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# Synthesis and Properties of an Aggregating Heterocyclic Helicene

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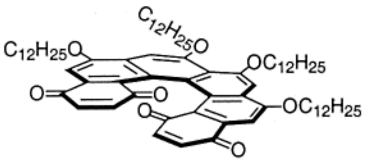
**Abstract:** Heterohelicene **10** is synthesized in six steps from 3,3′-bithienyl. Because the number of steps is small, because the yield is 95% in the last (the reaction of a bis-enol ether with 1,4-benzoquinone—a six-step one pot procedure that constructs the helicene skeleton), and because chromatography is not required to purify any of the products in the synthesis, significant amounts are easily prepared. To convert **10** into enantiopure **3**, a helicenebisquinone surrounded by four dodecyloxy groups, requires only a precedented three-step sequence. Enantiopure helicene **3**, either without solvent or in dodecane (but not in chloroform) aggregates into columnar structures whose optical properties differ markedly from those of the monomer but resemble those shown previously only by aggregates of **1**. Evidence of aggregation in the pure material includes optical microscopic observation of long fibrous structures and X-ray diffraction and combined transmission electron microscopic and electron diffraction analyses showing the molecules within the fibers to be organized in columnar arrays. The circular dichroism spectra, specific rotations, and fluorescent emission spectra of the aggregated structures are all distinctive, and, as reported elsewhere, the second harmonic response is very large. The linear polarizations of the monomers' and aggregates' fluorescent emissions differ greatly. The circular polarization of the aggregates' fluorescent emission, after excitation by unpolarized light, is large.

## Introduction

Helicene **1** is among few helical conjugated molecules that self-assemble into long corkscrew-shaped columns (structure **2**).[1] Others are an ester of the hydroquinone formed by reducing one of the quinone rings in **1**,[2] a phthalocyanine that is fused to four helicene structures,[3] a chiral *m*-phenylene ethynylene oligomer,[4] and a pyridine−pyridazine oligomer.[5] Enantiopure **1**, when dissolved in appropriate hydrocarbon solvents or when cooled from the melt, assembles into columnar structures.[1] In the pure material, these columns are hexagonally packed into very long micrometer-wide lamellar fibers that are easily seen under an optical microscope.[6] The columnar assemblies also appear to be the source of unusual optical properties. For example, enantiopure **1** when photoirradiated generates significant second harmonics,[7] which, because the major components of the second-order susceptibility tensor change sign when the chirality is inverted, can be quasi-phase matched by using interdigitated layers of the enantiomers to generate the second harmonics.[8]



**1**

**2**

We consider here whether there are helicenes, specifically derivatives of structure **3**, that are easier to prepare than **1**, but that exhibit properties just as uncommon. The reasons for considering structure **3** are the following: replacing benzenes by thiophenes has beneficial effects on the nonlinear optical properties of previously known achiral conjugated structures,[9] the Friedel−Crafts procedure should transform the heteroaromatic nucleus of the benzo[1,2-*b*:4,3-*b*′]-dithiophene into its diacetyl derivative **4**,[10,11] and the wealth of electrons in the conjugated systems of double bonds, oxygen, and sulfur atoms

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(1) Nuckolls, C.; Katz, T. J.; Katz, G.; Collings, P. J.; Castellanos, L. *J. Am. Chem. Soc.* **1999**, *121*, 79, and references therein.

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(7) (a) Verbiest, T.; Van Elshocht, S.; Kauranen, M.; Hellemans, L.; Snauwaert, J.; Nuckolls, C.; Katz, T. J.; Persoons, A. *Science* **1998**, *282*, 913. (b) Van Elshocht, S.; Verbiest, T.; de Schaetzen, G.; Hellemans, L.; Phillips, K. E. S.; Nuckolls, C.; Katz, T. J.; Persoons, A. *Chem. Phys. Lett.* **2000**, *323*, 340. (c) Verbiest, T.; Van Elshocht, S.; Persoons, A.; Nuckolls, C.; Phillips, K. E. S.; Katz, T. J. *Langmuir* **2001**, *17*, 4685.

(8) Busson, B.; Kauranen, M.; Nuckolls, C.; Katz, T. J.; Persoons, A. *Phys. Rev. Lett.* **2000**, *84*, 79.

(9) (a) Jen, A. K.-Y.; Rao, V. P.; Wong, K. Y.; Drost, K. J. *J. Chem. Soc., Chem. Commun.* **1993**, 90. (b) Varanasi, P. R.; Jen, A. K.-Y.; Chandrasekhar, J.; Namboothiri, I. N. N.; Rathna, A. *J. Am. Chem. Soc.* **1996**, *118*, 12443, and referencs therein. (c) Kim, O.-K.; Fort, A.; Barzoukas, M.; Blanchard-Desce, M.; Lehn, J.-M. *J. Mater. Chem.* **1999**, *9*, 2227.

(10) The parent benzo[1,2-*b*:4,3-*b*′]dithiophene undergoes acylation at the two positions adjacent to the sulfur atoms. See: (a) Gronowitz, S.; Dahlgren, T. *Chem. Scr.* **1977**, *12*, 97. However, benzo[*b*]thiophene acylates mainly at the 3-position. Substituents significantly affect the orientations of such reactions. See: (b) Katritzky, A. R.; Taylor, R. *Adv. Heterocycl. Chem.* **1990**, *47*, Chapter 8, and references therein.

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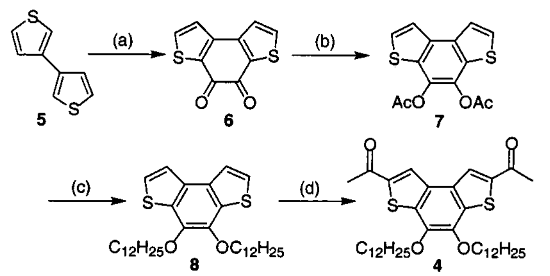
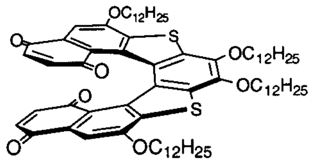
**Scheme 1**[a]

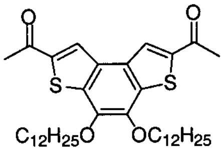


[a] Reagents and conditions: (a) oxalyl chloride, 1,2-dichloroethane, reflux, 68% yield; (b) Zn, $Ac_2O$, $CH_2Cl_2$, 83% yield; (c) $Cs_2CO_3$, $C_{12}H_{25}I$, $CH_3CN$, 94% yield; (d) AcCl, $AlCl_3$, 1,2-dichloroethane, 83% yield.

of this diacetyl compound's bis-enol ethers should, as in other electron-rich heteroaromatics,[12] make the Diels–Alder reactions with 1,4-benzoquinone and the subsequent oxidations of the Diels–Alder adduct take place easily.[1,13,14] The experiments described below demonstrate that a derivative of **3** can indeed be prepared easily and in high yield, that its enantiomers can be resolved by a procedure whose underlying theory is understandable and whose applicability has proven widely useful,[15] that enantiopure **3** aggregates both in solution and as the pure material, and that it gives rise to significantly circularly polarized fluoresence. In a separate paper, it is also shown that **3** is better than **1** in generating second harmonics.[16]



**3**



**4**

## Results

**Synthesis.** 2,7-Diacetyl-4,5-didodecyloxybenzo[1,2-*b*:4,3-*b*′]-dithiophene (**4**) was synthesized in five steps from commercially available 3-bromothiophene (Scheme 1). Thus, following Jayasuria and Kagan,[17] the bromothiophene was combined with its Grignard reagent in the presence of Ni(dppp)$Cl_2$, giving 3,3′-bithienyl, **5**. Although this bithienyl had previously been transformed into benzo[1,2-*b*:4,3-*b*′]dithiophene-4,5-dione (**6**),[18] an alternative way to effect the transformation was considered, that is a Friedel–Crafts acylation with oxalyl chloride. We thought this procedure could be beneficial because it requires only one step, whereas the previous one requires three—bromination,[18a] conversion of the resulting 2,2′-dibromo-3,3′-bithienyl into the corresponding dialdehyde (*n*-butyllithium and then DMF),[18b] and condensation and oxidation through reflux with ethanolic sodium cyanide in air[18b]—and in the last step gives a yield of only 50%. The precedents for installing the diketone bridge in one step include preparations of a number of substituted benzils,[19] a phenanthrene-9,10-dione,[20] and dixobenzo[1,2-*b*:4,3-*b*′]dipyrroles[21] from aromatic compounds, oxalyl chloride, and aluminum chloride.

The facts are that when the procedures used before (employing dichloromethane as the solvent at −85 °C,[19b] carbon disulfide at 0 °C,[19a,20] or 1,2-dichloroethane plus pyridine at −20 to −30 °C[18d]) or related procedures using other Lewis acids[22] were applied to 3,3′-bithienyl, they failed to produce diketone **6** in more than 15% yield, and they required much effort to separate even this small amount from tarry byproducts.[23,24] However, although thiophenes, unlike pyrroles[21,25] and anisoles,[26] seem not to have been found to undergo Friedel–Crafts acylations without the aid of Lewis acids,[27] it turns out that the diketone can be installed in one step and 50% yield simply by refluxing 3,3′-bithienyl with oxalyl chloride in 1,2-dichloroethane. The time required to complete the reaction, 7–10 days, is long, but the product precipitates as it forms, and the only steps required to obtain it pure are to filter it, wash it with hexanes, and triturate it with warm ethanol. In this way, 18 g of benzo[1,2-*b*:4,3-*b*′]dithiophene-4,5-quinone (**6**) were made at one time.

To convert dithienoquinone **6** into dodecyloxy-substituted benzodithiophene **8**, zinc in the presence of acetic anhydride was used to convert **6** into **7**,[3,28] and 1-iodododecane and cesium carbonate in acetonitrile was used to replace **7**'s acetate ester

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[11] Alternatives would make use of benzo[1,2-*b*:4,3-*b*′]dithiophene lithiating at the positions adjacent to the sulfur atoms. See ref 8a and the following: (a) Groen, M. B.; Schadenberg, H.; Wynberg, H. *J. Org. Chem.* **1971**, *36*, 2797. (b) Lehman, P. G.; Wynberg, H. *Aust. J. Chem.* **1974**, *27*, 315. (c) Yoshida, S.; Fuji, M.; Aso, Y.; Otsubo, T.; Ogura, F. *J. Org. Chem.* **1994**, *59*, 3077. (d) Larsen, J.; Bechgaard, K. *Acta Chem. Scand.* **1996**, *50*, 71.

[12] Dreher, S. D.; Weix, D. J.; Katz, T. J. *J. Org. Chem.* **1999**, *64*, 3671.

[13] (a) Katz, T. J.; Liu, L.; Willmore, N. D.; Fox, J. M.; Rheingold, A. L.; Shi, S.; Nuckolls, C.; Rickman, B. H. *J. Am. Chem. Soc.* **1997**, *119*, 10054. (b) Fox, J. M.; Goldberg, N. R.; Katz, T. J. *J. Org. Chem.* **1998**, *63*, 7456. (c) Paruch, K.; Katz, T. J.; Incarvito, C.; Lam, K.-C.; Rhatigan, B.; Rheingold, A. L. *J. Org. Chem.* **2000**, *65*, 7602. (d) Paruch, K.; Vyklick, L.; Katz, T. J.; Incarvito, C. D.; Rheingold, A. L. *J. Org. Chem.* **2000**, *65*, 8774.

[14] (a) Davies, W.; Porter, Q. N. *J. Chem. Soc.* **1957**, 4958. (b) Ghosh, A.; Maiti, S. B.; Chatterjee, A.; Raychaudhuri, S. R. *Indian J. Chem., Sect. B: Org. Chem. Incl. Med. Chem.* **1989**, *28B*, 724. (c) Sasaki, T.; Ishibashi, Y.; Ohno. *Heterocycles* **1983**, *20*, 1933. (d) Sasaki, T.; Ishibashi, Y.; Ohno. *J. Chem. Res. (S)* **1984** 218. (e) Abarca, B.; Ballesteros, R.; Enriquez, E.; Jones, G. *Tetrahedron* **1985**, *41*, 2435.

[15] (a) Thongpanchang, T.; Paruch, K.; Katz, T. J.; Rheingold, A. L.; Lam, K.-C.; Liable-Sands, L. *J. Org. Chem.* **2000**, *65*, 1850. (b) Paruch, K.; Katz, T. J.; Incarvito, C.; Lam, K.-C.; Rhatigan, B.; Rheingold, A. L. *J. Org. Chem.* **2000**, *65*, 7602.

[16] Verbiest, T.; Van Elshocht, S.; Persoons, A.; Nuckolls, C.; Phillips, K. E. S.; Katz, T. J. *Langmuir* **2001**, *17*, 4685.

[17] Jayasuria, N.; Kagan, J. *Heterocycles* **1986**, *24*, 2261.

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[21] Carter, P.; Fitzjohn, S.; Halazy, S.; Magnus, P. *J. Am. Chem. Soc.* **1987**, *109*, 2711.

[22] Conditions tried were $AlCl_3$ in $CH_2Cl_2$ at 0, −10, −15, and −78 °C; in $CS_2$ at 0, −15, and −78 °C; $SnCl_4$ in $CH_2Cl_2$ at 0 and −78 °C; in 1,2-dichloroethane at 60 °C and reflux; $BF_3{\cdot}OEt_2$ in $CH_2Cl_2$ and in 1,2-dichloroethane at 0 °C; $TiCl_4$ in 1,2-dichloroethane at 25 °C; $FeCl_3$ in $CH_2Cl_2$ at −10 and 25 °C and at reflux.

[23] Exposure to $AlCl_3$ causes thiophenes to polymerize (Kovacic, P.; McFarland, K. N. *J. Polym. Sci., Polym. Chem. Ed.* **1979**, *17*, 1963).

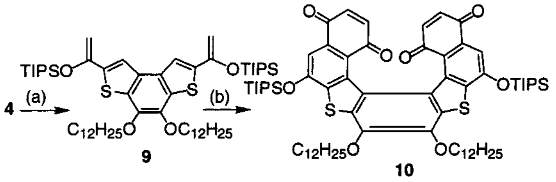
[24] Oxalyl chloride plus aluminum chloride in methylene chloride combines with benzenes at temperatures higher than −85 °C to give arylcarbonyl chlorides and diaryl ketones. [(a) Neubert, M. E.; Fishel, D. L. *Mol. Cryst. Liq. Cryst.* **1979**, *53*, 101. (b) Neubert, M. E.; Fishel, D. L. *Organic Syntheses*; Wiley: New York, 1990; Collect. Vol. VII, p 420.] However, in 1,2-dichloroethane-pyridine, it combines with 2,5-dimethylthiophene at −20 to −30 °C to give a diketone.[19d]

[25] (a) Nenitzescu, C. D.; Necsoiu, I.; Zalman, M. *Comun. Acad. Repub. Pop. Rom.* **1958**, *8*, 659; *Chem. Abstr.* **1959**, *53*, 17092c. (b) Archibald, J. L.; Freed, M. E. *J. Heterocycl. Chem.* **1967**, *4*, 335. (c) Treibs, A.; Kreuzer, F.-H. *Justus Liebigs Ann. Chem.* **1969**, *721*, 105.

[26] Pearson, D. E.; Buehler, C. A. *Synthesis* **1972**, 533, and references therein.

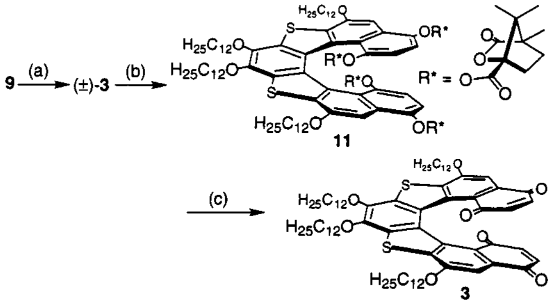
[27] 3,3′-Bithienyl is acylated by a Vilsmeier reagent (Nenajdenko, V. G.; Baraznenok, I. L.; Balenkova, E. S. *J. Org. Chem.* **1998**, *63*, 6132).

**Scheme 2**[a]



[a] TIPS = $i$-Pr$_3$Si. Reagents and conditions: (a) TIPSOTf, Et $_3$N, CH$_2$Cl$_2$, 100% yield; (b) $p$-benzoquinone, heptanes, reflux, 95% yield.

**Scheme 3**[a]



[a] Reagents and conditions: (a) CsF, C$_{12}$H$_{25}$I, DMF, 93% yield; (b) Zn, Et$_3$N, (1$S$)-(−)-camphanoyl chloride, DMAP, 1,2-dichloroethane, 90% yield (−)-diastereomer and 70% yield (+)-diastereomer; (c) (i) BuLi, Et$_2$O and (ii) chloranil, 88% yield (−)-enantiomer, 85% yield (+)-enantiomer.

functions with dodecyloxy groups.[3] Friedel−Crafts acylation with acetyl chloride and aluminum chloride then gave diacetyl derivative **4**, which required only trituration with cold methanol to be obtained pure. The yield was 83%. The NMR spectra show that the molecules of this product have a plane of symmetry, but to verify the structure, an alternative synthesis was carried out. Benzodithiophene **8** was combined with $n$-butyllithium, then with dimethylacetamide, and finally with aqueous acid. The resulting diacetyl derivative was identical to the one from the Friedel−Crafts procedure. The yield was impractically low, approximately 7%, and to purify the product required preparative TLC. However, since thiophenes and benzodithiophenes are known to lithiate α to their sulfur atoms,[11] the experiment shows that the acetyl groups in **4** are in the thiophenes' α positions.

To obtain helicenebisquinone **10** (Scheme 2), enol ether **9** was first prepared by combining **4** with triisopropylsilyl triflate and triethylamine in dichloromethane.[29] The yield was quantitative, and purification required only trituration with methanol. The amount of **9** prepared at one time was 22 g. When combined with 1,4-benzoquinone, it gave helicene **10**. The yield was extraordinary. *Although the conversion of* **9** *to* **10** *is comprised of six transformations (two Diels−Alder reactions and four dehydrogenations), 25 g of* **10** *were obtained in a single experiment in 95% yield. Chromatography is not required to purify any of the products in the entire synthesis.*

The silyl groups were then replaced by aliphatic chains, and the enantiomers were resolved (Scheme 3). Cesium fluoride and 1-iodododecane in DMF[29a,30] gave, in 93% yield, the racemic tetradodecyloxyhelicenebisquinone **3**, which could be purified simply by precipitating it by adding ethanol and methanol to its solutions in dichloromethane.

In accord with analogies and a theory described previously,[18] chromatography on silica gel separated the diastereomeric tetracamphanate esters that formed when the bis-quinone was reductively acylated by means of zinc in the presence of (1$S$)-(−)-camphanoyl chloride.[1,13b,31] Cleaving the camphanate moieties from the helicene skeletons with the aid of methyllithium and oxidizing with chloranil[1,13a] then gave the pure enantiomers of **3**. As expected,[15a,b] the enantiomer derived from the tetracamphanate with the lower $R_f$ (the more polar tetracamphanate) is dextrorotatory. Its UV and CD spectra are similar to those of similar [6]- and [7]carbohelicenebisquinones[13b,32] but are shifted ca. 50 nm to longer wavelengths. It is on the basis of these optical properties and the $R_f$s of the tetracamphanates that dextrorotatory **3** is assigned the ($P$)-stereochemistry.

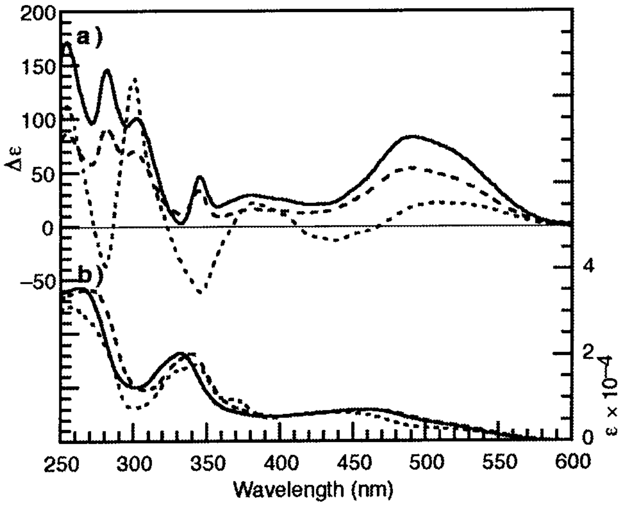


**Figure 1.** (a) CD spectra (ordinate on the left) and (b) UV−vis absorption spectra (ordinate on the right) of solutions of (+)-**3** in dodecane whose concentrations are as follows: (--) 2 × 10$^{-5}$, (− −) 2 × 10$^{-3}$, and (—) 2 × 10$^{-2}$ M.

**CD and UV−Visible Absorption Spectra of 3.** The specific rotations of solutions of enantiopure **3** in dodecane change appreciably when their concentrations are increased from 2 × 10$^{-5}$ to 2 × 10$^{-2}$ M. [α]$_D$ is 2800 at the former concentration, 10 400 at the latter, and 5000 at the intermediate concentration of 2 × 10$^{-3}$ M. The CD spectra of these solutions also change markedly. Figure 1 displays some of these spectra,[33] as well as the UV−visible absorption spectra of the same solutions. For example, the circular dichroism at 281 nm changes from $\Delta\epsilon = +146$ to $\Delta\epsilon = -37$ and that at 346 nm from $\Delta\epsilon = +44$ to $\Delta\epsilon = -62$. When the solvent is chloroform instead of dodecane, the changes due to high concentration disappear. (The CD spectra are in the Supporting Information. The specific rotation of a 2 × 10$^{-3}$ M solution in CHCl$_3$ is 3100.) When the solvent is dodecane and the concentration is increased further, or when there is no solvent, the changes, illustrated in Figure 2, become more pronounced. The figure displays the CD spectra of a 0.05 M solution in dodecane and of a film formed by evaporating the solvent from a nonane solution, and it compares them to the spectrum of the most concentrated solution in Figure 1. This last solution, like others of **3** in dodecane that are more

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(28) Katz, T. J.; Liu, L.; Willmore, N. D.; Fox, J. M.; Rheingold, A. L.; Shi, S.; Nuckolls, C.; Rickman, B. H. *J. Am. Chem. Soc.* **1997**, *119*, 10054, and ref 19 therein.

(29) In related syntheses, silyl enol ethers give higher yields than alkyl enol ethers. (a) Fox, J. M.; Goldberg, N. R.; Katz, T. J. *J. Org. Chem.* **1998**, *63*, 7456. (b) See footnote 7 in ref 13c.

(30) Paruch, K.; Vyklick, L.; Katz, T. J.; Incarvito, C. D.; Rheingold, A. L. *J. Org. Chem.* **2000**, *65*, 8774.

(31) See footnote 28 in ref 13b.

(32) The assignment of absolute stereochemistry to the [7]helicenebisquinones in ref 13b was later confirmed (in ref 13c) by X-ray crystallographic analysis.

(33) The CD spectrum of a 2 × 10$^{-4}$ M solution in dodecane is much more similar to the spectrum of a solution that is 10 times more dilute than to that of a solution that is 10 times more concentrated (see the Supporting Information).

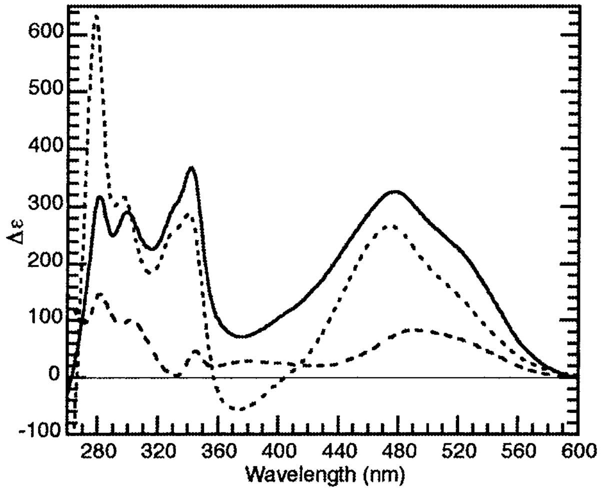

**Figure 2.** CD spectra of **(+)−3**: (− −) as a 2 × $10^{-2}$ M solution in dodecane, (--) as a 0.05 M solution in dodecane, and (—) as a drop-cast film. To facilitate comparison with Figure 1, the latter two spectra are the negatives of the spectra of the material analyzed, the (−)-enantiomer. The circular dichroisms of the film are arbitrarily scaled so they are similar to those of the concentrated solution.

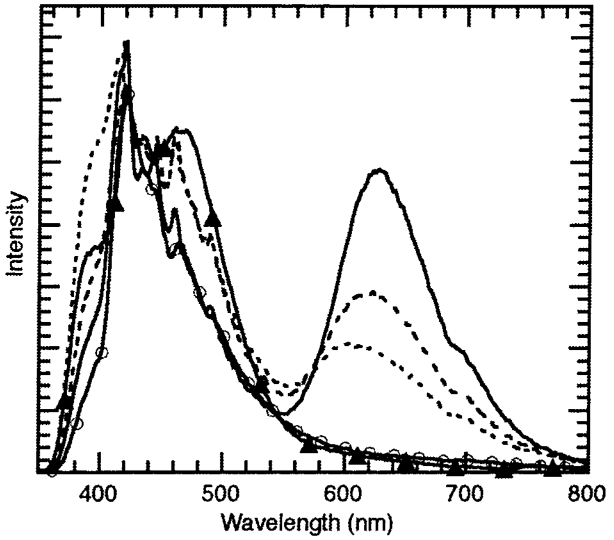

**Figure 3.** Fluorescence spectra of solutions of (+)-**3** in dodecane and in chloroform after excitation at 325 nm: (−▲−) 2 × $10^{-6}$ M (in dodecane); (--) 2 × $10^{-5}$ M (in dodecane); (− −) 2 × $10^{-4}$ M (in dodecane); (− −) 2 × $10^{-2}$ M (in dodecane); (−○−) 2 × $10^{-3}$ M (in $CHCl_3$). The intensities are normalized to the peak at 440 nm.

concentrated than 2 × $10^{-3}$ M, is noticeably viscous. The 0.05 M solution is a gel. The spectrum of the film in Figure 2 is the average of twelve spectra (all very similar) measured as the sample in a circular holder was rotated through successive 30° angles, a procedure that should eliminate effects of linear birefringence and linear dichroism.[34] Lowering the temperature of dodecane solutions affects the CD spectra in much the same way as increasing their concentration. The Supporting Information shows this for a 1 × $10^{-4}$ M solution whose temperature varies between −5 and +20 °C.

**Fluorescence Emissions and Their Linear and Circular Polarization.** Figure 3 shows the spectra of fluorescence emission from solutions at various concentrations of (+)-**3** in dodecane. At the lowest concentration (2 × $10^{-6}$ M), monomers are likely to predominate, and the observed fluorescence, centered at ca. 440 nm, is attributed to them. As the concentration is increased, another emission, centered at ca. 620 nm, appears and increases in intensity when compared to the emission at 440 nm. It is attributed to aggregates. Also shown in Figure 3 is that, in accord with these assignments and the absence, noted above, of circular dichroism characteristic of aggregates when chloroform is the solvent, no peak at ca. 620 nm is seen in the fluorescence from chloroform solutions of (+)-**3**, even when their concentration is high (2 × $10^{-3}$ M). Only a peak at ca. 440 nm is seen.

The assignments of the fluorescence peaks at 440 nm to monomers and at 620 nm to aggregates is supported by experiments that show how rotationally mobile the fluorescing species are. The exciting light for these experiments is linearly polarized. The light from fluorophores that are unable to rotate before they emit should be polarized parallel to the exciting light. The magnitude of the polarization ($P$) should be the maximum possible, 0.5.[35] The polarization of the light from fluorophores that do rotate before they emit should be less. Indeed, the polarization of the emission at 440 nm from a 2 × $10^{-5}$ M dodecane solution of (+)-**3** is low ($P = 0.02 \pm 0.01$), while that of the emission at 620 nm from a 1 × $10^{-3}$ M dodecane solution of (+)-**3** is very high ($P = 0.39 \pm 0.01$).

Also significant are the extent to which this emission is circularly polarized and the comparison of the dissymmetry factors for emission and absorption between the ground- and first-excited electronic states.[35,36] As Figure 4 shows, when unpolarized light excites 1 × $10^{-3}$ M solutions of (+)- or (−)-**3**, the magnitudes of the emissions by the aggregates of the two enantiomers, between 600 and 700 nm, are measured to be essentially the same. Their signs differ. The dissymmetry factor, $g_{\mathrm{lum}} = 2(I_L - I_R)/(I_L + I_R)$, where $I_L$ and $I_R$ are the intensities of left- and right-circularly polarized emissions, is high ($|g_{\mathrm{lum}}| = 0.01$). It is also similar to the dissymmetry factor measured for absorption of light[35] at this same solution's longest wavelength peak (${g_{\mathrm{abs}}}^{500-550\mathrm{nm}} = \Delta\epsilon/\epsilon = 0.01$).

**Polarized Light Microscopy and Differential Scanning Calorimetry.** Samples of (+)-**3** are seen by polarized light microscopy to be birefringent below 245 °C and, when cooled from the isotropic melt to 232 °C, to crystallize into thin long uniaxial and negatively birefringent fibers,[6a] displayed in Figure 5. Differential scanning calorimetric analyses (DSC, displayed in the Supporting Information) show sharp transitions at 245 °C ($\Delta H$ = 48.0 kJ/mol) in the first heating cycle and two transitions, at 232 and at 211 °C, in the first cooling cycle. As expected, the helicene appears to racemize significantly at these high temperatures. Thus, in subsequent cycles, two peaks appear in the heating phase, and peaks in both the heating and cooling phases become broader and shift to lower temperature. In still later cycles, peaks merge so there is only one on heating (at 220 °C) and one on cooling (at 208 °C). These last thermograms are essentially the same as those of racemic **3**, which shows a phase transition at 221.4 °C ($\Delta H$ = 44.6 kJ/mol) on heating and at 206.3 °C ($\Delta H$ = −42.1 kJ/mol) on cooling. Like the enantiopure material, racemic **3** between crossed polarizers is seen to be birefringent at temperatures below 220 °C. However, unlike the enantiopure material, when cooled from this temperature, it does not form visible fibers.

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(34) (a) Kuball, H.-G.; Schönhofer, A. In *Circular Dichroism: Principles and Applications*; Nakanishi, K., Berova, N., Woody, R., Eds.; VCH: New York, 1994; Chapter 4. (b) Schönhofer, A.; Kuball, H.-G. *Chem. Phys.* **1987**, *115*, 159. (c) Nordén, B. *Acta Chem. Scand.* **1972**, *26*, 1763. (d) Tunis-Schneider, M. J. B.; Maestre, M. F. *J. Mol. Biol.* **1970**, *52*, 521. (e) Cornell, D. G. *J. Colloid Interface Sci.* **1979**, *70*, 167.

(35) Kliger, D. S.; Lewis, J. W.; Randall, C. E. *Polarized Light in Optics and Spectroscopy*; Academic Press: San Diego, CA, 1990.

(36) (a) Riehl, J. P.; Richardson, F. S. *Chem. Rev.* **1986**, *86*, 1. (b) Brittain, H. G. *Chirality* **1996**, *8*, 357.

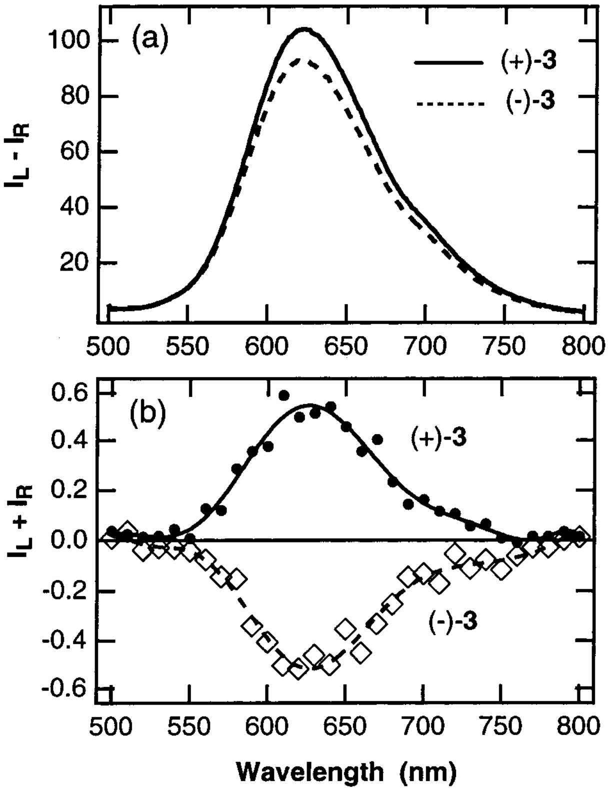

**Figure 4.** Spectra of (a) total luminescence and (b) circularly polarized luminescence from solutions at 23 °C of (+)- and (−)-**3** in dodecane ($1 \times 10^{-3}$ M) after excitation with unpolarized light ($\lambda_{ex} = 325$ nm). $I_L$ and $I_R$ are, respectively, the luminescence intensities of the left and right circularly polarized emission.

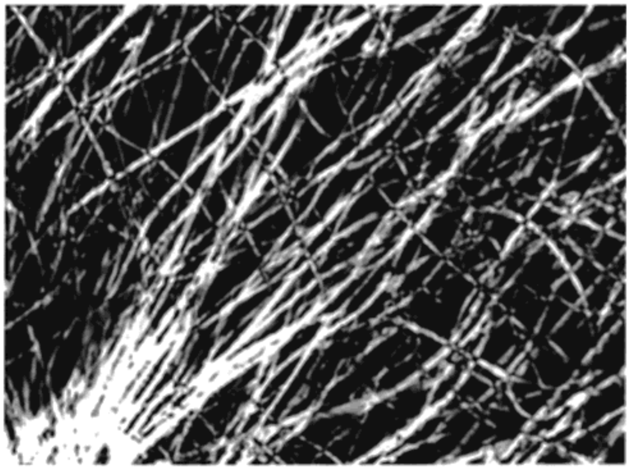

**Figure 5.** Fibers between crossed polarizers of (+)-**3** that had been cooled from the isotropic melt to 232 °C. The magnification is 160×.

**Transmission Electron Microscopy and Electron Diffraction.** The transmission electron microscopy (TEM) images in Figure 6 shows that the fibrous crystals of (+)-**3** adopt a lamellar morphology similar to that of nonracemic **1**.[25] The electron diffraction patterns from these crystals are consistent with the hypothesis that the molecules are stacked in columns that are packed into a hexagonal lattice. When thin areas of the fibrous crystals are tilted by 30° about the axis of the fibers, intense reflections, otherwise not seen, become apparent (Figure 7) at 3.4, 1.7, and 1.13 nm, transverse to the direction of the fibers' long axes. These are assigned to the first-, second- and third-order reflections from {110}/(020) planes in the hexagonal lattice that the tilt brings parallel to the electron beam. When fairly thick regions of the sample are examined, reflections are also seen without tilting, at spacings of 1.99 and 0.99 nm (Figure 8), corresponding to successive orders of reflection from the (200) planes. In thicker samples, there is an additional reflection, at 0.395 nm, (Figure 9) on a line parallel to the long axis of the fibers.

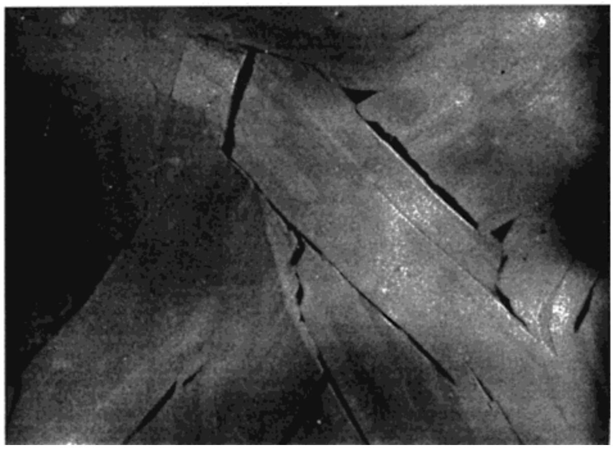

**Figure 6.** Transmission electron micrograph of fibers of (+)-**3**.

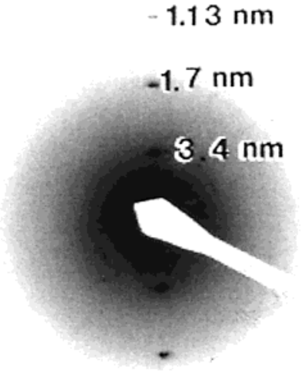

**Figure 7.** Electron diffraction pattern from a thin region of fibers of (+)-**3** tilted about the axis of the substrate by 30°.

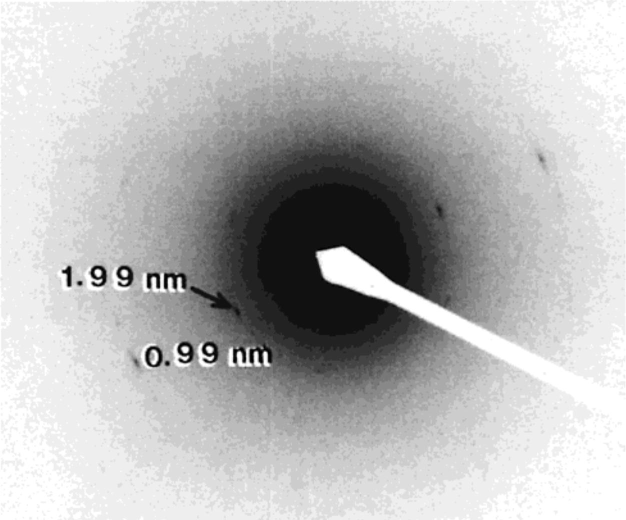

**Figure 8.** Electron diffraction from thick pack of fibers of (+)-**3**. The electron beam is perpendicular to the sample plane.

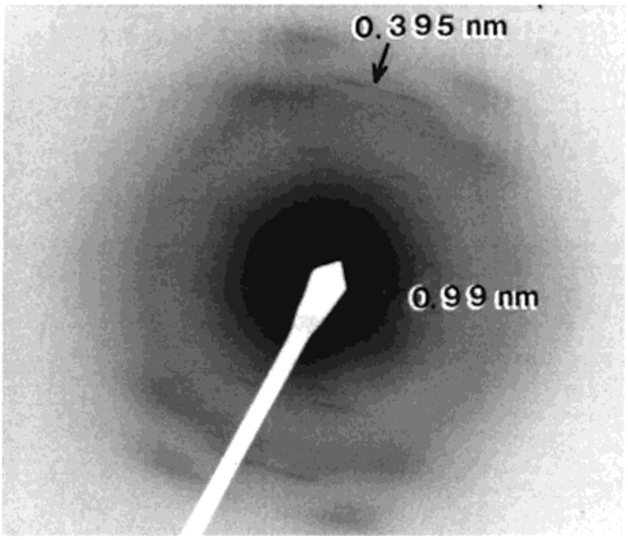

**Figure 9.** Pattern of reflected electrons from a thick region of fibrous (+)-**3** showing a meridional reflection (at 0.395 nm) corresponding to the spacing between aromatic cores.

**X-ray Diffraction.** The structure of (+)-**3** was also analyzed by X-ray diffraction. Samples were prepared on a glass substrate by evaporating the solvent from solutions in nonane. The resulting films were heated to 242 °C, cooled to 220 °C at 10 °C/min, and then cooled further to room temperature. The diffraction pattern of X-rays reflected from the surface, shown in the Supporting Information, is dominated by a peak at 3.45 nm, at the same position as the major peak in the electron diffraction pattern in Figure 7, and there are small second- and third-order peaks at 1.75 and 1.14 nm, respectively. There is a broad peak centered at ca. 0.4 nm, ascribed to diffraction by mobile side chains. No sharp peak is seen that is the analogue of one in the electron diffraction pattern in Figure 9 that was ascribed to the reflection from planes of stacked aromatic rings.

## Discussion

Enantiopure **1**, either dissolved in dodecane or as the pure material, assembles into columnar aggregates.[1,6a,b,7a,37] The columns assemble into hexagonal arrays, forming long fibers that are easily seen under an optical microscope.[6b] The aggregates, both in solution and pure, exhibit circular dichroisms and specific rotations distinctly different from those of the monomer.[1,6b,37] Enantiopure **3** appears to exhibit essentially similar properties.

A number of observations described above imply that molecules of enantiopure **3** self-assemble when solutions in dodecane or nonane are concentrated or cooled. These observations are the following: the changes recorded in Figures 1 and 2 that occur in the CD spectra;[1,6b,37] the changes that occur in the specific rotations;[1,6b] the absence of changes in the CD spectra and specific rotations when the solvent is chloroform rather than dodecane (because in chloroform the molecules do not aggregate);[1,3,38] the changes in the CD spectra that occur when the temperature is changed (Figure 3);[4,39] and the increased viscosity noted above when the solutions are concentrated.[40]

In addition, the two peaks in the fluoresence emission spectra in Figure 3 show that molecules of enantiopure **3** dissolved in dodecane aggregate.[41] Thus, the emission at ca. 440 nm appears to be from monomers of **3**, and that at ca. 620 nm from its aggregates. When the concentration is as small as $2 \times 10^{-6}$ M or when the solvent is chloroform, the only emission observed is from the monomer. However, when the concentration in dodecane is $2 \times 10^{-5}$ M, emission from the aggregates is also seen, and as the concentration is increased further, its intensity, compared to emission from the monomers, increases (as should aggregation). The assignments of the emission at 620 nm to aggregates and of the emission at 440 nm to monomers are supported by the fluorescence depolarization measurements. Thus, the polarization of the fluorescence from the aggregates ($P = 0.39 \pm 0.01$) is close to the maximum value ($P = 0.5$) for molecules that do not rotate appreciably in the interval between the time they are excited and the time they emit light,[35] while the polarization of the fluorescence from the monomers is essentially nil ($P = 0.02 \pm 0.01$). The implication is that the species emitting at 620 nm rotate more slowly in solution than those emitting at 440 nm, which is reasonable since the former are larger. Moreover, the wavelength of the emission attributed to the aggregates is, as it should be, higher than that attributed to the monomer.[41]

Chiral aggegates, which should be more dissymmetric than their monomers,[42] are known to emit circularly polarized fluorescence,[39a,b] and accordingly it is not surprising that the fluoresence from aggregates of enantiopure **3** is circularly polarized.[43] However, it is interesting that the dissymmetry factors of the emission, and absorption from the solutions are in fact very high. Although considerably smaller than the very large values reported for absorption and emission by *films* of some chiral poly(fluorene)s[44] and absorption by some films of chiral poly(*p*-phenylene)s,[45] they are slightly higher than those reported for absorption by solutions and films of some poly(*p*-phenyleneethynylene)s,[39e] comparable to those for absorption and emission by solutions and films of some chiral poly(phenylenevinylene)s,[46] and 0.5−4 times as large as those of the absorptions and emissions from aggregated chiral sexithiophenes[39a] and polythiophenes.[39b] That the dissymmetry found for the circular polarization of the emission is not an artifact caused by the anisotropy of the samples[47] is shown by the essentially perfect inversion of the sign of the polarization, displayed in Figure 4b, when enantiomers are interchanged. The similarity of the dissymmetry factors of the aggregates' lumi-

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(37) Nuckolls, C.; Katz, T. J.; Verbiest, T.; Van Elshocht, S.; Kauranen, M.; Kuball, H.-G.; Kiesewalter, S.; Lovinger, A. J.; Persoons, A. *J. Am. Chem. Soc.* **1998**, *120*, 8656.

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(40) Reference 1 and references therein.

(41) Fluorescence spectra showing two peaks, from monomers at lower wavelengths and from aggregates at higher wavelengths, are reported for phenylene ethynylene oligomers in: (a) Prince, R. B.; Saven, J. G.; Wolynes, P. G.; Moore, J. S. *J. Am. Chem. Soc.* **1999**, *121*, 3114. (b) Lahiri, S.; Thompson, J. L.; Moore, J. S. *J. Am. Chem. Soc.* **2000**, *122*, 11315. (c) Reference 39e and references therein. They are reported for poly(phenylbenzodithiazole) in (d) Moldowan, J. M.; Dahl, J.; Huizinga, B. J.; Fago, F. J.; Hickey, L. J.; Peakman, T. M.; Taylor, D. W. *Science* **1994**, *265*, 768, and for chiral polythiophenes in the following references: for $\alpha,\omega$-disubstituted sexithiophenes in ref 39a and for poly{3,4-di[(*S*)-2-methylbutoxy]thiophene} in ref 39b.

(42) Inai, Y.; Sisido, M.; Imanishi, Y. *J. Phys. Chem.* **1990**, *94*, 8365.

(43) (a) Dekkers, H. P. J. M. In *Circular Dichroism*; Nakanishi, K., Berova, N., Woddy, R. W., Eds.; VCH: New York, 1994; Chapter 6. (b) Riehl, J. P.; Richardson, F. S. *Chem. Rev.* **1986**, *86*, 1.

nescence and absorption at longest wavelength ($g_{\text{lum}}{}^{550-750\text{nm}} = g_{\text{abs}}{}^{500-550\text{nm}} = 0.01$) implies that the ground and excited states have similar geometries.[48]

Like enantiopure **1**, enantiopure **3** when cooled from the melt crystallizes into long fibers (Figure 5). The enthalpy changes accompanying the melting of both materials are similar (48 kJ/mol for enantiopure **3**, 45 kJ/mol for enantiopure **1**)[1] and significantly greater than those accompanying the clearing of columnar discotic mesophases (1−20 kJ/mol).[49] The implication may be that the fibrous materials are plastic crystals.

TEM images show fibers of enantiopure **3** (Figure 6) and **1**[6a] to have similar lamellar morphologies. That the underlying organization is hexagonal is proven by the 30° tilt about the fiber axes required for strong {110}/(020) reflections to be seen and by the observation of the (200) reflections when the sample is not tilted. The 3.40−3.45 nm distance between reflection planes measured both by electron and X-ray diffraction is consistent with a structure for enantiopure **3** that consists of hexagonally arrayed columns of helicenes, each $(3.40-3.45) \times (2/\sqrt{3}) = 3.9-4.0$ nm in diameter. This diameter is approximately that expected (4.3 nm) for two extended dodecyloxy side chains (ca. 2 × 1.73 nm) plus the diameter of the helicene core (ca. 0.8 nm), reduced by the side chains interdigitating.[50] The negative birefringence is consistent with the planes of the aromatic rings being approximately perpendicular to the long axes of the fibers,[51] as is the observation of electron diffraction, but not X-ray diffraction, by planes separated by 3.95 Å, the likely separation of these rings.[52]

Thus the morphology of pure **3** and the aggregating properties of **3** in solution are similar to the morphology and aggregating properties of **1**. Moreover, as reported elsewhere, the nonlinear optical properties are also similar.[7a,53] The second-order nonlinear optical response of Langmuir−Blodgett films of **3** is large because the material is chiral.[7a,53] And because it aggegates into columnar structures, the response varies sinusoidally as the sample, especially one that has been heated to the clearing temperature and cooled, is rotated about an axis perpendicular to the surface.[7b,53] However, films of higher symmetry and higher optical quality can be formed by spin-coating both **1** and **3**, and the second-order susceptibility of these films is higher for **3** than for **1**.[7c]

## Conclusions

The experiments show that helicenebisquinone **3** is easy to prepare in large amounts. Enantiopure, just like **1**, it self-assembles into columnar aggregates both when dissolved in saturated hydrocarbon solvents and in the absence of solvent. Moreover, the nonlinear optical properties of **3** are similar to or superior to those of **1**, previously the only material to exhibit a significant spontaneous[54] second harmonic response and to generate quasi phase-matched second harmonics from layers of enantiomers.[8]

## Experimental Section

THF and $Et_2O$ were distilled from Na/benzophenone, $CH_2Cl_2$, $(ClCH_2)_2$, and $Et_3N$ from $CaH_2$. 1,4-Benzoquinone (Aldrich, 98%) was purified by slurrying it in $CH_2Cl_2$ with 4 times its weight of basic alumina, filtering through Celite, removing the solvent, and drying under a vacuum. Zn dust (Aldrich, <10 μm, 98%) was activated prior to use.[55] The following were used without further purification: $AlCl_3$ (99%), acetyl chloride (99%), acetic anhydride (99%), $CH_3CN$ (anhydrous, 99.8%), $Cs_2CO_3$ (99%), CsF (99%), DMAP (99%), DMF (anhydrous, 99.8%), and 1-iodododecane (98%)—all from Aldrich, *n*-BuLi (2.6M in hexanes) and heptane (99%) from Acros, and triisopropylsilyl triflate (98%) from GFS. 3,3′-Bithienyl was synthesized according to ref 17. Glassware was flame-dried under vacuum and cooled under $N_2$. Unless otherwise specified, reactions were run under $N_2$, and reaction mixtures were stirred magnetically.

**Benzo[1,2-*b*:4,3-*b*′]dithiophene-4,5-quinone (6).** Oxalyl chloride (6.0 mL, 69 mmol) was added to a flask containing 3,3′-bithienyl (20.0 g, 120 mmol) dissolved in 1,2-dichloroethane (350 mL), and the mixture, under a $CaCl_2$ drying tube open to the atmosphere, was refluxed for 5 days. More oxalyl chloride (6.0 mL, 69 mmol) was added, and reflux was continued for another 5 days, after which time the mixture was cooled to 25 °C and left to stand overnight. It was filtered, and the filter cake was triturated thoroughly with hexanes and warm ethanol. Obtained were 18 g of red solid **6** (68% yield); mp (from EtOH) 240 °C (with decomposition); lit.[14b] (from *n*-propanol) 240 °C.[17b] $^1$H NMR ($CDCl_3$, 500 MHz): δ 7.82 (d, 2H, 5 Hz), 7.29 (d, 2H, 5 Hz).

**4,5-Diacetoxybenzo[1,2-*b*:4,3-*b*′]dithiophene (7).** Dry $CH_2Cl_2$ (300 mL) was added by cannula to a flask containing **6** (5.6 g, 25 mmol) and Zn dust (16.6 g, 250 mmol). Acetic anhydride (24 mL, 250 mmol) and triethylamine (53 mL, 380 mmol) were sequentially syringed in. The mixture was stirred for 4 h at 25 °C and then filtered through Celite. The filtrate was washed with water, 1 M HCl, saturated aqueous $NaHCO_3$, and again with water. The organic layer was dried ($Na_2SO_4$), filtered, treated with activated charcoal, and filtered again through Celite. Removal of solvent under reduced pressure and further drying under high vacuum yielded 6.34 g of **7** (83% yield), an off-white solid; mp (from $CH_2Cl_2$/MeOH) 194 °C. IR ($CCl_4$): 1787 cm$^{-1}$. $^1$H NMR ($CDCl_3$, 400 MHz): δ 7.62 (d, 2H, 5.4 Hz), 7.51 (d, 2H, 5.4 Hz), 2.41 ppm (s, 6H). $^{13}$C NMR ($CDCl_3$, 75 MHz): δ 167.5, 134.0, 133.6, 131.5,127.1, 122.2, 20.4 ppm. Anal. Calcd for $C_{14}H_{10}O_4S_2$: C, 54.89; H, 3.29. Found: C, 54.58; H, 3.31.

**4,5-Didodecyloxybenzo[1,2-*b*:4,3-*b*′]dithiophene (8).** A flask containing **7** (6.34 g, 20.7 mmol) and $Cs_2CO_3$ (16 g, 103 mmol) was fitted with a reflux condenser. Acetonitrile (300 mL) was added through a cannula and 1-iodododecane (26 mL, 103 mmol) was syringed in. The mixture was stirred and refluxed for 3 days, after which it was cooled to 25 °C. The solvent was removed under reduced pressure, and the remaining solids were partitioned between $CH_2Cl_2$ and water. The organic layer was washed with 1 M HCl and with water, dried ($Na_2SO_4$), and filtered. The solvent was removed, and the product was triturated thoroughly with cold ethanol and dried under high vacuum, yielding 11.1 g (94% yield) of **8**, an off-white, waxy solid; mp (from $CH_2Cl_2$/MeOH) 39−40 °C. $^1$H NMR ($CDCl_3$, 400 MHz): δ 7.62 (d, 2H, 5.4 Hz), 7.45 (d, 2H, 5.4 Hz), 4.25 (t, 4H, 6.6 Hz), 1.84 (quint, 4H, 7.5 Hz), 1.54 (quint, 4H, 7.6 Hz), 1.20−1.40 (m, 32H), 0.87 ppm (t, 6H, 6.8 Hz). $^{13}$C NMR ($CDCl_3$, 75 MHz): δ 142.3, 133.6, 131.2, 125.6, 122.1, 73.7, 31.9, 30.4, 29.7−29.4 (m), 26.1, 22.7, 14.1 ppm.

**2,7-Diacetyl-4,5-didodecyloxybenzo[1,2-*b*:4,3-*b*′]dithiophene (4).** Acetyl chloride (2.63 mL, 37 mmol) was syringed into a cold (0 °C) suspension of $AlCl_3$ (4.9 g, 35 mmol) in 100 mL of 1,2-dichloroethane. The mixture was stirred at 0 °C for 45 min, during which time it turned

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[44] Dissymmetry factors greater than 0.15 and up to 0.25 for absorption and emission from extensively annealed films are reported in the following. The details are not yet available. (a) Oda, M.; Meskers, S. C. J.; Nothofer, H. G.; Scherf, U.; Neher, D. *Synth. Met.* **2000**, *111−112*, 575. (b) Oda, M.; Nothofer, H. G.; Lieser, G.; Scherf, U.; Meskers, S. C. J.; Neher, D. *Adv. Mater.* **2000**, *12*, 362.

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[46] Peeters, E.; Christiaans, P. T.; Janssen, R. A. J.; Schoo, H. F. M.; Dekkers, H. P. J. M.; Meijer, E. W. *J. Am. Chem. Soc.* **1997**, *119*, 9909.

[47] Dekkers, H. P. J. M.. In *Circular Dichroism: Principles and Applications*; Nakanishi, K., Berova, N., Woody, R., Eds.; VCH: New York, 1994; Chapter 6, p 134.

[48] Brittain, H. G. In *Molecular Luminescence Spectroscopy: Methods and Applications, Part 1*; Schulman, S. G., Ed.; Wiley: New York, 1985; Chapter 6.

[49] Reference 2 and footnote 15 therein.

[50] See ref 6a and footnotes 19 and 20 therein.

[51] See ref 6a and footnotes 23−26 therein.

[52] Reference 2 and the references in footnotes 14, 15b, and 23 therein.

[53] Sioncke, S.; Van Elshocht, S.; Verbiest, T.; Persoons, A.; Mauranen, M.; Phillips, K. E. S.; Katz, T. J. *J. Chem. Phys.* **2000**, *113*, 7578.

[54] That is, a response in the absence of an external orienting force.

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clear. A solution of **8** (9.0 g, 16 mmol) in 1,2-dichloroethane (100 mL), also at 0 °C, was then added by cannula, and 25 mL of 1,2-dichloroethane was used to complete the transfer. The resulting mixture was stirred at 0 °C for 5 h, allowed to warm to 25 °C, quenched by the addition of water (250 mL), and transferred to a separatory funnel. The organic layer was washed with two portions of water, dried ($Na_2SO_4$), and filtered. The solvent was then removed under reduced pressure. The remaining solid was triturated with cold methanol and then dried under high vacuum. This gave 8.6 g (83% yield) of **4**, a lemon-yellow solid; mp (from $CH_2Cl_2$/MeOH) 69 °C. IR ($CCl_4$): 1669 $cm^{-1}$. $^1H$ NMR ($CDCl_3$, 400 MHz): $\delta$ 8.23 (s, 2H), 4.27 (t, 4H, 6.6 Hz), 2.71 ppm (s, 6H). $^{13}C$ NMR ($CDCl_3$, 75 MHz): $\delta$ 191.6, 144.2, 144.0, 138.7, 131.9, 126.9, 77.0, 74.0, 31.9, 30.4, 29.7−29.4 (m), 29.0, 26.1, 22.7, 14.1 ppm. Anal. Calcd for $C_{38}H_{58}O_4S_2$: C, 70.98; H, 9.09. Found: C, 70.79; H, 9.20.

**Triisopropylsilyl Enol Ether 9.** A solution of **4** (14.6 g, 22.7 mmol)-in $CH_2Cl_2$ (800 mL) contained in a round-bottomed flask was cooled in an ice bath. Triethylamine (32 mL, 227 mmol) and triisopropylsilyl triflate (13.4 mL, 49.5 mmol) were sequentially syringed in. The mixture was stirred at 0 °C for 10 min and then allowed to warm to 25 °C during 1 h, after which it was transferred to a separatory funnel and washed with 10% aqueous NaOH and saturated aqueous $NaHCO_3$. The organic layer was dried ($Na_2SO_4$) and filtered, and the solvent was removed under reduced pressure. The remaining yellowish-brown oil was triturated repeatedly with methanol until the wash was colorless. Drying under high vacuum gave 22.0 g (100% yield) of **9**, an amber oil. $^1H$ NMR ($CDCl_3$, 400 MHz): $\delta$ 7.69 (s, 2H), 4.91 (d, 2H, 2.2 Hz), 4.46 (d, 2H, 2.2 Hz), 4.23 (t, 4H, 6.5 Hz), 1.83 (quint, 4H, 7.9 Hz), 1.54 (quint, 4H, 7.7 Hz), 1.38−1.68 (m, 74H), 0.88 ppm (t, 6H, 6.8 Hz). $^{13}C$ NMR ($CDCl_3$, 75 MHz): $\delta$ 151.6, 142.4, 142.1, 133.0, 131.6, 118.8, 91.1, 73.7, 32.0, 30.5, 29.7−29.4 (m), 26.2, 22.7, 18.1, 14.2, 12.8 ppm.

**Thiohelicenebisquinone 10.** A mixture of **9** (21.5 g, 22.5 mmol), 1,4-benzoquinone (36.5 g, 337 mmol), and heptane (200 mL) was refluxed for 30 h, during which time it turned deep brownish-red. After it had cooled to 25 °C, the solvent was removed under reduced pressure. The remaining solids at a pressure of ca. 20 mmHg were heated to 100 °C, which sublimed away most of the residual 1,4-benzoquinone and hydroquinone. The product was then dissolved in hexanes, and insoluble materials were filtered. After the solvent had been evaporated, the remaining solid was dissolved in a small volume of $CH_2Cl_2$, and a portion, precipitated by the addition of excess methanol, was filtered. The filter cake was dissolved in $CH_2Cl_2$, which was subsequently evaporated, leaving the deep burgundy **10**, which was dried under high vacuum. The yield was 25.0 g, 95%; mp (from $CH_2Cl_2$-MeOH) 108 °C. $^1H$ NMR ($CDCl_3$, 400 MHz): $\delta$ 7.47 (s, 2H), 6.74 (d, 2H, 10.1 Hz), 6.52 (d, 2H, 10.1 Hz), 4.47−4.42 (m, 2H), 4.31−4.27 (m) 1.94−1.87 (quint, 4H, 6.5 Hz), 1.64−1.19 (m, 78H), 0.88 ppm (t, 6H, 6.8 Hz). $^{13}C$ NMR ($CDCl_3$, 75 MHz) :$\delta$ 185.3, 184.0, 155.1, 143.9, 139.5, 138.9, 137.3, 137.2, 136.3, 132.0, 129.0, 124.9, 110.1, 74.2, 31.9, 30.4, 29.7−29.4 (m) 26.2, 22.7, 18.0, 14.1, 12.9 ppm. Anal. Calcd for $C_{68}H_{98}O_8S_2Si_2$: C, 70.18; H, 8.49. Found: C, 69.98; H, 8.31.

**Preparation of Racemic 3.** DMF (150 mL) was added through a cannula to a flask containing **10** (3.00 g, 2.58 mmol) and CsF (1.96 g, 12.9 mmol). The resulting black solution was stirred and heated for 90 min in an oil bath at 65 °C. 1-Iodododecane (4.5 mL, 18.0 mmol) was syringed into the mixture, which was then heated for an additional 3 h. The mixture was cooled to 25 °C and partitioned between water and diethyl ether. The organic extract was washed twice more with water, dried ($Na_2SO_4$), and filtered. The solvent was removed under reduced pressure, and the product was precipitated from a small volume of $CH_2Cl_2$ by adding ethanol and evaporating. The ethanolic suspension was then filtered, and the filter cake was washed with cold ethanol. The yield of deep burgundy solid (±)-**3**, after it had been dried under high vacuum, was 2.86 g (93%); mp (from $CH_2Cl_2$-MeOH) 220 °C. IR ($CCl_4$): 1663 $cm^{-1}$. $^1H$ NMR ($CDCl_3$, 400 MHz): $\delta$ 7.49 (s, 2H), 6.75 (d, 2H, 10.1 Hz), 6.51 (d, 2H, 10.1 Hz), 4.4−4.29 (m, 8H), 2.00−1.91 (m, 8H), 1.61−1.55 (m, 8H), 1.49−1.20 (m, br, 64H), 0.90−0.87 ppm (m, 12H). $^{13}C$ NMR ($CDCl_3$, 75 MHz): $\delta$ 185.5, 183.9, 157.6, 144.0, 139.3, 137.3, 136.8, 135.6, 132.1, 128.7, 124.7, 103.2, 74.2, 69.7, 32.0, 30.4, 29.7−29.4 (m), 29.0, 26.1, 22.7, 14.1 ppm. Anal. Calcd for $C_{74}H_{106}O_8S_2$: C, 74.83; H, 9.00. Found: C, 74.76; H, 9.11.

**Resolution of 3. Preparation of 11.** Dichloroethane (250 mL) was added to a flask containing (±)-**3** (7.6 g, 6.4 mmol), Zn (21 g, 320 mmol), (1*S*)-(−)-camphanoyl chloride (11 g, 51 mmol), and DMAP (1.6 g, 13 mmol). $Et_3N$ was syringed in, and the mixture was stirred at 60 °C overnight. After it had cooled to 25 °C, it was filtered through Celite, and the filtrate was diluted with $CH_2Cl_2$. It was then washed with 1 M HCl and then saturated aqueous $NaHCO_3$ and dried ($Na_2SO_4$). Evaporation of the solvent under vacuum and column chromatography on silica gel using 25−30% EtOAc in hexanes yielded the two diastereomeric esters, **11a** (less polar) and **11b** (more polar) in 90 and 70% yields, respectively. Both are pale yellow solids.

**(a) Properties of 11a.** Mp (from $CH_2Cl_2$−MeOH) 141 °C. IR ($CCl_4$): 1798, 1753 $cm^{-1}$. $^1H$ NMR ($CDCl_3$, 500 MHz): $\delta$ 7.27 (s, 2H), 7.01 (d, 2H, 8.3 Hz), 6.09 (d, 2H, 8.3 Hz), 4.45 (m, 4H), 4.29−4.23 (m, 4H), 2.73 (m, 2H), 2.40 (m, 2H), 2.10−1.87 (m, 12H), 1.63−1.57 (m, 92H), 1.04 (m, 2H), 0.90−0.87 (m, 18H), 0.45−0.38 (m, 8H), 0.34 ppm (s, 6H). $^{13}C$ NMR ($CDCl_3$, 75 MHz): $\delta$ 177.9, 177.0, 166.3, 165.1, 153.4, 143.1, 142.7, 142.5, 134.3, 133.3, 130.3, 128.8, 127.2, 120.8, 118.1, 113.9, 96.7, 91.3, 89.1, 74.0, 68.9, 55.1, 54.6, 54.3, 54.0, 32.0, 31.2, 30.5, 29.7−28.9 (m), 28.5, 26.2 (d), 22.7, 17.2−17.1 (d), 16.0−15.8 (d), 14.1, 9.8, 9.5 ppm. Anal. Calcd for $C_{114}H_{158}O_{20}S_2$: C, 71.59; H, 8.33. Found: C, 71.37; H, 8.24.

**(b) Properties of 11b.** Mp (from $CH_2Cl_2$−MeOH) 110 °C. IR ($CCl_4$): 1801, 1751 $cm^{-1}$. $^1H$ NMR ($CDCl_3$, 500 MHz): $\delta$ 7.16 (s, 2H), 7.01 (d, 2H, 8.3 Hz), 6.15 (d, 2H, 8.3 Hz), 4.49 (m, 2H), 4.36−4.25 (m, 6H), 2.73 (m, 2H), 2.42 (m, 2H), 2.10−1.82 (m, 14H), 1.00−0.80 (m, 24H); $^{13}C$ NMR ($CDCl_3$, 75 MHz) $\delta$ 177.6, 176.8, 166.6, 165.0, 153.0, 143.6, 143.0, 142.7, 135.3, 132.3, 130.2, 128.5, 127.0, 121.4, 118.7, 115.1, 96.5, 90.9, 90.1, 74.2, 69.1, 54.9, 54.4, 54.2, 53.9, 31.9, 31.3, 30.5, 29.7−28.8 (m), 27.6, 26.5, 26.1, 22.7, 17.1−17.0 ($\delta$), 16.3−16.2 ($\delta$), 14.1, 9.7, 9.5. Anal. Calcd. for $C_{114}H_{158}O_{20}S_2$: C, 71.59; H, 8.33. Found: C, 71.31; H, 8.37.

**Conversion of 11 into Enantiopure 3.** Distilled $Et_2O$ (200 mL) was added to **11b** (3.1 g, 1.6 mmol), and the resulting solution was cooled to 0 °C. MeLi (23 mL, 1.4 M) was then added slowly from a syringe, and the mixture was stirred at 0 °C for 3 h and then allowed to warm to 25 °C during the course of 1 h. A deoxygenated solution of saturated aqueous $NH_4Cl$, added through a cannula, was stirred vigorously with the reaction mixture for 30 min. After extraction with $CH_2Cl_2$, washing with 1 M HCl and water, drying ($Na_2SO_4$), and filtering, the $CH_2Cl_2$ solution was stirred at 25 °C for 20 min with chloranil (1.2 g, 4.9 mmol). The solvent was then evaporated, and the crude solid product was filtered through a plug of silica gel, eluting first with 25% hexanes in $CH_2Cl_2$ and then with 20% hexanes in $CH_2Cl_2$. After the solvent had been evaporated, the remaining solid was dissolved in a small volume of $CH_2Cl_2$, to which excess MeOH was then added to precipitate the pure burgundy (*P*)-(+)-**3**, the yield of which, after drying, was 1.6 g (85%). The levorotatory enantiomer, (*M*)-**3**, was obtained by the same procedure starting from **11a**. The yield was 1.7 g (88%)

**(a) Properties of (*M*)-(−)-3.** Mp (from $CH_2Cl_2$-MeOH) 245 °C. IR ($CCl_4$): 1663 $cm^{-1}$. $^1H$ NMR ($CDCl_3$, 400 MHz): $\delta$ 7.49 (s, 2H), 6.75 (d, 2H, 10.1 Hz), 6.51 (d, 2H, 10.1 Hz), 4.4−4.29 (m, 8H), 2.00−1.91 (m, 8H), 1.61−1.55 (m, 8H), 1.49−1.20 (m, br, 64H), 0.90−0.87 ppm (m, 12H). $^{13}C$ NMR ($CDCl_3$, 75 MHz): $\delta$ 185.5, 183.9, 157.6, 144.0, 139.3, 137.3, 136.8, 136.3, 135.6, 132.1, 128.7, 124.7, 103.2, 74.2, 69.7, 32.0, 30.4, 29.7−29.4 (m) 29.0, 26.1, 22.7, 14.1 ppm. Anal. Calcd for $C_{74}H_{106}O_8S_2$: C, 74.83; H, 9.00. Found: C, 74.89; H, 8.85.

**(b) Properties of (*P*)-(+)-3.** The mp (from $CH_2Cl_2$−MeOH), IR spectrum ($CCl_4$), $^1H$ NMR spectrum ($CDCl_3$, 400 MHz), and $^{13}C$ NMR spectrum ($CDCl_3$, 75 MHz) was identical to that of the (−)-enantiomer. Anal. Calcd for $C_{74}H_{106}O_8S_2$: C, 74.83; H, 9.00. Found: C, 74.49; H, 9.11.

**CD and UV−Visible Absorption Spectra and Specific Rotations.** The dodecane used in these and other experiments was either purchased in olefin-free form from Fluka or was freed of olefin by shaking it with concentrated $H_2SO_4$, washing, drying over basic alumina and distilling. The cells used to measure the spectra of $2 \times 10^{-5}$, $2 \times 10^{-4}$, $2 \times 10^{-3}$, and $2 \times 10^{-2}$ M solutions were quartz and had path lengths of 1.0, 0.10, 0.010, and 0.0010 cm, respectively. The spectra of solutions more concentrated than $2 \times 10^{-2}$ M were also measured using the 0.0010 cm cell. The optical densities of the solutions at all reported wavlengths was ≤1.4. A solvent-free sample for CD analysis was prepared by drop-casting (−)-**3** from a solution in nonane onto a quartz disk. After most of the solvent had evaporated at 25 °C, any remaining traces were driven off by heating the film to 170 °C.

**Fluorescence Emission and Circularly Polarized Luminescence.** A Fluorolog-1680, 0.22 m double spectrometer (SPEX) was used to record the steady state fluorescence emission and excitation spectra. This same instrument was used to measure circular polarized fluorescence after a photoelastic modulator (PEM-90, Hinds Instruments) had been placed between the sample cell and the emission monochromator. The photoelastic modulator, operated in the quarter wave retardation mode at a frequency of 50 kHz, transformed circularly polarized light emitted by the sample into linearly polarized light, which was analyzed with a Glan-Thompson Polarizer (Oriel). The photocurrent of a R928 photomultiplier (Hamamatzu) was amplified with a SR560 preamplifier (Stanford Research Systems) and processed with a SR530 lock-in-amplifier (Stanford Research Systems) operating at 50 kHz. To measure the total emission intensity, the excitation light was chopped at 300 Hz, and the fluorescence was analyzed with the lock-in-amplifier operating at 300 Hz. Similar setups were reported previously.[56] To avoid artifacts that might result if the exciting light were polarized, a scrambler (SPEX) was placed between the light source and the sample. A FluoroMax-2 spectrometer (SPEX) with Glan Thompson polarizers was used to make the linear fluorescence polarization measurements.

**Polarized Light Microscopy and Differential Scanning Calorimetry.** The optical microscope was a Leica DMRXP polarizing microscope equipped with a Wild Leitz MPS46 Photoautomat along with a Linkam LTS 350 hot stage and a Linkam TP 92 controller. Differential scanning calorimetry was measured using a Perkin-Elmer DSC 7 with a Perkin-Elmer Pyris thermal analysis data station.

**Transmission Electron Microscopy and Electron Diffraction.** Samples were prepared by casting films from a solution in nonane onto a freshly cleaved mica substrate. The nonane was evaporated by heating the samples to 160 °C. The resulting thin films were heated further to 242 °C, then cooled to 220 °C at 10 °C/min, and returned to room temperature. They were obliquely shadowed with Pt, which was evaporated at an angle of $\tan^{-1}$ 0.5 to the surface, and then coated with a thin layer of amorphous carbon.[57] The mica substrate was then cut into small squares, and the films were floated off, transferred to copper grids, and dried. The JEOL transmission electron microscope used to study the samples was operated at 100 keV and equipped with a rotating tilt stage. The samples were scanned in the diffraction mode under low-dose conditions, and the diffraction patterns were recorded whenever a suitable region was found. The morphology of the region was then photographed using bright-field TEM.

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**Supporting Information Available:** Figures showing $^1$H NMR, $^{13}$C NMR, and IR spectra of (+)-**3**, (−)-**3**, (±)-**3**, **4**, **7**, **8**, **10**, (+)-**11**, and (−)-**11**, comparison of the CD spectra of (−)-**3** in $CHCl_3$ and in dodecane, CD spectra of (−)-**3** in dodecane at −5, 0, +10, and +20 °C, DSC thermograms of (+)- and racemic **3**, and the X-ray diffractogram from (+)-**3** (PDF). This material is available free of charge via the Internet at http://pubs.acs.org.

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