

# Supporting information

## Fluorination of Terminal Groups Promoting Electron Transfer in Small Molecular Acceptors of Bulk Heterojunction Films

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### Fabrication of hole-only device

The hole-only devices were fabricated with a configuration of ITO/PEDOT:PSS/BHJ/spiro-TBD/Au (Figure S8b). The ITO substrates were cleaned in deionized water, acetone, ethanol, and isopropanol with ultrasonic treatment for 20 min. These ITO substrates were then treated by UV-ozone for 15 min to improve their work function. PEDOT:PSS was spin-coated on ITO substrates with 4000 rpm for 50 s and then annealed at 150 °C for 15 min in air. Subsequently, PM6:Y6 (1:1 wt%, 24mg/ml) was dissolved by heating and stirring at 40 °C in chlorobenzene (12 hours). Then the dissolved solution was spin-coated onto the ITO substrates in a nitrogen-filled glove box, and the spin-coated active layer was annealed at 100 °C for 10 minutes. Finally, spiro-TPD (8nm) and Au (80nm) were deposited by thermal evaporation.

### The Calculation of Crystalline Coherence Length

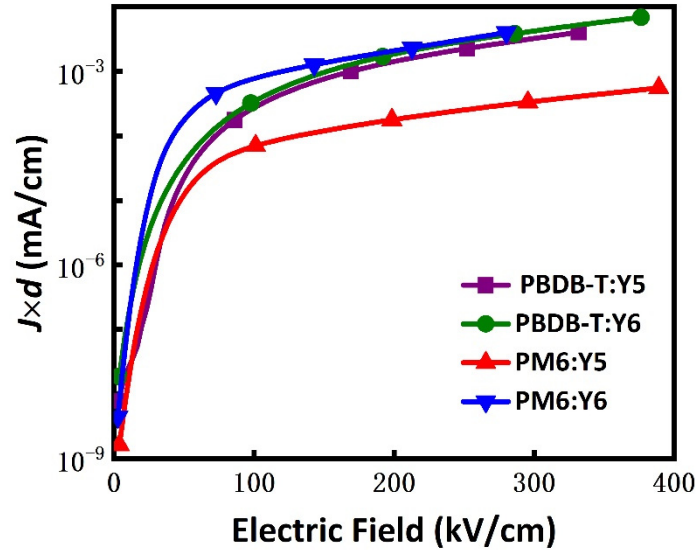
GIWAXS characterizes the molecular packing and crystallinity of the active layer. The d-spacing associated with the  $\pi$ - $\pi$  stacking peak indicates the molecular interlayer spacing, which can be calculated from the following equation:

$$d = \frac{2\pi}{q_{z(010)}}$$

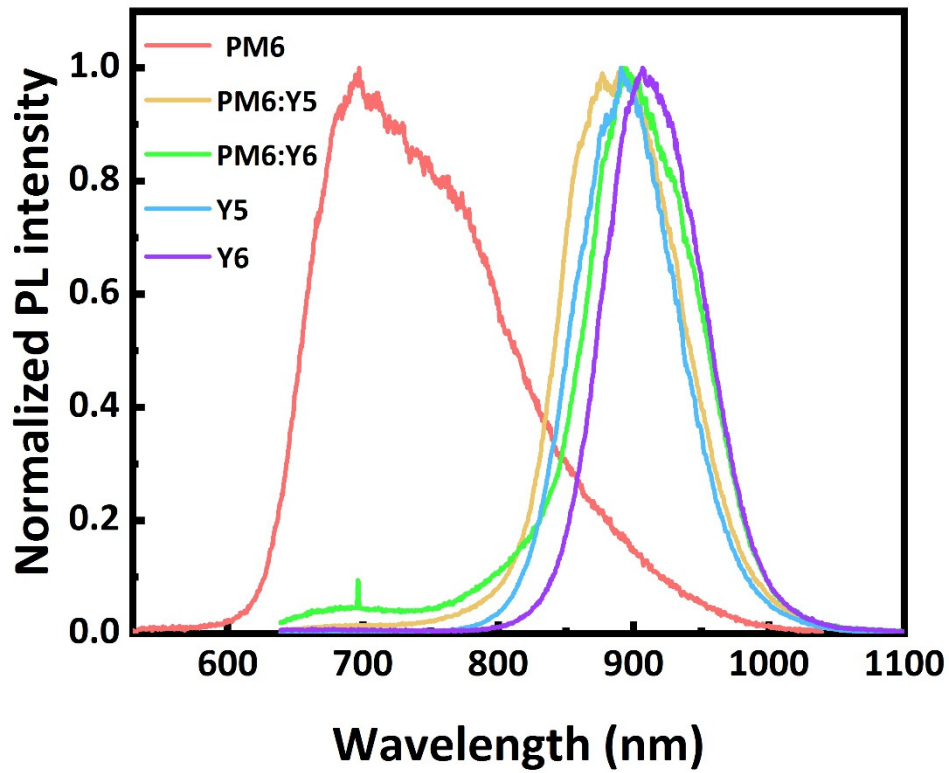
In which,  $q_{z(010)}$  is the position of the  $\pi$ - $\pi$  stacking peak in Q space. We further calculated the crystalline coherence length (CCL) using the Scherrer equation and quantitatively compared the crystallinity of the blend films:

$$CCL = \frac{2\pi k}{FWHM}$$

In which,  $k$  is the shape factor (0.9) and  $FWHM$  is the full width at half maximum of the  $\pi$ - $\pi$  stacking peak.

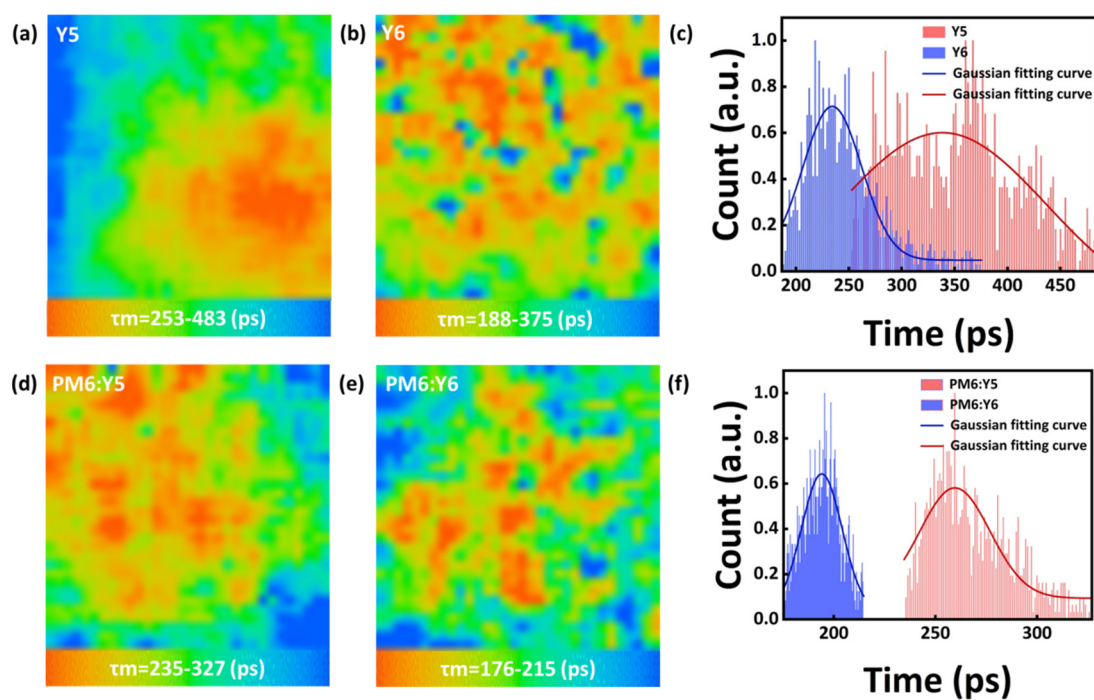


**Figure S1.** Hole carrier transport results for the PBDB-T:Y5, PBDB-T:Y6, PM6:Y5 and PM6:Y6 BHJ films:  $J \times d$  as a function of the applied electric field.

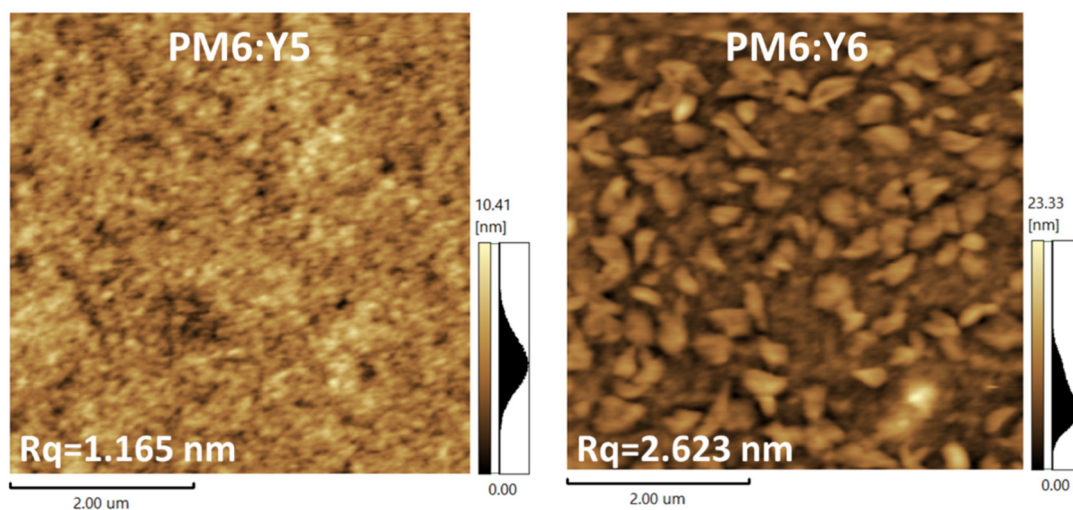


**Figure S2.** Normalized PL spectra of the PM6, Y5, Y6 and their blend films. The films were excited

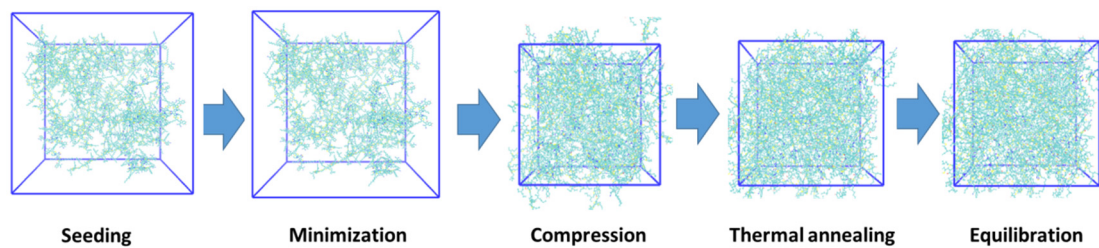
at 400nm.



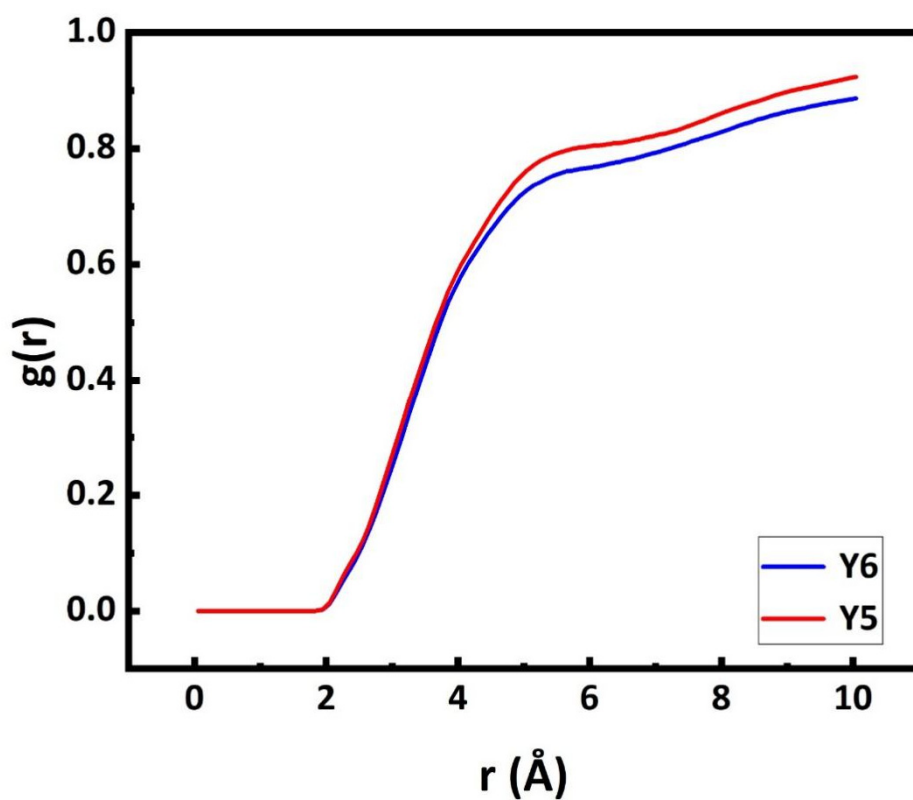
**Figure S3.** 2D time-resolved fluorescence images ( $10\ \mu\text{m} \times 10\ \mu\text{m}$ ) of (a) neat Y5, (b) neat Y6 and (d) PM6:Y5, (e) PM6:Y6 blend films and (c, f) the corresponding distribution histogram of exciton lifetime as a function of storage time.



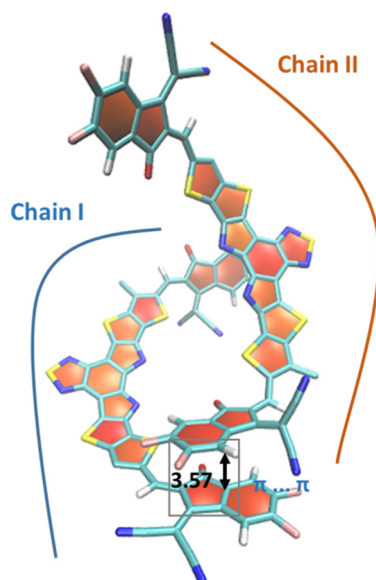
**Figure S4.** Morphology images ( $5\ \mu\text{m} \times 5\ \mu\text{m}$ ) of the blend films: AFM height images of PM6:Y5 and PM6:Y6 BHJ films.



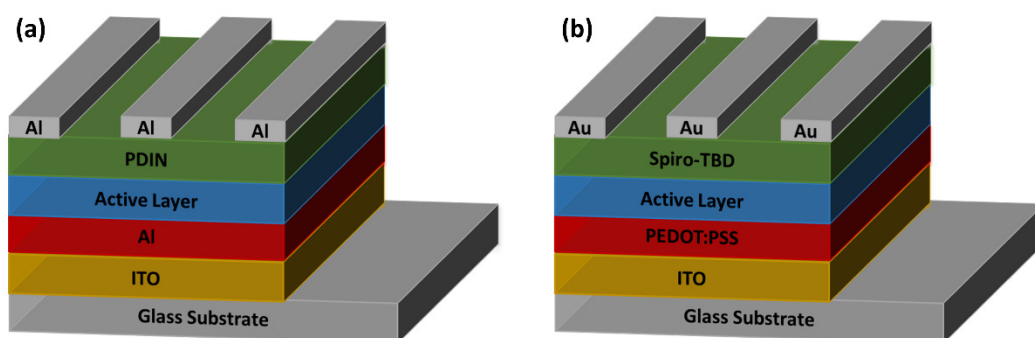
**Figure S5.** The procedure of molecular dynamics (MD) simulations from molecular seeding to equilibration of the molecular systems, taken PM6:Y6 as an example.



**Figure S6.** Radial distribution functions (RDFs) for Y6 in PM6:Y6 film and Y5 in PM6:Y5 film.



**Figure S7.** Representative configurations of Y6 dimer of “A-to-A” type J-aggregates.



**Figure S8.** Schematic diagram of (a) the electron-only device and (b) the hole-only device mentioned in this work.

**Table S1.** A summary of charge transport parameters of PM6:Y6, PM6:Y5, PBDB-T:Y6, and PBDB-T:Y5 BHJ films.

Device	$\mu_e/10^{-5} \text{ cm}^2 \text{ v}^{-1} \text{ s}^{-1}$	$\mu_h/10^{-5} \text{ cm}^2 \text{ v}^{-1} \text{ s}^{-1}$	$\sigma_e/\text{meV}$
PM6:Y6	5.02	35.4	47
PM6:Y5	0.0576	2.79	59
PBDB-T:Y6	1.04	12.6	57
PBDB-T:Y5	2.05	9.69	63