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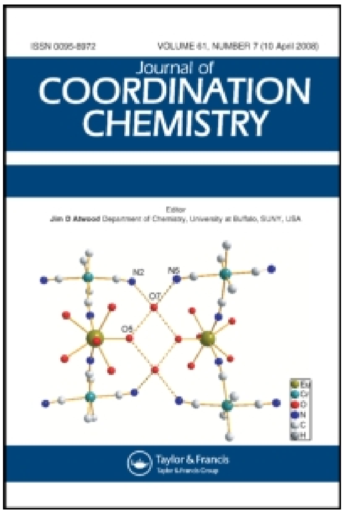

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Synthesis and characterization of a new unsymmetrical porphyrin liquid crystal and its lanthanide complexes

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Synthesis and characterization of a new unsymmetrical porphyrin liquid crystal and its lanthanide complexes

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A *meso*-substituted unsymmetrical porphyrin liquid crystal, 5-(4-myristyloxy)phenyl-10,15,20-triphenyl porphyrin, and a series of its lanthanide complexes, (lanthanide ions: Gd, Tb, Dy, Ho and Er) with acetylacetone were synthesized and characterized by elemental analyses, molar conductances, UV-Vis, IR and ^{1}H NMR spectra. A structure is proposed in which the porphyrin is as a tetradentate ligand and acetylacetonate is bidentate to the lanthanide. Luminescence spectra show that quantum yields of the Q band fluorescence are in the region 0.027–0.191. DSC data and an optical textural photo using a polarizing microscope indicates that the compounds have liquid crystalline character.

Keywords: Porphyrin; Acetylacetone; Lanthanide complexes; Liquid crystal

1. Introduction

Porphyrins and metalloporphyrins are core biological macromolecular structures such as the heme group of blood, the special pairs of chlorophyll, vitamin B_{12} and the cytochromes [1], and have received considerable attention because of their interesting excited state chemistry and catalytic behavior [2]. These centrosymmetric molecules have an extensive system of delocalized π electrons, can easily be modified, and have many different applications in nonlinear absorption [3] and artificial photosynthesis [4]. The free base of porphyrins is an excellent hole-burning photochemical pigment, so much attention has been given to the possibility of their use as high density information storage [5–6].

There has been increasing interest in designing and synthesizing discotic liquid crystals due to their potential application in fields like charge-transfer processes [7], photoconductivity [8], thermal switching [9] and organic electroluminescence [10]. Most discotic liquid crystals have a molecular structure that consists of a flat central core with several alkyl chains placed around the outside edge of the core [11]. Porphyrins substituted with long alkyl chains at the peripheral porphine are discotic liquid crystals. Since the discovery of the first porphyrin discotic liquid crystal in 1988 [12],

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liquid-crystalline porphyrins have been widely studied as materials for molecular electronics, due to their peculiar properties as uni-dimensional conductors [13] and semiconductors [14]. Many efforts to synthesize porphyrin liquid crystals and their complexes have been made [15–17]; but most were symmetrical and limited to transition metal porphyrin complexes. Lanthanide ions can exhibit long luminescence lifetimes and large Stoke shifts because of their f orbits. Although their absorption coefficients are quite low, porphyrins can be used as antennae to form stable lanthanide porphyrin complexes and lead to the direct excitation of lanthanide ions. The first monoporphyrinate lanthanide complexes were used as nuclear magnetic resonance (NMR) shift reagents and dipolar probes [18]. Recently, studies showed that they could be used as CD probes for chirality sensing of biological substrates [19], electroactive materials [20] and have applications in fluoroimmuno assays [21], optical amplification [22] and laser systems [23].

In this article, a new *meso*-substituted unsymmetrical porphyrin liquid crystal, 5-(4-myristyloxy)phenyl-10,15,20-triphenyl porphyrin, MPTPP, and a series of lanthanide complexes with it and acetylacetone, Ln(MPTPP)acac, (where Ln = Gd, Tb, Dy, Ho, Er; MP = 5-(4-myristyloxy)phenyl; TPP = triphenyl porphyrin; acac = acetylacetone) were synthesized. They have been characterized by elemental analyses, molar conductances, UV-Vis, IR, ^{1}H NMR, and luminescence spectra. The liquid crystalline phase was characterized by differential scanning calorimetry (DSC), and the optical texture was observed by viewing the birefringence of the samples between crossed polarizers in a polarizing microscope. The structures of the ligand, MPTPP, the complexes, Ln(MPTPP)acac and the synthetic route are shown in scheme 1.

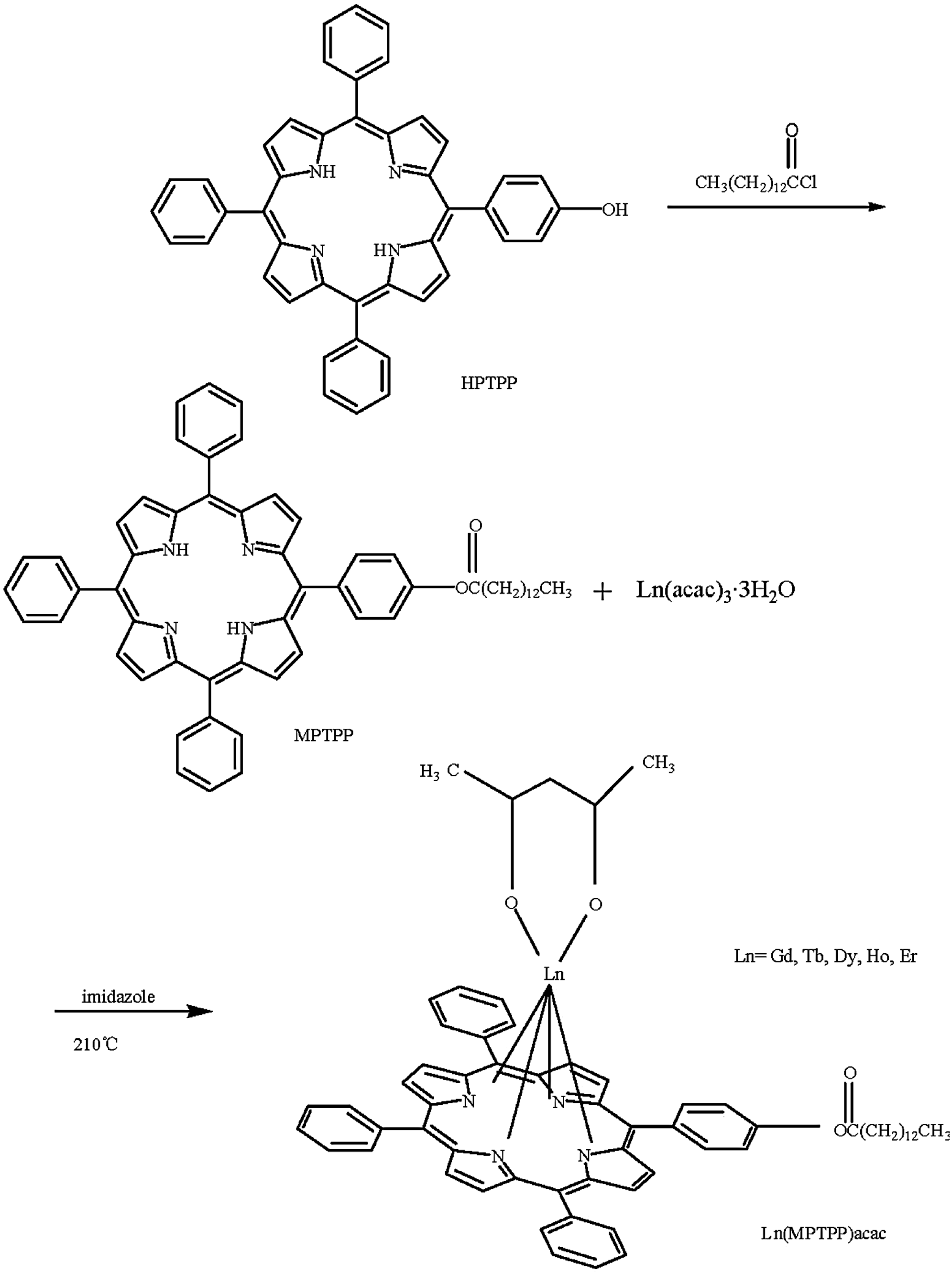
2. Experimental

2.1. *Reagents, apparatus and conditions*

All chemicals were reagent grade and were dried before use. Elemental analyses were carried out with a Perkin-Elmer 240C auto-elementary analyzer. The IR spectra (KBr pellets) were recorded on a Nicolet 5PC-FT-IR spectrometer in the region 400–4000 cm^{-1}. ^{1}H NMR spectra were obtained on a Varian-Unity-500 (MHZ) NMR spectrometer in $CDCl_3$ with TMS as internal standard. Electronic absoption spectra in the 350–700 nm region were recorded on a Shimadzu UV-240 spectrophotometer using chloroform as solvent. Excitation and emission spectra were recorded on a FS 920 Steady State Fluorescence Spectrometer at room temperature in the region 300–800 nm. Molar conductances at 25°C and 10^{-3} M in chloroform were measured on a DDX-111A conductometer. Transition temperatures and heats of fusion were determined at scan rates of 10°C min^{-1} by differential scanning calorimetry using a NETESCH DSC 204. Optical microscopic properties were observed by a XinTian XP1 (CCD: TOTA-500II) polarized light microscope equipped with a variable temperature stage (Linkam TMS 94).

2.2. *Synthetic procedures*

2.2.1. Myristyl chloride. Myristyl chloride was synthesized from the reaction of myristic acid and thioylchloride according to the published procedure [24].


NH
N
N
HN
OH
HPTPP
O
CH3(CH2)12CCl
NH
N
N
HN
O
OC(CH2)12CH3
+ Ln(acac)3·3H2O
MPTPP
imidazole
210℃
H3 C
CH3
O
O
Ln
Ln= Gd, Tb, Dy, Ho, Er
N
N
N
N
O
OC(CH2)12CH3
Ln(MPTPP)acac

Scheme 1.

2.2.2. MPTPP. 5-(4-Hydroxy)phenyl-10,15,20-triphenylporphyrin, HPTPP, [HP = 4-hydroxyphenyl; TPP = triphenylporphyrin] was prepared and purified according to the literature [25].

5-(4-Myristyloxy)phenyl-10,15,20-triphenyl porphyrin, MPTPP (MP = 5-(4-myristyloxy)phenyl; TPP = triphenyl porphyrin) was prepared by the reaction of HPTPP with myristyl chloride.

HPTPP (1.00 g, 1.59 mmol) was dissolved in 270 mL hot benzene. To this solution while stirring briskly at 70°C, was added triethylamine (2.00 mL, 11.37 mmol) and then dropwise a solution of myristyl chloride (2.3 mL, 14 mmol) and 10 mL benzene within 0.5 h. The solution was refluxed for 8 h. Benzene was distilled from the mixture. It was then mixed with 2 volumes of chloroform and extracted three times with equal volumes of distilled water. Concentrated the chloroform solution and added to a neutral aluminum oxide column (2.5 × 15 cm). The first band containing HPTPP was eluted by chloroform. The second band containing MPTPP was eluted by chloroform containing 10% absolute ethanol. The product was dried *in vacuo*. The yield was 1.10 g (yield: 82.5%). ^{1}H NMR for $C_{58}H_{56}N_4O_2$ ($CDCl_3$): $\delta = 8.927$ (d, 6H, pyrrole ring), 8.67 (d, 2H, pyrrole ring), 7.56, 7.83, 8.30, 7.34 (m, 19H, phenyl), 2.81–2.84 (d, 2H, $-OOCCH_2$), 1.26–1.99 (m, 22H, $-(CH_2)_{11}-$), 0.95–0.97 (d, 3H, $-CH_3$) and -2.715 (s, 2H, pyrrole N–H). Anal. Calcd for $C_{58}H_{56}N_4O_2$ (%) (m.p. >400°C): C, 82.86; H, 6.67; N, 6.67. Found: C, 82.73; H, 6.61; N, 6.53.

2.2.3. Ln(MPTPP)acac. The lanthanide acetylacetonate complexes $Ln(acac)_3 \cdot 3H_2O$ (Ln = Gd, Tb, Dy, Ho, Er; Hacac = acetylacetone) were prepared according to the literature [26].

For synthesis of the complexes, Tb(MPTPP)acac can serve as the example. Tb(MPTPP)acac was prepared by reaction of $Tb(acac)_3 \cdot 3H_2O$ (0.50 g, 1.13 mmol) with MPTPP (0.20 g, 0.24 mmol) in melted imidazole (10 g) at 210°C under dry N_2 for about 3.5 h. The extent of the reaction was followed by measuring UV-Vis spectra of the solution. The reaction mixture was cooled to 70°C and 10 mL absolute ethanol was added. Chloroform (20 mL) was added and then the solution was extracted three times with two volumes of water. The chloroform solution was chromatographed on a neutral aluminum oxide column (1.5 × 15 cm). The first band containing unreacted MPTPP was eluted with chloroform containing 10% ethanol. The second band was eluted with dimethylsulphoxide containing 50% ethanol. Water was added to the second fraction and the product was extracted by chloroform. The yield was about 0.10 g (38%). ^{1}H NMR for $TbC_{63}H_{63}N_4O_4$ ($CDCl_3$): $\delta = 8.92$ (d, 6H, pyrrole ring), 8.25 (d, 2H, pyrrole ring), 7.337 (m, 19H, phenyl), 2.41 (d, 2H, $-OOCCH_2$), 1.74 (m, 22H, $-(CH_2)_{11}-$), 0.933 (d, 3H, $-CH_3$) and 1.307 (s, 6H, acetylacetonate CH_3). Anal. Calcd for $TbC_{63}H_{63}N_4O_4$ (%) (m.p. >200°C): C, 68.86; H, 5.74; N, 5.10. Found: C, 68.71; H, 5.81; N, 5.18.

Other lanthanide complexes were prepared by the same route. Anal. Calcd for $GdC_{63}H_{63}N_4O_4$: C, 68.90; H, 5.74; N, 5.10. Found: C, 68.82; H, 5.60; N, 5.21. Anal. Calcd for Dy $C_{63}H_{63}N_4O_4$: C, 68.57; H, 5.71; N, 5.08. Found: C, 68.49; H, 5.60; N, 5.11. Anal. Calcd for Ho $C_{63}H_{63}N_4O_4$: C, 68.42; H, 5.70; N, 5.07. Found: C, 68.35; H, 5.61; N, 5.10. Anal. Calcd for Er $C_{63}H_{63}N_4O_4$: C, 68.28; H, 5.69; N, 5.06. Found: C, 68.15; H, 5.75.

Table 1. UV-Vis spectra of the ligand and complexes.

	λ_{max} (nm) (log ε)				
Ligand/complexes	Soret (B) band	Q bands			
MPTPP	419 (5.48)	516 (4.43)	550 (4.26)	589 (4.24)	647 (4.24)
Gd(MPTPP)acac	422 (5.30)	517 (2.42)	552 (3.86)	591 (2.60)	
Tb(MPTPP)acac	422 (5.03)	515 (2.66)	552 (3.60)	591 (2.83)	
Dy(MPTPP)acac	421 (5.21)	516 (2.30)	552 (3.65)	591 (2.48)	
Ho(MPTPP)acac	422 (5.34)	516 (2.21)	552 (4.87)	590 (2.47)	
Er(MPTPP)acac	422 (5.44)	515 (2.10)	552 (3.98)	591 (3.56)	

Table 2. Infrared spectra of the ligand and complexes.

MPTPP	Gd	Tb	Dy	Ho	Er	Intensity	Assignment
3318						m	ν(N–H) (pyrrole)
2921	2921	2921	2921	2921	2921	w	ν(C–H) (phenyl)
2849	2850	2849	2849	2849	2850	w	ν(C–H) (phenyl)
1759	1763	1765	1760	1761	1762	w	ν(C=O) (carbony)
1601	1594	1601	1598	1602	1602	w	ν(C=C) (phenyl)
1506	1506	1510	1509	1510	1510	w	ν(C=C) (phenyl)
1469	1460	1463	1464	1465	1469	m	ν(C–H) (pyrrole)
1353	1323	1325	1326	1327	1331	m	ν(C–N) (pyrrole)
1197	1201	1200	1199	1198	1199	w	ν(C–O) (acyloxy)
962							δ(N–H)
723	725	726	726	726	726	w	δ(CH_2)
	1511	1514	1511	1510	1511	m	ν(C–C) (Hacac)

* s: strong, m: medium, w: weak.

3. Results and discussion

3.1. *UV-Vis spectra*

Characteristic Soret (B) and Q bands of porphyrin and metallophyrins in the visible region are assigned as transitions from ground state (S_0) to the second excited singlet state (S_2) and lowest excited singlet state (S_1). The maximum absorption wavelength of B and Q bands in the visible and near-ultraviolet region for the ligand and complexes are listed in table 1. Compared with the ligand, the Soret bands of complexes are red shifted. All the Q bands of complexes are quite different from those of the ligand. The number of Q bands is reduced to three due to an increase in symmetry, in aggreement with Gouteman's four-orbital model [27].

3.2. *Infrared spectra*

The main frequencies (cm^{-1}) and assignments of the ligand and complexes are given in table 2. The bands at 3320 cm^{-1} and 962 cm^{-1} in the free porphyrin are assigned to the N–H stretching vibration and the bending vibration of the porphyrin core. This band is absent in the complexes, because the hydrogen atoms have been replaced by the lanthanide ions to form Ln–N bands. Bands at 1510–1514 cm^{-1} in the complexes are due to the C–C stretching vibrations of the coordinated acetylacetonate ring [28].

The above spectra indicate that an acetylacetonate ring and porphyrinate ring are coordinated to the lanthanide ion [29].

3.3. ^{1}H NMR spectra

The ^{1}H NMR chemical shift values (δ, ppm) were measured in deuterated chloroform. We collected the corresponding data of ligand MPTPP and complex Tb(MPTPP)acac as above. Compared with the ligand, a signal of Tb(MPTPP)acac at 1.307 (6H, acetylacetonate CH_3) appeared, and the signal at −2.715 ppm disappeared, indicating that the ligand and acetylacetone are coordinated to the lanthanide ion. Other peaks of the complex were broadened because of the paramagnetism of the lanthanide ions.

3.4. *Molar conductances*

The molar conductance values of the ligand and its Gd, Tb, Dy, Ho and Er complexes are at 0.120, 0.022, 0.02, 0.02, 0.0195 and 0.023 $\Omega^{-1}\,cm^2\,mol^{-1}$, respectively, in 10^{-3} M chloroform solution at 25°C. The ligand and complexes show nonelectrolytic behavior [30].

All of the results are consistent with an unsymmetrical structure of free porphyrin. The myristyloxy group was introduced to the *para*-position on one phenyl of porphyrin. In the complexes the ligand, MPTPP, is coordinated to a lanthanide in a tetradentate fashion. Hacac is coordinated to the same lanthanide ion in a bidentate fashion. Therefore, the coordination number of the central lanthanide ion is six. The structure is shown in scheme l. The lanthanide ion is considered to lie above the porphyrin plane of the ring.

3.5. *Luminescence spectra*

In order to study the photophysical properties of the ligand and complexes, the luminescence spectra were examined. Table 3 gives the excitation spectral maximal wavelengths ($\lambda_{ex} = 620$ nm). Figure 1 gives the excitation spectra of the ligand and Dy(MPTPP)acac.

Compared with their UV-Vis absorption spectra, the Soret bands (except Tb) split into two spectral bands. The maximal wavelengths of complexes also undergo small red shifts.

Table 3. Excitation spectral data of ligand and complexes.

Compounds	Maxima (λ_{max}, nm)					
MPTPP	406	426	516	549	595	650
Gd(MPTPP)acac	408	428	517	551	590	
Tb(MPTPP)acac	415	518	551	597		
Dy(MPTPP)acac	412	427	518	549	595	
Ho(MPTPP)acac	412	431	517	551	595	
Er(MPTPP)acac	407	433	516	550	595	

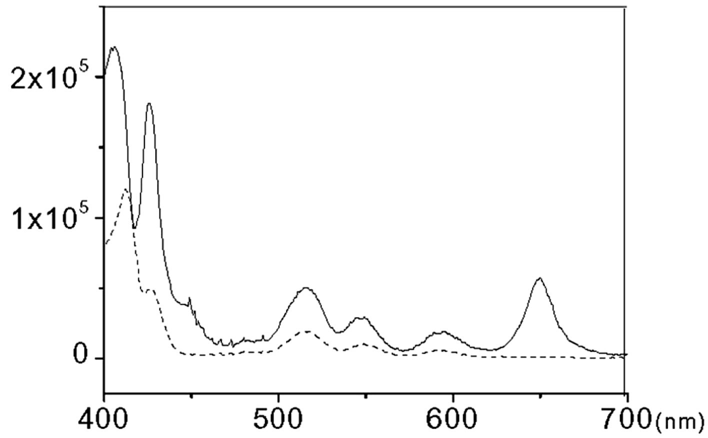


Figure 1. Excitation spectra of ligand (solid line) and complex Dy(MPTPP)acac (dash line).

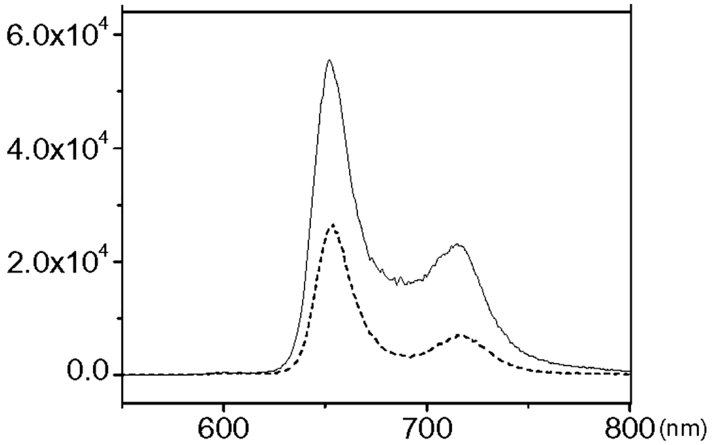


Figure 2. Emission spectra of ligand (solid line) and complex Dy(MPTPP)acac (dash line).

Table 4 gives the emission spectral data and quantum yields (Φ_f) of the ligand and complexes ($\lambda_{em} = 417$ nm, calculated using ZnTPP as a standard, the quantum yield of which is 0.033 [31]).

In porphyrin complexes there are fluorescence bands of S_2 (B band) and S_1 (Q band). B (Soret) band and Q band are attributed to transition from the second excited singlet state S_2 to the ground state S_0, $S_2 \rightarrow S_0$, and from the lowest excited singlet state S_1 to S_0, $S_1 \rightarrow S_0$, respectively. The Soret fluorescence is about two orders of magnitude weaker than Q band emission; its fluorescence is sometimes too low to be observed. This fluorescence emission does not occur at room temperature upon excitation at 417 nm. Φ_f of Q bands depends on the relative rates of the radiative process $S_1 \rightarrow S_0$ and two radiationless process $S_1 \rightarrow S_0$ and $S_1 \rightarrow Tn$. Table 4 shows that Φ_f of the complexes and ligand are less than 0.20. Therefore the spin forbidden process S_1Tn plays a dominant role in the radiationless deactivation of S_1 in porphyrin complexes [31]. Figure 2 shows the emission spectra of ligand and Dy(MPTPP)acac.

Table 4. Emission spectral data of ligands and complexes.

Compounds	Q (0–1)	Q (0–2)	Φ_f
MPTPP	652	715	0.115
Gd(MPTPP)acac	653	718	0.053
Tb(MPTPP)acac	653	716	0.163
Dy(MPTPP)acac	653	719	0.191
Ho(MPTPP)acac	654	715	0.086
Er(MPTPP)acac	654	719	0.027

3.6. *Liquid crystals*

The phase changes of porphyrin and complexes were characterized by differential scanning calorimetry (DSC). For the porphyrin, there are two distinct peaks in DSC curve which represent three phase changes at a heating rate of $10^{\circ}\mathrm{C\,min^{-1}}$. The phase change temperature and enthalpy of MPTPP was listed as follows.

$$\mathrm{C}\ \underset{-8.84^{\circ}\mathrm{C}\ (-0.098\,\mathrm{kJ\,mol^{-1}})}{\overset{-5.17^{\circ}\mathrm{C}\ (3.41\,\mathrm{kJ\,mol^{-1}})}{\rightleftharpoons}}\ \mathrm{LC}\ \underset{31.0^{\circ}\mathrm{C}\ (-4.125\,\mathrm{kJ\,mol^{-1}})}{\overset{43.9^{\circ}\mathrm{C}\ (4.12\,\mathrm{kJ\,mol^{-1}})}{\rightleftharpoons}}\ \mathrm{IL}$$

(Heating rate: $10^{\circ}\mathrm{C\,min^{-1}}$; C = crystal; LC = liquid crystal; IL = isotropic liquid; heating ($\rightharpoonup$); cooling ($\leftharpoondown$).)

This shows that the ligand, MPTPP, has one liquid crystalline phase at room temperature. For the complexes, Ln(MPTPP)acac, only one peak in the DSC curve makes it clear that they have no liquid crystalline phase.

The optical texture was observed by viewing the birefringence of the sample between crossed polarizers in a polarizing microscope. Figure 3 shows the birefringence texture micrograph of the ligand, MPTPP, at 25°C.

Lanthanide porphyrin complexes, Ln(MPTPP)acac (Ln: Gd, Tb, Dy, Ho and Er), show no liquid crystalline behavior. Because both acetylacetone and porphyrin were coordinated to the lanthanide ion and acetylacetone is very large, this structure is unfavorable for close packing of the macromolecule to form a columnar liquid crystal. Lanthanide porphyrin liquid crystals might be more readily made with an axial ligand [32].

4. Conclusions

A new unsymmetrical porphyrin and its lanthanide complexes with acetylacetone were prepared. Spectroscopic evidence indicates that the ligand is unsymmetric and the complexes can be considered as six-coordinate species with four N of the porphyrinate and two O of acetylacetonate coordinated to the lanthanide ion, as shown in scheme 1. The fluorescent emission of Q bands is in the region 652–719 nm and quantum yields are 0.027–0.191. These compounds may have applications as optical materials. DSC data and the optical texture seen in the polarizing microscope indicate that the ligand is a liquid crystalline compound at room temperature.

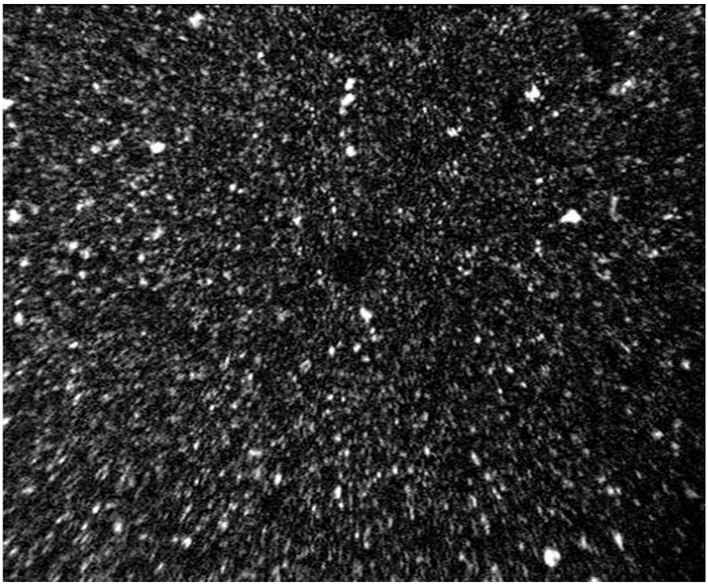


Figure 3. The birefringence texture micrograph of the ligand, MPTPP, at 25°C.

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