Supporting information

for

Small Molecules Incorporating Regioregular Oligothiophenes and Fluorinated Benzothiadiazole Groups for Solution-Processed Organic Solar Cells

Liu Yuan\textsuperscript{a,b}, Yifan Zhao\textsuperscript{a,c}, Kun Lu*\textsuperscript{a}, Dan Deng\textsuperscript{a,b}, Wei Yan\textsuperscript{c}, ZhiXiang Wei*\textsuperscript{a}

1. National Center for Nanoscience and Technology, Beijing 100190, China
2. University of Chinese Academy of Science, Beijing 100049, China
3. Department of Environmental Science and Engineering, Xi’an Jiaotong University, Xi’an 710049, PR China

*Corresponding author: e-mail: weizx@nanoctr.cn

\begin{scheme}
\begin{center}
\includegraphics[width=\textwidth]{scheme.png}
\end{center}
\end{scheme}

Scheme S1 Synthesis route of TAT and 3TA3T. Condition (a) Pd(PPh\textsubscript{3})\textsubscript{4}, toluene, Ar, 115 °C, 48 h.

**TAT** Compound 5,6-difluoro-2,1,3-benzothiadiazole (3.3 g, 10 mmol), tributyl-(4-hexyl-thiophen-2-yl)-stannane (13.7 g, 30 mmol), and toluene (60 ml) were added into a 100ml three-neck round-bottom flask., followed by the addition of Pd (PPh\textsubscript{3})\textsubscript{4} (115 mg, 0.1 mmol). The reaction flask was degassed three times and purged with argon for 5 minutes, then it was refluxed for 48 hours at 110 °C. The reaction mixture was cooled down to room temperature, and solvent was removed by rotary evaporation. The crude product was purified by flash column chromatography on silica gel using a mixture of dichloromethane and petroleum ether (1:10) as
eluent. TAT was collected as an orange solid (3.17 g, 63%). $^1$H NMR (400 MHz, CDCl$_3$, ppm) $\delta$ 8.07 (s, 2H), 7.16 (s, 2H), 2.63 (d, 4H), 1.65 (m, 2H), 1.22-1.45 (m, 16H), 0.80-0.95 (m, 12H).

$^{19}$F NMR (377 MHz, CDCl$_3$, ppm) $\delta$ -128.16. $^{13}$C(101 MHz, CDCl$_3$, ppm) $\delta$ 151.14, 150.93, 148.94, 148.90, 148.85, 148.56, 148.35, 143.67, 132.26, 132.22, 132.18, 131.20, 123.94, 123.92, 123.89, 111.73, 111.69, 111.64, 111.59, 31.71, 30.51, 30.48, 29.04, 22.65, 14.11. MS (MALDI): calculated: 504.15, found: 504.1 (M$^+$. Elemental Anal. Calcd. for (C$_{26}$H$_{30}$F$_2$N$_2$S$_3$): C, 61.87; H, 5.99; N, 5.55. Found: C, 61.85; H, 6.04; N, 5.61.

3TA3T 3TA3T was synthesized using the same procedure of TAT by reacting 2Br-2TA2T with tributyl-(4-hexyl-thiophen-2-yl)-stannane. $^1$H NMR (400 MHz, CDCl$_3$, ppm) $\delta$ 8.12 (s, 2H), 7.11 (s, 2H), 7.00 (s, 2H), 6.92 (s, 2H), 2.95-2.83 (m, 4H), 2.83-2.71 (m, 4H), 2.70-2.56 (m, 4H), 1.74 (d, 4H), 1.70 (d, 8H), 1.33 (d, 36H), 0.91 (m, 18H). $^{19}$F NMR (377 MHz, CDCl$_3$, ppm) $\delta$ 151.16, 148.79, 148.57, 148.37, 143.71, 139.74, 139.65, 135.46, 134.73, 134.10, 133.20, 131.72, 129.16, 128.97, 127.24, 120.13, 111.07, 31.71, 30.59, 30.52, 30.42, 29.54, 29.35, 29.32, 29.30, 29.04, 22.69, 22.67, 22.64, 14.13, 14.11. MS (MALDI): calculated: 1168.48, found: 1168.4 (M$^+$. Elemental Anal. Calcd. for (C$_{66}$H$_{86}$F$_2$N$_2$S$_7$): C, 67.76; H, 7.41; N, 2.39. Found: C, 67.63; H, 7.54; N, 2.44.

![Fig. S1 TGA plot of 4TA4T and 6TA6T under nitrogen atmosphere with a heating rate of 10 °C min$^{-1}$.](image)

**Table S1** Photovoltaic performances of 6TA6T: PC$_{71}$BM BHJ solar cells under AM 1.5 G-simulated solar illumination with different processing solvents.
<table>
<thead>
<tr>
<th>Solvent</th>
<th>D/A Ratio</th>
<th>$V_{oc}$ (V)</th>
<th>$J_{sc}$ (mA cm$^{-2}$)</th>
<th>FF</th>
<th>PCE</th>
</tr>
</thead>
<tbody>
<tr>
<td>CB 1:0</td>
<td>1:1</td>
<td>0.73</td>
<td>5.81</td>
<td>0.50</td>
<td>2.15%</td>
</tr>
<tr>
<td>CB/CF 4:1</td>
<td>1:1</td>
<td>0.76</td>
<td>6.90</td>
<td>0.56</td>
<td>2.96%</td>
</tr>
<tr>
<td>CB/CF 3:2</td>
<td>1:1</td>
<td>0.74</td>
<td>7.92</td>
<td>0.55</td>
<td>3.21%</td>
</tr>
<tr>
<td>CB/CF 1:1</td>
<td>1:1</td>
<td>0.75</td>
<td>7.31</td>
<td>0.57</td>
<td>3.15%</td>
</tr>
<tr>
<td>CB/CF 1:4</td>
<td>1:1</td>
<td>0.74</td>
<td>5.85</td>
<td>0.60</td>
<td>2.61%</td>
</tr>
<tr>
<td>CF 0:1</td>
<td>1:1</td>
<td>0.78</td>
<td>5.85</td>
<td>0.43</td>
<td>1.97%</td>
</tr>
</tbody>
</table>

**Fig. S2** SCLC model hole mobility measurement for 4TA4T and 6TA6T pristine films and their blended films with PC$_{71}$BM casted from CF or mixed solvents.
**Fig. S3** AFM height images of solar cell active layers of 4TA4T processed with (a) CF, (b) CB, (c) CB/CF 7:1 and 6TA6T processed with (d) CF, (e) CB, (f) CB/CF 3:2. All the image scales are 2 μm × 2 μm with RMS roughness below.

**Fig. S4.** MALDI-TOF spectrum of TAT
Fig. S5. MALDI-TOF spectrum of 2TA2T

Fig. S6. MALDI-TOF spectrum of 3TA3T
Fig. S6. MALDI-TOF spectrum of 4TA4T

Fig. S6. MALDI-TOF spectrum of 6TA6T