

Electronic Supplementary Information

Side-chain engineering of perylenediimide-vinylene polymeric acceptors for high-performance all-polymer solar cells

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Materials. Compounds **1**, **5**, **PDI-Br₂-C5**, **PDI-Br₂-C6**, **PDI-Br₂-C7** (see below) were synthesized as previously reported.^{1,4} *Trans*-1,2-bis(tri-*n*-butylstannyl)-ethylene was purchased from Alfa Aesar. PTB7-Th was purchased from 1-Material. Pd₂dba₃ and P(*o*-tol)₃ were purchased from J & K.

Optical characterizations. UV-Vis absorption spectra were acquired on a Hitachi U-4100 spectrometry. All film samples were spin-cast on ITO/ZnO substrates.

Electrochemical characterizations. Cyclic voltammetry was performed on a Gamry Interface 1000 electrochemical work-station with a three-electrode configuration, using Ag/AgCl as the reference electrode, a Pt plate as the counter electrode, and a glassy carbon as the working electrode. Polymer thin films were dropped on the working electrode and tetrabutylammonium hexafluorophosphate (0.1 mol L⁻¹) was dissolved in acetonitrile. The potentials were referenced to the ferrocenium/ferrocene couple, using ferrocene as the external standard in acetonitrile solution. The scan rate is 100 mV s⁻¹.

DFT calculation. The geometry was optimized with Density Functional Theory (DFT) using B3LYP hybrid functional with basis set 6-31g*. Quantum-chemical calculation was performed with the Gaussian09 package.^[2] Vibrational frequency calculations were performed to check that the stable structures had no imaginary frequency. All 1-hexylheptyl groups were replaced with methyl groups in the calculations.

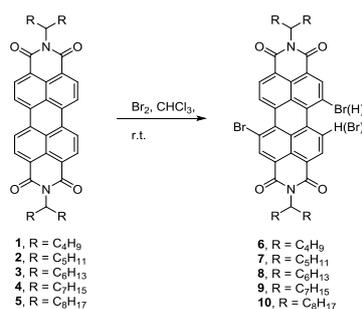
Hole and electron mobility measurements. The hole and electron mobilities were measured using the SCLC method, employing a device architecture of ITO/V₂O₅/blend film/V₂O₅/Al and ITO/ZnO/blend film/Ca/Al, respectively. The mobilities were obtained by fitting the current-voltage curves to a space charge limited form, where the SCLC is described by:

$$J = \frac{9\varepsilon_0\varepsilon_r\mu V^2}{8L^3}$$

In which ε_0 is the permittivity of free space, ε_r is the relative permittivity of the material (assumed to be 3), μ is the hole mobility and L is the thickness of the film. From the plots of $J^{1/2}$ vs V , hole and electron mobilities can be deduced.

AFM analysis. The AFM characterizations were performed using a Bruker's Dimension icon in tapping mode. All film samples were spin-cast on ITO/ZnO substrates.

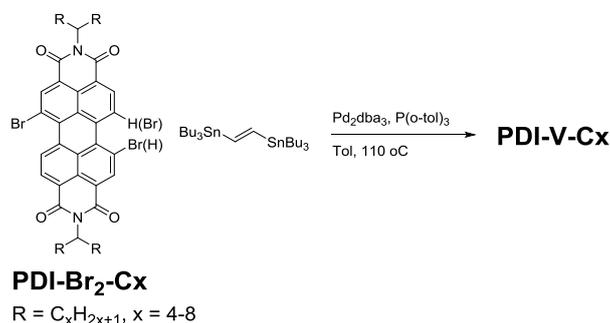
Synthetic procedures



PDI-Br₂-C4 A solution of **1** (1.05 g, 1.60 mmol) and bromine (13.95 g, 87.2 mmol) in chloroform (50 mL) was stirred at room temperature for 3 days. The solution was poured into an iced solution of sodium thiosulfate and then extracted with dichloromethane (DCM). The combined organic layers were dried over anhydrous sodium sulfate and concentrated under reduced pressure. The residue was purified with silica gel column chromatography (DCM:petroleum ether = 1:2). The red solid of **PDI-Br₂-C4** (1.23 g, 1.54 mmol) was obtained in 94% yield. ¹H-NMR (400 MHz, CDCl₃, ppm): δ 9.51-9.48 (m, 2H), 8.92 (m, 2H), 8.69 (m, 2H), 5.24-5.11 (m, 2H), 2.30-2.21 (m, 4H), 1.90-1.82 (m, 4H), 1.41-1.17 (m, 16 H), 0.87-0.84 (m, 12H). ¹³C-NMR (400 MHz, CDCl₃, ppm): δ164.1, 163.6, 163.0, 162.4, 138.4, 137.8, 133.0, 132.8, 132.7, 132.3, 130.3, 129.7, 129.2, 128.4, 128.1, 128.0, 127.2, 126.4, 123.8, 123.3, 121.6, 120.7, 54.9, 32.0, 29.1, 22.6, 14.1. HRMS: Calcd. for C₄₂H₄₅Br₂N₂O₄: 799.174. Found: 799.173. Elemental Anal.: Calcd. for C₄₂H₄₄Br₂N₂O₄: C, 63.01; H, 5.54; N, 3.50. Found: C, 63.03; H, 5.51; N, 3.53.

PDI-Br₂-C8 was synthesized using the similar procedures as described for **PDI-Br₂-C4**. The red solid of **PDI-Br₂-C8** (1.65 g, 1.61 mmol) was obtained in 92% yield. ¹H-NMR (400 MHz, CDCl₃, ppm): δ 9.51-9.47 (m, 2H), 8.93-8.90 (m, 2H), 8.70 (m, 2H), 5.24-5.13 (m, 2H), 2.28-2.22 (m, 4H), 1.85-1.80 (m, 4H), 1.35-1.21 (m, 48 H), 0.85-0.81 (m, 12H). ¹³C-NMR (400 MHz, CDCl₃, ppm): δ164.1, 163.6, 163.0, 162.4, 138.5, 137.8, 133.1, 132.8, 132.7, 132.3, 130.4, 129.8, 129.3, 128.4, 128.1, 127.9, 127.2, 126.5, 123.8, 123.4, 123.1, 122.7, 121.6, 120.7, 55.0, 32.3, 31.8, 29.5, 29.1, 26.9, 14.1. HRMS: Calcd. for C₅₈H₇₇Br₂N₂O₄: 1023.424. Found: 1023.424. Elemental Anal.: Calcd. for C₅₈H₇₆Br₂N₂O₄: C, 67.96; H, 7.47; N, 2.73. Found: C, 68.08; H, 7.44; N, 2.75.

General polymerization procedures



A Schlenk tube containing **PDI-Br₂-C_x**, *trans*-1,2-bis(tri-*n*-butylstannyl)ethylene (1:1 with **PDI-Br₂-C_x**), Pd₂(dba)₃ (2% molar ratio) and P(*o*-tol)₃ (8% molar ratio) was evacuated and re-filled with nitrogen three times, and then toluene (3 ml) was added using a syringe under nitrogen atmosphere. The reaction mixture was sealed under nitrogen atmosphere and stirred at 110 °C for 96 hours. Upon cooling to room temperature, an aqueous solution of potassium fluoride (1 g/3 mL) was added. This mixture was stirred at room temperature for 6 hours before it was extracted with chloroform (20 mL×3). The organic layers were combined, washed with water (30 mL × 3), dried over anhydrous sodium sulfate, and concentrated on a rotary evaporator. The residue was taken by a small amount of chloroform and precipitated in acetone. The obtained deep purple solid was purified with a size exclusion chromatography column filled with Bio-Beads S-X1 Beads, and then concentrated on a rotary evaporator. The solid residue was re-dissolved in chloroform (2 mL) and added slowly to methanol (50 mL). The precipitates were collected by filtration, washed with methanol, and dried in vacuum,

PDI-V-C4 (yield 68%). ¹H NMR (400 MHz, CDCl₃, ppm): δ 9.14-8.74 (m, 6H), 8.38-7.28 (m, 2H), 5.24 (m,

2H), 2.29 (m, 4H), 1.88 (m, 4H), 1.33-1.25 (m, 16H), 0.84 (m, 12H). GPC: $M_n = 13.4$ kDa, $M_w = 27.2$ kDa, PDI = 2.03. Elemental Anal.: Calcd. For $(C_{44}H_{46}N_2O_4)_n$: C, 79.25; H, 6.95; N, 4.20; Found: C, 77.55; H, 6.88; N, 4.09.

PDI-V-C5 (yield 72%). 1H NMR (400 MHz, $CDCl_3$, ppm): δ 9.14-8.74 (m, 6H), 8.38-7.28 (m, 2H), 5.24 (m, 2H), 2.29 (m, 4H), 1.88 (m, 4H), 1.33-1.25 (m, 24H), 0.84 (m, 12H). GPC: $M_n = 13.4$ kDa, $M_w = 26.3$ kDa, PDI = 1.96. Elemental Anal.: Calcd. For $(C_{48}H_{54}N_2O_4)_n$: C, 79.74; H, 7.53; N, 3.87; Found: C, 78.46; H, 7.49; N, 3.76.

PDI-V-C7 (yield 65%). 1H NMR (400 MHz, $CDCl_3$, ppm): δ 9.14-8.74 (m, 6H), 8.38-7.28 (m, 2H), 5.24 (m, 2H), 2.29 (m, 4H), 1.88 (m, 4H), 1.33-1.25 (m, 40H), 0.84 (m, 12H). GPC: $M_n = 13.7$ kDa, $M_w = 30.6$ kDa, PDI = 2.23. Elemental Anal.: Calcd. For $(C_{56}H_{70}N_2O_4)_n$: C, 80.53; H, 8.45; N, 3.35; Found: C, 80.16; H, 8.46; N, 3.32.

PDI-V-C8 (yield 77%). 1H NMR (400 MHz, $CDCl_3$, ppm): δ 9.14-8.74 (m, 6H), 8.38-7.28 (m, 2H), 5.24 (m, 2H), 2.29 (m, 4H), 1.88 (m, 4H), 1.33-1.25 (m, 48H), 0.84 (m, 12H). GPC: $M_n = 15.2$ kDa, $M_w = 31.6$ kDa, PDI = 2.08. Elemental Anal.: Calcd. For $(C_{55}H_{62}N_2O_4)_n$: C, 80.86; H, 8.82; N, 3.14; Found: C, 80.45; H, 8.82; N, 3.13.

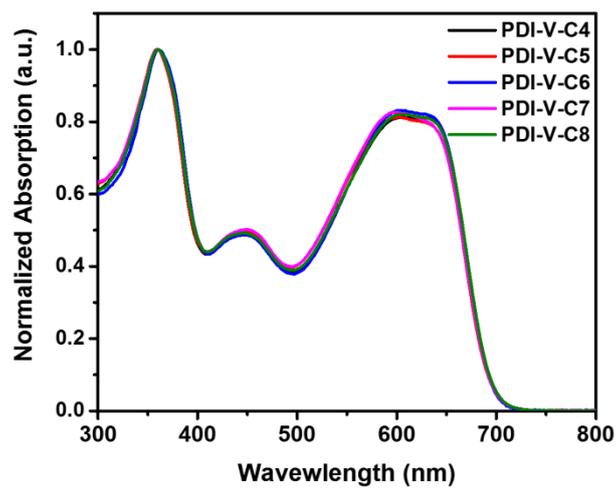


Fig. S1 Normalized absorption spectra of PDI-V-Cx in chloroform (10^{-5} M).

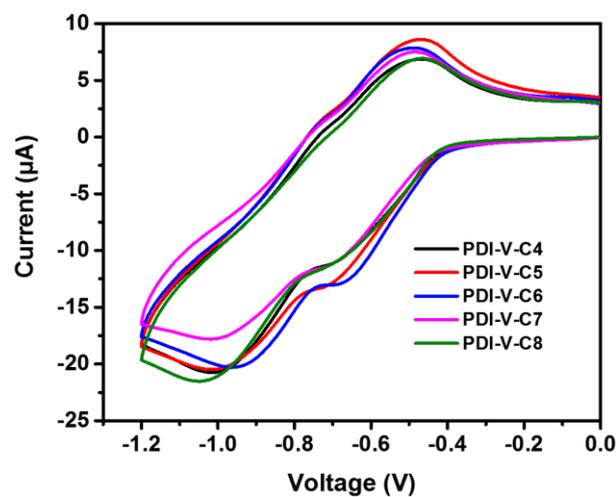


Fig. S2 Cyclic voltammograms of PDI-V-Cx.

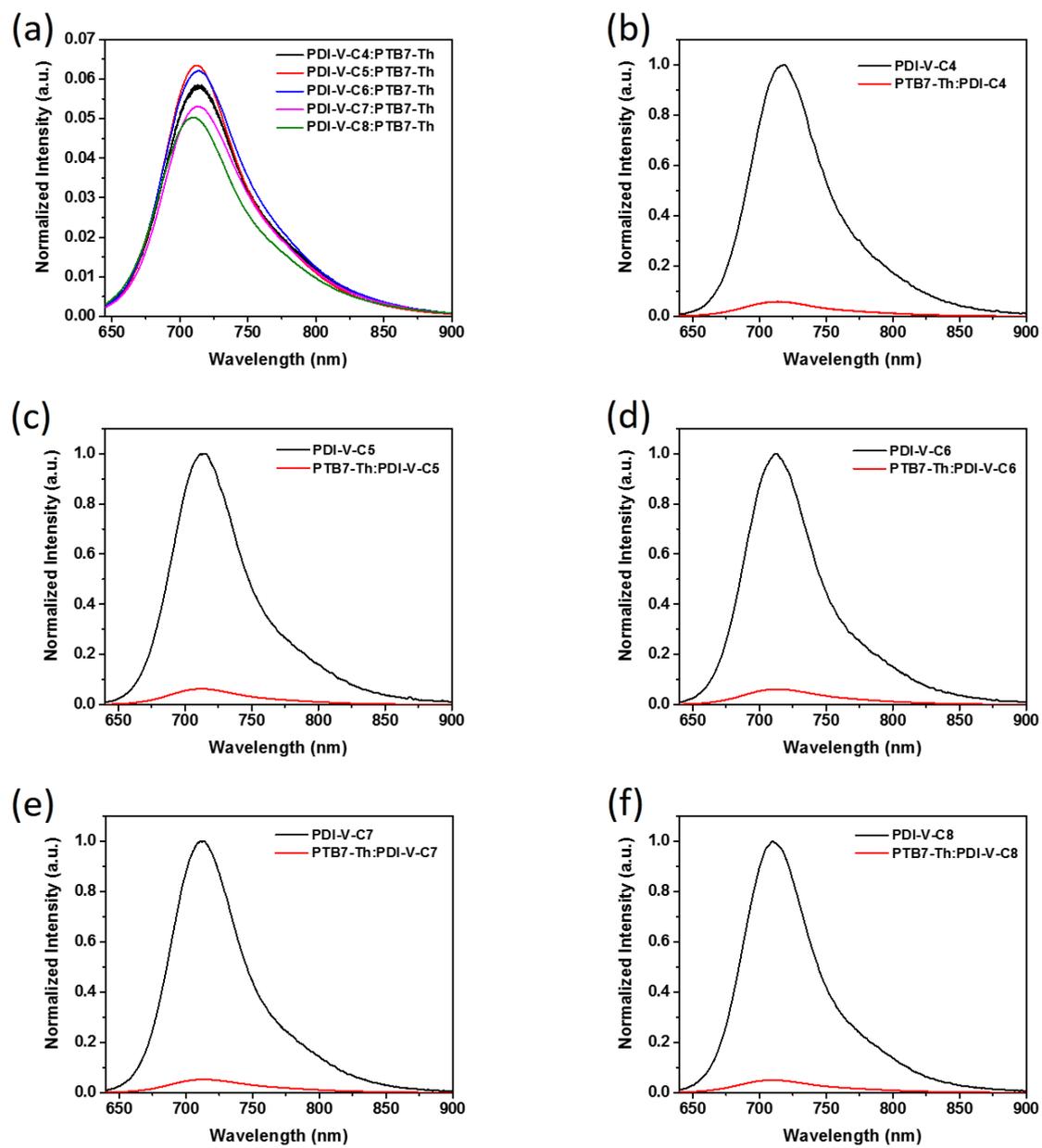


Fig. S3 Photoluminescence spectra of (a) different blends and (b-f) blend films in comparison with the corresponding neat acceptor films (the excitation wavelength was 633 nm)

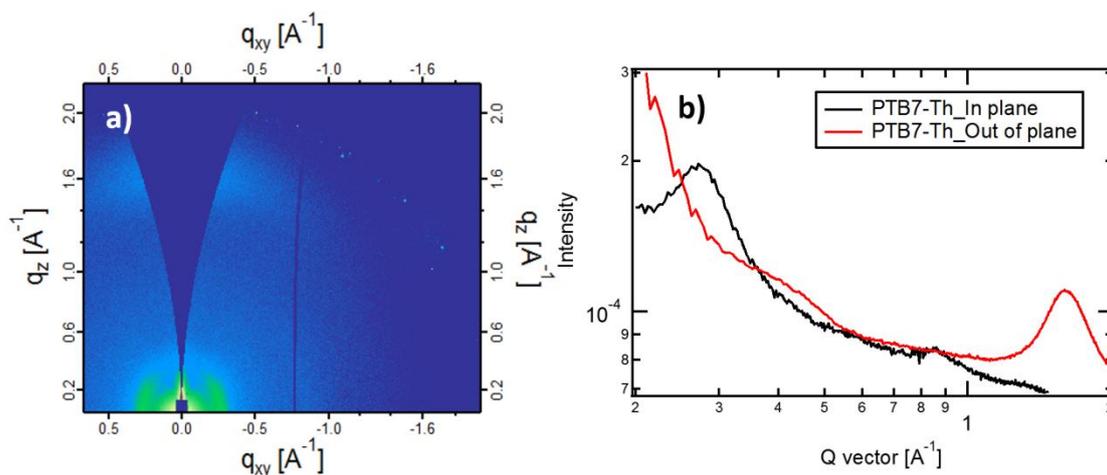


Fig. S4 GIWAXS characterizations of neat PTB7-Th: (a) 2-D pattern, (b) 1-D in-plane and out-of-plane profiles.

Table S1. Device performance of PTB7-Th:PDI-V-C7 with additives.

additives	V_{oc} (V)	J_{sc} ($mA\ cm^{-2}$)	FF	PCE (%)
1% DIO	0.73 ± 0.01	11.77 ± 0.12	0.65 ± 0.01	5.54 ± 0.17 (5.77)
1% CN	0.74 ± 0.01	14.77 ± 0.15	0.65 ± 0.01	7.10 ± 0.19 (7.33)

Table S2. Maximum EQE and J_{sc} values calculated from EQE spectra.

blends	EQE _{max} (%)	J_{sc} from EQE ($mA\ cm^{-2}$)	J_{sc} from J - V curves ($mA\ cm^{-2}$)	mismatch (%)
PTB7-Th:PDI-V-C4	69.04	14.69	14.44	1.7
PTB7-Th:PDI-V-C5	73.12	15.34	14.88	3.1
PTB7-Th:PDI-V-C6	77.14	15.94	15.55	2.5
PTB7-Th:PDI-V-C7	75.23	15.45	15.30	1.0
PTB7-Th:PDI-V-C8	72.98	15.31	14.83	3.2

References

- 1 S. Demmig and H. Langhals, *Chem. Ber.* 1988, **121**, 225.
- 2 H. Langhals, S. Demmig and T. Potrawa, *Journal fuer Praktische Chemie (Leipzig)* 1991, **333**, 733.
- 3 C. D. Schmidt, N. Lang, N. Jux and A. Hirsch, *Chem. Eur. J.* 2011, **17**, 5289.
- 4 Q. Yan and D. Zhao, *Org. Lett.* 2009, **11**, 3426.