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Synthesis, Redox Activity of Rigid Ferrocenyl Dendrimers, and Isolation of Robust Ferricinium and Class-II Mixed-Valence Dendrimers

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Abstract: The coupling reactions of ethynylferrocene with trihalogenoarenes do not lead to ethynylferrocenyl arenes that are soluble enough to form the basis of a suitable construction of stiff ferrocenylethynyl arene-cored dendrimers, which explains the previous lack of reports on stiff ferrocenyl dendrimers. However, rigid ferrocenyl-terminated dendrimers have been synthesized from 1,3,5-tribromo- and triiodobenzene through Sonogashira and Negishi reactions with 1,2,3,4,5-pentamethyl-1′-ethylnylferrocene (**1a**), according to 1→2 connectivity. With compound **1a**, the construction of a soluble dendrimer (**10a**) that contained 12 ethynylpentamethylferrocenyl termini was achieved. Stiff dendrimer **10a** shows a single, reversible cyclic voltammetry (CV) wave (with adsorption), which disfavors the hopping heterogeneous electron-transfer mechanism that is postulated for redox-terminated dendrimers that contain flexible tethers. The selectivity of these Sonogashira reactions allows the synthesis of an arene-cored dendron (**2c**) that contains both ethynylferrocenyl and 1,2,3,4,5-pentamethyl-ferrocenylethynyl redox groups, thus leading to the construction of a dendrimer (**7c**) that contains both types of differently substituted ferrocenyl groups with two well-separated reversible CV waves. Upon selective oxidation, this mixed dendrimer (**7c**) leads to a class-II mixed-valence dendrimer, **7c**$[PF_6]_3$, as shown by Mössbauer spectroscopy, whereas oxidation of the related fully pentamethylferrocenylated dendrimer (**7a**) leads to the all-ferricinium dendrimer, **7a**$[PF_6]_6$.

Keywords: cross-coupling · dendrimers · electrochemistry · ferrocene · mixed-valence compounds

Introduction

Electron-transfer reactions in multi-redox nanosystems, such as polymers,[1] dendrimers[2] and other nanoparticles,[3] are of interest for their relevance to biological redox processes,[4] molecular conductors and semiconductors,[5] mixed-valence stabilization,[6] catalysis,[7] and redox recognition.[8] Among the redox systems that are involved in dendritic frameworks, ferrocenes occupy a privileged place because of the stability of both their Fe^{II} and Fe^{III} forms, at least on the electrochemical timescale.[9] Although rigid dendrimers are known,[10–13] there are no reports of rigid ferrocene-containing dendrimers, presumably because of the synthesis problems related to their insolubility. Rigid dendrimers have been pioneered on the organic side by the work of Moore′s group with polyarylene dendrimers[1] and on the inorganic side by the reports of Balzani′s group on redox- and photoactive ruthenium and osmium poly(oligopyridine) dendrimers that are of specific interest as antenna models and for their optoelectronic properties.[2] Since the late 1990s, Humphrey and co-workers have synthesized and studied the non-linear optical properties of a series of stiff dendrimers that contain ruthenium complexes.[13] Giant polyarylene dendrimers also illustrative examples with these properties, as well as for biological applications in molecular recognition.[8,12] Recently, Yamamoto′s group introduced ferrocene derivatives into rigid polyazidomethine dendrimers by employing non-covalent charge-transfer interactions.[14] Vollhardt and co-workers reported the "impossible" hot molecule hexaferrocenylbenzene[15a] and, earlier, star-shaped hexa(ethynyl)benzene and hexa(diynyl)benzene.[15b,c] Recently, we also reported hexa(ferrocenylethyl)benzenes and their related electrostatic effects.[16] Herein, we report a convergent synthesis of rigid hexa- and dodecaferrocenyl arene-centered poly(ethynylphenylene) dendrimers with C_3 symmetry and 1→2 connectivity,[17] their electron-transfer properties, and the stabilization and isolation of ferricinium and class-II mixed-valence ferrocenyl dendrimers.

Results and Discussion

The convergent synthesis of the metallodendrimers that were used herein involved the Pd^0-catalyzed Sonogashira reactions[18] of ethynylferrocenes with 1,3,5-tribromobenzene. Whereas the Negishi reaction[19] of ferrocenylethynylzinc chloride with hexabromobenzene was reported to yield hexa(ferrocenylethynyl)benzene,[16] the Sonogashira reaction was much slower and selective because the favorable effect of the electron-withdrawing halogen atoms decreased with

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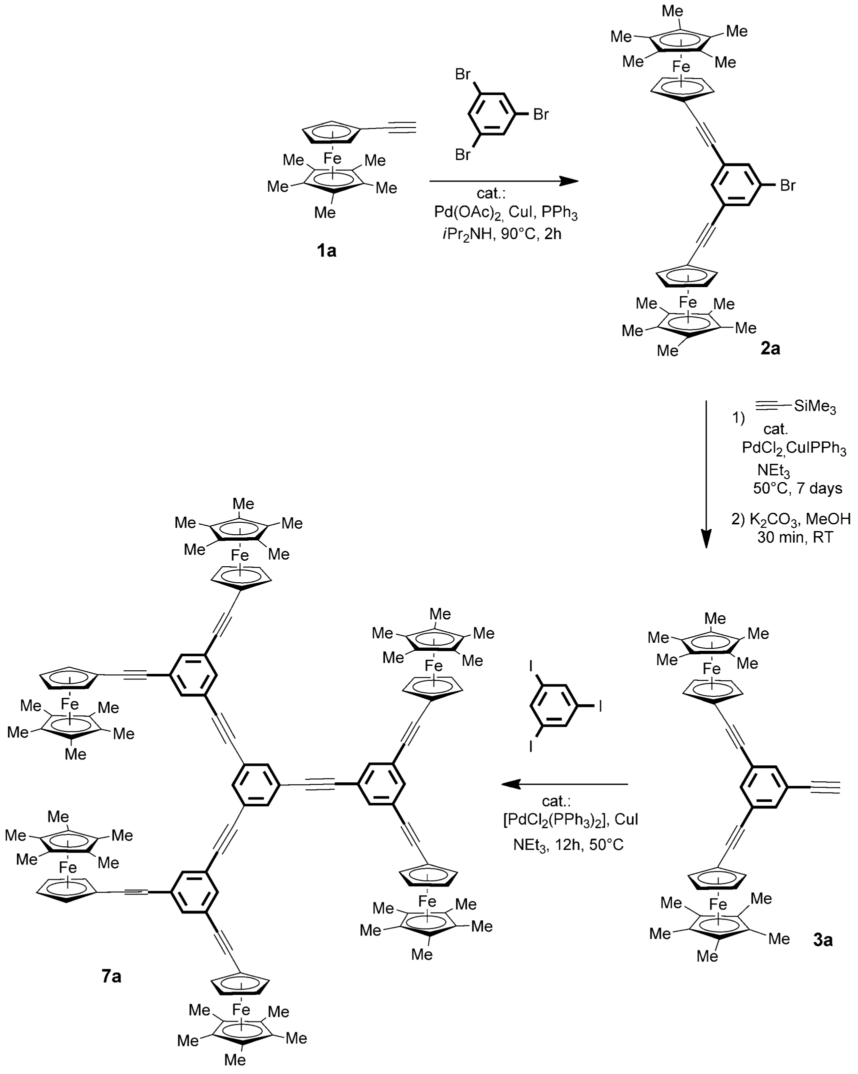
increasing substitution. Indeed, with 1,3,5-tribromobenzene, the Sonogashira reactions of the ethynylferrocenes rapidly yielded the monoethynylation products and, more slowly, the corresponding products of a second ethynylation step. On the other hand, the third ethynylation step, which required a reaction time of one week, could be easily avoided. We have taken advantage of this selectivity to carry out the convergent construction of poly(ferrocenylethynyl) dendrons, as shown in Scheme 1. Although 1,3-di(ferrocenylethynyl)-5-bromobenzene can be synthesized,[20] the convergent syntheses cannot progress any further, because of the insolubility of the hoped-for products. However, with 1,2,3,4,5-pentamethyl-1′-ethynyl ferrocene,[21] this drawback could be avoided and hexametallic dendrimer **7a** was successfully synthesized from the reaction of new metalladendron **3a** with 1,3,5-triiodobenzene, as shown in Scheme 1.

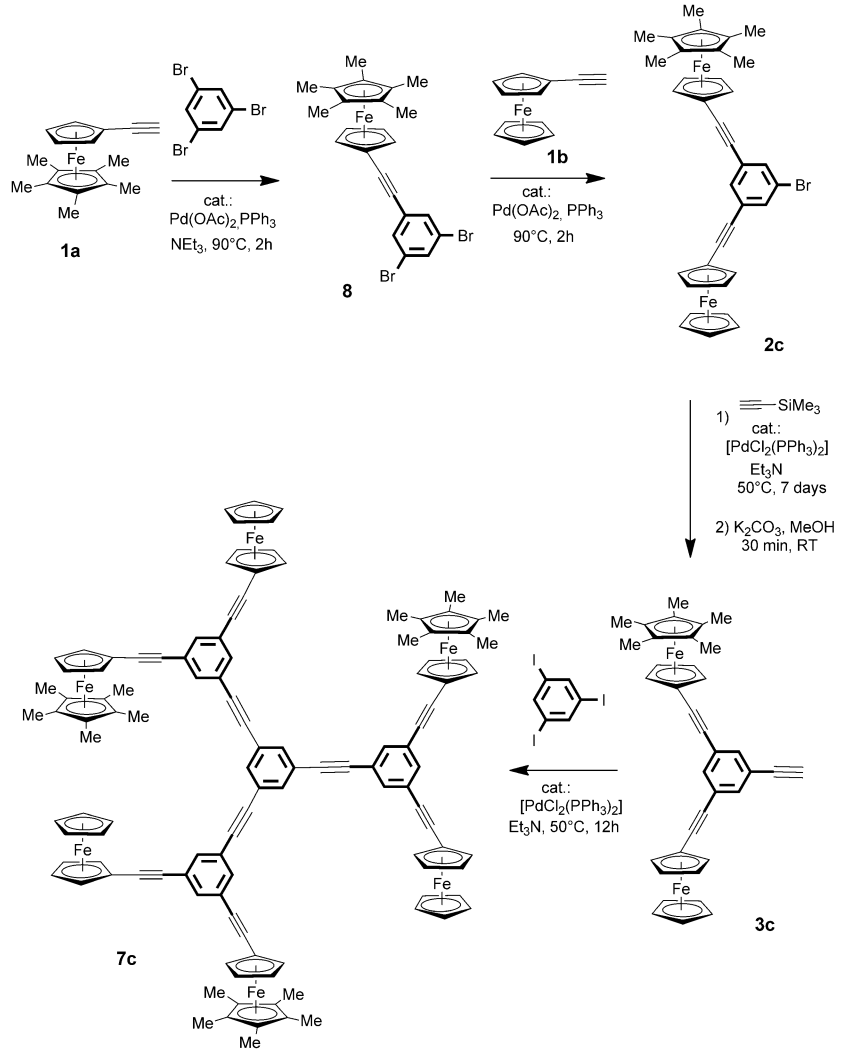
The cyclic voltammogram (CV) of compound **7a** in CH_2Cl_2 on a Pt anode shows a fully chemically and electrochemically reversible six-electron wave at −0.5 V (versus Cp_2Fe^+/Cp_2Fe). Contrary to the case of the star-shaped complex hexa(pentamethylferrocenylethynyl)benzene,[16] no electrostatic effect is observed by CV wave-splitting, even upon using the weak-ion-pairing salt $[n\mathrm{Bu}_4][\mathrm{BAr^F}_4]$ ($\mathrm{Ar^F}$ = 3,5-$C_6H_3(CF_3)_2$) as the supporting electrolyte,[22] owing to the relatively remote location of the redox groups from one another in compound **7a**. Because the electrostatic effect is close to zero, the binomial-law statistics indicate the presence of 31 % mixed-valence $\mathrm{Fe^{II}}_3\mathrm{Fe^{III}}_3$ dendrimer upon oxidizing half of compound **7a** in a homogeneous solution. The permethylated C_5Me_5 (Cp*) ring on the pentamethylferrocenyl termini in dendrimer **7a** allows a much better stabilization of the ferricinium species than the parent ferrocenyl dendrimers. Indeed, the synthesis of the fully oxidized, blue pentamethylferricinium dendrimer was carried out upon oxidation of compound **7a** with $[Cp_2Fe][PF_6]$ (6 equiv) in CH_2Cl_2, thus leading to the isolation of complex **7a**$[PF_6]_6$ as stable deep-blue microcrystals. The d^5, 17-electron electronic structure of this complex is shown by the rhombic distortion of the EPR signal. This synthesis represents a rare example of a ferricinium dendrimer.[23]



Scheme 1. Sonogashira synthesis of the hexa(pentamethylferrocenyl) G_1 dendrimer.

Remarkably, the monopentamethylferrocenylethynylation of 1,3,5-tribromobenzene with compound **1a** can be selective, thereby giving the corresponding monopentamethylferrocenyl arene derivative (**8**), which readily and selectively undergoes ferrocenylethynylation with ethynylferrocene. In this way, mixed, unsymmetrical disubstituted arene derivative **2c** was readily synthesized and further used in the dendrimer synthesis without being marred by solubility problems. Thus, either bis-1,3-(pentamethylferrocenyl)-5-ethynylbenzene **3a** (Scheme 1) or its unsymmetrical mixed homologue (**3c**, Scheme 2) reacted with 1,3,5-triiodobenzene to give symmetrical pentamethylferrocenylethynyl dendrimer **7a** (Scheme 1) or mixed dendrimer **7c** (Scheme 2), respectively, the first of which containing two distinct types of ferrocenyl groups.

The reaction of compound **7a** with $[FeCp_2][PF_6]$ (6 equiv) in CH_2Cl_2 yielded stable hexapentamethylferricinium dendrimer **7a**$[PF_6]_6$, which was precipitated by the addition of diethyl ether, thus affording the



Scheme 2. Sonogashira synthesis of the mixed ferrocenyl–pentamethylferrocenyl G_1 dendrimer.

complex as deep-blue microcrystals (Scheme 3). This hexapentamethylferricinium dendrimer was characterized by, among other things, elemental analysis and by the single broad band at I.S. = 0.6 mm s^{-1} (vs. Fe) and the nil quadrupole splitting, known for ferricinium derivatives, in the zero-field Mössbauer spectrum at 78 K (Figure 1).

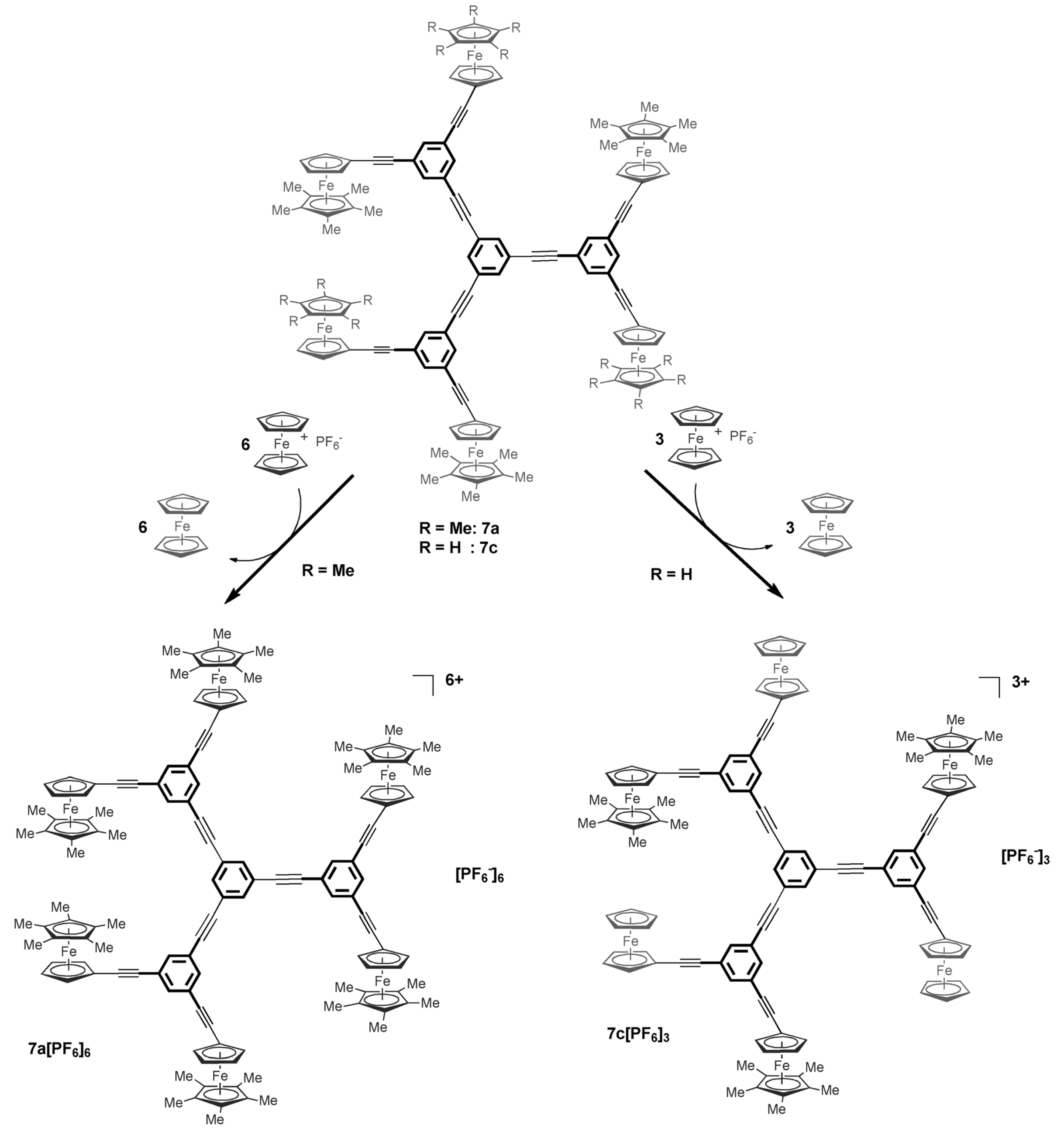
The CV of mixed dendrimer **7c** in CH_2Cl_2 on a Pt anode shows two fully chemically and electrochemically three-electron reversible waves (Figure 2): One at $E_{1/2} = -0.50$ V (vs. $CpFe_2^+/Cp_2Fe$), which corresponds to the oxidation of the three pentamethylferrocenyl groups, and the other at $E_{1/2} = -0.25$ V (vs. $CpFe_2^+/Cp_2Fe$), which corresponds to the oxidation of three ferrocenyl groups. This CV wave-splitting shows the stabilization of the mixed-valence trication, with a comproportionation constant (K_c) of the order of 10^4.

The partial oxidation of compound **7c** was performed by using $[FeCp_2][PF_6]$ (3 equiv) in CH_2Cl_2 and yielded metallodendrimer **7c**$[PF_6]_3$, which was precipitated as brown microcrystals by the addition of diethyl ether (Scheme 4). Gratifyingly, the more easily oxidizable pentamethylferrocenyl groups are also those that give the more robust ferricinium groups. Thus, mixed-valence ferricinium/ferrocene dendrimer **7c**$[PF_6]_3$ is robust, unlike genuine ferricinium derivatives that lack ring permethylation, which are sensitive to air and polar solvents. Various characterization methods were used to confirm the structure of complex **7c**$[PF_6]_3$, including elemental analysis and IR, UV/Vis, EPR, and Mössbauer spectroscopy. Its d^5, 17-electron electronic structure is shown by the rhombic distortion in the EPR signal. The class-II mixed-Fe^{II}/Fe^{III} valence is shown in the zero-field Mössbauer spectrum of compound **7c** by the presence of both the classical ferrocenyl-type doublet and the quadrupole doublet, with a very small value, which collapses into a broad singlet that is characteristic of ferricinium derivatives. (Figure 3).[24]

CV wave-splitting in ferrocenyl dendrimers has previously been observed by Casado's group with $SiFc_2$ branch termini (Fc = ferrocenyl); in that case, such wave-splitting was a signature of mixed-valence stabilization, but the oxidized or mixed-valence dendrimers were not isolated.[26]

Various characterization methods were used to confirm the structure of complex **7c**$[PF_6]_3$, including elemental analysis and IR, UV/Vis (see the Supporting Information), and Mössbauer spectroscopy. The class-II mixed-Fe^{II}/Fe^{III} valence is shown in the zero-field Mössbauer spectrum of complex **7c**$[PF_6]_3$ at 78 K by the presence of both the classical ferrocenyl-type doublet and the quadrupole doublet, with a quadrupole splitting, which collapse into a broad singlet that is characteristic of ferricinium derivatives (Figure 3).[24]

Further convergent dendronic construction involved the same Sonogashira reaction with 1,3,5-trimomobenzene, which was stopped after one day to essentially afford the substitution of only two bromine atoms of 1,3,5-tribromobenzene and the formation of dendron **11a**, which contained four iron-sandwich units. The third bromine atom was substituted by an ethynyl group upon Sonogashira reaction with trimethylsilylacetylene or Negishi reaction with trimethylsilylethynylzinc chloride, followed by deprotection, thus



Scheme 3. Oxidation of pentamethylferrocenyl (**7a**) and mixed pentamethylferrocenyl–ferrocenyl dendrimers (**7c**) and the isolation of thermodynamically stable, fully oxidized hexacationic (**7a**[PF$_6$]$_6$) and mixed-valence tricationic dendrimers (**7c**[PF$_6$]$_3$).

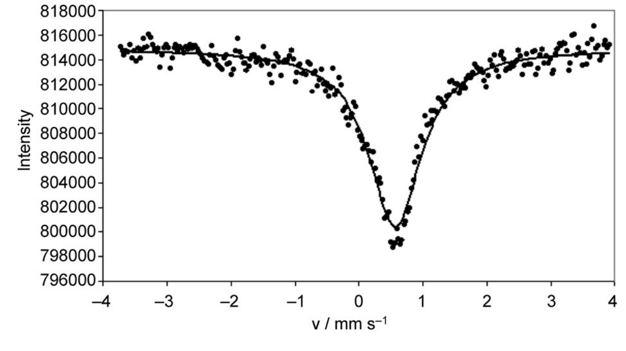


Figure 1. Zero-field Mössbauer spectrum of complex **7a**[PF$_6$]$_6$ at 78 K, which only shows the presence of pentamethylferricinium groups. Isomer shift (I.S.): 0.6 mm s^{-1} (vs. Fe); quadrupole splitting (Q.S.) = 0 mm^{-1}.

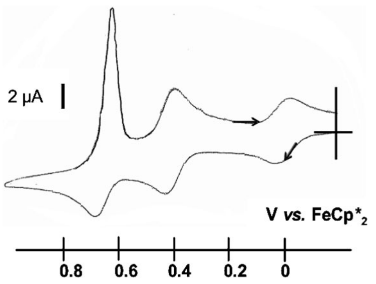
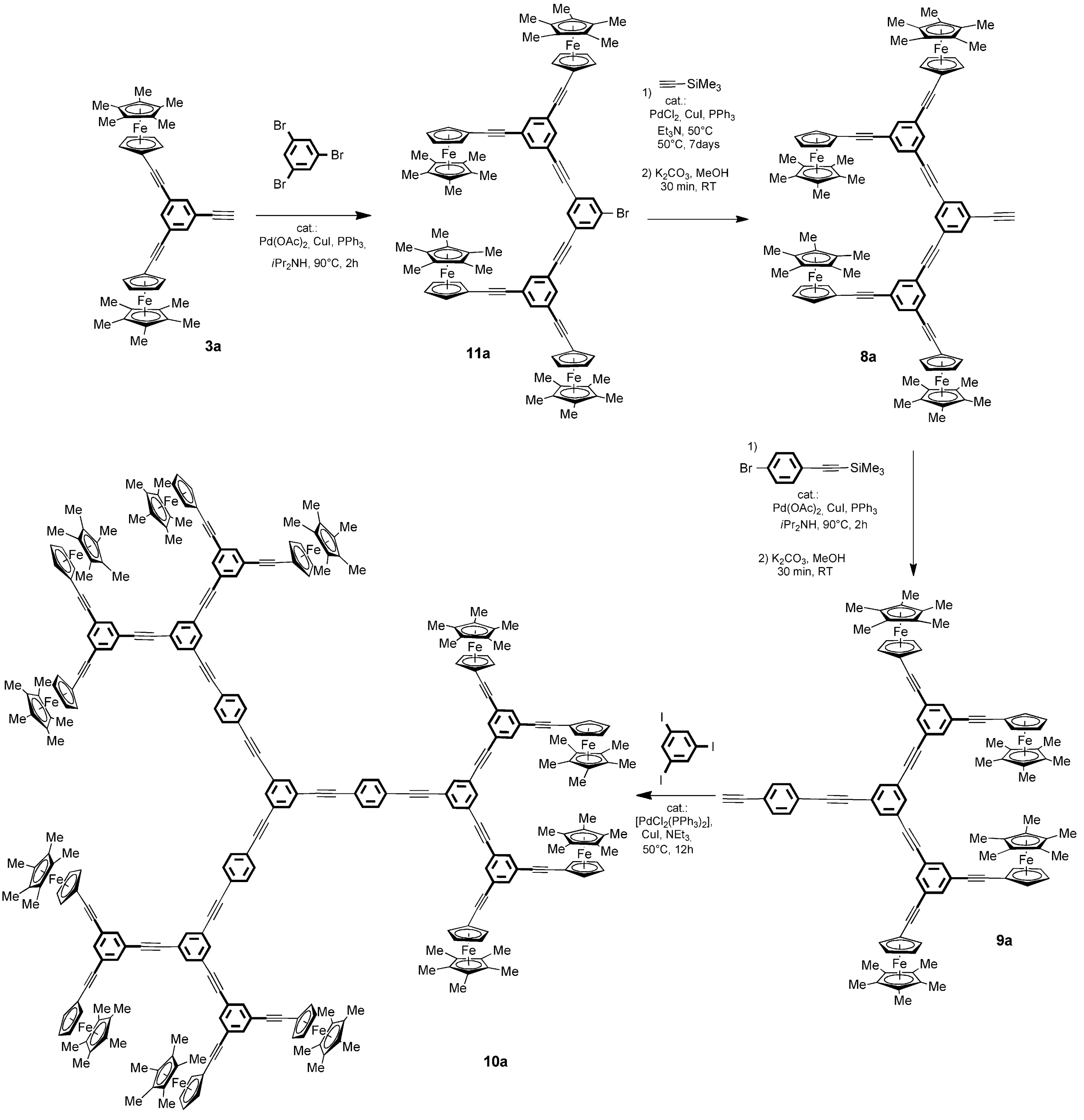


Figure 2. CV of dendrimer **7c** (c = 1 mM in CH_2Cl_2, 293 K, scan rate: 0.1 V s^{-1}): two reversible waves at $E_{1/2}$ = 0.4 and 0.64 V (cathodic adsorption, versus $Cp^*{}_2Fe$ as an internal reference,[25] supporting electrolyte: 0.1 M [(nBu)$_4$N][PF$_6$]).



Scheme 4. Convergent synthesis of rigid ferrocenyl-terminated G2 dendron and dendrimer.

yielding compound **8a**. Then, lengthening the tether at the focal point in compound **9a** is necessary to avoid excess steric bulk in the final convergent assembly step of this tetra-iron-sandwich dendron onto an arene core. Thus, the reaction of dendron **8a** with *para*-(bromo)trimethylsilylethynylbenzene, followed by deprotection, yielded dendron **9a**, which showed longer focal points that were terminated by an ethynyl group (Scheme 4).

Sonogashira reactions of dendron **9a** with 1,3,5-triiodobenzene yielded stiff dendrimer **10a**, which showed C_3 symmetry and contained 12 pentamethylferrocenyl groups (Scheme 4). Dendrimer **10a** was characterized by ^{1}H and ^{13}C NMR spectroscopy, MS (MALDI-TOF), and elemental analysis (see the Supporting Information).

The cyclic voltammogram (CV) of dodeca(pentamethylferrocenyl) metallodendrimer **10a** (Figure 4) shows a single chemically and electrochemically reversible 12-electron wave for the 12 pentamethylferrocenyl redox centers (with a weak cathodic adsorption), even with perfluorinated salt Na[BAr$^F_4$] (Ar^F = $C_6H_3\{3,5\text{-}(CF_3)_2\}_4$) as the supporting elec-

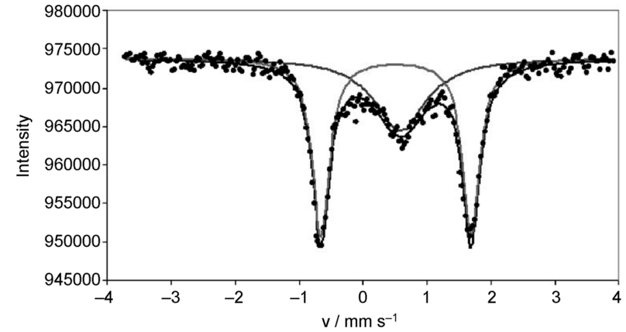


Figure 3. Zero-field Mössbauer spectrum of complex **7c**[PF$_6$]$_3$ at and 78 K, which shows the presence of both ferrocenyl (I.S. = 0.5 mm s^{-1} vs. Fe, Q.S. = 2.4 mm s^{-1}) and pentamethylferrocenyl groups (I.S. = 0.6 mm s^{-1} vs. Fe, Q.S. = 0 mm s^{-1}).

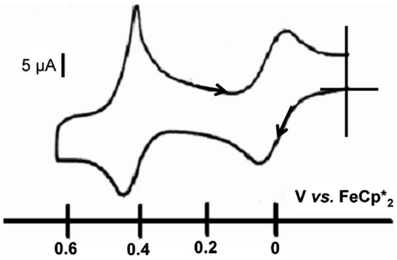


Figure 4. CV of compound **10a** (c = 1 mM in CH$_2$Cl$_2$, 293 K, scan rate: 0.1 V s^{-1}): reversible wave at $E_{1/2}$ = 0.42 V (versus decamethylferrocene as an internal reference, supporting electrolyte: 0.1 M [(nBu)$_4$N][PF$_6$]).

trolyte. Interestingly, the 12 pentamethylferrocenyl groups are oxidized in a single 12-electron wave, that is, the electrostatic effect is so weak that it is not observed, and the 12 distinct single redox potentials are so close to one another that they are not distinguishable.[27] Moreover, the rigidity of this metallodendrimer does not provide an adequate possibility of electron hopping, which is postulated in the cases of the ferrocenyl-terminated dendrimers with flexible tethers. Thus, fast rotation of the dendrimer, which brings all of the redox sites in turn into the vicinity of the electrode, appears here to be the privileged mechanism for fast heterogeneous electron transfer between all of these redox sites and the electrode.[28]

Conclusions

In conclusion, the synthetic strategies developed herein, which involved selective bromide substitution in 1,3,5-tribromobenzene, allowed the synthesis of the first stiff ferrocenyl, ferricinium, and mixed-valence dendrimers. The introduction of only the permethylferrocenylethynyl group onto the arene allowed the generation of robust all-ferricinium dendrons and dendrimers upon oxidation. The alkynylation reactions selectivity provided unsymmetrical dendrons, thus leading to the isolation and characterization of the first well-defined, robust class-II mixed-valence ferricinium/ferrocenyl dendrimers.

The comparative influence of the inter-site distances between the six redox centers on the electrostatic effects of hexa(Fc-ethynyl)benzene and hexa(Fc-ethynyl)-terminated dendrimer **7b** illustrates its crucial role in determining the electrostatic effects and mixed-valence stabilization of identical ferrocenyl sites.

Two electron-transfer mechanisms in metallodendrimers between the redox site and the electrode, that is, inter-site hopping and fast rotation, have been suggested.[27] In rigid metallodendrimers, the hopping mechanism is disfavored by the inter-site distance, as confirmed by the absence of an electrostatic effect. Thus, the fast-rotation mechanism remains the most likely.

Experimental Section

General data: ^{1}H NMR spectra were recorded at 25 °C on a Bruker AC 300 (300 MHz) spectrometer. ^{13}C NMR spectra were recorded in pulsed FT mode at 75.0 MHz on a Brucker AC 300 spectrometer. All chemical shifts (δ) are reported in parts per million (ppm) and are referenced to Me$_4$Si (TMS). Cyclic voltammetry (CV) measurements were recorded under a nitrogen atmosphere in CH$_2$Cl$_2$, 20 °C, supporting electrolyte: 0.1 M [nBu$_4$N][PF$_6$], working and counter electrodes: Pt, reference electrode: Ag, internal reference: FeCp*$_2$ (Cp* = η^5-C$_5$Me$_5$),[25] scan rate: 0.200 V s^{-1}. MS (MALDI-TOF) was performed by the CESAMO (Univ. Bordeaux I, France) on a Voyager mass spectrometer (Applied Biosystems). The instrument was equipped with a pulsed N$_2$ laser (337 nm) and a time-delayed extracted ion source. Spectra were recorded in positive-ion mode by using the reflection at an accelerating voltage of 20 kV. Samples were dissolved in CH$_2$Cl$_2$ at a concentration of 10 mg mL^{-1}. The dithranol matrix solution was prepared by dissolving 10 mg in 1 mL of CH$_2$Cl$_2$. The solution was combined in a 10:1 ratio (v/v) of the matrix to the sample. 1–2 µL of the obtained solution was deposited onto the sample target and vacuum-dried. Elemental analysis was performed at the Center of Microanalyses of CNRS at Lyon Solaize (France).

Synthesis of 1,3-dibromo-5-(1,2,3,4,5-pentamethylferrocenylethynyl)benzene) (8), 1-bromo-3,5-bis (pentamethylferrocenylethynyl)benzene (2a), and 1,3,5-tris(pentamethylferrocenylethynyl)benzene: A mixture of catalytic amounts of CuI (0.228 equiv, 1.26 mmol, 0.240 g), Pd(OAc)$_2$ (0.213 equiv, 1.17 mmol, 0.263 g), and PPh$_3$ (0.497 equiv, 2.74 mmol, 0.719 g) in diisopropylamine (100 mL) was stirred at 0 °C for 10 min. Then, the mixture was treated with 1,2,3,4,5-pentamethyl-1′-ethynylferrocene (2 equiv, 11 mmol, 3.082 g)[21] and 1,3,5-tribromobenzene (1 equiv, 5.51 mmol, 1.734 g) and stirring was continued at 0 °C for 1 h, before warming to RT and then heating at reflux for 2 h. After filtration and evaporation to dryness, the residue was washed with dilute HCl, Na$_2$CO$_3$ (10 %), and water and purified by column chromatography on silica gel (pentane/CH$_2$Cl$_2$, 90:10). Successive bands of compounds **1** (0.417 g, 15 % yield), **2** (2 g, 50 % yield), and **3** (0.150 g, 3 % yield) were obtained as solids after the removal of the solvent in vacuo.

1,3-Dibromo-5-(1,2,3,4,5-pentamethyl-ferrocenylethynyl)benzene (***8***): ^{1}H NMR (300 MHz, CDCl$_3$): δ = 1.88 (s, 15 H; Cp*), 3.85–3.92 (d, 4 H; CH of Cp), 7.55 ppm (m, 3 H; aromatic CH); ^{13}C NMR (75 MHz, CDCl$_3$): δ = 10.3 (CH$_3$), 64.8 (Cq of CpCH$_3$), 73.3, 74.3 (CH of CpC≡C), 81.4 (Cq of CpC≡C), 83.5, 92.3 (C≡C), 122.7 (Cq of aromatic-Br), 127.9 (Cq of aromatic-C≡C), 132.5, 133.0 ppm (aromatic CH); elemental analysis calcd (%) for C$_{23}$H$_{22}$Br$_2$Fe: C 53.74, H 4.31; found: C 53.95, H 4.26.

1-Bromo-3,5-bis(pentamethylferrocenylethynyl)benzene (***2a***): ^{1}H NMR (300 MHz, CDCl$_3$): δ = 1.91 (s, 30 H; Cp*), 3.84–3.93 (d, 8 H; CH of Cp), 7.53 ppm (m, 3 H; aromatic CH); ^{13}C NMR (75 MHz, CDCl$_3$): δ = 10.6 (*CH$_3$*Cp), 65.1 (Cq of *Cp*CH$_3$), 73.0, 74.1 (CH of *Cp*C≡C), 81.2 (Cq of

*Cp*C≡C), 84.2, 90.8 (C≡C), 121.9 (Cq of aromatic-Br), 126.3 (Cq of aromatic-C≡C), 132.2, 132.5 ppm (CH of aromatic); elemental analysis calcd (%) for $C_{40}H_{41}BrFe_2$: C 67.35, H 5.79; found: C 67.24, H 5.65.

Synthesis of 1-ethynyl-3,5-bis(pentamethylferrocenylethynyl)benzene (3a): To a mixture of compound **2a** (2 g, 3.11 mmol) in dry triethylamine (100 mL) were added $[PdCl_2(PPh_3)_2]$ (0.218 g, 10 mol%) and CuI (0.107 g, 18 mol%). The mixture was stirred at 50 °C and then trimethylsilylacetylene (0.9 mL, 6.22 mmol) was added. After 48 h, the same amounts of $[PdCl_2(PPh_3)_2]$, CuI, and trimethylsilylacetylene were added and the reaction mixture was stirred at 50 °C for 7 days. After evaporation of the solvent, the crude reaction mixture was purified by column chromatography on silica gel (CH_2Cl_2), thereby affording pure 1,3-bis(pentamethylferrocenylethynyl)-5-(trimethylsilylethynyl)benzene (**2a′**, 2.18 g, 2.98 mmol, 96% yield; for the structure, see the Supporting Information).

Complex **2a′** (2.18 g, 2.98 mmol) was dissolved in THF (25 mL) and MeOH (25 mL). Then, K_2CO_3 (0.824 g, 5.96 mmol) was added and the mixture was stirred at RT for 30 min. The reaction was quenched with a saturated aqueous solution of ammonium chloride and the product was extracted with CH_2Cl_2. The combined organic layers were dried over Na_2SO_4. After evaporation of the solvent, complex **4** (1.88 g, 2.86 mmol, 96% yield) was obtained.

*1-ethynyl-3,5-bis(pentamethylferrocenylethynyl)benzene (**3a**)*: ^1H NMR (300 MHz, $CDCl_3$): $\delta = 1.87$ (s, 30H; Cp*), 3.14 (s, 1H; CH≡C), 3.89–4.0 (d, 8H; CH of Cp), 7.55–7.60 ppm (d, 3H; CH of aromatic). ^{13}C NMR (75 MHz, $CDCl_3$): $\delta = 10.7$ (CH_3), 66.0 (Cq of $CpCH_3$), 73.5, 74.6 (CH of CpC≡C), 78.0 (CH≡C), 81.6 (Cq of CpC≡C), 82.5 (C≡CH), 84.7, 90.1 (C≡C), 122.7 (Cq of aromatic-C≡CH), 125.1 (Cq of aromatic-C≡C), 133.4, 133.9 ppm (CH of aromatic); MS (MALDI-TOF): *m*/*z* calcd for $C_{42}H_{42}Fe_2$: 658.49; found: 658.20; elemental analysis calcd (%) for $C_{42}H_{42}Fe_2$: C 76.61, H 6.43; found: C 76.61, H 6.55.

Synthesis of complex 7a: A mixture of 1,3,5-triiodobenzene (0.100 g, 0.219 mmol, 1 equiv), 1-ethynyl-3,5-bis(pentamethylferrocenylethynyl)-benzene (**3a**, 0.476 g, 0.723 mmol, 3.3 equiv), $[(PPh_3)_2PdCl_2]$ (0.009 g, 0.013 mmol, 0.06 equiv), and cuprous iodine (0.037 g, 0.197 mmol, 0.9 equiv) in triethylamine (10 mL) was magnetically stirred in a Schlenk flask overnight at 50 °C. The solvent was evaporated, and the residue was dissolved in CH_2Cl_2. The organic phase was washed with water and dried with sodium sulfate, the solvent was removed under vacuum, and the crude reaction mixture was purified by column chromatography on silica gel (pentane/CH_2Cl_2, 70:30), thereby affording compound **7a** (0.284 g, 0.118 mmol, 54% yield). ^1H NMR (300 MHz, $CDCl_3$): $\delta = 1.81$ (s, 90H; Cp*), 3.89–4.0 (d, 24H; CH of Cp), 7.55–7.70 ppm (d, 12H; CH of aromatic); ^{13}C NMR (75 MHz, $CDCl_3$): $\delta = 10.9$ (CH_3), 65.7 (Cq of $CpCH_3$), 73.2, 74.4 (CH of CpC≡C), 81.4 (Cq of CpC≡C), 84.8, 88.4, 89.7, 90.1 (C≡C), 123.4, 123.9, 125.2, 122.7 (Cq of aromatic-C≡C), 132.9, 133.8, 134.5 ppm (CH of aromatic); MS (MALDI-TOF): *m*/*z* calcd for $C_{132}H_{126}Fe_6$: 2407.534; found: 2047.7; elemental analysis calcd (%) for $C_{132}H_{126}Fe_6$: C 77.43, H 6.20; found: C 77.24, H 6.58**;** CV (CH_2Cl_2, 293 K): one reversible wave $E_{1/2} = 0.4$ V (versus decamethylferrocene, supporting electrolyte: 0.1 M $[(nBu)_4N][PF_6]$).

Synthesis of 1-bromo-3-(pentamethylferrocenylethynyl)-5-(ferrocenylethynyl)benzene (2c) and 1-(pentamethylferrocenylethynyl)-3,5-bis(ferrocenylethynyl)benzene: A mixture of catalytic amounts of CuI (0.06 equiv, 0.6 mmol, 0.114 g), $Pd(OAc)_2$ (0.06 equiv, 0.6 mmol, 0.135 g), and PPh_3 (0.122 equiv 1.22 mmol, 0.320 g) in diisopropylamine (100 mL) was stirred at 0 °C for 10 min. Then, the mixture was treated with ethynylferrocene (1 equiv 10 mmol, 2.101 g) and 1,3-dibromo-5-(pentamethylferrocenylethynyl)benzene (**8**, 1 equiv, 10 mmol, 5.141 g) and stirring was continued at 0 °C for 1 h before warming to RT and heating at reflux for 2 h. After filtration and evaporation to dryness, the residue was washed with dilute HCl, Na_2CO_3 (10%), and water and purified by column chromatography on silica gel with pentane/CH_2Cl_2 (90:10) to afford compound **6** (3.867 g, 60% yield) and then with pentane/CH_2Cl_2 (80:20) to afford compound **7** (0.532 g, 7% yield).

*Complex **2c***: ^1H NMR (300 MHz, $CDCl_3$): $\delta = 1.90$ (s, 15H; Cp*), 3.85–3.94 (d, 4H; CH of $C_5H_4FeCp^*$), 4.27–4.29 (m, 7H; CH of C_5H_4 and C_5H_5), 4.52–4.54 (m, 2H; CH of C_5H_4FeCp), 7.53–7.57 ppm (m, 3H; CH of aromatic); ^{13}C NMR (75 MHz, $CDCl_3$): $\delta = 10.7$ (CH_3), 64.3 (Cq of $CpCH_3$), 69.1, 70.0, 70.2, 73.1, 74.2 (CH of CpC≡C), 81.3 (Cq of CpC≡C), 83.8, 84.2, 90.6, 91.0 (C≡C), 121.9 (Cq of aromatic-Br), 125.9,126.3 (Cq of aromatic-C≡C), 132.3, 132.7 ppm (aromatic CH); elemental analysis calcd (%) for $C_{35}H_{31}BrFe_2$: C 65.36, H 4.86; found: C 65.26, H 4.83.

1-(Pentamethylferrocenylethynyl)-3,5-bis(ferrocenyl-ethynyl)benzene: ^1H NMR (300 MHz, $CDCl_3$): $\delta = 1.86$ (s, 15H; Cp*), 3.86–3.96 (d, 4H; CH of $C_5H_4FeCp^*$), 4.26 (m, 14H; CH of C_5H_4 and C_5H_5), 4.52- 4.53(m, 4H; CH of C_5H_4FeCp), 7.52–7.54 ppm (m, 3H; CH of aromatic); ^{13}C NMR (75 MHz, $CDCl_3$): $\delta = 10.5$ (CH_3), 64.5 (Cq of $CpCH_3$), 68.8, 69.8, 71.3, 73.0, 74.2 (CH of CpC≡C), 81.2 (Cq of CpC≡C), 84.3, 84.7, 89.2, 89.5 (C≡C), 124.2, 124.7 (Cq of aromatic-C≡C), 132.5, 132.6 ppm (aromatic CH); MS(MALDI-TOF): *m*/*z* calcd for $C_{47}H_{40}Fe_3$: 772.376; found: 772.18*;* elemental analysis calcd (%) for $C_{47}H_{40}Fe_3$: C 73.09, H 5.22; found: C73.47, H 5.26.

Synthesis of 1-ethynyl-3-(pentamethylferrocenylethynyl)-5-(ferrocenylethynyl)benzene (3c): To a mixture of compound **2c** (3.867 g, 6.01 mmol) in dry triethylamine (100 mL) were added $[PdCl_2(PPh_3)_2]$ (0.422 g, 10 mol%) and CuI (0.206 g, 18 mol%). The mixture was stirred at 50 °C and trimethylsilylacetylene (1.7 mL, 12.02 mmol) was added. After 48 h, the same amounts of $[PdCl_2(PPh_3)_2]$, CuI, and trimethylsilylacetylene were added and the reaction mixture was stirred at 50 °C for 7 days. After evaporation of the solvent, the crude reaction mixture was purified by column chromatography on silica gel (CH_2Cl_2), thereby leading to pure complex **2c′** (3.811 g, 5.77 mmol, 96% yield).

Complex **2c′** (3.811 g, 5.77 mmol) was dissolved in THF (50 mL) and MeOH (50 mL). Then, K_2CO_3 (1.595 g, 11.54 mmol) was added and the mixture was stirred at RT for 30 min. The reaction was quenched with a saturated aqueous solution of ammonium chloride and the product was extracted with CH_2Cl_2. The combined organic layers were dried over Na_2SO_4. After evaporation of the solvent, compound **3c** (3.259 g, 5.54 mmol, 96% yield) was obtained.

*1-Ethynyl-3-(pentamethylferrocenylethynyl)-5-(ferrocenylethynyl)benzene (**3c**)*: ^1H NMR (300 MHz, $CDCl_3$): $\delta = 1.94$ (s, 15H; Cp*), 3.16 (s, 1H; CH≡C), 3.87–3.97 (d, 4H; CH of $C_5H_4FeCp^*$), 4.30 (s, 7H; CH of C_5H_4 and C_5H_5), 4.56–4.57 (m, 2H; CH of C_5H_4FeCp), 7.59–7.64 ppm (m; 3H, CH of aromatic); ^{13}C NMR (75 MHz, $CDCl_3$): $\delta = 10.8$ (CH_3), 64.6 (Cq of $CpCH_3$), 69.2, 70.1, 71.6, 73.1, 74.3 (CH of CpC≡C), 78.2 (CH≡C), 81.3 (Cq of CpC≡C), 82.5, 83.8, 84.2, 90.6, 91.0 (C≡C), 122.8, 124.8, 125.2 (Cq of aromatic-C≡C), 133.5, 134.0 ppm (aromatic CH); MS (MALDI-TOF): *m*/*z* calcd for $C_{37}H_{32}Fe_2$: 588.355; found: 588.0; elemental analysis calcd (%) for $C_{37}H_{32}Fe_2$: C 75.53, H 5.48; found: C 75.19, H 5.31.

Synthesis of complex 7c: A mixture of 1,3,5-triiodobenzene (0.100 g, 0.219 mmol, 1 equiv), 1-ethynyl-3-(pentamethylferrocenylethynyl)-5-(ferrocenyl-ethynyl)benzene (**3c**, 0.425 g, 0.723 mmol, 3.3 equiv), $[(PPh_3)_2PdCl_2]$ (0.009 g, 0.013 mmol, 0.06 equiv), and cuprous iodine (0.037 g, 0.197 mmol, 0.9 equiv) in triethylamine (10 mL) was magnetically stirred in a Schlenk flask overnight at 50 °C. The solvent was evaporated under vacuum and the residue was dissolved in CH_2Cl_2. The organic phase was washed with water and dried with sodium sulfate, the solvent was removed under vacuum, and the crude reaction mixture was purified by column chromatography on silica gel (pentane/CH_2Cl_2, 70:30), thereby leading to product **7c** (0.226 g, 0.123 mmol, 56% yield). ^1H NMR (300 MHz, $CDCl_3$): $\delta = 1.91$ (s, 45H; Cp*), 3.83–3.93 (d, 12H; CH of $C_5H_4FeCp^*$), 4.26 (s, 21H; CH of C_5H_4 and C_5H_5), 4.53 (s, 6H; CH of C_5H_4FeCp), 7.58–7.69 ppm (d, 12H; aromatic CH); ^{13}C NMR (75 MHz, $CDCl_3$): $\delta = 10.7$ (CH_3), 64.6 (Cq of $CpCH_3$), 69.1, 70.1, 71.6, 73.7, 74.7 (CH of CpC≡C), 81.3 (Cq of CpC≡C), 84.4, 84.8, 88.5, 89.6, 89.9, 90.2 (C≡C), 123.3, 123.9, 124.8, 125.2 (Cq of aromatic-C≡C), 133.0, 133.2, 133.8, 134.4 ppm (aromatic CH); MS (MALDI-TOF): *m*/*z* calcd for $C_{117}H_{96}Fe_6$: 1837.131; found: 1837.2; elemental analysis calcd (%) for $C_{117}H_{96}Fe_6$: C 76.49, H 5.27; found: C 76.72, H 5.48. CV (CH_2Cl_2, 293 K): two reversible waves $E_{1/2} = 0.4$, 0.64 V (versus decamethylferrocene; supporting electrolyte $[(nBu)_4N]PF_6$).

Synthesis of complexes 6 and 11a: A mixture of catalytic amounts of CuI (0.09 equiv, 0.089 mmol, 0.017 g), $Pd(OAc)_2$ (0.075 equiv, 0.074 mmol, 0.017 g), and PPh_3 (0.183 equiv 0.180 mmol, 0.047 g) in diisopropylamine (50 mL) was stirred at 0 °C for 10 min. Then, the mixture was treated with 1-ethynyl-3,5-bis(pentamethylferrocenylethynyl)benzene (**3a**, 2 equiv 1.97 mmol, 1.30 g) and 1,3,5-tribromobenzene (1 equiv, 0.985 mmol, 0.310 g) and stirring was continued at 0 °C for 1 h before warming to RT and heating at reflux for 2 h. After filtration and evaporation to dryness, the residue was washed with dilute HCl, Na_2CO_3 (10 %), and water and purified by column chromatography on silica gel with pentane/CH_2Cl_2 (90:10) to afford compound **6** (137 mg, 15 % yield) and then with pentane/CH_2Cl_2 (80:20) to afford compound **11a** (700 mg, 48 % yield).

*Complex **6***: ^{1}H NMR (300 MHz, $CDCl_3$): $\delta = 1.87$ (s, 30 H; Cp*), 3.88–3.98 (d, 8 H; CH of Cp), 7.54–7.66 ppm (m, 6 H; aromatic CH); ^{13}C NMR (75 MHz, $CDCl_3$): $\delta = 10.7$ (CH_3), 66.4 (Cq of $CpCH_3$), 73.9, 74.8 (CH of $CpC\equiv C$), 81.8 (Cq of $CpC\equiv C$), 84.6, 87.0, 90.2, 90.8 ($C\equiv C$), 122.7, 125.2, 126.4 (Cq of aromatic-$C\equiv C$ and aromatic-Br), 132.8, 133.1, 134.0, 134.2 ppm (aromatic CH); MS (MALDI-TOF): *m*/*z* calcd for $C_{48}H_{44}Fe_2$: 892.379; found: 892.2; elemental analysis calcd (%) for $C_{48}H_{44}Fe_2$: C 64.61, H 4.97; found: C 64.25, H 5.43.

*Complex **11a***: ^{1}H NMR (300 MHz, $CDCl_3$): $\delta = 1.93$ (s, 60 H; Cp*), 3.90-4.01 (d, 16 H; CH of Cp), 7.62–7.73 ppm (m, 9 H; CH of aromatic); ^{13}C NMR (75 MHz, $CDCl_3$): $\delta = 10.5$ (CH_3), 65.2 (Cq of $CpCH_3$), 72.8, 74.0 (CH of $CpC\equiv C$), 81.1 (Cq of $CpC\equiv C$), 84.6, 87.5, 90.0 ($C\equiv C$), 121.8, 122.9, 125.0 (Cq of aromatic-$C\equiv C$ and aromatic-Br), 132.6, 133.3, 133.6, 134.0 ppm (aromatic CH); MS (MALDI-TOF): *m*/*z* calcd for $C_{90}H_{85}Fe_4$: 1469.957; found: 1470.5; elemental analysis calcd (%) for $C_{90}H_{85}Fe_4$: C 73.54, H 5.83; found: C 73.40, H 6.13.

*Complex **9a***: Same procedure as for **3c**; ^{1}H NMR (300 MHz, $CDCl_3$): $\delta = 1.89$ (s, 60 H; Cp*), 3.25 (s, 1 H; $CH\equiv C$), 3.93- 4.05 (d, 16 H; CH of Cp), 7.55–7.77 ppm (m, 13 H; aromatic CH); ^{13}C NMR (75 MHz, $CDCl_3$): $\delta = 10.8$ (CH_3), 66.1 (Cq of $CpCH_3$), 73.6, 74.7 (CH of $CpC\equiv C$), 79.4 ($CH\equiv C$), 81.6 (Cq of $CpC\equiv C$), 83.3, 84.8, 88.5, 89.7, 90.3 ($C\equiv C$), 122.5, 123.4, 124.0, 125.3 (Cq of aromatic-$C\equiv C$), 131.7, 132.2, 132.9, 133.8, 134.4 ppm (aromatic CH); MS (MALDI-TOF): *m*/*z* calcd for $C_{100}H_{90}Fe_4$: 1515.203; found: 1515.8. elemental analysis calcd (%) for $C_{100}H_{90}Fe_4$: C 79.27, H 5.99; found: C 79.40, H 6.15.

Synthesis of complex 10a: A mixture of 1,3,5-triiodobenzene (0.05 g, 0.110 mmol, 1 equiv), compound **9a** (0.550 g, 0.363 mmol, 3.3 equiv), $[(PPh_3)_2PdCl_2]$ (0.005 g, 6.6×10^{-3} mmol, 0.06 equiv), cuprous iodine (0.019 g, 9.9×10^{-2} mmol, 0.9 equiv) and triethylamine (10 mL) was magnetically stirred in a Schlenk flask overnight at 50 °C. The solvent was evaporated under vacuum and the residue was dissolved in CH_2Cl_2. The organic phase was washed with water and dried with sodium sulfate, the solvent was removed under vacuum, and the crude reaction mixture was purified by column chromatography on silica gel (pentane/CH_2Cl_2, 60:40) to afford compound **10a** (0.173 g, 3.74×10^{-2} mmol, 34 % yield). ^{1}H NMR (300 MHz, $CDCl_3$): $\delta = 1.86$ (s, 3 × 60 H; Cp*), 3.87–3.98 (d, 3 × 14 H; CH of $C_5H_4FeCp^*$), 7.54–7.70 ppm (d, 12 H; aromatic CH); ^{13}C NMR (75 MHz, $CDCl_3$): $\delta = 10.8$ (CH_3), 66.1 (Cq of $CpCH_3$), 73.6, 74.7 (CH of $CpC\equiv C$), 81.6 (Cq of $CpC\equiv C$), 84.8, 88.5, 89.7, 90.3 ($C\equiv C$), 122.5, 123.4, 124.0, 125.3 (Cq of aromatic-$C\equiv C$), 131.7, 132.2, 132.9, 133.8, 134.4 ppm (aromatic CH); MS (MALDI-TOF): *m*/*z* calcd for $C_{306}H_{270}Fe_{12}$: 4617.558; found: 4617.3; elemental analysis calcd (%) for $C_{306}H_{270}Fe_{12}$: C 77.89, H 7.90; found: C 77.25, H 7.70; CV (CH_2Cl_2, 293 K): one reversible wave $E_{1/2} = 0.42$ V (versus decamethylferrocene, supporting electrolyte $[(n\text{Bu})_4N]PF_6$).

Synthesis of complexes 7a[PF$_6$]$_6$ and 7c[PF$_6$]$_3$: Compound **7a** (75 mg, 3.66×10^{-2} mmol) and $Cp_2Fe^+PF_6^-$ (72.82 mg, 0.22 mmol, 6 equiv) were stirred in freshly distilled and degassed CH_2Cl_2 (20 mL). After evaporation of the solvent in vacuo and washing with diethyl ether (3 × 20 mL), complex **7a**$[PF_6]_6$ (85.42 mg, 80 % yield) was obtained as a dark-green salt. The same procedure was used with compound **7c** and $Cp_2Fe^+PF_6^-$ (3 equiv) to obtain complex **7c**$[PF_6]_3$.

*Complex **7a**[PF$_6$]$_6$*: IR (KBr): $\tilde{\nu} = 2219.82$ ($C\equiv C$), 836.96 cm^{-1} (PF_6^-); elemental analysis calcd (%) for $C_{132}H_{126}F_{36}Fe_6P_6 \cdot H_2O$: C 54.01, H 4.39; found: C 53.84, H 4.40. For the UV/Vis spectra of compounds **7a** and **7a**-$[PF_6]_6$ and the zero-field Mössbauer spectrum of compound **7a**$[PF_6]_6$, see the Supporting Information.

*Complex **7c**[PF$_6$]$_3$*: IR (KBr): $\tilde{\nu} = 2213.52$ ($C\equiv C$), 840.76 cm^{-1} (PF_6^-); elemental analysis calcd (%) for $C_{117}H_{96}F_{18}Fe_6P_3$: C 61.85, H 4.26; found: C 61.45, H 4.30.

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