Effects of Protonation and Deprotonation on Phthalocyanine's Spectra

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Abstract　The absorption and emission properties of $H_2Pc(O^iPr)_4$ were studied as a function of protonation and deprotonation. Stepwise protonation using TFA yielded $[H_2Pc(O^iPr)_4 \cdot H^+]^+$ and $[H_2Pc(O^iPr)_4 \cdot 2H^+]^{2+}$. $[H_2Pc(O^iPr)_4 \cdot 4H^+]^{4+}$ can be formed in concentrated sulfuric acid. Additionally, the NaOH/EtOH can deprotonate $H_2Pc(O^iPr)_4$ to $[Pc(O^iPr)_4]^{2-}$, the acid-dissociation of the two pyrrolic $-NH-$ occurred synchronous. Manifest bathochromic shifts of the Q band absorption for each bound proton indicated the basicity of phthalocyanine in the excited state is stronger than that in the ground state. In order to explain the experimental phenomena, the effects of protonation and deprotonation on MOs were proposed.

Keywords:　Phthalocyanine , Protonation, Deprotonation

Phthalocyanines (Pc) are a promising class of compounds with current and potential applications in many areas[1]. Structurally it is a polyvalent ampholyte with all four peripheral bridge (also called *meso*) nitrogen atoms as possible basic centers and the two pyrrolic type ($-NH-$) nitrogen atoms as possible acidic centers. Thus phthalocyanine may give rise to seven possible species under normally attainable acidic/basic conditions, namely $[Pc]^{2-}$, $[HPc]^-$, H_2Pc, $[H_2Pc \cdot H^+]^+$, $[H_2Pc \cdot 2H^+]^{2+}$, $\{H_2Pc \cdot 3H^+]^{3+}$ and $[H_2Pc \cdot 4H^+]^{4+}$. Such amphoteric behaviour is of particular interest[2−5], since dramatic stereochemical changes have been known caused by the protonation or deprotonation of these nitrogen atoms in porphyrins[6]. In the present work we have investigated reactions of phthalocyanine with acids and base in chloroform. The phthalocyanine unit has iso-propoxy groups substituted, ensuring its higher solubility in organic solvents. Our studies show acid-base equilibrium of phthalocyanine involving mono-, di-, tetra-protonated and dianion forms. The Q band electronic absorption of the macrocycle is greatly modified by the protonation and deprotonation, the difference in energy of the Q band between these

species with highest and lowest energy is around 3000 cm^{-1}. The use of molecular orbital diagram based on four-orbital transition permits a good interpretation of the observed phenomena[7,8].

1 Experimental

1.1 Chemicals

29H,31H-2, 9, 16, 23-tetraisopropoxy phthalocyanine ($H_2Pc \cdot O^iPr)_4$) was prepared according to the literature[9]. Elemental analysis for $C_{44}H_{42}N_8O_4$ found (calcd.) C 70.67 (70.76), H 5.59 (5.63), N 14.82 (15.00). Zinc-phthalocyanine (ZnPc) was supplied by Tokyo Kasei. Trifluoroacetic acid (TFA) was purchased from Merck-Schuchardt.
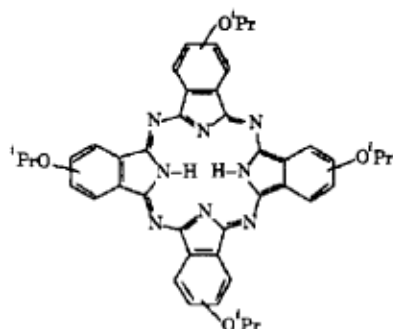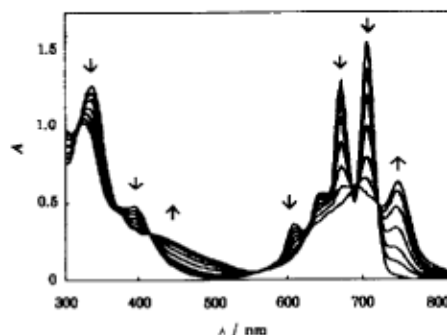

Fig.1 Chemical structure of $H_2Pc(O^iPr)_4$

Fig.2 The absorption changes showing the conversion of $H_2Pc(O^iPr)_4$ to $[H_2Pc(O^iPr)_4 \cdot H^+]^+$ (2.5×10^{-5} mol·L^{-1} in CHCl$_3$) on stepwise addition of TFA until the limiting spectrum

1.2 Instruments and methods

Electronic absorption spectra were recorded with a HP8452A spectrometer and a UV-2100S spectrometer. Fluorescence spectra were obtained on a PE LS50B Luminescence spectrometer with an excitation wavelength at 610 nm. Fluorescence quantum yields (Φ_f) were determined by comparative calibration method with ZnPc as a standard (Φ_f =0.3). Elemental analyses were performed in Institute of Chemistry, Academia Sinica. In order to study the spectral changes *in situ*, microliter quantities of TFA or 1% NaOH / EtOH were added gradually to 2.5 mL dry CHCl$_3$ solution of $H_2Pc(O^iPr)_4$ in a quartz cell equipped with a magnetic stirrer, the spectra were recorded after thoroughly mixing for each addition. $H_2Pc(O^iPr)_4$ was dissolved in concentrated sulfuric acid to obtain the electronic spectrum in highly acidic environment.

2 Results and discussion

2.1 Spectra of protonated and deprotonated species

During the titration of $H_2Pc(O^iPr)_4$, three limiting spectra in acid titration and one limiting spectrum in base titration were observed as shown in Fig.3. Limiting spectra so

called here are believed to be primarily the one species identified on the basis of their stage of formation during the titration, the existence of isosbestic points, the lack of contamination of the adjacent species, and the detail of the spectra themselves. For example, the first limiting spectra upon protonation can be obtained from Fig.2.
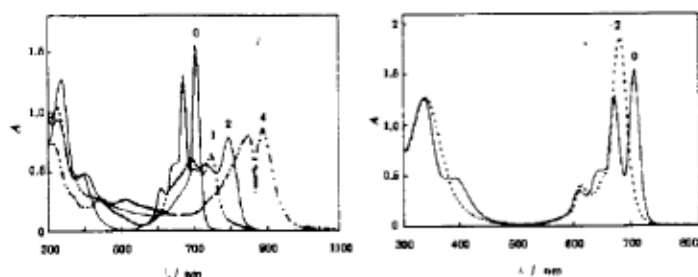

Fig.3 The absorption of protonated and deprotonated $H_2Pc(O^iPr)_4$
 (2.5×10^{-5} mol·L^{-1} in CHCl$_3$)
 (left) $\underline{0}$, $H_2Pc(O^iPr)_4$, no TFA; $\underline{1}$, $[H_2Pc(O^iPr)_4 \cdot H^+]^+$ at [TFA]=0.124 mol·L^{-1};
 $\underline{2}$, $[H_2Pc(O^iPr)_4 \cdot 2H^+]^{2+}$ at [TFA]=1.29 mol·L^{-1}; $\underline{4}$, $[H_2Pc(O^iPr)_4 \cdot 4H^+]^{4+}$
 in H_2SO_4; and (right) $\underline{0}$, $H_2Pc(O^iPr)_4$, no base; $\underline{-2}$, $[Pc(O^iPr)_4]^{2-}$ at
 [NaOH]=7.69×10^{-4} mol·L^{-1}

The determination of protonation degree for each protonated species may follow the Iodko's method[5] with the protonation reaction as

$$H_2Pc(O^iPr)_4 + 2nHA = [H_2Pc(O^iPr)_4 \cdot nH^+]^{n+} \cdot n[HA_2]^- \tag{1}$$
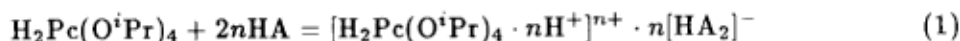
The product exists as $[H_2Pc(O^iPr)_4 \cdot nH^+]^{n+} \cdot n[HA_2]^-$ since the protonated species will be stabilized by ion pair $[HA_2]^{-[4,5]}$. The equilibrium constant K of this reaction is

$$K = \frac{c_p}{(c_0 - c_p) \cdot (c_{HA})^{2n}} \tag{2}$$

where c_0, c_p are the concentration of total phthalocyanine and the protonated species formed at the acid concentration c_{HA} ($c_{HA} \gg c_p$) (all in mol·L^{-1}), respectively, c_p can be deduced from the eq.(3)

$$c_p = \frac{A - \varepsilon_0 \cdot c_0}{\varepsilon_p - \varepsilon_0} \tag{3}$$

where A is the absorbance of solution at λ_{max} of the protonated species, ε_0, ε_p are the molar absorptivities (cm^{-1}·mol^{-1}·L) of unprotonated and protonated species at λ_{max}, respectively. Taking log with eq. (2) as

$$\log \frac{c_p}{c_0 - c_p} = \log K + 2n\log c_{HA} \tag{4}$$

By extracting the value of K and n for the reactions observed (Table 1) using eq. (4), we can identify each protonated species (Table 2). The mono- and di-protonated species can be formed in TFA . The tri-protonated species has not been identified since even dissolution in neat TFA yielded the di-protonated species. The protonated species in concentrated sulfuric acid was assigned to $[H_2Pc(O^iPr)_4 \cdot 4H^+]^{4+}$ (*vide infra*).

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Table 1 Summary of observed reactions for protonation and
deprotonation of $H_2Pc(O^iPr)_4$

Reaction	n	K
$H_2Pc(O^iPr)_4 + 2HA \Leftrightarrow [H_2Pc(O^iPr)_4 \cdot H^+]^+ \cdot [HA_2]^-$	1.2	5×10^3
$[H_2Pc(O^iPr)_4 \cdot H^+]^+ \cdot [HA_2]^- + 2HA \Leftrightarrow [H_2Pc(O^iPr)_4 \cdot 2H^+]^{2+} \cdot 2[HA_2]^-$	1.1	6
$H_2Pc(O^iPr)_4 + H_2SO_4 \Leftrightarrow [H_2Pc(O^iPr)_4 \cdot 4H^+]^{4+}$	–	–
$H_2Pc(O^iPr)_4 + 2NaOH \Leftrightarrow Na_2[Pc(O^iPr)_4]^{2-} + 2H_2O$	–	–

Table 2 Electronic absorption of protonated and deprotonated $H_2Pc(O^iPr)_4$ species

Species	λ / nm	Assignment	$\lg\varepsilon^{a)}$	$f^{b)}$
$H_2Pc(O^iPr)_4$	708	$Q_x(0'-0'')$	4.79	
(D_{2h})	672	$Q_y(0'-0'')$	4.72	0.36
	648	$Q_x(0'-1'')$	4.35	
	608	$Q_y(0'-1'')$	4.16	
	394	$B_1(0'-0'')$	4.28	1.29
	338	$B_2(0'-0'')$	4.71	
$[H_2Pc(O^iPr)_4 \cdot H^+]^+$	748	$Q_1(0'-0'')$	4.40	0.30
(C_s)	694	$Q_2(0'-0'')$	4.38	
	374	$B_1(0'-0'')$	4.25	1.13
	328	$B_2(0'-0'')$	4.61	
$[H_2Pc(O^iPr)_4 \cdot 2H^+]^{2+}$	794	$Q_1(0'-0'')$	4.50	
$(trans-, C_{2h})$	734	$Q_2(0'-0'')$	4.35	0.38
	698	$Q(0'-1'')$	4.31	
	402	$B_1(0'-0'')$	4.29	1.11
	326	$B_2(0'-0'')$	4.58	
$[H_2Pc(O^iPr)_4 \cdot 4H^+]^{4+}$	888	$Q_x(0'-0'')$	4.52	0.33
(D_{2h})	852	$Q_y(0'-0'')$	4.51	
	512	$B_1(0'-0'')$	4.03	0.90
	438	$B_2(0'-0'')$	4.05	
$[Pc(O^iPr)_4]^{2-}$	684	$Q(0'-0'')$	4.87	0.35
(D_{4h})	614	$Q(0'-1'')$	4.22	
	340	$B(0'-0'')$	4.71	1.32

Note: a) the molar absorption coefficient ε ($cm^{-1} \cdot mol^{-1} \cdot L^{-1}$); b) the oscillator strength

Theoretically, deprotonation of two pyrrolic –NH– will result in two different species $[HPc(O^iPr)_4]^-$ and $[Pc(O^iPr)_4]^{2-}$. However addition of NaOH / EtOH to the solution caused an immediate change in the Q band to single intense band at 684 nm and only one limiting spectrum could be observed ,resembling the spectrum of a metallophthalocyanine (D_{4h}). This led us to assume that the acid-dissociation of two –NH– occurred synchronously rather than consecutively, although it is different to Bernauer [10] in defining $[HPc]^-$. Determination of K and n for deprotonation as performed in protonation was disturbed by the H_2O formed in reaction.

2.2 Changes of MOs after protonation and deprotonation of the macrocycle

The four-orbital transition model[7] can be served to interpret the effects of protonation (or deprotonation) on MO's energy of phthalocyanine. In unprotonated phthalocyanine $H_2Pc(O^iPr)_4$ (D_{2h}), the two HOMOs and two LUMOs are b_{1u}, a_u and b_{3g}, b_{2g} respectively, which give $Q_x(0'-0'')$, $Q_y(0'-0'')$ and $B_1(0'-0'')$, $B_2(0'-0'')$ in combination. The a_u orbital has a nodal plane through the *meso* nitrogen atoms, so its energy will be conserved on protonation or deprotonation, while other orbitals have significant electron density on the *meso* nitrogen atoms and are stabilized by the addition of proton[11]. In mono-protonation, the symmetry depresses to C_s and the MOs change into a′ and a″. The orbitals are stabilized to certain extent except one and hence the Q band absorption shows red-shift. In di-protonation, the two protons reside on the opposite *meso* nitrogen atoms (trans-, C_{2h}) rather than adjacent ones (cis-, C_{2v}). The MO's energy will be lowered again due to the second proton. A schematic MO level diagram is shown in Fig.4 .
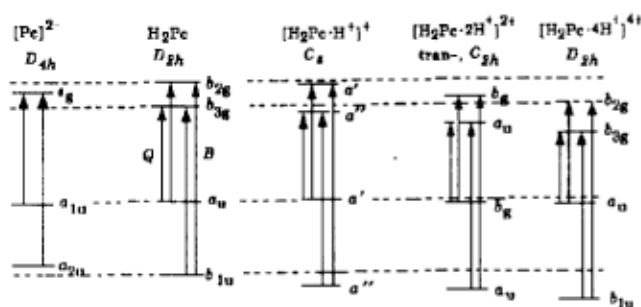

Fig.4 Effects of protonation and deprotonation on
MO's energy and electronic transitions

H_2Pc and $[H_2Pc \cdot 4H^+]^{4+}$ is similar in D_{2h} symmetry, the Q_x and Q_y states will be split into a pair of nondegenerate states, resulting in a pair of high peaks and a pair of weak peaks on coupling. Since the spectrum obtained in H_2SO_4 resembled the original one, the species formed in H_2SO_4 should be tetra-protonated. $[Pc]^{2-}$ is particular in that b_{2g} and b_{3g} will degenerate into e_g (D_{4h}) and give only one principle Q and Soret band, so it is easy to diagnose.

Table 3 Properties of excited states for protonated and deprotonated $H_2Pc(O^iPr)_4$

Species	ΔpK_a	λ_{em}/nm	Φ_f
$H_2Pc(O^iPr)_4$	-1.6	713	0.39
$[H_2Pc(O^iPr)_4 \cdot H^+]^+$	-1.6	825	~ 0.01
$[H_2Pc(O^iPr)_4 \cdot 2H^+]^{2+}$	-2.8	896	~ 0.002
$[H_2Pc(O^iPr)_4 \cdot 4H^+]^{4+}$			
$Pc(O^iPr)_4^{2-}$	-1.0	693	0.12

2.3 Excited state properties of protonated and deprotonated species

Red-shift of absorption on protonation indicates that phthalocyanine is stronger base in excited state than in ground state. Difference between the basicity of the excited state

and the ground state may be estimated by eq. (5)[12], where E_0 and E_p are the $Q(0'\text{-}0'')$ transition energy (in cm^{-1}) of unprotonated and protonated species respectively.

$$\Delta pK_a = pK_a^* - pK_a = \frac{0.625}{T} \cdot (E_p - E_0) \qquad (5)$$

As can be seen from Table 3, the fluorescence emission wavelength λ_{em} of protonated species tends to red-shift in company with the number of protons bound, while the λ_{em} of $[Pc(O^iPr)_4]^{2-}$ is typical of the metallo-phthalocyanines. The Φ_f diminished as protonation degree increased, and $[H_2Pc(O^iPr)_4 \cdot 4H^+]^{4+}$ was non-fluorescent.

The present work demonstrates that the two inner nitrogen atoms of the macrocycle show more less basicity than the *meso* ones and can not be protonated even in concentrated sulfuric acid , which may be due to the electrostatic effects upon protonation of the four *meso* nitrogen atoms.

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质子化和脱质子化对酞菁光谱的影响

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摘要　系统地研究了四异丙氧基酞菁的质子化和脱质子化对吸收和发射光谱的影响. 研究表明，三氟乙酸可对酞菁分子连续质子化，分别生成 $[H_2Pc(O^iPr)_4 \cdot H^+]^+$ 和 $[H_2Pc(O^iPr)_4 \cdot 2H^+]^{2+}$，而硫酸可使酞菁形成 $[H_2Pc(O^iPr)_4 \cdot 4H^+]^{4+}$. 此外， NaOH/EtOH 可使酞菁分子脱质子化生成 $[Pc(O^iPr)_4]^{2-}$，反应一步完成，表明分子中的两个吡咯 –NH– 同步酸解. 质子化可使吸收光谱的 Q 带和荧光发射峰显著红移，证明酞菁激发态的碱性强于基态. 对这些实验现象，利用四轨道电子跃迁模型作了合理的解释.

关键词: 酞菁，　质子化，　脱质子化