Anomalously Selective Quenching of S_2 Fluorescence from Upper Excited State of Zinc 5-(1′-Pyrenyl)-10,15,20-triphenylporphyrin Derivatives through Intramolecular Charge Transfer State

Kazutaka Hirakawa,*,† Keiko Saito,‡ and Hiroshi Segawa*,§

Department of Basic Engineering (Chemistry), Faculty of Engineering, Shizuoka University, Johoku 3-5-1, Naka-ku, Hamamatsu, Shizuoka 432-8561, Japan, Department of Chemistry, Faculty of Science, Kitasato University, Kitasato 1-15-1, Sagamihara, Kanagawa 228-8555, Japan, and Research Center for Advanced Science and Technology, The University of Tokyo, Komaba 4-6-1, Meguro-ku, Tokyo 153-8904, Japan

Received: April 22, 2009; Revised Manuscript Received: June 17, 2009

Zinc 5-(1′-pyrenyl)-10,15,20-tris(*p*-methoxyphenyl)porphyrin (ZnP−Py) and zinc 5-(1′-pyrenyl)-10,15,20-tris(pentafluorophenyl)porphyrin (ZnFP−Py), in which a pyrenyl group is directly connected at the *meso*-positions of their corresponding porphyrins, were synthesized and investigated on the photophysical properties. While the S_1 fluorescence of the porphyrin moieties was not quenched by the pyrenyl group at all, the S_2 fluorescence was remarkably quenched. The anomalously selective quenching of the S_2 fluorescence was dependent on the solvent polarity, and the quenching was enhanced in the polar solvent. The S_2 fluorescence quenching is considered to take place through an intramolecular charge transfer state. Interestingly, the charge transfer state relaxes to the S_1 state through the rapid charge recombination with high quantum yield. The charge transfer rate of ZnFP−Py, which was calculated from the S_2 fluorescence quenching, was larger than that of ZnP−Py, possibly due to the differences in the free-energy changes of the electron transfer and the electron densities at their *meso*-positions. This study has suggested that ultrafast electron transfer from the upper excited state and charge recombination to S_1 can occur in a directly connected electron donor−acceptor system.

Introduction

An enormous number of molecular systems composed of porphyrins have been investigated on the intramolecular electron transfer (ET) from the lowest singlet excited state (S_1), which is a notation of electronic states populated by excitation in the Q-band (500−650 nm).[1−3] On the other hand, the porphyrin derivatives have a characteristic intense absorption, namely the Soret-band (400−450 nm) owing to a transition to upper excited states with a large energy gap to S_1. The upper excited states have been denoted as the second excited singlet state (S_2), and some of the metalloporphyrins and diacid porphyrins emit an S_2 fluorescence whose quantum yields[4−8] and lifetimes[6c,9−14] were in the region of 10^{-3}−10^{-5} and 0.8−4.5 ps, respectively. Although the lifetimes of S_2 are remarkably shorter than those of S_1, intermolecular[9,15] and intramolecular[12−14] ET from S_2 within the S_2 lifetimes have been reported. When the ET from S_2 occurs against internal conversion (IC) from S_2 to S_1, the ET must be an ultrafast process, which is an attractive phenomenon in both basic and applied photochemistry. For example, the photosensitized DNA damage by using highly oxidative porphyrin S_2 has been investigated.[15] The S_2 fluorescence is a useful probe to investigate the ultrafast ET from the upper excited state.

The first investigation on intermolecular ET from S_2 by Chosrowjan et al.[9] was from the S_2 state of zinc tetraphenylporphyrin to solvent dichloromethane, which included undefined and irreversible solvent decomposition. Concerning the intramolecular ET from S_2 reported by LeGourriérec et al.,[12] a formation of a 50% charge separated state with a 50% S_1 state was observed. In this molecule, intramolecular energy transfer from S_2 should be excluded because it was reported for a molecule composed of similar units that can be both the energy acceptor and donor.[11] Mataga et al. reported the intramolecular ET in the zinc porphyrin-electron acceptor dyad systems.[13] Using these dyad systems, the bell-shaped energy gap law in the ET from porphyrin S_2 has been demonstrated. Recently, Fujitsuka et al. reported that the S_2 fluorescence quenching of tetraphenylporphyrin Sb(V) and P(V) complexes through ET from their axial ligands.[14] Although, the ET from porphyrin S_1 state can occur other than the ET from S_2 in the reported many molecular systems, the ultrafast ET from the S_2 is the possible photochemical process.

In the present study, we synthesized zinc *meso*-(1′-pyrenyl)-triphenylporphyrin derivatives (Chart 1) as simple models to investigate ET from S_2. In the molecules, (i) direct linkage between porphyrin and pyrene enhances intramolecular ET relative to intermolecular ET to solvent, (ii) the pyrene unit cannot become an energy acceptor of porphyrin S_2, and (iii) the energy level of the charge transfer (CT) state is below S_2 and above S_1; therefore, ET cannot occur from S_1. These molecules may be used as a model of photooxidative electron transfer to the porphyrin S_2. If a rapid ET from S_2 occurs in

---

* To whom correspondence should be addressed. (K.H.) Address: Department of Basic Engineering (Chemistry), Faculty of Engineering, Shizuoka University, Johoku 3-5-1, Naka-ku, Hamamatsu, Shizuoka 432-8561, Japan. Tel.: +81-53-478-1287. Fax: +81-53-478-1287. E-mail: tkhirak@ipc.shizuoka.ac.jp. (H.S.) Address: Research Center for Advanced Science and Technology, The University of Tokyo, Komaba 4-6-1, Meguro-ku, Tokyo 153-8904, Japan. Tel.: +81-3-5452-5295. Fax: +81-3-5452-5299. E-mail: csegawa@mail.ecc.u-tokyo.ac.jp.

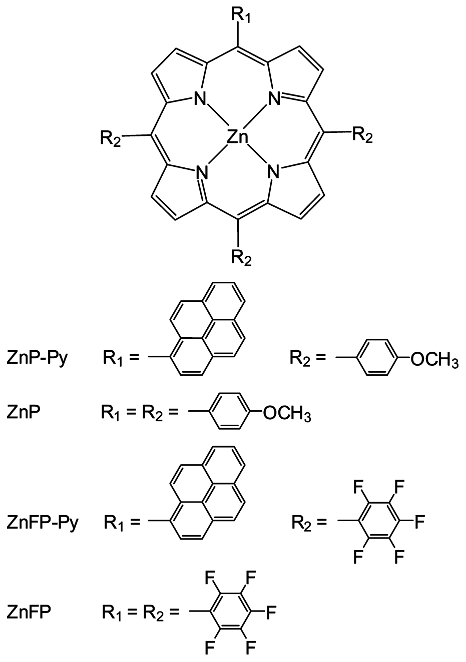
† Shizuoka University.

‡ Kitasato University.

§ The University of Tokyo.

10.1021/jp903743w CCC: $40.75 © 2009 American Chemical Society
Published on Web 07/09/2009

CHART 1



these molecules, the S_2 fluorescence quenching becomes an effective probe of the ET process under various conditions. Thus, the S_2 fluorescence quantum yields and its solvent dependence were investigated.

Experimental Section

Measurements. The 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 of the porphyrin moieties were determined relative to zinc tetraphenylporphyrin in benzene (S_1 fluorescence: $\Phi_f = 3.0 \times 10^{-2}$, S_2 fluorescence: $\Phi_f = 3.5 \times 10^{-4}$)[7c] and corrected by the refractive index of solvents.[16] 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.

Materials. The spectroscopic grade solvents of acetonitrile, dichloromethane, toluene (Dojin Chem. Ind., Kumamoto, Japan), and hexane (Kanto Chem. Com. Inc., Tokyo, Japan) were used for the measurement as received. Zinc 5-(1′-pyrenyl)-10,15,20-tris(*p*-methoxyphenyl)porphyrin (ZnP−Py) and zinc 5-(1′-pyrenyl)-10,15,20-tris(pentafluorophenyl)-porphyrin (ZnFP−Py) were synthesized by the following procedures. At first, free-base *meso*-(1′-pyrenyl)triphenylporphyrin derivatives were synthesized using a modified version of the procedure of Adler and co-workers.[17] Zinc ion was incorporated into the porphyrins according to the literature.[18] The products were identified by ^{1}H NMR, FAB-MS, and UV−vis spectroscopy (described in the following sections). Zinc 5,10,15,20-tetrakis(*p*-methoxyphenyl)porphyrin (ZnP)[17,18] and zinc 5,10,15,20-tetrakis(pentafluorophenyl)porphyrin (ZnFP)[19] were synthesized according to the literature.

Synthesis of ZnP−Py. Free-base 5-(1′-pyrenyl)-10,15,20-tris(*p*-methoxyphenyl)porphyrin (H_2P−Py) was synthesized by the following procedure: 1.73 g of 1-pyrenecarboxaldehyde (Aldrich Chem. Com. Inc., Milwaukee, WI) and 2.7 mL of *p*-methoxybenzaldehyde (WAKO Pure Chem. Ind.) were dissolved in 200 mL of propionic acid (WAKO Pure Chem. Ind., Osaka, Japan), and 2.1 mL of pyrrole (WAKO Pure Chem. Ind.) was added to the reflux for 1 h. The solvent propionic acid was removed by vacuum evaporation after the reaction. The crude product was washed by methanol several times and purified by column chromatography on silica gel with chloroform−hexane (9/1, v/v) as an eluent several times, the result being a pure product with a 3.3% (0.21 g) yield. ZnP−Py was prepared using 0.027 g of H_2P−Py. ^{1}H NMR ($CDCl_3$, TMS) δ 4.06 (s, 6H, methoxy-H of 10,20-phenyl), 4.11 (s, 3H, methoxy-H of 15-phenyl), 7.25 (d, 4H, $J_{H-H} = 10.5$ Hz, 10,20-*m*-phenyl-H), 7.30 (d, 2H, $J_{H-H} = 7.5$ Hz, 15-*m*-phenyl-H), 7.44 (d, 1H, $J_{H-H} = 9.5$ Hz, pyrenyl-H), 7.67 (d, 1H, $J_{H-H} = 9.0$ Hz, pyrenyl-H), 8.03−8.17 (m, 8H, 10,15,20-*o*-phenyl-H (6H) and pyrenyl-H (2H)), 8.32 (t, 2H, pyrenyl-H), 8.40 (d, 1H, $J_{H-H} = 9.0$ Hz, pyrenyl-H), 8.51 (d, 1H, $J_{H-H} = 7.5$ Hz, pyrenyl-H), 8.57 (d, 2H, $J_{H-H} = 4.5$ Hz, 3,7-βH), 8.80 (d, 1H, $J_{H-H} = 7.5$ Hz, pyrenyl-H), 8.87 (d, 2H, $J_{H-H} = 4.5$ Hz, 2,8-βH), 8.98−9.01 (m, 4H, 12,13,17,18-βH). FAB-MS: *m/z* 889.9 (M^+). UV−vis absorption peaks (λ_{max}/nm) in dichloromethane: 310, 322, 338, 428, 556, 598.

Synthesis of ZnFP−Py. Free-base 5-(1′-pyrenyl)-10,15,20-tris(pentafluorophenyl)porphyrin (H_2FP−Py) was synthesized by the following procedure: 3.9 g of 1-pyrenecarboxyaldehyde and 10.0 g of pentafluorobenzaldehyde (Aldrich Chem. Com. Inc.) were dissolved in 500 mL of propionic acid, and 5.0 mL of pyrrole was added to the reflux for 1 h. The solvent propionic acid was removed by vacuum evaporation after the reaction. The crude product was washed by methanol/water (9/1, v/v) several times and purified by column chromatography on silica gel with chloroform−hexane (9/1, v/v) as an eluent several times, and we obtained a mixture of H_2FP−Py and tetrakis(pentafluorophenyl)porphyrin (H_2FP). Zinc(II) ion was incorporated into H_2FP−Py and H_2FP, and pure ZnFP−Py was obtained by high-performance liquid chromatography (LC-10, Shimadzu, Kyoto, Japan, using a silica gel column) with chloroform−hexane (6/94, v/v) as an eluent. The purification of ZnFP−Py was difficult, and only a small amount of the sample could be obtained. ^{1}H NMR ($CDCl_3$, TMS) δ 7.33 (d, 1H, $J_{H-H} = 9.5$ Hz, pyrenyl-H), 7.73 (d, 1H, $J_{H-H} = 9.5$ Hz, pyrenyl-H), 8.07−8.14 (m, 2H, pyrenyl-H), 8.35−8.38 (m, 2H, pyrenyl-H), 8.43 (d, 1H, $J_{H-H} = 9.0$ Hz, pyrenyl-H), 8.56 (d, 1H, $J_{H-H} = 8.0$ Hz, pyrenyl-H), 8.71 (d, 2H, $J_{H-H} = 4.5$ Hz, 3,7-βH), 8.78 (d, 2H, $J_{H-H} = 4.5$ Hz, 2,8-βH), 8.79 (d, 1H, $J_{H-H} = 8.0$ Hz, pyrenyl-H), 8.99 (s, 4H, 12,13,17,18-βH). FAB-MS: *m/z* 1070.0 (M^+). UV−vis absorption peaks (λ_{max}/nm) in dichloromethane: 322, 341, 422, 552, 582.

Calculations. The equilibrium geometries of ZnP−Py and ZnFP−Py were calculated by the ab initio molecular orbital (MO) calculation at the Hartree−Fock 6-31G* level. The electron densities of the porphyrin and the pyrene moieties were also estimated from this method. These calculations were performed on Spartan 08 (Wavefunction Inc. CA).

Results

Absorption and Fluorescence Spectra of ZnP−Py and ZnFP−Py. The absorption feature of ZnP−Py (Figure 1a) coincides with the superposition of ZnP and pyrene, indicating that the $\pi-\pi$ interaction between the porphyrin and the pyrene moieties is weak.[20] The weak $\pi-\pi$ interaction is due to steric rotational hindrance of the pyrene moiety around the *meso*-position of the porphyrin, which keeps the two π-electronic systems nearly orthogonal to each other. The absorption feature

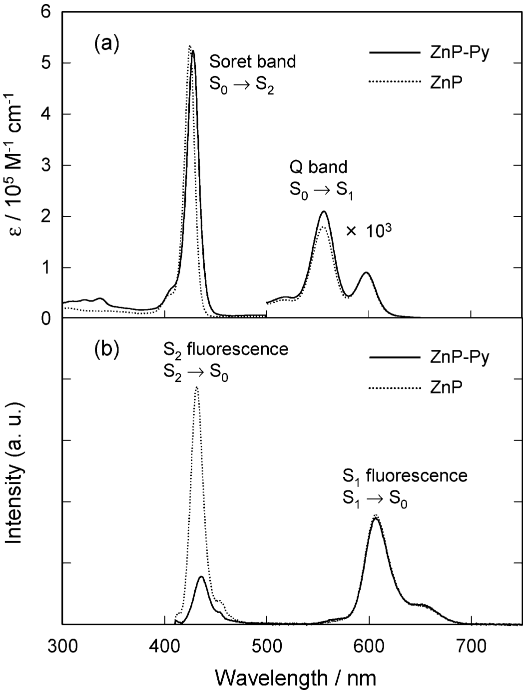


Figure 1. (a) Absorption spectra of ZnP−Py and ZnP in dichloromethane. (b) Fluorescence spectra of ZnP−Py and ZnP at 400 nm excitation in dichloromethane. The absorbance of these porphyrins was adjusted to 0.020 at the excitation wavelength.

TABLE 1: Fluorescence Quantum Yields

compound	solvent	Φ_{S2-S2}[a]	Φ_{S2-S1}[b]	Φ_{S1-S1}[c]
ZnP	toluene	2.90×10^{-4}	0.027	0.027
	CH_2Cl_2	4.10×10^{-4}	0.033	0.035
	CH_3CN	8.80×10^{-4}	0.017	0.018
ZnP−Py	toluene	1.40×10^{-4}	0.030	0.031
	CH_2Cl_2	0.98×10^{-4}	0.031	0.037
	CH_3CN	0.86×10^{-4}	0.017	0.020
ZnFP	hexane	1.00×10^{-4}	0.020	0.021
	toluene	1.30×10^{-4}	0.017	0.019
	CH_2Cl_2	0.41×10^{-4}	0.012	0.014
	CH_3CN	1.40×10^{-4}	0.011	0.011
ZnFP−Py	hexane	0.44×10^{-4}	0.019	0.021
	toluene	0.50×10^{-4}	0.019	0.019
	CH_2Cl_2	0.05×10^{-4}	0.013	0.016
	CH_3CN	0.20×10^{-4}	0.013	0.013

[a] S_2 fluorescence quantum yields at S_2 excitation (Ex = 400 nm). [b] S_1 fluorescence quantum yields at S_2 excitation (Ex = 400 nm). [c] S_1 fluorescence quantum yields at S_1 excitation (Ex = 550 nm).

TABLE 2: Estimated Energies of S_1, S_2, and CT[a]

compound	solvent	E_{S1} (eV)	E_{S2} (eV)	CT1 (eV)	CT2 (eV)
ZnP−Py	toluene	2.06	2.83	3.06	3.39
	CH_2Cl_2	2.04	2.83	2.72	3.05
	CH_3CN	2.04	2.86	2.63	2.96
ZnFP−Py	hexane	2.13	2.97	2.80	4.04
	toluene	2.10	2.84	2.68	3.92
	CH_2Cl_2	2.08	2.89	2.34	3.58
	CH_3CN	2.07	2.88	2.25	3.49

[a] E_{S1} and E_{S2} indicate the S_1 and S_2 energies of the porphyrin moieties, respectively. CT1 is the energy level of the porphyrin anion−pyrene cation pair. CT2 is the energy level of the porphyrin cation−pyrene anion pair.

of ZnFP−Py is similar to that of ZnP−Py. An ab initio MO calculation also indicated that the planes of the pyrene moieties are perpendicular to those of the porphyrins. This calculation showed that the highest occupied MO (HOMO) and lowest unoccupied MO (LUMO) of these porphyrins and pyrenes were localized on their corresponding moieties, supporting the results of absorption measurements.

The S_1 fluorescence spectra of ZnP−Py and ZnFP−Py were similar to those of the corresponding reference porphyrins (ZnP and ZnFP), indicating that the contribution of the CT state in S_1 is negligibly small. The fluorescence quantum yields of S_1 of the porphyrin moieties were almost the same as those of the corresponding reference porphyrins in any solvents when the porphyrins were photoexcited at the Q-bands (Table 1). Consequently, it is confirmed that the S_1 of the porphyrin derivatives is not quenched by the pyrene moiety. When ZnP−Py and ZnFP−Py were photoexcited at the Soret band, both the S_2 and S_1 fluorescence were observed (Figure 1b). Although the S_1 fluorescence quantum yields were almost the same as those of the corresponding reference porphyrins, the S_2 fluorescence was clearly quenched by the pyrene moiety (Figure 1b and Table 1).

Energies of Porphyrin S_2 and S_1 and of the CT State. The S_2 and S_1 states energies of porphyrins relative to the ground states were estimated from their fluorescence peaks and are listed in Table 2. The reduction potentials (vs SCE) of ZnP (−1.28 V) and ZnFP (−0.90 V), pyrene (−2.21 V),[21] and the oxidation potentials (vs SCE) of ZnP (0.84 V), ZnFP (1.37 V), and pyrene (1.44 V) in benzonitrile were obtained from cyclic voltammograms. The CT state energies relative to the ground states were estimated from these redox potentials using dielectric continuum theory (Table 2).[22,23] The energy levels of the CT1 state (the porphyrin anion−pyrene cation pair) were lower than the porphyrin S_2 energy, suggesting that ET from the pyrene to porphyrin S_2 is possible from an energetic viewpoint. The CT1 state energy of ZnP−Py in toluene is apparently higher than that of S_2, possibly due to an underestimation of the solvation energy of a less-polar solvent, toluene. The energy levels of the CT2 states (the porphyrin cation−pyrene anion pair) were higher than those of the CT1, supporting that the ET from the pyrene to porphyrin S_2.

Calculated Electron Densities of ZnP−Py and ZnFP−Py. Ab initio MO calculations indicated that the HOMO and the next HOMO of ZnP−Py are a_{2u} and a_{1u} symmetries, respectively, whereas those of ZnFP−Py are reversed, similarly to the case of other tris(pentafluorophenyl)porphyrin derivatives.[24-26] The a_{2u} orbital has electron density at the *meso* positions and the central nitrogens, whereas the a_{1u} orbital has nodes at these positions. The electron density at 5-C of the next HOMO of ZnFP−Py is significantly higher (6.4×10^{-2}) than that of ZnP−Py (6.2×10^{-6}). Since the electron densities at 1′-C of the pyrene moieties of ZnP−Py and ZnFP−Py are almost the same (8.9×10^{-2} and 8.5×10^{-2}, respectively), the electronic communication between the next HOMO of porphyrin and the HOMO of pyrene in ZnFP−Py becomes larger than that of ZnP−Py.

Discussion

The present study has demonstrated that the S_2 fluorescence of the porphyrin is quenched by the pyrene moiety, whereas the S_1 fluorescence is not. Since the energy levels of the excited state of the pyrene moiety and the CT state of these pyrenylporphyrins are higher than that of S_1 of the porphyrin, quenching through energy transfer and ET does not occur from the S_1. In the S_2, ET from the pyrene moiety to the porphyrin S_2 is energetically possible because the energy level of the CT state of a porphyrin anion and a pyrene cation pair is located between

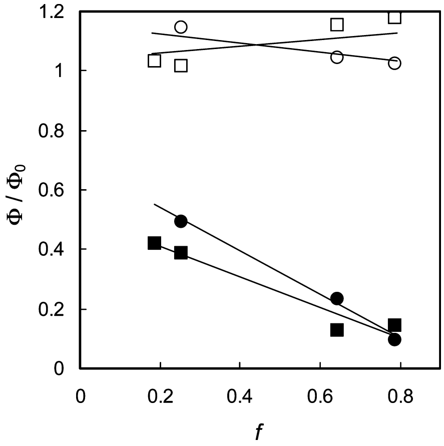


Figure 2. Dependence of the fluorescence quantum yield ratio (Φ/Φ_0) on the solvent polarity parameter ($f = (2(\varepsilon - 1))/(2\varepsilon + 1) - (n^2 - 1)/(2n^2 + 1)$, where ε is the dielectric constant, n is the refractive index): S_1 fluorescence of ZnP−Py (○) and ZnFP−Py (□) and S_2 fluorescence of ZnP−Py (●) and ZnFP−Py (■).

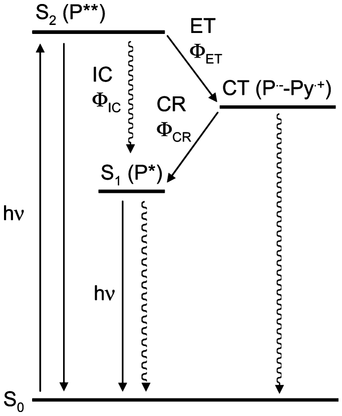


Figure 3. Schematic energy diagram of the deactivation processes. P and $P^{\bullet-}$−$Py^{\bullet+}$ indicate the porphyrin moiety and the porphyrin anion−pyrene cation pair in ZnP−Py or ZnFP−Py, respectively.

the S_2 and the S_1 energy levels of the porphyrins. The transient absorption spectrum measurement showed the absorption peak around 460 nm (Supporting Information). This absorption could be assigned to the radical cation of pyrene,[27] and did not coincide with the reported absorption peak of the radical anion of pyrene,[28] strongly suggesting the ET from the pyrene to porphyrin S_2. If the S_2 quenching is due to the ET, dependence of the fluorescence quenching on the solvent polarity is expected. The fluorescence quantum yields ratio (Φ/Φ_0), which results from the division of the fluorescence quantum yields of ZnP−Py and ZnFP−Py by those of the corresponding reference porphyrins, was plotted against the solvent polarity parameter (Figure 2). The Φ/Φ_0 of S_2 clearly decreased with increasing the solvent polarity, whereas the Φ/Φ_0 of S_1 was not affected. If the S_2 quenching process is due to enhancement of direct IC to S_1, the solvent dependence of S_2 fluorescence cannot be explained. For the purpose of careful investigation, the following deactivation processes from the S_2 of ZnP−Py and ZnFP−Py were assumed: (1) direct IC from S_2 to S_1 and (2) ET between pyrene and the porphyrin S_2, which is followed by charge recombination (CR) to the porphyrin S_1 or S_0, as shown in Figure 3. Since the S_1 fluorescence quantum yields of reference porphyrins (ZnP and ZnFP) are independent of the excitation wavelengths within experimental error (Table 1) similar to that of previous reports,[6b,c,7b] the main pathway of the deactivation processes of S_2 of these reference molecules are IC and S_2 emission. Consequently, the quantum yields of the ET (Φ_{ET}), the IC (Φ_{IC}), and the CR to the porphyrin S_1 ($\Phi_{CR\rightarrow S1}$) can be estimated by the following equations:

TABLE 3: Quantum Yields of Deactivation Processes and Estimated ET Rate Constants from the S_2 State

compound	solvent	Φ_{IC}	Φ_{ET}	$\Phi_{CR\rightarrow S1}$	$k_{ET}/10^{12}\ s^{-1}$
ZnP−Py	toluene	0.50	0.50	0.92	0.88
	CH_2Cl_2	0.24	0.76	0.81	2.00
	CH_3CN	0.10	0.90	0.82	2.60
ZnFP−Py	hexane	0.42	0.58	0.84	3.30
	toluene	0.39	0.61	0.96	3.10
	CH_2Cl_2	0.13	0.87	0.80	40.00
	CH_3CN	0.15	0.85	0.96	10.00

$$\Phi_{ET} = 1 - \frac{\Phi_{S2-S2}}{\Phi^0_{S2-S2}} \tag{1}$$

$$\Phi_{IC} = 1 - \Phi_{S2-S2} - \Phi_{ET} \tag{2}$$

$$\Phi_{CR\rightarrow S1} = \frac{\dfrac{\Phi_{S2-S1}}{\Phi_{S1-S1}} - \Phi_{IC}}{\Phi_{ET}} \tag{3}$$

where Φ^0_{S2-S2} is the S_2 fluorescence quantum yield of the reference porphyrin by the S_2 excitation. The quantum yields of these processes are listed in Table 3. The Φ_{ET} become large in polar solvent. For further investigation, the relative ET rate constant (k_{ET}) was roughly estimated from the following equation:

$$k_{ET} = \left(\frac{1}{\Phi_{S2-S2}} - \frac{1}{\Phi^0_{S2-S2}}\right)k_f \tag{4}$$

where k_f is the rate constant of S_2 fluorescence.[29] The k_{ET} values are mostly increasing with increasing the solvent polarity (Table 3), almost coinciding with the dependency of the Φ/Φ_0 on the solvent polarity. The k_{ET} value of ZnFP−Py in dichloromethane is larger than that in relatively high polar acetonitrile. This complicated result might be explained by the affect of charge transfer interaction between the porphyrin S_2 and solvent dichloromethane molecule.[9] The values of k_{ET} for ZnFP−Py are much larger than those of ZnP−Py. The ET should occur from the HOMO of the pyrene to the next HOMO of the porphyrin. Electron density at 5-C of the next HOMO of ZnFP−Py is larger than that of ZnP−Py, possibly resulting in an enhancement of electronic communication[24−26] between the porphyrin and the pyrene. Furthermore, the free energy changes ($-\Delta G$) of ET of ZnFP−Py, which were estimated from the values in Table 2 (0.16 eV in toluene, 0.55 eV in dichloromethane, and 0.63 eV in acetonitrile), were larger than those of ZnP−Py (−0.23 eV in toluene, 0.11 eV in dichloromethane, and 0.23 eV in acetonitrile). These findings support the observation that the ET from the porphyrin S_2 of ZnFP−Py is faster than that of ZnP−Py.

In addition, the high values of $\Phi_{CR\rightarrow S1}$ have indicated that the CT state predominantly decays into S_1. The $-\Delta G$s of the CR to S_0, which were estimated from the values in Table 2 (2.63−3.06 eV for ZnP−Py and 2.25−2.80 eV for ZnFP−Py), are much larger than the $-\Delta G$s of the CR to S_1 (0.59−1.00 eV for ZnP−Py and 0.18−0.67 eV for ZnFP−Py), indicating that CR to S_0 is a highly exothermic process. Therefore, CR to S_1 becomes the predominant process.

In summary, the present study has shown that the S_2 fluorescence of porphyrin is quenched through rapid ET from the pyrenyl group directly connected at the *meso* position, whereas the S_1 fluorescence cannot be quenched. The CT state relaxes to the S_1 state through rapid CR with a high quantum yield. The ET from the electron donor to the porphyrin S_2 can occur, suggesting that the photooxidation of various molecules by using porphyrin S_2 state, which has higher oxidative ability than the S_1, is possible.

Acknowledgment. This work was supported by grants from the Ministry of Education, Science and Culture of the Japanese Government and from the Japan Science and Technology Corporation.

Supporting Information Available: The transient absorption spectra of ZnP−Py. This material is available free of charge via the Internet at http://pubs.acs.org.

References and Notes

(1) (a) Wasielewski, M. R. Distance Dependencies of Electron Transfer Reactions. *Photoinduced Electron Transfer*; Fox, M. A., Chanon, M. , Eds.; Elsevier: Amsterdam, The Netherlands, 1988; Chapter 1.4. (b) Wasielewski, M. R. *Chem. Rev.* **1992**, *92*, 435.

(2) Kurreck, H.; Huber, M. *Angew. Chem., Int. Ed. Engl.* **1995**, *34*, 849.

(3) Piotrowiak, P. *Chem. Soc. Rev.* **1999**, *28*, 143.

(4) Bajema, R.; Gouterman, M. *J. Mol. Spectrosc.* **1971**, *39*, 421.

(5) Martarano, L. A.; Wong, C. P.; Horrocks, W. D., Jr.; Goncalves, A. M. P. *J. Phys. Chem.* **1976**, *80*, 2389.

(6) (a) Tsvirko, M. P.; Stelmakh, G. F.; Pyatosin, V. E.; Solovyov, K. N.; Kachura, T. F. *Chem. Phys. Lett.* **1980**, *73*, 80. (b) Stelmakh, G. F.; Tsvirko, M. P. *Opt. Spectrosc.* **1983**, *55*, 518. (c) Aaviksoo, J.; Freiberg, A.; Savikhin, S.; Stelmakh, G. F.; Tsvirko, M. P. *Chem. Phys. Lett.* **1984**, *111*, 275.

(7) (a) Tobita, S.; Kaizu, Y.; Kobayashi, H.; Tanaka, I. *J. Chem. Phys.* **1984**, *81*, 2962. (b) Kurabayashi, Y.; Kikuchi, K.; Kokubun, H.; Kaizu, Y.; Kobayashi, H. *J. Phys. Chem.* **1984**, *88*, 1308. (c) Ohno, O.; Kaizu, Y.; Kobayashi, H. *J. Chem. Phys.* **1985**, *82*, 1779. (d) Kaizu, Y.; Asano, M.; Kobayashi, H. *J. Phys. Chem.* **1986**, *90*, 3906. (e) Kaizu, Y.; Maekawa, H.; Kobayashi, H. *J. Phys. Chem.* **1986**, *90*, 4234.

(8) Fujitsuka, M.; Cho, D. W.; Solladié, N.; Troiani, V.; Qiu, H.; Majima, T. *J. Photochem. Photobiol. A: Chem.* **2007**, *188*, 346.

(9) Chosrowjan, H.; Taniguchi, S.; Okada, T.; Takagi, S.; Arai, T.; Tokumaru, K. *Chem, Phys. Lett.* **1995**, *242*, 644.

(10) Gurzadyan, G. G.; Tran-Thi, T. H.; Gustavsson, T. *J. Chem. Phys.* **1998**, *108*, 385.

(11) Harriman, A.; Hisseler, M.; Trompette, O.; Ziessel, R. *J. Am. Chem. Soc.* **1999**, *121*, 2516.

(12) LeGourriérec, D.; Andersson, M.; Davidsson, J.; Mukhtar, E.; Sun, L.; Hammarström, L. *J. Phys. Chem. A* **1999**, *103*, 557.

(13) (a) Mataga, N.; Shibata, Y.; Chosrowjan, H.; Yoshida, N.; Osuka, A. *J. Phys. Chem. B* **2000**, *104*, 4001. (b) Mataga, N.; Chosrowjan, H.; Shibata, Y.; Yoshida, N.; Osuka, A.; Kikuzawa, T.; Okada, T. *J. Am. Chem. Soc.* **2001**, *123*, 12422. (c) Mataga, N.; Chosrowjan, H.; Taniguchi, S.; Shibata, Y.; Yoshida, N.; Osuka, A.; Kikuzawa, T.; Okada, T. *J. Phys. Chem. A* **2002**, *106*, 12191. (d) Mataga, N.; Taniguchi, S.; Chosrowjan, H.; Osuka, A.; Yoshida, N. *Chem. Phys.* **2003**, *295*, 215. (e) Mataga, N.; Taniguchi, S.; Chosrowjan, H.; Osuka, A.; Kurotobi, K. *Chem. Phys. Lett.* **2005**, *403*, 163.

(14) (a) Fujitsuka, M.; Cho, D. W.; Shiragami, T.; Yasuda, M.; Majima, T. *J. Phys. Chem. B* **2006**, *110*, 9368. (b) Fujitsuka, M.; Cho, D. W.; Tojo, S.; Inoue, A.; Shiragami, T.; Yasuda, M.; Majima, T. *J. Phys. Chem. A* **2007**, *111*, 10574.

(15) Hirakawa, K.; Kawanishi, S.; Hirano, T.; Segawa, H. *J. Photochem. Photobiol. B: Biol.* **2007**, *87*, 209.

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

(17) Adler, A. D.; Longo, F. R.; Finarelli, J. D.; Goldmacher, J.; Assour, J.; Korsakoff, L. *J. Org. Chem.* **1967**, *32*, 476.

(18) Buchler, J. W. Static Coordination Chemistry of Metalloporphyrins. *Porphyrins and Metalloporphyrins;* Smith, K. M. , Ed.; Elsevier Scientific Publishing Company: New York, 1975; Chapter 5.

(19) Spellane, P. J.; Gouterman, M.; Antipas, A.; Kim, S.; Liu, Y. C. *Inorg. Chem.* **1980**, *19*, 386.

(20) Hirakawa, K.; Segawa, H. *J. Photochem. Photobiol. A Chem.* **1999**, *123*, 67.

(21) The reduction potential of pyrene was estimated from the oxidation potential (1.44 V vs SCE) and the 0−0 band of absorption maximum (340 nm).

(22) Weller, A. *Z. Phys. Chem. Neue Folge* **1982**, *133*, 93.

(23) The CT state energy in solvent x $(E^{CT})_x$ was calculated from the following equation:

$$(E^{CT})_x = (E_{1/2}{}^{+} - E_{1/2}{}^{-}) + \frac{e^2}{2}\left(\frac{1}{r_{por}} + \frac{1}{r_{py}}\right)\left(\frac{1}{\varepsilon_x} - \frac{1}{\varepsilon_m}\right) - \frac{e^2}{\varepsilon_x a}$$

where $E_{1/2}{}^{+}$, $E_{1/2}{}^{-}$, e, ε_x, and ε_m are half-wave one-electron oxidation and reduction potentials in solvent m, the electronic charge, and the static dielectric constants of solvent x and m, respectively. The r_{por} (6.2 Å) and the r_{py} (4.0 Å) are the effective ionic radius of porphyrin and pyrene, respectively. These values were obtained by the ab initio MO calculation at the Hartree−Fock 6-31G* level. Distance “*a*” is the center-to-center distance between the porphyrin and the pyrene moieties (7.7 Å). The following values were used as static dielectric constants: 36.0 (acetonitrile), 25.2 (benzonitrile), 9.10 (dichloromethane), 2.38 (toluene), and 1.88 (hexane).

(24) Fujii, H. *Chem. Lett.* **1994**, 1491.

(25) Strachan, J. P.; Gouterman, S.; Seth, J.; Kalsbeck, W. A.; Lindsey, J. S.; Holten, D.; Bocian, D. F. *J. Am. Chem. Soc.* **1997**, *119*, 11191.

(26) Yang, S. I.; Seth, J.; Balasubramanian, T.; Kim, D.; Lindsey, J. S.; Holten, D.; Bocian, F. *J. Am. Chem. Soc.* **1999**, *121*, 4008.

(27) Asahi, T.; Mataga, N. *J. Phys. Chem.* **1991**, *95*, 1956.

(28) Hirata, Y.; Saito, T.; Mataga, N. *J. Phys. Chem.* **1987**, *91*, 3119.

(29) The k_f was roughly estimated to be 2.5×10^8 s^{-1} from the fluorescence quantum yield $(\Phi^0{}_{S2-S2})$ and the lifetime (τ_0) of S_2 state of zinc tetraphenylporphyrin derivatives in acetonitrile by the following equation:

$$k_f = \frac{\Phi^0{}_{S2-S2}}{\tau_0}$$

For the calculation, the values for $\Phi^0{}_{S2-S2}$ of ZnP and τ_0 of zinc tetraphenylporphyrin ($\tau_0 = 3.5$ ps)[9] were used. The k_f was assumed to be the constant in all solvents for the calculation of the k_{ET}.

JP903743W