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Meso-tetra[(*p*-alkoxyl-*m*-ethyloxy)phenyl]porphyrins and their Transition Metal Complexes: Synthesis and Characterization

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Three meso-tetra[(*p*-alkoxyl-*m*-ethyloxy)phenyl]porphyrins and their transition metal (Zn, Cu, Ni, Co, Mn) complexes were synthesized. The molecular structures were confirmed by means of ^{1}H NMR, UV-Vis, IR, elemental analyses, etc., which indicate the valence state of Mn atom in the compound is +3 and Ni, Cu, Zn, Co atom is +2. Optical properties were discussed by fluorescence spectrum. The quantum yields of the complexes are much lower than the corresponding ligands.

Keywords luminescence spectroscopy, porphyrin, transition metal complex

INTRODUCTION

Porphyrins are tetrapyrrolic macrocycles and have special structures with big π-orbital on the carbon-nitrogen framework. Because of the large conjugational effect of the tetrapyrrolic macrocycle, porphyrins have special photophysical properties and have been used in many fields[1] such as oxygen transfer,[2] energy and electron transfer,[3] light harvesting,[4] molecular wires[5] and so on. Porphyrins can be synthesized flexibly by introducing different substituents at the meso- and β-position, and their photophysical and photochemical properties can be applied in many fields.[6] The meso-substituted porphyrins are a subgroup of porphyrins with interesting properties.[7–8] Meso-tetraaryl porphyrins show attractive properties such as easy synthesis and functionalization, and have been used in a wide variety of model systems. Metal porphyrin research is the center of porphyrin chemistry since the metal ions in porphyrin complexes can change porphyrins, electronic structure, which give them many characteristics.

It is well known that chlorophyll, haem and cytochrome, each of which plays a key role in life, are tetrapyrrole compounds that contain Mg^{2+}, Fe^{3+} ions, etc.[9] In recent years, dyads and triads containing porphyrins as electron acceptor or donor, have been proved of interest as photosynthetic model compounds[10]; metal porphyrins have also been widely used in photocatalysis, light-energy conversion and various medical applications.[11−13]

Fluorescein exhibits strong absorption and fluorescence in the UV-vis region; fluorescence is a convenient way of revealing electron transfer in photosynthesis model compounds. Fluorescein is a good candidate to form dyads with porphyrin in order to research the photoelectron properties. In the past few years, Sun et al. had synthesized a series of fluoresceine porphyrin dyads, and discussed their photoproperties.[14−15]

In this study, we synthesized three meso-tetra [(*p*-alkoxyl-*m*-ethyloxy) phenyl] porphyrins and their transition metal (Zn, Cu, Ni, Co, Mn) complexes. Their molecular structures were confirmed by ^{1}H NMR, UV-Vis, IR and elemental analyses. We also discussed the optical properties of these compounds (Scheme 1).

EXPERIMENTAL

Materials and Instrumentation

All reagents and solvents were of commercial reagent grade and used without further purification. All chemicals were reagent grade and dried before use. Pyrrole was newly distilled before use.

The proposed molecular structures of the compounds were confirmed by IR and ^{1}H NMR spectroscopy. The IR spectra were recorded on a Nicolet 5PC-FT-IR spectrometer in the region 200–4000 nm^{-1} using CsI pellets. ^{1}H NMR spectra were recorded on a Varian-Unity-500 NMR spectrometer

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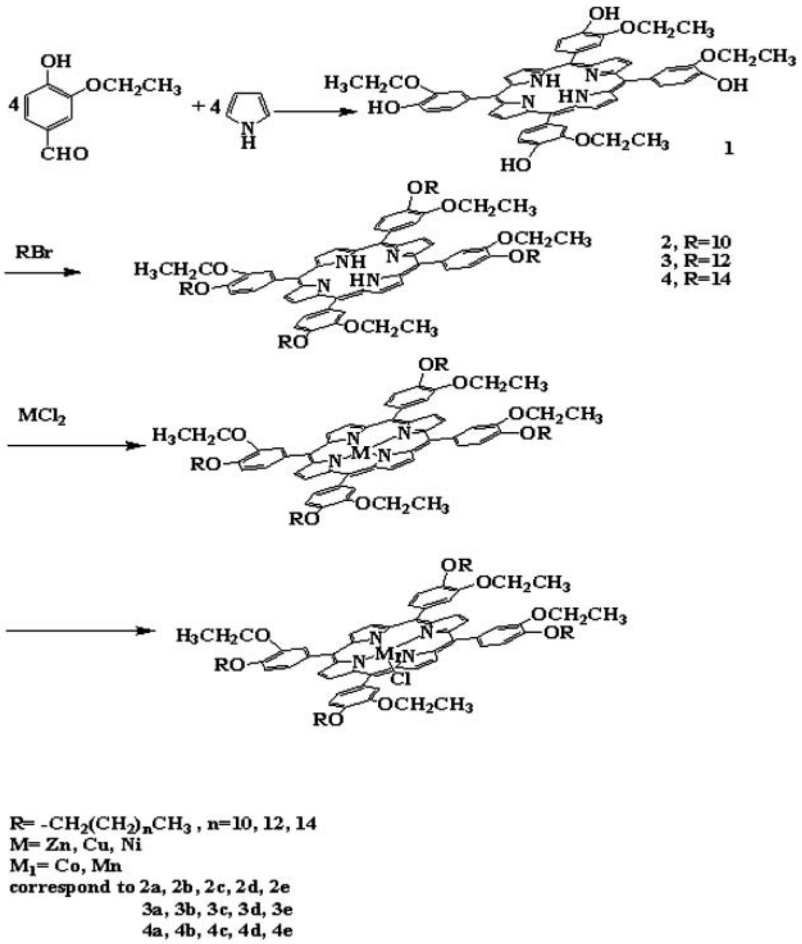

SCH. 1. Synthesis of the porphyrin ligands and complexes.

using $CDCl_3$ as solvent and tetramethylsilane (TMS) as internal standard. Further identification of the porphyrin derivatives was carried out by UV-vis spectroscopy on a Shimadzu UV-240 spectrophotometer using chloroform as solvent. Elemental analyses were carried out with a Perkin-Elmer 240C autoelementary analyzer. At room temperature, fluorescence spectra using 10^{-5} mol·dm^{-3} chloroform solution were measured by FS920 Steady State Fluorescence Spectrometer in the region 300–800 nm. Emission spectra were corrected by the sensitivity of the photomultiplier tube.

Preparation of Compounds

The porphyrin derivatives in this work were synthesized through the route as shown in Scheme 1. Meso-tetra-(*p*-hydroxy-*m*-ethyloxy) phenyl porphyrin (1) was prepared by the literatures method.[16]

Preparation of the ligand 3

Complex 1 (500 mg 0.6 mmol) and 1-bromotetradecane (1104 mg, 4 mmol) were refluxed in benzene under the protection of dry nitrogen for three hours. The crude product was purified by column chromatotgraphy on neutral alumina, eluted by chloroform, recrystallized from chloroform/hexane. Other ligands 3 and 4 were prepared by the similar method. The title compound was obtained as a purple solid (687 mg, 0.45 mmol, yield 75%). ^{1}H NMR ($CDCl_3$ 25°C): 8.9 (s, 8H, pyrrole ring); 7.78, 7.71 (t, 12H, meso-phenyl protons); 4.20 (m, 16H, C_6H_4-O-CH_2 protons); 0.88(t, 24H, CH_3); 1.26–1.64 (m, 96H, CH_2); -2.76 (s, 2H, pyrrole N-H).

Preparation of the complex 3a

Ligand 3 (0.2 g, 0.13 mmol) was dissolved in the mixture of 20 mL DMF and 20 mL chloroform, then $ZnCl_2{\cdot}2H_2O$ (0.09 g, 0.69 mmol) was added. The mixture was refluxed under the protection of dry nitrogen for about 1h. The extent of the reaction was measured by UV-Vis spectra of the solution at ten minute intervals. After evaporation of the solvent, the residue was purified by column chromatography (neutral aluminum oxide, $CHCl_3$). The title compound was obtained as a red solid (185 mg, 0.11mmol, 84%). ^{1}H NMR ($CDCl_3$ 25°C): 9.03 (s,

TABLE 1
Characterization data of the compounds

Compounds	Empirical formula	C (%)	H (%)	N (%)	Yield (%)	Dec.tem.(°C)
2	$C_{100}H_{142}N_4O_8$	78.60 (78.63)	9.31 (9.30)	3.66 (3.67)	75	> 400
3	$C_{108}H_{158}N_4O_8$	79.15 (79.12)	9.61 (9.64)	3.40 (3.41)	73	> 400
4	$C_{116}H_{174}N_4O_8$	79.56 (79.54)	9.45(9.44)	3.21(3.20)	75	> 400
2a	$ZnC_{100}H_{140}N_4O_8$	75.40 (75.46)	8.89 (8.87)	3.51 (3.52)	83	> 200
2b	$CuC_{100}H_{140}N_4O_8$	75.59 (75.55)	8.87 (8.88)	3.51 (3.52)	86	> 200
2c	$NiC_{100}H_{140}N_4O_8$	75.81 (75.78)	8.87 (8.90)	3.55 (3.54)	84	> 200
2d	$CoC_{100}H_{140}N_4O_8$	75.80 (75.77)	8.88 (8.90)	3.54 (3.53)	85	> 200
2e	$MnC_{100}H_{140}N_4O_8Cl$	74.25 (74.30)	8.72 (8.73)	3.45 (3.47)	86	> 200
3a	$ZnC_{108}H_{156}N_4O_8$	76.16 (76.13)	9.22 (9.23)	3.24 (3.23)	84	> 200
3b	$CuC_{108}H_{156}N_4O_8$	76.25 (76.22)	9.21 (9.24)	3.28 (3.29)	84	> 200
3c	$NiC_{108}H_{156}N_4O_8$	76.40 (76.43)	9.24 (9.26)	3.30 (3.30)	85	> 200
3d	$CoC_{108}H_{156}N_4O_8$	76.40 (76.42)	9.25 (9.26)	3.30 (3.30)	83	> 200
3e	$MnC_{108}H_{156}N_4O_8Cl$	75.07 (75.03)	9.11 (9.09)	3.25 (3.24)	85	> 200
4a	$ZnC_{116}H_{172}N_4O_8$	76.75 (76.72)	9.56 (9.55)	3.10 (3.09)	86	> 200
4b	$CuC_{116}H_{172}N_4O_8$	76.75 (76.80)	9.58 (9.56)	3.10 (3.09)	84	> 200
4c	$NiC_{116}H_{172}N_4O_8$	77.04 (77.00)	9.56 (9.58)	3.09 (3.10)	84	> 200
4d	$CoC_{116}H_{172}N_4O_8$	76.97 (76.99)	9.60 (9.58)	3.09 (3.10)	87	> 200
4e	$MnC_{116}H_{172}N_4O_8Cl$	75.62 (75.68)	9.40 (9.42)	3.05 (3.04)	88	> 200

Theoretical values are given in parentheses.

8H, pyrrole ring); 7.73–7.80 (t, 12H, meso-phenyl protons); 4.20–4.35 (m, 16H, C_6H_4-O-CH_2 protons); 0.89–0.92 (t, 24H, CH_3); 1.28–1.68 (m, 96H, CH_2);

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

RESULTS AND DISCUSSION

Composition of the Complexes

The complex consisted of a transition metal central ion and a coordinating porphyrin ligand. There are two kinds of structures, PM [P = porphyrin ligand; M = Zn (II), Cu (II), Ni (II), Co (II)] and PM_1C1 [M_1 = Mn (III)].

The elemental analysis data of the ligands and their complexes are given in Table 1.

Infrared Spectra

The main band frequencies (cm^{-1}) and assignments of the ligands and complexes are given in Table 2. The band at 3313 cm^{-1} and 971 cm^{-1} in the free porphyrins are assigned to the N-H stretching and bend vibrations of the porphyrin core, respectively. These bands are absent in the three series of complexes because the hydrogen atoms have been replaced by transition metal ions to form M-N bands.

All of above analysis prove that porphyrin ring are coordinated to transition metal ions to form Ni, Cu, Co and Zn complexes and porphyrin ring, and chlorine atom are coordinated to transition metal ions to form Mn complexes. Assignments of other absorption bands are also presented in Table 2.

UV-Vis Spectra

Table 3 gives UV-Vis spectral data of the three ligands and corresponding 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. As can be seen in Table 3, Ni, Cu, Co and Zn complexes show very similar absorptions, which differs from Mn complexes. Apparently, the chain length does not significantly influence the UV-Vis absorptions of the complexes. Figure 1 shows the UV-Vis spectra of **3** and its corresponding transition metal complexes. Compared with the ligands, the number of the absorption bands of the complexes decreases: it is due to symmetry of the complexes increase. The data of the complexes accord with TPP and the transition metal complexes of TPP, which indicate that the valence state of Mn atom in the compound is +3 and Co, Ni, Cu, and Zn atom is +2.[16−18]

Luminescence Studies

Excited-state processes in porphyrins are extremely important for their applications in molecular devices. The fluorescent emission data for the ligands and complexes are listed in Table 4. Both S_2(B, Soret bands) and S_1(Q band) of porphyrin complexes can be observed in the emission spectra. The B (Soret) band is

TABLE 2
Infrared spectra of the ligands and complexes

Compounds	N–H Str. (Pyrrole)	C–C Str. (Benzol)	C–H Bend (Pyrrole)	–C=N Str. (Pyrrole)	C–O–C Bend (Ethoxyl)	N–H Bend (Pyrrole)
2	3313	1591	1466	1345	1248	971
3	3313	1598	1466	1345	1248	971
4	3313	1586	1466	1345	1248	971
2a		1574	1470	1337	1253	
2b		1575	1470	1343	1253	
2c		1574	1470	1348	1253	
2d		1574	1470	1348	1253	
2e		1575	1470	1343	1254	
3a		1579	1470	1343	1254	
3b		1575	1470	1348	1254	
3c		1579	1469	1348	1254	
3d		1575	1469	1347	1254	
3e		1577	1470	1343	1254	
4a		1575	1469	1337	1254	
4b		1579	1469	1342	1254	
4c		1575	1470	1348	1255	
4d		1580	1465	1348	1259	
4e		1575	1465	1344	1258	

TABLE 3
UV-Vis spectra of the ligands and complexes

	λ_{max} [nm] (ε [10^3 $M^{-1}cm^{-1}$])				
Compounds	Soret band	Q_1 bands	Q_2 bands	Q_3 bands	Q_4 bands
2	426(300.8)	520(21.6)	558(18.2)	595(13.4)	651(13.0)
3	426(291.3)	520(19.7)	557(15.7)	592(10.0)	651(10.3)
4	426(268.9)	520(21.2)	557(17.6)	592(13.0)	651(13.1)
2a	430(1000.0)		554(16.6)		
2b	423(302.4)		542(14.9)		
2c	424(179.8)		528(20.0)		
2d	418(140.4)		531(11.4)		
2e	484(89.1)			587(8.2)	624(11.1)
3a	429(203.4)		550(9.5)		
3b	424(205.0)		541(14.3)		
3c	424(153.8)		531(11.6)		
3d	418(90.3)		529(6.6)		
3e	484(94.1)			587(9.0)	624(11.6)
4a	428(78.7)		548(12.1)		
4b	423(150.8)		542(8.0)		
4c	425(269.9)		533(19.8)		
4d	419(40.8)		537(4.4)		
4e	484(67.5)			589(6.3)	624(8.3)

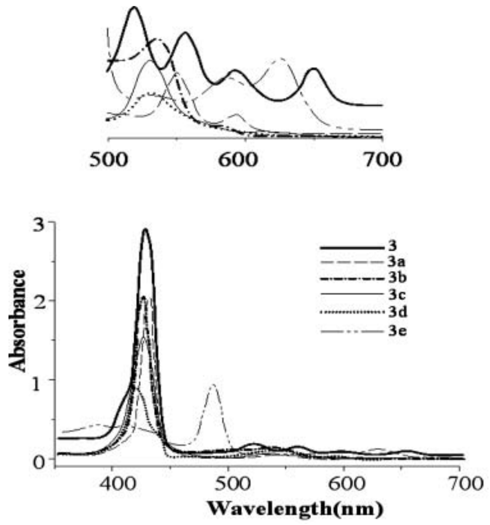

FIG. 1. UV-Vis spectra of a series of porphyrin complexes in chloroform at room temperature.

TABLE 4
Spectra data and quantum yields (Φf) of the ligands and complexes

Compounds	Q(0–0)	Q(0–1)	Q(0-2)	Φf
2		656	726	0.08411
3		659	722	0.1125
4		658	727	0.1145
2a	600	645		0.01671
2c	596	650		<0.001
2d	598	652		<0.001
2e		653		0.007708
3a	600	645		0.02444
3b	597	652		<0.001
3d	597	650		<0.001
3e	594	653		0.001967
4a	600	646		0.02131
4b	598	650		<0.001
4e	598	651		0.001806

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. The room-temperature fluorescence spectra of the ligands and complexes in chloroform (1×10^{-5} M) were recorded. The excitation spectra are approximately mirror images of the absorption spectra in the Q-band region. The emission spectra of zinc (a) and manganese (b) complexes obtained at an excitation wavelength of 425 nm are shown in Figure 2. The shapes of two series of complexes are so different. The Q (0–0) absorption intensity for the zinc complexes is stronger than that of manganese complexes. It should be noted that the Q (0–0) absorption bands around 600 nm do not appear in the emission spectra of complex 2e. This is probably because the band is too weak to be observed. Among these complexes, the absorption intensity decrease with the increasing of the chain length in the Ni, Co, Mn series of complexes and the complex 3a is the strongest. Its quantum yield is so low that sometimes fluorescence becomes unobservable. Q (0-0) fluorescence bands of the complexes are in the region 594–600 nm. Q (0-1) fluorescence bands of the complexes are in the region 645–653 nm. The quantum yields of the complexes are much lower than the corresponding ligands.

The $S_1 \rightarrow S_0$ (Q band) quantum yield depends on the relative rates of one radiative process $S_1 \rightarrow S_0$ and two radiationless processes $S_1 \rightsquigarrow S_0$ and $S_1 \rightsquigarrow$ Tn. The fluorescence quantum yields of our complexes are much less than 0.21. Thus, the excited state of the complexes S_1 is primarily deactivated by radiationless decay. Therefore, spin-forbidden process $S_1 \rightsquigarrow$ Tn[19] is the predominant route for radiationless deactivation of S_1 in the complexes.

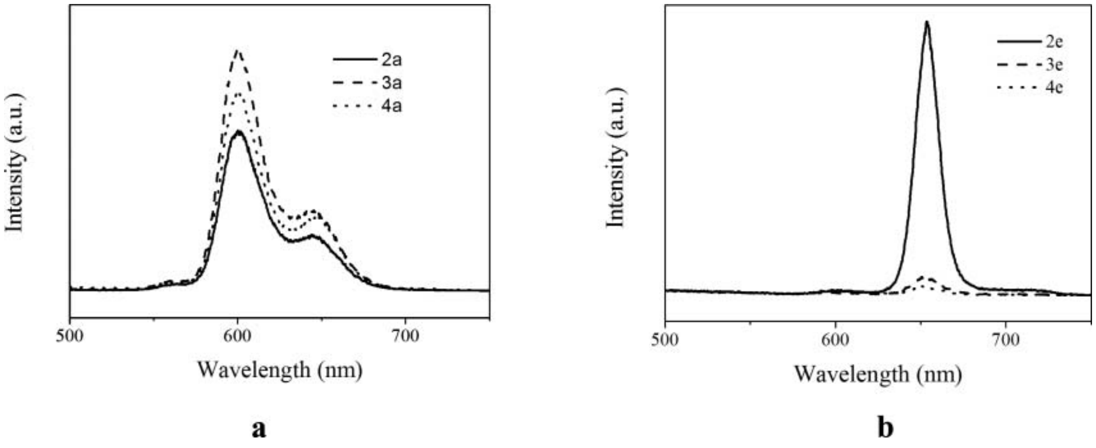

FIG. 2. Emission spectra of (a) three zinc complexes; (b) three manganese complexes.

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