Synthesis, Characterization, and Photophysical Properties of Chiral Dendrimers Based on Well-Defined Oligonaphthyl Cores

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ABSTRACT: Chiral dendrimers based on (*R*)-1,1′-bi-2-naphthyl and its oligomeric (*R*,*R*)-tetranaphthyl and (*R*,*R*,*R*)-hexanaphthyl chiral cores and Fréchet-type aryl-ether dendrons were synthesized using the Fréchet conditions or deprotonation of the chiral cores with NaH followed by nucleophilic attack on benzyl bromide moieties of the dendrons. These chiral dendrimers were characterized by ^{1}H and ^{13}C{^{1}H} NMR spectroscopy and mass spectrometric analyses. The UV absorption of the chiral dendrimers steadily increases as the generation grows. These dendrimers show significantly enhanced fluorescence compared to (*R*)-1,1′-bi-2-naphthol, and the fluorescence intensity increases as the generation grows for most of the dendrimers. Both CD and optical rotation data suggest that the increased steric bulk of the dendrons leads to larger dihedral angles between the naphthyl rings through their 1,1′-linkages. The absolute configuration of the chiral dendrimers remains the same as their chiral cores.

Introduction

Over the past 2 decades, there has been tremendous interest in the design and synthesis of dendrimers, a class of highly branched molecular architectures consisting of a well-defined number of generations and end groups.[1,2] There are numerous reasons for the investigation of these novel macromolecular systems, including unprecedented control over the positioning of constituent building units, general ease of construction, well-behaved solubility features that facilitate characterization, and the convincing evidence that such species can be constructed for utilitarian as well as aesthetic purposes. In fact, many interesting applications have been demonstrated for well-designed dendrimers. They are currently being explored for use as biomimetic catalysts,[3] building blocks for fabrication of functional materials,[4] molecular carriers for chemical catalysts,[5] potential vehicles for the delivery of drugs,[6] synthetic light-harvesting systems,[7] and light emitting materials.[8]

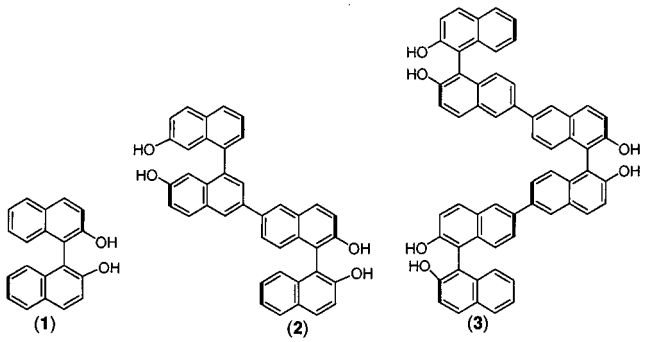
Dendritic structures and assemblies composed of optically active moieties have also received much attention.[9] These chiral supramolecular assemblies are potentially useful for enantioselective clathration, separation, catalysis,[10] and sensing.[11] Known chiral dendritic structures have included molecules with a chiral core,[12] chiral terminal units,[13] chiral branching units,[14] and combinations thereof. Dendrimers with constitutionally different segments on a chiral core or rigidly chiral conformation without possessing any stereogenic centers or chiral moieties have also been reported.[15]

We would like to report in this article the synthesis and characterization of a new class of optically pure dendrimers containing chiral binaphthyl and binaphthyl-based oligomer cores and Fréchet's aryl ether dendrons. Photophysical properties, including chiraloptical properties of these chiral dendritic architectures are also described.

Results and Discussion

1. Synthesis and Characterization of Chiral Dendrimers. 1,1′-Bi-2-naphthol, (*R*,*R*)-tetranaphthol, and (*R*,*R*,*R*)-hexnaphthol were used as the chiral cores for the assembly of chiral dendrimers (Scheme 1). (*R*,*R*)-Tetranaphthol, **2**, was prepared by Suzuki coupling between (*R*)-6-bromo-2,2′-diethoxy-1,1′-binaphthyl and (*R*)-2,2′-diethoxy-1,1′-binaphthyl-6-boronic acid, followed by deprotection with BBr_3.[16] (*R*,*R*,*R*)-Hexnaphthol, **3**, was also prepared by Suzuki coupling between (*R*)-6-bromo-2,2′-diethoxy-1,1′-binaphthyl and (*R*)-2,2′diethoxy-1,1′-binaphthyl-6,6′-diboronic acid, followed by deprotection with BBr_3.[16] 3,5-Substituted benzyl aryl ether dendrons (Fréchet dendrons) were prepared according to the literature methods.[17]

Scheme 1. Structures of the Chiral Cores



The coupling of dendritic benzyl bromide (from G0-Br to G2-Br) and the chiral cores was successfully carried out using the Fréchet conditions (K_2CO_3/18-crown-6, acetone, reflux)[18] to give the zeroth (G0) to second generation (G2) dendrimers. Similar procedures have failed to yield the third generation (G3) dendrimers presumably due to the incomplete deprotonatioin by weak base coupled with the steric bulk of the G3-Br dendron. Instead, the G3 dendrimers were successfully synthesized via deprotonation of the chiral cores by NaH in DMF followed by reacting with dendron G3-Br (Scheme 2). The structures of representative chiral dendrimers **3**-G0 to **3**-G3 are shown in Scheme 3.

The dendrimers are all white solid, and soluble in most common polar organic solvents such as ethyl acetate, methylene chloride, chloroform, THF, and acetonitrile. The identities of these dendrimers have been

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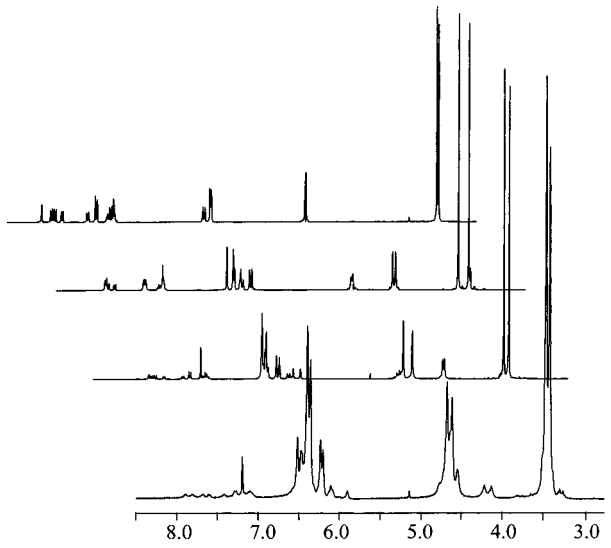
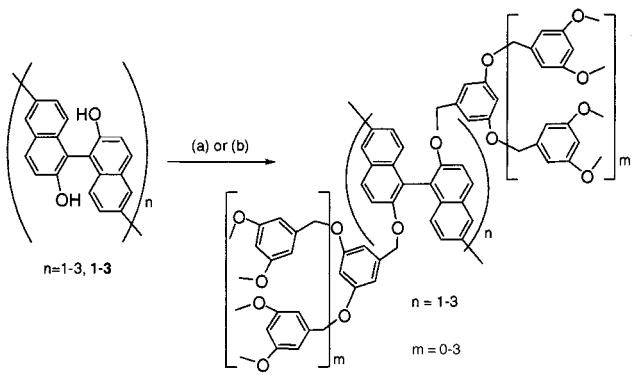


Figure 1. ^{1}H NMR Spectra of **2**-G0 to **2**-G3 (from top to bottom). The spectra have been shifted horizontally for clarity.

Scheme 2. Synthesis and Structures of Chiral Dendrimers



[a] Key: (a) for $m = 0$, 1, and 2: K_2CO_3, 18-C-6, acetone, reflux. (b) for $m = 3$: NaH, DMF, 0 °C to room temperature.

confirmed by ^{1}H and ^{13}C NMR and MS analyses. The proton signals of the ^{1}H NMR spectra are separated into four groups: signals between 8.2 and 7.1 ppm are attributed to the protons of chiral cores **1**−**3**, signals between 6.8 and 6.0 ppm belong to protons of phenyl groups of benzyl aryl ethers, signals between 5.2 and 4.2 ppm are attributed to methylene groups of the dendrons, and the peaks between 4 and 3 ppm are attributed to the peripheral methoxy groups. As the generation of the dendrimers grows, the benzyl aryl ether proton signal intensities increase significantly over those of the chiral cores. Representative ^{1}H NMR spectra of **2**-G0 to **2**-G3 are shown in Figure 1. The same tendency was also observed in the ^{13}C NMR spectra. The most characteristic features of the ^{1}H NMR spectra of these dendrimers lie in the peripheral methoxy protons. As expected from their structures, dendrimers **1**-G0 to **1**-G3 exhibit one set of singlet for the methoxy protons. Dendrimers **2**-G0 to **2**-G3 and dendrimers **3**-G0 to **3**-G3 exhibit two and three sets of singlets for the methoxy protons, respectively. Mass spectral analyses of these dendrimers were accomplished using a combination of EI/MS, FAB/MS, and MALDI−TOF/MS techniques, depending on molecular weights of the dendrimers. The detailed peak assignments are given in the Experimental Section.

Table 1. UV−Vis Spectral Data of Chiral Dendrimers in Acetonitrile

compd	C (mol/L)	peaks (nm)	ϵ (cm^2/mol) × 10^{-5}
1-G0	5×10^{-7}	203	1.95
		231	1.85
		269	0.38
		323	0.19
1-G1	1.24×10^{-5}	204	2.3
		231	1.6
		282	0.22
		324	0.066
		338	0.055
1-G2	5.4×10^{-6}	207	6.22
		228	3.36
		282	0.59
		337	0.10
		324	0.09
1-G3	7.0×10^{-6}	222	2.83
		282	0.59
		338	0.05
2-G0	6.0×10^{-7}	203	3.0
		229	2.0
		264	1.2
		319	0.43
2-G1	5.3×10^{-6}	205	4.6
		229	2.4
		266	1.1
		322	0.34
2-G2	5.4×10^{-7}	204	10.5
		264	2.26
		317	0.83
		323	0.80
2-G3	7.0×10^{-6}	234	3.37
		278	1.26
		324	0.23
3-G0	1.23×10^{-5}	203	3.2
		230	2.0
		266	1.6
		318	0.67
3-G1	4.7×10^{-6}	204	5.9
		270	1.5
		320	0.55
3-G2	2.5×10^{-6}	206	13.2
		274	2.13
		321	0.65
3-G3	1.5×10^{-6}	218	11.5
		276	3.12
		318	0.87

Table 2. Fluorescence Spectral Data of Chiral Dendrimers in Acetonitrile[a]

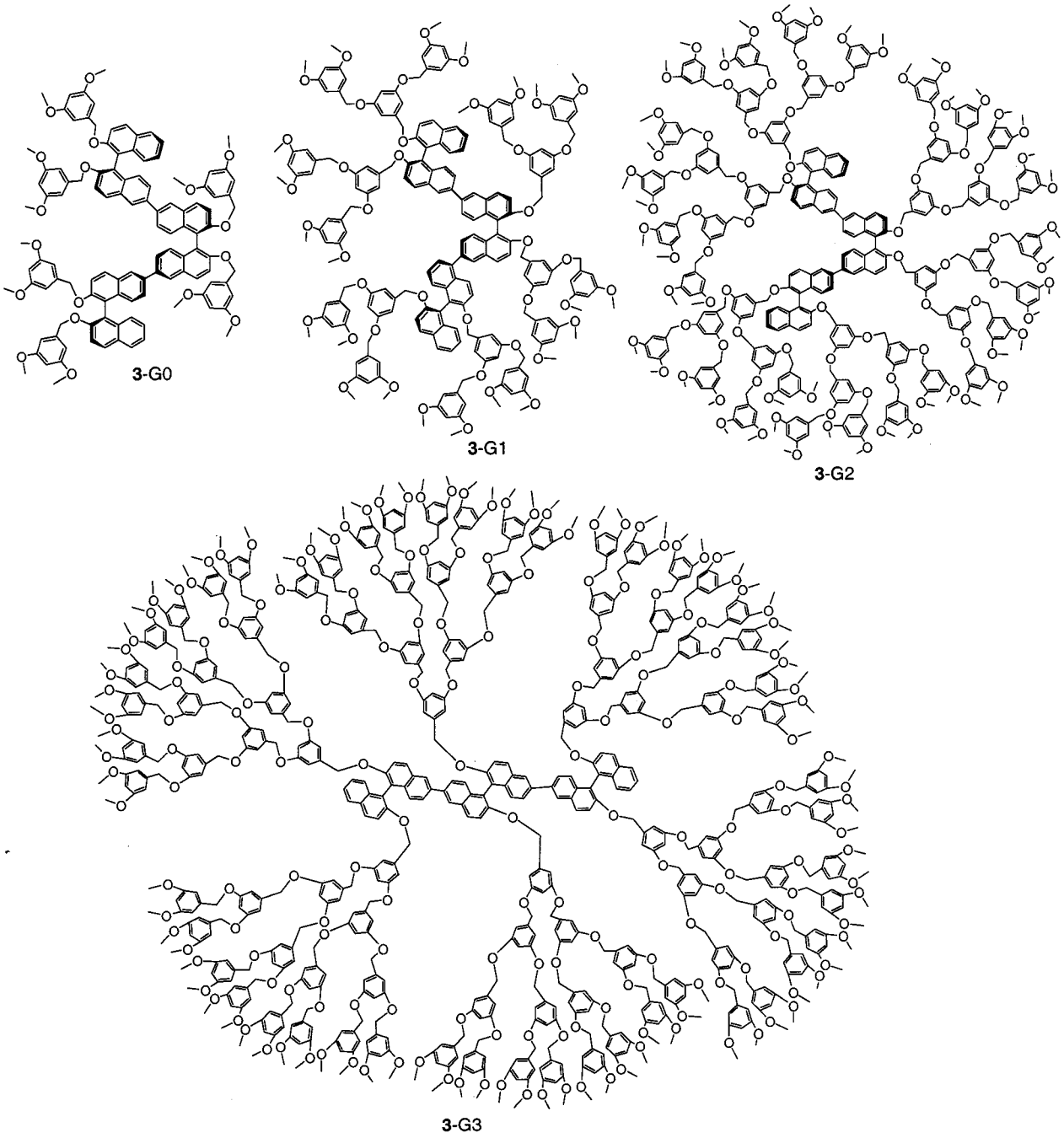
compd	excitation (nm)	emission (nm)	quantum yield
1-G0	320	360	0.17
1-G1	325	361	0.21
1-G2	324	382	0.57
1-G3	325	360	0.28
2-G0	321	383	0.32
2-G1	325	384	0.47
2-G2	324	384	0.26
2-G3	325	384	0.62
3-G0	320	383	0.48
3-G1	334	384	0.87
3-G2	325	386	0.57
3-G3	325	382	0.67
		396	

[a] The concentration of the dendrimers is 5×10^{-7} M.

2. Photophysical Properties of the Chiral Dendrimers. There are four major absorption bands around 203, 220, 270, and 320 nm in the UV spectra of these dendrimers. These absorptions can be assigned to the ^{1}B, ^1L_a, K, and ^1L_b transitions of the aromatic groups. Table 1 lists absorption maxima and their extinction coefficients for the dendrimers in acetonitrile. Molar extinction coefficients of the absorption bands around 203 nm increase significantly as the generation grows because of the increased number of phenyl groups.

The dendrimers emit strong blue light under UV irradiation. Table 2 shows the fluorescence spectral data

Scheme 3. Structures of Chiral Dendrimers 3-G0 to 3-G3



of the dendrimers in acetonitrile solution at 5×10^{-7} M. The emission bands center around 360 nm for the dendrimers derived from the binaphthyl core, around 380 nm for the dendrimers built from the tetranaphthyl core, and around 390 nm for those composed of the hexanaphthyl core (Figures 3−5). It is clear from Figures 3−5 that the fluorescence intensity of the chiral dendrimers increases as the generation grows for most of the dendrimers, consistent with the increased number of fluorophores. Quantum yields for these densrimers have been measured with the reference of 9,10-diphenylanthracene (Table 2), but no clear trend was observed with the increase of the dendrimer generation.

Optical rotation data for the chiral dendrimers were taken in THF. As Table 3 indicates, the sign of the molecular optical rotation of (*R*)-binaphthyl dendrimer **1**-G0 to **1**-G2 reverts from (+)-(*R*)-1,1′-binaphthol, and the value increases as the generation grows from G0 to G2. However, the sign for **1**-G3 reverts back to that of (+)-(*R*)-1,1′-binaphthol and the value decreases to that of **1**-G0. The signs of the (*R*,*R*)-tetranaphthyl and (*R*,*R*,*R*)-hexnaphthyl dendrimers are all the same as their chiral cores. As for (*R*,*R*)-tetranaphthyl dendrimers, the value of molecular optical rotation increases from G0 to G2, but decreases for G3. The value for (*R*,*R*,*R*)-hexanaphthyl dendrimers increases from the G0 to G1 and then decreases when the generation grows.

Circular dichroism (CD) spectra of the dendrimers were obtained in acetonitrile solution. The Cotton effects of these dendrimers are the same as their corresponding chiral cores, indicating that they maintain the same absolute configuration as their cores (Figures 5−7). The molar ellipticities of the two strongest Cotton effects which correspond to the ^{1}B transition of the naphtha-

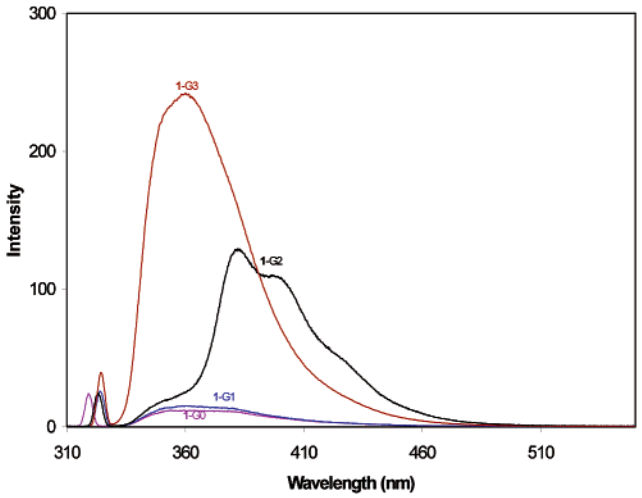


Figure 2. Fluorescence spectra of **1**-G0 to **1**-G3 in acetonitrile.

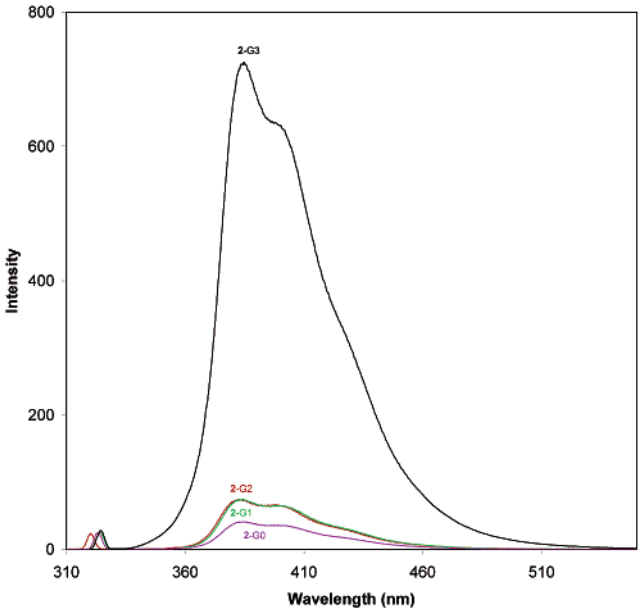


Figure 3. Fluorescence spectra of **2**-G0 to **2**-G3 in acetonitrile.

lene chromophores, decrease from the G0 generation to the G3 generation for all three series of chiral dendrimers, with the exception of **1**-G3. The molar ellipticity of (*R*)-**1**-G3 increases to above that of (*R*)-**1**-G0. This trend is consistent with that observed in optical rotation, and also agree with previous observations on BINOL-derived dendrimers with slightly different Frechét-type dendrons and poly(BINOL)-derived dendrimers.[19] One possible explanation for the abnormal behavior of (*R*)-**1**-G3 is that it may have adopt a dihedral angle above the critical angle of 110° and thus deviates significantly from the exciton approximation due to the strong coupling between the two naphthyl rings.[20] The decreasing trend of the molar ellipticities can be attributed two factors: (a) the CD signals of the chiral cores in higher generations of dendrimers have been diluted due to the presence of an increased number of nonchiral chromophores from the dendrons; (b) the dihedral angles between the naphthyl rings through their 1,1′-linkages may have increased as the generation grows owing to the steric bulk of the dendrons. It is also interesting to point out that all the chiroptical data suggest that no chirality transfer (expression) from the chiral core to the dendrons has occurred in the present system. This

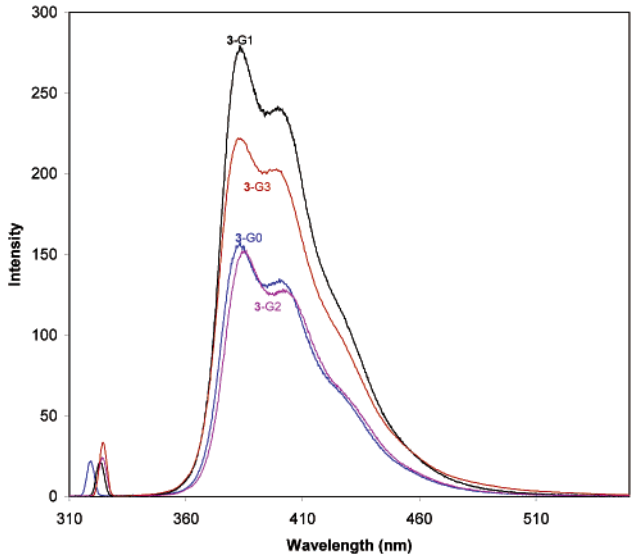


Figure 4. Fluorescence spectra of **3**-G0 to **3**-G3 in acetonitrile.

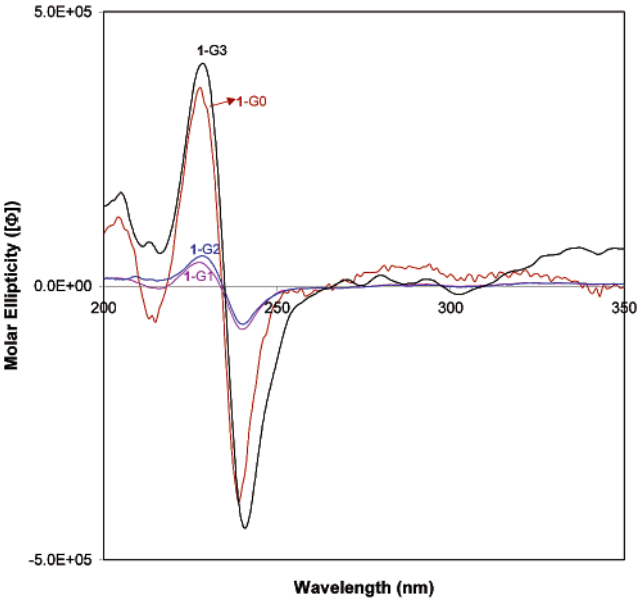


Figure 5. Circular dichroism spectra of **1**-G0 to **1**-G3 in acetonitrile.

Table 3. Optical Rotation Data of Chiral Dendrimers in THF

compd	*C* (g/100 mL)	[α] (deg)	$[\phi]_D$ (deg)
1-G0	0.5	−138.40	−8.120
1-G1	0.5	−175.87	−19.895
1-G2	0.34	−279.78	−62.724
1-G3	0.05	+20.62	+9.070
2-G0	0.5	−135.54	−15.876
2-G1	0.66	−120.30	−27.194
2-G2	0.6	−137.67	−61.110
2-G3	0.1	−9.27	−8.153
3-G0	0.52	−226.85	−39.834
3-G1	0.4	−261.00	−88.473
3-G2	1.0	−90.22	−60.059
3-G3	0.01	−23.92	−31.556

result is in contrast with those of a previous report in which more conformationally rigid ester-based dendrons were utilized.[21]

Conclusion

In summary, we have successfully synthesized three new series of chiral dendrimers based on (*R*)-1,1′-bi-2-

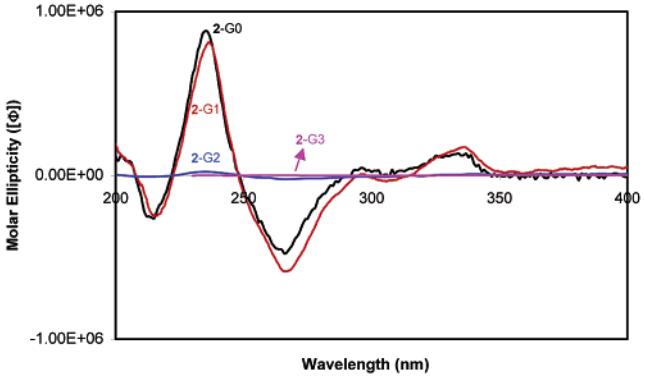


Figure 6. Circular dichroism spectra of **2**-G0 to **2**-G3 in acetonitrile.

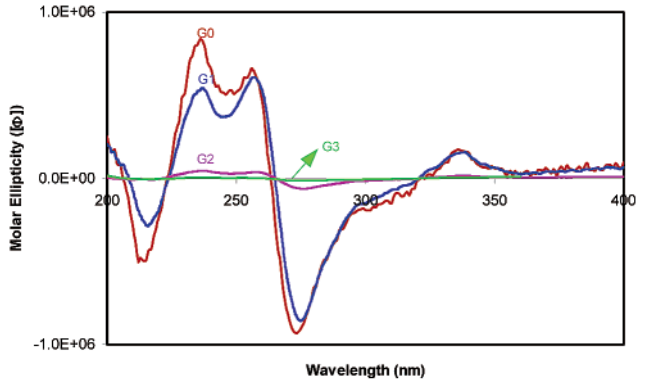


Figure 7. Circular dichroism spectra of **3**-G0 to **3**-G3 in acetonitrile.

naphthyl and its oligomeric (*R*,*R*)-tetranaphthyl and (*R*,*R*,*R*)-hexanaphthyl chiral cores and Fréchet-type aryl−ether dendrons. The UV absorption and blue fluorescence of these dendrimers steadily increase as the generation grows. Both CD and optical rotation data suggest an increase in the dihedral angles between the naphthyl rings through their 1,1′-linkages due to steric bulk of the higher generations of dendrons. CD spectroscopy indicates that absolute configurations of the chiral dendrimers are the same as their chiral cores.

Experimental Section

General Procedures. Column chromatography was performed on silica gel 60. NMR spectra were recorded in $CDCl_3$ on a Varian-400 MHz spectrometer (^1H at 400 MHz and ^{13}C at 100 MHz), with residual proton signal of $CDCl_3$ as reference (7.26 ppm). Mass spectrometric analyses were performed by the University of Illinois School of Chemical Science mass spectrometry facility. Optical rotation measurements were carried out on a JASCO DIP-370 digital polarimeter with a 1-dm cell at the Na D line ($\lambda = 589$ nm) at room temperature. The concentration c is given in g/100 mL. UV−visible spectra were recorded on an Agilent 8453 spectrophotometer. Circular dichroism spectra were recorded using a JASCO J-810 spectropolarimeter. Fluorescence spectroscopy was performed on a Shimadzu RF-5301 luminescence spectrometer.

All reactions were carried out under nitrogen. Solvents and reagents were reagent-grade from commercial sources and used without further purification unless otherwise stated. Solvents for spectroscopic measurement are spectroscopy or HPLC grade. THF was freshly distilled from sodium benzophenone ketyl; acetone and DMF were both distilled anhydrous solvents.

General Procedures for the Preparation of Dendrimers. (a) G0−G2 Dendrimers. An acetone solution of the chiral cores **1**−**3**, Fréchet-type dendron, anhydrous K_2CO_3, and 18-crown-6 in an appropriate ratio was refluxed under N_2. After appropriate length of time, the reaction mixture was concentrated under vacuum and the residue purified by flash chromatography on silica gel to give the pure product as a white solid.

(b) G3 Dendrimer. Under nitrogen, to a DMF solution of sodium hydride at room temperature was added an appropriate amount of the chiral cores. After a few hours of stirring at room temperature, the Fréchet-type dendron G3-Br in a solution of DMF was added to the above resulting yellow solution. The mixture was stirred at room temperature for 3 days and then quenched with water. The mixture was extracted with ethyl acetate and washed with copious amounts of 0.1 N HCl solution. The organic layer was dried over $MgSO_4$. After filtration, the filtrate was concentrated dry and the residue purified by flash chromatography on silica gel to give the pure product as a white solid.

1-G0. 43 h. Yield: 92%. $[\alpha]_D = -138.4°$ ($c = 0.5$, THF). ^1H NMR: δ 7.94 (d, $^3J = 9.4$ Hz, 2H), 7.86 (d, $^3J = 7.8$ Hz, 2H), 7.45 (d, $^3J = 8.6$ Hz, 2H), 7.33 (q, $^4J = 3.9$ Hz, 2H), 7.23 (d, 4H), 6.22 (t, $^3J = 1.6$ Hz, 2H), 6.11 (d, $^3J = 1.6$ Hz, 4H,), 5.00 (s, 4H, $-CH_2-$), 3.47 (s, 12H, $-OCH_3$). $^{13}C\{^1H\}$ NMR: δ 160.80, 154.10, 140.10, 134.36, 129.67, 129.49, 128.05, 126.63, 125.65, 123.99, 120.82, 115.92, 104.13, 100.13, 71.18, 55.29. MS (EI) for $C_{38}H_{34}O_6$, *m*/*z*: calcd, 586.2355; found, 586.2349 (M^+).

1-G1. 96 h. Yield: 70%. $[\alpha]_D = -175.9°$ ($c = 0.5$, THF). ^1H NMR: δ 7.94 (d, $^3J = 8.6$ Hz, 2H), 7.84 (d, $^3J = 7.9$ Hz, 2H), 7.48 (d, $^3J = 9.2$ Hz, 2H), 7.32 (m, 2 H), 7.25 (d, 4H), 6.52 (d, $^3J = 1.8$ Hz, 8H), 6.44 (t, $^3J = 1.8$ Hz, 4H), 6.37 (t, $^3J = 1.8$ Hz, 2H), 6.22 (d, $^3J = 1.8$ Hz, 4H,), 5.03 (s, 4H, $-CH_2-$), 4.58 (s, 8H, $-CH_2-$), 3.81 (s, 24H, $-OCH_3$). $^{13}C\{^1H\}$ NMR: δ 161.13, 159.92, 154.15, 140.14, 139.38, 134.36, 129.64, 129.58, 128.15, 126.71, 125.64, 124.07, 120.89, 115.91, 105.64, 105.27, 101.71, 100.05, 71.09, 69.96, 55.55. MS (FAB) for $C_{70}H_{66}O_{14}$, *m*/*z*: calcd, 1130.4453; found, 1130.4448 (M^+).

1-G2. 144 h. Yield: 63%. $[\alpha]_D = -279.8°$ ($c = 0.34$, THF). ^1H NMR: δ 7.82 (d, $^3J = 9.2$ Hz, 2H), 7.71 (dd, $^4J = 1.8$ Hz, $^3J = 7.3$ Hz, 2H), 7.42 (d, $^3J = 9.2$ Hz, 2H), 7.21 (m, 6H), 6.55 (m, 28H), 6.39 (t, $^3J = 1.8$ Hz, 8H), 6.27 (t, $^3J = 1.8$ Hz, 2H), 6.13 (d, $^3J = 1.8$ Hz, 4H,), 4.98 (d, 4H, $-CH_2-$), 4.92 (s, 16H, $-CH_2-$), 4.47 (s, 8H, $-CH_2-$), 3.75 (s, 48H, $-OCH_3$). $^{13}C\{^1H\}$ NMR: δ 161.16, 160.16, 159.82, 154.00, 140.05, 139.41, 139.38, 134.32, 129.58, 129.57, 128.16, 126.71, 125.56, 124.04, 120.80, 115.73, 106.81, 105.42, 105.20, 101.84, 101.46, 100.09, 70.86, 70.18, 69.85, 55.54. MS (MALDI−TOF): found, 2243.5 ($[M + Na]^+$) and 2259.3 ($[M + K]^+$); calcd 2243.4 ($[M + Na]^+$) and 2259.3 ($[M + K]^+$).

1-G3. Yield: 27%. $[\alpha]_D = 20.62°$ ($c = 0.05$,THF). ^1H NMR: δ 7.79 (d, $^3J = 9.2$ Hz, 2H), 7.70 (d,$^3J = 7.3$ Hz, 2H), 7.39 (d, $^3J = 9.2$ Hz, 2H), 7.20 (m, 6H), 6.64 (m, 16H), 6.52 (m, 48H), 6.36 (m, 16H), 6.25 (d, 2H), 6.13 (m, 4H,), 4.88 (m, 48H, $-CH_2-$), 4.85 (s, 4H, $-CH_2-$), 4.41 (s, 8H, $-CH_2-$), 3.71 (s, 96H, $-OCH_3$). $^{13}C\{^1H\}$ NMR: δ 161.16, 160.26, 160.14, 159.82, 154.00, 140.07, 139.51, 139.41, 139.34, 134.32, 129.55, 128.17, 126.67, 125.52, 124.01, 120.73, 115.66, 106.82, 106.56, 105.50, 105.44, 101.77, 100.13, 70.73, 70.19, 70.06, 69.82, 55.49. MS (MALDI−TOF): found, 4421.6 ($[M + Na]^+$); calcd, 4421.8 ($[M + Na]^+$).

2-G0. 96 h. Yield: 91%. $[\alpha]_D = -135.5°$ ($c = 0.5$, THF). ^1H NMR: δ 8.10 (s, 2H), 7.99 (d, $^3J = 9.2$ Hz, 2H), 7.94 (d, $^3J = 9.2$ Hz, 2H), 7.86 (d, $^3J = 8.6$ Hz, 2H), 7.56 (dd, $^4J = 1.8$ Hz, $^3J = 8.9$ Hz, 2H), 7.46 (d, $^3J = 8.6$ Hz, 4H), 7.30 (m, 8H), 6.21 (t, $^3J = 1.8$ Hz, 2H), 6.19 (t, $^3J = 1.8$ Hz, 2H), 6.13 (d, $^3J = 1.8$ Hz, 4H), 6.11 (d, $^3J = 1.8$ Hz, 4H), 5.01 (s, 4H, $-CH_2-$), 5.00 (s, 4H, $-CH_2-$), 3.47 (s, 12H, $-OCH_3$), 3.45 (s, 12H, $-OCH_3$). ^{13}C NMR: δ 160.81, 154.32, 154.23, 140.08, 136.58, 134.37, 133.51, 129.97, 129.80, 129.69, 129.57, 128.10, 126.72, 126.40, 126.32, 125.90, 125.66, 124.04, 120.74, 116.31, 115.94, 104.26, 104.14, 100.15, 100.09, 71.24, 71.16, 55.31, 55.28. MS (FAB) for $C_{76}H_{66}O_{12}$, *m*/*z*: calcd, 1170.4554; found, 1170.4558 (M^+).

2-G1. 120 h. Yield: 59%. $[\alpha]_D = -120.3°$ ($c = 0.66$, THF). ^1H NMR: δ 7.91 (m, 6 H), 7.82 (d, $^3J = 8.9$ Hz, 2H), 7.46 (m, 6H), 7.30 (m, 8H), 6.50 (d, $^3J = 2.4$ Hz, 8H), 6.43 (d, $^3J = 1.8$ Hz, 8H), 6.41 (t, $^3J = 2.4$ Hz, 4H), 6.35 (m, 6H), 6.31 (t, $^3J =$

1.8 Hz, 2H), 6.24 (d, ^3J = 1.8 Hz, 4H), 6.21 (d, ^3J = 1.8 Hz, 4H), 5.05 (d, 4H, − CH_2−), 5.03 (s, 4H, −CH_2−), 4.56 (s, 8H, −CH_2−), 4.52 (s, 8H, −CH_2−), 3.79 (s, 24H, − OCH_3), 3.66 (s, 24H, −OCH_3). $^{13}C\{^1H\}$ NMR: δ 161.13, 161.08, 159.93, 154.23, 154.16, 140.17, 140.11, 139.36, 139.25, 136.35, 134.37, 133.46, 129.94, 129.88, 129.6, 128.17, 126.78, 126.39, 126.17, 125.93, 125.61, 124.08, 120.75, 120.69, 116.20, 115.84, 105.66, 105.24, 105.16, 101.69, 101.65, 100.12, 100.05, 71.08, 71.05, 70.12, 69.97, 55.56, 55.44. MS (MALDI−TOF): found, 2284.5 ([M + Na]$^+$) and 2300.6 ([M + K]$^+$); cacld, 2283.6 ([M + Na]$^+$) and 2299.6 ([M + K]$^+$).

2-G2. 144 h. Yield: 41%. $[\alpha]_D = -137.7°$ (c = 0.6, THF). ^1H NMR: δ 7.86 (s, 2H), 7.82 (d, ^3J = 9.2 Hz, 2H), 7.78 (d, ^3J = 9.2 Hz, 2H), 7.68 (d, ^3J = 7.3 Hz, 2H), 7.46 (d, ^3J = 8.8 Hz, 2H), 7.38 (d, ^3J = 9.2 Hz, 4H), 7.21 (m, 8H), 6.55 (d, ^3J = 2.4 Hz, 32H), 6.53 (m, 12H), 6.50 (d, ^3J = 1.8 Hz, 8H), 6.48 (d, ^3J = 2.4 Hz, 4H), 6.38 (t, ^3J = 1.8 Hz, 8H), 6.35 (t, ^3J = 2.4 Hz, 8H), 6.26 (t, ^3J = 1.8 Hz, 2H), 6.23 (t, ^3J = 1.8 Hz, 2H), 6.19 (d, ^3J = 1.8 Hz, 4H), 6.11 (d, ^3J = 1.8 Hz, 4H), 4.98 (s, 4H, −CH_2−), 4.96 (s, 4H, − CH_2−), 4.91 (s, 16H, −CH_2−), 4.81 (s, 16H, −CH_2−), 4.45 (s, 8H, −CH_2−), 4.43 (s, 8H, − CH_2−), 3.74 (s, 48H, −OCH_3), 3.69 (s, 48H, −OCH_3). $^{13}C\{^1H\}$ NMR: δ 161.20, 161.15, 160.18, 160.15, 159.87, 159.82, 154.14, 154.06, 140.11, 140.06, 139.43, 139.35, 136.26, 134.31, 133.42, 129.95, 129.88, 129.54, 128.14, 126.73, 126.33, 126.13, 125.90, 125.56, 124.02, 120.68, 120.59, 115.98, 115.73, 106.83, 105.43, 105.42, 101.86, 101.68, 100.05, 70.18, 70.08, 69.84, 55.52, 55.47. MS (MALDI−TOF): found, 4462.2 ([M + Na]$^+$) and 4478.1 ([M + K]$^+$); calcd, 4461.9 ([M + Na]$^+$) and 4478.0 ([M + K]$^+$).

2-G3. Yield: 20%. $[\alpha]_D = -9.27°$ (c = 0.1,THF). ^1H NMR: δ 7.93 (s, 2H), 7.85 (d, ^3J = 9.2 Hz, 2H), 7.73 (d, ^3J = 9.2 Hz, 2H), 7.65 (d, ^3J = 7.3 Hz, 2H), 7.47 (m, 2H), 7.34 (d, ^3J = 9.2 Hz, 4H), 7.18 (m, 8H), 6.50 (m, 144H), 6.33 (m, 24H), 6.20 (m, 8H), 6.03 (m, 4H), 4.83 (m, 104H, −CH_2−), 4.42 (s, 8H, −CH_2−), 4.34 (s, 8H, −CH_2−), 3.69 (s, 96H, −OCH_3), 3.65 (s, 96H, −OCH_3). $^{13}C\{^1H\}$ NMR: δ 161.13, 161.10, 160.24, 160.19, 160.11, 159.89, 159.74, 154.12, 153.98, 139.97, 139.51, 139.33, 136.26, 134.30, 133.42, 131.08, 129.74, 129.47, 129.00, 128.14, 126.71, 125.94, 125.21, 124.03, 123.98, 120.68, 120.47, 115.73, 115.69, 106.83, 106.55, 105.42, 105.40, 101.75, 100.09, 100.06, 70.15, 70.09, 69.84, 60.07, 55.46, 55.41. MS (MALDI−TOF): found, 8822.1 ([M + Na]$^+$) and 8837.5 ([M + K]$^+$); calcd, 8818.6 ([M + Na]$^+$) and 8834.7 ([M + K]$^+$).

3-G0. 120 h. Yield: 74%. $[\alpha]_D = -226.8°$ (c = 0.5, THF). ^1H NMR: δ 8.11 (s, 4H), 8.00 (m, 4H), 7.94 (d, J = 8.8 Hz, 2H), 7.86 (d, J = 8.8 Hz, 2H), 7.58 (m, 4H), 7.47 (m, 6H), 7.30 (m, 10H), 6.21 (t, ^3J = 1.8 Hz, 2H), 6.19 (t, ^3J = 1.8 Hz, 4H), 6.14 (d, ^3J = 1.8 Hz, 4H), 6.12 (d, ^3J = 1.8 Hz, 4H), 6.11 (d, ^3J = 1.8 Hz, 4H), 5.03 (s, 4H, −CH_2−), 5.012 (s, 4H, −CH_2−), 5.010 (s, 4H, −CH_2−), 3.47 (s, 12H, − OCH_3), 3.45 (s, 12H, −OCH_3), 3.44 (s, 12H, −OCH_3). $^{13}C\{^1H\}$ NMR: δ 160.81, 154.33, 154.32, 154.23, 140.07, 140.04, 140.01, 136.61, 136.56, 134.37, 133.50, 129.98, 129.86, 129.80, 129.68, 129.56, 128.09, 126.71, 126.47, 126.40, 126.32, 125.91, 125.66, 124.04, 120.74, 120.67, 116.32, 115.95, 104.26, 104.14, 100.15, 100.09, 71.25, 71.16, 55.48, 55.30, 55.28. MS (MALDI−TOF): found, 1778.0 ([M + Na]$^+$) and 1796.1 ([M + K]$^+$); calcd, 1779.0 ([M + Na]$^+$) and 1795.1 ([M + K]$^+$).

3-G1. 120 h. Yield: 40%. $[\alpha]_D = -261.0°$ (c = 0.4, THF). ^1H NMR: δ 7.90 (m, 10H), 7.82 (d, J = 8.8 Hz, 2H), 7.47 (m, 10H), 7.27 (m, 10H), 6.50 (d, ^3J = 1.8 Hz, 8H), 6.44 (d, ^3J = 2.4 Hz, 8H), 6.43 (d, ^3J = 1.8 Hz, 8H), 6.41 (m, 8H), 6.32 (m, 10H), 6.25 (d, ^3J = 1.8 Hz, 4H), 6.24 (d, ^3J = 2.4 Hz, 4H), 6.21 (d, ^3J = 1.8 Hz, 4H), 5.06 (d, 4H, −CH_2−), 5.04 (d, 4H, −CH_2−), 5.02 (s, 4H, −CH_2−), 4.55 (s, 8H, −CH_2−), 4.54 (s, 8H, −CH_2−), 4.52 (s, 8H, −CH_2−), 3.78 (s, 24H, − OCH_3), 3.66 (s, 24H, −OCH_3), 3.65 (s, 24H, −OCH_3). $^{13}C\{^1H\}$ NMR: δ161.12, 161.08, 159.95, 159.92, 154.25, 154.22, 154.16, 140.16, 140.10, 139.35, 139.24, 136.32, 134.36, 133.47, 129.93, 129.92, 129.60, 128.17, 126.78, 126.45, 126.40, 126.17, 125.93, 125.61, 124.08, 120.75, 120.67, 120.58, 116.19, 115.83, 105.64, 105.22, 105.17, 101.64, 100.10, 100.04, 71.04, 69.99, 55.56, 55.43. MS (MALDI−TOF): found, 3413.0 ([M + Na]$^+$) and 3430.0 ([M + K]$^+$); calcd, 3412.8 ([M + Na]$^+$) and 3428.9 ([M + K]$^+$).

3-G2. 240 h. Yield: 40%. $[\alpha]_D = -90.22°$ (c = 1.0, THF). ^1H NMR: δ 7.81 (m, 10H), 7.67 (d, J = 7.9, 2H), 7.45 (m, 4H), 7.37 (m, 6H), 7.23 (m, 10H), 6.52 (s, 24H), 6.50 (m, 48H), 6.35 (m, 24H), 6.20 (m, 24H), 6.09 (m, 6H), 4.96 (m, 12H, −CH_2−), 4.90 (s, 16H, −CH_2−), 4.80 (s, 32H, −CH_2−), 4.43 (m, 24H, −CH_2−), 3.74 (s, 48H, −OCH_3), 3.67 (s, 48H, −OCH_3), 3.66 (s, 48H, −OCH_3). $^{13}C\{^1H\}$ NMR: δ 161.18, 160.16, 160.14, 159.86, 159.84, 159.78, 154.13, 154.12, 154.02, 140.10, 140.05, 139.86, 139.42, 139.33, 136.21, 134.30, 134.06, 133.41, 129.87, 129.76, 129.52, 128.15, 126.47, 126.45, 126.40, 126.17, 126.13, 125.96, 125.90, 122.30, 120.58, 120.45, 120.31, 115.92, 106.82, 105.42, 104.91, 101.84, 101.48, 100.07, 100.02, 70.16, 70.05, 69.85, 69.73, 55.53, 55.46, 53.98. MS (MALDI−TOF): found, 6680.0 ([M + Na]$^+$) and 6694.9 ([M + K]$^+$); calcd, 6680.3 ([M + Na]$^+$) and 6696.4 ([M + K]$^+$).

3-G3. Yield: 21% (about 90% pure). $[\alpha]_D = -23.92°$ (c = 0.01,THF). ^1H NMR ($CDCl_3$, 400 MHz): δ 7.81−7.23 (m, 32 H), 6.68−6.32 (m), 4.96−4.42 (m, −CH_2−), 3.76 (s, 96 H, −OCH_3), 3.72 (s, 96 H, −OCH_3), 3.69 (s, 96 H, −OCH_3). MS (MALDI−TOF): found, 13221 ([M + Na] $^+$); calcd, 13215.4 ([M + Na] $^+$).

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Supporting Information Available: Figures S1 and S2, NMR spectra for **1**-G0 to **1**-G3 (S1) and **3**-G0 to **3**-G2 (S2), and Figures S3 and S4, CD spectra for **3**-G2 (S3) and **3**-G3 (S4). This material is available free of charge via the Internet at http://pubs.acs.org.

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