Supporting Information

Donor–Acceptor Polymers Containing Thiazole-Fused Benzothiadiazole Acceptor Units for Organic Solar Cells

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Thermogravimetric Analysis

**Fig. S1** Thermogravimetric analysis of D–A polymers under nitrogen atmosphere with a heating rate of 10 °C min⁻¹.

**Tauc Plots**

**Fig. S2** Thin film Tauc plots of the D–A polymers and PC₇₁BM.
Cyclic Voltammetry (CV)

Cyclic voltammetry (CV) was performed on an ALS/chi-620C electrochemical analyzer. The CV cell consisted of a thin film sample on ITO electrode, a Pt wire counter electrode, and an Ag/AgNO$_3$ reference electrode. The measurement was carried out using acetonitrile with 0.1 M tetrabutylammonium hexafluorophosphate (Bu$_4$N$^+$PF$_6^-$) as a supporting electrolyte. The redox potentials were calibrated with ferrocene as an internal standard.

**Fig. S3** Cyclic voltammograms of D–A polymers using thin film samples on ITO and 0.1 M Bu$_4$N$^+$PF$_6^-$ as a supporting electrolyte. HOMO and LUMO energy level were estimated from the onset potential of the first oxidation and reduction peak ($E_{\text{HOMO}} = -E_{\text{ox,onset}} - 5.1$ eV and $E_{\text{LUMO}} = -E_{\text{red,onset}} - 5.1$ eV), respectively.$^1$
Theoretical Calculations for the Model Compounds

Fig. S4 (a) Chemical structure, and (b) calculated energy diagram and depiction of the frontier orbitals for the tetramer model compounds of the polymers. Calculations were carried out by the DFT method at B3LYP/6-31G(d) level of theory and the alkyl side chains were replaced with methyl groups to simplify the calculation.
Thin Film Absorption Spectra

Fig. S5 Thin film absorption spectra of (a) neat films and (b) polymer:PC$_{71}$BM blends.
Fig. S6 Surface topographic AFM images of the thin films of P1:PC71BM blend on ITO substrates: (a) without DIO and (b) with 3% DIO, P2:PC71BM blend (c) without DIO and (d) with 3% DIO.
Photovoltaic Characterization

Fig. S7 (a) $J-V$ characteristics and (b) incident photon to current conversion efficiency (IPCE) spectra of $\text{P1}:\text{PC}_{71}\text{BM}$ cells. The amount of 1,8-diiodooctane (DIO) is varied from 1 vol% to 3 vol%.

Table S1 Influence of 1,8-Diiodooctane (DIO) Concentration on the Photovoltaic Parameters of $\text{P1}:\text{PC}_{71}\text{BM}$ Cells

<table>
<thead>
<tr>
<th>DIO</th>
<th>$J_{SC}$ [mA cm$^{-2}$]</th>
<th>$V_{OC}$ [V]</th>
<th>FF</th>
<th>PCE [%]</th>
</tr>
</thead>
<tbody>
<tr>
<td>1 vol%</td>
<td>3.4</td>
<td>0.77</td>
<td>0.41</td>
<td>1.07</td>
</tr>
<tr>
<td>2 vol%</td>
<td>6.5</td>
<td>0.76</td>
<td>0.47</td>
<td>2.32</td>
</tr>
<tr>
<td>3 vol%</td>
<td>12.1</td>
<td>0.78</td>
<td>0.65</td>
<td>6.13</td>
</tr>
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</table>
Space Charge Limited Current (SCLC) Measurements

The hole mobility in the films of materials were measured from the space-charge limited current (SCLC) \( J-V \) characteristics obtained in the dark for hole-only devices. Hole mobility was calculated using the Mott-Gurney law by fitting Equation 1, where \( J \) is the current density, \( \varepsilon_0 \) is the permittivity of free space \( (8.85 \times 10^{-12} \text{ F m}^{-1}) \), \( \varepsilon \) is the relative permittivity of the material (approaching 3 for organic semiconductors), \( \mu \) is the hole mobility, \( V \) is the applied voltage, and \( d \) is the thickness of the active layer, respectively.

\[
J = \frac{9}{8} \varepsilon \varepsilon_0 \mu \frac{V^2}{d^3}
\]  

(1)

The ITO-coated glass substrate \( (5 \, \Omega \, \text{cm}^{-2}, 2.5 \, \text{cm} \times 2.5 \, \text{cm}, \text{GEOMATEC}) \) was washed carefully under ultrasonic irradiation using water (15 min), acetone (15 min), detergent solution (Semico Clean 56, Furuuchi chemical) (15 min), water (15 min) and ethanol (15 min). The substrate was further cleaned with a Filgen UV230 UV/ozone cleaner. A thin layer of PEDOT:PSS (Clevioous P VP AI 4083) was prepared onto the ITO surface by the spin-coating (5000 rpm, 60 s). The resulting substrate was heated at 140 °C for 20 min under ambient conditions. Then, the active layer was deposited by the spin-coating of the chlorobenzene solutions (same for solar cell fabrication) at 600 rpm for 60 s. The film thicknesses were measured with Alphastep IQ (Yamato Scientific Co., Ltd.). As counter electrode, Au was deposited on the film by vacuum evaporation. The current density–voltage curves of the devices were taken with a Keithley 2400 source.
Fig. S8 $J-V$ curves of polymer:PC$_{71}$BM blend films.

Table S2 Hole Mobility ($\mu_h$) Estimated from $J-V$ Curves of Hole-only Polymer:PC$_{71}$BM Blend Films

<table>
<thead>
<tr>
<th>Polymer</th>
<th>Thickness [nm]</th>
<th>$\mu_h$ [cm$^2$ V$^{-1}$ s$^{-1}$]$^a$</th>
</tr>
</thead>
<tbody>
<tr>
<td>P1</td>
<td>96</td>
<td>$\left(1.06 \pm 0.09\right) \times 10^{-5}$</td>
</tr>
<tr>
<td>P2</td>
<td>116</td>
<td>$\left(1.21 \pm 0.08\right) \times 10^{-5}$</td>
</tr>
</tbody>
</table>

$^a$Average hole mobility with standard deviation from 6 samples.
References


NMR spectra.

$^1$H NMR spectrum of 3 (500 MHz, CDCl$_3$)

$^{13}$C NMR spectrum of 3 (126 MHz, CDCl$_3$)
$^1$H NMR spectrum of 5 (500 MHz, CDCl$_3$)

$^{13}$C NMR spectrum of 5 (126 MHz, CDCl$_3$)
$^1$H NMR spectrum of 6 (500 MHz, CDCl$_3$)

$^{13}$C NMR spectrum of 6 (126 MHz, CDCl$_3$)
$^1$H NMR spectrum of 7 (500 MHz, CDCl$_3$)

$^{13}$C NMR spectrum of 7 (126 MHz, CDCl$_3$)