Effective Energy Transfer Process in a Dyad Molecule of Pyrene and C_{60}

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Photoexcitation dynamics of a pyrene-C_{60} dyad molecule has been investigated. From the excitation spectrum and fluorescence lifetime measurements, effective energy transfer processes from the singlet excited pyrene-moiety were confirmed both in polar and nonpolar solvents. The transient absorption suggested that the triplet excited C_{60} was generated effectively upon excitation of the pyrene-moiety via the singlet energy transfer and the intersystem crossing process.

Recently, various functionalized fullerenes have been reported.[1] For the photoactive molecular devices, energy transfer is one of the important functions, in addition to electron transfer properties.[2,3] Both the energy transfer and electron transfer processes in C_{60}-dyad molecules play an important role to establish efficient photosynthesis. In the present study, we investigated the photophysical properties of a novel dyad molecule of pyrene and C_{60} (Py-C_{60}, Figure 1(a)), in which bonds are connecting C_{60} with 3,4-positions of pyrene-ring. Pyrene-moiety will act as an efficient photon receiver in the blue region and also as a good fluorescence probe. Using steady-state fluorescence measurements, Nakamura et al. reported energy transfer process of a similar dyad of pyrene and C_{60}, in which 1,2-positions of pyrene-ring and C_{60} were connected with methylene bonds.[2,3] In the present letter, we estimated kinetic aspects of the energy transfer process of the dyad by fluorescence lifetime measurements.

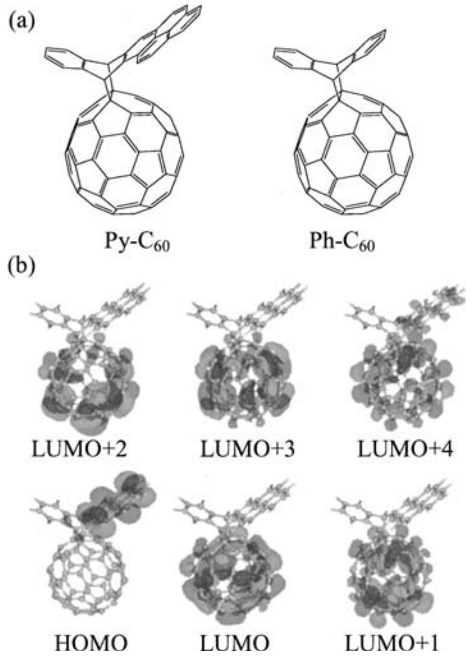

Figure 1. (a) Molecular structures of Py-C_{60} and Ph-C_{60} and (b) MO patterns of Py-C_{60}.

The Py-C_{60} was synthesized by cycloaddition of C_{60} with naphtho[2,3-*a*]pyrene.[4] From the MO calculations at the HF/3-21G level, MO is localized on C_{60}-moiety through LUMO to LUMO + 3 (Figure 1(b)). Thus, contribution of the C_{60}-moiety will be dominant in the lowest excited state. Consequently, excited state of the pyrene-moiety is expected to donate its excitation energy to the C_{60}-moiety of the dyad.

Figure 2 shows an absorption spectrum of Py-C_{60} in $CHCl_3$. The absorption spectrum of Py-C_{60} is well expressed as a super position of pyrene and Ph-C_{60} (Figure 1(a)),[5–7] which was synthesized from anthracene and C_{60}: absorption bands at 352.0 335.5, and 255.0 nm are attributed to the pyrene-moiety while bands at 705.0, 458.4, and 433.0 nm are ascribed to C_{60}-moiety. This finding indicates that the interaction between the pyrene- and C_{60}-moieties is weak in the dyad molecule.

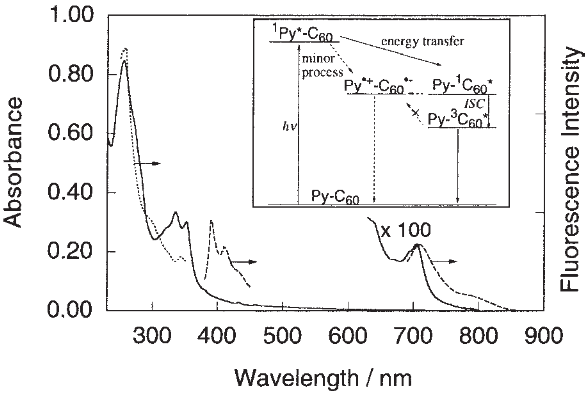

Figure 2. Absorption (solid line) and fluorescence (broken line) spectra of Py-C_{60} in $CHCl_3$. Excitation spectrum for the fluorescence band at 708 nm was indicated by dot line. Inset: schematic energy diagram for photoexcitation processes of the dyad.

Upon excitation of the dyad in $CHCl_3$ with 350 nm-light, the dyad showed fluorescence bands at 708, 412, and 390 nm (Figure 2). The fluorescence band at 708 nm is attributed to that from the C_{60}-moiety,[8] while the other are ascribed to the pyrene-moiety. Since the 350 nm-light was absorbed by the pyrene-moiety mainly, the appearance of the fluorescence band of the C_{60}-moiety indicates that the energy transfer process takes place. An excitation spectrum monitoring fluorescence intensity at 708 nm shows peaks at 340 and 258 nm (Figure 2), which correspond well to the absorption bands due to the pyrene-moiety of Py-C_{60} dyad. This finding supports the singlet energy transfer process from ^{1}Py*-C_{60} to Py-$^1C_{60}$*.

Dynamic aspects of the photoinduced processes of the present dyad molecule can be obtained by fluorescence lifetime measurements using an N_2 laser (337.1 nm, fwhm 300 ps) as an excitation source, which excites mainly the pyrene-moiety of the dyad. The lifetime of the fluorescence from the pyrene-moiety was estimated to be 11.9, 7.7, and 6.2 ns in toluene, $CHCl_3$, and benzonitrile, respectively. The respective fluorescence lifetimes of pristine pyrene in these solvents were 148, 140, and 130 ns. Thus, the accelerated fluorescence lifetimes of the dyad indicate the efficient photoinduced process via the singlet excited state of the pyrene-moiety of the dyad including the singlet energy transfer as discussed above. The lifetime of the excited singlet state of the pyrene-moiety found to become shorter with increasing solvent polarity. This finding perhaps indicates that charge separation occurred from the singlet excited pyrene-moiety to the C_{60}-moiety. But the contribution of the charge separation seems to be small, since any transient species such as radical cation or anion was not observed in the transient absorption experiments. In Figure 3, an observed transient absorption band at 700 nm was attributed to the triplet excited state of the C_{60}-moiety,[8] of which lifetime was estimated to be 28 μs. It is interesting to note that the transient absorption bands due to the triplet excited state of pyrene-moiety were not observed in Figure 3, even though the sample was excited with the 355 nm-laser which excites the pyrene-moiety mainly. This finding indicates that the triplet excited C_{60} was produced by the intersystem crossing process (ISC) from the singlet excited C_{60} which was generated by the energy transfer from the singlet excited pyrene-moiety. Thus, contribution of the triplet energy transfer from the pyrene- to C_{60}-moiety can be ignored. Most of excitation energy moved to the C_{60}-moiety from the singlet excited pyrene-moiety.

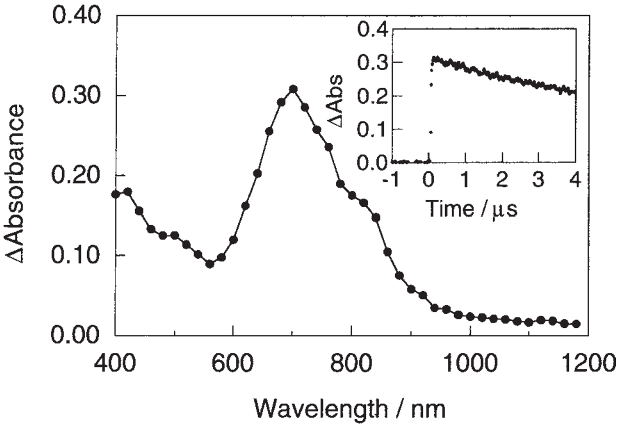

Figure 3. Transient absorption spectrum of Py-C_{60} in benzonitrile at 250 ns after the 355 nm laser irradiation. Inset: Absorption-time profile at 700 nm.

Table 1 shows oxidation and reduction potentials of Py-C_{60} dyad as well as Ph-C_{60} and pyrene. The oxidation and reduction potentials of the dyad are essentially the same as those of pyrene and Ph-C_{60}, respectively, supporting small interaction between the pyrene- and C_{60}-moieties. From these potentials, free energy change for the charge separation from singlet excited pyrene- to C_{60}-moiety was calculated to be −1.62 eV in benzonitrile.[9] Since the reorganization energy for dyad molecules including C_{60} is reported to be as small as 0.2–0.5 eV,[10] charge separation process from the singlet excited pyrene will be in the Marcus "inverted region". Thus, the charge separation process in the present dyad molecules would be quite slow and is considered to be an ineffective process (Inset of Figure 2).

Table 1. Oxidation and reduction potentials of Py-C_{60}, Ph-C_{60}, and pyrene[a]

compounds	pyrene (+1/0)[b]	C_{60} (0/−1)[b]
Py-C_{60}	0.85	−1.03
Ph-C_{60}	—	−1.04
pyrene	0.86	—

[a] Cyclic voltammetry experiments were carried out at 100 mV s^{-1} of scan rate in *o*-dichlorobenzene solvent including 100 mM tetrabutylammonium perchlorate. [b] V vs Fc/Fc^+.

Consequently, the rates of the singlet energy transfer process are calculated to be 7.7×10^7, 1.2×10^8, and $1.5 \times 10^8\ s^{-1}$ in toluene, $CHCl_3$, and benzonitrile, respectively, from the observed fluorescence lifetimes. The energy transfer rates on the order of 10^7–$10^8\ s^{-1}$ will be resulted from small spectral overlap of fluorescence of pyrene and absorption of C_{60} because of small extinction coefficient of C_{60} in the visible region. Furthermore, the respective yields for the energy transfer are estimated to be 92, 92, and 94%. These results indicate that the energy transfer in the dyad is effective almost independent of the solvent polarity.

As for the singlet excited state of the C_{60}-moiety, photoinduced processes between the pyrene- and C_{60}-moieties can be ignored, since the fluorescence lifetimes of the C_{60}-moiety were 1.3, 1.2, and 1.2 ns in toluene, $CHCl_3$, and benzonitrile, respectively. These lifetimes were essentially the same as that of Ph-C_{60}. Thus, the pyrene-moiety does not affect the deactivation process of the singlet excited state of the C_{60}-moiety, indicating efficient intersystem crossing process of C_{60}. In each solvent, fluorescence decay profiles show two-components decays, of which minor components show 6–12 ns of lifetimes, which are almost same as the lifetimes of the pyrene-moiety in each solvent. Thus, observation of the minor components supports the energy transfer process from the pyrene-moiety.

In the present study, we showed effective energy transfer process in a pyrene-C_{60} dyad. The energy transfer system is important to attain effective photo sensitization system. Thus, studies on combination of energy transfer and charge separation system are in progress.

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References and Notes

1 D. M. Guldi and P. V. Kamat, in "Fullerenes," ed. by K. M. Kadish and R. S. Ruoff, Wiley, New York (2000), Chap. 5, p 225.

2 T. Tago, T. Minowa, Y. Okada, and J. Nishimura, *Tetrahedron Lett.*, **93**, 8461 (1993).

3 Y. Nakamura, T. Minowa, S. Tobita, H. Shizuka, and J. Nishimura, *J. Chem. Soc., Perkin Trans. 2*, **1995**, 2351.

4 Y. Murata, N. Kato, K. Fujiwara, and K. Komatsu, *J. Org. Chem.*, **64**, 3483 (1999).

5 K. Komatsu, Y. Murata, N. Sugita, K. Takeuchi, and T. S. M. Wan, *Tetrahedron Lett.*, **34**, 8473 (1993).

6 J. A. Schlueter, J. M. Seaman, S. Taha, H. Cohen, K. R. Lykke, J. J. Wang, and J. M. Williams, *J. Chem. Soc., Chem. Commun.*, **1993**, 972.

7 M. Tsuda, T. Ishida, T. Nogami, S. Kurono, and M. Ohashi, *J. Chem. Soc., Chem. Commun.*, **1993**, 1296.

8 C. Luo, M. Fujitsuka, A. Watanabe, O. Ito, L. Gan, Y. Huang, and C.-H. Huang, *J. Chem. Soc., Faraday Trans.*, **94**, 527 (1998).

9 Free energy change was calculated assuming the radii of pyrene and C_{60} and center to center distance are to be 3.2, 4.2, and 7.8 Å.

10 H. Imahori, K. Hagiwara, T. Akiyama, M. Aoki, S. Taniguchi, T. Okada, M. Shirakwa, and Y. Sakata, *Chem. Phys. Lett.*, **263**, 545 (1996).