

Effects of hydrogen bonding interaction and solvent polarity on the competition between excitation energy and photo-induced electron transfer processes in hydroxy(1-pyrenebutoxy)phosphorus(V)porphyrin

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ABSTRACT

The solvent effects on an excitation energy transfer and a photo-induced electron transfer processes were examined using synthesized hydroxy(1-pyrenebutoxy)phosphorus(V)porphyrin. In the photoexcited state of the pyrene moiety, the intramolecular energy transfer to the porphyrin competed with the electron transfer from the pyrene to the porphyrin. The quantum yield of energy transfer in non-alcoholic solvents decreased with an increase of the solvent polarity due to the enhancement of electron transfer. However, the energy transfer was predominant process in alcoholic solvents with high polarity. The energy transfer yield increased with an increase in the ratio of methanol in the mixture of acetonitrile and methanol, of which solvent polarity is almost the same as that of acetonitrile. The redox potential measurements and *ab initio* molecular orbital calculation at Hartree-Fock 6-31G* level have shown that the electron affinity of the porphyrin moiety decreased through the hydrogen bonding with alcoholic solvents, resulting in that the electron transfer is suppressed and the excitation energy transfer becomes the predominant process. In conclusion, the hydrogen bonding interaction with alcoholic solvent contributes to the competition between energy and electron transfer by the changing of the energy level of charge transfer state rather than the effect of solvent polarity.

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1. Introduction

Excitation energy transfer (ENT) and photo-induced electron transfer (ELT) are essential processes for photochemical processes [1–3], photo-information operations [4–7], biological system [8–10], and medicinal application such as photodynamic therapy [11,12]. Intramolecular ENT and ELT systems between two chromophores involving the porphyrin chromophore have received much attention in elucidation of the natural photosynthetic system [13–18]. The effects of the surroundings of chromophores play an important role in ENT and ELT processes. Solvent properties such as polarity [19,20], hydrogen bonding [21], pH [4–7,22,23], and ion strength [4–7,22] are closely correlated with the governing factor of ENT and ELT rates. The competition between ENT and ELT in the photoexcited pyrene to the P(V)porphyrin in bispyrenylP(V)porphyrins was previously reported [19]. These

electronic transition processes are selected by the control of the ELT rate depending on the charge transfer (CT) state energy level due to solvent polarity. In general, alcohols are high polar solvents, and exhibit a hydrogen bonding interaction with the donor and/or the acceptor molecules. It has been reported that hydrogen bonding interaction significantly affects the electronic state of porphyrin derivatives [21]. Therefore, evaluation of contributions of solvent polarity and hydrogen bonding interaction to the governing factor of ENT and ELT would provide us the significance of an effect of surroundings on the electronic transition processes.

In this study, hydroxy(1-pyrenebutoxy)P(V)porphyrin (Py-POH, Fig. 1) was synthesized to investigate the solvent effects on the selectivity of ENT and ELT from the pyrene to the porphyrin. The main reasons for using pyrene and hydroxyP(V)porphyrin are that both ENT and ELT from the pyrene to the porphyrin are energetically possible in the photoexcited state of the pyrene [19], and the axial hydroxyl group can act as hydrogen bonding site with solvent molecules. Solvent effects on the photochemical and electrochemical properties of Py-POH were examined by spectroscopic methods and redox potential measurement. The interaction between Py-POH and alcohol molecule was investigated using *ab initio* molecular orbital (MO) calculation.

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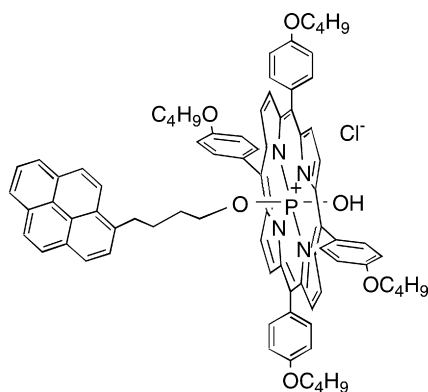


Fig. 1. Structure of Py-POH.

2. Experimental details

2.1. Measurements

^1H NMR spectra were taken on a JNM-A 500 (500 MHz) FT-NMR spectrometer (JEOL, Tokyo, Japan). Chemical shifts of ^1H were measured in δ (ppm) units relative to the tetramethylsilane internal standard. Absorption and fluorescence spectra were taken on a V-570 UV/VIS/NIR spectrophotometer (JASCO, Tokyo, Japan) and a FP-777 spectrophotometer (JASCO), respectively. The fluorescence quantum yields (Φ) of the pyrene and porphyrin moieties were determined relative to pyrene ($\Phi=0.65$ in acetonitrile) [24] and diphenoxyporphyrin ($\Phi=0.037$ in acetonitrile) [25–27]. These values were corrected by refractive index of solvents [28]. The fluorescence lifetime (τ_f) was measured by the previously reported method [25–27]. All the samples for the emission measurement were purged with nitrogen. Cyclic voltammograms were measured with a three-electrode system using a platinum working, a platinum counter, and a saturated calomel reference electrode (SCE), which were assembled with a HABF501 potentiogalvanostat (Hokuto Denko, Tokyo, Japan). All the electrolysis solutions were purged with nitrogen. To compare the redox potentials in different solvents, these values were corrected by the redox potential of one-electron oxidation of ferrocene (Fc/Fc^+ vs. SCE: 0.43 V in acetonitrile and 0.46 V in methanol).

2.2. Materials

The spectroscopic grade solvents of acetonitrile, dichloromethane, tetrahydrofuran, toluene, methanol, *iso*-butylalcohol (Dojin Chem. Ind., Kumamoto, Japan), ethanol, 2-propanol, and pyridine (Kanto Chem. Com. Inc., Tokyo, Japan) were used for the measurement as received. 1-Pyrenebutanol was from Aldrich Chemical Co. (Milwaukee, WI, USA). Silver nitrate was from Wako Pure Chemical Ind. (Tokyo, Japan).

Py-POH was synthesized by the following procedure according to the previously reported [29]. DichloroP(V)tetrakis(*n*-*p*-butoxyphenyl)porphyrin chloride [30] (0.100 g), 1-pyrenebutanol (0.200 g), and silver nitrate (0.500 g) were dissolved in 11 mL of acetonitrile and stirred at room temperature for 3 h. The reaction was supervised by absorption spectra and thin-layer chromatograph. At the end of the reaction, the solvent was removed by vacuum evaporation. The product was purified by column chromatography on silica gel with a chloroform-methanol (10/1, v/v) as an eluent, the result being a pure product in an 11% (0.013 g) yield. ^1H NMR (CDCl_3 , TMS): δ -2.41 (dt, 2H, $J_{\text{P-H}}=12$ Hz, $J_{\text{H-H}}=6.0$ Hz, P-OCH₂CCC-pyrenyl), -1.96 (d, 1H, $J_{\text{P-H}}=26$ Hz, P-OH), -1.29 (tt, 2H, P-OCCH₂CC-pyrenyl), -0.39 (tt, 2H, P-OCCCH₂C-pyrenyl), 1.05 (t, 12H, $J_{\text{H-H}}=7.2$ Hz, *meso*-phenyl-OCCCH₃), 1.59 (m, 8H, *meso*-

Table 1

Absorption properties of Py-POH in various solvents.

Solvent	Absorption ($\lambda_{\text{max}}/\text{nm}$)		
	Pyrene moiety	Soret band	Q band
AN	312, 327, 343	441	556, 612
Pyr	317, 330, 347	448	568, 645
DCM	314, 328, 345	444	567, 614
THF	314, 328, 344	442	566, 612
TOL	316, 330, 346	443	566, 612
MT	312, 326, 342	436	561, 605
ET	313, 326, 343	435	559, 605
PR	312, 326, 343	434	558, 600
BT	314, 327, 344	438	562, 608

AN: acetonitrile, Pyr: pyridine, DCM: dichloromethane, THF: tetrahydrofuran, TOL: toluene, MT: methanol, ET: ethanol, PR: 2-propanol, and BT: *iso*-butylalcohol.

phenyl-OCCCH₂C), 1.85–1.95 (m, 10H, *meso*-phenyl-OCCCH₂CC (8H) and P-OCCCH₂-pyrenyl (2H)), 4.16 (t, 8H, $J_{\text{H-H}}=6.2$ Hz *meso*-phenyl-OCH₂CCC), 6.91 (d, 1H, $J_{\text{H-H}}=7.5$ Hz, 2'-pyrenyl-H), 7.16 (d, 1H, $J_{\text{H-H}}=9.5$ Hz, 10'-pyrenyl-H), 7.18 (d, 8H, $J_{\text{H-H}}=8.5$ Hz, *meso*-*m*-phenyl-H), 7.74 (d, 1H, $J_{\text{H-H}}=7.5$ Hz, 3'-pyrenyl-H), 7.78 (d, 1H, $J_{\text{H-H}}=9.5$ Hz, 9'-pyrenyl-H), 7.89 (d, 9H, $J_{\text{H-H}}=8.5$ Hz, 4'-pyrenyl-H (1H) and *meso*-*o*-phenyl-H (8H)), 7.96 (d, 1H, $J_{\text{H-H}}=8.5$ Hz, 5'-pyrenyl-H), 7.98 (t, 1H, $J_{\text{H-H}}=7.8$ Hz, 7'-pyrenyl-H), 8.10–8.14 (m, 2H, 6',8'-pyrenyl-H), 8.85 (br. s, 8H, β H). FAB-MS: m/z 1221.4 (M^+). UV-vis absorption spectrum in dichloromethane: $\lambda_{\text{max}}/\text{nm}$ 314, 328, 345, 444, 567, 614.

2.3. *Ab initio* MO calculation of Py-POH

The equilibrium geometry of intermolecular complex of Py-POH with alcoholic molecules and the energy of the lowest unoccupied MO (LUMO) were estimated from *ab initio* MO calculation at Hartree-Fock 6-31G* level. The calculations were performed on a Spartan 08[®] Windows (Wavefunction Inc, CA, USA).

3. Results

3.1. Absorption property of Py-POH in various solvents

The absorption spectrum of Py-POH is almost a superposition of the pyrene moiety and Soret and Q bands of the P(V)porphyrin moiety. The absorption peaks of the Soret and the Q bands in alcoholic solvents were blue-shifted compared to those in non-alcoholic solvents (Table 1).

3.2. Fluorescence property of Py-POH in various solvents

The fluorescence spectrum of Py-POH was shown in Fig. 2 (A). The shapes of fluorescence spectra of the pyrene and the porphyrin moieties were quite similar to those of 1-pyrenebutanol and alkoxyP(V)porphyrin derivatives. Fluorescence from the pyrene moiety (quantum yield in dichloromethane: $\Phi_{\text{py} \rightarrow \text{py}}=0.0099$) was remarkably decreased compared to the 1-pyrenebutanol ($\Phi_{\text{pyO}}=0.50$) by the ENT and the ELT (described later). The fluorescence lifetime of the pyrene moiety was also decreased compared to the reference pyrene (e.g. 60.6 ns in acetonitrile) (Table 2). The fluorescence from the porphyrin moiety was observed clearly in the wavelength region of 570–750 nm by excitation of the pyrene moiety. The absorption feature of the pyrene moiety was observed in the fluorescence excitation spectrum by monitoring this porphyrin fluorescence, indicating the ENT from the pyrene to the porphyrin (Fig. 2(B)).

Fluorescence peak of the pyrene was not significantly affected by the kinds of solvents, whereas those of the porphyrin was blue-shifted in alcoholic solvents compared to those in non-alcoholic

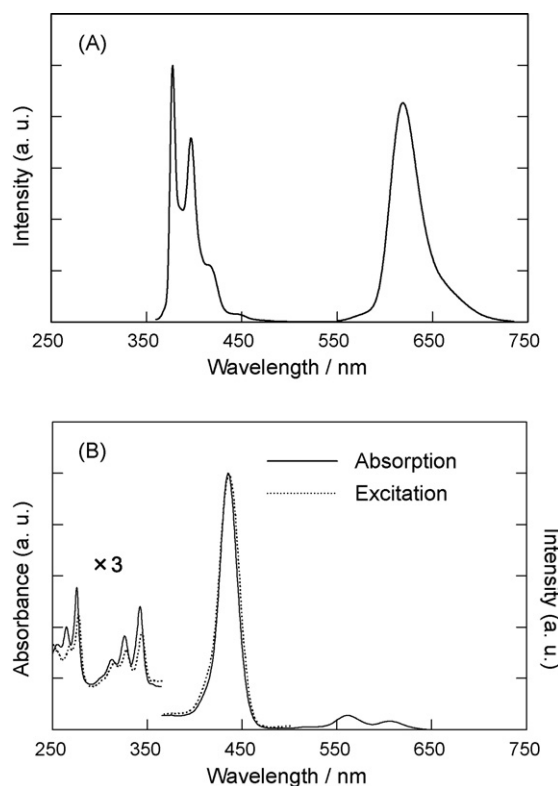


Fig. 2. Fluorescence and fluorescence excitation spectra of Py-POH in methanol. The fluorescence spectrum was measured by pyrene excitation (Ex = 337 nm) (A). The fluorescence excitation spectrum was measured by monitoring of the porphyrin fluorescence (Em = 630 nm) (B).

solvents, similar to the absorption spectra (Table 2). Fluorescence quantum yields of the porphyrin moiety in alcoholic solvents also become larger than those in non-alcoholic solvents. The fluorescence lifetime of the porphyrin moiety in non-alcoholic solvents was slightly shorter than those in alcoholic solvents. These results have shown that an interaction with alcoholic solvent molecules affects the electronic states of the porphyrin moiety of Py-POH.

3.3. Solvent effect on the competition between ENT and ELT from the photoexcited pyrene moiety to the porphyrin moiety

In the photoexcited pyrene, both the ENT and the ELT are energetically possible. The ENT was demonstrated as described in the above section. Previous study using transient absorption spectrum measurement has shown the formation of the pyrene cation radical

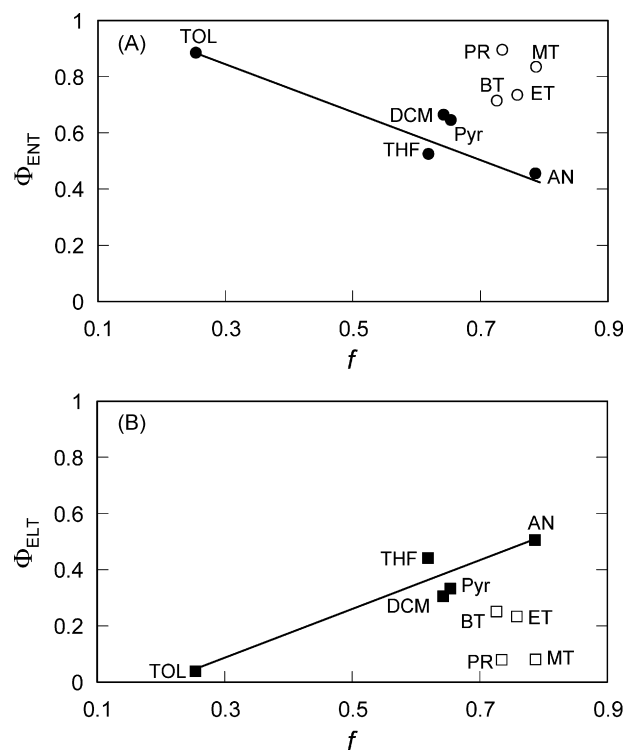


Fig. 3. Dependence of Φ_{ENT} and Φ_{ELT} on solvent polarity parameter (f).

and the P(V)porphyrin radical through ELT by photo-excitation of pyrenebutoxyP(V)porphyrin [19]. Thus, the quantum yield of the ENT (Φ_{ENT}) can be calculated by following equation:

$$\Phi_{ENT} = \frac{\Phi_{py \rightarrow por}}{\Phi_{por \rightarrow por}} \quad (1)$$

where $\Phi_{py \rightarrow por}$ and $\Phi_{por \rightarrow por}$ are fluorescence quantum yields from the porphyrin by photo-excitation of the pyrene (Ex = 337 nm) and the porphyrin (Ex = 560 nm), respectively. Since the fluorescence quenching is caused by both of the ENT and the ELT, the quantum yields of the ELT (Φ_{ELT}) can be calculated by following equation assuming that the radiative and nonradiative rates of the pyrene moiety in Py-POH are not affected by the presence of the porphyrin moiety:

$$\Phi_{ELT} = 1 - \frac{\Phi_{py \rightarrow py}}{\Phi_{py0}} - \Phi_{ENT} \quad (2)$$

The calculated values of Φ_{ENT} decreased with the solvent polarity parameter (f) [31], and Φ_{ELT} increased with f in non-alcoholic

Table 2
Fluorescence properties of Py-POH in various solvents.

Solvent	Pyrene moiety			Porphyrin moiety			
	λ_{max}/nm	$\Phi_{py \rightarrow py}^a$	τ_f/ns	λ_{max}/nm	$\Phi_{por \rightarrow por}^b$	$\Phi_{py \rightarrow por}^c$	τ_f/ns
AN	378, 397	0.020	1.4	630	0.014	0.0065	0.8
Pyr	378, 398	0.0067	1.0	630	0.016	0.0095	0.9
DCM	378, 398	0.0099	0.9	632	0.018	0.012	1.0
THF	378, 397	0.012	1.4	628	0.018	0.0095	1.0
TOL	378, 398	0.033	3.1	627	0.028	0.025	1.6
MT	378, 396	0.037	1.6	619	0.037	0.031	2.1
ET	377, 396	0.011	1.2	617	0.039	0.029	2.2
PR	377, 396	0.0075	1.1	614	0.031	0.028	1.7
BT	377, 396	0.012	1.2	618	0.036	0.026	2.0

Abbreviations of solvents are the same as Table 1.

^a Fluorescence quantum yield of the pyrene by the pyrene excitation.

^b Fluorescence quantum yield of the porphyrin by the porphyrin excitation.

^c Fluorescence quantum yield of the porphyrin by the pyrene excitation.

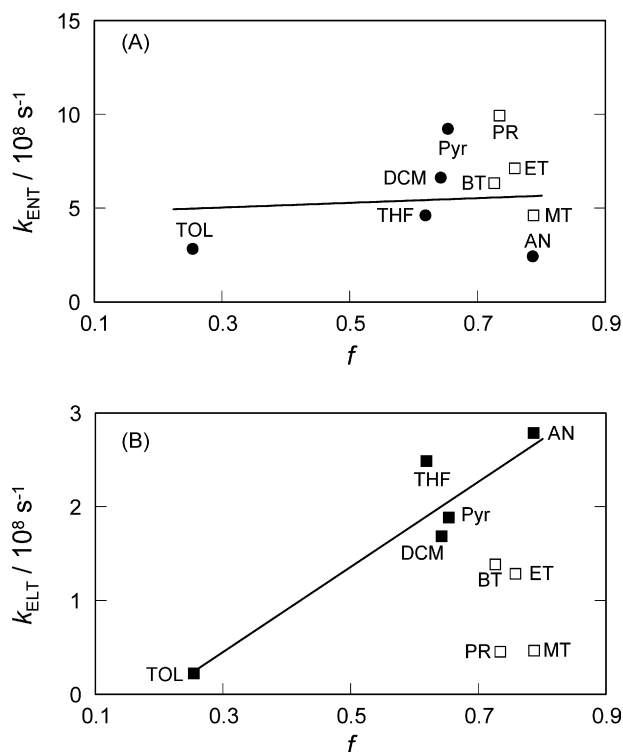


Fig. 4. Dependence of k_{ENT} and k_{ELT} on solvent polarity parameter (f).

solvents (Fig. 3). This solvent effect can be reasonably explained by that ELT is favorable in high polar solvent due to lowering of CT state energy. The values of Φ_{ENT} and Φ_{ELT} in alcoholic solvents deviated from the relation between those in non-alcoholic solvents and f , showing that ENT preferentially occurs in alcoholic solvent compared to non-alcoholic solvent.

The rate constants of ENT (k_{ENT}) and ELT (k_{ELT}) were estimated using the following equations:

$$k_{\text{ENT}} = \frac{\Phi_{\text{ENT}}}{\tau_f} \quad (3)$$

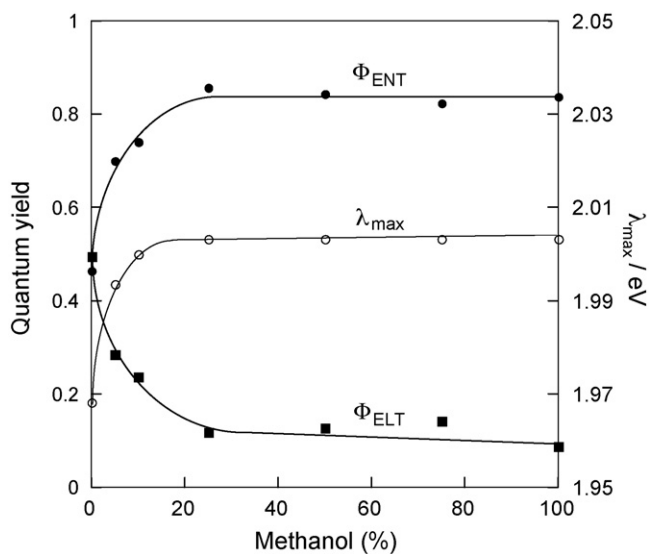
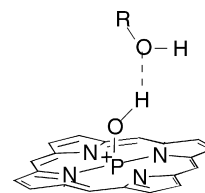


Fig. 5. Dependence of fluorescence peaks, Φ_{ENT} , and Φ_{ELT} on the ratio of methanol in the acetonitrile/methanol solvent. The fluorescence peaks are represented as the photon energy.



Scheme 1.

and

$$k_{\text{ELT}} = \frac{\Phi_{\text{ELT}}}{\tau_f}, \quad (4)$$

respectively. The estimated values of k_{ELT} increased with f in non-alcoholic solvents, similarly to those of Φ_{ELT} (Fig. 4). On the other hand, clear relationship between the k_{ENT} and f was not observed.

3.4. Effect of methanol on the photophysical property of Py-POH in acetonitrile/methanol

The absorption and the fluorescence spectra were measured in the mixture of acetonitrile and methanol. Since the solvent polarity of acetonitrile is almost the same as that of methanol, the polarity of this mixture does not significantly depend on the ratio of these solvents. The absorption and fluorescence peaks shifted to a shorter wavelength region as the ratio of methanol was increased. At the same time, the fluorescence quantum yields were also increasing. The ENT quantum yields estimated from Eq. (1) increased depending on the ratio of methanol as the same tendency of the fluorescence peaks changing (Fig. 5). On the other hand, the ELT yields decreased with an increase of the ratio of methanol. These findings have shown that the ELT is inhibited and the ENT becomes favorable in methanol.

3.5. Redox potential of Py-POH in acetonitrile and methanol

Redox potentials of Py-POH were measured by the cyclic voltammogram in acetonitrile or methanol. Reduction potentials of the porphyrin moiety were -1.00 V (in acetonitrile) and -1.17 V (in methanol) vs. fc/fc^+ . Oxidation potentials of the pyrene moiety were 0.82 V (in acetonitrile), 0.85 (in methanol) vs. fc/fc^+ . The energy levels of the CT states (E^{CT}) of Py-POH in the solvents were estimated from the difference in the reduction potential of porphyrin and the oxidation potential of pyrene with ion-pair formation free enthalpy [32,33]. The value of E^{CT} in acetonitrile was calculated to be 1.82 eV and slightly lower than that in methanol (2.02 eV), suggesting that ELT is favorable in acetonitrile rather than in methanol.

3.6. Calculation study of effect of hydrogen bonding between the axial hydroxyl group of Py-POH and alcoholic solvent molecule

The interaction between Py-POH and alcoholic solvent molecule was examined by *ab initio* MO calculation at Hartree-Fock 6-31G*

Table 3

Center-to-center distances between the oxygen and the hydrogen atoms of axial hydroxyl group of Py-POH (d_{OH}) and LUMO energy estimated from *ab initio* MO calculation.

Solvent	d_{OH} (Å)	LUMO (eV)	ΔE (eV)
No Solvent	0.965	-2.75	
MT	0.989	-2.53	+0.22
ET	0.991	-2.56	+0.19
PR	0.991	-2.58	+0.17
BT	0.993	-2.56	+0.19

Abbreviations of solvents are the same as Table 1. ΔE : Energy gap between LUMO of Py-POH with alcohol molecule and that without solvent molecule.

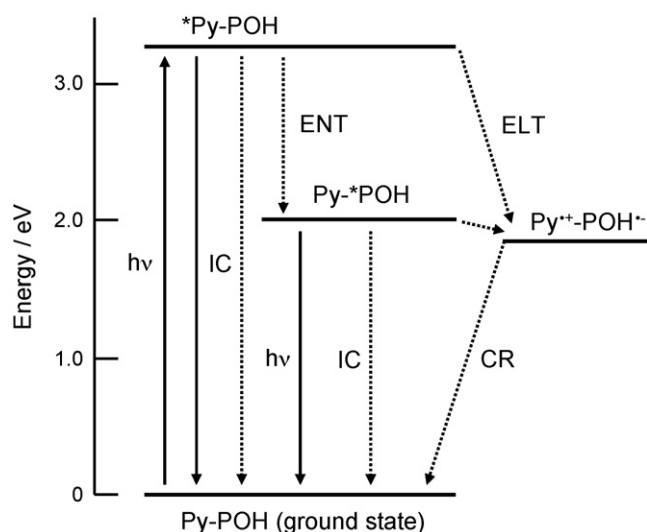


Fig. 6. Schematic diagram of deactivation processes of the photoexcited pyrene moiety of Py-POH. IC and CR indicate the internal conversion and the charge recombination, respectively.

level. The calculation of the equilibrium geometry of intermolecular complex of Py-POH with alcoholic solvent has shown that hydrogen bonding interaction between Py-POH and solvent molecule (Scheme 1). The bond length between H and O atoms of the hydroxyl group of Py-POH becomes larger by the interaction with alcoholic solvent molecule (Table 3). The energy of LUMO of Py-POH increases through the interaction with alcoholic solvent (Table 3). These results suggest that the axial hydroxyl group of Py-POH acts as proton donor, resulting in an increase of reduction potential.

4. Discussion

In the photoexcited state of the pyrene of Py-POH, ENT to the porphyrin competes with ELT to the porphyrin as shown in Fig. 6. The Φ_{ELT} increased with an increase in the solvent polarity in non-alcoholic solvents due to the lowering of CT state energy. ENT preferentially occurs in alcoholic solvents independent of solvent polarity. The calculated critical distance of ENT from the photoexcited pyrene moiety to the P(V) porphyrin through dipole-dipole interaction (Förster mechanism) is 42 Å [34,35]. Because the center-to-center distance between the pyrene moiety and the porphyrin ring, which was estimated from the *ab initio* MO calculation, is 8.5 Å, the high yield of ENT reasonably occurs in this molecular system in the absent of ELT process. The Φ_{ENT} increased with an increase of the ratio of methanol in the mixture of acetonitrile/methanol. The absorption and fluorescence peaks of the porphyrin ring in alcoholic solvents were blue-shifted compared to those in non-alcoholic solvents, suggesting that the electronic state of the porphyrin moiety is affected by the interaction with alcoholic solvents. *Ab initio* MO calculation has shown that the electron affinity of the por-

Table 4
Parameters for ENT and ELT from the photoexcited pyrene moiety to the porphyrin ring.

Solvent	J (10^{-11} cm ⁶ mol ⁻¹)	$-\Delta G$ (eV)	λ (eV)
AN	5.89	1.51	0.952
Pyr	5.69	1.47	0.644
DCM	5.73	1.45	0.695
THF	5.94	1.43	0.674
TOL	5.53	1.21	0.047
MT	5.86	1.31	0.963
ET	5.52	1.29	0.897
PR	5.84	1.28	0.849
BT	5.43	1.28	0.825

Abbreviations of solvents are the same as Table 1.

phyrin moiety of Py-POH decreases due to the hydrogen bonding interaction with alcoholic solvent molecule. Indeed, the reduction potential of the porphyrin moiety increases in methanol than that in acetonitrile, indicating that the electron affinity of the porphyrin decreases in methanol than that in acetonitrile. These results can be reasonably explained by that the axial hydroxyl group of Py-POH acts as proton donor and the positive charge of the P(V)porphyrin is partially transferred to alcoholic molecule, resulting in an increase of reduction potential as shown in Fig. 7. This is supported by that negative charge of the axial ligand of P(V)porphyrin causes blue-shift of the absorption spectrum [36].

According to the Förster mechanism [34], the ENT rate constant depends on the spectral overlap (J) between the fluorescence of donor and the absorption of the acceptor as follows:

$$J = \int F(\nu)\epsilon(\nu)\nu^{-4}d\nu. \quad (5)$$

Although the absorption spectra of the porphyrin moiety were slightly blue-shifted through the interaction with alcoholic solvents, the calculated values of J were almost the same in the all solvents used in this study (Table 4). Therefore, the switching of ENT and ELT should be due to the change of ELT rate constant rather than the increase of ENT rate constant. The interaction between the porphyrin and alcoholic solvent decreases the ELT rate, resulting in an enhancement of the ENT. Indeed, the ENT rate constants were rarely affected by the kind of solvents. The ELT rate constants in non-alcoholic solvents became larger than those in alcoholic solvents. The P(V)porphyrin is a strong electron acceptor by the central cationic phosphorus atom [37–40]. The strength as an electron acceptor depends on the electron affinity of an axial ligand connected at the central phosphorus atom. The CT state energies of Py-POH in various solvents calculated from the experimental value in acetonitrile using the dielectric continuum theory [32,41] decreases with dielectric constant of solvents (Fig. 8). The CT state energies in alcoholic solvents estimated from the experimental value in methanol by the above method are clearly higher than those in non-alcoholic solvents and comparable with that in toluene, least polar solvent used in this study. These findings suggest that the hydrogen bonding interaction affects the increase of

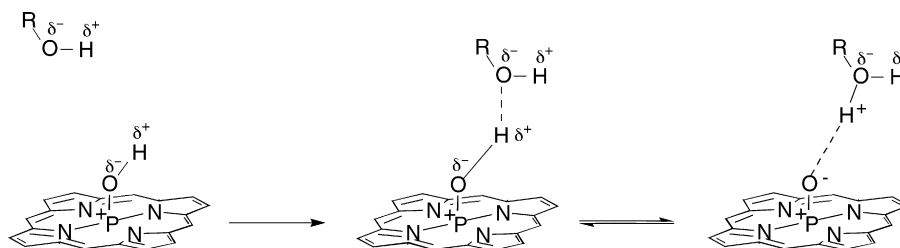


Fig. 7. Proposed scheme of the hydrogen bonding interaction between the axial hydroxyl group of Py-POH and alcoholic solvent molecule.

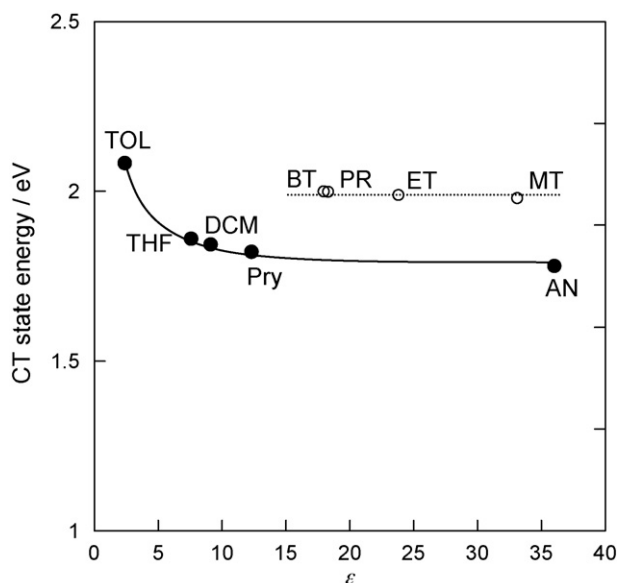


Fig. 8. Dependence of the calculated CT state energy on dielectric constant of solvent.

CT energy level rather than the effect of solvent polarity. The driving force of the ELT ($-\Delta G$) was calculated from the excitation energy of the pyrene moiety, which was estimated from the fluorescence peak, and the CT energy of Py-POH (Table 4). These obtained values were larger than the reorganization energy (λ) of the Marcus theory (Table 4) [42,43], suggesting that the ELT of this system is in the inverted region. However, the ELT of this system was enhanced depending on the $-\Delta G$. The flexibility of the bridge butoxy chain between the pyrene and porphyrin might change the λ , resulting in the enhancement of ELT depending on the $-\Delta G$.

In summary, this study has shown that hydrogen bonding between the axial hydroxyl group of Py-POH and surroundings can control the competition process between the intramolecular ENT and ELT. Hydrogen bonding interaction showed larger contribution to the selection of these processes rather than solvent polarity.

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