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Photochemistry and photophysics of coordination compounds: An extended view

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Contents

Abstract

Coordination chemistry is much more than the coordination of transition-metal ions by organic or inorganic ligands. Its scope extends to the binding of all kinds of substrates (cationic, anionic, and neutral molecular species). Therefore coordination chemistry merges into the big field of supramolecular chemistry. Coordination compounds (with or without metals) exhibit by definition a high level of organization and therefore they are quite suitable to exploit the energy and information content of photons. In this paper we illustrate specific examples concerning the similarity between the photochemical behavior of classical coordination compounds (i.e. metal complexes) and supramolecular species not containing metals. We

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also describe coordination compounds not containing metals that undergo photochemically, electrochemically, or chemically induced mechanical movements (molecular-level machines) and behave as logic gates. © 1998 Elsevier Science S.A.

Keywords: Supramolecular systems; Cage-type compounds; Azobenzene; Charge-transfer complexes; Photochemistry; Photophysics

1. Introduction

The birth year of coordination chemistry is assumed to be 1892, when Alfred Werner conceived his theory of metal complexes [1]. Since then, the term coordination chemistry has mostly been used with reference to the chemistry of transition-metal complexes and it has been considered as a part of the realm of inorganic chemistry. This is the reason why in 1970 a monograph on the photochemistry of transition-metal complexes was entitled Photochemistry of Coordination Compounds [2].

In the last 20 years it has become clearer and clearer that coordination chemistry is, in fact, much more than the coordination of transition-metal ions by organic or inorganic ligands. Pedersen, Cram and Lehn (Nobel Prize winners in 1987) and several other scientists have extended the scope of coordination chemistry to the binding of all kinds of substrates: cationic, anionic, and neutral molecular species of either organic, inorganic, or biological nature [3]. Nowadays coordination chemistry merges into the big field of supramolecular chemistry. An extended view of coordination chemistry within the frame of supramolecular chemistry allows one to discover interesting analogies between apparently different chemical systems and can therefore suggest ideas for the design of novel compounds and the development of systems capable of performing useful functions. This is particularly true as far as photochemistry is concerned, since the possibility to exploit the interaction of light with matter for energy or information purposes depends on the degree of organization of the receiving matter [4–7]. Coordination compounds (with or without metals) exhibit by definition a high level of organization and therefore they are quite useful as components of molecular-level photochemical devices [8].

In this paper we illustrate specific examples concerning the similarity between the photochemical behavior of classical coordination compounds (i.e. metal complexes) and supramolecular species not containing metals. We also describe some new supramolecular species where classical transition-metal complexes are used as components of larger, functionally integrated supramolecular systems in an attempt to achieve specific functions.

2. Cage-type coordination compounds

2.1. Caged metal ions

When a metal ion is encapsulated in a cage-type ligand, quite peculiar properties may appear. As far as the photochemical and photophysical behavior is concerned,

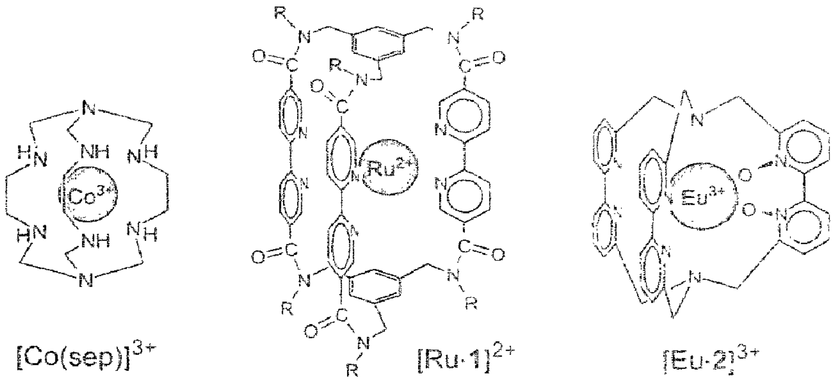

Fig. 1. Cage-type metal complexes: [Co(sep)]$^{3+}$ [9,10]; [Ru·1]$^{2+}$ [11]; [Eu·2]$^{3+}$ [12].

there are at least three very interesting cases (Fig. 1) of cage-type metal complexes [13].

Cobalt sepulchrate [9,10] is a caged version of [Co(NH$_3$)$_6$]$^{3+}$. These two complexes exhibit quite similar absorption spectra, but very different photochemical properties. While [Co(NH$_3$)$_6$]$^{3+}$ undergoes an efficient ($\Phi = 0.16$) redox decomposition on excitation in the ligand-to-metal charge transfer (LMCT) bands, [Co(sep)]$^{3+}$ is completely photoinert ($\Phi < 10^{-6}$) [14]. The reason for this very different photochemical behavior is quite simple: in the hexaamine complex, the formally Co(II) excited state undergoes fast and irreversible (in acid solution) dissociation of the amine ligands, whereas in the sepulchrate the ligand units are kept around the reduced metal by the caged structure, so that back electron transfer from Co(II) to the oxidized ligand takes place, giving back the ground state complex.

In the case of [Ru(bpy)$_3$]$^{2+}$, a ligand dissociation photoreaction takes place (with low quantum yield) in a metal-centered (MC) excited state [15,16]. For the same reason described above, the quantum yield of ligand photodissociation decreases by about four orders of magnitude in [Ru·**1**]$^{2+}$ (Fig. 1), which is the caged version of [Ru(bpy)$_3$]$^{2+}$ [11]. Because of their great stability towards photodecomposition, caged Co(III) and Ru(II) complexes can be used as photosensitizers [13].

The case of Eu^{3+} cryptates is completely different since it does not concern photochemistry, but luminescence [13,17,18]. The lowest MC excited state of Eu^{3+} exhibits an intense and long-lived phosphorescence, which in H$_2$O solution is strongly quenched by coupling with the high energy OH vibrations of the coordinated water molecules [13,19]. When Eu^{3+} is encapsulated into a cage-type ligand (see e.g. [Eu·**2**]$^{3+}$, Fig. 1), it is shielded from interaction with water molecules. As a consequence, its phosphorescence becomes much more intense and longer lived [12]. When the cage contains suitable chromophoric units, it can absorb light and transfer the resulting electronic energy to the emitting metal-centered level, thereby playing the role of "antenna" for light harvesting [12,17,18,20]. Such changes in the photophysical properties [illegible] important for the use of Eu^{3+} complexes as luminescent labels, particularly in immunoassay [17,18]. It should also be noted that the

Eu^{3+} ion plays the role of a "reporter" about the interior of the cage through its luminescence properties, since some features of the phosphorescence spectrum depend on the coordination symmetry.

2.2. *Caged molecules*

The development of supramolecular chemistry has led to the synthesis of several cage-type species capable of hosting neutral molecules in their cavities [21,22]. Particularly interesting hosts are the so-called hemicarcerands synthesized by Cram and co-workers [23,24]. Hemicarcerands are cage-type molecules with large voids and with "portals" through which molecules having the right size can enter at high temperature and then remain imprisoned at room temperature ("constrictive binding"). Biacetyl (2,3-butanedione) has been imprisoned into a hemicarcerand [Fig. 2(a)] with the dual purpose of (i) improving its luminescence properties, and (ii) obtaining information on the cavity of the hemicarcerand [25].

A very interesting feature of biacetyl is its strong and structured phosphorescence band ($\lambda_{max} = 518$ nm in CH_2Cl_2) which originates from the lowest triplet excited state T_1 [27]. The lifetime of the T_1 excited state is intrinsically long (millisecond time scale), but it is strongly affected by oxygen quenching. In fact, the phosphorescence band can hardly be observed in air equilibrated solutions. In carefully deaerated CH_2Cl_2 solutions the lifetime of the T_1 excited state is 0.43 ms.

When biacetyl is imprisoned into the hemicarcerand shown in Fig. 2(a) [25], its spectroscopic and excited state properties do not depend on the solvent nature. Furthermore, the lifetime of the T_1 excited state and the phosphorescence quantum yield of imprisoned biacetyl are unaffected by the presence of dioxygen. These results show that inclusion into the hemicarcerand (i) shields biacetyl from interaction with

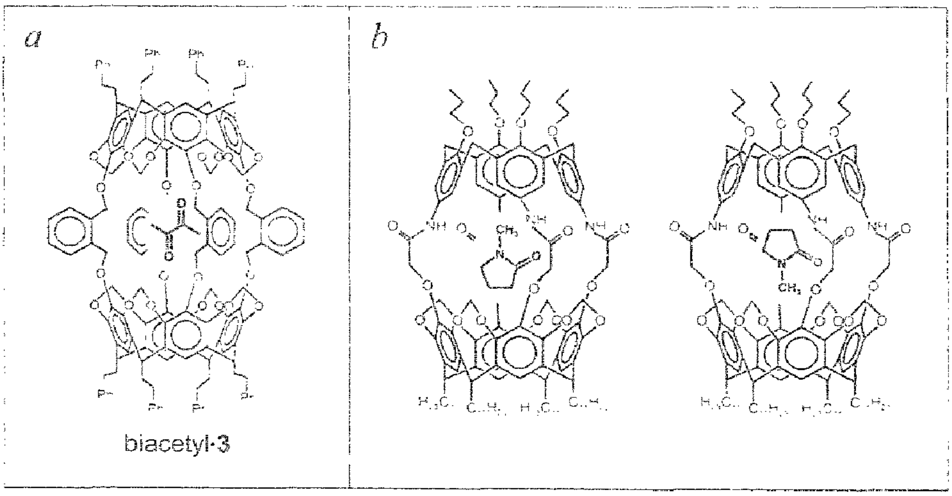

Fig. 2. Caged molecules: (a) biacetyl imprisoned in a hemicarcerand [25]; (b) the two different orientations of the guest 1-methyl-2-pyrrolidinone inside a non-symmetric calix[4]arene-based hemicarcerand [26].

Table 1
Emission properties of free and encapsuled species[a]

	Eu^{3+} [b]		Biacetyl[c]	
	Free	Caged in 2	Free	Caged in 3
λ_{max} (nm)	580[d]	580[d]	518	533
τ (ms)	0.11	0.46	$< 10^{-4}$	0.84
Φ_{rel}	~25	100[e]	< 1	100

[a] For references, see text; the formulae of cages 2 and 3 are shown in Figs. 1 and 2(a), respectively.
[b] H_2O solution, 298 K.
[c] Air equilibrated CH_2Cl_2 solution, 298 K.
[d] $^5D_0 \rightarrow {}^7F_0$ transition.
[e] Excitation performed on the ligand 2.

the solvent molecules and (ii) prevents deactivation of its long-lived T_1 excited state by energy transfer to dioxygen. A systematic investigation has recently shown that the T_1 excited state of imprisoned biacetyl can undergo energy- and electron-transfer processes with suitable species present in the solution, but the rate constants of such processes are orders of magnitude smaller than those of the processes involving free biacetyl [28].

Since imprisoned biacetyl molecules are shielded from interaction with the solvent, their spectroscopic and excited state properties must reflect the environment constituted by the internal cavity of the hemicarceplex. Comparison of the position of the phosphorescence maximum for the imprisoned molecules with the values obtained in a variety of solvents suggests that the perturbation provided by the cavity is much smaller than that provided by even the most "innocent" solvent [25].

Clearly, encapsulation on Eu^{3+} and biacetyl gives rise to very similar effects (Table 1), in spite of the different nature of the two systems. Such similarities may well extend to applications, since the lack of oxygen quenching on the strong and long-lived phosphorescence of incarcerated biacetyl could open the way to a new family of luminescent labels for immunoassay.

An important difference between caged metal ions and caged molecules should be emphasized. Whereas metal ions are species with high symmetry[1], molecules may have a variety of shapes. The relationship between the shape of the guest molecule and the characteristics of the hosting cage may play an important role in determining the properties of the system and may also become a means to exploit new functions. In the case of 9-cyanoanthracene hosted in a hemicarcerand, the –CN substituent leans out of a window of the cage and prevents the host from rotating [29]. In a hemicarcerand based on calix[4]arene, the cavity is non-centrosymmetric and therefore guests like 1-methyl-2-pyrrolidinone [Fig. 2(b)] or ethyl methyl sulfoxide can exhibit two different orientations, giving rise to a pair of "carceroisomers" [26,30].

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[1] An isolated metal ion has spherical symmetry. The most common geometries in metal complexes are the octahedral, tehrahedral, and square planar ones.

This phenomenon may offer a basis for information recording on a molecular scale [22,31–34].

3. Compounds containing the azobenzene unit

It is well known that crown ethers can play the role of ligands for alkaline metal ions [35,36]. Linking such ligands to photoisomerizable azo groups has led to a variety of systems where the coordination ability can be controlled by light [37,38]. A classical example is shown in Fig. 3(a) [39]. In the *trans* configuration of the azobenzene chromophore, the system exhibits a weak coordination ability for large cations. Light excitation causes the *trans*→*cis* isomerization yielding a configuration suitable to enclose large cations between the two crown ethers, with a strong increase in the coordination ability. The *trans* form extracts Na^+ 5.6 times more efficiently than the *cis* form, whereas the *cis* form extracts K^+ 42.5 times more efficiently than the *trans* form. Such a device offers a means of controlling the rate of ion transport through membranes.

A non-metal-containing supramolecular system working on the same principle has recently been reported [40]. Such a system is illustrated in Fig. 3(b). Amidoadenosine and *p*-nitrophenyl ester can react to give an amide. The two reactants (schematized by shaded areas in the figure) can be linked by H-bonds to receptor units mounted on an azobenzene moiety. The *trans* form of the receptor is

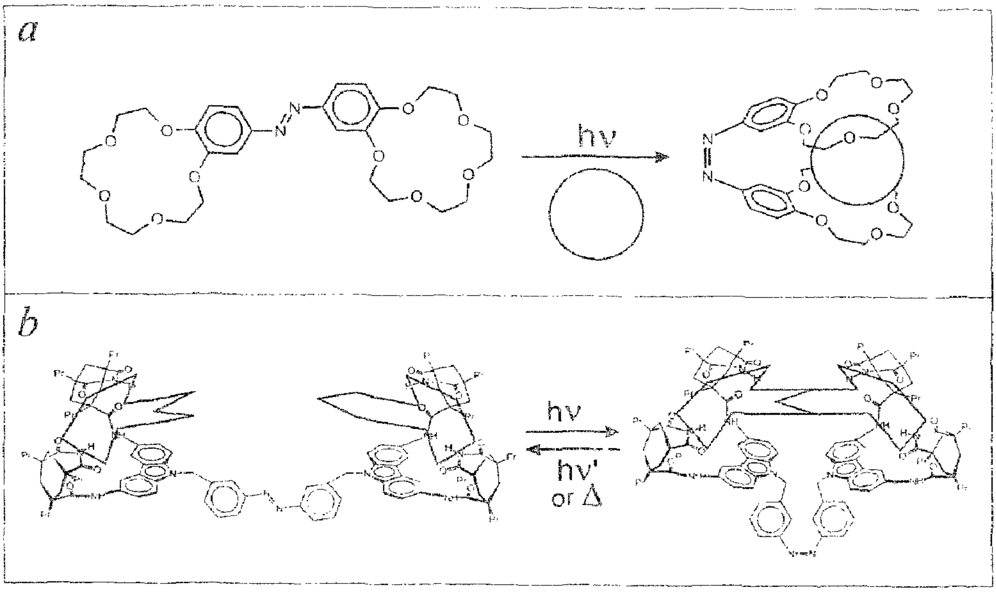


Fig. 3. (a) A photoresponsive crown ether capable of performing photoswitching of metal-coordination ability [39]. (b) A photoresponsive host capable of performing photocontrolled template catalysis. The two reactants, schematized by the shaded areas, are aminoadenosine and *p*-nitrophenyl ester [40].

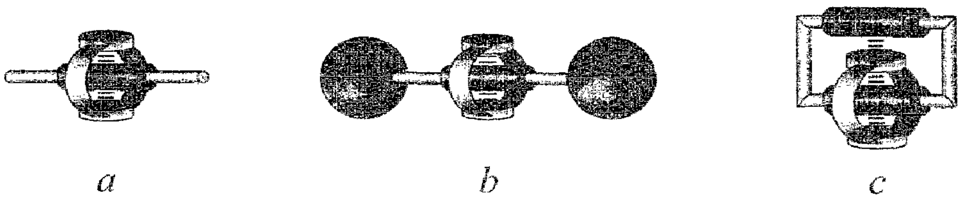


Fig. 4. Schematic representations of pseudorotaxanes (a), rotaxanes (b), and catenanes (c).

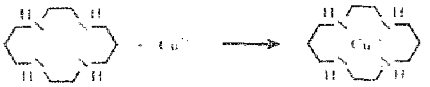
not able to catalyze the reaction. Light excitation at 365 nm causes the *trans*→*cis* isomerization of the azobenzene-based ditopic receptor, thereby bringing the two substrates close together. At the photostationary state, a nearly ten-fold enhancement of the coupling rate has been observed. This system provides an example of photo-controlled template catalysis.

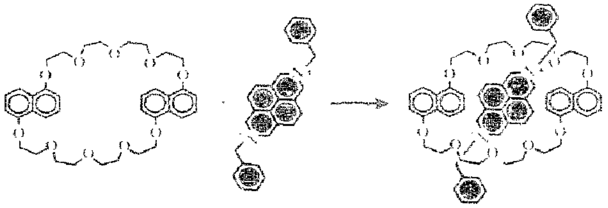
4. Pseudorotaxanes, rotaxanes and catenanes as coordination compounds

4.1. Pseudorotaxanes, rotaxanes, catenanes

In the last few years, Stoddart and co-workers [41] have shown that self-assembly of a macrocyclic ring and a thread-type species containing suitable electron donor or acceptor units can lead to formation of supramolecular species called pseudorotaxanes [Fig. 4(a)]. Addition of two bulky groups at the end of the threaded component or cyclization of this component can lead to rotaxanes [Fig. 4(b)] and, respectively, catenanes [Fig. 4(c)]. A variety of pseudorotaxanes, rotaxanes and catenanes have been prepared by several research groups. Particularly worth mentioning are those reported by Sauvage and co-workers [42], which are obtained by the templating action of Cu^+ ions.

For space reasons, we will only deal with pseudorotaxanes based on electron donor/acceptor interactions. Such pseudorotaxanes can certainly be considered coordination compounds even when they do not contain any metal. This is clearly shown by the analogy between Eq. (1) [43] and Eq. (2) [44]:

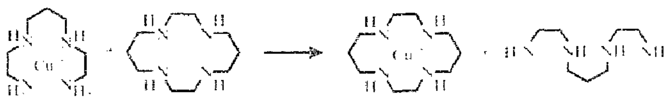




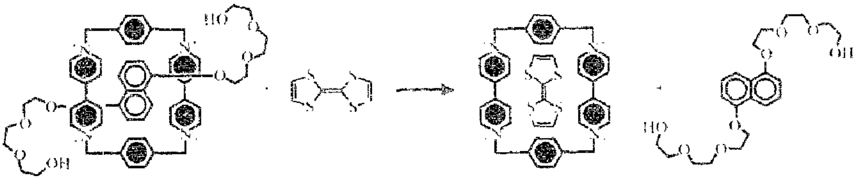
The similarity between such pseudorotaxanes and transition-metal complexes is not only formal, but extends to important properties.

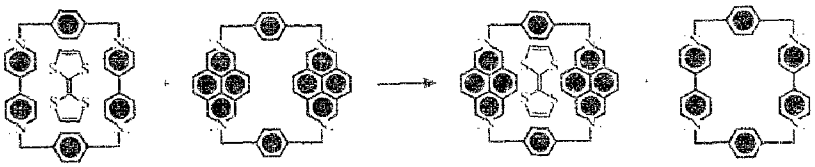
4.2. *Exchange reactions*

In a metal complex, the metal or ligand(s) can be replaced by another metal {Eq. (3) [45]} or ligand(s) {Eq. (4) [46]}:



Similarly, in a pseudorotaxane the thread or the cycle can be replaced by another thread [Eq. (5)] or cycle [Eq. (6)] [47]:





4.3. *Absorption and luminescence spectra*

Metal complexes may exhibit metal-centered, ligand-centered, and charge-transfer (either metal-to-ligand or ligand-to-metal) absorption bands. The metal-centered and ligand-centered bands are more or less perturbed by coordination. Emission takes place from the lowest excited state, but it can only occur when such an excited state is not distorted compared to the ground state. Similarly, in pseudorotaxanes we can find absorption bands concerning the two separated components (thread-centered or cycle-centered) more or less perturbed by association, and charge-transfer bands (either thread-to-cycle or cycle-to-thread). Fig. 5 shows the spectra of a pseudorotaxane and its two components [48]. Emission, if any, can again occur only from the lowest excited state. Since in pseudorotaxanes based on donor–acceptor interactions the charge-transfer excited states lie at very low energy and are distorted by their own nature, fast radiationless decay to the ground state usually prevents the occurrence of luminescence.

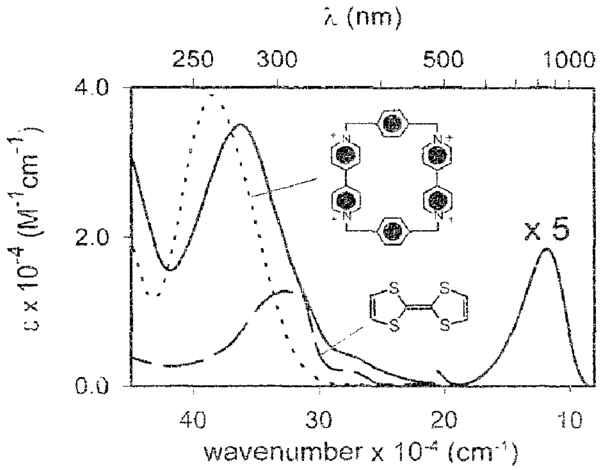


Fig. 5. Absorption spectra of an electron-acceptor cyclophane (dotted line), the tetrathiafulvalene electron donor (dashed line), and their pseudorotaxane-type adduct (full line) [48,49].

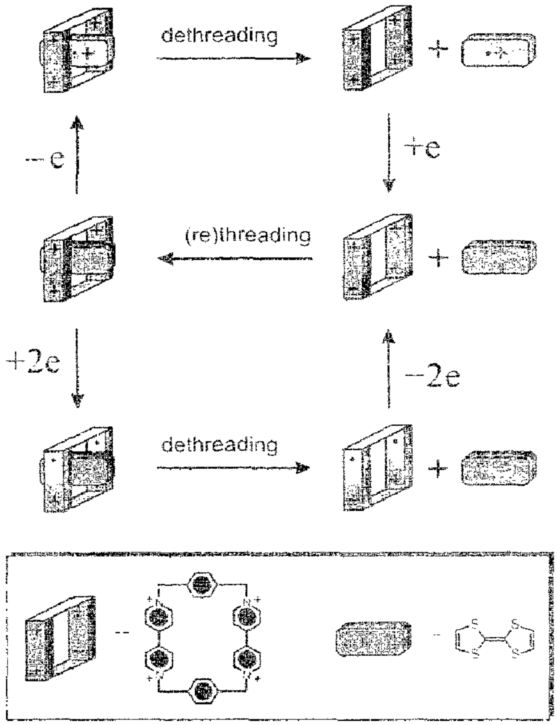


Fig. 6. Electrochemically-driven dethreading and rethreading processes in a pseudorotaxane [48].

4.4. Electrochemistry

Several transition-metal complexes undergo reversible outer-sphere redox reactions [50]. For example:

$$[\mathrm{Ru(bpy)_3}]^{2+} + e^- \rightleftarrows [\mathrm{Ru(bpy)_3}]^+ \qquad (7)$$

Other complexes undergo irreversible ligand dissociation upon electrochemical reduction or oxidation. Classical examples are Co(III) complexes of amine-type ligands [51], e.g.:

$$\mathrm{Co(en)_3^{3+}} + e^- \rightarrow \mathrm{Co^{2+}} + 3\mathrm{en} \qquad (8)$$

The electrochemical behavior of pseudorotaxanes based on electron donor/acceptor interactions is, in some way, a combination of the two types of behavior exhibited by metal complexes. An interesting example is shown in Fig. 6 [48,49]. Reduction of the electron-acceptor moiety or oxidation of the electron-donor one destroys the charge-transfer interaction which is at the basis of the threading process and therefore causes dethreading, a process similar to ligand release from $\mathrm{Co(en)_3^{3+}}$ shown in Eq. (8). However, the reduction and oxidation processes of pseudorotaxane compo-

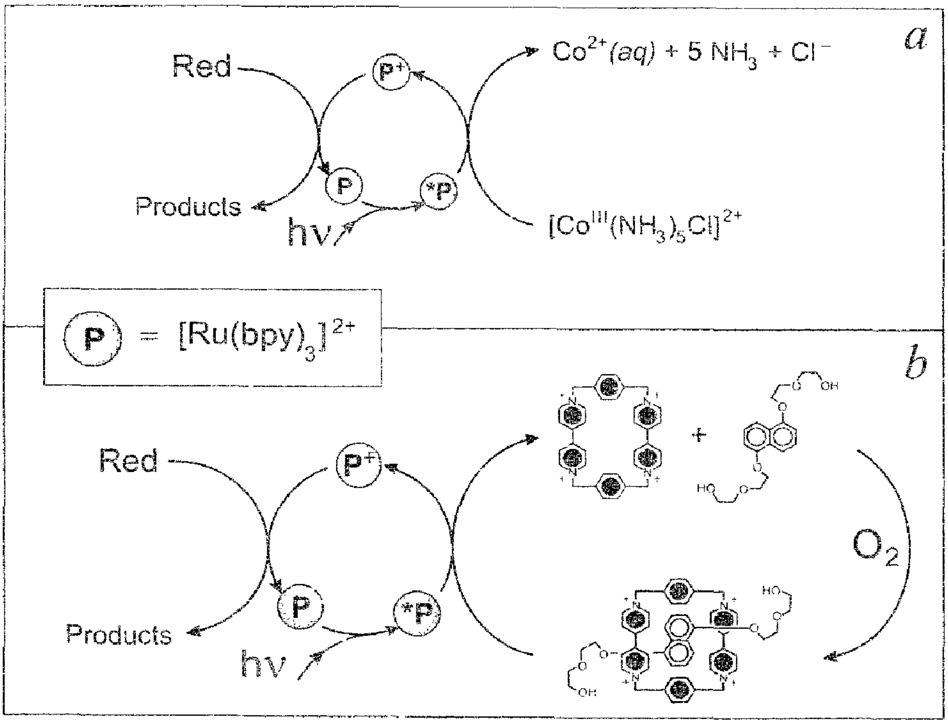


Fig. 7. Electron-transfer photosensitization: (a) decomposition of a metal complex [52,53]; (b) dethreading of a pseudorotaxane [54].

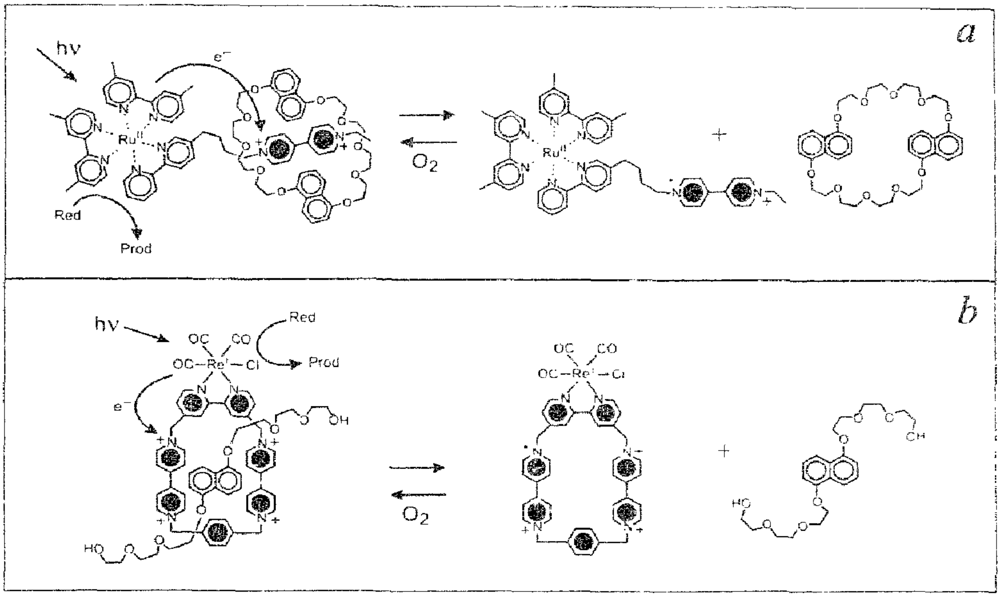


Fig. 8. Photochemically-driven dethreading of pseudorotaxanes, where the photosensitizer is incorporated (a) in the thread and (b) in the cycle.

nents, like those shown in Fig. 6, are reversible as happens for outer-sphere redox reactions of metal complexes [Eq. (7)], so that upon back oxidation or reduction rethreading takes place. The threading, dethreading, and rethreading processes are accompanied by strong changes in the absorption spectrum of the system.

4.5. *Photoinduced processes*

From the above discussion on the electrochemical properties it is clear that electron-transfer photosensitization can be used to decompose a metal complex as well as to dethread a pseudorotaxane. In the last few years, the expertise gathered with catalytic systems based on transition-metal complexes for water splitting [52,53] has been profitably used to perform photoinduced dethreading of pseudorotaxanes [54] by means of a bimolecular electron-transfer reaction (Fig. 7). Second generation systems, based on integrated structures that incorporate the photosensitizer and the thread [55] [Fig. 8(a)] or the photosensitizer and the cycle [56] [Fig. 8(b)] have recently been developed.

4.6. *Molecular-level mechanical machines and logic gates*

As we have seen above, the dethreading/rethreading processes of pseudorotaxanes can be induced by photons or electrons. In some cases, these processes can also be induced by suitable chemical reactions [57]. These photochemically-,

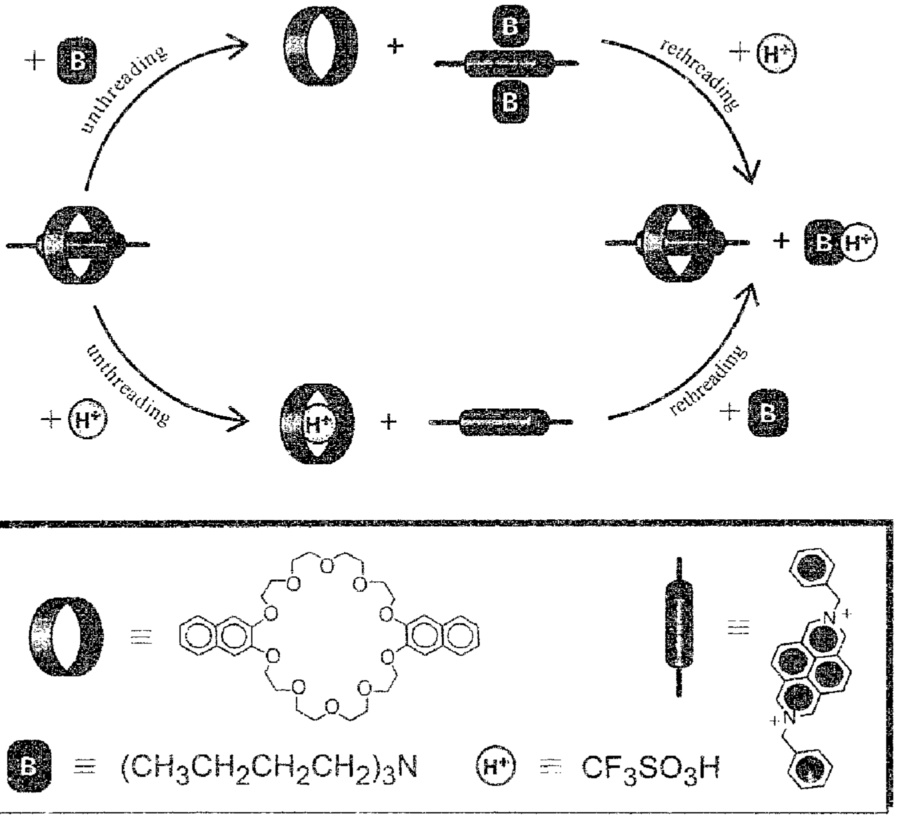


Fig. 9. Acid- and base-driven unthreading rethreading of a pseudorotaxane. The input (chemical) output (luminescence) characteristics of this system correspond to those of a XOR logic gate [58].

electrochemically-, or chemically-driven processes are interesting for two reasons: (i) they represent a simple example of a mechanical movement in a molecular-level system that can be controlled by an external stimulus; (ii) the input (photon, electron, proton, etc.)/output (absorption spectrum, emission spectrum, etc.) characteristics of these molecular-level systems often correspond to those of a logic operation. For example, the behavior of the system shown in Fig. 9 corresponds to that of a XOR logic gate [58].

Mechanical-like movements under the action of photochemical, electrochemical, or chemical stimuli can also be obtained in rotaxanes [59–61] and catenanes [59,62–68].

Acknowledgements

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