

Electronic Supplementary Information (ESI)

Molecular Design toward Efficient Polymer/PbS Hybrid Solar Cells

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Experimental Section

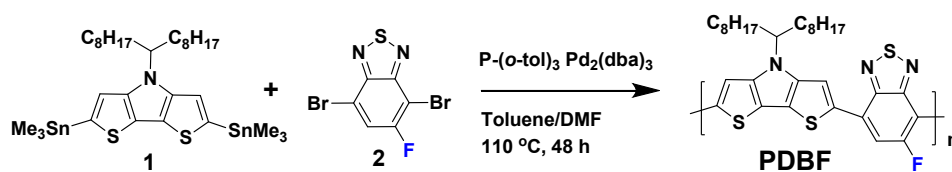
Characterization

¹H NMR data were performed on a Varian Unity Inova 400 MHz spectrometer with CDCl₃ as solvent and tetramethylsilane (TMS) as internal standard. The peaks are given in ppm, relative to TMS (0 ppm). Molecular weight and molecular weight distribution (PDI) were determined against a polystyrene standard by gel permeation chromatography (GPC) on a PL-GPC 50 apparatus at a flow rate of 1.0 mL/min at 40 °C, using THF as an eluent. Cyclic voltammetric (CV) measurements were carried out on a Zahner IM6 electrochemical workstation. Typically, a three-electrode cell equipped with a Pt plate coated with polymer as working electrode, a Ag/AgCl (0.01 M in anhydrous acetonitrile) reference electrode, and a Pt-wire counter electrode was employed. The measurements were conducted in anhydrous acetonitrile with tetrabutylammonium hexafluorophosphate (0.1M) under an argon atmosphere at a scan rate of 100 mV/s.

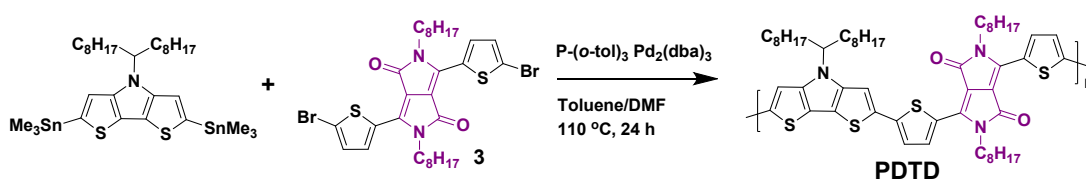
Polymer synthesis:

2,6-Di(trimethyltin)-N-(1-octylonyl)dithieno[3,2-b:2',3'-d]-pyrrole (1)¹, 4,7-Dibromo-5-fluorobenzo[c][1,2,5]thiadiazole (2)², 3,6-bis(5-bromo thien-2-yl)-2,5-b(2-ethylhexyl)pyrrolo[3,4-c]-pyrrole-1,4(2H, 5H)-dione (3)³, 4,7-di-2-thienyl-2,1,3-

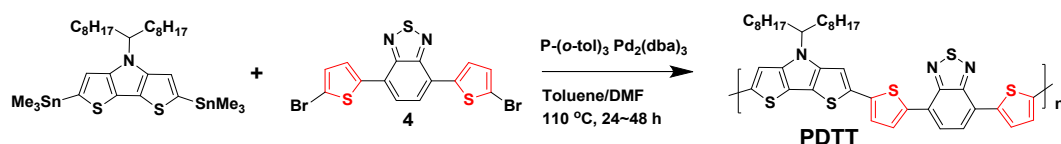
benzothiadiazole (4)⁴, 4,7-di-2-furan-2,1,3-benzothiadiazole (5)⁴ were prepared according to the previous report or with the similar procedure. **PDBT** were prepared according to the literature¹ with reaction time of 24 h; P3HT was purchased from Rieke Mental, inc.



PDBF: In a 50 mL reaction tube, compound **1** (0.22 g, 0.3 mmol), compound **2** (0.09 g, 0.3 mmol) tri(*o*-tolyl)phosphine (0.02 g, 0.08 mmol), and Pd₂(dba)₃ (0.01 g, 0.01 mmol) were dissolved in dry toluene/DMF (5 mL/0.5 mL) under argon. After stirred at 110 °C for 48 h, the mixture was cooled to room temperatures and precipitated in methanol (70 mL). The precipitate was filtered and washed with methanol (24 h) and hexane (24 h) successively in a soxhlet apparatus to remove oligomers and catalyst residue. Finally, the polymer was extracted with chloroform (10 h). The chloroform fraction was concentrated and precipitated in methanol. The precipitate was filtered and dried in vacuum at 80 °C overnight. **PDBF:** obtain as dark blue solid (110 mg, 61 %), GPC: $M_n=12.0 \text{ kg mol}^{-1}$, PDI=1.61. ¹H NMR (400 MHz, CDCl₃): 8.50-8.10 (br, 1 H), 7.80-7.20 (br, 2H), 4.50-4.21 (br, 1 H), 2.60-1.80 (m, 4 H), 1.70-0.30 (m, 30 H).

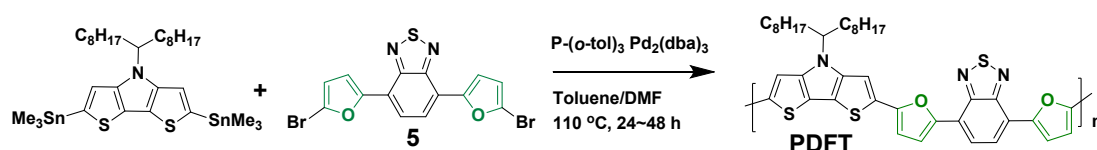


PDTD: In a 50 mL reaction tube, compound **1** (0.22 g, 0.3 mmol), compound **3** (0.21 g, 0.3 mmol) tri(*o*-tolyl)phosphine (0.02 g, 0.08 mmol), and Pd₂(dba)₃ (0.01 g, 0.01 mmol) were dissolved in dry toluene/DMF (5 mL/0.5 mL) under argon. After stirred at 110 °C for 24 h, the mixture was cooled to room temperatures and precipitated in methanol (70 mL). The precipitate was filtered and washed with methanol (24 h) and hexane (24 h) successively in a soxhlet apparatus to remove oligomers and catalyst residue. Finally, the polymer was extracted with chloroform (10 h). The chloroform fraction was concentrated and precipitated in methanol. The precipitate was filtered and dried in vacuum at 80 °C overnight. **PDTD:** obtain as dark green solid (230 mg, 80 %), GPC: $M_n=32.6 \text{ kg mol}^{-1}$, PDI=1.75. ¹H NMR (400 MHz, CDCl₃): δ (ppm) 9.20-8.50 (br, 2H), 7.60-6.85 (br, 4H), 4.20-3.55 (br, 3H), 2.25-1.80 (br, 4H), 1.72-0.75 (br, 62H).



PDTT: In a 50 mL reaction tube, compound **1** (0.22 g, 0.3 mmol), compound **4** (0.14 g, 0.3 mmol) tri(*o*-tolyl)phosphine (0.02 g, 0.08 mmol), and Pd₂(dba)₃ (0.01 g, 0.01 mmol) were dissolved in 5 mL dry toluene under argon. After stirred at 110 °C for 24 h, the mixture was cooled to room temperatures and precipitated in methanol (70 mL). The precipitate was filtered and washed with methanol (24 h) and hexane (24 h) successively in a soxhlet apparatus to remove oligomers and catalyst residue. Finally, the polymer was extracted with chloroform (10 h). The chloroform fraction was

concentrated and precipitated in methanol. The precipitate was filtered and dried in vacuum at 80 °C overnight. **PDTT**: obtain as dark purple solid (210 mg, 94 %) GPC: $M_n=32.6 \text{ kg mol}^{-1}$, PDI=1.75. $^1\text{H NMR}$ (400 MHz, CDCl_3): δ (ppm) 8.20-8.00 (br, 2H), 8.00-7.60 (br, 4H), 7.30-7.00 (br, 2H), 4.40-4.20 (br, 1H), 2.20-1.80 (br, 4H), 1.20-0.50 (br, 30H).



PDFT: In a 50 mL reaction tube, compound **1** (0.22 g, 0.3 mmol), compound **5** (0.13 g, 0.3 mmol) tri(*o*-tolyl)phosphine (0.02 g, 0.08 mmol), and $\text{Pd}_2(\text{dba})_3$ (0.01 g, 0.01 mmol) were dissolved in 5 mL dry toluene under argon. After stirred at 110 °C for 24 h, the mixture was cooled to room temperatures and precipitated in methanol (130 mL). The precipitate was filtered and washed with methanol (24 h) and hexane (24 h) successively in a soxhlet apparatus to remove oligomers and catalyst residue. Finally, the polymer was extracted with chloroform (10 h). The chloroform fraction was concentrated and precipitated in methanol. The precipitate was filtered and dried in vacuum at 80 °C overnight. **PDFT**: obtain as dark purple solid (200 mg, 93 %), GPC: $M_n=37.2 \text{ kg mol}^{-1}$, PDI=2.14. $^1\text{H NMR}$ (400 MHz, CDCl_3): δ (ppm) 8.20-7.80 (br, 4H), 7.80-7.60 (br, 2H), 7.30-6.80 (br, 2H), 4.40-4.20 (br, 1H), 2.20-1.80 (br, 4H), 1.50-0.75 (br, 30H).

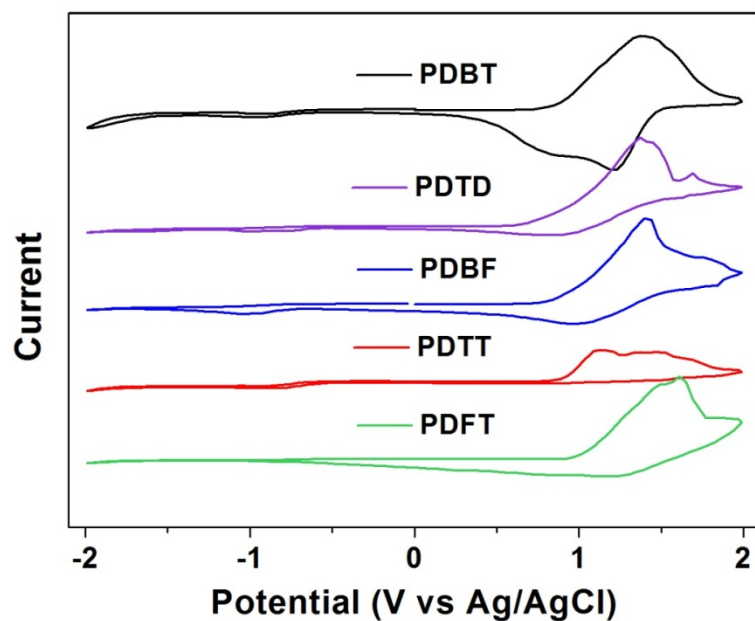


Figure S1 Cyclic voltammograms of PBDT-T-TPDs in the CH₃CN solution at a scan rate of 100 mV s⁻¹

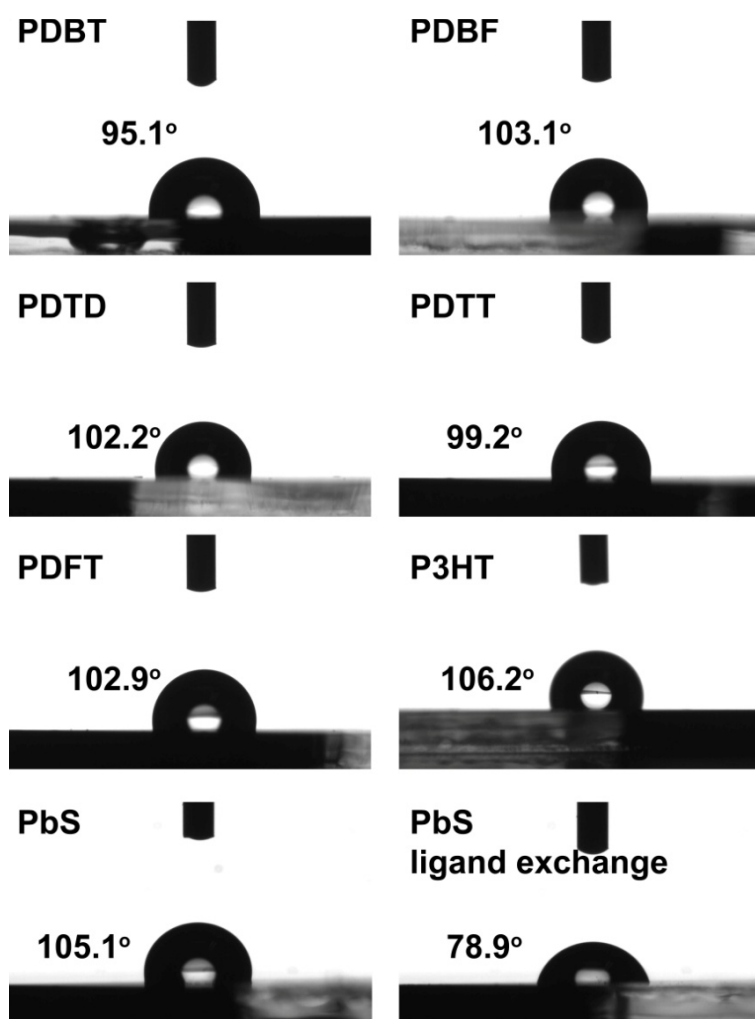


Figure S2 Contact angle measurements of pristine polymers and PbS QD.

Table S1. Summary of the devices performance based on polymer and PbS with varying first exciton energies.

Polymer	QD Growth Temperature (°C)	V_{oc} (V)	J_{sc} (mA/cm ²)	FF	PCE (%)
PDBF	60	0.45±0.00	9.98±0.1	0.27±0.04	1.21±0.19
PDBF	80	0.58±0.01	11.06±0.2	0.56±0.02	3.60±0.25
PDBF	100	0.47±0.01	13.87±0.2	0.46±0.02	3.00±0.22
PDBF	120	0.47±0.01	13.12±0.2	0.52±0.01	3.20±0.18
PDBF	140	0.43±0.01	10.15±0.1	0.44±0.02	1.92±0.14
PDTD	60	0.26±0.01	8.32±0.1	0.27±0.03	0.58±0.10
PDTD	80	0.51±0.00	10.21±0.2	0.42±0.02	2.19±0.13
PDTD	100	0.52±0.00	11.14±0.1	0.55±0.01	3.19±0.06
PDTD	120	0.49±0.01	12.76±0.1	0.56±0.01	3.50±0.15
PDTD	140	0.38±0.01	9.69±0.1	0.27±0.04	0.99±0.20
PDTT	60	0.40±0.01	9.34±0.0	0.33±0.03	1.23±0.13
PDTT	80	0.46±0.00	10.01±0.1	0.41±0.02	1.89±0.10
PDTT	100	0.44±0.01	12.35±0.2	0.51±0.01	2.82±0.4
PDTT	120	0.45±0.01	11.25±0.1	0.43±0.02	2.17±0.13
PDTT	140	0.40±0.01	9.71±0.1	0.34±0.03	1.32±0.17
PDFT	60	0.31±0.02	8.06±0.3	0.26±0.04	0.65±0.18
PDFT	80	0.40±0.01	9.73±0.2	0.33±0.03	1.28±0.19
PDFT	100	0.41±0.01	12.06±0.3	0.49±0.00	2.42±0.13
PDFT	120	0.44±0.01	10.89±0.2	0.44±0.02	2.10±0.19
PDFT	140	0.41±0.01	9.28±0.1	0.30±0.03	1.14±0.16
P3HT	60	0.23±0.01	7.49±0.2	0.26±0.04	0.45±0.07
P3HT	80	0.46±0.00	8.79±0.3	0.45±0.02	1.82±0.14
P3HT	100	0.44±0.01	10.70±0.2	0.43±0.02	2.02±0.14
P3HT	120	0.44±0.01	11.82±0.1	0.46±0.01	2.39±0.12
P3HT	140	0.51±0.00	11.62±0.2	0.42±0.02	2.49±0.16

The data shown are the average values obtained from 6 devices with standard deviation

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