1016 © 1993 The Chemical Society of Japan Bull. Chem. Soc. Jpn., 66, 1016—1023(1993) [Vol. 66, No. 4

Solvent Effects on Electronic States of Phthalocyanines

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(Received September 17, 1992)

The absorption spectra of a π–π^* transition (the Q band) of titanium (IV) oxide phthalocyaninate (TiOpc) and phthalocyanine (H_2pc) were measured in various organic solvents. It has been shown that the wavelength of the π–π^* transition is dependent on 1) the permanent dipole moment of the solvent, 2) the coordination of the solvent, and 3) the dispersion force and induced dipole moment of the solvent. A single π–π^* peak and its significant red-shift in the absorption spectrum of H_2pc in trifluoroacetic acid (TFA) suggested a protonation of the inner nitrogen atoms, leading to H_4pc^{2+}. TiOpc in TFA was cleaved, followed by the release of H_2pc. The overall reaction was proposed to be as follows; $TiOpc+4CF_3COOH \rightleftharpoons Ti(CF_3COO)_4+H_2O+H_2pc$.

Recently, dual-layered photoreceptors using phthalocyanines compounds have attracted considerable attention owing to their high photosensitivity in the near-infrared region (600—850 nm) for a laser beam printer. In phthalocyanines compounds, titanium(IV) oxide phthalocyaninate has been well known to have a higher photosensitivity as a CGM (charge generator material) in an organic photoconductor. The popular polymorphic forms of TiOpc are known to be A,B,C,D-TiOpc.[1,2] Most recently, a polymorph of m-TiOpc was reported to have been developed.[3] The crystal structures of A- and B-TiOpc were determined by Hiller et al.[1] However, thus far no structure analysis of C- or D-TiOpc by X-ray diffraction has been accomplished. Generally, such organic pigments as phthalocyanines are extremely insoluble in organic solvents. It has therefore been impossible to recrystallize phthalocyanines from organic solvents. However, it is noted that even a slight amount of impurity may inhibit the electrical characteristics of electric materials, such as an organic semiconductor or a solar battery. We found that TiOpc is comparatively soluble in hexamethylphosphoric triamide (HMPA). On the basis of this information we developed "the method for purification of organic pigments" using HMPA.[4]

Very few investigations on the spectral properties of TiOpc and H_2pc have been reported, because of their poor solubilities in organic solvents.[5] The absorption spectra of H_2pc were indicated in pyridine,[6] dimethylsulfoxide (DMSO),[7,8] *N*,*N*-dimethylacetamide (DMA),[7] 1-Cl-naphthalene,[9,10] 1-Br-naphthalene,[11] and HMPA.[8] Edwards et al.[8] mentioned that the absorption spectrum of H_2pc in DMSO and HMPA appeared as a superposition of the normal free-base spectrum and a metal-type spectrum. On the other hand, reports concerning the absorption spectra of TiOpc relative to H_2pc are rather scarce. Thus far, the absorption spectra of TiOpc have been reported only for 1-Cl-naphthalene,[12] DMSO,[8] dichlorobenzene,[8] and HMPA.[8] Edwards et al.[8] suggested the presence of a new species in DMSO and HMPA, due to a considerable perturbation appearing in the absorption spectrum of TiOpc in DMSO and HMPA. We obtained a normal absorption spectrum of TiOpc in HMPA as well as in 1-Cl-naphthalene. Investigations involving the absorption spectra of TiOpc and H_2pc have thus been very few, and making their behavior and situations uncertain.

In this paper we describe details concerning the relationship between π–π^* transitions called the Q band near to 650—750 nm, and the characteristics of organic solvents, i.e., the solvent effects on the electronic state of phthalocyanines. For this purpose we have measured the absorption spectra of TiOpc and H_2pc in such organic solvents as [Group I: TFA, QN (quinoline), 1CNP (1-Cl-naphthalene), ODCB (*o*-dichlorobenzene), DCM (dichloromethane), TEA (triethylamine); Group I′: PY (pyridine), THF (tetrahydrofuran); Group II: HMPA, DMSO, DMA, DMF, TBP (tributylphosphate); Group III: CS_2 (carbon disulfide)].

The behaviors of H_2pc and TiOpc in TFA, which is a protic solvent, are remarkable different from the case in other solvents. The absorption spectrum of H_2pc in TFA exhibited a single π–π^* peak which was significantly red-shifted compared to the peak position observed in other solvents. On the other hand, it was found that TiOpc in TFA was cleaved followed by a release of H_2pc. We also studied the reason for the red-shift of the H_2pc peak in TFA as well as the cleavage mechanism of TiOpc in TFA.

Experimental

Reagents. All of the reagents used were of reagent grade prepared by Tokyo Kasei Co., Kishida Chemical Co., or Junsei Chemical Co., and used without further purification.

Preparation of Compounds. **$TiCl_2$pc.** A flask (2 l) fitted with a condenser, a magnetic stirring bar and a thermometer was charged with *o*-dicyanobenzene (184 g) and 1-Cl-naphthalene (120 ml). Titanium tetrachloride (40 ml) was then added to the mixture. After the reaction mixture was refluxed for 5 h at 200°C, it was allowed to cool to 120°C, followed by filtration, to produce a crude cake of $TiCl_2$pc. The obtained crude cake was washed with 1-Cl-naphthalene (1 l) and methanol (600 ml), and dried to give a blue powder of pure $TiCl_2$pc (163 g).

A-TiOpc. A mixture of $TiCl_2$pc (9 g) and *N*-methylpyrrolidone (150 ml) in a flask (200 ml) equipped with a condenser, a magnetic stirring bar and thermometer was refluxed for 3 h at 140°C, and then cooled to 80°C. The reaction mixture was filterd; the precipitated cake was washed with methanol and dried to give a blue powder of pure A-TiOpc (7.2 g).

B-TiOpc. A flask (1 l) equipped with the apparatus mentioned above was charged with $TiCl_2pc$ (88 g) and *n*-buthanol (600 ml). The reaction mixture was refluxed for 3 h at 118°C, and cooled to 80°C. The mixture was filterd and washed with methanol, and then dried to give a blue powder of pure B-TiOpc (75 g).

D-TiOpc. A mixture of $TiCl_2pc$ (8 g) and phenol (150 g) in a flask (200 ml) was heated to 110°C and refluxed for 5 h with stirring. Water (150 ml) was then added to the reaction mixture, which was allowed to cool to 50°C. The mixture was filtrated and washed with methanol (100 ml). After the crude product in *o*-dichlorobenzene (20 ml) and water (150 ml) was refluxed for 1 h at 60°C, the water fraction was removed. The organic fraction was filterd and washed with methanol, and then dried to give a pure powder of D-TiOpc (6.2 g).

Apparatus and Procedures. Elemental Analysis. Elemental analyses of the complexes were carried out by using a Perkin–Elmer 240C analyzer. Calcd for $TiCl_2pc$: C, 60.88; H, 2.55; N, 17.75; Cl, 11.23%. Found: C, 60.66; H, 2.37; N, 17.68; Cl, 11.08%. Calcd for A,B,D-TiOpc: C, 66.68; H, 2.80; N, 19.44%. Found for A-TiOpc: C, 66.51, H, 2.71; N, 19.33%. Found for B-TiOpc: C, 66.40; H, 2.59; N, 19.23%. Found for D-TiOpc: C, 66.88; H, 2.81; N, 19.61%.

Absorption Spectra. The absorption spectra of sample solutions were measured using a Shimadzu UV-3100S spectrophotometer at room temperature.

Measurement of Water. The amount of water contained in the samples was determined according to a method of Karl Fischer using a MCI model KF-06 or UA-06 analyzer under dry air.

X-Ray Powder Diffraction. X-ray powder diffraction with monochromated Cu *Kα* was carried out using a Philips PW1700 diffractometer at room temperature.

Results and Discussion

Solvent Effects on the Electronic State of TiOpc. The structures of TiOpc and H_2pc are shown in Fig. 1. In Fig. 2, the characteristic X-ray powder diffraction patterns of A,B,D-TiOpc are given. The polymorphs have the characteristic Bragg's angles ($2\theta\pm0.2°$), as follows: A-TiOpc (9.3°, 10.5°, 13.3°, 15.3°, 20.8°, 26.3°); B-TiOpc (7.6°, 10.2°, 22.3°, 25.3°, 28.6°); D-TiOpc (9.5°, 24.1°, 27.3°). Figure 3 shows the absorption spectra of TiOpc in HMPA, 1-Cl-naphthalene, pyridine, and DMSO. A sharp peak appeared in the spectra of HMPA and 1-Cl-naphthalene; a broad band appeared in DMSO near to 700 nm, the peak or band of which was called the Q band based on the π–π^* ($^1A_1$–^1E) transition. Only one π–π^* peak of TiOpc in other solvents appeared in the spectrum due to the C_{4v} symmetry of TiOpc.[5] The peak positions of solutions which were prepared by dissolving A,B,D-TiOpc into organic solvents were the same, regardless of their morphologies. A plot of the peak wavelength of a solution containing TiOpc vs. the dielectric constant of the solvent, and that vs. the dipole moment of the solvent are given in Figs. 4 and 5, respectively. Generally, the wavelength of the π–π^* transition is known to be red-shifted as the polarity of the solvent increases.[14] The peak wavelength of TiOpc indicated the four kinds of dependency on the dielectric constant and dipole moment of the solvent, as can be seen in Figs. 4 and 5; that is, the wavelength depended on those of the group-I, -I′, -II, and -III solvents. Although the solvents in group I have a permanent dipole moment, they have no coordination ability. On the other hand, the solvents in group II have both a permanent dipole moment and some coordinating ability. Also, the permanent dipole moment in carbone disulfide in group III is zero. The absorption spectra of TiOpc in group-I and -III solvents, which have no coordinating ability, showed a sharp peak at near to 700 nm and a flat absorbance (nearly zero) in the region of about 400 to 600 nm. On the other hand, in group-II solvents, such as DMSO, the spectral shape was very distorted, as can be seen in Fig. 3. Although pyridine and THF have a coordinating ability, the spectral shape was intermidiate between that in group-I solutions and group-II solutions. It is considered to be better to classify pyridine and THF as being in group I′ rather than group II′, since the spectral shapes in those solvents are similar to those in group I, rather than in group II. For the reasons mensioned above we concluded that the solvent effects observed in the π–π^* transition can be primarily classified into three different groups. Thus, the π–π^* transition can be dependent on (I) the permanent dipole moment of the solvent (in group I); (II) the coodination of the solvent (in group II); and (III) the dispersion force and induced dipole moment of the solvent (in group III). A detailed discussion concerning solvent effects is presented in the next section.

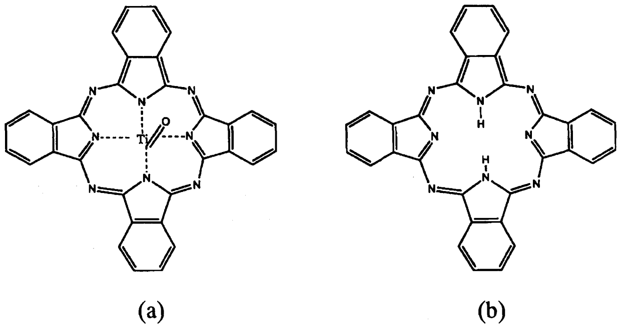

Fig. 1. Structures of TiOpc (a) and H_2pc (b).

Theory of Solvent Effects on the Absorption Spectrum of TiOpc. A qualitative interpretation of the solvent shifts on the absorption spectra is possible by considering (a) the momentary transition dipole moment during an optical absorption (dispersion force); (b) the difference in the permanent dipole moment be-

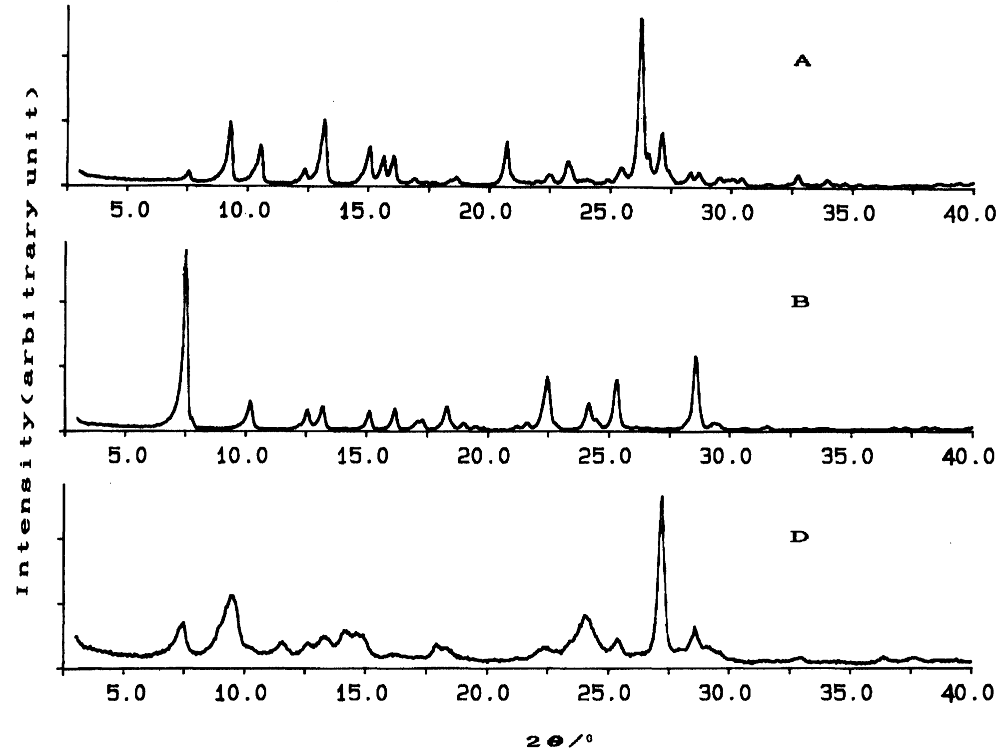

Fig. 2. X-Ray powder diffraction patterns of A,B,D-TiOpc. A: A-TiOpc; B: B-TiOpc; D: D-TiOpc.

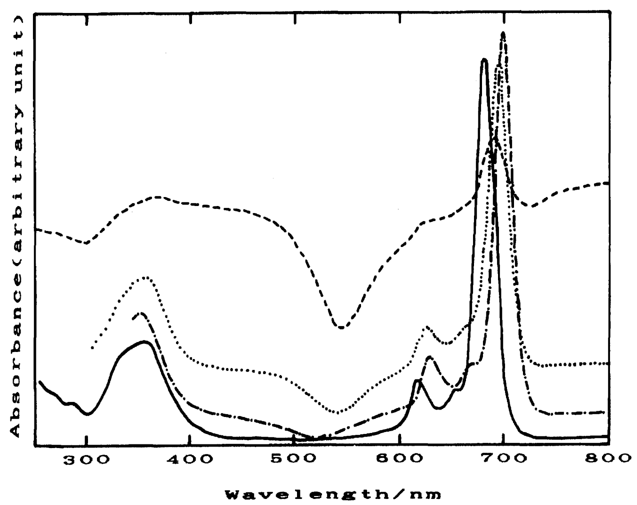

Fig. 3. Absorption spectra of TiOpc in HMPA (—), 1-Cl-naphthalene (-•-), pyridine (••••), and DMSO (---). HMPA and DMSO, 1-Cl-naphthalene, and pyridine are classfied as group -II, -I, and -I′, respectively.

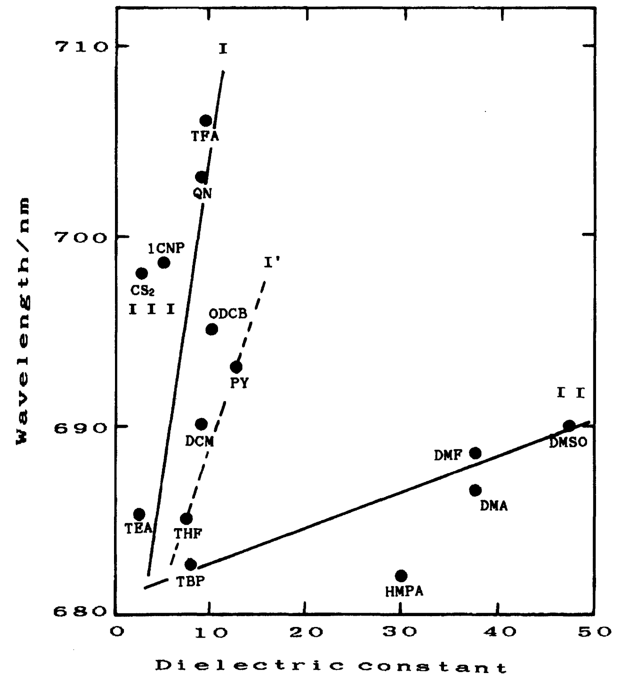

Fig. 4. Plot of the peak wavelength of a solution containing TiOpc vs. the dielectric constant of the solvent.

tween the ground and excited states of the solute; (c) the change in the ground state dipole moment of the solute induced by solvent; and (d) the Frank–Condon principle.[14] Four limiting cases can be considered for electronic transitions:[14]

(1) A non-polar solute in a polar solvent.

(2) A non-polar solute in a non-polar solvent.

In these cases, only dispersion forces contribute to the solvation of the solute.

(3) A dipolar solute in a polar solvent.

(3-1) The first of this case is "TiOpc in a group-I solvent".

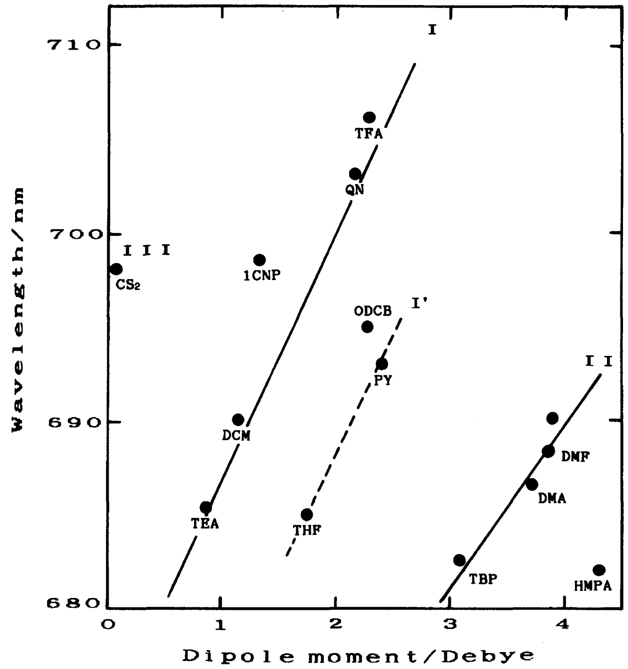

Fig. 5. Plot of the peak wavelength of a solution containing TiOpc vs. the dipole moment of the solution.

Since the ground-state solvation results from dipole–dipole forces, there is an oriented solvent cage around the dipolar solute molecule, TiOpc. The observed π–π^* transition peak of TiOpc is more red-shifted as the permanent dipole moment of solvent increases, as can be seen in Fig. 5. These facts mean that the dipole moment of TiOpc increases during the transition, i.e., $\mu_g < \mu_e$, where μ_g and μ_e are the dipole moments of the ground state and the excited state of TiOpc, respectively. Since a Franck–Condon excited state is formed in a solvent cage of already partly oriented dipoles, a greater stabilization state is obtained with increasing solvent polarity.[15] This effect of the solvation energy is illustrated in Fig. 6a.

(3-2) The second case of (3) is "TiOpc in a group-II solvent".

A red-shift was also observed in a coordinating solvent (in group II) with increasing solvent polarity, except in the case of HMPA. A large red-shift may be expected in the coordinating solvents in group II relative to the dipolar solvents in group I, since the dipole moments of the coordinating solvents are larger than those of the dipolar solvents. However, the observed wavelength in a coordinating solvent is not longer than that in a dipolar solvent. The reason is believed to be that the strong stabilization of the ground state energy of TiOpc in the coordinating solvent is caused by the coordination of solvent molecules. That is, the energy of the ground state in the coordinating solvent is lowered more than that in the dipolar solvent, as illustrated in Fig. 6b. We systematically studied the solvent effects on the π–π^* transition in such solvents having some coordinating ability. It was elucidated that the solvent shifts on the absorption spectra of TiOpc in coordinating solvents can be interpreted in terms of the larger dipole moment of the Franck–Condon excited state of TiOpc, relative to the ground state, and by the stronger solute–solvent interaction of the ground state than that in the dipolar solvent.

(4) A dipolar solute in a non-polar solvent.

In this case, the forces which contribute to solvation are dispersion and dipole-induced dipole forces. The absorption spectrum of TiOpc in CS_2 (in group III) is the only example, since TiOpc is extremely insoluble in other non-polar solvents. The energy of dispersion is expressed as

$$E_{\mathrm{dis}} = -3\alpha^2 I/4r^6, \quad ^{16)} \tag{1}$$

where α is the polarizability, I is the ionization energy of the interacting molecules, and r is the distance between molecules. The dispersion forces increase with α^2, which is a function of $(n^2-1)/(2n^2+1)$, where n is the solvent refractive index. Therefore, strong dispersion forces appear in a solvent molecule with a large polarizability or refractive index. Carbon disulfide has the highest refractive index (1.6280) of all the organic solvents as well as a large polarizability ($15.14/\mathrm{A}^3$; along with the principal axis).[17] For carbon disulfide, the dispersion force is expected to be considerable strong due to its large polarizability. The magnitude of the dipole-induced dipole interaction is given by

$$E_{\text{dipole-induced dipole}} = -2\alpha\mu^2/r^6, \tag{2}$$

which depends on the solvent n.[18] The observed wavelength of TiOpc in CS_2 is more red-shifted than the wavelength extrapolated to $\mu=0$ in wavelength vs. μ plots for dipolar solvents. This result is reasonably taken into account by the dispersion and strong dipole-induced dipole interactions, as mentioned above.

Figure 7 shows the absorption wavelength of TiOpc as a function of the donor number[19,20] of a solvent which is related to the ability of coordination. As the donicity of the solvent becomes stronger, the absorption peak becomes more red-shifted, except in the case of the HMPA solution. Although the donor number of HMPA is the strongest, the absorption peak of the HMPA solution was most blue-shifted. The reason for this is considered to be based on the bulkiness of the HMPA molecule. In other words, if the HMPA molecule is bulky, the number of HMPA molecules occupied in the first-coordination sphere of TiOpc will be fewer than that of other solvent molecules, i.e., DMSO, DMF, and so on. In addition, the interaction between π electrons of TiOpc and HMPA will become smaller, since the HMPA molecule has difficulty getting close to TiOpc. As a result, the overall interaction between TiOpc and HMPA becomes smaller. This assumption can be also supported by the peak shape in the spectrum. The absorption peak of

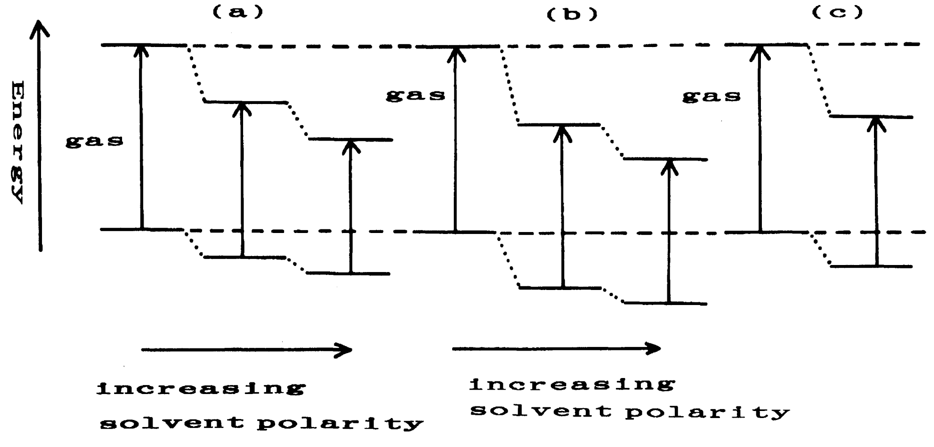

Fig. 6. Schematic energy diagram of solvent effects on the electronic transition of TiOpc in solvents. (a) in dipolar solvent, (b) in coordinating solvent, (c) in CS_2.

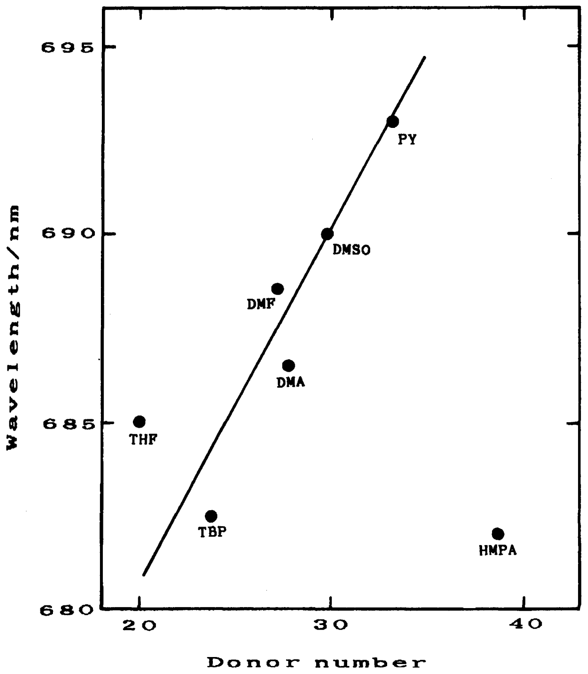

Fig. 7. Plot of the peak wavelength of a solution containing TiOpc vs. the donor number of the solvent.

TiOpc in HMPA is sharp, as well as in the case of 1-Cl-naphthalene, which has no coordinating ability. These results provide confirmative evidence that HMPA hardly coordinates to TiOpc. On the contrary, the spectra of TiOpc in TBP, DMSO, DMF, and DMA showed a perturbed broad peak. These results suggest that such solvents as TBP, DMSO, DMF, and DMA strongly coordinate to TiOpc. Thus, "(II) the coordination of solvent" was further closely related to two factors: II-1) the strength of the electron donicity of the solvent and II-2) the size of the solvent molecule. Edwards et al. reported that the spectra of TiOpc in HMPA and DMSO showed a considerable perturbation, thus indicating the presence of a new species. However, we observed the normal spectrum of TiOpc in HMPA, indicated in Fig. 3. When A-TiOpc was dissolved in HMPA and recrystallized, the molphology of A-TiOpc was obtained. This is a reasonable result, since A-TiOpc is the most stable molphology of all the molphologies of TiOpc.3,12)

Solvent Effects on the Electronic State of H_2pc. The absorption spectra H_2pc in 1-Cl-naphthalene, HMPA, and DMSO are given in Fig. 8. Two peaks of H_2pc were observed in a 1-Cl-naphthalene solution, and one broad band in DMSO. Furthermore, in an HMPA solution, the spectrum appeared as a superposition of two peaks and a broad band. As a result of the D_{2h} molecular symmetry of H_2pc, two optical transitions in the Q band are allowed: Q_x (^1A_g–$^1B_{2u}$), Q_y (^1A_g–$^1B_{3u}$). Plots of the longer peak wavelengths (i.e., the Q_x band vs. the dielectric constant, the dipole moment, and the donor number of the solvent) are given in Figs. 9, 10, and 11, respectively. The experimental results also indicate that the solvent effects on the π

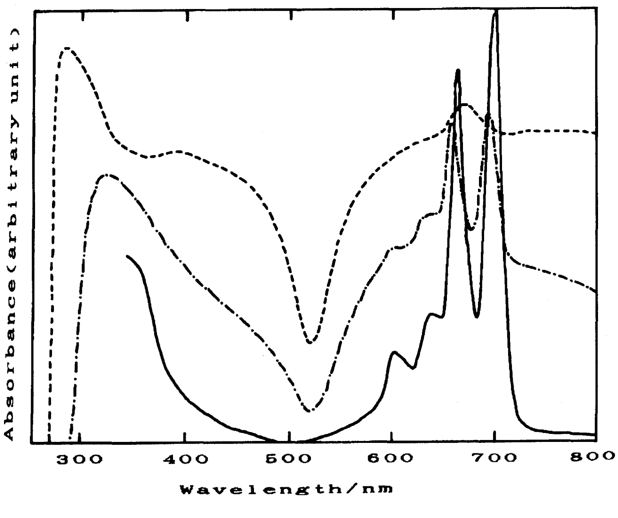

Fig. 8. Absorption spectra of H_2pc in 1-Cl-naphthlene (—), HMPA (-·-), and DMSO (---).

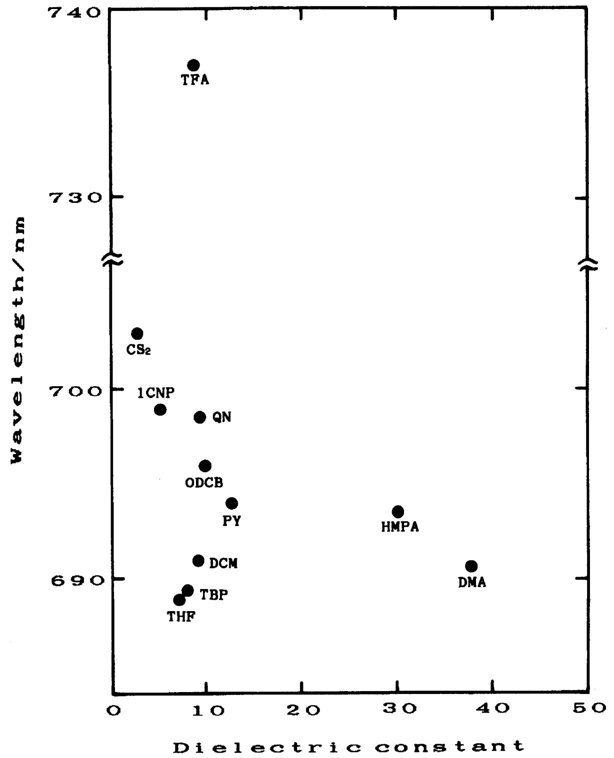

Fig. 9. Plot of the Q_x band wavelength of a solution containing H_2pc vs. the dielectric constant of the solvent.

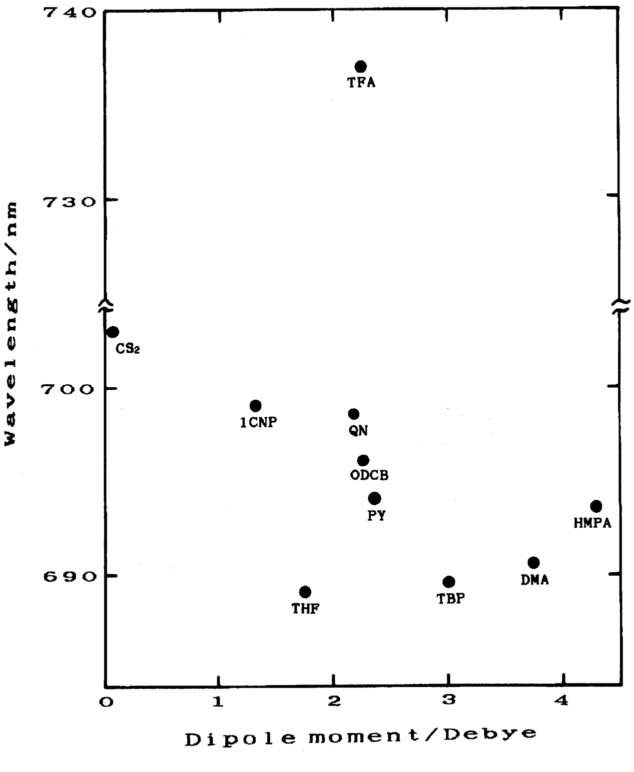

Fig. 10. Plot of the Q_x band wavelength of a solution containing H_2pc vs. the dipole moment of the solvent. A single peak was observed in TFA.

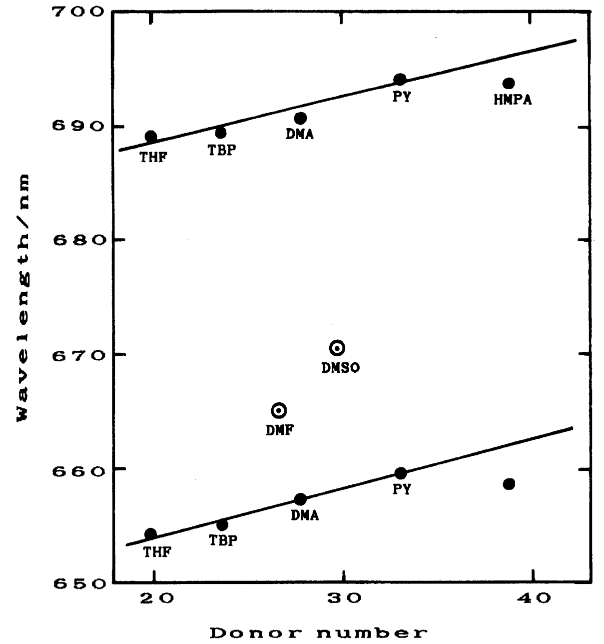

Fig. 11. Plot of the Q_x band wavelength of a solution containing H_2pc vs. the donor number of the solvent. Only a broad peak in DMF and DMSO was recorded.

electrons of H_2pc are very similar to those of TiOpc. The spectra of H_2pc exhibited only a broad band in DMSO and DMF. From these results, DMSO and DMF molecules are suggested to coordinate strongly to H_2pc. It was speculated from the peak shapes in the spectra that H_2pc was solvated due to the strong coordination of solvents in DMSO, DMA, DMF, TBP, and pyridine, and that H_2pc was weakly coordinated by solvent molecules in HMPA, THF, and *o*-dichlorobenzene. Such solvents as DMSO, DMA, and DMF have played important roles, since the coordination enhances the solubility; yet, at the same time, due to the coordination, they were not appropriate for recrystallization solvents. HMPA might, in turn, be noteworthy as a solvent for the recrystallization of phthalocyanines, due to its wesk coordination to phthalocyanines.

H_2pc in Trifluoroacetic Acid. The absorption spectrum of H_2pc in TFA is shown in Fig. 12. If exhibits a single π–π^* peak, which is significantly red-shifted compared to the peak positions observed in other solvents. Further, it exhibits a red shift of the peak position by 31 nm, compared with that of TiOpc in TFA. These results suggest that the protonations of inner nitrogens lead to H_4pc^{2+} with D_{4h} symmetry. TFA is a strong acid with the following equilibrium:

$$CF_3COOH \rightleftharpoons CF_3COO^- + H^+. \tag{3}$$

The equilibrium constant of dissociation K_a is

$$K_a = \frac{[CF_3COO^-][H^+]}{[CF_3COOH]} = 0.59.^{21)} \tag{4}$$

Ledson et al.[22)] reported that only the four outer bridg-

Table 1. Determination of the Amount of Water in a Solution of D-TiOpc Dissolved in TFA

Operation No.	1.	2.
Amount of water in CF_3COOH (ppm)	66.61	66.61
Amount of water in TiOpc (ppm)	1626.7	1626.7
Stock solution TiOpc (g)	0.0291	0.0275
CF_3COOH (g)	0.9709	0.9725
Amount of water expected for Eq. 6 (ppm)	1020	968
Amount of water expected for Eq. 7 (ppm)	112.0	109.5
Experimental value of amount of water (ppm)	1165	1170
Method of titration	Volumetric titration	
Model of apparatus	KF-06 UA-06 Titrant SS (MITSUBISHI) Solvent MS (MITSUBISHI)	

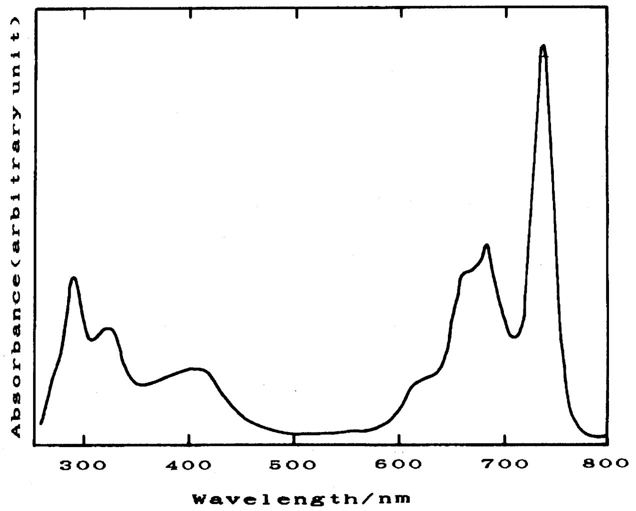

Fig. 12. Absorption spectrum of H_2pc in TFA.

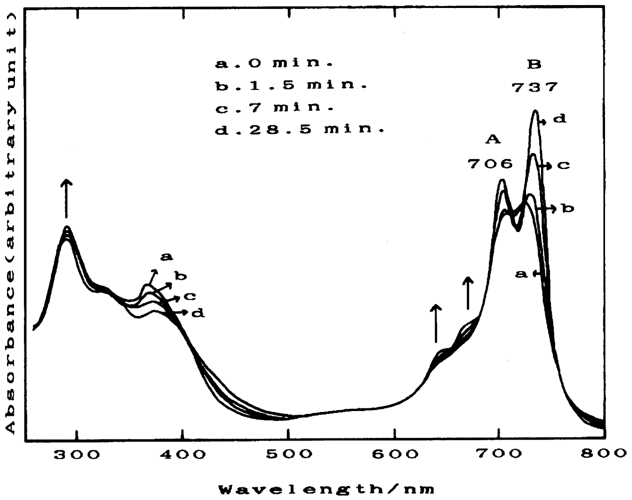

Fig. 13. Spectral changes of A-TiOpc dissolved in TFA. (a), 0 min; (b), 1.5 min; (c), 7 min; (d), 28.5 min.

ing nitrogen atoms of H_2pc were protonated, not the inner ones in a chlorosulphuric acid solution based on the results of conductivity data. There is some controversy concerning which nitrogens (inner or outer) are protonated. The phthalocyanine protonated on the outer four nitrogens has D_{2h} symmetry; on the other hand, that on the inner two nitrogens has D_{4h} symmetry, in which conjugation occurs between two hydrogens and two protons. The D_{4h}-type spectrum is characterized by an intense band near to 700 nm between A_{1g} and E_u.[5] Because the Q band of H_2pc in TFA exhibited the D_{4h} spectrum (Fig. 12), it might be suggested that protonatin occurs on the inner nitrogen, i.e., the aza nitrogen of H_2pc as follows:

$$H_2pc + 2H^+ \rightleftharpoons H_4pc^{2+} + 2CF_3COO^-. \qquad (5)$$

Thus, the red-shifted peak of H_2pc in TFA is considered to be observed as a result of conjugation between two imino hydrogens and two protons.

TiOpc in Trifluoroacetic Acid. Figure 13 shows changes in the absorption spectrum of TiOpc dissolved in TFA. In additon to the initial peak at 706 nm (A), another peak at 737 nm (B) appeared with an elapse of time. The peak height of peaks A and B became constant after approximately 30 min. After TiOpc was dissolved in TFA, the spectrum remained unchanged, even after 2 d. The peak position at 737 nm (B) and its shape are very consistent with the spectrum of H_2pc in TFA. Therefore, peak B at 737 nm was identified as that of H_2pc in TFA. On the other hand, peak A at 706 nm may be that of TiOpc in TFA. It was elucidated that TiOpc in TFA was cleaved, followed by the release of H_2pc, as mentioned above. Two paths were assumed for the reaction mechanism for TiOpc cleavage: (1) a Ti=O bond cleavage and the formation of water and H_2pc (overall reactions were expressed as Eq. 6); (2) Ti=O bond conservation and the formation of H_2pc (Eq. 7).

$$\begin{aligned}&(Ti{=}O)pc + 4CF_3COOH \\ &\quad \rightleftharpoons Ti(CF_3COO^-)_4 + H_2O + H_2pc, \qquad (6)\end{aligned}$$

$$\begin{aligned}&(Ti{=}O)pc + 2CF_3COOH \\ &\quad \rightleftharpoons (Ti{=}O)(CF_3COO^-)_2 + H_2pc. \qquad (7)\end{aligned}$$

It would be interesting to clarify which path (Eq. 6 or Eq. 7) is operative. We determined the amount of water in TFA solutions according to the method of Karl Fischer. The results are tabulated in Table 1. The experimental values of the amounts of water in all operations were in fair agreement with the values expected for the reaction given by Eq. 6. We therefore concluded that the path of Ti=O bond cleavage, as expressed by Eq. 6, would be operativbe.

The authors wish to express their thanks to Dr. Takao Matsuzaki, Mitsubishi Kasei Co., for valuable discussions and comments.

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