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Review

From the photochemistry of coordination compounds to light-powered nanoscale devices and machines

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Contents

Abstract

The photosensitivity of metal complexes has been known for a long time. Early studies on ligand photosubstitution and photoredox decomposition reactions of metal complexes of simple inorganic ligands (e.g. NH_3, CN^-) have been followed by accurate investigations on the photophysical behavior (luminescence quantum yields and lifetimes) and on the use of metal complexes in bimolecular processes (energy and electron transfer). A large number of complexes, stable towards photodecomposition, but capable of undergoing excited state redox processes, have been used for interconverting light and chemical energy. More recently, combination of supramolecular chemistry and photochemistry has led to the design and construction of multicomponent 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. Examples of molecular devices for processing light signals and of molecular machines powered by light energy, based on coordination compounds, are illustrated.

Keywords: Photochemistry; Coordination compounds; Luminescence; Electron transfer; Energy transfer; Supramolecular photochemistry; Molecular devices; Molecular machines

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1. Photochemistry of coordination compounds: milestones

The photosensitivity of metal complexes has been known for a long time [1]. 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 [2]. The light sensitivity of other metal complexes (particularly $[Fe(CN)_6]^{4-}$) was also observed very early [1]. 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, Professor of Chemistry at the University of Bologna, who was also the first scientist to suggest the development of artificial photosynthesis for solving the problem of energy supply [3,4]. 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. [5]). Several quantitative studies also appeared on the photochemical behavior of $[Fe(CN)_6]^{4-}$ [6], but the lack of a theory on the absorption spectra and on the nature of the excited states prevented any mechanistic interpretation of the observed photoreactions.

In the late 1950s, the interpretation of the absorption spectra started thanks to the development of the ligand field theory [7] and the first attempts to rationalize the charge-transfer bands [8,9]. Following these developments, investigations in the field of the photochemistry and photophysics of coordination compounds have proceeded along several routes. In a few years, four important laboratories published their first photochemical paper [10–13]. Much of the interest was focused on Cr(III) complexes, whose luminescence was also investigated in some detail [14]. Later, Co(III) complexes attracted a great deal of attention since their photochemical behavior was found to change drastically with excitation wavelength [15,16]. A few, isolated flash photolysis investigations began to appear, but this technique remained unavailable to most inorganic photochemists for several years.

Since the middle 1960s, the great development of photochemical and luminescence investigations on organic compounds led to the publication of books [17–20] illustrating fundamental photochemical concepts that were quickly exploited also for coordination compounds [1]. In the late 1960s, the spectroscopic properties of several bipyridine-type metal complexes were characterized and the red luminescence of $[Ru(bpy)_3]^{2+}$ (bpy = 2,2′-bipyridine) was assigned to its lowest triplet metal-to-ligand charge-transfer excited state, ^{3}MLCT [21]. Presently $[Ru(bpy)_3]^{2+}$ is by far the most popular complex used in photochemistry and photophysics, but in the exhaustive monograph on the photochemistry of coordination compounds [1] published in 1970 it was hardly mentioned at all and all the photochemistry of the Ru and Os complexes was dealt with in less than one page, whereas 51 pages were dedicated to Cr and 52 pages to Co complexes. In 1972 it was discovered that the ^{3}MLCT excited state of $[Ru(bpy)_3]^{2+}$, hereafter indicate as $^*[Ru(bpy)_3]^{2+}$, is quenched by $[Co(NH_3)_5Cl]^{2+}$ in a bimolecular electron transfer process [22]. Such a discovery had a strong impact on the photochemical community since at that time excited state outer-sphere electron-transfer reactions were not common, even in the more mature field of organic photochemistry. Several laboratories [23–26] became immediately interested in the use of $^*[Ru(bpy)_3]^{2+}$ as a reactant and in a few years it was clear that this complex shows an outstanding combination of high chemical stability, strong luminescence, long excited state lifetime, and strong tendency to undergo redox reactions [27]. Shortly thereafter it was recognized that, because of its photoredox properties, $[Ru(bpy)_3]^{2+}$ might function as a photocatalyst for the decomposition of water into hydrogen and oxygen [28]. Since then, the interest in the study of the photochemistry of Ru(II) bipyridine-type (and, to some degree, Os(II) bipyridine-type) complexes increased exponentially. In a special issue on the state-of-the-art in inorganic photochemistry, published by the Journal of Chemical Education in 1983, an entire article [29] was dedicated to ruthenium polypyridyls as a case study, and several other articles dealt with $[Ru(bpy)_3]^{2+}$ (particularly, on its use in energy [30] and electron [31] transfer processes). In the middle 1980s, most of the properties of $[Ru(bpy)_3]^{2+}$ were fully elucidated and in a few years several hundreds of Ru–polypyridine complexes were synthesized since it became clear that the redox and excited state properties can be tuned by changing the ligands or ligand substituents [32,33]. In the period 1975–1985 a real revolution occurred in the field of the photochemistry of coordination compounds. Studies of intramolecular ligand photosubstitution, photoredox decomposition, and photoisomerization reactions were carried out and, thanks to an extensive use of pulsed techniques, a huge amount of data was collected on the rate constants of bimolecular processes [34]. The high exoergonicity 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 [35], with particular attention to the so-called Marcus inverted region.

In the middle 1980s the interest of several research groups moved from molecular to supramolecular chemistry, a discipline consecrated by the award of the Nobel Prize in Chemistry to Pedersen [36], Cram [37], and Lehn [38]. In 1987 a NATO Workshop held at Capri (Italy) [39] marked the birth place of supramolecular photochemistry [40,41] that in a few years opened the way to the bottom-up construction of molecular devices and machines [42–50]. Coordination compounds are indeed essential photoactive components in a great number of such nanoscale devices and machines.

2. Supramolecular (multicomponent) chemistry

The classical definition of supramolecular chemistry is that given by 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” [51]. With supramolecular

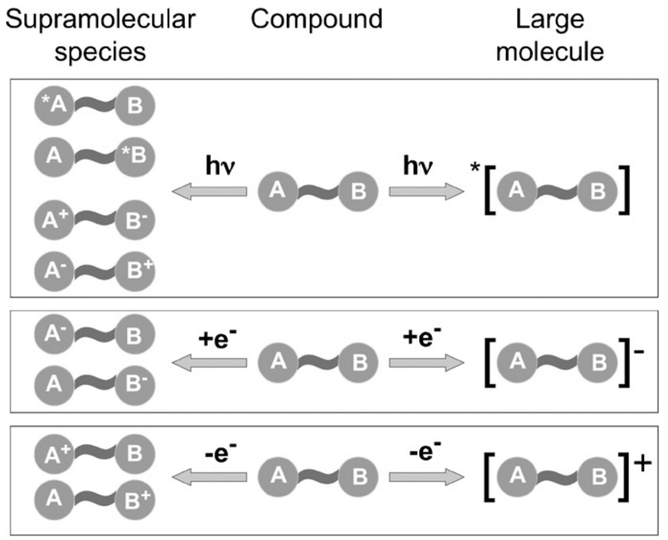


Fig. 1. Schematic representation of the difference between a supramolecular system and a large molecule based on the effects caused by a photon or an electron input [52].

chemistry there has been a change in focus from molecules to molecular assemblies or multicomponent systems but, according to the original definition, when the components of a chemical system are linked by covalent bonds, the system should be considered a molecule instead of a supramolecular species. This point is particularly important in dealing with light powered molecular devices and machines (vide infra), that are usually multicomponent systems in which the components can be linked by chemical bonds of various nature. Therefore, although the classical definition of supramolecular chemistry as "the chemistry beyond the molecule" [51] 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 [52]. This concept is illustrated, for example, in Fig. 1. In the case of a photon stimulation, a system A∼B, consisting of two units (∼indicates any type of "bond" that keeps the units together), can be defined 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. 1), 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 lead 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. 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.

3. Photoinduced processes in supramolecular systems

A supramolecular system can be preorganized so as to favor the occurrence of photoinduced energy and electron transfer processes. This is indeed the basis for the bottom-up construction of light-powered nanoscale devices and machines.

Consider, for example, an A–L–B supramolecular system, where A is the light-absorbing molecular unit (Eq. (1)), 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, since the two reaction partners can already be at an interaction distance suitable for electron (Eqs. (2) and (3)) and energy transfer (Eq. (4)):

$$\text{A–L–B} + h\nu \rightarrow {}^*\text{A–L–B} \quad \text{photoexcitation} \tag{1}$$

$$^*\text{A–L–B} \rightarrow \text{A}^+\text{–L–B}^- \quad \text{oxidative electron transfer} \tag{2}$$

$$^*\text{A–L–B} \rightarrow \text{A}^-\text{–L–B}^+ \quad \text{reductive electron transfer} \tag{3}$$

$$^*\text{A–L–B} \rightarrow \text{A–L–}^*\text{B} \quad \text{electronic energy transfer} \tag{4}$$

In the absence of subsequent processes (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. (5) and (6)), and photoinduced energy transfer is followed by radiative and/or non-radiative deactivation of the excited acceptor (Eq. (7)):

$$\text{A}^+\text{–L–B}^- \rightarrow \text{A–L–B} \quad \text{back oxidative electron transfer} \tag{5}$$

$$\text{A}^-\text{–L–B}^+ \rightarrow \text{A–L–B} \quad \text{back reductive electron transfer} \tag{6}$$

$$\text{A–L–}^*\text{B} \rightarrow \text{A–L–B} \quad \text{excited state decay} \tag{7}$$

In supramolecular systems electron- and energy-transfer processes can involve even very short lived excited states. Many light-powered nanoscale devices and machines are based on the occurrence of processes (1)–(7).

Photoinduced electron and energy transfer processes have been the object of extensive experimental and theoretical investigations in the last 30 years. The rates of these processes depend on the free energy change and on nuclear and electronic factors in a complex way. This topic cannot be discussed here for space reasons. The interested reader can refer to many books and reviews, e.g. [53–56]. On the basis of the acquired knowledge, it is indeed possible to interpret, or even to predict with reasonable confidence, the rate of most photoinduced energy and electron transfer processes.

In the following we will illustrate some examples of light-powered nanodevices and nanomachines based on classical transition metal complexes. For a more exhaustive discussion, the reader should refer to [42–45,47–50] and to a forthcoming monograph [56].

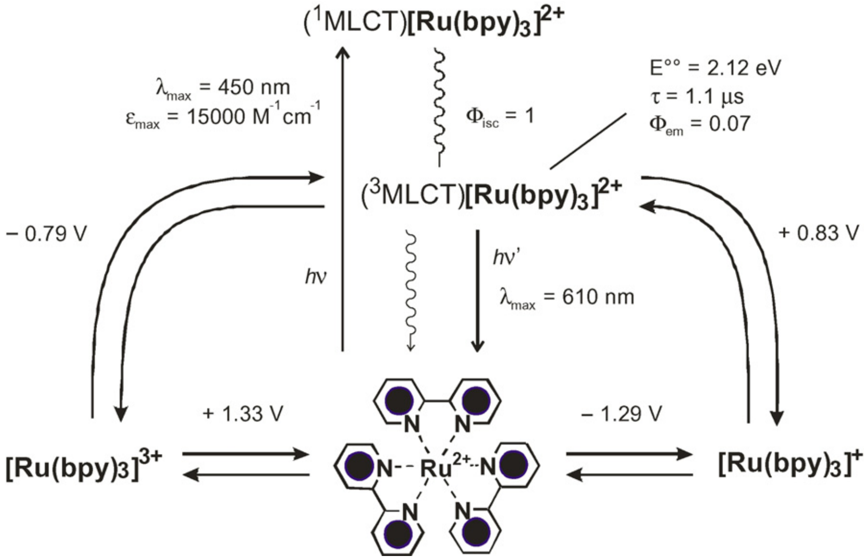


Fig. 2. Schematic representation of some important properties of $[Ru(bpy)_3]^{2+}$ in deaerated acetonitrile solution at 298 K. The potential values are referred to SCE [32].

4. Light-powered nanoscale devices

4.1. Molecular wires

An important function at the molecular level is photoinduced electron and energy transfer over long distances and/or along predetermined directions. This function can be obtained by linking donor and acceptor components by a rigid spacer. Most of the systems investigated are based on coordination compounds and contain polypyridine metal complexes as donor and acceptor units. In several cases, the photoexcited chromophoric group is $[Ru(bpy)_3]^{2+}$. The excited state of $[Ru(bpy)_3]^{2+}$, playing the role of energy donor or of redox reagent, is the lowest, formally triplet, metal-to-ligand charge-transfer excited state, ^{3}MLCT. This lies ~2.1 eV above the ground state and can be obtained by visible light excitation ($\lambda_{max} \sim 450$ nm). It is a good oxidant as well as a good reductant and has a lifetime of ~1 μs in deaerated solutions [32] (Fig. 2). This relatively long lifetime is very useful because it enables study of energy transfer over long distances. Other very interesting systems are those based on porphyrins, which will not be discussed for space limitations.

4.1.1. Photoinduced electron transfer

Several bi- and poly-metallic wire-type systems, capable of performing photoinduced electron transfer, have been designed and investigated [57]. An example of a systematic study is that performed on compounds $\mathbf{1}^{5+}$–$\mathbf{5}^{5+}$ (Fig. 3) [58]. When excitation is selectively performed in the Ru(II) chromophoric unit, prompt intersystem crossing from the originally populated singlet metal-to-ligand charge-transfer (^{1}MLCT) excited state leads to the long lived ^{3}MLCT excited state which transfers an electron to the Rh(III) unit, a process that is then followed by a back electron-transfer reaction. Comparison of compounds $\mathbf{1}^{5+}$ and $\mathbf{2}^{5+}$ shows that, despite the longer metal–metal distance, the forward electron transfer is faster across the phenylene spacer ($k = 3.0 \times 10^9\ s^{-1}$) than across the two methylene groups ($k = 1.7 \times 10^8\ s^{-1}$). This result can be related to the lower energy of the LUMO of the phenylene group, which facilitates the superexchange interaction. In the homogeneous family of compounds $\mathbf{2}^{5+}$–$\mathbf{4}^{5+}$, the rate constant decreases exponentially with increasing metal–metal distance. For compound $\mathbf{5}^{5+}$, which is identical to $\mathbf{4}^{5+}$ except for the presence of two solubilizing hexyl groups on the central phenylene ring, the photoinduced electron-transfer process is 10 times slower, presumably because the substituents increase the twist angle between the phenylene units, thereby reducing electronic coupling.

A very interesting system is the 4-nm long triad $\mathbf{6}^{3+}$ shown in Fig. 4, consisting of an Ir(III) bis-terpyridine complex connected to a triphenylamine electron donor (D) and a naphthalene bisimide electron acceptor (A) [59]. Upon excitation of the electron donor D (or even the Ir-based moiety) a charge separated state D^+–Ir^-–A is formed with 100% yield in less than 20 ps that successively leads to D^+–Ir–A^- with 10% efficiency in 400 ps. Remarkably, the fully charge-separated state D^+–Ir–A^- has a lifetime of 120 μs at room temperature in deaerated acetonitrile solution.

4.1.2. Photoinduced energy transfer

Several examples have been reported in which the photoexcited chromophoric group is $[Ru(bpy)_3]^{2+}$ and the energy acceptor is an $[Os(bpy)_3]^{2+}$ unit. The occurrence of the energy-transfer process promotes the ground state $[Os(bpy)_3]^{2+}$ acceptor unit to its lowest energy excited state ^{3}MLCT, which lies approximately 0.35 eV below the ^{3}MLCT excited state of the Ru complex. Both the donor and the acceptor excited states are luminescent, so that the occurrence of energy transfer can be monitored by quenching and/or sensitization experiments with both continuous and pulsed excitation techniques.

The most interesting systems are those in which the two chromophoric units are connected by rigid, modular spacers, as in the case of the $[Ru(bpy)_3]^{2+}$–$(ph)_n$–$[Os(bpy)_3]^{2+}$ (ph = 1,4-

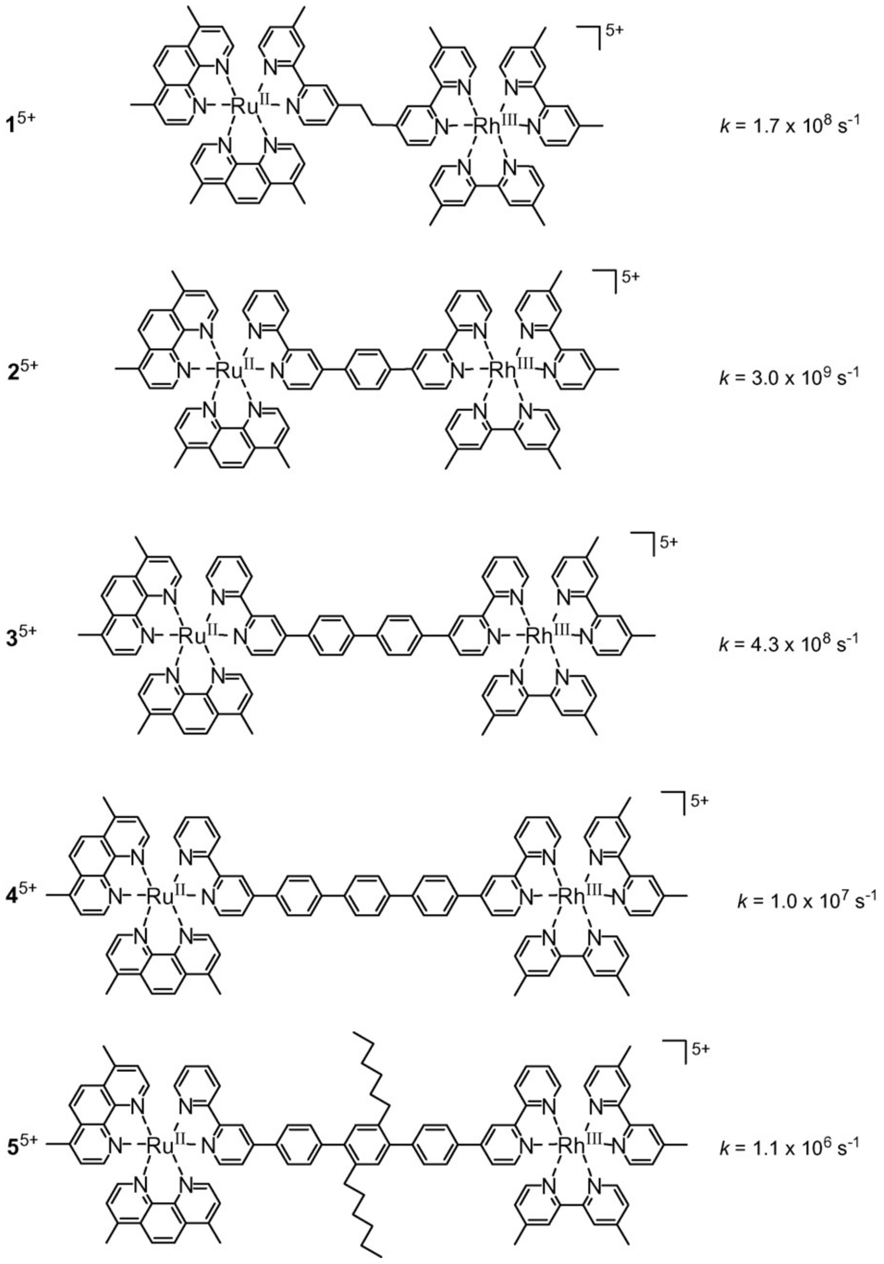


Fig. 3. Dinuclear metal complexes $\mathbf{1}^{5+}$–$\mathbf{5}^{5+}$ used for photoinduced electron-transfer experiments [58].

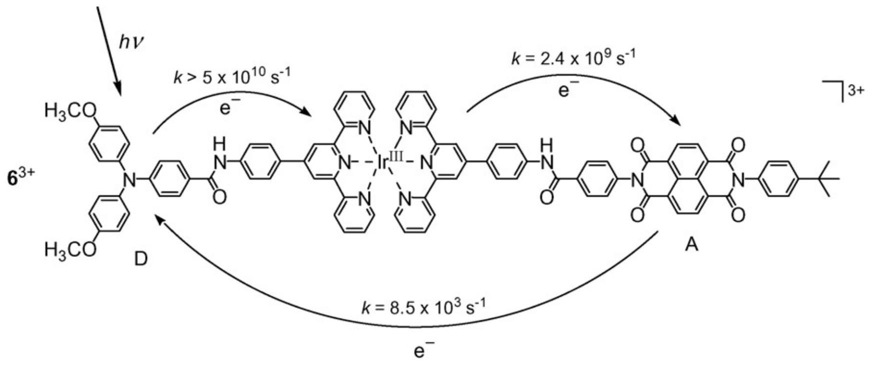


Fig. 4. Electron-transfer processes in triad $\mathbf{6}^{3+}$ [59].

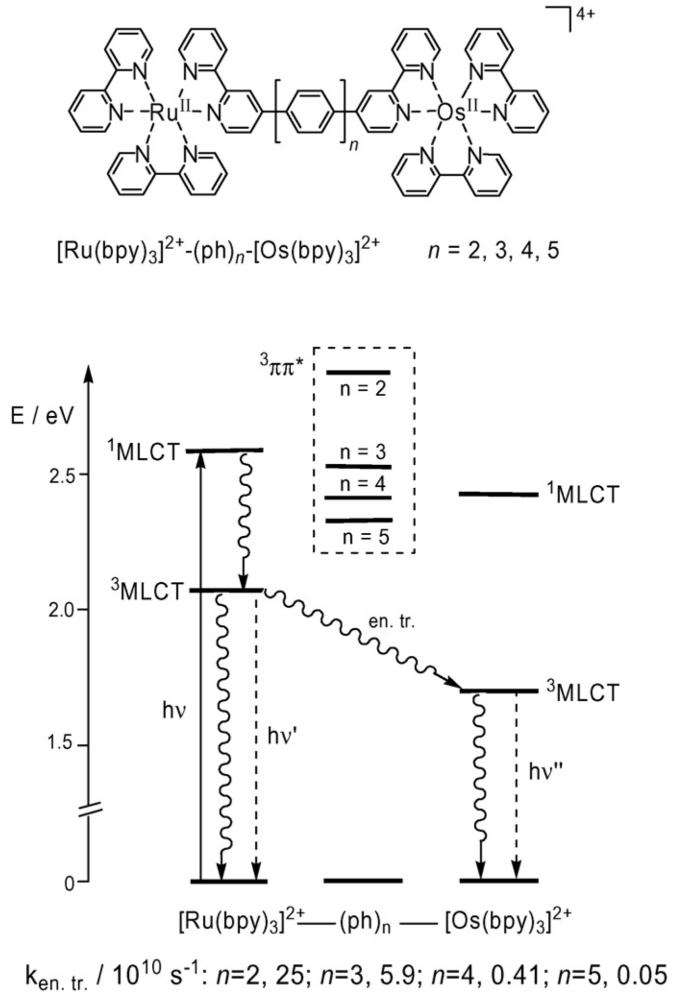


Fig. 5. Structure of compounds $[Ru(bpy)_3]^{2+}$–$(ph)_n$–$[Os(bpy)_3]^{2+}$, energy-level diagram and rate constants for the energy-transfer process [60].

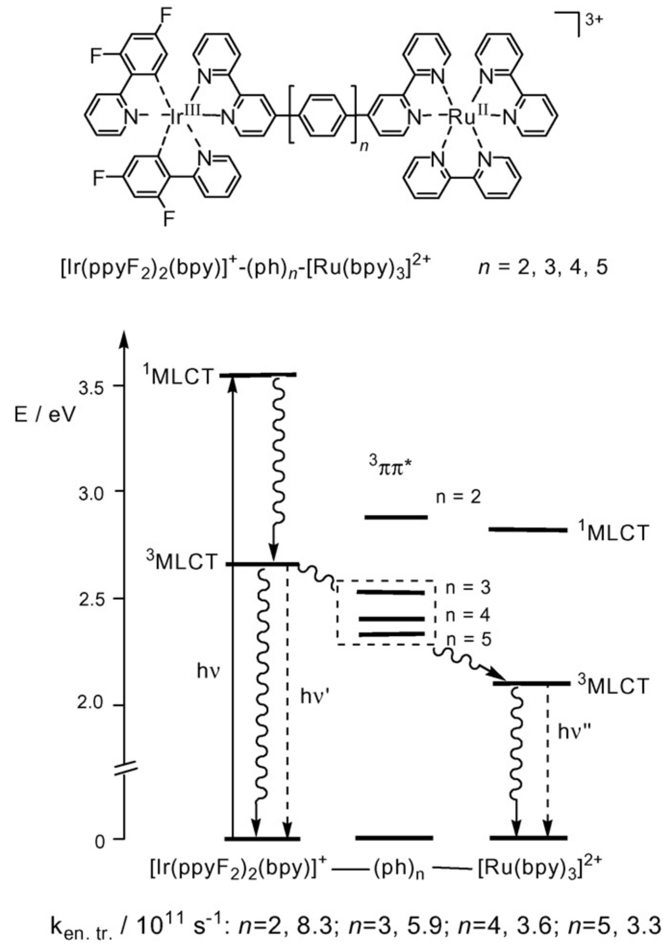


Fig. 6. Structure of compounds $[Ir(ppyF_2)_2(bpy)]^{+}$–$(ph)_n$–$[Ru(bpy)_3]^{2+}$, energy-level diagram and rate constants for the energy transfer process [62].

phenylene; $n = 2, 3, 4, 5$) species (Fig. 5) [60]. The lowest energy level of the bridge decreases slightly as the number of phenylene units is increased, but always lies above the donor and acceptor levels involved in energy transfer. A further decrease in the energy of the triplet excited state of the spacer would be expected to switch the energy-transfer mechanism from superexchange-mediated to hopping. In the series of compounds shown in Fig. 5, the energy-transfer rate decreases with increasing the length of the oligophenylene spacer. Such rate constants are much higher than those expected for a Förster-type mechanism, whereas they can be accounted for by a superexchange Dexter mechanism. The values obtained for the energy transfer rate in the series of compounds $[Ru(bpy)_3]^{2+}$–$(ph)_nR_2$–$[Os(bpy)_3]^{2+}$ [61], in which the central phenylene unit carries two hexyl chains (R), are much lower than those found for the unsubstituted compounds, most likely because the bulky substituents increase the tilt angle between the phenyl units.

The energy-level diagram of the $[Ir(ppyF_2)_2(bpy)]^{+}$–$(ph)_n$–$[Ru(bpy)_3]^{2+}$ (ph = 1,4-phenylene; $n = 2, 3, 4, 5$) systems (Fig. 6) [62] shows that in this case the energy level of the donor is almost isoenergetic with the triplet state of the spacers. The energy of the Ir-based donor can, therefore, be transferred to the Ru-based acceptor via the bridging ligand, at least for $n > 2$. This hopping mechanism accounts for the very low dependence of the energy-transfer rate constants on the length of the spacer (Fig. 6).

4.2. Molecular switches

Energy or electron transfer between components of supramolecular systems can occur directly (through space) or can be mediated by the intervening matter. In the latter case, manipulation of the interposed matter (e.g. the bridge in a three component system) can switch the process on/off. In principle, any kind of input causing a reversible modification in a bridging component can be used.

A simple, albeit not fully satisfactory, example of energy transfer switching is given by compound $\mathbf{7}^{4+}$ (Fig. 7), which consists of $[Ru(bpy)_3]^{2+}$ and $[Os(bpy)_3]^{2+}$ moieties bridged by an anthracene unit [63,64]. Because the lowest triplet energy level of the anthracene bridge lies between the lowest triplet metal-to-ligand charge transfer (MLCT) excited state of the Ru- and Os-based complexes, energy transfer from the $[Ru(bpy)]_3{}^{2+}$ to the $[Os(bpy)]_3{}^{2+}$ moiety is very efficient. Continuous irradiation with visible light in deaerated acetonitrile solution causes only the sensitized emission of the Os-based complex. In aer-

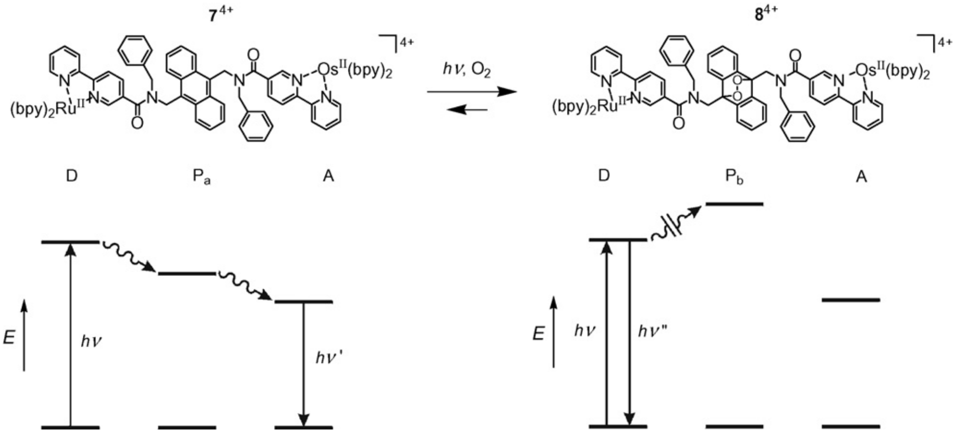


Fig. 7. Switching energy transfer in compound $\mathbf{7}^{4+}$ [63].

ated solution, however, the relatively long-lived excited state of the $[Os(bpy)_3]^{2+}$ moiety sensitizes the formation of singlet oxygen which attacks the anthracene ring to form the endoperoxide derivative $\mathbf{8}^{4+}$ (Fig. 7). As a consequence delocalization of the π-system on the bridge is reduced, the lowest energy excited state of the bridge moves to much higher energy, and energy transfer is switched off. In principle, the endoperoxide could be transformed back to anthracene but such a reaction is rather difficult to perform.

4.3. Molecular plug-socket and extension-cable systems

Supramolecular species comprising donor and acceptor units connected by means of noncovalent forces can be disassembled and re-assembled by modulating the interactions that keep the two components together [65], thereby enabling switching of electron- or energy-transfer processes. Systems of this type are reminiscent of plug and socket electrical devices and, like their macroscopic counterparts, are characterized by the possibility of connecting/disconnecting the two components in a reversible way, and the occurrence of an electron or electronic energy flow from the socket to the plug when the two components are connected.

The plug-socket concept has been used to design molecular systems which mimic the function of a macroscopic electrical extension cable. An example involving a metal complex is shown in Fig. 8 [66,67]. It comprises the three components $\mathbf{9}^{2+}$, $[\mathbf{10}H]^+$, and $\mathbf{11}^{2+}$. Component $\mathbf{9}^{2+}$ consists of two moieties: a $[Ru(bpy)_3]^{2+}$ unit, which behaves as an electron donor under light excitation, and a dibenzo[24]crown-8 macrocycle, capable of playing the role of a hydrogen-bonding socket. The extension cable $[\mathbf{10}H]^+$ is made up of a dialkylammonium ion, that can insert itself as a plug into a dibenzo[24]crown-8 socket by virtue of hydrogen-bonding interactions, a biphenyl spacer, and a benzonaphtho[36]crown-10 moiety, which fulfils the role of a π-electron rich socket. Finally, the 1,1′-dioctyl-4,4′-bipyridinium dication $\mathbf{11}^{2+}$ can play the role of an electron drain when plugged into the benzonaphtho[36]crown-10 moiety of $[\mathbf{10}H]^+$. In CH_2Cl_2 solution, reversible connection–disconnection of the two plug and socket junctions can be controlled independently by acid–base and red-ox stimulation, respectively, and monitored by changes in the absorption and emission spectra, owing to the different nature of the interactions (hydrogen bonding and π-electron donor–acceptor) that connect the components. In the fully assembled system, $\mathbf{9}^{2+} \supset [\mathbf{10}H]^+ \supset \mathbf{11}^{2+}$, light excitation of the Ru-based unit of $\mathbf{9}^{2+}$ is followed by electron transfer to $\mathbf{11}^{2+}$, with $[\mathbf{10}H]^+$ playing the role of an extension cable (Fig. 8). The occurrence of this process is demonstrated by nanosecond-laser flash-photolysis experiments which show the formation of the reduced $\mathbf{11}^{2+}$ species upon light excitation of $\mathbf{9}^{2+}$ in the self-assembled triad. Interestingly, the photoinduced electron-transfer process can be powered by sunlight because the $[Ru(bpy)_3]^{2+}$-type component $\mathbf{9}^{2+}$ shows a broad and intense absorption band in the visible spectral region.

4.4. Molecular antennas

An antenna for light harvesting is an organized multicomponent system in which several chromophoric molecular species absorb the incident light and channel the excitation energy to a common acceptor component [68]. Antenna systems are widely used by nature to solve the problem of light-harvesting efficiency in the photosynthetic process where light is converted into chemical energy [69]. Collecting light by an artificial antenna system may also be useful for other purposes, e.g. for signal amplification in luminescence sensors [70].

The antenna effect can only be obtained in supramolecular arrays suitably organized in the dimensions of time, energy, and space. Each molecular component has to absorb the incident light and the excited state so obtained (donor) has to transfer electronic energy to a nearby component (acceptor), before undergoing radiative or nonradiative deactivation (organization in the time dimension). In order for energy transfer to occur, the energy of the acceptor excited state has to be lower or, at most, equal to the energy of the excited state of the donor (organization in the energy dimension). Finally, the successive donor-to-acceptor energy-transfer steps must result in an overall energy-transfer process leading the excitation energy towards a selected component of the array (organization in the space dimension).

Such an organization in the dimensions of time, energy, and space can be obtained in suitably designed dendrimers. Several light harvesting dendrimers based on transition metal complexes have been constructed and investigated [71–73]. Here we mention only a couple of recent examples.

Dendrimer **12**, shown in Fig. 9, contains in the interior 18 amide groups, which are known to strongly coordinate lanthanide ions, and in the periphery 24 chromophoric dansyl units, which have intense absorption bands in the near UV spectral region and an intense fluorescence band in the visible region [74]. Addition of lanthanide ions to 5:1 (v/v) acetonitrile–dichloromethane solutions of dendrimer **12** causes a quenching of the fluorescence of the dansyl units. At low metal ion concentration, each dendrimer hosts only one metal ion and, when the encapsulated metal ion is Nd^{3+}, the fluorescence of all the 24 dansyl units is completely quenched and is accompanied by the sensitized emission in the near infrared region ($\lambda_{max} = 1064$ nm) of the lanthanide ion. These results show that a very efficient energy transfer takes place from the peripheral dansyl units to the coordinated metal ion.

Another interesting system is that illustrated in Fig. 10. Dendrimer **13** consists of a cyclam core appended with 12 dimethoxybenzene and 16 naphthyl units. The absorption spectrum is dominated by naphthalene absorption bands and the emission consists of three types of bands, assigned to naphthyl localized excited states ($\lambda_{max} = 337$ nm), naphthyl excimers (λ_{max} ca. 390 nm), and naphthyl–amine exciplexes ($\lambda_{max} = 480$ nm) [75]. Upon titration with trifluoroacetic acid, the tetraamine cyclam core undergoes two successive protonation reactions that, preventing exciplex formation, cause a strong increase of the naphthyl localized emission. $[Ru(bpy)(CN)_4]^{2-}$ (Fig. 10) exhibits two moderately intense ^{1}MLCT absorption bands at 373 and 535 nm and a very weak ^{3}MLCT emission at 770 nm. Upon titration with trifluoroacetic acid, successive protonation of two CN^- ligands takes place with displacement of the absorption and emission bands to higher energies. In acetonitrile–dichloromethane 1:1 (v/v) solution, the absorption and emission spectra of a 1:1 mixture of $[Ru(bpy)(CN)_4]^{2-}$ and **13** consist of the absorption and emission bands of the isolated components, showing that there is no interaction between the two species. Titration of this mixture with trifluoroacetic acid, however, causes strong spectral changes with isosbestic points maintained up to the addition of two equivalents of acid [76]. The results obtained show that protons promote association of $[Ru(bpy)(CN)_4]^{2-}$ and **13** and that, after addition of two equivalents of acid, a $\{[Ru(bpy)(CN)_4]^{2-}\bullet(2H^+)\bullet\mathbf{13}\}$ adduct is formed, in which the two original species share two protons (Fig. 10). Interestingly, whereas the exciplex type band of **13** disappears upon adduct formation, as expected because of the protonation of the cyclam nitrogen atoms, the intensity of the naphthyl band does not increase, as would be expected by disappearance of the exciplex, but decreases. This shows that a new deactivation channel, namely energy transfer to the lower lying excited state of the Ru complex, is available for the naphthyl excited state in the adduct. Quantitative measurements have shown that such an energy transfer process does take place with an efficiency of 85%. Therefore, dendrimer **13** plays the role of a light-harvesting second coordination sphere that transfers the collected energy to the $[Ru(bpy)(CN)_4]^{2-}$ complex. Such a system shows another interesting feature. The $\{[Ru(bpy)(CN)_4]^{2-}\bullet(2H^+)\bullet\mathbf{13}\}$ adduct can be disrupted not only, of course, by addition of a base

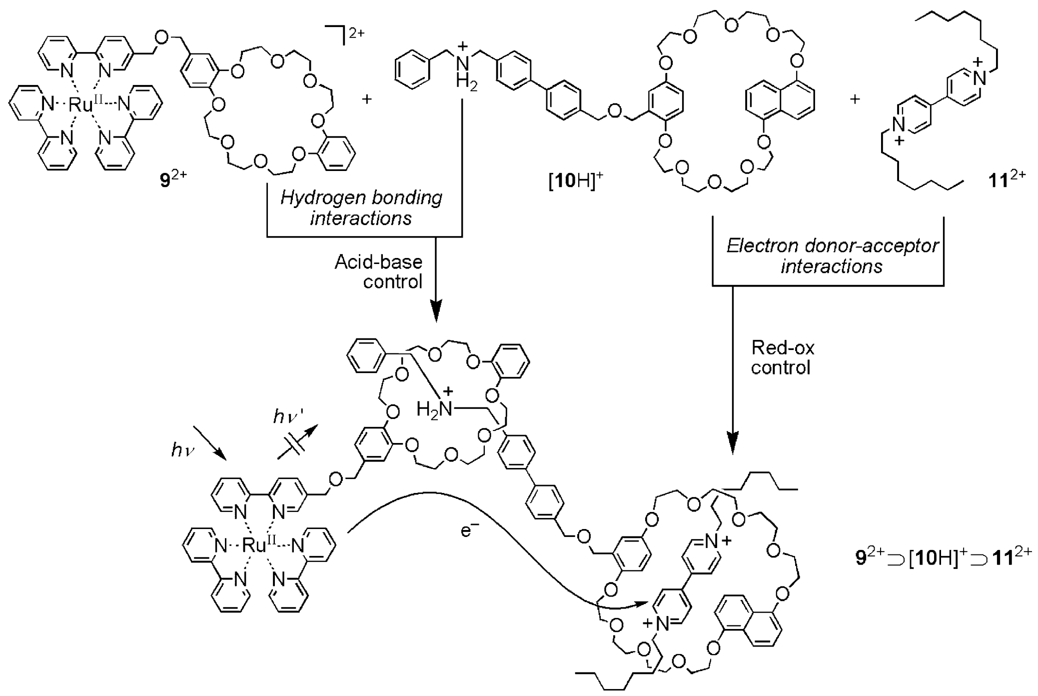


Fig. 8. A supramolecular system constituted by components $\mathbf{9}^{2+}$, $[\mathbf{10}H]^+$, and $\mathbf{11}^{2+}$ which mimics the function played by a macroscopic extension cable [66].

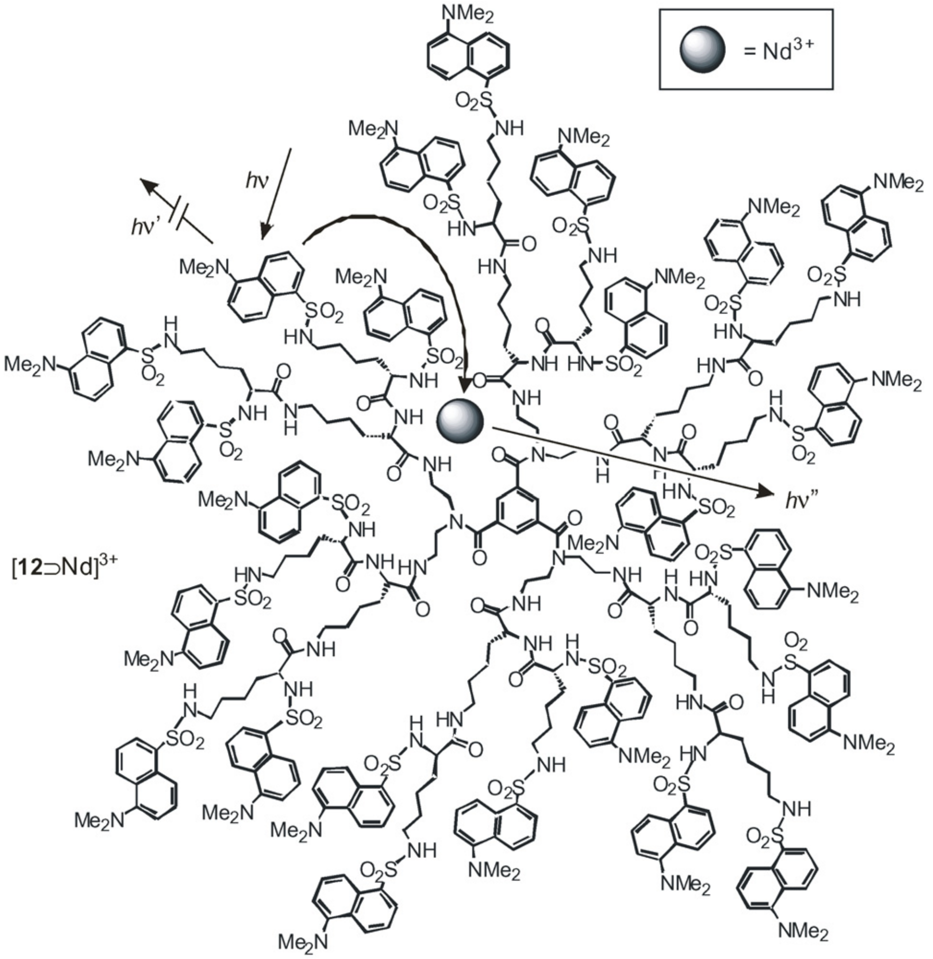


Fig. 9. Schematic representation of the energy-transfer process occurring in dendrimer **12** hosting a Nd^{3+} ion [74].

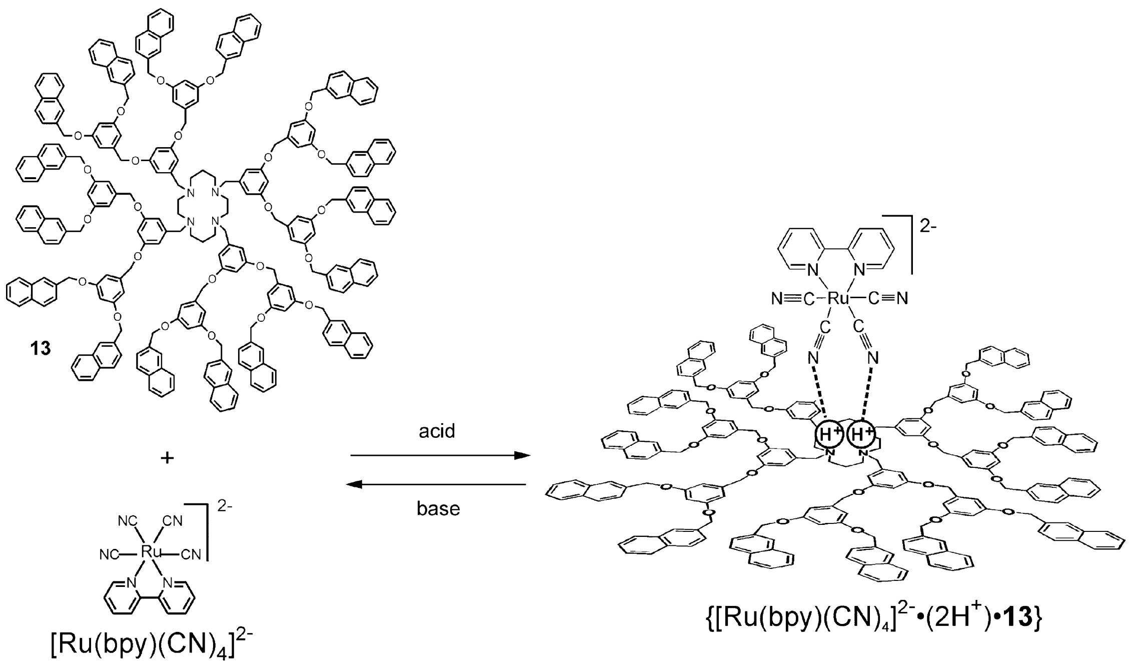


Fig. 10. Schematic representation of the formation of the {[Ru(bpy)(CN)$_4$]$^{2-}$•(2H$^+$)•**13**} adduct [76].

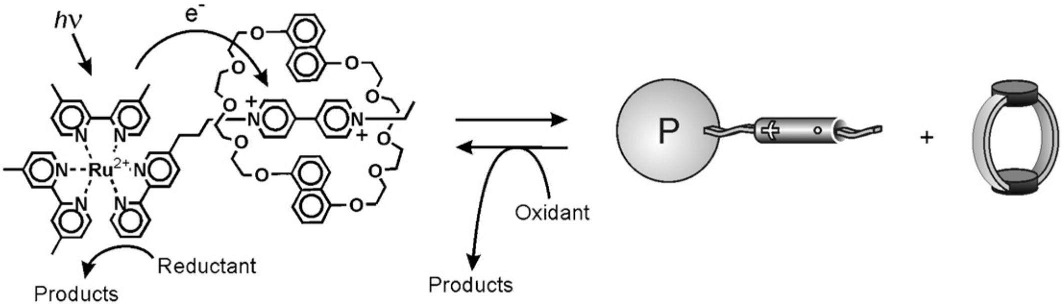


Fig. 11. Light-driven dethreading of a pseudorotaxane by excitation of a photosensitizer contained in the wire-type component [78].

(1,4-diazabicyclo[2.2.2]octane), yielding the starting species $[Ru(bpy)(CN)_4]^{2-}$ and **13**, but also by further addition of acid, with formation of ($\mathbf{13}\bullet 2H)^{2+}$ and protonated forms of $[Ru(bpy)(CN)_4]^{2-}$. It is shown that upon stimulation with two chemical inputs (acid and base) $\{[Ru(bpy)(CN)_4]^{2-}\bullet(2H^+)\bullet\mathbf{13}\}$ exhibits two distinct optical outputs (a naphthalene-based and a Ru(bpy)-based emissions) that behave according to an XOR and an XNOR logic, respectively [76].

5. Light-powered nanoscale machines

5.1. Dethreading/rethreading of pseudorotaxanes

Dethreading/rethreading of the wire and ring components of a pseudorotaxane reminds us of the movement of a piston in a cylinder. In order to achieve a light-induced dethreading in such piston/cylinder systems, pseudorotaxanes have been designed which incorporate a “light-fueled” motor [77] (i.e. a photosensitizer) in the wire (Fig. 11) [78] or in the macrocyclic ring [79]. In deaerated solution, excitation of the photosensitizer with visible light in the presence of a sacrificial electron donor (e.g. triethanolamine) causes reduction of the electron–acceptor unit and, as a consequence, dethreading takes place. Rethreading can be obtained by allowing oxygen to enter the solution. It is worth noting that through a repeated sequence of deoxygenation and irradiation followed by oxygenation many dethreading/rethreading cycles can be performed on the same solution without any appreciable loss of signal until most of the reductant scavenger is consumed. Photochemical systems which rely on such a sensitizer-scavenger strategy, however, produce waste species from the decomposition of the reductant scavenger and from the consumption of dioxygen.

The shuttling of the macrocyclic component of rotaxane $[\mathbf{14}\bullet Cu]^+$ (Fig. 12) along the linear portion of its dumbbell-shaped component can be induced photochemically [80]. Irradiation (464 nm) of a CH_3CN solution of the rotaxane, in the presence of *p*-nitrobenzylbromide, leads the Cu(I)-based chromophoric unit to its metal-to-ligand charge-transfer excited state. Electron transfer from the photoexcited rotaxane to *p*-nitrobenzylbromide follows, generating a tetracoordinated Cu(II) center. Since the Cu(II) ion prefers a pentacoordination geometry, the macrocycle shuttles away from the bidentate phenanthroline ligand of the dumbbell and encircles the terdentate terpyridine ligand. On addition of ascorbic acid the

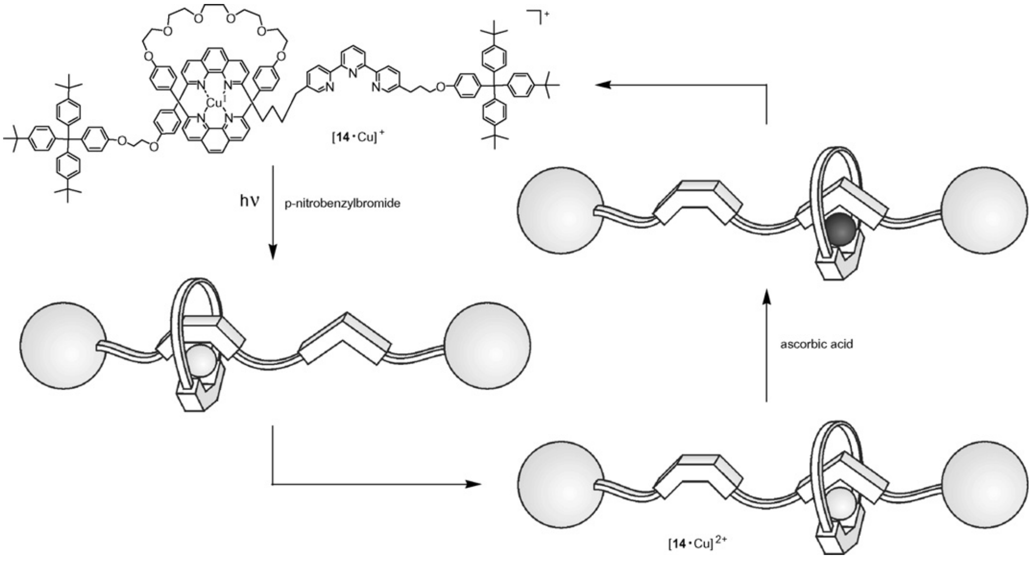


Fig. 12. Shuttling of the macrocyclic component of $[\mathbf{14}\bullet Cu]^+$ along its dumbbell-shaped component can be controlled photochemically by excitation of the metal complex [80]. Dark and light circles represent Cu(I) and Cu(II), respectively.

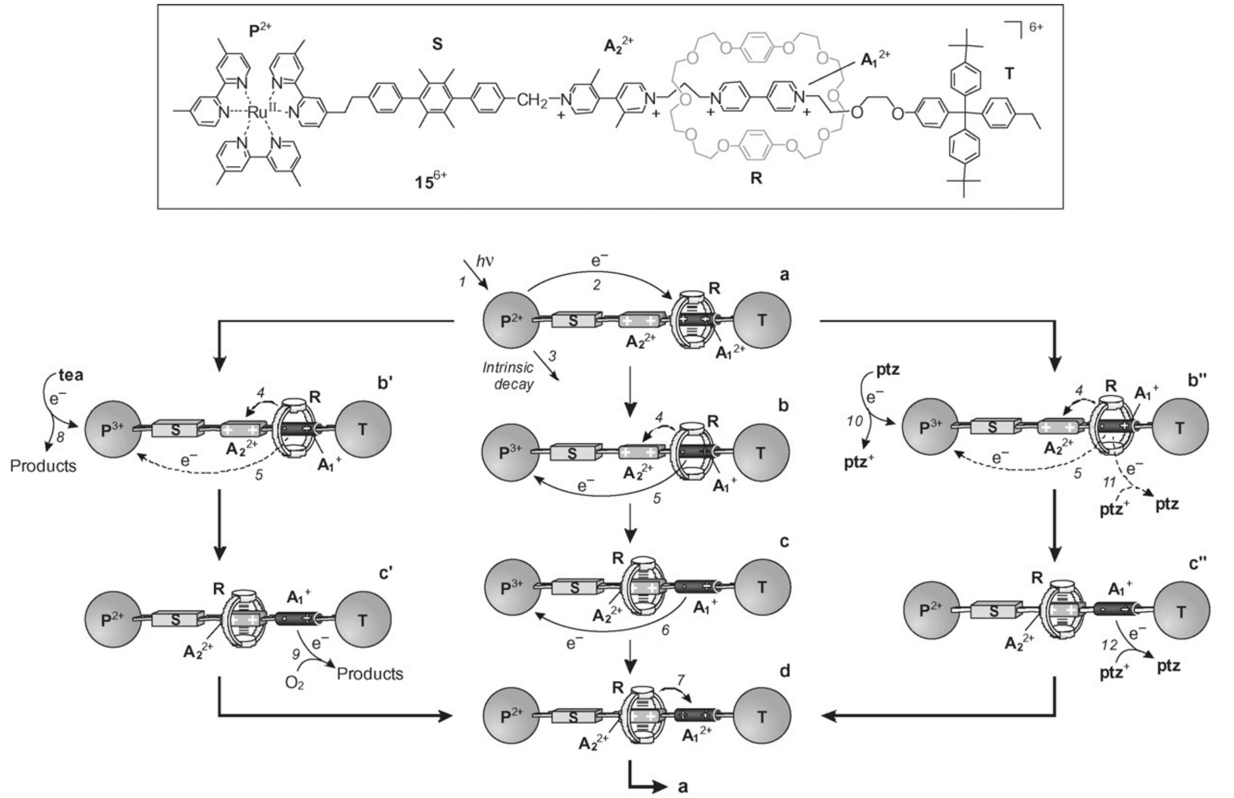


Fig. 13. Rotaxane $\mathbf{15}^{6+}$ and schematic representation of the intramolecular (center) sacrificial (left) and relay (right) mechanisms for the photoinduced shuttling movement of macrocycle **R** between the two stations $\mathbf{A_1}^{2+}$ and $\mathbf{A_2}^{2+}$ [82].

pentacoordinated Cu(II) center is reduced to a pentacoordinated Cu(I) ion. In response to the preference of Cu(I) for a tetracoordination geometry the macrocycle moves away from the terdentate terpyridine ligand and encircles the bidentate phenanthroline ligand to restore the original conformation.

Reversible threading/dethreading of pseudorotaxane has also been obtained by exploiting the well-known reversible *trans-cis* photoisomerization of the azobenzene group [81].

5.2. Shuttling processes in rotaxanes

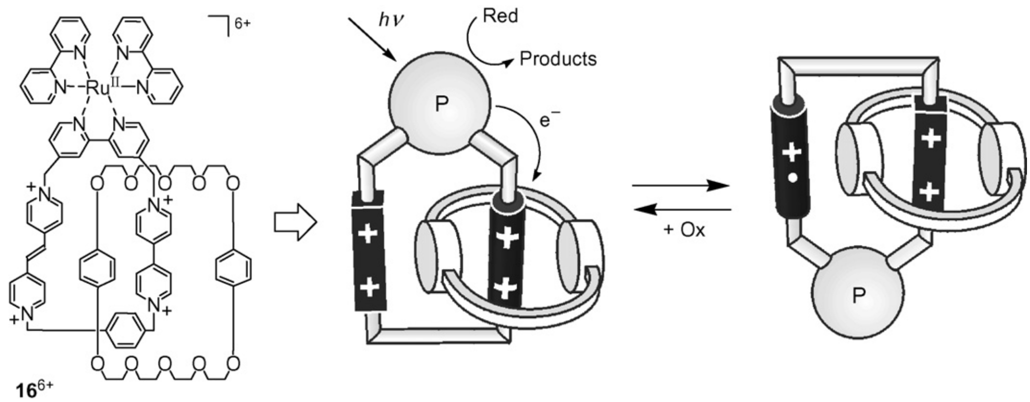
Photoinduced ring switching in a rotaxane containing two different recognition sites in the dumbbell-shaped component has been achieved with compound $\mathbf{15}^{6+}$ shown in Fig. 13 [82]. This compound consists of six molecular components suitably chosen and assembled in order to achieve the devised function. It comprises a bis-*p*-phenylene-34-crown-10 electron donor macrocycle **R** (hereafter called the ring), and a dumbbell-shaped component which contains two electron acceptor recognition sites for the ring, namely a 4,4′-bipyridinium ($\mathbf{A_1}^{2+}$) and a 3,3′-dimethyl-4,4′-bipyridinium ($\mathbf{A_2}^{2+}$) units, that can play the role of "stations" for the ring **R**. Furthermore, the dumbbell-shaped component incorporates a $[\mathrm{Ru(bpy)_3}]^{2+}$-type electron transfer photosensitizer **P** which is able to operate with visible light and also plays the role of a stopper, a *p*-terphenyl-type rigid spacer **S** which has the task of keeping the photosensitizer far from the electron acceptor units, and finally a tetraarylmethane group **T** as the second stopper. The stable translational isomer is the one in which the **R** component encircles the $\mathbf{A_1}^{2+}$ unit because this station is a better electron acceptor than the other one.

The photoinduced shuttling is triggered by the $[\mathrm{Ru(bpy)_3}]^{2+}$-type component which, on excitation with visible light, transfers an electron to the $\mathbf{A_1}^{2+}$. As schematized in Fig. 13, three shuttling mechanisms have been investigated [82]: (i) a mechanism involving an energetic contribution from low energy fuels (Fig. 13, left); (ii) a mechanism involving the kinetic assistance of an external electron relay (Fig. 13, right); and (iii) a purely intramolecular photochemical mechanism (Fig. 13, center). The quantum yield of ring displacement is 0.16, 0.12, and 0.02, respectively. When shuttling occurs via mechanisms (ii) and (iii), rotaxane $\mathbf{15}^{6+}$ behaves as an autonomous "four-stroke" linear motor powered only by visible light.

Several other examples of shuttling movement promoted by light excitation in rotaxanes not containing coordination compounds have been reported [83–90].

5.3. Ring switching processes in catenanes

Derivatives of the $[\mathrm{Ru(bpy)_3}]^{2+}$-type photosensitizer can be incorporated in catenated structures [91] and in suitably designed catenanes of this type it is possible to cause photochemical switching between two different conformations [92]. For example, in catenane $\mathbf{16}^{6+}$ (Fig. 14), excitation of the Ru-based complex should be followed by electron transfer to the bipyridinium unit. In the presence of a sacrificial electron



16^{6+}

Fig. 14. A suggested system for achieving light-driven switching in catenanes [92].

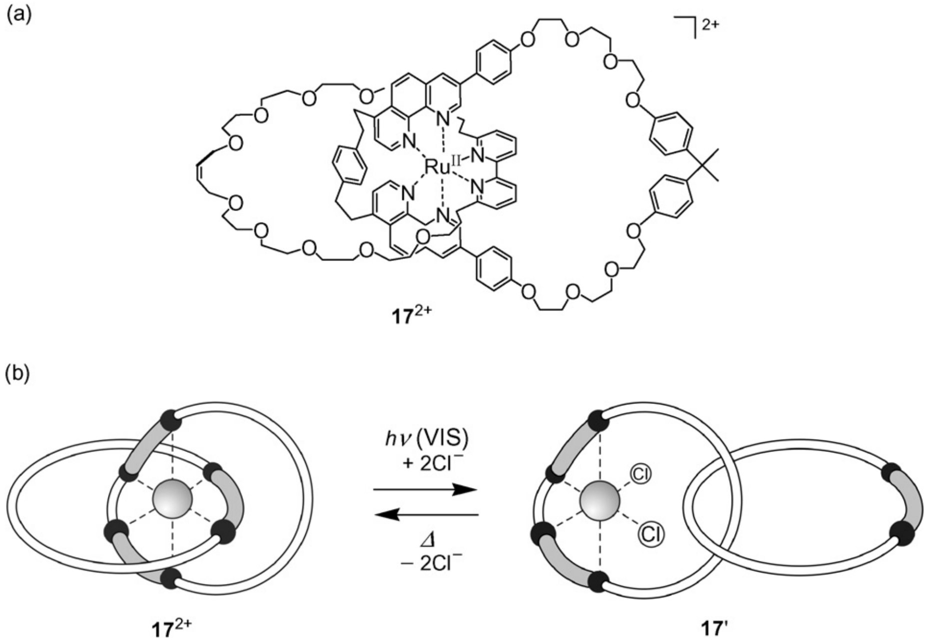


Fig. 15. (a) Structure of catenane **17**$^{2+}$ and (b) schematic representation of its reversible rearrangement on irradiation with visible light [93].

donor the oxidized Ru-based complex would be immediately reduced and circumrotation of the cyclophane would occur to enable the formation of a more stable configuration in which the *trans*-bis(pyridinium)ethylene unit occupies the inside position. Oxidation of the reduced bipyridinium unit would then lead back to the original configuration.

Catenane **17**$^{2+}$ (Fig. 15) consists of a 63-membered ring which incorporates two phenanthroline units and a 42-membered ring which contains a bpy unit. The light induced motion and the thermal back reaction exhibited by **17**$^{2+}$ are illustrated in Fig. 15 [93]. The photoproduct **17**′ consists of two disconnected rings because the photoexcitation of the Ru(II) moiety leads to decomplexation of the bpy unit contained in the 42-membered ring.

Unidirectional rotation in a catenane requires a careful design of the system [42,94,50]. A clever example, based on the photoisomerization of a fumaramide and a succinamide units has been recently reported [95].

6. Conclusions

The results reviewed in this paper show that the photochemistry of coordination compounds has evolved in four stages until now: (1) investigations on intramolecular photochemical reactions (ligand photosubstitution, photoredox decomposition, photoisomerization); (2) identification of intrinsically photostable, luminescent compounds and their use in bimolecular energy and electron transfer processes; (3) incorporation of photostable and luminescent complexes in supramolecular (multicomponent) systems with the aim of understanding the role of nuclear and electronic factors in determining the rates of energy and electron transfer processes; (4) use of coordination compounds as essential components for the bottom-up construction of simple, light-powered nanoscale devices and machines.

Up until now, the most useful compounds for stages 2–4 have been those of the $[Ru(bpy)_3]^{2+}$ family. Hopefully, in the next few years other families of coordination compounds will become available for the development of nanoscience and nanotechnology.

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References

[1] V. Balzani, V. Carassiti, Photochemistry of Coordination Compounds, Academic Press, London, 1970.

[2] D.H.D. John, G.T.J. Field, A Textbook of Photographic Chemistry, Chapman and Hall, London, 1963.

[3] G. Ciamician, Science 36 (1912) 385.

[4] N. Armaroli, V. Balzani, Angew. Chem. Int. Ed. 46 (2007) 52.

[5] W.G. Leighton, G.S. Forbes, J. Am. Chem. Soc. 52 (1930) 3139.

[6] (a) S. Ašpergěr, I. Murati, O. Cūpahin, J. Chem. Soc. (1953) 1041;
(b) G. Emschwiller, Comp. Rend. 239 (1954) 1451;
(c) G. Emschwiller, Ric. Sci. Suppl. 3 (1957) 1.

[7] F. Basolo, R.G. Pearson, Mechanisms of Inorganic Reactions, Wiley, New York, 1958.

[8] L.E. Orgel, Q. Rev. London 8 (1954) 422.

[9] C.K. Jorgensen, Absorption Spectra and Chemical Bonding in Complexes, Pergamon Press, Oxford, 1962.

[10] H.L. Schlaefer, Z. Phys. Chem. 11 (1957) 65.

[11] R.A. Plane, J.P. Hunt, J. Am. Chem. Soc. 79 (1957) 3843.

[12] V. Carassiti, M. Claudi, Ann. Chim. (Rome) 49 (1958) 1697.

[13] A.W. Adamson, A.H. Sporer, J. Am. Chem. Soc. 80 (1958) 3865.

[14] G.B. Porter, H.L. Schlaefer, Ber. Bunsenges Physik. Chem. 68 (1964) 316.

[15] J.F. Endicott, M.Z. Hoffman, J. Am. Chem. Soc. 87 (1965) 3348.

[16] V. Balzani, V. Carassiti, L. Moggi, N. Sabbatini, Inorg. Chem. 4 (1965) 1247.

[17] J.G. Calvert, J.N. Pitts Jr., Photochemistry, Wiley, New York, 1966.

[18] N.J. Turro, Molecular Photochemistry, Benjamin, New York, 1967.

[19] R.P. Wayne, Photochemistry, Butterworths, London, 1970.

[20] J.P. Simons, Photochemistry and Spectroscopy, Wiley-Interscience, London, 1971.

[21] (a) D.M. Klassen, G.A. Crosby, J. Chem. Phys. 43 (1965) 1498;
(b) G.A. Crosby, R.J. Watts, D.H.W. Carstens, Science 170 (1970) 1195.

[22] A.D. Gafney, A.W. Adamson, J. Am. Chem. Soc. 94 (1972) 8238.

[23] N. Sabbatini, V. Balzani, J. Am. Chem. Soc. 94 (1972) 7587.

[24] P. Natarajan, J.F. Endicott, J. Phys. Chem. 77 (1973) 971.

[25] G. Navon, N. Sutin, Inorg. Chem. 13 (1974) 2159.

[26] C.R. Bock, T.J. Meyer, D.G. Whitten, J. Am. Chem. Soc. 96 (1974) 4710.

[27] V. Balzani, F. Bolletta, M.T. Gandolfi, M. Maestri, Top. Curr. Chem. 75 (1978) 1.

[28] C. Creutz, N. Sutin, Proc. Natl. Acad. Sci. USA 72 (1975) 2858.

[29] R.J. Watts, J. Chem. Educ. 60 (1983) 814.

[30] F. Standola, V. Balzani, J. Chem. Educ. 60 (1983) 834.

[31] N. Sutin, C. Creutz, J. Chem. Educ. 60 (1983) 809.

[32] A. Juris, V. Balzani, F. Barigelletti, S. Campagna, P. Belser, A. von Zelewski, Coord. Chem. Rev. 84 (1988) 85.

[33] K. Kalyanasundaram, Photochemistry of Polypyridine and Porphyrin Complexes, Academic Press, London, 1992.

[34] M.Z. Hoffman, F. Bolletta, L. Moggi, G.L. Hug, J. Phys. Chem. Ref. Data 18 (1989) 219.

[35] N. Sutin, Prog. Inorg. Chem. 30 (1983) 441.

[36] C.J. Pedersen, Angew. Chem. Int. Ed. Engl. 27 (1988) 1021.

[37] D.J. Cram, Angew. Chem. Int. Ed. Engl. 27 (1988) 1009.

[38] J.-M. Lehn, Angew. Chem. Int. Ed. Engl. 27 (1988) 89.

[39] V. Balzani (Ed.), Supramolecular Photochemistry, Reidel, Dordrecht, 1987.

[40] V. Balzani, L. Moggi, F. Scandola, in: V. Balzani (Ed.), Supramolecular Photochemistry, Reidel, Dordrecht, 1987, p. 1.

[41] V. Balzani, F. Scandola, Supramolecular Photochemistry, Horwood, Chichester, England, 1991.

[42] R. Ballardini, V. Balzani, A. Credi, M.T. Gandolfi, M. Venturi, Acc. Chem. Res. 34 (2001) 445.

[43] J.-P. Collin, C.O. Dietrich-Buchecker, P. Gaviña, M.C. Jimenez-Molero, J.-P. Sauvage, Acc. Chem. Res. 34 (2001) 477.

[44] Struct. Bond. 99 (2001) (Special Volume on Molecular Machines and Motors, Guest Editor J.-P. Sauvage).

[45] V. Balzani, Photochem. Photobiol. Sci. 2 (2003) 459.

[46] V. Balzani, A. Credi, M. Venturi, Molecular Devices and Machines. A Journey into the Nano World, Wiley-VCH, Weinheim, 2003, p. 1.

[47] M. Venturi, V. Balzani, R. Ballardini, A. Credi, M.T. Gandolfi, Int. J. Photoenergy 6 (2004) 1.

[48] Top. Curr. Chem. 262 (2005) (Special Volume on Molecular Machines, T.R. Kelly (Ed.)).

[49] V. Balzani, A. Credi, M. Venturi, Nanotoday 2 (2007) 18.

[50] E.R. Kay, D.A. Leigh, F. Zerbetto, Angew. Chem. Int. Ed. 46 (2007) 72.

[51] J.-M. Lehn, Supramolecular Chemistry: Concepts and Perspectives, VCH, Weinheim, 1995.

[52] V. Balzani, A. Credi, M. Venturi, Chem. Eur. J. 8 (2002) 5524.

[53] R.A. Marcus, N. Sutin, Biochim. Biophys. Acta 811 (1985) 265.

[54] P.F. Barbara, T.J. Meyer, M.A. Ratner, J. Phys. Chem. 100 (1996) 13148.

[55] V. Balzani (Ed.), Electron Transfer in Chemistry, vol.1–5, Wiley-VCH, Weinheim, 2001.

[56] V. Balzani, A. Credi, M. Venturi, Molecular Devices and Machines. Concepts and Perspectives for the Nanoworld, Wiley-VCH, Weinheim, 2008.

[57] (a) F. Barigelletti, L. Flamigni, Chem. Soc. Rev. 29 (2000) 1;
(b) F. Scandola, C. Chiorboli, M.T. Indelli, M.A. Rampi, in: V. Balzani (Ed.), Electron Transfer in Chemistry, vol. 3, Wiley-VCH, Weinheim, 2001, p. 337;
(c) J.P. Launay, Chem. Soc. Rev. 30 (2001) 386;
(d) C. Chiorboli, M.T. Indelli, F. Scandola, Top. Curr. Chem. 257 (2005) 63.

[58] (a) M.T. Indelli, C.A. Bignozzi, A. Harriman, J.R. Schoonover, F. Scandola, J. Am. Chem. Soc. 116 (1994) 3768;
(b) M.T. Indelli, C. Chiorboli, L. Flamigni, L. De Cola, F. Scandola, Inorg. Chem. 46 (2007) 5630.

[59] L. Flamigni, E. Baranoff, J.-P. Collin, J.-P. Sauvage, Chem. Eur. J. 12 (2006) 6592.

[60] S. Welter, N. Salluce, P. Belser, M. Groeneveld, L. De Cola, Coord. Chem. Rev. 249 (2005) 1360.

[61] B. Schlicke, P. Belser, L. De Cola, E. Sabbioni, V. Balzani, J. Am. Chem. Soc. 121 (1999) 4207.

[62] S. Welter, F. Lafolet, E. Cecchetto, F. Vergeer, L. De Cola, ChemPhysChem 6 (2005) 2417.

[63] P. Belser, R. Dux, M. Baak, L. De Cola, V. Balzani, Angew. Chem. Int. Ed. Engl. 34 (1995) 595.

[64] L. De Cola, V. Balzani, P. Belser, R. Dux, M. Baak, Supramol. Chem. 5 (1995) 297.

[65] V. Balzani, A. Credi, M. Venturi, Proc. Natl. Acad. Sci. USA 99 (2002) 4814.

[66] (a) B. Ferrer, G. Rogez, A. Credi, R. Ballardini, M.T. Gandolfi, V. Balzani, Y. Liu, H.-R. Tseng, J.F. Stoddart, Proc. Natl. Acad. Sci. USA 103 (2006) 18411;
(b) R. Ballardini, V. Balzani, M. Clemente-Leon, A. Credi, M.T. Gandolfi, E. Ishow, J. Perkins, J.F. Stoddart, H.-R. Tseng, S. Wenger, J. Am. Chem. Soc. 124 (2002) 12786.

[67] G. Rogez, B. Ferrer Ribeira, A. Credi, R. Ballardini, M.T. Gandolfi, V. Balzani, Y. Liu, J.F. Stoddart, J. Am. Chem. Soc. 129 (2007) 4633.

[68] V. Balzani, P. Ceroni, M. Maestri, V. Vicinelli, Curr. Opin. Chem. Biol. 7 (2003) 657.

[69] R.E. Blankenship, Molecular Mechanism of Photosynthesis, Blackwell Science, Oxford, 2002.

[70] V. Balzani, P. Ceroni, S. Gestermann, C. Kauffmann, M. Gorka, F. Vögtle, Chem. Commun. (2000) 853.

[71] V. Balzani, S. Campagna, G. Denti, A. Juris, S. Serroni, M. Venturi, Acc. Chem. Res. 31 (1998) 26.

[72] V. Balzani, P. Ceroni, M. Maestri, C. Saudan, V. Vicinelli, Top. Curr. Chem. 228 (2003) 159.

[73] V. Balzani, G. Bergamini, F. Marchioni, P. Ceroni, F. Vögtle, Coord. Chem. Rev. 251 (2007) 525.

[74] V. Vicinelli, P. Ceroni, M. Maestri, V. Balzani, M. Gorka, F. Vögtle, J. Am. Chem. Soc. 124 (2002) 6461.

[75] C. Saudan, V. Balzani, P. Ceroni, M. Gorka, M. Maestri, V. Vicinelli, F. Vögtle, Tetrahedron 59 (2003) 3845.

[76] G. Bergamini, C. Saudan, P. Ceroni, M. Maestri, V. Balzani, M. Gorka, S.-K. Lee, J. van Heyst, F. Vögtle, J. Am. Chem. Soc. 126 (2004) 16466.

[77] M. Freemantle, Chem. Eng. News (October 26, 1998) 37.

[78] P.R. Ashton, R. Ballardini, V. Balzani, E.C. Constable, A. Credi, O. Kocian, S.J. Langford, J.A. Preece, L. Prodi, E.R. Schofield, N. Spencer, J.F. Stoddart, S. Wenger, Chem. Eur. J. 4 (1998) 2413.

[79] P.R. Ashton, V. Balzani, O. Kocian, L. Prodi, N. Spencer, J.F. Stoddart, J. Am. Chem. Soc. 120 (1998) 11190.

[80] N. Armaroli, V. Balzani, J.-P. Collin, P. Gaviña, J.-P. Sauvage, B. Ventura, J. Am. Chem. Soc. 121 (1999) 4397.

[81] V. Balzani, A. Credi, F. Marchioni, J.F. Stoddart, Chem. Commun. (2001) 1860.

[82] V. Balzani, M. Clemente-León, A. Credi, B. Ferrer, M. Venturi, A.H. Flood, J.F. Stoddart, Proc. Natl. Acad. Sci. 103 (2006) 1178.

[83] A.M. Brouwer, C. Frochot, F.G. Gatti, D.A. Leigh, L. Mottier, F. Paolucci, S. Roffia, G.W.H. Wurpel, Science 291 (2001) 2124.

[84] H. Murakami, A. Kawabuchi, R. Matsumoto, T. Ido, N. Nakashima, J. Am. Chem. Soc. 127 (2005) 15891.

[85] Q.-C. Wang, D.-H. Qu, J. Ren, K. Chen, H. Tian, Angew. Chem. Int. Ed. 43 (2004) 2661.

[86] D.-H. Qu, Q.-C. Wang, X. Ma, H. Tian, Chem. Eur. J. 11 (2005) 5929.

[87] D.-H. Qu, Q.-C. Wang, H. Tian, Angew. Chem. Int. Ed. 44 (2005) 5296.

[88] X. Ma, D. Qu, F. Ji, Q. Wang, L. Zhu, Y. Xu, H. Tian, Chem. Commun. (2007) 1409.

[89] M.N. Chatterjee, E.R. Kay, D.A. Leigh, J. Am. Chem. Soc. 128 (2006) 4058.

[90] V. Serreli, C.-F. Lee, E.R. Kay, D.A. Leigh, Nature 445 (2007) 523.

[91] P.R. Ashton, V. Balzani, A. Credi, O. Kocian, D. Pasini, L. Prodi, N. Spencer, J.F. Stoddart, M.S. Tolley, M. Venturi, A.J.P. White, D.J. Williams, Chem. Eur. J. 4 (1998) 590.

[92] R. Ballardini, V. Balzani, A. Credi, M.T. Gandolfi, M. Venturi, Int. J. Photoenergy 3 (2001) 63.

[93] P. Mobian, J.-M. Kern, J.-P. Sauvage, Angew. Chem. Int. Ed. 43 (2004) 2392.

[94] R.D. Astumian, Proc. Natl. Acad. Sci. USA 102 (2005) 1843.

[95] J.V. Hernandez, E.R. Kay, D.A. Leigh, Science 306 (2004) 1532.