

Porphyrin Octaesters: New Discotic Liquid Crystals

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Six liquid crystalline porphyrins are described which exhibit discotic mesophases over a broad temperature range before melting to stable, low viscosity, isotropic liquids suitable for capillary filling into photovoltaic cells.

For many applications thin, large area films of semiconductors are needed, for example, to address optical displays or for the conversion of solar energy.¹ Often the cost of using conventional inorganic semiconductors in these systems is prohibitive. A recent report of a liquid crystalline semiconductor² opens the possibility of combining the semiconducting properties of organic compounds³ with the liquid crystal's inherent tendency to flow until it forms an ordered phase. Liquid crystal (LC) displays are known where a single crystal covers an area of *ca.* 500 cm² with a thickness of only 5 μm (*e.g.* Tektronix Liquid Crystal Color Shutter). These displays are formed by vacuum filling the isotropic liquid between two sheets of glass (treated with the appropriate aligning agent) and cooling into the liquid crystalline phase. The originally reported LC copper phthalocyanine² had no fluid phases⁴ and so could not be used in this manner. We reasoned that by going from the phthalocyanine to the smaller porphyrin ring system as the central LC core some fluid phases might appear. We report here the synthesis and the liquid crystalline properties of a series of porphyrin octaesters.

A liquid crystalline porphyrin has been previously reported;⁵ however, it exhibited a mesophase of only 0.1 °C on

cooling. The compounds reported here have one or two LC phases, in one case (**3b**) extending over a range of 170 °C, before melting to isotropic liquids.

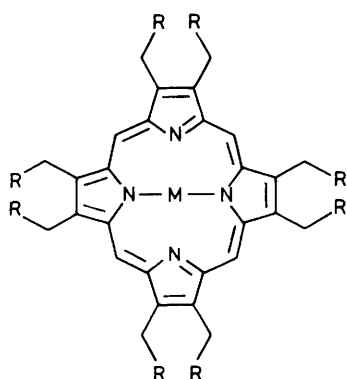
The octaesters (**2**)—(**4**) were obtained by warming a solution of (**1**)⁶ in the appropriate alcohol in the presence of H₂SO₄ (50 °C, 48 h). The products were purified by column chromatography [silica gel; eluant: chloroform–methanol (0.5–2%)] and recrystallized from a chloroform–methanol mixture. Treatment of the free base with zinc acetate in refluxing chloroform–methanol yielded the metal complex. The spectral (u.v.–vis., i.r., ¹H n.m.r., ¹³C n.m.r., fast atom bombardment mass) data[†] are in agreement with the assigned structures. Differential scanning calorimetry (D.S.C.) was performed with a Perkin-Elmer DSC 2. A Leitz Laborlux D polarizing microscope with heating stage was used to observe

[†] Spectral data for compound (**3b**): λ_{max} in CH₂Cl₂: 408, 536, and 572 nm; ν_{max} (solid): 1725 and 1170 cm⁻¹; ¹H n.m.r. (Me₄Si, CDCl₃, 500 MHz): δ 0.66 (t, 24H), 1.0–1.3 (m, 48H), 1.62 (m, 16H), 4.19 (t, 16H), 5.19 (s, 16H), and 10.31 (s, 4H); ¹³C n.m.r. (Me₄Si, CDCl₃, 500 MHz): δ 13.77, 22.34, 25.44, 28.56, 31.27, 65.50, 96.12, 99.57, 135.54, 147.59, 171.32; fast atom bombardment: *M*⁺ *m/z* 1512.

Table 1. Calorimetric data for compounds (2)–(4).

Compound	$T/^\circ\text{C}^a$ $(\Delta H/\text{kcal mol}^{-1})$		
(2a)	K ^b $\xrightarrow[0.29]{178}$ D ^c $\xrightarrow[11.4]{222}$ I ^d		
(2b)	K $\xrightarrow[0.72]{184}$ D $\xrightarrow[11.2]{273}$ I		
(3a)	K $\xrightarrow[3.6]{59}$ D1 $\xrightarrow[4.3]{132}$ D2 $\xrightarrow[7.1]{220}$ I		
(3b)	K $\xrightarrow[3.2]{61}$ D1 $\xrightarrow[5.3]{136}$ D2 $\xrightarrow[10.6]{232}$ I		
(4a)	K $\xrightarrow[4.5]{96}$ D1 $\xrightarrow[4.2]{99}$ D2 $\xrightarrow[4.9]{166}$ I		
(4b)	K $\xrightarrow[4.3]{91}$ D1 $\xrightarrow[4.3]{101}$ D2 $\xrightarrow[5.9]{208}$ I		

^a Heating rate $10^\circ\text{C min}^{-1}$; cal = 4.184 J. ^b K = crystal. ^c D = discotic mesophase. ^d I = isotropic liquid.



a; M = H₂
b; M = Zn

- (1), R = CO₂H (M = H₂ only)
(2), R = CO₂[CH₂]₃Me
(3), R = CO₂[CH₂]₅Me
(4), R = CO₂[CH₂]₇Me

the optical textures of the phases. The calorimetric data for compounds (2)–(4) are given in Table 1.

On cooling from the isotropic liquid, the n-butyl esters (2a) and (2b) gave a single, highly viscous, birefringent mesophase. The fan-like texture changed very little on crystallization consistent with the small enthalpy of transition.

The n-hexyl esters (3a) and (3b) showed two broad LC phases separated by sharp peaks in the D.S.C. (see Figure 1). Both phases exhibit the textures characteristic of highly ordered discotic phases^{7,8} although the viscosity decreases substantially in going from D1 to D2. The textures of these phases resemble the published textures of the LC phthalocyanines;^{4b,4c} a description of the exact structure of these mesophases must await the results of an X-ray analysis which is in progress.

Increasing the ester chain length to n-octyl, compounds (4a) and (4b), sharply increases T_{K-D1} while decreasing T_{D1-D2} and

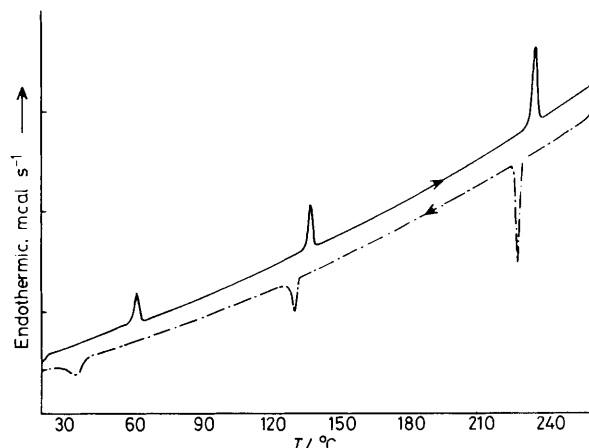


Figure 1. D.S.C. trace for (3b) (8.10 mg); heating rate $10^\circ\text{C min}^{-1}$.

T_{D2-I} . Thus the D1 phase becomes quite narrow and the whole LC range is decreased relative to the hexyl esters.

The incorporation of zinc into the porphyrin stabilizes the D2 phase, *i.e.*, it increases the clearing point, while it exerts only a modest effect on the other transitions.

It should be noted that none of these compounds shows a nematic, N_D,⁷ phase. This is seen both by the lack of a phase with a schlieren texture and by the observation that a crystal, on first heating, does not deform until it melts to an isotropic liquid. Since a nematic phase is often useful in the alignment of discotic LCs,⁹ attempts are being made to synthesize an LC porphyrin with an N_D phase. Nevertheless, the viscosity of the isotropic phase of *e.g.* (3b) is low enough to allow it to be capillary filled into a cell so that its electrical properties can be measured. Such experiments are in progress.

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