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Supporting Information

Charge photogeneration and recombination dynamics in non-fullerene solar cells based on a polymer donor with mono-fluorinated π-bridge

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SI. The detailed calculation about exciton dissociation efficiency in blend films based on steady state spectroscopy measurements

When calculating the exciton dissociation efficiency using steady-state spectroscopy, it was ensured that the test conditions for both the blended film and the neat acceptor film were identical.

For the measurement of PL of acceptor in neat and blend films, an excitation wavelength of 780 nm was employed for selectively exciting the acceptor in neat and blended films. Taking into the absorption of neat acceptor film and the blend film at 780 nm, the number of photons absorbed by the acceptor in neat acceptor film (n_{Abs}^{neat}) and the blend film (n_{Abs}^{blend}) can be determined as

$$n_{Abs}^{neat} = N\cdot\left(1 - 10^{-A_{neat}}\right)\#(1)$$

$$n_{Abs}^{blend} = N\cdot\left(1 - 10^{-A_{blend}}\right)\#(2)$$

where N is the number of photons for the excitation light, A_{neat} and A_{blend} represent the absorbance of neat acceptor and blend films at 780 nm, respectively. Assuming the PL quenching efficiency of the acceptor exciton in the blend film is η, the PL quantum yield of neat acceptor film is Q. Then, the number of emitted photons for acceptor in neat ($n_{neat\,PL}^{ex\,780}$) and blend ($n_{blend\,PL}^{ex\,780}$) films after excitation at 780 nm can be expressed as

$$n_{neat\,PL}^{ex\,780} = n_{Abs}^{neat}\cdot Q\#(3)$$

$$n_{blend\,PL}^{ex\,780} = n_{Abs}^{blend}\cdot(1-\eta)\cdot Q\#(4)$$

From equations (3) and (4), η can be extracted as

$$\eta = 1 - \frac{n_{blend\,PL}^{ex\,780}}{n_{Abs}^{blend}}\cdot\frac{n_{Abs}^{neat}}{n_{neat\,PL}^{ex\,780}} = 1 - \frac{1 - 10^{-A_{neat}}}{1 - 10^{-A_{blend}}}\cdot\frac{n_{blend\,PL}^{ex\,780}}{n_{neat\,PL}^{ex\,780}}\#(5)$$

where $\frac{1 - 10^{-A_{neat}}}{1 - 10^{-A_{blend}}}$ can be determined by measuring absorbance of neat acceptor and blend films at 780 nm, $\frac{n_{blend\,PL}^{ex\,780}}{n_{neat\,PL}^{ex\,780}}$ can be determined by the ratio of integrated PL intensity of acceptor material in the blend and neat films after excitation at 780 nm.

To determine the exciton dissociation efficiency of donor in blend films, an excitation wavelength of 532 nm is elected for the PL measurement of neat donor and blend films. At this wavelength, both donor and acceptor in the blend films can be excited. Therefore, compared to the measurement of exciton dissociation efficiency of acceptor above, an additional process is required to determine the proportion of donor absorption in the blend film. By normalizing absorption spectrum of neat acceptor film and blend film at 850 nm (the main absorption peak of neat acceptor film), the proportion of donor absorption in the blend film can be determined as

$$1 - \frac{A_{acceptor}}{A_{blend}} \#\ (6)$$

where $A_{acceptor}$ and A_{blend} are the absorption of neat acceptor film and blend film at 532 nm. The detailed calculation can be found in the reference [1].

Table SI. The exciton-exciton annihilation coefficient (γ), exciton lifetime (τ), exciton diffusion length (L_{3d} and L_d) and exciton diffusion coefficient (D) of PTzBI-*d*F and PTzBI-Cl films.

Material	γ **(cm^3·s^{-1})**	τ **(ps)**	L_{3d} **(nm)**	L_d **(nm)**	D **(cm^2·s^{-1})**
PTzBI-*d*F	1.4×10^{-8}	327.8	33.5	13.7	5.7×10^{-3}
PTzBI-Cl	6.9×10^{-9}	281	21.5	8.8	2.7×10^{-3}

Table SII. The detailed parameters for the fitting of early time TA kinetics of PTzBI-*d*F:Y6 blend films at ~650 nm after 800 nm excitation, with an excitation fluence of 1.5×10^{13} photons·cm^{-2}·pulse^{-1}.

Active layers	A_1	τ_1 **(ps)**	A_2	τ_2 **(ps)**
PTzBI-*d*F:Y6	0.48	IRF	0.44	17.1

IRF: Instrument Response Function

Table SIII. The detailed parameters for the fitting of early time TA kinetics of PTzBI-*d*F:Y6 blend films at ~845 nm after 400 nm excitation, with an excitation fluence of 2.1×10^{13} photons·cm^{-2}·pulse^{-1}.

Active layers	A_1	τ_1 **(ps)**	A_2	τ_2 **(ps)**
PTzBI-*d*F:Y6	0.69	IRF	0.20	1.7

IRF: Instrument Response Function

Table SIV. The detailed parameters for the fitting of charge recombination kinetics of PTzBI-*d*F:Y6 blend films with and without thermal annealing at the probing wavelength of ~650 nm after photoexcitation at 800 nm with various excitation fluences.

Active layer	Excitation fluence (photons·cm^{-2}·pulse^{-1})	A	τ (ps)
Without thermal annealing	1.5×10^{13}	0.82	5248
With thermal annealing	1.5×10^{13}	0.81	5402
Without thermal annealing	1.5×10^{14}	0.45	3091
With thermal annealing	1.5×10^{14}	0.48	3353

Table SV. The detailed parameters for the fitting of charge recombination kinetics of PTzBI-Cl:Y6 blend films at the probing wavelength of ~630 nm after photoexcitation at 800 nm with various excitation fluences.

Active layer	Excitation fluence (photons·cm^{-2}·pulse^{-1})	A	τ (ps)
PTzBI-Cl:Y6	7.7×10^{13}	0.66	4320
PTzBI-Cl:Y6	7.7×10^{14}	0.26	2723

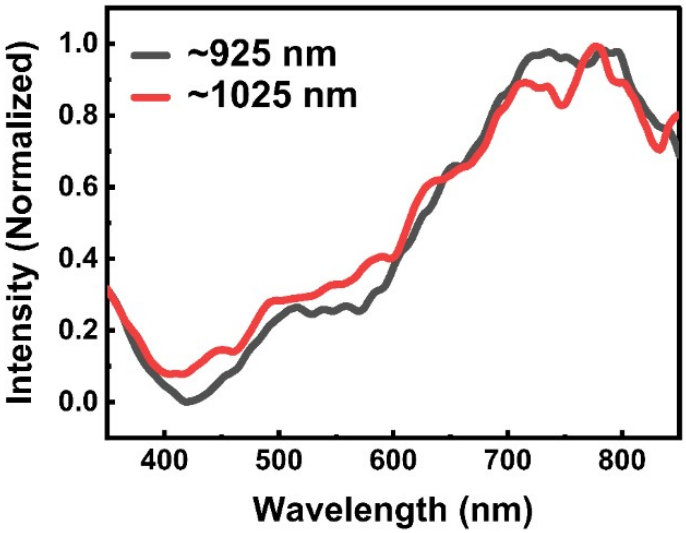

Figure S1. The excitation spectra of Y6 film at the probing wavelength of ~925 nm and ~1025 nm.

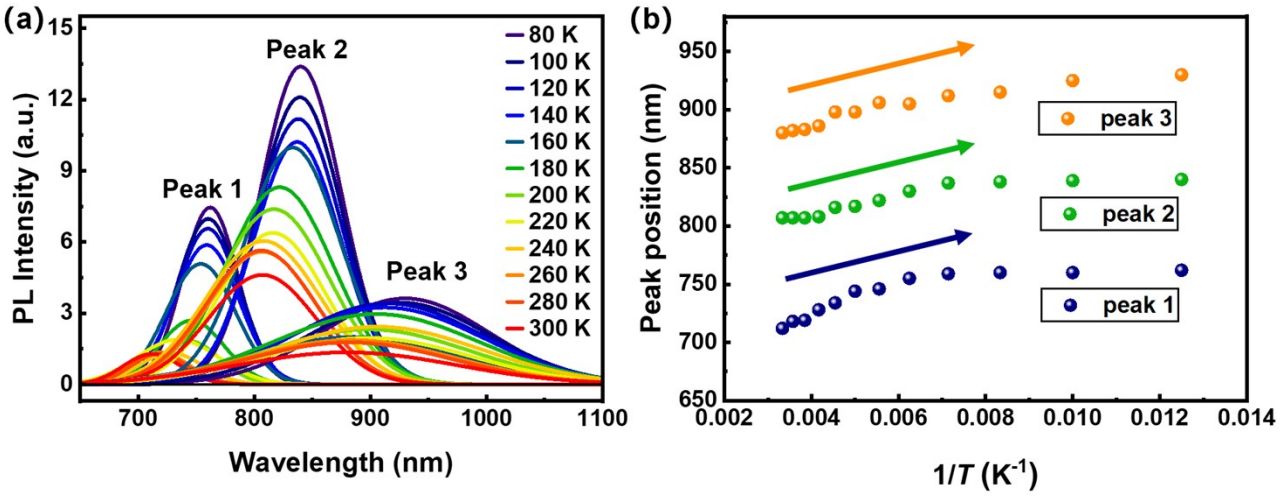

Figure S2. **(a)** Extracted emission bands of PL spectra of neat PTzBI-*d*F film at varies temperatures with three Gaussian-peaks fitting after excitation at 532 nm. **(b)** The correlations between PL emission peak positions and 1/*T* for neat PTzBI-*d*F film.

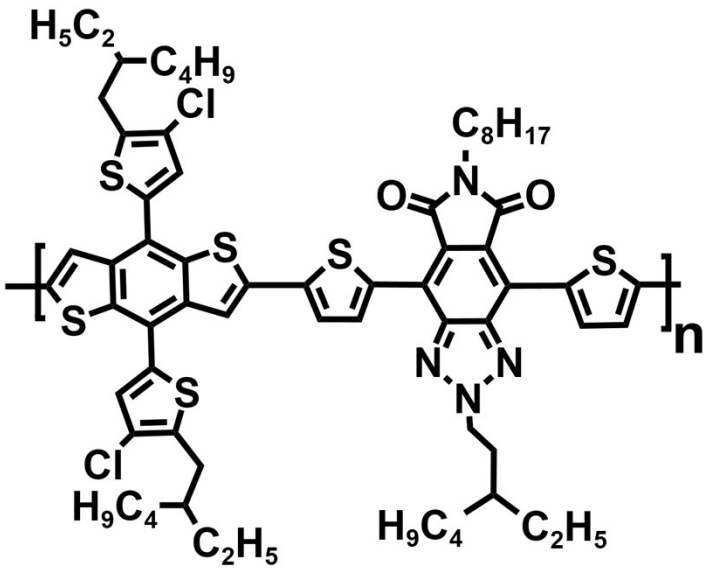

Figure S3. The molecule structure of PTzBI-Cl.

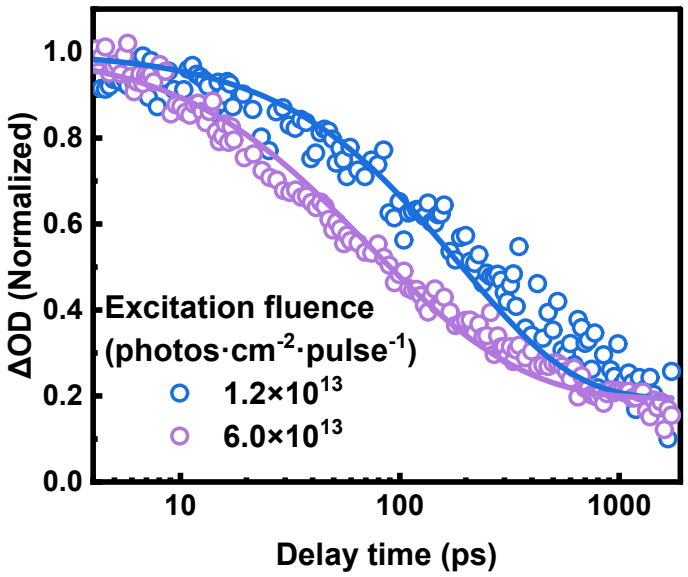

Figure S4. TA kinetics of PTzBI-Cl film probing at ~830 nm under indicated excitation fluences.

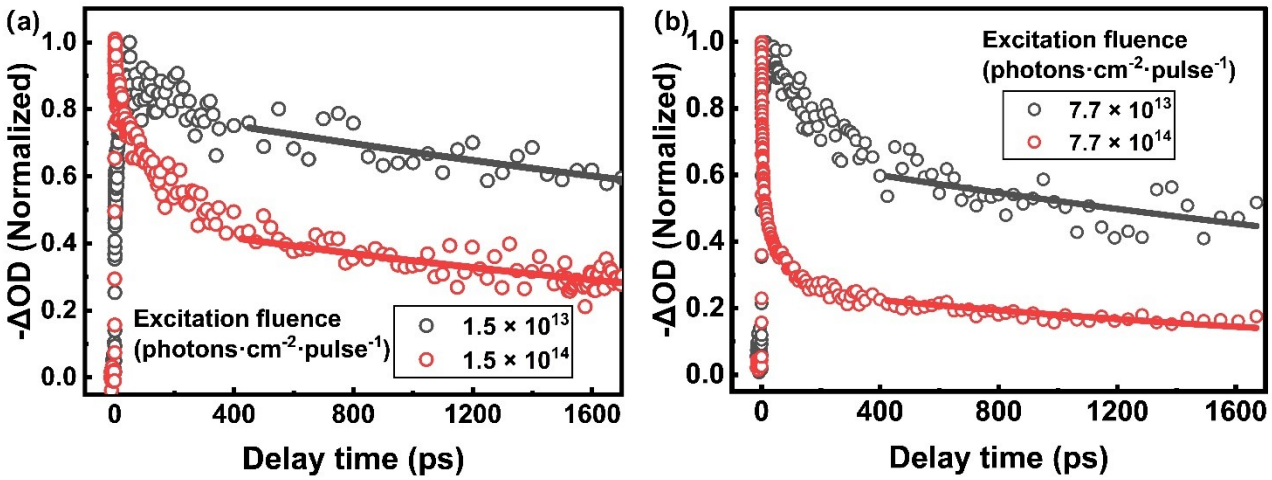

Figure S5. **(a)**The charge recombination kinetics at the probe wavelength of ~650 nm for PTzBI-*d*F:Y6 blend film after photoexcitation at 800 nm with excitation fluences of 1.5×10^{13} and 1.5×10^{14} photons·cm^{-2}·pulse^{-1}. **(b)**The charge recombination kinetics at the probe wavelength of ~630 nm for PTzBI-Cl:Y6 blend film after photoexcitation at 800 nm with excitation fluences of 7.7×10^{13} and 7.7×10^{14} photons·cm^{-2}·pulse^{-1}.

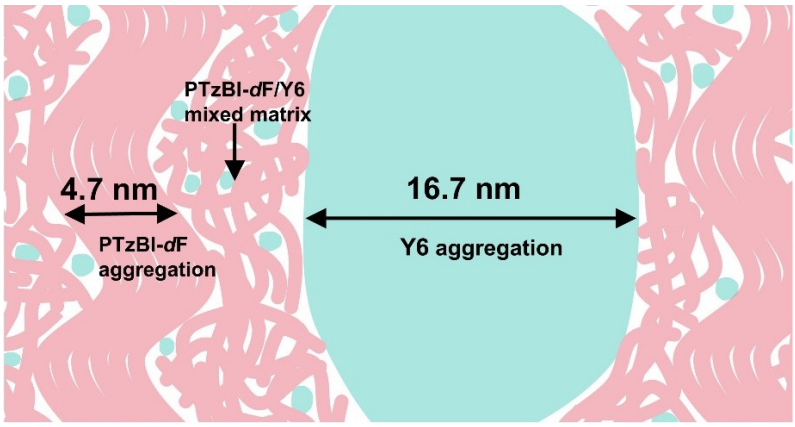

Figure S6. Morphology domains in PTzBI-*d*F:Y6 film.

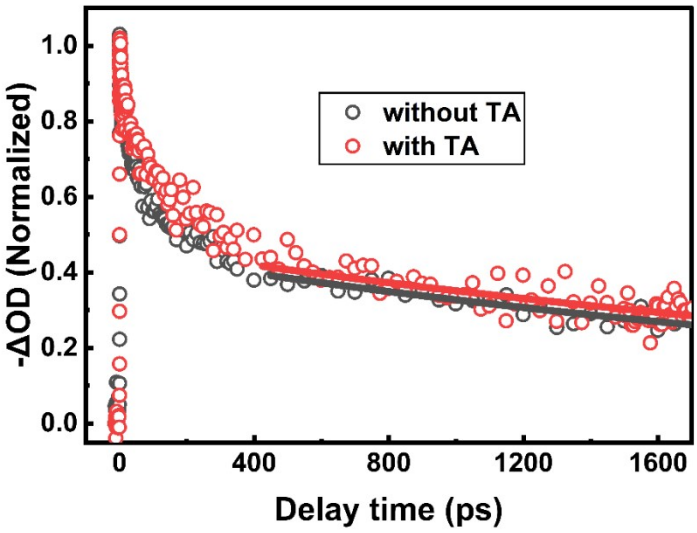

Figure S7. After excitation at 800 nm, TA kinetics of PTzBI-*d*F:Y6 films with and without thermal annealing at the probe wavelength of ~650 nm with an excitation fluence of 1.5×10^{14} photons·cm^{-2}·pulse^{-1}.

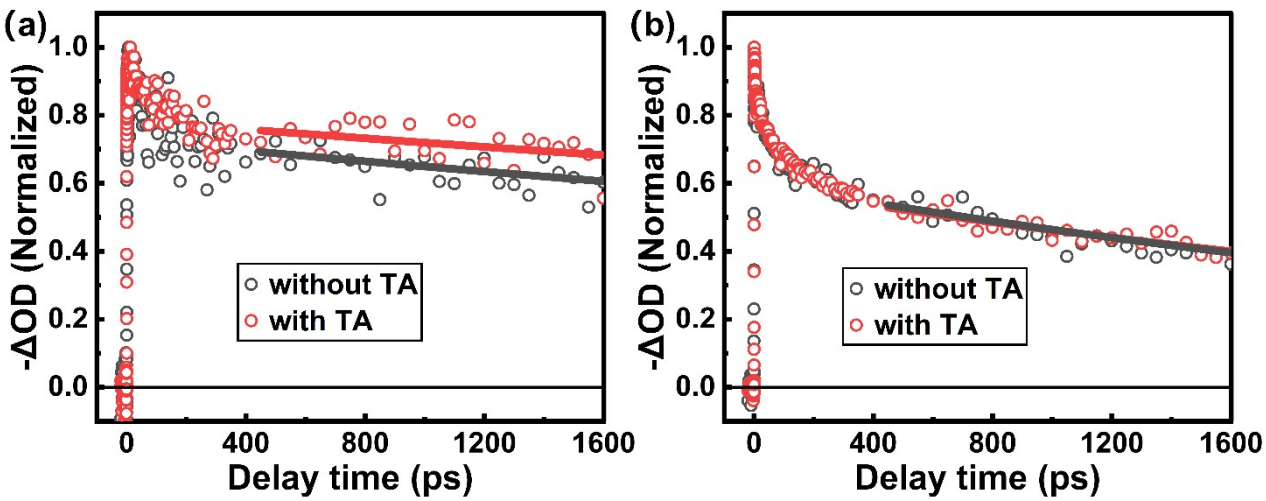

Figure S8. Charge recombination kinetics at the probe wavelength of ~845 nm for PTzBI-*d*F:Y6 blend films after photoexcitation at 400 nm with various excitation fluences. The excitation fluences are 2.1×10^{13} and 1.5×10^{14} photons·cm^{-2}·pulse^{-1}.

References

1 Z. Li, W. Zhang, X. Xu, Z. Genene, D. D. C. Rasi, W. Mammo, A. Yartsev, M. R. Andersson, R. A. J. Janssen and E. Wang, *Adv. Energy Mater.*, 2017, **7**, 1602722.