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Electron Transfer in the Supramolecular Donor–Acceptor Dyad of Zinc Hemiporphycene

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In the present study, photoinduced electron transfer (ET) processes of supramolecular donor–acceptor dyads of Zn 2,3,7,8,11,12,17,18-octaethylhemiporphycene (ZnHPc) and axial ligands were investigated by using various spectroscopic methods. The formation of 1:1 dyads was confirmed by absorption spectral change during titration of axial ligand. The association constants were determined from the spectral change. Quenching of the fluorescence intensity was observed when electron acceptor ability of the axial ligand increased. The driving forces for ET were estimated based on the estimated redox potentials and structural parameters. It became clear that various ZnHPc dyads showed ET because of slightly higher donor-ability and larger excitation energy of ZnHPc when compared to the corresponding dyads of Zn porphycene (ZnPcn). The transient absorption spectra during the sub-picosecond laser flash photolysis showed the formation of charge separated state, that is, radical cation of ZnHPc and radical anion of axial ligand, from the singlet excited ZnHPc. The observed ET rates were compared with the previously reported values for Zn porphyrins and ZnPcn. The ET rates of ZnHPc were located between those observed with porphyrins and ZnPcn supramolecular dyads, even when the $-\Delta G$ values were similar to each other. This observation was explained on the basis of the variation in reorganization energy and electronic coupling (V) values. Furthermore, distribution of HOMO electron density gave a plausible explanation for the variation in V values of these dyads.

Introduction

Porphyrin derivatives have been employed to develop various photofunctional molecular devices, including artificial photosynthesis systems.¹ For porphyrins, a series of well-defined isomers have been synthesized, namely, porphycene, hemiporphycene, and corrphecyne.² Compared to porphyrin, these isomers have a large absorption in the red and near-IR regions because of their lower symmetry compared to porphyrins. This point is attractive from the viewpoint of application to photodynamic therapy, photocatalyst, and so on.^{3–5}

Compared to a number of studies on the electron transfer (ET) process of porphyrin derivatives, examples of ET of these porphyrin isomers are rather limited. In the case of porphycene, some researchers have investigated the inter- and intramolecular ET processes.^{6–10} But for other isomers, there is no report on ET processes to the best of our knowledge. In the previous paper,⁹ we investigated photoinduced ET processes of the supramolecular donor–acceptor dyad molecules using zinc 2,3,6,7,12,13,16,17-octaethylporphycene (ZnPcn). As an electron acceptor, axial ligands consisting of phthalimides or pyromellitic diimide bearing a pyridine ring, which can coordinate to the central Zn ion of ZnPcn, were employed. Various spectroscopic studies revealed the charge separation (CS) upon photoexcitation of ZnPcn of the supramolecular dyads. The comparison of the ET rates of ZnPcn with those of corresponding supramolecules of Zn 5,10,15,20-tetraphenylporphyrin (ZnTPP) and Zn 2,3,7,8,12,13,17,18-octaethylporphyrin (ZnOEP) indicated larger reor-

ganization energy and smaller electronic coupling of ZnPcn supramolecules, although the origin of which was not clarified.

In the present paper we investigate photoinduced ET processes of supramolecular donor–acceptor dyads of zinc 2,3,7,8,11,12,17,18-octaethylhemiporphycene (ZnHPc) with the axial ligands, of which molecular structures are indicated in Figure 1. By using the same acceptors, comparison with the previous reports became possible.^{9,11} By using the sub-picosecond laser flash photolysis mainly, ET processes in the supramolecular dyads were revealed. From the comparison of the ET rates, characteristics of ET of ZnHPc were pointed out. On the basis of the molecular orbital theory, the difference in ET rates of ZnOEP, ZnPcn, and ZnHPc was discussed.

Experimental Section

Materials. 2,3,7,8,11,12,17,18-Octaethylhemiporphycene (HPc) was synthesized according to the reported procedure.¹² Zinc complex (Figure 1, ZnHPc) was prepared in a manner similar to that previously reported.² The syntheses of pyromellitic diimide and phthalimides bearing a pyridine ring at the N-position (Figure 1, PI, Cl₂Ph, ClPh, and CH₃Ph) were reported in the previous papers.^{9,11}

Apparatus. The sub-picosecond transient absorption spectra were measured by the pump-and-probe method using a regeneratively amplified titanium sapphire laser as reported previously.¹³ In the present study, the sample was excited using a 610 nm laser pulse that was generated by an optical parametric amplifier.

The fluorescence decay profiles were measured by the single photon counting method using a streakscope.¹⁴ The ultrashort laser pulse was generated by a Ti:sapphire laser. For excitation of the sample, the output of the Ti:sapphire laser was converted

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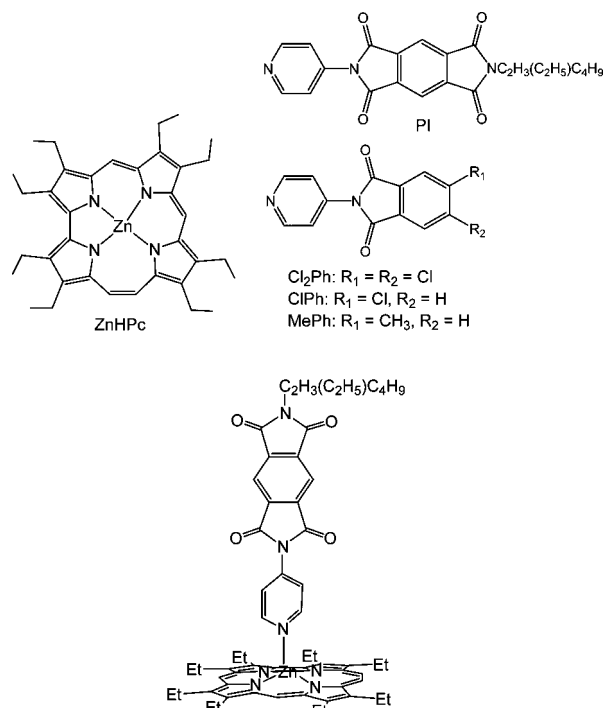


Figure 1. Molecular structures of ZnHPc, PI, phthalimides, and PI-ZnHPc, as an example of supramolecular dyad.

to the second harmonic oscillation (420 nm) using a harmonic generator (Spectra-Physics, GWU-23FL).

γ -Ray radiolysis of the sample was carried out using the ^{60}Co source of ISIR, Osaka University. After the freeze-pump-thaw cycles, the sample was cooled at 77 K to form a transparent glass, which was then irradiated with γ -ray. In the present study, *n*-butylchloride was used as a solvent to form the radical cation of the substrate.¹⁵

The cyclic voltammograms (CV) were measured using a BAS ALS model 630c electrochemical analyzer. A three-electrode cell equipped with 1.6 mm diameter platinum wires as the working and counter electrodes and an Ag/AgCl (3.0 M NaCl) electrode as the reference was used. Nonaqueous dichloromethane solution containing a substrate (5.0×10^{-4} M) and tetraethylammonium perchlorate (TEAClO_4) (5.0×10^{-2} M) was deaerated prior to each measurement, and a nitrogen atmosphere was maintained inside the cell throughout each measurement. All measurements were carried out at room temperature.

The steady-state absorption and fluorescence spectra were measured using a Shimadzu UV-3100PC and Hitachi 850, respectively. Optimized structures were estimated at the B3LYP/6-31G(d) level using the Gaussian 03 package.¹⁶ For simplicity of the calculation, alkyl groups of the compounds were reduced to methyl groups.

Results and Discussion

Steady-State Absorption and Fluorescence Spectra. Figure 2a shows absorption spectra of ZnHPc and PI in toluene. In the present study, toluene was used as a solvent for all the spectroscopic studies because formation of the pentacoordinated ZnHPc was reported,² and measurements in this solvent allow us comparison with the experimental results of the previous measurements on other supramolecular dyads of porphyrinoids.^{9,11} In toluene, ZnHPc showed absorption peaks at 608 and 421 nm. When PI was added to the solution of ZnHPc, the absorption

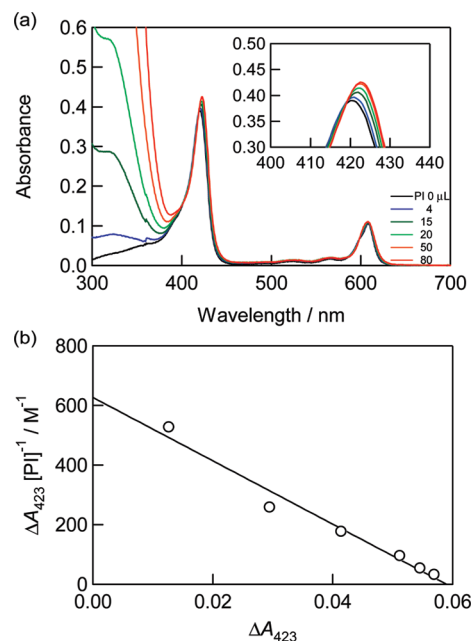


Figure 2. (a) Absorption spectra during the complexation of ZnHPc and PI in toluene. 0, 4, 15, 20, 50, and 80 μL of PI solution (12 mM) was added to ZnHPc (1.6 μM , 2 mL). Optical path length is 10 mm. Inset: Magnified spectrum. (b) Scatchard plot.

peak in the UV region shifted to 423 nm and the absorption tail of the band in the red region shifted to the longer wavelength side. During these spectral changes, isosbestic points were observed at 599, 587, 419, and 401 nm (inset of Figure 2a). Furthermore, the observed peak positions of the complex of ZnHPc and PI are the same as those of the 1:1 complex of ZnHPc and pyridine (Py).² These results indicate that the present spectral changes can be attributed to the formation of the 1:1 complex of PI and ZnHPc. Thus, it can be concluded that a pentacoordinated PI-ZnHPc supramolecular dyad was formed by coordination of the Py ring of PI to the central Zn ion of ZnHPc. Formation of the 1:2 complex can be ruled out under the present experimental conditions taking the reported association constant for the 1:2 complex into account.² Essentially the same behavior was confirmed with other supramolecular dyad of ZnHPc and phthalimide acceptors in Figure 1. By applying the Scatchard plot¹⁷ to the present absorption change (Figure 2b), the association constants were estimated as summarized in Table 1. The estimated values were similar to the reported values for A-ZnPc, A-ZnOEP, and so on, where A is PI or phthalimides.^{9,11}

ZnHPc in toluene showed a fluorescence band with a peak at 613 nm with a minor peak at 663 nm. The fluorescence quantum yield (Φ_f) was estimated to be 0.063 by employing Zn tetraphenylporphyrin in toluene as a standard (0.033).¹⁸ The fluorescence of ZnHPc decayed according to the single exponential function with 2.8 ns of lifetime (τ_f). When Py was coordinated to ZnHPc, the fluorescence peaks were shifted to the longer wavelength side, namely, 616 and 668 nm, respectively. The Φ_f and τ_f values were estimated to be 0.039 and 2.3 ns, respectively. The decrease in the Φ_f and τ_f values upon Py coordination is the same trend as observed with other porphyrinoids.⁹ The fluorescence properties such as peak positions, Φ_f , and τ_f values of the supramolecular dyads were estimated as summarized in Table 1. For example, when the toluene solution including ZnHPc (1.4 μM) and PI (1.5 mM) was excited at 570 nm, very weak fluorescence peaks were observed at 613 and 663 nm, indicating that the emitting species is ZnHPc not in

TABLE 1: Absorption, Fluorescence, and Association Constant of ZnHPc and Its Complexes in Toluene

	λ_{abs} (nm)	λ_{f} (nm)	Φ_{f}	τ_{f} (ns)	K_{a} (M^{-1})
ZnHPc	421, 608	613, 663	0.063 ^b	2.8 (100%)	
Py-ZnHPc	424, 608	616, 668	0.039 ^c	2.3 (100%)	14 000
PI-ZnHPc	423, 608	613, 663	0.001 ^c	0.038 (82%), 2.8 (18%)	11 000
Cl ₃ Ph-ZnHPc	423, 608	613, 663	0.020 ^c	0.84 (73%), 2.8 (27%)	11 000
ClPh-ZnHPc	424, 608	615, 665	0.029 ^c	2.0 (97%), 2.8 (3%)	6800
MePh-ZnHPc	424, 608	615, 666	0.039 ^c	2.4 (100%)	11 000

^a λ_{abs} , λ_{f} , Φ_{f} , and τ_{f} indicate absorption and fluorescence peaks, fluorescence quantum yield, and fluorescence lifetime, respectively. ^b The Φ_{f} value of ZnHPc in toluene was estimated using the Φ_{f} value of Zn tetraphenylporphyrin (0.033) as standard.¹⁸ ^c The Φ_{f} value of complex was estimated by applying the correction to the apparent fluorescence intensity based on the molar ratio of ZnHPc in the complex and uncomplexed form.

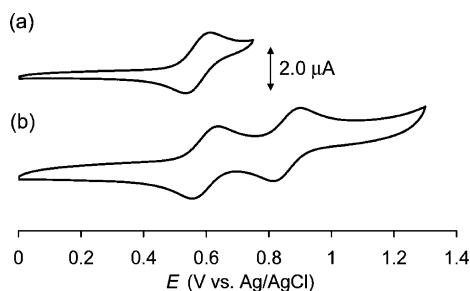


Figure 3. Cyclic voltammograms of Py-ZnHPc (a) and ZnHPc (b) in dichloromethane including TEAClO₄ as supporting electrolyte. Scan rate was 100 mV s⁻¹.

the complex form and PI-ZnHPc is almost nonfluorescent, because 6% of ZnHPc is not in the complex form under the present condition based on the estimated association constant. This is supported by the fact that the fluorescence exhibited two-components decay of 0.038 and 2.8 ns of τ_{f} values, of which the longer component is the same as the τ_{f} value of pristine ZnHPc. Thus, the Φ_{f} value of PI-ZnHPc was estimated to be 0.001 by subtracting the fluorescence from the pristine ZnHPc. It is clear in Table 1 that when phthalimide or PI was coordinated to the ZnHPc, fluorescence intensity was decreased as electron-acceptor-ability of the axial ligand was increased. This tendency indicates ET in the supramolecular dyads upon excitation of ZnHPc.

Driving Force for the Electron Transfer. To estimate the driving force for the ET in the supramolecular dyads, information on the redox properties and structures of supramolecular dyads is needed. Figure 3 shows the CV of Py-ZnHPc, which was measured with the solution including 100 equiv. of Py in addition to ZnHPc. Under this condition, > 99% of ZnHPc is in the pentacoordinated form. The first oxidation wave was observed, as shown in Figure 3a, from which the oxidation potential of Py-ZnHPc was estimated to be 0.43 V vs SCE. The estimated oxidation potentials was located at slightly cathodic by 0.02 V compared to pristine ZnHPc, indicating that a serious effect was not induced to the π -electron system of ZnHPc by formation of the pentacoordination. The oxidation potential of Py-ZnHPc was lower by 0.04 V in the comparison with Py-ZnPcn, indicating a slightly increased donor-ability of Py-ZnHPc.

The molecular structure of the supramolecular dyads was estimated by using molecular orbital calculation. Figure S1 (Supporting Information) shows the optimized structure and molecular orbital patterns of PI-ZnHPc as a representative. The central Zn ion of ZnHPc was coordinated by four pyrrole rings of HPC ligand and N atom of the Py ring of PI, forming pentacoordination. The bond length of the N atom of the Py ring—Zn ion was estimated to be 2.18 Å, which is the almost

the same as those of PI-ZnPcn (2.17 Å) and PI-ZnOEP (2.19 Å).^{9,11} By forming the pentacoordination, Zn ion is pulled out from the HPC mean plane by 0.44 Å, which is also the same value as PI-ZnPcn and PI-ZnOEP, indicating that the center-to-center distance of donor and acceptor of these supramolecules of PI and porphyrinoids are the same (9.8 Å). For phthalimides-ZnHPc dyads, the center-to-center distance was estimated to be 8.6 Å, which is also the same as that of other porphyrinoids.

For PI-ZnHPc, the HOMO and LUMO are localized on ZnHPc and PI, respectively (Figure S1). The LUMO of pristine ZnHPc corresponds to the LUMO+3 of PI-ZnHPc. Thus, upon excitation of ZnHPc moiety of the dyad, CS is possible. Because both HOMO and LUMO do not have electronic density on the Py ring of PI, the Py ring will act as a spacer, that is, ET should be a single-step process that does not include a charged state of the Py ring.

By using the oxidation potential and structural parameters estimated above as well as the reported reduction potentials of the ligands and the excitation energy of Py-ZnHPc (2.01 eV), the driving forces for the CS and charge recombination (CR) (ΔG_{CS} and ΔG_{CR} , respectively) were estimated according to the Weller's equation¹⁹ as summarized in Table 2. Although the $-\Delta G_{\text{CS}}$ value for MePh-ZnHPc is 0.01 eV, sufficiently negatively large driving force is expected for the other supramolecular dyad systems. This result seems to be reasonable, because the Φ_{f} and τ_{f} values of MePh-ZnHPc are the same as those of Py-ZnHPc, while both values decreased with the increase of $-\Delta G_{\text{CS}}$ values, supporting the fluorescence quenching due to CS. It should be pointed out that the $-\Delta G_{\text{CS}}$ values of the supramolecular donor—acceptor dyads of ZnHPc are larger than those of the corresponding dyads of ZnPcn (Table S1 of Supporting Information).⁹ The increase in the $-\Delta G_{\text{CS}}$ values can be attributed to the slightly enhanced donor ability and larger excitation energy of ZnHPc (1.87 eV for the pentacoordinated ZnPcn).

Absorption Spectrum of Radical Cation of ZnHPc. To investigate the ET process by the transient absorption spectroscopy, observation of radical anion of the acceptor and radical cation of the donor is essential. Although an absorption spectrum of the radical anion of PI is known,^{21,22} that of the radical cation of ZnHPc has not been reported. To generate the radical cation of ZnHPc, γ -ray irradiation to a glassy matrix was carried out in this study, because it has been established that γ -ray irradiation to a substrate in a low-temperature glassy matrix of *n*-butylchloride selectively generates the radical cation of the substrate.^{15,23} Figure 4 shows the absorption spectra of ZnHPc in *n*-butylchloride at 77 K before and after the γ -ray irradiation. After the irradiation, a new absorption peak appeared at 756 nm, which becomes obvious in a difference spectrum (inset of Figure 4). The new peak can be assigned to the radical cation of ZnHPc.

TABLE 2: Oxidation and Reduction Potentials of Complexes, Driving Force for Electron Transfers, and Electron Transfer Rates

	E_{ox} (V vs SCE)	E_{red} (V vs SCE) ^b	$-\Delta G_{\text{CS}}$ (eV) ^c	$-\Delta G_{\text{CR}}$ (eV) ^c	k_{CS} (s ⁻¹)	k_{CR} (s ⁻¹)
Py-ZnHPc	0.43 ^a					
PI-ZnHPc		-0.83	0.86	1.15	2.8×10^{10}	3.6×10^9
Cl ₂ Ph-ZnHPc		-1.44	0.27	1.74	7.6×10^8	^d
ClPh-ZnHPc		-1.56	0.15	1.86	0.7×10^8	^d
MePh-ZnHPc		-1.70	0.01	2.00	^d	^d

^a Potential estimated using an Ag/AgCl reference electrode was expressed using V vs SCE for the comparison with the previous report.

^b From ref 9. The reduction potentials were estimated for noncoordinated ligands by cyclic voltammetry. ^c The listed values were calculated using 5.0 Å as r_{D} , r_{A} for PI and phthalimides were 3.5 and 3.0 Å, respectively. r for PI-ZnHPc and phthalimide-ZnHPc were 9.8 and 8.6 Å, respectively. The ΔG_{S} value was decreased by 0.35 eV according to ref 20. ^d Not observed.

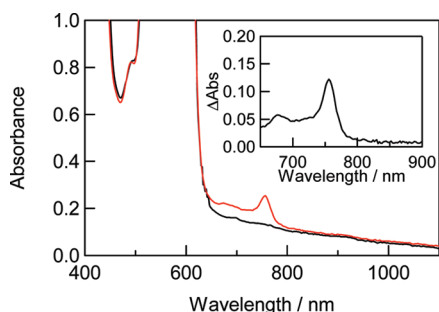


Figure 4. Absorption spectra of ZnHPc in *n*-butylchloride at 77 K before (black) and after (red) γ -ray irradiation. Inset: difference spectrum.

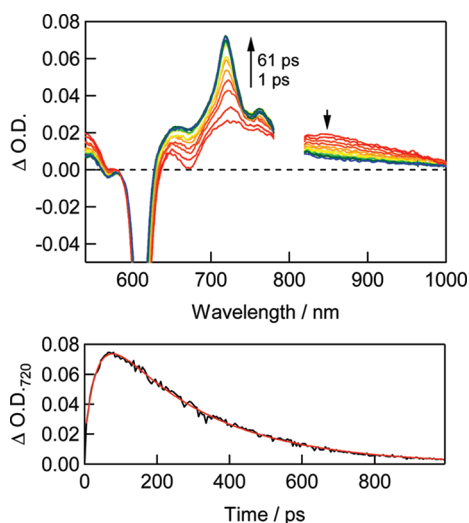


Figure 5. Transient absorption spectra of PI-ZnHPc in toluene during the laser flash photolysis using 610 nm femtosecond pulse for excitation. Spectra were obtained from 1 to 61 ps (5 ps step) after the laser excitation. Lower panel is the kinetic trace of $\Delta\text{O.D.}$ at 720 nm during the laser flash photolysis. Red curve is a fitted curve.

Transient Absorption Spectroscopy of the Supramolecular Donor–Acceptor Dyads. Figure 5 shows the transient absorption spectra of PI-ZnHPc in toluene obtained by the femtosecond laser excitation at 610 nm, which selectively excites the ZnHPc of the dyad. In the present transient absorption study, all experiments were carried out under the conditions, where an excess amount (100 equiv.) of electron acceptor was added to the sample solution to ensure that photoinduced processes of the pentacoordinated form can be elucidated. Under this condition, >99% of ZnHPc is in the pentacoordinated form. Immediately after the laser excitation, a broad absorption band ranging from 680–1000 nm as well as negative absorption at 616 nm due to breaching of the Q-band and stimulated emission

of ZnHPc were observed. These spectral features can be assigned to the singlet excited state of ZnHPc from the similarity of the spectral shape with the singlet excited state of Py-ZnHPc as shown in the Figure S2 of Supporting Information. With the delay time, the absorption band due to the singlet excited ZnHPc around 850 nm diminished and new absorption peaks appeared at 720 and 760 nm, which can be assigned to the radical anion of PI and the radical cation of ZnHPc, respectively, from the comparison with the previously reported spectrum and Figure 4.^{9,11,21,22} The lower panel of Figure 5 is a kinetic trace of $\Delta\text{O.D.}$ at 720 nm during the laser flash photolysis. The rise and decay time constants of the absorption band at 720 nm were estimated to be 2.8×10^{10} and 3.6×10^9 s⁻¹, respectively. Because the radical ions appeared with the decay of the singlet excited ZnHPc and the rise time constant is the same as the reciprocal of the fluorescence lifetime of PI-ZnHPc, it can be reasonably concluded that the CS occurred from the singlet excited ZnHPc of the supramolecular donor–acceptor dyad. The decay of the generated ion pair corresponds to CR. Thus, the lifetime of the charge-separated state was calculated to be 280 ps.

The laser flash photolysis experiments were also carried out with phthalimide-ZnHPc dyads. Figure S3 of Supporting Information shows the transient absorption spectra of Cl₂Ph-ZnHPc. In this case, with the decay of the absorption band of single-excited ZnHPc around 850 nm, an absorption peak around 760 nm became obvious. The absorption band around 760 nm can be attributed to the radical cation of ZnHPc, indicating generation of the charge-separated state. The spectral change over several hundreds picosecond coincides with the fluorescence lifetime of Cl₂Ph-ZnHPc, supporting the CS from the singlet excited state. Unfortunately, the lifetime of the charge separated state could not be estimated because of the instrumental limitation. The time constant of CS (k_{CS}) was determined from the fluorescence lifetime according to the relation, $k_{\text{CS}} = \tau_{\text{f}}(\text{A-ZnHPc})^{-1} - \tau_{\text{f}}(\text{Py-ZnHPc})^{-1}$, where $\tau_{\text{f}}(\text{A-ZnHPc})$ and $\tau_{\text{f}}(\text{Py-ZnHPc})$ are τ_{f} of supramolecular dyad and Py-ZnHPc, respectively. The estimated k_{CS} values are summarized in Table 2. It is clear that the k_{CS} values increased with increase in the $-\Delta G_{\text{CS}}$ values.

In the previous paper,⁹ we have reported the CS and CR rates of the supramolecular dyads of ZnPcn with the same set of the axial ligands that act as electron acceptors (Table S1). From the comparison with those of porphyrins, characteristics of ZnPcn supramolecular donor–acceptor dyads, namely, smaller electronic coupling and larger reorganization energy, were elucidated. For comparison, the estimated electron transfer rates (k_{ET} , i.e., k_{CS} and k_{CR}) of ZnHPc supramolecular dyads were plotted against the driving forces (ΔG) as well as the previously obtained data sets of ZnPcn, ZnOEP, and ZnTPP. The k_{ET} rates of ZnHPc are located between those of ZnPcn and porphyrins, when the ΔG values are similar to each other. For example,

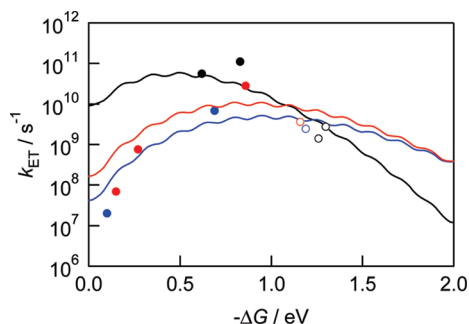


Figure 6. Free energy change ($-\Delta G$) dependence of ET rate (k_{ET} , i.e., k_{CS} (filled circle) and k_{CR} (open circle)) of porphyrins (black), ZnPcn (blue), and ZnHPc (red) complexes. Black curve was calculated using eq 1 by assuming $\lambda_s = 0.05$ eV, $V = 0.002$ eV, $\hbar\langle\omega\rangle = 0.15$ eV, and $\lambda_v = 0.5$ eV for porphyrins. Blue curve for ZnPcn was calculated by changing V and λ_v to 0.0007 and 1.0 eV, respectively. For ZnHPc (red curve), the V and λ_v values were 0.001 and 0.9 eV, respectively.

the k_{CS} values for PI complex are in the order of ZnOEP > ZnTPP > ZnHPc > ZnPcn. Usually, the ET processes can be explained on the basis of the Marcus theory, eqs 1–3,²⁴

$$k_{\text{ET}} = \frac{\pi}{\hbar^2 \lambda_s k_B T} |V|^2 \sum_m (e^{-S} (S^m / m!)) \exp\left(-\frac{(\lambda_s + \Delta G + m\hbar\langle\omega\rangle)^2}{4\lambda_s k_B T}\right) \quad (1)$$

$$\lambda_s = e^2 \left(\frac{1}{2r_D} + \frac{1}{2r_A} - \frac{1}{r} \right) \left(\frac{1}{n^2} - \frac{1}{\epsilon_s} \right) \quad (2)$$

$$S = \frac{\lambda_v}{\hbar\langle\omega\rangle} \quad (3)$$

In eq 1, λ_s is the solvent reorganization energy given by eq 2, V is the electronic coupling, S is the electron-vibration coupling constant given by eq 3, and $\langle\omega\rangle$ is the averaged angular frequency. In eq 2, n is the refractive index. In eq 3, λ_v is the internal reorganization energy. Using the values listed in the footnote of Table 2, the λ_s value was estimated to be 0.05 eV. In Figure 6, eq 1 was calculated as a black curve for porphyrins by assuming λ_v , V , and $\hbar\langle\omega\rangle$ to be 0.5, 0.002, and 0.15 eV, respectively. The calculated curve became wavy due to smaller solvent reorganization energy. Here, 0.5 eV of λ_v was employed, because the λ_v values for ET from the various S_1 -excited Zn porphyrin derivatives have been reported to be 0.3–0.6 eV.²⁵ For ZnPcn dyads, smaller λ_s and $\hbar\langle\omega\rangle$ values had to be assumed as indicated above. The blue curve for ZnPcn was obtained by assuming 1.0 and 0.0007 eV for the λ_v and V values, respectively. As indicated above, the k_{ET} rates of ZnHPc are located between ZnPcn and porphyrins. To reproduce the ΔG dependence of k_{ET} , the red curve was calculated as indicated in Figure 6 by using 0.9 and 0.001 eV of λ_v and V values, respectively. Thus, both λ_v and V values of ZnHPc are also between those of ZnPcn and porphyrins.

To assess the observed tendency of ET rates of ZnHPc supramolecular dyads, MOs were compared with other porphyrinoids. Usually ET rates from the excited porphyrinoids relate to HOMO electronic densities.²⁶ It is well-known that the two HOMOs of Zn porphyrin have a_{1u} and a_{2u} symmetry.²⁷ The substitution of alkyl chains to β -position of pyrrole rings makes

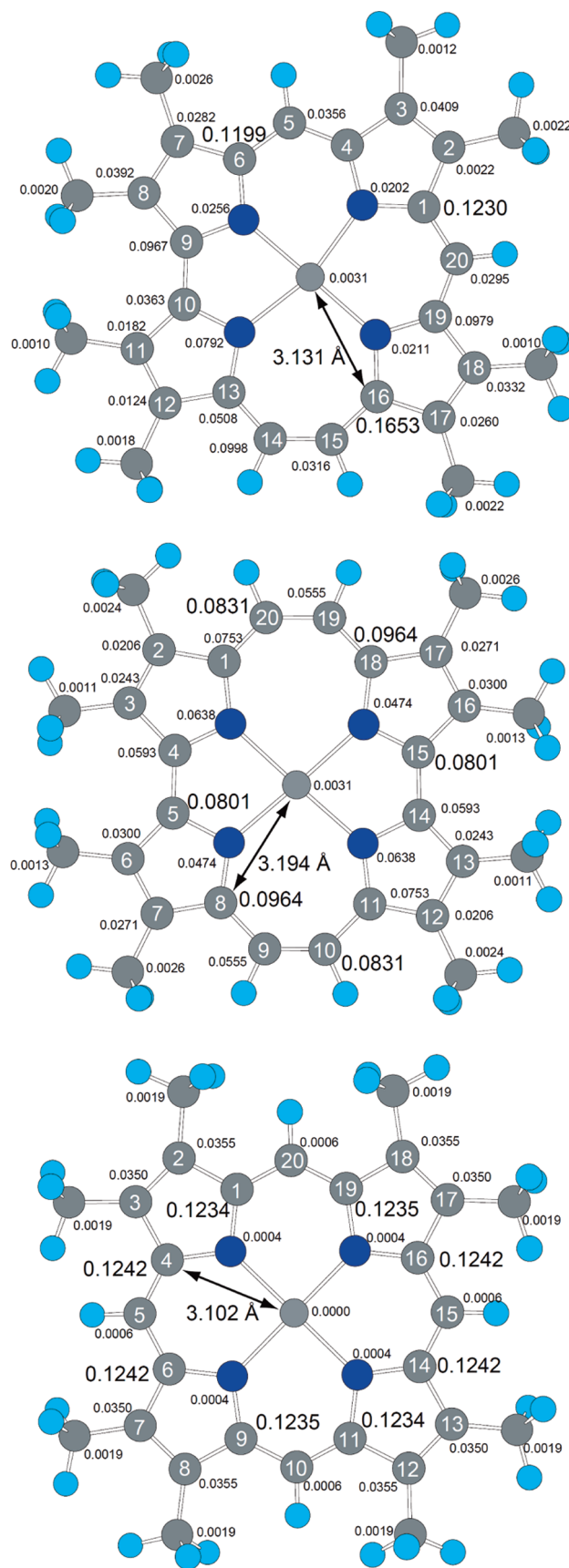


Figure 7. HOMO electron densities of PI-ZnHPc (top), PI-ZnPcn (middle), and PI-ZnOEP (bottom) estimated at B3LYP/6-31G(d) level. PI of each dyad was not drawn to avoid complexity of the figure. Large HOMO electron densities were indicated by larger character size. Arrows indicate the distance between the Zn ion and the carbon with the highest HOMO electron density.

a_{2u} orbital HOMO. As shown in Figure S4, HOMO patterns of ZnHPc and ZnPcn have similar characteristics to that of ZnOEP, that is, absence of a node between α - and β -carbon of pyrrole rings, no electronic density on Zn ion, and so on. This similarity comes from the same substitution patterns. Thus, comparison based on the MO patterns among these porphyrinoids is possible. In Figure 7, HOMO electron densities of these porphyrinoids were indicated. The largest HOMO electron density can be found at the α -carbon of pyrrole ring of each porphyrinoids, that is, C16 of ZnHPc, C8 and C18 of ZnPcn, and C4, C6, C14, and C16 of ZnOEP. In the electronic coupling of donor and acceptor moieties for ET, contribution of these carbons should be larger one. Distance between donor and acceptor is an important factor governing the electronic coupling. Because the same acceptor was employed in the calculation of Figure 7, the distance between Zn ion and the carbon with the largest HOMO electron density reflects the distance for the electronic coupling. The distance was estimated to be 3.13, 3.19, and 3.10 Å for ZnHPc, ZnPcn, and ZnOEP, respectively. This is the same order with that of the estimated V value in Figure 6. Thus, distribution of the HOMO electron density will give a plausible explanation for the variation in the V value for ET dependent on porphyrinoids for supramolecular donor–acceptor dyads. That is, the shorter (longer) distance between the acceptor and the carbon with the largest HOMO electron density accelerates (decelerates) ET in supramolecule of ZnOEP (ZnPcn). It should be noted that the present results indicate importance of molecular design to achieve an efficient ET process, because the efficient ET will become possible with ZnHPc or ZnPcn like ZnOEP if the acceptor is attached at an adequately close position to the carbon with the largest HOMO electron density.

Conclusion

In the present study, we investigated the photoinduced ET processes of supramolecular donor–acceptor dyads of ZnHPc. Because of slightly higher donor-ability and larger excitation energy, various ZnHPc dyad showed ET processes. The transient absorption spectra during the laser flash photolysis were explained on the basis of the ET from the singlet excited ZnHPc. The observed ET rates were located between those observed with porphyrins and ZnPcn supramolecular dyads, even when the $-\Delta G$ values were similar to each other. This observation was explained on the basis of the variation in λ_V and V values. Furthermore, distribution of HOMO electron density gave a plausible explanation for the variation in the V values.

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Supporting Information Available: Molecular orbital patterns of PI-ZnHPc, transient absorption spectra of Py-ZnHPc and Cl₂Ph-ZnHPc, HOMO patterns, and the driving forces and electron transfer rates of relevant compounds. These materials are available free of charge via the Internet at <http://pubs.acs.org>.

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