

## Electronic Supplementary Information

### Geometrically Controlled Organic Small Molecule Acceptors for Efficient Fullerene-free Organic Photovoltaic Devices

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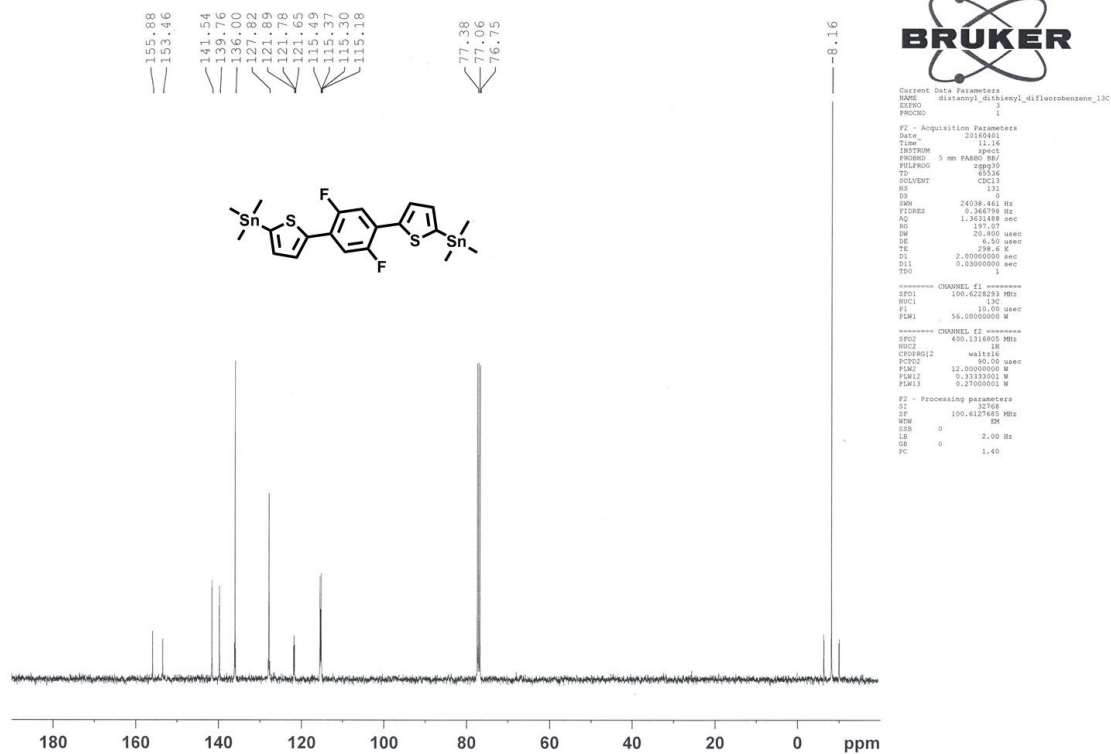
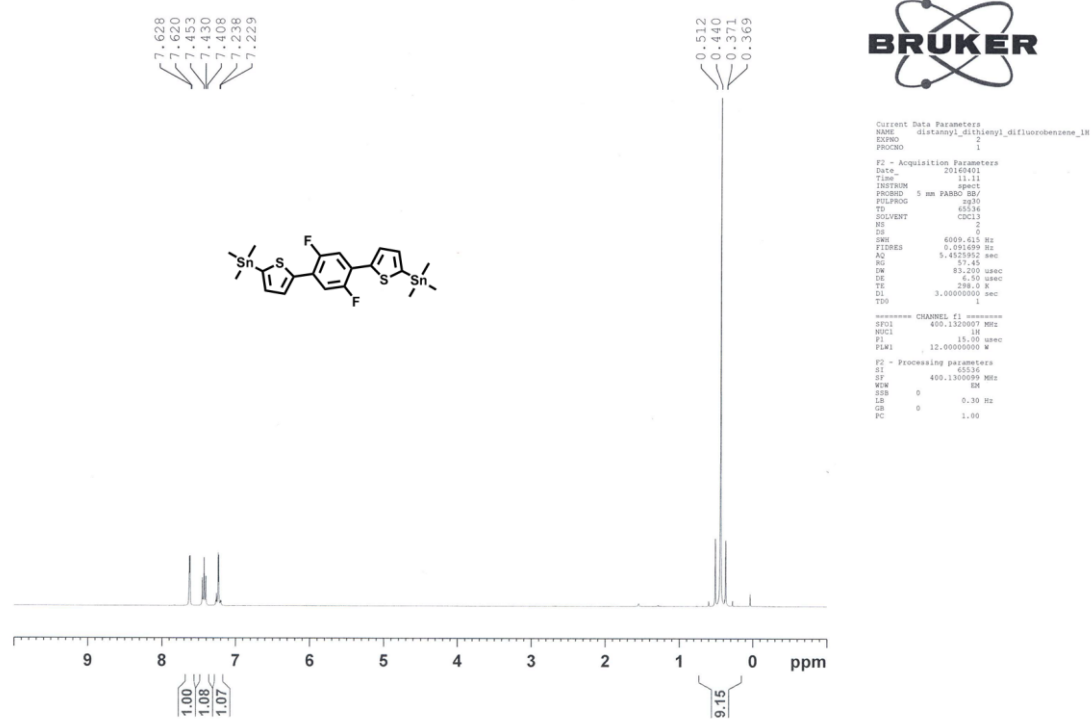
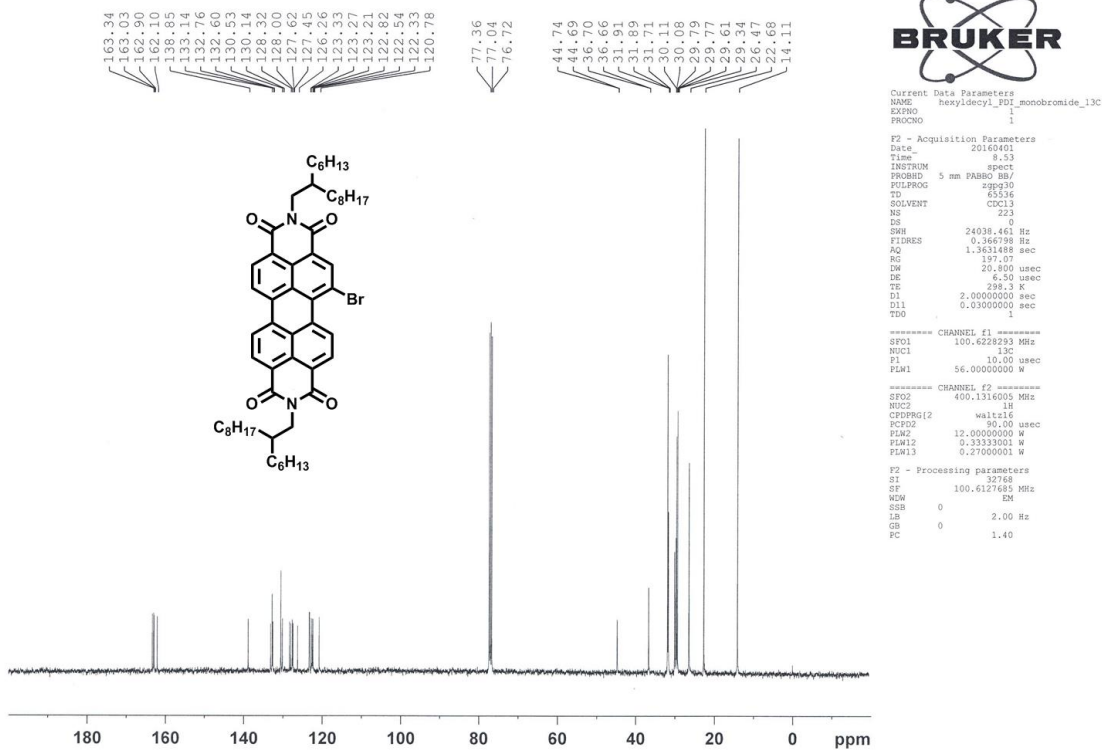
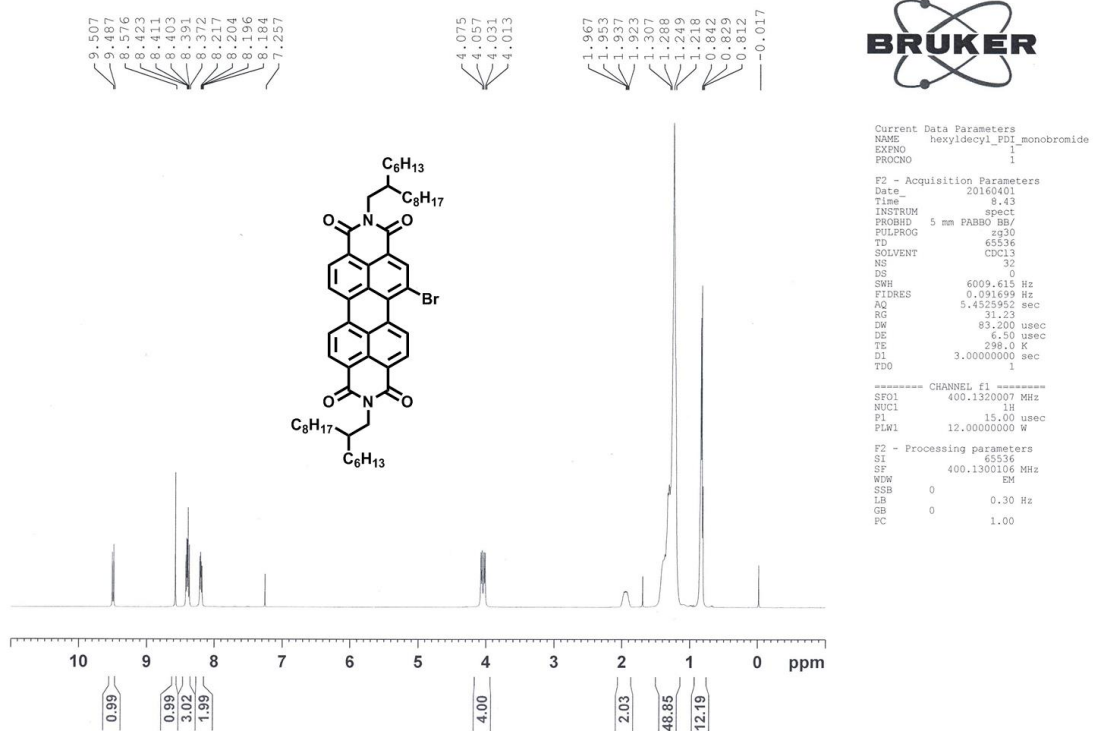
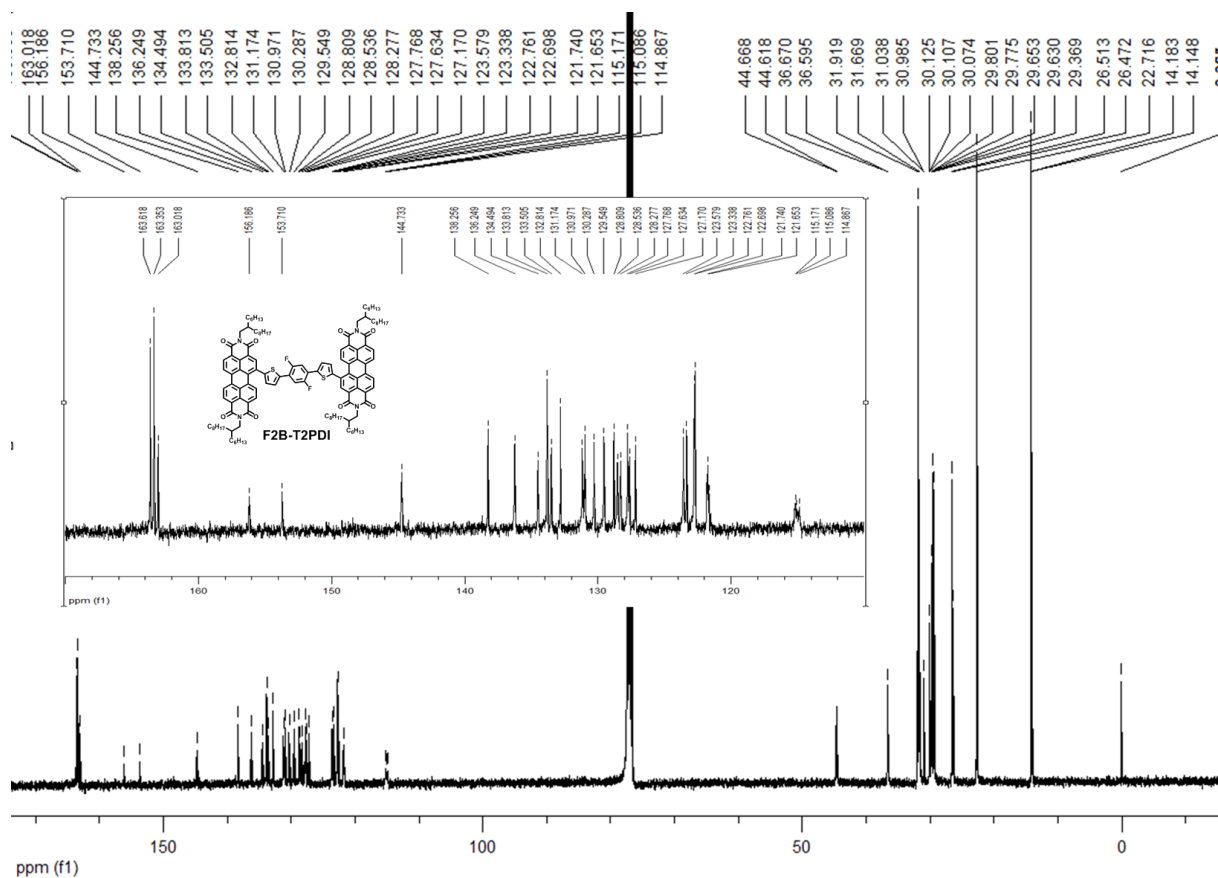
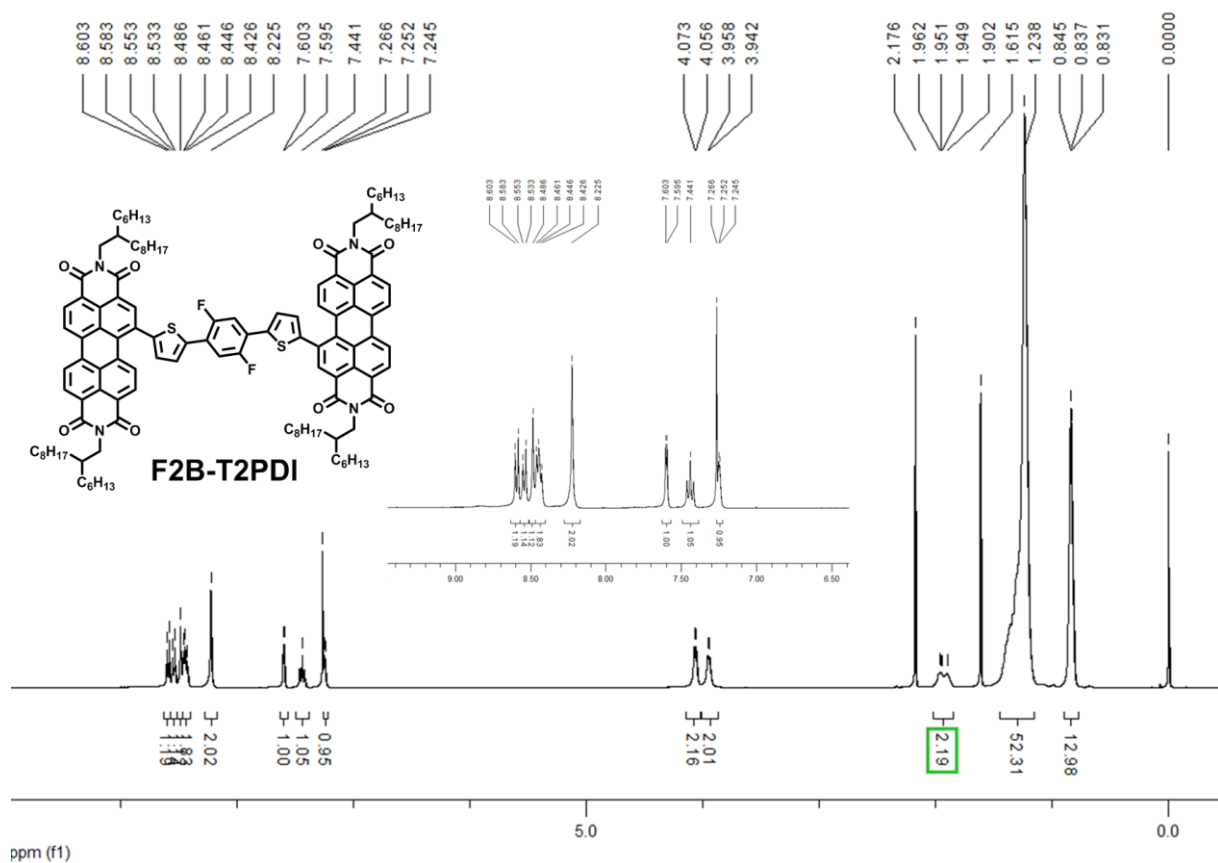


Fig. S1. <sup>1</sup>H and <sup>13</sup>C NMR spectrum of ((2,5-difluoro-1,4-phenylene)bis(thiophene-5,2-diyl))bis(trimethylstannane) (2)



**Fig. S2.** <sup>1</sup>H and <sup>13</sup>C NMR spectrum of 1-bromo-N,N'-bis(2-ethylhexyl)-3,4,9,10-perylene tetracarboxylic diimide (3)



**Fig. S3.** <sup>1</sup>H and <sup>13</sup>C NMR spectrum of F2B-T2PDI

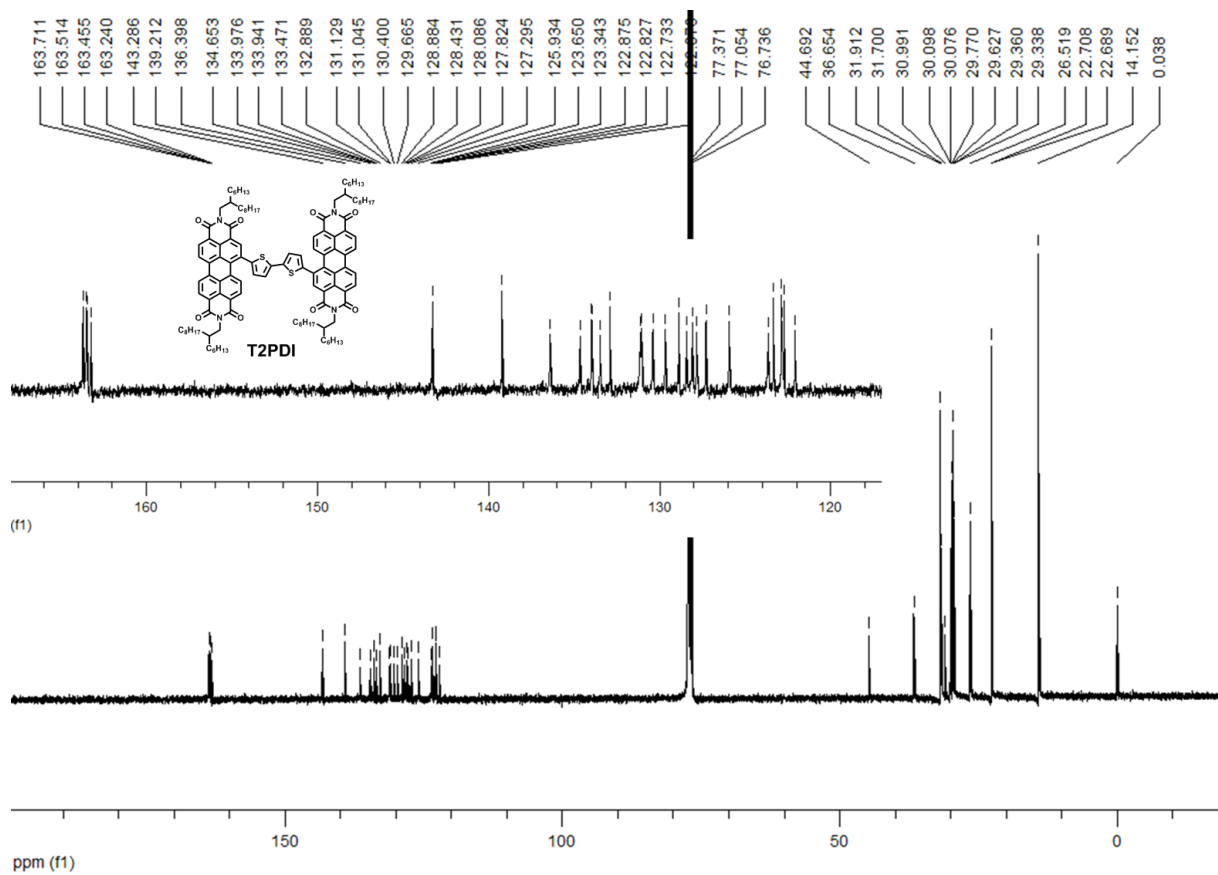
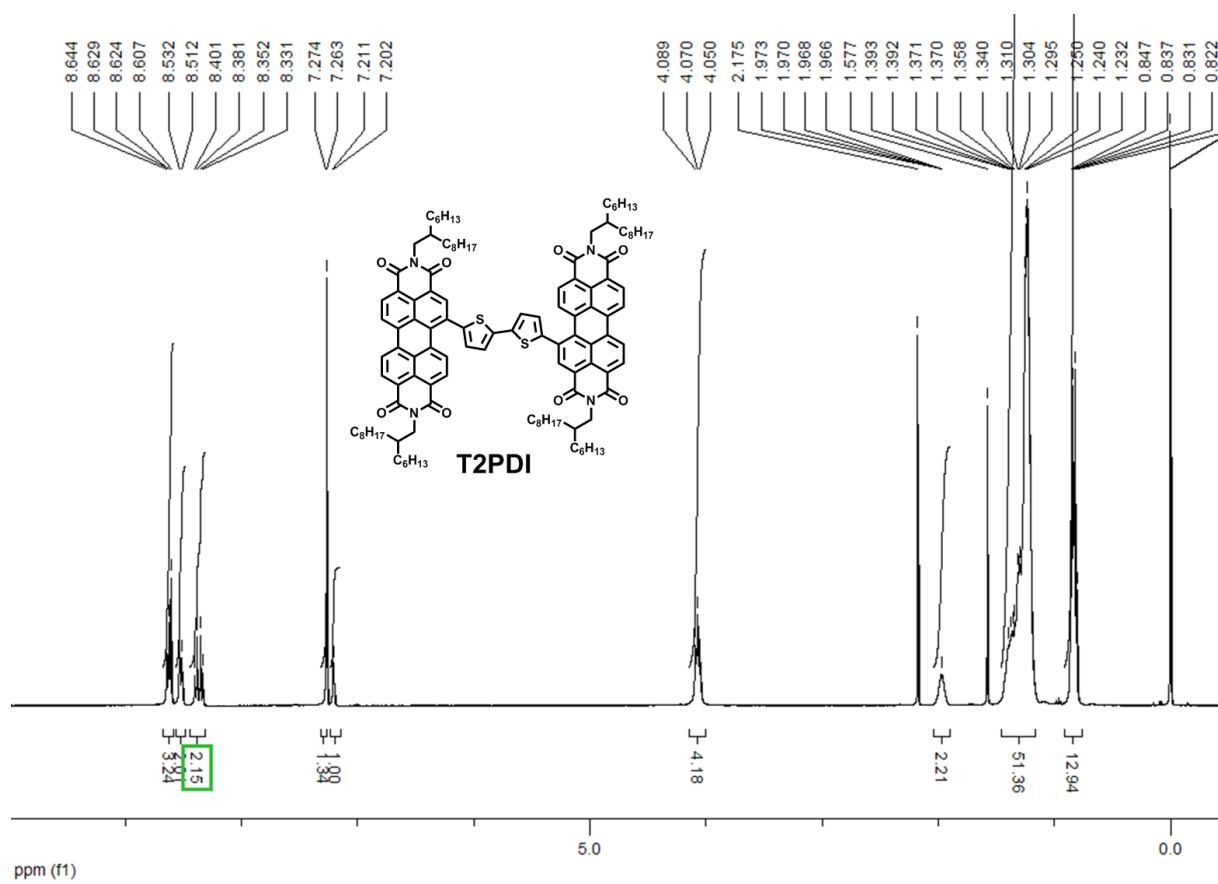
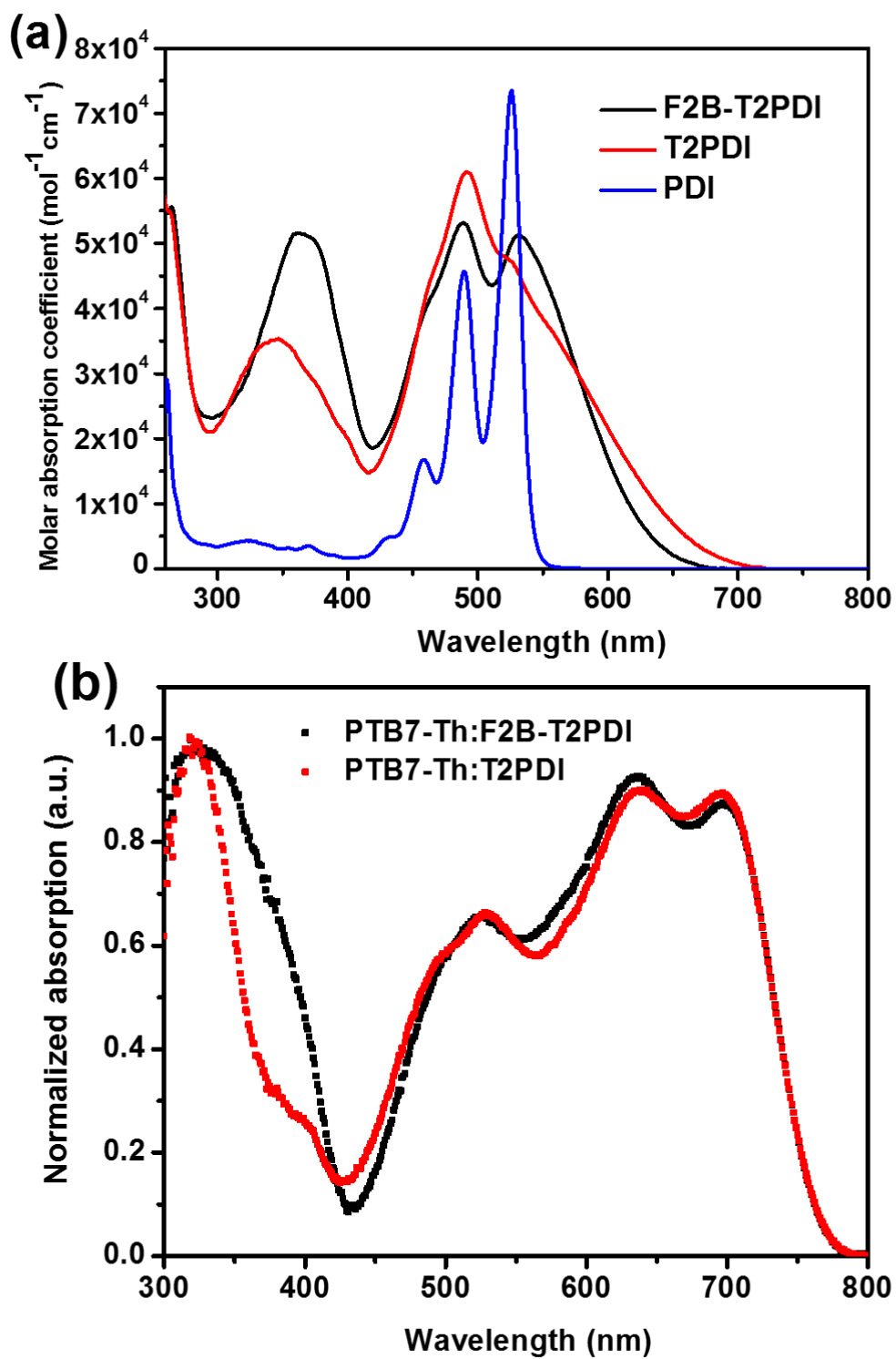
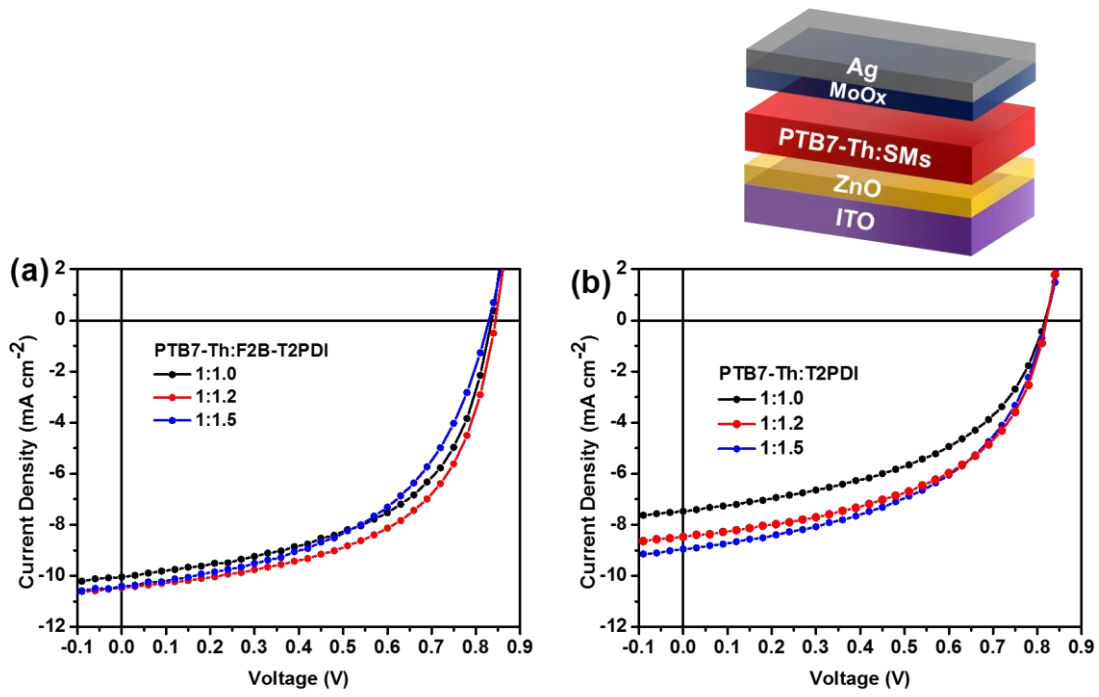


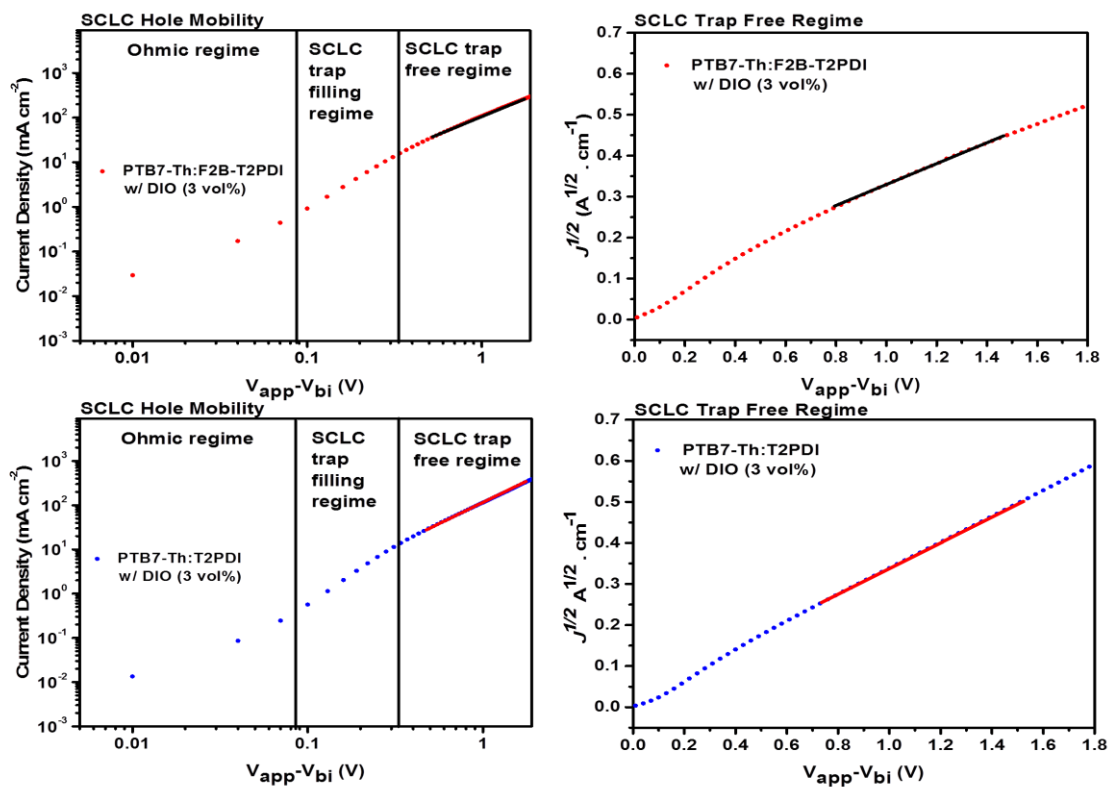
Fig. S4. <sup>1</sup>H and <sup>13</sup>C NMR spectrum of T2PDI



**Fig. S5.** (a) Molar absorption coefficients of F2B-T2PDI, T2PDI acceptors and PDI monomer in chloroform solution and (b) Absorption spectra



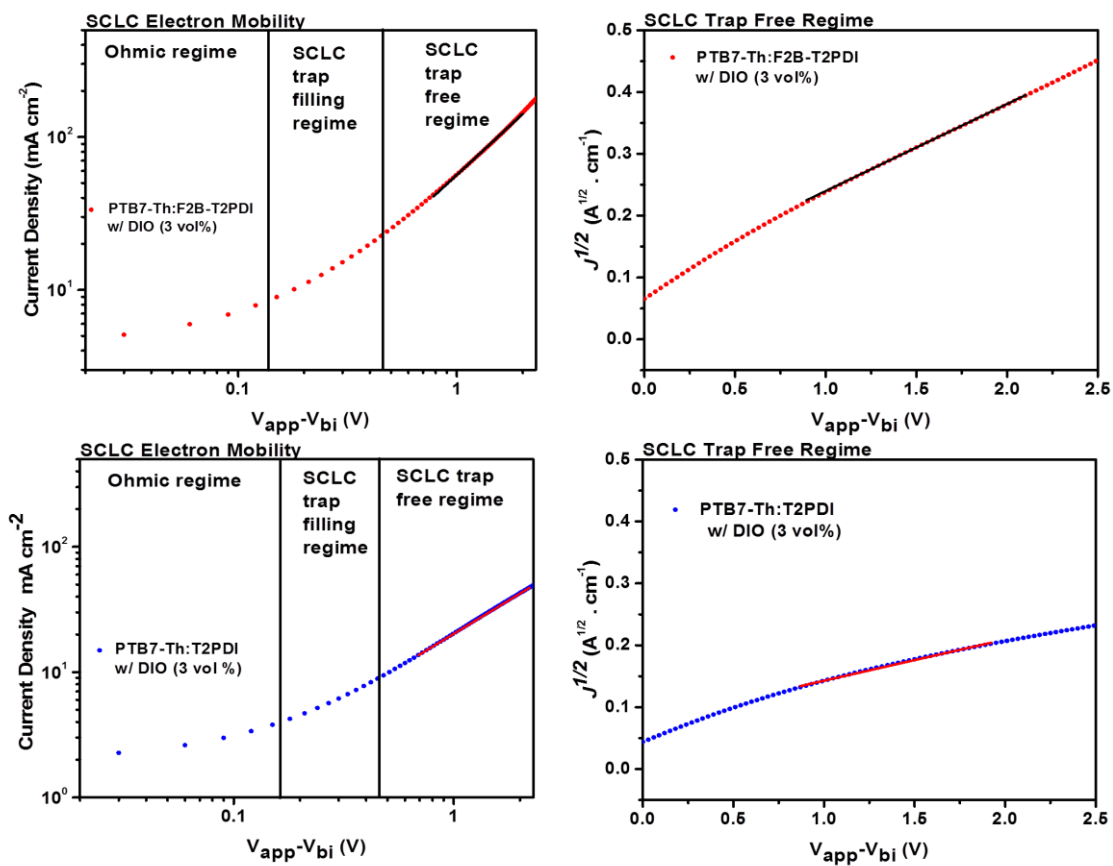
**Fig. S6.** *J*-*V* characteristics of PTB7-Th:F2B-T2PDI (or T2PDI) films at different blend ratio under AM 1.5G illumination.



**Fig. S7.**  $J$ - $V$  characteristics of the hole-only devices using PTB7-Th:SM acceptor blend films.

The charge mobilities were calculated by fitting the  $J$ - $V$  curves in the SCLC regime.





**Fig. S8.**  $J$ - $V$  characteristics of the electron-only devices using PTB7-Th:SM acceptor blend films. The charge mobilities were calculated by fitting the  $J$ - $V$  curves in the SCLC regime.

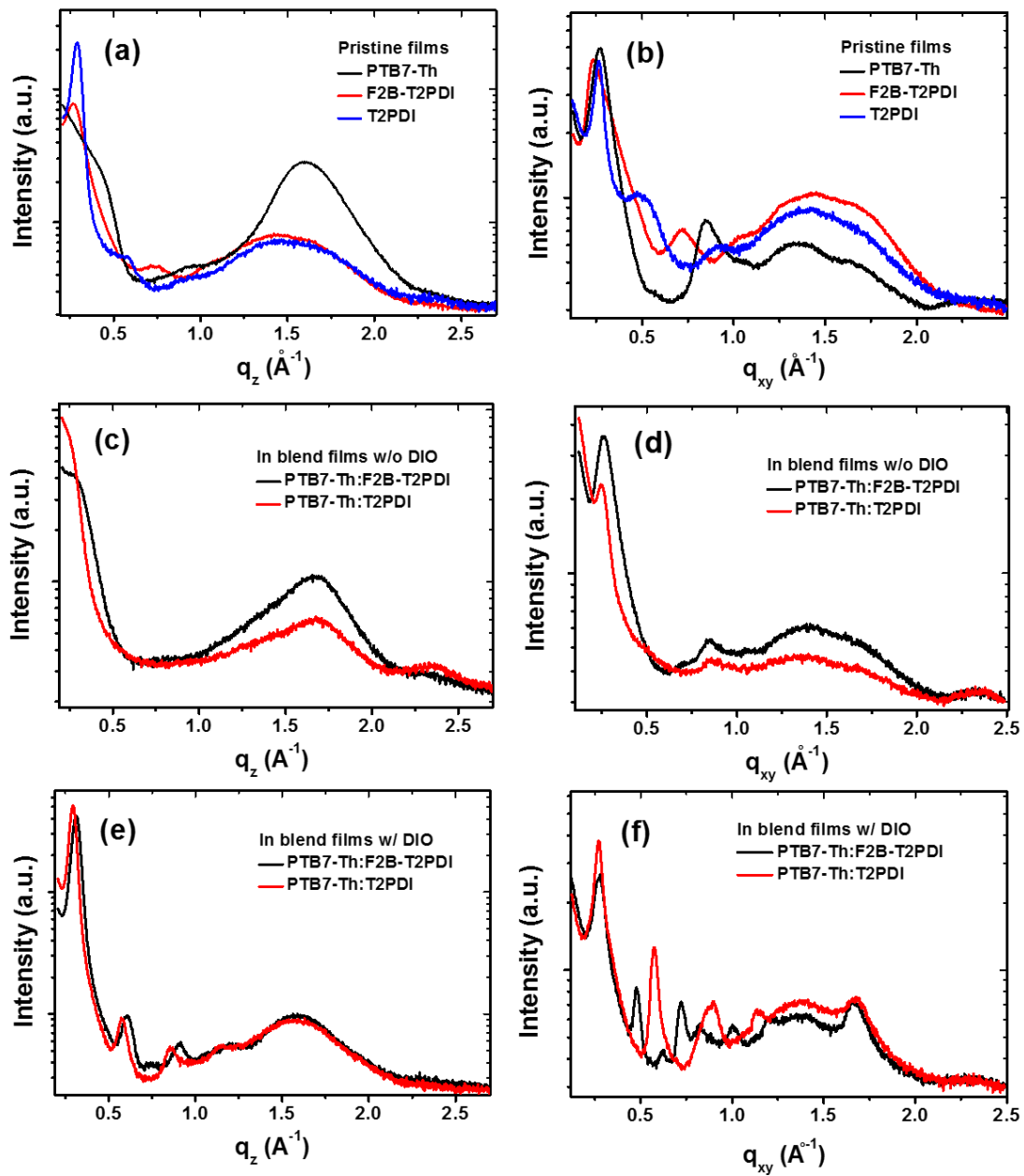


Fig. S9. Out-of-plane and in-plane line cuts from 2D-GIXRD results of neat and blend films.

**Table S1.** Summary of photovoltaic properties in Figure S6.

PTB7- Th:acceptor	blend ratio	$J_{sc}$ (mA cm <sup>-2</sup> )	$V_{oc}$ (V)	Fill factor	PCE <sub>max</sub> (ave) [%]
F2B-T2PDI	1.0 : 1.0	0.83	9.96	0.53	4.36 (4.26)
F2B-T2PDI	1.0 : 1.2	0.84	10.60	0.57	5.05 (4.79)
F2B-T2PDI	1.0 : 1.5	0.84	10.58	0.56	4.99 (4.70)
T2PDI	1.0 : 1.0	0.82	7.47	0.49	2.98 (2.91)
T2PDI	1.0 : 1.2	0.82	8.48	0.52	3.59 (3.53)
T2PDI	1.0 : 1.5	0.82	8.95	0.49	3.63 (3.57)