Synthesis, Structure, and Properties of a Helical Columnar Liquid Crystal

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Abstract: Helicene **2b** can be prepared by acylating the disproportionation product formed by combining **1** with the bis-hydroquinone that **1** gives when it is reduced. At room temperature, the nonracemic material forms a liquid crystalline phase, which upon heating becomes isotropic at 85 °C. Hexagonal columnar ordering in the pure material is demonstrated by X-ray diffraction, and columnar organization in dodecane solutions is indicated by all of the following increasing with concentration: the circular dichroisms, specific rotations, fluorescent emission shifts, and ^{1}H NMR shieldings. The material is the first columnar mesophase with a nonracemic helical core.

Introduction

Nonracemic columnar liquid crystalline materials include planar discotic mesogens in which the asymmetry is in the side-chains,[1] but the only examples in which the cores are chiral are derivatives of saccharides,[2] inositols,[2,3] and cyclotriveratrylene.[4] Remarkably, no property of any of these latter materials' mesophases has yet been detected that is consequent on the cores' chirality. In their review in 1992,[2b] Jeffrey and Wingert asserted that to their knowledge "there is no basic distinction between the mesophases formed by [derivatives of] a chiral molecule, such as D-glucitol, and a meso molecule, such as galactitol." This distinction appears not to have been made in the few years since that review. While attempts have been made to synthesize mesogenic materials in which the planar aromatic cores of molecules constituting disk-shaped liquid crystals are twisted helically,[5] in part because chiral columnar liquid crystals have the capacity to undergo ferroelectric switching,[1a,b,e,6] none that is nonracemic has been obtained until now. We describe below the synthesis of the first, a nonracemic helical columnar liquid crystal. We show that in addition to organizing into helical columns in the mesophase, it also aggregates in solution into similar columnar structures, and we show that the chiroptical properties of both the pure material and the aggregates in solution are enhanced in comparison to the isolated molecules.

This work is derived from the earlier synthesis of the nonracemic helicenebisquinone **1**,[7] which both in solution[7,8] and as the pure material[9] assembles into corkscrew-shaped columns that, compared to the isolated molecules, exhibit very large optical activity, circular dichroisms,[7,8] and second-harmonic-generating ability.[10] In pure **1**, the columns are hexagonally stacked into very long fibrous structures.[7,9] The fibrous material, unlike a liquid crystal, is not fluid. The questions considered subsequently, which are the basis for the work described below, are whether only one of the two quinone rings of **1** could be reduced and alkylated and what the properties would be of the resulting structure **2**, which has donor functions at one end of the helix and acceptors at the other.

Results and Discussion

Synthesis. Scheme 1 shows how nonracemic **2b** was synthesized, by using sodium dithionite to reduce *both* quinone functions of enantiomerically pure **1**[11] to hydroquinones. ^{1}H NMR analysis detected no significant amounts of other products in the crude reaction mixture, but the bis-hydroquinone oxidized so easily in the air that it could not be isolated and characterized. The crude bis-hydroquinone was therefore combined with an equimolar amount of the bis-quinone, **1**, and the quinone−

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[1] Triphenylenes, dibenzopyrenes, and phenanthrenes: (a) Malthête, J.; Jacques, J.; Tinh, N. H.; Destrade, C. *Nature* **1982**, *298*, 46. (b) Bock, H.; Helfrich, W. *Liq. Cryst.* **1992**, *12*, 697. (c) Bock, H.; Helfrich, W. *Liq. Cryst.* **1995**, *18*, 387. (d) Jákli, A.; Müller, M.; Krüerke, D.; Heppke, G. *Liq. Cryst.* **1998**, *24*, 467. (e) Scherowsky, G.; Chen, X. H. *J. Mater. Chem.* **1995**, *5*, 417. Radial pentaynes: (f) Langer, M.; Praefcke, K.; Krüerke, D.; Heppke, G. *J. Mater. Chem.* **1995**, *5*, 693. Phthalocyanines: (g) Cho, I.; Lim, Y. *Bull. Korean Chem. Soc.* **1988**, *9*, 98. (h) van Nostrum, C. F.; Bosman, A. W.; Gelinck, G. H.; Schouten, P. G.; Warman, J. M.; Kentgens, A. P. M.; Devillers, M. A. C.; Meijerink, A.; Picken, S. J.; Sohling, U.; Schouten, A.-J.; Nolte, R. J. M. *Chem. Eur. J.* **1995**, *1*, 171. Metallomesogens: (i) Barberá, J.; Iglesias, R.; Serrano, J. L.; Sierra, T.; de la Fuente, M. R.; Palacios, B.; Pérez-Jubindo, M. A.; Vázquez, J. T. *J. Am. Chem. Soc.* **1998**, *120*, 2908. Side-chain triphenylene polymers: (j) Green, M. M.; Ringsdorf, H.; Wagner, J.; Wüstefeld, R. *Angew. Chem., Int. Ed. Engl.* **1990**, *29*, 1478. Folic acid salts in water: (k) Gottarelli, G.; Mezzina, E.; Spada, G. P.; Carsughi, F.; Di Nicola, G.; Mariani, P.; Sabatucci, A.; Bonazzi, S. *Helv. Chim. Acta* **1996**, *79*, 220 and references therein. DNA in water: (l) Livolant, F.; Levelut, A. M.; Doucet, J.; Benoit, J. P. *Nature* **1989**, *339*, 724.

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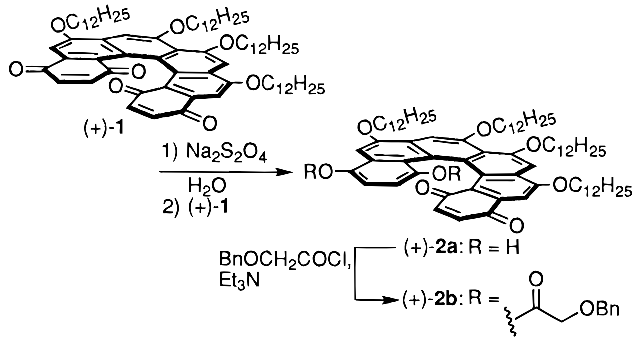
Scheme 1



hydroquinone that was presumed to result, **2a**, was acylated directly with α-benzyloxyacetyl chloride, producing (+)-**2b** in a yield (from **1**) of 72%. This ester was chosen in part because a number of triphenylenes and benzenes that are substituted with six ester groups display mesogenic properties only when a methylene in the side-chains is replaced by an ether, especially at the 3-position, presumably because the oxygens impart flexibility to aliphatic chains.[12]

Polarized Light Microscopy. (+)-**2b** is a yellow-orange viscous liquid that is birefringent at room temperature. As it is heated it becomes a mobile liquid, which becomes isotropic at 85 °C. No crystalline phase was seen. The texture displayed in Figure 1 forms when an isotropic liquid sample on a unidirectionally rubbed glass plate[13] is cooled to 84.6 °C and held at this temperature for 30 min. The features seen in the figure are ca. 13 μm × 5 μm in size, uniaxial, and negatively birefringent. However, the sample's absorption of visible light obscured details,[14] and we failed to identify the texture. Although it may be unique, it resembles that in a published photograph of a chiral cyclotriveratrylene.[4]

Differential Scanning Calorimetry. Heated in the calorimeter at a rate of 2 °C/min, (+)-**2b** undergoes a broad endothermic transition (16.14 kJ/mol) beginning at 74.3 °C and maximizing at 83.6 °C. No other phase transition was detected up to 150 °C. On cooling, the sample undergoes an exothermic transition (−19.30 kJ/mol) beginning at 74.0 °C and maximizing at 71.8 °C. The absence of other transitions and the similarity of the enthalpies measured to the ca. 1−20 kJ/mol associated with transitions from columnar discotic mesophases to isotropic liquids[15] supports the hypothesis that (+)-**2b** is liquid crystalline from room temperature to its clearing point.

CD Spectra, UV−Vis Absorption Spectra, and Specific Rotations. When solutions of (+)-**2b** in dodecane are concentrated, their CD spectra, UV−vis absorption spectra, specific rotations, and viscosity all change, just as these properties change when solutions of nonracemic **1** in dodecane are concentrated. The implication is that the molecules of nonracemic **2b**, like those of nonracemic **1**[7] and a number of other molecules,[16] aggregate in solution. Thus, when the concentration of a solution of (+)-**2b** in dodecane is increased from 2.0 × 10^{-5} M to 2.0 × 10^{-2} M, the viscosity increases and the specific rotation rises from 773 deg·cm^2/10 g to 2810 deg·cm^2/10 g. Moreover, the changes that occur in the CD spectra, the UV−vis absorption spectra (Figures 2a and 2b), the fluorescence emission spectra (Figure 2c), and the chemical shifts of the ^{1}H NMR spectra are similar to those that occur when solutions of nonracemic **1** are concentrated.

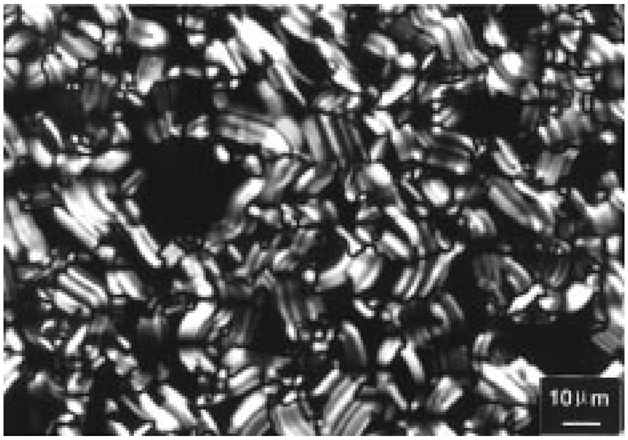


Figure 1. Optical micrograph of (+)-**2b**, cooled from the isotropic liquid to 84.6 °C between crossed polarizers.

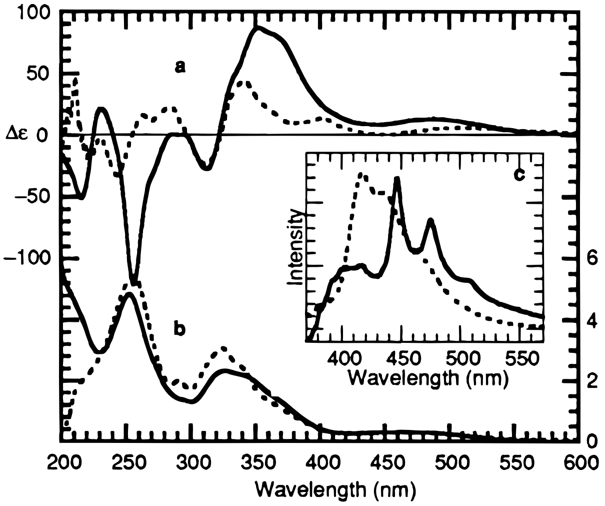


Figure 2. (a) CD spectra (ordinate on the left, displaying molar circular dichroism) and (b) UV−vis absorption spectra (ordinate on the right, displaying molar extinction coefficients) of (+)-**2b** in *n*-dodecane: (—) when the concentration is 2.0 × 10^{-2} M and the path length is 10 μm and (---) when the concentration is 2.0 × 10^{-5} M and the path length is 1 cm. The inset (c) displays the emission spectra (excitation at 320 nm) of the same solutions, both in 10 μm cells.

An intense circular dichroism appears in the concentrated solution at 256 nm ($\Delta\epsilon = -120$), whereas there is no appreciable circular dichroism at this wavelength in the dilute

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[11] Reference 7 and its Supporting Information give the details of the original synthesis and the evidence for the enantiomeric purity. A manuscript in preparation provides an improved preparation.

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[15] Some representative examples: (a) For a hexasubstituted benzene the value is 22 kJ/mol [Chandrasekhar, S.; Sadashiva, B. K.; Suresh, K. A.; Madhusudana, N. V.; Kumar, S.; Shashidhar, R.; Venkatesh, G. *J. Phys., Colloq. (Orsay, Fr.)* **1979**, *C3*, 120]. (b) For some metallomesogens the values are between 0.4 and 7.5 kJ/mol [Serrette, A. G.; Lai, C. K.; Swager, T. M. *Chem. Mater.* **1994**, *6*, 2252]. (c) For triphenylenes the values are between 0.7 and 18.8 kJ/mol [Destrade, C.; Mondon, M. C.; Malthete, J. *J. Phys., Colloq. (Orsay, Fr.)* **1979**, *C3*, 17]. (d) For a truxene the value is 2 kJ/mol [Warnerdam, T. W.; Nolte, R. J. M.; Drenth, W.; van Miltenburg, J. C.; Frenkel, D.; Zijlstra, R. J. J. *Liq. Cryst.* **1988**, *3*, 1087].

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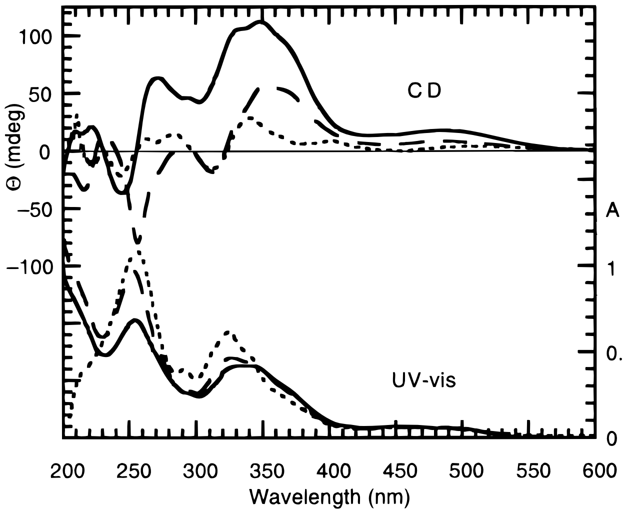

Figure 3. CD and UV−vis spectra (—) of a thin film, (− −) of a 2.0 × 10^{-2} M solution in dodecane (path length 10 μm), and (- - -) of a 2.0 × 10^{-5} M solution in dodecane (path length 1 cm). The UV−vis and CD spectra of the film were multiplied by 1.18 to make the film's UV−vis absorbance at 344 nm equal those of the solutions.

solution. (In the spectra of nonracemic **1**, the new CD peak that appears on concentration is at 251 nm.) In the spectrum of the concentrated solution of (+)-**2b**, a broad and intense CD appears at 352 nm, while in the spectra of nonracemic **1**, the similar peak is at 343 nm. The UV−vis absorption spectrum of (+)-**2b** changes much less than the CD spectrum when the solutions are concentrated (Figure 2), which is true also for the solutions of **1**.[7] However, the fluorescence emission spectrum shifts considerably (30 nm in Figure 2c), as does that of nonracemic **1**, and the shifts in both cases—to the red on concentration—are in the same direction as when hexapentyloxytriphenylene assembles into columnar discotic mesophases[17] and when its solutions in cyclohexane are concentrated.[18] The implications are that nonracemic **2b**, like nonracemic **1**[7,8] and like hexapentyloxytriphenylene,[19] aggregates when its solutions in dodecane are concentrated and that the structure of the aggregates is columnar.

The changes that occur in the ^{1}H NMRs when a solution in deuterated dodecane is concentrated accord with such a structure. All seven of the eight aromatic proton resonances that were observed shifted to higher fields by between 0.04 and 0.13 ppm, similar to the shifts seen when solutions of **1** are concentrated.[7]

Thin Films. Films were produced by spin-coating (+)-**2b** from a 1 × 10^{-3} M hexane solution onto quartz plates. Shown in Figure 3 are the CD and UV−vis absorption spectra of one of these films. The CD spectra did not change appreciably when the sample was rotated in a plane perpendicular to the light beam, but to eliminate any effects due to linear dichroism or linear birefringence, the CD spectrum displayed is the average of the spectra determined as the sample was rotated through six 30° increments.[20] Both the CD and UV−vis absorption spectra of the films differ from the spectra of a 2.0 × 10^{-5} M solution in dodecane (also in Figure 3), at which concentration the molecules are presumably isolated from one another. The films rotate plane polarized light at the D-wavelength (589 nm) by 0.018 ± 0.004° (this value too is the average of six measured as the sample was rotated through 30° increments). If the assumption is made that the extinction coefficient of the film at 344 nm is the same as that of the two solutions in dodecane, $[\alpha]_D$ can be estimated to be 9,600 deg·cm^2/10 g, a value much larger than the $[\alpha]_D$ of 773 deg·cm^2/10 g measured for the 2.0 × 10^{-5} M dodecane solution.

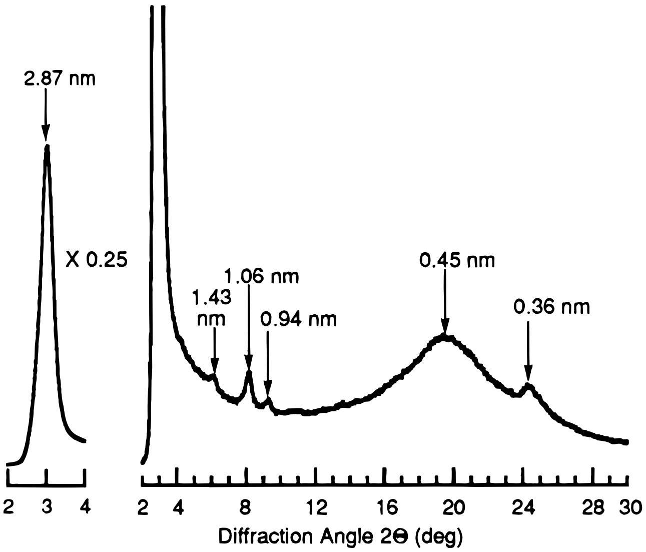

Figure 4. Diffraction pattern from a capillary tube filled with (+)-**2b** at 75 °C.

The most noteworthy observation drawn from Figure 3, which compares the CD and UV−vis absorption spectra of (+)-**2b** as a 2.0 × 10^{-5} M solution in dodecane, as a 2.0 × 10^{-2} M solution in dodecane, and as a thin film of the pure material, is that as the concentration increases, the CDs increase and the absorption intensities decrease. That is, the *g*-values ($\Delta\epsilon/\epsilon$) rise greatly, which agrees with the hypothesis that assembly into columns increases with concentration.[21] For the 2.0 × 10^{-5} M solution, the *g*-value at 244 nm is 5.8 × 10^{-4}; for the film, it is 2.8 × 10^{-3}. The corresponding values for the peaks at 350 nm are 1.8 × 10^{-3} for the dilute solution and 9.1 × 10^{-3} for the film.

X-ray Diffraction. Figure 4 shows the diffraction pattern of (+)-**2b** that had been warmed in a capillary tube to 100 °C and then cooled to 75 °C. The diffractogram is essentially the same if the material is cooled further to room temperature. The peaks at low angles can be indexed as reflections from a hexagonal lattice: 2.87 nm (100), 1.43 nm (200), 1.06 nm (210), and 0.94 nm (300). These peaks, as well as the broad one at 0.45 nm, are characteristic of the diffractograms of **1** and of columnar discotic liquid crystals, the former set representing reflections from planes of columns and the latter the distance between the alkyl side-chains.[22] The reflection at 0.36 nm is also observed in the diffractions from many ordered columnar discotic liquid crystals and has been attributed to their $\pi-\pi$ stacking distance.[14,15b,23]

There are two notable differences between the X-ray diffractograms of (+)-**2b** and of **1**. One is that the 0.36 nm reflection, observed for **2b**, is not seen in the diffractogram of **1**,[5] which

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[21] (a) Kuhn, W. *Trans. Faraday. Soc.* **1930**, *26*, 293. (b) Eliel, E. L.; Wilen, S. H.; Mander, L. N. *Stereochemistry of Organic Compounds*; Wiley: New York, 1994; Chapter 13.

[22] Reference 9 and references therein.

suggests that the order along the lengths of the columns is greater in the former than in **1**.[14,23] The other is that the column diameter is smaller in **2b** (3.3 nm) than in **1** (4.1 nm), which while it might be attributed to greater interpenetration or folding of the side-chains in **2b**, might more plausibly be a consequence of the rings being tilted. This could be a consequence of steric crowding by the substituent on the interior of the ring system or of the molecules of **2b** having a dipole moment that is not parallel to the helix axis, the rings tilting to minimize the intermolecular dipolar interaction energy. The greater order along the lengths of the columns in **2b**, compared to **1**, might also be a consequence of greater dipole−dipole (or donor−acceptor) interactions. How the structural differences account for the lower clearing temperature of **2b** than of **1** is, however, unclear.

Conclusions

Helicene **2b** can be prepared according to Scheme 1. The nonracemic material forms a columnar mesophase at room temperature and columnar aggregates in dodecane solution, both of which when compared to the isolated molecules show enhanced circular dichroisms and specific rotations and shifted fluorescent emissions.

Experimental Section

Synthesis. THF was distilled from Na plus benzophenone, CH_2Cl_2 and Et_3N from CaH_2. Benzyloxyacetyl chloride (95%) was purchased from Aldrich Chemical Co. and used without further purification.

(+)-2b: THF (3 mL) was added to (+)-**1** (30 mg, 2.7×10^{-5} mol) and $Na_2S_2O_4$ (60 mg, 3.45×10^{-4} mol) under N_2, followed by deoxygenated water (1.5 mL). The mixture was stirred until the deep wine-red color had changed to a brilliant lemon-yellow (ca. 10 min). CH_2Cl_2 (3 mL) was injected, and the lower organic layer, followed by two further CH_2Cl_2 extracts, was transferred to another dry round-bottomed flask.

After concentration under reduced pressure and drying for 12 h in a vacuum, THF (3 mL) containing (+)-**1** (30 mg, 2.7×10^{-5} mol) was added under N_2, and after the mixture had stirred for 5 min at room temperature and been cooled to 0 °C, α-benzyloxyacetyl chloride (42 μL, 2.7×10^{-4} mol) was injected, followed by Et_3N (200 μL, 1.43×10^{-3} mol), added in drops. The reaction mixture was stirred at room temperature for 3 h, and after saturated aqueous $NaHCO_3$ (ca. 2 mL) had been added, it was stirred for 1 h. After extraction with benzene (3 ×), washing with 1 N aqueous HCl, water and saturated aqueous $NaHCO_3$, drying ($MgSO_4$), filtering, and removal of solvent, the crude product was chromatographed 3 times on a 1 in. × 6 in. silica gel column, eluting with 2% EtOAc/benzene. The yield of (+)-**2b**, an orange oily wax, was 55 mg (72%). IR (KBr) 2923, 2853, 1772, 1662, 1599, 1516, 1498, 1467, 1375 cm^{-1}; ^1H NMR (400 MHz, $CDCl_3$) δ 0.88 (t, 12 H, $J = 6.5$ Hz), 1.20−1.50 (m, 72 H), 1.53−1.65 (m, 8 H), 1.92−2.05 (m, 8 H), 2.93 (d, 1 H, $J = 16.8$ Hz), 3.41 (d, 1 H, $J = 16.8$ Hz), 4.18 (s, 2 H), 4.10−4.40 (m, 8 H), 4.56 (s, 2 H), 4.84 (d, 2H, $J = 1.8$ Hz), 6.22 (d, 1 H, $J = 10.2$ Hz), 6.41 (d, 1 H, $J = 10.2$ Hz), 6.70 (d, 1 H, $J = 8.4$ Hz), 7.01 (s, 1 H), 7.09 (d, 1 H, $J = 8.4$ Hz), 7.17−7.19 (m, 2 H), 7.26−7.48 (m, 9 H), 7.54 (s, 1 H), 7.74 (s, 1 H); ^{13}C NMR (75 MHz, $CDCl_3$) δ 14.11, 22.69, 26.20, 26.39, 26.47, 29.06, 29.12, 29.38−29.75 (m), 31.92, 66.31, 67.24, 68.43, 69.22, 69.33, 69.56, 73.06, 73.66, 96.6, 97.7, 101.6, 101.8, 116.8, 118.2, 119.5, 121.1, 121.6, 124.9, 127.4, 127.7, 127.9, 128.1, 128.2, 128.3, 128.5, 128.6, 128.6, 130.0, 130.3, 134.5, 136.8, 136.9, 139.8, 143.0, 143.3, 153.3, 156.4, 156.5, 158.0, 167.5, 169.2, 185.2, 185.7. HRMS (M + 1) calcd for $C_{92}H_{127}O_{12}$ 1423.9328, found 1423.9349.

Concentration Effects—CD, UV−vis Absorption, Fluorescence Emission, and ^{1}H NMR Spectra; Polarimetry. UV−vis absorption spectra were recorded with a Perkin-Elmer Lambda 19 UV−vis spectrometer, circular dichroism spectra with a JASCO 720 spectrometer, fluorescence spectra with a Spex Fluorolog 86 fluorimeter, and optical rotations with a JASCO Dip 1000 polarimeter. The solvent used was olefin-free dodecane from Fluka. To measure the spectra of the 2.1×10^{-2} M solutions, a 10 μm quartz cell from Starna Cells was used, and for the 2.1×10^{-5} M solutions a 1 cm quartz cell. The fluorescence spectra were measured by front-face emission from the 10 μm quartz cell. The neat samples were prepared by spin coating from a 1×10^{-3} M hexane solution at 6000 rpm. A plate holder allowed the samples to be rotated through 360° at 30° increments. ^{1}H NMR spectra of 2×10^{-2} and 2×10^{-4} M solutions in deuterated dodecane (Cambridge Isotope Labs) at 50 °C were acquired on a 500 MHz Bruker NMR spectrometer, and the chemical shifts were referenced to internal TMS.

X-ray Diffraction, DSC, and Polarized Light Microscopy. A Leica DMRXP polarizing microscope and an attached Wild Leitz MPS46 camera were used to view and photograph samples sandwiched between a microscope slide and a coverslip. The samples were heated in a Mettler FP 82 HT hot stage controlled by a Mettler FP 80 HT central processor. We prepared the rubbed glass samples using a coverslip and microscope slide both of which had been rubbed multiple times in the same direction, first with a lint-free wiper and then with a lint-free wiper wetted with a drop of ethanol.

The sample for X-ray diffraction was warmed, made to flow into a 1.5 mm Lindemann capillary tube, and thermostated in a heating block whose temperature was controlled to ±1 °C by a Minco CT 137 controller. Ni-filtered Cu Kα radiation from a fine-focus X-ray tube and XRG 2000 generator and an Inel CPS 120 position-sensitive detector, calibrated with a mica standard from the National Bureau of Standards, were used to record the X-ray diffractogram.

A Perkin-Elmer DSC 7 equipped with a Perkin-Elmer 7700 was used for the differential scanning calorimetry measurements.

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