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Dendrimer Models

How Do Redox Groups Behave around a Rigid Molecular Platform? Hexa(ferrocenylethynyl)benzenes and Their "Electrostatic" Redox Chemistry

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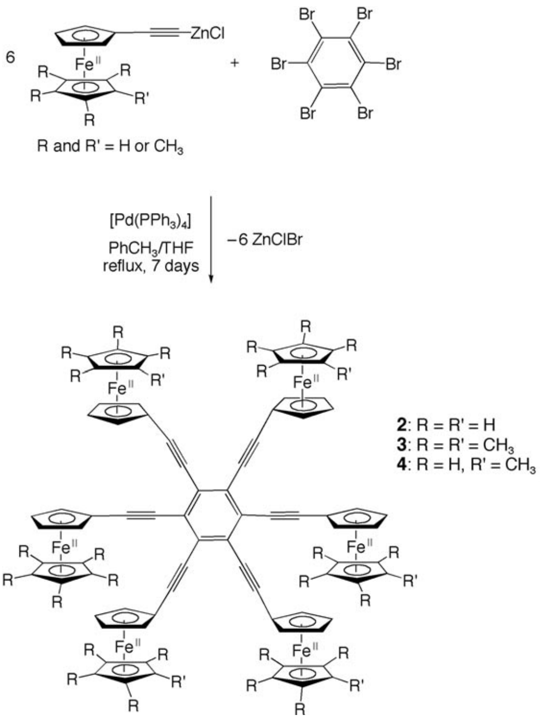
Ferrocenyl polymers[1] and dendrimers[2] are a key class of redox materials with electronic properties that include useful mixed-valency-induced sensing[1] and electrochemically based molecular recognition.[2] For instance, the splitting of the ferrocenyl cyclic voltammetry wave in ferrocenyl polymers was shown to be crucial for colorimetric sensing.[3] When four equivalent ferrocene redox centers are assembled around a small metal core, the ferrocenyl cyclic voltammetry wave can be split by using a supporting electrolyte that contains a perfluorinated anion.[4] Such a splitting is not seen in ferrocenyl-terminated dendrimers, as fast single-electron transfer to the electrode occurs because of the optimal connection between the ferrocenyl redox centers, which results from the flexibility of the tethers.[2c,5] The situation might be different in rigid dendrimers, however, because the rigidly held termini cannot communicate through space, unlike in flexible dendrimers. Although rigid polyarene dendrimers are well-known,[6] rigid ferrocenyl dendrimers have not been reported to date. The electronic properties for these compounds would solely result from intramolecular communication and electrostatic interactions around the ferrocenyl termini. In order to obtain an insight into such phenomena, we have synthesized a family of hexaferrocenylethynylferrocenes and examined their redox and electronic properties. This unique family of complexes is unprecedented, presumably because of synthetic and solubility problems that have now been overcome. Vollhardt and co-workers have recently reported the rather extraordinary hexaferrocenylbenzene, including its X-ray crystal structure, which shows extreme bulk and distortion.[7] Several organic-substituted hexaethynylbenzenes are known[8] as well as arene-centered stars with remote ferrocenyl termini, in which the length of the tethers and lack of conjugation precludes electronic interactions.[9]

The Negishi reaction[10] of a fourfold excess of [ZnCl(C_2Fc)] (Fc = ferrocenyl)[10b], C_6Br_6, and [Pd(PPh_3)$_4$] catalyst was heated at 80 °C in a toluene/THF (2:1) mixture for 7 days [Eq. (1)]. This reaction gave, in addition to [FcC_4Fc], a dark-red solid that is almost insoluble in all solvents and the ether-soluble dark-red new compound pentakis(ferrocenylethynyl)benzene (**1**) in 7 % yield.



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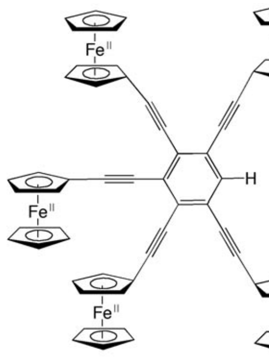

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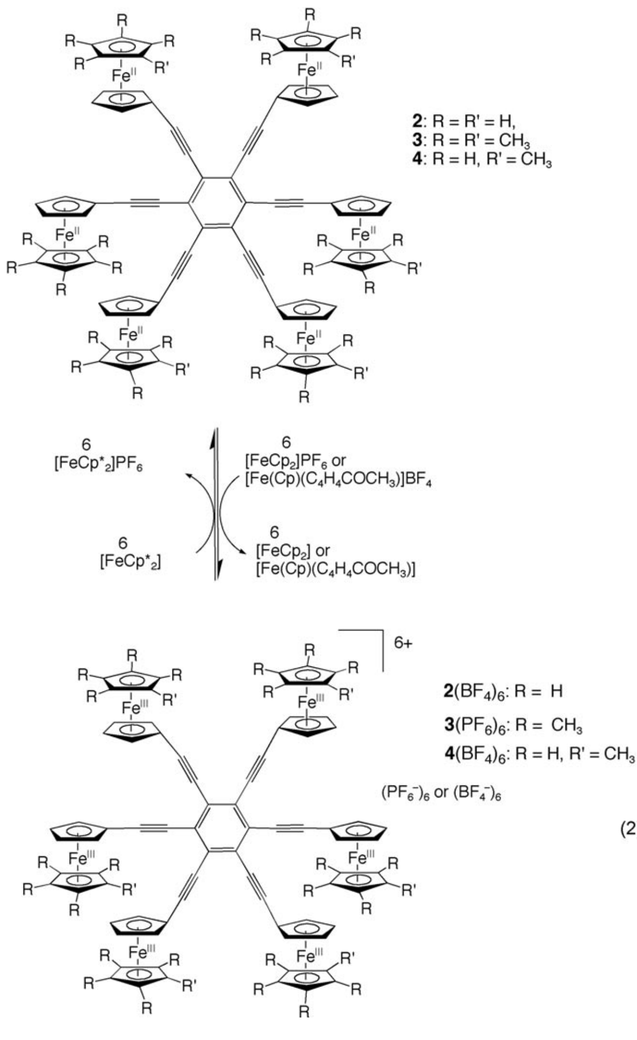
Dehalogenation has been frequently encountered in reactions of organometallic ethynyl reagents and hexahalogenobenzenes;[7,11] this effect can possibly be attributed to side electron transfer from the electron-rich organometallic reagent to the bulky pentaethynylated halogenoarene derivative.[11b] The almost-insoluble product could be removed from the soluble residues by Soxhlet extraction with toluene, and was analyzed by ^{13}C NMR spectroscopy and MALDI TOF mass spectroscopy, which confirmed the molecular structure of hexakis(ferrocenylethynyl)benzene (**2**) by the presence of the expected molecular ion peak and no other product peaks. The Mössbauer spectrum of **2** shows the ferrocene-type frame (the clean cyclovoltammograms are discussed below); six-electron oxidation using acetylferrocenium gives the corresponding hexacation that was characterized by elemental analysis as **2**$(BF_4)_6$ [Eq. (2)].



(2)

In order to obtain a more soluble and workable analogue of **2**, we reacted 1,2,3,4,5-pentamethyl-1′-ethynyl ferrocene[12] with C_6Br_6 in an analogous Negishi reaction under identical conditions. This reaction gave the red hexakis(1,2,3,4,5-pentamethyl-1′-ferrocenylethynyl)benzene (**3**) in 27% yield. The structure of **3** is confirmed by the molecular ion peak at *m/z* 1742.52 (calcd *m/z* 1747.18, Figure S7 in the Supporting Information), ^{1}H and ^{13}C NMR spectroscopy, IR and UV/Vis spectrometry, and elemental analysis. The air stability of solutions of **3** in various organic solvents is remarkable, even over several weeks, whereas solutions of ferrocene in organic solvents decompose in air during this period of time. The crystal structure of **3** shows that, although three ferrocenyl groups are located on each side of the benzene plane, they do not alternate because of packing forces, including those of the isooctane solvent molecules (Figure 1).[13]

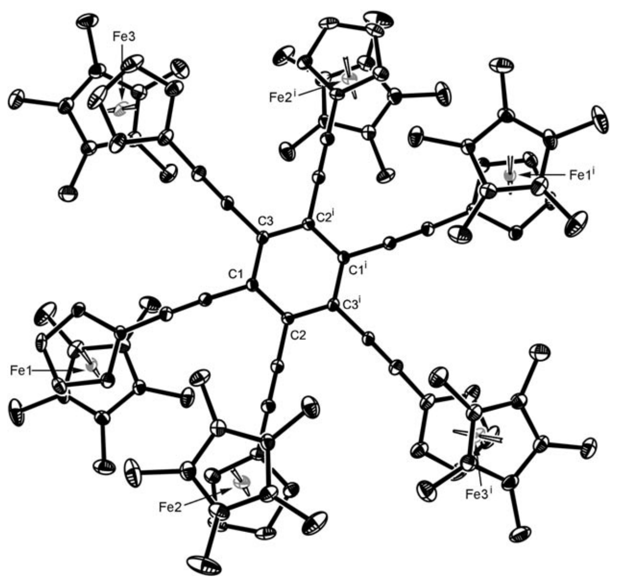


Figure 1. Molecular view of **3**. Ellipsoids are drawn at the 30% probability level. H atoms are omitted for clarity. (Symmetry code *i*: 1−*x*, 1−*y*, 1−*z*).

Reaction of **3** with six equivalents of ferrocenium hexafluorophosphate in dichloromethane yielded the dark-green salt **3**$(PF_6)_6$, the ferrocenium-type structure of which was confirmed by elemental analysis and IR and UV/Vis spectroscopy. The zero-field Mössbauer spectra of **3** and **3**$(PF_6)_6$ are compared in Figure 2 (the Mössbauer doublet of **3**$(PF_6)_6$ collapses to a slightly broad single band, a classic feature of ferrocenium salts[14]). The complex **3**$(PF_6)_6$ was quantitatively reduced back to **4** using six equivalents of decamethylferrocene [[FeCp*$_2$], Eq. (1), bottom]; six equivalents of decamethylferrocenium hexafluorophosphate were also formed in

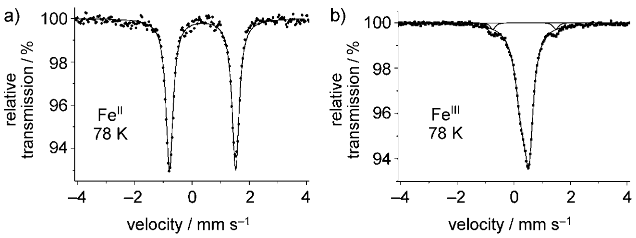
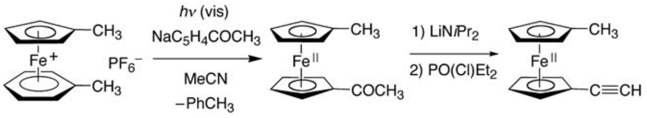


Figure 2. Zero-field Mössbauer spectra of a) **3** b) **3**$(PF_6)_6$ at 78 K.

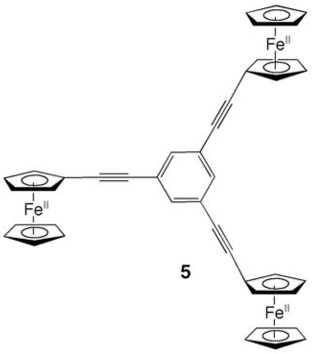
this reaction. Thus, the six-electron transfer is fully chemically reversible and occurs without any decomposition [Eq. (2)].

Finally, in order to introduce an intermediate situation between the parent complex **2** and complex **3** that contains 30 methyl groups, we undertook the synthesis of a third member of the series, which has only one methyl group on each Cp ring. For this purpose, the synthesis of an heterodisubstituted ethynylferrocene (Scheme 1) was required, which used the convenient photochemical ligand exchange reaction of the complex [Fe(η^6-$C_5H_4CH_3$)(η^6-toluene)]PF_6[15] followed by the conversion of the acetyl to an ethynyl substituent. In this case, the Negishi reaction was as effective as that for the other two ethynylferrocene derivatives [Eq. (1)], and afforded the moderately soluble deep-red hexakis(1-methylferrocenyl-1′-ethynyl)benzene complex **4** in 60% yield. These three reactions establish the general access to this new family of ferrocenyl-terminated rigid stars and their hexacationic ferrocenium derivatives. The interconversion between the neutral complexes and their oxidized form using the appropriate mononuclear ferrocene or ferrocenium derivative for exergonic hexaelectron transfer reactions is virtually quantitative and reversible, without any decomposition [Eq. (2)].



Scheme 1. Synthesis of the ferrocenyl precursor of **4**

In the cyclovoltammetric (CV) study, we compared parent complex **2** with both the known 1,3,5-tris(ferrocenylethynyl)-benzene (**5**), which had been reported to show a single CV wave, and 1,4-bis(ferrocenylethynyl)benzene (**6**).[16,17] The lack of CV wave splitting reported for **5** and **6** indicated that there is no significant communication between the iron centers of the ferrocenyl groups through the polyethynylbenzene core in these two complexes, unlike in the complex 1,4-(diironethynyl)benzene (**7**), in which the iron atoms are directly located on the ethynyl groups.[18]



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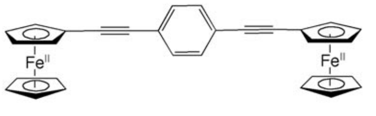

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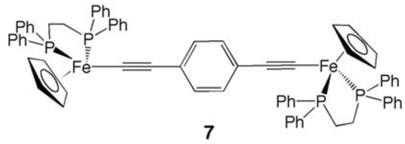

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Thus, as expected, the CVs of **2**, **3**, and **4** in CH_2Cl_2 also showed a single wave when nBu_4NPF_6 was used as the supporting electrolyte. We also recorded these CVs, as well as those of **5** and **6**, with $nBu_4NBAr^F_4$ ($Ar^F = [3,5\text{-}C_6H_3(CF_3)_2]$) as the supporting electrolyte, whose interesting ion-pairing properties and application in electrochemistry have been reported previously.[4,19] Interestingly, we find that, by using this perfluorinated electrolyte in CH_2Cl_2, the CVs of **2** and **5** split into three well-separated waves, whereas that of **6** still shows a single wave (Figure 3).

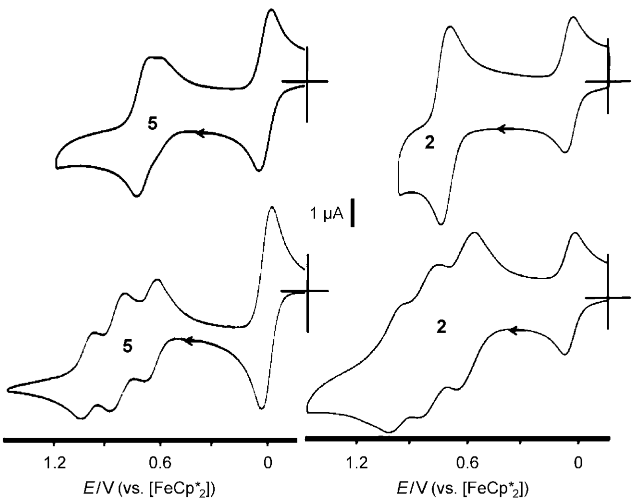
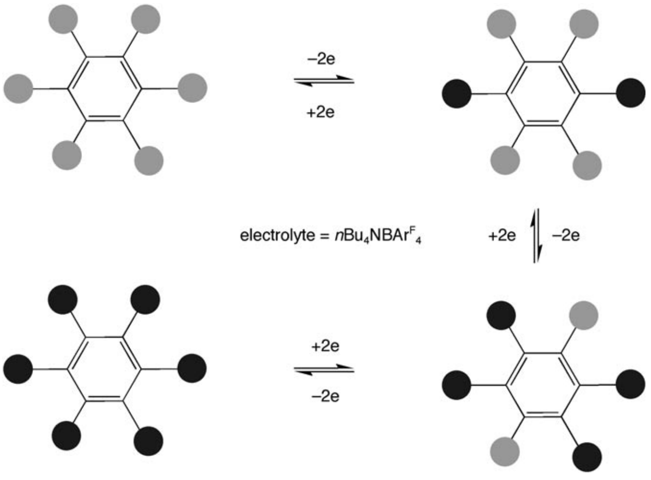


Figure 3. Cyclic voltammograms of a) **5** and b) **2** with NBu_4PF_6 (top) and $NBu_4BAr^F_4$ (bottom) in CH_2Cl_2.

Electronic communication is well known to occur between substituents around a *para*-substituted benzene core, but occurs less efficiently between substituents around a *meta*-substituted core.[20] These results therefore confirm that electronic communication does not proceed between the redox center (iron-based) of the ferrocenyl groups of **6** (contrary to **7**), which suggests that this must also be the case in the family of the hexakis(ferrocenylethynyl)benzenes **2**, **3**, and **4**. This also means that the splitting, only observed for **2** and **5** with $nBu_4NBAr^F_4$, does not result from electronic communication among the redox centers, but from electrostatic effects that arise from ion pairing with the electrolyte anion upon anodic oxidation of the neutral compounds.

It is remarkable that, although the parent complexes **2** and **2**$(PF_6)_6$ are almost insoluble in all solvents, the permethylated analogues **3** and **3**$(PF_6)_6$ are extremely soluble in pentane (**3**) and CH_2Cl_2 (**3** and **3**$(PF_6)_6$). This tremendous solubility difference is related to the considerable change in solute–solvent and ion-pairing energies when the bulky methyl groups increase the distance between the organometallic hexacation and the solvent or anions. This difference also shows that the nature of the anion has an enormous influence when using such ion pairs in both synthesis and electrochemistry.

The similarities of the CVs of **2** and **5** with $n\mathrm{Bu_4NBAr^F_4}$ in $\mathrm{CH_2Cl_2}$ (Figure 3) is also striking and indicates that the redox process in **2** involves three two-electron waves. The appearance of the *para*-ferrocenyl groups in the same CV wave confirms their mutual independence. The electrostatic effect is thus essentially the only reason for the distinction between the three two-electron oxidation steps shown in Scheme 2, which are distinguished by the large differences between these electrostatic effects in the *ortho*, *meta*, and *para* positions of **2**.



Scheme 2. Mechanism of the oxidation of **2** in the presence of $\mathrm{NBu_4BAr^F_4}$ in $\mathrm{CH_2Cl_2}$, which occurs by a cascade of three two-electron oxidation steps (shown in Figure 3). The ferrocenylethynyl groups are shown as gray circles and the ferroceniumethynyl groups are shown as black circles.

A close inspection of the CVs of **2** and **5** shows, however, that the splitting of the three CV waves is not as well defined for **2** as for **5**, because the electrostatic (and eventually, to a minor extent, if any, electronic) influence of each ferrocenyl group on its neighbor in *ortho* position is not zero. The CV of **2** with $n\mathrm{Bu_4NBAr^F_4}$ indicates that the mixed-valent species $[\mathrm{Fe^{III}_2Fe^{II}_4}](\mathrm{BAr^F_4})_2$ ($K_{\mathrm{disp}} = 172$ at 20 °C) and $[\mathrm{Fe^{II}_2Fe^{III}_4}](\mathrm{BAr^F_4})_4$ ($K_{\mathrm{disp}} = 43$ at 20 °C)[21], unlike $[\mathrm{Fe^{III}_3Fe^{II}_3}](\mathrm{BAr^F_4})_3$, are rather stable (both thermodynamically and kinetically within the electrochemical time scale), which arises from the electrostatic effect.[22] On the other hand, the mixed-valence compounds of **2** in the series $[\mathrm{Fe^{III}}_n\mathrm{Fe^{II}}_{6-n}](\mathrm{PF_6})_n$ $(0 < n < 6)$ only follow a statistical distribution, which includes a major contribution of $[\mathrm{Fe^{III}_3Fe^{II}_3}](\mathrm{PF_6})_3$.[23]

Finally, the CVs of **3** and **4** recorded with $n\mathrm{Bu_4NPF_6}$ show a single wave, as in the CV of **2**. The CV of **3** with $n\mathrm{Bu_4NBAr^F_4}$ versus decamethylferrocene is a broad envelope of overlapping waves between 0.3 and 0.7 V (see Figure S10 in the Supporting Information). This observation is consistent with a strong shielding of the electrostatic effect by the five methyl groups around each ferrocenyl center. For **4**, the envelope is better resolved and, despite the overlap, one can distinguish six waves that correspond to the six single-electron oxidation steps (Figure 4). Thus, the influence of a single methyl group on each ferrocenyl redox center has a dramatic effect on the perturbation of the ion-pairing strength, which results in both the CV modification and the large difference in solubility of both the neutral compounds and hexacationic salts with the same anions.

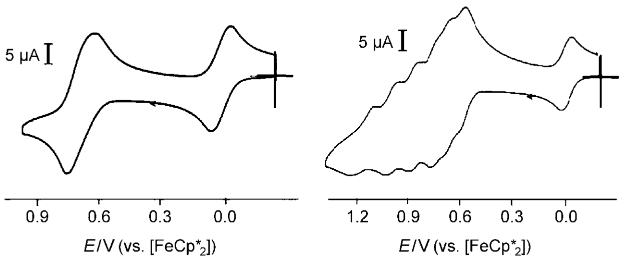


Figure 4. CVs of **4** in $\mathrm{CH_2Cl_2}$ at 20 °C with a) $n\mathrm{Bu_4NPF_6}$ and b) $n\mathrm{Bu_4NBAr^F_4}$ as the supporting electrolyte.

In conclusion, we have synthesized the first family of rigid stars with terminal redox groups that contain both neutral hexaferrocene and hexaferrocenium compounds, which can be fully and reversibly interconverted. Both solubility and cyclic voltammetry studies show that, despite the lack of electronic communication between the redox centers, the six-electron wave usually observed for all the family members with the standard electrolyte $n\mathrm{Bu_4NPF_6}$ can be split either into three two-electron waves or into six overlapping single-electron waves by simple variation of the number of methyl groups on the ferrocenyl groups, and of the counterion of the supporting electrolyte. This result shows that rigidly planar molecular platforms surrounded by redox groups undergo a redox chemistry that is extraordinarily sensitive to ion-pairing-dependent electrostatic effects. Such engineering of these rigid redox dendrimer models could find applications in materials science for the design of multielectron transfer catalysis and in biologically relevant anion sensing.[24]

Experimental Section

Negishi reaction between ethynylferrocene and hexabromobenzene: Hexabromobenzene (42 mg, 0.076 mmol), $[\mathrm{Pd(PPh_3)_4}]$ (66 mg, 0.057 mmol, 0.75 equiv), and toluene (freshly distilled over Na, 10 mL), were successively added to a Schlenk flask. A solution of ferrocenylethynyl zinc chloride[10b] in THF (2 mmol, 4 equiv per bromide group) was then added. The mixture was heated at 80 °C for 24 h, an additional portion of $[\mathrm{Pd(PPh_3)_4}]$ (66 mg, 0.057 mmol, 0.75 equiv) and ferrocenylethynyl zinc chloride (2 mmol, 4 equiv) in toluene were added by syringe under $\mathrm{N_2}$. The mixture was kept at 80 °C for six days and then cooled to room temperature. Following Soxhlet extraction to remove soluble residues, hexakis(ferrocenylethynyl)benzene (**2**) was obtained as a dark-red solid (47 mg, 47 % yield), which was almost insoluble in all solvents and characterized by using MALDI-TOF mass spectroscopy, Mössbauer spectroscopy, and cyclic voltammetry. The soluble residue was purified by column chromatography on $\mathrm{SiO_2}$ eluting with pentane to give 1,4-bis(ferrocenyl)butadiyne (75 mg), and eluting with pentane/dichloromethane (70:30) to give pentakis(ferrocenylethynyl)benzene (**1**) as dark-red solid (6 mg, 7 % yield; see the Supporting Information). The same reaction conditions were used for the synthesis of **3** and **4**, and the pure compounds were separated from the reaction mixtures by column chromatography (see the Supporting Information).

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Keywords: dendrimers · electron transfer · ferrocene · ion pairs · redox chemistry

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[1] P. Nguyen, P. Gomez-Elipe, I. Manners, *Chem. Rev.* **1999**, *99*, 1515 – 1548; I. Manners, *Science* **2001**, *294*, 1664 – 1666; G. R. Whittell, I. Manners, *Adv. Mater.* **2007**, *19*, 3239 – 3468.

[2] For reviews on ferrocenyl dendrimers and their electrochemical properties, see: a) C. M. Casado, I. Cuadrado, M. Moran, B. Alonso, B. Garcia, B. Gonzales, J. Losada, *Coord. Chem. Rev.* **1999**, *185–186*, 53 – 79; b) S. H. Hwang, C. D. Shreiner, C. N. Moorefield, G. N. Newkome, *New J. Chem.* **2007**, *31*, 1027 – 1038; c) D. Astruc, C. Ornelas, J. Ruiz, *Acc. Chem. Res.* **2008**, *41*, 841 – 856.

[3] R. Rulkens, A.-J. Lough, I. Manners, S. R. Lovelace, C. Grant, W. E. Geiger, *J. Am. Chem. Soc.* **1996**, *118*, 12683 – 12695; N. Camine, U. T. Mueller-Westerhoff, W. E. Geiger, *J. Organomet. Chem.* **2001**, *637*, 823 – 826.

[4] F. Barrière, N. Camine, W. E. Geiger, *J. Am. Chem. Soc.* **2002**, *124*, 7262 – 7263; F. Barrière, W. E. Geiger, *J. Am. Chem. Soc.* **2006**, *128*, 3980 – 3989; see also Ref. [3].

[5] C. Ornelas, J. Ruiz, C. Belin, D. Astruc, *J. Am. Chem. Soc.* **2009**, *131*, 590 – 601; J. Camponovo, J. Ruiz, E. Cloutet, D. Astruc, *Chem. Eur. J.* **2009**, *15*, 2990 – 3002.

[6] N. Rosenfeldt, N. Dingenouts, D. Pötschke, M. Ballauff, A. J. Berresheim, K. Müllen, P. Lindner, *Angew. Chem.* **2004**, *116*, 111 – 114; *Angew. Chem. Int. Ed.* **2004**, *43*, 109 – 112; C. G. Clark, Jr., R. J. Wenzel, E. V. Andreitchenko, W. Steffen, R. Zenobi, K. Müllen, *New J. Chem.* **2007**, *31*, 1300 – 1306.

[7] Y. Yu, A. D. Bond, P. W. Leonard, U. J. Lorenz, T. V. Timofeeva, K. P. C. Vollhard, D. W. Glenn, A. A. Yakovenko, *Chem. Commun.* **2006**, *24*, 2572 – 2574.

[8] a) For the first synthesis of hexaethynylbenzene, see: J. C. Armstrong, R. Boese, K. P. C. Vollhardt, *Angew. Chem.* **1986**, *98*, 270 – 271; *Angew. Chem. Int. Ed. Engl.* **1986**, *25*, 268 – 269; b) R. Boese, J. R. Green, J. Mittendorf, K. P. C. Vollhardt, *Angew. Chem.* **1992**, *104*, 1643 – 1645; *Angew. Chem. Int. Ed. Engl.* **1992**, *31*, 1643 – 1645; c) J. D. Tovar, N. Jux, T. Jarrosson, S. I. Khan, Y. Rubin, *J. Org. Chem.* **1997**, *62*, 3432 – 3433; d) J. E. Anthony, S. I. Khan, Y. Rubin, *Tetrahedron Lett.* **1997**, *38*, 3499 – 3502; e) U. H. F. Bunz, Y. Rubin, Y. Tobe, *Chem. Soc. Rev.* **1999**, *28*, 107 – 119; f) D. M. Bowles, G. J. Palmer, C. A. Landis, J. L. Scott, J. E. Anthony, *Tetrahedron* **2001**, *57*, 3753 – 3758.

[9] a) J.-L. Fillaut, J. Linares, D. Astruc, *Angew. Chem.* **1994**, *106*, 2540 – 2542; *Angew. Chem. Int. Ed. Engl.* **1994**, *33*, 2460 – 2462; b) J. Nierle, D. Barth, D. Kuck, *Eur. J. Org. Chem.* **2004**, 867 – 872; c) V. J. Chebny, D. Dhar, S. V. Lindeman, *Org. Lett.* **2006**, *8*, 5041 – 5044.

[10] a) E. Negishi, F. Liu in *Metal-Catalyzed Cross-Coupling Reactions* (Eds.: F. Diederich, P. J. Stang), Wiley-VCH, New York, **1997**, p. 1; b) A. Carella, G. Rapenne, J.-P. Launay, *New J. Chem.* **2005**, *29*, 288 – 290.

[11] a) J. Nierle, D. Barth, D. Kuck, *Eur. J. Org. Chem.* **2004**, 867 – 872; b) D. Astruc, *Organometallic Chemistry and Catalysis*, Springer, Heidelberg, **2007**, p. 502.

[12] B. Bildstein, A. Hradsky, H. Kopacka, R. Malleier, K.-H. Ongania, *J. Organomet. Chem.* **1997**, *540*, 127 – 145.

[13] Crystal data for **8**: $C_{108}H_{114}Fe_6$, $2\,C_8H_{18}$, $M_r = 1975.54$, monoclinic, $a = 18.7113(7)$, $b = 12.5738(4)$, $c = 22.4110(9)$ Å, $U = 5246.1(3)$ Å^3, $T = 180$ K, space group $P2_1/n$ (no. 14), $Z = 2$, $\mu(\mathrm{Mo}_{K\alpha}) = 0.856\ \mathrm{mm}^{-1}$, 92321 reflections measured, 10708 unique ($R_{\mathrm{int}} = 0.030$) which were used in all calculations. $R = 0.0409$ and $wR2 = 0.1020$ (8609 reflections with $I > 2\sigma(I)$). CCDC 686494 contains the supplementary crystallographic data for this paper. These data can be obtained free of charge from The Cambridge Crystallographic Data Centre via www.ccdc.cam.ac.uk/data_request/cif.

[14] R. L. Collins, *J. Chem. Phys.* **1965**, *42*, 1072 – 1080; A. Stebler, A. Furrer, J. H. Ammeter, *Inorg. Chem.* **1984**, *23*, 3493 – 3500. The Mössbauer spectrum of **3** shows the classic ferrocene doublet with Q.S. = $2.0\ \mathrm{mm\,s^{-1}}$ and I.S. = $0.5\ \mathrm{mm\,s^{-1}}$. The spectrum of $\mathbf{3}(PF_6)_6$ collapses into a broad line (Figure 2).

[15] T. P. Gill, K. R. Mann, *Inorg. Chem.* **1983**, *22*, 1986; D. Catheline, D. Astruc, *J. Organomet. Chem.* **1983**, *248*, c9 – c12; D. Catheline, D. Astruc, *J. Organomet. Chem.* **1984**, *272*, 417 – 426; D. Catheline, D. Astruc, *Organometallics* **1984**, *3*, 1094 – 1100.

[16] P. Jutzi, B. Kleinebekel, *J. Organomet. Chem.* **1997**, *545–546*, 573 – -576.

[17] H. Fink, N. J. Long, A. J. Martin, G. Opromolla, A. J. P. White, D. J. Williams, P. Zanello, *Organometallics* **1997**, *16*, 2646 – 2650.

[18] a) M. Sato, Y. Hayashi, M. Katada, S. Kawata, *J. Organomet. Chem.* **1994**, *471*, 179 – 184; b) M. Sato, Y. Hayashi, S. Kumakura, N. Shimizu, M. Katada, S. Kawata, *Organometallics* **1996**, *2*, 721 – 728; c) F. Paul, C. Lapinte, *Coord. Chem. Rev.* **1998**, *178*, 431 – 509.

[19] W. E. Geiger, *Organometallics* **2007**, *27*, 5738 – 5765.

[20] a) W. Adam, H. M. Harrer, F. Kita, W. M. Nau, *J. Org. Chem.* **1997**, *62*, 1419 – 1426; b) A. H. Winter, D. E. Falvey, C. J. Cramer, *J. Am. Chem. Soc.* **2004**, *126*, 9661 – 9668; c) B. Le Guennic, K. Costuas, J.-F. Halet, C. Nervi, M. A. J. Paterson, M. A. Fox, R. L. Roberts, D. Albesa-Jove, H. Puschmann, J. A. K. Howard, P. J. Low, *C. R. Chim.* **2005**, *8*, 1883 – 1896; d) W. T. G. Johnson, M. B. Sullivan, C. J. Cramer, *Int. J. Quantum Chem.* **2001**, *85*, 492 – 508.

[21] The disproportionation constant $K_{\mathrm{disp}} = \exp(\Delta E^\circ/2RT)$: D. E. Richardson, H. Taube, *Inorg. Chem.* **1981**, *20*, 1278 – 1285; D. E. Richardson, H. Taube, *J. Am. Chem. Soc.* **1983**, *105*, 40 – 51.

[22] Contributions to the mixed valency: $\Delta G^\circ c = \Delta G_e$ (entropy) + ΔG_E (electrostatic) + ΔG_D (delocalization) + ΔG_S (synergy): J. E. Sutton, P. M. Sutton, H. Taube, *Inorg. Chem.* **1979**, *18*, 1017.

[23] If the electrostatic and delocalization factors are zero, the distribution is only statistic (entropy)[22] and follows a simple binomial law, that is, for instance the half-oxidized [Fe_6] product contains 31.2% [$Fe^{II}{}_3Fe^{III}{}_3$], 23.4% [$Fe^{II}{}_4Fe^{III}{}_2$], 23.4% [$Fe^{II}{}_2Fe^{III}{}_4$], 9.4% [$Fe^{II}{}_5Fe^{III}$], 9.4% [$Fe^{II}Fe^{III}{}_5$], 1.6% [$Fe^{II}{}_6$], and 1.6% [$Fe^{III}{}_6$].

[24] P. D. Beer, P. A. Gale, *Angew. Chem.* **2001**, *113*, 502 – 532; *Angew. Chem. Int. Ed.* **2001**, *40*, 486 – 516; U. Dreshler, B. Erdogan and V. M. Rotello, *Chem. Eur. J.* **2004**, *10*, 5570 – 5579; D. Astruc, M.-C. Daniel, J. Ruiz, *Chem. Commun.* **2004**, 2637 – 2649.