

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

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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 ¹H 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.

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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

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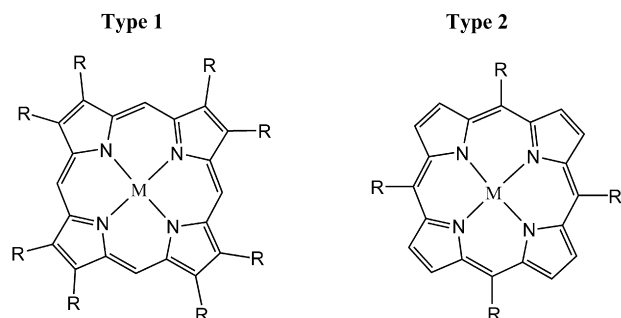


Fig. 1. Two types of mesogenic porphyrin derivatives reported to date.

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

The proposed molecular structures of the compounds were confirmed by IR and ^1H NMR spectroscopy. ^1H 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 $10\text{ }^\circ\text{C min}^{-1}$). 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 $K\alpha$ radiation.

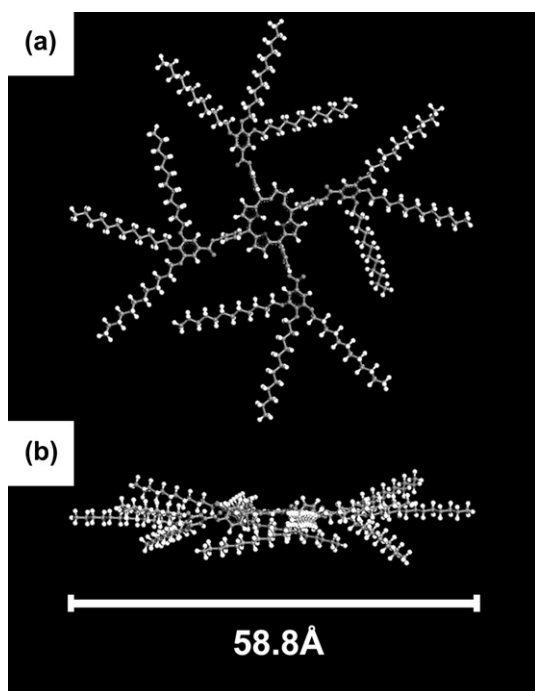


Fig. 2. Molecular structure of porphyrin **4b**: (a) view from above of the porphyrin ring; (b) edge-on-view with the porphyrin ring.

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 $<25\text{ }^\circ\text{C}$. ^1H NMR (CDCl_3 , δ , ppm): 7.25 (s, 2H, Ar–H), 4.33–4.37 (m, 2H, $-\text{COOCH}_2\text{CH}_3$), 4.00–4.02 (m, 6H, $-\text{O}-\text{CH}_2-$), 1.79–1.84 (m, 4H, m-to-COOH $-\text{O}-\text{C}-\text{CH}_2-$), 1.73–1.76 (m, 2H, p-to-COOH $-\text{O}-\text{C}-\text{CH}_2-$), 1.44–1.49 (m, 6H, $-\text{CH}_2-\text{CH}_3$), 1.34–1.40 (t, 3H, $-\text{COOCH}_2\text{CH}_3$), 1.26–1.35 (m, 18H, $-\text{O}-\text{C}-\text{C}-(\text{CH}_2)_3-\text{C}-\text{CH}_3$), 0.87–0.89 (t, 9H, $-\text{O}-\text{C}-\text{C}-(\text{CH}_2)_3-\text{C}-\text{CH}_3$). IR (KBr, ν , cm^{-1}): 2956 (ν_{CH_3}), 2918, 2850 (ν_{CH_2}), 1717 ($\nu_{\text{C}=\text{O}}$), 1584 ($\nu_{\text{C}=\text{C}}$, Ar), 1217 ($\nu_{\text{C}-\text{O}}$).

Compound **2b**: yield: 80%, mp $42.5\text{ }^\circ\text{C}$. ^1H NMR (CDCl_3 , δ , ppm): 7.25 (s, 2H, Ar–H), 4.33–4.37 (m, 2H, $-\text{COOCH}_2\text{CH}_3$), 4.00–4.02 (m, 6H, $-\text{O}-\text{CH}_2-$), 1.79–1.84 (m, 4H, m-to-COOH $-\text{O}-\text{C}-\text{CH}_2-$), 1.73–1.76 (m, 2H, p-to-COOH $-\text{O}-\text{C}-\text{CH}_2-$), 1.44–1.49 (m, 6H, $-\text{CH}_2-\text{CH}_3$), 1.34–1.40 (t, 3H, $-\text{COOCH}_2\text{CH}_3$), 1.26–1.35 (m, 48H, $-\text{O}-\text{C}-\text{C}-(\text{CH}_2)_8-\text{C}-\text{CH}_3$), 0.87–0.89 (t, 9H, $-\text{O}-\text{C}-\text{C}-(\text{CH}_2)_8-\text{C}-\text{CH}_3$). IR (KBr, ν , cm^{-1}): 2956 (ν_{CH_3}), 2918, 2850 (ν_{CH_2}), 1717 ($\nu_{\text{C}=\text{O}}$), 1584 ($\nu_{\text{C}=\text{C}}$, Ar), 1217 ($\nu_{\text{C}-\text{O}}$).

Compound **2c**: yield: 85%, mp $56\text{ }^\circ\text{C}$. ^1H NMR (CDCl_3 , δ , ppm): 7.25 (s, 2H, Ar–H), 4.33–4.37 (m, 2H, $-\text{COOCH}_2\text{CH}_3$), 4.00–4.02 (m, 6H, $-\text{O}-\text{CH}_2-$), 1.79–1.84 (m, 4H, m-to-COOH $-\text{O}-\text{C}-\text{CH}_2-$), 1.73–1.76 (m, 2H, p-to-COOH $-\text{O}-\text{C}-\text{CH}_2-$), 1.44–1.49 (m, 6H, $-\text{CH}_2-\text{CH}_3$), 1.34–1.40 (t, 3H, $-\text{COOCH}_2\text{CH}_3$), 1.26–1.35 (m, 72H, $-\text{O}-\text{C}-\text{C}-(\text{CH}_2)_{12}-\text{C}-\text{CH}_3$), 0.87–0.89 (t, 9H, $-\text{O}-\text{C}-\text{C}-(\text{CH}_2)_{12}-\text{C}-\text{CH}_3$). IR (KBr, ν , cm^{-1}): 2956 (ν_{CH_3}), 2918, 2850 (ν_{CH_2}), 1717 ($\nu_{\text{C}=\text{O}}$), 1584 ($\nu_{\text{C}=\text{C}}$, Ar), 1217 ($\nu_{\text{C}-\text{O}}$).

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 $43\text{ }^\circ\text{C}$. ^1H NMR (CDCl_3 , δ , ppm): 7.32 (s, 2H, Ar–H), 4.01–4.06 (m, 6H, $-\text{O}-\text{CH}_2-$), 1.79–1.84 (m, 4H, m-to-COOH $-\text{O}-\text{C}-\text{CH}_2-$), 1.73–1.76 (m, 2H, p-to-COOH $-\text{O}-\text{C}-\text{CH}_2-$), 1.45–1.51 (m, 6H, $-\text{CH}_2-\text{CH}_3$), 1.26–1.35 (m, 18H, $-\text{O}-\text{C}-\text{C}-(\text{CH}_2)_3-\text{C}-\text{CH}_3$),

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