

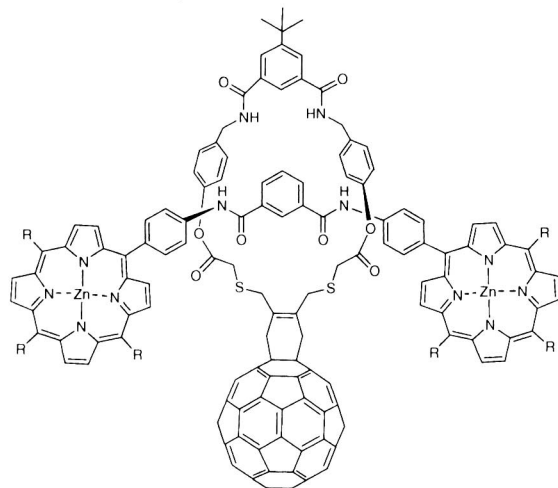
Photoinduced Electron Transfer Reaction in Rotaxane Structure containing C₆₀ and Zinc Porphyrin

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In the photosynthetic center of bacteria, charge separation proceeds via a series of electron transfer steps between porphyrin components and quinones that are spatially oriented in proteins. Numerous synthetic models for covalently connected donor-acceptor systems have been proposed, based on the coordination bond between donor and acceptor. Recently, photoinduced electron transfer systems between donors and acceptors in rotaxanes have been reported.[1,2] On the other hand, it is well known that ZnP-C₆₀ connected system shows a relatively long lifetime of the charge-separated state, in addition to high charge-separation efficiency.[3]



We considered the allocation of a ZnP (donor) and a C₆₀ (acceptor) with a rotaxane skeleton to mimic the photosynthesis reaction center. In the present study, we designed a ZnP-rotaxane with C₆₀ as shown in Fig. 1, in which through-space forward and backward electron transfer processes between the ZnP-moieties and the C₆₀-moiety are expected.

The time profile of the fluorescence of the rotaxane shows bi-exponential decay in PhCN; the lifetimes of the ZnP moieties in rotaxane ($\tau_1 = 93$ ps (80%) and $\tau_2 = 1560$ ps (20%) in PhCN) were evaluated by the least square curve-fitting method. The τ_1 value became short compared with that of rotaxane ZnP without C₆₀ ($\tau = 1790$ ps (100%)), while the τ_2 value remained similar to that of τ . From these lifetimes, the quantum yield (Φ_{CS}) and rate constant of the charge-separation (k_{CS}) were calculated to be 0.95 and $1.0 \times 10^{10} \text{ s}^{-1}$, respectively.

To ensure the longer lifetime of CS state, nanosecond transient absorption of rotaxane ZnP with C₆₀ in PhCN was observed by 532 nm laser light excitation (6 ns laser pulse), which is shown in Fig. 2. The inserted time profile in Fig. 2 shows the decay of the anion radical of C₆₀ at 1000 nm. The decay obeys first-order kinetic giving the rate constant of $5.5 \times 10^9 \text{ s}^{-1}$ (180 ns), which is the charge-recombination rate constant (k_{CR}). The charge-recombination rates (k_{CR}) showed slight temperature dependency; from the semi-empirical Marcus equation, the activation free-energy (ΔG_{CR}^\ddagger) was evaluated at 57 meV, which is quite smaller than the usual dyad system; i.e., the ΔG_{CR}^\ddagger of retinyl-C₆₀ was 160 meV.[4] Although it was still larger value compared with the complete through space electron transfer

case, we considered that this decrement of the ΔG_{CR}^\ddagger in rotaxane may be attributed to the flexibility of the relative configuration of the ZnP and C₆₀ moieties. The electronic coupling constant (V) evaluated from the semiempirical Marcus equation was 0.77 cm^{-1} , almost twice that of the retinyl-C₆₀ dyad ($V = 0.34 \text{ cm}^{-1}$ in PhCN).[4] This difference in V value suggests that not only is the donor-acceptor

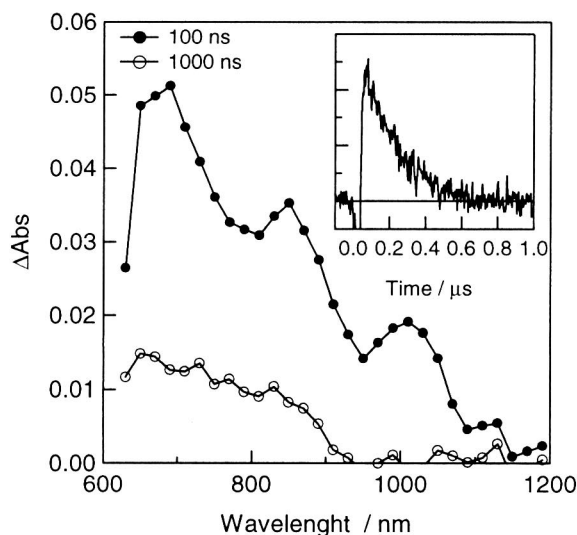


Figure 2 Transient Absorption Spectra of Rotaxane ZnP with C₆₀ obtained in PhCN.

er-to-center, r_{cc} , ca. 10 \AA) than in retinyl-C₆₀ dyad ($r_{cc} = 11.4 \text{ \AA}$), but also that it shows a more suitable orientation for electron transfer.

References

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