## Organic photovoltaics based on a cross-linkable PCPDTBT analogue; synthesis, morphological studies, solar cell performance and enhanced lifetime

Huw Waters, Shu-Wei Chang, Jeff Kettle\*, Chun-Jen Su, Wei-Ru Wu, U-Ser Jeng, Ya-Ching Tsai, and Masaki Horie\*

School of Electronic Engineering, Bangor University, Dean st., Bangor, Gwynedd, LL57 1UT, Wales, UK.

Frontier Research Center on Fundamental and Applied Sciences of Matters, Department of Chemical Engineering, National Tsing-Hua University, 101, Sec. 2, Kuang-Fu Road, Hsin-Chu, 30013 Taiwan.

National Synchrotron Radiation Research Center, 101, Hsin-Ann Rd. Science Park, Hsinchu, 30076, Taiwan

## **Supplementary Information**

## **Correspondence Address**

Dr. Jeff Kettle

School of Electronic Engineering, Bangor University, Dean st., Bangor, Gwynedd, LL57 1UT, Wales, UK.

E-mail: j.kettle@bangor.ac.uk

## **Co-correspondence Address**

Dr. Masaki Horie

Department of Chemical Engineering, National Tsing-Hua University, 101, Sec. 2, Kuang-Fu Road, Hsin-Chu, 30013 Taiwan.

E-mail: mhorie@mx.nthu.edu.tw



**Fig. SI-1** <sup>1</sup>H and <sup>13</sup>C NMR (500 MHz, CDCl<sub>3</sub>) spectra of 4,4-bis(5-hexenyl)-CPDT.



Fig. SI-2 <sup>1</sup>H and <sup>13</sup>C NMR (500 MHz, CDCl<sub>3</sub>) spectra of 2,6-dibromo-4,4-bis(5-hexenyl)-CPDT.



Fig. SI-3 FAB mass spectrum of 4,4-bis(5-hexenyl)-CPDT.



Fig. SI-4 FAB mass spectrum of 2,6-dibromo-4,4-bis(5-hexenyl)-CPDT.



**Fig. SI-5** <sup>1</sup>H NMR (500 MHz, CDCl<sub>3</sub>) spectrum of polymer **5**.



**Fig. SI-6** <sup>1</sup>H NMR spectrum (500 MHz,  $CDCl_3$ ) of resulting product(s) of the model reaction. Integration ratio between -OMe and -CH<sub>3</sub> is 2:1, supposed two anisole additives.



**Fig. SI-7** ESI mass spectrum of resulting product(s) of the model reaction.  $[M - OMe_2]^+ = 279$ , supposed two anisole additives.



(b)

**Fig. SI-8** Fourier Transform infrared (FTIR) measurements of polymers **4**, and **7** before and after crosslinking/annealing. Polymer 7 showed consistent changes to polymer **5**. Polymer **4** and **6** (not shown) displayed minor changes due to lower reactive site concentration (5%)

(a)



(c)

**Fig. SI-9** Photographic images of vials of (a) polymer **4**, (b) polymer **5** and (c) polymer **6** before (left hand vial) and after crosslinking (right hand vial).

**S**8



(c)

Annealed at	$V_{OC}(V)$	$J_{SC}$ (mA/cm <sup>2</sup> )	FF	PCE (%)
80°C				
Polymer 4	0.6351	12.84	44.75	3.65
Polymer 5	0.6591	12.44	46.24	3.80

**Fig. SI-10** (a) OPV performance of 5 after annealing the active layer at 260°C; no photocurrent was observed due to PCBM aggregation and PEDOT:PSS degradation. Similar performance was observed in polymer 4 after annealing the active layer at 260°C. The likely cause was due to PCBM aggregation and also PEDOT:PSS degradation. Figure (b) shows the active layer surface before and after annealing at 260°C for a  $5x5\mu m$  area showing PCBM aggregation. Both polymer 4 and 5 performed well at temperatures below crosslinking temperatures (see table SI-10 c)



**Fig. SI-11** Absorption spectra of (a) **1** and **6** (neat) at 100nm film thickness and (b) **1** and **6** blended with  $PCB_{71}BM$  and using 1,8-octanedithiol processing additive at 120nm film thickness.