

## In situ monitoring drying process to disclose the correlation between molecular weights of polymer acceptor with flexible spacer and performance of all-polymer solar cells

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### 1. Supporting Figures

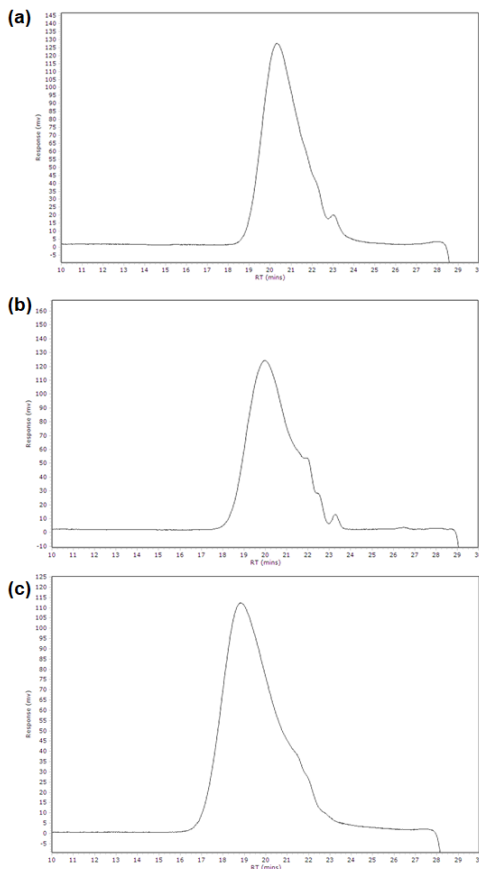


Figure S1. GPC profiles of PYTS samples with different molecular weight, (a) PYTS<sub>L</sub>, (b) PYTS<sub>M</sub> and (c) PYTS<sub>H</sub>.

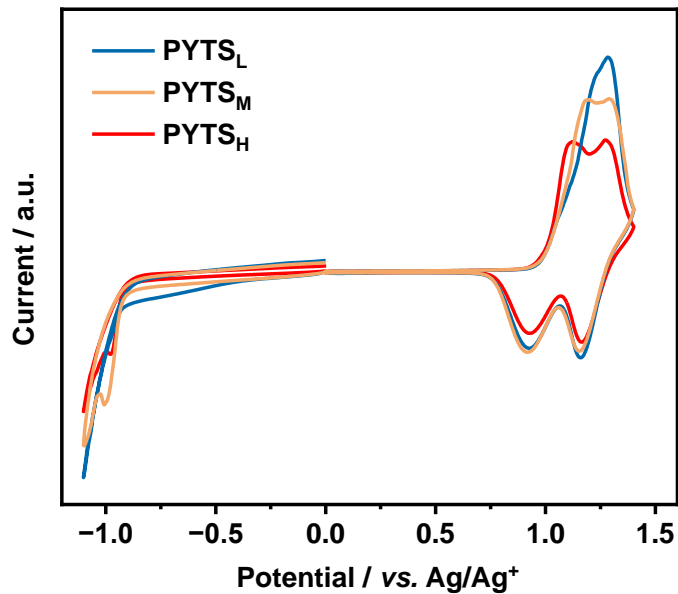


Figure S2. Cyclic voltammogram for reduction of PYTS thin film of different molecular weights.

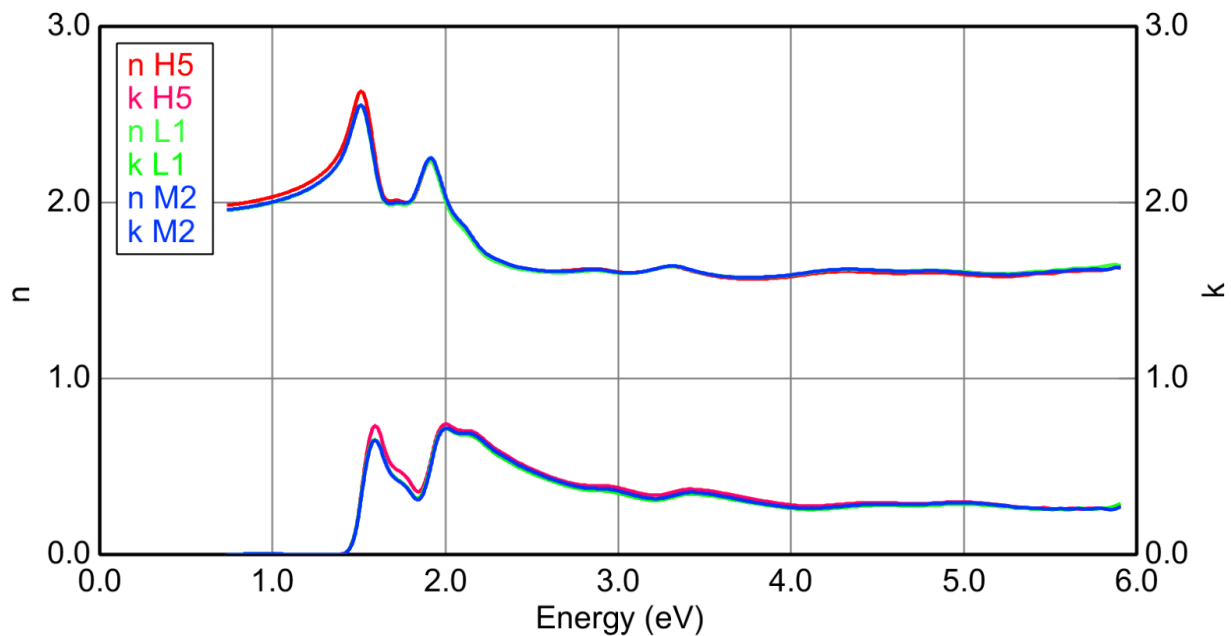


Figure S3.  $n$ ,  $k$  values of PYTS with different  $M_n$ . L1 represents PYTS<sub>L</sub>, M2 represents PYTS<sub>M</sub>, H5 represents PYTS<sub>H</sub>.

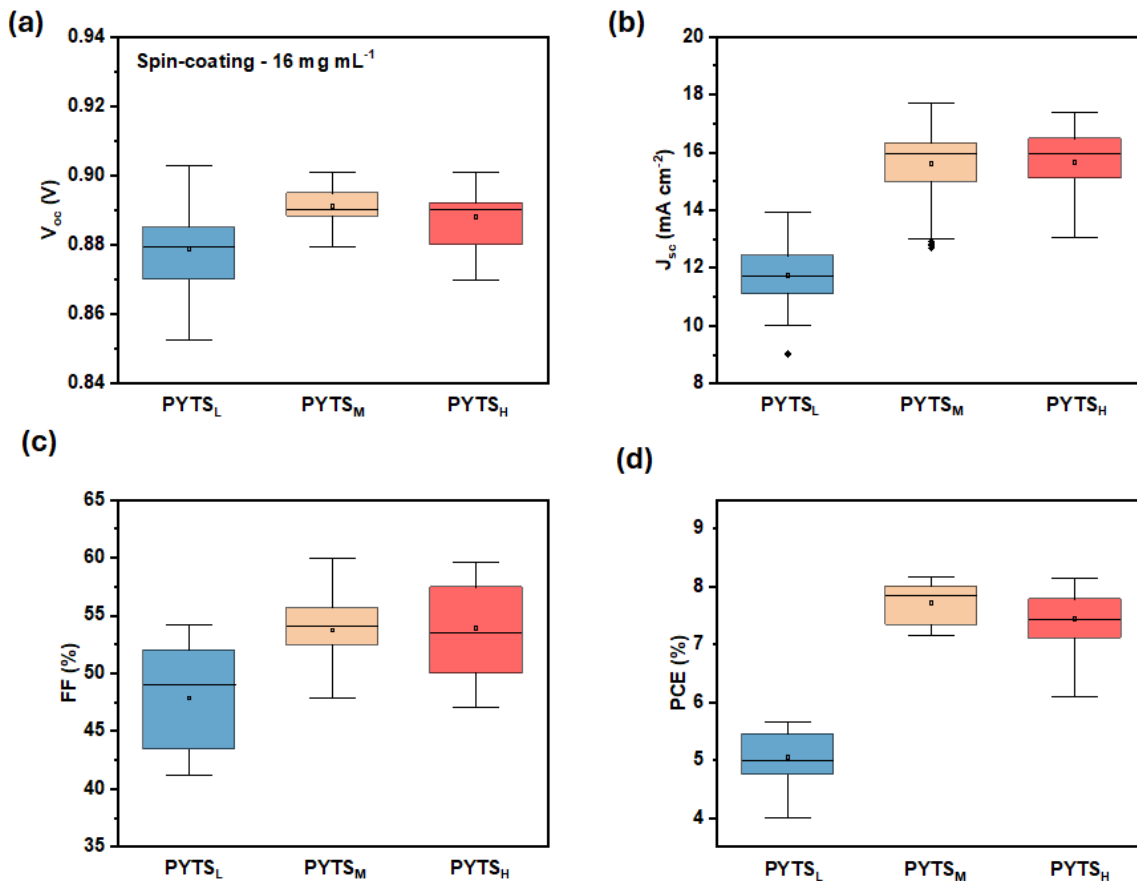


Figure S4. The relationships of photovoltaic parameters ( $V_{oc}$ ,  $J_{sc}$ ,  $FF$ , and  $PCE$ ) with the  $M_n$  of acceptor polymer PYTS in PBDB-T:PYTS all-PSC devices with concentration of  $16 \text{ mg mL}^{-1}$  via spin-coating: (a)  $V_{oc}$ , (b)  $J_{sc}$ , (c)  $FF$ , and (d)  $PCE$ . The error bars were generated from over 24 devices at each  $M_n$ .

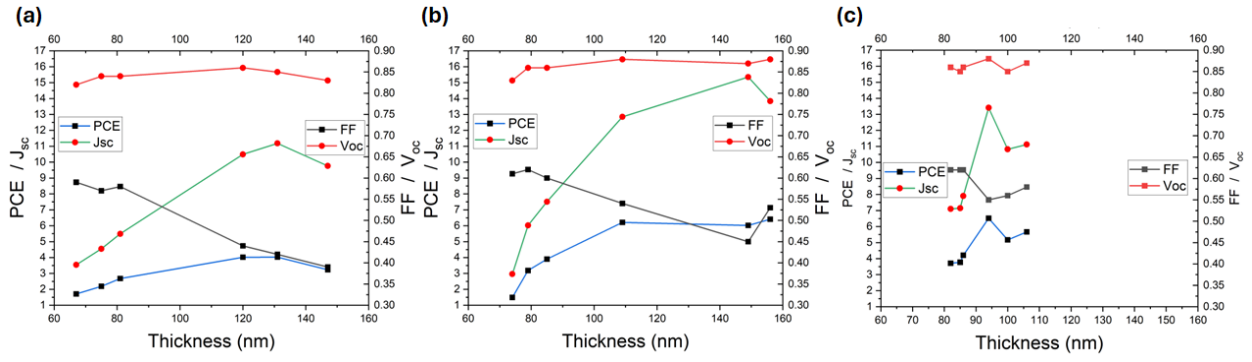


Figure S5. The relationships of photovoltaic parameters ( $V_{oc}$ ,  $J_{sc}$ ,  $FF$ , and  $PCE$ ) with the thickness of active layer in PBDB-T:PYTS all-PSC devices via blade-coating: (a) PYTS<sub>L</sub>, (b) PYTS<sub>M</sub>, and (c) PYTS<sub>H</sub>.

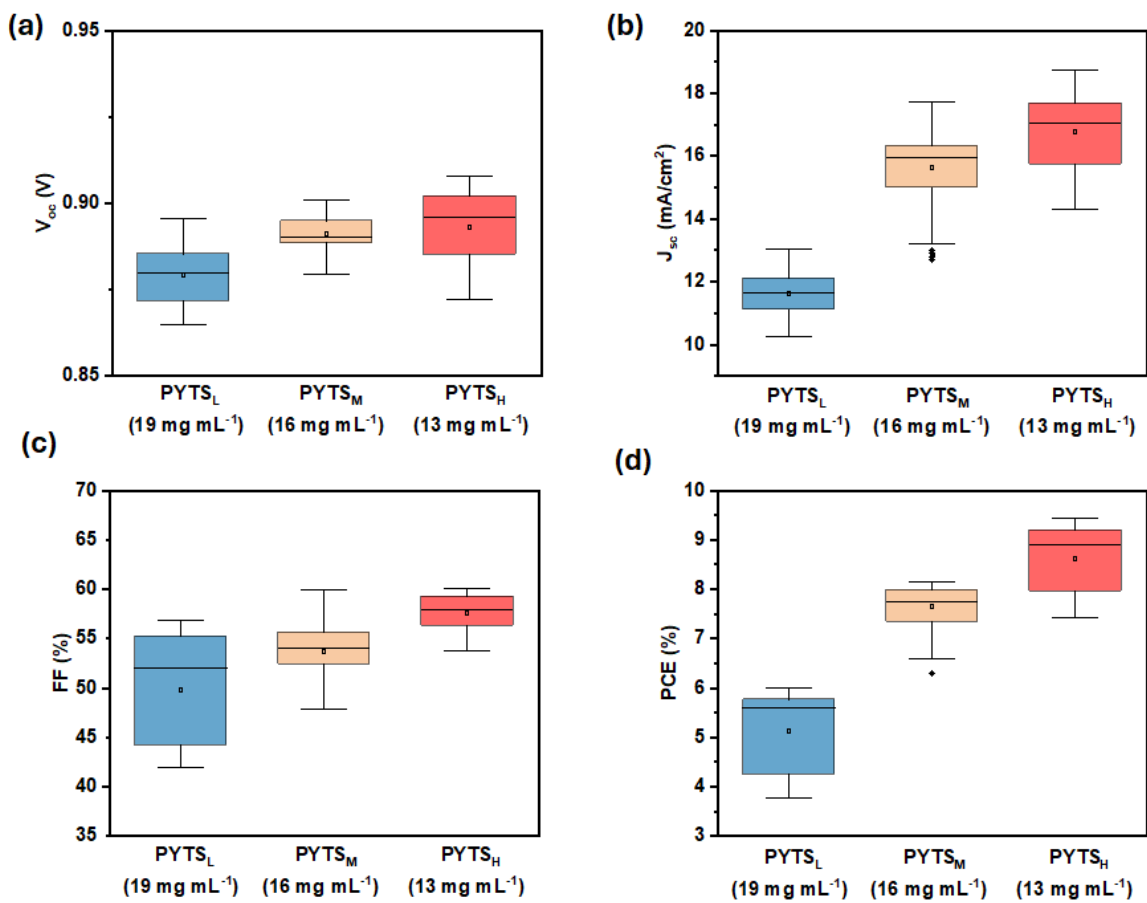


Figure S6. The relationships of photovoltaic parameters ( $V_{oc}$ ,  $J_{sc}$ ,  $FF$ , and  $PCE$ ) with the  $M_n$  of acceptor polymer PYTS in PBDB-T:PYTS all-PSC devices with different concentration via spin-coating: (a)  $V_{oc}$ , (b)  $J_{sc}$ , (c)  $FF$ , and (d)  $PCE$ . The error bars were generated from over 24 devices at each  $M_n$ .

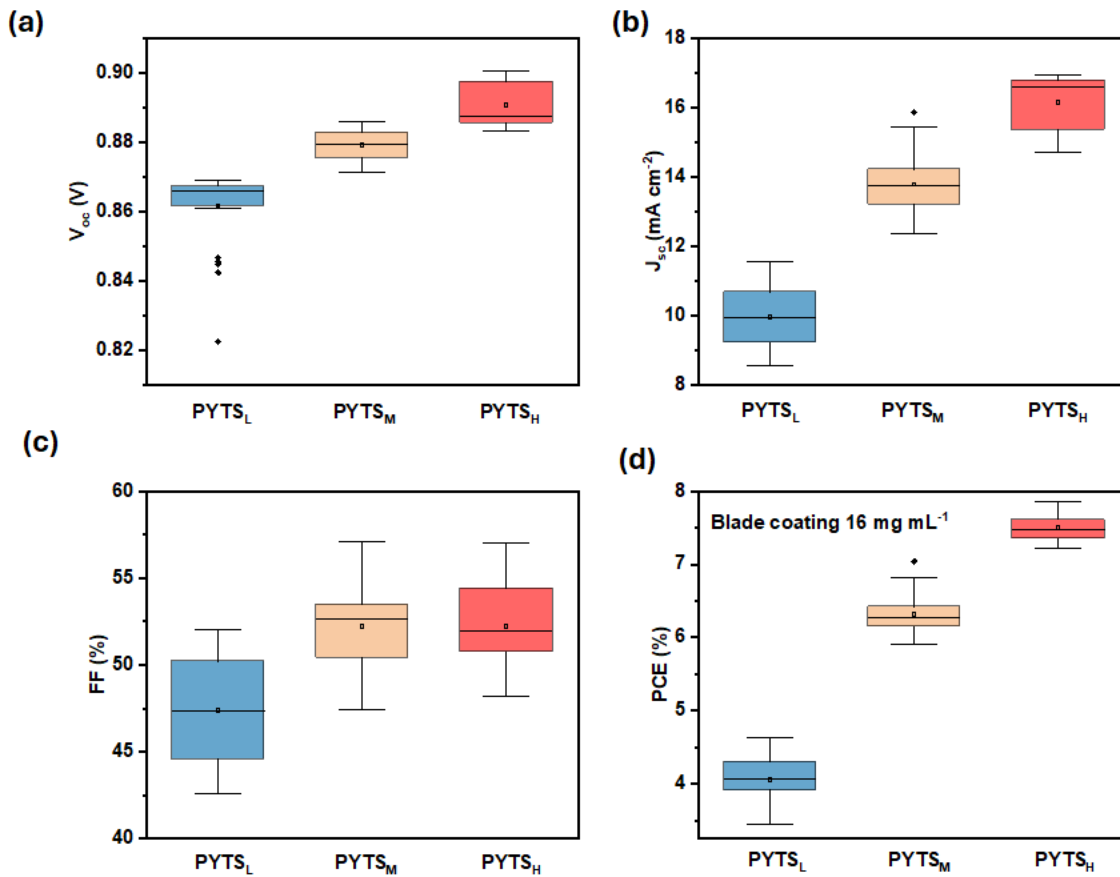


Figure S7. The relationships of photovoltaic parameters ( $V_{oc}$ ,  $J_{sc}$ ,  $FF$ , and  $PCE$ ) with the  $M_n$  of acceptor polymer PYTS in PBDB-T:PYTS all-PSC devices with concentration of  $16\ mg\ mL^{-1}$  via blade-coating: (a)  $V_{oc}$ , (b)  $J_{sc}$ , (c)  $FF$ , and (d)  $PCE$ . The error bars were generated from over 24 devices at each  $M_n$ .

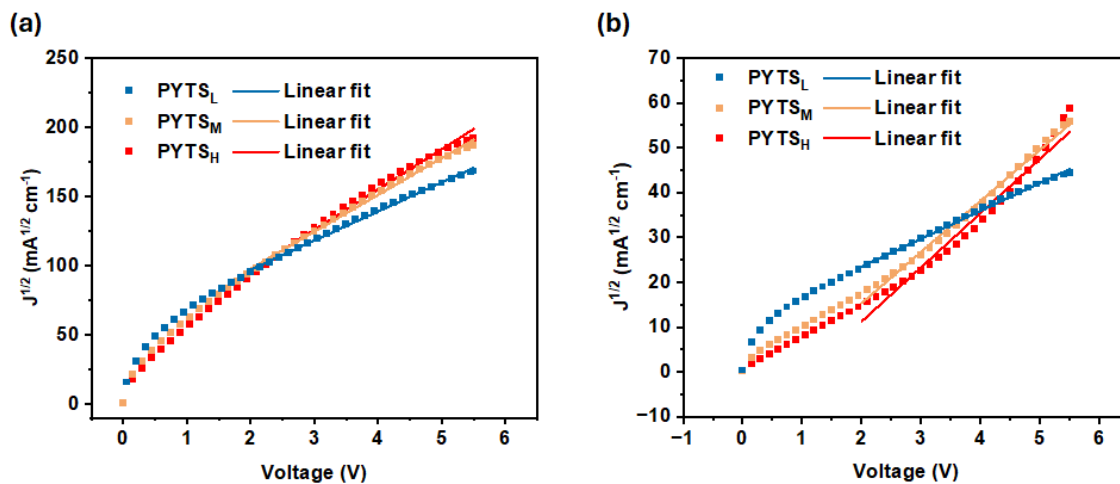


Figure S8.  $J^{0.5}$ -V curves of the (a) hole-only and (b) electron-only devices derived from SCLC.

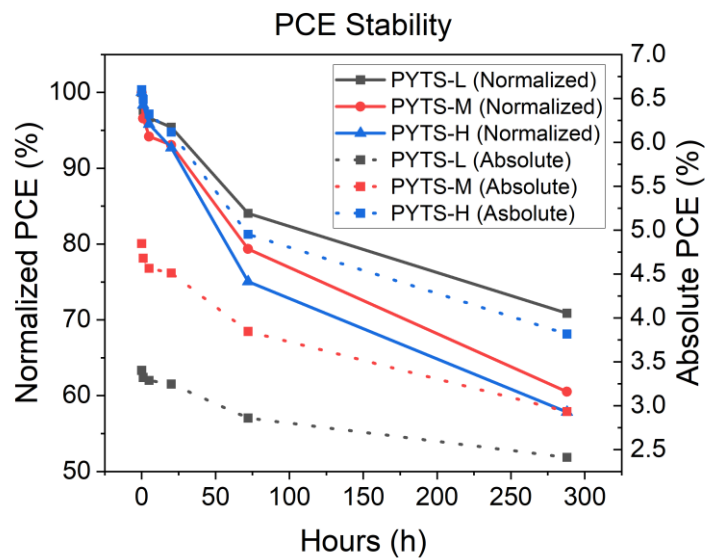


Figure S9. Storage stability of all-PSCs with different  $M_n$ , devices were stored in ambient air after encapsulation.



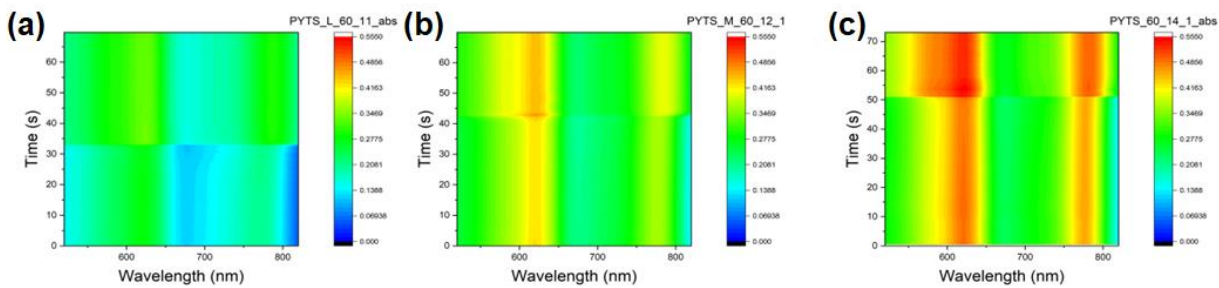


Figure S10. Time-dependent contour maps of UV-vis absorption spectra measured on different blends. (a) PBDB-T:PYTS<sub>L</sub>, (b) PBDB-T:PYTS<sub>M</sub>, and (c) PBDB-T:PYTS<sub>H</sub>.

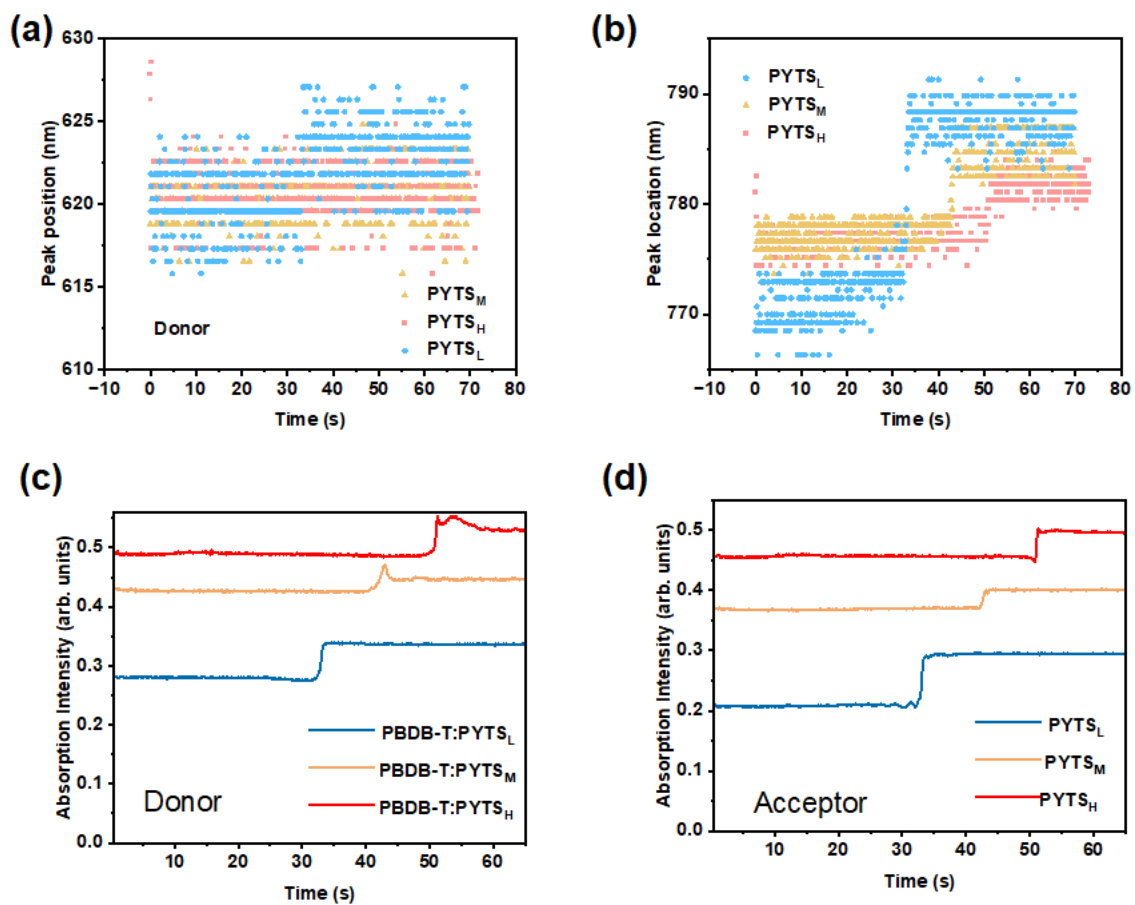


Figure S11. Plots of spectral evolution probed at the (a) donor and (b) acceptor absorption peaks based on the results in time-dependent contour maps.

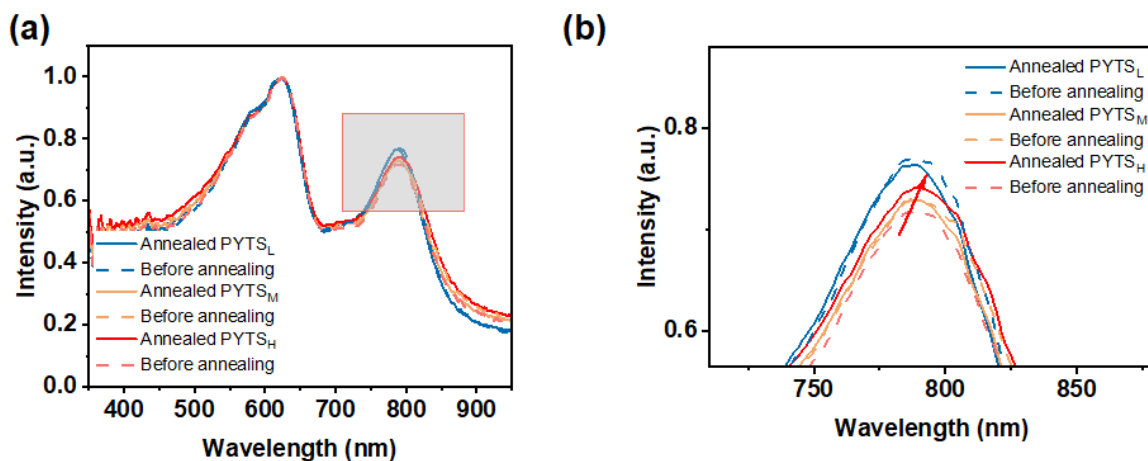


Figure S12. (a) Thin-film optical absorption spectra of the PBDB-T:PYTS acceptor copolymer at different number-average molecular weights  $M_n$  before and after heat annealing. (b) The enlarged view of the gray area in (a).

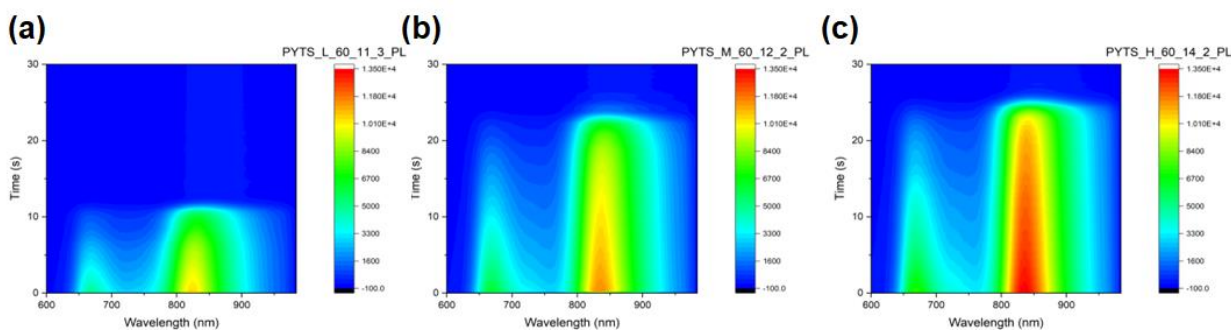


Figure S13. Time-dependent contour maps of PL spectra measured on different blends. (a) PBDB-T:PYTS<sub>L</sub>, (b) PBDB-T:PYTS<sub>M</sub>, and (c) PBDB-T:PYTS<sub>H</sub>.

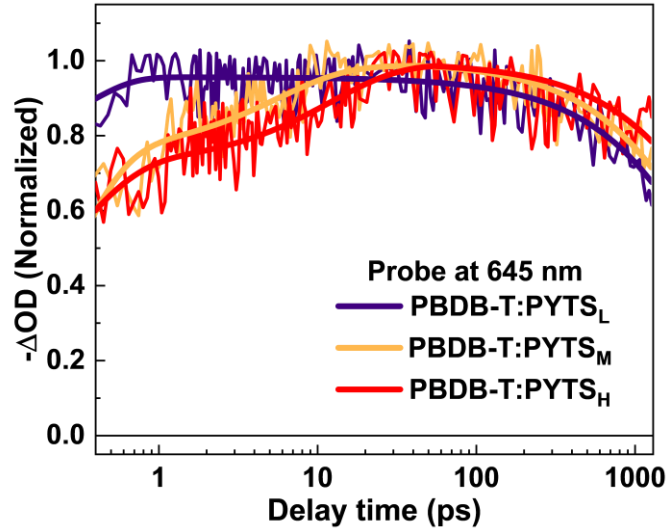


Figure S14. The extracted TA kinetics of  $\sim 645$  nm of three blend films after excitation at 800 nm with an excitation fluence of  $3.6 \times 10^{13}$  photons $\cdot$ cm $^{-2}$  $\cdot$ pulse $^{-1}$ .

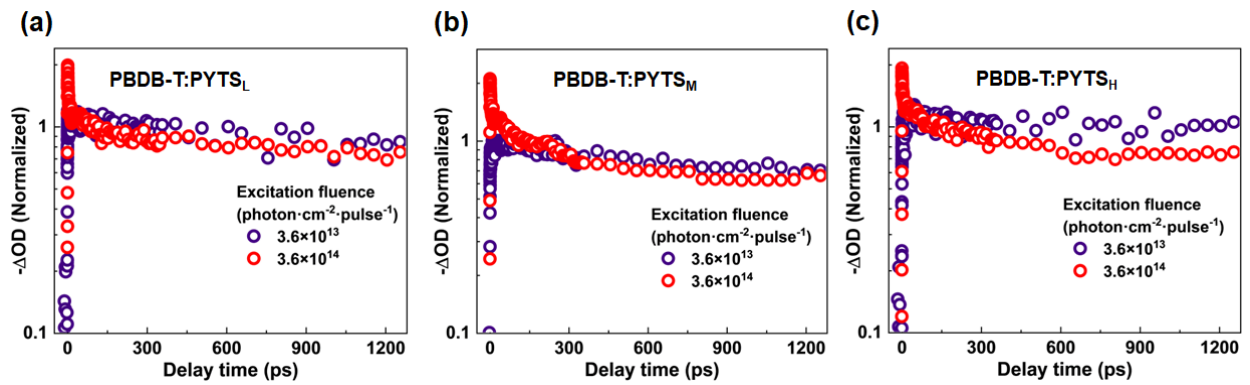


Figure S15. The extracted TA kinetics of  $\sim 645$  nm of three blend films after excitation at 800 nm with various excitation fluencies. The TA kinetics normalized at  $\sim 30$  ps.

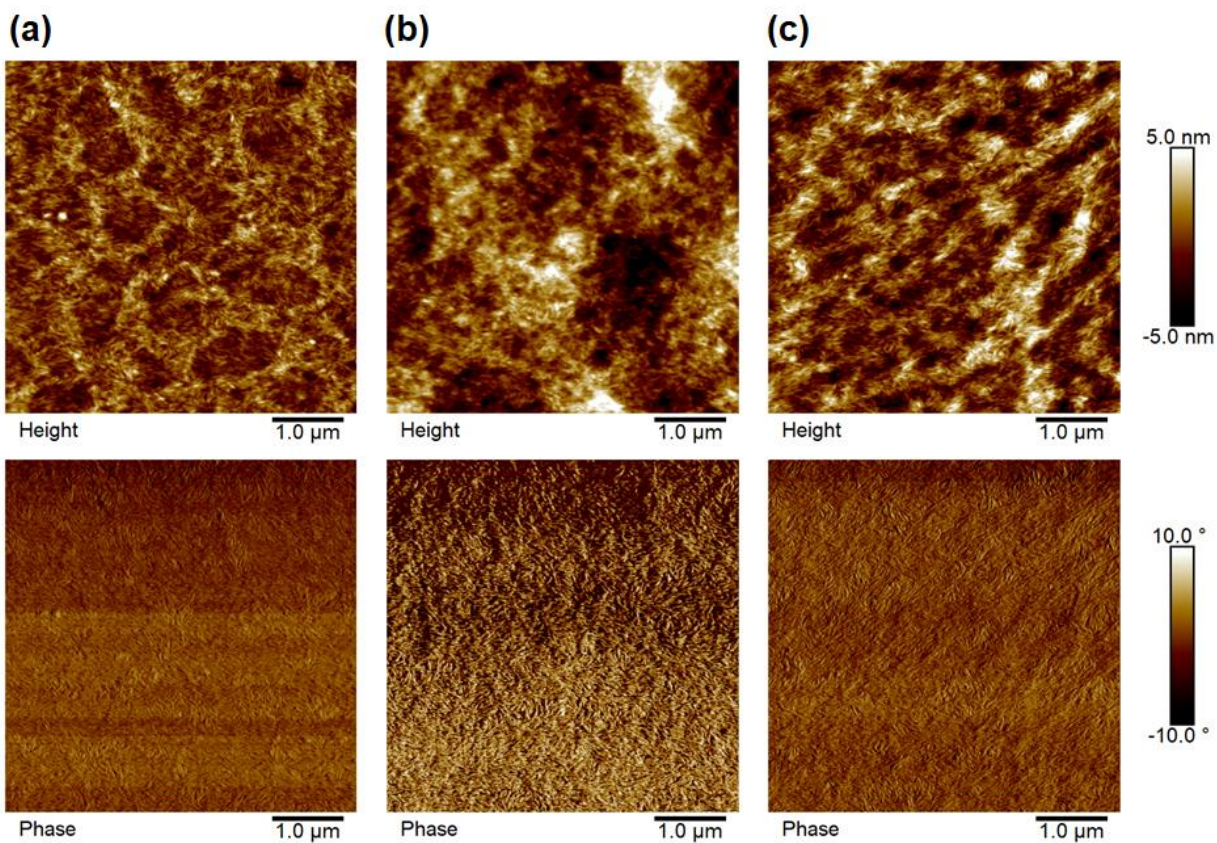


Figure S16. AFM height and phase images. (a) PBDB-T:PYTS<sub>L</sub>, (b) PBDB-T:PYTS<sub>M</sub>, and (c) PBDB-T:PYTS<sub>H</sub>.

## 2. Supporting Tables

Table S1. PV performances of the all-PSCs depending on the Mn of P<sub>As</sub> with concentration of 16 mg mL<sup>-1</sup> via spin-coating.

	$V_{oc}$ (V)	$J_{sc}$ (mA cm <sup>-2</sup> )	$FF(\%)$	$PCE (\%)$
PBDB-T:PYTS <sub>L</sub>	0.88 (0.88±0.01)	12.80 (11.74±0.93)	50.13 (47.86±4.33)	5.67 (5.05±0.39)
PBDB-T:PYTS <sub>M</sub>	0.90 (0.89±0.01)	16.21 (15.61±1.17)	55.93 (53.73±2.45)	8.16 (7.71±0.33)
PBDB-T:PYTS <sub>H</sub>	0.89 (0.89±0.01)	17.35 (15.68±1.05)	52.70 (53.89±3.62)	8.14 (7.44±0.46)

Table S2. PV performances of the all-PSCs depending on the Mn of P<sub>As</sub> with concentration of 16 mg mL<sup>-1</sup> via blade-coating.

	$V_{oc}$ (V)	$J_{sc}$ (mA cm <sup>-2</sup> )	$FF(\%)$	$PCE (\%)$
PBDB-T:PYTS <sub>L</sub>	0.87 (0.86±0.01)	11.27 (9.96±0.86)	47.35 (47.40±3.06)	4.62 (4.05±0.29)
PBDB-T:PYTS <sub>M</sub>	0.88 (0.88±0.00)	15.43 (13.78±0.81)	51.90 (52.23±2.38)	7.04 (6.32±0.24)
PBDB-T:PYTS <sub>H</sub>	0.90 (0.89±0.01)	16.89 (16.16±0.72)	51.76 (52.19±2.43)	7.85 (7.50±0.18)

Table S3. The detailed fitting parameters of the rising process in ~645 nm for three blend films after excitation at 800 nm.

Active layer	$A_1$	$\tau_1$ (ps)	$A_2$	$\tau_2$ (ps)
PBDB-T:PYTS <sub>L</sub>	/	/	/	/
PBDB-T:PYTS <sub>M</sub>	0.76	0.21	0.23	5.70
PBDB-T:PYTS <sub>H</sub>	0.71	0.27	0.27	12.32

Table S4. The detailed fitting parameters of charge recombination process for three blend films after excitation at 800 nm and probe at ~645 nm.

Active layer	A	$\tau$ (ps)
PBDB-T:PYTS <sub>L</sub>	0.96	3756.89
PBDB-T:PYTS <sub>M</sub>	0.99	3884.01
PBDB-T:PYTS <sub>H</sub>	0.99	5450.44

Table S5. Detailed data of GIWAXS Characterization.

	(100)				(010)			
	Position ( $\text{\AA}^{-1}$ )	FWHM( $\text{\AA}^{-1}$ )	Distance ( $\text{\AA}$ )	CCL ( $\text{\AA}$ )	Position ( $\text{\AA}^{-1}$ )	FWHM ( $\text{\AA}^{-1}$ )	Distance ( $\text{\AA}$ )	CCL ( $\text{\AA}$ )
PBDB-T:PYTS <sub>L</sub>	0.281	0.089	22.44	78.44	1.66	0,434	3.78	16.08
PBDB-T:PYTS <sub>M</sub>	0.281	0.085	22.44	82.13	1.68	0,395	3.74	17.67
PBDB-T:PYTS <sub>H</sub>	0.281	0.095	22.44	73.48	1.68	0,319	3.74	21.88