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

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Supplementary Information

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Fig. SI-1 $^1\text{H}$ and $^{13}\text{C}$ NMR (500 MHz, CDCl$_3$) spectra of 4,4-bis(5-hexenyl)-CPDT.
Fig. SI-2 ¹H and ¹³C NMR (500 MHz, CDCl₃) 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 $^1$H NMR (500 MHz, CDCl$_3$) spectrum of polymer 5.
Scheme SI-1. Model reaction

\[ \text{excess} \quad \text{Br} \quad \text{OMe} \quad \xrightarrow{\text{Pd(PPh\textsubscript{3})\textsubscript{4}, K\textsubscript{2}CO\textsubscript{3}}} \quad \text{toluene} \quad \text{R = H and 2 of } \text{OMe} \]

**Fig. SI-6** \( ^1\text{H} \) NMR spectrum (500 MHz, CDCl\textsubscript{3}) of resulting product(s) of the model reaction. Integration ratio between -OMe and -CH\textsubscript{3} is 2:1, supposed two anisole additives.
Fig. SI-7 ESI mass spectrum of resulting product(s) of the model reaction. [M – OMe₂]^+ = 279, supposed two anisole additives.
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%).

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).
Annealed at 80°C

<table>
<thead>
<tr>
<th></th>
<th>$V_{OC}$ (V)</th>
<th>$J_{SC}$ (mA/cm$^2$)</th>
<th>FF</th>
<th>PCE (%)</th>
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<tr>
<td>Polymer 4</td>
<td>0.6351</td>
<td>12.84</td>
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<td>Polymer 5</td>
<td>0.6591</td>
<td>12.44</td>
<td>46.24</td>
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**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 5x5μm 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 PCB71BM and using 1,8-octanedithiol processing additive at 120nm film thickness.