Electronic Supplementary Information (ESI)

Relating polymer chemical structure to the stability of polymer:fullerene solar cells

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1. Synthesis of BDT-monomers
All reactions were performed using oven-dried glassware and dry solvents unless otherwise specified. THF was taken from an Mbraun solvent purification system (SPS-800). All other reagents were purchased from Sigma–Aldrich, TCI Europe, or Acros Organics and were used without further purification unless noted otherwise. $^1$H NMR spectra were recorded on a Varian AMX600 (600MHz). Chemical shift values are reported in ppm with the solvent resonance as the internal standard. Data are reported as follows: chemical shifts, multiplicity (s = singlet, d = doublet, t = triplet, q = quartet, dd = double doublet, dq = double quartet, qd = quarter doublet, m = multiplet, br = broad), coupling constants (Hz), and integration. Flash chromatography: Merck silica gel type 9385 230–400 mesh. TLC: Merck silica gel 60, 0.25 mm. Compounds were visualised by UV.

1.1. Synthetic Procedures of $M_{R-O}$:

Benzo[1,2-b:4,5-b']dithiophene-4,8-dione was synthesized according to previously reported methods.$^1$

4,8-bis((2-ethylhexyl)oxy)benzo[1,2-b:4,5-b']dithiophene: 4,8-dihydrobenzo[1,2-b:4,5-b']-dithiophen-4,8-dione (0.22 g, 1.0 mmol), zinc powder (0.16 g, 2.5 mmol), and water (6 mL) were put into a 25 mL flask, then NaOH (0.6 g, 15.0 mmol) was added into the mixture. After the mixture was stirred and refluxed for 1 hour, 1-bromoisooctane (0.58 g, 3.0 mmol) and a catalytic amount of tetrabutylammonium bromide (0.06 g, 0.2 mmol) were added into the flask. The reactant was refluxed for 8 hours and then was poured into cold water and extracted by diethyl ether three times. The organic layer was dried over anhydrous MgSO$_4$. After the solvent had been removed, the crude product was purified by column chromatography (hexane/DCM: 8/2). Compound 2 (0.28 g, yield 62%) was obtained as a pale yellow oil. $^1$H NMR (400 MHz, CDCl$_3$) $\delta$ 7.48 (d, $J = 5.2$ Hz, 2H), 7.37 (d, $J = 5.6$ Hz, 2H), 4.18 (d, $J = 5.6$ Hz, 4H), 1.85–1.75 (m, 2H), 1.73–1.49 (br, 8H), 1.46-1.37 (br, 8H), 1.01 (t, $J = 7.4$ Hz, 6H), 0.94 (t, $J = 7.2$ Hz, 6H).
1.2. Synthetic Procedures of M_{R-T}:

BDT-Monomer (M_{R-T})

\[
\begin{align*}
1 & + 3 \\
\text{1) n-BuLi, THF} & \text{2) SnCl}_2\cdot2\text{H}_2\text{O, HCl}
\end{align*}
\]

2-(2-ethylhexyl)thiophene (3) was synthesized according to previously reported methods.\(^2\)

4,8-bis(5-(2-ethylhexyl)thiophen-2-yl)benzo[1,2-b:4,5-b']dithiophene (4): 3.0 mL of n-Butyllithium (4.8 mmol, 1.6 M) was added dropwise to the solution of 2-(2-ethylhexyl)thiophene (0.79 g, 4.0 mmol) in 12 mL of anhydrous THF at -30° C under nitrogen atmosphere. The mixture was heated up to 50° C for 2 hours. Then the solvent was cooled in ice-water bath, subsequently, 4,8-dihydrobenzo[1,2-b:4,5-b']-dithiophen-4,8-dione (0.22 g, 1.0 mmol) was added in one portion, and the mixture was heated at 50° C for another 2 hours. After cooling the mixture down to RT, a mixture of SnCl\(_2\cdot2\text{H}_2\text{O} (1.81 g, 8.0 mmol) in 5 mL of aqueous HCl (10%) was added, and the mixture was stirred overnight. The reaction mixture was poured into cold water and extracted by diethyl ether three times. The combined organic layer was washed with water and brine, dried with MgSO\(_4\), filtered, concentrated via rotary evaporation. Further purification was carried out by column chromatography on silica gel eluting with petroleum ether to obtain pure compound 4 as a yellow liquid (0.44 g, 77%). \(^1\)H NMR (400 MHz, CDCl\(_3\)) \(\delta 7.65 (d, J = 6.0 \text{ Hz}, 2H), 7.46 (d, J = 5.6 \text{ Hz}, 2H), 7.30 (d, J = 3.2 \text{ Hz}, 2H), 6.89 (d, J = 3.2 \text{ Hz}, 2H), 2.86 (d, J = 6.8 \text{ Hz}, 4H), 1.72–1.65 (m, 2H), 1.47-1.26 (br, 16H), 0.97-0.89 (m, 12H).

2. Absorption
Fig. s1: Absorption spectra of (a,b) R-T devices with onset Red-shifted compared to R-O devices; and of unexposed (Blue) and exposed (Red) films of (c) R-O\textsubscript{2} and (d) R-T\textsubscript{2}.

3. Effects of DIO

Table s1: Photovoltaic performances of conventional PSCs of the different blends with and without DIO under same conditions. Average values are for at least 20 selected devices without DIO, and for a lesser number of devices with DIO.
<table>
<thead>
<tr>
<th>Devices</th>
<th>L. (nm)</th>
<th>J_sc (mA.cm(^{-2}))</th>
<th>V_oc (mV)</th>
<th>FF (%)</th>
<th>PCE (%)</th>
<th>Average PCE (%)</th>
</tr>
</thead>
<tbody>
<tr>
<td>PTB7 DIO</td>
<td>~100</td>
<td>10.10</td>
<td>798</td>
<td>56.4</td>
<td>4.54</td>
<td>4.22±0.51</td>
</tr>
<tr>
<td>PTB7-Th DIO</td>
<td>~110</td>
<td>15.60</td>
<td>804</td>
<td>68.7</td>
<td>8.62</td>
<td>8.67±0.40</td>
</tr>
<tr>
<td>PBDTTT-C DIO</td>
<td>~130</td>
<td>12.33</td>
<td>743</td>
<td>45.5</td>
<td>4.17</td>
<td>3.78±0.20</td>
</tr>
<tr>
<td>PBDTTT-C-T DIO</td>
<td>~110</td>
<td>11.32</td>
<td>839</td>
<td>54.8</td>
<td>5.21</td>
<td>5.27±0.28</td>
</tr>
</tbody>
</table>

Fig. s2: Current-Voltage characteristics of blend devices with and without DIO of (a) R-O\(_1\), and (b) all polymers; (c) PCE degradation curves of blend R-O\(_1\) devices with and without DIO.

4. PCE Degradation Curves for Different Interfaces
Fig. s3: Current-Voltage characteristics PCE degradation curves: of devices (just with ITO) without PEDOT:PSS (a) R-O₁ and R-T₁ and (b) R-O₂ and R-T₂; of devices with pH-neutral PEDOT:PSS (c) R-O₁ and R-T₁ and (d) R-O₂ and R-T₂; and of devices with (e) Ca/Al as top electrodes.

5. ¹HNMR Spectrum
1H NMR Spectrum after 10 min's exposure

1H NMR Spectrum after 20 min's exposure

1H NMR Spectrum after 30 min's exposure

1H NMR Spectrum after 40 min's exposure

1H NMR Spectrum after 50 min's exposure

1H NMR Spectrum after 60 min's exposure

1H NMR Spectrum after 70 min's exposure

1H NMR Spectrum after 80 min's exposure

1H NMR Spectrum after 90 min's exposure

1H NMR Spectrum after 100 min's exposure

Original 1H NMR Spectrum

BDT-monomer (M_{R-O})

(2)
(3)

1H NMR Spectrum after 70 min's exposure with integration

BDT-monomer (M\textsubscript{R-O})

1H NMR Spectrum after 10 min's exposure with integration

(b)

1H NMR spectrum after 100 min's exposure

1H NMR spectrum after 90 min's exposure

1H NMR spectrum after 80 min's exposure

1H NMR spectrum after 70 min's exposure

1H NMR spectrum after 60 min's exposure

1H NMR spectrum after 50 min's exposure

1H NMR spectrum after 40 min's exposure

1H NMR spectrum after 30 min's exposure

1H NMR spectrum after 20 min's exposure

1H NMR spectrum after 10 min's exposure

Original 1H NMR Spectrum
Fig. s4: \(^1\)H NMR spectra (initial and after exposure to a shuttered UV flood light in steps of 10 mins for 100 mins) of monomer solutions of (a) R-O (P1 ~ 1\(^{st}\) peak to P10 ~ 10\(^{th}\) peak) and (b) R-T (P1 ~ 1\(^{st}\) peak to P11 ~ 11\(^{th}\) peak). Normal (1) and relative integrated peaks to: (2) solvent (CDCl\(_3\)) and (3) for peaks >7.3 ppm and between 0.5 and 2.25 ppm as used in fig. 2f,g.
6. Charge Transport

Fig. s5: Current-Voltage characteristics of unexposed (Blue if R-T, Red if R-O) and exposed (1 hour – Brown) (a) pristine R-T\textsubscript{2} polymer hole only device; (b) pristine R-O\textsubscript{2} polymer hole only device; (c) blend R-T\textsubscript{2} polymer hole only device; (d) blend R-O\textsubscript{2} polymer hole only device; (e) blend R-T\textsubscript{2} polymer electron only devices; and (f) blend R-O\textsubscript{2} polymer electron only device.
7. Light Intensity Measurements

Table S2: $V_{OC}$ light intensity dependence of PSC of the different blends: Light exposure time dependent $n$ values as a function of $n$-Fresh (i.e. $n$ of unexposed devices).

<table>
<thead>
<tr>
<th>Polymer</th>
<th>$n$-Fresh</th>
<th>$n$-1 hour</th>
<th>$n$-2 hours</th>
<th>$n$-3 hours</th>
</tr>
</thead>
<tbody>
<tr>
<td>R-O$_1$</td>
<td>~1.50</td>
<td>~1.16 $n_{Fresh}$</td>
<td>~1.18 $n_{Fresh}$</td>
<td>~1.20 $n_{Fresh}$</td>
</tr>
<tr>
<td>R-T$_1$</td>
<td>~1.09</td>
<td>~1.19 $n_{Fresh}$</td>
<td>~1.23 $n_{Fresh}$</td>
<td>~1.24 $n_{Fresh}$</td>
</tr>
<tr>
<td>R-O$_2$</td>
<td>~1.07</td>
<td>~1.13 $n_{Fresh}$</td>
<td>~1.20 $n_{Fresh}$</td>
<td>~1.24 $n_{Fresh}$</td>
</tr>
<tr>
<td>R-T$_2$</td>
<td>~1.00</td>
<td>~1.20 $n_{Fresh}$</td>
<td>~1.26 $n_{Fresh}$</td>
<td>~1.28 $n_{Fresh}$</td>
</tr>
</tbody>
</table>

Fig. s6: Light Intensity dependence of $V_{OC}$ of (a) R-O$_1$ (PTB7) and R-T$_1$ (PTB7-Th), and (b) R-O$_2$ (PBDTTT-C) and R-T$_2$ (PBDTTT-C-T) blended with [70]PCBM devices.
8. Lamp

![Spectrum of lamp used during the (degradation) experiment.](image)

Fig. s7: Spectrum (black line) of lamp used during the (degradation) experiment.³

9. AFM images

![AFM images of films.](image)

Fig. s8: Two films of PTB7:[70]PCBM spin-coated on glass under the same conditions (a) as cast (1 micron and 200 nm) and (b) after 2 hours UV-exposure (1 micron and 200 nm)

References

