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Ferrocenyl-Functionalized Poly(propylenimine) Dendrimers

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Summary: New ferrocenyl dendritic macromolecules based on flexible poly(propylenimine) dendrimer cores, built up to the fifth generation, containing 4, 8, 16, 32, and 64 peripheral ferrocenyl moieties, have been prepared and characterized. Solution electrochemical studies showed that all the ferrocenyl redox centers attached to the dendritic surface are electrochemically independent and that, in CH_2Cl_2 and THF as solvents, the neutral dendrimers undergo oxidative precipitation onto the electrode surfaces.

Research interest in dendrimers,[1] which are well-defined highly branched macromolecules that emanate from a central core, formed by iterative reaction sequences, has recently been focused toward the modification of the valuable properties of such molecules by either the introduction of internal functionalities into the dendrimer structure or the functionalization of the dendritic surfaces.[2] As part of our ongoing studies of organometallic dendrimers[3,4] we recently reported several families of silicon-based dendritic macromolecules containing ferrocenyl,[5] (η^6-arene)$Cr(CO)_3$,[6] cyclopentadienyl, and cobalt and iron carbonyl moieties[7] as surface functionalities. So far, the redox-active ferrocenyl dendrimers are the only dendritic macromolecules which have been used successfully in the modification of electrode surfaces.[8]

Ferrocene-based polymers are attractive materials because of their redox properties and their possible applications as electrode coatings, electrochemical biosensors, and nonlinear optical (NLO) systems. We have reported the preparation of silicon-based polymers possessing ferrocenyl units attached to the polymer backbone through amide linkages, which were prepared via condensation reactions.[9] This approach has now been extended to cover dendritic surfaces with organometallic moieties. We report here the preparation of poly(propylenimine)-based ferrocenyl dendrimers built up to the fifth generation, which contains 64 peripheral ferrocenyl moieties.[10] To our knowledge this is the highest number of organometallic functionalities attached to a dendritic surface ever reported.

The synthesis of the new dendritic organometallic macromolecules DAB-*dend*-(NHCOFc)$_x$ ($x = 4, 8, 16, 32, 64$)[11] was cleanly achieved by condensation reactions of 1-(chlorocarbonyl)ferrocene[12] with the first-, second-, third-, fourth-, and fifth-generation diaminobutane-based poly(propylenimine) dendrimers functionalized with terminal NH_2 groups, DAB-*dend*-(NH_2)$_x$, as shown in Scheme 1.[13] The condensation reactions were completed in a few minutes, as monitored by IR spectroscopy. Interestingly, no marked differences in the yields of the reactions are observed on going from the first- to the fifth-generation dendrimer, which in all cases are considerably high (95−98%). All five organometallic dendrimers were isolated as air-stable orange solids, soluble in solvents such as dichloromethane, THF, and

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(1) Recent reviews: (a) Newkome, G. R. *Advances in Dendritic Macromolecules*; JAI Press: Greenwich, CT, 1994; Vol. 1; *Ibid*., 1995; Vol. 2. (b) Tomalia, D. A.; Durst, H. D. In *Topics in Current Chemistry*; Weber, E., Ed.; Springer-Verlag: Berlin, 1993; Vol. 165, p 193. (c) Issberner, J.; Moors, R.; Vögtle, F. *Angew. Chem., Int. Ed. Engl.* **1994**, *33*, 2413. (d) Fréchet, J. M. *Science* **1994**, *263*, 1710. (e) Ardoin, N.; Astruc, D. *Bull. Soc. Chim. Fr.* **1995**, *132*, 875.

(2) See for example: (a) Slany, M.; Bardají, M.; Casanove, M. J.; Caminade, A.-M.; Majoral, J.-P.; Chaudret, B. *J. Am. Chem. Soc.* **1995**, *117*, 9764. (b) Campagna, S.; Denti, G.; Serroni, S.; Juris, A.; Venturi, M.; Ricevuto, V.; Balzani, V. *Chem. Eur. J.* **1995**, *1*, 211. (c) Newkome, G. R.; Güther, R.; Moorefield, C. N.; Cardullo, F.; Echegoyen, L.; Pérez-Cordero, E.; Luftmann, H. *Angew. Chem., Int. Ed. Engl.* **1995**, *34*, 2023. (d) Lange, P.; Schier, A.; Schmidbaur, H. *Inorg. Chem.* **1996**, *35*, 637. See also ref 4.

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(4) For organometallic dendrimers see for example: (a) Seyferth, D.; Kugita, T.; Rheingold, A.; Yap, G. P. A. *Organometallics* **1995**, *14*, 5362. (b) Liao, Y. H.; Moss, J. R. *Organometallics* **1995**, *14*, 2130. (c) Huck, W. T. S.; van Veggel, F. C. J. M.; Kropman, B. L.; Blank, D. H. A.; Keim, E. G.; Smithers, M. M. A.; Reinhoudt, D. N. *J. Am. Chem. Soc.* **1995**, *117,* 8293. (d) Knapen, J. W. J.; van der Made, A. W.; de Wilde, J. C.; van Leeuwen, P. W. N. M.; Wijkens, P.; Grove, D.; van Koten, G. *Nature* **1994**, *372*, 659. (e) Fillaut, J.-L.; Linares, J.; Astruc, D. *Angew. Chem., Int. Ed. Engl.* **1994**, *33*, 2460. (f) Achar, S.; Puddephatt, R. J. *J. Chem. Soc., Chem. Commun.* **1994**, 1895.

(5) Alonso, B.; Cuadrado, I.; Morán, M.; Losada, J. *J. Chem. Soc., Chem. Commun.* **1994**, 2575.

(6) Lobete, F.; Cuadrado, I.; Casado, C. M.; Alonso, B.; Morán, M.; Losada, J. *J. Organomet. Chem.* **1996**, *509*, 109.

(7) Cuadrado, I.; Morán, M.; Moya, A.; Casado, C. M.; Barranco, M.; Alonso, B. *Inorg. Chim. Acta*, in press.

(8) Alonso, B.; Morán, M.; Casado, C. M.; Lobete, F.; Losada, J.; Cuadrado, I. *Chem. Mater.* **1995**, *7*, 1440.

(9) Casado, C. M.; Morán, M.; Losada, J.; Cuadrado, I. *Inorg. Chem.* **1995**, *34*, 1668.

(10) Part of these results were first presented at the 211th National Meeting of the American Chemical Society, New Orleans, LA, March 24−28, 1996, and at the NATO Advanced Research Workshop on Physical Supramolecular Chemistry, Miami, FL, Jan 7−10, 1996.

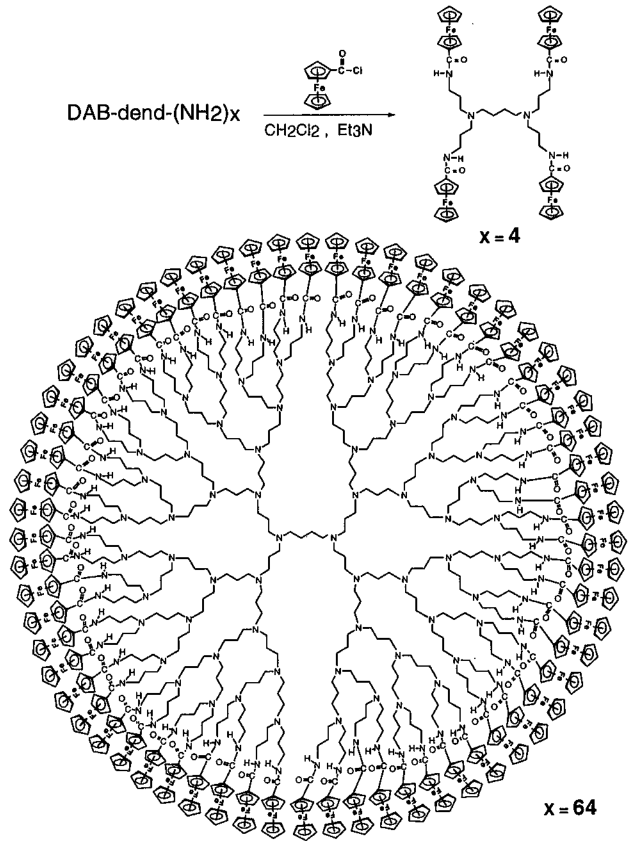
(11) The nomenclature of the new ferrocenyl poly(propylenimine)-dendrimers is DAB-*dend*-(NHCOFc)$_x$, where DAB (=diaminobutane) is the dendritic core and NHCOFc species (Fc = (η^5-C_5H_4)Fe(η^5-C_5H_5)) are the terminal groups.

(12) Pauson, P. L.; Watts, W. E. *J. Chem. Soc.* **1963**, 2990.

(13) Syntheses of dendrimers DAB-*dend*-(NHCOFc)$_x$. All dendrimers have been prepared following the same procedure. A mixture of the dendritic polyamine DAB-*dend*-(NH_2)$_x$ ($x = 4, 8, 16, 32, 64$), purchased from DSM, and triethylamine in CH_2Cl_2 was added dropwise to a stirred CH_2Cl_2 solution of the corresponding equivalent of 1-(chlorocarbonyl)ferrocene,[12] under argon at room temperature. The reaction completion was confirmed by FTIR spectroscopy. The resulting solution was washed with saturated $NaHCO_3$ aqueous solution and brine to remove the triethylamine hydrocloride byproduct and dried over $MgSO_4$. After the removal of the solvent the products were purified by repeated reprecipitations from CH_2Cl_2/hexane.

S0276-7333(96)00594-8 CCC: $12.00

Scheme 1



DMF and insoluble in acetonitrile and *n*-hexane. We have noticed that in the fourth- and fifth-generation dendritic molecules it is not possible to completely remove the *n*-hexane used during the purification procedures because of its inclusion into the inner dendritic cavities.[14]

The structures of the new dendrimers in which 4, 8, 16, 32, and 64 amide-linked ferrocenyl moieties are located at the dendritic surface have been established on the basis of ^{1}H and ^{13}C NMR and IR spectroscopy, mass spectrometry, and elemental microanalysis.[15] Because of the high symmetry of these molecules, ^{1}H and ^{13}C NMR spectroscopy has proved very useful in confirming the structure and assessing the purity of these materials.[16] Figure 1 shows the ^{1}H NMR spectra of the new ferrocenyl dendritic macromolecules, from the first to the fifth generation, which combine the signals assigned to the diaminobutane-based poly(propylenimine) framework within the dendritic structure, with the pattern of resonances in the cyclopentadienyl region characteristic of the newly introduced peripheral monosubstituted ferrocenes. The transition from a small organometallic molecule to a polymer-like structure was clearly evident by the peak broadness in the ^{1}H NMR spectra. Evidence of the condensation reaction was provided in the ^{1}H NMR by the total absence of the NH_2 signals of the starting dendritic polyamines around 1.3 ppm, as well as by the appearance of a new signal in the 6.8−8 ppm range and the downfield chemical shift (from 2.6 to 3.4 ppm) corresponding to the protons of the amide group and the adjacent methylene, respectively. In addition, estimations based on the signal intensities also confirm the complete functionalization of the NH_2 end groups of the starting dendritic polyamines. Interestingly, Figure 1 shows also that, in $CDCl_3$ ^{1}H NMR spectra, the chemical shifts of the protons corresponding to the amide spacer groups residing on the surface of the poly(propylenimine) dendrimer core vary in a generation-dependent manner. This observation is consistent with the participation of NH and C=O groups in hydrogen bonds. This NH···O hydrogen-bonding effect is greater in the higher generations because the presence of bulky molecular skeletons, in which the peripheral ferrocenyl moieties on adjacent dendritic branches are in close contact, leads to a greater number of NH···O intramolecular hydrogen bonds.

The structures of the first- and second-generation dendrimers DAB-*dend*-$(NHCOFc)_4$ and DAB-*dend*-$(NHCOFc)_8$ were corroborated by fast atom bombardment (FAB) mass spectrometry, which showed the molecular ions at *m/z* 1165 and 2471, respectively. Likewise, the matrix-assisted laser desorption and ionization time of flight detection (MALDI-TOF) mass spectrum of the third-generation species DAB-*dend*-$(NHCOFc)_{16}$ shows a single signal at *m/z* 5072.4 (5180.3 − 107.9 for Ag), which corresponds to the correct molecular mass.[17] The sizes of these novel ferrocenyl-functionalized dendritic

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(14) The same phenomenon has been also observed in large poly(propylenimine) dendrimers functionalized at the periphery with organic groups. See: (a) Jansen, J. F. G. A.; de Brabander-van den Berg, E. M. M.; Meijer, E. W. *Science* **1994**, *266*, 1226. (b) Moszner, N.; Völkel, T.; Rheinberger, V. *Macromol. Chem. Phys.* **1996**, 621.

(15) Selected spectroscopic and analytical data for DAB-*dend*-$(NHCOFc)_4$: ^{1}H NMR ($CDCl_3$) δ 6.81 (t, 4H, N*H*), 4.77 (t, 8H, C_5H_4), 4.33 (t, 8H, C_5H_4), 4.20 (s, 20H, Cp), 3.45 (quartet, 8H, $NHCH_2$), 2.51 (t, 8H, $CH_2CH_2CH_2N$), 2.43 (br, 4H, $NCH_2CH_2CH_2CH_2N$), 1.77 (quint, 8H, $CH_2CH_2CH_2$), 1.48 (br, 4H, $NCH_2CH_2CH_2CH_2N$); ^{13}C{^{1}H} NMR ($CDCl_3$) δ 170.34 (*C*O), 70.27 and 68.17 (C_5H_4), 69.68 (Cp), 54.00 and 52.11 (CH_2NCH_2), 38.52 (NH−CH_2), 25.00 and 27.24 ($CH_2CH_2CH_2$); MS (FAB; *m/z* (%)) 1165 (M^+, 100); IR (KBr) amide I (ν(CO)) 1627 cm^{-1}, amide II (ν(CN), δ(NH)) 1540 cm^{-1}. Anal. Calcd for $C_{60}H_{72}N_6Fe_4O_4$: C, 61.84; H, 6.23; N, 7.22. Found: C, 61.67; H, 6.19; N, 7.18. DAB-*dend*-$(NHCOFc)_8$: ^{1}H NMR ($CDCl_3$) δ 7.32 (t, 8H, N*H*), 4.93 (t, 16H, C_5H_4), 4.34 (t, 16H, C_5H_4), 4.22 (s, 40H, Cp), 3.42 (br, 16H, $NHCH_2$), 2.46 (br, 36H, CH_2NCH_2), 1.74 (br, 28H, CH_2CH_2N), 1.43 (br, 4H, $NCH_2CH_2CH_2CH_2N$); ^{13}C{^{1}H} NMR ($CDCl_3$) δ 170.70 (*C*O), 70.38 (C_5H_4), 69.72 (Cp), 68.43 (C_5H_4), 51.78 (CH_2NCH_2), 38.15 (NH−CH_2), 27.16 ($CH_2CH_2CH_2$); MS (FAB; *m/z* (%)) 2471 (M^+, 50); IR (KBr) amide I 1630 cm^{-1}, amide II 1540 cm^{-1}. Anal. Calcd for $C_{128}H_{160}N_{14}Fe_8O_8$: C, 62.25; H, 6.53; N, 7.94. Found: C, 62.03; H, 6.47; N, 7.87. DAB-*dend*-$(NHCOFc)_{16}$: ^{1}H NMR ($CDCl_3$) δ 7.48 (t, 16H, N*H*), 4.93 (t, 32H, C_5H_4), 4.34 (t, 32H, C_5H_4), 4.22 (s, 80H, Cp), 3.45 (br, 32H, $NHCH_2$), 2.47 and 2.38 (br, 84H, CH_2NCH_2), 1.75 (m, 56H, $CH_2CH_2CH_2$), 1.43 (br, 4H, $NCH_2CH_2CH_2CH_2N$); ^{13}C{^{1}H} NMR ($CDCl_3$) δ 170.61 (*C*O), 70.32 and 68.46 (C_5H_4), 69.71 (Cp), 52.48 and 51.80 (CH_2NCH_2), 38.75 (NH-CH_2), 27.31 ($CH_2CH_2CH_2$); MS (MALDI-TOF; *m/z* (%)) 5180 (M + Ag^+, 100); IR (KBr) amide I 1629 cm^{-1}, amide II 1539 cm^{-1}. Anal. Calcd for $C_{264}H_{336}N_{30}Fe_{16}O_{16}$: C, 62.44; H, 6.62; N, 8.27. Found: C, 62.27; H, 6.74; N, 8.16. DAB-*dend*-$(NHCOFc)_{32}$: ^{1}H NMR ($CDCl_3$) δ 7.66 (t, 32H, N*H*), 4.97 (t, 64H, C_5H_4), 4.34 (t, 64H, C_5H_4), 4.22 (s, 160H, Cp), 3.44 (br, 64H, $NHCH_2$), 2.46 and 2.37 (br, 180H, CH_2NCH_2), 1.75 (br, 60H, $CH_2CH_2CH_2$), 1.43 (br, 4H, $NCH_2CH_2CH_2CH_2N$); ^{13}C{^{1}H} NMR ($CDCl_3$) δ 170.71 (*C*O), 70.34 and 68.53 (C_5H_4), 69.73 (Cp), 52.47 and 51.79 (CH_2NCH_2), 38.34 (NH−CH_2), 27.33 ($CH_2CH_2CH_2$); IR (KBr) amide I 1631 cm^{-1}, amide II 1539 cm^{-1}. DAB-*dend*-$(NHCOFc)_{64}$: ^{1}H NMR ($CDCl_3$) δ 7.86 (br, 64H, N*H*), 5.00 (br, 128H, C_5H_4), 4.33 (br, 128H, C_5H_4), 4.21 (s, 320H, Cp), 3.43 (br, 128H, $NHCH_2$), 2.35 (br, 372H, CH_2NCH_2), 1.75 and 1.56 (br, 252H, CH_2CH_2N); ^{13}C{^{1}H} NMR ($CDCl_3$) δ 170.78 (*C*O), 70.39 and 68.60 (C_5H_4), 69.75 (Cp), 51.70 (CH_2NCH_2), 38.28 (NH-CH_2), 27.35 ($CH_2CH_2CH_2$); IR (KBr) amide I 1628 cm^{-1}, amide II 1537 cm^{-1}. Microanalytical data for the fourth and fifth generations are not included because of the *n*-hexane inclusion. Optimization of the GPC analyses conditions is currently under investigation at DSM research laboratories and will be detailed in the full paper.

(16) NMR spectroscopy has been used as a valuable technique for detecting and assigning structural defects in poly(propylenimine)-based dendrimers even at the stage of the higher generations and for the characterization of large organometallic dendrimers. See: (a) de Brabander-van den Berg, E. M. M.; Meijer, E. W. *Angew. Chem., Int. Ed. Engl.* **1993**, *32*, 1308. (b) Wörner, C.; Mülhaupt, R. *Angew. Chem., Int. Ed. Engl.* **1993**, *32*, 1306. See also refs 2d, 4b, and 14a.

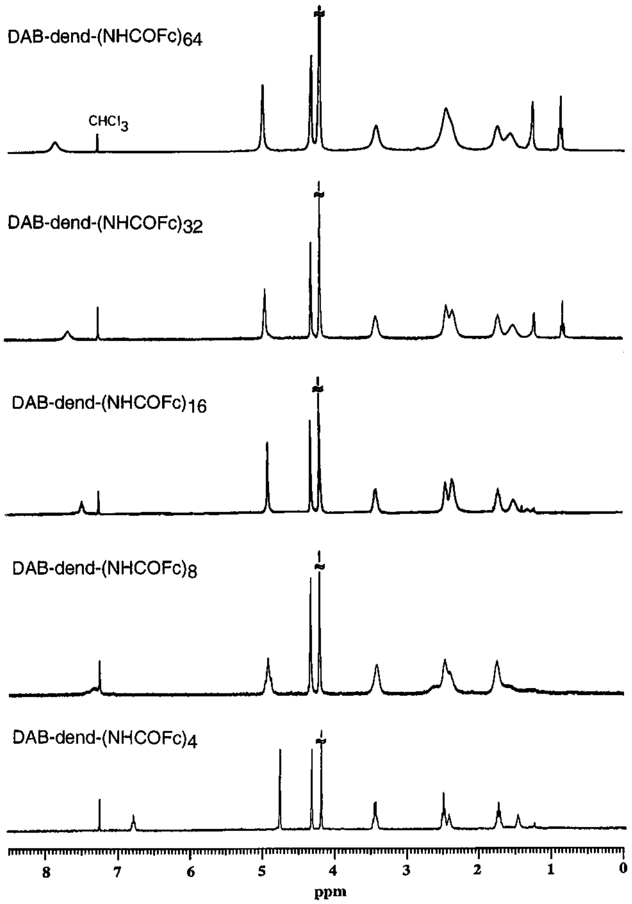

Figure 1. ^{1}H NMR (300 MHz, $CDCl_3$) spectra of dendrimers DAB-*dend*-$(NHCOFc)_x$ ($x = 4, 8, 16, 32, 64$).

molecules have been determined from CACHe molecular mechanic calculations, and the estimated diameters vary from about 25 to 52 Å, on going from the first to the fifth generation.

The electrochemistry of the new organometallic dendrimers has been examined.[18] In all cases, in CH_2Cl_2 and THF as solvents, a single reversible oxidation process was observed (see Figure 2). It is worth noting that the redox behavior of the dendrimers in such solvents is marked by changes in solubility with the change in the oxidation state of the ferrocene units on the dendritic surface. Whereas the anodic wave has a typical diffusional shape, in contrast, a sharp cathodic stripping peak was observed, which indicates the precipitation of the dendrimers onto the electrode upon oxidation. In addition, for all dendrimers upon continuous scanning in either CH_2Cl_2 or THF, there is an increase in the peak current with successive scans, which indicates that the formation of an electroactive film occurs on the electrode surface. From normal pulse voltammetry (NPV),[19] the values of the slopes of the plots of E vs $\log[(i_{\text{lim}} - i)/i]$ indicate that, for all dendrimers, all the ferrocenyl moieties attached to the dendritic surfaces behave independently and are oxidized at the same potential.

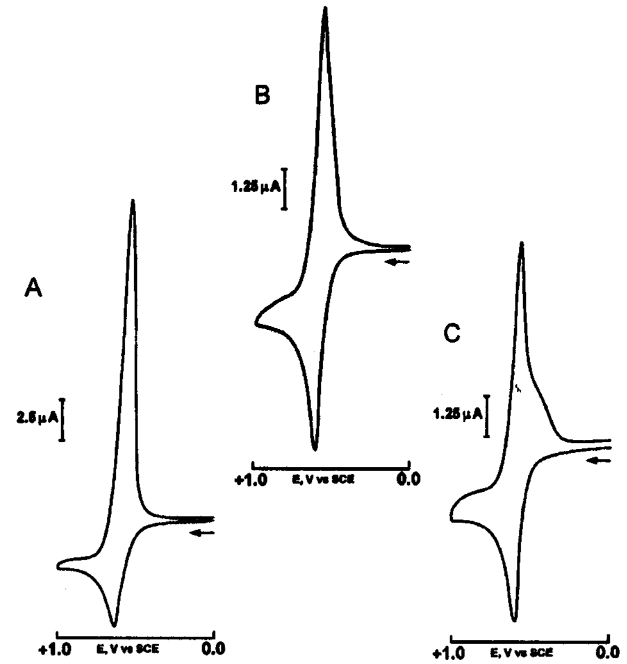

Figure 2. Cyclic voltammograms, measured in CH_2Cl_2/0.1 M TBAH, at a Pt-disk electrode of (A) DAB-*dend*-$(NHCOFc)_8$, (B) DAB-*dend*-$(NHCOFc)_{32}$, and (C) DAB-*dend*-$(NHCOFc)_{64}$. The scan rate was 100 mV/s. The concentration of ferrocene centers is the same (1.0 mM) for all solutions.

In summary, a novel evaluation of the reactivity of the surface functionalities of the NH_2-terminated dendrimers toward organometallic entities has been effected, affording good yields of a new family of ferrocenyl-containing dendritic macromolecules. Preliminary studies have shown that these dendritic molecules containing redox-active ferrocenyl moieties and amide CO−NH hydrogen-bonding functionalities act as a new type of receptor system capable of electrochemically recognizing anionic guest species. Further work will now be focused on exploring this area and also on studying the ability of these redox-active dendritic macromolecules to modify electrode surfaces.

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(17) The matrix for FAB-MS was 3-nitrobenzyl alcohol, and for MALDI-TOF-MS determinations silver trifluoroacetate was used as a cationization compound. The characterization of the fourth- and fifth-generation ferrocenyl dendrimers by MALDI-TOF mass spectrometric analysis will be published elsewhere.

(18) Formal potentials from cyclic voltammetry (*vs* saturated calomel electrode, SCE), in CH_2Cl_2, with 0.1 M NBu_4PF_6 (TBAH) for dendrimers DAB-*dend*-$(NHCOFc)_x$ are as follows: $E_{1/2} = +0.59, +0.57, +0.59, +0.58$, and $+0.59$ V, for $x = 4, 8, 16, 32$, and 64 respectively. For details of the electrochemical equipment, see ref 9.

(19) The NPV technique has been used in order to minimize precipitation of the oxidized dendrimers. See: (a) Flanagan, J. B.; Margel, S.; Bard, A. J.; Anson, F. C. *J. Am. Chem. Soc.* **1978**, *100*, 4248. (b) Albagly, D.; Bazan, G.; Wrighton, M. S.; Schrock, R. R. *J. Am. Chem. Soc.* **1992**, *114*, 4150.