Electronic Supplementary Information

Enhancing P3HT/PCBM blend stability by thermal crosslinking using poly(3-hexylthiophene)-*S,S*-dioxide

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1. X-Ray Photoelectron Spectroscopy (XPS)

Low-resolution XPS analysis of P3HT-TDO shows significant presence of oxygen, in comparison with P3HT, due to oxidation of sulfur atoms.

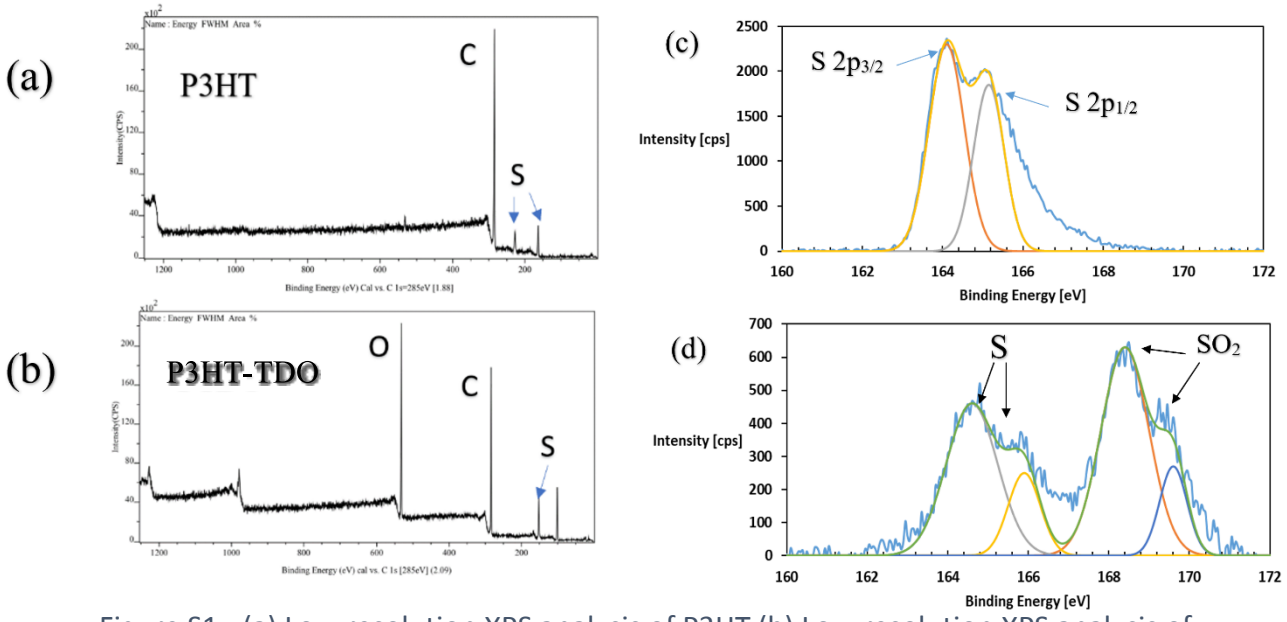

Figure S1 - (a) Low resolution XPS analysis of P3HT (b) Low resolution XPS analysis of P3HT-TDO (c) XPS analysis deconvolution of S 2p signal in P3HT (d) XPS analysis deconvolution of S 2p signal in P3HT-TDO.

Further XPS analysis was conducted in order to generate atomic compositions of SO_2/S, S/C, and SO_2/C for P3HT-TDO thin films, before and after annealing for 20 min at 150 °C.

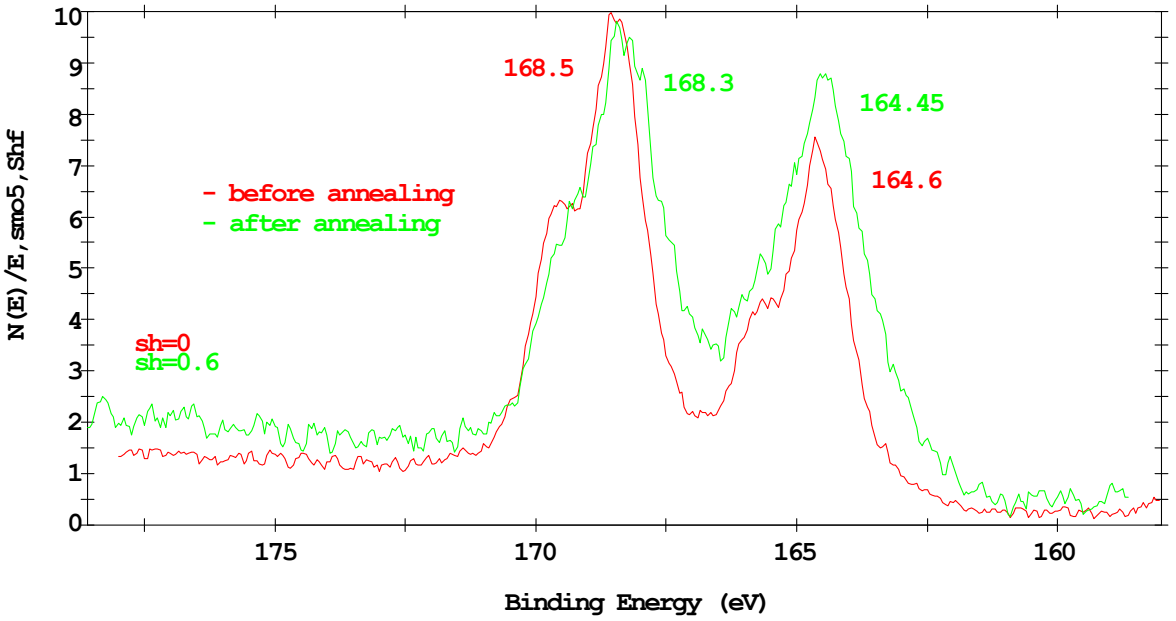

Figure S2 - Low resolution XPS analysis of P3HT-TDO S 2p signal before and after annealing for 20 min at 150 °C.

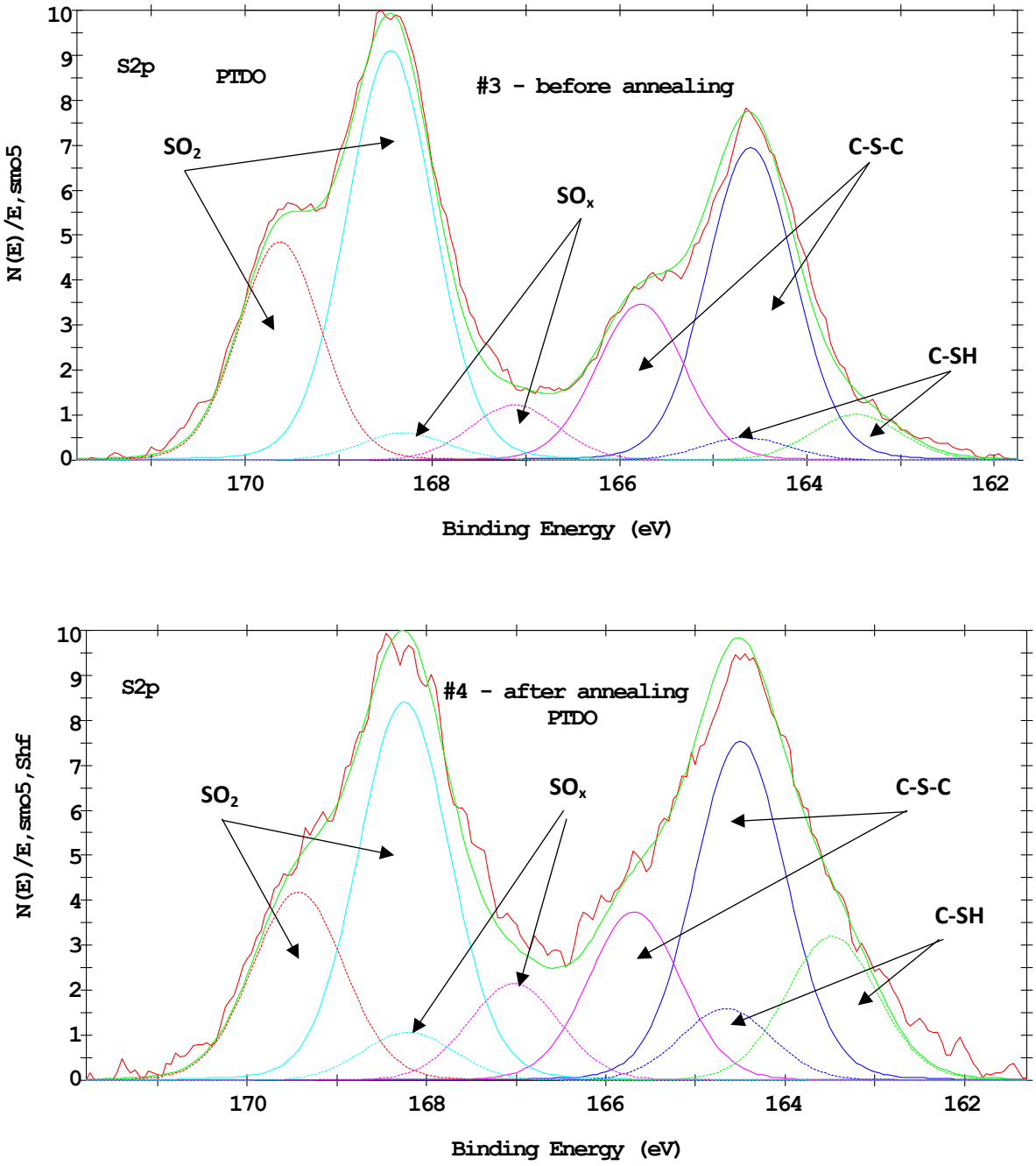

Figure S3 - XPS analysis deconvolution of S 2p signal in P3HT-TDO (a) before and (b) after annealing for 20 min at 150 °C.

Following component bonds were determined from high-resolution XPS analysis of sulfur:

		C-SH	C-S-C	SO_x	SO_2
P3HT-TDO	**Before anneal.**	5.53%	38.02%	6.68%	49.77%
		Total C-S - 43.55%		**Total SO_x – 56.45%**	
	After anneal.	15.01%	35.36%	10.01%	39.54%
		Total C-S - 50.37%		**Total SO_x – 49.55%**	

Table S1 – Component bonds percentage in P3HT-TDO XPS analysis of S 2p signal before and after annealing for 20 min at 150 °C.

Following atomic compositions were determined from high-resolution XPS analysis of S/C for P3HT-TDO and P3HT/P3HT-TDO (1:1) thin films, before and after annealing for 20 min at 150 °C.

	P3HT-TDO **Before annealing**	**P3HT-TDO** **After annealing**
C	**70.87 %**	**73.37 %**
S	**4.18 %**	**3.45 %**

Table S2 – Atomic compositions percentage in P3HT-TDO XPS analysis before and after annealing for 20 min at 150 °C.

Summary of SO_2/S, S/C, and SO_2/C for P3HT-TDO thin film, before and after annealing for 20 min at 150 °C:

	P3HT-TDO **Before annealing**	**P3HT-TDO** **After annealing**
SO_2 : S	**1.30 : 1**	**0.98 : 1**
C : SO_2	**30.03 : 1**	**42.91 : 1**
C : S_{total}	**17.95 : 1**	**21.27 : 1**

Table S3 – Atomic compositions ratios in P3HT-TDO XPS analysis before and after annealing for 20 min at 150 °C.

2. Attenuated Total Reflectance

Oxidation of thiophene units was confirmed by ATR infrared analysis with peaks at 1142cm^{-1} and 1314cm^{-1} corresponding to symmetric and asymmetric stretching of SO_2 accordingly (see Fig. 1). Additional groups appear at 1714 cm^{-1} and 1770 cm^{-1} which are probably the result of additional oxidation reactions of P3HT with mCPBA.

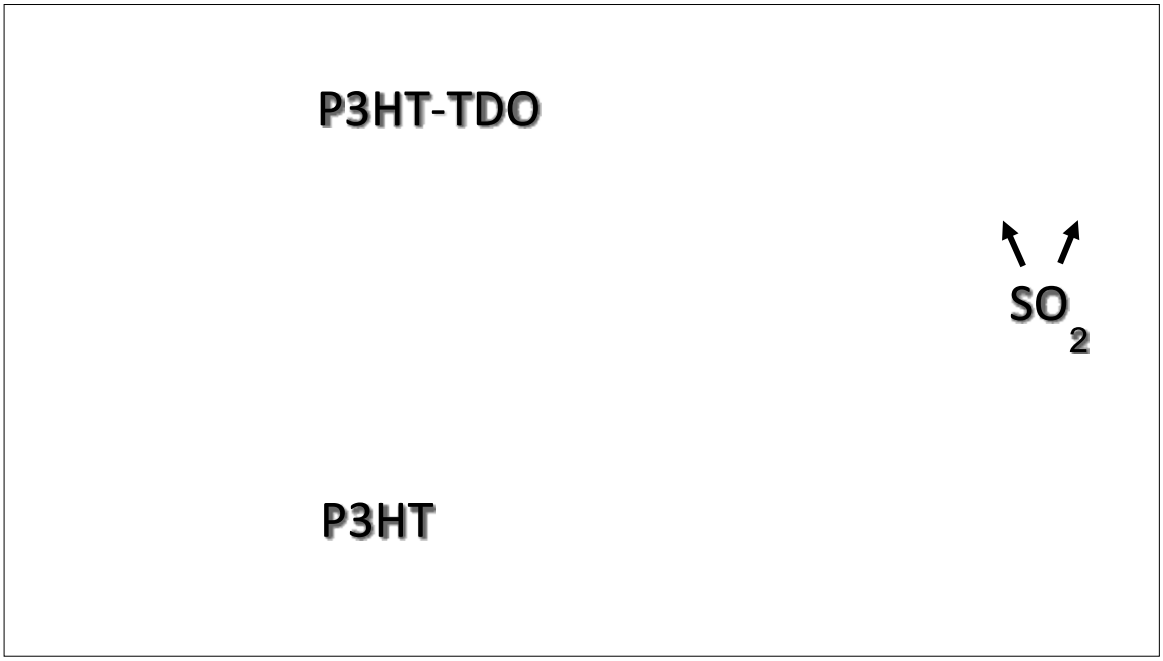

Figure S4 - FTIR spectrum of P3HT and P3HT-TDO.

3. [1]H-NMR Analysis

To analyze the structure of P3HT-TDO in more detailed manner, [1]H-NMR analysis was performed. It can be seen that [1]H-NMR spectrum of P3HT-TDO have several noticeable differences in comparison with P3HT. Aromatic protons at δ 6.98 ppm shifts to δ7.35 ppm due to oxidation of the thiophene rings. Protons in α position on alkyl chain display two signals – δ 2.76 ppm attributed to unoxidized thiophene rings and δ 2.95 ppm attributed to oxidized thiophene

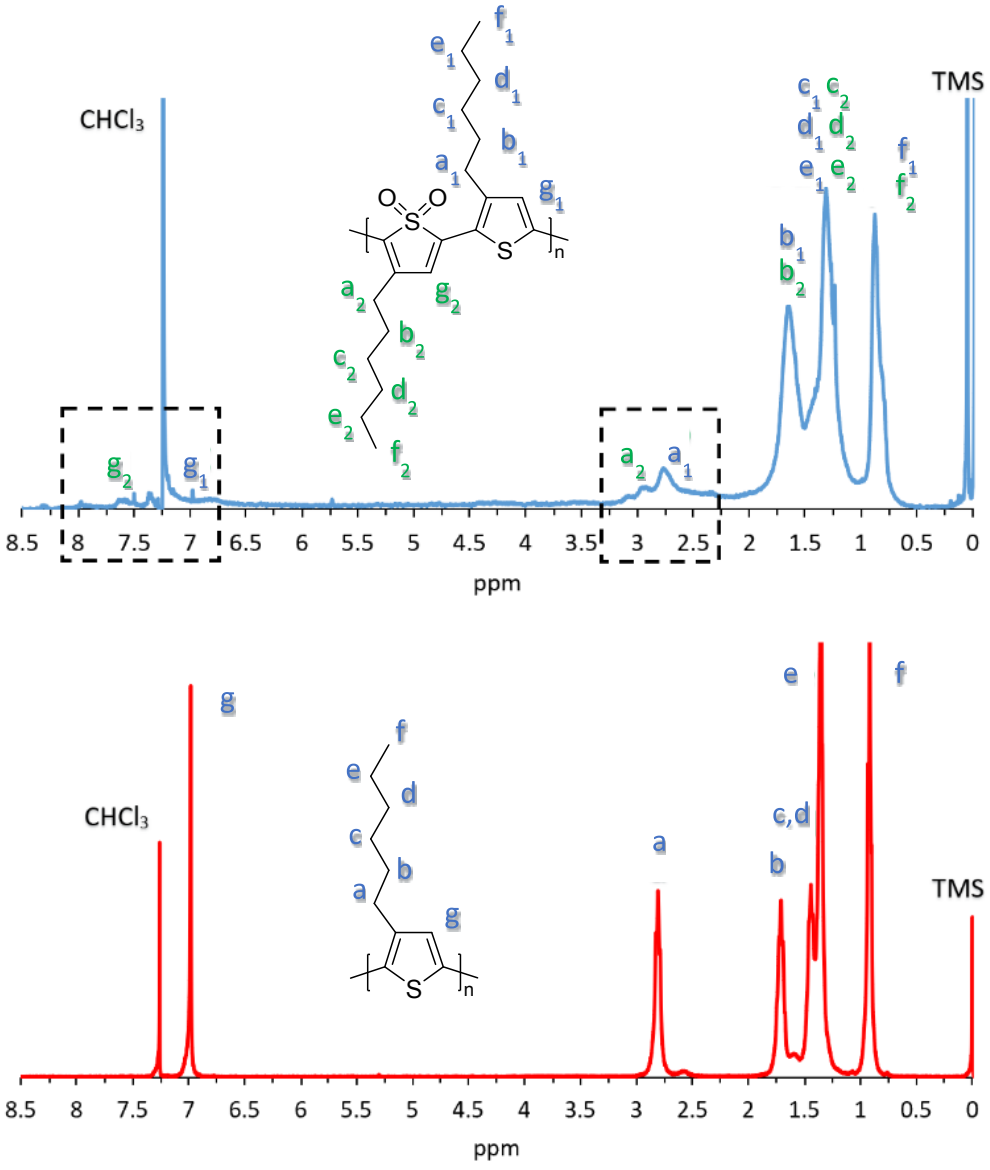

Figure S5 - [1]H-NMR spectra of P3HT-TDO (a) and P3HT(b).

rings.

4. DSC Analysis

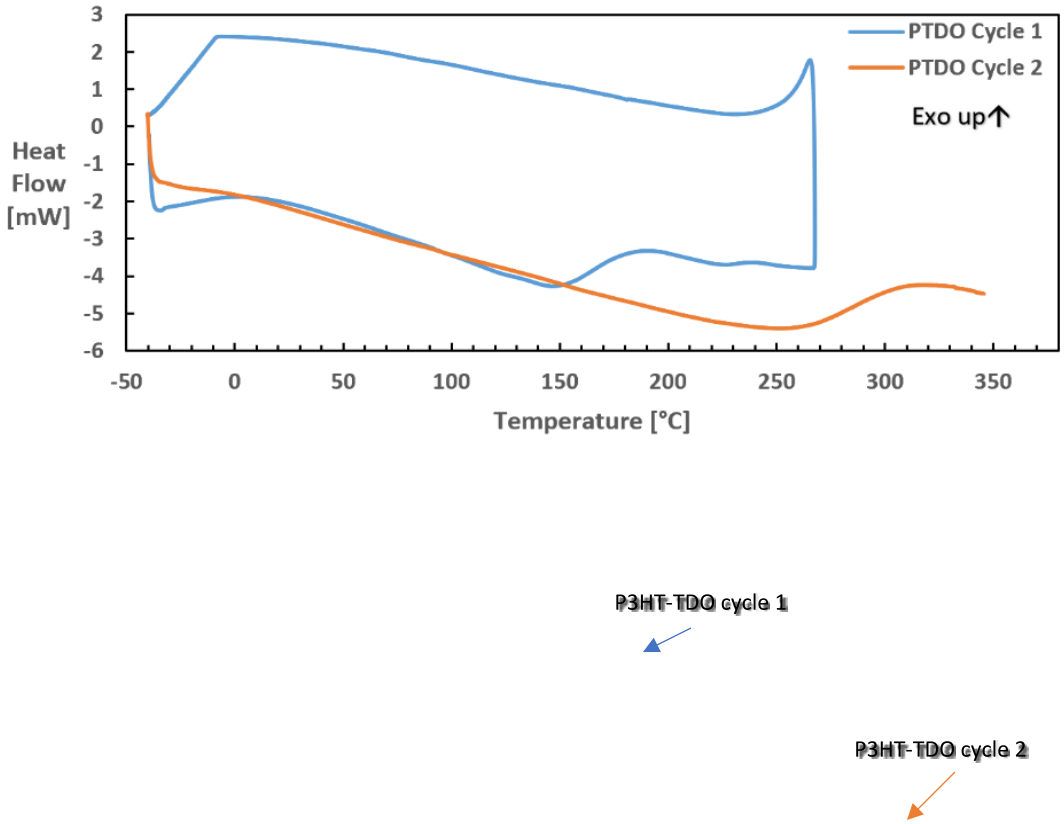

Figure S6 - DSC analysis of P3HT-TDO.

5. TGA-IR Analysis

FTIR analysis of gaseous products was performed on bulk P3HT-TDO via TGA-FTIR apparatus under air atmosphere. P3HT-TDO analysis shows presence of CO_2, SO_2 and gaseous polymer segments (Figure S3). Gaseous SO_2 evolved in two stages, first stage related to cross-

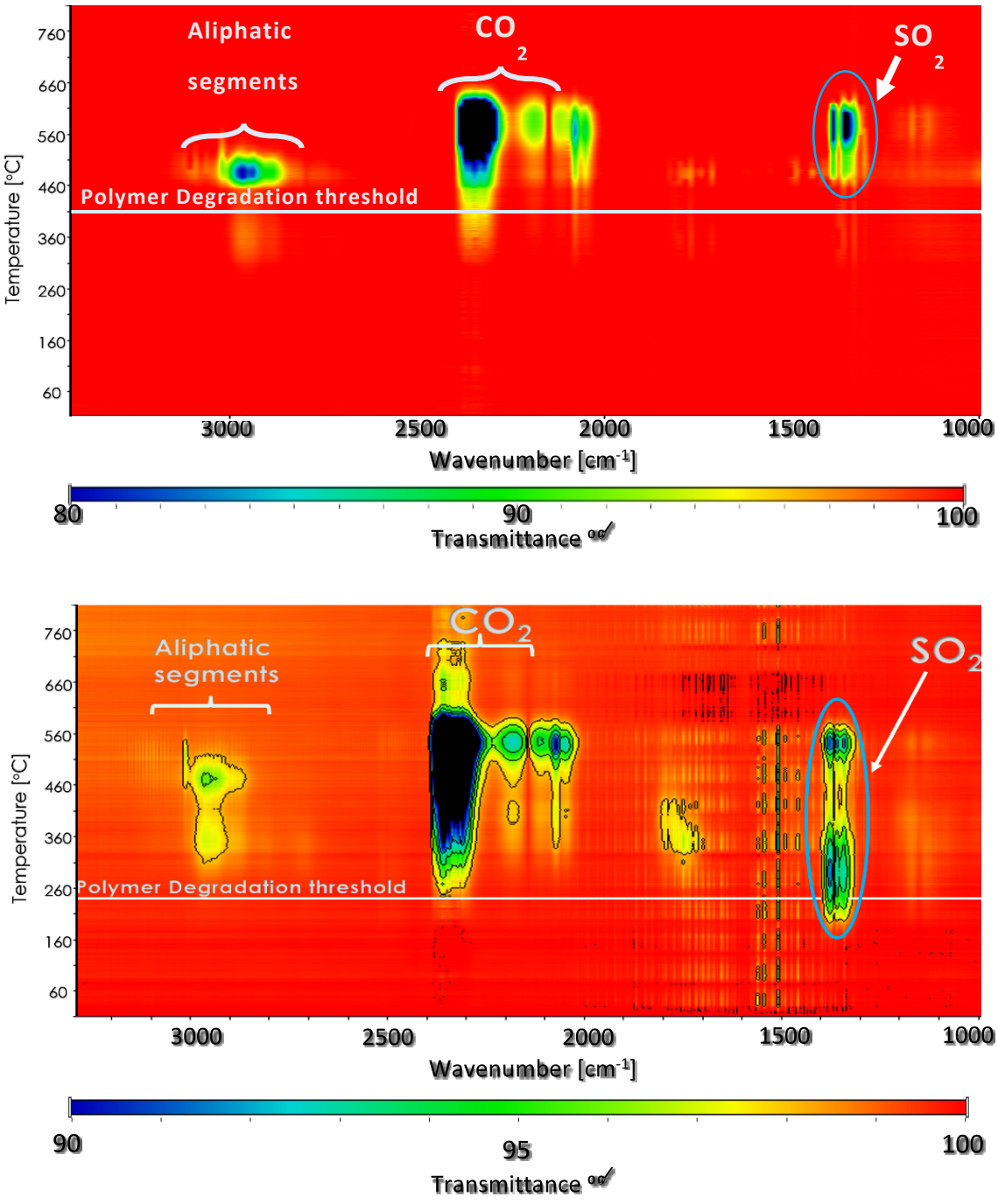

Figure S7 - TGA-IR analysis of TGA gaseous products transmittance as function of temperature at different wavenumbers for (a) P3HT (b) P3HT-TDO.

linking reaction while the second stage corresponds to thermal decomposition of the polymer. Transmittance analysis shows release of SO_2 between 150°C and 420°C in the first stage associated with cross-linking, while release of CO_2 begins only at 250°C. Analysis of P3HT under same conditions shows no significant presence of SO_2 or CO_2 up to 300°C, while release of SO_2 is correlated with release of CO_2 – both due to thermal oxidation and decomposition of polymer structure.

6. PCBM crystal formation kinetics

P3HT/P3HT-TDO/PCBM thin films were prepared from 20 mg/ml solution in chlorobenzene (0.5:0.5:1; w/w) with 20 mg/ml P3HT/PCBM films as reference (1:1; w/w). The films were annealed at 170°C, 150°C and 130°C under vacuum for different periods of time.

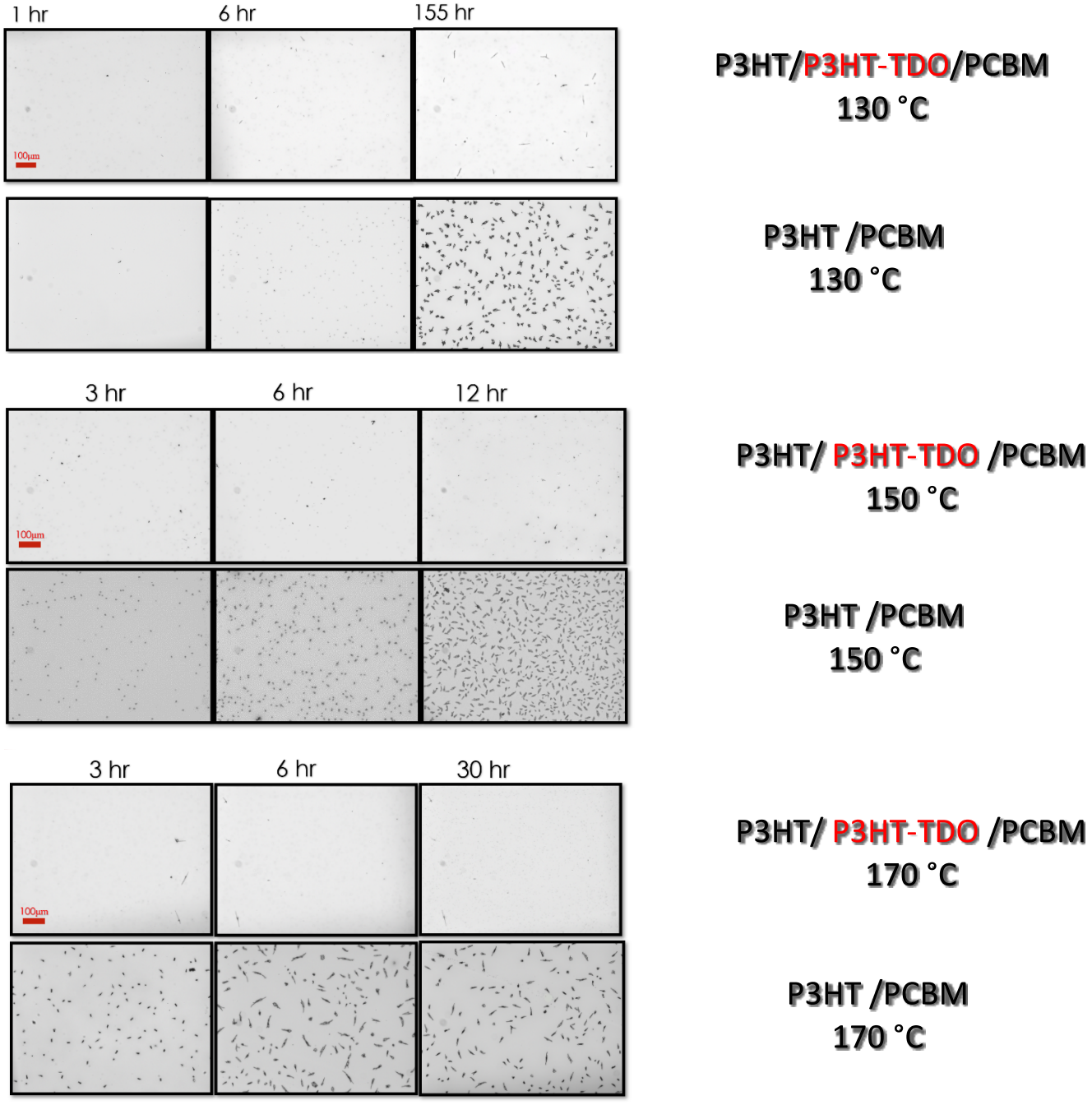

Figure S8 - Microscopy images of thin films of P3HT/PCBM and P3HT/P3HT-TDO/PCBM annealed at different temperatures and periods of time.

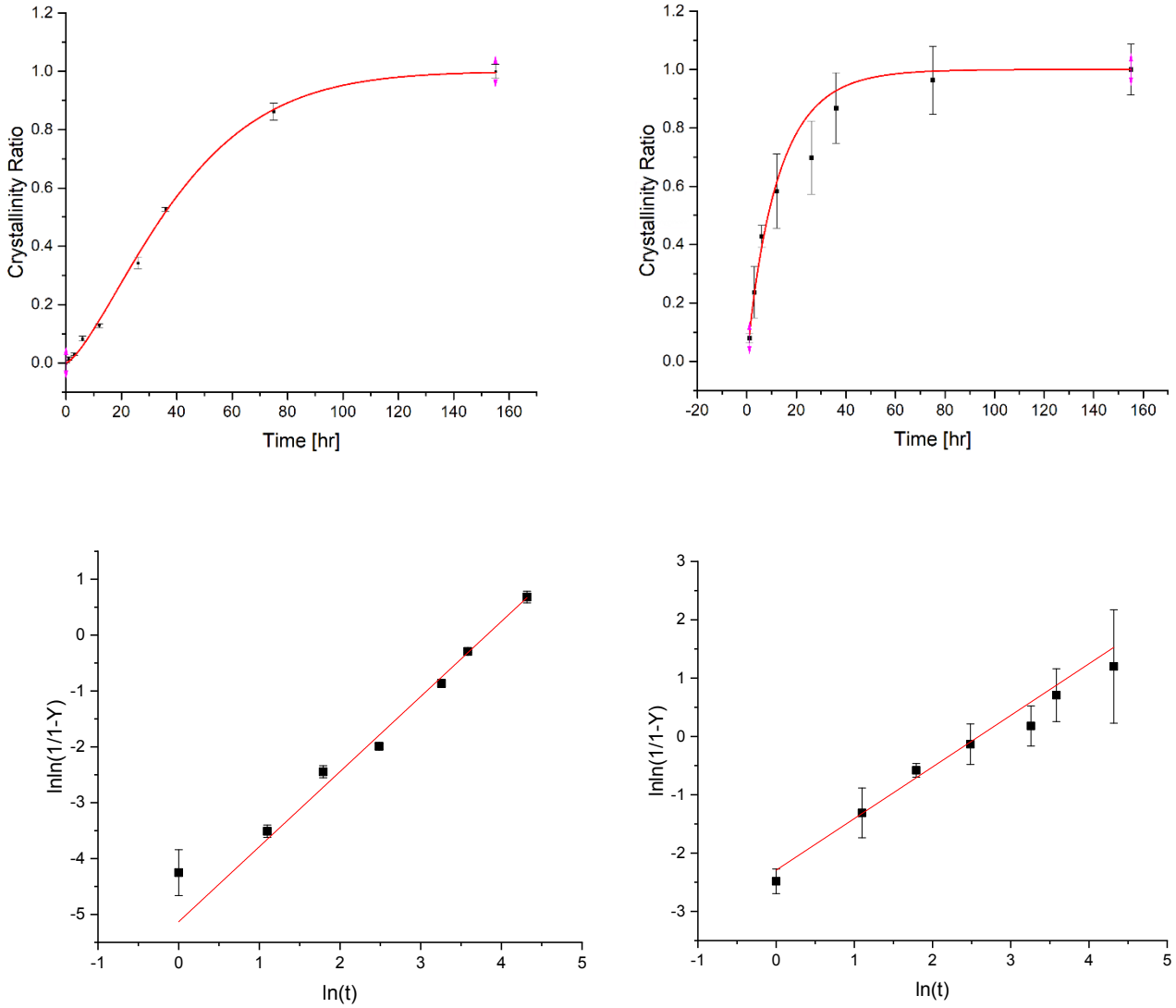

Figure S9. Kinetics of PCBM crystal growth in (a) P3HT/PCBM and (b) P3HT/P3HT-TDO/PCBM anne[redacted]30°C. Linearized expression of crystal growth for (c) P3HT/PCBM and (d) P3HT[redacted]DO/PCBM (parameter Y is crystallinity Ratio).

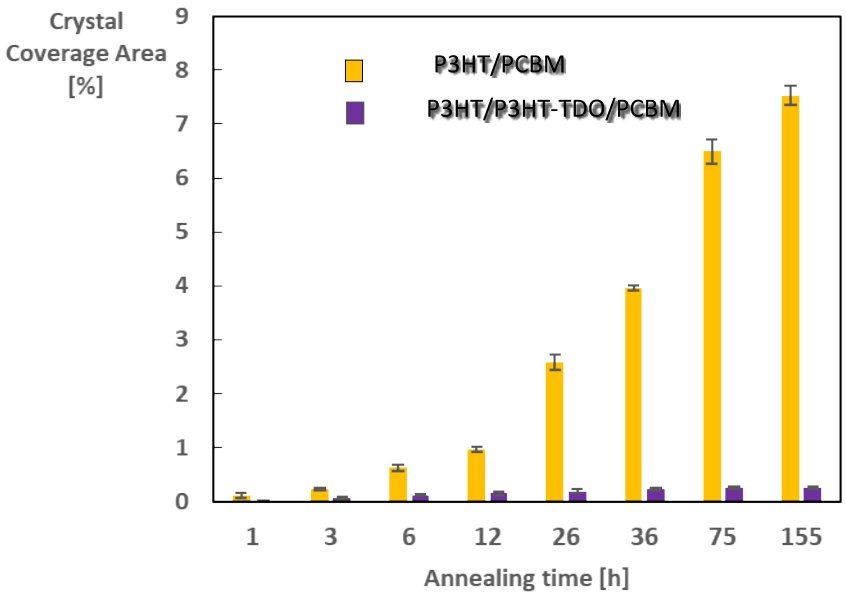

Figure S10 - Percent areas of P3HT/PCBM and P3HT/P3HT-TDO/PCBM thin films covered by PCBM crystals as a function of annealing time at 130 °C calculated based on microscopy images.

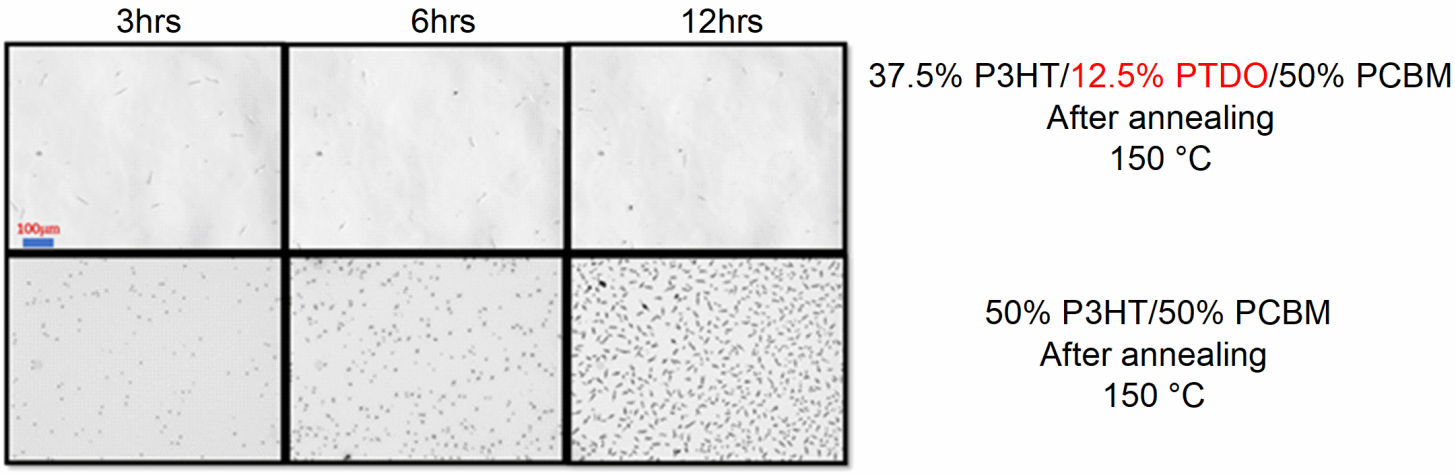

Figure S11 - Microscopy images of thin films of P3HT/PCBM and P3HT/P3HT-TDO/PCBM with 12.5% PTDO, annealed at 150 °C for different periods of time.

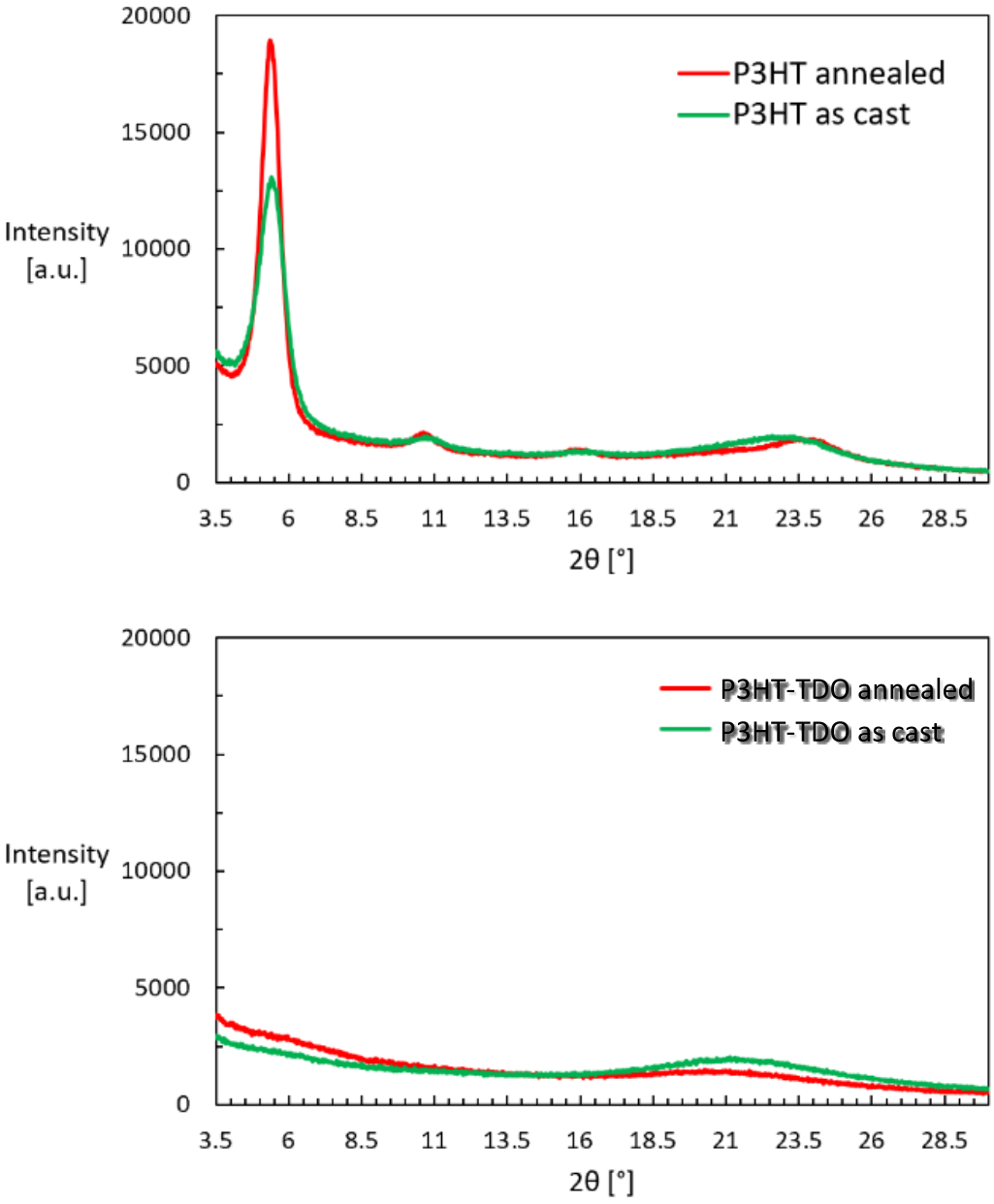

Figure S12- XRD analysis of (a) P3HT and (b)P3HT-TDO thin films as cast and after annealing.