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Volume Editors: Vincenzo Balzani · Sebastiano Campagna

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Preface

Photochemistry (a term that broadly speaking includes photophysics) is a branch of modern science that deals with the interaction of light with matter and lies at the crossroads of chemistry, physics, and biology. However, before being a branch of modern science, photochemistry was (and still is today), an extremely important natural phenomenon. When God said: "Let there be light", photochemistry began to operate, helping God to create the world as we now know it. It is likely that photochemistry was the spark for the origin of life on Earth and played a fundamental role in the evolution of life. Through the photosynthetic process that takes place in green plants, photochemistry is responsible for the maintenance of all living organisms. In the geological past photochemistry caused the accumulation of the deposits of coal, oil, and natural gas that we now use as fuels. Photochemistry is involved in the control of ozone in the stratosphere and in a great number of environmental processes that occur in the atmosphere, in the sea, and on the soil. Photochemistry is the essence of the process of vision and causes a variety of behavioral responses in living organisms.

Photochemistry as a science is quite young; we only need to go back less than one century to find its early pioneer [1]. The concept of coordination compounds is also relatively young; it was established in 1892, when Alfred Werner conceived his theory of metal complexes [2]. Since then, the terms coordination compound and metal complex have been used as synonyms, even if in the last 30 years, coordination chemistry has extended its scope to the binding of all kinds of substrates [3, 4].

The photosensitivity of metal complexes has been recognized for a long time, but the photochemistry and photophysics of coordination compounds as a science only emerged in the second half of the last century. The first attempt to systematize the photochemical reactions of coordination compounds was carried out in an exhaustive monograph published in 1970 [5], followed by an authoritative multi-authored volume in 1975 [6]. These two books gained the attention of the scientific community and certainly helped several inorganic and physical chemists to enter the field and to enrich and diversify their research activities. Interestingly, 1974 marked the beginning of the series of International Symposia on the Photochemistry and Photophysics of Coordi-

nation Compounds. The venue of the 17th symposium of this series is Dublin and will be held in June 2007.

Up until about 1975, most activity was focused on intramolecular photochemical reactions. Subsequently, due partly also to the more diffuse availability of flash techniques, the interest of several groups moved to investigations of luminescence and bimolecular energy and electron transfer processes. In the last decade of the past century, with the development of supramolecular chemistry, it was clear that photochemistry would play a very important role in the achievement of valuable functions, such as charge separation, energy migration and conformational changes [7], related to applications spanning from solar energy conversion to signal processing and molecular machines [8, 9]. In the last few years, an increasing number of scientists have become involved in these fields. Because of their unique ground and excited state properties, metal complexes have become invaluable components of molecular devices and machines exploiting light (often sunlight) to perform useful functions [8, 9, 10]. The photochemistry of coordination compounds can also contribute to solving the energy crisis by converting sunlight into electricity or fuel [11]. In the meantime, the basic knowledge of the excited state properties of coordination compounds of several metal ions has increased considerably. However, this has resulted in an unavoidable loss of general knowledge and an increase in specialization. Currently, all scientists working in the field of the photochemistry and photophysics of coordination compounds have their own preferred metal. There is, therefore, an urgent need to spread the most recent developments in the field among the photochemical community. To write an exhaustive monograph like [5], however, would now be an impossible enterprise. For this reason, we decided to ask experts to write separate chapters, each one dealing with a specific metal whose complexes are currently at the frontier of research. It has been a delight as well as a privilege to work with an outstanding group of contributing authors and we thank them for all their efforts. We would also like to thank all the members of our research groups for their support.

Bologna and Messina, March 2007

Vincenzo Balzani
Sebastiano Campagna

References

1. Ciamician G (1912) *Science* 36:385
2. Werner A (1893) *Zeit Anorg Chem* 3:267
3. Lehn J-M (1992) From coordination chemistry to supramolecular chemistry. In: Williams AF, Floriani C, Merbach AE (eds) *Perspectives in coordination chemistry*. VCH, Weinheim, p. 447
4. Balzani V, Credi A, Venturi M (1998) *Coord Chem Rev* 171:3
5. Balzani V, Carassiti V (1970) *Photochemistry of Coordination Compounds*. Academic Press, London

6. Adamson AW, Fleischauer PD (eds) (1975) Concepts in inorganic photochemistry. Wiley-Interscience, New York
7. Balzani V, Scandola F (1991) Supramolecular photochemistry. Horwood, Chichester
8. Balzani V, Credi A, Venturi M (2003) Molecular devices and machines. Wiley-VCH, Weinheim
9. Kelly TR (ed) (2005) Molecular machines, Topics Current Chem 262
10. Kay EU, Leigh DA, Zerbetto F (2007) Angew Chem Int Ed 46:72
11. Armaroli N, Balzani V (2007) Angew Chem Int Ed 46:52

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Photochemistry and Photophysics of Coordination Compounds: Overview and General Concepts

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And God said: “Let there be light”;
 And there was light.
 And God saw that the light was good.
 (*Genesis, 1, 3–4*)

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Abstract Investigations in the field of the photochemistry and photophysics of coordination compounds have proceeded along several steps of increasing complexity in the last 50 years. Early studies on ligand photosubstitution and photoredox decomposition reactions of metal complexes of simple inorganic ligands (e.g., NH_3 , CN^-) were followed by accurate investigations on the photophysical behavior (luminescence quantum yields and lifetimes) and use of metal complexes in bimolecular processes (energy and electron transfer). The most significant differences between Jablonski diagrams for organic molecules and coordination compounds are illustrated. A large number of complexes stable toward photodecomposition, but capable of undergoing excited-state redox processes, have been used for interconverting light and chemical energy. The rate constants of a great number of photoinduced energy- and electron-transfer processes involving coordination compounds have been measured in order to prove the validity and/or extend the scope of modern kinetic theories. More recently, the combination of supramolecular chemistry and photochemistry has led to the design and construction of supramolecular systems capable of performing light-induced functions. In this field, luminescent and/or photoredox reactive metal complexes are presently used as essential components for a bottom-up approach to the construction of molecular devices and machines. A few examples of molecular devices for processing light signals and of molecular machines powered by light energy, based on coordination compounds, are briefly illustrated.

Keywords Coordination compounds · Electron transfer · Energy transfer · Excited-state properties · Photochemistry · Supramolecular photochemistry

1

Early History

The photosensitivity of metal complexes has been known for a long time. The first paper exhibiting some scientific character was that of Scheele (1772) on the effect of light on AgCl , and photography was becoming established in several countries in the 1830s [1]. The light sensitivity of other metal complexes (particularly $\text{Na}_4[\text{Fe}(\text{CN})_6]$) was also observed very early [2]. At the beginning of the last century the importance of photochemistry became more widely recognized, mainly due to the work and the ideas of Giacomo Ciamician [3], Professor of Chemistry at the University of Bologna. In the same period (1912–1913), modern physics introduced the concept that light absorption corresponds to the capture of a photon by a molecule. This concept, and the distinction (sometimes difficult) between primary and secondary photoprocesses, led to the definition of quantum yield. In the following years, investigations on Fe^{3+} and UO_2^{2+} complexes were performed in looking for useful chemical actinometers (see, e.g., [4]). Several quantitative works also appeared on the photochemical behavior of $[\text{Fe}(\text{CN})_6]^{4-}$ and Co(III)-amine complexes in aqueous solution [2]. The lack of a theory on the absorption spectra and on the nature of the excited states, however, prevented any mechanistic interpretation of the observed photoreactions as well as of the few scattered reports on luminescent complexes.

After the Second World War, the interpretation of the absorption spectra started thanks to the development of the ligand field theory [5, 6] and the first attempts to rationalize the charge-transfer bands [7, 8]. Following these developments, the photochemistry of coordination compounds could take its first steps as a modern science and in a time span of 2 years four important laboratories published their first photochemical paper [9–12]. Much of the attention was focused on Cr(III) complexes, whose luminescence was also investigated in some detail [13]. Later, Co(III) complexes attracted a great deal of attention since their photochemical behavior was found to change drastically with excitation wavelength [14, 15]. A few, isolated flash photolysis investigations began to appear, but this technique remained unavailable to most inorganic photochemists for several years.

Since the late 1960s, the great development of photochemical and luminescence investigations on organic compounds led to the publication of books [16–19] illustrating fundamental photochemical concepts that were also quickly exploited for coordination compounds [2]. From that period, it became common to discuss the photochemical and photophysical behavior of a species (be it an organic molecule or a charged metal complex) on the basis of electronic configurations, selection rules, and energy level diagram, as we do today.

2

Molecular Photochemistry

Molecules are multielectron systems. Approximate electronic wavefunctions of a molecule can be written as products of one-electron wavefunctions, each consisting of an orbital and a spin part:

$$\Psi = \Phi S = \prod_i \varphi_i s_i. \quad (1)$$

The φ_i s are appropriate molecular orbitals (MOs) and s_i is one of the two possible spin eigenfunctions, α or β . The orbital part of this multielectron wavefunction defines the *electronic configuration*.

We illustrate now the procedure to construct energy level diagrams, using as examples an organic molecule and a few coordination compounds.

2.1

Organic Molecules

The MO diagram for formaldehyde is shown in Fig. 1 [20]. It consists of three low-lying σ -bonding orbitals, a π -bonding orbital of the CO group, a non-bonding orbital n of the oxygen atom (highest occupied molecular orbital, HOMO), a π -antibonding orbital of the CO group (lowest unoccupied molecular orbital, LUMO), and three high-energy σ -antibonding orbitals. The

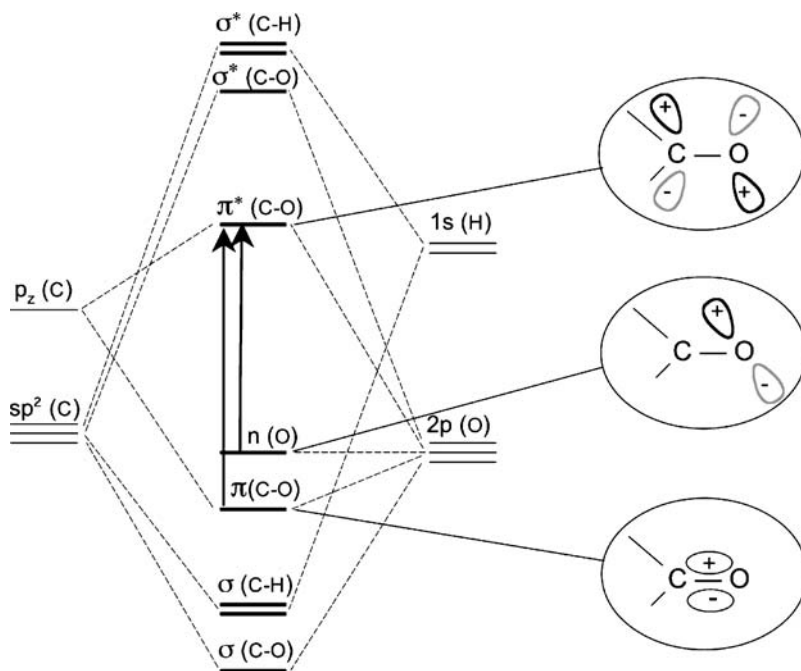


Fig. 1 Molecular orbital diagram for formaldehyde. The arrows indicate the $n \rightarrow \pi^*$ and $\pi \rightarrow \pi^*$ transitions

lowest-energy electronic configuration is (neglecting the filled low-energy orbitals) $\pi^2 n^2$. Excited configurations can be obtained from the ground configuration by promoting one electron from occupied to vacant MOs. At relatively low energies, one expects to find $n \rightarrow \pi^*$ and $\pi \rightarrow \pi^*$ electronic transitions (Fig. 1), leading to $\pi^2 n \pi^*$ and $\pi n^2 \pi^*$ excited configurations (Fig. 2a).

In a very crude zero-order description, the energy associated with a particular electronic configuration would be given by the sum of the energies of the occupied MOs. In order to obtain a more realistic description of the energy states of the molecule, two features should be added to the simple configuration picture: (1) spin functions must be attached to the orbital functions describing the electronic configurations, and (2) interelectronic repulsion must be taken into account. These two closely interlocked points have important consequences, since they may lead to the splitting of an electronic configuration into several states.

In the case of formaldehyde, the inclusion of spin and electronic repulsion leads to the schematic energy level diagram shown in Fig. 2b: each excited electronic configuration is split into a pair of triplet and singlet states, with the latter at higher energy because electronic repulsion is higher for spin-paired electrons. It can be noticed that the singlet-triplet splitting for the states arising from the $\pi\pi^*$ configuration is larger than that of the states cor-

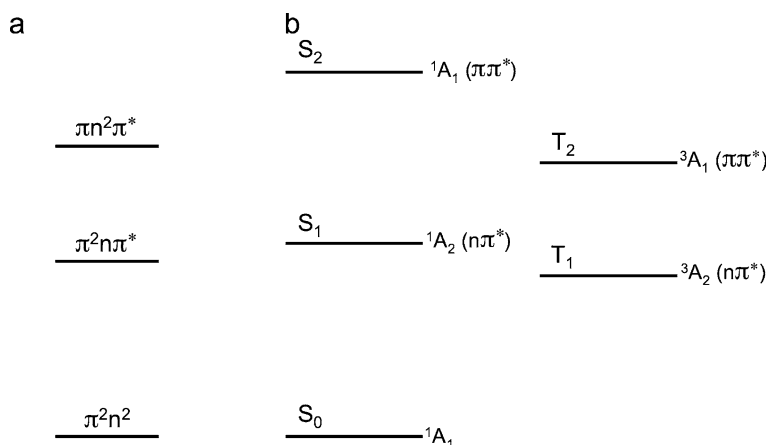


Fig. 2 Configurations (a) and states (b) diagrams for formaldehyde

responding to the $n\pi^*$ configuration. This result arises from the dependence of the interelectronic repulsions on the amount of spatial overlap between the MOs containing the two electrons, and this overlap is greater in the first than in the second case (see the MO shapes in Fig. 1). The electronic states can be designated by symbols that specify the symmetry of the wavefunction in the symmetry group of the molecule (e.g., A_1 , A_2 , etc. in the C_{2v} group of formaldehyde) and the spin multiplicity (number of unpaired electrons + 1) as a left superscript. In organic photochemistry, it is customary to label the singlet and triplet states as S_n and T_n , respectively, with $n = 0$ for the singlet ground state and $n = 1, 2$, etc. for states arising from the various excited configurations (often indicated in parentheses). Both notations are shown for formaldehyde in Fig. 2b. The situation sketched above (i.e., singlet ground state, pairs of singlet and triplet excited states arising from each excited configuration, lowest excited state of multiplicity higher than the ground state) is quite general for organic molecules that usually exhibit a closed-shell ground-state configuration.

State energy diagrams of this type, usually called “Jablonski diagrams”, are used for the description of light absorption and of the photophysical processes that follow light excitation (vide infra).

2.2

Metal Complexes

For metal complexes, the construction of Jablonski diagrams via electronic configurations from the MO description follows the same general lines described above for organic molecules [2]. A schematic MO diagram for an octahedral transition metal complex is shown in Fig. 3. The various MOs can be conveniently classified according to their predominant atomic orbital

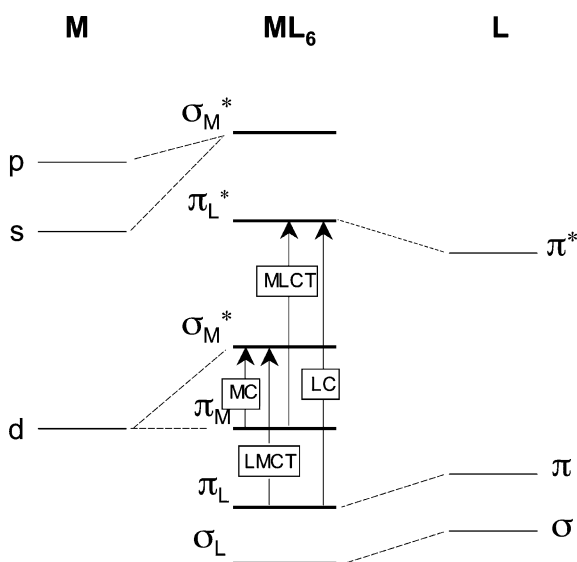


Fig. 3 Molecular orbital diagram for an octahedral complex of a transition metal. The arrows indicate the four types of transitions based on localized MO configurations. For more details, see text

contributions as: (1) strongly bonding, predominantly ligand centered σ_L orbitals; (2) bonding, predominantly ligand-centered π_L orbitals; (3) essentially nonbonding, metal-centered π_M orbitals of t_{2g} symmetry; (4) antibonding, predominantly metal-centered σ_M^* orbitals of e_g symmetry; (5) antibonding, predominantly ligand-centered π_L^* orbitals; and (6) strongly antibonding, predominantly metal-centered σ_M^* orbitals. In the ground electronic configuration of an octahedral complex of a d^n metal ion, orbitals of types 1 and 2 are completely filled, while n electrons reside in the orbitals of types 3 and 4.

As for organic molecules, excited configurations can be obtained from the ground configuration by promoting one electron from occupied to vacant MOs. At relatively low energies, one expects to find electronic transitions of the following types (Fig. 3): *metal-centered* (MC) transitions from orbitals of type 3 to orbitals of type 4; *ligand-centered* (LC) transitions of type 2 $\rightarrow$ 5; *ligand-to-metal charge-transfer* (LMCT) transitions, e.g., of type 2 $\rightarrow$ 4; and *metal-to-ligand charge-transfer* (MLCT) transitions, e.g., of type 3 $\rightarrow$ 5. The relative energy ordering of the resulting excited electronic configurations depends on the nature of metal and ligands in more or less predictable ways. Low-energy metal-centered transitions are expected for metals of the first transition row, low-energy ligand-to-metal charge-transfer transitions are expected when at least one of the ligands is easy to oxidize and the metal is easy to reduce, low-energy metal-to-ligand charge-transfer transitions are expected when the metal is easy to oxidize and a ligand is easy to reduce,

and low-energy ligand-centered transitions are expected for aromatic ligands with extended π and π^* orbitals (vide infra).

The step from configurations to states is conceptually less simple than for organic molecules because coordination compounds may have high symmetry (i.e., degenerate MOs) and open-shell ground configurations (i.e., partially occupied HOMOs).

For octahedral complexes of Co(III), Ru(II), and the other d^6 metal ions, the σ_L and π_L orbitals are fully occupied and the ground-state configuration is closed-shell since the HOMO, $\pi_M(t_{2g})^6$, is also completely occupied. The ground state is therefore a singlet, and the excited states are either singlets or triplets, as in the case of formaldehyde. In octahedral symmetry, the ground-state configuration gives rise to the state $^1A_{1g}$. In the case of $[M(NH_3)_6]^{n+}$ complexes (e.g., $M = Co$ or Ru), whose ligands do not possess π_L and π_L^* orbitals, the lowest-energy transition is metal centered and the resulting $\pi_M(t_{2g})^5\sigma_M^*(e_g)$ configuration gives rise to the singlet states $^1S_{1g}$ and $^1S_{2g}$ and the corresponding triplets $^3T_{1g}$ and $^3T_{2g}$. The energy level diagram (at low energies) for $[Ru(NH_3)_6]^{2+}$ is shown in Fig. 4 (the triplet-state energy has been obtained by comparison with the analogous Ir(III) complex [21]). In the case of $[M(bpy)_3]^{2+}$ ($M = Ru$ or Os), however, since the M(II) metal is easy to oxidize and the 2,2'-bipyridine ligands are easy to reduce, the lowest triplet and singlet excited states are metal-to-ligand charge-transfer in character (Fig. 4). For the corresponding $[M(bpy)_3]^{3+}$ complexes, the lowest triplet and singlet excited states are ligand-to-metal charge-transfer in character [22], since the M(III) metal can be easily reduced and the 2,2'-bipyridine ligands are not too difficult to oxidize (Fig. 4).

In Cr(III) complexes (d^3 metal ion), there are three electrons in the HOMO $\pi_M(t_{2g})$ orbitals. Therefore, these complexes exhibit an open-shell ground-state configuration, $\pi_M(t_{2g})^3$, that splits into quartet and doublet states

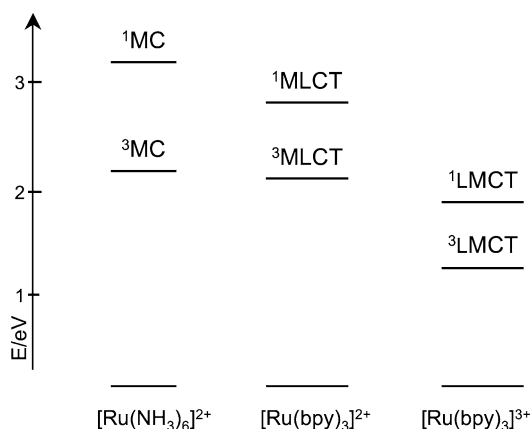


Fig. 4 Schematic energy level diagrams for $[Ru(NH_3)_6]^{2+}$, $[Ru(bpy)_3]^{2+}$, and $[Ru(bpy)_3]^{3+}$

(Fig. 5). For most Cr(III) complexes, e.g., for $[\text{Cr}(\text{NH}_3)_6]^{3+}$, the lowest-energy transition is metal centered and the resulting $\pi_M(t_{2g})^2\sigma_M^*(e_g)$ configuration gives rise to ${}^4T_{2g}$ and ${}^4T_{1g}$ excited states (Fig. 5). Several other coordination compounds, including the complexes of the lanthanide ions, have an open-shell ground-state configuration and, as a consequence, a ground state with high-multiplicity and low-energy intraconfigurational metal-centered excited states.

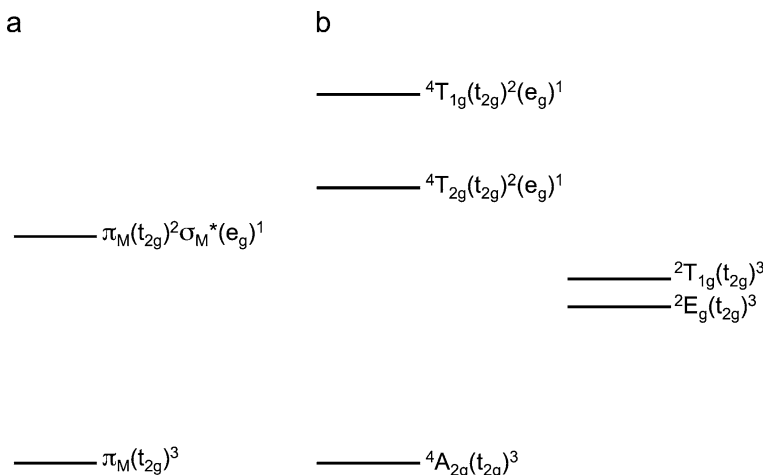


Fig. 5 Configurations (a) and state (b) diagrams for an octahedral Cr(III) complex. Only the lower-lying excited states of each configuration are shown [20]

In conclusion, metal complexes tend to have more complex and specific Jablonski diagrams than organic molecules. Points to be noticed are: (1) spin multiplicity other than singlet and triplet can occur, but for each electronic configuration the state with highest multiplicity remains the lowest one; (2) excited states can exist that belong to the same configuration of the ground state (this implies that the ground state has the highest multiplicity); and (3) more than one pair of states of different multiplicity can arise from a single electron configuration. In the following, in order to discuss some general concept of molecular photochemistry we will make use of a generic Jablonski diagram based on singlet and triplet states.

2.3

Light Absorption and Intramolecular Excited-State Decay

Figure 6 shows a schematic energy level diagram for a generic molecule [23]. In principle, transitions between states having the same multiplicity are allowed, whereas those between states of different multiplicity are forbidden. Therefore, the electronic absorption bands observed in the UV-visible spec-

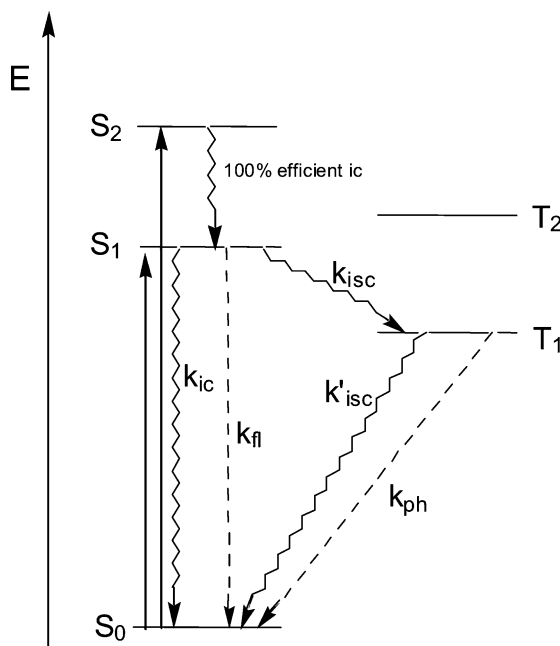


Fig. 6 Schematic energy level diagram for a generic molecule

trum of such a generic molecule would display bands corresponding to the $S_0 \rightarrow S_n$ transitions of the diagram. For metal complexes, which usually are highly symmetric species, symmetry selection rules can also play a role in determining the intensity of the absorption bands. Furthermore, the presence of a heavy atom (namely, the metal) relaxes the spin-conservation rule.

The excited states are unstable species that decay not only by intramolecular chemical reactions (e.g., dissociation, isomerization) but also (actually, more often) by intramolecular radiative and nonradiative deactivations. When a species is excited to upper spin-allowed excited states, it usually undergoes a fast and 100% efficient radiationless deactivation (internal conversion, ic) to the lowest spin-allowed excited (S_1 in Fig. 6). Setting aside the intramolecular photochemical processes, such an excited state undergoes deactivation via three competing first-order processes: nonradiative decay to the ground state (internal conversion, rate constant k_{ic}); radiative decay to the ground state (fluorescence, k_{fl}); and intersystem crossing (isc) to the lowest triplet state T_1 (k_{isc}). In its turn, T_1 can undergo deactivation via nonradiative (intersystem crossing, k'_{isc}) or radiative (phosphorescence, k_{ph}) decay to the ground state S_0 . When the species contains heavy atoms, as in the case of metal complexes, the formally forbidden intersystem crossing and phosphorescence processes become faster. The lifetime (τ) of an excited state, i.e., the time needed to reduce the excited-state concentration by 2.718, is given

by the reciprocal of the summation of the deactivation rate constants. For the molecule of Fig. 6,

$$\tau(S_1) = \frac{1}{(k_{ic} + k_{fl} + k_{isc})} \quad (2)$$

$$\tau(T_1) = \frac{1}{(k'_{isc} + k_{ph})} . \quad (3)$$

The lifetimes of the lowest spin-allowed and spin-forbidden excited state ($\tau(S_1)$ and $\tau(T_1)$ in the example of Fig. 6) are approximately 10^{-9} – 10^{-7} s and 10^{-3} – 10^0 s, respectively, for organic molecules, but they become shorter by several orders of magnitude for metal complexes. For example, the lifetime of the lowest spin-forbidden excited state of naphthalene is around 2 s, whereas that of $[\text{Ru}(\text{bpy})_3]^{2+}$, because of the presence of the heavy Ru ion, is about 1 μs [24].

The quantum yields of fluorescence (ratio between the number of photons emitted by the lowest spin-allowed excited state, S_1 in Fig. 6, and the number of absorbed photons) and phosphorescence (ratio between the number of photons emitted by the lowest spin-forbidden excited state, T_1 in Fig. 6, and the number of absorbed photons) can range between 0 and 1 and are given by the following expressions:

$$\Phi_{fl} = \frac{k_{fl}}{(k_{ic} + k_{fl} + k_{isc})} \quad (4)$$

$$\Phi_{ph} = \frac{k_{ph} \times k_{isc}}{(k'_{isc} + k_{ph}) \times (k_{ic} + k_{fl} + k_{isc})} . \quad (5)$$

The excited-state lifetimes and fluorescence and phosphorescence quantum yields of a great number of organic molecules and metal complexes are known [24].

3 Bimolecular Processes

3.1 General Features

In fluid solution, when the intramolecular deactivation processes are not too fast, i.e., when the lifetime of the excited state is sufficiently long, an excited molecule $^*A$ may have a chance to encounter a molecule of another solute B. In such a case, some specific interaction can occur leading to the deactivation of the excited state by second-order kinetic processes. The two most important types of interactions in an encounter are those leading to electron or

energy transfer:



Bimolecular electron- and energy-transfer processes are important because they can be used (1) to quench an electronically excited state, i.e., to prevent its luminescence and/or intramolecular reactivity, and (2) to sensitize other species, for example, to cause chemical changes of, or luminescence from, species that do not absorb light.

Simple kinetic arguments show that only the excited states that live longer than ca. 10^{-9} s may have a chance to be involved in encounters with other solute molecules. Usually, in the case of metal complexes only the lowest excited state satisfies this requirement. The kinetic aspects of energy- and electron-transfer processes are discussed in detail elsewhere [17, 20, 23]. A point that must be stressed is that an electronically excited state is a species with quite different properties compared with those of the ground-state molecule. In particular, because of its higher energy content, an excited state is both a stronger reductant and a stronger oxidant than the corresponding ground state. To a first approximation, the redox potentials of the excited-state couples may be calculated from the potentials of the ground-state couples and the one-electron potential corresponding to the zero-zero excited-state energy, E^{0-0} , as shown by Eqs. 9 and 10 [25]:

$$E(A^+/^*A) \approx E(A^+/A) - E^{0-0} \quad (9)$$

$$E(^*A/A^-) \approx E(A/A^-) + E^{0-0} \quad (10)$$

3.2

Bimolecular Processes Involving Metal Complexes

From an exhaustive monograph that appeared in 1970 [2] and a multiauthored volume of 1975 [26], it clearly appears that most of the interest was then focused on ligand photosubstitution reactions, photoredox decomposition, and photoisomerization reactions, while bimolecular processes were barely investigated. This picture, however, changed profoundly in a few years following the extensive work carried out by several research groups on the luminescence of coordination compounds [27–29] and the discovery that the lowest excited state of a number of Cr(III), Ru(II), and Os(II) complexes exhibits a sufficiently long lifetime in fluid solution to be able to participate as a reactant in bimolecular reactions [25, 30]. A further advantage offered by Ru(II) and Os(II) bipyridine-type complexes is that they can undergo reversible redox reactions both in the ground and excited state, so they were soon used as reactants and, even more interesting, as mediators, in light-

induced [30–34] and light-generating [35, 36] electron-transfer processes. Such studies were further boosted by the fact that, after the energy crisis of the early 1970s, several photochemists became involved in the problem of solar energy conversion. Particular interest arose around photosensitized water splitting [37–41] and it was soon realized [42] that $[\text{Ru}(\text{bpy})_3]^{2+}$ and related complexes, because of their excited-state redox properties, might function as photocatalysts for such a process.

As a matter of fact, in the period 1975–1985 a real revolution occurred in the field of the photochemistry of coordination compounds. The study of intramolecular ligand photosubstitution, photoredox decomposition, and photoisomerization reactions was almost completely set apart, about 300 Ru(II) bipyridine-type complexes were synthesized and investigated in an attempt (mostly vain) to improve the already outstanding excited-state properties of $[\text{Ru}(\text{bpy})_3]^{2+}$ [43], and, thanks to an extensive use of pulsed techniques, huge amounts of data were collected on the rate constants of bimolecular processes [44]. The high exergonicity of the excited-state electron-transfer reactions (and/or of their back reactions) offered the opportunity for the first time to investigate some fundamental aspects of electron-transfer theories [45], with particular attention to the so-called Marcus inverted region.

4

Supramolecular Photochemistry

4.1

Operational Definition of Supramolecular Species

In the late 1980s, following the award of the 1987 Nobel prize to Pedersen, Cram, and Lehn, there was a sudden increase of interest in supramolecular chemistry, a highly interdisciplinary field based on concepts such as molecular recognition, preorganization, and self-assembling.

The classical definition of supramolecular chemistry is that given by J.-M. Lehn, namely “the chemistry beyond the molecule, bearing on organized entities of higher complexity that result from the association of two or more chemical species held together by intermolecular forces” [46]. There is, however, a problem with this definition. With supramolecular chemistry there has been a change in focus from molecules to molecular assemblies or multicomponent systems. According to the original definition, however, when the components of a chemical system are linked by covalent bonds, the system should not be considered a supramolecular species, but a molecule. This point is particularly important in dealing with light-powered molecular devices and machines (*vide infra*), which are usually multicomponent systems in which the components can be linked by chemical bonds of various natures.

To better understand this point, consider, for example, the three systems [47] shown in Fig. 7, which play the role of photoinduced charge-separation molecular devices [48]. In each one of them, two components, a Zn(II) porphyrin and an Fe(III) porphyrin, can be immediately singled out. In **1**, these two components are linked by a hydrogen-bonded bridge, i.e., by intermolecular forces, whereas in **2** and **3** they are linked by covalent bonds. According to the above-reported classical definition of supramolecular chemistry, **1** is a supramolecular species, whereas **2** and **3** are (large) molecules. In each one of the three systems, the two components substantially maintain their intrinsic properties and, upon light excitation, electron transfer takes place from the Zn(II) porphyrin unit to the Fe(III) porphyrin one. The values of the rate constants for photoinduced electron transfer ($k_{\text{el}} = 8.1 \times 10^9$, 8.8×10^9 , and $4.3 \times 10^9 \text{ s}^{-1}$ for **1**, **2**, and **3**, respectively) show that the electronic interaction between the two components in **1** is comparable to that in **2**, and is slightly stronger than that in **3**. Clearly, as far as photoinduced electron transfer is concerned, it would sound strange to say that **1** is a supramolecular species, and **2** and **3** are molecules.

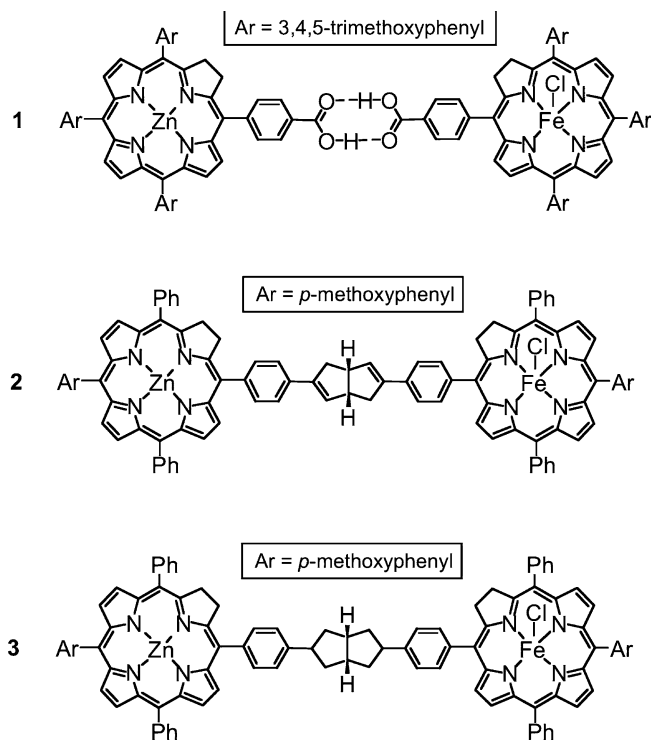


Fig. 7 Three dyads possessing Zn(II) porphyrin and Fe(III) porphyrin units linked by an H-bonded bridge (**1**), a partially unsaturated bridge (**2**), and a saturated bridge (**3**) [47]

The example discussed above shows that, although the classical definition of supramolecular chemistry as “the chemistry beyond the molecule” [46] is quite useful in general, from a functional viewpoint the distinction between what is molecular and what is supramolecular can be better based on the degree of intercomponent electronic interactions [20, 49–52]. This concept is illustrated, for example, in Fig. 8 [53]. In the case of photon stimulation, a system $A \sim B$, consisting of two units ($\sim$ indicates any type of “bond” that keeps the units together), can be defined as a supramolecular species if light absorption leads to excited states that are substantially localized on either A or B, or causes an electron transfer from A to B (or vice versa). By contrast, when the excited states are substantially delocalized on the entire system, the species can be better considered as a large molecule. Similarly (Fig. 8), oxidation and reduction of a supramolecular species can substantially be described as oxidation and reduction of specific units, whereas oxidation and reduction of a large molecule leads to species where the hole or the electron are delocalized on the entire system. In more general terms, when the interaction energy between units is small compared to the other relevant energy parameters, a system can be considered a supramolecular species, regardless of the nature of the bonds that link the units. Species made of covalently linked (but weakly interacting) components, e.g., 2 and 3 shown in Fig. 7, can therefore be regarded as belonging to the supramolecular domain when they are stimulated by photons or electrons. It should be noted that the properties of each component of a supramolecular species, i.e., of an assembly of weakly interacting molecular components, can be known from the study of the isolated components or of suitable model molecules.

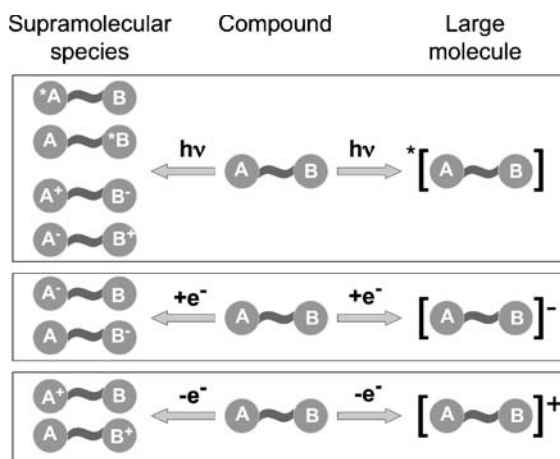


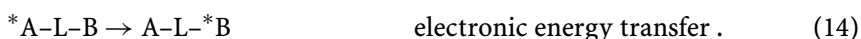
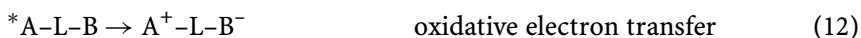
Fig. 8 Schematic representation of the difference between a supramolecular system and a large molecule based on the effects caused by a photon or an electron input. For more details, see text

4.2

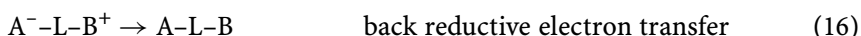
Photoinduced Processes in Supramolecular Systems

Clearly, preorganization is a most valuable property from a photochemical viewpoint since a supramolecular system, for example, can be preorganized so as to favor the occurrence of energy- and electron-transfer processes [20].

Consider, for example, an A–L–B supramolecular system, where A is the light-absorbing molecular unit (Eq. 11), B is the other molecular unit to be involved in the light-induced processes, and L is a connecting unit (often called bridge). In such a system, after light excitation of A there is no need to wait for a diffusion-controlled encounter between $^*A$ and B, as in molecular photochemistry (*vide supra*), since the two reaction partners can already be at an interaction distance suitable for electron and energy transfer:



In the absence of chemical complications (e.g., fast decomposition of the oxidized and/or reduced species), photoinduced electron-transfer processes are followed by spontaneous back electron-transfer reactions that regenerate the starting ground-state system (Eqs. 15 and 16), and photoinduced energy transfer is followed by radiative and/or nonradiative deactivation of the excited acceptor (Eq. 17):



In supramolecular systems, electron- and energy-transfer processes take place by first-order kinetics. As a consequence, in suitably designed supramolecular systems these processes can involve even very short lived excited states.

In most cases, the interaction between excited and ground-state components in a supramolecular system is weak. When the interaction is strong, new chemical species are formed, which are called excimers (from excited dimers) or exciplexes (from excited complexes), depending on whether the two interacting units have the same or different chemical nature (Fig. 9). It is important to notice that excimer and exciplex formation is a reversible process and that both excimers and exciplexes are sometimes luminescent.

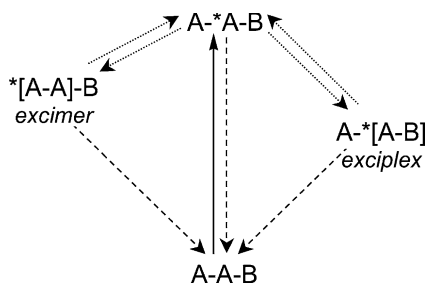


Fig. 9 Schematic representation of excimer and exciplex formation in a supramolecular system

Compared with the “monomer” emission, the emission of an excimer or exciplex is always displaced to lower energy (longer wavelengths) and usually corresponds to a broad and rather weak band.

Excimers are usually obtained when an excited state of an aromatic molecule interacts with the ground state of a molecule of the same type. For example, between the excited and ground states of anthracene units. Exciplexes are obtained when an electron donor (acceptor) excited state interacts with an electron acceptor (donor) ground-state molecule; for example, between excited states of aromatic molecules (electron acceptors) and amines (electron donors). Excited states of coordination compounds are seldom involved in excimers or exciplexes, since their components (metal and ligands) have already used their electron donor or acceptor properties in forming the complex. Furthermore, the three-dimensional structure of coordination compounds usually prevents strong electronic interaction with other species. However, for some square planar complexes excimer emission has long been reported [54] and can indeed be found for some families of Au and Pt complexes, as discussed in other chapters of this volume.

The working mechanisms of a number of biological and artificial molecular devices and machines are based on photoinduced electron- and energy-transfer processes [20, 48, 55]. Since these processes have to compete with the intrinsic decays of the relevant excited states, a key problem is that of maximizing their rates. It is therefore appropriate to summarize some basic principles of electron- and energy-transfer kinetics. [56].

4.3

Electron Transfer

4.3.1

Marcus Theory

Electron-transfer processes involving excited-state and/or ground-state molecules can be dealt with in the frame of the Marcus theory [57] and of the

successive, more sophisticated theoretical models [58, 59]. Of course, when excited states are involved, the redox potential of the excited-state couple has to be used (Eqs. 9 and 10).

According to the Marcus theory [57], the rate constant for an electron-transfer process can be expressed as

$$\kappa_{\text{el}} = \nu_{\text{N}} \kappa_{\text{el}} \exp \left(- \frac{\Delta G^\ddagger}{RT} \right), \quad (18)$$

where ν_{N} is the average nuclear frequency factor, κ_{el} is the electronic transmission coefficient, and $\Delta G^\ddagger$ is the free energy of activation. This last term can be expressed by the Marcus quadratic relationship

$$\Delta G^\ddagger = \frac{\lambda}{4} \left(1 + \frac{\Delta G^0}{\lambda} \right)^2, \quad (19)$$

where ΔG^0 is the standard free energy change of the reaction and λ is the nuclear reorganizational energy (Fig. 10). This equation predicts that for a homogeneous series of reactions (i.e., for reactions having the same λ and κ_{el} values), a $\ln k_{\text{el}}$ vs ΔG^0 plot is a bell-shaped curve (Fig. 11) involving (1) a “normal” region for endoergonic and slightly exoergonic reactions, in which $\ln k_{\text{el}}$ increases with increasing driving force; (2) an activationless maximum for $\lambda \approx -\Delta G^0$; and (3) an “inverted” region for strongly exoergonic reactions, in which $\ln k_{\text{el}}$ decreases with increasing driving force.

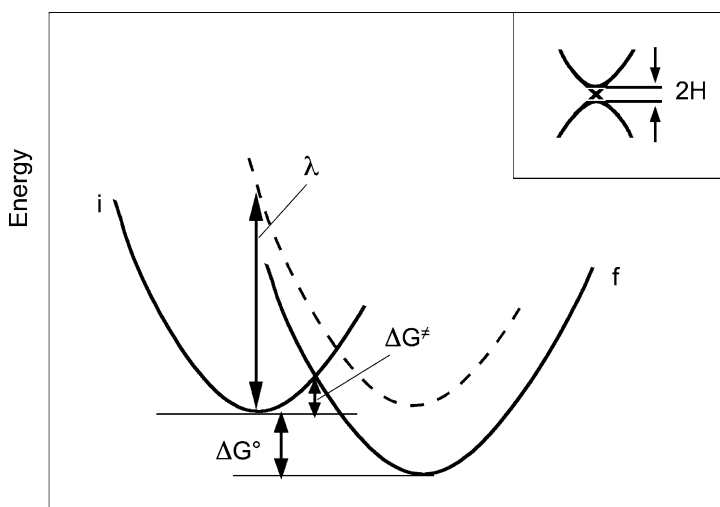


Fig. 10 Profile of the potential energy curves of an electron-transfer reaction: *i* and *f* indicate the initial and final states of the system. The *dashed curve* indicates the final state for a self-exchange (isoergonic) process. For more details, see text

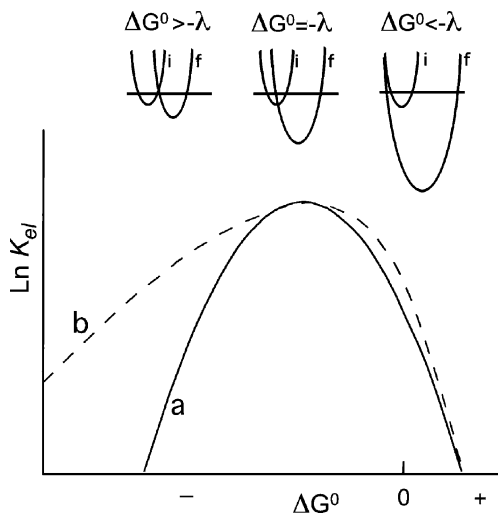


Fig. 11 Free energy dependence of electron-transfer rate (*i*, initial state; *f*, final state) according to the Marcus (a) and quantum mechanical (b) treatments. The three kinetic regimes (normal, activationless, and “inverted”) are shown schematically in terms of Marcus parabolas

The reorganizational energy λ can be expressed as the sum of two independent contributions corresponding to the reorganization of the “inner” (bond lengths and angles within the two reaction partners) and “outer” (solvent reorientation around the reacting pair) nuclear modes:

$$\lambda = \lambda_i + \lambda_o. \quad (20)$$

The electronic transmission coefficient κ_{el} is related to the probability of crossing at the intersection region (Fig. 10). It can be expressed by the equation

$$\kappa_{el} = \frac{2 [1 - \exp(-\nu_{el}/2\nu_N)]}{2 - \exp(-\nu_{el}/2\nu_N)}, \quad (21)$$

where

$$\nu_{el} = \frac{2 (H^{el})^2}{h} \left(\frac{\pi^3}{\lambda RT} \right)^{1/2}, \quad (22)$$

and H^{el} is the matrix element for electronic interaction (Fig. 10).

If H^{el} is large, $\nu_{el} \gg \nu_N$, $\kappa_{el} = 1$ and

$$k_{el} = \nu_N \exp \left(\frac{-\Delta G^\ddagger}{RT} \right) \quad (\text{adiabatic limit}). \quad (23)$$

If H^{el} is small, $\nu_{\text{el}} \ll \nu_{\text{N}}$, $\kappa_{\text{el}} = \nu_{\text{el}}/\nu_{\text{N}}$ and

$$k_{\text{el}} = \nu_{\text{el}} \exp\left(\frac{-\Delta G^\ddagger}{RT}\right) \quad (\text{nonadiabatic limit}). \quad (24)$$

Under the latter condition, k_{el} is proportional to $(H^{\text{el}})^2$. The value of H^{el} depends on the overlap between the electronic wavefunctions of the donor and acceptor groups, which should decrease exponentially with increasing donor-acceptor distance.

It should be noticed that the amount of electronic interaction required to promote photoinduced electron transfer is very small. By substituting reasonable numbers for the parameters in Eq. 24, for an activationless reaction H^{el} values of a few wavenumbers are sufficient to give rates in the sub-nanosecond timescale, while a few hundred wavenumbers may be sufficient to reach the limiting adiabatic regime (Eq. 23).

4.3.2

Quantum Mechanical Theory

From a quantum mechanical viewpoint, both the photoinduced and back electron-transfer processes can be viewed as radiationless transitions between different, weakly interacting electronic states of the A-L-B supermolecule (Fig. 12). The rate constant of such processes is given by an appropriate Fermi "golden rule" expression:

$$k_{\text{el}} = \frac{4\pi^2}{h} (H^{\text{el}})^2 \text{FC}^{\text{el}}, \quad (25)$$

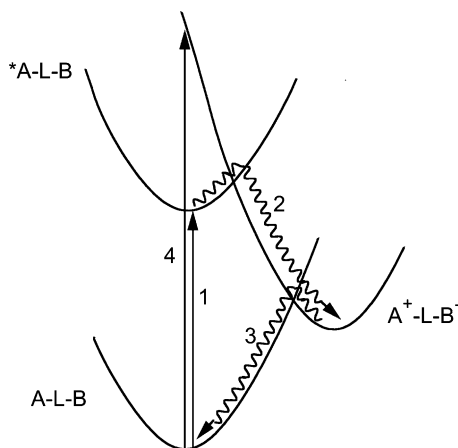


Fig. 12 Electron-transfer processes in a supramolecular system: 1 photoexcitation; 2 photoinduced electron transfer; 3 thermal back electron transfer; 4 optical electron transfer

where H^{el} and FC^{el} are the electronic coupling and the Franck–Condon density of states, respectively.

In the absence of any intervening medium (through-space mechanism), the electronic factor decreases exponentially with increasing distance:

$$H^{\text{el}} = H^{\text{el}}(0) \exp \left[-\frac{\beta^{\text{el}}}{2} (r_{\text{AB}} - r_0) \right], \quad (26)$$

where r_{AB} is the donor–acceptor distance, $H^{\text{el}}(0)$ is the interaction at the “contact” distance r_0 , and β^{el} is an appropriate attenuation parameter.

For donor–acceptor components separated by vacuum, β^{el} is estimated to be in the range $2\text{--}5 \text{ \AA}^{-1}$. When donor and acceptor are separated by “matter” (e.g., a bridge L), the electronic coupling can be mediated by mixing of the initial and final states of the system with virtual, high-energy electron-transfer states involving the intervening medium (superexchange mechanism) [60, 61].

The FC^{el} term of Eq. 25 is a thermally averaged Franck–Condon factor connecting the initial and final states. In the high temperature limit ($h\nu < k_{\text{B}}T$), an approximation sufficiently accurate for many room-temperature processes, the nuclear factor takes the simple form:

$$\text{FC}^{\text{el}} = \left(\frac{1}{4\pi\lambda k_{\text{B}}T} \right)^{1/2} \exp \left[-\frac{(\Delta G^0 + \lambda)^2}{4\lambda k_{\text{B}}T} \right], \quad (27)$$

where λ is the sum of the inner (λ_{i}) and outer (λ_{o}) reorganizational energies. The exponential term of Eq. 27 is the same as that predicted by the classical Marcus model based on parabolic energy curves for initial and final states. The quantum mechanical model, however, predicts a linear, rather than a parabolic, decrease of $\ln k_{\text{el}}$ with increasing driving force in the inverted region (Fig. 11).

4.3.3

Optical Electron Transfer

Reactants and products of an electron-transfer process are intertwined by a ground/excited-state relationship. As shown in Fig. 12, for nuclear coordinates that correspond to the equilibrium geometry of A–L–B, $\text{A}^+-\text{L}-\text{B}^-$ is an electronically excited state. Therefore, optical transitions connecting the two states are possible, as indicated by arrow 4 in Fig. 12.

The Hush theory [62] correlates the parameters that are involved in the corresponding thermal electron-transfer process by means of Eqs. 28–30:

$$E_{\text{op}} = \lambda + \Delta G^0 \quad (28)$$

$$\Delta \bar{\nu}_{1/2} = 48.06 (E_{\text{op}} - \Delta G^0)^{1/2} \quad (29)$$

$$\varepsilon_{\text{max}} \Delta \bar{\nu}_{1/2} = (H^{\text{el}})^2 \frac{r^2}{4.20 \times 10^{-4} E_{\text{op}}}, \quad (30)$$

where E_{op} , $\Delta \bar{\nu}_{1/2}$ (both in cm^{-1}), and ε_{max} are the energy, halfwidth, and maximum intensity of the electron-transfer band, respectively, and r is the center-to-center distance. As shown by Eqs. 28–30, the energy depends on both reorganizational energy and thermodynamics, the halfwidth reflects the reorganizational energy, and the intensity of the transition is mainly related to the magnitude of the electronic coupling between the two redox centers.

In principle, therefore, important kinetic information on a thermal electron-transfer process could be obtained from the study of the corresponding optical transition. In practice, it can be shown that weakly coupled systems may undergo relatively fast electron-transfer processes without exhibiting appreciably intense optical electron-transfer bands. More details on optical electron transfer and related topics (i.e., mixed valence metal complexes) can be found in the literature [63–65].

4.4

Energy Transfer

The thermodynamic ability of an excited state to intervene in energy-transfer processes is related to its zero-zero spectroscopic energy, E^{0-0} . Bimolecular energy-transfer processes involving encounters can formally be treated using a Marcus-type approach with $\Delta G^0 = E_{\text{A}}^{0-0} - E_{\text{B}}^{0-0}$ and $\lambda \sim \lambda_{\text{i}}$ [66].

Energy transfer in a supramolecular system can be viewed as a radiationless transition between two “localized” electronically excited states. Therefore, the rate constant can again be obtained by an appropriate “golden rule” expression, similar to that seen above for electron transfer:

$$k_{\text{en}} = \frac{4\pi^2}{h} (H^{\text{en}})^2 \text{FC}^{\text{en}}, \quad (31)$$

where H^{en} is the electronic coupling between the two excited states interconverted by the energy-transfer process and FC^{en} is an appropriate Franck–Condon factor. As for electron transfer, the Franck–Condon factor can be cast either in classical [67] or quantum mechanical [68–70] terms. Classically, it accounts for the combined effects of energy gradient and nuclear reorganization on the rate constant. In quantum mechanics terms, the FC factor is a thermally averaged sum of vibrational overlap integrals. Experimental information on this term can be obtained from the overlap integral

between the emission spectrum of the donor and the absorption spectrum of the acceptor.

The electronic factor H^{en} is a two-electron matrix element involving the HOMOs and LUMOs of the energy-donor and energy-acceptor components. By following standard arguments [20, 23], this factor can be split into two additive terms, a *coulombic* term and an *exchange* term. The two terms depend differently on the parameters of the system (spin of ground and excited states, donor-acceptor distance, etc.) and each of them can become predominant depending on the specific system and experimental conditions. The orbital aspects of the two mechanisms are schematically represented in Fig. 13.

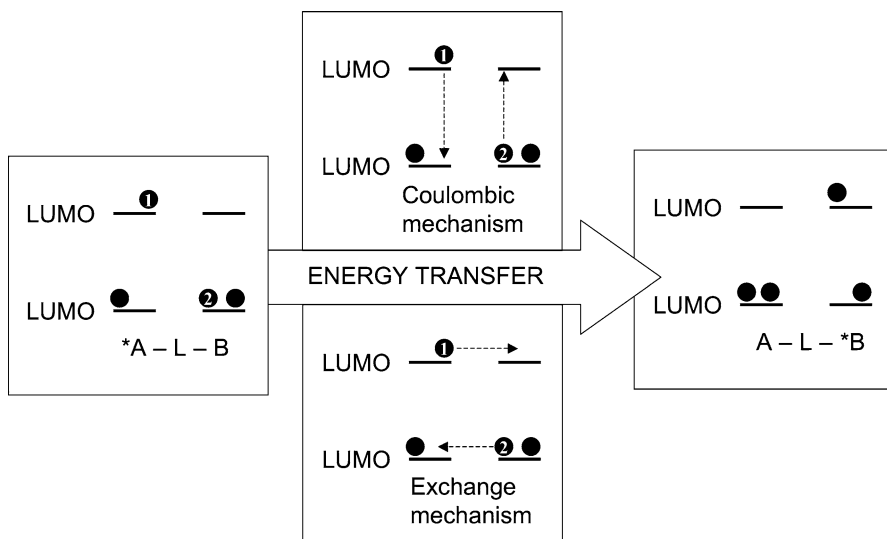


Fig. 13 Pictorial representation of the coulombic and exchange energy-transfer mechanisms

4.4.1

Coulombic Mechanism

The coulombic (also called resonance, Förster-type [71], or through-space) mechanism is a long-range mechanism that does not require physical contact between donor and acceptor. It can be shown that the most important term within the coulombic interaction is the dipole-dipole term, which obeys the same selection rules as the corresponding electric dipole transitions of the two partners ($*A \rightarrow A$ and $B \rightarrow *B$, Fig. 13). Therefore, coulombic energy transfer is expected to be efficient in systems in which the radiative transitions connecting the ground and the excited states of each partner have high oscillator strength. The rate constant for the dipole-dipole coulombic energy

transfer can be expressed as a function of the spectroscopic and photophysical properties of the two molecular components:

$$k_{\text{en}}^{\text{F}} = 8.8 \times 10^{-25} \frac{K^2 \Phi}{n^4 r_{\text{AB}}^6 \tau} J_{\text{F}} \quad (32)$$

$$J_{\text{F}} = \frac{\int F(\bar{\nu}) \varepsilon(\bar{\nu}) / \bar{\nu}^4 d\bar{\nu}}{\int F(\bar{\nu}) d\bar{\nu}}, \quad (33)$$

where K is an orientation factor which accounts for the directional nature of the dipole–dipole interaction ($K^2 = 2/3$ for random orientation), Φ and τ are the luminescence quantum yield and lifetime of the donor, respectively, n is the solvent refractive index, r_{AB} is the distance (in Å) between donor and acceptor, and J_{F} is the Förster overlap integral between the luminescence spectrum of the donor, $F(\bar{\nu})$, and the absorption spectrum of the acceptor, $\varepsilon(\bar{\nu})$, on an energy scale (cm^{-1}). With a good spectral overlap integral and appropriate photophysical properties, the $1/r_{\text{AB}}^6$ distance dependence allows energy transfer to occur efficiently over distances largely exceeding the molecular diameters. The typical example of an efficient coulombic mechanism is that of singlet–singlet energy transfer between large aromatic molecules, a process used by nature in the “antenna” systems of the photosynthetic apparatus [72]:



4.4.2

Exchange Mechanism

The exchange (also called Dexter-type [73]) mechanism requires orbital overlap between donor and acceptor, either directly or mediated by the bridge (through-bond), and its rate constant, therefore, decreases with increasing distance:

$$k_{\text{en}}^{\text{D}} = \frac{4\pi^2}{h} (H^{\text{en}})^2 J_{\text{D}}, \quad (35)$$

where

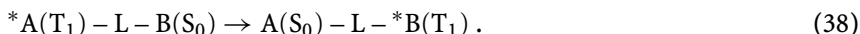
$$H^{\text{en}} = H^{\text{en}}(0) \exp \left[-\frac{\beta^{\text{en}}}{2} (r_{\text{AB}} - r_0) \right] \quad (36)$$

$$J_{\text{D}} = \frac{\int F(\bar{\nu}) \varepsilon(\bar{\nu}) d\bar{\nu}}{\int F(\bar{\nu}) d\bar{\nu} \int \varepsilon(\bar{\nu}) d\bar{\nu}}. \quad (37)$$

The exchange interaction can be regarded (Fig. 13) as a double electron-transfer process, one electron moving from the LUMO of the excited donor to the LUMO of the acceptor, and the other from the acceptor HOMO to the donor HOMO. Therefore, the attenuation factor β^{en} for exchange energy

transfer should be approximately equal to the sum of the attenuation factors for two separated electron-transfer processes, i.e., β^{el} for electron transfer between the LUMOs of the donor and acceptor, and β^{ht} for the electron transfer between the HOMOs (superscript ht is for hole transfer from the donor to the acceptor). This prediction has been confirmed by experiments [74].

The spin selection rules for this type of mechanism arise from the need to obey spin conservation in the reacting pair as a whole. This allows the exchange mechanism to be operative in many cases in which the excited states involved are spin-forbidden in the usual spectroscopic sense. Thus, the typical example of an efficient exchange mechanism is that of triplet–triplet energy transfer:



Exchange energy transfer from the lowest spin-forbidden excited state is expected to be the rule for metal complexes [61, 75].

Although the exchange mechanism was originally formulated in terms of direct overlap between donor and acceptor orbitals, it is clear that it can be extended to cover the case in which coupling is mediated by the intervening medium (i.e., the connecting bridge), as discussed above for electron-transfer processes (superexchange mechanism) [61].

5

Coordination Compounds as Components of Photochemical Molecular Devices and Machines

In the last few years, a combination of supramolecular chemistry and photochemistry has led to the design and construction of supramolecular systems capable of performing interesting light-induced functions. Photoinduced energy and electron transfer are indeed basic processes for connecting light energy inputs with a variety of optical, electrical, and mechanical functions, i.e., to obtain molecular-level devices and machines [48, 55]. We will now describe a few classical examples of molecular devices and machines in which coordination compounds are used to process light signals or to exploit light energy. Other examples are, of course, described in the chapters dealing with the complexes of the various metals.

5.1

A Molecular Wire

An important function at the molecular level is photoinduced energy and electron transfer over long distances and/or along predetermined directions. This function can be obtained by linking donor and acceptor components by a rigid spacer, as illustrated in Fig. 14.

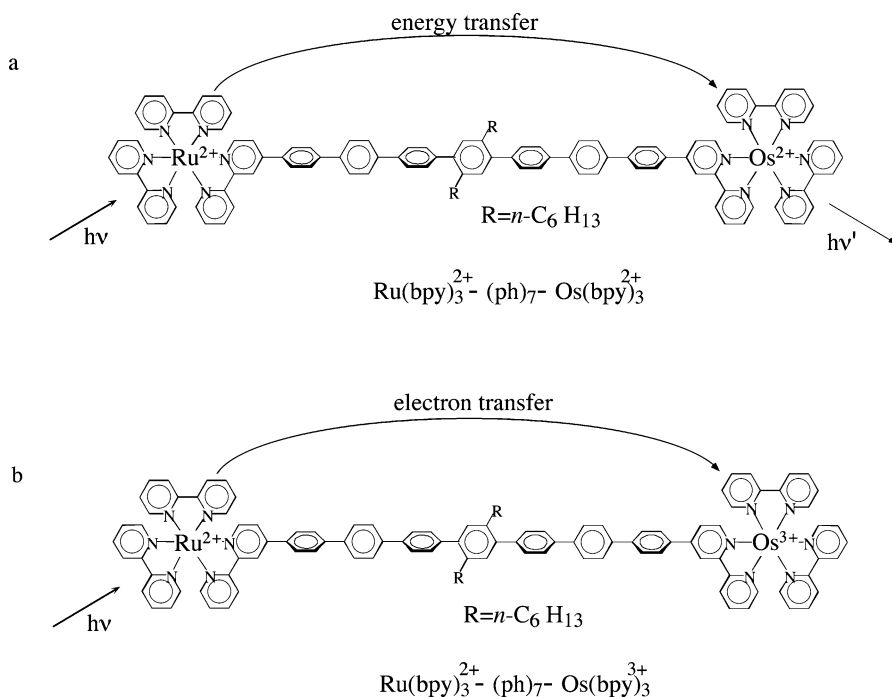


Fig. 14 Photoinduced energy (a) and electron (b) transfer processes in a molecular wire based on coordination compounds [76]

An example [76] is given by the $[\text{Ru}(\text{bpy})_3]^{2+} - (\text{ph})_n - [\text{Os}(\text{bpy})_3]^{2+}$ compounds (bpy = 2,2'-bipyridine; ph = 1,4-phenylene; $n = 3, 5, 7$), in which excitation of the $[\text{Ru}(\text{bpy})_3]^{2+}$ unit is followed by electronic energy transfer to the ground state $[\text{Os}(\text{bpy})_3]^{2+}$ unit, as shown by the sensitized emission of the latter. For the compound with $n = 7$ (Fig. 14a), the rate constant for energy transfer over the 4.2-nm metal-to-metal distance is $1.3 \times 10^6 \text{ s}^{-1}$. In the $[\text{Ru}(\text{bpy})_3]^{2+} - (\text{ph})_n - [\text{Os}(\text{bpy})_3]^{3+}$ compounds, obtained by chemical oxidation of the Os-based moiety, photoexcitation of the $[\text{Ru}(\text{bpy})_3]^{2+}$ unit causes the transfer of an electron to the Os-based one with a rate constant of $3.4 \times 10^7 \text{ s}^{-1}$ for $n = 7$ (Fig. 14b). Unless the electron added to the $[\text{Os}(\text{bpy})_3]^{3+}$ unit is rapidly removed, a back electron-transfer reaction (rate constant $2.7 \times 10^5 \text{ s}^{-1}$ for $n = 7$) takes place from the $[\text{Os}(\text{bpy})_3]^{2+}$ unit to the $[\text{Ru}(\text{bpy})_3]^{3+}$ one.

Spacers with energy levels or redox states in between those of the donor and acceptor may help energy or electron transfer (hopping mechanism). Spacers whose energy or redox levels can be manipulated by an external stimulus can play the role of switches for the energy- or electron-transfer processes [48]. For a more thorough discussion of photoinduced energy- and electron-transfer processes in systems involving metal complexes, see [61].

5.2

An Antenna System

In suitably designed dendrimers, electronic energy transfer can be channeled toward a specific position of the array. Compounds of this kind play the role of antennas for light harvesting. We briefly illustrate an example involving luminescent lanthanide ions. For a more extended discussion of dendritic antenna systems, see [77].

Lanthanide ions are known to show a very long-lived luminescence which is a potentially useful property. Because of the forbidden nature of their electronic transitions, however, lanthanide ions exhibit very weak absorption bands, which is a severe drawback for applications based on luminescence. In order to overcome this difficulty, lanthanide ions are usually coordinated to ligands containing organic chromophores whose excitation, followed by energy transfer, causes the sensitized luminescence of the metal ion (antenna effect). Such a process can involve either direct energy transfer from the singlet excited state of the chromophoric group with quenching of the chromophore fluorescence [78], or, most frequently, via $S_1 \rightarrow T_1$ intersystem crossing followed by energy transfer from the T_1 excited state of the chromophoric unit to the lanthanide ion [79, 80].

Amide groups are known to be good ligands for lanthanide ions. The dendrimer shown in Fig. 15 is based on a benzene core branched in the 1, 3, and 5 positions, and it contains 18 amide groups in its branches and 24 chromophoric dansyl units in the periphery [81]. The dansyl units show strong absorption bands in the near-UV spectral region and an intense fluorescence band in the visible region. In acetonitrile/dichloromethane (5 : 1 v/v) solutions, the absorption spectrum and the fluorescence properties of the dendrimer are those expected for a species containing 24 noninteracting dansyl units. Upon addition of lanthanide ions to dendrimer solutions the following effects were observed [81]: (a) the fluorescence of the dansyl units is quenched; (b) the quenching effect is very large for Nd^{3+} and Eu^{3+} , moderate for Yb^{3+} , small for Tb^{3+} , and very small for Gd^{3+} ; and (c) in the case of Nd^{3+} , Er^{3+} , and Yb^{3+} the quenching of the dansyl fluorescence is accompanied by the sensitized near-infrared emission of the lanthanide ion. Interpretation of the results obtained on the basis of the energy levels and redox potentials of the dendrimer and of the metal ions has led to the following conclusions: (1) at low metal ion concentrations, each dendrimer hosts only one metal ion; (2) when the hosted metal ion is Nd^{3+} or Eu^{3+} , all 24 dansyl units of the dendrimer are quenched with unitary efficiency; (3) quenching by Nd^{3+} takes place by direct energy transfer from the fluorescent (S_1) excited state of dansyl to a manifold of Nd^{3+} energy levels, followed by sensitized near-infrared emission from the metal ion ($\lambda_{max} = 1064 \text{ nm}$ for Nd^{3+}); (4) quenching by Eu^{3+} does not lead to any sensitized emission since a ligand-to-metal charge-transfer level lies be-

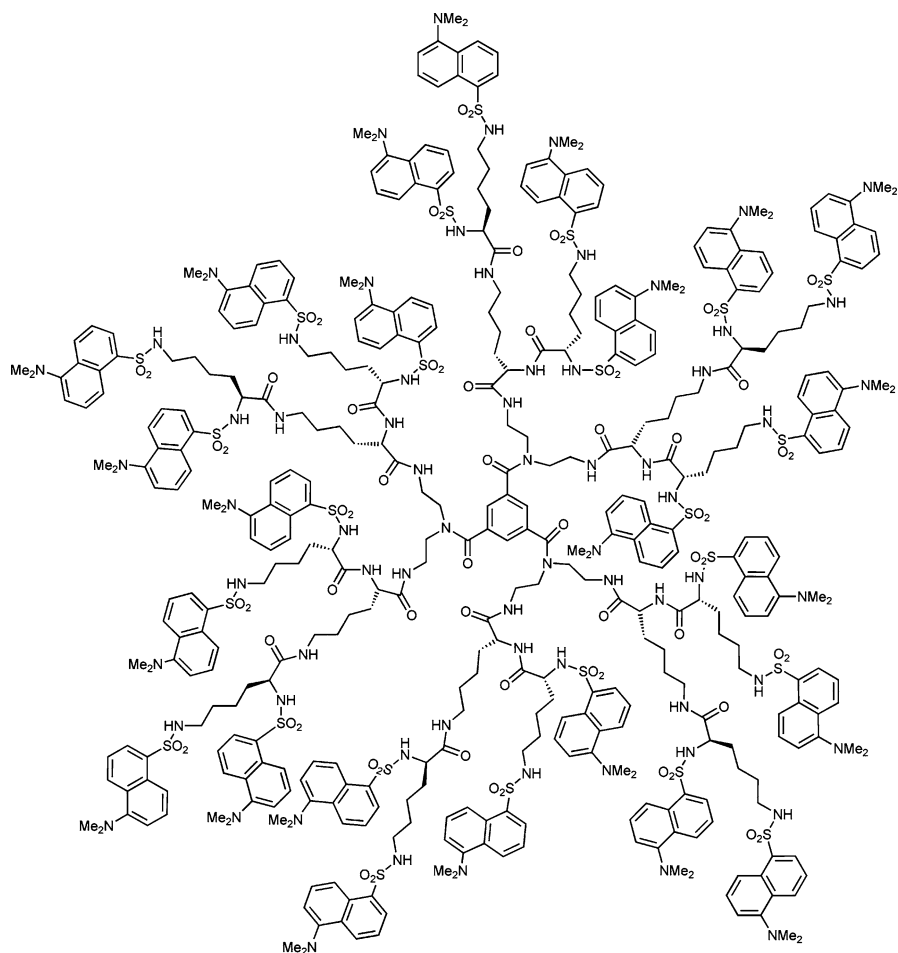


Fig. 15 Dendrimer based on a benzene core branched in the 1, 3, and 5 positions, which contains 18 amide groups in its branches and 24 chromophoric dansyl units in the periphery [81]

low the luminescent Eu^{3+} excited state; (5) in the case of Yb^{3+} , the sensitization of the near-infrared metal-centered emission occurs via the intermediate formation of an upper lying charge-transfer excited state; (6) the small quenching effect observed for Tb^{3+} is partly caused by a direct energy transfer from the fluorescent (S_1) excited state of dansyl; and (7) the very small quenching effect observed for Gd^{3+} is assigned to either induced intersystem crossing or, more likely, to charge perturbation of the S_1 dansyl excited state.

5.3

An Extension Cable

In the attempt of constructing a molecular-level extension cable, the [3]pseudorotaxane shown in Fig. 16, made of the three components A^{2+} , $[BH]^{3+}$, and **C**, has been synthesized and studied [82]. Component A^{2+} consists of two moieties: a $[Ru(bpy)_3]^{2+}$ unit, which plays the role of electron donor under light excitation, and a crown ether, which plays the role of a first socket. The ammonium center of $[BH]^{3+}$, driven by hydrogen-bonding interactions, threads as a plug into the first socket, whereas the bipyridinium unit, owing to charge-transfer (CT) interactions, threads as a plug into the third component, **C**, which plays the role of a second socket. In CH_2Cl_2/CH_3CN (98 : 2 v/v) solution, reversible connection/disconnection of the two plug/socket functions can be controlled independently by acid-base and redox stimulation, respectively. In the fully connected triad, light excitation of the $[Ru(bpy)_3]^{2+}$ unit of component A^{2+} is followed by electron transfer to the bipyridinium unit of component $[BH]^{3+}$, which is plugged into component **C**. Although the transferred electron does not reach the final component of the assembly, the intercomponent connections employed fulfill an important requirement, namely, they can be controlled reversibly and independently. An improved example of a molecular extension cable based on $[Ru(bpy)_3]^{2+}$ has been reported more recently [83].

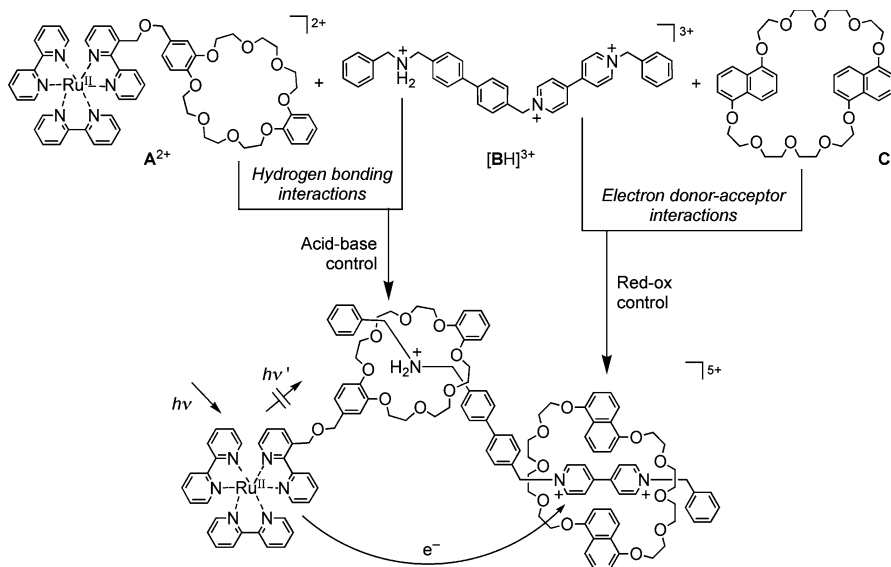
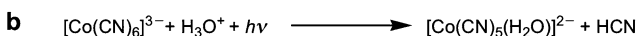
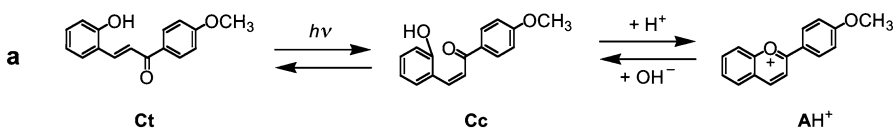


Fig. 16 Schematic representation of a supramolecular system that behaves as a molecular-level extension cable [82]

5.4

An XOR Logic Gate with an Intrinsic Threshold Mechanism

A system based on the photochemistry of a metal complex has been reported to mimic some elementary properties of neurons [84]. Such a system consists of an aqueous solution containing the *trans*-chalcone form (Ct, Fig. 17a) of the 4'-methoxyflavylium ion (AH^+), and the $[Co(CN)_6]^{3-}$ complex ion (as a potassium salt). Excitation by 365-nm light of Ct, which is the thermodynamically stable form of the flavylium species in the pH range 3–7, causes a *trans* $\rightarrow$ *cis* photoisomerization reaction ($\Phi = 0.04$). If the solution is sufficiently acid (pH < 4), the Cc isomer is rapidly protonated with conversion to the 4'-methoxyflavylium ion AH^+ , which is kinetically stable under such pH conditions and exhibits an intense absorption band with maximum at 434 nm and an emission band with maximum at 530 nm. At higher pH values, however, protonation does not occur and the Cc photoproduct is back converted to Ct. As far as $[Co(CN)_6]^{3-}$ is concerned, excitation by 254- or 365-nm light



XOR



c

In ₁ (Flash 1)	In ₂ (Flash 2)	Out (434 nm) ^a
0	0	0
0	1	1
1	0	1
1	1	0

^a Absorption

Fig. 17 An XOR logic system under control of an intrinsic threshold mechanism: the two photoreactions involved (**a** and **b**), and the truth table and symbolic representation of the XOR behavior (**c**) [84]

in acid or neutral aqueous solution causes the dissociation of a CN^- ligand from the metal coordination sphere ($\Phi = 0.31$), with a consequent increase in pH (Fig. 17b).

When an acid solution ($\text{pH}=3.6$) containing $2.5 \times 10^{-5} \text{ mol L}^{-1}$ Ct and $2.0 \times 10^{-2} \text{ mol L}^{-1}$ $[\text{Co}(\text{CN})_6]^{3-}$ is irradiated at 365 nm most of the incident light is absorbed by Ct, which undergoes photoisomerization to Cc. Since the pH of the solution is sufficiently acid, Cc is rapidly protonated (Fig. 17a), with the consequent appearance of the absorption band with maximum at 434 nm and of the emission band with maximum at 530 nm characteristic of the AH^+ species. On continuing irradiation, it can be observed that such absorption and emission bands increase in intensity, reach a maximum value, and then decrease up to complete disappearance. In other words, AH^+ first forms and then disappears with increasing irradiation time. The reason for the off-on-off behavior of AH^+ under continuous light excitation is related to the effect of the $[\text{Co}(\text{CN})_6]^{3-}$ photoreaction (Fig. 17b) on the Ct photoreaction (Fig. 17a). As Ct is consumed with formation of AH^+ , an increasing fraction of the incident light is absorbed by $[\text{Co}(\text{CN})_6]^{3-}$, whose photoreaction causes an increase in the pH of the solution. This change in pH not only prevents further formation of AH^+ , which would imply protonation of the Cc molecules that continue to be formed by light excitation of Ct, but also causes the back reaction to Cc (and, then, to Ct) of the previously formed AH^+ molecules. Clearly, the examined solution performs like a threshold device as far as the input (light)/output (spectroscopic properties of AH^+) relationship is concerned.

Instead of a continuous light source, pulsed (flash) irradiation can be used [83]. Under the input of only one flash, a strong change in absorbance at 434 nm is observed, due to the formation of AH^+ . After two flashes, however, the change in absorbance practically disappears. In other words, an output (434-nm absorption) can be obtained only when *either* input 1 (flash 1) *or* input 2 (flash 2) are used, whereas there is no output under the action of *none* or *both* inputs. This finding shows that the above-described system behaves according to XOR logic, under control of an intrinsic threshold mechanism (Fig. 17c).

Two important features of the above system should be emphasized: (1) intermolecular communication takes place in the form of H^+ ions, and (2) the input and output signals have the same nature (light) and the fluorescence output can be fed, in principle, into another device [85].

5.5

A Sunlight-Powered Nanomotor

In the last few years, a great number of light-driven molecular machines have been developed and the field has been extensively reviewed [48, 55, 86–92]. In several cases, the working principle of such machines exploits photoinduced electron transfer by $[\text{Ru}(\text{bpy})_3]^{2+}$ or related coordination compounds.

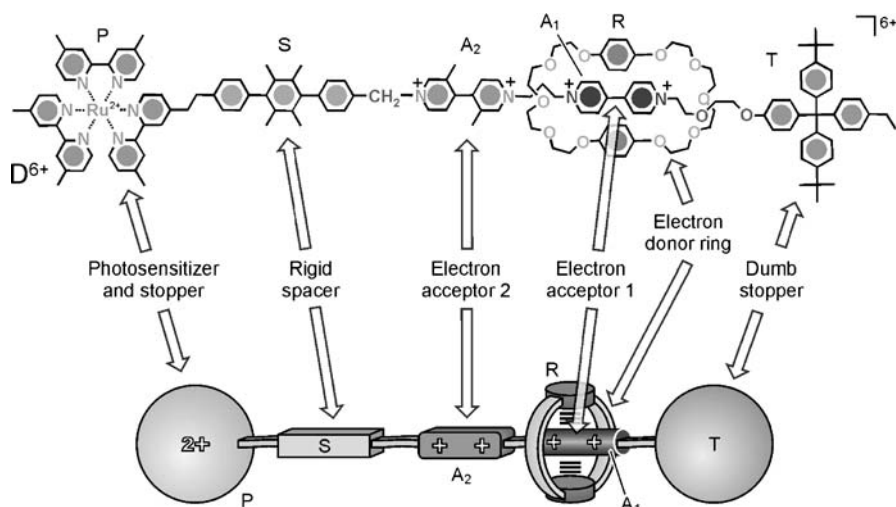


Fig. 18 Chemical formula and cartoon representation of the rotaxane D^{6+} , showing its modular structure [94]

In order to achieve photoinduced ring switching in rotaxanes containing two different recognition sites in the dumbbell-shaped component, the thoroughly designed rotaxane (D^{6+}) shown in Fig. 18 was synthesized [93–95]. This compound is made of the electron-donor macrocycle **R**, and a dumbbell-shaped component which contains (1) $[Ru(bpy)_3]^{2+}$ (**P**) as one of its stoppers, (2) a 4,4'-bipyridinium unit (**A₁**) and a 3,3'-dimethyl-4,4'-bipyridinium unit (**A₂**) as electron-accepting stations, (3) a *p*-terphenyl-type ring system as a rigid spacer (**S**), and (4) a tetraarylmethane group as the second stopper (**T**). The stable translational isomer is the one in which the **R** component encircles the **A₁** unit, in keeping with the fact that this station is a better electron acceptor than the other one. The strategy devised in order to obtain the photoinduced abacus-like movement of the **R** macrocycle, between the two stations **A₁** and **A₂** illustrated in Fig. 19, is based on the following four operations:

- (a) *Destabilization of the stable translational isomer*: light excitation of the photoactive unit **P** (step 1) is followed by the transfer of an electron from the excited state to the **A₁** station, which is encircled by the ring **R** (step 2), with the consequent “deactivation” of this station; such a photoinduced electron-transfer process has to compete with the intrinsic excited-state decay (step 3).
- (b) *Ring displacement*: the ring moves by Brownian motion from the reduced station **A₁^{•−}** to **A₂** (step 4), a step that has to compete with the back electron-transfer process from **A₁^{•−}** (still encircled by **R**) to the oxidized photoactive unit **P⁺** (step 5).

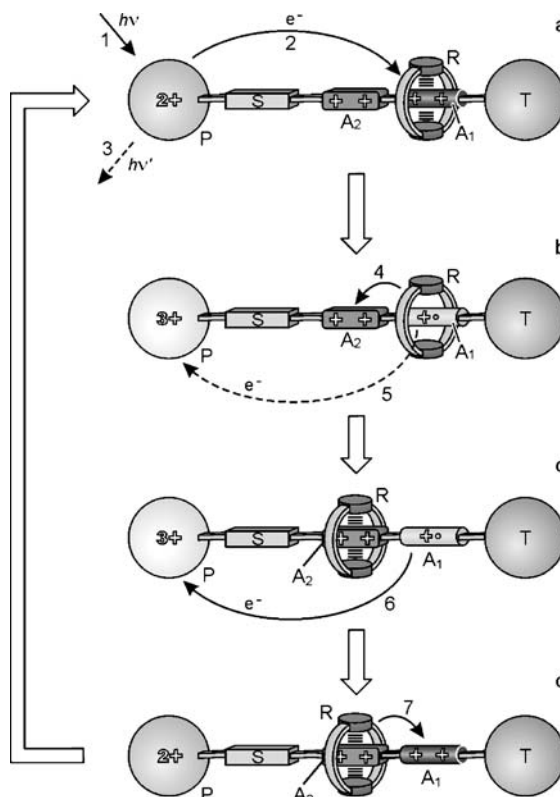


Fig. 19 Schematic representation of the operation of rotaxane D^{6+} as a four-stroke linear nanomotor powered by sunlight [94]

(c) *Electronic reset*: a back electron-transfer process from the “free” reduced station A_1^- to P^+ (step 6) restores the electron-acceptor power to the A_1 station.

(d) *Nuclear reset*: as a consequence of the electronic reset, back movement of the ring from A_2 to A_1 takes place (step 7).

The crucial point is the competition between ring displacement (step 4) and back electron transfer (step 5). The results revealed that in acetonitrile solution at room temperature the ring shuttling rate is one order of magnitude slower than the back electron transfer. Hence, the absorption of light can cause the occurrence of a forward and back ring movement (i.e., a full cycle) with a 2% quantum yield. The low efficiency is compensated by the following features: (1) the operation of the system relies exclusively on intramolecular processes, without generation of any waste product; and (2) since $[Ru(bpy)_3]^{2+}$ shows an intense absorption band in the visible region, the system works simply upon exposure to sunlight. A much higher efficiency

can be obtained by using an electron relay, again consuming only sunlight without generation of waste products [95].

6

Conclusions

Research on the photochemistry and photophysics of coordination compounds has shown an extraordinary quantitative development as well as profound qualitative changes over the years. Studies on intramolecular photoreactions and luminescence properties of coordination compounds of simple ligands have been followed by investigations on compounds containing complex synthetic ligands. Characterization of excited-state properties has been followed by extensive use of metal complexes in bimolecular processes. With the advent of supramolecular chemistry, luminescent and/or photoredox reactive metal complexes have been used as essential components in a bottom-up approach to the construction of molecular devices and machines. In the next few years research on the photochemistry and photophysics of coordination compounds will largely be concentrated on the development of supramolecular systems for solar energy conversion and information processes. In this regard, it should be noted that the photoactive components presently used are very limited in number. Therefore, there is a need to extend basic research in order to discover novel mononuclear coordination compounds capable of exhibiting long excited-state lifetimes, reversible redox behavior, and stability toward photodecomposition. The large number of metals that can be used and the endless number of ligands that can be designed and synthesized open an ample horizon to these studies, as illustrated in the other chapters in this volume.

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References

1. John DHD, Field GTJ (1963) A textbook of photographic chemistry. Chapman and Hall, London
2. Balzani V, Carassiti V (1970) Photochemistry of coordination compounds. Academic, London
3. Ciamician G (1912) Science 36:385
4. Leighton WG, Forbes GS (1930) J Am Chem Soc 52:3139
5. Basolo F, Pearson RG (1958) Mechanisms of inorganic reactions. Wiley, New York
6. Ballhausen CJ (1962) Introduction to ligand field theory. McGraw-Hill, New York
7. Orgel LE (1954) Q Rev London 8:422
8. Jorgensen CK (1962) Absorption spectra and chemical bonding in complexes. Pergamon, Oxford

9. Schlaefer HL (1957) *Z Phys Chem* 11:65
10. Plane RA, Hunt JP (1957) *J Am Chem Soc* 79:3843
11. Adamson AW, Sporer AH (1958) *J Am Chem Soc* 80:3865
12. Carassiti V, Claudi M (1958) *Ann Chim (Rome)* 49:1697
13. Porter GB, Schlaefer HL (1964) *Ber Bunsenges Phys Chem* 68:316
14. Endicott JF, Hoffman MZ (1965) *J Am Chem Soc* 87:3348
15. Balzani V, Carassiti V, Moggi L, Sabbatini N (1965) *Inorg Chem* 4:1247
16. Calvert JG, Pitts JN Jr (1966) *Photochemistry*. Wiley, New York
17. Turro NJ (1967) *Molecular photochemistry*. Benjamin, New York
18. Wayne RP (1970) *Photochemistry*. Butterworths, London
19. Simons JP (1971) *Photochemistry and spectroscopy*. Wiley-Interscience, London
20. Balzani V, Scandola F (1991) *Supramolecular photochemistry*. Horwood, Chichester
21. Schmidtke HH (1966) *Inorg Chem* 5:1683
22. Nazeeruddin MK, Zakeeruddin SM, Kalyanasundaram K (1993) *J Phys Chem* 97:9607
23. Gilbert A, Baggot J (1991) *Essentials of molecular photochemistry*. Blackwell Science, London
24. Montalti M, Credi A, Prodi L, Gandolfi MT (eds) (2006) *Handbook of photochemistry*, 3rd edn. CCR, Taylor and Francis, New York
25. Balzani V, Bolletta F, Gandolfi MT, Maestri M (1978) *Top Curr Chem* 75:1
26. Adamson AW, Fleishauer PD (1975) (eds) *Concepts of inorganic photochemistry*. Wiley-Interscience, New York
27. DeArmond MK (1974) *Acc Chem Res* 7:309
28. Crosby GA (1975) *Acc Chem Res* 8:231
29. Turro NJ (1978) *Modern molecular photochemistry*. Benjamin, Menlo Park
30. Gafney HD, Adamson AW (1972) *J Am Chem Soc* 94:8238
31. Balzani V, Moggi L, Manfrin MF, Bolletta F, Laurence GS (1975) *Coord Chem Rev* 15:321
32. Meyer TJ (1978) *Acc Chem Res* 11:94
33. Whitten DG (1980) *Acc Chem Res* 13:83
34. Sutin N, Creutz C (1980) *Pure Appl Chem* 52:2717
35. Balzani V, Bolletta F, Ciano M, Maestri M (1983) *J Chem Educ* 60:447
36. Velasco JG, Rubinstein I, Crutchley RJ, Lever ABP, Bard AJ (1983) *Inorg Chem* 22:822
37. Balzani V, Moggi L, Manfrin MF, Bolletta F, Gleria M (1975) *Science* 189:852
38. Lehn JM, Sauvage JP (1977) *Nouv J Chim* 1:449
39. Kalyanasundaram K, Graetzel M (1979) *Angew Chem Int Ed Engl* 18:701
40. Gray HB, Maverick AW (1981) *Science* 214:1201
41. Harriman A (1984) *J Photochem* 25:33
42. Creutz C, Sutin N (1975) *Proc Natl Acad Sci USA* 72:2858
43. Juris A, Balzani V, Barigelletti F, Campagna S, Belser P, Von Zelewsky A (1988) *Coord Chem Rev* 84:277
44. Hoffman MZ, Bolletta F, Moggi L, Hug GL (1989) *J Phys Chem Ref Data* 18:219
45. Sutin N (1983) *Prog Inorg Chem* 30:441
46. Lehn JM (1995) *Supramolecular chemistry: concepts and perspectives*. VCH, Weinheim
47. de Rege PJE, Williams SA, Therien MJ (1995) *Science* 269:1409
48. Balzani V, Venturi M, Credi A (2003) *Molecular devices and machines*. Wiley-VCH, Weinheim
49. Schneider HJ, Yatsimirsky A (2000) *Principles and methods in supramolecular chemistry*. Wiley, Chichester
50. Steed JW, Atwood JL (2000) *Supramolecular chemistry*. Wiley, Chichester

51. Lehn JM (1993) In: Kiskörek MV (ed) *Organic chemistry: its language and its state of the art*. VCH, Weinheim, p 77
52. Kaifer AM, Gómez-Kaifer M (1999) *Supramolecular electrochemistry*. Wiley-VCH, Weinheim
53. Balzani V, Scandola F (1996) In: Atwood JL, Davies JED, Macnicol DD, Vögtle F (eds) *Comprehensive supramolecular chemistry*, vol 10. Pergamon, Oxford, p 687
54. Kunkely H, Vogler A (1990) *J Am Chem Soc* 112:5625
55. Balzani V (2003) *Photochem Photobiol Sci* 2:459
56. Balzani V (ed) (2001) *Electron transfer in chemistry*. Wiley-VCH, Weinheim
57. Marcus RA, Sutin N (1985) *Biochim Biophys Acta* 811:265
58. Newton MD (2001) In: Balzani V (ed) *Electron transfer in chemistry*, vol 1. Wiley-VCH, Weinheim, p 3
59. Scandola F, Chiorboli C, Indelli MT, Rampi MA (2001) In: Balzani V (ed) *Electron transfer in chemistry*, vol 3. Wiley-VCH, Weinheim, p 337
60. McConnell HM (1961) *J Chem Phys* 35:508
61. Chiorboli C, Indelli MT, Scandola F (2005) *Top Curr Chem* 257:102
62. Hush NS (1967) *Prog Inorg Chem* 8:391
63. Nelsen SF (2001) In: Balzani V (ed) *Electron transfer in chemistry*, vol 1. Wiley-VCH, Weinheim, p 342
64. Launay JP, Coudret C (2001) In: Balzani V (ed) *Electron transfer in chemistry*, vol 5. Wiley-VCH, Weinheim, p 3
65. Brunschwig BS, Creutz C, Sutin N (2002) *Chem Soc Rev* 31:168
66. Balzani V, Indelli MT, Maestri M, Sandrini D, Scandola F (1980) *J Phys Chem* 84:852
67. Balzani V, Bolletta F, Scandola F (1980) *J Am Chem Soc* 102:2152
68. Orlandi G, Monti S, Barigelletti F, Balzani V (1980) *Chem Phys* 52:313
69. Murtaza Z, Zipp AP, World LA, Graff D, Jones WE Jr, Bates WD, Meyer TJ (1991) *J Am Chem Soc* 113:5113
70. Naqvi KR, Steel C (1993) *Spectrosc Lett* 26:1761
71. Förster T (1959) *Discuss Faraday Soc* 27:7
72. Pullerits T, Sundström V (1996) *Acc Chem Res* 29:381
73. Dexter DL (1953) *J Chem Phys* 21:836
74. Closs GL, Johnson DM, Miller JR, Piotrowiak P (1989) *J Am Chem Soc* 111:3751
75. Scandola F, Balzani V (1983) *J Chem Educ* 60:814
76. Schlicke B, Belser P, De Cola L, Sabbioni E, Balzani V (1999) *J Am Chem Soc* 121:4207
77. Ceroni P, Bergamini G, Marchioni F, Balzani V (2005) *Prog Polym Sci* 30:453
78. Hebbink GA, Klink SI, Grave L, Oude Alink PGB, van Veggel FCJM (2002) *Chem Phys Chem* 3:1014
79. Parker D, Dickens RS, Puschmann H, Crossland C, Howard JAK (2002) *Chem Rev* 102:1977
80. Sabbatini N, Guardigli M, Lehn J-M (1993) *Coord Chem Rev* 123:201
81. Vicinelli V, Ceroni P, Maestri M, Balzani V, Gorka M, Vögtle F (2002) *J Am Chem Soc* 124:6461
82. Ballardini R, Balzani V, Clemente-León M, Credi A, Gandolfi MT, Ishow E, Perkins J, Stoddart JF, Tseng HR, Wenger S (2002) *J Am Chem Soc* 124:12786
83. Ferrer B, Rogez G, Credi A, Ballardini R, Gandolfi MT, Balzani V (2006) *Proc Natl Acad Sci USA* 103:18411
84. Pina F, Melo MJ, Maestri M, Passaniti P, Balzani V (2000) *J Am Chem Soc* 122:4496
85. Balzani V, Venturi M, Credi A (2003) *Logic gates*. In: *Molecular devices and machines*. Wiley-VCH, Weinheim, p 235
86. Balzani V, Credi A, Raymo FM, Stoddart JF (2000) *Angew Chem Int Ed* 39:3348

87. Stoddart JF (ed) (2001) Special issue on molecular machines. *Acc Chem Res* 34:409
88. Venturi M, Credi A, Balzani V (2001) Electron-transfer processes in pseudorotaxanes. In: Balzani V (ed) *Electron transfer in chemistry*, vol 3. Wiley-VCH, Weinheim, p 501
89. Ballardini R, Gandolfi MT, Balzani V (2001) Electron-transfer processes in rotaxanes and catenanes. In: Balzani V (ed) *Electron transfer in chemistry*, vol 3. Wiley-VCH, Weinheim, p 539
90. Ballardini R, Balzani V, Credi A, Gandolfi MT, Venturi M (2001) *Acc Chem Res* 34:445–455
91. Sauvage JP (ed) (2001) *Molecular machines and motors*. Springer, Berlin
92. Kelly TR (ed) (2005) *Molecular machines*. *Top Curr Chem*, vol 262. Springer, Berlin
93. Ashton PR, Ballardini R, Balzani V, Credi A, Dress R, Ishow E, Kleverlaan CJ, Kocian O, Preece JA, Spencer N, Stoddart JF, Venturi M, Wenger S (2000) *Chem Eur J* 6:3558
94. Balzani V, Credi A, Ferrer B, Silvi S, Venturi M (2005) In: Kelly TR (ed) *Molecular machines*. *Top Curr Chem* 262:1
95. Balzani V, Clemente-León M, Credi A, Ferrer B, Venturi M, Flood AH, Stoddart JF (2006) *Proc Natl Acad Sci USA* 103:1178

Photochemistry and Photophysics of Coordination Compounds: Chromium

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Abstract The study of the photochemistry and photophysics of octahedral and pseudo-octahedral Cr(III) complexes has a rich history. An initial discussion is devoted to a general appraisal of the state of these two subjects up to December 1998, after providing a framework of state energy levels and radiative and non-radiative relaxation processes relevant to Cr(III) systems. The remaining sections cover some of the more active areas in the Cr(III) field, such as ultrafast dynamics, photosubstitution, thermally activated

excited state relaxation, energy transfer, and photoactivated redox processes (both intermolecular and intramolecular). Each of these sections begins with an overview of the subject area, and then one or more representative papers from the recent literature are selected for more detailed discussion.

Keywords Energy transfer · Photoredox · Photosubstitution · Thermal excited state relaxation · Ultrafast dynamics

1

Introduction

Investigations of the photobehavior of octahedral (O_h) or pseudo-octahedral chromium(III) complexes have played a pivotal role in the development of transition metal photochemistry as a vital scientific discipline. Except for the case of ruthenium(II), the photochemistry and photophysics of Cr(III) systems have been explored more fully than those of any other transition metal ion. Their photoactivity has been extensively reviewed previously, and readers are directed to the coverage in three texts [1–3], and the excellent discussion in the most recent comprehensive review of the topic by Kirk (which covered the literature up to December 1998) [4]. Several shorter Cr(III) reviews have since appeared, which have focused on a diverse range of more specific topics such as the excited state chemistry of pentacyanochromate(III) anions [5], intermediates in Cr(III) photochemistry [6], emission properties of hexam(m)ine Cr(III) systems [7], the interaction of $[M(\text{diimine})_3]^{n+}$ complexes of Ru(II) and Cr(III) with DNA [8], and thermal excited state relaxation [9].

The Cr(III) field remains an active one, and the objective of the present chapter is to provide an overview of some of the interesting developments in the area from 1999 to December 2006.

2

State Energy Levels and General Excited State Behavior

The electronic configuration of the Cr^{3+} ion is $[\text{Ar}]3d^3$. In its octahedral (O_h) complexes the degeneracy of the Cr d orbitals is lifted, resulting in two orbital subsets of t_{2g} and e_g symmetry. The $^4A_{2g}$ (quartet) ground state has the electronic configuration $(t_{2g})^3$, with the d orbitals filled according to Hund's Rule. Two excited states with $(t_{2g})^2(e_g)^1$ electronic configuration result from promotion of a t_{2g} electron to an e_g orbital while preserving electronic spin. Six such spin-allowed promotions are possible, which in O_h symmetry are divided into two sets differing in the magnitude of the interelectronic repulsion terms. The associated quartet excited states generated are labeled $^4T_{2g}$

and $^4T_{1g}$, respectively, with the former level being the more stable. For almost all octahedral Cr(III) complexes studied, the two lowest-lying excited states are the $^2T_{1g}$ and ^2E_g (doublet) levels of $(t_{2g})^3$ electronic configuration, where spin-pairing has occurred within the t_{2g} subshell. A qualitative orbital energy level diagram depicting the electron occupation of the pertinent electronic ground and excited states discussed above is provided in Fig. 1.

A representative state energy level diagram for octahedral Cr(III) compounds was presented in Chap. 1 of this volume (Fig. 5b). Consistent with this diagram, for the preponderance of Cr(III) complexes the ^2E_g state has the lower energy of the two doublet excited states [1, 2]. However, exceptions occur occasionally for mixed ligand systems such as *trans*-[CrN₄F₂]⁺ of D_{4h} symmetry, where splitting of the $^2T_{1g}$ (O_h) excited state (into $^2A_{2g}$ and ^2E_g in D_{4h} symmetry) results in its ^2E_g (D_{4h}) component lying lower in energy than the components of the ^2E_g (O_h) level [10, 11]. The generic Jablonski diagram shown in Chap. 1 of this volume (Fig. 6) has been modified in Fig. 2 of this chapter for the specific case of octahedral Cr(III) complexes.

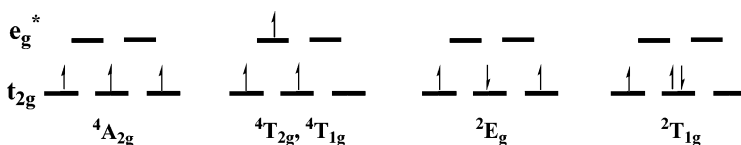


Fig. 1 The d orbital diagram for the electronic ground and excited states for d^3 Cr(III) complexes assuming O_h symmetry

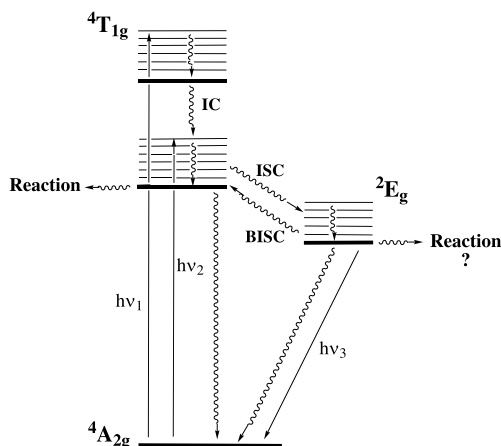


Fig. 2 Jablonski state energy level diagram for O_h Cr(III) complexes, showing the principal processes that may occur subsequent to vertical excitation to a $^4T_{2g}$ or $^4T_{1g}$ Franck–Condon excited state. *Full arrows* represent radiative processes (absorption or emission), whereas *wavy arrows* designate radiationless deactivation processes

The dominant ligand field bands in the UV-visible absorption spectra are associated with the ${}^4A_{2g} \rightarrow {}^4T_{2g}$ and ${}^4A_{2g} \rightarrow {}^4T_{1g}$ transitions, since the corresponding absorptions generating the two doublet excited states are both Laporte and spin multiplicity forbidden. Photochemical and photophysical studies of Cr(III) species are, therefore, usually restricted to initial excitation into one of the quartet excited states. The spin-allowed absorption bands for the ${}^4A_{2g} \rightarrow {}^4T_{2g}$ and ${}^4A_{2g} \rightarrow {}^4T_{1g}$ transitions are broad. This is a consequence of the ${}^4T_{2g}$ and ${}^4T_{1g}$ excited states both having an electron residing in an e_g antibonding σ^* orbital (Fig. 1), which results in a large nuclear displacement relative to the ground state. For excitation into the higher lying ${}^4T_{1g}$ level, very fast internal conversion (IC) occurs to the ${}^4T_{2g}$ state with near unit efficiency. Under normal photochemical conditions (i.e., in solution near room temperature) ${}^4T_{2g} \rightarrow {}^4A_{2g}$ fluorescence is rarely observed [12, 13], due to ${}^4T_{2g} \rightarrow {}^2E_g$ intersystem crossing (ISC) being an unusually rapid process [4, 13–15] and often occurring with high efficiency (see Table 4 in [4]). With only occasional exceptions, Cr(III) complexes in rigid low temperature media exhibit intense, long-lived phosphorescence from the ${}^2E_g$ level generated by ISC. Very little geometric change is expected between the ${}^4A_{2g}$ ground state and ${}^2E_g$ excited state, due their common $(t_{2g})^3$ orbital parentage. As a result, low temperature ${}^2E_g \rightarrow {}^4A_{2g}$ phosphorescence spectra often display sharp, highly resolved fine structure, which has led to a very extensive literature (including medium and temperature effects) on the photophysical properties of these systems [2, 4, 9, 11, 16].

In room temperature (rt) solution, ${}^4A_{2g} \rightarrow {}^4T_{2g}$ (or ${}^4A_{2g} \rightarrow {}^4T_{1g}$) excitation often leads to facile substitution of one or more bound ligands by solvent or an added nucleophile [1–4]. This observation does not, however, preclude the possibility of reaction out of the lower lying ${}^2E_g$ level, since this state is subsequently populated by rapid and efficient ${}^4T_{2g} \rightarrow {}^2E_g$ ISC. An enormous effort has been expended over the last 30 years in an attempt to determine the relative photochemical roles of the ${}^4T_{2g}$ and ${}^2E_g$ excited states. Importantly, a significant number of Cr(III) complexes exhibit relatively long-lived (≥ 100 ns) phosphorescence in solution near rt, and this emission can be bimolecularly quenched by added reagents. Comparing photoreaction data for experiments carried out in the presence and absence of these added reagents (an approach first pioneered by Chen and Porter [17]) has in many instances proved very informative.

The most definitive quenching studies have been for the strong field hexacyano complex $[Cr(CN)_6]^{3-}$ [18] and the pentacyano species $[Cr(CN)_5(X)]^{n-}$, where $X = NH_3$ [19], pyridine (py) [20], and NCS^- [5]. Under experimental conditions of total emission quenching, no reaction quenching was detected. Such data provide compelling evidence for the reaction proceeding exclusively out of the ${}^4T_{2g}$ level (a similar conclusion was reached for $[Cr(CN)_6]^{3-}$ based on sensitization studies [21, 22]). For most Cr(III) systems, however,

total phosphorescence quenching is accompanied by significant but less than total reaction quenching. Definitively establishing the precise role of the doublet level in this quenched reaction component has proven an elusive goal, with competing options including direct ^2E_g reaction, ^2E_g tunneling to a ground state intermediate (GSI) surface, or “delayed” quartet excited state reaction via thermally activated $^2E_g \rightarrow ^4T_{2g}$ back-intersystem crossing, BISC (Fig. 2).

This debate has been exhaustively discussed elsewhere [4, 6, 23, 24], and will not be a focus of this review. From the outset, it was appreciated that the $^4T_{2g}$ level of $(t_{2g})^2(e_g)^1$ orbital parentage was an attractive candidate for substitution chemistry, based on the occupation of an e_g orbital which is σ^* antibonding with respect to the metal–ligand (M–L) bond. At present, the most widely employed theoretical model for rationalizing Cr(III) photosubstitution behavior, assuming quartet reactivity, is the semi-empirical symmetry restricted angular overlap model (AOM) developed by Vanquickenborne and Ceulemans [25–27]. For mixed ligand systems it has had considerable success in predicting relative ligand labilities based on identifying the plane of labilization and assuming that the ligand with the smallest excited state M–L bond strength is preferentially substituted. A further strength of the model is the rationalization it provides for the stereochemical change that is a common feature of Cr(III) photochemistry (in contrast to their corresponding thermal behavior), especially for cases of axial ligand loss in mixed ligand systems of D_{4h} or C_{4v} symmetry [4, 28]. A more recent *ab initio* study of the photochemistry of Cr(III) ammine systems yielded results in good agreement with the earlier AOM calculations [29]. Tris-polypyridyl Cr(III) complexes may prove to be an exception to this apparent preference for quartet excited state reactivity. Early quenching studies on $[\text{Cr}(\text{phen})_3]^{3+}$ (where phen = 1,10-phenanthroline) revealed up to 95% reaction quenching in the presence of doublet quenchers such as I^- and NCS^- [30, 31], and the data from subsequent and more detailed investigations were most readily interpreted in terms of a direct doublet excited state reaction pathway [32–34].

The remaining sections of this chapter are devoted to a discussion of developments since December 1998 in a range of different focus areas of Cr(III) photochemistry and photophysics. For convenience, the state term symbols for O_h symmetry shown in Fig. 2 are usually employed during these discussions.

3

Ultrafast Dynamics of Cr(III) Ligand Field Excited States

Ultrafast time-resolved absorption spectroscopy constitutes one of the most exciting and promising new frontiers in transition metal photochemistry and photophysics. The term ultrafast is applied to photoprocesses that occur on

the time scale of nuclear motion, and have until recently been most frequently associated with intramolecular processes such as vibrational equilibration and conformational dynamics and with medium effects such as solvation shell reorientation. The time frames involved are in the femtosecond to low picosecond range, and because of the challenging experimental demands, the field of ultrafast transition metal spectroscopy is still in its infancy [35–37].

As depicted earlier (Fig. 2), for the Franck–Condon excited level generated by initial light absorption, evolution down to lower-energy excited states involves processes such as IC, ISC, and vibrational relaxation (VR). Conventional wisdom based on organic experience suggests that the rate constants for these three processes would normally be in the order: $k_{VR} > k_{IC} > k_{ISC}$ [38]. However, the observation that $\text{Cr(III)}\ ^2E_g \rightarrow ^4A_{2g}$ phosphorescence yields and emission/reaction quenching ratios showed some dependence on the wavelength chosen for $^4A_{2g} \rightarrow ^4T_{2g}$ excitation led to the suggestion that $^4T_{2g} \rightarrow ^2E_g$ ISC may compete successfully with $^4T_{2g}$ vibrational cooling [39–43]. This possibility received support from picosecond pulse laser studies that showed that the rise time for ^2E_g excited state transient absorption was shorter than the instrument time response [12–14].

3.1

Ultrafast Dynamics of ^2E_g State Formation in Cr(acac)_3

The first Cr(III) femtosecond spectroscopic study addressing the questions raised above has been very recently reported in an elegant study by Juban and McCusker for the test case of $[\text{Cr(acac)}_3]$ (where acac = acetylaceto-

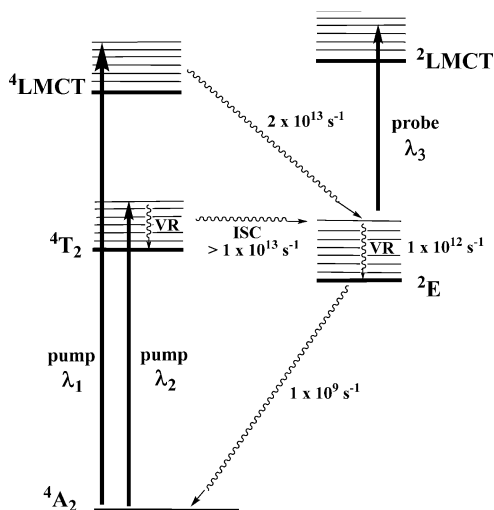


Fig. 3 Simplified Jablonski state energy level diagram for $[\text{Cr(acac)}_3]$

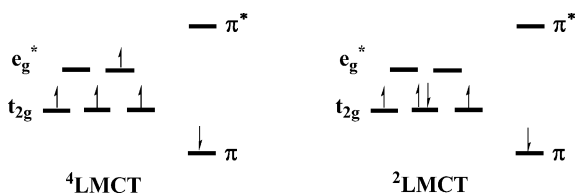


Fig. 4 A one-electron representation of the orbital electron populations for the $^4\text{LMCT}$ and $^2\text{LMCT}$ excited states of $[\text{Cr}(\text{acac})_3]$

nate) [15, 37]. The state and orbital energy level diagrams for this molecule are shown in Figs. 3 and 4, respectively.

Both ligand-field $^4\text{A}_2 \rightarrow ^4\text{T}_2$ and charge transfer $^4\text{A}_2 \rightarrow ^4\text{LMCT}$ pulse excitation experiments were performed, the former being the first such study for any transition metal system. Time evolution for ^2E excited state formation in CH_3CN solution at ambient temperature was followed by monitoring the transient signal associated with the $^2\text{E} \rightarrow ^2\text{LMCT}$ transition. Data analysis yielded the rate constants shown in Fig. 4, and provides convincing evidence that $^4\text{T}_2 \rightarrow ^2\text{E}$ ISC competes effectively with vibrational relaxation in the initially formed $^4\text{T}_2$ state. Coupling these results with those from related studies on $[\text{Fe}(\text{tren}(\text{py})_3)]^{2+}$ (where tren is tris(2-pyridylmethyliminoethyl)amine) [44], the authors argue that for transition metal systems the relative nuclear equilibrium displacements of potential energy surfaces and the high density of states may have a larger influence on the time-course of Franck–Condon excited state relaxation than spin selection rules [15, 37].

4

Photosubstitution Studies

A survey of the literature since 1999 reveals a marked decrease in activity in this foundation area of transition metal photochemistry, concomitant with the rapid development of the new areas of interest identified in Chap. 1 of this volume. For the case of octahedral or pseudo-octahedral $\text{Cr}(\text{III})$ species, only ten articles have been identified where ligand photosubstitution studies were the primary activity investigated [5, 6, 45–52]. Highlights from some of these papers are presented below.

4.1

$[\text{Cr}(\text{phen})_3]^{3+}$ Photoracemization/Hydrolysis

The loss of optical activity of Λ - $[\text{Cr}(\text{phen})_3]^{3+}$ upon photolysis in aqueous solution exhibits a strong pH dependence [31, 32]. Under acidic conditions,

the rate of direct racemization is much larger than that of acid hydrolysis to a *cis*-[Cr(phen)₂(H₂O)₂]³⁺ product. In contrast, at pH ≥ 11, the rate of optical activity loss matches closely that for base hydrolysis to a *cis*-[Cr(phen)₂(OH)₂]⁺ product, and it was suggested that the loss of optical activity under basic conditions occurs primarily via the hydrolysis path. However, these data did not preclude the possibility that a substantial fraction of rotation loss might occur via direct racemization, provided there is significant retention of optical configuration in the base hydrolysis reaction.

A recent paper demonstrates that chiral capillary electrophoresis (CE) provides a very effective direct probe of the extent of racemization of parent Λ -[Cr(phen)₃]³⁺, while simultaneously determining the optical purity of the hydrolysis product [49]. The electropherogram shown in Fig. 5 (electropherogram A) is for a mixture of *rac*-[Cr(phen)₃]³⁺ and *cis-rac*-[Cr(phen)₂(H₂O)₂]³⁺ (where 50 mM dibenzoyl-L-tartrate was employed as the capillary chiral additive), while the electropherogram for parent Λ -[Cr(phen)₃]³⁺ prior to photolysis is provided in Fig. 5 (electropherogram B).

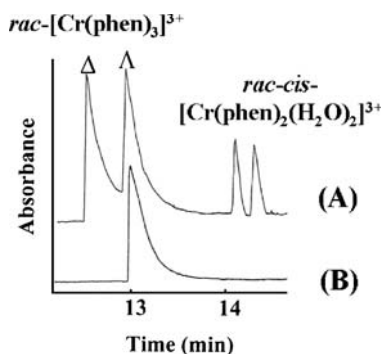


Fig. 5 Electropherograms of A an aqueous mixture of 1 mM *rac*-[Cr(phen)₃]³⁺ and 1 mM *cis-rac*-[Cr(phen)₂(H₂O)₂]³⁺, and B a 1 mM aqueous solution of Λ -[Cr(phen)₃]³⁺, using 50 mM sodium dibenzoyl-L-tartrate as chiral additive in 25 mM borate buffer, pH 9.2 (20 °C). Detection wavelength = 320 nm

The corresponding electropherograms for Λ -[Cr(phen)₃]³⁺ solutions irradiated for 24 min at 350 nm at pH 2.2 and pH 11.6, respectively, are presented in Fig. 6.

The pH 2.2 data (Fig. 6) show significant formation of Δ -[Cr(phen)₃]³⁺, but no bands (in agreement with expectation) for *cis*-[Cr(phen)₂(H₂O)₂]³⁺ product. The corresponding pH 11.6 results (Fig. 6) are strikingly different. There is no evidence for direct Λ -[Cr(phen)₃]³⁺ racemization, while extensive hydrolysis is observed with no apparent retention of absolute configuration. In a control experiment, no loss of optical activity was observed on irradiating a Δ -*cis*-[Cr(phen)₂(OH)₂]⁺ solution for 60 min at pH 11.6. These results provide direct verification that optical rotation loss for Λ -[Cr(phen)₃]³⁺

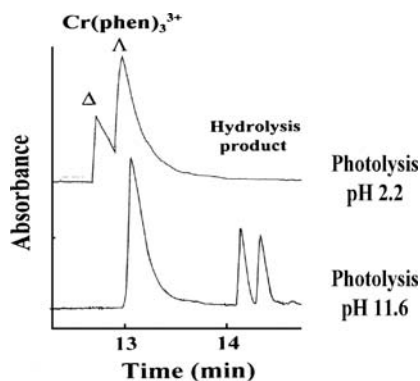


Fig. 6 Electropherograms of 5 mM aqueous solutions of Λ -[Cr(phen)₃]³⁺ after 350 nm photolysis for 24 min at pH 2.2 and pH 11.6, using 50 mM sodium dibenzoyl-L-tartrate as chiral additive in 25 mM borate buffer, pH 9.2 (20 °C). Detection wavelength = 320 nm

under strongly basic conditions is predominantly a consequence of hydrolysis.

4.2

Axial Ligand Photodissociation in Cr(III) Porphyrins

In a series of nanosecond laser photolysis studies, Inamo and coworkers have recently explored the details of axial ligand photosubstitution (and recombination) for a range of Cr(III) porphyrin systems of the type [Cr(porphyrin)(Cl)(L)] in toluene and dichloromethane solution [46, 47, 50, 51]. Interest in this area derives from the possible biological implications and the role of Cr(III) porphyrins in a variety of photocatalytic reactions.

The presence of the highly conjugated porphyrin ring leads to orbital and state energy level diagrams considerably different from those normally encountered for Cr(III) complexes. Iterative extended Huckel calculations [52] predict that a vacant d_z^2 and half-filled d_{xy} , d_{xz} , and d_{yz} orbitals of the Cr(III) center are located between the HOMO π and LUMO π^* orbitals of the porphyrin ring, while the empty Cr $d_x^2 - y^2$ orbital lies well above the porphyrin LUMO π^* orbital. Weak coupling of the porphyrin (π, π^*) states with the paramagnetic Cr(III) center results in the singlet ground and excited $^1(\pi, \pi^*)$ states becoming $^4S_0$ and $^4S_1$ levels, respectively, whereas the excited triplet $^3(\pi, \pi^*)$ state is split into tripdoublet $^2T_1$, tripquartet $^4T_1$, and tripsextet $^6T_1$ levels. The resultant state energy level diagram is shown in Fig. 7 [52].

In the studies by Inamo and coworkers, several porphyrin ring systems were utilized (tetraphenylporphyrin, octaethylporphyrin, and tetramesitylporphyrin) as well as a range of leaving axial ligands (L = H₂O, pyridine, piperidine, 1-methylimidazole, triphenylphosphine, and triphenylphosphine oxide). Analysis of the transient spectra observed, following initial pulse exci-

As shown in Fig. 8, the quenchable and non-quenchable dissociation pathways are both thought to proceed through lower-lying porphyrin π -Cr d_{π} charge transfer (CT) states [48]. For example, an increase in the electron density in a Cr d_{π} orbital with a z -axis component should lead to a weakening in the Cr-axial ligand bond. The rich photobehavior of these systems suggests that they would make good candidates for future ultrafast spectroscopic studies.

5

Thermally Activated ^2E_g Excited State Relaxation Studies of Sterically Constrained Systems

Early studies on Cr(III) complexes of the type $[\text{Cr}(\text{N}_4)\text{X}_2]^{n+}$ where N_4 is the macrocyclic ligand cyclam or tet a (see Fig. 9) and $\text{X} = \text{Cl}^-$ [53, 54], CN^- [55, 56], NH_3 [56–58], and F^- [59] revealed a marked difference in the photobehavior of the geometric isomers. All the *trans* isomers are photoinert while the *cis* species are photoreactive. The cyano, ammine, and fluoro systems drew particular attention because of their strong emission in rt solution, with accompanying lifetimes almost identical to those reported at 77 K. These observations were attributed to the steric rigidity of the macrocyclic ring restricting access to the thermally activated photochemical relaxation channels available to their non-macrocyclic analogs.

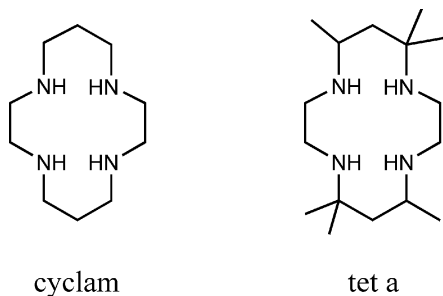


Fig. 9 Macrocyclic- N_4 ligands, cyclam and tet a

An extensive literature now exists on the effects of ligand steric constraint on ^2E_g excited state relaxation [4, 60–71], with studies by Endicott and coworkers being especially noteworthy. Hexaam(m)ine Cr(III) systems have been one key area of study of Endicott's group, where a range of complexes were synthesized containing ligands that would be trigonally strained if coordinated octahedrally to Cr(III). Their studies provided convincing evidence that the more trigonally strained ligand systems underwent more rapid ^2E_g deactivation. In an illustrative example [63], the photobehavior of $[\text{Cr}(\text{en})_3]^{3+}$ was

compared with that of the quasi-cage complex $[\text{Cr}(\text{sen})]^{3+}$, where $[\text{Cr}(\text{sen})]^{3+}$ can be regarded as a $[\text{Cr}(\text{en})_3]^{3+}$ analog with a neopentyl cap bonded in a facial position.

X-ray crystallographic data revealed that the CrN_6 microsymmetry is virtually identical for these two complexes, with the NCrN bond angles in $[\text{Cr}(\text{sen})]^{3+}$ being slightly closer to octahedral. These data and MM2 calculations also established considerable trigonal strain in the neopentyl cap for $[\text{Cr}(\text{sen})]^{3+}$.

Both compounds were found to have similar ${}^2\text{E}_g \rightarrow {}^4\text{A}_{2g}$ emission lifetimes at 77 K (120 μs and 171 μs for the en and sen complexes, respectively), and fairly comparable quantum yields for photoaquation in rt solution (0.27 and 0.10, respectively). However, the ${}^2\text{E}_g$ lifetime for $[\text{Cr}(\text{sen})]^{3+}$ in ambient solution was a factor of 10^4 times shorter than that for $[\text{Cr}(\text{en})_3]^{3+}$. The authors attributed this difference to a thermally activated ${}^2\text{E}_g$ deactivation channel promoted by steric factors associated with the sen complex. The general conclusion from this body of work was that large amplitude trigonal twists can facilitate thermally activated ${}^2\text{E}_g$ relaxation for a range of sterically constrained hexaam(m)ine $\text{Cr}(\text{III})$ complexes [64]. The authors also suggest that this relaxation pathway may have mechanistic implications for the photoracemization of $\text{Cr}(\text{III})$ species with D_3 symmetry [63]. Such a reaction channel could, for example, facilitate the trigonal twist pathway invoked for the observed photoinversion of Λ -*fac*- $[\text{Cr}(\text{S-trp})_3]$ to Δ -*fac*- $[\text{Cr}(\text{S-trp})_3]$ (where S-trp is the bidentate amino acid ligand S-tryptophan) [72].

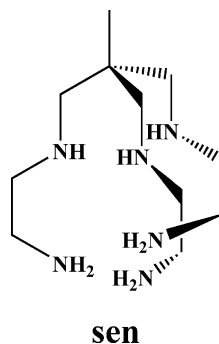


Fig. 10 Quasi-cage N_6 ligand, sen

The earlier studies on macrocyclic *cis*- and *trans*- $[\text{Cr}(\text{N}_4)\text{X}_2]^{n+}$ complexes (where X is NH_3 or CN^-) were also expanded by Endicott's group to include systems where stereochemical perturbations were introduced by the presence of methyl substituents in the macrocyclic ring in positions near the Cr-X coordination sites [65]. Their analysis of X-ray data and MM2 calculations supported the hypothesis that the more facile thermally activated ${}^2\text{E}_g$ relaxation of the *cis*- $[\text{Cr}(\text{N}_4)\text{X}_2]^{n+}$ systems is predominantly a stereochemi-

cal effect. It was also argued that ^2E_g back-intersystem crossing (BISC) was not likely to be an important component of ^2E_g excited state deactivation for Cr(III) complexes with N_6 or N_4C_2 chromophores [64]. This latter conclusion has been questioned by Kirk [4, 68], and in Sect. 5.1 the subject is discussed further. In Sect. 5.2 some very recent work by the Wagenknecht group employing a new series of sterically constrained N_4 -macrocycles is featured [69–71].

5.1

$[Cr(sen)]^{3+}$ and $[Cr[18]aneN_6]^{3+}$

5.1.1

$[Cr(sen)_3]^{3+}$

In a recent report, Kirk and coworkers have reinvestigated the photobehavior of $[Cr(sen)]^{3+}$, and compared it with that for the macrocyclic complex, $[Cr[18]aneN_6]^{3+}$ [68].

The data obtained for $[Cr(sen)]^{3+}$ supported the earlier report of a very short doublet lifetime in rt aqueous solution, and the photoaquation quantum yield of 0.10 determined upon $^4A_{2g} \rightarrow ^4T_{2g}$ excitation was in excellent agreement with that recorded earlier.

However, based on a more detailed investigation of $[Cr(sen)]^{3+}$ photoaquation, it was proposed that this process occurs via the $^4T_{2g}$ excited state after back-intersystem crossing (BISC). The more convincing argument presented was that direct irradiation into the ^2E_g state yielded a photoaquation quantum yield 22% lower than that for $^4T_{2g}$ excitation. However, as noted by the authors, direct spin-forbidden doublet excitation experiments are fraught with difficulties. Their second argument was based on a deter-

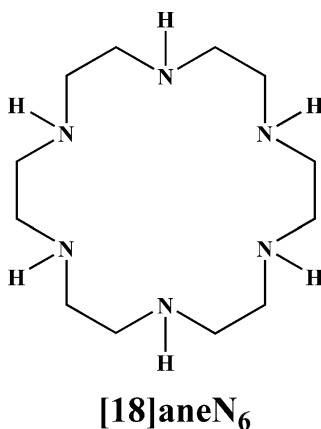


Fig. 11 Macrocyclic- N_6 ligand, $[18]aneN_6$

mination of the stereochemistry of the $[\text{Cr}(\text{sen-NH})(\text{H}_2\text{O})]^{4+}$ photoaquation product via chiral capillary electrophoresis analysis (CE), employing D-tartrate as the chiral capillary additive. The primary aquation product exhibited only a single peak, consistent with the presence of *trans* product – a result anticipated by AOM theory assuming quartet excited state reactivity. However, a control thermal aquation experiment (where isomerism is not expected) also yielded the same data. Although an explanation was offered for this latter result, the reviewer notes from experience [49, 73] that the CE separation of the Δ and Λ isomers of *cis* hydrolysis products is often difficult, and a definitive assignment of a single peak to the *trans* isomer can be made confidently only after several chiral additives have been tested in the capillary buffer medium.

5.1.2

$[\text{Cr}18]\text{aneN}_6]^{3+}$

No emission was detectable from this compound in rt solution, despite the presence of strong, long-lived ${}^2\text{E} \rightarrow {}^4\text{A}_{2g}$ phosphorescence (162 μs) at 77 K [67]. A temperature dependence study of the lifetime for this transition showed the usual low and high temperature regimes, with a single-exponential fit to the high temperature region giving an apparent activation energy of 34 kJ mol^{-1} . Interestingly, however, the compound was also photoinert in ambient solution. X-ray crystallographic data on $[\text{Cr}18]\text{aneN}_6]^{3+}$ indicated S_6 point group symmetry for the complex, with no evidence for trigonal twist strain in the 18aneN_6 ligand. The authors argue, therefore, that the Endicott thermally activated ${}^2\text{E}_g$ relaxation model is unlikely to be operative in this case. Instead, they propose that fast radiationless decay at rt is a consequence of the S_6 distortion from octahedral geometry, which leads to a mixing of states with doublet and quartet character and a facilitation of ${}^2\text{E}_g$ ISC to the ground state. In the light of data to be presented in Sect. 5.2, one could also conjecture whether a contributing factor to the short rt lifetimes might be a non-productive reaction pathway involving transient Cr – N bond cleavage.

Finally, note is made of the recent communication by Sargeson and co-workers on the remarkable photobehavior of the caged hexamine complex, $[\text{Cr}(\text{fac-Me}_5\text{-D}_{3h}\text{tricosaneN}_6)]^{3+}$ [74]. This photoinert compound exhibits unique photophysical behavior for an N_6 chromophoric Cr(III) species in rt aqueous solution. In addition to displaying an exceptionally long ${}^2\text{E}_g$ state lifetime ($\tau = 235 \mu\text{s}$), the emission shows a very strong isotope effect upon N – H deuteration ($\tau = 1.5 \text{ ms}$). These observations demonstrate that ${}^2\text{E}_g$ excited state decay in solution at ambient temperature is dominated by ${}^2\text{E}_g \rightarrow {}^4\text{A}_{2g}$ radiationless deactivation, promoted by high frequency N – H stretching acceptor modes. Importantly, the results also argue against thermally activated back-intersystem crossing being a significant ${}^2\text{E}_g$ deactivation pathway for this CrN_6 system.

5.2

***trans*-[Cr(N₄)(CN)₂]⁺ (where N₄ = cyclam, 1,11-C₃-cyclam, and 1,4-C₂-cyclam)**

The Wagenknecht group has very recently studied a set of *trans*-dicyanochromium(III) complexes of topologically constrained tetraazamacrocycles, namely *trans*-[Cr(1,11-C₃-cyclam)(CN)₂]⁺ and *trans*-[Cr(1,4-C₂-cyclam)(CN)₂]⁺ (Fig. 12) to determine the effect that the additional strap has on the overall chemistry and photophysics relative to the cyclam parent complex [69–71].

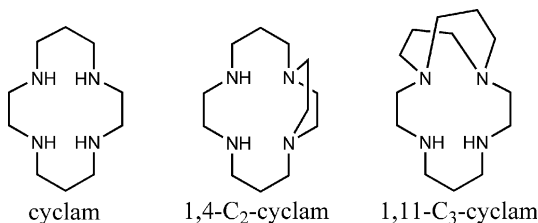


Fig. 12 Parent cyclam ligand, and the strapped derivatives 1,4-C₂-cyclam and 1,11-C₃-cyclam

In their initial work [69, 70], differences in thermal reactivity, UV-visible absorption spectra, and low temperature photophysics were adequately explained on the basis of steric and symmetry arguments, and differences in numbers of N – H oscillators in the molecule. However, marked differences in their rt photobehavior eluded explanation. For example, the 1,11-C₃-cyclam and 1,4-C₂-cyclam complexes have rt ²E_g excited state lifetimes one and three orders of magnitude lower, respectively, than the corresponding cyclam complex.

Furthermore, the lifetimes for complexes with the topologically constrained ligands are strongly temperature dependent near rt in acidified aqueous solution and the Arrhenius plots are linear [70]. Potential radiationless deactivation pathways for the ²E_g level in these systems are depicted in Fig. 13.

Of these possibilities, back-intersystem crossing (BISC) was considered unlikely on energetic grounds, while net photoreaction was rejected as a significant relaxation pathway due to the very low quantum yields for photoaquation for all three complexes. Additionally, MM2 studies suggested that neither solvent association nor symmetry destroying molecular “twists” are likely causes for the data in the temperature-dependent regime [70]. In their most recent paper [71], the authors present evidence that a photodissociation pathway involving transient Cr-macrocylic N-bond cleavage (followed by rapid ring closure) was the most plausible explanation for the thermally activated ²E_g relaxation. This conclusion received strong support from the observation of photodeuteration of the NH protons upon photolysis of the cyclam complex in acidified D₂O (where thermal deuteration was shown to

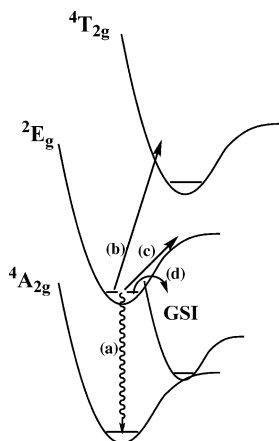


Fig. 13 Qualitative potential energy level diagram for O_h Cr(III) complexes showing possible radiationless ${}^2E_g$ relaxation processes, including *a* direct deactivation to the ground state, *b* back-intersystem crossing (BISC), *c* direct doublet reaction, or *d* surface crossing to a ground state intermediate surface (GSI)

be minimal). The proposed mechanism for this photodeuteration is shown in Fig. 14.

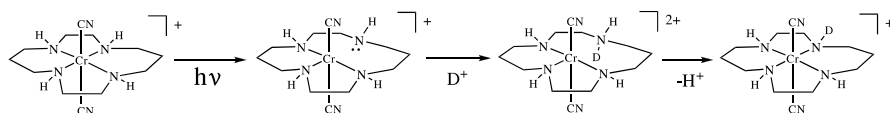


Fig. 14 Possible mechanism for photoinitiated macrocyclic N–H deuteration in acidic aqueous solution

A related paper on the corresponding difluorosystems has recently been published [75].

6

Energy Transfer Studies

Cr(III) complexes were employed as acceptor species in room temperature energy transfer experiments between transition metal complexes as early as 1972 [21, 76], and several years later the first cases appeared where the donor and acceptor were both Cr(III) compounds [77, 78]. In the survey since 1999, eight articles were identified where energy transfer studies involving Cr(III) species were the primary research activity [79–86]. The paper chosen for discussion in Sect. 6.1 describes the first report of electronic energy self-exchange between Cr(III) complexes [81].

6.1

Self-Exchange Energy Transfer Between Identical Chromophores

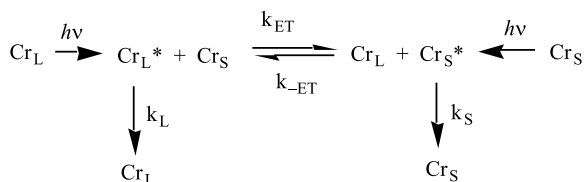
As noted earlier (Chap. 1 of this volume, Sect. 4.4.2), electronic energy transfer involving Cr(III) complexes is expected to proceed via an exchange mechanism, and thus effective donor-acceptor orbital overlap is a necessity. A large number of cross-exchange energy transfer studies utilizing Cr(III) donors and/or acceptors have been undertaken with the objective of determining the relative importance of thermodynamics, electronic factors (such as orbital overlap), and nuclear factors associated with Franck-Condon restrictions [87–92].

The study of self-exchange energy transfer is an attractive complementary approach, since the effect of thermodynamics on the rate is eliminated. However, monitoring self-exchange has proven a serious experimental challenge, since the absorption and emission characteristics of the donor and acceptor are identical. The only prior report of virtual self-exchange involving transition metal systems is that of Balzani and coworkers on several Ru(II) polypyridyl systems [93, 94]. In the paper to be discussed [81], advantage was taken of the marked enhancements in emission lifetimes and steady-state intensities in rt solution for the Cr(III) complexes listed in Table 1 upon deuteration of the amine N – H protons.

For each complex, the solution absorption and emission maxima of the deuterated and undeuterated compounds were essentially identical, indicating the presence of effectively identical chromophores. Irradiation of acidified mixtures of the isotopically labeled and unlabeled chromophores leads to the

Table 1 Emission lifetimes of Cr(III) complexes at 20 °C

Complex	Solvent	τ_H (μs)	τ_D (μs)	Refs.
<i>trans</i> -[Cr(cyclam)(CN) ₂] ⁺	H ₂ O	335	1500	[55]
<i>trans</i> -[Cr(cyclam)(NH ₃) ₂] ³⁺	DMSO	135	1620	[57]
<i>trans</i> -[Cr(tet a)F ₂] ⁺	H ₂ O	30	234	[59]



Scheme 1 Energy transfer between long-lived (Cr_L) and short-lived (Cr_S) complexes

reaction sequence shown in Scheme 1. In this scheme, the long-lived and short-lived Cr(III) species are labeled Cr_L and Cr_S , respectively, while k_ET and $k_{-\text{ET}}$ are the corresponding rate constants for forward and reverse energy transfer. Likewise, the terms k_L and k_S are the reciprocals of the lifetimes of Cr_L and Cr_S , respectively, in the absence of energy transfer. Emission quenching of Cr_L and Cr_S could then be followed by analyzing the decay profile following pulsed excitation according to the mathematical formulation developed by Maharaj and Winnik [95].

For the *trans*-dicyano and *trans*-diammine systems, energy transfer rate constants at 20 °C ($\mu = 1.0$) were determined to be $k_\text{ET} \gg 7 \times 10^6 \text{ M}^{-1} \text{ s}^{-1}$ and $9.7 \times 10^6 \text{ M}^{-1} \text{ s}^{-1}$, respectively. However, for *trans*-[Cr(tet a)F₂]⁺ no energy transfer was observed, which implied that the rate constant was $\ll 3 \times 10^5 \text{ M}^{-1} \text{ s}^{-1}$. Analysis of these results using Marcus theory lead to the important conclusion that electronic effects play a significant role in determining the rates of energy transfer self-exchange for these series of complexes.

7

Photoredox Behavior of [Cr(diimine)₃]³⁺ Systems

Arguably, the seminal report by Gafney and Adamson in 1972 [96] that the ³MLCT excited state of [Ru(bpy)₃]²⁺ (where bpy is 2,2'-bipyridine) could function as an electron transfer agent was the catalytic event that led to the extraordinary growth of transition metal photochemistry and photophysics over the last three decades [94, 97–99]. Today, the polypyridyl compounds of Ru(II) still hold a favored status, due to a coalescence of desirable properties including an intense, relatively long-lived luminescence signature, and a remarkable thermal robustness in a range of oxidation states.

The analogous polypyridyl complexes of Cr(III) are the next most investigated [M(diimine)₃]ⁿ⁺ systems. A few years after the Gafney and Adamson article appeared, Bolletta et al. presented the first evidence that the ligand-field ²E_g excited state of [Cr(bpy)₃]³⁺ was a strong one-electron photooxidant [100]. This involvement of polypyridyl Cr(III) species in direct bimolecular electron transfer reactions of the generic type represented in Eq. 1 has since been thoroughly documented for numerous substrates, Q [101–106]:



Importantly, [Cr(diimine)₃]³⁺ complexes are more powerful photooxidants than their [Ru(diimine)₃]²⁺ analogs. The oxidizing power of the Cr(III) ²E_g excited state can be assessed from the value of the ²E_g excited state reduction potential, E^o(*Cr³⁺/Cr²⁺). It has been shown [102, 103] that this latter quantity can be reliably estimated from the difference between the ²E_g → ⁴A_{2g}

emission energies in eV units and the ground state standard reduction potentials, $E^{\circ}(\text{Cr}^{3+}/\text{Cr}^{2+})$, obtained from cyclic voltammetry (CV) measurements. A representative illustration of the relevant energetics is shown in Fig. 15 for the case of $[\text{Cr}(\text{bpy})_3]^{3+}$, from which $E^{\circ}(*\text{Cr}^{3+}/\text{Cr}^{2+})$ is determined to be 1.44 V versus NHE in aqueous solution [103].

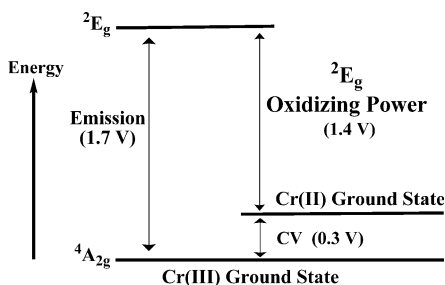
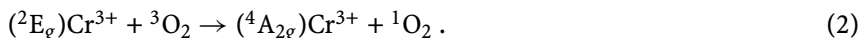


Fig. 15 Energetics associated with $^2\text{E}_g$ excited state oxidizing power

In contrast, the corresponding $E^{\circ}(*\text{Ru}^{2+}/\text{Ru}^+)$ value for $[\text{Ru}(\text{bpy})_3]^{2+}$ (where $*\text{Ru}^{2+}$ is the $^3\text{MLCT}$ excited state) is reported as 0.84 V [107]. The primary reason for these differences is the relatively minor energetic cost of ground state $\text{M}^{n+} \rightarrow \text{M}^{(n-1)+}$ reduction in the Cr(III) case, which leaves approximately 85% of the free energy of the $^2\text{E}_g$ excited state available for photoredox (as opposed to 40% for the Ru(II) analog).

Another important observation is that the $^2\text{E}_g \rightarrow ^4\text{A}_{2g}$ emission signal of $[\text{Cr}(\text{diimine})_3]^{3+}$ complexes in ambient solution is significantly quenched by the presence of dissolved oxygen, $^3\text{O}_2$, as the result of an energy transfer process generating excited state singlet oxygen ($^1\text{O}_2$) [103, 105, 108]:



Singlet oxygen production in Eq. 2 then provides an alternative method for substrate oxidation, where the Cr(III) $^2\text{E}_g$ excited state is functioning as a photocatalyst. During the present review period, Pagliero and Argüello examined the role of O_2 in the photooxidation of phenols in aqueous solution, employing $[\text{Cr}(\text{phen})_3]^{3+}$ as the photocatalyst [109]. Although direct phenol oxidation according to Eq. 1 is thermodynamically feasible, under air-saturated conditions the net photochemistry is dominated by a singlet oxygen mediated pathway leading to benzoquinone as the sole organic product. The results confirm and amplify the observations from an earlier study [110], and have practical relevance to the emerging field of photoremediation of waste waters [111].

Despite the large number of molecules that have been shown to quench the $^2\text{E}_g$ excited state of $[\text{Cr}(\text{diimine})_3]^{3+}$ complexes via Eq. 1, biological substrates have very rarely been employed in this role. Several recent studies

utilizing DNA as the potential quenching species are highlighted in the following section.

7.1

DNA Interactions

The last 20 years have witnessed the emergence of a rich chemistry associated with the non-covalent interaction of chiral $[M(\text{diimine})_3]^{n+}$ complexes with duplex DNA, with the ultimate goal of developing new diagnostic and therapeutic agents [112, 113]. Of particular interest in the present context is the potential utility of $[M(\text{diimine})_3]^{n+}$ systems as DNA photocleavage agents via excited state redox processes, which could lead to applications in the general field of photodynamic therapy [111]. The most widely explored systems have been $[\text{Ru}(\text{diimine})_3]^{2+}$ species. However, except for a few notable exceptions [114], values for $E^0(*\text{Ru}^{2+}/\text{Ru}^+)$ fall well short of the 1.2 V value required for direct one-electron oxidation of guanine (the most readily oxidized nucleobase [115]) via a reaction pathway analogous to Eq. 1 above. Although $[\text{Ru}(\text{diimine})_3]^{2+}$ systems are known to photoinitiate DNA oxidation, this damage normally occurs via the intermediacy of a singlet oxygen pathway analogous to Eq. 2 [116, 117].

In view of the markedly higher oxidative power of the ^2E_g excited state of Cr(III) polypyridyl complexes (approximately 1.4 V versus NHE), such species would appear to be more attractive candidates for photoinitiated direct oxidation of DNA via Eq. 1 (where $Q = \text{DNA}$). Another potential advantage of these d^3 systems with regard to bimolecular redox activity is their longer-lived $^2E_g \rightarrow ^4A_{2g}$ emission (often two orders of magnitude greater than that for the analogous Ru(II) $^3\text{MLCT}$ emission signals [106]). These photoredox expectations have been experimentally confirmed in several reports in the present review period [118–120].

In the first of these studies, the interaction of the complexes $[\text{Cr}(\text{phen})_3]^{3+}$ and $[\text{Cr}(\text{bpy})_3]^{3+}$ with duplex DNA and a range of mononucleotides was explored [118]. A key observation was that the Cr(III) emission signals were strongly quenched in the presence of guanine-containing nucleotides, but not by the mononucleotides of adenine, cytosine, or thymidine, nor by the synthetic polynucleotide, $\text{poly}(\text{dA-dT}) \cdot \text{poly}(\text{dA-dT})$. A representative example of Cr(III) emission quenching is shown in Fig. 16 for the case of $[\text{Cr}(\text{phen})_3]^{3+}$ in the presence of calf thymus B-DNA (which has 40% GC base pairs).

Such behavior provides strong evidence for direct oxidation of the guanine base of DNA via Eq. 1, since the corresponding oxidation of the other nucleobases is thermodynamically more difficult [115]. Since guanine oxidation has been shown in other systems to serve as a genesis point for DNA strand scission [115], these Cr(III) complexes show potential as a new class of DNA photocleavage agents (photonucleases). This expectation receives support from our recent observation of permanent DNA damage (strand

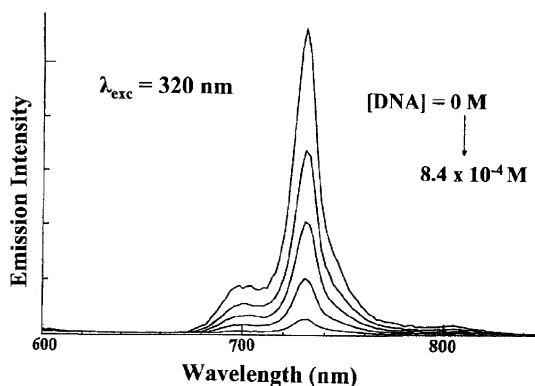


Fig. 16 Quenching of $[\text{Cr}(\text{phen})_3]^{3+}$ steady-state emission in air-saturated 50 mM Tris-HCl buffer (pH 7.4) by calf thymus B-DNA (22 °C)

scission) from agarose gel electrophoresis studies of $[\text{Cr}(\text{phen})_3]^{3+}$ bound to supercoiled ΦX174 RF plasmid DNA following photolysis at 350 nm (see Fig. 17) (Barnett et al., unpublished observations). In such studies, the detection of open-circular DNA following photolysis is clear evidence for a single strand break in the DNA [116].

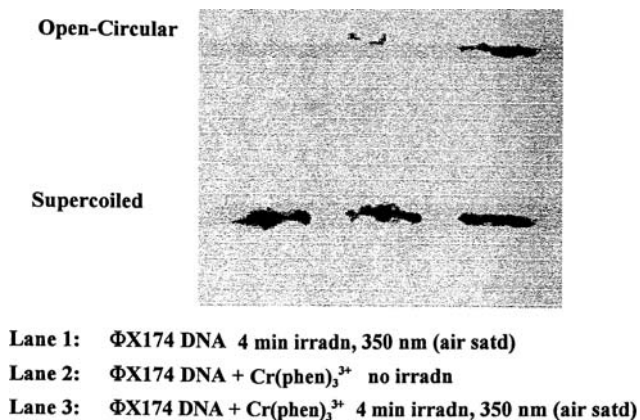


Fig. 17 Photoactivated cleavage at pH 7.4 of $5\ \mu\text{M}$ ΦX174 plasmid DNA by $200\ \mu\text{M}$ $[\text{Cr}(\text{phen})_3]^{3+}$ following irradiation at 350 nm (Rayonet). Samples were subjected to electrophoresis on 1% agarose gels for 3 h at 70 V, followed by staining with ethidium bromide

It is also noteworthy that while photodamage in the analogous Ru(II) cases is dramatically decreased in the absence of O_2 (consistent with a singlet O_2 pathway), photodamage by $[\text{Cr}(\text{phen})_3]^{3+}$ is considerably greater under a N_2 atmosphere (Barnett et al., unpublished observations). Since many cancer

cells are hypoxic [111], the increase in photodamage at lower O_2 levels may provide a selectivity advantage for these $[Cr(diimine)_3]^{3+}$ reagents in terms of their future potential as phototherapeutic agents.

In another aspect of this study [118], a mathematical analysis of the emission quenching data was undertaken. Representative steady-state intensity and lifetime Stern–Volmer (SV) plots for quenching of $[Cr(phen)_3]^{3+}$ emission by calf thymus B-DNA are shown in Fig. 18. From the lifetime data, a bimolecular quenching rate constant of $1.1 \times 10^8 \text{ M}^{-1} \text{ s}^{-1}$ was extracted (a value close to that anticipated for a diffusion controlled process). In contrast, the steady-state SV plot showed strong upward curvature at higher DNA concentrations. This observation was attributed to the formation of a non-luminescent $[Cr(phen)_3]^{3+}/\text{DNA}$ ion pair, and allowed an estimation to be made for the binding constant with DNA ($K_{\text{DNA}} \approx 4000 \text{ M}^{-1}$).

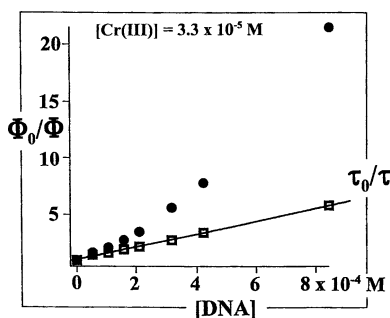


Fig. 18 Stern–Volmer plots for $[Cr(phen)_3]^{3+}$ emission quenching in air-saturated 50 mM Tris-HCl buffer (pH 7.4) by calf thymus B-DNA at 22 °C: ● steady-state data, □ lifetime data

A limitation of this initial work with $[Cr(bpy)_3]^{3+}$ and $[Cr(phen)_3]^{3+}$ is the relatively small binding constants of these compounds with DNA. In a subsequent study [119], the photoredox behavior of the complex $[Cr(phen)_2(DPPZ)]^{3+}$ with DNA was investigated, where the third diimine ligand is dipyridophenazine, DPPZ. The value of K_{DNA} increased by two orders of magnitude, consistent with the known ability of the DPPZ ligand to intercalate into DNA base stacks [113]. Perhaps more importantly, the complex was found to have an $E^0(*Cr^{3+}/Cr^{2+})$ value 80 mV more positive than that for $[Cr(phen)_3]^{3+}$, which placed it in the thermodynamic threshold range required for direct oxidation of the nucleobase adenine [115]. In accord with this thermodynamic argument, SV plots of the quenching of the emission lifetime of $[Cr(phen)_2(DPPZ)]^{3+}$ in the presence of deoxyguanosine-5'-monophosphate and deoxyadenosine-5'-monophosphate yielded quenching rate constants of $2.4 \times 10^9 \text{ M}^{-1} \text{ s}^{-1}$ and $1.8 \times 10^7 \text{ M}^{-1} \text{ s}^{-1}$, respectively [119].

More recently [120], a report by Vaidyanathan and Nair describes nucleobase photooxidation by the terpyridine Cr(III) derivatives $[Cr(tpy)_2]^{3+}$

and $[\text{Cr}(\text{Brphtpy})_2]^{3+}$ (where $\text{ttpy} = p\text{-tolylterpyridine}$ and $\text{Brphtpy} = p\text{-bromophenylterpyridine}$). The two complexes were reported to emit strongly in rt aqueous solution, although no emission lifetimes or spectra (except wavelength maxima) were provided. Such emission is quite remarkable in view of the exceedingly weak emission and very short lifetime ($\approx 0.05 \mu\text{s}$) found for the parent terpyridine complex, $[\text{Cr}(\text{tpy})_2]^{3+}$ [103]. Based on CV data and the reported emission spectral maxima, exceptionally high values for $E^\circ(*\text{Cr}^{3+}/\text{Cr}^{2+})$ were assessed for $[\text{Cr}(\text{ttpy})_2]^{3+}$ and $[\text{Cr}(\text{Brphtpy})_2]^{3+}$ (1.65 V and 1.85 V, respectively). Consistent with these thermodynamic observations, both complexes were demonstrated to be very powerful photooxidants. This was especially true for $[\text{Cr}(\text{Brphtpy})_2]^{3+}$, where its emission was quenched by all four mononucleotides (including deoxythymidine-5'-monophosphate). This statement, however, requires that the labels for Figs. 4A and B in the paper were accidentally reversed.

8

Photoredox Involving Coordinated Ligands

Whereas Sect. 7 was concerned with examples of intermolecular electron transfer between Cr(III) excited states and external substrates, attention is directed in the present section to cases of intramolecular redox chemistry involving the coordinated ligands. These studies have usually involved photoexcitation into high-energy LMCT excited states involving the ligand in question, which often results in the transient formation of a Cr(II)/ligand radical pair. The subject has been reviewed by Kirk [4], and some representative examples of molecules previously investigated are $[\text{Cr}(\text{NH}_3)_5\text{Br}]^{2+}$ [121] and *trans*- $[\text{Cr}(\text{tfa})_3]$ (where tfa is the anion of 1,1,1-trifluoro-2,4-pentanedione) [122]. Some of the more recent contributions in this area are discussed in the following two sections.

8.1

Photolabilization of NO from Cr(III)-Coordinated Nitrite

It has been recently established that nitric oxide (NO) regulates a number of mammalian biological processes, including blood pressure, neurotransmission, and smooth muscle relaxation [123]. Additionally, tumor cells are particularly sensitive to NO, which induces programmed cell death [124] and limits metasis [125]. In response to these findings, Ford and coworkers have developed a range of air-stable, water-soluble nitrito-Cr(III) macrocyclic complexes, which display photochemically activated NO release [126–128]. The initial study involved the complex *trans*- $[\text{Cr}(\text{cyclam})(\text{ONO})_2]^+$ [126], which for convenience is labeled structure I in Fig. 19.

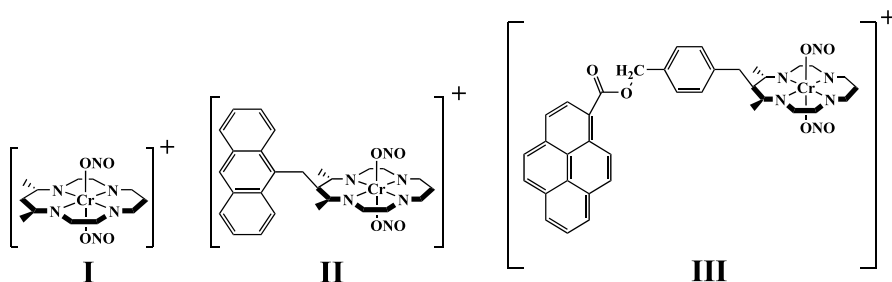
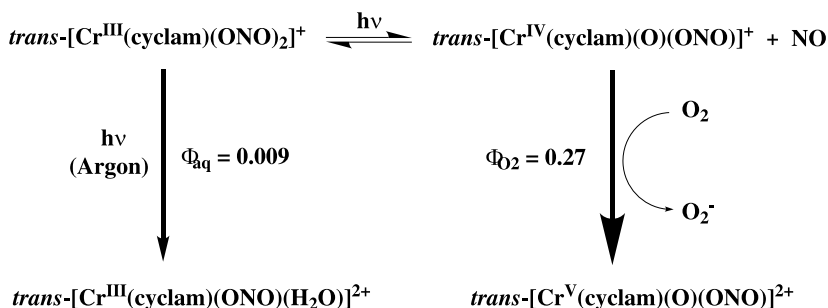


Fig. 19 Representative $trans$ -[Cr(macrocycle)(ONO)₂]⁺ complexes

The only product of 436 nm continuous photolysis of **I** in deaerated pH 7 aqueous solution was $trans$ -[Cr(cyclam)(H₂O)(ONO)]²⁺, formed in a substitution step in only low quantum yield ($\phi_{aq} = 0.009$). However, when the same photolysis was performed in air-saturated solution, a very different product was formed in much higher yield ($\phi_{O_2} = 0.27$). On the basis of mass spectral and EPR evidence, this Cr final product was formulated as the oxo-Cr(V) species, $trans$ -[Cr(cyclam)(O)(ONO)]²⁺. In addition, NO gas release was confirmed employing an NO-specific electrode sensor. Transient absorption spectral studies indicated that NO release occurred in a rapidly reversible earlier step (see Scheme 2) involving homolytic cleavage of coordinated nitrite ion in **I** to yield the transitory oxo-Cr(IV) product, $trans$ -[Cr(cyclam)(O)(ONO)]⁺.



Scheme 2 Photoinitiated reaction scheme for $trans$ -[Cr(cyclam)(ONO)₂]⁺

In deaerated solution, the transient rapidly reforms the parent complex, resulting in simple photoaquation being the only observed net reaction. Under air-saturated conditions, however, the transient species is very rapidly scavenged by dissolved O₂ to generate the oxo-Cr(V) final product, leading to the net release of NO gas. The overall mechanism is summarized in Scheme 2.

In an effort to utilize this reaction scheme in a more practical NO delivery system, the Ford group subsequently synthesized a series of complexes where

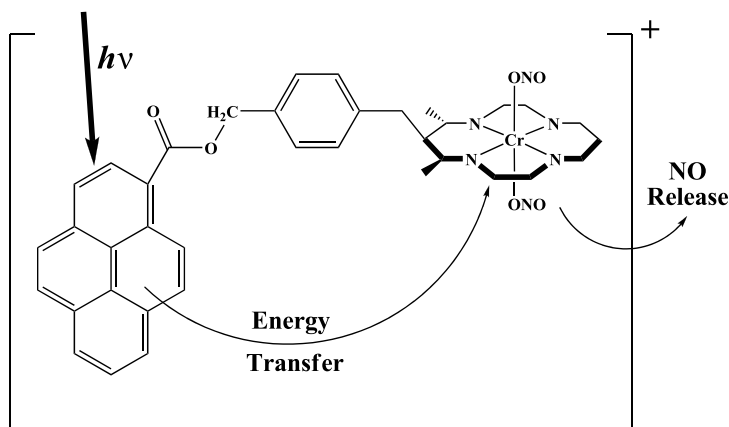


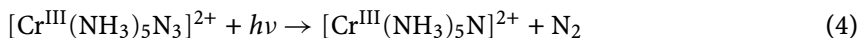
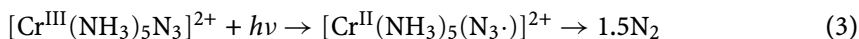
Fig. 20 Mechanism of NO release following light absorption by a pendant aromatic antennae

strongly absorbing pendant aromatic chromophores were attached to the macrocyclic ring [128–130]. Two of these second-generation Cr(III)nitrito systems are shown in Fig. 19, where molecules **II** and **III** have anthracenyl and pyrenyl pendant arms, respectively. The normally strong fluorescence of these tethered aromatics was largely quenched upon Cr(III) coordination, consistent with fast intramolecular energy transfer to the lower lying Cr(III) ligand field excited states followed by NO gas release according to Scheme 2 [128]. The overall NO-generating process for these promising light-gathering antennae systems is depicted in Fig. 20 for the pyrenyl-pendant complex (molecule **III**).

8.2

Photogeneration of Nitrido Complexes from Cr(III) Coordinated Azide

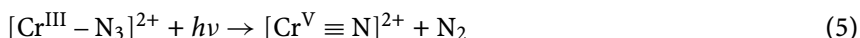
The complex $[\text{Cr}(\text{NH}_3)_5\text{N}_3]^{2+}$ containing the azido ligand, N_3^- , was the subject of several photochemical studies during the 1970s [131–134]. The results from irradiations in the LMCT region ($\lambda \leq 330$ nm) identified the presence of two competing processes, involving the formation of azide radical, $\text{N}_3^\cdot$ and nitrene, $\text{N}^\cdot$, intermediates (Eqs. 3 and 4, respectively) [132–134]:



Product analysis was complicated by the thermal reactions of the radical species generated. However, based in part on the differences expected in the N_2 gas yields for the two processes, Katz and Gafney [132, 134] concluded that initial nitrene formation was the dominant reaction pathway. Although the fi-

nal fate of the nitrene intermediate was not established, Sriram and Endicott noted that quasi-thermodynamic calculations suggested the lowest energy product ground state for this system would be a Cr(V) species [133].

More recent photochemical investigations on azido complexes of Cr(III) have focused on systems containing tetradentate ligands such as N_2O_4 Schiff-bases [135] and N_3 or N_4 macrocyclic ligands [136, 137] as stable non-leaving groups. For many of these systems, air-stable, solid products have been isolated, and have been fully characterized by a variety of spectroscopic probes (including X-ray crystallography). These studies provide convincing evidence for the formation of stable Cr(V) complexes containing the nitrido ligand, N^{3-} , formed via the generic photoreaction shown in Eq. 5:



Evidence for a Cr(V) product is based on the diagnostic EPR signature displayed by this d^1 metal ion. The presence of a $Cr \equiv N$ triple bond in the product is also in accord with the short Cr – N bond distances observed in X-ray crystallographic studies, and the presence of a strong infrared absorption in the 1020–1150 cm^{-1} region [135–138].

During the present review period, the charge transfer photochemistry of several azido-Cr(III) complexes containing new Schiff-base ligands as the non-leaving groups were examined [139, 140]. In the first of these papers, no crystallographic evidence was presented for Cr(V)-nitrido product formation, but this product assignment was strongly supported by EPR and infrared spectral results [139]. In the second contribution, a potentially valuable biochemical application of azido-Cr(III) photochemistry is reported by Shrivastava and Nair [140]. An azido-Cr(III) Schiff-base complex was irradiated in the presence of bovine serum albumin (BSA), and the photolyte examined by sodium dodecyl sulfate-polyacrylamide disc electrophoresis (SDS-PAGE). The SDS-PAGE results revealed that the BSA protein was cleaved at multiple sites, non-specifically into smaller peptide fragments. The protein cleavage was attributed to the azido-Cr(III) complex binding at multiple sites, and being subsequently converted to the reactive nitrido-Cr(V) species upon light activation. This light-promoted protease activity bears some analogies with the photonuclease activity discussed earlier for $[Cr(diimine)_3]^{3+}$ interactions with DNA (Sect. 7.1). A non-selective photonuclease could be utilized in a variety of applications, including protein sequencing.

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Final Comments

In this chapter, the author has attempted to provide an overview of recent progress in the field of Cr(III) photochemistry and photophysics, with a more detailed focus on certain topics of interest. For cohesiveness, it was not pos-

sible to cover some aspects of the field that did not naturally fit within the scope of those focus areas.

Included in the material not covered, is the recent contribution by Ronco and coworkers [141], where advantage is taken of the sometimes exquisite dependence on environmental factors of the emission intensity and lifetime of Cr(III) polypyridyls. This sensitivity was used to probe hydrophobic sites in anionic polyelectrolytes, where such information may provide useful guidance in attempts to enhance the rates of photoactivated electron transfer processes and/or retard recombination events. More recently [142], in an effort to more finely tune ^2E_g excited state properties, their group synthesized a range of mixed ligand polypyridyls of Cr(III), using a procedure we had developed earlier [143]. Another area not addressed is the increasing use of Cr(III) complexes in spectral hole-burning experiments to overcome spectral broadening in condensed phases [144, 145]. Finally, one of the more intriguing topics omitted is a report in *Nature* in 2000 describing an experimental confirmation [146] of a theoretical prediction, termed magnetochiral dichroism, that a chiral medium would absorb light traveling parallel to a magnetic field differently from light traveling antiparallel [147]. The compound investigated was $[\text{Cr}(\text{oxalate})_3]^{3-}$, and a very small, strongly excitation wavelength-dependent, induction of optical activity was observed on laser irradiation in a very powerful magnetic field (up to 15 Tesla).

In conclusion, it is noted that although the subject of Cr(III) photochemistry and photophysics is unlikely to reassume the degree of prominence it held up until the early 1970s, the present condition of the field is good and the long-term prognosis is excellent. Who is to say that the sign on my laboratory door which boldly states: "Chromium – The Final Frontier", will not one day be more than just a catchy phrase?

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References

1. Balzani V, Carassiti V (1970) Photochemistry of coordination compounds. Academic, London
2. Zinato E (1975) Substitutional photochemistry of first-row transition metal elements. In: Adamson AW, Fleischauer PD (eds) Concepts in inorganic photochemistry. Wiley, New York (Chap 4)
3. Roundhill DM (1994) Photochemistry and photophysics of metal complexes. Plenum, New York
4. Kirk AD (1999) Chem Rev 99:1607
5. Zinato E, Ricciari P (2001) Coord Chem Rev 211:5
6. Irwin G, Kirk AD (2001) Coord Chem Rev 211:25

7. Derwahl A, Wasgestian F, House DA, Robinson WT (2001) *Coord Chem Rev* 211:45
8. Kane-Maguire NAP, Wheeler JF (2001) *Coord Chem Rev* 211:145
9. Forster LS (2002) *Coord Chem Rev* 227:59
10. Fucaloro AF, Forster LS, Glover SG, Kirk AD (1985) *Inorg Chem* 24:4242
11. Forster LS (1990) *Chem Rev* 90:331
12. Rojas G, Magde D (1983) *Chem Phys Lett* 102:399
13. Rojas GE, Dupuy C, Sexton DA, Magde D (1986) *J Phys Chem* 90:87
14. Kirk AD, Hoggard PE, Porter GB, Rockley MG, Windsor MW (1976) *Chem Phys Lett* 37:199
15. Juban EA, McCusker JK (2005) *J Am Chem Soc* 127:6857
16. Forster LS (1969) *Transition Met Chem* 5:1
17. Chen SN, Porter GB (1970) *Chem Phys Lett* 6:41
18. Wasgestian F (1972) *J Phys Chem* 76:1947
19. Ricciari P, Zinato E (1990) *Inorg Chem* 29:5035
20. Ricciari P, Zinato E, Aliboni A (1997) *Inorg Chem* 36:2279
21. Sabbatini N, Balzani V (1972) *J Am Chem Soc* 94:7587
22. Balzani V, Moggi L, Manfrin MF, Bolletta F, Laurence GS (1975) *Coord Chem Rev* 15:321
23. Endicott JF, Ramasami T, Tamilarasan R, Lessard RB, Ryu CK (1987) *Coord Chem Rev* 77:1
24. Endicott JF (1985) *Comments Inorg Chem* 3:349
25. Vanquickenborne LG, Ceulemans A (1978) *J Am Chem Soc* 100:475
26. Vanquickenborne LG, Ceulemans A (1979) *Inorg Chem* 18:3475
27. Vanquickenborne LG, Ceulemans A (1983) *Coord Chem Rev* 48:157
28. Kirk AD (1993) *Comments Inorg Chem* 14:89
29. Vanquickenborne LG, Coussens B, Postelmans D, Ceulemans A, Pierloot K (1992) *Inorg Chem* 31:539
30. Kane-Maguire NAP, Langford CH (1972) *J Am Chem Soc* 94:2125
31. Kane-Maguire NAP, Langford CH (1976) *Inorg Chem* 15:464
32. Jamieson MA, Serpone N, Hoffman MZ (1981) *Coord Chem Rev*, p 121
33. Bolletta F, Maestri M, Moggi L, Jamieson MA, Serpone N, Henry MS (1983) *Hoffman Inorg Chem* 22:2502
34. Lilie J, Waltz WL, Lee SH, Gregor LL (1986) *Inorg Chem* 25:4487
35. Vleck A Jr (2000) *Coord Chem Rev* 933:200–202
36. McCusker JK (2003) *Acc Chem Res* 36:876
37. Juban EA, Smeigh AL, Monat JE, McCusker JK (2006) *Coord Chem Rev*, p 783
38. Turro NJ (1991) *Modern molecular photochemistry*. University Science Books, Mill Valley, CA
39. Kane-Maguire NAP, Richardson DE, Toney CG (1976) *J Am Chem Soc* 98:3996
40. Kane-Maguire NAP, Phifer JE (1976) *Toney Inorg Chem* 15:593
41. Sandrini D, Gandolfi MT, Moggi L, Balzani V (1978) *J Am Chem Soc* 100:1463
42. Sasseville RLP, Langford CH (1980) *Inorg Chem* 19:2850
43. Langford CH (1984) *Acc Chem Res*, p 96
44. Monat JE, McCusker JK (2000) *J Am Chem Soc* 122:4092
45. Yang G, Leng W, Zhang Y, Chen Z, Van Houten J (1999) *Polyhedron* 18:1273
46. Inamo M, Hoshino M (1999) *Photochem Photobiol* 70:596
47. Inamo M, Nakaba H, Nakajima K, Hoshino M (2000) *Inorg Chem* 39:4417
48. Jeoung SC, Kim D, Cho DW, Yoon M (2000) *J Phys Chem A* 104:4816
49. Mytykh OV, Martin SE, Wheeler JF, Kane-Maguire NAP (2000) *Inorg Chim Acta* 311:143

50. Inamo M, Eba K, Nakano K, Itoh N (2003) *Inorg Chem* 42:6095
51. Inamo M, Matsubara N, Nakajima K, Iwayama T, Okimi H, Hoshino M (2005) *Inorg Chem* 44:6445
52. Gouterman M, Hanson LK, Khalil GE, Leenstra WR, Buchler JW (1975) *J Chem Phys* 62:2343
53. Kutal C, Adamson AW (1971) *J Am Chem Soc* 93:5581
54. Kutal C, Adamson AW (1973) *Inorg Chem* 12:1990
55. Kane-Maguire NAP, Crippen WS, Miller PK (1983) *Inorg Chem* 22:696
56. Kane-Maguire NAP, Wallace KC, Cobranchi DP, Derrick JM, Speece DG (1986) *Inorg Chem* 25:2101
57. Kane-Maguire NAP, Wallace KC, Miller DB (1985) *Inorg Chem* 24:597
58. Friesen DA, Lee SH, Lilie J, Waltz WL, Vincze L (1991) *Inorg Chem* 30:1975
59. Kane-Maguire NAP, Wallace KC, Speece DG (1986) *Inorg Chem* 25:4650
60. Ramasami T, Endicott JF, Brubaker GR (1983) *J Phys Chem* 87:5057
61. Endicott JF, Lessard RB, Lei Y, Ryu CK, Tamilarasan R (1986) *ACS Symp Ser* 307:85
62. Perkovic MW, Endicott JF (1990) *J Phys Chem* 94:1217
63. Perkovic MW, Heeg MJ, Endicott JF (1991) *Inorg Chem* 30:3140
64. Endicott JF, Perkovic MW, Heeg MJ, Ryu CK, Thompson D (1997) *Adv Chem Ser* 253:199
65. Lessard RB, Heeg MJ, Buranda T, Perkovic MW, Schwartz CL, Rudong Y, Endicott JF (1992) *Inorg Chem* 31:3091
66. Comba P, Mau AWH, Sargeson AM (1985) *J Phys Chem* 89:394
67. Comba P, Creaser II, Gahan LR, Harrowfield JM, Lawrance GA, Martin LL, Mau AWH, Sargeson AM, Sasse WHF, Snow MR (1986) *Inorg Chem* 25:384
68. Irwin G, Kirk AD, Mackay I, Nera J (2002) *Inorg Chem* 41:874
69. Wright-Garcia K, Basinger J, Williams S, Hu C, Wagenknecht PS (2003) *Inorg Chem* 42:4885
70. Wagenknecht PS, Hu C, Ferguson D, Nathan LC, Hancock RD, Whitehead JR, Wright-Garcia K, Vagnini MT (2005) *Inorg Chem* 44:9518
71. Vagnini MT, Kane-Maguire NAP, Wagenknecht PS (2006) *Inorg Chem* 45:3789
72. Kane-Maguire NAP, Hanks TW, Jurs DG, Tollison RM, Heatherington AL, Ritzenthaler LM, McNulty LM, Wilson HM (1995) *Inorg Chem* 34:1121
73. Harris JE, Desai, Seaver KE, Watson RT, Kane-Maguire NAP, Wheeler JF (2001) *J Chromat A* 919:427
74. Brown KN, Geue RJ, Moran G, Ralph SF, Riesen H, Sargeson AM (1998) *Chem Commun*, p 2291
75. Vagnini MT, Rutledge WC, Hu C, VanDerveer DG, Wagenknecht PS (2007) *Inorg Chim Acta* 360:1482
76. Bolletta F, Maestri M, Moggi L, Balzani V (1973) *J Am Chem Soc* 95:7864
77. Bolletta F, Maestri M, Balzani V (1976) *J Phys Chem* 80:2499
78. Kane-Maguire NAP, Toney CG, Swiger B, Adamson AW, Wright RE (1977) *Inorg Chim Acta* 22:L11
79. Chen Y, Perkovic MW (2001) *Inorg Chim Acta* 317:127
80. Iwamura M, Otsuka T, Kaizu Y (2002) *Inorg Chim Acta* 333:57
81. Wagenknecht PS, Kane-Maguire NAP, Speece DG, Helwic N (2002) *Inorg Chem* 41:1229
82. Von Arx ME, Hauser A (2002) *J Phys Chem A* 106:7106
83. Subhan MDA, Nakata H, Suzuki T, Choi JH, Kaizaki S (2003) *J Lumin* 101:307
84. Iwamura M, Otsuka T, Kaizu Y (2004) *Inorg Chim Acta* 357:1565
85. Iwamura M, Morita M (2004) *Inorg Chim Acta* 357:3451

86. Otsuka T, Iwamura M, Kaizu Y (2006) *Inorg Chim Acta* 359:1351
87. Balzani V, Indelli MT, Sandrini D, Scandola F (1980) *J Phys Chem* 84:852
88. Gandolfi MT, Maestri M, Sandrini D, Balzani V (1983) *Inorg Chem* 22:3435
89. Endicott JF, Ramasami T, Gaswick DC, Tamilarasan GR, Heeg MJ, Brubaker GR, Pyke SC (1983) *J Am Chem Soc* 105:5301
90. Gamache RE, Rader RA, McMillin DR (1985) *J Am Chem Soc* 107:1141
91. Endicott JF (1985) *Coord Chem Rev* 64:293
92. Tamilarasan R, Endicott JF (1986) *J Phys Chem* 90:1027
93. Maestri M, Sandrini D, Balzani V, Belser P, Von Zelewski A (1984) *Chem Phys Lett* 110:611
94. Balzani V, Juris A (2001) *Coord Chem Rev* 211:97
95. Maharaj U, Winnik MA (1981) *Chem Phys Lett* 82:29
96. Gafney HD, Adamson AW (1972) *J Am Chem Soc* 94:8238
97. Juris A, Balzani V, Barigelletti F, Campagna S, Belser P, von Zelewsky A (1988) *Coord Chem Rev* 84:85
98. Balzani V, Juris A, Venturi M, Campagna S, Serroni S (1996) *Chem Rev* 96:759
99. Balzani V, Venturi M, Credi A (2003) *Molecular Devices and Machines*. Wiley, Weinheim
100. Bolletta F, Maestri M, Moggi L, Balzani V (1975) *J Chem Soc Chem Commun*, p 901
101. Ballardini R, Varani G, Scandola F (1976) *J Am Chem Soc* 98:7432
102. Ballardini R, Varani G, Indelli MT, Scandola F, Balzani V (1978) *J Am Chem Soc* 100:7219
103. Brunschwig B, Sutin N (1978) *J Am Chem Soc* 100:7568
104. Juris A, Manfrin MF, Maestri M, Serpone N (1978) *Inorg Chem* 17:2258
105. Serpone N, Jamieson MA, Henry MS, Hoffman MZ, Bolletta F, Maestri M (1979) *J Am Chem Soc* 101:2907
106. Jamieson MA, Serpone N, Hoffman MZ (1981) *Coord Chem Rev* 39:121
107. Navin G, Sutin N (1976) *Inorg Chem* 15:496
108. Tiyyabhorn A, Zahir KO (1996) *Can J Chem* 74:336
109. Pagliero D, Argüello GA (2001) *J Photochem Photobiol A* 138:207
110. Pizzocaro C, Bolte M, Sun H, Hoffman MZ (1994) *New J Chem* 18:737
111. DeRosa MC, Crutchley RJ (2002) *Coord Chem Rev* 233–234:351
112. Kirsch-De Mesmaeker A, Lecomte J-P, Kelly JM (1996) *Top Curr Chem* 177:25
113. Erkkila KE, Odom DT, Barton JK (1999) *Chem Rev* 99:2777
114. Lecomte J-P, Kirsch-De Mesmaeker A, Feeny MM, Kelly JM (1995) *Inorg Chem* 34:6481
115. Burrows CJ, Muller JG (1998) *Chem Rev* 98:1109
116. Fleisher MB, Waterman KC, Turro NJ, Barton JK (1986) *Inorg Chem* 25:3549
117. Mei H-Y, Barton JK (1988) *Proc Natl Acad Sci USA* 85:1339
118. Watson RT, Desai N, Wildsmith J, Wheeler JF, Kane-Maguire NAP (1999) *Inorg Chem* 38:2683
119. Barker KD, Benoit BR, Bordelon JA, Davis RJ, Delmas AS, Mytykh OV, Petty JT, Wheeler JF, Kane-Maguire NAP (2001) *Inorg Chim Acta* 322:74
120. Vaidyanathan VG, Nair BU (2004) *Eur J Inorg Chem*, p 1840
121. Sriram R, Endicott JF (1976) *J Chem Soc Chem Commun*, p 683
122. Kutal C, Yang DB, Ferraudi G (1980) *Inorg Chem* 19:2907
123. Fukuto JM, Wink DA (1999) *Metal Ions Biol Syst* 36:547
124. Boyd CS, Cadenas E (2002) *J Biol Chem* 383:411
125. Xie K, Huang S (2003) *Free Radic Biol and Med* 34:969
126. DeLeo M, Ford PC (1999) *J Am Chem Soc* 121:1980

127. DeLeo M, Ford PC (2000) *Coord Chem Rev* 208:47
128. DeRosa F, Bu X, Ford PC (2005) *Inorg Chem* 44:4157
129. DeRosa F, Bu X, Ford PC (2003) *Inorg Chem* 42:4171
130. DeRosa F, Bu X, Pohaku K, Ford PC (2005) *Inorg Chem* 44:4166
131. Vogler A (1971) *J Am Chem Soc* 93:5912
132. Katz M, Gafney HD (1976) *J Am Chem Soc* 98:7458
133. Sriram R, Endicott JF (1977) *Inorg Chem* 16:2766
134. Katz M, Gafney HD (1978) *Inorg Chem* 17:93
135. Arshankov SI, Poznjak ALZ (1981) *Z Anorg Allg Chem* 481:201
136. Niemann A, Bossek U, Haselhorst G, Weighardt K, Nuber B (1996) *Inorg Chem* 35:906
137. Meyer K, Bendix J, Bill E, Weyhermüller T, Wieghardt K (1998) *Inorg Chem*
138. Bendix J, Wilson SR, Prussak-Wiechowska T (1998) *Acta Crystallogr C* 54:923
139. Kanthimathi M, Nair BU (2004) *Transition Met Chem* 29:751
140. Shrivastava HY, Nair BU (2004) *J Inorg Biochem* 98:991
141. Ronco S, Persing B, Mortinsen R, Barber J, Shotwell S (2000) *Inorg Chim Acta* 308:107
142. Isaacs M, Sykes AG, Ronco S (2006) *Inorg Chim Acta* 359:3847
143. Barker K, Barnett K, Connell S, Glaeser J, Wallace A, Wildsmith J, Herbert B, Wheeler JF, Kane-Maguire NAP (2001) *Inorg Chim Acta* 316:41
144. Lewis ML, Riesen H (2002) *Phys Chem Chem Phys* 4:4845
145. Riesen H, Wallace L (2003) *Phys Chem Comm* 6:9
146. Rikken GLJA, Raupach E (2000) *Nature* 405:932
147. Wagnière G, Meir A (1982) *Chem Phys Lett* 93:78

Photochemistry and Photophysics of Coordination Compounds: Copper

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Abstract Cu(I) complexes and clusters are the largest class of compounds of relevant photochemical and photophysical interest based on a relatively abundant metal element. Interestingly, Nature has given an essential role to copper compounds in some biological systems, relying on their kinetic lability and versatile coordination environment. Some basic properties of Cu(I) and Cu(II) such as their coordination geometries and electronic levels are compared, pointing out the limited significance of Cu(II) compounds (*d*⁹ configuration) in terms of photophysical properties. Well-established synthetic protocols are available to build up a variety of molecular and supramolecular architectures

(e.g. catenanes, rotaxanes, knots, helices, dendrimers, cages, grids, racks, etc.) containing Cu(I)-based centers and exhibiting photo- and electroluminescence as well as light-induced intercomponent processes. By far the largest class of copper complexes investigated to date is that of Cu(I)-bisphenanthrolines ($[\text{Cu}(\text{NN})_2]^+$) and recent progress in the rationalization of their metal-to-ligand charge-transfer (MLCT) absorption and luminescence properties are critically reviewed, pointing out the criteria by which it is now possible to successfully design highly emissive $[\text{Cu}(\text{NN})_2]^+$ compounds, a rather elusive goal for a long time. To this end the development of spectroscopic techniques such as light-initiated time-resolved X-ray absorption spectroscopy (LITR-XAS) and femtosecond transient absorption have been rather fruitful since they have allowed us to firmly ground the indirect proofs of the molecular rearrangements following light absorption that had accumulated in the past 20 years. A substantial breakthrough towards highly emissive Cu(I) coordination compounds is constituted by heteroleptic Cu(I) complexes containing both N- and P-coordinating ligands ($[\text{Cu}(\text{NN})(\text{PP})]^+$) which may exhibit luminescence quantum yields close to 30% in deaerated CH_2Cl_2 solution and have been successfully employed as active materials in OLED and LEC optoelectronic devices. Also copper clusters may exhibit luminescence bands of halide-to-metal charge transfer (XMCT) and/or cluster centered (CC) character and they are briefly reviewed along with miscellaneous Cu(I) compounds that recently appeared in the literature, which show luminescence bands ranging from the blue to the red spectral region.

Keywords Clusters · Copper · Electron transfer · Energy transfer · Luminescence · OLED · Phenanthroline

1

An Overview of Copper

1.1

Historical Notes, Current Use, Consumption Trends

Copper was known to some of the oldest civilizations on record, and has a history of use that is at least 10 000 years old. A copper pendant was found in what is now northern Iraq that dates to 8700 B.C. and by 5000 B.C. there are signs of copper smelting from simple copper compounds such as malachite or azurite. This process appears to have been developed independently in several parts of the world since several centuries B.C., including Anatolia, China, Central America and West Africa. The Egyptians found that, upon addition of small amounts of tin, copper becomes easier to cast, and bronze alloys were extensively found in the Nile valley. The use of bronze was so pervasive in a certain era of civilization that the period spanning from 2500 to 600 B.C. is named the Bronze Age. In Roman times, copper became known as *aes Cyprium*, *aes* being the generic Latin term for copper alloys such as bronze or other metals, and *Cyprium* because so much of it was mined in the island of Cyprus. From this, the phrase was simplified to *cuprum* (originating the current chemical symbol) and then eventually Anglicized into *copper*.

Copper is usually found in Nature in association with sulfur. Pure copper metal is generally produced from a multistage process, beginning with the mining and concentrating of low-grade ores containing copper sulfide minerals, and followed by smelting and electrolytic refining to produce a pure copper cathode. An increasing share of this metal is produced from acid leaching of oxidized ores. Because of its properties which include high ductility, malleability, thermal and electrical conductivity, and resistance to corrosion, copper has become a major industrial metal, ranking third after iron and aluminum in terms of quantities consumed. Electrical uses of copper, including power transmission and generation, building wiring, telecommunication, and electronic products, account for about three quarters of total employment. Today, copper by-products from manufacturing and obsolete copper products are readily recycled and contribute significantly to supply. This is becoming a necessity due to the increasing difficulty of production to meet current world demand which has led to a quintuplication of the copper price during the last seven years, rising from \$0.60/pound in June 1999 to \$3.75/pound in May 2006. In 2005 14.9 million tons of copper were mined around the world; the global world reserves, economically recoverable with current technologies, amount to 470 million tons [1]. It has been recently estimated that ca. 25% of the copper stock initially available in the lithosphere has been already placed in use or in wastes from which it will probably never be recovered. This poses concern about the sustainability of current consumption trends of such a valuable commodity in the mid-long term [2].

1.2

Chemical Properties, Coordination Geometries, Excited States—Cu(I) vs. Cu(II)

Copper is a transition element belonging to the same group of the periodic table as gold and silver, these elements are sometimes referred to as the coinage metals in recognition of their historically widespread use in stamping coins. Copper has a single *s* electron outside the filled 3*d* shell but its properties have essentially nothing in common with alkali metals except for the possibility of assuming the +1 oxidation state. The filled *d* shell is not very effective in shielding the *s* electron from the nuclear charge, so the first ionization enthalpy of Cu is higher than that of the alkali metals. Since the electrons of the *d* shell are also involved in metallic bonding, the heat of sublimation and the melting point of Cu are also much higher than those of the alkalis. The above factors, taken together, are responsible for the noble character of copper. Indeed copper is the only industrial pure metal, used on a massive scale, exhibiting a positive electrochemical potential: for this reason it is not corroded by acids, unless they are strongly oxidizing like HNO₃ and H₂SO₄.

Copper in solution has two common oxidation states: +1 and +2. Because of their intrinsically superior photochemical and photophysical properties (vide infra), in this review our attention is focused on Cu(I) complexes, which

can be classified in three main categories, i.e. anionic complexes (e.g. al-complexes), neutral clusters and cationic complexes. The photochemistry of Cu(I) complexes, also related to environmental aspects, has already been reviewed [3, 4], here we will essentially focus on photophysics. Anionic complexes do not exhibit attractive photophysical properties (e.g. luminescence), unlike cluster and cationic complexes which show a very rich photophysical behavior. Among the latter, the most extensively investigated are NN-type (where NN indicates a chelating imine ligand, typically 1,10-phenanthroline) or PP-type (where PP denotes a bisphosphine ligand). Both homoleptic $[\text{Cu}(\text{NN})_2]^+$ and heteroleptic $[\text{Cu}(\text{NN})(\text{PP})]^+$ motifs have been investigated.

The coordination behavior of Cu(I) is strictly related to its electronic configuration. The complete filling of *d* orbitals (d^{10} configuration) leads to a symmetric localization of the electronic charge. This situation favors a tetrahedral disposition of the ligands around the metal center in order to locate the coordinative sites far from one another and minimize electrostatic repulsions (Fig. 1). Clearly, the complete filling of *d* orbitals prevents *d-d* metal-centered electronic transitions in Cu(I) compounds. On the contrary, such transitions are exhibited by d^9 Cu(II) complexes and cause relatively intense absorption bands in the visible (VIS) spectral window. The lowest ones extend into the near infrared (NIR) region (above 800 nm for the Cu(II) aqua ion) [5] and deactivate via ultrafast non-radiative processes. The fact that the lowest electronic states of Cu(II) complexes are ultra-short lived make them far less interesting than Cu(I) complexes from the photophysical point of view.

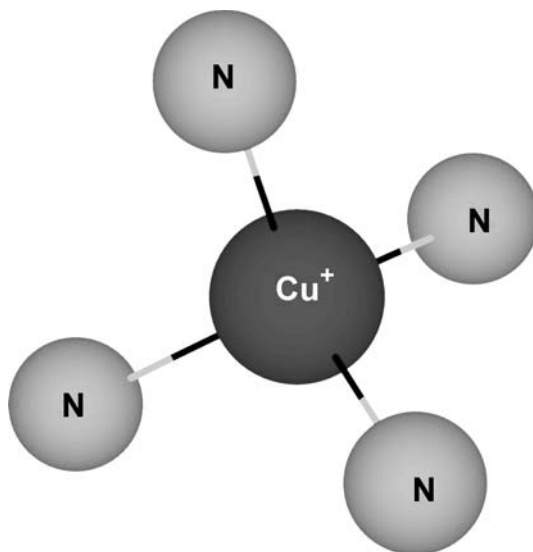


Fig. 1 Tetrahedral coordination environment typical of Cu(I) complexes

Cu(I) cluster compounds are characterized by a variety of emitting electronic levels whereas Cu(I) cationic complexes show only luminescence originating from metal-to-ligand charge-transfer (MLCT) states, as long as empty π orbitals are easily accessible in the ligands. Such MLCT transitions, which clearly take advantage of the low oxidation potential of Cu(I), are also commonly observed in other classes of coordination compounds, for example those of d^6 metals like Ru(II)-bipyridines [6] and Ir(III)-phenylpyridine complexes [7].

MLCT electronic transitions in coordination compounds are normally more intense when compared to MC (metal-centered) ones since they do not undergo the same prohibitions by orbital symmetry; accordingly MLCT absorption bands exhibit relatively high molar extinction coefficients. As far as emission is concerned, when MLCT excited states are the lowest-lying, they are generally characterized by long lifetimes, and potentially intense luminescence, even though exceptions are possible (*vide infra*). Complexes exhibiting long-lived MLCT excited states have been extensively investigated in the last decades both for a better comprehension of fundamental phenomena [8, 9] and for potential applications related to solar light harvesting and conversion [10–12]. Among them the highest attention was probably devoted to Ru(II) [13], Os(II) [14] and, more recently, Ir(III) [7] complexes, however, economical and environmental considerations make Cu(I) compounds interesting alternatives [15].

As extensively discussed in the literature, long-lived luminescent MLCT excited states of d^6 metal complexes, in particular those of Ru(II), can be strongly affected by the presence of upper lying MC levels. The latter can be partially populated through thermal activation from the MLCT states and prompt non-radiative deactivation pathways and photochemical degradation [6, 16]. Closed shell d^{10} copper(I) complexes cannot suffer these kinds of problems, but undesired non-radiative deactivation channels of their MLCT levels can be favored by other factors, as will be discussed in detail further on in this review. An orbital diagram illustrating the electronic transitions of Ru(II) and Cu(I) complexes is reported in Fig. 2.

1.3

Copper in Biology

Copper, even if present in traces, is an essential metal for the growth and development of biological systems. Copper plays a fundamental role in cerebral activity, nervous and cardiovascular systems, oxygen transport and cell protection against oxidation. Copper is important to strengthen the bones and to guarantee the performances of the immune system [17].

Metals are commonly found as natural constituents of proteins and, in the course of evolution, Nature has learned how to use the special properties of metal ions to perform a wide variety of specific functions associated

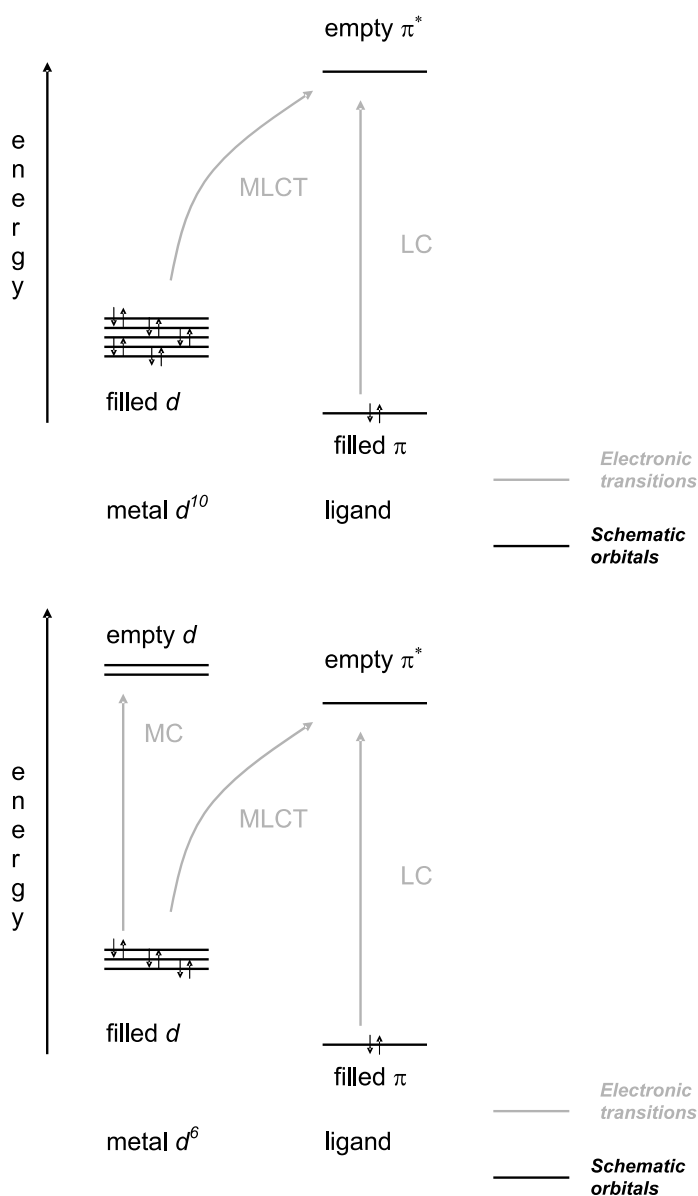


Fig.2 Qualitative comparison of orbitals and related electronic transitions in metal complexes having d^6 (e.g. Ru(II)) and d^{10} (e.g. Cu(I)) configurations

with life processes. It is puzzling that only a limited number of transition elements of the periodic table are utilized in biological systems, among them iron, copper, and zinc are of key importance. The criteria by which Nature chooses metals in biological systems are rather intriguing. One factor that

seems to be quite important is their relative abundance on Earth. A second factor is related to the fact that active centers of metalloproteins consist of kinetically labile and thermodynamically stable units. Kinetic lability facilitates rapid assembly/disassembly of the metal centers as well as fast association/dissociation of substrates. Both the above criteria are fulfilled by copper, which has been present in living organisms since the early stages of evolution, representing a fundamental constituent of many biological systems, particularly proteins, with the function of transporting oxygen and transferring electrons.

A key diversity between Cu(I) and Cu(II) is the different preferential coordination geometry. Cu(I) prefers tetrahedral four-coordinate geometries whereas Cu(II) complexes are typically square-planar or, in some biosystems, trigonal planar; occasionally, square planar compounds bind two additional weakly bonded axial ligands. In metalloproteins undergoing electron transfer processes, copper experiences a wealth of slightly different coordination environments: a tetrahedral ligand arrangement usually stabilizes Cu(I) over Cu(II), decreasing the Cu(II)/Cu(I) reduction potential, whereas high reduction potentials are achieved through distortion towards trigonal planar. In general, the thermodynamic stability of a metal center in biological environments is determined not only by inherent preferences of the metal for a particular oxidation state, ligand donor set, and coordination geometry, but also by the ability of the biopolymer to control, through its three-dimensional structure, the stereochemistry and the actual nearby ligand available for coordination. Non-coordinating residues also contribute to shape the local environment via hydrophilic/hydrophobic effects or steric blocking of coordination sites [17]. The complex pattern of factors occurring in biological systems make it possible to reach coordination geometries, such as trigonal planar, which can hardly be reproduced via synthetic chemistry.

Two examples of copper containing metalloproteins, namely the blue copper site and the mixed-valence binuclear Cu_A center, can be illustrated to better understand how Nature organizes metal complexed centers, with the aim of optimizing their properties for a specific function, in this case electron transfer [18].

In the blue copper site, which occurs in the plastocyanin that couples photosystem I with photosystem II through electron transfer (ET) [19], the X-ray geometrical structure of the Cu(II) center is distorted tetrahedral and not square planar, as normally observed for cupric complexes. The coordination environment is provided by two histidine nitrogen atoms giving 2.05 Å long N-Cu bonds, one thiolate sulfur of cysteine with a short Cu-S bond of ≈ 2.1 Å length and one thioether methionine at a longer distance (S-Cu ≈ 2.9 Å), Fig. 3.

The unusual geometry and ligation are responsible for the unique spectroscopic features of the blue copper site. In contrast to the weak *d-d* tran-

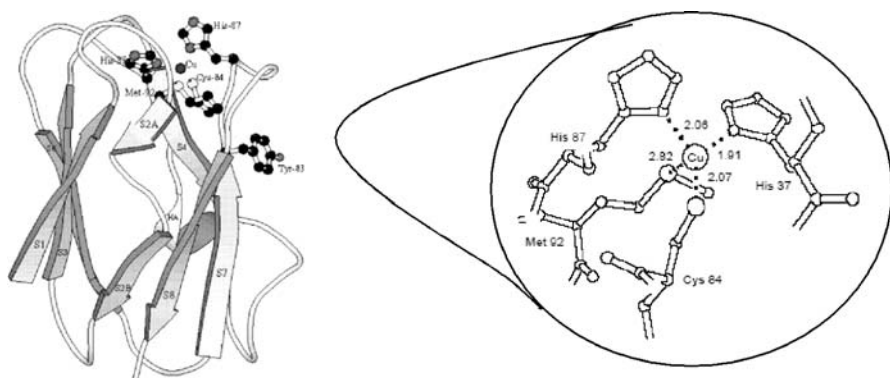


Fig. 3 The blue copper site inside plastocyanin

sitions of normal tetragonal Cu(II) complexes with $\varepsilon \approx 40 \text{ M}^{-1} \text{cm}^{-1}$ at ca. $16\,000 \text{ cm}^{-1}$ ($\approx 620 \text{ nm}$), the blue copper site has an intense absorption band at $16\,000 \text{ cm}^{-1}$ with $\varepsilon \approx 5000 \text{ M}^{-1} \text{cm}^{-1}$ Fig. 4 [20]. This result is a consequence of an inversion of the ligand-to-metal charge transfer (LMCT) pattern for the blue copper site that rises from its particular ligands distribution. As can be seen in Fig. 5 variation of the typical overlapping between the orbitals of copper and those of the ligands leads to an inversion of the relative absorption intensity, the final result is an enhancement of the absorption on the low energy side [21].

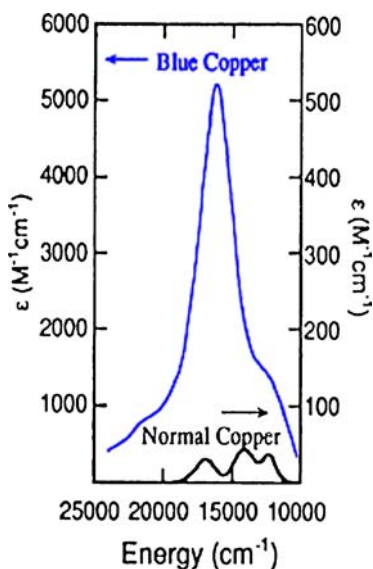


Fig. 4 Absorption spectrum of the blue copper site in plastocyanin (Reprinted from [20] with permission, © (2006) American Chemical Society)

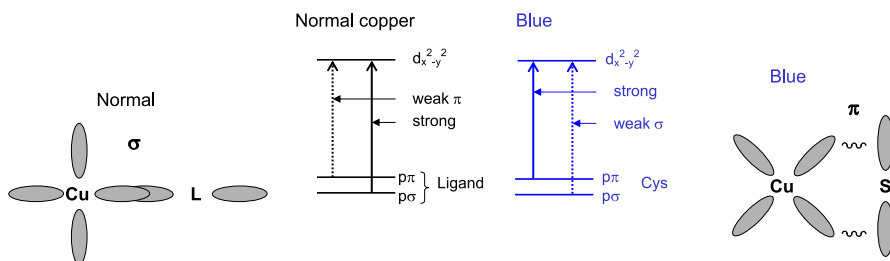


Fig. 5 Inverted intensity pattern of ligand-to-metal charge transfer absorption transitions for the blue copper site compared to a regular Cu(II) complex. L = generic organic ligand; S = sulfur coordinating site of a cysteine residue

In photosynthesis, plastocyanin functions as an electron transfer relay between cytochrome *f* (inside cytochrome *b₆f* complex) and P700⁺. Cytochrome *b₆f* complex (from photosystem II) and P700⁺ (from photosystem I) are both membrane-bound proteins with exposed residues on the lumen-side of the thylakoid membrane of chloroplasts. Cytochrome *f* acts as an electron donor while P700⁺ accepts electrons from reduced plastocyanin (Fig. 6) [18].

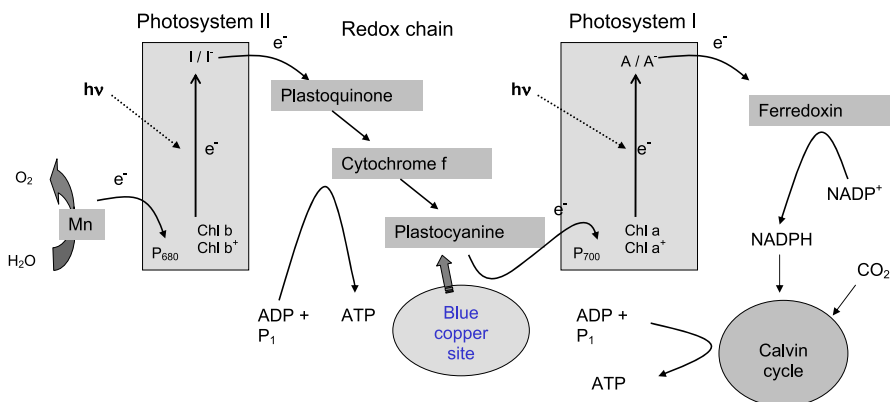


Fig. 6 The so-called Z-scheme of photosynthesis

Plastocyanin (Cu²⁺Pc) is reduced by cytochrome *f* to Cu⁺Pc which eventually diffuses through the lumen until recognition/binding occurs with P700⁺, which oxidizes Cu⁺Pc back to Cu²⁺Pc. The electronic structure of the blue copper is crucial for an efficient electron transfer in which Cu(II) is reduced to Cu(I). The tetrahedral organization of the Cu(II) site minimizes the reorganizational energy λ increasing the rate of the process, according to Marcus theory [22].

In the Cu_A mixed-valence binuclear site (Fig. 7), present for example in the terminal aerobic respiration enzyme (cytochrome c oxidase), a similar situation occurs [23]. The efficient electron transfer is promoted by the three-dimensional organization and by electronic factors. The presence of two coordinated anionic cysteine thiolates in a monomeric Cu complex, however, would severely decrease the rate of the electron transfer process by stabilizing the oxidized Cu^{2+} state and making the reduction potential too negative (Fig. 7).

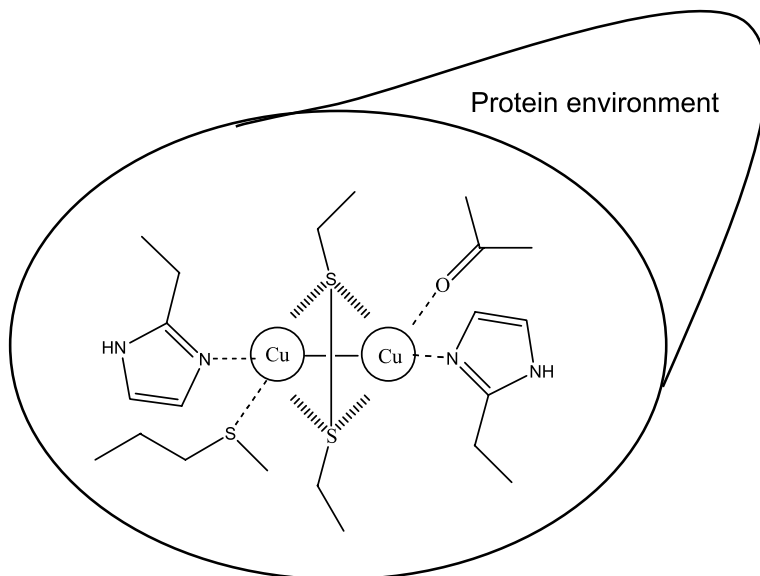


Fig. 7 Schematic structure of the Cu_A mixed valence dinuclear site, present in some terminal aerobic respiration enzymes

In Cu_A this is avoided by weakening axial bonding interactions and by delocalizing the charge over two Cu ions [24].

In conclusion, Nature makes extensive use of the coordination flexibility of copper complexes and of the related tuning of electronic properties, to optimize processes of crucial importance in living organisms.

1.4

Cu(I) in Supramolecular Chemistry

In the frame of the spectacular development of synthetic supramolecular chemistry over the last two decades [25], coordination chemistry has played a primary role [26] and, in this context, bisphenanthroline Cu(I) complexes (hereafter indicated as $[\text{Cu}(\text{NN})_2]^+$) have been major players [15]. Cu(I)

has a strong tendency to bind phenanthroline-type ligands [27] originating a wealth of simple tetrahedral $[\text{Cu}(\text{NN})_2]^+$ complexes with high yields. The parent compound $[\text{Cu}(\text{phen})_2]^+$ (phen = 1,10-phenanthroline) has been scarcely studied, probably due to the lack of long-lived electronic excited states in solution, a problem that is partially avoided in the solid state, where some emission has been detected [28]. The most common $[\text{Cu}(\text{NN})_2]^+$ complexes are those 2,9 or 4,7 disubstituted phenanthrolines, due to an easier synthetic accessibility of the related ligands.

The development of sophisticated synthetic strategies, which take advantage of this metal-ligand affinity, has afforded a number of complicated molecular architectures like catenanes [29–31], rotaxanes [7, 32, 33],

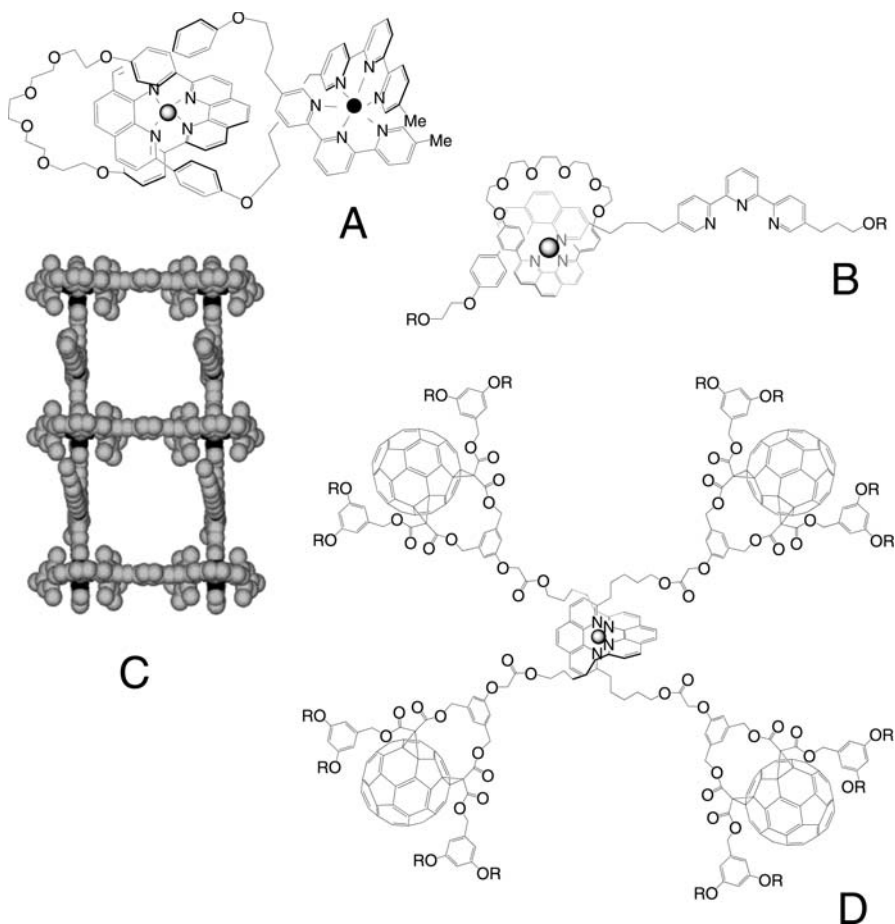


Fig. 8 Selected examples of multicomponent arrays containing Cu(I)-bisphenanthroline centers: **A** catenane, **B** rotaxane ($\text{R}=4\text{-[tris-(4-tert-butyl-phenyl)-methyl]-phenolato}$), **C** grid, **D** dendrimer ($\text{R}=\text{C}_8\text{H}_{17}$)

pseudo-rotaxanes [34, 35], knots [36, 37], dendrimers [38, 39], helices [40–42], polynuclear hosts [43] etc. as originally developed by Sauvage, Dietrich-Buchecker and coworkers [44]. Some of these fascinating structures are depicted in Fig. 8.

Most notably, some suitably engineered supramolecular architectures based on $[\text{Cu}(\text{NN})_2]^+$ cores are able to carry out motion at the molecular level upon chemical [45], or electrochemical/photochemical stimulation [32, 46] behaving as molecular machine prototypes [47, 48]. For instance a [2]-catenate made of two different rings, one with a phenanthroline fragment the other bearing both a phenanthroline and a terpyridine unit, undergoes spontaneous and reversible molecular rearrangements (Fig. 9 steps (B) and (D)) upon oxidation (step A) and subsequent reduction (step C). Rearrangements are driven by the different preferential coordination geometries of Cu(I) and Cu(II), i.e. tetra- vs. pentacoordination [46].

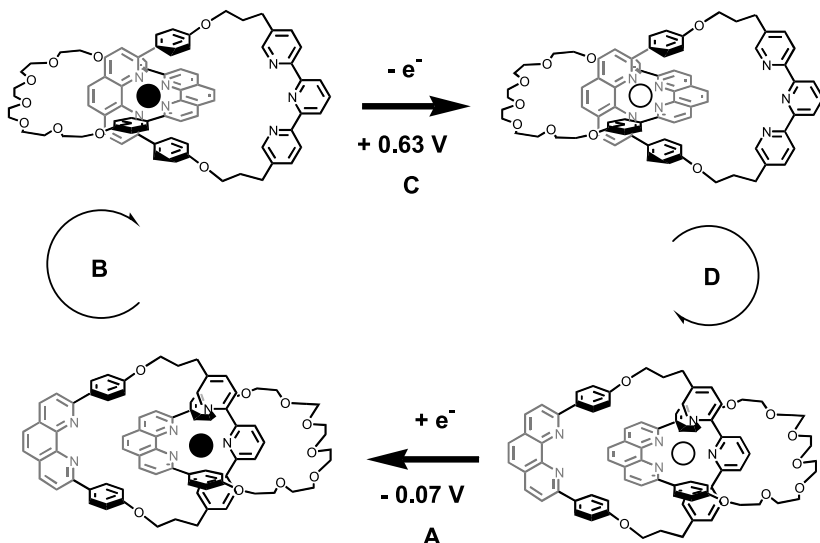


Fig. 9 Electrochemically induced molecular motions in a catenane containing a $[\text{Cu}(\text{NN})_2]^+$ center and a free tpy ligand. The spontaneous motion is driven by the different preferential coordination geometry of Cu(I) vs. Cu(II)

More recently, Schmittl and coworkers have made new supramolecular systems based on $[\text{Cu}(\text{NN})_2]^+$ -type building blocks such as racks [49], grids [50], boxes [51], and macrocycles [52]. Control of the sophisticated heteroleptic architectures has been achieved by exploiting the HETPHEN (HETeroleptic bisPHENanthroline) concept [53]. This approach is based on the kinetic control of the metal complexation equilibrium and, in the target complex, the Cu(I) ion turns out to be bound to a simple and a bulky phenanthroline ligand; this concept is schematically illustrated in Fig. 10.

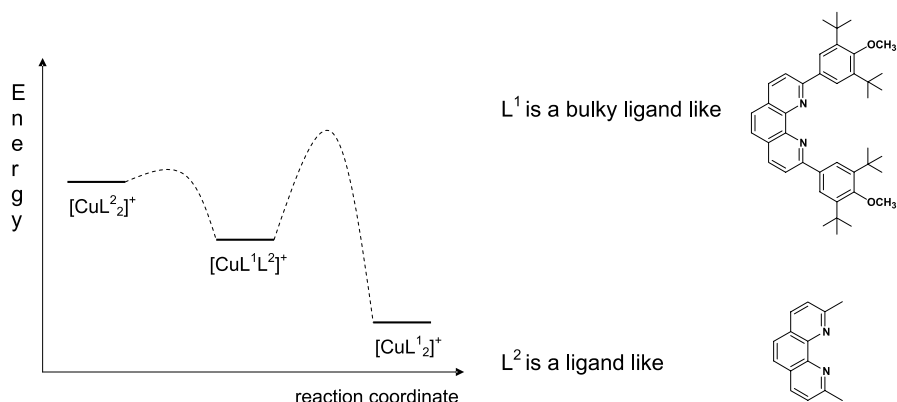


Fig. 10 Kinetic control in the formation of heteroleptic $[\text{CuL}^1\text{L}^2]^+$ complexes (HETPHEN approach)

Simple and supramolecular Cu(I)-bisphenanthroline complexes exhibit very interesting and largely tunable photophysical properties that will be illustrated in the next sections.

2

Cu(I)-Bisphenanthroline Complexes

2.1

Ground State Geometry

Cu(I)-bisphenanthroline complexes generally display distorted tetrahedral geometries. The distortion from D_{2d} symmetry can be visualized with the aid of Fig. 11 [54].

θ_x , θ_y , and θ_z define the interligand angles based on the CuN_4 core of the complex. When a molecule possesses a perfect tetrahedral geometry (D_{2d}), $\theta_x = \theta_y = \theta_z = 90^\circ$, whereas the square planar geometry D_2 implies $\theta_x = \theta_y = 90^\circ$ and $\theta_z = 0^\circ$. Practically, θ_z is the dihedral angle between the ligand planes and a decrease from 90° indicates a flattening distortion of the molecule that progressively lowers its symmetry to D_2 . The θ_x and θ_y values indicate the degree of “rocking” and “wagging” distortions [55].

These distortions are due to intra- and intermolecular (in solid state crystals) π -stacking interactions which also cause considerable displacement from D_{2d} symmetry. In practice, combinations of various types of distortions occur in $[\text{Cu}(\text{NN})_2]^+$ complexes and their extent is dictated by the size, chemical nature, and positions of the phenanthroline substituents. Recently, the parameter ξ_{CD} has been proposed to quantify the degree of distortion as

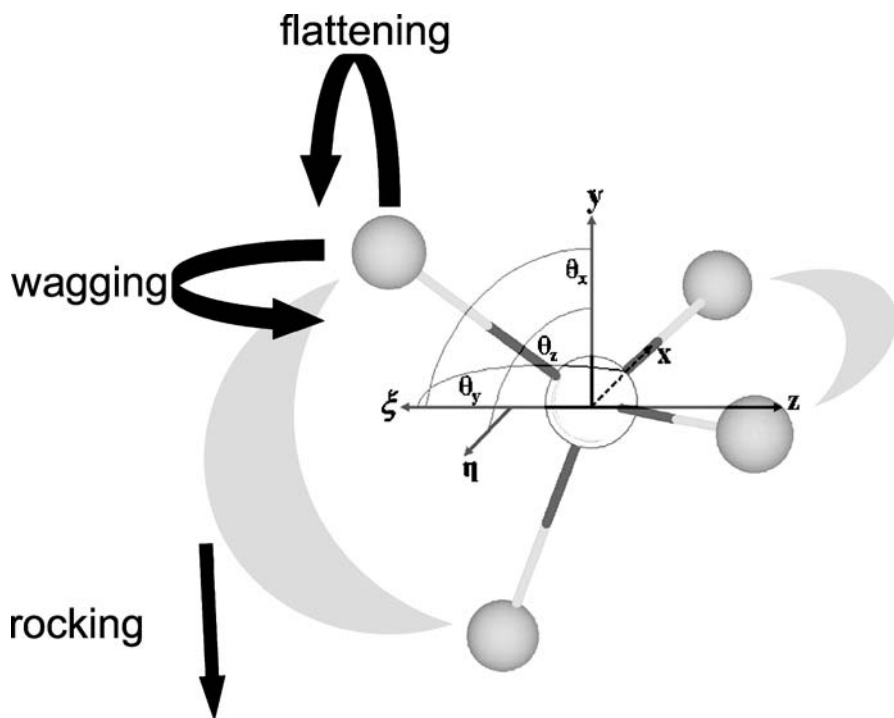


Fig. 11 Relative orientation of the two ligand planes (xz and yz) and of the reference θ_x (rocking), θ_y (wagging), and θ_z (flattening) angles. θ_z is on the plane of the sheet; the grey circles represent the N phenanthroline atoms; the Cu ion is centered on the origin of the reference axes; the vector ξ lies on the yz plane, the vector η is perpendicular to it. In this schematic representation the phenanthroline on the *left-hand* side is assumed to be placed on the plane of the sheet (yz) and that on the *right-hand* side on the xz plane perpendicular to it

a combination of θ_x , θ_y and θ_z (Eq. 1) [56]:

$$\xi_{CD} = \frac{(90^\circ + \theta_x)(90^\circ + \theta_y)(90^\circ + \theta_z)}{180^3} \quad (1)$$

where CD stands for “combined distortion”.

Detailed X-ray crystallographic studies have shown that the specific geometry in the solid state is dictated by packing forces and considerable variation is found for the *same* complex as a function of the counteranion. In the case of $[\text{Cu}(\text{1})_2]$ (Fig. 12) θ_z varies from 88° in the tetrafluoroborate and tosylate salts to 73° in the picrate [57].

As an example, the θ_z dihedral angles between the two phenanthroline planes in $[\text{Cu}(\text{1})_2]\text{PF}_6$, $[\text{Cu}(\text{2})_2]\text{PF}_6$ and $[\text{Cu}(\text{3})_2]\text{PF}_6$ are 79.4° [57], 87.5° [56, 58] and 79.8° [59], respectively, according to X-ray crystal structures; ligands 1, 2 and 3 are depicted in Fig. 12.

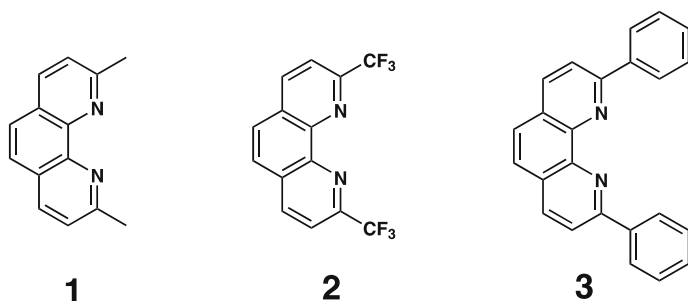


Fig. 12 Ligands 1 (2,9-dimethyl-1,10-phenanthroline), 2 (2,9-ditrifluoromethyl-1,10-phenanthroline), 3 (2,9-diphenyl-1,10-phenanthroline)

Substantial geometric distortion is possible with small methyl residues in $[\text{Cu}(\mathbf{1})_2]\text{PF}_6$, whereas bulkier trifluoromethyl groups force a more rigid quasi-tetrahedral arrangement in $[\text{Cu}(\mathbf{2})_2]\text{PF}_6$. In the case of $[\text{Cu}(\mathbf{3})_2]\text{PF}_6$, instead, the distortion is dictated by intramolecular π - π stacking interactions between phenyl rings and phenanthroline cores of the other ligand. The strong and sometimes hardly predictable effects of steric and/or electronic factors on the ground state geometry of $[\text{Cu}(\text{NN})_2]^+$ complexes is reflected in the wide tuning of electronic absorption spectra.

2.2

Absorption Spectra

In Fig. 13 are depicted the absorption spectra of three homoleptic complexes of 2,9-disubstituted phenanthrolines in CH_2Cl_2 solution, namely $[\text{Cu}(\mathbf{1})_2]^+$, $[\text{Cu}(\mathbf{4})_2]^+$, and $[\text{Cu}(\mathbf{5})_2]^+$. Ligands 1, 4, and 5 (Figs. 12 and 14) have alkyl- or aryl-type substituents and serve as paradigmatic cases.

The ultraviolet (UV) portion of the spectra are characterized by the intense ligand-centered (LC) bands typical of the $\pi\pi$ transitions of the phenanthroline ligands [60]; the molar absorption coefficients (ϵ) are of the order of $50\,000$ – $60\,000\text{ M}^{-1}\text{ cm}^{-1}$. Some mixing with MLCT states cannot be excluded according to density functional theory (DFT) calculations [61]. The bands lying in the VIS spectral region are much weaker than those in the UV (ϵ typically below $10\,000\text{ M}^{-1}\text{ cm}^{-1}$) and have been assigned to metal-to-ligand charge-transfer (MLCT) electronic transitions [61–64]. These levels occur at low energy because the Cu^+ ion can be easily oxidized [65] and the phen-type ligands possess low-energy empty π orbitals. Direct evidence of the localized nature of the lowest-lying MLCT state of Cu(I)-bisphenanthrolines was achieved via resonance Raman [66] and transient absorption spectroscopy [67].

In a number of papers McMillin et al. [68–71] and others [72–74] have presented and discussed the absorption spectra of several mononuclear Cu(I)-

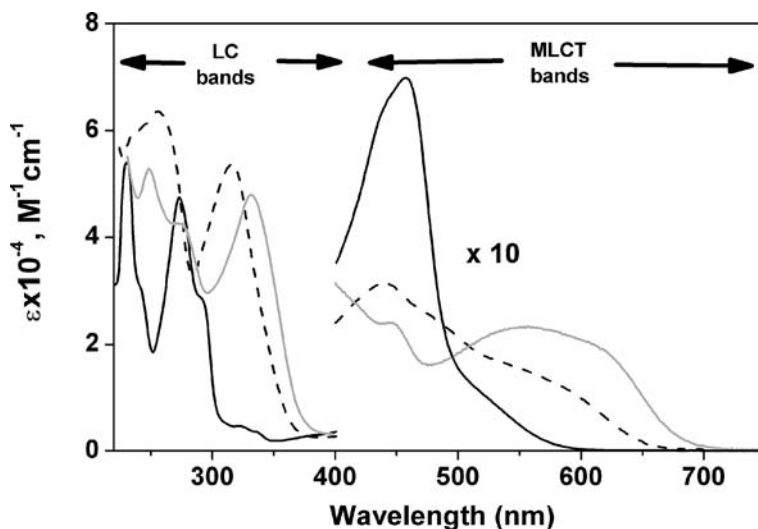


Fig. 13 Absorption spectra of $[\text{Cu}(\mathbf{1})_2]^+$ (full black line), $[\text{Cu}(\mathbf{4})_2]^+$ (dashed line) and $[\text{Cu}(\mathbf{5})_2]^+$ (full grey line) in CH_2Cl_2 solution at room temperature

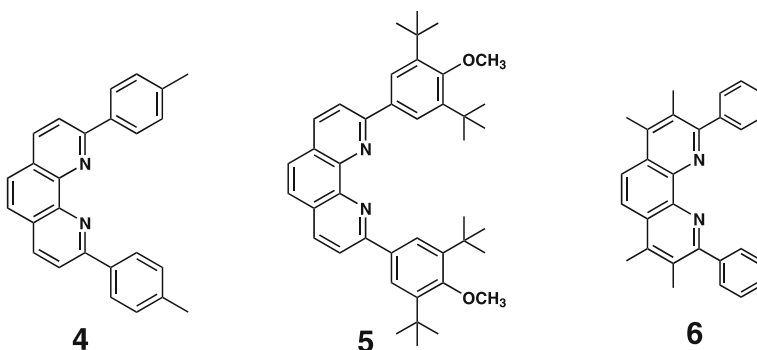


Fig. 14 Ligands **4** (2,9-di-*p*-tolyl-1,10-phenanthroline), **5** (2,9-bis(3,5-di-*tert*-butyl-4-methoxyphenyl)-1,10-phenanthroline), **6** (2,9-Diphenyl-3,4,7,8-tetramethyl-1,10-phenanthroline)

bisphenanthrolines. In general, at least three MLCT bands can be identified in the VIS spectral region [68]. They are termed band I (above 500 nm), band II (maximum around 430–480 nm, the most prominent, attributed to $S_0 \rightarrow S_3$ transitions [61]), and band III (390–420 nm, often hidden by the onset of band II). The envelope of such MLCT bands defines the shape of the VIS absorption spectrum (400–700 nm). Spectral intensities are strictly related to the symmetry of the complex (D_{2d} vs. D_2 , Fig. 15) that, in turn, is affected by the distortion from the tetrahedral geometry (see above).

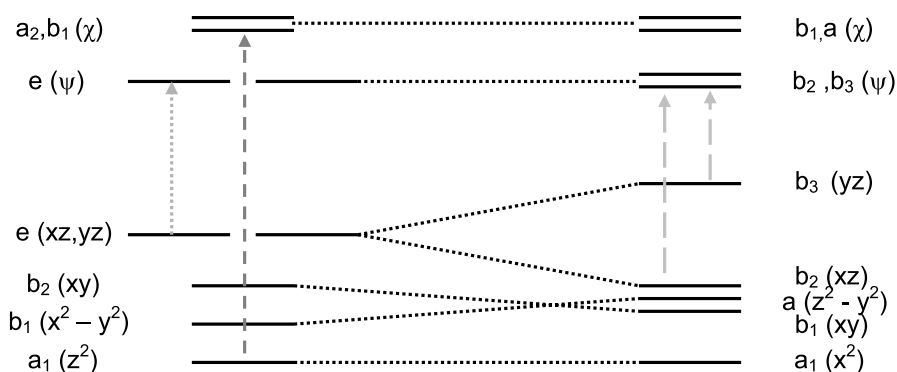


Fig. 15 Schematic orbital splitting diagrams for $[\text{Cu}(\text{NN})_2]^+$. *Left*, D_{2d} symmetry; *right*, D_2 symmetry. Grey arrows represent the transitions leading to bands I (— —), band II ($\cdots$), and band III (— —)

A simple picture able to rationalize the MLCT absorption patterns of these complexes in solution is difficult, nevertheless some general trends have been found by analyzing the MLCT absorption maxima and molar extinction coefficients of series of $[\text{Cu}(\text{NN})_2]^+$ compounds and have been reported elsewhere [15].

The spectrum of $[\text{Cu}(\mathbf{4})_2]^+$ in Fig. 13 exhibits a well-established fingerprint for complexes with 2,9-aryl substitution of the phenanthroline ring, i.e. a pronounced low-energy shoulder extending down to 650 nm (band I, see above), which is practically absent in the case of $[\text{Cu}(\mathbf{1})_2]^+$. This pattern is related to the above mentioned intramolecular π -stacking interactions, which make the transition corresponding to band I more permitted. The absorption spectrum of $[\text{Cu}(\mathbf{5})_2]^+$ is somewhat different if compared to both $[\text{Cu}(\mathbf{4})_2]^+$ and $[\text{Cu}(\mathbf{1})_2]^+$. The low energy band is wider and more intense and the peak around 440, which is typically the most intense in $[\text{Cu}(\text{NN})_2]^+$ complexes, appears as just a weak shoulder [74]. This trend is due to the presence of the cumbersome *tert*-butyl groups on the phenyl residues, that limit π - π stacking interactions and make the structure of the complex particularly rigid. The MLCT absorption profile of $[\text{Cu}(\mathbf{5})_2]^+$ is found to be similar to that of a Cu(I)-catenate complex made of two interlocked 27-membered rings containing a phenanthroline moiety and exhibiting a very rigid coordination environment [75]. The structural peculiarity of $[\text{Cu}(\mathbf{5})_2]^+$, as revealed by the absorption spectrum, is in accord with its extraordinary kinetic inertness towards demetallation [74].

Interestingly, it has been found that the complex $[\text{Cu}(\mathbf{6})_2]^+$ (Fig. 14) exhibits a very weak band above 500 nm despite the presence of phenyl rings in the 2 and 9 positions [71]. Indeed this confirms the above described model: the methyl groups in the 3 and 8 position contrast the flattening distortion,

leading to a coordination geometry (and a spectrum) very similar to that of the much simpler $[\text{Cu}(\text{I})_2]^+$ complex.

Some Cu(I)-bisphenanthroline compounds have also been utilized as receptors for dicarboxylic acids [76] and spherical inorganic anions [77]. The recognition motif is established by suitably functionalizing one phenyl residue in the 2 or 9 position of the phenanthroline chelating units, which are made able to pinch the pertinent substrate. The formation of the supra-molecular adducts is monitored through the substantial changes of the MLCT absorption bands that occur as a consequence of the modification of the coordination geometry and related symmetry [76].

2.3

Excited State Distortion: Pulsed X-ray and Transient Absorption Spectroscopy

Upon light excitation of $[\text{Cu}(\text{NN})_2]^+$ complexes the lowest MLCT excited state is populated, thus the metal center changes its formal oxidation state from Cu(I) to Cu(II) [15]. The Cu(I) MLCT excited complex undergoes further flattening compared to its ground state and assumes a geometry similar to that of ground state Cu(II)-bisphenanthroline complexes [59]. In this excited state flattened tetrahedral structure a fifth coordination site is made available for the Cu(II) d^9 ion, that can be filled by nucleophilic species such as solvent molecules and counterions. The intermediate species thus obtained is termed “pentacoordinated exciplex”. The process, which is schematically depicted in Fig. 16, had been proposed by McMillin and coworkers nearly 20 years ago on the basis of classical photochemical experiments on series of $[\text{Cu}(\text{NN})_2]^+$ complexes with increasingly nucleophilic counteranions [78].

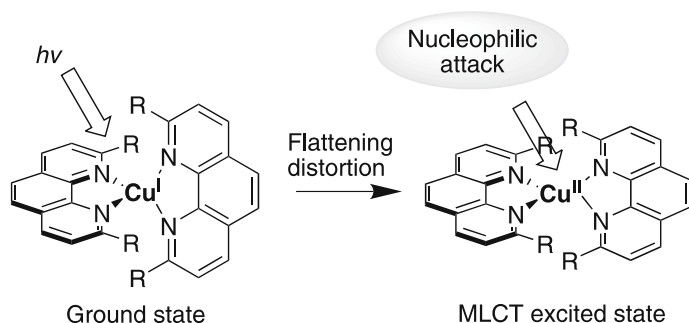


Fig. 16 Flattening distortion and subsequent nucleophilic attack by solvent, counterion, or other molecules following light excitation in Cu(I)-phenanthrolines. The size (and position) of the R substituents is of paramount importance in determining both the extent of the distortion and the protection of the newly formed Cu(II) ion from nucleophiles

In recent years this hypothesis has been nicely confirmed thanks to the development of light-initiated time-resolved X-ray absorption spectroscopy

(LITR-XAS) [79]. This pump-and-probe technique allows one to catch the transient oxidation state of a metal atom as well as its surrounding structures following photoexcitation via an ultrafast laser source; accordingly, it is particularly suited to investigating the process depicted in Fig. 16. Practically, the information obtained via LITR-XAS is a sort of snapshot of electronic excited states in disordered media (e.g. solution), which are generated via a UV-VIS femtosecond pump laser and subsequently probed with a 30–100 ps intense X-ray pulse produced by 3rd generation large synchrotron facilities [80].

This technique has been applied in solution studies to $[\text{Cu}(\text{1})_2]^+$ and unambiguously confirmed that, in the thermally equilibrated MLCT excited state, the copper ion is pentacoordinated both in poorly donor (toluene) [81] or highly donor (CH_3CN) [82] solvents; in addition, the copper ion has the same oxidation state as the corresponding ground state $\text{Cu}(\text{II})$ complex in both cases. Analogous investigations have been carried out also on $\text{Cu}(\text{I})$ complexes as solid crystals (“photocrystallography”) [55, 83]. LITR-XAS studies of $[\text{Cu}(\text{1})_2]^+$ in solution have been complemented by optical time-resolved spectroscopy, which evidenced spectroscopic features in the ps timescale, associated to excited state structural rearrangements, possibly flattening distortion [82].

We have also carried out femtosecond transient absorption studies on $[\text{Cu}(\text{7})_2]^+$ and $[\text{Cu}(\text{8})_2]^+$ in CH_2Cl_2 (Fig. 17) [84]. These complexes are characterized by alkyl- and more cumbersome phenyl-residues in the 2 and 9 position of the phenanthroline ligand, which imparts rather different photo-physical properties (i.e. shape of UV-VIS absorption, luminescence spectra, excited state lifetime) [85]. Despite this diversity, femtosecond transient absorption spectra have revealed a dynamic process lasting 15 ps in both cases Fig. 18.

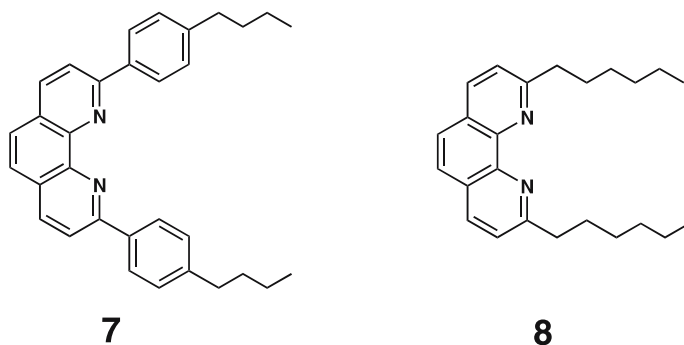


Fig. 17 Ligands 7 (2,9-bis(4-*n*-butylphenyl)-1,10-phenanthroline) and 8 (2,9-di-*n*-hexyl-1,10-phenanthroline)

Specific assignment of the observed spectral variation to (i) flattening distortion or (ii) extra ligand pick-up, two processes that might also occur sim-

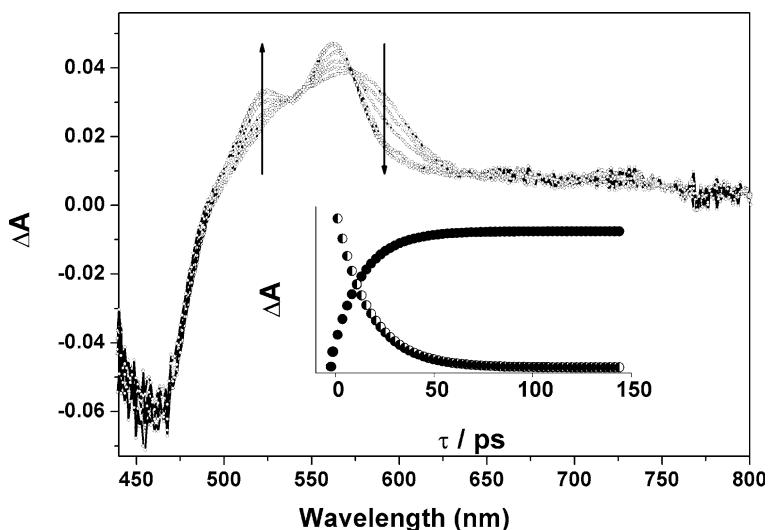


Fig. 18 Transient absorption spectral changes observed for $[\text{Cu}(\mathbf{8})_2]^+$ in CH_2Cl_2 at $\lambda_{\text{exc}} = 400$ nm (150 fs Ti:Sapphire laser pulse). The spectra were recorded at delays of 2, 5, 10, 25, 100, 1000 ps following the excitation pulse. In the inset are depicted spectral decays at two selected wavelengths, $\lambda_{\text{obs}} = 520$ (full circles) and 590 (half-empty circles)

ultaneously, is not straightforward. Access to the fifth coordinating position is likely to be less favored for the more congested phenyl-phenanthroline complex $[\text{Cu}(\mathbf{7})_2]^+$. Hence the identical rate constant observed for the two compounds in CH_2Cl_2 , as well as in CH_3CN for another $[\text{Cu}(\text{NN})_2]^+$ complex [82], is likely to be associated with the flattening distortion which is expected to be less solvent- and ligand-dependent than picking up an external unit for coordination expansion. Transient absorption studies leading to similar results have also been carried out with monophenanthroline complexes [86].

2.4

Emissive Excited State(s) and Luminescence Spectra

The first report on $[\text{Cu}(\text{NN})_2]^+$ luminescence in fluid solution dates back to 1980, when it was shown that, upon excitation into the MLCT band region, $[\text{Cu}(\mathbf{1})_2]^+$ exhibits a luminescence spectrum peaking around 700 nm and an excited state lifetime of 54 ns in air-equilibrated CH_2Cl_2 [87]. Luminescence from $[\text{Cu}(\text{NN})_2]^+$ complexes is observed in poorly electron donor solvents, typically CH_2Cl_2 . At room temperature, the emission band is wide and exhibit λ_{max} peaking between 680 and 740 nm, with rather low quantum yield ($\Phi_{\text{em}} 10^{-3} - 10^{-4}$) [15]. Excited state lifetimes in CH_2Cl_2 solution are strongly dependent on the degree of excited state distortion and the protection to-

wards exciplex quenching. It has been hypothesized that emission stems from the pentacoordinated exciplex itself that deactivates to a pentacoordinated ground state species which eventually loses the “fifth” nucleophilic ligand to regenerate the initial ground state pseudotetrahedral complex [81]. In recent years it has also been evidenced that some $[\text{Cu}(\text{NN})_2]^+$ complexes exhibit a prompt luminescence signal with a lifetime of the order of 13–16 ps, which is attributed to deactivation of $^1\text{MLCT}$ [88], whereas the long-lived component (above 50 ns) would be phosphorescence from $^3\text{MLCT}$, which borrows intensity from upper lying singlet levels [89].

The shortest and longest values reported to date (oxygen-free CH_2Cl_2 solution, longer-lived component) are 80 [68] and 930 ns [71] and refer to homoleptic $[\text{Cu}(\text{NN})_2]^+$ complexes of the two phenanthroline ligands depicted in Fig. 19.

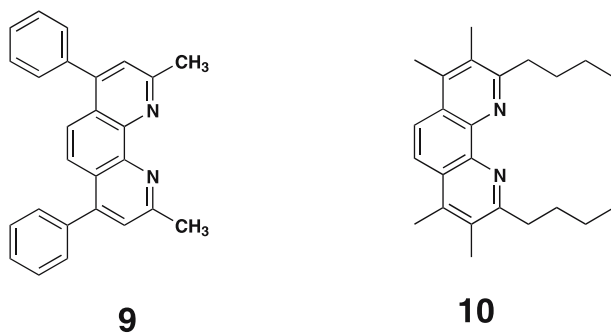


Fig. 19 Ligand **9** (2,9-dimethyl-4,7-diphenyl-1,10-phenanthroline) and **10** (2,9-di-*n*-butyl-3,4,7,8-tetramethyl-1,10-phenanthroline). Lifetime values of their $[\text{Cu}(\text{NN})_2]^+$ complexes differ by more than one order of magnitude

The value for $[\text{Cu}(\mathbf{9})_2]^+$ is very similar to that of $[\text{Cu}(\mathbf{1})_2]^+$ under the same conditions (80 ns), suggesting that electronic delocalization of the ligands [73], very strong for **9**, is less important than steric factors in determining the lifetimes value. Notably, substitution on the 3 and 8 position with a simple methyl residue in **10** is particularly effective to limit exciplex quenching and yields a lifetime of almost 1 μs . In general, the large majority of $[\text{Cu}(\text{NN})_2]^+$ homoleptic complexes exhibit excited state lifetimes in the range 80–350 ns in oxygen-free solution [15]. A longer lifetime (730 ns, $\Phi_{em} = 0.01$, oxygen-free CH_2Cl_2) has been found with the suitably designed heteroleptic complex $[\text{Cu}(\mathbf{1})(\mathbf{11})]^+$ [90], Fig. 20, in which excited state distortion is strongly limited by the cumbersome *tert*-butyl substituent. Interestingly, steric constraints make the formation of the homoleptic analogue $[\text{Cu}(\mathbf{11})_2]^+$ very difficult.

The picture describing the luminescent excited states of Cu(I)-bisphenanthrolines is not straightforward although Parker et al., in light of the ob-

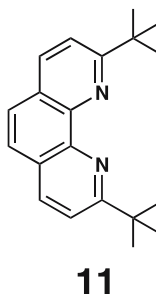


Fig. 20 Ligand 11 2,9-di-*tert*-butyl-1,10-phenanthroline

served large Stokes shift (over 5000 cm^{-1}) had attributed it to the lowest $^3\text{MLCT}$ excited state [91], likewise the popular family of octahedral Ru(II) -polypyridines [6]. McMillin and coworkers, instead, suggested that emission of $[\text{Cu}(\text{NN})_2]^+$ compounds arises from two MLCT excited states in thermal equilibrium, i.e. a singlet ($^1\text{MLCT}$) and a triplet ($^3\text{MLCT}$) [92]. The energy gap between these states was found to be about $1500\text{--}2000\text{ cm}^{-1}$ and, at room temperature, the population of the lower lying $^3\text{MLCT}$ level exceeds that of $^1\text{MLCT}$. At 77 K where the excited state population is largely frozen in the triplet, the emission band is red-shifted and much weaker compared to room temperature, a rather unusual trend. Recent studies have confirmed and refined this rationale [81, 85, 89].

A few years ago our group discussed detailed temperature-dependent luminescence studies of a series of $[\text{Cu}(\text{NN})_2]^+$ complexes of 2,9-disubstituted phenanthroline ligands [85]. The above-described two-level model, which implies red-shift and intensity decrease of the emission band upon temperature lowering, is always obeyed except when long alkyl chains are utilized as substituents of the phenanthroline chelating agent. In this case the “regular” trend is obeyed only until the matrix remains fluid ($T > 150\text{ K}$) but, when the matrix becomes rigid ($T < 120\text{ K}$), a substantial blue shift and intensity increase is observed. At 95 K these compounds are bright emitters as intense as Ru(II) complexes [85]. The two trends (i.e. “classical” vs. “odd”) in the luminescence intensity of $[\text{Cu}(\text{NN})_2]^+$ as a function of temperature are illustrated in Fig. 21 for $[\text{Cu}(\mathbf{7})_2]^+$ and $[\text{Cu}(\mathbf{8})_2]^+$.

We rationalized the unusual behavior observed for complexes having ligands with long alkyl chains to steric, rather than electronic factors. This interpretation has been confirmed by Siddique et al. who found that the radiative constant (k_r) of the lowest $^3\text{MLCT}$ level is structure-sensitive and increases dramatically when the dihedral angle θ_z is approaching 90° [89]. In other words the long-alkyl chain blocks the ground state geometry in a rigid matrix and grants intense orange luminescence from the lowest $^3\text{MLCT}$ level. We recently observed that the 77 K intense luminescence can also be observed for homoleptic complexes of the phenyl-substituted ligand, such as **12**

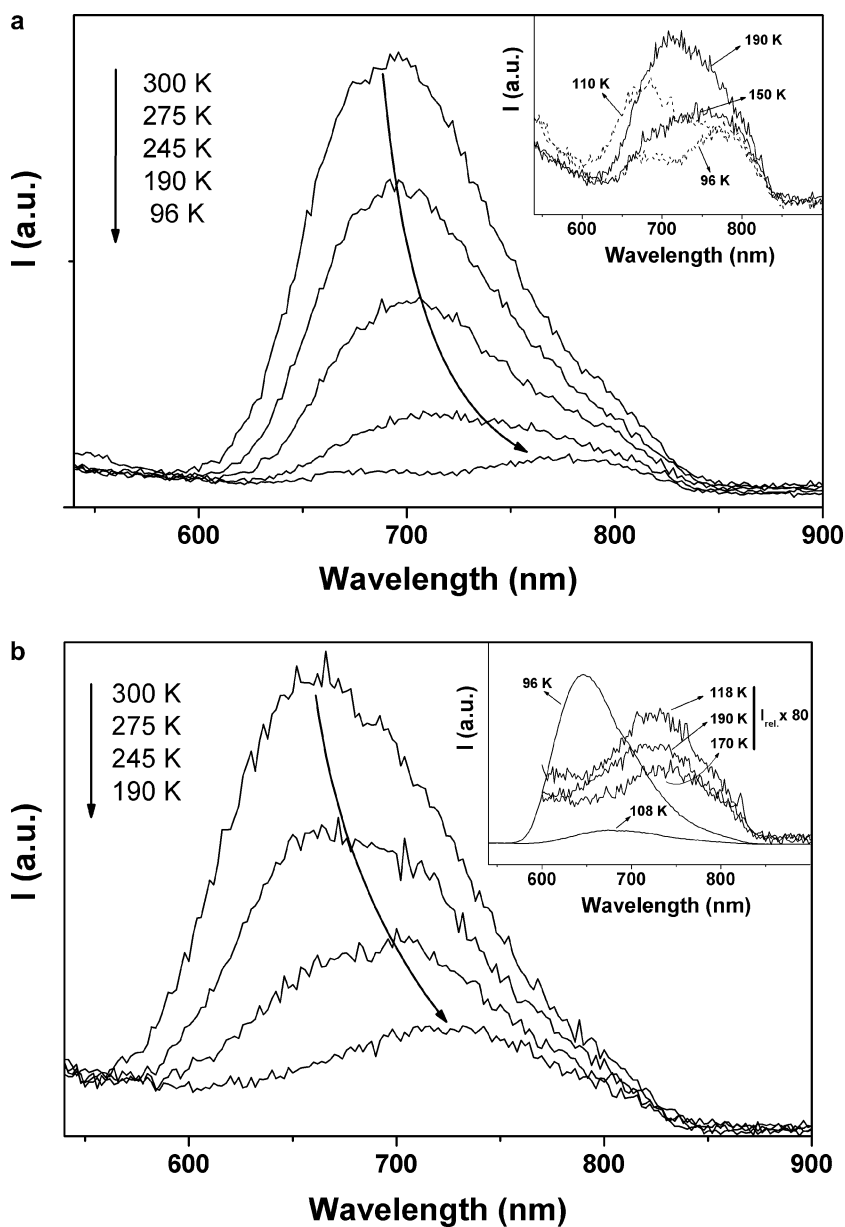


Fig. 21 Temperature dependence of the luminescence spectra of $[\text{Cu}(\mathbf{7})_2]^+$ (top) and $[\text{Cu}(\mathbf{8})_2]^+$ (bottom) in CH_2Cl_2 MeOH 1:1 (v/v). In the fluid domain (up to 170 K) emission intensity decrease and spectral red-shifting is observed by lowering temperature in both cases. By contrast when the solvent matrix becomes rigid (around 120 K), the two compounds behave differently. For the 2,9-dialkylphenanthroline complex (bottom panel) a complete reversal of the previous trend is observed with intensity recovery and blue shift. At 96 K a very strong luminescence band is recorded

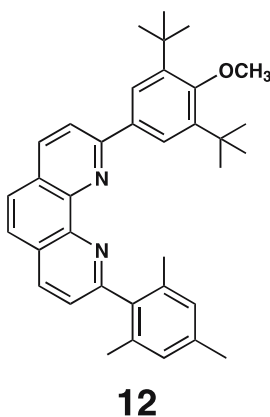


Fig. 22 Ligand 12, 2-(3,5-di-*tert*-butyl-4-methoxyphenyl)-9-(2,4,6-trimethylphenyl)-1,10-phenanthroline

(Fig. 22). This finding gives further support to the notion that steric factors are by far more important than electronic factors.

The room temperature lifetime of $[\text{Cu}(\mathbf{12})_2]^+$ in oxygen free solution (285 ns) is scarcely affected under air-equilibrated conditions (266 ns) and is remarkably high also in CH_3OH (182 ns), a solvent where most $[\text{Cu}(\text{NN})_2]^+$ do not show any luminescence. This rather unusual solvent insensitivity of the lifetime is observed also for $[\text{Cu}(\mathbf{5})_2]^+$ (Fig. 14) suggesting that *tert*-butyl groups are very effective in preventing the formation of the pentacoordinated exciplex at room temperature [74]. On the other hand, in striking contrast with $[\text{Cu}(\mathbf{12})_2]^+$, $[\text{Cu}(\mathbf{5})_2]^+$ is virtually non-luminescent in 77 K rigid matrix, highlighting once again the subtle factors affecting the molecular structure and, accordingly, the emission performance. Probably, in $[\text{Cu}(\mathbf{12})_2]^+$, the key structural features causing good luminescence performance are the methyl residues on the 2 and 6 position of a phenyl substituent (Fig. 22).

Solid state measurements confirm the strong dependence of the excited state lifetimes of $[\text{Cu}(\text{NN})_2]^+$ complexes on geometric distortions. In particular it has been found that there is a good linear correlation between the ξ_{CD} parameter (see Sect. 2.1, Eq. 1) and the measured lifetime both at room temperature and at 17 K: the smaller the distortion from the ideal pseudo-tetrahedral geometry (high ξ_{CD} parameter), the longer the lifetime [56].

2.5

Photoinduced Processes in Multicomponent Systems Based on $[\text{Cu}(\text{NN})_2]^+$ Complexes

Templated synthesis of Cu(I)-bisphenanthrolines has prompted the design and construction of sophisticated multicomponent architectures comprising one or more $[\text{Cu}(\text{NN})_2]^+$ centers in tandem with other chromophores, typ-

ically porphyrins and fullerenes. Intercomponent light-induced energy- and electron-transfer processes have been investigated in [2]- [93, 94] and [3]-catenanes [29, 95, 96], dinuclear knots [97], fullerene- [98] and porphyrin-stoppered rotaxanes [99–108], dendrimers with $[\text{Cu}(\text{NN})_2]^+$ cores [38], and helicates with Cu(I)-complexed cores and peripheral methano- [109] or bismethano-fullerenes [41, 109, 110]. The latter, which constitute the most recently investigated systems, are depicted in Fig. 23.

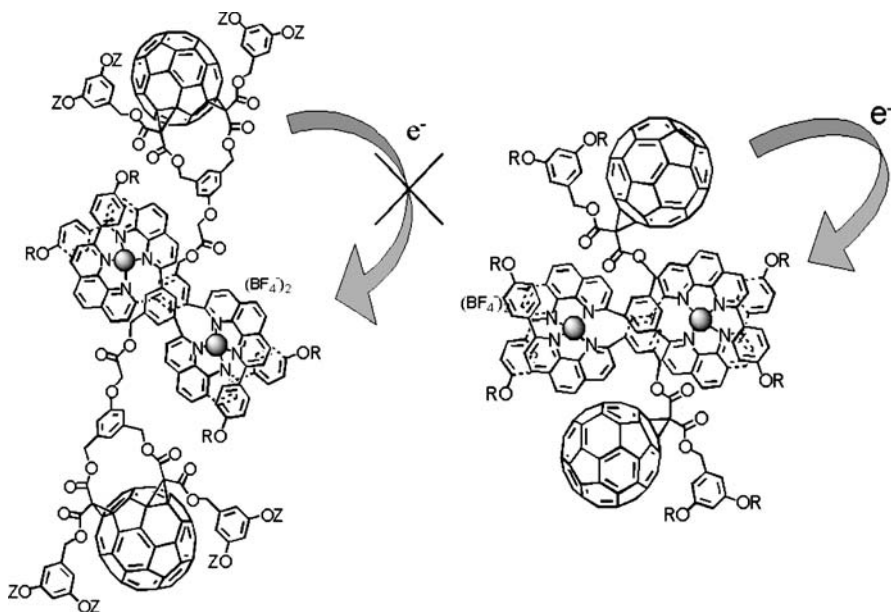


Fig. 23 Fullerohelicates based on a dinuclear $[\text{Cu}(\text{NN})_2]^+$ complex ($\text{Z}=\text{C}_8\text{H}_{17}$, $\text{R}=\text{C}_{12}\text{H}_{25}$). The peripheral moieties are different in the two cases, namely bismethano (*left*) vs. methanofullerenes (*right*)

Upon excitation of the Cu(I)-complexed moiety and population of the related MLCT level, electron transfer to the fullerene subunit is observed for both compounds shown in Fig. 23. By contrast, although the same process is thermodynamically allowed also by populating the fullerene lowest singlet state, it is observed only in the case of the methanofullerene system. This is related to the inherently different electronic structure of the two fullerene derivatives. By means of an analysis of their fluorescence spectra, which are substantially different, it was possible to conclude that the singlet excited state of methanofullerenes is more prone to undergo electron transfer than that of bismethanofullerenes, thanks to the associated smaller internal reorganization energy [109]. In addition, methanofullerenes are slightly easier to reduce than bismethanofullerenes, giving also a thermodynamic advantage for electron transfer in multicomponent arrays containing the monofunc-

tionalized derivative. The combined effect of these two factors (kinetic and thermodynamic) can explain the different and unexpected trend in photoprocesses of multicomponent arrays containing Cu(I)-phenanthrolines linked to methanofullerenes vs. bismethanofullerenes, which has been found in a variety of molecular architectures such as dendrimers [38], rotaxanes [98] and sandwich-type dyads [110].

Exhaustive review articles presenting photophysical investigations on fullerene- and porphyrin-type arrays built-up around $[\text{Cu}(\text{NN})_2]^+$ centers have been published recently and we suggest the reader refers to these papers for a comprehensive and updated overview on this topic [15, 25, 111, 112].

2.6

Bimolecular Quenching Processes

Excited state electrochemical potentials can be obtained from the *ground state* monoelectronic electrochemical potentials and the spectroscopic energy (E° in eV units, to be considered divided by a unitary charge) related to the involved transition, according to Eqs 2 and 3 [6]:

$$E(A^+/*A) = E(A^+/A) - E^\circ \quad (2)$$

$$E(*A/A^-) = E(A/A^-) + E^\circ \quad (3)$$

Hence the variation of the electron-donating or accepting capability of a given molecule A, upon light excitation, can be easily assessed. In Eqs 2 and 3: $*A$ denotes the lowest-lying electronically excited state of A and its spectroscopic energy (E°) can be estimated from the onset of emission spectra [6].

Oxidation from Cu(I) to Cu(II) is easily accomplished and the MLCT excited states of Cu(I)-bisphenanthrolines are, therefore, potent reductants. For example $[\text{Cu}(\text{3})_2]^+$ is a more powerful reductant than the very popular photosensitizer $[\text{Ru}(\text{bpy})_3]^{2+}$ ($A^+/A = -1.11$ and -0.85 V, respectively) owing to its more favorable ground state $2+/+$ potential ($+0.69$ vs. $+1.27$ V), that largely compensates the lower content of excited state energy (1.80 vs. 2.12 eV) [15]. By contrast reduction of Cu(I)-bisphenanthrolines is strongly disfavored and they are mild excited state oxidants; accordingly, only a few examples of reductive quenching of $[\text{Cu}(\text{NN})_2]^+$ complexes are reported in the literature, with ferrocenes as donors [113, 114].

Oxidative quenching of $[\text{Cu}(\text{NN})_2]^+$'s by Co(III) and Cr(III) complexes as well as nitroaromatic compounds and viologens has been reported and comprehensively reviewed [115]. Some attempts to sensitize wide band-gap semiconductors with Cu(I) complexes were also carried out [115] but so far they do not seem to be competitive in terms of stability and efficiency with those based on Ru(II) complexes [12]. Energy transfer quenching to molecules possessing low-lying triplets such as anthracene has been demonstrated via transient absorption spectroscopy [116, 117], whereas oxygen quenching,

which in principle can occur both via energy- and electron transfer, was evidenced by monitoring sensitized singlet oxygen luminescence in the NIR region [29, 36]. Optically pure dicopper trefoil knots with $[\text{Cu}(\text{NN})_2]^+$ -type cores have been reported to quench the emission of the Λ or Δ forms of Tb(III) and Eu(III) complexes, a very rare example of enantioselective luminescence quenching [118].

$[\text{Cu}(\text{NN})_2]^+$ complexes have also been used as substrates for DNA binding, trying to take advantage of the sensitivity of the luminescence of Cu(I)-phenanthrolines to the local environment [63]. The structure of the associates has not been clarified: both electrostatic binding and intercalation of the aromatic ligands between adjacent bases are possible. Cu(I)-porphyrins seem to be more promising substrates for DNA [63].

3

Heteroleptic Diimine/Diphosphine $[\text{Cu}(\text{NN})(\text{PP})]^+$ Complexes

3.1

Photophysical Properties

Heteroleptic Cu(I) complexes containing both N- and P-coordinating ligands, $[\text{Cu}(\text{NN})(\text{PP})]^+$, have been studied since the late 1970s [119]. The replacement of one N-N ligand with a P-P unit is often aimed at improving the emission properties. Accordingly, the relentless quest for highly performing luminescent metal complexes [7] has sparked revived interest in these compounds in recent years [120–122].

The absorption and luminescence spectrum of $[\text{Cu}(\text{dbp})(\text{POP})]^+$ (dbp = 2,9-butyl-1,10-phenanthroline and POP = bis[2-(diphenylphosphino)phenyl] ether) is reported in Fig. 24, as a representative example for this class of compounds [123]. Substantial blue-shifts of the lower-energy bands are observed compared to typical spectra of $[\text{Cu}(\text{NN})_2]^+$ compounds (see Sect. 2).

UV spectral features above 350 nm are due to ligand-centered transitions whereas those in the 350–450 nm window are attributed to MLCT levels. $[\text{Cu}(\text{NN})(\text{PP})]^+$ complexes are subject to dramatic oxygen quenching, as deduced from the strong difference in excited state lifetimes passing from air-equilibrated to oxygen-free CH_2Cl_2 solution, 250 ns and 17 600 ns in the case of $[\text{Cu}(\text{dbp})(\text{POP})]^+$ [123]. The character of the emitting state in $[\text{Cu}(\text{NN})(\text{PP})]^+$ complexes has been discussed since their first characterization [119] and now its MLCT nature is established experimentally and theoretically [120, 124, 125]. The electron-withdrawing effect of the P–P unit on the metal center tends to disfavor the Cu(I)→N–N electron donation, as also reflected by the higher oxidation potential of the Cu(I) center compared to $[\text{Cu}(\text{NN})_2]^+$ compounds [126], leading to a blue shift of MLCT transitions. This, according to the energy gap law [127], explains the emission enhance-

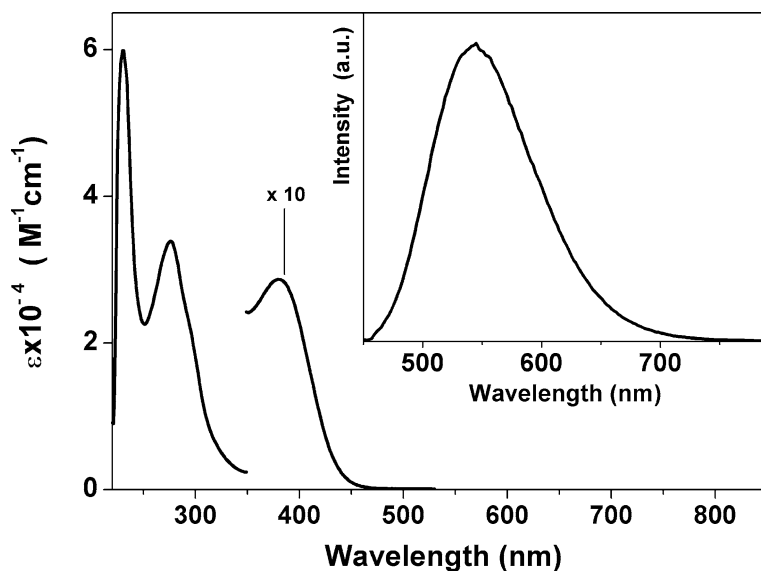


Fig. 24 Absorption and (inset) emission spectra of $[\text{Cu}(\text{dbp})(\text{POP})]^+$ in CH_2Cl_2

ment of $[\text{Cu}(\text{NN})(\text{PP})]^+$, that typically falls in the green spectral window, compared to weaker red-emitting $[\text{Cu}(\text{NN})_2]^+$ complexes.

The luminescence efficiency of MLCT excited states in $[\text{Cu}(\text{NN})(\text{PP})]^+$ compounds is strongly solvent- and oxygen-dependent because it can be decreased by exciplex quenching [128, 129], in line with what is observed for the $[\text{Cu}(\text{NN})_2]^+$ analogues (see above). Therefore, the geometry of $[\text{Cu}(\text{NN})(\text{PP})]^+$ complexes plays a central role in addressing the extent of luminescence efficiency, even though this is hard to predict a priori.

A variety of bidentate phosphine ligands has been prepared to coordinate Cu(I) in tandem with phenanthroline-type units: bis[2-(diphenylphosphino)phenyl]ether (POP), triphenylphosphine (PPh_3), bis(diphenylphosphino)ethane (dppe), and bis(diphenylphosphino)methane (dppm), represent some recent examples [120, 122, 123, 130, 131], Fig. 25.

Among them, the family of mononuclear $[\text{Cu}(\text{phen})(\text{POP})]^+$ complexes proposed by McMillin (see Fig. 25 for the PP-type ligands), where phen indicates a variably substituted 1,10 phenanthroline, shows an impressive emission efficiency compared to $[\text{Cu}(\text{NN})_2]^+$ compounds [120]. Especially on passing from pristine phenanthroline to dimethyl- or diphenyl-substituted analogues, and thanks to the efficient steric and electron-withdrawing effects of the POP ligand, remarkable emission quantum yields ($\Phi_{em} \sim 0.15$ in CH_2Cl_2 oxygen-free solution) and long lifetimes ($\sim 15 \mu\text{s}$) have been measured. On the contrary, the replacement of the POP ligand with two PPh_3 units, gives less remarkable results due to the lower geometric rigidity which leads to weak and red-shifted emissions comparable to those of

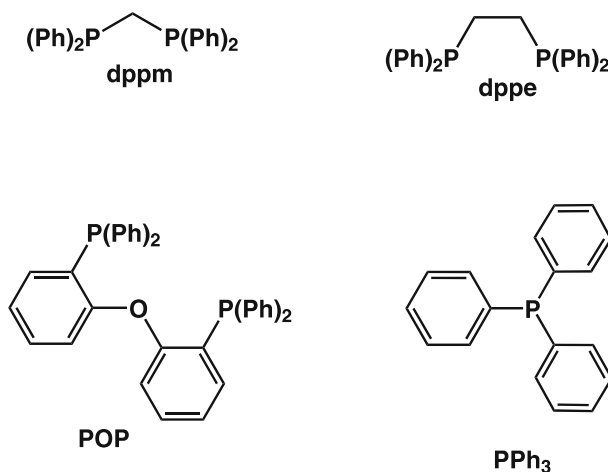


Fig. 25 Some ligands typically used as P-P units in $[\text{Cu}(\text{NN})(\text{PP})]^+$ complexes

bis-phenanthroline-type complexes. Importantly, the P-Cu-P angle decreases from 122.7° in $[\text{Cu}(\text{dmp})(\text{PPh}_3)_2]^+$ to 116.4° in $[\text{Cu}(\text{dmp})(\text{POP})]^+$ also allowing easier access for exciplex quenching over the fifth coordination position in the former. This example highlights the importance of having both conditions (i.e. steric protection and increased electron-withdrawing character of the P-P ligand) simultaneously satisfied for optimized photoluminescence performance of $[\text{Cu}(\text{NN})(\text{PP})]^+$ compounds.

The importance of the choice of the P-P ligand for the coordination of the metal ion is evidenced also by the systems recently investigated by Wang et al. [121], in which ligands other than phenanthroline have been utilized (Fig. 26).

By keeping the N-N ligand unchanged, the luminescence properties of the complexes (solid matrix, RT) increase on passing from dppe to POP to, sur-

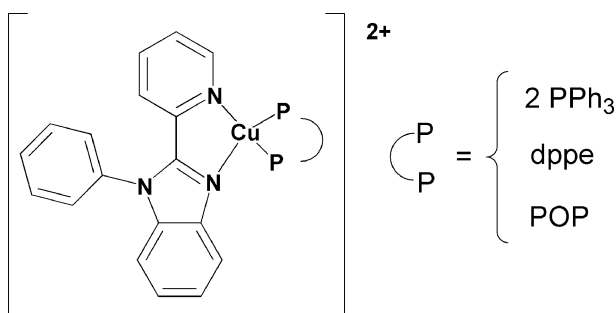


Fig. 26 General structure of $[\text{Cu}(\text{ppb})(\text{P})_2]^+$ complexes (ppb = 2-(2'-pyridyl)benzimidazolylbenzene)

prisingly, PPh_3 . Although POP provides the best emission performance when combined with phenanthroline ligands, a better result is found here for PPh_3 . This shows that subtle and combined steric and electronic effects of *both* P–P and N–N ligands are crucial for an enhanced light output, highlighting that general rules able to predict the photophysical behavior of $[\text{Cu}(\text{NN})(\text{PP})]^+$ complexes are not easy to draw. From an electronic point of view, both POP and PPh_3 units promote the usual blue shift of the MLCT state compared to $[\text{Cu}(\text{NN})_2]^+$ compounds, as predictable by the substantially higher oxidation potential of the Cu(I) center of heteroleptic $[\text{Cu}(\text{NN})(\text{PP})]^+$ complexes.

Dinuclear Cu(I) complexes have also been synthesized and investigated, two of them (A and B) are depicted in Fig. 27. Despite the presence of a P–P-type ligand, complex A shows a luminescence band peaked at 700 nm with a lifetime of 320 ns in the solid state [132]. The X-ray crystal structure indicates a distorted tetrahedral geometry which, combined to the scarcely protective 2,5-bppz N–N ligand (2,5-bis(2-pyridil)pyrazine) leads to a weakly red-emitting compound. By changing the N–N ligand (Fig. 27, B), a stronger

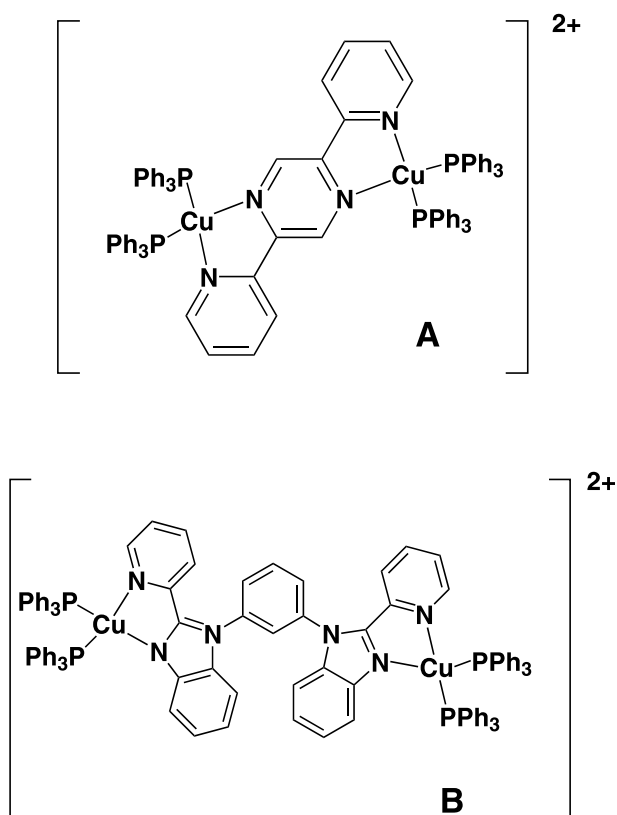


Fig. 27 Chemical structures of heteroleptic Cu(I) complexes A and B

green emission ($\lambda_{\max} = 550$ nm) is detected with a quantum yield of 0.17 at 77 K in CH_2Cl_2 matrix [133]. For complex B, although the geometric structure is similar to A, the oxidation potentials of the N–N ligand are substantially greater, pushing the MLCT levels at higher energy.

3.2

OLED and LEC Devices

The outstanding photophysical performances of some $[\text{Cu}(\text{NN})(\text{PP})]^+$ complexes make them potentially attractive for optoelectronic devices requiring highly luminescent materials [134–137]. This interest is also related to the lower cost and higher relative abundance of copper compared to more classical emitting metals such as europium or iridium. Some research groups have recently fabricated OLED devices with $[\text{Cu}(\text{NN})(\text{PP})]^+$ complexes [138]. It has been shown that they can be profitably used as electrophosphorescent emitters and provide device efficiency comparable to that of Ir(III) complexes in similar device structures (11.0 cd/A at 1.0 mA/cm², 23% wt Cu(I)-complex dispersed in PVK matrix). Also Li et al. have obtained a highly efficient electrophosphorescent OLED with the complex reported in Fig. 28 [139].

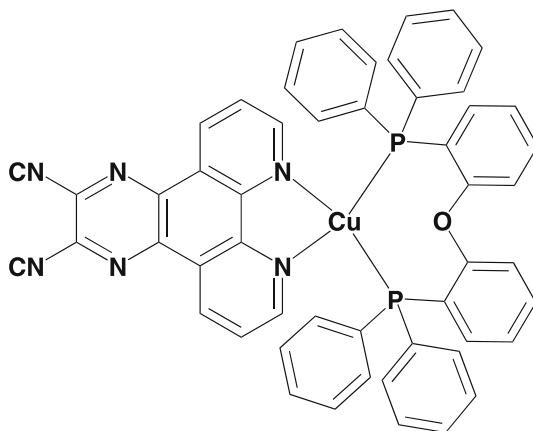


Fig. 28 The complex $[\text{Cu}(\text{Dicnq})(\text{POP})]^+\text{BF}_4^-$ used by Li et al. to make a highly efficient electroluminescent OLED device (Dicnq = 6,7-Dicyanodipyrido[2,2-*d'*:2'',3''-*f'*] quinoxaline)

The performances of OLEDs fabricated by the vacuum vapor deposition technique with this complex are among the best reported for devices incorporating Cu(I) complexes as emitters. A low turn-on voltage of 4 V, a maximum current efficiency up to 11.3 cd/A, and a peak brightness of 2322 cd/m² have been achieved.

A different type of electroluminescent device is a light-emitting electrochemical cell (LEC). LECs are substantially different from OLEDs due to the fact that mobile ions in the electroluminescent layer drift towards the electrodes when a voltage is applied over the device, thereby facilitating charge-carrier injection from the electrodes. This results in two important advantages compared to traditional OLEDs: (i) thick electroactive layers can be used without severe voltage penalties and shorts can be eliminated even for large-area pixels; (ii) matching of the work function of the electrodes with the energy levels of the electroluminescent material is not required.

We have recently described novel Cu(I) complexes with excellent PL performance (Q.Y. up to 0.28 in oxygen-free CH_2Cl_2) and the first LEC device made with a Cu(I) complex, Fig. 29 [123].

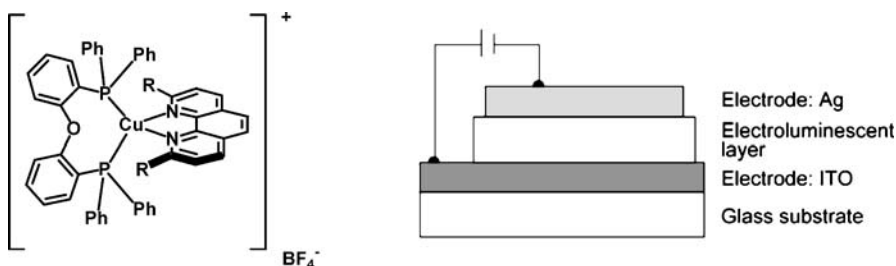


Fig. 29 Chemical structure of the complex used to make the first LEC device based on a Cu(I)-complex, $\text{R} = n$ -butyl. A schematic representation of the device structure is also depicted; in the electroluminescent layer the complex is dispersed in a polymethyl-metacrylate matrix (PMMA)

The device efficiency turned out to be moderate but comparable to LEC devices made with Ru(II)-type compounds [134]. Wang et al. used the same complex but, changing experimental conditions, could make a more efficient green light emitting device (CIE coordinates: 0.25, 0.60) with a maximum current efficiency of 56 cd/A at 4.0 V, corresponding to an external quantum yield of 16% [140]. This work notes the importance of the optimization of LEC device parameters such as the response time, which greatly depends on the counterion, driving voltage, and thickness of the emitting layer. Further efforts are needed to substantially improve the device stability and light output in order to take advantage of the low-cost and limited environmental damaging effects of copper materials.

Finally, it is worth pointing out that also the family of cuprous cluster (described in the next paragraph) has been tested in devices. In the late 1990s Ma et al. described the electroluminescence properties of a LED containing a tetranuclear Cu(I) cluster as the active component contributing to broaden the pool of electroluminescent materials outside the traditional boundaries of organic dyes and polymers [141].

4 Cuprous Clusters

4.1 Cuprous Halide Clusters

Cluster compounds contain a group of two or more metal atoms where direct and substantial metal-metal bonding is present. Cuprous halide clusters have been known for about 100 years [142], their general formula is $\text{Cu}_n\text{X}_n\text{L}_m$ ($\text{X} = \text{Cl}^-$, Br^- or I^- ; $\text{L} = \text{N}$ or P belonging to an organic molecule). For instance, in solution, mixtures of Cu(I) salts, iodine (I) and pyridine-type molecules (py) are primarily present as tetrahedral clusters $\text{Cu}_4\text{I}_4\text{py}_4$ and give origin to mononuclear or dinuclear structures only if forced by mass action law under high pyridine concentration. Normally, copper(I) complexes in solution are quite labile towards ligand substitution and the formation of new species is driven by thermodynamic stability rather than kinetic control.

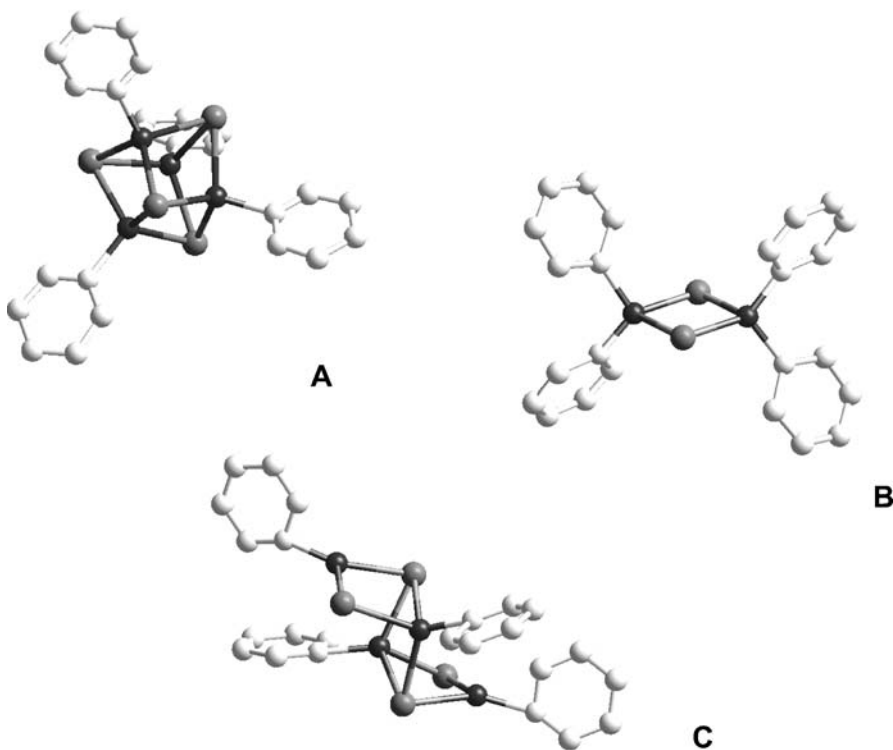


Fig. 30 Illustrations of $\text{Cu}_4\text{I}_4\text{py}_4$ (A), $\text{Cu}_2\text{I}_2\text{py}_4$ (B), $[\text{Cu}_3(\mu\text{-dppm})_3(\mu_3 - \eta^1\text{-C}\equiv\text{C-benzo-15-crown-5})_2]^+$ (C), and the repeating unit of a “stairstep” polymer $[\text{CuIpy}]_n$ (D) redrawn from the structural data. Black circles = copper atoms; grey circles = iodine; white rings = pyridine residues

Cuprous clusters display many structural formats that are characterized by largely different emission behavior (*vide infra*). The variety of structural motifs and stoichiometries is related to the remarkable flatness of their ground state potential energy surfaces [143]. The most extensive studies carried out on these Cu(I) complexes concern cubane-type clusters of general formula $[\text{CuXL}]_4$ [144, 145]. The solid state structural variety observed among cuprous clusters can be illustrated by examining some crystallographic data reported by Ford and co-workers, who found that compounds containing Cu(I), iodine, and pyridine generate different structures depending on the reaction stoichiometry, Fig. 30.

For a 1:1:1 Cu:I:L ratio (Fig. 30 A), the most common motif is the tetranuclear “cubane” structure ($\text{Cu}_4\text{I}_4\text{L}_4$) in which a tetrahedron of copper atoms is included by a larger I_4 tetrahedron where each iodine is placed on a triangular face of the Cu_4 cluster and the fourth coordination site of each copper is occupied by the ligand (L). For stoichiometry 1:1:2 (Fig. 30 B), the most common structure is an isolated rhombohedron of Cu_2I_2 with alternating copper and halide atoms. Sometimes, clusters with stoichiometry (1:1:1) exist in more than one crystalline structure. For example (Fig. 30 C) $\text{Cu}_4\text{I}_4\text{py}_4$ can also give rise to a polymeric “stair” made of an infinite chain of steps [146].

4.2

Cuprous Iodide Clusters

The interest in the luminescence properties of Cu(I) iodide clusters goes back to the pioneering work of Hardt and co-workers [144]. They found that the emission spectra of solid samples of $[\text{Cu}_x\text{I}_y(\text{py})_z]$ are markedly temperature-dependent and defined the term “luminescent thermochromism”.

In some cases cuprous iodide clusters exhibit two emission bands termed HE (high energy) and LE (low energy), which sharply change their relative intensities upon temperature variation. As an example, in Fig. 31 are depicted the temperature-dependent emission spectra of $\text{Cu}_4\text{I}_4(4\text{-phenylpyridine})_4$ [147]. The LE band dominates at room temperature, while the HE band is by far the strongest at temperatures below 80 K.

The HE band dominating at low temperature has been attributed, on the basis of *ab initio* calculations and experimental work, to ligand-to-ligand ($\text{I}^- \rightarrow \text{phenylpyridine}$) charge transfer states, also indicated as XLCT. The LE emission dominating at room temperature has been assigned to an excited state of mixed halide-to-metal charge transfer (XMCT) and $d \rightarrow s, p$ metal-centered character which is usually referred to as “cluster-centered” (CC). This term was introduced to highlight that these transitions are localized on the Cu_4I_4 cluster and are essentially independent on ligand L. The Cu–Cu distance is a fundamental parameter to allow the presence of CC bands and must be shorter than the orbital interaction radius, estimated to be 2.8 Å. If the distance between the two metal centers exceeds this critical value the metal

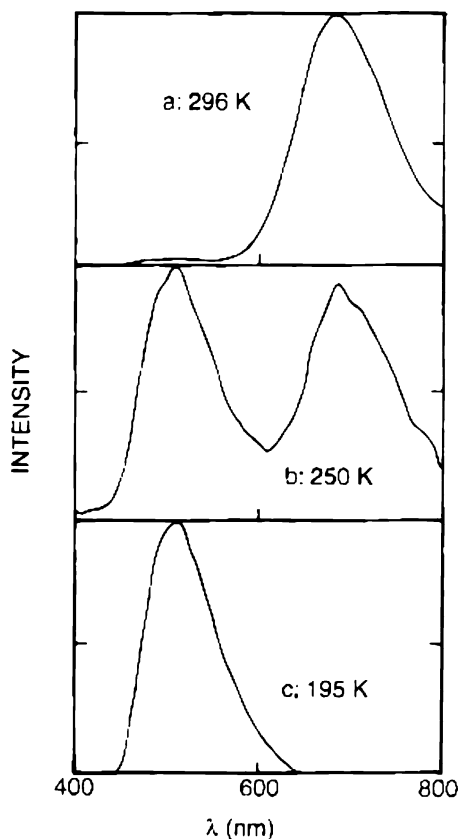


Fig. 31 Temperature dependence of the emission spectrum of $\text{Cu}_4\text{I}_4(4\text{-phenylpyridine})_4$ in toluene solution with relative intensities normalized to 1 in each case (Reprinted from [147] with permission, © (1991) American Chemical Society)

orbitals do not interact and the CC emission bands are not observed [148]. In Fig. 32 the relative position of the above-described excited states is schematically represented by means of potential energy curves.

When the amine aromatic ligand py is replaced by the aliphatic one piperidine (pip), the corresponding cluster $\text{Cu}_4\text{I}_4(\text{pip})_4$ preserves the CC band but does not display the high energy XLCT emission owing to the absence of ligands possessing π orbitals. Thus, luminescence thermochromism is the norm for $\text{Cu}_4\text{I}_4\text{L}_4$ clusters, but only when L is π -unsaturated.

Another factor contributing to the complicated pattern of the luminescence properties of $\text{Cu}_4\text{I}_4(4\text{-phenylpyridine})_4$ is the dramatic red-shift of the CC band in going from solid or frozen solution samples to fluid solutions, indicating that also rigidochromism effects are operative. Ab initio calculations and the Stokes shifts for $\text{Cu}_4\text{I}_4(4\text{-phenylpyridine})_4$ (up to $16\,300\text{ cm}^{-1}$ for the CC band in 296 K toluene solution; 7600 cm^{-1} for the XLCT band under the

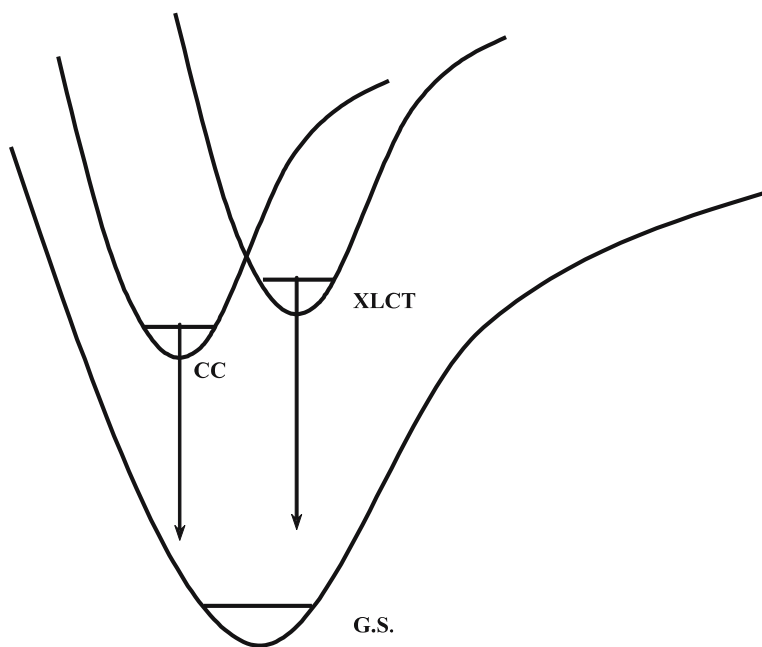


Fig. 32 Schematic representation describing the relative positions of the potential energy curves related to the emitting states of $\text{Cu}_4\text{I}_4\text{py}_4$

same conditions) also indicate that CC excited states are quite distorted relative to both the GS and XLCT levels. Such distortion was proposed as the cause for the lack of communication between CC and XLCT states, for the rigidochromism of the low CC energy band, and for the large reorganization energies of electron transfer reactions involving CC excited states [143].

In an interesting recent work on clusters of general formula CuXL ($\text{L} = \text{N}$ -heteroaromatic ligands), it was shown that the energy of the emitting level can be finely tuned [149]. The emission is attributed to a MLCT charge transfer state, because no clear correlation between Cu–Cu distances and emission maxima was observed and also because the effects of bridging halides were smaller than those of *N*-heteroaromatic ligands, therefore the position of the luminescence band can be varied by increasing the electron-accepting character of the ligand *L*, Fig. 33. In these compounds Cu–Cu distances are in the range 2.9–3.3 Å, accordingly the weak metal interaction prevent cluster-centered luminescence. Very recently, density functional theory calculations have confirmed the involvement of the triplet cluster-centered (CC) and triplet XLCT excited states as the origin of the dual emission [151].

It must be pointed out, however, that short Cu–Cu separation does not automatically imply the establishment of metal-metal bonds and the effect of the bridging ligands has to be taken into account. For example Cotton et al.

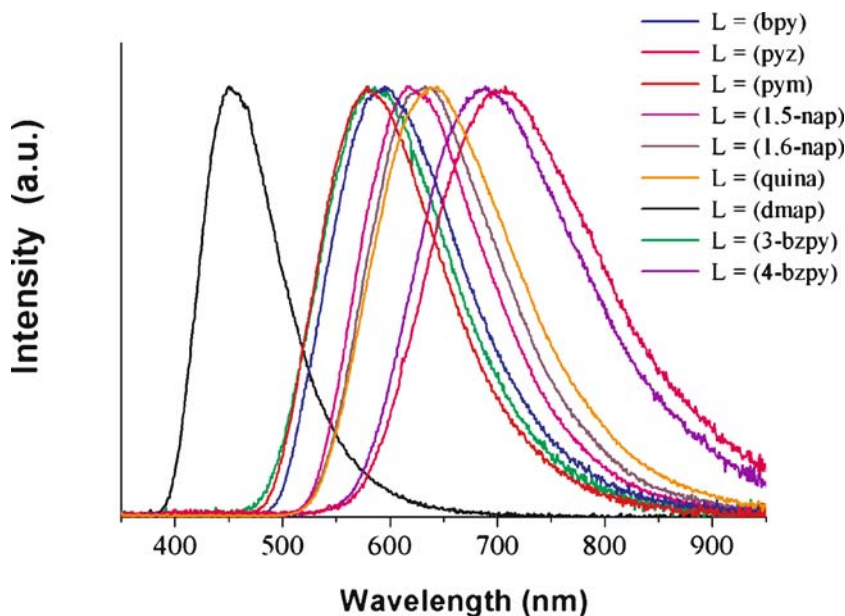


Fig. 33 Emission spectra of clusters CuXL ($\text{X} = \text{Br}^-$) at room temperature. The emission maxima of the complexes cover a wide range, from 450 to 740 nm depending on the *N*-heteroaromatic ligands. bpy = 4,4-bipyridine; pyz = pyrazine; pym = pyrimidine; pip = piperazine; 1,5-nap = 1,5-naphthyridine; 1,6-nap = 1,6-naphthyridine; quina = quina-zoline; dmap = *N,N*-dimethyl-amino-pyridine; 3-bzpy = 3-benzoyl-pyridine; 4-bzpy = 4-benzoyl-pyridine. (Reprinted from [149] with permission, © (2006) American Chemical Society)

have carried out DTF calculations on $[\text{Cu}_2(\text{hpp})_2]$, (where hpp^- = 1,3,4,6,7,8-hexahydro-2*H*pyrimido[1,2-*a*]pyrimidine) to investigate the possibility of metal-metal bonding in a complex where short metal-metal separations are present [$d_{\text{Cu} \cdots \text{Cu}} = 2.497(2) \text{ \AA}$]. They concluded that there is no Cu-Cu bond and the short intermetal distance is related to the strong Cu-N bonds and the small bite angle of the bridging ligand [150].

4.3

Other Copper Clusters

Recently, the synthesis of several polynuclear copper(I) alkynyl clusters has been reported and their luminescence properties investigated in detail [152, 153]; these compounds exhibit intense and long-lived luminescence upon photoexcitation. For instance, the tetranuclear copper(I) alkynyl complex $[\text{Cu}_4(\text{PPh}_3)_4(\text{L})_3]\text{PF}_6$, in Fig. 34 is characterized by an unusual open-cube structure, and exhibits a strong structured emission with two different max-

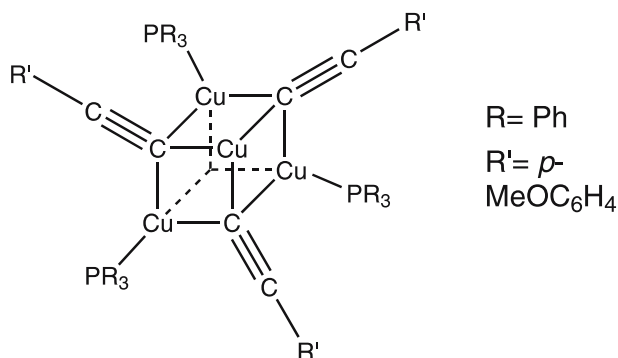


Fig. 34 A tetranuclear copper(I) alkynyl “open-cube” cluster

ima at 445 and 630 nm in solid state at 298 K and a single band with $\lambda_{\text{max}} = 445$ nm in rigid matrix at 77 K [154, 155].

For some of these open-cube compounds, an additional low-energy emission band at $\lambda > 623\text{--}665$ nm was observed in the solid-state spectra, similarly to what was observed for $[\text{Cu}_4\text{I}_4\text{L}_4]$ systems described above. In dichloromethane solution at ambient temperature they exhibit only an orange phosphorescence and the spectrum of $[\text{Cu}_4(\text{PPh}_3)_4(\text{L})_3]\text{PF}_6$ ($\text{L} = p\text{-}n\text{OctC}_6\text{H}_4$) is depicted in Fig. 35 as a representative example for this class of compounds.

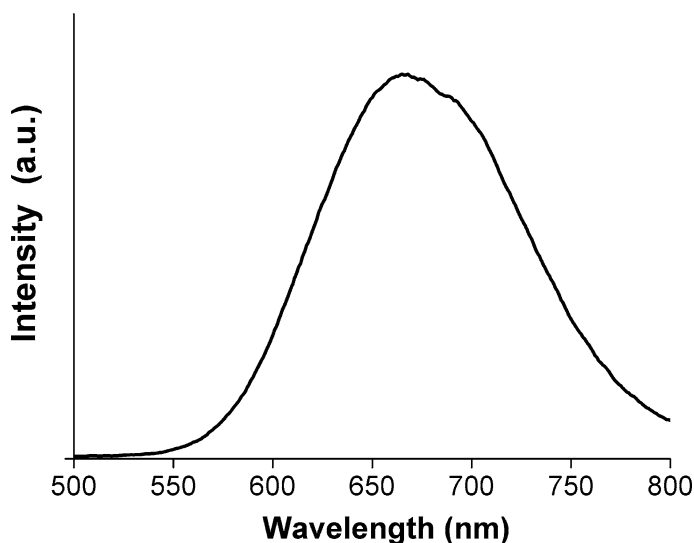


Fig. 35 Emission spectrum of $[\text{Cu}_4(\text{PPh}_3)_4(\text{L})_3]\text{PF}_6$ ($\text{L} = p\text{-}n\text{OctC}_6\text{H}_4$) in degassed dichloromethane at 298 K (Reprinted from [155] with permission, © (2006) Wiley)

There are other examples of luminescent clusters, for instance trinuclear copper(I) pyrazolates displaying emission bands over a wide spectral range [156], or others with a core made of four Cu(I) and four sulfur atoms [157, 158]. There are examples of Cu(I) luminescent clusters with a higher nuclearity, some of them are heterometallic (6–8 metal centers) [159] while others are homometallic but with a higher nuclearity (16–20 metal centers). In the latter case, which bear alkynyl ligands [160], an emission band is observed in the UV spectral region. Finally, the possible use of copper cluster units to assemble polymeric compounds with a wide range of possible structures, from one- to three-dimensional should be noted [161, 162].

5

Miscellanea of Cu(I) Luminescent Complexes

In the previous sections we have presented the three main classes of Cu(I) compounds exhibiting interesting photophysical properties, namely Cu(I)-bisphenanthrolines, $[\text{Cu}(\text{NN})(\text{PP})]^+$ complexes and cuprous clusters. However, especially in recent years, a growing number of Cu(I) luminescent complexes with less conventional ligands have appeared in the literature and some of them will be now briefly presented.

The homoleptic Cu(I) complexes of the benzo[*h*]quinoline ligands (BHQ) depicted in Fig. 36 exhibit excellent luminescence properties in CH_2Cl_2 with quantum yields as high as 0.10 and $\tau = 5.3 \mu\text{s}$ (ligand C in Fig. 36),

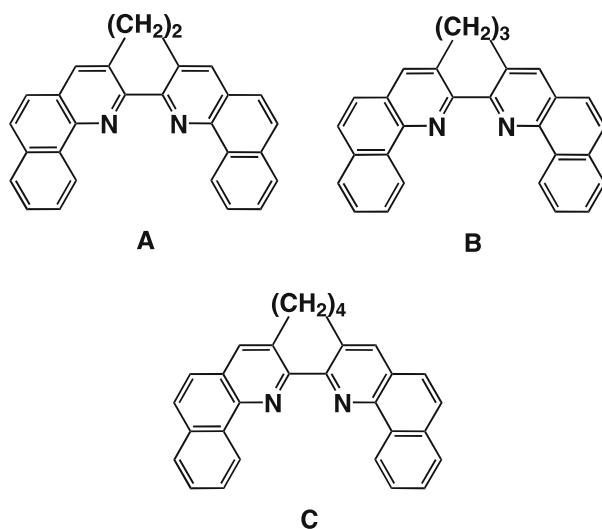


Fig. 36 Benzo[*h*]quinoline ligands which, upon complexation with Cu(I), provide highly luminescent complexes

which are values comparable to those of $[\text{Cu}(\text{NN})(\text{POP})]^+$ compounds (see Sect. 3.1) [163].

This relevant result has been rationalized assuming that the specific complex structure imposes minimal geometrical changes in the deactivation process of the luminescent excited state back to the ground state, while maintaining a significant energy gap. The BHQ ligands accomplish exactly this requirement by providing considerable steric congestion in the vicinity of chelation, which stabilizes Cu(I), while also providing interligand π -stacking that distorts the ground-state geometry and favors the (formal) oxidation of the metal with little structural change [163]. The same authors later proposed Cu(I) complexes made of bisphenanthroline ligands with structures identical to A, B and C (Fig. 36), but no emission data were presented [164].

2-Hydroxy-1,10-phenanthroline (**Hophen**) is a novel kind of substituted phenanthroline that was recently proposed (Fig. 37). With Cu(I) it gives origin to several compounds, as evidenced by X-ray crystallography, including an unusual neutral dinuclear complex $[\text{Cu}_2(\text{ophen})_2]$ which exists in three supramolecular isomeric forms and exhibits a broad and weak luminescence band centered around 630 nm, which has been tentatively attributed to deactivation of an MLCT state [165]. The same ligand, which is characterized by complicated coordination modes involving both the regular nitrogen sites and oxygen binding another metal ion (Fig. 37), was also used to make metal complexes of other d^{10} metal ions, i.e. Zn(II), Cd(II) and Hg(II), which show ligand centered (LC) emission bands in the blue-green region [166].

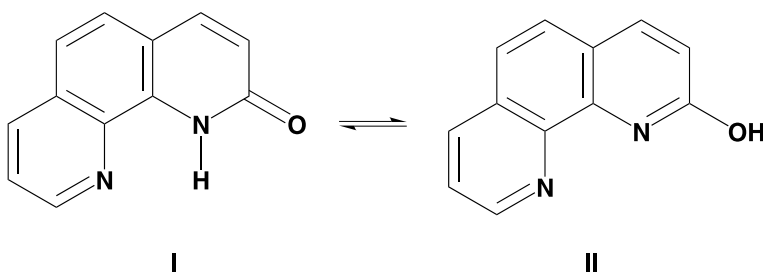


Fig. 37 The proposed ketone and hydroxy tautomers of **Hophen**

Vogler et al. have made several Cu(I) complexes exhibiting emission in different regions of the VIS spectral window, including blue and red, and having pure MLCT or mixed MLCT/LLCT character [167, 168]. For instance the complex depicted in Fig. 38 which is easily accessible from commercially available products shows a weak but distinct MLCT red luminescence peaking at 600 nm [167].

Several other unconventional ligands have been utilized recently to make luminescent Cu(I) complexes such as thia-calix[3]pyridine (orange MLCT

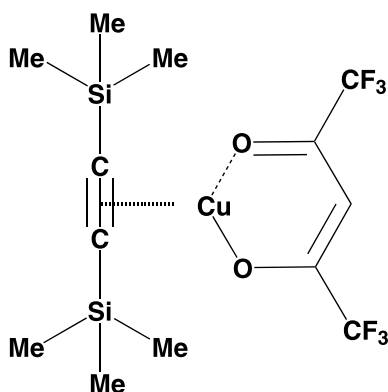


Fig. 38 The red-emitting complex $[\text{Cu}(\text{BTA})(\text{hfac})]$ with BTA = bis(trimethylsilyl)acetylene and hfac = 1,1,1,5,5,5-hexa-fluoroacetyl-acetonate

phosphorescence) [169], mononuclear and dinuclear azaindole-containing systems (blue LC) [170, 171], heteroleptic diphosphine/diisocyanide ligands (blue MLCT) [172], pyrazolylborates (blue LC phosphorescence) [173].

6

Conclusions and Perspectives

In recent years, the rationalization of the electronic and photophysical properties of Cu(I) compounds has made considerable progress, in parallel with a significant implementation of synthetic protocols to prepare both simple and complex Cu(I)-based structures with satisfactory yields. Now we know key design principles that allow one to make highly luminescent Cu(I) compounds and supramolecular architectures with programmable cascades of photoinduced processes. Such trends have taken Cu(I) complexes among the key players in the realm of photoactive complexes, where other metals such as Ru(II) and, more recently Ir(III) have traditionally played a prominent role. The relentless quest for luminescent metal compounds to be utilized in a variety of applications can find interesting answers among some classes of Cu(I) complexes, as pointed out in this review article. Obviously, the need for abundant, cheap, and environmentally friendly smart materials makes copper compounds an attractive alternative to more traditional choices based on precious metals. The current trends in literature and patenting [174] indeed suggest that Cu(I) complexes are attracting increasing attention for technological applications (e.g. OLEDs) and, although we are still at the level of prototypes and proofs of principles, further important breakthroughs may be anticipated in the years to come.

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References

1. US Geological Survey (2006) Mineral Commodity Summaries <http://minerals.er.usgs.gov/minerals/pubs/commodity/copper/>, last visited: January 2006
2. Gordon RB, Bertram M, Graedel TE (2006) *Proc Natl Acad Sci USA* 103:1209–1214
3. Horvath O (1994) *Coord Chem Rev* 135:303–324
4. Sykora J (1997) *Coord Chem Rev* 159:95–108
5. Jørgensen CK (1963) *Adv Chem Phys* 5:33–146
6. Juris A, Balzani V, Barigelletti F, Campagna S, Belser P, von Zelewsky A (1988) *Coord Chem Rev* 84:85–277
7. Lowry MS, Bernhard S (2006) *Chem Eur J* 12:7970–7977
8. Balzani V, Juris A, Venturi M, Campagna S, Serroni S (1996) *Chem Rev* 96:759–833
9. Roundhill DM (1994) *Photochemistry and Photophysics of Metal Complexes*. Plenum Press, NY
10. Bignozzi CA, Argazzi R, Kleverlaan CJ (2000) *Chem Soc Rev* 29:87–96
11. Balzani V, Ceroni P, Juris A, Venturi M, Campagna S, Puntoriero F, Serroni S (2001) *Coord Chem Rev* 219:545–572
12. Grätzel M (2005) *Inorg Chem* 44:6841–6851
13. Vos JG, Kelly JM (2006) *Dalton Trans* pp 4869–4883
14. Kober EM, Caspar JV, Lumpkin RS, Meyer TJ (1986) *J Phys Chem* 90:3722–3734
15. Armaroli N (2001) *Chem Soc Rev* 30:113–124
16. Maestri M, Armaroli N, Balzani V, Constable EC, Thompson A (1995) *Inorg Chem* 34:2759–2767
17. Lippard SJ, Berg JM (1994) *Principles of Bioinorganic Chemistry*. University Science Books, Mill Valley, California
18. Holm RH, Kennepohl P, Solomon EI (1996) *Chem Rev* 96:2239–2314
19. Colman PM, Freeman HC, Guss JM, Murata M, Norris VA, Ramshaw JAM, Venkatappa MP (1978) *Nature* 272:319–324
20. Solomon EI (2006) *Inorg Chem* 45:8012–8025
21. Gewirth AA, Solomon EI (1988) *J Am Chem Soc* 110:3811–3819
22. Marcus RA, Sutin N (1985) *Biochim Biophys Acta* 811:265–322
23. Babcock GT, Wikstrom M (1992) *Nature* 356:301–309
24. Gamelin DR, Randall DW, Hay MT, Houser RP, Mulder TC, Canters GW, de Vries S, Tolman WB, Lu Y, Solomon EI (1998) *J Am Chem Soc* 120:5246–5263
25. Armaroli N (2003) *Photochem Photobiol Sci* 2:73–87
26. Schmittel M, Kalsani V (2005) *Top Curr Chem* 245:1–53
27. Sammes PG, Yahiloglu G (1994) *Chem Soc Rev* 23:327–334
28. Cunningham CT, Moore JJ, Cunningham KLH, Fanwick PE, McMillin DR (2000) *Inorg Chem* 39:3638–3644

29. Armaroli N, Balzani V, Barigelletti F, De Cola L, Flamigni L, Sauvage JP, Hemmert C (1994) *J Am Chem Soc* 116:5211–5217
30. Dietrich-Buchecker C, Colasson B, Fujita M, Hori A, Geum N, Sakamoto S, Yamaguchi K, Sauvage JP (2003) *J Am Chem Soc* 125:5717–5725
31. Frey J, Kraus T, Heitz V, Sauvage JP (2005) *Chem Commun*, pp 5310–5312
32. Armaroli N, Balzani V, Collin JP, Gaviña P, Sauvage JP, Ventura B (1999) *J Am Chem Soc* 121:4397–4408
33. Weber N, Hamann C, Kern JM, Sauvage JP (2003) *Inorg Chem* 42:6780–6792
34. Baranoff E, Griffiths K, Collin JP, Sauvage JP, Ventura B, Flamigni L (2004) *New J Chem* 28:1091–1095
35. Kraus T, Budesinsky M, Cvacka JC, Sauvage JP (2006) *Angew Chem Int Ed* 45:258–261
36. Dietrich-Buchecker CO, Nierengarten JF, Sauvage JP, Armaroli N, Balzani V, De Cola L (1993) *J Am Chem Soc* 115:11237–11244
37. Perret-Aebi LE, von Zelewsky A, Dietrich-Buchecker CD, Sauvage JP (2004) *Angew Chem Int Ed* 43:4482–4485
38. Armaroli N, Boudon C, Felder D, Gisselbrecht JP, Gross M, Marconi G, Nicoud JF, Nierengarten JF, Vicinelli V (1999) *Angew Chem Int Ed* 38:3730–3733
39. Gumienka-Kontecka E, Rio Y, Bourgogne C, Elhabiri M, Louis R, Albrecht-Gary AM, Nierengarten JF (2004) *Inorg Chem* 43:3200–3209
40. Heuft MA, Fallis AG (2002) *Angew Chem Int Ed* 41:4520–4523
41. Cardinali F, Mamlouk H, Rio Y, Armaroli N, Nierengarten JF (2004) *Chem Commun*, pp 1582–1583
42. Zong RF, Thummel RP (2005) *Inorg Chem* 44:5984–5986
43. Ziessel R, Charbonniere L, Cesario M, Prange T, Nierengarten H (2002) *Angew Chem Int Ed* 41:975–979
44. Sauvage J-P, Dietrich-Buchecker CO (eds) (1999) *Molecular Catenanes, Rotaxanes and Knots. A Journey through the World of Molecular Topology*. Wiley-VCH, Weinheim, Germany
45. Jimenez-Molero MC, Dietrich-Buchecker C, Sauvage JP (2002) *Chem Eur J* 8:1456–1466
46. Livoreil A, Sauvage JP, Armaroli N, Balzani V, Flamigni L, Ventura B (1997) *J Am Chem Soc* 119:12114–12124
47. Sauvage JP (2005) *Chem Commun*, pp 1507–1510
48. Bonnet S, Collin JP, Koizumi M, Mobian P, Sauvage JP (2006) *Adv Mater* 18:1239–1250
49. Kalsani V, Bodenstedt H, Fenske D, Schmittel M (2005) *Eur J Inorg Chem* 1841–1849
50. Schmittel M, Kalsani V, Fenske D, Wiegrefe A (2004) *Chem Commun*, pp 490–491
51. Schmittel M, Ammon H, Kalsani V, Wiegrefe A, Michel C (2002) *Chem Commun*, pp 2566–2567
52. Kalsani V, Ammon H, Jäckel F, Rabe JP, Schmittel M (2004) *Chem-Eur J* 10:5481–5492
53. Schmittel M, Ganz A (1997) *Chem Commun*, pp 999–1000
54. Dobson JF, Green BE, Healy PC, Kennard CHL, Pakawatchai C, White AH (1984) *Aust J Chem* 37:649–659
55. Coppens P, Vorontsov II, Graber T, Kovalevsky AY, Chen YS, Wu G, Gembicky M, Novozhilova IV (2004) *J Am Chem Soc* 126:5980–5981
56. Kovalevsky AY, Gembicky M, Coppens P (2004) *Inorg Chem* 43:8282–8289
57. Kovalevsky AY, Gembicky M, Novozhilova IV, Coppens P (2003) *Inorg Chem* 42:8794–8802

58. Miller MT, Gantzel PK, Karpishin TB (1998) *Angew Chem Int Ed Engl* 37:1556–1558
59. Miller MT, Gantzel PK, Karpishin TB (1998) *Inorg Chem* 37:2285–2290
60. Armaroli N, De Cola L, Balzani V, Sauvage JP, Dietrich-Buchecker CO, Kern JM (1992) *J Chem Soc Faraday Trans* 88:553–556
61. Zgierski MZ (2003) *J Chem Phys* 118:4045–4051
62. McMillin DR, Buckner MT, Ahn BT (1977) *Inorg Chem* 16:943–945
63. McMillin DR, McNett KM (1998) *Chem Rev* 98:1201–1219
64. Scaltrito DV, Thompson DW, O'Callaghan JA, Meyer GJ (2000) *Coord Chem Rev* 208:243–266
65. Federlin P, Kern JM, Rastegar A, Dietrich-Buchecker C, Marnot PA, Sauvage JP (1990) *New J Chem* 14:9–12
66. Gordon KC, McGarvey JJ (1991) *Inorg Chem* 30:2986–2989
67. Armaroli N, Rodgers MAJ, Ceroni P, Balzani V, Dietrich-Buchecker CO, Kern JM, Bailal A, Sauvage JP (1995) *Chem Phys Lett* 241:555–558
68. Ichinaga AK, Kirchhoff JR, McMillin DR, Dietrich-Buchecker CO, Marnot PA, Sauvage JP (1987) *Inorg Chem* 26:4290–4292
69. Phifer CC, McMillin DR (1986) *Inorg Chem* 25:1329–1333
70. Everly RM, McMillin DR (1991) *J Phys Chem* 95:9071–9075
71. Cunningham CT, Cunningham KLH, Michalec JF, McMillin DR (1999) *Inorg Chem* 38:4388–4392
72. Miller MT, Gantzel PK, Karpishin TB (1999) *Inorg Chem* 38:3414–3422
73. Miller MT, Karpishin TB (1999) *Inorg Chem* 38:5246–5249
74. Kalsani V, Schmittel M, Listorti A, Accorsi G, Armaroli N (2006) *Inorg Chem* 45:2061–2067
75. Gushurst AKI, McMillin DR, Dietrich-Buchecker CO, Sauvage JP (1989) *Inorg Chem* 28:4070–4072
76. Goodman MS, Hamilton AD, Weiss J (1995) *J Am Chem Soc* 117:8447–8455
77. Amendola V, Boiocchi M, Colasson B, Fabbrizzi L (2006) *Inorg Chem* 45:6138–6147
78. Everly RM, McMillin DR (1989) *Photochem Photobiol* 50:711–716
79. Chen LX (2005) *Annu Rev Phys Chem* 56:221–254
80. Chen LX (2004) *Angew Chem Int Ed* 43:2886–2905
81. Chen LX, Jennings G, Liu T, Gosztola DJ, Hessler JP, Scaltrito DV, Meyer GJ (2002) *J Am Chem Soc* 124:10861–10867
82. Chen LX, Shaw GB, Novozhilova I, Liu T, Jennings G, Attenkofer K, Meyer GJ, Coppens P (2003) *J Am Chem Soc* 125:7022–7034
83. Coppens P (2003) *Chem Commun* pp 1317–1320
84. Gunaratne T, Rodgers MAJ, Felder D, Nierengarten JF, Accorsi G, Armaroli N (2003) *Chem Commun* pp 3010–3011
85. Felder D, Nierengarten JF, Barigelletti F, Ventura B, Armaroli N (2001) *J Am Chem Soc* 123:6291–6299
86. Cody J, Dennison J, Gilmore J, VanDerveer DG, Henary MM, Gabrielli A, Sherrill CD, Zhang YY, Pan CP, Burda C, Fahrni CJ (2003) *Inorg Chem* 42:4918–4929
87. Blaskie MW, McMillin DR (1980) *Inorg Chem* 19:3519–3522
88. Williams RM, De Cola L, Hartl F, Lagref JJ, Planeix JM, De Cian A, Hosseini MW (2002) *Coord Chem Rev* 230:253–261
89. Siddique ZA, Yamamoto Y, Ohno T, Nozaki K (2003) *Inorg Chem* 42:6366–6378
90. Miller MT, Gantzel PK, Karpishin TB (1999) *J Am Chem Soc* 121:4292–4293
91. Parker WL, Crosby GA (1989) *J Phys Chem* 93:5692–5696
92. Kirchhoff JR, Gamache RE, Blaskie MW, Del Paggio AA, Lengel RK, McMillin DR (1983) *Inorg Chem* 22:2380–2384

93. Cardenas DJ, Collin JP, Gaviña P, Sauvage JP, De Cian A, Fischer J, Armaroli N, Flamigni L, Vicinelli V, Balzani V (1999) *J Am Chem Soc* 121:5481–5488
94. Flamigni L, Talarico AM, Chambron JC, Heitz V, Linke M, Fujita N, Sauvage JP (2004) *Chem-Eur J* 10:2689–2699
95. Armaroli N, Balzani V, Barigelletti F, Decola L, Sauvage JP, Hemmert C (1991) *J Am Chem Soc* 113:4033–4035
96. Armaroli N, Balzani V, De Cola L, Hemmert C, Sauvage JP (1994) *New J Chem* 18:775–782
97. Dietrich-Buchecker CO, Sauvage JP, Armaroli N, Ceroni P, Balzani V (1996) *Angew Chem Int Ed Engl* 35:1119–1121
98. Armaroli N, Diederich F, Dietrich-Buchecker CO, Flamigni L, Marconi G, Nierengarten JF, Sauvage JP (1998) *Chem-Eur J* 4:406–416
99. Sandanayaka ASD, Watanabe N, Ikeshita KI, Araki Y, Kihara N, Furusho Y, Ito O, Takata T (2005) *J Phys Chem B* 109:2516–2525
100. Li K, Bracher PJ, Guldi DM, Herranz MA, Echegoyen L, Schuster DI (2004) *J Am Chem Soc* 126:9156–9157
101. Li K, Schuster DI, Guldi DM, Herranz MA, Echegoyen L (2004) *J Am Chem Soc* 126:3388–3389
102. Watanabe N, Kihara N, Furusho Y, Takata T, Araki Y, Ito O (2003) *Angew Chem Int Ed* 42:681–683
103. Linke M, Chambron SC, Heitz V, Sauvage SP, Encinas S, Barigelletti F, Flamigni L (2000) *J Am Chem Soc* 122:11834–11844
104. Andersson M, Linke M, Chambron JC, Davidsson J, Heitz V, Hammarström L, Sauvage JP (2002) *J Am Chem Soc* 124:4347–4362
105. Andersson M, Linke M, Chambron JC, Davidsson J, Heitz V, Sauvage JP, Hammarström L (2000) *J Am Chem Soc* 122:3526–3527
106. Flamigni L, Armaroli N, Barigelletti F, Chambron JC, Sauvage JP, Solladié N (1999) *New J Chem* 23:1151–1158
107. Chambron JC, Harriman A, Heitz V, Sauvage JP (1993) *J Am Chem Soc* 115:6109–6114
108. Chambron JC, Harriman A, Heitz V, Sauvage JP (1993) *J Am Chem Soc* 115:7419–7425
109. Holler M, Cardinali F, Mamlouk H, Nierengarten JF, Gisselbrecht JP, Gross M, Rio Y, Barigelletti F, Armaroli N (2006) *Tetrahedron* 62:2060–2073
110. Rio Y, Enderlin G, Bourgogne C, Nierengarten JF, Gisselbrecht JP, Gross M, Accorsi G, Armaroli N (2003) *Inorg Chem* 42:8783–8793
111. Clifford JN, Accorsi G, Cardinali F, Nierengarten JF, Armaroli N (2006) *C R Chim* 9:1005–1013
112. Flamigni L, Heitz V, Sauvage JP (2006) *Struct Bond* 121:217–261
113. Cunningham KL, McMillin DR (1998) *Inorg Chem* 37:4114–4119
114. Cunningham KL, Hecker CR, McMillin DR (1996) *Inorg Chim Acta* 242:143–147
115. Ruthkosky M, Kelly CA, Castellano FN, Meyer GJ (1998) *Coord Chem Rev* 171:309–322
116. Ruthkosky M, Castellano FN, Meyer GJ (1996) *Inorg Chem* 35:6406–6412
117. Castellano FN, Ruthkosky M, Meyer GJ (1995) *Inorg Chem* 34:3–4
118. Meskers SCJ, Dekkers H, Rapenne G, Sauvage JP (2000) *Chem-Eur J* 6:2129–2134
119. Buckner MT, McMillin DR (1978) *J Chem Soc-Chem Commun*, pp 759–761
120. Cuttall DG, Kuang SM, Fanwick PE, McMillin DR, Walton RA (2002) *J Am Chem Soc* 124:6–7
121. McCormick T, Jia WL, Wang SN (2006) *Inorg Chem* 45:147–155
122. Tsukuda T, Nakamura A, Arai T, Tsubomura T (2006) *Bull Chem Soc Jpn* 79:288–290

123. Armaroli N, Accorsi G, Holler M, Moudam O, Nierengarten JF, Zhou Z, Wegh RT, Welter R (2006) *Adv Mater* 18:1313–1316
124. Yang L, Feng JK, Ren AM, Zhang M, Ma YG, Liu XD (2005) *Eur J Inorg Chem* 1867–1879
125. Howell SL, Gordon KC (2004) *J Phys Chem A* 108:2536–2544
126. Kuang SM, Cuttall DG, McMillin DR, Fanwick PE, Walton RA (2002) *Inorg Chem* 41:3313–3322
127. Engelman R, Jortner J (1970) *Mol Phys* 18:145–164
128. Rader RA, McMillin DR, Buckner MT, Matthews TG, Casadonte DJ, Lengel RK, Whitaker SB, Darmon LM, Lytle FE (1981) *J Am Chem Soc* 103:5906–5912
129. Palmer CEA, McMillin DR, Kirmaier C, Holten D (1987) *Inorg Chem* 26:3167–3170
130. Tsubomura T, Takahashi N, Saito K, Tsukuda T (2004) *Chem Lett* 33:678–679
131. Saito K, Arai T, Takahashi N, Tsukuda T, Tsubomura T (2006) *Dalton Trans* pp 4444–4448
132. Tsubomura T, Enoto S, Endo S, Tamane T, Matsumoto K, Tsukuda T (2005) *Inorg Chem* 44:6373–6378
133. Jia WL, McCormick T, Tao Y, Lu JP, Wang SN (2005) *Inorg Chem* 44:5706–5712
134. Slinker J, Bernards D, Houston PL, Abruna HD, Bernhard S, Malliaras GG (2003) *Chem Commun*, pp 2392–2399
135. Schubert EF, Kim JK (2005) *Science* 308:1274–1278
136. Bolink HJ, Cappelli L, Coronado E, Gavina P (2005) *Inorg Chem* 44:5966–5968
137. Holder E, Langeveld BMW, Schubert US (2005) *Adv Mater* 17:1109–1121
138. Zhang QS, Zhou QG, Cheng YX, Wang LX, Ma DG, Jing XB, Wang FS (2004) *Adv Mater* 16:432–436
139. Che GB, Su ZS, Li WL, Chu B, Li MT, Hu ZZ, Zhang ZQ (2006) *Appl Phys Lett* 89:103511
140. Zhang QS, Zhou QG, Cheng YX, Wang LX, Ma DG, Jing XB, Wang FS (2006) *Adv Funct Mater* 16:1203–1208
141. Ma YG, Che CM, Chao HY, Zhou XM, Chan WH, Shen JC (1999) *Adv Mater* 11:852–857
142. Raston CL, White AH (1976) *J Chem Soc Dalton Trans* 21:2153–2156
143. Vitale M, Ford PC (2001) *Coord Chem Rev* 219:3–16
144. Hardt HD, Pierre A (1973) *Z Anorg Allg Chem* 402:107
145. Ford PC, Cariati E, Bourassa J (1999) *Chem Rev* 99:3625–3647
146. Eitel E, Oelkrug D, Hiller W, Strahle J (1980) *Z Naturforsch (B)* 35:1247–1253
147. Kyle KR, Ryu CK, DiBenedetto JA, Ford PC (1991) *J Am Chem Soc* 113:2954–2965
148. Rath NP, Holt EM, Tanimura K (1986) *J Chem Soc-Dalton Trans* pp 2303–2310
149. Araki H, Tsuge K, Sasaki Y, Ishizaka S, Kitamura N (2005) *Inorg Chem* 44:9667–9675
150. Cotton FA, Feng XJ, Timmons DJ (1998) *Inorg Chem* 37:4066–4069
151. De Angelis F, Fantacci S, Sgamellotti A, Cariati E, Ugo R, Ford PC (2006) *Inorg Chem* 45:10576–10584
152. Yam VWW, Lo KKW, Wong KMC (1999) *J Organomet Chem* 578:3–30
153. Yam VWW (2002) *Acc Chem Res* 35:555–563
154. Yam VWW, Choi SWK, Chan CL, Cheung KK (1996) *Chem Commun*, pp 2067–2068
155. Chan CL, Cheung KK, Lam WH, Cheng ECC, Zhu N, Choi SWK, Yam VWW (2006) *Chem-Asian J* 1–2:273
156. Dias HVR, Diyabalanage HVK, Eldabaja MG, Elbjeirami O, Rawashdeh-Omary MA, Omary MA (2005) *J Am Chem Soc* 127:7489–7501
157. Che CM, Xia BH, Huang JS, Chan CK, Zhou ZY, Cheung KK (2001) *Chem-Eur J* 7:3998–4006

158. Kharenko OA, Kennedy DC, Demeler B, Maroney MJ, Ogawa MY (2005) *J Am Chem Soc* 127:7678–7679
159. Wei QH, Yin GQ, Zhang LY, Shi LX, Mao ZW, Chen ZN (2004) *Inorg Chem* 43:3484–3491
160. Baxter CW, Higgs AC, Jones AC, Parsons S, Bailey PJ, Tasker PA (2002) *J Chem Soc Dalton Trans* 4395–4401
161. Peng R, Li D, Wu T, Zhou XP, Ng SW (2006) *Inorg Chem* 45:4035–4046
162. He X, Lu CZ, Wu CD, Chen LJ (2006) *Eur J Inorg Chem*, pp 2491–2503
163. Riesgo EC, Hu YZ, Bouvier F, Thummel RP, Scaltrito DV, Meyer GJ (2001) *Inorg Chem* 40:3413–3422
164. Riesgo EC, Hu YZ, Thummel RP (2003) *Inorg Chem* 42:6648–6654
165. Zhang XM, Tong ML, Gong ML, Lee HK, Luo L, Li KF, Tong YX, Chen XM (2002) *Chem-Eur J* 8:3187–3194
166. Zheng SL, Zhang JP, Chen XM, Huang ZL, Lin ZY, Wong WT (2003) *Chem-Eur J* 9:3888–3896
167. Kunkely H, Vogler A (2003) *Inorg Chem Commun* 6:543–545
168. Pawlowski V, Knor G, Lennartz C, Vogler A (2005) *Eur J Inorg Chem* 3167–3171
169. Kinoshita I, Hamazawa A, Nishioka T, Adachi H, Suzuki H, Miyazaki Y, Tsuboyama A, Okada S, Hoshino M (2003) *Chem Phys Lett* 371:451–457
170. Song DT, Jia WL, Wu G, Wang SN (2005) *Dalton Trans* pp 433–438
171. Zhao SB, Wang RY, Wang SN (2006) *Inorg Chem* 45:5830–5840
172. Fournier E, Lebrun F, Drouin M, Decken A, Harvey PD (2004) *Inorg Chem* 43:3127–3135
173. Omary MA, Rawashdeh-Omary MA, Diyabalanage HVK, Rasika Dias HV (2003) *Inorg Chem* 42:8612–8614
174. Tsuboyama A, Okada S, Takiguchi T, Igawa S, Kamatani J, Furugori M, Canon KK (2005) *JP Patent n. US Patent* 2005 014 024

Photochemistry and Photophysics of Coordination Compounds: Ruthenium

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Abstract Ruthenium compounds, particularly Ru(II) polypyridine complexes, are the class of transition metal complexes which has been most deeply investigated from a photochemical viewpoint. The reason for such great interest stems from a unique combination of chemical stability, redox properties, excited-state reactivity, luminescence emission, and excited-state lifetime. Ruthenium polypyridine complexes are indeed good visible light absorbers, feature relatively intense and long-lived luminescence, and can undergo reversible redox processes in both the ground and excited states. This chapter presents some general concepts on the photochemical properties of Ru(II) polypyridine complexes and gives an overview of various research topics involving ruthenium photochemistry which have emerged in the last 15 years. In particular, aspects connected to supramolecular photochemistry and photophysics are discussed, such as multicomponent systems for light harvesting and photoinduced charge separation, systems for photoinduced multielectron/hole storage, and photocatalytic processes based on supramolecular Ru(II) polypyridine species. Interaction with biological systems and dye-sensitized photoelectrochemical cells are also briefly discussed.

Keywords Ruthenium · Luminescence · Electron transfer · Energy transfer · Solar energy conversion · Light-powered molecular machines · Dye-sensitized solar cells

1

Introduction

The photochemistry of ruthenium complexes has undergone an impressive growth in the last few decades. The prototype compound $[\text{Ru}(\text{bpy})_3]^{2+}$ (bpy = 2,2'-bipyridine) has certainly been one of the molecules most extensively studied and widely used in research laboratories during the last 30 years. A unique combination of chemical stability, redox properties, excited-state reactivity, luminescence emission, and excited-state lifetime has attracted the attention of many researchers, first on this molecule and then on some hundreds of its derivatives. The study of this class of complexes has stimulated the growth of several branches of chemistry. In particular, Ru(II) polypyridine complexes have played and are still playing a key role in the development of

photochemistry, photophysics, photocatalysis, electrochemistry, photoelectrochemistry, chemi- and electrochemiluminescence, and electron and energy transfer. Mostly in the last 15 years, Ru(II) polypyridine complexes have also contributed highly to the development of supramolecular photochemistry, and in particular to its aspects related to photoinduced electron and energy transfer processes within multicomponent (supramolecular) assemblies, including luminescent polynuclear metal complexes, light-active dendrimers, artificial light-harvesting antennae, photoinduced charge-separation devices, luminescent sensors, and light-powered molecular machines.

Because of the enormous number of Ru(II) complexes investigated from a photochemical viewpoint and the variety of multicomponent structures prepared and light-based functions explored, it is impossible to make an exhaustive review. In this chapter, we recall some basic concepts on ruthenium photochemistry and discuss in some detail a few selected topics, particularly those that have developed or emerged during the last 15 years. In this way we also hope to give an overview of some research directions which ruthenium photochemistry allows to be explored. An exhaustive review [1] published about 20 years ago collects photochemical, photophysical, and redox data of several hundreds of Ru(II) polypyridine complexes. Another extensive review was published about 10 years ago [2], dealing with the luminescence properties of *polynuclear* transition metal complexes, most of them containing Ru(II) polypyridine subunits (interestingly, in the former review [1] less than ten polynuclear Ru complexes were reported). A review focused on the photophysical properties of Ru(II) complexes with tridentate polypyridine ligands [3] has also been published. All these review articles contain more or less comprehensive tables of data. Enlightening articles on some basic properties of Ru(II) polypyridine complexes are also available [4–8].

The very large majority of photochemical investigations on ruthenium complexes deal with Ru(II) polypyridine species. For such a reason, as also implicitly suggested above, we will limit our discussion to these species. Other photoactive compounds containing ruthenium metals, including ruthenium porphyrins, are not included in this article.

2

Structure, Bonding, and Excited States of Ru(II) Polypyridine Complexes

Ru^{2+} is a d^6 system and the polypyridine ligands are usually colorless molecules possessing σ donor orbitals localized on the nitrogen atoms and π donor and π^* acceptor orbitals more or less delocalized on aromatic rings. Following a single-configuration one-electron description of the excited state in octahedral symmetry (Fig. 1a), promotion of an electron from a π_M metal orbital to the π_L^* ligand orbitals gives rise to metal-to-ligand charge transfer (MLCT) excited states, whereas promotion of an electron from π_M to σ_M^* or-

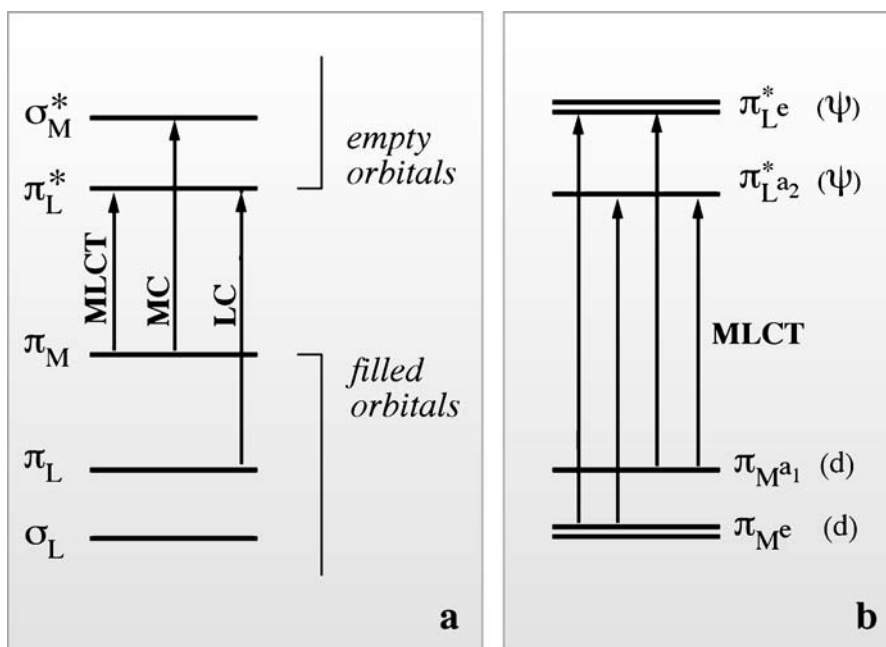


Fig. 1 **a** Simplified molecular orbital diagram for Ru(II) polypyridine complexes in octahedral symmetry showing the three types of electronic transitions occurring at low energies. **b** Detailed representation of the MLCT transition in D_3 symmetry

bitals gives rise to metal-centered (MC) excited states. Ligand-centered (LC) excited states can be obtained by promoting an electron from π_L to π_L^* . All these excited states may have singlet or triplet multiplicity, although spin-orbit coupling causes large singlet-triplet mixing, particularly in MC and MLCT excited states [6, 9–11].

The prototype $[\text{Ru}(\text{bpy})_3]^{2+}$ (Fig. 2), as well as most of the $\text{Ru}(\text{LL})_3^{2+}$ complexes (LL = bidentate polypyridine ligand), exhibits a D_3 symmetry [12]. Following Orgel's notation [13], the π^* orbitals may be symmetrical (χ) or

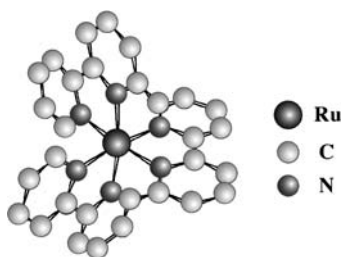


Fig. 2 Molecular structural formula of $[\text{Ru}(\text{bpy})_3]^{2+}$

antisymmetrical (ψ) with respect to rotation around the C_2 axis retained by each Ru(bpy) unit. A more detailed picture of the highest occupied molecular orbitals (HOMOs) and lowest unoccupied molecular orbitals (LUMOs) is shown in Fig. 1b [14–16]. The HOMOs are $\pi_{Ma_1}(d)$ and $\pi_{Me}(d)$, which are mainly localized on the metal; the LUMOs are $\pi_{La_2}^*(\psi)$ and $\pi_{Le}^*(\psi)$, which are mainly localized on the ligands. The ground state of the complex is a singlet, derived from the $\pi_{Me}(d)^4 \pi_{Ma_1}(d)^2$ electronic configuration.

According to Kasha's rule, only the lowest excited state and the upper states that can be populated on the basis of the Boltzmann equilibrium distribution may play a role in determining the photochemical and photophysical properties. The MC excited states of d^6 octahedral complexes are strongly displaced with respect to the ground-state geometry along metal–ligand vibration coordinates [17, 18].

When the lowest excited state is MC, it undergoes fast radiationless deactivation to the ground state and/or ligand dissociation reactions (Fig. 3). As a consequence, at room temperature the excited-state lifetime is very short, no luminescence emission can be observed [19], and very rarely bimolecular (or supramolecular) reactions can take place. LC and MLCT excited states are usually not strongly displaced compared to the ground-state geometry. Thus, when the lowest excited state is LC or MLCT (Fig. 3) it does not undergo fast radiationless decay to the ground state and luminescence can usually be observed. The radiative deactivation rate constant is somewhat higher for ^3MLCT than for ^3LC because of the larger spin–orbit coupling effect. For this reason, the ^3LC excited states are longer lived at low temperature in a rigid matrix and the ^3MLCT excited states are more likely to exhibit luminescence at room temperature in fluid solution.

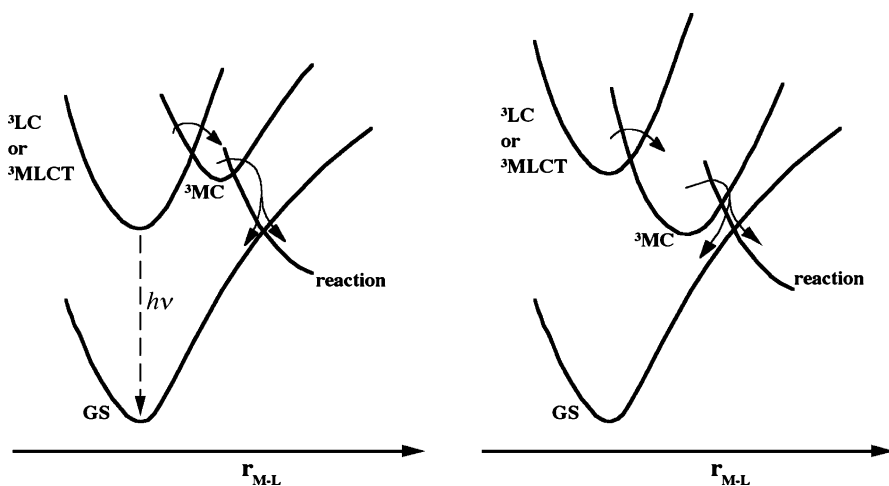


Fig. 3 Schematic representation of two limiting cases for the relative positions of ^3MC and ^3LC (or ^3MLCT) excited states

From the above discussion, it is clear that the excited-state properties of a complex are related to the energy ordering of its low-energy excited states and, particularly, to the orbital nature of its lowest excited state. The energy positions of the MC, MLCT, and LC excited states depend on the ligand field strength, the redox properties of metal and ligands, and intrinsic properties of the ligands, respectively [1, 2, 6]. Thus, in a series of complexes of the same metal ion, the energy ordering of the various excited states, and particularly the orbital nature of the lowest excited state, can be controlled by the choice of suitable ligands [1, 2, 5, 6]. It is therefore possible to design complexes having, at least to a certain degree, desired properties.

For most Ru(II) polypyridine complexes, the lowest excited state is a $^3\text{MLCT}$ level (or, better, a cluster [6] of closely spaced $^3\text{MLCT}$ levels, see later) which undergoes relatively slow radiationless transitions and thus exhibits relatively long lifetime and intense luminescence emission. Such a state is obtained by promoting an electron from a metal π_{M} orbital to a ligand π_{L}^* orbital (Fig. 1). The same π_{L}^* orbital is usually involved in the one-electron reduction process. For a long time it has been discussed whether in homoleptic complexes the emitting $^3\text{MLCT}$ state is best described with a multichelate ring-delocalized orbital (Fig. 4a) or a single chelate ring-localized orbital with a small amount of interligand interaction (Fig. 4b) [20]. This problem has been tackled with a variety of techniques on both reduced and excited complexes. Compelling evidence for “spatially isolated” [21] redox orbitals has been obtained from low-temperature cyclic voltammetry [22, 23], electron spin resonance [24], electronic absorption spectra of reduced species [25, 26], nuclear magnetic resonance [27], resonance Raman spectra [28, 29], and time-resolved infrared spectroscopy [30]. In the last 10 years, with the coming into play of ultrafast spectroscopic techniques, it has also been possible to investigate the nature of the Franck–Condon state and the rate constants of the localization/delocalization processes, as well as the interligand hopping (sometimes called “randomization of the excitation”) in the MLCT excited state. These issues will be discussed in more detail later.

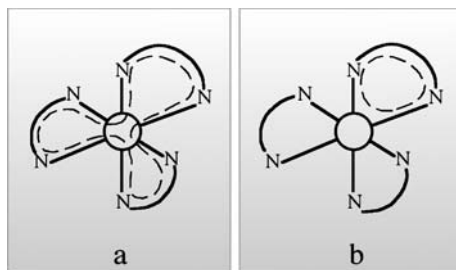


Fig. 4 Pictorial description of the electron promoted to the π_{L}^* orbital: **a** multichelate ring-delocalized orbital; **b** single chelate ring-localized orbital

3

[Ru(bpy)₃]²⁺: The Prototype

To discuss the general properties of Ru(II) polypyridine complexes, it is convenient to refer to the properties of the prototype of this class of compounds, that is, [Ru(bpy)₃]²⁺.

3.1

Absorption Spectrum

The absorption spectrum of [Ru(bpy)₃]²⁺ is shown in Fig. 5 along with the proposed assignments [1, 4, 6, 14–16, 31]. The bands at 185 nm (not shown in the figure) and 285 nm have been assigned to spin-allowed LC $\pi \rightarrow \pi^*$ transitions by comparison with the spectrum of protonated bipyridine [32]. The two remaining intense bands at 240 and 450 nm have been assigned to spin-allowed MLCT $d \rightarrow \pi^*$ transitions. The shoulders at 322 and 344 nm might be MC transitions. In the long-wavelength tail of the absorption spectrum a shoulder is present at about 550 nm ($\epsilon \sim 600 \text{ M}^{-1} \text{ cm}^{-1}$) in an ethanol-methanol glass at 77 K [33]. This absorption feature is thought to be due to spin-forbidden MLCT transition(s).

In spite of the presence of the heavy Ru atom, it has been established that it is reasonable to assign the electronic transitions of [Ru(bpy)₃]²⁺ as being due to “singlet” or “triplet” states. In particular, a singlet character $\leq 10\%$ has been estimated [10, 34] for the lowest-lying excited states of [Ru(bpy)₃]²⁺. The maximum of the ¹MLCT band at $\sim 450 \text{ nm}$ is slightly sensitive to solvent, suggesting an instantaneous sensing of the formation of the dipolar excited-state [Ru³⁺(bpy)₂(bpy)⁻]²⁺ [35].

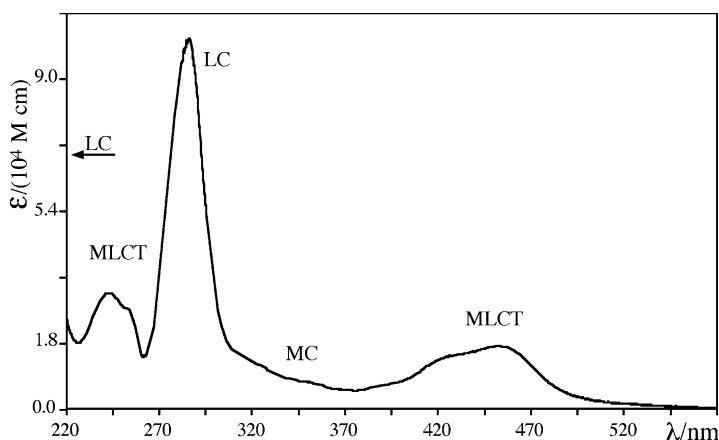


Fig. 5 Electronic absorption spectrum of [Ru(bpy)₃]²⁺ in alcoholic solution

3.2

Deactivation of Upper Excited States

As mentioned in the Introduction, the upper excited states of transition metal complexes usually undergo radiationless deactivation to the lowest excited state. For $[\text{Ru}(\text{bpy})_3]^{2+}$ the lowest excited state (or, better, the cluster of lowest excited states) is relatively long lived and its formation and disappearance can be easily monitored by flash spectroscopy and luminescence decay. The absorption spectrum of the lowest excited state is shown in Fig. 6 [36–39].

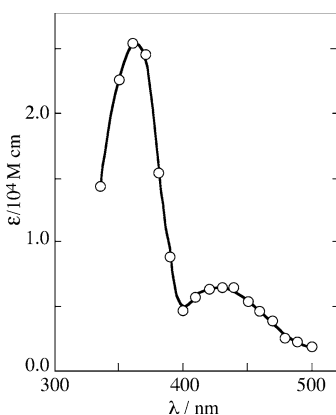


Fig. 6 Electronic absorption spectrum of the lowest excited state of $[\text{Ru}(\text{bpy})_3]^{2+}$ in alcoholic solution

The risetime of the lowest excited state upon excitation of spin-allowed excited states was initially estimated to be $\ll 1$ ns for $[\text{Ru}(\text{bpy})_3]^{2+}$ [40, 41]; successively, available ultrafast spectroscopic techniques demonstrated that intersystem crossing occurs in the subpicosecond timescale (see later). The efficiency of formation of the lowest excited state, $\Phi(^3\text{MLCT})$ (and thus, the efficiency of intersystem crossing from the upper singlets obtained by excitation to the lowest triplet, η_{isc}), is essentially unity [36, 37, 42–44].

3.3

Emission Properties

Excitation of $[\text{Ru}(\text{bpy})_3]^{2+}$ in any of its absorption bands leads to a luminescence emission (Fig. 7) whose intensity, lifetime, and energy position are more or less temperature dependent. Detailed studies on the temperature dependence [1, 4, 6, 45–49] of the luminescence lifetime and quantum yield in the temperature range 2–70 K showed that luminescence originates from a set of three closely spaced levels (ΔE , 10, and 61 cm^{-1}) in ther-

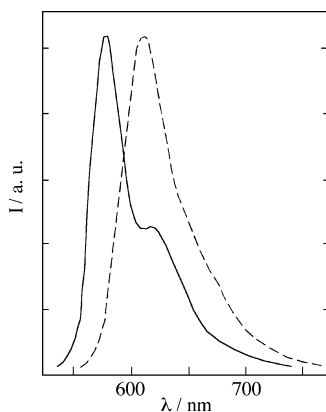


Fig. 7 Emission spectrum of $^*[Ru(bpy)_3]^{2+}$ in alcoholic solution at 77 K (solid line) and at room temperature (dashed line)

mal equilibrium. This cluster of luminescent, closely spaced excited states will be indicated in the following by $^*[Ru(bpy)_3]^{2+}$ or as the ^3MLCT state. $^*[Ru(bpy)_3]^{2+}$ has a substantial triplet character and a single ligand localized excitation.

In rigid glass at 77 K the emission lifetime of $^*[Ru(bpy)_3]^{2+}$ is $\sim 5 \mu s$ and the emission quantum yield is ~ 0.4 [1, 6, 8]. Taken together with the unitary intersystem crossing efficiency, these figures yield a value of $\sim 13 \mu s$ for the radiative lifetime. Values of this order of magnitude have been found for MLCT excited states of other transition metal complexes [50–53]. LC excited states of transition metal complexes usually exhibit radiative lifetimes in the millisecond range [1, 6, 49, 50, 53–60].

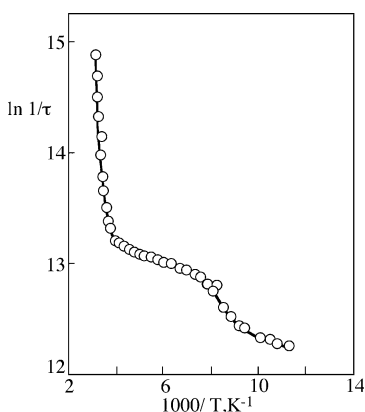


Fig. 8 Temperature dependence of the emission lifetime of $^*[Ru(bpy)_3]^{2+}$ in nitrile solution

With increasing temperature, the emission lifetime (Fig. 8) and quantum yield decrease [1, 4, 6, 8, 32, 61–79]. This behavior may be accounted for by a stepwise term and two Arrhenius terms [1–3]:

$$1/\tau = k_0 + \frac{B}{1 + \exp[C(1/T - 1/T_B)]} + A_1 \exp(-\Delta E_1/RT) + A_2 \exp(-\Delta E_2/RT). \quad (1)$$

The value of the various parameters is somewhat dependent on the nature of the solvent. In propionitrile–butyronitrile (4 : 5 v/v) the values are as follows [70, 71]: $k_0 = 2 \times 10^5 \text{ s}^{-1}$; $B = 2.1 \times 10^5 \text{ s}^{-1}$; $A_1 = 5.6 \times 10^5 \text{ s}^{-1}$; $\Delta E_1 = 90 \text{ cm}^{-1}$; $A_2 = 1.3 \times 10^{14} \text{ s}^{-1}$; $\Delta E_2 = 3960 \text{ cm}^{-1}$. Included in k_0 are the radiative $k_0(r)$ and nonradiative $k_0(nr)$ rate constants at 84 K. The stepwise term B is due to the melting of the matrix (100–150 K) and corresponds to the coming into play of vibrations capable of facilitating radiationless deactivation [8, 71]. In the same temperature range a red shift of $\sim 1000 \text{ cm}^{-1}$ is observed in the maximum of the emission band, and it is mainly attributed to reorganization of solvent molecules around the excited state in fluid solution before emission takes place [8, 71]. The Arrhenius term with $A_1 = 5.6 \times 10^5 \text{ s}^{-1}$ and $\Delta E_1 = 90 \text{ cm}^{-1}$ is thought to correspond to the thermal equilibration with a level lying at slightly higher energy and having the same electronic nature (so it would be a fourth MLCT state [6], considering the lowest-lying MLCT state is made of three sublevels as described before). The second Arrhenius term corresponds to a thermally activated surface crossing to an upper-lying ^3MC level which undergoes fast deactivation. Identification of this higher level as a ^3MC state is based upon the observed photosubstitution behavior at elevated temperatures [61], consistent with established photoreactivity patterns for d^6 metal complexes [17, 52].

Experiments carried out with $[\text{Ru}(\text{bpy})_3]^{2+}$ and $[\text{Ru}(\text{bpy}-d_8)_3]^{2+}$ in H_2O and D_2O [61, 80, 81] indicate that $k_0(nr)$ is sensitive to deuteration, as expected for a weak-coupled radiationless process [6, 82–84]. By contrast, A_2 is insensitive to deuteration, supporting a strong-coupled (surface crossing) deactivation pathway, which may be related to the observed photosensitivity. It should be noted that the decrease in lifetime on melting has also been explained on the basis of the energy gap law because of the corresponding red shift in the emission band [6].

Finally, it should be noted that at 77 K the emission spectrum of $[\text{Ru}(\text{bpy})_3]^{2+}$, as well as that of most $\text{Ru}(\text{II})$ polypyridine complexes, exhibits a vibrational structure (see Fig. 7). This structure is assigned to the vibrational progression, and its energy spacing is about 1300 cm^{-1} , equivalent to the C–N and C–C stretching energy of the aromatic rings, thus indicating that such stretchings are the dominant accepting modes for deactivation of the $^3\text{MLCT}$ state.

3.4

Photosubstitution and Photoracemization Processes

Although $[\text{Ru}(\text{bpy})_3]^{2+}$ is normally considered as photochemically inert toward ligand substitution, this is not strictly true [1, 6, 14, 15]. In aqueous solution the quantum yield of $[\text{Ru}(\text{bpy})_3]^{2+}$ disappearance is in the range 10^{-5} – 10^{-3} , depending on both the pH of the solution and temperature [1]. In chlorinated solvents such as CH_2Cl_2 , the photochemistry of $[\text{Ru}(\text{bpy})_3]\text{X}_2$ ($\text{X} = \text{Cl}^-$, Br^- , NCS^-) is well behaved [64, 85], giving rise to $[\text{Ru}(\text{bpy})_2\text{X}_2]$ as the final product. The quantum yields are in the range 10^{-1} – 10^{-2} . The PF_6^- salt is photoinert. A substantial difference between aqueous and CH_2Cl_2 solutions is that salts of $[\text{Ru}(\text{bpy})_3]^{2+}$ are completely ion-paired in the latter medium.

A detailed mechanism for the ligand photosubstitution reaction of $[\text{Ru}(\text{bpy})_2\text{X}_2]$ has been proposed [6, 64] (Fig. 9). According to this mechanism, thermally activated formation of a ^3MC excited state (vide supra) leads to the cleavage of a Ru–N bond, with formation of a five-coordinate square pyramidal species. In the absence of coordinating ions, as with the PF_6^- salt, this square pyramidal species returns to $[\text{Ru}(\text{bpy})_3]^{2+}$. When coordinating anions are present, as in the Cl^- salt, a hexacoordinated monodentate bpy intermediate is formed. Once formed, this monodentate bpy species can undergo loss of bpy and formation of $[\text{Ru}(\text{bpy})_2\text{X}_2]$, or a “self-annealing” process (chelate ring closure), with re-formation of $[\text{Ru}(\text{bpy})_3]^{2+}$. The “self-annealing” protective step is favored in aqueous solution, presumably because

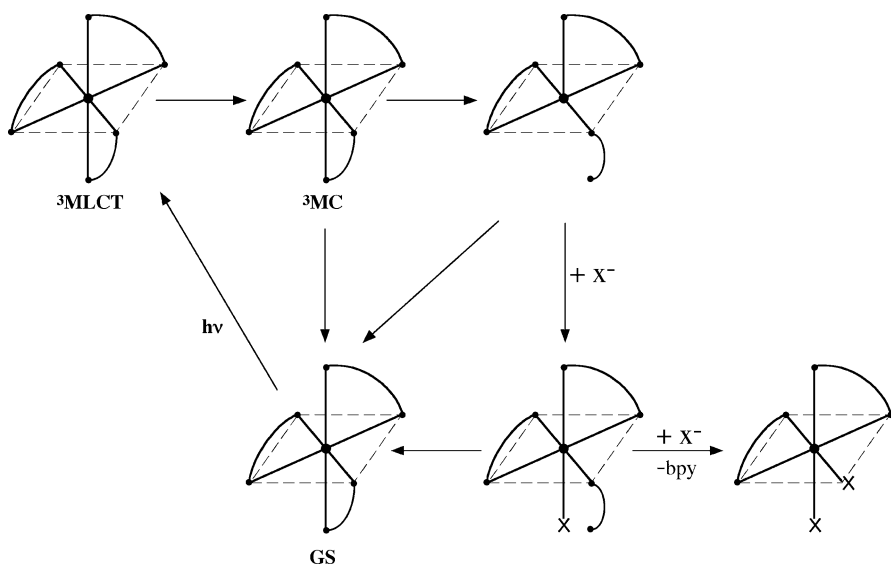


Fig. 9 Scheme of the proposed mechanism for ligand photosubstitution reactions of $[\text{Ru}(\text{bpy})_3]\text{X}_2$

of stabilization of the cationic $[\text{Ru}(\text{bpy})_3]^{2+}$ species, whereas formation of neutral $[\text{Ru}(\text{bpy})_2\text{X}_2]$ complexes is favored in low-polarity solvents. Photoracemization of $[\text{Ru}(\text{bpy})_3]^{2+}$ [86] also occurs with low quantum yield (2.9×10^{-4} in water at 25 °C). This process can be accounted for by a rearrangement of the square pyramidal primary photoproduct into a trigonal bipyramidal intermediate which can lead back to either the Δ or the Λ isomer [64].

Ligand photodissociation is, of course, a drawback for the use of $[\text{Ru}(\text{bpy})_3]^{2+}$ in practical applications. To avoid ligand photodissociation one should prevent population of ^3MC and/or ligand dissociation from ^3MC . Population of ^3MC can be prevented or at least reduced by: (a) addition of sufficient quencher to capture $^3\text{MLCT}$ before surface crossing to ^3MC can occur; (b) working at low temperature; (c) increasing the energy gap between $^3\text{MLCT}$ and ^3MC ; and (d) increasing pressure [87, 88]. Ligand dissociation from ^3MC can also be reduced by (e) avoiding coordinating anions in solvent of low dielectric constant and (f) linking together the three bpy ligands so as to form a single caging ligand which encapsulates the metal ion. Point (a) is experimentally difficult, since thermal equilibration is quite a fast process. Points (c) and (f) are particularly interesting and much effort has been made along such directions [1, 89, 90]. It should be considered that in most of the $[\text{Ru}(\text{bpy})_3]^{2+}$ derivatives, the $^3\text{MLCT}$ state is shifted to lower energies [1], whereas the energy of the ^3MC state usually does not change. This leads to an increased energy gap between MLCT and MC states and decreased photolability. As a consequence, photosubstitution is a minor problem in most ruthenium polypyridine complexes. It should be considered, however, that decreasing the energy of the $^3\text{MLCT}$ level increases the Franck–Condon factors for radiationless decay to the ground state, leading to decreased luminescence lifetimes and quantum yields. The rate of radiationless decay can be decreased by extending the delocalization of the promoted electron on suitable aromatic ligands [78, 91, 92].

Finally, it should also be noted that the photolabilization of ligands can be a profitable photochemical process: for example, a synthetic route to tris-heteroleptic Ru complexes involves photosubstitution of ligands [93] and photochemical, reversible ligand exchange has been proposed to be used to photoswitch the complexation activity in a ruthenium complex containing a scorpionate terpyridine ligand [94].

3.5

Quenching of the $^3\text{MLCT}$ Excited State: Energy and Electron Transfer Processes

The lowest $^3\text{MLCT}$ excited state of $[\text{Ru}(\text{bpy})_3]^{2+}$ lives long enough to encounter other solute molecules (even when these are present at relatively low concentration) and possesses suitable properties to play the role of energy

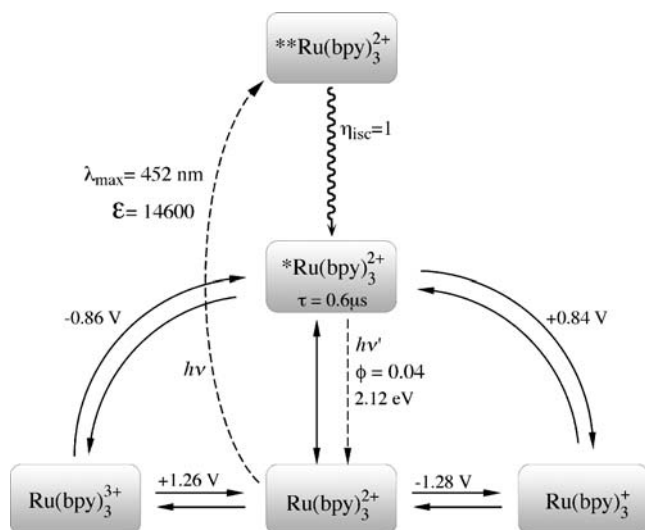
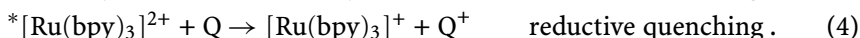
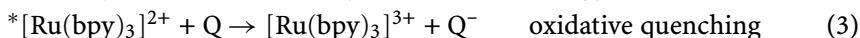
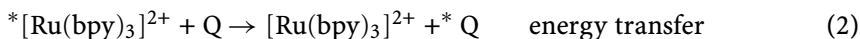


Fig. 10 Molecular quantities of $[\text{Ru}(\text{bpy})_3]^{2+}$ relevant for energy and electron transfer processes. ****Ru(bpy)₃²⁺** indicates higher-energy spin-allowed excited states and ***Ru(bpy)₃²⁺** indicates the lowest spin-forbidden excited state (³MLCT). Reported potentials are in aqueous solution vs SCE

donor, electron donor, or electron acceptor. As is also shown in Fig. 10, the energy available to $*[\text{Ru}(\text{bpy})_3]^{2+}$ for energy transfer processes is 2.12 eV and its reduction and oxidation potentials are + 0.84 and – 0.86 V (aqueous solution, vs SCE). It follows that $*[\text{Ru}(\text{bpy})_3]^{2+}$ is at the same time a good energy donor (Eq. 2), a good electron donor (Eq. 3), and a good electron acceptor (Eq. 4):



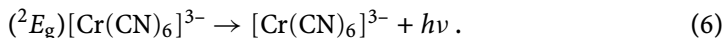
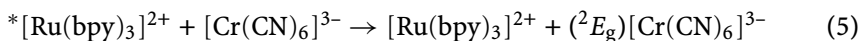
The direct observation of redox products represents the strongest evidence to support the occurrence of oxidative and reductive quenching mechanisms.

These observations can be performed in a few cases with continuous irradiation [95, 96] and more often in flash photolysis experiments, because usually the redox products rapidly decay either by back electron transfer reactions to re-form the starting materials or by secondary reactions to form other products. In practice, the possibility to observe transient absorptions is related to the changes in the optical density of the solution caused by the photoreaction. Bleaching and recovering of the $[\text{Ru}(\text{bpy})_3]^{2+}$ spectrum can be used for kinetic measurements. The absorption band at 680 nm typical of $[\text{Ru}(\text{bpy})_3]^{3+}$ is too weak to detect small $[\text{Ru}(\text{bpy})_3]^{3+}$ concentrations, so that in oxidative quenching processes one is forced to use the absorption spec-

trum of Q^- to monitor product formation. By contrast, $[\text{Ru}(\text{bpy})_3]^+$ exhibits a strong absorption band at 510 nm, which is particularly useful to investigate reductive quenching reactions.

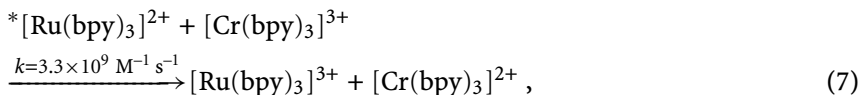
Following some pioneering works [96–100], literally hundreds of bimolecular excited-state reactions of $[\text{Ru}(\text{bpy})_3]^{2+}$ and of its derivatives have been studied [101]. Here we only illustrate a few examples to show that these excited-state reactions can be used for mechanistic studies as well as for potential applications of the greatest interest.

The early interest in $[\text{Ru}(\text{bpy})_3]^{2+}$ photochemistry arose from the possibility of using its long-lived excited state as energy donor in energy transfer processes. Although several sensitized reactions attributed to energy transfer processes (see, e.g., [102, 103]) were later shown to proceed via electron transfer [100], there are some very interesting cases in which energy transfer has been firmly demonstrated. A clear example is the quenching of $^*[\text{Ru}(\text{bpy})_3]^{2+}$ by $[\text{Cr}(\text{CN})_6]^{3-}$, where sensitized phosphorescence of the chromium complex has been observed both in fluid solution [104–108] and in the solid state [109–111]:

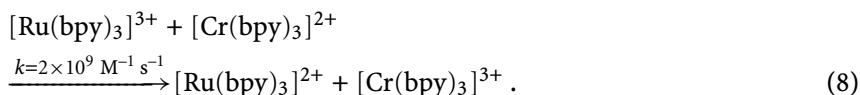


Energy transfer from $^*[\text{Ru}(\text{bpy})_3]^{2+}$ to $[\text{Cr}(\text{CN})_6]^{3-}$ was also used to demonstrate that the photosolvation reaction observed upon direct excitation of $[\text{Cr}(\text{CN})_6]^{3-}$ does not originate from the luminescent ${}^2E_g$ state of the chromium complex [104, 112].

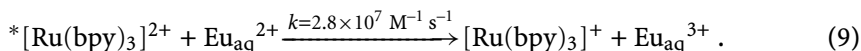
It should be pointed out that both reductive and oxidative $^*[\text{Ru}(\text{bpy})_3]^{2+}$ electron transfer quenchings by $[\text{Cr}(\text{CN})_6]^{3-}$ are thermodynamically forbidden because it is very difficult to reduce or oxidize $[\text{Cr}(\text{CN})_6]^{3-}$ [108]. $[\text{Cr}(\text{bpy})_3]^{3+}$, by contrast, can be very easily reduced and with this quencher oxidative electron transfer prevails over energy transfer



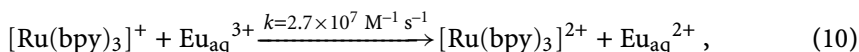
as is shown by the appearance of the $[\text{Cr}(\text{bpy})_3]^{2+}$ absorption spectrum in flash photolysis experiments [113]. Equation 7 converts 71% of the spectroscopic energy (2.12 eV) of the excited-state reactant into chemical energy of the products. As usually happens in these simple homogeneous systems, the converted energy cannot be stored but is immediately dissipated into heat by the back electron transfer reaction:



A carefully studied example of reductive electron transfer quenching (Eq. 9) is that involving $\text{Eu}_{\text{aq}}^{2+}$ as a quencher [114, 115]:



The difference spectrum obtained by flash photolysis after a 30-ns light pulse shows a bleaching in the region around 430 nm due to depletion of $[\text{Ru}(\text{bpy})_3]^{2+}$ and an increased absorption around 500 nm due to the formation of $[\text{Ru}(\text{bpy})_3]^+$ (note that both $\text{Eu}_{\text{aq}}^{2+}$ and $\text{Eu}_{\text{aq}}^{3+}$ are transparent in this spectral region). Clear kinetic evidence for reductive quenching comes from the observation that the growth of the absorption at 500 nm occurs at a rate equal to the rate of decay of the luminescence emission of $^*[\text{Ru}(\text{bpy})_3]^{2+}$. As it may happen in excited-state reactions, the products of Eq. 9 have a high energy content and thus they give rise to a back electron transfer reaction



which can be monitored (on a longer timescale) through the recovery of the 430-nm absorption or the disappearance of the 500-nm absorption.

In several cases direct evidence for energy transfer quenching (i.e., sensitized luminescence or absorption spectrum of the excited acceptor) or electron transfer quenching (i.e., absorption spectrum of redox products) is difficult or even impossible to obtain for bimolecular processes. In such cases, free energy correlations of rate constants are quite useful to elucidate the reaction mechanism [108, 116–118]. As we will see later, photoinduced energy and electron transfer processes can take place very easily in suitably organized supramolecular systems.

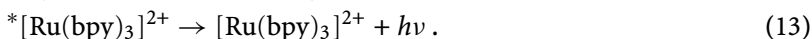
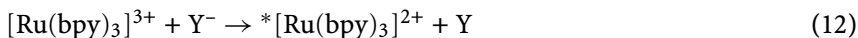
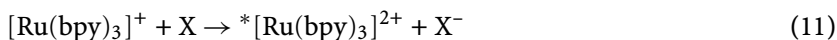
3.6

Chemiluminescence and Electrochemiluminescence Processes

As mentioned in the introductory chapter (Balzani et al. 2007, in this volume) [119], excited states can be generated in very exergonic electron transfer reactions. Formation of excited states can be easily demonstrated when the excited states are luminescent species. Because of its stability in the reduced and oxidized forms and the strong luminescence of its excited state, $[\text{Ru}(\text{bpy})_3]^{2+}$ is an extremely versatile reactant for a variety of chemiluminescent processes [32, 120–124].

In principle, there are two ways to generate the luminescent $^*[\text{Ru}(\text{bpy})_3]^{2+}$ excited state in chemical reactions. One way (Eq. 11) is to oxidize $[\text{Ru}(\text{bpy})_3]^+$ with a species X having reduction potential $E^0(\text{X}/\text{X}^-)$ more positive than 0.84 V, and another way (Eq. 12) is to reduce $[\text{Ru}(\text{bpy})_3]^{3+}$ with a species Y^-

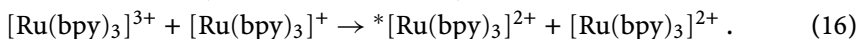
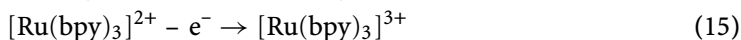
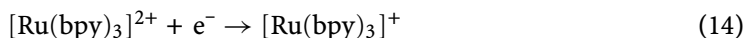
whose potential $E^0(Y/Y^-)$ is more negative than -0.86 V (see also Fig. 10).



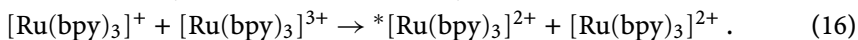
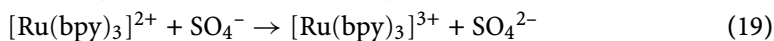
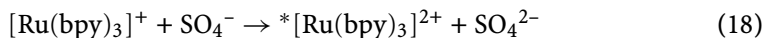
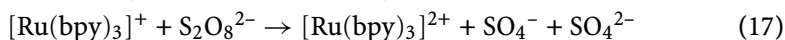
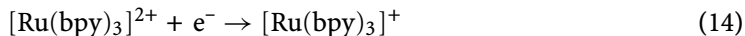
A variety of oxidants (e.g., $\text{S}_2\text{O}_8^{2-}$ [125, 126]) and reductants (e.g., e_{aq}^- [127], hydrazine and hydroxyl anion [128], oxalate ion [129, 130]) have been used in these chemiluminescent processes. In some cases (e.g., with OH^-), the reaction mechanism cannot be a simple outer sphere electron transfer reaction and the emitting species could be a slightly modified (on the ligands) complex. It should also be pointed out that minor amounts of oxidizing and reducing impurities are sufficient to produce luminescence in chemiluminescence and electrochemiluminescence experiments [131].

The most interesting way [132] to obtain chemiluminescence from $[\text{Ru}(\text{bpy})_3]^{2+}$ solutions is probably to produce the oxidized and/or reduced form of the complex “in situ” by electrochemical methods. Three classical experiments of this type can be performed:

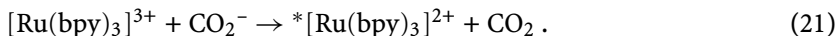
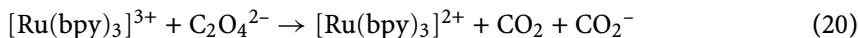
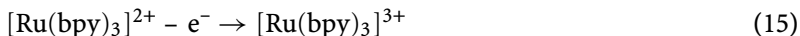
(a) To pulse the potential applied to a working electrode between the oxidation and reduction potentials of $[\text{Ru}(\text{bpy})_3]^{2+}$ in a suitable solvent [132, 133]. In such a way the reduced and oxidized forms produced in the same region of space can undergo a comproportionation reaction where enough energy is available to produce an excited state and a ground state (see also Fig. 10):



(b) To reduce $[\text{Ru}(\text{bpy})_3]^{2+}$ in the presence of a strong oxidant (reductive oxidation). For example, luminescence is obtained upon continuous reduction of $[\text{Ru}(\text{bpy})_3]^{2+}$ at a working electrode in the presence of $\text{S}_2\text{O}_8^{2-}$ [125, 126]. This oxidant in a first one-electron oxidation reaction generates the very powerful oxidant SO_4^- that can either oxidize $[\text{Ru}(\text{bpy})_3]^+$ to $*[\text{Ru}(\text{bpy})_3]^{2+}$ (Eq. 18) or $[\text{Ru}(\text{bpy})_3]^{2+}$ to $[\text{Ru}(\text{bpy})_3]^{3+}$ (Eq. 19), which then reacts with $[\text{Ru}(\text{bpy})_3]^+$ (Eq. 16) to yield the luminescent excited state:



(c) To oxidize $[\text{Ru}(\text{bpy})_3]^{2+}$ in the presence of a strong reductant (oxidative reduction). For example, light is generated upon continuous oxidation of $[\text{Ru}(\text{bpy})_3]^{2+}$ at a working electrode in the presence of $\text{C}_2\text{O}_4^{2-}$ [129, 130]. This reductant in a first one-electron reaction generates the strongly reducing CO_2^- radical that can reduce $[\text{Ru}(\text{bpy})_3]^{3+}$ to the excited $^*[\text{Ru}(\text{bpy})_3]^{2+}$



These chemiluminescent electron transfer reactions are quite interesting from an applicative [134–136] as well as from a theoretical viewpoint. Actually, method a is at the basis of electroluminescent materials, such as organic light-emitting diodes (OLEDs) and similar devices, which are receiving increasing interest for practical applications [137–141].

4

Some Important Features of Ru(II) Polypyridine Complexes

4.1

Nonradiative Decay Rate Constants and Emission Spectral Profiles of Ru(II) Polypyridine Complexes

Radiationless decay from MLCT states of metal polypyridine complexes occurs with energy release into medium-frequency (polypyridyl-based) modes and, to a lower degree, low-frequency modes and solvent [4, 142–149]. Averaging the medium-frequency modes which mainly promote the transition and combining low-frequency modes, including solvent, into a single mode, treated classically, the rate constant for radiationless decay k_{nr} is predicted to follow the so-called energy gap law [150–154]. Most of the work to define this topic has been made by using Ru(II) polypyridine complexes as models; however, the approach also applies to any MLCT emitter, as largely demonstrated for Os(II) [146, 147, 155] and Re(I) polypyridine [147, 149, 156] complexes. Actually, the energy gap law can be expressed by Eq. 22, where β_0 includes the vibrationally induced electronic matrix element and $F(\text{calc})$ is the vibrational overlap factor (the quantity $1s$ in Eq. 22 is used to give unitless expression):

$$\ln(k_{\text{nr}} \cdot 1s) = \ln \beta_0 + \ln[F(\text{calc})] . \quad (22)$$

In a simplified version, $F(\text{calc})$ can be expressed as in Eq. 23 [157]:

$$F(\text{calc}) \propto \left(\frac{-\gamma E_0}{\hbar\omega} \right) \quad \gamma = \ln \left(\frac{E_0}{S_M \hbar\omega} \right) - 1 . \quad (23)$$

In Eq. 23, the energy gap E_0 is related to the energy separation of the two coupled surfaces the $\hbar\omega$ term describes, assuming a single configurational coordinate model, the average energy of the medium-frequency vibrational (accepting) modes that couple the MLCT and ground states, that is, the vibrational spacing of the ground state, and S_M is the electron-vibrational coupling constant (Huang–Rhys factor). E_0 , $\hbar\omega$, and S_M are expressed in cm^{-1} , as well as $\Delta\nu_{1/2}$, the “classical” bandwidth that takes into account the low-frequency modes and is present in the detailed expression for $F(\text{calc})$ [146, 147], not shown here. If β_0 , the electronic term, remains roughly constant for a series of related complexes, Eq. 22 yields a straight line with intercept $\ln \beta_0$ [146].

It is interesting to note that the parameters E_0 , $\hbar\omega$, S_M , and $\Delta\nu_{1/2}$ also define the emission spectral profile, so they can be obtained by a single-mode Franck–Condon analysis of the emission spectra, using Eq. 24:

$$I(\bar{\nu}) = \sum_{x=0}^5 \left[\left(\frac{E_0 - x\hbar\omega}{E_0} \right)^3 \left(\frac{S_M^x}{x!} \right) \left(\exp \left[-4 \ln 2 \left(\frac{\bar{\nu} - E_0 + x\hbar\omega}{\Delta\nu_{1/2}} \right)^2 \right] \right) \right] \quad (24)$$

In Eq. 24, $I(\bar{\nu})$ is the relative emission intensity at energy $\bar{\nu}$ (in cm^{-1}), E_0 is the energy of the zero-zero transition (i.e., the energy of the emitting ³MLCT state), $\hbar\omega$ is the average of medium-frequency acceptor modes coupled to the MLCT transition, x is the quantum number of such an averaged medium-frequency mode which serves as the final vibronic state (note that x is usually limited to 5), $\Delta\nu_{1/2}$ is the half-width of the individual vibronic bands, and S_M is the Huang–Rhys factor.

Application of the above equations to Ru(II) polypyridine complexes allows important information to be obtained on the excited-state properties. It should be considered, however, that Eqs. 22–24 are based on several assumptions, the most important being the following. (1) For radiationless decay, the thermal population of higher-energy excited states is neglected; when such an activated route cannot be disregarded, Eq. 22 only gives a contribution to the observed radiationless rate constant, the one related to k_0 of Eq. 1. (2) The Franck–Condon analysis of the emission spectral profile here shown is based on a single coordinate; when more coordinates need to be considered, fitting of the spectral profile following Eq. 24 can give uncorrected parameter values. A simple refinement of Eq. 24 requires inclusion of a second (low energy) frequency acceptor mode due to solvent contributions [158–161].

More sophisticated theoretical methods to analyze the emission spectra of Ru(II) complexes have been introduced [162–166]. In particular, these methods allow for the detailed characterization of the high-frequency vibronic contributions to the emission spectra and the dependence of such contributions on various factors, such as the energy gap between ground and excited states. Extensive discussion can be found in the cited references.

Emission spectral profiles calculated by equations such as Eq. 24 have also been used, along with theoretical quantum mechanical expressions and experimentally determined rate constant values, to estimate the electronic coupling matrix element for such intercomponent processes for photoinduced energy transfer in dinuclear Ru(II) polypyridine complexes [160].

4.2

Ultrafast Time-Resolved Spectroscopy and Localization/Delocalization Issues

In the last 20 years, ultrafast pump–probe spectroscopy has become accessible to several research laboratories, including research groups interested in Ru photochemistry. The possibility of investigating the excited-state dynamics at very short time delays after the excitation pulse allowed clarification of several problems and shed light on many aspects of ruthenium photochemistry. New features, sometimes unexpected, have also been revealed and new questions and research topics have emerged. For example, as discussed in other parts of this chapter, it was found that singlet MLCT states can be involved in electron transfer and energy transfer processes, even before intersystem crossing and/or thermal relaxation. This is the case of photoinduced electron injection in semiconductors [167] and energy transfer/migration between Ru subunits of large, strongly coupled dendritic-shaped systems [168–170]. Fluorescence from ruthenium complexes has also been detected [171].

Powered by the availability of ultrafast techniques, the long-term issue of localization/delocalization of MLCT states has also been revitalized. As previously stated, the general view is that the emissive state is localized on a single ligand, even for homoleptic species. However, open questions remain concerning the nature of the Franck–Condon state and the early-time dynamics which leads to the emissive state.

As for the early-time dynamics, it is largely accepted that in $[\text{Ru}(\text{bpy})_3]^{2+}$ and analogous homoleptic species light excitation in the MLCT singlet manifold initially produces a Franck–Condon state that is delocalized, which is where the promoted electron is shared by all the polypyridine ligands. Then on the timescale of tens of femtoseconds, the promoted electron becomes localized on a single ligand, due to coupling with local solvent dipoles. Intersystem crossing then takes place in about 100 fs, producing a localized triplet state. The triplet MLCT state becomes “randomized” by interligand hopping on the timescale of 10 ps, the same scale of thermal (including vibrational and solvent reorganization) relaxation of the $^3\text{MLCT}$ state. This general figure is schematized in Fig. 11, and is based on results dealing with many Ru(II) polypyridine complexes, taking advantage of various experimental techniques (transient absorption anisotropy, time-resolved resonance Raman, pump–probe femtosecond transient absorption spectroscopy).

However, some experimental data contrast with the scheme shown in Fig. 11. For example, a time-resolved resonance Raman study indicates that in $[\text{Ru}(\text{bpy})_3]^{2+}$ even the initial excitation is localized [172]. Moreover, the recently reported femtosecond transient absorption spectrum of $[\text{Ru}(\text{bpy})_3]^{2+}$ in the UV region suggests that complete relaxation within the emitting triplet MLCT state takes several tens of picoseconds, and that randomization of triplet MLCT is complete in less than 500 fs [173]. If this latter point is correct, interligand hopping should largely occur from nonrelaxed states, probably even partly in the singlet state. In the relaxed triplet MLCT state, interligand hopping could be slower, but it would be difficult to measure since randomization would already have happened.

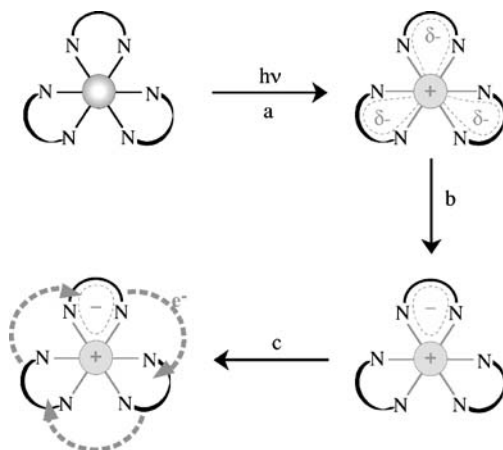


Fig. 11 Picture of the early-time dynamics of light excitation in the MLCT singlet of $[\text{Ru}(\text{bpy})_3]^{2+}$. A delocalized Franck–Condon state is formed (**a**), which becomes localized on a single ligand (**b**) and then becomes “randomized” by interligand hopping (**c**)

Related to the excited-state dynamics at short times after excitation, broadband femtosecond fluorescence spectroscopy of $[\text{Ru}(\text{bpy})_3]^{2+}$ has been recently reported, as already mentioned [171]. The authors get 15 ± 10 fs as the lifetime for the singlet emission, which is centered at about 520 nm.

4.3

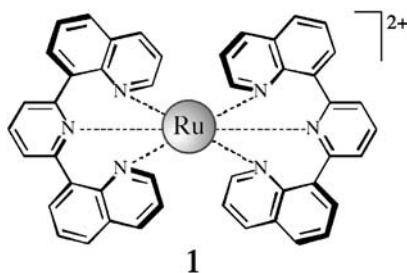
Ru(II) Complexes Based on Tridentate Polypyridine Ligands

An important family of Ru(II) polypyridine complexes is that based on tridentate ligands, with $[\text{Ru}(\text{terpy})_2]^{2+}$ as a prototype (terpy = 2,2' : 6',2''-terpyridine). The absorption, emission, and redox properties of $[\text{Ru}(\text{terpy})_2]^{2+}$ are similar to those of $[\text{Ru}(\text{bpy})_3]^{2+}$, except that $[\text{Ru}(\text{terpy})_2]^{2+}$ is essentially nonluminescent at room temperature, with a lifetime of the $^3\text{MLCT}$ state in degassed acetonitrile at room temperature of about 250 ps (meas-

ured by transient absorption spectroscopy [3]), compared with a value of about 1 μs exhibited by $[\text{Ru}(\text{bpy})_3]^{2+}$ under the same conditions [1]. Such a short excited-state lifetime is very disappointing, as $[\text{Ru}(\text{terpy})_2]^{2+}$ has some advantage over $[\text{Ru}(\text{bpy})_3]^{2+}$ from a structural point of view. Whereas $[\text{Ru}(\text{bpy})_3]^{2+}$ can exist as a mixture of Λ and Δ isomers, and the isomer problem can become even more complicated for polynuclear species based on “asymmetric” bidentate ligands such as 2,3-bis(2'-pyridyl)pyrazine (2,3-dpp), $[\text{Ru}(\text{bpy})_3]^{2+}$ is achiral. Moreover, by taking advantage of *para* substituents on the central pyridine of the terpy ligand, $[\text{Ru}(\text{terpy})_2]^{2+}$ can give rise to supramolecular architectures perfectly characterized from a structural viewpoint, in particular to multinuclear one-dimensional (“wire”-like) species. The reason for the poor photophysical properties of Ru(II) complexes with tridentate polypyridine ligands at room temperature, compared to Ru(II) species with bidentate chelating polypyridine, stems from the bite angle of the tridentate ligand that leads to a weaker ligand field strength and thus to lower-energy MC states as compared to Ru(II) complexes of bpy. The thermally activated process from the potentially emitting $^3\text{MLCT}$ state to the higher-lying ^3MC state is therefore more efficient in $[\text{Ru}(\text{terpy})_2]^{2+}$ and its derivatives and leads to fast deactivation of the excited state by nonradiative processes [1, 3, 4], although terpy-type Ru complexes are inherently more photostable than bpy-type ones because of a stronger chelating effect.

Much effort has been devoted to the design and synthesis of tridentate polypyridine ligands, leading to Ru(II) complexes with improved photophysical properties [3, 78, 92, 174–181]. For example, the use of ligands containing electron-withdrawing and -donor substituents on tpy increases the gap between the $^3\text{MLCT}$ and the ^3MC states [174]. An increase in such an energy gap has also been obtained by the use of cyclometallating ligands [177]. Unavoidably, the stabilization of $^3\text{MLCT}$ states causes an increase of the rate constant for radiationless decay to the ground state. This latter effect can be balanced by extension of the π^* orbital by appropriate substituents, which increases the delocalization of the acceptor ligand of the MLCT excited state leading to a smaller Franck–Condon factor for nonradiative decay [78, 175, 176, 178, 179, 182–188]. In this regard, species based on ethynyl-substituted terpy ligands feature particularly interesting photophysical properties [175, 176, 182]. Various approaches to improve the photophysical properties of Ru(II) complexes with tridentate polypyridine ligands have been reviewed [175, 182].

The bis-tridentate Ru(II) polypyridine complex with the best photophysical properties reported up to now is probably the species **1**, based on the 2,6-bis(8'-quinolinyl)pyridine ligand [189]. This species exhibits $^3\text{MLCT}$ emission with a maximum at 700 nm, with a lifetime of 3.0 μs and a quantum yield of 0.02 in deoxygenated methanol–ethanol solution at room temperature. The emission maximum blue-shifts to 673 nm at 77 K in the same solvent mixture, exhibiting a luminescence lifetime of 8.5 μs and a quantum



yield of 0.06. The authors attribute these excellent (particularly at room temperature) photophysical properties to the relief of structural distortion from the ideal octahedral geometry, due to ligand design. Actually, X-ray characterization of the compound reveals a quasi-ideal octahedral geometry around the metal center.

4.4

Interplay Between Multiple Low-Lying MLCT States Involving a Single Polypyridine Ligand

Usually, there is a linear relationship between redox data, namely first oxidation and reduction potentials of Ru complexes, and spectroscopic parameters such as MLCT absorption and emission bands, provided that the considered compounds constitute a homogeneous series [1, 4, 190–192]. This relationship is based on the fact that the orbitals involved in metal-based oxidation and ligand-based reduction processes are the same (to a first approximation) as those involved in the MLCT absorption and emission transitions. Differences in solvent effects for redox and spectroscopic processes should be constant, so that the relationship is still linear, although the slopes are not unitary [1, 191]. However, whereas until 20 years ago this relationship was followed by almost all the Ru complexes reported at that time, and exceptions were rare [193] and partly unexplained, Ru complexes which do not follow the rule, in particular as far as the absorption spectra are concerned, have become quite common in recent years. The availability of several examples allowed the development of a general interpretation of this behavior. In all the cases that do not obey the linear relationship, ligands characterized by a large aromatic framework are present.

It is now clear that the apparent mismatched relationship is linked to the presence of multiple low-energy MLCT transitions to a single polypyridine ligand, with one such transition being essentially almost invisible spectroscopically. The key feature here is that the “single” polypyridine ligand can actually be viewed as being made of two “separated” subunits (Fig. 12) with the LUMO centered on a part of the ligand framework which is not significantly coupled with the metal-based HOMOs (in other words, the LUMO does

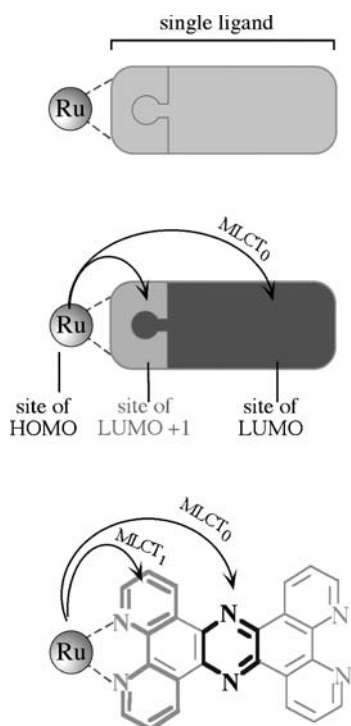
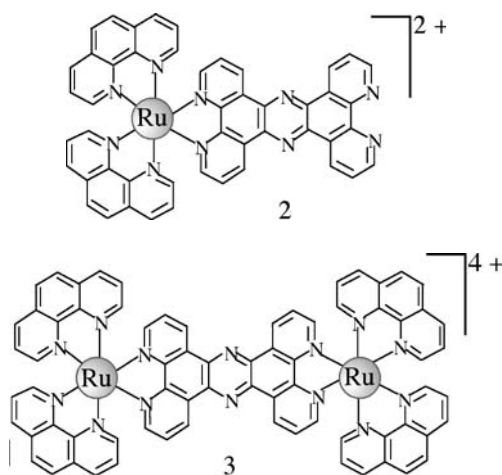


Fig. 12 Structural formula of two possible MLCT transitions in ruthenium complexes with large polypyridine ligands

not receive a significant contribution from the chelating nitrogens). In these systems, the lowest-energy MLCT transition ($MLCT_0$) can have vanishing oscillator strength and thus it does not significantly contribute to the absorption spectrum. On the contrary, a closely lying LUMO+1 (centered on a different moiety of the large ligand) receives a significant contribution from the chelating nitrogens, so it is largely coupled with the metal-based HOMO(s); as a consequence, its corresponding MLCT transition (the $MLCT_1$ transition) dominates the absorption spectrum. Since reduction takes place in the LUMO, the linear relationship between absorption spectra and redox potential cannot be followed. This case will also be discussed in Sects. 5 and 6, for specific systems.

As far as the relationship between emission spectra and redox potentials is concerned, whether it is followed or not depends on how fast the interconversion between the $MLCT_1$ and $MLCT_0$ states is, compared to the intrinsic decay of the $MLCT_1$ excited state (here it is assumed that $MLCT_0$ is lower in energy than $MLCT_1$; otherwise, the relationship is always followed, except for very particular cases). Solvent, temperature, driving force, and medium effects are very important in this regard. For example, at room temperature in fluid

solution the mononuclear complex $[(\text{phen})_2\text{Ru}(\text{tpphz})]^{2+}$ (**2**, phen = 1,10-phenanthroline; tpphz = tetrapyrido[3,2-*a*:2',3'-*c*:3'',2''-*h*:2'',3''-*j*]phenazine) exhibits emission from its MLCT_1 level ($\lambda_{\text{max}} = 625 \text{ nm}$, $\tau = 1.25 \text{ ms}$, $\Phi = 0.07$), while the dinuclear species $[(\text{phen})_2\text{Ru}(\text{tpphz})\text{Ru}(\text{phen})_2]^{4+}$ (**3**) emits from its MLCT_0 level ($\lambda_{\text{max}} = 710 \text{ nm}$, $\tau = 0.100 \text{ ms}$, $\Phi = 0.005$) [194]. The absorption spectra of both compounds in the visible region are very similar to one another (apart from the intensity), with the lowest-energy MLCT band maximizing at about 440 nm in both cases. In a rigid matrix at 77 K, both the mononuclear and dinuclear metal complexes exhibit emission at about 585 nm (lifetime in the microsecond timescale), typical of the MLCT_1 level. Such results are interpreted on considering that the ligand tpphz has two empty orbitals close in energy: the LUMO is centered on the central pyrazine, with negligible contribution from the chelating nitrogen atoms, and the LUMO+1 is essentially a bpy-type orbital. Reduction potential data of the complexes indicate that LUMO+1 of tpphz is hardly affected on passing from mononuclear to dinuclear species, whereas the LUMO of tpphz is stabilized. For both $[(\text{phen})_2\text{Ru}(\text{tpphz})]^{2+}$ and $[(\text{phen})_2\text{Ru}(\text{tpphz})\text{Ru}(\text{phen})_2]^{4+}$, the absorption spectrum is dominated by Ru-to-tpphz_{LUMO+1} charge transfer (i.e., MLCT_1) transition—almost coincident to the Ru-to-phen charge transfer transition—which occurs at roughly the same energy in mononuclear and dinuclear species, with the Ru-to-tpphz_{LUMO} charge transfer (i.e., MLCT_0) transition not contributing to the absorption feature. Because of the different stabilization of MLCT_1 and MLCT_0 on passing from mononuclear to dinuclear species (see above), the driving force for the MLCT_1 -to- MLCT_0 interconversion is more favorable, and therefore faster, in the dinuclear species. As a consequence, MLCT_1 -to- MLCT_0 decay does not compete with the direct decay of MLCT_1 to the ground state in the mononuclear species, whereas it is



faster and efficient in the dinuclear species. However, at 77 K the MLCT₁-to-MLCT₀ interconversion, which cannot occur without solvent reorganization, becomes inefficient in both systems. Essentially the same experimental behavior is featured by many other Ru(II) polypyridine complexes, and can be interpreted in a similar way [195–205].

Time-resolved transient absorption spectroscopy [206, 207] confirmed that the MLCT₁-to-MLCT₀ excited-state conversion in [(phen)₂Ru(tpphz)-Ru(phen)₂]⁴⁺ at room temperature is solvent dependent. Indeed, it was 120 ps in dichloromethane and faster than 40 ps in acetonitrile [206, 207]. The solvent dependence can be attributed to the difference in the MLCT₁/MLCT₀ energy gap in the two solvents. It has to be considered, in fact, that the “charge separation” between donor and acceptor orbitals, and, as a consequence, the coulombic stabilization, is quite different in the two types of MLCT states. A nonnegligible reorganization energy is therefore expected for the MLCT₁-to-MLCT₀ transition. A detailed study of the temperature dependence of the luminescence properties of species exhibiting this interesting behavior would be quite useful, but to our knowledge it has not yet been reported.

5

Ruthenium and Supramolecular Photochemistry

Supramolecular photochemistry has played a prominent role in chemical research since its definition in the late 1980s [208, 209]. The operational definition of supramolecular species is discussed (Balzani et al. 2007, in this volume) [119], so it will not be further commented on here. Since Ru(II) polypyridine complexes exhibit very interesting photochemical properties and can be prepared by relatively easy synthetic methods, even with made-to-order properties, the number of photoactive supramolecular species based on Ru(II) complexes has rapidly become extraordinarily large. Supramolecular systems in which donor and acceptor units are placed at designed distances can undergo photoinduced energy and electron transfer process (first-order kinetics) even in the case of short-lived excited states [208, 209].

Indeed, Ru(II) polypyridine compounds have been extensively used as photoactive units in supramolecular systems either exclusively made of metal-based components, such as molecular racks, grids, and dendrimers, or in systems whose other active components of the assemblies are of an organic nature. In both cases, the final goals of the supramolecular systems are essentially two, reflecting the nature of the whole of photochemical science: (1) systems designed for the conversion of light energy into other forms of energy, essentially chemical energy or electricity; and (2) systems focused on the elaboration of the information, including sensors. Quite often these two

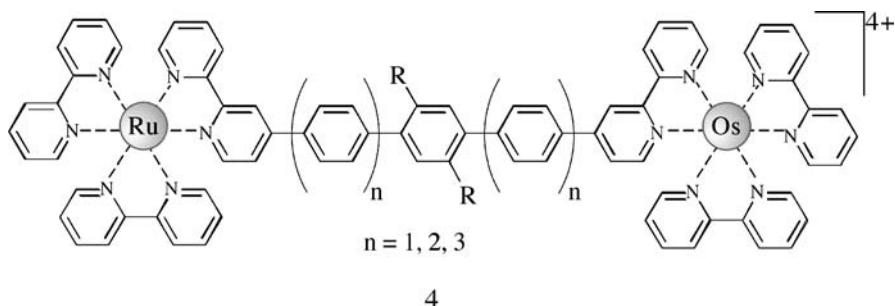
aspects are intertwined; for example, long-range photoinduced electron and energy transfer processes are important both for the elaboration of optical information signals and for light-harvesting systems.

5.1

Photoinduced Electron/Energy Transfer Across Molecular Bridges in Dinuclear Metal Complexes

Dinuclear metal complexes containing Ru(II) polypyridine subunits, where the metal centers are separated by molecular components (bridges), are particularly suited to investigating photoinduced electron and energy transfer processes, whose rate constants can give information on the electronic coupling mediated by the bridge. The latter topic has been recently reviewed and deeply discussed [210]. The number of photoactive (usually, luminescent) dinuclear metal complexes based on Ru(II) subunits is very large. The last exhaustive review dealing with such species was published about 10 years ago [2]. Today it is impossible to be exhaustive even in this relatively narrow field. Therefore, we will only present a few examples. In most cases, Ru(II) subunits, which play the role of donors, are coupled to Os(II) units, which play the role of acceptors in photoinduced energy transfer processes. In all cases, the dinuclear homometallic Ru(II) species have also been investigated for comparison purposes. Their photophysical properties can be found in the original references.

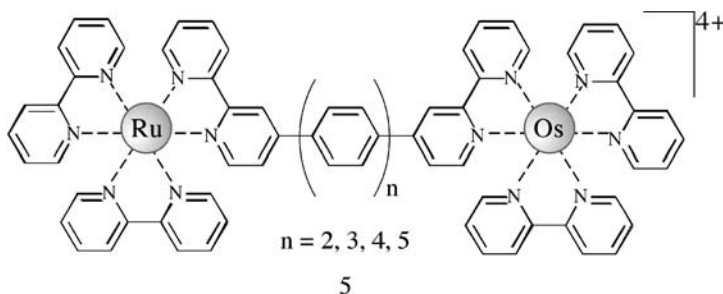
It is important to note that to have control of the distance between the metal centers, the bridges have to be rigid as much as possible. Therefore, it is not surprising that oligophenylenes have often been employed. In the series of dinuclear dyads **4** [211], having the general formula $[\text{Ru}(\text{bpy})_3]^{2+}-(\text{ph})_n-(\text{R}_2\text{ph})-(\text{ph})_n-[\text{Os}(\text{bpy})_3]^{2+}$ (ph = 1,4-phenylene; n = 1, 2, 3), excitation of the $[\text{Ru}(\text{bpy})_3]^{2+}$ unit is followed by energy transfer to the $[\text{Os}(\text{bpy})_3]^{2+}$ unit, as shown by the sensitized emission of the latter. For the compound with $n = 3$, with a total of seven phenylene spacers, the rate constant k_{en} for energy transfer over the 4.2-nm metal-to-metal distance is $1.3 \times 10^6 \text{ s}^{-1}$ in acetonitrile solution at room temperature. This was probably the first example of



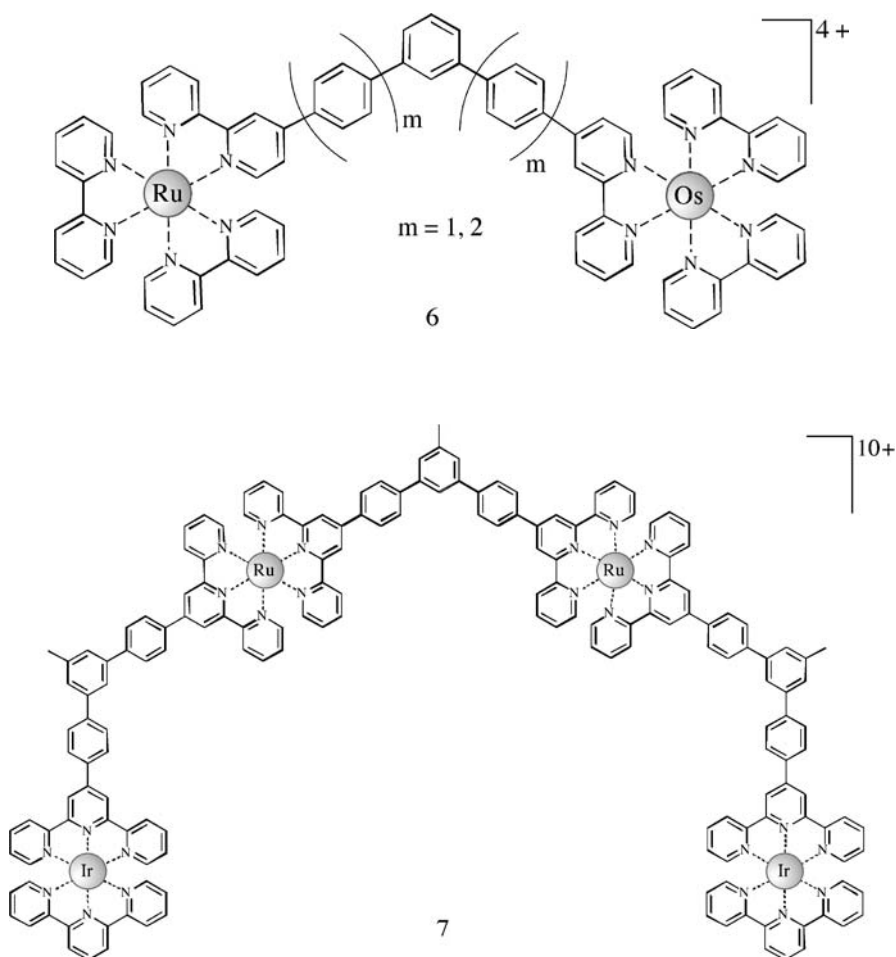
a systematic study on the distance dependence of energy transfer rates for Ru(II)–Os(II) dyads. A Dexter-type mechanism for the Ru(II)–Os(II) energy transfer was proposed, and an attenuation factor β of $0.32 \text{ \AA}^{-1}$ for photoinduced energy transfer was obtained from the $\ln k_{\text{en}}$ vs metal–metal distance plot.

In the $[\text{Ru}(\text{bpy})_3]^{2+}-(\text{ph})_n-[\text{Os}(\text{bpy})_3]^{3+}$ compounds, obtained by chemical oxidation of the Os-based moiety, photoexcitation of the $[\text{Ru}(\text{bpy})_3]^{2+}$ unit causes the transfer of an electron to the Os-based one with a rate constant (k_{el}) of $3.4 \times 10^7 \text{ s}^{-1}$ for $n = 3$. Unless the electron added to the $[\text{Os}(\text{bpy})_3]^{3+}$ unit is rapidly removed, a back electron transfer reaction (rate constant $2.7 \times 10^5 \text{ s}^{-1}$ for $n = 3$) takes place from the $[\text{Os}(\text{bpy})_3]^{2+}$ unit to the $[\text{Ru}(\text{bpy})_3]^{3+}$ one [211]. The rate constants of all the transfer processes in the series of complexes decrease, as expected, with decreasing length of the oligophenylene spacer, whereas they were practically unaffected by temperature.

Interestingly, a series of analogous dyads missing the central substituted phenylene (5) was successively prepared [212, 213] and the results of the two series have been compared: for the dyads containing bridges made of a total of three and five phenylene spacers, the rate constants of photoinduced energy transfer are higher in the nonsubstituted phenyl series. This was attributed to effects of inter-phenylene twist angle on the electronic coupling between donor and acceptor subunits [213].



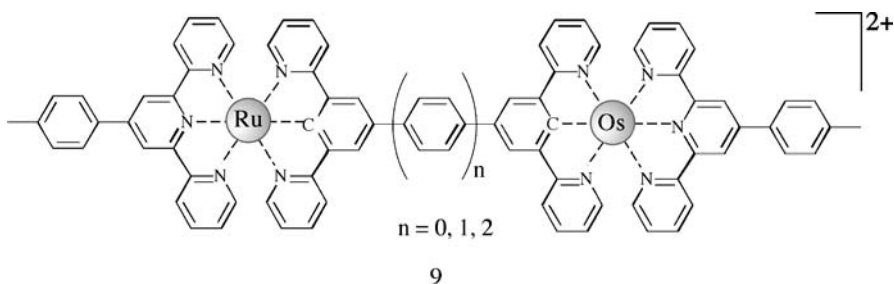
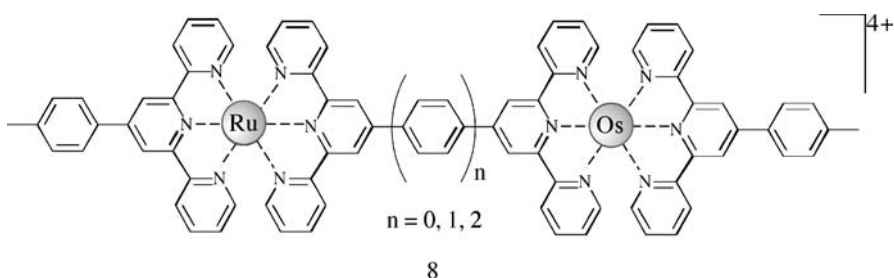
The presence of *meta* substitution in oligophenylene bridges versus the all-*para* systems have been evidenced by the dyads 6 [210, 213]. In these species, the photoinduced energy transfer rate constants are lower than the rates for the respective compounds containing all-*para* phenylene units: for example, for spacers made of three and five phenylenes, respectively, k_{en} is 1.32×10^9 and $6.67 \times 10^7 \text{ s}^{-1}$ for the *meta* series and 2.77×10^{10} and $4.90 \times 10^8 \text{ s}^{-1}$ for the *para* series. A related result has been reported for the tetranuclear Ir(III)/Ru(II) mixed-metal species 7 (although not linear, this species is briefly discussed here for convenience reasons) [214]. In 7, both Ir-based emission ($\lambda = 572 \text{ nm}$, $\tau = 2.9 \text{ }\mu\text{s}$) and Ru-based emission ($\lambda = 682 \text{ nm}$, $\tau = 82 \text{ ns}$) are present, showing that photoinduced energy transfer from the



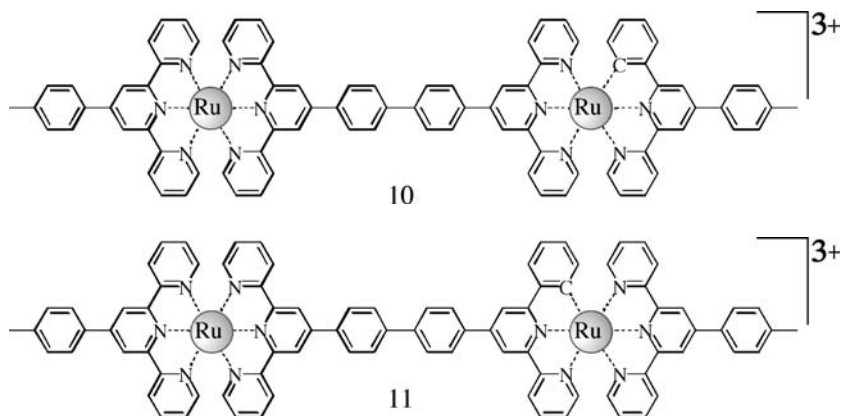
Ir(III) chromophores to the Ru(II) units is inefficient at room temperature in fluid solution. This suggests that the Ir-to-Ru photoinduced energy transfer rate constant in this tetranuclear species is lower than the intrinsic rate constant for Ir decay (about $3.7 \times 10^5 \text{ s}^{-1}$), in spite of the nonnegligible driving force (about 0.3 eV, from emission data). At 77 K, energy transfer from Ir-based to Ru-based chromophores is quantitative because of the much longer lifetime (205 μs) of the excited state of the Ir-based units. Indirectly, the room- and low-temperature results tend to suggest that Ir-to-Ru energy transfer in the tetranuclear mixed-metal species would occur with a rate constant of the order of 10^4 s^{-1} . The apparent discrepancy with the relatively fast energy transfer rate constant for the Ru-Os species with three phenylene unit bridges of the *meta* series discussed above (having a similar bridge to the Ir/Ru tetranuclear system here discussed) shows that the energy transfer

rates are significantly affected by the partner properties, as expected for both coulombic and (superexchange-assisted) Dexter-type mechanisms.

In the series of Ru–Os dyads with tridentate ligands **8** [215–217], both the donor Ru-based and acceptor Os-based MLCT states taking part in the energy transfer process involve the bridging ligand, while in the analogous, cyclometallated species **9** [215, 218] the donor and acceptor MLCT states are based on the peripheral ligands. In the larger systems, with two phenylene spacers, k_{en} for energy transfer from the Ru-based chromophore to the Os-based one is $5 \times 10^{10} \text{ s}^{-1}$ for the non-cyclometallated species [215–217] and $< 2 \times 10^7 \text{ s}^{-1}$ for the cyclometallated species [215, 218]. These different results are mainly attributed to the fact that the energy transfer pathway is longer for the cyclometallated system, although it is suggested that the different nature of the bridge could also play a role.

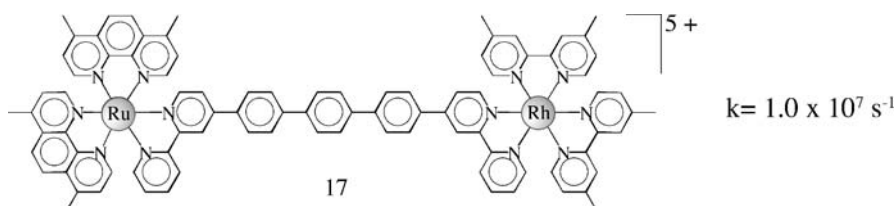
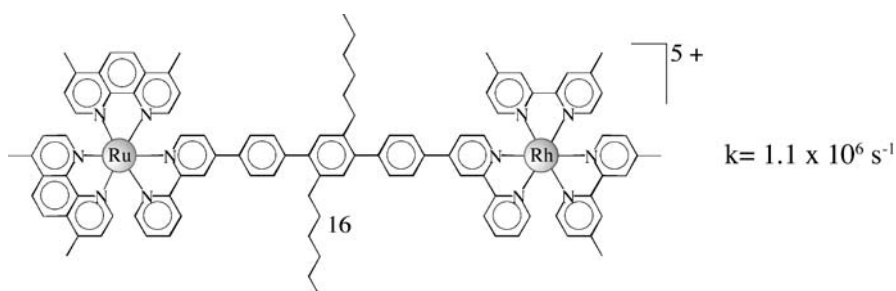
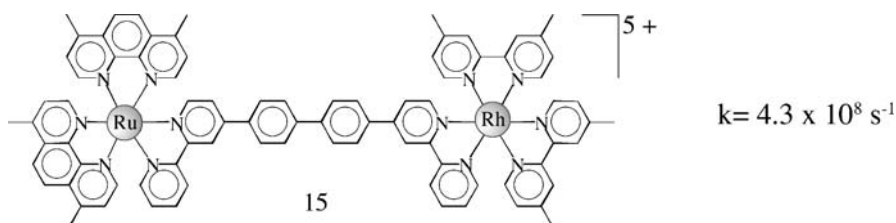
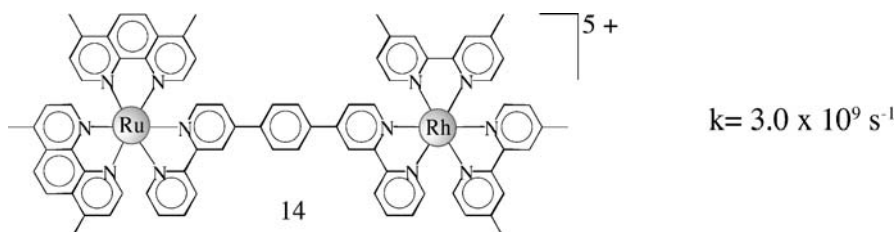
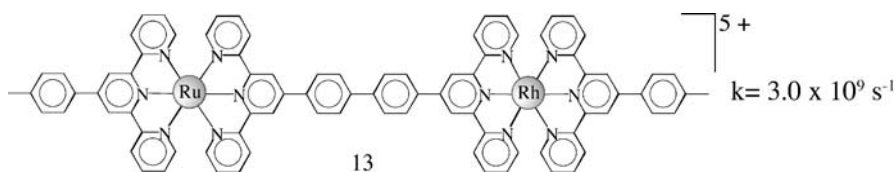
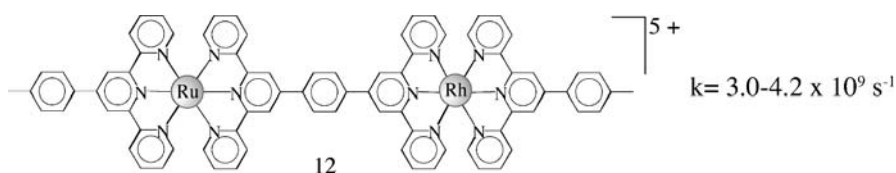


Possible effects of excited-state localization on intramolecular energy transfer kinetics are also shown by the results obtained for the two isomeric dinuclear Ru(II) species **10** and **11** [219]. In both complexes, energy transfer from the non-cyclometallated Ru subunit to the cyclometallated Ru subunit takes place by a Dexter mechanism. Ultrafast spectroscopic measurements yield different energy transfer time constants for the two isomers, with that related to the bridge-cyclometallated complex (2.7 ps) being faster than that related to the terminal-cyclometallated one (8.0 ps). This difference is explained in terms of different electronic factors for Dexter energy transfer. The lowest MLCT excited state in the Ru cyclometallated unit of the dinuclear

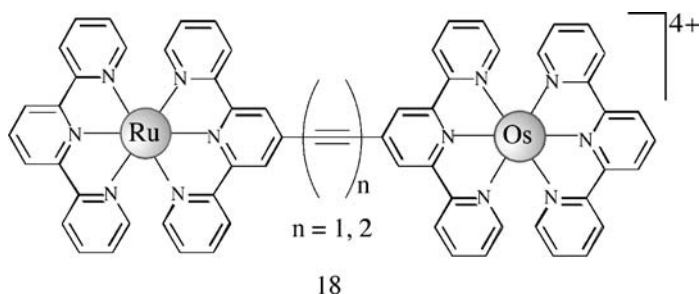


complexes (that is, the acceptor state of the energy transfer process) has the promoted electron on the non-cyclometallating ligand, i.e., on the bridging ligand for **10** and on the terminal ligand for **11**. The lowest MLCT excited state of the non-cyclometallated Ru(II) subunit (that is, the donor state of the energy transfer process) has the promoted electron on the bridging ligand in both cases. The energy transfer process, in a Dexter mechanism, is equivalent to simultaneous electron-hole transfer between the molecular components. The hole transfer process is the same (metal-to-metal) for both isomers. The electron transfer, on the other hand, is different for the two isomers, taking place between the two halves of the bridging ligand for **10** and from the bridging ligand of one unit to the terminal ligand of the other unit in the case of **11**. The exchange electronic coupling is clearly expected to be higher in the former than in the latter case. Interestingly, in both cases the energy transfer processes also have a slower component of about 40 ps, which was tentatively assigned to roughly isoenergetic electron hopping between terminal and bridging ligands in the non-cyclometallated Ru chromophore, in agreement with reported rate constants for isoenergetic electron hopping in Ru(II) polypyridine complexes, as discussed in Sect. 4.2. This study clearly highlights the peculiar intricacies of intramolecular energy transfer in inorganic dyads involving MLCT excited states.

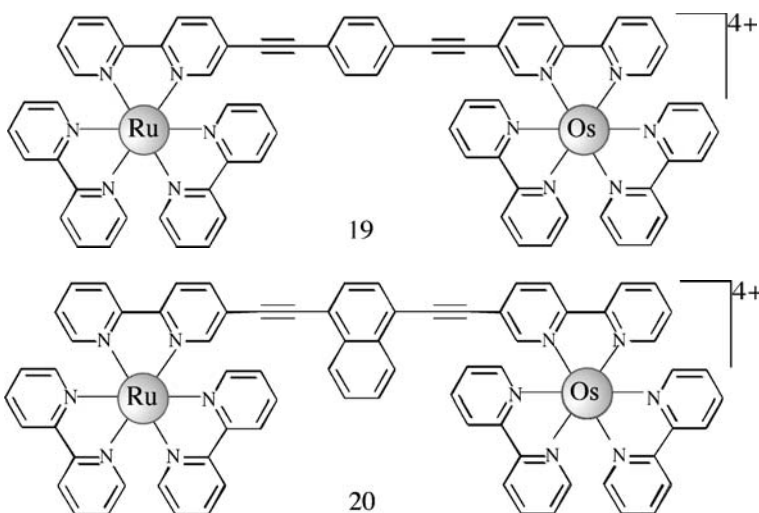
Oligophenylene bridges have also been employed for studying photoinduced electron transfer from Ru(II) chromophores to Rh(III) subunits. In this type of multicomponent species, electron transfer from the Ru-based MLCT state to the Rh(III) component takes place, followed by charge recombination. The compounds **12–17** are an interesting series of homologous systems [220, 221]. The rate constants of the photoinduced electron transfer processes reported confirm the distance dependence of the process, as well as the effect of the twist angle between adjacent spacers [106, 213, 222, 224, 225] on the electronic coupling (and, therefore, on the electron transfer kinetics) across the spacer.

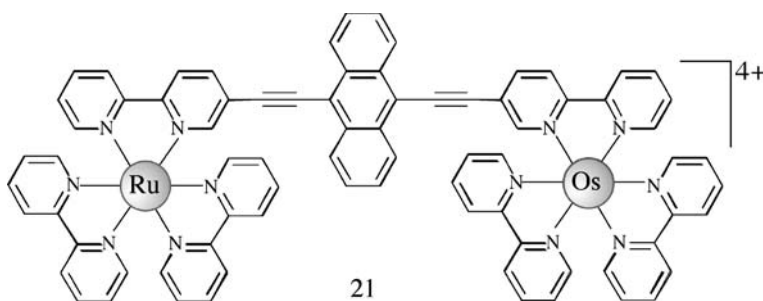


Another spacer subunit which allows for rigidity and controlled directionality is the alkynyl group. Dinuclear species incorporating an unsaturated polyacetylenic backbone in the spacer (18) have been extensively investigated [175, 226]. Energy transfer (electron exchange mechanism) from the Ru(II) chromophore to the Os(II) one takes place with a rate constant of 7.1×10^{10} and $5.0 \times 10^{10} \text{ s}^{-1}$ for $n = 1$ and $n = 2$, respectively [175]. The β attenuation factor [227] for the polyacetylenic systems was calculated to be $0.17 \text{ \AA}^{-1}$, indicating that the “electron conduction” for energy transfer through alkyne bridges is more efficient than that through oligophenylenic spacers [228].



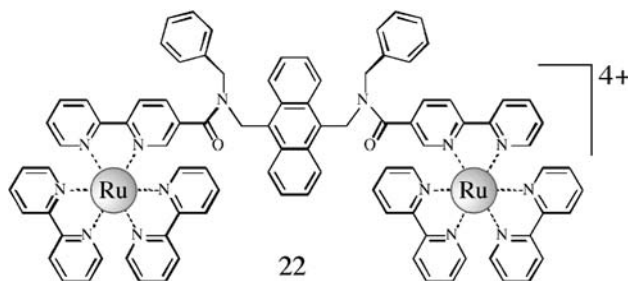
Several other differently connected multicomponent species based on Ru(II) chromophores as donors and incorporating polyacetylenic bridges have been studied. Interested readers can find information in [175, 176, 226, 229]. A special comment is warranted by the species 19–21 [230]. These compounds indicate the effect of the incorporation of additional units into the

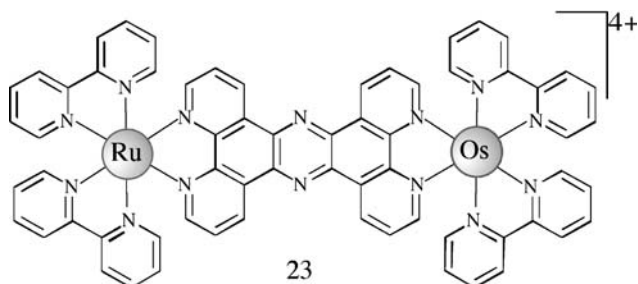




polyacetylenic backbone. For the phenyl-containing bridge system, the triplet state of the bridge is higher in energy than both the Ru(II) and Os(II) MLCT levels. Energy transfer takes place directly from the Ru(II) chromophore to the Os(II) one via a superexchange-assisted Dexter mechanism. In the naphthyl-bridged Ru–Os species, the triplet state of the bridge is intermediate in energy between donor and acceptor levels: the energy transfer from the Ru(II) subunit to the Os(II) one occurs in a stepwise manner, first to the central bis(alkyl)naphthalene unit of the bridge and then to the Os(II) site. In the anthryl-bridged species, the bis(alkyl)anthracene triplet is lower in energy than both Ru- and Os-based MLCT states, and the bridge plays the role of an energy trap [230].

The last Ru–Os compound discussed above has some similarity with the Ru–anthracene–Os species **22** [231, 232]. In this species, missing the ethynyl groups, the anthracene triplet lies in between the Ru donor and Os acceptor energy transfer subunits, so the behavior of the bridge is similar to that of the naphthyl-bridged species mentioned above. However, in air-equilibrated solution the energy transfer rate constant significantly decreases with increasing irradiation time. This effect is due to the formation of singlet oxygen by bimolecular energy transfer from the Os(II) excited state. The singlet oxygen reacts with the anthracene unit to give a peroxide species which cannot behave as the intermediate “station” for energy transfer, so that the overall process is significantly slowed down. This complex was called a “self-poisoning” species [231, 232].





Another example showing an “active” role of the bridge in mediating intercomponent transfer processes involving Ru(II) species is evidenced by **23** [233]. In this species, there are two close-lying MLCT states per metal center involving the bridging ligand (leaving aside the MLCT state involving the peripheral ligands), because of the particular nature of the bridge (see Sect. 5.9). The higher energy of such MLCT states (MLCT₁) involves a bridging ligand orbital mainly centered in the bpy-like coordinating site (LUMO+1), and the lower energy one (MLCT₀) is localized on the central phenazine-like site (LUMO). Light excitation of the Ru-based chromophore populates the singlet MLCT₁ state, which rapidly decays to its triplet counterpart. Direct light excitation into the singlet MLCT₀ level (and successive population of its triplet) is inefficient because of the negligible oscillator strength of the transition. For Ru-to-Os energy transfer, two possible pathways are possible: (1) Ru-to-Os energy transfer at the ³MLCT₁ level (EnT), followed by ³MLCT₁-to-³MLCT₀ relaxation within the Os(II) chromophore (a sort of intraligand electron transfer, ILET, within the Os(II) subunit); and (2) ³MLCT₁-to-³MLCT₀ relaxation within the Ru(II) chromophore (ILET in Ru(II) subunit), followed by Ru-to-Os energy transfer at the ³MLCT₀ level. The situation is schematized in Fig. 13 [210, 233].

Interestingly, ultrafast spectroscopy shows that pathway 1 is followed in dichloromethane and pathway 2 prevails in the more polar acetonitrile solvent.

Oligophenyl bridges are reported to play “active” roles in the dinuclear Ir(III)–Ru(II) species **24–27** [234]. In this series of complexes, the Ru-based component is the energy transfer acceptor subunit. Indeed, Ru-based emission takes place in all the species at about 625 nm (lifetime about 200 ns) in aerated acetonitrile at room temperature and at about 590 nm (lifetime about 6 μs) in butyronitrile at 77 K, whereas the high-energy Ir-based chromophore has a very short excited-state lifetime, determined by time-resolved emission and subpicosecond transient absorption spectroscopy, slightly dependent on the bridge. The energy transfer rate constant is very weakly slowed down by increasing the bridge length, passing from $8.3 \times 10^{11} \text{ s}^{-1}$ for the species with two phenyls as spacer to $3.3 \times 10^{11} \text{ s}^{-1}$ for the species with five interposed phenyls. The apparent attenuation parameter β for energy transfer rate con-

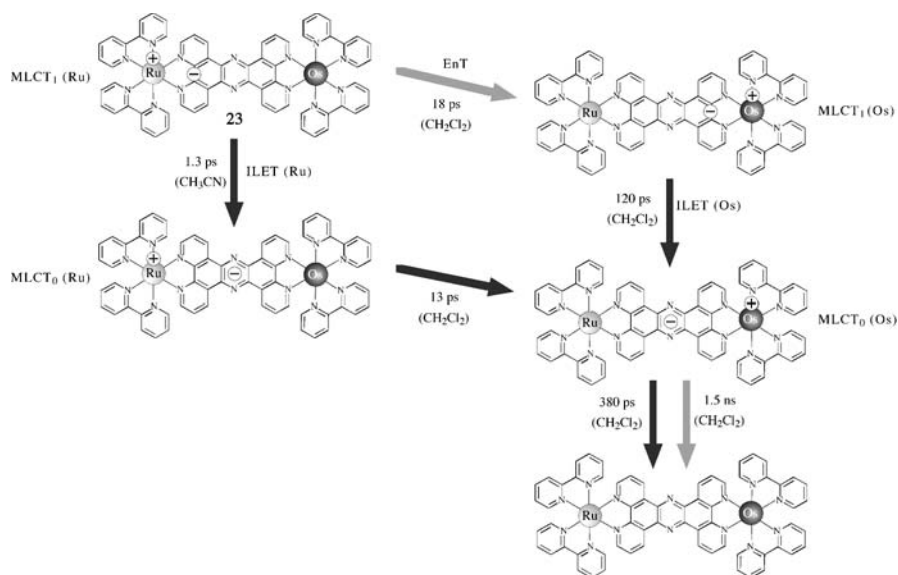
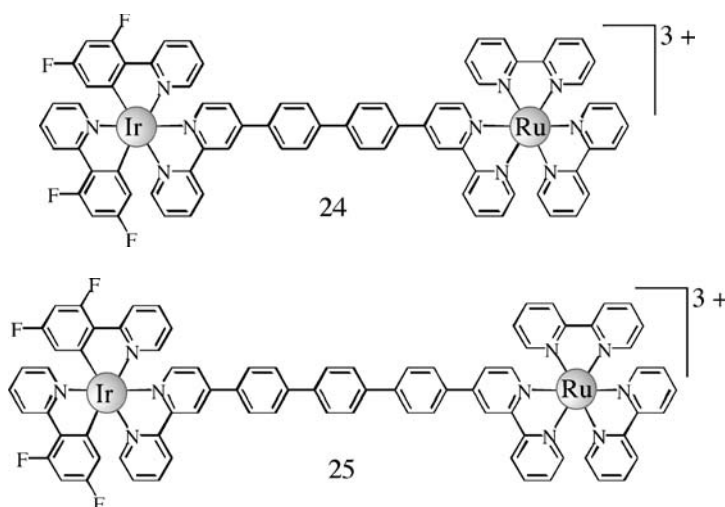
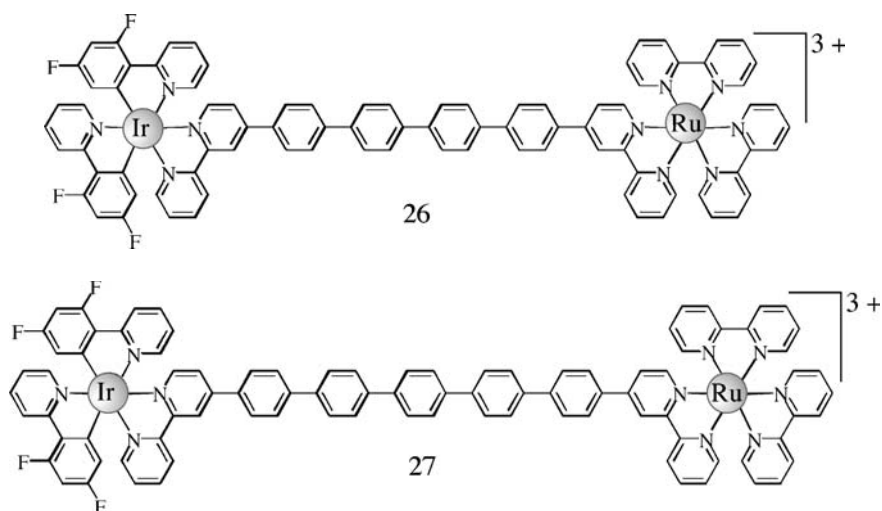


Fig. 13 Energy transfer pathways in a dinuclear Ru(II) – Os(II) species containing a π -extended bridge



stant would be $0.07 \text{ \AA}^{-1}$. However, increasing the bridge length changes the excited-state energy level of the bridge itself, and it is proposed that the MLCT excited state of the Ir center assumes an increasing LC character involving the bridge orbitals as the number of phenyls increases. As a consequence, metal–metal separation does not reflect the effective donor–acceptor separation for the energy transfer process; with the donor excited state largely involving the oligophenyl spacer, the energy transfer takes place by an in-



coherent hopping mechanism, and cannot be considered a through-bond, superexchange-assisted energy transfer. Interestingly, the use of the same spacers has already been mentioned for the couple Ru/Os (see above), where a normal through-bond superexchange mechanism was proposed to be operative: the reason for the difference between Ru/Os and Ir/Ru series is the energy level of the donor excited state. In Ir(III) complexes, such a state is much higher in energy and can interact significantly with oligophenyl-based excited states.

An interesting series of papers dealing with photoinduced electron transfer in a series of dinuclear Ru(II)–Co(III) species allowed the accumulation of further information on the role of the bridging ligand [207, 235, 236]. Typical studied complexes were $[(\text{terpy})\text{Ru}(\text{terpy-terpy})\text{Co}(\text{terpy})]^{5+}$, $[(\text{terpy})\text{Ru}(\text{terpy-ph-terpy})\text{Co}(\text{terpy})]^{5+}$, and $[(\text{bpy})_2\text{Ru}(\text{tpphz})\text{Co}(\text{bpy})_2]^{5+}$ (terpy-terpy = 6,6'-bis(2-pyridyl)-2,2':4',4'':2'',2'''-quarterpyridine, that is, the bridge with $n = 0$ in 5; terpy-ph-terpy is the bridge with $n = 1$ in 5; tpphz is the bridge in 3). In these studies, the quantum yields of the thermally equilibrated product of the photoinduced electron transfer from the Ru-based MLCT state to the Co(III) subunit were carefully measured [207]. Interestingly, $^*\text{Ru(II)}$ -to-Co(III) electron transfer takes place in less than 10 ps in all three above-mentioned species; however, the quantum yields of the thermally equilibrated electron transfer product were quite different in the series, with the tpphz-bridged dinuclear species exhibiting a quantum yield of about 0.8 and the other two compounds featuring significantly smaller values (0.53 and 0.41 for the terpy-terpy and the terpy-ph-terpy species, respectively) in butyronitrile at 298 K [207]. The authors proposed that the relatively low yield of photoinduced electron transfer in the two terpy-based complexes is due to formation of the d–d (MC) excited state of the $[\text{Co}(\text{terpy})_2]^{3+}$ moiety during solvent

relaxation within the electron transfer excited state. In fact, fast tunneling transition of the nonrelaxed electron transfer product to the lowest d–d excited states of the $[\text{Co}(\text{terpy})_2]^{3+}$ moiety can take place via hole transfer from $[\text{Ru}(\text{terpy})_2]^{3+}$ to the $[\text{Co}(\text{terpy})_2]^{2+}$, generating a $d\pi^6 d\sigma^*$ configuration. Strong through-ligand electronic coupling of $d\pi(\text{Ru})$ – $d\pi(\text{Co})$, as estimated from the strong intensity of the intervalence band of $[(\text{terpy})\text{Ru}(\text{terpy-terpy})\text{Ru}(\text{terpy})]^{5+}$, can effectively mediate the fast hole transfer process. For the tpphz-bridged system, through-ligand electronic coupling between $d\pi(\text{Ru}^{\text{III}})$ and $d\pi(\text{Co}^{\text{II}})$ orbitals is much smaller, as suggested by the absence of any sizeable intervalence band in $[(\text{bpy})_2\text{Ru}(\text{tpphz})\text{Ru}(\text{bpy})_2]^{5+}$ [207]. It turns out that the weak tpphz superexchange interaction between $d\pi(\text{Ru}^{\text{III}})$ and $d\pi(\text{Co}^{\text{II}})$ orbitals may be unable to open the channel of hole transfer during the relaxation of the electron transfer product, leading to a higher quantum yield of the charge-separated, thermally equilibrated product. However, the charge recombination rate constant was fast in all cases: in butyronitrile at room temperature it was $2.1 \times 10^7 \text{ s}^{-1}$ for the tpphz species and biphasic and faster for the other two compounds (81×10^9 and $5 \times 10^9 \text{ s}^{-1}$ for the terpy-ph-terpy containing species and 52×10^{10} and $3 \times 10^{10} \text{ s}^{-1}$ for the terpy-terpy species). Even in the charge recombination (back electron transfer) process, the different coupling offered by the bridging ligands could explain the results.

5.2

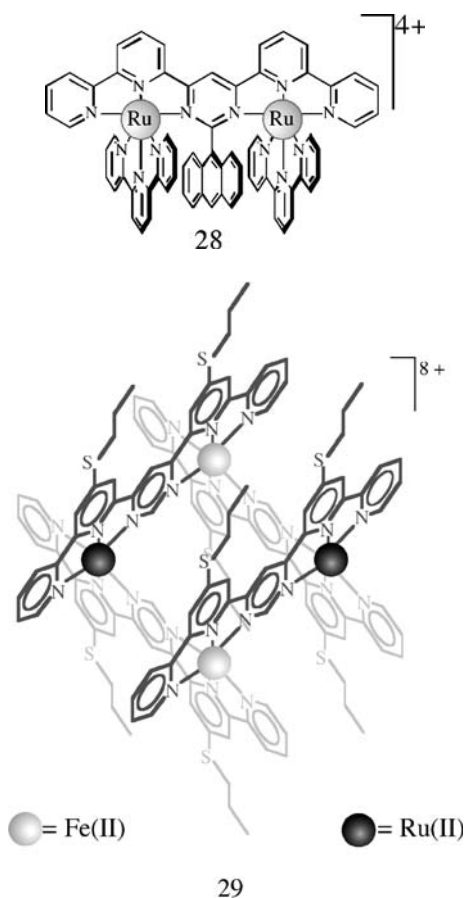
Photoactive Multinuclear Ruthenium Species Exhibiting Particular Topologies

5.2.1

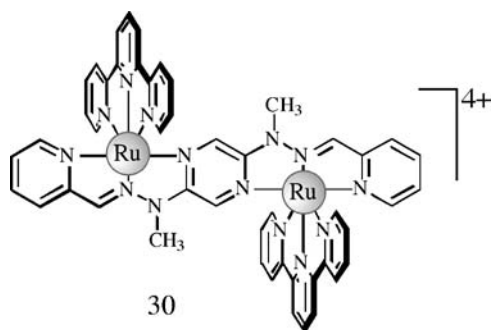
Racks and Grids

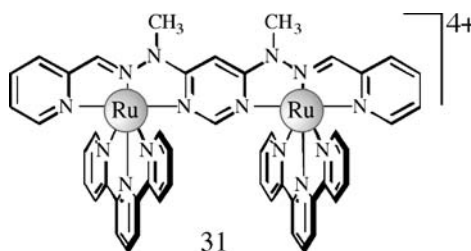
Rack-type metal complexes are linearly arranged species [237], but differ from the species discussed in the former section since they are made of several repeating, roughly identical, metal-based subunits orthogonally appended to a roughly linear and rigid polytopic molecular strand. The metal centers are never aligned along the main axis of the bridging ligand.

The first rack-type $\text{Ru}(\text{II})$ polypyridine complex investigated from a photochemical viewpoint is **28** [238]. In this species, the anthryl group has only the function of absorbing additional light energy; in fact, its triplet state is higher in energy than the MLCT triplet state(s) of the $\text{Ru}(\text{II})$ subunits (here, the lowest-lying MLCT states involve the bridging ligand, which is very easily reduced). For **28**, near-IR emission occurs ($\lambda_{\text{em}} = 845 \text{ nm}$) with a relatively long lifetime (60 ns). Such an emission is totally quenched in the somewhat related tetranuclear $\text{Ru} - \text{Fe}$ grid **29** [239], where energy transfer from the Ru -based MLCT state to the Fe -based MC levels is likely to occur. Kinetic data for the quenching processes were not reported.



Ru(II) racks based on different molecular strands (**30**, **31**) have also been recently studied [240] (S Campagna, unpublished results). The pyrimidine-containing Ru complex exhibits a $^3\text{MLCT}$ emission with maximum at 758 nm





in acetonitrile at room temperature ($\tau = 30$ ns), which moves to 740 nm in nitrile glass at 77 K ($\tau = 335$ ns) [240]. The pyrazine-containing species exhibits very similar emission properties (room temperature, acetonitrile: $\lambda_{\text{max}} = 765$ nm; $\tau = 60$ ns; 77 K, nitrile glass: 750 nm; $\tau = 400$ ns) (S Campagna, unpublished results). For these species, the lowest (emitting) MLCT state(s) involve(s) the bridging ligands, as for the former rack-type complex discussed above.

5.2.2

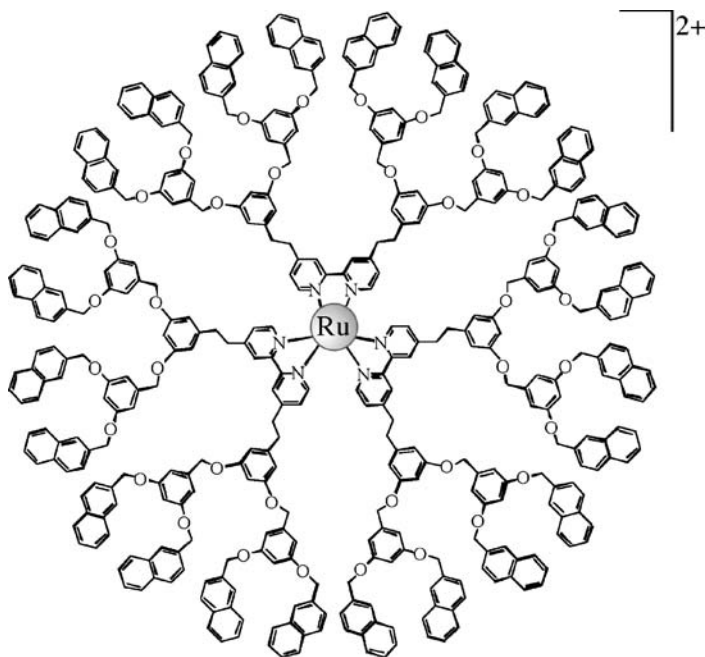
Dendrimers

Luminescent Ru(II) dendrimers have been deeply investigated and the field has been reviewed recently [2, 241–245]. We will only mention some examples.

5.2.2.1

Dendrimers Containing Only One Metal Center Unit

The ruthenium compound **32** is a classical example of a dendrimer containing a luminescent ruthenium complex core surrounded by organic wedges. In this dendrimer, the 2,2'-bipyridine (bpy) ligands of the $\{\text{Ru}(\text{bpy})_3\}^{2+}$ -type core carry branches containing 1,3-dimethoxybenzene- and 2-naphthyl-type chromophoric units [246]. All three types of chromophoric groups present in the dendrimer, namely, $\{\text{Ru}(\text{bpy})_3\}^{2+}$, dimethoxybenzene, and naphthalene, are potentially luminescent species. In **32**, however, the fluorescence of the dimethoxybenzene- and naphthyl-type units is almost completely quenched in acetonitrile solution, with concomitant sensitization of the $\{\text{Ru}(\text{bpy})_3\}^{2+}$ core luminescence. These results show that very efficient energy transfer processes take place, converting the very short-lived (nanosecond timescale) UV fluorescence of the aromatic units of the wedges to the relatively long-lived (microsecond timescale) orange luminescence of the metal-based dendritic core. This dendrimer is therefore an excellent example of a light-harvesting antenna system as well as of a species capable of acting as a frequency converter. It should also be noted that in aerated solution the phosphorescence intensity of the dendritic core is more than twice as intense as that of the

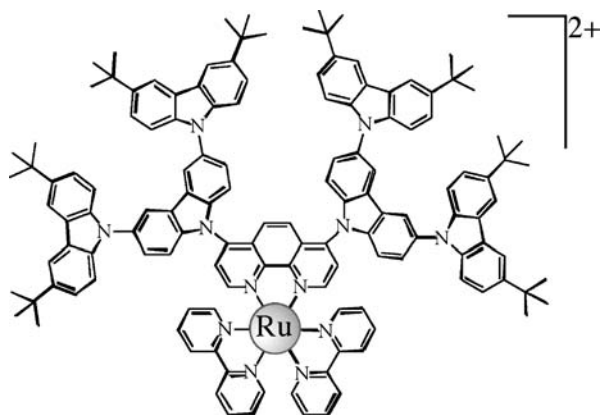


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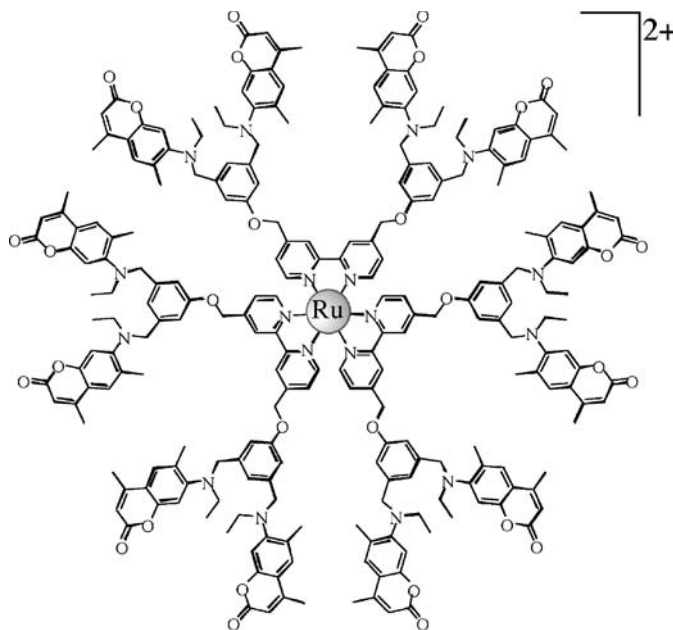
$[\text{Ru}(\text{bpy})_3]^{2+}$ parent compound, because the dendrimer branches protect the Ru-bpy-based core from dioxygen quenching [247].

More recently, dendrimers based on $\{\text{Ru}(\text{phen})_3\}^{2+}$ or $\{\text{Ru}(\text{bpy})_2(\text{phen})\}^{2+}$ (phen = 1,10-phenanthroline) cores with appended carbazole chromophoric units have been investigated (see, e.g., 33) [248]. In these compounds, energy transfer from the peripheral carbazole units to the metal-based core occurs with ca. 100% efficiency, with sensitization of the $^3\text{MLCT}$ luminescence at ca. 630 nm.

The $\{\text{Ru}(\text{bpy})_3\}^{2+}$ core was used to build a first-generation dendrimer containing 12 coumarin 450 units in the periphery (34). In acetonitrile solution, excitation of the coumarin 450 chromophores resulted in luminescence emission at 625 nm, typical of the $^3\text{MLCT}$ excited state of the $\{\text{Ru}(\text{bpy})_3\}^{2+}$ core, with only a minor residual fluorescence of the initially excited chromophores. An antenna effect is thus operative, with an estimated intramolecular energy transfer efficiency close to unity [249]. Using the same dendrimer and the $[\text{Ru}(\text{dmb})_3]^{2+}$ (dmb = 4,4'-methyl-2,2'-bipyridine) complex, which served as a model for the "naked" dendrimer core, it was possible to investigate the shielding effect of the dendritic structure on the intermolecular energy and electron transfer processes [250]. Bimolecular quenching constants were measured in acetonitrile solution for dioxygen, 9-methylanthracene (MA), phenothiazine (PTZ), and methyl viologen (MV^{2+}), using three dif-



33



34

ferent techniques: intensity and lifetime quenching, and transient absorption spectroscopy. These quenchers were chosen to explore different quenching mechanisms. Whereas in the case of dioxygen the quenching mechanism is still an object of controversy, and should involve both energy and electron transfer, it is known that the $[\text{Ru}(\text{bpy})_3]^{2+}$ excited state is quenched by MA, PTZ, and MV^{2+} via energy transfer, reductive and oxidative electron transfer mechanisms, respectively. The results obtained with the quenchers MA, PTZ,

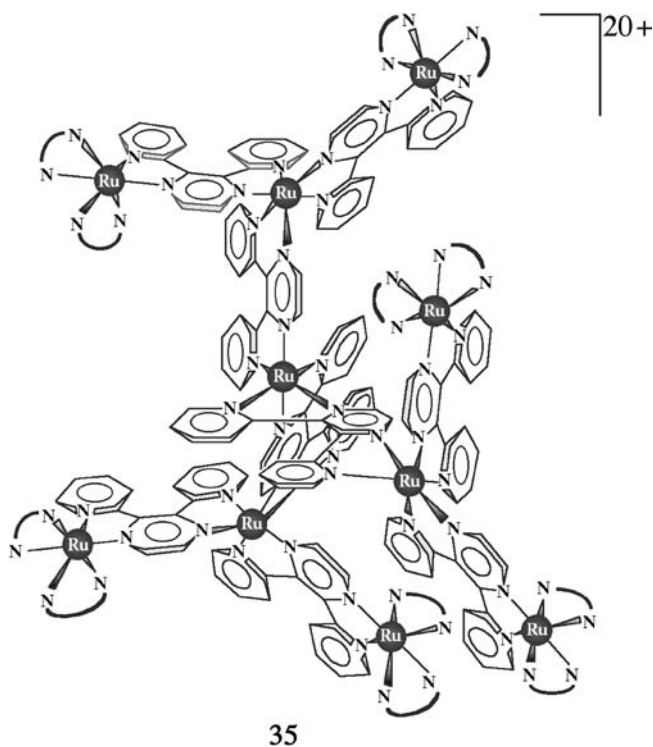
and MV^{2+} indicated that the first-generation dendritic structure of this class of dendrimers is unable to shield the Ru-based core from bimolecular energy and electron transfer reactions. On the contrary, quenching by dioxygen was attenuated in going from $[Ru(dmb)_3]^{2+}$ to larger dendrimers, suggesting an effect of the dendritic structure. As this effect is not observed with MA, PTZ, and MV^{2+} , which are certainly much bulkier species, the shielding effect observed in the case of dioxygen was attributed to lower O_2 solubility within the dendritic structure [250].

5.2.2.2

Multimetallic Dendrimers

For the class of dendrimers where metal complexes are the branching centers, a key role is played by polytopic chelating ligands (*bridging ligands*), which can control the shape of the polynuclear array and the electronic interaction between metal chromophores.

The largest family of these dendrimers is based on the 2,3-bis(2'-pyridyl)pyrazine (dpp) bridging ligand. Within such a series, the largest species contain 22 metal centers [251–253]. The decanuclear compound **35** is



a second-generation dendrimer of this family (in the sketch of the compound, the peripheral ligands, schematized as $N^{\wedge}N$, stand for 2,2'-bipyridine) [254]. For the dendrimers of this series, the modular synthetic strategy [252] allows a high degree of synthetic control in terms of the nature and position of metal centers, bridging ligands, and terminal ligands. Since the excited-state level of each metal center in the dendrimer depends on the nature of the metal, of its coordination sphere (which in its turn depends on the metal position, inner or outer, within the dendritic array) and on the ligands, each metal-based subunit is characterized by specific excited-state properties, which because of the symmetry of the dendritic structure are usually identical for each metal-based subunit belonging to the same dendritic layer. Therefore, the synthetic control translates into control of specific properties, such as the direction of electronic energy flow within the dendritic array (antenna effect) [245]. For example, in **35** the lowest excited-state level involves the peripheral subunit(s), and the emission of the species (acetonitrile, room temperature: $\lambda_{\max} = 780 \text{ nm}$; $\tau = 60 \text{ ns}$; $\Phi = 3 \times 10^{-3}$) is assigned to a $(\text{bpy})_2\text{Ru} \rightarrow \mu\text{-dpp}$ MLCT triplet state [254]. Excitation spectroscopy indicates that quantitative energy transfer takes place from inner subunits to the peripheral ones [254]. Because of the energy gradient between the dendritic layers, the energy transfer is ultrafast (see later), occurring in the femtosecond timescale. On the basis of the above discussion, it is not surprising that all the homometallic dendrimers of the same family, independent of the number of Ru subunits (i.e., tetranuclear [255, 256], decanuclear [253, 254], and docosanuclear [251–253], as well as hexanuclear [257, 258], heptanuclear [259], and tridecanuclear species [260], which have particular connections/geometries), exhibit practically identical photophysical properties, since the lowest-energy subunit(s) is in all cases the identical peripheral $(\text{bpy})_2\text{Ru}(\mu\text{-dpp})$ MLCT state(s). A nonanuclear species has also been prepared [261], but its photophysical properties have not yet been reported.

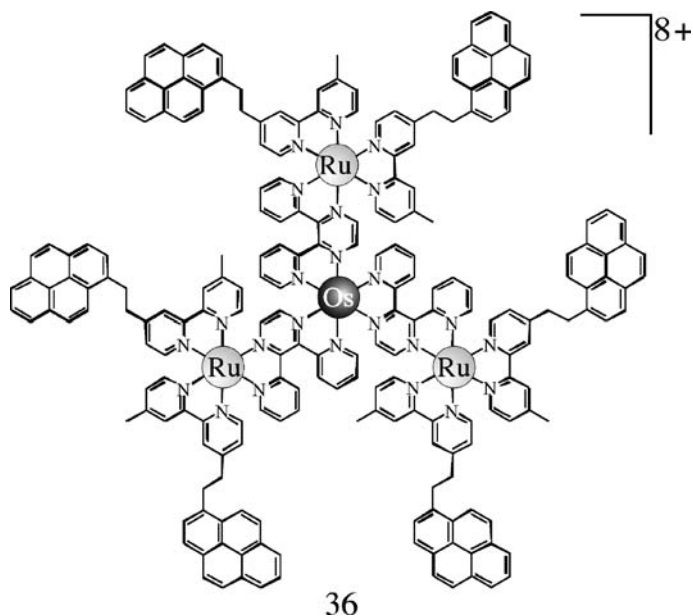
On increasing nuclearity, a unidirectional gradient (center-to-periphery or vice versa) for energy transfer is hardly obtained with only two types of metals (commonly, Ru(II) and Os(II)) and ligands (bpy and 2,3-dpp). In fact, by using a divergent synthetic approach starting from a metal-based core it becomes unavoidable that metal-based building blocks with high-energy excited states (*high-energy subunits*) are interposed between donor and acceptor subunits of the energy transfer processes [245]. For example, while in the tetranuclear $[\text{Os}\{(\mu\text{-dpp})\text{Ru}(\text{bpy})_2\}_3]^{8+}$ (OsRu_3) species, in which a central $\{\text{Os}(\mu\text{-dpp})_3\}^{2+}$ subunit is surrounded by three $\{\text{Ru}(\text{bpy})_2\}^{2+}$ subunits, only the osmium-based core emission is obtained (acetonitrile, room temperature: $\lambda_{\max} = 860 \text{ nm}$; $\tau = 18 \text{ ns}$; $\Phi = 1 \times 10^{-3}$) [262], indicating quantitative energy transfer from the peripheral Ru-based chromophore to the central Os-based site; for the larger systems the peripheral Ru-based emission is not quenched [245, 253]. This result highlights that although downhill or even isoergonic energy transfer between nearby building blocks in the dendrimers

based on the 2,3-dpp bridging ligand is fast and efficient, direct downhill energy transfer between partners separated by high-energy subunits is much slower and can be highly inefficient. This problem has been overcome (1) by using a third type of metal center, namely a Pt(II) one, to prepare decanuclear species (second-generation dendrimers) having different metal centers in each "generation" layer (schematically, OsRu₃Pt₆ species) [263] or, more recently, (2) in a heptanuclear dendron where the barrier made of high-energy subunits is bypassed via the occurrence of consecutive electron transfer steps [264]. Quite interestingly, this latter study suggests that long-range photoinduced electron transfer processes do not appear to be dramatically slowed down by interposed high-energy subunits in this class of dendrimers.

The efficiency of energy migration in 2,3-dpp-based dendrimers has attracted a large interest for the potential use of these species as synthetic antennae in artificial photosynthesis processes, and this has stimulated detailed kinetic investigations by means of ultrafast techniques. Studies on dinuclear model compounds have shown that esoergonic and isoergonic energy transfer between nearby units occurs within 200 fs, probably from nonthermalized excited states [168]. A direct consequence of such results is that energy transfer involving singlet states can compete with intersystem crossing. This conclusion is supported by the fact that the energy transfer from the peripheral Ru(II) subunits to the central Os(II) core in a tetranuclear OsRu₃ dendrimer takes place both by a singlet–singlet pathway, with a lifetime of less than 60 fs, and by triplet–triplet energy transfer, with a lifetime of 600 fs [169, 170]. The finding of singlet–singlet energy transfer is a particularly important result, since it indicates that the idea that any excited-state process involving metal polypyridine complexes had to be ascribed only to triplet states should be taken with caution when a significant electronic coupling between donor and acceptor is present. In some way, this finding also parallels the results obtained for photoinduced injection of electrons into semiconductors [167, 265–271].

An extension of this kind of antenna is a first-generation heterometallic dendrimer with appended organic chromophores like pyrenyl units (36) [272]. In this species, consisting of an Os(II)-based core surrounded by three Ru(II)-based moieties and six pyrenyl units in the periphery, 100% efficient energy transfer to the Os(II) core is observed, regardless of the light absorbing unit. A detailed investigation of the excited-state dynamics occurring in this multicomponent species on exciting in the UV region (267 nm) has also been performed [273]. Transient absorption spectra (in the range 420–700 nm) for the various intermediates have been reported by the acquisition of evolution-associated difference spectra.

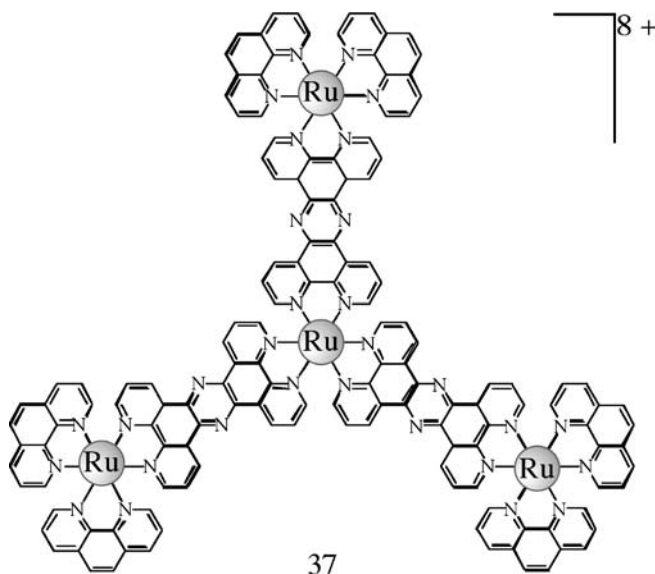
Energy transfer processes from the nonrelaxed and relaxed S₁ state of the peripheral pyrenyl chromophores to the lowest-lying Os-based MLCT triplet excited state occur with lifetimes of about 6 and 45 ps, respectively [273]. Subpicosecond energy transfer from the excited Ru manifold to the Os-based



chromophore and interconversion between the initially prepared S_3 state and the low-lying S_1 level within the pyrenyl subunits have also been evidenced. The rate constant of the energy transfer from the pyrenyl groups to the Ru/Os excited state manifold is in good agreement with the Förster mechanism when the relaxed S_1 pyrene state is taken into account. Energy transfer from the nonrelaxed state most likely involves folded conformations in which the pyrenyl subunits are strongly interacting with inner subunits of the tetranuclear core. Such interactions were also suggested by the ground-state absorption spectrum of the compound [272].

Because octahedral metal complexes can exist in two chiral forms, Λ and Δ , it could be expected that the photophysical properties of dendrimers containing metal complexes as branching centers could be different for the various isomers (the situation can be even more complicated in the case of geometrical isomers). However, the investigation of optically pure isomers of dinuclear and dendritic-shaped tetranuclear species (37 is the general structural formula of the tetranuclear systems: optical geometry is not evidenced) has shown that stereochemical isomerism does not cause any sizeable difference, at least for the studied compounds [194].

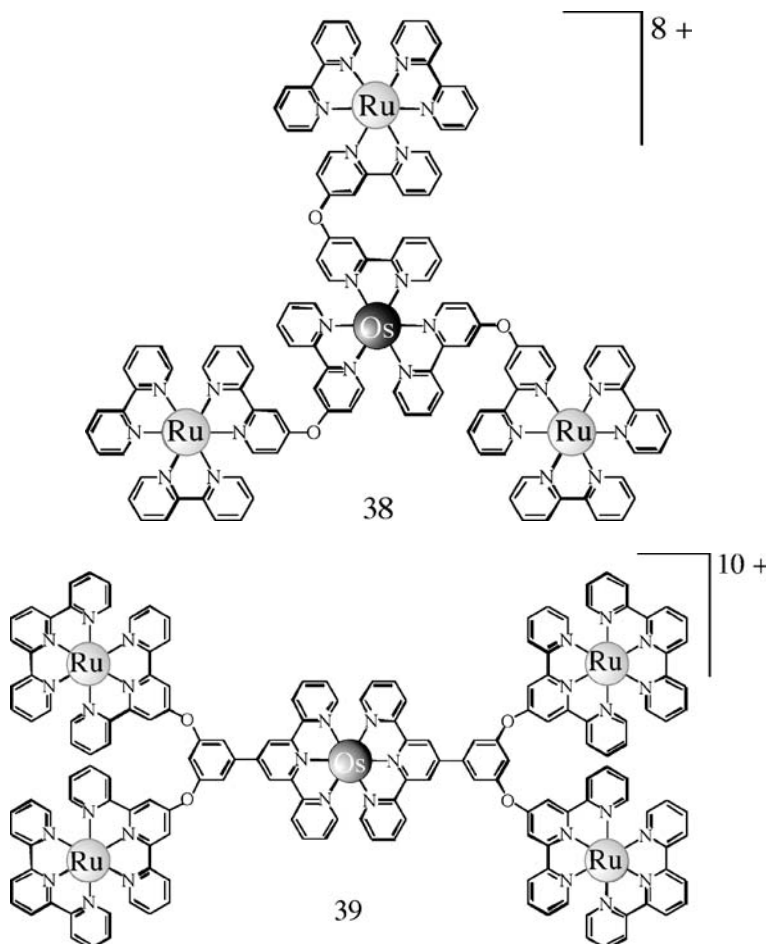
In 37 the emissive state, which involves the peripheral Ru(II) centers, does not have a sizeable absorption counterpart, since it is a special type of charge-separated state, with the formal “hole” localized on a peripheral Ru(II) center and the “electron” localized on an orbital mainly centered on the pyrazine moiety of the bridging ligand: the absorption related to such a state has negligible oscillator strength, due to the poor overlap of the orbitals involved



(for similar systems, see Sect. 4.4) [194]. A recently investigated, closely related tetranuclear dendritic-shaped compound, where the bridging ligand is the asymmetric PHEHAT ligand (PHEHAT = 1,10-phenanthroline[5,6-*b*]-1,4,5,8,9,12-hexaazatriphenylene), displays similar photophysical properties [274].

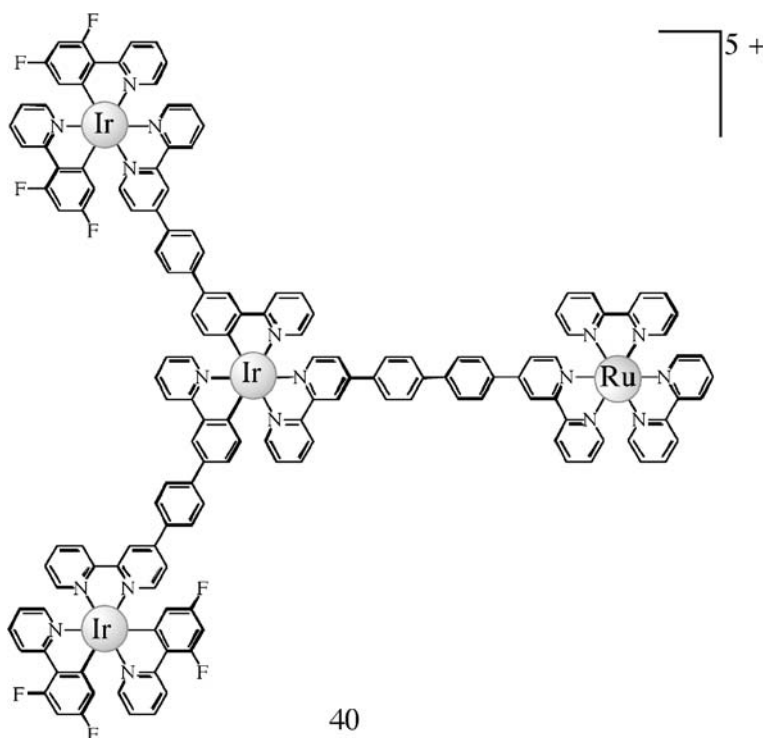
Mixed-metal Os(II)–Ru(II) dendrimers whose bridging ligands contain ether linkages have also been reported: compounds **38** and **39** are two examples [275, 276]. The tetranuclear species in **38** exhibits quantitative energy transfer from the Ru(II) chromophores to the Os(II) core [275], whereas for **39** the efficiency of the energy transfer process is highly temperature dependent; in fact the Ru-to-Os energy transfer is highly efficient at low temperature, whereas at room temperature it does not compete with the intrinsic decay of the Ru(II)-based subunits [276].

In most of the mixed-metal dendrimers featuring energy transfer and containing Ru(II) subunits, the Ru(II) centers play the role of the energy donor components (and usually Os(II) centers are the acceptors). Examples of photoactive dendrimers in which Ru(II) subunits behave as acceptor components are the tetranuclear compound **40** [277] and its higher-generation, Y-shaped octanuclear species, in which four additional Ir(III) chromophores have been connected at the two peripheral Ir(III) subunits of the compound **40** (JAG Williams, personal communication). Here, efficient energy transfer takes place for the Ir(III) cyclometallated subunits toward the single Ru(II) polypyridine chromophore, which acts as the energy trap of the assemblies. The Ru(II) subunit then emits with relatively high quantum yield (0.12 in degassed acetonitrile at room temperature) and long lifetime (1.6 μ s) [277].



The fluoro substituents which are present on the peripheral Ir chromophores have the role of increasing the excited-state energy levels of the outer Ir chromophores with regard to the inner ones, so generating the correct energy gradient.

Multi-ruthenium dendrimers of the 2,3-dpp family discussed above have also been functionalized with organic electron donor subunits, to yield integrated light-harvesting antennae/electron donor systems for charge separation. In particular, a triruthenium dendron has been coupled with a tetrathiafulvalene (TTF) derivative [278] and the tetranuclear OsRu₃ has been functionalized at the peripheral bpy ligands with up to six phenothiazine subunits [279]. In both cases, the light-harvesting antenna emission was totally quenched by reductive electron transfer from the electron donor subunit. Interestingly, the electron donor quenchers were not directly linked to the energy trap of the antenna; however, the electron transfer process was fast and



efficient, which confirms that in this type of artificial antenna metallodendrimer, long-range electron transfer can be quite effective, as in the case of the heptanuclear complex mentioned above [264], and could suggest interesting options to build up integrated donor-antenna-acceptor systems. This discussion leads us directly to the next section.

5.3

Donor–Chromophore–Acceptor Triads

Triad systems (Fig. 14) are key components of the early events in artificial photosynthesis: the light energy collected by the chromophore (P) is transformed into chemical (redox) energy by a sequence of electron transfer steps involving electron donor (D) and electron acceptor (A) units, ultimately leading to charge separation [208, 209, 228]. Charge separation is probably the most important photoinduced process on Earth, so it is not surprising that many triads based on Ru(II) complexes have been prepared and studied in the last 20 years [228, 280]. It should be noted that there are literally dozens of dyads based on Ru polypyridine complexes [228, 281]. Only some examples of triads (that is, species where Ru(II) chromophores are simultaneously coupled to electron donor and acceptor units) are discussed here.

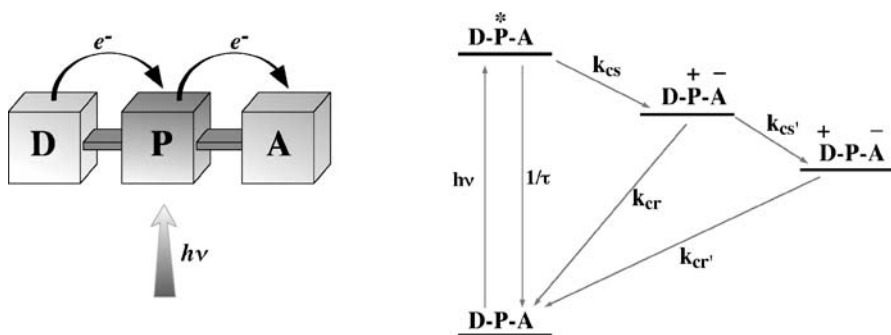


Fig. 14 Schematization of a triad for photoinduced charge separation. P, chromophore; D, donor; A, acceptor; cs, primary charge separation; cr, primary charge recombination; cs', secondary charge separation; cr', final charge recombination

Structurally speaking, Ru complexes with tridentate ligands like terpy are ideal systems for molecular triads: indeed, substitution at the 4 position of the central pyridine ring of terpy-like ligands allows a linear arrangement of subunits, with control of geometry and distance. Some of the first ruthenium triads based on such an arrangement are shown in Fig. 15 [282]. Whereas fully developed charge separation, with formation of the D^+-P-A^-

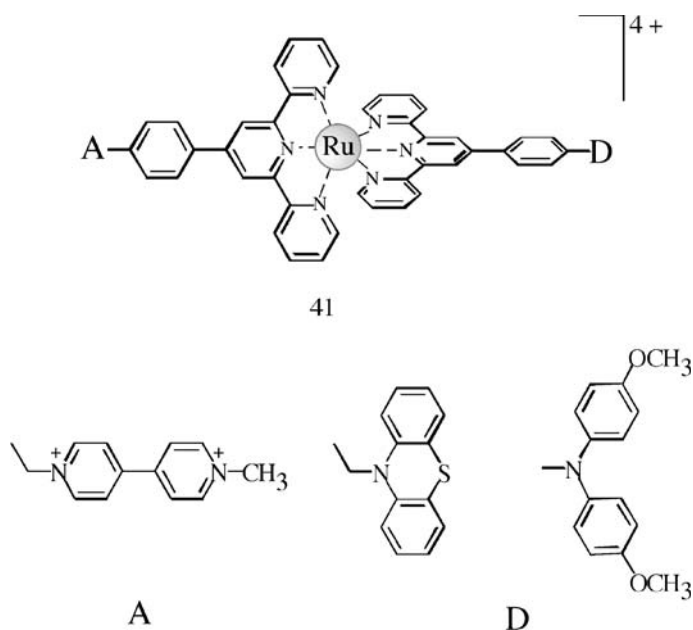
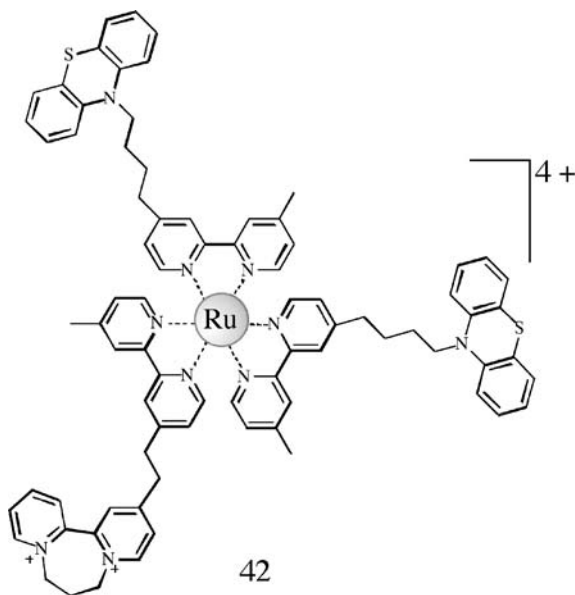


Fig. 15 Structural formulae of Ru(II) terpyridine triads containing acceptor (A) and donor (D) components

charge-separated state, did not take place in the triad with D = PTZ (PTZ = phenothiazine subunit), the formation of such a charge-separated species was inferred for the species with D = DPPA (DPPA = diphenylamino moiety) at 150 K, although it could not be evidenced spectroscopically because it did not accumulate as a consequence of a fast recombination rate [282].

In spite of less control of distance and orientation between donor and acceptor, better results have been reported for a series of systems exemplified by **42** [283–285]. The components of this series of triads are a tris-bipyridine Ru(II) chromophore covalently linked to one or two phenothiazine electron donors and to quaternized bipyridinium electron acceptors. The saturated alkyl chains bridging the molecular components are electrically insulating and flexible. This latter point is apparently a drawback since it does not allow for control of geometry. Moreover, even the octahedral arrangement of the bpy subunits adds some difficulties in defining the real structure: for example, geometrical isomers can also exist, since each bpy of **42** is non-symmetric. The compound **42** exhibited formation of the $D^+ - P - A^-$ charge-separated state in dichloromethane at room temperature with an initially reported efficiency of about 26%. Such a value was later corrected to about 86% by using a slightly different solvent (1,2-dichloroethane) [283, 286, 287]. Once formed, the charge-separated state decayed with a relatively fast rate ($k_{CR} = 6.3 \times 10^6 \text{ s}^{-1}$), corresponding to a lifetime of about 160 ns. On the basis of redox data, the charge-separated state stored about 1.3 eV.

Similar complexes were prepared that differed from one another by the length of the alkyl chains connecting the subunits and/or by changing



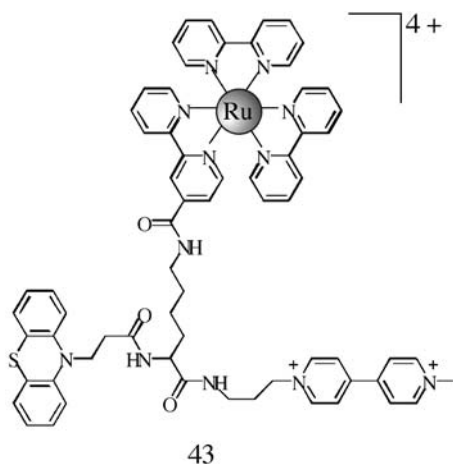
the methylene chains connecting the quaternary nitrogens (and, as a consequence, the reduction potential of the electron acceptor) [283–287]. In a homogeneous series of experiments performed on such species, however, the efficiency of charge separation does not change appreciably, remaining larger than 0.80, although the driving forces and the rate constants of the various electron transfer steps, as obtained by independent studies performed on isolated dyads of the type D–P or P–A, were different.

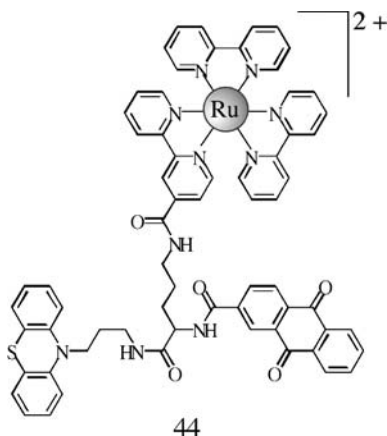
In D–P*–A systems, the fully developed charge-separated state can be obtained, in principle, by two different routes (excluding direct electron transfer from D to A): (1) a route initiated by oxidative quenching, that is, the series of events described by the sequence D–P*–A, D–P⁺–A[–], D⁺–P–A[–]; and (2) a route initiated by reductive quenching, described by the sequence D–P*–A, D⁺–P[–]–A, D⁺–P–A[–]. Both routes can also take place simultaneously. The comparison between the photophysical properties of the various triads and the corresponding isolated dyads of this family of compounds indicated that the emission decay rates of any D–P–A triad never differed by more than a factor of two from those of the P–A dyads, although the absolute decay rate values changed by over a factor of 10³ (over the whole collection of compounds). This prompted the authors to attribute the initial quenching event in all the D–P–A triads of this family to oxidative electron transfer, with formation of the D–P⁺–A[–] intermediate, with the route initiated by reductive quenching playing a negligible role [288]. However, in all the P–A dyad systems, it was always impossible to detect the A[–] radical anion [284], indicating that back electron transfer in the P–A dyads was faster than the forward, oxidative electron transfer. This posed some problems in justifying the efficiency of formation of the fully developed charge-separated state, where apparently reduction of P⁺ from D in D–P⁺–A[–] species efficiently competes with back electron transfer in the intermediate. In fact, this looks somewhat puzzling because the reductive electron transfer in D–P* dyads is reported to be of the order of 10⁶ s^{–1} [289], while oxidative electron transfer in P*–A dyads ranges from 10¹⁰ to 10⁷ s^{–1} [284, 285, 290–293] and, based on the circumstances mentioned above, back electron transfer in P⁺–A[–] (and for extension in D–P⁺–A[–]), opposing the formation of the fully developed charge-separated state, could be even faster. To justify the experimental data, electron transfer from D to P⁺ in D–P⁺–A[–] should be about 1 × 10¹⁰ s^{–1} or faster. Therefore, the exceptional properties of these compounds as far as the efficiency of charge separation is concerned remained largely unexplained.

A recent paper has shed light on the photophysical behavior of these triads [288]. A series of new experiments, including transient absorption measurements, emission decay, and a careful examination of the ground-state absorption spectra of the triads and of various separated dyad components, suggested that in the D–P–A triads of this family an association between the tethered phenothiazine electron donor subunit and the Ru(II) chromophore takes place, in a folded conformation. The association is already present in the

ground state, before excitation and any electron transfer process. The triad would then be better defined as a D/P–A system, and electron transfer between D and P⁺ subunits in the intermediate state D/P⁺–A[−] can be largely faster than that reported for the D–P* dyad, and even faster than charge recombination between C⁺ and A[−] in the assembly, justifying the high efficiency of formation of the fully developed charge separation. Ground-state association of tethered aromatic ligands (with flexible linkages) with Ru(II) chromophores was also known in a tetranuclear dendrimer [272, 273], further supporting these conclusions.

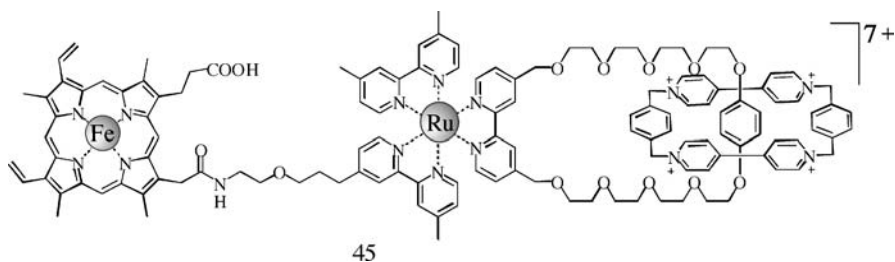
The triad **43** involves components similar to those used in the former discussed systems, but the connecting scheme is different [294]. Here, the chromophore and the electron donor and acceptor subunits are all linked to a lysine moiety. The charge-separated state of this triad stores 1.17 eV and lives for 108 ns (rate constant of charge recombination $k_{\text{CR}} = 9.26 \times 10^6 \text{ s}^{-1}$) in acetonitrile, as observed by transient spectroscopy. The efficiency of formation of the charge-separated state is about 34%. On the basis of detailed photophysical studies of isolated dyads [294], the authors believe that the only route leading to fully developed charge separation is reductive quenching of D–P*–A leading to D⁺–P[−]–A, followed by a second electron transfer leading to D⁺–P–A[−], whereas the route passing through the population of the D–P⁺–A[−] intermediate does not lead to the full charge-separated species, but leads directly to the ground state. Therefore, the occurrence of oxidative electron transfer of P* would be the main reason for the efficiency loss in the whole process. Better results were obtained by modifying the acceptor site of the triad, as shown in **44** [295]. In this species, the energy stored by the charge-separated species is higher (1.54 eV), since the anthraquinone has a less negative reduction potential than the methyl viologen subunit, and the lifetime of the charge-separated state is longer (174 ns, $k_{\text{CR}} = 5.7 \times 10^6 \text{ s}^{-1}$), but the





quantum yield is slightly smaller (26%). The longer lifetime of the charge-separated species of the anthraquinone-containing triad was attributed to the charge-recombination process being further in the inverted region (a similar reorganization energy λ , about 0.80 eV, is assumed in both cases). Even in this case, the main losses in the efficiency of formation of the fully developed charge separation were attributed to the inefficiency of the route in which the initial electron transfer is oxidative to produce the final $D^+ - C - A^-$ state.

Within the field of molecular triads, a peculiar example is 45 [296]. In this species, the Ru(II) subunit playing the role of the chromophore is mechanically linked with a cyclobis(paraquat-*p*-phenylene) unit (BV^{4+} , acceptor) and covalently linked with a protoheme unit (the donor), located in a myoglobin pocket (not shown in figure). The overall system is therefore a reconstituted protein bearing a molecular triad. Excitation of the ruthenium chromophore is followed by a series of photoinduced electron transfer steps (the first one being electron transfer to the electron acceptor), leading to the charge-separated species containing the porphyrin radical cation and the paraquat-based radical anion, $Mb(Fe^{III}OH_2)^+ - Ru^{2+} - BV^{3+}$. This species successively undergoes a series of deprotonation processes ultimately leading to another charge-separated species, identified as $Mb(Fe^{IV}=O) - Ru^{2+} - BV^{3+}$, with an ap-

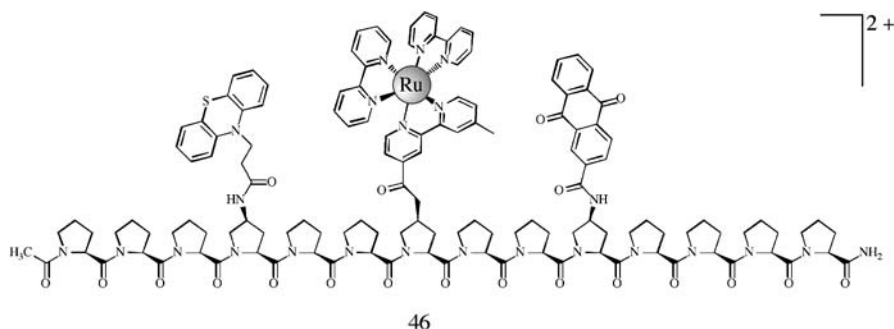


parent first-order rate constant of $6.6 \times 10^3 \text{ s}^{-1}$. This species is produced with a low quantum yield (0.5%), stores about 1.3 eV, and recombines to the ground state with a lifetime exceeding 2 ms. In spite of the low efficiency of the charge-separation process, there are several interesting points: (1) in the absence of myoglobin, charge separation is not obtained at all; (2) the complete process is pH dependent; (3) the final charge-separated state lifetime is comparable with that of natural photosynthetic reaction centers; and (4) back electron transfer is regulated by protonation/deprotonation of distal histidine moieties, which appears to be needed to reduce the $\text{Mb}(\text{Fe}^{\text{IV}}=\text{O})$ subunit. The low efficiency of the overall process is mainly attributed to charge recombination within the $\text{Mb}(\text{Fe}^{\text{III}}\text{OH}_2)^+ - \text{Ru}^{2+} - \text{BV}^{3+}$ state, which efficiently competes with the deprotonation processes. This study highlights the potential of mixed synthetic–natural systems for obtaining long-lived charge separation.

5.4

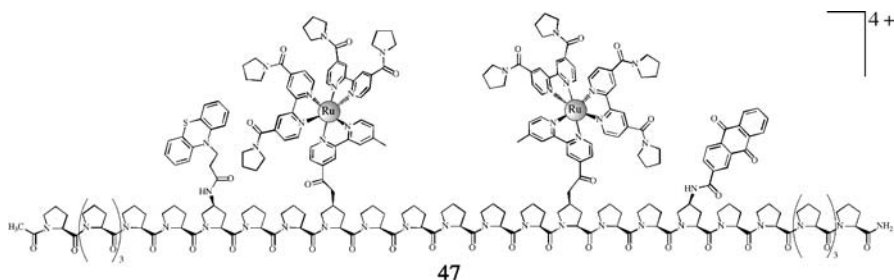
Polyads Based on Oligoproline Assemblies

The interesting results obtained by organizing D–P–A triads on the structure of the amino acid lysine (Sect. 5.3) prompted the preparation of D–P–A systems assembled on oligoproline scaffolds, by means of solid-state peptide synthesis [294, 297–299]. One such system is **46**. In this species, a phenothiazine (PTZ) group acts as the electron donor and an anthraquinone (Anq) subunit plays the role of the electron acceptor. Oligoprolines were selected, since it is known that oligoproline chains of nine or more proline units fold into stable helices even with large functional groups on the proline units. The terminal segments allow the helix to begin and end with capped Pro_3 turns which prevent unwinding of the helix. For **46**, a fully developed charge-separated state is gained in acetonitrile solution with good efficiency (53%). The charge-separated state stores 1.65 eV relative to the ground state and returns to the ground state with a rate constant of $5.7 \times 10^6 \text{ s}^{-1}$ ($\tau = 175 \text{ ns}$) [299, 300]. Quenching of the Ru-based excited state is domi-



nated by reductive electron transfer involving the PTZ electron donor, in a process which is largely solvent dependent, as is the driving force of the process. Then, there is a fast electron transfer from the reduced metal chromophore to the Anq subunit, which yields the charge-separated state. There is a strong solvent-dependent competition between such a second electron transfer, which allows for fully developed charge separation and back electron transfer in the D^+-P^--A intermediate. The consequence of this solvent dependence is that going from 1,2-dichloroethane to dimethylacetamide, the efficiency of charge separation changes from 33 to 96%. Also, the charge recombination is solvent dependent, and the electronic coupling between PTZ^+ and Anq^- was calculated to be about 0.13 cm^{-1} [300].

A more elaborated polyad based on the formerly described systems is the D-P-P-A tetrad **47** [301]. This is the evolution of a system quite related to **46**, where substituents on the terminal bpy ligands of the metal chromophore are used to favor the thermodynamics of the (reductive) first electron transfer step. This modification led to an efficiency of charge separation of 90% in acetonitrile for the corresponding triad. In the tetrad, 13 proline spacers are present between PTZ and Anq. The efficiency of formation of the charge-separated state in the tetrad is 60% and its lifetime is $2\text{ }\mu\text{s}$ ($k_{CR} = 5.0 \times 10^5\text{ s}^{-1}$). Excitation can occur in both the Ru chromophores, but apparently the result is not identical. Excitation of the Ru(II) complex adjacent to the PTZ electron donor gives the D^+-P^--P-A system. To produce the fully developed $D^+-P-P-A^+$ species, it is proposed that a stepwise mechanism occurs, with the species D^+-P-P^-A as an intermediate. Efficient, isoergonic electron transfer between the two chromophores is therefore foreseen. Excitation of the Ru(II) complex adjacent to the electron acceptor Anq subunit would be unproductive in a direct sense, since oxidative electron transfer by Anq is unfavorable thermodynamically and direct quenching from the PTZ unit is unlikely because of the large distance. However, even excitation of this Ru(II) chromophore can become productive, provided that isoergonic energy transfer to the Ru(II) chromophore adjacent to the PTZ unit takes place. Since the quantum efficiency of formation of the charge-separated state is 60%, and considering that excitation of the two identical Ru(II) chromophores



is equivalent (that is, 50% each), clearly interchromophoric energy transfer takes place, although not with a high efficiency.

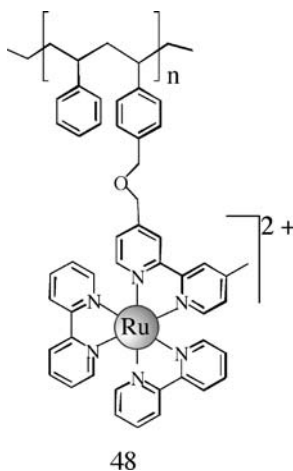
As far as the mechanism of the intrastrand energy and electron transfer in such oligoprolines is concerned, through-bond and through-space pathways can be considered. An important step to elucidate the mechanism was a systematic investigation of the reductive electron transfer in oligoprolines containing only PTZ and one Ru(II) chromophore [302]. From such a study, when the number of interposed prolines varies from two to five, it was demonstrated that a through-space mechanism is operative, with an apparent β value of $0.41 \text{ \AA}^{-1}$. Superexchange coupling with the solvent and oligoproline scaffold are proposed to play important roles in promoting electronic coupling [302].

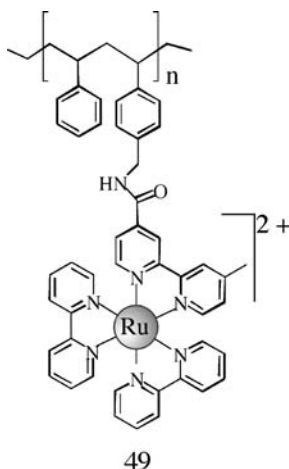
To complete the overview of these oligoproline-based systems, it has to be mentioned that also pentads of type D-P-P-P-A have been prepared and studied, where each functional subunit is separated from the adjacent ones by two prolines [297, 303]. The results obtained indicate that interchromophoric energy transfer is relatively slow across five proline units, but rapid across two prolines [297].

5.5

Multi-ruthenium Assemblies Based on Derivatized Polystyrene

A suitable choice to assemble a large number of chromophores is polymer derivatization: within this class of compounds, probably the largest series deals with polystyrene polymers. Indeed, up to 30 Ru-bpy-type chromophores have been linked to soluble styrene polymers [297, 304–308, 310, 318]. An early synthetic strategy [309] involved attachment of the chromophores to polystyrene by an ether linkage (48). Successively [310], the

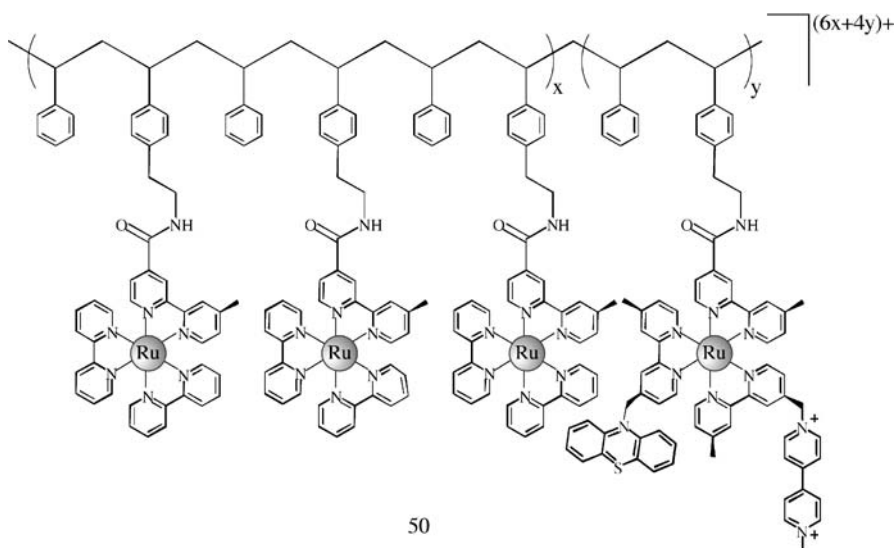




same authors developed an alternative route based on amide linkage (**49**), finding a dramatic enhancement in the ability of the polymeric arrays to promote intrastrand energy transfer. In the (amide-functionalized) mixed polymers containing a 3 : 13 ratio between the lower-energy Os-based chromophores and the higher-energy Ru-based ones, triplet–triplet energy transfer was found to occur with an efficiency higher than 0.90 in acetonitrile solution.

It was pointed out [310] that energy transfer from the excited Ru-based moieties to the ground-state Os-based moieties requires two processes: energy migration among the Ru-based units (site-to-site energy hopping) and a final energy transfer from a Ru-based to a nearby Os-based unit. For both processes the rate constants exceeded $2 \times 10^8 \text{ s}^{-1}$ for the amide-linked polymer, whereas in the ether-linked polymer the rate constant for intrastrand energy migration from $^*\text{Ru}$ to Ru was orders of magnitude slower. The rate constants for the amide-linked species, coupled with the relatively long excited-state lifetime of the Ru-based chromophores (910 ns), account for the ability of the polymer arrays containing the amide-linked chromophores to act as efficient antennae. The reason for the different behavior of the ether-linked and amide-linked arrays lies in the direction of the excited-state MLCT dipole of the chromophores involved in the energy transfer processes. This dipole is directed toward the polymer backbone in the most effective amide-linked antenna systems, whereas it is out from the polymer backbone in the less efficient ether-linked arrays. This difference affects the electronic coupling between donor and acceptor sites of the energy migration processes.

Ru(II) chromophores with appended electron acceptor (a methyl viologen species, A) and donor (a phenothiazine group, D) subunits have been incorporated within the antenna polystyrene system (**50**) [311], to play the role of “reaction center” (RC) units. In such an integrated antenna–RC polymer,



50

containing 17 normal Ru chromophores and three RCs, the D^+-A^+ charge-separated state is formed, as shown by transient absorption spectroscopy. Emission at the Ru(II) chromophores was quenched by about 34% compared to the homopolymer containing 20 “normal” Ru chromophores. Energy transfer from the normal Ru chromophores to the RC sites was favored by -0.1 eV. It was shown that about 50% of the charge-separated state was formed during the 7-ns laser pulse, indicating intrastrand sensitization, with the charge-separated state formed by direct excitation at the RC complex and by excitation to nonadjacent Ru chromophores followed by energy migration to the RC sites. In this system, 1.15 eV is stored in the charge-separated state and the efficiency of the process varies from 12 to 18% depending on laser irradiance, indicating excited-state annihilation at high irradiance. Charge recombination is similar to that of the “isolated” RC, but an additional long-lived transient (formed in low efficiency, about 0.5%) was observed, which decayed by second-order kinetics with $k = 48 \text{ M}^{-1} \text{ s}^{-1}$. This long-lived transient was attributed to polymers in which D^+ and A^- were formed on different RC units, by invoking mechanisms in which electron transfer quenching by oxidative or reductive electron transfer in a RC site is followed by intrastrand hole or electron transfer to a second RC site [311].

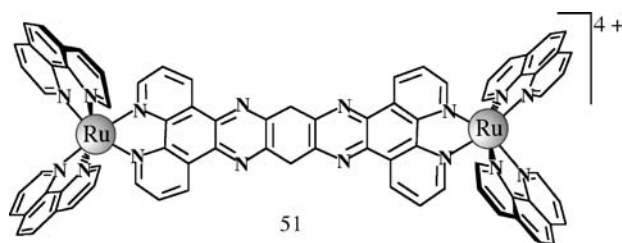
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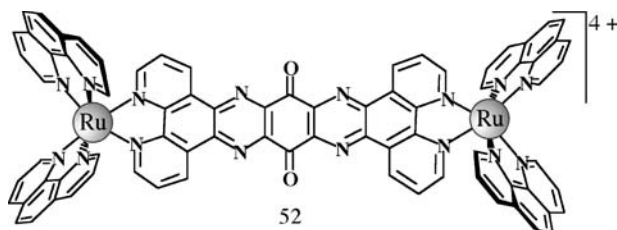
Photoinduced Collection of Electrons into a Single Site of a Metal Complex

An essential property of natural photosynthesis is the collection of multiredox equivalents at specific sites. Indeed, all the important light energy storage

processes require more than one electron to operate: for example, reduction of H^+ to H_2 is bielectronic, and oxidation of oxygen in water to produce O_2 is a four-electron process. Reduction of CO_2 to the high-energy content glucose species is also a multielectron process. Whereas artificial systems capable of performing photoinduced charge separation have been reported, species able to collect, by successive photoinduced processes, more than one single electron (or hole) in *one specific site* of their structure are very rare. These species differ from polymers or dendritic species, which are also able to reversibly store more than one single electron (or hole) in their structure (in several, roughly identical, but *spatially separated sites*), since the accumulated charges should be located in a single subunit and, at least in principle, could be more easily delivered simultaneously to a unique substrate.

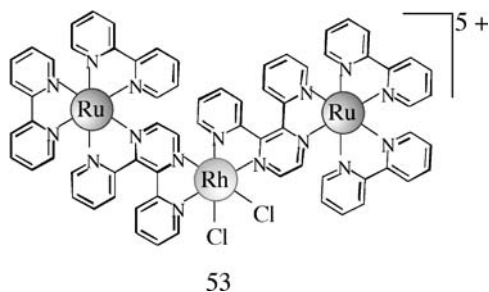
A breakthrough in this field was the study of the two dinuclear Ru complexes **51** and **52** [312]. These complexes are indeed able to collect two electrons (and two protons) and four electrons (and four protons), respectively, within their bridging ligand moieties upon successive light excitation and in the presence of sacrificial donor species. In a typical (schematized) sequence of events involving **51**: (1) light excitation produces a MLCT state involving the bpy-like subunit of the bridge; (2) a charge shift takes place from the bpy-like bridge moiety to the inner, phenazine-like portion of the bridge, so producing a sort of charge-separated state; (3) the sacrificial donor, a triethylamino (TEA) species, reduces the Ru(III) center, so restoring the chromophore; (4) the reduced central moiety of the bridge adds a proton (originated from irreversible TEA oxidation), so reaching charge neutrality; and (5) the sequence of events 1–4 is repeated and two electrons and two protons are collected [312]. However, a recent refinement of the ultra-fast spectroscopic results has evidenced that the product of step 2, initially identified as a sort of charge-separated state [313], receives a significant contribution also from a bridge-centered triplet state [314]. The overall process is perfectly reversible, and **51** is fully restored on leaving molecular oxygen reaching the complex [312]. For **52**, the formerly described sequence of events is repeated four times, thanks to the presence of the quinone subunits responsible for the addition of two extra electron/proton couples [312]. All the various steps of the multielectron processes occurring in **51** have also been characterized by UV/Vis spectroscopy and each intermediate has a unique





signature. This characterization was made by extensive work (including spectroelectrochemistry in various solvents, as well as at different pH values in aqueous solution) to identify the intermediates and to clarify the effect of pH on the processes [315–317]. Indeed, it has been demonstrated that in some solvents, processes 2 and 4 take place simultaneously, so it would be more correct to talk of proton-coupled electron transfer instead of successive electron/proton transfer events. At pH 4, only a fully reversible, coupled two-electron/two-proton transfer process is observed for **51**. This is a rare example of a proton-coupled multielectron transfer reaction [317] (FM MacDonnell, personal communication).

Another interesting example of photoinduced multielectron collection, this time at a metal center rather than at a ligand site, has been reported for a series of trimetallic mixed-metal species [318–320]. The most recent example of the series is **53** [320]. In this species, two Ru(II) chromophores (the light absorber units, LA) are linked to one Rh(III) center, which represents the electron collection (EC) core, through polyazine bridging ligands (BLs). The absorption spectrum of this species is dominated by the absorption of the Ru LA subunits, while the reduction properties identify the Rh($d\sigma^*$) orbital as the LUMO [319]. Upon excitation of the peripheral Ru(II) chromophore, an oxidative electron transfer to the Rh(III) center takes place ($k = 1.2 \times 10^8 \text{ s}^{-1}$), populating a triplet Ru(II)-to-Rh(III) charge transfer state. In the presence of a sacrificial donor, dimethylaniline, which restores the Ru(II) center(s), the starting compound undergoes a net photoreduction process with formation of $[\{(bpy)_2Ru(dpp)\}_2Rh^I]^{5+}$, as also demonstrated by spectroelectrochemistry, in which two chlorides have been lost (probably by irreversible chlo-



ride oxidation), and a two-electron reduced unit Rh(I) is formed [320]. The Rh center should simultaneously undergo a structural reorganization (most likely, octahedral/square planar). Interestingly, the photoreduced species is coordinatively unsaturated and therefore could be available to interact with substrates. It warrants mentioning that photoinitiated electron collection is obtained in a trimetallic species having an Ir(III) redox-active center instead of a Rh(III) one and similar Ru-based LA units [318].

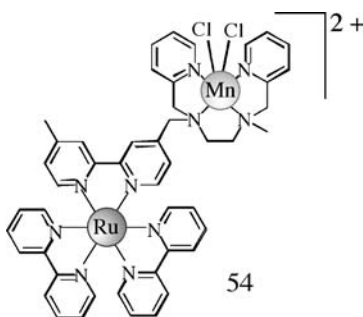
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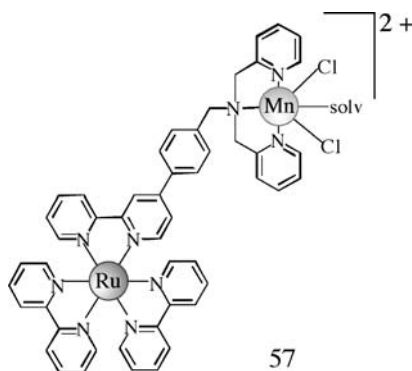
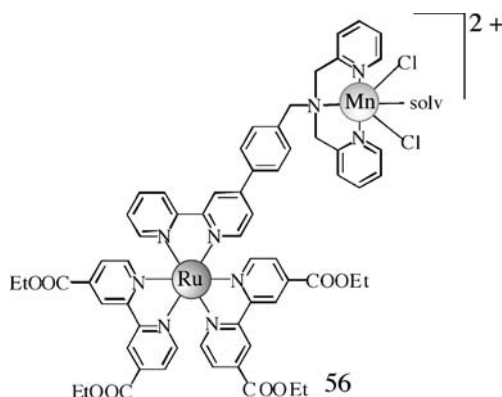
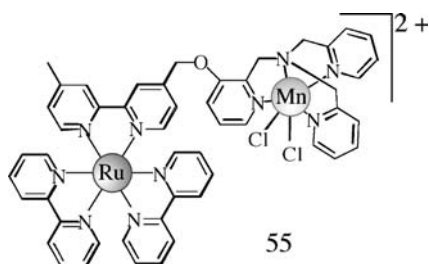
Photoinduced Multihole Storage: Mixed Ru–Mn Complexes

Complementary to the topic discussed in the previous section (that is, to accumulate multiple electrons in a single site of a (supra)molecular species) is the development of systems capable of accumulating holes, as happens in the oxygen evolving systems of natural photosynthesis. The source of inspiration is the photosystem II [321], where the excited primary chlorophyll donor, $^*P_{680}$, one of the most effective photooxidants of natural systems, is able to extract up to four electrons in consecutive steps from the so-called manganese cluster, whose structure—at least for a specific natural system—has recently been revealed [322–324]. The four-times oxidized manganese cluster successively produces molecular oxygen, thus returning to its initial state, ready for another photoinduced catalytic cycle.

Since the inspiration is photosystem II, it is not surprising that the largest family of complexes made to photochemically accumulate “holes” are Ru(II) polypyridine complexes coupled to manganese species. The field has been recently reviewed [325].

Several Ru–Mn dyads were initially studied to investigate some specific parameters for electron transfer (see for example 54–57 [326]). In a typical experiment, the excited Ru(II) chromophore is quenched via a bimolecular oxidative electron transfer by a sacrificial acceptor (usually methyl viologen), and the oxidized Ru(III) species oxidizes the attached Mn(II) subunit to Mn(III). Time constants of these latter processes spanned a large range, from





< 50 ns to 10 μ s, depending on the complex [326]. This study demonstrated that the reorganization energy for the Mn(II)-to-Ru(III) electron transfer was quite large (1.4–2.0 eV), suggesting significant inner reorganization of the manganese moiety during the process [327]. As an obvious consequence, very fast Mn(II)-to-Ru(III) electron transfer could not be expected. A further complication was that the manganese subunit could directly quench the excited ruthenium chromophore by Dexter energy transfer, competing with electron transfer quenching by the sacrificial acceptor for short Ru–Mn distances. These arguments led to the preparation of more elaborated systems in which intermediate donor species were interposed between ruthenium and

manganese subunits [328–330], with phenolate and tyrosine moieties playing the role of an intermediate donor. In most cases, proton-coupled electron transfer processes took place.

To achieve multielectron catalysts, more than one manganese ion was included in the systems. Figure 16 shows some examples [329,331,332] of Ru(II) species covalently linked to Mn dimers or trimers via phenolate ligands. In particular, for the Ru–Mn₂^{II,II} complex **58** reported in the figure, repeated flashes in the presence of a Co(III) sacrificial electron acceptor allowed three successive one-electron oxidations of the manganese moiety by the photooxidized Ru(III) subunit [333], as evidenced by the disappearance of the characteristic Mn₂^{II,II} signals and the appearance of the characteristic Mn₂^{III,IV} signals in EPR experiments. Manganese oxidation was suggested to involve a ligand exchange, in which acetate is released and water molecules are bound to form a di- μ -oxo bridge (see the reaction scheme in Fig. 16). According to the authors, this was the first example of a light-driven, multiple oxidation of a manganese complex attached to a photosensitizer. The ligand exchange at the manganese sites (presumably occurring in the Mn₂^{III,III} state, that is, after second electron release from the initial Mn₂^{II,II} center) is functional to the overall process, as it allows introduction of negative

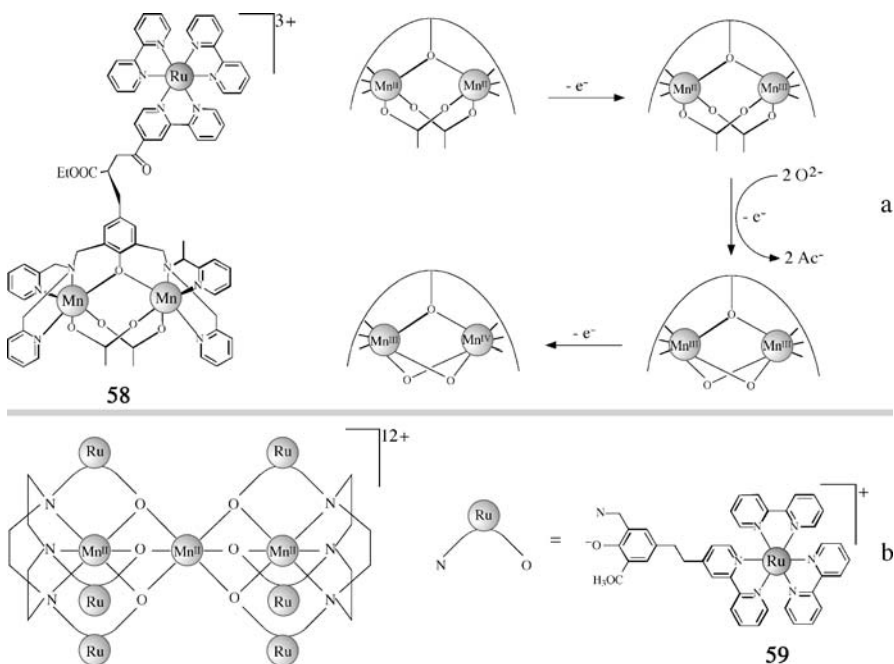


Fig. 16 Electron transfer from the manganese moiety to the photooxidized Ru(III) in **a** a Ru–Mn₂^{II,II} complex and **b** a Ru–Mn₃^{II,II,II} complex

charges to the complex thus making feasible oxidation to the $\text{Mn}_2^{\text{III,IV}}$ state, which would have otherwise been impossible on thermodynamic grounds. The ligand exchange and reorganization of the manganese ion coordination sphere, which has a nonneutral effect from the viewpoint of the charge, would be a charge compensating process, analogous to proton release occurring in most of the oxidation states of the “manganese cluster” in natural systems [321, 325]. It can be inferred that charge compensating processes are needed requirements to maintain the oxidation potential of the redox-active catalytic site roughly constant when moving along the various steps of the overall hole accumulating process, an aspect that should be well taken into account in designing new systems.

Recently a mixed Ru–Mn₂ species featuring a photoinduced charge-separation state with an impressive lifetime (0.6 ms at room temperature and 0.1–1 s at 140 K, comparable to many of the naturally occurring charge-separated states in photosynthetic systems) has been reported [334]. The slow charge-recombination rate obtained for such a species has been mainly attributed to the large reorganization energy connected with the inner reorganization of the manganese subunit already mentioned (about 2 eV for the compound in [334]). This would suggest that there is no need to look for charge-recombination processes occurring in the Marcus inverted region to obtain long-lived separated states, since the large inner reorganization energy typical of the manganese systems could lead to the same (or better) result.

5.8

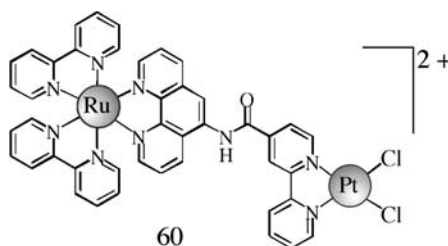
Photocatalytic Processes Operated by Supramolecular Species

5.8.1

Photogeneration of Hydrogen

Since the early papers appeared in the 1970s [335–339], Ru(II) polypyridine complexes have been extensively used to produce hydrogen in heterogeneous cycles under light irradiation, by using sacrificial donor species (most commonly amines), electron acceptor relays (usually methyl viologens), and colloidal metal catalysts (Pt, Rh, etc.). This aspect of Ru(II) photochemistry has been extensively reviewed [1, 340] and will not be discussed in detail here. We will discuss some recent papers in which a (supramolecular) multicomponent approach is used.

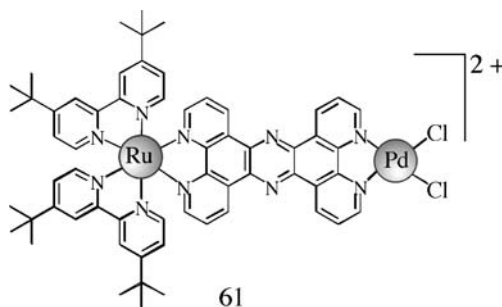
One of the important steps in designing a multicomponent hydrogen evolving system would be to assemble in the same (supramolecular) system as many key components as possible. Key components would be (based on the systems operating in heterogeneous schemes): (a) light-harvesting units (antennae); (b) a charge-separation unit made of a photosensitizer (the energy trap of the antenna, if an antenna is present), an electron acceptor, and an electron donor; and (c) a catalyst [280, 297, 341–345]. The compound **60** [346]



is a quite interesting example toward the preparation of functional supramolecular species of this type, where all the key components would be integrated into a single multicomponent system. Under visible irradiation, **60** evolves molecular hydrogen from water (in the presence of EDTA as sacrificial donor) with an efficiency of about 1%. A relatively low turnover number (4.8) is estimated on the basis of the total amount of H_2 evolved after 10 h ($2.4 \mu\text{mol}$) and the amount of the complex used ($1 \mu\text{mol}$). The hydrogen formation is immediate and is rather higher in its rate when UV light is eliminated by suitable filters. This latter observation suggests some photoinstability of the system upon UV irradiation.

The wavelength dependence in the visible region of the rate of H_2 formation agrees with the absorption spectrum of the complex. Moreover, the rate of H_2 formation increases linearly with the photon flux, indicating that one-photon excitation of the molecule operates. This multicomponent system integrates in its structure the light harvester/photosensitizer (the Ru(II) chromophore) and the electron acceptor, which also plays the role of the catalyst (the Pt(II) subunit). Compared to the formerly investigated systems [1, 335–337, 339, 456], neither the electron relay (usually a methyl viologen species) or the solid-state catalyst (usually colloidal platinum or rhodium) are required. Mechanistic aspects have not been discussed yet.

Another multicomponent system (**61**) has been recently reported [347]. When excited at 470 nm in acetonitrile and in the presence of triethylamine (TEA, 2.08 mol L^{-1}), such a species evolves H_2 from the solution with a turnover number of about 50 (mol of H_2 per mol of compound). No H_2 evolution is ob-



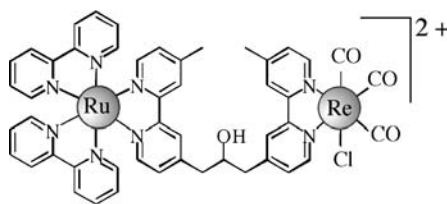
tained in the dark or when one of the key components (the Ru(II) chromophore, the Pd catalyst, or the particular bridging ligand) is missing. Interestingly, the same compound where the bridging ligand between the two metal sites is a bipyrimidine unit does not evolve molecular hydrogen. It is also reported that the amount of photocatalytically formed hydrogen depends strongly on the TEA concentration and the exposure time, and chloride ions inhibit the reaction. The amount of hydrogen produced increases steadily and levels off after 1200 min. After about 1800 min no more hydrogen is produced. The rate of hydrogen formation increases with increasing TEA concentration for low TEA concentration, but becomes independent at a TEA concentration $> 0.86 \text{ mol L}^{-1}$, where it is about $1600 \text{ nmol min}^{-1}$. Although detailed mechanistic data are not available, the authors suggest as a first step of the process a twofold photoinduced reduction of the compound by TEA, analogously to what was reported for the related photoinduced electron collection system **51**. Probably reduction is concomitant with proton extraction from TEA oxidation products: TEA should therefore be the proton source. The successive step should be reduction of the protons at the nearby Pd center. This latter step probably passes through a temporary chloride loss. The same paper also reports the photocatalyzed selective hydrogenation of tolane to *cis*-stilbene, accomplished by the same compound. Analogously to **60**, the Ru(II) chromophore of **61** acts as the light harvester/photosensitizer (which also contains in its structure the electron acceptor subunit, that is, the phenazine moiety of the bridging ligand), while the role of the catalytic unit is here played by the Pd(II) center.

Molecular hydrogen evolution under visible light irradiation has also been reported for trimetallic species like **53** [348]. Mechanistic details are not available.

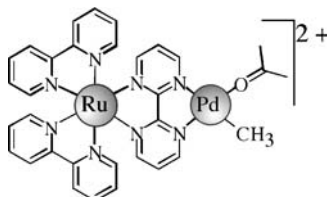
5.8.2

Other Photocatalytic Systems

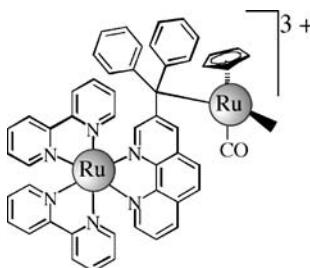
The catalytic potential of heterometallic species containing Ru(II) and Re(I) chromophores for the conversion of CO_2 to CO has been recently shown [349]. Compound **62** is one of the species in this regard. This investigation highlighted the fact that the photocatalytic activity is deeply influenced by the nature of both the bridging ligand and the peripheral ligands at the light-harvesting Ru(II) chromophore. The proposed mechanism is that upon light irradiation ($\lambda > 480 \text{ nm}$) in DMF/triethanolamine (TEOA, acting as base) with 1-benzyl-1,4-dihydronicotinamide (BNAH) as sacrificial donor, the initially produced Ru-based MLCT state is reduced by BNAH. Then intrabridging ligand electron transfer occurs, with formation of the reduced rhenium subunit. This latter species is known to react with CO_2 upon Cl ligand loss [350, 351]. The reduction of CO_2 is bielectronic, so it is assumed that the second electron transfer follows a similar route. The most efficient species of this series of compounds, which is exactly **62**, exhibits a turnover number of 170.



62



63



64

Two other dinuclear species (**63** and **64**) have been reported to show photocatalytic activity for specific reactions. The Ru–Pd dimer **63** is active for the photocatalytic dimerization of 1-methylstyrene [352], and the turnover numbers of the photocatalyzed reaction (> 90 within 4 h) and the high selectivity compete well with thermal catalytic systems. Compound **64** is active for the conversion of *trans*-4-cyanostilbene to its *cis* form [353]. Other aspects of the last mentioned works and of similar systems are also commented on in a very recent paper [354]. Photocatalytic processes based on photoelectrochemical cells in which the Ru chromophores are physically interfaced to electrodes or other solid systems are reported later.

5.9

Photoactive Molecular Machines Able to Perform Nuclear Motions

In the last 10 years there has been great interest in designing molecular machines [280]. As machines of the macroscopic world, even molecular machines need energy to operate, and a suitable form of energy to power

molecular machines is light. It is therefore almost obvious that several photoactive molecular machines containing Ru(II) polypyridine complexes as the photoactive subunits have been prepared and studied. For an exhaustive discussion, the reader should consult [355–358]. A recent outstanding example [359] is discussed Balzani et al. 2007, in this volume [119].

We mention here the case of photoinduced ring motion in the catenane **65** [360], illustrated in Fig. 17. Visible light excitation of this compound in acetonitrile leads to population of the MLCT triplet state and subsequent formation (via thermal activation) of the MC state which causes the decoordination of the sterically hindered bpy-type ligand. As a result, swinging of the bpy-containing ring occurs, and the catenane structure made of discon-

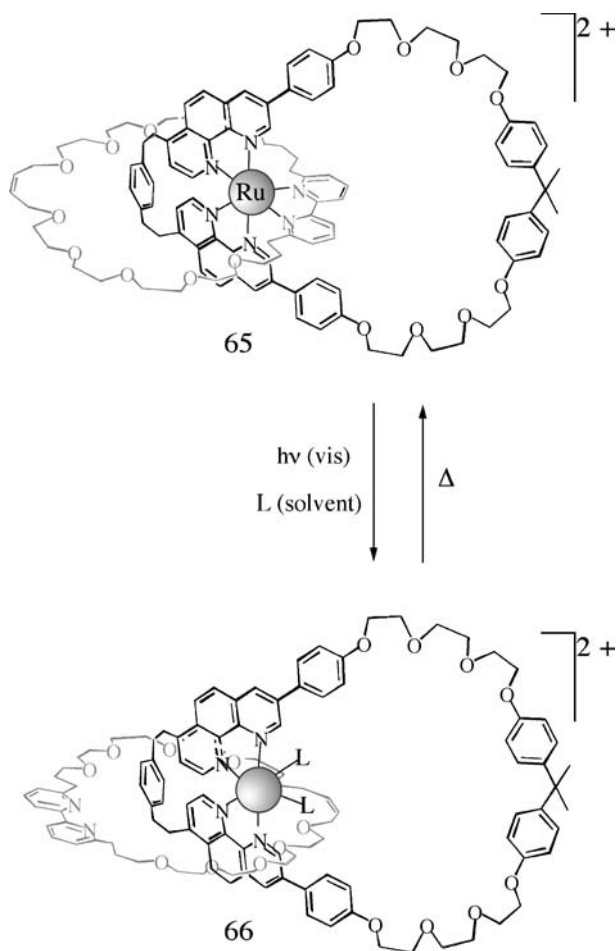


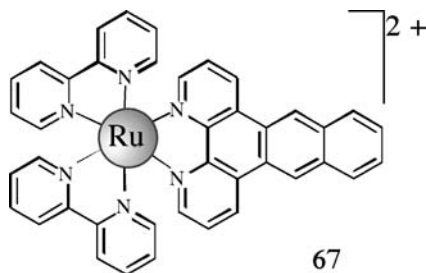
Fig. 17 Structural formula and photochemically and thermally induced motions of a Ru(II) catenane complex

nected rings is obtained (**66**). Heating regenerates the starting catenane. The process can be repeated at will, since both the reactions (coordination and decoordination) are quantitative. It can be noted that in this system the photostitution process, usually considered as an undesired property for Ru(II) complexes, is instead used to perform the desired function. More recently, light-induced motion on a rotaxane system has also been obtained by using the same strategy [361].

6

Ruthenium Complexes and Biological Systems

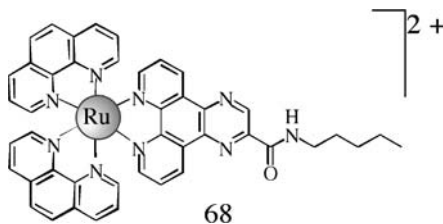
The effects of the interaction of photoactive ruthenium complexes with biological structures have been extensively studied. Because of the outstanding excited-state properties of Ru(II) polypyridine complexes, these systems have been employed as probes of biological sites, as well as photocleavage agents and, in recent times, as inhibitors of biological functions [362–369]. Among the species used as luminescent probes, one of the most studied compounds in the last 15 years is **67** [200–204, 362–379]. This complex is very weakly emissive in aqueous solution, but becomes strongly emitting in the presence of DNA, giving rise to the so-called light-switch effect [200, 201]. The reason for such a behavior lies in the electronic properties of this specific chromophore and in the intercalation ability of the dipyrido[3,2-*a*:2',3'-*c*]phenazine (dppz) ligand. In this species, there are several triplet excited states quite close in energy: (1) a MLCT state directly populated by light excitation, in which the excited electron resides in the LUMO+1 centered on the “bpy-like” portion of dppz ligand; (2) a MLCT state in which the excited electron is located in the LUMO centered on the “phenazine-like” portion of the dppz ligand; and (3) a ligand-centered (dppz-based) excited state. This compound represents another example of interplay between multiple MLCT states, discussed in more detail in Sect. 4.4. The energy gap and order of the three low-lying excited states mentioned above, as well as their dynamics, can be modulated by various parameters, including solvent dielectrics, protic ability of the solvent, and hydrophobic interactions. In a simplified schema-



tization, in aqueous solution the dominant (lowest energy) excited state is the MLCT involving the phenazine-like dppz subunit (populated by a sort of “charge shift” decay from the directly excited MLCT level), which deactivates largely by nonradiative processes. When the complex interacts with DNA, the MLCT state involving the bpy-like dppz subunit becomes dominant, and since such a state has better luminescent properties, the luminescence of the complex is switched on. Looking in more detail, the interplay among the various states, in this and related species and in the absence and presence of DNA, is more complicated, as demonstrated by various theoretical [379] and experimental techniques, including transient absorption femtosecond spectroscopy [370, 371, 378, 380, 381] and time-resolved resonance Raman spectroscopy [372, 373, 382]. Details can be found in the original references.

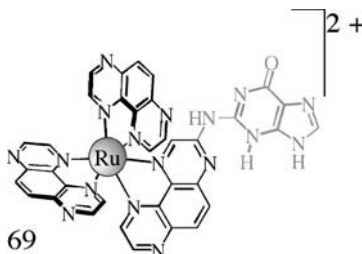
Besides **67**, many other Ru(II) polypyridine complexes have been reported to exhibit luminescence enhancement in the presence of DNA. In most cases, the luminescence enhancement is moderate and can be assigned to the protection offered toward oxygen quenching by DNA structures to the surface-attached Ru(II) complex (which can bind, essentially for electrostatic reasons, to the major or minor grooves). If the interaction is limited to surface binding, the luminescence enhancement is usually within 20–40% in the presence of oxygen, whereas it is negligible in deoxygenated samples. Several compounds, however, exhibit noticeable luminescence enhancement (one order of magnitude or higher): in most of these cases, the compounds quite often have a ligand with a large, flat framework and intercalation takes place. The compound **68** [383], which is nonemissive in water solution and strongly emissive in organic solvents ($\lambda = 610$ nm; $\tau = 1.1$ μ s; $\Phi = 0.12$) is an exception. In water, the presence of DNA switches the luminescence on. The authors suggest that in water solvent-specific interactions with the amido moiety promote radiationless decay of the (potentially) emitting MLCT state, and that the protection offered by DNA versus solvent interaction restores MLCT emission.

Ru(II) complexes whose luminescence is significantly quenched in the presence of DNA have also been reported. Usually, the excited state of these species is a very good oxidant, and photoinduced reductive electron transfer involving guanine residues is responsible for the luminescence quenching [362, 369, 384]. In some cases, it has been proposed that the quenching



process can occur via photoinduced proton-coupled electron transfer with guanosine-5'-monophosphate.

Besides being used as luminescent probes, ruthenium complexes have been reported to form photoadducts with DNA and other species of biological relevance. The most studied photoadducts are probably the ones formed by Ru(II) complexes containing 1,4,5,8-tetraazaphenanthrene (TAP) as ligand and guanine residues on DNA strands (see for example **69**) [386]. The mechanism of photoadduct formation has been extensively investigated. The initially formed MLCT state undergoes reductive electron transfer from guanine. This process is followed by fast formation of a covalent bond between the electron donor and acceptor, which leads to an adduct between the metallic complex and the nucleobase [386]. Such photoadduct formation has also been used to induce photocrosslinks between two nucleotide strands when one of the strands was chemically derivatized by the photoreactive metal complex and the complementary strand contained a guanine base in the proximity of the tethered complex [387]. The necessary requirement for this photoreaction to occur is a MLCT excited state which is a very strong oxidant, as guaranteed by the TAP ligand.



More recently, a photoadduct between similar Ru complexes and the amino acid tryptophan have also been reported [388]. The authors mention that this photoreaction appears very promising for a wide range of applications to peptides and proteins.

Ru(II) complexes have also been inserted into synthetic oligonucleotides to obtain specific information on the properties of DNA strands and/or to prepare particular (super)structures [389–393]. For example, Ru(II)-derivatized oligonucleotides have been used to investigate the distance dependence of the quenching of suitable Ru luminescence by guanine residues [393]. Oligonucleotide conjugates containing Ru(II) polypyridine units as photosensitizers have also been reported to induce photodamage on single-stranded DNA sites [394].

The potential of Ru(II)-derivatized oligonucleotides has been explored to synthesize novel, interesting, and beautiful nanometer-sized luminescent structures in which the DNA strands act as templates and the Ru complexes act as both template and photoactive units [395–397], giving rise to

3D-networked structures. In these systems, the Ru(II) polypyridine subunits carry their own photoluminescence properties in the networked assemblies.

Finally, it has been demonstrated that the photoexcitation of suitable Ru(II) complexes can inhibit biological functions; for example, in Ru(II)-labeled oligonucleotides DNA polymerase is inhibited by a photocrosslinking process [387]. On the basis of these and similar results, which indicate strong and even complete inhibition of gene transcription by photoexcited Ru(II) complexes [398], it has been proposed that properly designed compounds can be ideal candidates for a phototherapy with implemented fiber-optic light source [398–400]. It should be noted that the photoactivity of Ru(II) complexes for phototherapy does not depend on the presence of oxygen: this could represent a real advantage as compared to other dyes used in photodynamic therapy [398].

7

Dye-Sensitized Photoelectrochemical Solar Cells

One of the most important developments involving Ru(II) polypyridine complexes in the last two decades is related to the design of dye-sensitized photoelectrochemical solar cells, which have outstanding properties for application in the field of solar energy conversion, in particular photovoltaics. Since their appearance in the early 1990s [401, 402], dye-sensitized photoelectrochemical solar cells based on the principle of sensitization of wide-bandgap mesoporous semiconductors have indeed attracted the interest of the scientific community, due to their performances which started the vision of a promising alternative to conventional junction-based photovoltaic devices. For the first time a solar energy device operating on a molecular level showed the stability and the efficiency required for potential practical applications. In the last few years, several excellent review articles have been published in this field [403–405]. These articles indicated that research on dye-sensitized solar cells is strongly multidisciplinary, involving areas such as nanotechnology, materials science, interfacial electron transfer, and supramolecular photochemistry and electrochemistry [405]. Here we mention the main basic aspects and describe a few of recent Ru(II) photosensitizers which exhibit quite interesting performances.

7.1

General Concepts

The principle of dye sensitization of semiconductors can be traced back to the end of the 1960s [406]. However, the practical use of these systems was limited for a long time because the efficiencies obtained with single-crystal substrates were too low due to the poor light absorption of the adsorbed

monolayer of dye molecules. The breakthrough in the field was brought about by the introduction of mesoscopic films made of sintered nanoparticles of a semiconductor metal oxide with a large surface area, which allowed the adsorption, at monolayer coverage, of a much larger number of sensitizer molecules leading to absorbance values, of thin films of a few microns, well above unity [407].

Wide-bandgap semiconductor materials such as TiO_2 show a separation between the energy levels of the valence and conduction bands of the order of 3 eV, which means that the electron-hole pair needs to be produced by irradiation with light having a wavelength shorter than 400 nm, i.e., UV light. In order to use sunlight, mainly visible and near-IR, two general approaches have been developed: doping and molecular sensitization. The doping approach is the preferred choice for conventional photovoltaic devices [405]. Dye-sensitized photoelectrochemical cells rely on photosensitization. In this process, a photoexcited species, the sensitizer (S), is capable of injecting an electron into the conduction band (CB) or a hole into the valence band (VB) of the semiconductor (Fig. 18).

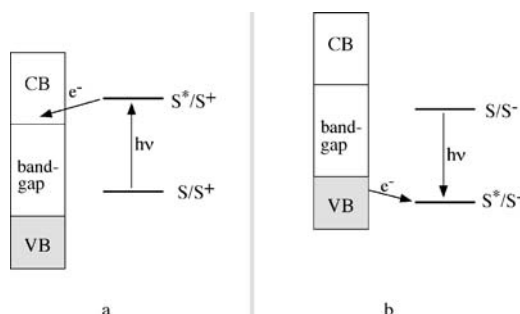


Fig. 18 Schemes for sensitized charge injection in the photoelectrochemical solar cells: **a** electron injection, **b** hole injection

In fact, when the excited-state energy level of the sensitizer is higher with respect to the bottom of the conduction band, an electron can be injected with no thermal activation barrier in the semiconductor, leaving the sensitizer in its one-electron oxidized form (Fig. 18a). When the excited state is lower in energy with respect to the top of the valence band, an electron transfer (formally a hole transfer) between the semiconductor and the sensitizer can take place, leaving the molecule in its one-electron reduced form (Fig. 18b) [408].

The operation of a dye-sensitized solar cell is schematized in Fig. 19 [403, 405]. The system is comprised of two facing electrodes, a photoanode and a counter electrode, with an electrolyte in between. The transparent conductive photoanode is covered with a thin film (7–10 μm) of a mesoporous

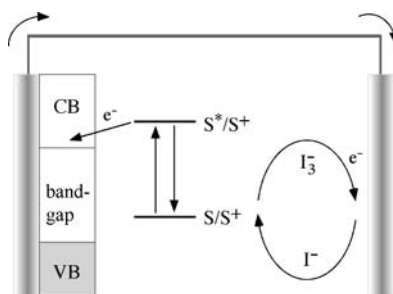
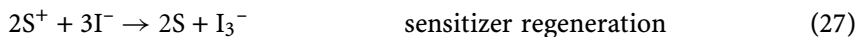


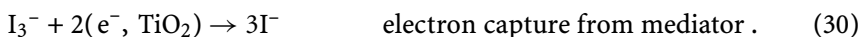
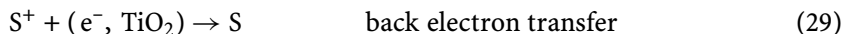
Fig. 19 Schematic operation principle of a dye-sensitized solar cell

semiconductor oxide obtained via a sol-gel procedure. Dye coverage of semiconductor nanoparticles is generally obtained from alcoholic solutions of the sensitizer, in which the sintered film is left immersed for a few hours. Sensitizers are usually designed to have functional groups such as $-\text{COOH}$, $-\text{PO}_3\text{H}_2$, or $-\text{B}(\text{OH})_2$ for stable adsorption onto the semiconductor substrate. The dye-covered film is in intimate contact with an electrolytic solution containing a redox couple dissolved in a suitable solvent. The electron donor member of the redox couple must reduce quickly and quantitatively the oxidized sensitizer, so closing the circuit. A variety of solvents with different viscosity and of redox mediators have been the object of intense studies, the most commonly used being the couple I_3^-/I^- in acetonitrile or methoxypropionitrile solution. The counter electrode is a conductive glass covered with a few clusters of metallic platinum, which has a catalytic effect in the reduction process of the electron mediator. Further details on the cells and on their preparation can be found in the literature [403–405].

The complete photoelectrochemical cycle of the device can be outlined as follows. The adsorbed sensitizer molecules (S) are brought into their excited state (S^*) by photon absorption and inject one electron into the empty conduction band of the semiconductor in a timescale of femtoseconds. Injected electrons percolate through the nanoparticle network and are collected by the conductive layer of the photoanode electrode, while the oxidized sensitizer (S^+) in its ground state is rapidly reduced by I^- ions in solution. Photoinjected electrons flow in the external circuit where useful electric work is produced and are available at the counter electrode for the reduction of the electron mediator acceptor I_3^- . The entire cycle consists in the quantum conversion of photons to electrons.



Photoinjected electrons should escape from any recombination process in order to have a unit charge collection efficiency at the photoelectrode back contact. The two major waste processes in a dye-sensitized solar cell are due to (1) back electron transfer, at the semiconductor/electrolyte interface, between electrons in the conduction band and the oxidized dye molecules (Eq. 29), and (2) reduction of the electron relay (I_3^- , in this case) at the semiconductor nanoparticle surface (Eq. 30).



A detailed knowledge of all the kinetic mechanisms occurring in a photoelectrochemical cell under irradiation is an essential feature toward optimization of the process.

7.2

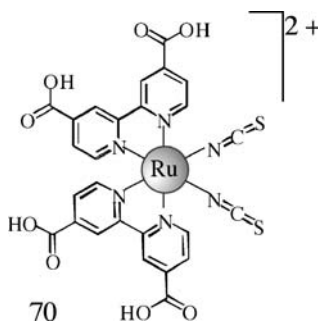
Ruthenium-Sensitized Photoelectrochemical Solar Cells

A major breakthrough in the field relied on the performance of dye-sensitized solar cells employing Ru(II) complexes as sensitizers [401–405, 409–411]. Several reasons are at the basis of the success of Ru(II) polypyridine complexes in playing this leading role:

1. Strong absorption throughout all the visible region, which can also extend to the near-IR. This result is obtained by means of intense MLCT bands due to a judicious choice and combination of ligands [1].
2. Strong electronic coupling between the MLCT excited state of the chromophore and the semiconductor conduction band. To fulfill this requirement, it has to be noted that the polypyridine ligand connected to the semiconductor via suitable functionalization of the ligand (usually carboxylated ligands) must be that involved in the lowest-lying MLCT state.
3. Tunability of the excited-state redox properties. This allows the preparation of compounds whose excited-state oxidation potential can ensure an efficient electron injection in the semiconductor conduction band. In this regard, it should be considered that to estimate a “reduction potential” (E_{cb}) for the semiconductor conduction band is not an easy task [404, 412–414], and in nonaqueous solvents adsorption of cations, which are present as electrolytes, also has a significant effect on E_{cb} values. For example, E_{cb} for nanostructured TiO_2 has been reported to be -1.0 V vs SCE in $0.1\text{M LiClO}_4/\text{acetonitrile}$ and about -2.0 V when Li^+ cations are replaced by tetrabutylammonium [413, 414].
4. Stability of the Ru(II) polypyridine complexes, in the ground state as well as in the excited and redox states. However, it is useful to note that photostability is not a strict requisite here, since the excited state is rapidly deactivated by electron injection. The same applies to chromophores hav-

ing intrinsic short excited-state lifetimes, provided that their intrinsic lifetime (that is, the reverse of the summation of the radiative and radiationless decay of the “isolated” chromophores) does not compete with the timescale for photoinjection.

The electronic coupling between MLCT states and TiO_2 conduction band is so efficient that electron injection takes place in the ultrafast regime. In particular, for the complex $[\text{Ru}(\text{dcbpy})_2(\text{NCS})_2]$ (dcbpy = 4,4'-carboxylbipyridine), also called N3 or “red dye” (70), biphasic kinetics was reported for photoinduced electron injection [266, 267, 270]: the first ultrafast component was estimated to have a risetime of 28 fs and the slower component was reported to occur within the 1–50 ps time range [270, 271]. This behavior was initially interpreted on the basis of a two-state mechanism, the fast and slow components being attributed to injection from the MLCT singlet and triplet states, respectively. Also, the singlet-state injection was from nonthermalized vibronic states. Whereas injection from the singlet state was later confirmed (although with risetime slightly different, shorter than 20 fs), the origin of the picosecond component has been questioned: it has been recently proposed that such a “slow” component of electron injection arises from sensitizer molecules which are loosely attached to the semiconductor or are present in aggregated forms [271].



Dozens of $\text{Ru}(\text{II})$ complexes have been explored as sensitizers in dye-sensitized solar cells of this type. We mention here some of the species exhibiting the best performances. The above mentioned N3 complex has very interesting properties: it shows a photoaction spectrum dominating almost the entire visible region, with incident photon-to-current conversion efficiency (IPCE) of the order of 90% between 500–600 nm. Short-circuit photocurrents exceeding 17 mA/cm^2 in simulated A.M. 1.5 sunlight and open-circuit photovoltages of the order of 0.7 V were obtained by using the couple I_3^-/I^- as redox electrolyte [415]. For the first time a photoelectrochemical device was found to give an overall conversion efficiency of 10%. These performances, in part expected for the high reducing ability of the $^3\text{MLCT}$ state (ca. -1 eV vs SCE) and the positive ground-state oxidation potential ($+0.85 \text{ eV}$

vs SCE), contrast with the lower IPCE observed for other sensitizers having comparable ground- and excited-state properties [416]. It has been suggested that a peculiar molecular level property of the *cis*-[Ru(dcbpy)₂(NCS)₂] complex could affect one of the key processes of the cell mechanism. This view is consistent with the results of photoelectron spectroscopy and INDO/S calculations indicating that the Ru d orbitals interact strongly with the π orbitals of NCS, resulting in MOs of mixed nature [417]. In particular, the calculations show that the sulfur 3p orbitals give a considerable contribution to the HOMO of the complex. Hole delocalization across the NCS ligands can thus be responsible for an increased electronic matrix element for the electron transfer reaction involving TiO₂/Ru^{III}NCS and I⁻. This would lead to an increase of the rate constant of the reductive process, and as a consequence of IPCE.

Even better photoelectrochemical performances, compared to those given by the complex [Ru(dcbpy)₂(NCS)₂], are featured by a species based on the terpyridine ligand [418]: TiO₂ electrodes covered with the complex [Ru(L)(NCS)₃] (L = 4,4',4''-tricarboxy-2,2':6',2''-terpyridine) display very efficient panchromatic sensitization covering the whole visible spectrum and extend the spectral response at the near-IR region up to 920 nm, with maximum IPCE values comparable to that obtained with the dithiocyanate complex. Another species based on a substituted terpyridine is the mixed ligand complex [Ru(HP-terpy)(dmb)(NCS)], where P-terpy = 4-phosphonato-2,2':6,2''-terpyridine and dmb = 4,4'-dimethyl-2,2'-bipyridine [419]. A quantitative study of dye adsorption on TiO₂ has shown that complexes containing the phosphonated terpyridine ligand adsorb more efficiently and strongly, giving an adsorption constant about 80 times larger than that for the dicarboxy bipyridine compounds. Since one of the problems encountered with the carboxy polypyridine class of sensitizers is the desorption from the semiconductor surface in the presence of water, the search for new anchoring groups is advisable. Along this line of research, complexes based on the derivatization of 2,2'-bipyridine with a phenylboronic functionality were prepared. The photoaction spectra of TiO₂ electrodes sensitized with the [Ru(4-phenylboronic-2,2'-bipyridine)₂(CN)₂] complex showed IPCE values comparable to those observed for [Ru(dcbH₂)₂(CN)₂], indicating that the new type of linkage does not reduce the electronic coupling between sensitizer and semiconductor [405].

7.3

Supramolecular Sensitizers

Besides mononuclear Ru(II) complexes, multinuclear (supramolecular) compounds, as well as chromophore-acceptor or chromophore-donor dyads made of Ru(II) species and organic quenchers, have been used as sensitizers. There are several aims that inspired the design of such systems:

1. To increase the absorption properties of the (multicomponent) sensitizer, by using systems featuring the antenna effect, with the energy trap of the antenna being the Ru(II) unit directly connected to the semiconductor. One example is the trinuclear Ru(II) species **71** shown in Fig. 20; in **71**, the light absorbed by the peripheral Ru(II) chromophores is transferred quantitatively to the central Ru(II) chromophore, from which electron injection takes place [420]. Experiments on this complex adsorbed on polycrystalline TiO₂ gave an overall conversion efficiency of ca. 7% with turnover numbers of at least 1×10^6 . The antenna effect is expected to be of relevance for applications requiring very thin TiO₂ layers.
2. To spatially separate the injected electron and the hole on the sensitizer, so decreasing losses due to charge recombination. A system designed for this aim (**72**) is shown in Fig. 21, where the possible electron transfer steps are indicated [421]. In **72**, the MLCT state of the Ru(II) unit is rapidly quenched by the Rh(III) species (step k_1 in Fig. 21), followed by injection of the electron onto the semiconductor conductance band from the reduced Rh unit (step k_2 , in competition with step k_4). The recombination process (k_5) is slow because of a very weak electronic coupling. To reach the same aim, the species **73** shown in Fig. 22 has been designed [422]. Here, the first step is the electron injection from the Ru unit. Then, electron transfer from the phenothiazine unit to the oxidized Ru unit takes place, resulting in a charge-separated species which decays to the ground state with a rate of $3.6 \times 10^3 \text{ s}^{-1}$ (lifetime, 0.3 ms). The dyad and model molecules were also tested in solar cells, with iodide as an electron donor. While the observed IPCE was of the order of 45% for both systems, the open circuit photovoltage was higher for the dyad by 100 mV. The effect was more pronounced in the absence of iodide with $V_{oc} = 180 \text{ mV}$. Applying the measured interfacial electron transfer rates to the diode equation

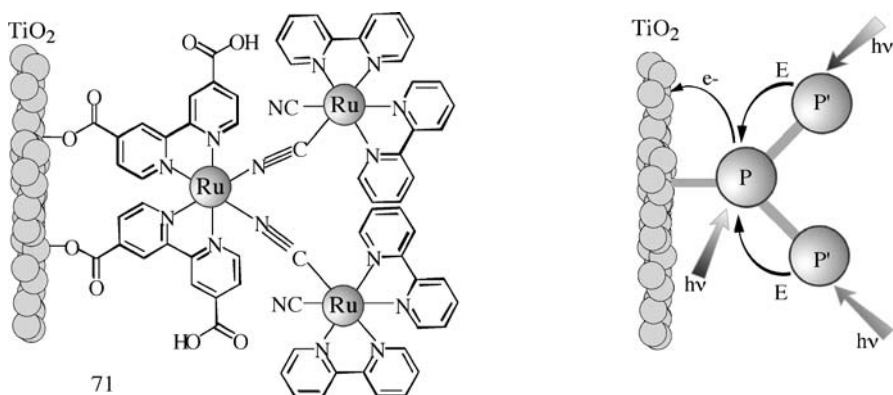


Fig. 20 Structural formula of a branched antenna system and schematization of energy transfer and charge injection in TiO₂. Complex charge is omitted for clarity

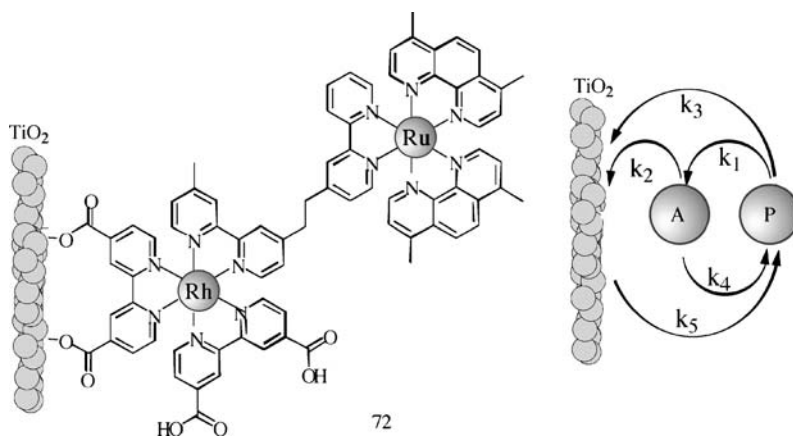


Fig. 21 Structural formula of a linear antenna system and schematization of energy transfer and charge injection in TiO_2 . Complex charge is omitted for clarity

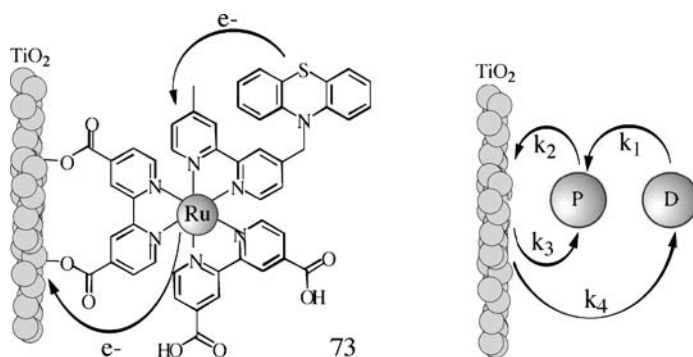
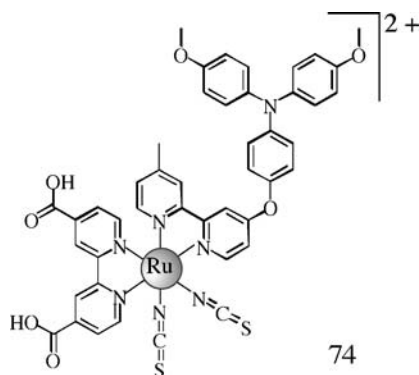


Fig. 22 Structural formula of $\text{TiO}_2/\text{Ru-PTZ}$ heterotriad system and schematization of the electron transfer steps. Complex charge is omitted for clarity



74

gave the predicted increase of V_{oc} of 200 mV, which was in agreement with the obtained value (180 mV) [422]. It is interesting that an increase of the lifetime of the interfacial charge-separated state $TiO_2(e^-)-Ru(II)-PTZ^+$ has a direct influence on the overall efficiency of the cell. A similar approach inspired the design of the supramolecular species **74**, based on the “red dye” N3 sensitizer. Optical excitation of a nanocrystalline TiO_2 film dye coated with such a species showed a long-lived charge-separated state [423].

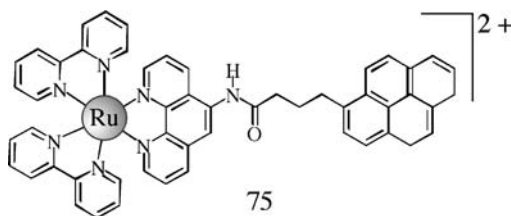
8

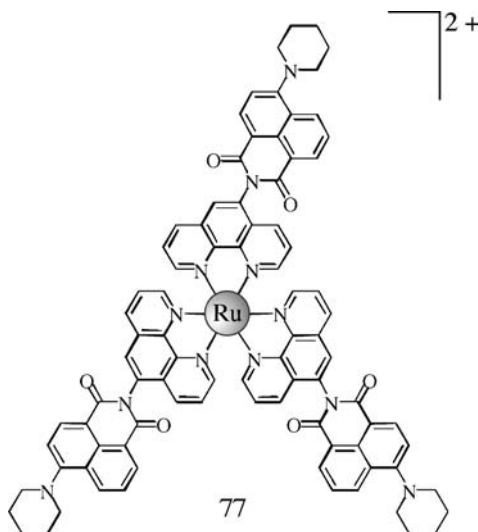
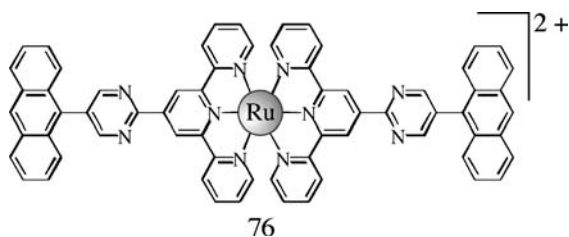
Miscellanea

The fields that have been recently powered by Ru photochemistry are much more than those reported in some detail in this article. A few of those that are not discussed above will be briefly mentioned.

Ru(II)-based chromophores have been linked to a plethora of receptor species, like calixarenes, crowns, and azacrowns, essentially for sensing purposes [280, 424, 425]. Ru(II) chromophores have also been embedded in oxygen-permeating polymers to yield luminescent sensors for molecular oxygen determination in atmosphere [426–429]. New systems have been designed and studied for obtaining OLED materials. In this regard, a dinuclear Ru complex has been used in conjunction with an organic luminophore to generate two-color electroluminescence [430].

Multichromophoric species made of Ru(II) chromophores interfaced with organic aromatics having suitable triplet-state levels have been studied to extend the lifetime of the MLCT excited state by a sort of delayed luminescence involving intercomponent energy transfer, with the organic triplet states used as excited-state energy storage systems [431–440, 442]. A few such species are compounds **75** (which is the first reported example of such a behavior [431]), **76** [437], and **77** [435]. Compound **77** is one of the species featuring the most outstanding behavior: its emission in fluid solution at room temperature (with maximum at about 600 nm) has lifetimes ranging from 43 μs (acetone solution) to 61 μs (acetonitrile) to 115 μs (DMSO solution) [435]. With the aim of increasing the excited-state lifetime as well as the luminescence





quantum yield, a goal which is missed by the formerly mentioned multichromophoric species, several Ru(II) chromophores having polypyridine ligands able to feature extended electron delocalization in their structure have been prepared [441]. In this case, the improved photophysical properties are due to reduced Franck–Condon factors for radiationless decay, a consequence of extended delocalization of the emitting MLCT state [78, 157, 443–446]. A typical example is the compound 78 shown in Fig. 23 [445]. In 78, in spite of the quite low emission energy at room temperature (820 nm), a relatively long luminescence lifetime and high quantum yield are found (420 ns and about 0.01, respectively).

Hydrogen-bonded or, generally, noncovalently linked supramolecular species exhibiting photoinduced electron and/or energy transfer have also been prepared to mimic natural systems (see, for example, 79–81) [447–452]. Efficient intercomponent energy transfer through the noncovalently linked frameworks is usually obtained. However, in some cases the interest in the potential application of these systems is reduced by the small value of the association constants.

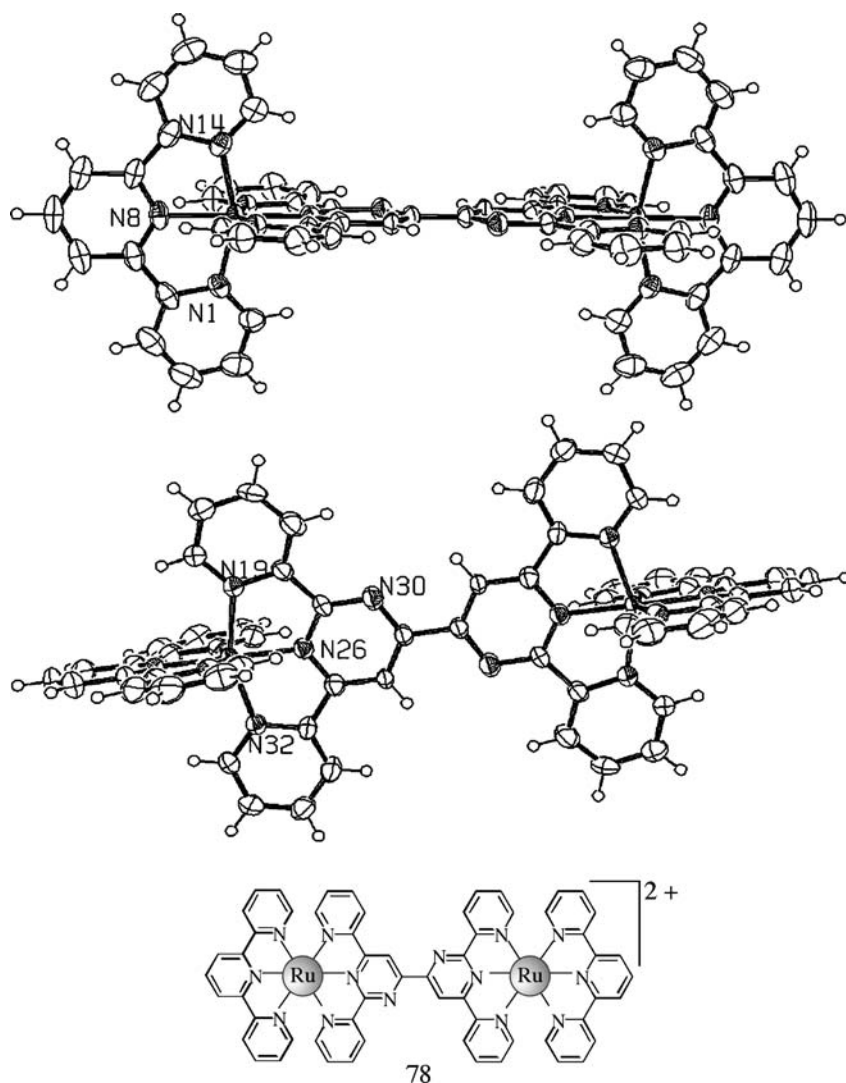
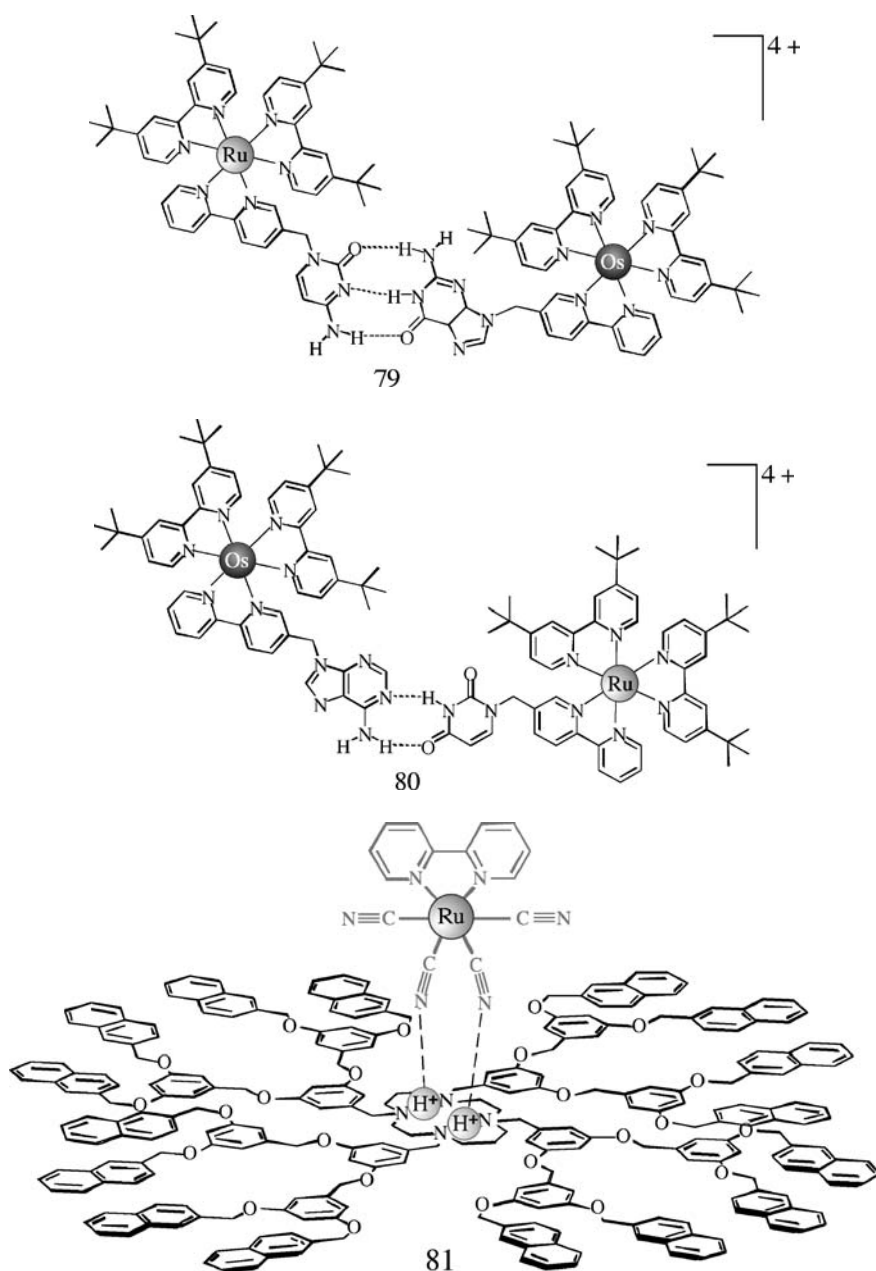


Fig. 23 Thermal ellipsoid views and structural formula of a dinuclear Ru(II) complex

Multiple emissions from Ru(II) polypyridine complexes have been reported. Besides multiple emission connected to supramolecular species featuring nonquantitative interchromophoric energy transfer (a relatively common and in some way an expected behavior), in some cases multiple emission from the same Ru(II) subunit has also been proposed at room temperature [453]. This behavior has not been fully explained yet.

Many efforts have aimed to take advantage of the photophysical properties of Ru(II) chromophores in electropolymerized thin film structures and



in SiO_2 -based sols-gels [342]. In some cases, these solid-interfaced systems allowed interesting photocatalytic results to be obtained, such as (1) the dehydrogenation of 2-propanol to acetone and molecular hydrogen, obtained in a photoelectrochemical cell in which a dinuclear Ru complex is adsorbed

to TiO_2 [454], and (2) the dehydrogenation of hydroquinone to quinone, by means of two Ru chromophores coadsorbed on TiO_2 at the anode of a photoelectrochemical cell, with molecular hydrogen produced at a platinized-platinum cathode [455]. These fields have been recently reviewed and several details can be found in [342]. Quite recently photoinduced charge transfer between CdSe nanocrystal quantum dots and Ru(II) complexes has also been reported [456].

Interesting results, from the photocatalysis point of view, have been reported for other heterogeneous systems. For example, the sensitization of platinized layered metal oxide semiconductors with Ru(II) polypyridine dyes enabled photolysis of aqueous hydrogen iodide to molecular hydrogen and triiodide using visible light [457–459]. Photocatalytic water oxidation has been accomplished with good efficiency in a system based on $[\text{Ru}(\text{bpy})_3]^{2+}$ as the photosensitizer and using a colloidal solution of IrO_2 as a catalyst [460, 461].

Ru(II) polypyridine complexes containing ligands which can be protonated/deprotonated have been extensively studied. Interesting effects of electronic coupling between metal centers in dinuclear systems with protonable/deprotonable bridging ligands have been reported [462–464], as well improved emissive properties in $\text{Ru}(\text{terpy})_2$ -like complexes [188]. Quite interesting light-controlled electronic coupling between the Ru(II) centers of dinuclear systems has also been obtained by inserting photoisomerizable subunits with the bridging ligands [465, 466].

Finally, the recently published X-ray time-resolved spectra of $[\text{Ru}(\text{bpy})_3]^{2+}$, obtained by different techniques [467–469], warrants recalling. These studies give information on the structural changes induced by excitation. Interestingly, they confirm the very small distortion of the $^3\text{MLCT}$ state in comparison with the ground state, as formerly predicted on the basis of other experimental results and theoretical arguments.

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References

1. Juris A, Balzani V, Barigelletti F, Campagna S, Belser P, von Zelewsky A (1988) *Coord Chem Rev* 84:85
2. Balzani V, Juris A, Venturi M, Campagna S, Serroni S (1996) *Chem Rev* 96:759
3. Sauvage JP, Collin JP, Chambron JC, Guillerez S, Coudret C, Balzani V, Barigelletti F, De Cola L, Flamigni L (1994) *Chem Rev* 94:993
4. Meyer TJ (1986) *Pure Appl Chem* 58:1193
5. Crosby GA, Watts RJ, Carstens DHW (1970) *Science* 170:1195
6. Crosby GA (1975) *Acc Chem Res* 8:231

7. Demas JN (1983) *J Chem Educ* 60:803
8. Chen Y, Meyer TJ (1998) *Chem Rev* 98:1439
9. Crosby GA (1976) *Adv Chem Ser* 150:149
10. Kober EM, Meyer TJ (1982) *Inorg Chem* 21:3967
11. Mandal K, Pearson TLD, Krug WP, Demas JN (1983) *J Am Chem Soc* 105:701
12. Rillema DP, Jones DS, Levy HA (1979) *J Chem Soc Chem Commun*, p 849
13. Orgel LE (1961) *J Chem Soc* 3683
14. Kalyanasundaram K (1982) *Coord Chem Rev* 46:159
15. Seddon EA, Seddon KR (1984) *The chemistry of ruthenium*, chap 15. Elsevier, Amsterdam
16. Watts RJ (1983) *J Chem Educ* 60:834
17. Balzani V, Carassiti V (1970) *Photochemistry of coordination compounds*. Academic, London
18. Adamson AW (1983) *J Chem Educ* 60:797
19. Fleischauer PD, Fleischauer P (1970) *Chem Rev* 70:199
20. DeArmond MK, Carlin CM (1981) *Coord Chem Rev* 36:325
21. DeArmond MK, Hanck KW, Wertz DW (1985) *Coord Chem Rev* 64:65
22. Ohsawa Y, DeArmond MK, Hanck KW, Morris DE (1983) *J Am Chem Soc* 105:6522
23. Ohsawa Y, Whangho MH, Hanck KW, DeArmond MK (1984) *Inorg Chem* 23:3426
24. Morris DE, Hanck KW, DeArmond MK (1983) *J Am Chem Soc* 105:3032
25. Elliott CM (1980) *J Chem Soc Chem Commun*, p 261
26. Heath GA, Yellowlees LJ, Braterman PS (1982) *Chem Phys Lett* 92:646
27. Ohsawa Y, DeArmond MK, Hanck KW, Moreland CG (1985) *J Am Chem Soc* 107:5383
28. Angel SM, DeArmond MK, Donohoe RJ, Hanck KW, Wertz DH (1984) *J Am Chem Soc* 106:3688
29. Dallinger RF, Woodruff WH (1979) *J Am Chem Soc* 101:4391
30. Omberg KM, Schoonover JR, Treadway JA, Leasure LM, Dyer RB, Meyer TJ (1997) *J Am Chem Soc* 119:7013
31. Balzani V, Bolletta F, Gandolfi MT, Maestri M (1978) *Top Curr Chem* 75:1
32. Lytle FE, Hercules DM (1969) *J Am Chem Soc* 91:253
33. Klassen DM, Crosby GA (1968) *J Chem Phys* 48:1853
34. Xie P, Chen YJ, Uddin J, Endicott JF (2005) *J Phys Chem A* 109:4671
35. Kober EM, Sullivan BP, Meyer TJ (1984) *Inorg Chem* 23:2098
36. Bensasson R, Salet C, Balzani V (1976) *J Am Chem Soc* 98:3722
37. Bensasson R, Salet C, Balzani V (1979) *CR Acad Sci Paris* 289B:41
38. Lachish U, Infelta PP, Grätzel M (1979) *Chem Phys Lett* 62:317
39. Creutz C, Chou M, Netzel TL, Okumura M, Sutin N (1980) *J Am Chem Soc* 102:1309
40. Bradley PC, Kress N, Hornberger BA, Dallinger RF, Woodruff WH (1981) *J Am Chem Soc* 103:7441
41. Brauenstein CH, Baker AD, Strekas TC, Gafney HD (1984) *Inorg Chem* 23:857
42. Demas JN, Crosby GA (1971) *J Am Chem Soc* 93:2841
43. Demas JN, Taylor DG (1979) *Inorg Chem* 18:3177
44. Bolletta F, Juris A, Maestri M, Sandrini D (1980) *Inorg Chim Acta* 44:L175
45. Harrigan RW, Crosby GA (1973) *J Phys Chem* 59:3468
46. Hager GD, Crosby GA (1975) *J Am Chem Soc* 97:7031
47. Hager GD, Watts RJ, Crosby GA (1975) *J Am Chem Soc* 97:7037
48. Hips KW, Crosby GA (1975) *J Am Chem Soc* 97:7042
49. Crosby GA, Elfring WH Jr (1976) *J Phys Chem* 80:2206

50. Sprouse S, King KA, Spellane PJ, Watts RJ (1984) *J Am Chem Soc* 106:6647
51. Maestri M, Sandrini D, Balzani V, Chassot L, Jolliet P, von Zelewsky A (1985) *Chem Phys Lett* 122:375
52. Roundhill DM (1994) *Photochemistry and photophysics of metal complexes*. Plenum, New York
53. Maestri M, Balzani V, Deuschel-Cornioley C, von Zelewsky A (1991) *Adv Photochem* 17:1
54. King KA, Spellane PJ, Watts RJ (1985) *J Am Chem Soc* 107:1431
55. Hillis JE, De Armond MK (1971) *J Lumin* 4:273
56. Shaw JR, Schmehl RH (1991) *J Am Chem Soc* 113:389
57. Guglielmo G, Ricevuto V, Giannetto A, Campagna S (1989) *Gazz Chim Ital* 119:457
58. Juris A, Campagna S, Bidd I, Lehn JM, Ziessel R (1988) *Inorg Chem* 27:4007
59. Ohsawa Y, Sprouse S, King KA, DeArmond MK, Hanck KW, Watts RJ (1987) *J Phys Chem* 91:1047
60. Maestri M, Sandrini D, Balzani V, von Zelewsky A, Jolliet P (1988) *Helv Chim Acta* 71:134
61. Van Houten J, Watts RJ (1976) *J Am Chem Soc* 98:4853
62. Van Houten J, Watts RJ (1978) *Inorg Chem* 17:3381
63. Elfring WH Jr, Crosby GA (1981) *J Am Chem Soc* 103:2683
64. Durham B, Caspar JV, Nagle JK, Meyer TJ (1982) *J Am Chem Soc* 104:4803
65. Caspar JV, Sullivan BP, Kober EM, Meyer TJ (1982) *Chem Phys Lett* 91:91
66. Calvert JM, Caspar JV, Binstead RA, Westmoreland TD, Meyer TJ (1982) *J Am Chem Soc* 104:6620
67. Agnew SF, Stone ML, Crosby GA (1982) *Chem Phys Lett* 85:57
68. Caspar JV, Meyer TJ (1983) *J Am Chem Soc* 105:5583
69. Barigelletti F, Juris A, Balzani V, Belser P, von Zelewsky A (1983) *Inorg Chem* 22:3335
70. Juris A, Barigelletti F, Balzani V, Belser P, von Zelewsky A (1985) *Inorg Chem* 24:1758
71. Barigelletti F, Belser P, von Zelewsky A, Juris A, Balzani V (1985) *J Phys Chem* 89:3680
72. Wacholtz WF, Auerbach RA, Schmehl RH (1986) *Inorg Chem* 25:227
73. Anderson S, Constable EC, Seddon KR, Turp JE, Baggott JE, Pilling MJ (1985) *J Chem Soc Dalton Trans*, p 2247
74. Barigelletti F, Juris A, Balzani V, Belser P, von Zelewsky A (1986) *J Phys Chem* 90:5190
75. Barigelletti F, Juris A, Balzani V, Belser P, von Zelewsky A (1987) *J Phys Chem* 91:1095
76. Kitamura N, Sato M, Kim HB, Obata R, Tazuke S (1988) *Inorg Chem* 27:651
77. Hiraga T, Kitamura N, Kim HB, Tazuke S, Mori N (1989) *J Phys Chem* 93:2940
78. Hammarström L, Barigelletti F, Flamigni L, Indelli MT, Armaroli N, Calogero G, Guardigli M, Sour A, Collin JP, Sauvage JP (1997) *J Phys Chem A* 101:9061
79. Abrahamson M, Wolpher H, Johansson O, Larsson J, Kritikos M, Eriksson L, Norrby PO, Bergquist J, Sun L, Akermark B, Hammarström L (2005) *Inorg Chem* 44:3215
80. Cherry WR, Henderson LJ Jr (1984) *Inorg Chem* 23:983
81. Van Houten J, Watts RJ (1975) *J Am Chem Soc* 97:3843
82. Englman R, Jortner J (1970) *Mol Phys* 18:145
83. Gelbart WM, Freed KF, Rice SA (1970) *J Chem Phys* 52:2460
84. Barbara P, Meyer TJ, Ratner MA (1996) *J Phys Chem* 100:13148
85. Gleria M, Minto F, Beggiato G, Bortolus P (1978) *J Chem Soc Chem Commun*, p 285
86. Porter GB, Sparks RH (1980) *J Photochem* 13:123

87. Fetterolf ML, Offen HW (1985) *J Phys Chem* 89:3320
88. Fetterolf ML, Offen HW (1986) *J Phys Chem* 90:1828
89. De Cola L, Barigelletti F, Balzani V, Belser P, von Zelewsky A, Vögtle F, Ebmeyer F, Grammenudi S (1988) *J Am Chem Soc* 110:7210
90. Barigelletti F, De Cola L, Balzani V, Belser P, von Zelewsky A, Vögtle F, Ebmeyer F (1989) *J Am Chem Soc* 111:4662
91. Treadway JA, Strouse GF, Anderson PA, Keene RF, Meyer TJ (2002) *J Chem Soc Dalton Trans*, p 3820
92. Medlycott EA, Hanan GS (2005) *Chem Soc Rev* 34:133
93. Juris A, Campagna S, Balzani V, Gremaud G, von Zelewsky A (1988) *Inorg Chem* 27:3652
94. Schofield ER, Collin JP, Gruber N, Sauvage JP (2003) *Chem Commun*, p 188
95. Bolletta F, Juris A, Maestri M, Sandrini D (1980) *Inorg Chim Acta* 44:L175
96. Laurence GS, Balzani V (1974) *Inorg Chem* 13:2976
97. Gafney HD, Adamson AW (1972) *J Am Chem Soc* 94:8238
98. Demas JN, Adamson AW (1973) *J Am Chem Soc* 95:5159
99. Bock CR, Meyer TJ, Whitten DG (1974) *J Am Chem Soc* 96:4710
100. Navon G, Sutin N (1974) *Inorg Chem* 13:2159
101. Hoffman MZ, Moggi L, Bolletta F, Hugh GL (1989) *J Phys Chem Ref Data* 18:219
102. Natarajan P, Endicott JF (1973) *J Phys Chem* 77:971
103. Natarajan P, Endicott JF (1973) *J Phys Chem* 77:1823
104. Sabbatini N, Scandola MA, Carassiti V (1973) *J Phys Chem* 77:1307
105. Sabbatini N, Scandola MA, Balzani V (1974) *J Phys Chem* 78:541
106. Juris A, Gandolfi MT, Manfrin MF, Balzani V (1976) *J Am Chem Soc* 98:1047
107. Ballardini R, Varani G, Scandola F, Balzani V (1976) *J Am Chem Soc* 98:7432
108. Juris A, Manfrin MF, Maestri M, Serpone N (1978) *Inorg Chem* 17:2258
109. Fujita I, Kobayashi H (1970) *J Chem Phys* 52:4904
110. Fujita I, Kobayashi H (1972) *J Chem Phys* 59:2902
111. Fujita I, Kobayashi H (1972) *Ber Bunsenges Phys Chem* 76:115
112. Sabbatini N, Balzani V (1972) *J Am Chem Soc* 94:7857
113. Bolletta F, Maestri M, Moggi L, Balzani V (1975) *J Chem Soc Chem Commun*, p 901
114. Creutz C, Sutin N (1976) *J Am Chem Soc* 98:6384
115. Creutz C (1978) *Inorg Chem* 17:1046
116. Sutin N, Creutz C (1978) *Adv Chem Ser* 168:1
117. Brunschwig B, Sutin N (1978) *J Am Chem Soc* 100:7568
118. Hoselton MA, Lin C-T, Schwarz HA, Sutin N (1978) *J Am Chem Soc* 100:2383
119. Balzani V, Bergamini G, Campagna S, Puntoriero F (2007) *Photochemistry and Photophysics of Coordination Compounds: Overview and General Concepts* (in this volume)
120. Balzani V, Bolletta F, Ciano M, Maestri M (1983) *J Chem Educ* 60:447
121. Balzani V, Bolletta F (1983) *Comments Inorg Chem* 2:211
122. Gafney HD, Adamson AW (1975) *J Chem Educ* 52:480
123. Bolletta F, Bonafede S (1986) *Pure Appl Chem* 58:1229
124. Liu DK, Brunschwig BS, Creutz C, Sutin N (1986) *J Am Chem Soc* 108:1749
125. Bolletta F, Ciano M, Balzani V, Serpone N (1982) *Inorg Chim Acta* 62:207
126. White HS, Bard AJ (1982) *J Am Chem Soc* 104:6891
127. Jonah CD, Matheson MS, Meisel D (1978) *J Am Chem Soc* 100:1449
128. Hercules LM, Lytle FE (1966) *J Am Chem Soc* 88:4795
129. Rubinstein I, Bard AJ (1981) *J Am Chem Soc* 103:512

130. Balzani V, Bolletta F (1981) *J Photochem* 17:179
131. Luttmer JD, Bard AJ (1978) *J Electrochem Soc* 125:1423
132. Tokel-Takvoryan NE, Hemingway RE, Bard AJ (1973) *J Am Chem Soc* 95:6582
133. Faulkner LR, Bard AJ (1977) In: Bard AD (ed) *Electroanalytical chemistry*, vol 10, chap 1. Dekker, New York
134. Bard AJ, Laser D (1975) *J Electrochem Soc* 122:632
135. Brilmyer GH, Bard AJ (1980) *J Electrochem Soc* 127:104
136. Ege D, Becker WG, Bard AJ (1984) *Anal Chem* 56:2413
137. Tung YL, Chen LS, Chi Y, Chou PT, Cheng YM, Li EY, Lee GH, Shu CF, Wu FI, Carty AJ (2006) *Adv Funct Mater* 16:1615
138. Kalyuzhny G, Buda M, McNeill J, Barbara P, Bard AJ (2003) *J Am Chem Soc* 125:6272
139. Slinker JD, Gorodetsky AA, Lowry MS, Wang S, Parker S, Rohl P, Bernhard S, Malliaras GG (2004) *J Am Chem Soc* 126:2763
140. Yang J, Gordon KC (2004) *Chem Phys Lett* 385:481
141. Chou PT, Chi Y (2006) *Eur J Inorg Chem* 3319
142. Caspar JV, Westmoreland TD, Allen GH, Bradley PJ, Meyer TJ (1984) *J Am Chem Soc* 106:3492
143. McClanahan SF, Dallinger R, Holler FJ, Kincaid JR (1985) *J Am Chem Soc* 107:4860
144. Mabrouk PA, Wrighton MS (1986) *Inorg Chem* 25:3004
145. Worl LA, Duesing R, Chen P, Della Ciana L, Meyer TJ (1991) *J Chem Soc Dalton Trans*, p 849
146. Kober EM, Caspar JV, Lumpkin RS, Meyer TJ (1986) *J Phys Chem* 90:3722
147. Claude JP, Meyer TJ (1995) *J Phys Chem* 99:51
148. Caspar JV, Meyer TJ (1983) *Inorg Chem* 22:2444
149. Caspar JV, Meyer TJ (1983) *J Am Chem Soc* 105:5583
150. Freed KF, Jortner J (1970) *J Chem Phys* 52:6272
151. Englman R, Jortner J (1970) *Mol Phys* 18:145
152. Bixon M, Jortner J (1968) *J Chem Phys* 48:715
153. Siebrand W, Williams DF (1967) *J Chem Phys* 46:403
154. Avouris P, Gelbart WM, El-Sayed MA (1977) *Chem Rev* 77:793
155. Caspar JV, Kober EM, Sullivan BP, Meyer TJ (1982) *J Am Chem Soc* 104:630
156. Y Wang, KS Schanze (1994) *Inorg Chem* 33:1354
157. Damrauer NH, Boussie TR, Devenney M, McCusker JK (1997) *J Am Chem Soc* 119:8253
158. Murtaza Z, Zipp AP, Worl LA, Graff DK, Jones WE Jr, Bates WD, Meyer TJ (1991) *J Am Chem Soc* 113:5113
159. Murtaza Z, Graff DK, Zipp AP, Worl LA, Jones WE Jr, Bates WD, Meyer TJ (1994) *J Phys Chem* 98:10504
160. Liang YY, Baba AI, Kim WY, Atherton SJ, Schmehl RH (1996) *J Phys Chem* 100:18408
161. Bergman SD, Gut D, Kol M, Sabatini C, Barbieri A, Barigelletti F (2005) *Inorg Chem* 44:7943
162. Seneviratne DS, Uddin MJ, Swayambunathan V, Schlegel HB, Endicott JF (2002) *Inorg Chem* 41:1502
163. Xie P, Chen YJ, Endicott JF, Uddin MJ, Seneviratne D, McNamara PG (2003) *Inorg Chem* 42:5040
164. Xie P, Chen YJ, Uddin MJ, Endicott JF (2005) *J Phys Chem A* 109:4671
165. Endicott JF, Chen YJ, Xie P (2005) *Coord Chem Rev* 249:343
166. Endicott JF, Chen YJ (2007) *Coord Chem Rev* 251:328

167. Moser JE, Grätzel M (2001) In: Balzani V (ed) *Electron transfer in chemistry*, vol 5. Wiley-VCH, Weinheim, p 589
168. Berglund Baudin H, Davidsson J, Serroni S, Juris A, Balzani V, Campagna S, Hammarström L (2002) *J Phys Chem A* 106:4312
169. Andersson J, Puntoriero F, Serroni S, Yartsev A, Pascher T, Polivka T, Campagna S, Sundström V (2004) *Chem Phys Lett* 386:336
170. Andersson J, Puntoriero F, Serroni S, Yartsev A, Pascher T, Polivka T, Campagna S, Sundström V (2004) *Faraday Discuss* 127:295
171. Cannizzo A, Van Nourik F, Gawelda W, Bressler C, Chergui M (2006) *Angew Chem Int Ed* 45:3174
172. Webb A, Knorr F, McHale J (2001) *J Raman Spectrosc* 32:481
173. Wallin S, Davidsson J, Modin J, Hammarström L (2005) *J Phys Chem A* 109:4697
174. Maestri M, Armaroli N, Balzani V, Constable EC, Thompson AMW (1995) *Inorg Chem* 34:2759
175. Harriman A, Ziessel R (1996) *Chem Commun*, p 1707
176. Benniston AC, Harriman A, Grosshenny V, Ziessel R (1997) *New J Chem* 21:405
177. Mamo A, Stefio I, Poggi A, Tringali C, Di Pietro C, Campagna S (1997) *New J Chem* 21:1173
178. El-Ghayoury A, Harriman A, Khatyr A, Ziessel R (2000) *J Phys Chem A* 104:1512
179. Polson MIJ, Medlycott EA, Mikelsons L, Taylor NJ, Watanabe M, Tanaka Y, Loiseau F, Passalacqua R, Campagna S (2004) *Chem Eur J* 10:3640
180. Duatti M, Tasca S, Lynch FC, Bohlen H, Vos JG, Stragni S, Ward MD (2003) *Inorg Chem* 42:8377
181. Medlycott EA, Hanan GS (2006) *Coord Chem Rev* 250:1763
182. Benniston AC, Grosshenny V, Harriman A, Ziessel R (1994) *Angew Chem Int Ed Engl* 33:1884
183. Hissler M, El-Ghayoury A, Harriman A, Ziessel R (1998) *Angew Chem Int Ed* 37:1717
184. Barbieri A, Ventura B, Barigelletti F, De Nicola A, Quesada M, Ziessel R (2004) 43:7359
185. Benniston AC, Harriman A, Li P, Sams CA (2005) *J Am Chem Soc* 127:2553
186. Galletta M, Puntoriero F, Campagna S, Chiorboli C, Quesada M, Goeb S, Ziessel S (2006) *J Phys Chem A* 110:4348
187. Benniston AC, Harriman A (2006) *Inorg Chim Acta* 359:753
188. Constable EC, Housecroft CE, Cargill Thompson A, Passaniti P, Silvi S, Maestri M, Credi A (2007) *Inorg Chim Acta* 360:1102
189. Abrahamsson M, Jäger M, Osterman T, Erikson L, Persson P, Becker HC, Johansson O, Hammarström L (2006) *J Am Chem Soc* 128:12616
190. Dodsworth ES, Lever ABP (1985) *Chem Phys Lett* 119:61
191. Dodsworth ES, Lever ABP (1986) *Chem Phys Lett* 124:152
192. Rillema DP, Mack KB (1982) *Inorg Chem* 21:3849
193. Juris A, Belser P, Barigelletti F, von Zelewsky A, Balzani V (1986) *Inorg Chem* 25:256
194. Campagna S, Serroni S, Bodige S, MacDonnell FM (1999) *Inorg Chem* 38:692
195. Warnmark K, Heyke O, Thomas JA, Lehn JM (1996) *Chem Commun*, p 2603
196. Ishow E, Gourdon A, Launay JP, Chiorboli C, Scandola F (1999) *Inorg Chem* 38:1504
197. Chiorboli C, Bignozzi CA, Scandola F, Ishow E, Gourdon A, Launay JP (1999) *Inorg Chem* 38:2402
198. Lopez R, Leiva AM, Zuloaga F, Loeb B, Norambuena B, Omberg KM, Schoonover JR, Striplin D, Devenney M, Meyer TJ (1999) *Inorg Chem* 38:2924
199. Torieda H, Yoshimura A, Nozaki K, Sakai S, Ohno T (2002) *J Phys Chem A* 106:11034

200. Amouyal E, Homsí A, Chambron JC, Sauvage JP (1990) *J Chem Soc Dalton Trans*, p 1841
201. Friedman AE, Chambron JC, Sauvage JP, Turro NJ, Barton JK (1990) *J Am Chem Soc* 118:4960
202. Tuite E, Lincoln P, Norden B (1997) *J Am Chem Soc* 119:239
203. Nair RB, Cullum BM, Murphy CJ (1997) *Inorg Chem* 36:962
204. Olson EJC, Hu D, Hormann A, Jonkman AM, Arkin MR, Stemp EDA, Barton JK, Barbara PF (1997) *J Am Chem Soc* 119:11458
205. Albano G, Belser P, De Cola L, Gandolfi MT (1999) *Chem Commun*, p 1171
206. Flamigni L, Encinas S, MacDonnell FM, Kim KJ, Puntoriero F, Campagna S (2000) *Chem Commun*, p 1185
207. Torieda H, Nozali K, Yoshimura A, Ohno T (2004) *J Phys Chem A* 108:4819
208. Balzani V, Moggi L, Scandola F (1987) In: Balzani V (ed) *Supramolecular photochemistry*. Reidel, Dordrecht, p 1
209. Balzani V, Scandola F (1991) *Supramolecular photochemistry*. Horwood, Chichester
210. Chiorboli C, Indelli MT, Scandola F (2005) *Top Curr Chem* 257:63
211. Schlike B, Belser P, De Cola L, Sabbioni E, Balzani V (1999) *J Am Chem Soc* 121:4207
212. Welter S, Salluce N, Belser P, Groeneveld M, De Cola L (2005) *Coord Chem Rev* 249:1360
213. Indelli MT, Chiorboli C, Flamigni L, De Cola L, Scandola F (2007) *Inorg Chem* (in press)
214. Cavazzini M, Pastorelli P, Quici S, Loiseau F, Campagna S (2005) *Chem Commun*, p 5266
215. Barigelletti F, Flamigni L, Collin JP, Sauvage JP (1997) *Chem Commun*, p 333
216. Collin JP, Gavina P, Hietz V, Sauvage JP (1998) *Eur J Inorg Chem* 1
217. Barigelletti F, Flamigni L (2000) *Chem Soc Rev* 29:1
218. Barigelletti F, Flamigni L, Guardigli M, Juris A, Beley M, Chodorowski-Kimmes S, Collin JP, Sauvage JP (1996) *Inorg Chem* 35:136
219. Polson M, Chiorboli C, Fracasso S, Scandola F (2007) *Photochem Photobiol Sci* 6:438
220. Indelli MT, Scandola F, Collin JP, Sauvage JP, Sour A (1996) *Inorg Chem* 25:303
221. Indelli MT, Scandola F, Flamigni L, Collin JP, Sauvage JP, Sour A (1997) *Inorg Chem* 26:4247
222. Helms A, Heiler D, McLendon G (1991) *J Am Chem Soc* 113:4325
223. Onuchic JN, Beratan DN (1987) *J Am Chem Soc* 109:6771
224. Lainé PP, Bedioui F, Loiseau F, Chiorboli C, Campagna S (2006) *J Am Chem Soc* 128:7510
225. Lainé PP, Loiseau F, Campagna S, Ciofini I, Adamo C (2006) *Inorg Chem* 45:5538
226. Grosshenny V, Harriman A, Ziessel R (1995) *Angew Chem Int Ed Engl* 34:1100
227. Paddon-Row MN (2001) In: Balzani V (ed) *Electron transfer in chemistry*, vol 3. Wiley-VCH, Weinheim, p 179
228. Scandola F, Chiorboli C, Indelli MT, Rampi MA (2001) In: Balzani V (ed) *Electron transfer in chemistry*, vol. 3. Wiley-VCH, Weinheim, p 337
229. Grosshenny V, Harriman A, Ziessel R (1995) *Angew Chem Int Ed Engl* 34:2705
230. Ziessel R, Hissler M, El-ghayoury A, Harriman A (1998) *Coord Chem Rev* 177:1251
231. Belser P, Dux R, Baak M, De Cola L, Balzani V (1995) *Angew Chem Int Ed Engl* 34:595
232. De Cola L, Balzani V, Dux R, Baak M, Belser P (1995) *Supramol Chem* 5:297
233. Chiorboli C, Rodgers MAJ, Scandola F (2003) *J Am Chem Soc* 125:483
234. Welter S, Laforet F, Cecchetto E, Vergeer F, De Cola L (2005) *ChemPhysChem* 6:2417

235. Torieda H, Yoshimura A, Nozaki K, Sakai S, Ohno T (2002) *J Phys Chem A* 106:11034
236. Torieda H, Yoshimura A, Nozaki K, Ohno T (2004) *J Phys Chem A* 108:2148
237. Ruben M, Rojo J, Romero-Salguero FJ, Uppadine LH, Lehn JM (2004) *Angew Chem Int Ed* 43:3644
238. Credi A, Balzani V, Campagna S, Hanan GS, Arana CR, Lehn JM (1995) *Chem Phys Lett* 243:105
239. Bassani DM, Lehn JM, Serroni S, Puntoriero F, Campagna S (2003) *Chem Eur J* 9:5936
240. Stadler AM, Puntoriero F, Campagna S, Kyritsakas N, Welter R, Lehn JM (2005) *Chem Eur J* 11:3997
241. Juris A (2003) *Annu Rep Prog Chem Sect C* 99:177
242. Balzani V, Ceroni P, Maestri M, Saudan C, Vicinelli V (2003) *Top Curr Chem* 228:159
243. Balzani V, Vögtle F (2003) *CR Chim* 6:867
244. Balzani V, Juris A, Puntoriero F, Campagna S (2007) In: Gleria M, De Jaeger R (eds) *Inorganic polymers*, chap 19. Nova Science, New York
245. Balzani V, Campagna S, Denti G, Serroni S, Juris A, Venturi M (1998) *Acc Chem Res* 31:26
246. Pleovets M, Vögtle F, De Cola L, Balzani V (1999) *New J Chem* 23:63
247. Vögtle F, Pleovets M, Nieger M, Azzellini GC, Credi A, De Cola L, De Marchis V, Venturi M, Balzani V (1999) *J Am Chem Soc* 121:6290
248. McClenaghan ND, Passalacqua R, Loiseau F, Campagna S, Verheyde B, Hameurlaine A, Dehaen W (2003) *J Am Chem Soc* 125:5356
249. Zhou XL, Tyson DS, Castellano FN (2000) *Angew Chem Int Ed* 39:4301
250. Tyson DS, Luman CR, Castellano FN (2002) *Inorg Chem* 41:3578
251. Serroni S, Denti G, Campagna S, Juris A, Ciano M, Balzani V (1992) *Angew Chem Int Ed Engl* 31:1493
252. Campagna S, Denti G, Serroni S, Juris A, Venturi M, Ricevuto V, Balzani V (1995) *Chem Eur J* 1:211
253. Serroni S, Juris A, Venturi M, Campagna S, Resino Resino I, Denti G, Credi A, Balzani V (1997) *J Mater Chem* 7:1227
254. Denti G, Campagna S, Serroni S, Ciano M, Balzani V (1992) *J Am Chem Soc* 114:2944
255. Campagna S, Denti G, Sabatino L, Serroni S, Ciano M, Balzani V (1990) *Inorg Chem* 29:4750
256. Serroni S, Campagna S, Denti G, Keyes TE, Vos JG (1996) *Inorg Chem* 35:4513
257. Campagna S, Denti G, Serroni S, Ciano M, Balzani V (1991) *Inorg Chem* 30:3728
258. Denti G, Serroni S, Campagna S, Ricevuto V, Juris A, Ciano M, Balzani V (1992) *Inorg Chim Acta* 198–200:507
259. Denti G, Campagna S, Sabatino L, Serroni S, Ciano M, Balzani V (1990) *Inorg Chim Acta* 176:175
260. Campagna S, Denti G, Serroni S, Juris A, Ciano M, Balzani V (1991) *Inorg Chem* 31:2982
261. Leveque J, Moucheron C, Kirsch-De Mesmaeker A, Loiseau F, Serroni S, Puntoriero F, Campagna S, Nierengarten H, Van Dorsselaer A (2004) *Chem Commun*, p 877
262. Campagna S, Denti G, Sabatino L, Serroni S, Ciano M, Balzani V (1989) *J Chem Soc Chem Commun*, p 1500
263. Sommovigo M, Denti G, Serroni S, Campagna S, Mingazzini C, Mariotti C, Juris A (2001) *Inorg Chem* 40:3318
264. Puntoriero F, Serroni S, Galletta M, Juris A, Licciardello A, Chiorboli C, Campagna S, Scandola F (2005) *ChemPhysChem* 6:129

265. Tachibana Y, Moser JE, Grätzel M, Klug DR, Durrant JR (1996) *J Phys Chem* 100:20056
266. Benkö G, Kallioinen J, Korppi-Tommola JEI, Yartsev AP, Sundström V (2002) *J Am Chem Soc* 124:489
267. Kallioinen J, Benkö G, Sundström V, Korppi-Tommola JEI, Yartsev AP (2002) *J Phys Chem B* 106:4396
268. Tachibana Y, Nazeeruddin MDK, Grätzel M, Klug DR, Durrant JR (2002) *Chem Phys* 285:127
269. Asbury JB, Anderson NA, Hao EC, Ai X, Lian TQ (2003) *J Phys Chem* 107:7376
270. Benkö G, Kallioinen J, Myllyperkiö P, Trif F, Korppi-Tommola JEI, Yartsev AP, Sundström V (2004) *J Phys Chem B* 108:2862
271. Wenger B, Grätzel M, Moser JE (2005) *J Am Chem Soc* 127:12150
272. McClenaghan ND, Loiseau F, Puntoriero F, Serroni S, Campagna S (2001) *Chem Commun*, p 2634
273. Larsen J, Puntoriero F, Pascher T, McClenaghan ND, Campagna S, Sundström V, Åkesson E (2007) *Chem Phys Chem* (in press)
274. Leveque J, Elias B, Moucheron C, Kirsch-De Mesmaeker A (2005) *Inorg Chem* 44:393
275. Börje A, Köthe O, Juris A (2002) *J Chem Soc Dalton Trans*, p 843
276. Constable EC, Handel RW, Housecroft CE, Farràn Morales A, Ventura B, Flamigni L, Barigelletti F (2005) *Chem Eur J* 11:4024
277. Arm KJ, Williams JAG (2005) *Chem Commun*, p 230
278. Campagna S, Serroni S, Puntoriero F, Loiseau F, De Cola L, Kleverlaan CJ, Becher J, Sørensen AP, Hascoat P, Thorup N (2002) *Chem Eur J* 8:4461
279. Puntoriero F, Nastasi F, Cavazzini M, Quici S, Campagna S (2007) *Coord Chem Rev* 251:536
280. Balzani V, Credi A, Venturi M (2003) *Molecular devices and machines*. Wiley-VCH, Weinheim
281. Schanze KS, Walters KA (1998) In: Ramamurthy V, Schanze KS (eds) *Organic and inorganic photochemistry*. Dekker, New York, p 75
282. Collin JP, Guillerez S, Sauvage JP, Barigelletti F, De Cola L, Flamigni L, Balzani V (1991) *Inorg Chem* 30:4230
283. Danielson E, Elliott CM, Merkert JW, Meyer TJ (1987) *J Am Chem Soc* 109:2519
284. Cooley LF, Larson SL, Elliott CM, Kelley DF (1991) *J Phys Chem* 95:10694
285. Larson SL, Elliott CM, Kelley DF (1995) *J Phys Chem* 99:6530
286. Klumpp T, Linsenmann M, Larson SL, Limoges BR, Buerssner D, Krissinel B, Elliott CM, Steiner UE (1999) *J Am Chem Soc* 121:4092
287. Klumpp T, Linsenmann M, Larson SL, Limoges BR, Buerssner D, Krissinel B, Elliott CM, Steiner UE (1999) *J Am Chem Soc* 121:1076
288. Weber JM, Rawls MT, MacKenzie VJ, Limoges BR, Elliott CM (2007) *J Am Chem Soc* 129:313
289. Larson SL, Elliott CM, Kelley DF (1996) *Inorg Chem* 35:2070
290. Schmehl RH, Ryu CK, Elliott CM, Headford CLE, Ferrere S (1990) *Adv Chem Ser* 226:211
291. Cooley LF, Headford CEL, Elliott CM, Kelley DF (1988) *J Am Chem Soc* 112:6673
292. Ryu CK, Wang R, Schmehl RH, Ferrere S, Ludwikow M, Merkert JW, Headford CEL, Elliott CM (1992) *J Am Chem Soc* 114:430
293. Yonemoto EH, Saupe GB, Schmehl RH, Hubig SM, Riley RL, Iverson BL, Mallouk TE (1994) *J Am Chem Soc* 116:4786
294. Meckenburg SL, Peek BM, Schoonover JR, McCafferty DJ, Wall CJ, Erickson BW, Meyer TJ (1993) *J Am Chem Soc* 115:5479

295. Meckenburg SL, McCafferty DJ, Schoonover JR, Peek BM, Erickson BW, Meyer TJ (1994) *Inorg Chem* 33:2974
296. Hu YZ, Tsukiji S, Shinkai S, Oishi S, Hamachi I (2000) *J Am Chem Soc* 122:241
297. Huynh MHV, Dattelbaum DM, Meyer TJ (2005) *Coord Chem Rev* 249:457
298. McCafferty DG, Bishop BM, Wall CG, Hughes SG, Meckenburg SL, Meyer TJ, Erickson BW (1995) *Tetrahedron* 51:1093
299. McCafferty DG, Friesen DA, Danielson E, Wall CG, Saederholm MJ, Erickson BW, Meyer TJ (1993) *Proc Natl Acad Sci USA* 93:8200
300. Striplin DR, Reece SY, McCafferty DG, Wall CG, Friesen DA, Erickson BW, Meyer TJ (2004) *J Am Chem Soc* 126:5282
301. Slate CA, Striplin DR, Moss JA, Chen PY, Erickson BW, Meyer TJ (1998) *J Am Chem Soc* 120:4885
302. Serron SA, Aldridge SA III, Fleming CN, Danell RM, Baik MH, Sykora M, Dattelbaum DM, Meyer TJ (2004) *J Am Chem Soc* 126:14506
303. Serron SA, Aldridge SA III, Danell RM, Meyer TJ (2000) *Tetrahedron* 41:4039
304. Strouse GF, Worl LA, Younathan JN, Meyer TJ (1989) *J Am Chem Soc* 111:9101
305. Jones WE Jr, Baxter SM, Strouse GF, Meyer TJ (1993) *J Am Chem Soc* 115:7363
306. Worl LA, Jones WE Jr, Strouse GF, Younathan JN, Danielson E, Maxwell KA, Sykora M, Meyer TJ (1999) *Inorg Chem* 28:2705
307. Dupray LM, Devenny M, Striplin DR, Meyer TJ (1997) *J Am Chem Soc* 119:10243
308. Fleming CN, Dupray LM, Papanikolas JM, Meyer TJ (2002) *J Phys Chem* 106:2328
309. Worl LA, Strouse GF, Younathan JN, Baxter SM, Meyer TJ (1990) *J Am Chem Soc* 112:7571
310. Baxter SM, Jones WE Jr, Danielson E, Worl LA, Strouse GF, Younathan JN, Meyer TJ (1991) *Coord Chem Rev* 111:47
311. Sykora M, Maxwell KA, DeSimone JM, Meyer TJ (2000) *Proc Natl Acad Sci USA* 97:7687
312. Konduri R, Ye H, MacDonnell FM, Serroni S, Campagna S, Rajeshwar K (2002) *Angew Chem Int Ed* 41:3185
313. Chiorboli C, Fracasso S, Scandola F, Campagna S, Serroni S, Konduri R, MacDonnell FM (2003) *Chem Commun*, p 1658
314. Chiorboli C, Fracasso S, Ravaglia M, Scandola F, Campagna S, Wouters K, Konduri R, MacDonnell FM (2005) *Inorg Chem* 44:1658
315. Konduri R, de Tacconi NR, Rajeshwar K, MacDonnell FM (2004) *J Am Chem Soc* 126:11621
316. de Tacconi NR, Lezna RO, Konduri R, Ongeri F, Rajeshwar K, MacDonnell FM (2005) *Chem Eur J* 11:4327
317. Wouters KL, de Tacconi NR, Konduri R, Lezna RO, MacDonnell FM (2006) *Photosynth Res* 87:1
318. Molnar SM, Nallas G, Bridgewater JS, Brewer KJ (1994) *J Am Chem Soc* 116:5206
319. Holder AA, Swavey S, Brewer KJ (2004) *Inorg Chem* 43:303
320. Elvington M, Brewer KJ (2006) *Inorg Chem* 45:5242
321. Barber J (2003) *Q Rev Biophys* 36:71
322. Ferreira KN, Iverson TM, Maghlaoui K, Barber J, Iwata S (2004) *Science* 303:1831
323. Iwata S, Barber J (2004) *Curr Opin Struct Biol* 14:447
324. McEvoy JP, Brudvig G (2006) *Chem Rev* 106:4455
325. Hammarström L (2003) *Curr Opin Chem Biol* 7:666
326. Berg KE, Tran A, Raymond MK, Abrahamsson M, Wolny J, Redon S, Andersson M, Sun L, Styring S, Hammarström L, Toflund H, Akermark B (2001) *Eur J Inorg Chem* 1019

327. Abrahamsson M, Baudin HB, Tran A, Philouze C, Berg KE, Raymond MK, Sun L, Akerman B, Styring S, Hammarström L (2002) *Inorg Chem* 41:1534
328. Magnusson A, Frapart Y, Abrahamsson M, Horner O, Akerman B, Sun L, Girerd JJ, Hammarström L, Styring S (1999) *J Am Chem Soc* 121:89
329. Burdinski D, Wieghardt K, Steenken S (1999) *J Am Chem Soc* 121:10781
330. Sjödin M, Styring S, Sun L, Akerman B, Hammarström L (2000) *J Am Chem Soc* 122:3932
331. Sun L, Raymond MK, Magnusson A, LeGourriérec D, Tamm M, Abrahamsson M, Huang-Kenez P, Martensson J, Stenhagen G, Hammarström L, Akerman B, Styring S (2000) *J Inorg Biochem* 78:15
332. Burdinski D, Eberhard B, Wieghardt K (2000) *Inorg Chem* 39:105
333. Huang P, Magnusson A, Lomoth R, Abrahamsson M, Tamm M, Sun L, van Rotterdam B, Park J, Hammarström L, Akerman B, Styring S (2002) *J Inorg Biochem* 91:150
334. Borgström M, Shaikh N, Johansson O, Anderlund MF, Styring S, Akerman B, Magnusson A, Hammarström L (2005) *J Am Chem Soc* 127:17504
335. Balzani V, Moggi L, Manfrin MF, Bolletta F, Gleria M (1975) *Science* 189:852
336. Lehn JM, Sauvage JP (1977) *Nouv J Chim* 1:449
337. Kalyanasundaram K, Grätzel M (1979) *Angew Chem Int Ed Engl* 18:701
338. Creutz C, Sutin N (1975) *Proc Natl Acad Sci USA* 72:2858
339. Kalyanasundaram K, Kiwi J, Grätzel M (1978) *Helv Chim Acta* 61:2720
340. Meyer TJ (1989) *Acc Chem Res* 22:163
341. Campagna S, Serroni S, Puntoriero F, Di Pietro C, Ricevuto V (2001) In: Balzani V (ed) *Electron transfer in chemistry*, vol. 5. Wiley-VCH, Weinheim, p 168
342. Alstrum-Acevedo JH, Brennaman MK, Meyer TJ (2005) *Inorg Chem* 44:6802
343. Armaroli N, Balzani V (2007) *Angew Chem Int Ed* 46:52
344. Wasielewski MR (1992) *Chem Rev* 92:435
345. Gust D, Moore TA, Moore AL (1993) *Acc Chem Res* 26:198
346. Ozawa H, Haga MA, Sakai K (2006) *J Am Chem Soc* 128:4926
347. Rau S, Schäfer B, Gleick D, Anders E, Rudolph M, Friedrich M, Görls H, Henry W, Vos JG (2006) *Angew Chem Int Ed* 45:6215
348. Brewer KJ, Elvington M (2006) US Patent 20060120954A1
349. Gholankhass B, Mametsuka H, Koite K, Tanabe T, Furue M, Ishitani O (2005) *Inorg Chem* 44:2326
350. Hawecker J, Lehn JM, Ziessel R (1983) *J Chem Soc Chem Commun*, p 536
351. Walther D, Ruben M, Rau S (1999) *Coord Chem Rev* 182:67
352. Inagaki A, Edure S, Yatsuda S, Akita M (2005) *Chem Commun*, p 5468
353. Osawa M, Hoshino M, Wakatsuki Y (2001) *Angew Chem Int Ed* 40:3472
354. Rau S, Walther D, Vos JG (2007) *Dalton Trans*, p 915
355. Ballardini R, Balzani V, Credi A, Gandolfi MT, Venturi M (2001) *Acc Chem Res* 34:445
356. Balzani V (2003) *Photochem Photobiol Sci* 2:459
357. Venturi M, Balzani V, Ballardini R, Credi A, Gandolfi MT (2004) *Int J Photoenerg* 6:1
358. Balzani V, Credi A, Venturi M (2007) *Nano Today* 2:18
359. Balzani V, Clemente-Leon M, Credi A, Ferrer B, Venturi M, Flod A, Stoddart JF (2006) *Proc Natl Acad Sci USA* 103:1178
360. Mobian P, Kern J-P, Sauvage J-P (2004) *Angew Chem Int Ed* 43:2392
361. Collin J-P, Jouvenot D, Koizumi M, Sauvage J-P (2005) *Eur J Inorg Chem* 1850
362. Kirsch-De Mesmaeker A, Lecomte JP, Kelly JM (1996) *Top Curr Chem* 177:25

363. Jenkins Y, Friedman AE, Turro NJ, Barton JK (1992) *Biochemistry* 31:10809
364. Friedman AE, Chambron JC, Sauvage JP, Turro NJ, Barton JK (1984) *Nucleic Acids Res* 13:6016
365. Tossi AB, Kelly JM (1989) *Photochem Photobiol* 49:545
366. Ortmans I, Moucheron C, Kirsch-De Mesmaeker A (1998) *Coord Chem Rev* 168:233
367. Kelly JM, Feeney M, Jacquet L, Kirsch-De Mesmaeker A, Lecomte JP (1997) *Pure Appl Chem* 69:767
368. Piérard F, Del Guerso A, Kirsch-De Mesmaeker A, Demeunynck M, Lhomme J (2001) *Phys Chem Chem Phys* 3:2911
369. Vos JG, Kelly JM (2006) *Dalton Trans*, p 4839
370. Hiort C, Lincoln P, Nordén B (1993) *J Am Chem Soc* 115:3448
371. Lincoln P, Broo A, Nordén B (1996) *J Am Chem Soc* 118:2644
372. Ujj L, Coates CG, Kelly JM, Kruger P, McGarvey JJ, Atkinson GH (2002) *J Phys Chem B* 106:4854
373. Coates CG, Callaghan PL, McGarvey JJ, Kelly JM, Kruger P, Higgins ME (2000) *J Raman Spectrosc* 31:283
374. Turro C, Bossman SH, Jenkins Y, Barton JK, Turro NJ (1995) *J Am Chem Soc* 117:9026
375. Sabatini E, Nikol HD, Gray HB, Anson FC (1996) *J Am Chem Soc* 118:1158
376. Nair RB, Cullum BM, Murphy CJ (1997) *Inorg Chem* 36:962
377. Guo XQ, Castellano FN, Li L, Lakowitz JR (1998) *Biophys Chem* 71:51
378. Brennaman MK, Alstrum-Acevedo JH, Fleming CN, Jang P, Meyer TJ, Papanikolas JM (2002) *J Am Chem Soc* 124:15094
379. Pourtois G, Beljonne D, Moucheron C, Schumm S, Kirsch-De Mesmaeker A, Lazzaroni R, Brédas JL (2004) *J Am Chem Soc* 126:683
380. Onfelt B, Lincoln P, Nordén B, Baskin JS, Zewail AH (2000) *Proc Natl Acad Sci USA* 97:5708
381. Coates CG, Olofsson J, Coletti M, McGarvey JJ, Onfelt B, Lincoln P, Nordén B, Tuite E, Matousek P, Parker AW (2001) *J Phys Chem B* 105:12653
382. Coates CG, Callaghan P, McGarvey JJ, Kelly JM, Jacquet L, Kirsch-De Mesmaeker A (2002) *J Mol Struct* 598:15
383. O'Donoghue K, Kelly JM, Kruger PE (2004) *Dalton Trans*, p 13
384. Moucheron C, Kirsch-De Mesmaeker A, Kelly JM (1997) *J Photochem Photobiol B* 40:91
385. Ortmans I, Elias B, Kelly JM, Moucheron C, Kirsch-De Mesmaeker A (2004) *Dalton Trans*, p 668
386. Jacquet L, Kelly JM, Kirsch-De Mesmaeker A (1995) *J Chem Soc Chem Commun*, p 913
387. Lentzen O, Defrancq E, Constant JF, Schumm S, Garcia-Fresnadillo D, Moucheron C, Dumy P, Kirsch-De Mesmaeker A (2004) *J Biol Inorg Chem* 9:100
388. Gicquel E, Boisdenghien A, Defrancq E, Moucheron C, Kirsch-De Mesmaeker A (2006) *Chem Commun*, p 2764
389. Jenkins Y, Barton JK (1992) *J Am Chem Soc* 114:8736
390. Hurley DJ, Tor Y (1998) *J Am Chem Soc* 120:2194
391. Telser J, Cruickshank A, Schanze KS, Netzel TL (1989) *J Am Chem Soc* 111:7221
392. Grimm GN, Boutorine AS, Lincoln P, Nordén B, Hélène C (2002) *ChemBioChem* 3:324
393. Lentzen O, Constant JF, Defrancq E, Prevost M, Schumm S, Moucheron C, Dumy P, Kirsch-De Mesmaeker A (2003) *ChemBioChem* 4:195

394. Crean CW, Kavanagh YT, O'Keefe CM, Lawler MP, Stevenson C, Davies JH, Boyle PH, Kelly JM (2002) *Photochem Photobiol Sci* 1:1024
395. Vargas-Baca I, Mitra D, Zulyniak HJ, Banerjee J, Sleiman HF (2001) *Angew Chem Int Ed* 40:4629
396. Mitra D, Di Cesare N, Sleiman HF (2004) *Angew Chem Int Ed* 43:5804
397. Chen B, Sleiman HF (2004) *Macromolecules* 37:5866
398. Pauly M, Kayser I, Schmitz M, Dicato M, Del Guerzo A, Kolber I, Moucheron C, Kirsch-De Mesmaeker A (2002) *Chem Commun*, p 1086
399. Ortmans I, Content S, Boutonnet N, Kirsch-De Mesmaeker A, Bannwarth W, Constant JF, Defrancq E, Lhomme J (1999) *Chem Eur J* 5:2712
400. Garcia-Fresnadillo D, Boutonnet N, Schumm S, Moucheron C, Kirsch-De Mesmaeker A, Defrancq E, Constant JF, Lhomme J (2002) *Biophys J* 82:978
401. O'Regan B, Grätzel M (1991) *Nature* 335:737
402. Hagfeldt A, Grätzel M (1992) *Chem Rev* 95:49
403. Grätzel M (2005) *Inorg Chem* 44:6841
404. Meyer G (2005) *Inorg Chem* 44:6852
405. Bignozzi CA, Argazzi R, Caramori S (2007) *Inorganic and bioinorganic chemistry*. In: Bertini I (ed) *Encyclopaedia of life supporting systems (EOLSS)*, developed under the auspices of UNESCO. Eolss, Oxford (in press) <http://www.eolss.net>
406. Gerischer H, Tributsch H (1968) *Ber Bunsenges Phys Chem* 72:437
407. DeSilvestro J, Grätzel M, Kavan L, Moser JE, Augustynski J (1985) *J Am Chem Soc* 107:2988
408. Memming R (1984) *Prog Surf Sci* 17:7
409. Nazeeruddin MK, Pechy P, Renouard T, Zakeeruddin SM, Humphry-Baker R, Comte P, Liska P, Cevey L, Costa E, Shklover V, Spiccia L, Deacon GB, Bignozzi CA, Grätzel M (2001) *J Am Chem Soc* 123:1613
410. Nazeeruddin MK, Wang Q, Cevey L, Aranyos V, Liska P, Figgemeier E, Klein C, Hirata N, Koops S, Haque SA, Durrant JR, Hagfeldt A, Lever ABP, Grätzel M (2006) *Inorg Chem* 45:787
411. Grätzel M (2001) *Pure Appl Chem* 73:459
412. Cao F, Oskam G, Searson PC, Stipkala J, Farzhad F, Heimer TA, Meyer GJ (1995) *J Phys Chem* 99:11974
413. Redmond G, Grätzel M, Fitzmaurice D (1993) *J Phys Chem* 97:6951
414. Boschlo G, Fitzmaurice D (1999) *J Phys Chem B* 103:7860
415. Nazeeruddin MK, Kay A, Rodicio R, Humphry-Baker R, Muller E, Liska P, Vlachopoulos M, Grätzel M (1993) *J Am Chem Soc* 115:6382
416. Argazzi R, Bignozzi CA, Hasselmann GM, Meyer GJ (1998) *Inorg Chem* 37:4533
417. Rensmo H, Sodergren S, Patthey L, Westermak L, Vayssieres L, Kohle O, Bruhwiler PA, Hagfeldt A, Siegbahn H (1997) *Chem Phys Lett* 274:51
418. Nazeeruddin MK, Pechy P, Grätzel M (1997) *Chem Commun*, p 1705
419. Zakeeruddin SM, Nazeeruddin MK, Pechy P, Rotzinger F, Humphry-Baker R, Kalyanasundaram K, Grätzel M, Shklover V, Haibach T (1997) *Inorg Chem* 36:5937
420. Argazzi R, Bignozzi CA, Heimer TA, Meyer GJ (1997) *Inorg Chem* 36:2
421. Indelli MT, Bignozzi CA, Harriman A, Schoonover JR, Scandola F (1994) *J Am Chem Soc* 116:3768
422. Argazzi R, Bignozzi CA, Heimer TA, Castellano FN, Meyer GJ (1997) *J Phys Chem B* 101:2591
423. Hirata N, Lagref JJ, Palomares EJ, Durrant JR, Nazeeruddin MK, Grätzel M, Di Censo D (2004) *Chem Eur J* 10:595

424. de Silva AP, Tecilla P (eds) (2005) Thematic issue on fluorescent sensors. *J Mater Chem* 15:2617–2976
425. Schmittel M, Lin HW (2007) *Angew Chem Int Ed* 46:893
426. Demas JN, DeGraff BA (1991) *Anal Chem* 63:829A
427. Demas JN, DeGraff BA, Coleman P (1999) *Anal Chem* 71:793A
428. Demas JN, DeGraff BA (2001) *Coord Chem Rev* 211:317
429. Borisov SM, Vasylevska AS, Krause C, Wolfbeis O (2006) *Adv Funct Mater* 16:1536
430. Welter S, Brunner K, Hofstraal JW, De Cola L (2003) *Nature* 421:54
431. Ford WE, Rodgers MAJ (1992) *J Phys Chem* 96:2917
432. Wilson GJ, Launikonis A, Sasse WHF, Mau AWH (1997) *J Phys Chem A* 101:4860
433. Simon JA, Curry SL, Schmehl RH, Schartz TR, Piotrowiak P, Jin X, Thummel RP (1997) *J Am Chem Soc* 119:11012
434. Harriman A, Hissler M, Khatyr A, Zissel R (1999) *Chem Eur J* 5:3366
435. Tyson DS, Lauman CR, Zhou X, Castellano FN (2001) *Inorg Chem* 40:4063
436. McClenaghan ND, Barigelletti F, Maubert B, Campagna S (2002) *Chem Commun*, p 602
437. Passalacqua R, Loiseau F, Campagna S, Fang YQ, Hanan GS (2003) *Angew Chem Int Ed* 42:1608
438. Leroy-Lhez S, Belin C, D'Aleo A, Williams R, De Cola L, Fages F (2003) *Supramol Chem* 15:627
439. Maubert B, McClenhagan ND, Indelli MT, Campagna S (2003) *J Phys Chem A* 107:447
440. Wang XY, Del Guerzo A, Schmehl RH (2004) *J Photochem Photobiol C* 5:55
441. McClenaghan ND, Leydet Y, Maubert B, Indelli MT, Campagna S (2005) *Coord Chem Rev* 249:1336
442. Wang J, Fang YQ, Bourget-Merle L, Polson MIJ, Hanan GS, Juris A, Loiseau F, Campagna S (2006) *Chem Eur J* 12:8539
443. Strouse GF, Schoonover JR, Duesing R, Boyde S, Jones WE, Meyer TJ (1995) *Inorg Chem* 34:473
444. Fang YQ, Taylor NJ, Hanan GS, Loiseau F, Passalacqua R, Campagna S, Nierengerten H, Van Dorsselaer A (2002) *J Am Chem Soc* 124:7912
445. Polson MIJ, Loiseau F, Campagna S, Hanan GS (2006) *Chem Commun*, p 1301
446. Fang YQ, Taylor NJ, Laverdière F, Hanan GS, Loiseau F, Nastasi F, Campagna S, Nierengerten H, Leize-Wagner E, Van Dorsselaer A (2007) *Inorg Chem* 46:2854
447. Encinas S, Simpson NRM, Andrews P, Ward MD, White CW, Armaroli N, Barigelletti F, Houlton A (2000) *New J Chem* 24:987
448. Ward MD, White CM, Barigelletti F, Armaroli N, Calogero G, Flamigni L (1998) *Coord Chem Rev* 171:481
449. Rau S, Schäfer B, Schebesta S, Grübing A, Poppitz W, Walther D, Duati M, Browne WR, Vos JG (2003) *Eur J Inorg Chem*, p 1503
450. Loiseau F, Marzanni G, Quici S, Indelli MT, Campagna S (2003) *Chem Commun*, p 286
451. Bergamini G, Saudan C, Ceroni P, Maestri M, Balzani V, Gorka M, Lee SK, van Heyst J, Vögtle F (2004) *J Am Chem Soc* 126:16466
452. Falz JA, Williams RM, Dilva MJJP, De Cola L, Pikramenou Z (2006) *J Am Chem Soc* 128:4520
453. Glazer EC, Madge D, Tor Y (2005) *J Am Chem Soc* 127:4190
454. Treadway JA, Moss JA, Meyer TJ (1999) *Inorg Chem* 38:4386
455. Gallaghaer LA, Serron SA, Wen X, Hornstein BJ, Dattelbaum DM, Schoonover JR, Meyer TJ (2005) *Inorg Chem* 44:2089

456. Sykora M, Petruska MA, Alstrum-Acevedo J, Bezel I, Meyer TJ, Klimov VI (2006) *J Am Chem Soc* 128:9984
457. Kim YI, Salim S, Huq MJ, Mallouk TE (1991) *J Am Chem Soc* 113:9561
458. Kim YI, Atherton SJ, Brigham ES, Mallouk TE (1993) *J Phys Chem* 97:11802
459. Saupe GB, Mallouk TE, Kim W, Schmehl RH (1997) *J Phys Chem* 101:2508
460. Hara, Waraksa CC, Lean JT, Lewis BA, Mallouk TE (2000) *J Phys Chem A* 104:5275
461. Morris ND, Suzuki M, Mallouk TE (2004) *J Phys Chem A* 108:9115
462. Haga MA, Ali MDM, Koseki S, Fujimoto K, Yoshimura A, Nozaki K, Ohno T, Nakajima K, Stufkens D (1996) *Inorg Chem* 35:3335
463. Di Pietro C, Serroni S, Campagna S, Gandolfi MT, Ballardini R, Fanni S, Browne W, Vos JG (2002) *Inorg Chem* 41:2871
464. Fanni S, Di Pietro C, Serroni S, Campagna S, Vos JG (2000) *Inorg Chem Commun* 3:42
465. Jukes TF, Adamo V, Hartl F, Belser P, De Cola L (2005) *Coord Chem Rev* 249:1327
466. Belser P, De Cola L, Hartl F, Adamo V, Bozic B, Chriqui Y, Iyer VM, Jukes TF, Kühni J, Querol M, Roma S, Salluce N (2006) *Adv Funct Mater* 16:195
467. Saes M, Bressler C, Abela R, Grolimund D, Johnson SL, Heimann PA, Chergui M (2003) *Phys Rev Lett* 90:47403
468. Gawelda W, Johnson M, de Groot FME, Abela R, Bressler C, Chergui M (2006) *J Am Chem Soc* 128:5001
469. Benfatto M, Della Longa S, Hatada H, Hayakawa K, Gawelda W, Bressler C, Chergui M (2006) *J Phys Chem B* 110:14035

Photochemistry and Photophysics of Coordination Compounds: Rhodium

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Abstract Rhodium(III) polypyridine complexes and their cyclometalated analogues display photophysical properties of considerable interest, both from a fundamental viewpoint and in terms of the possible applications. In mononuclear polypyridine complexes, the photophysics and photochemistry are determined by the interplay between LC and MC excited states, with relative energies depending critically on the metal coordination environment. In cyclometalated complexes, the covalent character of the C–Rh bonds makes the lowest excited state classification less clear cut, with strong mixing of LC, MLCT, and LLCT character being usually observed. In redox reactions, Rh(III) polypyridine units can behave as good electron acceptors and strong photo-oxidants. These properties are exploited in polynuclear complexes and supramolecular systems containing these units. In particular, Ru(II)-Rh(III) dyads have been actively investigated for the study of photoinduced electron transfer, with specific interest in driving force, distance, and bridging ligand effects. Among systems of higher nuclearity undergoing photoinduced electron transfer, of particular interest are polynuclear complexes where rhodium dihalo polypyridine units, thanks to their Rh(III)/Rh(I) redox behavior, can act as two-electron storage components. A large amount of work has been devoted to the use of

Rh(III) polypyridine complexes as intercalators for DNA. In this role, they have proven to be very versatile, being used for direct strand photocleavage marking the site of intercalation, to induce long-distance photochemical damage or dimer repair, or to act as electron acceptors in long-range electron transfer processes.

Keywords DNA intercalators · Electron transfer · Photophysics · Polynuclear complexes · Rhodium

Abbreviations

bpy	2,2'-bipyridine
bzq	Benzo(h)-quinoline
chrysi	5,6-chrysenequinone diimine
dpb	2,3-bis(2-pyridyl)benzoquinoxaline
DPB	4,4'-diphenylbipyridine
dpp	2,3-bis(2-pyridyl)pyrazine
dppz	dipyridophenazine
dpq	2,3-bis(2-pyridyl)quinoxaline
HAT	1,4,5,8,9,12-hexaazatriphenylene
Me ₂ bpy	4,4'-dimethyl-2,2'-bipyridine
Me ₂ phen	4,7-dimethyl-1,10-phenanthroline
Me ₂ trien	diamino-4,7-diazadecane
ox	Oxalato
phen	1,10-phenanthroline
phi	9,10-phenanthrenequinonediimine
PPh ₃	triphenylphosphine
ppy	2-phenylpyridine,
TAP	1,4,5,8-tetraazaphenanthrene
thpy	2-(2-thienyl)-pyridine
tpy	2,2' : 6',2''-terpyridine

1

Introduction

Although not as popular as other transition metals, e.g., ruthenium, rhodium has received considerable attention in the field of inorganic photochemistry. Few specific reviews on rhodium photochemistry are available, however. The literature preceding 1970 was reviewed in the classical book of Carassiti and Balzani [1]. The photochemistry of polypyridine metal complexes, including those of rhodium, has been reviewed by Kalyanasundaram in 1992 [2]. Several rhodium-containing species are considered in the extensive review written in 1996 by Balzani and coworkers on luminescent and redox active polynuclear complexes [3]. A number of photochemical investigations are included in the 1997 review article of Hannon on rhodium complexes [4]. Rhodium complexes are included in more recent reviews dealing with photoinduced processes in covalently linked systems containing metal complexes [5, 6].

In general terms, three main classes of rhodium complexes have attracted the attention of photochemists: (i) amino complexes and substituted derivatives; (ii) multiply bridged dirhodium complexes; (iii) rhodium polypyridine and related complexes.

Rhodium(III) halo/amino complexes have been actively investigated in the late 1970s and in the 1980s. They have low-lying metal centered (MC) excited states of $d-d$ type, and can be considered paradigmatic representatives of the ligand-field photochemistry of d^6 metal complexes. The subject has been summarized and clearly discussed by Ford and coworkers in their 1983 review articles [7, 8]. In more recent times, however, despite a number of interesting investigations [9–18], the activity in the field seems to have slowed down considerably.

Multiply bridged dirhodium complexes constitute a large family of compounds, the structure and properties of which depend strongly upon the oxidation state of the metals. The Rh(I)-Rh(I) species of formula $Rh_2(bridge)_4^{2+}$, where the two d^8 metal centers are bridged by four bidentate ligands (e.g., diisocynoalkanes) in square planar coordination, have $d\sigma^* \rightarrow p\sigma$ excited states with a greatly shortened metal-metal bond [19] that emit efficiently in fluid solution [20]. In the Rh(II)-Rh(II) species of formula $Rh_2(bridge)_4X_2^{n+}$, the two d^7 metal centers are bridged by four bidentate ligands (e.g., diisocynoalkanes, acetate) and complete their pseudo-octahedral coordination with a metal-metal bond and two-axial monodentate ligands (e.g., $X = Cl, Br$ $n = 2$). These dirhodium complexes have long-lived excited states of $d\pi^* \rightarrow d\sigma^*$ type, which do not emit in fluid solution but can undergo a variety of bimolecular energy and electron transfer reactions [21]. Dirhodium tetracarboxylato units of this type have also been used as building blocks for a variety of supramolecular systems of photophysical interest [22–24]. Particularly interesting triply bridged dirhodium complexes of type $X_2Rh(bridge)_3RhX_2$, $LRh(bridge)_3RhX_2$, and $LRh(bridge)_3RhL$ (bridge = bis(difluorophosphino)methylamine, $X = Br$, $L = PPh_3$) have been developed recently by Nocera [25]. These Rh(II)-Rh(II), Rh(0)-Rh(II) and Rh(0)-Rh(0) species, all possessing excited states of $d\pi^* \rightarrow d\sigma^*$ type, can be interconverted photochemically by means of two-electron redox processes. Such two-electron photoprocesses provide the basis for a recently developed light-driven hydrogen production system [26], with a Rh(0)-Rh(II) mixed valence species playing the role of key photocatalysts [27]. The interest in multiply bridged dirhodium systems is now largely driven by their potential and implications for photocatalytic purposes.

As for other transition metals, polyimine ligands (in particular, polypyridines and their cyclometalated analogues) have played a major role in the design of rhodium complexes of photophysical interest. This is due to an ensemble of factors, including chemical robustness, synthetic flexibility, electronic structure, excited-state and redox tunability. Thus, rhodium polypyridine and related complexes have been extensively studied from a photophysical

viewpoint, both as simple molecular species or as components of supramolecular systems featuring energy/electron transfer processes. Also, rhodium polypyridine complexes have played a major role in the active research field of DNA metal complex interactions. In recognition of the relevance of these systems, this review will be essentially focused on the photochemistry and photophysics of complexes of rhodium with polypyridine-type ligands and of supramolecular systems that contain such units as molecular components.

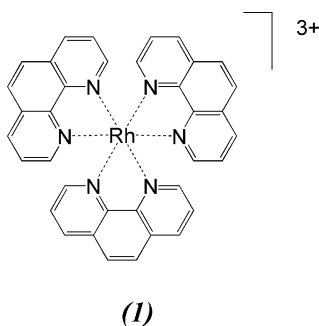
2

Mononuclear Species

2.1

Polypyridine Complexes

The fundamental features of the photophysics of Rh(III) polypyridine complexes have been extensively discussed in the book of Kalyanasundaram [2] and only a few general aspects are recalled here. The tris(1,10-phenanthroline)rhodium(III) ion, $\text{Rh}(\text{phen})_3^{3+}$ (**1**), can be used to exemplify the typical photophysical behavior of this class of complexes. $\text{Rh}(\text{phen})_3^{3+}$ exhibits in 77 K matrices an intense (Φ , ca. 1), long-lived (τ , ca. 50 ms), structured emission ($\lambda = 465, 485, 524, 571$ nm) assigned as ligand-centered (LC) phosphorescence, i.e., emission from a $\pi-\pi^*$ triplet state essentially localized on the phenanthroline ligands [28–31]. As is shown by high-resolution spectroscopy, the LC excitation is not delocalized, but rather confined to a single ligand [32, 33]. In room-temperature fluid solutions, $\text{Rh}(\text{phen})_3^{3+}$ is practically non-emitting (see below). The LC triplet state can be nevertheless easily monitored by transient absorption spectroscopy ($\lambda_{\text{max}} = 490$ nm, $\varepsilon_{\text{max}} = 4000 \text{ M}^{-1} \text{ cm}^{-1}$, $\tau = 250$ ns) [34]. The temperature-dependent behavior is explained on the basis of decay of the LC triplet via a thermally activated process involving an upper metal-centered (MC) state [34–36]. Indeed, the



properties of the very weak emission measured from room-temperature solutions of $\text{Rh}(\text{phen})_3^{3+}$ (bandshape, lifetimes) are consistent with a small amount of MC excited state being in thermal equilibrium with the lowest LC state [34]. In related 2,2'-bipyridine complexes, changes in LC-MC energy gap and emission spectral profile can be induced by methyl substitution in the 3,3' positions, as a consequence of changes in the degree of planarity of the ligand [37].

The interplay of LC and MC triplets in the photophysics of this type of complexes has been investigated in detail by studying the series of mixed-ligand complexes $\text{cis-Rh}(\text{phen})_2\text{XY}^{n+}$ ($\text{X} = \text{Y} = \text{CN}$, $n = 1$; $\text{X} = \text{Y} = \text{NH}_3$, $n = 3$; $\text{X} = \text{NH}_3$, $\text{Y} = \text{Cl}$, $n = 2$), where the energy of the MC states is controlled by the ligand field strength of the X, Y ancillary ligands [38]. While at room temperature all the complexes are very weakly emissive, at 77 K, the di-cyano and di-amino complexes give the typical, structured LC emission, whereas the amino-chloro complex exhibits a broad emission of MC type (Fig. 1a). This can be readily explained on the basis of the energy diagram of Fig. 1b, where the relative energies of the LC triplet (appreciably constant for the three complexes) and of the lowest MC state (dependent on the ligand field strength of the ancillary ligands) are schematically depicted. For the amino-chloro complex the MC state is the lowest excited state of the system. For the di-amino case the situation is similar to that of the $\text{Rh}(\text{phen})_3^{3+}$ complex, with LC as the lowest excited state but with MC sufficiently close in energy to provide an efficient thermally activated decay path for LC (actually, in an appropriate temperature regime the two states are in equilibrium). In the di-cyano complex, the MC state is sufficiently high in energy that the LC state has a substantial lifetime (1.2 μs) even in room-temperature solution [38]. The actual energy gap between the LC and MC states (2000 cm^{-1} for the di-cyano

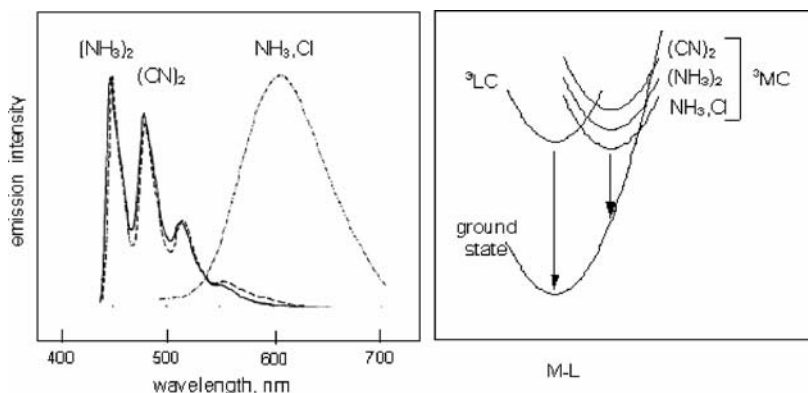
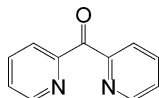


Fig. 1 **a** 77 K emission spectra of $\text{cis-Rh}(\text{phen})_2\text{XY}^{n+}$ complexes with different X, Y ancillary ligands. **b** Rationalization of the emission properties in terms of relative energies of ligand-centered (LC) and metal-centered (MC) excited states (adapted from [38])

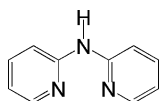
complex) can be evaluated by measuring the activation energy of the photo-solvation reaction originating from the MC state in low-temperature glycerol matrices [39].

As it is obvious from the trend sketched in Fig. 1b, the *cis*-Rh(phen)₂Cl₂⁺ complex has again a lowest MC excited state. It emits at ca. 710 nm [31] and, in keeping with the typical ligand-field photoreactivity of d⁶ metal complexes [7], undergoes in fluid solution photosolvation of the chloride ligands [40–42]. This type of reactivity that has been exploited by Morrison and coworkers [43] in an extensive series of studies on photoinduced binding to DNA and potential applications of this class of complexes as photo-toxic agents.

A number of analogues of the *cis*-Rh(NN)₂Cl₂⁺ complexes, where the NN represents various bidentate nitrogen donors, such as e.g., **2**, **3** behave similarly to *cis*-Rh(phen)₂Cl₂⁺, i.e., have lowest excited states of MC character and emit accordingly [44, 45].

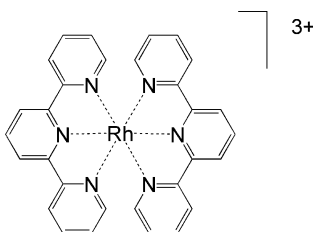


(2)



(3)

The same line of reasoning can be applied to rationalize the photophysical properties of the bis(2,2' : 6',2''-terpyridine)rhodium(III) ion, Rh(tpy)₂³⁺ (**4**), and analogous complexes. It is well known that, owing to a more unfavorable

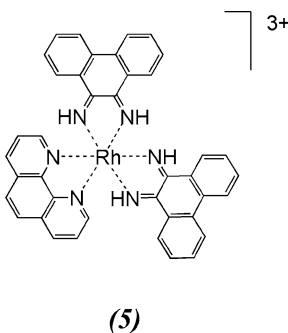


(4)

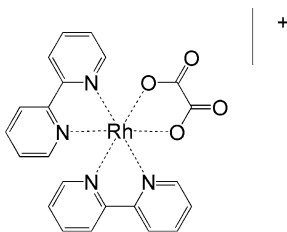
bite angle, two tpy ligands provide a lower ligand field strength compared to three phen (or bpy) ligands [46]. Accordingly, whereas $\text{Rh}(\text{bpy})_3^{3+}$ is a LC emitter, $\text{Rh}(\text{tpy})_2^{3+}$ and related compounds only show at 77 K broad structureless emissions of MC type [47].

In heteroleptic bis-imine $\text{Rh}(\text{III})$ complexes, multiple emissions originating from LC states localized on different ligands can be present at 77 K. For example, in complexes of type $[\text{Rh}(\text{bpy})_n(\text{phen})_{3-n}]^{3+}$, the LC emissions localized on bpy and phen are spectrally very similar but can be distinguished on the basis of their different lifetimes in time-resolved experiments [30, 48]. Clear indication that the excitation is trapped at either a bipyridyl or a phenanthroline ligand in the phosphorescent triplet state can also be obtained from phosphorescence microwave double resonance (PMDR) experiments [49]. The heteroleptic complex $\text{Rh}(\text{phi})_2(\text{phen})^{3+}$ (5) has been particularly developed as a DNA photocleavage agent (see Sect. 4). The complexes absorb strongly in UV region with a significant broad absorption in the visible range, which tails to ca. 500 nm [50]. The spectrum is dominated by overlapping of the ligand centered (LC) transitions of the component ligands with the phi centered bands at lower energy. These bands are strongly pH dependent with shifts to the blue upon increasing the pH. At 77 K the complex exhibits ligand centered (LC) dual emission from both phi and phen ligands. At room temperature no emission can be detected whereas a long-lived excited state ($\tau \approx 200$ ns in polar solvent) has been observed by transient absorption. On the basis of several experimental evidences this excited state, lying in energy at ca. 2 eV above the ground state, is assigned by the authors to be intraligand charge transfer in nature (ILCT). Quenching experiments with organic electron donors clearly indicate that the ILCT triplet state is a strong oxidizing agent with $E_{1/2}(*\text{Rh}^{3+}/\text{Rh}^{2+}) = 2.0$ V vs. NHE [50]. Multiple LC emissions have also been suggested to occur in heteroleptic complexes containing bipyridine or phenanthroline and pyridyl triazole ligands [51].

While for the vast majority of $\text{Rh}(\text{III})$ polypyridine complexes the photo-physics and photochemistry are dominated by LC and MC states, in a few

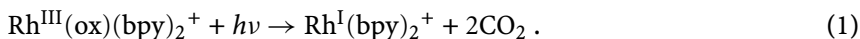


cases ligand-to-metal charge transfer (LMCT) photochemistry is observed. A clear example is provided by the $\text{Rh}(\text{bpy})_2(\text{ox})^+$ complex (**6**) [52].

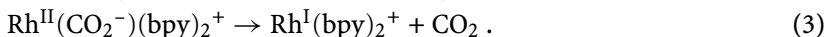
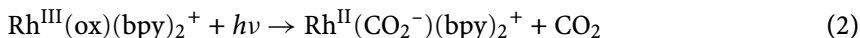


(6)

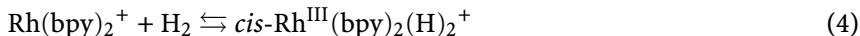
The spectrum of the colorless complex **6** is characterized by an intense band at ca. 300 nm assigned to oxalato-to-rhodium LMCT transitions. Upon UV irradiation, the following photoreaction is observed:



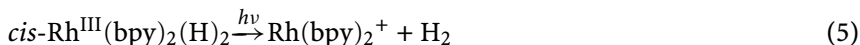
The $\text{Rh}(\text{bpy})_2^+$ product is formed rapidly (risetime in pulsed experiments, ca. 10 ns), probably via a sequence of processes comprising photochemical intramolecular electron transfer from the oxalate ligand to $\text{Rh}(\text{III})$ followed by the decomposition of the oxidized ligand into CO_2 and CO_2^- radical (Eq. 2) and thermal reduction of the $\text{Rh}(\text{II})$ center to $\text{Rh}(\text{I})$ by the reactive CO_2^- radical (Eq. 3) [52].



The violet $\text{Rh}(\text{bpy})_2^+$ product, with intense MLCT visible absorption, is a tetrahedrally distorted d^8 square planar complex [53]. This $\text{Rh}(\text{I})$ species, which can also be obtained by chemical [54], electrochemical [55], or radiation chemical [56, 57] reduction of $\text{Rh}(\text{III})$ complexes, is of great interest from the catalytic viewpoint. It undergoes facile oxidative addition by molecular hydrogen [58], to give the corresponding $\text{Rh}(\text{III})$ dihydride (Eq. 4). The reaction is fully reversible upon



removal of molecular hydrogen from the system. Interestingly, the release of molecular hydrogen from the dihydride complex can be obtained photochemically (Eq. 5). This photoreaction provides a

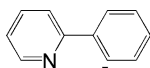


convenient means to perturb the equilibrium of Eq. 4 and to study the kinetics of hydrogen uptake in the thermal relaxation of the perturbed system. A detailed picture of the transition state of this interesting reaction has been obtained by such type of experiments [53].

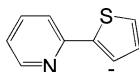
2.2

Cyclometalated Complexes

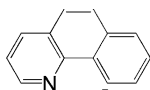
Ligands such as 2-phenylpyridine, 2-(2-thienyl)-pyridine, or benzo(h)-quinoline, in their ortho-deprotonated forms (ppy, 7; thpy, 8; bzq, 9), can bind in a bidentate N⁻C fashion to a variety of transition metals, including Rh(III). These complexes are generally indicated as cyclometalated (or orthometalated) complexes. The spectroscopy and photophysics of cyclometalated complexes [59] are usually very different from those of the corresponding polypyridine complexes, the main reason being the much stronger σ donor character of C⁻ relative to N. The consequences are (i) a high degree of covalency in the carbon-metal bond, (ii) a strongly enhanced ease of oxidation of the metal, (iii) high-energy MC excited states, (iv) relatively low-energy MLCT excited states.



(7)



(8)



(9)

The photophysics of Rh(III) cyclometalated complexes, though not as developed as that of analogous Ir(III) species (see Chap. 9), has been actively investigated in the last two decades. While some tris- [60] and mono-cyclometalated [61] compounds have been synthesized and studied, for synthetic reasons bis-cyclometalated complexes of Rh(III) are by far more common in the literature. All the bis-cyclometalated complexes have a C,C *cis* geometry [62]. The Rh(ppy)₂(bpy)⁺ (10) complex can be used here to exemplify the main photophysical features of this class of compounds.

The absorption spectrum of **10** (Fig. 2) shows LC transitions of the bpy and ppy ligands in the 240–310 nm range. In addition, a prominent band is present at 366 nm, which is attributed to MLCT transitions [63,64]. The presence of MLCT transitions at relatively low energy, a feature completely absent in analogous polypyridine complexes, is the result of the strongly electron donating character of the cyclometalating ligand, which makes the formally Rh(III) center relatively easy to oxidize (irreversible wave observed at ca. + 1.1 V vs. NHE) [63]. The complex, which is only very weakly emissive at room temperature, exhibits an intense, long-lived (τ , 170 μ s), structured emission at 77 K (Fig. 2). The emission has been attributed to ppy-based LC phosphorescence, although various degrees of mixing between LC and with MLCT triplet states have been invoked on the basis of absence of dual emissions [64], lifetime considerations [63], and high-resolution spectroscopy [65, 66]. In fact, because of the strong covalency of the carbon–metal bonds, the HOMO in this class of complexes has a mixed character, being delocalized on the central metal and on the cyclometalating ligand. This has been clearly shown by a number of recent TD/DFT calculations performed on Rh(III) [67] and related Ir(III) [68,69] cyclometalated complexes. Therefore, a classifica-

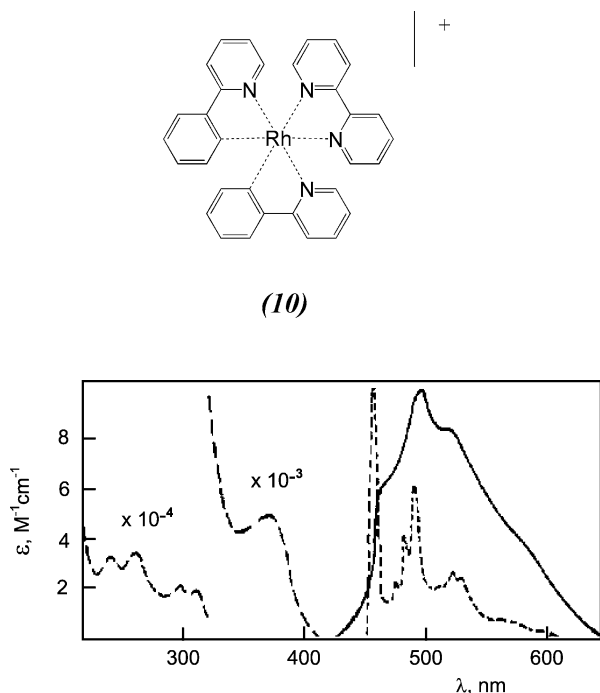
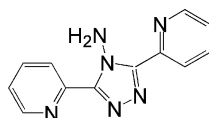


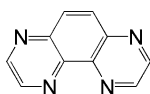
Fig. 2 Absorption spectrum (*dashed line*) and emission spectrum (room-temperature, *continuous line*; 77 K, *dotted line*) of $\text{Rh}(\text{ppy})_2(\text{bpy})^+$ in 4/1 EtOH/MeOH (adapted from [64])

tion of the excited states in classical, localized terms (MC, LC, MLCT) is not generally applicable for cyclometalated complexes.

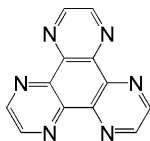
The general behavior of other $\text{Rh}(\text{N}^{\wedge}\text{C})_2(\text{N}^{\wedge}\text{N})^+$ complexes is similar to that described above for $\text{Rh}(\text{ppy})_2(\text{bpy})^+$, with some easily understandable specific differences. For instance, the main effect of substituting thpy (8) for ppy is an enhancement of emission intensity and lifetime in room-temperature solutions [63]. This is likely a result of the lower energy of the emission and the consequent lower efficiency of the thermally activated decay [70] via higher MC states. The remarkably long-lived (4.4–6.6 μs) emission observed in fluid solution for an analog of 10 with aldehyde substituents on the phenyl ring of the cyclometalating ligand [71] is probably justified by the same type of argument. On the other hand, the photophysical behavior of 10 is only slightly affected by substitution of bpy with similar $\text{N}^{\wedge}\text{N}$ ligands, such as, e.g., 1,10-phenanthroline, 2,2'-biquinoline [72], or 4-amino-3,5-bis(2-pyridyl)-4H-1,2,4-triazole (11) [73]. However, when strong π -deficient ligands such as 1,4,5,8-tetraazaphenanthrene (TAP, 12) or 1,4,5,8,9,12-hexaazatriphenylene (HAT, 13) are used as $\text{N}^{\wedge}\text{N}$ ligand [74], a definite switch in behavior is observed, with the presence of broad structureless 77 K emissions that have a clear charge transfer character. Indeed, for this type of complexes, TD/DFT calculations show that the HOMO involves the metal and the cyclometalating ligand-carbon bonds, but the LUMO is now exclusively localized on the non-cyclometalating ligand (Fig. 3) [67]. Thus, in this case the emission is best considered as having a mixed LLCT/MLCT character.



(11)



(12)



(13)

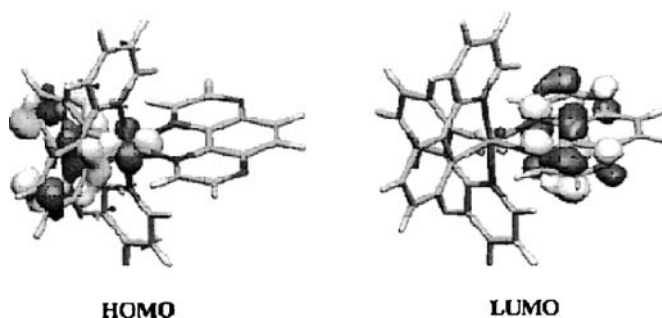
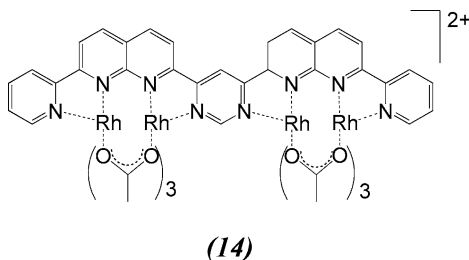


Fig. 3 Frontier orbitals of $\text{Rh}(\text{ppy})_2\text{TAP}^+$. From [67]

3 Polynuclear and Supramolecular Species

3.1 Homobinuclear Complexes

A few homobinuclear ligand-bridged $\text{Rh}(\text{III})$ polypyridine complexes have been studied [3, 75, 76]. Their photochemical interest is rather limited, however, as they behave generally like their mononuclear analogues, with minor differences in spectral shifts and lifetimes. An interesting type of systems, which bring together the complexities of ligand-bridged species and multiply bridged metal–metal bonded rhodium dimers, has recently been reported by Campagna et al. [77]. In (14) two quadruply bridged $\text{Rh}(\text{II})$ – $\text{Rh}(\text{II})$ dimers are the “molecular components” of a higher-order two-component system held together by the complex bis-naphthyridine-type ligand. As already observed for some related simple rhodium dimers (e.g., $\text{Rh}_2(\text{CH}_3\text{COO})_4(\text{PPh}_3)_2$) [21], the “binuclear” compound has a non-emissive but long-lived excited state in room-temperature solution. In the case of 14, the long-lived state has been assigned as an MLCT (metal–metal π^* to naphthyridine π^*) excited state [77].



3.2 Dyads

Heteronuclear bimetallic species containing rhodium polypyridine complexes are more interesting, as the Rh(III) unit can be involved in intercomponent processes, particularly of the electron transfer type. The thermodynamic requirements for the participation of Rh(III) polypyridine complexes in electron transfer processes are summarized in Fig. 4, where Rh(III), $^*\text{Rh(III)}$, and Rh(II) represent the ground state, the triplet LC excited state (see Sect. 2.1), and the one-electron reduced form, respectively, and the values of excited-state energy [31] and reduction potential [78] refer to Rh(phen)_3^{3+} (1). From these figures, it is apparent that Rh(III) polypyridine complexes can behave as extremely powerful photochemical oxidants and relatively good electron transfer quenchers. On the other hand, because of the high excited-state energy, these complexes are also good potential energy donors.

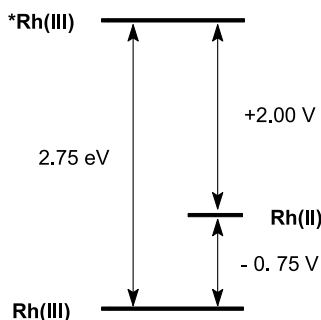


Fig. 4 Typical redox energy level diagram for Rh(III) polypyridine complexes. Values (reduction potential vs. SCE) appropriate for Rh(phen)_3^{3+} (1)

As a matter of fact, Rh(III) polypyridine complexes have been extensively used in bimolecular electron transfer processes, either as photoexcited molecule [79, 80] or as quencher [81–83], with motivations of both fundamental (testing electron transfer-free energy relationships) [80] and applied nature (photoinduced hydrogen evolution from water) [81, 82]. Here, on the other hand, we focus our attention on photoinduced processes where the reactants are pre-assembled in some kind of supramolecular system. The most common photoinduced processes taking place in simple two-component systems (often called “*dyads*”) involving a Rh(III) polypyridine unit are shown in Eqs. 6–8:

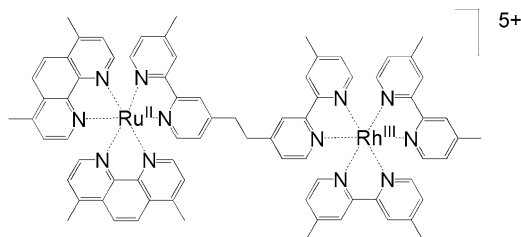


The dyads generically indicated in Eqs. 6–8 are actually heterobinuclear complexes when, as it is often the case, the photosensitizer P or the quencher Q are transition metal complex moieties, and the chemical linkage is provided by a bridging ligand. A number of examples of such processes are discussed in the following sections.

3.2.1

Photoinduced Electron Transfer in Ru(II)-Rh(III) Polypyridine Dyads

Though not exclusively, dyads containing Rh(III) polypyridine units have often involved as P or Q (Eqs. 7, 8) the chromophores *par excellence* of inorganic photochemistry, namely Ru(II) polypyridine complexes. The general behavior of Ru(II)-Rh(III) polypyridine dyads can be discussed taking dyad 15 as an example [84].



(15)

The absorption spectrum of dyad 15, as compared with those of the $\text{Ru}(\text{Me}_2\text{phen})_2(\text{Me}_2\text{bpy})^{2+}$ and $\text{Rh}(\text{Me}_2\text{bpy})_3^{3+}$ molecular components, is shown in Fig. 5. It shows that the spectra of the molecular components are strictly additive, as expected for weak intercomponent interaction, and that selective (100%) excitation of the Ru(II) chromophore can be easily performed in the visible region, whereas partial excitation of the Rh(III) component (ca. 70% at 300 nm) can be achieved in the ultraviolet. The energy level diagram for this dyad (Fig. 6) shows that, besides the photophysical processes taking place within each molecular component, a number of inter-component processes are thermodynamically allowed. They include:

- *Ru(II)-Rh(III) $\rightarrow$ Ru(III)-Rh(II) *electron transfer from excited Ru(II)* (a)
- Ru(II)-*Rh(III) $\rightarrow$ Ru(III)-Rh(II) *electron transfer to excited Rh(III)* (b)
- Ru(II)-*Rh(III) $\rightarrow$ *Ru(II)-Rh(III) *energy transfer from Rh(III) to Ru(II)* (c)
- Ru(III)-Rh(II) $\rightarrow$ Ru(II)-Rh(III) *back electron transfer* . (d)

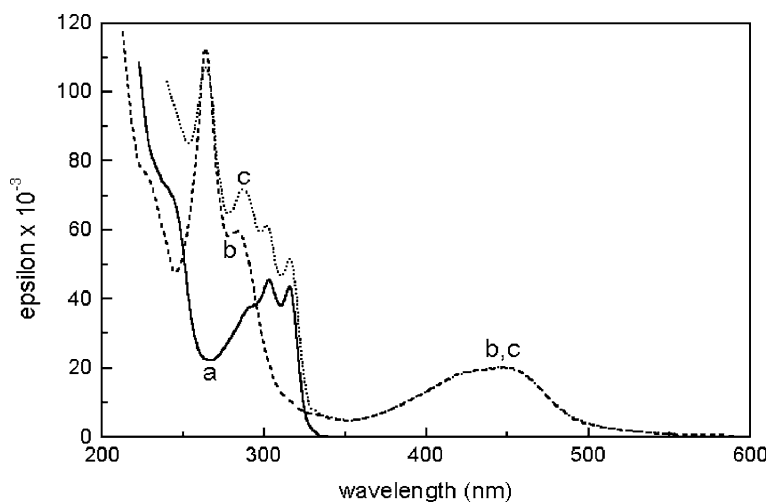


Fig. 5 Absorption spectra of the Ru(II)-Rh(III) dyad **15** (dotted line, **c**), and of the $\text{Ru}(\text{Me}_2\text{phen})_2(\text{Me}_2\text{bpy})^{2+}$ (dashed line, **b**) and $\text{Rh}(\text{Me}_2\text{bpy})_3^{3+}$ (continuous line, **a**) molecular components

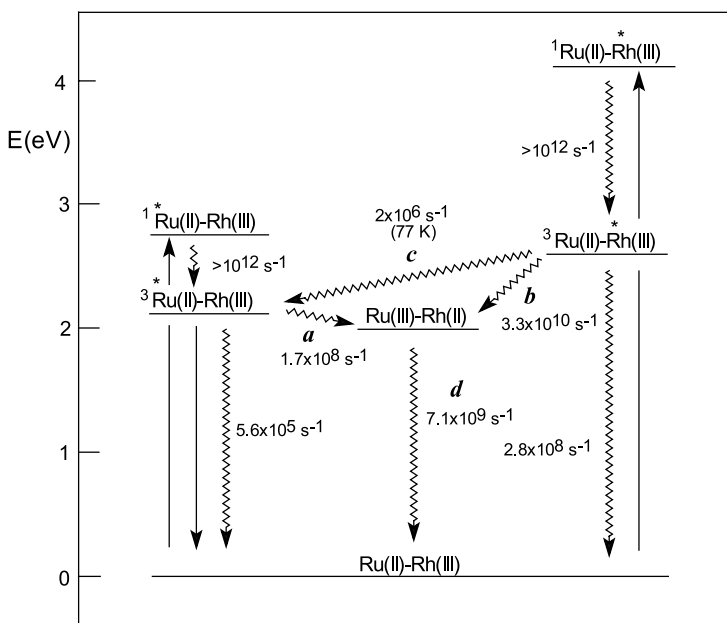


Fig. 6 Energy level diagram and photophysical processes for the Ru(II)-Rh(III) dyad **15**

For dyad **15**, all these processes could be time-resolved by nanosecond and picosecond techniques under the appropriate experimental conditions (visible excitation for *a*, UV excitation for *b* and *d*, rigid matrix for *c*), leading to the

detailed kinetic picture of Fig. 6 [84]. The widely different rates of the three ET processes (*a*, *b*, *d*) can be rationalized in terms of predominant driving force effects [84], as shown schematically in Fig. 7.

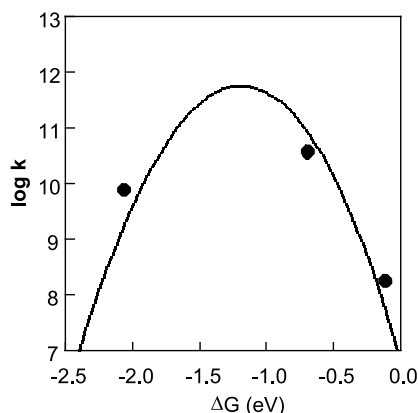
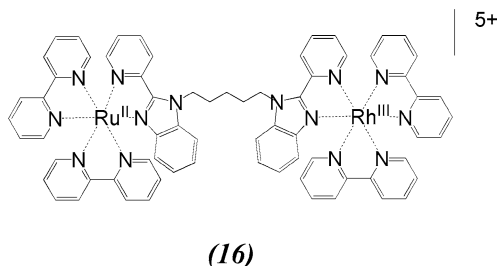


Fig. 7 Free-energy correlation of rate constants for the three electron transfer processes of dyad 15

Since most Ru(II)-Rh(III) polypyridine dyads have very similar energetics, the qualitative features illustrated above for dyad 15 can be safely generalized to this whole class of compounds. For example, in dyad 16 [85] the rate constants of processes *a*, *b*, and *d* are slower by a factor of ca. 3 but have the same *relative* magnitudes as for dyad 15. The slower rates are likely related to the longer aliphatic bridge, although for this and related [86] dyads, the flexibility of the bridges limits the validity of such comparisons.



Within this general type of behavior of Ru(II)-Rh(III) dyads, a number of experimental studies have been specifically aimed at investigating the role of the bridge in determining electron transfer rates. As has been the case for other types of bimetallic dyads [87–90], particular attention has been devoted to Ru(II)-Rh(III) dyads with modular bridges involving *p*-phenylene spacer units [6, 91, 92]. The dyads in Chart 1 provide a homogeneous series

with appreciably constant energetics but differing in the number (1–3) of *p*-phenylene spacers in the bridge and, in one of the two dyads with three spacers, for the presence of alkyl substituents on the central spacer. Upon excitation of the Ru(II)-based chromophore, the rate constants of photoinduced electron transfer (process a in the above general scheme) have been measured by time-resolved emission and transient absorption techniques in the nanosecond and picosecond time domains [6, 92]. The values for **Ru-ph-Rh**, **Ru-ph₂-Rh**, and **Ru-ph₃-Rh** (Chart 1), when plotted as a function of the metal–metal distance *r* (Fig. 8), display an exponential decrease (Eq. 9):

$$k = k(0) \exp(-\beta r) . \quad (9)$$

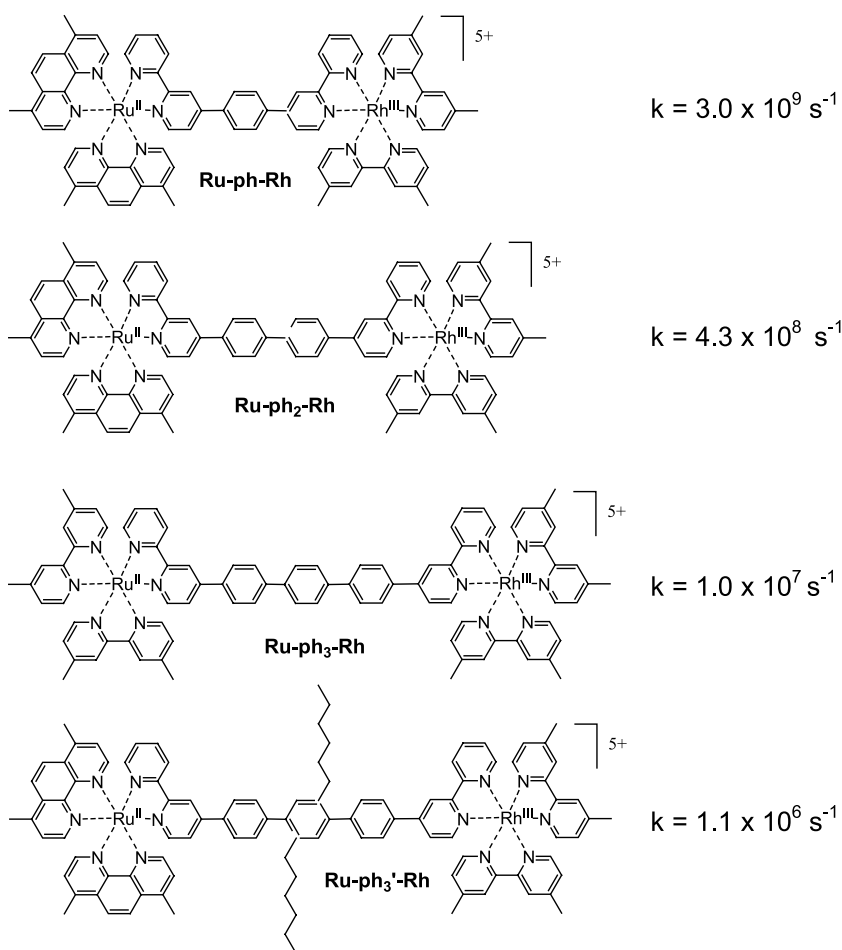


Chart 1

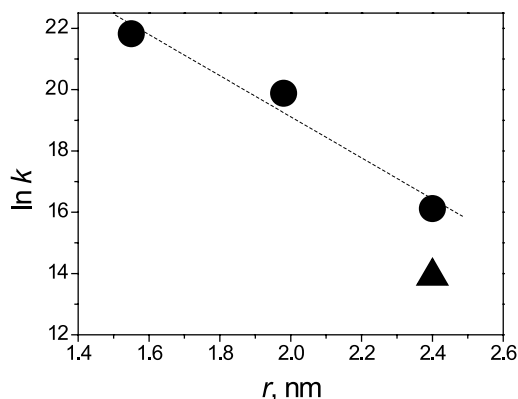


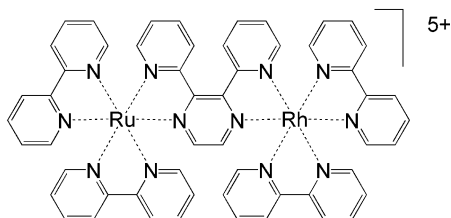
Fig. 8 Distance dependence of photoinduced electron transfer rates in the dyads of Chart 1: **Ru-ph-Rh**, **Ru-ph₂-Rh**, **Ru-ph₃-Rh** (dots), **Ru-ph'₃-Rh** (triangle)

This is the behavior predicted for electron transfer in the superexchange regime [5,93,95] if the distance dependence of the reorganizational energy term can be neglected. The β value obtained from the slope of the line in Fig. 8, $0.65 \text{ \AA}^{-1}$, should be regarded as an upper limiting value for the attenuation factor of the intercomponent electronic coupling (Eq. 9). This β value is in the range found for other oligophenylene-containing systems (organic dyads [96, 97], metal–molecules–metal junctions [98]). This underlines the good ability of this type of bridges to mediate donor–acceptor electronic coupling (for comparison, β is typically $0.8\text{--}1.2 \text{ \AA}^{-1}$ for rigid aliphatic bridges). In this regard, it is instructive to compare the electron transfer rate constant observed for **Ru-ph-Rh** ($k = 3.0 \times 10^9 \text{ s}^{-1}$) with that mentioned above for dyad **15** containing an aliphatic bis-methylene bridge ($k = 1.7 \times 10^8 \text{ s}^{-1}$). Despite the longer metal–metal distance ($15.5 \text{ \AA}$ for **Ru-ph-Rh** relative to $13.5 \text{ \AA}$ for **15**), the reaction is faster across the phenylene spacer by more than one order of magnitude.

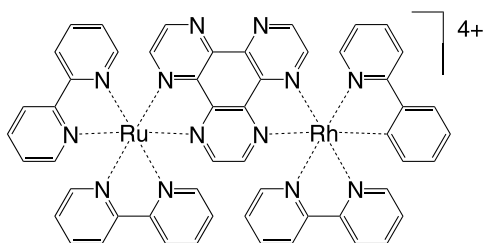
An interesting result [6, 92] is the fact that dyad **Ru-ph'₃-Rh**, which is identical to **Ru-ph₃-Rh** except for the presence of two solubilizing hexyl groups on the central phenylene ring, is one order of magnitude slower than its unsubstituted analog (Fig. 8). This is related to the notion that in a superexchange mechanism the rate is sensitive to the electronic coupling between adjacent modules of the spacer [5, 93, 95], and that in polyphenylene bridges this coupling is a sensitive function of the twist angle between adjacent spacers [99]. While the planes of unsubstituted adjacent phenylene units form angles of $20^\circ\text{--}40^\circ$ [100, 101], ring substitution leads to a substantial increase in the twist angle (to ca. 70°) [100] and, as a consequence, to a slowing down of the electron transfer process.

A number of Ru(II)-Rh(III) dyads have been reported where little or any photoinduced electron transfer quenching of the Ru(II)-based MLCT emis-

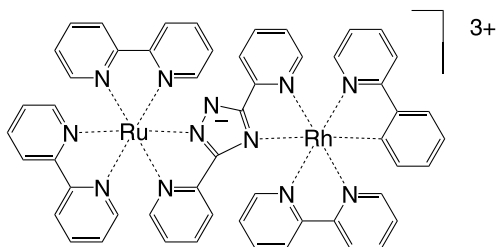
sion takes place [75, 76, 102]. In the case of dyad **17**, the plausible reason is that, owing to the comparable reduction potentials of the diphenylpyrazine bridging ligand and Ru(III) center, the driving force for intramolecular electron transfer is too small [102]. In the cases of dyads **18** and **19**, the presence of cyclometalated ancillary ligands makes the formally Rh(III) center very difficult to reduce and relatively easy to oxidize, thus yielding MLCT states at comparable energies on the two units [75, 76].



(17)

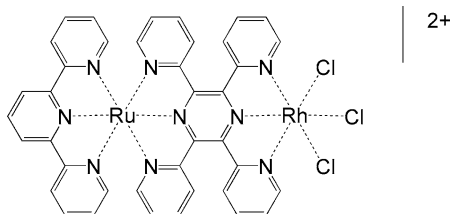


(18)



(19)

Low driving force arguments could also apply to the dyad **20**, where relatively slow quenching of the Ru(II) MLCT emission (estimated k , ca. $3.5 \times 10^7 \text{ s}^{-1}$) was observed and attributed to intramolecular electron transfer [103]. Here, however, a relevant aspect is also the presence a Rh(III)



2+

(20)

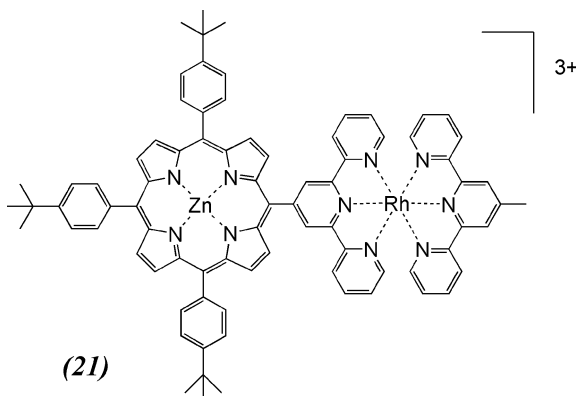
moiety with of coordinated chloride ligands. In fact, contrary to what happens for common Rh(III) polypyridine units (e.g., $\text{Rh}(\text{bpy})_3^{3+}$, $\text{Rh}(\text{phen})_3^{3+}$) where one-electron reduction is a quasi-reversible process, mixed-ligand units containing halide ions (e.g., $\text{Rh}(\text{bpy})_2\text{Cl}_2^+$, $\text{Rh}(\text{phen})_2\text{Cl}_2^+$) undergo strongly irreversible two-electron reductions accompanied by prompt halide ligand loss [78, 104]. While the use of these units as electron acceptors can be of interest towards photoinduced electron collection and multi-electron catalysis (see Sect. 3.4), from a kinetic viewpoint the large reorganizational energies involved are likely to lead to slow electron transfer rates.

3.2.2

Photoinduced Electron Transfer in Porphyrin-Rh(III) Conjugates

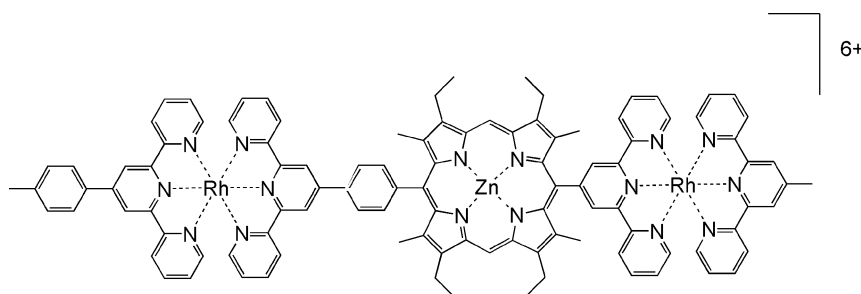
Though structurally quite different, the porphyrin-Rh(III) conjugates thoroughly studied by Harriman et al. [105] behave with regard to photoinduced electron transfer rather similarly to the above-discussed Ru(II)-Rh(III) dyads. The systems contain a zinc porphyrin unit connected directly with one (21) or via a phenylene spacer with two (22) rhodium terpyridine units.

The electron transfer processes thermodynamically allowed in these systems are indicated in Eqs. 10–14, where both 21 and 22 are schematized as



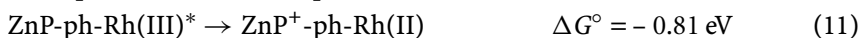
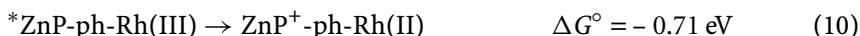
3+

(21)



(22)

dyads (indeed, **22** is a triad only in a formal sense), ZnP, Rh, and ph represent the zinc porphyrin and rhodium terpyridine molecular components and the phenylene spacer, respectively. The singlet excited state is considered for the zinc porphyrin chromophore and the triplet state for the rhodium terpyridine unit.



In **22**, where a phenylene spacer is interposed between the two molecular components, both photoinduced electron transfer following excitation of the zinc porphyrin (Eq. 10) and charge recombination (Eq. 12) have been time resolved, with values in acetonitrile of $3.2 \times 10^{11} \text{ s}^{-1}$ and $8.3 \times 10^9 \text{ s}^{-1}$, respectively. The wide difference in rates is attributed to the different kinetic regimes of the two processes, photoinduced electron transfer (Eq. 10) being almost activationless, and charge recombination (Eq. 12) lying deep into the Marcus inverted region [105]. For the directly linked system **21** (as well as for its free-base analogue), the disappearance of the porphyrin excited state, presumably by photoinduced electron transfer (Eq. 13), is extremely fast. In fact, the excited state lifetime of **21**, ca. 0.7 ps in acetonitrile, is comparable to the longitudinal relaxation time of the solvent, implying that the electron transfer process in this system is controlled by solvent reorientation [105].

3.3

Triads and Other Complex Systems

In dyads, including those discussed in the previous sections, photoinduced electron transfer is always followed by fast charge recombination. This greatly limits the use of dyads for practical purposes such as, e.g., conversion of light

into chemical energy. A strategy to overcome this problem, largely inspired by the architecture of natural photosynthetic reaction centers, is that of going to more complex supramolecular systems, triads, etc., in which a sequence of electron transfer steps is used to achieve long-range charge separation. The simplest of such system is a triad, as schematically illustrated in Fig. 9 for two possible reaction schemes. In Fig. 9a, the consecutive ET steps are from the excited chromophore, P, to an acceptor molecular component, A, and from a donor unit, D, to the oxidized chromophore. In Fig. 9b, the two consecutive electron transfer steps are from the excited chromophore, P, to a primary acceptor, A, and from the primary to a secondary acceptor unit, A'. These strategies have been extensively implemented using organic [106, 107] and, to a lesser extent, inorganic [108–110] molecular components.

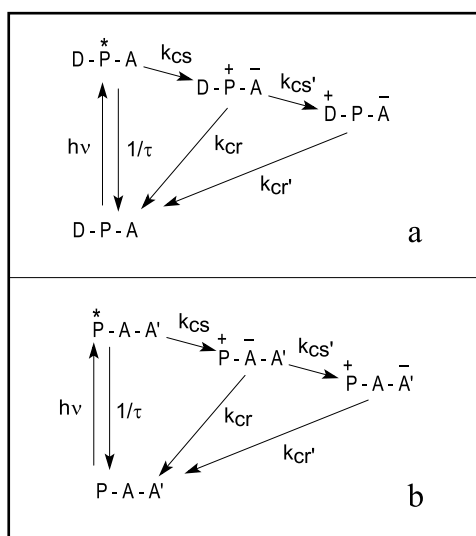
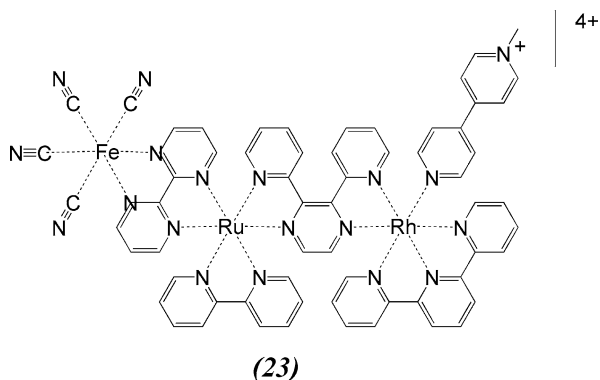


Fig. 9 Two types of triads for photoinduced charge separation. Molecular components: P (chromophore), D (donor), A (acceptor), A' (secondary acceptor). Electron transfer processes: *cs* (primary PET), *cr* (primary charge recombination), *cs'* (secondary charge separation), *cr'* (final charge recombination)

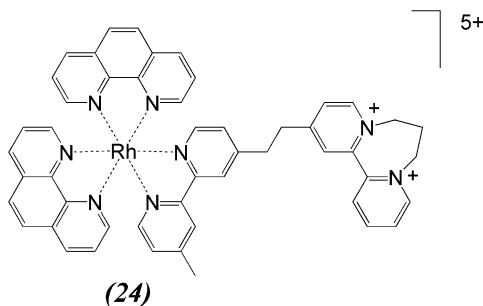
A number of systems involving Rh(III) molecular components that behave in some respects as triads (or pseudo-triads) are discussed in this section.

The trimetallic species **23** has been synthesized and studied by Petersen and coworkers [111] as a possible supramolecular system for photoinduced multi-step charge separation. This system comprises a Fe(II) electron donor, a Ru(II) photoexcitable chromophore, and a Rh(III) unit carrying a “monoquat” acceptor as ligand. Two different types of bridging ligand are present in **23**, a bipyrimidine between Fe(II) and Ru(II) and a dipyridylpyrazine between Ru(II) and Rh(III). All the other combinations of bridging ligands be-



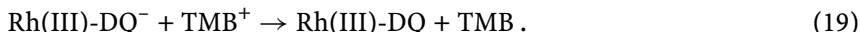
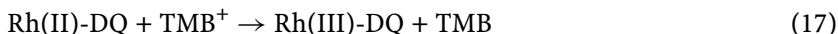
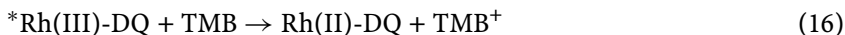
tween the three metal centers have been produced as well [111]. The ideal aim of the molecular design was to achieve complete photoinduced charge separation, with the positive hole on the iron donor and the electron on monoquat acceptor. Apparently, however, the redox properties of the molecular components were not quite ideal. Thus, the Ru(II)-based MLCT excited state is efficiently quenched. In the transient product obtained, however, the oxidized site is indeed the iron center but the reduced site seems to be a polypyridine ligand (in **23**, either the bridging dipyridylpyrazine or the terpyridine ligand). In **23**, this charge transfer state reverts to the ground state in 37 ns [111].

The simple chromophore-quencher system **24** also contains a quaternarized electron acceptor attached to a Rh(III) polypyridine unit. This dyad was designed [112] to study intramolecular *charge shift* processes, using a photochemical inter/intramolecular reaction scheme of the type shown in Eqs. 15–19.



The dyad, schematized as Rh(III)-DQ, undergoes Rh(III)-localized photoexcitation (Eq. 15). The excited state is then involved in reductive quenching (Eq. 16) by a suitable electron donor, 1,3,5-trimethoxybenzene, indicated as TMB. The reduced dyad originates from the quenching process with the extra electron on the metal complex moiety, i.e., on the thermodynamically less

avored (by ca. 0.2 eV) site. Therefore, in competition with primary bimolecular charge recombination (Eq. 17), it is expected to undergo intramolecular electron transfer (*charge shift* process, Eq. 18) from the metal complex to DQ. The system will be finally converted back to ground-state reactants by secondary charge recombination (Eq. 19):



The system performs indeed as predicted. The rate constants of all the processes in the above scheme have been experimentally determined, except for that of Eq. 17, inferred from experiments on appropriate model rhodium systems (without DQ pendant unit) [112]. In particular, the intramolecular charge shift process (Eq. 18) has been observed and time-resolved ($k = 3 \times 10^7 \text{ s}^{-1}$) by laser flash photolysis. It can be noticed that, from a formal viewpoint, the stepwise photoinduced electron transfer taking place in this dyad/quencher system is reminiscent of that of a triad for charge separation.

A system that, despite the chemical and physical differences, bears a close similarity to charge separating triads, is the heterogeneous assembly depicted in Fig. 10 [113]. It is based on a Ru(II)-Rh(III) polypyridine dyad of the same type as 15, that has been functionalized with carboxyl groups at the Rh(III) units. This gives the dyad the capability to adsorb on nanocrystalline titanium dioxide and to act as a photosensitizer in Graetzel-type photoelec-

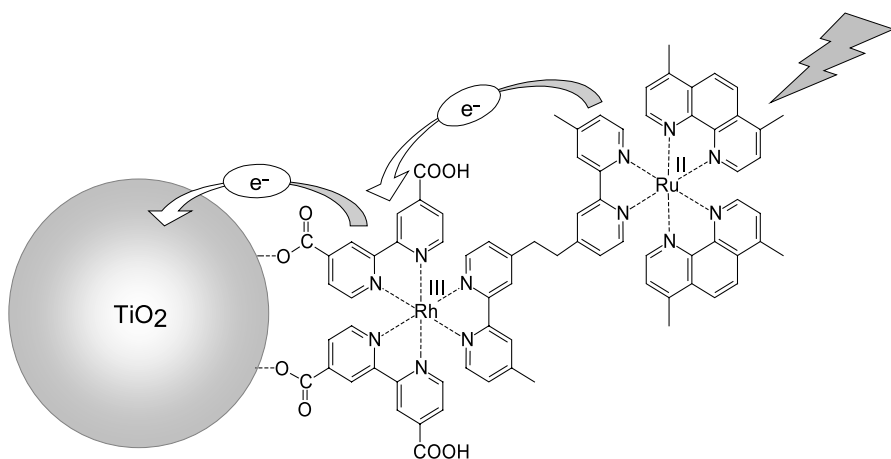


Fig. 10 Schematic picture of a Rh(III)-Ru(II) dyad anchored on nanocrystalline TiO_2 and of its behavior as a heterotriad system (from [113])

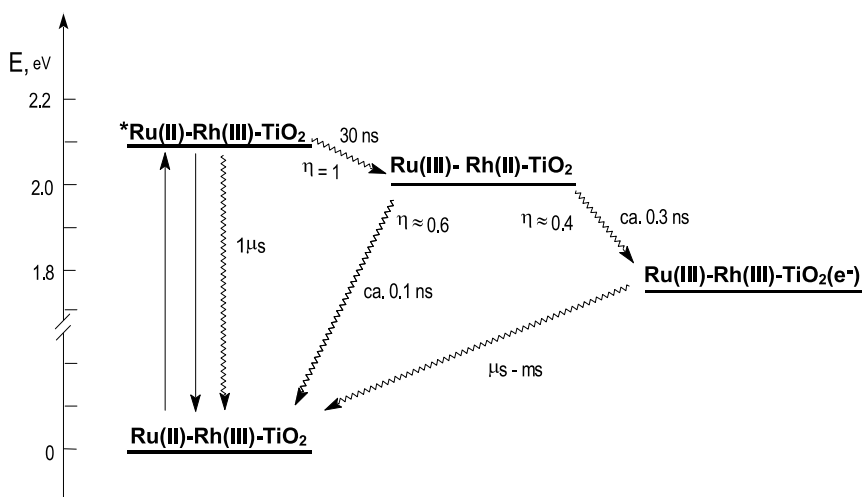


Fig. 11 Energy-level diagram and photophysical processes for the “heterotriad” of Fig. 10

trochemical cells. When photocurrent action spectra are measured with this dyad sensitizer, it is seen that light absorption by the Ru(II) chromophore leads to electron injection into the semiconductor. Furthermore, a detailed analysis of the transient behavior of the system indicates that the dyad performs a stepwise charge injection process, i.e., intramolecular Ru $\rightarrow$ Rh electron transfer followed by electron injection from the Rh unit into the semiconductor (Fig. 10). The first process has comparable rates and efficiencies as for the free dyads in solution. The second step is 40% efficient, because of competing primary recombination (Fig. 11). When the final recombination between injected electrons and oxidized Ru(III) centers is studied, a remarkable slowing down is obtained relative to standard systems containing simple mononuclear sensitizers. Stepwise charge separation and slow recombination between remote sites are distinctive features of charge separating triads (Fig. 9b). Therefore, the system can be considered as a “heterotriad” with the TiO₂ nanocrystal playing the role of the terminal electron acceptor [113].

3.4

Photoinduced Electron Collection

Central to the problem of light energy conversion into fuels (e.g., solar water splitting or light-driven carbon dioxide reduction) is the concept that the fuel-generating reactions are multielectron processes [3]. Progress in this field is therefore related to the design of systems capable of performing *photoinduced electron collection* [114]. A supramolecular system for photoinduced electron collection (PEC) can be constructed by coupling components capable of causing photoinduced electron transfer processes with compo-

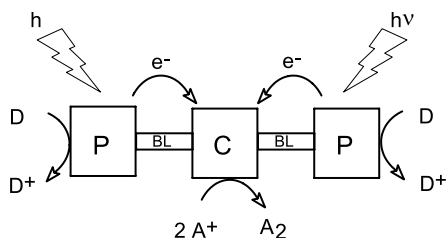
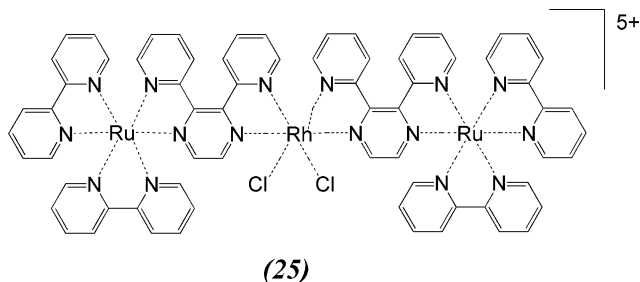


Fig. 12 Block diagram representation of a photochemical molecular device for photoinduced electron collection and two-electron redox catalysis

nents capable of storing electrons and using them in multielectron redox processes. A possible PEC scheme is shown in Fig. 12.

In this scheme, P are electron transfer photosensitizers, C an electron store component, and BL rigid bridging ligands. D is a sacrificial electron donor, and A_2 is a two-electron reduced product (e.g., H_2 starting from $2H^+$). The key molecular component C must have the ability to store two electrons following photoinduced electron transfer from P, and to deliver them to the substrate A^+ in a low-activation two-electron process that leads to the desired product A_2 .

Very few homogeneous systems for photoinduced electron collection (PEC) have been reported by now [115–122]. Trimetallic complexes incorporating polyazine bridging ligands have been designed and studied by Brewer's group for potential applications as PEC devices [123–126]. Most of these complexes have general formula $[(bpy)_2Ru(BL)]_2MCl_2^{n+}$ with BL = 2,3-bis(2-pyridyl)pyrazine (dpp), 2,3-bis(2-pyridyl)quinoxaline (dpq), or 2,3-bis(2-pyridyl)benzoquinoxaline (dpb) and M = Ir(III) or Rh(III) [123, 125]. The first functioning PEC system, $[(bpy)_2Ru(dpbb)]_2IrCl_2^{5+}$, was reported in 1994, employing π systems of polyazine bridging ligands to collect electrons [123]. Very recently, an analogous supramolecular trimetallic species has been reported where the central Ir-based moiety is replaced by a Rh(III) complex [127]. This new system, $[(bpy)_2Ru(dpp)]_2RhCl_2^{5+}$ (**25**), was obtained coupling two Ru chromophoric units which play the role of P, through



polyazine bridges (BL), to a central Rh core (C). In the presence of dimethylaniline (DMA) as sacrificial electron donor (D), **25** undergoes two-electron photoreduction at the rhodium center, producing the stable Rh(I) form $[(bpy)_2Ru(dpp)]_2Rh^{5+}$ via loss of two chlorides. This result is demonstrated by the observation that the spectroscopic changes associated with the photochemical reduction are identical with those seen in the electrochemical reduction experiments. On the basis of quenching experiments in the presence of different concentrations of DMA, the authors suggest that the monoreduced Rh(II) species can be formed by two alternative pathways following excitation of the peripheral Ru(II)-base chromophores: i) photoinduced electron transfer from the excited Ru(II)-based units followed by regeneration of the Ru(II)-based chromophores by oxidation of the sacrificial donor or ii) bimolecular quenching of the excited Ru(II)-based units by the sacrificial donor followed by reduction of the central Rh(III). No clear indication is given as to the mechanism for the formation of the stable two-electron-reduced Rh(I) product from the Rh(II) intermediate. According to the authors, the ability of $[(bpy)_2Ru(dpp)]_2RhCl_2^{5+}$ to undergo photoreduction at the rhodium center by multiple electrons and the fact that the photoreduced product $[(bpy)_2Ru(dpp)]_2Rh^{5+}$ is coordinatively unsaturated and thus available to interact with substrates are promising features in view of potential applications in light energy harvesting to produce fuels [127].

4

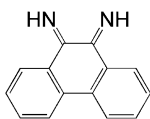
Rhodium Complexes as DNA Intercalators

4.1

Specific Binding to DNA and Photocleavage

The development and the study of transition metal complexes able to bind selectively to DNA sites, emulating the behavior of the DNA-binding proteins, ranks among the most fascinating and challenging issues in the field of current chemical and biological research [128–131]. This topic has been extensively investigated by Barton and coworkers, who devoted an impressive number of studies to the use of Rh(III) complexes with ligands containing nitrogen donors as DNA binding agents [129, 130]. Most of these studies center around complexes of the ligand 9,10-phenanthrenequinonediimine (phi) (**26**) [130, 132–138].

The phi Rh(III) complexes are indeed excellent DNA intercalators given the flat aromatic heterocyclic moiety of the phi ligand that deeply inserts and stacks in between the DNA base pairs (binding affinity constants range from 10^6 – 10^9 M⁻¹) [132, 139, 140]. The photophysical properties of phi Rh(III) complexes [50] have been discussed in Sect. 2.1. When bound to DNA, upon photoactivation with UV light, they are able to promote DNA strand cleav-

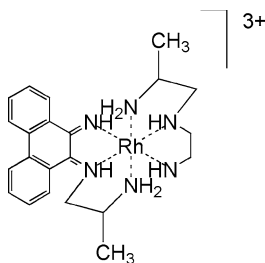


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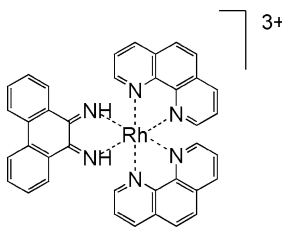
age, thanks to the outstanding oxidant properties of their excited states. The photocleavage ability offers a strategy for the use of these rhodium complexes as DNA targets. The approach used by the Barton's laboratory is the following: i) upon ultraviolet excitation, the excited state of DNA-bound rhodium complex promotes the scission of DNA sugar-phosphate backbone through oxidative degradation of the sugar moiety; ii) biochemical methods (e.g., gel electrophoresis) are used to determine where the strand scission occurred and therefore where, along the strand, the complex was bound. This method provides a powerful tool to mark specifically the sites of binding [129].

A variety of articles focused on DNA photocleavage by phi complexes containing different ligands in ancillary positions [130, 139–142]. The structural formula of the most extensively characterized complexes are reported below (27, 28, 29, 30).

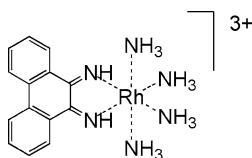
Irradiation with UV light of $\text{Rh}(\text{phen})_2(\text{phi})^{3+}$ (28) and $\text{Rh}(\text{bpy})(\text{phi})_2^{3+}$ (30) intercalated in DNA leads to direct DNA strand scission with products



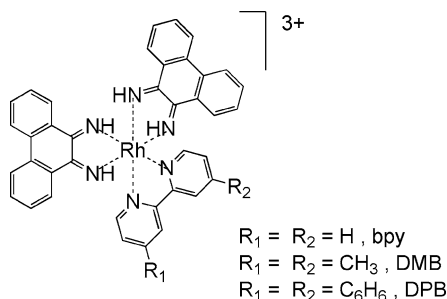
(27)



(28)



(29)



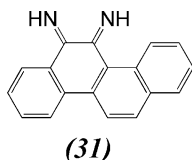
(30)

consistent with 3'-hydrogen abstraction from the deoxyribose sugar adjacent to the binding site [140, 141]. The photochemistry of these phi complexes intercalated in DNA has also been studied as a function of irradiation wavelength [143, 144]. Interestingly, the results showed that light of different wavelengths induces selectively different chemical reactions. In particular, the irradiation of the DNA-bound $\text{Rh}(\text{phi})_2(\text{L})^{3+}$ complexes with UV light ($\lambda = 313 \text{ nm}$) leads, as discussed above, to direct scission of the DNA-sugar backbone [141, 144]. If instead the complexes are excited with low-energy light ($\lambda \geq 365 \text{ nm}$) oxidative damage to the DNA bases is observed. The mechanism of these two photoprocesses is not discussed in great detail [130, 143]. It is proposed, however, which direct DNA scission takes place by hydrogen abstraction from the sugar by the phi ligand radical of a ligand-to-metal charge transfer (LMCT) state [130]. On the other hand, the oxidative damage is attributed to the population of a powerful oxidizing excited state (ILCT [50] or LC [143]) with longer wavelength light.

Photocleavage experiments have been used profitably for establishing how the phi complexes are associated to DNA [129, 130, 141]. Confirmation of site selectivity and greater structural definition were obtained later from high-resolution NMR studies [134–138, 145]. The important result is that all the phi complexes bind DNA noncovalently through intercalation in the major groove where the phi ligand is inserted between the base pairs so as to maximize stacking interactions. More recently a full crystal structure of $\Delta\text{-Rh}((R,R)\text{-Me}_2\text{trien})_2(\text{phi})^{3+}$ ($(R,R)\text{-Me}_2\text{trien} = 2R,9R\text{-diamino-4,7-diazadecane}$) bound to a DNA octamer provided a direct evidence of the

intercalation through the major groove [146]. A series of systematic NMR and photocleavage studies clearly showed that the binding of complexes containing different ancillary ligands occurs at a different specific DNA sequence. This site specificity results from both shape-selective steric interactions as well as stabilizing van der Waals and hydrogen bonding contacts. In particular, $\text{Rh}(\text{NH}_3)_4\text{phi}^{3+}$ and related amine complexes bind to $\text{d}(\text{TGGCCA})_2$ duplex through hydrogen bonding between the ancillary amine ligands and DNA bases [130, 136]. Evidence for specific intercalation was found also for $\text{Rh}(\text{phen})_2\text{phi}^{3+}$ in the hexanucleotide $\text{d}(\text{GTCGAC})_2$ [134]. In this case Barton proposed that the site specificity was based upon shape-selection. Since the phenanthroline ligands provide steric bulk above and below the plane of the phi ligand, the stacking occurs at sites which are more open in the major groove. The most striking example of site-specific recognition by shape selection with bulky ancillary ligands was found for $\text{Rh}(\text{DPB})_2\text{phi}^{3+}$ (DPB = 4,4'-diphenylbpy) [140]. For all the complexes studied enantioselectivity favoring the intercalation of the Δ -isomer was observed [130, 147]. Further control of sequence specificity has been achieved by using derivatives of $\text{Rh}(\text{phen})(\text{phi})_2^{3+}$ complexes where the nonintercalating phenanthroline ligand has been functionalized with pendant guanidinium group or with short oligopeptides [148, 149]. For metal-peptide complexes photocleavage experiments showed that the polypeptide chain is essential in directing the complex to a specific DNA sequence [149].

Among the rhodium intercalators explored as probes of DNA structure, Barton selected the $\text{Rh}(\text{bpy})_2\text{chrysi}^{3+}$ (chrysi = 5,6-chrysenequinone diimine, **31**) complex as an ideal candidate for mismatches recognition [150–152].



The specific recognition is based on the size of the intercalating ligand: the chrysene ring system is too large to intercalate in normal B-form DNA but it can do so at destabilized mismatch sites. The authors point out that sterically demanding intercalators such as $\text{Rh}(\text{bpy})_2\text{chrysi}^{3+}$ may have application both in mutation detection systems and as mismatch-specific chemotherapeutic agents.

Recently mixed-metal trimetallic complexes have been designed and studied by Brewer to obtain supramolecular system capable of DNA photocleavage [153, 154]. These complexes of general formula $[\{(\text{bpy})_2\text{M}(\text{dpp})\}_2\text{RhCl}_2](\text{PF}_6)_5$ with $\text{M} = \text{Ru}(\text{II})$ or $\text{Os}(\text{II})$ couple ruthenium or osmium chromophoric units to a central rhodium(III) core. When excited with visible light into their intense MLCT bands, these complexes exhibit DNA photocleavage

property. The authors discussed the role of the supramolecular architecture and in particular of the rhodium(III) unit on the photoreactivity

4.2

Rh(III) Complexes in DNA-Mediated Long-Range Electron Transfer

DNA-mediated electron transfer has been an active and much debated topic of research [155]. Several articles have dealt with DNA-mediated photoinduced electron transfer reactions involving metal complexes as photoactive units [156]. In this context, of particular interest are the studies of Barton and coworkers that used rhodium(III) intercalator complexes not only as ground-state but also as excited-state electron acceptor in electron transfer (ET) reactions through the DNA [144].

4.2.1

Rh(III) Complexes as Acceptors in Electron Transfer Reactions

In 1993, Murphy et al. [157], reported the surprising result that an efficient and rapid photoinduced electron transfer occurs over a large separation distance ($> 40 \text{ \AA}$) between DNA metallointercalators that are covalently tethered to opposite 5'-ends of a 15-base pair DNA duplex (Fig. 13).

In this oligomeric assembly $\text{Ru}(\text{phen})_2\text{dppz}^{2+}$ (dppz = dipyrrophenazine) plays the role of excited electron donor and the $\text{Rh}(\text{phen})_2(\text{phen})^{3+}$ is the electron acceptor. Both donor and acceptor bind to DNA with high affinities ($> 10^6 \text{ M}^{-1}$) by intercalation through the dppz [158, 159] and phen ligands, re-

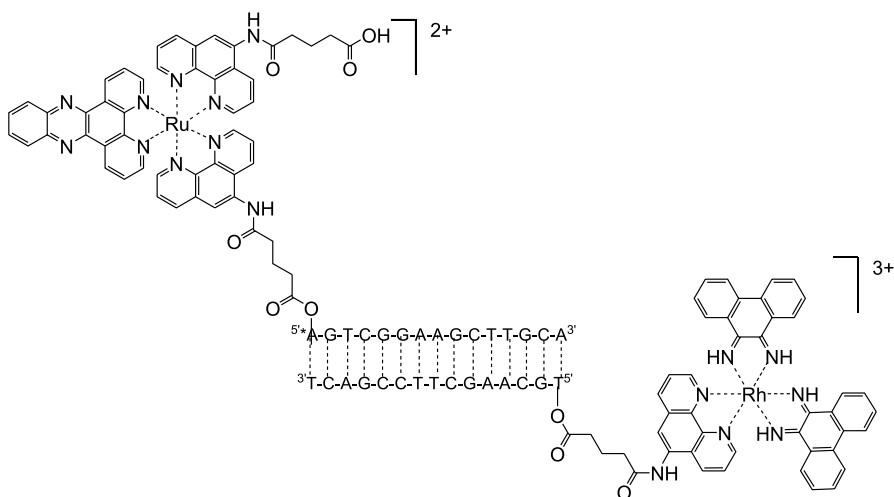


Fig. 13 A 15-base pair DNA duplex carrying covalently tethered Ru(II) and Rh(III) intercalators

spectively. A clear advantage of the tethered Ru/DNA/Rh system is that both the donor and acceptor are covalently held in a well-defined fixed distance range. On the other hand, the report of Murphy et al. was limited by the exclusive use of steady-state emission spectroscopy. A lower limit for the photoinduced electron transfer rate ($> 3 \times 10^9 \text{ s}^{-1}$) has been obtained measuring the quenching of the Ru(II) metal-to-ligand charge transfer (MLCT) emission by the tethered Rh(III) acceptor.

In a subsequent investigation, untethered Ru/DNA/Rh and related systems were studied by Barton et al. [160] using ultrafast laser spectroscopy. The study was focused mainly on the system shown in Fig. 14 constituted by Δ -Ru(phen)₂dppz²⁺ as excited donor, Δ -Rh(phi)₂bpy³⁺ as acceptor intercalated in the calf thymus DNA with the aim to determine the rate of excited-state electron transfer (k_{et}) that occurs from the lowest-lying MLCT state of the Ru donor, and the recombination electron transfer reaction (k_{rec}).

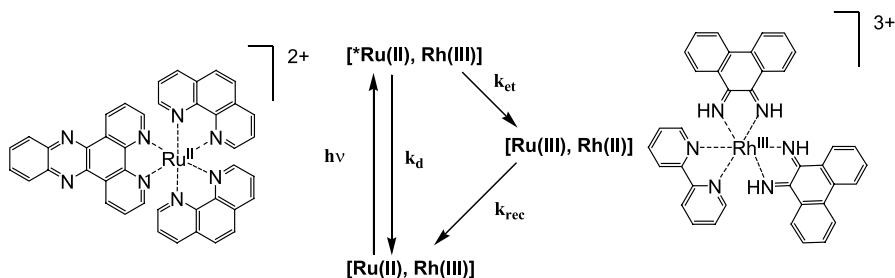


Fig. 14 Photoinduced electron transfer processes taking place between Ru(phen)₂dppz²⁺ and Rh(phi)₂bpy³⁺ DNA intercalators

Efficient and rapid quenching of luminescence of the Ru complex in the presence of Rh complex, even at surprisingly low acceptor loading on the DNA duplex was observed. All the experimental observations were consistent with complete intercalation of the donor and acceptor in DNA. A comparative experiment employing Ru(NH₃)₆³⁺ complex as electron acceptor, clearly indicates that much less efficient quenching is observed when the quencher is groove bound rather intercalated. To deepen the understanding of the mechanism of the electron transfer processes, the authors examined the photoinduced charge separation (k_{et}) and recombination electron transfer (k_{rec}) reactions on the picosecond time scale by monitoring both the kinetics of the emission decay and the kinetics of the recovery of ground state absorption of Ru(II) donor (Fig. 14). Time-correlated single photon counting failed to detect the lifetime of the excited state, clearly indicating that luminescent quenching by electron transfer proceeds faster ($k_{\text{et}} > 3 \times 10^{10} \text{ s}^{-1}$) than the time resolution of the instrument (ca. 50 ps). Ultrafast transient absorption measurements, on the other hand, revealed bleaching of the MLCT band of the Ru(II) complex in a picosecond time scale, assigned by the authors to the

Table 1 Rate constants for charge recombination following electron transfer from DNA-bound, photoexcited donors to Δ -Rh(phi)₂(bpy)³⁺ ^a

Donor	DNA	k_{rec} [10^9 s^{-1}]	$-\Delta G^\circ$ [V]
Δ -Ru(phen) ₂ (dppz) ²⁺	Calf thymus	9.2	1.66
<i>rac</i> -Ru(bpy) ₂ (dppz) ²⁺	Calf thymus	7.1	1.69
Δ -Ru(dmp) ₂ (dppz) ²⁺	Calf thymus	11	1.59
Δ -Ru(phen) ₂ (F ₂ dppz) ²⁺	Calf thymus	7.7	1.68
<i>rac</i> -Ru(phen) ₂ (Me ₂ dppz) ²⁺	Calf thymus	9.2	1.67
Δ -Os(phen) ₂ (dppz) ²⁺	Calf thymus	11	1.21
Λ -Ru(phen) ₂ (dppz) ²⁺	Calf thymus	4.5	
Δ -Ru(phen) ₂ (dppz) ²⁺	Poly-d(AT)	7.4	
Δ -Ru(phen) ₂ (dppz) ²⁺	Poly-d(GC)	0.21	

^a Based on [144]

presence of Ru(III) oxidized donor. The rate constants for charge recombination process (k_{rec}) were obtained from the decay of this signal. The data for seven donor–acceptor pairs are given in Table 1. Within this series, the driving force (ΔG°) is comparable but the donors vary with respect to intercalating ligand, ancillary ligands, chirality, and metal center. Despite such a range of chemical properties, the rate observed is centered around 10^{10} s^{-1} .

A significant difference in rate is observed, however, when the absolute configuration of the donor is varied. For the right-handed Δ -Ru(phen)₂dppz²⁺ the value is 2.5 times higher with respect the left-handed enantiomer indicating a deeper stacking of this complex into the double helix. This result, according to the authors, clearly suggests that the electron transfer process required the intervening aromatic base pairs. The notion of highly efficient ET through the stack of DNA base is also strongly supported by the finding that the largest change in electron transfer rate is observed when the sequence of the DNA bridge is changed: for the same donor and acceptor reactants the rate with poly d(AT) is 30 times higher than with poly d(GC). This is an important result that indicates that the π -stacked bases of the DNA provide an effective pathway for electron transfer reactions. However, the crucial point of this study that involves an untethered Ru/DNA/Rh system concerns the distances over which fast ET occurs. The question is: do the donor and acceptor complexes contact each other, or does electron transfer occur at long range? Two models were considered by the authors to interpret the experimental results: i) a cooperative binding model with ET over short D–A distance and ii) a random binding model with ET over long distances. On the basis of DNA photocleavage experiments, the first hypothesis was reject in favor of a rapid long range ET with a shallow distance dependence [160]. On the other hand, soon thereafter, Barbara [161] reinterpreted the experimental results on a quantitative basis using computational simulation procedures and demon-

strated the failure of long-distance electron transfer model to account for the data. Concurrently, Tuite and coworkers [162] arrived at a similar conclusion for the ET quenching of $\text{Ru}(\text{phen})_2\text{dppz}^{2+}$ emission in a very similar untethered DNA/metallointercalator system. In summary, considerable controversy persists in the estimates of the distances over which fast ET may occur in such type of untethered systems [144].

4.2.2

Long Range Oxidative DNA Damage by Excited Rh(III) Complexes

It is well known from a large variety of experimental studies and calculations that guanine (G) is the most easily oxidized of the nucleic acid bases [144, 163, 164]. Barton and coworkers have extensively exploited the ability of Rh(III)- ϕ complexes to induce oxidative damage specifically at the 5'-G of the 5'-GG-3' doublets, when irradiated with low-energy light. A first investigation was carried out using a 15-base duplex (Rh-DNA) which possesses an end-tethered $\text{Rh}(\phi)_2\text{bpy}^{3+}$ complex in one strand and two 5'-GG-3' sites in the complementary strand (Fig. 15). The peculiarity of this Rh-DNA assembly is that the rhodium complex is spatially separated in a well-defined manner from the potential sites of oxidation. Damage to DNA was demonstrated to occurred as a result of excitation of the intercalated rhodium complex, followed by long-range (30–40 Å) electron transfer through the DNA base pair stack [165]. The strategy used to analyze the mechanism is illustrated in Fig. 16.

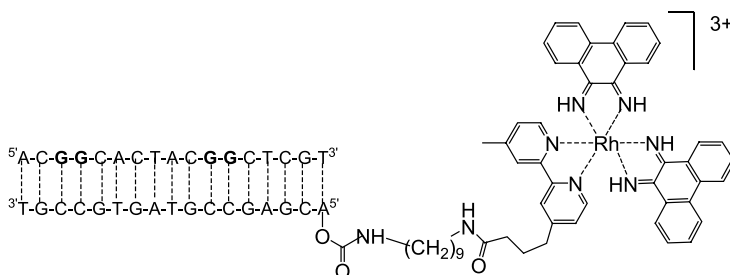


Fig. 15 A15-base duplex with an end-tethered $\text{Rh}(\phi)_2\text{bpy}^{3+}$ complex in one strand and two 5'-GG-3' sites in the complementary strand [165]

The Rh-DNA assembly was first irradiated at 313 nm to induce direct strand cleavage. This photocleavage step marks the site of intercalation, and permits determination of the distance separating the rhodium complex from potential sites of damage. Rh-DNA samples were then irradiated with low energy light at 365 nm, treated with hot piperidine, which promotes strand cleavage at the damaged sites, and examined by gel electrophoresis. This treatment reveals the position and yield of damage. The results clearly in-

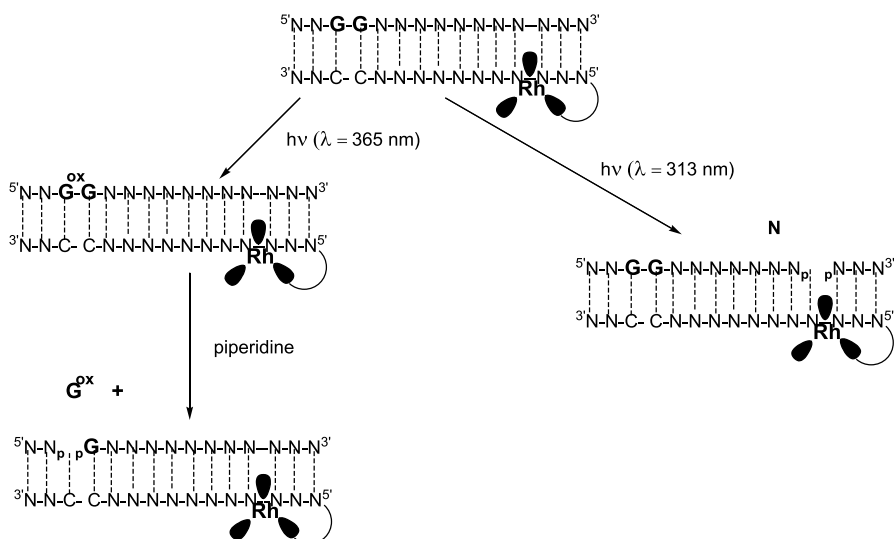


Fig. 16 Use of the tethered Rh(III) complex to (i) mark the site of intercalation by direct strand cleavage (313-nm irradiation) and (ii) promote damage via long-range electron transfer (365-nm irradiation) [165]

dicated that both the proximal and distal 5'-GG-3' doublets were equally damaged and the reaction was intraduplex. Two possible mechanisms for this process were discussed: i) concerted long-range electron transfer; and ii) oxidation of a base near the intercalated Rh acceptor followed by hole migration to the two GG sites. Sensitivity of the reaction to the intervening base pair stack was also observed. In subsequent studies, oxidation has been reported at sites that are up to 200 Å away from the site of intercalation of the photoactive rhodium complex [166].

The photooxidant properties of the phi rhodium (III) complexes have also been used to repair thymine dimers [167, 168], the most common photo-

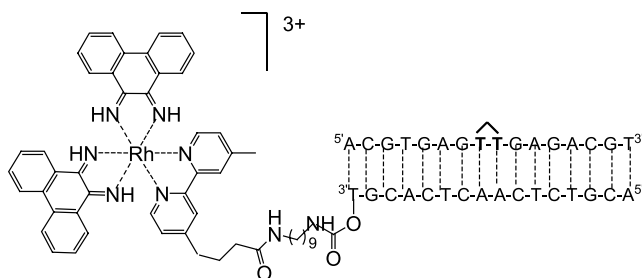


Fig. 17 DNA duplex containing a thymine dimer with tethered Rh(III) complex for photoinduced repair studies [167, 168]

chemical lesion in DNA. Investigations of photoinitiated repair of duplexes containing a single thymine dimer lesion were carried out with visible light (400 nm) using both nontethered and tethered complexes (Fig. 17).

The quantum yield for photorepair with a Rh(III)-tethered complex is substantially (about ca. 30 fold) reduced compared to the noncovalently bound complex. Since the repair efficiency does not appear to be very sensitive to the distance between intercalated rhodium complex and the thymine dimer, the authors suggest that the observed disparity likely results from differences in π -stacking. In addition, evidences that the repair efficiency diminished with disruption of the intervening π -stack confirm that the DNA helix mediates this long-range oxidative repair reaction.

5

Conclusion

A large number of rhodium(III) polypyridine complexes and their cyclometalated analogues have been investigated from the viewpoint of photochemistry, photophysics and of their possible applications.

As mononuclear species, Rh(III) polypyridine complexes display interesting photophysical properties, with lowest excited states of LC type for tris bis-chelated species, and increasing role of MC states for mixed-ligand halo-polypyridine species. In Rh(III) cyclometalated complexes, the covalent character of the C – Rh bonds makes the excited state classification less clearcut, with strong mixing of LC, MLCT, and LLCT character.

Many polynuclear and supramolecular systems containing Rh(III) polypyridine and related units have been synthesized and studied, taking advantage of the favorable properties of these units as good electron acceptors and strong photo-oxidants. In particular, Ru(II)-Rh(III) dyads have been actively investigated for the study of photoinduced electron transfer, with specific interest in driving force, distance, and bridging ligand effects. A limited number of supramolecular systems of higher nuclearity have also been produced. Among these, of particular interest are trinuclear species containing rhodium dihalo polypyridine units, which can act as two-electron storage components thanks to their Rh(III)/Rh(I) redox behavior.

Finally, a large amount of work has been devoted to the use of Rh(III) polypyridine complexes as intercalators for DNA. In this role, they have shown a very versatile behavior, being used for direct strand photocleavage marking the site of intercalation, to induce long-distance photochemical damage or dimer repair, or to act as electron acceptors in long-range electron transfer processes.

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References

1. Carassiti V, Balzani V (1970) *Photochemistry of Coordination Compounds*. Academic Press, New York
2. Kalyanasundaram K (1992) *Photochemistry of Polypyridine and Porphyrin Complexes*. Academic Press, London
3. Balzani V, Juris A, Venturi M, Campagna S, Serroni S (1996) *Chem Rev* 96:759
4. Hannon MJ (1997) *Coord Chem Rev* 162:477
5. Scandola F, Chiorboli C, Indelli MT, Rampi MA (2001) Covalently linked systems containing metal complexes. In: Balzani V (ed) *Electron Transfer in Chemistry*, Vol III, Chap 2.3. Wiley-VCH, Weinheim, p 337
6. Chiorboli C, Indelli MT, Scandola F (2005) *Top Curr Chem* 257:63
7. Ford PC (1983) *J Chem Ed* 60:829
8. Ford PC, Wink D, DiBenedetto J (1983) *Prog Inorg Chem* 40:213
9. Miller DB, Miller PK, Kane-Maguire NAP (1983) *Inorg Chem* 22:3831
10. Frink ME, Ford PC, Skibsted LH (1984) *Acta Chem Scand A* 38:795
11. Skibsted LH, Hancock MP, Magde D, Sexton DA (1984) *Inorg Chem* 23:3735
12. Skibsted LH (1985) *Coord Chem Rev* 64:343
13. Kane-Maguire NAP, Wallace KC, Cobranchi DP, Derrick JM, Speece DG (1986) *Inorg Chem* 25:2101
14. Skibsted LH, Hancock MP, Magde D, Sexton DA (1987) *Inorg Chem* 26:1708
15. McClure LJ, Ford PC (1992) *J Phys Chem* 96:6640
16. Carlos RM, Frink ME, Tfouni E, Ford PC (1992) *Inorg Chim Acta* 193:159
17. Islam K, Ikeda AN, Nozaki KT, Ohno T (1998) *J Chem Phys* 109:4900
18. Forster LS, Rund JV (2003) *Inorg Chem Commun* 6:78
19. Coppens P, Gerlits O, Vorontsov II, Kovalevsky AY, Chen Y-S, Graber T, Novozhilova IV (2004) *Chem Commun*, p 2144
20. Miskowski VM, Rice SF, Gray HB, Milder SJ (1993) *J Phys Chem* 97:4277
21. Bradley PM, Bursten BE, Turro C (2001) *Inorg Chem* 40:1376
22. Cotton FA, Lin C, Murillo CA (2001) *Acc Chem Res* 34:759
23. Lo Schiavo S, Serroni S, Puntoriero F, Tresoldi G, Piraino P (2002) *Eur J Inorg Chem* 79
24. Cooke MW, Hanan GS, Loiseau F, Campagna S, Watanabe M, Tanaka Y (2005) *Angew Chem Int Ed* 44:4881
25. Heyduk AF, Macintosh AM, Nocera DG (1999) *J Am Chem Soc* 121:5023
26. Heyduk AF, Nocera DG (2001) *Science* 293:1639
27. Gray TG, Nocera DG (2005) *Chem Commun*, p 1540
28. Hillis JE, De Armond MK (1971) *J Lumin* 4:273
29. Carstens DHW, Crosby GA (1970) *J Mol Spectrosc* 34:113
30. Crosby GA, Elfring WH Jr (1976) *J Phys Chem* 80:2206
31. De Armond MK, Hillis JE (1971) *J Chem Phys* 54:2247
32. Humbs W, Yersin H (1996) *Inorg Chem* 35:2220
33. Humbs W, Strasser J, Yersin H (1997) *J Lumin* 72–74:677
34. Indelli MT, Carioli A, Scandola F (1984) *J Phys Chem* 88:2685
35. Bolletta F, Rossi A, Barigelletti F, Dellonte S, Balzani V (1981) *Gazz Chim Ital* 111:155
36. Ohno T, Kato S (1984) *Bull Chem Soc Jpn* 57:3391
37. Nishizawa M, Suzuki TM, Sprouse S, Watts RJ, Ford PC (1984) *Inorg Chem* 23:1837
38. Indelli MT, Scandola F (1990) *Inorg Chem* 29:3056
39. Brozik JA, Crosby GA (2005) *Coord Chem Rev* 249:1310
40. Broomhead JA, Grumley W (1968) *Chem Commun*, p 1211

41. Muir MM, Huang WL (1973) *Inorg Chem* 12:1831
42. Loganathan D, Rodriguez JH, Morrison H (2003) *J Am Chem Soc* 125:5640
43. Menon EL, Perera R, Navarro M, Kuhn RJ, Morrison H (2004) *Inorg Chem* 43:5373–5381
44. Huang WL, Lee JR, Shi SY, Tsai CY (2003) *Trans Met Chem* 28:381
45. Tseng MC, Li FK, Huang JH, Su WL, Wang SP, Huang WL (2006) *Inorg Chim Acta* 359:401
46. Calvert JM, Caspar JV, Binstead RA, Westmoreland TD, Meyer TJ (1982) *J Am Chem Soc* 104:6620
47. Frink ME, Sprouse SD, Goodwin HA, Watts RJ, Ford PC (1988) *Inorg Chem* 27:1283
48. Watts RJ, Van Houten J (1978) *J Am Chem Soc* 100:1718
49. Westra J, Glasbeek M (1992) *J Lumin* 53:92
50. Turro C, Evenzahav A, Bossmann SH, Barton JK, Turro NJ (1996) *Inorg Chim Acta* 243:101
51. Burke HM, Gallagher JF, Indelli MT, Vos JG (2004) *Inorg Chim Acta* 357:2989
52. Shinozaki K, Takahashi N (1996) *Inorg Chem* 35:3917
53. Fujita E, Brunschwig BS, Creutz C, Muckerman JT, Sutin N, Szalda D, van Eldik R (2006) *Inorg Chem* 45:1595
54. Martin B, McWhinnie WR, Waind GM (1961) *J Inorg Nucl Chem* 23:207
55. Chou M, Creutz C, Mahajan D, Sutin N, Zipp AP (1982) *Inorg Chem* 21:3989
56. Mulazzani QG, Venturi M, Hoffman MZ (1982) *J Phys Chem* 86:242
57. Schwarz HA, Creutz C (1983) *Inorg Chem* 22:707
58. Yan SG, Brunschwig BS, Creutz C, Fujita E, Sutin N (1998) *J Am Chem Soc* 120:10553
59. Maestri M, Balzani V, Deuschel-Cornioley C, von Zelewsky A (1992) *Adv Photochem* 17:1
60. Colombo MG, Brunold TC, Riedener T, Guedel HU, Fortsch M, Buergi H-B (1994) *Inorg Chem* 33:545
61. Constable EC, Leese TA (1990) *Polyhedron* 9:1613
62. Maeder U, von Zelewsky A, Stoeckli-Evans H (1992) *Helv Chim Acta* 75:1320
63. Maestri M, Sandrini D, Balzani V, Mader U, von Zelewsky A (1987) *Inorg Chem* 26:1323
64. Ohsawa Y, Sprouse S, King KA, De Armond MK, Hanck KW, Watts RJ (1987) *J Phys Chem* 91:1047
65. Zilian A, Maeder U, von Zelewsky A, Guedel HU (1989) *J Am Chem Soc* 111:3855
66. Zilian A, Guedel HU (1991) *Coord Chem Rev* 111:33
67. Ghizdavu L, Lentzen O, Schumm S, Brodkorb A, Moucheron C, Kirsch-De Mesmaeker A (2003) *Inorg Chem* 42:1935
68. Hay PJ (2002) *J Phys Chem A* 106:1634
69. Polson M, Ravaglia M, Fracasso S, Garavelli M, Scandola F (2005) *Inorg Chem* 44:1282
70. Barigelletti F, Sandrini D, Maestri M, Balzani V, von Zelewsky A, Chassot L, Joliet P, Maeder U (1988) *Inorg Chem* 27:3644
71. Lo KK-W, Li C-K, Lau K-W, Zhu N (2003) *Dalton Trans* 24:4682
72. Sandrini D, Maestri M, Balzani V, Mader U, von Zelewsky A (1988) *Inorg Chem* 27:2640
73. Calogero G, Giuffrida G, Serroni S, Ricevuto V, Campagna S (1995) *Inorg Chem* 34:541
74. Didier P, Ortmans I, Kirsch-De Mesmaeker A, Watts RJ (1993) *Inorg Chem* 32:5239
75. Van Diemen JH, Hage R, Haasnoot JG, Lempers HEB, Reedijk J, Vos JG, De Cola L, Barigelletti F, Balzani V (1992) *Inorg Chem* 31:3518

76. Ortmans I, Didier P, Kirsch-De Mesmaeker A (1995) *Inorg Chem* 34:3695
77. Petitjean A, Puntoriero F, Campagna S, Juris A, Lehn J-M, (2006) *Eur J Inorg Chem* 3878
78. Kew G, Hanck K, DeArmond MK (1975) *J Phys Chem* 79:1828
79. Ballardini R, Varani G, Balzani V (1980) *J Am Chem Soc* 102:1719
80. Indelli MT, Ballardini R, Scandola F (1984) *J Phys Chem* 88:2547
81. Lehn J-M, Sauvage J-P (1977) *Nouv J Chim* 1:449
82. Chan S-F, Chou M, Creutz C, Matsubara T, Sutin N (1981) *J Am Chem Soc* 103:369
83. Creutz C, Keller AD, Sutin N, Zipp A P (1982) *J Am Chem Soc* 104:3618
84. Indelli MT, Bignozzi CA, Harriman A, Schoonover JR, Scandola F (1994) *J Am Chem Soc* 116:3768
85. Yoshimura A, Nozaki K, Ohno T (1997) *Coord Chem Rev* 159:375
86. Furue M, Hirata M, Kinoshita S, Kushida T, Kamachi M (1990) *Chem Lett* 2065
87. Collin J-P, Gavina P, Heitz V, Sauvage J-P (1998) *Eur J Inorg Chem* :1
88. Welter S, Salluce N, Belser P, Groeneveld M, De Cola L (2005) *Coord Chem Rev* 249:1360
89. Welter S, Lafolet F, Cecchetto E, Vergeer F, De Cola L (2005) *Chem Phys Chem* 6:2417
90. Barigelletti F, Flamigni I (2000) *Chem Soc Rev* 29:1
91. Indelli MT, Scandola F, Flamigni L, Collin J-P, Sauvage J-P, Sour A (1997) *Inorg Chem* 36:4247
92. Indelli MT, Chiorboli C, Flamigni L, De Cola L, Scandola F (2007) *Inorg Chem* (in press)
93. McConnell HM (1961) *J Chem Phys* 35:508
94. Newton MD (1991) *Chem Rev* 91:767
95. Paddon-Row MN (2001) Covalently linked systems based on organic components. In: Balzani V (ed) *Electron Transfer in Chemistry*, Vol III, Chap 2.1. Wiley-VCH, Weinheim, p 179
96. Helms A, Heiler D, McLendon G (1992) *J Am Chem Soc* 114:6227
97. Weiss EA, Ahrens MJ, Sinks LE, Gusev AV, Ratner MA, Wasielewski MR (2004) *J Am Chem Soc* 126:5577
98. Wold DJ, Haag R, Rampi MA, Frisbie CD (2002) *J Phys Chem B* 106:2814
99. Toutounji MM, Ratner MA (2000) *J Phys Chem A* 104:8566
100. Tour JM, Lamba JJS (1993) *J Am Chem Soc* 115:4935
101. Tsuzuki K, Tanabe J (1991) *J Phys Chem* 95:139
102. Kalyanasundaram K, Graetzel M, Nazeeruddin MK (1992) *J Phys Chem* 96:5865
103. Lee J-D, Vrana LM, Bullock ER, Brewer KJ (1998) *Inorg Chem* 37:3575
104. Kew G, DeArmond K, Hanck K (1974) *J Phys Chem* 78:727
105. Collin J-P, Harriman A, Heitz V, Odobel F, Sauvage J-P (1994) *J Am Chem Soc* 116:5679
106. Wasielewski MR (1992) *Chem Rev* 92:435
107. Gust D, Moore TA, Moore AL (2001) Covalently linked systems containing porphyrin units. In: Balzani V (ed) *Electron Transfer in Chemistry*, Vol III, Chap 2.2. Wiley-VCH, Weinheim, p 273
108. Larson SL, Elliott CM, Kelley DF (1995) *J Phys Chem* 99:6530
109. Huynh MHV, Dattelbaum DM, Meyer TJ (2005) *Coord Chem Rev* 249:457
110. Baranoff E, Collin J-P, Flamigni L, Sauvage J-P (2004) *Chem Soc Rev* 33:147
111. Ronco SE, Thompson DW, Gahan SL, Petersen JD (1998) *Inorg Chem* 37:2020
112. Indelli MT, Polo E, Bignozzi CA, Scandola F (1991) *J Phys Chem* 95:3889
113. Kleverlaan CJ, Indelli MT, Bignozzi CA, Pavanin LA, Scandola F, Hasselman GM, Meyer GJ (2000) *J Am Chem Soc* 122:2840

114. Balzani V, Scandola F (1991) *Supramolecular Photochemistry*. Horwood, Chichester
115. Konduri R, Ye H, MacDonnell FM, Serroni S, Campagna S, Rajeshwar K (2002) *Angew Chem Int Ed* 41:3185
116. Chiorboli C, Fracasso S, Ravaglia M, Scandola F, Campagna S, Wouters K, Konduri R, MacDonnell F (2005) *Inorg Chem* 44:8368
117. Heyduk AF, Nocera DG (2001) *Science* 293:1639
118. Esswein A, Veige A, Nocera D (2005) *J Am Chem Soc* 127:16641
119. Chang CC, Pfennig B, Bocarsly AB (2000) *Coord Chem Rev* 208:33
120. Watson DE, Tan HS, Schreiber E, Mordas CJ, Bocarsly AB (2004) *J Phys Chem A* 108:3261
121. Rau S, Schfer B, Gleich D, Anders E, Rudolph M, Friedrich M, Gorls H, Henry W, Vos JG (2006) *Angew Chem Int Ed* 45:6215
122. Ozawa H, Haga M, Sakai K (2006) *J Am Chem Soc* 128:4926
123. Molnar SM, Nallas G, Bridgewater JS, Brewer KJ (1994) *J Am Chem Soc* 116:5206
124. Nallas GNA, Jones SW, Brewer KJ (1996) *Inorg Chem* 35:6974
125. Molnar SM, Jensen GE, Vogler LM, Jones SW, Laverman L, Bridgewater JS, Richter MM, Brewer KJ (1994) *J Photochem Photobiol A Chem* 80:315
126. Swavey S, Brewer KJ (2002) *Inorg Chem* 41:4044
127. Elvington M, Brewer KJ (2006) *Inorg Chem* 45:5242
128. Barton JK (1986) *Science* 233:727
129. Pyle AM, Barton JK (1990) In: Lippard SJ (ed) *Progress in Inorganic Chemistry: Bioinorganic Chemistry*, Vol 38. Wiley, New York, p 413
130. Erkkila KE, Odom DT, Barton JK (1999) *Chem Rev* 99:2777
131. Jennette KW, Lippard SJ, Vassiliades GA, Bauer WR (1974) *Proc Natl Acad Sci USA* 71:3839
132. Crotz AH, Hudson BP, Barton JK (1993) *J Am Chem Soc* 115:12577
133. Pyle AM, Chiang MY, Barton JK (1990) *Inorg Chem* 29:4487
134. David SS, Barton JK (1993) *J Am Chem Soc* 115:2984
135. Crotz AH, Kuo LY, Barton JK (1993) *Inorg Chem* 32:5963
136. Collins J-C, Shield JK, Barton JK (1994) *J Am Chem Soc* 116:9840
137. Crotz AH, Barton JK (1994) *Inorg Chem* 33:1940
138. Hudson BP, Barton JK (1998) *J Am Chem Soc* 120:6877
139. Crotz AH, Kuo LY, Shields TP, Barton JK (1993) *J Am Chem Soc* 115:3877
140. Sitlani A, Dupureur C, Barton JK (1993) *J Am Chem Soc* 115:12589
141. Sitlani A, Long EC, Pyle AM, Barton JK (1992) *J Am Chem Soc* 114:2303
142. Kisko J, Barton JK (2000) *Inorg Chem* 39:4942
143. Turro C, Hall DB, Chen W, Zuilhof H, Barton JK, Turro NJ (1998) *J Phys Chem A* 102:5708
144. Holmlin RE, Dandliker PJ, Barton KJ (1997) *Angew Chem Int Ed* 36:2714
145. Hudson BP, Dupureur CM, Barton JK (1995) *J Am Chem Soc* 117:9379
146. Kielkopf CL, Erkkila KE, Hudson BP, Barton JK, Rees DC (2000) *Nat Struct Biol* 7:117
147. Pyle AM, Morii T, Barton JK (1990) *J Am Chem Soc* 112:9432
148. Sardesai NJ, Zimmermann, Barton JK (1994) *J Am Chem Soc* 116:7502
149. Terbrueggen RH, Johann T W, Barton JK (1998) *Inorg Chem* 37:6874
150. Jackson BA, Barton JK (1997) *J Am Chem Soc* 119:12986
151. Jackson BA, Alekseyev VY, Barton JK (1999) *Biochemistry* 38:4655
152. Kisko JL, Barton JK (2000) *Inorg Chem* 39:4942
153. Holder AA, Swavey A, Brewer KJ (2004) *Inorg Chem* 43:303
154. Swavey S, Brewer KJ (2002) *Inorg Chem* 41:6196

155. Lewis FD (2001) In: Balzani V (ed) *Electron Transfer in Chemistry*, Vol III, Chap 1.5. Wiley/VCH, Weinheim, p 105
156. Stemp EDA, Barton JK (1996) In: Sigel A, Sigel H (eds) *Metal Ions in Biological systems*, Vol 33. Marcel Dekker, New York, p 325
157. Murphy CJ, Arkin MR, Jenkins Y, Ghatlia ND, Bossmann S, Turro NJ, Barton JK (1993) *Science* 262:1025
158. Friedman AE, Chambron JC, Sauvage JP, Turro NJ, Barton JK (1990) *J Am Chem Soc* 112:4960
159. Hort C, Lincoln P, Norden B (1993) *J Am Chem Soc* 115:3448
160. Arkin MR, Stemp EDA, Holmlin RE, Barton JK, Hormann A, Olson EJC, Barbara PF (1996) *Science* 273:475
161. Olson EJC, Hu D, Hormann A, Barbara PF (1997) *J Phys Chem B* 101:299
162. Lincoln P, Tuite E, Norden B (1997) *J Am Chem Soc* 119:1454
163. Saito I, Takayama M, Sugiyama H, Nakatani K (1995) *J Am Chem Soc* 117:6406
164. Kittler L (1980) *J Electroanal Chem* 116:503
165. Hall DB, Holmlin RE, Barton JK (1996) *Nature* 382:731
166. Nunez ME, Hall DB, Barton JK (1999) *Chem Biol* 6:85
167. Dandliker PJ, Holmlin RE, Barton JK (1997) *Science* 275:1465
168. Dandliker PJ, Nunez ME, Barton JK (1998) *Biochemistry* 37:6491

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