Supporting Information

Synergistic Effects of Terpolymer Regioregularity on the Performance of All-Polymer Solar Cells

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Keywords: all-polymer solar cells, regioregular polymers, terpolymers, D1-A-D2-A, side chain engineering

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Materials and Synthesis

Materials and Synthesis: All reagents were used as obtained from commercial supplies (Sigma Aldrich, ACROS, and TCI) without further purification. (2,6-Bis(trimethyltin)-4,8-bis(5-((2-ethylhexyl)thio)thiophen-2-yl)benzo[1,2-b:4,5-b’]dithiophene (D1), 2,6-bis(trimethyltin)-4,8-bis(5-(2-ethylhexyl)thiophen-2-yl)benzo[1,2-b:4,5-b’]dithiophene (D2), 2-ethylhexyl-4,6-3-fluorothieno[3,4-b]-thiophene-2-carboxylate (A), and symmetric A-D2-A intermediate (TB7) were synthesized according to the literature procedures.1-4 All the PDs were synthesized by Stille polymerization. RR-(D1-A-D2-A) regioregular terpolymers were prepared in a two-step route via an A-D2-A intermediate (TB7), whereas D1-A alternating copolymer and Ra-(D1-A-D2-A) random terpolymers were synthesized by general routes for conventional polycondensation polymerizations.

Synthesis of D1-A: 2,6-Bis(trimethyltin)-4,8-bis(5-((2-ethylhexyl)thio)thiophen-2-yl)benzo[1,2-b:4,5-b’]dithiophene (0.150 g, 0.155 mmol) and 2-(ethylhexyl)-4,6-dibromo-3-fluorothieno[3,4-b]thiophene-2-carboxylate (0.072 g, 0.155 mmol) were mixed in toluene (3.0 mL) and DMF (2 mL). After being purged with argon for 30 min, [Pd(PPh3)4] (0.045 g, 0.039 mmol) was added as the catalyst, and the mixture was then purged with argon for 30 min. The reaction mixture was stirred and heated to 100 °C for 72 h then cooled to room temperature. The raw product was precipitated into methanol and collected by filtration through a Soxhlet thimble. The crude polymer was then subjected to Soxhlet extraction with methanol, acetone, hexanes, and chloroform. The purified polymer was collected and dried under vacuum overnight. Therefore, purified D1-A with a purple-black luster (0.106 g, 71.4%) was obtained. ^1H NMR (400 MHz, CDCl3): δ 8.10-6.38 (br, 6H), 4.70-4.01 (br, 2H), 3.35-2.05 (br, 4H), 2.22-
0.55 (br, 45H). Anal. Calcd (%) for (C_{30}H_{60}FO_{2}S_{8})_{n}: C, 62.00; H, 6.24; S, 26.49. Found: C, 61.78; H, 6.02; S, 26.97.

^1H NMR spectrum

Synthesis of Ra-(D1-A-D2-A): 2,6-Bis(trimethyltin)-4,8-bis(5-((2-ethylhexyl)thio)thiophen-2-yl)benzo[1,2-b:4,5-b']dithiophene (0.075 g, 0.077 mmol), 2,6-Bis(trimethyltin)-4,8-bis(5-(2-ethylhexyl)thiophen-2-yl)benzo[1,2-b:4,5-b']dithiophene (0.070 g, 0.077 mmol) and 2-(ethylhexyl)-4,6-dibromo-3-fluorothieno[3,4-b]thiophene-2-carboxylate (0.072 g, 0.155 mmol) were mixed in toluene (3 mL) and DMF (2 mL). After being purged with argon for 30 min, [Pd(PPh₃)₄] (0.045 g, 0.039 mmol) was added as the catalyst, and the mixture was then purged with argon for 30 min. The reaction mixture was stirred and heated to 100 °C for 72 h then cooled to room temperature. The raw product was precipitated into methanol and collected by filtration through a Soxhlet thimble. The crude polymer was then subjected to Soxhlet extraction with methanol, acetone, hexanes, and chloroform. The purified polymer was
collected and dried under vacuum overnight. Therefore, purified Ra-(D1-A-D2-A) with a purple-black luster (0.120 g, 83.1%) was obtained. $^1$H NMR (400 MHz, CDCl$_3$): $\delta$ 8.20-6.35 (br, 12H), 4.11-4.53 (br, 4H), 3.35-2.55 (br, 8H), 2.30-0.58 (br, 90H). Anal. Calcd (%) for (C$_{99}$H$_{117}$F$_2$O$_4$S$_{14}$)$_n$: C, 64.00; H, 6.35; S, 24.16. Found: C, 63.54; H, 6.41; S, 24.75.

$^1$H NMR spectrum

*Synthesis of RR-(D1-A-D2-A):* Monomeric TB7 (0.321 g, 0.236 mmol), 2,6-Bis(trimethyltin)-4,8-bis(5-((2-ethylhexyl)thio)thiophen-2-yl)benzo[1,2-b:4,5-b']dithiophene (0.229 g, 0.236 mmol), toluene (4.8 mL), and DMF (2.3 mL) were charged into a flask under a nitrogen atmosphere to obtain a clear solution. The solution was bubbled with nitrogen for 30 min. Then, [Pd(PPh$_3$)$_4$] (0.069 g, 0.060 mmol) was added to the solution. The mixed solution was stirred at 100 °C for 72 h. After polymerization, 4-bromobenzotrifluoride (0.8 mL) was added to the solution. It is known that the fluorine functionalization of the end group (trifluoromethyl-benzene) of the conjugated polymer can lead to the improved absorption and effective charge
transport due to the increased π-π interactions between the polymer chains, resulting in enhanced $J_{sc}$ and FF. Then, the resulting solution was stirred for 12 h and cooled to room temperature. Then, the reaction mixture was poured into methanol. The precipitated polymer was purified by Soxhlet extraction using methanol, acetone, hexane, dichloromethane, chloroform, and chlorobenzene. The chlorobenzene extract was concentrated and then poured into methanol to obtain the purified polymer. The purified polymer was collected and dried under vacuum overnight. As a result, purified $RR-(D_1-A-D_2-A)$ with a purple-black luster (0.272 g, 65.9%) was obtained. $^1$H NMR (400 MHz, CDCl$_3$): δ 8.10-6.35 (br, 12H), 4.65-3.85 (br, 4H), 3.22-2.58 (br, 8H), 2.24-0.58 (br, 90H). Anal. Calcd (%): for (C$_{99}$H$_{117}$F$_2$O$_4$S$_{14}$)$_n$: C, 64.00; H, 6.35; S, 24.16. Found: C, 63.29; H, 6.25; S, 24.15.

$^1$H NMR spectrum
• Fabrication of All-PSCs

Inverted structure all-PSC device were fabricated with the following structure: Indium tin oxide (ITO)/ZnO/Active layer/MoO$_3$/Ag. The ITO glass substrates were cleaned by ultrasonication in acetone, deionized water and isopropyl alcohol, sequentially. The ITO glass substrates were fully dried in an oven at 80 °C. After UV-ozone treatment of ITO substrates, a filtered ZnO solution was applied by spin-coating at 4000 rpm for 40 sec and baking for 20 min at 150 °C in ambient condition. All of the blend solutions of polymer donor/P(NDI2HD-DTAN) (1.3/1.0 w/w) with 2.5 vol% diphenyl ether (DPE) were prepared in chloroform (CF) solvent at concentration of 10mg/mL. These solutions were vigorously stirred at 45 °C for 3h prior to spin coating, and then each blend solution was spin-cast onto a ZnO layer at 3000 rpm for 40 sec. The active layer coated substrate were placed in thermal evaporation chamber and MoO$_3$ (10nm) and Ag (120nm) were thermally deposited sequentially under high vacuum state (<10$^{-6}$ Torr).

• Fabrication of Organic Field-Effect Transistor (OFET) devices

OFETs were fabricated in a bottom-gate and top-contact configuration to observe the electrical properties of polymer donors using 1,2-dichlorobenzene (oDCB) processing solvent. The SiO$_2$/Si wafers were treated with a trichlorosilane (OTS) self-assembled monolayer. The fully dissolved four polymer donors were spin-coated onto the OTS-treated SiO$_2$/Si substrate. Au electrode (40 nm) were thermally evaporated through a patterned shadow mask onto the semiconducting active layer. The electrical performance of the FETs was measured in a N$_2$-filled chamber using a Keithley 4200 semiconductor parametric analyzer.
**Characterization**

The photovoltaic performance of the devices was measured using a solar simulator (K201 LAB55, McScience), irradiating at 100 mW cm$^{-2}$ with a 150 W Xe short-arc lamp filtered by an air mass 1.5G filter. All the measurement of devices were carried out after light intensity calibration with a Si reference cell (K801S-K302, McScience). External Quantum Efficiencies (EQEs) were measured using a spectral measurement system (K3100 IQX, McScience), which applied monochromatic light from a xenon arc lamp at 300 W filtered by an optical chopper (MC 2000 Thorlabs) and a monochromator (Newport). For space-charge limited current (SCLC) measurements of hole and electron mobilities, SCLC devices were fabricated with the structure of ITO/poly(3,4-ethylenedioxythiphene) polymericstyrene sulfonate (PEDOT:PSS)/active layer/Au and ITO/ZnO/active layer/LiF/Al, respectively. Grazing incidence X-ray scattering (GIXS) were performed at beamline 9A in the Pohang Accelerator Laboratory (Republic of Korea), GIXS samples were prepared on Si wafers under same optimized device conditions.
**Figure S1.** Cyclic voltammetry curves of D1-A, Ra-(D1-A-D2-A) and RR-(D1-A-D2-A) films.

**Table S1.** Packing parameters extracted from GIXS measurements for pristine films.

<table>
<thead>
<tr>
<th>Pristine films</th>
<th>(d_{100}) (IP) (Å)</th>
<th>(d_{010}) (OOP) (Å)</th>
<th>CCL(_{100}) (Å)</th>
<th>CCL(_{010}) (Å)</th>
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</thead>
<tbody>
<tr>
<td>D1-A</td>
<td>24.6</td>
<td>3.9</td>
<td>83.7</td>
<td>23.4</td>
</tr>
<tr>
<td>Ra-(D1-A-D2-A)</td>
<td>23.5</td>
<td>4.0</td>
<td>78.5</td>
<td>18.9</td>
</tr>
<tr>
<td>RR-(D1-A-D2-A)</td>
<td>23.7</td>
<td>3.9</td>
<td>88.5</td>
<td>24.2</td>
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</table>

**Figure S2.** Transfer characteristics of (a) D1-A, (b) Ra-(D1-A-D2-A) and (c) RR-(D1-A-D2-A) for OFET devices.
Figure S3. Space-charge-limited $J$-$V$ characteristics of the D$_1$-A, Ra-(D$_1$-A-D$_2$-A) and RR-(D$_1$-A-D$_2$-A) films under dark conditions for hole-only devices.

Figure S4. Dependence of (a) $J_{sc}$ and (b) $V_{oc}$ on illuminated light intensity ($P$) of D$_1$-A, Ra-(D$_1$-A-D$_2$-A) and RR-(D$_1$-A-D$_2$-A) based all-PSCs.
**Figure S5.** (a) 2D-GIXS images of D1-A:PA, Ra-(D1-A-D2-A):PA and RR-(D1-A-D2-A):PA blend films. Line cuts of GIXS images: (b) in-plane and (c) out-of-plane.

**Table S2.** Packing parameters extracted from GIXS measurements for blend films.

<table>
<thead>
<tr>
<th>Blend films</th>
<th>$d_{100}$ (IP) (Å)</th>
<th>$d_{010}$ (OOP) (Å)</th>
<th>CCL$_{100}$ (Å)</th>
</tr>
</thead>
<tbody>
<tr>
<td>D$_1$-A:PA</td>
<td>24.0</td>
<td>3.9</td>
<td>60.4</td>
</tr>
<tr>
<td>Ra-(D$_1$-A-D$_2$-A):PA</td>
<td>23.7</td>
<td>3.9</td>
<td>61.0</td>
</tr>
<tr>
<td>RR-(D$_1$-A-D$_2$-A):PA</td>
<td>23.9</td>
<td>3.8</td>
<td>72.2</td>
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</table>
Figure S6. (a) 2D-GIXS images of P(NDI2HD-DTAN) pristine film. Line cuts of GIXS images: (b) in-plane and (c) out-of-plane.
REFERENCES


