Time-Resolved EPR Study on Photoinduced Charge-Transfer Trap State in Thiophene-Thiazolothiazole Copolymer Film

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To shed a light on fundamental optoelectronic properties of conjugated polymer films applicable to the organic photovoltaics (OPV), field-effect transistors (FET) and light-emitting diodes (LED), we have characterized interspin separation and exchange coupling of interchain charge-transfer (CT) states in a pristine film of thiophene–thiazolothiazole copolymer by using the time-resolved EPR method. It has been indicated that the CT state is generated at the disordered regions of the polymer films as deep trap sites via the singlet--exciton diffusion in polymer amorphous phase. These characteristics of the trapped charges may limit the device performances in the OPV, FET and LED applications and thus are informative for the device developments.

Keywords: Organic photovoltaic, Conjugated polymer, Charge-transfer, Trap state, Defect

1. Introduction

Great attentions have been attracted on the organic photovoltaic (OPV) devices as the next generation thin-film solar cells that can be low-cost, flexible and light.[1] Conjugated polymers have extensively been utilized in various organic electronic devices including the solar cells, field-effect transistors (FET) [2] and light-emitting diodes (LED) [3]. The spin coating method from mixed solutions consisting of the conjugated polymers as the electron donors (D) and fullerene derivatives as the acceptors (A) has been employed to produce the solid photoactive layer of the OPV cells [1]. In the organic photoactive layers, it is well known that the polymer molecules are self-organized to generate the bulk heterojunction (BHJ) [4] interfaces. Apart from the OPV applications, pristine films of the conjugated polymers are also utilized for the FET and LED applications [5]. The polymers usually form two dimensional lamellae structures as a result of close interchain packing interaction [4]. Such crystalline phases are known to play a key role for the mobilities of the charges and the excitons in the organic devices. Recent studies suggested that non-fluorescent CT characters exist as a competitive channel of the formation of emissive exciton-type states and determine the light emission efficiencies of the LED films [5].

Despite the significance of the non-fluorescent CT state, no study has experimentally characterized geometry and electronic character of the photoinduced CT state in the pristine polymer films. Consequently, the optoelectric properties of the polymer films have not been fully understood. In this study, we have directly observed the photoinduced CT state for a pristine film by thiophene–thiazolothiazole copolymer (PTzBT–BOHD in Fig.1) [6] fabricated by the spin–coating method using time-resolved EPR (TREPR) method to characterize the orbital geometries, the electronic property of the polymer CT state. We show that long-lived interchain CT states (P⁺⁺ P⁻⁻) are generated as deep trap states at disordered region as defects at a cryogenic temperature.
2. Experimental

Solutions of the PTzBT–BOHD were prepared by dissolving in 1,2-dichlorobenzene (ODCB) at 4 mg/mL. The pristine films were fabricated by the spin-coating method on the cleaned cover-glasses at 400 rpm for 20 s and subsequently at 1500 rpm for 5 s. Morphologies of the thin films were checked by the optical absorption bands of PTzBT–BOHD using the UV-vis spectrometer. The films in EPR quartz tubes were deaerated using a vacuum line to remove ODCB and oxygen. To conduct heat during the measurements and to avoid film exfoliation damages by the laser, 3:2 glycerol/water (v:v) mixture were added to the EPR tubes. These samples were deoxygenated by the freeze-pump-thaw cycles using the vacuum line. The X-band TREPR measurements were carried out using a Bruker EMX system at $T = 77$ K. Light excitations were performed by the second harmonics (532 nm) of a Nd:YAG laser (Continuum, Minilite II, fwhm ~5 ns) with and without a laser depolarizer.

3. Results and discussion

Figure 2a shows TREPR spectra of the pristine films of PTzBT–BOHD measured at 77 K. The negative signal denoted by ‘E’ is the TREPR intensity (transverse magnetization) by the microwave emission. The spectrum shapes are composed of a sharp peak around 337 mT and a broad signal ranging from 335.5 to 338 mT. In the previous TREPR study, the transient radical pairs were reported to be generated as microwave emissions in regioregular poly(3-hexylthiophene) – fullerene (P3HT–C60) linked dyad molecules [7]. The net E polarization was well explained by the photoinduced charge-separation (CS) via the triplet exciton in the P3HT moiety. The small g-anisotropy in $P^+$ and the larger g-anisotropy in $P^-$ are both coincident with the coexistence of the sharp (at 337.2 mT) and broad spectrum components in Fig. 2a, strongly supporting the above hypothesis of the CT generation. It is noted that the spectrum width obtained by the above anisotropies in the g-factors and the hyperfine couplings were smaller for the isolated radicals than the field range from 335.5 to 338 mT in Fig. 2a, indicating that the spin-spin dipolar interaction ($d$) and the exchange coupling ($J$) between the charges also contribute to the entire spectrum shapes [8]. No other TREPR bands were observed at a wider field-scan experiment for the pristine film.

Figure 2b shows time profile of the transient EPR intensity at 337.2 mT. The E polarization persists more than 5 $\mu$s which is attributable to the spin-lattice relaxation time ($T_1$). This is ten times larger than the reported $T_1 = 0.5$ $\mu$s in the photoinduced CS state generated at the BHJ domain interfaces in the RR–P3HT:PCBM blends at $T = 77$ K [9]. This denotes that the charge motions are highly restricted in the present film, suggesting that the charges in the
Fig. 3. Schematic representations of the spin polarization generation mechanism in the CT state (PTzBT\textsuperscript{+•} PTzBT\textsuperscript{–•}) to compute the emissive TREPR spectrum of the pristine film in Fig. 2 at $T = 77$ K. X, Y and Z are principal axes of the spin-spin dipolar coupling in $^3$PTzBT* and of the $g$-tensor in PTzBT\textsuperscript{–•}. The position of PTzBT\textsuperscript{–•} is represented by the bold arrow with respect to PTzBT\textsuperscript{+•}.

The CT state exist as deep trap sites rather than mobile charges to contribute to the photocurrent generation. We also measured the TREPR spectra using the polarized lasers to obtain effects of the polarization direction with respect to the external magnetic field [10]. No light polarization effects were however obtained on the spectrum shape in Fig. 2, demonstrating that the CT states lose the memory of the direction of the transition dipole moment of the polymer molecule. This indicates that the CT states are not located at the dominant polymer crystalline phase wherein the efficient singlet exciton diffusion takes place, supporting the above CT assignment as the deep trap state. The UV-vis absorption spectrum of PTzBT–BOHD is reported to be composed of low-energy strong sharp absorptions (570-575 nm and 620-630 nm) and a shoulder band around 530 nm in the film [6]. This broad shoulder-band is thus attributable to the excitation of the disordered polymer chains (amorphous domain) rather than the exciton-band by the crystalline phase [7]. The present laser excitation wavelength of 532 nm denotes that the singlet excited states are generated at the amorphous domain to contribute to the generation of the trapped CT state. The disappearance of the above light polarization effect strongly suggests that the CT states are generated after the random exciton diffusions in the disordered domains, as reported in our previous study for P3HT–C\textsubscript{60} in solution [7].

To characterize the geometry and the electronic interaction of the CT state, we computed the delay time dependence of the transient EPR signals as shown by the gray lines in Fig. 2a based upon the spin correlated radical pair (SCRP) model [11] utilizing the above g-factors and the hyperfine coupling constants with considering the spin density distribution as shown in Fig. 3. For this analysis, we applied the triplet electron spin polarization transfer (T-ESPT) theory [12,13], as shown in Fig. 3. The triplet exciton may be produced via the $S_1$-$T_1$ intersystem crossing (ISC) as a precursor of the CT state, generating the population in the $T_3$ sublevel by the spin-orbit coupling in the sulfur atomic orbitals in Fig. 1 to induce the angular momentum change along the long axis (X) in Fig. 3 between the $n$ and $\pi$ orbitals during the $^1n\pi^* \rightarrow ^3\pi\pi^*$ transition [7]. As for the triplet exciton, we observed a TREPR spectrum by the fine structure from PTzBT–BOHD dissolved in ODCB at 77 K. From this, the zero field splitting parameters of $D_T = 60$ mT and $E_T = -10$ mT were obtained with $P_X = 0.65$, $P_Y = 0.35$ and $P_Z = 0$ as the sublevel populations and were similar to the parameters in $^3$P3HT\textsuperscript{*} [7]. This gives rise to the overpopulation in the upper sublevel ($T_+$) in the presence of the external magnetic field via T-ESPT, resulting in the net E polarization in the CT state, as shown in Fig. 3. In the CT states, the coherent singlet-triplet (S-T\textsubscript{0}) mixing was also taken into account, as reported previously [7,12]. Since this mixing is influenced by the anisotropic $d$-coupling and by the isotropic $J$-coupling, the entire spectrum shape is highly dependent on these magnetic parameters. It was anticipated that the CT state is located at the disordered regions of the polymer films as the deep trap site. Thus, the PTzBT\textsuperscript{+•} position ($\theta$ in Fig. 3) was treated to be uniformly distributed in the X-Y-Z axis system of PTzBT\textsuperscript{+} at a certain spin-spin separation from the origin of the coordinate axes. The spectrum shapes were well...
reproduced by setting the dipolar coupling parameter of \( D = -0.8 \) mT and \( J = -0.5 \) mT, as shown by the grey lines in Fig. 2a.

From \( D = -0.8 \) mT, the center-to-center separation (\( r_{\text{CC}} \)) between the charges is estimated to be 1.5 nm in the present CT state. In the previous study, the photoinduced CS states generated at the BHJ domain interfaces were characterized to be \( J = +6 \) \( \mu \)T for \( r_{\text{CC}} = 1.5 \) nm in the RR–P3HT:PCBM blends at \( T = 77 \) K [14,15]. This significantly weak \( J \) coupling was explained by a weakened electronic coupling (\( V \)) between the charges due to highly delocalized distributions in the unpaired orbitals of the mobile holes at the polymer crystalline phase. On the other hand, the present strong \( J \) coupling denotes that the photoinduced charges in the CT state is rather localized to strengthen the orbital overlap. However, a highly strong coupling of \( J > 3 \) mT was obtained [7] for a larger \( r_{\text{CC}} \) of 1.8 nm in the covalently linked dyad of P3HT\(^{++} \)–C\(_{60}^{-} \). Thus, the present \( J \) coupling is not in line with an intrachain CT (P\(^{--} \)–P\(^{+} \) ) generation within the polymer backbone but the interchain CT state (P\(^{--} \)–P\(^{+} \) in Fig. 4). The stronger \( J \) of \(-0.5 \) mT than in the RR–P3HT:PCBM interface is well consistent with the above argument that the interchain CT states are not located at the dominant polymer crystalline phase but at minor disordered regions, as shown at the upper left in Fig. 4, generating the long–lived deep trap site in the pristine polymer film.

The negative \( J \)–coupling obtained in the pristine film represents that the singlet CT state is stabilized with respect to the triplet CT state, while the positive \( J \) specifies the destabilized singlet state. According to the configuration interaction model, the \( J \)–coupling is induced by the singlet perturbation from the ground state configuration: \( 2J = -|V|^2/\Delta E_{\text{CR}} \) where \( \Delta E_{\text{CR}} = \Delta G_{\text{CR}} + \lambda \) is the vertical energy gap (Fig. 5) for the charge–recombination to the ground state [16]. In the P3HT:PCBM domain interfaces, the free energy change of \(-\Delta G_{\text{CR}} > 1 \) eV in the CS state of P3HT\(^{++} \)–PCBM\(^{-} \) is evidently larger at the crystalline phase than the reorganization energy of \( \lambda \), [17] supporting the positive \( J \) because of the negative \( \Delta E_{\text{CR}} \). On the other hand, the negative \( J \) implies that a strong electrostatic binding is effective between the localized charges to reduce the \(-\Delta G_{\text{CR}} \) value in Fig. 5. Together with this, a larger intramolecular reorganization energy of \( \lambda \approx 1 \) eV is expected in Fig. 5 to result in a positive \( \Delta E_{\text{CR}} \), generating the negative \( J \)–coupling from \( 2J = -|V|^2/\Delta E_{\text{CR}} \). This large \( \lambda \) is consistent with the assignment of the long–lived deep traps at the polymer disordered regions which can be regarded as the defect[18] of the charge–conducting crystalline phase in the pristine film.

From the above results, one can argue how the stable CT trap is generated by the light irradiation, as shown at the upper left in Fig. 4. It is reported that the self-organized crystalline phase is dominantly formed by the \( \pi \)-\( \pi \) stackings both in the pristine and BHJ blend films [6]. However, the present 532 nm excitation may lead to the exciton generation at the amorphous domain, allowing the trapped CT state generation via the triplet exciton (Figs. 3 and 5) at polymer-polymer crossing regions where the two disordered polymer-chains are in close proximity, as shown in Fig. 4. The photoexcitation will also occur at the polymer crystalline phase and conduct the efficient exciton-diffusion. Such exciton may not contribute to the highly stable interchain CT generation because of the lack of the electronic stabilizations [5] in the CT character at the crystalline phase in Fig. 4, resulting in dominant radiative deactivations by the fluorescence. This scenario may also explain the absence of the EPR spectrum by the triplet exciton possessing the strong \( D_T \) coupling in the pristine film.

In conclusion, we have characterized the interspin separation and the exchange coupling of the interchain CT states in the pristine polymer film of PTzBT–BOHD generated by the 532 nm laser excitation at \( T = 77 \) K. It has been revealed that the triplet CT state is generated at the disordered regions of the polymer films as the deep trap site via the triplet exciton. These stable charge–traps would be produced at the polymer defect site possessing the large reorganization energy of \( \lambda \approx 1 \) eV. These characteristics of the trapped charges may limit the device performances in the OPV, FET and LED.

![Fig. 5. Schematic representation of the potential energy surface of the trapped CT state (PTzBT\(^{++} \)–PTzBT\(^{-} \)) stabilized by the strong electrostatic interaction as the reorganization energy (\( \lambda \)) induced by the localized charges at the polymer disordered region of the pristine PTzBT film at cryogenic temperature.](image-url)
applications. Thus, the TREPR method can provide us with the informative optoelectronic and structural properties of the polymer films for evaluations, designs, and developments of the highly efficient OPV, FET and LED systems.

**References**

1. G. Yu, J. Gao, J. C. Hummelen, F. Wudl, and A. J. Heeger, *Science*, **270** (1995) 1789.
2. C. B. Nielsen and I. McCulloch, *Prog. Polym. Sci.* **38** (2013) 2053.
3. I. F. Perepichka, D. F. Perepichka, H. Meng, and F. Wudl, *Adv. Mater.*, **17** (2005) 2281.
4. Y. Kim, S. Cook, S. M. Tuladhar, S. A. Choulis, J. Nelson, J. R. Durrant, D. D. C. Bradley, M. Giles, I. Mcculloch, C. S. Ha, and M. Ree, *Nat. Mater.*, **5** (2006) 197.
5. Z. J. Hu, A. P. Willard, R. J. Ono, C. W. Bielawski, P. J. Rossky, and D. A. Vanden Bout, *Nat. Commun.*, **6** (2015) 8246.
6. I. Osaka, M. Saito, T. Koganazawa, and K. Takimiya, *Adv. Mater.*, **26** (2014) 331.
7. T. Miura, R. Tao, S. Shibata, T. Umeyama, T. Tachikawa, H. Imahori, and Y. Kobori, *J. Am. Chem. Soc.*, **138** (2016) 5879.
8. S. Weber, T. Biskup, A. Okafuji, A. R. Marino, T. Berthold, G. Link, K. Hitomi, E. D. Getzoff, E. Schleicher, and J. R. Norris, *J. Phys. Chem. B*, **114** (2010) 14745.
9. Y. Kobori, R. Noji, and S. Tsuganezawa, *J. Phys. Chem. C*, **117** (2013) 1589.
10. M. Fuki, H. Murai, T. Tachikawa, and Y. Kobori, *J. Phys. Chem. B*, **120** (2016) 4365.
11. G. L. Closs, M. D. E. Forbes, and J. R. Norris, *J. Phys. Chem.* **91** (1987) 3592.
12. Y. Kobori, M. Fuki, and H. Murai, *J. Phys. Chem. B*, **114** (2010) 14621.
13. Y. Kobori and M. Fuki, *J. Am. Chem. Soc.*, **133** (2011) 16770.
14. Y. Kobori and T. Miura, *J. Phys. Chem. Lett.*, **6** (2015) 113.
15. T. Miura, T. Tachikawa, and Y. Kobori, *J. Photopolym. Sci. Technol.*, **29** (2016) 561.
16. Y. Kobori, S. Sekiguchi, K. Akiyama, and S. Tero-Kubota, *J. Phys. Chem. A*, **103** (1999) 5416.
17. T. Liu and A. Troisi, *J. Phys. Chem. C*, **115** (2011) 2406.
18. T. S. Ripolles, A. Guerrero, and G. Garcia-Belmonte, *Appl. Phys. Lett.*, **103** (2013) 243306.