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

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## Synthesis and Characterization of Novel Unsymmetrical Porphyrin and its Complexes

## Yuhua Shi, Xuexin Tang, Erjun Sun, Xiuli Cheng, Dong Wang, Shuangjiang Yu, and Tongshun Shi

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A novel unsymmetrical porphyrin meso-5-(p-octanoyloxyphenyl)-10,15,20-triPhenylporphyrin (OPTPPH<sub>2</sub>) and relative transition metal complexes (DPTPPM, M=Zn, Fe, Co, Ni, Cu, Mn) were synthesized and characterized by elemental analysis, UV-Vis spectra, mass spectra, <sup>1</sup>H NMR, infrared spectra, Raman spectra, and cyclic voltammetry. In dimethylformamide (DMF), 0.1 mol·L<sup>-1</sup> tetrabutylammonium perchlorate (TBAP), these compounds exhibit two or three one-electron reversible redox reactions. Quantum yields of the S<sub>1</sub>•S<sub>0</sub> fluorescence are measured at room temperature. These studies will contribute to further choice and application of the liquid crystals.

Keywords cyclic voltammetry, fluorescence spectra, luminescence spectra, Raman spectra, unsymmetrical porphyrin

#### INTRODUCTION

The study of porphyrins has received increased interest in recent years. Porphyrins have been utilized for the development of artificial receptors for molecular recognition and new chiral catalysts for asymmetric synthesis,<sup>[1-3]</sup> for the exploration of the mechanisms of biologically important reactions such as photosynthesis and P450-catalyzed redox reactions, and for the study of stereochemistry.

Metalloporohyrin chemistry is one of the most important areas of modern chemistry, the unique structure and novel reactivity promise metalloporphyrin complexes for expansive applications in biology, medicine, chemistry, material science fields, such as catalysis, new material, etc. In this paper, we report for the first time, the synthesis and characterization of a series of novel unsymmetrical porphyrin and complexes (Scheme 1).

#### MATERIALS AND METHODS

All reagents and solvent were commercial reagent grade and were used without further purification unless otherwise noted, except DMF was predried over activated 4Å molecular sieve and vacuum distilled from calcium hydride (CaH<sub>2</sub>) prior to use. Pyrrole was distilled under reduced pressure and stored in sealed ampoules

#### Instrumentation

Elemental analyses were obtained by a Perkin-Elmer 240 C auto elementary analyzer. UV-vis spectra were recorded on a Shimadzu UV-365 spectrometer using chloroform as solvent. IR spectra were recorded on a Nicolet 5PC-FT-IR spectrometer in the region 400–4000 cm-1 using KBr pellets. <sup>1</sup>HNMR spectra were obtained in CDCl<sub>3</sub> employing tetramethylsilane, (CH<sub>3</sub>)<sub>4</sub>Si as an internal reference on Varian Unity-500 (500 MHz) spectrometer, mass spectra (FBA) were obtained on a JEOL AX-505 spectrometer.

Flucrescence spectra were recorded with a Shimadzu RF5301PC spectrofluorometer. Ramn spectra were recorded with a Renishawinvia resonance raman spectroscopy.

Redox potentials of the porphyrin and its complexes  $(10^{-3} \text{ mol}\cdot\text{L}^{-1})$  in dried DMF containing 0.1 M TBAP as a supporting electrolyte using a glassy carbon working electrode, platinum counter electrode, and Ag+/Ag (0.01 mol·L<sup>-1</sup> AgNO<sub>3</sub> in CH<sub>3</sub>CN)pseudo-reference electrode under deaerated conditions and a CHI 660A electrochemical analyzer were determined at room temperature by cyclic voltammetry.

#### **Synthesis**

Octanoyl chloride was prepared and purified in our laboratory.

Meso-5-(p-hydroxy)phenyl-10,15,20-triphenylporphyrin (HTPP) was prepared and purified by known procedures.<sup>[4]</sup>

Synthesis of ligand ( $OPTPPH_2$ ). The HTPP(1.5 g) and Triethylamine were added to benzene (400 ml, distilled from CaCl<sub>2</sub>) in a 250 ml round bottom flask. Octanoyloxychlorin (diluted by 10 ml benzene) was trickled between 0.5h. The solution mixture was refluxed and stirred for 8h under the protection of a dry nitrogen stream. Then benzene was evaporated, triethylamine and overplus octanoyloxychlorin were was evaporated out under vacuum. The crude dry product was chromatographed

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SCHEME 1. The structure of the unsymmetrical porphyrin and its complexes.

on neutral aluminum oxid using CHCl<sub>3</sub> as the eluent. The first band (purple red) was collected and evaporated to dryness to give a purple red solid which was further recrystallized from CHCl<sub>3</sub> (83.4% yield). Elemental ana1. calc. (%) for  $C_{52}H_{44}O_2N_4$ : C 82.54,H 5.82,N 7.41; found (%): C 82.49, H 5.94, N 7.36.

Synthesis of OPTPPZn. OPTPPH<sub>2</sub> and ZnCl<sub>2</sub> were added to DMF (20 ml) and CH<sub>2</sub>Cl<sub>2</sub> (20 ml), then the solution was refluxed for about 20 min. The extent of the reaction was monitored by measuring the UV-visible spectrum of the reaction solution per 5 min. The CH<sub>2</sub>Cl<sub>2</sub> was evaporated out, then the solution was added to distilled water (500 ml), was suctionfiltered, and the crude product was purified by column chromatography on silica gel using a solvent of CHCl<sub>3</sub> as the eluent. The second band was collected and evaporated to dryness to give a purple red solid. Elemental ana1. calc.(%) for C<sub>52</sub>H<sub>42</sub>O<sub>2</sub>N<sub>4</sub>Zn: C 76.28, H 5.13, N 6.85; found(%): C 76.14, H 5.20, N 6.79

The synthetic methods of the other complexes(M = Cu, Ni) were similar to above-mentioned method.

Synthesis of OPTPPCo. OPTPPH<sub>2</sub> were added to DMF (20 ml) and CH<sub>2</sub>Cl<sub>2</sub> (20 ml), then the solution mixture was purged with dry nitrogen for about 30 min.  $CoCl_2 \bullet H_2O$  were added to mixture and refluxed for 30 min. The extent of the reaction was monitored by measuring the UV-visible spectrum of the reaction solution per 5 min. Then DMF and CH<sub>2</sub>Cl<sub>2</sub> were evaporated out under vacuum. The red-black was collected and the crude product was purified by column chromatography on neutral aluminum oxid using a solvent of CHCl<sub>3</sub> as the eluent. The second band was collected and evaporated to dryness to give a purple red solid. Elemental ana1. calc.(%) for C<sub>52</sub>H<sub>42</sub>O<sub>2</sub>N<sub>4</sub>Co:

The UV-visible spectra and data of the figure and the complexes in chlorotorm $(1.00 \times 10^{-6} \text{ mol/L})$								
Compounds	Solvent	Soret band						
Ligand	CHCl <sub>3</sub>	420 (3.10×10 <sup>5</sup> )	515 (1.91×10 <sup>4</sup> )	$550 (8.20 \times 10^3)$	590 ( $6.47 \times 10^3$ )	645 (6.01×10 <sup>3</sup> )		
OPTPPZn	CHCl <sub>3</sub>	$420(2.90 \times 10^5)$	545 $(2.26 \times 10^4)$	585 ( $4.35 \times 10^3$ )				
OPTPPCu	CHCl <sub>3</sub>	$415 (2.90 \times 10^5)$	$540(2.13 \times 10^4)$					
OPTPPNi	CHCl <sub>3</sub>	$415 (2.50 \times 10^5)$	$525 (1.78 \times 10^4)$					
OPTPPCo	CHCl <sub>3</sub>	$410(2.60 \times 10^5)$	525 (1.61×10 <sup>4</sup> )					
OPTPPFeCl	CHCl <sub>3</sub>	$415 (8.30 \times 10^4)$	$505 (9.27 \times 10^3)$	$570 (6.15 \times 10^3)$				

 $615(1.15 \times 10^4)$ 

 $580(1.07 \times 10^4)$ 

TABLE 1 The UV-visible spectra and data of the ligand and the complexes in chloroform  $(1.00 \times 10^{-6} \text{ mol/L})$ 

\*Molar extinction coefficients are in parentheses.

 $480 (1.00 \times 10^5)$ 

CHCl<sub>3</sub>

**OPTPPMnCl** 

TABLE 2 Fluorescence spectral data of the ligand and the complexes in chloroform  $(1.00 \times 10^{-6} \text{ mol/L})$ 

Compounds	λemm	ax/nm	Quantum yields (f)		
Ligand	650	711	0.066		
OPTPPZn	592	640	0.040		
OPTPPNi	653	710	0.033		

C 76.85, H 5.17, N 6.90; found(%): C 76.93, H 5.24, N 6.82.

The synthetic methods of the other complexes (M = Mn,Fe) were similar to above-mentioned method.

#### **RESULTS AND DISCUSSION**

#### **UV-vis Spectra**

The data of UV-visible spectra of the ligand and compounds were recorded in chloroform (see Table 1).

The UV-visible absorption bands of the porphyrin are due to the electronic transitions from the ground state( $S_0$ ) to the two lowest singlet excited states  $S_1$  (Q state ) and  $S_2$  (B state). The  $S_0$ - $S_1$  transition gives rise to the weak Q bands in visible region (550–650 nm), while  $S_0$ - $S_2$  transition produces the strong B band in near UV region (380–450 nm).

From Table 1, we know that  $OPTPPH_2$  have one Soret band (420 nm) and four Q bands (515, 550, 590, 645 nm). The Soret band of OPTPPM occurs to different degree shift and number of Q band reduced.

After the metal ion has entered the body of porphyrin because of the increasing of molecular symmetry from  $D_{2h}$  to  $D_{4h}$ , the number of Q band decreases, and the absorption frequencies shift.<sup>[5]</sup>



FIG. 1. Fluorescence spectra of ligand and complexes at room temperature in CHCI<sub>3</sub>.

#### Fluorescence Spectroscopy

The fluorescence emission spectra of the porphyrin compounds at room temperature are shown in Figure 1. Table 2 gives the excitation spectral maxima and the quantum yields of the fluorescent emission of the ligand and its complexes.

The porphyrin was disolved in dry chloroform and deaerated by Ar carefully. The compounds exhibit two emission bands in the regions 650, 592, 653 and 711, 640, 710 nm corresponding to Q(0,0) and Q(0,1) transition, respectively. To determine fluorescence quantum yield, fluorescence intensity makes the yield of S<sub>1</sub> fluorescence of meso-tetraphenylporphyrin zinc (TPPZn) in CHCl<sub>3</sub> (f = 0.033, ex = 420 nm) as a standard. There are fluorescences of the  $S_2$  (B band) and the  $S_1$  (Q band) in the porphyrin. The fluorescence of the B (Soret) band is attributed to the transition from the second excited singlet state  $S_2$  to the 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 the fluorescence becomes unobservable sometimes. This fluorescence emission was not observed at room temperature and the experimental excited wavelength of 420 nm. The fluorescence quantum yields of our complexes are less than 0.07. Thus, the excited state  $S_1$ is primarily deactivated by radiationless decay. This indicates fairly certainly that the spin forbidden process S  $_1 \sim \bullet$  Tn is predominant for radiationless deactivation of S<sub>1</sub> in porphyrin complexes.

#### **Infrared Spectra**

The important band frequencies and assignments of the ligand and complexes as presented in Table 3.

From Table 3, We can see that  $3317 \text{ cm}^{-1}$  and  $966 \text{ cm}^{-1}$  in the free porphyrin are due to N-H sretching vibration and winding vibration of porphyrin core, respectively. But the two bands in the complexes disappear since the two hydrogen atoms in the N–H bonding are replaced by a metal ion. The band in the range  $3052-3056 \text{ cm}^{-1}$  in the ligand and complexes are found that are assigned to the C–H stretching vibration of aromaticity. The band in the range  $1590-1598 \text{ cm}^{-1}$  in the ligand and complexes are found that are assigned to the C–H stretching vibration of aromaticity. The band in the range  $1590-1598 \text{ cm}^{-1}$  in the ligand and complexes are found that are assigned to the C=C stretching vibration of benzene ring. The bands at  $698-703 \text{ cm}^{-1}$  are assigned to the methylene in-plane rocking vibration of straight alkyl chain including over four carbons. Assignment of other absorption bands are also presented in Table 3.

#### **Raman Spectra**

The importa band frequencies and assignments of the ligand and complexes as presented in Table 4 according to literature.<sup>[6-9]</sup>

Figure 2 displays the Raman spectra of ligand and complexes excited at 514.5 nm. The  $C_{\beta}$ - $C_{\beta}$  and  $C_{\alpha}$   $C_m$  stretching frequencies are usually in 1450–1600 cm<sup>-1</sup> region due to the relatively large force constants of these bonds. The stretching motions of  $C_{\alpha}$ - $C_{\beta}$  and  $C_{\alpha}$ -N bonds are known to interact with each

Ligand	OPTPPZn	OPTPPCu	OPTPPCo	OPTPPNi	OPTPPFeCl	OPTPPMnCl	Assignment	
3317.1							υ(N-H)	
3056.7	3052.9	3054.8	3052.9	3056.7	3054.8	3054.8	v(C-H)(Ar)	
2927.6	2925.6	2923.7	2925.6	2919.8	2923.7	2923.7	v(C-H)	
2856.2	2852.3	2852.3	2854.3	2850.4	2852.3	2854.3	v(C-H)	
1758.8	1722.2	1758.8	1756.9	1756.9	1758.8	1758.8	v(C=0)	
1596.8	1596.8	1598.8	1598.8	1596.8	1596.8	1598.8	v(C=C)	
1471.5	1485.0	1490.8	1490.8	1490.8	1488.9	1488.9		
1440.6	1440.6	1440.6	1440.6	1440.6	1440.6	1440.6	C = C(benzene)	
1351.9	1338.4	1346.1	1348.1	1346.1	1338.4	1342.3	v(C-C)	
1199.6	1200.1	1201.4	1205.4	1201.4	1201.5	1203.4	v(C-O)	
1132.1	1166.8	1162.9	1164.9	1162.9	1164.8	1166.7	$\beta$ (C-H)	
1072.3	1068.4	1072.4	1070.4	1068.4	1072.3	1072.3	$\upsilon(C\alpha-N) \delta(CCN) \upsilon(C_{\alpha}-C_m)$	
	995.1	1002.9	1004.8	1002.9	1002.9	1010.6	Р	
966.2							$\delta$ (N-H)	
798.4	796.5	798.4	798.4	794.6	798.4	802.2		
698.1	702.0	700.1	698.1	700.1	702.0	703.9	-(CH <sub>2</sub> ) <sub>n</sub> -	





FIG. 2. Raman spectra of OPTPPH2 and OPTPPM (M=Ni, Cu, Mn).



FIG. 3. <sup>1</sup>HNMR spectra of OPTPPH<sub>2</sub>.



FIG. 4. <sup>1</sup>HNMR spectra of OPTPPZn.

other substantially. Raman bands in 1300–1450 cm<sup>-1</sup> region are due to the out-of-phase coupled  $(C_{\alpha}-C_{\beta})/(C_{\alpha}-N)$  stretching modes. In the 1008–995 cm<sup>-1</sup> region spectrum are due to the in-phase coupled  $(C_{\alpha}-C_{\beta})/(C_{\alpha}-N)$  stretching mode, while the 917 cm<sup>-1</sup> band of ligand can be assigned to the Pyr. breathing stretching modes. In the 363–390 cm<sup>-1</sup> region spectrum of complexes can be assigned to  $\delta(C_{\alpha}C_mC_{\alpha})$  and (M - N) stretching modes.

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

The <sup>1</sup>HNMR spectra of the ligand and the complex OPTPPZn (shown in Figures 3 and 4) were obtained in CDCl<sub>3</sub>. The <sup>1</sup>H-NMR chemical shift values in CDCl<sub>3</sub> ( $\delta$ , ppm) for ligand OPTPPH2 are at 8.843–8.864(8H, pyrrole ring), 7.481–8.224(19H, benzene ring), 2.733–2.763(2H, OOCH<sub>2</sub>), 1.373–1.911(10H, alkyl CH2), 0.929–0.956(3H, alkyl CH<sub>3</sub>),

-2.790(2H,pyrrole N-H). The <sup>1</sup>H-NMR chemical shift values in CDCl<sub>3</sub> ( $\delta$ , ppm) for OPTPPZn are at 8.948–8.969(8H, pyrrole ring), 7.476–8.227 (19H, benzene ring), 2.732–2.762 (2H, OOCH<sub>2</sub>), 1.254–1.912 (10H, alkyl CH<sub>2</sub>), 0.930–0.943 (3H, alkyl CH<sub>3</sub>).

From Figures 3 and 4, we can see that there are fewer peaks for the metalloporphyrins complexes than for the free base. In the complex OPTPPZn, the signal peak at -2.790 (2H, pyrrole N-H) disappears, since the hydrogen atom in the N-H bond is replaced by Zinc ion. Other peaks of the complex are similar as compared with those of the ligand.

#### Mass Spectra (FBA)

In the mass spectra (Figures 5 and 6), the molecular ion peak of the ligand OPTPPH<sub>2</sub> is 757.8 (100%), and the molecular ion peak of the OPTPPZn is 820.3(100%).

TABLE 4	
Characteristic Raman bands of ligand and complexes (cr	$m^{-1}$ )

Ligand	OPTPPZn	OPTPPCu	OPTPPCo	OPTPPNi	OPTPPFeCl	OPTPPMnCl	Assignment
1550.4vs	1545.9m	1560.9s	1541.5s	1553.4vs	1550.4vs	1578.9m	$(C_{\beta}-C_{\beta})$
1493.3s	1490.3w	1502.4m	1502.4m	1494.8w	1511.4m	1499.3m	$(C_{\beta}-C_{\beta})$
1361.0m	1350.2s	1364.0vs	1373.2s	1373.2s	1357.9s	1373.2m	$(C_{\alpha}-N) + (C_{\beta}-C_{\beta})$
1327.2m							$\delta$ (C-H)
1238.9s	1229.6w	1234.3s	1231.2w	1237.4m	1228.1m	1215.6w	$(C_{\alpha}-N)$
1134.1m	1173.4vm	1181.2s	1185.9m	1130.9w	1181.2m	1130.9w	$\delta(C_{\beta} - H)$
999.1m	1002.3w	1002.3s	995.9m	1002.3m	1000.7m	1008.7vm	$(C_{\alpha}-N) + (C_{\alpha}-C_{\beta})$
917.1w							Pyr.breathing
714.3m	724.3vw	729.2vw	715.9w	730.9w	722.6w	755.6m	
542.2m	570.9w	564.2vw	557.4w	547.3w	560.8w	532.1w	
	389.1vw	387.4vs	390.8vs	389.1m	387.4s	363.3s	$\delta(\mathbf{C}_{\alpha}\mathbf{C}_{m}\mathbf{C}_{\alpha}) + (\mathbf{M} - \mathbf{N})$
334.0m							

vs. very strong; s. strong; m. medium; w. weak; vw. very weak

**Reflectron Mode** Data: 756l0002.P14 13 Jun 2006 20:18 Cal: 14 Jun 2006 13:07 Kratos PC Axima CFR V2.3.1: Mode Linear, Power: 70, P.Ext. @ 756 (bin 57) %Int. 2218 mV Profiles 1-63: 757.8 Mass/Charge

FIG. 5. Mass spectra of OPTPPH<sub>2</sub>.

#### Reflectron Mode

Data: 8180001.P13 13 Jun 2006 20:12 Cat 14 Jun 2006 13:07 Kratos PC Avima CFR V2.3.1: Mode Linear, Power: 77, P.Ext. @ 818 (bin 57) %ht. 3239 mV Profiles 1-92:



FIG. 6. Mass spectra of OPTPPZn.



FIG. 7. Cyclic voltammograms of OPTPPH2 and OPTPPM (M=Zn,Co,Ni,Cu,Mn) dissolved in DMF containing 0.1M TBAP. Scan rate=0.1V/S.

#### Electrochemistry

The redox potentials of  $OPTPPH_2$  and OPTPPM (M=Zn, Co,Ni,Cu,Mn) were measured by cyclic voltammetry.

Cyclic voltammograms of OPTPPH<sub>2</sub> and OPTPPM(M=Zn, Co, Ni, Cu, Mn) dissolved in DMF are shown in Figure 7 and Table 5. From Figure 7 and Table 5, we can see that in the presence of 0.1 M TBAP of DPTPPH<sub>2</sub> undergoes one irreversible oxidation reaction at  $Ep = 0.63 \text{ V} (P^+/P^0)$  and one reversible reductive reaction at  $Ep = -1.46 \text{ V} (P^-/P^{2-})$  for a scan rate of 0.1 V/S. The difference in  $E_{1/2}$  was 2.10 V, which are in good agreement with  $E_{1/2}^{ox}(1)$ -  $E_{1/2}^{red}(1) = 2.25 \pm 0.15$ .

All voltammograms of OPTPPNi, OPTPPCu, OPTPPZn were similar in shape. Each compound undergoes two irreversible oxidation reactions and a single one reversible reductive reaction with the potential range of the solvent. From Figure 7, we can know two reductive reactions of cyclic voltammograms of OPTPPMnCl were obtained , the first at -0.59Vcorresponds to the reaction Mn(III) [Mn(II), and the second occurs at -1.73V, and can be assigned as formation of the anion radical.

In the DMF, OPTPPCo undergoes three redox reactions. The second reaction peak occurs to  $E_p = -0.12$ , corresponds to the reaction Co(III) [ Co(II); The second reaction peak occurs to  $E_p = -0.12$ , corresponds to the reaction Co(II) [ Co(I). Compared with the redox reaction of TPPCo [TPPCo(III)/TPPCo(II),  $E_p = -0.1$  V; TPPCo(II)/TPPCo(I),  $E_p = -1.154$  V], those of DPTPP are more negative. This behavior may be explained that octanoyloxy increases the electron density of the  $\pi$ -ring system and the energy of both the HOMO and the LUMO,

 TABLE 5

 Summary of redox potentials for the ligand and the complexes

	Ligand of $E_{1/2}(1)$	Exidation $E_{1/2}(2)$	Metal E <sub>1/2</sub>	Ligand reduction $E_{1/2}(1)$
OPTPPH <sub>2</sub>	0.63			-1.46
OPTPPMnCl			$-0.59(\bullet - \bullet)$	-1.73
OPTPPCo	0.73		$-0.12(\bullet - \bullet), -1.21(\bullet - \bullet)$	
OPTPPNi	0.56	0.39		-1.58
OPTPPCu	0.79	0.37		-1.58
OPTPPZn	0.67			

which makes them easier to oxidize and harder to reduce than TPPCo<sup>10</sup>.

#### **CONCLUSIONS**

From the above results of UV-vis spectra, infrared spectra, <sup>1</sup>H-NMR spectra, mass Spectra, we can propose the structure of the OPTPPH<sub>2</sub> and relative transition metal complexes is as we expected.

A series of meso-5-(p-octanoyloxyphenyl)-10,15,20triphenylporphyrin and relative transition metal complexes have been prepared. We have illustrated the application of cyclic voltammetry. The cyclic voltammetry contributes to the investigation of porphyrins.

The fluorescence intensity of OPTPPZn and OPTPPNi is much bigger than other transition metal complexes.

#### REFERENCES

 Z. Gross, S. Ini. Remarkable Effects of Metal, Solvent, and Oxidant on Metalloporphyrin-Catalyzed Enantiselective Epoxidation of Olefins. J. Org. Chem., 1997, 62, 5514–5521.

- J. P. Collman, X. Zhang, V. J. Lee, E. S. Uffelman, J. I. Brauman. SRegioselective and enantioselective epoxidation catalyzed by metalloporphyrins, Science, 1993, 261, 1404–1411.
- D. Mansuy. Activation of alkanes: The biomimetic approach. Coord. Chem. Rev., 1993, 125, 129–142.
- Ji Liangnian, Qin Xia, Huang Yinwan, The Synthesis and Characterization of a New Tailed Metalloporphyrin Coordination Compound. Acta Scientiarum Naturalium Universitatis Sunyatseni, 1993, 32, 1–7.
- W. D. Horrocks, Jr., C. P. Wong. Lanthanide Porphyrin Complexes. Evaluation of Nuclear Magnetic Resonance Dipolar Probe and Shift Reagent Capabilities. J. Am. Chem. Soc., **1976**, 98, 7157.
- G. S. S. Saini, Resonance Raman study of free-base tetraphenylporphine and its dication. Spectrochimica Acta Part A., 2006, 64, 981–986.
- Ingar Halvorsen, Erik Steene, Abhik Ghosh. Resonance Raman marker bands of β-octahalogeno-meso-tetraarylmetalloporphyrins. J. Porphyrins Phthalocyanines, 2001, 5, 721–730.
- Florian Paulat, V. K. K. Praneeth, Christian Nalther, and Nicolai Lehnert. Quantum Chemistry-Based Analysis of the Vibrational Spectra of 5-Coordinate Metalloporphyrins [M(TPP)CI]. Inorg. Chem., 2006, 45, 2835– 2856.
- Huiying Jia, Weiqing Xu. Spectral Study of 5, 10, 15, 20-Tetra (p-Chlorophenyl) Porphyrin Lanthanide Complexes. Chem Icai Journal of Chinese Universities, 2004, 2, 338–341.
- Wei Liu, Tongshun Shi, Synthesis and Characterization of Tetra-(poctanoyloxyphenyl) Porphyr in Cobalt complex. Acta Scientiarum Naturalium Universitatis Jilinensis, 1999, 01, 94–96.