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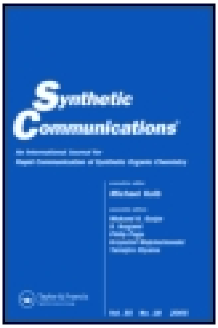

Synthetic Communications: An International Journal for Rapid Communication of Synthetic Organic Chemistry
Publication details, including instructions for authors and subscription information:
http://www.tandfonline.com/loi/lsyc20

Synthesis of Unsymmetrical Schiff-Base Porphyrin with O-Nitrobenzaldehyde and its Lanthanide Complexes

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Published online: 04 Dec 2007.

To cite this article: Dong-Mei Li , Zhi-Xin Zhao , Shu-Qing Liu , Guo-Fa Liu , Tong-Shun Shi & Xiao-Xun Liu (2000) Synthesis of Unsymmetrical Schiff-Base Porphyrin with O-Nitrobenzaldehyde and its Lanthanide Complexes, Synthetic Communications: An International Journal for Rapid Communication of Synthetic Organic Chemistry, 30:22, 4017-4026, DOI: 10.1080/00397910008087017

To link to this article: http://dx.doi.org/10.1080/00397910008087017

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SYNTHETIC COMMUNICATIONS, 30(22), 4017–4026 (2000)

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SYNTHESIS OF UNSYMMETRICAL SCHIFF-BASE PORPHYRIN WITH O-NITROBENZALDEHYDE AND ITS LANTHANIDE COMPLEXES

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Abstract: The synthesis of a new unsymmetrical Schiff-base porphyrin is reported from 5-(p-nitrophenyl)-10, 15, 20-triphenyl porphyrin and o-nitro benzaldehyde. Its lanthanide complexes are also reported. The ligand and its lanthanide complexes are characterized by UV, IR and ^{1}H NMR spectra.

Introduction

Porphyrins are widely studied for their interesting electronic, optoelectronic, optical and nonlinear optical properties [1, 2]. In recent years, synthetic mimics of the natural antenna complexes and photosynthesis reaction centers have been a major objective in the field of artificial photosynthesis [3-5]. Porphyrin units could

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be considered as a chromophore in electron transfer and energy transfer systems [6]. Therefore, tetra-phenyl porphyrin derivatives substituted with a conjugated system at the meso-position are of potential interest. Several groups reported the syntheses of meso-meso coupled arrays [7-9]. However, in general, this research work is limited to transition metal porphyrin complexes. Little work has been done on lanthanide porphyrin complexes because lanthanide ions have special electronic structures [10, 11].

In this paper, we report the first introduction of o-nitro benzaldehyde into porphyrin units as well as the preparation of its lanthanide complexes.

Experimental

All starting materials and solvents were commercial available analytical reagents grade. Hydrated tris (2,4-pentanedionato) lanthanides ($Ln(acac)_3 \cdot 3H_2O$) (Ln = Eu, Tb, Dy, Ho, Er, Tm, Yb) were prepared according to the literature [12].

Elemental analyses were obtained with a Perkin-Elmer 240C auto-elementary analyzer. Infrared spectra were recorded on a Nicolet 5PC-FT-IR spectrometer in the region 200-4000 cm^{-1} using KBr pellets. UV spectra were performed on a Shimadu UV-240 spectrophotometer using dichloromethane as solvent. ^1H NMR spectra were recorded on Varian-Unity-400 NMR spectrometer in $CDCl_3$ and the chemical shifts are reported relative to TMS.

1) Preparation of the Schiff-base porphyrin (H_2NBTpp)

0.6g of H_2NTpp (5-nitrophenyl-10, 15, 20-triphenyl porphyrin) [13, 14] was added to 40 mL of 25% hydrochloric acid, then 3.0 g of $SnCl_2 \cdot 2H_2O$ was added.

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After stirring at 65 °C for 25 min, the reaction mixture was cooled via an ice-water bath. The solution was adjusted to pH = 8.0 with concentrated NH_4OH and a gray precipitation appeared. The product was filtered and washed several times with dichloromethane. The dichloromethane solutions were combined, first washed with 2% NH_4OH, then water until the pH of the solution was 7.0, dried over anhydrous Na_2CO_3 and concentrated. The residue was chromatographed on neutral alumina (1.5×30 cm). The first eluting band (dichloromethane, R_f=0.70) was an impurity. The second band (dichloromethane, R_f=0.45) was collected, the fraction concentrated and the solid dried under vacuum to give violet microcrystalline H_2ATpp (5-aminophenyl-10, 15, 20-triphenyl porphyrin).

0.1 g of o-nitrobenzaldehyde was added to 20 mL of dimethylformamide (DMF) containing 0.3g of H_2ATpp. After refluxing for 4 h, the mixture was cooled to the room temperature, then washed three times with water. The insoluble part was filtered off and washed with chloroform for several times. The chloroform solution containing the crude product was collected, concentrated to about 30 mL and purified by column chromatography on neutral alumina using chloroform as eluant. The second band containing convalently linked Schiff base-porphyrin H_2NBTpp was collected, concentrated and dried under vacuum. The ligand was obtained. mp > 300 °C. *Anal.* Found (Calcd. for $C_{51}H_{34}N_6O_2$): C, 79.77 (80.26); H, 4.48 (4.49); N, 10.72 (11.01).

2) Preparation of the lanthanide complexes with porphyrin and acetylacetone (LnNBTpp(acac))

0.3 g of H_2NBTpp and 0.6 g of hydrated tris (2, 4-pentanedionato) lanthanide ($Ln(acac)_3 \cdot 3H_2O$) were refluxed in 40 mL of 1, 2, 4-trichlorobenzene solvent at 214 °C for 3 h to 4 h under the protection of a dry nitrogen stream. The reaction mixture was poured directly to the column (1.5×30 cm) and purified by chromatography on neutral alumina. The first band eluted by chloroform was the ligand. The second band eluted by dimethyl sulfoxide (DMSO) was the complex. Chloroform was added to DMSO solution to double the volume. The chloroform solution was washed several times with water, dried with anhydrous magnesium sulfate, concentrated and dried under vacuum. The violet microcrystalline was obtained. The yield was about 0.2g. mp >300 °C. *Anal.* Found (Calcd. for $TbC_{56}H_{39}N_6O_4$): C, 63.32 (65.09); H, 3.47 (3.80); N, 7.58 (8.13).

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Results and discussion

Elemental analyses show the composition of the complexes as $LnC_{56}H_{40}N_5O_2$, that is LnNBTpp(acac). The lanthanide complexes are characterized by electronic absorption spectra, Fourier Transform Infrared Photoacoustic spectra, and ^1H NMR.

The data of visible spectra of the free base H_2NBTpp and LnNBTpp(acac) were recorded in chloroform (see Table 1).

Table 1 reveals that the band 646.2 nm of the free base disappears in the complex [15]. Other bands between the schiff base porphyrin and LnNBTpp(acac) are apparently less different. Theoretically, conjugated degree of o-

Table 1 The UV-Visible spectra of the ligand and the complexes

Compounds	Solvent	Soret Band	Q_1	Q_2	Q_3	Q_4
H_2NBTpp	$CHCl_3$	420.8	515.4	551.2	591.2	646.2
DyNBTpp(acac)	$CHCl_3$	421.0	517.2	553.2	592.8	
HoNBTpp(acac)	$CHCl_3$	424.0	517.6	554.8	595.4	
TmNBTpp(acac)	$CHCl_3$	421.6	514.8	552.2	591.8	
EuNBTpp(acac)	$CHCl_3$	421.2	516.5	555.8	595.0	
ErNBTpp(acac)	$CHCl_3$	421.2	516.5	552.4	591.8	
TbNBTpp(acac)	$CHCl_3$	422.2	516.4	553.6	592.8	
YbNBTpp(acac)	$CHCl_3$	422.0	516.5	553.4	593.4	

nitrobenzaldehyde Shiff-base porphyrin is stronger than that of 5,10,15, 20-tetraphenyl porphyrin, however, the difference of UV-visible spectra is almost not found.

Fourier Transform Infrared Photoacoustic spectroscopy indicated the differences between H_2NBTpp and LnNBTpp (acac), see Figure 1. Apparently, no water peaks are seen, which means that water molecules are not coordinated to the lanthanide ions. 3326 cm^{-1}, 968 cm^{-1} in the free porphyrin are due to N-H stretching vibration and winding vibration of porphyrin core, respectively [16, 17]. But the two bands in the complexes disappear since the two hydrogen atoms are replaced by a lanthanide ion. 1620 cm^{-1} ~ 1624 cm^{-1} in the ligand and complexes are found which are assigned to the N=C stretching vibration of the Schiff-base

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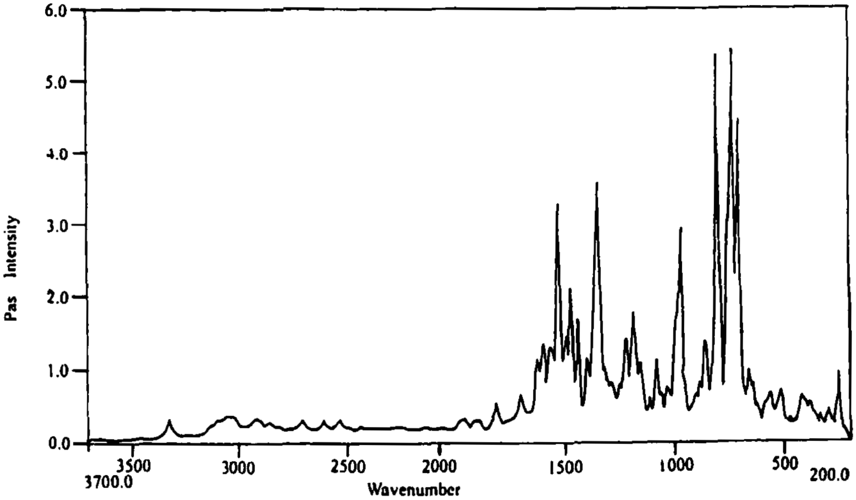

Figure 1 (a) Fourier transform infrared photoacoustic spectroscopy of the ligand

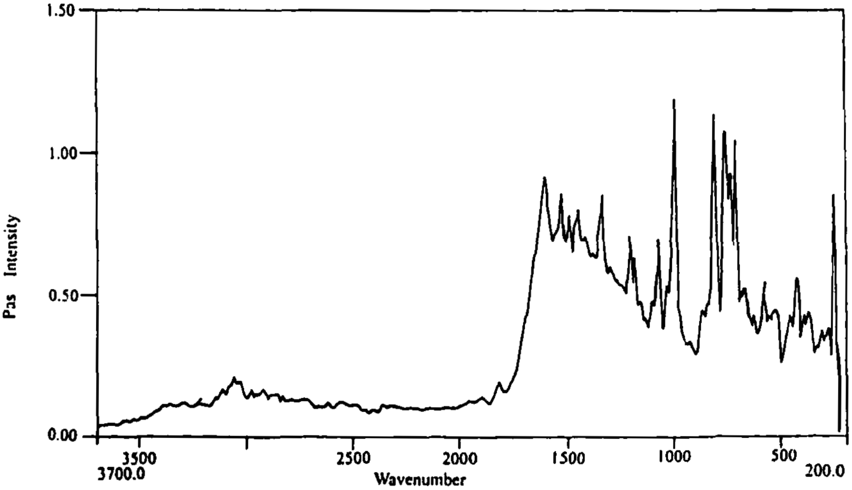

Figure 1 (b) Fourier transform infrared photoacoustic spectroscopy of ytterbium complex

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functionality. There are no distinctive shifts observed in the comparison of the ligand to the complexes. That is, coordination between the Schiff base and the metal ion does not occur. 1520 cm^{-1} ~ 1532 cm^{-1} of these compounds are ascribed to stretching vibration of $-NO_2$ group. The band at 355 ~ 367 cm^{-1} in the complexes is assigned to the Ln-O stretching vibration. This indicates the acetylacetonate ring is coordinated to the lanthanide atom.

^1H NMR spectra of H_2NBTpp and EuNBTpp (acac) were obtained in $CDCl_3$. There are fewer peaks for the lanthanide porphyrin complexes than for the free base. Signals of the ligand (ppm) are –2.76 (N-H of pyrrole), 7.25 ~ 7.83 (10H, phenyl), 8.14 ~ 8.29 (8H, phenyl), 8.48 ~ 8.50 (4H, phenyl), 8.85 ~ 8.90 (6H, pyrrole), 9.30 (2H, pyrrole), 10.40(1H, Schiff-base). Those of EuNBTpp(acac) were at 3.02 (6H, CH_3 of acetylacetone), 7.25 ~ 8.01(14H, phenyl), 8.21~ 8.27 (4H, phenyl), 8.83 ~8.94 (6H, pyrrole), 9.52(2H, pyrrole), 10.15(1H, Schiff-base). It is clearly that –2.76 ppm of the free base disappears in the complex, and a new signal 3.02 ppm emerges, indicating the acetylacetonate ring being coordinated to the lanthanide ion [18].

From the above results, the structure of the lanthanide unsymmetrical porphyrin complexes is proposed as depicted in Fig. 2. Lanthanide ion is coordinated in a tetradentated fashion with porphyrin and in a bidentated fashion with acetylacetonate. The central ion is outside of the porphyrin ring [19]. This structure is different from the first X-ray crystal structure of Tb(β-Cl_8tpp)(O_2CMe)($Me_2SO)_2$ [20]. The reasons are as followed: First, the purification

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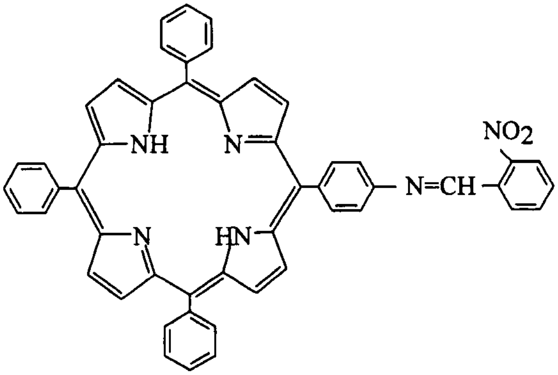

Figure 2(a) the structure of the ligand

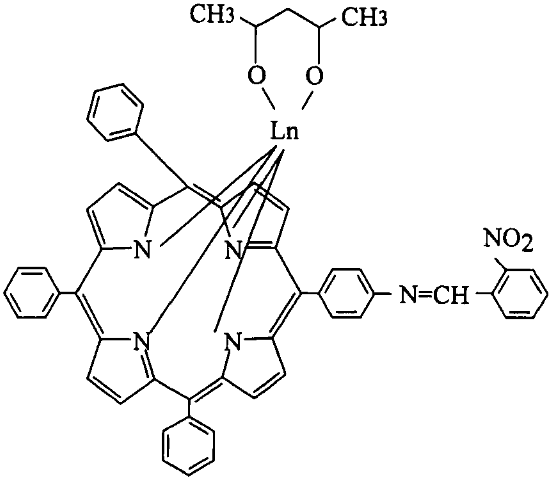

Figure 2(b) the structure of the lanthanide complexes described in the literature was done at about 170 °C. In our experiment, the whole purification procedure was performed at 70 °C. Dimethyl sulfoxide (DMSO) could not replace the acetylacetonate coordinated to lanthanide ion easily at lower temperature. Second, water is removed and can not coordinate to the lanthanide ion. The lanthanide ion only can adopt a six-coordinated mode. Whether it has optoelectronic properties or other application is being investigated.

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Acknowledgement:

The research works was supported by a grant from the National Natural Science Foundation (No. 29871013).

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(Received in the USA 3 February 2000)

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