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-C₆₀ 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), C₆₀ (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 C₆₀ moieties and a relatively long charge-separation lifetime are expected.

Rotaxane **4** was synthesized by the hydrogen-bondassisted method for *sec*-amide-based rotaxanes.^[9,10] Thus, the condensation of isophthaloyl dichloride (**2**) and 5,10,15tris(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 C₆₀ was carried out in refluxing 1,2-dichloro-

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benzene 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



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

mainly the Soret and Q bands, respectively, of ZnP moiety 5. The absorption bands of the C60 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 C₆₀, 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 C60 moiety at 725 nm was not observed, and this suggests that energy transfer from the excited singlet state of the ZnP moieties to the C₆₀ 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.

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 $5.5 \times 10^6 \text{ s}^{-1}$, 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** $(1 \times 10^{-4} \text{ m})$ and ZnP moiety **5** $(1 \times 10^{-4} \text{ m})$ 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 (\bullet) and 1000 ns (\odot). Inset: trace of the C₆₀ radical anion at 1000 nm.

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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, C₆₀-dimethylaniline (<1 ns),^[14] C₆₀-β-carotene (<1 ns),^[15] and C₆₀-TTF (2 ns).^[16] Rotaxane **7** has a $\tau_{\rm RIP}$ value similar to that of covalently linked C₆₀-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 C₆₀ 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 ΔG_{CR}^{*} was evaluated to be 57 meV, which is somewhat smaller than for conventional dyad systems; for example, ΔG_{CR}^{\dagger} of retinyl–C₆₀ is 160 meV.^[17] In general, a rather small ΔG^{*}_{CR} is expected for through-space electron transfer, while a considerably higher $\Delta G_{\rm CR}^{*}$ is anticipated for through-bond electron transfer. Thus, the small ΔG_{CR}^{\dagger} observed for rotaxane 7 suggests that charge recombination takes place by through-space electron transfer with a superexchange mechanism.^[7] The ΔG_{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 ΔG_{CR}^{*} of 7 can be attributed to the flexibility of the relative configuration of the ZnP and C₆₀ 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 $r_{cc} \approx 10$ Å) than in retinyl–C₆₀ dyad ($r_{cc} = 11.4$ Å), but also that 7 has a more suitable orientation for electron transfer. Further studies on electron transfer features are in progress.

- [1] D. Gust, T. A. Moore, A. L. Moore, *Acc. Chem. Res.* **2001**, *34*, 40.
- [2] S. Fukuzumi, D. M. Guldi in *Electron Transfer in Chemistry*, Vol. 2 (Ed.: V. Balzani), Wiley-VCH, Weinheim, 2001, pp. 270-337.
- [3] H. Imahori, M. E. El-Khouly, M. Fujitsuka, O. Ito, Y. Sakata, S. Fukuzumi, J. Phys. Chem. A 2001, 105, 325.
- [4] a) N. Armaroli, F. Diederich, C. O. Dietrich-Buchecker, L. Flamigni, G. Marconi, J.-F. Nierengarten, J.-P. Sauvage, *Chem. Eur. J.* **1988**, *4*, 406; b) N. Armaroli, G. Marconi, L. Echegoyen, J. P. Bourgeois, F. Diederich, *Chem. Eur. J.* **2000**, *6*, 1629; c) L. Flamigni, I. M. Dixon, J.-P. Collin, J.-P. Sauvage, *Chem. Commun.* **2000**, 2479.
- [5] F. D'Souza, G. R. Deviprasad, M. E. El-Khouly, M. Fujitsuka, O. Ito, J. Am. Chem. Soc. 2001, 123, 5277.
- [6] M.-J. Blanco, M. C. Jiménez, J.-C. Chambron, V. Heitz, M. Linke, J.-P. Sauvage, *Chem. Soc. Rev.* 1999, 28, 293.
- [7] P. R. Ashton, R. Ballardini, V. Balzani, A. Credi, K. R. Dress, E. Ishow, C. J. Kleverlaan, O. Kocian, J. A. Preece, N. Spencer, J. F. Stoddart, M. Venturi, S. Wenger, *Chem. Eur. J.* 2000, *6*, 3558.
- [8] M. Andersson, M. Linke, J.-C. Chambron, J. Davidsson, V. Heitz, J.-P. Sauvage, L. Hammarström, J. Am. Chem. Soc. 2000, 122, 3526.
- [9] N. Watanabe, N. Kihara, T. Takata, Org. Lett. 2001, 3, 3519.
- [10] a) N. Kihara, T. Takata, J. Synth. Org. Chem. Jpn. 2001, 59, 206;
 b) Y. Furusho, J. Shoji, N. Watanabe, N. Kihara, T. Adachi, T. Takata, Bull. Chem. Soc. Jpn. 2001, 74, 139; c) N. Watanabe, Y. Furusho, N. Kihara, T. Takata, K. Kinbara, K. Saigo, Chem. Lett. 1999, 915; d) R. Jäger, F. Vögtle, Angew. Chem. 1997, 109, 966; Angew. Chem. Int. Ed. Engl. 1997, 36, 930; e) F. Vögtle, T. Dünnwald, T. Schmidt, Acc. Chem. Res. 1996, 29, 451.
- [11] H. Imahori, K. Hagiwara, M. Aoki, T. Akiyama, S. Taniguchi, T. Okada, M. Shirakawa, Y. Sakata, J. Am. Chem. Soc. 1996, 118, 11771.
- [12] M. V. Martínez-Díaz, N. S. Fender, M. S. Rodríguez Morgade, M. Gómez-López, F. Diederich, L. Echegoyen, J. F. Stoddart, T. Torres, J. Mater. Chem. 2002, 12, 2095.
- [13] P. R. Ashton, F. Diederich, M. Gómez-López, J.-F. Nierengarten, J. A. Preece, F. M. Raymo, J. F. Stoddart, *Angew. Chem.* 1997, 109, 1611; Angew. Chem. Int. Ed. Engl. 1997, 36, 1448.
- [14] R. M. Williams, J. M. Zwier, J. W. Verhoeven, J. Am. Chem. Soc. 1995, 117, 4093.
- [15] H. Imahori, S. Cardoso, D. Tatman, S. Lin, L. Noss, G. R. Seely, L. Sereno, C. Silber, T. A. Moore, A. L. Moore, D. Gust, *Photochem. Photobiol.* **1995**, *62*, 1009.
- [16] N. Martín, L. Sánchez, M. A. Herranz, D. M. Guldi, J. Phys. Chem. A 2000, 104, 4648.
- [17] M. Yamazaki, Y. Araki, M. Fujitsuka, O. Ito, J. Phys. Chem. A 2001, 105, 8615.

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