Macromolecules **2001,** *34,* 7983−7988

Synthesis and Study of Optically Active Polydendrimers

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Received June 29, 2001; Revised Manuscript Received August 28, 2001

ABSTRACT: The first optically active polydendrimers have been synthesized by polymerization of binaphthyl-based dendrimers. Study of the chiral optical properties of the polydendrimers and their model compounds has revealed that the interaction of the dendritic side chains along the polybinaphthyl backbone cannot induce a secondary helical conformation. Energy migration from the dendritic side chains to the more conjugated polybinaphthyl main chain is observed through absorption and fluorescence spectroscopic studies. As the dendritic generation increases, the glass transition temperature of the polydendrimers decreases significantly. The dendritic substituents have made considerable influence on the thermal transition of the polybinaphthyls.

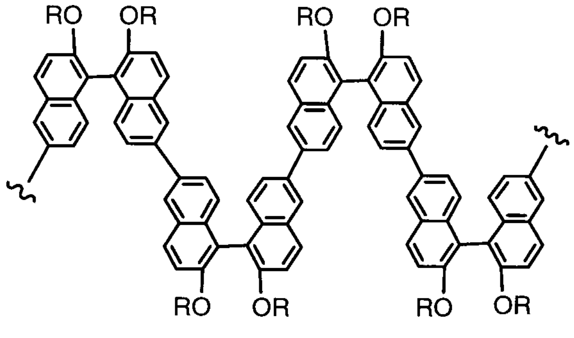
Introduction

In recent years, the study of dendrimer-based light-harvesting materials has received significant attention.[1−7] Among the representative examples of light-harvesting dendrimers are Balzani's metal-containing dendrimers,[2] Moore's phenylacetylene dendrimers,[3] the porphyrin-centered dendrimers made by Aida[4] and Lindsey,[5] the benzyl ether dendrimers studied by Fox,[6] and the dye-labeled dendrimers made by Fréchet.[7] These materials attempt to mimic the photosynthetic energy transfer process in nature[8] by using various dendritic units as antenna to absorb and transfer light energy to the lower band-gap focal points. Aida also connected dendritic arms to a conjugated polyphenyleneethynylene to generate light-emitting materials with enhanced photoluminescence.[9a] Other studies using dendritic units as electron and energy transporting moieties, as solubilizing units, and as bulky shields to prevent interchain aggregation in conjugated or nonconjugated polymers and oligomers have also been conducted.[9b−k]

In our laboratory, we have used both optically active and racemic 1,1′-binaphthyl molecules to build chiral conjugated polymers for electrical and optical applications.[10,11] In collaboration with Jen and co-workers, we have found that polybinaphthyl **1** exhibits very efficient electroluminescence (EL) in a double-layered light-emitting diode.[12] The nonplanar 1,1′-binaphthyl structure in **1** is believed to be important for the efficient EL response. The optically active version of the polybinaphthyl is potentially useful for polarized light emission. We have introduced light-harvesting dendritic side chains to the optically active polybinaphthyl to further develop its materials property. Herein, our synthesis and study of optically active polydendrimers containing the polybinaphthyl backbone and Fréchet's dendrons are reported.

Results and Discussion

Following the literature procedure, (*R*)-1,1′-bi-2-naphthol [(*R*)-BINOL] was brominated to give (*R*)-**2** (Scheme 1).[13] The bromination specifically occurred at the 6,6′-positions of BINOL. Reaction of (*R*)-**2** with benzyl bromide (**3**)[14] and Fréchet's dendritic bromides



1: R = n-C_6H_{13}

4 and **5** in the presence of base gave the desired chiral precursor dendrimers including generation zero (*R*)-**6**, generation one (*R*)-**7**, and generation two (*R*)-**8**.[11b,15a−c,16] Dendrimer (*S*)-**8** was prepared from optically pure (*S*)-BINOL.

Polymerization of the precursor dendrimers in the presence of a catalytic amount of $NiCl_2$ and excess zinc powder[17] led to the formation of the novel optically active polydendrimers (*R*)-**9**, (*R*)-**10**, and (*R*)-**11a** (Figure 1). The precursor dendrimers (*R*)-**8** and (*S*)-**8** were also polymerized by using a stoichiometric amount of $Ni(COD)_2$[17] (COD = 1,5-cyclooctadiene) to generate polydendrimers (*R*)-**11b** and (*S*)-**11** that have different molecular weights from (*R*)-**11a**. These materials were soluble in common organic solvents such as chloroform, methylene chloride, and THF. Their molecular weights were analyzed by gel permeation chromatography (GPC) relative to polystyrene standards. Multiangle laser light scattering (MALLS) technique was also used to measure the absolute molecular weights of the generation two polydendrimers (*R*)-**11a,b** and (*S*)-**11**. These molecular weight data are summarized in Table 1. As shown in Table 1, the molecular weights of (*R*)-**11b** and (*S*)-**11** are significantly higher than that of (*R*)-**11a**, indicating that the stoichiometric $Ni(COD)_2$ complex is better for the polymerization than the Ni(II)/Zn system. The MALLS study demonstrates that the absolute molecular weights of (*R*)-**11a,b** and (*S*)-**11** are about twice as much as the GPC results. Thus, using the polystyrene standard in GPC analysis significantly underestimates the actual molecular weight of these polydendrimers.[18]

The chiral optical properties of the polydendrimers were studied. We found that as the molecular weight

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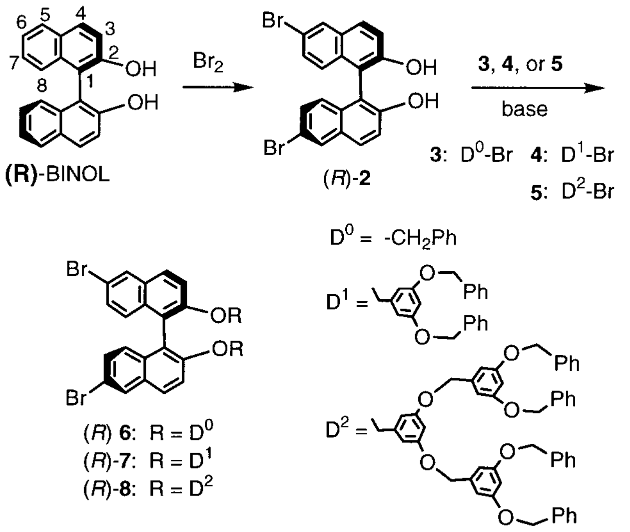
10.1021/ma011120+ CCC: $20.00

Table 1. Molecular Weights of the Polydendrimers

		GPC			MALLS			
polymer	polymerization method	M_w	M_n	PDI	M_w	M_n	PDI	isolated yield (%)
(*R*)-**9**	Ni(II)/Zn	6600	3600	1.8				62
(*R*)-**10**	Ni(II)/Zn	8200	5200	1.6				71
(*R*)-**11a**	Ni(II)/Zn	6800	5100	1.3	14 100	11 100	1.3	76
(*R*)-**11b**	$Ni(COD)_2$	11200	7200	1.6	26 200	19 300	1.4	86
(*S*)-**11**	$Ni(COD)_2$	16200	10500	1.5	35 300	23 000	1.5	82

Scheme 1. Synthesis of Precursor Dendrimers (*R*)-6, (*R*)-7, and (*R*)-8



increased from (*R*)-**11a,b** to (*S*)-**11**, their molar optical rotations (based on their binaphthyl units) also increased significantly from −254 of (*R*)-**11a** to +601 of (*S*)-**11**. To determine whether such an increase in optical rotation with respect to the molecular weights of the polymers is due to a secondary helical conformation of the polymer chain, the optical rotations of the polydendrimers are compared with those of precursor dendrimers (*R*)-**6**−(*R*)-**8** and Meijer's dendrimers (*S*)-**12**−(*S*)-**14**.[15a,b] We also prepared dendrimers (*R*)-**16**, (*R*)-**17**, and (*S*)-**18** that contain 6,6′-dinaphthyl substituents by carrying out the Suzuki coupling of naphthylboronic acid **15** with (*R*)-**6**, (*R*)-**7**, and (*S*)-**8**, respectively (Scheme 2). By analyzing the chain structures of polydendrimers **9**−**11**, it is clear that dendrimers (*R*)-**16**, (*R*)-**17**, and (*S*)-**18** should serve as better models for the repeating units of the polydendrimers than dendrimers (*S*)-**12**−(*S*)-**14**. Table 2 compares the optical rotations of the monobinaphthyl dendrimers with the polydendrimers. As shown in Table 2, dendrimers (*S*)-**12**−(*S*)-**14** not only have much smaller molar optical rotations than model dendrimers **16**−**18** but also have the opposite signs with respect to the same binaphthyl configuration. Similarly, precursor dendrimers (*R*)-**6**−(*R*)-**8** with 6,6′-dibromo substitution also give the opposite optical rotations as well as smaller values compared to the model dendrimers of the same binaphthyl configuration. This demonstrates that the 6,6′-dinaphthyl substituents in model dendrimers **16**−**18** have caused a dramatic electronic effect on their chiral optical response.[19] However, the molar optical rotation of the generation two model dendrimer (*S*)-**18** is very close to that of the high molecular weight generation two polydendrimer (*S*)-**11**. The molar optical rotations of model dendrimers (*R*)-**16** and (*R*)-**17** are also similar to those of (*R*)-**9** and (*R*)-**10**, respectively. The circular dichroism (CD) spectra of the polydendrimers exhibit similar Cotton effects to those of the model dendrimers (Figures 2 and 3). These results indicate that there is probably no predominately one-handed secondary helical conformation generated along the backbone of these polydendrimers beyond the chiral binaphthyl units. The observed increase in optical rotation from (*R*)-**11a**,**b** to (*S*)-**11** is thus attributed to the lower degree of polymerization of (*R*)-**11a**,**b** which raises the proportion of their end groups to the internal

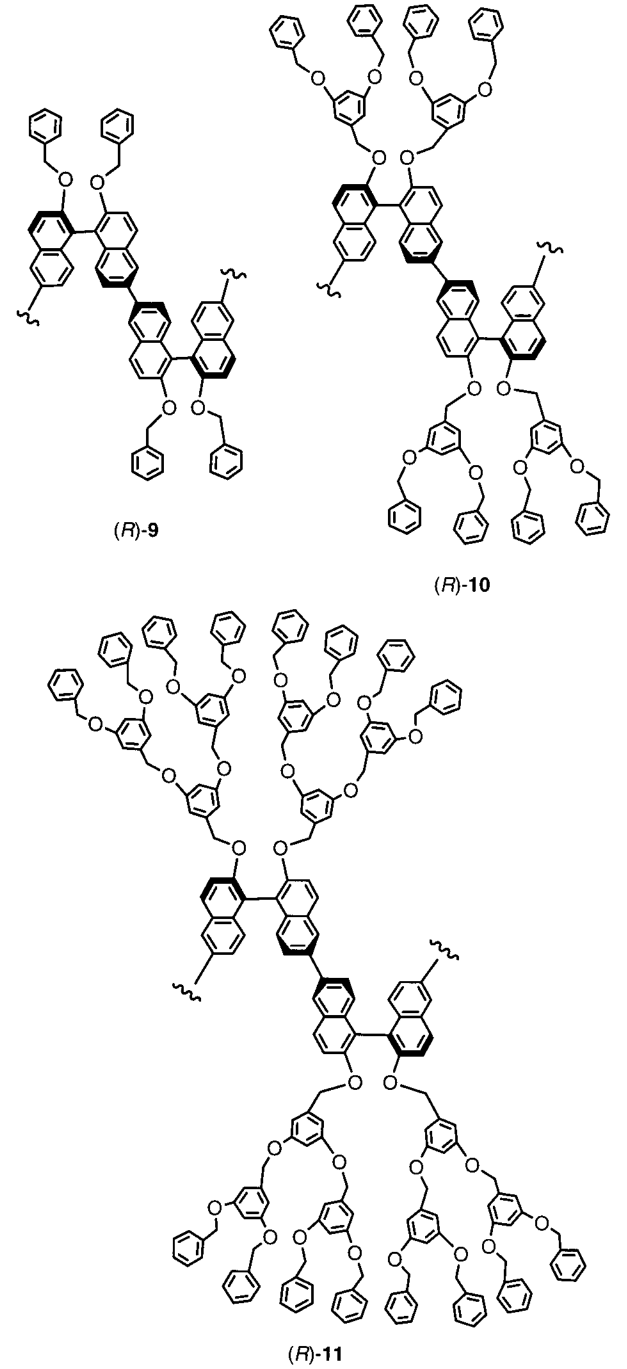


Figure 1. Optically active polydendrimers.

Table 2. Comparison of the Optical Rotations of the Polydendrimers with the Monobinaphthyl Dendrimers

	precursor dendrimer			polydendrimer[a]				Meijer's dendrimer			model dendrimer		
optical rotation	(*R*)-**6**	(*R*)-**7**	(*R*)-**8**	(*R*)-**9**	(*R*)-**10**	(*R*)-**11a**	(*R*)-**11b**	(*S*)-**11**	(*S*)-**12**	(*S*)-**13**	(*S*)-**14**	(*R*)-**16**	(*R*)-**17**	(*S*)-**18**
specific rotation $[\alpha]_D$	+30.3	+21.5	+20.5	−174.9	−89.7	−14.6	−30.5	+34.6	−45.5	−22.8	−15.6	−142.2	−73.5	+34.5
molar rotation $[\phi]$	+189	+225	+389	−812	−797	−254	−530	+601	−212	−203	−271	−1107	−885	+716

[a] The molar optical rotations of the polydendrimers are calculated based on their repeating binaphthyl units.

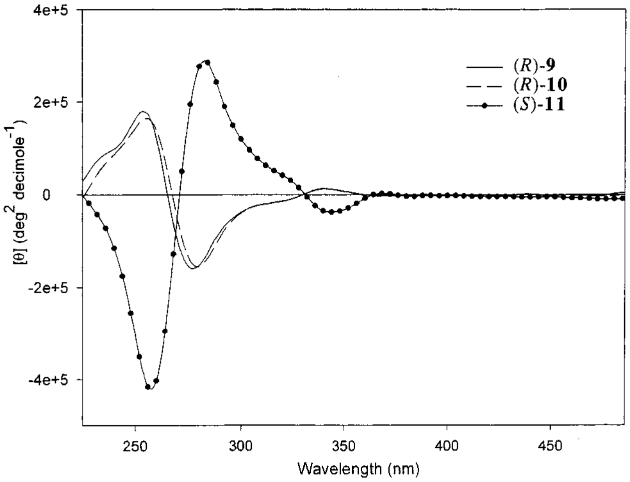


Figure 2. CD spectra of polydendrimers (*R*)-**9**, (*R*)-**10**, and (*S*)-**11** ($C = 2.5 \times 10^{-4}$ M THF).

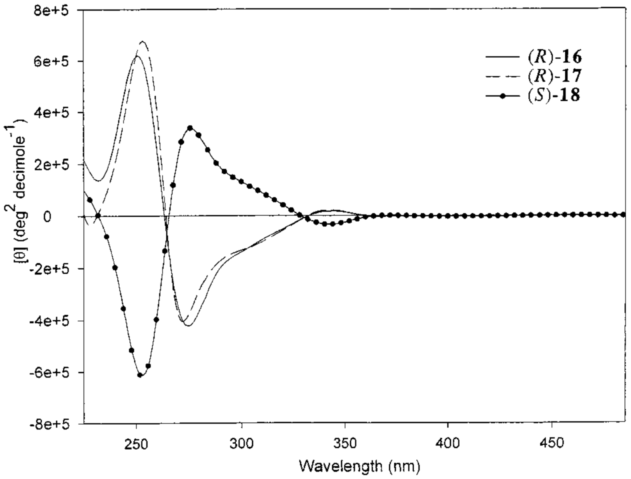
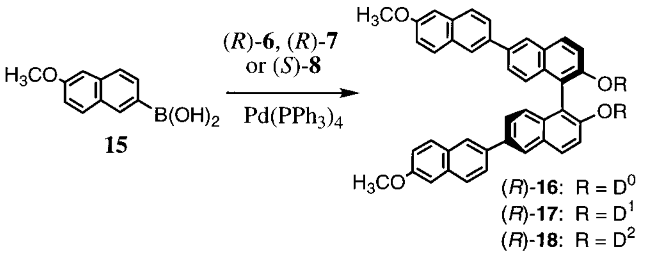


Figure 3. CD spectra of the model dendrimers (*R*)-**16**, (*R*)-**17**, and (*S*)-**18** ($C = 6.0 \times 10^{-6}$ M THF).

Scheme 2. Synthesis of Model Dendrimers 16–18



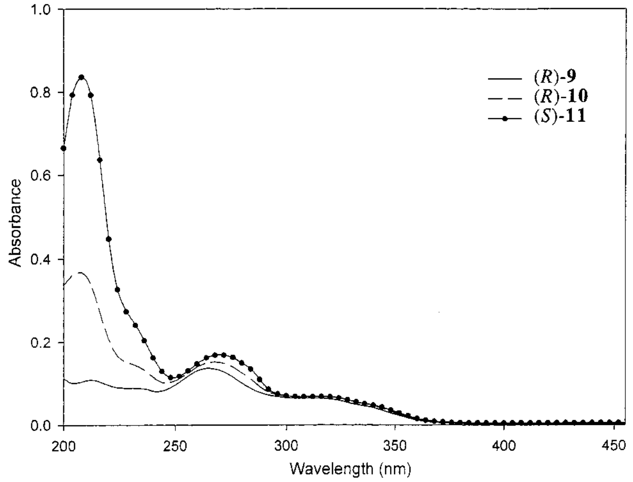
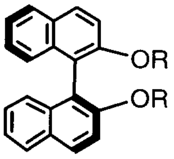


Figure 4. UV spectra of polydendrimers (*R*)-**9**, (*R*)-**10**, and (*S*)-**11** ($C = 2.5 \times 10^{-4}$ M THF).

repeating units over (*S*)-**11**. Because the end groups in these materials should contain either bromine or hydrogen atoms at the 6-positions of the binaphthyl unit, they are expected to give an opposite optical rotation from the 6,6′-dinaphthyl-substituted binaphthyls as shown by precursor dendrimers **6**–**8** and Meijer's dendrimers **12**–**14** in Table 2. This should cause an overall reduction of the optical rotations for the lower molecular weight polydendrimers.



(*S*)-**12**: R = D⁰
(*S*)-**13**: R = D¹
(*S*)-**14**: R = D²

Figure 4 gives the UV spectra of polydendrimers (*R*)-**9**, (*R*)-**10**, and (*S*)-**11**. All the polydendrimers (*R*)-**9**, (*R*)-**10**, and (*S*)-**11** display two similar absorptions at λ_{max} 265–270 and 308–317 nm, but a major difference appears at ca. 210 nm. At this wavelength, there is a large increase of absorption going from the generation zero polydendrimer (*R*)-**9** to the generation two polydendrimer (*S*)-**11** at the same molar concentration. This is attributed to the large increase of the phenylene units as the dendritic generation grows.

When the polydendrimers were excited at 320 nm, they all showed very strong emissions at 385 and 405 nm (Figure 5). The fluorescence quantum yields of polydendrimers (*R*)-**9**, (*R*)-**10**, and (*S*)-**11** were 46.0%, 54.1%, and 55.8%, respectively, measured in THF by using quinine sulfate as the standard.[20] When these materials were excited at 208 nm where the absorption was mostly due to the dendritic phenylenes, strong emissions were also observed at 385 and 405 nm. This demonstrates that there is energy migration from the dendritic side chains to the polybinaphthyl backbone. The dendritic arms alone exhibited emission at 312 nm, which was absent when the polydendrimers were excited in the range 208–270 nm. Because of the limitation of our fluorescence spectrometer at the short excitation wavelength, the efficiency of the energy migration was not quantified. The fluorescence quantum yield of model dendrimer (*S*)-**18** was 48.6% ($\lambda_{exc} = 270$ nm), similar to that of the polydendrimers.

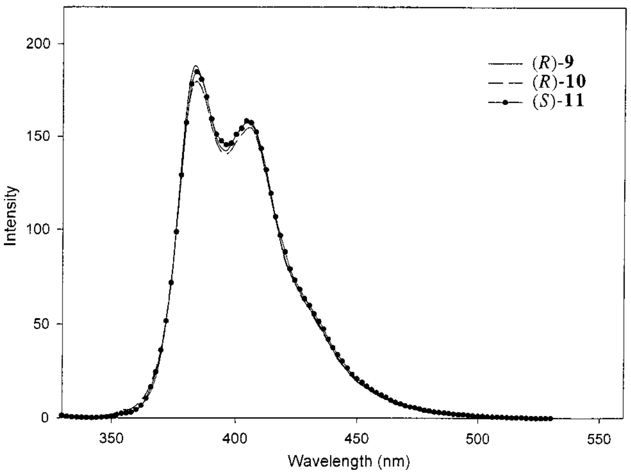


Figure 5. Fluorescence spectra of polydendrimers (*R*)-**9**, (*R*)-**10**, and (*S*)-**11** ($C = 1.5 \times 10^{-6}$ M THF; $\lambda_{exc} = 320$ nm).

Thermal gravemetric analysis of the polydendrimers showed that these materials were stable up to and above 300 °C before they started to lose their dendritic side chains. Differential scanning calorimetry study showed that the glass transition temperature (T_g) of these materials decreased significantly as the dendritic generation of the side chain increased.[22] The T_g's of (*R*)-**9**, (*R*)-**10**, and (*S*)-**11** were 162, 87, and 55 °C, respectively, and the T_g of polybinaphthyl **1** was 119 °C.[11b] Thus, introduction of the dendritic side chains has a strong effect on the thermal transition of the polybinaphthyl.

In summary, the first optically active polydendrimers have been synthesized by polymerization of chiral dendrimers.[23] Study of the chiral optical properties of the polydendrimers and their model compounds has revealed that the interaction of the dendritic side chain along the polybinaphthyl backbone cannot induce a secondary helical conformation. Significant reduction of glass transition temperature is observed as the dendritic generation of the polydendrimers increases. Energy migration from the dendritic side chains to the more conjugated polybinaphthyl main chain has been observed. Collaboration with colleagues to study the EL property as well as the circular polarized light emission of these optically active polydendrimers is in progress. We expect that the dendritic arms of the polybinaphthyl will not only conduct light harvesting but also may reduce the excimer formation of the solid films[12] and enhance the EL efficiency.

Experimental Section

General Data. NMR spectra were recorded using a General Electric QE-300 spectrometer (300 MHz) for ^{1}H and a Varian-300 spectrometer (75 MHz) for ^{13}C in either dimethyl-d_6 sulfoxide or chloroform-*d* purchased from Cambridge Isotope Laboratories, Inc. Ar, Ar′, and Ar″ refer to the successive generations (0−2) of aromatic units when discussing the ^{1}H NMR peak assignment of the dendritic arms. Elemental analyses were carried out using a Perkin-Elmer 2400 series II CHN S/O analyzer. Fluorescence measurements were recorded using a Perkin-Elmer LS-50B luminescence spectrometer. UV−vis spectra were measured on a Varian Cary 5E UV−vis−NIR spectrophotometer. Infrared data were taken on a Nicolet Impact 400D FT-IR spectrometer in KBr pellet form. Circular dichroism (CD) spectra were recorded on a JASCO J-720 spectropolarimeter. Specific optical rotation measurements were taken on a JASCO DIP-1000 digital polarimeter. Thermogravimetric analysis (TGA) and differential scanning calorimetry (DSC) were carried out using a TA Instruments TGA 2050 and DSC 2920, respectively. Molecular weight measurements on the polymers were collected and compared using both gel permeation chromatography (GPC) and multiangle laser light scattering (MALLS) techniques. GPC data were collected using a Waters Corp. 515 pump, a 410 differential refractometer, and Ultrastyragel linear GPC columns. MALLS data were collected using a Hewlett-Packard 1100 GPC with a diode array detector and a Wyatt Technology Corp. DAWN DSP laser photometer with a Optilab interferometric refractometer. Mass spectra were collected at both the University of Virginia on a Finnigan MAT LC-Q mass spectrometer system using positive ion atmospheric pressure chemical ionization (APCI) and by the University of California (Riverside) instrumentation facility on a PE-Biosystems MALDI TOF DE-STR system.

All reagents were puchased from Aldrich Chemical Co. unless otherwise noted. Bis(1,5-cyclooctadiene)nickel(0) and 2,2′-bipyridine were purchased from Strem Chemicals Inc. All reagents were used as received unless otherwise noted. Acetone, dichloromethane, and ethyl acetate were refluxed over K_2CO_3 and distilled under nitrogen before use. Hexanes and tetrahyrofuran (THF) were refluxed over sodium/benzophenone and distilled under nitrogen before use. Synthesis of compound 15 followed the literature procedure.[24]

Preparation and Characterization of Precursor Dendrimer (*R*)-6.[14] Under nitrogen, a mixture of (*R*)-**2** (3.00 g, 6.75 mmol), benzyl bromide (**3**) (2.7 equiv), and anhydrous K_2CO_3 (4.0 equiv) in acetone (40 mL) was heated at reflux with stirring for 48 h. The reaction was monitored by ^{1}H NMR and TLC. Upon completion of the reaction, water was added and the compound extracted with EtOAc several times. The organic layer was washed with brine (2 times), dried over Na_2SO_4, and then rotoevaporated to remove the solvent. The resulting oily residue crystallized upon sitting overnight to give (*R*)-**6** in 87% yield (3.42 g); mp 112−113 °C. FT-IR (KBr) cm^{-1}: 1614 (w), 1583 (s), 1494 (s), 1452 (m), 1328 (m), 1269 (s), 1067 (s), 911 (m), 874 (w), 736 (m). The ^{1}H and ^{13}C NMR data match those of the reported.[14] MS (APCI) *m*/*z*: 624 (M$^+$), 546, 457. Anal. Calcd for $C_{34}H_{24}O_2Br_2$: C, 65.41; H, 3.87. Found: C, 65.35; H, 3.74.

General Procedure for the Preparation of Precursor Dendrimers (*R*)-7, (*R*)-8, and (*S*)-8. Under nitrogen, a mixture of (*R*)- or (*S*)-**2** (1.00 equiv), dendritic bromide **4** or **5** (2.05 equiv), 18-crown-6 (0.20 equiv), and a large excess of anhydrous K_2CO_3 (6−10 equiv) in freshly distilled acetone was heated at reflux for 2 days. The reaction was monitored by ^{1}H NMR and TLC. Upon completion, the mixture was allowed to cool to room temperature, and the acetone was slowly removed via rotoevaporation. The solid residue was dissolved in CH_2Cl_2 and washed with water and brine. The organic layer was dried over Na_2SO_4 before rotoevaporation to dryness. The solid residue was dissolved in a minimum amount of CH_2Cl_2, precipitated with MeOH, and centrifuged (3 times). Further purification was required in some cases, using column chromatography on silica gel eluted with CH_2Cl_2/hexanes (3:1). Note: several attempts to carry out purification by recrystallization were unsuccessful.

Characterization of Precursor Dendrimer (*R*)-7. By starting with (*R*)-**2** (2.50 g, 5.63 mmol), the material (5.18 g) obtained after general workup underwent extensive purification by column chromatography on silica gel to yield pure (*R*)-**7** in 67% yield (3.98 g); mp 63−64 °C. FT-IR (KBr) cm^{-1}: 1596 (s), 1496 (w), 1450 (m), 1376 (w), 1269 (m), 1159 (s), 1062 (s), 670 (w). ^{1}H NMR ($CDCl_3$, 300 MHz): δ 4.65 (s, 8H, Ar′−CH_2), 5.00 (s, 4H, Ar−CH_2), 6.20 (d, $J = 2.4$ Hz, 4H, Ar−H), 6.37 (t, 2H, Ar−H), 7.02 (d, $J = 9.0$ Hz, 2H, H-8), 7.25−7.47 (m, Ar″−H, H-3, and H-7), 7.78 (d, $J = 9.0$ Hz, 2H, H-4), 7.92 (d, $J = 1.5$ Hz, 2H, H-5). ^{13}C NMR ($CDCl_3$, 75 MHz): δ 69.97, 70.87, 101.53, 105.33, 116.60, 117.88, 120.26, 127.20, 127.79, 128.14, 128.70, 128.80, 130.06, 130.51, 132.68, 136.87, 139.62, 154.36, 160.03. MS (APCI) *m*/*z*: 1050 (M$^+$), 606. Anal. Calcd for $C_{62}H_{48}O_6Br_2$: C, 71.00; H, 4.61. Found: C, 71.33; H, 4.58.

Characterization of Precursor Dendrimers (*R*)-8 and (*S*)-8. The precursor dendrimer (*R*)-**8** was obtained in 89% yield (2.27 g) by starting with (*R*)-**2** (0.60 g, 1.35 mmol); mp

65−66 °C. FT-IR (KBr) cm^{-1}: 1596 (s), 1496 (w), 1452 (m), 1374 (m), 1157 (s), 1058 (s), 697 (w). ^{1}H NMR (CDCl$_3$, 300 MHz): δ 4.52 (s, 8H, Ar′−CH$_2$), 4.98 (s, 20H, Ar−CH$_2$, Ar″−CH$_2$), 6.13 (d, J = 2.1, 4H, Ar−H), 6.28 (t, 2H, Ar−H), 6.54−6.60 (m, 12H, Ar′−H), 6.99 (d, J = 8.7, 2H, H-8), 7.20−7.43 (m, 44H, Ar‴−H, H-3, H-7), 7.70 (d, J = 9.3, 2H, H-4), 7.86 (d, J = 2.1, 2H, H-5). ^{13}C NMR (CDCl$_3$, 75 MHz): δ 69.91, 70.26, 70.93, 101.48, 101.86, 105.38, 106.77, 116.70, 117.91, 120.39, 127.74, 128.16, 128.78, 130.09, 130.57, 132.70, 137.03, 139.30, 139.65, 154.21, 159.92, 160.29. MS (MALDI) *m/z*: 1919 (M + Na$^+$), 1840. Anal. Calcd for $C_{118}H_{96}O_{14}Br_2$: C, 74.68; H, 5.10. Found: C, 74.30; H, 5.08. Precursor dendrimer (*S*)-**8** was obtained in 87% yield (2.97 g) by starting with (*S*)-**2** (0.80 g, 1.80 mmol). The characterization data matched those of (*R*)-**8**.

General Procedure for the Preparation of Polydendrimers (*R*)-9, **(*R*)-10**, **(*R*)-11a**, **(*R*)-11b, and (*S*)-11**. The polymerizations were carried out using two different methods (**I** and **II**, see below). Under nitrogen, a mixture of the precursor dendrimer (1 equiv) and the metal reagents in DMF was stirred at 85−90 °C. The reaction was followed by monitoring the disappearance of the precursor dendrimer with TLC. Once the reaction was complete, the mixture was cooled to room temperature, diluted with CH$_2$Cl$_2$, and washed with 1 N HCl and brine (2 times). The organic layer was then dried over Na$_2$SO$_4$ before rotoevaporation to dryness. The solid was dissolved in CH$_2$Cl$_2$, precipitated with MeOH, and centrifuged (3 times). The resulting solid was then dissolved in THF and filtered through silica gel, yielding the desired polydendrimer.

The Polymerization Methods. I. NiCl$_2$ (0.10 equiv), excess zinc (3.40 equiv), 2,2′-bipyridine (0.10 equiv), and triphenylphosphine (0.40 equiv). **II.** Ni-[COD]$_2$ (1.24 equiv), 2,2′-bipyridine (1.5 equiv), and cyclooctadiene (COD) (3.00 equiv).

Characterization of Polydendrimer (*R*)-9. By using (*R*)-**6** (1.53 g, 2.54 mmol) and method **I**, (*R*)-**9** was obtained in 62% yield (0.73 g). FT-IR (KBr) cm^{-1}: 1588 (m), 1497 (m), 1452 (m), 1325 (m), 1220 (s), 1055 (s), 1025 (s), 819 (w), 735 (m), 695 (m). ^{1}H NMR (CDCl$_3$, 300 MHz): δ 5.06 (s, 4H, CH$_2$, small peak at 5.08), 6.99 (br s), 7.08 (br s), 7.20−7.66 (several broad multiplets), 7.84 (br m), 8.14 (br s) (the small peaks may be due to the end groups). ^{13}C NMR (CDCl$_3$, 75 MHz): δ 71.30, 116.17, 116.52, 120.76, 123.92, 125.73, 125.97, 126.37, 126.91, 127.44, 128.08, 128.30, 129.50, 129.81, 129.93, 131.74−132.68, 133.50, 134.39, 136.52, 137.67, 154.42. Anal. Calcd for $C_{34}H_{24}O_2$: C, 87.91; H, 5.21. Found: C, 87.31; H, 5.34.

Characterization of Polydendrimer (*R*)-10. By using precursor dendrimer (*R*)-**7** (1.00 g, 0.95 mmol) and method **I**, (*R*)-**10** was obtained in 71% yield (0.60 g). FT-IR (KBr) cm^{-1}: 1595 (s), 1497 (w), 1451 (m), 1374 (w), 1325 (w), 1218 (m), 1157 (s), 1052 (s), 1025 (m), 821 (w), 736 (m), 696 (m). ^{1}H NMR (CDCl$_3$, 300 MHz): δ 4.56 (s, 8H, Ar′−CH$_2$, small peak at 4.61), 5.03 (s, 4H, Ar−CH$_2$), 6.13−6.39 (m, Ar−H), 7.05−7.55 (br m), 7.74−8.00 (br m) (the small peaks may be due to the end groups). ^{13}C NMR (CDCl$_3$, 75 MHz): δ 69.98, 71.06, 101.59, 105.22, 116.16, 120.62, 125.86, 126.23, 126.77, 127.85, 128.09, 128.66, 129.60, 129.90, 133.46, 136.20, 136.88, 140.06, 154.24, 160.00. Anal. Calcd for $C_{62}H_{48}O_6$: C, 83.76; H, 5.44. Found: C, 84.63; H, 5.79.

Characterization of Polydendrimers (*R*)-11a, 11b, and (*S*)-11. By using (*R*)-**8** (0.83 g, 0.44 mmol) and method **I**, polydendrimer (*R*)-**11a** was obtained in 76% yield (0.58 g). By using (*R*)-**8** (0.55 g, 0.29 mmol) and method **II**, polydendrimer (*R*)-**11b** was obtained in 86% yield (0.44 g). By using (*S*)-**8** (1.40 g, 0.74 mmol) and method **II**, polydendrimer (*S*)-**11** was obtained in 82% yield (1.05 g). FT-IR (KBr) cm^{-1}: 1596 (s), 1452 (m), 1375 (w), 1322 (w), 1217 (w), 1156 (s), 1055 (s), 831 (w), 736 (m), 697 (m). ^{1}H NMR (CDCl$_3$, 300 MHz): δ 4.31−4.55 (br m), 4.72−5.06 (br m), 6.06−6.31 (br m), 6.42−6.62 (br m), 6.93−7.94 (br m). ^{13}C NMR (CDCl$_3$, 75 MHz): δ 69.89, 70.13, 70.90, 101.56, 101.83, 106.82, 115.58−116.49, 120.31−121.14, 125.38−126.88, 127.31, 127.71, 128.11, 128.72, 129.55, 129.90, 131.82−132.70, 134.45, 134.33, 136.28, 137.03, 139.35, 140.07, 154.18, 159.86, 160.24. Anal. Calcd for $C_{118}H_{96}O_{14}$: C, 81.55; H, 5.57. Found for (*R*)-**11a**: C, 82.03; H, 5.65. Found for (*R*)-**11b**: C, 81.32; H, 5.87. Found for (*S*)-**11**: C, 81.16; H, 5.47.

Preparation and Characterization of Model Dendrimer (*R*)-16. Under nitrogen, to a flask containing naphthylboronic acid **15** (406 mg, 2 mmol) and (*R*)-**6** (317 mg, 0.5 mmol) in THF (20 mL) was added a degassed aqueous solution of K$_2$CO$_3$ (2 N, 5 mL) and then 5 mol % of Pd(PPh$_3$)$_4$ (28 mg).[25] The reaction mixture was heated under reflux for 24 h (80 °C bath temperature) and monitored with TLC (eluent: hexane: ethyl acetate = 2:1). A major blue fluorescence spots at Rf = 0.5 indicated the formation of the product. After the reaction mixture was cooled to room temperature, water (10 mL) was added. Ethyl acetate was used to extract, and the resulting organic layer was washed with brine and dried with Na$_2$SO$_4$. The solvent was removed with rotoevaporation, and the resulting residue was purified by flash chromatography on silica gel (eluent: hexane:ethyl acetate = 5:1−3:1). After removal of solvent, dendrimer (*R*)-**16** was obtained as a white solid in 63% yield (248 mg). ^{1}H NMR (CDCl$_3$, 300 MHz): δ 3.95 (s, 6H, OCH$_3$), 5.11 (s, 4H, OCH$_2$), 7.02−7.27 (m, 14 H), 7.37 (d, J = 9.0 Hz, 2H), 7.49 (d, J = 9.0 Hz, 2H), 7.65 (dd, J = 9.0, 1.8 Hz, 2H), 7.80−7.84 (m, 6H), 8.04 (d, J = 9.0 Hz, 2H), 8.07 (br s, 2 H), 8.21 (d, J = 1.8 Hz, 2 H). ^{13}C NMR (CDCl$_3$, 75 MHz): δ 50.89, 66.74, 101.15, 111.98, 114.67, 116.15, 121.17, 121.37, 121.75, 122.31, 122.88, 123.74, 125.27 (shoulders), 128.90, 129.24, 131.91, 133.08, 149.84, 153.25. MS (FIA-APCI) *m/z* 779.2 (M + H$^+$).

Preparation and Characterization of Model Dendrimer (*R*)-17. The same procedure as the preparation of (*R*)-**16** was used with the following stoichiometry: **15** (121 mg, 0.6 mmol), (*R*)-**7** (156 mg, 0.15 mmol), Pd(PPh$_3$)$_4$ (20 mg), and 2 N K$_2$CO$_3$ (5 mL). Dendrimer (*R*)-**17** was obtained in 67% yield (120 mg). ^{1}H NMR (CDCl$_3$, 300 MHz): δ 3.96 (s, 6H, OCH$_3$), 4.62 (shoulders, 8H, OCH$_2$), 5.08 (s, 4H, OCH$_2$), 6.27 (s, 4H), 6.36 (s, 2H), 7.17 (m, 4H), 7.27−7.29 (br m, 20 H), 7.39 (d, J = 9.0 Hz, 2H), 7.53 (d, J = 9.0 Hz, 2H), 7.64−7.78 (m, 8H), 7.92 (s, 2H), 8.02 (d, J = 9.0 Hz, 2H), 8.09 (s, 2H). ^{13}C NMR (CDCl$_3$, 75 MHz): δ 50.90, 65.38, 66.47, 97.04, 100.59, 101.11, 111.66, 114.60, 116.07, 121.08, 121.33, 121.56, 121.67, 121.83, 122.83, 123.28, 123.50, 124.06, 124.80, 125.32, 128.86, 129.25, 131.51, 131.91, 132.30, 135.45, 149.68, 153.26, 155.40. MS (FIA-APCI) *m/z*: 1204.1 (M + H$^+$).

Preparation and Characterization of Model Dendrimers (*S*)-18. The same procedure as the preparation of (*R*)-**16** was used with the following stoichiometry: **15** (90 mg, 0.42 mmol), (*S*)-**8** (200 mg, 0.106 mmol), Pd(PPh$_3$)$_4$ (12 mg), and 2 N K$_2$CO$_3$ (5 mL). (*S*)-**18** was obtained in 46% yield (100 mg). ^{1}H NMR (CDCl$_3$, 300 MHz): δ 3.88 (s, 6H, OCH$_3$), 4.47 (s, 8H, OCH$_2$), 4.90 (s, 16H, OCH$_2$), 5.06 (s, 4H, OCH$_2$), 6.19 (s, 4H), 6.27 (s, 2H), 6.56 (s, 12H), 7.04 (d, J = 2.4 Hz, 2H), 7.09 (dd, J = 2.1 Hz, 2H), 7.26−7.36 (m, 40H), 7.38 (d, J = 9.0 Hz, 2H), 7.50 (d, J = 9.0 Hz, 2H), 7.63 (d, J = 8.4 Hz, 4H), 7.68 (d, J = 8.4 Hz, 4H), 7.88 (s, 2H), 7.94 (d, J = 9.3 Hz, 2H), 8.03 (s, 2H). ^{13}C NMR (CDCl$_3$, 75 MHz): δ 55.47, 67.00, 70.18, 71.06, 101.63, 101.92, 105.17, 105.74, 106.87, 116.30, 119.25, 120.75, 125.70, 125.95, 126.15, 126.30, 126.50, 127.47, 127.76, 128.18, 128.77, 129.40, 129.97, 133.47, 133.87, 136.07, 136.55, 137.02, 139.32, 140.01, 154.23, 157.85, 159.89, 160.27. MS (MALDI) *m/z*: 2073.6 (M + Na$^+$).

Special Sample Cells. Fluorescence measurements were taken using a dye laser cell (inner cross section/light path: 10 × 0.5 mm; outside dimensions $H \times W \times D$: 40 × 12.5 × 12.5 mm) purchased from Hellma-Worldwide, part 115.072, with the light path of 0.5 mm. UV−vis and CD data were collected using a cell from JASCO Inc. with a 0.1 mm path length. Small path lengths were used to reduce the amount of solvent (HPLC grade THF) absorbance.

Quantum Yield Measurements. Polymer samples, dissolved in THF, were measured relative to a solution of quinine sulfate in 1.0 N aqueous H$_2$SO$_4$ (quantum yield = 0.55). Emission spectra were recorded on a Spex Fluorolog 2+2 spectrofluorometer. Excitation and emission slits were set to 4.0 and 3.0 mm, respectively, and scans were recorded at a rate of 1 nm/s over the range from 350 to 800 nm. Emission spectra were corrected for lamp intensity and detector sensitivity according to the method of Gardecki and Maroncelli,[26] and the integrated area under the corrected spectra was used for the intensity of each sample.

Acknowledgment. Support of this work from the Office of Naval Research (N00014-99-1-0531) is gratefully acknowledged. We thank Professor James N. Demas for his help on the fluorescence quantum yield measurement.

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MA011120+