Acceleration of Photoinduced Electron Transfer in Porphyrin-Linked C_{70}

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Porphyrin-linked C_{70} and porphyrin-linked C_{60} dyads have been designed and synthesized to evaluate the intrinsic properties of C_{70} in electron transfer. The photoinduced charge separation in the former is accelerated by a factor of about two compared with that in the latter. The result shows that C_{70} can be added to potential building blocks in artificial photosynthesis.

After discovery of C_{60} and subsequent production in large scale, fullerene chemistry has been rapidly developed during the last decade.[1] Unique chemical, physical, and biochemical properties of C_{60} have consequently been revealed. We[2] and other groups[3-5] have prepared a variety of porphyrin-linked C_{60} and have shown that C_{60} is an excellent acceptor in electron transfer (ET) process. In the course of these studies we found that the most peculiar properties of C_{60} are to accelerate photoinduced charge separation (CS) and decelerate charge recombination (CR) due to the small reorganization energy (λ) of C_{60} in ET.[2,6] The characteristic features are similar to the situation in photosynthetic ET where λ, which is mainly controlled by the surrounding protein residues, is small enough to achieve the optimized conditions.[7] Considering that higher fullerenes have similar three-dimensional size and shape to those of C_{60}, it is interesting to examine whether the unique property of C_{60} is maintained in the next most abundant, higher fullerene C_{70}. The structure of C_{70} has rugbyball shape (major axis, 9.8 Å; minor axis, 8.8 Å) in contrast with the soccerball shape for C_{60} (diameter, 8.8 Å). To clarify the ET properties in C_{70}, we designed compounds **1** and **2** where the same porphyrin unit is connected to C_{70} and C_{60}, respectively, using the same spacer (Figure 1). Since the first reduction potentials of C_{60} and C_{70} are reported to be quite similar,[8] the inherent shape and size effect of C_{70} in ET is expected to be evaluated accurately by comparing the ET rates of the two compounds. Free rotation around the spacer methylene in **1** and **2** would not affect ET as we reported in similar porphyrin-C_{60} linked systems.[2]

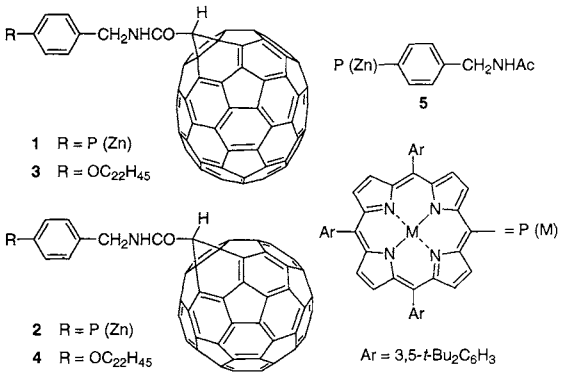
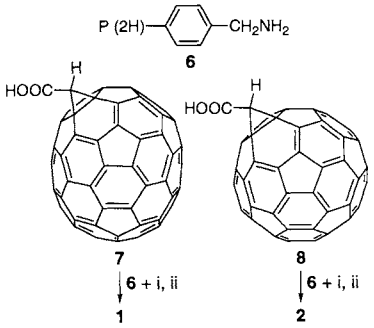


Figure 1. Porphyrin-linked C_{70} and C_{60} and the related references.



Scheme 1. Synthesis of **1** and **2**. i) DCC, 1-hydroxybenzotriazole, bromobenzene, DMSO; ii) $Zn(OAc)_2$, $CHCl_3$, reflux.

The synthesis of **1** and **2** is shown in Scheme 1. To eliminate the isomer problem in the functionalization of C_{70}, we applied Schuster's method to obtain selectively [1,9]methanofullerene[70] carboxylic acid **7**.[9] Condensation of **7** with aminomethylporphyrin **6**,[10] followed by treatment with $Zn(OAc)_2$, gave **1** in 56% yield. The porphyrin-C_{60} dyad **2** was synthesized from **6** and [6,6]methanofullerene[60] carboxylic acid **8**[9] by the same method as that described for **1**. The fullerene references **3** and **4** as well as the porphyrin reference **5** were also prepared. Various spectral data including ^{1}H- and ^{13}C-NMR and FAB mass spectra supported the expected structure for these molecules.[11]

Absorption spectra of **1** and **2** both in benzene and THF were essentially the linear combinations of the spectra of the corresponding components **3**-**5**, indicating no appreciable interactions between the two chromophores in the ground state. The absorption due to the C_{70} and C_{60} is much weaker and broader than that of the porphyrin, implying that selective excitation of the porphyrin is possible in **1** and **2**. The redox potentials of **1**-**5** were measured by a differential pulse voltammetry in dichloromethane using 0.1 M n-Bu_4NPF_6 as supporting electrolyte. The potentials of **1** and **2** (**1**: −1.83, −1.46, −1.10, +0.30, +0.64 V; **2**: −1.92, −1.46, −1.10, +0.31, +0.63 V vs. Fc/Fc^+) can be explained by the sum of **5** (+0.22, +0.70 V vs. Fc/Fc^+) and **3** and **4** (**3**: −1.83, −1.44, −1.09 V; **4**: −1.92, −1.45, −1.08 V vs. Fc/Fc^+), respectively. The first reduction potential (−1.10 V) of the C_{70} moiety in **1** is the same as that of the C_{60} moiety in **2**.[12]

Steady-state fluorescence spectra of **1**, **2**, and **5** were taken in THF and benzene with the same concentration exciting at the Soret band where the porphyrin absorbs mainly. The fluorescence spectra of **1** and **2** were strongly quenched compared with those of **5** (relative intensity: 0.005 for **1**, 0.016 for **2** in THF; 0.007 for **1**, 0.022 for **2** in benzene), showing the rapid

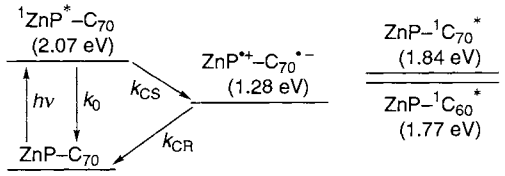


Figure 2. Energy diagram for **1** and **2** in THF. Numbers in parentheses indicate the values of the energy level.

quenching of the excited singlet state of the porphyrin (^{1}ZnP*) by the attached fullerene. In THF the emissions of **1** and **2** (580-750 nm) were observed only from the porphyrin. Therefore, there is no evidence for the existence of the singlet-singlet energy transfer (EN) from ^{1}ZnP* to the fullerenes.[13] Based on the energy diagram shown in Figure 2, CS from ^{1}ZnP* to the fullerenes is energetically feasible (Table 1). On the other hand, emissions from both the porphyrin and the fullerenes (λ_{max} = 690 nm for **1**, λ_{max} = 705 nm for **2**) were seen in benzene. The emission from the fullerene may be explained by the slower CS from the porphyrin to the excited singlet states of the C_{70} and C_{60} and/or the fast energy equilibrium between the charge-separated states and the excited singlet states of the C_{70} and C_{60}. From these results, we can conclude that CS from ^{1}ZnP* to the fullerenes is a dominant pathway in THF and benzene.

The fluorescence lifetimes of **1**, **2**, and **5** were measured by a picosecond single photon counting technique with excitation at 425 nm where the porphyrin absorbs mainly and monitoring at 605 nm where the fluorescence is due to only the porphyrin. The fluorescence decays of **1** and **2** in THF and benzene were analyzed to give only one significant component with lifetimes of 20-70 ps. The results are summarized in Table 1. Based on the data we can calculate the CS rates, k_{CS} ($= \tau^{-1} - \tau_{ref}^{-1}$; τ_{ref} = 2.0 ns for **5** in THF and benzene). In THF and benzene the k_{CS} for **1** is faster than that for **2** by a factor of about 2. The rate acceleration of CS is remarkable considering that the driving forces for the photoinduced CS as well as the electronic couplings between the two moieties are quite similar in **1** and **2**. This may be explained by the smaller λ in C_{70} compared with that in C_{60}.

In conclusion, zincporphyrin-C_{70} dyad **1** has been prepared for the first time. Photoinduced CS from ^{1}ZnP* to the C_{70} is accelerated compared with that of the C_{60}. This result shows that C_{70} acts as a good electron acceptor to produce charge-separated state efficiently.

Table 1. The Gibbs free energy changes for CS ($-\Delta G_{CS}$), fluorescence lifetimes (τ), and ET rate constants for CS (k_{CS}) of **1** and **2**

Compounds	Solvents	$-\Delta G_{CS}$/eV[a]	τ/ps	k_{CS} /10^{10} s^{-1}
1	THF	0.79	28	3.5
2	THF	0.77	50	1.9
1	benzene	0.40	36	2.7
2	benzene	0.39	71	1.4

[a] The free energy changes for CS were calculated by using the oxidation and reduction potentials in CH_2Cl_2 and the corrected term for the ion solvation energies by Born equation for the other solvents.[14] The radii of C_{70} and C_{60} and the center-to-center distances in **1** and **2** were estimated to be 4.7, 4.4, 10.6, and 10.9 Å, respectively. In benzene, the value of the corrected term (0.29 eV) in the similar zincporphyrin-C_{60} dyad was used tentatively.

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References and Notes

1 A. Hirsch, "The Chemistry of the Fullerenes," Georg Thieme Verlag, Stuttgart (1994).
2 H. Imahori, K. Hagiwara, T. Akiyama, S. Taniguchi, T. Okada, and Y. Sakata, *Chem. Lett.*, **1995**, 265; H. Imahori, K. Hagiwara, M. Aoki, T. Akiyama, S. Taniguchi, T. Okada, M. Shirakawa, and Y. Sakata, *J. Am. Chem. Soc.*, **118**, 11771 (1996); H. Imahori, K. Hagiwara, T. Akiyama, M. Aoki, S. Taniguchi, T. Okada, M. Shirakawa, and Y. Sakata, *Chem. Phys. Lett.*, **263**, 545 (1996); Y. Sakata, H. Imahori, H. Tsue, S. Higashida, T. Akiyama, E. Yoshizawa, M. Aoki, K. Yamada, K. Hagiwara, S. Taniguchi, and T. Okada, *Pure Appl. Chem.*, **69**, 1951 (1997); H. Imahori and Y. Sakata, *Adv. Mater.*, **9**, 537 (1997); H. Imahori, K. Yamada, M. Hasegawa, S. Taniguchi, T. Okada, and Y. Sakata, *Angew. Chem., Int. Ed. Engl.*, **36**, 2626 (1997).
3 P. A. Liddell, J. P. Sumida, A. N. Macpherson, L. Noss, G. R. Seely, K. N. Clark, A. L. Moore, T. A. Moore, and D. Gust, *Photochem. Photobiol.*, **60**, 537 (1994); D. Kuciauskas, S. Lin, G. R. Seely, A. L. Moore, T. A. Moore, D. Gust, T. Drovetskaya, C. A. Reed, and P. D. W. Boyd, *J. Phys. Chem.*, **100**, 15926 (1996); P. A. Liddell, D. Kuciauskas, J. P. Sumida, B. Nash, D. Nguyen, A. L. Moore, T. A. Moore, and D. Gust, *J. Am. Chem. Soc.*, **119**, 1400 (1997).
4 T. D. M. Bell, T. A. Smith, K. P. Ghiggino, M. G. Ranasinghe, M. J. Shephard, and M. N. Paddon-Row, *Chem. Phys. Lett.*, **268**, 223 (1997).
5 N. Martín, L. Sánchez, B. Illescas, and I. Pérez, *Chem. Rev.*, **98**, 2527 (1998).
6 D. M. Guldi and K. -D. Asmus, *J. Am. Chem. Soc.*, **119**, 5744 (1997).
7 "The Photosynthetic Reaction Center," ed by J. Deisenhofer and J. R. Norris, Academic Press, San Diego (1993), Vol. 1 and 2.
8 Q. Xie, E. Pérez-Cordero, and L. Echegoyen, *J. Am. Chem. Soc.*, **114**, 3978 (1992).
9 Y. Wang, D. I. Schuster, S. R. Wilson, and C. J. Welch, *J. Org. Chem.*, **61**, 5198 (1996).
10 H. Tamiaki, K. Nomura, and K. Maruyama, *Bull. Chem. Soc. Jpn.*, **67**, 1863 (1994).
11 **1**: ^{1}H NMR (270 MHz, $CDCl_3$:CS_2 = 5:1) δ 1.51 (s, 54H), 2.03 (s, 1H), 4.93 (br. d, J = 5 Hz, 2H), 6.73 (br. t, J = 5 Hz, 1H), 7.75 (s, 1H), 7.77 (s, 2H), 7.82 (d, J = 8 Hz, 2H), 8.00 (s, 2H), 8.03 (s, 4H), 8.32 (d, J = 8 Hz, 2H), 8.88 (s, 4H), 8.90 (d, J = 4 Hz, 2H), 8.94 (d, J = 4 Hz, 2H); MS (FAB) 1923 (M+H$^+$) and 840 (C_{70}^+); UV/Vis λ_{max} (THF) 276, 355, 370, 406, 426, 462, 510, 557, 597, 651 nm.
12 P. Boulas, F. D'Souza, C. C. Henderson, P. A. Cahill, M. T. Jones, and K. M. Kadish, *J. Phys. Chem.*, **97**, 13435 (1993); C. Boudon, J. -P. Gisselbrecht, M. Gross, A. Herrmann, M. Rüttimann, J. Crassous, F. Cardullo, L. Echegoyen, and F. Diederich, *J. Am. Chem. Soc.*, **120**, 7860 (1998).
13 We have demonstrated that the direct through-bond ET from the ^{1}ZnP* to the fullerenes is the main pathway in zincporphyrin-C_{60} linked systems where electronic coupling between the two chromophores is weak.[2] Considering that i) there is no apparent interaction between the two moieties in the ground state and ii) there is no large overlap of the fluorescence from the porphyrin and absorption of the fullerenes, it is concluded that the EN from ^{1}ZnP* to the fullerenes is, at least, not dominant in **1** and **2** in THF and benzene.
14 A. Weller, *Z. Phys. Chem.*, **133**, 93 (1982).