2358 *J. Org. Chem.* **2001,** *66,* 2358−2367

Optically Active Dendrimers with a Binaphthyl Core and Phenylene Dendrons: Light Harvesting and Enantioselective Fluorescent Sensing

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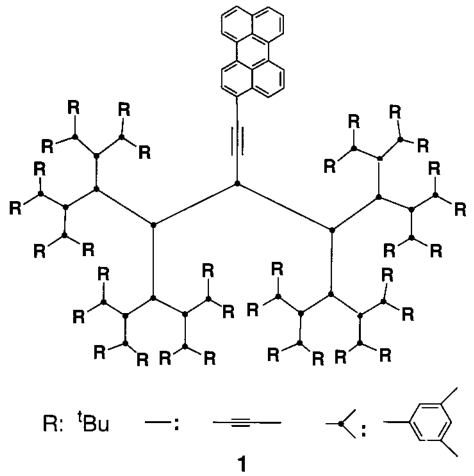
Received November 3, 2000

Optically active dendrimers containing a 1,1′-binaphthyl core and cross-conjugated phenylene dendrons were synthesized and characterized. The chiral optical properties of these phenylene-based dendrimers are different from the previously reported phenyleneethynylene-based dendrimers probably because of the increased steric interaction between the adjacent phenylene units. UV and fluorescence spectroscopic studies demonstrate that the energy harvested by the periphery of the dendrimers can be efficiently transferred to the more conjugated core, generating much enhanced fluorescence signal at higher generation. The fluorescence of these dendrimers can be quenched both efficiently and enantioselectively by chiral amino alcohols. The energy migration and light-harvesting effects of the dendrimers make the higher generation dendrimer more sensitive to fluorescent quenchers than the lower ones. Thus, the dendritic structure provides a signal amplification mechanism. These materials are potentially useful in the enantioselective recognition of chiral organic molecules.

Introduction

The discovery of light-harvesting phenomena in photosynthesis has stimulated a tremendous amount of research.[1] Various types of light-harvesting materials have been designed and synthesized to mimic the photosynthetic process. Among these studies, the use of dendrimers has received particular attention.[2−7] For example, a phenyleneethynylene-based dendrimer (**1**) prepared by Moore and co-workers shows that its dendritic arms can act as antenna to absorb as well as transfer light energy to the more conjugated center, leading to greatly enhanced fluorescence signal.[2] Fox and co-workers have studied the light harvesting properties of phenyl benzyl ether dendrimers.[3d] Jiang and Aida have found that porphyrin-centered dendrimers having a continuous array of aryl ether peripheral framework exhibit very efficient energy transfer from the dendritic antenna to the porphyrin core.[5a] Fréchet and co-workers also reported the use of dye-labeled dendrimers to carry out energy migration.[7]



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In our laboratory, we are interested in using the light-harvesting and energy-migration properties of chiral dendrimers[8] to develop efficient enantioselective fluorescent sensors. Chiral discrimination in luminescence has been studied in the past two decades.[9−11.] These studies involve a variety of luminescent materials including

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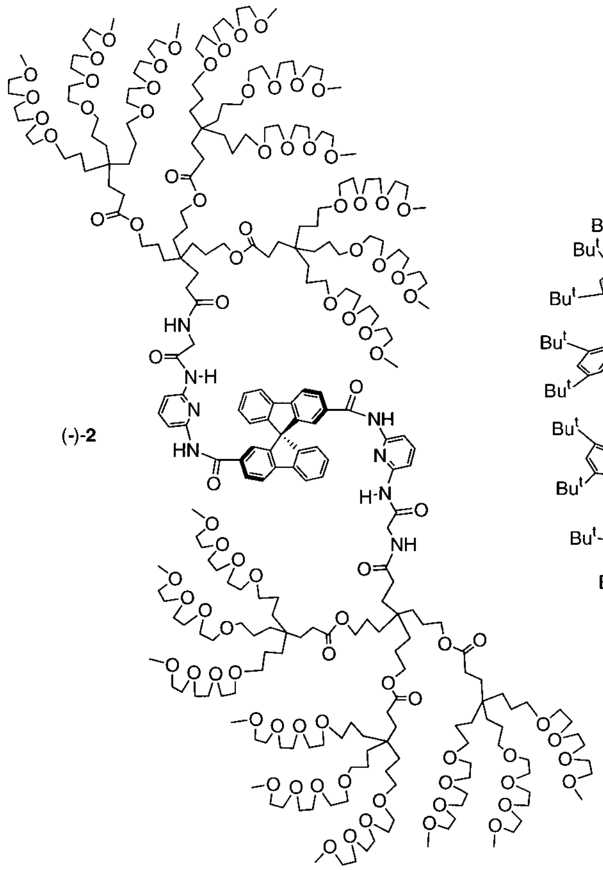
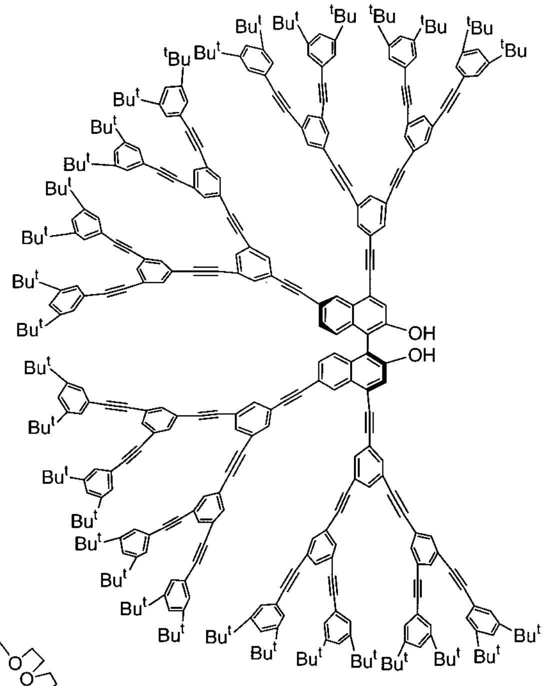
Chart 1

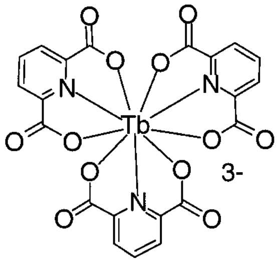


(-)-**2**

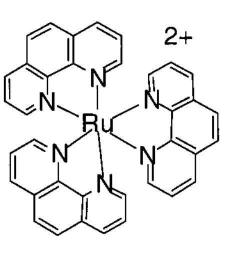


(*S*)-**3**

inorganic complexes,[9] organic molecules,[10,11] and enzymes.[11g,h] Enantioselective responses have been observed when chiral luminophores are treated with chiral quenchers or enhancers. In a few cases, the relationship between the fluorescence properties of the luminophores and the enantiomeric purity of the substrates have been established.[9b,10g,11a,b,h] For example, Richardson and co-workers studied the circular polarized luminescence of a racemic complex $Tb(dpa)_3^{3-}$ in the presence of the Λ and Δ enantiomers of $Ru(Phen)_3^{3+}$.[9b] A linear relationship between the enantiomeric composition of $Ru(Phen)_3^{3+}$ and the steady-state emission dissymmetry factor of $Tb(dpa)_3^{3-}$ was observed.



Λ and Δ $Tb(dpa)_3^{3-}$



Λ and Δ $Ru(phen)_3^{2+}$

Using ^1H NMR and CD spectroscopy, Diederich and co-workers have demonstrated that chiral dendrimers such as **2** are able to conduct enantioselective recognition of monosaccharides (Chart 1).[12] Recently, we have prepared the chiral cross-conjugated dendrimer (*S*)-**3** and have shown that it can be used as an enantioselective fluorescent sensor for the recognition of chiral amino alcohols.[13] The fluorescence intensity change of this dendrimer in the presence of amino alcohol quenchers

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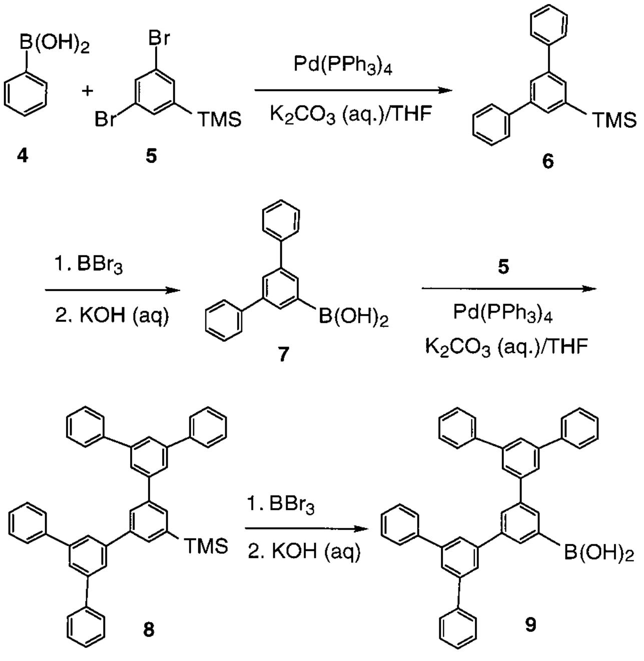
Scheme 1. Synthesis of Phenylene Dendrons



was found to be much larger than that of the small 1,1′-bi-2-naphthol molecule. This is because the fluorescence quenching occurs through the interaction of the quenchers with the binaphthyl core where the light energy harvested by the dendrons is transferred. Thus, the dendrimer is a much more sensitive fluorescent sensor than the corresponding small molecule. Efficient and enantioselective fluorescent sensors are potentially useful in the real-time determination of the enantiomeric composition of chiral organic compounds. A few binaphthyl-based chiral dendrimers containing flexible dendrons have also been studied by other researchers.[14,15] For example, Diederich and co-workers found that a binaphthyl-based chiral dendrimer was capable of molecular recognition.[15c] On the basis of our work on (*S*)-**3**, we have further prepared optically active phenylene-based dendrimers as enantioselective fluorescent sensors. Herein, our synthesis of these materials and their use in the fluorescent recognition of chiral amino alcohols are reported.

Results and Discussion

1. Synthesis and Characterization of the Structurally Rigid Chiral Dendrimers. Miller and co-workers have used the aryl boronic acids such as **4**, **7**, and **9** to synthesize *meta*-phenylene-based dendrimers.[16] To synthesize phenylene-based rigid chiral dendrimers, we have also prepared the aryl boronic acids by using a slightly modified procedure of Miller's (Scheme 1). The Suzuki coupling[17] of phenylboronic acid (**4**) with 1,3-dibromo-5-trimethylsilylbenzene (**5**)[18] gave 5-trimethylsilyl-1,3-diphenylbenzene (**6**). Reaction of **6** with BBr_3 followed by hydrolysis produced 3,5-diphenylphenylboronic acid (**7**). The Suzuki coupling of **7** with **5** gave **8**, which was then converted to **9**.

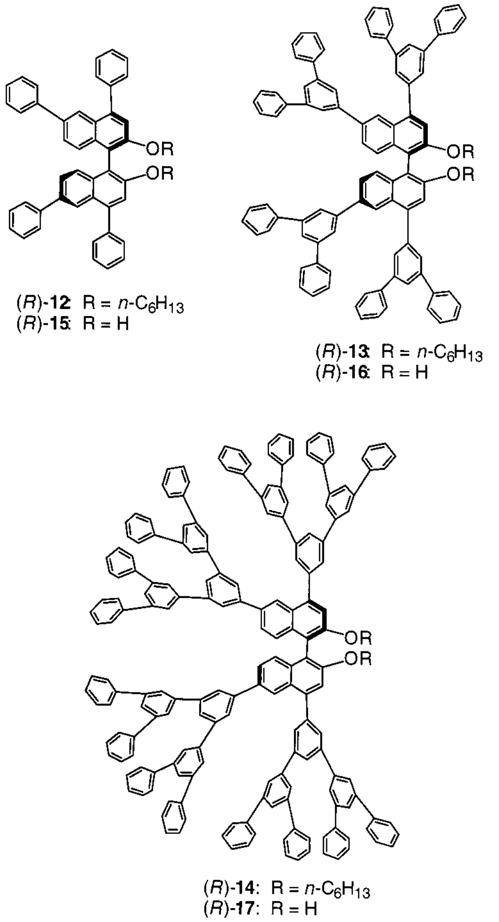


Figure 1. Phenylene-based chiral dendrimers.

The optically active (*R*)-4,4′,6,6′-tetrabromo-2,2′-dihexyloxy-1,1′-binaphthyl [(*R*)-**11**] was synthesized in two steps from (*R*)-1,1′-bi-2-naphthol [(*R*)-BINOL] (Scheme 2). Alkylation of (*R*)-BINOL gave (*R*)-**10** in over 95% yield, which was then brominated at room temperature to (*R*)-**11** in over 80% yield.[13]

The Suzuki coupling of the boronic acids **4**, **7**, and **9** with (*R*)-**11** in refluxing THF in the presence of 3 mol % of $Pd(PPh_3)_4$ and 2 M K_2CO_3 (aq) gave compounds (*R*)-**12**−(*R*)-**14**, respectively. Because their R_f values were very close to that of PPh_3, these compounds were difficult to purify by flash column chromatography. They were thus passed through a short plug of silica gel without further purification for the next step. Treatment of the crude (*R*)-**12**−(*R*)-**14** with BBr_3 followed by hydrolysis gave the corresponding BINOL-based generation zero dendrimer (*R*)-**15**, the generation one dendrimer (*R*)-**16**, and the generation two dendrimer (*R*)-**17**. These compounds were purified by flash chromatography on silica gel. After elution with ethyl acetate and hexane, (*R*)-**15**−(*R*)-**17** were obtained in 80%, 71%, and 58% yields, respectively. The lower yield of (*R*)-**17** was due to its lower solubility in the eluent.

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Table 1. Physical Properties of the Dendrimers (*R*)-15−(*R*)-17

	dendrimer		
	(*R*)-**15** (G0)	(*R*)-**16** (G1)	(*R*)-**17** (G2)
mass spectral data	CI, 591 $(M + H)^+$	EI, 1199 $(M + H)^+$	FAB, 2417 $(M + H)^+$
GPC Mn (PDI) (THF, polystyrene standard)	570 (PDI = 1.03)	1100 (PDI = 1.03)	2200 (PDI = 1.03)

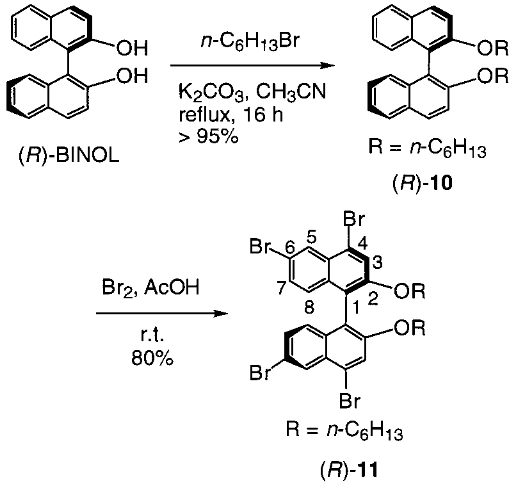
Table 2. Optical Rotation Data of the Chiral Dendrimers

	dendrimer		
	(*R*)-**15** (G0)	(*R*)-**16** (G1)	(*R*)-**17** (G2)
molecular weight	590.7	1199.5	2417.1
molar optical rotation (M)	−391	−704	−754
specific optical rotation $[\alpha]_D$ (THF)	−66.3 ($c = 1.03$)	−51.6 ($c = 1.04$)	−31.2 ($c = 1.04$)

Table 3. CD Spectral Data of the Dendrimers (*R*)-15−(*R*)-17

	dendrimer		
	(*R*)-**15** (G0)	(*R*)-**16** (G1)	(*R*)-**17** (G2)
CD [Θ] (λ, nm)	6.37×10^{-5} (254)	-4.75×10^{-5} (282)	2.72×10^{-5} (244)
(CH_2Cl_2)	-6.79×10^{-5} (272)		-3.64×10^{-5} (287)

Scheme 2. Synthesis of Optically Active (*R*)-11



Dendrimers (*R*)-**15**−(*R*)-**17** are pale yellow solids. They are soluble in common polar organic solvents such as acetone, ethyl acetate, methylene chloride, chloroform, and THF but are insoluble in nonpolar solvents such as hexane and toluene. In the ^{1}H NMR spectra of these dendrimers, a signal at δ 8.18 (d, $J = 1.8$ Hz), 8.49 (s), or 8.59 (s) is attributed to the 5,5′-protons of (*R*)-**15**, (*R*)-**16**, or (*R*)-**17**. This indicates a C_2 symmetric structure of these compounds in solution. The expected molecular ions of (*R*)-**15**−(*R*)-**17** were observed in their CI, EI, and FAB mass spectra, which support their structures. Table 1 summarizes the mass spectral results and gel permeation chromatography (GPC) data of these dendrimers. The GPC results are consistent with the monodisperse nature of these materials.

2. Optical Spectroscopic Studies of the Chiral Dendrimers. The optical rotation of the dendrimers was studied. As shown in Table 2, the molar optical rotation increases about two times as the molecular weight increases about four times from the generation zero dendrimer to the generation two dendrimer. Earlier, Chen[15a] and Meijer[14] have studied the effect of the dendritic branches at the 2,2′-positions of the 1,1′-binaphthyls on the optical rotation of the chiral binaphthyl-core-based dendrimers. They found that the growing steric interaction between the dendritic branches at the 2,2′-positions from the lower generation binaphthyl dendrimers to the higher generations increases the dihedral angle of the 1,1′-binaphthyl core, causing significantly increased molar optical rotation. However, we found that in the case of the phenyleneethynylene-based dendrimers represented by (*S*)-**3** there was only a 30% increase in molar optical rotation from generation zero to generation two. This indicates that substitution at the 4,4′,6,6′-positions of the binaphthyl core as in (*S*)-**3** cannot significantly change the 1,1′-binaphthyl dihedral angle at least from generation zero to generation two.

Therefore, we propose that the observed large increase in molar optical rotation from (*R*)-**15** to (*R*)-**17** might also not be due to the change of the binaphthyl dihedral angle. Instead, it might be contributed by the chiral conformations of the biaryl units in the dendrons induced by the chiral binaphthyl core. The steric interaction between the adjacent arylene units in the dendrons of (*R*)-**15**−(*R*)-**17** is much larger than that in (*S*)-**3**. This might have allowed the chiral effects of the binaphthyl core in (*R*)-**15**−(*R*)-**17** to propagate better along the dendritic branches, producing the significantly increased molar optical rotation.

The circular dichroism (CD) spectra of the dendrimers (*R*)-**15**−(*R*)-**17** in methylene chloride solution were obtained at 2.0×10^{-6} M (Figure 2). The molar ellipticities ([θ]) of the major CD signals are listed in Table 3. From the generation zero dendrimer to the generation two dendrimer, the major negative CD signal has shifted 15 nm to the red and the intensity is decreased to 54% of the original value. This is also very different from the phenyleneethynylene-based dendrimers, which show no significant change among different generations. Both the CD spectra and the optical rotations of (*R*)-**15**−(*R*)-**17** suggest that the dendritic arms of these materials might have made certain contributions to the chiral optical effects probably due to the increased steric interaction between the adjacent arylene units in the dendrons. The observed red-shift in the CD signals indicates that there is a small increase in conjugation from the lower generation dendrimers to the higher ones.

Figure 3 shows the UV−vis absorption spectra of (*R*)-**15**−(*R*)-**17** in CH_2Cl_2 at 2×10^{-6} M. The absorption maximum and molar extinction coefficients of these dendrimers as well as their dendron precursors **6** and **8** are summarized in Table 4. There are two major absorption bands in the UV spectra of the dendrimers. One

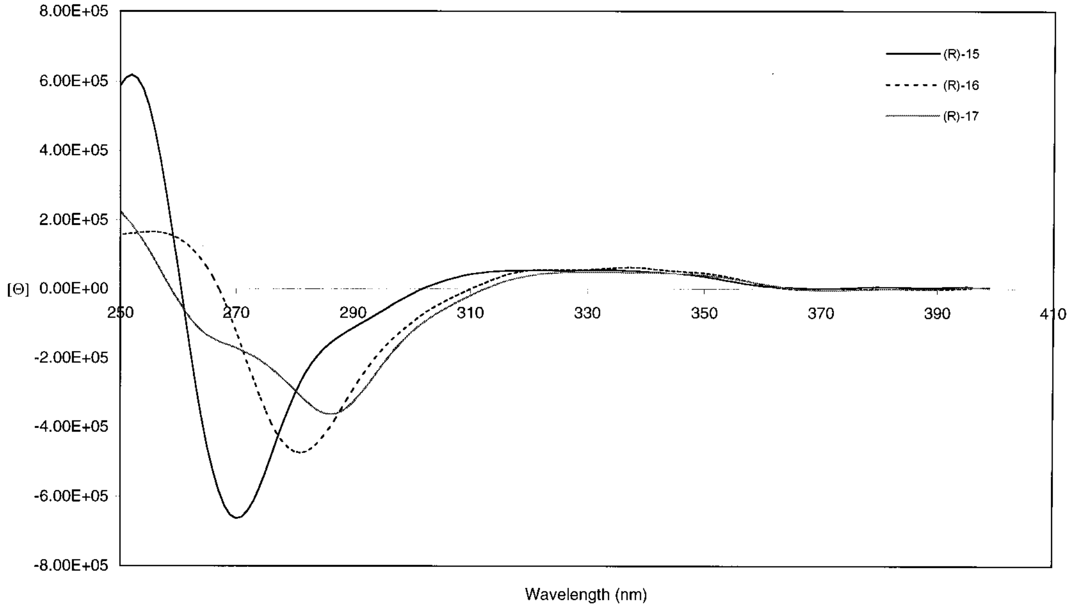


Figure 2. CD spectra of the dendrimers (*R*)-**15**−(*R*)-**17**.

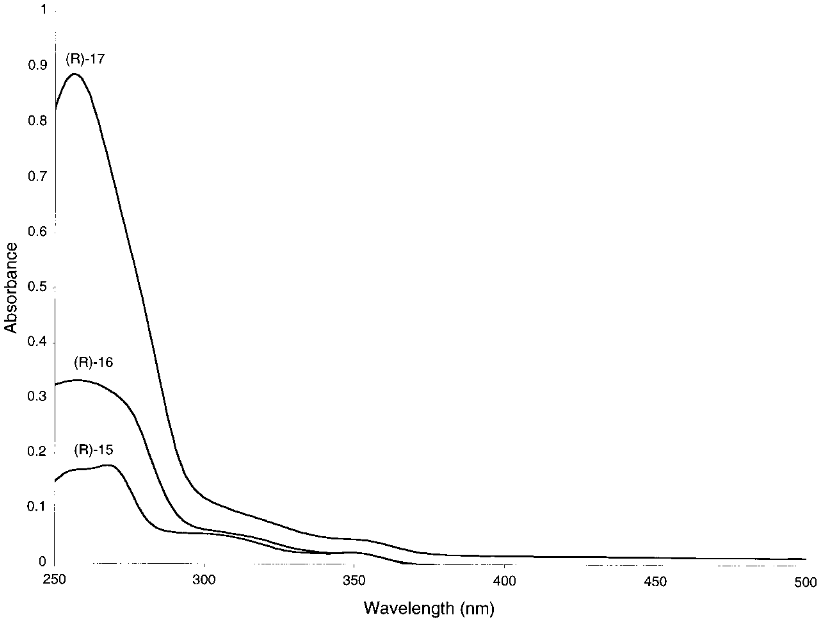


Figure 3. UV−vis absorption spectra of the dendrimers (*R*)-**15**−(*R*)-**17** in methylene chloride (2.0 × 10^{-6} M).

strong band at 250−300 nm is due to both the phenylene dendrons and the binaphthyl moieties. The absorption in this area increases significantly as the dendritic generation grows because of the increased phenylene units. The molar extinction coefficient of the dendrimers at 256 nm is increased over 5 times from the generation zero (*R*)-**15** to the generation two (*R*)-**17** when the number of phenylene units is increased 4 times. The second absorption band at 300−370 nm is due to the conjugated 4,4′,6,6′-tetraphenyl-1,1′-bi-2-naphthol core. Its intensity does not show significant change as the dendrimer generation increases.

The dendrimers emit strong blue light under UV irradiation. Figure 4 shows the fluorescence spectra of the dendrimers in CH_2Cl_2 solution at 2.0 × 10^{-7} M. When the dendrimer samples were excited at 256 nm where the absorption is mostly due to the benzene units of the dendrons, the emission wavelengths of these rigid dendrimers are almost identical with a maximum at 395 nm for (*R*)-**15**, 402 nm for (*R*)-**16**, and 405 nm for (*R*)-**17**, respectively. At the same molar concentration, the generation two dendrimer (*R*)-**17** emits about 2.5 times more intense than the generation one (*R*)-**16** which emits about three times more intense than the generation zero (*R*)-**15**. Thus, from the generation zero dendrimer to the generation two, the fluorescence intensity has increased about 7.5 times.

The fluorescence spectra of dendrons **6** and **8** are obtained (Figure 5). Comparison of these spectra with those of the dendrimers shows that the emissions at 340−350 nm for the monodendrons have disappeared in the dendrimers. Thus, the energy absorbed by the dendrons has completely migrated to the more conjugated core, leading to the greatly enhanced fluorescence intensity as the dendrimer generation grows.

The excitation spectra of the dendrimers also support

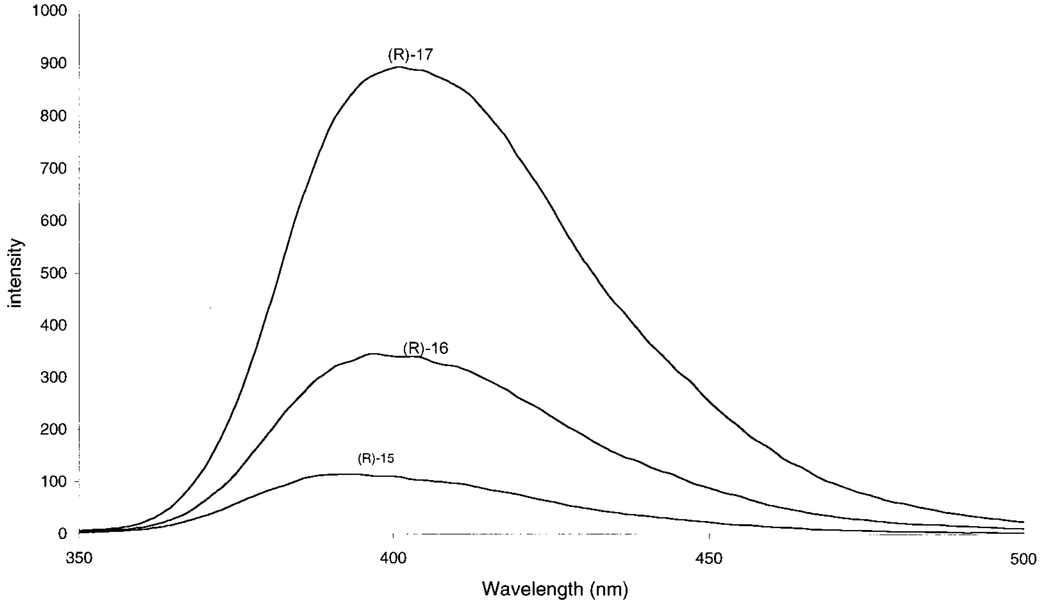


Figure 4. Fluorescence spectra of dendrimers (*R*)-**15**−(*R*)-**17** in methylene chloride (2.0×10^{-7} M) (uncorrected).

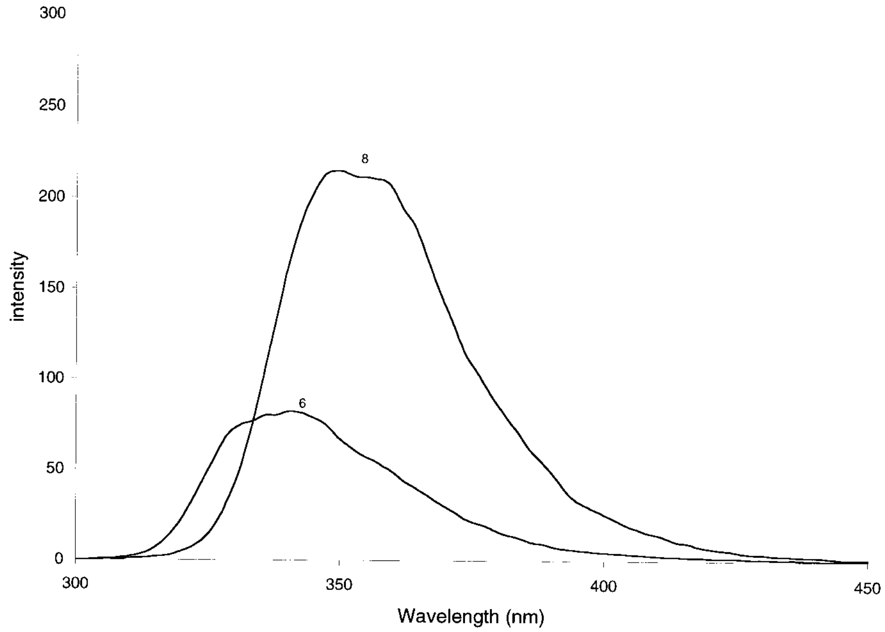


Figure 5. Fluorescence spectra of the generation one dendron **6** and the generation two dendron **8** (uncorrected).

Table 4. UV Absorption Maximums and Extinction Coefficients of the Dendrimers and Dendrons

	dendrimer			dendron	
	(*R*)-**15** (G0)	(*R*)-**16** (G1)	(*R*)-**17** (G2)	**6**	**8**
$\lambda_{\max}$ (nm) ($\epsilon \times 10^{-4}$)	351 (1.0)	351 (1.0)	356 (2.0)	252 (30.2)	256 (10.8)
	310 (2.5)	310 (2.7)	310 (5.0)		
	270 (8.8)	256 (16.6)	256 (44.3)		
	256 (8.4)				

the observed efficient energy migration (Figure 6). When the emission was set at 405 nm, the excitation maximum of the dendrimers at 256 nm increases dramatically from generation zero to generations one and two. The fluorescence intensity of (*R*)-**17** is also much stronger than that of (*R*)-BINOL at the same concentration of 2.0×10^{-7} M. To achieve a similar fluorescence intensity, the concentration of (*R*)-BINOL needs to be over 100 times higher than that of the generation two dendrimer. Therefore, the dendrimer is much more suitable as a fluorescent sensor and only a very small amount of the material is needed for the measurement.

3. Enantioselective Fluorescent Recognition of Chiral Amino Alcohols. We have studied the fluorescence of the generation two dendrimer (*R*)-**17** in the presence of chiral amino alcohols such as 2-amino-1-propanol (**18**).[10,13] In methylene chloride solution, the fluorescence of (*R*)-**17** was not significantly quenched by **18**. However, with the addition of hexane as a cosolvent, the fluorescence quenching became much more efficient.

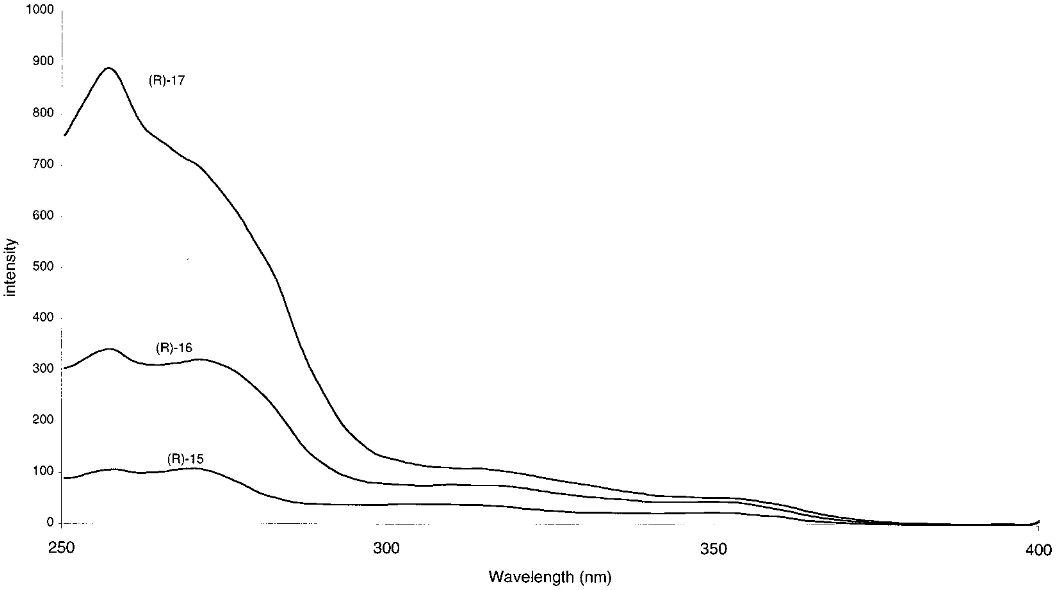


Figure 6. Excitation spectra of the dendrimers (*R*)-**15**–(*R*)-**17** in methylene chloride (2.0×10^{-7} M).

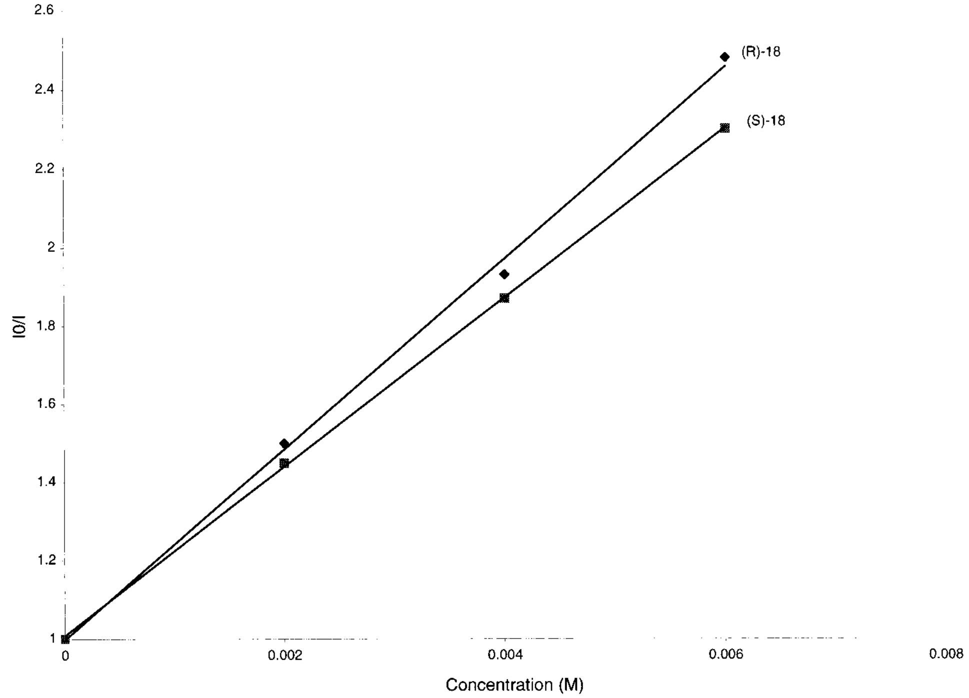


Figure 7. Stern–Volmer plot of (*R*)-**17** in the presence of (*R*)- and (*S*)-**18**.

This is probably due to better hydrogen bonding interaction in a less polar solvent between the hydroxyl groups of the dendrimer and the amino alcohol. The use of the mixed solvent of hexane and methylene chloride (9:1 by volume) allows the fluorescence of the dendrimer to be quenched by the amino alcohols in the desired range of 20–80% for minimum operational errors. Both the dendrimer and the amino alcohols are not soluble in pure hexane.

We found that the fluorescence quenching of dendrimer (*R*)-**17** at 1.0×10^{-7} M by the optically pure (*R*)- and (*S*)-**18** in the concentration range studied obeys the Stern–Volmer equation:[20]

$$I_0/I = 1 + \mathrm{Ksv}[Q]$$

where I_0 is the fluorescence intensity in the absence of a quencher and I the fluorescence intensity in the presence of a quencher. [Q] is the quencher concentration. K_{sv} is the Stern–Volmer constant, which measures the efficiency of quenching.

Figure 7 is the Stern–Volmer plot of the dendrimer in the presence of (*R*)- and (*S*)-**18**. From these plots, it is found that $K_{sv}{}^{R} = 243.5$ M^{-1} and $K_{sv}{}^{S} = 216.0$ M^{-1}. Thus, the fluorescence quenching of (*R*)-**17** by the amino alcohol is enantioselective with $K_{sv}{}^{R} - K_{sv}{}^{S} = 27.5$ and $K_{sv}{}^{R}/K_{sv}{}^{S} = 1.13$. The *R* enantiomer of the amino alcohol quenches

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(19) For a recent study of the conformation of chiral dendrimers, see: Recker, J.; Tomcik, D. J.; Parquette, J. R. *J. Am. Chem. Soc.* **2000**, *122*, 10298–10307.

(20) Lakowicz, J. R. *Principles of Fluorescence Spectroscopy*, 2nd ed.; Kluwer Academic/Plenum: New York, 1999.

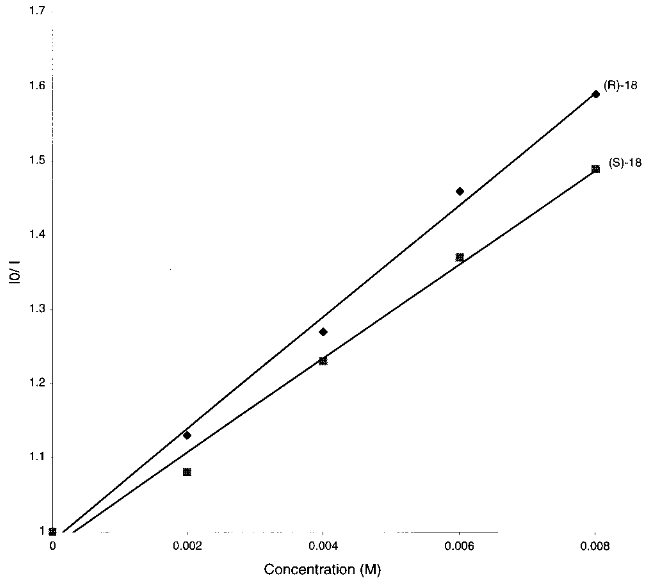


Figure 8. Stern–Volmer plot of (*R*)-**15** in the presence of (*R*)- and (*S*)-**18**.

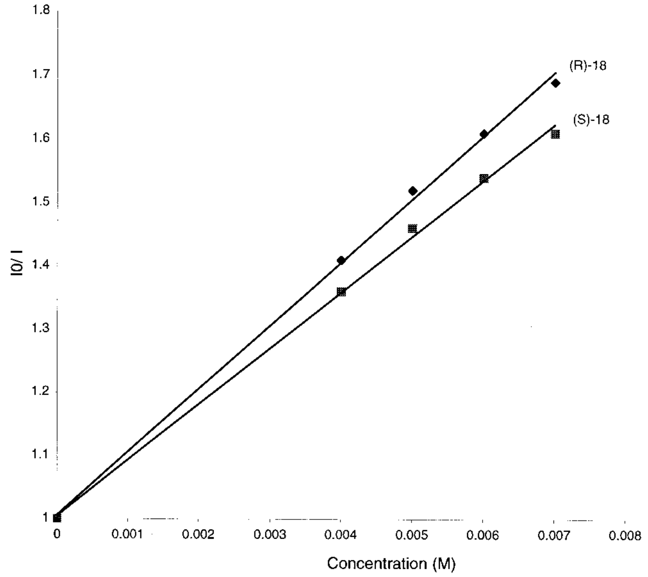


Figure 9. Stern–Volmer plot of (*R*)-**16** in the presence of (*R*)- and (*S*)-**18**.

the fluorescence of the dendrimer more efficiently than the *S* enantiomer.

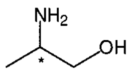
Under the same conditions, the fluorescence quenching of the generation zero dendrimer (*R*)-**15** and the generation one dendrimer (*R*)-**16** by (*R*)- and (*S*)-**18** also followed the Stern–Volmer equation (Figures 8 and 9). The observed Stern–Volmer constants are $K_{sv}^{R} = 75.5$ M^{-1} and $K_{sv}^{S} = 63.5$ M^{-1} for (*R*)-**15** ($K_{sv}^{R}/K_{sv}^{S} = 1.19$), and $K_{sv}^{R} = 99.9$ M^{-1} and $K_{sv}^{S} = 88.4$ M^{-1} for (*R*)-**16** ($K_{sv}^{R}/K_{sv}^{S} = 1.13$).

Thus, there is a significant increase in the Stern–Volmer constant as the dendrimer generation increases. This demonstrates that the fluorescence of the higher generation dendrimer is more sensitive toward quenchers than the lower ones. The increased nonpolar dendrons for the higher generation dendrimers may enhance the hydrogen bonding between their core hydroxyl groups and the amino alcohols. The difference between the fluorescence intensity of the sensor without and with the quencher is also much larger for the higher generation dendrimers than for the lower ones. The quenching of the dendrimer fluorescence probably occurs when the dendritic core hydroxyl groups interact with the amino alcohol quencher. This allows the light harvested by the dendrons to be quenched at the core where the energy is funneled. Therefore, the higher the dendrimer generation, the more the quenched emission.

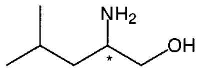
Table 5. Stern–Volmer Constants of the Dendrimer (*R*)-17 in the Presence of the Chiral Amino Alcohols 18–20

	amino alcohol					
	(*R*)-**18**	(*S*)-**18**	(*R*)-**19**	(*S*)-**19**	(*R*)-**20**	(*S*)-**20**
K_{sv} (M^{-1})	243.5	216.0	191.5	162.5	145.5	133.5
$K_{sv}^{R} - K_{sv}^{S}$	27.5		29.0		12.0	
K_{sv}^{R}/K_{sv}^{S}	1.13		1.18		1.09	

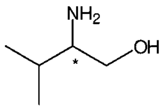
The fluorescence of (*R*)-**17** (1.0×10^{-7} M) in the presence of leucinol (**19**) (Figure 10) and 2-amino-3-methyl-butanol (**20**) (Figure 11) were also studied under the same conditions as above. The Stern–Volmer constants of (*R*)-**17** in the presence of the chiral amino alcohols **18**–**20** are summarized in Table 5. These studies demonstrate that the fluorescence response of the dendrimer to chiral amino alcohols is enantioselective. The enantioselectivity of dendrimer (*R*)-**17** is higher for the amino alcohol **19** than for **18** and **20**. The magnitude of the K_{sv}^{R}/K_{sv}^{S} ratio of dendrimer (*R*)-**17** for chiral amino alcohols is similar to those of (*S*)-**3**[13a] and BINOL,[10e,13a] but smaller than that of a calix[4]arene-based fluorescent sensor.[11b] The fluorescence of these dendrimers can be quenched both efficiently and enantioselectively by chiral amino alcohols. In all the cases, the (*S*)-amino alcohols quench the fluorescence of the chiral dendendrimers (*R*)-**15** - (*R*)-**17** more efficiently than the (*R*)-amino alcohols. This indicates that the interaction of the (*R*)-dendrimers with the (*S*)-amino alcohols is better than with the (*R*)-amino alcohols.



18



19



20

4. Conclusion

In summary, optically active dendrimers containing a 1,1′-binaphthyl core and cross-conjugated phenylene dendrons have been synthesized and characterized. The chiral optical properties of these phenylene-based dendrimers are different from our previously reported phenyleneethynylene-based dendrimers probably because of the increased steric interaction between the adjacent arylene units in the phenylene dendrons. These new dendrimers show significantly increased molar optical rotation as the dendrimer generation increases. UV and fluorescence spectroscopic studies demonstrate that the energy harvested by the periphery of the dendrimers is efficiently transferred to the more conjugated core, generating much enhanced fluorescence signal at higher generation. The energy migration and light harvesting

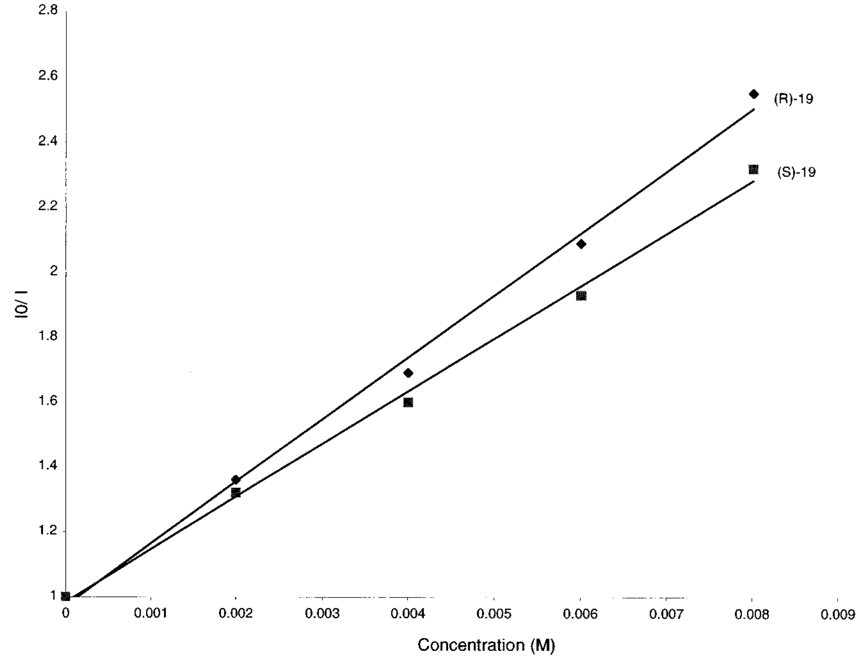


Figure 10. Stern–Volmer plot of (*R*)-**17** in the presence of (*R*)- and (*S*)-**19**.

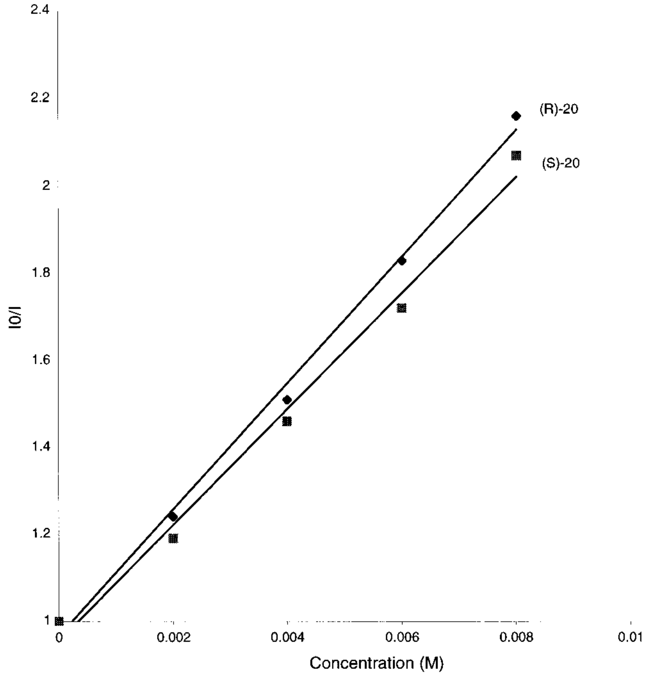


Figure 11. Stern–Volmer plot of (*R*)-**17** in the presence of (*R*)- and (*S*)-**20**.

effects of the dendrimers make the higher generation dendrimer more sensitive to fluorescent quenchers than the lower ones. Thus, the dendritic structure provides a signal amplification mechanism.[21] These materials are potentially useful in the enantioselective recognition of chiral organic molecules.

Experimental Section

General Data. NMR spectra were recorded on a Varian-300 MHz spectrometer. Elemental analysis was carried out using Perkin-Elmer 2400 Series II CHN S/O Analyzer. Gel permeation chromatography (GPC) analysis utilized Waters 510 HPLC pump, Waters 410 Differential Refractometer and Ultrastyragel Linear GPC columns. THF was used as the eluent solvent for GPC and polystyrene standards were used. UV–vis spectra were recorded on a Hewlett-Packard 8452A diode array spectrophotometer. Fluorescence spectra were recorded on a Perkin-Elmer LS-50B luminescence spectrometer. Both the excitation and emission slits were set at 2.5 nm, and the scan speed was set at 100 nm/min. Circular dichroism spectra were recorded using a JASCO J-710 spectropolarimeter. Optical rotations were measured on a JASCO polarimeter at $\lambda = 589$ nm. CI and EI mass spectra were recorded on LCQ FINNIGON. FAB mass spectroscopic analysis was performed by the University of California–Riverside mass spectroscopy facility. THF was dried with sodium/benzophenone. CH_2Cl_2 was dried with CaH_2. Tetrakis(triphenylphosphine)palladium was purchased from Strem and used directly. Other chemicals were purchased from Aldrich and used directly.

Preparation and Characterization of 3,5-Dibromo-1-(trimethylsilyl)benzene, 5.[16,18] Under nitrogen, to a solution of 1,3,5-tribromobenzene (9.4 g, 30 mmol) in THF (80 mL) was added *n*-BuLi (2.5 M in hexane, 12 mL, 30 mmol) at −78 °C. The resulting mixture was stirred at this temperature for 30 min, to which trimethylsilyl chloride (7.6 mL, 60 mmol) was added via a syringe. After another 30 min, the reaction mixture was warmed to room temperature and stirred overnight. To the resulting solution, saturated aqueous NH_4Cl was added to quench the excess *n*-BuLi. The aqueous layer was extracted with EtOAc, and the combined organic layer was washed with brine. After evaporation of the solvent, the residue was distilled under reduced pressure to give **5** as needle crystals in 79% yield (7.2 g, 23.7 mmol): mp 40–41 °C; ^1H NMR ($CDCl_3$, 300 MHz) δ 7.64 (d, $J = 1.8$ Hz, 1H), 7.51 (d, $J = 1.8$ Hz, 2H), 0.27 (s, 9H); ^{13}C NMR ($CDCl_3$, 75 MHz) δ 146.01, 134.45, 123.16, −1.37.

Preparation of 5-Trimethylsilyl-1,3-diphenylbenzene, 6. A 100 mL Schlenk flask charged with 3,5-dibromo-5-(trimethylsilyl)benzene (**5**) (6.16 g, 20 mmol) and phenylboronic acid (**4**) (5.36 g, 44 mmol) was brought into a drybox and was combined with $Pd(PPh_3)_4$ (1.39 g, 1.20 mmol). To the resulting mixture, aqueous K_2CO_3 (2 M, 25 mL, degassed with nitrogen) and THF (50 mL) were syringed in under nitrogen. The reaction mixture was degassed again by three freeze–pump–thaw cycles and was then refluxed under nitrogen. After 24

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[21] Using energy migration as a fluorescence signal amplification mechanism in linear conjugated polymers was studied by Swager: Zhou, Q.; Swager, T. M. *J. Am. Chem. Soc.* **1995**, *117*, 7017.

h, the reaction mixture was poured into a mixture of H_2O and EtOAc. The aqueous layer was extracted with EtOAc. The combined organic layer was washed with brine and dried over anhydrous Na_2SO_4. After removal of the solvent, the residue was passed through a silica gel column using hexanes as the eluent, and the resulting material was further recrystallized from EtOH to yield **6** as colorless crystals in 80% yield (4.8 g, 16 mmol). The ^{1}H and ^{13}C NMR data of **6** matched those in the literature.[16]

Preparation of 5-Trimethylsilyl-1,3-bis(1′,3′-diphenylphenyl)benzene, 8. The same procedure as the preparation of **6** was followed. The synthesis of **8** was carried out by using **5** (1.57 g, 5.1 mmol), **7** (3.1 g, 11.0 mmol), $Pd(PPh_3)_4$ (381 mg, 0.33 mmol) in THF (25 mL), and aqueous K_2CO_3 (2 M, 16 mL). The reaction mixture was heated at reflux under nitrogen for 48 h. The crude product was recrystallized from EtOH to give **8** as white crystals in 90% yield (2.8 g, 4.6 mmol). The ^{1}H and ^{13}C NMR data of **8** matched those in the literature.[16]

Preparation and Characterization of (*R*)-2,2′-Hexyloxy-1,1′-binaphthyl, (*R*)-10. To a solution of (*R*)-BINOL (6.0 g, 21.0 mmol) and 1-bromohexane (12 mL, 105.0 mmol) in acetonitrile (100 mL) was added K_2CO_3 (15 g, 105 mmol). The resulting mixture was degassed with nitrogen and then refluxed for 16 h. After the mixture was cooled to room temperature, H_2O was added and the mixture was extracted with hexanes. The organic layer was washed with brine. Evaporation of the solvent followed by flash chromatography on silica gel with hexane as eluent afforded (*R*)-**10** as a colorless oil in 95% yield (9.1 g, 20 mmol): $[\alpha]_D = +60.5$ ($c = 1.0$, THF); ^{1}H NMR ($CDCl_3$, 300 MHz) δ 7.92 (d, $J = 9.0$ Hz, 2H), 7.84 (d, $J = 8.1$ Hz, 2H), 7.41 (d, $J = 9.0$ Hz, 2H), 7.33−7.17 (m, 6 H), 3.98−3.89 (m, 4H), 1.44−1.37 (m, 4H), 1.07−0.91 (m, 12H), 0.77−0.72 (m, 6H); ^{13}C NMR ($CDCl_3$, 75 MHz) δ 154.54, 134.23, 129.27, 128.97, 127.72, 125.95, 125.50, 123.34, 120.76, 115.89, 69.79, 31.30, 29.35, 25.25, 22.41, 13.88.

Preparation and Characterization of (*R*)-4,4′,6,6′-Tetrabromo-2,2′-hexyloxy-1,1′-binaphthyl, (*R*)-11. To a solution of (*R*)-**10** (4.5 g, 10 mmol) in AcOH (100 mL) was added Br_2 (5.2 mL, 100 mmol) over 30 min at room temperature. The reaction mixture was stirred for 6 h and monitored by ^{1}H NMR spectroscopy. Then, $NaHSO_3$ was added to quench excess Br_2. After being extracted with EtOAc, the combined organic solution was washed with brine. After removal of the solvent, the residue was purified by column chromatography on silica gel with hexanes as the eluent to give (*R*)-**11** in 80% yield (6.1 g, 8 mmol) as a slightly yellow oil: $[\alpha]_D = +50.0$ ($c = 0.808$, THF); ^{1}H NMR ($CDCl_3$, 300 MHz) δ 8.39 (d, $J = 2.1$ Hz, 2H), 7.70 (s, 2H), 7.30 (dd, $J = 2.1$ Hz, 9.0 Hz, 2H), 6.97 (d, $J = 9.0$ Hz, 2H), 3.89−3.96 (m, 4H), 1.38−1.43 (m, 4H), 0.72−1.08 (m, 18H); ^{13}C NMR ($CDCl_3$, 75 MHz) δ 154.56, 133.26, 130.72, 129.55, 129.02, 127.49, 122.55, 120.52, 119.40, 119.36, 69.99, 31.37, 29.26, 25.47, 22.63, 14.04. Anal. Calcd for $C_{32}H_{34}Br_4O_2$: C, 49.90; H, 4.45. Found: C, 50.07; H, 4.39.

Preparation and Characterization of the Chiral Dendrimers. A typical procedure: Under nitrogen, to a mixture of (*R*)-**11** (0.764 g, 1 mmol), the boronic acid dendron **4** (0.536 g, 4.4 mmol), **7** (1.205 g, 4.4 mmol), or **9** (2.543 g, 4.4 mmol), and $Pd(PPh_3)_4$ (138 mg, 0.12 mmol) were added degassed THF (20 mL) and aqueous K_2CO_3 (2 M, 12 mL). After the mixture was degassed with three freeze−pump−thaw cycles, it was refluxed for 48 h and then cooled to room temperature. The resulting mixture was poured into a mixture of EtOAc and H_2O. The aqueous layer was extracted with EtOAc. The combined organic solution was washed with brine and dried over anhydrous Na_2SO_4. After concentration, the residue was passed through a silica gel column to remove the inorganic impurity. The crude mixture was dissolved in CH_2Cl_2 (20 mL), and BBr_3 (0.28 mL, 3 mmol) was added dropwise under nitrogen at −78 °C. The reaction solution was then warmed to room temperature for a period of 20 h and was quenched with H_2O. The aqueous layer was extracted with CH_2Cl_2. The combined organic solution was washed with brine and dried over anhydrous Na_2SO_4. After removal of the solvent, the residue was purified with a silica gel column (eluent: EtOAc/hexane = 1:10 to 1:4) to give the dendrimers as pale solids.

(*R*)-**15**: yield 80%; mp 164−167 °C dec; $[\alpha]_D = -66.3$ ($c = 1.03$, THF); ^{1}H NMR ($CDCl_3$, 300 MHz) δ 8.18 (d, $J = 1.8$ Hz, 2H), 7.32−7.68 (m, 26H), 5.21 (s, 2H); ^{13}C NMR ($CDCl_3$, 75 MHz) δ 152.28, 144.22, 141.03, 139.82, 136.97, 133.16, 129.93, 128.80, 128.54, 128.24, 127.85, 127.26, 127.17, 127.10, 125.25, 124.81, 119.17, 110.30; MS (CI) *m*/*e* 591 (M + H^+, 100); UV λ_{max} (CH_2Cl_2) nm 351, 310, 270, 256. Anal. Calcd for $C_{44}H_{30}O_2$: C, 89.40; H, 5.12. Found: C, 89.27; H, 4.96.

(*R*)-**16**: yield 71%; mp 207−210 °C dec; $[\alpha]_D = -51.6$ ($c = 1.04$, THF); ^{1}H NMR ($CDCl_3$, 300 MHz) δ 8.49 (s, 2H), 7.97 (d, $J = 1.2$ Hz, 6H), 7.76−7.78 (m, 16H), 7.57−7.64 (m, 12H), 7.34−7.51(m, 24H), 5.35 (s, 2H); ^{13}C NMR ($CDCl_3$, 75 Hz) δ 152.94, 144.58, 142.79, 142.71, 142.58, 141.40, 141.20, 137.77, 133.86, 129.36, 129.29, 128.72, 128.14, 128.07, 127.92, 127.78, 127.68, 126.21, 125.90, 125.75, 125.66, 119.85, 111.02; MS (EI) *m*/*e* 1199 (M + H^+); UV λ_{max} (CH_2Cl_2) nm 351, 310, 256. Anal. Calcd for $C_{92}H_{62}O_2$: C, 92.12; H, 5.21. Found: C, 92.07; H, 5.58.

(*R*)-**17**: yield 58%; mp 231−234 °C dec; $[\alpha]_D = -31.2$ ($c = 1.03$, THF); ^{1}H NMR ($CDCl_3$, 300 MHz) δ 8.59 (s, 2H), 8.07 (s, 6H), 7.97−7.76 (m, 32H), 7.67−7.60 (m, 36H), 7.30−7.44 (m, 48H), 5.36 (s, 2H); ^{13}C NMR ($CDCl_3$, 75 MHz) δ 152.58, 144.06, 142.67, 142.50, 142.25, 141.78, 140.91, 140.84, 136.85, 133.56, 128.78, 128.38, 128.20, 127.50, 127.30, 125.91, 125.58, 125.34, 119.45, 110.64; MS (FAB) *m*/*e* 2417 (M + H^+); UV λ_{max} (CH_2Cl_2) nm 356, 310, 256. Anal. Calcd for $C_{188}H_{126}O_2$: C, 93.33; H, 5.25. Found: C, 93.21; H, 5.37.

Acknowledgment. The support of this work from the National Institutes of Health (1R01GM58454) is gratefully acknowledged. We also acknowledge the partial support from the donors of the Petroleum Research Fund, administered by the American Chemical Society.

JO001565G