

Supporting information for:

# Dendrimers Based on a Three-Dimensionally Disposed AB<sub>4</sub> Monomer

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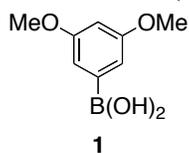
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## Experimental Section:

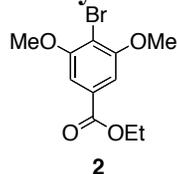
<sup>1</sup>H-NMR spectra were recorded on a 400 MHz or 300 MHz NMR spectrometer using the residual proton resonance of the solvent as the internal standard. Chemical shifts are reported in parts per million (ppm). When peak multiplicities are given, the following abbreviations are used: s, singlet; d, doublet; t, triplet; q, quartet; quin, quintet; d of d, doublet of a doublet; m, multiplet; br, broad. <sup>13</sup>C-NMR spectra were proton decoupled and recorded on a 100 MHz or 75 MHz NMR spectrometer using the carbon signal of the deuterated solvent as the internal standard. MALDI-ToF, EI and FAB mass spectra were obtained at the Coordinated Instrumentation Facility at University of Massachusetts. Flash chromatography was performed with 37-75 μm silica gel. Analytical thin layer chromatography was performed on silica plates with F-254 indicator and the visualization was accomplished by UV lamp or using an iodine chamber. THF was distilled over Na / Ph<sub>2</sub>CO ketyl. Dichloromethane was distilled over CaH<sub>2</sub>. All other chemicals were obtained from commercial sources and used as received, unless otherwise mentioned. 1-Bromo-3,5-dimethoxybenzene was synthesized by a literature procedure.<sup>1</sup> Fluorocarbonylferrocene or ferrocenyl-1,1'-diacid fluoride was prepared by a reported procedure.<sup>2</sup> Ethyl-4-bromo-3,5-dihydroxybenzoate was synthesized by a reported procedure.<sup>3</sup>

## Synthesis of 3,5-dimethoxyphenyl boronic acid (1):



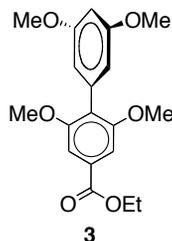
To a solution of 1-bromo-3,5-dimethoxybenzene in anhydrous THF (5.59 g, 25.75 mmol) was added *t*-BuLi (33.4 mL of 1.7 M pentane solution, 56.66 mmol) under argon atmosphere at -78°C and stirred for 45 min at that temperature. The B(OMe)<sub>3</sub> (10.1 mL, 90.13 mmol) was added and stirred at -78 to 20°C for 8h. The reaction was quenched with a satd. NH<sub>4</sub>Cl solution and extracted with EtOAc. The solvent was removed in vacuo and the crude boronic acid was taken to the next step without further purification or characterization.

## Synthesis of ethyl-4-bromo-3,5-dimethoxybenzoate (2):



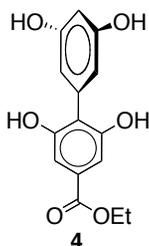
Ethyl-4-bromo-3,5-dihydroxybenzoate (13.1 g, 50.0 mmol), potassium carbonate (34.6 g, 250 mmol) and methyl iodide (15.6 mL, 250 mmol) were taken in 250 mL of acetone and refluxed overnight under nitrogen atmosphere. It was filtered through a Büchner funnel and concentrated in vacuo. The residue was washed with water and extracted twice with diethyl ether. The combined organic layers were washed with brine and dried with anhydrous sodium sulphate and evaporated. The residue was purified by silica gel column by eluting with EtOAc/hexane (10:90) to afford 13.7 g (95%) of **2** as a colorless solid. <sup>1</sup>H-NMR (400 MHz, CDCl<sub>3</sub>)  $\delta$  1.38 (t, J=7.0 Hz, 3H), 3.92 (s, 6H), 4.36 (q, J=7.0 Hz, 2H), 7.21 (s, 2H); <sup>13</sup>C-NMR (100 MHz, CDCl<sub>3</sub>)  $\delta$  14.29, 56.56, 61.39, 105.36, 106.39, 130.46, 156.87, 165.90

#### Synthesis of compound 3:



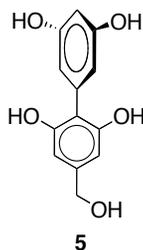
3,5-Dimethoxyphenyl boronic acid (**1**) (3 g, 16.5 mmol), ethyl-4-bromo-3,5-dimethoxybenzoate (**2**) (4.3 g, 15 mmol) and potassium phosphate (9.6 g, 45 mmol) were taken in anhydrous DME under argon atmosphere. Pd(PPh<sub>3</sub>)<sub>4</sub> (1.73 g, 1.5 mmol) was added and refluxed for 48 h. It was quenched with water and extracted twice with EtOAc. The combined organic layers were washed with brine and dried with anhydrous sodium sulfate and concentrated in vacuo. The residue was purified by silica gel column by elution with EtOAc/hexane (8:92) to afford 3.73 g (72%) of **3** as a colorless solid. <sup>1</sup>H-NMR (400 MHz, CDCl<sub>3</sub>)  $\delta$  1.42 (t, J=7.0 Hz, 3H), 3.80 (s, 12H), 4.42 (q, J=7.0 Hz, 2H), 6.46-6.50 (m, 3H), 7.33 (s, 3H); <sup>13</sup>C-NMR (100 MHz, CDCl<sub>3</sub>)  $\delta$  14.33, 55.19, 56.04, 61.15, 99.41, 105.25, 108.59, 123.85, 130.74, 135.16, 157.38, 160.08, 166.28; EI/MS m/z (r.i.) 346 (M<sup>+</sup>, 96), 290 (99), 288 (100), 245 (58), 243 (58), 84 (52).

#### Synthesis of compound 4:



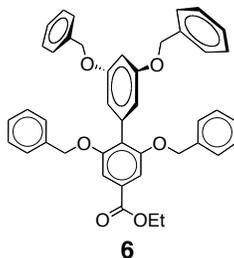
The biaryl ester **3** (2.5 g, 7.22 mmol) was dissolved in anhydrous CH<sub>2</sub>Cl<sub>2</sub> under nitrogen atmosphere, then it was cooled to  $-78^{\circ}\text{C}$ . BBr<sub>3</sub> (8.2 mL, 86.6 mmol) was added dropwise at  $-78^{\circ}\text{C}$  which was then allowed to warm to  $25^{\circ}\text{C}$  and stirred for 2 days. It was cooled again to  $-78^{\circ}\text{C}$  and quenched with slow and careful addition of ethanol (50 mL). The solvent was concentrated in vacuo and the residue was loaded on a silicagel column. Elution with EtOAc/hexane (40:60) afforded 1.75 g (84%) of **4**. <sup>1</sup>H-NMR (400 MHz, CD<sub>3</sub>COCD<sub>3</sub>)  $\delta$  1.32 (t, J=7.0 Hz, 3H), 3.61 (br s, 4H), 4.29 (q, J=7.2 Hz, 2H), 6.30-6.37 (m, 3H), 7.13 (s, 2H); <sup>13</sup>C-NMR (100 MHz, CD<sub>3</sub>COCD<sub>3</sub>)  $\delta$  13.39, 60.19, 101.52, 107.65, 108.74, 120.98, 130.07, 134.69, 155.08, 158.04, 165.49; EI/MS m/z (r.i.) 290 (M<sup>+</sup>, 100), 245 (49), 218 (22), 161 (19).

### Synthesis of compound 5:



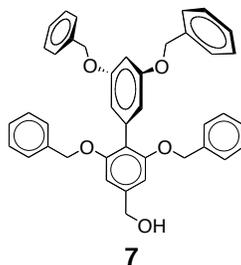
Lithium aluminium hydride (3.2 g, 83 mmol) was taken in anhydrous THF under nitrogen atmosphere. The compound **4** in anhydrous THF was added dropwise to the reaction flask at 0° C. After the addition it was warmed to 25° C and refluxed for 24 h. It was brought to 0° C and quenched with ethyl acetate (30 mL). It was washed with dil. HCl and extracted with EtOAc. The solvent was removed in vacuo and the residue was purified by silica gel column by eluting with 60% EtOAc, 10% methanol and 30% hexane. Gradually increasing the concentration of methanol afforded the product 2.4 g (82%) as a colorless solid. <sup>1</sup>H-NMR (400 MHz, CD<sub>3</sub>OD)  $\delta$  4.47 (s, 2H), 4.87 (br s), 6.24 (t, J=2.4 Hz, 1H), 6.30 (d, J=2.4 Hz, 2H), 6.41 (s, 2H); <sup>13</sup>C-NMR (100 MHz, CD<sub>3</sub>OD)  $\delta$  65.01, 102.35, 106.55, 110.62, 116.89, 137.30, 143.14, 156.14, 159.08; EI/MS m/z (r.i.) 248 (M<sup>+</sup>, 100), 231 (9), 219 (12), 161 (12), 115 (10).

### Synthesis of compound 6:



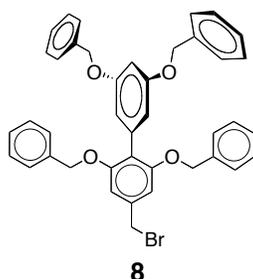
The phenolic ester **4** (1.45 g, 5 mmol), potassium carbonate (4.14 g, 30 mmol), 18-crown-6 (0.7 g, 2.5 mmol), and benzyl bromide (3.6 mL, 30 mmol) were all dissolved in acetone. The mixture was refluxed under nitrogen for 24 h. The mixture was allowed to cool and concentrated in vacuo. The residue was partitioned between water and dichloromethane and the aqueous layer extracted with dichloromethane. The combined organic layers were then dried and evaporated to dryness. The residue was purified by silica gel column using EtOAc/hexane (5:95) to afford 3.12 g (95%) of the product **6**. <sup>1</sup>H-NMR (300 MHz, CDCl<sub>3</sub>)  $\delta$  1.43 (t, J=7.1 Hz, 3H), 4.42 (q, J=7.1 Hz, 2H), 4.99 (s, 4H), 5.11 (s, 4H), 6.65 (t, J=2.3 Hz, 1H), 6.75 (d, J=2.3 Hz, 2H), 7.2-7.5 (m, 22H); <sup>13</sup>C-NMR (75 MHz, CDCl<sub>3</sub>)  $\delta$  14.31, 61.16, 69.99, 70.64, 101.59, 107.37, 107.73, 109.98, 125.38, 126.92, 127.49, 127.63, 127.81, 128.34, 128.45, 130.69, 135.03, 136.78, 137.02, 156.52, 159.24, 166.12; FAB/MS m/z (r.i.) 650 (M<sup>+</sup>, 24), 558 (19), 180 (78), 91 (100).

### Synthesis of compound 7:



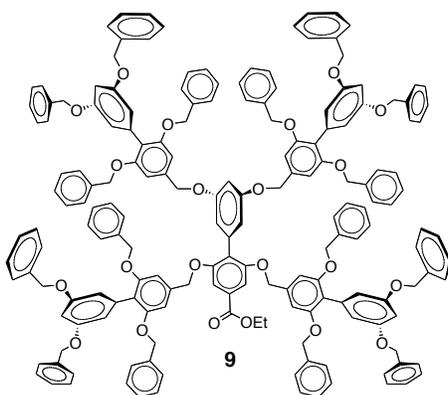
Lithium aluminium hydride (0.71 g, 18.64 mmol) was taken in anhydrous THF under nitrogen atmosphere. The compound **6** in anhydrous THF was added dropwise to the reaction flask at 0° C. After the addition it was stirred at 25° C for 8 h. It was quenched with EtOAc, washed with dil. HCl and extracted with EtOAc. The solvent was removed in vacuo and the residue was purified by silica gel column by elution with EtOAc/hexane (20:80) to obtain 2.38 g (84%) of **7**. <sup>1</sup>H-NMR (300 MHz, CDCl<sub>3</sub>)  $\delta$  4.64 (s, 2H), 4.95 (s, 4H), 5.02 (s, 4H), 6.58 (t, J=2.3 Hz, 1H), 6.69-6.74 (m, 4H), 7.2-7.4 (m, 20H); <sup>13</sup>C-NMR (75 MHz, CDCl<sub>3</sub>)  $\delta$  65.14, 69.96, 70.48, 101.19, 104.98, 110.32, 119.91, 126.79, 127.48, 127.76, 128.29, 128.42, 135.74, 137.08, 137.12, 141.98, 156.77, 159.15; EI/MS m/z (r.i.) 608 (M<sup>+</sup>, 44), 517 (29), 181 (15), 91 (100).

**Synthesis of compound 8:**



The alcohol **7** (0.7 g, 1.15 mmol) and triphenylphosphine (0.45 g, 1.72 mmol) was taken in 4 mL of anhydrous THF under nitrogen atmosphere. *N*-Bromosuccinimide (0.31 g, 1.72 mmol) was added in one portion at 25° C. After stirring for 1 min, it was quenched with water and extracted with dichloromethane. The solvent was removed in vacuo and the residue was purified by silica gel column by elution with ethyl acetate/hexane (10:90) to give the product 0.69 g (90%). <sup>1</sup>H-NMR (300 MHz, CDCl<sub>3</sub>)  $\delta$  4.47 (s, 2H), 4.99 (s, 4H), 5.06 (s, 4H), 6.65 (t, J=2.3 Hz, 1H), 6.76-6.80 (m, 4H), 7.20-7.50 (m, 20H); <sup>13</sup>C-NMR (75 MHz, CDCl<sub>3</sub>)  $\delta$  33.87, 69.94, 70.40, 101.40, 107.40, 110.20, 121.00, 126.80, 127.50, 127.60, 127.80, 128.30, 128.40, 135.30, 136.90, 137.10, 138.20, 156.70; FAB/MS m/z (r.i.) 670 (M<sup>+</sup>, 2), 447 (12), 259 (48), 219 (33), 149 (47), 91 (96), 57 (100).

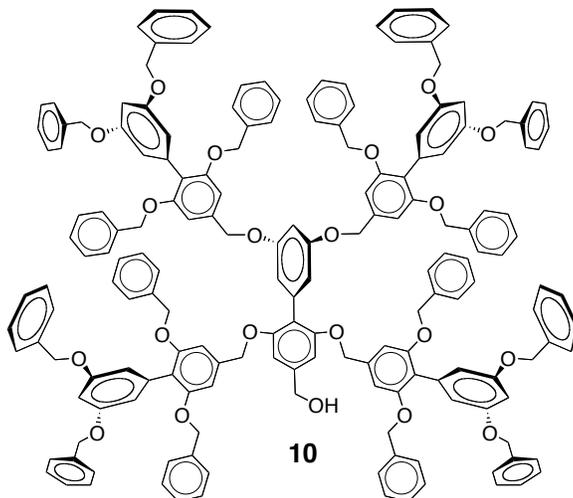
**Synthesis of compound 9:**



The phenolic ester **4** (0.12 g, 0.4 mmol), potassium carbonate (0.44 g, 3.2 mmol), 18-crown-6 (0.053 g, 0.2 mmol), and compound **8** (1.34 g, 2 mmol) were dissolved in acetone. The mixture was refluxed under nitrogen for 48 h. The work-up procedure used in the synthesis of **6** was followed. The residue was purified by silica gel column using EtOAc/hexane (20:80) to afford 1.02 g (93%) of the product. <sup>1</sup>H-NMR (300 MHz, CDCl<sub>3</sub>)  $\delta$  1.62 (t, J=5.2 Hz, 3H), 4.63 (q, J=5.8 Hz, 2H), 4.85-5.35 (m, 40H), 6.60-6.98 (m, 20H), 7.05-7.75 (m, 80H); <sup>13</sup>C-NMR (75 MHz, CDCl<sub>3</sub>)  $\delta$  14.42, 61.36, 69.79, 69.83,

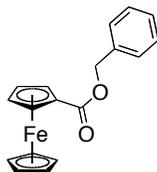
70.28, 70.34, 101.23, 101.75, 104.36, 106.10, 107.61, 109.88, 110.19, 119.91, 120.35, 126.75, 127.02, 127.32, 127.43, 127.52, 127.67, 128.12, 128.27, 128.35, 130.83, 131.18, 135.51, 135.89, 136.93, 137.01, 137.08, 137.69, 156.38, 156.72, 159.04, 159.09, 159.39, 166.01. MALDI-Tof: Calcd for  $C_{179}H_{150}O_{22}$ : 2653.09; Found: 2676.11 ( $M^+ + 23$ ).

**Synthesis of compound 10:**



Lithium aluminium hydride (0.12 g, 3.2 mmol) was taken in anhydrous THF under nitrogen atmosphere. The compound **9** (1.05 g, 0.4 mmol) in anhydrous THF was added dropwise to the reaction flask at 0° C. After the addition it was refluxed for 12 h. It was quenched with EtOAc, washed with dil. HCl and extracted with EtOAc. The solvent was removed in vacuo and the residue was purified by silica gel column by eluting with EtOAc/hexane (30:70) to give the product 0.8 g (77%).  $^1H$ -NMR (400 MHz,  $CDCl_3$ )  $\delta$  4.69-4.95 (m, 38H), 5.05-5.13 (m, 4H), 6.46 (t,  $J=2.2$  Hz, 2H), 6.54 (t,  $J=2.4$  Hz, 2H), 6.57-6.77 (m, 17H), 6.81 (s, 2H), 6.92 (d,  $J=2.4$  Hz, 2H), 7.08-7.38 (m, 80H);  $^{13}C$ -NMR (75 MHz,  $CDCl_3$ )  $\delta$  65.08, 69.81, 69.85, 70.31, 101.20, 101.27, 104.34, 104.75, 106.33, 110.23, 119.63, 119.81, 120.33, 126.64, 126.79, 127.05, 127.33, 127.45, 127.69, 128.13, 128.26, 128.36, 135.56, 136.67, 136.98, 137.02, 137.09, 137.22, 138.10, 142.45, 156.63, 156.68, 156.72, 159.05, 159.09, 159.33; MALDI-Tof: Calcd for  $C_{177}H_{148}O_{21}$ : 2611.06; Found: 2633.72 ( $M^+ + 23$ ).

**Synthesis of compound 11:**

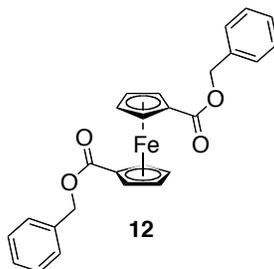


11

Ferrocenecarboxylic acid (0.23 g, 1 mmol) was dissolved in anhydrous DMF under nitrogen atmosphere. EDC {1-(3-dimethylaminopropyl)-3-ethylcarbodiimide hydrochloride} (0.29 g, 1.5 mmol) was added at 25° C and stirred for 10 min. 4-Dimethylamino pyridine (0.12 g, 1 mmol) and benzyl alcohol (0.16 mL, 1.5 mmol) was added and stirred at 25° C for 2 h. It was extracted with  $CH_2Cl_2$  (3  $\times$  50 mL) and washed with water. The solvent was removed and the residue was purified by silica gel column by eluting with ethyl acetate/hexane (10:90) to give the product 0.26 g (82%).  $^1H$ -NMR (300 MHz,  $CDCl_3$ )  $\delta$  4.09 (s, 5H), 4.38 (t,  $J=1.9$  Hz), 4.82 (t,  $J=1.9$  Hz, 2H), 5.26 (s, 2H), 7.28-7.49 (m, 5H);  $^{13}C$ -NMR (75 MHz,  $CDCl_3$ )  $\delta$  65.77, 69.64, 70.14, 70.97, 71.30,

128.14, 128.27, 128.50, 136.54, 171.41; EI/MS m/z (r.i.) 320 (M+, 100), 226 (18), 129 (10), 91 (23).

**Synthesis of compound 12:**

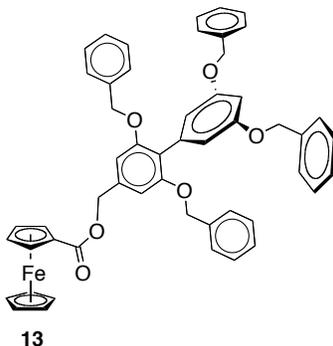


The procedure used for the synthesis of **11** was essentially followed except that 3 equivalents of EDC and 3 equivalents of benzyl alcohol were used. The residue was purified by silica gel column by elution with EtOAc/hexane (15:85) to give the product 0.35 g (80%). <sup>1</sup>H-NMR (300 MHz, CDCl<sub>3</sub>)  $\delta$  4.25 (t, J=1.9 Hz, 4H), 4.79 (t, J=1.9 Hz, 4H), 5.23 (s, 4H), 7.28-7.47 (m, 10H); <sup>13</sup>C-NMR (75 MHz, CDCl<sub>3</sub>)  $\delta$  66.06, 71.45, 72.54, 72.90, 128.20, 128.34, 128.50, 136.24, 170.16; EI/MS m/z (r.i.) 454 (M+, 100), 378 (28), 91 (42).

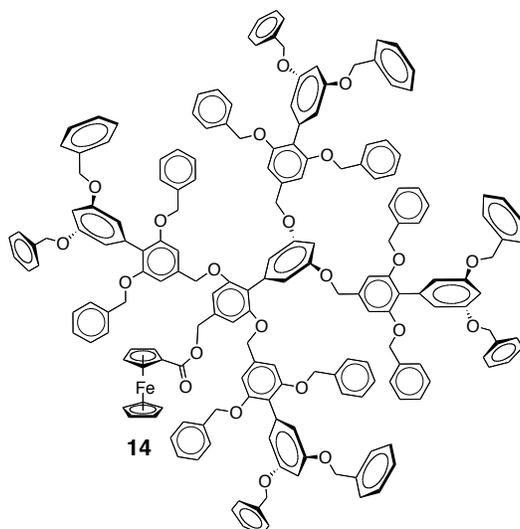
**Representative procedure for the reaction of fluorocarbonylferrocene or ferrocenyl-1,1'-diacid fluoride with dendritic alcohols:**

Fluorocarbonylferrocene or ferrocenyl-1,1'-diacid fluoride (1 equiv) was dissolved in anhydrous dichloromethane under nitrogen atmosphere. The dendritic alcohol (1.1 equiv for fluorocarbonylferrocene, 2.3 equiv for ferrocenyl-1,1'-diacid fluoride) and 4-dimethylamino pyridine (1.5 equiv for fluorocarbonylferrocene, 4 equiv for ferrocenyl-1,1'-diacid fluoride) was added at 25° C and stirred overnight. The solvent was removed and the residue was purified by silica gel column by elution with appropriate solvent combination to give the ferrocene-cored dendrimers.

**Synthesis of compound 13:**

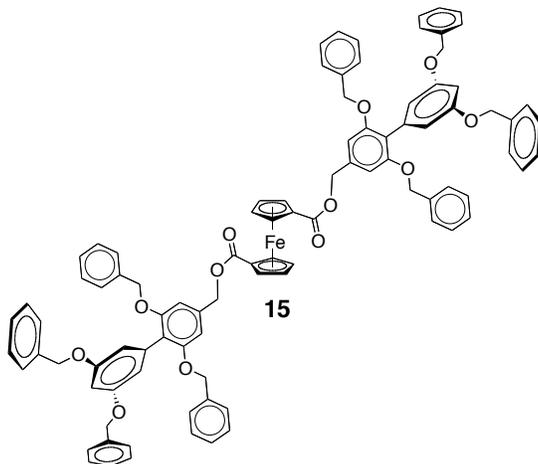


The crude reaction mixture was purified by elution with EtOAc/hexane (15:85) to give the product 0.17 g (88%). <sup>1</sup>H-NMR (300 MHz, CDCl<sub>3</sub>)  $\delta$  4.15 (s, 5H), 4.42 (br s, 2H), 4.80 (br s, 2H), 4.96 (s, 4H), 5.06 (s, 4H), 5.20 (s, 2H), 6.60 (t, J=2.3 Hz, 1H), 6.73 (d, J=2.3 Hz, 2H), 6.78 (s, 2H), 7.24-7.43 (m, 20H); <sup>13</sup>C-NMR (75 MHz, CDCl<sub>3</sub>)  $\delta$  65.84, 69.70, 69.97, 70.19, 70.67, 70.80, 71.37, 101.36, 106.72, 110.28, 120.85, 126.81, 127.46, 127.52, 127.74, 128.33, 128.41, 135.61, 137.07, 137.12, 137.30, 156.80, 159.21, 171.44; FAB/MS m/z (r.i.) 820 (M+, 35), 306 (24), 228 (19), 153 (100), 136 (84), 92 (75).**Synthesis of compound 14:**



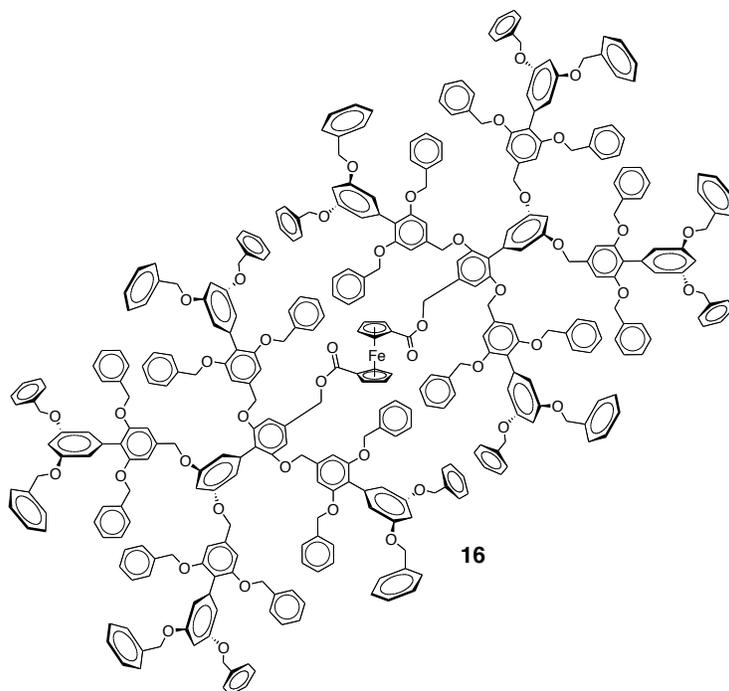
The crude reaction mixture was purified by elution with dichloromethane/chloroform (60:40) to give the product 0.14 g (75%).  $^1\text{H-NMR}$  (300 MHz,  $\text{CDCl}_3$ )  $\delta$  4.19 (s, 5H), 4.42 (br s, 2H), 4.74-4.95 (m, 38H), 5.14 (s, 4H), 5.33 (s, 2H), 6.45-6.98 (m, 25H), 7.08-7.40 (m, 80H);  $^{13}\text{C-NMR}$  (75 MHz,  $\text{CDCl}_3$ )  $\delta$  65.92, 69.78, 69.85, 69.89, 70.22, 70.34, 70.73, 71.60, 101.16, 101.28, 101.43, 104.36, 106.13, 106.78, 110.23, 113.86, 119.89, 120.37, 120.68, 126.81, 127.05, 127.36, 127.49, 127.54, 127.73, 128.17, 128.30, 128.40, 135.57, 136.46, 137.01, 137.06, 137.14, 137.22, 137.89, 138.00, 156.67, 156.75, 159.08, 159.13, 159.38, 171.63; MALDI-Tof: Calcd for  $\text{C}_{188}\text{H}_{156}\text{FeO}_{22}$ : 2823.08; Found: 2825.32 ( $\text{M}^+$ ), 2848.44 ( $\text{M}^+ + 23$ ).

#### Synthesis of compound 15:



The crude reaction mixture was purified by elution with EtOAc/hexane (20:80) to give the product 0.26 g (85%).  $^1\text{H-NMR}$  (300 MHz,  $\text{CDCl}_3$ )  $\delta$  4.43 (br s, 4H), 4.90 (br s, 4H), 4.99 (s, 8H), 5.09 (s, 8H), 5.27 (s, 4H); 6.67 (br s, 2H), 6.83 (s, 4H), 6.88 (s, 4H), 7.25-7.48 (m, 40H);  $^{13}\text{C-NMR}$  (75 MHz,  $\text{CDCl}_3$ )  $\delta$  66.20, 69.88, 70.55, 71.68, 72.68, 72.71, 101.27, 106.61, 110.23, 120.68, 126.82, 127.43, 127.48, 127.72, 128.28, 128.38, 135.51, 137.01, 137.07, 156.76, 159.15, 170.01; FAB/MS  $m/z$  (r.i.) 1455 ( $\text{M}^+$ , 79), 591 (100), 498 (58), 409 (49).

#### Synthesis of compound 16:



The contents were stirred at 25° C for 24 h. The reaction did not undergo completion. So, it was refluxed for 12 h. The crude reaction mixture was best purified by eluting with EtOAc/dichloromethane/hexane (10:10:80) and gradually increasing the concentration of EtOAc/dichloromethane to afford the product 0.27 g (72%). <sup>1</sup>H-NMR (400 MHz, CDCl<sub>3</sub>)  $\delta$  4.37 (t, J=1.8 Hz, 4H), 4.68-4.95 (m, 80H), 5.11 (br s, 4H), 5.28 (br s, 4H), 6.43 (t, J=2.2 Hz, 5H), 6.53 (t, J=2.2 Hz, 5H), 6.59-6.70 (m, 34H), 6.92 (br s, 6H), 7.05-7.35 (m, 160H); <sup>13</sup>C-NMR (75 MHz, CDCl<sub>3</sub>)  $\delta$  66.39, 68.56, 69.81, 69.89, 70.33, 70.37, 71.77, 72.87, 101.14, 101.28, 101.42, 104.47, 106.14, 106.70, 110.25, 113.88, 119.96, 120.38, 120.63, 126.82, 127.09, 127.35, 127.50, 127.73, 128.16, 128.29, 128.38, 128.41, 135.54, 136.48, 136.95, 137.06, 137.15, 137.21, 137.58, 137.98, 156.76, 159.08, 159.11, 159.43, 170.17; MALDI-Tof: Calcd for C<sub>366</sub>H<sub>302</sub>FeO<sub>44</sub>: 5460.13; Found: 5464.74 (M<sup>+</sup>).

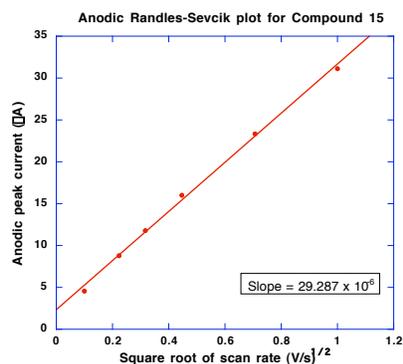
#### Electrochemical measurements:

All electrochemical measurements were carried out on Epsilon (BAS) electrochemical analyzer at ambient temperature with a standard three electrode configuration, consisting of platinum wire counter electrode and a glassy carbon working electrode (with a geometric surface area of 0.0707 cm<sup>2</sup>) and an Ag/AgCl reference electrode. The electroactive dendrimers (0.001 mol L<sup>-1</sup>) were dissolved in HPLC grade dichloromethane also containing tetrabutylammonium hexafluorophosphate as the supporting electrolyte (0.2 mol L<sup>-1</sup>). A nitrogen atmosphere was maintained over the solutions throughout the electrochemical experiments. IR compensation was not applied. Typical scan rate values of 0.010, 0.050, 0.100, 0.200, 0.500, 1.00 and 2.00 V/s were utilized.

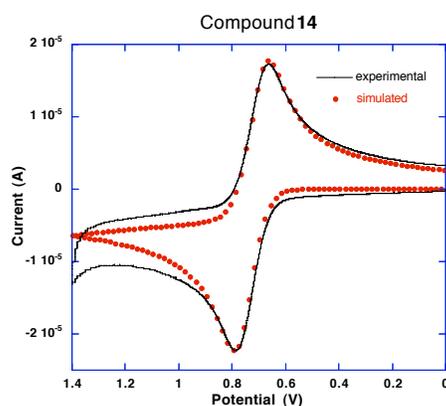
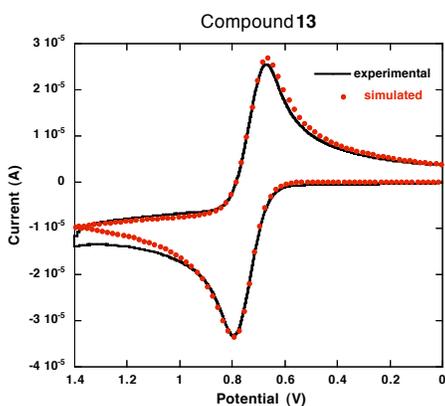
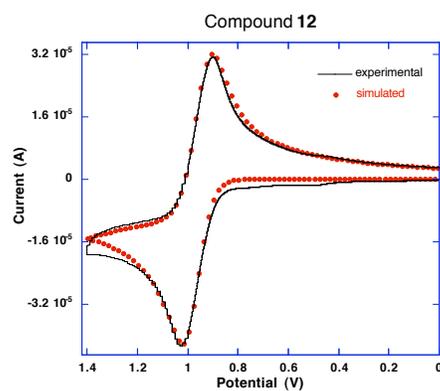
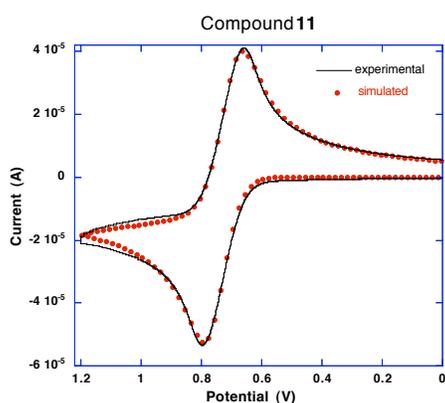
The electrochemical diffusion coefficients of the oxidized and reduced species were calculated by the Randles-Sevcik equation. From the slope obtained in the plot of anodic or cathodic peak current vs the square root of scan rate, the diffusion coefficient can be calculated.

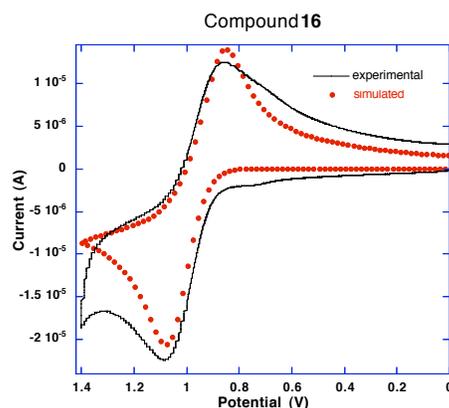
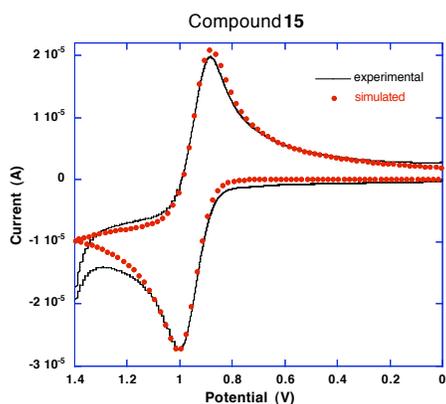
$$i_p = (2.69 \times 10^5) ACD^{1/2}v^{1/2}$$

A representative anodic Randles-Sevcik plot is shown here.

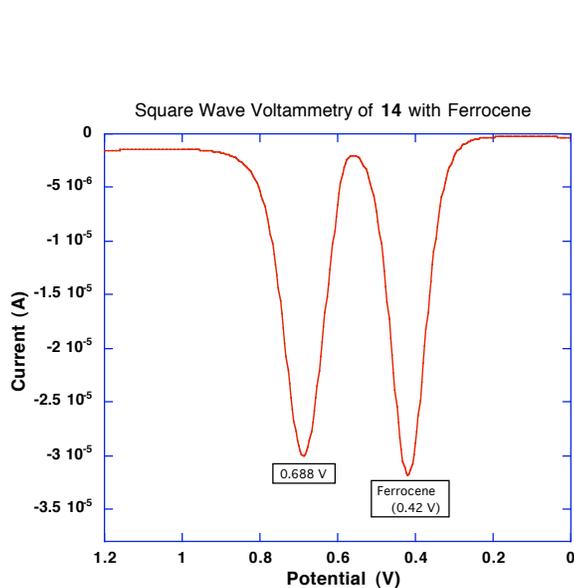


The  $D_0$  and  $k^0$  values were obtained by fitting digital simulations (DigiSim 3.0) to the experimental voltammograms at the scan rates of 0.100, 0.200, 0.500, 1.00 and 2.00 V/s for all the compounds. The digital simulations at lower scan rates 0.010 and 0.050 V/s were not successful for all the compounds. The experimental {Potential (V) vs Ag/AgCl} and simulated voltammograms for all compounds at 0.500 V/s scan rate are shown here.





Square wave voltammetry was used to determine the half wave potential ( $E_{1/2}$ ) values of all compounds relative to  $\text{Fc}/\text{Fc}^+$ . A representative square wave voltammogram of compound **14** with ferrocene is shown here.



#### References:

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- 3) Bharathi, P.; Zhao, H.; Thayumanavan, S. *Org. Lett.* **2001**, *3*, 1961.