Photoinduced Charge Separation in Supramolecules between Li$^+$@C$_{60}$ and Chlorins

Kei Ohkubo,[a] Yuki Kawashima,[a] Kentaro Mase,[a] and Shunichi Fukuzumi[a,b]

[a] *Department of Material and Life Science, Graduate School of Engineering, Osaka University, ALCA, Japan Science and Technology Agency, Suita, Osaka 565-0871, Japan*
[b] *Department of Bioinspired Science, Ewha Womans University, Seoul, 120-750, Korea*

ookubo@chem.eng.osaka-u.ac.jp,
fukuzumi@chem.eng.osaka-u.ac.jp

Extensive efforts have been devoted toward the preparation of electron donor-acceptor linked compounds which, upon photoexcitation, give rise to a long-lived photoinduced charge-separated state as achieved in the photosynthetic reaction center. Porphyrins and fullerenes, both of which have highly delocalized π systems, are suitable for efficient electron transfer because the uptake or release of electrons results in minimal structural and solvation changes upon electron transfer.[1] Thus, there have been many reports on photoinduced charge separation in porphyrin-fullrene linked- and supramolecular systems. In natural systems, however, reduced porphyrins, namely chlorins are the electron donor pigments of the electron-transfer processes. It is of great interest to examine the use of chlorophyll-like molecules such as chlorins. However, there has been no report of photoinduced charge separation using chlorin/fullerene supramolecular system in polar solvent. We report herein construction of chlorin/fullerene supramolecular system and photoinduced charge separation in a polar benzonitrile (PhCN) solution.

UV-vis absorption spectrum of an anionic zinc chlorin (ZnCh$^-$) in PhCN at 298 K was changed upon addition of a cationic lithium encapsulated C$_{60}$ (Li$^+$@C$_{60}$), where the Soret band at 665 nm and an absorption band at 617 nm are blue-shifted to 661 nm and 611 nm, respectively. The wavelength of absorbance maximum change exhibits saturation behavior with increasing Li$^+$@C$_{60}$ concentration. The formation constant (K) was determined from the titration to be 1.9×10^4 M^{-1}. This result indicates that strong supramolecular binding between ZnCh$^-$ and Li$^+$@C$_{60}$ occurs by ionic interaction in PhCN (eq 1).

Li$^+$@C$_{60}$ ZnCh$^-$ ZnCh$^-$/Li$^+$@C$_{60}$ (1)
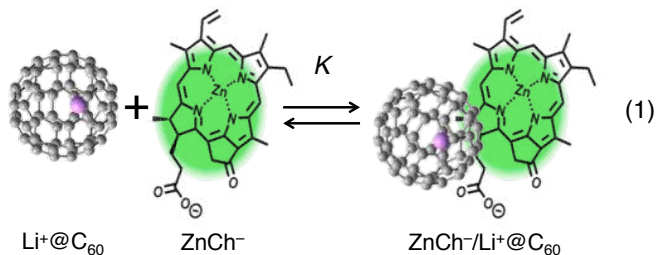
The transient absorption spectra of the ZnCh/Li$^+$@C$_{60}$ supramolecular complex were measured by nanosecond laser flash photolysis as shown in Figure 1a. The band of 470 nm observed at 2 μs is assigned to the ^{3}[ZnCh$^-$]*. The absorption band of ^{3}[ZnCh$^-$]* decays with increasing the

absorbances at 790 and 1035 nm, which can be assigned to [ZnCh$^-$]$^{•+}$ and Li$^+$@C$_{60}$$^{•-}$, respectively.[2,3] This clearly indicates the formation of the CS state by photoinduced electron transfer from ZnCh$^-$ to ^{3}[Li$^+$@C$_{60}$]*. Figure 1b shows time profiles of the decay of the CS state [ZnCh$^-$]$^{•+}$/Li$^+$@C$_{60}$$^{•-}$ in PhCN using different laser intensities. The first-order plots for the decay time profiles of the CS state at different laser intensity are shown in the inset of Figure 1b. The first-order plots afford linear correlations with the same slope irrespective of the difference in laser intensity. Thus, there is no or little contribution from the bimolecular charge-recombination (CR) process between [ZnCh$^-$]$^{•+}$ and Li$^+$@C$_{60}$$^{•-}$. The lifetimes of the triplet CS state in the supramolecular complex is determined to be 170 μs at 298 K. The quantum yield of the CS state is determined to be 0.62.
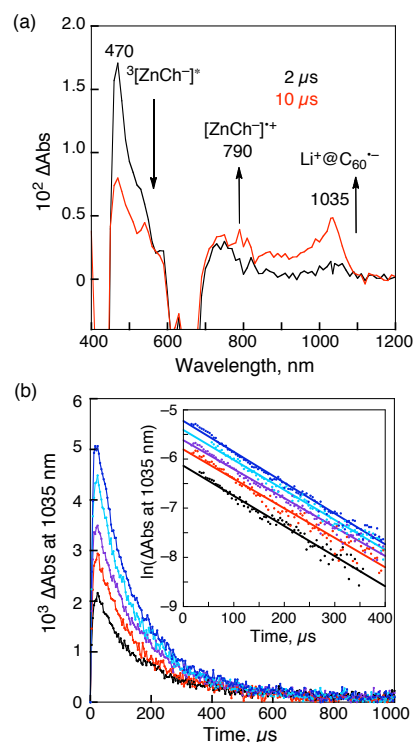

Figure 1 (a) Transient absorption spectra of ZnCh$^-$ (2.5×10^{-5} M) with Li$^+$@C$_{60}$ (5.0×10^{-5} M) in PhCN measured at 2.0 μs (Black) and 10 μs (red) after laser excitation at 450 nm. (b) Decay time profiles of absorbance at 1035 nm with different laser intensities (1, 2, 3, 4, 5 mJ/pulse). Inset: First-order plots.

References

[1] Fukuzumi, S.; Guldi, D. M. in *Electron Transfer in Chemistry*, Balzani, V., Ed.; Wiley-VCH: Weinheim, 2001, Vol. 2, pp 270-337.

[2] Fukuzumi, S.; Ohkubo, K.; Imahori, H.; Shao, J.; Ou, Z.; Zheng, G.; Chen, Y.; Pandey, R. K.; Fujitsuka, M.; Ito, O.; Kadish, K. M. *J. Am. Chem. Soc.* **2001**, *123*, 10676-10683.

[3] (a) Fukuzumi, S.; Ohkubo, K.; Kawashima, Y.; Kim, D. S.; Park, J. S.; Jana, A.; Lynch, V.; Kim, D.; Sessler, J. L. *J. Am. Chem. Soc.* **2011**, *133*, 15938-15941. (b) Ohkubo, K.; Kawashima, Y.; Fukuzumi, S. *Chem. Commun.* **2012**, *48*, 4314-4316. (c) Kawashima, Y; Ohkubo, K.; Fukuzumi, S. *J. Phys. Chem. A* **2012**, *116*, 8942-8948.