Synthesis and Photochemical Properties of the Orthogonal Porphyrin Triad Composed of Free-Base and Phosphorus(V) Porphyrins

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A novel triad molecule composed of three porphyrins was synthesized by the use of the axial substitution of phosphorus(V) porphyrin. Photochemical properties of the triad suggest that the photoinduced electron transfer was accomplished.

For the elucidation of the electron transfer function of the photosynthetic reaction center, a large number of multi-porphyrin systems have been investigated.[1] Especially, the triad molecules, in which the redox potentials of the chromophores were energetically terraced, have been synthesized to understand the sequential electron transfer mechanism and achieve efficient charge separation as natural system.[2] Although many groups have synthesized various porphyrin trimers so far,[3] it was difficult to construct the triad composed of three porphyrins whose redox potentials were energetically terraced. In this sense, the phosphorus(V) porphyrin (P(V) porphyrin) is useful in the construction of the multi-porphyrin systems because the stable axial bond could reduce the difficulty of the systematic molecular architecture[4] and provide the method for the change of the redox potential of the porphyrin ring.[5] Taking advantage of these points, we synthesized "center-to-edge-type" porphyrin dimers and trimers, whose porphyrin units were covalently connected between the central phosphorus atom of one P(V) porphyrin and phenoxy groups at meso-position of the other porphyrins (Figure 1.).[6] It is expected that such bonding types arrange the adjacent porphyrins orthogonal to one another. In this paper, we report the syntheses and photochemical properties of "center-to-edge-type" porphyrin dimers and trimers.

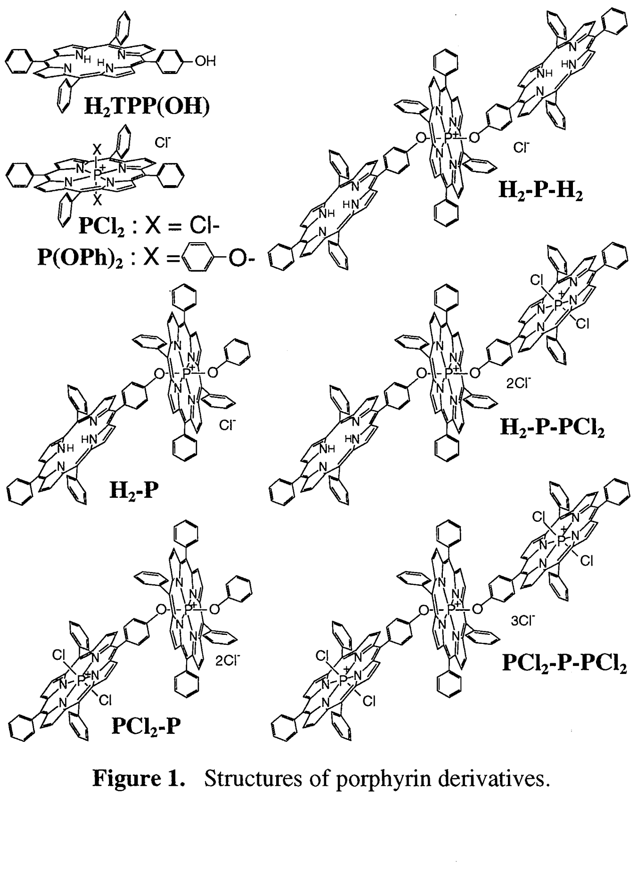

Figure 1. Structures of porphyrin derivatives.

PCl$_2$ and **P(OPh)$_2$** were synthesized as reported previously.[4,7] **H$_2$-P** and **H$_2$-P-H$_2$** were obtained by the axial substitution of **PCl$_2$**, which was refluxed with phenol and **H$_2$TPP(OH)** in dry pyridine. **H$_2$-P** and **H$_2$-P-H$_2$** were purified by column chromatography on alumina with CHCl$_3$-MeOH (50:1) and on silica gel with CHCl$_3$-MeOH (5:1) (27% yield for **H$_2$-P** and 22% yield for **H$_2$-P-H$_2$**). The insertion of phosphorus atoms to the free-base porphyrin units of **H$_2$-P-H$_2$** was accomplished by the reflux of dry pyridine solution of **H$_2$-P-H$_2$** and POCl$_3$ under nitrogen. The products were purified by column chromatography on silica gel with CHCl$_3$-MeOH (5:1). The desired triad **H$_2$-P-PCl$_2$** was obtained in 28% yield. In the same time, **PCl$_2$-P-PCl$_2$** was obtained in 52% yield. **PCl$_2$-P** was also prepared by similar procedure. The porphyrin dimers and trimers were characterized by UV-vis, ^{1}H-NMR, ^{31}P-NMR and FAB mass spectra.[8]

The fluorescence data of the porphyrin derivatives are listed in Table. **PCl$_2$-P** and **PCl$_2$-P-PCl$_2$** showed the properties similar to those of the reference monomer **PCl$_2$**. In **PCl$_2$-P** and **PCl$_2$-P-PCl$_2$**, the strong quenching by the electron transfer from the lowest excited singlet state is not considered to occur. On the other hand, the fluorescence of **H$_2$-P** and **H$_2$-P-H$_2$** was strongly quenched as compared with that of the monomers, **PCl$_2$-P** and **PCl$_2$-P-PCl$_2$**. In principle, both the energy transfer and the electron transfer should be considered as the reason for the fluorescence quenching. Since the energy levels of the lowest excited singlet states of **H$_2$TPP(OH)** and **P(OPh)$_2$** estimated from the fluorescence maxima (Table) were 1.89 and 1.99 eV, respectively, the energy transfer could occur from the P(V) porphyrin unit to the free-base porphyrin unit.

Table. Fluorescence Data for Porphyrin Derivatives in CH$_2$Cl$_2$

compounds	λ_{max}(nm)	Φ_f^{a}	τ_f(ns)
monomer			
H$_2$TPP(OH)	656, 719	0.042	8.36
P(OPh)$_2$	623, 674	0.037	2.92
PCl$_2$	624, 679	0.011	0.82
dimer			
PCl$_2$-P	629, 681	0.012	0.84
H$_2$-P	621, 666^b	$<1.0\times10^{-4}$	0.01^{c,d}
trimer			
PCl$_2$-P-PCl$_2$	629, 683	0.010	0.67
H$_2$-P-H$_2$	609, 655, 714^b	$<2.5\times10^{-4}$	0.01^d
H$_2$-P-PCl$_2$	626, 681^b	$<2.5\times10^{-4}$	0.03^d

^{a}Excitation at 560nm. ^{b}Estimated error limits are ±5nm. ^{c}Data for **H$_2$-P** derivative in which one axial substituent of **H$_2$-P** is changed from phenoxy group to ethyleneglycoxy group. ^{d}Fitting in the 690-740nm region.

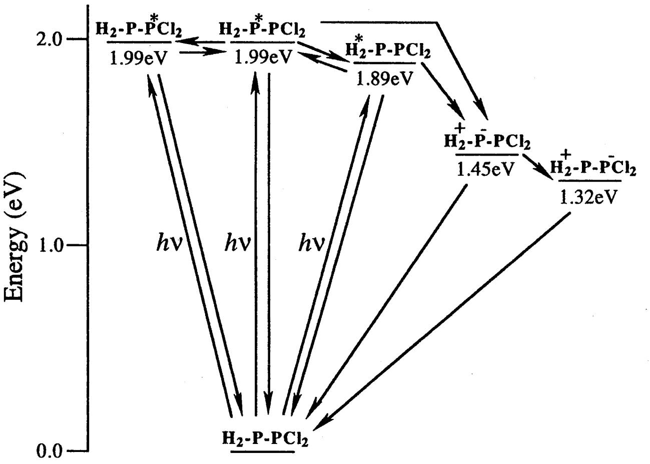

Figure 2. Energy level diagrams for excited singlet states and charge separated states of **H_2-P-PCl_2** in CH_2Cl_2.

However, the fluorescence excitation spectra of **H_2-P** suggested that the contribution of the energy transfer was not major, because the excitation of the P(V) porphyrin unit did not cause the emission from the free-base porphyrin unit significantly. Anyway, the lowest excited singlet states of **H_2-P** and **H_2-P-H_2** are localized on the free-base porphyrin unit and the quenching in them was due to only the electron transfer, although the contribution of the energy transfer from the P(V) porphyrin unit to the free-base porphyrin unit can not be negligible entirely.

In the case of the triad **H_2-P-PCl_2**, the fluorescence from the free-base porphyrin unit was also quenched. Especially, the fluorescence lifetime of the free-base porphyrin unit in **H_2-P-PCl_2** dramatically decreased as compared with that of the reference monomer **H_2TPP(OH)**. The fluorescence quenching in **H_2-P-PCl_2** is ascribed to the electron transfer from the free-base porphyrin to the P(V) porphyrin units as well as that in **H_2-P** and **H_2-P-H_2**. The electron transfer in **H_2-P-PCl_2** is in agreement with the connection of the energy level between the lowest excited singlet states of the monomer units and the charge separated states (Figure 2.).[9] Since the energy level of the charge separated state **H_2^+-P-PCl_2^-** is lower than that of **H_2^+-P^--PCl_2**, the sequential electron transfer from the free-base porphyrin to the terminal dichloro-P(V) porphyrin unit through the central P(V) porphyrin unit is probable in this triad. In fact the radical cation of the free-base porphyrin and the radical anion of the P(V) porphyrin were confirmed by the transient absorption just after the laser excitation. Interestingly, the transient absorption maxima for **H_2-P-PCl_2** (~470nm) were different from that for **H_2-P** (~460nm). These results suggest that the final charge separation state is not **H_2^+-P^--PCl_2** but **H_2^+-P-PCl_2^-**. Further electron transfer kinetics for a series of the triad molecules will be published separately.

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References and Notes

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8 ^{1}H- and ^{31}P-NMR data are relative to TMS and H_3PO_4, respectively. **H_2-P-PCl_2**: UV-vis(CH_2Cl_2) : λ_{max} = 418, 440, 516, 565, 613, 645nm. ^{1}H-NMR(500MHz, $CDCl_3$) : δ = -3.02(s, 2H, NH), 2.71(d, 2H, J_{H-H}=6.72Hz, 5-phenyl-H), 2.87(d, 2H, J_{H-H}=7.94Hz, 5-phenyl-H), 6.83(d, 2H, J_{H-H}=7.33Hz, 5-phenyl-H), 6.90(d, 2H, J_{H-H}=7.32Hz, 5-phenyl-H), 7.70~7.82(m, 30H, phenyl-H), 7.88~7.95(m, (6+2)H, phenyl-H and 3,7-β-H), 8.09~8.19(m, 14H, phenyl-H), 8.51(dd, 2H, J_{H-H}=J_{P-H}=4.89Hz, 3,7-β-H), 8.59(d, 2H, J_{H-H}=4.88Hz, 2,8-β-H), 8.79(s, 4H, 12,13,17,18-β-H), 8.96(d, 4H, 12,13,17,18-H), 9.00(dd, 2H, J_{H-H}=J_{P-H}=4.88Hz, 2,8-β-H), 9.30(d, 8H, β-H). ^{31}P-NMR(90MHz, $CDCl_3$) : δ = -194.8(s, inner P(V) porphyrin), -229.2(s, outer P(V) porphyrin). FAB HRMS : *m/z* 2000.562 (M^+), calcd for $C_{132}H_{84}N_{12}O_2P_2Cl_2$ 2000.5693. The spectral data of **H_2-P**, **H_2-P-H_2**, **PCl_2-P-PCl_2**, and **PCl_2-P** are reported in ref 6.

9 The energies of the lowest excited singlet states of each monomer unit were determined from the position of the (0,0) band of the fluorescence. The energies of the charge separated states were roughly estimated from the sum of the one-electron oxidation potential of the donor unit and the one-electron reduction potential of the acceptor unit. Redox potentials for the donor and acceptor units were determined in CH_3CN containing 0.1M n-Bu_4NBF_4 using platinum working and counter electrodes and a saturated calomel reference electrode. **H_2TPP(OH)**: E_{ox} = 0.92V, E_{red} = -1.18V; **P(OPh)$_2$**: E_{red} = -0.38V; **PCl_2**: E_{red} = -0.25V. The energies of the charge separated states in CH_2Cl_2 were corrected by using the dielectric continuum theory.