Synthesis and Chiroptical Properties of Dendrimers Elaborated from a Chiral, Nonracemic Central Core

Jean-Louis Chaumette, Matthew J. Laufersweiler, and Jon R. Parquette*

Department of Chemistry, The Ohio State University, Columbus, Ohio 43210

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Three generations of ester-terminated dendrimers have been constructed from (1*R*,2*S*)-2-amino-1-phenyl-1,3-propanediol, **1**, as the central core. The chiroptical properties of the dendrimers were measured revealing that the molar rotations [Φ] of the dendrimers decreased with increasing dendrimer generation. Comparison to a series of substituted benzoate derivatives of **1** suggested that the decrease in rotation was a consequence of a steric effect upon the conformational equilibrium of the central core that increased with increasing dendrimer generation. The optical rotations of dendrimers **7**−**9** were also observed to be solvent and temperature dependent.

Introduction

The stepwise synthesis and nanoscopic dimensions of dendrimeric molecules places this new class of macromolecules at the interface of traditional organic and polymer chemistry.[1] The well-defined structure and homogeneity of these materials provides an opportunity to investigate whether the chirality of a particular subunit can be transmitted to distal portions of the molecule.[2] Such conformational order,[3] if present, would be useful in developing asymmetric catalysts that derive function through asymmetric three-dimensional order. Several examples of dendrimers containing chiral branches,[4] or termini,[5,6] have been reported to exhibit rotations linearly proportionate to the number of chiral subunits present in the molecule suggesting the absence of conformational order. Seebach, however, has observed anomalies in chiroptical data for dendrimers that were either constructed from a chiral core with achiral branches or with fully chiral branches suggesting possible conformational order in the branches.[7]

Recent studies suggest that dendrimers constructed with Fréchet-type polyether dendritic wedges are conformationally quite flexible.[8] This program is directed at studying the properties of internally hydrophobic chiral dendrimers with polar groups on the periphery in aqueous media. Conformational order should be optimal in polar solvents such as water that interact favorably with the polar termini but poorly with the internal regions of the polymer. This effect should lead to a compression of the dendrimer that minimizes interactions of the polar solvent with the nonpolar interior thereby enforcing a more compact globular structure.[9] Chiral, amphiphilic dendrimers may be useful as enantioselective phase-transfer catalysts in aqueous media especially if conformational order can be induced throughout the dendritic branches.

In this paper, we report the synthesis and chiroptical properties of ester-terminated dendrimers constructed with achiral polyether branch segments from (1*R*,2*S*)-2-amino-1-phenyl-1,3-propanediol, **1** (Chart 1). The observed chiroptical properties are rationalized by changes occurring in the conformational equilibrium of the chiral, nonracemic central core as a function of dendrimer generation.

Results and Discussion

Dendrimer Synthesis and Characterization. An initial objective was focused on delineating a modular strategy to allow simple access to dendrimers containing polar termini and chiral, nonracemic central cores. Therefore, the convergent synthetic method of Fréchet[10] was exploited to prepare monodisperse dendrimers from

(1) Newkome, G. R.; Moorefield, C. N.; Vögtle, F. *Dendritic Molecules-Concepts-Synthesis-Perspectives*; VCH: New York, 1996.

(2) For a recent discussion of the chirality of dendrimer systems, see: (a) Peerlings, H. W. I.; Meijer, E. W. *Chem. Eur. J.* **1997**, *3*, 1563. (b) Thomas, C. W.; Tor, Y. *Chirality* **1998**, *10*, 53. (c) Seebach, D.; Rheiner, P. B.; Greiveldinger, G.; Butz, T.; Sellner, H. *Top. Curr. Chem.* **1998**, *197*, 125.

(3) We define "conformational order" as the presence of stable secondary structure within the branch segments of the polymer.

(4) (a) Chow, H.-F.; Fok, L. F.; Mak, C. C. *Tetrahedron Lett.* **1994**, *35*, 3547. (b) Chow H.-F.; Mak, C. C. *Tetrahedron Lett.* **1996**, *37*, 5935. (c) Chow, H.-F.; Mak, C. C. *J. Chem. Soc., Perkin Trans. 1* **1997**, 91. (d) McElhanon, J. R.; McGrath, D. V. *J. Am. Chem. Soc.* **1998**, *120*, 1647.

(5) (a) Newkome, G. R.; Lin, X.; Weis, C. D. *Tetrahedron: Asymmetry* **1991**, *10*, 957. (b) Lartigue, M.-L.; Caminade, A.-M.; Majoral, J.-P. *Tetrahedron: Asymmetry* **1997**, *8*, 2697.

(6) The examples in ref 5 exhibit rotations that increase with increasing numbers of chiral termini. However, in the following system, due to dense packing on the surface occurring due to hydrogen bonding, optical activity decreased as the number of amino acid termini present on poly(propylene imine) dendrimers was increased: Jansen, J. F. G. A.; Peerlings, J. H. W. I.; de Brabander-Van den Berg, E. M. M.; Meijer, E. W. *Angew. Chem., Int. Ed. Engl.* **1995**, *34*, 1206. Dyes encapsulated in the poly(propylene imine) system with an optical rotation of zero exhibited a small induced circular dichroism which could be the result of the achiral pockets adopting chiral, nonracemic conformations: Jansen, J. F. G. A.; de Brabander-van den Berg, E. M. M.; Meijer. E. W. *Recl. Trav. Chim.* **1995**, *114*, 225.

(7) (a) Seebach, D.; Lapierre, J.-M.; Greiveldinger, G.; Skobridis, K. *Helv. Chim. Acta* **1994**, *77*, 1673. (b) Seebach, D.; Lapierre, J.-M.; Skobridis, K.; Greiveldinger, G. *Angew. Chem., Int. Ed. Engl.* **1994**, *33*, 440. (c) Murer, P.; Seebach, D. *Angew. Chem., Int. Ed. Engl.* **1995**, *34*, 2116. (d) Murer, P. K.; Lapierre, J.-M.; Greiveldinger, G.; Seebach, D. *Helv. Chim. Acta* **1997**, *80*, 1648.

(8) (a) Peerlings, H. W. I.; Struijk, M. P.; Meijer, E. W. *Chirality* **1998**, *10*, 46. (b) Kremers, J. A.; Meijer, E. W. *J. Org. Chem.* **1994**, *59*, 4262. (c) Peerlings, H. W. I.; Trimbach, D. C.; Meijer, E. W. *J. Chem. Soc., Chem. Commun.* **1998**, 497 (d) Karakaya, B.; Claussen, W.; Gessler, K.; Saenger, W.; Schlüter, A. D. *J. Am. Chem. Soc.* **1997**, *119*, 3296.

(9) Tanford, C. *The Hydrophobic Effect: Formation of Micelles and Biological Membranes*, 2nd ed.; John Wiley and Sons: New York, 1980.

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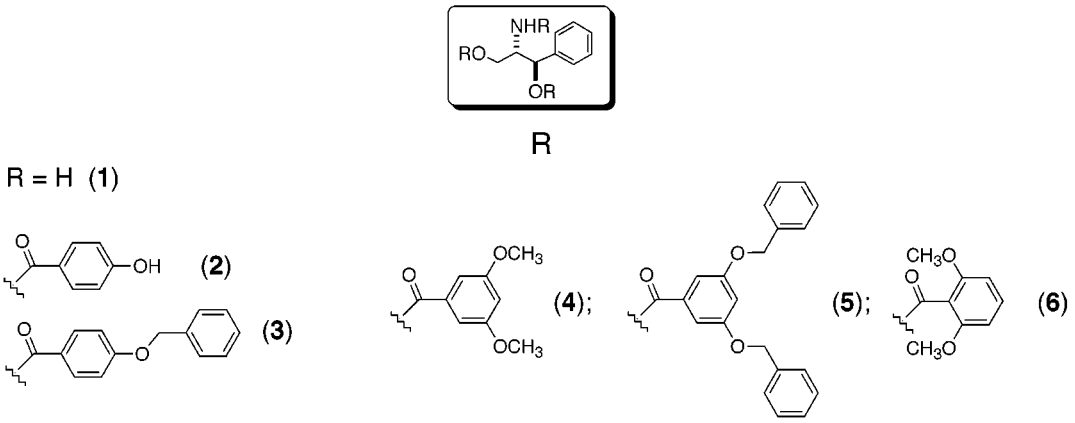
Chart 1



(1*R*,2*S*)-1-phenyl-2-amino-1,3-propanediol, **1**. We found that attaching a phenolic linker to **1** simplified alkylation with the ester-terminated dendron monobromides by preventing polyalkylation of the amine and transesterification of the ester termini with alkoxides generated from **1**. This strategy should afford a general method to introduce a series of chiral, nonracemic cores with diverse functional groups using a similar protocol for attachment of the dendron branch segments.

Accordingly, aminodiol **1** was acylated with 4-(*tert*-butyldimethylsiloxy)benzoyl chloride and then deprotected with $(n\text{-}C_4H_9)_4NF$ affording **2** in 56% overall yield. Alternatively, acylation with 4-(benzyloxy)benzoyl chloride followed by hydrogenation over Raney-Ni provided a more convenient, albeit lower yielding,[11] procedure to prepare **2**. Convergent trialkylation of the central core, **2**, with the first ($(MeO_2C)_2$[G-1]-Br), second ($(MeO_2C)_4$-[G-2]-Br), and third ($(MeO_2C)_8$[G-3]-Br)[12] generation polyether dendritic monobromides was achieved using K_2CO_3/18-C-6 in THF−DMF[13] (3:1) at 70 °C. Purification over silica gel afforded monodisperse dendrimers with molecular weights of 1781 (**7**, 74%), 3402 (**8**, 80%), and 6643 (**9**, 70%) (Chart 2) with 6, 12, and 24 terminal esters, respectively.[14]

Dendrimers **7**−**9** all showed gel permeation chromatography (GPC) traces with low polydispersities and the expected increase in M_w with increasing generation. The structure of the first generation dendrimer **7** was readily assigned by the ^{13}C and ^1H NMR spectra and electrospray mass spectrometry. However, the core protons of the second and third generation molecules were almost invisible due to the large number of resonances arising from the branch segments. Consequently, MALDI-TOF spectrometry[15] was performed for the larger dendrimers. Second generation dendrimer **8** exhibited a signal in the MALDI-TOF spectrum at m/z = 3425 (M + 23 (Na)), which verified the structure, and at m/z = 2306 resulting from a fragmentation at the benzylic position of the core.[16] The signal/noise in the MALDI-TOF spectrum of the third generation dendrimer **9** was low due to inefficient ionization but exhibited a signal at m/z = 6683 (M + 39 (K)). GPC analysis of **9** revealed a molecular weight, by comparison to polystyrene standards, also consistent with the expected structure (M_{calc} = 6643; M_w = 7178, M_n = 7156, polydispersity = 1.0032). Gel permeation analysis was definitive due to the large molecular weight changes that occurred upon going from the starting core (M_w = 527) to mono- (M_w = 2567), di- (M_w = 4608) and trialkylated (M_w = 6643) products.

Chiroptical Properties. The specific and molar optical activities of **1**−**9** are presented in Table 1. Both the molar and specific rotations of the dendrimers decrease going from the first to the third generation dendrimers (**7**−**9**). Several reports suggest that significant backfolding of the terminal groups occurs in dendrimers leading to a density maximum that is located near the central core region rather than at the periphery.[8d,17] Moreover, the sign and magnitude of optical rotation is extremely sensitive to shifts in conformational equilibrium that are brought about by changes in structure, solvent, or temperature.[18] Consequently, the decrease in molar rotation with increasing generation could be a manifestation of a steric effect on the population of certain conformations of the core that increases with increasing dendron size.[19] As the dendrimers increase in size, it is conceivable that the conformational mobility of the central core region should decrease. Support for this supposition was obtained by preparing a series of tribenzoate derivatives of **1** designed to impart increasing steric congestion

(10) (a) Hawker, C. J.; Fréchet, J. M. J. *J. Am. Chem. Soc.* **1990**, *112*, 7638. (b) Fréchet, J. M. J.; Hawker, C. J.; Wooley, K. L *J. Macromol. Sci., Pure Appl. Chem.* **1994**, *A31*, 1627.

(11) Hydrogenolysis of the secondary benzyloxy group competes with deprotection of the benzyl groups and is minimized by using Raney-Ni.

(12) The dendron monobromides were prepared using a slightly modified procedure developed by Fréchet: Hawker, C. J.; Wooley, K. L.; Fréchet, J. M. J. *J. Chem. Soc., Perkin Trans. 1* **1993**, 1287.

(13) In the absence of DMF, the alkylation efficiency decreases significantly.

(14) All dendrimers gave satisfactory combustion analysis and monodisperse GPC traces.

(15) Indoleacrylic acid was used as the matrix: Leon, J. W.; Fréchet, J. M. J. *Polym. Bull.* **1995**, *35*, 449.

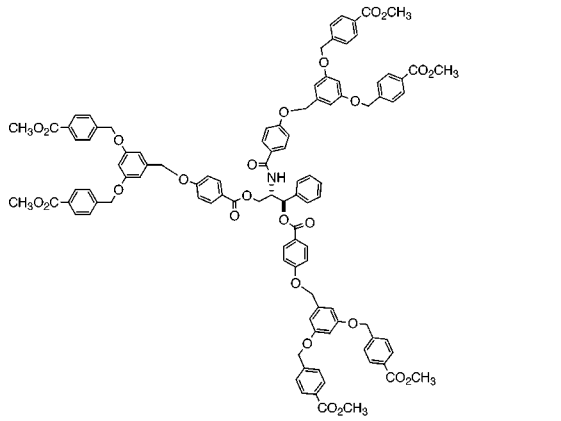
(16) Fragmentation at this benzylic position was also observed in the mass spectrum of central core **2**.

(17) (a) ^2H NMR T_1 relaxation time measurements of PAMAM dendrimers have revealed that internal segment density increases with increasing generation: Meltzer, A. D.; Tirrell, D. A.; Jones, A. A.; Inglefield, P. T. *Macromolecules* **1992**, *25*, 4549. Further studies: (b) Wooley, K. L.; Klug, C. A.; Tasaki, K.; Schaefer, J. *J. Am. Chem. Soc.* **1997**, *119*, 53. (c) Scherrenberg, R.; Coussens, B.; van Vliet, P.; Edouard, G.; Brackman, J.; de Brabander, E. *Macromolecules* **1998**, *31*, 456.

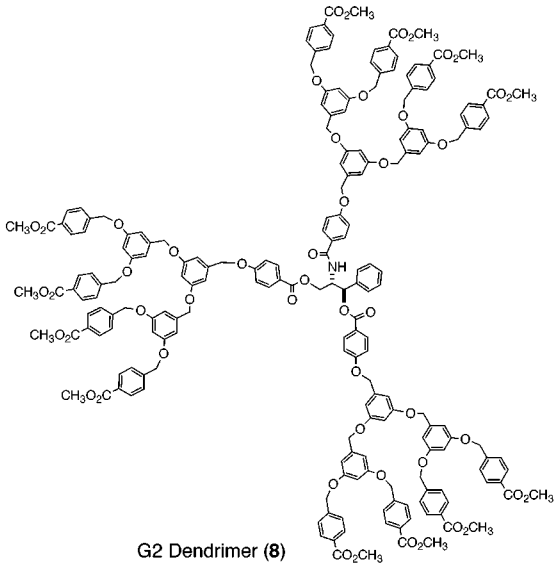
(18) (a) Djerassi, C.; Geller, L. E.; Eisenbraun, E. J. *J. Org. Chem.* **1960**, *25*, 1. (b) Kumata, Y.; Furukawa, J.; Fueno, T. *Bull. Chem. Soc. Jpn.* **1970**, *43*, 3920. (c) Menger, F. M.; Boyer, B. *J. Org. Chem.* **1984**, *49*, 1826. (d) Suga, T.; Ohta, S.; Aoki, T.; Hirata, T. *Chem. Lett.* **1985**, 1331. (e) Lauricella, R.; Kéchayan, J.; Bodot, H. *J. Org. Chem.* **1987**, *52*, 1577. (f) Polavarapu, P. L. *Tetrahedron: Asymmetry* **1997**, *8*, 3397. (g) Galisteo, D.; Gordaliza Ramos, G.; López Sastre, J. A.; Martinez Garcia, M. H.; Núñez Miguel, R. *J. Mol. Struct.* **1998**, *442*, 135.

(19) Peerlings, H. W. I.; Meijer, E. W. *Eur. J. Org. Chem.* **1998**, *4*, 573.

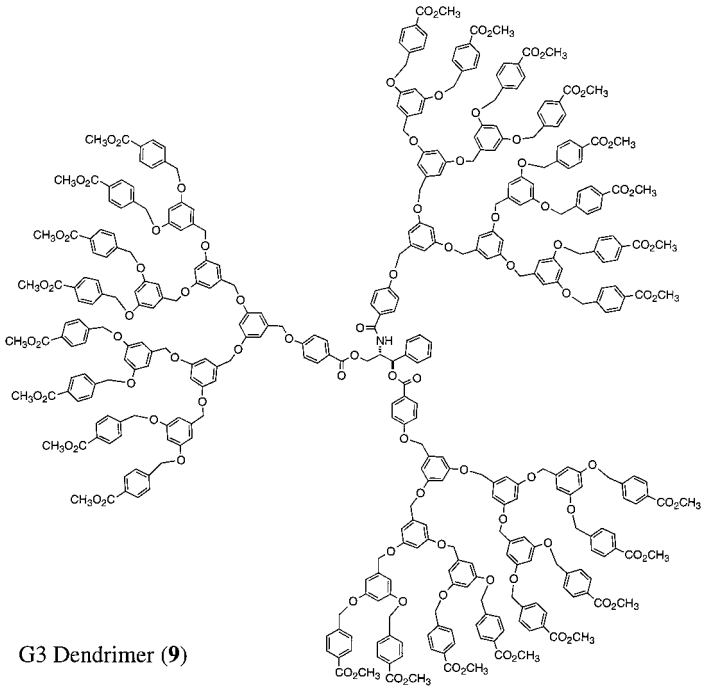
Chart 2



G1 Dendrimer (**7**)



G2 Dendrimer (**8**)



G3 Dendrimer (**9**)

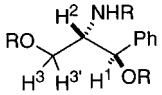
Table 1. Specific and Molar Rotations of 1−9 and Mass Spectral Data

compd	desc	fw[a]	$[\alpha]^{22}_{365}$[b,c]	$[\Phi]^{22}_{365}$[d]	MS[e]
1	AD	167.09	138	229	
2	4-OH	527.16	218	1148	390.1354 (M − $C_7H_5O_3$)
3	4-OBn	797.30	350	2792	798.3089 (MH)
4	3,5-diOMe	659.23	78.3	516	660.2619 (MH)
5	3,5-diOBn	1115.42	50.4	563	1116.4323 (MH)
6	2,6-diOMe	659.23	−213	−1402	660.2600 (MH)
7	G1	1781.58	132 (10.0)[f]	2352 (178)[f]	1782.8 (MH)
8	G2	3402.57	41.7 (9.5)[f]	1418 (323)[f]	3425.9 (M + Na)
9	G3	6643.19	18.2 (4.4)[f]	1209 (292)[f]	6683.4 (M + K)

[a] Exact mass. [b] Specific rotation in 10^{-1} deg cm^2 g^{-1}. [c] **1** and **2** measured in 1:10 MeOH/$CHCl_3$, **3**−**9** in $CHCl_3$. [d] Molar rotation in 10^{-1} deg cm^2 mol^{-1}. [e] **2**−**6** by FAB MS, **7** by electrospray MS, **8** and **9** by MALDI-TOF MS. [f] Values in parentheses measured in 1:4 THF/CH_3CN.

around the core going from **3** to **6**. As shown in Table 1, the 4-benzyloxy derivative (**3**) exhibited a rotation slightly more positive than the G1 dendrimer (**7**). However, both the 3,5-dimethoxy (**4**) and 3,5-dibenzyloxy (**5**) benzoates exhibited molar rotations less positive than **7**−**9** and *the most congested 2,6-dimethoxy derivative (**6**) displayed a negative rotation*.[20] Interestingly, whereas **6** is the most sterically congested benzoate derivative, the absolute value of the rotation is more than twice that of **4** or **5** suggesting a significant shift in conformational equilibrium favoring a conformation displaying a large negative rotation.[18] The reversal in the sign of rotation is a consequence of the 2,6-disubstitution of the benzoate which forces the carbonyl to rotate out of the plane of the phenyl group. This conformation also imparts an electronic perturbation to the central core resulting in a slight downfield shift of $H^{3'}$ in the proton NMR spectrum of **6** relative to **3**−**5**. These electronic and conformational changes are also reflected in the $J_{1,2}$ and $J_{2,3}$ coupling constants in the ^{1}H NMR spectrum which are significantly different in **6** than in **3**−**5** and **7** (Table 2). Therefore, we conclude that the observed decrease in rotatory power with increasing dendrimer generation is due, in part, to the increase in steric congestion developing around the central core as the dendritic wedges grow in size.

Table 2. ^{1}H NMR[a] Coupling Constants for 3−7



compd	δ_{H3}[b] ($J_{2,3}$)[c]	$\delta_{H3'}$($J_{2,3'}$)	δ_{H1} ($J_{1,2}$)
3	4.25 (4.7)	4.46 (3.7)	6.29 (8.4)
4	4.31 (4.8)	4.47 (3.0)	6.29 (7.7)
5	4.39 (5.3)	4.50 (3.6)	6.28 (8.3)
6	4.32 (3.9)	4.64 (9.0)	6.22 (9.1)
7	4.23 (4.7)	4.49 (3.2)	6.33 (8.6)

[a] Spectra recorded in $CHCl_3$ at 22 °C. [b] ppm. [c] Hz.

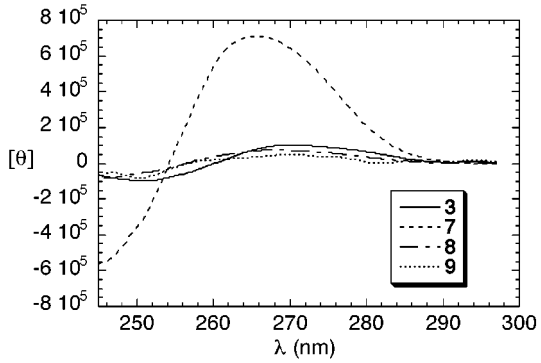


Figure 1. Molar ellipticity of **3** and **7**−**9** in $CHCl_3$ at 22 °C.

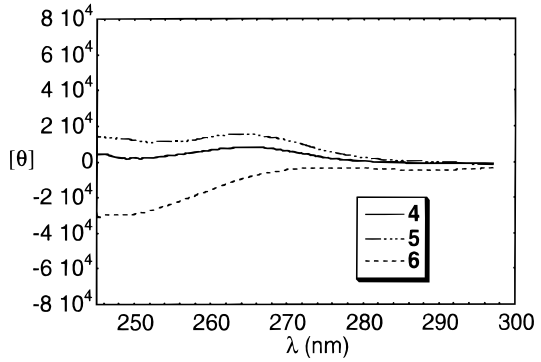


Figure 2. Molar ellipticity of **4**−**6** in $CHCl_3$ at 22 °C.

The circular dichroism spectra of **3** and **7**−**9** exhibit comparable excitonic couplings at 255−260 nm indicating that the tribenzoyl central core is primarily responsible for this coupling rather than interactions among the chromophores present in the branches or on the periphery (Figure 1).[21] The shape and amplitude of the Cotton effects (CE) for **3**, **8**, and **9** are similar; however, **7** exhibits a much more intense CE. The CD spectra of **4**−**6** exhibit CEs of significantly reduced intensity relative to **3** and **7**−**9** and without any observable excitonic coupling (Figure 2). Similar to the optical rotation, a reversal in the sign of the CE occurs in the spectrum of **6**. The origin of the anomalously large ellipticity for **7** cannot easily be rationalized. However, the central tribenzoyl core contains three potentially interacting chromophores and it is well established that the amplitude of the bisignate CE can be approximated by the addition of the amplitudes of each pairwise interaction.[22] Inspection of the lowest energy conformation[23] of the 4-methoxy derivative of **3** suggests that the 1,2- and 2,3-dibenzoyl chromophores are of opposing chirality which would lead to a CE of reduced amplitude as observed for **3**, **8**, and **9** (Figure 3). A conformation of **7** in which the relative orientation of one of these dibenzoate interactions changes could account for the augmented CE.

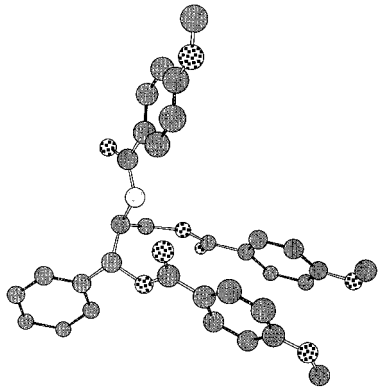


Figure 3. Minimum energy conformer of **3** (4-methoxy derivative) found using molecular mechanics.

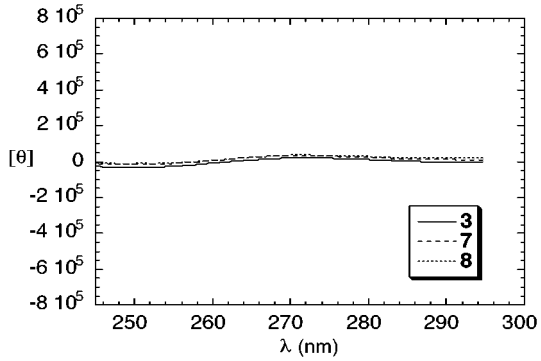


Figure 4. Molar ellipticity of **3**, **7**, and **8** in 1:4 THF−CH_3CN. **9** (not shown for clarity) exhibits no detectable CE.

Prompted by a report that *meta*-linked phenylacetylene oligomers organize into helices in acetonitrile but not in chloroform due to solvophobic effects,[24] we investigated the optical rotations (Table 1) and ellipticities of **7**−**9** in a 1:4 THF−acetonitrile solvent mixture (Figure 4). THF was necessary because **7**−**9** exhibited poor solubility in pure acetonitrile. The optical rotations and ellipticities of **7**−**9** were significantly diminished in this solvent system, and dendrimer **9** exhibited no detectable CE in the CD spectrum (Figure 4). Interestingly, the molar rotations in this solvent system increased slightly going from **7** to **8** but remained constant from **8** to **9**. The methyl benzoate termini of **7**−**9** interact more favorably with the polar solvent than the internal regions of the dendrimers. Therefore, in this poor solvent system, the

(20) **1**−**6** exhibit their most intense UV absorptions bands at 250−260 nm; however, **4**−**6** also exhibit a less intense absorption band at 308, 308, and 282 nm, respectively. Dendrimers **7**−**9** exhibit the most intense bands at 246 nm with a weaker absorption at 260−270 nm. These electronic differences are not solely responsible for the difference in optical rotatory power that is observed because the additional bands at longer wavelength in **4**−**6** should lead to a slight increase in rotation which is not observed.

(21) Since the terminal esters are electronically different than the tribenzoyl core, an interaction of these chromophores would be expected to generate a more complex Cotton effect than is observed.

(22) Nakanishi, K.; Liu, H.-W. *J. Am. Chem. Soc.* **1982**, *104*, 1178.

(23) The lowest energy conformation was generated by employing a Monte Carlo conformational search using the MM2* force field and the GB/SA model for $CHCl_3$ implemented in Macromodel 5.0.

(24) Nelson, J. C.; Saven, J. G.; Moore, J. S.; Wolynes, P. G. *Science* **1997**, *277*, 1793.

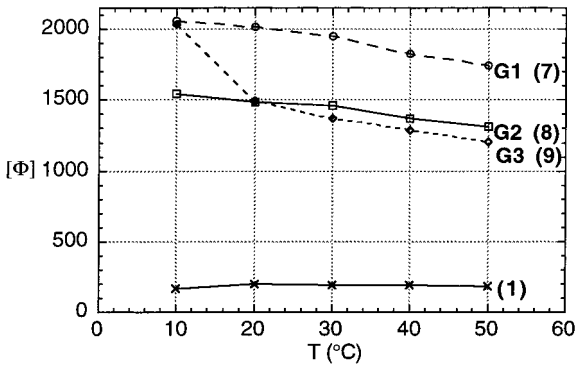


Figure 5. Molar rotation at 365 nm versus temperature (**7**−**9** in $CHCl_3$; **1** in 1:10 $CH_3OH/CHCl_3$).

nonpolar dendritic wedges could be expected to collapse upon the central core in an effort to minimize potentially unfavorable interactions with the solvent resulting in a corresponding conformational change of the central core.[25]

Due to the apparent conformational mobility of the central core and the resultant variation in optical activity, it is not possible at this point to determine the extent, if at all, that asymmetric conformational order contributes to the chiroptical properties; however, a few observations are noteworthy. Upon heating of the samples from 10 to 50 °C, **7** and **8** experience a reversible 15% decrease in optical rotation and the third generation dendrimer, **9**, shows a 41% decrease (Figure 5). While the rate of decrease is similar for **7**−**9** between 20 and 50 °C, the rotation of **9** decreases much more rapidly between 10 and 20 °C. If conformationally chiral substructures were present, an increase in temperature would lead to a decrease in the stability of these structures and a corresponding decrease in optical rotation. However, variation of optical activity of 1−2%/°C is not uncommon and could also reflect a perturbation in solvent−solute equilibria or in the degree of aggregation.[26] DSC analysis of **9** reveals a T_g at 45 °C, but no phase transitions were observed between 10 and 20 °C. Therefore, the steep decrease in rotation between 10 and 20 °C observed for **9** may be indicative of a change in conformational equilibrium that occurs in **9** at low temperatures.

Summary

A series of dendrimers with a chiral central core and methyl benzoate termini have been prepared. On the basis of the investigation of a series of model compounds, the observed decrease in optical activity with increasing generation has been attributed to an increasing steric effect that perturbs the conformational preference of the chiral core. CD measurements also suggest that the observed Cotton effects are due to changes in the population of certain conformations of the central core. We are currently preparing water-soluble derivatives of these and other chiral dendrimers so that the induced CD of achiral dyes can be used as a measure of conformational chirality in the branch segments of the dendrimers.

Experimental Section

General Methods. Melting points were determined in open capillaries and are uncorrected. ^{1}H NMR spectra were recorded at 200 or 300 MHz and ^{13}C NMR spectra at 62.5 or 75 MHz. EI or FAB mass spectra were recorded at The Ohio State University Chemical Instrument Center. MALDI-TOF spectrometry was performed using indoleacrylic acid as the matrix in tetrahydrofuran (THF). Electrospray mass spectrometry was performed on a triple quadrupole mass spectrometer, with positive ion electrospray. Optical rotations were measured at a concentration of 10 mg/mL ($c = 1$). Gel permeation chromatography (GPC) was performed using three divinylbenzene columns arranged in series (500, 10^3, and 10^4 Å) with RI detection. All runs were carried out using THF as the carrier solvent at 40 °C. All reactions were performed under an argon or nitrogen atmosphere. Dimethylformamide (DMF) was dried by distillation from barium oxide or magnesium sulfate, THF was distilled from sodium/benzophenone ketyl, and acetone was distilled from $CaSO_4$ and dichloromethane was distilled from calcium hydride. Chromatographic separations were performed on silica gel 60 (230−400 mesh, 60 Å) using the indicated solvents.

Acylation of (1*R*,2*S*)-2-Amino-1-phenyl-1,3-propanediol. Method 1. A. *tert*-Butyldimethylsilyl 4-((*tert*-Butyldimethylsilyl)oxy)benzoate. To a solution of 4-hydroxybenzoic acid (6.9 g, 50 mmol) in dry dimethylformamide (40 mL) was added a solution of imidazole (13.6 g, 200 mmol) in dimethylformamide (40 mL) followed by a solution of *tert*-butyldimethylsilyl chloride (15.8 g, 105 mmol) in dimethylformamide (40 mL). The mixture was stirred at 60 °C under argon for 16 h and then poured over ice water (ca. 200 g), and the aqueous phase was extracted with diethyl ether (5 × 50 mL). The combined extracts were washed with water (50 mL) and brine (50 mL) and dried over magnesium sulfate. The solvent was removed in vacuo affording 18.2 g (99%) of *tert*-butyldimethylsilyl 4-((*tert*-butyldimethylsilyl)oxy)benzoate as an oil which was used without further purification in part B. ^{1}H NMR (200 MHz, $CDCl_3$): δ 0.23 (s, 6H), 0.36 (s, 6H), 0.99 (s, 9H), 1.02 (s, 9H), 6.85 (d, $J = 8.7$ Hz, 2H), 7.93 (d, $J = 8.7$ Hz, 2H).

B. 4-((*tert*-butyldimethylsilyl)oxy)benzoyl Chloride. *tert*-Butyldimethylsilyl 4-((*tert*-butyldimethylsilyl)oxy)benzoate (18.2 g, 50 mmol, crude from part A) in dichloromethane (50 mL) containing 10 drops of DMF was treated with oxalyl chloride (1.5 equiv, 9.52 g, 6.5 mL, 75 mmol). After 40 h at room temperature, the solvents were evaporated in vacuo and the crude acyl chloride was used in part C without further purification. ^{1}H NMR (200 MHz, $CDCl_3$): δ 0.26 (s, 6H), 0.99 (s, 9H), 6.90 (d, $J = 9.0$ Hz, 2H), 8.03 (d, $J = 9.0$ Hz, 2H).

C. (1*R*,2*S*)-(2-(4-((*tert*-butyldimethylsilyl)oxy)benzamido)-1-phenyl-1,3-propanediyl)bis(4-((*tert*-butyldimethylsilyl)oxy)benzoate). 4-((*tert*-Butyldimethylsilyl)oxy)-benzoyl chloride (50 mmol, crude from part B) in dichloromethane (10 mL) was added dropwise to a cooled (0 °C) solution of (1*R*,2*S*)-2-amino-1-phenyl-1,3-propanediol (2.09 g, 12.5 mmol), (dimethylamino)pyridine (DMAP) (0.15 g, 1.25 mmol), and pyridine (10 mL) in dichloromethane (50 mL). After the addition was complete, the mixture was allowed to warm to room temperature overnight (14 h). Diethyl ether (100 mL) was added to the mixture, and the pyridinium hydrochloride that precipitated was removed by filtration. The filtrate solution was washed with 50 mL portions of 1 N hydrochloric acid (aqueous) until the aqueous phase remained acidic, then with 50 mL portions of 5% aqueous sodium bicarbonate until the aqueous solution remained basic, and finally with water (50 mL). The organic layer was then dried over magnesium sulfate and evaporated to dryness. ^{1}H NMR (200 MHz, $CDCl_3$): δ 0.19 (s, 6H), 0.21 (s, 6H), 0.25 (s, 6H), 0.96 (s, 9H), 0.97 (s, 9H), 1.00 (s, 9H), 4.21 (dd, $J = 11.6$, 4.6, Hz, 1H), 4.46 (dd, $J = 11.6$, 3.7 Hz, 1H), 5.09 (m, 1H), 6.34 (d, $J = 8.5$ Hz, 1H), 6.65 (d, $J = 9.1$ Hz, 1H), 6.71−6.91 (m, 6H), 7.26−7.60 (m, 7H), 7.90−7.97 (m, 4H).

D. (1*R*,2*S*)-(2-(4-hydroxybenzamido)-1-phenyl-1,3-propane*di*ylbis(4-hydroxybenzoate (2). The crude protected core from part C (12.5 mmol) in dry tetrahydrofuran (THF) (50 mL) was treated at 0 °C with a 1 M solution of tetrabutylammonium fluoride in THF (4 equiv, 50 mL, 50 mmol). After the addition was complete, the mixture was allowed to warm to room temperature for 1 h. The mixture was then quenched

(25) Such variation of rotation values with solvent is not unusual. For an example of a solvent-induced reorientation of dipoles that reverses the sign of an ORD curve, see ref 18c.

(26) Eliel, E. L.; Wilen, S. H. *Stereochemistry of Organic Compounds*; Wiley: New York, 1994; p 1076.

by adding 1 N aqueous hydrochloric acid solution (100 mL) and was stirred for an additional 5 min. The mixture was extracted into dichloromethane (4 × 50 mL), and the combined organic layers were dried over magnesium sulfate and evaporated to dryness. Purification by flash chromatography (SiO_2) with (1−5%) methanol/dichloromethane afforded (1*R*,2*S*)-(2-(4-hydroxybenzamido)-1-phenyl-1,3-propanediylbis(4-hydroxybenzoate) (**2**) (3.7 g, 56%) as a white solid: mp = 160−163 °C, ^{1}H NMR (300 MHz, $MeOD_4$) δ 4.25 (dd, J = 11.3, 7.3 Hz, 1H), 4.36 (dd, J = 11.3, 4.6 Hz, 1H), 5.09 (m, 1H), 6.20 (d, J = 7.9 Hz, 1H), 6.74−6.82 (m, 7H), 7.27−7.62 (m, 3H), 7.80−8.03 (m, 3H); ^{13}C NMR (75 MHz, MeOH-d_4) 54.6, 64.1, 76.9, 116.18, 116.32, 116.40, 121.98, 122.07, 126.73, 128.39, 129.87, 129.96, 130.01, 130.55, 133.11, 133.17, 133.29, 139.25, 162.21, 163.90, 167.42, 167.93, 170.97, 173.10 ppm; IR (KBr) 3302 (OH), 1687 (CO) cm^{-1}. HRMS for $C_{23}H_{20}NO_5$ (EI) ($M^+ - C_7H_5O_3$): calcd, *m/e* 390.1342; obsd, *m/e* 390.1354.

Method 2. (1*R*,2*S*)-(2-(4-(benzyloxy)benzamido)-1-phenyl-1,3-propanediylbis(4-(benzyloxy)benzoate) (3). Oxalyl chloride (4.5 g, 3.1 mL, 35.54 mmol) was added dropwise to a suspension of 4-(benzyloxy)benzoic acid (4.1 g, 18 mmol) in dichloromethane (20 mL) and DMF (3 drops), at 25 °C. After 3 h, the solvent was evaporated in vacuo and the yellow oil was dissolved in dichloromethane (25 mL) and added dropwise over 5 min to a solution of (*1R, 2S*)-(+)-2-amino-1-phenyl-1,3-propanediol (0.5 g, 3.0 mmol) and DMAP (0.04 g, 0.33 mmol) in pyridine (15 mL) at 0 °C. The reaction mixture was allowed to warm to 25 °C and was stirred for an additional 18 h. The reaction mixture was transferred to a separatory funnel and washed with 1.2 N aqueous hydrochloric acid (100 mL). The aqueous layer was extracted with dichloromethane (3 × 100 mL), and the combined organic layers were washed sequentially with 1.2 N hydrochloric acid (100 mL), 5% aqueous sodium bicarbonate (100 mL), and saturated aqueous sodium chloride (100 mL) and then dried over Mg_2SO_4 and evaporated to yield 3.97 g of a yellow oil The oil was purified via flash chromatography on silica gel (elution with 100% CH_2Cl_2 to 5% diethyl ether/ CH_2Cl_2) to yield **3** as a white solid (1.52 g, 1.91 mmol, 64%): R_f = 0.58 (5% ether/CH_2Cl_2), mp = 69−74 °C; ^{1}H NMR (300 MHz, $CDCl_3$) δ 4.25 (dd, J = 11.6, 4.7 Hz, 1H), 4.46 (dd, J = 11.6, 3.7 Hz, 1H), 5.06 (s, 2H), 5.08 (s, 2H), 5.13 (s, 2H), 6.29 (d, J = 8.4 Hz, 1H), 6.69 (d, J = 9 Hz, 1H), 6.9−7.0 (m, 6H), 7.26−7.55 (m, 20H), 7.64 (d, J = 8.8 Hz, 2H), 7.95−8.03 (m, 4H); ^{13}C NMR (62.5 MHz, $CDCl_3$) 53.3, 63.5, 70.02, 70.05, 70.11, 75.14, 114.4, 114.5, 114.6, 122.02, 126.47−128.8 (mult. overlapping carbons), 131.7, 131.8, 136.04, 136.24, 136.74, 161.28, 162.7, 165.9, 166.0, 167.03 ppm; IR (KBr) 1715, 1652 cm^{-1}; UV ($CHCl_3$) λ_{max} = 258 nm (ϵ 56 906). HRMS for $C_{51}H_{44}NO_8$ (FAB) (MH): calcd, *m/e* 798.3007; obsd, *m/e* 798.3089.

(1*R*,2*S*)-(2-(4-hydroxybenzamido)-1-phenyl-1,3-propanediylbis(4-hydroxybenzoate) (2). A solution of **3** (290 mg, 0.36 mmol) in 5 mL of methanol/ethyl acetate (1:1) was degassed by bubbling nitrogen through the solution for 5 min. W-2 Raney Ni (60 mg) was added, and the vessel was flushed with H_2 and fitted with a H_2 balloon at 1 atm. After 18 h, the Ni was removed by filtration through a pad of Celite and the filtrate was evaporated in vacuo affording a white solid. The crude solid was purified via flash chromatography on silica gel (elution with 1% methanol/CH_2Cl_2−4% methanol/CH_2Cl_2) to yield **2** (100 mg, 52%) as a white solid.

Preparation of Model Compounds 4−6. The acid chloride was either obtained commercially or prepared by the following procedure: The appropriate carboxylic acid (6 equiv) was treated with oxalyl chloride (12 equiv) and DMF (2 drops) in methylene chloride. After 2 h, the solvent was evaporated in vacuo and the acid chloride was dissolved in dichloromethane and added dropwise over 5 min to a solution of (*1R,2S*)-2-amino-1-phenyl-1,3-propanediol, **1** (1 equiv), and DMAP (10 mol %) in pyridine at 0 °C to obtain a final concentration of 0.25 M in **1**. The reaction mixture was allowed to warm to room temperature and stirred an additional 18 h. The mixture was transferred to a separatory funnel and washed with 1.2 N aqueous hydrochloric acid. The aqueous layer was extracted into dichloromethane (3×), and the combined organic layers were washed sequentially with 1.2 N aqueous hydrochloric acid, 5% aqueous sodium bicarbonate, and saturated aqueous sodium chloride and then dried over Mg_2SO_4 and evaporated. The crude material was purified via flash chromatography on silica gel.

(1*R*,2*S*)-(2-(3,5-dimethoxybenzamido)-1-phenyl-1,3-propanediylbis(3,5-dimethoxybenzoate) (4). This compound was prepared from 3,5-dimethoxybenzoyl chloride and purified via flash chromatography on silica gel (elution with 25% ethyl acetate/ hexanes) to yield **4** as a white solid (100 mg, 0.15 mmol, 51%): mp = 120−124 °C; ^{1}H NMR (300 MHz, $CDCl_3$) δ 3.75 (s, 6H), 3.79 (s, 6H), 3.81 (s, 6H), 4.31 (dd, J = 11.5, 4.8 Hz, 1H), 4.47 (dd, J = 11.5, 3.0 Hz, 1H), 5.15 (m, 1H), 6.29 (d, J = 7.7 Hz, 1H), 6.52 (t, J = 1.9 Hz, 1H), 6.62 (t, J = 2.2 Hz, 1H), 6.64 (t, J = 2.3 Hz, 1H), 6.78 (d, J = 2.0 Hz, 2H), 7.16 (d, J = 2.2 Hz, 2H), 7.18 (d, J = 2.2 Hz, 2H), 7.38 (m, 3H), 7.52 (m, 2H); ^{13}C NMR (75 MHz, $CDCl_3$) 53.1, 55.3, 55.4, 55.5, 63.9, 75.4, 103.9, 104.5, 104.6, 105.9, 106.0, 107.2, 107.3, 127.0, 128.9, 128.97, 131.16, 131.23, 133.35, 136.32, 136.38, 160.57, 160.62, 160.78, 165.85, 166.0, 167.24 ppm; IR (neat) 1722, 1669 cm^{-1}; UV ($CHCl_3$) λ_{max} = 256 nm (ϵ 12 104), 308 (ϵ 4288) nm. HRMS for $C_{36}H_{38}NO_{11}$ (FAB) (MH): calcd, *m/e* 660.2444; obsd, *m/e* 660.2619.

(1*R*,2*S*)-(2-(3,5-dibenzyloxybenzamido)-1-phenyl-1,3-propanediylbis(3,5-dibenzyoxybenzoate) (5). This compound was prepared from 3,5-dibenzyloxybenzoic acid,[27] and the resultant crude oil was purified via flash chromatography on silica gel (elution with 100% CH_2Cl_2 to 5% diethyl ether/ CH_2Cl_2) to yield **5** as a white solid (0.21 g, 0.19 mmol, 32%): mp = 56−60 °C; ^{1}H NMR (300 MHz, $CDCl_3$) δ 4.39 (dd, J = 11.7, 5.31 Hz, 1 H) 4.50 (dd, J = 11.7, 3.6 Hz, 1H), 4.95 (s, 4H), 5.01 (s, 4H), 5.10 (s, 4 H), 5.26 (m, 1H), 6.28 (d, J = 8.28 Hz, 1H), 6.57 (d, J = 7.8 Hz, 1H), 6.75 (t, J = 2.17 Hz, 1H), 6.86 (t, J = 2.24 Hz, 1H), 6.89 (t, J = 2.32 Hz, 1H), 7.04 (d, J = 1.92 Hz, 2H), 7.24−7.58 (m, 40 H); ^{13}C NMR (75 MHz, $CDCl_3$) 53.3, 64.1, 70.13, 70.25, 75.67, 105.6, 105.9, 107.7, 107.8, 108.4, 108.6, 127.2−129.1 (multiple overlapping carbons), 131.3, 131.4, 136.3, 136.4, 136.4, 136.5, 137.8, 159.8, 159.9, 160.0, 165.9, 166.1, 167.5 ppm; IR (cm^{-1}) 1720, 1664; UV ($CHCl_3$) λ_{max} = 256 nm (ϵ 17 330), 308 (ϵ 7882) nm. HRMS for $C_{72}H_{62}NO_{11}$ (FAB) (MH): calcd, *m/e* 1116.4323; obsd, *m/e* 1116.4323.

(1*R*,2*S*)-(2-(2,6-dimethoxybenzamido)-1-phenyl-1,3-propanediylbis(2,6-dimethoxybenzoate) (6). This compound was prepared from 2,6-dimethoxybenzoyl chloride, and the resultant crude oil was purified via flash chromatography on silica gel (elution with 50% ethyl acetate/ hexanes) to yield **6** as a white solid (0.09 g, 0.14 mmol, 46%): mp = 105−108 °C; ^{1}H NMR (300 MHz, $CDCl_3$) δ 3.59 (s, 6H), 3.71 (s, 6H), 3.80 (s, 6H), 4.32 (dd, J = 10.6, 3.9 Hz, 1H), 4.64 (dd, J = 10.6, 9.0 Hz, 1H), 4.99 (m, 1H), 6.22 (d, J = 9.1 Hz, 1H), 6.46 (d, J = 8.41 Hz, 2H), 6.56 (d, J = 8.45 Hz, 2H), 6.58 (d, J = 8.56 Hz, 2H), 7.23 (t, J = 8.37 Hz, 1H), 7.26−7.39 (m, 6H), 7.51 (d, J = 8.41 Hz, 2H); ^{13}C NMR (75 MHz, $CDCl_3$) 52.1, 55.6, 55.8, 56.0, 62.8, 73.6, 103.7, 126.3, 126.6, 127.6, 128.0, 130.5, 131.2, 137.2, 157.3, 157.5, 157.7, 164.9, 165.3, 165.9 ppm; IR (cm^{-1}) 3054, 2968, 1736, 1671, 1597, 1473; UV ($CHCl_3$) λ_{max} = 250 nm (ϵ 7999), 282 nm (ϵ 5731). HRMS for $C_{36}H_{38}NO_{11}$ (FAB) (MH): calcd, *m/e* 660.2444; obsd, *m/e* 660.2600.

Dendron Monobromide Synthesis. $(MeO_2C)_2$[G-1]-Br, $(MeO_2C)_4$[G-2]-Br, and $(MeO_2C)_8$[G-3]-Br were prepared by the method of Fréchet;[12] however, the starting methyl 4-(bromomethyl)benzoate was prepared as follows.

Methyl 4-(Bromomethyl)benzoate.[12] Methyl *p*-toluate (212 g, 1.4 mol) and 2 L of benzene were added to a 5-L three-necked flask fitted with a condenser, a mechanical stirrer, and a 1-L addition funnel. The mixture was heated to reflux, and a 250-W sunlamp was focused on the reaction. Bromine (72.6 mL, 1.4 mol) in 900 mL of benzene was then added dropwise via addition funnel over a period of 2 h while the solution was at reflux. After the addition of bromine was complete, the lamp

(27) Haddleton, D. M.; Sahota, H.; Taylor, P. C.; Yeates, S. G. *J. Chem. Soc., Perkin Trans. 1* **1996**, 649.

remained focused on the flask for an additional 10 minutes until the dark red color of the solution dissipated and the solution became pale yellow. The reaction mixture was then cooled to ambient temperature, and the solvent was evaporated in vacuo. The remaining oily residue crystallized at 4 °C overnight affording light yellow/orange crystals. Recrystallization from heptane afforded methyl 4-(bromomethyl)benzoate (157 g, 0.69 mol, 49%) as light yellow/white crystals.

General Procedure for Synthesis of Dendrimers 7−9. The dendron benzyl bromide (3.33 equiv), (1*R*,2*S*)-(2-(4-hydroxybenzamido)-1-phenyl-1,3-propanediylbis(4-hydroxybenzoate) (**2**) (1 equiv), finely powdered potassium carbonate (5 equiv), and 18-crown-6 (0.2 equiv) were mixed in a sealed vessel. The vessel was charged with THF (5 mL), and dimethylformamide (1.5 mL) was added to homogenize the suspension. The sealed vessel was heated to 70 °C for 12 h. After being cooled to room temperature, the pressure tube was opened and water was added. The mixture was then extracted with dichloromethane (3×), and the combined organic layers were washed with brine, dried over magnesium sulfate, and evaporated to dryness. Purification was accomplished by column chromatography over silica gel.

G1 Dendrimer (7). 6-Cascade: (1*R*,2*S*)-1-Phenylpropane [3-1,2,3]:2-[(4-(1-oxo-2-azaethyl)-1-phenylene):(5-(2-oxaethyl)-1,3-phenylene):(4-(2-oxaethyl)-1-(carbomethoxy)-benzene)]:1,3-bis[4-(1-oxo-2-oxaethyl)-1-phenylene):(5-(2-oxaethyl)-1,3-phenylene):(4-(2-oxaethyl)-1-(carbomethoxy)benzene). This compound was prepared from $(MeO_2C)_2$[G-1]-Br and **2**. Purification by flash chromatography (5−10% ether/dichloromethane) afforded the G1-$(COOMe)_6$ (**7**) dendrimer as a white solid in 74% yield (250 mg): ^{1}H NMR (200 MHz, $CDCl_3$) δ 3.90 (s, 18H), 4.23 (dd, J = 11.3, 4.7 Hz, 1H), 4.49 (dd, J = 11.3, 3.2 Hz, 1H), 5.06−5.09 (m, 19H), 6.33 (d, J = 8.6 Hz, 1H), 6.52−6.60 (m, 3H), 6.8−6.7 (m, 6H), 6.81−6.95 (m, 7H), 7.34−7.53 (m, 17H), 7.64 (d, J = 8.8 Hz, 2H), 7.94−8.06 (m, 16H); ^{13}C NMR (62.5 MHz, $CDCl_3$) 52.07, 53.26, 63.83, 69.43, 69.74, 75.21, 101.32, 101.79, 105.87, 106.32, 106.37, 106.45, 114.57, 121.91, 122.29, 126.71, 126.89, 126.97, 127.19, 127.60, 128.03, 128.41, 128.78, 128.87, 129.73, 129.83, 131.73, 131.86, 132.31, 136.92, 138.86, 139.04, 141.79, 159.90, 159.93, 161.09, 162.51, 165.88, 165.92, 166.71, 166.99 ppm; MS (electrospray) m/z 1783.8 (1782.87 calcd for $C_{105}H_{92}NO_{26}$, MH); IR ($CDCl_3$) 1719, 1605 cm^{-1}; UV ($CHCl_3$) λ_{max} = 246 nm (ϵ 75 166), 265 nm (ϵ 33 061). Anal. Calcd for $C_{105}H_{91}NO_{26}$: C, 70.74; H, 5.14; N, 0.79. Found: C, 70.49; H, 5.19; N, 0.79.

G2 Dendrimer (8). 12-Cascade: (1*R*,2*S*)-1-phenylpropane [3-1,2,3]:2-[(4-(1-oxo-2-azaethyl)-1-phenylene):(5-(2-oxaethyl)-1,3-phenylene)^2:(4-(2-oxaethyl)-1-(carbomethoxy)-benzene)]:1,3-bis[4-(1-oxo-2-oxaethyl)-1-phenylene):(5-(2-oxaethyl)-1,3-phenylene)^2:(4-(2-oxaethyl)-1-(carbomethoxy)benzene). This compound was prepared from $(MeO_2C)_4$[G-2]-Br and **2**. Purification was performed by flash chromatography (5−10% ether/dichloromethane) affording the G2-$(COOMe)_{12}$ (**8**) dendrimer as a white solid in 80% yield (520 mg): ^{1}H NMR (200 MHz, $CDCl_3$) δ 3.87 (s, 36H), 4.25 (br dd, 1H) 4.50 (br s, 1H), 4.93−5.03 (m, 43H), 6.33 (d, J = 8.3 Hz, 1H), 6.4−6.6 (m, 27H), 6.83−6.98 (m, 7H), 7.32−7.49 (m, 27H), 7.64 (d, J = 8.4 Hz, 2H), 7.97−8.02 (m, 30H); ^{13}C NMR (62.5 MHz, $CDCl_3$) 52 ($ArCO_2CH_3$'s), 53 (1*C*H−NH, core), 63 (1*C*H_2−O, core), 69.3−69.7 (*C*H_2O's), 75 (1PH*C*HO, core), 101, 107, 114, 121, 121−133 (multiple carbons), 137−142 (multiple carbons) 159−162 (multiple carbons) ppm; IR ($CDCl_3$) 1719, 1598 cm^{-1}; MS (MALDI-TOF) m/z 3425 (3425 calcd for $C_{201}H_{175}NO_{50}Na$ (M + Na)); UV ($CHCl_3$) λ_{max} = 246 nm (ϵ 148 216), 265 nm (ϵ 54 291). Anal. Calcd for $C_{201}H_{175}NO_{50}$: C, 70.91; H, 5.18; N, 0.41. Found: C, 70.65; H, 5.19; N, 0.43.

G3 Dendrimer (9). 24-Cascade: (1*R*,2*S*)-1-Phenylpropane [3-1,2,3]:2-[(4-(1-oxo-2-azaethyl)-1-phenylene):(5-(2-oxaethyl)-1,3-phenylene)^3:(4-(2-oxaethyl)-1-carbomethoxybenzene)]:1,3-bis[4-(1-oxo-2-oxaethyl)-1-phenylene):(5-(2-oxaethyl)-1,3-phenylene)^3:(4-(2-oxaethyl)-1-(carbomethoxy)benzene). This compound was prepared from $(MeO_2C)_8$[G-3]-Br and **2**. Purification was performed by flash chromatography (5% to 15% ether/dichloromethane) affording the G3-$(COOMe)_{24}$ (**9**) dendrimer as a white solid in 70% yield (880 mg): ^{1}H NMR (200 MHz, $CDCl_3$) δ 3.86 (s, 72H), 4.23 (br s, ca. 1H), 4.48 (br s, ca. 1H), 4.87−5.1 (m, 91H), 6.31 (d, J = 7.9 Hz, 1H), 6.49−6.62 (m, 63H), 6.80−6.92 (m, 7H), 7.38−7.43 (m, 52H), 7.62 (d, J = 8.8 Hz, 2H), 7.97−8.01 (m, 54H); ^{13}C NMR (62.5 MHz, $CDCl_3$) (multiple overlapping carbons) 52 ($ArCO_2CH_3$'s), 69.3 (*C*H_2O's), 69.8 (*C*H_2O's), 101, 107, 114, 126, 129, 138−139, 141, 159−160, 162.4, 162.5, 165.9, 166.6 ppm; IR ($CDCl_3$) 1719, 1598 cm^{-1}; UV ($CHCl_3$) λ_{max} = 244 nm (ϵ 313 096), 265 nm (ϵ 102 622); GPC analysis M_{calc} = 6648, M_w = 7178, M_n = 7156, polydispersity index = 1.0032; MS (MALDI-TOF) m/z 6683 (6682 calcd for $C_{393}H_{343}NO_{98}K$ (M + K)) Anal. Calcd for $C_{393}H_{343}NO_{98}$: C, 71.00; H, 5.20; N, 0.21. Found: C, 70.78; H, 5.21; N, 0.31.

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Supporting Information Available: Copies of ^{1}H NMR spectra for compounds **2**−**6** (5 pages). This material is contained in libraries on microfiche, immediately follows this article in the microfilm version of the journal, and can be ordered from the ACS; see any current masthead page for ordering information.

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