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## Liquid Crystals

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### Synthesis and characterization of liquid crystalline 5, 10, 15, 20-tetrakis(4-*n*-alkanoyloxyphenyl)porphyrins

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# Synthesis and characterization of liquid crystalline 5, 10, 15, 20-tetrakis(4-*n*-alkanoyloxyphenyl)porphyrins

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5,10,15,20-Tetrakis(4-*n*-alkanoyloxyphenyl)porphyrins and their Zinc complexes exhibit hexagonal columnar phases with low phase transition temperatures and wide mesophase ranges.

## 1. Introduction

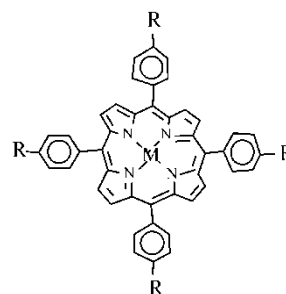
Metalloporphyrin complexes have been extensively studied in many applied chemistry fields such as photo-electronic conversion, non-linear optics, bio-sensors, bio-catalysts and liquid crystals [1–3]. It has been found in these studies that control of the orientation of porphyrin chromophores can play a very important role. Moreover, the properties of materials are affected by molecular alignments as well as by molecular structures. From this viewpoint, mesomorphic states, as well as the properties of materials may be effective realizing molecular functions. Columnar mesomorphic states are of particular significance in the study of the relationships between material functions and mesomorphic structures. At present, however, little is known of the mesomorphic functions of discotic/columnar mesogens, although columnar mesomorphic states have been extensively studied since their discovery in 1977 [4]. While liquid crystalline phthalocyanines have been extensively studied, the related porphyrins have received relatively little attention [5–11], possibly due to the more complex synthetic chemistry.

To our knowledge, the first liquid crystalline porphyrin was synthesized by Goodby *et al.* [7] through the esterification of acetic or propionic acid, with addition of side chains to the porphyrin I with dodecanol. The resulting octanoyloxyphenylporphyrin had a liquid crystalline phase range of only 0.1°C on cooling. In 1987, Gregg *et al.* [5] reported the synthesis and liquid crystalline properties of a series of porphyrin octaesters, which have one or two liquid crystalline phases; the LC-isotropic liquid phase transition temperature was higher than 170°C. In 1989 Gregg *et al.* [6]

reported the synthesis of octakis( $\beta$ -hydroxyethyl)-porphyrin. In 1991, tetrakis(4-*n*-dodecylphenyl)porphyrin was reported by Shimizu *et al.* [10], and in 1994, a rod-like liquid crystalline 5,15-disubstituted porphyrin was reported by Bruce *et al.* [11]. In all of the studies of mesogenic porphyrins, the extended disc-like core was peripherally substituted and can therefore be used as the basis for the construction of discotic materials. In this work we report the synthesis of a series of liquid crystalline tetraalkanoyloxyphenylporphyrins, based on 5,10,15,20-tetrakis(4-hydroxyphenyl)porphyrin (see figure 1), and investigate their liquid crystalline behaviour and structure. Their Zn complexes exhibit lower phase transition temperatures and wide mesophase ranges.

## 2. Experimental

5,10,15,20-tetrakis(4-Hydroxyphenyl)porphyrin **1a** was synthesized from 4-hydroxybenzaldehyde and pyrrole in propionic acid. Compound **1a** was esterified using the appropriate acyl chloride in benzene in the presence of triethylamine. The products, tetraalkanoyloxyphenylporphyrin **2–4** were purified by column chromatography (silica gel, chloroform/methanol) and recrystallized from a chloroform/methanol mixture.



- a. M=2H  
b. M=Zn  
(1) R=OH (M=2H, only)  
(2) R=OOC(CH<sub>2</sub>)<sub>6</sub>Me  
(3) R=OOC(CH<sub>2</sub>)<sub>8</sub>Me  
(4) R=OOC(CH<sub>2</sub>)<sub>10</sub>Me

Figure 1. Structure of the complexes.

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The free porphyrin base **4** and zinc acetate were heated under reflux in chloroform *N,N*-dimethylformamide to give the metal porphyrin complex. Spectral data were in agreement with the assigned structures.

**2a**: yield 86.4%. Elemental anal: calcd for  $C_{76}H_{86}O_8N_4$  C 77.13, H 7.32, N 4.73; found C 77.28, H 7.46, N 4.28%. UV-Vis ( $CHCl_3$ )  $\lambda_{max}/nm$ : 418, 514, 550, 590 and 645. IR (Cel) $\nu_{max}/cm^{-1}$ : 1755.5( $\nu_{C=O}$ ), 1199.9( $\nu_{C-H}$ ) and 722.4( $-(CH_2)_n-$ ).  $^1H$  NMR:  $\delta_H$  ( $C_6D_6$ , 400 MHz), 8.88(8H, s,  $\beta$ -pyrrole), 7.25–8.22(16H, m, Ar-H), 1.25–2.36(40H, m,  $-(CH_2)_n-$ ), 0.88–0.93(12H, s,  $-CH_3$ ), –2.83(2H, s, pyrrole, N-H).  $m/z = 1184$  (M + 1).

**2b**: yield 82.4%. Elemental anal: calcd for  $C_{76}H_{84}N_4O_8Zn$  C 73.26, H 6.80, N 4.50; found C 73.14, H 6.78, N 4.48%. UV-Vis ( $CHCl_3$ )  $\lambda_{max}/nm$ : 429.2, 561.0, 601.4. IR (Cel) $\nu_{max}/cm^{-1}$ : 1755( $\nu_{C=O}$ ), 1204( $\nu_{C-H}$ ), 722( $-(CH_2)_n-$ ).  $^1H$  NMR:  $\delta_H$  ( $C_6D_6$ , 400 MHz), 8.91(8H, s,  $\beta$ -pyrrole), 7.46–8.22(16H, m, Ar-H), 2.71–2.74(8H, m,  $-O-OC-CH_2-$ ), 1.25–1.92(40H, m,  $-(CH_2)_n-$ ), 0.93–0.95(12H, s,  $-CH_3$ ).  $m/z = 1246$  (M + 1).

**3a**: yield 87.6%. Elemental anal: calcd for  $C_{84}H_{102}N_4O_8$  C 77.86, H 7.93, N 4.32; found C 77.78, H 7.88, N 4.28%. UV-Vis ( $CHCl_3$ )  $\lambda_{max}/nm$ : 419.4, 515.0, 553.6, 582.6, 644.6. IR (Cel) $\nu_{max}/cm^{-1}$ : 1751( $\nu_{C=O}$ ), 1199( $\nu_{C-H}$ ), 722( $-(CH_2)_n-$ ).  $^1H$  NMR:  $\delta_H$  ( $C_6D_6$ , 400 MHz), 8.88(8H, s,  $\beta$ -pyrrole), 7.49–8.22(16H, m, Ar-H), 2.73–2.77(8H, m,  $-O-OC-CH_2-$ ), 1.25–2.37(56H, m,  $-(CH_2)_n-$ ), 0.88–0.93(12H, s,  $-CH_3$ ), –2.84(2H, s, pyrrole, N-H).  $m/z = 1296$  (M + 1).

**3b**: yield 83.6%. Elemental anal: calcd. for  $C_{84}H_{100}N_4O_8Zn$  C 74.29, H 7.42, N 4.13; found C 73.12, H 7.40, N 4.14%. UV-Vis ( $CHCl_3$ )  $\lambda_{max}/nm$ : 428.4, 557.0, 601.0. IR (Cel) $\nu_{max}/cm^{-1}$ : 1761( $\nu_{C=O}$ ), 1203( $\nu_{C-H}$ ), 722( $-(CH_2)_n-$ ).  $^1H$  NMR:  $\delta_H$  ( $C_6D_6$ , 400 MHz), 8.98(8H, s,  $\beta$ -pyrrole), 7.47–8.22(16H, m, Ar-H), 2.73–2.76(8H, m,  $-O-OC-CH_2-$ ), 1.25–1.93(56H, m,  $-(CH_2)_n-$ ), 0.92(12H, s,  $-CH_3$ ).  $m/z = 1465$  (M + 1).

**4a**: yield 86.8%. Elemental anal: calcd for  $C_{92}H_{118}N_4O_8$  C 78.48, H 8.45, N 3.98; found C 78.38, H 8.42, N 3.95%. UV-Vis ( $CHCl_3$ )  $\lambda_{max}/nm$ : 419.4, 514.8, 549.8, 589.6, 646.0. IR (Cel) $\nu_{max}/cm^{-1}$ : 1751( $\nu_{C=O}$ ), 1203( $\nu_{C-H}$ ), 722( $-(CH_2)_n-$ ).  $^1H$  NMR:  $\delta_H$  ( $C_6D_6$ , 400 MHz), 8.58(8H, s,  $\beta$ -pyrrole), 7.49–8.22(16H, m, Ar-H), 2.73–2.77(8H, m,  $-O-OC-CH_2-$ ), 1.26–1.93(72H, m,  $-(CH_2)_n-$ ), 0.88–0.91(12H, s,  $-CH_3$ ), –2.84(2H, s, pyrrole, N-H).  $m/z = 1408$  (M + 1).

**4b**: yield 82.8%. Elemental anal: calcd. for  $C_{92}H_{116}N_4O_8Zn$  C 75.42, H 7.98, N 3.82; found C 75.30, H 7.95, N 3.81%. UV-Vis ( $CHCl_3$ )  $\lambda_{max}/nm$ : 429.0, 561.2, 602.2. IR (Cel) $\nu_{max}/cm^{-1}$ : 1763( $\nu_{C=O}$ ), 1203( $\nu_{C-H}$ ), 1076( $\nu_{CCN}$ ), 826( $\nu_{C-H}$ ), 722( $-(CH_2)_n-$ ).  $^1H$  NMR:  $\delta_H$  ( $C_6D_6$ , 400 MHz), 8.98(8H, s,  $\beta$ -pyrrole), 7.48–8.22(16H, m, Ar-H), 2.73–3.02(8H, m,  $-O-OC-CH_2-$ ),

1.25–1.92(72H, m,  $-(CH_2)_n-$ ), 0.88–0.93(12H, s,  $-CH_3$ ).  $m/z = 1583$  (M + 1).

### 3. Results and discussion

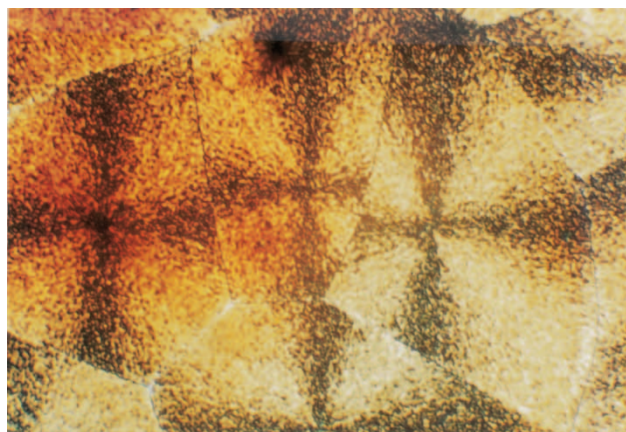
Differential scanning calorimetry (DSC) measurements were performed with a Perkin-Elmer 7 series thermal analysis system. A polarizing microscope with heating stage was used to observe phase textures. The calorimetric data for compounds **2–4** are listed in the table. The behaviour of phase transition enthalpies  $\Delta H$  and entropies  $\Delta S$  are similar to these of columnar mesogens, in which the  $\Delta H$  and  $\Delta S$  for the crystal to mesophase transition are larger than those for the mesophase to isotropic liquid transition. A comparison with 5,10,15,20-tetrakis(4-*n*-alkanolyloxyphenyl)porphyrins, which exhibit direct transition from the crystalline phase to the isotropic liquid, also demonstrates that compounds **2–4** are columnar mesogens.

According to the DSC thermograms, all phase transitions are enantiotropic. Compound **2a** melted at 90°C and gave a liquid crystal which persisted until around 134°C. On cooling from the isotropic liquid, the octanoyloxyphenylporphyrin **2a** gave a single mesophase at 142°C and a crystal phase at 27°C. The insertion of zinc into the porphyrin stabilizes the Col phase, i.e. it increases the clearing point, while exerting only a modest effect on other transitions. The decanoyloxyphenylporphyrins **3a** and **3b** showed two broad liquid crystalline phases between the isotropic liquid and crystalline phase, which were separated by sharp peaks in the DSC. Both phases exhibit textures

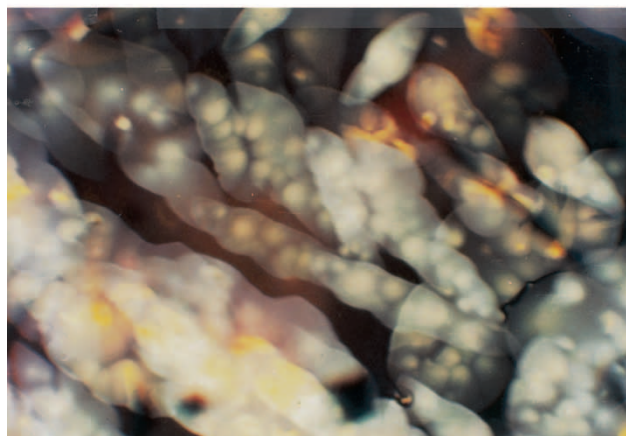
Table. Calorimetric data for compounds **2–4**. Cr = crystal, Col = columnar mesophase, I = isotropic liquid.

Compound	$T^a/^\circ C$ ( $\Delta H/kJ mol^{-1}$ )			
<b>2a</b>	90.64	133.9		
	Cr—Col—I (15.27) (12.77)			
<b>2b</b>	100.76	190.08		
	Cr—Col—I (13.05) (8.29)			
<b>3a</b>	24.03	48.39	124.66	
	Cr—Col <sub>1</sub> —Col <sub>2</sub> —I (20.59) (15.46) (12.15)			
	–8.987	35.53	166.0	
<b>3b</b>	Cr—Col <sub>1</sub> —Col <sub>2</sub> —I (0.151) (1.38) (5.13)			
	25.95	134.51		
<b>4a</b>	Cr—Col—I (36.00) (12.98)			
	–36.40	–19.26	10.88	39.78
<b>4b</b>	Cr—Col <sub>1</sub> —Col <sub>2</sub> —Col <sub>3</sub> —I (4.96) (0.78) (2.76) (1.31)			

<sup>a</sup>Heating rate 10°C min<sup>–1</sup>.



(a)



(b)

Figure 2. (a) Optical texture of compound **4a** obtained on cooling from the crystal at 42°C; (b) Optical texture of compound **4b** obtained on cooling from isotropic liquid at 13.5°C.

characteristic of highly ordered columnar phases, although the viscosity decreases substantially from Col<sub>1</sub> to Col<sub>2</sub>. The phase transition temperature  $T_{C-Col1}$  for compounds **3a** and **3b** sharply increases. Thus the Col<sub>1</sub> phase become narrow and the temperature range of whole liquid crystal decreased in comparison with

that of the octanoyloxyphenylporphyrin. The textures of these phases resemble those published for the liquid crystal phthalocyanines and tetrakis(4-*n*-dodecylphenyl)porphyrin.

On increasing the ester chain length to *n*-lauryl, the Col<sub>1</sub> phase of compound **4a** becomes quite narrow. The  $T_{C-Col1}$  and  $T_{Col1-I}$  transition temperatures for compound **4b** sharply decrease and the whole liquid crystal range is decreased relative to the octanoyloxyphenylporphyrins **2a** and **2b** and decanoyloxyphenylporphyrins **3a** and **3b**. Owing to the insertion of zinc into the porphyrin, the crystal to mesophase transition temperature for tetradodecanoyloxyphenylporphyrin **4b** is -36.4°C. The phases were identified by their characteristic optical texture as shown in figure 2. Compounds **3** and **4** exist in liquid crystalline phases at room temperature, so this lower phase transition temperature is very significant.

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