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Intramolecular Photoinduced Electron Transfer in Pyromellitimide-linked Porphyrins

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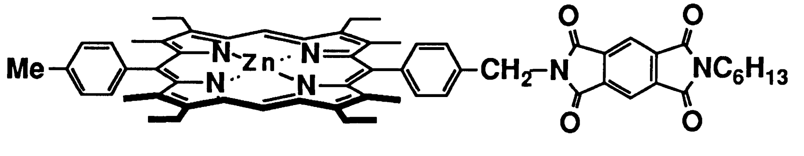
Characteristic absorption of the anion radical of pyromellitimide around 715 nm was demonstrated to be particularly useful for studies on photoinduced electron transfer reactions. Charge recombination in pyromellitimide-linked porphyrin was greatly retarded in benzene due to the large energy gap and small reorganization energy. A long-lived charge separated state (τ = 2.5 μs) was formed in the case of a diporphyrin-porphyrin-pyromellitimide triad system.

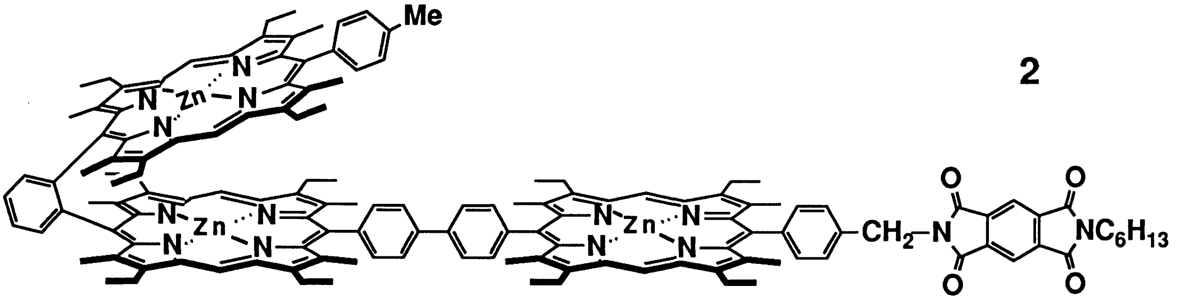
Electron transfer (ET) processes such as photoinduced charge separation (CS) and charge recombination (CR) of ion pair (IP) are regulated by a variety of parameters including the free energy gap ($-\Delta G^0$) between the initial and final state of ET, the magnitude of the electronic interaction between the donor (D) and acceptor (A) which is dependent upon the mutual distance and orientation, the reorganization energy (λ) involving the surrounding solvents, and the solvent dynamics.1) The bell-shaped energy gap dependence of ET rate constant covering inverted, top and normal regions as predicted by conventional theories has been only recently confirmed for CR decay of geminate radical ion pairs produced by the fluorescence quenching of uncombined D and A in polar solutions.2) In the case of CR reaction of covalently linked D-A pairs,3) however, no normal region but only the inverted region has been observed so far in contrast to the photoinduced CS reaction for both uncombined4,5) and combined D-A pairs,3,6) in which no inverted region but only the normal region has been observed. Several theoretical interpretations have been proposed to remedy this contradictory situations.7)

On the other hand, the appearance of the X-ray structure of bacterial photosynthetic reaction center (RC)8) has exerted a great impact on mechanistic as well as synthetic approaches toward this natural CS apparatus.9,10) In order to better understand the detailed mechanisms in RC, ultrafast laser photolysis investigations on the ET reactions of elaborated models consisting of acceptor-linked oligomeric porphyrins are highly desirable. However, it is not necessarily easy to identify a IP state when the acceptor is quinone, since the absorption spectra of the porphyrin cation radical are quite similar to those of S_1-state or T_1-state of porphyrin and the spectral characteristics of the quinone anion radical are rather obscure. One remarkable exception is the case of carotenoid-linked porphyrins, in which the carotenoid cation radical exhibits strong absorption around 980 nm in CH_2Cl_2 which has been used to detect the IP states.11)

We report here the picosecond dynamics of pyromellitimide-linked porphyrins **1** and **2**, in which the sharp absorption around 715 nm due to the anion radical of pyromellitimide $(Im)^-$ greatly facilitates the analysis of ET kinetics. Sanders et al. also conducted picosecond time-resolved flash photolysis on the pyromellitimide-capped porphyrins only in a narrow range of 420-540 nm, and thus missed observing the characteristic absorption of $(\mathrm{Im})^-$.[12] In the model **1**, the center-to-center distance between the porphyrin and pyromellitimide is restricted ca. 10 Å,[13] while a 1,2-phenylene-bridged diporphyrin (D) is connected via a 4,4'-biphenyl linkage with the pyromellitimide (Im)-linked porphyrin (M) in the model **2**. In the D moiety, strong interaction between the two porphyrins results in lowering of the S_1-excitation energy by 0.19 eV and also in the decrease of one-electron oxidation potential by 0.17 V.



1



2

In Fig. 1, the picosecond time-resolved transient absorption spectra of **1** and **2** observed in THF by exciting with 532 nm laser pulse were indicated.[14,15] As the S_n—S_1 absorption band of ZnP at 460 nm

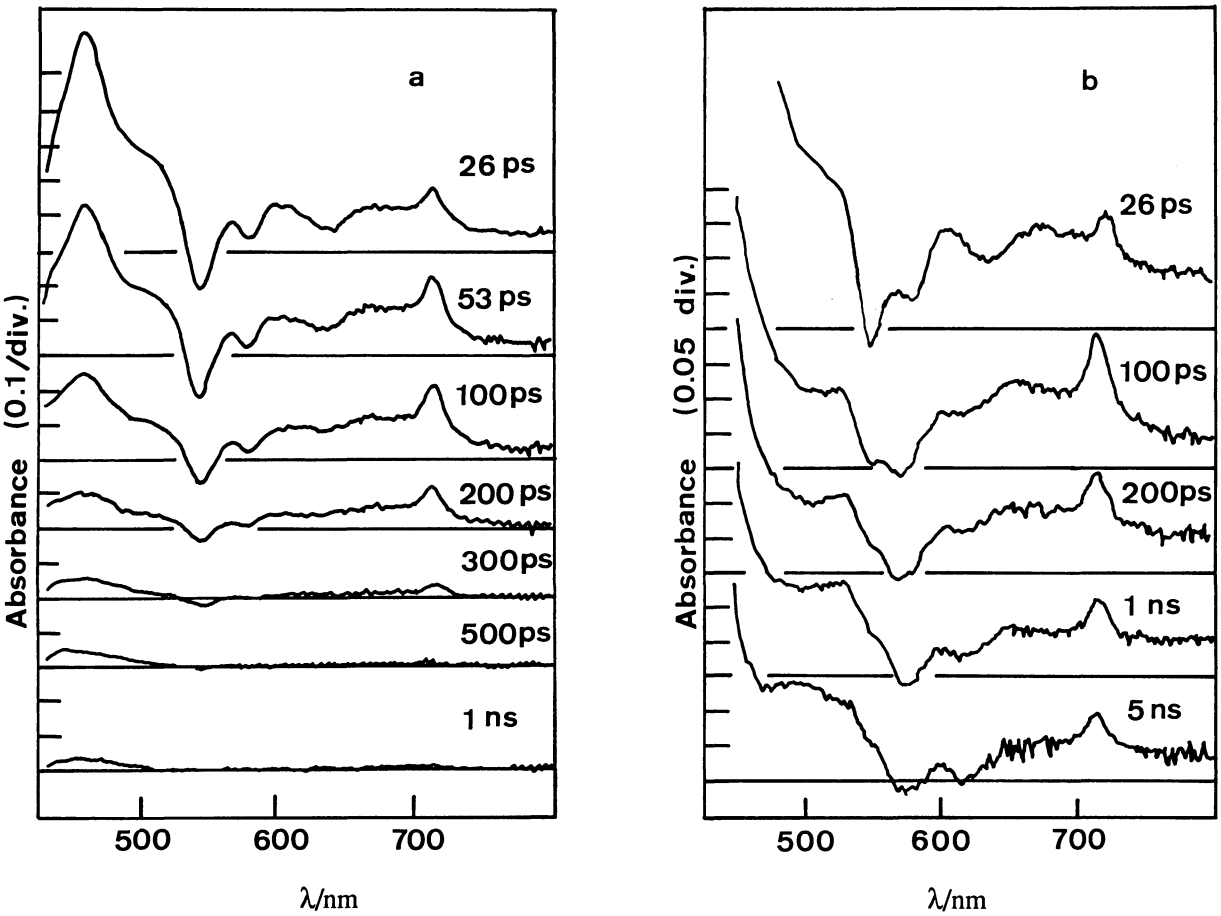
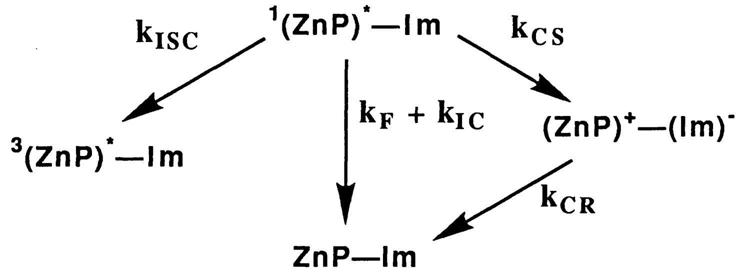


Fig. 1. Picosecond transient absorption spectra of **1**(a) and **2** (b) in THF at 25 °C excited at 532 nm.



Scheme 1.

decays with τ = 60 ps, a sharp absorption band at 715 nm appears with rise time of 60 ps and decays with τ = 100 ps. A broad absorption band around 670 nm exhibits the same time-profile as that of the 715 nm band. By referring to the spectra obtained by electrochemical oxidation or reduction of the relevant chromophores, the absorption bands at 670 nm and 715 nm have been assigned to $(ZnP)^+$ and $(Im)^-$, respectively. The long-lived absorption band around 460 nm can be assigned from its band shape to the $^3(ZnP)^*$, which may be produced by the intersystem crossing competing with the CS between the $^1(ZnP)^*$ and Im. We have obtained similar time-resolved transient absorption spectra also in benzene and dimethylformamide (DMF).

$$A_\lambda(t) = \alpha \exp(-t/\tau_S) + \beta \exp(-t/\tau_{IP}) + \gamma \qquad (1)$$

From the above results, the reaction scheme for **1** may be depicted as summarized in scheme 1. This reaction scheme gives Eq. 1 for the time dependence of the absorbance $A_\lambda(t)$ at a wavelength of λ, where $1/\tau_S = k_{CS} + 1/\tau_0$, $1/\tau_0 = k_F + k_{IC} + k_{ISC}$, $1/\tau_{IP} = k_{CR}$, and α, β, and γ are constant independent of time (t) and include initial concentration of $^1(ZnP)^*$, intersystem crossing yield of $^1(ZnP)^*$, yield of IP state formation, etc. By simulation of the observed time profiles at 715 nm and 460 nm with Eq. 1, k_{CS} and k_{CR} values have been obtained as indicated in Table 1, where the free energy gap $-\Delta G^0_{IP}$ for CR reaction estimated by using the oxidation and reduction potentials measured in DMF and corrected term for the ion solvation energies by Born formula16) for the other solvents are also given. It is evident from Table 1 that k_{CS} does not show large solvent polarity dependence but k_{CR} shows a large decrease with decrease of the solvent polarity. In general, with decrease of the solvent polarity, the free energy gap for the CR reaction of the IP state increases and that for the photoinduced CS reaction decreases, while the solvent reorganization energy decreases. Therefore, k_{CS} is not much affected by solvent polarity on the one hand, while k_{CR} shows a rather drastic decrease with the decrease of the solvent polarity. It should be noted here that such effect is very important in regulating the photoinduced CS processes even in the case of uncombined and combined porphyrin-quinone systems.17) In the present work, this effect has been most clearly demonstrated by using a fixed distance porphyrin-pyromellitimde molecule **1**.

Table 1. Electron transfer rate constants and free energy gaps between the IP state and ground state

Solvent	k_{CS} /s^{-1}	k_{CR} /s^{-1}	$-\Delta G^0_{IP}$/eV
Benzene	1.9×10^{10}	3.6×10^8	2.23
THF	1.7×10^{10}	9.3×10^9	1.60
DMF	8.0×10^9	$\approx 5 \times 10^{10}$	1.37

By extending the system to **2**, we have observed long-lived absorption due to $(\mathrm{Im})^-$ as indicated in fig 1(b). Deconvolution of the time dependence of the absorbances at 715 nm reveals the decay curve to be composed of two exponentials with lifetime of 70 ps and 2.5 μs, which can be ascribed to CR process from IP states, $\mathrm{D}\text{—}(\mathrm{M})^+\text{—}(\mathrm{Im})^-$ and $(\mathrm{D})^+\text{—}\mathrm{M}\text{—}(\mathrm{Im})^-$, respectively. The latter IP state is produced from the former one by hole transfer. Detailed features of the energetics and picosecond to microsecond photochemical dynamics of the triad **2** and its related models will be reported elsewhere.

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