SYNTHESIS OF NOVEL PORPHYRIN DERIVATIVES WITH MESOGENIC PROPERTIES

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GRAPHICAL ABSTRACT

Abstract Two novel porphyrin derivatives, 5,10,15,20-tetra(4-(N-octane-carboxamide)phenyl)porphyrin (4NC8-TPP) and 5,10,15,20-tetra(4-(N-stearyl-carboxamide)phenyl)porphyrin (4NC18-TPP), were synthesized. Their molecular structures were characterized by means of time-of-flight mass spectrometer (TOF-MS), nuclear magnetic resonance (NMR), and infrared spectra (IR). The thermal behavior and morphologies of 4NC8-TPP and 4NC18-TPP were examined by thermal gravity (TG), differential scanning calorimetry (DSC), x-ray diffraction (XRD), and polarizing

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optical microscope (POM). It was found that both 4NC$_8$-TPP and 4NC$_{18}$-TPP had mesogenic properties.

**Keywords** Mesogenic property; morphology; porphyrin derivative; thermal behavior

**INTRODUCTION**

Because porphyrin and their derivatives play important roles in nature, such as chlorophyll in photosynthesis and hemoglobin in human blood, they have received extensive attention and study in many years. They have been expected to be applied in many areas, for example, photodynamic therapy,[1] photoelectronic transition,[2] organic light-emitting diodes,[3] biosensors,[4] and optical information storage[5] because of their favorable optoelectronic properties and chemical and thermal stabilities.

Since porphyrin derivatives with liquid-crystalline properties were reported,[6] many mesogenic porphyrins have been synthesized.[7] Researchers have synthesized 2,3,7,8,12,13,17,18-octakis(3-hydroxyethyl) porphyrin and its octaalkyl ether derivatives, which exhibited a discotic liquid crystalline character,[8] and 2,3,7,8,12,13,17,18-octakis(ocetylthio)tetraazaporphyrin copper(II) complex, which showed a mesophase ranging from 67.6 to 151.7 °C.[9] These mesogenic compounds have a well-organized intermolecular arrangement, which benefits the transition of charge carrier. They can be used as semiconductor materials in photovoltaic devices. So far, the substituent groups of porphyrin derivatives with mesogenic properties are usually alkyl, alkoxy, or acyloxy, and there have been few reports regarding the alkylamide group as substituent groups of porphyrin derivatives with mesogenic properties.

In this article, we synthesized two novel porphyrin derivatives, 5,10,15,20-tetra(4-(N-stearyl-carboxamide)phenyl)porphyrin(4NC$_{18}$-TPP) and 5,10,15,20-tetra(4-(N-octane-carboxamide)phenyl)porphyrin (4NC$_{8}$-TPP) (Scheme 1), and their thermal behaviors and morphologies were investigated.

![Scheme 1. Molecular structures of 4NC$_8$-TPP and 4NC$_{18}$-TPP.](image-url)
RESULTS AND DISCUSSION

Thermal gravity (TG) and differential scanning calorimetry (DSC) were measured to examine the thermal properties. The initial decomposition temperature of 4NC₈-TPP and 4NC₁₈-TPP are 187 and 385 °C according to the TG (Fig. 1). Figure 2 shows the DSC curves of 4NC₈-TPP and 4NC₁₈-TPP under the first cooling and second heating. The DSC measurement of 4NC₈-TPP from room temperature to 350 °C showed that 4NC₈-TPP did not exhibit liquid-crystalline behavior either on heating or cooling, but showed only melting and crystallization transitions at 312 and 264 °C, respectively. In the cooling process, there was a small peak at 119 °C, which was the glass transition temperature. By contrast, when 4NC₁₈-TPP was heated from room temperature, it showed a small wide peak at 45 °C, which was the glass transition. On further heating, an endothermic peak was observed at 120 °C and the mesophase was obtained. The onset of the transition from the mesophase into isotropic liquid was observed at 271 °C and the peak at 283 °C. In the cooling process, the onset of the isotropic liquid transition into the mesophase was
observed at 272 °C and the peak at 268 °C. The mesophase crystallized at 122 °C. There was a wide mesomorphic state from crystal to liquid crystal lasting about 150 °C. The small peak at 61 °C was glass transition temperature like 4NC8-TPP. From the DSC curves of 4NC8-TPP and 4NC18-TPP, we conclude that the increase of the length of the side chain benefits the formation of liquid-crystalline phase. The phase transition temperatures and enthalpy changes are listed in Table 1.

The morphology of 4NC8-TPP and 4NC18-TPP was observed on the polarizing optical microscope (POM). Figure 3 shows the optical texture of 4NC8-TPP and 4NC18-TPP by slow cooling from isotropic liquid. Judging from the DSC of 4NC8-TPP, it should have a crystalline phase below melting temperature. However, in the POM image, a liquid-crystal-like texture was observed and some areas presented crystal morphology. This showed that there were both crystalline and liquid-crystalline phase in 4NC8-TPP below 264 °C on the cooling process but the liquid-crystalline phase was metastable. 4NC8-TPP tended to crystallize in the aluminum pan used in the DSC measurement but formed a liquid-crystalline phase on the glass substrate used for the POM.[10] For 4NC18-TPP, a birefringent fan-shaped texture was observed in the POM image, which was the evidence of columnar phase.[11]

X-ray diffraction was performed from 3° to 50° and the profile is shown in Fig. 4. 4NC8-TPP and 4NC18-TPP were vacuum deposited on the glass, and the thicknesses of the 4NC8-TPP and 4NC18-TPP film were about 100 nm and 100 nm respectively. The results showed that both of the 4NC8-TPP and 4NC18-TPP were amorphous on the glass at room temperature. These results conformed with the DSC results.

Table 1. Calorimetric data for 4NC8-TPP and 4NC18-TPP

| Compound     | Temp. [°C] (ΔH/kJ · mol⁻¹) | ΔTemp [°C] |
|--------------|----------------------------|------------|
| 4NC8-TPP     |                            |            |
| Heating      | C 312 (−56.00), I          |            |
| Cooling      | I 264 (52.30), Cr 118, g   |            |
| 4NC18-TPP    |                            |            |
| Heating      | g 45, Cr 120 (−46.72), Col 271 (−45.46), I | 151 |
| Cooling      | I 272 (38.37), Col 122 (31.65), Cr 61, g | 150 |

Notes. Heating rate 10 °C/min; cooling rate 10 °C/min. Cr, crystal; Col, columnar phase; I, isotropic liquid; g, glass.

Figure 3. POM texture of 4NC8-TPP and 4NC18-TPP cooling from the isotropic state, ×200.
For many of the conjugated compounds, the absorbance in the visible region is undoubtedly an important parameter. Figure 5 showed the UV-visible absorption spectra of 4NC₈-TPP and 4NC₁₈-TPP using CH₂Cl₂ as solvent, and the two curves were similar due to their similar conjugated structure. It was found that there were two major absorbances, the Soret band and the Q band. The Soret band of 4NC₈-TPP and 4NC₁₈-TPP were 422 and 421 nm, respectively. The Q band values of 4NC₈-TPP (or 4NC₁₈-TPP) were 517 (or 516), 552 (or 551), 592 (or 592), and 647 (or 647). According to the molecular orbital theory of porphyrin put forth by Gouterman, the Soret band was due to the electronic transition from the ground state (S₀) to the second singlet excited state S₂, and the Q band was from the S₀ to the first singlet excited state S₁. We also measured the UV-visible absorption of the two compounds’ films. The absorption edges of 4NC₈-TPP and 4NC₁₈-TPP were 673 and
According to the formula \( \Delta E = \frac{1240}{\lambda_{\text{edge}}} \), the optical band gaps (\( \Delta E \)) of 4NC\textsubscript{8}-TPP and 4NC\textsubscript{18}-TPP were 1.84 and 1.83 eV.

Figure 6 is the fluorescence emission spectra of 4NC\textsubscript{8}-TPP and 4NC\textsubscript{18}-TPP. It showed that they both had two emission bands at the same wavelength. These results illustrated that the electron emission occurred on the porphyrin rings and the length of the side chain had little influence on the emission spectra.

Electrochemical cyclic voltammetry was carried out to evaluate the oxidation and reduction properties. The cyclic voltammograms of 4NC\textsubscript{8}-TPP and 4NC\textsubscript{18}-TPP were obtained in a solution of tetra-n-butylammonium perchlorate (0.1 mol/L) in CH\textsubscript{2}Cl\textsubscript{2}, and an Ag/AgCl electrode was used as reference electrode as shown in Fig. 7. Both 4NC\textsubscript{8}-TPP and 4NC\textsubscript{18}-TPP exhibited two anodic oxidation and two cathodic reduction waves. The first oxidation potential was 0.79 V vs. Ag/AgCl while the second was 1.53 V vs. Ag/AgCl for 4NC\textsubscript{8}-TPP. The reduction values were −0.98 V and −1.33 V vs. Ag/AgCl, respectively. For 4NC\textsubscript{18}-TPP, the first oxidation
potential was 0.78 V vs. Ag/AgCl and the second was 1.53 V vs. Ag/AgCl while the reduction values were −0.96 V vs. Ag/AgCl and −1.32 V vs. Ag/AgCl. It was found that the difference between 4NC8-TPP and 4NC18-TPP was small because the porphyrin cores occurring from oxidation and reduction were the same. The highest occupied molecular orbital (HOMO) and the lowest unoccupied molecular orbital (LUMO) energy levels of porphyrin derivatives were calculated according to the following equations [14].

\[
\text{HOMO} = -e\left(\text{E}_{\text{onset}} + 4.71\right)\text{(ev)}
\]

\[
\text{LUMO} = -e\left(\text{E}_{\text{onset}} + 4.71\right)\text{(ev)}
\]

The HOMO levels of 4NC8-TPP and 4NC18-TPP were −5.50 and −5.49 eV while the LUMO levels of 4NC8-TPP and 4NC18-TPP were −3.73 and −3.75 eV, respectively. The HOMO-LUMO gap can be expressed as \(\Delta E\). The \(\Delta E\) values of 4NC8-TPP and 4NC18-TPP were 1.77 and 1.74 eV. Both the oxidation and reduction took place on the porphyrin ring.

CONCLUSIONS

Two novel porphyrin derivatives, 4NC8-TPP and 4NC18-TPP, were prepared and characterized. Both of the two compounds had high thermostability from TG analysis. 4NC8-TPP did not exhibit mesophase from the DSC curves but the POM image was typical liquid-crystalline texture. However, 4NC18-TPP had a broad column mesogenic phase about 150 °C. It indicated that the length of side chains influenced the liquid-crystalline property of the compounds. X-ray diffraction results showed that 4NC8-TPP and 4NC18-TPP were amorphous on the glass at room temperature. UV-vis spectra, fluorescence, and CV properties were similar in 4NC8-TPP and 4NC18-TPP. These liquid-crystalline materials may be useful for the practical applications in photovoltaic devices.

EXPERIMENTAL

Pyrrole was newly distilled before use because of its self-polymerization. Methyl 4-formylbenzoate and propionic acid were purchased and used without further purification. The MS were recorded on a Bruker Agilent 1100/Esquire HCT Plus (Bruker Autoflex III smartbean for TOF-MS). The \(^1\)H NMR was recorded on a Bruker Avance 400(MHz) NMR spectrometer in CDCl\(_3\) or dimethylsulfoxide (DMSO) using tetramethylsilane (TMS) as the internal standard. IR spectra were taken on a Nicolet 6700 Fourier transform (FT) IR spectrometer with KBr pellets. UV-vis spectra was obtained from Thermo Helios-\(\gamma\) spectrometer. The fluorescence spectra were recorded on a WGY-10 spectrofluorometer using CH\(_2\)Cl\(_2\) as solvent. TG was examined on Netzsch TGA209F3. DSC was performed with Netzsch 204-F1 thermal analysis system (scanning rate 10 °C/min). Optical texture was investigated on Olympus BX51-P LINKAMTHMS600 polarizing optical microscope (POM). The x-ray diffraction patterns were measured on a Bruker D8 Avance
instrument. The cyclic voltammetry curves were obtained from CHI750A electrochemical workstation (Zhenhua Apparatus Co., Ltd, Shanghai) using CH₂Cl₂ as solvent and Ag/AgCl as reference electrode.

**General Synthetic Procedure**

The primary material meso-tetra(4-methoxycarbonylphenyl)porphyrin (TCMPP) was synthesized through the ring formation of pyrrole and methyl 4-formylbenzoate according to the method reported in the literature by Alder-Longgo.¹⁵ The second material meso-tetra(4-carboxylphenyl)porphyrin (TCPP) was obtained through the saponification of TCMPP and the acylation and amidation of TCPP obtained the target products 4NC₈-TPP and 4NC₁₈-TPP under a nitrogen atmosphere. All of the intermediate products were characterized by MS, ¹H NMR, and IR spectra. The synthesis routes are illustrated in Scheme 2.

**Typical Procedure for the Synthesis of 4NC₈-TPP**

A mixture of TCPP (0.1 g, 0.126 mmol), SOCl₂ (5 ml), and CH₂ClCH₂Cl (30 ml) were refluxed for 8 h under a nitrogen atmosphere in a 100-ml, three-necked flask. The excess SOCl₂ and solvent were removed under reduced pressure after the reaction was finished. The remanent solid was dissolved in CH₂Cl₂ (40 ml) and trimethylamine (2 ml) and then n-octylamine was added into the flask. The mixture was stirred in ice water for 3 h and then at room temperature for 12 h under the nitrogen protection. The solvent was removed, and the residue was purified by silica-gel column chromatography using CHCl₃ as eluent. The first band was collected and condensed to obtain the target products 4NC₈-TPP (43.75 mg, 28%).

![Scheme 2. Synthesis route for porphyrin derivatives.](image-url)
**4NC₈⁻TPP**

TOF-MS: 1235.640, calcd. for C₈₀H₉₈N₈O₄: 1235.685; ¹H NMR (400 MHz, CDCl₃, TMS), δ (ppm): −2.78 (s, 2H, pyrrole NH), 0.88–0.90 (t, 12H, -CH₃), 1.27–1.59 (m, 48H, alkyl CH₂), 3.64–3.66 (t, 8H, -NH-CH₂/C₃/C₄), 6.45–6.49 (t, 4H, -CO-NH-), 8.16–8.56 (d, 16H, -C₆H₄), 8.85 (s, 8H, pyrrole ring); IR(KBr), ν (cm⁻¹) = 3315 (ν amide N-H and pyrrole N-H), 2924, 2852 (ν C-H), 1634 (ν C=O), 1554 (β, amide N-H), 966 (β, pyrrole N-H).

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**SUPPLEMENTAL MATERIAL**

Experimental details, characterization data of all compounds, and ¹H NMR, FT-IR, and mass spectra for this work can be accessed on the publisher’s website.

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