Supporting Information

Thiophene-Benzothiadiazole Based D-A₁-D-A₂ Type Alternating Copolymers for Polymer Solar Cells

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Experimental Section

1. General

$^1$H- and $^{13}$C-NMR spectra were measured on a Bruker AVANCE III HD 300 instrument operated at 400 and 100 MHz, respectively. Mass spectra were measured using a JEOL JMS-700 MStation. Thermogravimetric analysis was carried out using a Thermo Plus EVOII TG8120 under $\text{N}_2$ at a heating rate of 10 °C/min. UV-vis absorption measurements were carried out with a double-beam Shimadzu UV–2550 spectrophotometer. Cyclic voltammetry was carried out using an IviumStat instrument under argon using 0.1 M tetrabutylammonium hexafluorophosphate solution in acetonitrile at a scan rate of 50 mVs$^{-1}$ at 25 °C. A Pt wire, a Ag/AgCl electrode, and a platinum electrode coated with polymer film were used as the counter, reference, and working electrodes, respectively. AFM surface images (2 × 2 µm$^2$) were obtained using a scanning probe Multimode III instrument in tapping mode. 2D-GIWAX measurements were performed on the PLS–II 3C beam line at the Pohang Accelerator Laboratory in South Korea. The active materials were coated on a PEDOT:PSS/silicon substrate under the optimized device fabrication conditions. A monochromatic X-ray beam with an 11-keV intensity and an incident angle of 0.100–0.140° was used to irradiate the samples for 5 to 30 s. The scattered X-ray patterns were recorded with a charge-coupled device (CCD) detector.

2. PSC Device fabrication and characterization

All the polymer solar cells were fabricated using the conventional ITO/PEDOT:PSS/polymer:PC$_{71}$BM/Ca/Al device structure. First, the ITO glass substrate was cleaned in sequence with detergent, deionized water, acetone, and isopropyl alcohol in an ultrasonic treatment, followed by oven drying at 120 °C for 5 h. The ITO glass was then treated with UV-ozone (UVO) for 20 min and PEDOT:PSS (Heraeus Clevios™ P VP AI 4083) was spin coated at 5500 rpm for 60 s, followed by annealing at 150 °C for 20 min in air. The thickness of the PEDOT:PSS layer was ~30 nm. The
polymer:PC$_{71}$BM blends (1.0:1.5 by weight in CB with 3 vol% DPE) was spin-coated on top of the PEDOT:PSS layer in a glove box, and the thickness of the active layer was varied by changing the spin rate. Finally, Ca (2 nm) and Al (100 nm) were deposited onto the active layer in a vacuum (~3 × 10$^{-6}$ Torr). A shadow mask was used to define the active area (9 mm$^2$) of the PSC devices. The current density versus voltage ($J$-$V$) curves were measured under ambient conditions using a Keithley 236 and a xenon lamp (1000 W) fitted with an AM 1.5G filter. The light intensity was calibrated to 100 mW cm$^{-2}$. The external quantum efficiency curves were measured using a 100 W halogen lamp. The corresponding photocurrent was measured using a lock-in amplifier, and the absolute photocurrent was determined using a calibrated silicon photodiode.

3. Hole and electron mobility measurements.

The charge carrier mobilities of the polymers and blends were measured using the SCLC method based on the Mott-Gurney equation ($J = 9\varepsilon_0\varepsilon_r \mu V^2/8L^3$), where $J$ is the current density, $\varepsilon_r$ is the dielectric constant of the polymer, $\varepsilon_0$ is the permittivity of free space (8.85 × 10$^{-12}$ F m$^{-1}$), and $L$ is the active layer thickness). The potential loss arising from the series resistance ($V_r$) of the ITO contact and the built-in potential ($V_{bi}$) during the measurements were considered to ensure accuracy.

4. Materials: Synthesis of the intermediates and monomers

All chemicals were purchased from Aldrich, Alfa Aesar, and TCI Chemical Co. 5,6-Difluorobenzo[c][1,2,5]thiadiazole was purchased from 4Chem Co. The monomers 4,7-dibromo-5,6-bis(2-hexyldecyloxy)benzo[c][1,2,5]thiadiazole (M1)$^1$ and 5,6-difluoro-4,7-bis(5-(trimethylstannyl)thiophen-2-yl)benzo[c][1,2,5]thiadiazole (M6)$^2$ were prepared following previously reported methods.
Scheme S1 Synthetic routes to intermediate alcohols.
3-Hexylundecanoic acid (1a). To a stirred solution of magnesium (0.5 g, 19.65 mmol) in dry diethyl ether (50 mL) under argon, 7-(bromomethyl)pentadecane (1) (5 g, 16.37 mmol) was added dropwise. A flake of iodine was added as a reaction initiator. Then the reaction mixture was refluxed until the magnesium was completely consumed. The reaction solution was cooled to room temperature (RT), quenched with dry ice, and stirred for another 30 min. Finally, the residue was dissolved in water (50 mL) acidified with 6 M HCl (aq), and the resulting solution was extracted with dichloromethane (CH₂Cl₂) (3 × 200 mL). The combined organic layer was dried over anhydrous MgSO₄. The solvent was evaporated, and the product was obtained (1a) (3 g, 68%) as a pale-yellow oil, which was used for the next step without further purification. ¹H-NMR (300 MHz, CDCl₃): δ (ppm) 2.27 (d, J = 6.78 Hz, 2H), 1.85 (m, 1H), 1.32–1.16 (m, 24H), 0.87 (m, 6H).

3-Hexylundecan-1-ol (2). To a stirred solution of lithium aluminum hydride (LAH) (0.9 g, 22.2 mmol) in anhydrous tetrahydrofuran (THF), compound (1a) (1.5 g, 5.54 mmol) in THF was added dropwise at 0 °C and the reaction mixture was stirred at RT for 12 h. The reaction solution was cooled to 0 °C and quenched with water and 1.5 N HCl, the resulting mixture was extracted with ethyl acetate (EA) (3 × 100 mL). The organic layer was combined and dried over anhydrous MgSO₄. The crude product was purified by column chromatography using EA:hexane (1:1 by volume) as the eluent, affording the product (2) (0.45 g, 33%) as a pale yellow oil. ¹HNMR (300 MHz, CDCl₃): δ (ppm) 3.66 (t, J = 7.0Hz, 2H), 1.52 (m, 2H), 1.42 (m, 1H), 1.32-1.14 (m, 24H), 0.88 (m, 6H). MS (EI): Calcd for [C₁₇H₃₆O], m/z (M⁺) = 256.47; found: 257.

Ethyl 3-octylundec-2-enoate (3a). Ethyl 2-(diethoxyphosphoryl)acetate (5 g, 23.57 mmol) was slowly added to a solution of sodium hydride (60 w/w% mineral oil suspension, 0.95 g, 23.57 mmol) in THF at 0 °C and stirred for 30 min. To the resulting solution, 9-heptadecanone (3) (2 g, 7.85 mmol) was added at
RT, and the mixture was refluxed for 18 h. The reaction solution was brought to RT and quenched with distilled water. The organic layer was dried over anhydrous MgSO<sub>4</sub> and concentrated under reduced pressure. The residue was purified by flash chromatography (silica gel, hexane:DCM = 5:1 by volume) to give 3a (2 g, 80%) as a colorless oil. <sup>1</sup>HNMR (300 MHz, CDCl<sub>3</sub>): δ (ppm) 5.61 (br s, 1H), 4.13 (m, 3H), 2.58 (m, 2H), 2.12 (m, 2H), 1.44 (m, 4H), 1.27 (m, 23H), 0.88 (m, 6H). MS (EI): Calcd for [C<sub>21</sub>H<sub>40</sub>O<sub>2</sub>], m/z (M<sup>+</sup>) = 324.55; found: 324.

**Ethyl 3-octylundecanoate (3b).** A mixture of 3a (2g, 6.17 mmol) and platinum oxide (60 mg) in CHCl<sub>3</sub>/MeOH (5:1, v:v) (30 mL) was stirred vigorously under H<sub>2</sub> (1 atm) at room temperature. The residue was filtered on a celite bed, and the residue was concentrated. The colorless crude oil (3b) (1.8 g, 93%) was used for the next step without further purification. <sup>1</sup>HNMR (300 MHz, CDCl<sub>3</sub>): δ (ppm) 4.13 (m, 3H), 2.22 (m, 2H), 1.84 (m, 1H), 1.25 (m, 23H), 0.88 (m, 6H). MS (EI): Calcd for [C<sub>21</sub>H<sub>42</sub>O<sub>2</sub>], m/z (M<sup>+</sup>) = 326.57; found: 326.

**3-Octylundecan-1-ol (4).** To a stirred solution of LAH (1.2 g, 32 mmol) in anhydrous THF (20 mL), ethyl 3-octylundecanoate (3b) (2.5 g, 8 mmol) in THF was added dropwise at 0 °C. The resulting solution was stirred at RT for 12 h and was cooled to 0 °C and quenched with water and 1.5 N HCl. The reaction mixture was extracted with EA (3 × 100 mL), and the combined organic layer was dried over anhydrous MgSO<sub>4</sub>. The crude product was purified by the column chromatography using EA:hexane (1:1, v/v) as the eluent to afford product 4 (2 g, 88%) as a pale-yellow oil. <sup>1</sup>HNMR (300MHz, CDCl<sub>3</sub>): δ (ppm) 3.66 (t, J = 8Hz, 2H), 1.54 (m, 2H), 1.49 (m, 1H), 1.32-1.14 (m, 9H), 0.88 (m, 6H). MS (EI): Calcd for [C<sub>19</sub>H<sub>40</sub>O], m/z (M<sup>+</sup>) = 284.53; found: 284.
3-Octyltridecan-1-ol (6). To a stirred solution of magnesium (0.35 g, 14.40 mmol) in dry diethyl ether (50 mL) under argon, 9-(bromomethyl)nonadecane (5) (4 g, 11.08 mmol) was added dropwise. A flake of iodine was added as a reaction initiator. Then, the reaction solution was refluxed until magnesium was completely consumed, cooled to RT, quenched with dry ice, and stirred for another 30 min. The residue was dissolved in water (50 mL) acidified with 6 M HCl (aq.) and extracted with CH$_2$Cl$_2$ (3 × 200 mL). The combined organic layer was dried over anhydrous MgSO$_4$ and concentrated under reduced pressure, yielding 3-octyltridecanoic acid (5a) (3 g, 83%) as a pale-yellow oil that was used for next step without further purification. To the stirred solution of LAH (1.4 g, 36.77 mmol) in anhydrous THF, crude compound (5a) (3 g, 9.19 mmol) in THF was added dropwise at 0 °C and the reaction mixture was stirred at RT for 12 h. The resulting solution was cooled to 0 °C and quenched with water and 1.5 N HCl, and extracted with EA (3 × 100 mL). The organic layer was combined and dried over anhydrous MgSO$_4$. The crude product was purified by column chromatography using EA:hexane (1:1, v:v) as the eluent to afford product 6 (0.8 g, 23% yield for the two successive steps) as a pale yellow oil. $^1$H-NMR (300 MHz, CDCl$_3$): $\delta$ (ppm) 3.66 (t, $J$ = 7.06 Hz, 2H), 1.51 (q, 2H), 1.39 (m, 1H), 1.29–1.22 (m, 33H), 0.88 (m, 6H). MS (EI): Calcd for [C$_{21}$H$_{44}$O], m/z (M$^+$) = 312.58; found: 312.

3-Decyltridecyl acetate (7a). To a stirred solution of 11-(2-iodoethyl)heneicosane (7) (2.5 g, 5.54 mmol) in anhydrous DMF (60 mL), sodium acetate (0.91 g, 11.09 mmol) was added and stirred at 100 °C for 12 h. After cooling the reaction mixture to RT, the DMF solution was concentrated, water was added, and the resulting mixture was extracted with EA. The organic layers were combined and dried over anhydrous MgSO$_4$. The crude product was purified by column chromatography using EA:hexane (1:9, v:v) as the eluent to afford 7a (1.7 g, 80%) as a pale-yellow oil. $^1$H-NMR (300 MHz, CDCl$_3$): $\delta$ (ppm) 4.07 (t, $J$ =
7.14 Hz, 2H), 2.04 (s, 3H), 1.56 (q, 2H), 1.29-1.24 (m, 37H), 0.87 (m, 6H). MS (EI): Calcd for [C_{25}H_{50}O_2], m/z (M+) = 382.67; found: 382.

**3-Decyltridecan-1-ol (8).** To a stirred solution of 3-decyltridecyl acetate (7a) (0.8 g, 2.1 mmol) in DMF (60 mL) and 10 mL 1N NaOH, potassium carbonate (0.87 g, 6.27 mmol) was added, and the reaction solution was stirred at room temperature for 12 h. After cooling the reaction mixture to RT, the DMF solution was concentrated, water was added, and the resulting mixture was extracted with EA. The organic layer was combined and dried over MgSO_4. The crude product was purified by column chromatography using EA:CH_2Cl_2 (4:6, v:v) as the eluent to afford product 8 (0.55 g, 65%) as a pale-yellow oil. ^1H NMR (300 MHz, CDCl_3): δ (ppm) 3.66 (t, J= 7.14 Hz, 2H), 1.52 (q, 2H), 1.40 (m, 1H), 1.29-1.24 (m, 37H), 0.87 (m, 6H). MS (EI): Calcd for [C_{23}H_{48}O], m/z (M+) = 340.64; found: 340.

**General procedure for the synthesis of the ROBT monomers.**

Hydroxyl-functionalized 2, 4, 6, or 8 (2.5 eq.) was added into a two-neck round bottom flask containing anhydrous THF (25 mL) under argon. After the reaction solution had been cooled to 0 °C, sodium hydride (3 eq.) was added as one portion, and the solution was stirred for 1 h at 0 °C. Then, difluorobenzo[c][1,2,5]thiadiazole (9) (1 eq.) was added, and the reaction mixture was refluxed overnight. The reaction solution was quenched by adding water (100 mL) and extracted with diethyl ether. The organic extract was dried over anhydrous magnesium sulfate and then concentrated by rotary evaporation. After concentration, the crude product was used directly for bromination without purification. To a stirred solution of the crude product in chloroform (30 mL) and hydrobromic acid (5 mL), bromine (2.5 eq.) was added at room temperature, and the resulting solution was refluxed overnight. Then, the reaction solution was cooled down to RT, and the mixture was quenched by adding aqueous sodium sulfide solution and then extracted with chloroform (3 × 50 mL). The organic phase was dried over anhydrous magnesium
sulfate and then concentrated under reduced pressure. The residue was purified by flash chromatography (silica gel, hexane:DCM = 4:1 (v:v)) to afford the product (M2–M5).

4,7-Dibromo-5,6-bis(3-hexylundecyloxy)benzo[c][1,2,5]thiadiazole (M2). Yield: 0.4 g, 88%. $^1$H NMR (300 MHz, CDCl$_3$): $\delta$ (ppm) 4.18 (t, J = 7.09 Hz, 4H), 1.86 (q, 4H), 1.55 (m, 2H), 1.34-1.24 (m, 48H), 0.87 (m, 12H).$^{13}$C NMR (100 MHz, CDCl$_3$): $\delta$ (ppm) 154.59, 150.39, 106.24, 73.65, 34.46, 34.19, 33.70, 31.93, 30.12, 29.77, 29.69, 29.38, 26.57, 26.54, 22.70, 14.12. MS (EI): Calcd for [C$_{40}$H$_{70}$Br$_2$N$_2$O$_2$S], m/z (M$^+$) = 802.88; found: 802.

4,7-Dibromo-5,6-bis(3-octylundecyloxy)benzo[c][1,2,5]thiadiazole (M3). Yield: 0.7 g, 40% as colorless oil. $^1$H NMR (300 MHz, CDCl$_3$): $\delta$ (ppm) 4.18 (t, J = 7.10 Hz, 4H), 1.87 (q, 4H), 1.6 (m, 2H), 1.34-1.24 (m, 56H), 0.87 (m, 12H).$^{13}$C NMR (100 MHz, CDCl$_3$): $\delta$ (ppm) 154.59, 150.39, 106.24, 73.65, 34.46, 34.20, 33.70, 31.94, 30.12, 29.69, 29.39, 26.58, 22.70, 14.13. MS (EI): Calcd for [C$_{44}$H$_{78}$Br$_2$N$_2$O$_2$S], m/z (M$^+$) = 858.99; found: 858.

4,7-Dibromo-5,6-bis(3-octyltridecyloxy)benzo[c][1,2,5]thiadiazole (M4). Yield: 0.5 g, 75% as colorless oil. $^1$H NMR (300 MHz, CDCl$_3$): $\delta$ (ppm) 4.18 (t, J = 7.10 Hz, 4H), 1.86 (q, 4H), 1.6 (m, 2H), 1.34-1.24 (m, 64H), 0.87 (m, 12H).$^{13}$C NMR (100 MHz, CDCl$_3$): $\delta$ (ppm) 154.59, 150.39, 106.24, 73.65, 34.46, 34.20, 33.70, 31.94, 30.12, 29.74, 29.69, 29.58, 26.57, 26.54, 22.70, 14.13. MS (EI): Calcd for [C$_{48}$H$_{86}$Br$_2$N$_2$O$_2$S], m/z (M$^+$) = 915.10; found: 915.

4,7-Dibromo-5,6-bis(3-decyltridecyloxy)benzo[c][1,2,5]thiadiazole (M5). Yield: 0.4 g, 86% as colorless oil. $^1$H NMR (300 MHz, CDCl$_3$): $\delta$ (ppm) 4.18 (t, J = 7.02 Hz, 4H), 1.85 (q, 4H), 1.6 (m, 2H), 1.34-1.24 (m, 72H), 0.87 (m, 12H).$^{13}$C NMR (100 MHz, CDCl$_3$): $\delta$ (ppm) 154.59, 150.39, 106.25, 73.65, 34.46, 34.20, 33.71, 31.95, 30.13, 29.74, 29.69, 29.39, 26.57, 26.59, 22.70, 14.12. MS (EI): Calcd for [C$_{52}$H$_{94}$Br$_2$N$_2$O$_2$S], m/z (M$^+$) = 971.20; found: 971.
General synthetic procedure for the polymers

To a 5-mL microwave vial, ROBT monomers (M1–M5) (0.3 mmol), 5,6-difluoro-4,7-bis(5-(trimethylstannyl)thiophen-2-yl)benzo[c][1,2,5]thiadiazole (M6) (0.3 mmol), Pd2(dba)3 (3 mol%), tri-(o-tolyl)phosphine (6 mol%), and anhydrous chlorobenzene (1 mL) were added. The resulting reaction mixture was heated at 100 °C for 10 min, 120 °C for 10 min, and 140 °C for 60 min in a microwave reactor. The crude polymers were purified by Soxhlet extraction with methanol for 12 h, acetone for 12 h, hexane for 12 h, and chloroform or chlorobenzene (CB) for 12 h. The chloroform or CB portion was then concentrated under reduced pressure, precipitated into methanol, and filtered to give the polymers P1–P5. The polymer was then dried in a vacuum oven for 24 h. Due to the instrument limit and the strong interchain aggregation, the high quality NMR spectra could not be obtained. Although the NMR spectra were obtained in chlorobenzene-d5 at 80 °C, the aromatic protons in thiophene were not discernible.

P1: 170 mg, 59% yield, \( M_n = 68,300 \) g/mol (PDI=3.0). \(^1\)H NMR (500 MHz, C\(_6\)D\(_5\)Cl): \( \delta \) (ppm) 4.05-3.64 (br, 4H), 2.23-0.43 (br, 62H).

P2: 220 mg, 75% yield, \( M_n = 74,200 \) g/mol (PDI=2.7). \(^1\)H NMR (500 MHz, C\(_6\)D\(_5\)Cl): \( \delta \) (ppm) 3.97-3.68 (br, 4H), 2.49-0.26 (br, 66H).

P3: 195 mg, 63% yield, \( M_n = 77,800 \) g/mol (PDI=2.8). \(^1\)H NMR (500 MHz, C\(_6\)D\(_5\)Cl): \( \delta \) (ppm) 4.08-3.60 (br, 4H), 2.58-0.43 (br, 74H).

P4: 170 mg, 52% yield, \( M_n = 70,400 \) g/mol (PDI=2.8). \(^1\)H NMR (500 MHz, C\(_6\)D\(_5\)Cl): \( \delta \) (ppm) 3.96-3.64 (br, 4H), 2.69-0.23 (br, 82H).

P5: 200 mg, 58% yield, \( M_n = 86,000 \) g/mol (PDI=3.2). \(^1\)H NMR (500 MHz, C\(_6\)D\(_5\)Cl): \( \delta \) (ppm) 4.23-3.52 (br, 4H), 2.58-0.34 (br, 90H).
Fig. S1 (a) DSC thermograms and cyclic voltammograms of polymers.

Fig. S2 $J$-$V$ curves of hole-only devices under dark.
Fig. S3 $J$-$V$ characteristics of $P2$:PC$_{71}$BM with changing D:A blend ratio (solvent: CB/3vol% DPE).

Fig. S4 $J$-$V$ characteristics of $P2$:PC$_{71}$BM with varying the active layer thickness.
Fig. S5 J-V characteristics of P2:PC$_{71}$BM with different solvent additives.
Fig. S6 $J$–$V$ characteristics of (a) hole-only and (b) electron-only devices based on polymer:PC$_{71}$BM blend films (solvent: CB/3vol% DPE). The solid line is a fitting curve using the Mott–Gurney relationship.
Fig. S7 Photocurrent density ($J_{ph}$) versus effective voltage ($V_{eff}$) for polymer:PC$_7$BM devices.
Fig. S8. J-V curves of polymer:PC$_{71}$BM under varying light intensity (3.2 - 100 mWcm$^{-2}$).
Fig. S9 $^1$H NMR (above) and $^{13}$C NMR (below) spectra of M1 in CDCl$_3$. 
Fig. S10 ¹H NMR (above) and ¹³C NMR (below) spectra of M2 in CDCl₃.
Fig. S11 $^1$H NMR (above) and $^{13}$C NMR (below) spectra of M3 in CDCl$_3$. 
Fig. S12 $^1$H NMR (above) and $^{13}$C NMR (below) spectra of M4 in CDCl$_3$.
Fig. S13 $^1$H NMR (above) and $^{13}$C NMR (below) spectra of M5 in CDCl$_3$. 
Table S1 Device characteristics of P2:PC$_{71}$BM PSCs processed with different blend ratios (solvent: CB/3vol % DPE).

<table>
<thead>
<tr>
<th>Weight Ratio (P2:PC$_{71}$BM)</th>
<th>$V_{oc}$ [V]</th>
<th>$J_{sc}$ [mA/cm$^2$]</th>
<th>FF [%]</th>
<th>PCE [%]</th>
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<tr>
<td>1.0:1.0</td>
<td>0.84</td>
<td>14.09</td>
<td>66</td>
<td>7.83</td>
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<tr>
<td>1.0:1.5</td>
<td>0.85</td>
<td>14.49</td>
<td>67</td>
<td>8.27</td>
</tr>
<tr>
<td>1.0:2.0</td>
<td>0.84</td>
<td>13.24</td>
<td>67</td>
<td>7.43</td>
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Table S2 Summary of photovoltaic parameters of P2:PC$_{71}$BM (1:1.5) with varying film thickness (solvent: CB/3vol % DPE).

<table>
<thead>
<tr>
<th>Thickness [nm]</th>
<th>$V_{oc}$ [V]</th>
<th>$J_{sc}$ [mA/cm$^2$]</th>
<th>FF [%]</th>
<th>PCE [%]</th>
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<tr>
<td>~180</td>
<td>0.83</td>
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<td>65</td>
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<td>~130</td>
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<td>67</td>
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<tr>
<td>~100</td>
<td>0.85</td>
<td>14.49</td>
<td>67</td>
<td>8.27</td>
</tr>
<tr>
<td>~75</td>
<td>0.85</td>
<td>13.02</td>
<td>68</td>
<td>7.57</td>
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Table S3 Summary of photovoltaic parameters of P2:PC$_{71}$BM (1:1.5) with different solvent additives.

<table>
<thead>
<tr>
<th>Solvent</th>
<th>$V_{oc}$ [V]</th>
<th>$J_{sc}$ [mA/cm$^2$]</th>
<th>$FF$ [%]</th>
<th>PCE [%]</th>
</tr>
</thead>
<tbody>
<tr>
<td>CB</td>
<td>0.87</td>
<td>8.82</td>
<td>54</td>
<td>4.12</td>
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<tr>
<td>CB+ 3 vol% CN</td>
<td>0.87</td>
<td>12.91</td>
<td>65</td>
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</tr>
<tr>
<td>CB+ 3 vol% DPE</td>
<td>0.85</td>
<td>14.49</td>
<td>67</td>
<td>8.27</td>
</tr>
<tr>
<td>CB+ 3 vol% DIO</td>
<td>0.84</td>
<td>13.54</td>
<td>69</td>
<td>7.84</td>
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Table S4 Summary of GIWAXS Packing parameters.

<table>
<thead>
<tr>
<th>Film</th>
<th>Solvent</th>
<th>(100)$^a$ [Å]</th>
<th>(010)$^a$ [Å]</th>
<th>(100)$^b$ [Å]</th>
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<tbody>
<tr>
<td>P1:PC$_{71}$BM</td>
<td>CB+DPE</td>
<td>20.8</td>
<td>3.7</td>
<td>20.1</td>
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<tr>
<td>P2:PC$_{71}$BM</td>
<td>CB+DPE</td>
<td>23.4</td>
<td>3.5</td>
<td>21.8</td>
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<tr>
<td>P3:PC$_{71}$BM</td>
<td>CB+DPE</td>
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<td>3.6</td>
<td>22.5</td>
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<tr>
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<td>CB+DPE</td>
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<td>23.4</td>
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<td>CB+DPE</td>
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$^a$Out-of-plane direction. $^b$In-plane direction.
References
