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Review

Ru(II)-bipyridine complexes in supramolecular systems, devices and machines

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Contents

Abstract

Because of a unique combination of chemical stability, redox properties, excited-state reactivity, and excited-state lifetime, $[Ru(bpy)_3]^{2+}$ (bpy = 2,2′-bipyridine) and related complexes have long been used to obtain photoinduced intermolecular energy and electron-transfer processes. More recently these compounds have been employed as components to build up supramolecular species that exhibit peculiar photochemical and/or electrochemical properties. When suitably designed, such supramolecular species can behave as light-powered nanoscale electronic devices (e.g. wires, switches, antennas) or mechanical machines (e.g. shuttles). This paper reviews the results obtained in our research group on supramolecular species, devices and machines that exploit the properties of Ru(II) bipyridine complexes.

Keywords: Photochemistry; Photophysics; Electrochemistry; Supramolecular chemistry; Molecular devices; Molecular machines

1. Introduction

In the late 1960s the group of Crosby et al. [1] characterized the spectroscopic properties of several bipyridine-type metal complexes and assigned the red luminescence of $[Ru(bpy)_3]^{2+}$ (bpy = 2,2′-bipyridine) to its lowest triplet metal-to-ligand charge-transfer excited-state, ^{3}MLCT. In an exhaustive mono-

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Abbreviations: bpy, 2,2′-bipyridine; ph, 1,4-phenylene; 2,3-dpp, 2,3-bis(2-pyridyl)pyrazine; 2,5-dpp, 2,5-bis(2-pyridyl)pyrazine; biq, 2,2′-biquinoline

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graph on the photochemistry of coordination compounds [2] published in 1970, $[Ru(bpy)_3]^{2+}$ was mentioned as a luminescent, but not photoreactive, compound and all the photochemistry of the Ru and Os complexes was dealt within less than one page, whereas 51 pages were dedicated to Cr and 52 pages to Co complexes. In 1972, Gafney and Adamson [3] discovered the reductive electron-transfer quenching of the ^{3}MLCT excited-state of $[Ru(bpy)_3]^{2+}$ by $Co(NH_3)_5Cl^{2+}$:

$$^*[Ru(bpy)_3]^{2+} + [Co(NH_3)_5Cl^{2+}] \rightarrow [Ru(bpy)_3]^{3+} + [Co(NH_3)_5Cl^{+}] \rightarrow \text{products} \quad (1)$$

Such a discovery had a strong impact on the photochemical community since at that time excited-state electron-transfer reactions were not common, even in the more mature field of organic photochemistry. Several laboratories [4–7] 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 a unique combination of chemical stability, redox properties, excited-state reactivity, and excited-state lifetime. 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 [8]. Since then, the interest in the study of the photochemistry of bipyridine-type Ru(II) complexes has 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 [9] 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 [10] and electron [11] transfer processes). In middle 1980s, most of the properties of $[Ru(bpy)_3]^{2+}$ were fully characterized (Fig. 1) [12]. By choosing the right counter ion, $[Ru(bpy)_3]^{2+}$ can be dissolved in a variety of solvents, from dichloromethane to water. It is thermodynamically stable and kinetically inert and shows very intense ligand-centered absorption bands in the UV spectral region and a broad and intense MLCT band in the visible region with maximum at 450 nm. Its lowest excited-state, ^{3}MLCT, is reached with unitary efficiency from the upper lying excited-states, is relatively long-lived (1.1 μs in deaerated acetonitrile solution at 298 K, 5 μs in rigid matrix at 77 K), and exhibits a moderately intense emission around 600 nm ($\phi = 0.07$ in deaerated acetonitrile at 298 K). $[Ru(bpy)_3]^{2+}$ has also very interesting electrochemical properties [13]. It shows a metal-centered oxidation process in acetonitrile at room temperature and six distinct ligand-centered reduction processes in dimethylformamide at 219 K [14]. In its ^{3}MLCT excited-state, $[Ru(bpy)_3]^{2+}$ is both a good reductant and a good oxidant (Fig. 1). Several hundreds of Ru–polypyridine complexes have been synthesized and characterized since it has been found that the redox and excited-state properties can be tuned by changing the ligands or ligand substituents [12].

In middle 1980s the interest of several research groups moved towards supramolecular chemistry, a discipline consecrated by the award of the Nobel Prize in Chemistry to Pedersen [15], Cram [16], and Lehn [17] in 1987, and in the same year a Nato Workshop on Supramolecular Photochemistry was held at Capri (Italy), with participation of more than one hundred scientists belonging to several different disciplines [18]. In retrospect, the Capri meeting can perhaps be considered the birth place of a new branch of chemistry, that dealing with photochemical molecular devices [19]. In the following years it became clear that Ru(II) bipyridine-type complexes are very useful building blocks for the construction of supramolecular species capable of exhibiting peculiar photochemical and/or electrochemical properties [20–22] and since the middle 1990s a variety of molecular devices and machines comprising a Ru–bpy complex as photoactive component have been constructed [23–25].

Our group has been heavily involved in research on complexes of the Ru(II) bipyridine-type family since the early 1970s [4,26]. In this paper we will review some recent work carried

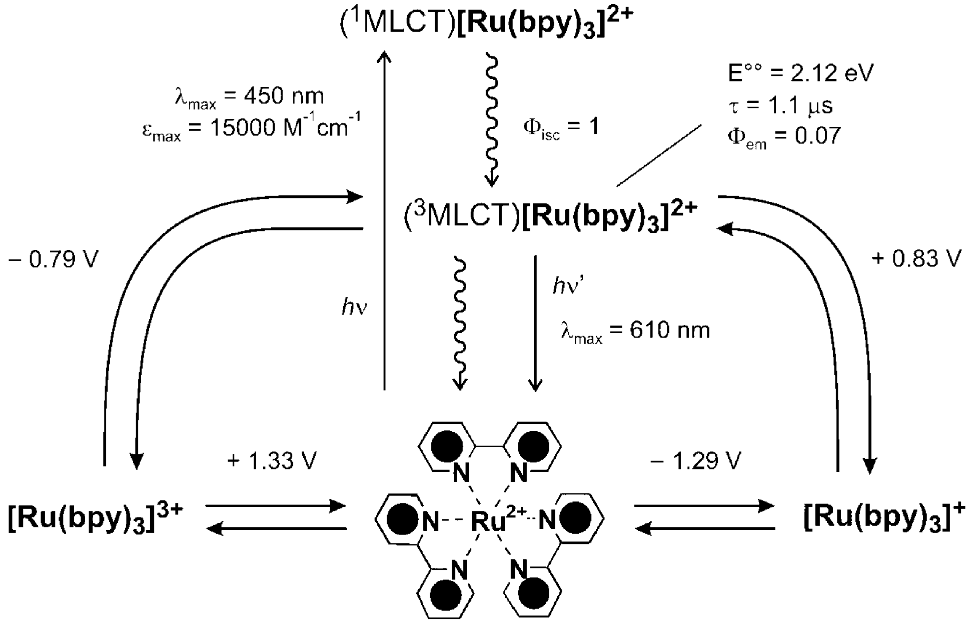


Fig. 1. Schematic representation of some important properties of $[Ru(bpy)_3]^{2+}$ in deaerated acetonitrile solution at 298 K. The potential values are referred to SCE.

out in our laboratory on supramolecular species, devices and machines exploiting the properties of these complexes.

2. Photoinduced energy or electron-transfer processes

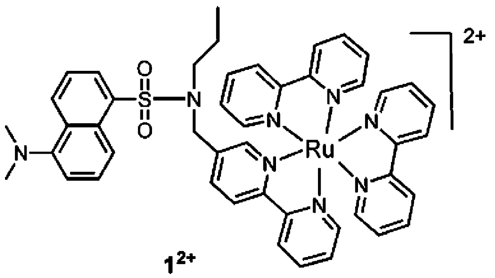
Photoinduced energy and electron-transfer are basic processes for connecting light energy inputs with a variety of optical, electrical, and mechanical functions. Several devices have been designed for delivering electronic energy or electrons, in a controlled way, to predetermined components in a supramolecular system.

2.1. A dansyl-[Ru(bpy)$_3$]$^{2+}$ dyad

In order to elucidate the excited-state behavior of the dansyl chromophoric group, which is extensively used for labeling purposes in supramolecular systems and dendrimers [27], we have studied the photochemical, photophysical and electrochemical properties of dyads made of a propyldansylamide unit covalently linked to other components, including [Ru(bpy)$_3$]$^{2+}$ (compound **1**$^{2+}$ in Fig. 2) [28]. In the emission spectrum of the dyad **1**$^{2+}$ the band of the dansyl unit is quenched by at least 100 times compared to that of the free propyldansylamide unit, whereas the characteristic band of [Ru(bpy)$_3$]$^{2+}$ is practically unaffected. Careful comparison between the emission intensities obtained at different excitation wavelengths has shown that only 25% of the quenching of the dansyl fluorescence is due to energy transfer. This result is consistent with the fact that electron-transfer quenching of the fluorescent excited-state of the dansyl unit (2.8 eV) is thermodynamically allowed since dansyl can be oxidized at +0.96 V and the Ru complex can be reduced at −1.30 V (versus SCE in acetonitrile).

2.2. Wire-type bridges

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. An example [29] is given by the [Ru(bpy)$_3$]$^{2+}$-(ph)$_n$-[Os(bpy)$_3$]$^{2+}$ compounds (ph = 1,4-phenylene; $n = 3, 5, 7$) in which excitation of the [Ru(bpy)$_3$]$^{2+}$ unit is followed by electronic energy transfer to the ground state [Os(bpy)$_3$]$^{2+}$ unit, as shown by the sensitized emission of the latter (a schematic energy level diagram is reported in Fig. 3a). For compound **2**$^{4+}$ with $n = 7$ (Fig. 4a), the rate constant for energy transfer over the 4.2 nm metal-to-metal distance is $1.3 \times 10^6\ \mathrm{s}^{-1}$. In the [Ru(bpy)$_3$]$^{2+}$-(ph)$_n$-[Os(bpy)$_3$]$^{3+}$ compounds, obtained by chemical oxidation of the Os-based moiety, photoexcitation of the [Ru(bpy)$_3$]$^{2+}$ unit causes the transfer of an electron to the Os-based one (schematic energy level diagram in Fig. 3b) with a rate constant of $3.4 \times 10^7\ \mathrm{s}^{-1}$ for $n = 7$ (compound **2**$^{5+}$ in Fig. 4b). Unless the electron added to the [Os(bpy)$_3$]$^{3+}$unit is rapidly removed, a back electron-transfer reaction (rate constant $2.7 \times 10^5\ \mathrm{s}^{-1}$ for $n = 7$) takes place from the [Os(bpy)$_3$]$^{2+}$ unit to the [Ru(bpy)$_3$]$^{3+}$ one.



1^{2+}

Fig. 2. Structure of a dyad consisting of a propyldansylamide unit linked to [Ru(bpy)$_3$]$^{2+}$ [28].

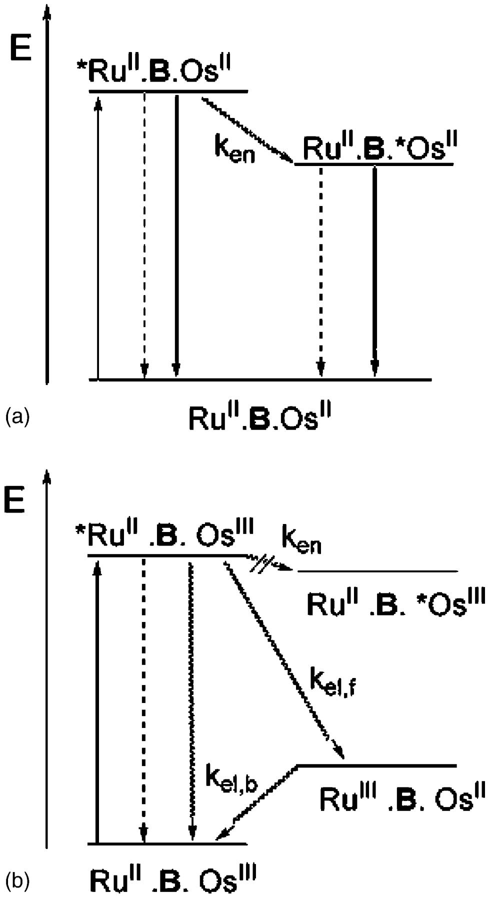


Fig. 3. Energy-level diagram showing the photoinduced energy- or electron-transfer processes that occur in systems containing a Ru(II) and an Os(II) (a) or a Ru(II) and an Os(III) (b) complexes linked by a bridge B. Key: full line, excitation; dashed line, luminescence; wavy line, radiationless decay.

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.

2.3. Shape-persistent macrocyclic bridges

The photophysical behavior of the dinuclear [(bpy)$_2$Ru(**3**)Os-(bpy)$_2$]$^{4+}$ complex, where **3** is a phenylacetylene macrocycle which incorporates two bpy chelating units in opposite sites

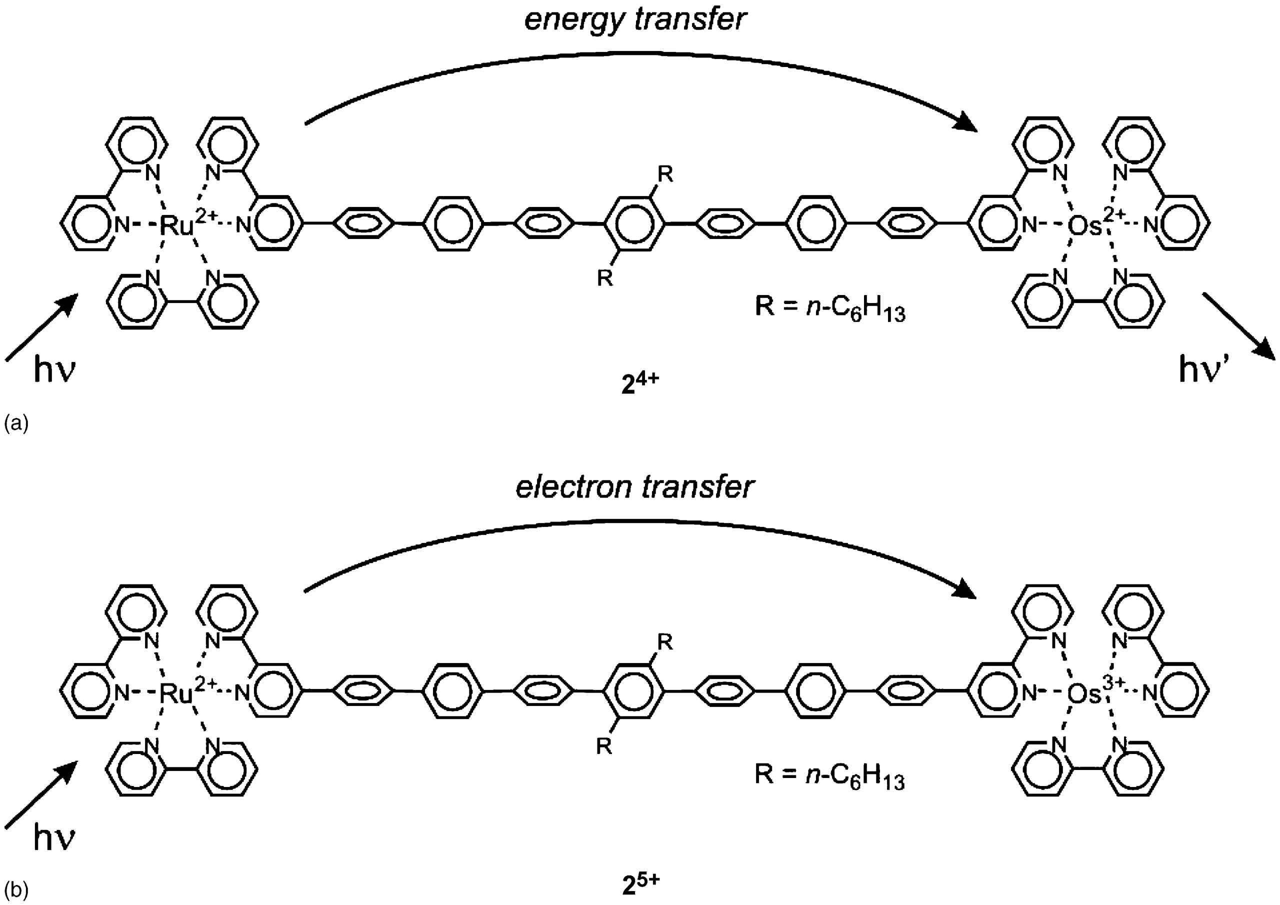


Fig. 4. Examples of photoinduced energy (a) and electron (b) transfer processes over long distances [29].

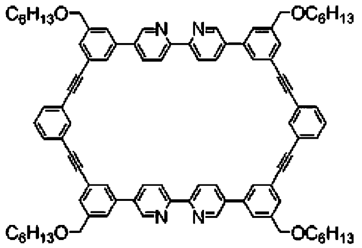
of its shape-persistent structure (Fig. 5), has been investigated [30]. In acetonitrile solution, the Ru-based and Os-based units display their characteristic absorption spectra and electrochemical properties as in the parent homodinuclear compounds [31]. The luminescence spectrum, however, shows that the emission band of the Ru(II) unit is almost completely quenched with concomitant sensitization of the emission of the Os(II) unit (Fig. 3a). Electronic energy transfer from the Ru(II) to the Os(II) unit takes place by two distinct processes (rate constants 2.0×10^8 and $2.2 \times 10^7\ s^{-1}$ at 298 K). Oxidation of the Os(II) unit of $[(bpy)_2Ru(\mathbf{3})Os(bpy)_2]^{4+}$ by Ce(IV) or nitric acid leads quantitatively to the $[(bpy)_2Ru^{II}(\mathbf{3})Os^{III}(bpy)_2]^{5+}$ complex which exhibits a band with $\lambda_{max} = 720$ nm and $\varepsilon_{max} = 250\ M^{-1}\ cm^{-1}$. Comparison with the spectral changes observed upon oxidation of $[(bpy)_2Os^{II}(\mathbf{3})Os^{II}(bpy)_2]^{4+}$ shows that such a band is not due to intervalence transfer, but to a bpy-to-Os^{III} charge-transfer transition. Light excitation of the Ru(II) unit of $[(bpy)_2Ru^{II}(\mathbf{3})Os^{III}(bpy)_2]^{5+}$ is followed by electron-transfer from the Ru(II) to the Os(III) unit ($k_{el,f} = 1.6 \times 10^8$ and $2.7 \times 10^7\ s^{-1}$), resulting in the transient formation of the $[(bpy)_2Ru^{III}(\mathbf{3})Os^{II}(bpy)_2]^{5+}$ complex (Fig. 3b). The latter species relaxes to the $[(bpy)_2Ru^{II}(\mathbf{3})Os^{III}(bpy)_2]^{5+}$ one by back electron-transfer ($k_{el,b} = 9.1 \times 10^7$ and $1.2 \times 10^7\ s^{-1}$). The biexponential decays of the $[(bpy)_2{}^*Ru^{II}(\mathbf{3})Os^{II}(bpy)_2]^{4+}$, $[(bpy)_2{}^*Ru^{II}(\mathbf{3})Os^{III}(bpy)_2]^{5+}$ and $[(bpy)_2Ru^{III}(\mathbf{3})Os^{II}(bpy)_2]^{5+}$ species are likely related to the presence of two conformers, as expected because steric hindrance between hydrogen atoms of pyridine and phenyl rings forces the Ru-based and Os-based subunits to assume a *cis* or *trans* conformation. Comparison of the results obtained with those previously reported for other Ru–Os polypyridine complexes show that the macrocyclic ligand **3** is a relatively poor conducting bridge.

3. Host–guest systems

Supramolecular species whose components are connected by means of non-covalent forces can be disassembled and re-assembled [32] by modulating the interactions that keep the components together, thereby allowing switching of electron- or energy-transfer processes. Ru(II) bipyridine complexes can be useful components to build up this kind of systems.

3.1. A proton-driven assembling process

1,4,8,11-Tetraazacyclotetradecane (cyclam), which is one of the most extensively investigated ligands in coordination chemistry, in its protonated forms, can play the role of host towards cyanide metal complexes. We have investigated the acid-driven adducts formed in acetonitrile–dichloromethane 1:1 v/v solution by $[Ru(bpy)(CN)_4]^{2-}$ with 1,4,8,11-tetrakis(naphthylmethyl)-cyclam (**4**) and a dendrimer consisting of a cyclam core appended with 12 dimethoxybenzene and 16 naphthyl units (**5**, see Fig. 6)



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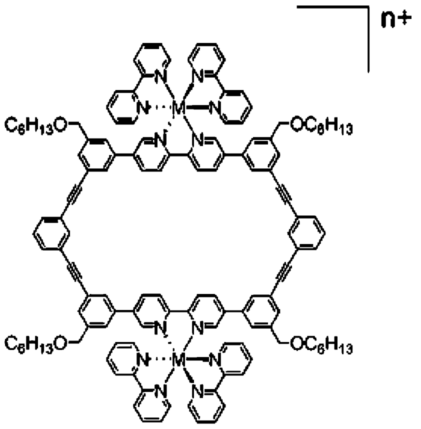
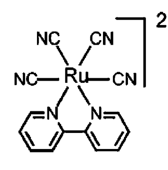


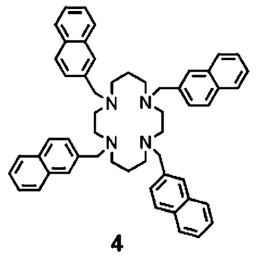
$[(bpy)_2Ru(3)Os(bpy)_2]^{4+}$ $Ru^{II}.3.Os^{II}$

$[(bpy)_2Ru(3)Os(bpy)_2]^{5+}$ $Ru^{II}.3.Os^{III}$

Fig. 5. Structures of the macrocyclic ligand **3** and its Ru and Os complexes [30].



$[Ru(bpy)(CN)_4]^{2-}$



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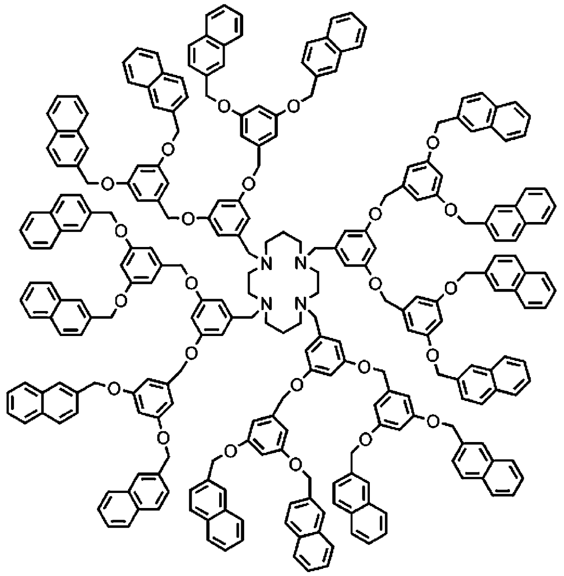


5

Fig. 6. Structures of $[Ru(bpy)(CN)_4]^{2-}$ complex and of two cyclam-cored dendrimers **4** and **5** [33].

[33]. $[Ru(bpy)(CN)_4]^{2-}$, **4** and **5** exhibit characteristic absorption and emission bands that are strongly affected by addition of acid. When a solution containing equimolar amounts of $[Ru(bpy)(CN)_4]^{2-}$ and **4** or **5** is titrated by trifluoroacetic acid, or when $[Ru(bpy)(CN)_4]^{2-}$ is titrated with $(\mathbf{4}{\cdot}2H)^{2+}$ or $(\mathbf{5}{\cdot}2H)^{2+}$, $\{[Ru(bpy)(CN)_4]^{2-}{\cdot}(2H^+){\cdot}\mathbf{4}\}$ or $\{[Ru(bpy)(CN)_4]^{2-}{\cdot}(2H^+){\cdot}\mathbf{5}\}$ adducts are formed (Fig. 7) in which the fluorescence of the naphthyl units is strongly quenched by very efficient energy transfer to the metal complex, as shown by the sensitized luminescence of the latter. The $\{[Ru(bpy)(CN)_4]^{2-}{\cdot}(2H^+){\cdot}\mathbf{4}\}$ and $\{[Ru(bpy)(CN)_4]^{2-}{\cdot}(2H^+){\cdot}\mathbf{5}\}$ adducts can be disrupted (i) by addition of a base (1,4-diazabicyclo[2.2.2]octane), yielding the starting species $[Ru(bpy)(CN)_4]^{2-}$ and **4** or **5**, or (ii) by further addition of triflic acid, with formation of $(\mathbf{4}{\cdot}2H)^{2+}$ or $(\mathbf{5}.2H)^{2+}$ and protonated forms of

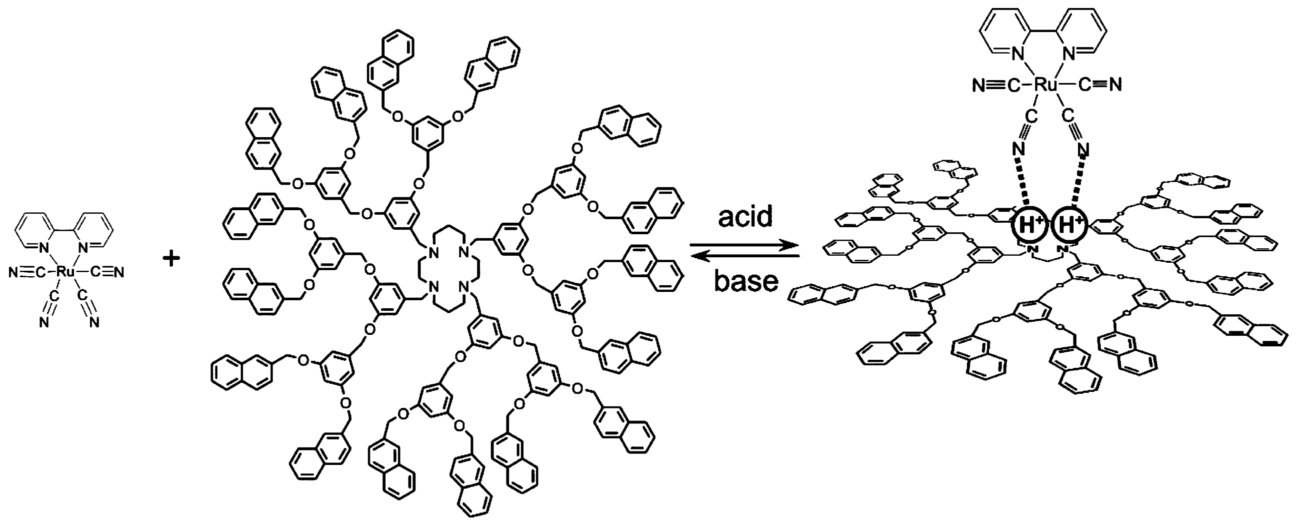


Fig. 7. Schematic representation of the formation of the $\{[Ru(bpy)(CN)_4]^{2-}{\cdot}(2H^+){\cdot}\mathbf{5}\}$ adduct [33].

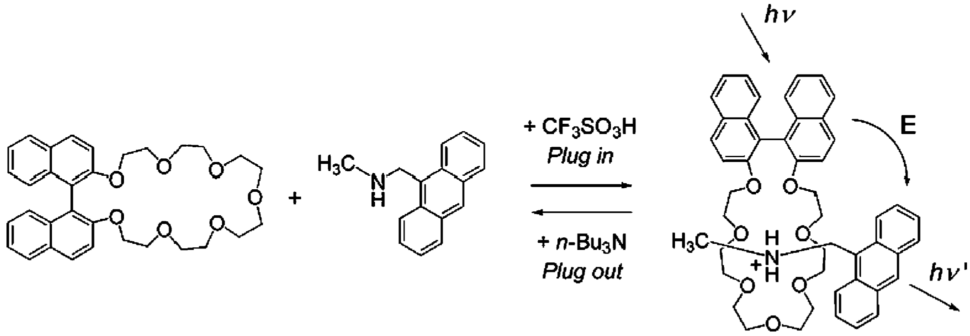


Fig. 8. A plug-socket system: switching of photoinduced energy transfer by acid/based controlled plug in/plug out of suitable molecular components [34].

$[Ru(bpy)(CN)_4]^{2-}$. Upon stimulation with two chemical inputs (acid and base) both $\{[Ru(bpy)(CN)_4]^{2-}\cdot(2H^+)\cdot\mathbf{4}\}$ and $\{[Ru(bpy)(CN)_4]^{2-}\cdot(2H^+)\cdot\mathbf{5}\}$ exhibit two distinct optical outputs (a naphthalene-based and a Ru(bpy)-based emissions) that behave according to an XOR and an XNOR logic, respectively.

3.2. Molecular plug/socket and extension cable

Hydrogen-bonding interactions between ammonium ions and crown ethers are particularly convenient for constructing molecular-level plug/socket devices since they can be switched on and off quickly and reversibly by means of acid–base inputs (see, e.g. Fig. 8) [34].

The plug/socket concept can then be extended to design molecular systems which mimic the function played by a macroscopic electrical extension cable. An extension cable is more complex than a plug/socket device since there are three components held together by two connections that have to be controllable reversibly and independently; in the fully connected system, an electron or energy flow must take place between the remote donor and acceptor units (Fig. 9).

In the attempt of constructing a molecular-level extension cable, the [3]pseudorotaxane shown in Fig. 10, made of the three components $\mathbf{6}^{2+}$, $[\mathbf{7}H]^{3+}$, and **8**, has been synthesized and studied [35]. Component $\mathbf{6}^{2+}$ 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 $[\mathbf{7}H]^{3+}$, 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, **8**, 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 red/ox stimulation, respectively. In the fully connected triad, light excitation of the $[Ru(bpy)_3]^{2+}$ unit of component $\mathbf{6}^{2+}$ is followed by electron-transfer to the bipyridinium unit of component $[\mathbf{7}H]^{3+}$, which is plugged into component **8**. 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. Possible schemes to improve the system have also been discussed [35]. Currently, we are trying to construct an improved version of a molecular extension system [36].

4. Dendrimers as antenna systems

In suitably designed dendrimers, electronic energy transfer can be channeled towards a specific position of the array. Compounds of this kind play the role of antennas for light harvesting [27]. Several light harvesting dendrimers based on Ru–bipyridine type complexes have been investigated. Some examples are illustrated below.

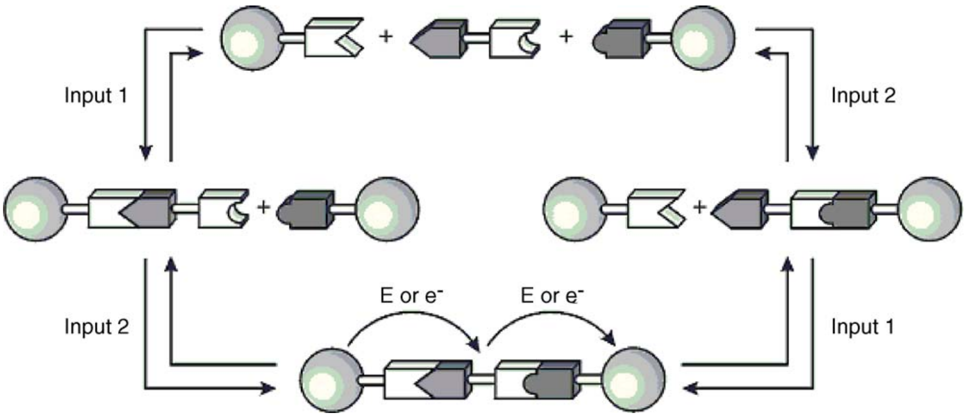


Fig. 9. Schematic representation of an extension cable.

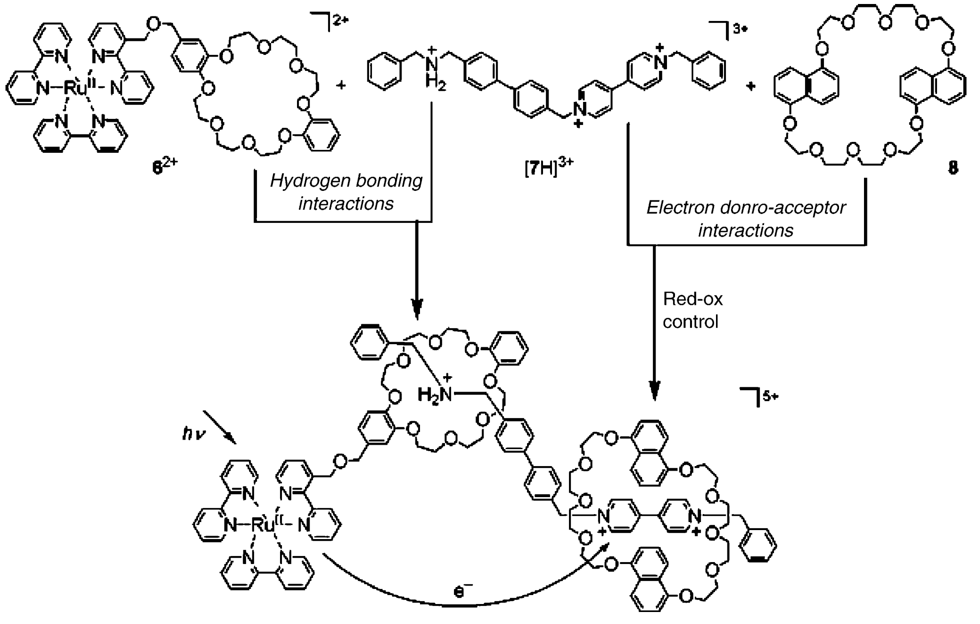
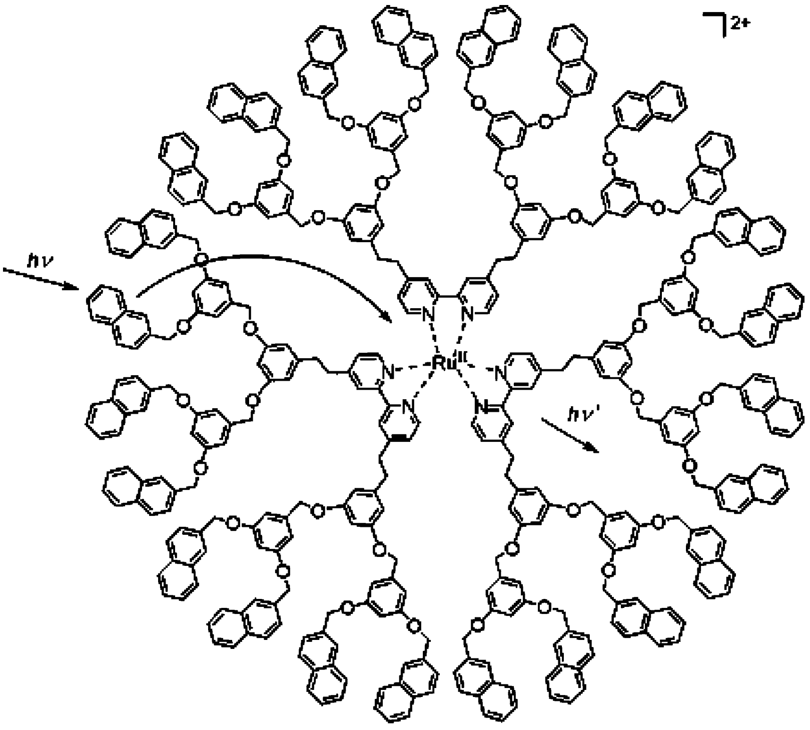


Fig. 10. A supramolecular system that behaves as a molecular-level extension cable [35].

4.1. A dendrimer with a metal complex as a core

In the dendritic complex **9**$^{2+}$ (Fig. 11), the bpy ligands of the $[Ru(bpy)_3]^{2+}$-type core carry branches containing 1,2-dimethoxybenzene- and 2-naphthyl-type chromophoric units [37]. Since such units (as well as the core) are separated by aliphatic connections, the interchromophoric interactions are weak and the absorption spectra of the dendrimer is substantially equal to the sum of the spectra of the chromophoric groups that are present in its structures. The three types of chromophoric groups, namely, $[Ru(bpy)_3]^{2+}$, dimethoxybenzene, and naphthalene, are potentially luminescent species. In the dendrimer, however, the fluorescence of the dimethoxybenzene- and naphthyl-type units is almost completely quenched in



9^{2+}

Fig. 11. Antenna effect in a dendrimer [37].

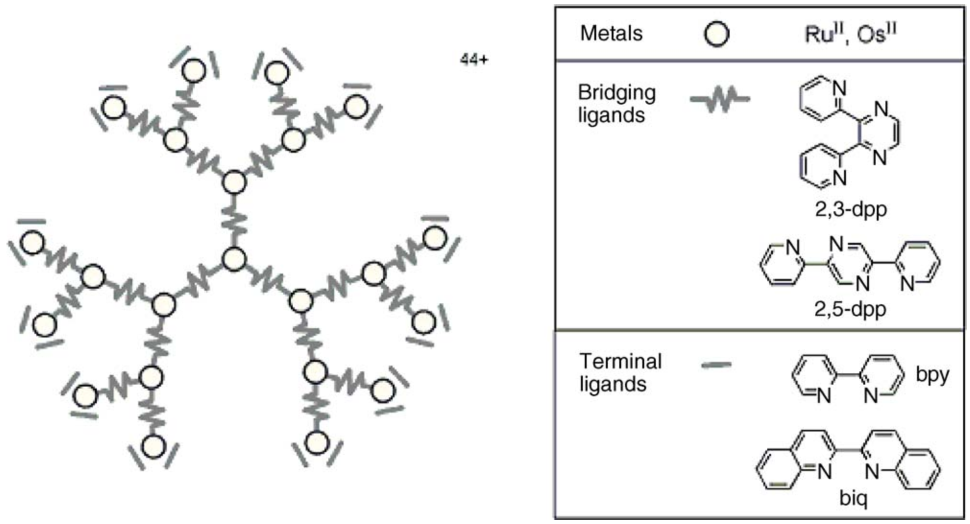


Fig. 12. Schematic representation of a dendrimer containing Ru and/or Os complexes in each branching site. The formulae of the 2,3- and 2,5-dpp bridging ligands and of the bpy and biq terminal ligands are also shown.

acetonitrile solution, with concomitant sensitization of the luminescence of the $[Ru(bpy)_3]^{2+}$ core ($\lambda_{max} = 610$ nm). These results show that a very efficient energy-transfer process takes place converting the very short lived UV fluorescence of the aromatic units of the wedges to the long-lived orange emission of the metal-based dendritic core. In aerated solution the luminescence intensity of the dendrimer core is more than twice as intense as that of the $[Ru(bpy)_3]^{2+}$ parent compound because the dendrimer branches protect the Ru–bpy-based core from dioxygen quenching [37]. In conclusion, because of the very high absorbance of the naphthyl groups in the UV spectral region, the high energy-transfer efficiency, and the strong emission of the $[Ru(bpy)_3]^{2+}$-type core, dendrimer $\mathbf{9}^{2+}$ (Fig. 11) exhibits a strong visible emission upon UV excitation even in very dilute (10^{-7} mol L^{-1}) solutions.

4.2. Dendrimers with metal complexes in each branching center

In the past 10 years a great number of dendrimers containing Ru(II) and Os(II) as metals, 2,3- and 2,5-bis(2-pyridyl)pyrazine (2,3- and 2,5-dpp) as bridging ligands and bpy and 2,2′-biquinoline (biq) as terminal ligands (Fig. 12) have been carefully investigated from the photophysical viewpoint [38].

The typical strategy used to prepare dendrimers containing the 2,3- and 2,5-dpp bridging ligands is the so-called "complexes as metals and complexes as ligands" approach [39] which has allowed the construction of species containing 4, 6, 10, 13 and 22 metal-based units. A docosanuclear dendrimer of that family, such as that schematically shown in Fig. 12, is a 44^+ cationic species made of 1090 atoms, with an estimated size of

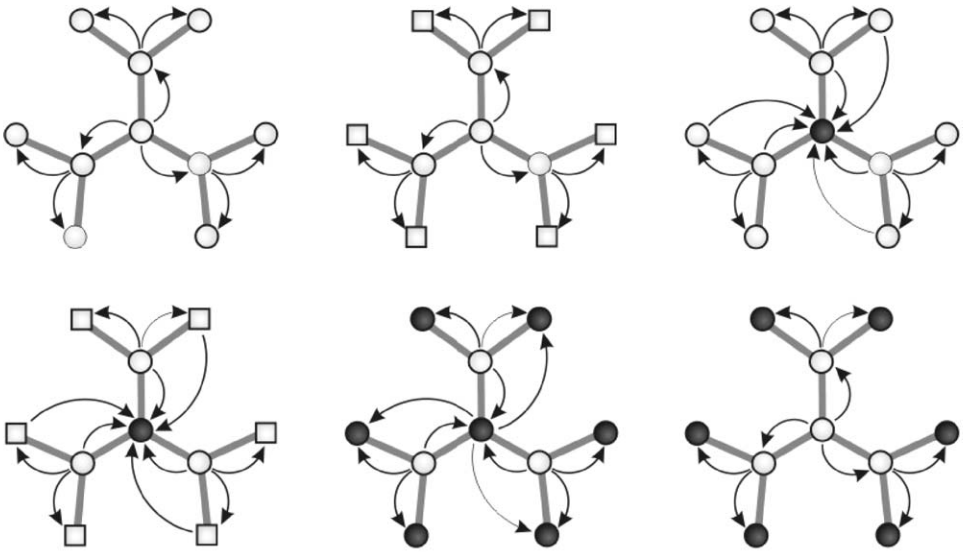


Fig. 13. Schematic representation of the different energy-transfer patterns that can be obtained in decanuclear dendrimer-type compounds on choosing different metals and ligands. The arrows indicate the energy transfer steps; gray and black circles indicate Ru(II) and Os(II), respectively; in the peripheral positions, circles and squares indicate $M(bpy)_2$ and $M(biq)_2$ moieties, respectively. The compounds have 20+ electric charge.

5 nm. Besides the 22 metal atoms, it contains 24 terminal ligands and 21 bridging ligands. Such dendrimers can be viewed as ordered ensembles of $[M(L)_n(BL)_{3-n}]^{2+}$ complexes [M = Ru(II) or Os(II); L = bpy or biq; BL = 2,3- or 2,5-dpp] which are known to exhibit (i) intense ligand-centered (LC) absorption bands in the UV region and moderately intense metal-to-ligand charge-transfer (MLCT) bands in the visible region, and (ii) a relatively long-lived luminescence in the red spectral region, originating from the lowest ^{3}MLCT level. In the dendrimers, there is only a relatively small electronic interaction between nearby mononuclear units and therefore the absorption spectrum is practically the sum of the spectra of the constituent units. In the dendrimers of higher nuclearity, the molar absorption coefficient is huge throughout the entire UV–visible spectral region ($\varepsilon = 202000\ \mathrm{L\,mol^{-1}\,cm^{-1}}$ at 542 nm for a docosanuclear dendrimer in which all the metal ions are Ru(II)), so that most of the photochemically active part of sunlight can be absorbed.

In these dendrimers, the small but not negligible electronic interaction between nearby units is sufficient to cause a very fast energy transfer that leads to the quenching of the potentially luminescent units having higher energy ^{3}MLCT levels and the sensitization of the luminescence of the units having lower energy ^{3}MLCT levels. Recent studies have suggested that energy transfer between nearby units occurs within 200 fs, probably from non thermalized excited-states [40].

The energy of the ^{3}MLCT excited-state of each unit depends on metal and ligands in a predictable way and the modular synthetic strategy used enables a high degree of synthetic control in terms of the nature and position of metal centers, bridging ligands, terminal ligands. Such a synthetic control translates into a high degree of control on the direction of energy flow within the dendritic array, as shown by the decanuclear compounds represented in Fig. 13. On increasing nuclearity, however, an unidirectional gradient (center-to-periphery or vice versa) for energy transfer cannot be obtained with only two types of metals [Ru(II) and Os(II)] and ligands (bpy and 2,3-dpp) [38].

Other investigations on this type of polynuclear complexes have been carried out recently [41].

5. Switching electron and energy transfer processes

The movement of electrons or electronic energy in a molecular-level wire can be switched on/off by an external stimulus applied to a suitably designed molecular device, incorporated in the wire.

In an appropriately designed compound, the external stimulus can be light. Since, by definition, switching has to be reversible, reversible photochemical reactions have to be used. Photochromic molecules are particularly useful in this regard [42].

A switching-related system investigated in our laboratory is the triad **10**$^{4+}$ shown in Fig. 14, which consists of a $[Ru(bpy)]_3^{2+}$ and a $[Os(bpy)]_3^{2+}$ moieties bridged by an anthracene unit [43,44]. Since the lowest triplet energy level of the anthracene bridge lies in between the lowest triplet 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 aerated solution, however, the relatively long-lived excited-state of the $[Os(bpy)]_3^{2+}$ moiety sensitises the formation of singlet oxygen which attacks the anthracene ring to form the endoperoxide derivative (Fig. 14). As a consequence, the 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 difficult to perform. Energy transfer in the starting compound has been defined a “self-poisoning” process. The intriguing possibility of designing “self-repairing” processes has been advanced [44].

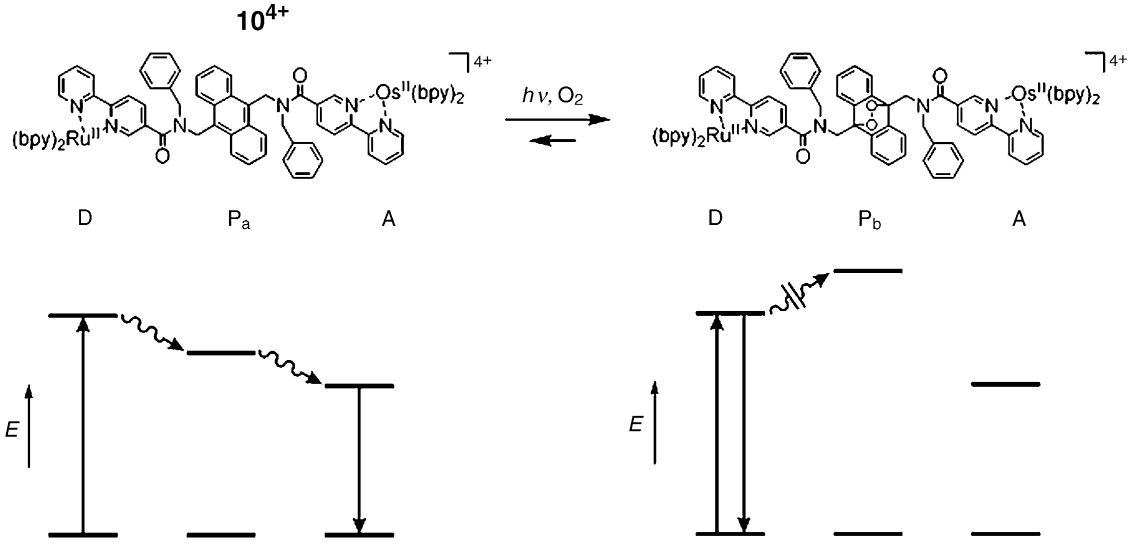


Fig. 14. “Self-poisoning” of energy transfer in a compound consisting of a $[Ru(bpy)]_3^{2+}$ and a $[Os(bpy)]_3^{2+}$ moieties bridged by an anthracene unit [43,44].

6. Photochemically driven molecular machines

In supramolecular species, photoinduced electron-transfer reactions can often cause large displacement of molecular components [45,46]. Indeed, working with suitable systems, an endless sequence of cyclic molecular-level movements can in principle be performed making use of light-energy inputs without generating waste products. Compared to chemical energy inputs, photochemical energy inputs offer other advantages, besides the fundamental one of not generating waste products: (i) light can be switched on/off easily and rapidly; (ii) lasers provide the opportunity of working in very small space and very short time domains; (iii) photons, besides supplying the energy needed to make a machine work, can also be useful to "read" the state of the system and thus to control and monitor the operation of the machine. In the last few years, a great number of light-driven molecular machines have been developed and the field has been extensively reviewed [25,46–51].

6.1. Dethreading/rethreading of pseudorotaxanes

Dethreading/rethreading of the wire and ring components of a pseudorotaxane reminds the movement of a piston in a cylinder. In order to achieve a light-induced dethreading in piston/cylinder systems, pseudorotaxanes have been designed which incorporate a "light-fueled" motor [52] (i.e. a photosensitizer) in the wire (Fig. 15) [53] or in the macrocyclic ring (Fig. 16) [54]. In both cases, 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. 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. As previously pointed out, however, photochemical systems which rely on such a sensitizer-scavenger strategy produce waste species from the decomposition of the reductant scavenger and from the consumption of dioxygen.

6.2. A photocontrollable molecular shuttle

Just like their macroscopic counterparts, molecular-level machines have to be organized structurally and work as functionally integrated multicomponent systems. In order to achieve photoinduced ring switching in rotaxanes containing two different recognition sites in the dumbbell-shaped component, the thoroughly designed rotaxane **11**$^{6+}$ shown in Fig. 17 was synthesized [55]. This compound consists of as many as 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 (A_1) and a 3,3′-dimethyl-4,4′-bipyridinium (A_2) units, that can play the role of "stations" for the ring R. Furthermore, the dumbbell-shaped component incorporates a $[Ru(bpy)_3]^{2+}$-type (bpy = 2,2′-bipyridine) 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 structure of the rotaxane was characterized by mass spectrometry and NMR spectroscopy. The stable translational isomer is the one in which the R component encircles the A_1 unit, in keeping with the fact that this station is a better electron acceptor than the other one.

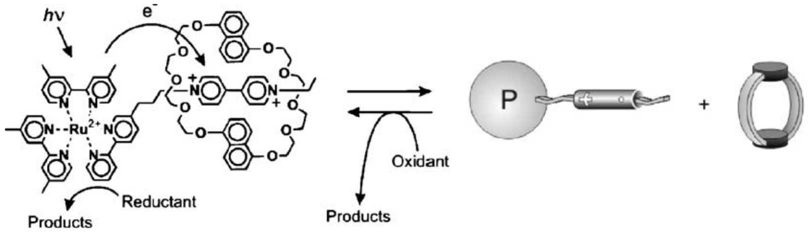


Fig. 15. Light-driven dethreading of pseudorotaxanes by excitation of a photosensitizer contained in the wire-type component [53].

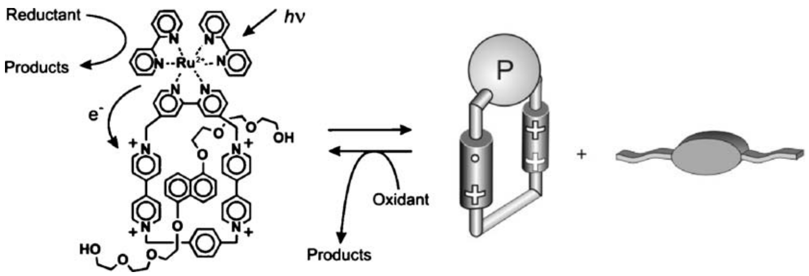


Fig. 16. Light-driven dethreading of pseudorotaxanes by excitation of a photosensitizer incorporated in the macrocyclic ring [54].

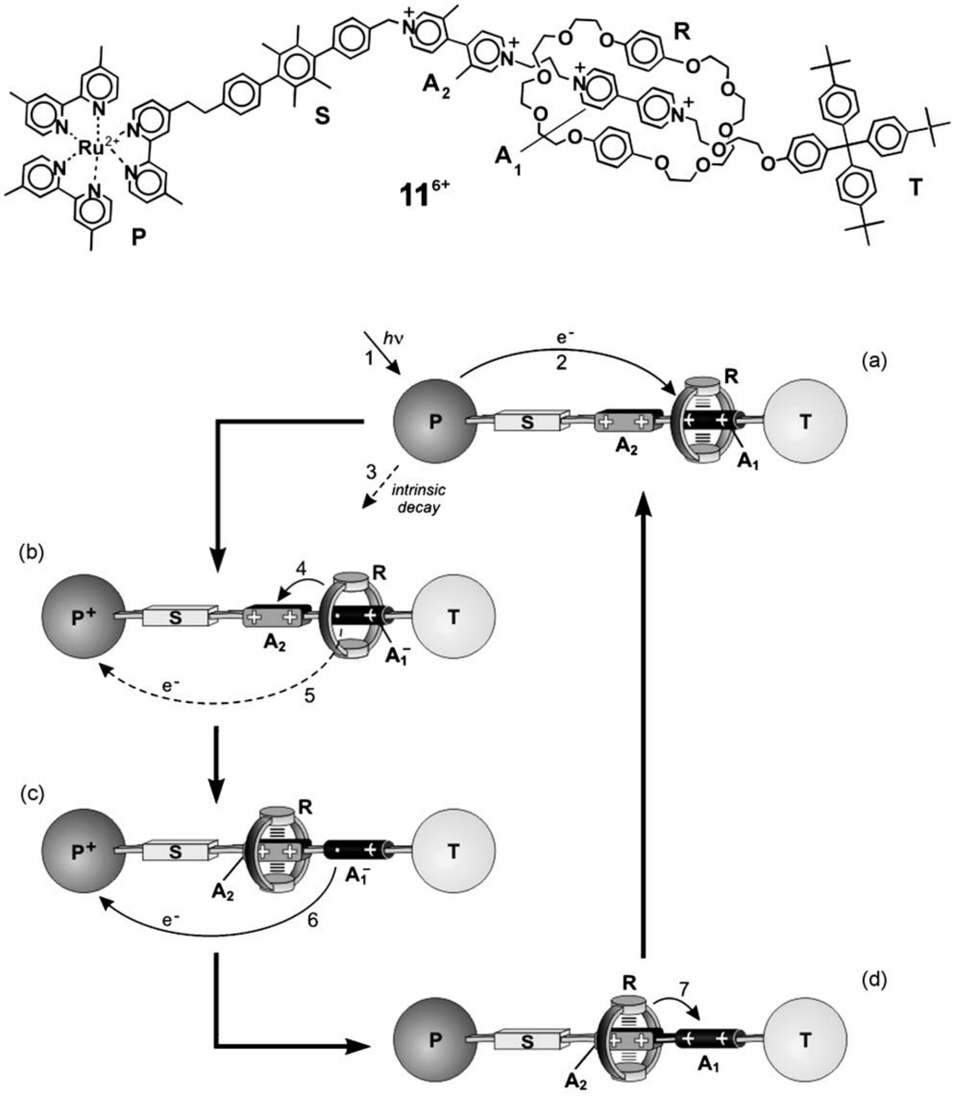


Fig. 17. Structure of a rotaxane and schematic representation of the intramolecular mechanisms for its photoinduced shuttling movement [55,56].

A shuttling movement of the ring between the two stations A_1 and A_2 can be obtained in solution at room temperature by electrochemical or light energy inputs. The photoinduced shuttling, which operates with visible light, can take place in three distinct ways: (i) by a mechanism involving an energetic contribution from low energy fuels, (ii) by a mechanism involving the kinetic assistance of an external electron relay, and (iii) by a purely intramolecular photochemical mechanism [55,56]. When shuttling occurs via mechanisms (ii) and (iii), rotaxane $\mathbf{11}^{6+}$ behaves as an autonomous "four-stroke" linear motor powered only by visible light.

The intramolecular mechanism, illustrated in Fig. 17, is based on the following four operations [55,56]:

(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 A_1 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 from the reduced station A_1^- to A_2 (Step 4), a step that has to compete with the back electron-transfer process from A_1^- (still encircled by R) to the oxidized photoactive unit P^+ (Step 5). This is the most difficult requirement to meet in the intramolecular mechanism.

(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).

According to the above mechanism, in a fully optimized system of this kind, each light energy input (i.e. each absorbed photon) would cause the occurrence of a forward and backward movement (i.e. a full cycle) of ring R between the two stations A_1 and A_2. The rotaxane would therefore operate as an autonomous "four-stroke" linear motor, powered by visible light and relying only upon intramolecular processes. Each phase corresponds, in kind, to the (a) fuel injection and combustion, (b) piston displacement, (c) exhaust removal, and (d) piston replacement of a four-stroke motor. However, the timing of the strokes is intrinsic to the molecular motor and cannot be tuned up externally, such as in modern fuel-injected car engines.

At 303 K the quantum yield for the shuttling process, Φ_{sh}, is about 2%. The low efficiency of this motor may seem disappointing, particularly if compared with the performance of natural motors [57]. It should be considered, however, that the operation of the system is based on the challenge that a complex nuclear motion can compete with an electron-transfer process. The low efficiency is compensated by the fact that the operation of the system relies exclusively on intramolecular processes. Therefore, this artificial molecular motor does not need the assistance of external species and, in principle, it can work at the single molecule level. This is the first example of an autonomous artificial linear motor working by an intramolecular mechanism powered by visible light.

7. Conclusions

The results reviewed in this paper show that $[Ru(bpy)_3]^{2+}$ and related compounds have given an outstanding contribution to the development of photochemistry and supramolecular chemistry. In particular, they are very useful building blocks to construct devices capable of using light for information processing (wires, antennas, switches, plug/socket and extension system) and for driving machines (pyston cylinder systems, shuttles) at the molecular level.

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