

Observation of Large Orientation Effect on Photoinduced Electron Transfer in Rigid Porphyrin-Quinone Compounds

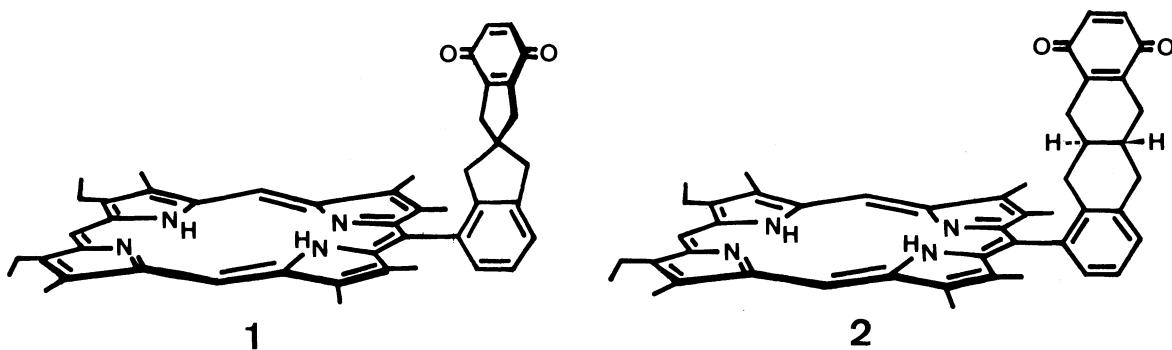
Yoshiteru SAKATA,* Hirohito TSUE, Yasushi GOTO, Soichi MISUMI, Tsuyoshi ASAHI,[†]
Shinya NISHIKAWA,[†] Tadashi OKADA,[†] and Noboru MATAGA[†]

The Institute of Scientific and Industrial Research, Osaka University, Mihoga-oka, Ibaraki, Osaka 567
+Department of Chemistry, Faculty of Engineering Science, Osaka University, Toyonaka, Osaka 560

In order to understand the mutual orientation effect in photosynthetic electron transfer, two different kinds of quinone-linked porphyrins **1** and **2** with fixed orientation were synthesized. In the two compounds only orientation is different among various factors which control electron transfer. It has been found that the electron transfer of **1** is faster than **2** by a factor of nine.

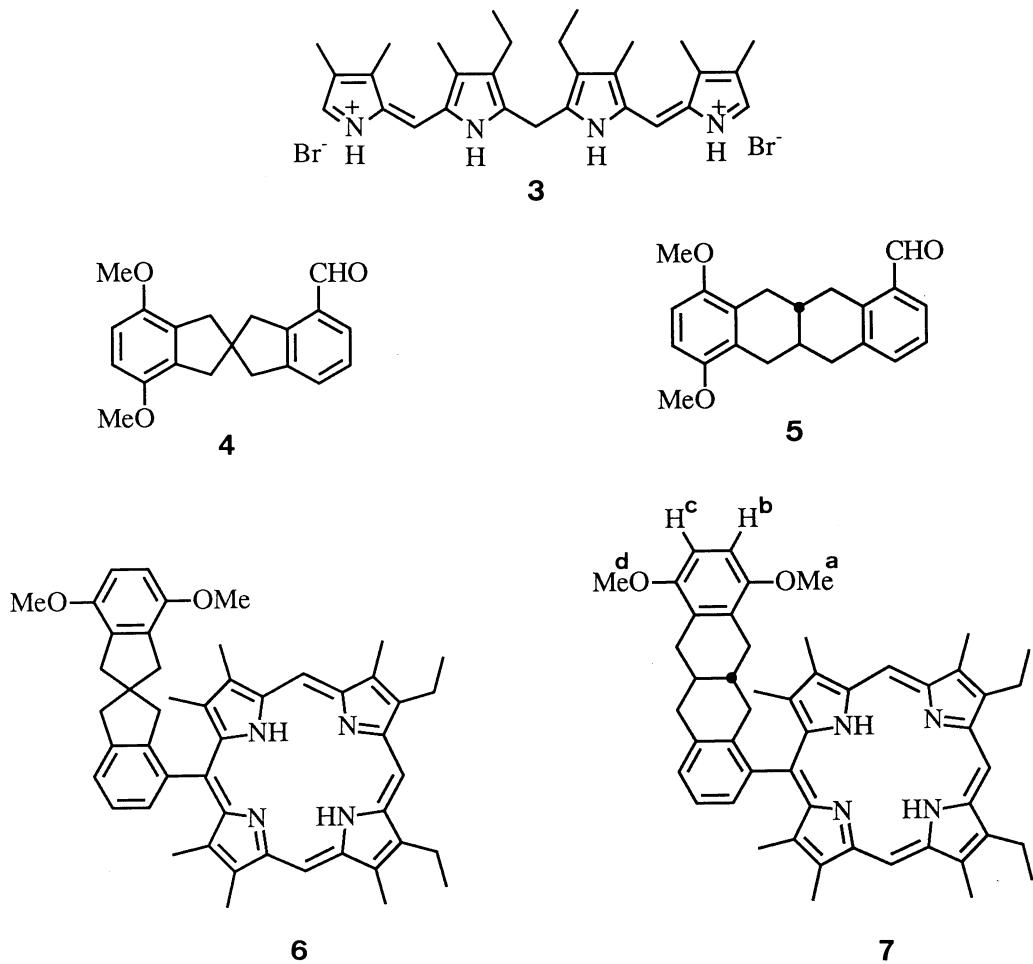
It is well known that photosynthetic electron transfers occur between chromophores fixed with peculiar orientations in protein.¹⁾ In order to understand such orientation effect on electron transfer reactions, theoretical studies have been carried out in various systems,²⁾ but experimental results for which the effects have been explicitly studied are rather few. This is mainly due to the difficulties in synthesizing a series of suitable model compounds where a set of donor-acceptor pair is fixed without rotational freedom by a rigid spacer with the same distance, but different orientation. Several synthetic systems which satisfy the above conditions have been reported³⁻⁵⁾ and orientation-dependent electron transfers were observed. However, more examples are still needed for the general understandings of the orientation effect.

We now report large orientation effect on photoinduced electron transfer for **1** and **2**, which were designed to have the same rigid spacers as the previous models,³⁾ but have shorter distance between the chromophores, so that large orientation effect is expected. Based on molecular model considerations, the edge-to-edge (or center-to-center) distances between the porphyrin and quinone rings are almost the same [6.4 Å (9.0 Å) for **1**⁶⁾ and 6.3 Å (9.3 Å) for **2**]. Moreover, the number of the intervening bonds, which affects greatly the electron transfer rate in



intramolecular systems,⁷⁾ is the same (6 bonds). Therefore, the main differences in the structures of **1** and **2**, which relates to electron transfer, are the relative orientation of the both chromophores and of the intervening σ -framework.

The syntheses⁸⁾ of the compounds **1** and **2** were achieved in a manner similar to those described previously.³⁾ Thus, acid catalysed condensation of tetrapyrrole **3** with functionalized benzaldehydes **4** and **5** gave **6** (11% yield) and **7** (24% yield), respectively. Demethylation of **6** and **7** with boron tribromide in dichloromethane, followed by oxidation with PbO₂ gave the desired compounds **1**⁹⁾(66% yield) and **2**¹⁰⁾(88% yield). The starting materials **4** and **5** were prepared using modifications of methods which we have reported.³⁾



The restricted rotation around the single bond at meso position of the porphyrin ring is confirmed by NMR spectra. Thus, the ring current effect due to the porphyrin ring, for example, in **7** is obtained for protons H_a - H_d by subtracting the chemical shifts of the corresponding protons of **5** from those of **7**. On the other hand, this effect is calculated by the well established method¹¹⁾ in which 8 point dipoles in a porphyrin ring are assumed. This calculation was performed for **7** assuming that the structure has the dihedral angle of 90° between the porphyrin and meso-substituted phenyl rings. Good agreement between the calculated and observed values in Table 1 indicates that this conformation is frozen in a solution at an ambient temperature.

Electronic spectra of **1** and **2** in THF do not show any detectable interaction between the chromophores:the spectra exhibit normal porphyrin spectra superimposed upon the spectra of **6** and **7**, respectively.

Table 1. Found and Calculated Ring Current Effect^{a)} for H_a - H_d of 7

	Found (ppm)	Calcd (ppm)
H _a	-0.543	-0.539
H _b	-0.277	-0.284
H _c	-0.138	-0.126
H _d	-0.032	-0.011

a) Minus sign means up-field shift.

Fluorescence lifetimes of **1** and **2**, and reference compounds **6** and **7** were measured in two solvents (THF and DMF). Reflecting rigid structures, their decay curves fit well to single exponential ones. The fluorescence lifetimes of **1**, **2**, **6**, and **7** were used to determine photoinduced electron transfer rates in **1** and **2**. As seen from Table 2, large differences in electron transfer rate between **1** and **2** were observed in the both

Table 2. Fluorescence Lifetimes and Electron Transfer Rates

	THF		DMF	
	τ^a /ns	k_{et}^b /s ⁻¹	τ^a /ns	k_{et}^b /s ⁻¹
1	0.28	3.5×10^9	0.26	3.8×10^9
2	2.1	4.0×10^8	1.5	5.8×10^8
6	17.5		17.5	
7	15.0		16.3	

a) Fluorescence lifetimes were measured by the method of time correlated single photon counting using a picosecond dye laser (second harmonic of pyridine-1) exciting at 355 nm with a pulse width of 0.8 ps (fwhm).

b) Electron transfer rate was calculated using the formula $k_{et} = 1/\tau - 1/\tau_{ref}$.

solvents. Since the other factors controlling the electron transfer in the two compounds are almost the same, as discussed earlier, the orientation effect is responsible for the differences. The remarkably large value, a factor of nine, for **1** against **2** in THF is compatible to the value of the separation-distance effect¹²⁾ for the reduction of each 1.5-2.0 Å. Moreover, the value (a factor of nine) is much larger than the previous models (a factor of five), where the same two chromophores are linked by the same spacers with longer distances. (One more intervening bond is present.) This indicates clearly that the orientation effect becomes larger as a decrease of separation distance between chromophores. In general, orientation effect includes two types of effects, i.e., "through bond" and "through space". In the through-bond mechanism, which is believed to be mainly operative in intramolecular electron transfer systems, the electron transfer rates are dependent upon the conformation of intervening σ -framework; being optimal for an all-trans, antiperiplanar arrangement.⁵⁾ Contrary to the all-trans rule,¹³⁾ compound **2** with all-trans conformation of the spacer shows smaller k_{et} than **1**. This indicates that through-space mechanism is dominant in **1** and **2** or that the all-trans rule in through-bond mechanism is not applicable to the present systems. The large orientation effect observed in this study will give useful information in the designing of artificial photosynthetic molecular assemblies.

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- 6) Planar conformation for indan framework in **1** was assumed for the estimation of the separation distance. See, Ref. 9 in Ref. 3 of this article.
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- 8) Synthesis of **1** and **2** will be reported elsewhere.
- 9) **1**: UV-vis (THF) 401, 500, 532, 571, 625 nm; ^1H NMR (360 MHz, CDCl_3) δ 10.14 (s, 2H), 9.93(s, 1H), 7.87(d, 1H, $J=7.0$ Hz), 7.62(s, 1H), 7.58(dd, 1H, $J=7.3, 7.0$ Hz), 6.45(s, 2H), 4.05(q, 4H, $J=7.6$ Hz), 3.62(s, 6H), 3.59(s, 2H), 3.54(s, 6H), 3.25(s, 2H), 2.91(d, 2H, $J=16.2$ Hz), 2.59(d, 2H, $J=16.2$ Hz), 1.86(t, 6H, $J=7.6$ Hz), -3.20(br s, 2H); MS 698 (M^+).
- 10) **2**: UV-vis (THF) 401, 500, 531, 571, 626 nm; ^1H NMR (360 MHz, CDCl_3) δ 10.16(s, 1H), 10.14(s, 1H), 9.95(s, 1H), 7.71(d, 1H, $J=7.1$ Hz), 7.56(d, 1H, $J=7.4$ Hz), 7.51(dd, 1H, $J=7.1, 7.4$ Hz), 6.56(d, 1H, $J=9.9$ Hz), 6.42(s, 1H, $J=9.9$ Hz), 4.07(q, 4H, $J=7.6$ Hz), 3.64(s, 3H), 3.54(s, 3H), 3.53(s, 3H), 2.48(s, 3H), 2.43(s, 3H), 1.87(t, 6H, $J=7.6$ Hz), 1.78-3.46(m, 10H), -3.14(br s, 1H), -3.29(br s, 1H); MS(FAB) 715 ($\text{M}+2$) $^+$; MS(EI) 713 (M^+).
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