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Synthesis, spectroscopic and electrochemical property of an unsymmetrical porphyrin and its Zn compound

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Abstract

In this article, a new 5-(*p*-maleicaminophenyl)-10,15,20-triphenylporphyrin (H_2P) and relative zinc compound (ZnP) were synthesized and characterized by means of elemental analyses, UV–vis, IR, MS and ^1H NMR spectroscopies. Furthermore, we have investigated the fluorescence spectroscopy of these compounds. The oxidation and reduction properties of the compounds were studied by the cyclic voltammetry, the oxidation–reduction potentials were obtained.

Keywords: Synthesis; Porphyrin; Cyclic voltammetry; Fluorescence

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In recent years, extensive effort has been devoted to designing and synthesizing various porphyrin compounds. Especially, the diverse modification of porphyrins at the β-pyrrolic or/and *meso*-positions by a variety of functional groups will bring about the exploration of new molecular devices, such as molecular wires, photovoltaic devices, light-emitting diodes, molecular optoelectronic devices and nonlinear optical devices, etc [1–3]. Toward this goal, there have been a number of reports on design a new class of zinc porphyrin–imide, in which an electron-donating ZnP moiety is directly connected to an electron accepting imide moiety in the *meso*-position. People have recently demonstrated that the combination of imide and porphyrin units leads to novel conjugates [4,5].

In this article, we have synthesized the H_2P and ZnP. They have been characterized by elemental analyses, UV–vis spectra, infrared spectra, mass spectra and ^1H NMR spectra. Luminescence spectra and cyclic voltammetry have been investigated.

1. Experimental

^1H NMR spectra were recorded on a Varian MERCORY-300 (300 MHz) NMR spectrometer. Elemental analyses were measured by a Perkin-Elmer 240 C auto elementary analyzer. UV–vis spectra were collected on a Shimadzu UV-365 spectrometer. Infrared spectra were recorded on a Nicolet 5PC-FT-IR spectrometer in the region of

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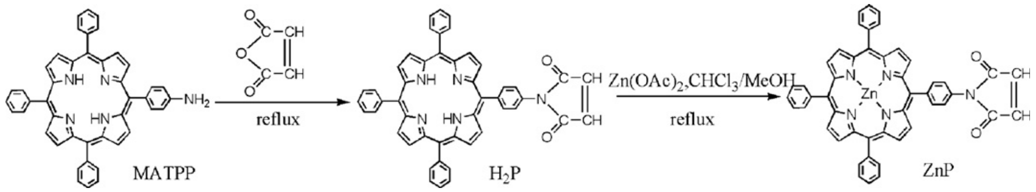

Scheme 1. Synthetic route of the H_2P and ZnP.

4000–400 cm^{-1}. Redox potentials were determined at room temperature by cyclic voltammetry with a CHI 660A electrochemical analyzer. Fluorescence spectra were recorded with a SPEX Fluorolog-2T2 spectrofluorometer.

All reagents and solvents were of the commercial reagent grade and were used without further purification except DMF was predried over activated 4 Å molecular sieve and vacuum distilled from calcium hydride (CaH_2) prior to use.

The synthetic route of the target compound is depicted as shown in Scheme 1.

MATPP was synthesized according to the published procedure [6].

MATPP (210 mg) and maleic anhydride (30 mg) were dissolved in 18 mL anhydrous dimethylformamide. The mixture solution was stirred and refluxed for 13 h under nitrogen atmosphere. After being cooled to room temperature, the mixture was diluted with chloroform and washed with the deionized water (3× 150 mL). After the organic solution was dried by sodium sulfate, the filtered solution was reduced to a smaller volume on a rotary evaporator. The product was purified by means of chromatography on silica gel column with chloroform as the eluent. The porphyrin H_2P was obtained in about 38.5% yield. ^1H NMR ($CDCl_3$): δ 8.823–8.893 (m, 8H, β-pyrrole), 8.307–8.346 (m, 2H, *o*-phenyl), 8.187–8.248 (m, 6H, *o*-triphenyl), 7.718–7.799 (m, 9H + 2H, *p*/*m*-triphenyl + *m*-phenyl), 7.005 (s, 2H, –CH=CH–), −2.783 (s, 2H, pyrrole N–H). MS: *m/z* 709.7$[M]^+$; Elemental analyses: $C_{48}H_{31}N_5O_2$ (709.81), Calcd. C: 81.22, H: 4.40, N: 9.87; found: C: 81.16, H: 4.62, N: 9.74.

ZnP was prepared by the reaction of the H_2P (0.20 g) and Zn $(Ac)_2$ (2.00 g) in the mixture solution of $CHCl_3$ (20 mL) and MeOH (10 mL) at 70 °C under nitrogen atmosphere for about 0.5 h. The extent of the reaction was monitored by measuring the UV–vis spectrum of the reaction solution. The reaction mixture then was chromatographed on silica gel column with chloroform as the eluent giving the ZnP as a purple red solid (yield 81.0%). Elemental analyses: $C_{48}H_{29}N_5O_2$ Zn, Calcd. C: 74.57, H: 3.78, N: 9.06; found: C: 74.15, H: 3.82, N: 8.94.

2. Results and discussion

From the ^1H NMR spectra of the H_2P, the ^1H NMR chemical shift values in deuterium $CDCl_3$ for ligand are at 8.823–8.893 (m, 8H, β-pyrrole), 8.307–8.346 (m, 2H, *o*-phenyl), 8.187–8.248 (m, 6H, *o*-triphenyl), 7.718–7.799 (m, 9H + 2H, *p*/*m*-triphenyl + *m*-phenyl), 7.005 (s, 2H, –CH=CH–), −2.783 (s, 2H, pyrrole N–H). The characteristic inner NH of the basic porphyrin hole and β-pyrrole chemical shifts are found at −2.783 and 8.823–8.893 ppm, respectively. In the ZnP, the signal peak at −2.783 (2H, pyrrole N–H) disappears, because the hydrogen atom in the N–H bond is replaced by zinc ion. Other peaks of the ZnP are similar to the H_2P.

In the mass spectra (Fig. 1), the molecular ion peak of the H_2P is 709.7.

Fig. 2a shows the UV–vis spectra of the H_2P and ZnP at room temperature in $CHCl_3$. The UV–vis 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) [7]. The $S_0 \rightarrow S_1$ transition gives rise to the weak Q bands in visible region while $S_0 \rightarrow S_2$ transition produces the strong Soret band in near UV region. In this work, the absorption bands of the H_2P appear at 420, 520, 555, 595 and 650 nm. The ZnP has an intense Soret band at 420 nm; with Q bands appear at 510, 550 and 595 nm. Compared with the H_2P, the number of the absorption bands of the ZnP decrease, which attributed to symmetry increase of the ZnP [8].

The IR spectra of H_2P and ZnP show in Fig. 2b. They display characteristic IR absorptions which are helpful to identify the functional groups, the IR bands at 3315, 966 cm^{-1} of the H_2P are due to the N–H stretching and bending vibration of the porphyrin core, but they disappear in ZnP because the hydrogen atom in the N–H bonding is replaced by zinc ion to form Zn–N bond [9]. Compared with the H_2P, a new band appears at about 1003 cm^{-1} in the IR spectrum of the ZnP. In addition, the intense bands at 1717 cm^{-1} of the H_2P and 1705 cm^{-1} of the ZnP assign to symmetric C=O stretching vibrations from imido groups.

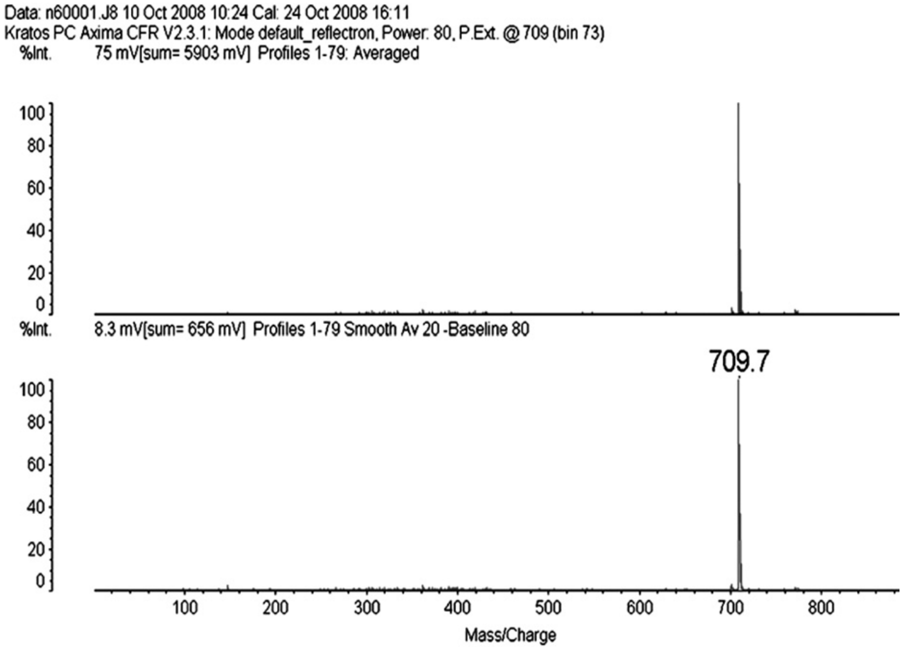

Fig. 1. Mass spectra of H_2P.

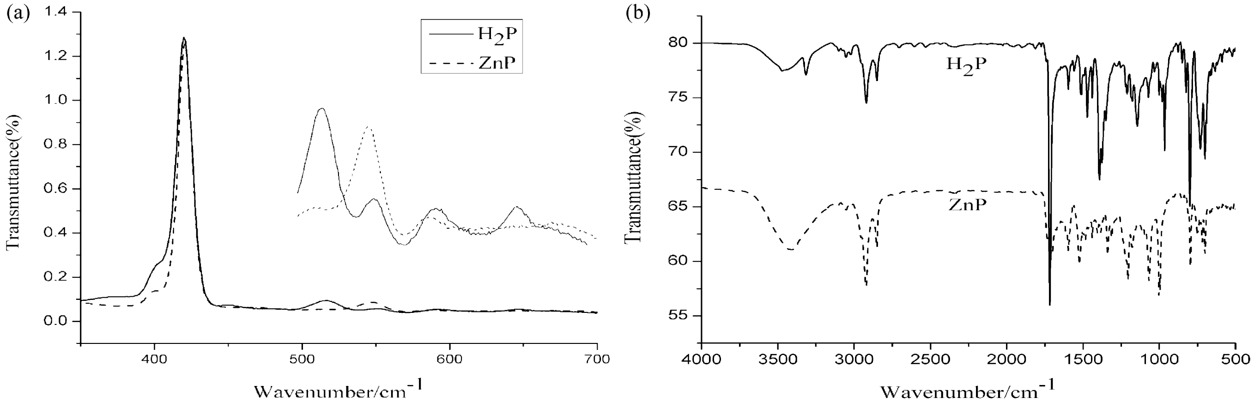

Fig. 2. UV−vis (a) and IR (b) spectra of H_2P and ZnP.

Fig. 3a shows the excitation spectra of H_2P and ZnP at room temperature in $CHCl_3$ and the excitation wavelength is 650 nm. In the 400–700 nm regions, the excitation spectra of H_2P and ZnP follow the absorption spectra well, indicating that they are corresponding to similar electron transition process.

Fig. 3b shows the emission spectra of H_2P and ZnP in $CHCl_3$ and the excitation wavelength is 420 nm. The fluorescence of the B band is attributed to the transition from the second excited singlet state S_2 to the ground state S_0, $S_2 \rightarrow S_0$, which is much weaker than that of the $S_1 \rightarrow S_0$ transition of the Q band emission [10]. Fluorescence of S_1 consists of two bands, Q (0–1) bands are at 649 and 594 nm and Q (0–2) are at 716 and 646 nm of H_2P and ZnP, respectively. These spectra are approximately mirror symmetric to the absorption spectra.

Quantum yields of the Q bands depend on the relative rates of radiative process $S_1 \rightsquigarrow S_0$ and two radiationless processes $S_1 \rightsquigarrow S_0$ and $S_1 \rightsquigarrow$ Tn. According to the known result, the fluorescence quantum yields of the porphyrin complexes are low [11]. The fluorescence quantum yields of H_2P and ZnP are 0.096 and 0.089, respectively. In our experiment, because the spin forbidden process $S_1 \rightsquigarrow$ Tn plays a predominant role in radiation absent deactivation of S_1 in porphyrin complexes, the fluorescence quantum yields of complexes are much less than 0.21 [11].

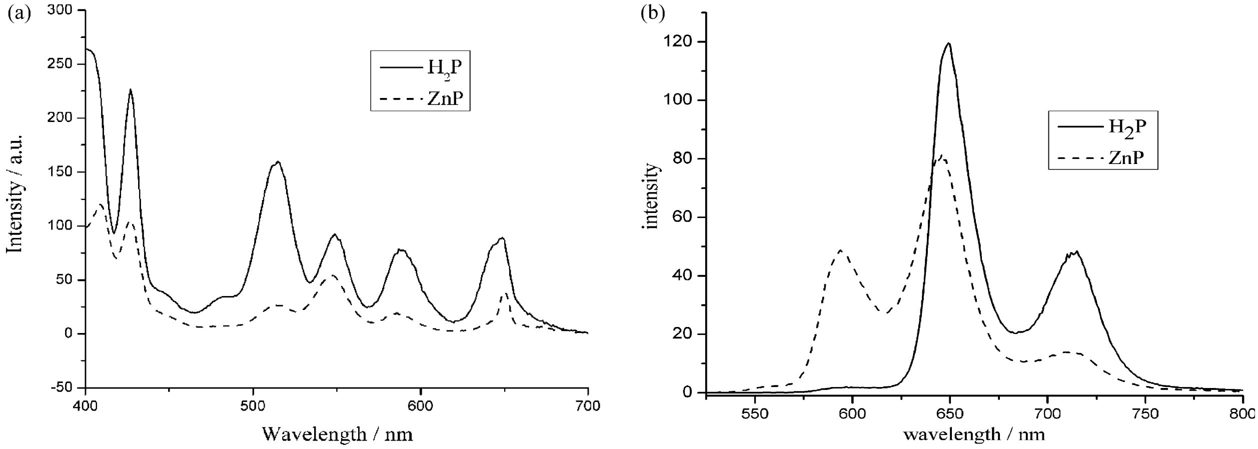

Fig. 3. Excitation (a) and emission (b) spectra of H_2P and ZnP in 10–5 mol/L $CHCl_3$. (a. λem = 650 nm and b. λex = 420 nm).

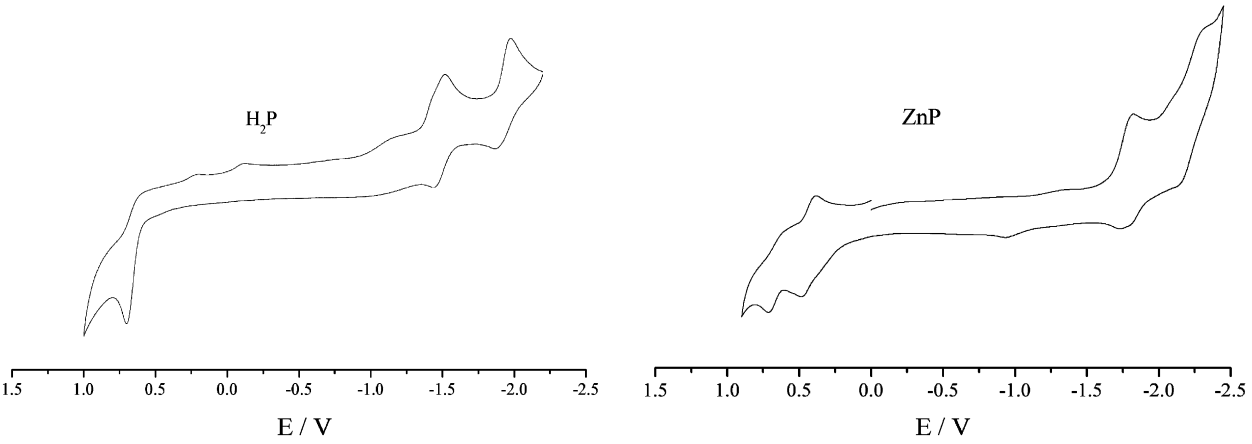

Fig. 4. Cyclic voltammetric of H_2P and ZnP.

Cyclic voltammograms of the H_2P in DMF containing 0.1 mol dm^{-3} TBAP as supporting electrolyte is shown in Fig. 4. The redox potentials for MATPP and H_2P are summarized in Table 1.

The H_2P undergoes one reversible oxidation at $E_p = 0.72$ V and two reversible reductions at $E_{1/2} = -1.47$ V and $E_{1/2} = -1.92$ V. The redox half wave potentials corresponding to the porphyrin ring reaction of the ZnP is located at $E_{1/2} = 0.66, 0.43, -1.78, -2.23$ V. The difference of H_2P and ZnP in $E_{1/2}$'s between the first ring oxidation yielding π cation radicals and the first ring reduction yielding π anion radicals is 2.19 and 2.21 V, and the difference between the first and second ring reduction is 0.45 and 0.45 V, which are in good agreement with $E_{1/2}^{ox}(1) - E_{1/2}^{red}(1) = 2.25 \pm 0.15\,V, E_{1/2}^{red}(1) - E_{1/2}^{red}(1) = 0.42 \pm 0.05\,V$ [12].

Table 1
The redox potentials of MATPP, H_2P and ZnP (V).

Compound	Ring oxidation	Ring reduction	
	1st	1st	2nd
MATPP [13]	0.70	−1.49	−2.00
H_2P	0.72	−1.47	−1.92
ZnP	0.43	−1.78	−2.23

Comparing the redox potentials of H_2P with MATPP, all the values of the former are shifted obviously toward positive potentials. The reason for this is that the formation of maleimide onto tetraphenylporphyrin instead of electron-donating group, amido, decreases the electron density of the π-ring system and the energy of both the HOMO and the LUMO, which makes them more difficult to oxidize and easier to reduce than the corresponding monomeric species.

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