Supporting Information

Charge Separation from an Intra-moiety Intermediate State in the High-Performance PM6:Y6 Organic Photovoltaic Blend

Rui Wang,[†] Chunfeng Zhang,[*,†] Qian Li,[†] Zhiguo Zhang,[‡] Xiaoyong Wang,[†] Min Xiao[,†,§]

[†]National Laboratory of Solid State Microstructures, School of Physics, and Collaborative Innovation Center for Advanced Microstructures, Nanjing University, Nanjing 210093, China.

[‡]College of Materials Science and Engineering, Beijing University of Chemical Technology, Beijing 100029, China.

[§]Department of Physics, University of Arkansas, Fayetteville, Arkansas 72701, United States.

*E-mail: cfzhang@nju.edu.cn

1. Additional experimental details

Nanosecond-resolved transient absorption (TA) spectroscopy was employed to probe the dynamics on the late stage using an electronic delay generator. The pump pulse was generated by a picosecond laser diode emitted at 670 nm (LDH-P-C-670M, Picoquant). The probe was the supercontinuum generated by the Ti: Sapphire regenerative amplifier. The time delay between the two lasers were synchronized and enabled by a digital delay generator (DG645, Stanford Research System).

The control TA measurement with pump wavelength at 910 nm was conducted using a Yb:KGW laser (Pharos, Light Conversion). The wavelength of fundamental output was at ~ 1030 nm. We used a home-built noncollinear optical parametric amplifier as described in literature[1] to generate the pump pulse at 910 nm. A long pass filter (FGL850, Thorlabs) was placed in the pump light path to reduce the short-wavelength spectral coverage. The probe beam was supercontinuum by focusing a small fraction of the fundamental 1030 beam to a 5 mm sapphire plate. A short pass filter (10SWF-1000-B, Newport) or a long pass filter (FELH1200, Thorlabs) was employed in the supercontinuum to exclude the fundamental beam for visible detection (600-950 nm) or infrared detection (1200 -1600 nm), respectively. The pump and visible probe were compressed by chirp mirrors and wedge pairs to maintain time resolution better than 30 fs. The detection system was the same as described in the main text. Temperature-dependent measurements were performed using a cryostat (MicrostatHe, Oxford Instruments).

2. Device performance

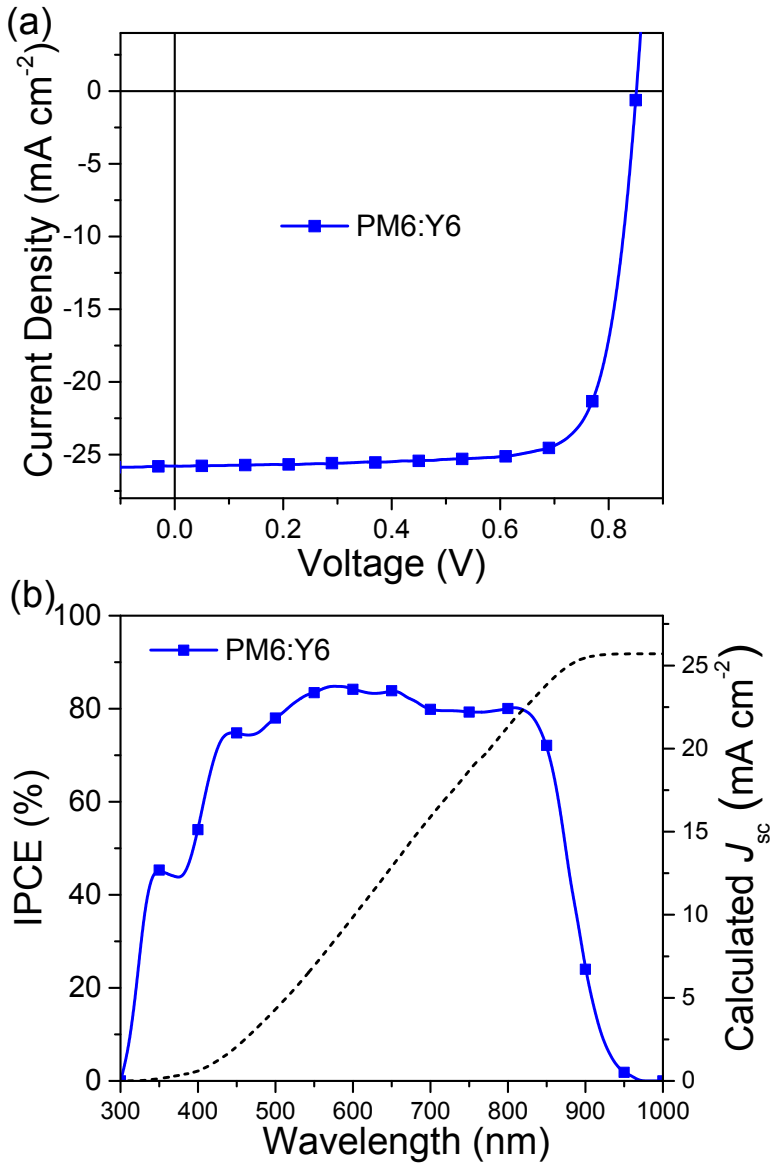

Figure S1. Device performance. (a) Current-voltage curve of a typical organic solar cell with the active layer of PM6:Y6 with power conversion efficiency of 17.2%. (b) The spectrum of incident-photon-conversion efficiency (IPCE) and integrated current density of the device. The average values of power conversion efficient is ~ 17%.

3. Absorption and photoluminescence spectra

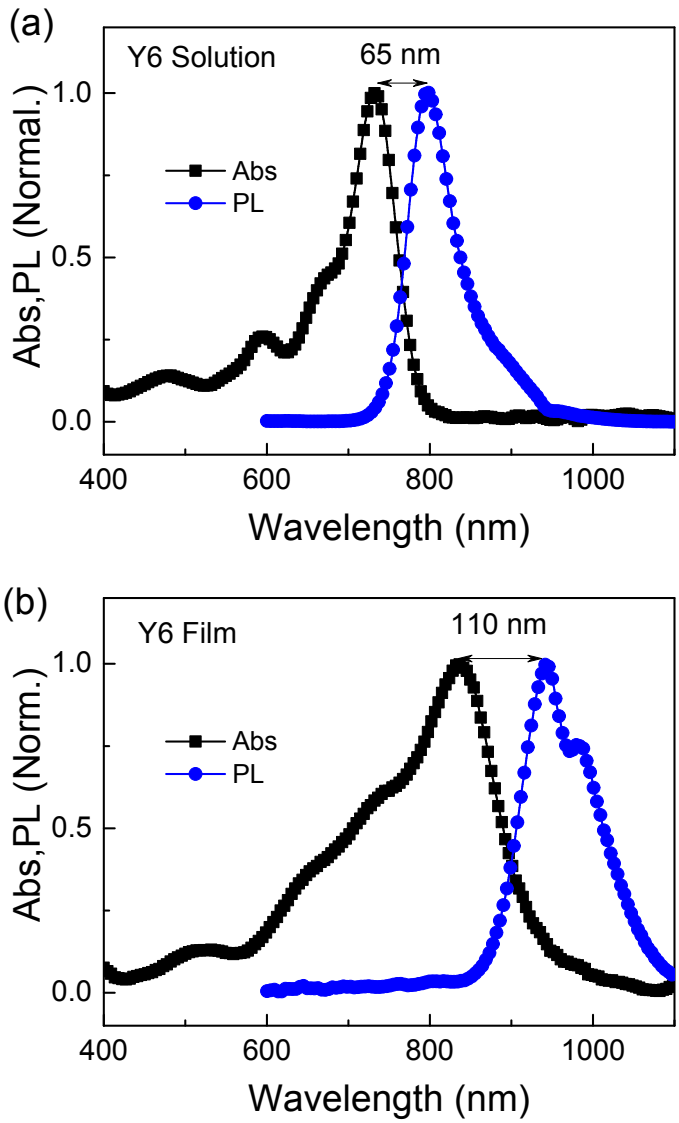

Figure S2. Absorption and photoluminescence (PL) spectra of the (a) solution and (b) film samples of Y6, respectively. In Y6 film, the shift between PL and emission spectra is much larger than that in the Y6 solution, implying a larger nuclear displacement for the intra-moiety excited state in the Y6 film.

4. Pump-wavelength selection

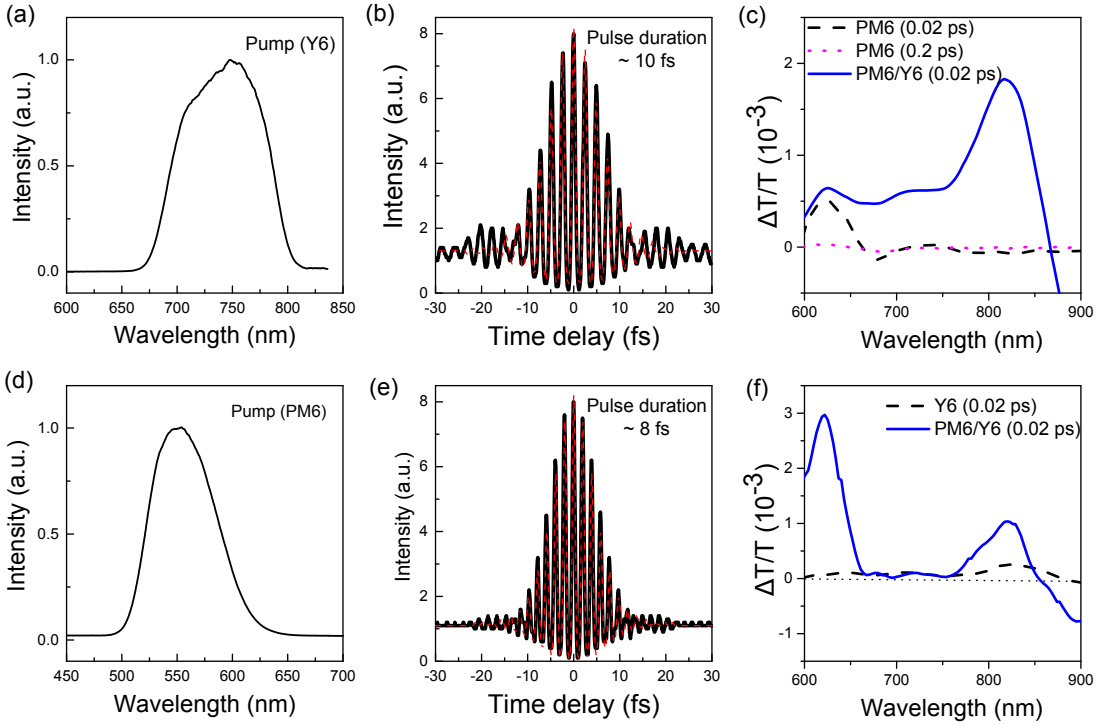

Figure S3. Pump pulses adopted for selective excitations of donor and acceptors for transient absorption (TA) measurements. (a) The spectrum centered at 750 nm is used for selective excitation of Y6. (b) FRAC trace of the pulse at 750 nm. The dashed line of is the Sech^2-fit curve suggests the pulse duration of ~ 10 fs. (c) The TA spectra of the neat PM6 film recorded at the zero delay of 0.02 and 0.2 ps are compared with that of the blend film at the delay of 0.02 ps under the same pump condition of Figure 2a. Nearly no signal is recorded from the neat PM6 film expected the optical Stark effect within the time pulse duration. (d) The pump spectrum at 550 nm used for selective excitation of PM6. (e) FRAC trace of the pulse at 550 nm. The dashed line of is the Sech^2-fit curve suggests the pulse duration of ~ 8 fs. (f) The TA spectrum of the neat Y6 film recorded at 0.02 ps is compared with that of the blend film under the same pump condition of Figure 4a. The TA signal from the neat Y6 film is negligibly weaker if compared with that from the blend PM6/Y6 or PM6 films (Figure 4 in the main text). Notably, the signal near 830 nm in the spectrum of the blend is mainly caused by the coherent electron transfer within the pulse duration. The data suggest that the TA signals from the blend film are mainly induced by the excitation of Y6 or PM6 with pump wavelengths centered at 750 nm or 550 nm, respectively.

5. Excitation fluence-dependent TA measurements.

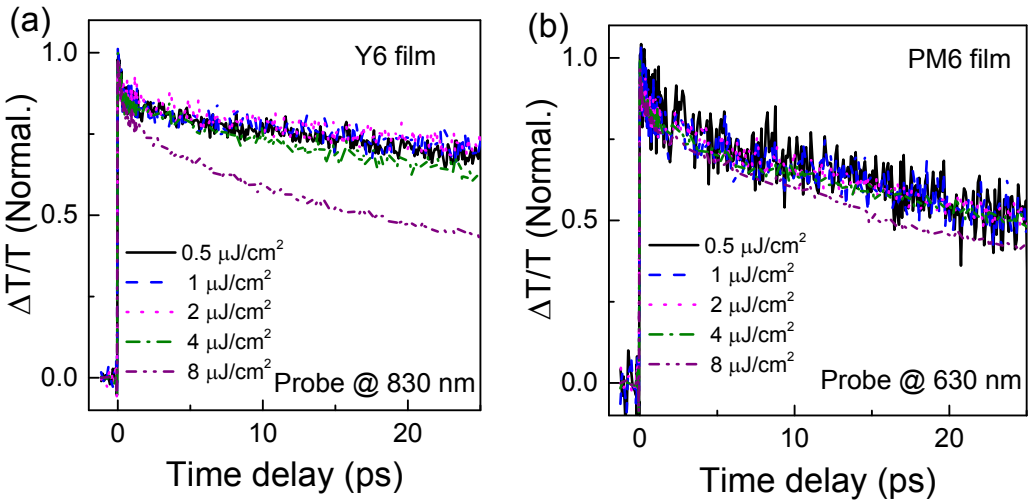

Figure S4. Normalized curves of the dynamics of ground-state bleaching of (a) the neat Y6 film at 830 nm and (b) the neat PM6 film under pump at 750 nm and 550 nm of different fluences, respectively. The decay dynamics are independent of the power fluence in the weak regime (< 2 μJ/cm^2)

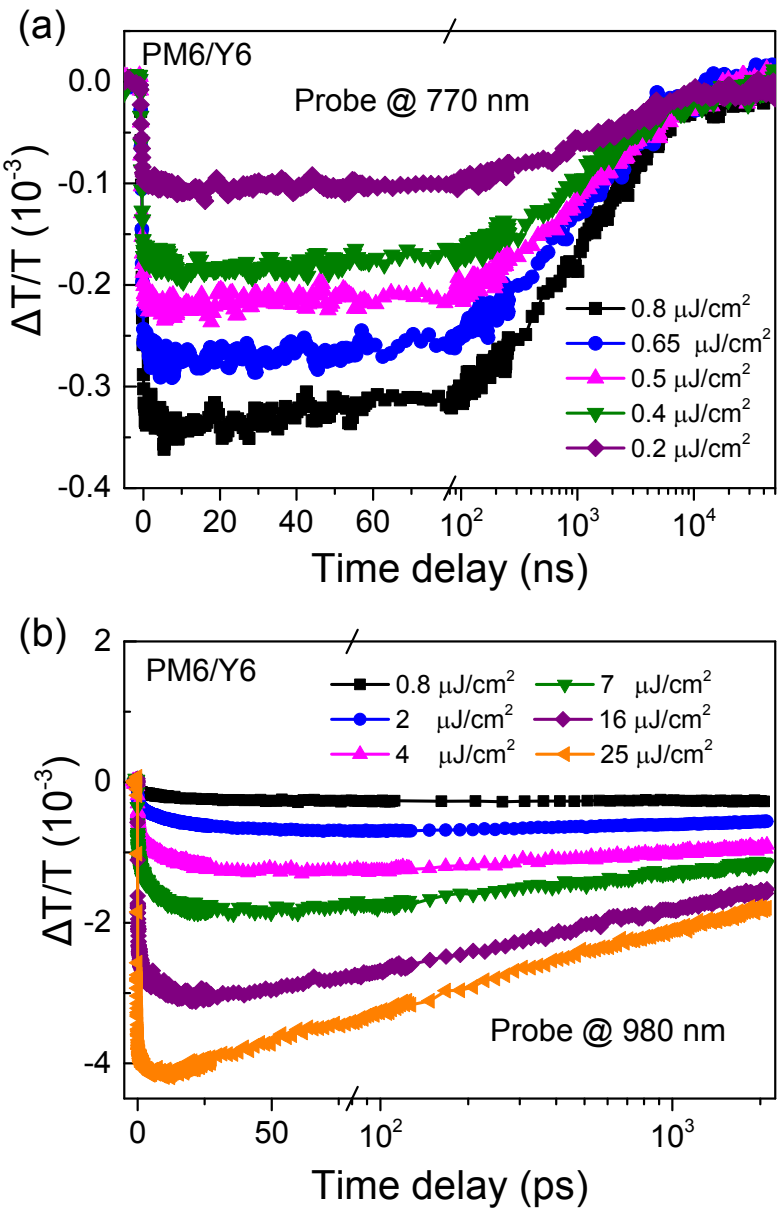

Figure S5. (a) Ns-resolved decay dynamics probed at 770 nm recorded under different pump fluences in the weak regime. (b) Ps-resolved decay dynamics probed at 980 nm recorded at different pump fluences showing similar fluence dependences to that probed at 770 nm due to bimolecular recombination. The data are recorded from the blend PM6/Y6 film.

6. TA measurements on the solution sample of Y6

In comparison with that in the Y6 film, molecular interaction can be neglected in the solution sample of Y6. Upon optical pump, the Frenkel type local excitation (LE) is created with electron and hole localized at individual Y6 molecules. As shown in Figure S6, TA spectra of Y6 solution show a ground-state bleaching (GSB) feature at 750 nm and an excited-state absorption (ESA) feature at 870 nm. The ESA feature appearing at the red tail of the absorption band is similar to the feature at 920 nm in the Y6 film (Figure 2 in the text) except a slight spectral shift. The results suggest that primary excitation in the Y6 film is also the LE state. The spectral shift is caused by the absorption wavelength shift between the solution and film samples (Figure S2). The early-state spectral transfer from the ESA feature at 920 nm to the ESA feature at 1550 nm in the Y6 film (Figure 2) is not observed in Y6 solution, indicating that the ESA feature at 1550 nm is related to a new excited species arising from the molecular interaction, i.e., an intra-moiety excited state, in the Y6 film.

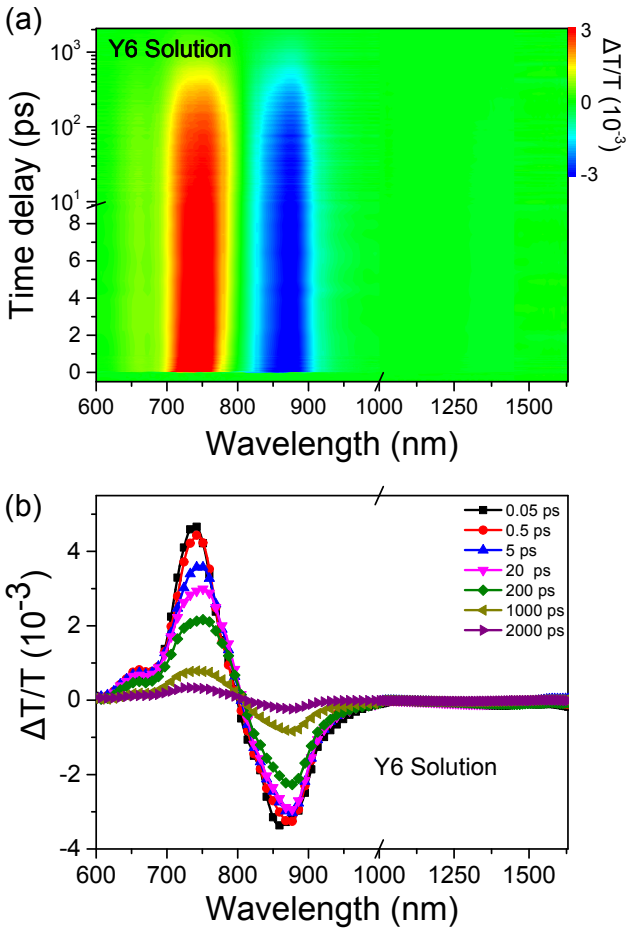

Figure S6. (a) TA data and (b) TA spectra recorded at different time delays of Y6 solution. The ESA feature is similar to the feature probed at 920 nm recorded from the Y6 film except for a slight wavelength shift. The wavelength shift corresponds to the shift between the absorption of solution and film Y6 samples.

7. Pump wavelength-dependent measurements

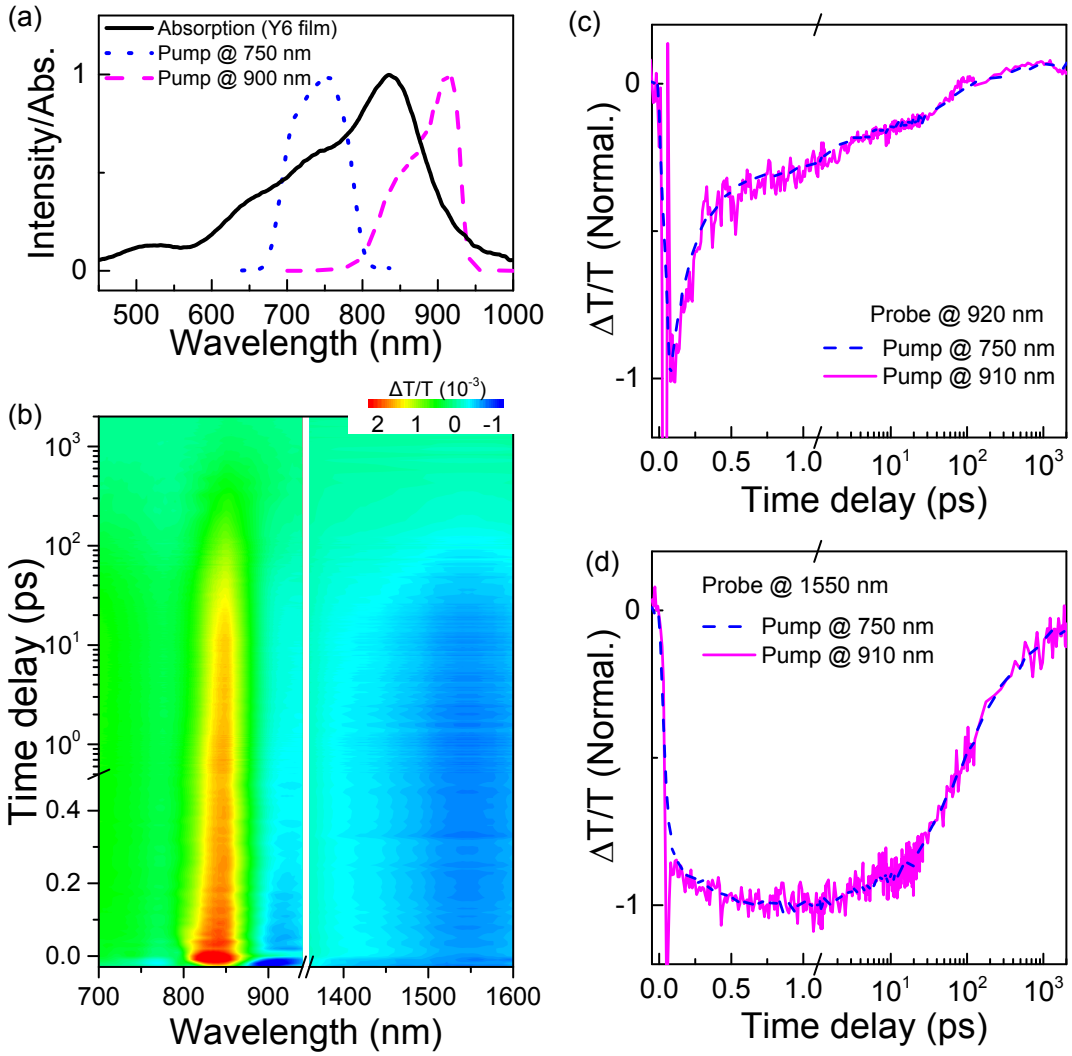

Figure S7. (a) The absorption spectrum of Y6 film is compared with the spectral coverage of pump beams with wavelengths centered at 750 nm and 910 nm, respectively. (b) TA data recorded from the Y6 film under pump at 910 nm. The normalized kinetic curves probed at (c) 920 nm and (d) 1550 nm recorded with pump wavelength centered at 750 and 910 nm, respectively.

8. Annealing effect on hole transfer dynamics.

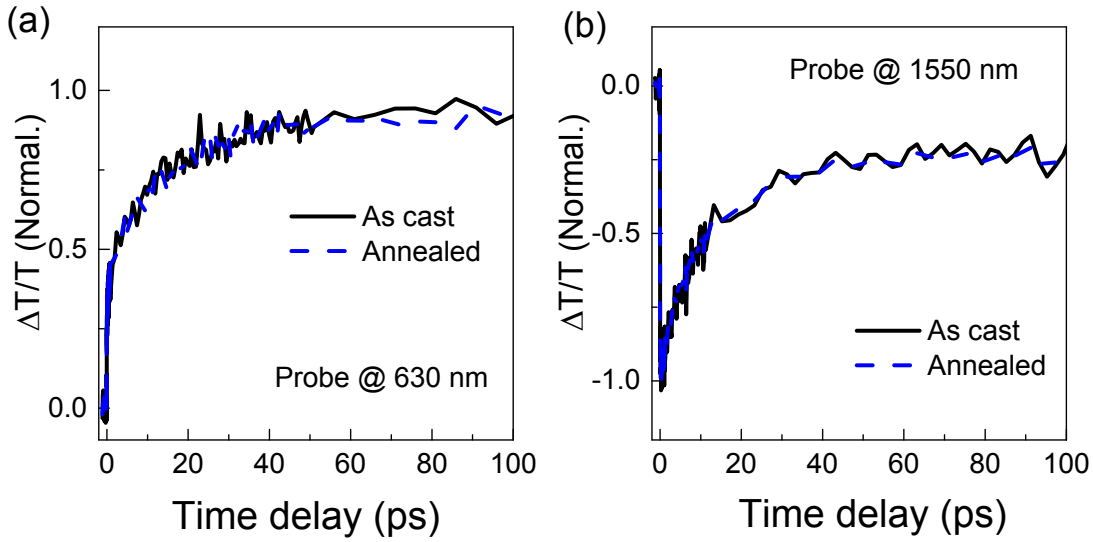

Figure S8. Annealing effect on hole transfer in PM6/Y6 blend. The dynamics probed at 630 nm and 1550 nm recorded from films with and without thermal annealing at 110 ℃ are compared in (a) and (b), respectively.

9. Spectral characteristic of the charge-separated state

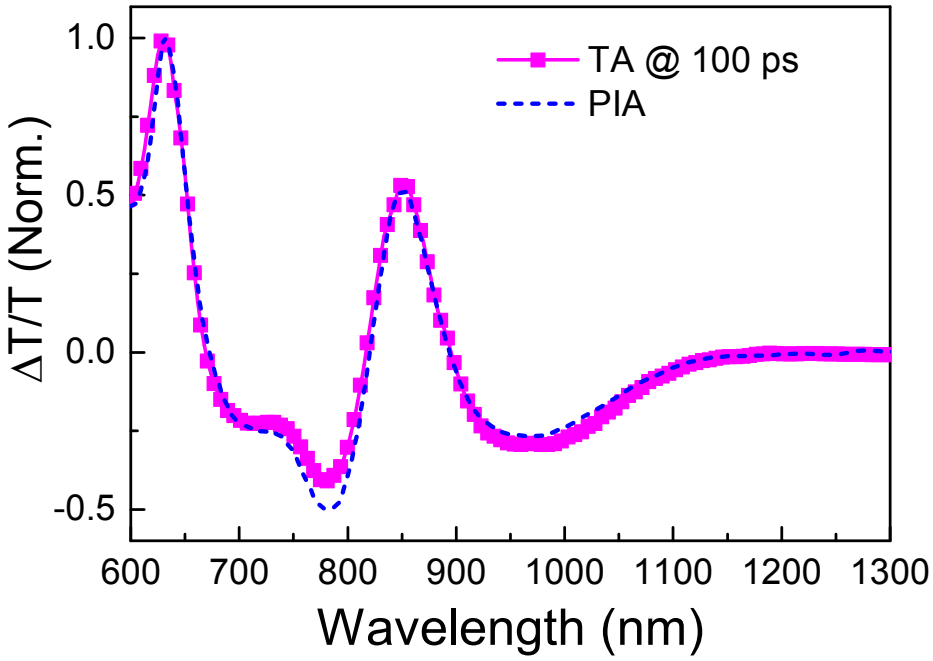

Figure S9. The normalized TA spectrum recorded from the blend PM6/Y6 film at 100 ps upon pump at 550 nm is compared with the photo-induced absorption spectrum recorded under weak continuous wave excitation. The coincidence of the two spectra verifies the long-lived component in TA spectra (Figure 4) is induced by the charge separated state of free polarons.

10. Temperature-dependent measurements

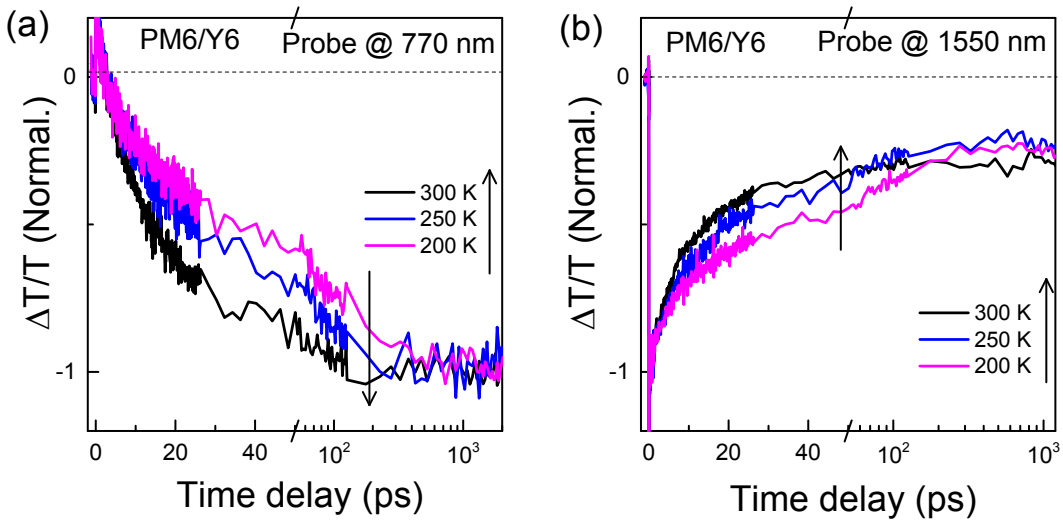

Figure S10. Normalized kinetic curves probed at 770 nm and 1550 nm recorded at different temperatures upon pump centered at 910 nm.

Reference

(1) Liebel, M.; Schnedermann, C.; Kukura, P., Sub-10-Fs Pulses Tunable from 480 to 980 Nm from a Nopa Pumped by an Yb:Kgw Source, *Opt. Lett.* **2014**, *39*, 4112.