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# Synthesis and Reactivity in Inorganic, Metal-Organic, and Nano-Metal Chemistry

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## Synthesis, Characterization and Properties of Asymmetrical Porphyrin with [p-Flourobenzoyl]-m-Ethyloxy] Phenyl and its Metal Complexes

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## Synthesis, Characterization and Properties of Asymmetrical Porphyrin with [*p*-Flourobenzoyl]-*m*-Ethyloxy] Phenyl and its Metal Complexes

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A new asymmetrical 5-[*p*-(4-flourobenzoyloxy)-*m*-ethyloxy] phenyl-10, 15, 20-triphenyl porphyrin and its transition metal (Zn, Cu, Ni, Co, Mn) complexes were synthesized. Their constitute and structure were characterized by elemental analyses, UV-vis, IR, molar conductances and <sup>1</sup>H NMR. Optical properties were discussed by fluorescence spectrum, and their high thermal stability was explained by thermal analytical results.

Keywords asymmetrical porphyrin, characterization, synthesis, transition metal complexes

#### INTRODUCTION

The synthesis of functionalized porphyrins is of growing interest for their use as model compounds.<sup>[1]</sup> Such substituted porphyrins have also been employed in various materials applications.<sup>[2]</sup> Porphyrins also play important roles in vital biological processes, in particular photosynthesis (chlorophyll), oxygen transport (hemoglobin), and oxygen activation (cytochrome) processes, and they have been characterized as "pigments of life."<sup>[3]</sup> Notably, metalloporphyrins play an important role in biological activities as for instance hemoprotens, chlorophylls and vitamin B<sub>12</sub>. They participate in essential biological process such as photosynthesis,<sup>[4]</sup> dioxygen transport and storage.<sup>[5]</sup> Metalloporphyrin are also used as powerful photodynamic druges and photosensitizers.<sup>[6]</sup> It has been found that in the above-mentioned properties, the orientation of the porphyrin chromophores plays a very important role. On the other

hand, the functions of materials are related to the molecular alignments as well as the molecular structures.<sup>[7]</sup>

Porphyrin synthesis has always been hampered by numerous side reactions leading to low product yields. Even with this synthetic shortcoming, a vast array of porphyrins containing practically every imaginable meso-substituent exist in literature.<sup>[8–11]</sup> There also have been a number of reports on transition metal complexes. In this paper, a new *meso*-substituted unsymmetrical porphyrin, 5-[p-(4-flourobenzoyloxy)- m-ethyloxy] phenyl-10, 15, 20–triphenyl porphyrin and its transition metal (Zn, Cu, Ni, Co, Mn) complexes were synthesized. They have been characterized by elemental analyses, molar conductances, UV-vis, IR and <sup>1</sup>H NMR spectra. We also studied their luminescent properties by emission spectra and thermal stabilities by differential thermal analyses.

#### **EXPERIMENTAL**

#### Apparatus and Measurements

All chemicals were reagent grade and were dried before use. Elementary analyses were obtained on a Perkin-Elmer 240C auto elementary analyzer. Infrared spectra were recorded on a Nicolet 5PC-FT-IR spectrometer using KBr pellets in the region 400-4000 cm<sup>-1</sup>. Uv-visible spectra were recorded on a Shimadzu UV-240 spectrophotometer in the range 350-700 nm using chloroform as solvent. Molar conductances of  $10^{-3}$  mol· dm<sup>-3</sup> chloroform solution at 25°C were measured on a DDX-111A conductometer. <sup>1</sup>H NMR spectra were recorded on a Varian-Unity-400 NMR spectrometer using CDCl<sub>3</sub> as solvent and tetramethylsilane (TMS) as internal standard. The excitation and emission spectra were given at room temperature on a FS 920 Stead State Fluorescence Spectrometer in the region 300-800 nm. TGA and DTA were carried out by DTG-60 simultaneous DTA-TGA apparatus (sample: 3-4 mg, heating rate:  $10^{\circ}$ C· min<sup>-1</sup>, atmosphere: static air).

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Compounds	Empirical formula	C(%)	H(%)	N(%)
FBOEPTPP	C <sub>53</sub> H <sub>37</sub> N <sub>4</sub> O <sub>3</sub> F	79.43(79.90)	4.61(4.65)	6.93(7.04)
Ni(FBOEPTPP)	C <sub>53</sub> H <sub>35</sub> N <sub>4</sub> O <sub>3</sub> FNi	74.60(74.59)	4.08(4.10)	6.54(6.57)
Cu(FBOEPTPP)	C <sub>53</sub> H <sub>35</sub> N <sub>4</sub> O <sub>3</sub> FCu	74.19(74.17)	4.11(4.08)	6.56(6.53)
Zn(FBOEPTPP)	C <sub>53</sub> H <sub>35</sub> N <sub>4</sub> O <sub>3</sub> FZn	74.03(74.01)	4.05(4.07)	6.54(6.52)
Co(FBOEPTPP)	C <sub>53</sub> H <sub>35</sub> N <sub>4</sub> O <sub>3</sub> FCo	74.59(74.57)	4.12(4.10)	6.55(6.57)
Mn(FBOEPTPP)Cl	C <sub>53</sub> H <sub>35</sub> N <sub>4</sub> O <sub>3</sub> FMnCl	71.92(71.91)	3.98(3.96)	6.31(6.33)

TABLE 1 Characterization data of the compounds\*

\*Theoretical values are given in parentheses.

#### Preparation of Ligand and Complexes

*Synthesis* of*FBOEPTPP*. [5-(4-hydroxy-3-ethyloxy) phenyl-10, 15, 20-tri-phenyl]porphyrin, HEPTPP, (HEP=(4hydroxy-3-ethyloxy)phenyl; TPP = triphenyl porphyrin)was prepared and purified according to the literature.<sup>[12]</sup> 4-flourobenoyl chloride was prepared by the reaction of 4-flourobenzoic acid and thioylchloride. 5-[p-(4-flourobenzoyloxy)phenyl-10, 15, 20- triphenyl porphyrin, m-ethyloxy] FBOEPTPP, was prepared by the reaction of HEPTPP with 4-flourobenzoyl chloride. HEPTPP (1.00 g, 1.45 mmol) was dissolved in 75 mL heating benzene, and added triethylamine (2.00 mL, 11.37 mmol). Then added dropwise the solution of 4-flourobenoyl chloride (0.18 mL, 1.52 mmol) and 25 mL benzene within 2 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 the residual with 2 volumes of distilled water and extracted three times with equal volumes of water. Concentrated the chloroform solution and added to a neutral aluminum oxide column ( $2.5 \times 15$  cm). The first band containing HEPTPP was eluted by chloroform. The second band containing FOEPTPP was eluted by chloroform containing 10% absolute ethanol. This eluant was concentrated and cooled. Then the product was dried in vacuo. The yield was 1.0 g.

Synthesis of transition metal complexes. We take Zn(FBOEPTPP) for example.

FBOEPTPP (0.2 g, 0.23 mmol) was dissolved in the mixture of 20 mL DMF and 20 mL chloroform, and ZnCl<sub>2</sub>· 2H<sub>2</sub>O

Co(FBOEPTPP)

Mn(FBOEPTPP)Cl

(0.09 g, 0.69 mmol) was added. The mixture was refluxed under the protection of dry nitrogen atmosphere for about 1 h. The extent of the reaction was followed by measuring the UV-Vis spectra of the solution at ten minute intervals. After evaporation of the solvent, the residue was purified by column chromatography (netural aluminum oxide, CHCl<sub>3</sub>). The title compound was obtained as a red solid (200 mg, 0.20 mmol, 88%).

There are similar preparation methods and results for other transition metal complexes.

#### **RESULTS AND DISCUSSION**

#### **Elemental Analyses**

The elemental analyses of the ligand and complexes are given in Table 1.

#### **UV-Vis Spectra**

530(4.28)

581(4.08)

617(4.10)

Table 2 gives ultra-violet visible spectral data of ligand FBOEPTPP and complexes.

Characteristic Q and B (Soret) bands of porphyrins and metal porphyrins in visible and near-ultra violet ranges are assigned as the transitions from ground state  $(S_0)$  to the lowest excited singlet  $(S_1)$  and second lowest excited singlet state  $(S_2)$ , respectively. Compared with the ligand  $H_2(P-Cl)TPP$ , the number of the absorption bands of the complexes decreases, it is due to symmetry of the complexes increase. In comparison these complexes and TPP and its transition complexes, the data is accord,

UV-vis spectra of the ligand and complexes							
Ligand/complexes	$\lambda \max (nm) (lg \varepsilon)$						
	Soret (B) band	Q bands					
FBOEPTPP	417(5.46)	515(4.35)	549(4.08)	590(3.99)	637(3.94)		
Ni(FBOEPTPP)	415(5.26)		528(4.22)				
Cu(FBOEPTPP)	415(5.45)		539(4.33)				
Zn(FBOEPTPP)	422(5.44)		552(4.27)	594(3.93)			

410(5.41)

479(4.93)

TABLE 2

	-		-		-	
FBOEPTPP	Ni	Cu	Zn	Co	Mn	Assignment
3320w <sup>a</sup>						v (N–H)(pyrrole)
2922w	2920w	2922w	2922w	2922w	2922w	$\nu$ (C–H) (phenyl?pyrrole)
2852w	2850w	2852w	2852w	2852w	2852w	
1743s	1743s	1743s	1747s	1743s	1743s	ν (C=O)
1601s	1601s	1601s	1601s	1604s	1606s	$\nu$ (C–C)(phenyl)
1469w	1463w	1461w	1441w	1467w	1442w	$\delta$ (C–H)(pyrrole)
1350w	1352w	1344w	1338w	1350w	1342w	$\nu$ (C–N)(pyrrole)
1259s	1257s	1259s	1259s	1259s	1259s	ν (C-O-C)
1120s	1120s	1120s	1117s	1120s	1122s	$\nu$ (C–F)(phenyl)

 TABLE 3

 Infrared spectra frenquenceies (cm<sup>-1</sup>) of the ligand and complexes

<sup>*a*</sup>s: strong, w: weak.

which indicate that the valence state of manganese atom in the compound is +3 and that of the nickel, copper, zinc and cobalt atom is +2.<sup>[13]</sup>

#### **Infrared Spectra**

The main band frequencies  $(cm^{-1})$  and assignments of the ligand and complexes were given in Table 3. The bands at about 1743  $cm^{-1}$  which assigned to the C=O stretching vibration appeared. This showed that the 4-flourobenoyl chloride had been linked to oxygen. The band at 3320  $cm^{-1}$  in the free porphyrin is assigned to the N-H stretching of the porphyrin core. While this band is absent in the complexes, the hydrogen atoms has been replaced by the transition metal ions to form M-N bands.

#### **Molar Conductances**

The molar conductance values of the ligand and its Ni, Cu, Zn, Co complexes are at 0.015, 0.01, 0.015, 0.015 and 0.01  $\Omega^{-1}$  cm<sup>2</sup> mol<sup>-1</sup>, respectively, in 10<sup>-3</sup> mol· L<sup>-1</sup> chloroform solution at 25°C. But Mn complex is at 53  $\Omega^{-1}$  cm<sup>2</sup> mol<sup>-1</sup>, and it is very clear that the ligand and Ni, Cu, Zn, Co complexes show nonelectrolytic behavior, but Mn complex shows 1:1 type electrolytes.<sup>[14]</sup> This suggests that the valence state of manganese atom in the compound is +3. The structure is Mn(FBOEPTPP)Cl.

TABLE 4 Emission spectral data of ligand and complexes

Compounds	Q(0-0)	Q(0-1)	Q(0-2)	$\Phi_{\mathrm{f}}$
FBOEPTPP		651	719	0.02
Ni(FBOEPTPP)	600	651	716	0.0096
Cu(FBOEPTPP)		654	717	0.002
Zn(FBOEPTPP)	603	649		0.043
Co(FBOEPTPP)	602	653	715	0.0016
Mn(FBOEPTPP)Cl	600	651	715	0.0401

#### <sup>1</sup>H NMR

We take Mn comples for example.

The <sup>1</sup>H NMR chemical shift values ( $\delta$ , ppm) were measured in deuterium chloroform. The <sup>1</sup>H NMR data of the ligand FBOEPTPP are given as follows: 9.038–8.931 (8H, pyrrole, ring), 4.97 (2H, flouro-phenyl-2,6-protons), 7.368 (2H, flouro-phenyl-3,5-protons), 8.29–8.31 (10H, 10, 20-phenyl), 7.61–7.97 (8H,5,15-phenyl) and -2.71 (2H, pyrrole, N-H). In the complexes, Mn(FBOEPTPP)Cl, the singal peak of ligand at -2.71 (2H, pyrrole, N-H) disapperars because the hydrogen atom of N-H bond has been replaced by Mn ion to form Mn-N. Other peaks are analogous to the ligand.

From the above results, we can draw the following conclusions: The valence state of nickel, copper, zinc and cobalt atom in the compound is +2 and manganese is +3. The structure of the ligand, FBOEPTPP and complexes, M(FBOEPTPP) and Mn(FBOEPTPP)Cl are shown in Figure 1.

#### Luminescence of the Ligand and Complexes

There are fluorescence of the  $S_2(B, \text{Soret band})$  and  $S_1(Q, B)$ 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 O band emission. Its quantum yield is so low that sometimes fluorescence becomes unobservable. This fluorescence emission was not observed at room temperature in the experimental excited wavelength, 417 nm. Q(0-1) bands of the complexes are in the region 649-654 nm and Q(0-2) bands 715-717 nm. They are mirror symmetric to the absorption spectra. Quantum yields( $\Phi_f$ ) of Q band for the complexes are in the range 0.0016– 0.043. The  $S_1 \rightarrow S_0$  quantum yield depends on the relative rates of the radiative process  $S_1 \rightarrow S_0$  and two radiationless processes  $S_1 \rightarrow S_0$  and  $S_1$  means The fluorescence quantum yield of our complexes is far less than 0.20. Thus, the excited state S<sub>1</sub> is primarily deactivated by radiationless decay. This indicates that the spin-forbidden process  $S_1$   $\cdots$  Tn is the



FIG. 1. The structure of the complexes: a. M(FBOEPTPP) (M = Ni, Cu, Zn, Co); b. Mn(FBOEPTPP)Cl.

predominant route for radiationless deactivation of  $S_1$  in the complexes.

From the quantum yield of the sampes, the  $\Phi_f$  of Co and Cu porphyrins are the lowest. Since Co and Cu are open-shell metal ions with paramagnetic property, and d orbital in electron configuration of external layer has single electron, those single electrons destroy the conjugate system when metal ions coordinate with conjugate porphyrin ring.<sup>[15]</sup> While close-shell metal Zn can not destroy the conjugate configuration of porphyrin, so the  $\Phi_f$  of Zn-porphyrin is stronger than that of porphyrin ligand.

#### Thermal Stability of the Ligand and Complexes

Figures 2 and 3 are TGA and DTA pictures of the ligand, FBOEPTPP and complex Cu(FBOEPTPP), respectively. Figure 2 shows that DTA curve of the ligand has two exothermic peaks and TGA curve two stages. Ligand FBOEPTPP has begun to be decomposed at 395°C and decomposed completely at 613°C. TGA and DTA curves of the ligand do not have stages or peaks up to 395°C, therefore it is stable under 395°C. Figure 3 indicates that DTA of the Cu(FBOEPTPP) has two exothermic peaks and TGA curve one stage. For the complex, it began to decompose at about 298°C, and at about 555°C, about 8% of it remained



FIG. 2. DTA(—) and TGA(.....) pictures of ligand, FBOEPTPP.



which represented the content of CuO. It is very easy to see that porphyrin and its complexes have higher thermal stability. And they are stable in air, can be dried under 298°C.

#### **CONCLUSIONS**

In this article, we have described the synthesis and characterization of a new unsymmetrical porphyrin and its transition metal (Zn, Cu, Ni, Co, Mn) complexes. Spectroscopy and molar conductances evidences suggests that the structure of Zn, Cu, Ni and Co complexes can be considered as 4 coordinated species with four N of the porphyrinate coordinated to the metal centre. The valence state of nickel, copper, zinc and cobalt atom in the compound is +2 and the complexes show nonelectrolytic behavior. Mn(III) porphyrin is a 1:1 type of electrolyte. The analysis of photoluminescence(PL) spectrum shows that the PL of close-shell Zn porphyrin is stronger and the PL of open-shell Co and Cu porphyrin with paramagnetic property is weaker. The data of thermal analysis indicate that porphyrin and metallic porphyrin have a better thermal stability, and they are a kind of important compound as bio-labels.<sup>[16]</sup>

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