

Fullerene [C₆₀] and Amine Donors Tethered Rotaxanes: Photoinduced Electron Transfer Processes via Excited Triplet States of C₆₀

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With the advent of supramolecular chemistry, efficient synthetic route of rotaxanes have been built-up by using cooperative noncovalent bonding interactions. Fullerene-based derivatives have been shown a wide range of physical and chemical properties that make them attractive for the preparation of supramolecular assemblies and new advanced materials for optoelectronic and molecular electronic devices. In the present study the intra-rotaxane photoinduced electron transfer processes of C₆₀/triphenylamine (TPA) rotaxane and C₆₀/di(biphenyl)benzamine (BBA) rotaxane have been investigated by time-resolved transient absorption and fluorescence measurements with changing solvent polarity and temperature. Nanosecond transient absorption measurements (Figures 1 and 2) of the rotaxane demonstrated that the long-lived charge separated state (C₆₀^{•-}; TPA^{•+})_{rotaxane} is formed via the excited triplet state of C₆₀ (³C₆₀^{*}). In case of C₆₀/BBA rotaxane radical ion pair (C₆₀^{•-}; BBA^{•+})_{rotaxane} is produced both via ¹C₆₀^{*} and ³C₆₀^{*} in polar solvents. The rate constants for the charge-separation process were evaluated in the range of (5 – 8) × 10⁷ s⁻¹, while the rate constants of charge recombination were in the range of (3 – 6) × 10⁶ s⁻¹ corresponding to the lifetimes of the charge-separated states (τ_{RIP}) of 170 – 400 ns. Both rate constants depended on the rotaxane structure, solvent polarity, and temperature. The activation free energy changes of charge-separation and recombination processes were evaluated by the temperature dependences. The observed low activation energies clearly suggested that the electron transfer in these rotaxanes takes place through space. These lifetimes were longer than those of the covalently bonded C₆₀-amine dyad systems, in which the fast CS process takes place via the ¹C₆₀^{*} moiety.

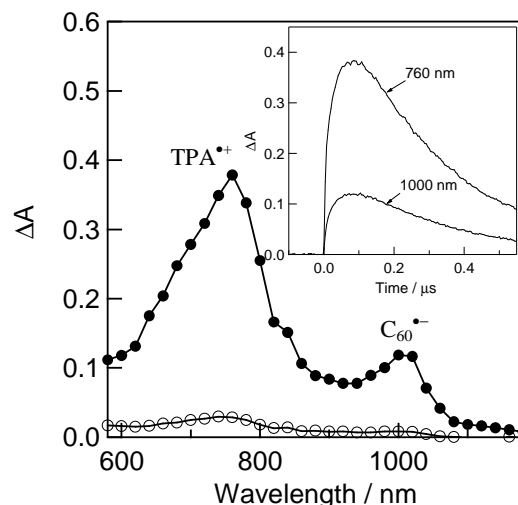
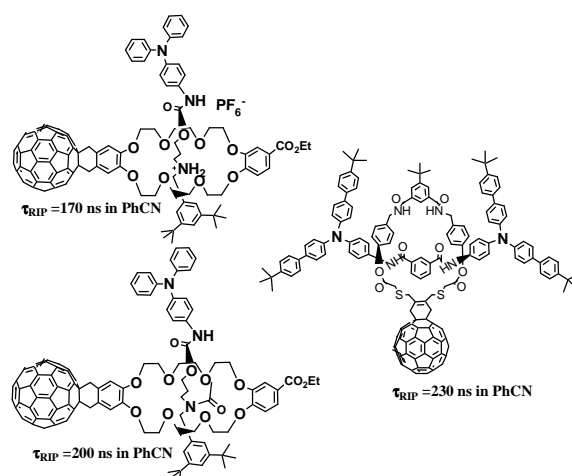
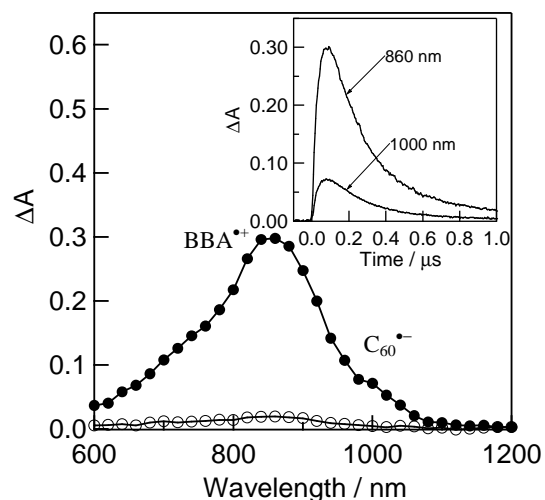


Figure.1. Nanosecond transient absorption spectra of



rotaxane (C₆₀;TPA)_{rotaxane} in PhCN

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