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Journal of Photochemistry and Photobiology A: Chemistry 92 (1995) 39–46

Journal of PHOTOCHEMISTRY AND PHOTOBIOLOGY A:CHEMISTRY

Control of photophysical properties of "wheel-and-axle-type" phosphorus(V) porphyrin dimers by electronic symmetry breaking

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Abstract

The excited state properties of "wheel-and-axle-type" phosphorus(V) porphyrin dimers, whose central phosphorus atoms are covalently connected via an ethylenedioxy bridge, were investigated to determine the contribution of the charge transfer (CT) state. The lifetime of the excited singlet state of each dimer decreased with increasing solvent polarity. The lifetime of the symmetry-disturbed dimer, in which the redox potentials of the two porphyrin rings are differentiated by unsymmetrical axial substitution, was much shorter than that of the symmetrical dimer. The decrease in lifetime suggests the enhancement of non-radiative decay through the CT state. Similar phenomena were also observed for the quenching of the excited singlet state of porphyrin dimers possessing orthogonally oriented porphyrin rings. In addition, analogous trimers with parallel or orthogonal configurations showed stronger fluorescence quenching than that of the corresponding dimers.

Keywords: Phosphorus(V) Porphyrins; Charge transfer; Dimers

1. Introduction

Various molecular systems containing multiple porphyrin units have been investigated extensively in an attempt to determine the electron transfer function of cofactors in the bacterial photosynthetic reaction centre [1–27]. In particular, investigation of the function of the excited state of the porphyrin dimer is important for clarification of the ultrafast electron transfer from the "special pair", i.e. partially stacked bacteriochlorophyll dimer. Recently, the contribution of charge transfer (CT) character in the excited state of the special pair has been suggested by photochemical hole burning experiments [28], Stark effect spectroscopy [29] and theoretical calculations [30]. In order to consider the contribution of the CT state in dimers such as the special pair, the existence of the CT state should be confirmed in partially stacked and relatively symmetrical dimers.

With this in mind, we have synthesized symmetrical phosphorus(V) tetraphenylporphyrin (P(V)TPP) dimers, whose central phosphorus atoms are connected by an ethylenedioxy bridge [31,32]. The axial spacers of the P(V)TPP dimers keep the two porphyrin rings in close proximity without large overlap of their π systems. For comparison, symmetry-disturbed dimers were synthesized by different axial substitution for parallel and orthogonal dimers. Although the tunability of the redox potentials of the P(V)TPP dimers enables the influence of the CT state in the excited state to be controlled, the object of this study is the understanding of the influence of the CT state. In addition, the corresponding trimers were synthesized and investigated.

2. Experimental section

2.1. Measurements

The absorption spectra were recorded on a Shimadzu UV-2200 spectrophotometer and the fluorescence spectra on a Shimadzu RF-503A spectrofluorometer.

Fluorescence lifetimes were measured on a Horiba NAES-550 time-correlated, single-photon-counting equipment. The excitation light was passed through a Toshiba glass bandpass filter V-42 (maximum transmittance at 420 nm), and the emission was detected through a monochromator.

Time-resolved transient absorption spectra were measured with a microcomputer-controlled picosecond laser photolysis system, with the second harmonic excitation pulse (395 nm; full width at half-maximum (FWHM), 500 fs) of a mode-

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Elsevier Science S.A.
SSDI 1010-6030(95)04169-9

locked Ti–sapphire laser pumped by an Ar ion laser (Tsunami, Spectra Physics).

Cyclic voltammograms were measured in acetonitrile solution with 0.1 M n-Bu_4NBF_4 as supporting electrolyte, platinum working and counter electrodes, a saturated calomel reference electrode (SCE), a Nikko Keisoku NPGS-301 potentiogalvanostat and an NFG-6 function generator. All the solutions were purged with nitrogen during the measurements.

2.2. Materials

The porphyrin derivatives used in this study are listed in Fig. 1. Symmetrical P(V)TPP monomer (M2), dimer (D2)

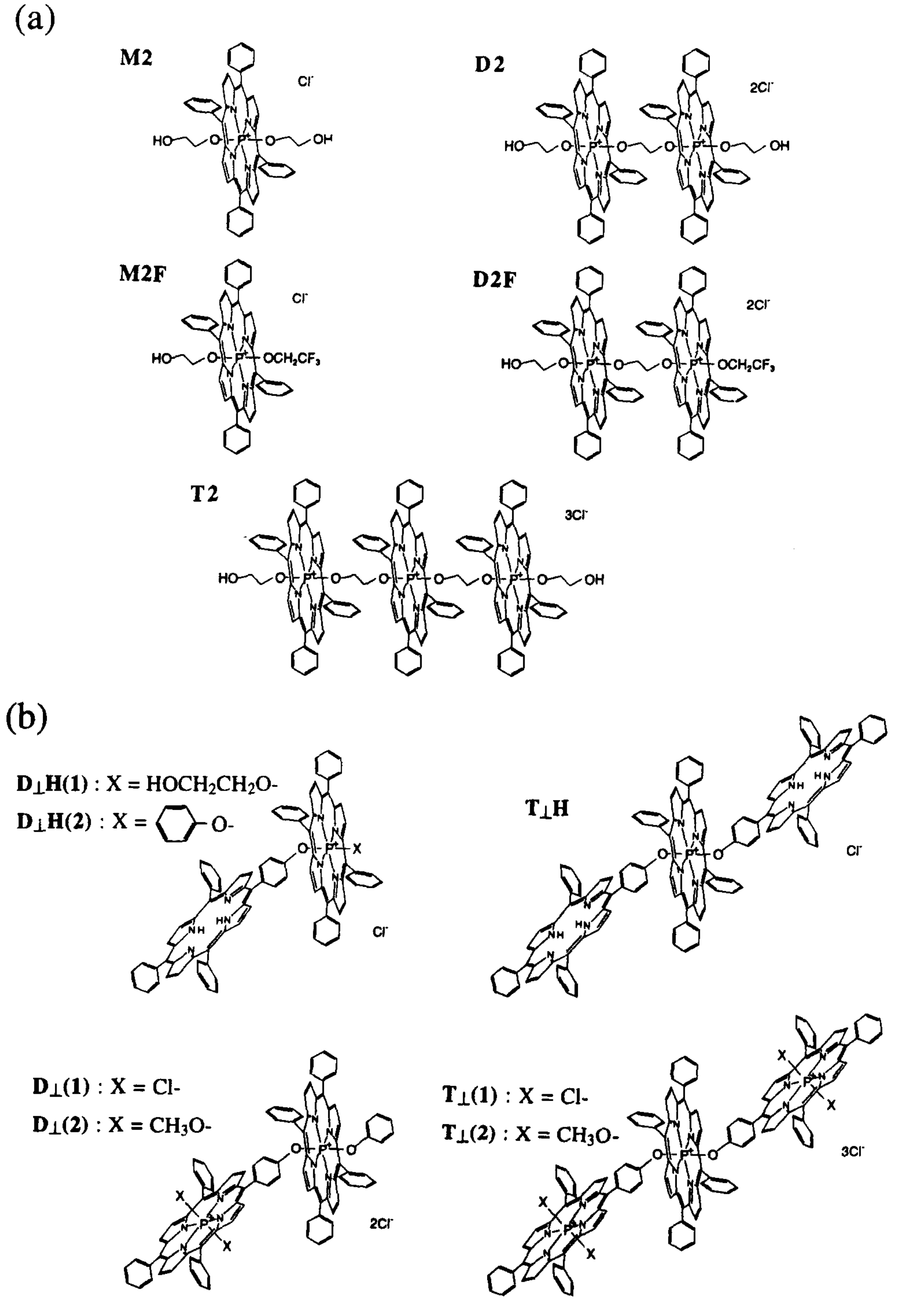

Fig. 1. Structures of the phosphorus(V) porphyrin derivatives: (a) "wheel-and-axle-type" P(V)TPP monomers, dimers and trimer; (b) porphyrin dimers and trimers possessing orthogonally oriented porphyrin rings.

and trimer (T2) were prepared as described previously [31]. Unsymmetrical P(V)TPP monomer (M2F) and dimer (D2F) were also prepared as described previously [32]. The other porphyrin derivatives used in this study were synthesized as follows.

2.2.1. Heterodimer $D_{\perp}H(1)$ and heterotrimer $T_{\perp}H$

Dichlorophosphorus(V) tetraphenylporphyrin chloride (0.202 g), ethylene glycol (0.015 ml) and 5-(4-hydroxyphenyl)-10,15,20-triphenylporphyrin (0.230 g) were dissolved and refluxed in 4 ml of dry pyridine. After the reaction, the P(V) porphyrin derivatives (heterodimer $D_{\perp}H(1)$ and heterotrimer $T_{\perp}H$) were separated by repeated column chromatography on silica gel with $CHCl_3$–CH_3OH (10:1). Finally, heterodimer $D_{\perp}H(1)$ and heterotrimer $T_{\perp}H$ were further chromatographed on alumina with $CHCl_3$–CH_3OH (50:1) to remove hydroxyl derivatives of P(V) porphyrin, and were obtained in 7% (0.0267 g) and 27% (0.097 g) yields respectively.

2.2.2. Heterodimer $D_{\perp}H(2)$

This compound was prepared in a similar manner to $D_{\perp}H(1)$ in 27% yield.

2.2.3. Dimer $D_{\perp}(1)$

Dimer $D_{\perp}H(2)$ (0.1123 g) and $POCl_3$ (3.5 ml) were dissolved and refluxed in 10 ml of dry pyridine under nitrogen. The solvent and excess $POCl_3$ were removed in vacuo. The residues were separated by column chromatography on silica gel with $CHCl_3$–CH_3OH (5:1) to yield 0.0925 g (75%) of $D_{\perp}(1)$.

2.2.4. Trimer $T_{\perp}(1)$

This compound was prepared in a similar manner to $D_{\perp}(1)$ in 52% yield.

2.2.5. Dimer $D_{\perp}(2)$ and trimer $T_{\perp}(2)$

These compounds were prepared by substitution reactions of axial chloride ligands of dichlorophosphorus(V) porphyrin unit(s) of $D_{\perp}(1)$ or $T_{\perp}(1)$ with methanol as described previously [33].

2.3. Nuclear magnetic resonance (NMR) spectroscopy and mass spectrometry

The compounds were characterized by ^1H NMR, ^{31}P NMR and fast atom bombardment (FAB) mass spectra. The ^1H and ^{31}P NMR data in $CDCl_3$ were determined relative to tetramethylsilane (TMS) and H_3PO_4 respectively. In the FAB mass spectra, the parent peak of each derivative coincided with the expected molecular weight in the absence of counterion.

Heterodimer $D_{\perp}H(1)$. ^1H NMR (90 MHz, $CDCl_3$) δ: -3.03 (br s, 2H, NH), -1.91 (dt, 2H, $POCH_2$), 0.89 (m, 2H, $POCCH_2$), 2.54 (dd, 2H, $J_{H-H}=8.58$ Hz, 5-phenyl-H), 6.75 (d, 2H, $J_{H-H}=8.35$ Hz, 5-phenyl-H), 7.5–8.3 (m, 35H, phenyl-H), 7.88 (d, 2H, $J_{H-H}=4.84$ Hz, 3,7-β-H), 8.57 (d, 2H, $J_{H-H}=4.62$ Hz, 2,8-β-H), 8.79 (s, 4H, 12,13,17,18-β-H), 9.14 (d, 8H, $J_{P-H}=3.08$ Hz, β-H). ^{31}P NMR (90 MHz, $CDCl_3$) δ: -186.0 (s). FAB HRMS m/z: 1333.473 (M^+). Calculated for $C_{90}H_{62}N_8O_3P$, 1333.4683.

Heterotrimer $T_{\perp}H$. ^1H NMR (90 MHz, $CDCl_3$) δ: -3.00 (br s, 4H, NH), 2.76 (d, 4H, $J_{H-H}=8.57$ Hz, 5-phenyl-H), 6.87 (d, 4H, $J_{H-H}=7.47$ Hz, 5-phenyl-H), 7.5–8.4 (m, 50H, phenyl-H), 7.92 (d, 4H, $J_{H-H}=4.83$ Hz, 3,7-β-H), 8.60 (d, 4H, $J_{H-H}=4.84$ Hz, 2,8-β-H), 8.80 (s, 8H, 12,13,17,18-β-H), 9.35 (d, 8H, $J_{P-H}=3.52$ Hz, β-H). ^{31}P NMR (90 MHz, $CDCl_3$) δ: -193.5 (s). FAB HRMS m/z: 1901.688 (M^+). Calculated for $C_{132}H_{86}N_{12}O_2P$, 1901.6734.

Heterodimer $D_{\perp}H(2)$. ^1H NMR (90 MHz, $CDCl_3$) δ: -3.04 (br s, 2H, NH), 2.33 (d, 2H, axial phenyl-H), 2.63 (d, 2H, 5-phenyl-H), 5.86–6.36 (m, 3H, axial phenyl-H), 6.79 (d, 2H, 5-phenyl-H), 7.56–8.35 (m, (35+2)H, phenyl-H and 3,7-β-H), 8.57 (d, 2H, $J_{H-H}=4.84$ Hz, 2,8-β-H), 8.78 (s, 4H, 12,13,17,18-β-H), 9.19 (d, 8H, $J_{P-H}=3.30$ Hz, β-H). ^{31}P NMR (90 MHz, $CDCl_3$) δ: -194.0 (s).

Dimer $D_{\perp}(1)$. ^1H NMR (90 MHz, $CDCl_3$) δ: 2.29 (d, 2H, axial phenyl-H), 2.73 (d, 2H, 5-phenyl-H), 5.76–6.34 (m, 3H, axial phenyl-H), 6.79 (d, 2H, 5-phenyl-H), 7.48–8.23 (m, 35H, phenyl-H), 8.42 (dd, 2H, 3,7-β-H), 8.97 (m, 6H, 2,8,12,13,17,18-β-H), 9.15 (d, 8H, $J_{P-H}=3.52$ Hz, β-H). ^{31}P NMR (90 MHz, $CDCl_3$) δ: -195.3 (s, diphenoxyP(V) porphyrin unit), -229.2 (s, axial dichloroP(V) porphyrin unit). FAB HRMS m/z: 1464.376 (M^+). Calculated for $C_{94}H_{60}N_8O_2P_2Cl_2$, 1464.3692.

Trimer $T_{\perp}(1)$. ^1H NMR (90 MHz, $CDCl_3$) δ: 2.80 (d, 4H, 5-phenyl-H), 6.77 (d, 4H, 5-phenyl-H), 7.59–8.20 (m, 50H, phenyl-H), 8.39 (dd, 4H, 3,7-β-H), 8.97 (m, (8+4)H, β-H of inner P(V) porphyrin and 2,8-β-H of outer P(V) porphyrin), 9.26 (d, 8H, 12,13,17,18-β-H). ^{31}P NMR (90 MHz, $CDCl_3$) δ: -195.8 (s, inner P(V) porphyrin), -229.2 (s, outer P(V) porphyrin).

Dimer $D_{\perp}(2)$. ^1H NMR (90 MHz, $CDCl_3$) δ: -2.20 (d, 6H, $J_{P-H}=25.94$ Hz, $POCH_3$), 2.19 (d, 2H, axial phenyl-H), 2.61 (d, 2H, 5-phenyl-H), 5.72–6.18 (m, 3H, axial phenyl-H), 6.60 (d, 2H, 5-phenyl-H), 7.44–8.03 (m, 35H, phenyl-H), 8.15 (dd, 2H, 3,7-β-H), 8.73 (dd, 2H, 2,8-β-H), 8.81 (d, 4H, $J_{P-H}=2.86$ Hz, 12,13,17,18-β-H), 9.05 (d, 8H, $J_{P-H}=3.30$ Hz, β-H). ^{31}P NMR (90 MHz, $CDCl_3$) δ: -178.2 (s, axial dimethoxyP(V) porphyrin unit), -195.3 (s, diphenoxyP(V) porphyrin unit). FAB HRMS m/z: 1456.475 (M^+). Calculated for $C_{96}H_{66}N_8O_4P_2$, 1456.4682.

Trimer $T_{\perp}(2)$. ^1H NMR (90 MHz, $CDCl_3$) δ: -2.09 (d, 12H, $J_{P-H}=25.94$ Hz, $POCH_3$), 2.78 (d, 4H, 5-phenyl-H), 6.68 (d, 4H, 5-phenyl-H), 7.63–8.31 (m, (50+4)H, phenyl-H and 3,7-β-H), 8.82 (m, 4H, 2,8-β-H), 8.93 (d, 8H, $J_{P-H}=2.86$ Hz, β-H), 9.27 (d, 8H, $J_{P-H}=3.52$ Hz, 12,13,17,18-β-H). ^{31}P NMR (90 MHz, $CDCl_3$) δ: -178.2 (s, outer P(V) porphyrin), -195.7 (s, inner P(V) porphyrin). FAB HRMS m/z: 2083.648 (M^+). Calculated for $C_{136}H_{94}N_{12}O_6P_3$, 2083.6632.

Table 1
Absorption data for P(V)TPP monomers and dimers

Compound	Band	λ_{max} (nm) [FWHM[a] (cm^{-1})]				
		$CHCl_3$	$(CH_3)_2CO$	CH_3CN	H_2O–CH_3CN (95:5)	H_2O
M2	Soret	431 [850]	429 [860]	428 [850]	427 [870]	427 [900]
	Q(0, 1)	560	559	559	558	559
	Q(0, 0)	600	599	600	599	599
M2F	Soret	431 [890]	428 [880]	427 [880]	427 [890]	[b]
	Q(0, 1)	560	559	558	558	[b]
	Q(0, 0)	602	600	600	598	[b]
D2	Soret	425 [910]	422 [940]	421 [940]	421 [980]	420 [1010]
	Q(0, 1)	561	560	559	559	560
	Q(0, 0)	603	603	601	602	603
D2F	Soret	425 [920]	422 [920]	421 [970]	421 [970]	[b]
	Q(0, 1)	561	560	559	560	[b]
	Q(0, 0)	605	603	600	603	[b]

[a] The full width at half-maximum of the Soret band. Estimated error limits of FWHM are within ± 40 cm^{-1}.

[b] Insoluble in H_2O.

3. Results and discussion

3.1. *Solvent polarity dependence of the absorption spectra of the parallel dimers*

The "wheel-and-axle-type" P(V)TPP dimers and the corresponding monomers are soluble in various solvents with a wide range of polarity. This characteristic solubility enables the solvent polarity-dependent photophysics to be investigated. The absorption data of the P(V)TPP monomers and dimers in various solvents are summarized in Table 1. In each solvent, the Soret bands of the dimers are shifted to shorter wavelengths compared with those of the corresponding monomers. According to exciton coupling theory [34], these results can be explained by the structure, where the parallel arrangement of the two porphyrin rings results in a blue shift of the absorption maximum. In addition, a small absorption shoulder is observed for each dimer at longer wavelengths than the Soret absorption in polar solvents. Interestingly, the absorption shoulder of the dimers becomes more distinguishable with an increase in the solvent polarity as shown in Fig. 2. These results suggest that the two porphyrin rings are partially stacked in polar solution and located predominantly in an oblique orientation due to bending of the axial spacer induced by hydrophobic interaction of the porphyrin rings.

3.2. *Deactivation process of the excited singlet state of the parallel dimers in polar solvents*

Table 2 shows the fluorescence spectral data for the dimers and the corresponding monomers in various solvents. Since the emission peaks of the dimers are almost the same as those of the corresponding monomers, the excitation energies of the dimers determined from the (0,0) fluorescence bands are almost the same as those of the monomers. However, the fluorescence quantum yields (Table 3) of the dimers are smaller than those of the monomers.

The fluorescence lifetimes (Table 4) of the dimers and the corresponding monomers in various solvents were measured by a single-photon-counting method, and each of the decay curves obtained showed good single-exponential fitting. Two characteristic types of behaviour of the solvent polarity-dependent lifetimes were observed. One is the decrease in the lifetimes of both dimers and monomers in $CHCl_3$. This result can be explained by enhanced intersystem crossing induced by the heavy atom effect of $CHCl_3$. The other is an apparent decrease in the lifetimes of dimers compared with those of monomers in aqueous solution, in which the two porphyrin rings of the dimer are located predominantly in a partially stacked orientation. The radiative and non-radiative decay rate constants (k_r and k_{nr}) were calculated by

$$k_r = \Phi_f / \tau_f$$

$$k_{nr} = (1 - \Phi_f) / \tau_f$$

where Φ_f and τ_f are the fluorescence quantum yield and lifetime respectively. Considering that the fluorescence quantum yield of P(V)TPP is comparatively low (0.03–0.05), the decrease in the lifetimes of the dimers can be ascribed to the enhancement of non-radiative decay rather than radiative decay. Thus the presence of a new decay channel in polar solvents suggests that the contribution of CT character to the non-radiative decay of the excited singlet state is enhanced and the non-radiative decay rate is accelerated. Moreover, in the case of the symmetry-disturbed dimer D2F, the emission energy, fluorescence intensity and lifetime are similar to those of the symmetrical dimer D2 in $CHCl_3$, $(CH_3)_2CO$ and CH_3CN, whereas the fluorescence intensity and lifetime are apparently decreased in H_2O–CH_3CN (95:5) relative to those of D2. It is assumed that the introduction of the terminal axial groups with different electron-donating power creates a dif-

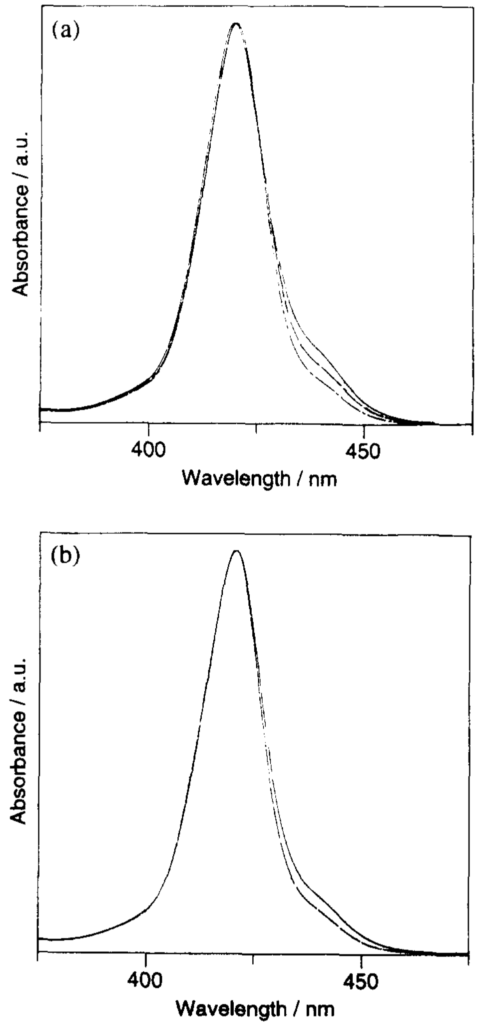

Fig. 2. Soret absorption spectra of P(V)TPP dimers: (a) D2 in CH_3CN (- - -), H_2O–CH_3CN (95:5) (– –) and H_2O (——); (b) D2F in CH_3CN (– –) and H_2O–CH_3CN (95:5) (——). The absorbances were normalized at the maximum intensities.

Table 2
Fluorescence data for P(V)TPP monomers and dimers

Compound	λ_{max} (nm) ($E(S_1)$ (eV))				
	$CHCl_3$	$(CH_3)_2CO$	CH_3CN	H_2O–CH_3CN (95:5)	H_2O
M2	617, 670 (2.01)	617, 670 (2.01)	617, 669 (2.01)	617, 669 (2.01)	616, 668 (2.01)
M2F	617, 671 (2.01)	617, 670 (2.01)	617, 670 (2.01)	617, 670 (2.01)	–
D2	621, 673 (2.00)	620, 672 (2.00)	619, 671 (2.00)	619, 671 (2.00)	618, 670 (2.01)
D2F	622, 674 (1.99)	620, 673 (2.00)	618, 671 (2.01)	619, 671 (2.00)	–

ference in the redox potential between the porphyrin rings. As a result, the CT state is more stabilized in D2F than in D2, and the contribution of CT character to the non-radiative decay of the excited singlet state is considered to be enhanced.

3.3. Consideration of the CT character in the excited state of the dimers

Strictly speaking, CT state formation within a symmetrical dimer (D2) is symmetry forbidden [20]. For a symmetrical dimer P–P, the equal contributions of the charge resonance terms P^+–P^- and P^-–P^+ to the excited state cause no net change in the dipole moment of the state. However, by interaction with polar solvent molecules, the symmetry of the dimer can be broken, and CT state formation can be allowed. This type of intramolecular CT state in symmetrical bichromophoric molecules is known as a twisted intramolecular charge transfer (TICT) state [35], e.g. 9,9′-bianthryl, which undergoes CT state formation in the excited state as a result of symmetry breaking induced by polar solvents despite its symmetrical structure [36,37]. In the case of 9,9′-bianthryl, a new, red-shifted, fluorescence emission band appears relative to that of the original band in non-polar solvents and moves to longer wavelengths as the polarity of the solvent increases. The red-shifted emission results from an intramolecular CT state of 9,9′-bianthryl which is stabilized by the polar solvent. As the solvent polarity increases, the CT state is stabilized because of the asymmetrical charge distribution in the molecules. However, no new, red-shifted band is observed in the present porphyrin dimers, and the emission from the dimers is essentially independent of the solvent polarity. This result shows that the fluorescence of the dimers is not due to an emissive CT state. Thus the deactivation of the excited state via the CT state participates in non-radiative decay.

D2F shows a significant decrease in the fluorescence intensity and lifetime in H_2O–CH_3CN (95:5) compared with D2. It is probable that the contribution of the CT state to the excited singlet state is enhanced by electronic symmetry breaking. Indeed, symmetry-disturbed bianthryl derivatives,

Table 3
Fluorescence quantum yields for P(V)TPP monomers and dimers

Compound	$CHCl_3$	$(CH_3)_2CO$	CH_3CN	H_2O–CH_3CN (95:5)	H_2O
M2	0.042	0.044	0.043	0.042	0.048
M2F	0.042	0.046	0.046	0.041	–
D2	0.034	0.038	0.038	0.036	0.030
D2F	0.033	0.039	0.038	0.028	–

Table 4
Fluorescence lifetimes (ns) for P(V)TPP monomers and dimers

Compound	$CHCl_3$	$(CH_3)_2CO$	CH_3CN	H_2O–CH_3CN (95:5)	H_2O
M2	3.4_7	4.3_1	4.2_2	4.3_6	4.5_2
M2F	3.4_8	4.3_1	4.3_5	4.5_9	–
D2	3.3_6	4.3_6	4.4_3	4.1_3	3.9_8
D2F	3.5_3	4.4_4	4.3_3	3.6_9	–

Estimated error limits of all data are within 1.2%.

such as 10-chloro-9,9′-bianthryl, show faster CT rates than the symmetrical derivatives [38]. In this case, two possible CT states, P^+–$P(F)^-$ and P^-–$P(F)^+$, can be expected. Since the P(F) part is more easily reduced than the P part, the CT energy is lower in P^+–$P(F)^-$ than in the CT state of the symmetrical dimer (P^+–P^-) as well as in P^-–$P(F)^+$. Thus the activation energy must be reduced via the P^+–$P(F)^-$ state in the symmetry-disturbed dimer.

However, direct evidence for the presence and contribution of the CT state in such dimers is very difficult to obtain due to other competitive relaxation pathways which are also rapid. In order to overcome these fundamental difficulties, it is necessary to increase gradually the degree of symmetry distribution by suitable molecular design. With this in mind, dimers and trimers possessing orthogonally oriented porphyrin rings were synthesized and investigated.

In the orthogonal phosphorus(V) porphyrin dimer $D_\perp(2)$, the fluorescence quantum yield is significantly decreased from 0.022 in CH_2Cl_2 to 0.0041 in CH_3CN. A similar quenching phenomenon of the excited singlet state is also observed for the orthogonal heterodimer $D_\perp H(1)$. In the case of the heterodimer, the complete CT state (i.e. charge separated radical ion pair) was confirmed by picosecond transient absorption measurements, where the radical ion pair ($\lambda_{max} \approx 460$ nm) was observed just after excitation. The corresponding trimers ($T_\perp(2)$ and $T_\perp H$) exhibit a similar behaviour with respect to fluorescence quenching. Following these results, it is concluded that quenching is due to the contribution of the CT state, although the measured CT state should have a significantly lower energy level compared with that of the excited singlet state. From a comparison of the fluorescence of the dimers (D2, $D_\perp(2)$ and $D_\perp H(1)$) and corresponding trimers (T2, $T_\perp(2)$ and $T_\perp H$), it is obvious that fluorescence quenching is more efficient in the trimers than in the corresponding dimers regardless of the orientation of the porphyrin rings, suggesting that there are other CT states and non-radiative decay processes in the trimers.

3.4. Redox properties and energetics of the dimers

The excitation energies to the lowest excited singlet states can be determined from the position of the (0,0) band of the fluorescence emission. The CT state energies can be estimated roughly from the sum of the one-electron oxidation and reduction potentials of the dimers in CH_3CN by using the dielectric continuum theory [39]. From this information, we can estimate the relationship between the energy levels of the lowest excited singlet state and the CT state. The cyclic voltammograms of the monomers and dimers are shown in Fig. 3. With regard to the reduction of the porphyrin ring, the peak separation of the dimers is larger than that of the monomers. This observation indicates that the reductions of the two porphyrin rings are not independent of each other because of the enhanced interaction in the ground state. It is well known that the voltammetric waves merge and are observed as only a single wave with a large peak separation when two coupled redox potentials are sufficiently close [40]. Moreover, a shoulder appears by the side of the peak of the cyclic voltammogram in D2F. This observation indicates that the difference between the redox potentials of the two porphyrin rings in D2F is a result of the modulation of the redox properties in the porphyrin ring by unsymmetrical substitution of the terminal axial groups. The oxidation of the porphyrin ring yields irreversible cyclic voltammograms in both monomers and dimers. Therefore the oxidation peak potentials are used as the oxidation potentials. Dielectric continuum theory gives the energy stabilization derived from the solvation of charge as a function of solvent polarity as follows

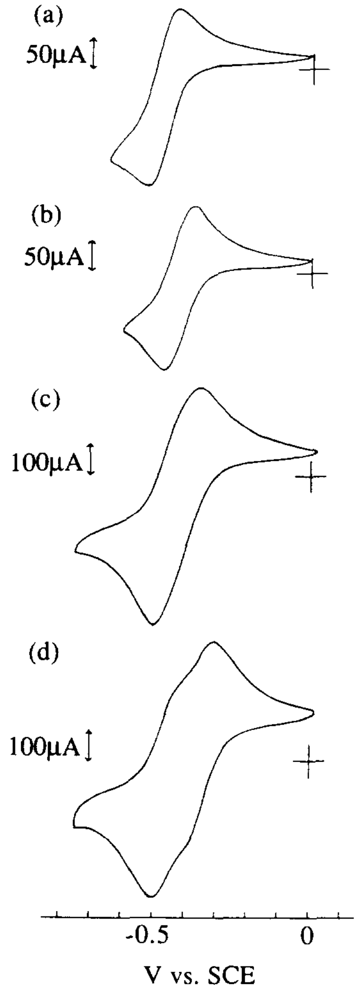

Fig. 3. Cyclic voltammograms of P(V)TPP in CH_3CN, 0.1 M n-Bu_4NBF_4 (platinum electrode; scan rate, 0.1 V s^{-1}; vs. SCE): (a) M2; (b) M2F; (c) D2; (d) D2F.

$$
\begin{aligned}
(\Delta G_{CT})_x = {} & (E_{1/2}{}^+ - E_{1/2}{}^-)_m + (z^2 e_0{}^2/2) \\
& \times (1/r_+ + 1/r_-)(1/\epsilon_x) - z^2 e_0{}^2/ \\
& \epsilon_x a - (z^2 e_0{}^2/2)(1/r_+ + 1/r_-)(1/\epsilon_m)
\end{aligned}
$$

where $(\Delta G_{CT})_x$ is the CT state energy in solvent x, $E_{1/2}{}^+$ and $E_{1/2}{}^-$ are the one-electron oxidation and reduction potentials of the dimer respectively in solvent m (CH_3CN), z is the charge number, e_0 is the electronic charge, r_+ and r_- are

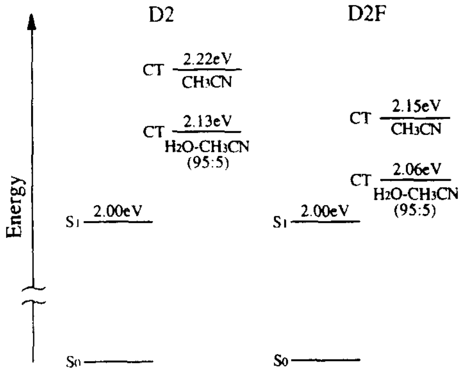

Fig. 4. Energy level diagrams for the lowest excited singlet and CT states of D2 and D2F.

the ionic radii of the positive ion and negative ion respectively, ϵ_x and ϵ_m are the static dielectric constants of solvents x and m respectively and a is the distance between the ions. In the excited CT state of the P(V)TPP dimer, one porphyrin ring produces divalent positive charge, while the other porphyrin ring produces no net charge. Therefore we can neglect the Coulomb interaction between the two porphyrin rings. As a result, the distance between the ions and the ionic radius of the negative ion are eliminated from this equation. Considering these points, this equation is simplified to

$$(\Delta G_{CT})_x = (E_{1/2}{}^+ - E_{1/2}{}^-)_m + (2e_0{}^2/r)(1/\epsilon_x - 1/\epsilon_m)$$

where $z = 2$ and $r_+ = r$. The estimated energy level diagrams for the lowest excited singlet states and CT states of D2 and D2F are shown in Fig. 4. For the ion with 5 Å radius, the CT state energies $(\Delta G_{CT})_x$ of D2 and D2F in CH_3CN are 2.22 and 2.15 eV respectively (the dielectric constant of CH_3CN was assumed to be 36.0 and that of H_2O–CH_3CN (95:5) was assumed to be 76.4). The energy levels are 0.22 and 0.15 eV above the observed lowest excited singlet state energy of the dimers (2.00 eV) respectively. In CH_3CN, the energy gap between S_1 and the CT state is too large to produce a new decay channel. However, the CT state energies $(\Delta G_{CT})_x$ of D2 and D2F in H_2O–CH_3CN (95:5) are 2.13 and 2.06 eV respectively. Considering the partial stacking of the two porphyrin rings in H_2O–CH_3CN (95:5) and the overestimation of the oxidation potentials, the CT state energy should lie closer to the lowest excited singlet state. The CT state is stabilized by the solvation of charge as the solvent polarity increases. As a result of this stabilization, it is possible that non-radiative transitions between S_1 and S_0 in the dimers are enhanced by the mixing of a low-lying CT state into S_1. In the P(V)TPP dimers, the CT state energy can be controlled by exchanging terminal axial groups, and therefore this property should be applied to artificial systems to achieve directional ultrafast electron transfer and efficient charge separation.

4. Conclusions

In "wheel-and-axle-type" phosphorus(V) porphyrin dimers with an ethylenedioxy bridge as axial spacer, it is possible to obtain the partially stacked conformation, such as in the special pair, due to the hydrophobic interaction between the porphyrin rings in highly polar solvents. The P(V)TPP dimers D2 and D2F show an enhancement of the non-radiative transition in highly polar solvents compared with the corresponding monomers M2 and M2F; this indicates a new decay channel from the lowest excited singlet state. This solvent polarity-dependent feature originates from the contribution of CT character to the lowest excited singlet state. In particular, the non-radiative decay of the symmetry-disturbed dimer D2F is enhanced relative to that of the symmetrical dimer D2 and the monomers. Such an enhancement of the contribution of CT character is considered to be responsible for the slightly pre-solvated nature of the ground state and the stabilization of the CT state energy by modulation of the redox properties in the porphyrin rings. It is suggested from an estimation of the CT state energy using dielectric continuum theory that the excited CT state lies slightly above the lowest excited singlet state. The non-radiative transitions between S_1 and S_0 in the P(V)TPP dimers are enhanced by mixing of a low-lying CT state into S_1.

Acknowledgment

This work was partially supported by grants from the Ministry of Education, Science and Culture of the Japanese Government.

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