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An unsymmetrical porphyrin and its metal complexes: synthesis, spectroscopy, thermal analysis and liquid crystal properties

CHANGFU ZHUANG, XUEXIN TANG, DONG WANG, AIQING XIA, WENHUI LIAN, YUHUA SHI* and TONGSHUN SHI

College of Chemistry, Jilin University, Changchun 130023, P. R. China

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Abstract: The synthesis and characterization of a new unsymmetrical porphyrin liquid crystal, 5-(4-stearoyloxyphenyl)phenyl-10,15,20-triphenylporphyrin ($SPTPPH_2$) and its transition metal complexes (SPTPPM, M(II) = Zn, Fe, Co, Ni, Cu or Mn) are reported. Their structure and properties were studied by elemental analysis, and UV–Vis, IR, mass and ^{1}H-HMR spectroscopy. Their luminescent properties were studied by excitation and emission spectroscopy. The quantum yields of the $S_1 \rightarrow S_0$ fluorescence were measured at room temperature. According to thermal studies, the complexes have a higher thermal stability (no decomposition until 200 °C). Differential scanning calorimetry (DSC) data and an optical textural photograph, obtained using a polarizing microscope (POM), indicate that the porphyrin ligand had liquid crystalline character and that it exhibited more than one mesophase and a low-lying phase transition temperature, with transition temperatures of 19.3 and 79.4 °C; the temperature range of the liquid crystal (LC) phase of the ligand was 70.1 °C.

Keywords: porphyrin; transition metal complex; fluorescence spectroscopy; liquid crystal.

INTRODUCTION

Porphyrin and metalloporphyrins have always received considerable attention from scientists because of their photostability, high visible molar extinction coefficients, interesting excited state chemistry and electron transfer processes. These properties make them useful materials for charge transport, photoelectronic conversion, non-linear optics, organic light emitting diodes and optical information storage.[1–5] Porphyrin liquid crystals[6] are of interest for optoelectronic and other device applications due to their synthetic versatility, thermal stability, large electron systems and photochemical properties.[7] Considerable scientific and technological effort has been devoted to discotic liquid crystals since the first

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* Corresponding author. E-mail: cfzhuang_2008@yahoo.com.cn

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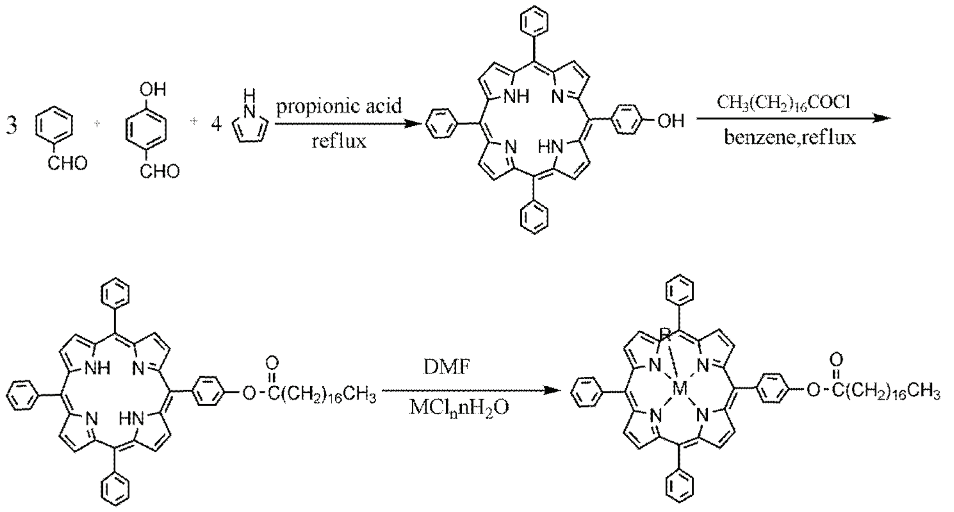
discovery of discotic mesogens.[8] The studies of previously reported liquid crystal compounds concentrated mainly on a certain aspect of their properties, such as fluorescence.[9]

Hence, chemists have made efforts to synthesize different porphyrins by peripheral modification of porphyrin.[10–12] However, most of the porphyrin derivatives substituted with a conjugated system at the meso-position were symmetrical[13] and limited to transition metal–porphyrin complexes.[14,15] In this paper, the synthesis and characterization of a novel unsymmetrical porphyrin liquid crystal and its transition metal complexes are reported for the first time (Scheme 1).



M=Zn,Cu,Co,Ni(no R); M=Mn,Fe,R=Cl

Scheme 1. Synthesis route to the porphyrin ligand and its metal complexes.

RESULTS AND DISCUSSION

Characterization and spectroscopy

5-(4-Stearoyloxyphenyl)phenyl-10,15,20-triphenylporphyrin (SPTPPH$_2$). Yield: 81.7 %; purple solid. M.p. > 300 °C. Anal. Calcd. for $C_{62}H_{64}N_4O_2$: C, 82.94; H, 7.13; N, 6.22 %; found: C, 82.99; H, 7.13; N, 6.24 %. IR (KBr, cm^{-1}): 3319 (N–H (pyrrole)), 2919, 2850 (C–H), 1762 (C=O), 1199 (C–O), 966 (N–H (pyrrole)). 725 ($–(CH_2)_n–$ ($n > 4$)). ^{1}H-NMR (500 MHz, $CDCl_3$, δ / ppm): –2.756 (2H, pyrrole N–H,), 0.858–0.901 (3H, $–CH_3$), 1.544–1.932 (30H ($–CH_2)_{15}$), 2.721––2.772 (2H, $OOCCH_2–$), 7.452–8.230 (19H, meso-phenyl protons), 8.844–8.856 (8H, pyrrole ring). MS (m/z): 897.3 (M^+). UV–Vis ($CHCl_3$) (λ_{max} / nm): 420 (Soret band), 515, 550, 590, 645 (four Q bands).

SPTPPZn. Yield: 88.3 %, purple red solid. M.p. > 300 °C. Anal. Calcd. for $C_{62}H_{62}N_4O_2Zn$: C, 77.45; H, 6.45; N, 5.82 %; found: C, 77.52; H, 6.50; N, 5.83

%. IR (KBr, cm^{-1}): 2917, 2850 (C–H), 1760 (C=O), 1193 (C–O), 719 (–(CH$_2$)$_n$– ($n > 4$)). ^{1}H-NMR (CDCl$_3$, 500 MHz): 0.845–0.881 (3H, –CH$_3$), 1.533–1.937 (30H, –(CH$_2$)$_{15}$), 2.721–2.772 (2H, OOCCH$_2$–), 7.471–8.233 (19H, meso-phenyl protons), 8.950–8.948 (8H, pyrrole ring). MS (m/z): 960.5 [M]$^+$. UV–Vis (CHCl$_3$) (λ_{max} / nm): 425 (Soret band), 555, 595 (two Q bands).

SPTPPCu. Yield: 87.6 %, green solid. M.p. > 300 °C. Anal. Calcd. for $C_{62}H_{62}N_4O_2Cu$: C, 77.61; H, 6.47; N, 5.82 %; found: C, 77.67; H, 6.51; N, 5.84 %. IR (KBr, cm^{-1}): 2919, 2850 (C–H), 1760 (C=O), 1199 (C–O), 717 (–(CH$_2$)$_n$– ($n > 4$)). MS (m/z): 957.9 [M+1]$^+$. UV–Vis (CHCl$_3$) (λ_{max} / nm): 415 (Soret band), 540 (Q bands).

SPTPPNi. Yield: 83.2 %, purple red solid. M.p. > 300 °C; Anal. Calcd. for $C_{62}H_{62}N_4O_2Ni$: C, 77.98; H, 6.49; N, 5.85 %; found: C, 78.06; H, 6.55; N, 5.87. IR (KBr, cm^{-1}): 2917, 2848 (C–H), 1762 (C=O), 1199 (C–O), 721 (–(CH$_2$)$_n$– ($n > 4$)). MS (m/z): 953.1 [M]$^+$. UV–Vis (CHCl$_3$) (λ_{max} / nm): 415 (Soret band), 530 (Q bands).

SPTPPCo. Yield: 81.3 %, purple red solid. M.p. > 300 °C. Anal. Calcd. for $C_{62}H_{62}N_4O_2Co$: C, 77.98; H, 6.55; N, 5.84 %; found: C, 78.04; H, 6.55; N, 5.87 %. IR (KBr, cm^{-1}): 2917, 2848 (C–H), 1760 (C=O), 1197 (C–O), 717 (–(CH$_2$)$_n$– ($n > 4$)). MS (m/z): 954.1 [M+1]$^+$. UV–Vis (CHCl$_3$) (λ_{max} / nm): 410 (Soret band), 530, 575 (two Q bands).

SPTPPFeCl. Yield: 80.1 %, purple black solid. M.p. > 300 °C. Anal. Calcd. for $C_{62}H_{62}N_4O_2ClFe$: C, 75.46; H, 6.29; N, 5.64 %; Found: C, 75.48, H, 6.33; N, 5.67 %. IR (KBr, cm^{-1}): 2919, 2850 (C–H), 1764 (C=O), 1202 (C–O), 721 (–(CH$_2$)$_n$– ($n > 4$)). MS (m/z): 953.1 [M]$^+$. UV–Vis (CHCl$_3$) (λ_{max} / nm): 420 (Soret band), 510 (Q bands).

SPTPPMnCl. Yield: 80.8 %, purple black solid. M.p. > 300 °C. Anal. Calcd. for $C_{62}H_{62}N_4O_2ClMn$: C, 75.48, H, 6.29; N, 5.65 %; found: C, 75.55; H 6.34; N, 5.68 %. IR (KBr, cm^{-1}): 2923, 2854 (C–H), 1758 (C=O), 1201 (C–O), 715 (–(CH$_2$)$_n$– ($n > 4$)). MS (m/z): 953.1 [M]$^+$. UV–Vis (CHCl$_3$) (λ_{max} / nm): 480 (Soret band), 580 (Q bands).

The characteristic Q and B (Soret) bands of the ligand and metal porphyrins in the visible and near UV ranges were assigned as transitions from the ground state (S$_0$) to the lowest excited singlet (S$_1$) and second lowest excited singlet state (S$_2$), respectively. SPTPPH$_2$ has one Soret band (420 nm) and four Q bands (515, 550, 590 and 645 nm). Compared with the ligand, the number of Q band decreased and the absorption frequencies shifted after the metal ion entered the hole of the porphyrin because of the increase in molecular symmetry from D$_{2h}$ to D$_{4h}$.[16]

The spectral bands at 3319 and 966 cm^{-1} in the IR spectrum of the porphyrin ligand are due to the N–H stretching vibration and the winding vibration of the porphyrin core, respectively. The two vibration bands of in the spectra of the complexes disappeared because the two hydrogen atoms of the porphyrin core are replaced by the transition metal ion to form an M–N bond. The bands found in the 1758–1764 cm^{-1} range in the spectra of the ligand and complexes are assigned to the C=O stretching vibration. The bands at 715–725 cm^{-1} correspond to the methylene in-plane rocking vibration of the straight alkyl chain consisting of over four carbon atoms.

The fluorescence emission spectra of SPTPPH$_2$ and SPTPPM at room temperature were measured. Their peak values and the quantum yields of the fluorescent emission of SPTPPH$_2$ and SPTPPZn are given in Table I.

TABLE I. Fluorescence spectral data of the ligand and Zn complex

Compound	λ_{emmax} / nm		Quantum yields (ϕ_f)
Ligand	650	709	0.050
SPTPPZn	594	639	0.035

The samples were dissolved in dry chloroform and deaerated under argon. Two emission bands, Q (0–1) bands at 650 and 594 nm and Q (0–2) bands at 709 and 639 nm were registered for SPTPPH$_2$ and SPTPPZn, respectively. The quantum yields (ϕ_f) of the Q bands of the complexes were calculated to be 0.050 and 0.035. The quantum yield was determined from the following equation:

$$\phi_{\text{sample}} = \frac{F_{\text{sample}}}{F_{\text{ZnTPP}}} \frac{A_{\text{ZnTPP}}}{A_{\text{sample}}} \phi_{\text{ZnTPP}}$$

where F_{sample} and F_{ZnTPP} are the measured integral areas of the fluorescence peaks of the sample and the reference ZnTPP, respectively; A_{sample} and A_{ZnTPP} are the absorbencies of the sample and the reference (ZnTPP), respectively, at the same excitation wavelength, and ϕ_{ZnTPP} (equals 0.033)[17] is the quantum yield of the reference. Porphyrin exhibited two fluorescence peaks: one from S$_2$ (B band) and the other from S$_1$ (Q band). The fluorescence of the B (Soret) band is attributed to the transition from the second excited singlet state S$_2$ to the ground state S$_0$, S$_2$ → S$_0$. The Soret fluorescence was about two orders of magnitude weaker than the S$_1$ → S$_0$ transition of the Q band emission. Its quantum yield is so low that the fluorescence sometimes becomes unobservable. This fluorescence emission was not observed at room temperature, which indicates certainly that the spin forbidden process S$_1$ → Tn is predominant for the radiationless deactivation of S$_1$ in porphyrin complexes.

Thermal analysis

Non-isothermal thermogravimetric analyses were performed in an air atmosphere at a heating rate of 10 °C/min. The TG and DTA curves of the ligand SPTPPH$_2$ are shown in Fig. 1. There are four stages in the TG curve of the ligand. The ligand began to decompose at 200 °C. At 360 °C, about 40 % of the mass had been lost due to loss of the meso-phenyl and palmitoyl groups. At 445 °C, about 66 % of the mass had been lost, corresponding to loss of the triphenyl group. The residual mass was zero at 600 °C. Simultaneously, there were three exothermal peaks at 310, 505 and 595 °C on the DTA curve of the ligand. The exothermic peaks correspond to the decomposition of the ligand. Decomposition began at 200 °C and was completely finished at 600 °C. It is a continuous decomposition process; the small exothermic peaks correspond to the loss of chains of the porphyrin ring and the large exothermic peak at 505 °C corresponds to the collapse of the porphyrin skeleton. It is very easy to see that this porphyrin complex is so stable in air that it could be dried at temperatures up to 200 °C.

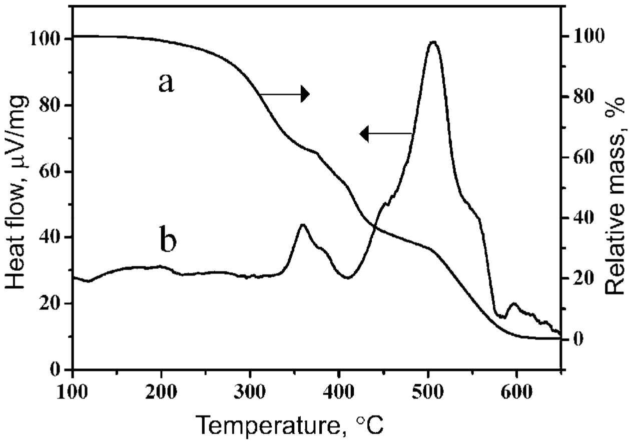


Fig. 1. TG Curve (a) and DTA curve (b) of $SPTPPH_2$.

Liquid crystalline behaviour

The liquid crystal properties were investigated by DSC and POM. The results showed that only the porphyrin ligand exhibited liquid crystalline, behaviour, while all the investigated metal porphyrin complexes were not liquid crystals. The phase change temperatures and enthalpies for $SPTPPH_2$ are as follows at heating and cooling rate of 10 °C min^{-1}:

$$\mathrm{C} \xleftrightarrow[9.4\ ^{\circ}\mathrm{C}\ (-43.1\ \mathrm{kJ\ mol^{-1}})]{19.3\ ^{\circ}\mathrm{C}\ (7.78\ \mathrm{kJ\ mol^{-1}})} \mathrm{D_1} \xleftrightarrow[21.6\ ^{\circ}\mathrm{C}\ (-2.57\ \mathrm{kJ\ mol^{-1}})]{37.0\ ^{\circ}\mathrm{C}\ (26.5\ \mathrm{kJ\ mol^{-1}})} \mathrm{D_2} \xleftrightarrow[69.5\ ^{\circ}\mathrm{C}\ (-23.5\ \mathrm{kJ\ mol^{-1}})]{79.4\ ^{\circ}\mathrm{C}\ (20.3\ \mathrm{kJ\ mol^{-1}})} \mathrm{I}$$

where → represents heating and ← coling; C is crystal phase, D_1 and D_2 are discotic mesophases and I is isotropic liquid phase.

Importantly, the ligand porphyrin exhibited an enantiotropy mesophase. A melting similar transition temperature of 19.3 °C for the ligand was observed during the first heating scan. Moreover, the porphyrin resulting from the ligand could be melted; a melting transition temperature of 37.0 °C for the ligand collected from the second heating scan was obtained. On cooling from the isotropic liquid, the ligand changed to the mesophase D at 69.5 °C, which persisted until about 9.4 °C. The phases were identified by their characteristic optical texture as shown in Fig. 2. Single liquid domains were obtained by annealing them from their clearing temperature. Due to alignment of the molecules with the polarizer and the analyzer, a classic Maltese cross extinction pattern was observed in the polarizer direction (vertical in the figure) and the analyzer direction (horizontal in the figure).

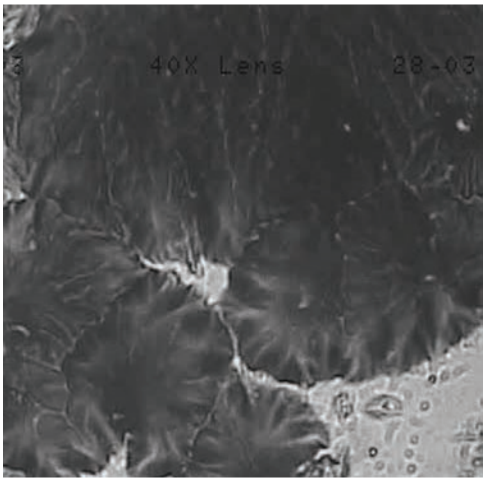


Fig. 2. Optical texture of SPTPPH$_2$ at 40 °C.

EXPERIMENTAL

Chemicals

All reagents and solvent were commercial reagent grade and were used without further purification except DMF that was predried over activated 4 Å molecular sieve and vacuum distilled from calcium hydride (CaH$_2$) prior to use. Pyrrole was distilled under reduced pressure.

Stearoyl chloride was prepared and purified according to a published procedure. Meso-5--(*p*-hydroxy)phenyl-10,15,20-triphenylporphyrin (HTPPH$_2$) was prepared and purified by known procedures.[18]

Synthesis of ligand (SPTPPH$_2$)

HTPPH$_2$ (1.5 g) was dissolved in 400 mL of heated distilled benzene in a 250 mL round bottom flask and 2.00 mL triethylamine was added. Then a solution of stearoyl chloride in 10 mL benzene was added dropwise over 0.5 h to the above solution under vigorous stirring at 70 °C. The solution was refluxed for 8 h under the protection of a dry nitrogen stream. The benzene was removed from the mixture by distillation. Then the mixed residue was extracted three times with two volumes of distilled water. A concentrated chloroform solution was added to a neutral aluminum oxide column and eluented with CHCl$_3$. The first band (purple red) was collected and evaporated to dryness to give a purple solid, which was further recrystallized from CHCl$_3$.

Synthesis of SPTPPZn

The complex SPTPPZn was prepared according to a published procedure. The ligand and $ZnCl_2$ were added to a mixture of DMF (20 mL) and CH_2Cl_2 (20 mL) and the solution refluxed for about 20min. The extent of the reaction was monitored by measuring the UV–Vis spectrum of the reaction solution every 5 min. After cooling to room temperature, 200 mL distilled water was added to the reaction mixture and extracted three times. The chloroform solution was concentrated and the crude product was chromatographed on a silica gel column using $CHCl_3$ as the eluent. The second band was collected, condensed and dried under vacuum to give a purple red solid.

The other complexes were synthesized in a similar manner to the above-described procedure.

Instrumentation

The UV–Vis spectra were recorded on a Shimadzu UV-240 spectrometer using chloroform as the solvent. The IR spectra were recorded on a Nicolet 5PC-FT-IR spectrometer in the region 400–4000 cm^{-1} using KBr pellets. The ^{1}H-NMR spectra were recorded on a Varian Unity-500 (MHz) NMR spectrometer. The chemical shifts are reported on the δ-scale relative to tetramethylsilane (TMS). The elemental analyses were realized using a Perkin–Elmer 240 C auto elementary analyzer. The mass spectra (FBA) were obtained on an AXIMA-CFR spectrometer. The fluorescence spectra were recorded on a Shimadzu RF5301PC spectrofluorometer. The thermogravimentic analyses (TGA) and differential thermal analyses (DTA) were performed on a TA SDT 2960 thermoanalyzer in air atmosphere at a heating rate of 10 °C/min.

CONCLUSIONS

A new unsymmetrical porphyrin and its transition metal complexes (SPTPPM, M(II) = Zn, Fe, Co, Ni, Cu) were prepared. The application of fluorescence, thermal studies, differential scanning calorimetry (DSC) and polarized optical microscopy (POM) in the analyses were illustrated. The fluorescence intensities of the ligand and SPTPPZn were much larger than the other transition metal complexes. The thermal studies showed that the porphyrin complexes were stable up to nearly 200 °C and that the decomposition of the complexes was a continuous process. Importantly, the porphyrin is a new class of liquid-crystal material, as verified by the combination of the DSC and POM techniques. This research may open a new vista in materials and devices using porphyrin.

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ИЗВОД

АСИМЕТРИЧНИ ПОРФИРИН И ЊЕГОВИ МЕТАЛНИ КОМПЛЕКСИ: СИНТЕЗА, СПЕКТРОСКОПИЈА, ТЕРМИЧКА АНАЛИЗА И СВОЈСТВА ТЕЧНОГ КРИСТАЛА

CHANGFU ZHUANG, XUEXIN TANG, DONG WANG, AIQING XIA, WENHUI LIAN, YUHUA SHI и TONGSHUN SHI

College of Chemistry, Jilin University, Changchun 130023, P. R. China

Приказана је синтеза и карактеризација новог асиметричног течног кристала порфирина 5-(4-стеароилоксифенил)фенил-10,15,20-трифенилфосфирин ($SPTPPH_2$) и његових металних комплекса (SPTPPM, M(II) = Zn, Fe, Co, Ni, Cu, Mn). Њихова структура и својства су изучавани елементалном анализом, UV–Vis, IR, MS и ^{1}H-HMR спекторскопијом. Луминисцентна својства су проучавана ексцитационим и емисионим спектрима, квантним приносима $S_1 \rightarrow S_0$ флуоресценције и мерене на собној температури. На основу термалне анализе комплекси имају већу стабилност (распадају се до 200 °C). Подаци диференцијалне скенирајуће калориметрије (DSC) и оптичкке тектуралне фотографије помоћу поларизујућег микроскопа (POM) указују да порфирински лиганд има карактер течног кристала и поседује више од једне мезофазе и ниско-лежеће фазе температурног прелаза, чије се температуре фазног прелаза мењају од 19,3 до 79,4 °C; температурни опсег за фазу течног кристала (LC) лиганда одржава се на 70,1 °C.

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