

Photophysical Properties of Novel Phthalocyanines: Multi Emission by Excited at Short Wavelength

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Two novel phthalocyanines: tetra-azobenzene substituted zinc phthalocyanine $ZnPc.(Oazo)_4$ and polymeric ytterbium phthalocyanine carboxyl ($YbPPc.COOH$) have been synthesized and their electronic adsorption and emission spectra have been investigated by spectrometric method. Both of the synthesized compounds can emit two fluorescent peaks when excited at short wavelength (below 400 nm) and one peak when excited at long wavelength (higher than 600 nm) as well. For $YbPPc.COOH$, in pH 7.4 buffer solution, when excited at 330 nm, beside normal fluorescent peak at 720 nm, a second emission peak appeared at 455 nm. The fluorescence quantum yield of two emission was 0.35 (720 nm em, 635 nm ex) and 0.33 (455 nm em, 330 nm ex), respectively. This equivalent multi-emission phenomenon by different excited wavelength indicates good applied potential in photodynamic diagnose and fluorescence imagination.

Key Words: Phthalocyanine, Fluorescence, Photophysical.

INTRODUCTION

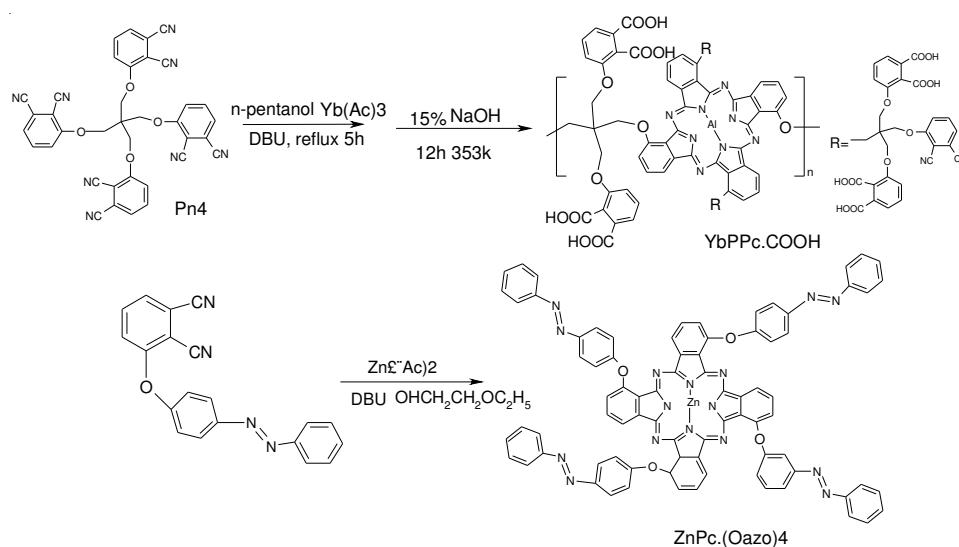
The multi fluorescence emission phenomenon of guaiazulene¹ and porphyrins² have been observed for a long times. The special luminescence related to the emission from the second excited state S_2 , it expressed as more than one emission peak occurrence when excited at short wavelength³. Usually the second emission peaks at short wavelength was ascribed to the transition from S_2 to S_0 , though the transition from S_2 excited state to S_0 state is forbidden in the photochemical theory⁴. Another explanation of the intermolecular charge transfer (ICT) was accepted in lager molecule with electronic donor and accepted groups in two sides⁵.

Phthalocyanine is a kind of azacyclic compound with complicated photochemical excited states. The fluorescence, triplet excited state and singlet oxygen producing of them has been investigated extensively⁶. However, only denumerable documents of porphyrins, the originating compound of phthalocyanine, are reported of the dual florescence emission behaviour^{7,8}. No unambiguous result for the multi-fluorescence of phthalocyanine are reported as so far. The phthalocyanines, applied as photosensitizer in photodynamic therapy as well, have long adsorption wavelength and higher quantum yield than normal used florescence compounds, so its multi-

fluorescence emission are valuable for investigation. In this study, two novel phthalocyanine compounds are synthesized and investigated their photophysical properties in detail.

EXPERIMENTAL

The synthesis of tetra-azobenzene substituted phthalocyanine [ZnPc.(Oazo)₄] and ytterbium polymeric phthalocyanine carboxyl (YbPPc.COOH) was referenced our previous work^{9,10}, the synthesis route are shown in **Scheme-I**.



Scheme-I: Synthesis of two compounds

A mixture of 3-(phenylazophenoxy)phthalonitrile (1.00 g), zinc acetate (0.12 g) and 1,8-diazabicyclo[5.4.0]undec-7-ene (DBU; 0.15 g) in 2-ethoxyethanol (30 mL) was refluxed for 2 h under argon atmosphere. The mixture was cooled to room temperature and poured into 150 mL water. Collect the participate and purify it by chromatography on silica gel with chloroform as the eluent. ZnPc.(Oazo)₄ (52 mg) was obtained as final product. MALDI-TOF: calcd. 1362.7, found 1362.9. ¹H NMR (300 MHz, DMSO-*d*₆; ppm) 7.3-7.6 (m, 23H), 7.6-8.2 (m, 22H), 8.4-8.5 (t, 1H), 8.5-9.1 (q, 1H), 9.2-9.3 (q, 1H). Elemental analysis calcd. for C₈₀H₄₈N₁₆O₄Zn: C, 70.51; H, 3.55; N, 16.45. Found: C, 70.23; H, 3.38; N, 16.59.

The ytterbium polymeric phthalocyanine carboxyl was synthesized from the tetramerization of a tetra-phthalonitrile and successive hydrolysis. 1.28 g (0.002 mol) *tetrakis*-(2,3-dicyanophenoxy)methan¹¹ was mixed with 0.7 g (0.002 mol) ytterbium triacetate anhydrate in 10 mL *n*-pcta, 1-ol by stirring, then the mixture was heated to reflux for 4 h after add 1 mL DBU as catalyst. Then filtrate out the solid and wash with 6 mol/L HCl, DMF and acetone successively. The green solid was hydrolyzed in 15 mL of 30 % NaOH solution for 12 h at 353 K. Then collect

the solution by centrifuge, adjust the pH of solution to 1 by 6 mol/L HCl, obtain the participate by centrifuge as the raw product. Purify the raw product by acidic alumina chromatography using DMF as eluent. The final product was green powder 0.35 g. FT-IR (KBr, ν_{\max} , cm^{-1}): 1740, 3600-3300, 1150, 1320, 1485, 1650; ^{13}C NMR (in DMF): 176-178 (carboxyl C), 102.3, 116.7, 118.3, 126.5, 136.1, 158.6 (aromatic C) 48.2, 68.2 (alkyl C) ppm; MOLDI-TOF: found: 8730-8850, 9130-9200, 10300-10400, 11200-11300, 12800-13200; Elemental analysis: found C, 68.93, H 4.23, N, 16.33, O, 7.22; COOH, 2.8, Yb (atom), 5.1 % (ICP-AAS).

The electronic spectra was recorded on an HP 5324A Uv-vis array spectrometer. The electric emission and excitation were recorded by a Hitachi F4500 spectrometer with a setting of 5 nm grating slit and 700 V amplifier of photomultiplier. The $\text{ZnPc}(\text{Oazo})_4$ was prepared as 10^{-5} mol/L solution in CH_2Cl_2 ; while $\text{YbPPc}(\text{COOH})$ was dissolved in pH 7.4 buffer solution at 0.1g/L conc. The quantum yield of fluorescence was determined by comparative methods¹² in pH 7.4 buffer using ZnPcS^2 ($\Phi_F = 0.18$) for 720 nm emission and fluorescein ($\Phi_F = 0.45$) for 450 nm emission in DMF as standard, respectively. The Φ_F was calculated by:

$$\Phi_F = \Phi_{F,\text{std}}(S A_{\text{std}} n^2 / S_{\text{std}} A n_{\text{std}}^2)$$

where S and S_{std} are the areas under the emission curves of the sample and standard, respectively. A and A_{std} are the absorbances of the sample and standard, respectively and n and n_{std} are the refractive indexes of the solvents used for sample and standard, respectively. The error in the determination was about 10 %. The absorbance of the solutions at the excitation wavelength was about 0.3.

RESULTS AND DISCUSSION

The electronic spectra of the two compounds are shown in Fig. 1. The broad Q band of $\text{YbPPc}(\text{COOH})$ from 680-720 nm indicated a strong aggregation tendency in pH 7.4 buffer solution¹³. It suggested that the anionic carboxyl groups in pH 7.4 buffer increased the electronic density of phthalocyanine and enhanced the aggregation. The location of Q band at 690 nm is the collective result of heavy rare metal atom and polymeric effect, the former lead hypsochromic shift and the latter influence resulted in bathochromic shift of Q band¹⁴.

The $\text{ZnPc}(\text{Oazo})_4$ showed little aggregation in low-polarity solvent dichloride methane. The strong adsorption of Soret band in $\text{YbPPc}(\text{COOH})$ at 350 nm attributed to the cyano groups in their structure. The largest adsorption wavelength of Q band for $\text{ZnPc}(\text{Oazo})_4$ located at 695 nm due to the participation of electronic-rich azophenoxy groups in the conjugated system of phthalocyanine rings.

The detail electronic emission and excitation spectra of $\text{YbPPc}(\text{COOH})$ are shown in Fig. 2. The normal fluorescent emission of phthalocyanine located at 720 nm when excited with 625 nm wavelength laser. It is corresponded to the emission from S1 excited state transit to ground S0 state (Q bands). The quantum yield of fluorescence of this emission was 0.35. When the excitation spectrum of 720 nm

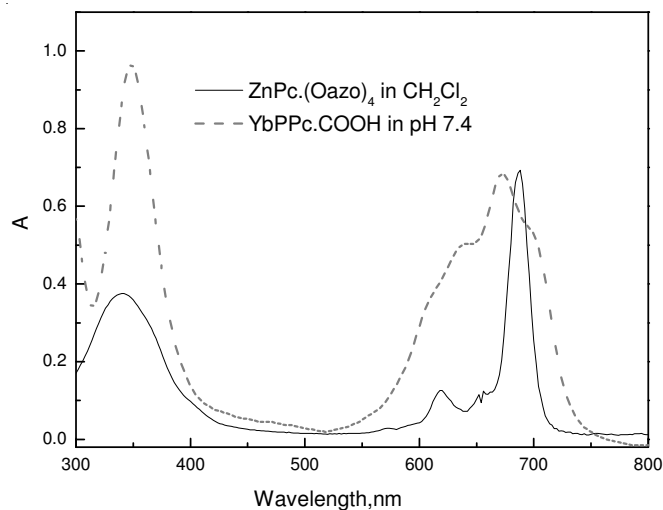


Fig. 1. Electronic adsorption spectrum of ZnPc.(Oazo)₄ and YbPPc.COOH in different solutions

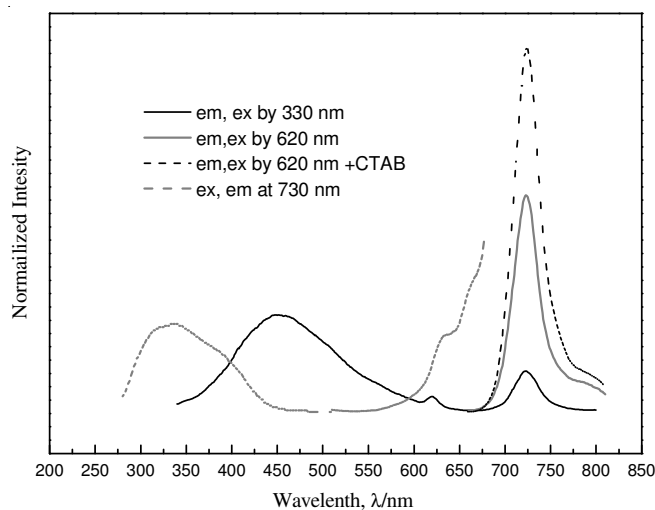


Fig. 2. Electronic spectrum (emission and excitation) of YbPPc.COOH in pH 7.4 buffer solution

emission peak checked, the result was a similar spectrum with its adsorption spectrum. As shown in Fig. 2, two peaks appeared at 330 and 625 nm. The excitation peak at 330 nm indicated the existence of second emission peak. When excited from 330 nm, it proved the described deduction. The emission peaks located at 450 nm and 720 nm, while former peak showed larger strength than the latter. Here, it is supposed that the emission at 450 nm originated from Soret band of phthalocyanine (the transition from S₂ excited state to S₀ state). The photophysical parameters

listed in Table-1 showed the quantum yield of fluorescence was 0.15 for 450 nm emissions. The short wavelength emission peak of porphyrins only has 1/100 strengthen than Q band emission as ever reported^{7,8}. The similar phenomenon for non polymeric phthalocyanine ZnPc.(Oazo)₄ (Fig. 3) was observed as well. Beside the normal emission at 750 nm excited by 665 nm, when excited at 260 nm, two fluorescent peaks located at 320 and 750 nm with similar strengthen. The excitation spectrum of 750 nm emission also showed the excited peaks at 260 and 600 nm; while the emission of azo-benzene cyclic located at about 450 nm, which had no affect in this spectrum.

TABLE-1
PHOTOPHYSICAL PARAMETERS of ZnPc.(Oazo)₄ AND YbPPc.COOH

	Q band λ_{\max} (nm)	Emission λ_{\max} (nm)	Stokes shift, Δ (nm)	Φ_F S1	Φ_F S2	Φ_F S1 with CTAB
ZnPc.(Oazo) ₄	690.3	740.0	49.7	0.12	0.06	–
YbPPc.COOH	683.3	721.1	37.8	0.35	0.15	0.71

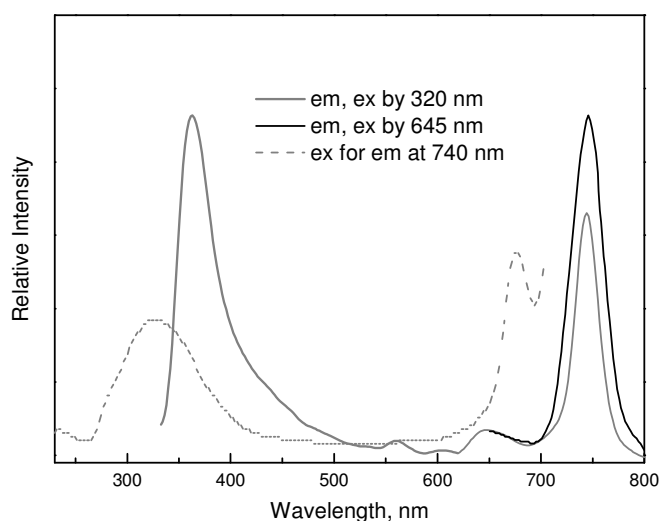


Fig. 3. Electronic emission spectrum of ZnPc.(Oazo)₄ excited at 260 nm and its excitation spectrum in CH₂Cl₂ solution

The aggregation of Pc also influenced their electronic emission behaviour; CTAB can effectively dissociate the aggregation and elevate the quantum yield of fluorescence as ever reported¹⁵. Here we also added 0.1 % CTAB solution in YbPPc.COOH, the result in Fig. 2 showed the emission peak at 720 nm was enhanced but the emission in short wavelength have no manifest variation. The fluorescence quantum yield increased from 0.23 to 0.71 after the addition of CTAB.

Though there is dispute that the dual fluorescence of phthalocyanine emitted by impurity, such as phthalonitrile or fragment, which resulted in the emission at low wavelength. But in this study, both of the polymeric and monomeric phthalocyanine in different solvents was found dual fluorescent emission. A previous report by our lab indicated the phthalocyanine analogue: nitro substituent phosphorus tetrabenzotriazacorrole (Ptbc)¹⁶ has the similar dual fluorescent emission, when excited at. From another points, the excited spectrum corresponding to 720 nm emission showed the excitation peak at 320-350 nm. For impurity phthalonitrile, there is no emission over 400 nm wavelength, so no excitation spectrum can be detected when scanned at 720 nm. Based on above evidences, it is considered that the emissions in Figs. 2 and 3 are from the S2 state to S0 state.

Conclusion

The unique fluorescent emission excited at short wavelength was observed for polymeric ytterbium phthalocyanine carboxyl and tetra-azobenzene substituted zinc phthalocyanine in aqueous and dichloride methane, respectively. The emissions at low wavelength and long wavelength had the equivalent strength for two compounds. This multi-emission property has potential application in multi-wavelength fluorescence imaging and diagnose.

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