Synthesis and Photoinduced Electron Transfer of Pyromellitimide-Linked Porphyrin in Constrained Hydrophobic Environment of Unimer Micelle

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Pyromellitimide-linked zincporphyrin dyad was covalently incorporated into hydrophobic cluster of amphiphilic polysulfonate. Accelerated photoinduced electron transfer of the dyad in the copolymer was observed as compared with that of the corresponding dyad in THF, indicating the large contribution of the constrained microenvironment for electron transfer.

Photosynthetic electron transfer (ET) takes place among the well-arranged pigments in the protein matrix. The factors controlling ET such as free energy changes, electronic coupling, reorganization energy, and temperature have been so far well studied,[1] while the environmental effect in the protein remains unclear because of the difficulty in experimental access. Here we report our novel approach to this problem by preparing pyromellitimide (Im)-linked zincporphyrins (ZnP) and comparing their ET rates between in organic solvent and in constrained hydrophobic cluster (Figure 1). The spacer between the redox pair constitutes a monomethylene unit so that their conformations are relatively fixed.[2] It is well established that copolymers having sulfonate and cyclododecyl groups form unimer micelles with constrained hydrophobic clusters.[3] When the dyad is covalently incorporated into the unimer micelles, it should be tightly "compartmentalized" in the cluster. Therefore, it is expected that the orientational changes of the hydrophobic moieties surrounding the dyad during ET are much reduced, in contrast to the dynamic motion of solvents accompanied with ET in solution.

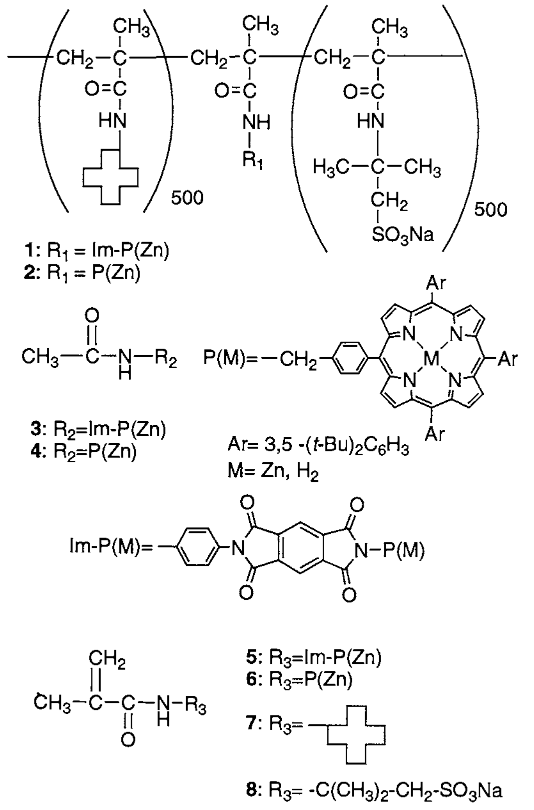
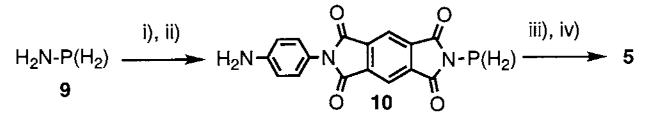


Figure 1.



Scheme 1. Synthesis of **5**; i) pyromellitic dianhydride, 4-trifluoroacetoamidoaniline, DMF, reflux; ii) K_2CO_3, 18-crown-6; iii) methacryloyl chloride, triethylamine; iv) zinc acetate.

Synthetic route of **5** is shown in Scheme 1. Cross-condensation of the corresponding aminomethylporphyrin **9**,[4] pyromellitic dianhydride, and mono-protected 1,4-phenylenediamine in DMF, followed by deprotection of the amino group gave pyromellitimide-substituted porphyrin **10** in 55% yield.[5] Methacrylamide **5** was prepared from **10** following the same procedures as described in the previous paper.[6] The synthesis of porphyrin-containing copolymers **1** and **2** was carried out according to the literature[7] by heating a mixture of **7** (49.95 mol%) and **8** (49.95 mol%) with **5** or **6** (0.1 mol%) in DMF in the presence of AIBN at 60 °C for 12 h. The crude polymer was

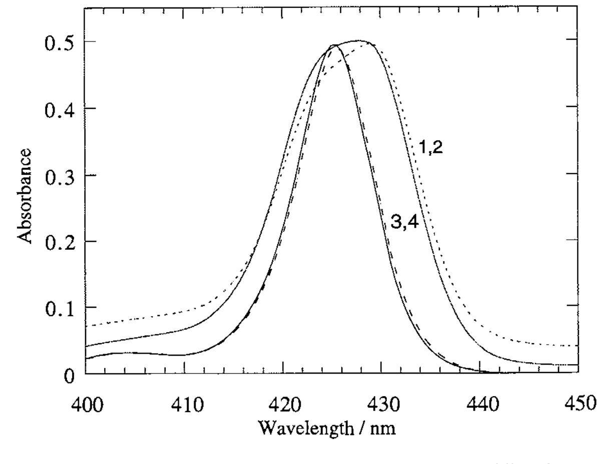


Figure 2. Absorption spectra of **1** (dashed line) and **2** (solid line) in water and **3** (dashed line) and **4** (solid line) in THF. Absorbances at the Soret bands were adjusted to 0.5 for a comparison.

purified by reprecipitation from a methanol solution into excess ether for three times and by dialysis against pure water for three weeks. References **3** and **4** were also prepared. The structures of **3**-**6** were confirmed on the basis of spectroscopic data.[8]

A sharp Soret band was observed in the absorption spectra of **3** and **4** as shown in Figure 2, while in the case of **1** and **2** the band appeared with a broader shape at longer wavelength reflecting the polymeric environment.[6,9] Fluorescence spectra of polymers **1** and **2** are different from those of monomers **3** and **4** in shape and peak position. The 0-1 emission band in **1** and **2** are blue-shifted by about 10 nm compared with those in **3** and **4**, while no appreciable difference was observed for the 0-0 emission bands. Furthermore, the intensities of the 0-1 band against the 0-0 band are larger in **1** and **2**, whereas the tendency is reversed in **3** and **4**. The fluorescence intensities of **1** and **3** are quenched by 30% and 70% as compared with the reference with single chromophore **2** and **4**, respectively, implying that photoinduced ET occurs from ^{1}ZnP* to Im.[2]

Fluorescence lifetimes of **1**-**4** were measured by picosecond time-resolved single-photon counting technique exciting at 524 nm and monitoring at 600 nm. The decay curves of **3** and **4** in THF could be analyzed by a single exponential decay (**3**: 0.42 ns, **4**: 2.10 ns). This shows that photoinduced ET takes place in **3** with a rate constant of $k_{et} = 1.9 \times 10^9\ s^{-1}$ ($= 1/(0.42 \times 10^{-9}) - 1/(2.1 \times 10^{-9})$) from ^{1}ZnP* to Im. Osuka et al. reported a similar zincporphyrin-pyromellitimide dyad.[2] The rate constant of k_{et} ($1.3\text{-}1.7 \times 10^{10}\ s^{-1}$) in THF is one order of magnitude larger than that in **3**. Considering that the free energy changes between the two system are quite similar, this may be explained by the difference of the reorganization energy and/or the electronic coupling. In contrast, the fluorescence of **2** in water displayed multi-exponential decays,[10] indicating that ^{1}ZnP* is influenced by the different microenvironments within the copolymer. However, a fast decay component (<50 ps) with a ratio of >40% was detected in **1**, in addition to the slow components similar to those of **2**.[11] Assuming that the fast decay is responsible for ET, we can estimate the rate constant of k_{et} from ^{1}ZnP* to Im in **1**; k_{et} ($> 2 \times 10^{10}\ s^{-1} = 1/(50 \times 10^{-12}) - 1/(2.1 \times 10^{-9})$) in **1** is at least one order of magnitude larger than that in **3**.

The internal dielectric constant of unimers **1** and **2** is estimated to be 2,[12] which is somewhat lower than the value (7.4) of THF.[13] It is known that the rate of photoinduced ET is relatively insensitive to the nature of the solvents employed.[14] As the solvent polarity decreases, both the solvent reorganization energy and the driving force decrease simultaneously, thus the ET rate constant does not vary much. Therefore, the remarkable acceleration of the ET observed in **1** can be interpreted by the microenvironmental effect of internal medium upon ET. Since the hydrophobic moieties surrounding the dyad within **1** are constrained, some of them may be well-oriented for ET in the dyad. Thus, some of the surrounding polarization produced by ET would be pre-optimized so that no dynamical motion of the hydrophobic moieties is required, resulting in the fast formation of the charge-separated state.[15] However, some of the dyad within the copolymer did not show any acceleration of ET. This is probably due to the unfavorable orientation of the hydrophobic moieties surrounding the dyad, which is consistent with the fact that the steady-state fluorescence of **1** is less quenched compared with **3** in THF, as we described before.

In conclusion, accelerated photoinduced ET was observed in the hydrophobic cluster of amphiphilic polysulfonate. For such preoptimized arrangement of the environments the fast formation of the charge-separated state is expected. Elaborated design of the amphiphilic polysulfonate will make it possible to develop novel polymers where most of ET processes are optimized.

References and Notes

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8 Spectral data for **3**: ^{1}H-NMR ($CDCl_3$, 270 MHz) δ=1.51 (s, 54H), 2.21 (s, 3H), 3.47 (s, 1H), 5.26 (s, 2H), 7.44 (d, 2H, J=9 Hz), 7.69 (d, 2H, J=9 Hz), 7.78 (s, 3H), 7.81 (d, 2H, J=8 Hz), 8.07 (s, 6H), 8.21 (d, 2H, J=8 Hz), 8.47 (s, 2H), 8.88 (d, 2H, J=5 Hz), 8.96 (d, 2H, J=5 Hz), 8.99 ppm (s, 4H). MALDI-TOF-MS 1376 (M+H$^+$). Spectral data for **4**: ^{1}H-NMR ($CDCl_3$, 270 MHz) δ=1.52 (s, 54H), 1.54 (s, 3H), 2.19 (s, 3H), 4.80 (d, 2H, J=5 Hz), 6.00 (br.s, 1H) 7.64 (d, 2H, J=8 Hz), 7.79 (t, 3H, J=1 Hz), 8.09 (t, 6H, J=1 Hz), 8.20 (d, 2H, J=8 Hz), 8.92 (d, 2H, J=5 Hz), 9.00 (d, 2H, J=5 Hz), 9.00 ppm (s, 4H). MALDI-TOF-MS 1086 (M+H$^+$). Spectral data for **5**: ^{1}H-NMR ($CDCl_3$, 270 MHz) δ=1.51 (s, 36H), 1.56 (s, 18H), 2.09 (s, 3H), 3.45 (s, 1H), 5.25 (s, 2H), 5.52 (s, 1H), 5.83 (s, 1H), 7.47 (d, 2H, J=9 Hz), 7.76 (d, 2H, J=9 Hz), 7.78 (s, 3H), 7.81 (d, 2H, J=9 Hz), 7.96 (s, 6H), 8.21 (d, 2H, J=9 Hz), 8.45 (s, 2H), 8.89 (d, 2H, J=5 Hz), 8.96 (d, 2H, J=5 Hz), 9.00 ppm (s, 4H). MALDI-TOF-MS 1403 (M+H$^+$). Spectral data for **6**: ^{1}H-NMR ($CDCl_3$, 270 MHz) δ=1.54 (s, 57H), 3.90 (d, 2H, J=5 Hz), 4.96 (s, 1H), 5.00 (s, 1H), 5.86 (t, 1H, J=5 Hz), 7.31 (d, 2H, J=8 Hz), 7.80 (s, 3H), 8.14 (s, 6H), 8.14 (d, 2H, J=8 Hz), 8.88 (d, 2H, J=5 Hz), 9.00 (d, 2H, J=5 Hz), 9.04 ppm (s, 4H). MALDI-TOF-MS 1113 (M+H$^+$).

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11 The lifetime due to the fast component (<50 ps) is beyond the time resolution of our instrumentation.

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