Supporting information

Design of Benzodithiophene-Diketopyrrolopyrrole Based Donor-Acceptor Copolymers for Efficient Organic Field Effect Transistors and Polymer Solar Cells

Jianyu Yuan,
Fengjiao Zhang, Jialing Lu, Zhicun Zai, Chongan Di, Zuoquan Jiang, and Wanli Ma*

\(^{a}\) Institute of Functional Nano & Soft Materials (FUNSOM), Soochow University 199 Ren-Ai Road, Suzhou Industrial Park, Suzhou, Jiangsu 215123, P. R. China

\(^{b}\) Key Laboratory of Organic Solids Institute of Chemistry Chinese Academy of Sciences Beijing 100190, P. R. China

E-mail: wlma@suda.edu.cn; dicha@iccas.ac.cn

Hole Mobility Measure (SCLC)\(^{1}\)

Hole-only devices were fabricated to measure the hole mobility using the space charge limited current (SCLC) method with a device structure of ITO/PEDOT/Active layer/MoO_3/Al. The mobility was determined by fitting the dark current to the model of a single carrier SCLC, described by the equation:

\[
J = \frac{9}{8} \varepsilon_0 \varepsilon_r \mu_h \frac{V^2}{d^3}
\]

where \(J\) is the current density, \(\mu_h\) is the mobility under zero field, \(\varepsilon_0\) is the permittivity of free space, \(\varepsilon_r\) is the material relative permittivity, \(d\) is the active layer thickness, and \(V\) is the effective voltage. The effective voltage can be obtained by subtracting the built-in voltage \((V_{bi})\) and the voltage drop \((V_s)\) from the substrate’s series resistance from the applied voltage \((V_{appl})\), \(V = V_{appl} - V_{bi}\). The hole-mobility can be calculated from the slope of the \(J_{1/2} - V\) curves.
**Figure S1** DSC curves of copolymers at a scanning rate of 10 °C/min under nitrogen.

**Figure S2** AFM tapping-mode images (heights) of copolymers spin-cast from CF on OTS-treated Si-SiO$_2$ substrates under different annealing temperatures.
**Figure S3** Normalized UV–vis. absorption spectra of PBDT-T-TDP in o-DCB at room temperature or 180 °C. The high temperature solution spectra of the polymer shows a 15nm blue-shift compared to the room temperature spectra, indicating a breakup of aggregates.

**Figure S4** $J^{1/2} - V$ characteristics of Polymer/PC$_{71}$BM hole-only devices
Table S1. Summary of field effect mobilities, on/off ratios ($I_{on}/I_{off}$) and threshold voltages (V) for the copolymers

<table>
<thead>
<tr>
<th>Polymer</th>
<th>Annealing Temperature °C</th>
<th>Mobility cm²V⁻¹s⁻¹ Avg(Max)</th>
<th>Threshold Voltage V Avg(Min)</th>
<th>Log($I_{on}/I_{off}$)</th>
</tr>
</thead>
<tbody>
<tr>
<td>PBDT-FDP</td>
<td>RT</td>
<td>0.022(0.026)</td>
<td>-2.3(-0.4)</td>
<td>5-9</td>
</tr>
<tr>
<td></td>
<td>60</td>
<td>0.018(0.023)</td>
<td>-2.9(-2.5)</td>
<td>7</td>
</tr>
<tr>
<td></td>
<td>80</td>
<td>0.023(0.054)</td>
<td>-1.7(-1.7)</td>
<td>6-9</td>
</tr>
<tr>
<td></td>
<td>100</td>
<td>0.010(0.018)</td>
<td>-10.2(-2.6)</td>
<td>6-8</td>
</tr>
<tr>
<td></td>
<td>140</td>
<td>0.016(0.017)</td>
<td>-6.6(-6.0)</td>
<td>6-7</td>
</tr>
<tr>
<td></td>
<td>180</td>
<td>0.026(0.028)</td>
<td>-11.5(-7.9)</td>
<td>8</td>
</tr>
<tr>
<td>PBDT-T-TDP</td>
<td>RT</td>
<td>0.003(0.003)</td>
<td>1.2(0.5)</td>
<td>5-7</td>
</tr>
<tr>
<td></td>
<td>60</td>
<td>0.008(0.011)</td>
<td>-0.3(-1.8)</td>
<td>6-7</td>
</tr>
<tr>
<td></td>
<td>80</td>
<td>0.055(0.106)</td>
<td>0.3(-0.1)</td>
<td>6-8</td>
</tr>
<tr>
<td></td>
<td>100</td>
<td>0.016(0.021)</td>
<td>-1.8(2.0)</td>
<td>6-7</td>
</tr>
<tr>
<td></td>
<td>140</td>
<td>0.029(0.034)</td>
<td>-4.6(-4.4)</td>
<td>7-8</td>
</tr>
<tr>
<td></td>
<td>180</td>
<td>0.025(0.027)</td>
<td>-4.3(-3.5)</td>
<td>6-8</td>
</tr>
<tr>
<td>PBDT-T-FDP</td>
<td>RT</td>
<td>0.052(0.065)</td>
<td>-0.4(-0.3)</td>
<td>7-8</td>
</tr>
<tr>
<td></td>
<td>60</td>
<td>0.089(0.111)</td>
<td>-2.3(-0.7)</td>
<td>8</td>
</tr>
<tr>
<td></td>
<td>80</td>
<td>0.063(0.158)</td>
<td>-4.4(-2.3)</td>
<td>7-9</td>
</tr>
<tr>
<td></td>
<td>100</td>
<td>0.060(0.086)</td>
<td>-5.8(-2.7)</td>
<td>8-10</td>
</tr>
<tr>
<td></td>
<td>140</td>
<td>0.062(0.067)</td>
<td>-4.6(-3.6)</td>
<td>3-8</td>
</tr>
<tr>
<td></td>
<td>180</td>
<td>0.053(0.062)</td>
<td>-4.8(-4.5)</td>
<td>6-8</td>
</tr>
</tbody>
</table>

Table S2. Effect of solvents on the performance of devices using PC₆₀BM

<table>
<thead>
<tr>
<th>Polymer</th>
<th>Solvent</th>
<th>Donor:PC₆₀BM</th>
<th>$J_{sc}$ (mA cm⁻²)</th>
<th>$V_{oc}$ (V)</th>
<th>FF (%)</th>
<th>PCE (%)</th>
</tr>
</thead>
<tbody>
<tr>
<td>PBDT-FDP</td>
<td>o-DCB</td>
<td>1:2</td>
<td>4.47</td>
<td>0.72</td>
<td>59</td>
<td>1.90</td>
</tr>
<tr>
<td>PBDT-FDP</td>
<td>o-DCB, 2% DIO</td>
<td>1:2</td>
<td>7.58</td>
<td>0.73</td>
<td>60</td>
<td>3.32</td>
</tr>
<tr>
<td>PBDT-FDP</td>
<td>CF</td>
<td>1:2</td>
<td>1.93</td>
<td>0.74</td>
<td>55</td>
<td>0.79</td>
</tr>
<tr>
<td>PBDT-FDP</td>
<td>CF, 2% DIO</td>
<td>1:2</td>
<td>7.87</td>
<td>0.73</td>
<td>56</td>
<td>3.24</td>
</tr>
<tr>
<td>PBDT-T-TDP</td>
<td>o-DCB</td>
<td>1:2</td>
<td>8.19</td>
<td>0.68</td>
<td>51</td>
<td>2.85</td>
</tr>
<tr>
<td>PBDT-T-TDP</td>
<td>o-DCB, 2% DIO</td>
<td>1:2</td>
<td>8.41</td>
<td>0.65</td>
<td>52</td>
<td>2.84</td>
</tr>
<tr>
<td>PBDT-T-TDP</td>
<td>CF</td>
<td>1:2</td>
<td>6.37</td>
<td>0.66</td>
<td>41</td>
<td>1.71</td>
</tr>
<tr>
<td>PBDT-T-TDP</td>
<td>CF, 2% DIO</td>
<td>1:2</td>
<td>8.86</td>
<td>0.65</td>
<td>42</td>
<td>2.42</td>
</tr>
<tr>
<td>PBDT-T-FDP</td>
<td>o-DCB</td>
<td>1:2</td>
<td>8.80</td>
<td>0.77</td>
<td>52</td>
<td>3.50</td>
</tr>
<tr>
<td>PBDT-T-FDP</td>
<td>o-DCB, 2% DIO</td>
<td>1:2</td>
<td>6.98</td>
<td>0.73</td>
<td>59</td>
<td>3.03</td>
</tr>
<tr>
<td>PBDT-T-FDP</td>
<td>CF</td>
<td>1:2</td>
<td>9.95</td>
<td>0.76</td>
<td>49</td>
<td>3.74</td>
</tr>
<tr>
<td>PBDT-T-FDP</td>
<td>CF, 2% DIO</td>
<td>1:2</td>
<td>10.80</td>
<td>0.78</td>
<td>51</td>
<td>4.25</td>
</tr>
</tbody>
</table>
### Table S3. Effect of solvents on the performance of devices using PC$_{71}$BM

<table>
<thead>
<tr>
<th>Polymer</th>
<th>Solvent</th>
<th>Donor:PC$_{71}$BM mg/mL</th>
<th>RPM</th>
<th>$J_{sc}$ (mA cm$^{-2}$)</th>
<th>$V_{oc}$ (V)</th>
<th>FF (%)</th>
<th>PCE (%)</th>
</tr>
</thead>
<tbody>
<tr>
<td>PBDT-FDP</td>
<td>$o$-DCB</td>
<td>5:10</td>
<td>800</td>
<td>4.97</td>
<td>0.73</td>
<td>61</td>
<td>2.22</td>
</tr>
<tr>
<td>PBDT-FDP</td>
<td>$o$-DCB, 2% DIO</td>
<td>5:10</td>
<td>800</td>
<td>7.71</td>
<td>0.71</td>
<td>62</td>
<td>3.42</td>
</tr>
<tr>
<td>PBDT-FDP</td>
<td>$o$-DCB/CF=1/1, 2% DIO</td>
<td>5:10</td>
<td>800</td>
<td>8.30</td>
<td>0.70</td>
<td>51</td>
<td>2.97</td>
</tr>
<tr>
<td>PBDT-T-TDP</td>
<td>$o$-DCB</td>
<td>5:10</td>
<td>1500</td>
<td>6.91</td>
<td>0.67</td>
<td>57</td>
<td>2.66</td>
</tr>
<tr>
<td>PBDT-T-TDP</td>
<td>$o$-DCB, 2% DIO</td>
<td>5:10</td>
<td>1500</td>
<td>7.39</td>
<td>0.66</td>
<td>60</td>
<td>2.92</td>
</tr>
<tr>
<td>PBDT-T-TDP</td>
<td>$o$-DCB/CF=1/1, 2% DIO</td>
<td>5:10</td>
<td>1500</td>
<td>9.80</td>
<td>0.68</td>
<td>59</td>
<td>3.91</td>
</tr>
<tr>
<td>PBDT-T-FDP</td>
<td>CF</td>
<td>5:10</td>
<td>1500</td>
<td>5.34</td>
<td>0.73</td>
<td>34</td>
<td>1.31</td>
</tr>
<tr>
<td>PBDT-T-FDP</td>
<td>CF, 2% DIO</td>
<td>5:10</td>
<td>1500</td>
<td>11.76</td>
<td>0.76</td>
<td>59</td>
<td>5.15</td>
</tr>
<tr>
<td>PBDT-T-FDP</td>
<td>$o$-DCB/CF=1/1, 2% DIO</td>
<td>5:10</td>
<td>1200</td>
<td>12.55</td>
<td>0.73</td>
<td>60</td>
<td>5.54</td>
</tr>
</tbody>
</table>

### Table S4. The hole mobility of Polymers/PC$_{71}$BM blend films measured by SCLC method

<table>
<thead>
<tr>
<th>Polymer</th>
<th>Thickness (nm)</th>
<th>Mobility (cm$^2$V$^{-1}$s$^{-1}$)</th>
</tr>
</thead>
<tbody>
<tr>
<td>PBDT-FDP</td>
<td>95</td>
<td>1.37*10$^{-4}$</td>
</tr>
<tr>
<td>PBDT-T-TDP</td>
<td>80</td>
<td>1.27*10$^{-4}$</td>
</tr>
<tr>
<td>PBDT-T-FDP</td>
<td>90</td>
<td>7.10*10$^{-5}$</td>
</tr>
</tbody>
</table>