Supporting Information

Efficiently Chemical Structure and Device Engineering for Achieving Difluorinated 2,2′-Bithiophene-Based Small Molecular Organic Solar Cells with 9.0% Efficiency

Min Li, Zhongbin Qiu, Guangjun Zhang, Yu Liu, Lin Xiong,

Dan Bai, Mengbing Zhu, Qiang Peng, Weiguo Zhu*

a College of Chemistry, Key Lab of Environment-Friendly Chemistry and Application in the Ministry of Education, Xiangtan University, Xiangtan 411105, China.
b School of Materials Science and Engineering, Jiangsu Engineering Laboratory of Light-Electricity-Heat Energy-Converting Materials and Applications, Jiangsu Collaborative Innovation Center of Photovoltaic Science and Engineering, National Experimental Demonstration Center for Materials Science and Engineering, Changzhou University, Changzhou 213164, China.
c Key Laboratory of Green Chemistry and Technology of Ministry of Education, College of Chemistry, and State Key Laboratory of Polymer Materials Engineering, Sichuan University, Chengdu 610065, China.
d Department of Biochemistry and Molecular Biology, School of Medicine, Xi’an Jiaotong University Xi’an, Shaanxi Province 710061, China.

*Email addresses:
(W, Z) zhuwig18@126.com
(Q. P) qiangpeng@scu.edu.cn

(Y. L) liuyu03b@126.com
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8. Photovoltaic properties of the FBT(IID-T)$_2$/PC$_{71}$BM-based OPV cells.
1. Characterization and Measurement

Nuclear magnetic resonance (NMR) spectra were recorded on a Bruker AV-400 spectrometer using tetramethylsilane (TMS) as a reference in deuterated chloroform solution at 298 K. Mass spectrometric measurements were performed on Bruker Biflex III MALDI-TOF. Thermogravimetric analyses (TGA) were conducted under a dry nitrogen gas flow at a heating rate of 20 °C min⁻¹ on a Perkin-Elmer TGA 7. Differential scan calorimetry (DSC) measurements were carried out with a Netzsch DSC-204 under N₂ flow at heating and cooling rates of 10 °C min⁻¹. UV-Vis absorption spectra were recorded on a HP-8453 UV visible system. Cyclic voltammograms (CV) were carried out on a CHI660A electrochemical work station with a three electrode electrochemical cell in a 0.1 M tetrabutylammonium hexafluorophosphate (TBAPF₆) acetonitrile solution with a scan 100 mV s⁻¹ at room temperature (RT) under argon atmosphere. In this three-electrode cell, a platinum rod, platinum wire and Ag/AgCl electrode were used as a working electrode, counter electrode and reference electrode, respectively. The surface morphology of the SMs:PC₇₁BM blend film was investigated by an atomic force microscopy (AFM) on a Veeco, DI multimode NS-3D apparatus in a tapping mode under normal air condition at RT with a 5 µm scanner. The HOMO and LUMO distributions of SMs were calculated by the density functional theory (DFT) (B3LYP; 6-31G*) method.
2. $^1$H NMR and $^{13}$C NMR Spectra

Fig. S1. $^1$H NMR spectrum of BrPyDPP-TR$_1$

Fig. S2. $^1$H NMR spectrum of BrIID-TR$_1$
Fig. S3. $^1$H NMR spectrum of BrTDPP-TR$_1$

Fig. S4 $^1$H-NMR spectrum of FBT(PyDPP-T)$_2$
Fig. S5. $^1$HNMR spectrum of FBT(TDPP-T)$_2$

Fig. S6. $^1$H-NMR spectrum of FBT(IID-T)$_2$
Fig. S7. $^{13}$C-NMR spectrum of FBT(PyDPP-T)$_2$
Fig. S8. $^{13}$C-NMR spectrum of FBT(TDPP-T)$_2$

Fig. S9. MS spectrum of FBT(PyDPP-T)$_2$

Fig. S10. MS spectrum of FBT(IID-T)$_2$
3. The absorption molar coefficient in different conditions.

Fig. S12. Absorption spectra of SMs in a) dilute CHCl₃ and b) in their blend films with PC₇₁BM at an optimized ratio of 1:1 (w/w), respectively.
4. Tauc plot of SMs to determine optical bandgap.

![Tauc plot of SMs to determine optical bandgap](image)

Fig.S13. Tauc plot of SMs to determine optical bandgap, from the equation of the related band gap $E_{g_{\text{opt}}}$ and absorbance $A$: $(Ahv)^2 = B(hv - E_{g_{\text{opt}}})$.

5. Fabrication and Characterization of Organic Solar Cells

A sandwich structure of: ITO/PEDOT:PSS(5000 rpm, 140 °C 30min)/SM:PC$_{71}$BM (2000 rpm)/Ca (10 nm)/Al (100 nm), was used in the solar cells. The photosensitive layer was subsequently prepared by spin-coating rate of 2000 rpm with a solution of the SM/PC$_{71}$BM (1:1, w/w) at room temperature in chloroform (CF) with 0.4% CN (CN/CF, v/v) on the PEDOT:PSS layer with a typical concentration of 10 mg mL$^{-1}$, followed by CS$_2$-SVA treatment for 20 s. Ca (10 nm) and Al (100 nm) were successively deposited on the photosensitive layer in vacuum and used as top electrodes. The current-voltage ($I$–$V$) characterization of the devices was carried out on a computer-controlled Keithley source measurement system. A solar simulator was used as the light source and the light intensity was monitored by a standard Si solar cell. The active area was 0.1 cm$^2$ for each cell. The thicknesses of the spun-cast films were recorded by a profilometer (Alpha-Step 200, Tencor Instruments). The external quantum efficiency ($EQE$) was measured with a Stanford Research Systems model SR830 DSP lock-in amplifier coupled with WDG3 monochromator and a 150 W xenon lamp.
6. Photovoltaic properties of the FBT(PyDPP-T)$_2$/PC$_{71}$BM-based OPV cells.

![J-V curve of the FBT(PyDPP-T)$_2$/PC$_{71}$BM-based OSCs under AM.1.5G illumination (100 mW/cm$^2$) with SM/PC$_{71}$BM CN ratios optimization.](image)

**Fig. S14.** $J$-$V$ curve of the FBT(PyDPP-T)$_2$/PC$_{71}$BM-based OSCs under AM.1.5G illumination (100 mW/cm$^2$) with SM/PC$_{71}$BM CN ratios optimization.

**Table S1.** Photovoltaic parameters of the FBT(PyDPP-T)$_2$/PC$_{71}$BM-based PSCs under AM.1.5G illumination (100 mW/cm$^2$) with SM/PC$_{71}$BM CN ratios optimization.

<table>
<thead>
<tr>
<th>CN</th>
<th>$V_{oc}$ (V)</th>
<th>$J_{sc}$ (mA/cm$^2$)</th>
<th>FF (%)</th>
<th>PCE (%)</th>
</tr>
</thead>
<tbody>
<tr>
<td>0.2%</td>
<td>0.77</td>
<td>11.85</td>
<td>50.92</td>
<td>4.65(4.31)</td>
</tr>
<tr>
<td>0.4%</td>
<td>0.77</td>
<td>12.03</td>
<td>54.46</td>
<td>5.04(4.89)</td>
</tr>
<tr>
<td>0.6%</td>
<td>0.76</td>
<td>11.79</td>
<td>50.89</td>
<td>4.56(4.32)</td>
</tr>
</tbody>
</table>

Device condition:
(1) chloroform(CF);
(2) concentration: 10 mg/mL of FBT(PyDPP-T)$_2$ in CF;
(3) Structure: ITO/PEDOT:PSS(5000 rpm, 140 °C 30min)/SM1:PC71BM (2000 rpm)/Ca (10 nm)/Al (100 nm).
(4) Spin-coating temperature: at room temperature.
**Fig. S15.** $J$-$V$ curve of the FBT(PyDPP-T)$_2$/PC$_{71}$BM-based SM-OSC under AM.1.5G illumination (100 mW/cm$^2$) with CS$_2$ solvent annealing.

<table>
<thead>
<tr>
<th>Solvent</th>
<th>$V_{oc}$ (V)</th>
<th>$J_{sc}$ (mA/cm$^2$)</th>
<th>FF (%)</th>
<th>PCE (%)</th>
</tr>
</thead>
<tbody>
<tr>
<td>CS$_2$</td>
<td>0.765</td>
<td>13.53</td>
<td>61.81</td>
<td>6.40(6.15)</td>
</tr>
</tbody>
</table>

Device condition:
(1) chloroform (CF);
(2) concentration: ITO/PEDOT:PSS(5000 rpm, 140 °C 30min)/SM1:PC$_{71}$BM (2000 rpm)/Ca (10 nm)/Al (100 nm)
(3) Solvent vapor annealing time: 20 s
Fig. S16. $J$-$V$ curve of the FBT(IID-T)$_2$/PC$_{71}$BM-based SM-OSCs under AM.1.5G illumination (100 mW/cm$^2$) with CN ratios optimization.

Table. S3. $J$-$V$ curve of the FBT(IID-T)$_2$/PC$_{71}$BM-based SM-OSCs under AM.1.5G illumination (100 mW/cm$^2$) with CN ratios optimization.

<table>
<thead>
<tr>
<th>CN</th>
<th>$V_{oc}$ (V)</th>
<th>$J_{sc}$ (mA/cm$^2$)</th>
<th>FF (%)</th>
<th>PCE (%)</th>
</tr>
</thead>
<tbody>
<tr>
<td>0.2%</td>
<td>0.79</td>
<td>12.46</td>
<td>54.91</td>
<td>5.41(5.14)</td>
</tr>
<tr>
<td>0.4%</td>
<td>0.79</td>
<td>12.54</td>
<td>57.06</td>
<td>5.65(5.35)</td>
</tr>
<tr>
<td>0.6%</td>
<td>0.78</td>
<td>12.41</td>
<td>54.85</td>
<td>5.31(5.05)</td>
</tr>
</tbody>
</table>

Device condition:

(1) chloroform(CF);
(2) concentration: 10 mg/mL of FBT(IID-T)$_2$ in CF;
(3) Structure: ITO/PEDOT:PSS(5000 rpm, 140 °C 30min)/SM1:PC$_{71}$BM (2000 rpm)/Ca (10 nm)/Al (100 nm).
(4) Spin-coating temperature: at room temperature.
**Fig. S17.** $J$-$V$ curve of the FBT(IID-T)$_2$/PC$_{71}$BM-based SM-OSCs under AM.1.5G illumination (100 mW/cm$^2$) with CS$_2$ solvent annealing.

**Table. S4.** $J$-$V$ curve of the FBT(IID-T)$_2$/PC$_{71}$BM-based SM-OSCs under AM.1.5G illumination (100 mW/cm$^2$) with CS$_2$ solvent annealing.

<table>
<thead>
<tr>
<th>Solvent</th>
<th>$V_{oc}$ (V)</th>
<th>$J_{sc}$ (mA/cm$^2$)</th>
<th>FF (%)</th>
<th>PCE (%)</th>
</tr>
</thead>
<tbody>
<tr>
<td>CS$_2$</td>
<td>0.785</td>
<td>14.74</td>
<td>67.26</td>
<td>7.78(7.54)</td>
</tr>
</tbody>
</table>

Device condition:

(1) chloroform (CF);

(2) concentration: ITO/PEDOT:PSS(5000 rpm, 140 $^\circ$C 30min)/SM2:PC71BM (2000 rpm)/Ca (10 nm)/Al (100 nm)

(3) Solvent vapor annealing time: 20 s
Fig. S18. J-V curve of the FBT(TDPP-T)$_2$/PC$_{71}$BM-based OSCs under AM.1.5G illumination (100 mW/cm$^2$) with SM/PC$_{71}$BM CN ratios optimization.

Table. S5. J-V curve of the FBT(TDPP-T)$_2$/PC$_{71}$BM-based SM-OSCs under AM.1.5G illumination (100 mW/cm$^2$) with CN ratios optimization.

<table>
<thead>
<tr>
<th>CN</th>
<th>$V_{oc}$ (V)</th>
<th>$J_{sc}$ (mA/cm$^2$)</th>
<th>FF (%)</th>
<th>PCE (%)</th>
</tr>
</thead>
<tbody>
<tr>
<td>0.2%</td>
<td>0.76</td>
<td>13.61</td>
<td>59.91</td>
<td>6.20(6.01)</td>
</tr>
<tr>
<td>0.4%</td>
<td>0.76</td>
<td>14.61</td>
<td>61.75</td>
<td>6.86(6.51)</td>
</tr>
<tr>
<td>0.6%</td>
<td>0.75</td>
<td>13.93</td>
<td>62.27</td>
<td>6.40(6.13)</td>
</tr>
</tbody>
</table>

Device condition:
(1) chloroform(CF);
(2) concentration: 10 mg/mL of FBT(TDPP-T)$_2$ in CF;
(3) Structure: ITO/PEDOT:PSS(5000 rpm, 140 ºC 30min)/SM3:PC$_{71}$BM (2000 rpm)/Ca (10 nm)/Al (100 nm).
(4) Spin-coating temperature: at room temperature.
Fig. S19. J-V curve of the FBT(TDPP-T)$_2$/PC$_{71}$BM-based SM-OSCs under AM.1.5G illumination (100 mW/cm$^2$) with CS$_2$ solvent annealing.

Table S6. J-V curve of the FBT(TDPP-T)$_2$/PC$_{71}$BM-based SM-OSCs under AM.1.5G illumination (100 mW/cm$^2$) with CS$_2$ solvent annealing.

<table>
<thead>
<tr>
<th>Solvent</th>
<th>$V_{oc}$ (V)</th>
<th>$J_{sc}$ (mA/cm$^2$)</th>
<th>FF (%)</th>
<th>PCE (%)</th>
</tr>
</thead>
<tbody>
<tr>
<td>CS$_2$</td>
<td>0.758</td>
<td>16.14</td>
<td>73.52</td>
<td>9.00(8.85)</td>
</tr>
</tbody>
</table>

Device condition:

(1) chloroform (CF);

(2) concentration: ITO/PEDOT:PSS(5000 rpm, 140 °C)

30min)/SM3:PC$_{71}$BM (2000 rpm)/Ca (10 nm)/Al (100 nm)

(3) Solvent vapor annealing time: 20 s