Supporting Information

Benzobisthiadiazole-based conjugated donor-acceptor polymers for organic thin film transistors: effects of \(\pi\)-conjugated bridges on ambipolar transport

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Fig. S1 $^1$H NMR spectrum of compound 1.

Fig. S2 $^{13}$C NMR spectrum of compound 1.
Fig. S3 $^1$H NMR spectrum of compound 2.

Fig. S4 $^{13}$C NMR spectrum of compound 2.
Fig. S5 $^1$H NMR spectrum of compound 3.

Fig. S6 $^{13}$C NMR spectrum of compound 3.
Fig. S7 $^1$H NMR spectrum of compound 4.

Fig. S8 $^{13}$C NMR spectrum of compound 4.
Fig. S9 ¹H NMR spectrum of compound 5.

Fig. S10 ¹³C NMR spectrum of compound 5.
Fig. S11 $^1$H NMR spectrum of PBBT-FT.

Fig. S12 $^1$H NMR spectrum of PBBT-T-FT.
Fig. S13 $^1$H NMR spectrum of PBBT-Tz-FT.
Fig. S14 (a) TGA of the polymers under nitrogen flow (50 mL min$^{-1}$) at the heating rate of 10 °C min$^{-1}$ and DSC curves of (b) PBBT-FT, (c) PBBT-T-FT, and (d) PBBT-Tz-FT. All the DSC curves are the second heating and cooling processes under nitrogen flow (50 mL min$^{-1}$) at the scan rate of 10 °C min$^{-1}$. 
Fig. S15 Normalized absorption spectra of (a) PBBT-FT and (b) PBBT-T-FT in dilute CHCl₃, as-cast thin film, and annealed film at 150 °C for 30 min.
Fig. S16 (a) Current–voltage (I–V) characteristics of TFTs fabricated by spin-coating in air. Comparison of transfer characteristics for (a),(b) PBBT-FT; (c),(d) PBBT-T-FT; (e),(f) PBBT-Tz-FT films under optimized conditions stored in air (hole-enhancement operation with $V_{DS} = -80$ V and electron-enhancement operation with $V_{DS} = 80$ V; $L = 100 \mu m$ and $W = 1$ mm).
**Fig. S17** Tapping-mode AFM topography images (left: as-cast, right: after thermal annealing at 200 °C for 10 min) of the PBBT-T-FT films spin-cast from a chloroform solution. AFM size: 10 × 10 µm².

**Fig. S18** Comparison of the TFT performances (a: average hole mobility values from 5 to 10 devices, b: average electron mobility values from 5 to 10 devices) of the devices fabricated in air and in a glove box under optimized conditions.
Fig. S19 Current–voltage ($I$–$V$) characteristics of TFTs fabricated by spin-coating in a glove box under optimized conditions. Transfer characteristics for PBBT-FT films (a: hole, b: electron), for PBBT-T-FT films (c: hole, d: electron), and for PBBT-Tz-FT films (e: hole, f: electron) at the carrier-enhancement operation with $V_{DS} = -80$ and $+80$ V, respectively ($L = 100$ μm and $W = 1$ mm, all the measurements were done under vacuum ($10^{-4}$-$10^{-5}$ mbar)).
### Table S1 Summary of TFT device performances stored in air

<table>
<thead>
<tr>
<th>Polymer</th>
<th>$\mu_h$ (cm$^2$ V$^{-1}$ s$^{-1}$)</th>
<th>$\mu_e$ (cm$^2$ V$^{-1}$ s$^{-1}$)</th>
<th>$I_{on}/I_{off}$</th>
</tr>
</thead>
<tbody>
<tr>
<td><strong>PBBT-FT</strong></td>
<td>1.3×10$^{-1}$ (9.2×10$^{-2}$)</td>
<td>3.1×10$^{-3}$ (2.3×10$^{-3}$)</td>
<td>p:10$^4$-10$^5$; n:10$^2$-10$^3$</td>
</tr>
<tr>
<td>One week</td>
<td>1.0×10$^{-1}$ (5.9×10$^{-2}$)</td>
<td>2.6×10$^{-3}$ (2.0×10$^{-3}$)</td>
<td>p:10$^4$-10$^5$; n:10$^1$-10$^2$</td>
</tr>
<tr>
<td>Two weeks</td>
<td>9.5×10$^{-2}$ (5.6×10$^{-2}$)</td>
<td>2.4×10$^{-3}$ (1.9×10$^{-3}$)</td>
<td>p:10$^4$-10$^5$; n:10$^2$-10$^3$</td>
</tr>
<tr>
<td>Four weeks</td>
<td>9.0×10$^{-2}$ (5.5×10$^{-2}$)</td>
<td>2.1×10$^{-3}$ (1.6×10$^{-3}$)</td>
<td>p:10$^4$-10$^5$; n:10$^1$-10$^2$</td>
</tr>
<tr>
<td><strong>PBBT-T-FT</strong></td>
<td>6.5×10$^{-3}$ (4.8×10$^{-3}$)</td>
<td>1.2×10$^{-3}$ (8.3×10$^{-4}$)</td>
<td>p:10$^2$-10$^3$; n:10$^1$-10$^2$</td>
</tr>
<tr>
<td>One week</td>
<td>6.0×10$^{-3}$ (5.6×10$^{-3}$)</td>
<td>7.7×10$^{-4}$ (5.1×10$^{-4}$)</td>
<td>p:10$^2$-10$^3$; n:10$^1$-10$^2$</td>
</tr>
<tr>
<td>Two weeks</td>
<td>4.8×10$^{-3}$ (3.7×10$^{-3}$)</td>
<td>6.0×10$^{-4}$ (3.8×10$^{-4}$)</td>
<td>p:10$^3$-10$^4$; n:10$^1$-10$^2$</td>
</tr>
<tr>
<td>Four weeks</td>
<td>4.4×10$^{-3}$ (3.5×10$^{-3}$)</td>
<td>3.8×10$^{-4}$ (1.5×10$^{-4}$)</td>
<td>p:10$^3$-10$^4$; n:10$^1$-10$^2$</td>
</tr>
<tr>
<td><strong>PBBT-Tz-FT</strong></td>
<td>6.8×10$^{-3}$ (5.8×10$^{-3}$)</td>
<td>1.5×10$^{-2}$ (1.3×10$^{-2}$)</td>
<td>p:10$^1$-10$^2$; n:10$^2$-10$^3$</td>
</tr>
<tr>
<td>One week</td>
<td>3.8×10$^{-3}$ (2.0×10$^{-3}$)</td>
<td>1.6×10$^{-3}$ (1.4×10$^{-3}$)</td>
<td>p:10$^2$-10$^3$; n:10$^3$-10$^4$</td>
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<tr>
<td>Two weeks</td>
<td>2.9×10$^{-3}$ (1.9×10$^{-3}$)</td>
<td>6.8×10$^{-4}$ (4.1×10$^{-4}$)</td>
<td>p:10$^2$-10$^3$; n:10$^2$-10$^3$</td>
</tr>
<tr>
<td>Four weeks</td>
<td>1.7×10$^{-3}$ (1.3×10$^{-3}$)</td>
<td>5.5×10$^{-4}$ (3.0×10$^{-4}$)</td>
<td>p:10$^2$-10$^3$; n:10$^2$-10$^3$</td>
</tr>
</tbody>
</table>

* Maximum values of the hole/electron mobilities measured under vacuum (10$^{-4}$-10$^{-5}$ Pa). The average values are in parentheses (from 5 to 10 devices).