

# PHOTOINDUCED PROCESSES OF -FULLERENE LINKED POLYCARBAZOLE IN SOLUTION

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Light induced photocurrent has been generated by the excitation of fullerene ( $C_{60}$ ) containing poly(vinylcarbazole) (PVCz) films.[1] Photoinduced bimolecular electron transfer between  $C_{60}$  and PVCz and oligocarbazole has been previously reported [2]. In the present study, photoinduced charge-separation (CS) and recombination (CR) processes of fullerene ( $C_{60}$ ) pendant polycarbazoles (PVCz- $C_{60}$ ), which were designed to change the composition of  $C_{60}$  by copolymerization of  $C_{60}$ -styrene and VCz as shown in Scheme 1, have been investigated by time-resolved fluorescence and absorption spectroscopic methods. The absorption spectra are shown in Fig. 1, in which the peak at 700 nm is attributed to the  $C_{60}$  moiety; however, broad absorptions in the visible region indicate the charge-transfer interaction between the  $C_{60}$  and Cz moiety. By the selective excitation of the  $C_{60}$  moiety of PVCz- $C_{60}$  in benzonitrile (PhCN), charge-separation takes place via the excited singlet state of  $C_{60}$ . The nanosecond transient spectra observed by the selective excitation of  $C_{60}$  are shown in Fig. 2, in which the absorption of the radical cation of the carbazole moiety ( $Cz^+$ ) appeared at 780 nm and the charge-resonance band of dimer radical cation of carbazole ( $Cz_2^+$ ) appeared at near-IR region, while the radical anion of  $C_{60}$  ( $C_{60}^-$ ) appeared at 1000 nm, indicating that the charge-separated state  $PVCz^+-C_{60}^-$  was produced via  $PVCz-C_{60}^*$ . The lifetimes of the charge-separated states ( $\tau_{CS}$ ) of  $PVCz^+-C_{60}^-$  vary with the composition of  $C_{60}$  in PVCz- $C_{60}$ ;  $\tau_{CS} = 2.80$  ms for PVCz- $C_{60}$  (1%),  $\tau_{CS} = 0.43$  ms for PVCz- $C_{60}$  (3%), and  $\tau_{CS} = 0.24$  ms for PVCz- $C_{60}$  (5%). These changes in the  $\tau_{CS}$  values with the composition of  $C_{60}$  in PVCz- $C_{60}$  afforded rich information about the flow of the electron and hole along the PVCz- $C_{60}$  as shown in Scheme 2. Simulation (Fig. 3) gave the rate constants as summarized in scheme 2. Variation of the compositions of  $C_{60}$  in PVCz- $C_{60}$  affects the rate parameters, which rationalized the observed  $\tau_{CS}$  values and rate parameters of the flow of the electron and hole along the PVCz- $C_{60}$  appreciably.

[1] (a) Wang, Y. *Nature*, **1992**, 356, 585. (b) Wang, Y.; Herron, N.; Casper, J.; *Mater. Sci. Eng. B, Solid State Mater. Adv. Tech.* **1993**, B19, 61.

[2] (a) Fujitsuka, M.; Yahata, Y.; Watanabe, A.; Ito, O.; *Polymer*, **2004**, 41, 2807. (b) Komamine, S.; Fujitsuka, M.; Ito, O.; Itaya, A. *J. Photochem. Photobiol. A*, **2000**, 135, 111.

## Scheme 1

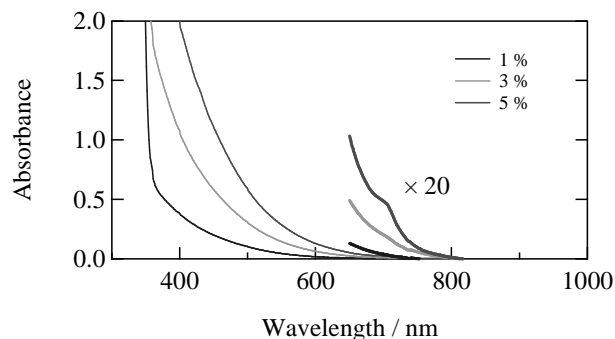
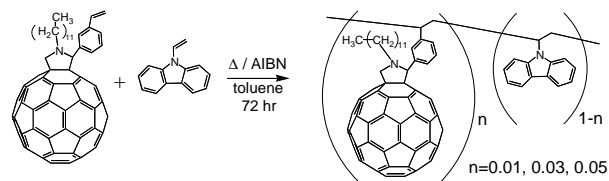


Figure 1. UV-Vis absorption spectra of PVCz- $C_{60}$  (n%) (2mM, monomer unit) in THF.

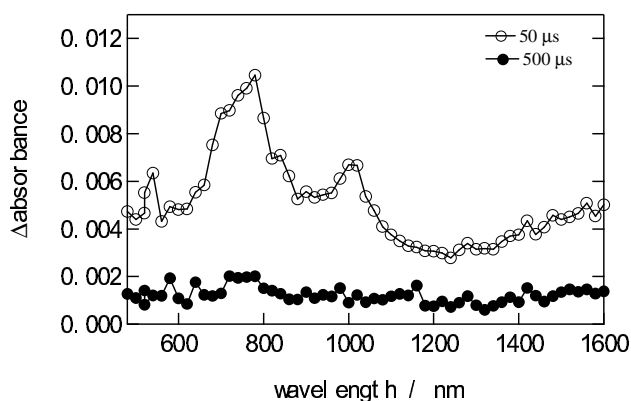


Figure 2. Transient absorption spectra observed by 532 nm-laser irradiation of PVCz- $C_{60}$  (5%) (2 mM; monomer unit) in deaerated PhCN.

## Scheme 2

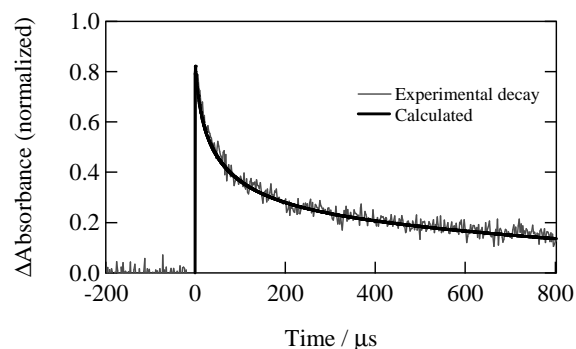
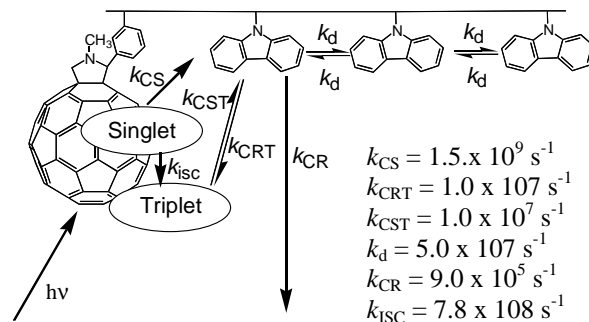


Figure 3. Time-profile of PVCz- $C_{60}$  (1%) in benzonitrile at 1500 nm and calculated decay.