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Redox-active ferrocenyl dendrimers and polymers in solution and immobilised on electrode surfaces

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Contents

Abstract

This article reviews the electrochemical properties of different families of redox-active silicon- and amine-based ferrocenyl polymers and dendrimers prepared in our laboratory

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over the last few years. The electrochemical behaviour of the ferrocenyl polymers both in solution and immobilised on the electrode depends on the polymer structure. Solution electrochemical studies of silicon-based ferrocenyl polymers showed that all the redox centres were electrochemically independent and that polymers containing pendant ferrocenyl moieties undergo oxidative precipitation, yielding polymer films on electrode surfaces. The application of electrodes modified with a ferrocenyl polymer containing octakis(dimethylsiloxy)-octasilsesquioxane as framework, as mediator in the electrocatalytic oxidation of ascorbic acid is described. The electrochemical behaviour of silicon- and amine-based dendrimers in which ferrocenyl moieties behave as electronically isolated centres, and also of dendritic macromolecules containing interacting ferrocenyl units has been studied. The feasibility of modifying electrode surfaces with these redox-active metallo-dendrimers containing a controlled number of metal centres has been demonstrated. The application of ferrocenyl dendrimers as electron transfer mediators in amperometric biosensors and in the electrochemical recognition of anions, as well as the use of dendritic terminal ferrocenyl groups for inclusion complexation by cyclodextrins has been outlined.

Keywords: Electrochemistry; Ferrocene; Polymers; Dendrimers; Silicon; Modified electrodes

1. Introduction

Over the past decades, organometallic polymers have emerged as an important category of new materials. The interest in developing these materials resulted from the fact that the incorporation of transition metals into polymeric structures allows access to materials with unusual and attractive characteristics including electrical, magnetic, preceramic and catalytic properties, and non-linear optical (NLO) effects [1–6].

In the last several years, our group began a research with the goal of synthesising new types of redox-active organometallic polymers derived from metal–cyclopentadienyl and metal–arenes, from silicon-containing monomers and dimers functionalised with easily polymerisable groups. In this way, we have reported the synthesis of some siloxanyl polymeric compounds containing $[(\eta^5\text{-}C_5R_4)Fe(CO)(\mu\text{-}CO)]_2$ $(R = H, Me)$ and $[(\eta^6\text{-arene})Cr(CO)_3]$ moieties along the backbone, which display interesting electrochemical properties [7,8].

On the other hand, the ferrocene entity has proved to be a versatile building block with excellent thermal and photochemical stability, which displays a reversible redox reaction in organic solvents. Thus, ferrocene-containing polymers are currently receiving much attention due to their increasing role in the rapidly growing area of materials science [9]. With this in mind, and in order to extend our investigations on organometallic polymers, we have recently reported the synthesis and electrochemical behaviour of new classes of ferrocenyl polymers with linear [10], cyclic [11] and polyhedral [12] siloxanes as frameworks.

Over the past few years the development of a new class of well-defined tree-like macromolecules, known as dendrimers, has become an area of growing interest

[13–19]. Dendrimers are nano-sized, highly branched molecules emanating from a central core to a periphery that becomes more dense with increasing generation number. Recently, the emphasis has been focused on the modification of the properties of dendritic molecules by either the introduction of internal functionalities into the dendrimer structure or the functionalisation of dendritic surfaces. In particular, the incorporation of metal centres within or on the periphery of dendritic structures is now attracting widespread attention [19–47], as it provides access to materials capable of novel magnetic, electronic, photo-optical or catalytic properties. Likewise, the properties of dendrimers containing redox-active units are of great interest because the number of electrochemically active functional groups can be precisely controlled. Thus, redox-active dendrimers are good candidates to play a key role as multielectron transfer mediators in electrocatalytic processes of biological and industrial importance.

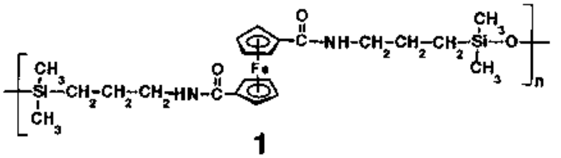
Over the last few years, several families of organometallic dendrimers have been prepared in our laboratory by surface functionalisation of silicon and amine-based dendritic structures with ferrocene, cobaltocenium, cyclopentadienyl, chromium, iron and cobalt carbonyl moieties [19,36–47]. In particular, ferrocenyl-containing dendrimers represented the first target organometallic dendritic molecules. The same reasons for the interest in incorporating ferrocene units into polymers also provided us motivation for the synthesis of dendritic macromolecules of well-defined size and structure containing ferrocenyl units. Such macromolecules raise the possibility of combining the unique and valuable redox properties associated with the ferrocene nucleus with the highly structured macromolecular chemistry. This may afford entrance to materials of nanoscopic-size possessing unusual symmetrical architectures, as well as specific physical and chemical properties, which would be expected to differ from those of the ferrocene-containing materials prepared to date.

This article is an overview of our most recent work on ferrocenyl polymers and dendrimers and in particular, summarises our efforts to understand the relationship between the structure and the redox properties of these ferrocene-based materials.

2. Silicon-based ferrocenyl polymers

Two different synthetic routes were developed for incorporating ferrocenyl moieties into silicon-containing polymer backbones.

The first method consisted of exploiting the ability of chlorocarbonylferrocene and 1,1′-bis(chlorocarbonyl)ferrocene on one hand, and β-aminoethylferrocene and 1,1′-bis(β-aminoethyl)ferrocene on the other, to undergo classical condensation reactions, with amine- and acid chloride-functionalised siloxanes, respectively. This approach has provided access to polyamides **1**–**2** in which the amide-linked ferrocenyl moieties are part of the main polymer chain, and also to a series of poly(methylsiloxanes) **3**–**6**, containing pendant ferrocenyl moieties attached to the polymer backbone through amide linkages, with varying degrees of ferrocene substitution [10].



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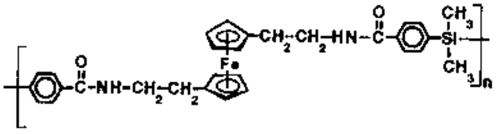

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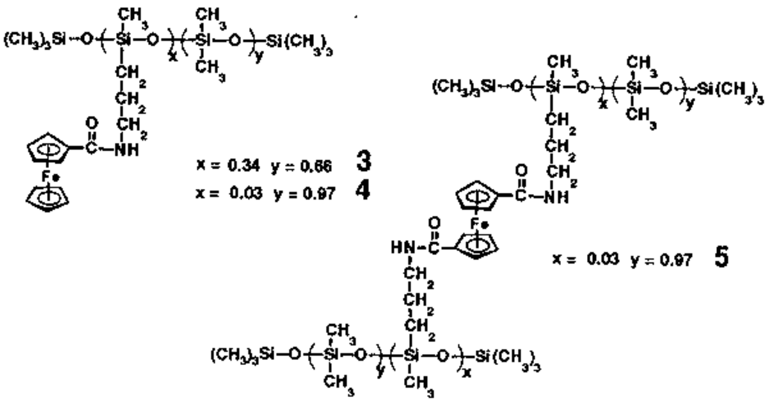
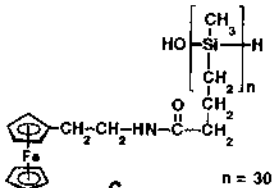


x = 0.34 y = 0.66 **3**

x = 0.03 y = 0.97 **4**

x = 0.03 y = 0.97 **5**



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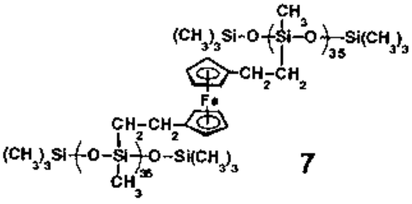
n = 30



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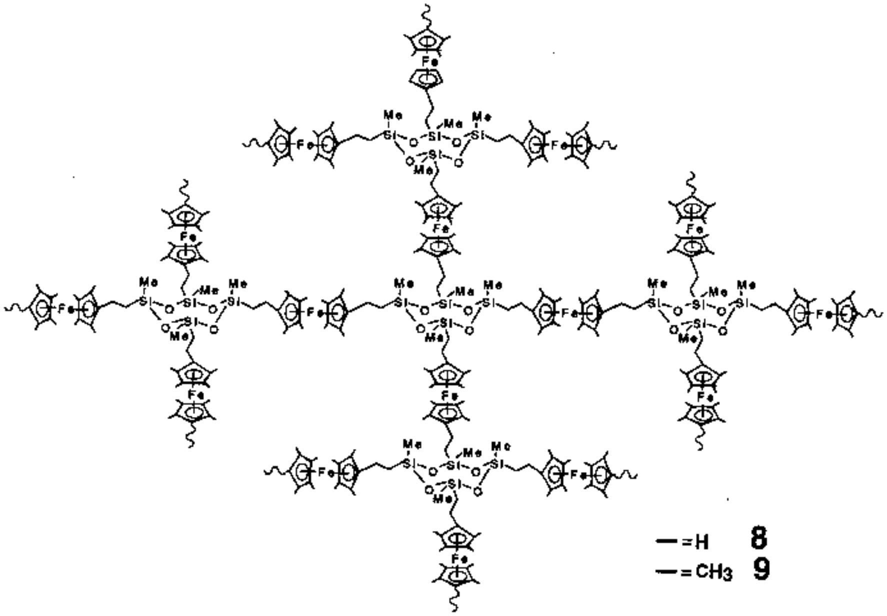
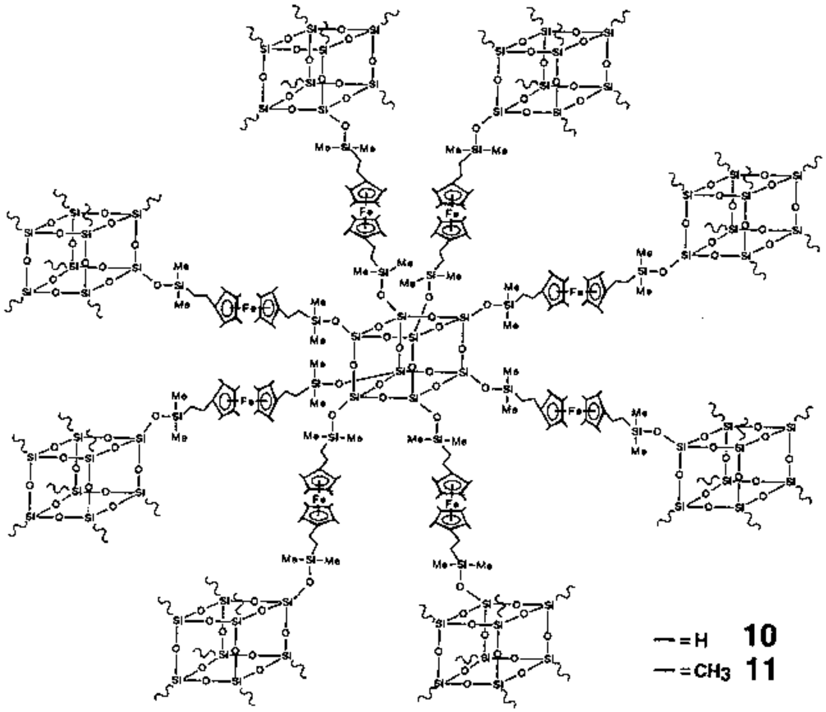
Likewise, hydrosilylation reactions of vinyl-substituted ferrocenyl monomers with Si–H functionalised frameworks also represent a second versatile synthetic route for the preparation of new organometallic polymers. In this way, redox-active ferrocenyl polymers constructed from linear siloxanes (**7**), cyclosiloxanes (**8**–**9**) and silsesquioxanes (**10**–**11**) have been prepared [11,12].



— =H **8**
— =CH3 **9**



— =H **10**
— =CH3 **11**

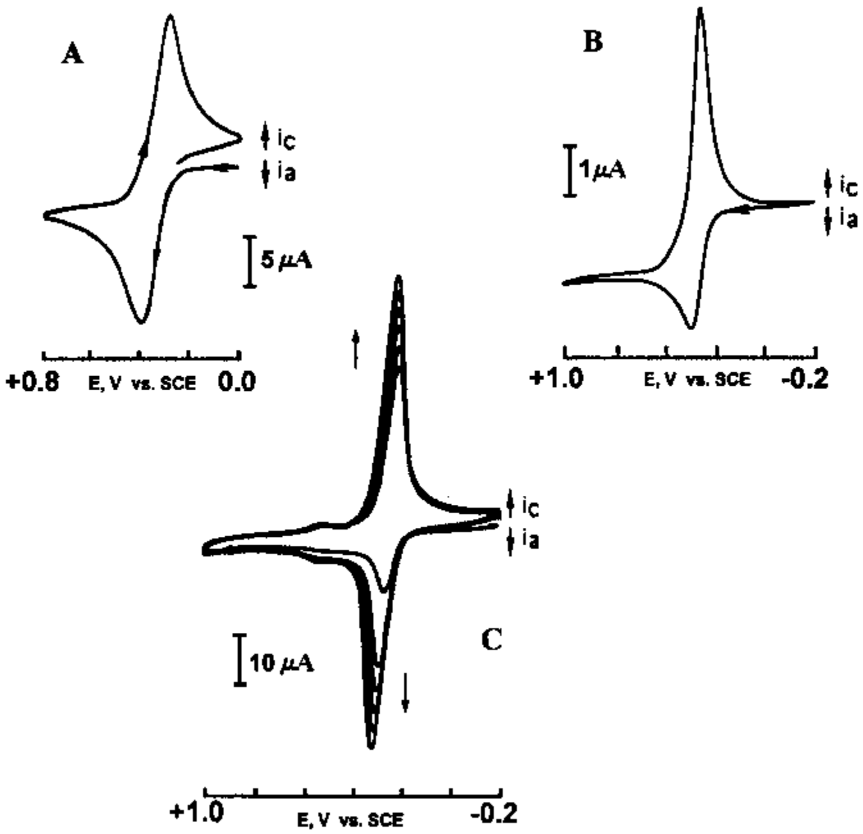


Fig. 1. Cyclic voltammograms in CH_2Cl_2/0.1 M TBAH solution at a Pt disk electrode of (A) polymer **1**, (B) polymer **6**, (C) polymer **8**, consecutive scans. Scan rate for A and B 50 mV s^{-1}, for C 100 mV s^{-1}.

2.1. Redox behaviour in solution

The electrochemical behaviour of the silicon-based ferrocenyl polymers **1**–**11** dissolved in CH_2Cl_2, THF or DMF containing 0.1 M Bu_4NPF_6 (TBAH), was studied by cyclic voltammetry, at platinum, gold or glassy carbon electrodes [10–12]. Interestingly, the solution redox behaviour of these polymers seems to depend on the polymer structure. Thus, although each one of the polymers exhibits particular features, such as formal potential values $E°$, two different types of cyclic voltammetric behaviours have been observed which are illustrated in Fig. 1.

Polymers **1** and **2**, with electroactive ferrocenyl moieties fixed in the main polymer chain exhibit a single reversible oxidation process (Fig. 1A), indicating that all the iron centres are essentially non-interacting [48]. Moreover, oxidation and reduction in CH_2Cl_2, THF or DMF solutions, does not affect the solubility of these polymers. The cyclic voltammograms (CVs) have the characteristics of one-electron,

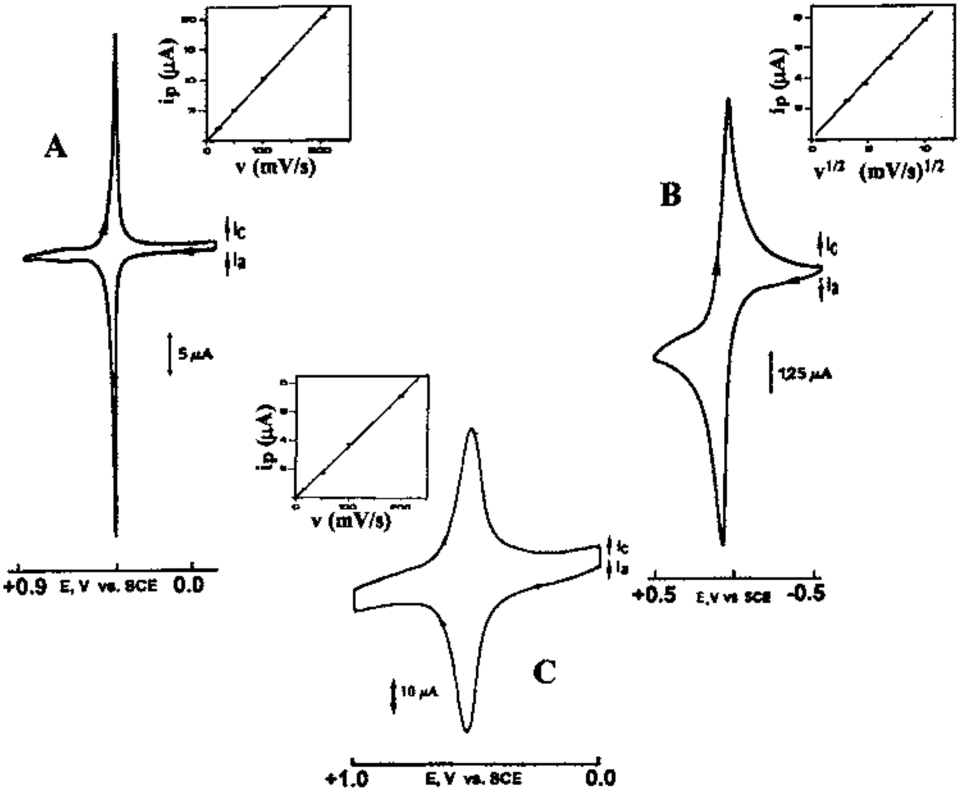


Fig. 2. Cyclic voltammograms at 100 mV s^{-1} in CH_3CN/0.1 M TBAH, of Pt disk electrodes modified with electro-deposited films of (A) polymer **8**, $\Gamma = 1.46 \times 10^{-8}$ mol Fc cm^{-2}, (B) polymer **9**, $\Gamma = 7.11 \times 10^{-8}$ mol Fc cm^{-2} (C) polymer **7**, $\Gamma = 6.65 \times 10^{-9}$ mol Fc cm^{-2}. Insets: plots of peak current vs. sweep rate (adapted from Ref. [11]).

reversible, Nernstian redox couples, and no increase of the peak current upon continuous scanning was detected. Therefore, **1** and **2** do not appear to precipitate when present as oxidised polymers.

In contrast, for polymers **3**–**7**, in which the electroactive ferrocenyl groups are more free to rotate as side chains, and polymers **8**–**11**, with cyclic and polyhedral siloxanes as frameworks, changes in solubility with the change in the oxidation state in the ferrocene units, were observed (Fig. 1B and 1C). Thus, in CH_2Cl_2 and THF solutions, although the anodic wave has the form required if transport to the electrode is controlled by diffusion, the cathodic wave does not. The shape of the reduction peak is characteristic of redox couples in which the oxidised form is insoluble and the reduced form is soluble, i.e. a stripping peak. In addition, upon continuous scanning, there is an increase in the peak current with each successive scan, which indicates that formation of an electroactive polymer film occurs on the electrode surface (Fig. 1C).

For the silicon-based ferrocenyl polymers that undergo oxidative precipitation, the number of electrons in the process has been estimated by using the normal pulse voltammetry (NPV) technique. From the normal pulse voltammograms, the values of the slopes of the plots E vs. $\log[(i_{\text{lim}} - i)/i]$ are in the range of 75–80 mV. Thus, all the ferrocenyl redox-active units in these polymers behave independently, and exchange electrons with the electrode in a wave characteristic of a one-electron process.

2.2. Modification of electrode surfaces

For the ferrocenyl polymers **3**–**11**, the oxidative deposition effects observed in the solution voltammetric studies described above, have allowed the preparation of polymer-modified electrode surfaces [10–12]. Films of these polymers were electrodeposited on platinum surfaces by continuous scanning (at 50 or 100 mV s^{-1}) between the appropriate potential limits, in degassed CH_2Cl_2 or THF polymer-containing solutions with 0.1 M TBAH. Electrodes thus coated were rinsed with CH_2Cl_2 or THF to remove any adhering solution, and dried in air. Ferrocenyl polymer films were characterised by cyclic voltammetry in fresh CH_2Cl_2 or CH_3CN solutions containing only supporting electrolyte. Some of the more representative redox responses of electrodes modified with these ferrocenyl polymers are shown in Fig. 2. In all CVs, reversible redox waves with potential values corresponding to the ferrocene/ferricenium system are observed. However, the shapes and features of these waves are quite different, and this seems to be strongly related with the polymer structure and also with the nature of the substituents on the cyclopentadienyl rings. For example, Fig. 2A corresponds to an electrode modified with the ferrocenyl polymer **8**, which contains tetracyclosiloxane backbones. A very sharp oxidation–reduction wave is observed, with a linear relationship of peak current with potential sweep rate v, typical of surface-confined redox couples [49–51]. The anodic and cathodic wave shapes are extremely narrow, and values of the full width at half maximum, $\Delta E_{\text{FWHM}} \approx$ 5 mV, are measured at a scan rate of 20 mV s^{-1}, which reflect attractive interactions among the ferrocene sites and suggest a phase transition.

There is a substantial difference in the redox response of electrodes modified with films of polymer **9**, containing permethylated ferrocenyl units, in comparison with the analogous non-methylated **8**. Thus, the surface redox wave observed for films of **9** is broader and shows diffusional features (Fig. 2B). In addition, at scan rates between 10 and 300 mV s^{-1}, the peak current increases linearly with the square root of the sweep rate $v^{1/2}$, which suggests that in this case the charge transport through the film is limited by the electrolyte diffusion into the polymer film. This can be attributed to the less porous morphology of the polymer film. For the voltammetric peaks of films of the permethylated polymer, a ΔE_{FWHM} value of ca. 125 mV was measured at 20 mV s^{-1}, which indicates repulsive interactions. It is interesting to note that a formal potential value of $E_{1/2} = +0.05$ V vs. SCE was found for films of this polymer, which is considerably more negative than that of films of the non-methylated ferrocenyl polymer **8** ($E_{1/2} = +0.35$ V). This lower redox potential for electrodes modified with the methylated polymer is due to the enhanced electron donating ability of the permethylated cyclopentadienyl rings. To our knowledge this was the first example of electrodes derivatised with an octamethylated ferrocenyl polymer.

The third example included in Fig. 2C corresponds to polymer **7** in which each ferrocenyl moiety is linked to two different linear chains of polymethylsiloxanes. Films of this polymer exhibit voltammetric responses very similar to the ideal behaviour predicted for surface confined species. Thus, the ferrocene oxidation and ferricenium reduction peaks are symmetric with a ΔE_{FWHM} of ca. 90 mV and no splitting between the oxidation and reduction peaks is observed. This is the behaviour expected for non-interacting electroactive groups attached to the surface and in rapid equilibrium with the electrode.

We have also checked the stability of some of these ferrocenyl polymers-modified electrodes in aqueous media [45]. The voltammetric response of an electro-deposited film of the polymer **10**, constructed from a cubic silsesquioxane, in aqueous solution (0.5 M acetic acid, 0.1 M $LiClO_4$) is shown in Fig. 3. A well-defined, symmetrical oxidation–reduction wave is observed, with the expected linear relationship of peak current with potential sweep rate v. The sur-

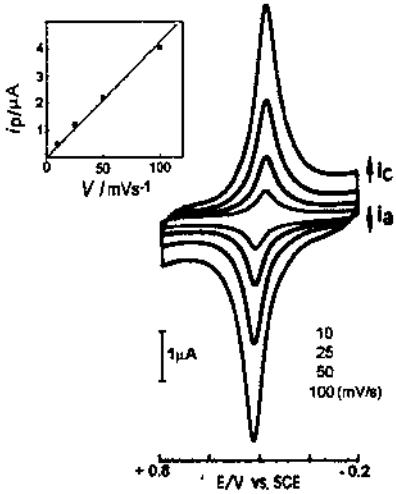


Fig. 3. Cyclic voltammogram of a glassy carbon electrode modified with a film of polymer **10**, measured in 0.5 M acetic acid solution with 0.1 M $LiClO_4$ (adapted from Ref. [45]).

face coverage of electroactive ferrocenyl sites in the polymer film Γ (mol cm^{-2}), was determined from the integrated charge of the cyclic voltammetric wave resulting in a value of 8.9×10^{-7} mol Fc cm^{-2}.

One remarkable feature of electrodes modified with films of these silicon-based ferrocenyl polymers is that they are very stable and reproducible. Indeed, cyclic voltammetric scans can be carried out in either organic or aqueous electrolyte solutions hundreds of times with no loss of electroactivity. The electroactivity of the modified electrodes was retained after storage in air several weeks after preparation.

2.2.1. Catalysis of ascorbic acid

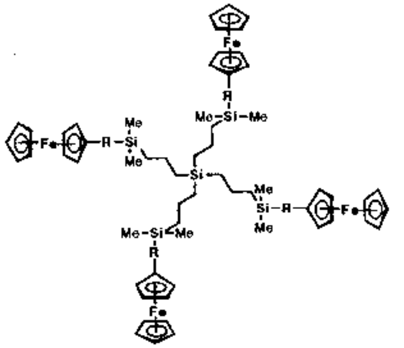
One of the most important properties of chemically modified electrodes is their potential ability to mediate the electrolysis of solutes whose oxidation or reduction occurs only slowly at the corresponding bare electrode surfaces. For this reason, we decided to examine the ability of the electrodes modified with films of the ferrocenyl octasilsesquioxane-based polymer **10** to catalyse the ascorbic acid oxidation [45]. The results displayed in Fig. 4 indicate that electrodes modified with films of **10** are effective in the electrocatalytic oxidation of ascorbic acid. The curve A represents the voltammetric response at a platinum electrode modified with a film of **10** in 0.1 M acetic buffer. The curve B represents the voltammetric response of the ascorbic acid (10^{-3}M) in 0.1 M acetic buffer at the same modified electrode. It can be observed that the anodic peak current of the ferrocenyl polymer film is greatly enhanced while the corresponding cathodic wave disappears, which is consistent with a catalytic process. Catalytic activity of the ferrocenyl polymer modified electrode is confirmed by the decrease in the oxidation potential (225 mV) and by the increase of the anodic peak current relative to the oxidation of the ascorbic acid at a bare electrode in the same medium (curve C in Fig. 4).

3. Ferrocenyl dendrimers

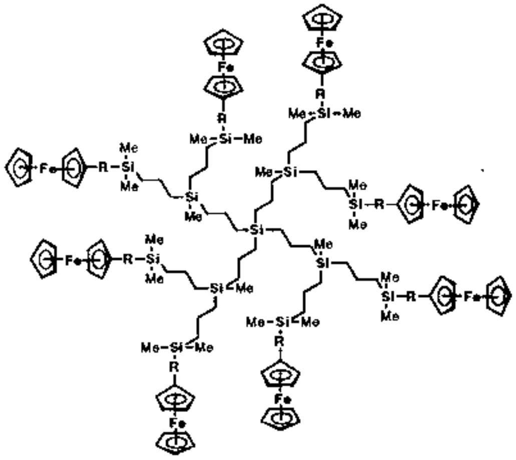
A synthetic challenging target is the construction of dendrimers containing organometallic moieties that undergo reversible multielectron redox processes, and exhibiting predetermined redox patterns. To pursue this aim, we have followed three different synthetic strategies to build up ferrocenyl dendrimers of varying constitution and sizes, capable of acting as multielectron sources or reservoirs, where the redox groups may act independently in multielectron processes or in contrast, they may interact with one another [19,36–39,42–46].

3.1. Silicon-based ferrocenyl dendrimers constructed via a divergent approach

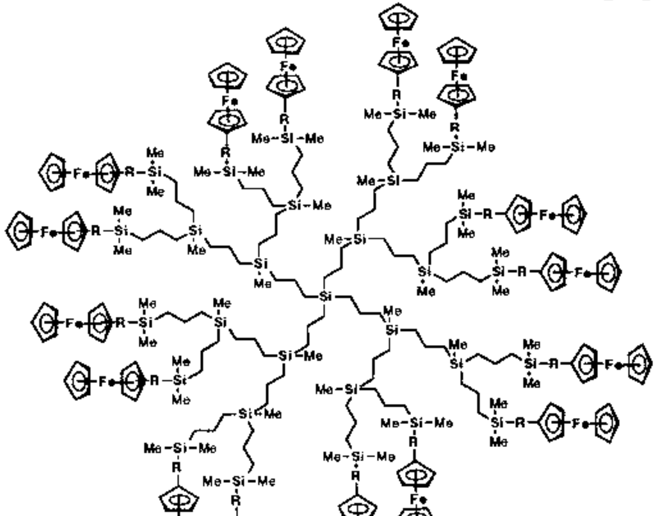
By using a divergent approach [52–54], four different families of silicon-based ferrocenyl dendritic macromolecules possessing four, eight and 16 peripheral ferrocenyl units have been prepared starting from tetraallylsilane and tetramethylcyclotetrasiloxane as four-directional centres of branching [19,44,45].



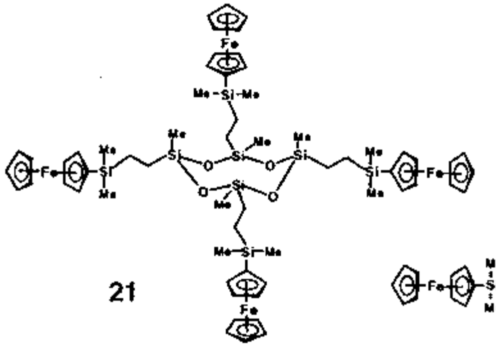
R = — **12**
R = CH₂CH₂ **15**
R = NHCH₂CH₂ **18**



R = — **13**
R = CH₂CH₂ **16**
R = NHCH₂CH₂ **19**



R = — **14**
R = CH₂CH₂ **17**
R = NHCH₂CH₂ **20**



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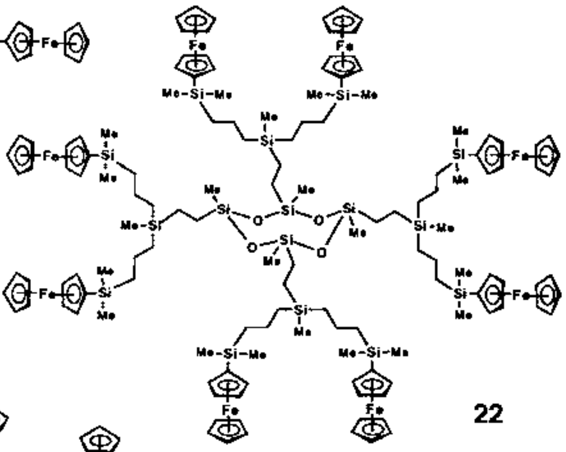

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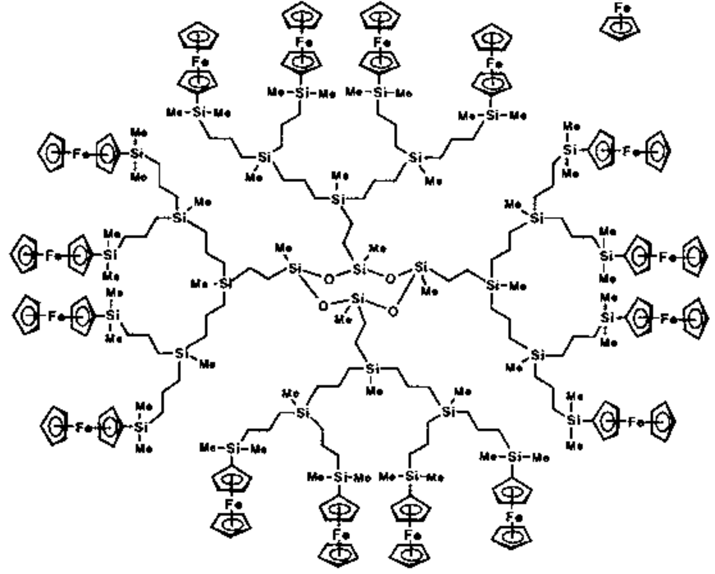

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In these molecules, the ferrocenyl moieties are linked to the organosilicon dendritic framework through spacers of different nature and length. Thus, in dendrimers **12**–**14** and **21**–**23**, ferrocenyl units are directly bonded to the external silicon atoms, while for **15**–**17** the ferrocenyl moieties are attached to the dendritic surface through a two-methylene flexible spacer, and finally **18**–**20** contain N–H linked ethylferrocenyl moieties.

The redox behaviour of these metallodendrimers has been studied by cyclic voltammetry, differential pulse voltammetry and bulk coulometry [19,43,45]. The CVs show a single reversible oxidation process at potentials that depend on the

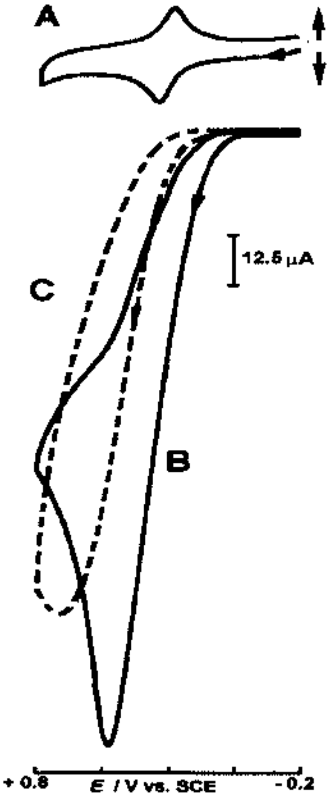


Fig. 4. Cyclic voltammogram in 0.1 M acetate buffer + 0.1 M $LiClO_4$ of: (A) a glassy carbon electrode modified with polymer **10**, (B) same electrode as in A with 10^{-3} M ascorbic acid, (C) a bare glassy carbon electrode in 10^{-3} M ascorbic acid (adapted from Ref. [45]).

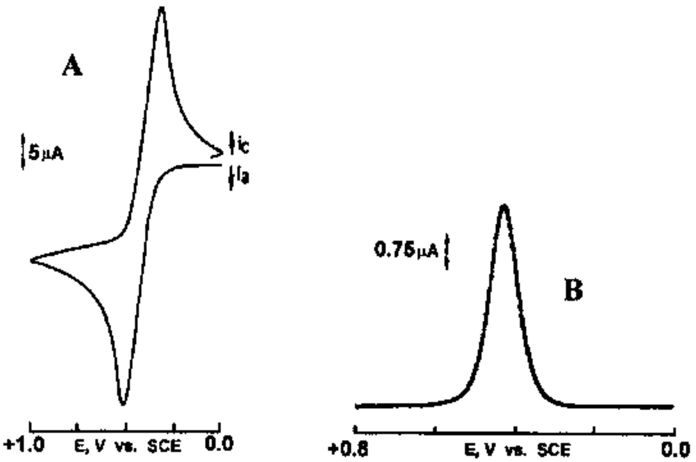


Fig. 5. (A) Cyclic voltammogram at a Pt disk electrode of dendrimer **13** in CH_2Cl_2/0.1 M TBAH solution, (B) differential pulse voltammogram of **13** in CH_2Cl_2/CH_3CN (14:1), 0.1 M TBAH solution.

electron donating ability of the different substituents attached to the ferrocenyl moieties (see a representative example in Fig. 5A). In addition, in the differential pulse voltammograms only one oxidation wave is observed (Fig. 5B), which clearly shows that the reversible oxidation wave observed, corresponds to a simultaneous multielectron transfer of four, eight or 16 electrons, depending on the dendrimer. Therefore, the multiple iron centres in each dendrimer are essentially non-interacting. Particularly, we note that for dendrimers **12**–**17** and **21**–**23**, careful coulometry measurements not only result in the removal of the expected number of electrons for all the peripheral ferrocenyl groups (four, eight or 16 electrons per molecule), but in addition reelectrolysis quantitatively regenerated the starting neutral polynuclear compounds.

These polyferricenium cations have been also prepared by chemical oxidation of the neutral dendrimers with $NOPF_6$ and have been characterised by UV–Vis and IR spectroscopy and EPR [19,43].

Without doubt, the most noteworthy aspect of the redox behaviour of some of these dendritic macromolecules is their ability to modify electrode surfaces. And thus, we have successfully prepared the first example of electrodes derivatised with organometallic dendrimers containing a well-defined number of redox centres [43].

The ferrocenyl dendrimers (**12**–**20**) were electro-deposited in their oxidised forms onto electrode surfaces either by controlled potential electrolysis or by repeated cycling between the appropriate anodic and cathodic potential limits; therefore, the amount of electroactive material electro-deposited can be controlled with the electrolysis time or the number of scans. The electrochemical behaviour of films of the polyferrocenyl dendrimers was studied by cyclic voltammetry in dendrimer-free CH_2Cl_2 and CH_3CN solutions. The voltammetric response of an electro-deposited film of dendrimer **13** in different solvents is shown in Fig. 6 as a representative example. In a CH_2Cl_2 solution containing only supporting electrolyte (Fig. 6A), a well-defined, symmetrical oxidation–reduction wave is observed, which is characteristic of surface-immobilised reversible redox couples, with the expected linear relationship of peak current with potential sweep rate v. The electroactive dendrimer film behaved almost ideally with rapid charge transfer kinetics. These voltammetric features unequivocally indicate the surface-confined nature of the electroactive ferrocenyl moieties in the dendrimer. Surface coverage of electroactive ferrocenyl sites in the film $\Gamma = 2.01 \times 10^{-10}$ (mol cm^{-2}), was determined from the integrated charge of the cyclic voltammetric wave. The electrochemical response of this octanuclear dendrimer films is solvent-dependent as in contrast to the electrochemical behaviour exhibited in CH_2Cl_2, a narrower surface redox wave is observed in CH_3CN likely due to the poor solvating effect of the CH_3CN solution (Fig. 6B).

One of the most noteworthy features of Pt electrodes modified with films of these dendrimers is that they are extremely durable and reproducible. Cyclic voltammetric scans can be carried out in either organic or aqueous electrolyte solutions hundreds of times with no loss of electroactivity. In addition, the wave shapes as well as the surface coverages are reproducible for a number of independent preparations.

Ferrocenyl dendrimers also afford electroactive films on indium tin oxide (ITO) electrodes (Fig. 7B). UV–vis spectroelectrochemical measurements of this modified

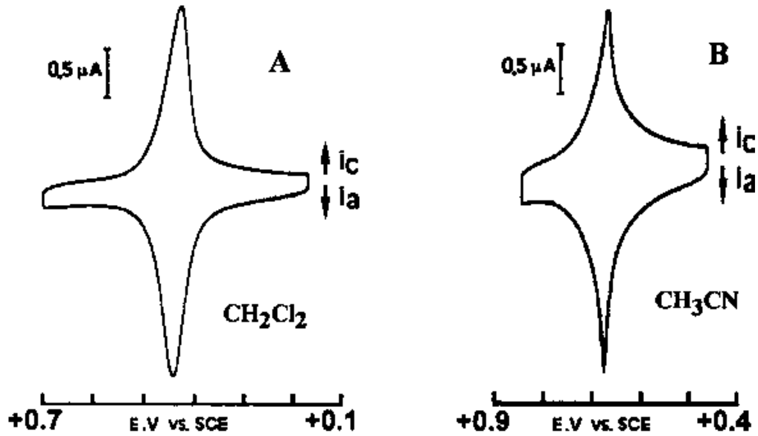


Fig. 6. Cyclic voltammograms of a Pt disk electrode modified with dendrimer **13** (A) measured in CH_2Cl_2/0.1 M TBAH, (B) measured in CH_3CN/0.1 M TBAH.

electrodes on oxidation show changes characteristic for the formation of ferricenium cations. Thus, Fig. 7A shows the UV–vis absorption spectrum of a film of **13** electro-deposited on a transparent ITO electrode (measured after the film was

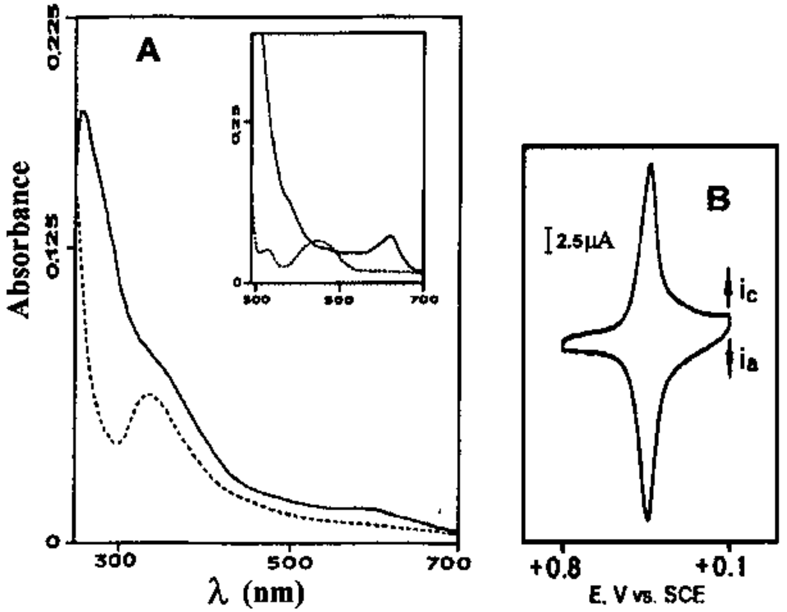


Fig. 7. (A) UV–vis spectra of a film of an ITO electrode modified with dendrimer **13**, measured after the film was oxidised at + 0.70 V (—) and subsequently reduced at 0.0 V (---). Inset: UV–vis spectra of **[13^{8+}][PF_6^-]** (—) and **13** (---) in CH_2Cl_2 solution, (B) cyclic voltammogram of an ITO electrode modified with a film of **13** measured in CH_2Cl_2/0.1 M TBAH (adapted from Refs. [19,43]).

oxidised at an E_{appl} of $+0.7$ V), which exhibits a strong band at 260 nm and a weak absorption band centred at 600 nm that agree with those observed for the cationic dendrimer $\mathbf{[13^{8+}][PF_6^-]_8}$ in solution (Fig. 7A, inset), obtained by chemical oxidation of the corresponding neutral dendrimer with $NOPF_6$ [19,43].

It is interesting to note that in contrast to the results commented above, for ferrocenyl dendrimers **21**–**23** grown from tetramethylcyclotetrasiloxane as core, oxidation and reduction does not affect the solubility of the dendrimers, so that no oxidised dendritic material deposits on the electrode surface [45]. This can be attributable to the cyclosiloxane nature of the dendritic core, which modifies the oxidised peripheral ferrocenes/solvent interaction in a manner that keeps the dendrimer in solution.

3.1.1. Ferrocenyl dendrimers as mediators in amperometric biosensors

Over the last few years, amperometric enzyme electrodes with electroactive species acting as mediators replacing the natural electron acceptor, dissolved oxygen, have been developed. Monomeric mediators, such as ferrocene, were initially used as electron-shuttling redox couples. The solubility of the oxidised form would inevitably be a source of long-term instability, due to loss of ferricenium ions that can diffuse away from the electrode surface. Increasing the molecular weight of the mediator should significantly decrease this possible loss.

Potentially, our ferrocene-containing dendritic macromolecules with relatively high molecular weights and in which the ferrocenyl units are at the end of long flexible silicon-containing branches, can serve to electrically connect the enzyme, facilitating a flow of electrons from the enzyme to the electrode. For this reason, in order to test the ability of ferrocenyl dendrimers to act as electron mediating species, a study of the efficiency of dendrimer/glucose–oxidase/carbon paste electrodes was undertaken [19,42]. Some of the most significant results for dendrimers **12**, **13**, **15** and **16** of this study are illustrated in Fig. 8.

Cyclic voltammograms of these carbon paste electrodes show that the addition of glucose leads to the enhancement of the oxidation current, while cathodic current is not observed (Fig. 8A). This fact is indicative of enzyme-dependent catalytic reduction of the ferricenium cations. In addition, the electrodes are clearly sensitive to small changes in glucose concentration, and display a good response over long periods of time. Dependence of glucose response on dendrimer structure has been examined. For equimolar amounts of the ferrocene moieties, the octanuclear dendrimers **13** and **16**, possessing the longer organosilicon branches, have proved to mediate electron transfer more efficiently than the relay systems based on the tetranuclear dendrimers **12** and **15** (Fig. 8B and C). On the other hand, it is clear that dendrimers **15** and **16**, in which the ferrocenyl units are attached to the dendritic framework through a two methylene flexible spacer, are more effective at mediating electron transfer between reduced glucose oxidase and the carbon paste electrode, than the respective related dendrimers of same nuclearity **12** and **13**. This result clearly suggests that the flexibility of the dendritic mediator is an important factor in the ability to facilitate the interaction between the mediating species and the flavin adenine dinucleotide (FAD) redox centres of glucose oxidase. Studies of

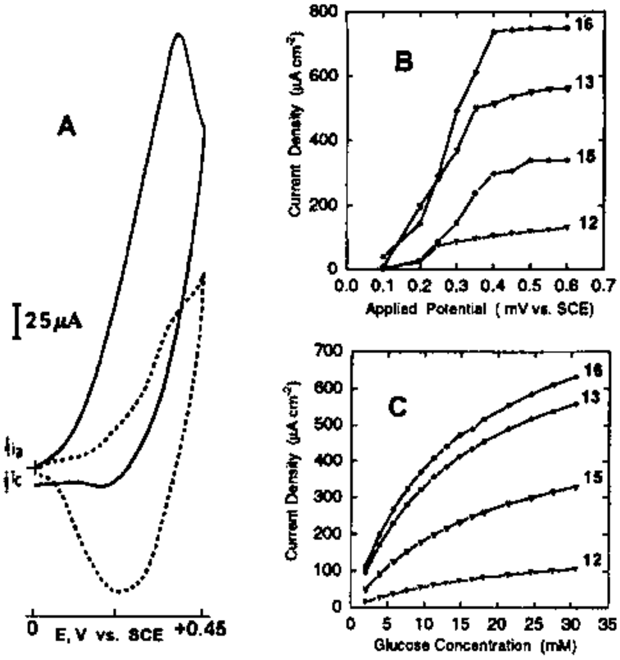


Fig. 8. (A) Cyclic voltammograms for the dendrimer **16**/glucose oxidase/carbon paste electrode, recorded at 5 mV s^{-1} in pH 7.0 sodium phosphate buffer (with 0.1 M KCl) solution, with no glucose present (---), and in the presence of 0.1 M glucose (—). (B) Steady-state polarisation curves of the dendrimer/glucose oxidase/carbon paste electrodes in the presence of 25 μM glucose. (C) Variation of the steady-state current of the dendrimer/glucose oxidase/carbon paste electrodes with glucose concentration (at +350 mV vs. SCE) (adapted from Ref. [42]).

comparison with monomeric and polymeric mediators show that the sensors based on the octanuclear ferrocenyl dendrimers display a similar response to glucose as sensors based on monomeric ferrocene mediators but they show better operational stabilities because their oxidised forms are less soluble than those of the freely diffusing mediators. Furthermore, ferrocenyl dendrimers-based sensors exhibit a higher sensitivity than ferrocene-modified polymers mediated electrodes.

3.1.2. Electrochemical recognition of anions

The molecular recognition of anionic guest species by positively charged or neutral receptors constitutes a relatively new area of research of growing interest [55,56]. This is due to the key roles that anions play in biological and chemical processes as well as the importance of developing novel sensors for environmentally important anions, such as nitrate and phosphate. Redox-responsive receptor molecules are able to selectively bind and recognise electrochemically guest species through the perturbation of the redox system provoked by the host–guest interactions.

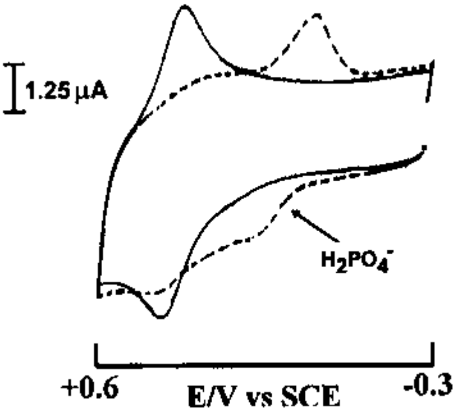


Fig. 9. Cyclic voltammograms of **19** in Bu_4NPF_6/CH_2Cl_2, in the absence (–), and in the presence (---) of $H_2PO_4^-$ anion (adapted from Ref. [46]).

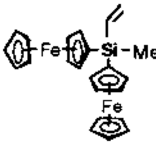
Ferrocenyl dendrimers **18**–**20** that contain suitable cavities as well as multiple N–H groups, can co-ordinate anion guest species via the co-operative forces of favourable hydrogen bonding interactions in the neutral state and electrostatic attractions after the electrochemical oxidation of the ferrocenyl moieties in the receptor [19,46]. Cyclic voltammograms of these dendrimers in CH_2Cl_2/0.1 M TBAH solution, showed significant anion induced cathodic perturbations. Thus, the addition of increasing amounts of $[Bu_4N][H_2PO_4]$ or $[Bu_4N][HSO_4]$ causes a decrease in the intensity of the redox wave, along with the progressive appearance of a new redox wave of increasing intensity at a less positive potential (see e.g. Fig. 9). The current associated with the new redox couple increases linearly with the concentration of anions until the original wave disappears and the new redox couple reaches full development. It is noteworthy that the largest magnitude of cathodic shift was observed with the $H_2PO_4^-$ anion. These CVs suggest that the shape of the oxidation wave changes from a reversible redox process to an EC mechanism. The addition of Cl^- and Br^- salts to the ferrocenyl dendrimer does not give rise to a new wave but only a progressive cathodic shift of the initial wave is observed. The fact that the most striking changes of the CVs are obtained for large and tetrahedral anions, such as $H_2PO_4^-$ and HSO_4^-, could be related to the presence of cavities in the receptor with complementary dimensions to these anions. To establish the selectivity of the receptor in the electrochemical recognition, competition experiments were carried out. In this way, the CV recorded when $H_2PO_4^-$ is added to a CH_2Cl_2/TBAH solution of dendrimer **19** in the presence of tenfold excess of HSO_4^-, Cl^- and Br^-, results to be closely similar to that recorded for **19** in the presence of $H_2PO_4^-$ alone. In a like manner, HSO_4^- can be detected, unambiguously, in the presence of Cl^- and Br^-. The results obtained indicated that the dendrimer displays the selectivity trend $H_2PO_4^- > HSO_4^- > Cl^- > Br^-$.

In addition, it is interesting to note that the voltammetric response of electrodes derivatised with electroactive films of **19** is sensitive to the presence and concentration of the $H_2PO_4^-$ anion [46].

3.2. Silicon-based ferrocenyl dendrimers constructed via a convergent approach

We are particularly interested in the construction of well-defined dendrimers possessing redox-active organometallic units in which the metal atoms are in close proximity so that there is electronic communication between the metal sites in the dendritic structure. This would provide access to new multimetallic dendrimers with appreciable electron mobility and consequently with interesting electrical, redox, optical and magnetic properties.

With this goal in mind, a stepwise convergent growth approach [57,58] has been accomplished to prepare silicon-based dendrons (**24** and **25**), and dendrimers (**26** and **27**) containing in each branch two ferrocenyl units linked together in close proximity through a silicon bridge.



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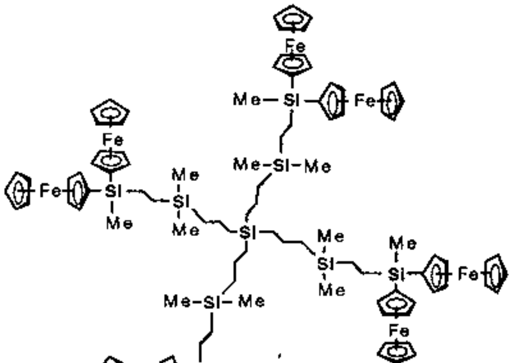

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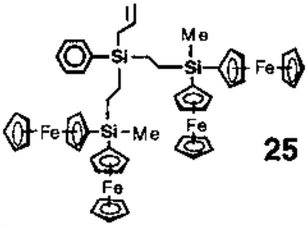

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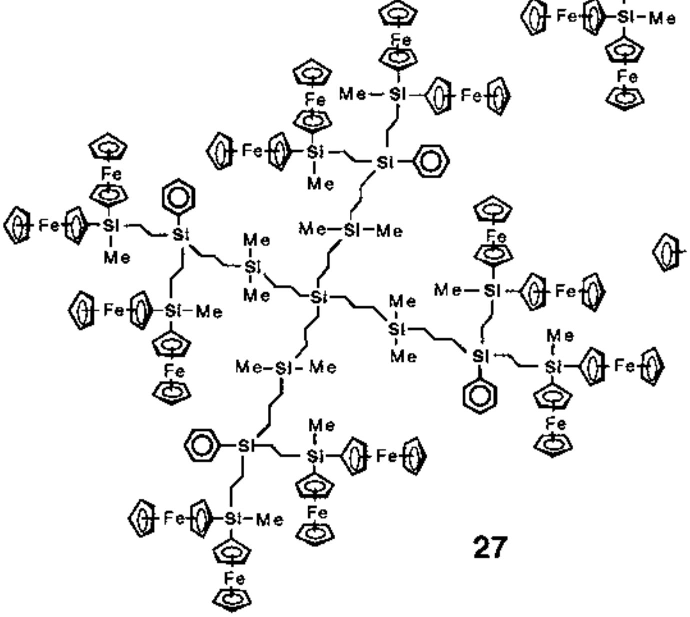

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To our knowledge these are the first organometallic dendritic molecules displaying electronic interactions between transition metal atoms in the dendritic structure reported so far [36].

The key dendritic wedge for the synthesis of the new dendrimers is the silicon-bridged biferrocene **24**, which functions as a valuable model with respect to the electrochemical properties of the dendrimers of higher nuclearity. This dendron exhibits a CV in CH_2Cl_2 solution (Fig. 10A) characterised by two well-separated and reversible oxidation waves of equal intensity, at $^{1}E_{1/2} = +0.45$ and $^{2}E_{1/2} = +0.63$ V. A similar cyclic voltammetric response was observed for the growth dendron **25** and dendrimers **26** and **27** possessing four, eight and 16 ferrocenyl groups, respectively. Nevertheless, it should be noted that for these dendrimers in CH_2Cl_2, a change in solubility accompanied the change in oxidation state, so that upon scan reversal after the second oxidation process, the reduction wave was sharpened, giving rise to a cathodic stripping peak (Fig. 10C). Thus, the complete oxidation of **24** and **25** results in the precipitation of the oxidised dendrimers onto the electrode surface, and on the reverse scan the dendrimer redissolves as it is reduced. However, if a small amount of CH_3CN is added to the CH_2Cl_2 electrolyte medium, the cathodic stripping peak disappears (Fig. 10D), and the CVs become similar to that observed for the model dendron **24**. Likewise, differential pulse

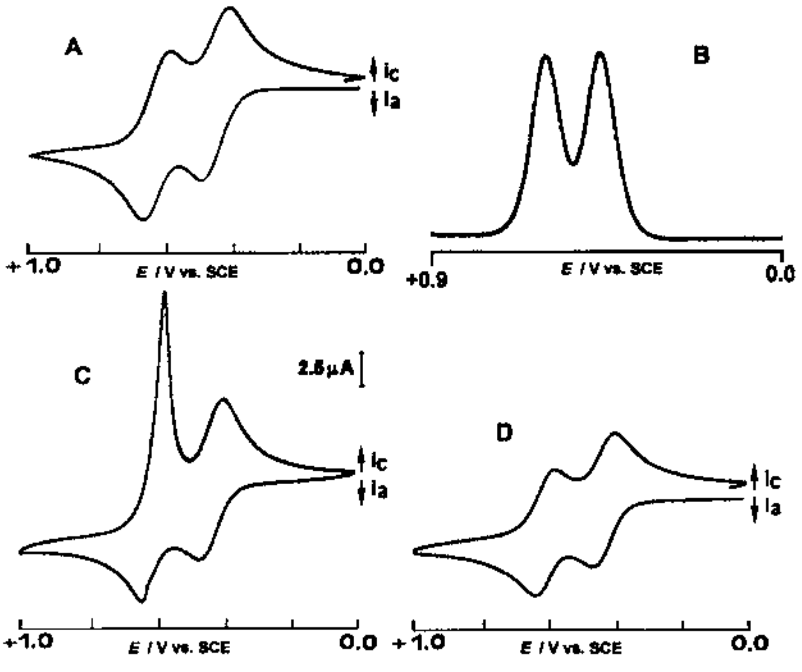


Fig. 10. (A) CV of **24** in CH_2Cl_2, (B) DPV of **24** in CH_2Cl_2, (C) CV of **26** in CH_2Cl_2, (D) CV of **26** in CH_2Cl_2/CH_3CN (5:1 by volume). Supporting electrolyte: 0.1 M TBAH, Pt disk electrode, scan rate 100 mV s^{-1} (adapted from Ref. [36]).

voltammetry (DPV) measurements for all dendritic molecules exhibited two separated oxidation waves of the same area (Fig. 10B).

This electrochemical behaviour observed for these dendritic molecules is consistent with the existence of significant interactions between the two ferrocenyl units that are linked together by the bridging silicon atom. The first oxidation of **24**–**27** occurs in the dendritic wedges at non-adjacent ferrocene sites, which makes the subsequent removal of electrons from the remaining ferrocenyl centres, neighbouring those already oxidised, more difficult. The difference in the redox potentials ($\Delta E = {}^2E_{1/2} - {}^1E_{1/2}$) observed for the two waves, provides an indication of the degree of interaction between the two iron sites. From the wave splitting, which varies from $\Delta E = 190$ mV (for **26**) and 180 mV (for **24**), to 160 mV (for **25** and **27**), the comproportionation constant K_c relative to the equilibrium $\mathrm{Fe(II)-Fe(II)} + \mathrm{Fe(III)-Fe(III)} \leftrightarrows 2\mathrm{Fe(II)-Fe(III)}$ was calculated, resulting in values of $K_c =$ 1630 for **26**, 1104 for **24**, and 507 for **25** and **27**. These values indicate that the partially oxidised dendritic molecules **24**–**27** can be classified as Robin and Day class II mixed-valence species [59].

It is worth noting that the redox-active multimetallic dendrimers **26** and **27** have demonstrated to be suitable for the modification of electrode surfaces. The voltammetric response of an electro-deposited film of the octanuclear **26**, in dendrimer-free CH_2Cl_2 solution, shows two successive well-defined, reversible oxidation–reduction waves (Fig. 11). A linear relationship of peak current with potential sweep rate v was observed, and the potential difference between the cathodic and anodic peak is smaller than 10 mV at scan rates of 0.1 V s^{-1} or less. These voltammetric features unequivocally indicate the surface-confined nature of the electroactive dendrimer film. To our knowledge, this is the first example of electrode surfaces modified with films of redox-active dendrimers possessing a controlled number of interacting metal centres.

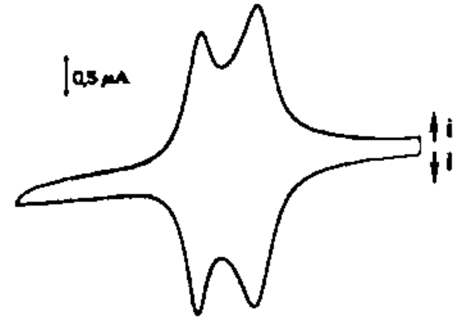
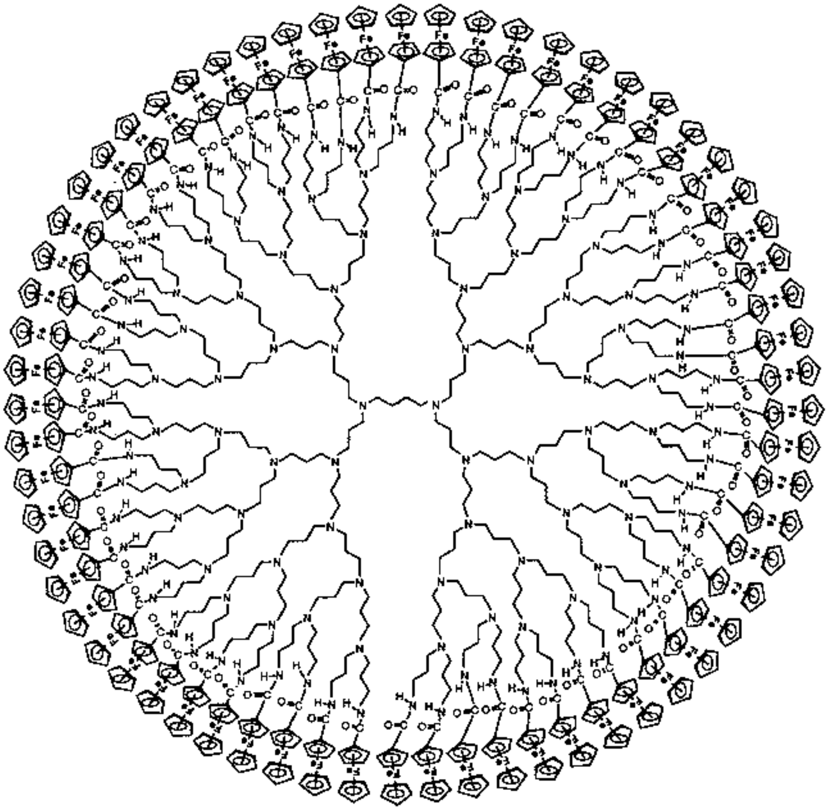


Fig. 11. Voltammetric response of a platinum disk electrode modified with a film of dendrimer **26**, measured in CH_2Cl_2/0.1 M TBAH.

3.3. Amine-based ferrocenyl dendrimers

We have also prepared five generations of organometallic dendrimers by surface functionalisation of a series of diaminobutane-based dendritic structures DAB-dend-(NHCOFc)$_x$ with four, eight, 16, 32 and 64 ferrocenyl moieties, **28**–**32**, respectively [39].



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For all generations of this dendritic family, a single redox process is observed in CH_2Cl_2 solution, which implies a simultaneous multielectron transfer of all the ferrocene centres at the same potential. In addition, the solution redox behaviour of these dendrimers appears to be solvent-dependent. Thus, in CH_2Cl_2 solution, changes in solubility with the change in the oxidation state of the ferrocene units are observed (Fig. 12A), while in CVs measured in THF, the precipitation effects are considerably less pronounced (Fig. 12B). Finally, when DMF is used as solvent, an irreversible electron transfer occurs (Fig. 12C). Therefore, the oxidised dendritic species are not stable in DMF solution in the cyclic voltammetry time scale. This fact could be explained if we assume the existence of strong hydrogen bonds between CO groups in DMF and the NH groups in the amidoferrocenyl moiety.

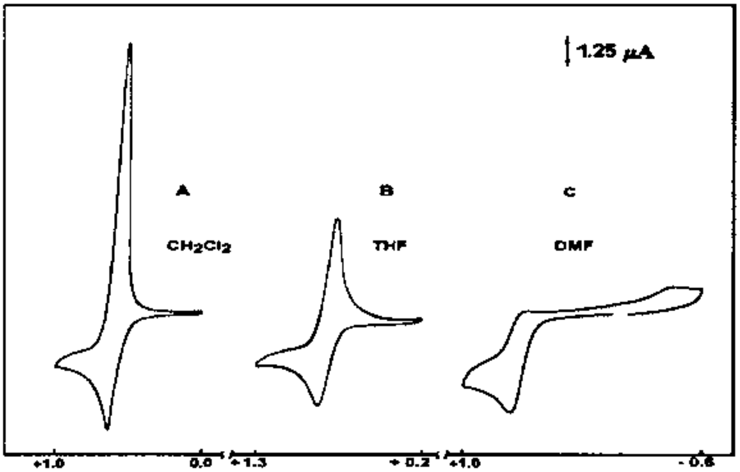

Fig. 12. Cyclic voltammograms of dendrimer **29** (A) in CH_2Cl_2, (B) in THF, (C) in DMF. Supporting electrolyte: 0.1 M TBAH, Pt disk electrode, scan rate 100 mV s^{-1}.

On the other hand, it is interesting to note the ability of these amine-based dendrimers to adsorb onto electrode surfaces both under controlled potential as well as at open circuit. The thermodynamics and kinetics of adsorption of the redox-active dendrimers have been studied using electrochemical and electrochemical quartz crystal microbalance (EQCM) techniques [37]. The adsorption thermodynamics of the reduced form of the dendrimers in a CH_2Cl_2 solution are well-represented by the Langmuir adsorption isotherm. The kinetics of adsorption appears to be activation-controlled rather than diffusion-controlled and to be dependent upon the identity of the dendrimer, but independent of concentration. With the EQCM technique and, in particular, from an analysis of admittance measurements of the resonator, it appears that the oxidised form of the dendrimers deposit onto the Pt electrode, likely due to low solubility of the salt of oxidised dendrimer (ferricenium form) and ClO_4^- anions, whereas the reduced form of the dendrimers easily redissolves except for the first monolayer, which appears to be strongly adsorbed. Further, the mass transfer process during the redox reaction of the adsorbed dendrimers in CH_3CN solution was found to be of the anion exchange type. In addition, it was determined that the ClO_4^- anions are accompanied by CH_3CN molecules, whose numbers appear to depend on the charge density (density of ferrocenyl groups) of each dendrimer.

In addition, we have been able to obtain molecularly resolved images of the dendrimer with 64 peripheral ferrocenyl units adsorbed onto a Pt (111) single crystal electrode, using non-contact AFM also known as tapping mode AFM (Fig. 13) [37]. Prior to modification, the surface appears essentially smooth and featureless (Fig. 13A). However, upon modification there is clear evidence of the presence of adsorbed dendrimer (Fig. 13B). The circular features that can be seen over the entire image represent individual dendrimer units. Also from the figure, it is evident that in some cases there appears to be aggregates present on the surface. We ascribe these brighter spots to the presence of adsorbates that are two dendrimer units in height and which likely result from the evaporation of the CH_2Cl_2 solvent. A preliminary analysis of these images suggests that the apparent size of the adsorbed dendrimer is significantly larger than the calculated value. We believe that this is due, in part, to a convolution of the tip profile and the sample as well as to a flattening of the dendrimer upon adsorption.

3.3.1. Inclusion complexation of dendrimers by β-cyclodextrin

The first, second and third generation of diaminobutane-based dendrimers containing four, eight and 16 peripheral ferrocene groups, **28**–**30**, were investigated as guests for inclusion complexation by the hosts β-cyclodextrin (β-CD) and dimethyl-β-cyclodextrin (DM-β-CD) [38].

Electrochemical and spectroscopic data along with the competitive binding experiments indicate that the aqueous solubility of such hydrophobic dendritic molecules results from the inclusion complexation of the ferrocenyl moieties in the dendrimers by the CD hosts in the solution. The enhancement in solubility decreases with increasing dendrimer generation, as more ferrocenyl moieties are packed on the surface of the guest, and therefore the individual complexation, events become sterically hindered. Because of these steric effects, a fraction of the 16 ferrocenyl units on the surface of the larger dendrimer **30** are not accessible to inclusion complexation by the CD hosts. Moreover, cyclic voltammetry of the cyclodextrin-complexed dendrimer **29** shows only one redox wave (Fig. 14A), which indicates that all the peripheral ferrocenyl moieties are complexed and equivalent. In contrast, the CV of dendrimer **30** solubilised by β-CD exhibits two different voltammetric waves corresponding to uncomplexed ($E_{1/2} = 0.38$ V vs. SCE) and complexed ($E_{1/2} = 0.51$ V vs. SCE) ferrocenyl units in the dendrimer (Fig. 14B). These results indicate that complete complexation of all the peripheral ferrocene

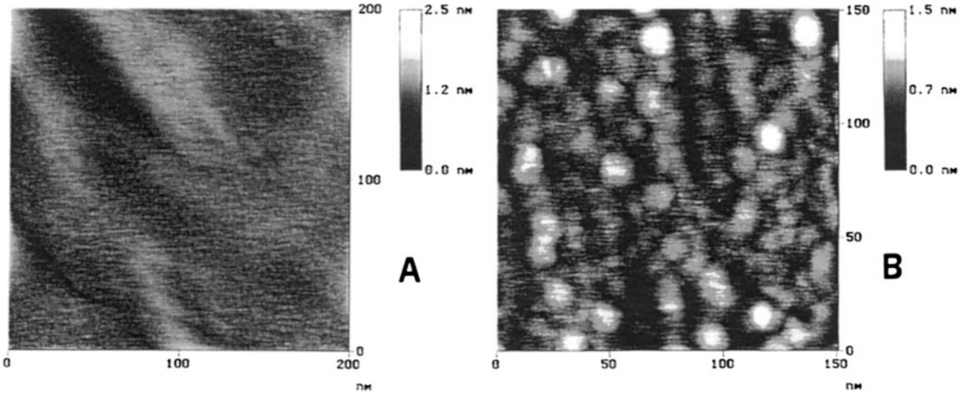

Fig. 13. (A) 200 × 200 nm^2 TMAFM image of a freshly annealed Pt (111) single crystal surface and (B) 150 × 150 nm^2 TMAFM image of a dendrimer **32** modified Pt (111) single crystal surface (adapted from Ref. [37]).

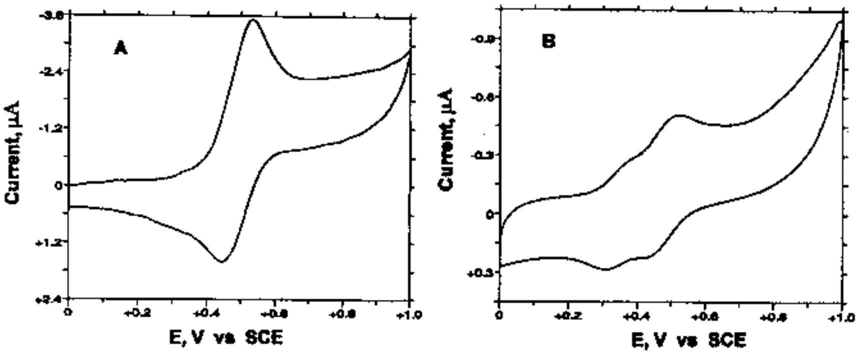

Fig. 14. (A) CV of a solution containing 0.074 mM **29**, 6 mM β-CD and 0.1 M NaCl, (B) CV of a solution containing 2.4 µM **30**, 6 mM β-CD and 0.1 M NaCl. Glassy carbon electrode, scan rate 20 mV s^{-1}.

units by cyclodextrin is not possible in dendrimer **30**, although it is feasible in the less-branched dendrimers **28** and **29**.

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