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Syntheses and characterization of some porphyrins and metalloporphyrins

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Abstract

We have previously reported [1] that metalloporphyrins can be regarded as an active centre of cytochrome P-450 model enzyme systems. In this report, twelve derivatives of tetraphenyl porphyrins with electron-withdrawing and -donating substituents in the benzene ring, and their Fe(III) and Mn(III) complexes have been prepared, some of which have not been reported.

The synthetic compounds were identified by element analysis, mass spectrometry and paramagnetic susceptibility. Their structures were confirmed by UV–Vis, IR and ^{1}H NMR spectrometry. The spectral characteristics of the compounds are also discussed.

Introduction

The reaction mechanism of the hydroxylation of benzene to phenol under mild experimental conditions by the system consisting of the synthetic iron porphyrins and thiol compounds has been reported [1]. This system can be considered as a model system of cytochrome P-450 and will be further investigated. Recently the nature of the 'active oxygen species' and the oxygen-transfer event in the catalytic cycle of cytochrome P-450 have been the subject of intensive investigations. The formation of the oxidizing species involves the complexing of enzymes with substrate, reduction, addition of O_2, and a second reduction which could be the rate determining step [2]. The structure of the intermediate which is related to O–O activation by the cytochrome P-450 catalytic system is difficult to investigate because of the difficulty in its isolation. Therefore the modification of the structure of synthetic metalloporphyrins with different substituting groups becomes one of the approaches to study the O–O activation. An electron-donating group in the benzene rings of porphyrins activates the reduction of oxygen. On the other hand, an electron-withdrawing group would promote the efficiency of a catalyst by preventing its self-oxidation. The side chains in the porphyrin ring, especially the substituting groups in the *meta* position, also attribute some resistances to the formation of the inactive $(MP)_2O$ [3].

More than ten derivatives of TPP and their Fe(III) and Mn(III) complexes have been synthesized of which TENPP, MnTHMPPCl, MnTTOMPPCl and MnTOBPPCl have not been reported. In this report, the compositions of synthetic compounds were analyzed by elemental analysis and mass spectrometry and the structures of some porphyrins and metalloporphyrins were studied by using UV–Vis, IR and ^{1}H NMR spectrometry.

Experimental

Materials

Pyrrole (A.R. grade) was distilled before use. Chloroform (A.R. grade) was dried with P_2O_5 and distilled. 3,4,5-Trimethoxy-benzaldehyde, $(CH_3O)_3$-C_6H_2CHO, (85%) was washed twice by the sequence of 10% HCl, water, 10% NaOH, water, and finally it was dried in vacuum at 60 °C. Neutral alumina (100–200 mesh) used for column chromatography was reflexed with CH_2Cl_2 for 12 h, and then vacuum dried (180 °C, 0.1 mm Hg) for 12 h before use.

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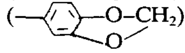
TABLE 1. Yield of synthesis and purification of some porphyrin derivatives

No.	Phenyl substituents	Porphyrins	Yield (%)	Purification method[a]	Yield (%)
1	$(3,4,5\text{-}OCH_3)_4$	TTOMPP	16.2	A	85.0
2	$(o\text{-}OCH_3)_4$	TOMPP	10.2	B	77.0
3	$(o\text{-}OC_2H_5)_4$	TOEPP	6.5	B	70.4
4	$(p\text{-}Cl)_4$	TPCPP	21.7	A	92.0
5	$(o\text{-}Br)_4$	TOBPP	5.1	B	63.0
6	$(p\text{-}NO_2)_4$	TNPP	6.0	C	43.3
7	$(o\text{-}NO_2, p\text{-}NO_2)_4$	TENPP	2.2	C	50.0
8	$(p\text{-}OCH_3)_4$	TEMPP	18.2	B	80.5
9	$(m\text{-}OCH_3, p\text{-}OH)_4$	THMPP	16.3	D	77.3
10		TPMPP	9.25	D	60.5
11	$(m\text{-}Cl)_4$	TMCPP			

[a] A: oxidation column chromatography, B: column chromatography, C: extraction rinse, D: recrystallization.

TABLE 2. Synthesis and purification of metalloporphyrins

Metalloporphyrin	Yield (%)	Purification (%)	Metalloporphyrin	Yield (%)	Purification (%)
MnTPPCl	37.0	95.2	FeTPPCl	95.0	86.4
MnTTOMPPCl	52.3	96.0	FeTTOMPPCl	73.4	80.2
MnTOMPPCl	62.0	50.3	FeTOMPPCl	70.3	45.0
MnTOEPPCl	46.8	50.4	FeTOEPPCl	52.3	43.0
MnTHMPPCl	56.4	60.4	FeTHMPPCl	68.5	67.9
MnTOBPPCl	40.3	45.0	FeTOBPP·OAc	37.8	48.2
MnTMPPCl	56.2	62.3	FeTMPPCl	93.0	73.2
MnTPMPP·OAc	42.0	58.6	FeTPMPP·OAc	52.3	63.0
MnTPCPPCl	77.0	90.3	FeTMCPPCl	69.2	67.0

Other reagents were A.R. grade chemicals as supplied.

Syntheses and purification of porphyrins

Synthesis of TENPP

Freshly distilled pyrrole (56 ml, 0.8 mol) and an equal molar quantity of reagent grade 3,5-dinitrobenzaldehyde were added to 150 ml of refluxing reagent grade glacial acetic acid. After refluxing for 1 h, the colour of solution changed from pale brown to brown and finally to dark purple. After heating, the solution was cooled to room temperature and filtered. The precipitate was washed thoroughly with methanol. The resulting purple crystals were air dried, and finally dried in vacuum to remove adsorbed acid to yield 15 g of TENPP.

The product obtained was purified by a simple extraction rinse method. TENPP (1.0 g) was dissolved in 6 M HCl and the solution appeared greyish green. It was filtered and neutralized by NaOH solution and finally sodium carbonate was added. A dark brown precipitate was obtained and finally dried in vacuum. The precipitate was extracted by chloroform (containing 15% pyridine) several times and the chloroform layer was immediately passed through a fresh bed of Florex. The greyish brown coloured band was collected using chloroform as an extraction solvent which was finally removed in vacuum. Due to adsorption, there is a loss of approximately 50% of the starting material.

Other porphyrins were synthesized by using the method of Adler *et al.* [4] and were purified by one of the following methods:

(A) Oxidation column chromatography
(B) Column chromatography
(C) Extraction rinse
(D) Recrystallization [5].

The yield of synthesized porphyrins are listed in Table 1.

Syntheses and purification of metalloporphyrins

The synthetic methods for Fe(III) and Mn(III) porphyrin complexes and their purification are similar to those previously described [6] and the results are listed in Table 2.

Synthesis and purification of MnTTOMPPCl($MnC_{56}H_{52}N_4O_{12}Cl$)

The porphyrin TTOMPP (2.0 g) was dissolved in 200 ml DMF. A total of 1.6 g of manganese acetate $Mn(Ac)_2 \cdot 4H_2O$ was then added. After waiting for several minutes to allow TTOMPP and $Mn(Ac)_2 \cdot 4H_2O$ to dissolve, the solution was allowed to reflux for 1 h. At this point a visible spectrum in $CHCl_3$ taken from the reaction mixture will reveal the absence of any remaining free-base porphyrin. Had the visible spectrum revealed the presence of TTOMPP, an additional quantity of manganese acetate (0.1 g) would be added and refluxing continued for another 20 min. The process of adding small amounts of manganese acetate would be continued until no free-base porphyrin bands were found in the visible spectrum. After refluxing, the mixture was allowed to cool to room temperature and was poured into 200 ml ice-cooled 30% NaCl solution. The precipitate formed was collected, washed with distilled water (100 ml) and air dried. The dried precipitate was dissolved in 400 ml CH_3OH and filtered. The solution was poured into 400 ml 6 M HCl solution. The precipitate formed was filtered again and washed with distilled water and air dried. It was then extracted by CH_2Cl_2 and concentrated. n-hexane was added to the concentrated solution and finally the crystal formed was dried by infrared. Yield 2.0 g of MnTTOMPPCl (52.3% based on TTOMPP).

Syntheses and purification of MnTHMPPCl($MnC_{48}H_{36}N_4O_8Cl$) and MnTOBPPCl($MnC_{56}H_{24}N_4Br_4Cl$)

Similar procedures to those described above were used to prepare MnTHMPPCl and MnTOBPPCl and the yields were 56.4 and 40.3%, respectively.

In the purification of the metal complexes, the mixed solvent $CHCl_3$–HoAC (vol./vol. 3/5) was used. Crude Fe(III) and Mn(III) complexes were purified by recrystallization to remove impurities which can cause dimerization.

Results and discussion

Compositions of synthetic compounds and their complexes

The compositions of the synthesized porphyrins and their metalloporphyrins were determined using an element analyzer (Perkin-Elmer 240C). The results which are listed in Table 3 are close to the calculated values. Some results were cross-examined by mass spectrometry (VG, ZAB-HS mass spectrometer) and were found close to the theoretical values. For example, the mass data of $(MnTTOMPP)^+$ and $(FeTOMPP)^+$ are 1028 and 789 compared to the calculated values of 1028.87 and 788.61, respectively. In order to establish the oxidation state of the metal ion, the magnetic susceptibility was measured using the method of Evans (JEOL, FX-90Q) [7] and the results are shown in Table 4. In column 2, the magnetic susceptibility of FeTOMPPCl, χ_μ, with high electron spin indicates that the complex is a single one, since its oxo-dimer has a μ_{eff} value of 1.85 [9]. The same principle can be applied to explain the Mn(III)–porphyrin complexes. $\chi_{\mu,corr}$ is χ_μ after the correction for the diamagnetic susceptibility of porphyrin. The value of effective magnetic moment μ_{eff} is related to the number of unpaired electrons n and the calculated n values are listed in column 5 of Table 4. From the number of unpaired electrons, a larger magnetic susceptibility is expected.

Visible spectra of porphyrins and their metalloporphyrin complexes

The visible spectra were obtained using a Shimadzu MPS-2000 spectrometer. The results are listed in Table 5. The synthetic metalloporphyrins are believed not to exist as an oxo-dimer since there are no peaks at 565 and 610 nm for the oxo-dimer $(FeP)_2O$ [12] and no peaks at 353–358 nm for $(MnP)_2O$ [13]. At the 500–650 nm visible range, four peaks from low to high energy are normally observed for porphyrins and its derivatives as shown in Fig. 1. These four peaks can be explained by using a four orbital model [14] named as peak I to IV. The wavelengths of the maximum absorption λ_{max} for four visible bands I–IV in order of increasing energy in consistence with the nomenclature of Gouterman [15] are also listed. It is due to the electron transition between the highest energy occupied orbitals and the lowest energy empty orbitals. Some visible spectra for synthetic porphyrins can be explained as follows.

Electron donating substituents on para position of phenyl group

The following gradual spectral changes were observed with the increasing electron donating power of the *para* substituents: (i) all peaks shift to the red, (ii) the ratios of the transition dipoles of the Q(0–0) (bands I and III) to those of Q(0–1) (bands II and IV) increase markedly. These predictions are consistently verified by the progressive shift to longer wavelengths in the visible bands with increasingly stronger electron donating substituents on the methine bridged carbon atoms such as TOMPP, THMPP and TTOMPP.

TABLE 3. Element analysis for the porphyrins (P) and metalloporphyrins (MP)[a]

P or MP	Formula	C (%)	H (%)	N (%)	M^{n+} (%)
TPCPP	$C_{44}H_{26}N_4Cl_4$	70.39 (70.21)	3.46 (3.48)	7.54 (7.44)	
FeTPCPPCl	$FeC_{44}H_{24}N_4Cl_5$	62.61 (62.76)	2.83 (2.87)	6.37 (6.65)	6.60 (6.63)
MnTPCPPCl	$MnC_{44}H_{24}N_4Cl_5$	62.98 (62.89)	2.60 (2.88)	6.56 (6.66)	6.55 (6.53)
TTOMPP	$C_{56}H_{54}N_4O_{12}$	68.70 (68.98)	5.50 (5.58)	5.39 (5.74)	
FeTTOMPPCl	$FeC_{56}H_{52}N_4O_{12}Cl$	63.46 (63.19)	5.02 (4.92)	5.28 (5.26)	5.06 (5.23)
MnTTOMPPCl	$MnC_{56}H_{52}N_4O_{12}Cl$	63.17 (63.25)	4.82 (4.93)	5.36 (5.27)	5.09 (5.17)
TOMPP	$C_{48}H_{38}O_4N_4$	78.20 (78.46)	5.14 (5.21)	7.23 (7.62)	
FeTOMPP·OAc	$FeC_{50}H_{41}O_6N_4$	70.42 (70.84)	4.88 (4.64)	6.29 (6.61)	6.40 (6.59)
TOBPP	$C_{44}H_{26}N_4Br_4$	56.75 (56.81)	2.94 (2.81)	6.01 (6.02)	
TNPP	$C_{44}H_{26}N_8O_8$	65.96 (66.50)	3.88 (3.30)	14.02 (14.09)	
TOEPP	$C_{52}H_{46}N_4O_4$	78.93 (78.96)	5.89 (5.86)	6.90 (7.08)	
MnTHMPPCl	$MnC_{48}H_{36}N_4O_8Cl$	64.72 (64.98)	4.14 (4.09)	6.03 (6.31)	6.22 (6.19)
TENPP	$C_{44}H_{22}N_{12}O_8$	67.20 (67.52)	2.76 (2.83)	12.33 (12.47)	

[a]Calculated values are given in parentheses.

TABLE 4. Paramagnetic susceptibility of metalloporphyrins

Metalloporphyrin	Magnetic susceptibility of complexes χ_μ ($\times 10^{-6}$ cgs)	$\chi_{\mu,\mathrm{corr}}$[a] ($\times 10^{-6}$ cgs)	Magnetic moment, μ_{eff}[b]	Number of unpaired electrons n[c]
FeTOMPPCl	13625.68	14425.68	5.86	5
MnTTOMPPCl	9704.20	10549.20	4.96	4
MnTOEPPCl	9372.37	10072.33	4.90	4
MnTOBPPCl	8925.69	9678.23	4.82	4

[a]Correction of diamagnetic susceptibility of porphyrin ligands [8] and Pascal constant. [b]Effective magnetic moment: $\mu_{\mathrm{eff}}=2.84\sqrt{\chi_{\mu,\mathrm{corr}}T}$, T=temperature. [c]μ_{eff} (theory)$=\sqrt{n(n+1)}$, where n is the number of unpaired electrons.

Spectral effect of electron-withdrawing substituents in ortho position

For TOBPP, the peaks shift to the blue, bands I and III are largely diminished, and the effect on bands II and IV is negligible. A similar result was observed for TOMPP and TOEPP. It is preferable to interpret this by the effects of steric hindrance of the a_{2u} electrons toward the molecular periphery rather than the shift of electron density.

Visible spectra of high spin metalloporphyrin derivatives

The spectral bands I–IV and Soret band for the high spin metalloporphyrin derivatives are listed in Table 5. Each band behaves somewhat differently as the electronic effects of the substituents are changed. The band shifting is due to the effects of the substituents and was described elsewhere [10]. Visible spectra for bands IV–I are similar for all

TABLE 5. Electronic absorption spectrum data of porphyrins and metalloporphyrins

Compounds	Solvent[a]	λ_{max} (nm)							$\frac{Q_{(0-0)}}{Q_{(0-1)}}$
		Sh	Soret	Sh	IV $Q_{y(0-1)}$	III $Q_{y(0-0)}$	II $Q_{x(0-1)}$	I $Q_{x(0-0)}$	
TPP	B		419.0	486.0	515.0	548.0	592.0	648.0	0.46
TPP [4b]	B		419.0	485.0	514.0	549.0	591.0	647.0	
TPCPP	B		419.9	485.0	514.7	549.1	590.9	646.9	0.48
TPCPP [10]	B		420.9	485.0	515.0	550.0	592.0	647.0	
TOMPP	C		419.7	483.0	513.7	547.7	590.3	651.3	0.33
TOMPP [10]	C		420.0	483.0	513.0	546.0	590.0	652.0	
TOBPP	C		419.9	480.3	513.7	544.7	588.3	646.5	0.18
TOBPP [4b]	C		418.5	479.2	512.7	541.9	587.8	643.1	
TOEPP	C		419.3		514.9	547.9	590.1	650.9	0.34
TOEPP [11]	B		418.0		513.4	546.2	591.3	651.6	
TTOMPP	C		419.9		517.1	553.3	591.3	651.3	0.54
THMPP	C		422.7	480.9	517.7	554.9	593.3	650.3	0.81
TMPP	B		422.7	486.9	517.9	555.5	595.1	651.3	0.67
TMPP [10]	B		423.8	488.0	518.0	556.0	595.0	652.0	
TMCPP	C	358.0	420.9		513.2	547.5	587.9	645.5	0.41
TMCPP [4b]	B	357.5	419.5	480.5	512.5	546.5	588.5	644.5	
TNPP [10]	B		427.3	486.0	517.8	553.0	592.3	646.1	
TNPP	B		428.0	487.0	518.0	554.0	593.0	647.0	
TENPP	C		419.5		517.0	564.2	592.0	647.2	
FeTPPCl	B	372.0	418.0		507.0		572.0	689.0	
FeTPPCl [10]	B	372.1	418.0		506.8		572.0	688.2	
FeTPCPPCl	C	377.7	415.7		509.9		575.7	609.3	
FeTOMPPCl	C	376.9	417.7		508.9		578.1	650.5	
FeTOEPPCl	C	381.9	418.3		510.9		589.7	656.3	
FeTOBPP·OAc	C	341.1	417.5	480.3			590.2		
FeTPMPPCl	C		420.8		511.7		576.7	694.3	
FeTTOMPPCl	C	383.1	422.1		510.3	528.3	582.9	619.3	
FeTHMPPCl	C	364.3	423.7		512.2		572.7	650.0	
FeTMPPCl	C	385.9	420.9		512.7				
FeTMCPPCl			416.3	477.1	512.9		586.9	644.3	
MnTPPCl	C	362.5	406.9	475.2	522.5			625.3	
MnTPPCl [10]	C	370.1	405.8	474.7	523.0			624.7	
MnTPCPPCl	C	384.0	414.2	478.3	527.4		582.1	617.5	
MnTOMPP·OAc	C	377.9	401.5	479.3	523.2		580.1	614.9	
MnTOEPP·OAc	C	378.3	403.3	480.0	525.8		581.5	615.3	
MnTOBPP·OAc	C	374.1	418.9	479.5	512.1		583.5		
MnTTOMPPCl	C	381.3	406.1	482.3	528.3		582.9	619.3	
MnTHMPPCl	C	380.1	419.5	480.5	521.2		587.1	624.1	
MnTENPP·OAc	C		434.7	488.3				645.5	
MnTMPPCl	C	382.3	406.1	480.3	531.3		589.6	644.3	

[a] B = benzene, C = chloroform.

metalloporphyrins indicating that the influence of the d orbital from the metal ion is generally weak.

The electron spectra for Mn(III)P complexes are abnormal and interesting as shown in Fig. 2. Two strong new bands (V and VI) were observed. In general, a very broad band III appears as a shoulder peak at the longer wavelength side of band IV, and hence band III disappears in Fig. 2. This abnormal behaviour indicates that the Mn^{3+} ion has a strong influence on the π orbital of the porphyrin ring system.

Vibrational spectroscopy

IR spectra were measured on a Nicolet SDX-FT IR spectrometer using the KBr pellet method. The spectra data for TTOMPP, TOEPP, MnTHMPPCl, MnTOBPPCl and FeTTOMPPCl are listed in Table 6. The IR spectra were more complicated due to

TABLE 6. IR spectral data of porphyrins and metalloporphyrins (cm^{-1}) using the KBr pellet method

TTOMPP	TOEPP	MnTHMPPCl	MnTOBPP	FeTTOMPPCl	Band Assignment
		3400(m)			ν_{O-H}
3350(m)	3325(m)				ν_{N-H}
2943(m)	2981(m)	2937(m)		2943(m)	$\nu_{C-H\ (OCH_3)}$
	2875(m)				$\nu_{C(\beta)-H}$
1581(s)	1581(m)	1600(m)	1562(s)	1581(s)	$\nu_{C=C\ (Bz)}$
1500(s)	1481(s)	1512(s)	1468(s)	1500(s)	ν_{Cp-Cp}
1461(s)	1443(s)			1462(s)	ν_{Cp-N}, δ_{C-CN}
1406(s)			1425(s)	1406(s)	δ_{C-H}
1356(s)		1337(m)	1343(s)	1350(s)	ν_{Cp-Cp}, δ_{Cp-H}
1237(s)		1268(s)		1237(s)	$\nu_{C-O\ (C-OCH_3)}$
	1237(s)				$\nu_{C-O\ (C-OC_2H_5)}$
		1206(s)			ν_{O-H}
1125(s)		1118(m)		1125(s)	$\nu_{C-O-C\ (C-OCH_3)}$
	1118(m)				$\nu_{C-O-C\ (C-OC_2H_5)}$
			1012(s)		ν_{C-Br}
1006(m)					δ_{Cp-Cp}, Bz(*p*)
	1043(m)				δ_{Cp-Cp}, Bz(*o*)
		1018(m)		1000(s)	δ_{Cp-Cp}, Bz(*p*, *m*)
925(m)	968(m)	935(m)	960(w)	937(s)	ν_{Cp-Cp}, ν_{Cp-N}
	920(m)		881(w)		
800(m)	800(m)	806(m)	800(m)	812(m)	π_{C-H}
735(m)	750(s)	718(w)	750(s)	725(m)	δ_{C-H} (out of plane)
648(m)	650(w)	618(w)	640(m)	643(m)	π (ring deformation)
466(m)	455(w)				
		450(w)	448(w)	475(m)	ν_{Fe-N}

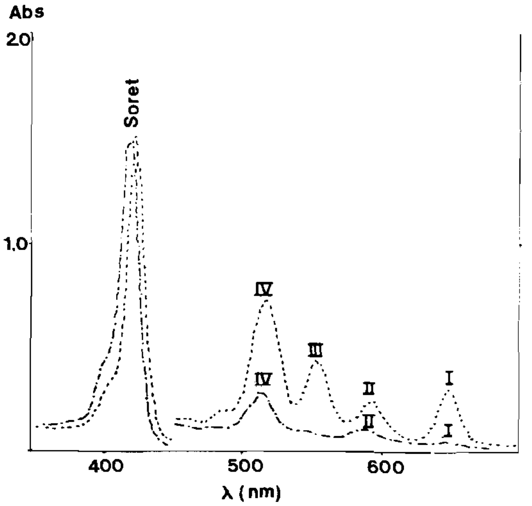


Fig. 1. Electronic absorption spectra for THMPP (– – –) and TOBPP (– · –).

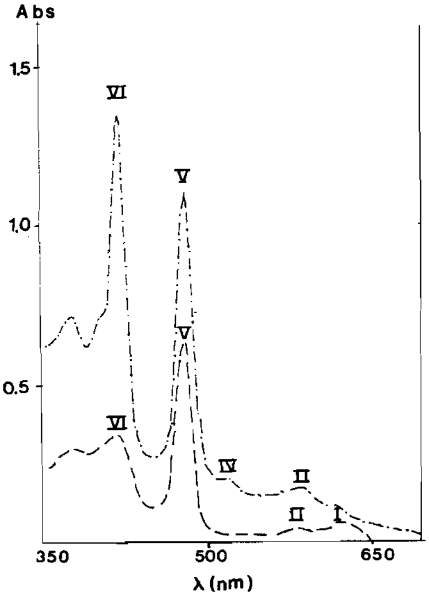


Fig. 2. Electronic absorption spectra for MnTOBPPOAc (– · –) and MnTHMPPCl (– – –).

the inducting by the substituting group in the *ortho* position of TPP, the lowering of the symmetry of the molecule and the increasing steric hindrance of the conjugate system. For example, TOEPP with the functional group $-OC_2H_5$ at the *ortho* positions exhibits an absorption band, $\nu(C-OC_2H_5)$, at 1118 cm^{-1} and a characteristic vibrational band of Bz(*o*) at 1043 cm^{-1}. In addition, this functional group also has a strong influence at a low frequency range. For

TABLE 7 Chemical shifts for the porphyrins

Compound	Chemical shifts (ppm)					
TOEPP	Pyrrol-H	Bz *o*-H	Bz *p*-H	Bz *m*-H	$OC_2H_5\alpha H$	$OC_2H_5\beta H$
	8 74	7 95	7 73	7 34	3 88	0 74
Ratio of H atom	8	4	4	8	8	12
TTOMPP	Pyrrol-H	Bz *o*-H	Bz *p*-OCH_3, H	Bz *m*-OCH_3, H		
	8 97	7 48	4 19	3 98		
Ratio of H atom	8	8	12	24		
THMPP	Pyrrol-H	Bz *o*-H	Bz *m*-OCH_3, H	Bz *p*-OH, H		
	8 90	8 79	3 90	9 50		
Ratio of H atom	8	8	12	4		
TPP	Pyrrol-H	Bz *o*-H	Bz *m*-H	Bz *p*-H		
	8 84	8 22	7 78	7 77		
Ratio of H atom	8	8	8	4		

example, the band at 425 cm^{-1} for porphyrin ring deformation of TPP is shifted to a longer frequency of 455 cm^{-1} for TOEPP [16]

When porphyrins form complexes with a metal ion, the most obvious change in IR spectra is the disappearance of ν(N–H) (about 3360 cm^{-1}) On the other hand, a strong band appears at 900–1000 cm^{-1} due to the deformation of the porphyrin ring by the interaction of M–N bonding [1]

^1H NMR spectra of porphyrin derivatives

A Fourier transform NMR spectrometer (JEOL, FX-90Q) was used for measurement, $CDCl_3$ was used as a solvent and TMS as an internal standard The chemical shifts for TOEPP, TTOMPP, THMPP and TPP are listed in Table 7 It was found for all the porphyrins that the ratio of hydrogen atoms in the spectra is consistent with the hydrogen atoms in the porphyrins and hence the proposed structure of porphyrin molecules is proved From the spectra, pyrrole-H shows a single peak which indicates the plane symmetry of the porphyrin molecules [17]

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