Electronic supplementary information (ESI)

for

Vinylene-bridged difluorobenzo[c][1,2,5]thiadiazole (FBTzE):
a new electron-deficient building block for high-performance
semiconducting polymers in organic electronics

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1. Experimental Procedures and Spectroscopic Data for Compounds.

**Scheme S1.** Synthetic procedure of 4-bromo-5,6-difluoro[10]benzo[c][1,2,5]thiadiazole (1)

\[
\begin{align*}
\text{NH}_2 & \xrightarrow{\text{Ac}_2\text{O} (1.2 \text{ equiv})} \text{NHAc} \\
\text{F} & \xrightarrow{1,4-\text{dioxane} \quad 0^\circ\text{C}, \quad 1 \text{ h}} \quad 99\% \quad \text{F} \\
\text{NHAc} & \xrightarrow{\text{KNO}_3 (1.2 \text{ equiv})} \text{NHAc} \\
\text{F} & \xrightarrow{\text{H}_2\text{SO}_4 \quad 0^\circ\text{C}, \quad 3 \text{ h}} \quad \text{quant} \quad \text{F} \\
\end{align*}
\]

\[
\begin{align*}
\text{O}_2\text{N} & \xrightarrow{1 \text{ M HCl} (1.8 \text{ equiv})} \text{NH}_2 \\
\text{F} & \xrightarrow{\text{reflux, 3 h}} \text{Br}_2 (2 \text{ equiv}) \quad 87\% \\
\text{F} & \xrightarrow{\text{AcOH} \quad 50-56^\circ\text{C}, \quad 2.5 \text{ h}} \quad 84\% \\
\text{F} & \xrightarrow{\text{SnCl}_2 \cdot 2\text{H}_2\text{O} (5 \text{ equiv})} \text{H}_2\text{N} \quad \text{Br} \\
\text{F} & \xrightarrow{\text{AcOEt/EtOH} (7/3) \quad 75^\circ\text{C}, \quad 3 \text{ h}} \quad 99\% \\
\text{F} & \xrightarrow{\text{SOCl}_2 (2 \text{ equiv})} \text{NH}_2 \quad \text{F} \\
\text{F} & \xrightarrow{\text{TEA (4 equiv)}} \text{Br} \\
\end{align*}
\]

**Scheme S2.** Synthesis of standard PffBT4T-DT

\[
\begin{align*}
\text{DFBT2T-DT-Br} & \xrightarrow{\text{Pd}_2(\text{dba})_3 \cdot \text{CHCl}_3 (2 \text{ mol%}), \quad \text{P(o-toly)}_3 (8 \text{ mol%})} \text{MW, 160^\circ\text{C}, 45 min} \quad \text{PffBT4T-DT}
\end{align*}
\]

**Synthesis of Standard Polymers PffBT4T-DT.** Monomers DFBT2T-DT-Br (116.7 mg, 0.1 mmol), 5,5'bis(trimethylstannyl)-2,2'-bithiophene (7, 49.2 mg, 0.1 mmol), tris(dibenzylideneacetone)dipalladium(0)-chloroform adduct (Pd2(db)3·CHCl3, 2.1 mg, 2 μmol), tri(o-tolyl)phosphine (P(o-toly)3, 2.4 mg, 8 μmol) and chlorobenzene (3.0 mL) were added to a reaction vessel, which was sealed and refilled with argon.
reaction mixture was heated at 160 °C for 45 min in a microwave reactor. After being cooled to room temperature, the reaction mixture was poured into 100 mL of methanol containing 5 mL of concentrated hydrochloric acid and stirred for 3 h. The precipitate was then subjected to sequential Soxhlet extraction with methanol and hexane to remove low molecular-weight fractions. The residue was extracted with chloroform, and concentrated solution was poured into 50 mL of methanol. The formed precipitates were collected by filtration and dried in vacuo to afford \textbf{PffBT4T-DT} (103.3 mg, 88%) as a metallic purple solid. GPC ($\alpha$-DCB, 140 °C): $M_n = 23.9$ kDa, $M_w = 39.9$ kDa, PDI = 1.67.
Table S1. Optimization of the Catalysts, Oxidants, and Additives in Dehydrogenative Coupling\textsuperscript{1-3}

\begin{align*}
\text{Pd cat.} & \quad \text{oxidant} & \quad \text{additive} & \quad \text{NMR yield (%)} \\
\hline
1^a & \text{Pd(OAc)}_2 & \text{Ag}_2\text{O} & \text{none} & 11 & 63 & 37 \\
2 & \text{Pd(OAc)}_2 & \text{Ag}_2\text{CO}_3 & \text{none} & 13 & 45 & 6 \\
3 & \text{Pd(OAc)}_2 & \text{Ag}_2\text{CO}_3 & \text{AcOH} & 13 & 39 & 9 \\
4 & \text{Pd(OAc)}_2 & \text{Ag}_2\text{CO}_3 & \text{PivOH} & 29 & 37 & \text{trace} \\
5 & \text{Pd(OAc)}_2 & \text{Ag}_2\text{CO}_3 & \text{1-AdCOOH} & 13 & 9 & 2 \\
6^b & \text{Pd(OAc)}_2 & \text{Ag}_2\text{CO}_3 & \text{PivOH} & 22 (26^a) & 32 (23^a) & 3 \\
7 & \text{Pd(OAc)}_2 & \text{Ag}_2\text{O} & \text{PivOH} & 26 & 39 & 1 \\
8 & \text{Pd(tfa)}_2 & \text{Ag}_2\text{CO}_3 & \text{PivOH} & 33 & 33 & \text{trace} \\
9 & \text{PdCl}_2(\text{NCPH})_2 & \text{Ag}_2\text{CO}_3 & \text{PivOH} & 33 & 27 & \text{trace} \\
10 & \text{PdCl}_2(\text{PPh}_3)_2 & \text{Ag}_2\text{CO}_3 & \text{PivOH} & 27 & 32 & 1 \\
11^d & \text{Pd(tfa)}_2 & \text{Ag}_2\text{CO}_3 & \text{PivOH} & 54 (51^e) & 12 & \text{trace} \\
12 & \text{Pd(OAc)}_2 & \text{AgOAc} & 2\text{-methylpyridine} & 9 & 33 & 25
\end{align*}

\textsuperscript{a}Pd(OAc)\textsubscript{2} (5 mol %), 80 °C. \textsuperscript{b}Additional Pd(OAc)\textsubscript{2} (10 mol %) and 4a (2 equiv) were added after 12 h. \textsuperscript{c}An isolated yields. \textsuperscript{d}Pd(tfa)\textsubscript{2} (20 mol %), Ag\textsubscript{2}CO\textsubscript{3} (8 equiv), PivOH (6 equiv).
2. Copies of $^1H$, $^{13}C(^1H)$, and $^{19}F(^1H)$ NMR Charts for the New Compounds
The $^1$H, $^{13}$C$^1$H, and $^{19}$F$^1$H NMR spectra of 3 (in CDCl$_3$).
5a
The $^1\text{H}$, $^{13}\text{C}{^1\text{H}}$, and $^{19}\text{F}{^1\text{H}}$ NMR spectra of 5a (in CDCl$_3$).
The $^1\text{H}$, $^{13}\text{C}$,$^1\text{H}$, and $^{19}\text{F}$,$^1\text{H}$ NMR spectra of 5b (in CDCl$_3$).
The $^1$H, $^{13}$C($^1$H), and $^{19}$F($^1$H) NMR spectra of 5c (in CDCl$_3$).
The $^1$H NMR spectra of 3T (in toluene-$d_8$, 80 °C).
The $^1$H NMR spectra of 4T (in toluene-$d_8$, 80 °C).
The $^1$H NMR spectra of 2TTT (in toluene-$d_8$, 80 °C).
3. DFT Calculations of Model Compound of FBTzE Derivatives

**Figure S1.** Energy diagrams calculated by using DFT at B3LYP/6-31G(d); (a) DFBT and FBTzE derivatives, and (b) dimer structure of model compound for PFBTzE3T-OD (3T), PFBTzE4T-DT (4T), and PFBTzE2TTT-DT (2TTT).
Figure S2. Four possible conformations of (a) FBTzE core and (b) bis(4-methylthienyl)FBTzE (FBTzE2T). Geometry optimization was performed by using DFT at B3LYP/6-31G(d).
Figure S3. Geometry of HOMO and LUMO orbitals for (a) parent DFBT, and bis(alkylthienyl) DFBT derivatives (DFBT2T and DFBT4T), and (b) parent FBTzE, and bis(alkylthienyl) FBTzE derivatives (FBTzE2T and FBTzE4T) calculated by using DFT at B3LYP/6-31G(d).
(a) ffBT4T dimer
$\phi_1 = 8.5^\circ, \phi_2 = 11.1^\circ, \phi_3 = 0.4^\circ$

LUMO

HOMO

(b) FBTzE3T dimer
$\phi_2 = 12.0^\circ, \phi_3 = 0.4^\circ, \phi_4 = 0.0^\circ$

LUMO

HOMO
Figure S4.  The optimized dimer structure of model compound for (a) PFBT4T-DT, (b) PFBTzE3T-OD (3T), (c) PFBTzE4T-DT (4T), and (d) PFBTzE2TTT-DT (2TTT) calculated by using DFT at B3LYP/6-31G(d). Branched alkyl chains were replaced with methyl groups, respectively, to simplify the calculation.
4. GPC Charts of FBTzE-Based Copolymers

![Figure S5. GPC charts of PFBTzEAr polymers; (a) 3T, (b) 4T, and (c) 2TTT.](image)

<table>
<thead>
<tr>
<th>PFBTzEAr</th>
<th>Conc./mg mL$^{-1}$</th>
<th>$M_n$/kDa $^b$</th>
<th>PDI$^b$</th>
<th>DP$_n$ $^c$</th>
</tr>
</thead>
<tbody>
<tr>
<td>3T</td>
<td>0.6</td>
<td>46.9</td>
<td>1.98</td>
<td>40</td>
</tr>
<tr>
<td>4T</td>
<td>0.6</td>
<td>133.8</td>
<td>2.39</td>
<td>97</td>
</tr>
<tr>
<td></td>
<td>0.2</td>
<td>71.4</td>
<td>3.32</td>
<td>52</td>
</tr>
<tr>
<td>2TTT</td>
<td>0.6</td>
<td>76.4</td>
<td>2.18</td>
<td>56</td>
</tr>
<tr>
<td></td>
<td>0.2</td>
<td>53.6</td>
<td>2.98</td>
<td>40</td>
</tr>
</tbody>
</table>

$^a$Concentrations of polymer solution for the measurement of GPC. $^b$Determined by GPC measurements using polystyrene standards and o-dichlorobenzene (o-DCB) as the eluent at 140 °C. $^c$Degree of polymerization (DP$_n$) based on the repeating unit.
5. Physicochemical Properties of Difluorobenzothiadiazole (DFBT) Derivatives and Copolymer

Figure S6. UV-vis absorption spectra of (a) DFBT derivatives in CH$_2$Cl$_2$ and (c) PffBT4T-DT in chlorobenzene and thin film, and cyclic voltammograms of (b) DFBT derivatives in CH$_2$Cl$_2$ and (d) PffBT4T-DT in thin films.
6. Temperature Dependence of UV-vis Absorption Spectra of PFBTzEAr in PhCl Solution

Figure S7. UV-vis absorption spectra of PFBTzEAr polymers in chlorobenzene solution; (a) 3T, (b) 4T, and (c) 2TTT.

Table S3. Optical Properties of PFBTzEAr in Chlorobenzene Solution

<table>
<thead>
<tr>
<th>PFBTzEAr</th>
<th>λ\text{max,rt} (λ\text{max,heat})/nm\textsuperscript{a}</th>
<th>ε\text{rt} (ε\text{heat})/10\textsuperscript{-4} M\textsuperscript{-1} cm\textsuperscript{-1}\textsuperscript{b}</th>
<th>λ\text{edge}/nm\textsuperscript{c}</th>
<th>E\textsubscript{g,opt}/eV\textsuperscript{d}</th>
</tr>
</thead>
<tbody>
<tr>
<td>3T</td>
<td>629, 693 (625, 687 [sh])</td>
<td>5.82, 4.36 (5.15, 3.78)</td>
<td>781</td>
<td>1.59</td>
</tr>
<tr>
<td>4T</td>
<td>643, 704 (633, 701 [sh])</td>
<td>6.61, 6.41 (5.64, 4.58)</td>
<td>800</td>
<td>1.55</td>
</tr>
<tr>
<td>2TTT</td>
<td>648, 708 (642, 696)</td>
<td>5.78, 5.60 (4.88, 4.13)</td>
<td>790</td>
<td>1.57</td>
</tr>
</tbody>
</table>

\textsuperscript{a}Absorption maxima in chlorobenzene solution at rt (out of parentheses) and at ca. 80 °C (in parentheses). \textsuperscript{b}Molar absorption coefficient in chlorobenzene solution at rt (out of parentheses) and at ca. 80 °C (in parentheses). \textsuperscript{c}Absorption edge (λ\text{edge}) in chlorobenzene solution at rt. \textsuperscript{d}Optical energy gap in chlorobenzene solution at rt estimated from λ\text{edge}. 

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### 7. Photovoltaic Properties of PFBTzEAr-Based OPVs

Table S4. Solar Cell Performances of Polymer/PC$_{61}$BM-based Devices

<table>
<thead>
<tr>
<th>PFBTzEAr</th>
<th>p/n ratio</th>
<th>solvent</th>
<th>$J_{sc}$/mA cm$^{-2}$</th>
<th>$V_{oc}$/V</th>
<th>FF</th>
<th>PCE$<em>{max}$ (PCE$</em>{avg}$)/%</th>
</tr>
</thead>
<tbody>
<tr>
<td>3T</td>
<td>1:1</td>
<td>CB</td>
<td>2.92</td>
<td>0.87</td>
<td>0.35</td>
<td>0.87 (0.83)</td>
</tr>
<tr>
<td></td>
<td>1:2</td>
<td>CB</td>
<td>2.09</td>
<td>0.95</td>
<td>0.39</td>
<td>0.76 (0.68)</td>
</tr>
<tr>
<td></td>
<td>1:1</td>
<td>CB+1 vol% DIO</td>
<td>4.08</td>
<td>0.86</td>
<td>0.42</td>
<td>1.48 (1.42)</td>
</tr>
<tr>
<td></td>
<td>1:1</td>
<td>CB+1 vol% DPE</td>
<td>4.86</td>
<td>0.87</td>
<td>0.41</td>
<td>1.73 (1.50)</td>
</tr>
<tr>
<td></td>
<td>1:1</td>
<td>CB+2.5 vol% DPE</td>
<td>7.00</td>
<td>0.88</td>
<td>0.43</td>
<td>2.66 (2.60)</td>
</tr>
<tr>
<td></td>
<td>1:1</td>
<td>DCB</td>
<td>4.11</td>
<td>0.87</td>
<td>0.41</td>
<td>1.46 (1.32)</td>
</tr>
<tr>
<td>4T</td>
<td>1:1</td>
<td>CB</td>
<td>no photovoltaic response</td>
<td></td>
<td></td>
<td></td>
</tr>
<tr>
<td></td>
<td>1:1</td>
<td>CB+1 vol% DIO</td>
<td>no photovoltaic response</td>
<td></td>
<td></td>
<td></td>
</tr>
<tr>
<td>2TTT</td>
<td>1:1</td>
<td>CB</td>
<td>8.36</td>
<td>0.79</td>
<td>0.47</td>
<td>3.09 (2.97)</td>
</tr>
<tr>
<td></td>
<td>1:1</td>
<td>DCB</td>
<td>9.38</td>
<td>0.80</td>
<td>0.49</td>
<td>3.70 (3.37)</td>
</tr>
<tr>
<td></td>
<td>1:2</td>
<td>DCB</td>
<td>9.79</td>
<td>0.80</td>
<td>0.50</td>
<td>3.92 (3.67)</td>
</tr>
<tr>
<td></td>
<td>1:2</td>
<td>CB+2 vol% DIO</td>
<td>11.02</td>
<td>0.78</td>
<td>0.42</td>
<td>3.65 (3.46)</td>
</tr>
<tr>
<td></td>
<td>1:2</td>
<td>CB+2 vol% CN</td>
<td>9.59</td>
<td>0.82</td>
<td>0.61</td>
<td>4.80 (4.58)</td>
</tr>
<tr>
<td></td>
<td>1:2</td>
<td>CB+1 vol% DPE</td>
<td>10.31</td>
<td>0.81</td>
<td>0.59</td>
<td>4.89 (4.39)</td>
</tr>
<tr>
<td></td>
<td>1:2</td>
<td>CB+2 vol% DPE</td>
<td>9.62</td>
<td>0.81</td>
<td>0.65</td>
<td>5.12 (4.83)</td>
</tr>
<tr>
<td></td>
<td>1:2</td>
<td>CB+4 vol% DPE</td>
<td>11.47</td>
<td>0.80</td>
<td>0.57</td>
<td>5.23 (5.09)</td>
</tr>
</tbody>
</table>

$^a$Weight ratios of polymers and PC$_{61}$BM.  $^b$CB = chlorobenzene. DCB = o-dichlorobenzene. DIO = 1,8-diiodooctane. DPE = diphenyl ether. CN = 1-chloronaphthalene.
Table S5. Substrate Temperature Dependence of Solar Cell Performances in Polymer/PC_{61}BM-based Devices

<table>
<thead>
<tr>
<th>PFBTzEAr</th>
<th>Substrate temp./°C&lt;sup&gt;a&lt;/sup&gt;</th>
<th>$J_{sc}$/mA cm$^{-2}$</th>
<th>$V_{oc}$/V</th>
<th>$FF$</th>
<th>PCE&lt;sub&gt;max&lt;/sub&gt; (PCE&lt;sub&gt;avg&lt;/sub&gt;)%/&lt;sup&gt;5&lt;/sup&gt;</th>
</tr>
</thead>
<tbody>
<tr>
<td>3T&lt;sup&gt;b&lt;/sup&gt;</td>
<td>rt</td>
<td>7.00</td>
<td>0.88</td>
<td>0.43</td>
<td>2.66 (2.60)</td>
</tr>
<tr>
<td></td>
<td>70</td>
<td>3.40</td>
<td>0.86</td>
<td>0.42</td>
<td>1.22 (1.15)</td>
</tr>
<tr>
<td></td>
<td>140</td>
<td>1.85</td>
<td>0.84</td>
<td>0.30</td>
<td>0.47 (0.41)</td>
</tr>
<tr>
<td>2TTT&lt;sup&gt;c&lt;/sup&gt;</td>
<td>rt</td>
<td>11.35</td>
<td>0.79</td>
<td>0.55</td>
<td>4.92 (4.62)</td>
</tr>
<tr>
<td></td>
<td>140</td>
<td>11.47</td>
<td>0.80</td>
<td>0.57</td>
<td>5.23 (5.09)</td>
</tr>
</tbody>
</table>

<sup>a</sup>The substrates were preheated on hot plate before the spin-coating.  
<sup>b</sup>For 3T, the polymer/PC_{61}BM blend ratio is 1:1 (w/w), solvent = chlorobenzene (CB) + 2.5 vol% diphenyl ether (DPE).  
<sup>c</sup>For 2TTT, the polymer/PC_{61}BM blend ratio is 1:2 (w/w), solvent = CB + 4 vol% DPE.
8. SCLC Hole Mobility of PFBTzEAr-Based Hole-Only Devices

Figure S8. $J-V$ characteristics of PFBTzEAr-based hole-only devices with configuration of ITO/(PEDOT:PSS)/(polymer:PC$_{61}$BM)/MoO$_3$/Al; (a) 3T and (b) 2TTT. The thickness of active layer is 240 nm for 3T, and 220 nm for 2TTT.
9. The Calculated Interlayer Distances of PFBTzEAr and Blended Films with PC61BM

Table S5. The calculated interlayer distances of pure polymer and blended films with PC61BM.

<table>
<thead>
<tr>
<th>compound</th>
<th>q/Å⁻¹</th>
<th>d₀/Å</th>
<th>q/Å⁻¹</th>
<th>dₗ/Å</th>
</tr>
</thead>
<tbody>
<tr>
<td>3T</td>
<td>0.300</td>
<td>20.9</td>
<td>1.777</td>
<td>3.54</td>
</tr>
<tr>
<td>3T/PC61BM</td>
<td>0.298</td>
<td>21.1</td>
<td>1.760</td>
<td>3.57</td>
</tr>
<tr>
<td>2TTT</td>
<td>0.298</td>
<td>21.1</td>
<td>1.805</td>
<td>3.48</td>
</tr>
<tr>
<td>2TTT/PC61BM</td>
<td>0.292</td>
<td>21.5</td>
<td>1.800</td>
<td>3.49</td>
</tr>
</tbody>
</table>
10. References