

Photoinduced Electron-Transfer From Two-Electron Donor to C₆₀ and C₇₀

Kenichi Yamanaka, Mamoru Fujitsuka, Osamu Ito

Institute of Multidisciplinary Research for Advanced
Materials, Tohoku University, CREST, Japan Science
and Technology, Katahira, Sendai, Miyagi 980-8577,
Japan

Toshihide Aoyama, Takanori Fukushima,
Tsutomu Miyashi

Department of Chemistry, Graduate School,
Tohoku University, Aoba, Sendai 980-8587, Japan

For the electron-donors having two-electron oxidation ability, it would be expected that the two-electron-transfer processes take place by one-photon excitation of the materials with highly reduction abilities such as C₆₀ and C₇₀ in polar solvents. In the present study, the tetrathienylethylene (TTE) derivatives are used as two-electron donors. In neutral TTE, four thiophene moieties has the planer structure around the ethylene group, although the thiophene rings bent each other. Under the two-electron oxidation, TTF dication has the perpendicular structure with respect to the ethylene dication moieties (Scheme 1). With the electrochemical oxidation of TTE, only the absorption band of the dications was observed at 690 nm.

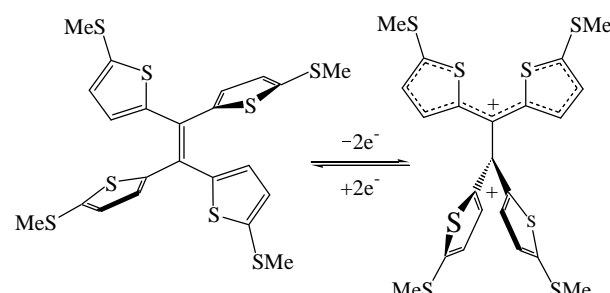
Upon laser excitation of C₆₀ and C₇₀ in the presence of TTE, the absorption bands of the radical anions of C₆₀ and C₇₀ were observed with the decay of their triplet states. In the case of C₆₀-TTE, a the new absorptions appeared at 690 nm for dication of TTF in addition to bands in the 900 - 1200 nm with the decay of the triplet state of C₆₀ at 740 nm (Figure 1). This indicates that in the 900 - 1200 nm region, the monocation-radical of TTE and the mono-anion radical of C₆₀ are included.¹ With increase in the laser power keeping the concentration of TTE and C₆₀ at constant, the absorption intensity of the dication of TTE at 690 nm was increased. This suggests that the triplet state of C₆₀ generates monocation-radical of TTE by the first encounter and that another triplet state of C₆₀ generates dication of TTE with the second encounter with monocation radical of TTE.

Although the absorption bands of the dianion of C₆₀ were reported at 950 and 830 nm, the formation of dianion of C₆₀ could not be confirmed by overlapping with the absorption bands of one electron-transfer species, such as monoanion-radical of C₆₀ and monocation radical of TTE.

For the transient absorption spectra observed by the 532-nm laser light excitation of C₇₀, the absorption band of the dication of TTE was also observed in the low intensity in addition to the monoion-radicals in the wide region of 900 - 1400 nm;² however, the absorption bands of the dianion of C₇₀, which would be expected to appear at 1170 nm and 670 nm, may not be confirmed by overlapping with the absorptions of monoion-radicals.

Although it is expected that the dication of TTF may be long-lived, most of the transient absorption bands decay with second-order kinetics in the long-time measurements, giving the diffusion controlled rate constants.

It is necessary to find the two-electron donors with more high donor abilities and with the absorption bands which do not overlap with the anion radicals of fullerenes.



Scheme 1. Structure change of tetrathienylethylene (TTE) by two-electron oxidation.

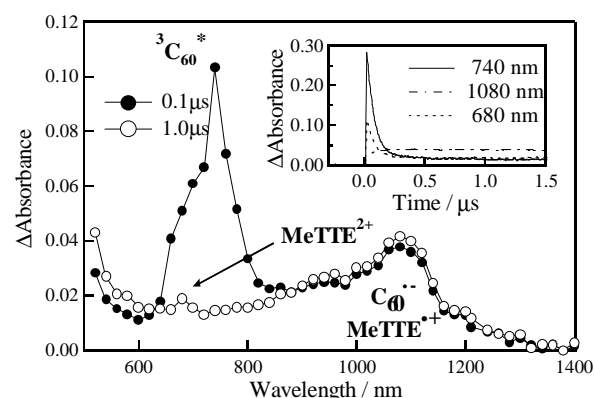


Figure 1. Transient absorption spectra observed 532-nm laser light excitation of C₆₀ in the presence of TTE in deaerated benzonitrile. Inset: Time-profiles.

References.

- 1) M. M. Alam, A. Watanabe and O. Ito, J. Photochem. Photobiol. A, 104, 59 - 64 (1997).
- 2) M. M. Alam, Akira Watanabe, and Osamu Ito, Bull. Chem. Soc. Jpn., 70 (8), 1833 - 1838 (1997).