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Holmium porphyrin compound liquid crystals: Synthesis and properties

Miao Yu [a,b], Yu J. Zhang [b], Jian H. Shi [b], Guo F. Liu [b], Hong J. Zhang [a,*]

[a] State Key Laboratory of Rare Earth Resource Utilization, Changchun Institute of Applied Chemistry, Chinese Academy of Sciences, Changchun 130022, Jilin, PR China
[b] College of Chemistry, Jilin University, Changchun 130023, PR China

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ABSTRACT

5,10,15,20-Tetra-[(p-alkoxy-m-ethyloxy)phenyl]porphyrin and [5-(p-alkoxy)phenyl-10,15,20-tri-phenyl]porphyrin and their holmium(III) complexes are reported. They display a hexagonal columnar discotic columnar (Col_h) liquid crystal phase and were studied by cyclic voltammetry, surface photovoltage spectroscopy (SPS), electric-field-induced surface photovoltage spectroscopy (EFISPS) and luminescence spectroscopy. Within the accessible potential window, all these compounds exhibit two one-electron reversible redox reactions. Quantum yields of Q band are in the region 0.0045–0.21 at room temperature. The SPS and EFISPS reveal that all the compounds are p-type semiconductors and exhibit photovoltaic response due to π–π^* electron transitions.

1. Introduction

Porphyrins, as a series of functional materials, are playing a more and more important role in science and technology owing to their synthetic versatility, good thermal stability, large π-electron transition, and excellent photochemical properties [1–6]. These properties make them extensive useful materials in the electrophotographic, photovoltaic, photo-electrochemical, and high density optical storage fields [7–11]. Among the numerous porphyrins and metalloporphyrin complexes, much attention has been focused on their liquid-crystalline property [12–14]. Liquid-crystalline porphyrins are unique for their sub-phase aggregations under different temperatures or under different effects of solvent. The liquid-crystalline porphyrins have been demonstrated to tend to form large crystallites, which strongly affects the energetics and transport properties of the material [15–19]. Therefore, it is very attractive to investigate the surface photovoltage (SPV) response of the porphyrins.

Surface photovoltage spectroscopy (SPS) is an effective tool to investigate the photophysics of excited states generated by absorption in the aggregate state [20]. This technique has been successfully employed to the study of the charge transfer in photostimulated surface interaction, dye sensitization processes and photocatalysis [21], and has a very high sensitivity, about 10^8 q/cm^2, or one elementary charge per 10^7 surface atoms, which exceed many orders of magnitude of conventional spectroscopies, such as XPS and Auger spectroscopy [22]. The electric-field-induced surface photovoltage spectroscopy (EFISPS) has its superiority in investigating the optoelectric properties of organic thin films [23,24].

Metal-containing porphyrins are multifuncational molecules; nevertheless, most of the studies are focused on transition metal porphyrins that show photovoltaic effect so far [25,26]. Only a few examples of lanthanide-containing porphyrins have been described in the literature although lanthanide ions have unique optical properties, such as line-like emission bands and relatively long luminescence lifetimes [27–30]. Furthermore, most of the investigations in the field of luminescent lanthanide complexes have been devoted to Eu^{3+}, Tb^{3+}, Dy^{3+} and Sm^{3+} compounds [31,32]. In this paper, we synthesized a series of holmium porphyrin complexes and comprehensively studied electrochemistry, semiconductor, and luminescence properties of the compounds by cyclic voltammetry, surface photovoltage, and excitation and emission spectroscopies. The structures of the compounds are shown in Chart 1.

2. Experimental section

2.1. Materials and instrumentation

All reagents and solvent were of commercial reagent grade and were used without further purification except DMF. DMF was predried over activated 4 Å molecular sieves and vacuum distilled

* Corresponding author. Tel.: +86 1350 4329737; fax: +86 0431 85168439.
E-mail addresses: yumiao@jlu.edu.cn (M. Yu), hongjie@ciac.jl.cn (H.J. Zhang).

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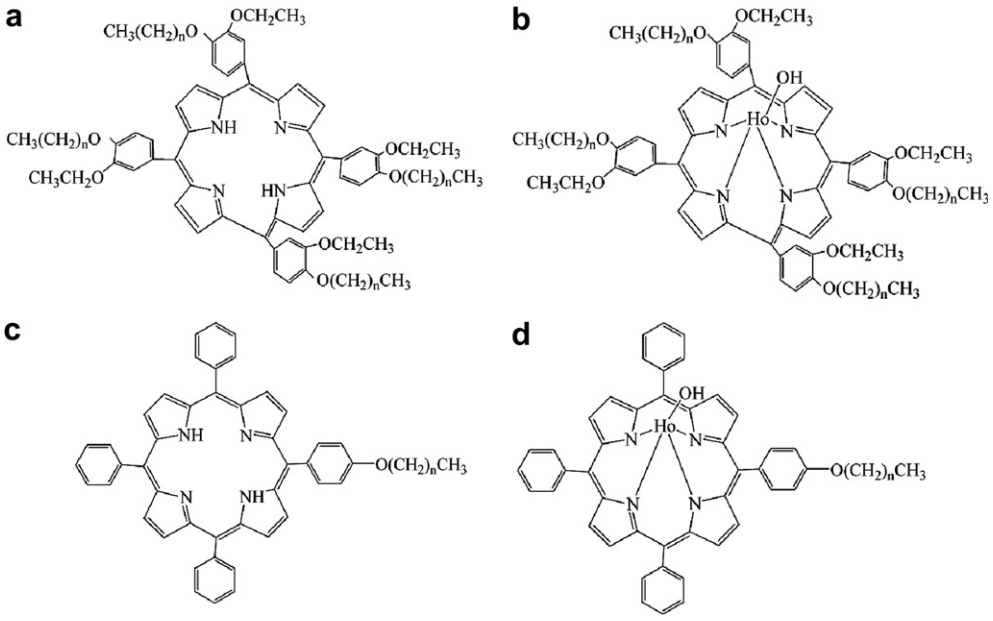


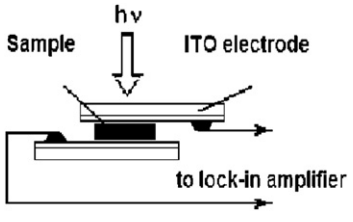
Chart 1. Porphyrin liquid-crystalline compounds: 5,10,15,20-tetra-[(p-alkoxy-m-ethyloxy)phenyl]porphyrin (a), $n = 11, 13, 15$ correspond to $12L_2$, $14L_2$, $16L_2$, respectively; 5,10,15,20-tetra-[(p-alkoxy-m-ethyloxy)phenyl]porphyrin holmium(III) complex (b), $n = 11, 13, 15$ correspond to $12(HoOH)_2$, $14(HoOH)_2$, $16(HoOH)_2$, respectively; [5-(p-alkoxy)phenyl-10,5,20-tri-phenyl] porphyrin (c), $n = 11$, 13, 15 correspond to $12L_1$, $14L_1$, $16L_1$, respectively; [5-(p-alkoxy)phenyl-10,15,20-tri-phenyl]porphyrin holmium(III) complex (d), $n = 11$, 13, 15 correspond to $12(HoOH)_1$, $14(HoOH)_1$, $16(HoOH)_1$, respectively.

from calcium hydride (CaH_2) prior to use. UV–visible spectra were recorded on a shimadzu UV-240 spectrophotometer in the range 350–700 nm using chloroform as solvent. Infrared spectra were recorded on a Nicolet 5PC-FT-IR spectrometer using KBr pellets in the region 400–4000 cm^{-1}. ^1H NMR spectra were recorded on a Varian-Unity-500 NMR spectrometer using $CDCl_3$ as solvent and tetramethylsilane (TMS) as internal standard. Elementary analyses were obtained on a Pekin–Elmer 240C auto elementary analyzer. Molar conductances of 10^{-3} mol dm^{-3} chloroform solution at 25 °C were measured on a DDX-111A conductometer. The optical textures were observed with a XinTian XP1 (CCD: TOTA-500 II) polarized light microscope equipped with a variable temperature stage (Linkam TMS 94). Transition temperatures and heats of fusion were determined at scan rates of 10 °C/min by differential scanning calorimetry using a NETESCH DSC 204. Fluorescence spectra at room temperature in the region 300–800 nm using 10^{-5} mol dm^{-3} chloroform solution were measured by FS920 Steady State Fluorescence Spectrometer. Emission spectra were corrected by the sensitivity of the photomultiplier tube, and excitation spectra were corrected by the intensity of the xenon lamp. X-ray diffraction was recorded by a Shimadzu XRD-6000. Surface photovoltage spectroscopy was measured with a solid junction photovoltaic cell (ITO/Sample/ITO) using a light source-monochromator-lock-in detection technique. Monochromatic light was obtained by passing light from a 500 W xenon lamp (CHF XQ500 W, Global xenon lamp power made in China) through a double-prism monochromator (Hilger and Watts, D 300 made in England). The slit width of entrance and exit is 1 mm. A lock-in amplifier (SR830-DSP, made in USA), synchronized with a light chopper (SR540, made in USA), was employed to amplify the photovoltage signal. The range of modulating frequency is from 20 to 70 Hz. The spectral resolution is 1 nm. The raw SPS data were normalized using the illuminometer (Zolix UOM-IS, made in China). The contact between samples and indium tin oxide (ITO) electrode is not ohmic contact since we carried out the measurement of surface photovoltage. The construct of the photovoltaic cell is a sandwich structure, see Scheme 1. Redox potentials of the porphyrins (10^{-3} M) in dried DMF containing 0.1 M TBAP as a supporting electrolyte was determined at room temperature by cyclic voltammetry using a three-electrode system under deaerated conditions and a CHI 600A electrochemical analyzer.

2.2. Synthesis

Compound 16L₁. [5-(p-Hydroxy)phenyl-10,15,20-tri-phenyl]-porphyrin (HPTPP) was prepared by general procedure [33]. The HPTPP (500 mg, 0.8 mmol) and 1-bromohexadecane (1221 mg, 4 mmol) were heated in DMF with stirring for 2.5 h in a dry nitrogen atmosphere. The crude product was purified by column chromatography (silica gel, $CHCl_3$). The title compound was obtained as a purple solid (560 mg, 0.6 mmol, yield 82%). UV–visible ($CHCl_3$) (10^{-4} ε M^{-1} cm^{-1}) 419 (10.2) 516 (0.40) 551 (0.28) 590 (0.20) 647 (0.15); IR (KBr): 3313, 2927, 2855, 1581, 1467, 1349, 1250, 978; Anal. Calcd. for $C_{60}N_4H_{62}O$: C, 84.31; H, 7.26; N, 6.56; Found: C, 84.39; H, 7.24; N, 6.57. Molar conductance value (MCV) (CH_3Cl, 25 °C, Ω^{-1} cm^2 mol^{-1}) 0.14 (nonelectrolyte) [23]. ^1H NMR ($CDCl_3$, 25 °C): 8.89 (s, 8H, pyrrole ring); 7.26–8.22(m, 19H, meso-phenyl protons); −2.78 (s, N–H); 0.89–0.87 (t, 3H, CH_3); 1.26–1.98 (m, 28H, CH_2); 3.64–3.39 (t, 2H, CH_2).

Compound 16(HoOH)₁. A mixture of $16L_1$ (300 mg, 0.35 mmol) and $HoCl_3 \cdot 6H_2O$ (228 mg, 0.6 mmol) in imidazole (1.0×10^4 mg) was heated at 210 °C were heated with stirring for 2.5 h in a dry



Scheme 1. The structure of the photovoltaic cell.