

**Photoinduced Electron Transfer
from $\text{Sc}_3\text{N}@C_{80}$ to $\text{Li}^+@C_{60}$**

Yuki Kawashima,^a Kei Ohkubo,^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

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

Fullerene, which has a highly delocalized three-dimensional π -system, is suitable for efficient electron acceptor because the uptake or release of electrons results in minimal structural and solvation changes upon electron transfer.[1] Therefore, fullerene has been employed as an electron acceptor for the donor-acceptor charge separation systems. Because C_{60} is essentially spherical, it is an ideal molecule to examine the electron-transfer reactions involving C_{60} in light of the Marcus theory of electron transfer.[2] Endohedral fullerenes have recently gained increased attention with regard to the potential applicability due to the specific reactivities, being spherical molecules (I_h -symmetry) like fullerene.[3] For instance, lithium ion encapsulated fullerene, $\text{Li}^+@C_{60}$ has I_h -symmetric C_{60} cage. It shows enhanced electron acceptability than pristine C_{60} . [4] On the other hand, trimetal nitride fullerenes, $\text{M}_3\text{N}@I_h-C_{80}$ also have I_h -symmetric C_{80} fullerene cage, which is stabilized by encapsulating M_3N cluster to donate six electrons to C_{80} cage.[5] However, there has been no report of electron-transfer reactions between an I_h -symmetric fullerene to other fullerenes. We report herein the electron-transfer reaction from $\text{Sc}_3\text{N}@I_h-C_{80}$ to $\text{Li}^+@I_h-C_{60}$.

The one-electron reduction potential of triplet excited state of $\text{Li}^+@C_{60}$ [$^3(\text{Li}^+@C_{60})^*$] is determined to be 1.67 V vs SCE in benzonitrile (PhCN) from the one-electron reduction potential of $\text{Li}^+@C_{60}$ (0.14 V) and the triplet excited energy (1.53 eV).[4] The one-electron oxidation potential of $\text{Sc}_3\text{N}@C_{80}$ as an electron donor is determined to be 1.09 V, which is more positive than the one-electron reduction potential of $^3(\text{Li}^+@C_{60})^*$, when the driving force of electron transfer from $\text{Sc}_3\text{N}@C_{80}$ to $^3(\text{Li}^+@C_{60})^*$ is highly positive ($-\Delta G_{\text{et}} = 0.58$ eV). Upon nanosecond laser excitation at 355 nm of a PhCN solution of $\text{Li}^+@C_{60}$, a transient triplet-triplet (T-T) absorption spectrum is observed at $\lambda_{\text{max}} = 750$ nm. The T-T absorbance decays obeying first-order kinetics. The addition of $\text{Sc}_3\text{N}@C_{80}$ to a solution of $\text{Li}^+@C_{60}$ in PhCN results in electron transfer from $\text{Sc}_3\text{N}@C_{80}$ to $^3(\text{Li}^+@C_{60})^*$ to produce $\text{Sc}_3\text{N}@C_{80}^{2+}$ and $\text{Li}^+@C_{60}^{\cdot-}$ ($\lambda_{\text{max}} = 1035$ nm [4]). The absorption spectrum of $^3(\text{Li}^+@C_{60})^*$ observed at 3 μs after laser excitation is converted to the spectrum of radical ion pair at 30 μs in Figure 1. The second-order rate constant of electron transfer from $\text{Sc}_3\text{N}@C_{80}$ to $^3(\text{Li}^+@C_{60})^*$ was determined to be $k_{\text{et}} = 1.5 \times 10^9 \text{ M}^{-1} \text{ s}^{-1}$ from dependence of decay rate

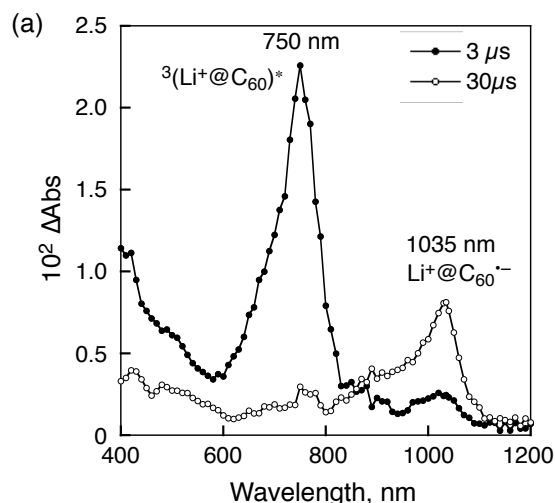


Figure 1. Transient absorption spectra observed in photoinduced electron transfer from $\text{Sc}_3\text{N}@C_{80}$ to $\text{Li}^+@C_{60}$ taken at 3 (●) and 30 μs (○) after laser excitation at 355 nm in deaerated PhCN at 298 K.

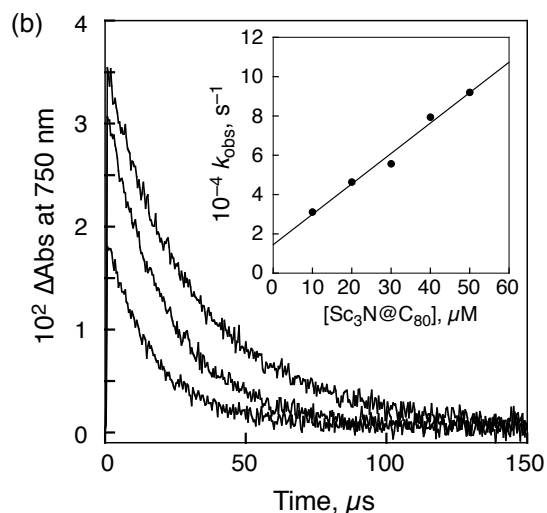


Figure 2. Time profiles at 750 nm of $\text{Li}^+@C_{60}$ (50 μM) in the presence of various concentration of $\text{Sc}_3\text{N}@C_{80}$. Inset: Plot of observed decay rate constants vs the concentration of $\text{Sc}_3\text{N}@C_{80}$.

constant of $^3(\text{Li}^+@C_{60})^*$ on the $\text{Sc}_3\text{N}@C_{80}$ concentration (inset of Figure 2). The decay of radical ion pair obeyed second-order kinetics monitored at 1035 nm. The rate constant was determined to be $k_{\text{bet}} = 5.6 \times 10^9 \text{ M}^{-1} \text{ s}^{-1}$ which is close to be the diffusion limited value in PhCN.

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] (a) Marcus, R. A. *Annu. Rev. Phys. Chem.* **1964**, *15*, 155-196. (b) Marcus, R. A. *Angew. Chem., Int. Ed. Engl.* **1993**, *32*, 1111-1121
- [3] *Chemistry of Nanocarbons*, Akasaka, T., Wuldi, F., Nagase, S., Eds.: Wiley, London, 2010.
- [4] Kawashima, Y.; Ohkubo, K.; Fukuzumi, S. *J. Phys. Chem. A* **2012**, *116*, 8942-8948.
- [5] Rudolf, M.; Wolfrum, S.; Guldi, D. M.; Feng, L.; Tsuchiya, T.; Akasaka, T.; Echegoyen, L. *Chem.-Eur. J.* **2012**, *18*, 5136-5148.