Supplementary Information

Synthesis and Photovoltaic Properties of Thieno[3,2-b]thiophenyl Substituted Benzo[1,2-b:4,5-b’]dithiophene Copolymers

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General Experimental Information

Unless noted, all materials were reagent grade and used as received without further purification. Chromatographic separations were performed using standard column methods with silica gel (Merck 9385 Kieselgel 60). Thin layer chromatography was performed on Merck Kieselgel 60 silica gel on glass (0.25 mm thick).

Infrared (IR) spectra were obtained on a Perkin Elmer Spectrum One FT-IR spectrometer and UV-vis spectra were recorded using a Cary 50 UV-Vis spectrometer. Photoluminescence was measured with a Varian Cary Eclipse fluorimeter. Melting points were determined on a Büchi 510 melting point apparatus. $^1$H NMR and $^{13}$C NMR spectra were carried out on a 400 MHz spectrometer. All NMR data was referenced to the chloroform signal and peak multiplicity was reported as follows: s = singlet, d = doublet, t = triplet, q = quartet, p = pentet, dd = doublets of doublets, m = multiplet, br = broad). Differential scanning calorimetry (DSC) experiments were performed on a Perkin-Elmer Sapphire DSC.

High temperature gel permeation chromatography (HT-GPC): Molecular weights of polymer were characterized by HT-GPC performed in 1,2,4-trichlorobenzene (TCB) with 500 ppm 3,5-di-tert-butyl-4-hydroxytoluene (1.0 mL/min) at 120°C using a Malvern Viscotek 350A HT-GPC system with a Refractive Index Detector, a Viscotek 2600 Photodiode Array Detector, a Viscometry Detector, a series of four Malvern high temperature columns (1×Guard + 3×HT6000M), and OmniSEC Software. The GPC was calibrated with narrow polydispersity polystyrene standards (Malvern PolyCal PS standards, MW from 1050 to 4.2×10$^6$), and molecular weights are reported both as polystyrene equivalents based on the refractive index detector, and absolute values using universal calibration based on a combination of the refractive index detector and the viscosity detector. The sample was dissolved in TCB with 500 ppm BHT at a concentration around 2.5 mg/mL at 120 °C for 2 hours before injection.

Cyclic voltammetry (CV) experiments were performed at a sweep rate of 50 mV/s. CVs were carried out in a three-electrode cell consisting of a glassy carbon working electrode, a platinum wire auxiliary electrode, and a Ag/Ag$^+$ pseudo-reference electrode. The supporting electrolyte was 0.10 M tetrabutylammonium hexafluorophosphate (Bu$_4$NPF$_6$) in CH$_3$CN. The solutions were deoxygenated by sparging with argon prior to each scan and blanketed with argon during the scans. The glassy carbon working electrode was prepared by polishing with 5 mm alumina and washed and dried before the polymer was drop-casted on the electrode from chlorobenzene solution to form a film. Ferrocene/ferroceium redox couple was used as the internal standard. The HOMO energy level was calculated from the onset of the oxidation potential of the polymer using the following: $E_{\text{HOMO}} = -(4.8 + E_{\text{ox, onset}})$ eV.
Figure S1. High temperature GPC trace of P1.
Figure S2. High temperature GPC trace of P2.
Figure S3. Differential scanning calorimetry data for polymers (a) P1 and (b) P2.

Figure S4. Solution UV-vis absorption spectrum of polymers P1 and P2 in chloroform (0.04 g/L).

Figure S5. Solution and solid film emission spectra of polymers P1 and P2.
Figure S6. Absorption spectra from films of polymers P1 and P2 blended with PC_{71}BM in a 1:2 weight ratio.
Solar cell device data

Table S1 Additional photovoltaic data of the polymer and PC$_{71}$BM blend films.$^{a,b}$

<table>
<thead>
<tr>
<th>Active layer</th>
<th>$V_{oc}$ (V)</th>
<th>$J_{sc}$ (mA cm$^{-2}$)</th>
<th>FF</th>
<th>PCE (%)</th>
</tr>
</thead>
<tbody>
<tr>
<td>P1:PC$_{71}$BM (1:2)</td>
<td>0.85</td>
<td>10.2</td>
<td>45</td>
<td>3.87</td>
</tr>
<tr>
<td>P2:PC$_{71}$BM (1:2)$^c$</td>
<td>0.96</td>
<td>3.5</td>
<td>37</td>
<td>1.26</td>
</tr>
<tr>
<td>P2:PC$_{71}$BM (1:2)$^d$</td>
<td>0.92</td>
<td>2.6</td>
<td>37</td>
<td>0.88</td>
</tr>
<tr>
<td>P2:PC$_{71}$BM (1:2)$^{c,d}$</td>
<td>0.94</td>
<td>2.6</td>
<td>35</td>
<td>0.84</td>
</tr>
</tbody>
</table>

$^a$ Inverted structure. $^b$ weight ratio. $^c$ with 2.5% of DIO. $^d$ Thermally annealed at 120 °C for 3 min.
**SCLC measurement**

The space charge limited current (SCLC) in the polymers were studied using hole-only devices to find the charge-transport properties. The hole-only devices, consisting of active layer sandwiched between a PEDOT:PSS coated ITO electrode and Au counter-electrode as the electron-blocking contact, were fabricated as shown in Fig. S8. From the current density as a function of voltage data, the hole mobility in the space-charge limited current (SCLC) region can be estimated using the Mott-Gurney equation.

**Hole only device**

![Image of hole only device configuration](image)

Figure S6. Configuration of the hole only device.

![Graph of J^1/2-V plots](image)

Figure S7. Hole only device: $J^{1/2}$-$V$ plots of the dark currents of hole-only with films of polymers P1 and P2 blended with PC$_{71}$BM in a 1:2 weight ratio.
Electron only device

(a) Device structure:
- Al (100 nm)
- Ca (20 nm)
- P1/P2:PC$_{71}$BM (1:2)
- ZnO (25 nm)
- ITO
- Glass substrate

(b) Current density vs. voltage curve.

<table>
<thead>
<tr>
<th>Active layer</th>
<th>Hole Mobility (cm$^2$/Vm)</th>
</tr>
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<tbody>
<tr>
<td>P1:PC$_{71}$BM</td>
<td>1.9 x $10^{-4}$</td>
</tr>
<tr>
<td>P2:PC$_{71}$BM</td>
<td>1.1 x $10^{-4}$</td>
</tr>
</tbody>
</table>

Figure S8. The electron mobility was measured by the space charge limited current (SCLC) method using an electron-only device with a structure of ITO/ZnO/Active layer/Ca/Al. a) Device structure; b) Current density vs. voltage curve.
NMR Spectra

\[^1\text{H} \text{NMR spectrum of compound 6}\]

\[^1\text{H} \text{NMR spectrum of compound 7}\]
$^1$H NMR spectrum of compound 8

$^1$H NMR spectrum of compound 9
$^1$H NMR spectrum of compound 10

$^1$H NMR spectrum of polymer P1
$^1$H NMR spectrum of polymer P2