Electron Transfer in Rotaxanes

Photoinduced Intrarotaxane Electron Transfer between Zinc Porphyrin and [60]Fullerene in Benzonitrile**

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In the photosynthetic center of bacteria, charge separation proceeds by a series of electron-transfer steps between porphyrin(P)-like components and quinones that are spatially oriented in proteins. Numerous synthetic models for covalently connected donor–acceptor systems have been proposed,[1–4] based on coordinative bonds between donor and acceptor.[5] Recently, photoinduced electron transfer between donors and acceptors in rotaxanes was reported.[6,7] Rotaxanes containing ZnP (donor) and AuP (acceptor) show photoinduced superexchange forward electron transfer between noncovalently linked chromophores.[8] Imahori et al. reported that a ZnP–C_{60} linked dyad system shows a relatively long lifetime of the charge-separated state, in addition to high charge-separation efficiency.[3] We envisaged that the combination of a ZnP (donor), C_{60} (acceptor), and a rotaxane skeleton could mimic the photosynthesis reaction center. Herein we report on the ZnP/C_{60} rotaxane **7**, designed as shown in Scheme 1, in which through-space forward and backward electron transfer processes between the ZnP and C_{60} moieties and a relatively long charge-separation lifetime are expected.

Rotaxane **4** was synthesized by the hydrogen-bond-assisted method for *sec*-amide-based rotaxanes.[9,10] Thus, the condensation of isophthaloyl dichloride (**2**) and 5,10,15-tris(3,5-di-*tert*-butylphenyl)-20-(4-aminophenyl)porphyrin (**3**)[11] was carried out in chloroform in the presence of macrolactam **1**[9] at 0 °C to afford **4** in 17 % yield. The conversion of **4** into the corresponding zinc porphyrin rotaxane **5** was achieved by treatment with zinc acetate in refluxing chloroform. The Diels–Alder reaction of **4** and five equivalents of C_{60} was carried out in refluxing 1,2-dichlorobenzene to give rotaxane **6** in 69 % yield. Finally, **6** was converted into zinc porphyrin rotaxane **7** in 82 % yield by treatment with zinc acetate. The rotaxanes were characterized by satisfactory NMR and FAB-MS spectra corresponding to their structures. To our knowledge, these are the first rotaxane porphyrin–C_{60} conjugates, although such a pseudorotaxane has been reported.[12] On the other hand, some fullerene-containing catenanes have also been reported.[13]

The steady-state absorption spectrum of **7** is shown in Figure 1; the absorption bands at 420 and 500–600 nm are mainly the Soret and Q bands, respectively, of ZnP moiety **5**. The absorption bands of the C_{60} moiety appear at 700 nm and below 350 nm. The absorption spectrum of **7** is almost a superimposition of those of **5** and C_{60}. Figure 1 also shows the fluorescence spectrum of **7** above 600 nm; the fluorescence peaks at 620 and 670 nm are attributed to the ZnP moiety **5**, while the fluorescence peak of C_{60}, which is expected to appear at 725 nm, may be hidden in the fluorescence bands of the ZnP moieties. The fluorescence intensity of **7** was quite weak compared to that of **5** in benzonitrile. Furthermore, an enhancement in the fluorescence of the C_{60} moiety at 725 nm was not observed, and this suggests that energy transfer from the excited singlet state of the ZnP moieties to the C_{60} moiety may not have taken place. These observations indicate that electron transfer predominantly takes place from the excited singlet state of the ZnP moieties to the C_{60} moiety.

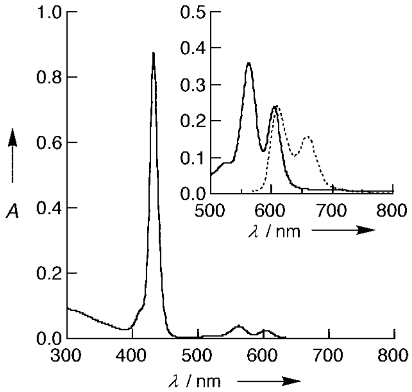

Figure 1. Steady-state absorption spectrum of **7** (1×10^{-6} M) in PhCN. Inset: steady-state absorption spectrum (solid line) and fluorescence spectrum (dashed line) of **7** (1×10^{-5} M).

The time profile of the fluorescence of rotaxane **7** shows biexponential decay in benzonitrile (Figure 2); the lifetimes of the ZnP moieties in **7** [$\tau_{f1} = 93$ ps (80 %) and $\tau_{f2} = 1560$ ps (20 %)] were evaluated by the curve-fitting method. The τ_{f1} value is small relative to that of **5** [$\tau_{fr} = 1790$ ps (100 %)], while the τ_{f2} value remained similar to that of τ_{fr}. From these lifetimes, the quantum yield Φ_{CS} and rate constant k_{CS} for charge separation were calculated to be 0.95 and 1.0×10^{10} s^{-1}, respectively, by using the ordinal equations [$\Phi_{CS} = 1/\tau_{fr}/(1/\tau_{fr} - 1/\tau_{f1})$ and $k_{CS} = (1/\tau_{fr} - 1/\tau_{f1})$).[3]

Figure 3 shows the nanosecond transient absorption spectra of rotaxane **7** in benzonitrile, observed by 532 nm laser excitation (6 ns laser pulse). The transient absorption band at 1000 nm observed immediately after laser pulse (6 ns)

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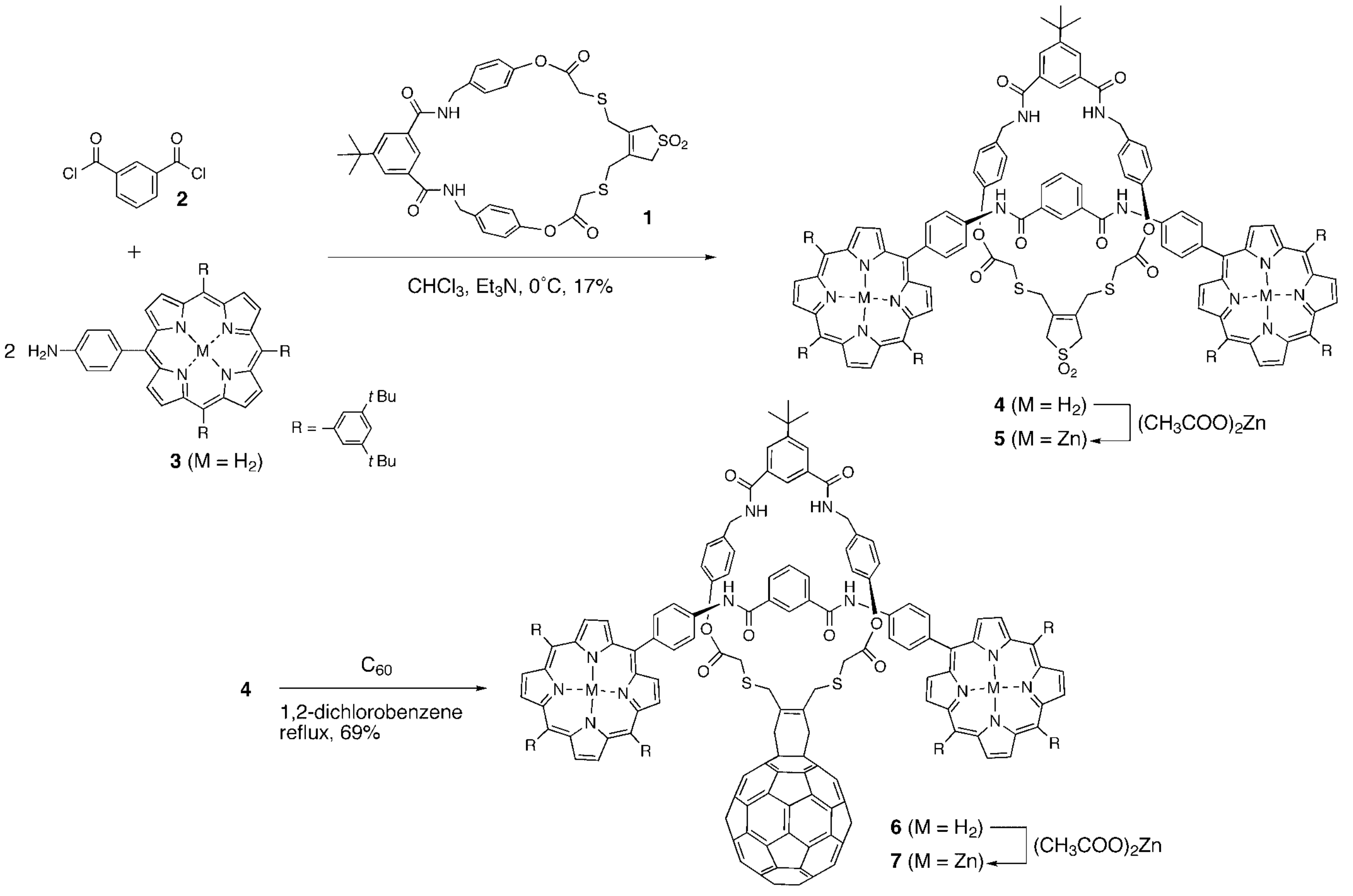

Scheme 1. Synthesis of **4**–**7**.

was assigned to the anion radical of the C_{60} moiety; the absorption bands in the visible region, centered around 700 nm and 850 nm, were attributed to the triplet states of the C_{60} and ZnP moieties, respectively, with which the cation radical of the ZnP moieties may overlap.[3] These observations confirm that charge separation takes place immediately after laser exposure. The transient absorptions at 1000 ns were mostly attributed to the triplet states of C_{60} and ZnP in rotaxane **7**, which have longer lifetimes than the charge-separated state.

The inset time profile in Figure 3 shows the decay of the radical anion of C_{60} at 1000 nm. The decay obeys first-order kinetics with a rate constant of $5.5\times10^6\,s^{-1}$, which is the charge-recombination rate constant k_{CR}. This value corresponds to a lifetime τ_{RIP} of 180 ns for the charge-separated state (radical ion pair). This τ_{RIP} value is significantly larger

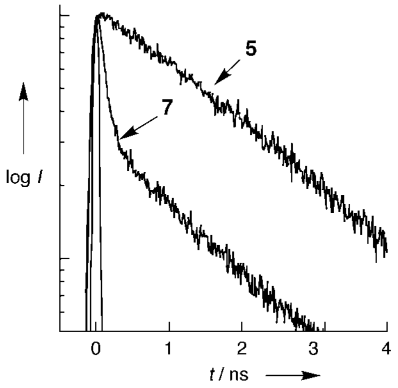

Figure 2. Time profiles of the fluorescence of rotaxane **7** (1×10^{-4} M) and ZnP moiety **5** (1×10^{-4} M) in PhCN. Excitation wavelength was 410 nm.

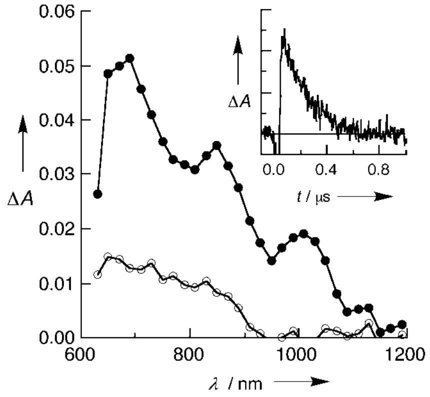

Figure 3. Nanosecond transient absorption spectra of **7** (1×10^{-4} M) observed by 532 nm laser excitation in PhCN after 100 (●) and 1000 ns (○). Inset: trace of the C_{60} radical anion at 1000 nm.

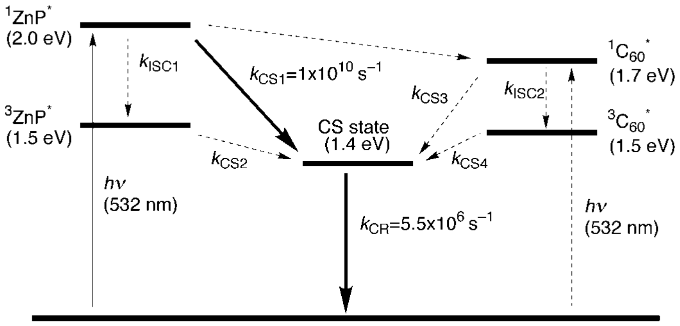

Figure 4. Energy diagram for charge separation (CS) and charge recombination (CR) of **7** after photoexcitation in PhCN. ISC = intersystem crossing.

than those reported for covalently connected dyad molecules; for example, C_{60}–dimethylaniline (< 1 ns),[14] C_{60}–β-carotene (< 1 ns),[15] and C_{60}-TTF (2 ns).[16] Rotaxane **7** has a τ_{RIP} value similar to that of covalently linked C_{60}–ZnP (770 ns).[3]

The energy diagram for the charge separation and recombination processes after photoexcitation is shown in Figure 4. The ion-pair state was evaluated from the first oxidation potential of the ZnP moiety (0.29 V vs ferrocene/ferrocene$^+$) and the first reduction potential of the C_{60} moiety (-1.1 V vs ferrocene/ferrocene$^+$) of rotaxane **7** in benzonitrile. The shortening of fluorescence lifetimes indicates that charge separation takes place mainly from the excited singlet state of the ZnP moiety to produce a radical ion pair. The rate of this charge-separation process was as high as 10^{10} s^{-1}. The slow recombination rate suggests that this process lies in an inverted region far more negative than the charge-separation process.

The charge-recombination rates k_{CR} showed slight temperature dependence; from the semiempirical Marcus equation,[3] the free-energy of activation $\Delta G^{\ddagger}_{\mathrm{CR}}$ was evaluated to be 57 meV, which is somewhat smaller than for conventional dyad systems; for example, $\Delta G^{\ddagger}_{\mathrm{CR}}$ of retinyl–C_{60} is 160 meV.[17] In general, a rather small $\Delta G^{\ddagger}_{\mathrm{CR}}$ is expected for through-space electron transfer, while a considerably higher $\Delta G^{\ddagger}_{\mathrm{CR}}$ is anticipated for through-bond electron transfer. Thus, the small $\Delta G^{\ddagger}_{\mathrm{CR}}$ observed for rotaxane **7** suggests that charge recombination takes place by through-space electron transfer with a superexchange mechanism.[7] The $\Delta G^{\ddagger}_{\mathrm{CR}}$ value of 57 meV for **7** is slightly larger than that expected for the complete through-space electron transfer system; hence, this slight increase in $\Delta G^{\ddagger}_{\mathrm{CR}}$ of **7** can be attributed to the flexibility of the relative configuration of the ZnP and C_{60} moieties. The electronic coupling constant V, evaluated with the semiempirical Marcus equation, is 0.77 cm^{-1}, almost twice that of the retinyl–C_{60} dyad ($V = 0.34$ cm^{-1} in PhCN).[17] This difference in V value suggests that not only is the donor–acceptor distance smaller in **7** (center-to-center distance $r_{\mathrm{cc}} \approx 10$ Å) than in retinyl–C_{60} dyad ($r_{\mathrm{cc}} = 11.4$ Å), but also that **7** has a more suitable orientation for electron transfer. Further studies on electron transfer features are in progress.

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