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Morphological Characterization of a New Low-Bandgap Thermocleavable Polymer Showing Stable Photovoltaic Properties

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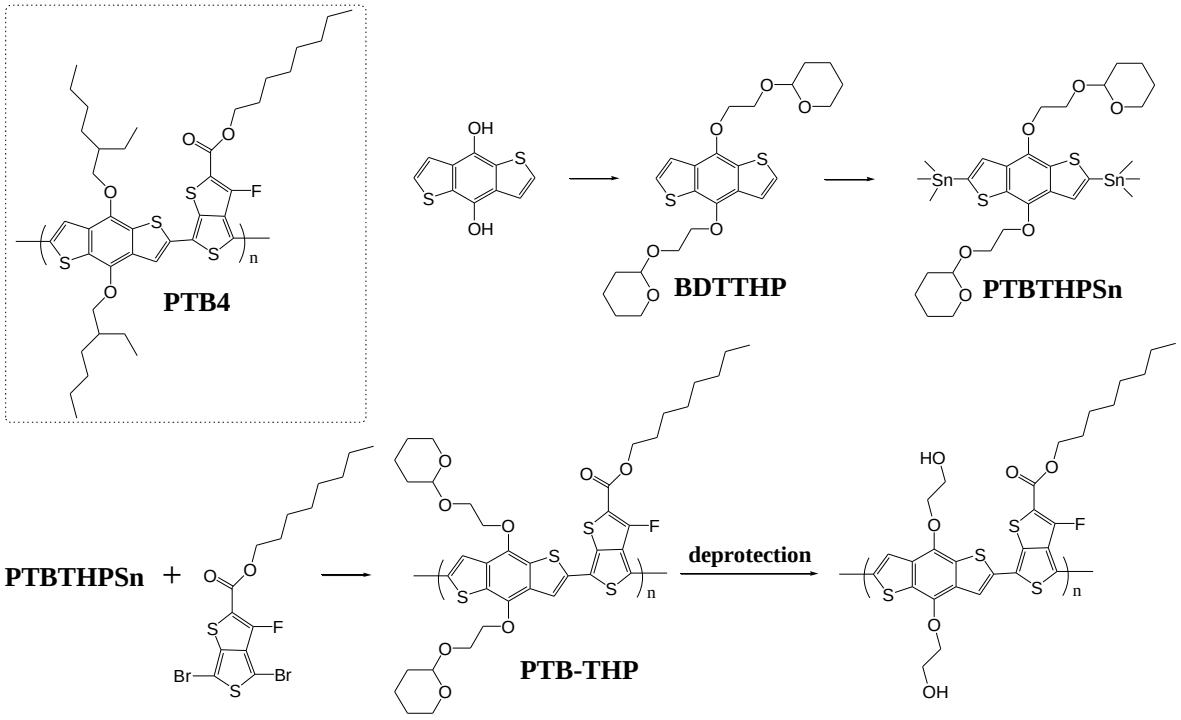
Supporting Information



Scheme 1. Chemical structures and synthetic routes for monomer and polymer. To avoid deterioration of the THP groups, 4,8-Dihydroxybenzo[1,2-b:4,5-b']dithiophene was used as the starting compound. The chemical structures of all the compounds and polymers reported were confirmed by NMR spectroscopy. Molecular weight (Mn) of the obtained polymer was determined by gel permeation chromatography (GPC).

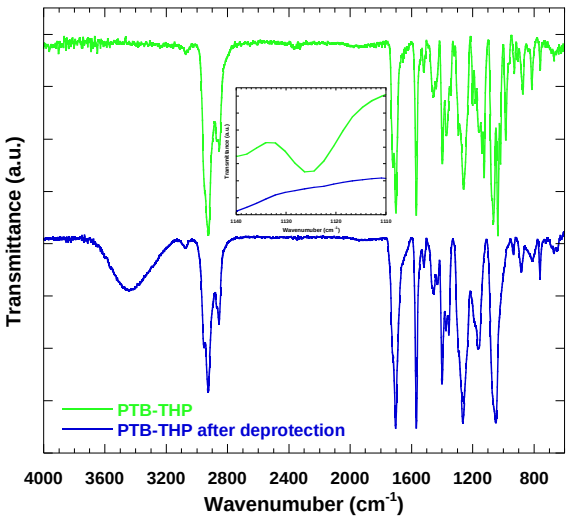


Figure S1. FTIR spectra of the polymer before and after thermal treatment at 150 ℃ in the presence of CSA also confirms the cleavage of THP attachment upon heating. Inset: Expanded FTIR spectrum at the wavenumber ~1120 cm^{-1}.

(a) (b)

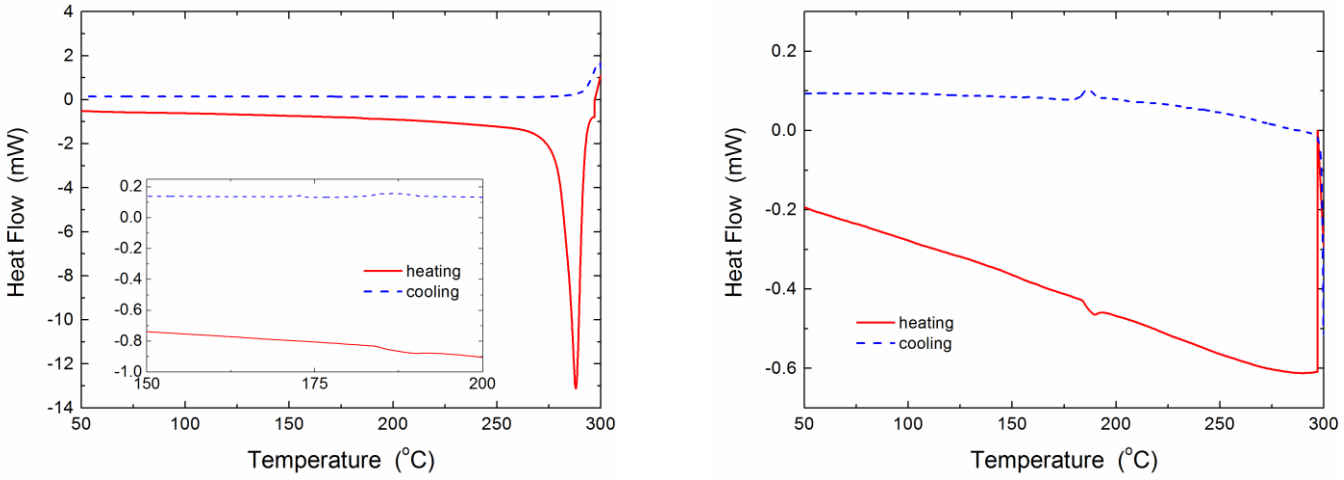


Figure S2. Differential scanning calorimetry (DSC) results for PTB(THP): (a) first scan, (b) second scan completed at a scan rate of 10 °C per minute. Both scans show a reversible thermal transition at around 185 °C, which we attribute to the glass transition in the bulk polymer; please see the inset in part (a) for details of the first scan near this temperature. The prominent endothermic peak in the first scan at 270 °C correlates with the deprotection observed in TGA. In the second scan, the deprotection peak is no longer observed, confirming the completion of the deprotection process. The deprotection of the 3.45 mg sample finished in 2.2 minutes. The glass transition temperature T_g remained the same after the deprotection, indicating that the deprotection process did not result in a significant change of the polymer's physical properties.

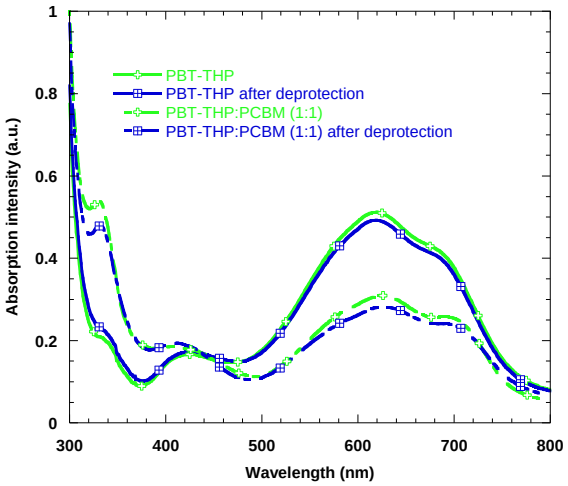


Figure S3. UV-Vis absorption spectra of PTB(THP) polymer films, before and after deprotection. Also shown are absorption spectra of PTB(THP) and $PC_{61}BM$ blends (1:1, w/w), before and after deprotection. Deprotection results in a small reduction (< 10%) in the absorption intensity in the long wavelength range of 500-730 nm.

Table S1. Photovoltaic properties of PTB:PCBM, PTB(THP):PCBM, and dPTB:PCBM, shown in columns labeled **a**, **b**, and **c**, respectively, after annealing at 120 ℃ for the times shown as extracted from the JV curves shown in Figure S4. The table shows the short circuit current J_{SC}, open circuit voltage V_{OC}, the fill factor *FF*, and the photo conversion efficiency *PCE*.

Time (hours)	Jsc (mA/cm^2)			Voc (V)			FF (%)			PCE (%)		
	a	**b**	**c**	**a**	**b**	**c**	**a**	**b**	**c**	**a**	**b**	**c**
0	7.98	14.6	6.37	0.73	0.62	0.57	54.5	37.5	41.5	3.2	3.4	1.5
1	5.84	9.74	10.22	0.73	0.62	0.64	46.3	37.1	38.5	2.0	2.2	2.5
2	4.87	3.97	8.34	0.71	0.56	0.62	44.7	31.3	34.3	1.6	0.7	1.8
3	3.82	3.67	7.84	0.37	0.56	0.62	26.6	30.8	33.9	0.4	0.6	1.6
4	4.00	3.33	7.65	0.52	0.56	0.62	29.0	30.5	33.9	0.6	0.6	1.6
5	2.07	3.33	7.22	0.37	0.56	0.62	25.7	30.5	34.1	0.2	0.6	1.5
6	2.01	3.39	7.59	0.44	0.55	0.62	27.1	30.7	33.6	0.2	0.6	1.6

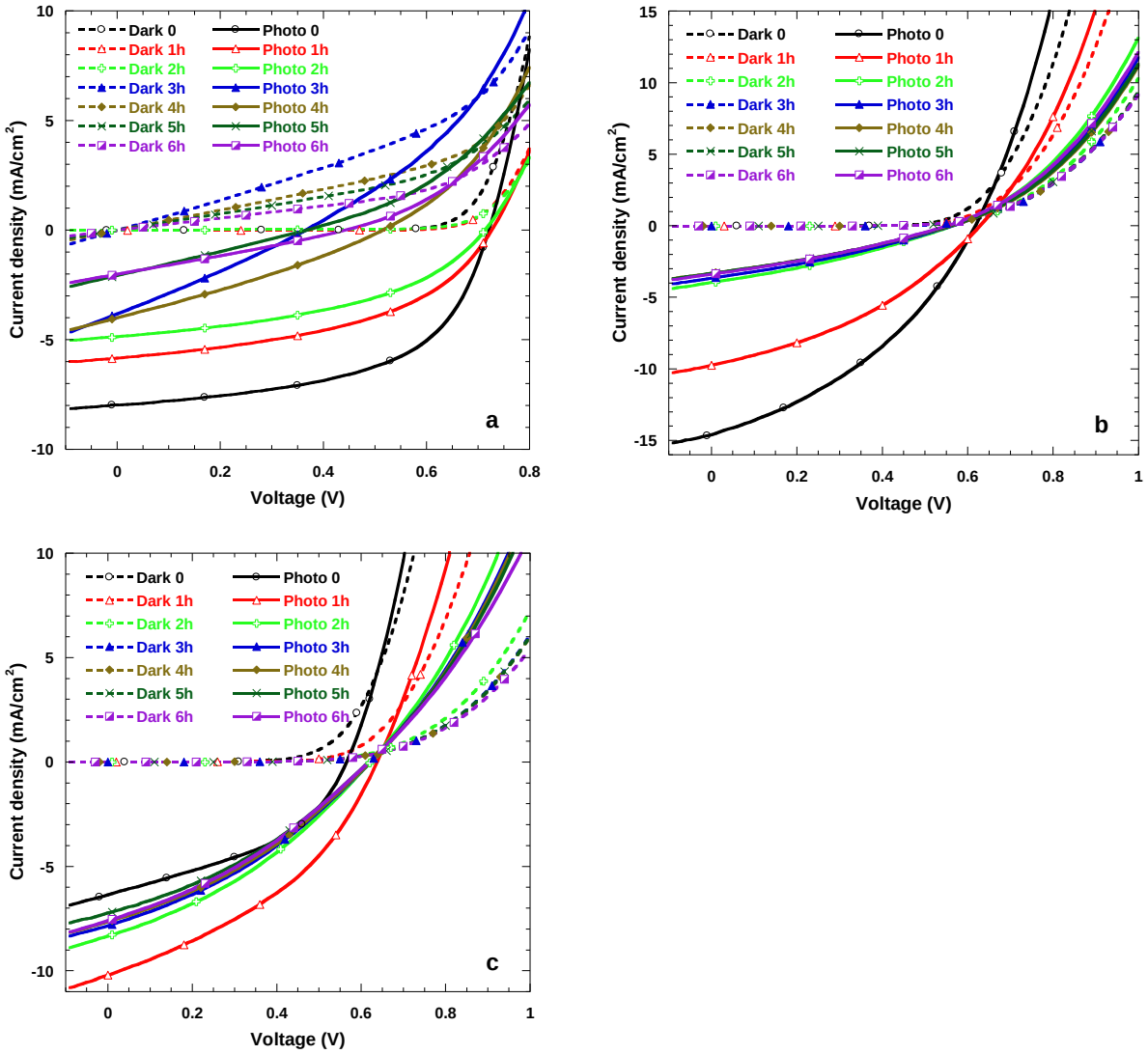


Figure S4. J-V curves of the devices based on a) PTB4:PCBM, b) PTB(THP):PCBM, and c) dPTB:PCBM annealed at 120 ^{o}C for 0, 1, 2, 3, 4, 5, and 6 hr.

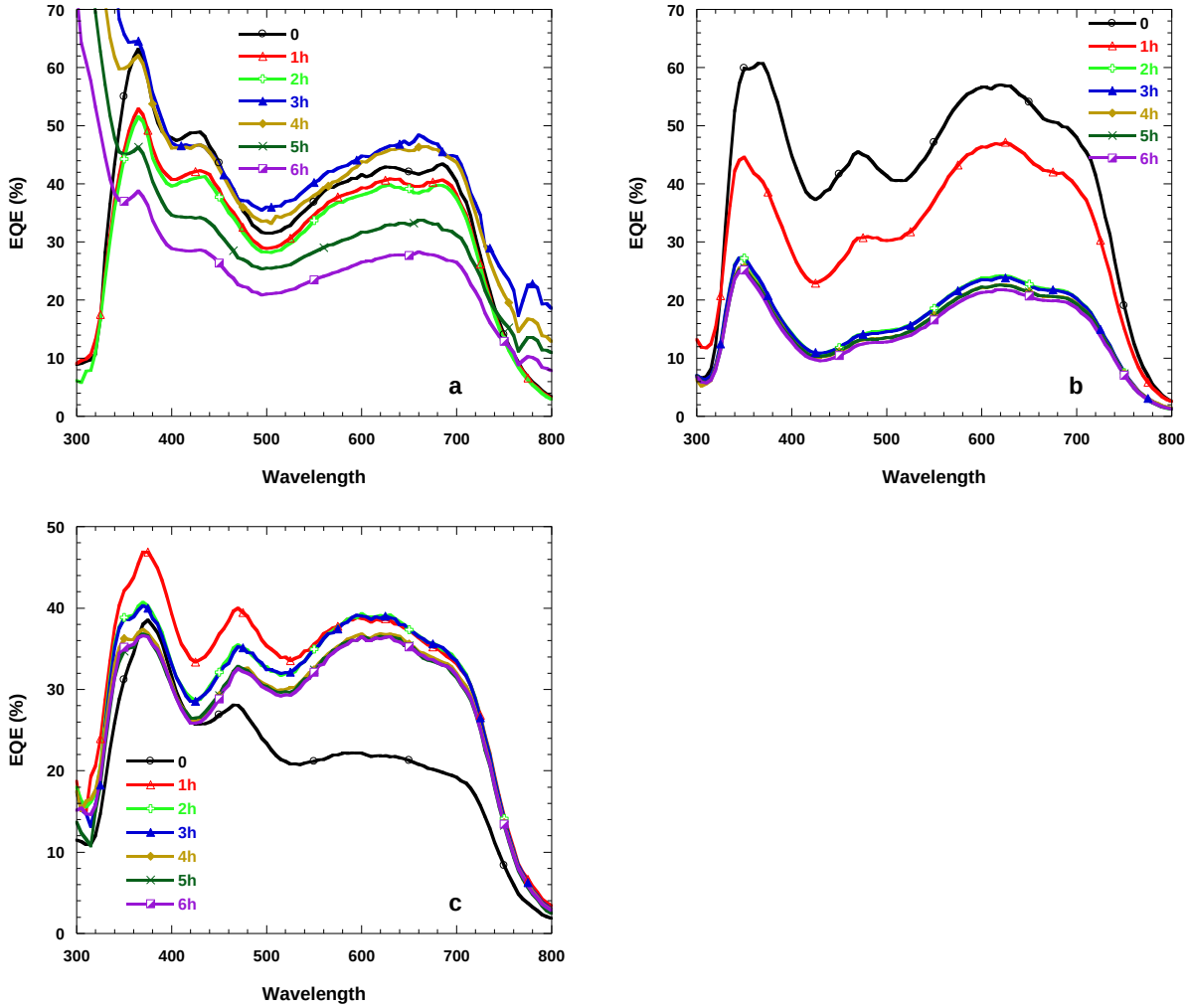


Figure S5. External quantum efficiency of photovoltaic devices based on a) PTB4:PCBM, b) PTB(THP):PCBM, and c) dPTB:PCBM annealed at 120 ^{o}C for 0, 1, 2, 3, 4, 5, and 6 hr.

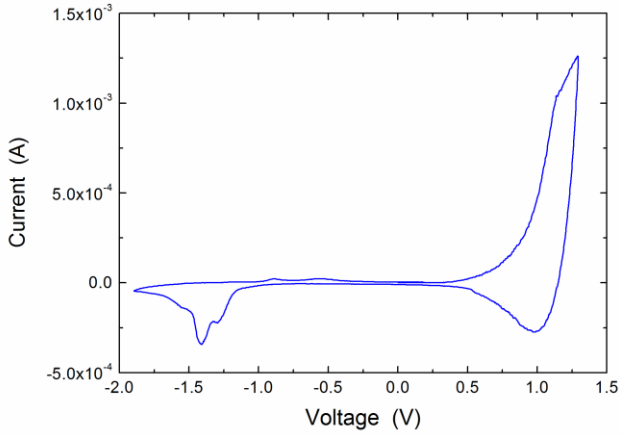
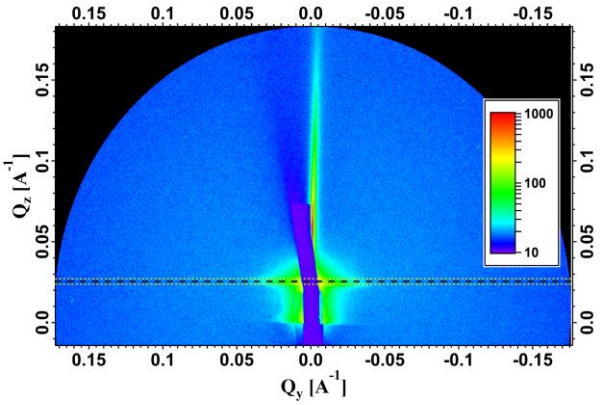
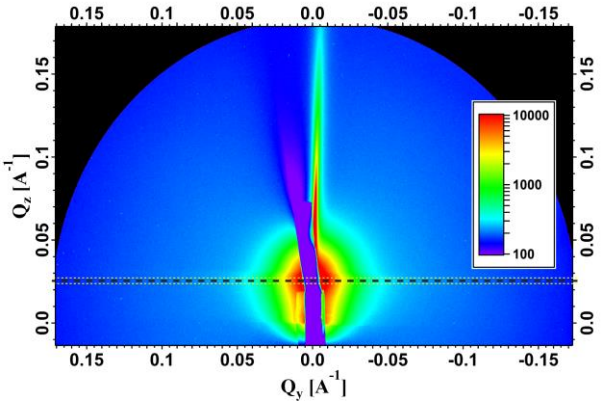


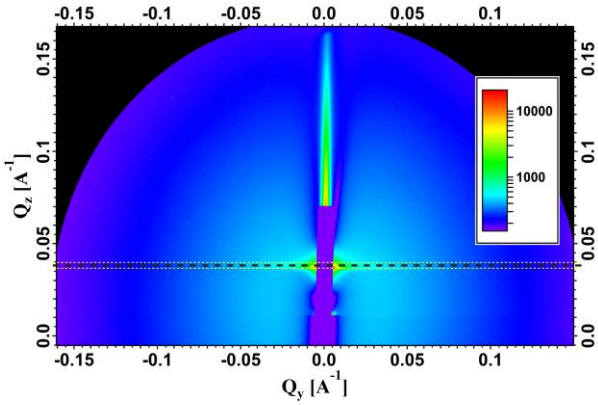
Figure S6. Cyclic voltammetry (CV) results for PTB(THP). The HOMO and LUMO of PTB(THP) are found at -4.9 eV and -3.4 eV respectively, corresponding to a bandgap of 1.5 eV, which is consistent with the optical bandgap of 1.57 eV found through UV-vis spectroscopy.


0.15 0.1 0.05 0.0 -0.05 -0.1 -0.15
Qz [A-1]
Qy [A-1]
1000
100
10

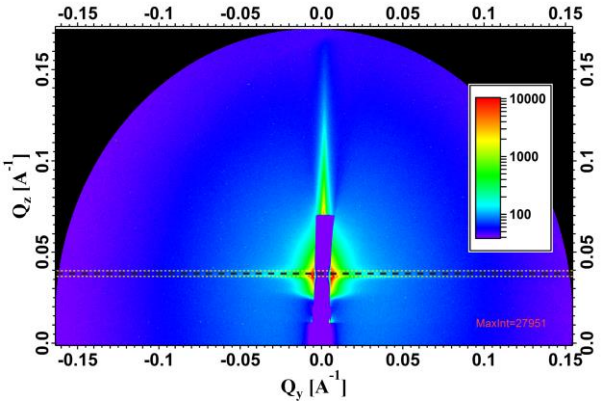
(a)


0.15 0.1 0.05 0.0 -0.05 -0.1 -0.15
Qz [A-1]
Qy [A-1]
10000
1000
100

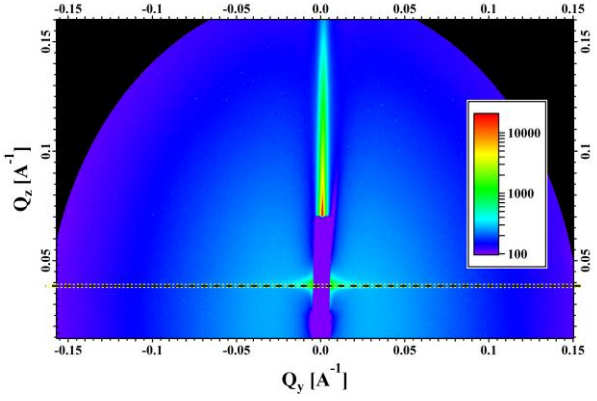
(b)


-0.15 -0.1 -0.05 0.0 0.05 0.1
Qz [A-1]
Qy [A-1]
10000
1000

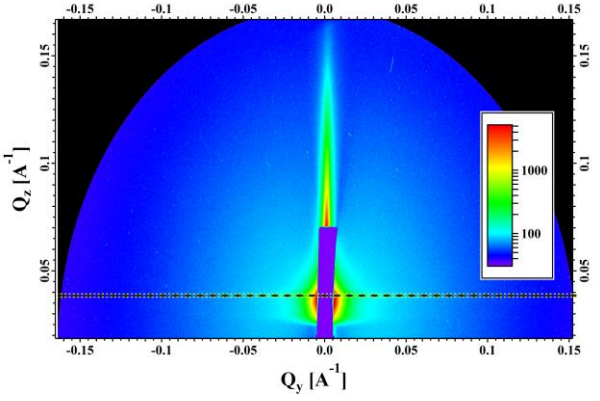
(c)


-0.15 -0.1 -0.05 0.0 0.05 0.1 0.15
Qz [A-1]
Qy [A-1]
10000
1000
100
MaxInt=27951

(d)


-0.15 -0.1 -0.05 0.0 0.05 0.1 0.15
Qz [A-1]
Qy [A-1]
10000
1000
100

(e)


-0.15 -0.1 -0.05 0.0 0.05 0.1 0.15
Qz [A-1]
Qy [A-1]
1000
100

(f)

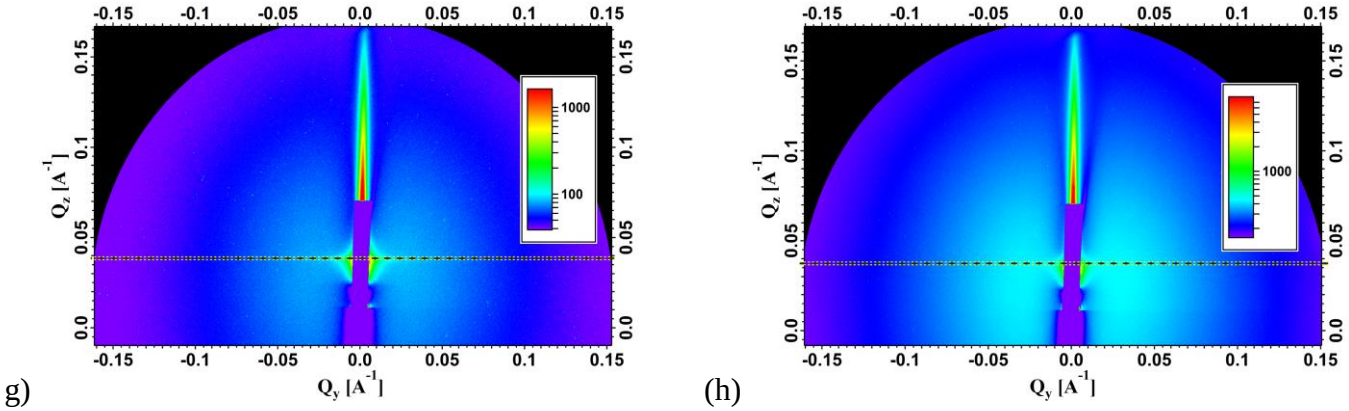


Figure S7. GISAXS data for P3HT:PCBM films thermally annealed for (a) 0 and (b) 6 hr; PTB4:PCBM films thermally annealed for (c) 0 and (d) 6 hr; PTB(THP):PCBM films thermally annealed for (e) 0 and (f) 6 hr; and dPTB(THP):PCBM films thermally annealed for (g) 0 and (h) 6 hr.

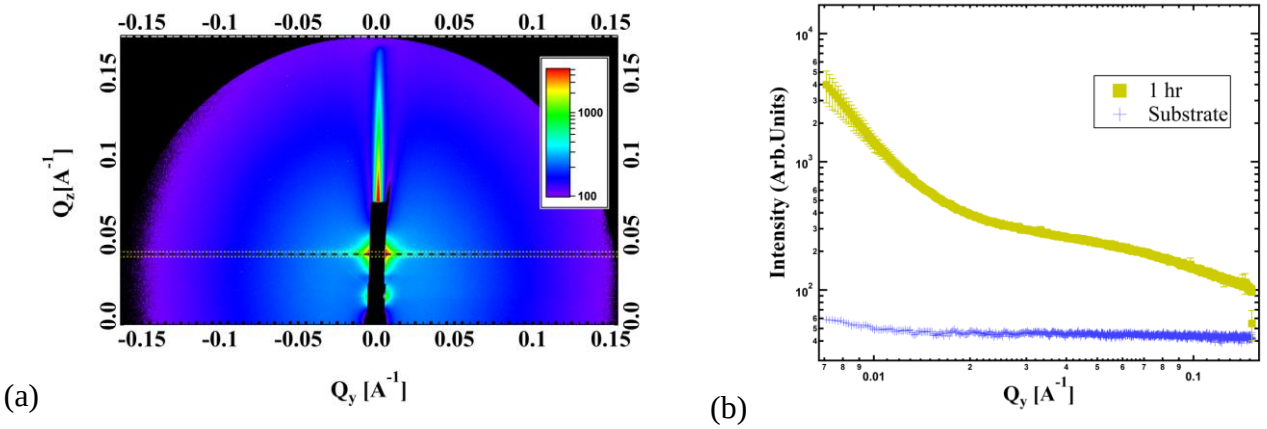


Figure S8. (a) GISAXS data for PTB4:PCBM blend film thermally annealed for 1 hr. (b) The data is integrated along a stripe 10 pixels in width parallel to the Q_y axis at the position of specular beam. Results for scattering from a bare substrates are included for comparison.