

Supplementary Information

Synthesis and photovoltaic properties of three different types of terpolymers

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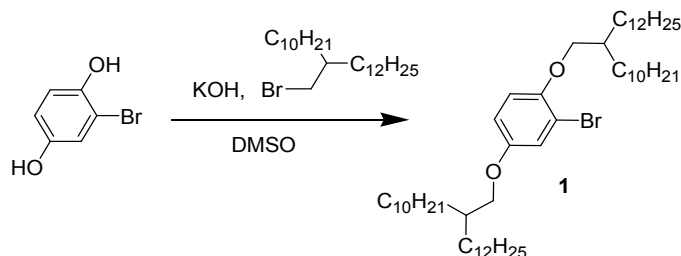
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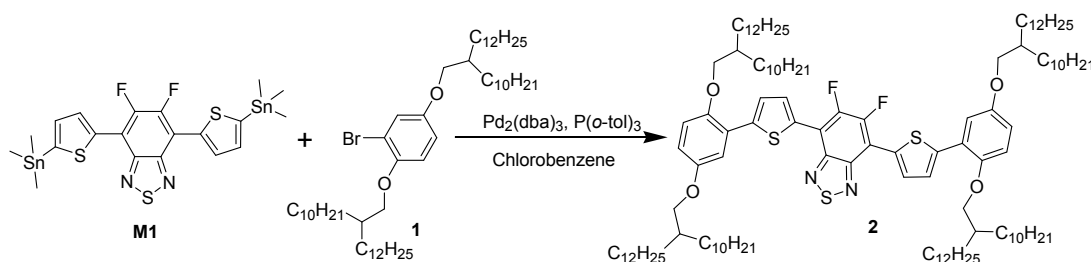
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Synthesis

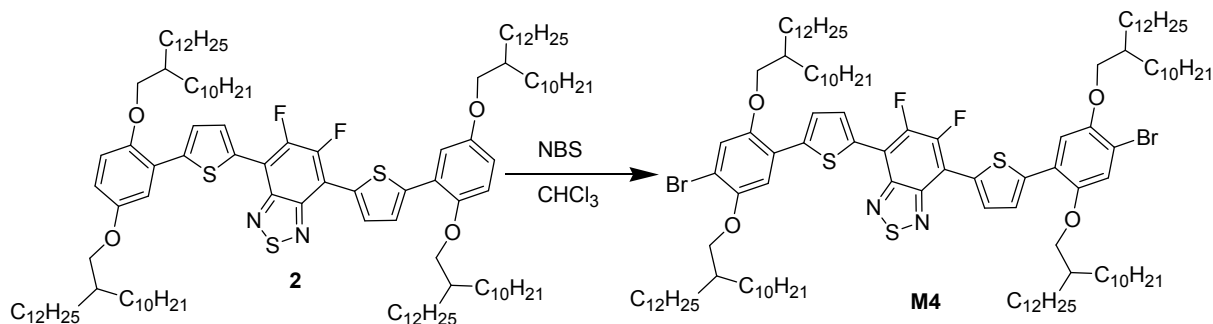


1-Bromo-2,5-bis(2-decyltetradecyloxy)benzene (1). Into a suspension of KOH solution (2.5 g, 0.044 mol) in dimethylsulfoxide (DMSO, 50 mL), 2-bromohydroquinone (2.1 g, 0.011 mol) and 1-bromo-2-decyltetradecane (18.4 g, 0.044 mol) were added and the reaction mixture was stirred at 60 °C for 10 h. The reaction solution was cooled down to room temperature and poured into ice water and the mixture was extracted with chloroform. The solvent was removed under reduced pressure and the crude compound was purified by silica gel column chromatography, using hexane as the eluent to yield compound 1 (44% yield) of a colorless oil. ¹H NMR (300 MHz, CDCl₃): δ (ppm) 7.10 (s, 1H), 6.78 (dd, 2H), 3.82 (d, 2H), 3.75 (d, 2H), 1.78 (m, 2H), 1.78 (m, 1H), 1.73 (m, 1H), 1.49-1.20 (br, 80H), 0.88 (m, 12H). ¹³C NMR (75 MHz, CDCl₃): δ (ppm) 153.7, 149.9, 119.5, 114.2, 112.7, 72.8, 71.6, 38.0, 32.0, 31.3, 30.0, 29.7, 29.4, 26.9, 22.7, 14.1.



4,7-Bis(5-(2,5-bis(2-decyltetradecyloxy)phenylene)-2-thienyl)-5,6-difluoro-2,1,3-benzothiadiazole (2). 4,7-Bis(5-trimethylstannylthiophen-2-yl)-5,6-difluoro-2,1,3-benzothiadiazole (M1) (1.0 g, 1.50 mmol), 1-bromo-2,5-bis(2-decyltetradecyloxy)benzene (1) (3.2 g, 3.75 mmol), tris(dibenzylideneacetone)dipalladium(0) (4 mol%) and tri(o-tolyl)phosphine (8 mol%) were added in a 30 mL microwave vial. The vial was sealed and purged with nitrogen. Chlorobenzene (10 mL) was added to the vial and the reaction mixture was heated at 80 °C for 10 min and at 140 °C for 60 min in

a microwave reactor. After the reaction was completed, the solvent was removed under reduced pressure and the compound 2 was purified by column chromatography (eluent: hexane/CHCl₃ = 4/1, v/v). Yield: 90%. ¹H NMR (300 MHz, CDCl₃): δ (ppm) 8.30 (d, 2H), 7.65 (d, 2H), 7.33 (d, 2H), 6.92 (d, 2H), 6.92 (dd, 2H), 3.96 (d, 4H), 3.86 (d, 4H), 1.92 (m, 2H), 1.78 (m, 2H), 1.61 (m, 4H), 1.40 (m, 8H), 1.36-1.10 (br, 68H), 0.84 (m, 12H). ¹³C NMR (75 MHz, CDCl₃): δ (ppm) 150.7, 149.2, 148.2, 137.4, 133.4, 131.4, 120.6, 117.7, 116.4, 113.4, 110.6, 72.6, 72.2, 37.7, 31.7, 31.2, 31.1, 29.8, 29.5, 29.4, 29.1, 26.6, 22.4, 13.9.



4,7-Bis(5-(4-bromo-2,5-bis(2-decyltetradecyloxy)phenylene)-2-thienyl)-5,6-difluoro-2,1,3-

benzothiadiazole (M4). Compound 2 (1 g, 0.5 mmol) was dissolved in 25 mL of CH₃CN in a 50 mL flask under N₂ atmosphere. 0.1 g (1.2 mmol, 2.2 equiv.) of *N*-bromosuccinimide (NBS) was added portionwise and stirred for 24 h. Excess solvent was distilled out. The crude product was purified by column chromatography (eluent: hexane/CHCl₃ = 5/1, v/v). Yield: 65%. ¹H NMR (300 MHz, CDCl₃): δ (ppm) 8.30 (d, 2H), 7.65 (d, 2H), 7.19 (s, 2H), 7.12 (s, 2H), 3.89 (d, 4H), 3.82 (d, 4H), 1.82 (m, 2H), 1.71 (m, 2H), 1.49 (m, 4H), 1.36 (m, 8H), 1.26-1.10 (br, 68H), 0.86 (m, 12H). ¹³C NMR (75 MHz, CDCl₃): δ (ppm) 153.3, 149.9, 125.6, 123.5, 114.6, 114.4, 113.4, 72.2, 71.7, 38.3, 38.1, 31.9, 31.5, 31.4, 30.1, 29.7, 29.4, 27.0, 26.9, 22.7, 14.1.

General Procedure of polymerization.

In a N₂ filled glovebox, corresponding monomers (1:1 mole ratio), tris(dibenzylideneacetone)dipalladium(0) (3 mol%), and tri(*o*-tolyl)phosphine (8 mol%) were added in a 5 mL microwave vial. The vial was sealed, and chlorobenzene was added as a solvent. The polymerization reaction was carried out in a microwave reactor: 10 min at 80 °C, 10 min at 100 °C, 40 min at 140 °C. The polymer was end-capped by addition of 0.1 equiv of 2-

(tributylstannyl)thiophene and reacted further at 140 °C for 20 min. The polymer solution was cooled, 0.2 equiv of 2-bromothiophene was added by syringe, and the reaction solution was further reacted at 140 °C for 20 min. The crude polymer was precipitated into a mixture of methanol:HCl (350 mL:10 mL) and purified by Soxhlet extraction with acetone, hexane, and chloroform. The dissolved portion in CHCl₃ was concentrated under reduced pressure and precipitated into cold methanol. The polymer was dried under vacuum for 24 h.

Poly[(2,5-bis(2-decyltetradecyloxy)phenylene)-*alt*-(5,6-difluoro-4,7-di(thiophen-2-yl)benzo[c][1,2,5]thiadiazole)] (PPDT2FBT_{DT}). 4,7-Bis(5-trimethylstannylthiophen-2-yl)-5,6-difluoro-2,1,3-benzothiadiazole (M1) and 1,4-dibromo-2,5-bis(2-decyltetradecyloxy)benzene (M3) (1:1 mole ratio) was reacted by following the above polymerization procedure. Yield: 65%. Number-average molecular weight (GPC, *o*-dichlorobenzene): $M_n = 31,000$ g/mol (PDI = 2.0)

Poly[(2,5-bis(2-decyltetradecyloxy)phenylene)-*alt*-(5,6-dicyano-4,7-di(thiophen-2-yl)benzo[c][1,2,5]thiadiazole)] (PPDT2CNBT). 4,7-bis(5-trimethylstannylthiophen-2-yl)-5,6-dicyano-2,1,3-benzothiadiazole (M2) and 1,4-dibromo-2,5-bis(2-decyltetradecyloxy)benzene (M3) (1:1 mole ratio) were reacted. Yield: 67%. $M_n = 28,000$ g/mol (PDI = 2.2).

PPDT2FBT_{DT}-*random*-PPDT2CNBT. M1:M2:M3 (0.5:0.5:1 mole ratio). Yield: 71%. $M_n = 30,000$ g/mol (PDI = 2.6).

PPDT2FBT_{DT}-*regular*-PPDT2CNBT. M2:M4 (1:1 mole ratio). Yield: 73%. $M_n = 34,000$ g/mol (PDI = 2.3).

PPDT2FBT_{DT}-Br. Polymerization was done similarly as for PPDT2FBT_{DT} and end-capped by addition of 1 equiv. of 2-(tributylstannyl)thiophene. $M_n = 20,000$ g/mol (PDI = 2.2)

PPDT2FBT_{DT}-*block*-PPDT2CNBT. M2 and M3 (1:1 mole ratio) were reacted with PPDT2FBT_{DT}-Br by following a similar procedure for PPDT2FBT_{DT}. Yield: 69%. Number-average molecular weight: $M_n = 28,000$ g/mol (PDI = 2.6).

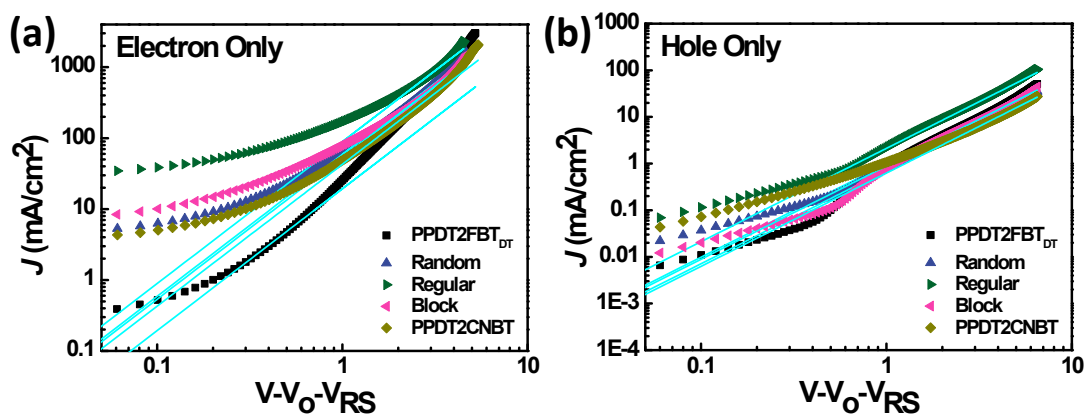


Fig. S1. J - V characteristics of (a) electron-only and (b) hole-only devices. Sky blue lines represent fits of the curves using the Mott-Gurney relationship.

Table S1. Summary of electron and hole mobilities for five BHJ PSCs.

Polymer	Thickness [nm]	Electron mobility [$\text{cm}^2 \text{V s}^{-1}$]	Thickness [nm]	Hole mobility [$\text{cm}^2 \text{V s}^{-1}$]	μ_e/μ_{hole}
PPDT2FBT _{DT}	260	1.10×10^{-3}	320	1.06×10^{-4}	10.4
Random	230	2.37×10^{-3}	330	8.41×10^{-5}	28.2
Regular	200	2.32×10^{-3}	250	1.15×10^{-4}	20.2
Block	170	8.67×10^{-4}	250	4.70×10^{-5}	18.5
PPDT2CNBT	200	1.20×10^{-3}	260	3.56×10^{-5}	33.7

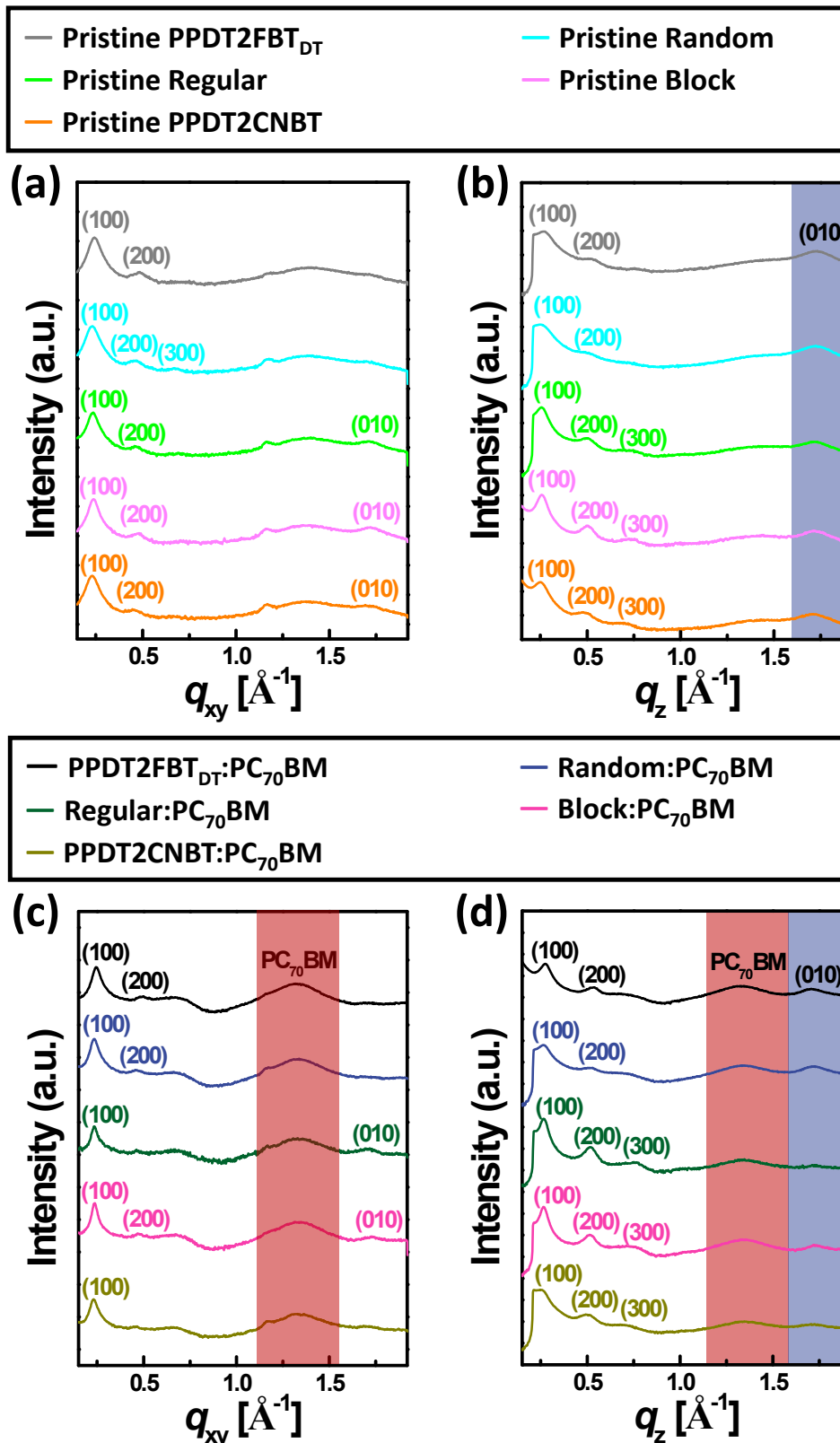


Fig. S2. Scattering line-cuts along (a and c) in-plane and (b and d) out-of-plane direction for (a-b) pristine polymers and (c-d) polymer:PC₇₀BM blend films.

Table S2. Summary of GIWAXS packing parameters.

Type	Direction	Scattering vector (q) of π - π stacking [\AA^{-1}]	d-spacing [\AA]	Scattering vector (q) of lamella peak [\AA^{-1}]	d-spacing [\AA]
Pristine PPD2T2FBT _{DT}	In-plane (q_{xy})	-	-	0.245	25.664
	Out-of- plane (q_z)	1.721	3.652	0.270	23.305
Pristine Random	In-plane (q_{xy})	-	-	0.232	27.080
	Out-of- plane (q_z)	1.722	3.648	0.250	25.140
Pristine Regular	In-plane (q_{xy})	1.715	3.664	0.236	26.628
	Out-of- plane (q_z)	1.705	3.685	0.258	24.373
Pristine Block	In-plane (q_{xy})	1.720	3.652	0.290	26.300
	Out-of- plane (q_z)	1.721	3.652	0.257	24.488
Pristine PPD2T2CNBT	In-plane (q_{xy})	1.696	3.706	0.231	27.198
	Out-of- plane (q_z)	1.712	3.670	0.253	24.870
PPD2T2FBT _{DT} :PC ₇₀ BM	In-plane (q_{xy})	-	-	0.247	25.459
	Out-of- plane (q_z)	1.707	3.681	0.274	22.906
Random :PC ₇₀ BM	In-plane (q_{xy})	-	-	0.234	26.852
	Out-of- plane (q_z)	1.722	3.648	0.266	23.651
Regular :PC ₇₀ BM	In-plane (q_{xy})	1.717	3.660	0.234	26.852
	Out-of- plane (q_z)	1.738	3.616	0.266	23.651
Block :PC ₇₀ BM	In-plane (q_{xy})	1.731	3.630	0.236	26.628
	Out-of- plane (q_z)	1.721	3.652	0.266	23.651
PPD2T2CNBT :PC ₇₀ BM	In-plane (q_{xy})	1.697	3.702	0.232	27.080
	Out-of- plane (q_z)	1.704	3.688	0.248	25.340