DENDRIMERS BASED ON ELECTROACTIVE METAL COMPLEXES. A REVIEW OF RECENT ADVANCES

Alberto JURIS[a1,*], Margherita VENTURI[a2], Paola CERONI[a3], Vincenzo BALZANI[a4], Sebastiano CAMPAGNA[b1] and Scolastica SERRONI[b2]

[a] *Dipartimento di Chimica "G. Ciamician", Università di Bologna, 40126 Bologna, Italy; e-mail: [1] juris@ciam.unibo.it, [2] mventuri@ciam.unibo.it, [3] ceroni@ciam.unibo.it, [4] vbalzani@ciam.unibo.it*

[b] *Dipartimento di Chimica Inorganica, Chimica Analitica e Chimica Fisica, Università di Messina, 98166 Messina, Italy; e-mail: [1] photochem@chem.unime.it, [2] serroni@chem.unime.it*

Received November 10, 2000
Accepted November 30, 2000

In memory of Professor Antonín A. Vlček.

Recent studies in the field of dendrimers based on electroactive metal complexes are reviewed. The electroactive units may be present (i) in the core, (ii) in the branches, (iii) in the surface, (iv) in the core and in the branches, (v) in the core and in the surface, (vi) in the branches and in the surface, and (vii) in the core, branches and surface. Depending on the dendrimer structure, the electroactive units can either interact or behave independently. The most interesting features are the shielding of electroactive cores by non electroactive branches, the great number of electrons that can be exchanged in a very narrow potential region by high generation surface-functionalized dendrimers, and the tailor-made redox patterns that can be obtained by dendrimers based on metal complexes at each branching centre. A review with 42 references.

Keywords: Dendrimers; Polypyridine ligands; Transition metal complexes; Ferrocenes; Ruthenium; Osmium; Phthalocyanines; Electrochemistry.

doi: 10.1135/cccc20010001

1. INTRODUCTION

Highly branched molecules having tree-like structures are called dendrimers. Research in this field began in 1978 with a report by Vögtle *et al.*[1] on the synthesis of cascade molecules, and started to spread explosively around 1985 with the works of Newkome[2] and Tomalia[3]. Dendrimers[4] are currently attracting the interest of a great number of scientists because of their unusual chemical and physical properties and the wide range of potential applications in such different fields as medicine, biology, chemistry, physics, and engineering.

Dendrimers are complex, but well defined, chemical compounds characterized by three-dimensional architectures, a high degree of order, and the possibility of bearing selected chemical functions in predetermined sites of their structure. From a topological viewpoint, three different regions can be identified in a dendrimer: core, branches, and surface (Fig. 1). Functional groups can be incorporated into each of these three regions[5]. Schematically, we can distinguish dendrimers containing functions (i) in the core, (ii) in the branches, (iii) in the surface, (iv) in the core and in the branches, (v) in the core and in the surface, (vi) in the branches and in the surface, and (vii) in the core, branches and surface (structures a–g in Fig. 2). Furthermore, functional units can be non-covalently hosted in the cavities of a dendritic

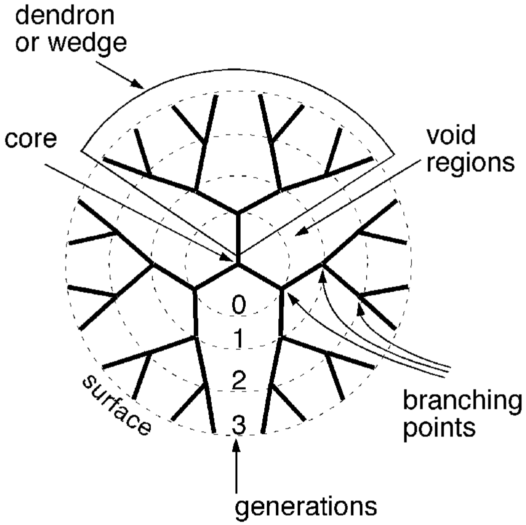


FIG. 1
Schematic representation of the structure of a dendrimer

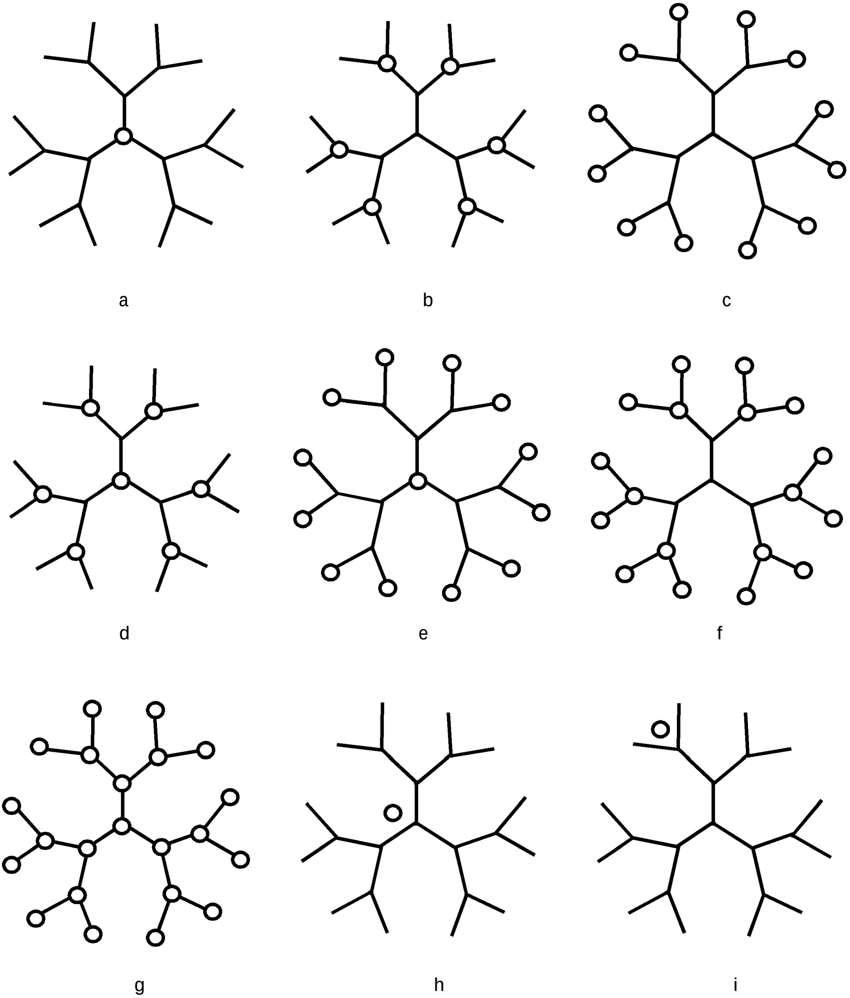


FIG. 2
Schematic representation of dendrimers with positions where electroactive units (circles) can be located

structure[6] (type h in Fig. 2) or associated to the dendrimer surface[7] (type i in Fig. 2). Because of their proximity, the various functional groups of a dendrimer may easily interact with one another and, in any case, the resulting properties are modulated by the dendrimer as a whole. Therefore, dendrimers incorporating functional units can be considered as supramolecular species.

From the electrochemical viewpoint, dendrimers are very interesting species for several reasons. Potentially electroactive units can be buried in the dendrimer core, thus preventing the exchange of electrons. A very large number of equivalent, non-interacting electroactive units can be linked to the surface of a dendrimer, giving rise to simultaneous exchange of a large and predetermined number of electrons. Electroactive units of the same or different types can be located in topologically equivalent or non-equivalent sites of a dendrimer to obtain tailor-made redox patterns. The interest in dendrimers containing electroactive units rests on the fact that electrochemistry is a powerful technique (i) for elucidation of the structure of dendrimers, (ii) for evaluation of the degree of electronic interaction of their chemically and/or topologically equivalent or non-equivalent moieties, and (iii) for investigation of their endo- and exo-receptor capabilities.

In this paper we will review some recent advances in the field of dendrimers containing electroactive units based on transition metal complexes. Recent advances on photochemical properties of this kind of dendrimers are reviewed elsewhere[8].

Transition metal complexes are characterized by a precise molecular geometry related to the coordination number of the metal ion and, in some cases, also to the rigid structure of the ligands. Furthermore, they can usually undergo reduction and oxidation processes at easily accessible potentials. By using metal complexes to construct a dendrimer, it is therefore possible to incorporate in the dendritic structure many *pieces of information* that, when placed in suitable sites of the array, can be used to perform valuable functions.

As discussed in detail elsewhere[8,9], many metal-based dendrimers, because of their ability to absorb in the visible spectral region and to exhibit predetermined energy migration patterns, can play the role of antennas for light harvesting. Therefore, it is particularly interesting to couple in a dendrimer the light harvesting function with the capability of exchanging several electrons with the aim of exploiting successive one-photon/one-electron events to perform multielectron transfer processes[10].

2. ELECTROACTIVE METAL-BASED UNITS

The electroactive units in the dendrimers that we are going to discuss are metal-based moieties. An important requirement for any kind of application is the chemical redox reversibility of such moieties. The most common metal complexes capable of exhibiting a chemically reversible redox behaviour are ferrocene and its derivatives, and iron, ruthenium and osmium complexes of polypyridine ligands. Therefore, it is not surprising that most of the investigated dendrimers contain such metal-based moieties. In the electrochemical window accessible in the usual solvents, 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. Dendrimers containing electroactive porphyrins have also been investigated.

When the only metal complex of a dendrimer is that constituting the core of the structure (Fig. 2, type a), the most interesting problem is whether and, if so, how much electrochemical properties (redox potential, electrochemical reversibility) of the metal-based core are modified by the surrounding branches.

In b–f type dendrimers (Fig. 2), a number of equivalent metal-based centres are present, as dendrimers are usually highly symmetric species. The metal-based centres may well or not interact, depending on the distance and nature of the linking units. Multielectron redox processes can therefore be observed, with specific patterns related to the degree of interaction of the various units.

In dendrimers based on metals at each branching centre (Fig. 2, type g), the electrochemical behaviour is even more complex since (i) each component unit of the dendrimer is electroactive, (ii) the chemical nature of the metal-based units may be different, (iii) chemically equivalent units can be different from the topological viewpoint, and (iv) the degree of interaction of the moieties depends on their chemical nature and distance.

It should be pointed out that in the recent literature we have not found any report on dendrimers with electroactive units in the core and in the branches (Fig. 2, type d), in the branches and in the surface (Fig. 2, type f), and on dendrimers hosting metal complexes (Fig. 2, types h and i).

3. DENDRIMERS WITH AN ELECTROACTIVE UNIT IN THE CORE

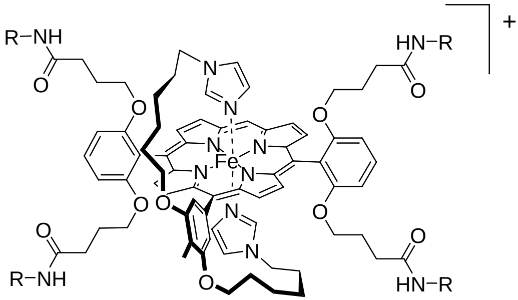
Porphyrin complexes are particularly suitable for construction of dendrimers with an electroactive unit in the core (Fig. 2, type a) and for investigation of the modified behaviour of an electroactive species when surrounded by dendritic branches. In particular, dendritic porphyrins can be regarded as models for electron-transfer proteins like cytochrome c (ref.[11]).

Very recently, the iron porphyrin core has been modified in order to control the axial ligation to the iron centre by means of two imidazoles attached to the porphyrin ring[12]. Dendrimers **1**, **2** and **3** of the generation zero, one and two, respectively, have been prepared and the redox behaviour of the $Fe^{III/II}$ couple has been examined in three solvents of increasing polarity, namely dichloromethane, acetonitrile, and water. The redox potential of the $Fe^{III/II}$ couple becomes more positive with increasing dendrimer generation, the process being reversible in all cases. For dendrimers **1** and **2** the potential value is solvent-dependent, increasing with increasing solvent polarity. Interestingly, for the larger dendrimer **3** the potential value is the same in all of the three solvents, indicating that the dendritic branches are dense enough to prevent solvent access to the iron core, which thus experiences a unique local microenvironment, independently of the solvent. This shielding behaviour is similar to that exercised by the peptide shell around the $Fe^{III/II}$ couple in cytochromes.

Another recent example of a redox-active dendrimer which can mimic the behaviour of redox proteins is **4** (ref.[13]). This dendrimer contains a single, unsymmetrically located ferrocene unit that reminds a prosthetic group partially buried in a polypeptide framework. The behaviour of dendrimer **4** compared with that of smaller dendrimers of the same family shows that, upon increasing dendrimer generation, the half-wave potential and the diffusion coefficient for ferrocene oxidation decrease. These results demonstrate that the ferrocene oxidation is hindered by the hydrophobic environment. Upon hydrolysis of the peripheral esters in **4**, a series of carboxyl-terminated dendrimers can be obtained[14]. Their electrochemical response on a cysteamine-covered electrode is extremely sensitive to pH. At pH 7, the carboxylic groups are deprotonated and a strong electrostatic interaction with the cysteamine residues takes place: the ferrocene unit is therefore far from the electrode surface and the electron transfer kinetics is very slow.

4. DENDRIMERS WITH ELECTROACTIVE UNITS IN THE BRANCHES

Very few examples exist of dendrimers functionalized in the branches with redox-active metal units (Fig. 2, type b)[4k,5,15]; apparently, electrochemical data are available[16] only for dendrimers **5** and **6**. Units $[Ru(tpy)_2]^{2+}$ (tpy = 2,2′:6′,2″-terpyridine) are present in the branches of these dendrimers that have the same molecular formula and are the first example of dendritic



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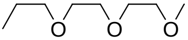

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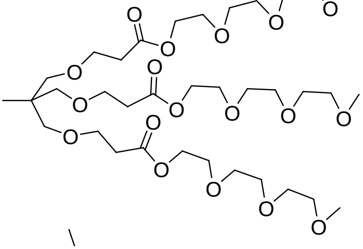

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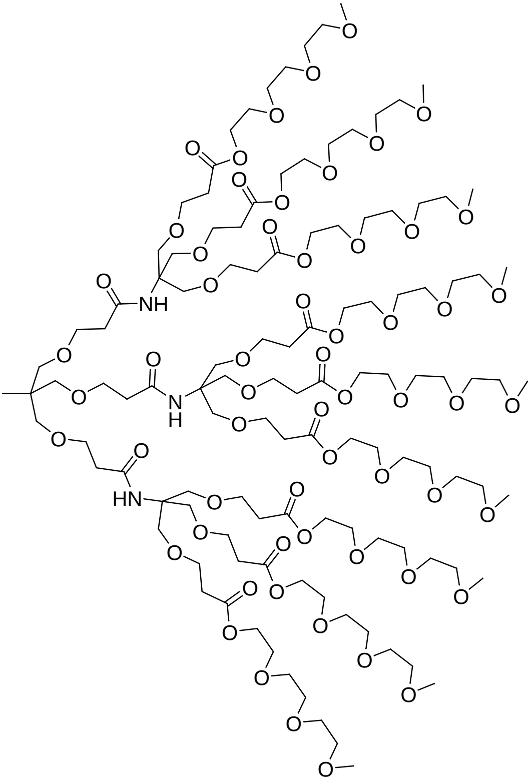

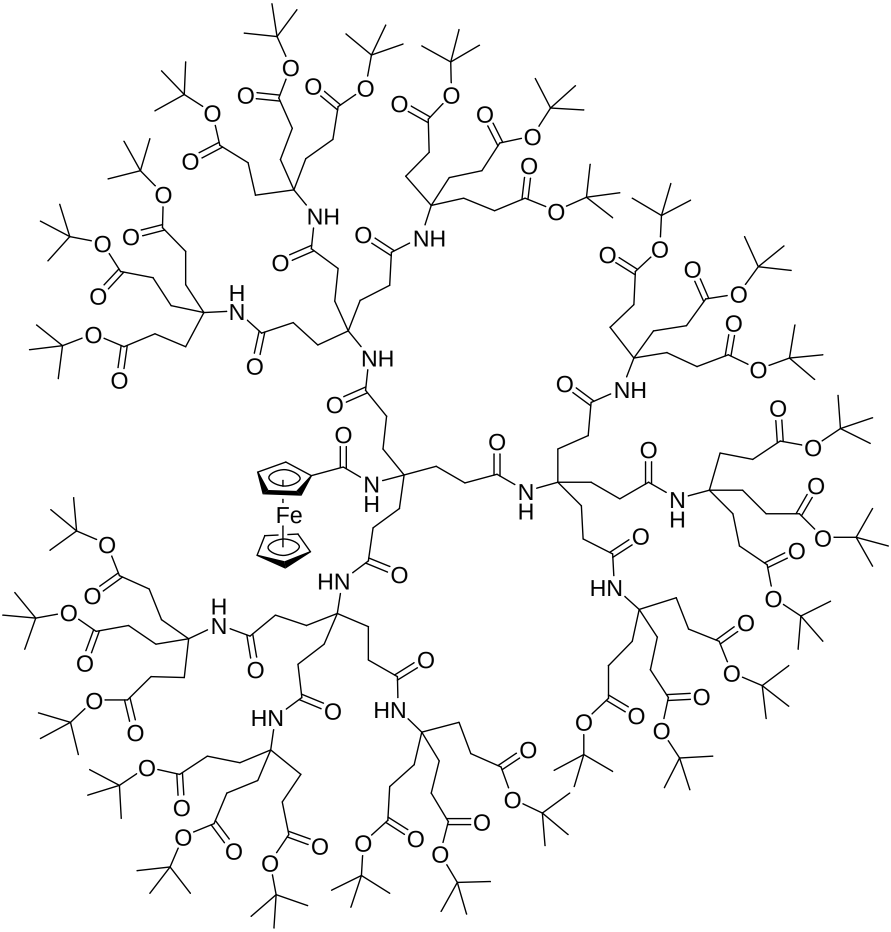

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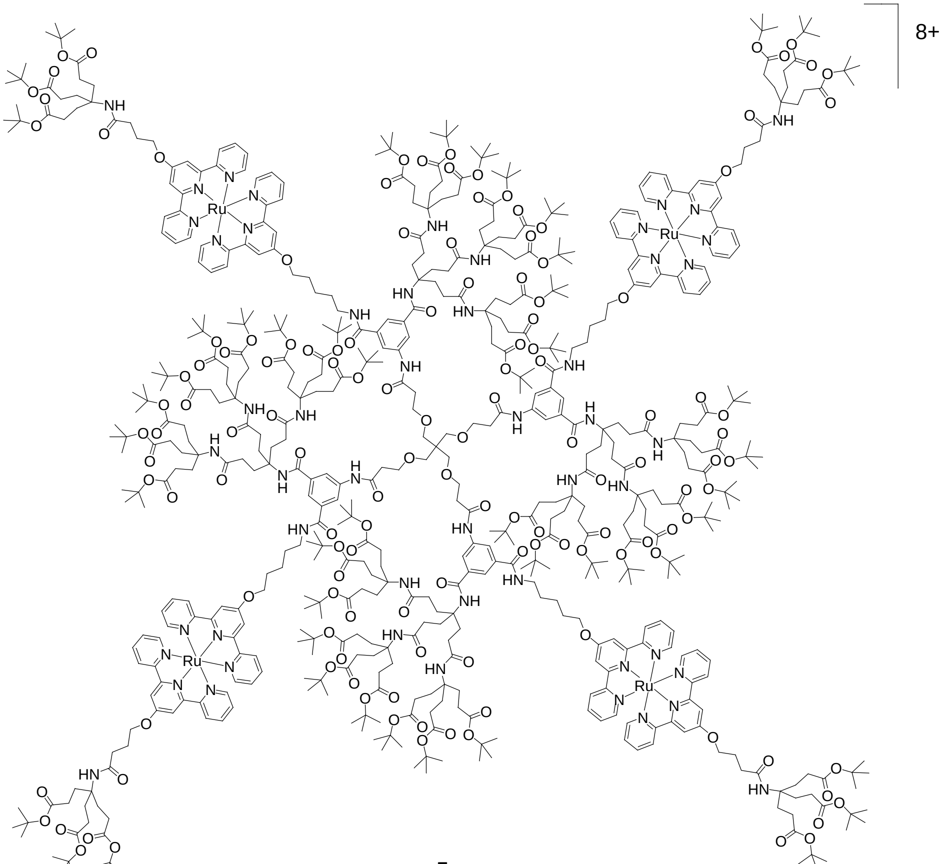
constitutional isomers. These isomers feature similar solubility and decomposition temperature, whereas their electrochemical behaviour (in acetonitrile), due to the four $[Ru(tpy)_2]^{2+}$ units, is different. Reduction of the two isomers evidences two quasi-reversible processes due to the terpyridine ligands. The $E_{1/2}$ values for isomer **6** are slightly more negative than those of **5**. Oxidation of the Ru(II) ions occurs in a single quasi-reversible process for isomer **6**, whereas two processes are observed for **5**. The results obtained for the two isomers can be accounted for by differences in chemical environment, internal density, void regions, and, possibly, structural rigidity. For more details on the electrochemical behaviour of Ru(II) polypyridine complexes, see section 7.1.



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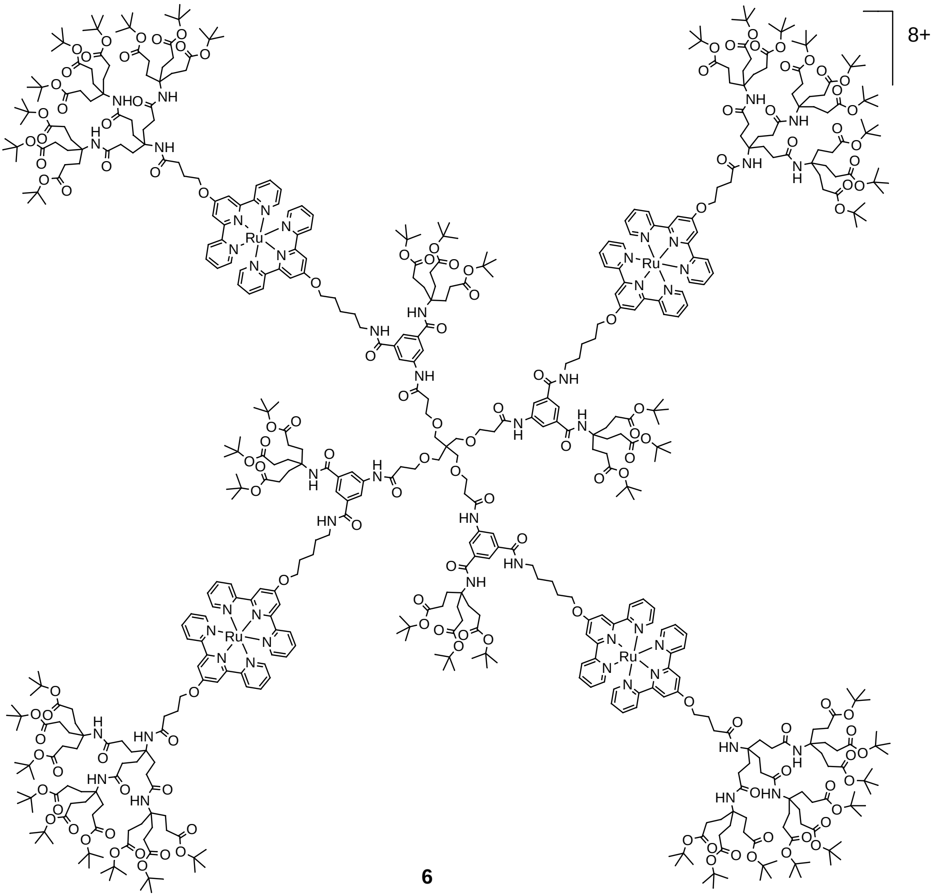

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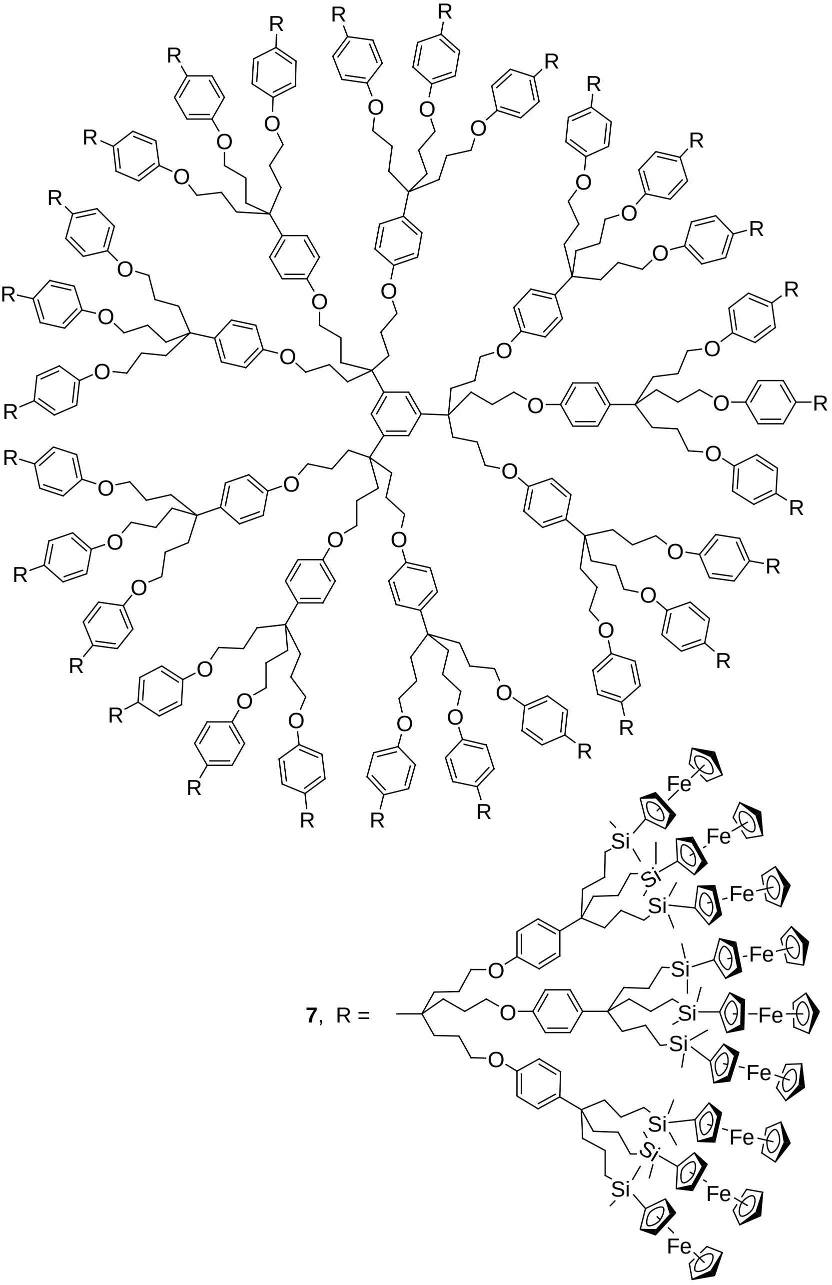
5. DENDRIMERS WITH ELECTROACTIVE UNITS IN THE SURFACE

Ferrocene is the most commonly used electroactive unit for peripheral functionalization of dendrimers (Fig. 2, type **c**). Many dendrimers of this kind have been studied and the field has already been reviewed[4k,5,15]. A few selected examples taken from recent literature will be illustrated here.

Dendrimers containing up to 243 peripheral ferrocenyl groups (**7**) have been obtained, and their electrochemical properties have been investigated[17]. In *N*,*N*-dimethylformamide solution, oxidation of the ferrocenyl units occurs in a single reversible wave, at a potential showing no or only minor dependence on the dendrimer generation. The number of exchanged



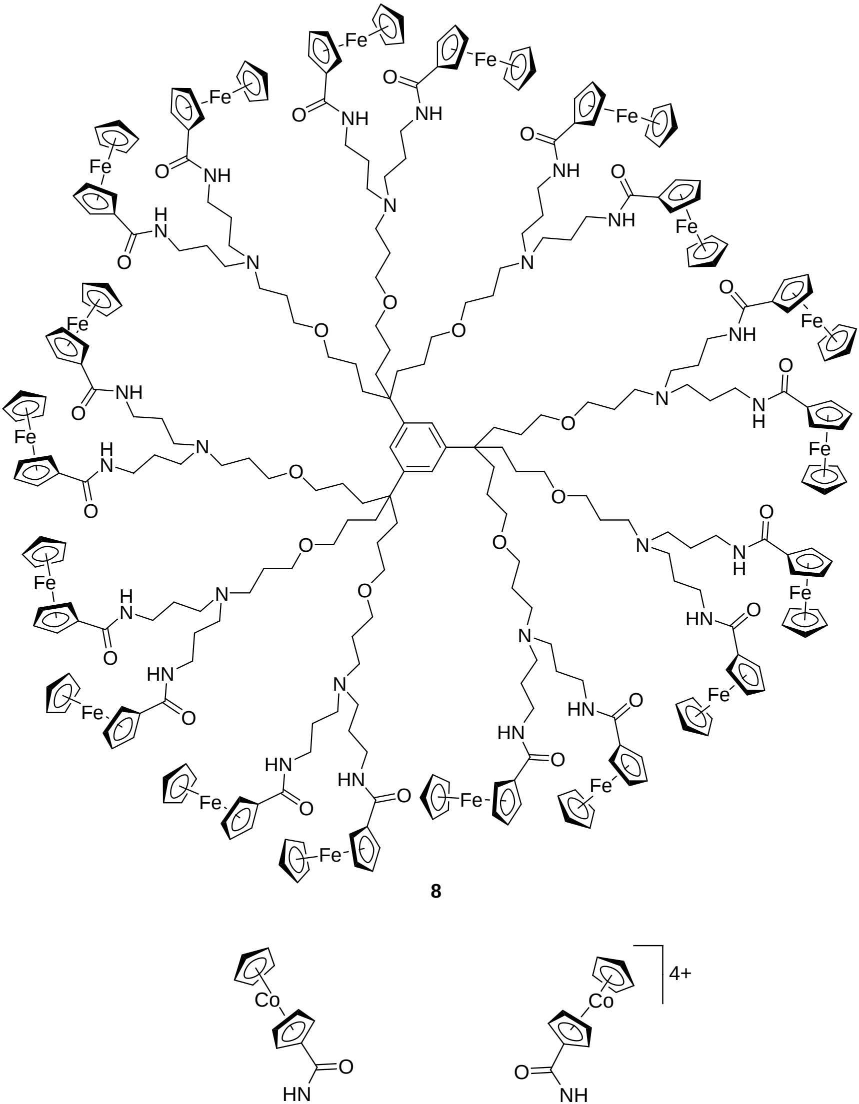
7, R =

electrons in the oxidation is equal to the number of expected peripheral ferrocenyl units. This result confirms the structure of the dendrimers and indicates that the ferrocenyl units are non-interacting. The electrochemical reversibility observed for the higher-generation species indicates that all the ferrocenyl units undergo fast heterogeneous electron transfers. This behaviour has been ascribed to rapid rotation of the dendrimer molecule near the electrode surface, although other relay mechanisms facilitating transfer of electrons from the electrode to remote ferrocenyl groups cannot be excluded.

In dichloromethane, oxidation of the higher-generation species gives rise to adsorption processes, thus allowing the fabrication of functionalized electrodes[17]. Chemical oxidation with $NOPF_6$ produces the oxidized species that precipitates. The solid can be reduced back to the original ferrocenyl dendrimer without any decomposition. Thus these species could find application as molecular batteries in molecular electronic devices[17].

Ferrocenyl-functionalized dendrimers have also been investigated for recognition of anions. Dendrimer **8** contains 18 equivalent and independent ferrocene units in the periphery, and only a single anodic reversible wave is observed in cyclic voltammetry experiments in dichloromethane solution[18]. Progressive addition of $H_2PO_4^-$ induces the growing of a new wave at less positive potential, while the original wave is lowered in intensity. In contrast, addition of HSO_4^-, Cl^-, and NO_3^- only produces a cathodic shift of the original wave. The lower-generation analogues, carrying nine and three peripheral ferrocene units, were also tested; a clear dendritic effect is observed, in the sense that the ion-sensing ability increases with increasing dendrimer generation. Similar dendrimers using cobaltocenium as electroactive units for anion sensing have also been studied[19].

Host–guest dendrimer chemistry has been investigated by electrochemical techniques. An interesting example concerns dendrimers based on the iminopropane-1,3-diyl framework, which have been functionalized with four (**9**), eight, sixteen, and thirtytwo cobaltocenium units[20]. Dendrimer **9** was examined in greater detail; its electrochemical reduction in aqueous solution occurs in an irreversible single-wave process that transforms the cobaltocenium into cobaltocene units. As a result, the dendrimer becomes hydrophobic and deposits on the electrode. Addition of the well-known host species β-cyclodextrin (β-CD) prevents dendrimer precipitation and the cyclic voltammogram exhibits a shape which is consistent with a reversible process. This result indicates that β-CD interacts with the reduced form of the dendrimer, forming an inclusion complex with cobaltocene. The described system is an example where electrochemical activation is required in order to trigger the host–guest interaction. As far as higher-



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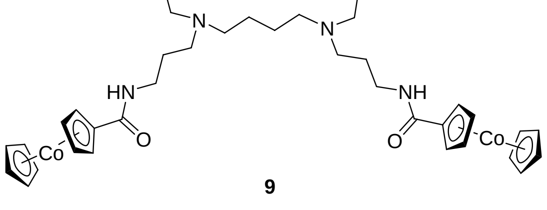

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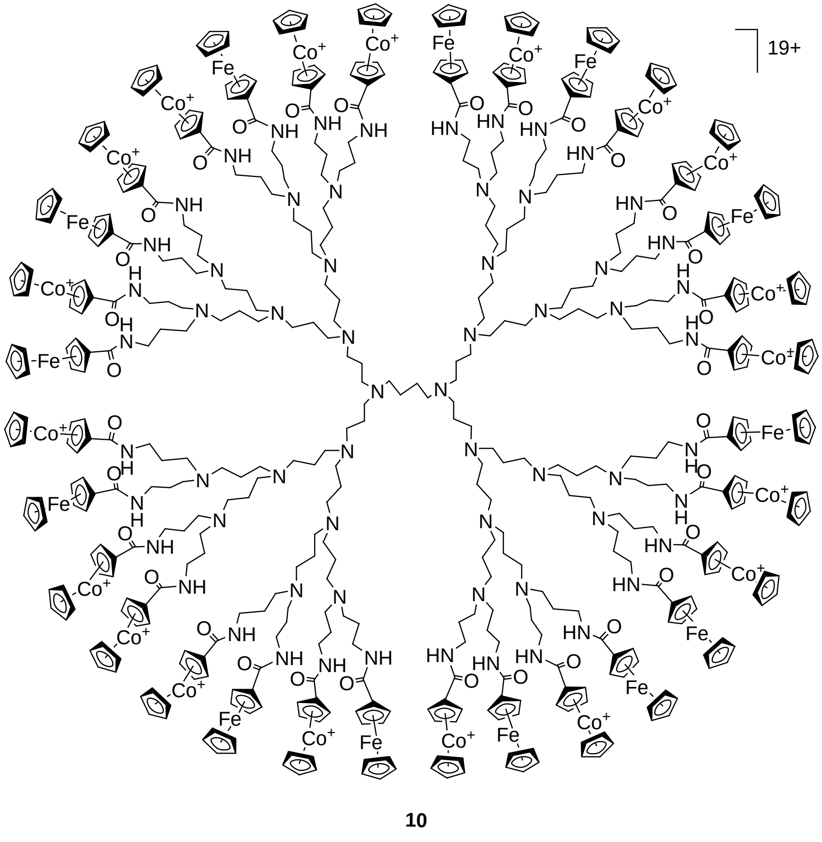
generation analogues are concerned, their solubility in aqueous media decreased with increasing size, so that qualitatively similar results were obtained only for the species functionalized with eight and sixteen cobaltocenium units.

An interesting example of mixed-metal functionalization has been published very recently. Iminopropane-1,3-diyl dendrimers terminated with up to thirtytwo NH_2 groups were treated with an equimolecular mixture of appropriate ferrocene and cobaltocenium species, thus producing for the first time dendrimers containing both neutral and cationic redox-active organometallic species[21]. X-Ray fluorescence analysis shows that the ratio of the cobaltocenium to ferrocene units is not 1 : 1, but close to 19 : 13, as indicated in the formula of dendrimer **10**. Cyclic voltammetry experiments in acetonitrile solution evidenced a single reversible oxidation process at about +0.60 V (*vs* SCE) due to multiple non-interacting ferrocenyl units,



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and a single reduction wave at about –0.70 V attributed to multiple non-interacting cobaltocenium units. The ferrocene/cobaltocenium ratio obtained from the cyclic voltammetric measurements agrees with the other analytical data. Precipitation of the dendrimer occurs upon reduction; this behaviour was exploited to produce for the first time functionalized electrodes containing both ferrocene and cobaltocenium redox sites. These modified electrodes are very stable, showing no loss of activity even after hundreds of cyclic voltammetric scans, and have also been tested as a novel type of glucose sensors.

6. DENDRIMERS WITH ELECTROACTIVE UNITS IN THE CORE AND THE SURFACE

A few examples of dendrimers belonging to this family (Fig. 2, type e) are reported in the literature.

The two-direction 1,1′-bis[dimethyl(vinyl)silyl]ferrocene was used for the synthesis of two small dendrimers, namely the homometallic compound **11** and the heterometallic compound **12** (ref.[22]). In compound **11**, oxidation occurs in three consecutive processes, involving the exchange of two, one, and two electrons. This shows that the four terminal, topologically equivalent ferrocene units do not behave independently. The first process can be assigned to the oxidation of two terminal ferrocenes linked to different Si atoms, the second process involves the oxidation of the central ferrocene unit, and the third one the oxidation of the two remaining, non-adjacent terminal ferrocene units. The difference in the potentials at which the oxidation of the peripheral units takes place, provides a measure of the degree of interaction between such units. Interestingly, in the similarly structured compound **12**, no interaction is observed between the adjacent $Cr(\eta^6\text{-}C_6H_5)(CO)_3$ units, as evidenced by its electrochemical behaviour. A first one-electron process, assigned to the oxidation of the ferrocenyl core, is followed by a four-electron process corresponding to the simultaneous oxidation of the four peripheral chromium units.

Ten-fold functionalization of ferrocene with allyl groups has been used to construct dendrimer **13** which contains the ferrocene core and ten peripheral ferrocene units[23]. Cyclic voltammetric experiments have shown that the peripheral ferrocene units are oxidized at the same potential. At a slightly negative potential, a much weaker cyclic voltammetric wave, assigned to the oxidation of the core, is also observed.

Compound **14** contains seven ferrocene units[24]. The six peripheral units are chemically and topologically equivalent, whereas the core has a different chemical nature. Accordingly, two redox processes are observed, *i.e.*, ox-

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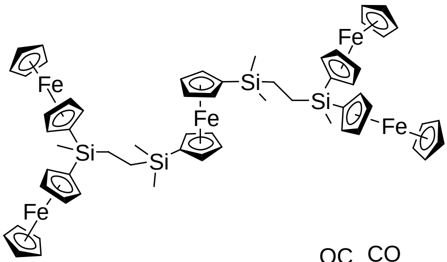

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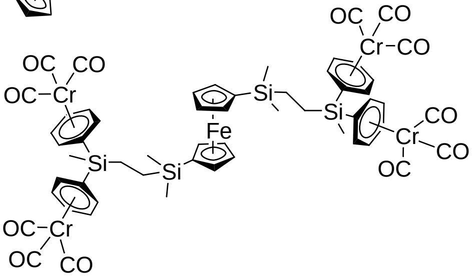

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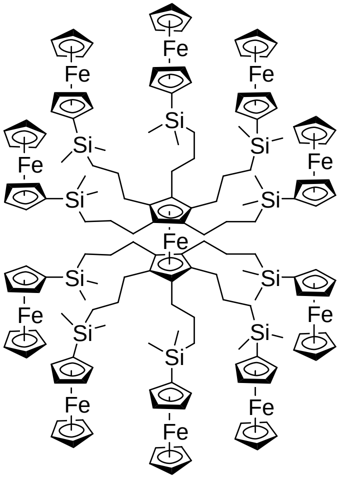

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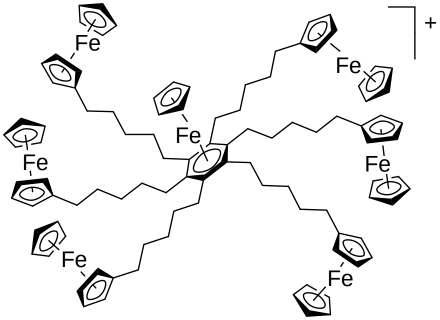
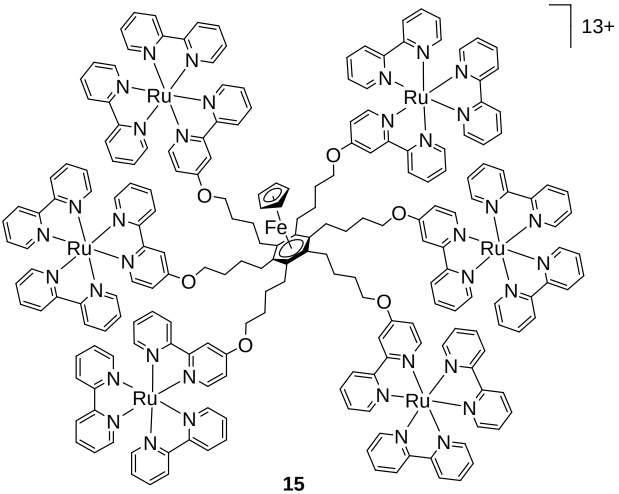


idation of the peripheral ferrocene units and reduction of the core, with corresponding cyclic voltammetric waves in the 6 : 1 current intensity ratio. Clearly, the one-electron process of the core is a convenient internal standard to calibrate the number of electrons exchanged in the multielectron process involving the peripheral units.

The same core of dendrimer **14** was used to construct dendrimers **15** and **16** bearing in the periphery six $[Ru(bpy)_3]^{2+}$ (bpy = 2,2′-bipyridine), and six



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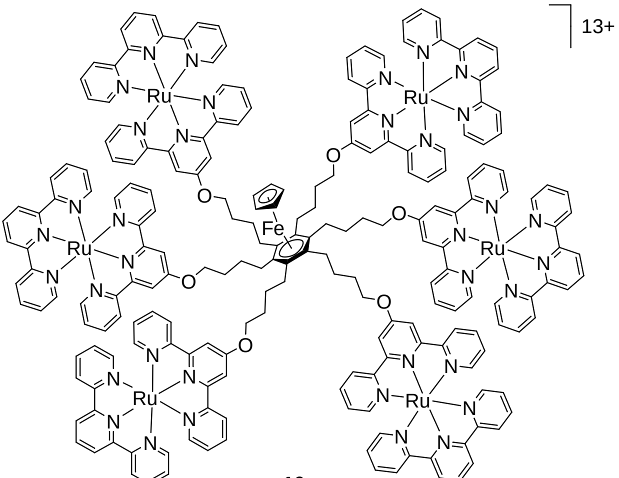

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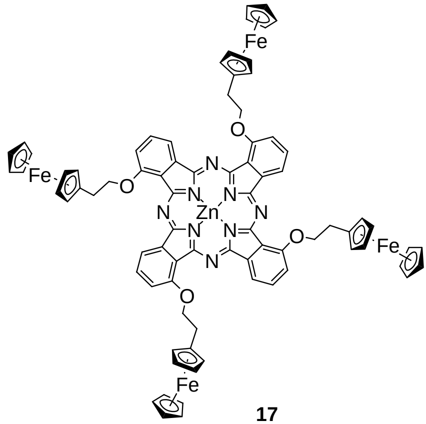
$[Ru(tpy)_2]^{2+}$ units, respectively[25]. Cyclic voltammetric experiments have evidenced that in the two compounds, the six equivalent Ru-based units are reversibly oxidized at the same potential, showing that they are non-interacting. The reduction of the core, which would be useful as an internal reference for the exchange of one electron, is partly masked by bpy- and tpy-based reduction processes.

Dendrimers **17** and **18**, with four and eight ferrocene units, respectively, have been obtained by functionalization of the Zn(II)-phthalocyanine core[26]. All the ferrocene units linked to the phthalocyanine core undergo oxidation at the same potential, showing that they behave independently. This process is accompanied by two oxidation and three reduction processes attributed to the phthalocyanine π-system. No attempt has been made to establish the number of the electrons exchanged in various processes.



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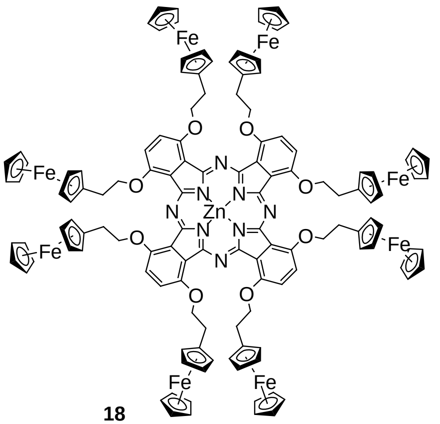

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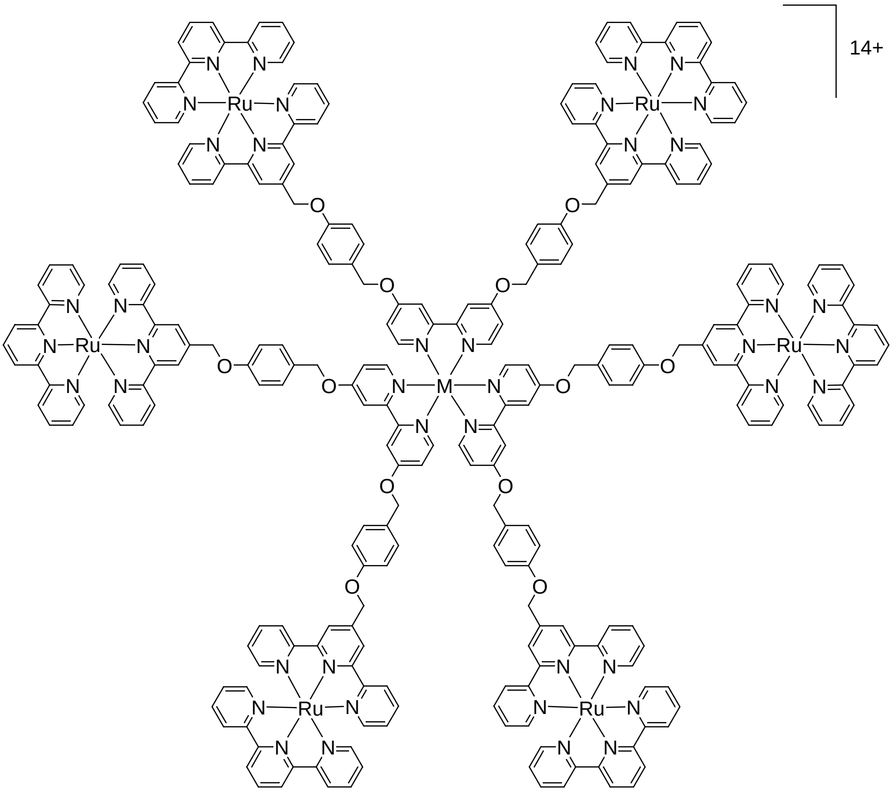
Compounds **19** and **20** are the only examples of dendrimers containing polypyridine transition metal complexes both in the core and in the periphery[27]. In compound **19**, oxidation of the core is an irreversible process, as often observed for encapsulated redox units. This process is followed, at a more positive potential, by simultaneous and reversible oxidation of the six Ru-based units, indicating that there is no interaction among them. In dendrimer **20**, the behaviour of the Ru-based units is essentially that observed in the case of compound **19**, but no oxidation of the Co-based core was evidenced. Interestingly, also treatment with a chemical oxidant was ineffective in this regard.



19, M = Fe
20, M = Co

7. DENDRIMERS WITH ELECTROACTIVE UNITS IN EACH BRANCHING CENTRE

In this section we will discuss recent advances in the field of dendrimers containing electroactive metal complexes as branching centres (Fig. 2, type g), which can be considered extended, tree-like versions of long-known oligonuclear metal complexes. As we will see, such dendrimers have been constructed using Ru(II) and Os(II) as metals and the polypyridine ligands shown in Fig. 3.

7.1. Component Units

In the last 20 years extensive investigations have shown that Ru(II) and Os(II) complexes of polypyridine-type ligands exhibit outstanding ground- and excited-state redox properties[28]. Figure 4 illustrates the case of

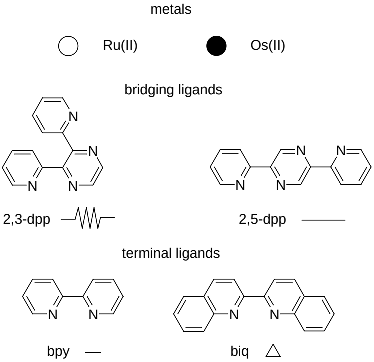


FIG. 3
Formulas of ligands, abbreviations, and graphic symbols used to represent the components of the investigated dendrimers of type g in Fig. 2

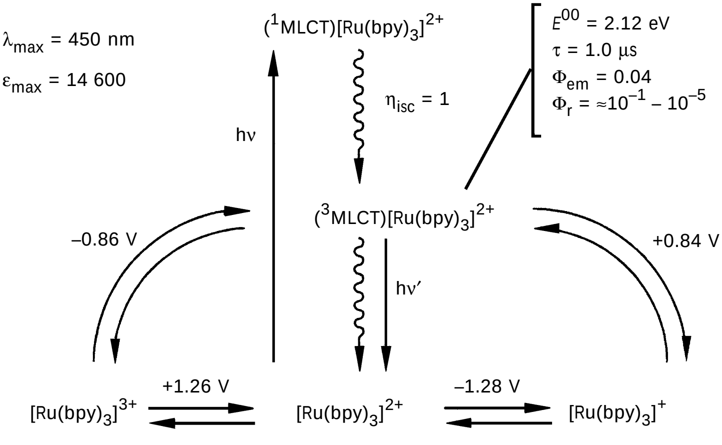


FIG. 4
Schematic representation of some relevant ground- and excited-state properties (energy of the lowest triplet excited state, E^{00}; lifetime, τ; emission quantum yield, Φ_{em}; photosubstitution quantum yield, Φ_r; intersystem crossing efficiency, η_{isc}) of $[Ru(bpy)_3]^{2+}$ in aqueous solution at room temperature, except Φ_r which refers to a variety of experimental conditions. The potentials are *vs* NHE

$[Ru(bpy)_3]^{2+}$, which is the prototype of this class of compounds. Figure 5 shows the cyclic voltammogram of $[Ru(bpy)_3]^{2+}$ in which seven redox processes are evidenced. The oxidation process corresponds to the oxidation of Ru(II) to Ru(III), whereas the two triplets of reduction processes correspond to the first and the second reduction of the three bpy ligands.

Several hundreds of complexes of this family have been synthesized and it has been shown that their redox properties can be tuned significantly by changing ligands or ligand substituents[28,29]. More recently, as a prelude to the construction of dendrimers based on metals as branching centres, a great number of oligonuclear metal complexes containing Ru(II) and Os(II) have been prepared and their electrochemical properties have been investigated[28d,29,30]. In these compounds, the oxidation processes (observed below 3 V *vs* SCE) are essentially metal-localized and the reduction processes are essentially ligand-localized. All the observed processes are, in general, reversible.

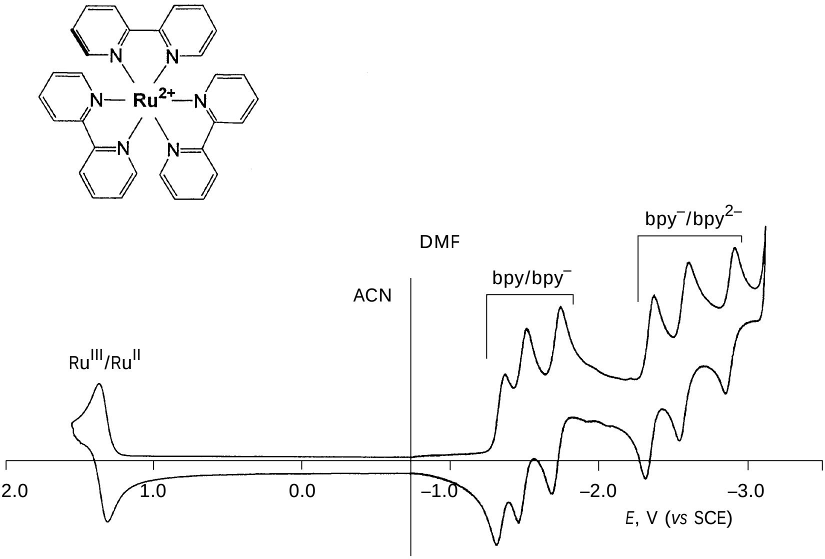


FIG. 5
Electrochemical behaviour of $[Ru(bpy)_3]^{2+}$. The solvent is acetonitrile for oxidation and dimethylformamide for the reduction processes

7.2. *Bridging the Metal-Based Units*

In this kind of dendrimers (Fig. 2, type g), the metal-containing units are linked together by bridging ligands. The role played by the bridging ligands is extremely important for the following reasons: (i) their structure and the orientation of their coordination sites determine the architecture of the dendrimer, (ii) their coordinating sites contribute (together with the coordination sites of the "terminal" ligands) to influence properties of the metal-based electroactive units, and (iii) their chemical nature controls the electronic communication between the metal-based units. The bridging ligands, of course, must also satisfy requirements that make the synthetic process efficient and controllable in each step.

Figure 3 shows the doubly chelating 2,3- and 2,5-bis(2-pyridyl)pyrazine (2,3- and 2,5-dpp) bridging ligands and 2,2′-bipyridine or 2,2′-biquinoline (biq) terminal ligands, that have been used to construct most of the dendrimers of this type[28d]. Figure 6 shows different schematic representations of a dendrimer containing ten metal atoms[31,32]. For the sake of clarity, graphic representations like that shown in the middle of Fig. 6 are normally used when discussing the electrochemical behaviour of these compounds.

Each dendrimer of this family can be viewed as an ordered assembly of metal-based $[M(BL)_n(L)_{3-n}]^{2+}$ units (M = Ru(II) or Os(II); L = bpy or biq; BL = 2,3- or 2,5-dpp) which are known[28d] to exhibit reversible redox-processes. For each unit, only one, metal-based, process is observed on oxidation in the potential window usually investigated (< +2 V *vs* SCE). This process occurs at a potential which depends strongly on the nature of the metal ion (Os(II) is oxidized at less positive potentials compared to Ru(II)) and, less dramatically, on the nature of the coordinated ligands, whose electron-donor power increases in the series μ-2,5-dpp < μ-2,3-dpp < biq < bpy (alternatively, one can say that the electron-acceptor power decreases in the same series). The reduction processes are ligand-localized. The reduction potential of each ligand depends on its electronic properties and, to a smaller extent, on the nature of the metal and the other ligands coordinated to the metal. The first reduction potential becomes more negative in the ligand series μ-2,5-dpp < μ-2,3-dpp < biq < bpy. Each L ligand is reduced twice and each BL ligand is reduced four times, when coordinated to a metal ion, in the potential window –0.5/–3.1 V *vs* SCE (ref.[35]).

In the dendritic species each unit brings its own redox properties, more or less affected by component 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 very

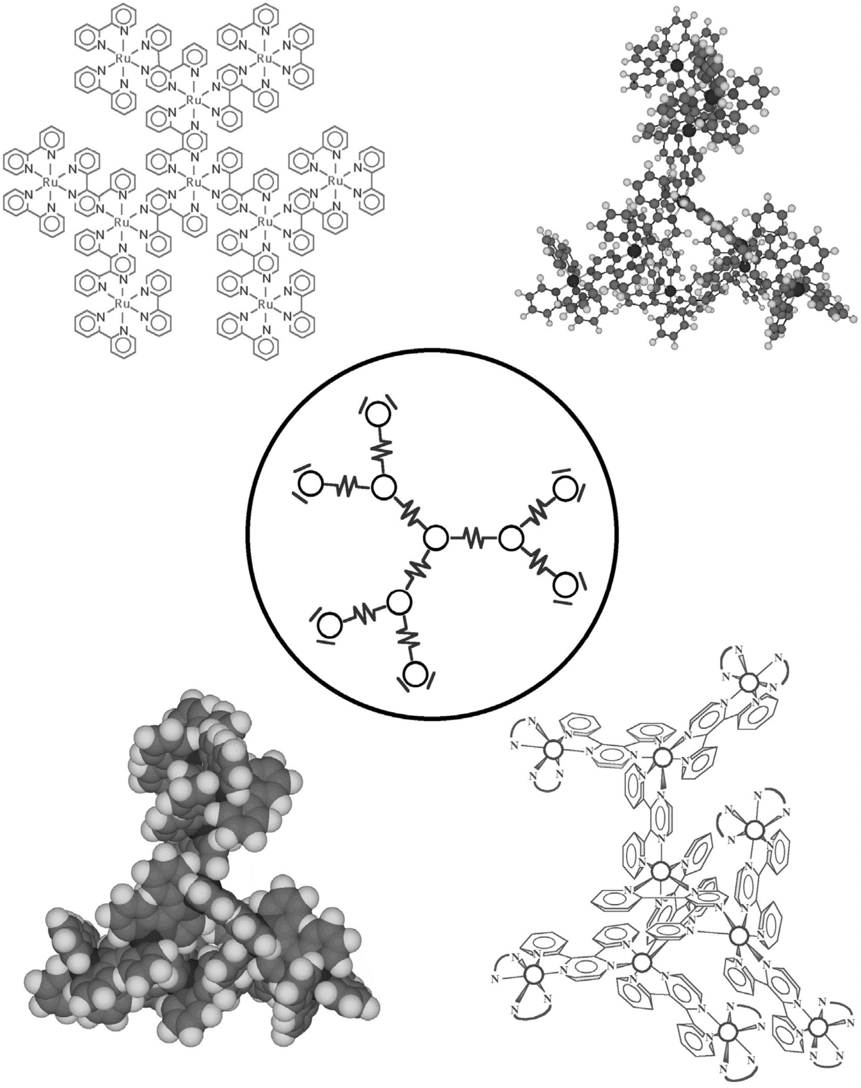


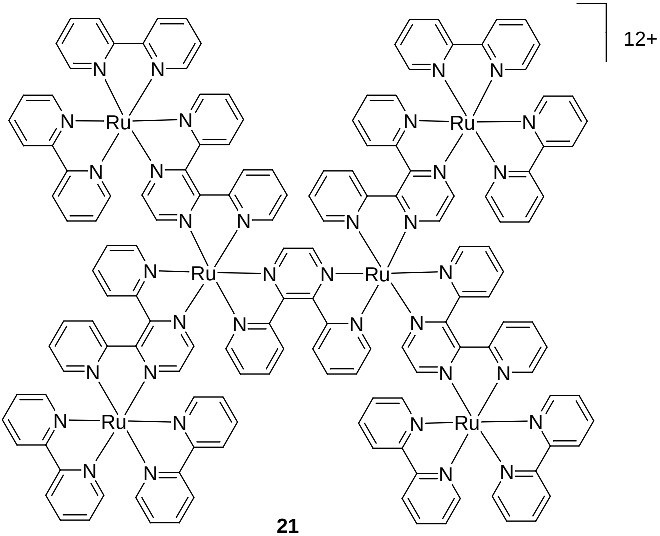
FIG. 6
Different schematic representation of a decanuclear metal-containing dendrimer. The graphic symbols used to draw the central picture are explained in Fig. 3

small for metals or ligands that are sufficiently far apart. By placing in the dendrimer the desired number of suitable equivalent and non-interacting units, it is possible to control the number of electrons lost or gained at a certain potential.

In order to illustrate the most interesting electrochemical features of this family of dendrimers, we report the results obtained for a hexanuclear complex and three strictly related decanuclear complexes.

7.3. Hexanuclear Dendrimers

The electrochemical behaviour of the small dendrimer $\{[(bpy)_2Ru(\mu\text{-}2,3\text{-}dpp)]_2Ru(\mu\text{-}2,3\text{-}dpp)Ru[(\mu\text{-}2,3\text{-}dpp)Ru(bpy)_2]_2\}^{12+}$ (**21**) has been accurately investigated in the potential window from +4.3 to –3.1 V *vs* SCE. Oxidation[36] was studied in liquid sulfur dioxide at –70 °C and reduction[37] in highly purified dimethylformamide at –55 °C.



21

On oxidation, the cyclic voltammogram of this compound (Fig. 7) shows four waves corresponding to Nernstian four-, two-, four- and four-electron transfers, respectively. Wave IV exhibits a partial chemical irreversibility. On the basis of the electrochemical behaviour of related mono- and dinuclear complexes, the observed processes have been assigned as follows. Waves I and II correspond to the simultaneous oxidation of the four external Ru(II) centres and the two internal ones, respectively. This assignment is based on the fact that the 2,3-dpp ligand has a stronger π-back-bonding power than the bpy ligand (π*-dpp levels are lower than π*-bpy ones). Therefore, the inner metals, that are bonded to three 2,3-dpp ligands, are more difficult to oxidize than the peripheral metals (coordinated only to one 2,3-dpp ligand). The first four-electron transfer was previously observed in acetonitrile[38]. The experimental observation that the oxidation of the two internal centres occurs at the same potential is surprising on the basis of electronic communication through the bridging ligand and electrostatic repulsion. It can be rationalized, considering that in the four-electron oxidized compound the four electron-withdrawing peripheral groups cause a stabilizing of the d_π orbitals of the two central Ru(II) ions and, therefore, a low overlap between the metal-d_π and π^*_{BL} orbitals. This results in a smaller interaction between the two central Ru(II) ions and in virtually coincident oxidation potentials. Finally, waves III and IV are ascribed to bpy oxidations[39].

On reduction, the cyclic voltammogram (Fig. 8a) shows six multielectron waves I–VI corresponding to a total number of twentysix successive one-electron redox processes. Waves I, IV, V, and VI correspond to four one-electron closely spaced redox processes, while II and III to five one-electron reductions each. The digital simulation of the cyclic voltammetric curve, shown in Fig. 8b, is in fairly good agreement with the experimental curve

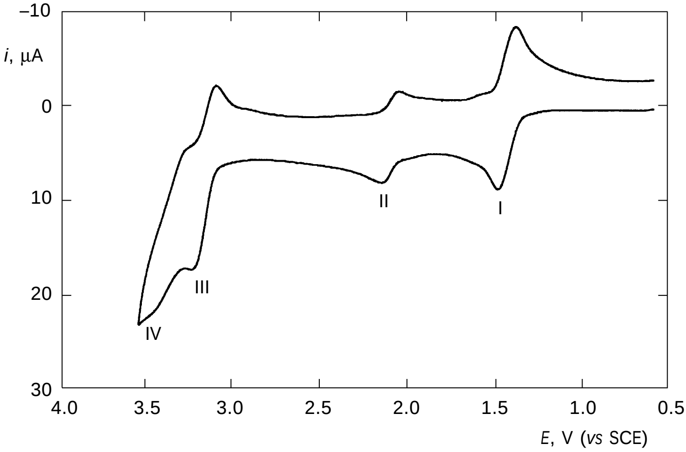


FIG. 7
Oxidation of dendrimer **21** in liquid sulfur dioxide at –70 °C

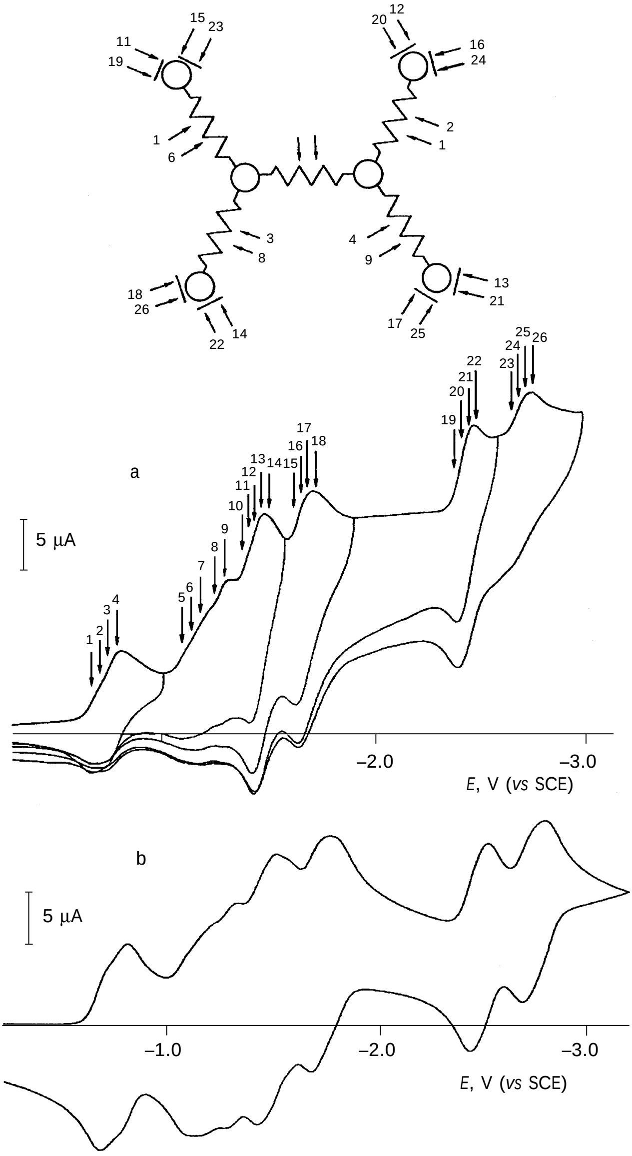


FIG. 8

a Reduction of dendrimer **21** in dimethylformamide at –55 °C; the assignment of the observed processes is shown. b Digital simulation of the cyclic voltammetric curve and shows that slow, irreversible chemical reactions are coupled to the last redox processes (those comprised in wave VI). The $E_{1/2}$ potentials for each process was obtained from the simulation. Assignment of the twentysix processes could be easily made on the basis of the patterns observed for the reduction of mono-, di-, tri-, and tetranuclear compounds of the same family[35,37]. The four processes within wave I are localized on the four outer 2,3-dpp ligands. The first out of the five processes comprised in II is localized on the central 2,3-dpp ligand. The other four processes in II represent the electron pairing into the same redox orbital of the outer 2,3-dpp ligands. The first process manifesting itself in III corresponds to the electron pairing for the central bridging ligand. The remaining four processes in III and those in IV are the first reductions of the eight bpy ligands, and the last two voltammetric waves (V and VI) involve the second reduction of the same ligands. Thus, the wide cathodic potential window explored (up to *ca* –3.1 V *vs* SCE) has allowed the observation of the most extensive ligand-centred redox series reported so far (twentysix reduction processes). The small dendrimer **21** shows as many as 40 redox processes.

7.4. Decanuclear Dendrimers

For dendrimers of higher nuclearity, only the electrochemical behaviour under normal conditions (in acetonitrile at room temperature) has usually been investigated. Very interesting oxidation patterns have been obtained for the series of decanuclear dendrimers shown in Fig. 9. In the $[Ru\{(\mu\text{-}2,3\text{-dpp})Ru[(\mu\text{-}2,3\text{-dpp})Ru(bpy)_2]_2\}_3]^{20+}$ dendrimer ($\mathbf{Ru_{10}}$, Fig. 9a)[31], the peripheral Ru-based units are expected to be oxidized at less positive potentials than the inner units, as already observed for the hexanuclear dendrimer, because the bpy ligands are worse electron acceptors than the bridging 2,3-dpp ligands. Furthermore, the six peripheral Ru-based units are not expected to interact with each other, because they are not directly linked. In accord with this expectation, the oxidation process observed for this dendrimer (+1.53 V *vs* SCE) involves the exchange of six electrons at the same potential[40].

In the $[Os\{(\mu\text{-}2,3\text{-dpp})Ru[(\mu\text{-}2,3\text{-dpp})Ru(bpy)_2]_2\}_3]^{20+}$ dendrimer ($\mathbf{Ru_9Os}$, Fig. 9b)[31a,41], which is made of the Os(II)-based core and nine Ru(II)-based units, the Os(II) centre is expected to be oxidized at less positive potentials than the nine Ru(II) centres. Furthermore, because of different electron-donor properties of the ligands, the six peripheral Ru(II) centres are expected to be oxidized at less positive potentials than the three intermediate Ru(II) centres. Since the core and the peripheral units are not directly linked, they are not expected to affect each other. Therefore, a 1 : 6 pattern is predicted for the electrons exchanged on oxidation. In agreement with these expectations, this compound shows a one-electron process at +1.35 V and a six-electron process at +1.55 V (*vs* SCE). On the basis of the potential values and the number of electrons exchanged, the former process can be

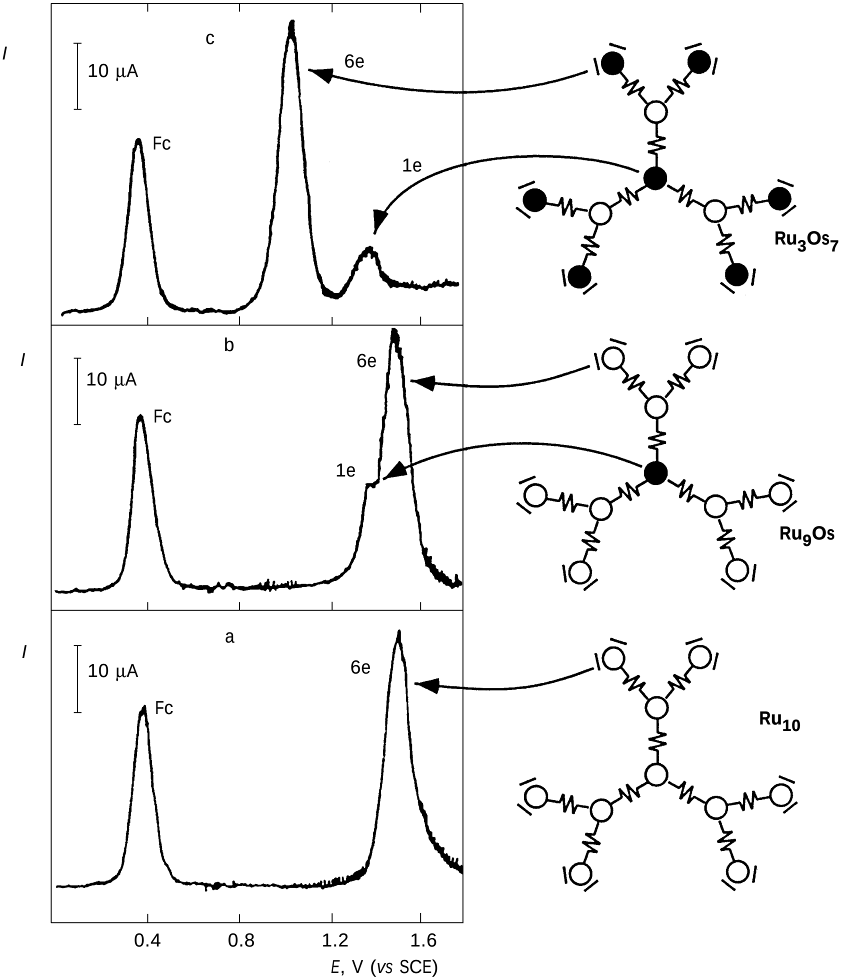


Fig. 9
Oxidation patterns (differential pulse voltammetric peaks) for three decanuclear dendrimers. Peak Fc indicates oxidation of ferrocene used as internal standard

assigned to oxidation of the central Os(II) metal ion and the latter to the simultaneous one-electron oxidation of the six peripheral non-interacting Ru(II) ions. Oxidation of the three intermediate Ru(II) ions is further shifted to more positive potentials and cannot be observed in the potential window accessible in acetonitrile solution.

For the $[Os\{(\mu\text{-}2,3\text{-dpp})Ru[(\mu\text{-}2,3\text{-dpp})Os(bpy)_2]_2\}_3]^{20+}$ dendrimer (**Ru_3Os_7**, Fig. 9c)[31a], made of the Os(II)-based core, three Ru(II)-based units in the intermediate positions, and six Os(II)-based units in the peripheral positions, one may expect that oxidation involves first the six peripheral Os(II) ions (which contain the weaker π-acceptor bpy ligand in their coordination sphere), and then the central ion, yielding for the electron exchange a 6 : 1 pattern instead of the 1 : 6 one observed in the case of **Ru_9Os**. This expectation is fully consistent with the experimental results that show a six-electron process at +1.05 V and a one-electron process at +1.39 V (*vs* SCE). Oxidation of the intermediate Ru(II)-based units is not observed in the potential window accessible in acetonitrile solution.

In larger dendrimers, the number of equivalent units becomes huge and a variety of electron exchanged patterns can be expected. In the docosanuclear dendrimer made of the Os(II)-based core and twentyone Ru(II)-based units, one-electron oxidation at +1.42 V (*vs* SCE), localized at the Os(II) ion, is followed by a 12-electron process at +1.54 V (*vs* SCE), due to the simultaneous oxidation of the 12 equivalent and non-interacting peripheral Ru(II)-based units[41]. The situation is even more complex as far as reduction is concerned, because each ligand can exchange at least two electrons.

In conclusion, the knowledge of electrochemical properties of the mononuclear component $[M(BL)_n(L)_{3-n}]^{2+}$ units and the synthetic control of the supramolecular structure allow to design dendrimers with predetermined redox patterns. The tailor-made synthesis of systems with reversible exchange (storage and release) of a controlled number of electrons at a certain potential is an attractive goal for the design of molecular batteries and multielectron-transfer catalysts. It should also be noted that the electrochemical data offer a fingerprint of the chemical and topological structure of the dendrimers.

8. CONCLUSIONS

Two of the most important research fields of modern chemistry are artificial photosynthesis[10] and information processing at the molecular level[42]. The achievement of these two goals is related to the construction of molecular-level devices capable of processing photon and/or electron inputs in a suitable way. As reported elsewhere[8], suitably designed dendrimers containing specific transition metal-based units at appropriate places of a three-dimensional structure can harvest sunlight and process light signals. In this paper we have shown that such dendrimers can exchange large, well defined numbers of electrons according to a variety of predetermined patterns, which will likely lead to applications in the fields of molecular batteries and multielectron catalysis. Furthermore, potentially electroactive units, when placed in a dendrimer core, can be insulated so as to become a site for information (charge) storage. Because of these and other not yet fully investigated properties (*e.g.*, non-linear optics), we can expect that research on dendrimers containing electro- and photoactive units will become the object of increasing interest in the next few years.

We thank the University of Bologna (Funds for Selected Research Topics), MURST (Artificial Photosynthesis Project) and CNR (Sensori Fluorescenti Supramolecolari) for financial support.

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