

Electronic Supporting Information

Correlation between blend morphology and recombination dynamics in additives-added P3HT:PCBM solar cells

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1. Normalized Absorption Spectra

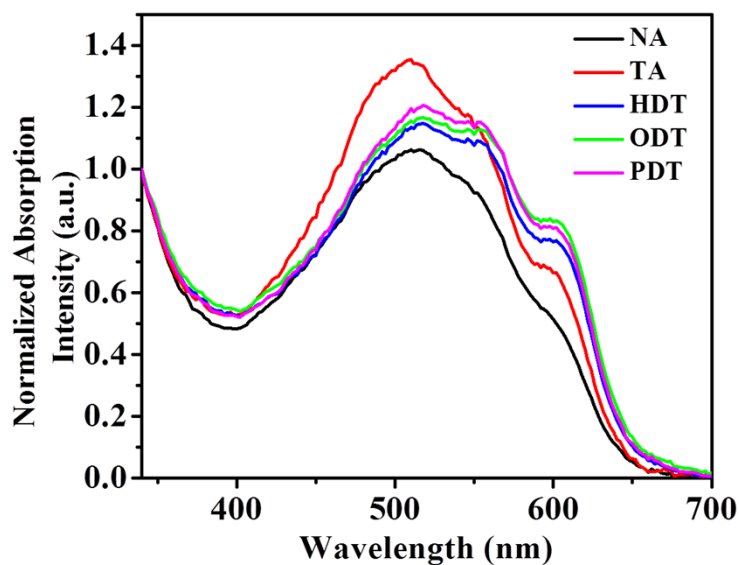


Figure S1: Normalized absorption spectra of the NA, TA and additives-added P3HT:PCBM blend film. P3HT crystallinity is highly sensitive to the interchain interaction represented by the vibronic shoulder at 600 nm and thus the photoabsorption. Although it can indeed be inferred that the pi-pi* transition (~ 500 nm) in the TA film gives the highest peak absorption, the additive-added blend films are more organized as a result of the stronger interchain interactions. The total amount of absorbed photons is calculated by integrating the absorption spectrum of these blend films – see main text for more details.

2. X-ray Diffraction Pattern

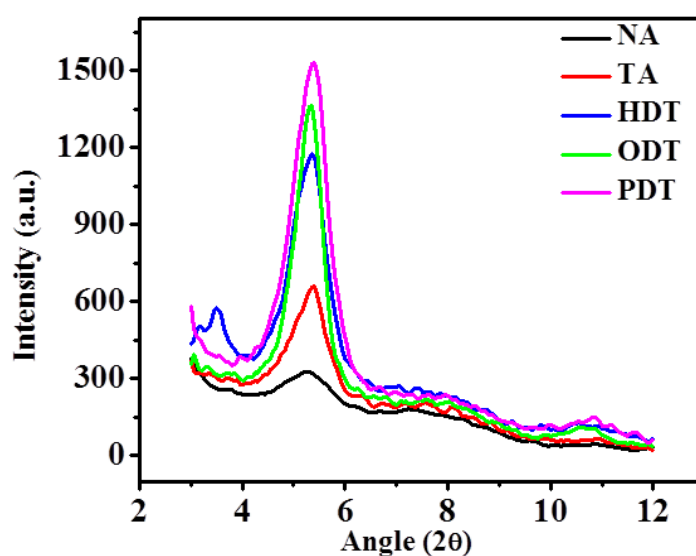


Figure S2: X-ray diffraction patterns of different P3HT:PCBM blend films. The samples were prepared on Si/SiO₂ substrates.

3. Morphology study by Atomic Force Microscope

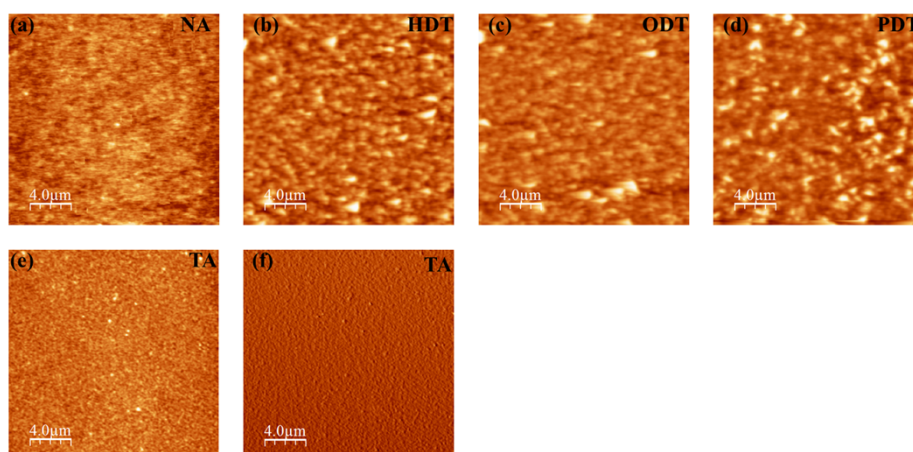


Figure S3: Topographic height image from AFM scan of (a) NA, (b) HDT, (c) ODT, (d) PDT, (e) TA and (f) thermally annealed P3HT:PCBM (phase) blend film. The scan area is $20 \times 20 \mu\text{m}^2$ for these images.

4. Femtosecond Transient Absorption Spectroscopy (fs-TAS).

Transient absorption measurements were performed using a commercially available integrated HeliosTM and EOSTM setup (Ultrafast Systems LLC). Helios and EOS were used to measure transient absorption dynamics in the fs-ns and ns- μs time regimes, respectively. The pump pulse (500 nm) was generated from an optical parametric amplifier (OPerA Solo) that was pumped by a 1-kHz regenerative amplifier (Coherent Libra). The beam from the regenerative amplifier has a center wavelength at 800 nm, a pulse width of around 50 fs and a power of 4 mJ per pulse and was seeded by a mode-lock Ti-sapphire oscillator (Coherent Vitesse, 80MHz). The pump beam energy was set to be around $35 \mu\text{J}\cdot\text{cm}^{-2}$ per pulse. The probe beam for Helios was a white light continuum generated from either a 3 mm sapphire crystal for visible part (400 nm-800 nm) or one centimeter sapphire plate for NIR part (800 nm-1600 nm) using 800 nm fs pulse from the regenerative amplifier above. The probe beam for EOS was a white continuum generated from a photonic fiber using a Nd:YAG laser

(center wavelength: 1064 nm). The probe beam was collected using a dual detector for UV-Vis (CMOS sensor) and NIR (InGaAs diode array sensor).

5. Femtosecond Transient Absorption Spectra of thermally annealed (TA) P3HT:PCBM blend.

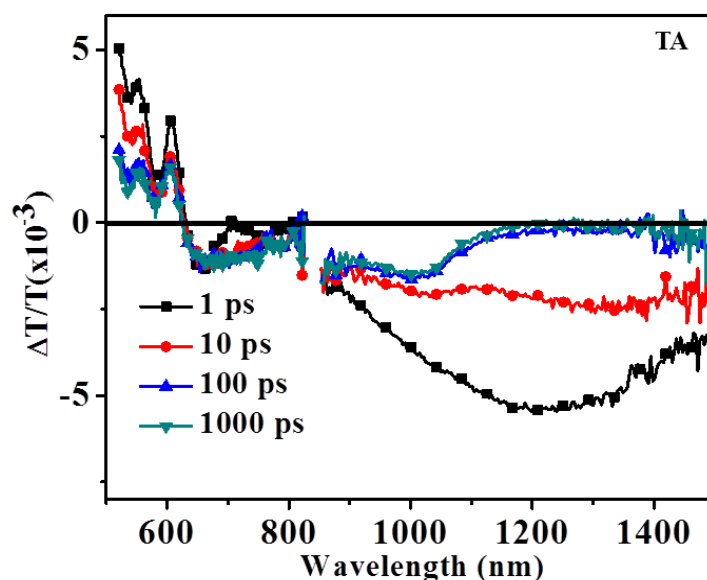


Figure S4: Femtosecond Transient Absorption (TAS) spectra of thermally annealed (TA) P3HT:PCBM blend film.

6. Normalized decay dynamics of 0-0 GSB peak in NA and TA P3HT:PCBM blend films

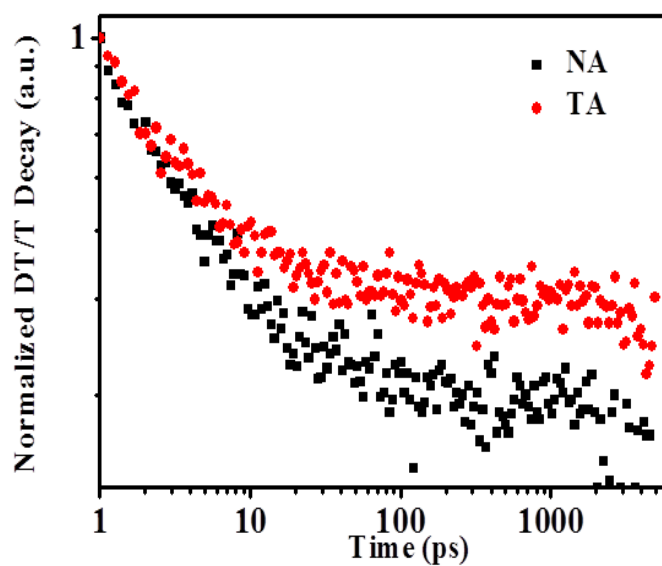


Figure S5: Normalized decay dynamics of 0-0 GSB peak in NA and TA P3HT:PCBM blend films excited with $35 \mu\text{J}\cdot\text{cm}^{-2}$ pump fluence.

7. Transient profile for the signal rise at from 710-740 nm in NA and HDT added blend film

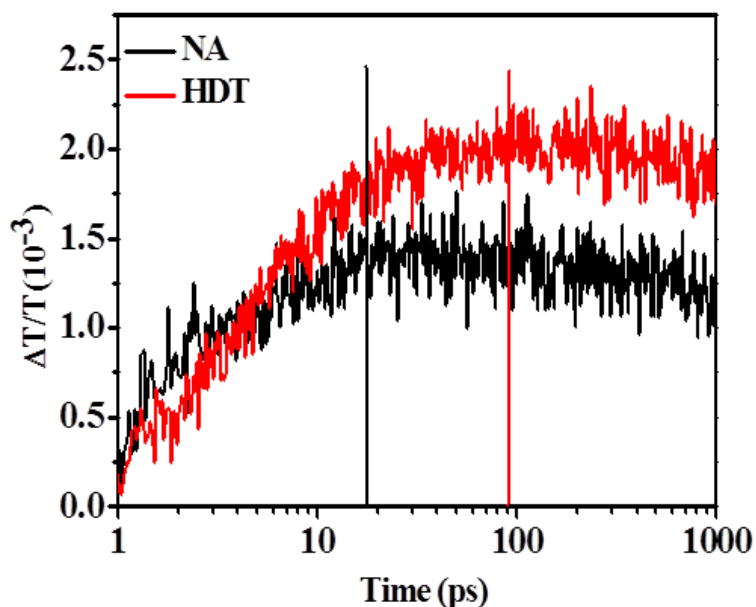


Figure S6: Polaron dynamics of NA and HDT-added P3HT:PCBM blend film between 710-740 nm.

8. Global Fitting of transient absorption spectrum of thermally annealed blend

To examine the mechanisms of the exciton and polaron formation in the different blend films, a singular value decomposition (SVD) and global fitting analysis for the transient absorption spectra were also performed. In this method, the 3D matrix of the transient absorption data is decomposed into its principal spectra and dynamics using SVD. A multi-exponential function convolved with a Gaussian function was used to globally fit these principal dynamics. Applying this method to the different P3HT:PCBM blend films, we obtained three exponential components and a constant component.

Fig. S7 shows the separation of the different features using global analysis of all different blend films over the time range from 100 fs to 5 ns at $35 \mu\text{J}\cdot\text{cm}^{-2}$ pump fluence and

the extracted time constants are summarized in Table S1. The first two most prominent decay time constants (τ_1 - black line and τ_2 - red line) are mainly due to singlet excitons (dominant around 1230 nm); first constant τ_1 is due to the excitons present in the amorphous or intermixed phase of P3HT:PCBM while the second τ_2 is assigned to the delayed exciton dissociation due to the migration in larger P3HT domains. Fig S7 (a) and Table S1 shows that in the NA blend film, the excitons present in the intermixed polymer phase dissociate faster ($\tau_1 < 1$ ps) than in the crystalline phase ($\tau_2 \sim 13$ ps). On adding the HDT in P3HT:PCBM blend film, τ_1 becomes slightly delayed ($\tau_1 \sim 1.4$ ps) while τ_2 remains almost invariant. The lengthening of τ_1 can be attributed to the transition of intermixed phase to the more ordered or segregated phase and to the enlargement of the crystalline P3HT domains (as a result of the interaction with HDT) which resulted in the migration of excitons to the interface before dissociation. All the spectra fits of the other additive-added blend films show similar τ_2 values, suggesting that exciton dissociation in these additive-treated films occurs in larger P3HT domains which could be of similar average size. The third and last decay constant τ_3 in all blend films can be attributed to the long-lived free polarons which persist longer than the temporal window of the measurement. In short, the singlet excitons decay faster in the NA P3HT:PCBM film than in the other additive-added blend films due to the presence of intermixed phase while dynamics (within this time window) remains unaffected regardless of the choice of processing additives.

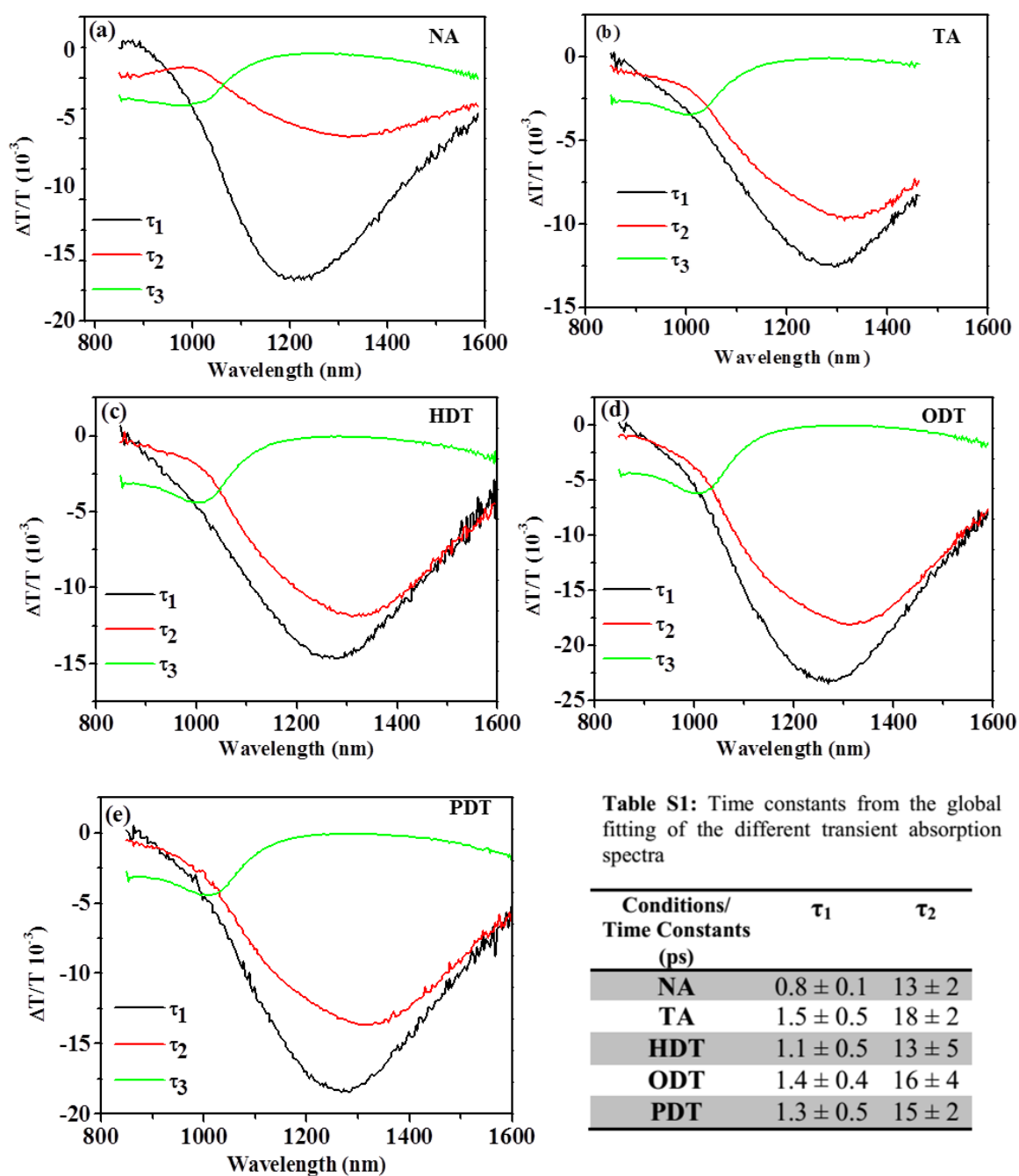


Figure S7: Pre-exponential coefficient spectrum obtained by SVD and global fitting analysis of (a) NA, (b) TA, (c) HDT, (d) ODT and (e) PDT-added P3HT:PCBM blend films at $35 \mu\text{J}\cdot\text{cm}^{-2}$ pump fluence. τ_1 represents the excitons in the intermixed phase, τ_2 for excitons in the larger domains and τ_3 represents polarons in P3HT.

9. Pump fluence dependent decay dynamics for thermally annealed P3HT:PCBM

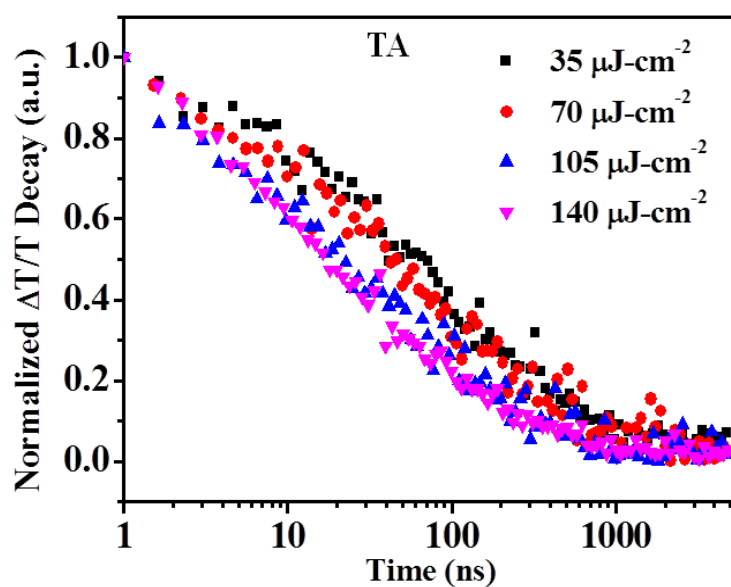


Figure S8: Normalized decay dynamics in TA P3HT:PCBM blend film between 710-740 nm.

10. Photoluminescence Spectra

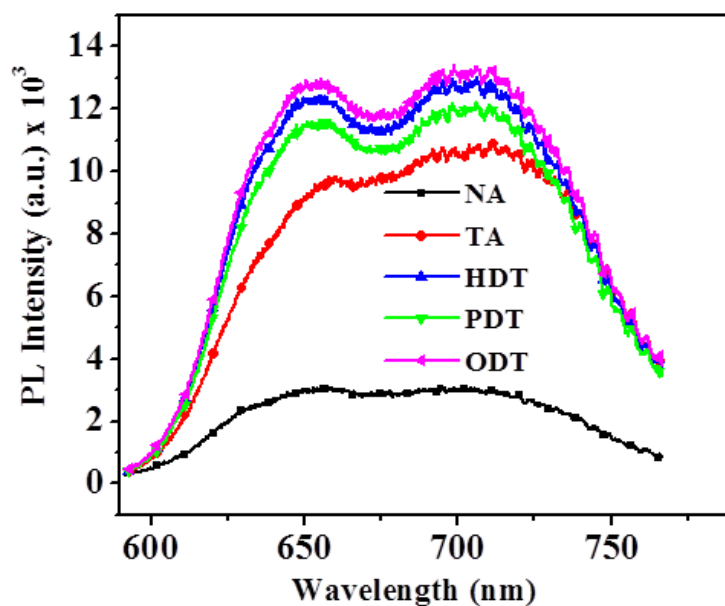


Figure S9: Photoluminescence spectra of different blend films.