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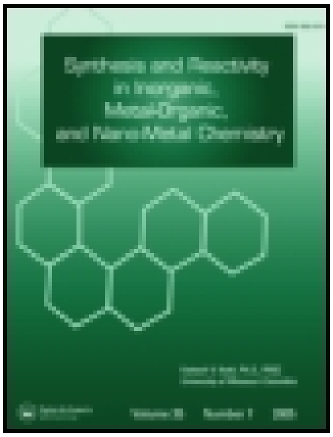

Synthesis and Reactivity in Inorganic, Metal-Organic, and Nano-Metal Chemistry
Publication details, including instructions for authors and subscription information:
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Lanthanide Porphyrin Complexes: Synthesis and Properties

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Published online: 10 Nov 2009.

To cite this article: Yujing Zhang , Jianhui Shi , Yan Zheng , Miao Yu & Guofa Liu (2009) Lanthanide Porphyrin Complexes: Synthesis and Properties, Synthesis and Reactivity in Inorganic, Metal-Organic, and Nano-Metal Chemistry, 39:9, 605-608

To link to this article: http://dx.doi.org/10.1080/15533170903328537

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Synthesis and Reactivity in Inorganic, Metal-Organic, and Nano-Metal Chemistry, 39:605–608, 2009
Copyright © Taylor & Francis Group, LLC
ISSN: 1553-3174 print / 1553-3182 online
DOI: 10.1080/15533170903328537

Lanthanide Porphyrin Complexes: Synthesis and Properties

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A new *meso*-substituted unsymmetrical porphyrin, 5-(4-myristyloxy)phenyl- 10,15,20-triphenyl porphyrin, and a series of its hydroxy lanthanide complexes, (lanthanide ions: Gd, Tb, Dy, and Ho) were synthesized and characterized by elemental analyses, molar conductances, UV-Vis, IR and ^{1}H NMR spectra. Their luminescent properties are studied by emission spectra. Q (0-0) fluorescence bands of the complexes are in the region 649–650 nm and Q (0-1) bands 714–715 nm. Quantum yields (Φf) of Q band for the complexes are in the range 0.00151–0.08433 and ligand 0.07459.

Keywords complexes, hydroxyl, lanthanide, porphyrin

INTRODUCTION

The porphyrins are a class of macrocyclic compounds that has high chemical and thermal stability.[1] For these centrosymmetric molecules have an extensive system of delocalized π electrons, moreover molecules can easily be modified,[2] they have many different applications in nonlinear absorption[3] and artified photo synthesis.[4] Besides, the porphyrin ring can coordinate a wide range of metal ions and it is available with a range of peripheral substitution, some of which are fairly easy to synthesize. These features not only provide for structural diversity but also allow the electronic and optical properties to be fine-tuned.[5] Among abundant porphyrins and metalloporphyrin complexes, lanthanide porphyrins have attracted an increasing interest for their potential applications in electroactive materials,[6] laser system,[7] molecular information storage,[8] CD probes for chirality sensing of biological substrates,[9] nuclear magnetic resonance (NMR) shift reagents and dipolar probes[10] and so forth.

Our previous studies have provided some results on the lanthanide complexes.[11–16] In this paper, a new *meso*-substituted unsymmetrical porphyrin, 5-(4-myristyloxy) phenyl-10, 15, 20–triphenyl porphyrin (**2**) and a series of lanthanide compounds (**3**) are reported. They also have been characterized by elemental analyses, molar conductances, UV -Vis, IR and ^{1}H NMR spectra. We also studied their luminescent properties by emission spectra.

EXPERIMENTAL

Reagents, Apparatus and Measured 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 (MH_Z) NMR spectrometer in $CDCl_3$ and TMS as internal standard. Electronic absorption spectra in the 350–700 nm region were recorded on a Shimadzu UV-240 spectrophotometer using chloroform as solvent, emission spectra on a FLR006 fluorescence spectrometer at room temperature in the region 300–800 nm. Molar conductances at 25°C and 10^{-3} mol·L^{-1} in chloroform were measured on a DDX-111A conductometer.

Synthetic Procedures

The synthesis procedure for the porphyrin is illustrated in Scheme 1. Myristyl chloride was synthesized from the reaction of myristic acid and thioylchloride according to the published procedure.[17] The unsymmetrically phenyl-substituted porphyrin **1** was prepared and purified according to the literature.[18] The synthesis of porphyrin **2** was based on the following procedures (see Scheme 1.)

Porphyrin **1** (1.00 g, 1.59 mmol) was dissolved in 270 ml heating benzene, and triethylamine (2.00 ml, 11.37 mmol) was added. Then added dropwise the solution of myristyl chloride (2.3 ml, 14 mmol) and 10 ml benzene within 0.5 h to the above solution with quickly stirring at 70°C. The solution was refluxed for 8 h. Benzene was distilled out of the mixture. then mixed with 2 volumes of distilled water and extracted three times with equal volumes of water. Concentrated chloroform solution and added to a neutral aluminum oxide column (2.5 × 15 cm). The first band containing **1** was eluted by chloroform. The second band containing **2** was eluted by chloroform containing 10%

Reccieved 11 July 2009; accepted 11 September 2009.

We would like to thank the National Natural Science Foundation of China for financial support of this work (No. 20801022).

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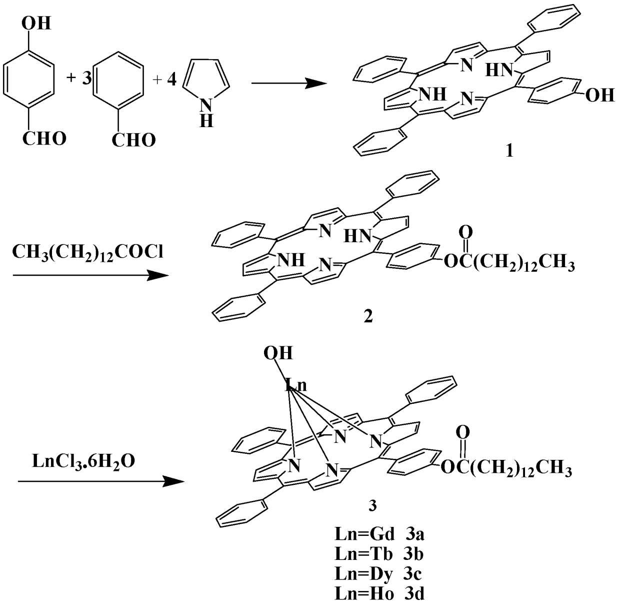

SCH. 1. Synthesis of the porphyrin ligand and complexes.

absolute ethanol. The product was dried in vacuum. The yield was 1.10 g.

$C_{58}H_{56}N_4O_2$(840.44): calcd. C, 82.82; H, 6.71; N, 6.66. Found C, 82.82; H, 6.71; N, 6.66.^{1}H NMR (500 MHz, $CDCl_3$): $\delta = 8.927$ (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).

The hydroxy lanthanide complexes **3** were prepared according to the following method. We take 3a for example. A mixture of **2** (300 mg, 0.4 mmol) and hydration $GdCl_3 \cdot 6H_2O$ (600 mg, 1.5 mmol) were heated in an imidazole (10.0 g) melt at 210°C under the protection and stirring of a dry nitrogen stream for two hours. The extent of the reaction was followed by measuring the Uv-visible spectra of the reaction solution at ten minute intervals. After cooling the reaction mixture to 100°C, 150 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 chloroform (200 ml). The solution was shaken with 100 ml 0.1% aqueous $AgNO_3$ and the chloroform layer was separated. The mixture of chloroform (30 ml) and methanol (20 ml) were added to the separated chloroform. The mixture was again shaken with 100 ml 0.1% aqueous $AgNO_3$. This procedure was repeated until no more AgCl precipitated. The chloroform solution was concentrated and applied to chromatography aluminum oxide column. The first band containing a small amount ligand, **2**, was eluted by chloroform. The second band eluted by chloroform containing 20% methanol, obtained the solution of the complex. The product was crystallized by concentrated the solution and finally product was dried under vacuum. Other lanthanide complexes (**3b**, **3c**, **3d**) were prepared according to the same route above.

RESULTS AND DISCUSSION

Elemental Analyses

The elemental analyses for carbon, hydrogen, nitrogen, empirical formulas, yields and decomposition temperature are given in Table 1.

Uv-Vis Spectra

The maximum absorption values (λ_{max}) of the ligand and complexes are given in Table 2. The absorption bands of the free base **2** appear at 418, 515, 550, 591 and 646 nm. The relative intensities of these bands are as follows: $418 \gg 515 > 550 > 591 > 646$ nm. The absorption bands of the complexes **3d** appear at 418, 516, 552, 591 nm. The relative intensities are $418 \gg 552 > 591 > 516$ nm. Compared with the ligand **2**, the number of the absorption bands of the complexes decreases and the absorption bands exhibit small shifts to longer wave lengths.

The UV spectra of the complexes show bands characteristic of metalloporphyrins.[19] The absorption band behaviors of other complexes (Gb, Tb, Dy) are also similar to the complex **3d**.

Infrared Spectra

The main band frequencies (cm^{-1}) and assignments of the ligand **2** and complexes **3a**, **3b**, **3c**, **3d** were given in Table 3.

The bands at 3322 cm^{-1} and 965 cm^{-1} in the free porphyrin, are assigned to the N-H stretching and bend vibrations of the porphyrin core, respectively. These two vibration bands

TABLE 1
Characterization data of the compounds[a]

Compounds	Empirical formula	C (%)	H (%)	N (%)	Yield (%)	Dec.tem.(°)
2	$C_{58}H_{56}N_4O_2$	82.80 (82.82)	6.72 (6.71)	6.66 (6.66)	82.5	>400
3a	$GdC_{58}H_{55}N_4O_3$	68.78 (68.74)	5.45 (5.47)	5.54 (5.53)	84.3	>200
3b	$TbC_{58}H_{55}N_4O_3$	68.60 (68.63)	5.46 (5.46)	5.53 (5.52)	83.2	>200
3c	$DyC_{58}H_{55}N_4O_3$	68.40 (68.39)	5.42 (5.44)	5.51 5.50)	86.5	>200
3d	$HoC_{58}H_{55}N_4O_3$	68.20 (68.23)	5.42 (5.43)	5.50 (5.49)	84.7	>200

[a] Theoretical values are given in parentheses.

TABLE 2
UV-Vis spectra of the ligand and complexes

Compounds	λ_{max}/ nm(ε [$10^3M^{-1}cm^{-1}$])				
2	418 (1000)	515 (13.4)	550 (6.83)	591 (5.52)	646 (4.86)
3a	419 (1010)	514 (16.0)	551 (8.80)	591 (6.17)	
3b	423 (1000)	513 (5.52)	553 (1.93)	592 (4.86)	
3c	418 (2640)	516 (3.60)	552 (1.60)	591 (4.20)	
3d	422 (214)	516 (3.39)	551 (1.10)	590 (2.48)	

of complexes disappear, since the hydrogen atoms have been replaced by the lanthanide ions to form Ln-N bands. Existence of the Ln-OH bending vibration band in the region 1067–1071 cm^{-1} show that the oxygen atom of hydroxy group is bonded to lanthanide ion. All of above analysis prove that a hydroxyl and porphyrin ring are coordinated to the lanthanide ions to form complexes, **3a**, **3b**, **3c**, **3d**. Assignments of other absorption bands are also presented in Table 2.

^{1}H NMR Spectra

The ^{1}H NMR chemical shift values (δ, ppm) were measured in deuterium chloroform. We collected the corresponding data of ligand **2** and complex **3b** as above. Compared with the ligand, the signal peak of **3b**, at 0.19 ppm (1H, -OH) appeared, and the signal peak at -2.715 ppm disappeared. They indicated that the ligand and hydroxyl group are all coordinated to the lanthanide ion. Other peaks of the complex were broaded because of the paramagnetism of the lanthanide ions.

Molar Conductances

The molar conductance values of the ligand and hydroxy complexes, Gd, Tb, Dy, Ho, are at 0.120, 0.340, 0.202, and 0.342 $\Omega^{-1}cm^2mol^{-1}$, respectively, in 10^{-3} mol·L^{-1} chloroform solution at 25°C. And it is very clear that the ligand and complexes show all nonelectrolytic behavior[20].

TABLE 3
Infrared spectra of the ligand and complexes

2	3a	3b	3c	3d	Intensity	Assignment
3322					m	ν (N—H)(pyrrole)
2922	2922	2922	2922	2920	w	ν(C—H)(phenyl)
2849	2849	2849	2849	2850	w	ν(C—H)(phenyl)
1749	1748	1748	1748	1748	w	ν(C=O)(carbony)
1581	1578	1576	1576	1579	w	ν(C=C) (phenyl)
1508	1515	1517	1517	1516	w	ν(C=C) (phenyl)
1439	1441	1438	1438	1438	m	ν(C—H) (pyrrole)
1344	1329	1328	1328	1328	m	ν(C—N) (pyrrole)
1197	1196	1198	1200	1199	w	ν(C—O) (acyloxy)
965					m	δ(N—H)
723	721	722	722	722	w	δ(CH_2)
	1071	1069	1069	1067	m	ν(Ln—OH)

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

Luminescence Studies

Table 4 gives the emission spectral data and quantum yields of the ligand and complexes. The emission spectra of the ligand and complexes are shown in Figure 1.

There are fluorescence of the S_2 (B, Soret band) and S_1 (Q band) in porphyrin complexes. Fluorescence of the B (Soret) band is attributed to transition from the second excited singlet state S_2 to ground state S_0, $S_2 \rightarrow S_0$. The Soret fluorescence is about two orders of magnitude weaker than the $S_1 \rightarrow S_0$ of Q band emission. Its quantum yield is so low that sometimes fluorescence becomes unobservable. This fluorescence emission does not occur yet at room temperature in our experimental excited wavelength, 415 nm. Q (0-0) fluorescence bands of the complexes are in the region 649–650 nm and Q (0-1) bands 714–5 nm. Quantum yields (Φf) of Q band for the complexes are in the range 0.00151–0.08433 and ligand 0.07459. Quantum yields of the Q bands ($S_1 \rightarrow S_0$) depend on the relative rates of radiative process $S_1 \rightarrow S_0$ and two radiationless process internal conversion $S_1 \rightarrow S_0$ and intersystem crossing $S_1 \rightarrow$ Tn. Because the spin forbidden process $S_1 \rightarrow$ Tn play a predominant role for radiationless deactivation of S_1 in porphyrin complexes, the fluorescence quantum yields of complexes are much less than 0.2.[21]

The quantum yield is determined from the following equation:

$$Yu = Ys(Fu/Fs)(Au/As)$$

TABLE 4
Emission spectra of the ligand and complexes

	Peak values(nm)			
Compounds	Q(0-0)	Q(0-1)	Q(0-2)	Quantum yields, ϕ_f
2	607	649	712	0.07459
3a	600	649	715	0.08433
3b	605	648	716	0.00151
3c	604	651	710	0.02121
3d	605	647	698	0.03013

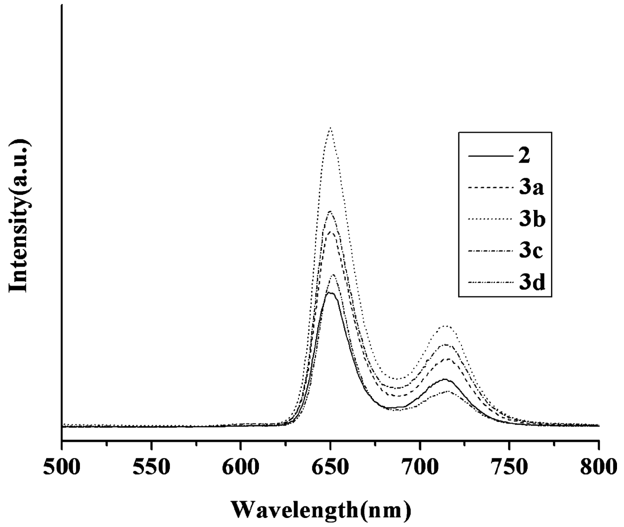

FIG. 1. Emission spectra of the ligand and complexes.

where Fu (F_{ZnTPP}) and F_{S}(F sample) are the measured fluorescence integral area of the the reference ZnTPP and sample, respectively, Au (A_{ZnTPP}) and As (A sample) are the absorbances of the the reference (ZnTPP) and sample, respectively, and Y_{ZnTPP} ($Y_{\mathrm{ZnTPP}} = 0.033$)[21] is the quantum yield of the reference at the same excitation wavelength.

CONCLUSION

In the work, we synthesized a new *meso*-substituted unsymmetrical porphyrin, 5-(4-myristyloxy) phenyl-10, 15, 20-triphenyl porphyrin, and a series of its hydroxy lanthanide complexes, (Lanthanide ions: Gd, Tb, Dy, and Ho). We thoroughly investigated their electronic absorption spectra, and luminescent property. A lanthanide porphyrin complex, one molecular porphyrin ligand is coordinated to a lanthanide ion in a tetradentate fashion and a hydroxyl group is coordinated to the same lanthanide ion. Therefore, the coordination number of the central rare earth ion is five.[22,23] The rare earth ion is expected to lie above the porphyrin molecular plane (see Scheme 1).

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