

Notes

Convergent Synthesis of Ferrocene Dendrimers: The Use of Multitopic Dendrons with Disrupted Conjugation

Saumitra Sengupta* and Subir Kumar Sadhukhan

Department of Chemistry, Jadavpur University, Calcutta 700 032, India

Received December 6, 2000

Summary: Convergent synthesis of a redox-stable nona-ferrocenyl dendrimer using a tritopic dendron with disrupted conjugation is described.

Introduction

Dendrimers that are peripherally functionalized with electrochemically active groups can be potentially used as multielectron redox catalysts, electron reservoirs, electrode modifiers, ion sensors, and mimics of biological redox processes.¹ In view of this, syntheses of peripherally functionalized redox-active dendrimers have been the focus of many recent studies.² Since ferrocenes show stable redox properties and are easy to functionalize,³ ferrocene dendrimers are a widely studied class of redox-active dendrimers.⁴ Until now, most of these ferrocene dendrimers have been prepared via the divergent approach where multiple ferrocene residues were coupled to the surface of a preformed dendrimer in the ultimate synthetic step. Such a strategy often leads to constitutional defects due to incomplete couplings, especially at higher generations. This, in turn, can severely affect the

overall electrochemical properties of the dendrimers. To circumvent this, convergent syntheses⁵ of ferrocene dendrimers, albeit a few, have recently appeared in the literature,⁶ which prompted us to disclose here our own results.

Results and Discussion

Our objective was to prepare a dendrimer having multiple but identical ferrocene units on its surface. For this purpose, we have used a topologically new tritopic dendron **4** having a quarternary branching point. We envisaged that **4**, by virtue of its disrupted conjugation at the central carbon atom, would allow no communication whatsoever between its attached ferrocene rings, hence providing three electrochemically equivalent ferrocene moieties. Consequently, any dendrimer derived from **4** was assured of $3n$ identical ferrocene units at the periphery.

In the event, we started with the cheap commercial dye New Fuchsin (**1**), which via 3-fold diazotization (NaNO_2 , H_2SO_4) followed by a Sandmeyer reaction (KI , H_2O) was converted to the tris(iodoaryl) carbinol **2** in 40% overall yield (Scheme 1).⁷ A Friedel–Crafts type reaction of phenol with **2**, in the presence of concentrated H_2SO_4 , then produced the key AB_3 tecton **3** (85%), which upon 3-fold Heck reaction with vinyl ferrocene under Jefferey's condition ($\text{Pd}(\text{OAc})_2$, Bu_4NBr , KOAc , DMF)⁸ gave rise to the desired triferrocenyl dendron **4** (70%) after chromatographic separation from a small amount of the (1,1-ferrocenylaryl)vinylene regioisomeric product. Cyclic voltammetric (CV) study on **4** (CH_3CN , Pt anode, TBAP, 25 °C) produced a single reversible redox wave ($E_{1/2} = 0.32$ V vs SCE, $\Delta E_p = 70$ mV, unaltered at different scan rates), indicating that the three ferrocene units in **4**, as expected, were electrochemically equivalent.

* Corresponding author. Fax: 91-033-4734266. E-mail: jusaumitra@yahoo.co.uk.

(1) (a) Bard, A. J. *Nature* **1995**, *374*, 13. (b) Beer, P. D. *Acc. Chem. Res.* **1998**, *31*, 71. (c) Astruc, D. *Acc. Chem. Res.* **2000**, *33*, 287.

(2) (a) Bryce, M. R.; Devenport, W. In *Advances in Dendritic Macromolecules*; Newkome, G. R., Ed.; JAI Press: CT, 1996; Vol. 3, p 115. (b) Chow, H.-F.; Mong, T. K.-K.; Nongrum, M. F.; Wan, C.-W. *Tetrahedron* **1998**, *54*, 8543. (c) Gorman, C. *Adv. Mater.* **1998**, *10*, 295. (d) Balzani, V.; Campagna, S.; Denti, G.; Juris, A.; Serroni, S.; Venturi, M. *Acc. Chem. Res.* **1998**, *31*, 26. (e) Hearshaw, M. A.; Moss, J. R. *J. Chem. Soc., Chem. Commun.* **1999**, 1. (f) Cuadrado, I.; Moran, M.; Casado, C. M.; Alonso, B.; Losada, J. *Coord. Chem. Rev.* **1999**, *193–195*, 395. (g) Newkome, G. R.; He, E.; Moorefield, C. N. *Chem. Rev.* **1999**, *99*, 1689.

(3) *Ferrocenes*; Togni, A., Hayashi, T., Eds.; VCH: Weinheim, 1995.

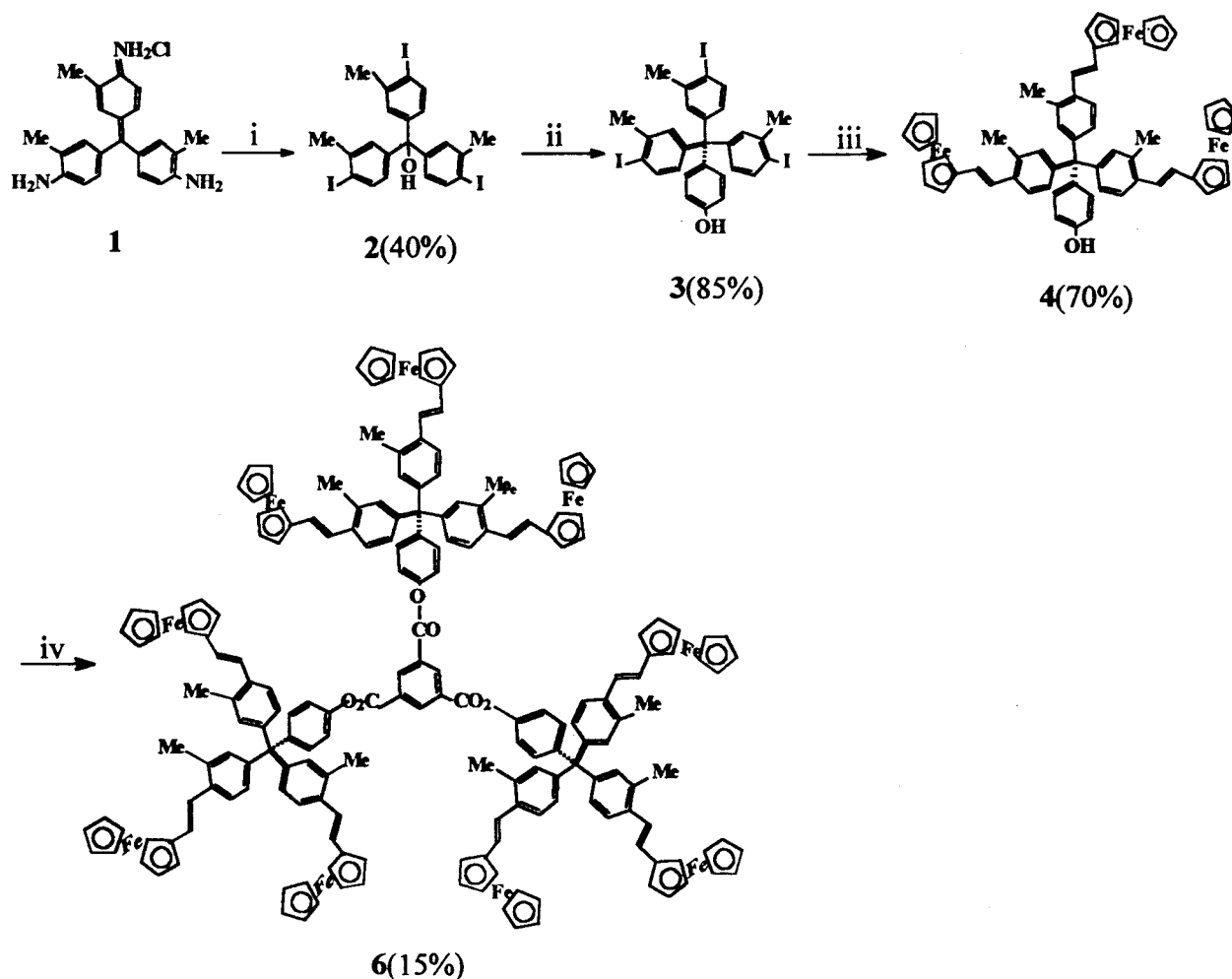
(4) Reviews: (a) Ardoin, N.; Astruc, D. *Bull. Soc. Chim. Fr.* **1995**, *132*, 875. (b) Casado, C. M.; Cuadrado, I.; Moran, M.; Alonso, B.; Garcia, B.; Gonzalés, B.; Losada, J. *Coord. Chem. Rev.* **1999**, *185–186*, 53. Recent works: (c) Cuadrado, I.; Moran, M.; Casado, C. M.; Alonso, B.; Lobete, F.; Garcia, B.; Ibisate, M.; Losada, J. *Organometallics* **1996**, *15*, 5278. (d) Losada, J.; Cuadrado, I.; Moran, M.; Casado, C. M.; Alonso, B.; Barranco, M. *Anal. Chim. Acta* **1997**, *338*, 191. (e) Cuadrado, I.; Casado, C. M.; Alonso, B.; Moran, M.; Losada, J.; Belsky, V. *J. Am. Chem. Soc.* **1997**, *119*, 7613. (f) Castro, R.; Cuadrado, I.; Alonso, B.; Casado, C. M.; Moran, M.; Kaifer, A. E. *J. Am. Chem. Soc.* **1997**, *119*, 5760. (g) Takada, T.; Diaz, D. J.; Abruna, H. D.; Cuadrado, I.; Casado, C.; Alonso, B.; Morán, M.; Losada, J. *J. Am. Chem. Soc.* **1997**, *119*, 10763. (h) Valério, C.; Fillaut, J. L.; Ruiz, J.; Guittard, J.; Blais, J. C.; Astruc, D. *J. Am. Chem. Soc.* **1997**, *119*, 2588. (i) Valério, C.; Alonso, E.; Ruiz, J.; Blais, J. C.; Astruc, D. *Angew. Chem., Int. Ed. Engl.* **1999**, *38*, 1747. (j) Valério, C.; Moulines, F.; Ruiz, J.; Blais, J. C.; Astruc, D. *J. Org. Chem.* **2000**, *65*, 1996. (k) Nlate, S.; Ruiz, J.; Sartor, V.; Navarro, R.; Blais, J.-C.; Astruc, D. *Chem. Eur. J.* **2000**, *6*, 2544.

(5) (a) Hawker, C. J.; Fréchet, J. M. J. *J. Am. Chem. Soc.* **1990**, *112*, 7638. (b) Miller, T. M.; Neenan, T. X. *Chem. Mater.* **1990**, *2*, 346. (c) Moore, J. S.; Xu, Z. *Macromolecules* **1991**, *24*, 5893.

(6) (a) Shu, C. F.; Shen, H. M. *J. Mater. Chem.* **1997**, *7*, 47. (b) Achar, S.; Immoos, C. E.; Hill, M. G.; Catalano, V. J. *Inorg. Chem.* **1997**, *36*, 2314. (c) Köllner, C.; Pugin, B.; Togni, A. *J. Am. Chem. Soc.* **1998**, *120*, 10274. (d) Schneider, R.; Köllner, C.; Weber, I.; Togni, A. *J. Chem. Soc., Chem. Commun.* **1999**, 2415. (e) Nlate, S.; Ruiz, J.; Blais, J.-C.; Astruc, D. *J. Chem. Soc., Chem. Commun.* **2000**, 417.

(7) Sengupta, S.; Sadhukhan, S. K. *Tetrahedron Lett.* **1999**, *40*, 9157.

(8) (a) König, B.; Zieg, H.; Bubenitschek, P.; Jones, P. G. *Chem. Ber.* **1994**, *127*, 1811. (b) Jefferey, T. *Tetrahedron* **1996**, *52*, 10113.

Scheme 1^a

^a (i) NaNO₂, conc. H₂SO₄, 0 °C then KI, H₂O, rt to 80 °C; (ii) phenol, conc. H₂SO₄, 80 °C; (iii) vinyl ferrocene, Pd(OAc)₂, Bu₄NBr, KOAc, DMF, 80 °C; (iv) trimesic acid (5), DCC, DMAP, CH₂Cl₂, rt.

The utility of **4** in dendrimer assembly was exemplified by its 3-fold esterification reaction (DCC, DMAP, CH₂Cl₂, 25 °C) with trimesic acid (**5**), which produced the first-generation nonaferrocenyl dendrimer **6** (15%), after purification by silica gel chromatography (light petroleum–CHCl₃–MeOH). The dendrimer was characterized by ¹H and ¹³C NMR spectroscopy. Interestingly, the ¹H NMR spectrum of **6** showed the central benzene ring protons at a much downfield region (δ 9.20, 3H, s), perhaps due to anisotropic effects caused by the folded nature of the centrally tetrahedral wedges. The MALDI-TOF mass spectrum of **6** (Figure 1) showed a dominant M + 1 peak at m/z 3181. Cyclic voltammetric studies on **6** (CH₂Cl₂, Pt anode, TEAP, 25 °C) produced a single redox wave ($E_{1/2}$ = 0.38 V vs Ag/AgCl) with a cathodic stripping peak (Figure 2). It is interesting to note that the three triferrocenyl clusters in **6** are placed furthest apart from each other, despite which the dendrimer showed a single redox wave. Therefore, during CV scanning, the dendrimer must undergo fast rotational changes so that all of its nine ferrocene units are able to approach the electrode within the electrochemical time scale. Moreover, the appearance of a stripping peak indicated a change in the solubility of the dendrimer after oxidation. Presumably, due to its large molecular weight, the dendrimer, upon oxidation, precipitates onto the cathode surface and redissolves,

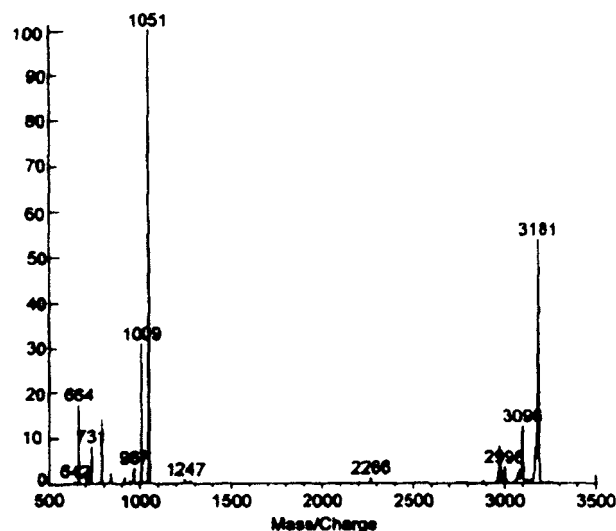


Figure 1. MALDI-TOF mass spectrum of **6**, as it gets reduced during the reverse scan. Similar phenomena have also been reported during CV studies on large ferrocenyl poly(propyleneimine) dendrimers.^{4c–e}

Experimental Section

All reactions were carried out under a dry nitrogen atmosphere using dry, distilled solvents. IR spectra were taken on

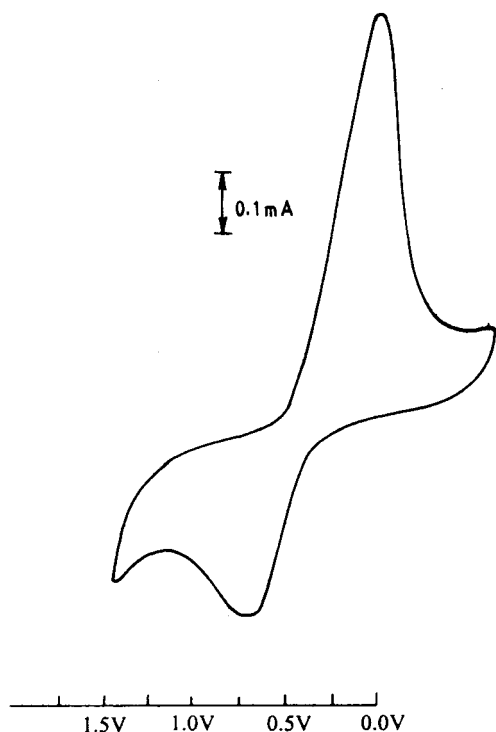


Figure 2. Cyclic voltammogram of **6** (CH_2Cl_2 , Pt anode TEAP, 25 °C) at 0.4 v/s scan rate.

a Perkin-Elmer 297 spectrophotometer. NMR spectra were recorded on a Bruker Avance 300 (300 MHz) instrument. Chemical shifts are expressed in the δ scale, ppm downfield from tetramethylsilane internal standard. Coupling constants, J , are given in hertz. Light petroleum refers to the fraction boiling at 60–80 °C. Electrochemical measurements were made using a PAR model 270 potentiostat. A platinum disk working electrode (of area 0.02 cm^2), a platinum wire auxiliary electrode, and an aqueous saturated calomel reference electrode (SCE) or a silver/silver chloride reference electrode (Ag/AgCl) were used in a three-electrode configuration. All electrochemical experiments were carried out under a nitrogen atmosphere at 25 °C using 0.43×10^{-3} M sample concentrations either in CH_3CN (for **4**) or in CH_2Cl_2 (for **6**) with tetrabutylammonium perchlorate (TBAP) or tetraethylammonium perchlorate (TEAP) as the supporting electrolyte.

Tris(4-iodo-3-methylphenyl)methanol (2). A solution of NaNO_2 (0.62 g, 9.0 mmol) in water (2 mL) was added dropwise during 10 min to a stirred solution of New Fuchsin (**1**, 1.0 g, 2.73 mmol) in concentrated H_2SO_4 (1.7 mL, 30.6 mmol) and water (5 mL) kept at 0 °C. It was stirred at 0 °C for 15 min and then treated dropwise with a solution of KI (5.0 g, 30 mmol) in water (5 mL) during 15 min. The mixture was stirred at room temperature for 5 h and then heated at 80 °C for 30 min. It was then cooled and the precipitated product was filtered and washed thoroughly with water. The residue was purified by silica gel chromatography (5% EtOAc in light petroleum) to give **2** as a white solid (0.74 g, 40%); mp 98–99 °C (MeOH); IR (CHCl_3 , cm^{-1}) 3560, 1450, 1365, 1185, 1000; ^1H NMR (300 MHz, CDCl_3) δ 2.40 (s, 9 H), 6.72 (dd, $J = 8.4$, 2.1 Hz, 3 H), 7.18 (d, $J = 2.1$ Hz, 3 H), 7.74 (d, $J = 8.4$ Hz, 3 H); ^{13}C NMR (75 MHz, CDCl_3) δ 28.2, 81.0, 100.3, 126.9, 128.9, 138.5, 141.2, 146.2. Anal. Calcd for $\text{C}_{22}\text{H}_{19}\text{I}_3\text{O}$: C, 38.86; H, 2.79. Found: C, 38.54; H, 3.11.

4-Tris(4'-iodo-3'-methylphenyl)methylphenol (3). A mixture of **2** (1.0 g, 1.47 mmol), phenol (0.41 g, 4.41 mmol), and concentrated H_2SO_4 (2 drops) was heated at 80 °C for 4 h. After being cooled to room temperature, the mixture was treated with 10% aqueous NaOH solution (10 mL). The precipitated solid was filtered, washed thoroughly with water, and dried in air. It was then purified by silica gel chromatography (10% EtOAc in light petroleum) to give **3** as a white solid (0.95 g, 85%); mp 206–207 °C (MeOH); IR (KBr, cm^{-1}) 3400, 1605, 1500, 1460, 1370, 1170, 1010; ^1H NMR (300 MHz, CDCl_3) δ 2.33 (s, 9 H), 6.65 (dd, $J = 8.4$, 2.1 Hz, 3 H), 6.70 (d, $J = 6.6$ Hz, 2 H), 6.99 (d, $J = 6.6$ Hz, 2 H), 7.02 (d, $J = 2.1$ Hz, 3 H), 7.65 (d, $J = 8.4$ Hz, 3 H); ^{13}C NMR (75 MHz, CDCl_3) δ 28.2, 63.3, 98.7, 114.5, 130.1, 131.9, 138.0, 140.5, 146.5, 153.6. Anal. Calcd for $\text{C}_{28}\text{H}_{23}\text{I}_3\text{O}$: C, 44.48; H, 3.04. Found: C, 44.56; H, 3.19.

(E,E,E)-4-Tris(4'-ferrocenylvinyl-3'-methylphenyl)methylphenol (4). $\text{Pd}(\text{OAc})_2$ (0.009 g, 0.39 mmol) was added to a solution of **3** (0.20 g, 0.26 mmol), vinyl ferrocene (0.25 g, 1.18 mmol), KOAc (0.19 g, 1.95 mmol), and Bu_4NBr (0.28 g, 0.79 mmol) in DMF (5 mL), and the mixture was heated at 80 °C for 30 h. It was then concentrated under reduced pressure, and water (5 mL) was added and extracted with CH_2Cl_2 (3×7 mL). The organic layer was washed with water, dried (Na_2SO_4), and evaporated under reduced pressure. The residue was purified by preparative thin-layer chromatography (10% EtOAc in light petroleum) to give **4** as an orange solid (0.20 g, 70%); mp 161–162 °C ($\text{CHCl}_3/\text{MeOH}$); IR (KBr, cm^{-1}) 2920, 1630, 1500, 1170, 1100; ^1H NMR (300 MHz, CDCl_3) δ 2.30 (s, 9 H), 4.13 (s, 15 H), 4.27 (s, 6 H), 4.45 (s, 6 H), 6.73 (d, $J = 8.7$ Hz, 2 H), 6.74 (d, $J = 16$ Hz, 3 H), 6.88 (d, $J = 16$ Hz, 3 H), 7.03–7.12 (m, 6 H), 7.15 (d, $J = 8.6$ Hz, 3 H), 7.42 (d, $J = 8.7$ Hz, 2 H); ^{13}C NMR (75 MHz, CDCl_3) δ 20.3, 63.7, 66.8, 68.9, 69.2, 83.9, 114.2, 123.5, 123.9, 127.7, 129.0, 132.2, 132.7, 133.7, 134.1, 139.4, 145.6, 153.3. Anal. Calcd for $\text{C}_{64}\text{H}_{56}\text{Fe}_3\text{O}$: C, 76.24; H, 5.55. Found: C, 76.51; H, 5.36.

Preparation of the Dendrimer 6. DCC (0.015 g, 0.075 mmol) was added to a solution of **4** (0.04 g, 0.037 mmol), trimesic acid (**5**, 0.0026 g, 0.012 mmol), and DMAP (0.005 g, 0.037 mmol) in CH_2Cl_2 (5 mL), and the mixture was stirred at room temperature for 96 h. It was then cooled to 0 °C and filtered. The filtrate was washed successively with water, 10% HCl solution, and again with water. The organic layer was dried (Na_2SO_4) and evaporated under reduced pressure. The residue was purified by preparative thin-layer chromatography (30% CHCl_3 –1% MeOH in light petroleum) to give **6** as an orange powder (0.007 g, 15%); IR (CHCl_3 , cm^{-1}) 2940, 1790, 1455, 1370, 1210; ^1H NMR (300 MHz, CDCl_3) δ 2.31 (s, 27 H), 4.13 (s, 45 H), 4.27 (s, 18 H), 4.45 (s, 18 H), 6.75 (d, $J = 16$ Hz, 9 H), 6.88 (d, $J = 16$ Hz, 9 H), 7.04–7.13 (m, 18 H), 7.17 (d, $J = 8.0$ Hz, 9 H), 7.40 (d, $J = 8.5$ Hz, 6 H), 7.44 (d, $J = 8.5$ Hz, 6 H), 9.21 (s, 3 H); ^{13}C NMR (75 MHz, CDCl_3) δ 20.3, 64.0, 67.0, 69.2, 69.5, 84.5, 120.3, 123.7, 124.1, 127.9, 129.0, 131.4, 132.2, 132.7, 134.0, 134.3, 136.0, 145.2, 147.1, 148.4, 163.3. MS (MALDI-TOF): m/z 3181 ($M + 1$).

Acknowledgment. S.K.S. thanks CSIR, New Delhi, for a senior research fellowship. Indranil Bhattacharya and Parbati Sengupta are thanked for the electrochemical studies. Dr. M. Vairamani (IICT, Hyderabad) is thanked for MALDI-TOF mass spectral analysis.

OM001043R