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# Radical ion pair mediated triplet formation in polymer–fullerene blend films†

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**Efficient triplet formation is observed for films of high ionisation potential polythiophenes blended with a fullerene derivative, and assigned to formation *via* geminate charge recombination of bound radical ion pair states.**

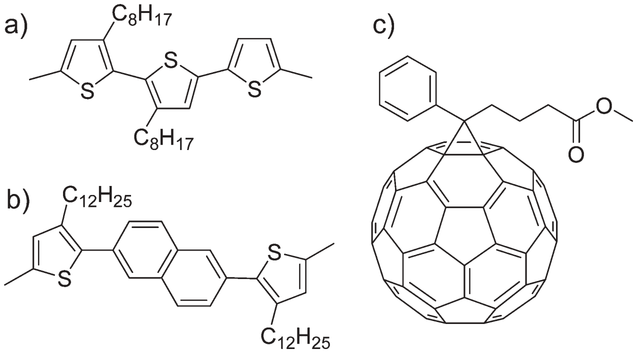

**Chart 1** Chemical structures of a repeating unit in polythiophenes and a fullerene derivative used in this study: a) P($T_8T_8T_0$), b) P($T_{12}NpT_{12}$), c) PCBM.

Organic solar cells are attracting extensive academic and commercial interest. It has been shown that efficient charge separation (CS) can be achieved by blending a conjugated polymer and a fullerene derivative, resulting in a high interface area at which CS can occur.[1,2] Recently, energy conversion efficiencies exceeding 4% have been reported by several groups for blend films of regioregular poly(3-hexylthiophene) (P3HT) and 1-(3-methoxycarbonyl)propyl-1-phenyl-(6,6)$C_{61}$ (PCBM).[3] Such devices exhibit near optimum charge generation per absorbed photons, with short-circuit external quantum efficiencies of up to ~ 70%. Device efficiencies for such devices are, however, significantly limited by their relatively modest open-circuit voltage, $V_{OC}$ ~ 0.6 V. A close correlation has recently been demonstrated between device $V_{OC}$ and polymer ionisation potential (IP), with the relatively low IP of P3HT (4.8 eV) correlating directly with low device $V_{OC}$.[4] It is therefore of particular interest to develop analogous polythiophenes with higher IPs (*i.e.* more positive oxidation potentials). In this paper we report a steady state and transient spectroscopic study of the exciton and charge separated states generated by excitation of polymer–PCBM blend films employing two high IP thiophene copolymers: P($T_8T_8T_0$) (5.6 eV) and P($T_{12}NpT_{12}$) (5.4 eV), as shown in Chart 1.

As shown in Fig. 1, the P($T_8T_8T_0$) pristine film exhibited an absorption peak around 440 nm and an emission peak around 570 nm. Compared with regioregular P3HT films, these spectra are less structured and blue-shifted, with a larger Stokes shift, suggesting that the film is largely amorphous, with reduced π orbital overlap along the polymer backbone. The absence of thermal transitions, confirmed by differential scanning calorimetry (DSC) data (see supplementary information), supported a more amorphous film structure. From the absorption and photoluminescence (PL) spectra, the energy level of the lowest singlet excited state ($S_1$) of the P($T_8T_8T_0$) polymer was evaluated to be $E_S$ = 2.5 eV. Addition of 5% PCBM to the film did not change the absorption spectrum, but resulted in a strong quenching of the PL (quenching efficiency $Q_e$ ~ 95%). This efficient quenching suggests that in the blend film there is an additional reaction pathway from the polymer singlet exciton such as CS or energy transfer (EnT) to PCBM. We previously reported efficient EnT in a polyfluorene–PCBM blend film.[5] In this previous system, evidence for EnT was obtained from the observation that optical excitation of the polyfluorene in the blend film resulted in the appearance of a characteristic PCBM singlet exciton emission band at 700 nm. No

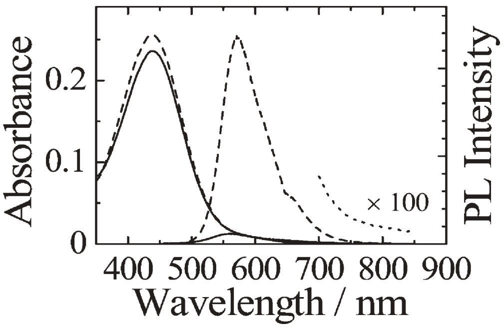

**Fig. 1** Absorption and PL spectra of P($T_8T_8T_0$)/PCBM blend (——) and P($T_8T_8T_0$) pristine (– – –) films. The PL intensity was corrected for variations in the absorption at an excitation wavelength of 440 nm. The PL tail of P($T_8T_8T_0$)/PCBM blend films is multiplied by 100 (········).

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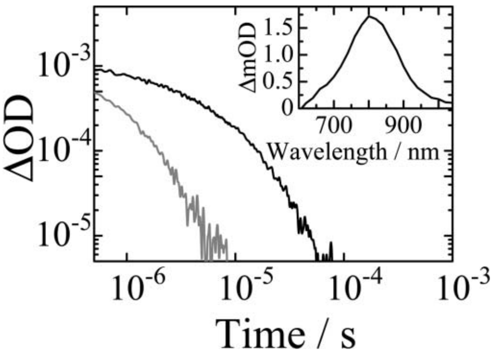


**Fig. 2** Transient absorption decays at 800 nm of the $P(T_8T_8T_0)$ pristine film excited at 440 nm under Ar (black line) and $O_2$ (grey line) atmospheres. The inset shows the transient absorption spectrum at 1 μs after the laser excitation under Ar atmosphere.

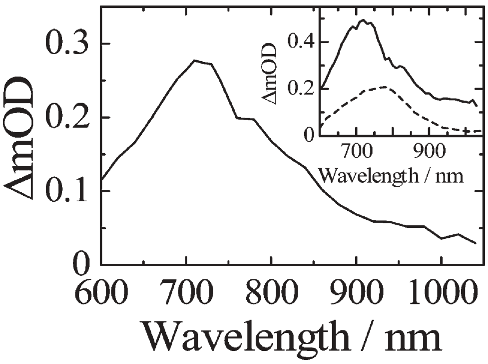


**Fig. 4** Transient absorption spectrum of the $P(T_{12}NpT_{12})$/PCBM blend film at 1 μs after the laser excitation at 440 nm under Ar atmosphere. The inset shows transient absorption spectra of the PCBM/PS blend film excited at 337 nm (——) and the $P(T_{12}NpT_{12})$ pristine film excited at 440 nm (– – –) under Ar atmosphere, assigned to the PCBM and $P(T_{12}NpT_{12})$ triplet states respectively.

such 700-nm emission band could be observed for $P(T_8T_8T_0)$/PCBM blend films, suggesting that there should be another quenching pathway resulting in the strong emission quenching shown in Fig. 1. We therefore employed transient absorption studies to address further the origin of the observed strong PL quenching.

Transient absorption spectra of pristine $P(T_8T_8T_0)$ films showed an induced absorption band around 800 nm, as shown in Fig. 2. This band decayed monoexponentially with a lifetime of 6 μs, too long to be assigned to singlet excitons. As shown in Fig. 2, this transient absorption decayed more rapidly under $O_2$ atmosphere. From all these data, we can safely ascribe the 800-nm absorption to triplet–triplet ($T_1 \rightarrow T_n$) transition of the $P(T_8T_8T_0)$ polymer. No other long-lived transients could be observed for the pristine film.

Fig. 3 shows transient absorption decays of the $P(T_8T_8T_0)$/PCBM blend film. As for the pristine film, a strong photoinduced absorption was observed at 800 nm, with a lifetime of 4 μs, assigned to polymer triplet formation. The quantum yield of these triplets was observed to be only reduced 50% relative to the pristine film. This high triplet yield in the blend film is in contrast to the greatly reduced PL intensity observed for the blend, as we discuss below. In addition to the $P(T_8T_8T_0)$ triplet transient, the absorption data for the blend film showed an additional, slower, decay phase, which exhibited a power law decay with a slope of $\alpha = 0.4$. Such power law decays are characteristic of charge recombination of dissociated charged species in conjugated polymer–PCBM blend films in the presence of energetic disorder.[6] This long lived decay is therefore assigned to $P(T_8T_8T_0)^+$ and $PCBM^-$ generated by charge separation at the polymer–PCBM interface. A more detailed study of such long lived transients will be presented elsewhere.

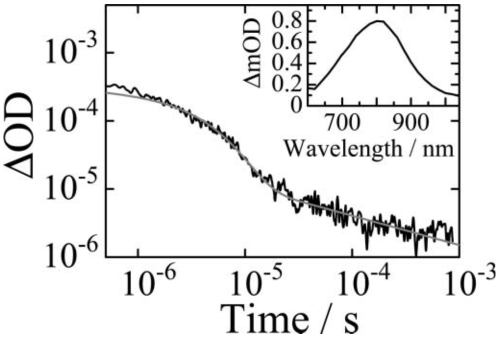
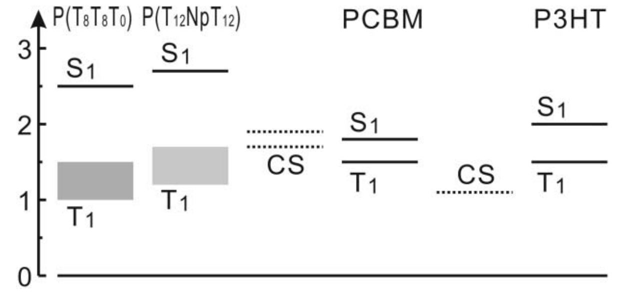


**Fig. 3** Transient absorption decays at 800 nm of the $P(T_8T_8T_0)$/PCBM blend film excited at 440 nm. The grey line represents the fitting curve with a sum of single exponential and power law functions: $\Delta OD = A\exp(-t/\tau) + B\,t^{-\alpha}$. The inset shows the transient absorption spectrum at 1 μs after the laser excitation under Ar atmosphere.

We now turn to transient absorption studies of the analogous polymer $P(T_{12}NpT_{12})$. As for $P(T_8T_8T_0)$, blending with 5% PCBM resulted in strong polymer PL quenching ($Q_e \sim 80\%$). Again no PCBM singlet exciton emission could be observed (in contrast to films of 5% PCBM in an inert polystyrene (PS) matrix, where strong 700-nm PCBM emission could be observed). Typical transient absorption data are shown for $P(T_{12}NpT_{12})$/PCBM blend films in Fig. 4. This figure shows data for the blend film, while the inset shows data for the pristine $P(T_{12}NpT_{12})$ and PCBM/PS films. In this case, the transient spectrum for the blend exhibits a maximum at 720 nm and closely matches the $T_1 \rightarrow T_n$ absorption of PCBM rather than $P(T_{12}NpT_{12})$ triplet excitons. The quantum yield of PCBM triplets observed following excitation of the $P(T_{12}NpT_{12})$ polymer was estimated to be approximately 50% of that observed following direct excitation of the PCBM in the PCBM/PS film. The slightly broader absorption for the $P(T_{12}NpT_{12})$/PCBM blend compared with the $T_1 \rightarrow T_n$ absorption of PCBM might be due to a small contribution from $P(T_{12}NpT_{12})$ triplet absorption. As for the $P(T_8T_8T_0)$/PCBM blend films, the transient decay of the $P(T_{12}NpT_{12})$/PCBM blend film absorbance was well fitted with a sum of a single exponential function and a power law decay. The monoexponential lifetime was 11 μs, consistent with the PCBM triplet lifetime. Thus the transient absorption data for the $P(T_{12}NpT_{12})$/PCBM film are assigned primarily to the PCBM triplet formation, with an additional low yield of dissociated polarons.

In the pristine $P(T_{12}NpT_{12})$ and $P(T_8T_8T_0)$ films, polymer triplet exciton formation can be assigned to intersystem crossing (ISC) from singlet excitons, with the high ISC efficiency resulting from sulfur heavy atoms in the main chain.[7] The strong PL quenching observed for the blend films indicates that the addition of PCBM results in strong quenching of these polymer singlet excitons. Such



**Scheme 1** Energy diagram for polythiophene–PCBM blend films. The energy scale unit is eV. The $T_1$ states of the two polymers are drawn with shaded areas to give the range. The CS states are roughly estimated from IP − EA (3.7 eV).

ISC from these singlet excitons should also be strongly quenched in the blend films. In this context, it is remarkable that we observe a high yield of $P(T_8T_8T_0)$ triplet excitons in the $P(T_8T_8T_0)$/PCBM blend film. We furthermore note that the absence of PCBM singlet exciton emission from the $P(T_{12}NpT_{12})$/PCBM blend films indicates that the PCBM triplets observed for this blend film cannot originate from direct ISC from PCBM singlet excitons. We therefore conclude that the polymer and PCBM triplet states observed for the blend films cannot originate from direct ISC from either polymer or PCBM singlet excitons. Rather we conclude that these triplet excitons are formed by charge recombination for bound polymer–PCBM radical ion states, as we discuss in detail below.

Triplet formation *via* charge recombination from bound radical ion pair states has been widely reported for other experimental systems, including photosynthetic reaction centres,[8] molecular donor–acceptor systems in solution[9] and polymer–polymer blend films.[10] In all cases, the mechanism is based upon the weaker spin–spin interactions in the charge separated state compared to the singlet exciton, allowing rapid mixing of the singlet and triplet radical ion pairs. The distinct formation of either polymer or PCBM triplet excitons can be attributed to the relative energies of these triplet excitons. Our observation of a high triplet yield concomitant with strong PL quenching indicates that such radical ion pair mediated triplet formation may also be important for polymer–fullerene blend films.

In the blend films, our transient absorption data provide evidence not only for triplet formation but also the formation of a low yield of long lived, dissociated polarons. The yield of these long lived polarons depended upon the polythiophene employed, as we discuss in detail elsewhere; for both $P(T_8T_8T_0)$ and $P(T_{12}NpT_{12})$, it was approximately one order of magnitude lower than that observed for P3HT/PCBM films. We note that the microsecond transients assigned to triplet excitons for the $P(T_8T_8T_0)$ and $P(T_{12}NpT_{12})$/PCBM blend films cannot be assigned to charge recombination from these dissociated radical ion pairs (due to the slow timescale for charge recombination from the species). Rather these triplet excitons are assigned to geminate charge recombination of bound radical ion pairs. Previous studies have suggested that geminate recombination of bound radical ion pairs may be important in determining the efficiency of P3HT/PCBM solar cells.[11] The results we present here raise the possibility that geminate charge recombination to polymer or PCBM triplet states may be a significant recombination pathway competing with charge dissociation.

The importance of the recombination pathway reported here will depend critically upon the energetics of the triplet and radical ion pair states, as we illustrate in Scheme 1. For this scheme, the energies of radical ion pair states were estimated from the polymer IP, using an electron affinity (EA) for PCBM of 3.7 eV. Singlet exciton energies were estimated from ground state absorption and PL spectra. For $P(T_8T_8T_0)$ and $P(T_{12}NpT_{12})$, the singlet–triplet exciton separations, $\Delta E_{ST}$, were assumed to be close to those of short oligothiophenes (1.48–1.06 eV)[12] as their twisted structures are expected to limit their conjugation length. $\Delta E_{ST}$ for P3HT was taken from literature data for highly ordered regioregular poly(3-octylthiophene) films (0.45 eV).[13] The energy levels in Scheme 1 are consistent with our observation of significant triplet formation in $P(T_8T_8T_0)$ and $P(T_{12}NpT_{12})$/PCBM blend films, contrasting with efficient generation of dissociated polarons in P3HT/PCBM films. These observations suggest that the energetics of radical ion pair states *versus* triplet exciton energies is a new parameter to be considered in optimising the efficiency of polythiophene–PCBM solar cells.

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