

PHOTOINDUCED REACTIONS OF FULLERENES STUDIED BY TRANSIENT ABSORPTION SPECTRA IN NIR

Osamu Ito and Mamoru Fujitsuka

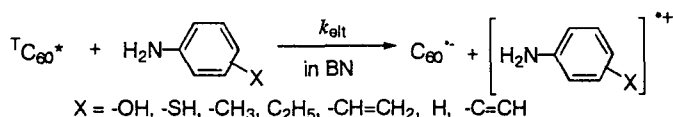
Institute for Chemical Reaction Science, Tohoku University,
Katahira, Aoba-ku, Sendai, 980-8577, Japan

Introduction

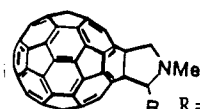
The photo-induced electron transfer processes of fullerenes can be revealed by measuring their transient absorption spectra in the near-IR region over the wide time-scales. Such measurements are useful to elucidate the successive reaction mechanism including photo-current generation mechanism.

Results and Discussion

1) Substituent effect: Substituent effect of electron donors on the electron transfer rate was observed for the system of ${}^1\text{C}_{60}^*$ with substituted anilines. One of the linear-free energy relationship, Hammett plot, can be used as



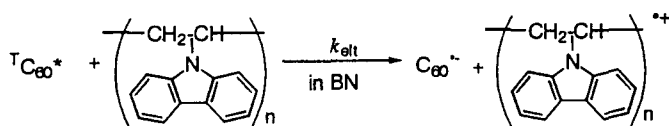
log *k* vs. Δ*G*⁰ plots. In the case of *p*-amino-styrene and *p*-aminophenyl acetylene, oligomerization reactions via their cation radicals were confirmed.



R = *p*-C₆H₄NO₂ (1), *p*-C₆H₄CHO (2), C₆H₅ (3),
p-C₆H₄OMe (4), and *p*-C₆H₄NMe₂ (5)

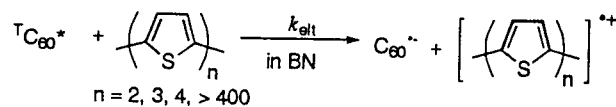
The substituent effects in the side of C₆₀ cage were observed in various kinds of excited state dynamics including electron transfer processes both via the singlet and triplet states.

2) Polymer effect: In the case of polyvinylcarbazole, slow electron transfer via ${}^1\text{C}_{60}^*$ was observed in addition to the fast electron transfer via ${}^3\text{C}_{60}^*$. The



electron transfer rate via ${}^1\text{C}_{60}^*$ was faster than that of ethylcarbazole, suggesting a considerable polymer effect. For polyvinylcarbazole, with direct excitation of polycarbazole moiety, electron transfer via direct photoejection also takes place.

The electron transfer occurs with oligothiophenes larger than trimer. In the case of polythiophenes (*n* = 400), C₆₀^{·-} and cation radical of polythiophene



were observed by the photoexcitation of both C₆₀ and polythiophene. The polymer effect on the back electron rates was also observed for both polymers.

3) Steric effect: Comparing with the planar naphthalene donor, perpendicular bi-naphthyl donor shows slower electron transfer rate via ${}^1\text{C}_{60}^*$. This may be caused by the hindrance of approach of spherical fullerene to perpendicular binaphthyl moieties. In the case of optically active binaphthyl amine, optical active C₆₀-binaphthylamine adduct was obtained. For binaphthol, addition of bases such as pyridine accelerates the electron transfer.

