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Thermochromism of 5,10,15,20-Tetraarylporphyrins at Low Temperature

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5,10,15,20-Tetrakis(4-aminophenyl)porphyrin [T(*p*-NH$_2$)PP] exhibited thermochromism in 2-methyltetrahydrofuran. In the electronic spectrum at 77 K four Q bands largely shifted to longer wavelength and relative intensities changed. The electronic spectrum of T(*p*-NH$_2$)PP was also influenced by the nature of solvents. In strong hydrogen-bond accepting solvents Q bands were red-shifted and the resulting spectrum resembles that recorded at low temperature. Based on the solvent effect and substituent effects, the thermochromism of T(*p*-NH$_2$)PP can be attributed to enhancement of hydrogen-bonds between *p*-NH$_2$ group and solvent molecules at lower temperature, which causes increase of effective electron-donating ability of *p*-NH$_2$ group. In alcoholic solvents T(*p*-NH$_2$)PP and T(*p*-OH)PP showed another type of temperature dependence of absorption spectra.

Electronic spectra of porphyrins and metalloporphyrins have been extensively investigated both experimentally and theoretically,[1] and the spectral properties are interpreted on the basis of the four-orbital model.[2] Meot-Ner and Adler[3a] and Dalton et al.[3b] investigated a series of *meso*-tetraarylporphyrins and reported correlation between the absorption maximum of Q band and Hammet's σ values of the substituents. On the other hand, effects of temperature or solvent on electronic spectra of porphyrins have not yet been discussed except for a report on thermochromism of *meso*-tetraphenylporphyrin (TPP) in an aqueous solution.[4] In the present study, we have investigated temperature dependence of electronic spectra for *meso*-tetraarylporphyrins having various substituents including strongly electron-donating groups such as OH, NH$_2$, and NMe$_2$, at para- or ortho-positions on the phenyl rings, and found that *p*-amino and *p*-hydroxyl derivatives exhibit thermochromism in several solvents between room temperature and 77 K. Effect of the nature of solvents on spectral properties of these porphyrins will be also discussed.

Table 1. Absorption Maxima and Spectral Type of Q Band for *meso*-Tetraarylporphyrins in MTHF[a)]

No	Compound	λ_{max}/nm				Type
		I	II	III	IV	
1	T(*p*-NO$_2$)PP	644	590	548	512	$\varepsilon_I<\varepsilon_{II}<\varepsilon_{III}<\varepsilon_{IV}$
2	TPP	646	589	546	511	
3	T(*p*-Me)PP	648	591	547	512	
4	T(*p*-OMe)PP	650	594	552	515	
5	T(*p*-NHAc)PP	651	595	554	516	$\varepsilon_{II}<\varepsilon_I<\varepsilon_{III}<\varepsilon_{IV}$
6	T(*p*-OH)PP	652	595	554	517	
7	T(*p*-NH$_2$)PP	659	600	565	523	$\varepsilon_{II}<\varepsilon_I<\varepsilon_{IV}<\varepsilon_{III}$
8	T(*p*-NMe$_2$)PP	663	—	570	525	
	T(*p*-O$^-$)PP[b)]	665	—	575	525	
9	T(*o*-NH$_2$)PP	651	590	549	514	$\varepsilon_I<\varepsilon_{III}<\varepsilon_{II}<\varepsilon_{IV}$

a) Concentration 3×10^{-5}—6×10^{-5} M; Temperature ca. 295 K. b) In MeOH (Ref. 10).

Experimental

Porphyrins were synthesized by the reported methods.[5—9] T(*p*-NH$_2$)PP could be obtained also by hydrolysis of T(*p*-NHAc)PP with hydrochloric acid. T(*p*-NMe$_2$)PP was commercially available and used without further purification. Solvents used for electronic spectrum measurements were of spectroscopic grade. 2-Methyltetrahydrofuran (MTHF) was distilled over LiAlH$_4$ just before use. Hexamethylphosphoric triamide (HMPT) was distilled over CaH$_2$ under reduced pressure. Electronic spectra were recorded on a Shimadzu UV-240 spectrophotometer. Beer's law was obeyed in the concentration range investigated (1×10^{-5}—6×10^{-5} M; 1 M=1 mol dm^{-3}).

Results and Discussion

All the porphyrins investigated exhibit electronic spectra typical of free base porphyrins, i.e., a strong B (Soret) band around 420 nm and four Q bands (I, II, III, and IV from the longest absorption band) in 700—450 nm. Table 1 summarizes absorption maximum (λ_{max}) of Q band and spectral type of these porphyrins in MTHF. As electron-donating ability of the para substituents increased, (a) all the four bands (I—IV) were red-shifted, and (b) the ratio of the intensities of Q(0–0) (I and III) to Q(0–1) (II and IV) increased. These substituent effects are qualitatively in good correspondence with those reported for a series of tetraarylporphyrins in DMF by Meot-Ner and Adler.[3a] They reported that frequency shifts of band I compared with *meso*-tetraphenylporphyrin (TPP) showed a good correlation with a combined Hammet coefficient 0.8 σ_R+0.2 σ_I. In the present series of para-substituted derivatives, however, the Hammet-type plot (Fig. 1) did not give a straight line. T(*p*-NH$_2$)PP and T(*p*-NMe$_2$)PP exhibited larger frequency shifts than expected assuming linear relationship. Furthermore, for these porphyrins the spectrum belongs to a new type ($\varepsilon_{II}<\varepsilon_I<\varepsilon_{IV}<\varepsilon_{III}$) (Table 1). It can be seen that the spectrum of T(*p*-NMe$_2$)PP resembles to that of a KOH–MeOH solution of T(*p*-OH)PP. The basic solution of T(*p*-OH)PP exhibits olive-green color, and the electronic spectrum is

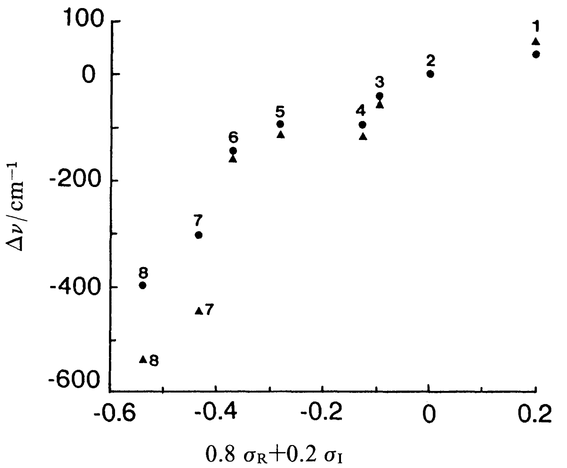

Fig. 1. Plots of frequency shift of band I vs. the combined Hammet substituent coefficient $0.8\ \sigma_R + 0.2\ \sigma_I$ for *meso*-tetraarylporphyrins in MTHF (●) and in DMF (▲). The numbers in the figure indicate the compounds listed in Table 1.

rationalized in terms of delocalization onto the pyrrole nitrogen atoms of the negative charges on the phenoxide oxygens.[10] These facts suggest that strong electron-donating para-substituents, especially NMe_2 groups in the *meso*-phenyl rings give large perturbation to the electronic state of the porphyrin π system.

In the case of T(*o*-NH_2)PP red-shift of absorption band is much smaller than that observed for T(*p*-NH_2)PP and the spectral type is different. Since the *o*-aminophenyl group in T(*o*-NH_2)PP is sterically hindered from free rotation around the C_{ipso}–C_{meso} bond,[11] mesomeric electron-donating power of *o*-NH_2 group is poorly transmitted to the porphyrin π system. Furthermore, it was reported that direct steric interaction between substituents and the porphyrin ring causes blue-shift of Q band for T(*o*-Me)PP and T(*o*-OEt)PP.[3a]

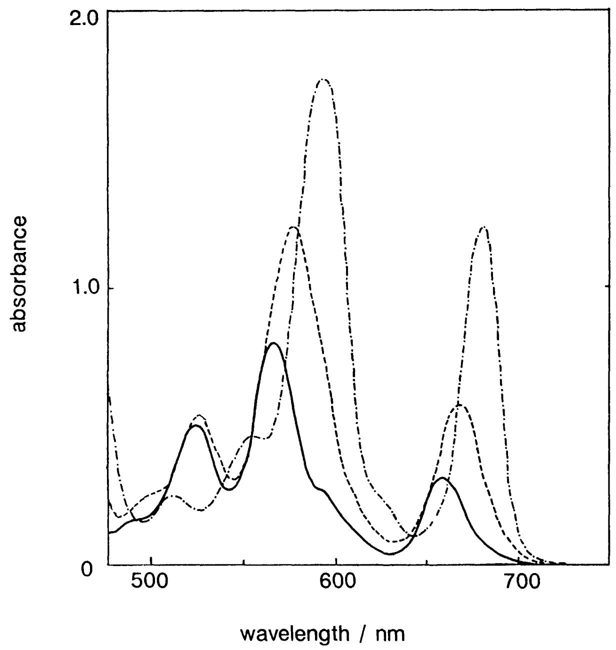

Fig. 2. Temperature dependence of electronic spectrum of T(*p*-NH_2)PP in MTHF. (a) 295 K (——), (b) around 150 K (------), and (c) 77 K (—·—).

Table 2. Comparison of Absorption Maxima of Q Band for *meso*-Tetraarylporphyrins at 77 K and Those at 295 K[a]

No	Compound	$\Delta\lambda_{max}(\lambda_{max})/\mathrm{nm}$[b]			
		I	II	III	IV
1	T(*p*-NO_2)PP	−5(639)	−6(584)	−2(546)	1(513)
2	TPP	−4(642)	−1(588)	2(548)	1(512)
3	T(*p*-Me)PP	−4(644)	−3(588)	3(550)	2(514)
4	T(*p*-OMe)PP	1(651)	0(594)	4(556)	3(518)
5	T(*p*-NHAc)PP	1(652)	1(596)	6(560)	6(522)
6	T(*p*-OH)PP	5(657)	7(602)	10(564)	9(526)
7	T(*p*-NH_2)PP	21(680)	25(625)	27(592)	29(552)
8	T(*p*-NMe_2)PP	14(677)	—	20(590)	17(542)
9	T(*o*-NH_2)PP	−2(649)	−1(589)	3(552)	5(519)

a) Solvent: MTHF, Concentration: 3×10^{-5}—6×10^{-5} M.
b) Values in parentheses are absorption maxima at 77 K.

Although an MTHF solution of T(*p*-NH_2)PP exhibited red color at room temperature, on cooling down to 77 K the solution turned deep green. The green solution became red again as temperature rose, i. e. a new thermochromic phenomenon was observed. Figure 2 shows variation of electronic spectrum of T(*p*-NH_2)PP in MTHF at different temperatures. As temperature decreased, all the four bands were red-shifted with marked change of the intensity ratio. The spectral type of T(*p*-NH_2)PP at 77 K was similar to those of T(*p*-NMe_2)PP obtained at room temperature and also of T(*p*-O^-)PP. Considering the substituent effects discussed above, it was suggested that effective electron-donating ability of *p*-NH_2 group is significantly enhanced at low temperature. As are shown in Table 2, all the porphyrins examined showed more or less shifts of absorption maxima at 77 K, however, no color change was observed except for T(*p*-NH_2)PP. It is noteworthy that the absorption maxima of T(*p*-NH_2)PP were more red-shifted than those of T(*p*-NMe_2)PP at 77 K. The fact suggested that the electronic state of the porphyrins will be influenced by not only intrinsic electron-donating ability of the para substituents but also another factor which is more significant at lower temperature. In order to clarify the factor solvent effects on the electronic spectra of *meso*-tetraarylporphyrins were investigated. The nature of solvent made a significant effect on Q bands of T(*p*-NH_2)PP, and as a result remarkable solvatochromism was observed (Table 3). Absorption maximum of band I of T(*p*-NH_2)PP showed relatively good correlation with donor number (DN) (Fig. 3a),[12] while it poorly correlated with $E_T(30)$ (Fig. 3b).[13] In the electronic spectrum of T(*p*-NH_2)PP in hexamethylphosphoric triamide (HMPT), which has very high DN, the four absorption bands (I—IV) collapsed to two intense bands and the

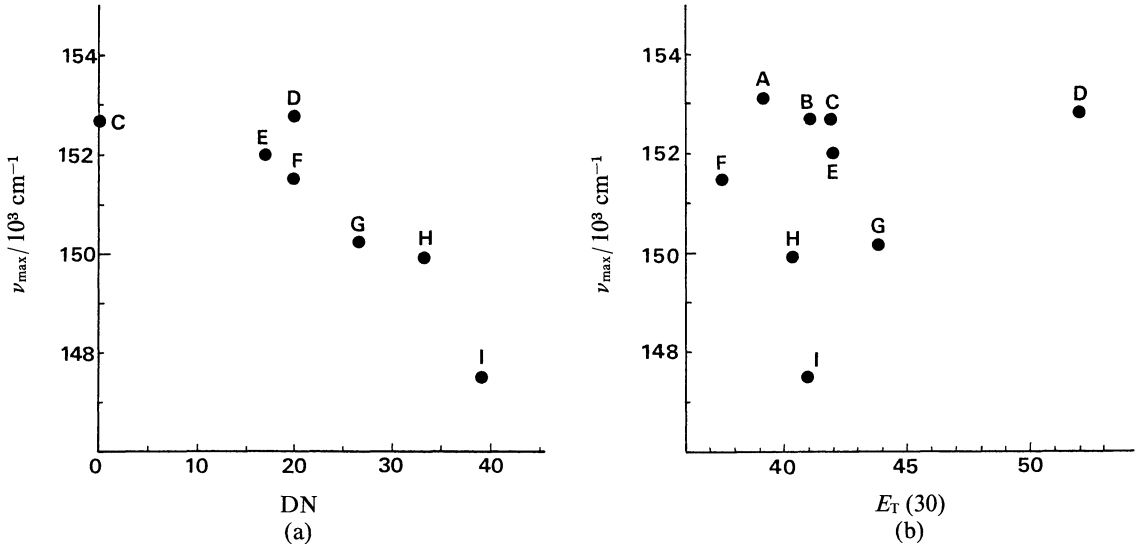

Fig. 3. Correlation between the absorption maximum of band I of T(p-NH_2)PP and (a) donor number (DN) or (b) E_T(30) of solvents at 293 K. A: $CHCl_3$, B: CH_2Cl_2, C: 1,2-dichloroethane, D: EtOH, E: acetone, F: THF, G: DMF, H: pyridine, I: HMPT.

Table 3. Solvent Effect on the Electronic Spectra of T(p-NH_2)PP, T(p-NMe_2)PP, and T(p-OH)PP[a)]

Solvent	λ_{max}/nm				Color
	I	II	III	IV	
(A) T(p-NH_2)PP					
$CHCl_3$	653	594	562	522	Violet
CH_2Cl_2	655	594	562	522	Reddish violet
Dichloroethane	655	595	564	523	Reddish violet
EtOH	654	593	563	522	Red
Acetone	658	599	565	522	Red
THF	660	600	565	523	Red
DMF	666	—	574	527	Brown
Pyridine	667	—	575	529	Deep green
HMPT	678	—	590	—	Deep green
(B) T(p-NMe_2)PP					
CH_2Cl_2	665	—	575	530	
MTHF	663	—	569	525	
DMF	670	—	581	527	
HMPT	671	—	581	527	
(C) T(p-OH)PP					
MeOH	649	592	553	517	
MTHF	652	595	554	517	
DMF	652	595	556	519	
Pyridine	653	596	560	521	
HMPT	656	597	561	522	

a) Concentration 3×10^{-5}—8×10^{-5} M; Temperature ca. 295 K.

spectrum resembled to that of T(p-O^-)PP. These facts indicate that electronic spectrum of T(p-NH_2)PP is influenced mainly by electron-pair donating ability of solvent molecules rather than macroscopic polarity of media. Since molecules with high DN can serve as a good hydrogen-bond acceptor, it is likely that such solvent molecules will form hydrogen-bonds with p-NH_2 hydrogens of T(p-NH_2)PP causing spectral change. Solvent dependence of the spectrum of T(p-NMe_2)PP was smaller than that of T(p-NH_2)PP, indicating that interaction of NMe_2 groups with hydrogen-bond acceptors is rather small as can be expected. The solvatochromic behavior of T(p-NH_2)PP can be explained as follows: Hydrogen-bonding between p-NH_2 hydrogens and hydrogen-bond accepting solvents increases effective electron-donating ability of the NH_2 group and this effect is transmitted into the porphyrin moiety through the phenyl rings to cause the spectral changes. It was expected that p-OH groups in T(p-OH)PP also interact with hydrogen-bond accepting solvents. In fact the electronic spectrum of T(p-OH)PP exhibited solvent dependence similar to that of T(p-NH_2)PP, although the observed spectral change was smaller. For the other porphyrins including T(o-NH_2)PP, each absorption band in DMF was slightly (0—3 nm) red-shifted compared with that recorded in MTHF.

On the basis of the solvent effect discussed above, it can be considered that the thermochromism of T(p-NH_2)PP in MTHF involves hydrogen-bonding interaction with the solvent. As temperature decreases the hydrogen-bonds between the p-NH_2 groups and the solvent molecules become stronger and as a result the electronic spectrum resembles that observed in solvents with higher hydrogen-bond accepting ability such as pyridine and HMPT. In the case of T(o-NH_2)PP it is likely that the o-NH_2 group forms hydrogen-bonds with the solvent molecules as the p-NH_2 group in T(p-NH_2)PP, but the enhancement of effective electron-donating ability of the o-NH_2 groups could little affect electronic state of the porphyrin π-system since the ortho-substituted phenyl groups are nearly perpendicular to the porphyrin ring.

On the other hand, the electronic spectra of T(p-OH)PP and T(p-NH_2)PP in alcoholic solvents exhibited

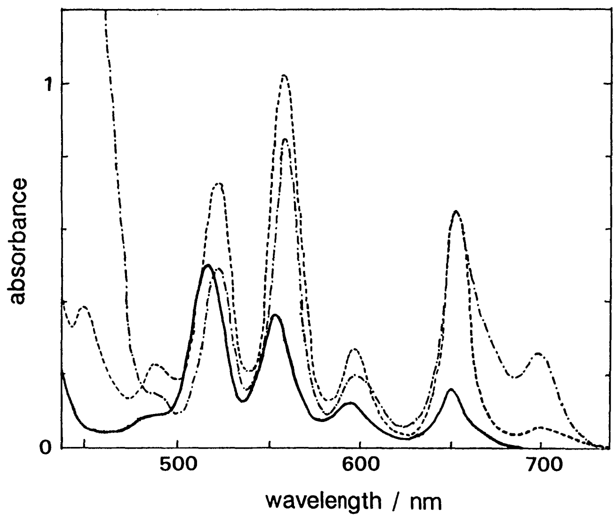

Fig. 4. Temperature dependence of electronic spectrum of T(p-OH)PP in MeOH–EtOH (2:1). [T(p-OH)PP]=7.4×10^{-5} M. (a) 295 K (——), (b) 77 K (------), and (c) 77 K in the presence of CF_3CO_2H (2.2×10^{-5} M) (—·—).

different type of temperature dependence from that observed in MTHF. A violet solution of T(p-OH)PP in MeOH–EtOH turned brown at 77 K, and the spectrum exhibited new absorption bands at 697 and 448 nm (Fig. 4). To clarify the mechanism of the color change for T(p-OH)PP with decrease of temperature we examined the effect of solvent acidity on the electronic spectrum. In the presence of a small amount of trifluoroacetic acid (TFA) (ca. 0.3 molar amount of porphyrin) the spectrum obtained at 295 K was little affected, however, as shown in Fig. 4, at 77 K the resulting spectrum also showed new bands at 698 and 447 nm with increase of absorbances. With rise of temperature the spectrum returned to the original one and the cycles were observed repeatedly. The spectral change with decrease of temperature in alcoholic solvents with or without small amount of TFA was similar to that obtained on addition of increasing amount of TFA at 295 K. It has been known that the species having absorption maxima at ca. 700 nm (Q band) and ca. 450 nm (Soret band) is the dication of the porphyrin,[10] and the species having other four Q bands (I, II, III, and IV) in the spectrum is free-base of T(p-OH)PP. From these facts the new bands observed at 77 K are assigned to the absorption of the dication of T(p-OH)PP, and the formation of the monocation of the porphyrin is considered to be negligible. Thus, the observed thermochromic phenomenon of T(p-OH)PP in alcoholic solutions can be explained in terms of temperature dependence of free-base–dication equilibrium, i.e., at lower temperature protonation of pyrrole nitrogen in the porphyrin ring is facilitated. This temperature effect on the protonation equilibrium of porphyrins coincides with that reported for TPP by Tsukahara et al.,[4] although the temperature range where the thermochromism is observed is quite different. T(p-NH_2)PP showed similar temperature dependence of electronic spectrum: New absorption bands appeared at 747 and 460 nm with color change from red to brown at 77 K. Because of the too low solubility of T(p-NMe_2)PP into alcoholic solvents measurements of electronic spectrum could not be succeeded. In the cases of T(p-OMe)PP and T(o-OH)PP no new band was observed and the color of the solution was unchanged on cooling. Since introduction of strong electron-donating para-substituents on the *meso*-phenyl groups increases basicity of the pyrrole nitrogens,[3a] T(p-OH)PP and T(p-NH_2)PP are partially converted to the dication on cooling in the presence of water or small amount of acid, and use of carefully dried solvents suppressed appearance of the new bands.

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