Geometry and Solvent-Polarity Dependences of the Relaxation Dynamics of the Singlet Excited State of Center-to-Edge Phosphorus(V) Porphyrin Heterodimers

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Received: December 6, 2004; In Final Form: December 10, 2005

Para- and meta-isomers of center-to-edge phosphorus(V) porphyrin heterodimers (*p*- and *m*-Pm−PCl_2) composed of a phosphorus(V) tetraphenylporphyrin (P) and a phosphorus(V) tetrakis(4-methoxyphenyl)-porphyrin (Pm) were synthesized to investigate the geometry and solvent-polarity dependences of the relaxation dynamics of the lowest singlet excited state (S1) of the porphyrin dimer. The geometrical difference between *m*- and *p*-Pm−PCl_2 in solution was confirmed by ^{1}H NMR on the basis of the porphyrin ring current model. By the photoexcitation of the dimers, only the fluorescence from ^{1}Pm*−P was observed in both dimers because of the efficient singlet energy transfer from the higher energy ^{1}P* to the lower energy ^{1}Pm*. However, the ^{1}Pm*−P fluorescence had features that differ from the typical fluorescence from monomeric ^{1}Pm*, especially for the solvent-polarity dependence of the quantum yields. Furthermore, all the fluorescence decay curves of ^{1}Pm*−P were double-exponential. The special fluorescence features of ^{1}Pm*−P are due to the equilibrium between ^{1}Pm*−P and the charge-transfer (CT) excited state of the dimer ((Pm−P)^{CT}). By the excited-state equilibrium, ^{1}Pm*−P is efficiently quenched through (Pm−P)^{CT} in highly polar solvents. The contribution of (Pm−P)^{CT} to the decay process of ^{1}Pm*−P is more remarkable in *m*-Pm−PCl_2 than in *p*-Pm−PCl_2, depending on the interaction between the two porphyrin π-systems in the heterodimer.

Introduction

A very large number of porphyrin oligomers,[1−3] which mimic the chromophoric sequence of the photosynthetic reaction centers (RCs),[4−8] have been synthesized and investigated to elucidate the electron-transfer function of natural photosynthetic systems.[9−11] Among the porphyrin oligomers, studies on excited dimers are important for the understanding of the initial electron transfer from a special pair (SP).[9−11] Early studies on photochemical hole-burning experiments[12−15] and Stark-effect spectroscopy[16,17] of the RCs have suggested that the photoexcited SP possesses a charge-transfer (CT) character. From the theoretical aspect,[18−20] the CT character has also been discussed on the molecular orbital of the excited state of the SP.[20] As to the contribution of the CT state in the photoinduced electron transfer of the model systems, directly linked chlorophyll−porphyrin heterodimers were reported by Wasielewski et al.[21] Other porphyrin oligomers possessing similar properties were also reported by Tran-Thi et al.[22]

Recently, we reported that the lowest singlet excited state (S1) of phosphorus(V) porphyrin (P(V)porphyrin) oligomers, namely *wheel-and-axle* and *center-to-edge* P(V)porphyrin arrays, decayed via the CT state.[23] The P(V)porphyrin arrays were composed of *homo-chromophores* except for a difference in the axial ligands. In the case of wheel-and-axle P(V)porphyrin dimers, in which the central phosphorus atoms of two tetraphenylporphyrins were connected to each other by various lengths of the alkyldioxy bridge, the S1 decayed via the CT state only in the highly polar and water-containing solvent in which the two porphyrin rings were stacked.[23a] The CT decay process was enhanced for a symmetry-disturbed dimer, in which one of the central phosphorus atoms of the P(V)porphyrin dimer connects to a trifluoroethoxy terminal axial group.[23a] The decay enhancement was quite remarkable for center-to-edge P(V)porphyrin dimers, in which the central phosphorus atom of one P(V)-porphyrin connects to the *meso*-phenoxy edge of the other.[23b,c] In this case, the two monomer units have an asymmetrical orientation to each other, which allows the relaxation through the CT in the dimers.[24] However, their structure was still far from the partly stacked SP in the geometry. Thus, studies on the CT contribution to the excited state of bichromophores, in which the π planes are fixed more closely to each other, are important.

Since the geometry of the center-to-edge P(V)porphyrin dimers can be varied by the substitution position of the phenoxy bridge, we can investigate the geometry dependence of the decay process by using the P(V)porphyrin dimers. In this study, para- and meta-isomers of center-to-edge P(V)porphyrin *heterodimers* (*p*- and *m*-Pm−PCl_2 (Figure 1)), composed of a phosphorus-(V) tetrakis(4-methoxyphenyl)porphyrin (Pm) as the center unit and a phosphorus(V) tetraphenylporphyrin (P) as the edge one, were synthesized and investigated with regard to the geometry and solvent-polarity dependences of the relaxation dynamics of the S1.

Since Pm has a relatively higher electron-donating level than P in the reported center-to-edge P(V)porphyrin dimers,[23b,23c] the energy levels of the CT state of the heterodimers will be lower than those in the reported model;[23c] as a result, the marked contribution of the CT state on the decay process of S1 is expected in both *p*- and *m*-Pm−PCl_2 heterodimers. Since the CT state of the heterodimers is not a contact ion pair as reported on the tightly stacked porphyrin heterodimer,[25] it is expected to be a good model for the medium-coupled CT state as a

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10.1021/jp044468q CCC: $33.50
Published on Web 02/17/2006

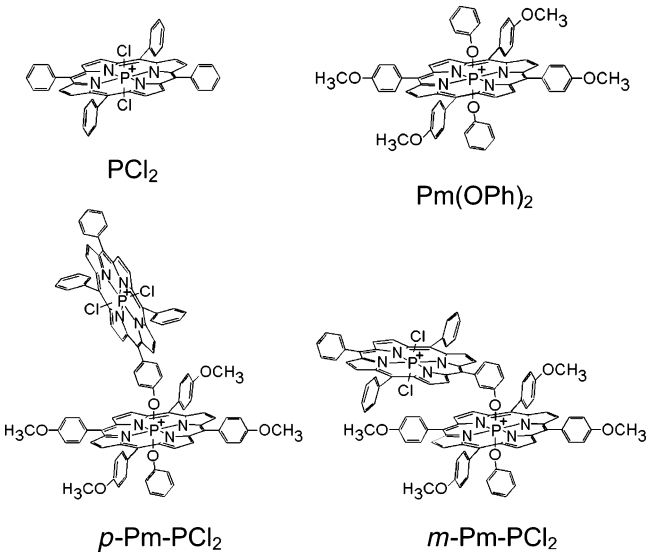

Figure 1. Structures of phosphorus(V) porphyrin monomers and heterodimers.

bacteriochlorophyll−bacteriopheophytin heterodimer in a genetically modified bacterial reaction center.[26,27]

Experimental Section

Materials. Since the axial ligands of dichlorophosphorus(V) porphyrin are easily converted to stable axial ligands,[23,28−40] a series of P(V)porphyrin oligomers was obtained.[23,34,37,38,40,41] In this study, the heterodimers (*p*- and *m*-Pm−PCl_2, Figure 1) were synthesized by reaction of dichlorophosphorus(V) tetrakis(4-methoxyphenyl)porphyrin chloride ($PmCl_2$) with 5-(hydroxyphenyl)-10,15,20-triphenylporphyrin ($H_2TPP(OH)$)[42] and phenol followed by the insertion of a phosphorus atom to the free-base moiety. The heterodimers were characterized by UV−vis, ^{1}H NMR, and FAB mass spectra. Diphenoxyphosphorus(V) tetrakis(4-methoxyphenyl)porphyrin, $Pm(OPh)_2$, was synthesized as described previously.[23]

Diphenoxyphosphorus(V) Tetrakis(4-methoxyphenyl)porphyrin Chloride, $Pm(OPh)_2$. Tetrakis(4-methoxyphenyl)porphyrin (1.63 g, 2.22 mmol) and phosphorus oxychloride ($POCl_3$, 9 mL) were dissolved and refluxed in dry pyridine (8.5 mL) under nitrogen for 24 h. After the solvent and excess $POCl_3$ were removed in vacuo, the residues were separated by column chromatography on silica gel with $CHCl_3$−MeOH (5:1) to yield pure dichlorophosphorus(V) tetrakis(4-methoxyphenyl)porphyrin ($PmCl_2$; 71.5%). UV−vis (CH_2Cl_2; λ_{max}, nm): 460, 579, 630. ^{1}H NMR (500 MHz, $CDCl_3$): δ 4.01 (s, 12H, methoxy-H of *meso*-phenyl group), 7.28 (d, 8H, J_{H-H} = 8.5 Hz, *meso*-*m*-phenyl-H), 7.88 (d, 8H, J_{H-H} = 8.5 Hz, *meso*-*o*-phenyl-H), 9.10 (d, 8H, J_{P-H} = 4.5 Hz, β-H). FAB/MS: *m*/*z* 833 (M^+).

$PmCl_2$ (0.1 g, 0.12 mmol) and phenol (0.017 g, 0.18 mmol) were dissolved and refluxed in dry pyridine (3 mL) under nitrogen for 24 h. After the solvent was removed in vacuo, the residues were separated by column chromatography on silica gel with $CHCl_3$−MeOH (5:1) to yield pure $Pm(OPh)_2$ (50.0%). UV−vis ($CHCl_3$; λ_{max}, nm (ϵ)): 455 (166 000), 573 (12 400), 621 (13 600). ^{1}H NMR (500 MHz, $CDCl_3$): δ 2.21 (d, 4H, J_{H-H} = 7.5 Hz, axial *o*-phenyl-H), 4.01 (s, 12H, methoxy-H of *meso*-phenyl group), 5.92 (d, 4H, J_{H-H} = 7.5 Hz, axial *m*-phenyl-H), 6.11 (d, 2H, J_{H-H} = 7.5 Hz, axial *p*-phenyl-H), 7.24 (d, 8H, J_{H-H} = 8.5 Hz, *meso*-*m*-phenyl-H), 7.68 (d, 8H, J_{H-H} = 8.5 Hz, *meso*-*o*-phenyl-H), 9.03 (d, 8H, J_{P-H} = 3.5 Hz, β-H). FAB/MS: *m*/*z* 949 (M^+).

***p*-Pm-PCl_2.** $PmCl_2$ (0.302 g, 0.36 mmol), 5-(4-hydroxyphenyl)-10,15,20-triphenylporphyrin (0.289 g, 0.46 mmol), and phenol (0.033 g, 0.35 mmol) were dissolved and refluxed in dry pyridine (10 mL) under nitrogen for 24 h. After the solvent was removed in vacuo, the residues were separated by column chromatography on silica gel with $CHCl_3$−MeOH (5:1) to yield the crude product containing *p*-Pm−H_2 (FAB/MS: *m*/*z* 1485 (M^+)). The crude product containing *p*-Pm−H_2 (0.171 g) and $POCl_3$ (2 mL) was dissolved and refluxed in dry pyridine (2 mL) under nitrogen for 2 days. The solvent and excess $POCl_3$ were removed in vacuo. The residues were separated by column chromatography on silica gel with $CHCl_3$−MeOH (5:1) to yield *p*-Pm−PCl_2 (0.015 g). UV−vis ($CHCl_3$; λ_{max}, nm (ϵ)): 443 (323 000), 572 (25 200), 620 (21 300). ^{1}H NMR (500 MHz, $CDCl_3$): δ 2.31 (d, 2H, J_{H-H} = 7.5 Hz, axial *o*-phenyl-H of the center porphyrin), 2.72 (d, 2H, J_{H-H} = 8.5 Hz, bridge *o*-phenyl-H), 3.98 (s, 12H, methoxy-H of *meso*-phenyl group of the central porphyrin), 5.95 (t, 2H, J_{H-H} = 7.5 Hz, axial *m*-phenyl-H of the central porphyrin), 6.13 (t, 1H, J_{H-H} = 7.5 Hz, axial *p*-phenyl-H of the central porphyrin), 6.69 (d, 2H, J_{H-H} = 7.5 Hz, bridge *m*-phenyl-H), 7.91−7.89 (m, 6H, *meso*-*o*-phenyl-H of the distal porphyrin), 7.84 (d, 8H, J_{H-H} = 6.5 Hz, *meso*-*o*-phenyl-H of the central porphyrin), 7.77−7.73 (m, 9H, *meso*-*m*,*p*-phenyl-H of the distal porphyrin), 7.26 (d, 8H, J_{H-H} = 8.0 Hz, *meso*-*m*-phenyl-H of the central porphyrin), 8.30 (dd, 2H, J_{P-H} = 4.5 Hz, 3,7-β-H of the distal porphyrin), 8.93 (dd, 2H, J_{P-H} = 4.5 Hz, 2,8-β-H of the distal porphyrin), 8.96 (dd, 4H, J_{P-H} = 4.0 Hz, 12,13,17,18-β-H of the distal porphyrin), 9.12 (d, 8H, J_{P-H} = 3.5 Hz, β-H of the central porphyrin). FAB/MS: *m*/ *z* 1585 (M^+).

***m*-Pm-PCl_2.** $PmCl_2$ (0.194 g, 0.23 mmol), 5-(3-hydroxyphenyl)-10,15,20-triphenylporphyrin (0.188 g, 0.30 mmol), and phenol (0.0194 g, 0.21 mmol) were dissolved and refluxed in dry pyridine (10 mL) under nitrogen for 24 h. After the solvent was removed in vacuo, the residues were separated by column chromatography on silica gel with $CHCl_3$−MeOH (5:1) to yield the crude product containing *m*-Pm−H_2 (FAB/MS: *m*/*z* 1485 (M^+)). The crude product containing *m*-Pm−H_2 (0.427 g) and $POCl_3$ (2.5 mL) was dissolved and refluxed in dry pyridine (4 mL) under nitrogen for 2 days. The solvent and excess $POCl_3$ were removed in vacuo. The residues were separated by column chromatography on silica gel with $CHCl_3$−MeOH (5:1) to yield *m*-Pm−PCl_2 (0.022 g) UV−vis ($CHCl_3$; λ_{max}, nm (ϵ)): 441 (344 000), 571 (24 800), 618 (18 700). ^{1}H NMR (500 MHz, $CDCl_3$): δ 2.13 (d, 2H, J_{H-H} = 7.5 Hz, axial *o*-phenyl-H of the central porphyrin), 2.58 (d, 2H, J_{H-H} = 8.0 Hz, bridge *o*-phenyl-H), 3.90 (s, 12H, methoxy-H of the *meso*-phenyl group of the central porphyrin), 5.84 (t, 2H, J_{H-H} = 7.5 Hz, axial *m*-phenyl-H of the center porphyrin), 6.04 (t, 1H, J_{H-H} = 7.5 Hz, axial *p*-phenyl-H of the central porphyrin), 6.51 (t, 1H, J_{H-H} = 7.5 Hz, bridge *m*-phenyl-H), 6.93 (d, 8H, J_{H-H} = 7.5 Hz, *meso*-*m*-phenyl-H of the central porphyrin), 7.45 (s, 8H, *meso*-*o*-phenyl-H of the central porphyrin), 7.77−7.76 (m, 6H, 10,-20-*meso*-*m*,*p*-phenyl-H of the distal porphyrin), 7.81−7.80 (m, 3H, 15-*meso*-*m*,*p*-phenyl-H of the distal porphyrin), 7.93 (dd, 4H, J_{P-H} = 2.0 Hz, J_{H-H} = 7.0 Hz, 10,20-*meso*-*o*-phenyl-H of the distal porphyrin), 8.00 (dd, 2H, J_{P-H} = 3.0 Hz, J_{H-H} = 7.5 Hz, 15-*meso*-*o*-phenyl-H of the distal porphyrin), 8.05 (dd, 2H, J_{P-H} = 5.0 Hz, J_{H-H} = 5.0 Hz, 3,7-β-H of the distal porphyrin), 8.93 (s, 8H, β-H of the central porphyrin), 9.09 (dd, 2H, J_{P-H} = 5.0 Hz, J_{H-H} = 5.0 Hz, 2,8-β-H of the distal porphyrin), 9.10 (dd, 2H, J_{P-H} = 5.0 Hz, J_{H-H} = 5.0 Hz, 12,18-β-H of the distal porphyrin), 9.13 (dd, 2H, J_{P-H} = 5.0 Hz, J_{H-H} = 5.0 Hz, 13,17-β-H of the distal porphyrin). FAB/MS: *m*/*z* 1585 (M^+)).

Measurement. The ^{1}H NMR spectra were measured with a JNM-A 500 (500 MHz) FT-NMR spectrometer (JEOL). The

absorption and fluorescence spectra were taken using a V-570 UV−vis−near-IR spectrophotometer (JASCO) and an RF-503A spectrofluorimeter (Shimadzu), respectively. The fluorescence quantum yields of the dimers were determined relative to diphenoxyphosphorus(V) tetraphenylporphyrin, $(PhO)_2P(V)TPP$ ($\Phi_f = 0.037$ in CH_2Cl_2, $\Phi_f = 0.014$ in acetone, and $\Phi_f = 0.016$ in CH_3CN).[23]

The fluorescence lifetimes were determined by a two-dimensional photon-counting technique using a streak camera (Hamamatsu Photonics K. K., C4334 steakscope) and the excitation pulse source of a model-locked Ti-sapphire laser (Spectra Physics, Tsunami; frequency-doubled excitation pulse: 400 nm). The total apparatus response function was about 30 ps. A glass cutoff filter was used to isolate the fluorescence from the scattered laser light.

All the samples were carefully purified by column chromatography, and the purity of each sample was checked by thin-layer chromatography before each measurement.

Results and Discussion

Geometry of the Center-to-Edge P(V)Porphyrin Heterodimers. The induced magnetic fields of the porphyrin ring strongly affect the chemical shifts of the ^1H NMR, where the simple ring current model can be applied to understand the chemical shifts.[43−46] According to the model, the ring current shifts are determined by the distance and orientation to the porphyrin ring (Figure 2a). In the case of the porphyrin dimer, one porphyrin shifts the signal of the proton on the other porphyrin relative to the corresponding monomers; therefore, the conformations of the porphyrin rings can be estimated from the shifts.

In *p*-Pm−PCl_2, all β and axial protons on the Pm unit showed downfield shifts compared to the corresponding monomer Pm-$(OPh)_2$ (Table 1), indicating that the Pm unit is in the deshielding region of the ring current of the P unit (Figure 2b). On the other hand, all β protons on the P unit, which were inequivalent, showed upfield shifts depending on the distance to the Pm unit, indicating that the P unit is in the shielding region (Figure 2b). The opposite ring current effects in Pm and P can be explained if the two porphyrins are nearly perpendicular to each other, as depicted in Figure 2b. Since further anisotropic splitting was not observed for the four *meso*-4-methoxyphenyl groups on the Pm unit, the rotation around the *p*-phenylene bridge would be fast enough to conceive of the four meso-groups as equivalent at room temperature.

On the other hand, all the protons on the Pm unit in the *m*-Pm−PCl_2 showed upfield shifts (Table 1), confirming that the Pm unit is in the shielding region of the P unit (Figure 2c). Although no further anisotropic splitting of *m*-Pm−PCl_2 was observed for the four 4-methoxyphenyl groups on the Pm unit due to the rotation around the bridge *m*-phenylene as well as the *p*-Pm−PCl_2, the resonances of the β and *meso*-*o*-phenyl protons on the Pm unit were considerably broadened (Supporting Information Figure 1), suggesting that the P unit rotates near the Pm unit in parallel, as shown by a rotating arrow in Figure 2c. The β protons on the P unit of *m*-Pm−PCl_2 were also inequivalent and shifted to the upfield region as did those of *p*-Pm−PCl_2. The shift of the β protons nearest to the bridge (β1) was larger than that of the para-derivative, whereas the β protons (β3 and β4) opposite to the bridge showed very small upfield shifts (Table 1). To explain the results, the plane of the P unit in *m*-Pm−PCl_2 should be nearer the Pm unit than the para-derivative, and the two porphyrin rings in *m*-Pm−PCl_2 should be in nearly parallel conformation, as shown in Figure 2c.

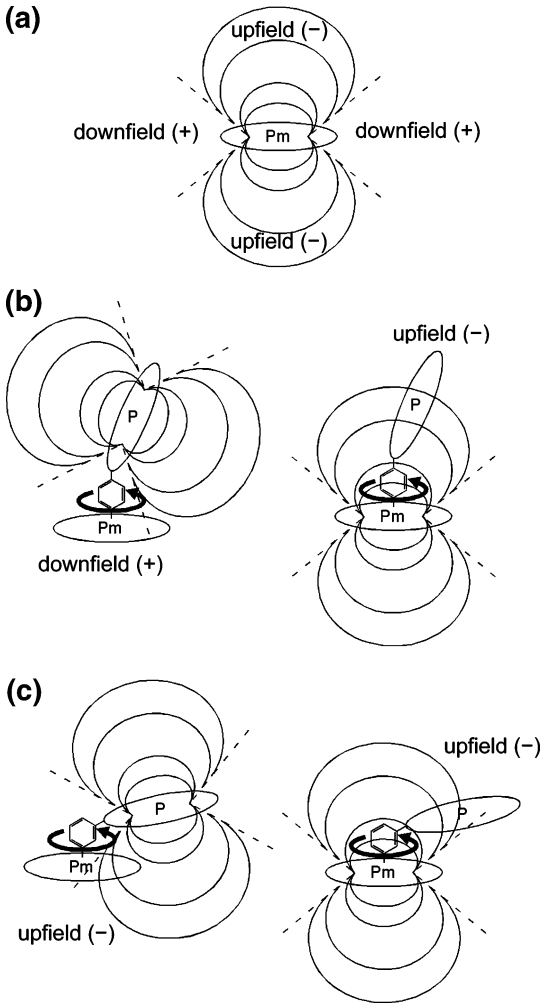

Figure 2. Shielding (upfield(−)) and deshielding (downfield(+)) regions of the P(V)porphyrin monomer (a) and heterodimers, *p*-Pm−PCl_2 (b) and *m*-Pm−PCl_2 (c).

Steady-State Absorption and Fluorescence Properties. The absorption maxima of PCl_2, $Pm(OPh)_2$, *p*-Pm−PCl_2, and *m*-Pm−PCl_2 were slightly blue-shifted as the solvent polarity was increased (Table 2). This is a typical feature of P(V)-porphyrins.[23] The absorption spectra of the heterodimers were roughly consistent with the superposition of PCl_2 and $Pm(OPh)_2$, and a new absorption band was not observed (Figure 3, Supporting Information Figure 2). However, the main Soret band assigned to the P unit absorption was much weaker than that of the PCl_2 monomer.[23] The hypochromic effect of the absorption spectra for the dimer suggested a $\pi-\pi$ interaction.[47] Interestingly, the absorption spectra of *m*-Pm−PCl_2 were slightly different from those of *p*-Pm−PCl_2 in each solvent, revealing that the inter-porphyrin interactions in the heterodimers are dependent on the geometry.

The steady-state fluorescence spectra of the heterodimers were assigned as the emission from $^1Pm^*-P$ (Figure 4, Supporting Information Figure 3) suggesting efficient intradimer singlet energy transfer from higher energy $Pm-^1P^*$ to lower energy $^1Pm^*-P$, as shown in Table 2. The half-width at half-maximums (hwhms) of the (0, 0) fluorescence band of the heterodimers were slightly larger than those of the $Pm(OPh)_2$ monomer, and the (1, 0) band of the heterodimers broadened, particularly in the highly polar solvents. These results suggested that the $^1Pm^*-P$ had, to some degree, a weak CT character and the vibrational structure of the $^1Pm^*-P$ fluorescence had become obscured.

TABLE 1: ^{1}H NMR of P(V)Porphyrin Monomers and Heterodimers[a]

	$\delta_{P-\beta}$	$\delta_{Pm-\beta}$	$\delta_{Pm-meso-o-Ph}$	$\delta_{Pm-meso-m-Ph}$	$\delta_{Pm-axial-o-Ph}$	$\delta_{Pm-axial-m-Ph}$	$\delta_{Pm-axial-p-Ph}$
PCl_2	9.15						
$Pm(OPh)_2$		9.03	7.68	7.24	2.21	5.92	6.11
p-Pm−PCl_2	8.30 (−0.85)	9.12 (+0.09)	7.84 (+0.16)	7.26 (+0.02)	2.31 (+0.10)	5.95 (+0.03)	6.13 (+0.02)
	8.93 (−0.22)						
	8.96 (−0.19)						
m-Pm−PCl_2	8.05 (−1.1)	8.93 (−0.10)	7.45 (-0.23)	6.93 (−0.31)	2.13 (−0.08)	5.84 (−0.08)	6.04 (−0.07)
	9.09 (−0.06)						
	9.10 (−0.05)						
	9.13 (−0.02)						

[a] The chemical shift difference, $\Delta\delta$, between the heterodimer and the corresponding monomers is in parentheses.

TABLE 2: Absorption and Fluorescence Data of P(V)porphyrin Monomers and Heterodimers at Room Temperature

compd	solvent	absorption [fluorescence excitation][a] λ_{max}/nm			fluorescence[b] λ_{max}/nm [hwhm/cm^{-1}]		$E(S_1)$/eV	Φ (10^{-2})
		Soret band	Q (0.1) band	Q (0.0) band	Q (0.0) band	Q (1.0) band		
PCl_2	CH_2Cl_2	439 [440]	568 [567]	612 [609]	621 [305]	677	2.00	1
	acetone	437 [437]	567 [566]	611 [609]	622 [307]	677	1.99	1
	CH_3CN	436 [436]	566 [566]	610	621 [360]	676	2.00	1
$Pm(OPh)_2$	CH_2Cl_2	453 [453]	572 [569]	619 [620]	647 [508]	703	1.92	4
	acetone	451 [451]	571 [568]	619 [618]	648 [531]	700	1.91	6
	CH_3CN	449 [450]	570 [568]	618 [618]	648 [544]	700	1.91	4
p-Pm−PCl_2	CH_2Cl_2	442 [445]	571 [569]	619 [620]	650 [577]		1.91	0.9
	acetone	440 [440]	570 [570]	617	648 [612]		1.91	0.3
	CH_3CN	438 [444]	569 [568]	616	647 [597]		1.92	0.4
m-Pm−PCl_2	CH_2Cl_2	440 [444]	571 [570]	617 [620]	649 [558]		1.91	0.5
	acetone	438 [438]	570 [565]	616	646 [578]		1.92	0.2
	CH_3CN	437 [438]	569 [564]	615	645 [605]		1.92	0.2

[a] Fluorescence excitation spectra were measured for the emission at 700 nm. [b] Fluorescence spectra were measured by the excitation at 440 nm.

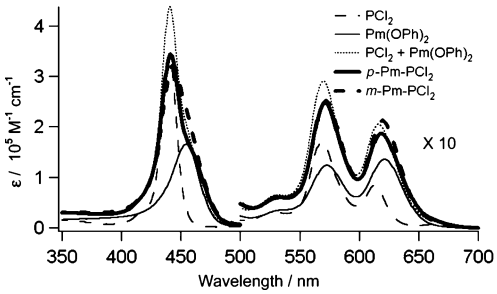

Figure 3. Soret and Q band absorption spectra of P(V)porphyrin monomers and heterodimers in $CHCl_3$.

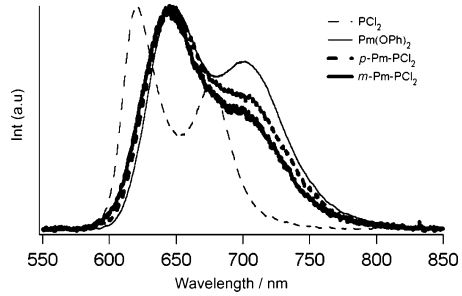

Figure 4. Fluorescence spectra of P(V)porphyrin monomers and heterodimers with excitation at 440 nm in CH_3CN. The intensities are normalized at each maximum. The fluorescence spectra are independent of excitation wavelength.

A simple expression of the real wave function of ^{1}Pm*−P ($\Psi[^1Pm^*-P]$) is given by the linear combination of the pure S1 completely localized on the Pm unit ($\Psi[^1Pm^*]$) and the pure intradimer CT state ($\Psi[(Pm-P)^{CT}]$), as shown in eq 1, where α and $(1-\alpha^2)^{1/2}$ are the relative amplitudes of the two components, $\Psi[^1Pm^*]$ and $\Psi[(Pm-P)^{CT}]$, respectively.

$$\Psi[^1Pm^* - P] = \alpha\Psi[^1Pm^*] + (1-\alpha^2)^{1/2}\Psi[(Pm-P)^{CT}] \quad (1)$$

In the case of the present P(V)porphyrin dimers, the energy of $(Pm-P)^{CT}$ ($E[(Pm-P)^{CT}]$) is very close to that of ^{1}Pm* ($E[^1Pm^*]$).[40] Since the mixing of the two states is dependent on the energy gap between $E[^1Pm^*]$ and $E[(Pm-P)^{CT}]$, which falls with increasing solvent polarity, the value of α depends on the solvent polarity. Consequently, the CT character of $\Psi[^1Pm^*-P]$ was enhanced in the highly polar solvent. The main CT state is probably Pm^+-P^- because the Pm unit has the electron-donating *meso*-methoxylphenyl groups and PCl_2 is a good electron acceptor.[40] Strictly speaking, Pm^+-P^- should be represented by $Pm^{\delta+}-P^{\delta-}$. However, the δ would be very close to unity; thus, "Pm^+-P^-" is appropriate in the heterodimers.

The fluorescences of the dimers were quenched compared to those of the $Pm(OPh)_2$ monomer, and the quenchings were enhanced in the polar solvents (Table 2). The fluorescence quantum yields of *m*-Pm−PCl_2 were smaller than those of *p*-Pm−PCl_2 in each solvent. The solvent-polarity dependence reveals the transition from ^{1}Pm*−P to non-emissive $(Pm-P)^{CT}$, which decays to ^{1}Pm*−P or to the ground state nonradiationally.

The fluorescence excitation spectra of the PCl_2 monomer and the $Pm(OPh)_2$ monomer coincided with the absorption spectra (Table 2). However, the fluorescence excitation spectra of the heterodimers measured for the fluorescence of the Pm unit were not identical to the absorption spectra of the dimers (Table 2, Figure 5 and Supporting Information Figure 4). The differences between the absorption spectra and the fluorescence excitation spectra indicate that the efficiency of the energy transfer from the P unit to the Pm unit is not unity. Furthermore, the solvent dependence of the fluorescence excitation spectra suggests that the energy-transfer efficiency is dependent on the solvent property.

Decay Processes of the Singlet Excited State of the Heterodimers. The time-resolved fluorescence spectra of the dimers were measured by a two-dimensional photon-counting technique using a streak camera and the 400 nm excitation pulse of a frequency-doubled model-locked Ti-sapphire laser pulse.

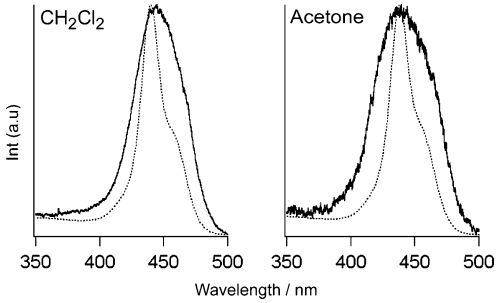

Figure 5. Comparison of absorption (dotted line) and flurorescence excitation (solid line) spectra of *m*-Pm−PCl_2 in CH_2Cl_2 and acetone. The fluorescence was monitored at 700 nm. The intensities are normalized at the maximum. The fluorescence excitation spectra are independent of the monitored fluorescence wavelength.

TABLE 3: Fluorescence Decay Kinetics of P(V)porphyrin Monomer and Heterodimers

compd	solvent	C_1	λ_1 ($\times 10^9$)	C_2	λ_2 ($\times 10^9$)
$Pm(OPh)_2$	$CHCl_3$	1	0.44		
	CH_2Cl_2	1	0.51		
	acetone	1	0.53		
	$CHCN_3$	1	0.60		
	DMSO[a]	1	0.42		
p-Pm−PCl_2	CH_2Cl_2	0.85	6.0	0.15	1.1
	acetone	0.93	21	0.07	1.2
	CH_3CN	0.93	17	0.07	1.0
m-Pm−PCl_2	$CHCl_3$	0.65	5.1	0.35	1.5
	CH_2Cl_2	0.74	14	0.26	1.8
	acetone	0.87	33	0.13	1.2
	CH_3CN	0.90	36	0.10	1.2
	DMSO	0.87	42	0.13	0.97

[a] DMSO = dimethyl sulfoxide.

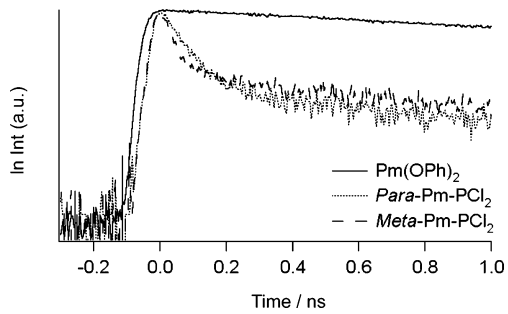

Figure 6. Fluorescence decays of P(V)porphyrin monomers and heterodimers in the 580−760 nm region in CH_3CN by a laser pulse excitation at 400 nm. The fluorescence decays are independent of the observed wavelength region.

Since the total apparatus response function was about 30 ps, no fluorescence rise resulting from the ultrafast intramolecular energy transfer from the P unit to the Pm unit was observed, and only the lowest singlet excited state emission from the ^{1}Pm*−P was measured without any obstruction by Pm−^{1}P* (Supporting Information Figures 5 and 6). In fact, the time-resolved fluorescence spectral shape was independent of the time and assigned to the ^{1}Pm*−P fluorescence (Supporting Information Figure 7). However, the fluorescence decays of the dimers were not single-exponential but double-exponential (Table 3, Figure 6). Since the fluorescence decays of the $Pm(OPh)_2$ and PCl_2 monomers were single-exponential in all solvents at ambient temperature, the double-exponential decays were a feature of the heterodimers. The possibility that the heterodimer samples have a small impurity of monomer was excluded because both lifetime components of the heterodimers were shorter than that of the monomer. The possibility of two short-lived metastable conformers[48,49] in nanosecond time scale was not ruled out by the NMR measurement. However, the permitted

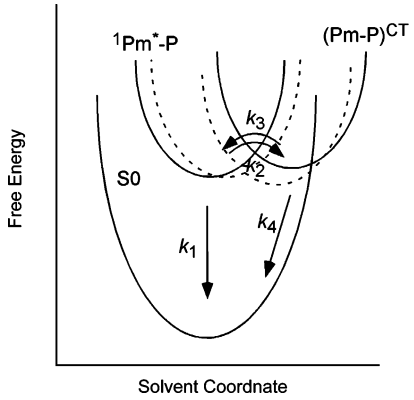

Figure 7. Outline of the potential energy surface of S0, ^{1}Pm*−P, and (Pm−P)^{CT}. The surfaces of ^{1}Pm*−P and (Pm−P)^{CT} are changed from the isolated system (solid line) to a weakly mixed system (dotted line) as the solvent polarity is increased.

conformational changes in the present porphyrin dimers are very limited because no long alkyl chain and no flexible unit existed in the bridge moiety. Only a P−O−Ph bond can affect the conformation between the two porphyrin rings, but the P−O−Ph rotation and angle change are not enough to form two different types of metastable conformers with ten-times different lifetimes. If the continual conformation changes in the nanosecond time scale affected the decay of the fluorescence, the decay would not be double-exponential but, rather, multiexponential. Consequently, the other excited-state equiliblium of the heterodimers should be taken into account. In the present P(V)-porphyrin heterodimers, intramolecular back-energy-transfer from ^{1}Pm*−P to Pm−^{1}P* is ruled out because of the large endothermic energy gap and negligible higher energy Pm−^{1}P* emission. A reasonable explanation is that the double-exponential decay is due to the equilibrium between ^{1}Pm*−P and (Pm−P)^{CT}, as depicted in Figure 7.[50−52]

Under these conditions, the rate constant of the transition from ^{1}Pm*−P to (Pm−P)^{CT} (k_2), the back-reaction from (Pm−P)^{CT} to ^{1}Pm*−P (k_3), and the decay from (Pm−P)^{CT} to the S0 of the dimers (k_4) can be calculated using eq 2, where λ_1 and λ_2 are the lifetimes of the two fluorescence decay components of ^{1}-Pm*−P, C_1 and C_2 are the relative amplitudes of these two components, and k_1 is assumed to be the reciprocal of the fluorescence lifetime of the $Pm(OPh)_2$ monomer. By changing the temperature to 77 K in CH_3CN, the fluorescence decay of *m*-Pm−PCl_2 became considerably slower than that at ambient temperature (Supporting Information Figure 6), although the decay was still double-exponential ($C_1 = 0.47$, $\lambda_1 = 6.4 \times 10^9$, $C_2 = 0.53$, $\lambda_2 = 0.77 \times 10^9$).

$$\lambda_1 = \frac{1}{2}[(X+Y) + \sqrt{(X-Y)^2 + 4k_2k_3}]$$

$$\lambda_2 = \frac{1}{2}[(X+Y) - \sqrt{(X-Y)^2 + 4k_2k_3}]$$

$$X = k_1 + k_2 \qquad Y = k_3 + k_4 \qquad C_1 = \frac{X - \lambda_2}{\lambda_1 - \lambda_2} \qquad (2)$$

From the fluorescence spectra mentioned above, it was suggested that E[(Pm−P)^{CT}] was very close to E[^{1}Pm*−P]. Therefore, the driving forces for k_2 and k_3, which are in the "normal region" if the typical electron-transfer scheme is used, are assumed to be very small.[53,54] Interestingly, the k_2 and k_3 of *m*-Pm−PCl_2 were larger than those of *p*-Pm−PCl_2, as listed in Table 4. These results suggest that k_2 and k_3 are strongly dependent on the geometry of the two porphyrin rings in the

TABLE 4: Rate Constants of the P(V)porphyrin Monomer and Heterodimers ($\times 10^9$ s^{-1})

compd	solvent	k_1	k_2	k_3	k_4
$Pm(OPh)_2$	$CHCl_3$	0.44			
	CH_2Cl_2	0.51			
	acetone	0.53			
	CH_3CN	0.60			
	DMSO[a]	0.42			
p-Pm−PCl_2	CH_2Cl_2		4.8	0.64	1.2
	acetone		19	1.3	1.2
	CH_3CN		15	1.1	1.0
m-Pm−PCl_2	$CHCl_3$		3.4	0.87	1.9
	CH_2Cl_2		10	2.8	2.2
	acetone		28	4.0	1.3
	CH_3CN		32	3.4	1.3
	DMSO		36	5.3	1.1

[a] DMSO = dimethyl sulfoxide.

dimer. Although the geometry controls the electronic coupling matrix element,[55] the reorganization energy, and the $E[(Pm-P)^{CT}]$,[56] the electronic coupling matrix element is assumed to be the predominant factor. Due to the larger overlap between the two porphyrin rings of *m*-Pm−PCl_2 than those of the *p*-Pm−PCl_2, the transition between $^1Pm^*-P$ and $(Pm-P)^{CT}$ should be accelerated. As to the energy gap dependence, k_2 was accelerated by the highly polar solvents, which pull the $E[(Pm-P)^{CT}]$ down. However, the solvent-polarity dependence of k_3 is not clear. In these cases, the solvent-polarity dependence of the electronic coupling matrix element[57,58] might be taken into account because the electronic coupling matrix element is expressed as eq 3, where α and $E[(Pm-P)^{CT}]$ depend on the solvent polarity.

$$V = \frac{\sqrt{(1-\alpha^2)}}{\alpha}(E[^1Pm^*] - E[(Pm-P)^{CT}]) \qquad (3)$$

Surprisingly, the charge recombination rate k_4 of the heterodimers was only slightly dependent on the solvent polarity. The driving force for k_4 is sufficiently large; as a result, the energy-gap dependence of k_4 is in the "inverted region" if the typical electron-transfer scheme is used.[53,54] For a thorough discussion of the present relaxation dynamics of center-to-edge P(V)porphyrin dimers, the typical outer-sphere electron-transfer scheme might not be appropriate. Since $\Psi[(Pm-P)^{CT}]$ has a $\Psi[^1Pm^*]$ character and $\Psi[^1Pm^*-P]$ has a $\Psi[(Pm-P)^{CT}]$ character, the nuclear coordination of $(Pm-P)^{CT}$ and $^1Pm^*-P$ is somewhat closer than the typical outer-sphere electron transfer (see the dotted line in Figure 7). In this case, the transition between $^1Pm^*$-P and $(Pm-P)^{CT}$ and the charge recombination of $(Pm-P)^{CT}$ are in the boundary between the intramolecular nonradiative transition and the outer-sphere electron transfer. The charge recombination of $(Pm-P)^{CT}$ could decay to the ground state through the vibrational levels before crossing over the barrier.[54,59] Since natural photosynthetic systems have a similar complex structure, the boundary between the intramolecular nonradiative transition and the outer-sphere electron transfer should continue to be investigated.

Conclusion

In this study, the contribution of the CT state to the decay process of the singlet excited state of center-to-edge P(V)-porphyrin heterodimers was investigated. Interestingly, *m*-Pm−PCl_2 with the larger overlap between the two porphyrin rings shows the large contribution of $(Pm-P)^{CT}$. The $(Pm-P)^{CT}$ contribution to $^1Pm^*-P$ would be mostly Pm^+-P^-, which nonradiationally decays to the S0 with only a slight dependence on the solvent polarity. We conclude that *m*-Pm−PCl_2 is an effective component in the supramolecular system for fast and sequential electron transfer via the CT state.[60−62]

Acknowledgment. This work was partly supported by a Grant-in-Aid for Scientific Research on Priority Areas 417 from the Ministry of Education, Culture, Sports, Science, and Technology, Japan.

Supporting Information Available: Figures showing ^1H NMR spectra of P(V)porphyrin monomers and dimers, Soret and Q band absorption spectra, fluorescence spectra, fluorescence excitation spectra, and fluorescence decays of P(V)-porphyrin monomers and heterodimers, and time-resolved fluorescence spectra of *m*-Pm−PCl_2. This material is available free of charge via the Internet at http://pubs.acs.org.

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