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Synthesis and mesomorphic behaviour of novel discotic *meso*-tetra(3,4,5-*n*-trialkoxybenzoylaminophenyl)porphyrins

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Novel porphyrin derivatives with twelve flexible alkyl chains, namely *meso*-tetra[4-(3,4,5-*n*-trialkoxybenzoylamino)phenyl]porphyrins (**1a**, n=12; **1b**, n=16) and the zinc complex (**2a**) were synthesized. The mesomorphic properties were investigated by DSC, WAXD and polarizing optical microscopy; the results showed that **1a** and **2a** exhibit a pseudo-hexagonal columnar phase, and **1b** a rectangular (Col) phase over a wide temperature range including room temperature.

1. Introduction

Since the discovery of discotic mesogens [1], a large number of disc-shaped molecules have been found to form columnar and/or nematic mesophases [2–4]. Much attention has been paid to discotic liquid crystals due to their potential application in fields such as charge transport, photoelectronic conversion, nonlinear optics and organic light-emitting diodes [5–8].

Porphyrin derivatives and their metal complexes have received considerable attention due to their remarkable electro-optical properties and potential application as semiconductors and one-dimensional conductors [9]. Since the report of the first liquid crystalline porphyrin which showed mesomorphism within 0.5°C by Goodby *et al.* [10], considerable effort has been devoted to the design, synthesis, and characterization of liquid crystalline porphyrins [10–12]. During the last two decades, Ohta and co-workers reported several porphyrin and phthalocyanine derivatives [2, 4, 13], most of which exhibit wider liquid crystalline phase ranges, but usually less than 180°C. Tetra-substituted porphyrins at the *meso* positions often show lamellar discotic phases over relatively narrow ranges (30–40°C) [12]. Here, we report the synthesis and mesomorphic behaviour of *meso*-tetra-substituted porphyrins with twelve flexible alkyl chains. All showed room temperature liquid crystalline behaviour and wide mesophase temperature ranges, particularly porphyrin **1a**, for which the temperature range is more than 250°C. Interestingly, the *meso*-tetra-substituted porphyrins investigated do not exhibit a lamellar but a columnar mesophase.

2. Experimental

2.1. *Materials and characterization*

p-Nitrobenzaldehyde was purchased from Acros and used without further purification. Pyrrole was freshly distilled before use; dichloromethane was dried with magnesium sulphate and then distilled. Other reagents were all analytical grade reagents.

^{1}H NMR spectra were measured on a Bruker Avance 500 MHz spectrometer using tetramethylsilane (TMS) (δ=0.00) as an internal chemical shift standard. FTIR measurements were carried out on a Perkin-Elmer Spectrum One B spectrometer; the samples were pressed tablets using potassium bromide. UV-Vis spectra were obtained using a Shimadzu UV-3100 UV-Vis spectrometer. DSC measurements were conducted on a Mettler Toledo DSC 821^e at a heating or cooling rate of 10°C min^{-1}. Optical texture was observed using a Leica DMLP polarizing optical microscope equipped with a Leitz 350 microscope heating stage. X-ray diffraction (XRD) measurements were obtained using a Rigaku X-ray diffractometer with Cu-K$_\alpha$ radiation.

2.2. *Synthesis*

The synthetic route is shown in scheme 1. Tetra(*p*-aminophenyl)porphyrin **3** was obtained by reducing tetra(*p*-nitrophenyl)porphyrin which was synthesized from *p*-nitrobenzaldehyde and pyrrole [14]. Porphyrins **1a** and **1b** were prepared through the reaction between **3** and 3,4,5-trialkoxybenzoyl chloride in the presence of

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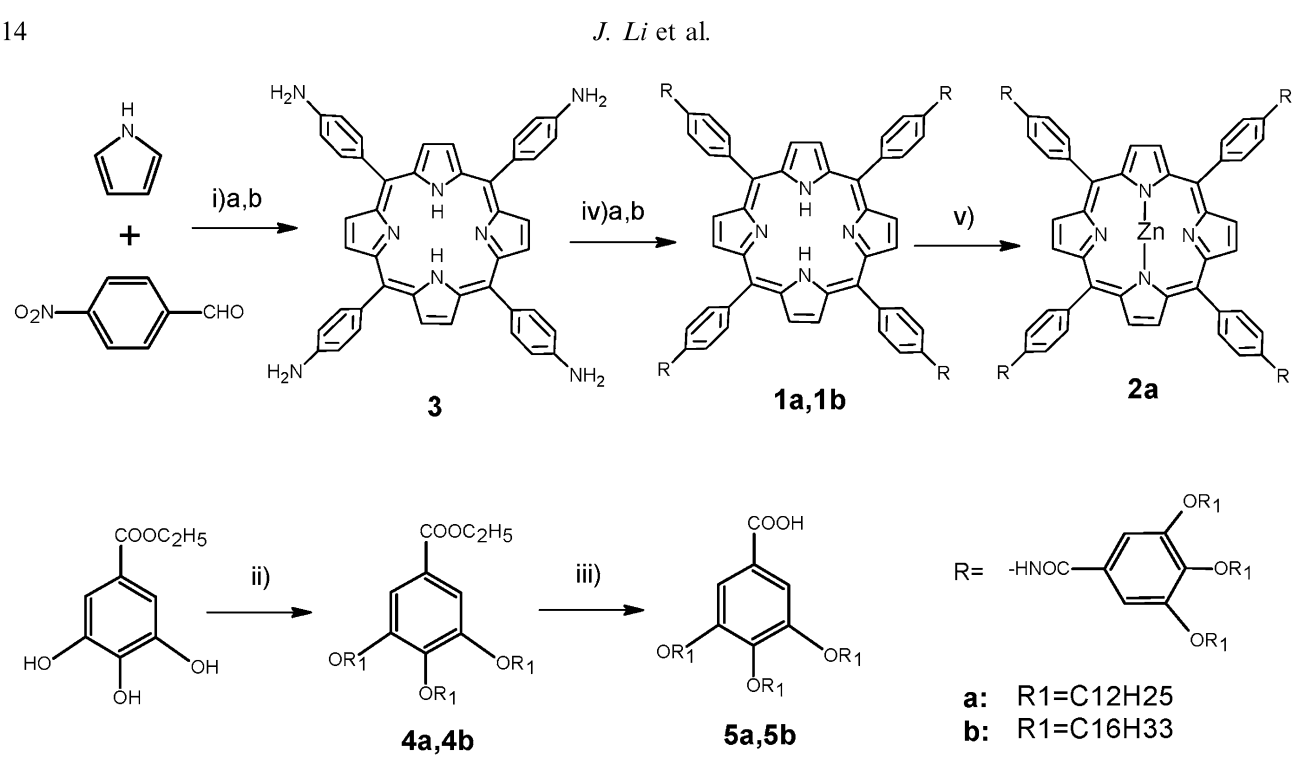

Scheme 1. Synthesis route for porphyrins **1a**, **1b** and **2a**. Reagents and conditions: i) a, lactic acid, *p*-nitrobenzene, 40 min; b, $SnCl_2•2H_2O$, HCl (37%), 65–70°C, 90 min. ii) $C_{12}H_{25}Br$, K_2CO_3, KI, acetone, reflux, 40 h. iii) KOH, ethanol, reflux, 30 h. iv) a $SOCl_2$, reflux, 15 h; b CH_2Cl_2, Et_3N, reflux, 24 h. v) $ZnAc_2•2\ H_2O$, CH_2Cl_2, CH_3OH, 24 h.

the catalyst triethylamine [15]. Porphyrin **1a** and zinc acetate were heated under reflux in a mixture of dichloromethane and methanol for 24 h to give porphyrin **2a** [16]. The proposed molecular structures of the compounds were confirmed with FTIR, ^1H NMR and elemental analysis.

2.2.1. *meso*-Tetra(*p*-nitrophenyl)porphyrin ($T_{NO2}PP$).

p-Nitrobenzaldehyde (10 g, 68.75 mmol) and pyrrole (4.43 ml, 68.75 mmol) were dissolved in *p*-nitrobenzene (60 ml). The solution was slowly added to a boiling solution containing *p*-nitrobenzene (90 ml) and lactic acid (5.5 ml). The resulting dark solution was heated under reflux for 40 min; it was cooled in an ice bath to 25°C followed by the addition of methanol (140 ml), and the purple crystalline product was isolated by filtration. The crude product was recrystallized from dimethylformamide (DMF), washed with chloroform ($CHCl_3$) and then dried under vacuum at 60°C for 48 h. The free porphyrin, $H_2T_{NO2}PP$, is insoluble in most organic solvents and hence no further purification was performed; yield 27.8%. IR (KBr, ν, cm^{-1}): 3319 ($\nu_{N\text{-}H}$), 1595 ($\nu_{C=C,\ Ar}$; $\nu_{C=N}$), 1520, 1348 ($\nu_{N=O}$).

2.2.2. *meso*-Tetra(*p*-aminophenyl)porphyrin ($T_{AM}PP$).

The nitroporphyrin ($T_{NO2}PP$, 2.5 g) was dissolved in concentrated hydrochloric acid (150 ml) at room temperature, followed by the addition of excess $SnCl_2•2H_2O$ (10.8 g). The resulting mixture was heated at 65–70°C for 90 min, and then cautiously neutralized with concentrated aqueous ammonia. The dark crystalline product was filtered off, dissolved in DMF, and the solution filtered. 150 ml H_2O was added, and the product filtered and washed with methanol. This product was recrystallized from $CHCl_3$/methanol (2/1) and dried under vacuum; yield 85%. ^1H NMR: δ_H (DMSO), 8.88 (s, 8H, β-pyrrole), 7.86 (d, 8H, *ortho*-phenyl), 7.01 (d, 8H, *meta*-phenyl), 5.58 (s, 2H, $-NH_2$), -2.79 (s, 2H, pyrrole, N–H). IR (KBr, ν cm^{-1}): 3435, 3361, 1618 (ν_{NH2}), 3217 ($\nu_{N\text{-}H,\ pyrrole}$), 1606 ($\nu_{C=C,\ Ar}$; $\nu_{C=N}$). UV-Vis ($CDCl_3$) λ/nm: 427, 522, 563, 596 and 654.

2.2.3. Ethyl 3,4,5-trialkoxybenzoates, 4a and 4b.

Compounds **4a** and **4b** were synthesized by a method similar to that described elsewhere [15], and were recrystallized from acetone. **4a**: yield 80%, m.p. 42.5°C. ^1H NMR ($CDCl_3$): δ=7.25 (s, 2H, Ar–H), 4.33–4.37 (m, 2H, $-COOC\underline{H}_2CH_3$), 4.00–4.02 (m, 6H, $-O-CH_2-$), 1.79–1.84 (m, 4H, *m* to COOH, $-O-C-C\underline{H}_2-$), 1.73–1.76 (m, 2H, *p* to COOH, $-O-C-C\underline{H}_2-$) 1.44–1.49 (m, 6H, $-C\underline{H}_2-CH_3$), 1.34–1.40 (t, 3H, $-COOCH_2C\underline{H}_3$) 1.26–1.35 (m, 48H, $-O-C-C-(C\underline{H}_2)_8-C-CH_3$), 0.87–0.89 (t, 9H, $-O-C-C-(CH_2)_8-C-C\underline{H}_3$). IR (KBr, ν, cm^{-1}): 2956 ($\nu_{\text{-}CH3}$), 2918, 2850 ($\nu_{\text{-}CH2\text{-}}$), 1717 ($\nu_{C=O}$), 1584 ($\nu_{C=C,Ar}$), 1217 ($\nu_{C\text{-}O}$). **4b**: yield 85%, m.p. 56°C. ^{1}HNMR (CDCl$_3$): δ=7.25 (s, 2H, Ar–H), 4.33–4.37 (m, 2H, –COOC$\underline{H}_2$CH$_3$), 4.00–4.02 (m, 6H, –O–CH$_2$–), 1.79–1.84 (m, 4H, *m* to COOH, –O–C–C$\underline{H}_2$–), 1.73–1.76 (m, 2H, *p* to COOH, –O–C–C$\underline{H}_2$–) 1.44–1.49 (m, 6H, –C$\underline{H}_2$–CH$_3$), 1.34–1.40 (t, 3H, –COOCH$_2$C$\underline{H}_3$) 1.26–1.35 (m, 72H, –O–C–C–(C$\underline{H}_2$)$_{12}$–C–CH$_3$), 0.87–0.89 (t, 9H, –O–C–C–(CH$_2$)$_{12}$–C–C$\underline{H}_3$). IR (KBr, ν cm^{-1}): 2956 (ν_{CH3}), 2918, 2850 (ν_{CH2}), 1717 ($\nu_{C=O}$), 1584 ($\nu_{C=C,Ar}$), 1217 ($\nu_{C\text{-}O}$).

2.2.4. 3,4,5-Trialkoxybenzoic acids, 5a and 5b. Compounds **5a** and **5b** were synthesized by a method similar to that described in previous papers [15*b*], and were recrystallized from ethanol. **5a**: yield 85%, m.p. 60°C. ^{1}H NMR (CDCl$_3$): δ=7.32 (s, 2H, Ar–H), 4.01–4.06 (m, 6H, –O–CH$_2$–), 1.79–1.84 (m, 4H, *m* to COOH, –O–C–CH$_2$–), 1.73–1.76 (m, 2H, *p* to COOH, –O–C–CH$_2$–), 1.45–1.51 (m, 6H, –C$\underline{H}_2$–CH$_3$), 1.26–1.35 (m, 48H, –O–C–C–(C$\underline{H}_2$)$_8$–C–CH$_3$), 0.87–0.89 (t, 9H, –O–C–C–(C)$_8$–C–C$\underline{H}_3$). IR (KBr, ν cm^{-1}): 3106–2641 (ν_{OH}), 2918, 2849 ($\nu_{\text{-CH2-}}$), 1683 ($\nu_{C=O}$), 1588 ($\nu_{C=C,\ Ar}$), 1223 ($\nu_{C\text{-}O}$). **5b**: yield 83%, m.p. 78°C. ^{1}HNMR (CDCl$_3$, δ, ppm): 7.32 (s, 2H, Ar–H), 4.01–4.06 (m, 6H, –O–CH$_2$–), 1.79–1.84 (m, 4H, *m* to COOH, –O–C–CH$_2$–), 1.73–1.76 (m, 2H, *p* to COOH, –O–C–CH$_2$–), 1.45–1.51 (m, 6H, –C$\underline{H}_2$–CH$_3$), 1.26–1.35 (m, 72H, –O–C–C–(C$\underline{H}_2$)$_{12}$–C–CH$_3$), 0.87–0.89 (t, 9H, –O–C–C–(C)$_{12}$–C–C$\underline{H}_3$). IR (KBr, ν cm^{-1}): 3106–2641 ($\nu_{\text{-OH}}$), 2918, 2849 ($\nu_{\text{-CH2-}}$), 1683 ($\nu_{C=O}$), 1588 ($\nu_{C=C,\ Ar}$), 1223 ($\nu_{C\text{-}O}$).

2.2.5. *meso*-Tetra[4-(3,4,5-tridodecyloxybenzoylamino)phenyl]porphyrin, 1a [15]. 1.32 g (2.1 mol) of 3,4,5-tridodecyloxybenzoic acid was dissolved in 20 ml thionyl chloride (SOCl$_2$) and heated under reflux for 15 h. The solvent was evaporated under reduced pressure, and dried dichloromecane (30 ml) was stirred in. A solution of 0.22 g (0.32 mmol) T$_{AM}$PP and 3 ml triethylamine in 20 ml of dried dichloromethane was then slowly added and the mixture heated under reflux for 24 h. The mixture was reduced to 20 ml on a rotary evaporator and 80 ml of acetone was added to precipitate the product. The crude product was isolated and further purified by column chromatography (silica gel, CHCl$_3$, then silica gel, CHCl$_3$ ethyl acetate=20/1); yield 73%. Anal: calcd for C$_{216}$H$_{338}$N$_8$O$_{16}$ C 78.54, H 10.31, N 3.39; found C 78.15, H 10.26, N 3.16%. ^{1}H NMR: δ_H (CDCl$_3$), 8.92 (s, 8H, β-pyrrole), 8.23–8.25 (d, 8H, ortho phenyl), 8.07 (s, 4H, –CON–H), 8.04–8.06 (d, 8H, *meta*-phenyl), 7.22 (s, 8H, s, Ar–H), 4.07–4.15 (m, 24H, –O–CH$_2$–), 1.80–1.90 (m, 24H, –O–C–CH$_2$–), 1.45–1.51 (m, 24H, –C$\underline{H}_2$–CH$_3$), 1.26–1.35 (m, 192H, –O–C–C–(CH$_2$)$_8$–C–CH$_3$), 0.86–0.90 (t, 36H, –O–C–C–(C)$_8$–C–CH$_3$), –2.75 (s, 2H, pyrrole N–H). IR (KBr, ν cm^{-1}): 3315 ($\nu_{N\text{-}H,\ pyrrole;}\ \nu_{N\text{-}H,\ NHCO}$), 2925, 2854 ($\nu_{\text{-CH2-}}$), 1649, 1670 ($\nu_{C=O}$), 1583 ($\nu_{C=C,\ Ar;}\ \nu_{C=N}$), 1235 ($\nu_{C\text{-}O}$). UV-Vis (CHCl$_3$) λ/nm: 423, 518, 555, 592 and 649.

2.2.6. *meso*-Tetra[4-(3,4,5-tricetyloxybenzoylamino)phenyl]porphyrin, 1b. The compound **1b** was synthesized by a method similar to that for **1a.** Anal: calcd for C$_{264}$H$_{434}$N$_8$O$_{16}$ C 79.74, H 11.00, N 2.82; found C 79.45, H 11.02, N 2.80%. The characterization of **1b** (^{1}H NMR, FTIR and UV-Vis spectra) was similar to that of **1a**.

2.2.7. *meso*-Tetra[4-(3,4,5-tridodecyloxybenzoylamino)phenyl]porphyrin Zn, 2a [16]. 0.30 g of porphyrin **1a** and excess ZnAc$_2$•2H$_2$O was dissolved in a mixture of dichloromethane and methanol (3/1) and heated under reflux for 24 h. The mixture was then reduced to about 10 ml, and 80 ml methanol was added to precipitate the product. The crude product was isolated and purified by column chromatography (silica gel, CHCl$_3$ ethyl acetate=20/1); yield 90%. Anal: calcd for C$_{216}$H$_{336}$N$_8$O$_{16}$Zn C, 77.06, H, 10.06, N, 3.33; found C 76.77, H 10.28, N 3.23%. ^{1}H NMR: δ_H (CDCl$_3$), 9.02 (s, 8H, β-pyrrole), 8.24–8.25 (d, 8H, *ortho*-phenyl), 8.06 (s, 4H,–CON–H), 8.04–8.05 (d, 8H, *meta* to phenyls), 7.22 (s, 8H, s, Ar–H), 4.07–4.15 (t, 24H, –O–CH$_2$–), 1.81–1.90 (m, 24H, –O–C–CH$_2$–), 1.45–1.51 (m, 24H, –C$\underline{H}_2$–CH$_3$), 1.26–1.39 (m, 192H, –O–C–C–(C$\underline{H}$2)$_8$–C–CH$_3$), 0.87–0.91 (t, 36H, –O–C–C–(C)$_8$–C–CH$_3$). IR (KBr, ν cm^{-1}): 3318 ($\nu_{N\text{-}H,\ \text{-NHCO}}$), 2925, 2854 ($\nu_{\text{-CH2-}}$), 1650, 1670 ($\nu_{C=O}$), 1585 ($\nu_{C=C,\ Ar;}\ \nu_{C=N}$), 1235 ($\nu_{C\text{-}O}$). UV-Vis (CHCl$_3$) λ/nm: 427, 555 and 597.

3. Results and discussion

The DSC curves of the porphyrin derivatives are given in figure 1. The transition temperatures and associated enthalpy changes of the porphyrins are summarized in table 1. All the porphyrin derivatives show weak birefringence at room temperature, but could be easily sheared, to give stronger birefringence. This behaviour suggested that their liquid crystalline phases may be easily aligned. Figure 2 shows the LC textures of the porphyrins. On cooling from the isotropic liquid, porphyrin **1a** exhibited a dendritic texture, **1b** showed a steatite texture, and zinc complex **2a** a spherical texture, typical for a columnar phase.

The wide angle XRD (WAXD) patterns of the porphyrins in the liquid crystalline phase are shown in figure 3. The WAXD pattern of **1a** at room temperature shows one diffraction peak with a *d*-spacing of 36.6 Å and two broad halos around 4.0 and 3.6 Å corresponding

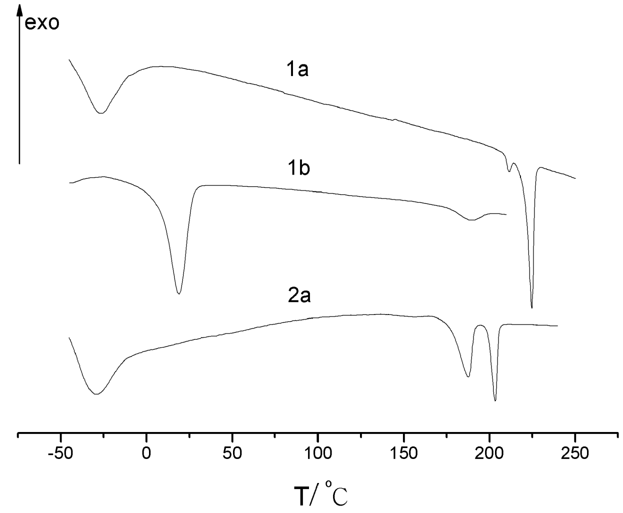

Figure 1. DSC curves of porphyrin **1a**, its zinc complex **2a** and porphyrin **1b** on the second heating run.

to the disordered alkoxy chains and the mean intermolecular distance, respectively, in the wide angle region. Although the presence of only one peak in the low angle region in the diffraction pattern does not allow an assignment of the specific type of columnar phase, we obtained reasonable estimates for the macroscopic density by assuming ordered hexagonal columns (see [17]). Assuming a hexagonal columnar phase, the lattice parameter ($a=2d/\sqrt{3}$) of 42.3 Å is obtained, which is equal to the diameter of the self-assembled column and the inter-columnar distance. Assuming that the packing density (ρ) of porphyrin **1a** is close to 1.0 gcm^{-3} and the average inter-disc distance h in the columnar phase is 3.6 Å, then Z, the number of molecules per unit cell, is about 1.02 according to equations (1) and (2):

$$\rho=(M/N_A)/(V/Z) \tag{1}$$

$$V=(\sqrt{3}/2)a^2h\times10^{-24} \tag{2}$$

where N_A is the Avogadro constant, M the molecular mass, and V the volume of the local unit cell.

It is clear that there is one molecule per unit cell, and then the calculated ρ is 0.98 g cm^{-3}. Considering the observed density (ρ=0.95 g cm^{-3}) of porphyrin **1a**, we may conclude that porphyrin **1a** shows a hexagonal columnar mesophase. As the peak was broad, we cannot entirely rule out a rectangular phase (almost a pseudo-hexagonal phase) where (2 0) and (1 1) reflections are close to each other. Considering the discrepancy between the molecular diameter of **1a** (55.5 Å calculated using the Material Studio 3.0) and the lattice parameter (a=42.3 Å) at the pseudo hexagonal phase, the mesophase of **1a** is assigned as a rectangular columnar phase with lattice parameters a=73.2 Å and b=42.3 Å. The ratio a/b in the rectangular columnar phase of **1a** is $\sqrt{3}$, suggesting that **1a** exhibits a pseudo-hexagonal columnar phase [18].

The XRD pattern of **1b** in the low angle region shows three diffraction peaks with d-spacing of 42.47, 33.21 and 29.45 Å, corresponding to the (1 1), (2 0) and (2 1) reflections, respectively, which are typical for a rectangular columnar structure with lattice parameters of a=66.4 Å and b=55.24 Å [4]. In addition, the broad halo around 4.0 Å can be attributed to the disordered alkoxy chains, and diffraction peak of 3.6 Å is the mean intermolecular distance. The XRD pattern of **2a** in its LC phase exhibits one diffraction peak with a d-spacing of 37.7 Å in the low angle region and two broad halos around 4.0 and 3.6 Å, corresponding to the disordered

Table 1. Thermal properties of **1a**, **1b** and **2a**. Cr=crystal, Col$_r$=rectangular columnar mesophase, I=isotropic.

Compound	T/°C (ΔH/kJ mol^{-1})
1a	$\mathrm{Cr} \underset{-26.5(46.0)}{\overset{-26.0(41.1)}{\rightleftharpoons}} \overset{213.9(1.2)\swarrow}{\mathrm{Col_r}} \underset{218.8(22.1)}{\overset{225.7(24.2)}{\rightleftharpoons}} \mathrm{I}$
1b	$\mathrm{Cr} \underset{15.0(162.9)}{\overset{19.3\ (165.0)}{\rightleftharpoons}} \mathrm{Col_r} \underset{173.8(10.3)}{\overset{189.3(14.2)}{\rightleftharpoons}} \mathrm{I}$
2a	$\mathrm{Cr} \underset{-30.0(56.9)}{\overset{-29.9(56.9)}{\rightleftharpoons}} \mathrm{Col_r} \underset{158.7(6.4)}{\overset{187.6(16.5)}{\rightleftharpoons}} \mathrm{Col} \underset{198.1(10.4)}{\overset{203.1(10.1)}{\rightleftharpoons}} \mathrm{I}$

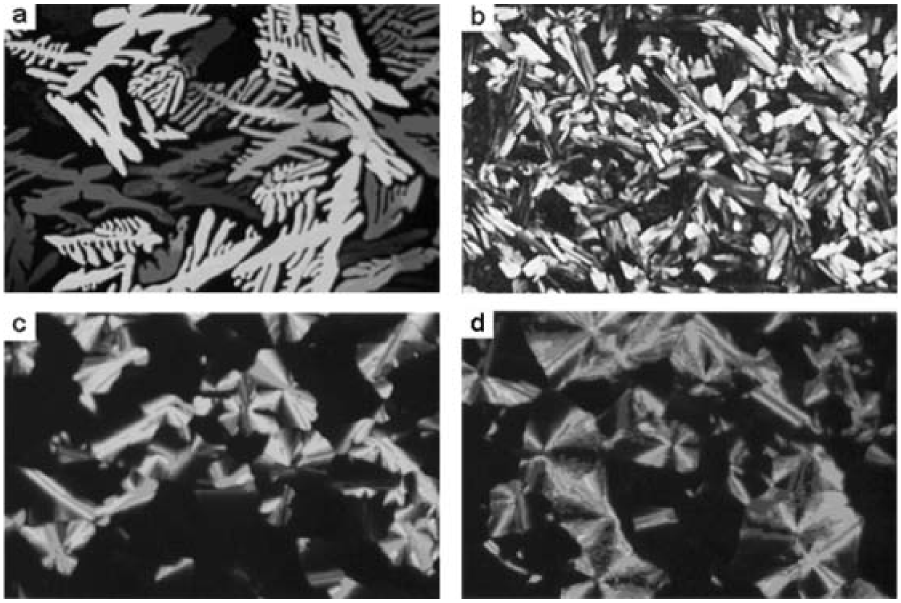

Figure 2. Polarizing optical microphotographs (× 200) of (*a*) porphyrin **1a** at 25°C, (*b*) porphyrin **1b** at 30°C, (*c*) porphyrin **2a** at 194°C and (*d*) porphyrin **2a** at 25°C on cooling.

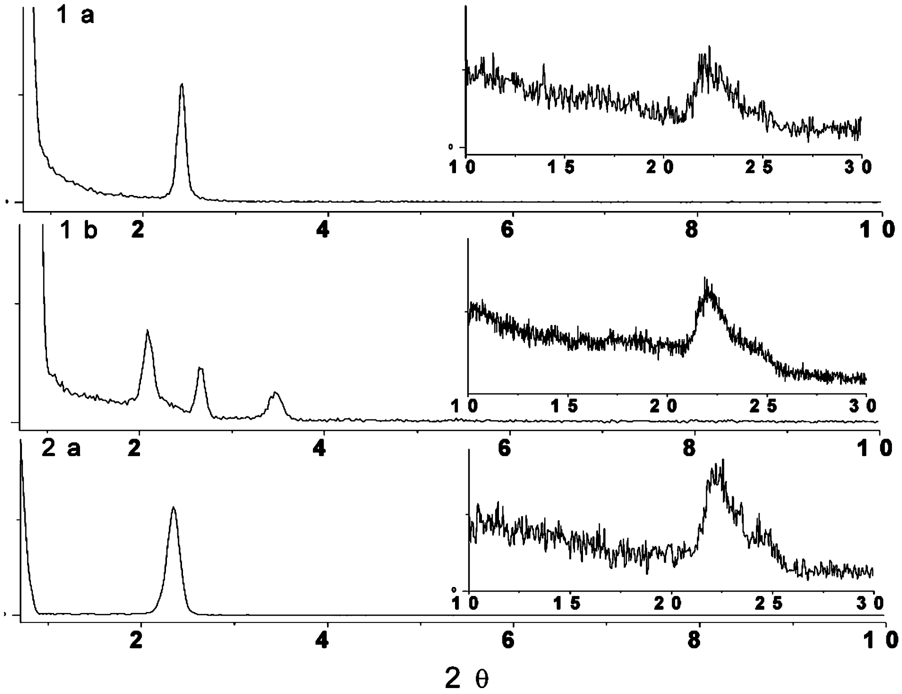

Figure 3. Wide angle X-ray diffraction patterns of **1a**, **1b** and **2a**.

Table 2. Wide angle X-ray diffraction data and the cell parameters for porphyrins **1a**, **1b** and **2a**, sheared in the isotropic state, annealed at 80°C for 12 h, then measured at 25°C.

Compound	Observed *d*-spacing/Å	(*h k l*)	Mesophase parameter/Å	Calculated diameter/Å	Molecular density/ g cm^{-3}
1a	36.61 3.5–4.4	(2 0), (1 1) alkoxy chains	($P2_1/a$) Col$_r$ a=73.2, b=42.3	55.5	0.98
1b	42.47 33.21 29.45 3.5–4.4	(1 1) (2 0) (2 1) alkoxy chains	($P2_1/a$) Col$_r$ a=66.4, b=55.2	66.6	—
1c	37.70 3.5–4.4	(2 0), (1 1) alkoxy chains	($P2_1/a$) Col$_r$ a=75.4, b=43.5	56.7	0.95

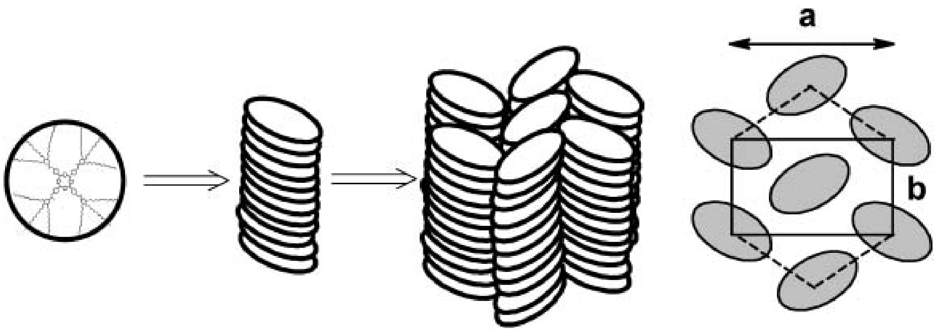

Figure 4. Schematic representation of the molecular packing of the porphyrins in their LC phases.

alkoxy chains and the mean intermolecular distance, respectively, in the wide angle; the phase was assigned as a rectangular columnar phase with lattice parameters of a=75.4 Å and b=43.5 Å. The *d*-spacings and lattice parameter of the porphyrins are listed in table 2.

Based on the results of XRD, a schematic molecular arrangement of the porphyrins in their LC phases is given in figure 4, in which a molecule of the porphyrin derivative is depicted as a disc. The discs are tilted and the aliphatic chains interdigitate among adjacent columns resulting in a rectangular columnar phase.

In summary, novel porphyrins **1a** and **1b**, and a zinc complex **2a** were synthesized and characterized. They all exhibit columnar mesophases over a wide temperature range including room temperature.

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References

[1] S. Chandrasekhar, B.K. Sadashiva, K.A. Suresh. *Pramana*, **9**, 471 (1977).

[2] K. Ohta, N. Yamaguchi, I. Yamamoto. *J. mater. Chem.*, **8**, 2637 (1998).

[3] S. Kumar, S.K. Varshney. *Org. Lett.*, **4**, 157 (2002).

[4] F. Maeda, K. Hatsusaka, K. Ohta, M. Kimura. *J. mater. Chem.*, **13**, 243 (2003).

[5] R.E. Hughes, S.P. Hart, D.A. Smith, B. Movaghar, R.J. Bushby, N. Boden. *J. phys. Chem.ô B*, **106**, 6638 (2002).

[6] K.Q. Jian, H.S. Shim, D. Tuhus-Dubrow, S. Bernstein, C. Woodward, D. Steingart, T. Gournay. *Carbon*, **41**, 2073 (2003).

[7] L.R. Milgrom, G. Yahioglu, D.W. Bruce, S. Morrone, F.Z. Henari, W.J. Blau. *Adv. Mater.*, **9**, 313 (1997).

[8] N. Boden, R.J. Bushby, A.N. Cammidge, G. Headdock. *J. mater. Chem.*, **5**, 2275 (1995).

[9] C.Y. Liu, H.L. Pan, M.A. Fox, A.J. Bard. *Chem. Mater.*, **9**, 1422 (1997).

[10] J.W. Goodby, P.S. Robinson, B.K. Teo, P.E. Cladis. *Mol. Cryst. liq. Cryst.*, **56**, 303 (1980).

[11] (*a*) M. Castella, F. López-Calahorra, D. Velasco. *Liq. Cryst.*, **29**, 559; (*b*) A. Nagata, Y. Shimizu, H. Nagamoto and M. Miyi. *Inorg. Chim. Acta*, **238**, 169 (1995); (*c*) H.D. Burroes, A.M. Rocha Gonsalves, M.L.P. Leitão, M. Miguel, G. Da and M.M. Pereira. *Supramol. Sci.*, **4**, 241 (1997); (*d*) D.W. Bruce, D.A. Dunmur, L.S. Santa and M.A. Wali. *J. Mater. Chem.*, **2**, 363 (1992); (*e*) Q.M.

Wang and D.W. Bruce. *Tetrahedron Lett.*, **37**, 7641 (1996).

[12] M. Castella, F. Lopez-Calahorra, D. Velasco, H. Finkelmann. *Chem. Commun.*, **20**, 2348 (2002).

[13] (*a*) K. Ohta, S. Azumane, W. Kawahara, N. Kobayashi, I. Yamamoto. *J. mater. Chem.*, **9**, 2313 (1999); (*b*) K. Hatsusaka, K. Ohta, I. Yamamoto and H. Shirai. *J. mater. Chem.*, **11**, 423 (2001); (*c*) T. Nakai, K. Ban, K. Ohta and M. Kimura. *J. mater. Chem.*, **12**, 844 (2002).

[14] (*a*) P.C. James, R.G. Robert, R. Christopher, R.H. Thomas, L. George, T. Ward. *J. Am. chem. Soc.*, **97**, 1427 (1975); (*b*) B.K. Zhu, Z.K. Xu and Y.Y. Xu. *Chin. J. appl. Chem.*, 68 (1999).

[15] W. Liu, Y.H. Shi, T.S. Shi, G.F. Liu, Y.X. Liu, C. Wang. *Liq. Cryst.*, **30**, 1255 (2003).

[16] (*a*) T. Ohtake, M. Ogasawara, K. Ito-Akita, N. Nishina, S. Ujiie, H. Ohno, T. Kato. *Chem. Mater*, **12**, 782 (2000); (*b*) V. Percec, G. Johansson, G. Ungar and J. Zhou. *J. Am. chem. Soc.*, **118**, 9855 (1996).

[17] A. Kraft, A. Reichert, R. Kleppinger. *Chem. Commun.*, **12**, 1015 (2000).

[18] J. Barberá, R. Iglesias, J.L. Serrano, T. Sierra, B. Palacios. *J. Am. chem. Soc.*, **120**, 2098 (1998).