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Photochemistry and photophysics of Ru(II)–polypyridine complexes in the Bologna group. From early studies to recent developments

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Contents

Abstract

The investigations carried out in the Bologna group on $Ru(bpy)_3^{2+}$ (bpy = 2,2′-bipyridine) and related systems are reviewed. The following topics are discussed: (i) bimolecular energy and electron-transfer processes (including the measure of the rate of self-exchange energy-transfer); (ii) tuning the excited state properties by changing the ligands (including a caged

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version of $Ru(bpy)_3^{2+}$); (iii) chemi- and electrochemiluminescent processes (including the description of an artificial firefly); (iv) photochemistry without light; (v) molecular-level wires for energy and electron transfer; (vi) dendrimers for light harvesting; (vi) light-powered molecular machines. © 2001 Elsevier Science B.V. All rights reserved.

Keywords: Electron-transfer processes; Electrochemiluminescence; Dendrimers; Molecular wires; Molecular machines

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1. Introduction

In the late 1960s Crosby and co-workers [1] characterized the luminescence properties of the $Ru(bpy)_3^{2+}$ complex (bpy = 2,2′-bipyridine) and of other polypyridine-type compounds. In 1972, Gafney and Adamson [2] reported the electron-transfer quenching of the triplet charge-transfer excited state of $Ru(bpy)_3^{2+}$, $(^3CT)Ru(bpy)_3^{2+}$, by $Co(NH_3)_5Cl^{2+}$:

$$(^3CT)Ru(bpy)_3^{2+} + Co(NH_3)_5Cl^{2+} \rightarrow Ru(bpy)_3^{3+} + Co(NH_3)_5Cl^{+} \qquad (1)$$

This Gafney–Adamson paper, as was usually the case for the papers of Adamson's group, had a strong impact on the photochemical community because at that time excited-state electron-transfer reactions were not common, even in the more mature field of organic photochemistry. Following that paper, several laboratories [3–6] became interested in the use of $(^3CT)Ru(bpy)_3^{2+}$ 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 [7]. Since then, the interest in the study of the photochemistry of Ru–polypyridine complexes has increased exponentially. In an exhaustive monograph on the photochemistry of coordination compounds [8] 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 with in less than one page. By contrast, 51 pages were dedicated to Cr and 52 pages to Co complexes. In an authoritative multi-author book on inorganic photochemistry [9], which appeared a few years later, the use of $Ru(bpy)_3^{2+}$ in photoinduced energy and electron transfer processes was briefly mentioned. 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 [10] 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 [11] and electron-transfer [12] processes). In the last decade, Ru–polypyridine complexes have become one of the main topics of photochemistry [13–16].

Along the past 30 years our group has been heavily involved in research on complexes of the Ru–polypyridine family. In this paper we would like to review some of the work carried out in our laboratory on several aspects of this fascinating chemistry.

2. Bimolecular energy- and electron-transfer processes

2.1. Energy transfer

In the early 1970s our group began to investigate the quenching of the luminescent triplet charge-transfer excited state of $Ru(bpy)_3^{2+}$ by energy transfer, with the purpose of elucidating the mechanism of photoaquation $Cr(CN)_6^{3-}$ [3]. We showed that energy transfer from $(^3CT)Ru(bpy)_3^{2+}$ to $Cr(CN)_6^{3-}$ was able to sensitize the emission of the lowest excited state, ^2E_g, of the Cr complex, but not the photoaquation reaction. This result contributed to solve the controversy about the nature of the photoreactive state in $Cr(CN)_6^{3-}$. Sensitization/quenching experiments were then extended to other Cr(III) complexes [17] and to a variety of complex anions [18]. For the latter systems, the presence of both static and dynamic quenching was evidenced.

The possibility to design Ru(II)–polypyridine complexes having specific properties (vide infra) allowed us to investigate the problem of *self-exchange energy-transfer* processes

$$^*A + A \rightarrow A + {}^*A \qquad (2)$$

which is much more difficult to tackle than that of self-exchange electron transfer. We prepared $Ru(L)_3^{2+}$, $Ru(bpy)_2(L)^{2+}$ and $Ru(bpy)(L)_2^{2+}$ complexes (L = 2,2′-biquinoline or a 2,2′-biquinoline derivative) having very different luminescence lifetimes, but practically the same excited state energy. Using the complexes with long lifetime as donors and those with short lifetime as acceptors, we measured the quenching rate constants. Since the excited states of the donor and acceptor have not only the same energy, but also the same spin and orbital nature, the values obtained for the rate constants (which range from 3.4×10^7 to 6.6×10^7 M^{-1} s^{-1}) are a measure of the self-exchange energy-transfer rates in Ru(II)–polypyridine complexes [19].

2.2. Electron transfer

We did not consider the possibility of using the $(^3CT)Ru(bpy)_3^{2+}$ excited state as an electron transfer reactant until we read the above mentioned Gafney and Adamson paper [2] describing the electron-transfer quenching of $(^3CT)Ru(bpy)_3^{2+}$ by $Co(NH_3)_5Cl^{2+}$, Eq. (1). That work prompted us to investigate other aspects of the $(^3CT)Ru(bpy)_3^{2+}$ reactivity, and in 1974 we reported the oxidative quenching of $(^3CT)Ru(bpy)_3^{2+}$ using the Tl_{aq}^{3+} ion as a quencher [20]:

$$(^3CT)Ru(bpy)_3^{2+} + Tl_{aq}^{3+} \rightarrow Ru(bpy)_3^{3+} + Tl_{aq}^{2+} \qquad (3)$$

Interestingly, we also found that the limiting quantum yield for the photoreaction between $Ru(bpy)_3^{2+}$ and Tl_{aq}^{3+} is 2, which indicates that the initially formed Tl_{aq}^{2+} ion oxidizes, as expected from the redox potentials, a ground state $Ru(bpy)_3^{2+}$ molecule, thereby yielding a second $Ru(bpy)_3^{3+}$ species. Incidentally, this was also the first evidence for unitary efficiency for the intersystem crossing process from the

$(^1\mathrm{CT})\mathrm{Ru(bpy)}_3^{2+}$ excited state originally populated by light excitation to the $(^3\mathrm{CT})\mathrm{Ru(bpy)}_3^{2+}$ reactive excited state.

Eqs. (1) and (3) lead to permanent redox products because of the fast disappearance of the $\mathrm{Co(NH_3)_5Cl^+}$ and $\mathrm{Tl}_{\mathrm{aq}}^{2+}$ primary products via secondary reactions. In most cases, however, as for the frequently used MV^{2+} (N,N′-dimethyl-4,4′-bipyridinium cation) quencher, the forward excited state electron-transfer reaction is followed by a back reaction leading to the original reactants:

$$(^3\mathrm{CT})\mathrm{Ru(bpy)}_3^{2+} + \mathrm{MV}^{2+} \rightarrow \mathrm{Ru(bpy)}_3^{3+} + \mathrm{MV}^{+} \tag{4}$$

$$\mathrm{Ru(bpy)}_3^{3+} + \mathrm{MV}^{+} \rightarrow \mathrm{Ru(bpy)}_3^{2+} + \mathrm{MV}^{2+} \tag{5}$$

In such cases, the occurrence of the excited state electron-transfer reaction and of the back reaction was monitored following the transient absorption of the MV^+ radical in flash photolysis experiments [6,21]. In the case of reductive quenching, e.g.

$$(^3\mathrm{CT})\mathrm{Ru(bpy)}_3^{2+} + \mathrm{Eu}_{\mathrm{aq}}^{2+} \rightarrow \mathrm{Ru(bpy)}_3^{+} + \mathrm{Eu}_{\mathrm{aq}}^{3+} \tag{6}$$

$$\mathrm{Ru(bpy)}_3^{+} + \mathrm{Eu}_{\mathrm{aq}}^{3+} \rightarrow \mathrm{Ru(bpy)}_3^{2+} + \mathrm{Eu}_{\mathrm{aq}}^{2+} \tag{7}$$

the monitored species was the strongly absorbing $\mathrm{Ru(bpy)}_3^{+}$ complex [22].

Flash photolysis experiments were used in our group to measure the absorption spectrum of $(^3\mathrm{CT})\mathrm{Ru(bpy)}_3^{2+}$ [23], which offers an alternative way to monitor the disappearance of the excited state.

We found that $(^3\mathrm{CT})\mathrm{Ru(bpy)}_3^{2+}$ is quenched by $\mathrm{Cr(bpy)}_3^{3+}$ by electron transfer and, interestingly, that also the lowest metal-centered (MC) excited state of $\mathrm{Cr(bpy)}_3^{3+}$ is quenched by $\mathrm{Ru(bpy)}_3^{2+}$ by electron transfer [24]:

$$(^3\mathrm{CT})\mathrm{Ru(bpy)}_3^{2+} + \mathrm{Cr(bpy)}_3^{3+} \rightarrow \mathrm{Ru(bpy)}_3^{3+} + \mathrm{Cr(bpy)}_3^{2+} \tag{8}$$

$$(^2\mathrm{MC})\mathrm{Cr(bpy)}_3^{3+} + \mathrm{Ru(bpy)}_3^{2+} \rightarrow \mathrm{Cr(bpy)}_3^{2+} + \mathrm{Ru(bpy)}_3^{3+} \tag{9}$$

Reaction (9) showed for the first time that also the spectroscopic energy of the metal-centered excited states can be used for redox reactions.

3. Tuning the excited state properties by changing the ligands

In 1978 there was already a fair amount of information on bimolecular photoinduced electron-transfer reactions involving $\mathrm{Ru(bpy)}_3^{2+}$, $\mathrm{Ru(phen)}_3^{2+}$, and a few other complexes containing substituents on the bpy or phen ligands [25]. In 1980 our group initiated [26] a very productive collaboration with the group of von Zelewsky, Belser and co-workers (Fribourg, Switzerland). In a long series of papers we reported the synthesis and the photochemical and photophysical properties of a great number of complexes of the Ru–polypyridine family, including temperature and viscosity effects [27], complexes that exhibit long-lived ligand-centered phosphorescence [28] and the first examples of tris-heteroleptic complexes [29]. A review article published in 1988 (updated to mid-1986) on the photochemical, photophysical, and electrochemical properties of Ru–polypyridine complexes [30] is 193 pages long (compared with the single page dedicated to ruthenium and osmium complexes in [8]), covers 518 references, and lists the properties of more than 300 luminescent complexes of about 200 different ligands. (It may be interesting to note that, as pointed out by Professor von Zelewsky, with 200 bidendate polypyridine type ligands LL, one can obtain 200 homoleptic $Ru(LL)_3^{2+}$, 39 800 bis-heteroleptic $Ru(LL)_{3-n}(LL')_n^{2+}$, and 1 313 400 tris-heteroleptic $Ru(LL)(LL'(LL'')^{2+}$ complexes!) The above-mentioned review is apparently the most cited paper in the field of Ru–polypyridine chemistry. In 1989 another very interesting review (325 pages long) by our group, in collaboration with Hoffman et al., listed all the available data on the rate constants for the quenching of excited states of metal complexes in fluid solution [31].

We also extended our investigations on mononuclear Ru–polypyridine compounds in a completely new direction, obtaining a remarkable result. As $Ru(bpy)_3^{2+}$ is not fully stable under light excitation, we prepared a caged version of this complex (Fig. 1). As expected, this cage-type complex exhibits all the properties that make $Ru(bpy)_3^{2+}$ a widely used photosensitizer, with the additional advantages of a longer excited state lifetime (1.7 vs. 0.80 μs, in deaerated acetonitrile solution at room temperature (r.t.)) and a 10^4 higher stability towards ligand dissociation [32].

4. Chemiluminescence

The generation of light upon reduction of $Ru(bpy)_3^{3+}$ was first reported in 1971 [33]. In the following years Bard and co-workers carried out a systematic investigation on the electroluminescence generated in $Ru(bpy)_3^{2+}$ solutions by successive oxidation/reduction cycles or by electrochemical oxidation in the presence of a strong reductant [34]. Working in this field, we found that electrochemical reduc-

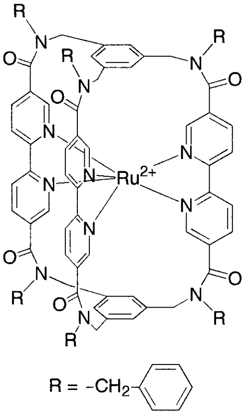


Fig. 1. A caged version of $Ru(bpy)_3^{2+}$ [32].

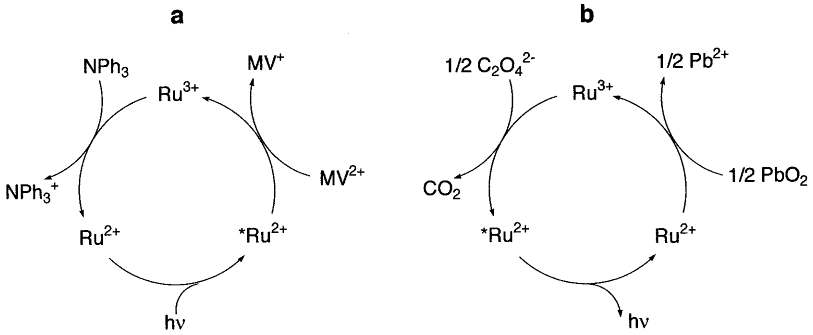


Fig. 2. $\mathrm{Ru(bpy)_3^{2+}}$ as a light-absorption [38,39] and (b) a light-emission sensitizer [37,39].

tion of polypyridine complexes of Ru(II), Os(II), and Cr(III) in the presence of $\mathrm{S_2O_8^{2-}}$ ions is accompanied by light emission [35,36]. Taking $\mathrm{Ru(bpy)_3^{2+}}$ as an example, the reaction mechanism can be described as follows:

$$\mathrm{Ru(bpy)_3^{2+} + e^- \rightarrow Ru(bpy)_3^{+}} \tag{10}$$

$$\mathrm{Ru(bpy)_3^{+} + S_2O_8^{2-} \rightarrow Ru(bpy)_3^{2+} + SO_4^{-} + SO_4^{2-}} \tag{11}$$

$$\mathrm{Ru(bpy)_3^{+} + SO_4^{-} \rightarrow (^3MC)Ru(bpy)_3^{2+} + SO_4^{2-}} \tag{12}$$

$$\mathrm{(^3MC)Ru(bpy)_3^{2+} \rightarrow Ru(bpy)_3^{2+}} + h\nu \tag{13}$$

Rubistein and Bard [37] have also found that reduction of lead dioxide by oxalate produces light when it is mediated by $\mathrm{Ru(bpy)_3^{2+}}$. Therefore the chemiluminescence results show another outstanding property of $\mathrm{Ru(bpy)_3^{2+}}$: it can be used not only as a *light absorption sensitizer* (i.e. to carry on a reaction that does not occur in the dark, Eqs. (14) and (15) [38], Fig. 2(a)),

$$\mathrm{MV^{2+} + NPh_3 \not\rightarrow MV^{+} + NPh_3^{+}} \tag{14}$$

$$\mathrm{MV^{2+} + NPh_3} + h\nu \xrightarrow{\mathrm{Ru(bpy)_3^{2+}}} \mathrm{MV^{+} + NPh_3^{+}} \tag{15}$$

but also as *light emission sensitizer* (i.e. to convert the free energy of a dark reaction into light, Eqs. (16) and (17) [37], Fig. 2(b)) [39,40]:

$$\mathrm{1/2PbO_2 + 1/2C_2O_4^{2-} + 2H^+ \not\rightarrow 1/2Pb^{2+} + CO_2 + H_2O} + h\nu \tag{16}$$

$$\mathrm{1/2PbO_2 + 1/2C_2O_4^{2-} + 2H^+} \xrightarrow{\mathrm{Ru(bpy)_3^{2+}}} \mathrm{1/2Pb^{2+} + CO_2 + H_2O} + h\nu \tag{17}$$

We have also discovered that $\mathrm{Ru(bpy)_3^{2+}}$ can be used to construct an *artificial firefly* system [41]. At that time we were interested in oscillating reactions and we noticed that polypyridine complexes, including $\mathrm{Ru(bpy)_3^{2+}}$, were commonly used as catalysts in the Belousov–Zhabotinskii (BZ) reaction (reduction of bromate by malonic acid). As it was known that the concentration of the oxidized form of the catalyst oscillates during the reaction and that $\mathrm{Ru(bpy)_3^{3+}}$ gives rise to chemiluminescence in the presence of organic acids, we thought that the oscillating BZ reaction has to be accompanied by an oscillating chemiluminescence emission. An oscillating emission was indeed recorded when we performed the reaction in a spectrofluorimeter cell (Fig. 3).

5. Photochemistry without light

$Ru(bpy)_3^{2+}$ is fairly stable in the dark and also under light excitation. Nevertheless, in acetonitrile (AN) solution it undergoes a photochemical ligand-substitution reaction with quantum yield 2×10^{-5}. The state responsible for the photoreaction is the $(^3MC)Ru(bpy)_3^{2+}$ level:

$$Ru(bpy)_3^{2+} + h\nu \rightarrow (^3MC)Ru(bpy)_3^{2+} \xrightarrow{AN} Ru(bpy)_2(AN)_2^{2+} + bpy \quad (18)$$

The chemiluminescent experiments discussed above show that this excited state can be generated by means of chemical or electrochemical reactions. This opens the possibility to carry on the photochemical reaction (18) *without* using light excitation.

$$Ru(bpy)_3^{2+} \xrightarrow{red/ox} (^3MC)Ru(bpy)_3^{2+} \xrightarrow{AN} Ru(bpy)_2(AN)_2^{2+} + bpy \quad (19)$$

This expectation was indeed verified [42]. Therefore, besides being able 'to sensitize' photochemical reactions (Eq. (15)) and light emission (Eq. (17)), $Ru(bpy)_3^{2+}$ can also 'be sensitized' in the sense that its excited state ligand-substitution reaction can

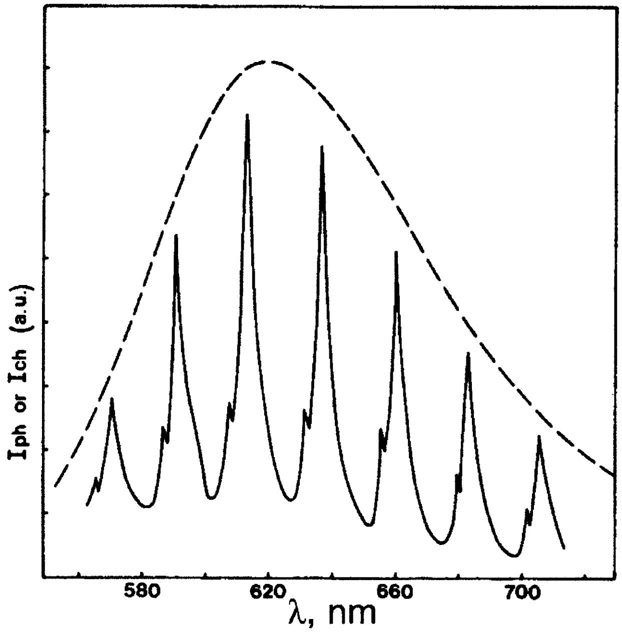


Fig. 3. Oscillating chemiluminescence emission spectrum of the $Ru(bpy)_3^{2+}$ catalyzed Belousov–Zhabotinskii reaction (solid line) compared with the photoluminescence spectrum of $Ru(bpy)_3^{2+}$ [41].

be induced by an oxidation/reduction (or vice versa) process involving electrodes or suitable chemical species. This adds another dimension to the extraordinarily rich chemistry of $Ru(bpy)_3^{2+}$.

6. Molecular-level wires

In the mid-1980s our group became interested in photoinduced energy- and electron-transfer processes taking place in supramolecular species [43], and in 1986 we organized a NATO meeting on supramolecular photochemistry. In a paper published in the proceedings of that meeting, the possibility to construct molecular-level devices was discussed [44]. Since then, the need to explore the construction of molecular-level devices has been widely recognized [45–48].

As light is going to play a major role in signal generation, processing, and storage, there is a need to design molecular-level systems capable of elaborating light signals. Particularly important are molecular-level systems where photoinduced energy- and electron-transfer processes can be obtained over long distances and/or along predetermined directions. In collaboration with several European laboratories (see, e.g. [49–52]), and particularly with the groups of Belser, Vötgle, Barigelletti, Campagna and Denti (vide infra) we have dedicated much attention to the design of oligonuclear metal complexes capable of performing these tasks [53].

The modular approach used is illustrated in Fig. 4. As photo/electro-active units we have used Ru(II) and Os(II) polypyridine complexes, connected by a bridging ligand whose two chelating moieties are separated by a suitable spacer. In all the investigated heterodinuclear compounds, a quenching of the phosphorescence of the $Ru(bpy)_3^{2+}$ chromophoric unit and a parallel sensitization of the phosphorescence of the $Os(bpy)_3^{2+}$ chromophoric unit has been observed, indicating the occurrence of electronic energy transfer. In these systems, the bridging ligand plays an important role. When the spacer linking the coordinating sites of the bridging ligand is not rigid (i.e. a $-(CH_2)_n-$ chain), the discussion of the experimental results (particularly, the rates of energy- and electron-transfer processes in the frame of current theoretical treatments) can only be vague since the geometry of the system (e.g. the metal–metal distance) is not defined. Such systems are also of limited applicative interest because practical devices usually require the occurrence of vectorial energy or electron transfer over long distances [13]. Therefore rigid spacers, which are much more difficult to synthesize, have to be preferred.

To further illustrate the role of the bridging ligands consider, for example, dinuclear Ru(II) complexes based on bridging ligands containing bpy, phen, and tpy (phen = 1,10-phenanthroline; tpy = 2,2′,2″-terpyridine) chelating units (Fig. 4(b)). From the viewpoint of the excited state properties, bpy and phen are much better ligands than tpy for Ru(II). It is well know, in fact, that at r.t. in fluid solution $Ru(bpy)_3^{2+}$ and $Ru(phen)_3^{2+}$ exhibit a strong and long-lived luminescence (^{3}CT lifetime of the order of 10^2–10^3 ns [30]), whereas $Ru(tpy)_2^{2+}$ does not show any luminescence (^{3}CT lifetime of the order of 250 ps, from transient absorption measurements) [54]. From the viewpoint of structure, however, bridging ligands

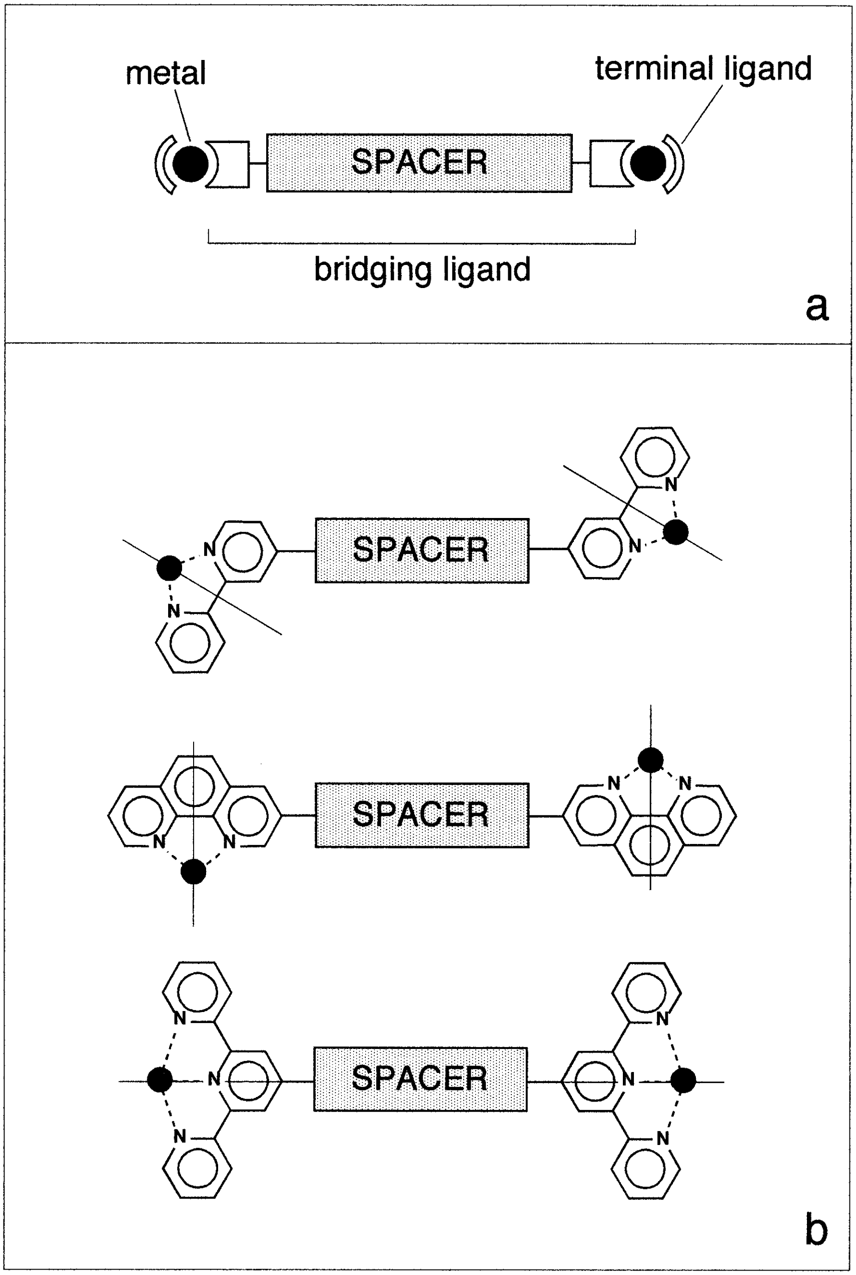
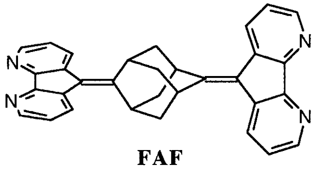
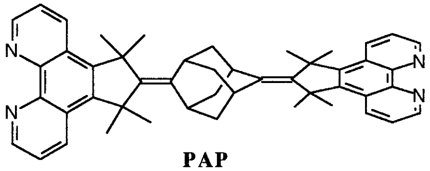


Fig. 4. (a) Schematic representation of a dinuclear complex and (b) schemes showing the geometrical structure of representative examples of dinuclear complexes based on bpy, phen, and tpy bridging ligands [53].



FAF



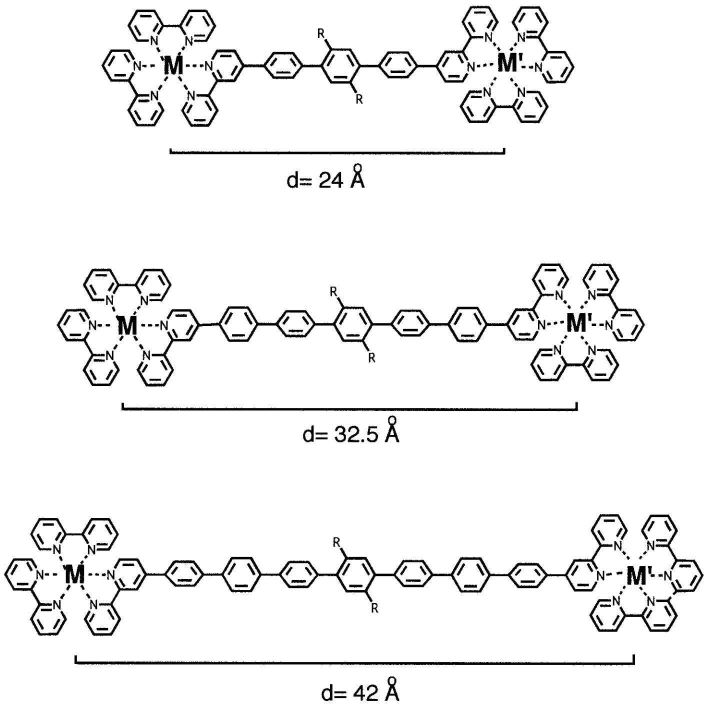
PAP

Fig. 5. Structural formulas of the FAF [56] and PAP [57] bridging ligands.

based on tpy are much more appealing than those based on bpy or phen. One reason is that bipyridines give rise to stereoisomerism at six-coordinated centers due to their bidentate nature and therefore an M(bpy)$_3^{n+}$ complex exists in two enantiomeric forms. In contrast to this behavior, a six-coordinate metal forms an achiral M(tpy)$_2^{n+}$ complex upon reaction with tpy. The introduction of a single substituent in the 4′-position of each tpy ligands presents no additional problems. Another important structural difference is illustrated in Fig. 4(b): connection between bpy- or phen-type ligands with a spacer cannot occur along the coordination axis, whereas this can be obtained by 4′-substitution of the tpy ligand. The tridentate tpy ligand is therefore more appealing than the bidentate bpy and phen ligands from the point of view of constructing linear, rod-like polynuclear complexes [54b].

From the above discussion, it is clear that there is the need for ligands with the electronic properties of bpy or phen and, at the same time, the structural properties of tpy. To achieve this goal, two approaches have been recently attempted. On one side, the lifetime of the Ru(tpy)$_2^{2+}$-based chromophoric unit has been noticeably increased by electron-acceptor substituents on the 4′-position of the tpy ligand (for Ru(tpy-MeSO$_2$)(tpy)$^{2+}$, the luminescence lifetime at r.t. is 36 ns and the luminescence quantum yield is 4×10^{-4}) [55]. On the other side, attempts have been made to construct bpy- and phen-based bridging ligands where the axis of the rigid spacer coincides with the coordination axes of the two bidentate ligands. Belser and co-workers have achieved this goal by preparing the bridging ligands FAF [56] and PAP [57] shown in Fig. 5. In FAF the improvement of the structural properties has partially compromised the good electronic properties of bpy because the five-membered ring constructed to obtain an anchoring point for the spacer along the metal–ligand coordination axis opens the bite angle of the metal coordination site and therefore reduces the ligand field strength, with the same consequences previously discussed for tpy. In PAP the construction of the anchoring point along the metal–ligand coordination axis has not affected the phenanthroline coordination sites, so that this bridging ligand combines the excellent electronic properties of phen and the possibility, typical of 4′-tpy derivatives, to give linear rod-like dinuclear complexes.

Current developments in this field include the design of bridging ligands where the spacer is made of a progressively increasing number of rigid subunits. This allows one to obtain families of dinuclear compounds in which the metal–metal distance can be tuned without changing the nature of the active units. With such systems it is possible to perform systematic studies on the distance dependence of electron- and/or energy-transfer rates. Along this line, our group has recently synthesized nine rod-like compounds of nanometric dimension (Fig. 6) with general formula $\mathrm{M(bpy)_3{-}(ph)}_n\mathrm{{-}M'(bpy)_3^{4+}}$ (M = M′ = Ru(II); M = M′ = Os(II); M = Ru(II), M′ = Os(II); ph = 1,4-phenylene: $n = 3, 5, 7$; the central phenylene unit



M = M'= Ru : $[\mathrm{Ru(bpy)_3\text{-}(ph)_n\text{-}Ru(bpy)_3}]^{4+}$
M = M'= Os : $[\mathrm{Os(bpy)_3\text{-}(ph)_n\text{-}Os(bpy)_3}]^{4+}$
M = Ru; M'= Os : $[\mathrm{Ru(bpy)_3\text{-}(ph)_n\text{-}Os(bpy)_3}]^{4+}$
n = 3, 5, 7
R = n-hexyl

Fig. 6. Rigid, rod-like, modular dinuclear complexes [58].

bears two alkyl chains for solubility reason; the metal-to metal distance is 4.2 nm for the longest spacer) [58]. The absorption spectra and the luminescence properties (emission spectra, quantum yields and excited state lifetimes) of the nine dinuclear complexes have been investigated in acetonitrile solution at 293 K and in butyronitrile rigid matrix at 77 K. We have found again that in the heteronuclear compounds energy transfer from the $Ru(bpy)_3^{2+}$ to the $Os(bpy)_3^{2+}$ unit takes place, with a rate which is practically temperature independent and decreases with increasing length of the oligophenylene spacer (in acetonitrile solution at 293 K, $k_{en} = 6.7 \times 10^8$ s^{-1} for $n = 3$; $k_{en} = 1.0 \times 10^7$ s^{-1} for $n = 5$; $k_{en} = 1.3 \times 10^6$ s^{-1} for $n = 7$). It is shown that such an energy-transfer process takes place via a Dexter-type mechanism (superexchange interaction) with an attenuation coefficient of 0.32 Å^{-1} and 1.5 per interposed phenylene unit.

A very peculiar system is that made of $Ru(bpy)_3^{2+}$- and $Os(bpy)_3^{2+}$-type units linked to the 9,10-positions of an anthracene ring [59]. This arrangement was chosen so has to have a gradient for energy transfer along the Ru–An–Os sequence. In this compound the quenching of the Ru moiety is accompanied by the sensitization of the Os-based emission. In air-equilibrated solutions, however, oxygen quenching of the Os-based ^{3}CT excited state of Ru–An–Os takes place with formation of singlet oxygen, followed by attack of singlet oxygen on an anthracene ring to form an endoperoxide derivative and other products where the central ring of anthracene has lost its aromatic character. As a consequence, in the photoreaction product the bridge has no low lying energy level and the energy transfer from the Ru to the Os moiety takes place with rate constant about 80 times smaller than that found for the original Ru–An–Os species. Results of this kind can open the way to the construction of molecular-level switches [60].

7. Dendrimers

Dendrimers are a new class of well-defined macromolecules exhibiting a tree-like structure [61]. Dendrimer chemistry was initially developed in the field of organic chemistry. More recently, a number of dendrimers based on metal complexes have been synthesized [62]. Metal complexes are characterized by a precise molecular geometry related to the characteristic coordination number of the metal ion and can exhibit valuable properties such as absorption of visible light, luminescence, and reduction and oxidation levels at accessible potentials. By using metal complexes it is therefore possible to incorporate in the dendritic structure specific 'pieces of information' that, when placed in suitable sites of the array, can be used to perform valuable functions. From a structural viewpoint, most of the metal-containing dendrimers can be classified according to four categories: (i) dendrimers built around a metal complex as a core; (ii) dendrimers containing metal complexes as peripheral units; (iii) dendrimers containing metal complexes in the branches; (iv) dendrimers based on metals as branching centers [62].

In 1988 we began a fruitful collaboration with Campagna and co-workers on the design of polynuclear metal complexes capable of exhibiting interesting photophys-

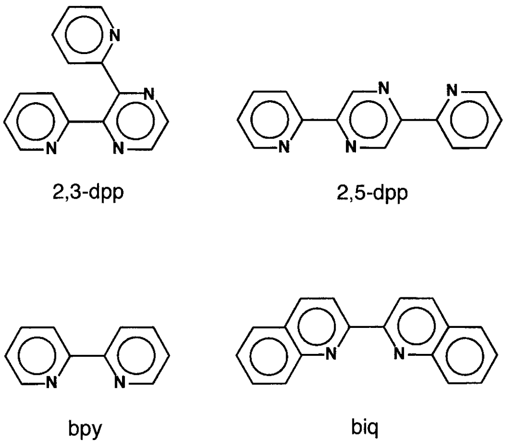


Fig. 7. Ligands employed to obtain polynuclear complexes of large nuclearity [63].

ical and electrochemical properties. Using 2,3-dpp and 2,5-dpp as bridging ligands (dpp = bis(2-pyridyl)pyrazine), Ru(II) and Os(II) as metal centers, and bpy or biq (biq = 2,2′-biquinoline) as terminal ligands (Fig. 7) and the so called complexes-as-metals and complexes-as-ligands synthetic strategy [63,64], we have prepared a large variety of homo- and heterometallic di- [65], tri- [66], tetra- [67], hexa- [68], hepta- [69], deca- [70], trideca- [71], and docosanuclear [72] complexes. The structure of a decanuclear complex of this family is schematized in Fig. 8. Such complexes, which have a dendrimer-type structure [73], are very interesting because, depending on the number and location of the metal and ligand components, predetermined energy migration (Fig. 9) and redox patterns (Fig. 10) can be obtained [53,62]. The use of this kind of dendrimers as molecular-level antennas to harvest sunlight has been recently reviewed [74].

In collaboration with the group of Vögtle (Bonn University), we have investigated dendrimers built around a $Ru(bpy)_3^{2+}$ core. In a compound bearing 24 naphthyl units in the periphery, the intense emission band of the naphthyl chromophoric groups is absent, and the metallodendrimer exhibits only the visible emission band characteristic of the $Ru(bpy)_3^{2+}$ core [75]. These results show that a very efficient energy-transfer process takes place from the potentially fluorescent excited states of the aromatic units of the wedges to the metal-based dendritic core (antenna effect). We have also found that the dendrimer branches protect the Ru–bpy based core from dioxygen quenching, so that in aerated solutions the quantum yield of the Ru-based phosphorescence of the dendrimer is about three times that of $Ru(bpy)_3^{2+}$. Electrochemical experiments carried out on other dendrimers of this family have shown that the $Ru(bpy)_3^{2+}$ core behaves as an encapsulated electroactive unit and that the rate constant for the quenching of the luminescent excited state of the $Ru(bpy)_3^{2+}$ core by bipyridinium dication, tetrathiafulvalene, and anthraquinone-2,6-disulfonate anion decreases with increasing number and size of the dendritic branches [76]. A peculiar effect of the charge of the quencher has also been observed.

8. Light-powered molecular machines

Our research on solar energy conversion has recently led to an interesting spin-off. In collaboration with the group of Stoddart, we have shown that light can be used to induce the mechanical movement of molecules [77]. The investigated systems are pseudorotaxanes (Fig. 11), where dethreading/rethreading of the wire and ring components reminds one of the movements of a piston in a cylinder.

Our first attempt at designing a photochemically driven molecular-level machine of a pseudorotaxane type was based (Fig. 11(a)) on the use of an external electron-transfer photosensitizer [78]. In aqueous solution, the ring made of two bipyridinium-type electron-acceptor units and the naphtho-based electron-donor wire self-assemble as a result of a CT interaction. Irradiation with visible light of an external electron-transfer photosensitiser (e.g. Ru(bpy)$_3^{2+}$) causes reduction of one of the bipyridinium-type units of the ring (the back electron-transfer reaction is prevented by the presence of a sacrificial reductant like triethanolamine). Once the ring has received an electron, the donor–acceptor interaction responsible for

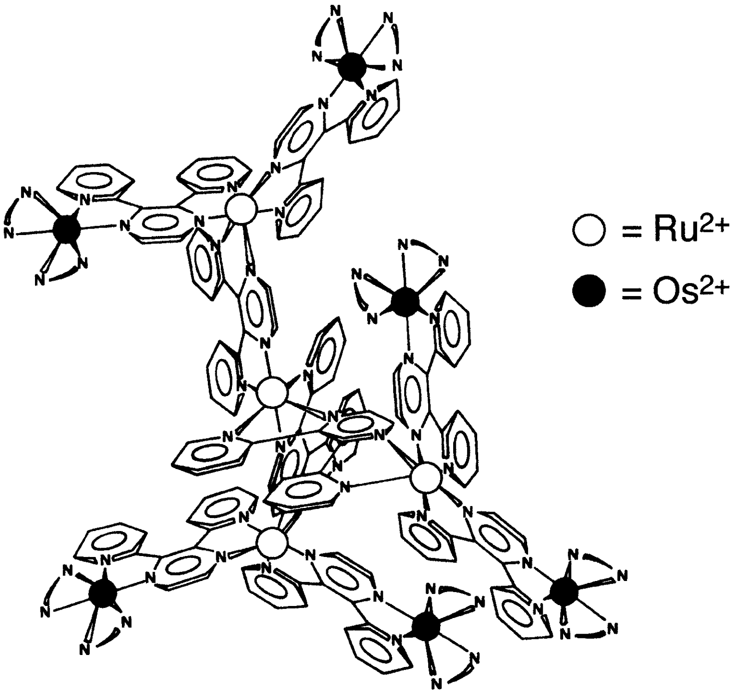


Fig. 8. Schematic view of the structure of a decanuclear complex containing six Os and four Ru ions [70].

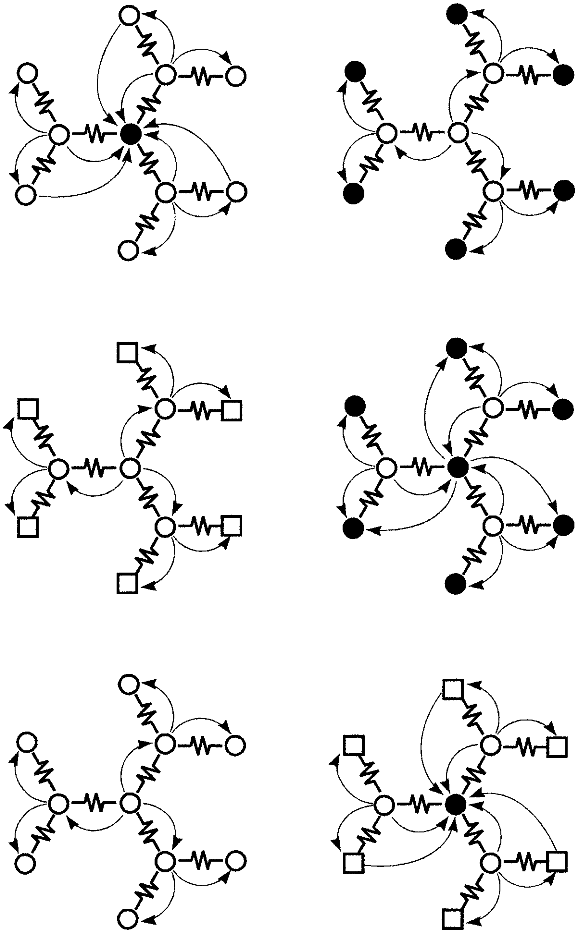


Fig. 9. Schematic representation of the energy-transfer processes in decanuclear compounds. Empty and full labels indicate Ru and Os ions, respectively. In the peripheral positions, circles and squares indicate $M(bpy)_2$ and $M(biq)_2$ components, respectively. For the bridging ligands, wavy lines, 2,3-dpp; straight lines, 2,5-dpp [53].

the self assembly is partly destroyed and therefore the wire dethreads from the reduced ring. If oxygen is allowed to enter the solution, oxidation of the reduced bipyridinium-type unit restores the donor–acceptor interaction and causes rethreading. The threading, dethreading, and rethreading processes can be easily followed by absorption and fluorescence spectroscopy.

Second generation photochemically driven machines have then been designed where the piston–cylinder pseudorotaxane structure incorporates the 'light-fueled' motor (i.e. the photosensitizer) in the wire (Fig. 11(b)) [79] or in the macrocyclic ring (Fig. 11(c)) [80]. We have shown that in both cases excitation of the photosensitizer with visible light in the presence of a sacrificial donor causes reduction of the electron-acceptor unit and, as a consequence, dethreading. Rethreading can again be obtained by allowing oxygen to enter the solution.

9. Conclusions

The pioneering work of Gafney and Adamson on the photoinduced electron-transfer reactions of Ru(bpy)$_3^{2+}$ [2] has opened up an important avenue to chemical research. The complexes of the Ru–polypyridine family have played and are still playing a key role in the development of photochemistry, photophysics, photocatalysis, electrochemistry, radiation chemistry, chemi- and electrochemiluminescence, electron and energy transfer. They are also extensively used for present and futuristic applications such as solar energy conversion, luminescent and electroluminescent sensors, non-linear optics, molecular-level wires, switches, and antennae, and, very recently, as light-fueled motors for simple molecular-level machines.

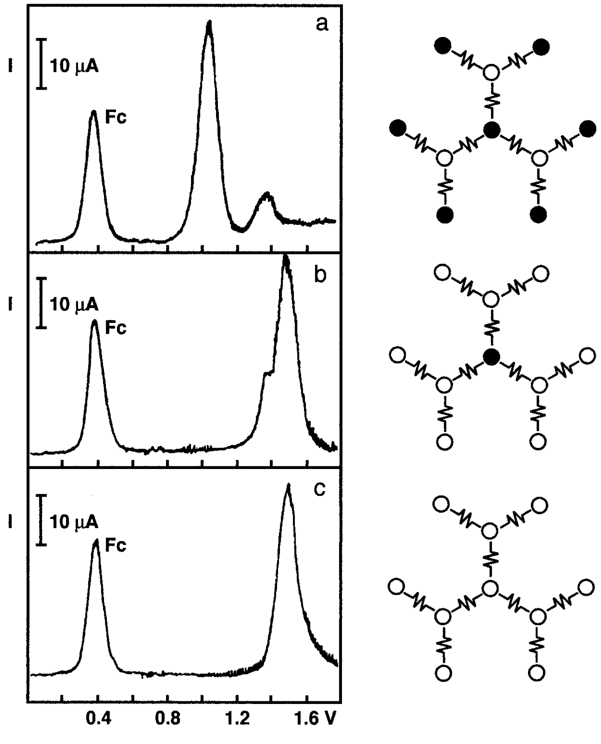


Fig. 10. Differential pulse voltammetric patterns for oxidation of three decanuclear compounds. For the graphic symbols, see caption to Fig. 9. Fc indicates the oxidation peak of ferrocene, used as an internal standard [62].

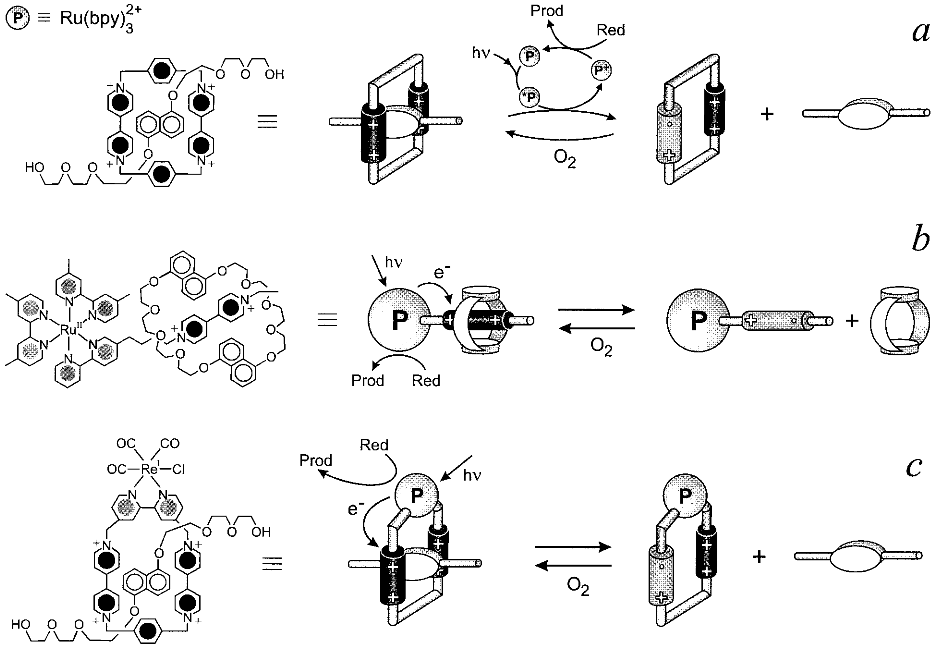


Fig. 11. Light-driven dethreading of: (a) a pseudorotaxane by excitation of Ru(bpy)$_3^{2+}$ as an external photosensitizer [78]; (b) a pseudorotaxane incorporating a Ru(bpy)$_3^{2+}$ photosensitizer as a stopper in the wire-type component [79]; (c) a pseudorotaxane incorporating a Re-based photosensitizer (preferred to Ru(bpy)$_3^{2+}$ for spectroscopic reasons) in the macrocyclic component [80].

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