

Supplementary Information

Small Band Gap Polymers Based on Diketopyrrolopyrrole

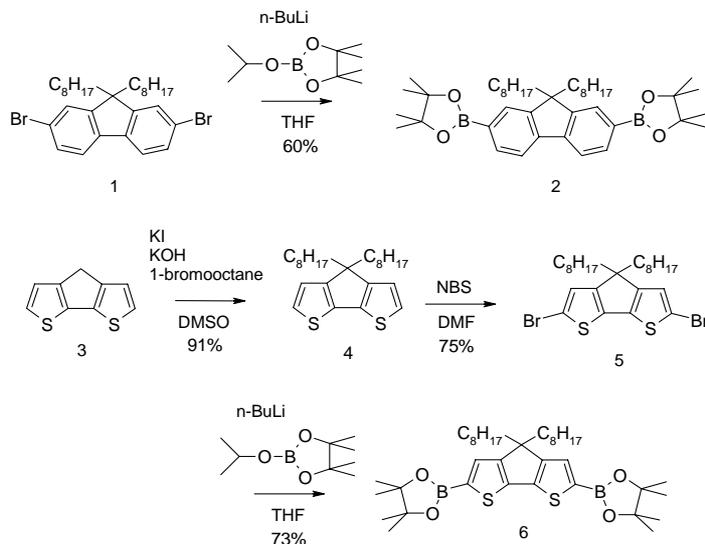
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1. Synthesis

The synthetic routes toward monomers **2** and **6** are depicted in Scheme 1. Both monomers are functionalized to be applied in a Suzuki-type polymerization reaction. Starting from the commercially available 2,7-dibromo-9,9-dioctylfluorene (**1**), lithiation using *n*-butyllithium followed by addition of excess 2-isopropoxy-4,4,5,5-tetramethyl-1,3,2-dioxaborolane allows the formation of bis(boronic acid pinacol ester) **2**. Recrystallizing several times from acetone gave pure **2** as white crystals in good yield.

The synthetic route leading to monomer **6** starts with 4H-cyclopenta[2,1-b:3,4-b']dithiophene (CPDT) (**3**), which was synthesized according to a literature procedure.^{S1} Deprotonation and subsequent alkylation of **3** affords compound **4**, that was brominated with 2 equivalents of *N*-bromosuccinimide (NBS) in dimethylformamide (DMF) to give 2,6-dibromo-4,4-dioctylcyclopenta[2,1-b:3,4-b']dithiophene (**5**). The last step involves again the boronation leading to bis(boronic acid pinacol ester) **6**. Purification of monomer **6** was achieved by recycling gel permeation chromatography in chloroform (CHCl₃).



Scheme 1 Synthetic route towards monomers **2** and **6**.

2,7-Bis(4,4,5,5-tetramethyl-1,3,2-dioxaborolan-2-yl)-9,9-dioctylfluorene (2). To a solution of 2,7-dibromo-9,9-dioctylfluorene **1** (1.02 g, 1.8 mmol) in THF (20 mL) cooled to $-84\text{ }^{\circ}\text{C}$, *n*-butyllithium (3.7 mL, 7.4 mmol) was added dropwise during 15 min. After stirring at $-84\text{ }^{\circ}\text{C}$ for 1.5 h, 2-isopropoxy-4,4,5,5-tetramethyl-1,3,2-dioxaborolane (2 mL, 9.8 mmol) was added dropwise during 15 min. The reaction mixture was allowed to slowly reach room temperature and left to stir for 16 h, followed by the addition of water (50 mL). The product was extracted with heptane ($2 \times 100\text{ mL}$), the organic layer washed with water ($2 \times 100\text{ mL}$), brine ($2 \times 100\text{ mL}$) and dried with Na_2SO_4 . The solvent was removed under reduced pressure and recrystallization of the residue from acetone afforded 716 mg of white crystals (60% yield). $^1\text{H-NMR}$ (400 MHz, CDCl_3): δ 7.80 (dd, 2H, $J = 7.6\text{Hz}$, $J = 1.0\text{Hz}$), 7.74 (s, 2H), 7.71 (d, 2H, $J = 7.5\text{Hz}$), 1.99 (m, 4H), 1.39 (s, 24H), 1.25-0.95 (m, 20H), 0.81 (t, 6H, $J = 7.2\text{Hz}$), 0.54 (m, 4H). $^{13}\text{C-NMR}$ (400 MHz, CDCl_3): δ 150.45, 143.89, 133.63, 128.89, 119.35, 83.69, 55.17, 40.07, 31.77, 29.92, 29.19, 29.14, 24.93, 23.58, 22.58, 14.06. MALDI-TOF MS ($M_w = 642.59$): $m/z = 642.55\text{ [M}^+]$.

4H-Cyclopenta[2,1-b:3,4-b']dithiophene (3). Compound **3** was synthesized according to a literature procedure,^{S1} giving 0.73 g of beige needles (47% yield). ¹H-NMR (400 MHz, CDCl₃): δ 7.18 (d, 2H, *J* = 5.2Hz), 7.09 (d, 2H, *J* = 4.8Hz), 3.54 (s, 2H). ¹³C-NMR (400 MHz, CDCl₃): δ 149.65, 138.64, 124.45, 122.94, 31.81. GC-MS (*M*_w = 178.28): *m/z* = 178.00 [*M*⁺].

4,4-Dioctylcyclopenta[2,1-b:3,4-b']dithiophene (4). To a solution of **3** (654 mg, 3.7 mmol), KOH (810 mg, 14.4 mmol) and KI (64 mg, 0.4 mmol) in DMSO (20 mL), 1-bromooctane (1.85 g, 9.6 mmol) was added. After stirring at room temperature for 16 h, water was added (100 mL) and subsequently the mixture was extracted with heptane (3 × 100 mL), washed with water (2 × 100 mL) and dried with Na₂SO₄. The solvent was removed under reduced pressure and purification of the residue by column chromatography on silica (heptane) gave 1.35 g of a slightly green colored oil (91% yield). ¹H-NMR (400 MHz, CDCl₃): δ 7.14 (d, 2H, *J* = 4.9Hz) 6.92 (d, 2H, *J* = 4.8Hz), 1.81 (m, 4H), 1.30-1.05 (m, 20H), 0.93 (m, 4H), 0.84 (t, 6H, *J* = 7.0Hz). ¹³C-NMR (400 MHz, CDCl₃): δ 158.11, 136.41, 124.38, 121.63, 53.23, 37.71, 31.80, 30.01, 29.34, 29.23, 24.51, 22.61, 14.08. MALDI-TOF MS (*M*_w = 402.71): *m/z* = 402.16 [*M*⁺].

2,6-Dibromo-4,4-dioctylcyclopenta[2,1-b:3,4-b']dithiophene (5). *N*-Bromosuccinimide (1.25 g, 7.0 mmol) was added in portions during 30 min to a solution of **4** (1.32 g, 3.3 mmol) in DMF (50 mL) at room temperature. After 16 h, the mixture was poured out into water (200 mL), extracted with heptane (3 × 100 mL), the organic phase washed with water (3 × 100 mL), dried with Na₂SO₄ and concentrated under reduced pressure. Purification of the residue by column chromatography on silica (heptane) gave 1.38 g of a slightly green colored oil (75% yield). ¹H-NMR (400 MHz, CDCl₃): δ 6.92 (s, 2H), 1.74 (m, 4H), 1.30-1.05 (m, 20H), 0.89 (m, 4H), 0.85 (t, 6H, *J* = 7.0Hz). ¹³C-NMR (400 MHz, CDCl₃): δ 155.92, 136.27, 124.56, 111.05, 55.01, 37.52, 31.78, 29.91,

29.28, 29.23, 24.40, 22.61, 14.08. MALDI-TOF MS ($M_w = 560.50$): $m/z = 560.00 [M^+]$.

2,6-Bis(4,4,5,5-tetramethyl-1,3,2-dioxaborolan-2-yl)-4,4-dioctylcyclopenta[2,1-b:3,4-b']dithiophene (6). To a solution of **5** (486 mg, 0.9 mmol) in THF (20 mL) cooled to $-84\text{ }^\circ\text{C}$, *n*-butyllithium (2.7 mL, 4.3 mmol) was added dropwise during 20 min. After stirring at $-84\text{ }^\circ\text{C}$ for 1 h, 2-isopropoxy-4,4,5,5-tetramethyl-1,3,2-dioxaborolane (0.9 mL, 4.4 mmol) was added dropwise during 10 min. The reaction mixture was allowed to slowly reach room temperature and left to stir for 16 h, followed by the addition of water (50 mL). The product was extracted with heptane ($2 \times 100\text{ mL}$), washed with water ($2 \times 100\text{ mL}$), brine ($2 \times 100\text{ mL}$) and dried with Na_2SO_4 . The solvent was removed under reduced pressure and purification by recycling GPC afforded 412 mg of a beige solid (73% yield). $^1\text{H-NMR}$ (400 MHz, CDCl_3): δ 7.41 (s, 2H), 1.79 (m, 4H), 1.35 (s, 24H), 1.30-1.05 (m, 20H), 0.92 (m, 4H), 0.84 (t, 6H, $J = 7.1\text{ Hz}$). $^{13}\text{C-NMR}$ (400 MHz, CDCl_3): δ 161.45, 143.85, 131.07, 84.02, 52.76, 37.81, 31.79, 30.03, 29.28, 24.79, 24.49, 22.61, 14.08. MALDI-TOF MS ($M_w = 654.64$): $m/z = 654.38 [M^+]$.

Monomers a, b and c. All three monomers 3,6-bis(5-bromo-2-thienyl)-2,5-dihydro-2,5-bis(2-hexyldecyl)pyrrolo[3,4-c]pyrrole-1,4-dione (**a**),^{S2} 3,6-bis(5-bromo-2-thienyl)-2,5-dihydro-2,5-bis(2-butyloctyl)pyrrolo[3,4-c]pyrrole-1,4-dione (**b**),^{S2} 3,6-bis(5-bromo-2-thienyl)-2,5-dihydro-2,5-bis(2-ethylhexyl)pyrrolo[3,4-c]pyrrole-1,4-dione (**c**)^{S2} were generously provided by BASF.

PFPPP2T-a. To a solution of **a** (224 mg, 0.25 mmol) and **2** (159 mg, 0.25 mmol) in toluene (5 mL, degassed for 30 min), aliquat 336 (3 drops) and $\text{Pd}(\text{PPh}_3)_4$ (6.7 mg, 5.8 μmol) were added. The reaction mixture was heated to $120\text{ }^\circ\text{C}$, after which 2 M degassed (30 min) aqueous K_2CO_3 (0.6 mL, 1.2 mmol) was added. After 3 days water (10 mL) was added, followed by an extraction with CHCl_3 (200 mL). Ammonia (100 mL of 25% aq. sol.) was

added to the organic phase and the mixture was refluxed for 2 h. After washing with water (2×100 mL) and stirring in presence of an excess EDTA in CHCl_3 for at least 3 h, the mixture was washed again with water (3×100 mL). The organic phase was concentrated under reduced pressure. The polymer was precipitated in methanol, filtered through a Soxhlet thimble and fractionated by Soxhlet extraction using methanol, hexane and CHCl_3 , respectively. The polymer was obtained in 153 mg as a blue solid (54% yield). $^1\text{H-NMR}$ (400 MHz, CDCl_3): δ 8.99 (br, 2H), 7.76 (d, 2H, $J = 8.4\text{Hz}$), 7.71 (d, 2H, $J = 8.1\text{Hz}$), 7.64 (br, 2H), 7.55 (br, 2H), 4.13 (br, 4H), 2.04 (br, 6H), 1.47-0.98 (m, 68H), 0.91-0.55 (m, 22H). GPC (ODCB at 80°C): $M_w = 62$ kg/mol, PDI = 1.6.

PFDPP2T-b. Using monomers **b**, **2** and an identical procedure as discussed for PFDPP2T-a, afforded 149 mg of a blue solid (93% yield). $^1\text{H-NMR}$ (400 MHz, CDCl_3): δ 8.98 (br, 2H), 7.77 (d, 2H, $J = 8.5\text{Hz}$), 7.71 (d, 2H, $J = 8.1\text{Hz}$), 7.64 (br, 2H), 7.55 (br, 2H), 4.13 (br, 4H), 2.04 (br, 6H), 1.48-0.98 (m, 52H), 0.95-0.57 (m, 22H). $M_w = 31$ kg/mol, PDI = 2.2.

PFDPP2T-c. Using monomers **c**, **2** and an identical procedure as discussed for PFDPP2T-a, afforded 160 mg of a blue solid (75% yield). $^1\text{H-NMR}$ (400 MHz, CDCl_3): δ 9.01 (br, 2H), 7.77 (d, 2H, $J = 7.6\text{Hz}$), 7.72 (d, 2H, $J = 8.0\text{Hz}$), 7.64 (br, 2H), 7.55 (br, 2H), 4.13 (br, 4H), 2.02 (br, 6H), 1.49-1.00 (m, 36H), 1.00-0.55 (m, 22H). $M_w = 17$ kg/mol, PDI = 2.2.

PCPDTDPP2T-b. Using monomers **b**, **6** and an identical procedure as discussed for PFDPP2T-a, afforded 377 mg of a green solid (89% yield). $^1\text{H-NMR}$ (400 MHz, CDCl_3): δ 8.87 (br, 2H), 7.17 (br, 2H), 6.91 (br, 2H), 4.07 (br, 4H), 1.94 (br, 6H), 1.62-1.05 (m, 56H), 0.98-0.67 (m, 18H). $M_w = 68$ kg/mol, PDI = 1.3.

PCPDTDPP2T-c. Using monomers **c**, **6** and an identical procedure as discussed for PFDPP2T-a, afforded 176 mg of a green solid (73% yield). $^1\text{H-NMR}$ (400 MHz, CDCl_3): δ 8.89 (br, 2H), 7.17 (br, 2H), 6.95 (br, 2H), 4.07

(br, 4H), 1.89 (br, 6H), 1.60-1.09 (m, 40H), 1.06-0.56 (m, 18H). $M_w = 12$ kg/mol, PDI = 1.8.

PDPP2T-a. A solution of **a** (200 mg, 0.2 mmol) in toluene (6 mL) was heated to 80 °C. Subsequently, Ni(cod)₂ (215 mg, 0.8 mmol) and bipyridine (106 mg, 0.7 mmol) were added in one portion. After 20 h a mixture of methanol/acetone/0.1 M HCl (1:1:1, 100 mL) was added and left to stir for 1 h. The polymer was extracted with CHCl₃ (200 mL) and the organic phase stirred with an excess EDTA for 3 h. After washing with water (3 × 200 mL), the polymer was precipitated in methanol, filtered through a Soxhlet thimble and fractionated by Soxhlet extraction using methanol, hexane, CHCl₃ and ODCB respectively. The polymer was obtained in 63 mg as a green solid (38% yield). ¹H-NMR (400 MHz, CDCl₃): δ 9.24 (br, 2H), 7.08 (br, 2H), 4.05 (br, 4H), 1.95 (br, 2H), 1.65-1.02 (m, 48H), 1.01-0.67 (m, 12H). $M_w = 322$ kg/mol, PDI = 3.8.

2. Optical properties in films

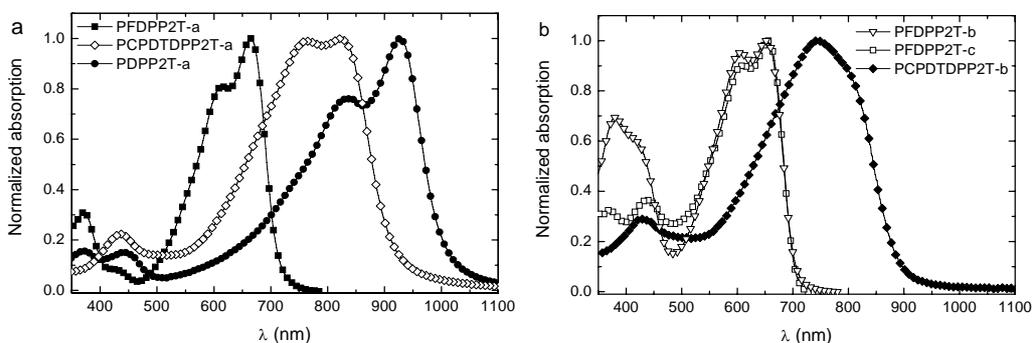


Figure S1. Room temperature UV-vis absorption spectra of the DPP polymers as thin films spin coated from CHCl₃.

3. Temperature dependent UV-vis spectra

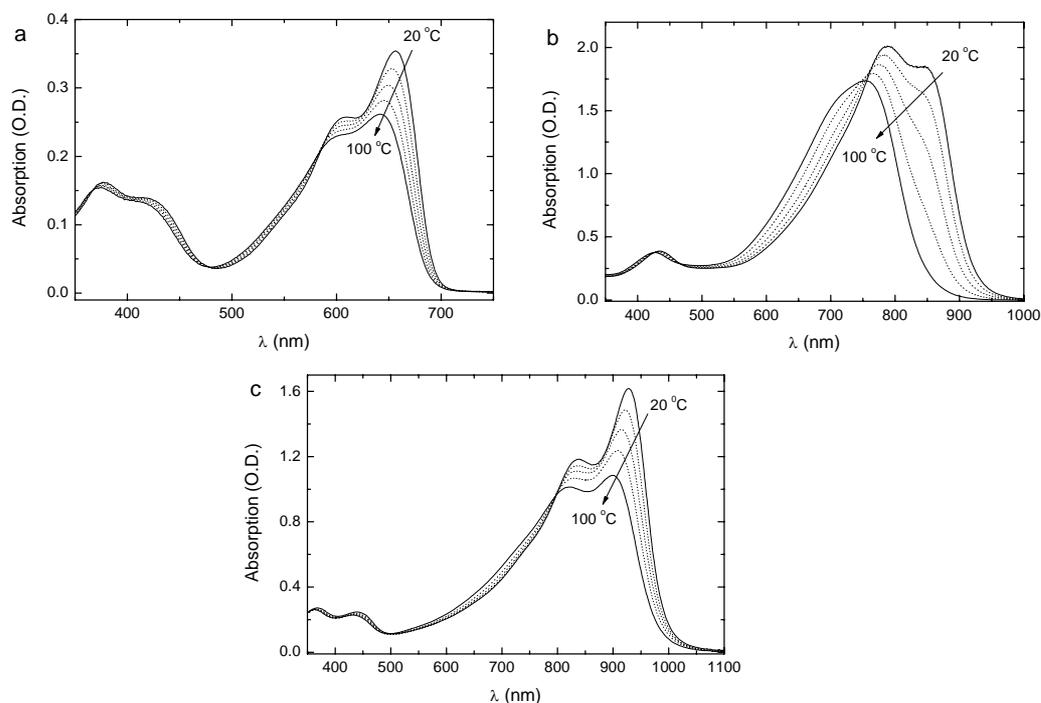


Figure S2. Temperature dependent absorption of (a) PFDDPP2T-c, (b) PCPDTDPP2T-b and (c) PDPP2T-a in ODCB. The solutions were heated from 20 to 100 °C.

4. Cyclic voltammetry

For PCPDTDPP2T, the redox potentials were determined for two different molecular weight fractions (Figures S4 b and c). The onset of reduction is nearly identical for each polymer, regardless the M_w . However, at high M_w , an additional oxidation peak appears (indicated by the arrows) that is attributed to aggregated polymer chains. The onset of this oxidation peak for both PCPDTDPP2T-b and PCPDTDPP2T-c varies between -0.10 and -0.15 V and this would set the electrochemical gap at about 1.35-1.40 V, resembling

the optical gap of the aggregated polymer. Polymer PFDPP2T-c exhibits a similar additional oxidation wave (Figure S4a) at about -0.12 V, which would give an electrochemical gap of 1.42 V. The precise origin of the oxidation peak is unclear and further research is required to clarify these observations.

Some of the high M_w materials showed an additional peak at a lower oxidation potential. If the $E_{\text{onset}}^{\text{OX}}$ corresponding to this peak is used to determine E_g^{CV} , it in fact nicely corresponds to the E_g of the aggregated polymer.

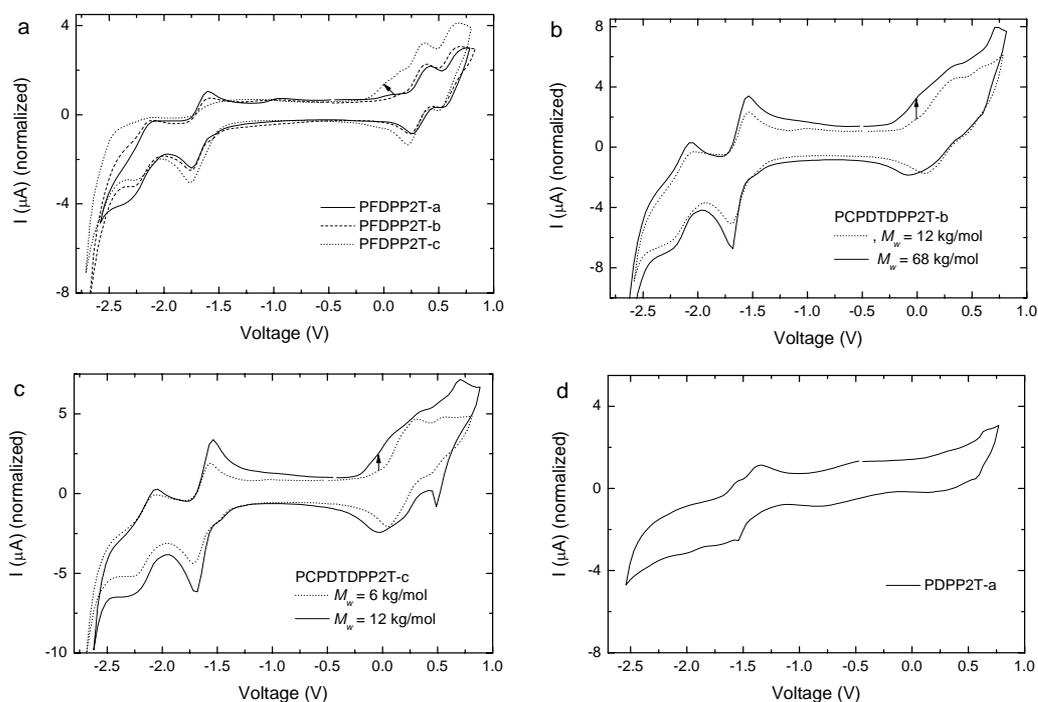


Figure S3. Cyclic voltammograms of PFDPP2T (a), PCPDTDPP2T-b (b), PCPDTDPP2T-c (c) and PDPP2T-a (d) recorded in ODCB at room temperature.

5. PCPDTDPP2T-b:[60]PCBM cells using different processing conditions.

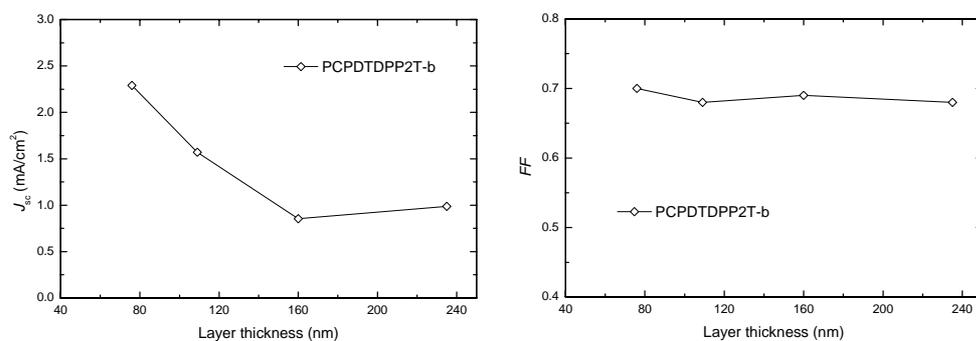


Figure S5. J_{sc} and FF of solar cells made from PCPDTDPP2T-b:[60]PCBM (1:4) blends spin coated from CHCl_3 plotted versus layer thickness.

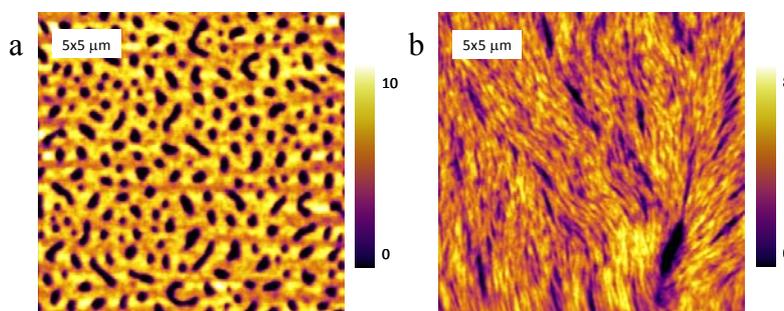


Figure S6. Panels (a) and (b) show images of PCPDTDPP2T-b:[60]PCBM (1:3) blends spin coated spin coated from ODCB at 100 °C and from TCB/ CHCl_3 (1:3) at 60 °C, respectively.

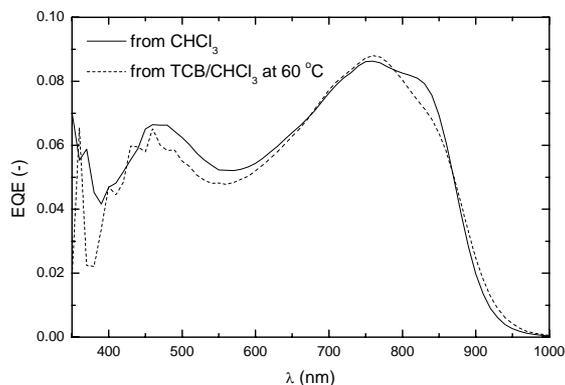


Figure S7. External quantum efficiency (EQE) of solar cells made from PCPDTDPP2T-b:[60]PCBM blends spin coated from CHCl₃ (solid line) and from TCB/CHCl₃ (1:3) at 60 °C (dotted line), respectively. Although the topography of the active layers is completely different, their photovoltaic performance is nearly identical, as can be seen from their EQEs.

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- S1 Kraak, A.; Wiersema, A. K.; Jordens, P.; Wynberg, H. *Tetrahedron* **1968**, 24, 3381-3398.
- S2 Turbiez, M. G. R.; Janssen, R. A. J.; Wienk, M. M.; Kirner, H. J.; Düggeli, M.; Tieke, B.; Zhu, Y.; WO 2008000664, **2008**, p 72