

Synthesis and Electrochemistry of Molecular Dumbbells. Triblock Copolymers of Dendrons and Rigid Rods

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Received June 3, 2002. Revised Manuscript Received September 25, 2002

Polyether dendrons, generations 1–4, were connected to naphthalene diimides and rigid rod naphthalene diimide-benzidine oligomers. This provided a series of well-defined triblock copolymers with flexible dendrons on both ends of rigid rods. The largest of these used generation-4 dendrons with a 4.4-nm rigid rod containing two diimides and three benzidines. The estimated length of this molecule is 10 nm. Electrochemical reduction in DMF provided anion radicals on each diimide of the rigid rod. The diffusion coefficients and rates of these reductions were measured using cyclic voltammetry. The diffusion coefficients were successfully compared with predictions for diffusing prolate ellipsoids. Comparison of the heterogeneous rate constants showed that larger dendrons slowed the electrochemical reaction, and had slightly larger effects when the rod was shorter. It is proposed that the bulky dendrons prevent access of the diimide groups to the electrode even when they are not directly connected to the diimide. A zinc porphyrin substituted with two generation-3 poly(benzyl ether) dendrons was prepared and reduced for comparison. The heterogeneous rate constants for all these compounds were compared with literature values for related compounds.

Introduction.

In this project we set out to prepare triblock copolymers with unusual structures that incorporated bulky dendrimers on each end of rigid rods. These dumbbell-shaped molecules should have extremely disparate physical and chemical properties associated with the two types of units, and we imagined that this would have a variety of interesting consequences, especially in materials chemistry. We have previously communicated some initial results concerning two compounds of this type.¹ Here we report the synthesis of a number of dumbbells, and an investigation of their diffusion coefficients and electrochemical electron-transfer rates.

The compounds of choice are labeled **D_n-B-A-B-D_n** where **D_n** represents a poly(benzyl ether) dendron of generation *n*, **B** represents dimethoxybenzidine, and **A** represents naphthalene diimide. The dendrons, generations 1–4 of Frechet poly(benzyl ethers), were chosen for ease of synthesis and because much is known about their structure and properties.² The rigid rods were chosen based on our past work in which we have prepared **BAB** (2.7 nm), and **BABAB** (4.4 nm) rods.³ Although the individual **A** and **B** moieties can rotate

around the molecular axis of these rods, the rods should be nearly linear and quite rigid. To our knowledge the only comparable dumbbell-shaped compounds with long connectors that have been reported involve oligothiophenes⁴ or an oligo(thienylene-vinylene)⁵ flanked by poly(benzyl ether) dendrons. In contrast with oligoimides, oligothiophenes and oligo(thienylene vinylene)s can adopt nonlinear conformations by rotation about the bonds connecting the conjugated units.

The electrochemistry of oligoimide rods and various naphthalene diimides has been investigated in some detail.⁶ The naphthalene diimide groups are easily reduced to stable anion radicals and dianions. It has been shown that anion radicals along the rod are localized, although electrons can hop from one dimide to another. The aggregation of the monomeric anion radicals in aqueous solution has been demonstrated, and conducting polymer films have been developed using these anion radicals. One of the first reports of electrochemistry of any dendrimer involved poly(amidoamine) dendrimers to which these naphthalene diimides were attached.⁷ Although stable dendrimeric poly(anion radicals) were generated and studied in solution, the electrochemical studies showed unmistakable evidence for adsorption of the reduced species on the electrode surface in either DMF or water.

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More recently there have been a number of reports of dendrimers containing redox active groups at their core. These reports are especially pertinent to the present study in that they probed electron transfer using electrochemistry, and they explicated the basic ideas of steric hindrance to electron transfer by the dendrimer and of "micro-solvation"⁸ of the redox site by the surrounding dendrimer. Considering flexible-rod dumbbell molecules with poly(benzyl ether) dendrons, a D3-quatrathiophene-D3 dumbbell showed qualitative evidence for inhibition of electron transfer, but dumbbells composed from oligomers larger than quatraphiophene showed no evidence for this inhibition.⁴ A similar lack of inhibition was noted for a D3-oligo(thienylene vinylene)-D3.⁵ Also of interest here is a zinc porphyrin to which four poly(benzyl ether) dendrons are attached. These compounds show apparently complete inhibition of the electrochemical events for a D3 modified porphyrin.⁹

A number of other electrochemical studies have been reported for redox core dendrimers including studies of ferrocenes modified with a polyester amide.¹⁰ Here, even a single attachment of a small G2 or G3 dendron led to inhibition of the ferrocene electron transfer. Interesting because of the control of dendrimer rigidity and the careful investigation of electrochemistry, are the studies of Gorman and co-workers who used an iron cluster at the core and surrounded it with either rigid poly(phenylene ethynylene) or flexible polyether dendrons.¹¹ They also found inhibition of the electron transfer and quantified its effects. Other studies probed dendrimers with core moieties of ruthenium bipyridyls,¹² viologens,¹³ and dimolybdates.¹⁴ These and related studies make it clear that the dendrimer can have important inhibitory effects on the electrochemical electron-transfer process. Although the origin of these effects seems to be steric, there is a lot not understood about the detailed mechanism that has to do with the structure and orientation of polymers on surfaces, and the polymer's effects on the double layer. For these large molecules, dumbbell and solvent reorientation at the electrode surface can be an important consideration. In our preliminary communication¹ we presented no evidence for inhibition of electron transfer. Since then we have found such effects and quantified them. The data allow some conclusions and insights into the inhibitory effects for rigid and flexible-rod dumbbells and the general phenomenon of dendron inhibition.

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Experimental Section

Chemicals and Instrumentation. All chemicals were purchased from Aldrich Chemical Co. and used without further purification. Dimethylacetamide (DMA) and dimethylformamide (DMF) were stored over activated molecular sieves. ¹H NMR spectra were recorded on a Varian Unity spectrometer at 200 or 300 MHz using the solvent proton signal as the internal standard. ¹³C NMR spectra were recorded at 50 or 75 MHz on a Varian Unity spectrometer using the solvent carbon signal as the internal standard. Electrochemical experiments were done in 0.1 M Bu₄NBF₄ in DMF with a BAS 100 electrochemical analyzer. A glassy carbon disk and carbon fiber microelectrode were used for cyclic voltammetry. Mass spectra were obtained with a VG7070E-HF FAB with *m*-nitrobenzyl alcohol as the matrix (MNBA), a Finnigan FT/MS MALDI with dihydroxybenzene (DHB) as the matrix, or a MALDI/TOF with dianthranol as matrix. PEG was used as an internal standard for high-resolution MS. Dendron bromides **Dn-Br** and oligoimides **ABA**, **BAB**, and **BABAB** were prepared according to the literature^{2b,3,15} and had spectra compatible with structure. The syntheses of **D1-B**, **D1-B-D1**, **D1-BAB-D1**, **D2-B**, **D2-BABAB-D2**, **D4-CO₂CH₂CCl₃**, **D4-CO₂H**, **D4-B**, and **D4-BABAB-D4** have been reported in the supporting information for ref 1.

General Procedure for the Synthesis of Dendritic Methyl Esters. The dendritic benzyl bromide (2 equiv),^{2b} methyl 3,5-dihydroxybenzoate (1 equiv), anhydrous potassium carbonate (2.5 equiv), and 18-crown-6 (0.2 equiv) were refluxed in dried acetone for 48 h. The solution was evaporated to dryness and the remaining residue was partitioned between methylene chloride and water and extracted 3 times with methylene chloride. The organic layers were combined and dried over anhydrous sodium sulfate. The solvent was evaporated under reduced pressure and the crude product was purified as reported for each compound.

General Procedure for the Synthesis of Dendritic Carboxylic Acids. The dendritic methyl ester (1 equiv) and potassium hydroxide (8 equiv) were dissolved in ethanol/THF 10:3 mixture and heated to reflux for 4 h. The mixture was evaporated to dryness and dissolved in THF/water, which was then acidified with dilute HCl to a pH of 1. The ppt was filtered and purified as reported for each compound.

General Procedure for the Synthesis of Dendritic Acid Chlorides. Thionyl chloride (10 equiv) was added to a solution of the dendritic carboxylic acid (1 equiv) in freshly distilled benzene and heated to 80 °C for 8 h. The excess thionyl chloride and benzene were evaporated under reduced pressure. The product was then placed in a vacuum desiccator for 24 h and used without further purification.

General Procedure for the Synthesis of D-BAB-D and D-BABAB-D from Acid Chlorides. **BAB**¹⁵ or **BABAB**¹⁵ (1.0 equiv) was dissolved in freshly distilled methylene chloride and slowly added to a solution of the dendritic acid chloride (2.4 equiv) dissolved in freshly distilled methylene chloride under argon. The reaction mixture was stirred vigorously for 4 to 6 h and then washed with saturated sodium bicarbonate. The aqueous layer was washed twice with methylene chloride and the combined organic layers were dried over sodium sulfate. The solvent was evaporated under reduced pressure and the crude product was purified as reported for each compound.

D2-CO₂Me. The crude product was purified by recrystallizing from hexanes/toluene 4:1 to give the pure product: 89%. ¹H NMR (CDCl₃) δ: 3.91 (s, 3H, OMe), 5.01 (s, 4H, OCH₂), 5.04 (s, 8H, OCH₂), 6.59 (t, 2H, *J* = 2.4 Hz, ArH), 6.69 (d, 4H, *J* = 2.4 Hz, ArH), 6.78 (t, 1H, *J* = 2.4 Hz, ArH), 7.29 (d, 2H, *J* = 2.4 Hz, ArH), 7.32–7.44 (m, 20H, ArH, PhH). ¹³C NMR (CDCl₃) δ: 52.37, 70.18, 101.71, 106.43, 107.21, 108.46, 127.62, 128.09, 128.66, 132.11, 136.79, 138.92, 159.72, 160.23, 166.79. Mass spectrum C₅₀H₄₄O₈ (MALDI) dianthranol matrix found (M + Na)⁺ = 795.3040; calcd. (M + Na)⁺ = 795.2933.

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D2-CO₂H. The crude product from hydrolysis of the methyl ester was purified by recrystallization from ethanol/acetone 10:1 to give the pure product: 92%. ¹H NMR (DMSO-*d*₆) δ : 5.05 (s, 12H, OCH₂), 6.61 (t, 2H, *J* = 2 Hz, ArH), 6.71 (d, 4H, *J* = 2 Hz, ArH), 6.89 (t, 1H, *J* = 2 Hz, ArH), 7.14 (d, 2H, *J* = 2 Hz, ArH), 7.26–7.42 (m, 20H, ArH), 13.03 (s, 1H, COOH). ¹³C NMR (DMSO-*d*₆) δ : 69.82, 101.62, 106.92, 107.03, 108.54, 128.24, 128.34, 128.91, 133.35, 137.41, 139.65, 159.80, 160.07, 167.41. Mass spectrum C₄₉H₄₂O₈ (FAB) MNBA matrix found (M + Na)⁺ = 781.2773; calcd. (M + Na)⁺ = 781.2777.

D2-COCl. ¹H NMR (CDCl₃) δ : 5.01 (s, 4H, OCH₂), 5.03 (s, 8H, OCH₂), 6.58 (t, 2H, *J* = 2.4 Hz, ArH), 6.66 (d, 4H, *J* = 2.4 Hz, ArH), 6.84 (t, 1H, *J* = 2.4 Hz, ArH), 7.31–7.43 (m, 22H, ArH, PhH). ¹³C NMR (CDCl₃) δ : 70.19, 70.38, 101.82, 106.44, 109.37, 110.29, 127.58, 128.10, 128.65, 134.99, 136.70, 138.38, 159.83, 160.29, 168.18.

D2-BAB. A mixture of **D2-COCl** (53.9 mg, 0.0694 mmol) was dissolved in freshly distilled methylene chloride (25 mL) under argon. BAB (100 mg, 0.139 mmol) was dissolved in freshly distilled methylene chloride (25 mL) under argon. The solution of the **D2-COCl** was added dropwise to the solution of BAB over a period of 30 min. A ppt formed within 15 min upon the addition of the acid chloride. The mixture was stirred at room temperature for an additional 8 h to ensure a completed reaction. The mixture was then washed with saturated sodium bicarbonate (25 mL). The aqueous layer was washed twice with 30 mL of CH₂Cl₂ and the organic layers were combined and dried over anhydrous sodium sulfate. The mixture was evaporated to dryness under reduced pressure to give a mixture of mono- and di-substituted BAB rods. The crude product was purified by flash chromatography, eluting with 100:1 CH₂Cl₂/THF and gradually increasing to 20:1 CH₂Cl₂/THF to give **D2-BAB** as a brown solid: 58 mg, 57%. ¹H NMR (CDCl₃) δ : 3.85–8 (m, 6H, OCH₃), 3.96 (s, 3H, OCH₃), 3.99 (s, 3H, OCH₃), 5.05 (s, 12H, CH₂O), 6.60 (t, 2H, *J* = 2.4 Hz, ArH), 6.71 (d, 4H, *J* = 2.4 Hz, ArH), 6.77 (t, 1H, *J* = 2.1 Hz, ArH), 6.87 (dd, 1H, *J* = 1.5, 8.4 Hz, ArH), 7.11 (sb, 1H, ArH), 7.13 (d, 2H, *J* = 2.1 Hz, ArH), 7.17 (d, 1H, *J* = 1.5 Hz, ArH), 7.24 (sb, 1H, ArH), 7.28–7.44 (m, 27H, ArH, PhH), 8.53 (s, 1H, NH), 8.63 (d, 1H, *J* = 8.4 Hz, ArH), 8.86 (s, 4H, ArH). ¹³C NMR (CDCl₃) δ : 55.79, 56.01, 56.08, 70.23, 70.36, 101.77, 105.32, 106.36, 106.56, 109.25, 109.91, 110.81, 111.09, 119.76, 120.02, 120.30, 121.73, 122.45, 127.13, 127.23, 127.58, 127.67, 128.15, 128.70, 129.80, 129.99, 131.42, 136.78, 137.48, 138.85, 144.13, 144.48, 148.48, 154.89, 154.94, 155.01, 155.05, 160.12, 160.32, 162.85, 164.99. Mass spectrum C₉₁H₇₂N₄O₁₅ (MALDI-TOF) dithranol matrix found M⁺ = 1460.4983; calcd. M⁺ = 1460.4989.

D2-BAB-D2. D2-B. (196 mg, 0.199 mmol) was dissolved in anhydrous DMA (6 mL) and heated to 90 °C while stirring. Naphthalene dianhydride (17.8 mg, 0.0663 mmol) was added in portions over a 5-min period, and after 1 h the temperature was raised to 135 °C for 16 h. The DMA was evaporated under reduced pressure and the crude product was purified via flash chromatography, eluting with methylene chloride and gradually increasing to 25:1 methylene chloride/acetone to give **D2-BAB-D2** as an orange solid: 60 mg, 41%. ¹H NMR (CDCl₃) δ : 3.88 (s, 3H, OCH₂), 3.89 (s, 3H, OCH₃), 4.00 (s, 6H, OCH₃), 5.06 (s, 24H, OCH₂), 6.61 (t, 4H, *J* = 2.1 Hz, ArH), 6.72 (d, 8H, *J* = 2.1 Hz, ArH), 6.78 (t, 2H, *J* = 2.4 Hz, ArH), 7.14 (d, 4H, *J* = 2.4 Hz, ArH), 7.18 (d, 2H, *J* = 1.2 Hz, ArH), 7.29–7.46 (m, 48H, ArH, PhH), 8.55 (s, 2H, NH), 8.64 (d, 2H, *J* = 8.4 Hz, ArH), 8.87 (s, 4H, ArH). ¹³C NMR (CDCl₃) δ : 56.09, 70.24, 70.36, 101.76, 106.36, 106.56, 109.25, 110.09, 111.05, 120.03, 120.30, 122.43, 127.18, 127.57, 127.69, 128.16, 128.72, 130.00, 131.44, 136.77, 137.46, 138.85, 144.10, 148.48, 155.00, 160.12, 160.31, 162.85, 165.03. Mass spectrum C₁₄₀H₁₁₂N₄O₂₂ (MALDI-TOF) dithranol matrix found (M + Ag)⁺ = 2309.9; calcd. (M + Ag)⁺ = 2309.7.

D3-CO₂Me. The crude product was purified via flash chromatography, eluting with 7:3 methylene chloride/hexanes and gradually increasing to 17:3 to give **D3-CO₂Me** as a white solid: 92%. ¹H NMR (CDCl₃) δ : 3.87 (s, 3H, OMe), 4.95 (s, 8H, CH₂O), 4.98 (s, 4H, CH₂O), 5.01 (s, 16H, CH₂O), 6.53 (t, 2H, *J* = 2.4 Hz, ArH), 6.55 (t, 4H, *J* = 2.4 Hz, ArH), 6.64 (d, 4H, *J* = 2.4 Hz, ArH), 6.66 (d, 8H, *J* = 2.4 Hz, ArH), 6.78 (t,

1H, *J* = 2.4 Hz, ArH), 7.25–7.42 (m, 42H, PhH). ¹³C NMR (CDCl₃) δ : 52.80, 70.07, 70.16, 101.68, 101.75, 106.44, 106.51, 107.21, 108.48, 127.64, 128.08, 128.65, 132.15, 136.85, 138.95, 139.27, 159.77, 160.15, 160.24, 166.78. Mass spectrum for C₁₀₆H₉₂O₁₆ (MALDI-TOF) DT matrix found (M + Na)⁺ = 1683.5; calcd. (M + H)⁺ = 1683.4.

D3-CO₂H. The crude product was purified by recrystallization from 5:1 ethanol/acetone to give **D3-CO₂H** as a white powder: 90%. ¹H NMR (CDCl₃) δ : 4.98 (s, 8H, CH₂O), 5.00 (s, 4H, CH₂O), 5.03 (s, 16H, CH₂O), 6.58–6.61 (m, 6H, ArH), 6.70–6.72 (m, 12H), 6.87 (t, 1H, *J* = 2.4 Hz, ArH), 7.30–7.45 (m, 42H, PhH). ¹³C NMR (CDCl₃) δ : 70.08, 70.16, 101.68, 101.82, 106.46, 106.58, 108.10, 109.00, 127.67, 128.10, 128.68, 131.25, 136.85, 138.85, 139.27, 159.82, 160.17, 160.23, 171.42.

D3-COCl. ¹H NMR (CDCl₃) δ : 4.97 (s, 8H, CH₂O), 4.99 (s, 4H, CH₂O), 5.02 (s, 16H, CH₂O), 6.55–6.58 (m, 6H, ArH), 6.65 (d, 4H, *J* = 2.1 Hz, ArH), 6.67 (d, 8H, *J* = 2.4 Hz, ArH), 6.88 (t, 1H, *J* = 2.1 Hz, ArH), 7.31–7.43 (m, 40H, PhH). ¹³C NMR (CDCl₃) δ : 70.10, 70.18, 70.43, 101.64, 101.87, 106.44, 106.54, 109.41, 110.31, 127.67, 128.11, 128.69, 135.03, 136.80, 138.41, 139.18, 159.89, 160.21, 160.24, 168.23.

D3-B. A mixture of **D3-CO₂H** (200 mg, 0.125 mmol), hydroxybenzotriazole (HOBT) (18.6 mg, 0.138 mmol), and diisopropylcarbodiimide (DIC) (17.4 mg, 0.138 mmol) was dissolved in anhydrous DMA (3 mL) and stirred vigorously under argon for 1 h. **B** (91.6 mg, 0.375 mmol) was dissolved in anhydrous DMA (3 mL) under argon. The solution of the activated D₃-ester was slowly added to the solution of **B** over a period of 15 min. The mixture was stirred at 50 °C for 24 h. The DMA was then evaporated under reduced pressure to give a solid. The crude product was purified by flash chromatography, eluting with methylene chloride and gradually increasing to 30:1 methylene chloride/acetone to give **D3-B** as an orange solid: 185 mg, 81%. ¹H NMR (CDCl₃) δ : 3.93 (s, 3H, OCH₃), 3.95 (s, 3H, OCH₃), 5.00 (s, 8H, CH₂O), 5.04 (s, 20H, CH₂O), 6.60–6.62 (m, 6H, ArH), 6.72–6.74 (m, 12H, ArH), 6.81–6.86 (m, 2H, ArH), 7.06–7.10 (m, 3H, ArH), 7.18 (d, 2H, *J* = 2.1 Hz, ArH), 7.22 (dd, 1H, *J* = 2.1, 8.4 Hz, ArH), 7.30–7.46 (m, 40H, PhH), 8.53 (s, 1H, NH), 8.60 (d, 1H, *J* = 8.4 Hz, ArH). ¹³C NMR (CDCl₃) δ : 55.73, 55.95, 70.10, 70.17, 70.34, 101.68, 101.80, 105.18, 106.48, 106.63, 108.45, 109.38, 115.62, 119.29, 119.71, 120.08, 126.34, 127.67, 128.10, 128.68, 132.19, 136.86, 137.66, 138.92, 139.27, 147.86, 148.52, 160.13, 160.22, 160.26, 164.79. Mass spectrum for C₁₁₉H₁₀₄N₂O₁₇ (MALDI-TOF) dithranol matrix found (M + Ag)⁺ = 1939.6334; calcd. (M + Ag)⁺ = 1939.6386.

D3-BAB-D3. D3-COCl and BAB was purified via flash chromatography, eluting with methylene chloride and gradually increasing to 30:1 methylene chloride/acetone to give solid **D3-BAB-D3**: 72%. ¹H NMR (CDCl₃) δ : 3.86 (s, 3H, OCH₃), 3.87 (s, 3H, OCH₃), 3.95 (s, 6H, OCH₃), 4.98 (s, 16H, CH₂O), 5.02 (s, 32H, CH₂O), 5.03 (s, 8H, CH₂O), 6.56–6.58 (m, 12H, ArH), 6.68–6.70 (m, 24H, ArH), 6.79 (t, 2H, *J* = 2.1 Hz, ArH), 7.18 (d, 8H, *J* = 2.1 Hz, ArH), 7.30–7.46 (m, 86H, PhH), 8.54 (s, 2H, NH), 8.63 (d, 2H, *J* = 8.4 Hz, ArH), 8.86 (s, 4H, ArH). ¹³C NMR (CDCl₃) δ : 56.06, 70.11, 70.18, 70.37, 101.66, 101.79, 105.23, 106.46, 106.63, 109.22, 110.11, 111.08, 120.01, 120.28, 122.43, 127.18, 127.66, 128.11, 128.69, 130.00, 131.43, 136.83, 137.50, 138.84, 139.22, 144.10, 148.49, 155.05, 160.16, 160.22, 160.25, 162.83, 164.96. Mass spectrum for C₂₅₂H₂₀₈N₄O₃₈ (MALDI-TOF) dithranol matrix found (M + Ag)⁺ = 4008.2; calcd. (M + Ag)⁺ = 4008.36.

D3-BABAB-D3. The crude product from the reaction of **D3-COCl** with **BABAB**¹⁵ was purified via flash chromatography, eluting with methylene chloride and gradually increasing to 10:1 methylene chloride/acetone to give **D3-BABAB-D3** as an orange solid: 46%. ¹H NMR (CDCl₃) δ : 3.88 (s, 3H, OCH₃), 3.89 (s, 3H, OCH₃), 3.91 (s, 3H, OCH₃), 3.92 (s, 3H, OCH₃), 3.97 (s, 6H, OCH₃), 5.00 (s, 16H, CH₂O), 5.04 (s, 40H, CH₂O), 6.58–6.60 (m, 12H, ArH), 6.70–6.71 (m, 26H, ArH), 6.81 (t, 2H, *J* = 2.1 Hz, ArH), 7.17 (d, 8H, *J* = 2.1 Hz, ArH), 7.30–7.44 (m, 90H, PhH), 8.56 (s, 2H, NH), 8.64 (d, 2H, *J* = 8.4 Hz, ArH), 8.90 (s, 8H, NH). ¹³C NMR (CDCl₃) δ : 55.94, 70.09, 70.28, 101.62, 106.39, 106.54, 109.13, 110.99, 111.59,

119.87, 119.99, 120.15, 120.36, 122.41, 127.08, 127.12, 127.47, 127.92, 128.50, 129.88, 129.99, 131.27, 136.75, 137.39, 138.76, 139.14, 143.93, 143.96, 148.40, 154.97, 160.14, 162.65, 164.81, 167.82. Mass spectrum for $C_{280}H_{224}N_6O_{44}$ (MALDI-TOF) dithranol matrix found ($M + Ag$)⁺ = 4484.2; calcd. ($M + Ag$)⁺ = 4484.46.

D4-CO₂Me. The crude product was purified by flash chromatography, eluting with CH_2Cl_2 /hexanes 5:1 and gradually increasing to 100:1 CH_2Cl_2 /acetone to give **D4-CO₂Me** as a clear, colorless, glassy solid: 85%. ¹H NMR ($CDCl_3$) δ : 3.87 (s, 3H, OCH_3), 4.95 (s, 28H, CH_2O), 5.01 (s, 32H, OCH_2Ph), 6.54–6.59 (m, 16H, ArH), 6.68–6.69 (m, 28H, ArH), 6.79 (t, 1H, J = 1.8 Hz, ArH), 7.28–7.42 (m, 80H, PhH). ¹³C NMR ($CDCl_3$) δ : 52.34, 70.16, 101.70, 106.48, 107.21, 108.58, 127.65, 128.07, 128.66, 132.18, 136.88, 139.03, 139.31, 159.79, 160.16, 160.25, 166.78. Mass spectrum for $C_{218}H_{188}O_{32}$ (MALDI-TOF) dithranol matrix found ($M + Ag$)⁺ = 3427.0; calcd. ($M + Ag$)⁺ = 3427.2.

D4-COCl. ¹H NMR ($CDCl_3$) δ : 4.93 (s, 28H, CH_2O), 4.99 (s, 32H, CH_2O), 6.54–6.57 (m, 16H, ArH), 6.65–6.67 (m, 28H, ArH), 6.84 (t, 1H, J = 2.4 Hz, ArH), 7.27–7.41 (m, 80H, PhH). ¹³C NMR ($CDCl_3$) δ : 70.05, 70.15, 101.64, 106.46, 110.35, 127.66, 128.10, 128.45, 128.67, 134.97, 136.84, 138.50, 139.22, 139.27, 159.85, 160.14, 160.22.

D4-BAB-D4. The crude product from reaction of **D4-COCl** with **BAB** was purified by flash chromatography, eluting with CH_2Cl_2 and gradually increasing to 50:1 CH_2Cl_2 /acetone to give **D4-BAB-D4** as a glassy orange solid: 40%. ¹H NMR ($CDCl_3$) δ : 3.81 (s, 3H, OCH_3), 3.83 (s, 3H, OCH_3), 3.89 (s, 6H, OCH_3), 4.91 (s, 48H, CH_2O), 4.93 (s, 8H, CH_2O), 4.96 (s, 64H, CH_2O), 6.51–6.54 (m, 24H, ArH), 6.56 (t, 4H, J = 2.1 Hz, ArH), 6.64 (d, 48H, J = 2.4 Hz, ArH), 6.67 (d, 8H, J = 2.1 Hz, ArH), 6.74 (t, 2H, J = 2.1 Hz, ArH), 7.09–7.11 (m, 6H, PhH); 7.24–7.37 (m, 168H, PhH), 8.50 (s, 2H, NH), 8.60 (d, 2H, 8.1 Hz, ArH), 8.85 (s, 4H, ArH). ¹³C NMR ($CDCl_3$) δ : 55.87, 69.88, 69.98, 101.47, 106.28, 110.37, 110.89, 118.86, 119.88, 122.27, 127.02, 127.47, 127.90, 128.48, 129.79, 131.25, 135.21, 136.65, 137.29, 138.72, 139.05, 139.09, 143.95, 148.30, 159.95, 160.03, 162.62, 164.74. Mass spectrum for $C_{476}H_{400}N_4O_{70}$ (MALDI-TOF) dithranol matrix found ($M + Ag$)⁺ = 7403.0; calcd. ($M + Ag$)⁺ = 7403.7.

General Procedure for Synthesis of Dx-A-Dx. To a round-bottom flask under a nitrogen atmosphere was added a 2:1 mixture of **Dn-Br** and the dipotassium salt of **A** in a minimum amount of dry DMF. The reaction was allowed to stir for 16 h. The reaction mixture was treated with CH_2Cl_2 and water and extracted four times with CH_2Cl_2 . The product was purified by column chromatography on silica gel. The percent yields reported refer to percentage of desired compound collected relative to the percentage of bromide that was converted.

D1-A-D1. **D1-Br** (0.500 g, 1.31 mmol) and **A** (0.223 g, 0.652 mmol) were stirred under nitrogen at 100 °C for 18 h in 30 mL of DMF. The product was worked-up as described above and purified by column chromatography eluting with CH_2Cl_2 , hexanes, and Et_2O (4:4:0.6) gradually increasing to a 3:1:1 mixture to give the product as a yellow powder (150 mg, 0.186 mmol): 55% yield. ¹H NMR δ 8.76 (s, 4H, A–H), 7.33 (m, 20H, Ph–H), 6.72 (d, 4H, Ar–H), 6.52 (t, 2H, Ar–H), 5.33 (s, 4H, Bn–H), and 5.00 (s, 8H, Bn–H). Mass spectrum (MALDI-TOF) m/z calcd 893.3 (100), 894.3 (65), 895.3 (25), and 896.3 (7); found 893.5 (100), 894.5 (88), 895.5 (44), and 896.5 (12).

D2-A-D2. **D2-Br** (1.03 g, 1.28 mmol) and **A** (0.218 g, 0.638 mmol) were stirred under nitrogen at 105 °C for 16 h in 30 mL of DMF. The product was worked-up as described above and purified by column chromatography eluting with CH_2Cl_2 , hexanes, and Et_2O (5:5:0.5) gradually increasing to a 3:1:1 mixture to give the product as a yellow powder (145 mg, 0.082 mmol): 22% yield. ¹H NMR δ 8.67 (s, 4H, A–H), 7.33 (m, 40H, Ph–H), 6.64 (m, 18H, Ar–H), 5.30 (s, 4H, Bn–H), 4.98 (s, 16H, Bn–H), and 4.94 (s, 8H, Bn–H). Mass spectrum (MALDI-TOF) m/z calcd 1741.6 (80), 1742.6 (100), 1743.6 (65), and 1744.6 (28); found 1741.6 (79), 1742.6 (100), 1743.5 (70), and 1744.5 (34).

D3-A-D3. **D3-Br** (1.21 g, 0.73 mmol) and **A** (0.125 g, 0.36 mmol) were stirred under nitrogen at 105 °C for 16 h in 10 mL of DMF. The product was worked-up as described above and purified by column chromatography eluting with CH_2Cl_2 and hexanes (1:1) gradually increasing to a 3:1 mixture to give the product as a yellow powder (220 mg, 0.064 mmol): 23% yield. ¹H NMR δ 8.60 (s, 4H, A–H), 7.33 (m, 80H, Ph–H), 6.61 (m, 42H, Ar–H), 5.25 (s, 4H, Bn–H), and 4.94 (m, 56H, Bn–H). Mass spectrum (MALDI-TOF) m/z calcd 3438.3 (30), 3439.3 (78), 3440.3 (100), 3441.3 (88), 3442.3 (58), 3443.3 (32), 3444.3 (12), and 3445.3 (4); found 3438.4 (28), 3439.4 (77), 3440.4 (100), 3441.4 (88), 3442.4 (60), 3443.4 (34), 3444.4 (16), and 3445.3 (8).

D4-A-D4. **D4-Br** (1.68 g, 0.50 mmol) and **A** (0.086 g, 0.25 mmol) were stirred under nitrogen at 105 °C for 16 h in 8 mL of DMF. The product was worked-up as prescribed above and purified by column chromatography eluting with CH_2Cl_2 and hexanes (1:1) gradually increasing to a 2:1 mixture to give the product as an amber colored glass (480 mg, 0.07 mmol): 37% yield. ¹H NMR δ 8.50 (s, 4H, A–H), 7.33 (m, 160H, Ph–H), 6.62 (m, 106H, Ar–H), 5.17 (s, 4H, Bn–H), and 4.94 (m, 56H, Bn–H). Mass spectrum (MALDI-TOF) m/z calcd 6832.6 (18), 6833.6 (43), 6834.6 (74), 6835.6 (95), 6836.6 (100), 6837.6 (88), 6838.7 (67), and 6840.7 (27); found 6832.5 (17), 6833.6 (40), 6834.5 (70), 6835.5 (90), 6836.5 (100), 6837.4 (87), 6838.4 (62), and 6840.6 (28).

Naphthalenediimide Dipotassium Salt.²¹ Naphthalenediimide (0.54 g, 2.0 mmol) and potassium hydroxide (5.0 g) were refluxed in 150 mL of ethanol for 6 h. The precipitate was filtered off, washed with ethanol, and dried. The salt was isolated as a green powder in 92% yield (0.64 g, 1.9 mmol).

5,15-Bis(3,5-dimethoxyphenyl)porphyrin. 3,5-Dimethoxybenzaldehyde (1.68 g, 10.12 mmol) and dipyrromethane²² (1.42 g, 10.12 mmol) were dissolved in dry chloroform (1 L) under nitrogen. BF_3 etherate (0.21 mL, 1.7 mmol) was added, and the reaction mixture was shielded from ambient light while the reaction stirred at room temperature for 90 min. After adding DDQ (3.45 g, 15.2 mmol), the reaction stirred for an additional 90 min when triethylamine (0.24 mL, 1.67 mmol) was added to neutralize any unreacted BF_3 etherate. The solvent was evaporated and the solid were adsorbed onto silica gel. Using 25 g of silica gel, the crude product was purified using a 2:1 mixture of hexanes to dichloromethane, and eluting to a 20:1 mixture, dichloromethane to ether. Upon evaporation of solvent, the product was obtained as a purple crystal, yield 12% (350 mg, 0.60 mmol).

5,15-Bis(3,5-dihydroxyphenyl)porphyrin. 5,15-bis(3,5-Dimethoxyphenyl)porphyrin (290 mg, 0.50 mmol) was dissolved in dry CH_2Cl_2 (15 mL) under a nitrogen atmosphere. The solution was cooled to 0 °C, and then BBr_3 (1.99 mL, 1.99 mmol, 1 M in CH_2Cl_2) was added slowly to the reaction. After the addition, the solution was allowed to warm to room temperature while stirring for 18 h. Distilled water (25 mL) was added, and the mixture was stirred for 2 h. After evaporation of the organic solvents, a brown-green powder was filtered from the water. The product was dissolved in ether, washed twice with saturated $NaHCO_3$, washed once with water, and then dried over Na_2SO_4 . The solvent was evaporated, and the product was isolated as a purple powder that was dried under vacuum at 40 °C affording 80% yield (212

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mg, 0.399 mmol). ^1H NMR δ 10.62 (s, 2H, methyne), 9.62 (d, 4H, β -H), 9.08 (m, 4H, γ -H), 7.12 (m, 4H, *p*Ph-H), and 6.72 (m, 2H, *o*Ph-H).

Zinc 5,15-Di(dihydroxyphenyl)porphyrin. 5,15-bis(3,5-dihydroxyphenyl)porphyrin (185 mg, 0.349 mmol) and $\text{Zn}(\text{OAc})_2 \cdot 2\text{H}_2\text{O}$ (84 mg, 0.384 mmol) were dissolved in methanol (10 mL). The solution was heated to a reflux for 4 h, when distilled water (40 mL) was added. The methanol was evaporated under vacuum. The turbid solution was placed in refrigeration overnight, and the purple crystalline solid was filtered and dried in vacuo at 40 °C, yield 90%.

D3-Zn-D3. Zinc 5,15-di(dihydroxyphenyl)porphyrin (105 mg, 0.18 mmol), **D2-Br** (714 mg), K_2CO_3 (0.220 g, 1.59 mmol), and 18-cr-6 (37 mg, 0.14 mmol) were dissolved in dry acetone under a nitrogen atmosphere. The solution was heated to reflux and allowed to stir for 48 h. The solvent was evaporated, and the residue was dissolved in CH_2Cl_2 and portioned with water. The layers were separated, and the aqueous layer was washed 3× with CH_2Cl_2 . The organic fractions were dried over Na_2SO_4 . The product was purified via flash column chromatography starting with 4:1, hexanes/ CH_2Cl_2 and eluting to pure CH_2Cl_2 . The product fractions were collected, and the solvent was evaporated. The product was dissolved in a minimum amount of CHCl_3 and precipitated into methanol. The precipitate was dissolved in a minimum amount of ethyl acetate and precipitated into ether. The product was obtained as a purple powder in 43% yield. ^1H NMR δ 10.20 (s, 2H, methyne), 9.35 (s, 4H, β -H), 8.87 (m, 4H, γ -H), 7.29 (m, 80H, Ph-H), 6.77 (m, 42H, Ar-H), and 5.00 (m, 56H, Bn-H).

Results and Discussion

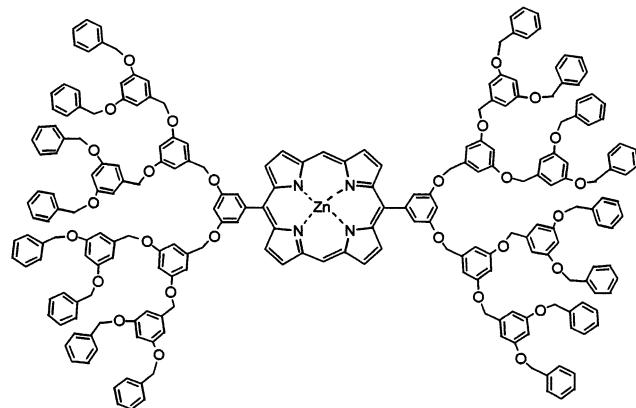
Synthesis. The four dendrons **D1-Br** through **D4-Br** were prepared following the literature with minor modifications. In our hands the overall yields of these dendrimers were similar to those previously reported. Compounds **D1-A-D1** through **D4-A-D4** were prepared by converting naphthalene diimide to its dipotassium salt and then coupling the isolated salt with **Dn-Br** in an appropriate 1:2 stoichiometric ratio.

A zinc porphyrin bound to two **D3** dendrons (**D3-Zn-D3**) was prepared starting with pyrrole, which was converted to dipyrromethane and then to the 5,15-(3,5-dihydroxyphenyl) substituted porphyrin. This was reacted with **D3-Br** giving **D3-Zn-D3**. Disubstituted **D3-Zn-D3** is an exact analogue of a zinc porphyrin substituted with four poly(benzyl ether) dendrons,⁹ which has been previously investigated electrochemically.

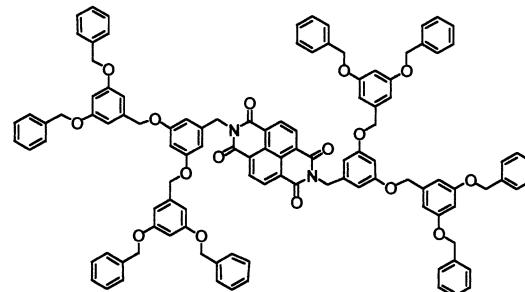
Dendrons **Dn-CO₂H** were prepared by coupling the dendritic bromide, **D(n-1)-Br**, to methyl 3,5-dihydroxybenzoate in refluxing in acetone, with crown ether as the phase transfer catalyst for the base, potassium carbonate.^{2b} Initial experiments using 1,1,1-trichloroethyl 3,5-dihydroxybenzoate proved less satisfactory than the use of the methyl ester, which was solid and led to a recrystallizable **Dn-CO₂H**.

Rods and rod precursors were synthesized by the methods of Stallman.¹⁵ **ABA** was prepared from dimethoxybenzidine (**B**) with excess naphthalene dianhydride (**A**). **BAB** came from **A** with excess **B**. **BABAB** was prepared from **ABA** with excess **B**.

Three routes have been used in the synthesis of dumbbells, with each method having advantages and disadvantages. The first method used activated ester–amine coupling in which the carboxylic acid was activated with hydroxybenzotriazole (HOBt) and the coupling was catalyzed with diisopropylcarbodiimide (DIC). The dendrons with carboxylic acids as their focal point



D3-Zn-D3



D2-A-D2

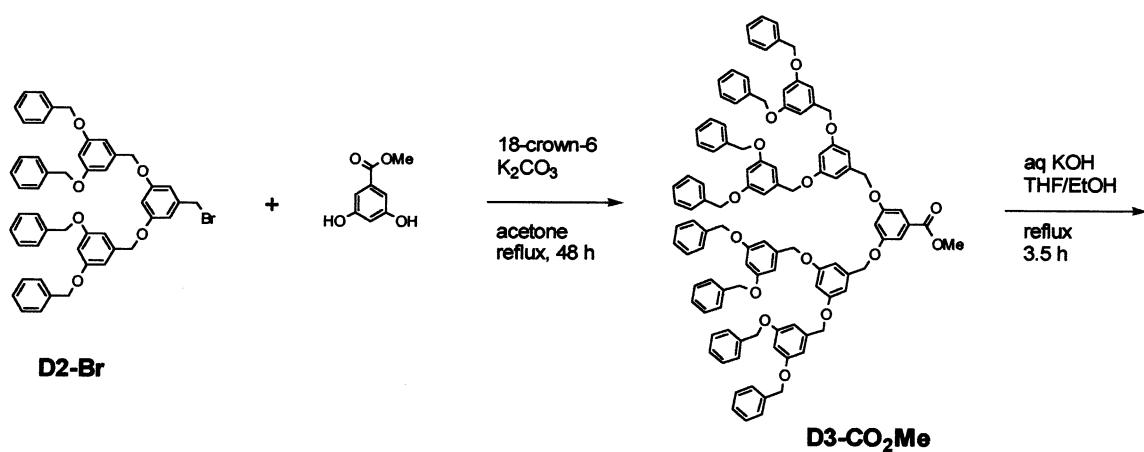
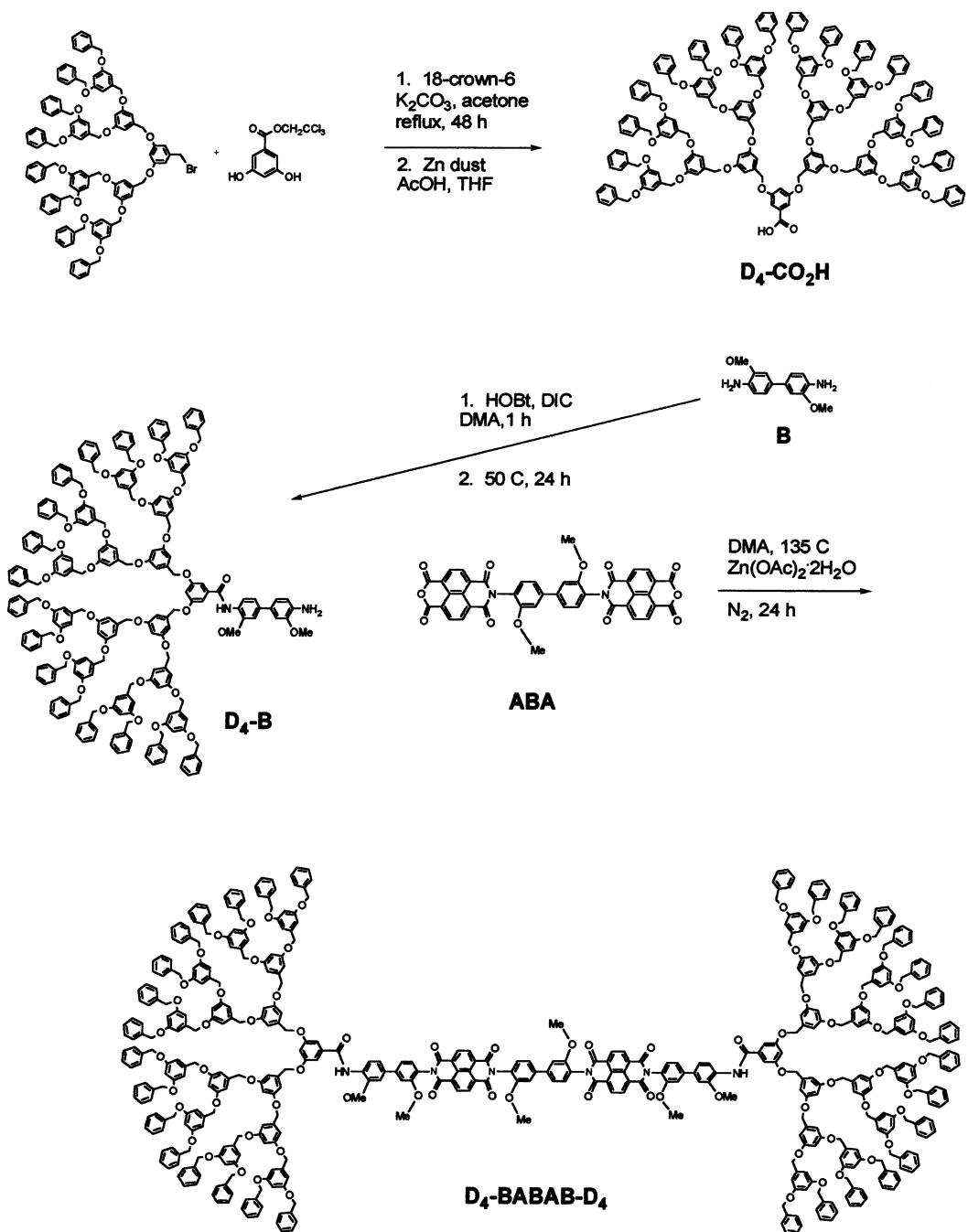
functionality **Dn-CO₂H** were coupled directly to **B** for all generations to give **Dn-B** when **B** was in excess, and **Dn-B-Dn** when the ratio of dendron to **B** was 2:1. This method was also used with oligoimide **BAB** to synthesize **D1-BAB-D1** and **D2-BAB-D2** dumbbells as shown in Scheme 1. This method failed, however, when employed to produce generations three and four dumbbells. The yields were very low and isolation was not feasible due to the myriad of byproducts.

The second method involved condensation of **Dn-B** molecules with naphthalene dianhydride under conditions that do not require a great excess of amine.¹⁵ This was as effective as the activated ester–amine coupling for forming compounds such as **D2-BAB-D2**, but for generations three and four the reaction was again unproductive. The observed result may stem from the interaction of the dendritic arms on the larger generation dendrons with the amine functionality at the focal point. However, this method did allow for the formation of **D4-BABAB-D4** by reacting **D4-B** with **ABA**, which was more reactive than **A** in forming a diimide.

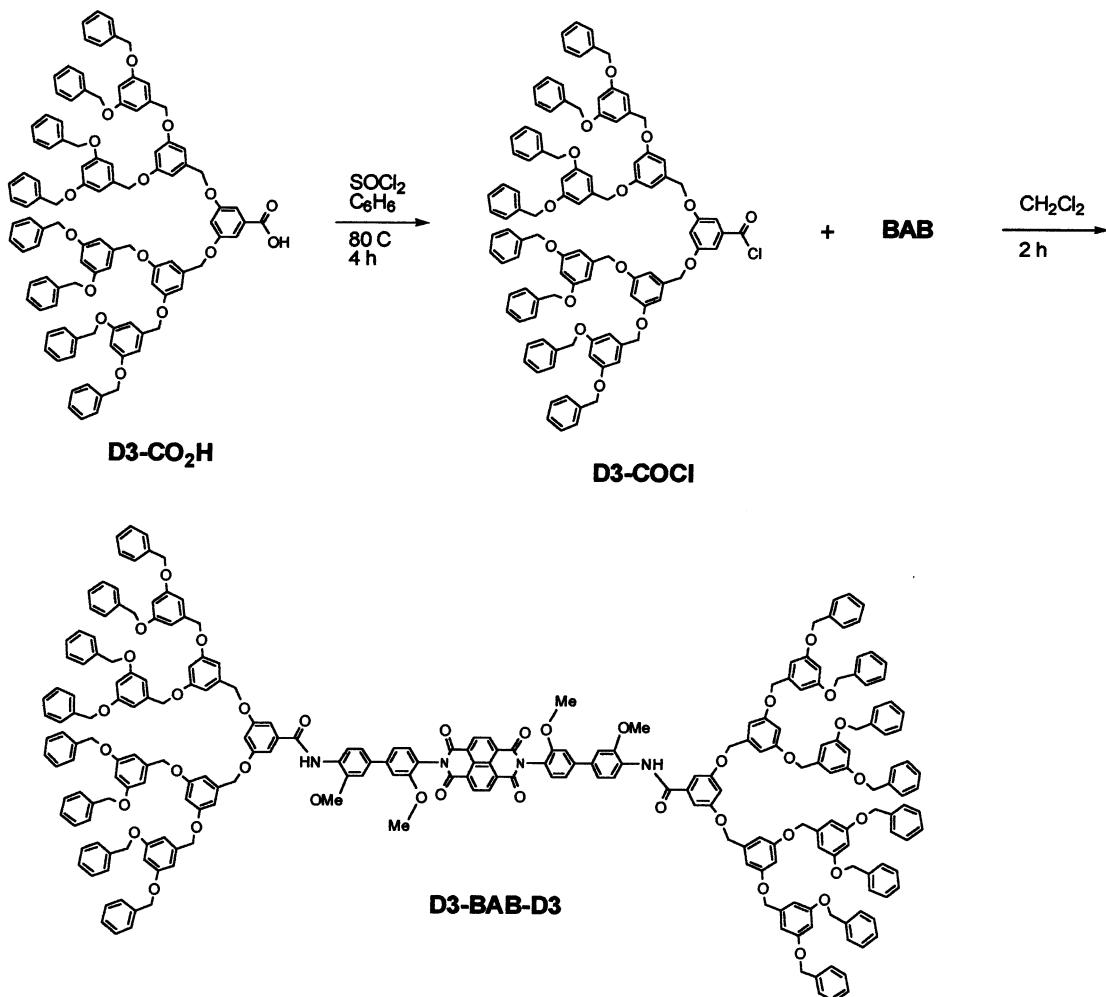
The third method involved the synthesis of the acid chloride from the carboxylic acid terminated dendron followed by coupling with **B** terminated rods (Scheme 1). This method generally improved yields for the lower generation dumbbells and successfully allowed for the synthesis and purification of **D3-BAB-D3** and **D4-BAB-D4**. **D2-COCl** was also reacted with **BAB** or **BABAB** to give a high overall yield of **D2-BAB-D2** and **D2-BABAB-D2**. Similarly, **D3-COCl** was used to prepare **D3-BAB-D3** and **D3-BABAB-D3**, which were purified chromatographically.

All of the above compounds were pure by TLC and had expected NMR and mass spectra. We note in particular that the mass spectra had the expected isotope ratios for the molecular ions. There was one

Scheme 1



Scheme 1 (continued)



interesting aspect to the ^1H NMR spectra. As expected, **D-B-D** dumbbells show only one peak for the two methoxy groups of **B**. **D-BAB-D** and **D-BABAB-D**, however, show more methoxy peaks than the number expected for symmetrical molecules. For example, **D-BAB-D** dumbbells in CDCl_3 show one sharp singlet (6 protons) and two overlapping singlets (6 protons) instead of the expected two peaks. In deuterated dimethyl sulfoxide a similar, but less well-resolved, pattern is observed. Upon heating the **D-BAB-D** samples in $\text{DMSO}-d_6$ to higher temperatures, coalescence of the doublet is observed and the peak sharpens. A very similar pattern emerges with **D-BABAB-D** dumbbells as the $\text{DMSO}-d_6$ spectrum shows one sharp singlet (6 protons), and two (6 protons each) overlapping peaks that look like singlets undergoing initial coalescence.

These observations indicate the nonequivalence of certain methoxy groups next to **A** moieties. Because this phenomenon is not present in **D-B-D** molecules it should not be due to the methoxy groups near the dendron, and because higher temperatures equilibrate the signals it is proposed that the nonequivalence arises from rotamers that slowly interconvert at room temperature.¹⁶ It is proposed that **D-BAB-D** exists in two conformations. Twisting about the bond connecting **A** and **B** leads to one conformation in which the inner methoxys are on the same side of the diimide (Z), and one in which they are on opposite sides of the diimide (E). These two conformations give rise to the additional NMR signals

because of the hindered rotation around the carbon and imide–nitrogen bond due to the close proximity of the methoxy group on the 3' position of **B** to the imide–oxygen on **A**. The rotation around carbon–amide–nitrogen bonds and the carbon–carbon bonds between the phenyl rings is fast, and therefore the “outer” methoxys have no affect on the “inner” methoxy signals. If it is assumed that E and Z are present in nearly equal amounts, this explains why **D-BAB-D** has three signals: one for the “outer” methoxy groups next to dendrimers (6 protons), one for the “inner” methoxy groups of the E configuration (3 protons), and one for the “inner” methoxy groups of the Z configuration (3 protons).

Electrochemistry. Initial studies demonstrated that the dumbbells could be reduced in DMF solvent to give stable anion radicals and dianions as expected. Each of the reductions used one electron per **A** group. Cyclic voltammetric studies were performed on about 1-mM solutions in degassed DMF/ Bu_4NBF_4 using a glassy carbon disk or a carbon fiber microelectrode. Once cleaned, these electrodes gave reproducible data throughout a series of scans without further cleaning. In contrast, a platinum working electrode gave distorted peaks and evidence that the dumbbells were adsorbing strongly to the surface. A silver wire was the reference electrode, but all potentials were calibrated to the ferrocene/ferrocenium couple from ferrocene present in the solution. The apparent E° was the same within

Table 1. Dumbbell Diffusion Coefficients^a

cmpd	D_d (10 ⁷ cm ² /s)	cmpd	D_d (10 ⁷ cm ² /s)	cmpd	D_d (10 ⁷ cm ² /s)
D1-A-D1	25 (31)	D1-BAB-G1	24 (24)		
D2-A-D2	19 (20)	D2-BAB-G2	18 (17)	D2-BABAB-D2	16 (15)
D3-A-D3	12 (17)	D3-BAB-G3	13 (14)	D3-BABAB-D3	10 (13)
D4-A-D4	8 (12)	D4-BAB-G4	7 (11)	D4-BABAB-D4	5 (10)

^a Experimental and (calculated) D_d values.

Table 2. Heterogeneous Rate Constants for Dumbbell Reduction

cmpd	k (10 ³ cm/s)	cmpd	k (10 ³ cm/s)	cmpd	k (10 ³ cm/s)
D3-A-D3	5	D3-BAB-D3	10	D3-BABAB-D3	11
D4-A-D4	0.7	D4-BAB-D4	1.7	D4-BABAB-D4	6.5

experimental error for the first reduction potential of all the dumbbells. As expected from previous studies of redox sites in poly(benzyl ether) dendrimers^{4,5,9,13} there was no effect on the E° by the dendrons. Within experimental error each compound had $E^\circ = -0.96$ V vs ferrocene/ferrocenium. The following then focuses on dumbbell diffusion coefficients and the rates of reduction, which were sensitive to molecular architecture. Only the first reduction process was studied in detail. When the first process was quasi-reversible the second reduction peak also broadened and it became difficult to measure the peak potential.

At slow sweep rates many of the dumbbells gave reversible voltammograms with peak separations of about 65 mV and equal anodic and cathodic currents for both reduction processes. The diffusion coefficients D_d (Table 1) were measured using the voltammetric peak currents. **Dn-BABAB-Dn** currents were corrected for the coulometric fact of two electrons per molecule. In these molecules the **A** groups (separated by **B** groups) are noninteracting as previously shown by ESR and electrochemical studies.³ The D_d values were consistent with those obtained from linear sweep voltammetry, from chronocoulometry and from comparison of the diffusion current with that of ferrocene on a microelectrode.¹⁷ For example, chronocoulometric measurements gave values within 15% of those from CV for each of the four compounds tested, and microelectrode measurements on five compounds gave values within experimental error of the values reported in Table 1. Table 1 makes it clear that the larger the dendrimer or the longer the rod, the smaller is D_d . This is expected and the data form a qualitatively self-consistent set. Furthermore, we can compare the D_d for **D3-A-D3** (1.2×10^{-6} cm²/s) to that for **D3-methyl viologen²⁺-D3** (3×10^{-6} cm²/s).¹³ These compounds are quite similar in size and if one corrects for the difference in solvent viscosity between acetonitrile and DMF the values are in good agreement.

Because the hydrodynamic radii of poly(benzyl ether) dendrons have been estimated,^{2c} and the rigid rods have lengths estimable from molecular models, it was possible to estimate the size of the dumbbells and use this to calculate the diffusion coefficients. To do this we could not reasonably use the Stokes–Einstein equation for diffusion of spherical objects. Even **D4-A-D4** should have a long dimension nearly twice that of its short dimension, and longer rods, especially with smaller dendrons, will be even less spherical. The diffusion equation for prolate ellipsoids¹⁸ (eq 1) with input of a , the long axis radius, and ρ , the ratio of short to long radii, was used to estimate diffusion coefficients in DMF (tetrabutylammonium fluoroborate), which has a viscos-

ity, η , of about 0.88 pa.¹⁹ The dimensions for dendrons (assumed to be spherical) were estimated for **D1** (0.5 nm) and taken from the literature^{2c} for **D2** (0.8 nm), **D3** (1.0 nm), and **D4** (1.4 nm). The rod lengths were **A** (0.9 nm), **BAB** (2.7 nm), and **BABAB** (4.4 nm). The width of **A** was taken as 0.8 nm. The results (Table 1) show remarkable agreement with the experimental results, especially considering that the calculation assumes a rigid cigar-shaped object and the dumbbells are slim rigid rods between nonrigid fuzzy balls.

$$D_d = \frac{KT}{6\pi\eta a} \left[\frac{1}{(1 - \rho^2)^{1/2}} \ln \left(\frac{1 + (1 - \rho^2)^{1/2}}{\rho} \right) \right] \quad (1)$$

As the glassy carbon disk electrode sweep rate was increased from 20 mV/s to 2 V/s the peak separation became larger for **D2**, **D3**, and **D4** dumbbells indicating slow electron-transfer kinetics. In each case the apparent E° did not change with sweep rate and the anodic/cathodic peak current ratio remained equal to one within experimental error. Linear sweep voltammetry analysis of the cathodic peak shape was also consistent with slow kinetics. Over this range of sweep rates the ferrocene peak separation was less than 70 mV, indicating that the dumbbell data did not need correction for iR drop. **D2** dumbbells showed slightly increased peak separations above 1.5 V/s, but the data were not considered good enough to extract rate constants. (At 1.5 V/s **D2-A-D2** had a peak separation of 87 mV). In Table 2 are gathered the heterogeneous rate constant (k) values for **D3** and **D4** dumbbells calculated using the Nicholson method²⁰ for analyzing the peak separation changes with sweep rate. In this analysis, n , the number of electrons, was taken as one, even for the **BABAB** dumbbells because each of the reactions is one electron per **A** unit and the reversible separations correspond to 60 mV, not 30 mV, as would be expected for an n -equals-two process. Closely similar k values were measured for a few examples using chronocoulometry. The rate constants were reproducible within 20% from experiment to experiment using freshly made solutions.

As expected, larger dendrons gave slower rates. **D2** dumbbells gave detectable inhibition, **D3** dumbbells were more inhibited and the **D4** dumbbells gave strong indications of inhibition even at slow sweep rates. We were concerned that adsorption of one molecule would inhibit the reduction of others, especially for larger polymers. We checked this possibility by reducing small dumbbells in the presence of large dendrons, e.g., **D1-A-D1** in the presence of **D4-Br**. There was no inhibition, and so we conclude that adsorptive inhibition of this

type was not a significant problem in this case. Using **D4-CO₂Me** in 10, 20, 30, or 40-fold excess in the presence of **D3-BAB-D3** (0.8 mM) demonstrated visibly large effects on the solution viscosity, and substantial effects on the diffusion coefficient of the dumbbell, but only small effects (k diminished by less than one-half) on the rate of dumbbell reduction.

Three mechanisms can be considered for dendron inhibition. In one, the dendrons fold back and encapsulate the **A** group to some extent, screening **A** from the electrode. In the second mechanism, the dendrons, even when remote from **A**, prevent the rigid rod containing **A** from easily reaching the electrode surface (imagine the dumbbell parallel to the electrode surface with the slim, rigid rod held away from the surface by the dendrons). And in the third possibility, slow molecular rotation to orient the dumbbells at the electrode surface contributes to the slow rates. The dumbbells have approximate cylindrical symmetry and the slow molecular rotation would be end-to-end. When a molecule presented a dendron to the surface with the rod length perpendicular to the surface it might have to reorient to get the electrophore nearer the surface. This process could be slow, but considering molecules with longer rods have faster rates than equivalent ones with short rods this third argument seems not to be a determining factor.

Consider now "folding back" as an explanation for the difference between short and long rods with the same dendrons attached, for example, the relative rates for **D4-A-D4** (0.7×10^{-3} cm/s), **D4-BAB-D4** (1.7×10^{-3} cm/s), and **D4-BABAB-D4** (6.5×10^{-3} cm/s). In **D4-A-D4**, which is slowest of the three, **A** is separated from each of the two dendrons by only one methylene group, and the dendritic chains can both fold back to cover **A**. In **D4-BAB-D4** the **A** is separated from the two dendrons by a **B** unit, which is nearly 1 nm long and an amide linkage. Thus, the **A** groups cannot be well covered by dendritic chains that fold back on the rod, and the rate is faster. In **D4-BABAB-D4** each electrophore **A** is spaced apart from only one dendron by a **B** group and the rate is again faster. However, on the basis of the folding back mechanism one might have expected larger differences between these rates and we suggest that mechanism two, in which the dendrons hold the rigid rod away from the surface, is important.

This inhibition from the rigid rod dumbbells can be compared with that for dumbbells with more flexible rods. Neither **D3-oligothiophene-D3**⁴ molecules, when the oligothiophene has five thiophenes, nor **D3-oligo(thienylenevinylene)-D3**⁵ with four thiophenes and five vinyls, show inhibition. Extended to be linear these rods would be of a length intermediate between those of **A** and **BAB**. Considering both **D3-A-D3** and **D3-BAB-D3** give slow electron transfer it seems clear that the more flexible rods that have the electrophore extending all along the rod give faster electrochemistry than our rigid rods. It could be interpreted that the flexible rods can have easier access to the electrode by making the chain nonlinear, thus allowing the dendrons to be away from the surface. This is not easy for the rigid rod examples studied here.

Also quite fast is the reduction of the viologen-flanked-with-poly(benzyl ether) dendrons, **D3-MV²⁺-D3**,¹³ in acetonitrile. Although the voltammograms are distorted by adsorption of the product it is indicated that the first reduction peak is "Nernstian" at scan rates up to 10 V/s. The voltammetric shape was not analyzed to give a rate constant, but it seems that the heterogeneous rate is as high as, or higher than, that of **D3-A-D3**.

To vary the electroactive group and to make comparison with porphyrins modified with dendrimers, we studied the disubstituted zinc porphyrin **D3-Zn-D3**. Here the dendrons are directly attached to the porphyrin, without the intervening methylene of **D3-A-D3** or amide of **D3-BAB-D3**. Electrochemically, this compound had a diffusion coefficient of 1.3×10^{-6} cm²/s, which is similar to that for **D3-A-D3**. The k value was estimated at 1×10^{-2} cm/s, a value similar to that for **D3-A-D3** (0.5×10^{-2} cm/s). This suggests that the porphyrin and **A** have similar access to the electrode.

Consider now the observations⁹ previously reported on the same zinc porphyrin tetrasubstituted with the same **D3** dendrons in the same solvent, DMF. Although the electrochemical reduction was not studied extensively the voltammogram shows no evidence for reversibility. This could come from very slow electron transfer and that would be consistent with our results. However, since the return anodic peak did not correspond in size or shape to the cathodic one it is also quite possible that the reduction product was not stable or adsorption played a significant role. No coulometric, spectroscopic, or sweep rate studies were reported to examine that possibility. Thus, we are unsure whether the four dendrons give larger inhibition than two.

Comparison can also be made to a "G_n-Flex" compound of Gorman.¹⁰ These compounds have iron–sulfur cores and four benzyl ether dendrons of a type slightly different from the Frechet type. The core was attached to the dendrons with a short, flexible chain. Although **G4-Flex** was irreversible (no reverse peak), **G3-Flex** gave voltammograms from which a rate constant 0.8×10^{-3} cm/s could be calculated. **D3-A-D3** has a rate constant in the same range, but six times larger. It seems reasonable that the four dendrons would inhibit the rate more than two and so the data are consistent.

Summarizing all of these data one can conclude that for the compounds composed of a redox center attached to two or four dendrons of flexible poly(benzyl ether) type the electrochemical reaction rates are relatively fast for **D1** and **D2** dendrons, but can be slowed for **D3**. The **D3** compounds have relative rates that can be rationalized in terms of the extent to which the electrophore has access to the electrode. **D4** compounds are also slow, but interpretation is often complicated by complete irreversibility, which could come from effects other than slow electron transfer.

Acknowledgment. Help from Professors T. Lodge and J. Frechet with estimation of molecular dimensions, and financial support from the National Science Foundation are acknowledged.