

## Synthesis and Characterization of Liquid Crystal with Lower Temperature of Phase Change of meso-tetra-(4-n-lauroyloxyphenyl)porphyrin

Wei LIU<sup>1\*</sup>, Tong Shun SHI<sup>2</sup>

<sup>1</sup> Department of chemistry, The Forth Military Medical University, Xian 710032

<sup>2</sup> Department of chemistry, Jilin University, Changchun 130023

**Abstract :** The synthesis and characterization of meso-tetra (4-n-lauroyloxy phenyl) porphyrin with long ester chains are reported. The domains of stability and the structure of the liquid crystalline phases are determined by optical microscopy and differential scanning calorimetry (DSC).

**Keywords :** Porphyrin, liquid crystal, lower temperature of phase change.

Metalloporphyrin complexes have been extensively studied in many functional chemistry fields such as photo-electronic conversion non-linear optics, biomimetic studies and catalytic effects. To our knowledge, the first liquid crystalline porphyrin was synthesized by Goodby *et al*<sup>1</sup>. In 1987, Gregg *et al*<sup>2</sup> reported the synthesis and the liquid crystalline properties of a series of porphyrin octanol esters. In 1987, Gregg *et al*<sup>3</sup> synthesized octakis ( $\beta$ -hydroxyethyl) porphyrin. In 1991, tetrakis (4-n-lauroylphenyl) porphyrin was prepared by Shimizu *et al*<sup>4</sup>. In 1994, 5, 15-disubstituted porphyrin, a rod-like liquid crystal, was synthesized by Bruce<sup>5</sup>. Above mentioned compounds have a high temperature of liquid crystal phase change, a high viscosity of liquid crystal phase and a narrow mesophase range. In an attempt to solve these problems, we synthesized meso-tetra- (4-lauroyloxy-phenyl) porphyrin [TLPPH<sub>2</sub>] and Zn<sup>++</sup> complex [TLPPZn]. The liquid crystalline behavior and structures of these compounds are investigated in this paper.

The preparation method of meso-tetra (4-lauroyloxyphenyl) porphyrin is as follows: A mixture of 300 mL of dried benzene, 1.5 g (0.441mmol) of tetra (4-hydroxyphenyl) porphyrin (prepared in our laboratory) and 3 mL of triethylamine were put into a 500 mL Wolff bottle with a N<sub>2</sub> inlet. 4.5 mL (27mmol) of lauroyl chloride (prepared in our laboratory) diluted by 10 mL of benzene was added in 0.5 h under dry nitrogen. The reaction solution was refluxed for 10 h. The solvent was evaporated. A deep purple residue was dissolved in chloroform and twice chromatographed on a column of neutral aluminum using chloroform as an eluent. The second band contained the desired porphyrin. The second fraction was recrystallized in chloroform. The product was

dried in *vacuo* to obtain 1.4 g. Elementary analysis was carried out with a Perkin-Elmer 240 C auto elementary analyser. Elementary Anal. for compound: calcd. C: 78.48, H: 8.45, N: 3.98 (%) found. C: 78.06, H: 8.42, N: 3.95. UV-Vis spectra were recorded on a Shimadzu UV-240 spectra photometer with chloroform as the solvent. Ultra-violet visible spectrum (nm): 419.4 (soret), 514.8, 549.8, 589.6 and 646.0 nm. Infrared spectra were recorded on a Fourier transform infrared photoacoustic spectral system consisting of a JDV-1 infrared photoacoustic cell (made in Jilin University) and Nicolet FTIR-5PC spectrometer with CsI photosystem (made in American) in the region of 190-3600  $\text{cm}^{-1}$ . IR ( $\nu/\text{cm}^{-1}$ ): 3318 ( $\nu_{\text{N-H}}$ , pyrrole), 968 ( $\delta_{\text{N-H}}$ , pyrrole), 721 ( $\nu_{\text{-(CH}_2\text{)}_n^-}$ ), 1751 ( $\nu_{\text{C=O}}$ ), 1203 ( $\nu_{\text{C-O}}$ ), 823 ( $\nu_{\text{C-CH}}$ , p-substituted benzene ring)<sup>6</sup>. The  $^1\text{H}$  NMR spectra were recorded on a Varian-Unity-400NMR spectrometer in  $\text{CDCl}_3$  and chemical shifts were relative to external standard TMS.  $^1\text{H}$  NMR ( $\delta$ ): 8.579 (pyrrole, 8H), 7.256-8.222 (benzene ring, 16H), 2.733-2.770 ( $-\text{O-OC-CH}_2$ , 8H), 1.255-1.931 ( $\nu_{\text{-(CH}_2\text{)}_n^-}$ , 72H), 0.879-0.912 ( $-\text{CH}_3$ , 12H) and -2.834 (N-H, 2H)<sup>6</sup>. The molar conductance of the compound in DMF at 25°C is  $12.66 \text{ S}\cdot\text{cm}^2\cdot\text{mol}^{-1}$ <sup>7</sup>.

The preparation method of Zn complex is as follows: The complex was prepared by the reaction of TLPPH<sub>2</sub> 0.15 g with  $\text{ZnCl}_2$  (1.0 g) in  $\text{CH}_2\text{Cl}_2$  (20 mL) and DMF (20 mL) at 60°C under nitrogen. After the reaction, O<sub>2</sub> was bubbled through the solution for 10 min. Most of the DMF was evaporated. The crude product was chromatographed twice on neutral alumina column using chloroform as an eluent. The second band containing the desired porphyrin complex was collected. The complex was obtained from the chloroform solution by recrystallization and the yield was 0.14 g. Elementary Anal. for compound: calcd. C: 75.10, H: 7.95, N: 3.81 (%); found. C: 74.68, H: 7.90, N: 3.78. Ultra-violet visible spectrum (nm): 429.0 (soret), 561.2 and 602.2 nm. After the metal ion entered the body of porphyrin, because of the increasing of molecular symmetry from D<sub>2h</sub> to D<sub>4h</sub>, the number of Q bands decreases and the absorption frequencies shift. IR ( $\nu/\text{cm}^{-1}$ ): 721 ( $\nu_{\text{-(CH}_2\text{)}_n^-}$ ), 1763 ( $\nu_{\text{C=O}}$ ), 1203 ( $\nu_{\text{C-O}}$ ), 856 ( $\nu_{\text{C-CH}}$ , p-substituted benzene ring), 243.1 ( $\nu_{\text{M-N}}$ ). The bands at 3318, 968  $\text{cm}^{-1}$  disappear in the complex, since the hydrogen atom in the N-H bonding is replaced by a Zn atom.  $^1\text{H}$  NMR ( $\delta$ ): 8.978 (pyrrole, 8H), 7.262-7.501 (benzene ring, 16H), 2.731-3.022 ( $-\text{O-OCCH}_2$ , 8H), 1.254-1.913 ( $\nu_{\text{-(CH}_2\text{)}_n^-}$ , 72H) disappears, since the hydrogen atom in the N-H band is replaced by a Zn<sup>++</sup>. The molar conductance of the complex in DMF at 25°C is  $12.55 \text{ S}\cdot\text{cm}^2\cdot\text{mol}^{-1}$ <sup>7</sup>.

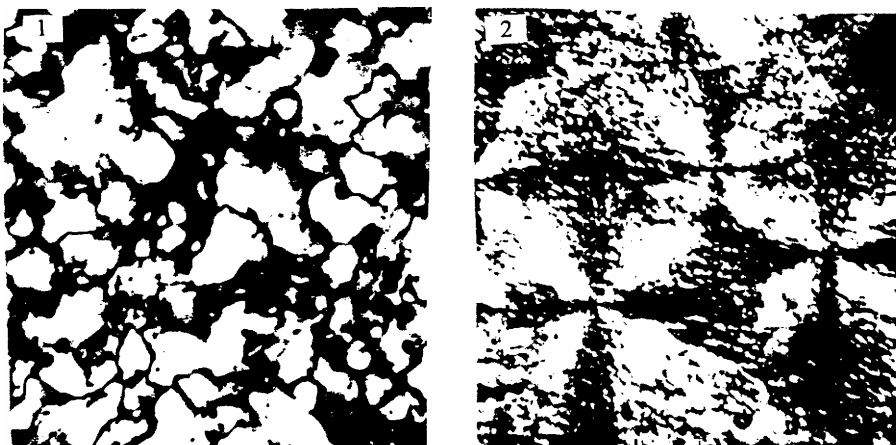
**Table.** Calorimetric data for compounds

Compounds	T <sup>a</sup> /°C		
	(T/°C) / ( $\Delta\text{H}/\text{KJ} \cdot \text{mol}^{-1}$ )		
TLPPH <sub>2</sub> 1	25.95	38.22	134.51
	C <sup>b</sup> —	D <sub>1</sub> —	D <sub>2</sub> <sup>c</sup> — I <sup>d</sup>
	(36.00)	(10.76)	(12.98)
TLPPZn 2	-36.40	10.88	39.78
	—C—	—D <sub>1</sub> —	—D <sub>2</sub> — I
	(4.96)	(2.76)	(1.31)

a. Heating rate 10°C/min b. C=crystal c. D=discotic mesophase d. I=isotropic liquid

Differential scanning calorimetry (DSC) measurement was performed with a Perkin-Elmer 7 series thermal analysis system. Polarizing microscope with a heating stage was used to observe the optical texture of the phases. The calorimetric data for the compounds are given in **Table**. All phase transitions are enantiotropic.

**Figure.** Optical texture of the mesophase of porphyrin



- (1) obtained on cooling from the isotropic liquid at 89°C  
(2) obtained on cooling from the isotropic liquid at 19°C

The lauroyloxy phenyl porphyrin **1** and **2** showed two broad liquid crystalline phases between the isotropic liquid and crystalline phase and the two phases were separated by sharp peak in the DSC. Both phases exhibit the textures characteristic of highly ordered discotic phase and lower phase transition temperature.

According to the DSC thermogram of compounds, compound **2** melted at -36.4°C and D<sub>1</sub> phase was obtained, which persisted until around 10.88°C and began D<sub>2</sub> phase which persisted until around 39.78°C. On cooling from the isotropic liquid, the laurolyoxyphenyl porphyrin **2** changed to one mesophase D<sub>2</sub> at 93.11°C and another mesophase D<sub>1</sub> at 30.21°C which persisted until near -50.67°C. The phases were identified by their characteristic optical texture as shows in **Figure**. On inserting zinc into the porphyrin, the phase transition temperature from crystalphase to mesophase decreases.

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