Available online at www.sciencedirect.com
ScienceDirect
Dyes and Pigments 77 (2008) 395–401
DYES and PIGMENTS
www.elsevier.com/locate/dyepig

The synthesis and characterization of novel liquid crystalline, *meso*-tetra[4-(3,4,5-trialkoxybenzoate)phenyl]porphyrins

Jianzhong Li [a,b], Tao Tang [b], Fan Li [a], Min Li [a,*]

[a] *Key Laboratory for Automobile Materials, MOE and Department of Materials Science and Engineering, Jilin University, Changchun 130012, China*
[b] *State Key Laboratory of Polymer Physics and Chemistry, Changchun Institute of Applied Chemistry, Chinese Academy of Sciences, Changchun 130022, China*

Received 28 January 2007; received in revised form 5 July 2007; accepted 5 July 2007
Available online 27 July 2007

Abstract

Five, novel, *meso*-tetra[4-(3,4,5-trialkoxybenzoate)phenyl]porphyrins and their metal complexes were synthesized and their molecular structures were confirmed by ^{1}H NMR, FTIR spectroscopy and elemental analysis. Mesomorphic studies using DSC, polarizing optical microscope and X-ray diffraction revealed that all compounds exhibited thermotropic columnar mesophases over a wide mesophase temperature range and low liquid crystalline–crystalline transition temperature.

Keywords: Discotic; Liquid crystals; Porphyrin; Columnar mesophase; Self-assembly; Organometallic complexes

1. Introduction

Considerable scientific and technological efforts have been devoted to discotic liquid crystals since the first discovery of discotic mesogens [1]. And there has been an increasing interest in designing and synthesizing discotic liquid crystals due to their potential applications in several fields such as charge transport, photoelectronic conversion, nonlinear optics, organic light emitting diodes and optical information storage during the past decades [2–6].

The mesomorphic behavior of porphyrin derivatives usually arises from their flat structure of the porphyrin core consisting of four pyrrole units linked by four methane bridges [7]. Since the first report of the liquid crystalline porphyrin which showed mesomorphism within 0.5 °C by Goodby et al. [8], liquid crystalline porphyrin derivatives have received considerable attention due to their remarkable electro-optical properties as semiconductors and one-dimensional conductor [9]. Liquid crystalline porphyrins reported to date can be classified into two types in virtue of their molecular shapes (Fig. 1). On one hand, β-substituted porphyrin derivatives (type 1) usually show columnar mesophases with wide mesophase range but rather difficult to synthesize [10,11]. On the other hand, porphyrins di- and tetra-substituted at the *meso* positions (type 2) usually exhibit nematic/smectic phases or lamellar discotic phases, respectively, in a narrow range (30–40 °C) [11]. Recently, Ohta et al. [12] and other groups [13] reported a large number of *meso*-substituted porphyrin derivatives, most of which exhibited wider mesophase range. Herein, we report the synthesis and liquid crystalline behavior of *meso*-substituted porphyrins. They all show columnar phase in a wide mesophase range including room temperature. For example, porphyrin **4b** (Fig. 2) exhibits columnar phase with a temperature range as wide as 180 °C and crystallization temperature down to −33 °C.

2. Experimental

2.1. Material and characterization

Pyrrole was newly distilled before use. Dichloromethane and acetone were dried with magnesium sulfate

* Corresponding author. Tel.: +86 431 85168254; fax: +86 431 85168444.
E-mail address: minli@mail.jlu.edu.cn (M. Li).

0143-7208/$ - see front matter © 2007 Elsevier Ltd. All rights reserved.
doi:10.1016/j.dyepig.2007.07.008

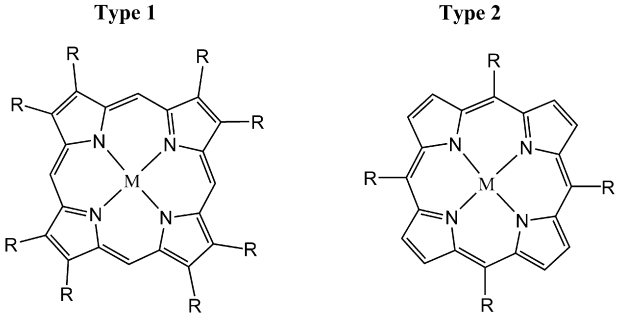


Fig. 1. Two types of mesogenic porphyrin derivatives reported to date.

and then distilled. Other reagents were all of analytic standard.

The proposed molecular structures of the compounds were confirmed by IR and ^{1}H NMR spectroscopy. ^{1}H NMR spectra were measured on a Bruker Avance 300 MHz spectrometer using tetramethylsilane (TMS) ($\delta = 0.00$) as an internal chemical shift standard. IR measurements were carried out on a Perkin–Elmer spectrometer (Spectrum One B). Further identification of the porphyrin derivatives was carried out by UV–vis spectroscopy on a Shimadzu UV-3100 UV–vis spectrometer. Thermal properties were determined by differential scanning calorimetry (DSC) on a Netzsch DSC 204 system (scanning rate 10 °C min^{-1}). Optical texture observations were conducted on a Leica DMLP polarizing optical microscope (POM) equipped with a Leitz 350 microscope heating stage. X-ray diffraction (XRD) measurements were measured using a Rigaku X-ray diffractometer with Cu Kα radiation.

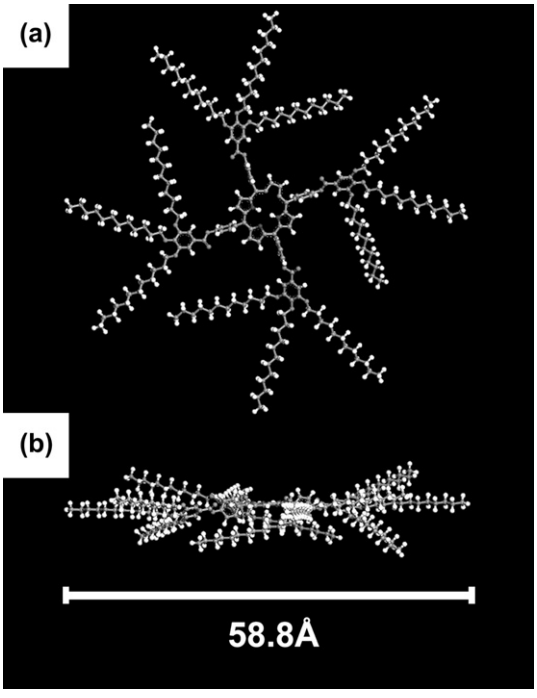


Fig. 2. Molecular structure of porphyrin **4b**: (a) view from above of the porphyrin ring; (b) edge-on-view with the porphyrin ring.

2.2. Synthesis

The porphyrin derivatives in this work were synthesized through the synthetic route as shown in Scheme 1. Tetra (4-hydroxyphenyl)porphyrin **1** was synthesized through the reaction between 4-hydroxybenzaldehyde and pyrrole in the presence of propionic acid [13]. Porphyrin derivatives (**4a**, **4b** and **4c**) were prepared through the esterification of **1** with 3,4,5-trialkoxybenzoyl chloride using triethylamine as catalyst. The metal porphyrin complexes (**4b–Zn/Ni**) were obtained from free porphyrin **4b** and zinc/nickel acetate.

2.2.1. Ethyl 3,4,5-trialkoxybenzoate (*2a*, *2b*, *2c*)

Compounds **2a**, **2b** and **2c** were synthesized through a similar method described in previous papers [14]. Compound **2a** was recrystallized from methanol, and others were recrystallized from acetone.

Compound **2a**: yield: 77%, mp <25 °C. ^{1}H NMR ($CDCl_3$, δ, ppm): 7.25 (s, 2H, Ar–H), 4.33–4.37 (m, 2H, $-COOCH_2CH_3$), 4.00–4.02 (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 $-O-C-CH_2-$), 1.44–1.49 (m, 6H, $-CH_2-CH_3$), 1.34–1.40 (t, 3H, $-COOCH_2CH_3$), 1.26–1.35 (m, 18H, $-O-C-C-(CH_2)_3-C-CH_3$), 0.87–0.89 (t, 9H, $-O-C-C-(CH_2)_3-C-CH_3$). IR (KBr, ν, cm^{-1}): 2956 (ν_{CH_3}), 2918, 2850 (ν_{-CH_2-}), 1717 ($\nu_{C=O}$), 1584 ($\nu_{C=C,\ Ar}$), 1217 (ν_{C-O}).

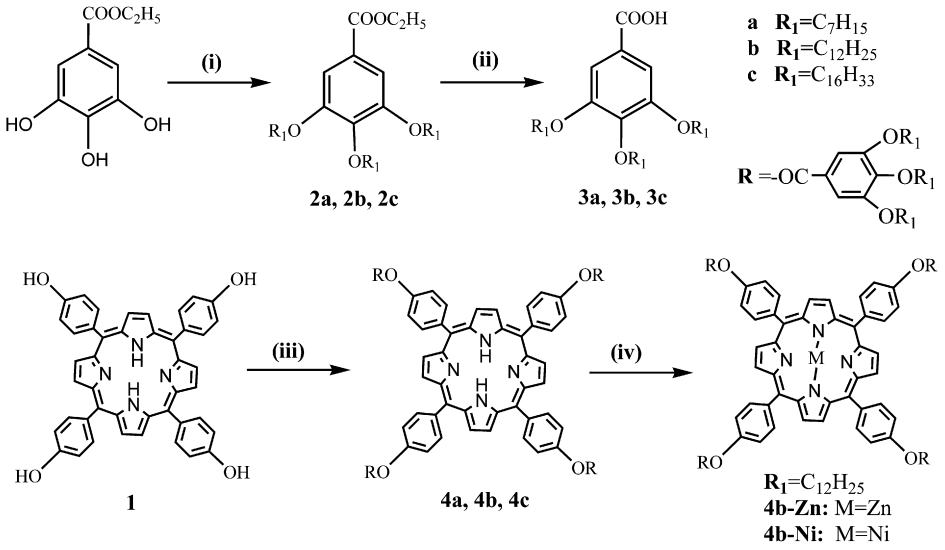
Compound **2b**: yield: 80%, mp 42.5 °C. ^{1}H NMR ($CDCl_3$, δ, ppm): 7.25 (s, 2H, Ar–H), 4.33–4.37 (m, 2H, $-COOCH_2CH_3$), 4.00–4.02 (m, 6H, $-O-CH_2-$), 1.79–1.84 (m, 4H, m-to-COOH $-O-C-CH_2-$), 1.73–1.76 (m, 2H, p-to-COOH $-O-C-CH_2-$) 1.44–1.49 (m, 6H, $-CH_2-CH_3$), 1.34–1.40 (t, 3H, $-COOCH_2CH_3$), 1.26–1.35 (m, 48H, $-O-C-C-(CH_2)_8-C-CH_3$), 0.87–0.89 (t, 9H, $-O-C-C-(CH_2)_8-C-CH_3$). IR (KBr, ν, cm^{-1}): 2956 (ν_{CH_3}), 2918, 2850 (ν_{CH_2}), 1717 ($\nu_{C=O}$), 1584 ($\nu_{C=C,\ Ar}$), 1217 (ν_{C-O}).

Compound **2c**: yield: 85%, mp 56 °C. ^{1}H NMR ($CDCl_3$, δ, ppm): 7.25 (s, 2H, Ar–H), 4.33–4.37 (m, 2H, $-COOCH_2CH_3$), 4.00–4.02 (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 $-O-C-CH_2-$), 1.44–1.49 (m, 6H, $-CH_2-CH_3$), 1.34–1.40 (t, 3H, $-COOCH_2CH_3$), 1.26–1.35 (m, 72H, $-O-C-C-(CH_2)_{12}-C-CH_3$), 0.87–0.89 (t, 9H, $-O-C-C-(CH_2)_{12}-C-CH_3$). IR (KBr, ν, cm^{-1}): 2956 (ν_{CH_3}), 2918, 2850 (ν_{CH_2}), 1717 ($\nu_{C=O}$), 1584 ($\nu_{C=C,\ Ar}$), 1217 (ν_{C-O}).

2.2.2. 3,4,5-Trialkoxybenzoic acid (*3a*, *3b*, *3c*)

Compounds **3a**, **3b** and **3c** were prepared according to literature [14]. Compound **3a** was recrystallized from methanol and others were recrystallized from ethanol.

Compound **3a**: yield: 80%, mp 43 °C. ^{1}H NMR ($CDCl_3$, 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, $-CH_2-CH_3$), 1.26–1.35 (m, 18H, $-O-C-C-(CH_2)_3-C-CH_3$),



Scheme 1. Synthesis route for porphyrin derivatives. *Reagents and conditions*: (i) $C_nH_{2n+1}Br$, K_2CO_3, KI, acetone, reflux, 40 h; (ii) KOH, ethanol, reflux, 30 h; (iii) $SOCl_2$, reflux, 15 h; CH_2Cl_2, DMF, triethylamine, reflux, 24 h; (iv) $M(Ac)_2 \cdot nH_2O$, chloroform/methanol = 3:1, reflux, 30 h.

0.87–0.89 (t, 9H, –O–C–C–(C)$_3$–C–C*H*$_3$). IR (KBr, ν, cm^{-1}): 3106–2641(ν_{OH}), 2918, 2849 (ν_{CH_2}), 1683 ($\nu_{C=O}$), 1588 ($\nu_{C=C,\ Ar}$), 1223 (ν_{C-O}).

Compound **3b**: yield: 85%, mp 60 °C. ^{1}H NMR ($CDCl_3$, δ, ppm): 7.32 (s, 2H, Ar–H), 4.01–4.06 (m, 6H, –O–C*H*$_2$–), 1.79–1.84 (m, 4H, m-to-COOH –O–C–C*H*$_2$–), 1.73–1.76 (m, 2H, p-to-COOH –O–C–C*H*$_2$–), 1.45–1.51 (m, 6H, –C*H*$_2$–CH$_3$), 1.26–1.35 (m, 48H, –O–C–C–(C*H*$_2$)$_8$–C–CH$_3$), 0.87–0.89 (t, 9H, –O–C–C–(C)$_8$–C–C*H*$_3$). IR (KBr, ν, cm^{-1}): 3106–2641(ν_{OH}), 2918, 2849 (ν_{-CH_2-}), 1683 ($\nu_{C=O}$), 1588 ($\nu_{C=C,\ Ar}$), 1223 (ν_{C-O}).

Compound **3c**: yield: 85%, mp 78 °C. ^{1}H NMR ($CDCl_3$, δ, ppm): 7.32 (s, 2H, Ar–H), 4.01–4.06 (m, 6H, –O–C*H*$_2$–), 1.79–1.84 (m, 4H, m-to-COOH –O–C–C*H*$_2$–), 1.73–1.76 (m, 2H, p-to-COOH –O–C–C*H*$_2$–), 1.45–1.51 (m, 6H, –C*H*$_2$–CH$_3$), 1.26–1.35 (m, 72H, –O–C–C–(C*H*$_2$)$_{12}$–C–CH$_3$), 0.87–0.89 (t, 9H, –O–C–C–(C)$_{12}$–C–C*H*$_3$). IR (KBr, ν, cm^{-1}): 3106–2641(ν_{-OH}), 2918, 2849 (ν_{-CH_2-}), 1683 ($\nu_{C=O}$), 1588 ($\nu_{C=C,\ Ar}$), 1223 (ν_{C-O}).

2.2.3. *meso*-Tetra[4-(3,4,5-tridodecyloxybenzoate)phenyl] porphyrin (*4b*)

Compound **3b** (1.32 g, 2.1 mmol) was dissolved in thionyl chloride ($SOCl_2$, 20 mL) and the mixture was refluxed for 15 h. The solvent was evaporated completely under reduced pressure. Then dried dichloromethane (60 mL), triethylamine (3.0 mL) and a solution of porphyrin **1** (1.22 g, 0.32 mmol) in dried DMF (30 mL) were added into the system, respectively. The mixture was stirred and refluxed for 24 h, and then condensed to about 20 mL on a rotary evaporator. Acetone (80 mL) was used to precipitate the product. The product was isolated and further purified by column chromatography (silica gel, $CHCl_3$; and then silica gel, $CHCl_3$: ethyl acetate = 20:1). Yield: 73%. Anal. Calcd for $C_{216}H_{334}N_4O_{20}$: C, 78.45; H, 10.18; N, 1.69. Found: C, 78.15; H, 10.04; N, 1.55. ^{1}H NMR ($CDCl_3$, δ, ppm): 8.95 (s, 8H, β-pyrrole), 8.27–8.30 (d, 8H, ortho phenyl), 7.62–7.68 (d, 8H, meta phenyl), 7.57 (s, 8H, Ar–H), 4.11–4.20 (m, 24H, –O–C*H*$_2$–), 1.79–1.96 (m, 24H, –O–C–C*H*$_2$–), 1.42–1.55 (m, 24H, –C*H*$_2$–CH$_3$), 1.35–1.42 (m, 192H, –O–C–C–(CH$_2$)$_8$–C–CH$_3$), 0.90–0.98 (t, 36H, –O–C–C–(C)$_8$–C–CH$_3$), –2.75 (s, 2H, pyrrole N–H). IR (KBr, ν, cm^{-1}): 3315 ($\nu_{N-H,\ pyrrole}$), 2925, 2854 (ν_{CH_2}), 1734 ($\nu_{c=O}$), 1586 ($\nu_{C=C,\ Ar;}$ $\nu_{C=N}$). UV–vis ($CHCl_3$) λ/nm: 419, 515, 551, 590 and 647.

2.2.4. *meso*-Tetra[4-(3,4,5-triheptyloxybenzoate)phenyl] porphyrin (*4a*)

Compound **4a** was synthesized and purified in a similar method to that described for compound **4b**. Yield: 78%. Anal. Calcd for $C_{156}H_{214}N_4O_{20}$: C, 76.00; H, 8.75; N, 2.27. Found: C, 75.59; H, 9.01; N, 2.46. ^{1}H NMR ($CDCl_3$, δ, ppm): 8.95 (s, 8H, β-pyrrole), 8.27–8.30 (d, 8H, ortho phenyl), 7.61–7.68 (d, 8H, meta phenyl), 7.57 (s, 8H, Ar–H), 4.10–4.21 (m, 24H, –O–C*H*$_2$–), 1.80–1.95 (m, 24H, –O–C–C*H*$_2$–), 1.45–1.51 (m, 24H, –C*H*$_2$–CH$_3$), 1.33–1.42 (m, 72H, –O–C–C–(CH$_2$)$_3$–C–CH$_3$), 0.86–0.95 (t, 36H, –O–C–C–(C)$_3$–C–CH$_3$), –2.75 (s, 2H, pyrrole N–H). IR (KBr, ν, cm^{-1}): 3318 ($\nu_{N-H,\ pyrrole}$), 2925, 2854 (ν_{CH_2}), 1735 ($\nu_{C=O}$), 1586 ($\nu_{C=C,\ Ar;}$ $\nu_{C=N}$). UV–vis ($CHCl_3$) λ/nm: 419, 515, 551, 591 and 647.

2.2.5. *meso*-Tetra[4-(3,4,5-tricetyloxybenzoate)phenyl] porphyrin (*4c*)

Compound **4c** was prepared in a similar method as described for compound **4b**. Yield: 83%. Anal. Calcd for $C_{264}H_{430}N_4O_{20}$: C, 79.66; H, 10.89; N, 1.41. Found: C, 79.28; H, 11.21; N, 1.41. ^{1}H NMR ($CDCl_3$, δ, ppm): 8.96 (s, 8H, β-pyrrole), 8.26–8.30 (d, 8H, ortho phenyl), 7.61–7.68 (d, 8H, meta phenyl), 7.56 (s, 8H, Ar–H), 4.10–4.23 (m, 24H, –O–C*H*$_2$–), 1.80–1.94 (m, 24H, –O–C–C*H*$_2$–),

1.48–1.53 (m, 24H, $-CH_2-CH_3$), 1.33–1.44 (m, 288H, $-O-C-C-(CH_2)_{12}-C-CH_3$), 0.86–0.94 (t, 36H, $-O-C-C-(C)_{12}-C-CH_3$), −2.75 (s, 2H, pyrrole N–H). IR (KBr, ν, cm^{-1}): 3321 ($\nu_{N-H,\ pyrrole}$), 2925, 2854 (ν_{CH_2}), 1736 ($\nu_{C=O}$), 1586 ($\nu_{C=C,\ Ar;}\ \nu_{C=N}$). UV–vis ($CHCl_3$) λ/nm: 419, 515, 551, 590 and 647.

2.2.6. Zinc meso-tetra[4-(3,4,5-tridodecyloxybenzoate) phenyl]porphyrin (*4b–Zn*)

Porphyrin **4b** (0.15 g) and excess $ZnAc_2 \cdot 2H_2O$ were dissolved in a mixture of dichloromethane and methanol (3:1). The reaction mixture was refluxed for 24 h, and then condensed to about 10 mL. Methanol (80 mL) was added to precipitate the product. The product was isolated and purified by column chromatography (silica gel, $CHCl_3$: ethyl acetate = 20:1). Yield: 90%. Anal. Calcd for $C_{216}H_{332}N_4O_{20}Zn$: C, 76.97; H, 9.93; N, 1.66. Found: C, 76.65; H, 10.14; N, 1.64. ^1H NMR ($CDCl_3$, δ, ppm): 8.95 (s, 8H, β-pyrrole), 8.27–8.30 (d, 8H, ortho phenyl), 7.62–7.68 (d, 8H, meta phenyl), 7.57 (s, 8H, Ar–H), 4.11–4.20 (m, 24H, $-O-CH_2-$), 1.79–1.96 (m, 24H, $-O-C-CH_2-$), 1.42–1.55 (m, 24H, $-CH_2-CH_3$), 1.35–1.42 (m, 192H, $-O-C-C-(CH_2)_8-C-CH_3$), 0.90–0.98 (t, 36H, $-O-C-C-(C)_8-C-CH_3$). IR (KBr, ν, cm^{-1}): 2925, 2854 (ν_{CH_2}), 1733 ($\nu_{C=O}$), 1587 ($\nu_{C=C,\ Ar;}\ \nu_{C=N}$). UV–vis ($CHCl_3$) λ/nm: 426, 555 and 596.

2.2.7. Nickel meso-tetra[4-(3,4,5-tridodecyloxybenzoate) phenyl]porphyrin (*4b–Ni*)

Porphyrin **4b** (0.15 g) and excess $NiAc_2 \cdot 4H_2O$ were dissolved in a mixture of dichloromethane and methanol (3:1). The reaction mixture was refluxed for 72 h. The purification of **4b–Ni** was done in a similar method as described for compound **4b–Zn**. Yield: 80%. Anal. Calcd for $C_{216}H_{332}N_4O_{20}Ni$: C, 77.13; H, 9.95; N, 1.67. Found: C, 76.89; H, 10.18; N, 1.64. ^1H NMR ($CDCl_3$, δ, ppm): 8.76 (s, 8H, β-pyrrole), 8.27–8.30 (d, 8H, ortho phenyl), 7.61–7.68 (d, 8H, meta phenyl), 7.57 (s, 8H, Ar–H), 4.13–4.20 (m, 24H, $-O-CH_2-$), 1.79–1.96 (m, 24H, $-O-C-CH_2-$), 1.42–1.55 (m, 24H, $-CH_2-CH_3$), 1.35–1.42 (m, 192H, $-O-C-C-(CH_2)_8-C-CH_3$), 0.90–0.98 (t, 36H, $-O-C-C-(C)_8-C-CH_3$), −2.75 (s, 2H, pyrrole N–H). IR (KBr, ν, cm^{-1}): 2925, 2854 (ν_{CH_2}), 1734 ($\nu_{C=O}$), 1586 ($\nu_{C=C,\ Ar;}\ \nu_{C=N}$). UV–vis ($CHCl_3$) λ/nm: 420 and 526.

3. Result and discussion

The mesomorphic behavior of the porphyrin derivatives was investigated by DSC, X-ray diffraction and polarizing optical microscopy.

Fig. 3 shows the first cooling and the second heating DSC thermograms of the porphyrin derivatives. The phase transition temperatures and enthalpy changes of all compounds are summarized in Table 1. It is noteworthy that the phase behavior of **4a–c** is greatly dependent on the length of the alkyl chains. Compound **4a** shows only one endothermic peak at 169.1 °C corresponding to liquid crystalline (LC)–isotropic transition on heating cycle. On cooling from its isotropic phase, the isotropic–LC transition is observed at 119.6 °C. Neither exothermic crystallization nor glass transition behavior is seen on cooling below −80 °C. Compound **4b** exhibits a crystalline phase with a wide temperature range from −33.0 to 146.5 °C upon the second heating run. The DSC curves of compound **4c** during the second heating cycle shows three endothermic peaks at 17.5, 97.7 and 109.5 °C corresponding to crystalline–LC, LC–LC and LC–isotropic transition, respectively. Upon cooling, three exothermic peaks at 102.8, 80.6 and 12.4 °C are observed. Compared with porphyrin **4b**, its metal complexes (**4b–Zn** and **4b–Ni**) show liquid crystalline phase with a narrower temperature range. Considerable supercooling effect was observed for the porphyrin complexes.

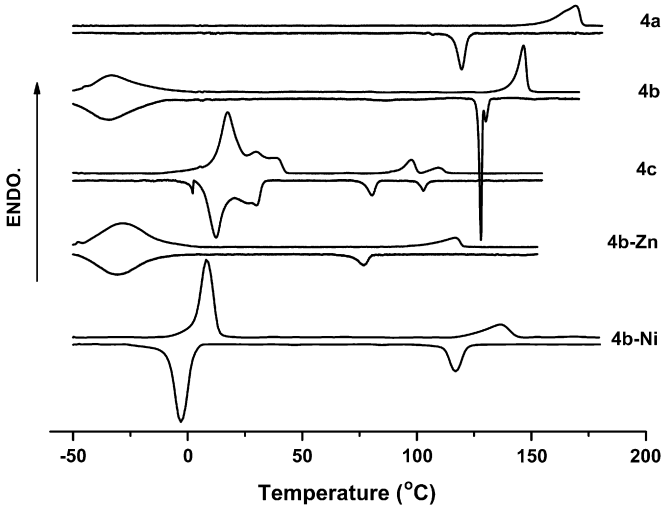


Fig. 3. DSC curves of the porphyrin derivatives on the first cooling and the second heating runs.

POM observations showed that all the compounds were birefringent at room temperature. They can be sheared easily leaving a pasty birefringent trace expected for a highly viscous phase. Upon heating, they become less viscous, suggesting that

Table 1
Thermal properties of the porphyrin derivatives

Compound	T/°C (H, kJ mol^{-1}) Phase 1 ⇌ Phase 2
4a	Col_r 169.1(15.8) / 119.6(15.2) I
4b	Cr -33.0(45.5) / -33.6(44.8) Col_r 146.5(31.2) / 102.8(33.0) I
4c	Cr 17.5(156.7) / 12.4(156.4) Col_r 97.7(12.3) / 80.6(12.1) Col_x 109.5(4.6) / 102.8(4.8) I
4b–Zn	Cr -28.5(45.1) / -30.1(45.9) Col_r 116.5(5.2) / 77.4(4.8) I
4b–Ni	Cr 8.6(62.2) / -2.7(61.5) Col_r 136.7(16.3) / 117.0(15.9) I

Cr: crystal, Col_r: rectangular columnar mesophase, I: isotropic liquid.

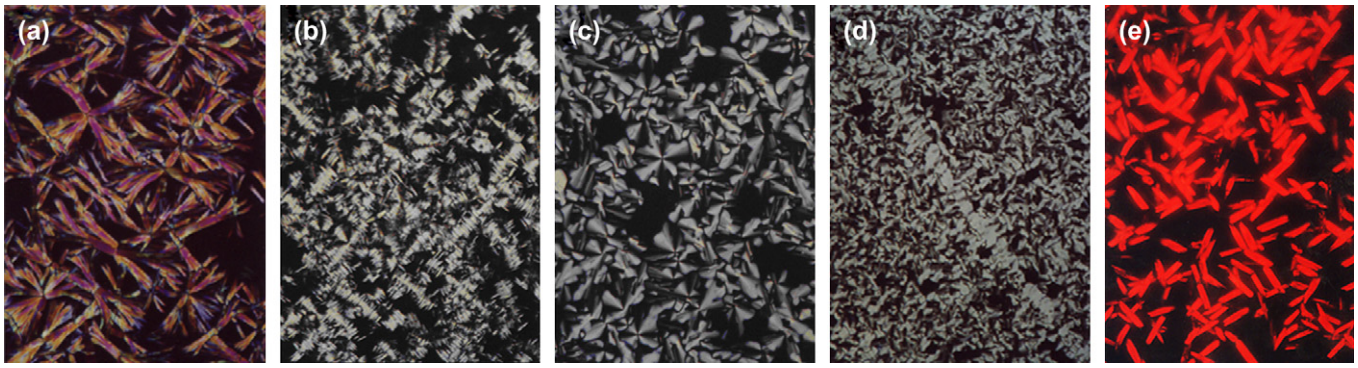


Fig. 4. Polarizing optical textures (×200) of (a) **4a** at 130 °C, (b) **4b** at 127 °C, (c) **4c** at 104 °C, (d) **4c** at 78 °C and (e) **4b–Ni** at 103 °C.

the liquid crystalline domains are aligned easily in their liquid crystalline phases. The LC textures of these porphyrin derivatives at their LC phases upon cooling from their isotropic liquid are shown in Fig. 4, which are typical textures of columnar mesophase [12–14]. No texture is observed for **4b–Zn**.

X-ray diffraction experiments further confirm the presence of liquid crystalline mesophases of porphyrin derivatives. The *d*-spacings of the diffraction peaks are summarized in Table 2. The ratio of the *d*-spacings in the low angles of the compounds in their mesophases is not 1:1/2:1/3, indicating that their mesophases do not show lamellar structure. X-ray diffraction pattern of **4b** shows one diffraction peak with *d*-spacing of 40.7 Å in the low angle region and a broad halo around 4.4 Å in the wide angle region at room temperature. Though the presence of only one peak in the low angle region cannot allow an assignment of the specific type of columnar arrangement, we obtain reasonable estimation for the macroscopic density by assuming columns [15]. In combination with model of a hexagonal columnar phase (Col_h), the diffraction with *d*-spacing of 40.7 Å can be indexed as (10) columnar lattice with the lattice parameter of $a = 47.0$ Å, which is equal to the diameter of the self-assembled column and the inter-columnar distance. Then the number of the molecules in the hexagonal lattice, *Z*, can be calculated according to Eqs. (1) and (2) by assuming the packing density (ρ) as 1.0 g cm^{-3}:

$$\rho = (M/N_A)/(V/Z) \quad (1)$$

$$V = \left(\sqrt{3}/2\right)a^2 h \times 10^{-24} \quad (2)$$

where N_A is Avogadro constant; *M*, molecular mass; *V*, the volume of the local unit cell; *h*, the inter-discs distance ($h = 3.6$ Å) [10,12a]. The calculated *Z* is about 1.25 and we consider the number of the molecules is 1. Then the packing density ρ can be calculated as 0.80 g cm^{-3}, which is smaller than the found density ($\rho = 0.95$ g cm^{-3}). Additionally, considering the difference between the molecular diameter (calculated by the Material Studio 3.0 program in Fig. 2) of 58.8 Å and the assumed lattice parameter ($a = 47.0$ Å), we propose that **4b** should not show hexagonal columnar mesophase. As the peak is relatively broad (Fig. 5), we can assume a rectangular phase where (20) and (11) reflections are close to each other. Thus the mesophase of **4b** is assigned to a rectangular columnar phase, commonly referred to a pseudo hexagonal columnar phase. The lattice parameters are $a = 81.4$, $b = 47.0$ Å, with $a/b = \sqrt{3}$ [16]. In addition, the broad halo around 4.4 Å

Table 2
Powder X-ray diffraction data for the porphyrin derivatives

Compounds [a]	Observed *d*-spacing/Å	(*h k l*)	Mesophase parameter/Å	Calculated molecular diameter/Å	Calculated density/[g cm^{-3}] [b]
4a	34.5	(11), (20)	($P2_1/a$) Col_r, $a = 68.9$, $b = 39.8$	47.1	0.80
	13.5	(21)			
	4.4	Alkoxy chains			
4b	40.7	(11), (20)	($P2_1/a$) Col_r, $a = 81.4$, $b = 47.0$	58.8	0.80
	4.4	Alkoxy chains			
4c	46.0	(11), (20)	($P2_1/a$) Col_r, $a = 92.0$, $b = 53.1$	68.1	0.75
	4.4	Alkoxy chains			
4b–Zn	40.5	(11), (20)	($P2_1/a$) Col_r, $a = 81.1$, $b = 46.8$	57.3	0.82
	4.4	Alkoxy chains			
4b–Ni	37.0	(11)	($C2/m$) Col_r, $a = 68.2$, $b = 44.0$	56.7	–
	34.1	(20)			
	17.1	(40)			
	4.4	Alkoxy chains			

[a] All the compounds were sheared in the isotropic state, annealed at 70 °C for 12 h, and measured at 25 °C except **4c** at 50 °C.
[b] The calculated density based on a hexagonal columnar phase (Col_h) is lower than the assumed packing density, thus the possibility of forming Col_h phase can be ruled out.

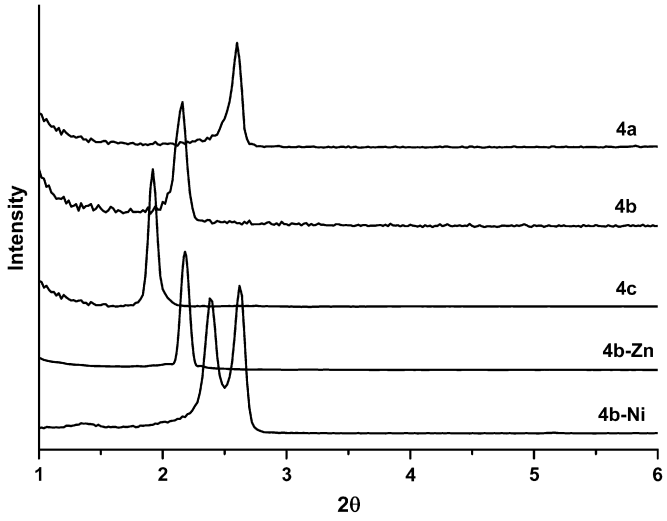


Fig. 5. X-ray diffraction patterns in the liquid crystalline phases measured at room temperature except **4c** at 50 °C.

can be attributed to the disordered alkoxy chains. As no sharp peak appears in the wide angle region, compound **4b** shows a disordered rectangular columnar mesophase Col_r.

X-ray diffraction pattern of **4a** at its LC phase exhibits two diffraction peaks with *d*-spacings of 34.5 and 13.5 Å in the low angle region and a broad halo around 4.4 Å in the wide angle region at room temperature. Similarly, pseudo hexagonal columnar phase (rectangular columnar phase) with lattice parameters of $a = 68.9$ and $b = 39.8$ Å is assigned. Similar X-ray diffraction patterns of **4c** and **4b−Zn** have been observed, and thus both **4c** and **4b−Zn** exhibit pseudo hexagonal columnar phase (rectangular columnar phase) with lattice parameters of $a = 92.0$, $b = 53.1$ Å and $a = 81.1$, $b = 46.8$ Å, respectively. Although the XRD pattern of **4c** at high temperature is not obtained, it is reasonable to propose that **4c** exhibits columnar phase considering its typical texture shown in Fig. 4(c).

X-ray diffraction pattern of **4b−Ni** at its LC phase consists of three diffraction peaks with *d*-spacing of 37.0, 34.1 and 17.1 Å in the low angle region, corresponding to the (11), (20) and (40) reflections, respectively. This phase, which is different from the above pseudo hexagonal columnar phase, can be assigned to a rectangular columnar mesophase (*C*2/*m*) with lattice parameters of $a = 68.2$ and $b = 44.0$ Å.

As we know that the columnar structure of a mesophase depends greatly on the molecule structure, discotic molecules would prefer to form columnar mesophase, while rod-like molecules to form a layered structure. Compared with the most reported *meso*-substituted porphyrins with 4 alkyl chains showing lamellar mesophase, the present porphyrin derivatives show disc-like shape due to the 12 flexible chains around their rigid porphyrin ring. The formation of columnar mesophase of the present porphyrins rather than a lamellar mesophase might be due to their flat disc-like structures, which have been confirmed through the simulation by Material Studio 3.0 program (see in Fig. 2).

Based on the results of POM, DSC and XRD, it can be concluded that these compounds show columnar mesophase Col at room temperature. Schematic molecular arrangement of the porphyrins in their LC phases is given in Fig. 6, 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.

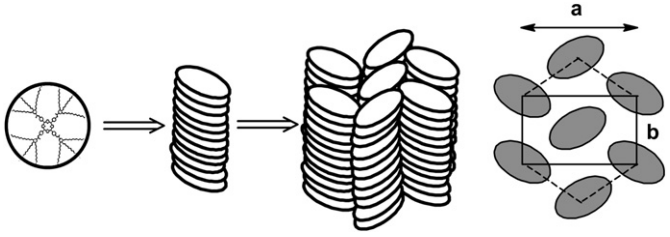


Fig. 6. Schematic molecular packing model of the porphyrin derivatives.

4. Conclusions

The novel porphyrin derivatives carrying 12 flexible alkyl chains were synthesized and characterized by X-ray diffraction and polarizing optical microscopy. They displayed rectangular columnar mesophases of relatively wide liquid crystalline phase temperature range that included room temperature. The results confirm that both alkyl chain length and metalisation can influence mesomorphic behavior of the compounds. The mesomorphic properties of the compounds indicate that they offer potential usage in photoelectronic fields.

References

[1] Chandrasekhar S, Sadashiva BK, Suresh KA. Pramana 1977;9:471−80.
[2] Kumar S, Varshney SK. Org Lett 2002;4:157−9.
[3] Jian KQ, Shim HS, Tuhus-Dubrow D, Bernstein S, Woodward C, Steingart D, et al. Carbon 2003;41:2073−83.
[4] Boden N, Bushby RJ, Cammidge AN, Headdock G. J Mater Chem 1995;5:2275−81.
[5] Milgrom LR, Yahioglu G. Adv Mater 1997;9(4):313−6.
[6] Hughes RE, Hart SP, Smith DA, Movaghar B, Bushby RJ, Boden N. J Phys Chem B 2002;106:6638−45.
[7] Jaung J-Y. Dyes Pigments 2007;72:315−21.
[8] Goodby JW, Robinson PS, Teo B-K, Cladis PE. Mol Cryst Liq Cryst 1980;56:303−9.
[9] Liu C, Pan H-L, Fox MA, Bard AJ. Chem Mater 1997;9:1422−9.
[10] Segade A, Castella M, Lopez-Calahorra F, Velasco D. Chem Mater 2005;17:5366−74.
[11] (a) Castella M, Lopez-Calahorra F, Velasco D, Finkelmann H. Chem Commun 2002;2348−9;
(b) Wang QM, Bruce DW. Tetrahedron Lett 1996;37:7641−4.
[12] (a) Ohta K, Yamaguchi N, Yamamoto I. J Mater Chem 1998;8:2637−50;
(b) Ohta K, Azumane S, Kawahara W, Kobayashi N, Yamamoto I. J Mater Chem 1999;9:2313−20;
(c) Hatsusaka K, Ohta K, Yamamoto I, Shirai H. J Mater Chem 2001;11:423−33;
(d) Nakai T, Ban K, Ohta K, Kimura M. J Mater Chem 2002;12:844−50.

[13] (a) Liu W, Shi YH, Shi TS, Liu GF, Liu YX, Wang C, et al. Liq Cryst 2003;30:1255–7;
(b) Nagata A, Shimizu Y, Nagamoto H, Miyi M. Inorg Chim Acta 1995;238:169–71;
(c) Burrows HD, Gonsalves AMR, Leitao MLP, Miguel MG. Supramol Sci 1997;4:241–6.
[14] (a) Ohtake T, Ogasawara M, Ito-Akita K, Nishina N, Ujiie S, Ohno H, et al. Chem Mater 2000;12:782–9;
(b) Percec V, Johansson G, Ungar G, Zhou J. J Am Chem Soc 1996;118:9855–66;
(c) Lehmann M, Gearba RI, Koch MHJ, Ivanov DA. Chem Mater 2004;16:374–6.
[15] Kraft A, Reichert A, Kleppinger R. Chem Commun 2000; 1015–6.
[16] Barberá J, Iglesias R, Serrano JL, Sierra T, Palacios B. J Am Chem Soc 1998;120:2908–18.