Photoinduced Electron Transfer Reactions, Magnetic Field Effects on the Decay Process of Charge-Separated State, and Time-Resolved EPR Spectra in Fullerene-Donor Systems

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Photoinduced electron transfer reactions of fullerene (C_{60})-donor linked compounds have been extensively investigated. The electron transfer of a singlet excited state of C_{60} ($^1C_{60}$*) has been intensively studied, while that of an excited triplet of C_{60} ($^3C_{60}$*) has been scarcely studied.[1,2] In addition, magnetic field effects (MFEs) on photoinduced electron transfer reactions using C_{60} have also been hardly studied.

MFEs and time-resolved EPR measurements have been useful for verifying the contribution of triplet biradicals, generated by photoinduced intramolecular electron transfer from donor to $^3C_{60}$*, to those electron transfer reactions in the C_{60}-donor system.[3] In addition, the MFEs and the time-resolved EPR of C_{60} are interesting because C_{60} has no nuclei spin and is a highly symmetric molecule.[4] MFEs and time-resolved EPR in various C_{60}-donor linked compounds are expected to provide information for studying spin chemistry of C_{60}.

In the present paper, we have examined photoinduced electron transfer reactions in C_{60}-donor linked compounds such as C_{60}-phenothiazine (PH) linked compounds (**C_{60}(n)PH**) as shown in Fig. 1 by the measurements of fluorescence lifetime, time-resolved transient absorption in visible and near-IR regions, MFEs, and time-resolved EPR.[5-7]

The fluorescence lifetime of **C_{60}(n)PH** was small than that of a reference C_{60} compound without PH moiety in benzonitrile (PhCN) and THF. The result indicated that the photoinduced intramolecular electron transfer from PH to $^1C_{60}$* occurred in PhCN and THF.

In the transient absorption spectra of **C_{60}(n)PH** by laser excitation at 532 nm, the broad absorption band around 700 nm due to $^3C_{60}$* was observed in benzene. In PhCN and THF, the absorption band at 700 nm ($^3C_{60}$*) immediately appeared after the laser pulse. With decreasing the band (~700 nm) of $^3C_{60}$*, concomitant rises of the absorption bands at 1000 nm due to C_{60} anion radical ($C_{60}{\cdot}^-$) and 520 nm due to PH cation radical ($PH{\cdot}^+$) were observed. The results clearly indicated that the triplet biradical, $^3(PH{\cdot}^+\text{-}C_{60}{\cdot}^-)$, was generated from the photoindued intramolecular electron transfer from PH to $^3C_{60}$* in **C_{60}(n)PH** in PhCN and THF, while not in benzene.

Thermodynamic parameters for the electron transfer processes were evaluated from the redox potentials and were compared with each other. Solvent effects on the fluorescence lifetime and the transient absorption spectra can be explained thermodynamically by using the Gibbs free energy changes for the corresponding intramolecular electron transfer reactions.

In the case of PhCN, 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 on the decay rate constants are interpreted in terms of isotropic hyperfine coupling and spin-lattice relaxation mechanisms, and verified the formation of the triplet biradical, $^3(PH{\cdot}^+\text{-}C_{60}{\cdot}^-)$, from the intramolecular electron transfer from PH to $^3C_{60}$*.

In the time-resolved EPR spectra of **C_{60}(10)PH** in benzonitrile, the characteristic antiphase emission/ absorption pattern of spin polarization was observed and was assignable to spin-correlated radical pairs formed by photoinduced electron transfer from PH to $^3C_{60}$*. In the case of **C_{60}(n)PH** in benzene, on the other hand, only absorption pattern was observed and it indicated the formation of $^3C_{60}$*. These results in the time-resolved EPR measurements are consistent with the reaction mechanism obtained from those of the fluorescence lifetime, the transient absorption spectra, and the MFEs.

We will also discuss photoinduced electron transfer reactions, MFEs, and time-resolved EPR in other C_{60}-donor linked compounds.

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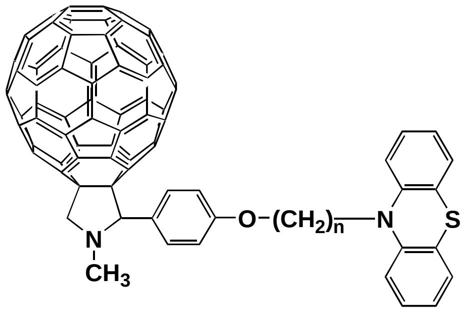

C_{60}(n)PH (n=8, 10, and 12)

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