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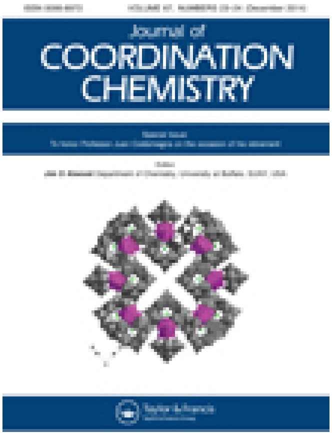

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Review: Mixed-valent metallodendrimers: design and functions

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Review: Mixed-valent metallodendrimers: design and functions

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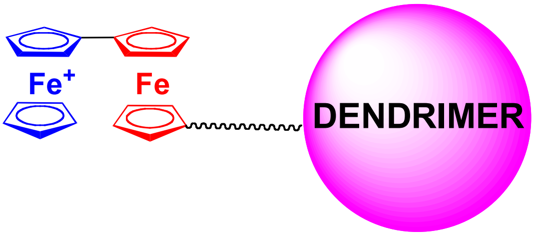

Various types of mixed-valent metallodendrimers and star-shaped macromolecules containing ferrocenyl, biferrocenyl, or other redox-robust iron groups with rigid or flexible tethers of short and long lengths mostly studied in the authors' laboratory including the class type in terms of Robin-Day classification and their functions including electrode modification, sensing, and nanoparticle templates are discussed in this mini review.

Keywords: Dendrimer; Ferrocene; Iron complexes; Mixed valence, Redox; Molecular recognition; Electrostatic effect

1. Introduction

Metallopolymers are nanomaterials of interest both for their morphologies and applications [1]. In particular, metallodendrimers that are precise macromolecules [2] have found potential applications in materials science [3], catalysis [4], and biomedicine [5]. When the metal complex moieties that are contained in the polymer or dendrimer are redox-robust, it is possible to isolate the nanomaterial in two distinct oxidation states with potential applications in nanobatteries, electrochromes, sensors, and redox catalysts. Such research lines have been pursued in particular by the group of Manners [1] with polymers especially using the elegant and efficient ring-opening polymerization of silyl-bridged [1] ferrocenophanes [6].

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Metallodendrimers are different from polymers because their morphology recalls metalloproteins [7] and other biological structures [8], they are well defined with a polydispersity of 1.0, and their globular shape leads to unique encapsulation and sensing properties as exo-receptors [9]. In this micro review, metallodendrimers containing terminal redox groups in two distinct oxidation states are discussed including the electronic and electrostatic factors that are responsible for the mixed valency and the function and application of this property to the synthesis of new nanomaterials. The type of redox group that is used is based on first-row late transition-metal sandwich and piano-stool complexes for which the delocalized electronic system of the π-ligands provides orbital degeneracies resulting in stabilization of several redox states [10], i.e. the complexes $[Fe(\eta^5\text{-}Cp)_2]$ [11], $[Fe(\eta^5\text{-}Cp)(\eta^6\text{-}C_6Me_6)]$ [12], $[Fe(\eta^6\text{-}C_6Me_6)]_2$ [13], $[Co(\eta^5\text{-}Cp)_2]$ [14], and $[Fe(\eta^5\text{-}Cp)(dppe)(alkynyl)]$ [15] ($Cp = C_5H_5$ or C_5Me_5), and their substituted functional derivatives.

2. Metallodendrimers with redox-active peripheral groups

Star, dendrimer core, and dendron syntheses in our research group are based on the $CpFe^+$ perallylation of polymethylarenes [16], in particular mesitylene and *p*-ethoxytoluene that proceed according to 1→3 connectivity [17], followed by hydrosilylation, then Williamson reaction, cross metathesis, or click chemistry [18]. Redox-active groups, such as typically ferrocenyl groups, located at the dendrimer periphery disclose a single chemically and electrochemically reversible wave in cyclic voltammetry (CV), even with up to the last generation (G6) containing up to about 15,000 ferrocenyl termini [19]. The reason is that the redox potentials of the various groups are seemingly the same and only distinguished by a statistic factor and an electrostatic factor that is extremely weak and usually not detectable, due to the relatively large distance between the groups that are flexible and separated by many bonds [20]. Under ideal conditions, this redox CV wave is chemically and electrochemically reversible if the redox system is sufficiently robust under the experimental conditions and if there is no significant structural change between the reduced and oxidized form of this system [21]. It is remarkable that even with large dendrimers, the redox system of the peripheral redox groups remains electrochemically reversible, i.e. the heterogeneous electron transfer is fast in spite of the large distance between the remote redox sites and the electrode (see G2 in figure 1) [22].

Two mechanisms have been invoked to explain this property: (i) rotation of the metallodendrimer that eventually is faster than the electrochemical timescale bringing all the redox centers near the electrode within this timescale [23] and (ii) electron hopping from one redox site to the other resulting from the fast movement of the vicinal redox centers due to their flexibility, this fast movement providing the ideal mutual distance and relative conformation of the two redox sites are involved in tunneling [24]. The consequence of what appears as a single-electron CV wave is that redox recognition and sensing of supramolecularly interacting guests become facile, the metallodendrimer functioning as an exo-receptor. Such experiments might be perturbed by significant adsorption [21], but this inconvenience is usually minimized by an adequate choice of solvent. In such a case, it is possible to determine the number of redox sites using Bard–Anson's equation upon measuring the current intensities of the metallodendrimer and a monomer reference and their diffusion coefficients [20]. It is also possible to improve this determination by combining steady-state conditions (long timescale experiment) with transient conditions (short timescale

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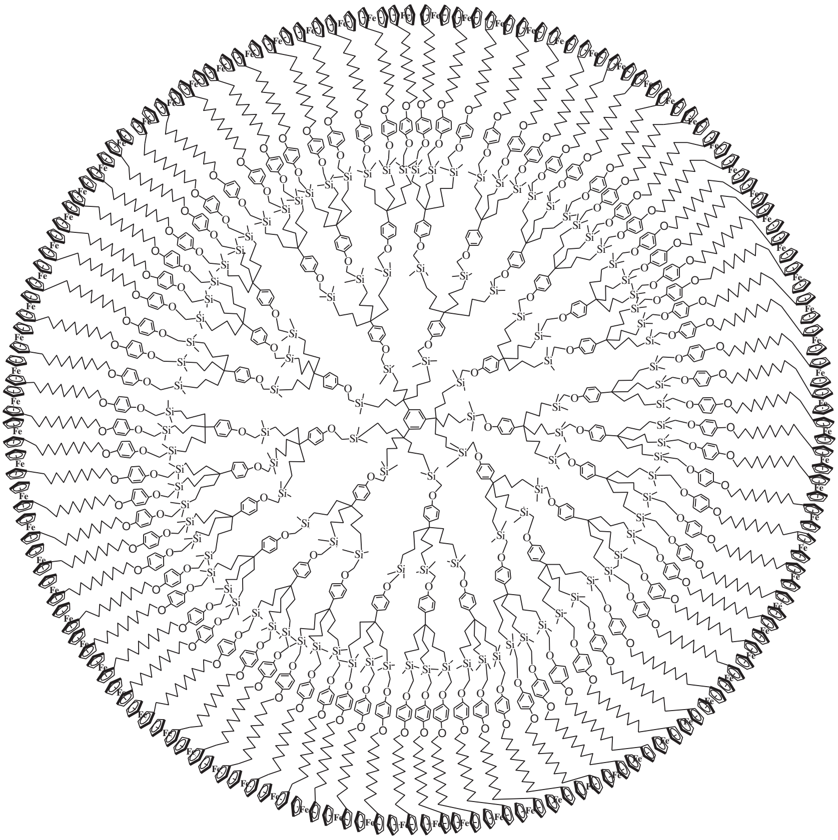

Figure 1. Example of ferrocenyl-terminated dendrimers with 1→3 connectivity and 81 ferrocenyl termini: 2nd generation (G2) [19].

experiment) using the same sample in the absence of absorption, i.e. for low-generation dendrimers [25]. The prototype of such metallodendrimers is ferrocenyl-terminated dendrimers that were first used for anion sensing in the mid-1990s [26]. Later, dendrimers of the same family as that shown in figure 1 with up to 15,000 ferrocenyl centers (G6) were synthesized and thoroughly characterized with such a single reversible CV wave [27].

3. Mixed-valent metallodendrimers with peripheral ferrocenyl/ferricenium groups

Mixed-valent complexes have been extensively studied by Taube and Hush who rationalized the parameters responsible for the localization (mixed valence) or delocalization (average valence) of the binuclear systems with identical sites separated by a short molecular bridge, i.e. the delocalization, the synergy, the electrostatic force, and the entropy [28]. Complexes of this type were classified as class-2 (for which the synergy is dominant) and class-3 mixed-valent compounds (for which the delocalization is dominant), respectively [29]. Mixed-valent compounds have been involved since the pioneering time in ferrocene

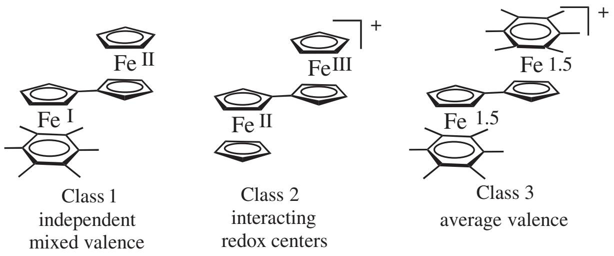

Figure 2. Bis-iron-sandwich complexes representing the three classes of the Robin-Day classification of mixed-valent complexes. The counter anion is PF_6^- [32(e)].

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chemistry upon linking two iron-sandwich units with the three classes of the Robin-Day classification. In 1970, Cowan and Kaufman published biferrocenium, a class-2 mixed-valent complex [30], and the average-valent (class-3) biferrocenylene monocation was reported shortly afterward [31]. Other odd-electron bis-sandwich iron complexes were reported to belong to either class-2 or class-3 of mixed valence [32], a subject for which research has continued up to recently (figure 2) [33].

Following the synthesis of ferrocenyl-terminated dendrimers, their oxidized d^5, 17-electron ferricenium derivatives were prepared by exergonic chemical oxidation using acetylferricenium tetrafluoroborate in dichloromethane in the case of a fifth-generation dendrimer that possesses a theoretical number of 2187 iron-sandwich-terminated branches (the measured actual average number is 2000 ± 100 terminal ferrocenyl groups) [27]. Whereas, the ferrocenyl dendrimer shows by AFM a size of (4.5 ± 0.4 nm), the ferricenium derivative shows an almost 50% size increase up to 6.6 ± 0.6 nm, essentially due to charge repulsion of the redox termini (figure 3).

The mixed-valent ferrocenyl–ferricenium dendrimers were then formed by mixing equimolar amounts of the ferrocenyl dendrimers and ferricenium dendrimers, and the sample was analyzed by electron force microscopy (EFM). With this technique, the nanomolecules that possess a charge density can be distinguished, and it was observed that the nanomolecules in the EFM image have a charge density with a value, on average, of half (0.44) of

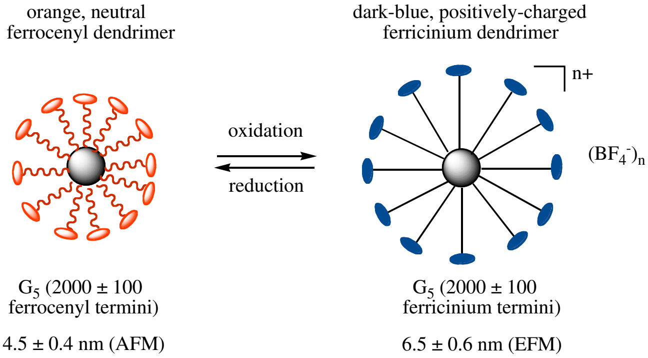

Figure 3. Redox "breathing" of the fifth generation ferrocenyl dendrimer with approx. 2000 ferrocenyl termini upon oxidation to ferricenium: large size increase upon oxidation to ferricenium dendrimer [27].

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the charge density of a pure sample of fifth-generation ferricenium dendrimer (0.82), which is a clear evidence of the presence of mixed-valent dendrimers. In these mixed-valent dendrimers, the delocalization is nil because there are many single bonds between the redox centers. The electrostatic factor is not nil, but extremely weak, because the nanomolecules are very large, and the flexible redox centers are well separated from one another. What remains is the statistic factor that is responsible for the observed existence of the mixed valence. Note that this factor has been taken into account by both inorganic chemists [28] and electrochemists [20, 25].

4. Mixed-valent metallodendrimers with interacting redox centers

In 1997, metallodendrimers containing electronically communicated redox centers were reported by the Casado group with bi(ferrocenyl)silyl termini in which two separated ferrocenyl waves were observed by CV [34], and these metallodendrimers were further applied as biosensors [35]. Silicon transfers some electronic communication between the two iron redox centers through the Cp-Si-Cp organic bridge, and it is possible that the electrostatic factor plays some role, but whether the electronic or electrostatic factor dominates the difference of redox potential between the two waves is uncertain. Although the mixed-valent dendrimers have not been isolated, it might be anticipated that they belong to class-2 of the Robin-Day classification, because electronic communication through the Cp-Si-Cp bridge is insufficient for class-3 (figure 4).

Metallodendrimers have been synthesized by the Casado group with both ferrocenyl and cobalticenium termini that are introduced simultaneously and randomly located at the dendrimer periphery; these metallodendrimers are of interest as class-1 mixed-valent systems [36].

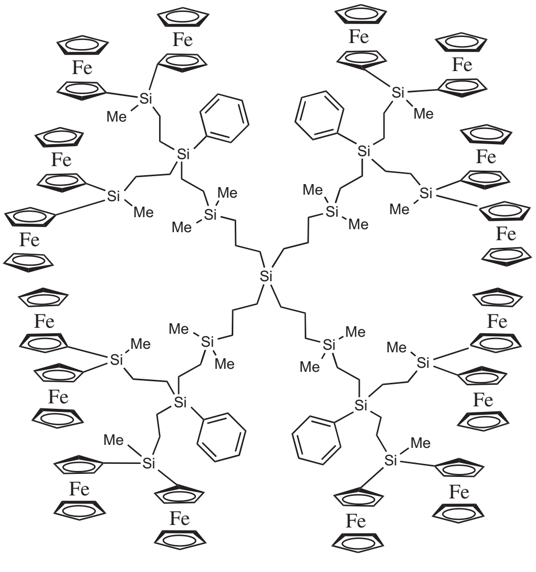

Figure 4. Dendritic molecule by the Casado group containing $SiFc_2$ termini (Fc = ferrocenyl) and showing two CV waves at $E^{1/2} = 0.42$ resp. 0.58 V *vs.* SCE; Pt disk electrode, in CH_2Cl_2-CH_3CN (5 : 1 by volume). Supporting electrolyte: $[N(n\text{-}Bu)_4[PF_6]$ [34].

Recently, small dendrimers have been fabricated with both ethynylferrocenyl and ethynylpentamethylferrocenyl substituents in *meta* positions of arene groups linked to central cores by another apical ethynyl group. In this case again, electronic communication is weak between the two ethynylferrocenyl groups, but permethylation of one of these two ferrocenyl groups permits selective oxidation of this group to robust pentamethylferricenium. The robustness of pentamethylferricenium allows easy handling, contrasting with the fragility of ferricenium, especially in aerobic solution. In this way, the mixed-valent ferrocenyl dendrimers were isolated with precisely located ferrocenyl and pentamethylferricenium redox centers on the terminal arene dendrons, and characterized as class-2 mixed-valent systems by Mössbauer spectroscopy (figure 5) [36].

5. The renaissance of biferrocene in class-2 mixed-valent dendrimers: selective recognition by its two connected redox sites

At the turn of this century, acylbiferrocenes were used by the Hiroshi Nishihara group to introduce distinct redox centers onto nanodevices [39, 40], in particular at the periphery of thiolate gold nanoparticles, and especially in a remarkable series of reports in collaboration

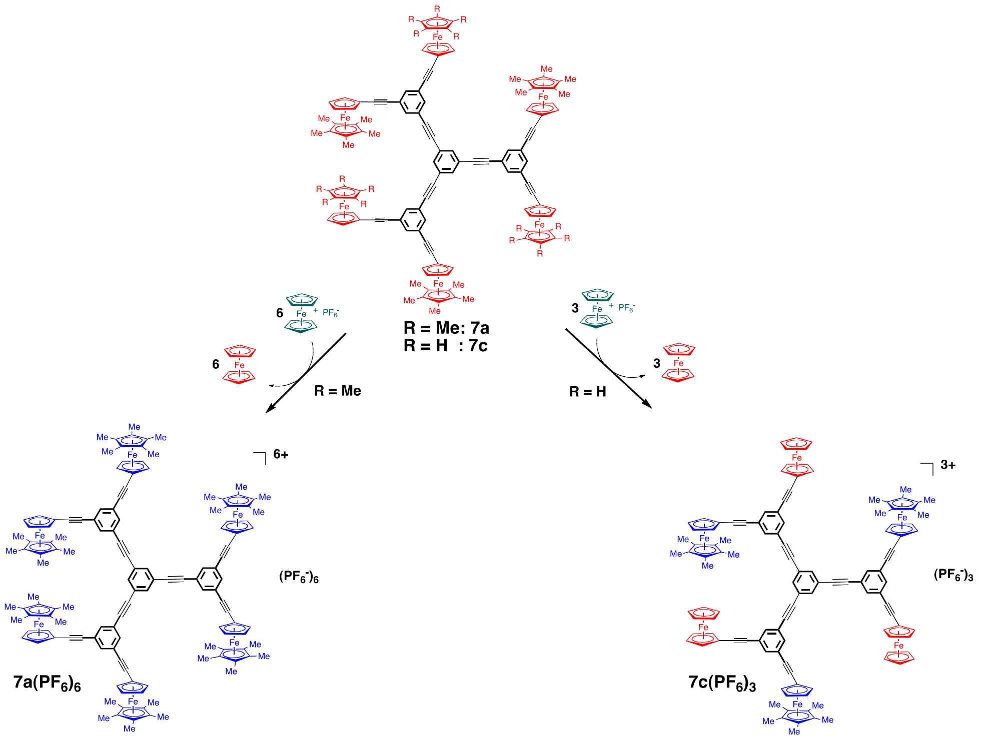

Figure 5. Fe^{II}, Fe^{III}, and mixed-valent $Fe^{II}Fe^{III}$ stiff dendrimers. The latter are intermediate between class-1 and class-2 mixed-valent dendrimers, because the electronic interactions between the ferricenium and pentamethylferricenium redox centers within each arene metallodendron are very weak [37].

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with Mami Yamada [40]. The group of Reinhoudt and Ravoo also demonstrated that small acylbiferrocenyl dendrimers formed inclusion complexes with self-assembled monolayered β-cyclodextrin as "molecular printboards" [41]. In another elegant work with arylazidomethine dendrimers from the Kimihisa Yamamoto and Hiroshi Nishihara groups, biferrocene was incorporated intradendritically without covalent bonding as the mixed-valent biferrocenium charge-transfer complex [42]. In other works, biferrocene has been astutely used as a bridge connecting metal centers [43]. Single electron tunneling was recently observed in large-scale nanojunction arrays with biferrocene-gold nanoparticle hybrids [44]. Studies of electron transfer and mixed valence in biferrocene derivatives are presently continuing with, for instance, di(biferroceny)ethyne involving the class-2 mixed valence (figure 5) [45], biferrocenium salts in which Fe^{3+} and $Fe^{2.5+}$ coexist in the crystal [46], and stiff arene-cored poly(biferrocenes) [47].

The recent "click" synthesis of a series of 1,2,3-triazolylbiferrocenyl-terminated dendrimers by Cu^I-catalyzed azide alkyne cycloaddition including large metallodendrimers containing up to a theoretical number of 729 biferrocenyl termini provided the opportunity to distinguish the properties of the inner and outer ferrocenyl groups. The outer ferrocenyl group bearing only the electron-releasing inner ferrocenyl group is indeed more easily oxidized ($E^{1/2}{}_1 = 0.43$ V *versus* $[Fe(\eta^5\text{-}C_5Me_5)_2]^{+/0}$) than the inner ferrocenyl group ($E^{1/2}{}_2 = 0.75$ V *versus* $[Fe(\eta^5\text{-}C_5Me_5)_2]^{+/0}$) bearing the electron-withdrawing triazolyl substituent. Whereas, the large metallodendrimers readily adsorb on a Pt electrode allowing facile fabrication of modified electrodes, smaller dendrimers such as the second-generation metallodendrimer containing 81 biferrocenyl termini that allows selective molecular recognition and sensing in solution. As a consequence, these metallodendrimers recognize oxo-anions such as ATP^{2-} (in the form of $[n\text{-}Bu_4N]_2[ATP]$) in dichloromethane by interaction with the outer ferricenium groups, because the outer ferrocenes are first oxidized to ferricenium upon scanning towards positive potentials. Meanwhile, the inner ferrocenyl group recognizes metal cations such as Pd^{II} (in the form of $Pd(OAc)_2$) that coordinate with the triazolyl group which withdraws electron density from the inner ferrocenyl group and renders its oxidation even more difficult (figure 6) [48].

6. Electrostatic mixed-valence in star-shaped hexaferrocenes

Biferrocene is the typical example of class-2 mixed-valent compounds presenting two well-separated waves in CV, at 0.31 and 0.64 V, respectively, in CH_2Cl_2-MeCN (1 : 1) with $[n\text{-}Bu_4N][PF_6]$ 0.2 M as the supporting electrolyte ($\Delta E = 330$ mV) for which it is not possible to separate the electronic factor from the electrostatic factor causing the mixed valency and wave separation, although we know that both factors are present because of the very close proximity of the two redox centers (figure 7). In diferrocenylmethane, the electronic factor almost completely disappears because of the lack of electronic communication between the two redox centers, but the two CV waves are still separated, although to a lesser extent than in biferrocene ($\Delta E = 120$ mV in CH_2Cl_2 on Pt electrode with $[n\text{-}Bu_4N][PF_6]$ 0.2 M as the supporting electrolyte) [49]. The wave separation is then presumbly due to the electrostatic factor resulting from the small distance between the two redox centers. We have been interested in the possibility of separating the electronic and electrostic factors in mixed-valent complexes using the examples of 1,3,5-tri(ferrocenylethynyl)benzene [50] and hexa(ferrocenylethynyl)-benzene [51]. In both cases, CV using $[n\text{-}Bu_4N][PF_6]$ as the

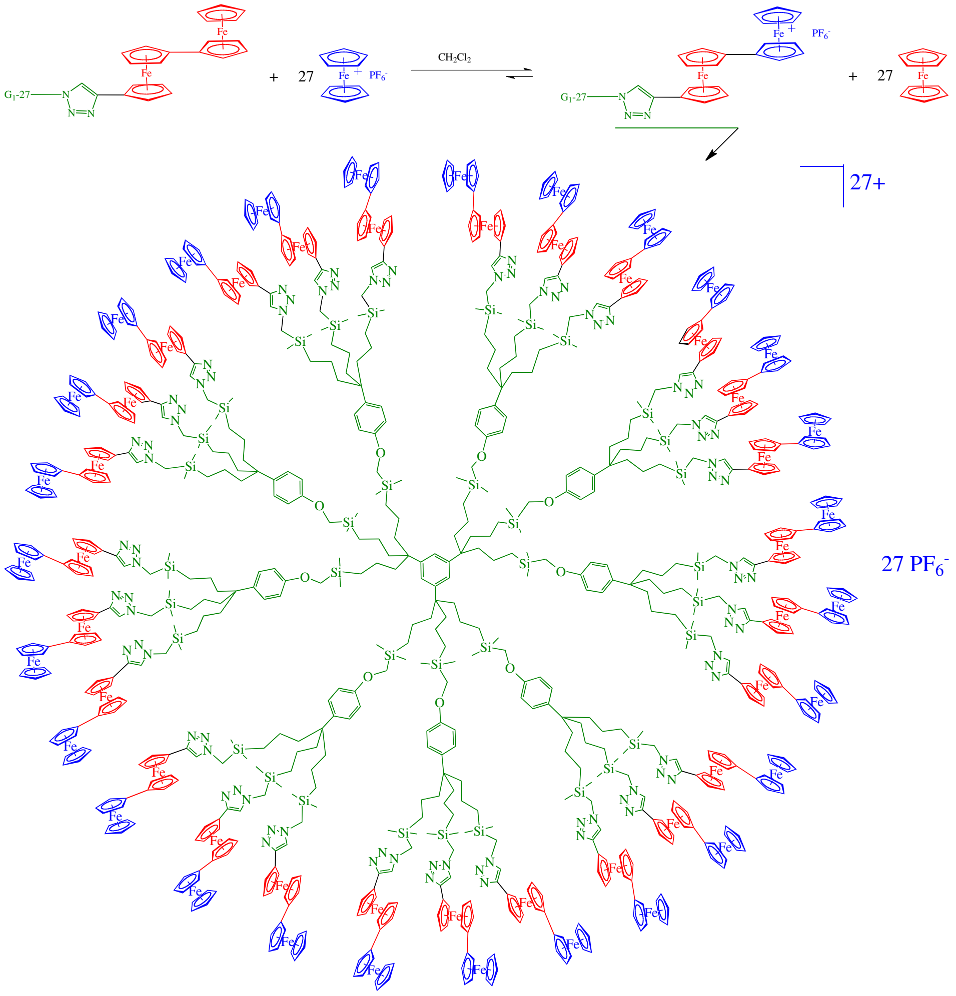

Figure 6. Example of isolated class-2 mixed-valent dendrimers. The outer ferrocenyl groups are first oxidized to ferricenium [38].

supporting electrolyte shows a single CV wave [50, 51]. Geiger and his group have shown that the separation between two CV waves is enhanced upon using perfluorinated electrolyte anions due to reduced anion pairing [52]. We have recorded the CVs of these two complexes also using [n-Bu$_4$N][BAr$^F{}_4$] {Ar^F = 3,5-C$_6$H$_3$(CF$_3$)$_2$} and observed three distinct waves for both complexes, although the wave separation is more clear-cut in the case of the 1,3,5-trisubstituted complex [50, 52]. The single wave observed for this complex using [n-Bu$_4$N][PF$_6$] as the supporting electrolyte shows that there is no electronic effect, which is not surprising in meta position and given the weak Cp character of the ferrocenyl groups in the redox orbital [50]. Upon comparison of a series of polysubstituted arene complexes, it appears that it is the forced frustration among the three ferrocenyl groups that provokes the wave splitting resulting from the electrostatic effect. This frustration results from the fact that two of the three groups must be on the same side of the arene plane at the same

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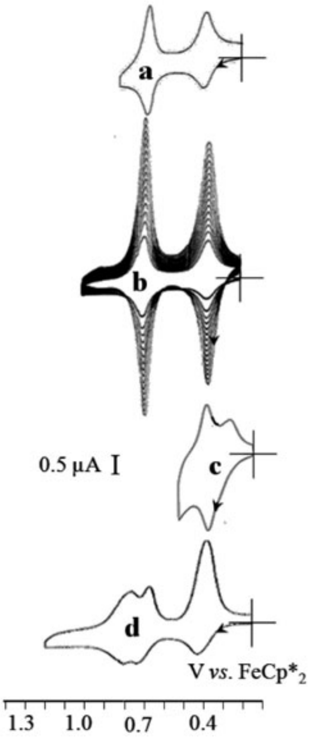

Figure 7. Cyclic voltammograms of the G2-81-biferrocenyl dendrimer: (a) in CH_2Cl_2 [*n*-Bu_4N][PF_6], 0.1 M; (b) progressive adsorption upon scanning around the potential of the biFc area; (c) splitting of the outer ferrocenyl CV wave at 0.4 V upon addition of [ATP][*n*-Bu_4N]$_2$; (d) addition of $Pd(OAc)_2$ provoking the splitting of the inner ferrocenyl wave at 0.7 V [38].

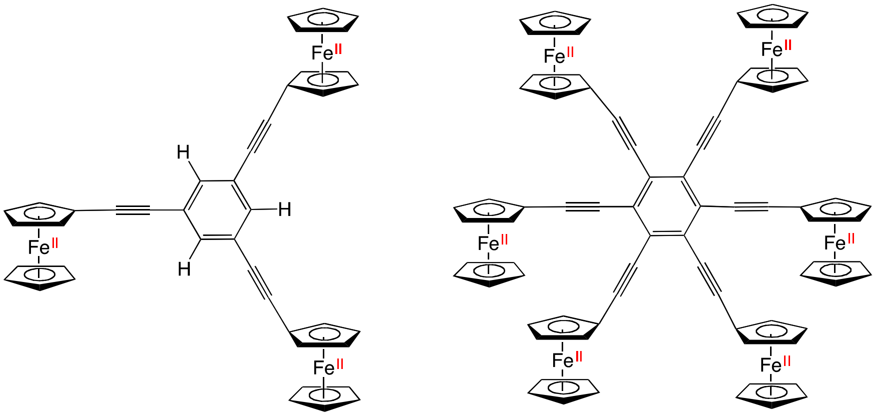

Figure 8. 1,3,5-Tris- and hexa-(ferrocenylethynyl)benzene, both showing three separated cyclic voltammery waves on Pt electrode with *n*-$Bu_4NBAr^F{}_4$ {$Ar^F = 3,5\text{-}C_6H_3(CF_3)_2$} as the supporting electrolyte in CH_2Cl_2 [51, 53].

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time (although an average situation must be considered because of the fast rotation of the ferrocenyl groups compared with the electrochemical timescale). This situation largely enhances the electrostatic effect in the absence of electronic effect [53]. Indeed, in *p*-disubstituted bis(ferrocenylethynyl)-benzene, only one wave is observed regardless the supporting electrolyte, indicating that the electronic factor is too weak to be observed, and the electrostatic factor is also too weak in *transoid* positions, because the two redox centers are too far from each other. Thus, in the hexasubstituted complex, it may consequently be assumed that the *trans* substituents are independent and appear in a single two-electron wave. This explains why a similar situation is observed for the tris- and hexa-substituted complexes, both showing three separated CV waves that are mono- and bi-electronic, respectively (figure 8).

7. Metallodendrimers in three isolable oxidation states including class-2 mixed-valent dendrimers and the size-selective formation of gold nanoparticles

1,3,5-Trisubstituted arene-centered dendrons [54] have been designed with two interacting ethynyl iron fragments in meta positions [55] and a focal-point connection to various dendrimer cores. The two Fe^{II} centers within each dendron have redox potentials that are separated enough, so that mixed-valent complexes can be synthesized either upon oxidation with one equiv. ferricenium salt or upon mixing equal amounts of the neutral Fe^{II} complexes and the cationic Fe^{III} salts. When several dendrons are connected to a dendrimer core, they are independent and all identical, so that the metallodendrimers only present two separated reversible redox waves by CV, as for the multiple redox centers that are discussed in Section 2. The isolation of three redox states of these metallodendrimers (figure 9)

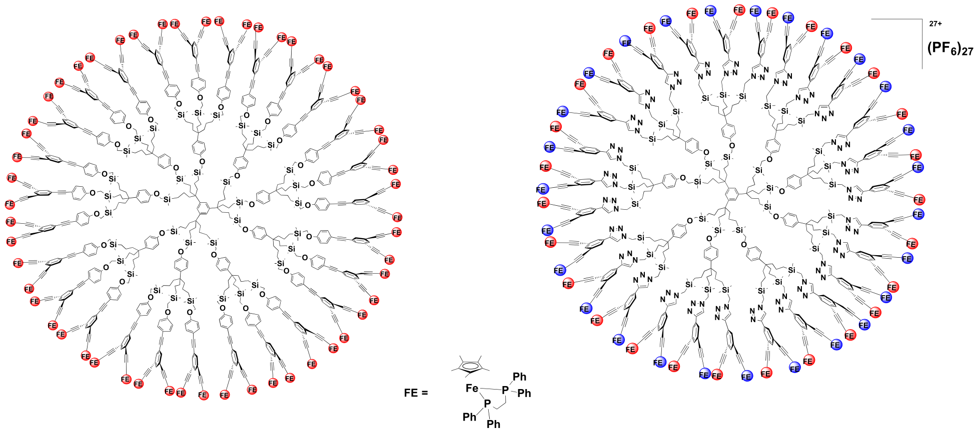

Figure 9. Two metallodendrimers containing 54 $[Fe(\eta^5\text{-}C_5Me_5)(dppe)]$ termini have been isolated in the three oxidation states $Fe^{II}Fe^{II}$, $Fe^{III}Fe^{III}$, and $Fe^{II}Fe^{III}$, the latter being class-2 mixed-valent with interacting redox centers in meta positions of the arene dendrons. The Fe^{II} (all red) dendrimer on the left was synthesized using Sonogashira coupling between an iodophenyl-terminated dendritic core and the bimetallic arene dendron at the alkynyl focal point. The class-2 mixed-valent (Fe^{II}: red; Fe^{III}: blue) dendrimer on the right was synthesized by “click” reaction between an azido-terminated dendritic core and the same alkynyl dendron, followed by oxidation of half the redox groups by ferricenium hexafluorophosphate or $HAuCl_4$ or by mixing equal amounts of the Fe^{II} and Fe^{III} dendrimers [54] (see http://dx.doi.org/10.1080/00958972.2014.939648 for color version).

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($Fe^{II}Fe^{II}$, $Fe^{II}Fe^{III}$, and $Fe^{III}Fe^{III}$) offers considerable flexibility in terms of redox processes in nanosystems. In particular, it has been possible to manipulate the generation of size-selected gold nanoparticles by reactions of the Fe^{II} dendrimers with $HAuCl_4$. In short, the 54 Fe^{II}-dendrimer that possesses internal triazole ligands allows coordination of Au^{III} to the intradendritic triazole ligands; then reduction leads to the intradendritic formation of small gold nanoparticles (1.4 nm). On the other hand, when structurally related 54-Fe^{II} metallodendrimers do not possess such ligands, gold nanoparticle formation only proceeds outside the dendrimer; then in the absence of template, large gold nanoparticles are formed (3.3 nm) [54].

8. Concluding remarks

Since the discovery by the painter Heinrich Diesbach in 1704 in Berlin of a new blue pigment, $Fe_4[Fe(CN)_6]_3(H_2O)_x$ ($x = 14–18$), named Prussian Blue, that has become the archetype of mixed-valent compounds (mixed valency: Fe^{III}-CN-Fe^{II} *versus* Fe^{II}-CN-Fe^{III}), this family of compounds has become popular [56] and has been classified by Robin and Day according to the nature of interaction between the metal moieties [28]. Taube and Hush have rationalized and refined the distinct parameters to understand the metal–metal interactions, also leading to a new science, molecular electronics that now expands in nanosciences with implication in biology and various nanomaterials [29]. Here we have illustrated various types of mixed-valent metallodendrimers and their potential applications. The apparent "simultaneous" electrochemical oxidation of all the analogous redox sites in a single cyclic voltammertry wave that is split in the case of class-2 interacting metal centers is an extremely convenient basis that is gratifyingly utilized for redox recognition, sensing and multi-redox manipulation of nanomaterials. Consequences of electronic interactions in and electron transfer with such soft nanomaterials and others should spread toward redox catalysis, redox recognition, and designed redox-mediated synthesis of specific nanoparticles.

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