

Electronic supplementary information (ESI)

A Femtosecond Transient Absorption Study of Charge Photogeneration and Recombination Dynamics in Photovoltaic Polymers with Different Side-Chain Linkages

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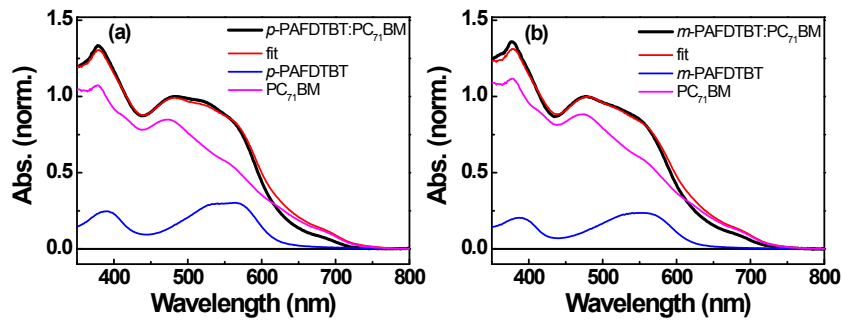


Figure S1. The fitting results of UV-vis absorption spectra for *p*-PAFDTBT:PC₇₁BM (a) and *m*-PAFDTBT:PC₇₁BM (b) films by linear combination of characteristic spectra of neat *p*-PAFDTBT and PC₇₁BM films.

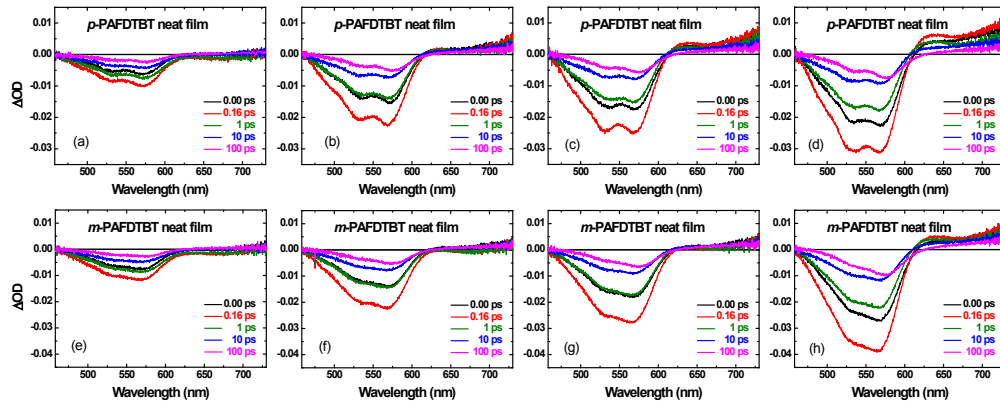


Figure S2. Transient absorption spectra of neat films under different excitation photon fluences. The excitation photon fluence (in photons·cm⁻²·pulse⁻¹) was varied as follows: (a) 6.3×10^{12} , (b) 1.4×10^{13} , (c) 1.6×10^{13} , (d) 2.0×10^{13} for *p*-PAFDTBT films, and (e) 3.6×10^{12} , (f) 7.3×10^{12} , (g) 8.6×10^{12} , (h) 1.2×10^{13} for *m*-PAFDTBT films.

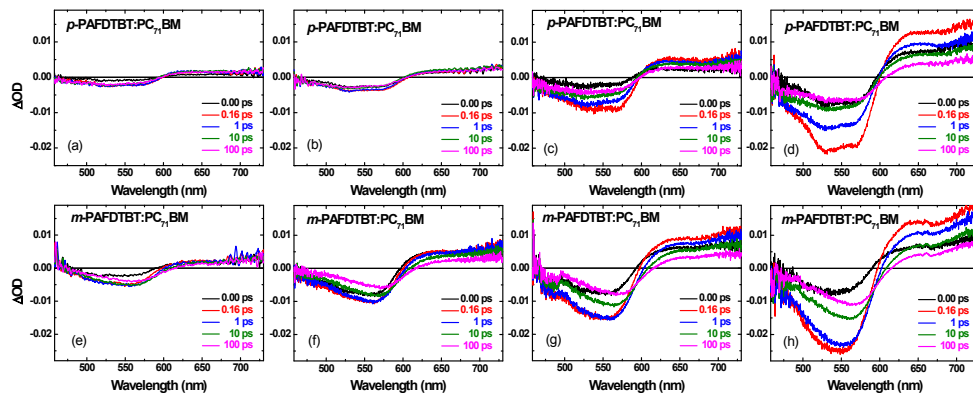


Figure S3. Transient absorption spectra of blend films under different excitation photon fluences. The excitation photon fluence (in photons·cm⁻²·pulse⁻¹) was varied as follows: (a) 1.3×10^{12} , (b) 2.3×10^{12} , (c) 3.5×10^{12} , (d) 7.8×10^{12} for *p*-PAFDTBT:PC₇₁BM films, and (e) 1.8×10^{12} , (f) 3.2×10^{12} , (g) 5.3×10^{12} , (h) 6.5×10^{12} for *m*-PAFDTBT:PC₇₁BM films.

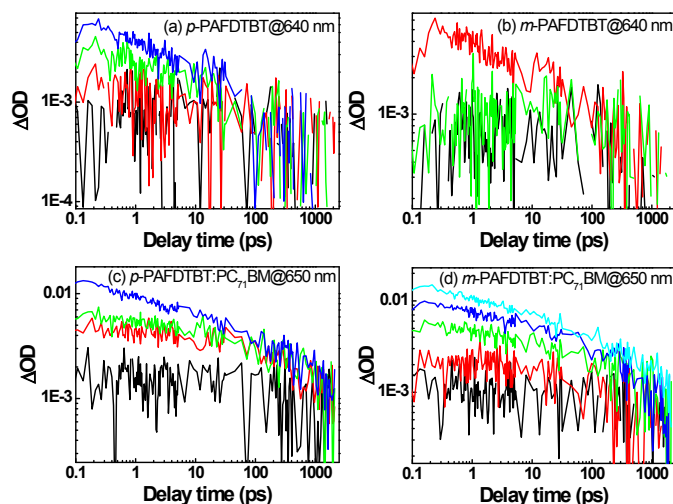


Figure S4. Kinetic curves at ~ 650 nm of neat films (a,b) and blends (c,d) under different excitation photon fluences. For (a), the excitation photon fluence was varied over 2.0×10^{13} , 1.6×10^{13} , 1.4×10^{13} and 1.2×10^{13} photons $\cdot\text{cm}^{-2}\cdot\text{pulse}^{-1}$ from top to bottom; For (b), the excitation photon fluence was varied over 1.2×10^{13} , 8.6×10^{12} and 7.7×10^{12} photons $\cdot\text{cm}^{-2}\cdot\text{pulse}^{-1}$ from top to bottom; For (c), the excitation photon fluence was varied over 7.8×10^{12} , 5.9×10^{12} , 3.5×10^{12} and 1.3×10^{12} photons $\cdot\text{cm}^{-2}\cdot\text{pulse}^{-1}$ from top to bottom; For (d), the excitation photon fluence was varied over 6.5×10^{12} , 5.3×10^{12} , 3.2×10^{12} , 1.8×10^{12} and 9.3×10^{11} photons $\cdot\text{cm}^{-2}\cdot\text{pulse}^{-1}$ from top to bottom.

We also carried out the UV-vis transient measurement for films. As shown in Figure S2, for the neat film, in the visible region both the GSB and SE signals are observed under lower excitation photon fluence; however, under higher excitation photon fluence the SE signals are replaced by positive PIA signals. The PIA signals in the range of 630–730 nm most probably come from polarons because this similar signal is also observed in the case of blend films even if under the lower excitation photon fluence (Figure S3). Polaron signals at 640 nm in neat films generate under higher excitation fluence owing to more polaron formations led to by exciton-exciton annihilation, while these in blends arise from electron transfer from polymer to fullerene. The polarons absorbing at 640 nm can be ascribed to the delocalized polarons (DP) based on the P3HT system. In neat films, the SE signals at 640 nm are also involved which can be excluded in blends due to the efficient exciton dissociation. Therefore, for neat films, the signals at 640 nm are complicated and it is difficult to analyze them owing to the overlap of spectral components. The kinetic curves at 640 nm are shown in Figure S4, including both cases of neat and blend films. Under lower excitation photon fluences, the transient signals at 640 nm of both neat and blend films remain almost constant, which means most of delocalized polarons are free from the bimolecular recombination up to nanosecond timescale. Under higher excitation photon fluences, on the other hand, the signals at 640 nm are linear on the log-log plots which suggest distinctly bimolecular recombination behavior, and decay faster with the excitation photon fluence. These phenomena further support our assignment that the transient signals at 640 nm comes from the contribution of delocalized polarons. Herein the interchain polaron pairs in neat films or charge transfer states at the polymer-fullerene interface in blends are not observed together with polarons. In the maintext, we have mentioned that transient signals at 900 nm involves the contribution polaron pairs or charge transfer states. This assignment is much analogous with the case of

PFDTBT, a polymer similar with *p*-/*m*-PAFDTBT.^{S1} However, in contrast to PFDTBT, the spectral features of polaron pairs in neat film or charge transfer states in blends and localized polarons are not differentiable based on the near-infrared transient absorption spectra in the case of *p*-/*m*-PAFDTBT.

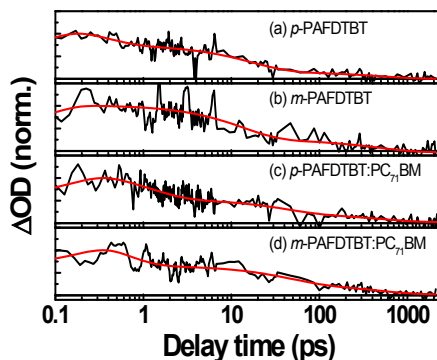


Figure S5. Time evolutions of decays at 1300 nm for neat and blend films. The red lines represent fitting curves with a sum of three or two exponential functions. For blends, the longest lifetime was fixed to the lifetime derived from neat films.

Table S1. Fitting parameters for transient absorption decays of films at 1300 nm.

sample	τ_1 (ps)	τ_2 (ps)	τ_3 (ps)	τ_{av}^a (ps)
<i>p</i> -PAFDTBT	0.33±0.11	17.1±2.5	516±57	462
<i>m</i> -PAFDTBT	—	13.4±1.8	478±92	443
<i>p</i> -PAFDTBT:PC ₇₁ BM	1.16±0.16	40.8±6.4	462 (fix)	—
<i>m</i> -PAFDTBT:PC ₇₁ BM	0.50±0.10	45.5±9.8	443 (fix)	—

^a The averaged lifetime τ_{av} was calculated with the relation^{S2} $\tau_{av} = \sum_{i=1}^n A_i \tau_i^2 / \sum_{i=1}^n A_i \tau_i$ ($n = 3$), where τ_i and A_i , respectively, are the individual decay time constant and the fraction of the *i*th component

The time-kinetics of excitons can be monitored by extracting the 1300 nm dynamics from the transient absorption matrix. These data were plotted in Figure S5 and their fitting parameters were summarized in Table S1. For neat films, excitons decay exponentially and their averaged lifetimes are 462 ps and 443 ps for *p*-PAFDTBT and *m*-PAFDTBT, respectively. For blend films, the longest lifetime of decays at 1300 nm were fixed to the exciton lifetime derived from neat films. On the other hand, the fastest decay component (τ_1) is ascribable to the exciton-exciton annihilation as seen in the GSB dynamics at 570 nm or 575 nm (Figures 6,7 in the maintext). Under the comparative excitation photon fluence, the fastest decay lifetime coincides with the rise lifetime observed in Figure 7a. In addition, the medium decay component originates from the exciton diffusion to the polymer-fullerene interface. Comparing the cases of *p*-PAFDTBT film and *m*-PAFDTBT film, we do not discover distinct discrepancies between the excitons decay behaviors of *p*-PAFDTBT and *m*-PAFDTBT. The absence of exciton discrepancy between *p*-PAFDTBT and *m*-PAFDTBT suggests the substitution pattern have no significant impact on the exciton decay.

Reference

(S1) W. Zhang, Y. W. Wang, R. Hu, L. M. Fu, X. C. Ai, J. P. Zhang and J. H. Hou, *J. Phys. Chem. C*, 2013, **117**, 735.

(S2) K. Masuda, Y. Ikeda, M. Ogawa, H. Benten, H. Ohkita and S. Ito, *ACS Appl. Mater. Interfaces*, 2010, **2**, 236.