

## 2,3,7,8,12,13,17,18-Octakis( $\beta$ -hydroxyethyl)porphyrin (Octaethanolporphyrin) and Its Liquid Crystalline Derivatives: Synthesis and Characterization

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**Abstract:** A synthesis is reported for 2,3,7,8,12,13,17,18-octakis( $\beta$ -hydroxyethyl)porphyrin (octaethanolporphyrin) and a series of its octaalkyl ether derivatives. A number of the octakis(alkoxyethyl)porphyrins exhibit a discotic liquid crystalline phase, and all exhibit an isotropic liquid phase. These materials can be prepared as ordered thin films for testing as large-area organic semiconductor devices.

Porphyrin thin films have received considerable attention because of their interesting excited-state chemistry and catalytic behavior and because of Nature's ubiquitous use of porphyrins in electron-transfer processes.<sup>1</sup> Their photostability, high visible extinction coefficients, and low processing costs make them attractive candidates for electrophotographic,<sup>2</sup> photovoltaic,<sup>3</sup> and photoelectrochemical<sup>4</sup> applications. Especially intriguing is the ability to adjust the porphyrin's structural and electrical properties by synthetic means, thus making them ideal model compounds for the study of semiconduction in the organic solid state.<sup>5</sup>

A great deal of current research is being devoted to the understanding of systems, biomimetic and otherwise, that self-assemble into organized structures.<sup>6</sup> Liquid crystals<sup>7,8</sup> represent one of the best known classes of self-organizing materials, exhibiting properties that range from surfactants that can form micelles, monolayers, and membranes, to the rodlike molecules used in liquid crystal displays, to the recently discovered disklike

liquid crystals.<sup>9</sup> All of these compounds will spontaneously form ordered but fluid structures, and, if disturbed, the more fluid phases tend to reorder themselves. This self-ordering/self-healing property is an essential part of all biological cells; our interest in it, however, is more mundane: we wish to use it to form ordered organic electronic structures.

In electronic applications, it is well-known that a highly crystalline phase has superior properties relative to the same material in an amorphous phase. In semiconductors, the effect of order is to increase the carrier mobility and lifetime by decreasing the defect density.<sup>10</sup> However, the attainment of large-area single crystals of semiconductors is difficult and expensive. Hence, for example, there has been a great deal of effort expended on the growth of crystalline silicon ribbon and an even larger effort on improving the semiconductor properties of polycrystalline and amorphous silicon.<sup>11,12</sup>

Given the inherent tendency of liquid crystals (LCs) to self-order, it is tempting to speculate about the possibility of liquid crystalline electronic devices. LC displays are known<sup>13</sup> in which a single (liquid) crystal, 5  $\mu\text{m}$  thick, covering an area of ca. 500  $\text{cm}^2$ , is formed by simple capillary-filling of the isotropic material between two sheets of conducting glass (coated with the appropriate aligning agents) and cooling into the liquid crystalline phase. These inexpensive, thin, large-area crystals are precisely what is needed in some applications such as in the matrix addressing of flat panel displays<sup>14</sup> and in the conversion of solar energy.<sup>15</sup> Of course, the above-mentioned LCs are electronic insulators; what is required is a liquid crystalline semiconductor.

Because of their symmetry (spherical), no elemental semiconductor can be a liquid crystal. In fact, it would appear that, without a substantial organic (or silicone?) component to provide the necessary asymmetry, no inorganic semiconductor can be a liquid crystal. Therefore, LC semiconductors should be sought in the realm of organic semiconductors,<sup>5,16</sup> in which the porphyrins and the phthalocyanines are among the best known.

To our knowledge, the first LC semiconductor was synthesized by Goodby et al.<sup>17</sup> by esterifying the acetic and propionic acid

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side chains of uroporphyrin I with dodecanol. The resulting octaester had an LC phase over a range of 0.1 °C only on cooling. Apparently no other derivatives were synthesized, and no attempt was made to measure its electrical or photophysical properties. Two years later, in 1982, Piechocki et al.<sup>18</sup> published the synthesis of an LC phthalocyanine (Pc). This compound, copper octakis((dodecyloxy)methyl)phthalocyanine, melted at 53 °C to a columnar discotic mesophase<sup>19–22</sup> that was stable up to its decomposition point near 300 °C. However, the viscosity of the columnar phase was so high that it would barely flow, even under pressure, at temperatures just below its decomposition point.<sup>23</sup> Since this compound possessed no isotropic liquid phase, it was not possible to capillary-fill it into a device. Also, without an isotropic phase or a fluid mesophase, it would be extremely difficult to align<sup>24</sup> (order) this material.

In an attempt to solve these problems, we decided to synthesize a porphyrin analogue of the LC phthalocyanine. A porphyrin, having a smaller central core and 16 fewer  $\pi$  electrons than a phthalocyanine, should inherently be much less viscous than the Pc. Also, it should require shorter alkyl side chains to induce mesophase formation, further decreasing the viscosity. One final consideration: the replacement of the meso nitrogens in the Pc for carbons in the porphyrin allows the possibility of derivatizing the semiconductor (at the meso positions) with electron-donating or -withdrawing groups. Thus, the redox potential, dielectric constant, and polarizability of the porphyrin could be adjusted without (greatly) affecting crystal packing.

We recently reported the synthesis of a series of LC porphyrin octaesters<sup>25</sup> based on (octaacetic acid)porphyrin.<sup>26</sup> We now describe a much improved synthetic procedure that leads to a new series of LC porphyrin octaethers. The parent compound of this series is the hitherto unreported octaethanolporphyrin. We show that the appearance and the temperature range of a liquid crystalline phase depend markedly on the presence of a central metal and on the length of the ether side chains. These compounds melt to isotropic liquids well below their decomposition points and exhibit a relatively low viscosity, columnar discotic mesophase.

## Experimental Section

**Instrumentation.** High-resolution carbon and proton NMR spectra were measured on either a General Electric GN-500 (500 MHz) or a General Electric QE-300 (300 MHz) spectrometer, while the low-resolution proton NMR spectra were measured on a Varian EM-390 (90 MHz) instrument. High-resolution mass spectra were obtained with a Consolidated Electro Dynamics Corp. 110-21C mass spectrometer equipped with an electron impact ionization source. Fast atom bombardment mass spectra were performed on a Finnigan TSQ 70 instrument with the sample in a 3-nitrobenzyl alcohol matrix. Differential scanning calorimetry

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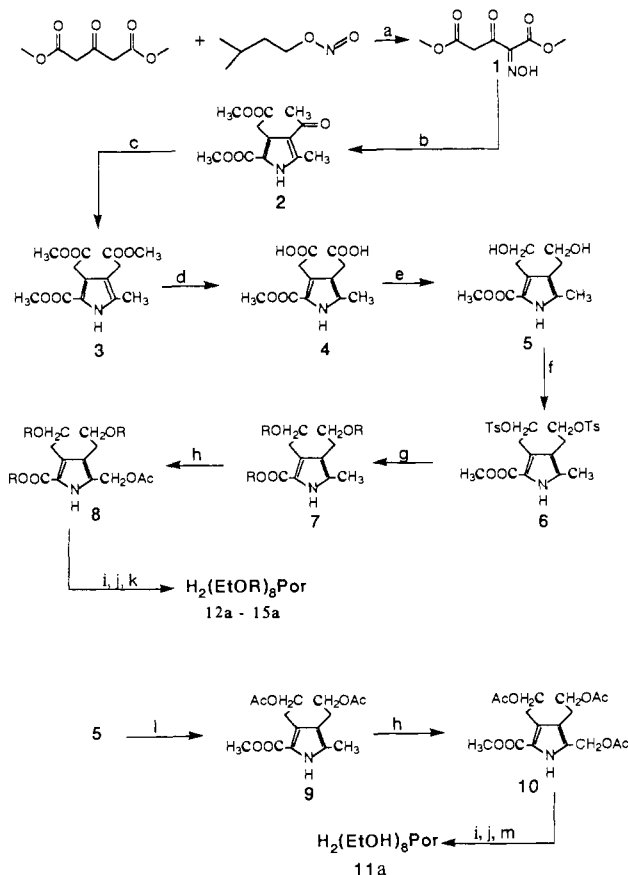
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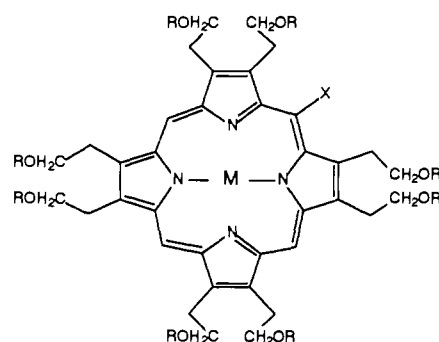
(24) To align a liquid crystal is to prepare the sample as a single domain with a specific orientation, e.g., with the optical axis perpendicular to the substrate. In general, the less viscous a mesophase, the easier it is to align. In the relatively new field of discotic liquid crystals, a general method for the alignment of large-area samples has not yet been found. For a discussion of this problem, see: (a) Chandrasekhar, S. In ref 8, 1982, Vol. V. (b) Vauchier, C.; Zann, A.; LeBarny, P.; DuBois, J. C.; Billard, J. *Mol. Cryst. Liq. Cryst.* **1981**, *66*, 103–114. (c) Levelut, A. M.; Hardouin, F.; Gasparoux, H.; Destrade, C.; Tinh, N. H. *J. Phys. (Paris)* **1981**, *42*, 147–152. (d) Safinya, C. R.; Clark, N. A.; Liang, K. S.; Varady, W. A.; Chiang, L. Y. *Mol. Cryst. Liq. Cryst.* **1985**, *123*, 205–216. (e) Chiang, L. Y.; Stokes, J. P.; Safinya, C. R.; Bloch, A. N. *Mol. Cryst. Liq. Cryst.* **1985**, *125*, 279–288.

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**Figure 1.** Schematic synthesis of octaethanolporphyrin ( $H_2(EtOH)_8Por$ ) and its octaether derivatives ( $H_2(ETOR)_8Por$ ): (a) HCl; (b) 2,4-pentanedione/ $Zn/AcOH/ca. 75\text{ }^\circ\text{C}$ ; (c)  $Ti(NO_3)_3/MeOH/HClO_4$ ; (d) NaOMe/MeOH; (e)  $BH_3/THF$ ; (f) TsCl/pyridine; (g) ROH/toluene; (h)  $Pb(OAc)_2$ ; (i) KOH/EtOH; (j) HBr/EtOH; (k) chloranil; (l) AcCl/ $NEt_3$ ; (m)  $O_2$ .



11. R = H	X = H	M(EtOH) <sub>8</sub> Por
12. R = n-C <sub>6</sub> H <sub>9</sub>	X = H	M(EtOBu) <sub>8</sub> Por
13. R = n-C <sub>6</sub> H <sub>13</sub>	X = H	M(EtOHex) <sub>8</sub> Por
14. R = n-C <sub>8</sub> H <sub>17</sub>	X = H	M(EtOOct) <sub>8</sub> Por
15. R = n-C <sub>10</sub> H <sub>21</sub>	X = H	M(EtODec) <sub>8</sub> Por
16. R = n-C <sub>8</sub> H <sub>17</sub>	X = CN	CN-M(EtOOct) <sub>8</sub> Por
17. R = n-C <sub>8</sub> H <sub>17</sub>	X = NO <sub>2</sub>	NO <sub>2</sub> -M(EtOOct) <sub>8</sub> Por

**Figure 2.** Octaethanolporphyrin (11), the octakis(alkoxyethyl)porphyrins, and their abbreviated names.

metry<sup>27</sup> was performed with a Perkin-Elmer DSC 2. UV-visible spectra were taken on a Hewlett-Packard 8451A spectrophotometer. The optical

(27) For an introduction, see: Barrall, E. M., II; Johnson, J. F. In ref 7, Vol. II.

textures<sup>28</sup> were observed as a function of temperature between crossed polarizers in a Leitz polarizing microscope, equipped with a hot stage, at 100× magnification.

**Synthesis.** The synthesis is outlined in Figure 1. The resulting family of octaethers is shown in Figure 2.

**Methyl 3-acetyl-5-(methoxycarbonyl)-2-methylpyrrole-4-acetate (2)** was prepared in 54% yield from 2,4-pentanedione and dimethyl 1,3-acetonedicarboxylate oxime (1) by a standard Knorr pyrrole synthesis.<sup>26a,29</sup> Mp 140–141 °C (lit. mp 141 °C). <sup>1</sup>H NMR (90 MHz, CDCl<sub>3</sub>) δ 2.36 (s, 3 H), 2.45 (s, 3 H), 3.67 (s, 3 H), 3.75 (s, 3 H), 4.17 (s, 2 H), 9.70 (br, 1 H).

**Dimethyl 5-(methoxycarbonyl)-2-methylpyrrole-3,4-diacetate (3)** was prepared in 80% yield by the method of Franck.<sup>26a</sup> Mp 91–92 °C (lit. mp 92 °C). <sup>1</sup>H NMR (90 MHz, CDCl<sub>3</sub>) δ 2.21 (s, 3 H), 3.38 (s, 2 H), 3.60 (s, 3 H), 3.62 (s, 3 H), 3.75 (s, 3 H), 3.82 (s, 2 H), 8.93 (br, 1 H).

**5-(Methoxycarbonyl)-2-methylpyrrole-3,4-diacetic Acid (4).** NaH (32 g, 1.3 mol) was dissolved in 1600 mL of dry methanol, and 83 g of finely powdered 3 (0.29 mol) was added. The mixture was heated at reflux for 6 h and then concentrated by rotary evaporation to 300 mL. H<sub>2</sub>O (700 mL) was added, and the solution was filtered, washed twice with ether, and acidified to pH = 5 with concentrated HCl. After standing at 5 °C for several hours, the precipitate was filtered, washed with H<sub>2</sub>O and cold acetone, and dried in vacuo. The yield of light pink solid was 64 g (86%). Mp 245–250 °C (dec). HRMS P<sup>+</sup> *m/e* calcd for C<sub>11</sub>H<sub>13</sub>O<sub>6</sub>N 255.0743, *m/e* found 255.0736. <sup>1</sup>H NMR (300 MHz, D<sub>2</sub>O/DOK) δ 1.82 (s, 3 H), 2.88 (s, 2 H), 2.99 (s, 3 H), 3.36 (s, 2 H).

**5-(Methoxycarbonyl)-3,4-bis(β-hydroxyethyl)-2-methylpyrrole (5).** Finely powdered 4 (15 g, 0.059 mol) was dispersed in 1600 mL of dry THF under N<sub>2</sub>, and 110 mL of 1 M BH<sub>3</sub> in THF was added. After 2 h at room temperature, 30 mL of methanol was added and the solution was concentrated to 800 mL before being washed 4 times with a total of 30 g of KOH in 70 mL of H<sub>2</sub>O and then twice with saturated NaCl. The organic layer was filtered and carefully (*T* < 30 °C) evaporated to dryness under vacuum. The product was recrystallized from 2-propanol/hexanes. The yield of light yellow solid was 11 g (82%). The solid was found to polymerize if heated. HRMS P<sup>+</sup> *m/e* calcd for C<sub>11</sub>H<sub>17</sub>O<sub>4</sub>N 227.1158, *m/e* found 227.1164. <sup>1</sup>H NMR (500 MHz, CD<sub>3</sub>OD) δ 2.19 (s, 3 H), 2.62 (t, *J* = 7 Hz, 2 H), 2.94 (t, *J* = 7 Hz, 2 H), 3.54 (t, *J* = 7 Hz, 2 H), 3.62 (t, *J* = 7 Hz, 2 H), 3.78 (s, 3 H). <sup>13</sup>C NMR (125.76 MHz, CD<sub>3</sub>OD) δ 11.24, 28.46, 29.68, 51.21, 63.68, 63.93, 117.48, 119.19, 129.72, 132.85, 163.28.

**5-(Methoxycarbonyl)-3,4-bis(β-tosyloxyethyl)-2-methylpyrrole (6).** The ditosylate was prepared by a standard method<sup>30</sup> in 84% yield. <sup>1</sup>H NMR (300 MHz, CDCl<sub>3</sub>) δ 2.22 (s, 3 H), 2.50 (s, 3 H), 2.51 (s, 3 H), 2.75 (t, *J* = 7 Hz, 2 H), 2.96 (t, *J* = 7 Hz, 2 H), 3.82 (s, 3 H), 4.07 (t, *J* = 7 Hz, 2 H), 4.14 (t, *J* = 7 Hz, 2 H), 7.36 (m, 4 H), 7.74 (m, 4 H), 9.40 (s, 1 H). <sup>13</sup>C NMR (75.48 MHz, CDCl<sub>3</sub>) δ 11.41, 21.47 (2 C), 23.91, 25.08, 50.93, 69.99, 70.16, 116.50, 117.28, 125.49, 127.72, (4 C), 129.70 (4 C), 131.15, 133.43 (2 C), 144.58 (2 C), 160.55.

**5-((Octyloxy)carbonyl)-3,4-bis(β-(octyloxy)ethyl)-2-methylpyrrole (7, R = *n*-octyl).** 6 (9.5 g, 0.0177 mol) was dissolved in 30 mL of toluene, 70 mL of octanol was added, and the solution was heated under reflux overnight. The resulting solution was concentrated under vacuum to ca. 20 mL, taken up in ether, washed with 1 M NaOH and H<sub>2</sub>O, dried over MgSO<sub>4</sub>, and evaporated. Methanol (100 mL) was added and the solution was slowly cooled to –78 °C. The precipitate was filtered (cold) and the resulting dark oil was filtered through a short silica gel column in CHCl<sub>3</sub> to remove colored impurities. The product was then again recrystallized from methanol at –78 °C. The yield of light yellow oil was 7.6 g (79%). Mp ca. 18 °C. HRMS P<sup>+</sup> *m/e* calcd for C<sub>34</sub>H<sub>63</sub>O<sub>4</sub>N 549.4757, *m/e* found 549.4773. <sup>1</sup>H NMR (500 MHz, CDCl<sub>3</sub>) δ 0.86 (t, *J* = 7 Hz, 9 H), 1.25 (m, 30 H), 1.53 (m, 4 H), 1.69 (m, 2 H), 2.20 (s, 3 H), 2.65 (t, *J* = 7 Hz, 2 H), 2.97 (t, *J* = 7 Hz, 2 H), 3.38 (m, 6 H), 3.48 (t, *J* = 7 Hz, 2 H), 4.21 (t, *J* = 7 Hz, 2 H), 8.80 (s, 1 H). <sup>13</sup>C NMR (125.76 MHz, CDCl<sub>3</sub>) δ 11.62, 14.07 (3 C), 22.64–31.82 (alkyls, 14 resolved peaks, 20 C), 64.01, 70.97, 71.11, 71.35, 71.45, 117.09, 118.61, 127.80, 130.60, 161.48.

**5-((Octyloxy)carbonyl)-3,4-bis(β-(octyloxy)ethyl)-2-(acetoxymethyl)pyrrole (8)** was made by a standard procedure<sup>29,31</sup> in 95% yield.

(28) Examination of a sample between crossed polarizers allows the observation of only that light which has been refracted by a (birefringent) ordered phase (i.e., one that is anisotropic) (see Figure 4). Thus, upon melting to an isotropic liquid, the sample appears black. For an introduction to the polarized microscopy of liquid crystals, see: Hartshorne, N. H. In ref 7, Vol. II, Chapter 2.

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(30) Fieser, L. F.; Fieser, M. *Reagents for Organic Synthesis*; Wiley: New York, 1967; Vol. 1, p 1180.

Mp 41–42 °C. <sup>1</sup>H NMR (500 MHz, CDCl<sub>3</sub>) δ 0.84 (t, *J* = 7 Hz, 9 H), 1.24 (m, 30 H), 1.52 (m, 4 H), 1.68 (m, 2 H), 2.03 (s, 3 H), 2.72 (t, *J* = 7 Hz, 2 H), 2.97 (t, *J* = 7 Hz, 2 H), 3.35 (m, 6 H), 3.47 (t, *J* = 7 Hz, 2 H), 4.21 (t, *J* = 7 Hz, 2 H), 5.03 (s, 2 H), 9.33 (s, 1 H). <sup>13</sup>C NMR (125.76 MHz, CDCl<sub>3</sub>) δ 14.01 (3 C), 20.84, 22.59–31.77 (alkyls, 14 resolved peaks, 20 C), 57.21, 64.30, 70.94, 71.12, 71.28, 71.51, 119.41, 121.73, 126.97, 128.24, 161.21, 171.48.

**Zinc 2,3,7,8,12,13,17,18-Octakis(β-(octyloxy)ethyl)porphyrin (Zn-(EtOOct)<sub>8</sub>Por (14b)). Method a.** 8 (7.4 g, 0.0122 mol) was dissolved in 120 mL of 95% ethanol, and 5 g of KOH in 20 mL of H<sub>2</sub>O was added. The mixture was heated under reflux in the dark under N<sub>2</sub> for 4 h before being cooled to room temperature and diluted with another 500 mL of 95% ethanol. After N<sub>2</sub> was bubbled through the solution for 20 min, 20 mL of 48% HBr was added and the solution was reheated in the dark with continuous bubbling of N<sub>2</sub>. After heating under reflux for 30 min, the solution was allowed to cool to room temperature and 2.54 g (0.0103 mol) of *p*-chloranil was added. The mixture was stirred overnight, diluted with 150 mL of H<sub>2</sub>O, and filtered. The crude product was chromatographed on a silica gel column in the dark (elution with 0.8% methanol in CHCl<sub>3</sub>) and then recrystallized from CHCl<sub>3</sub> and methanol. The free base was metalated with excess Zn(OAc)<sub>2</sub> in refluxing CH<sub>2</sub>Cl<sub>2</sub>/methanol, chromatographed on a silica gel column (eluent, 2% THF in toluene), and recrystallized from toluene/methanol to yield 2.3 g (47%). FAB P<sup>+</sup> *m/e* calcd for C<sub>100</sub>H<sub>172</sub>N<sub>4</sub>O<sub>8</sub>Zn 1621, *m/e* found 1621. UV/vis (CH<sub>2</sub>Cl<sub>2</sub>) λ<sub>max</sub> (nm) = 404, 534, 568. <sup>1</sup>H NMR (300 MHz, CDCl<sub>3</sub>) δ 0.84 (t, *J* = 7 Hz, 24 H), 1.21 (m, 80 H), 1.70 (m, 16 H), 3.63 (t, *J* = 7 Hz, 16 H), 4.26 (t, *J* = 6 Hz, 16 H), 4.36 (t, *J* = 6 Hz, 16 H), 10.07 (s, 4 H). <sup>13</sup>C NMR (75.47 MHz, CDCl<sub>3</sub>) δ 13.95, 22.58, 26.32, 27.74, 29.25, 29.53, 30.03, 31.81, 71.61, 73.23, 98.31, 138.75, 147.86.

**Zinc 2,3,7,8,12,13,17,18-Octakis(β-(octyloxy)ethyl)porphyrin (Zn-(EtOOct)<sub>8</sub>Por (14b)). Method b.** Zn(EtOH)<sub>8</sub>Por (11b; 110 mg, 0.152 mmol) was dissolved in 5 mL of dry DMSO and 10 mL of dry THF, and 100 mg of NaH (4.35 mmol) was added followed by 1.0 mL of 1-octanol (6.35 mmol). The mixture was stirred in the dark under N<sub>2</sub> for 4 days at room temperature. The crude product was precipitated with H<sub>2</sub>O, filtered, and twice chromatographed and recrystallized as described in method a. The yield was 22 mg (9%). The characterization was identical with that given in method a.

**5-(Methoxycarbonyl)-3,4-bis(β-acetoxyethyl)-2-methylpyrrole (9).** 5 (1.0 g, 0.0044 mol) was dispersed in 100 mL of CH<sub>2</sub>Cl<sub>2</sub>. Triethylamine (15 mL) was added, followed by 7 mL of acetic anhydride. After stirring at room temperature for 7 h, the solution was washed with dilute HCl, 1 N NaOH, and saturated NaCl before being dried over MgSO<sub>4</sub> and evaporated to dryness. The product was recrystallized from CH<sub>2</sub>Cl<sub>2</sub>/hexanes. The yield of white crystals was 1.3 g (95%). Mp 85–86 °C. HRMS P<sup>+</sup> *m/e* calcd for C<sub>15</sub>H<sub>21</sub>N<sub>1</sub>O<sub>6</sub> 311.1369, *m/e* found 311.1374. <sup>1</sup>H NMR (300 MHz, CDCl<sub>3</sub>) δ 2.03 (s, 3 H), 2.04 (s, 3 H), 2.24 (s, 3 H), 2.73 (t, *J* = 7 Hz, 2 H), 3.03 (t, *J* = 7 Hz, 2 H), 3.82 (s, 3 H), 4.08 (t, *J* = 7 Hz, 2 H), 4.18 (t, *J* = 7 Hz, 2 H), 8.97 (s, 1 H). <sup>13</sup>C NMR (75.47 MHz, CDCl<sub>3</sub>) δ 11.44, 20.85 (2 C), 23.51, 24.71, 50.94, 64.43, 64.72, 117.34, 117.64, 127.16, 130.78, 161.35, 170.82 (2 C).

**5-(Methoxycarbonyl)-3,4-bis(β-acetoxyethyl)-2-(acetoxymethyl)pyrrole (10)** was made from 9 as described earlier for the conversion of 7 to 8 in almost quantitative yield. Mp 99–101 °C. <sup>1</sup>H NMR (500 MHz, CDCl<sub>3</sub>) δ 2.01 (s, 3 H), 2.02 (s, 3 H), 2.06 (s, 3 H), 2.80 (t, *J* = 7 Hz, 2 H), 3.03 (t, *J* = 7 Hz, 2 H), 3.82 (s, 3 H), 4.09 (t, *J* = 7 Hz, 2 H), 4.17 (t, *J* = 7 Hz, 2 H), 5.04 (s, 2 H), 9.23 (s, 1 H). <sup>13</sup>C NMR (125.76 MHz, CDCl<sub>3</sub>) δ 20.92 (2 C), 20.99, 23.11, 24.34, 51.38, 56.83, 64.58, 64.76, 119.56, 120.59, 126.35, 128.33, 160.94, 170.91, 171.00, 171.75.

**Zinc 2,3,7,8,12,13,17,18-Octakis(β-hydroxyethyl)porphyrin (Zn-(EtOH)<sub>8</sub>Por (11b)).** 10 (1.4 g, 0.0038 mol) was dissolved in 95% ethanol, 1.5 g of KOH in 10 mL of H<sub>2</sub>O was added, and the solution was heated under reflux under N<sub>2</sub> in the dark for 5 h. After the solution cooled to room temperature, N<sub>2</sub> was bubbled through it for 30 min. Then 4 mL of 48% HBr in 120 mL of 95% ethanol was added. The solution was heated under reflux for 30 min, cooled to room temperature, and then left open to the air but protected from light for 5 days. After the solution was neutralized with triethylamine, the solids were filtered and washed with H<sub>2</sub>O. The crude product was dissolved in hot DMF and filtered. Excess Zn(OAc)<sub>2</sub> was added and the solution was heated under reflux for 15 min after which a little H<sub>2</sub>O was added and the solution was cooled slowly. The crystals were filtered and washed with H<sub>2</sub>O and methanol. The yield was 0.44 g (64%). <sup>1</sup>H NMR (500 MHz, DMSO-*d*<sub>6</sub>) δ 4.27 (m, 32 H), 5.23 (t, *J* = 5 Hz, 8 H), 10.12 (s, 4 H). <sup>13</sup>C NMR (125.76 MHz, DMSO-*d*<sub>6</sub>) δ 30.44, 64.04, 97.41, 138.50, 147.13.

**Zinc 2,3,7,8,12,13,17,18-Octakis(β-(hexanoyloxy)ethyl)porphyrin (18b).** H<sub>2</sub>(EtOH)<sub>8</sub>Por (14a; 400 mg, 0.55 mmol) was dissolved in a

(31) Siedel, W.; Winkler, F. *Liebigs Ann. Chem.* **1943**, *554*, 162–201.

mixture of 3 mL of DMF and 3 mL of triethylamine (21.5 mmol). *n*-Hexanoyl chloride (2 mL, 14.3 mmol) was then added and the solution was stirred at room temperature for 1 h. Dry THF (25 mL) was added followed by an additional 3 mL of triethylamine and 2 mL of acid chloride. This was stirred at room temperature for 2 days, extracted with CH<sub>2</sub>Cl<sub>2</sub>, washed with dilute HCl and NaOH, dried over MgSO<sub>4</sub>, and evaporated. The crude material was chromatographed in the dark on SiO<sub>2</sub> (eluent: 0.8% MeOH in CHCl<sub>3</sub>), metalated in the usual fashion, and rechromatographed as before. The product was recrystallized from CHCl<sub>3</sub>/MeOH. The yield was 43 mg (5%). FAB P<sup>+</sup> *m/e* calcd for C<sub>84</sub>H<sub>124</sub>N<sub>4</sub>O<sub>16</sub>Zn 1509, *m/e* found 1509. <sup>1</sup>H NMR (300 MHz, CDCl<sub>3</sub>) δ 0.74 (t, *J* = 7 Hz, 24 H), 1.20 (m, 32 H), 1.56 (m, 16 H), 2.35 (t, *J* = 7 Hz, 16 H), 4.50 (t, *J* = 7 Hz, 16 H), 4.99 (t, *J* = 7 Hz, 16 H), 10.44 (s, 4 H).

**Cu(EtOOct)<sub>8</sub>Por (14c)** was prepared by heating H<sub>2</sub>(EtOOct)<sub>8</sub>Por (14a) to reflux under N<sub>2</sub> for 20 min in DMF containing excess Cu(OAc)<sub>2</sub>.<sup>32</sup>

**Pd(EtOOct)<sub>8</sub>Por (14d)** was prepared by heating 14a to reflux for 1 h under N<sub>2</sub> in phenol containing a tenfold excess of Pd(OAc)<sub>2</sub>.

**Cd(EtOOct)<sub>8</sub>Por (14e)** was prepared by heating 14a to reflux for 10 min under N<sub>2</sub> in DMF containing excess Cd(OAc)<sub>2</sub>.<sup>33</sup>

Metal insertion for all the metalloporphyrins was verified by visible absorption spectroscopy, and all products were purified by chromatography on SiO<sub>2</sub> (elution with CHCl<sub>3</sub>/methanol) and recrystallization from CHCl<sub>3</sub>/methanol. Yields were >90%.

**meso-CN-Zn(EtOOct)<sub>8</sub>Por (16b)** was prepared in 67% yield by the procedure of Smith et al.<sup>34</sup> (method c).

**meso-NO<sub>2</sub>-Zn(EtOOct)<sub>8</sub>Por (17b)** was prepared in 72% yield by the method of Fanning et al.<sup>35</sup>

## Discussion

**Synthesis.** The pyrrole trimethyl ester 3 can be selectively hydrolyzed in high yield to the diacid monoester 4 with NaOCH<sub>3</sub> in methanol followed by an acidic workup. The crude product was quite pure and was not noticeably improved by recrystallization from ethanol/H<sub>2</sub>O.

Diacid 4 is efficiently reduced by BH<sub>3</sub> in THF to diol 5. The diacid has a limited solubility in THF and so was reduced as a fine dispersion, which quickly became transparent upon BH<sub>3</sub> addition. The product diol is relatively soluble in H<sub>2</sub>O and also adsorbs tightly (chelates?) to insoluble salts such as Na<sub>2</sub>SO<sub>4</sub> used as drying agents. Therefore the workup involved washing with a minimum of concentrated KOH solution and then with concentrated brine. The yellow, light green fluorescent solution was evaporated to dryness under vacuum at approximately room temperature. The solid diol, if heated, will polymerize, presumably through intermolecular transesterification. The dry diol 5 was dissolved in 2-propanol, filtered away from remaining salts, and recrystallized with addition of hexane.

Attempts to alkylate diol 5 directly through a Williamson ether synthesis failed, so ditosylate 6 was prepared in pyridine at 0 °C. Crude 6 is a waxy semisolid at room temperature that is ca. 95% pure by NMR. Attempts to purify it by recrystallization from hexane led to no further improvement.

In the presence of even weak bases, the ditosylate 6 undergoes elimination and subsequent polymerization rather than the desired substitution. Therefore the substitution was carried out in the appropriate alcohol with just enough toluene to dissolve the starting material, and no attempt was made to neutralize the toxic acid byproduct. These conditions also led to the transesterification of the pyrrolic α-ester. This product, 7, was rigorously purified (see Experimental Section) before proceeding, as it is difficult to purify the following product.

Compound 7 was oxidized to 8 almost quantitatively with a 5% excess of Pb(OAc)<sub>4</sub> in acetic acid/acetic anhydride.

The final three steps were done in one pot without isolation of intermediates and with exclusion of light and O<sub>2</sub>. The α-ester group of 8 was first hydrolyzed, and then HBr was added at ca.

**Table I.** Calorimetric Data for Compounds 12–19

compd <sup>b</sup>	R	M	X	T <sub>l</sub> /°C <sup>a</sup>	
				(ΔH/(kcal mol <sup>-1</sup> ))	
12a	Bu <sup>c</sup>	H <sub>2</sub>	H	K <sup>g</sup> $\xrightarrow[154]{(14.4)}$	I <sup>h</sup>
13a	Hex <sup>d</sup>	H <sub>2</sub>	H	K $\xrightarrow[111]{(12.6)}$	I
14a	Oct <sup>e</sup>	H <sub>2</sub>	H	K $\xrightarrow[84]{(11.9, \text{sum of transitions})}$	D <sup>i</sup> $\xrightarrow[89]{(11.9, \text{sum of transitions})}$ I
15a	Dec <sup>f</sup>	H <sub>2</sub>	H	K $\xrightarrow[69]{(18.8)}$	I
12b	Bu	Zn	H	K $\xrightarrow[159]{(6.3, \text{sum of transitions})}$	D $\xrightarrow[164]{(6.3, \text{sum of transitions})}$ I
13b	Hex	Zn	H	K $\xrightarrow[114]{(8.8)}$	D $\xrightarrow[181]{(5.7)}$ I
14b	Oct	Zn	H	K $\xrightarrow[107]{(10.8)}$	D $\xrightarrow[162]{(5.9)}$ I
15b	Dec	Zn	H	K $\xrightarrow[86]{(14.9)}$	D $\xrightarrow[142]{(5.2)}$ I
14b/15b <sup>j</sup>	Oct/ Dec	Zn	H	K $\xrightarrow[61]{(9.4)}$	D $\xrightarrow[147]{(5.1)}$ I
14c	Oct	Cu	H	K $\xrightarrow[84]{(7.6)}$	D $\xrightarrow[132]{(5.0)}$ I
14d	Oct	Pd	H	K $\xrightarrow[89]{(8.6)}$	D $\xrightarrow[123]{(5.2)}$ I
14e	Oct	Cd	H	K $\xrightarrow[103]{(9.0)}$	D $\xrightarrow[136]{(3.9)}$ I
16b	Oct	Zn	CN	K $\xrightarrow[85]{(8.1)}$	D $\xrightarrow[140]{(2.9)}$ I
17b	Oct	Zn	NO <sub>2</sub>	K $\xrightarrow[93]{(12.7)}$	D $\xrightarrow[118]{(3.4)}$ I
18b	COC <sub>3</sub> H <sub>11</sub>	Zn	H	K $\xrightarrow[169]{(11.1)}$	I
19b <sup>k</sup>		Zn	H	K $\xrightarrow[61]{(3.2)}$	D1 $\xrightarrow[136]{(5.3)}$ D2 $\xrightarrow[232]{(10.6)}$ I

<sup>a</sup> Heating rate 10 °C/min. <sup>b</sup> See Figure 2 for the structures of the compounds. <sup>c</sup> Bu = *n*-butyl. <sup>d</sup> Hex = *n*-hexyl. <sup>e</sup> Oct = *n*-octyl. <sup>f</sup> Dec = *n*-decyl. <sup>g</sup> K = crystal. <sup>h</sup> I = isotropic liquid. <sup>i</sup> D = discotic mesophase. <sup>j</sup> 1:1 (molar) mixture. <sup>k</sup> See text or ref 25 for the structure.

20 °C. After a brief reflux, the solution was again cooled to ca. 20 °C before the addition of the oxidizing agent; any oxidation occurring at higher temperature resulted in lower yields.

The resulting product, H<sub>2</sub>(EtOR)<sub>8</sub>Por or M(EtOR)<sub>8</sub>Por, is identical with the corresponding octaethylporphyrin (OEP) as far as its photophysical and electrochemical properties are concerned; only its solubility and solid-state thermal behavior are different.<sup>36</sup>

We employed method b (direct alkylation of Zn(EtOH)<sub>8</sub>Por) for the synthesis of the original set of octakis(alkoxyethyl)porphyrins. This method allowed us to relatively quickly screen a number of different side chain lengths and determine which products possessed liquid crystalline phases. However, the yield from method b is quite low. Method a was subsequently developed to synthesize larger quantities of a specific derivative, in our case, the (octyloxy)ethyl compound, in higher yields. Thus, the butyl, hexyl, and decyl derivatives have been prepared only by method b while the octyl derivative has been prepared by both methods.

**Octaethanolporphyrin (H<sub>2</sub>(EtOH)<sub>8</sub>Por) (11a)** was prepared from diol 5 by first protecting the alcohol functionalities as the acetates, 9, and then oxidizing as before with Pb(OAc)<sub>4</sub> to give 10. H<sub>2</sub>(EtOH)<sub>8</sub>Por was prepared in an analogous manner to H<sub>2</sub>(EtOR)<sub>8</sub>Por, although the final oxidation was done with O<sub>2</sub> rather than *p*-chloranil. The product is insoluble in H<sub>2</sub>O and THF, very slightly soluble in ethanol, and quite soluble in DMF, DMSO, and pyridine.

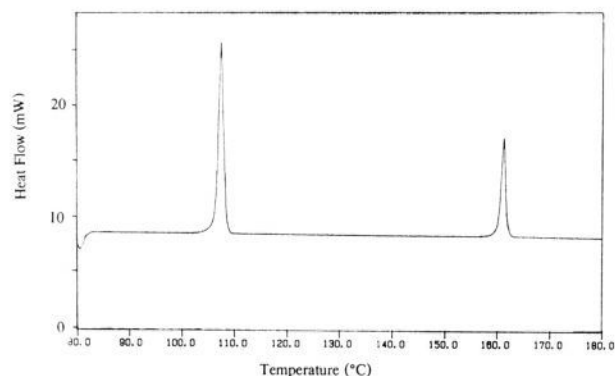
(36) (a) Gregg, B. A.; Fox, M. A.; Bard, A. J. *J. Phys. Chem.*, in press. (b) Gregg, B. A.; Fox, M. A.; Bard, A. J., submitted to *J. Phys. Chem.*

(32) Adler, A. D.; Longo, F. R.; Kampas, F.; Kim, J. J. *Inorg. Nucl. Chem.* 1970, 32, 2443–2445.

(33) Rodesiler, P. F.; Griffith, E. A. H.; Charles, N. G.; Lebioda, L.; Amma, E. L. *Inorg. Chem.* 1985, 24, 4595–4600.

(34) Smith, K. M.; Barnett, G. H.; Evans, B.; Martynenko, Z. *J. Am. Chem. Soc.* 1979, 101, 5953–5961.

(35) Fanning, J. C.; Mandel, F. S.; Gray, T. L.; Datta-Gupta, N. *Tetrahedron* 1979, 35, 1251–1255.



**Figure 3.** Differential scanning calorimogram of Zn(EtOOct)<sub>8</sub>Por (**14b**). Endothermic transitions are plotted upward.

**Characterization of Porphyrin Octaalkyl Ethyl Ethers.** The transition temperatures and enthalpies of the various porphyrin octaalkyl ethyl ethers are given in Table I. Figure 3 shows a differential scanning calorimetry (DSC) trace of Zn(EtOOct)<sub>8</sub>Por. Two major differences between the octaethers and the previously reported octaesters<sup>25</sup> are apparent from the DSC results. First, the liquid crystalline octaethers have only a single discotic LC phase, while four of the six octaesters had two discotic LC phases. Second, the free base ( $M = 2H$ ) octaethers have very little tendency to form liquid crystalline phases; only one of the four derivatives has an LC phase, and that only over a temperature range of 5 °C. Apparently, the metal plays an important role in the formation of these mesophases. This is in contrast to the octaesters,<sup>25</sup> where the presence or absence of a metal had only subtle effects on the thermal transitions.

Table I shows that the clearing (melting to isotropic<sup>28</sup>) points of the free bases decrease, as expected, with increasing chain length. The butyl derivative melts directly to an isotropic liquid at 154 °C. The hexyl derivative shows a broad peak at 111 °C, which could not be resolved into two peaks even at the slowest scan rate employed, 1.25 °C/min. The octyl derivative of the free base shows a very narrow mesophase from 84 to 89 °C that has an optical texture similar to that of the corresponding zinc derivative (Figure 4). When the chain length is increased to decyl, the free base again melts directly to an isotropic liquid (69 °C).

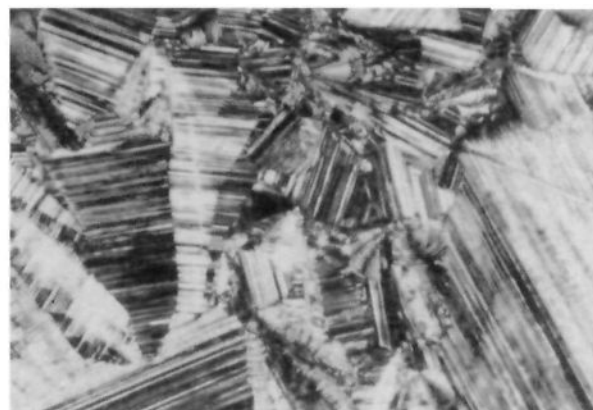
The zinc derivative of the butyl ether has a very narrow mesophase from 159 to 164 °C. The corresponding hexyl, octyl, and decyl ethers each have a single broad mesophase ranging over 67, 55, and 56 °C, respectively, with the clearing point decreasing by ca. 20 °C with each two-carbon increase in chain length.

Mixtures of liquid crystals are commonly employed to expand the LC temperature range relative to the individual components. To test if this behavior extended to the LC porphyrins, a 1:1 (molar) mixture of the zinc octyl and the zinc decyl ethers was prepared. This mixture had a  $K \rightarrow D$  (crystal to discotic LC) transition that was 25 °C lower than that of the decyl ether and 46 °C below that of the octyl ether. Its clearing point was intermediate between that of its two constituents, giving it an LC range of 86 °C. Thus, it is possible to greatly extend the LC range of the porphyrins by making mixtures of homologous compounds.

The central metal has a dramatic effect on mesophase formation in the porphyrin octaethers (Table I), which was absent in the corresponding octaesters.<sup>25</sup> Although it is often difficult to predict mesophase stability (even among the better known rodlike liquid crystals), one obvious mechanism for this effect of the central metal had to be considered: this is an analogue to the well-known tendency of porphyrins to aggregate in organic solvents. As described by Caughey et al.,<sup>37</sup> the participation of the porphyrin  $\pi$  system in donor-acceptor type interactions can lead to aggregation. They showed that the tendency of porphyrins to aggregate in solution increased in proportion to the electron-withdrawing character of the meso substituent. More recently, Abraham et



**a**



**b**

**Figure 4.** Optical texture of Zn(EtOOct)<sub>8</sub>Por (**14b**) in a capillary-filled cell (thickness ca. 2.5  $\mu\text{m}$ , crossed polarizers, area of view  $3.7 \times 2.6 \text{ mm}^2$ ): (a) in the liquid crystal phase, 140 °C; (b) in the solid phase at room temperature.

al.<sup>38</sup> have demonstrated a correlation between the porphyrin oxidation potential and its dimerization constant. In their model, the central cavity of the porphyrin ring (containing the metal or  $2H$ ) is considered a center of positive charge surrounded by a ring of negative charge (the  $\pi$  system). The porphyrins have a tendency to stack up with the  $\pi$  cloud of one ring attracted to the central metal of the next. Thus, porphyrins containing electropositive metals such as Cd, which donate substantial electron density to the ring (and are correspondingly easily oxidized), aggregate quite readily. The Pd or free base derivatives, which are harder to oxidize, have a much lower tendency to aggregate. If this mechanism is also operative in mesophase formation, the predicted order of mesophase stability is  $\text{Cd} > \text{Zn} > \text{Cu} > \text{Pd} \approx 2H$ . That is, the liquid crystalline temperature range should decrease in this order. When the metallo derivatives of the octyl ether were compared, the order (with the temperature range in parentheses) was  $\text{Zn}(55 \text{ }^\circ\text{C}) > \text{Cu}(48 \text{ }^\circ\text{C}) > \text{Pd}(34 \text{ }^\circ\text{C}) > \text{Cd}(33 \text{ }^\circ\text{C}) > 2H(5 \text{ }^\circ\text{C})$ . Clearly, no direct correlation exists between mesophase stability and the oxidation potential of the ring. Neither is there any obvious correlation with the size of the central ion. As yet we have no explanation for this order of mesophase stability.

One of the advantages of using porphyrins is that the meso carbons can be derivatized with electron donors or acceptors without drastically changing the crystal packing. Two preliminary attempts in this direction, the meso nitro and the meso cyano derivatives of Zn(EtOOct)<sub>8</sub>Por, are shown also in Table I. In the cyano derivative (**16b**) both transition temperatures are reduced by 22 °C, leaving the LC range at 55 °C. (Note that this is further

(37) Caughey, W. S.; Eberspaecher, H.; Fuchsmann, W. H.; McCoy, S. *Ann. N.Y. Acad. Sci.* **1969**, *153*, 722-737.

(38) Abraham, R. J.; Eivaz, F.; Pearson, H.; Smith, K. M. *J. Chem. Soc., Chem. Commun.* **1976**, 698-699, 699-701.

evidence against the dipole–dipole attraction mechanism for mesophase formation; vide supra.) The nitro derivative (**17b**) has a much reduced LC range of only 25 °C, presumably associated with the buckling of the porphyrin ring caused by the bulky nitro group in the meso position.<sup>39</sup>

Finally, we wished to compare the mesomorphic properties of an ester of octaethanolporphyrin (M(EtOH)<sub>8</sub>Por) to that of an ester of (octaacetic acid)porphyrin, M(AcOH)<sub>8</sub>Por.<sup>25</sup> The last two entries in Table I are isomers; they are the octa-*n*-hexanoate of Zn(EtOH)<sub>8</sub>Por and the octa-*n*-hexyl ester of Zn(AcOH)<sub>8</sub>Por, respectively. That is, they differ only in the directionality of the ester linkage. Quite surprisingly, their mesomorphic properties are completely different. The ester of Zn(EtOH)<sub>8</sub>Por (**18b**) is not a liquid crystal at all, melting to an isotropic liquid at 169 °C. The ester of Zn(AcOH)<sub>8</sub>Por (**19b**) shows two broad LC phases extending over a range of 171 °C before melting to an isotropic liquid at 232 °C.<sup>25</sup> Clearly, there is still much art contained in the science of liquid crystals.<sup>40</sup>

**Phase Behavior of Zinc Octakis(β-(octyloxy)ethyl)porphyrin.** Zn(EtOOct)<sub>8</sub>Por (**14b**) is a waxy solid at room temperature that crystallizes in long threads that are unsuitable for single-crystal X-ray analysis. When crystals are placed between microscope cover slips and heated, one observes by microscopy between crossed polarizers a definite decrease in viscosity at the crystalline to liquid crystalline phase transition (107 °C). The compound becomes translucent, allowing observation of the optical texture (without requiring any shear or pressure). On further heating, there is some minor rearrangement of the compound and the cover slips but the LC does not begin to flow. The optical texture (Figure 4) resembles that of a columnar discotic phase.<sup>42</sup> The disclinations are more curved than was the case with the octaesters,<sup>25</sup> and the viscosity of the mesophase is substantially lower. If the temperature is held at 5–10 °C below the clearing point (e.g., 155 °C), the LC will flow slightly under the weight of the cover slips

(39) Bonnett, R.; Stevenson, G. F. *J. Org. Chem.* **1965**, *30*, 2791–2798.

(40) Although the reversal of ester functions is known to affect the transition temperatures of the rodlike liquid crystals, this effect is much less dramatic than that seen here.<sup>41</sup> Furthermore, it is often attributed to a change in conjugation,<sup>41</sup> which, clearly, does not apply to compounds **18b** and **19b**.

(41) Gray, G. W. In ref 8, Vol. 2.

(42) (a) Guillon, D.; Weber, P.; Skoulios, A.; Piechocki, C.; Simon, J. *Mol. Cryst. Liq. Cryst.* **1985**, *130*, 223. (b) Guillon, D.; Skoulios, A.; Piechocki, C.; Simon, J.; Weber, P. *Ibid.* **1983**, *100*, 275.

and wet the surface of the glass. Any sharp crystal protrusions will become rounded. Thus, although the LC phase is definitely not nematic,<sup>21,22,43</sup> it does have enough conformational mobility at this temperature to seek a lower energy conformation, i.e., to self-order. This ordering process in the LC phase can be observed by changes in the absorption and emission spectra of the sample.<sup>36a</sup> If one repeats this procedure on a sample that appears amorphous (i.e., black) between crossed polarizers, the spectral shifts will be evident, although no order appears in the microscope. This implies that the spectral shifts are consequences of a short-range order that can appear under these conditions, although no longer range order, as seen in the microscope, is achieved. If heated to above the clearing point and then cooled slowly, the porphyrin will form a polycrystalline array on the surface.

These materials can be easily capillary-filled into thin cells between conducting substrates, resulting in large-area devices with unusual photoelectrical properties.<sup>36b</sup> Figure 4 shows the optical textures of such a cell (ca. 2.5 μm thick) in both the solid and the liquid crystalline phases. It is also possible to spin-coat these porphyrins onto a support and monitor their photophysical properties as a function of increasing order.<sup>36a</sup>

### Conclusion

An efficient synthesis has been described for a new series of liquid crystalline porphyrins based on the hitherto unreported octaethanolporphyrin. The thermotropic behavior of these compounds has been investigated as a function of the length of the ether side chains and of the central metal. The LC phase is fluid enough to permit some short-range ordering of the material, and the isotropic phase permits capillary-filling and longer range ordering.

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(43) We have not yet identified the type of discotic mesophase formed. The standard miscibility tests for LC phase identification are rendered problematic by (a) the lack of commercially available discotic LCs and (b) the fact that discotic liquid crystals of the same phase are known to be immiscible if they are of substantially different molecular sizes.<sup>21</sup>

## Glucosamine-6-phosphate Synthase from *Escherichia coli*: Mechanism of the Reaction at the Fructose 6-Phosphate Binding Site

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**Abstract:** A mechanistic study on the pure glucosamine-6-phosphate synthase from *Escherichia coli* has been undertaken. The stereochemistry of the reaction and the existence of a small intramolecular hydrogen transfer allow us to propose a mechanism consistent with its classification in the 2*R* aldose/ketose isomerase class. The fate of solvent tritium in substrate and product shows that proton transfer is followed by a slower step and that formation of a fructosimine 6-phosphate intermediate is rate limiting.

The first step in amino sugar metabolism is the interconversion of fructose 6-phosphate and glucosamine 6-phosphate catalyzed by glucosamine-6-phosphate isomerase<sup>1</sup> (glucosamine-6P deaminase, EC 5.3.1.10) and by L-glutamine:D-fructose-6-phosphate

amidotransferase<sup>2</sup> (glucosamine-6P synthase, EC 2.6.1.16). The *nagB*- (deaminase) and *glmS*- (synthase) encoded proteins, mapping respectively at minutes 15 and 84 on *Escherichia coli* chromosome,<sup>3</sup> are able to synthesize glucosamine-6P, but only the

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