Axial Ligand Dependences of the Relaxation Dynamics of the Singlet Excited State of Center-to-Edge Phosphorus(V)porphyrin Heterodimers

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Center-to-edge phosphorus(V)porphyrin heterodimers (*meta*-Pm-PCl₂ and *mata*-Pm-P(OPh)₂), composed of a phosphorus(V)tetrakis(4-methoxyphenyl)porphyrin (Pm) and a phosphorus(V)-tetraphenylporphyrin (P) with two chloride (-Cl) or two phenoxide (-OPh) axial ligands were investigated with regard to the relaxation dynamics of the singlet excited state (S1) of the dimers. Under the steady-state photo-excitation of the heterodimers, fluorescence from only the ¹Pm^{*}-P state was observed because of the efficient intramolecular excitation energy transfer. The ¹Pm^{*}-P fluorescence intensity of the dimers was lower than that of the corresponding ¹Pm^{*} monomer and decrease with increasing the solvent polarity. Furthermore, some of the ¹Pm^{*}-P fluorescence decay curves became double-exponential. The fluorescence properties of the heterodimers revealed that ¹Pm^{*}-P equilibrates with (Pm-P)^{CT} and is quenched through the (Pm-P)^{CT} state. A comparison of the photophysical properties of the two heterodimers with different axial ligands suggested that decay through (Pm-P)^{CT} is more obvious for *meta*-Pm-PCl₂ than for *meta*-Pm-P(OPh)₂.

Key words: Phosphorus(V)porphyrin, Heterodimer, Charge Transfer, Solvent Polarity, Axial Ligand.

1. INTRODUCTION

In natural photosynthetic reaction centers (RCs),¹ initial electron transfer in nano-space occurs from the singlet excited state (S1) of a special pair (SP) to a bacteriopheophytin (BPh) unidirectionally.² Recently, it was reported that the mutation of the amino-acid residue around SP controls the initial electron transfer rate.³ On the other hand, several experimental ⁴ and theoretical ⁵ studies have suggested that the excited SP possesses a charge transfer (CT) character. If the CT character of the excited SP can be induced and controlled by the surroundings around SP, the initial unidirectional electron transfer and its dependences on the mutation can be elucidated by the CT character. In fact, the difference of the mutation position varies the CT character of the SP.^{4a} With regard to the CT state of synthesized porphyrin oligomers,⁶ it was reported that the S1 of the directly-linked chlorophyll-porphyrin heterodimers ^{6b} and the face-to-face porphyrin oligomers ^{6c} decays via the CT state. Recently, we have reported that the S1 of phosphorus (V)porphyrin (P(V)porphyrin) arrays decays through the CT state.^{6d-6f, 6i} In wheel-and-axle ^{6d, 6e} and center-to-edge ^{6e, 6f, 6h, 6i} P(V)porphyrin arrays, the contribution of the CT state depended strongly upon the molecular structures of the arrays. With this in mind, we synthesized a new center-to-edge heterodimers ⁶ⁱ in which P(V)tetrakis(4-methoxyphenyl)porphyrin (Pm) and P(V)tetraphenylporphyrin (P) were connected at the meta position of the axial phenoxy bridge of the Pm.⁶ⁱ Since the heterodimers are asymmetric in both the structure and the electronic state, a marked contibition of the CT state is expected. In this study, the electronic perturbation by the axial ligands to the relaxation dynamics of the S1 of the center-to-edge P(V) porphyrin heterodimers (meta-Pm-P(OPh)₂, meta-Pm-PCl₂⁶ⁱ (Fig. 1)) was investigated.

2. EXPERIMENTAL

Axial chloride ligands of dichloro P(V)tetraphenylporphyrin (PCl₂) can be changed to phenoxy ligands.^{6, 7} Meta-Pm-P(OPh)₂ was synthesized by the ligand exchange reaction of meta-Pm-PCl₂ reported previously.⁶¹ As reference monomers, PCl₂,⁶⁷



Fig. 1. Structures of P(V)porphyrin heterodimers

diphenoxy P(V)tetraphenylporphyrin $(P(OPh)_2)$, ^{6f} and diphenoxy P(V)tetrakis(4-methoxyphenyl)porphyrin $(Pm(OPh)_2)$ ⁶ⁱ were used. All samples were purified by column chromatography, and the purity of each sample was checked by thin layer chromatography before each measurement.

The geometry between the two porphyrins in meta-Pm-PCl₂ and meta-Pm-P(OPh)₂ was estimated by ¹H-NMR on the basis of the porphyrin ring current model.⁸ In meta-Pm-P(OPh)₂, the two porphyrin ring was in nearly parallel conformation as was meta-Pm-PCl₂.⁶ⁱ

The absorption and fluorescence spectra were taken using a V-570 UV/VIS/NIR spectrophotometer (JASCO) and a RF-503A spectrofluorimeter (Shimadzu), respectively. The fluorescence quantum yields of the dimers were determined relative to P(OPh)2.^{6f} The fluorescence lifetimes were determined by a twodimensional photon-counting technique using a streak camera (Hamamatus Photonics K. K., C4334 streakscope, time resolution: ca. 15 ps) and the excitation pulse source of a model-locked Ti-sapphire laser (Spectra Physics, Tsunami, frequency-doubled excitation pulse: 400 nm, FWHM: 200 fs). The total apparatus response function was about 30 ps.

3. RESULTS AND DISCUSSION

3.1 Steady-state photophysical properties

The steady-state fluorescence spectra of the heterodimers by the excitation at 440 nm were observed at an energy level near the S1 of Pm(OPh)₂ (Table I), indicating that the heterodimer fluorescence state was assigned as ¹Pm^{*}-P. The absence of fluorescence from Pm-¹P^{*} is due to an efficient intradimer energy transfer from the P unit to the Pm unit. The fluorescences of the dimers were quenched relative to that of the Pm(OPh)₂ monomer, and the fluorescence intensity decreased in highly polar solvents such as acetone and CH₃CN (Table I). The solvent polarity dependence of the fluorescence quantum yield reveals that the ¹Pm^{*}-P decays to the ground state through the CT state of the dimer ((Pm-P)^{CT})).⁶ Interestingly, the *meta*-Pm-PCl₂ fluorescence was more quenched than the meta-Pm-P(OPh)₂ fluorescence (Table I). Furthermore, the fluorescence spectral shape of meta-Pm-PCl₂ differed from that of meta-Pm-P(OPh)₂ and Pm(OPh)₂. Although Pm(OPh)₂ and meta-Pm-P(OPh)₂ clearly had a (1, 0) band even in the polar solvents, the (1, 0)band of meta-Pm-PCl₂ decreased and coalesced to the (0, 0) band in the polar solvents. Additionally, the meta-Pm-PCl₂ fluorescence had larger HWHMs of

the (0, 0) band in the polar solvents than that of the Pm(OPh)₂. The fluorescence features suggest that (Pm-P)^{CT} is more markedly mixed to the ¹Pm^{*}-P of *meta*-Pm-PCl₂ than *meta*-Pm-P(OPh)₂. The mixing of (Pm-P)^{CT} to ¹Pm^{*}-P is considered to be enhanced by the strong electron-accepting character of the PCl₂ unit than the P(OPh)₂ unit and the small steric hindrance of -Cl than -OPh.

The Soret-band and Q-band absorptions of meta-Pm-PCl₂ and meta-Pm-P(OPh)₂ are roughly consistent with the superposition of the corresponding monomers, and no new absorption band was observed. However, the Soret band of the fluorescence excitation spectra of the dimers measured for the ¹Pm^{*}-P fluorescence was not completely identical with that of the absorption spectra of the heterodimers. The difference between the absorption and the fluorescence excitation spectra indicates that the efficiency of the energy transfer from the P unit to the Pm unit is not unity.

3.2 Decay processes of the singlet excited state of the heterodimers

Under the excitation of the heterodimers by a 400 nm laser pulse, both the P unit and the Pm unit were excited. However, no fluorescence rise of $^{1}Pm^{*}$ -P by the excitation energy transfer from the P unit to the Pm unit was observed. Since the total apparatus response function was about 30 ps, the intradimer energy transfer from the P unit to the Pm unit was too fast for the fluorescence rise to be measured.

The ¹Pm^{*}-P fluorescence decays of heterodimers were double-exponential except for that of meta-Pm-P(OPh)₂ in CH₂Cl₂ (Table I), although the ¹Pm^{*} fluorescence decays of Pm(OPh)₂ were single-exponential in all the solvents used in this study. The typical explanations of the doublefluorescence decays of exponential the heterodimers are the presence of the conformers of the dimers 9 or the excited-state equilibrium between the two distinguishable excited states of the dimers.¹⁰ If several conformers of the P(V)porphyrin heterodimers existed as in a former case, the drastic solvent polarity dependences on the decay processes as shown in Table I could not be clearly explained. stable conformers Furthermore. were not confirmed by ¹H-NMR because of the rapid free rotation around a P-O bond of the phenoxy bridge. In a latter case of distinguishable excited states,

Table I. Wavelength, quantum yield, and decay kinetics ² of the fluorescence of phosphorus(V)porphyrin derivatives.

compounds	solvent	λ_{max}/nm [hwł	m/cm^{-1}]	$\Phi_{\rm f}({\rm X}\ 10^{-2})$	C1	$\lambda_1 (X \ 10^9)$		$\lambda_2 (X \ 10^9)$
$Pm(OPh)_2$	CH_2Cl_2	647 [508]	703	4	1	0.51		
	acetone	648 [531]	700	6	1	0.53		
	CH₃CN	648 [544]	700	4	1	0.60		
Meta-Pm-PCl ₂	CH_2Cl_2	649 [558]		0.5	0.74	14	0.26	1.8
	acetone	648 [578]		0.2	0.87	33	0.13	1.2
	CH ₃ CN	647 [605]		0.2	0.90	36	0.10	1.2
Meta-Pm-P(OPh) ₂	CH_2Cl_2	647 [537]	707	3	1	0.71		
	acetone	647 [548]	707	1	0.89	1.6	0.11	0.87
	CH ₃ CN	646 [577]	706	0.7	0.99	1.8	0.01	0.48

^aI(t) = C₁exp($-\lambda_1$ t)+C₂exp($-\lambda_2$ t).



Fig. 2. Outline of typical energy surfaces of S0, ¹Pm^{*}-P, and (Pm-P)^{CT} under weak interaction.

Table II. Rate constants of P(V)porphyrin hetreodoimers.

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compounds	solvent	k_2	k_3	k_4	
Meta-Pm-PCl ₂	CH ₂ Cl ₂	10	2.8	2.2	
	acetone	28	4.0	1.3	
	CH ₃ CN	32	3.4	1.3	
Meta-Pm-P(OPh) ₂	CH_2Cl_2	0.29			
. ,	acetone	1.1	0.047	0.90	
	CH₃CN	1.3	0.013	0.48	

the equilibrium between ${}^{1}Pm^{*}-P$ and $Pm^{-1}P^{*}$ is one of the typical explanations. However, $E[Pm^{-1}P^{*}]$ is about 0.1 eV higher than $E[{}^{1}Pm^{*}-P]$, and no $Pm^{-1}P^{*}$ fluorescence was observed; as a result, the intramolecular back energy transfer from ${}^{1}Pm^{*}-P$ to $Pm^{-1}P^{*}$ can be excluded. Consequently, it can be concluded that the transition from ${}^{1}Pm^{*}-P$ to $(Pm-P)^{CT}$ with the equilibrium between ${}^{1}Pm^{*}-P$ and $(Pm-P)^{CT}$ as shown in Fig. 2 is a reasonable explanation for the decay of the present P(V)porphyrin heterodimers.¹⁰

In the case of the single-exponential decay curve of the meta-Pm-P(OPh)₂ in CH₂Cl₂, the back transition from (Pm-P)^{CT} to ¹Pm^{*}-P (k_3) can be negligible, and the rate constant from the ¹Pm^{*}-P to the (Pm-P)^{CT} (k_2) can be calculated from the Eq. 1, where λ_1 is the reciprocal of the fluorescence lifetime of the ¹Pm^{*}-P and k_1^{6i} is assumed to be the reciprocal of fluorescence lifetime of Pm(OPh)₂.

$$k_2 = \lambda_1 - k_1$$
 (Eq. 1)

On the other hand, the equilibrium between ¹Pm^{*}-P and (Pm-P)^{CT} leads to double-exponential decay according to Eq. 2, where k_1 , k_2 , k_3 , and k_4 are rate constants as indicated in Fig. 2. The λ_1 and λ_2 are the reciprocal of the lifetimes of the two decay components of ¹Pm^{*}-P, and C₁ and C₂ are the relative amplitudes of the two components, respectively. The experimental deta for three solvents are listed in Table I. All the rate constants estimated according to Eq.2 are listed in Table II.

As to the equilibrium between ${}^{1}Pm^{*}-P$ and $(Pm-P)^{CT}$, the driving forces of the k_2 and k_3 determined by the difference between $E[{}^{1}Pm^{*}-P]$ and $E[(Pm-P)^{CT})]$

$$\lambda_{1} = \frac{1}{2} \left[(X + Y) + \sqrt{(X - Y)^{2} + 4k_{2}k_{3}} \right]$$
$$\lambda_{2} = \frac{1}{2} \left[(X + Y) - \sqrt{(X + Y)^{2} + 4k_{2}k_{3}} \right]$$
$$X = k_{1} + k_{2} \quad Y = k_{3} + k_{4} \quad C = \frac{X - \lambda_{2}}{\lambda_{1} - \lambda_{2}} \quad (Eq. 2)$$

are very small values in the normal region of the Marcus theory.¹¹ The solvent dependences of k_2 and k_3 of *meta*-Pm-P(OPh)₂ seemed to be explained by the typical electron transfer along with the Marcus theory.¹¹ However, both k_2 and k_3 were considerably large in *meta*-Pm-PCl₂. Since the two heterodimers have same geometry between the two porphyrins, the kinetical difference should be attributed to the difference of the axial ligands.

The central Pm unit in the heterodimers has an electron-donating methoxy group at the 4-position of the meso-phenyl groups. Thus, the energy level of Pm^+-P^- is lower than that of $Pm^{-}P^{+}$, and the contribution of $Pm^{+}P^{-}$ to $^{1}Pm^{*}P$ is considered to be larger than that of Pm^--P^+ . Since the reduction potential of PCl_2 is higher than that of $P(OPh)_2$,^{6h} the $E[Pm^+-P^-]$ of meta-Pm-PCl₂ is lower than that of meta-Pm-P(\overline{OPh})₂. Although the difference of k_2 seemed to be due to the driving force, the k_3 cannot be explained by the driving force alone.¹¹ Particularly, the very fast back electron transfer rate k_3 of meta-Pm-PCl₂ compared to that of meta-Pm-P(OPh)₂ cannot be explained by the typical electron transfer.¹¹ As described for the steady-state fluorescence properties, the mixing of (Pm-P)^{CT} to ¹Pm^{*}-P is considered to be enhanced by the strong electron accepting character of the PCl₂ unit than the P(OPh)₂ unit and by the small steric hindrance of -Cl than -OPh. Therefore, the excited state equilibrium between ¹Pm^{*}-P and (Pm-P)^{CT} should also be enhanced for the same reason. Since the mixings of $(Pm-P)^{CT}$ to ${}^{1}Pm^{*}-P$ and of ${}^{1}Pm^{*}-P$ to (Pm-P)^{CT} might change the nuclear coordinations of both ¹Pm^{*}-P and (Pm-P)^{CT}, the activation energy of the



Fig. 3. Outline of partly mixed energy surfaces of S0, $^{1}Pm^{*}-P$, and $(Pm-P)^{CT}$ under strong interaction, where complete S1 and ion pair surfaces shown by the dotted line are partly mixed to form a solid line.

excited state equilibrium is considered to decrease in the case of meta-Pm-PCl₂. In addition, the enhancement of electronic coupling between ¹Pm^{*}-P and (Pm-P)^{CT} should occur as depicted in Fig. 3. In the strong coupling condition, the typical outer-sphere electron transfer is not adequate.

As for the charge recombination to the ground state, k_4 of *meta*-Pm-PCl₂ is larger than that of the *meta*-Pm-P(OPh)₂. The energy-gap between the (Pm-P)^{CT} and the S0 of the heterodimers is sufficiently large and, in the inverted region,¹¹ the difference of the k_4 between *meta*-Pm-P(OPh)₂ and *meta*-Pm-PCl₂ seemed to be explained by the typical electron transfer theory. However, the solvent-polarity dependence of k_4 of each heterodimer did not follow the typical energy gap law as in previous study.⁶¹ Since the mixing of ¹Pm^{*}-P to (Pm-P)^{CT} might change the nuclear coordination of (Pm-P)^{CT}, the decay from (Pm-P)^{CT} to S0 should not be the typical outer-sphere electron transfer but have some of the feature of the intramolecular nonradiative transition through the vibrational levels.¹²

CONCLUSION

In this study, the comparison of the photophysical properties of meta-Pm-P(OPh)₂ and meta-Pm-PCl₂ suggests that the axial ligand is important for the decay kinetics of S1 through the CT state. The mechanism may provide an important clue to the unidirectional electron transfer in the nano-space as observed for the excited SP in RCs.

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