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Zhixin Zhao; Guofa Liu

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The first lanthanide(III) monoporphyrin complex liquid crystal

ZHIXIN ZHAO and GUOFA LIU*
Department of Chemistry, Jilin University, Changchun, 130023, PR China

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Hydroxy [5,10,15,20-tetra[*p*-decyloxy-*m*-methyloxy)phenyl]porphyrin Yb(III) exhibits a discotic hexagonal columnar phase, it is the first example of a monoporphyrin rare earth complex liquid crystal.

1. Introduction

Metalloporphyrin compounds have been extensively studied in many functional chemistry fields such as photoelectronic conversion, non-linear optics and biomimetic studies [1]. For many applications, large area thin films of semiconductors are needed, for example, to address optical displays or for the conversion of solar energy [2]. Often the cost of using conventional inorganic semiconductors in these systems is prohibitive. Liquid crystal displays, however, may easily form large area thin films. Because of the inherent tendency of liquid crystals to self-order, it is tempting to speculate about the possibility of liquid crystalline electronic devices [3]. A liquid crystal electro-optical memory effect has been observed for zinc octalis (β-decyloxyethyl)porphyrin (ZnODEP). Its charge trapping and detrapping rise time is on the nanosecond time scale; such a data storage system would be non-volatile and rewritable, with a storage density of about 8×10^{10} bits cm^{-2} under 6 V bias [4–6]. There have been many reports on transition metal porphyrin liquid crystal complexes [7, 8]; we now report the first example of a lanthanide monoporphyrin complex discotic metallomesogen with four alkyl tails—hydroxy[5,10,15,20-tetra[*p*-decyloxy-*m*-methyloxy)phenyl]porphyrin ytterbium, Yb[$(C_{10}BOMP)_4P$]OH (see figure 1).

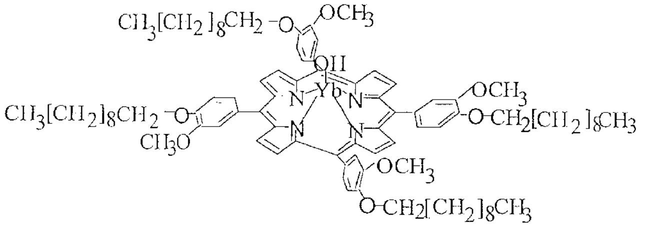

Figure 1. Structure of the complex Yb[$(C_{10}BOMP)_4P$]OH.

2. Experimental

The ligand 5,10,15,20-tetra[(*p*-decyloxy-*m*-methyloxy)-phenyl]porphyrin was prepared by usual procedures from the corresponding *p*-decyloxy-*m*-methyloxybenzaldehyde and pyrrole in propionic acid. It was purified by column chromatography (neutral aluminum oxide column, chloroform eluent) and crystallized from chloroform/hexane; yield 10%. IR(KBr) ν_{max}/cm^{-1} 3318: (N–H str.), 918 (N–H bend). ^{1}H NMR: δ_H ($CDCl_3$, 400 MHz), 8.91 (s, 8H, pyrrole ring), 7.73 (m, 12H, meso-phenyl protons), 4.30 (t, 20H, phenyl methyloxy protons), 3.97 (t, 8H, C_6H_4–O–CH_2), 0.88 (t, 12H, CH_3), 1.26, 1.32, 1.46, 1.64 (m, 64H, $[CH_2]_8$), −2.75 (s, 2H, pyrrole N–H). Elemental analysis: calcd for $C_{88}H_{118}N_4O_8$ C 77.76, H 8.69, N 4.12; found C 77.71, H 8.65, N 4.14%. UV-Vis ($CHCl_3$) λ_{max}/nm (ε_{max}/1 mol^{-1} cm^{-1}): 649 (5.41×10^3), 593 (6.65×10^3), 556 (8.46×10^3), 519 (1.98×10^4), 420 (3.19×10^5).

The complex Yb[$(C_{10}COMP)_4P$]OH (see figure 1) was synthesized and purified by literature methods [9]. The free base $H_2(C_{10}BOMP)_4P$ (0.3 g, 0.22 mmol) and anhydrous $YbCl_3$ (0.6 g, 2.14 mmol) were heated in an imidazole (10 g) melt at 210°C under the protection and stirring of a dry nitrogen stream for one hour. The extent of the reaction was followed by measuring the UV-Vis spectra of the reaction solution at ten minute intervals. After cooling the reaction mixture to 100°C, 200 ml distilled water was added and the solution filtered, washed several times with distilled water in a separating funnel, and finally the product was dried under vacuum.

The crude product was dissolved in a mixture of chloroform (300 ml) and methanol (30 ml). The solution was shaken with 100 ml of 0.1% aqueous $AgNO_3$ and the chloroform layer was separated. To the chloroform layer, 20 ml methanol and 30 ml chloroform were added. The mixture was again shaken with 100 ml of 0.1% aqueous $AgNO_3$. This procedure was repeated until no more AgCl precipitated. The chloroform solution was

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*Author for correspondence; e-mail: zhixin-zhao@yeah-net

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concentrated and applied to a silica gel column. The first band containing a small amount ligand, $H_2(C_{10}BOEP)_4P$, was eluted by chloroform. The second band eluted by methanol contained the hydroxy complex; yield 90%. IR(CeI) ν_{max}/cm^{-1}: 3578 (OH str.), 1138 (Ln–OH, bend), 378 (Ln–OH str.). $m/z = 1547$ (M$^+$), 1532 ([M–HO + 1])$^+$. ^{1}H NMR: δ_H (C_6D_6, 400 MHz), 9.30 (s, 8H, pyrrole ring), 7.46 (m, 12H, meso-phenyl protons), 4.33 (t, 20H, phenyl methyloxy protons), 3.58 (t, 8H, C_6H_4–O–CH_2), 1.02 (t, 12H, CH_3), 1.40 (m, 64H, $[CH_2]_8$), 0.39 (s, broad, OH). ^{13} Elemental analysis: calcd for $C_{88}H_{117}N_4O_9Yb$ C 67.9; H 7.26, N 3.73; found C 67.8, H 7.27, N 3.74%. UV-Vis ($CHCl_3$) λ_{max}/nm (ε_{max}/1 mol^{-1} cm^{-1}): 594 (3.21×10^3), 556 (1.37×10^4), 520 (2.61×10^3), 427 (3.77×10^5).

3. Results and discussion

The molar conductance values of the complex and the ligand in chloroform were 0.26 and 0.15 Ω^{-1} cm^2 mol^{-1}, respectively. It is clear that the complex and ligand show non-electrolytic behaviour [10].

Figure 2 shows the DSC thermogram of Yb-$[(C_{10}COMP)_4P]OH$ (heating rate: 10°C min^{-1}). Two endothermic peaks can be seen at -10.6°C ($\Delta H =$ 55.9 kJ mol^{-1}) and at 42.3°C ($\Delta H = 14.7$ kJ mol^{-1}), corresponding to the melting and cleaning points, respectively. Two rather broad exothermic peaks at 23°C ($\Delta H = -1.85$ kJ mol^{-1}) and at -34.3°C (-64.2 kJ mol^{-1}) were observed on cooling. When a sample of Yb-$[(C_{10}BOMP)_4P]OH$ was cooled from room temperature to -38°C, it changed into a crisp, powered crystal with a sheen. On slowly heating, the sample changed to a highly viscous liquid in the range -8–40°C, showing the liquid crystal state. At 45°C, its fluidity was obvious enhanced and it became an isotropic liquid. The complex is apparently stable up to 250°C, where upon decomposition begins.

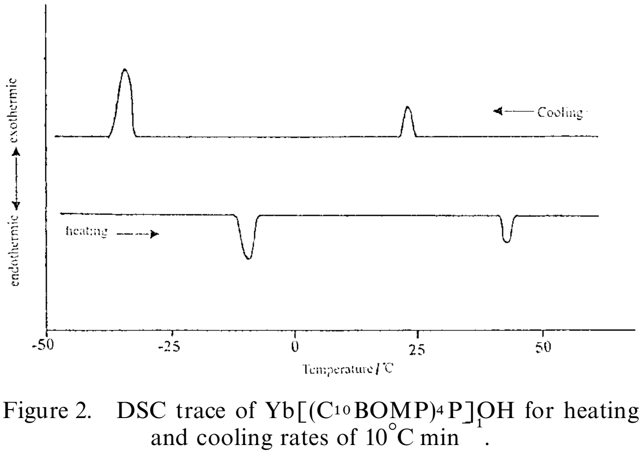

Figure 2. DSC trace of $Yb[(C_{10}BOMP)_4P]OH$ for heating and cooling rates of 10°C min^{-1}.

The metallomesogen phase was confirmed by polarizing optical microscopy. When the metallomesogen was slowly cooled from the isotropic phase to 0°C, we observed a liquid crystal phase texture of the complex $Yb[(C_{10}BOMP)_4P]OH$ (see figure 3).

The X-ray scattering at 0°C (see figure 4) shows reflections with d-spacings of 39.9 and 23.2 Å, corresponding to the first two reflections of a hexagonal columnar structure (reciprocal d-spacings of $1:\sqrt{3}$) [11]. We conclude that the mesophase structure is probably a hexagonal columnar discotic columnar Col_h (previously designated D_h). In the wider angle region, a sharp reflection appeared at $2\theta = 12°$ (*c*. 7.4 Å); it may indicate the presence of dimers in the mesophase. This peak (at 7.4 Å) had also been observed for the columnar mesophase of 2,3,9,10,16,17,23,24-octakis (octadecylthio)-phthalocyaninatooxotitanium(IV) [12]. Moreover, there is a broad halo centred at $2\theta = 20°$ (*c*. 4.4 Å) derived from alkyl chain melting.

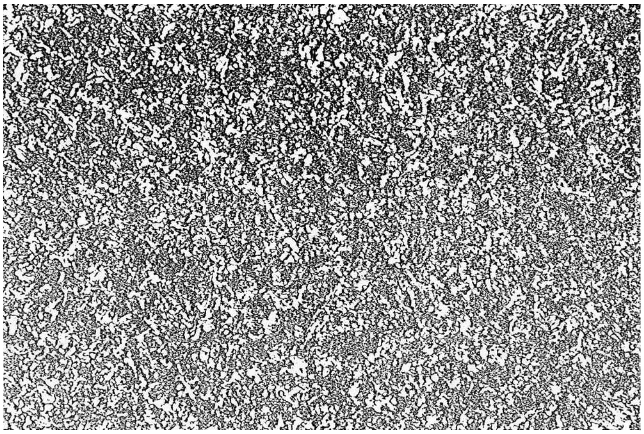

Figure 3. Optical texture of $Yb[(C_{10}BOMP)_4P]OH$ obtained on cooling from the isotropic liquid to 0°C.

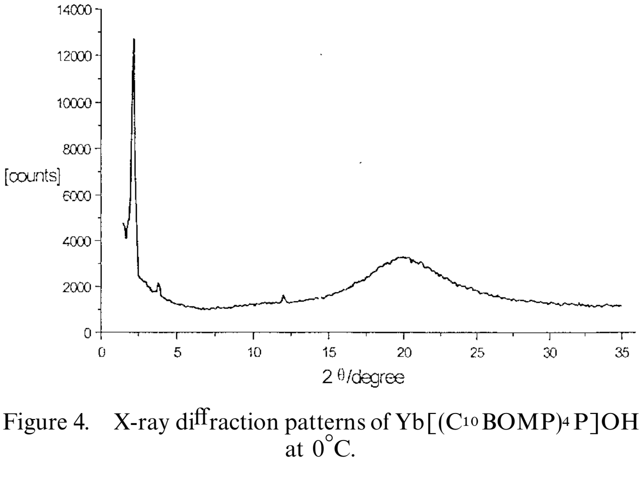

Figure 4. X-ray diffraction patterns of $Yb[(C_{10}BOMP)_4P]OH$ at 0°C.

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