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Electrochemistry of coordination compounds: an extended view

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Abstract

Nowadays coordination chemistry has merged into the big field of supramolecular chemistry. In this paper we illustrate specific examples concerning analogies between the electrochemical behaviour of mononuclear metal complexes and supramolecular species containing metal complexes as component units. This similarity is extended to apparently very different systems, such as pseudorotaxanes, rotaxanes and catenanes not containing metal ions. In some cases the described compounds undergo electrochemically induced molecular movements and can be considered as prototypes of molecular-level machines. The importance of electrochemistry as a tool for obtaining information on the structure of the supramolecular system and as an energy input to induce mechanical movements at the molecular level is outlined.

Keywords: Supramolecular systems; Dendrimers; Catenanes; Rotaxanes; Charge-transfer systems; Electrochemistry

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1. Introduction

In the last decade it has become evident that coordination chemistry extends beyond the interactions of metal ions with organic and inorganic ligands and merges into the field of supramolecular chemistry [1–3]. 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 to perform useful functions. Coordination compounds, with or without metals, exhibit a high level of organization and therefore they are quite useful as components of molecular-level devices [1–4].

In this paper we illustrate examples concerning analogies between the electrochemical behaviour of mononuclear metal complexes and supramolecular species containing metal complexes as component units. This similarity is then extended to systems, such as pseudorotaxanes, rotaxanes and catenanes, not containing metal ions and apparently very different from those mentioned above. In some cases the described compounds undergo electrochemically induced molecular movements and can be considered as prototypes of molecular-level machines.

2. Mononuclear metal complexes

It is well known that metal ions, in the presence of organic or inorganic ligands, can spontaneously give rise to metal complexes.

$$\mathrm{M} + n\mathrm{L} \rightarrow \mathrm{ML}_n \tag{1}$$

As far as the electrochemical behaviour is concerned, mononuclear metal complexes can be divided in the following three categories.

2.1. Complexes which undergo reversible electrochemical processes

The prototypical example of metal complexes belonging to this category is $Ru(bpy)_3{}^{2+}$ (bpy = 2,2′–bipyridine) whose electrochemical behaviour has been extensively investigated [5–7]. Complexation makes the Ru(II)/Ru(III) oxidation process more difficult compared to the solvated ion because of the stabilization of Ru(II) due to coordination, whereas the bpy ligands become easier to reduce compared to free bpy, indicating that the energy of the π^*-orbitals is lowered upon coordination. In general, the change in the potential values at which the metal is oxidized and the ligands are reduced is a proof that complexation took place. The reversibility of the redox processes involving the metal complex indicates that addition or extraction of electrons is not followed by a chemical reaction in the time scale of the electrochemical scan.

As it happens for $Ru(bpy)_3{}^{2+}$ several transition-metal complexes, not only those containing polypyridine-type ligands, undergo reversible outer-sphere redox reactions.

2.2. Complexes which undergo irreversible ligand dissociation upon electrochemical reduction or oxidation

Typical examples are Co(III) complexes of amine-type ligands, e.g. $Co(NH_3)_6{}^{3+}$ and $Co(en)_3{}^{3+}$ (en = ethylenediamine) [7].

$$Co(NH_3)_6^{3+} + e^- \rightarrow Co^{2+} + 6NH_3 \tag{2}$$

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

For these complexes the redox behaviour changes substantially when the metal ion is encapsulated in a cage-type ligand. This is the case of $Co(sep)^{3+}$ (sep = sepulchrate, 1,3,6,8,10,13,16,19-octaazabicyclo[6.6.6]eicosane) [8,9], a caged version of the Co(III) amine-type complexes, for which the Co(III)/Co(II) reduction process is reversible since the ligand units are kept around the reduced metal by the caged-like structure.

$$Co(sep)^{3+} + e^- \rightleftarrows Co(sep)^{2+} \tag{4}$$

2.3. Complexes which undergo structural changes upon electrochemical reduction or oxidation

Copper(I) complexes are interesting examples of this category [10–13]. $Cu(phen)_2^+$ (phen = 1,10-phenanthroline) [12], for example, exhibits one oxidation and one reduction process, both metal-centred and poorly reversible. This is attributed to the strong tendency of Cu^{2+} to form octahedral species by coordination of solvent molecules, and to the fact that the Cu^0 complexes undergo ligand dissociation. Substitution of phen with dmphen (2,9-dimethyl-1,10-phenanthroline) [12] has a profound effect on the electrochemical behaviour. Oxidation is still metal-centred but it is reversible and strongly shifted towards positive potential values; this is due to the presence of the α-substituents to the nitrogen atoms which prevent a change in geometry and protect the metal ion from solvent coordination. The reduction process becomes reversible as well and takes place on the ligand's π*-orbital.

Many other cases of metal complexes characterized by complicated sequences of electrochemical and chemical processes are known [14,15].

3. Supramolecular systems containing metal complexes

Metal complexes are characterized by a precise molecular geometry related to the coordination number of the metal ion and, in some cases, to the rigid structure of the ligands. Furthermore, they can exhibit interesting properties such as light absorption and luminescence, and redox processes at accessible potential values. Therefore, by using metal complexes, it is possible to incorporate in a supramolecular structure many 'pieces of information' that can be used to perform valuable functions [16–19]. In the last decade a great variety of very interesting supramolecular species of this type have been prepared and studied. Here we will focus on the electrochemical properties of metal-based dendrimers, interlocked compounds and other supramolecular metal complexes that can be regarded as prototypes of molecular-level devices [18,20].

3.1. Dendrimers

Dendrimers are macromolecules exhibiting a tree-like structure, first developed by organic chemists [21], and more recently extended into the realm of coordination chemistry. From a structural viewpoint, metal-containing dendrimers can be subdivided into species: (a) built around a metal complex core; (b) containing metal complexes as peripheral units; (c) containing metal complexes in the branches; and (d) based on metals as branching centres (Fig. 1).

The electroactive units in these dendrimers are the metal-based moieties. An important requirement for any kind of application is the chemical redox reversibility of such moieties. The most common metal complexes able to exhibit a chemically reversible redox behaviour are ferrocene and its derivatives, and the iron, ruthenium and osmium complexes of polypyridine ligands. Therefore it is not surprising that most of the investigated dendrimers contain such metal-based moieties [18], with particular interest in ferrocene-type compounds [18,22,23]. In the electrochemical window accessible in the usual solvents (around $+2/-2$ V) ferrocene-type complexes undergo only one redox process, whereas iron, ruthenium and osmium polypyridine complexes undergo a metal-based oxidation process and at least three ligand-based reduction processes.

For space reasons, and because of our own interest, we describe only dendrimers containing transition-metal polypyridine complexes which belong to the categories (a) and (d).

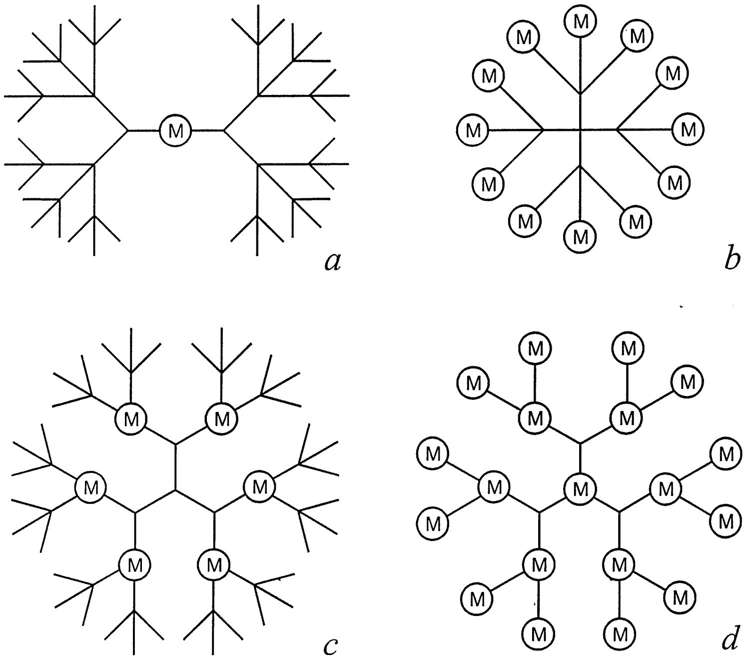
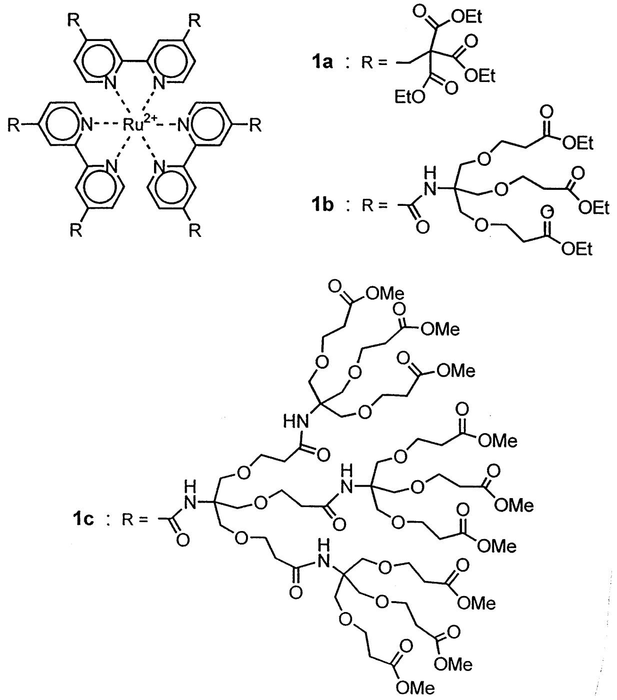


Fig. 1. Schematic representation of dendrimers: (a) built around a metal complex core; (b) containing metal complexes as peripheral units; (c) containing metal complexes in the branches; and (d) based on metals as branching centres.

When the only metal complex of a dendrimer is that constituting the core of the structure, the most interesting problem is whether and, if so, how much the electrochemical properties (potential value, kinetic reversibility) of the metal-based core are modified by the surrounding branches. In compounds **1a**–**c** [24] a $Ru(bpy)_3^{2+}$ core is linked to ester- and amide-based branches. The behaviour of the first generation species **1a** in MeCN solution is practically identical to that of $Ru(bpy)_3^{2+}$; on going to the second and third generation compounds **1b** and **1c** the electrochemical reversibility of both the metal-centred oxidation and the ligand-centred reduction processes decreases. This effect can be ascribed to encapsulation of the redox active units into the insulating dendritic structure, a behaviour similar to that observed for porphyrin-based dendrimers [25,26] and reminiscent of that of electron-transfer proteins like cytochrome *c*. In addition, in **1b**–**c** the Ru(II) oxidation takes place at more positive potential while the ligand-centred reductions occur at less negative potentials with respect to **1a**. While the reduction behaviour can be accounted for by the presence of different substituents on the ligands, alkyl versus amide, the oxidation shift can be explained considering that the dendritic shell hamper solvation thereby stabilizing the less charged species.

The same behaviour is exhibited by dendrimers containing a $Ru(tpy)_2^{2+}$ (tpy = 2,2′:6′,2″-terpyridine) core with appended two hydrocarbon long chains bearing



dendritic branches [27] and by dendrimers constituted of a $Fe(tpy)_2^{2+}$ core with two branches appended as substituents of the tpy ligands [28].

In dendrimers based on metals as branching centres, the electrochemical behaviour is more complex since: (i) each unit of the dendrimer is electroactive; (ii) the chemical nature of the metal-based units constituting the dendrimer may be different; (iii) chemically equivalent units can be different from the topological viewpoint; and (iv) the degree of interaction among the moieties depends on their chemical nature and distance. In the past few years a great number of dendrimers of this type has been synthesized and investigated [29–35]. In general, it has been shown that each mononuclear component brings its own redox properties, more or less affected by intercomponent interactions. Metal–metal and ligand–ligand interactions are noticeable for metals coordinated to the same bridging ligand and for ligands coordinated to the same metal, whereas they are negligibly small for metals or ligands that are sufficiently far apart. Since non-interacting units undergo electrochemical processes at the same potential, the number of electrons lost or gained at a certain potential can be controlled by placing in the dendrimer the desired number of suitable, equivalent, and non-interacting units.

An interesting series of such kind of dendrimers has been obtained using Ru(II) and/or Os(II) as metal centres, 2,3-dpp [2,3–bis(2-pyridyl)pyrazine] as bridging ligand, and bpy as terminal ligand (Fig. 2). Considering that Os(II) is easier to oxidize than Ru(II), and bpy is a better electron donor than 2,3-dpp, predetermined oxidation patterns can be obtained by changing the nature and the position of the metal ions, as shown in Fig. 3 [33,34]. Also the nature of the terminal ligands can

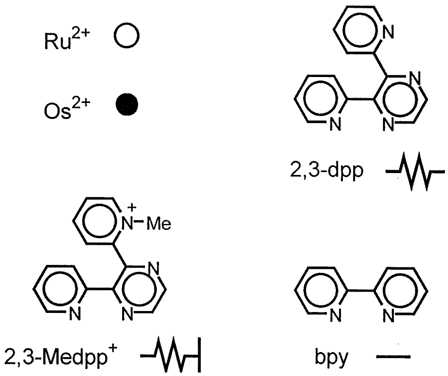


Fig. 2. Building blocks employed for the construction of dendrimers based on Ru(II)- and Os(II)-polypyridine metal complexes as branching centres [34,35].

affect the electrochemical properties of the dendrimers. The replacement of bpy with 2,3-Medpp$^+$ {2-[2-(1-methyl-pyridiniumyl)]-3-(2-pyridyl)pyrazine} (Fig. 2) in the periphery of the dendrimer causes big changes in the redox pattern, as illustrated in Fig. 4. This behaviour is attributed to the differences in charge and electron-donor power of the two ligands [35].

In conclusion, the electrochemical data offer a fingerprint of the chemical and topological structure of these dendrimers. Furthermore, the knowledge of the electrochemical properties of the mononuclear components allows the design of dendrimers with predetermined redox patterns [34].

3.2. Interlocked systems

Catenanes, rotaxanes and knots, schematically represented in Fig. 5 [36] are topologically intriguing chemical species that are currently the object of much interest. Catenanes are constituted of interlocked molecular rings, while rotaxanes are made of one or more macrocycles surrounding a thread-like molecule; dethreading of the system is prevented by the presence of bulky groups at the ends of the molecular thread.

The preparation of such type of compounds was very difficult until the advent of synthetic strategies based on various kinds of template effects [37]. Coordination of ligands around a transition-metal ion has been used by Sauvage et al. [38,39] to preorganize the molecular components towards the formation of the desired interlocked compound.

In such species, as in the classical transition-metal complexes discussed in Section 2, the electroactive units are the metal ion and the ligands. Electrochemical oxidation or reduction of these units can lead to changes in their mutual interaction. In particular, since the stereoelectronic requirements of the metal depend on its oxidation state, it can be possible, by means of electrochemical stimuli, to influence the structure and properties of the overall supramolecular assembly. This principle can be exploited to obtain molecular rearrangements on systems containing suitable metal ions and ligands. When such rearrangements imply the displacement of some components of the supramolecular architecture with respect to the others, the system can be said to behave as an electrochemically driven molecular machine [40,41].

A nice prototypical system in which molecular movements are caused and monitored by electrochemical techniques is provided by catenane **2** (Fig. 6) [42]. The components of this species are a Cu(I) ion and two interlocked macrocycles, one containing a phen-type bidentate site, and the other one incorporating two

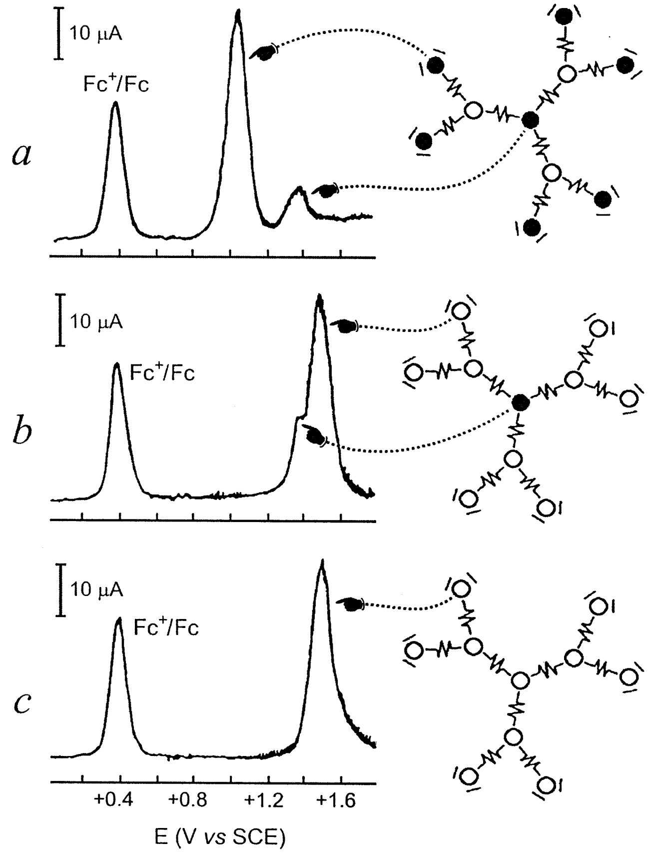


Fig. 3. Differential pulse voltammograms (MeCN/n-Bu$_4$NPF$_6$, glassy carbon electrode, scan rate 20 mV s^{-1}, pulse height 75 mV, pulse duration 40 ms) of three decanuclear Ru(II)/Os(II) dendrimers [33,34]. The symbols used are defined in Fig. 2. (a) The simultaneous one-electron oxidation of the six peripheral Os(II) ions is followed by the oxidation of the central one. Oxidation of the three intermediate Ru(II) ions cannot be observed within the accessible potential window. (b) The monoelectronic oxidation of the central Os(II) ion is followed by the simultaneous one-electron oxidation of the six peripheral Ru(II) ions. Oxidation of the three intermediate Ru(II) ions cannot be observed within the accessible potential window. (c) Only the simultaneous one-electron oxidation of the six peripheral Ru(II) ions is observed. Oxidation of the other metal ions cannot be observed within the accessible potential window.

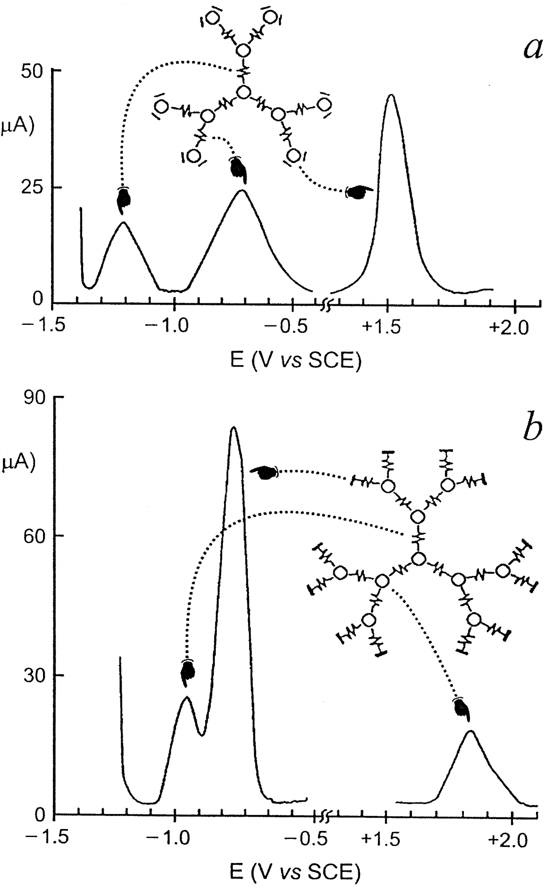


Fig. 4. Differential pulse voltammograms (MeCN/n-Bu_4NPF_6, glassy carbon electrode, scan rate 20 mV s^{-1}, pulse height 75 mV, pulse duration 40 ms) of two decanuclear Ru(II) dendrimers [35]. The symbols used are defined in Fig. 2. (a) The six-electron oxidation process is assigned to the simultaneous one-electron oxidation of the six peripheral Ru(II) ions; on the reduction side, the simultaneous one-electron reduction of the six outer dpp bridging ligands is followed by the simultaneous one-electron reduction of the three inner dpp ligands. (b) The three-electron oxidation process is assigned to the simultaneous one-electron oxidation of the three intermediate Ru(II) ions; on the reduction side, the simultaneous one-electron reduction of the 12 2,3-$Medpp^+$ terminal ligands is followed by the simultaneous one-electron reduction of the three inner dpp ligands.

different coordinating sites, namely, a phen-type bidentate and a tpy-type terdentate unit. Depending on the mutual arrangement of the two macrocyclic rings, the central metal ion can be tetrahedrally complexed (two phen-type ligands) or pentacoordinated (one phen-type and one tpy-type ligands); since Cu(I) prefers a tetrahedral geometry, catenane **2** exists as the $Cu(phen)_2^+$-type complex. Such a compound exhibits a reversible process at $+0.63$ V versus SCE in acetonitrile solution corresponding to Cu(I)–Cu(II) oxidation in a tetrahedral environment. Oxidation of **2** leads to the formation of Cu(II) tetracoordinated species, which

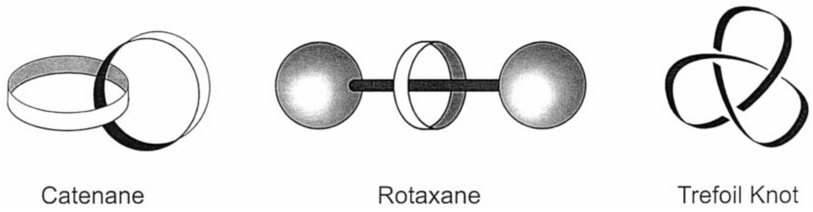


Fig. 5. Cartoon representation of a catenane, a rotaxane, and a trefoil knot.

then slowly rearrange to give pentacoordinated Cu(II) species. The occurrence of this process is demonstrated not only by the change in colour but also by the presence in the cyclic voltammogram of a wave at –0.07 V versus SCE that can be attributed to the reduction of Cu(II) in a pentacoordinated environment. Thus, interconversion between the two complexing modes, which imply a complete pirouetting of the two-site macrocyclic ring, can be induced by oxidation/reduction stimuli on the Cu(I)/Cu(II) couple (Fig. 6). The same approach has been used to synthesize another catenane [43] and a rotaxane [44] which exhibit similar electrochemically triggered movements. In the latter system, a macrocyclic ring containing a phen-type bidentate site can be displaced between two different coordinating positions on a thread-like molecule by changing the oxidation state

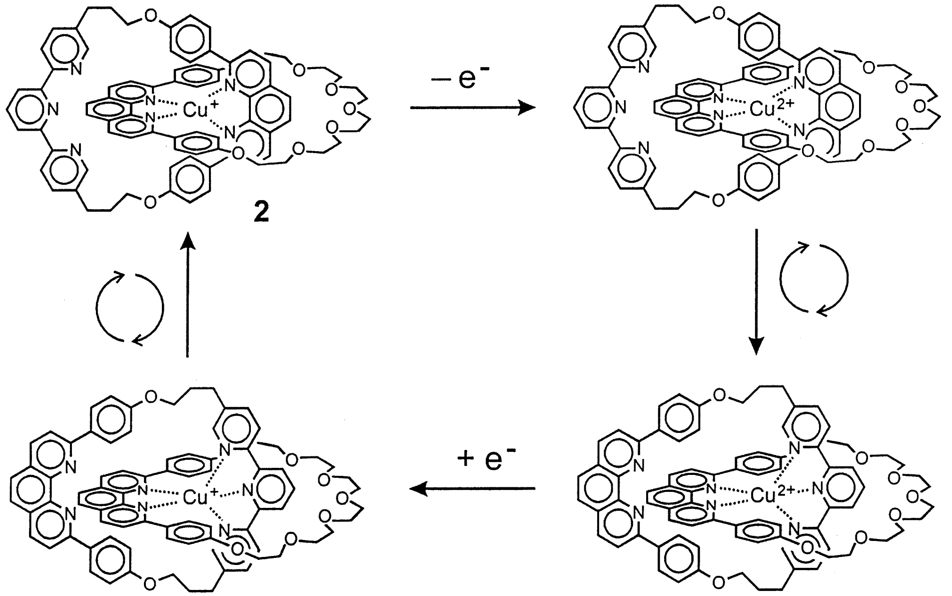
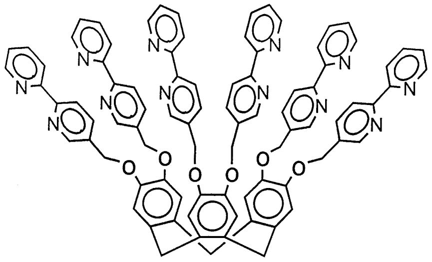


Fig. 6. Square scheme of the redox processes involving the Cu(I)/Cu(II) couple, and subsequent chemical rearrangements, that occur on catenane **2** [42].

of the Cu metal ion, which moves along with the ring. A system of this kind can be termed a ‘molecular shuttle’. The movements can again be monitored by means of controlled potential electrolysis and cyclic voltammetry.

3.3. Other systems

The difference in the coordination properties of Cu(I) and Cu(II) ions has been exploited to obtain another type of redox-induced conformational switch.



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In the presence of Cu(I) ions the six pendant bpy groups of ligand **3** lead to the formation of a trinuclear complex where each tetrahedral Cu(I) centre is coordinated to two bpy units linked to vicinal dioxybenzene units of the calixarene rim [45]. Upon electrochemical oxidation of the three Cu(I) ions to Cu(II), a rearrangement occurs to give a structure in which each square planar Cu(II) centre binds two bpy units linked to the same dioxybenzene group. This chemical rearrangement, which corresponds to decoordination–rotation–recoordination of at least three bpy units, is reflected in the cyclic voltammetric behaviour of the trinuclear Cu(I) and Cu(II) complexes.

Another interesting system exploits the Ni(II)/Ni(III) redox change in a multicomponent species to cause the electrochemically induced intramolecular translocation of an anion [46]. Such a multicomponent species (Fig. 7) was obtained linking to a Cu(II) cation two Ni(II) cyclam-like (cyclam = 1,4,8,11-tetraazacyclotetradecane) complexes containing an appended bpy unit. While the Ni(II) centres are insensitive to the addition of anions, the $Cu(bpy)_2^{2+}$ fragment binds anions like NCO^- with a 1:1 stoichiometry, as probed by the change in its reduction potential. Since Ni(III) shows much more affinity than Cu(II) towards anionic species, oxidation of the two Ni(II) centres induces the translocation of the anion bound to the central Cu(II) ion onto one of the two peripheral Ni(III) ions. Conversely, reduction of Ni(III) to Ni(II) makes the anion move back to the Cu(II) centre. The occurrence of these processes have been demonstrated by cyclic and differential pulse voltammetric experiments.

Examples of redox-active supramolecular metal complexes of biological importance are provided by proteins, in which electrochemical techniques extend the conventional spectroscopic approaches to study protein folding and, in some cases, are used to trigger and monitor folding/defolding processes [47–49].

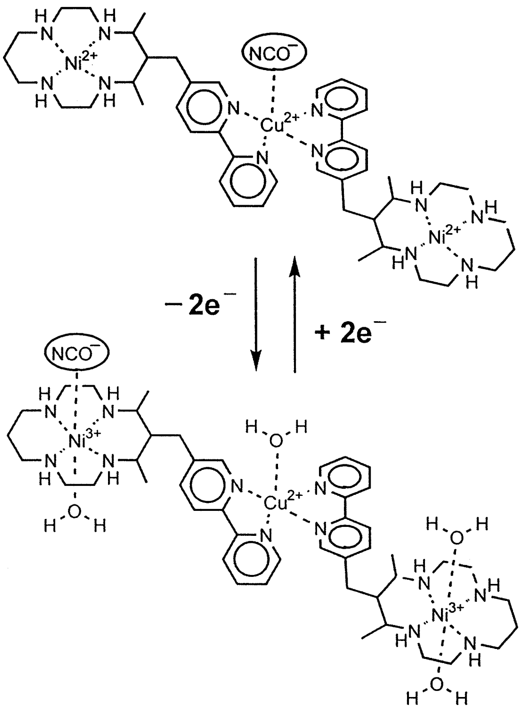


Fig. 7. Electrochemically driven intramolecular anion translocation in a supramolecular metal complex [46].

4. Supramolecular systems not containing metal complexes

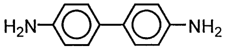
It is well known that two (or more) organic compounds with complementary π-electron or hydrogen-bonding acceptor/donor properties can self-assemble leading to the formation of supramolecular species [37,50].

$$D + A \rightarrow D \cdot A \qquad (5)$$

Such species can be considered coordination compounds since: (i) their formation occurs in a way similar to that of metal complexes (Eq. (1)) and, as it happens for metal complexes, the interaction between the components (ii) leads to a much higher degree of organization, and (iii) causes predictable changes in several properties, including the electrochemical ones.

4.1. Charge-transfer complexes

In the last few years Stoddart and co-workers [51] have shown that self-assembly of a macrocyclic ring and a guest species containing suitable electron donor and acceptor units can lead to formation of charge-transfer inclusion complexes. As an example, addition of electron-rich guests like **4** and **5** to a solution of the electron acceptor tetracationic cyclophane **6** results in the formation of a charge-transfer complex in which the electron donor guest is included into the cavity of the cyclophane [52].



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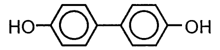

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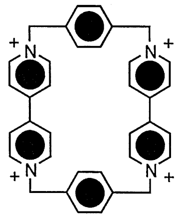

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A convenient way to monitor the occurrence of complexation is by means of electrochemical methods since, as a result of the mutual stabilization, the complexed electron donor and acceptor components become more difficult to oxidize and to reduce, respectively. For instance, the oxidation potential of benzidine **4** shifts anodically by 23 mV in the presence of an excess of **6**, while the monoelectronic reduction of each of the two bipyridinium units of **6** shifts by 27 mV towards more negative potentials in the presence of an excess of **4**. This behaviour reminds that of classical metal complexes where coordination causes shifts in the metal and ligand redox potentials (see Section 2).

A similar behaviour is observed in the self-complexing macrocycle **7** (Fig. 8) [53], where an electron donor 1,5-dioxynaphthalene fragment is inserted between two electron acceptor bipyridinium units. In such a compound, the two bipyridinium units get reduced simultaneously and reversibly at a potential which is 60 mV more negative than that measured for **8**, the parent compound without the naphthalene tether. These results (i) confirm the self-threaded structure of **7** (also demonstrated by NMR spectroscopy), and (ii) evidence that the two bipyridinium units remain equivalent in the charge-transfer complex and, therefore, that the 1,5-dioxynaphthalene moiety is positioned symmetrically between them. The most interesting aspect of the behaviour of **7** concerns the second reduction of its bipyridinium units, which occurs simultaneously and reversibly for both units, and at a potential value identical to that of the corresponding process in **8**. This result indicates that at the time of the second reduction of **7** the two bipyridinium units are no longer engaged in any donor/acceptor interaction; if this were not the case, also the second reduction process would be shifted to more negative potential values [53]. One can therefore draw the conclusion that dethreading/rethreading is obtained upon reduction/oxidation of the bipyridinium units of **7** (Fig. 8). This is an expected result since reduction of the electron acceptor moieties (or oxidation of the electron donor ones) destroys the charge-transfer interaction which stabilizes the supramolecular structure and causes dethreading, a process similar to ligand release from transition-metal complexes like $Co(en)_3^{3+}$ (Eq. (3)).

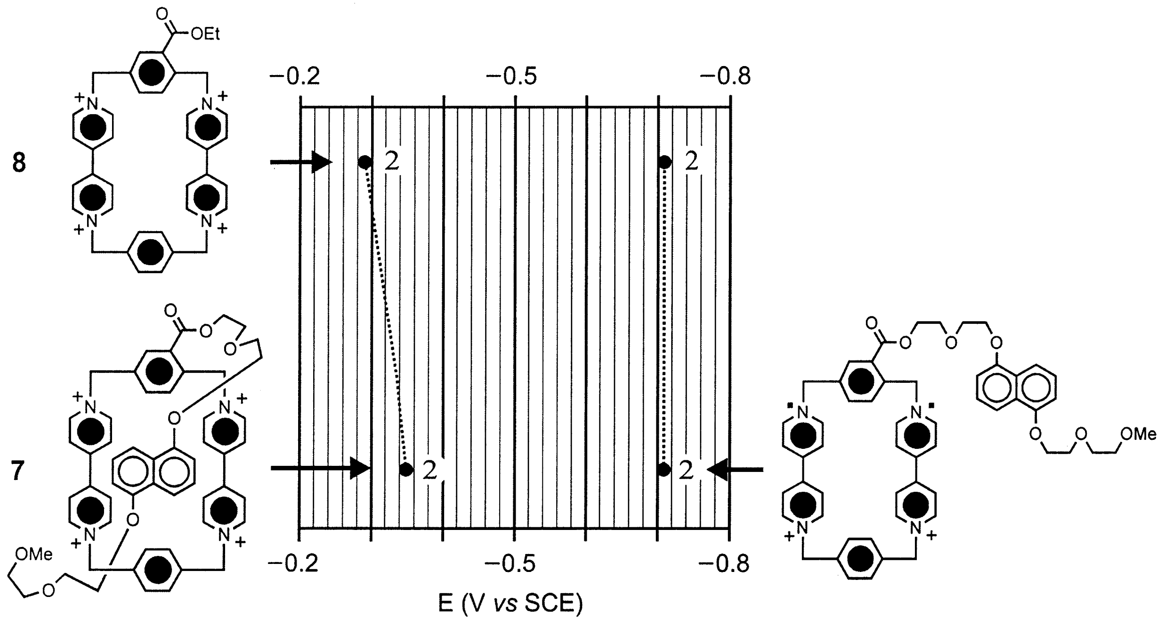

Fig. 8. Genetic diagram of the electrochemical processes taking place on the self-complexing macrocycle **7** and on its model compound **8** [53].

4.2. Charge-transfer interlocked systems

Catenanes and rotaxanes have been synthesized by Stoddart et al. using template effects based on donor/acceptor interactions and hydrogen bonding [51]. The electron acceptor cyclophane **6** shows two reversible bielectronic reduction processes attributed to the simultaneous first and second reduction, respectively, of the two topologically equivalent bipyridinium units (Fig. 9). Catenation of **6** with a crown ether containing two dioxybenzene electron donor units causes big changes in the electrochemical behaviour. Catenane **9** (Fig. 9) [54,55] shows three reversible cyclic voltammetric waves: the first two waves correspond to the separate monoelectronic reductions of the two bipyridinium moieties, while the third one, which is bielectronic, is assigned to the simultaneous second reduction of both moieties. The fact that two separate reductions are observed for the first redox processes is attributed to the topological difference between the 'inside' and 'alongside' positions. The 'alongside' unit, which experiences the interaction with only one of the dioxybenzene units, is easier to reduce than the 'inside' one, stabilized to a greater extent by the two electron donor units. Interestingly, the second reduction of the two bipyridinium units splits in the case of the naphtho-catenane **10** (Fig. 9) [55]. These observations suggest that in bireduced **9** the two bipyridinium units become equivalent, whereas they continue to be non-equivalent in bireduced **10**.

The changes in the electrochemical behaviour on passing from non-interlocked charge-transfer complexes to catenanes are reminiscent of those shown by some metal complexes where the metal ion is encapsulated in cage-type ligands. For example, as discussed in Section 2, Co(III) complexes with amine-type ligands (e.g. $Co(NH_3)_6^{3+}$) undergo irreversible ligand dissociation upon electrochemical reduction, while reduction of caged Co(III) complexes (e.g. $Co(sep)^{3+}$) is reversible since the ligand units are kept around the reduced metal by the cage structure. The behaviour of $Co(sep)^{3+}$ reminds that of interlocked supramolecular systems, in which the electron-acceptor and the electron-donor components are forced to interact, while the ligand release of amine-type complexes recalls the electrochemically induced dethreading of non-interlocked supramolecular species. An important difference, however, resides in the possibility for charge-transfer systems to obtain rethreading of the molecular components by conferring opposite electrochemical inputs, whereas in metal complexes the released ligand is usually irreversibly replaced by solvent molecules.

Catenanes where one of the rings is asymmetric can display a peculiar behaviour. This is the case of catenane **11** (Fig. 10) [56], whose crown ether ring contains a tetrathiafulvalene (TTF) and a dioxynaphthalene (DMN) moiety. While the reduction pattern of such species is similar to that of **10**, its oxidation behaviour is more interesting. Cyclic voltammetric studies have shown that (i) the most stable conformation for **11** is that having the TTF unit inside the cyclophane, and (ii) upon oxidation of the TTF unit circumrotation of the crown ether takes place, giving the conformation with the DMN unit positioned inside the cyclophane (Fig. 10). Contrary to what happens for the self-complexing species **7**, the molecular movements taking place in **11** occur on the time scale of the electrochemical experiments,

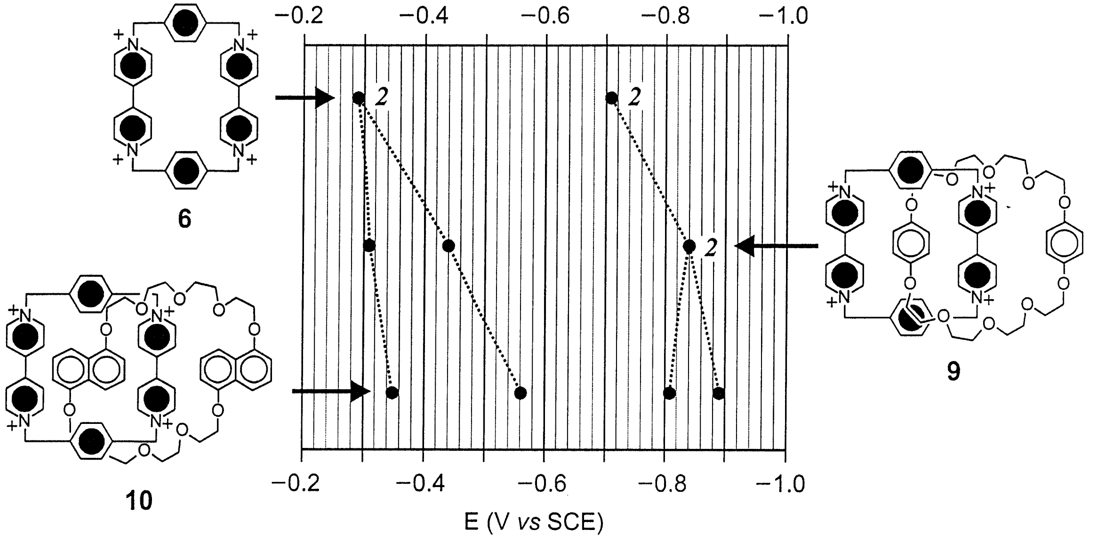

Fig. 9. Genetic diagram of the electrochemical processes taking place on catenanes **9** and **10**, and on their cyclophane component **6** [54,55].

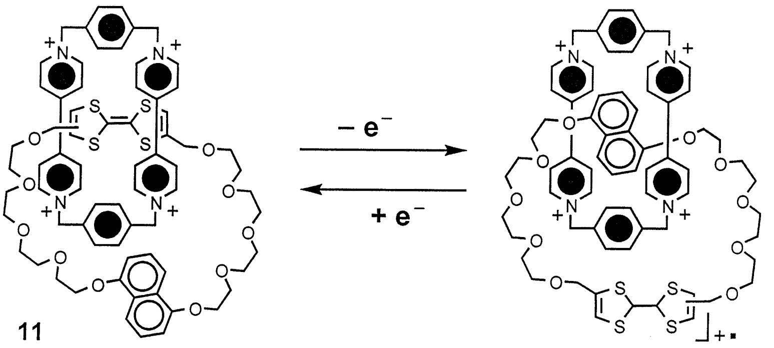
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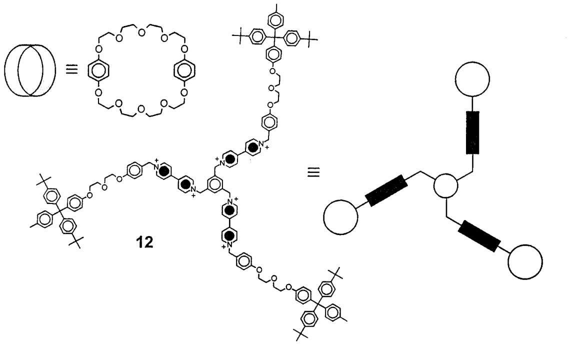
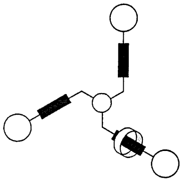
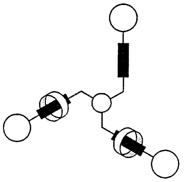
Fig. 10. Conformational changes occurring in catenane **11** by modulating the oxidation state of its tetrathiafulvalene moiety [56].

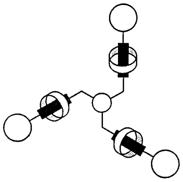
as evidenced by the scan-rate dependence of the cyclic voltammetric waves involving the TTF unit.

An example of the structural information that can be obtained by electrochemical studies on rotaxanes is given by the investigation of the branched species **12** and **13** [57].


12


13a


13b


13c

Since the bipyridinium units change their reduction potential when encircled by the electron donor crown ether, one obtains different electrochemical signals for ‘free’ and ‘complexed’ bipyridinium. It is therefore possible to count the number of the bipyridinium groups surrounded by the macrocyclic polyether by measuring the number of electrons exchanged at the potential values corresponding to the ‘free’ and ‘complexed’ electron acceptor units (Fig. 11).

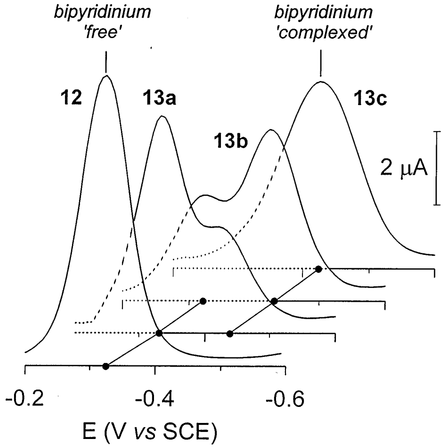
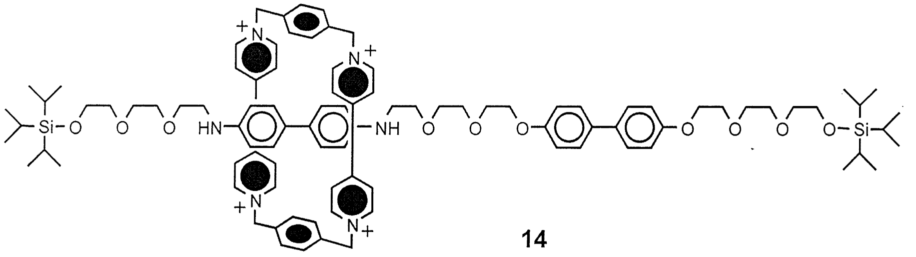


Fig. 11. Differential pulse voltammetric peaks (MeCN/n-Bu_4NPF_6, glassy carbon electrode, scan rate 20 mV s^{-1}, pulse height 75 mV, pulse duration 40 ms) corresponding to the first reduction of the branched species **12** and its rotaxanes **13a–c** [57].

An interesting class of rotaxanes are the so called 'molecular shuttles'. The first working example, reported by Kaifer et al. [58], is rotaxane **14**, made of the electron acceptor cyclophane **6** and a dumbbell species containing two different electron donors, namely, a benzidine and a biphenol unit.



14

The macrocycle can be reversibly moved from the benzidine to the biphenol site by either oxidation/reduction or protonation/deprotonation cycles on the benzidine unit. The switching is followed by cyclic voltammetry, and NMR and absorption spectroscopy.

Very recently, a rotaxane has been studied in which two different types of interactions are exploited to achieve the shuttling process [59]. This rotaxane (compound **15**, Fig. 12) is made of a crown ether ring containing two dioxybenzene electron donor units and a dumbbell-shaped component with two different recognition sites—a dialkylammonium centre and a π-electron-acceptor bipyridinium unit. The ring can interact with the ammonium centre through the formation of hydrogen bonds, and with the bipyridinium unit through charge-transfer interactions; the crown ether, however, exhibits complete selectivity for the ammonium site and, as a consequence, the rotaxane exists as only one of the two possible translational isomers. This is confirmed by the comparison of the cyclic voltammetric behaviour of **15** (Fig. 12) and of the free dumbbell component, which shows that the reduction processes of the bipyridinium unit are not at all affected by the presence of the crown ether. Addition of a base able to deprotonate the ammonium centre results in dramatic changes in the first reduction process of the bipyridinium unit, which is strongly shifted towards more negative potentials and displays a large, scan-rate dependent separation between the anodic and cathodic cyclic voltammetric peak. The second reduction process, in contrast, is completely unaffected (Fig. 12). Subsequent addition of an acid in a stoichiometric amount with respect to the added base restores the electrochemical behaviour observed before addition of base. These results, also supported by NMR spectroscopic studies, indicate that deprotonation of the ammonium centre causes complete displacement of the ring component to the bipyridinium unit, and reprotonation leads back the crown ring on the ammonium centre. In addition, the voltammetric behaviour of the deprotonated rotaxane (particularly, the scan-rate dependence of the first reduction process of the bipyridinium group and the lack of changes in its second reduction) shows that electrochemical reduction of bipyridinium induces the displacement of the crown ring from such unit since it destroys the charge-transfer interaction. Therefore, the described system behaves as a chemically driven molecular machine which, in its deprotonated form, can also be electrochemically driven.

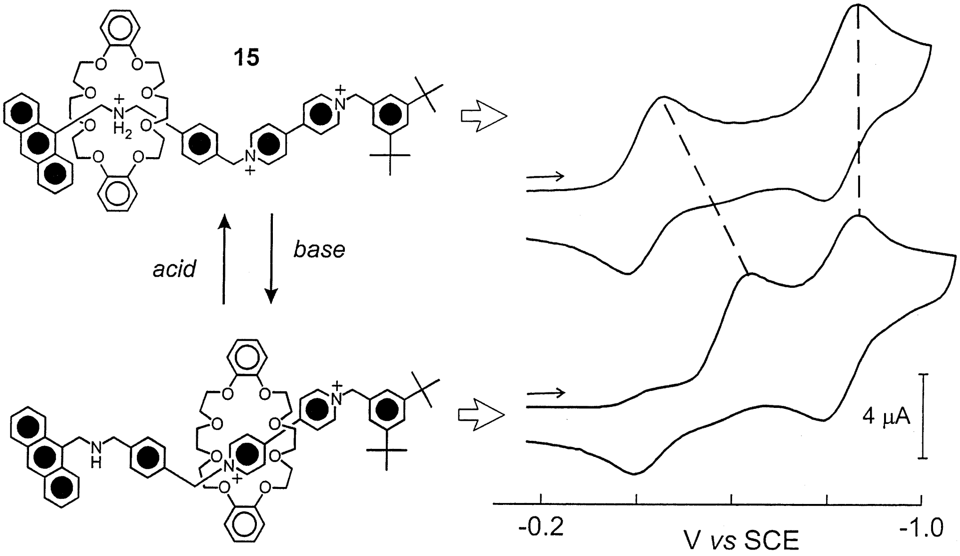
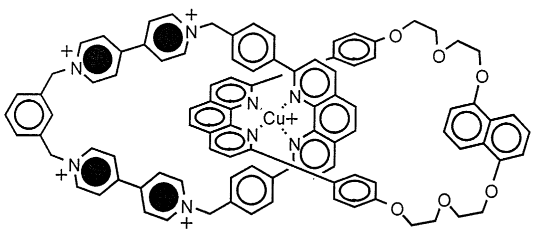


Fig. 12. Cyclic voltammetric behaviour on reduction of **15** and its deprotonated form (MeCN/*n*-Bu_4NPF_6, glassy carbon electrode, scan rate 50 mV s^{-1}) [59].



16

5. 'Hybrid' systems

In the frame of the present discussion, it is worth describing supramolecular systems containing both types of coordination modes, namely, metal complexation and charge-transfer interactions. The bimodal catenane **16** [60] contains both a Cu(I) coordination site and a set of electron rich and electron deficient aromatic units suitable for the formation of donor/acceptor complexes. This species shows one monoelectronic process concerning the oxidation of the Cu(I) complex, and two bielectronic processes corresponding to the simultaneous first and second reduction of the two equivalent bipyridinium units.

Incorporation of transition-metal ions in pseudorotaxane, rotaxane and catenane structures based on charge-transfer interactions has also been performed with the aim to exploit the peculiar excited–state properties of transition-metal complexes [61]. Suitably designed systems of this type can behave as photodriven molecular machines in which the covalently linked metal-based moiety plays the role of photosensitizer [62,63]. With this purpose, a variety of mono and dinuclear Ru(II) and Re(I) complexes based on a cyclophane, derived from **6**, containing one or two bpy coordination sites has been synthesized (Fig. 13) [64]. Such complexes exhibit several redox processes that can be assigned to: (i) reduction of the bipyridiniun and

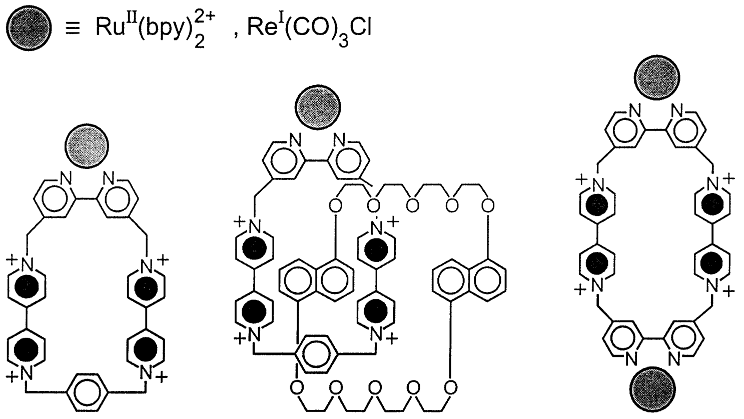


Fig. 13. Structure formulae of mono and dinuclear Ru(II) and Re(I) complexes containing a cyclophane or a catenane ligand [64].

bpy moieties of the cyclophane; (ii) reduction of the bpy ligands in the case of the Ru complexes; (iii) oxidation of the metals; and (iv) oxidation of the dioxynaphthalene units of the crown ether in the complexes containing the catenane ligands. For instance, complex **17** (Fig. 14) exchanges up to a total of nine electrons. On reduction, it shows two monoelectronic and one bielectronic processes involving the bipyridinium units, and three monoelectronic processes concerning the bpy moieties (Fig. 14). On oxidation, two monoelectronic processes are observed; the first process, being reversible, is assigned to the oxidation of the metal centre, and the second one, not fully reversible, to the oxidation of the 'alongside' dioxynaphthalene unit of the crown ether catenated to the cyclophane.

6. Conclusion

The electrochemical properties of classical coordination compounds (i.e. mononuclear metal complexes) are maintained and, in several cases, emphasized when metal complexes are used as components of supramolecular structures. The similarities existing between metal complexes and supramolecular charge-transfer systems not containing metals have also been pointed out.

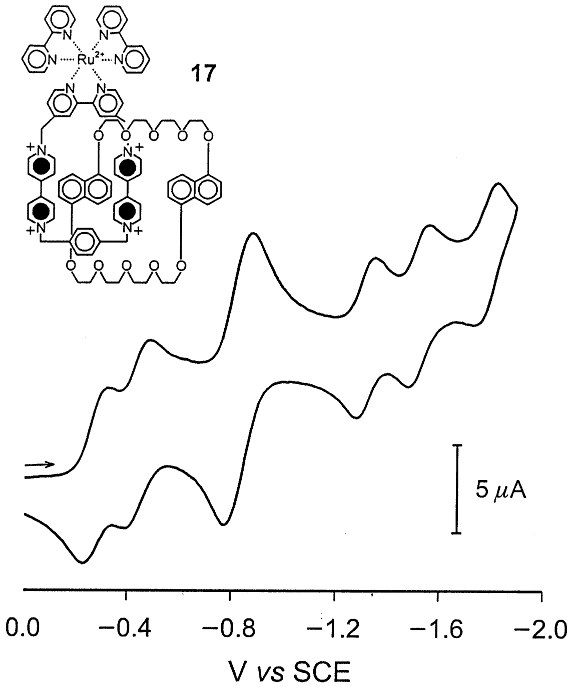


Fig. 14. Cyclic voltammetric behaviour on reduction of **17** (MeCN/n-Bu_4NPF_6, glassy carbon electrode, scan rate 50 mV s^{-1}) [64].

Most of the systems described illustrate the supramolecular approach to the construction of molecular-level devices. When a number of molecular components are suitably assembled and organized, the simple *acts* (e.g. uptake or loss of electrons, absorption of photons, etc.) performed by the single components can result in a valuable *function* (e.g. multielectron exchange at a predetermined potential, sophisticated molecular movements, energy transfer along predetermined pathways, photoinduced charge separation, etc.) characteristic of the whole supramolecular species.

The importance of electrochemical techniques [65,66] (i) as a tool for obtaining information on complex structures (e.g. on the degree of organization of the supramolecular system) and (ii) as an energy input to induce movements at the molecular level has been evidenced.

Acknowledgements

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