

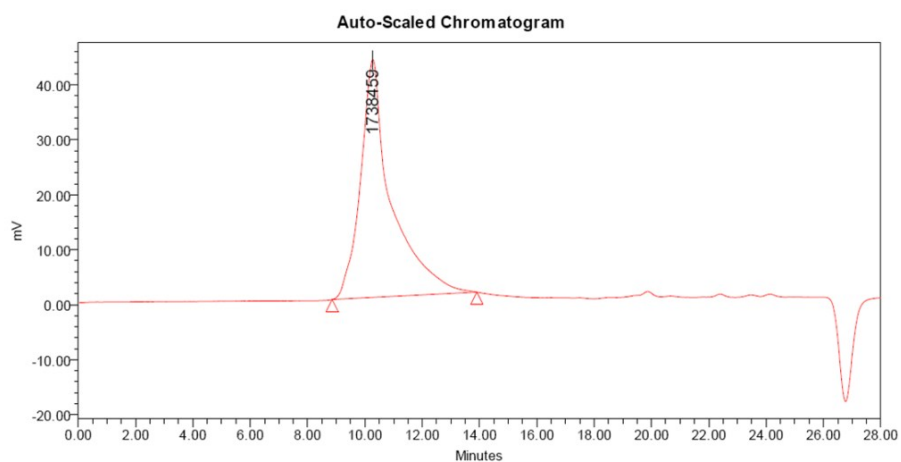
Electronic Supplementary Information

For

Steric Minimization Towards High Planarity and Molecular Weight for Aggregation and Photovoltaic Studies

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GPC Results

Dist Name	Mn	Mw	Mv	MP	Mz	Mz+1	Poly dispersity	K	alpha
1	343374	819653		1738459	1244697	1474694	2.387051		

Fig. S1 GPC chromatogram of **PTOBDTDTffBT**, chloroform as an eluent at a column temperature of 25 °C.

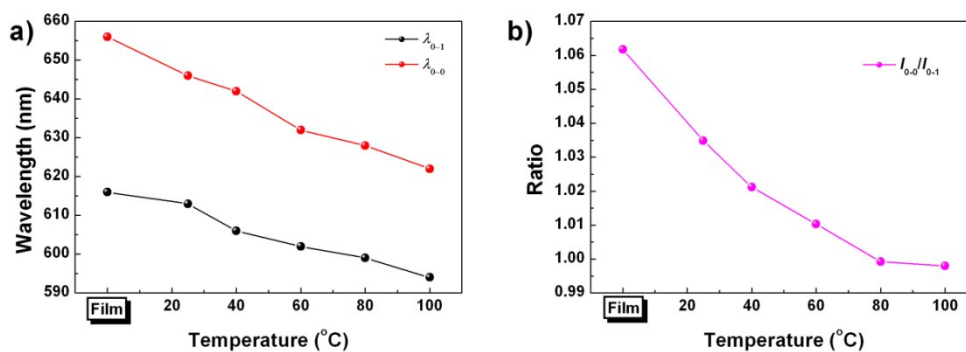


Fig. S2 λ_{0-0} and λ_{0-1} displacement (a), intensity ratio value of λ_{0-0} and λ_{0-1} (b) of **PTOBDTDTffBT** in *o*-DCB solution at different temperature and in its neat film state.

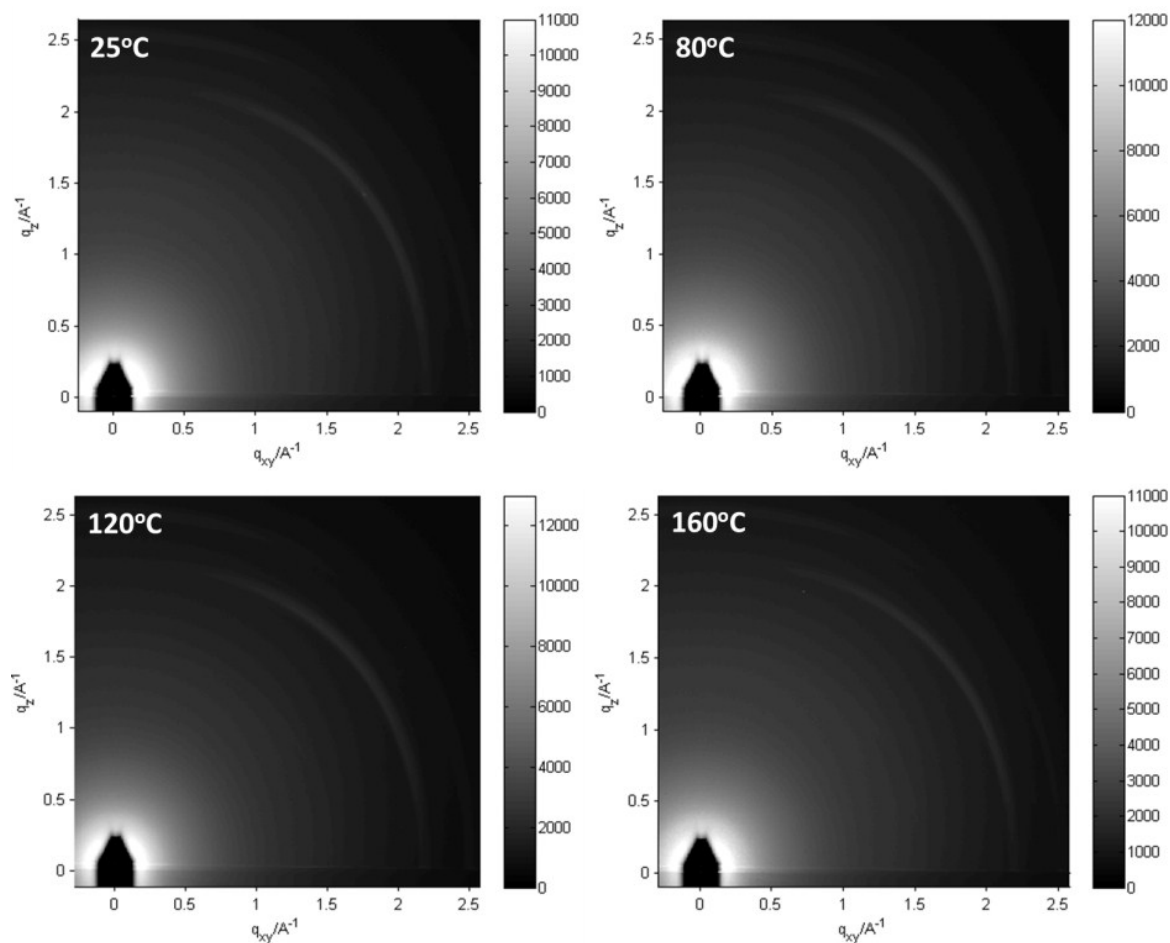


Fig. S3 2D GIXD patterns of PTOBDTDTffBT films spin-coated from *o*-DCB solution at 25 °C, 80 °C, 120 °C and 160 °C.

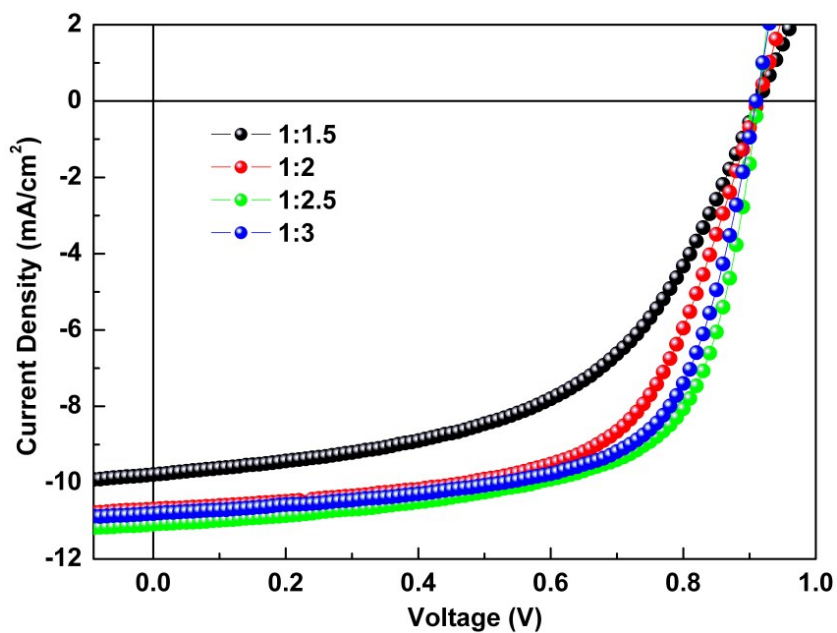


Fig. S4 J - V curves of PTOBDTDTffBT/PC₇₁BM based devices with different donor/acceptor ratios.

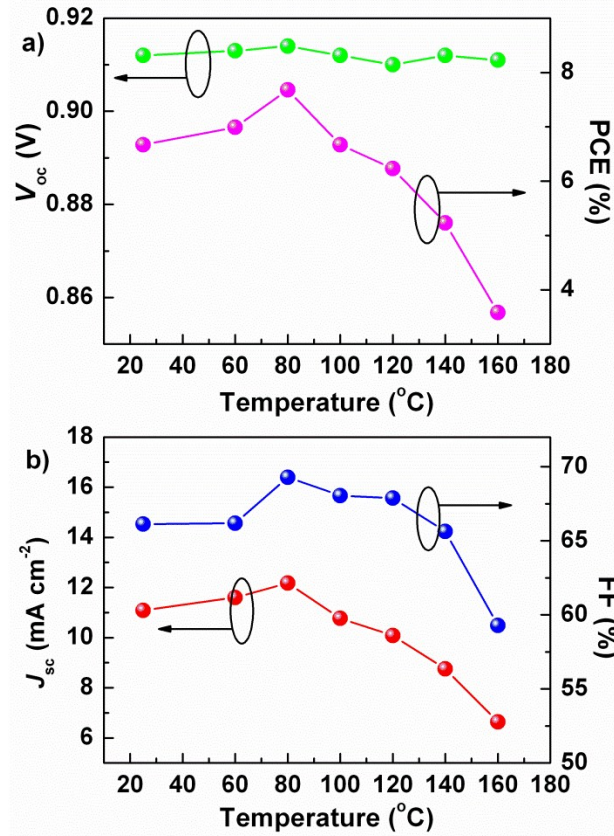


Fig. S5 V_{oc} (a), PCE (a), J_{sc} (b) and FF (b) changes of the active layer spin coated at different temperature from 25 °C to 160 °C.

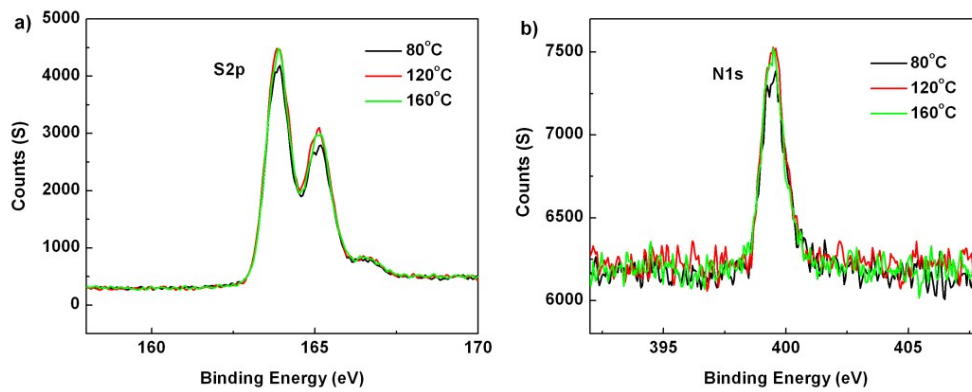


Fig. S6 XPS spectra of S2p (a) and N1s (b) in the **PTOBDDTffBT/PC₇₁BM** surface spin coated at 80 °C, 120 °C and 160 °C.

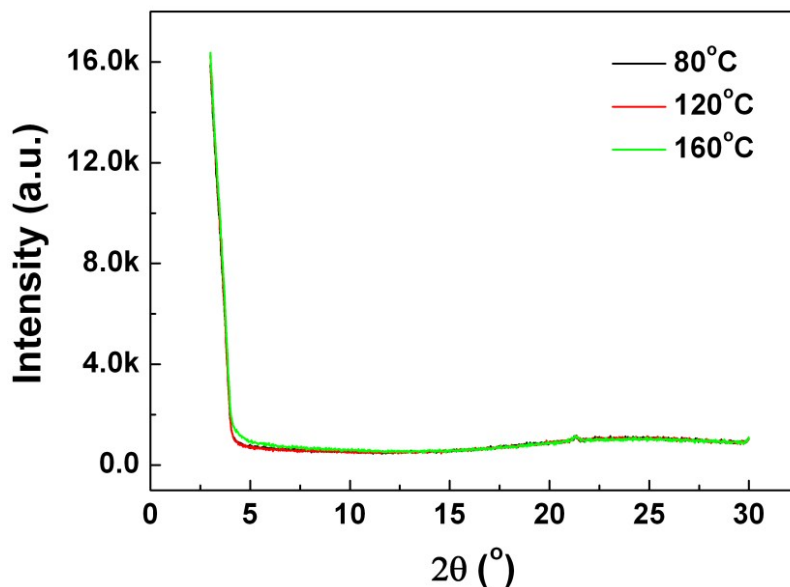


Fig. S7 XRD patterns of PTOBDTDTTffBT/PC₇₁BM blends spin-coated from *o*-DCB solution at 80 °C, 120 °C and 160 °C.

Table S1. Summary of the peak wavelength and the intensity of λ_{0-0} and λ_{0-1} .

Temperatur e	λ_{0-1}	λ_{0-0}	I_{0-1}	I_{0-0}	I_{0-0}/I_{0-1}
25 ^a	616	656	1.03607	1.1	1.0617
25 ^b	613	646	0.96632	1	1.0349
40 ^b	606	642	0.88128	0.9	1.0212
60 ^b	602	632	0.79185	0.8	1.0103
80 ^b	599	628	0.69845	0.69788	0.9992
100 ^b	594	622	0.59945	0.59826	0.9980

^a Film. ^b Solution.

Table S2. Summary of device parameters based on the active layers with different polymer/PC₇₁BM ratios spun cast from *o*-DCB solutions at 25 °C.

Polymer/PC ₇₁ BM ratio	Thickness [nm]	V_{oc} [V]	J_{sc} [mA cm ⁻²]	FF [%]	PCE ^a [%]
1:1.5	110	0.91	9.74	52.99	4.69 (4.38)
1:2	109	0.91	10.67	61.97	6.02 (5.73)
1:2.5	108	0.91	11.09	66.12	6.67 (6.39)
1:3	108	0.91	10.82	65.85	6.48 (6.20)

^a Average PCE in brackets (at least 10 devices).