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# The Effect of Macromolecular Architecture in Nanomaterials: A Comparison of Site Isolation in Porphyrin Core Dendrimers and Their Isomeric Linear Analogues

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***Abstract:*** The influence of macromolecular architecture on the physical properties of polymeric materials has been studied by comparing poly(benzyl ether) dendrons with their exact linear analogues. The results clearly confirm the anticipation that dendrimers are unique when compared to other architectures. Physical properties, from hydrodynamic volume to crystallinity, were shown to be different, and in a comparative study of core encapsulation in macromolecules of different architecture, energy transduction from the polymer backbone to a porphyrin core was shown to be different for dendrimers as compared to that of isomeric four- or eight-arm star polymers. Fluorescence excitation revealed strong, morphology dependent intramolecular energy transfer in the three macromolecular isomers investigated. Even at high generations, the dendrimers exhibited the most efficient energy transfer, thereby indicating that the dendritic architecture affords superior site isolation to the central porphyrin it surrounds.

## Introduction

The controlled preparation of functionalized nanoscale materials has rapidly become a vigorous research topic due to their application as active components in advanced materials.[1−4] In surveying materials for the growing needs of nanotechnology, a range of different macromolecular architectures has been developed in recent years to meet this demand. These include shell cross-linked nanoparticles,[5] hyperbranched macromolecules,[6] dendrimers,[7] etc. The latter have received particular attention due to their unique structural features including the following: (i) their regularly layered and symmetrically branched three-dimensional architecture, (ii) their near-perfect monodisperse nature, and (iii) their accurately controlled placement of functionalities.[8] Such features, not found in other synthetic polymers, have spurred rapid growth of the field of dendrimer research, largely based on the assumption that inherent differences in architecture can lead to a range of new and improved properties for dendrimers when compared to more traditional polymers.

While a number of studies have addressed the effect of macromolecular architecture on physical and chemical properties,[9] comparative studies involving different macromolecular

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architectures[10,11] have seldom been performed, mainly due to the synthetic difficulties intrinsic to the preparation of molecular structures sufficiently similar to enable comparisons between dendrimers and their architectural isomers.[11−13] In this paper, we report on the synthesis and characterization of monodisperse architectural isomers of poly(benzyl ethers) dendrons and dendrimers with a porphyrin core, ranging from exact linear analogues to four- and eight-arm star polymers also containing a central porphyrin. In an effort to fully understand the steric environment and encapsulation behavior of these architectural isomers, a detailed investigation into intramolecular energy transfer involving the polymer backbone is presented and the results related to previously reported morphology and antenna effects in porphyrin-core dendrimers of the poly(benzyl ether) type.[14]

## Experimental Section

**General Methods.** Tetrakis(3,5-dimethoxyphenyl)porphyrin, **24**,[15] and tetrakis(4-methoxyphenyl)porphyrin, **25,**[16] were prepared from pyrrole and the respective aromatic aldehydes using Adler−Longo condensation conditions.[17] Tetrakis(4-hydroxy-phenyl)porphyrin (THPP) and tetrakis(3,5-dihydroxyphenyl)porphyrin[18] (TDHPP) were prepared by boron tribromide deprotection[19] of **25** and **24**, respectively. 3,5-Dimethoxybenzyl methyl ether **22** was prepared as described in the literature.[20] Column chromatography was carried out with Merck silica gel for flash columns, 230−400 mesh. NMR spectra were recorded on a Bruker AM 200 (200 MHz) spectrometer with the residual protonated solvent peak as internal standard. GPC was carried out on a Waters chromatograph connected to a Waters 410 differential refractometer with THF as the carrier solvent. Absorption spectra were recorded in degassed THF solution (containing no stabilizers) on a Cary 50 UV−visible spectrophotometer. Fluorescence spectra were measured of degassed solutions (1 cm cells, $OD_{max} < 0.2$) using an ISA/SPEX Fluorolog 3.22 equipped with a 450 W Xe lamp, double excitation and double emission monochromators, and a digital photon-counting photomultiplier. Excitation spectra of compounds **19b−d**, **20b−d**, and **21b−d** were acquired at $\lambda_{em} = 653$ nm with slit widths set to 2 nm band-pass for both excitation and emission. Emission spectra of model compounds **22** and **23** were measured at $\lambda_{exc} = 280$ nm and $\lambda_{exc} = 258$ nm, respectively, and slit widths were set to 2 nm band-pass for excitation as well as 4 nm band-pass for emission. Correction for variations in lamp intensity over time and wavelength was achieved with a solid-state silicon photodiode as the reference. The spectra were further corrected for variations in photomultiplier response over wavelength and for the path difference between the sample and the reference by multiplication with emission correction curves generated on the instrument. The energy transfer efficiencies for compounds **19b−d**, **20b−d**, and **21b−d** were calculated from the ratio of the integrated donor excitation and absorption spectra normalized at the acceptor Soret band.

**Nomenclature.** The nomenclature used for the linear macromolecules is as follows: X-[*n*]-Y, where X describes the functional group at the one chain end, either P for phenacyl ether or HO for phenol; *n* is the number of repeat units; and Y describes the functional group at the other chain end, either hydroxymethyl, OH, or bromomethyl, Br. Dendritic porphyrins are denoted as D-[G-*n*]$_8$Por, where D indicates a dendritic framework, *n* gives its generation ($n = 1-4$), while the particular substituent number identifies the porphyrin core moiety (Por). Similarly, for the linear and branched analogues, L-[G-*n*]$_4$Por and L-[G-*n*]$_8$Por will denote linear and branched architectures about their porphyrin cores ($n = 2-5$ and $1-4$, respectively). Note that the first generation linear and dendritic substituents are identical. For this reason, no linear analogue for D-[G-1]$_8$Por was prepared.

**General Procedure for Bromination. 3-Benzyloxy-5-phenacyloxybenzyl Bromide, 4.** To a solution of the alcohol **3**[13] (32.0 g, 132 mmol) in tetrahydrofuran (80 mL) was added carbon tetrabromide (54.9 g, 165 mmol) followed by the portion-wise addition of triphenylphosphine (43.3 g, 165 mmol). The reaction was quenched immediately with 40 mL of water after the slightly yellow clear solution changed to a deep yellow-green suspension in ca. 5 min. THF was evaporated, and dichloromethane (400 mL) and water (150 mL) were added. The organic layer was dried with $MgSO_4$ and evaporated to dryness. The crude product was purified by flash chromatography eluting with 8:1 dichloromethane/hexane to give the bromide, **4**, as a white solid in 88% yield. mp 101−102 °C. IR: 1685, 1605, 1375, and 1170 cm$^{-1}$. $^1$H NMR ($CDCl_3$): $\delta$ 4.36 (s, 2H, $CH_2Br$), 5.04 (s, 2H, $CH_2O$), 5.23 (s, 2H, $CH_2O$), 6.55, 6.68, 6.72 (each t, 3H, ArH), 7.20−7.35 (m, 8H, PhH), and 8.07 (A of $AB_2$, $J = 9$ Hz, 2H, ArH). $^{13}$C NMR ($CDCl_3$): $\delta$ 33.34, 70.76, 114.87, 115.49, 122.32, 128.14, 128.90, 129.99, 133.98, 134.50, 139.35, 158.20, 194.10. Anal. Calcd for $C_{22}H_{19}BrO_3$: C, 64.25; H, 4.66. Found: C, 64.4; H, 4.93.

**General Procedure for Alkylation. P-[2]-OH, 5.** To a solution of the bromide **4** (12.5 g, 20 mmol) and 3-benzyloxy-5-hydroxybenzyl alcohol,[13] **1** (8.64 g, 19.5 mmol), in acetone (200 mL) were added potassium carbonate (7.9 g) and 18-crown-6 (70 mg). The reaction mixture was then heated at reflux under nitrogen for 16 h, filtered, and evaporated to dryness. The crude product was partitioned between water (200 mL) and dichloromethane (200 mL), the aqueous layer was extracted with dichloromethane (2 × 100 mL), and the combined extracts were dried and evaporated to dryness. Purification by flash chromatography eluting with dichloromethane, gradually increasing to 1:4 ether/dichloromethane gave the alcohol, **5**, as a colorless oil (yield 87%). IR: 3400−3100, 1690, 1600, 1380, and 1165 cm$^{-1}$. $^1$H NMR ($CDCl_3$): $\delta$ 1.80 (br s, 1H, OH), 4.59 (s, 2H, $CH_2OH$), 5.04, 5.08 (each s, 6H, $CH_2O$), 5.27 (s, 2H, $COCH_2$), 6.47−6.68 (complex m, 6H, ArH), 7.29−7.60 (complex m, 13H, PhH), and 7.94 (A of $AB_2$, $J = 7$ Hz, 2H, PhHCO). $^{13}$C NMR ($CDCl_3$): $\delta$ 53.45, 65.27, 69.81, 70.07, 70.18, 70.74, 101.35, 101.64, 105.71, 105.87, 106.08, 106.97, 125.19, 127.54, 127.62, 128.01, 128.11, 128.61, 128.87, 133.93, 134.50, 136.66, 136.84,


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139.52, 143.51, 159.33, 159.97, 160.15, 160.21, 194.21. Anal. Calcd for $C_{36}H_{32}O_6$: C, 77.1; H, 5.76. Found: C, 76.8; H, 5.80.

**General Procedure for Deprotection of the Phenacyl Protecting Group. HO-[2]-OH, 6.** The phenacyl ether, **5** (42.0 g, 75 mmol), was dissolved in tetrahydrofuran (70 mL) and acetic acid (200 mL). To this solution was added zinc dust (40 g, 640 mmol) portion-wise, and the solution was stirred vigorously overnight under argon. The reaction mixture was filtered and evaporated to dryness with the acetic acid being removed by several azeotropes with toluene. The crude product was purified by flash chromatography eluting with dichloromethane, gradually increasing to 1:3 ether/dichloromethane to obtain the deprotected alcohol, **6**, as a white solid in 88% yield. IR: 3400−3100, 1690, 1600, 1380, and 1165 $cm^{-1}$. $^1H$ NMR ($CDCl_3$): $\delta$ 4.55 (s, 2H, $CH_2OH$), 4.95, 4.99, 5.01 (each s, 2H, $CH_2O$), 6.70−6.90, 7.12−7.24 (each m, 16H, ArH). $^{13}C$ NMR ($CDCl_3$): $\delta$ 65.07, 65.97, 69.66, 113.42, 114.33, 114.38, 115.07, 119.41, 119.66, 129.68, 138.63, 142.05, 156.09, 158.85. Anal. Calcd for $C_{28}H_{26}O_5$: C, 76.0; H, 5.92. Found: C, 76.1; H, 5.67.

**P-[2]-Br, 7.** This compound was prepared from the alcohol **5** according to the general procedure with carbon tetrabromide and triphenylphosphine in THF. The crude product was purified by flash chromatography eluting with 5:1 dichloromethane/hexane to give the bromide, **7**, as a white solid in 84% yield. mp 105−106 °C. IR: 1680, 1605, 1380, and 1180 $cm^{-1}$. $^1H$ NMR ($CDCl_3$): $\delta$ 4.39 (s, 2H, $CH_2Br$), 4.94, 5.00, 5.01 (each s, 6H, $CH_2O$), 5.24 (s, 2H, $COCH_2$), 6.50−6.63 (complex m, ArH), 7.33−7.51 (complex m, 13H, PhH), 7.96 (A of $AB_2$, $J$ = 10 Hz, 2H, PhHCO). $^{13}C$ NMR ($CDCl_3$): $\delta$ 33.59, 69.91, 70.16, 101.72, 102.20, 106.13, 107.01, 108.14, 108.29, 127.60, 128.11, 128.63, 128.87, 133.93, 134.52, 136.61, 139.26, 139.79, 159.37, 159.89, 160.07, 160.23, 194.09. Anal. Calcd for $C_{36}H_{31}BrO_5$: C, 69.3; H, 5.01. Found: C, 69.1; H, 5.22.

**P-[4]-OH, 8.** This compound was prepared from the bromide **7** and the monophenol **6**, according to the general procedure for alkylation with potassium carbonate and 18-crown-6 in acetone. The reaction mixture was evaporated to dryness, and the crude product was partitioned between water (200 mL) and dichloromethane (200 mL); the organic layer was dried with $MgSO_4$ and evaporated to dryness. The crude product was purified by flash chromatography eluting with dichloromethane to give **8** as colorless crystals (96% yield). IR: 3300−3100, 1710, 1685, 1605, 1380, and 1165 $cm^{-1}$. $^1H$ NMR ($CDCl_3$): $\delta$ 1.69 (br s, 1H, $CH_2OH$), 4.51 (s, 2H, $CH_2OH$), 4.86 (s, 6H, $ArCH_2OAr$), 4.93 (s, 8H, $PhCH_2O$), 5.14 (s, 2H, $COCH_2O$), 6.44−6.58 (complex m, 12H, ArH), 7.22−7.42 (complex m, 23H, PhH), 7.86 (A of $AB_2$, $J$ = 10 Hz, 2H, PhHCO). $^{13}C$ NMR ($CDCl_3$): $\delta$ 65.27, 69.93, 70.00, 70.07, 70.13, 70.18, 70.74, 101.31, 101.62, 101.68, 105.73, 105.80, 106.15, 106.32, 106.43, 106.51, 107.01, 127.53, 127.60, 128.03, 128.11, 128.61, 128.86, 133.91, 134.52, 136.67, 136.78, 136.85, 139.29, 139.35, 139.44, 143.52, 159.34, 160.01, 160.07, 160.17, 160.21, 160.33, 194.13. Anal. Calcd for $C_{64}H_{56}O_{10}$: C, 78.0; H, 5.73. Found: C, 77.8; H, 5.89.

**P-[4]-Br, 26.** This compound was prepared from the alcohol **8** according to the general procedure for bromination with 2.5 equiv of carbon tetrabromide and 2.5 equiv of triphenylphosphine. The crude product was purified by flash chromatography eluting with 5:1 dichloromethane/hexane, gradually increasing to dichloromethane to give the bromide, **26**, as a colorless solid in 91% yield. mp 110−112 °C. IR: 1680, 1605, 1380, and 1180 $cm^{-1}$. $^1H$ NMR ($CDCl_3$): $\delta$ 4.39 (s, 2H, $CH_2Br$), 4.51 (s, 2H, $CH_2OH$), 4.95 (s, 6H, $ArCH_2OAr$), 5.00 (s, 8H, $PhCH_2O$), 5.28 (s, 2H, $COCH_2OH$), 6.53−6.66 (complex m, 12H, ArH), 7.32−7.47 (complex m, 23H, PhH), 7.96 (A of $AB_2$, $J$ = 10 Hz, 2H, PhHCO). $^{13}C$ NMR ($CDCl_3$): $\delta$ 33.63, 69.90, 70.03, 70.15, 70.76, 101.67, 102.22, 106.15, 106.37, 106.51, 107.01, 108.16, 108.26, 127.59, 128.05, 128.11, 128.62, 128.87, 133.90, 134.53, 136.62, 136.67, 136.78, 139.10, 139.26, 139.45, 139.80, 159.36, 159.98, 160.02, 160.09, 160.19, 194.09. Anal. Calcd for $C_{64}H_{55}BrO_9$: C, 73.3; H, 5.29. Found: C, 73.1; H, 5.15.

**HO-[4]-OH, 14.** This compound was prepared from **8** according to the general procedure for deprotection with Zn dust and acetic acid in THF. Because the remaining product is very crystalline, the Zn was filtered off and washed with hot THF. The filtrate was evaporated to dryness with the acetic acid being removed by several azeotropes with toluene. The crude product was precipitated out of ether to give a white crystalline product, **14**, in 90% yield. mp 122−124 °C. IR: 3500−3100, 1600, 1375, and 1175 $cm^{-1}$. $^1H$ NMR ($CDCl_3$): $\delta$ 4.55 (s, 2H, $CH_2OH$), 4.69−4.98 (complex m, 14H, $CH_2O$), 6.37−6.66 (complex m, 12H, ArH), 7.24−7.41 (complex m, 20H, PhH). $^{13}C$ NMR ($CDCl_3$): $\delta$ 65.21, 69.76, 69.91, 70.04, 70.06, 70.11, 101.46, 101.85, 105.81, 105.93, 106.05, 106.31, 106.40, 106.47, 107.02, 126.96, 127.63, 128.04, 128.61, 136.75, 139.31, 139.47, 143.15, 157.21, 159.99, 160.12, 160.28, 160.12. Anal. Calcd for $C_{56}H_{50}O_9$: C, 73.6; H, 5.81. Found: C, 73.5; H, 5.72.

**L-[G-2]-OH, 12.** This compound was prepared from **6** and **11** according to the general procedure for alkylation with potassium carbonate and 18-crown-6 in acetone. The crude product was purified by flash chromatography eluting with dichloromethane, gradually increasing to 5% diethyl ether/dichloromethane to give the exact linear analogue of the dendrimer, L-[G-2]-OH, **12**, as a colorless solid in 91% yield. mp 126−127 °C. IR: 3300−3100, 1600, 1380, and 1170 $cm^{-1}$. $^1H$ NMR ($CDCl_3$): $\delta$ 1.73 (br s, 1H, $CH_2O\mathit{H}$), 4.60 (s, 2H, $C\mathit{H}_2OH$), 4.96 (s, 4H, $ArC\mathit{H}_2OAr$), 5.02 (s, 8H, $PhC\mathit{H}_2O$), 6.53−6.68 (complex m, 9H, $Ar\mathit{H}$), 7.31−7.43 (complex m, 20H, PhH). $^{13}C$ NMR ($CDCl_3$): $\delta$ 65.29, 69.95, 70.02, 70.10, 70.14, 101.34, 101.61, 105.73, 105.8, 106.41, 127.56, 127.61, 128.05, 128.63, 136.80, 136.86, 130.28, 139.35, 143.15, 168.09, 160.18. Anal. Calcd for $C_{49}H_{44}O_7$: C, 79.0; H, 5.95. Found: C, 79.2; H, 6.17.

**L-[G-2]-Br, 13.** This compound was prepared from **12** according to the general procedure for bromination with 3 equiv of carbon tetrabromide and 3 equiv of triphenylphosphine. The crude product was purified by flash chromatography eluting with 9:1 dichloromethane/hexane, gradually increasing to dichloromethane to give the bromide, **13**, as a colorless solid in 88% yield. mp 102−103 °C. IR: 1600, 1375, and 1175 $cm^{-1}$. $^1H$ NMR ($CDCl_3$): $\delta$ 4.42 (s, 2H, $CH_2Br$), 4.98, 5.00 (each s, 4H, $ArCH_2OAr$), 5.04, 5.06 (each s, 8H, $PhCH_2O$), (each s, 8H, $PhCH_2O$), 6.57−6.73 (complex m, 9H, ArH), 7.11−7.47 (complex m, 20H, PhH). $^{13}C$ NMR ($CDCl_3$): $\delta$ 33.68, 70.07, 70.18, 101.67, 101.71, 102.27, 106.45, 106.53, 108.21, 108.31, 127.64, 128.09, 128.14, 128.32, 128.67, 136.86, 139.16, 139.31, 139.86, 160.04, 160.14, 160.25. Anal. Calcd for $C_{49}H_{44}BrO_6$: C, 72.9; H, 5.37. Found: C, 73.2; H, 5.43.

**L-[G-3]-OH, 15.** This compound was prepared from **13** and **14** according to the general procedure for alkylation with potassium carbonate and 18-crown-6 in acetone. The crude product was purified by flash chromatography eluting with dichloromethane, gradually increasing to 5% diethyl ether/dichloromethane to give the alcohol, **15**, in 93% yield as a colorless solid. mp 128−129 °C. IR: 3300−3100, 1605, 1375, and 1170 $cm^{-1}$. $^1H$ NMR ($CDCl_3$): $\delta$ 1.70 (t, 1H, $CH_2OH$), 4.42 (d, $J$ = 5.7 Hz, 2H, $CH_2OH$), 4.82 (s, 12H, $ArCH_2OAr$), 4.88 (s, 16H, $PhCH_2O$), 6.40−6.56 (complex m, 21H, ArH), 7.16−7.35 (complex m, 40H, PhH). $^{13}C$ NMR ($CDCl_3$): $\delta$ 65.24, 70.04, 70.14, 101.33, 101.66, 105.71, 105.79, 106.44, 106.53, 127.64, 128.65, 136.83, 136.90, 139.34, 139.40, 143.59, 160.12, 160.21. Anal. Calcd for $C_{105}H_{92}O_{15}$: C, 79.1; H, 5.82. Found: C, 78.9; H, 6.05.

**P-[8]-OH, 9.** This compound was prepared from **14** and **26** according to the general procedure for alkylation with potassium carbonate and 18-crown-6 in acetone. Because the product is moderately insoluble in acetone, the addition of more solvent was required during the reaction as necessary. The reaction mixture was evaporated to dryness and the crude product partitioned between dichloromethane and water. The organic phase was dried with $MgSO_4$, and the protected alcohol, **9**, was purified by precipitation out of diethyl ether (yield: 96%). mp 132−134 °C. IR: 3300−3100, 1680, 1605, 1380, and 1165 $cm^{-1}$. $^1H$ NMR ($CDCl_3$): $\delta$ 1.69 (br s, 1H, $CH_2OH$), 4.51 (s, 2H, $CH_2OH$), 4.85

(s, 12H, $ArCH_2OAr$), 4.92 (s, 16H, $PhCH_2O$), 5.18 (s, 2H, $COCH_2O$), 6.40−6.56 (complex m, 24H, ArH), 7.25−7.42 (complex m, 48H, PhH), 7.86 (A of $AB_2$, $J = 10$ Hz, 2H, PhCO). $^{13}C$ NMR ($CDCl_3$): $\delta$ 65.25, 70.00, 70.11, 101.29, 101.62, 105.69, 105.77, 106.13, 106.36, 106.48, 107.01, 127.59, 128.03, 128.10, 128.60, 128.85, 133.89, 134.50, 136.67, 136.78, 139.27, 139.43, 143.53, 159.34, 160.01, 160.17, 194.08. Anal. Calcd for $C_{120}H_{104}O_{18}$: C, 78.6; H, 5.72. Found: C, 78.9; H, 5.55.

**P-[8]-Br, 28.** This compound was prepared from **9** according to the general procedure for bromination with 1.5 equiv of carbon tetrabromide and 1.5 equiv of triphenylphosphine. The crude product was purified by flash chromatography eluting with hexane, gradually increasing to pure 2.5% diethyl ether/dichloromethane. The bromide, **28**, was obtained as a colorless solid in 91% yield. mp 135−136 °C. IR: 1685, 1605, 1380, and 1180 $cm^{-1}$. $^1H$ NMR ($CDCl_3$): $\delta$ 4.38 (s, 2H, $CH_2Br$), 4.86 (s, 12H, $ArCH_2OAr$), 5.00 (s, 16H, $PhCH_2O$), 5.21 (s, 2H, $COCH_2O$), 6.52−6.67 (complex m, 24H, ArH), 7.29−7.46 (complex m, 48H, PhH), 7.96 (A of $AB_2$, $J = 10$ Hz, 2H, PhHCO). $^{13}C$ NMR ($CDCl_3$): $\delta$ 33.64, 69.89, 70.02, 70.13, 70.73, 101.64, 102.22, 106.15, 106.38, 106.49, 107.02, 108.16, 108.26, 127.60, 128.04, 128.18, 128.61, 128.86, 128.90, 134.53, 136.63, 136.68, 136.79, 139.11, 139.27, 139.45, 139.81, 159.93, 160.02, 160.10, 106.18, 194.08. Anal. Calcd for $C_{120}H_{103}BrO_{17}$: C, 76.0; H, 5.47. Found: C, 76.2; H, 5.45.

**HO-[8]-OH, 16.** This compound was prepared from **9** according to the general procedure for deprotection with Zn dust and acetic acid in THF. Because the material is very crystalline, the Zn was filtered off and washed with hot THF. The filtrate was evaporated to dryness with the acetic acid being removed by several azeotropes with toluene. The crude product was precipitated out of ether to give **16** as a white crystalline product in 90% yield. mp 136−138 °C. IR: 3500−3100, 1605, 1370, and 1175 $cm^{-1}$. $^1H$ NMR ($CDCl_3$): $\delta$ 4.56 (s, 2H, $CH_2OH$), 4.88−5.00 (complex m, 30H, $CH_2O$), 5.7 (br s, 1H, ArOH), 6.37, 6.41 (s, 2H, ArHOH), 6.52−6.66 (complex m, 22H, ArH), 7.27−7.42 (complex m, 40H, PhH). $^{13}C$ NMR ($CDCl_3$): $\delta$ 69.74, 70.02, 70.13, 101.38, 101.67, 101.83, 105.74, 105.85, 106.05, 106.52, 106.99, 127.56, 127.62, 128.05, 128.61, 136.78, 139.50, 143.37, 157.19, 160.06, 160.16, 160.30. Anal. Calcd for $C_{112}H_{98}O_{17}$: C, 78.4; H, 5.76. Found: C, 78.4; H, 5.93.

**L-[G-3]-Br, 29.** This compound was prepared from **15** according to the general procedure for bromination employing 2 × 1.5 equiv of carbon tetrabromide and 2 × 1.5 equiv of triphenylphosphine. The crude product was purified by flash chromatography eluting with hexane, gradually increasing to dichloromethane to give the bromomethyl derivative, **29**, as a colorless solid (yield: 84%). mp 127−129 °C. IR: 1605, 1380, and 1175 $cm^{-1}$. $^1H$ NMR ($CDCl_3$): $\delta$ 4.41 (s, 2H, $CH_2Br$), 4.91−5.04 (complex m, 28H, $CH_2O$), 6.56−6.72 (complex m, 21H, ArH), 7.32−7.51 (complex m, 40H, PhH). $^{13}C$ NMR ($CDCl_3$): $\delta$ 33.71, 70.06, 101.69, 105.27, 106.45, 108.21, 108.32, 127.65, 127.91, 128.67, 136.70, 136.86, 139.17, 139.34, 139.86, 160.03, 160.15, 160.24. Anal. Calcd for $C_{105}H_{91}BrO_{15}$: C, 75.4; H, 5.48. Found: C, 75.2; H, 5.40.

**L-[G-4]-OH, 17.** This compound was prepared from **15** and **16** according to the general procedure for alkylation with potassium carbonate and 18-crown-6, except that a 4:1 mixture of THF/acetone was used as the solvent mixture. The product was purified by flash chromatography eluting with dichloromethane, gradually increasing to 5% diethyl ether/dichloromethane to give the fourth generation linear analogue, **17**, as a colorless solid in 81% yield. mp 142−144 °C. IR: 3300−3100, 1605, 1380, and 1175 $cm^{-1}$. $^1H$ NMR ($CDCl_3$): $\delta$ 4.59 (s, 2H, $CH_2OH$), 4.97 (s, 28H, $ArCH_2OAr$), 5.03 (s, 32H, $PhCH_2O$), 6.58−6.70 (complex m, 45H, ArH), 7.32−7.51 (complex m, 80H, PhH). $^{13}C$ NMR ($CDCl_3$): $\delta$ 53.57, 65.23, 70.05, 70.15, 101.34, 101.68, 105.71, 105.80, 106.45, 106.56, 127.67, 128.67, 136.87, 139.37, 143.68, 160.15, 160.24. Anal. Calcd for $C_{217}H_{188}O_{31}$: C, 79.2; H, 5.76. Found: C, 79.0; H, 5.59.

**P-[16]-OH, 30.** This compound was prepared from **16** and **28** according to the general procedure for alkylation with potassium carbonate and 18-crown-6 in acetone. The crude product was purified by flash chromatography eluting with dichloromethane, gradually increasing to 5% diethyl ether/dichloromethane to give the alcohol, **30**, as a colorless solid in 81% yield. mp 137−138 °C. IR: 3300−3100, 1690, 1600, 1380, and 1170 $cm^{-1}$. $^1H$ NMR ($CDCl_3$): $\delta$ 4.57 (d, $J = 6$ Hz, 2H, $CH_2OH$), 4.94 (s, 33H, $ArCH_2OAr$), 5.08 (s, 32H, $PhCH_2O$), 5.20 (s, 2H, $COCH_2O$), 6.54−6.68 (complex m, 48H, ArH), 7.24−7.59 (complex m, 83H, PhH), 7.95 (A of $AB_2$, $J = 10$ Hz, 2H, PhHCO). $^{13}C$ NMR ($CDCl_3$): $\delta$ 53.51, 65.22, 70.01, 70.12, 101.31, 101.64, 105.69, 105.78, 106.18, 106.40, 106.52, 107.04, 127.12, 127.62, 128.33, 128.63, 128.88, 133.91, 134.53, 136.72, 136.91, 139.32, 139.40, 139.48, 143.63, 159.38, 160.11, 160.20, 194.08. Anal. Calcd for $C_{232}H_{200}O_{34}$: C, 78.9; H, 5.71. Found: C, 79.2; H, 5.88.

**L-[G-4]-Br, 31.** This compound was prepared from the alcohol **17** according to the general procedure for bromination with 4.0 equiv of carbon tetrabromide and 4.0 equiv of triphenylphosphine. The crude product was purified by flash chromatography eluting with hexane, gradually increasing to 5% diethyl ether/dichloromethane to give the bromide, **31**, as a colorless solid in 89% yield. mp 139−141 °C. IR: 1600, 1370, and 1175 $cm^{-1}$. $^1H$ NMR ($CDCl_3$): $\delta$ 4.37 (s, 2H, $CH_2Br$), 4.93 (s, 28H, $ArCH_2OAr$), 5.00 (s, 32H, $PhCH_2O$), 6.50−6.66 (complex m, 45H, ArH), 7.26−7.41 (complex m, 80H, PhH). $^{13}C$ NMR ($CDCl_3$): $\delta$ 33.64, 70.00, 70.11, 101.62, 102.21, 106.49, 108.15, 108.26, 127.59, 128.03, 128.61, 136.63, 136.79, 139.10, 139.80, 159.97, 160.09, 160.18. Anal. Calcd for $C_{217}H_{187}BrO_{30}$: C, 77.7; H, 5.62. Found: C, 78.0; H, 5.61.

**HO-[16]-OH, 32.** This compound was prepared from the alcohol **30** according to the general procedure for deprotection with Zn dust and acetic acid in THF. The crude product was purified by flash chromatography eluting with dichloromethane, gradually increasing to 10% diethyl ether/dichloromethane to give the phenol, **32**, as a colorless solid in 83% yield. mp 140−142 °C. IR: 3400−3100, 1600, 1370, and 1170 $cm^{-1}$. $^1H$ NMR ($CDCl_3$): $\delta$ 4.57 (d, $J = 6$ Hz, 2H, $CH_2OH$), 4.88 (s, 30H, $ArCH_2OAr$), 5.00 (s, 32H, $PhCH_2O$), 5.52 (s, 1H, ArOH), 6.36, 6.37 (each s, 2H, Ar*H*OH), 6.52−6.72 (complex m, 46H, ArH), 7.28−7.49 (complex m, 80H, PhH). $^{13}C$ NMR ($CDCl_3$): $\delta$ 33.62, 69.73, 70.02, 70.13, 101.35, 101.66, 105.73, 105.83, 106.12, 106.42, 106.54, 106.99, 127.63, 128.06, 128.63, 136.81, 139.31, 139.54, 143.49, 157.13, 160.10, 160.19. Anal. Calcd for $C_{224}H_{194}O_{33}$: C, 78.8; H, 5.73. Found: C, 78.7; H, 5.49.

**P-[16]-Br, 33.** This compound was prepared from **30** according to the general procedure from bromination with 5.0 equiv of carbon tetrabromide and 5.0 equiv of triphenylphosphine in THF. The crude product was purified by flash chromatography eluting with 5:1 dichloromethane/hexane, gradually increasing to dichloromethane to give the bromide, **33**, as a colorless solid in 86% yield. mp 143−144 °C. IR: 1680, 1605, 1375, and 1180 $cm^{-1}$. $^1H$ NMR ($CDCl_3$): $\delta$ 4.39 (s, 2H, $CH_2Br$), 4.87 (s, 24H, $ArCH_2OAr$), 5.02 (s, 32H, $PhCH_2O$), 5.21 (s, 2H, $COCH_2O$), 6.50−6.68 (complex m, 24H, ArH), 7.25−7.45 (complex m, 48H, PhH), 7.94 (A of $AB_2$, $J = 10$ Hz, 2H, PhHCO). $^{13}C$ NMR ($CDCl_3$): $\delta$ 33.62, 69.90, 70.02, 70.08, 70.15, 70.70, 101.68, 102.25, 106.10, 106.35, 106.55, 107.08, 108.27, 127.62, 128.04, 128.10, 128.63, 128.90, 134.52, 136.68, 136.82, 139.16, 139.42, 139.85, 159.44, 159.95, 160.04, 160.19, 194.10. Anal. Calcd for $C_{232}H_{199}BrO_{33}$: C, 77.5; H, 5.58. Found: C, 77.7; H, 5.33.

**L-[G-5]-OH, 34.** This compound was prepared from **31** and **32** according to the general procedure for alkylation with potassium carbonate and 18-crown-6 in 4:1 THF/acetone. The crude product was purified by flash chromatography eluting with dichloromethane, gradually increasing to 5% diethyl ether/dichloromethane to give the alcohol, **34**, as a colorless solid in 76% yield. mp 148−150 °C. IR: 3300−3100, 1600, 1375, and 1175 $cm^{-1}$. $^1H$ NMR ($CDCl_3$): $\delta$ 4.61 (s, 2H, $CH_2OH$), 4.97 (s, 56H, $ArCH_2OAr$), 5.04 (s, 66H, $PhCH_2O$), 6.55−6.70 (complex m, 93H, ArH), 7.25−7.53 (complex m, 160H, PhH). $^{13}C$ NMR ($CDCl_3$): $\delta$ 65.34, 70.02, 70.14, 101.38, 101.70, 105.78, 105.86, 106.54, 127.70, 128.14, 128.73, 136.82, 139.33, 143.64, 160.15,

160.15, 160.25. Anal. Calcd for $C_{441}H_{380}O_{63}$: C, 79.2; H, 5.73. Found: C, 79.4; H, 5.87.

**L-[G-5]-Br, 36.** This compound was prepared from **34**, according to the general procedure for bromination with 5.0 equiv of carbon tetrabromide and 5.0 equiv of triphenylphosphine. The crude product was purified by flash chromatography eluting with 9:1 dichloromethane/hexane, gradually increasing to dichloromethane to give the bromide, **36**, as a colorless solid in 81% yield. mp 145−147 °C. IR: 1605, 1375, and 1180 $cm^{-1}$. $^1H$ NMR ($CDCl_3$): $\delta$ 4.39 (s, 2H, $CH_2Br$), 4.94 (s, 60H, $ArCH_2OAr$), 5.05 (s, 64H, $PhCH_2O$), 6.50−6.71 (complex m, 93H, ArH), 7.25−7.45 (complex m, 160H, PhH). $^{13}C$ NMR ($CDCl_3$): $\delta$ 33.7, 69.82, 70.14, 101.56, 102.20, 106.43, 108.20, 127.44, 128.09, 128.55, 136.69, 139.13, 139,91, 160.00, 160.25. Anal. Calcd for $C_{441}H_{379}BrO_{62}$: C, 78.5; H, 5.66. Found: C, 78.7; H, 5.54.

**General Procedure for the Preparation of Porphyrin Cored Dendrimers.** The preparation of these materials was accomplished using the conventional alkylation procedure described above, with two notable exceptions. At higher generations, alkylation in acetone proved to be extremely slow, and so the procedure of Weintraub and Parquette[38] using a mixture of THF and DMF, which is repeatedly evaporated/concentrated, was employed to increase the rate of reaction and dramatically improve yields. In addition, the products were purified by fractional precipitation rather than column chromatography. This was accomplished by dissolving the filtered reaction mixture in a minimal amount of dichloromethane and adding ethyl ether slowly until the product starts to precipitate. The supernatant was poured off, and the process is repeated until no more precipitates. Analysis of the different fractions by GPC permitted the pure fractions to be identified and combined.

**D-[G-1]$_8$Por, 19a.** The first generation benzylic bromide, **11** (1.0 g, 2.6 mmol), was dissolved in acetone (20 mL), followed by the addition of tetrakis(3,5-dihydroxyphenyl)porphyrin, **37** (232 mg, 31 mmol), $K_2CO_3$ (3.0 g, 22 mmol), and 18-crown-6 (50 mg). The mixture was heated at reflux under $N_2$ for 5 days in the dark and purified by fractional precipitation from ethyl ether. This afforded purple crystals of **19a** in 90% yield. $^1H$ NMR (250 MHz, $CDCl_3$): $\delta$ 4.88 (s, 32H, Ar-C$H_2$-O), 5.22 (s, 16H, PhC$H_2$O), 6.36 (t, 8H, $J$ = 2 Hz, Ar-*H*), 6.66 (t, 16H, $J$ = 2 Hz, Ar*H*), 6.97 (t, 4H, $J$ = 2 Hz, Ar*H*), 7.10−7.30 (m, 48H, Ph*H*), 7.38 (d, 12H, ArH), 8.78 (s, 8H, Pyrrol).

**D-[G-2]$_8$Por, 19b.** The second generation benzylic bromide, **38** (2.0 g, 2.5 mmol),[13] was dissolved in acetone (40 mL), followed by the addition of tetrakis(3,5-dihydroxyphenyl)porphyrin, **37** (297 mg, 0.40 mmol), $K_2CO_3$ (4.0 g, 29 mmol), and 18-crown-6 (50 mg). The mixture was heated at reflux under $N_2$ for 6 days in the dark and purified by fractional precipitation from ethyl ether. This afforded the dendritic porphyrin, **19b**, as a purple solid in 61% yield. $^1H$ NMR (250 MHz, $CDCl_3$): $\delta$ 4.81 (s, 96H, Ar-C$H_2$-O), 5.01 (s, 16H, PhC$H_2$O), 6.32 (t, 16H, $J$ = 2 Hz, Ar*H*), 6.52 (t, 8H, $J$ = 2 Hz, Ar*H*), 6.53 (d, 32H, $J$ = 2 Hz, Ar*H*), 6.66 (d, 16H, $J$ = 4 Hz, Ar*H*), 7.00 (t, 4H, $J$ = 2H, Ar*H*), 7.14−7.24 (m, 160H, Ph*H*), 7.42 (d, 8H, $J$ = 4 Hz, Ar*H*), 8.85 (s, 8H, Pyrrol).

**D-[G-3]$_8$Por, 19c.** The third generation benzylic bromide, **39** (2.0 g, 1.08 mmol),[13] was dissolved in a 4:1 mixture of THF/DMF (40 mL), followed by the addition of tetrakis(3,5-dihydroxyphenyl)porphyrin, **37** (75 mg, 0.1 mmol), $K_2CO_3$ (3.0 g, 22 mmol), and 18-crown-6 (50 mg). The mixture was heated at reflux under $N_2$ for 14 h with solvent cycling through an addition funnel in the dark and purified by fractional precipitation from diethyl ether. This afforded the dendritic porphyrin, **19c**, as a dark purple/brown solid in 57% yield. $^1H$ NMR (250 MHz, $CDCl_3$): $\delta$ 4.66 (s, 224H, Ar-$CH_2$-O), 4.73 (s, 16H, Ph$CH_2$O), 6.37 (m, 96H, Ar*H*), 6.46 (m, 40H, Ar*H*), 6.63 (m, 32H, Ar*H*), 7.12−7.24 (m, 320H, Ph*H*), 8.88 (s, 8H, Pyrrol).

**D-[G-4]$_8$Por, 19d.** The fourth generation benzylic bromide, **40** (2.0 g, 0.597 mmol),[13] was dissolved in a 4:1 mixture of THF/DMF (50 mL), followed by the addition of tetrakis(3,5-dihydroxyphenyl)-porphyrin, **37** (35 mg, 0.05 mmol), $K_2CO_3$ (3.0 g, 22 mmol), and 18-crown-6 (50 mg). The mixture was heated at reflux under $N_2$ for 12 h with solvent cycling through an addition funnel in the dark and purified by fractional precipitation from diethyl ether. This afforded the dendritic porphyrin, **19d**, as a dark purple/brown solid in 57% yield. $^1H$ NMR (250 MHz, $CDCl_3$): $\delta$ 4.90 (s, 480H, Ar-$CH_2$-O), 4.99 (s, 16H, $CH_2$O), 6.37 (m, 96H, Ar*H*), 6.42 (m, 40H, Ar*H*), 6.60 (m, 32H, Ar*H*), 7.12−7.33 (m, 640H, Ph*H*), 8.87 (s, 8H, Pyrrol).

**L-[G-2]$_8$Por, 20b.** The linear benzylic bromide, **13** (1.50 g, 1.86 mmol), was dissolved in acetone (40 mL), followed by the addition of tetrakis(3,5-dihydroxyphenyl)porphyrin, **37** (113 mg, 0.153 mmol), $K_2CO_3$ (3.5 g, 25 mmol), and 18-crown-6 (50 mg). The mixture was heated at reflux under $N_2$ for 6 days in the dark and purified by fractional precipitation from diethyl ether. This afforded purple crystals of **20b** in 51% yield. $^1H$ NMR (250 MHz, $CDCl_3$): $\delta$ 4.79 (m, 32H, Ar$CH_2$O), 4.86 (s, 32H, PhC$H_2$O), 5.02 (s, 16H, $ArCH_2O$), 6.44−6.66 (complex m, 72H, Ar*H*), 6.98 (s, 4H, ArH), 7.17−7.41 (complex m, 160H, Ph*H*), 7.41 (d, $J$ = 4 Hz, ArH), 8.84 (s, 8H, Pyrrol).

**L-[G-3]$_8$Por, 20c.** The linear third generation benzylic bromide, **29** (0.75 g, 0.45 mmol), was dissolved in a 4:1 THF:DMF solution (20 mL), followed by the addition of tetrakis(3,5-dihydroxyphenyl)-


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porphyrin, **37** (20 mg, 27.0 $\mu$mol), $K_2CO_3$ (1.5 g, 11 mmol), and 18-crown-6 (25 mg). The mixture was heated and cycled at reflux under $N_2$ for 6 h in the dark and purified by fractional precipitation from diethyl ether. This afforded **20c** as a dark purple/brown solid in 67% yield. $^1$H NMR (250 MHz, $CDCl_3$): $\delta$ 4.76−4.92 (complex m, 224H, $ArCH_2O$, $PhCH_2O$), 6.42−6.53 (complex m, 168H, Ar*H*), 7.12−7.25 (complex m, 320H, Ph*H*), 8.85 (s, 8H, Pyrrol).

**L-[G-4]$_8$Por, 20d.** The linear fourth generation benzylic bromide, **31** (0.75 g, 0.224 mmol), was dissolved in a 4:1 THF:DMF solution (20 mL), followed by the addition of tetrakis(3,5-dihydroxyphenyl)-porphyrin, **37** (9.8 mg, 14 $\mu$mol), $K_2CO_3$ (2.5 g, 18 mmol), and 18-crown-6 (40 mg). The mixture was heated and cycled at reflux under $N_2$ for 6 h in the dark and purified by fractional precipitation from diethyl ether. This afforded **21a** as a dark purple/brown solid in 71% yield. $^1$H NMR (250 MHz, $CDCl_3$): $\delta$ 4.82−489 (complex m, 494H, $ArCH_2O$, $PhCH_2O$), 6.43−6.54 (complex m, 360H, Ar*H*), 7.19−7.25 (complex m, 640H, Ph*H*), and 8.83 (s, 8H, pyrrol).

**L-[G-2]$_4$Por, 21a.** The linear second generation benzylic bromide, **13** (2.06 g, 2.52 mmol), was dissolved in acetone (40 mL), followed by the addition of tetrakis(4-hydroxyphenyl)porphyrin, **38** (279 mg, 0.40 mmol), $K_2CO_3$ (4.0 g, 29 mmol), and 18-crown-6 (52 mg). The mixture was heated at reflux under $N_2$ for 6 days in the dark and purified by fractional precipitation from diethyl ether. This afforded **21a** as purple crystals in 71% yield. $^1$H NMR (250 MHz, $CDCl_3$): $\delta$ 4.96 (s, 16H, $ArCH_2O$), 5.25−5.28 (m, 32H, $PhCH_2O$), 6.52−6.84 (complex m, 36H, Ar*H*), 7.24−7.47 (complex m, 80H, Ph*H*), 8.07 (d, 8H, $J$ = 8 Hz), 8.83 (s, 8H, pyrrol).

**L-[G-3]$_4$Por, 21b.** The linear third generation benzylic bromide, **29** (0.500 g, 0.285 mmol), was dissolved in a 4:1 THF:DMF solution (40 mL), followed by the addition of tetrakis(4-hydroxyphenyl)porphyrin, **38** (24 mg, 36 $\mu$mol), $K_2CO_3$ (1.5 g, 11 mmol), and 18-crown-6 (25 mg). The mixture was heated and cycled at reflux under $N_2$ for 6 h in the dark and purified by fractional precipitation from diethyl ether. This afforded **21b** as a purple solid in 61% yield. $^1$H NMR (250 MHz, $CDCl_3$): $\delta$ 4.88 (complex m, 96H, $CH_2O$), 5.06 (s, 8H, $CH_2O$), 5.21 (s, 8H, $CH_2O$), 6.49−6.85 (complex m, 76H, Ar*H*), 6.85 (d, 8H, $J$ = 4 Hz, Ar*H*), 7.24−7.42 (complex m, 160H, Ph*H*), 8.05 (d, 8H, $J$ = 8 Hz, Ar*H*), 8.82 (s, 8H, Pyrrol).

**L-[G-4]$_4$Por, 21c.** The linear fourth generation benzylic bromide, **31** (980 mg, 0.293 mmol), was dissolved in a 4:1 THF:DMF solution (40 mL), followed by the addition of tetrakis(4-hydroxyphenyl)-porphyrin, **38** (25 mg, 36 $\mu$mol), $K_2CO_3$ (1.7 g, 12 mmol), and 18-crown-6 (25 mg). The mixture was heated and cycled at reflux under $N_2$ for 6 h in the dark and purified by fractional precipitation from diethyl ether. This afforded **21c** as a dark purple/brown solid in 37% yield. $^1$H NMR (250 MHz, $CDCl_3$): $\delta$ 4.81 (complex m, 216H, $CH_2O$), 4.89 (s, 8H, $CH_2O$), 6.54 (complex m, 180H, Ar*H*), 7.18−7.25 (complex m, 328H, Ph*H*), 8.01 (s, 8H, Ar*H*), 8.85 (s, 8H, Pyrrol).

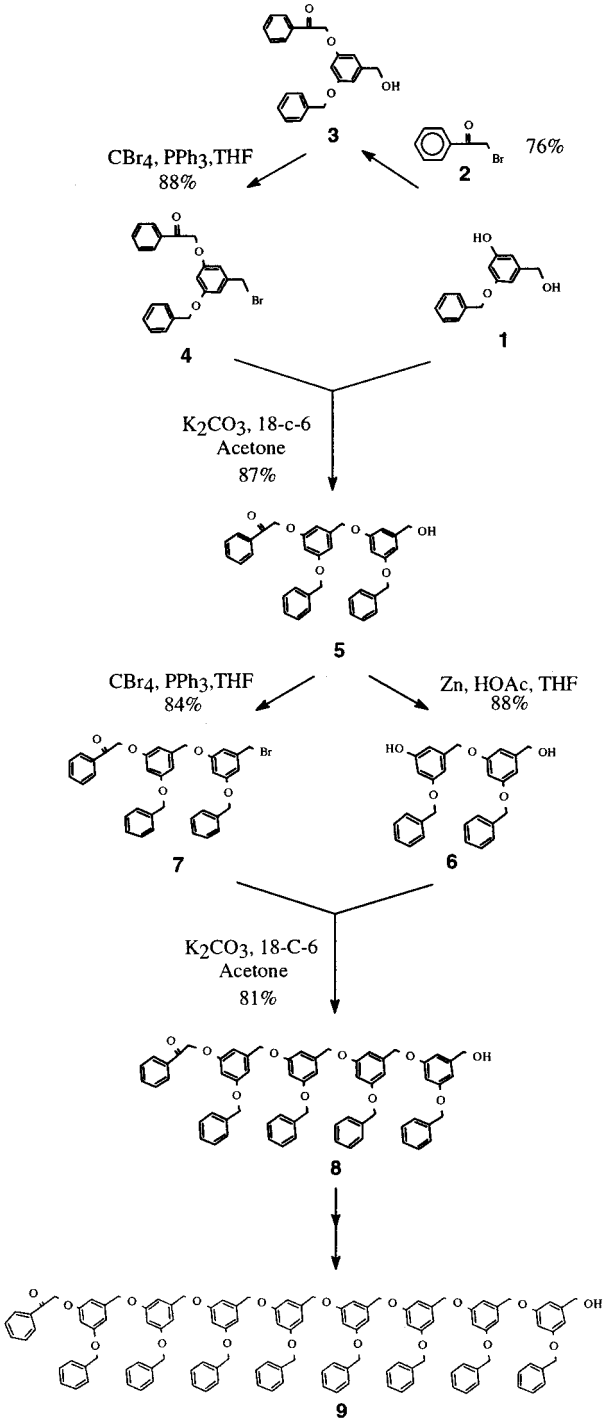
**L-[G-5]$_4$Por, 21d.** The linear fifth generation benzylic bromide, **36** (1.05 g, 0.157 mmol), was dissolved in a 4:1 THF:DMF solution (50 mL), followed by the addition of tetrakis(4-hydroxyphenyl)porphyrin, **38** (8.9 mg, 13 $\mu$mol), $K_2CO_3$ (1.7 g, 12 mmol), and 18-crown-6 (25 mg). The mixture was heated and cycled at reflux under $N_2$ for 12 h in the dark and purified by fractional precipitation from diethyl ether. This afforded **21d** as a wine red solid in 42% yield. $^1$H NMR (250 MHz, $CDCl_3$): $\delta$ 4.82−4.88 (complex m, 240H, $CH_2O$), 4.90 (complex m, 256H, $CH_2O$), 6.56 (complex m, 372H, ArH), 7.12−7.27 (complex m, 640H, PhH), 8.85 (s, 8H, Pyrrol).

## Results and Discussion

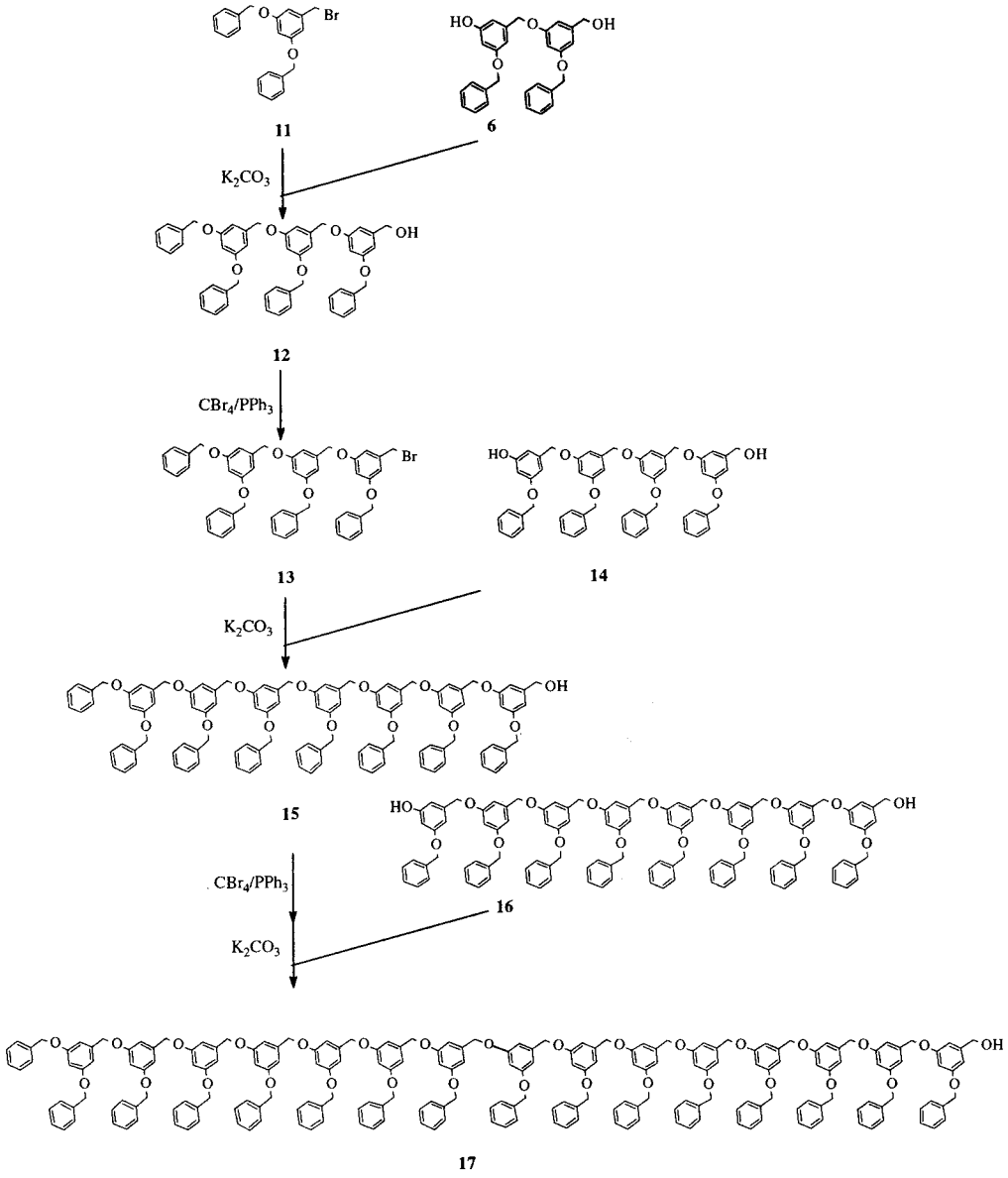
**Synthesis and Characterization.** To preserve the compositional analogy of the various architectural isomers, new synthetic procedures had to be developed to mimic the special features of the dendritic architecture with its incremental growth in the number of monomer units. For example, a generation four dendron derived from 3,5-dihydroxybenzyl alcohol, D-[G-4]-OH, has an odd number, 15 or ($2^4 - 1$), of repeat units and an even number, 16 or ($2^4$), of chain end benzyl groups. Such features preclude a traditional exponential growth strategy[21,22] involving the synthesis of well-defined oligomers with an even number of repeat units, that is, 2, 4, 8 ($2^n$). A combination of two growth strategies was therefore adopted to overcome this problem and allow the preparation of a linear series of oligomers with ($2^n - 1$) repeat units.

Initially, a series of oligomers with an even number of repeat units was constructed using a standard exponential growth strategy from 5-benzyloxy-3-hydroxybenzyl alcohol, **1**. The two

***Scheme 1.*** Synthesis of Oligomeric Benzyl Ethers



***Scheme 2.*** Synthesis of Exact Linear Analogues




dormant functionalities in this strategy were a phenacyl protected phenol group and a hydroxymethyl group. The latter could be activated by reaction with $CBr_4/PPh_3$ to give a bromomethyl group, while the phenacyl group could be deprotected with zinc in acetic acid to give the desired phenol. By using these activation reactions and a coupling step based on Williamson ether chemistry, oligomeric linear poly(benzyl ethers) could be prepared in high yield (Scheme 1). Reaction of **1** with phenylacyl bromide, **2**, gave the alcohol, **3**, which is activated with $CBr_4/PPh_3$ to afford the protected bromide, **4**. Coupling of **1** with **4** then gives the dimer, **5**, which like **3** is either deprotected with Zn/HOAc to give the monophenol, **6**, or brominated to give the bromomethyl derivative, **7**. Coupling of **6** and **7** resulted in the linear tetramer, **8**, which can be subsequently carried forward to the octamer, **9**, hexadecamer, **10**, etc., using the same series of reactions. To achieve the necessary number of repeat units matching that found in regular dendrimers, the monophenolic derivatives from the above synthetic sequence were coupled with a series of bromomethyl substituted oligomers containing an odd number of repeat units. In this way, linear oligomers could be built up with the correct number sequence of repeat units, $2^n - 1$. Therefore, 3,5-bis-(benzyloxy)benzyl bromide, **11**, which is actually the first generation dendritic bromide, is coupled with the monophenolic dimer, **6**, in the presence of potassium carbonate to give the trimer, **12**. Activation of the hydroxymethyl group with $CBr_4/PPh_3$ gives the bromomethyl derivative, **13**, which in turn can be coupled with the tetramer, **14**, to afford the septamer, **15**. Repetition of this activation/coupling strategy with the monophenolic octamer, **16**, finally gives the pentadecamer, **17**, the exact linear analogue of the fourth generation dendrimer, D-[G-4]-OH, **18**, described above.

Significantly, **17** contains 15 repeat units, 16 benzyl "chain ends", and a single hydroxymethyl functional group (Scheme 2). MALDI-TOF analysis of the linear analogue, **17**, and the corresponding dendrimer, D-[G-4]-OH, **18**, showed that both are essentially monodisperse and have a molecular ion at 3288 amu (Figure 1). This is in total agreement with the synthetic strategy and the observation that **17** and **18** are architectural isomers that differ only in the linear versus dendritic placement

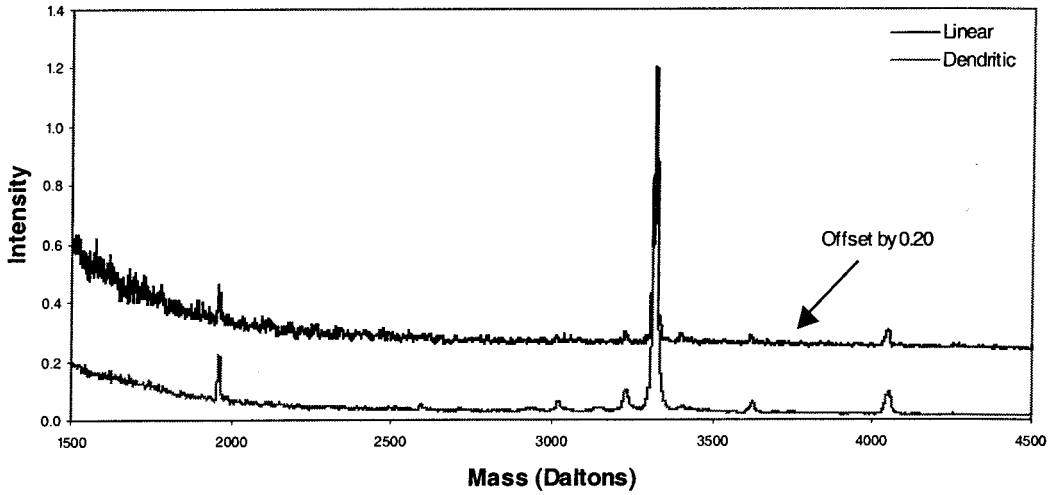



***Figure 1.*** MALDI-TOF analysis for the linear analogue, L-[G-4]-OH **17**, and the corresponding dendrimer, D-[G-4]-OH **18**.

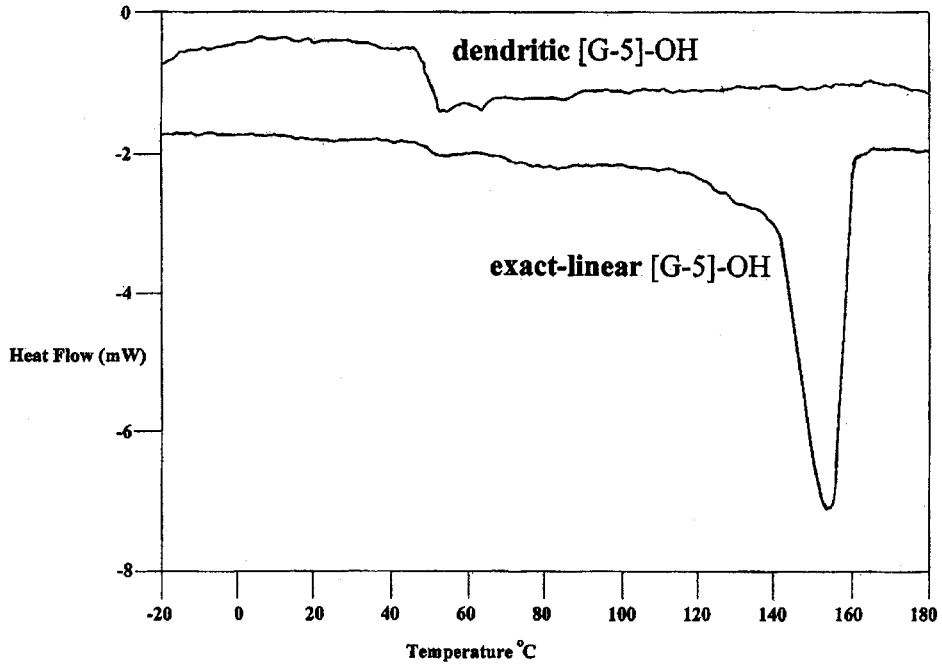



***Figure 2.*** DSC analysis of the linear analogue, L-[G-5]-OH **34**, and the corresponding dendrimer, D-[G-5]-OH **35**.

of their repeat units. The preparation of the exact linear analogues of poly(benzyl ether) dendrimers from generation one to generation six now permits a direct comparison of the physical properties of these two series of macromolecular isomers. From the synthetic work, it was immediately apparent that the linear analogues were highly crystalline at both low and high generation numbers.

This is in direct contrast to the corresponding dendrimers, which are crystalline at generation one and two but become totally amorphous at generation four and above. As can be seen in Figure 2, DSC analysis shows that the dendrimer, D-[G-5]-OH, **35**, has a glass transition temperature of 43 °C as compared with that of the exact linear analogue, **34**, which shows a prominent melting transition at 153 °C. This high level of crystallinity was also apparent for the third, fourth, and sixth generation exact linear analogues and impacted the synthetic efforts through their decreased solubility. This change in solubility has also been observed in vapor−liquid equilibrium experiments.[23]

Another difference in physical characteristics between the linear and dendritic poly(benzyl ethers) was in the hydrodynamic volume of the macromolecules.[13] Comparison of the two isomeric series by gel permeation chromatography showed a marked nonlinear change in hydrodynamic volume on going from the linear molecule to the corresponding dendrimer. At low generation numbers, $G = 1$ to 4, the linear macromolecules are only marginally larger than the corresponding dendrimers. However, this difference increases dramatically upon reaching generations five and six with both linear molecules having a hydrodynamic volume approximately 40−50% larger than that of the corresponding dendrimers (Figure 3).

This result is fully consistent with the dendrimers having a more compact and globular structure than do their linear architectural isomers, which would be expected to assume a more random coil structure in THF solution.[24] It is of interest to note that similar generation dependent discontinuities in physical properties are observed between generation four and five for a number of other dendritic systems.[25] In this case, however, the

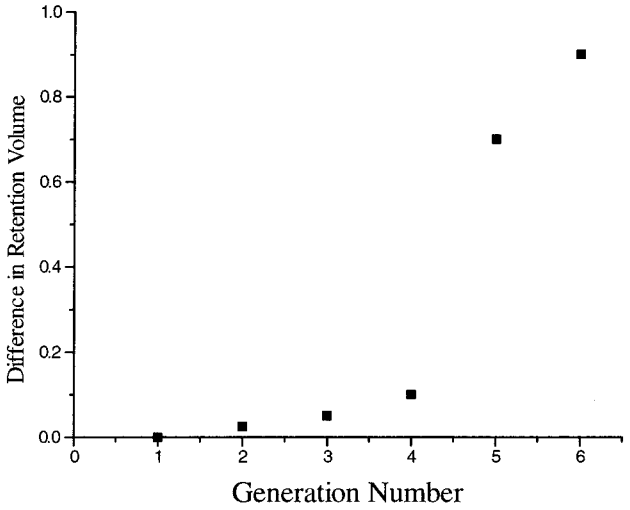



***Figure 3.*** Difference in GPC retention volume for the exact linear analogues versus the corresponding dendrimers ($Rt_{lin} - Rt_{den}$) as a function of generation number.

comparison with linear isomers having exactly the same molecular weight and composition permits the difference to be directly attributed to the architectural change in the polymer and suggests that these architectural changes only manifest themselves as actual changes in the physical properties at higher generations, $G = 5$ or above, where the dendrimer adopts a compact globular architecture.

To obtain the desired structural isomers for evaluation of the effect of architecture on photophysical properties, a range of porphyrin core poly(benzyl ether) macromolecular architectures was also prepared. These isomeric architectures ranged from four- or eight-arm stars to dendrimers. Synthetically, the latter two were obtained by coupling an octaphenolic porphyrin core with the appropriate linear or isomeric dendritic bromides of the same generation, while the former was obtained by coupling a tetraphenolic core to the linear analogues of the next higher generation. In this way, three different porphyrin core poly(benzyl ether) architectures **19a**−**d**, **20b**−**d**, **21a**−**d** were prepared (Scheme 3). In analogy with previous work using highly functionalized cores,[26] the formation of partially functional porphyrin cores, that is, di-, tri-alkylated, etc., was not favored, and the predominant product was the fully alkylated derivative for all the structures studied. Table 1 detailing the chemical composition of the various macromolecules demonstrates their isomeric relationship. Of particular note is the fact that the dendritic and eight-arm series of macromolecules have the same molecular formulas and are exact structural isomers. In contrast, the series of four-arm star polymers is based on a central tetraphenyl porphyrin core and, therefore, contains four extra phenyl rings, which leads to a slight increase in molecular weight as compared to the other two series.

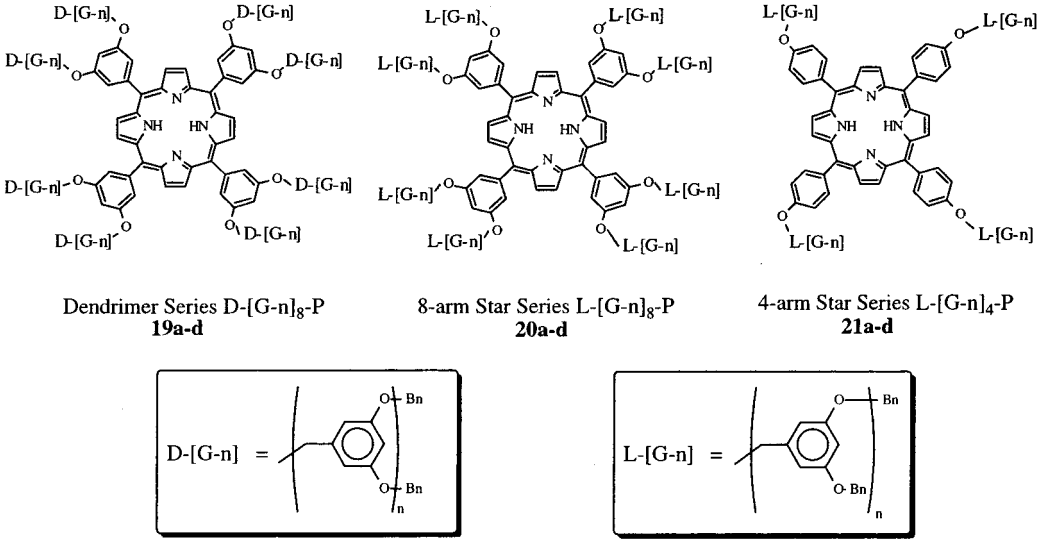
***Table 1.*** Chemical Composition of Isomeric Porphyrin Core Poly(benzyl ether) Macromolecules **19a**−**d**, **20b**−**d**, and **21a**−**d** (**20a** Has the Same Structure as **19a**)

| compound | series | generation | formula | internal units | terminal units |
|---|---|---|---|---|---|
| **19a** | D-[G-*n*]$_8$P | $n = 1$ | $C_{212}H_{174}N_4O_{24}$ | 8 | 16 |
| **19b** | | $n = 2$ | $C_{436}H_{366}N_4O_{56}$ | 24 | 32 |
| **19c** | | $n = 3$ | $C_{884}H_{750}N_4O_{120}$ | 56 | 64 |
| **19d** | | $n = 4$ | $C_{1780}H_{1518}N_4O_{248}$ | 120 | 128 |
| **20a** | L-[G-*n*]$_8$P | $n = 1$ | $C_{212}H_{174}N_4O_{24}$ | 8 | 16 |
| **20b** | | $n = 2$ | $C_{436}H_{366}N_4O_{56}$ | 24 | 32 |
| **20c** | | $n = 3$ | $C_{884}H_{750}N_4O_{120}$ | 56 | 64 |
| **20d** | | $n = 4$ | $C_{1780}H_{1518}N_4O_{248}$ | 120 | 128 |
| **21a** | L-[G-*n*]$_4$P | $n = 2$ | $C_{240}H_{198}N_4O_{28}$ | 12 | 16 |
| **21b** | | $n = 3$ | $C_{464}H_{390}N_4O_{60}$ | 28 | 32 |
| **21c** | | $n = 4$ | $C_{912}H_{774}N_4O_{124}$ | 60 | 64 |
| **21d** | | $n = 5$ | $C_{1808}H_{1542}N_4O_{252}$ | 124 | 128 |

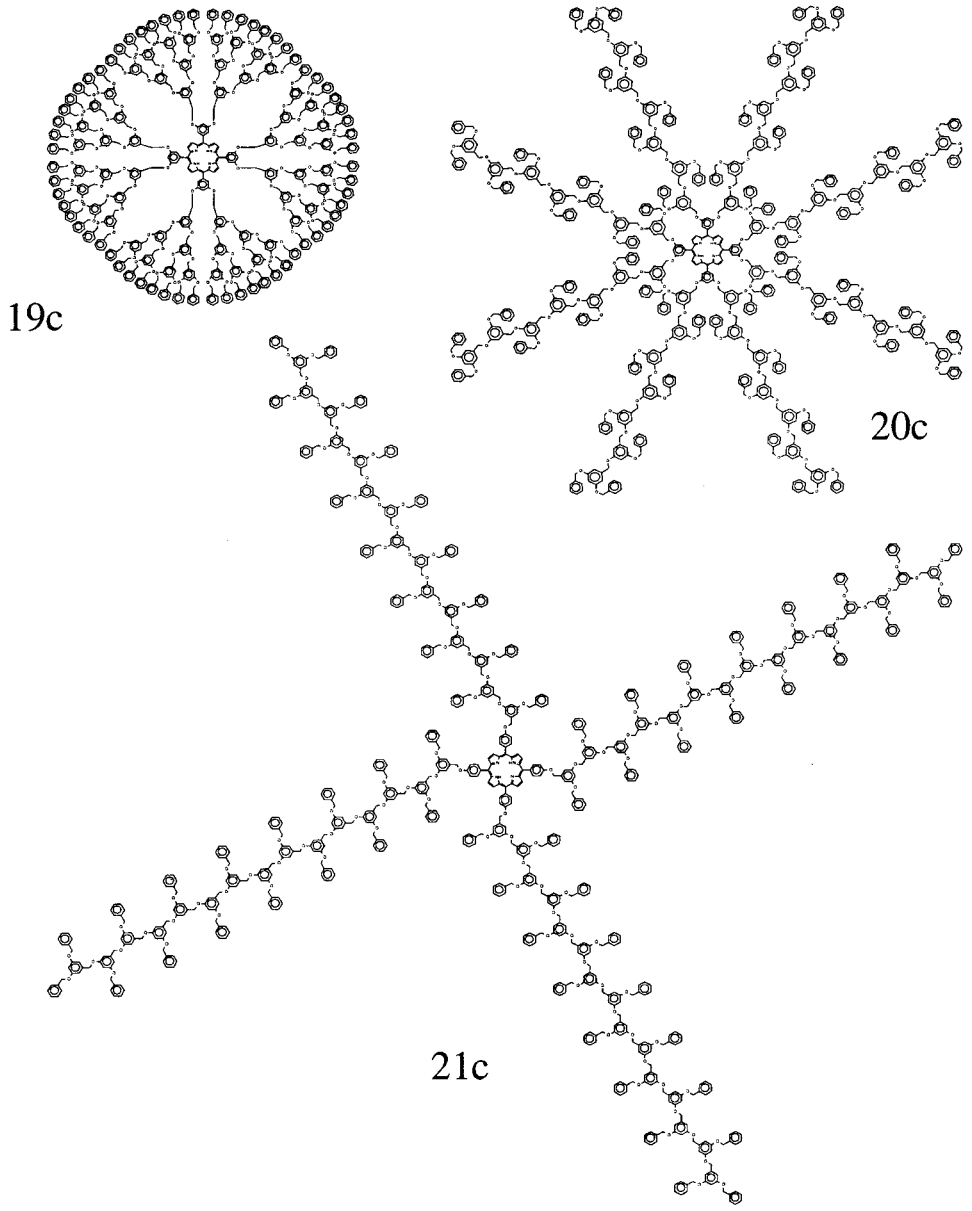
For illustration purposes, the actual chemical structures of the three third generation isomers **19c**, **20c**, and **21c** are shown in Scheme 4 (structures drawn to scale in their extended conformations).

Characterization of the different architectural isomers by gel permeation chromatography (GPC) gave evidence for the influence of macromolecular configuration on hydrodynamic volume. As can be seen in Figure 4, the dendritic D-[G-4]$_8$-Por derivative, **19d**, has a substantially smaller hydrodynamic volume than does the isomeric eight-arm star, **20d**, which in turn is substantially smaller than the four-arm star, **21d**. Interestingly, calibration of the GPC using linear polystyrene standards led to surprisingly accurate molecular weight values for the linear four-arm series **21a**−**d**. Hence, the linear portion of the macromolecule seems to dominate the hydrodynamic

***Scheme 3.*** Structure of Porphyrin Derivatives



***Scheme 4.*** Chemical Structures of Third Generation Isomers **19c**, **20c**, and **21c**



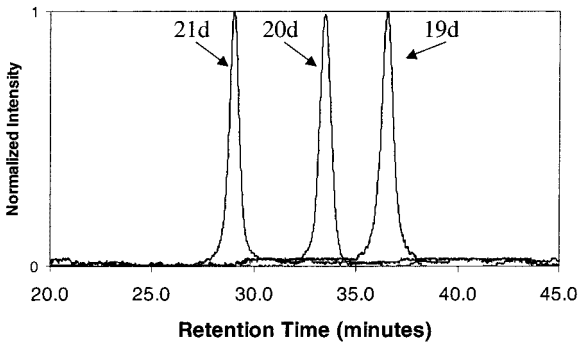




***Figure 4.*** GPC traces for the fourth generation isomeric porphyrin core poly(benzyl ether) macromolecules, dendritic **19d**, eight-arm star **20d**, four-arm star **21d**.

properties of the four-arm star leading to a less globular conformation in solution (Table 2). In the case of the eight-arm series **20a**−**d** and the true dendrimers **19a**−**d**, the increased branching causes a progressively larger deviation when compared to linear polystyrene standards (Figure 5).

***Table 2.*** GPC Characterization of the Isomeric Porphyrin Core Poly(benzyl ether) Macromolecules **19a**−**d**, **20a**−**d**, and **21a**−**d**

| compound | $t_R$/min | $M_n$/D | $MW_{theory}$/D | PD |
|---|---|---|---|---|
| **19a** | 40.4 | 3261 | 3162 | 1.005 |
| **19b** | 38.8 | 5496 | 6558 | 1.009 |
| **19c** | 37.3 | 8857 | 13 350 | 1.026 |
| **19d** | 36.4 | 13 347 | 26 933 | 1.050 |
| **20a** | 40.4 | 3261 | 3162 | 1.005 |
| **20b** | 38.6 | 5828 | 6558 | 1.008 |
| **20c** | 36.6 | 12 030 | 13 350 | 1.024 |
| **20d** | 33.4 | 22 500 | 26 933 | 1.020 |
| **21a** | 39.4 | 4515 | 3586 | 1.007 |
| **21b** | 37.6 | 8183 | 6982 | 1.014 |
| **21c** | 34.3 | 15 000 | 13 774 | 1.010 |
| **21d** | 29.0 | 28 000 | 27 358 | 1.010 |

The more globular, three-dimensional shape in solution for the dendrimer may also result in greater shielding of the porphyrin core when compared to the isomeric eight- and four-arm stars. To evaluate the effect of architecture on core shielding, the photophysical properties for these isomeric series of porphyrin core poly(benzyl ether) macromolecules were

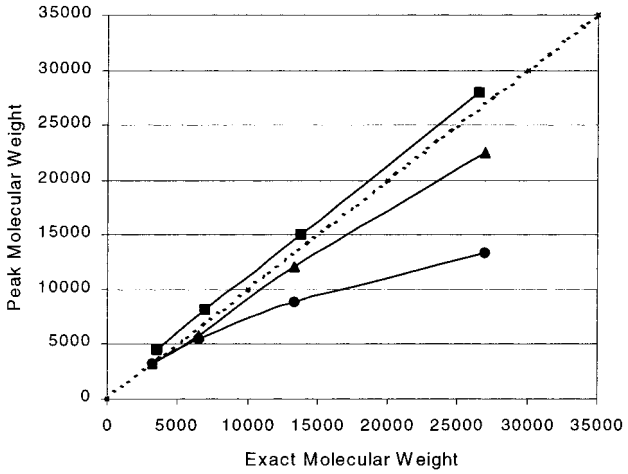



***Figure 5.*** Correlation of molecular weight by GPC and actual molecular weight for the dendritic series **19a**−**d** (●), the eight-arm linear series **20b**−**d** (▲), and the four-arm linear series **21a**−**d** (■). Linear polystyrene standard calibration (·····) is shown.

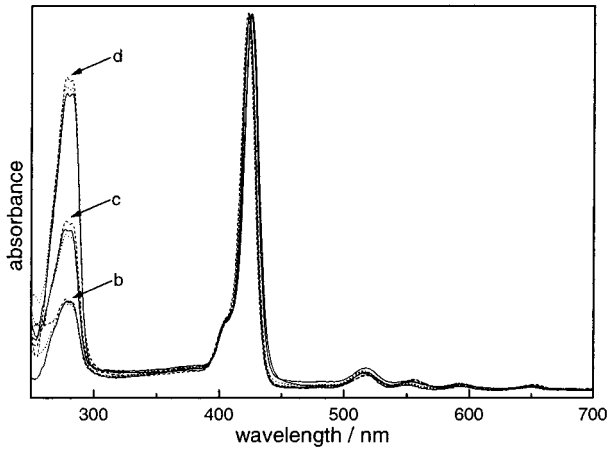


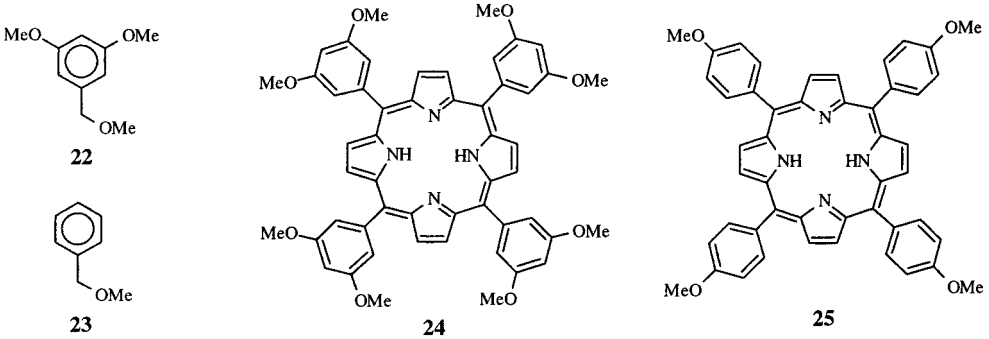

***Figure 6.*** Absorption spectra of isomer series **19b**−**d** (—), **20b**−**d** (·····), and **21b**−**d** (- - -) in THF (25 °C).

investigated. To fully understand these systems, compounds modeling individual chromophore subunits were also prepared. 3,5-Dimethoxybenzyl methyl ether, **22**, and benzyl methyl ether, **23**, were chosen as model compounds for the internal and terminal units, respectively, while tetrakis(3,5-dimethoxyphenyl)porphyrin, **24**, and tetrakis(4-methoxyphenyl)porphyrin, **25**, served as models for the core (Scheme 5).

**Absorption/Emission Properties and Energy Transfer Studies.** The encapsulation of functional cores within dendritic[27,28] shells has attracted considerable attention in recent years.[29] This approach enables the tailoring of the overall molecular properties via peripheral modification while also allowing the tuning of the properties of the core itself. In some cases, there have been observations of dramatic influence of morphology[30] and focal point geometry[31] on the efficiency of energy transduction, that is, the "antenna effect", within the dendrimer architecture, in particular for those of the poly(benzyl ether) type. The antenna effect, arising from indirect excitation of a dendritic core moiety via efficient light-harvesting of the poly(benzyl ether) dendrimer backbone and subsequent energy transfer to the core, was found to lead to considerably enhanced emission from the core[30,31] and even multiphoton processes[30a] for rigidified structures with sufficient site isolation.[29] Furthermore, the focal point geometry seemed to play an important role in energy funneling.[31] While Jiang and Aida have varied the number of dendron subunits around a free base porphyrin core,[30b] a different approach was taken to investigate morphology effects on the energy transfer process by comparing the structural isomer series **19b**−**d**, **20b**−**d**, and **21b**−**d**. Because of the negligible absorption of the dendritic backbone in low generations, compounds **19a** and **21a** could not be investigated. These stimulating early findings have encouraged us to further investigate these properties attributed to the dendritic state. With regard to site isolation, porphyrins and their metal complexes have been thoroughly investigated as core moieties due to their distinct photophysical, electrochemical, and catalytic characteristics.[30b,32] Recently, we have reported on approaches to site isolation involving alternative architectures based on star-shaped branched-linear copolymers.[33] It is clear that further insight into the role of the polymer backbone in site isolation of core functionality could be gained by the study of isomeric molecules in which a porphyrin probe is surrounded by building block assemblies with different architectures. The absorption spectra of the three different isomer series clearly show that the absorbance of the poly(benzyl ether) backbone is essentially the same for all isomers within a given generation, while the absorbance doubles with each increase in generation number (Figure 6). It should be noted that compounds **21b**−**d** show slightly higher absorbencies due to the incorporation of four more phenyl rings (Table 1). The Soret bands of the porphyrin core exhibit minor bathochromic shifts in the order of 3−4 nm that are most pronounced in the dendrimer series **19b**−**d** and are attributed to increasing core encapsulation.[30b]

Emission from the porphyrin core was observed by either direct excitation (Soret or Q-bands) or by indirect excitation (dendrimer backbone). This can be demonstrated by obtaining the corresponding excitation spectra showing all chromophore subunits that are responsible for population of the emitting

***Scheme 5.*** Structure of Model Compounds **22**−**25**



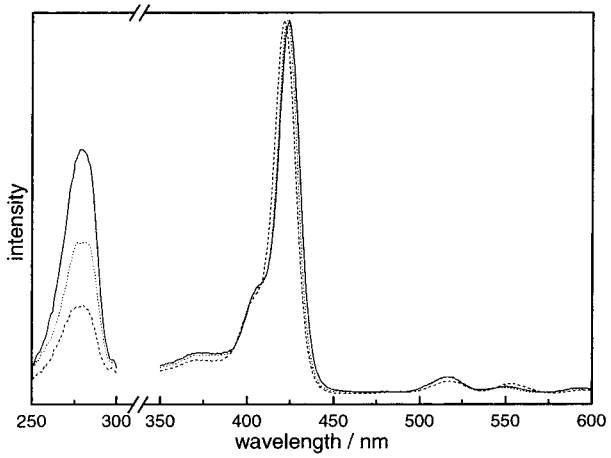



***Figure 7.*** Excitation spectra ($\lambda_{em}$ = 653 nm) for isomers **19d** (—), **20d** (·····), and **21d** (- - -) in THF (25 °C).

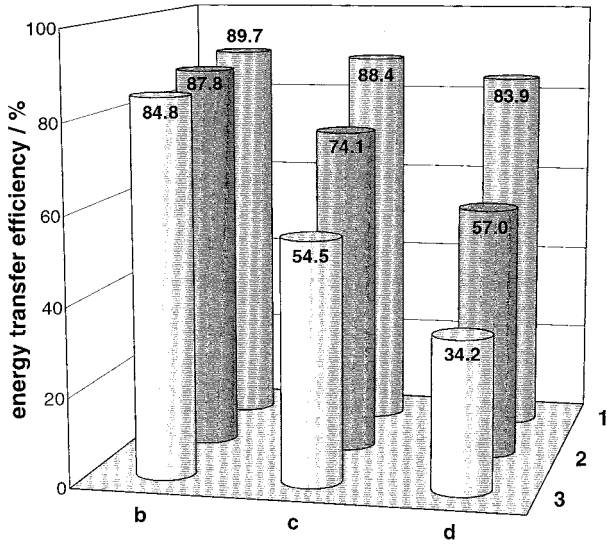



***Figure 8.*** Energy transfer efficiencies of isomer series **19b**−**d**, **20b**−**d**, and **21b**−**d** in THF (25 °C).

excited state of the porphyrin core. For example, one set of isomers (**19d**, **20d**, **21d**) depicted in Figure 7 clearly shows different contributions of the poly(benzyl ether) backbone in the energy transfer.

Comparison of the excitation and the absorption spectra allows quantification of the energy transfer efficiency ($\Phi_{ET}$).[34] With increasing generation, the dendrimer series **19b**−**d** exhibits only a slight decline in $\Phi_{ET}$, while the branched linear series **20b**−**d** shows a significant decrease, and the linear series **21b**−**d** shows the steepest decrease in $\Phi_{ET}$ (Figure 8). Clearly, there is a pronounced morphology dependence on the energy transfer event in the investigated molecules.

To explain these results, the individual chromophore subunits were studied. UV/vis spectroscopy revealed a much stronger absorbance for **22** as compared to that of **23**, indicating that the photophysical properties of the dendrimer backbone are dominated by the interior branching units. This is further supported by the observed absorption maximum and the vibrational fine structure (Figure 9, inset). By adding the absorbencies of all individual components to construct "ensemble" spectra, a good correlation with the absorption spectra of the actual macromolecule was found (Figure 9). This spectral

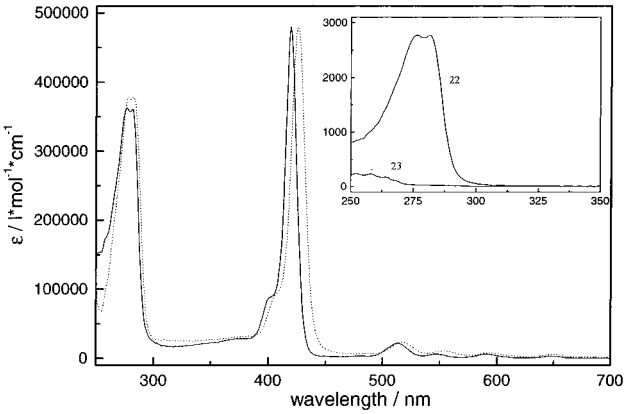



***Figure 9.*** Comparison of an "ensemble" spectrum consisting of the combined absorption spectra of all individual chromophore subunits (120 × 22 + 128 × 23 + 24, —) with compound **19d** (·····). The inset shows the absorption spectra of the model compounds for the branched (**22**) and terminal units (**23**).

comparison furthermore demonstrates the apparent core isolation in the dendrimers as indicated by the relatively large shift of the Soret band.

This finding suggests no significant electronic cooperativity of the dendron fragments. Hence, in a first approximation, we can assume that the observed macroscopic energy transfer arises from a combination of individual events involving single chromophore subunits. Therefore, the overall average distance of the 3,5-dialkoxybenzyl donor chromophores to the central porphyrin acceptor will determine $\Phi_{ET}$ in the system as illustrated in Figure 10 (see also Scheme 3). Obviously, this average distance will largely depend on the molecular architecture, that is, connectivity, and should therefore differ significantly by comparing the isomer series as found in the energy transfer experiments.

To further validate this assumption, a more detailed analysis of the resonance energy transfer[35] in the model systems was carried out by calculating the Förster radius $R_0$,[36] that is, the distance at which $\Phi_{ET} = 0.5$, using

$$R_0 = \sqrt[6]{\frac{0.5291\kappa^2 J}{n^4 N_A}} \qquad (1)$$

where $\kappa^2$ is the orientation factor, $J$ is the overlap integral of the fluorescence intensity of the donor and the molar extinction coefficient of the acceptor normalized by the frequency expressed in wavenumbers, $n$ is the index of refraction of the solvent, and $N_A$ is Avogadro's constant. The overlap integrals were calculated to be $J$(**22** → **24**) = 1.788 × $10^{-14}$ mol$^{-1}$ cm$^6$ and $J$(**22** → **25**) = 1.697 × $10^{-14}$ mol$^{-1}$ cm$^6$ giving rise to Förster radii of $R_0$(**22** → **24**) = 3.73 nm (series **19b**−**d** and **20b**−**d**) and $R_0$(**22** → **24**) = 3.70 nm (series **21b**−**d**). Although the $R_0$ values for energy transfer from **23** → **24** and **23** → **25** were calculated to be 3.50 nm in both cases, the contribution of the terminal groups to the overall energy transfer process is almost negligible due to their very low absorbance. This is supported by the few available experimental size data, since compound **19c** has a hydrodynamic radius of approximately 1.7 nm in THF, which is much smaller than the Förster radius (3.73 nm) allowing efficient energy transfer to take place ($\Phi_{ET}$ = 88.4%). For the linear poly(benzyl ether) chains, on the other

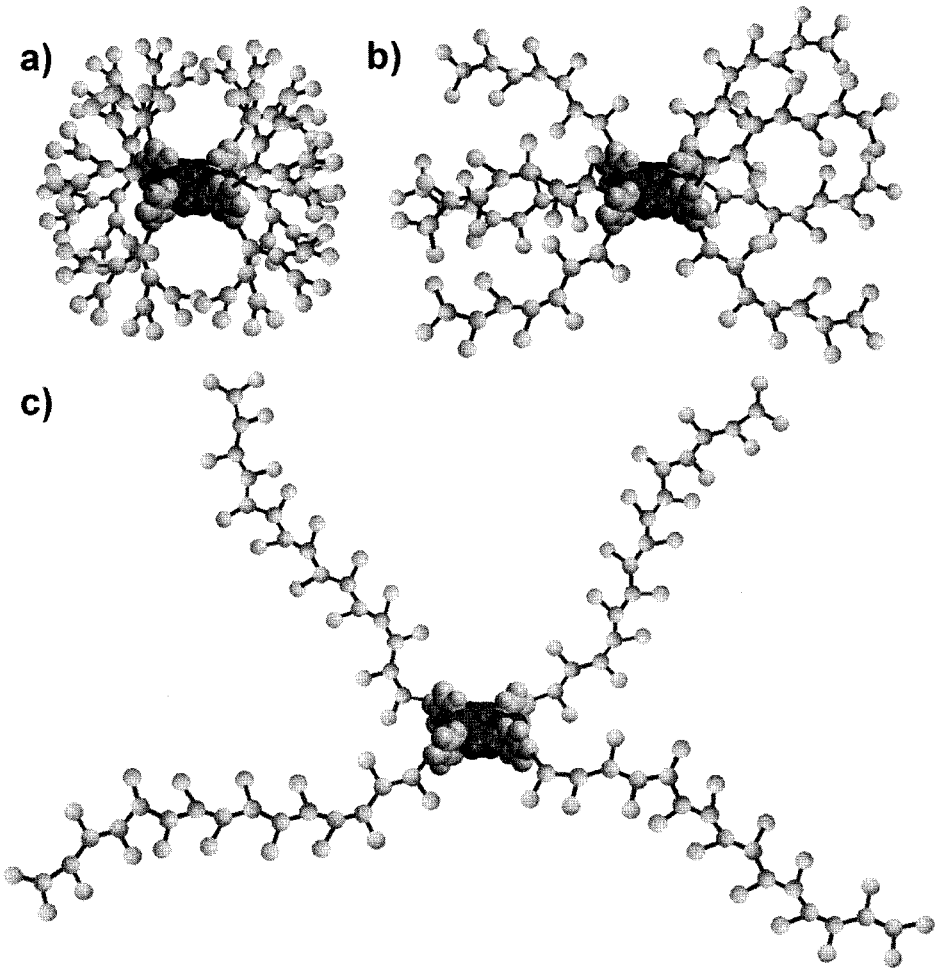



***Figure 10.*** Illustration of morphology dependent energy transfer arising from a collective interaction of individual donor chromophores with an acceptor core. The *average* donor−acceptor separation increases with the linearity of the system from (a) dendritic (**19c**) over (b) branched linear (**20c**) to (c) linear (**21c**) leading to a reduced energy transfer efficiency.

hand, we have to rely on molecular modeling that predicts a 0.6 nm separation of adjacent 3,5-dialkoxybenzyl chromophores. Therefore, in a good solvent for the polymer such as THF,[37] compound **21c** in its fully extended conformation would have a radius of approximately 9.0 nm (15 × 0.6 nm), giving rise to an average donor−acceptor distance of 4.5 nm, which is in good agreement with the observed value of 3.7 nm ($\Phi_{ET} = 0.55$, which corresponds approximately to the Förster radius).

## Conclusion

For the first time, a comparative study of site isolation as a function of the architecture of the shielding polymer backbone has been carried out. The design of exact linear analogues of dendritic poly(benzyl ether) wedges allowed the synthesis of three architectural isomer series having a porphyrin probe at the core. The isomers displayed dramatically different hydrodynamic properties, crystallinity, and solubility characteristics when compared to those of their dendritic analogues. Photophysical studies also showed significant differences based on architecture. First static absorption and emission experiments led to the observation of strongly morphology dependent intramolecular energy transfer in the different porphyrin core isomers series. The energy transduction from the poly(benzyl ether) backbone to the core was found to be facilitated in the dendritic case, whereas significant decreases in the energy transfer efficiencies were observed in the linear cases at higher molecular weights. Initial spectral analysis revealed the 3,5-dialkoxybenzyl ether internal units as the donor chromophores, whose average distance to the porphyrin core dictates the energy transfer efficiency. The extremely efficient energy transfer of the dendrimers, even in higher generations, derives from the relatively short distances that are maintained between the internal donor units and the acceptor core, clearly suggesting the superior encapsulation properties of the dendritic architecture.

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