[June, 1992] © 1992 *The Chemical Society of Japan* *Bull. Chem. Soc. Jpn.*, *65*, *1475—1481 (1992)* 1475

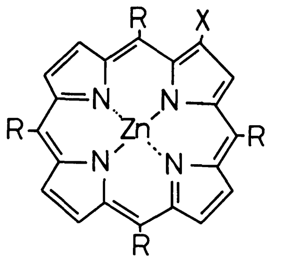
The Fluorescence Properties of (2-Nitro-5,10,15,20-tetraphenylporphyrinato)zinc

Kohshin TAKAHASHI,* Shino HASE, Teruhisa KOMURA,
Hiroto IMANAGA, and Osamu OHNO†
Department of Chemistry and Chemical Engineering, Faculty of Technology,
Kanazawa University, Kodatsuno, Kanazawa 920
†Department of Chemistry, Tokyo Institute of Technology,
O-okayama, Meguro-ku, Tokyo 152

(Received August 21, 1991)

The photophysical and redox properties of (2-substituted porphyrinato)zinc derivatives in various solvents are investigated. Zinc complexes of 2-bromo-, 2-cyano-, and 2,3-(1,4-phenylenedinitrilo)-substituted porphyrins as well as (tetraphenylporphyrinato)zinc (Zntpp(H,H)) exhibit well-resolved $Q_{0,0}$ and $Q_{0,1}$ fluorescence peaks, while (2-nitro-substituted porphyrinato)zincs emit a red-shifted fluorescence with a less resolved vibrational fine structure. Stokes shift of (2-nitro-5,10,15,20-tetraphenylporphyrinato)zinc (Zntpp(H,NO_2)) is considerably larger than that of Zntpp(H,H), and increases with the increase in the dielectric constant of aprotic solvents. The results are ascribed to the intramolecular charge transfer from the porphyrin ring to 2-nitro group in the lowest singlet excited state of Zntpp(H,NO_2).

Photoinduced redox chemistry of porphyrin derivatives has been extensively studied from the standpoint of the conversion of solar to chemical and/or electrical energy.[1-10] Porphyrin sensitization is achieved by an enhanced electron-donating or -accepting tendency in the electronic excited state. Therefore the fundamental properties in the electronic excited state of porphyrin derivatives are of interest in connection with the photosensitization and photoelectrical characteristics. Gross et al. reported the effects of 2-substituents on the redox potential of tetraphenylporphyrins.[11-13] The shift of the reduction potentials induced by strong electron withdrawing substituents(CN,NO_2) was larger than that of oxidation potential. Recently, Binstead et al. reported the redox potentials and absorption spectra of a series of (2-substituted 5,10,15,20-tetraphenylporphyrinato)copper(II).[14] They discussed the modulation of valence orbital levels with the substitution on 2-position, and concluded that the substitution modulates more significantly the lowest unoccupied e_g (in D_{4h} symmetry) and the next highest occupied a_{1u} π orbitals than the highest occupied a_{2u} orbital. In this paper, we present the redox properties and the photophysical properties including the absorption and fluorescence spectra, the fluorescence lifetime, and the fluorescence quantum yields of (2-substituted porphyrinato)zinc derivatives (Fig. 1).



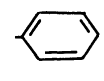
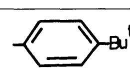
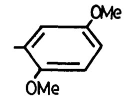
R	X	Zntpp(R,X)
	H	Zntpp(H,H)
	NO_2	Zntpp(H,NO_2)
	Br	Zntpp(H,Br)
	CN	Zntpp(H,CN)
	$C_6H_4N_2$	Ztpp(H,$C_6H_4N_2$)
	H	Zntpp(Bu^t,H)
	NO_2	Zntpp(Bu^t,NO_2)
	H	Zntpp(MeO,H)
	NO_2	Zntpp(MeO,NO_2)

Fig. 1. Structures and abbreviations of zinc porphyrins.

Experimental

5,10,15,20-Tetraphenylporphyrin (H_2tpp(H,H)) and its derivatives were synthesized and purified by the literature method.[15] The zinc porphyrins were also synthesized by the literature method.[16] The products were purified by column chromatography on alumina and silica. (2-Nitro-5,10,15,20-tetraphenylporphyrinato)zinc (Zntpp(H,NO_2)) and [2-nitro-5,10,15,20-tetrakis(4-*t*-butylphenyl)porphyrinato]zinc (Zntpp(Bu^t,NO_2)) as well as [2-nitro-5,10,15,20-tetrakis(2,5-dimethoxyphenyl)porphyrinato]zinc (Zntpp(MeO,NO_2)) were synthesized and purified by the literature method.[17] Further (2-bromo-5,10,15,20-tetraphenylporphyrinato)zinc (Zntpp(H,Br)),[18] (2-cyano-5,10,15,20-tetraphenylporphyrinato)zinc (Zntpp(H,CN)),[18] and [2,3-(1,4-phenylenedinitrilo)-5,10,15,20-tetraphenylporphyrinato]zinc (Zntpp(H,$C_6H_4N_2$))[19,20] were synthesized and purified by the literature methods. Calcd for $C_{44}H_{27}N_5O_2Zn$ (Zntpp(H,NO_2)) (MW 723.12): C, 73.08; H, 3.76; N, 9.69%. Found: C, 72.86; H, 3.63; N, 9.43%. Calcd for $C_{50}H_{32}N_6OZn$ (Zntpp(H,$C_6H_4N_2$)·H_2O) (MW 798.24) C, 75.23; H, 4.04; N, 10.53%. Found: C, 75.34; H, 3.98; N, 10.35%. Tetrabutylammonium perchlorate (TBAP) was commercially available and was recrystallized twice from ethanol, and then was dried in vacuo at 60 °C. Solvents, dichloromethane (CH_2Cl_2), 1,2-dichlorobenzene (*o*-

DCB), benzonitrile (BN), *N,N*-dimethylformamide (DMF), acetonitrile (AN), dimethyl sulfoxide (DMSO), used for cyclic voltammetric measurement were purified by repeated distillation or rectification after dehydration. Solvents used for other measurements were purified by distillation.

The absorption spectra were recorded on a Hitachi U-3210 spectrophotometer. The emission and excitation spectra were taken on a Shimadzu RF-540 spectrofluorometer equipped with a Hamamatzu Photonics R928 photomultiplier. The spectral response was corrected by the use of the standard solution.[21,22] The quantum yields of the emissions in air-equilibrated solutions were determined with reference to the yield of Zntpp(H,H) in benzene ($\phi_f^{S1}=0.033$[23]), using the optical dilute method.[24] The fluorescence lifetimes were measured on a Horiba time-resolved spectrofluorometer NAES-1100. Cyclic voltammetry was performed in a N_2-purged solution, using a Pt wire (diameter; 0.1 mm) as the working electrode, a Pt wire as the counter electrode, and Ag/0.1 M $AgNO_3$ in acetonitrile as the reference electrode (1 M=1 mol dm^{-3}). Electrode potential was controlled by using a Hokuto Denko HA-501 potentiostat and a HB-104 function generator. Cyclic voltammograms were recorded on a Yokogawa 3025 X-Y recorder. The average of the cathodic and anodic peak potentials, measured at the scan rate of 100 mV s^{-1}, is regarded as the half-wave potentials. The half-wave potential of ferrocene/ferricinium ion (Fc/Fc$^+$) was used as the internal reference.

Results and Discussion

The Photophysical and Redox Properties of (2-Substituted Porphyrinato)zinc Derivatives in DMF and CH_2Cl_2. Figure 2 shows the absorption and fluorescence spectra of the representative (2-substituted porphyrinato)zincs in DMF. Zntpp(H,Br) and Zntpp(H,$C_6H_4N_2$) as well as Zntpp(H,H) exhibit $Q_{0,0}$ and $Q_{0,1}$

Table 1. The Fluorescence Lifetimes (τ_{s1}^f)$^{a)}$ and the Quantum Yields (ϕ_{s1}^f)$^{b)}$ of Zinc Porphyrin Derivatives in CH_2Cl_2 at Room Temperature

Porphyrin	τ_{s1}^f/ns	$\phi_{s1}^f/10^{-2}$
Zntpp(H,H)	1.7	2.8
Zntpp(H,NO_2)	2.2	2.7
Zntpp(Bu^t,H)	—	3.2
Zntpp(Bu^t,NO_2)	—	2.9
Zntpp(MeO,H)	2.1	2.1
Zntpp(MeO,NO_2)	—	1.0
Zntpp(H,Br)	—	0.39
Zntpp(H,$C_6H_4N_2$)	2.2	1.8

a) Excitation at 420 nm. b) Excitation at 520 nm.

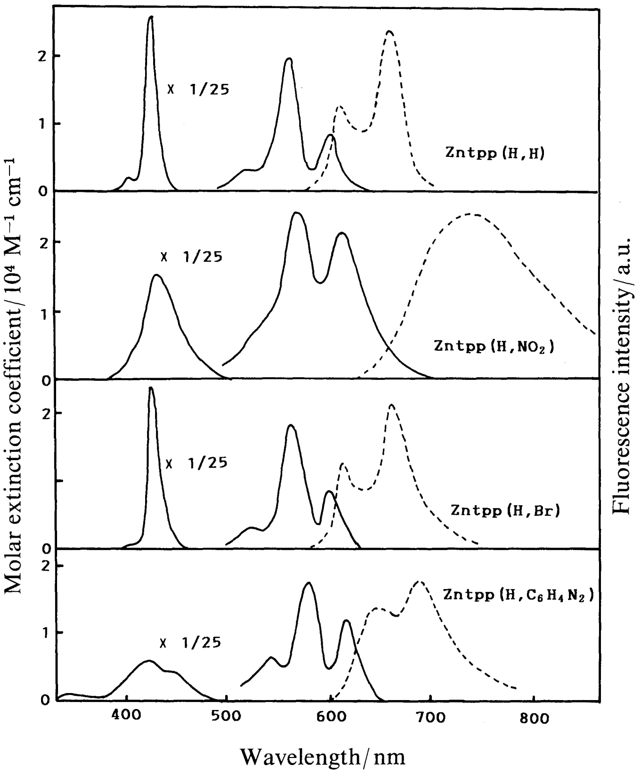


Fig. 2. Absorption (—) and fluorescence(----) spectra of zinc porphyrins in DMF at room temperature.

Table 2. The Half-Wave Potentials ($E_{1/2}$/V vs. Fc/Fc$^+$) of Zinc Porphyrin Derivatives in DMF and CH_2Cl_2 Containing 0.1 M TBAP at Room Temperature

Solvent	Porphyrin	$E_{1/2}^{II}$(red)	$E_{1/2}^{I}$(red)	$E_{1/2}^{I}$(ox)	$E_{1/2}^{II}$(ox)
DMF	Zntpp(H,H)	−2.18	−1.79	0.38	0.61
	Zntpp(H,NO_2)	−1.76	−1.41	0.50	
	Zntpp(Bu^t,H)	−2.21	−1.80	0.34	
	Zntpp(Bu^t,NO_2)	−1.78	−1.43	0.44	
	Zntpp(MeO,H)		−1.80	0.32	0.57
	Zntpp(MeO,NO_2)	−1.82	−1.47	0.49	
	Zntpp(H,Br)		−1.71	0.46	
	Zntpp(H,CN)	−1.97	−1.52	0.50	
	Zntpp(H,$C_6H_4N_2$)	−2.02	−1.61	0.43	
CH_2Cl_2	Zntpp(H,H)		−1.83	0.30	0.60
	Zntpp(H,NO_2)		−1.54	0.39	0.72
	Zntpp(Bu^t,H)		−1.85	0.26	0.57
	Zntpp(Bu^t,NO_2)		−1.48	0.33	0.65
	Zntpp(MeO,H)		−1.88	0.30	0.48
	Zntpp(MeO,NO_2)		−1.43	0.44	0.68
	Zntpp(H,$C_6H_4N_2$)	−1.95	−1.66	0.32	0.53

fluorescence peaks, while Zntpp(H,NO$_2$) emits a rather diffuse and red-shifted fluorescence with a less resolved vibrational fine structure. The other (2-nitro substituted porphyrinato)zincs, Zntpp(Bu^t,NO$_2$) and Zntpp(MeO,NO$_2$), exhibit also the similar fluorescence profile to Zntpp(H,NO$_2$), but the fluorescence spectrum of Zntpp(H,CN) displays resolved $Q_{0,0}$ and $Q_{0,1}$ peaks. The red-shifted diffuse fluorescence of (tetraphenylporphyrinato)zinc is also found with the substitution of one meso-phenyl group with a methyl-pyridinium group.[25] The decay lifetimes (τ_{S1}^{f}) and the quantum yields (ϕ_{S1}^{f}) of the zinc porphyrins in the lowest singlet excited state (S$_1$) in CH$_2$Cl$_2$ are summarized in Table 1. In spite of the significant difference in emission spectrum, the quantum yield and the decay rate hardly depend on the peripheral substitutions except Zntpp(H,Br), where an intramolecular heavy atom effect reduces the fluorescence yield.[26] The half-wave potentials of these zinc porphyrins in DMF and CH$_2$Cl$_2$ are also summarized in Table 2. The first oxidation and reduction potentials, $E_{1/2}^{I}$ (ox) and $E_{1/2}^{I}$ (red) respectively, of Zntpp(H,Br) in DMF are more positive than those of Zntpp(H,H), and the differences between the potentials of Zntpp(H,Br) and Zntpp(H,H), $\Delta E_{1/2}^{ox}$ (Zntpp(H,Br))=$E_{1/2}^{I}$ (ox) (Zntpp(H,Br))$-E_{1/2}^{I}$ (ox) (Zntpp(H,H)) and $\Delta E_{1/2}^{red}$ (Zntpp(H,Br))=$E_{1/2}^{I}$ (red) (Zntpp(H,Br))$-E_{1/2}^{I}$ (red) (Zntpp(H,H)), are 0.08 V respectively. Further the values of $\Delta E_{1/2}^{ox}$ (Zntpp(H,C$_6$H$_4$N$_2$)), $\Delta E_{1/2}^{ox}$ (Zntpp(H,CN)) and $\Delta E_{1/2}^{ox}$ (Zntpp(H,NO$_2$)) are 0.05, 0.12, and 0.12 V, respectively, while the values of $\Delta E_{1/2}^{red}$ (Zntpp(H,C$_6$H$_4$N$_2$)), $\Delta E_{1/2}^{red}$ (Zntpp(H,CN)), and $\Delta E_{1/2}^{red}$ (Zntpp(H,NO$_2$)) are 0.18, 0.27 and 0.38 V, respectively. The $\Delta E_{1/2}^{red}$ values are larger than the $\Delta E_{1/2}^{ox}$ ones as demonstrated by Gross et al.,[11] when the 2-substituents are 1,4-phenylenedinitrilo, cyano, and nitro groups. The results indicate the 2-substituent effects more strongly on the e$_g$ (LUMO) orbital than the a$_{2u}$ (HOMO) orbitals.[14] The energies of the $Q_{0,0}$ absorption and S$_1$ fluorescence peaks, ΔE_{abs} and ΔE_f respectively, are shown in Fig. 3a as a function of the difference between $E_{1/2}^{I}$ (ox) and $E_{1/2}^{I}$ (red), $\Delta E_{1/2}^{I}$ (ox−red). The different ΔE_f values are obtained for the (2-substituted porphyrinato)zincs, but the ΔE_{abs} values hardly change. Figure 3b shows the relation between $\Delta E_{1/2}^{I}$ (ox−red) and Stokes shift (=$\Delta E_{abs}-\Delta E_f$). Stokes shifts of (2-nitro-substituted porphyrinato)zincs are fairly large, and increase with the decrease in the values of $\Delta E_{1/2}^{I}$ (ox−red). On the other hand, Stokes shifts of other zinc porphyrins are very small. Such unusual fluorescence properties of (2-nitro-substituted porphyrinato)zincs are discussed later in detail.

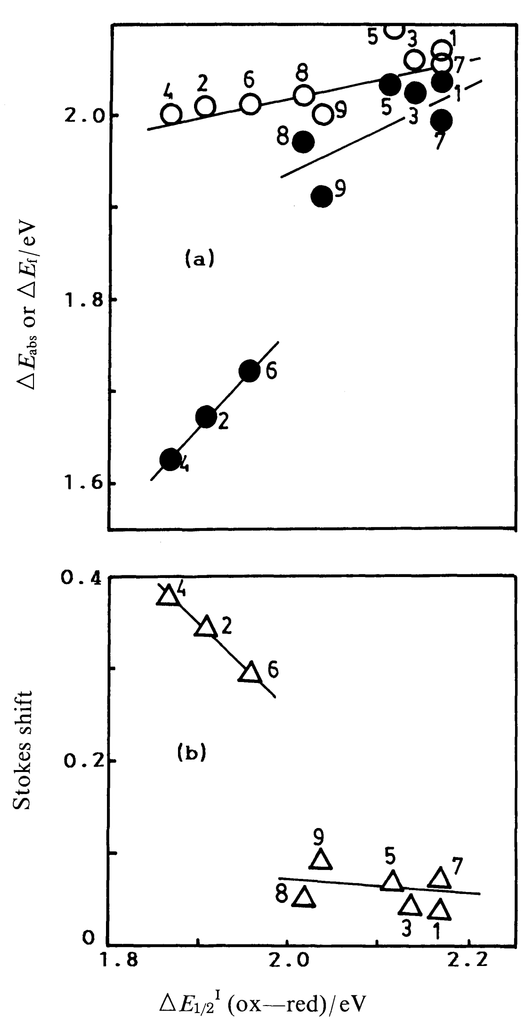


Fig. 3. The plots of ΔE_{abs} (○), ΔE_f (●), and Stokes shift (△) versus $\Delta E_{1/2}^{I}$ (ox−red) of different zinc porphyrins in DMF at room temperature. ΔE_{abs} and ΔE_f denote the energies of the $Q_{0,0}$ absorption and S$_1$ fluorescence peaks, respectively. $\Delta E_{1/2}^{I}$ (ox−red) denotes also the difference between the first oxidation and reduction potentials. 1, Zntpp(H,H); 2, Zntpp(H,NO$_2$); 3, Zntpp(Bu^t,H); 4, Zntpp(Bu^t,NO$_2$); 5, Zntpp(MeO,H); 6, Zntpp(MeO,NO$_2$); 7, Zntpp(H,Br); 8, Zntpp(H,CN); 9, Zntpp(H,C$_6$H$_4$N$_2$).

The Fluorescence Properties of Zntpp(H,NO$_2$) in Aprotic Solvents. Figure 4 shows the S$_1$ fluorescence spectra of Zntpp(H,NO$_2$) in various aprotic solvents.

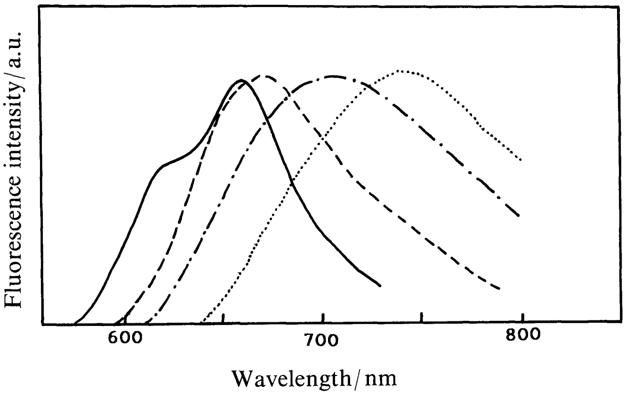


Fig. 4. The solvent effect on the S$_1$ fluorescence spectra of Zntpp(H,NO$_2$) at room temperature. —, hexane; ----, toluene; —·—, CH$_2$Cl$_2$; ·····, DMF.

Table 3. The Solvent Effect on Stokes Shift of Zntpp(H,NO_2)

Aprotic solvent	Stokes shift/eV	Alcohol	Stokes shift/eV
Toluene	0.20	1-Butanol	0.29
1,2-Dichlorobenzene	0.24	1-Propanol	0.28
Dichloromethane	0.30	Ethanol	0.27
Benzonitrile	0.32	Methanol	0.26
N,N-Dimethylformamide	0.34	Ethylene glycol	0.20
Nitromethane	0.39		
Acetonitrile	0.37		
Dimethylsulfoxide	0.37		

Table 4. The Half-Wave Potentials ($E_{1/2}$/V vs. Fc/Fc^+) of Zntpp(H,H) and Zntpp(H,NO_2) in Various Solvents Containing 0.1 M TBAP at Room Temperature

Solvent	Porphyrin	$E_{1/2}^{\mathrm{II}}$(red)	$E_{1/2}^{\mathrm{I}}$(red)	$E_{1/2}^{\mathrm{I}}$(ox)	$E_{1/2}^{\mathrm{II}}$(ox)
o-DCB	Zntpp(H,H)		−1.94	0.26	0.60
	Zntpp(H,NO_2)		−1.56	0.50	0.72
CH_2Cl_2	Zntpp(H,H)		−1.83	0.30	0.60
	Zntpp(H,NO_2)		−1.54	0.39	0.72
BN	Zntpp(H,H)		−1.81	0.34	0.68
	Zntpp(H,NO_2)		−1.46	0.45	0.78
DMF	Zntpp(H,H)	−2.18	−1.79	0.38	0.61
	Zntpp(H,NO_2)	−1.76	−1.41	0.50	
AN	Zntpp(H,H)			0.37	0.68
	Zntpp(H,NO_2)		−1.41	0.47	0.78
DMSO	Zntpp(H,H)		−1.75	0.42	
	Zntpp(H,NO_2)		−1.36	0.48	

The diffuse fluorescence band with less resolved vibrational fine structure remarkably shifts to the shorter wavelength region with the decrease in the dielectric constant of the solvent. The solvent effect on Stokes shift of Zntpp(H,NO_2) is summarized in Table 3. The Stokes shift approximately increases with the increase in the dielectric constant of the aprotic solvents. The half-wave potentials of Zntpp(H,NO_2) and Zntpp(H,H) in various solvents are summarized in Table 4. The $E_{1/2}^{\mathrm{I}}$ (red) value of Zntpp(H,NO_2) approximately increases with the increase in the dielectric constant of the aprotic solvent, that is to say, the reduced species may be stabilized by the solvation in polar solvents rather than nonpolar ones. However the $E_{1/2}^{\mathrm{I}}$ (ox) values hardly change. The values of $\Delta E_{1/2}^{1}$ (ox−red) of Zntpp(H,NO_2) consequently decrease with the increase in the dielectric constant of the solvent. The regular dependence of $\Delta E_{1/2}^{\mathrm{I}}$ (ox−red) of Zntpp (H, H) on the solvent polarity is not observed. Figure 5a shows the relation between $\Delta E_{1/2}^{\mathrm{I}}$ (ox−red) and ΔE_{abs} (or ΔE_{f}) of Zntpp(H,NO_2) and Zntpp(H,H) in various aprotic solvents. The values of ΔE_{abs} and ΔE_{f} of Zntpp(H,H) are hardly dependent on the dielectric constant of the solvent. On the other hand, those of Zntpp(H,NO_2) decrease with the increase in the dielectric constant of the solvent, and the magnitude of the decrease in ΔE_{f} is considerably larger than that in ΔE_{abs}. The Stokes shift of Zntpp(H,NO_2) consequently increases with the increase in the dielectric constant of the solvent as shown in Fig. 5b. It may be concluded from these results that the intramolecular charge transfer from the porphyrin ring to 2-nitro group takes place in the S_1 excited state of Zntpp(H,NO_2), because the 2-nitro group can conjugate with the π-electron system in porphyrin ring.[27−30] Therefore Zntpp(H,NO_2) must have larger dipole moment in the excited state than the ground state, and consequently, in the excited state, must be more stable in the polar solvents than Zntpp(H,H). Figure 6 shows the energy diagrams of Zntpp(H,H) and Zntpp(H,NO_2). A Franck-Condon S_1 excited state (S_1^{F}) is formed by the absorption of light in the visible region, and then a S_1 equilibrium state is achieved by the reorientation of solvating molecules around a porphyrin. Further the excited porphyrins inactivate to a Franck-Condon ground state (S_0^{F}) through emitting the fluorescence, and then lead to an equilibrium ground state (S_0) through the reorientation of solventing molecules around the porphyrin. The energy difference between S_1^{F} and S_1 states, ΔE ($S_1^{\mathrm{F}}-S_1$), and that between S_0^{F} and S_0, ΔE ($S_0^{\mathrm{F}}-S_0$), may almost correspond to the reorientation energies of the solvating molecules. The values of ΔE ($S_1^{\mathrm{F}}-S_1$) and ΔE ($S_0^{\mathrm{F}}-S_0$) of Zntpp(H,NO_2) may be fairly larger than those of Zntpp(H,H), and also increase with the increase in the dielectric constant of the solvent because of the large dipole moment of Zntpp(H,NO_2) in the S_1 excited state. Therefore the Stokes shift of Zntpp(H,NO_2), which is equal to the sum of ΔE ($S_1^{\mathrm{F}}-S_1$) and

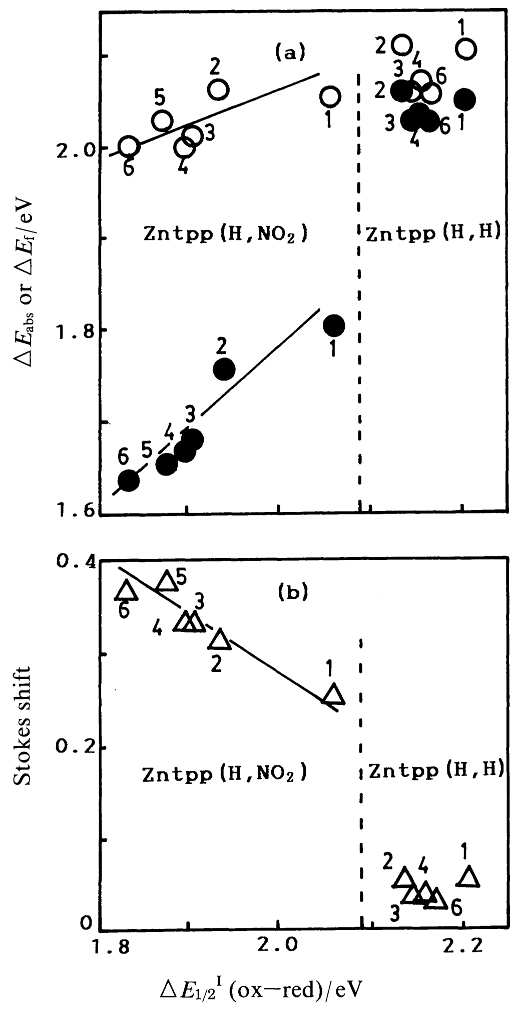


Fig. 5. The plots of ΔE_{abs} (○), ΔE_f (●) and Stokes shift (△) versus $\Delta E_{1/2}{}^{I}$ (ox−red) of Zntpp(H,H) and Zntpp(H,NO$_2$) in different solvents at room temperature. 1, *o*-DCB; 2, CH$_2$Cl$_2$ 3, BN; 4, DMF; 5, AN; 6, DMSO.

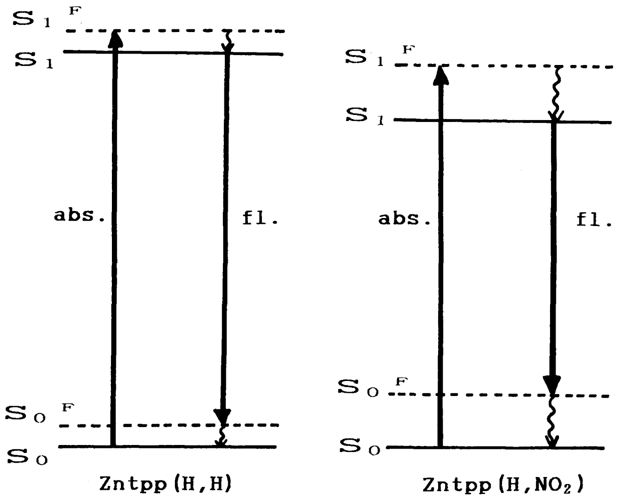


Fig. 6. Schematic energy level diagrams of Zntpp(H,H) and Zntpp(H,NO$_2$). $S_1{}^F$ and $S_0{}^F$ denote a Franck-Condon S_1 excited state and a Franck-Condon ground state respectively.

ΔE ($S_0{}^F$−S_0), becomes very large in the polar solvent.

The Fluorescence Properties of Zntpp(H,NO$_2$) in Alcohols. Figure 7 shows the S_1 fluorescence and excitation spectra of Zntpp(H,NO$_2$) in ethanol and toluene at room temperature, 203 K (Dry Ice-methanol temperature) and 77 K (liquid nitrogen temperature). Zntpp(H,H) in various solvents shows the same emission and excitation profiles at different temperatures, while the profiles of Zntpp(H,NO$_2$) are dependent on the temperature. The emission in rigid media such as ethanol, toluene, CH$_2$Cl$_2$ and DMF at 77 K exhibits well-resolved vibronic bands, and the Stokes shift is remarkably small, compared with at higher temperatures. This result indicates that the reorientation of solvating molecules is limited in the rigid media. On the other hand, a diffuse emission is observed in fluid solution even at low temperature (203 K). The Stokes shift at 203 K is large in aprotic solvents but small in alcohols, compared with those at room temperature respectively. Although the reason for the increased Stokes shift in aprotic solvents is not clear, the increase in the dielectric constant at low temperature may be a candidate. However, it is impossible to interpret the Stokes shift in protic solvents in a simple way based on the polarity of solvent. As shown in Table 3, the Stokes shifts of Zntpp(H,NO$_2$) in alcohols decrease with the increase in the dielectric constant in contrast to those in aprotic solvents. It is also noted that the Stokes shift is prominently small in viscous ethylene glycol. In protic solvents, the reorientational motion seems to be restricted by hydrogen bonding of solvent molecules onto the nitro group. High viscosity and/or effective hydrogen bonding interaction at low temperature inhibit the solvent relaxation in the excited state and result in small Stokes shifts.

The reorientation of solvating molecules in the excited state may be accompanied with the conformational change including the rotation of the nitro group with respect to the porphyrin plane. The conjugation between nitro group and porphyrin ring materializes in a coplaner conformation.

The *Q* band absorption of Zntpp(H,NO$_2$) in ethanol at room temperature exhibits resolved vibronic structure, but has a long tail to lower energy region. This red-shifted and diffuse absorption should be attributed to some minor conformers of coplaner structure in the ground state. The diffuse absorption, however, disappears in the excitation spectrum observed in ethanol at 77 K. Preliminary measurements of resonance Raman spectra show that Zntpp(H,NO$_2$) in ethanol at room temperature exhibits a diffuse and intense vibrational band at 1350 cm^{-1} which could be assigned to an internal stretching mode in the NO$_2$ group, whereas only a sharp but rather weak band is observed at 77 K around this wavenumber region. This result substantiates that the coplaner conformer hardly exists at 77 K. From these observations, it is expected that coplaner conformation is unstable in the ground state, but conforma-

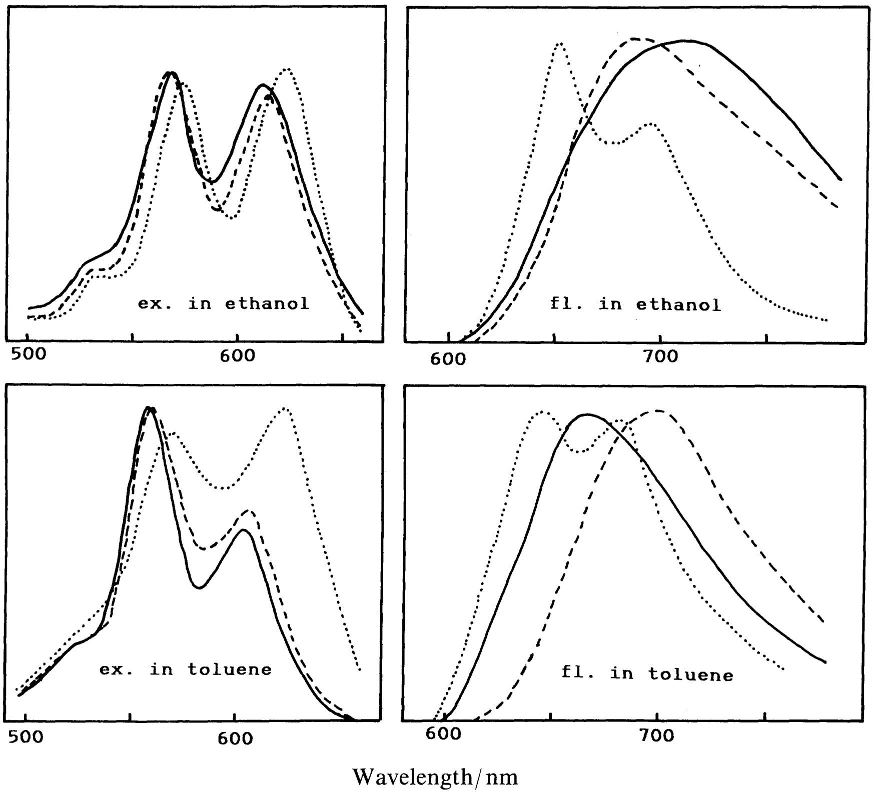


Fig. 7. The S_1 fluorescence (fl.) and excitation spectra (ex.) of Zntpp(H, NO_2) in ethanol and toluene at 293 K (—), 203 K (----) and 77 K (.....).

tional change is likely to occur in fluid media. In this case, the diffuse and red-shifted emission observed in fluid media could be attributed to the fluorescence from a planer conformer, and the conformation must be changed within the excited state lifetime. The conformational change amplifies the charge transfer character of the lowest singlet states, and the large dipole moment thus induced must stabilize the excited state significantly in polar solvents.

In conclusion, the charge transfer into the nitro group accompanying a conformational change takes place in the lowest singlet excited state of Zntpp(H,NO_2), although it is not so much clear whether the coplaner conformation is inherently prefered in the excited state or only with the aid of solvation. The correlation between the Stokes shift and reduction potentials in aprotic solvents suggests that such a conformational change may occur in the one-electron reduction of Zntpp(H,NO_2).

The authors are deeply indebted to Professor N. Takeuchi, Mr. S. Taniguchi, and Mr. S. Nakamura for the fluorescence lifetime measurements.

References

1) K. Takahashi, T. Komura, and H. Imanaga, *Bull. Chem. Soc. Jpn.*, **56**, 3203 (1983).

2) K. Takahashi, Y. Kamatsuchi, T. Komura, and H. Imanaga, *Nippon Kagaku Kaishi*, **1988**, 1756.

3) K. Takahashi, T. Komura, and H. Imanaga, *Bull. Chem. Soc. Jpn.*, **62**, 386 (1989).

4) K. Takahashi, T. Terashima, T. Komura, and H. Imanaga, *Bull. Chem. Soc. Jpn.*, **62**, 3069 (1989).

5) K. Takahashi, H. Katsurada, T. Komura, and H. Imanaga, *Bull. Chem. Soc. Jpn.*, **63**, 3315 (1990).

6) K. Yamashita, Y. Harima, and T. Matsubayashi, *J. Phys. Chem.*, **93**, 5311 (1989).

7) K. Kalyanasundaram and M. Grätzel, *Helv. Chem. Acta*, **63**, 478 (1980).

8) R. H. Schmehl and D. G. Whitten, *J. Phys. Chem.*, **85**, 3473 (1981).

9) G. S. Nahor, J. Rabani, and F. Grieser, *J. Phys. Chem.*, **85**, 697 (1981).

10) A. Harriman, G. Porter, and M. C. Richoux, *J. Chem. Soc., Faraday Trans. 1*, **77**, 833 (1981).

11) A. Giraudeau, H. J. Callot, and M. Gross, *Inorg. Chem.*, **18**, 201 (1979).

12) A. Giraudeau, H. J. Callot, J. Jordan, I. Ezhar, and M. Gross, *J. Am. Chem. Soc.*, **79**, 3857 (1979).

13) H. J. Callot, A. Giraudeau, and M. Gross, *J. Chem. Soc., Perkin Trans. 2*, **1975**, 1321.

14) R. A. Binstead, M. J. Crossley, and N. S. Hush, *Inorg. Chem.*, **30**, 1259 (1991).

15) R. G. Little, J. A. Anton, P. A. Loach, and J. A. Ibers, *J. Heterocycl. Chem.*, **12**, 343 (1975).

16) A. D. Adler, F. R. Longo, F. Kampas, and J. Kim, *J. Inorg. Nucl. Chem.*, **32**, 2443 (1970).

17) J. E. Baldwin, M. J. Crossley, and J. F. DeBernardis, *Tetrahedron*, **38**, 685 (1982).

18) E. Samuels, R. Shutleworth, and T. S. Stevens, *J. Chem. Soc. C,* **1968**, 145.

19) M. J. Crossley and L. G. King, *J. Chem. Soc., Chem. Commun.,* **1984**, 920.

20) M. J. Crossley and P. L. Burn, *J. Chem. Soc., Chem. Commun.,* **1987**, 39.

21) E. Lippert, W. Nagele, I. Seibold-Blankenstein, V. Staiger, and W. Voss, *Z. Anal. Chem.,* **170**, 1 (1959).

22) W. H. Melhuish, *J. Res. Natl. Bur. Stand., Sect. A,* **76**, 547 (1972).

23) P. G. Seybold and M. Gouterman, *J. Mol. Spectrosc.,* **31**, 1 (1969).

24) J. N. Demas and G. A. Crosby, *J. Phys. Chem.,* **75**, 991 (1971).

25) K. Takahashi, O. Ohno, Y. Kaizu, and H. Kobayashi, unpublished results.

26) D. J. Quimby and F. R. Longo, *J. Am. Chem. Soc.,* **97**, 5111 (1975).

27) W. H. Fuchsman, Q. R. Smith, and H. M. Stein, *J. Am. Chem. Soc.,* **99**, 4190 (1977).

28) E. W. Baker, C. B. Storm, G. McGrew, and A. H. Corwin, *Bioinorg. Chem.,* **3**, 49 (1973).

29) N. H. Inhoffen and P. Jäger, *Tetrahedron Lett.,* **1964**, 1317.

30) M. Zerner and M. Gouterman, *Theor. Chim. Acta,* **4**, 44 (1966).