Supporting Information

Charge Generation in Non-Fullerene Donor-Acceptor Blends for Organic Solar Cells

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Calculation of the acceptor concentration

For A1, A2 and A3 the mass density ρ was assumed to be approximately the same as that of PTB7 and 1.1 g/cm^3. It was also assumed that the mass ratio of the materials in the solutions used for spin-coating was the same as that in the formed films. Hence, the number of acceptor molecules per cm^3, *n*, was calculated using

$$n = \frac{\rho f}{M_W} N_A, \quad \text{(S1)}$$

where *f* is the weight fraction of the acceptor in the blend, M_W is the molecular weight of the acceptor and N_A is Avogadro's number. As the mass density of PC70BM is greater than that of PTB7 at ~1.6 g/cm^3,[1] the effective mass density of the blend in this case, given by

$$\rho_{eff} = f\rho_{PC70BM} + (1 - f)\rho_{PTB7}, \quad \text{(S2)}$$

was substituted into Equation S1 and used to calculate the number of PC70BM molecules per cm^3.

To calculate the acceptor chromophore concentration the number of acceptor molecules per cm^3 was multiplied by the number of chromophores per molecule, which was 1 for A1 and PC70BM and 4 for A2 and A3.

Intermediate CT-state model for charge generation

The changes in the population of the ground state [GS], CT-states [CT] and separated charges [SC] over time was described with the following rate equations (see Figure 8a for a schematic representation):

$$\frac{d[CT]}{dt} = -k_{CT-GS}[CT] - k_{CT-SC}[CT] + \gamma[SC]^{\lambda+1} \quad \text{(S3)}$$

$$\frac{d[SC]}{dt} = k_{CT-SC}[CT] - \gamma[SC]^{\lambda+1} \quad \text{(S4)}$$

$$\frac{d[GS]}{dt} = k_{CT-GS}[CT] \quad \text{(S5)}$$

where k_{CT-GS} is the rate of recombination to the ground state from the CT-state, k_{CT-SC} is the rate of CT-state dissociation to separated charges, γ is the rate of recombination for separated charges and λ is the order of the recombination.

As the data was limited to 3 ns with no non-geminate recombination (see Figure S3) at low fluences the rate equations can be simplified to give:

$$\frac{d[CT]}{dt} = -k_{CT-GS}[CT] - k_{CT-SC}[CT] \quad \text{(S6)}$$

$$\frac{d[SC]}{dt} = k_{CT-SC}[CT] \quad \text{(S7)}$$

$$\frac{d[GS]}{dt} = k_{CT-GS}[CT] \quad \text{(S8)}$$

Supplementary figures

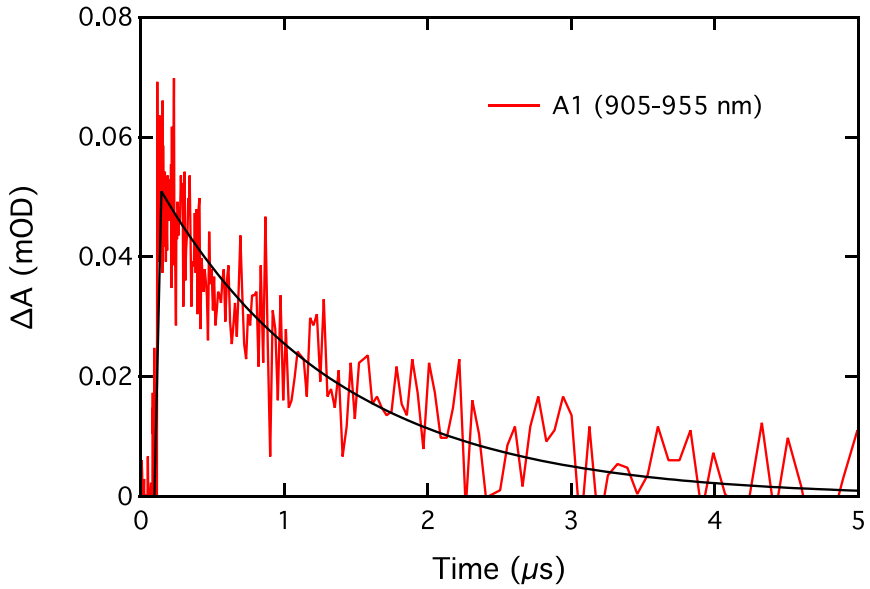

Figure S1. Triplet exciton decay in a neat film of A1 excited at 520 nm with a fluence of 5.4 μJ/cm^2. The signal was integrated between 905-955 and decayed exponentially (fit represented with a black line).

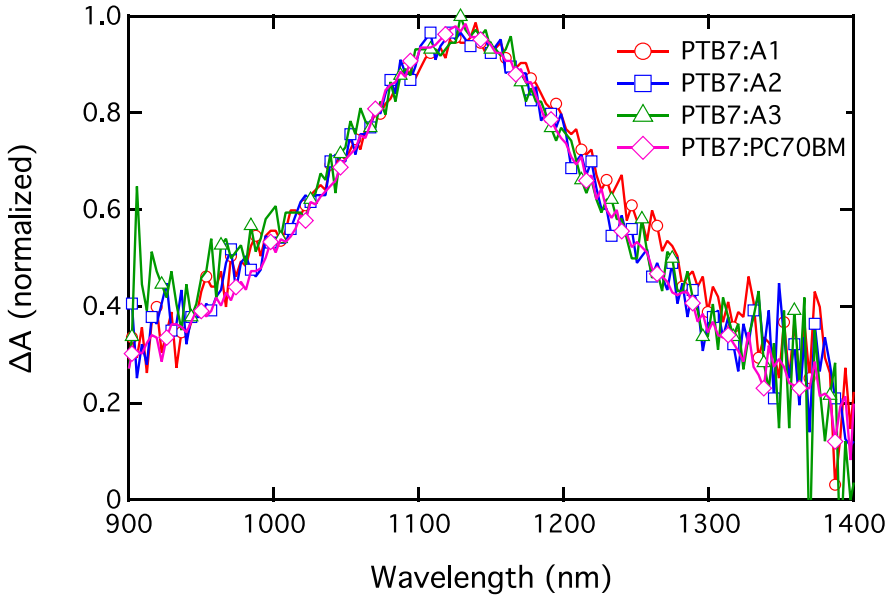

Figure S2. Comparison of the shape of the polaron absorption spectra at 1.5 ns for PTB7 blends containing 5 wt % acceptor. Films were excited at 650 nm with a fluence of 3.4 μJ/cm^2.

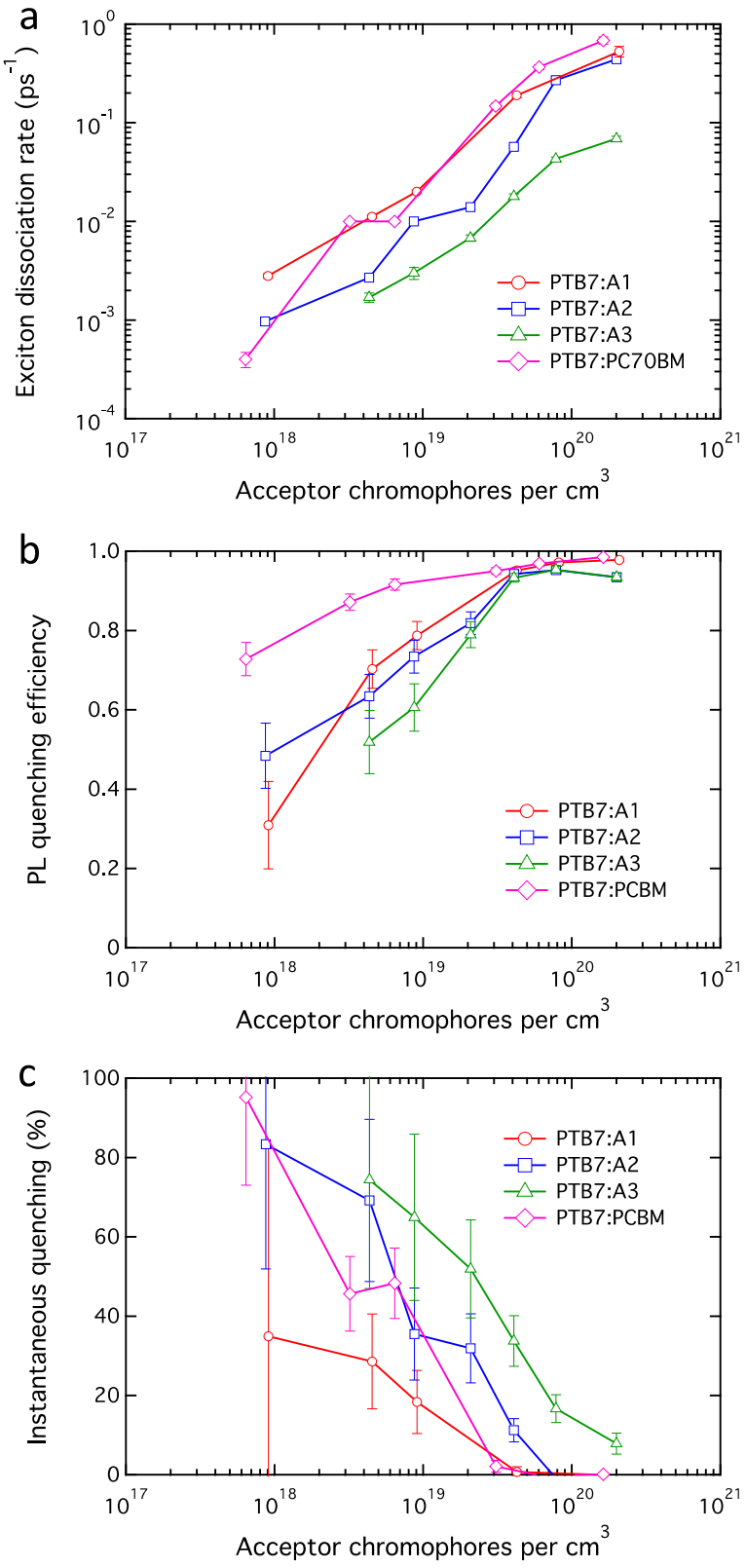

Figure S3. (a) Singlet exciton quenching rate in PTB7:acceptor blends versus acceptor chromophore concentrations. (b) Steady-state photoluminescence (PL) quenching efficiency of PTB7:acceptor blends with acceptor chromophore concentration. (c) Proportion of donor excitons that are quenched within the temporal resolution of the measurements with acceptor chromophore concentration.

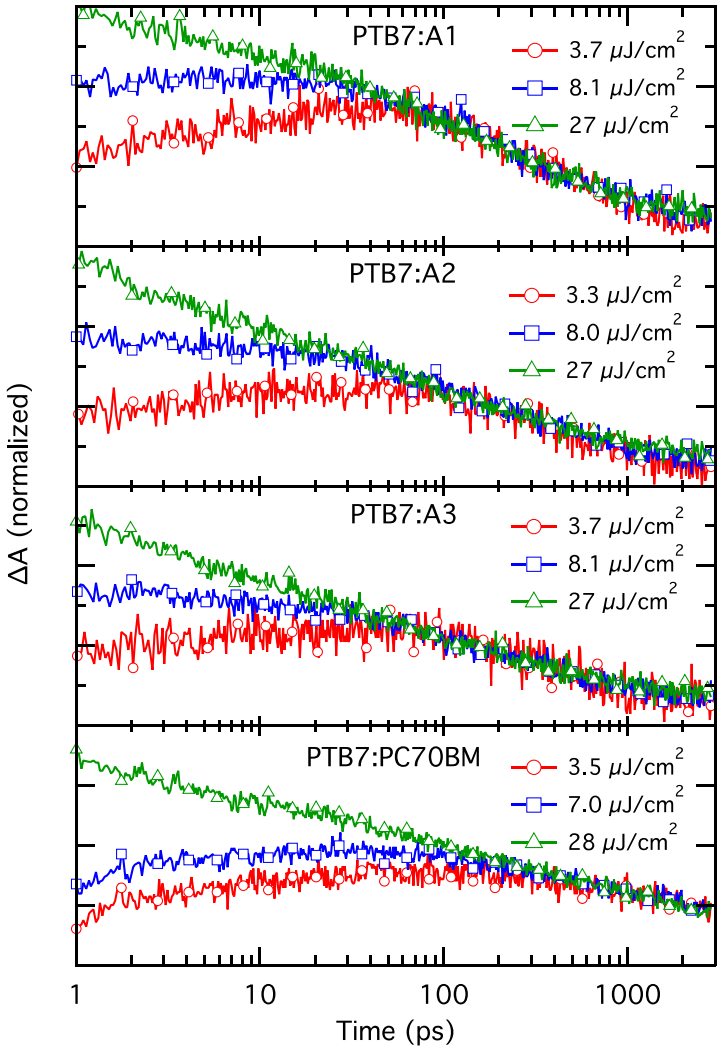

Figure S4. Pump power dependence of the kinetics at for blends containing 1 wt % acceptor. The blends were photo-excited at 650 nm. The signals have been normalized so that the decay at later times align.

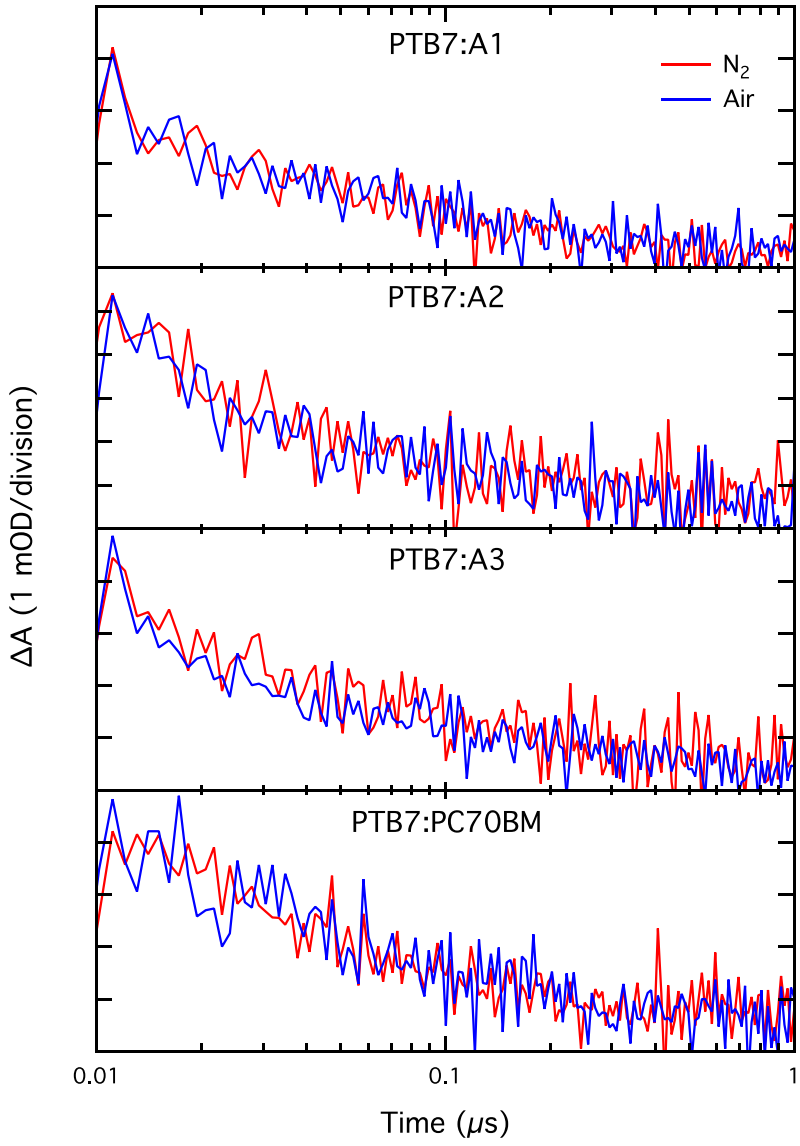

Figure S5. Decay kinetics of the polaron signal in PTB7 blends containing similar concentrations of acceptor molecule per cm^3 in a nitrogen atmosphere and in air: 1 wt % of A1 (9.1×10^{18} cm^3) and PC70BM (6.4×10^{18} cm^3), 5 wt % of A2 (1.0×10^{19} cm^3) and A3 (1.0×10^{19} cm^3). The films were photo-excited at 650 nm with a pump fluence of 2.3 μJ/cm^2 and the signal was integrated between 1152-1252 nm.

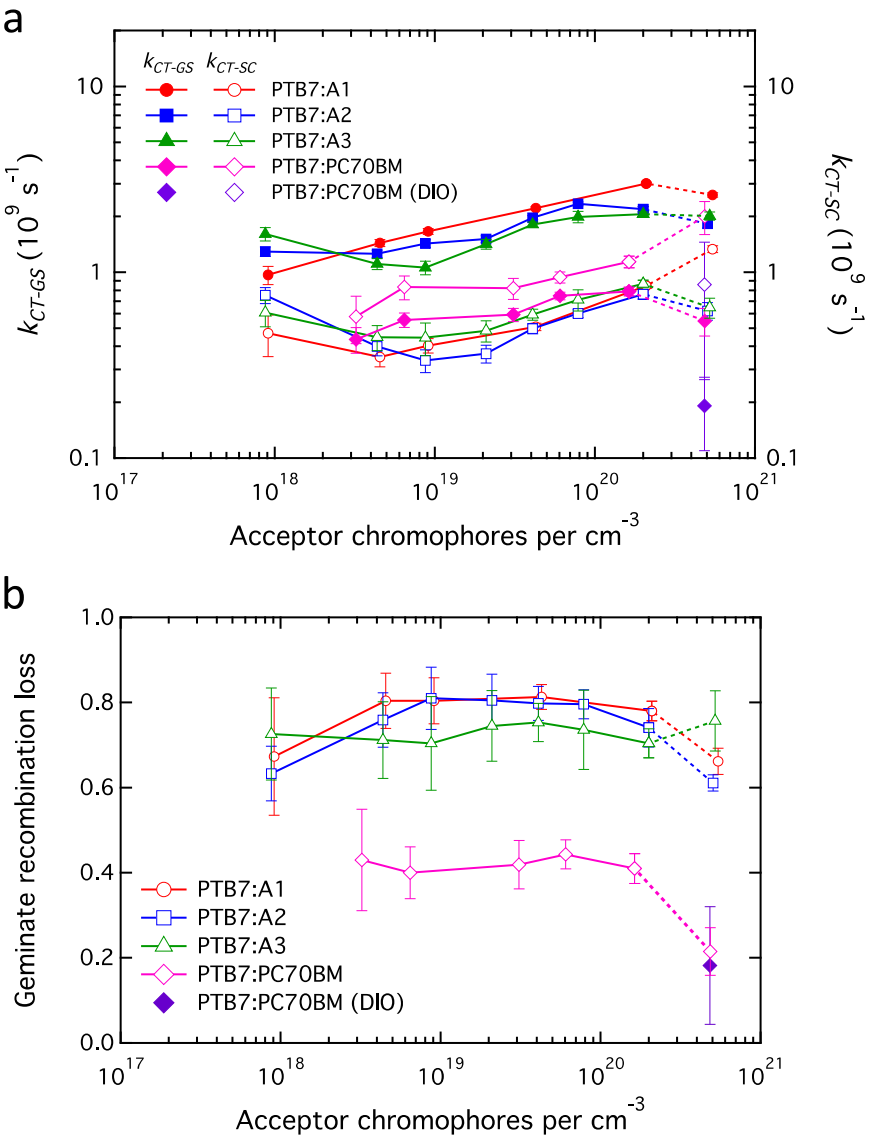

Figure S6. (a) Rates for geminate recombination to the ground state (k_{CT-GS}) and dissociation of the CT-state to separated charges (k_{CT-SC}) versus acceptor chromophore concentration. (b) Losses to geminate recombination versus acceptor chromophore concentration.

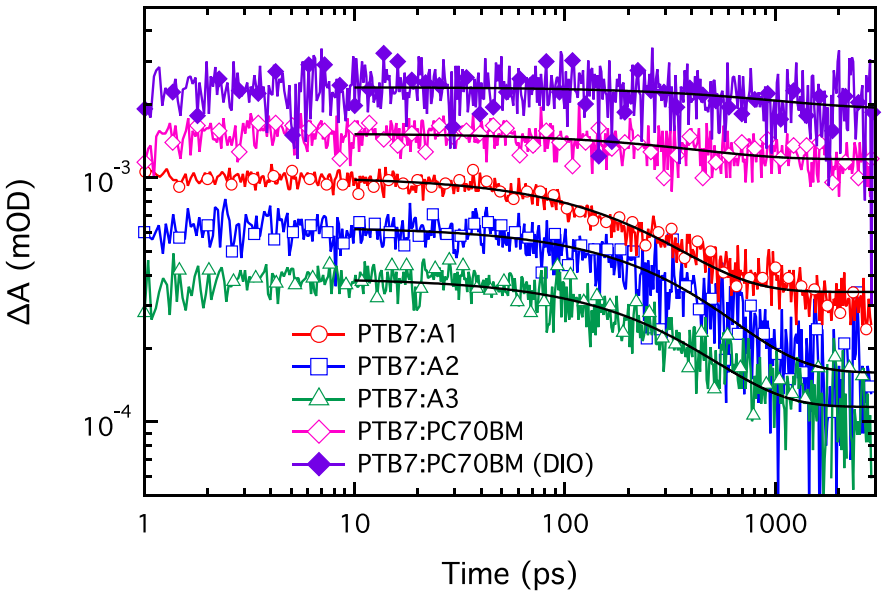

Figure S7. Polaron signal for blends of PTB7 with 60 wt % acceptor probed between at 902 nm, which have been offset for clarity. The blends were photo-excited at 650 nm with a fluence of 1.5 μJ/cm^2. The black lines are fits to the data using the intermediate CT-state model.

Supplementary reference

(1) Clulow, A. J.; Armin, A.; Lee, K. H.; Pandey, A. K.; Tao, C.; Velusamy, M.; James, M.; Nelson, A.; Burn, P. L.; Gentle, I. R.; et al. *Langmuir* **2014**, *30* (5), 1410.