

Magnetic Field Effects on Lifetimes of Triplet Biradicals Generated from Photoinduced Electron Transfer in Fullerene-Phenothiazine Systems

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Recently, photochemical and photoelectrochemical properties of fullerene (C_{60}) have extensively been studied (1). Photoinduced electron transfer reactions of C_{60} -donor linked molecules have been reported (1),(2). However, in those papers, the intramolecular electron transfer of an excited singlet ($^1C_{60}^*$) state of C_{60} has been studied in spite of very-high quantum yield for the triplet ($^3C_{60}^*$) state of C_{60} .

Magnetic field effects (MFEs) have been powerful for verifying the reaction mechanism via triplet intermediate states in photochemical reactions (3). The MFEs are expected to be observed, if the triplet biradical is obtained by photoinduced electron transfer in the C_{60} -donor linked compound.

In the present paper, we have examined photoinduced electron transfer reactions and magnetic field effects (MFEs) on intramolecular electron transfer for C_{60} -donor linked systems such as C_{60} -phenothiazine (PH) linked compounds ($C_{60}(n)PH$) as shown in Fig. 1, since the contribution of triplet biradicals, generated by intramolecular electron transfer from donor to $^3C_{60}^*$, to those electron transfer reactions was verified by the MFEs (4),(5).

In the case of $C_{60}(10)PH$, transient absorption spectra by laser excitation at 532 nm indicated that the intramolecular electron transfer occurred in polar solvents such as benzonitrile, while not in nonpolar solvents such as benzene. The result is due to the solvent effect on energy levels of the photogenerated biradical. In benzonitrile, the lifetime (118 ns) of the photogenerated biradical was very longer, in spite of being around the top region in Marcus theory.

In benzonitrile, the decay at 520 nm followed first-order reaction kinetics. It indicates that the intramolecular process is responsible for disappearance of the biradical of the PH cation and the C_{60} anion radicals. The decay of the biradical was suppressed in the presence of magnetic field. The decay rate constant quickly decreased with the increase of magnetic field and reached a plateau region at above 0.2 T. The MFEs are explained by relaxation mechanism and verified that the triplet biradical was generated from the intramolecular electron transfer from PH to $^3C_{60}^*$. The long lifetime of the biradical is most likely ascribed to spin multiplicities of the biradical.

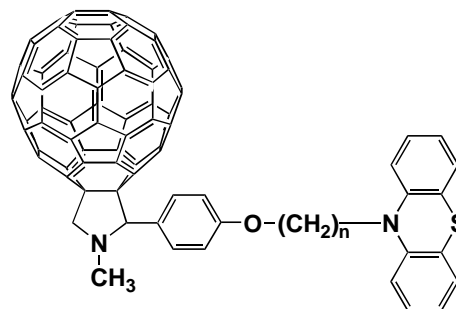
We will also discuss the effects of methylene chain length ($n=8, 10, \text{ and } 12$) as shown in Fig. 1, solvent, and salt on the MFEs.

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$C_{60}(n)PH$ ($n=8, 10, \text{ and } 12$)

Fig.1 . Structural Formulae for C_{60} -PH linked compounds ($C_{60}(n)PH$) used in this study.

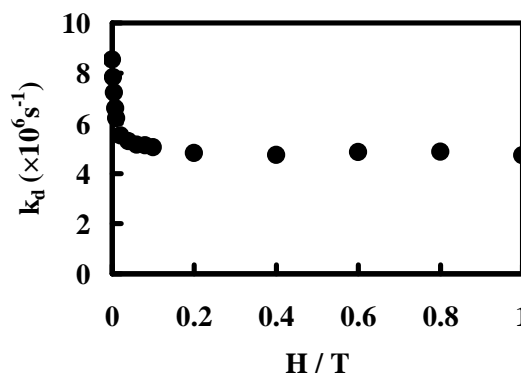


Fig.2 . MFEs on the decay rate constant (k_d) for the biradical of $C_{60}(10)PH$.