

Electronic Supplementary Information

Cyanovinylene-Based Copolymers by Tin-free Knoevenagel

Polycondensation for High Efficiency Polymer Solar Cells

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EXPERIMENTAL SECTION

Materials: All solvents and reagents were purchased from commercial sources and used without further purification unless stated otherwise. All reactions were carried out under the nitrogen atmosphere. Tetrahydrofuran (THF) was distilled over sodium/benzophenone before use to ensure an anhydrous state. Anhydrous N,N-Dimethylformamide (DMF), toluene and chlorobenzene (CB) were purchased from Sigma-Aldrich and used as received. 1,4-Bis(cyanomethyl)-2,5-bis(dodecyloxy)benzene (M1) was reported by Reynolds et al¹ with safe, easy and convenient synthetic steps from hydroquinone. The other intermediates, 4,8-Bis(2-octyldodecyloxy)benzo[1,2-b:3,4-b] dithiophene (5), 2,6-Bis(trimethyltin)-4,8-bis(2-octyldodecyloxy)benzo[1,2-b:3,4-b']dithiophene (6)², 4,8-Bis(2,4-dioctylthiophene-5-yl)benzo[1,2-b;4,5-b'] dithiophene (7), 2,6-Bis(trimethyltin)-4,8-bis(2,4-dioctylthiophene-5-yl)benzo[1,2-b;4,5-b']dithiophene (8)³ were synthesized according to previously reported methods. 2,6-Bis(carbaldehyde)-4,8-bis(2-octyldodecyloxy) benzo[1,2-b:3,4-b] dithiophene(M2),2,6-Bis(carbaldehyde)-4,8-bis(2,4-dioctylthiophene-5-yl)benzo [1,2-b:3,4-b']dithio-phene (M4) were synthesized from 5 and 7 according to the previous reports.⁴ 2,6-Bis(thiophene-2-carbaldehyde)-4,8-bis(2,4-dioctylthiophene-5-yl) benzo[1,2-b;4,5-b'] dithiophene (M3) and 2,6-Bis(thiophene-2-carbaldehyde)-4,8-bis(2,4-dioctylthiophene-5-yl) benzo[1,2-b;4,5-b'] dithiophene (M5) were synthesized from 6 and 8 respectively. (2E, 2'E)-3,3'-(2,5-bis(2-ethylhexyloxy)-1,4-phenylene) bis(2-(5-(bromo)thiophen-2-yl)acrylonitrile) (M6) was synthesized by Knoevenagel condensation from M1 and 5-Bromo-2-thiophenecarbaldehyde.⁵

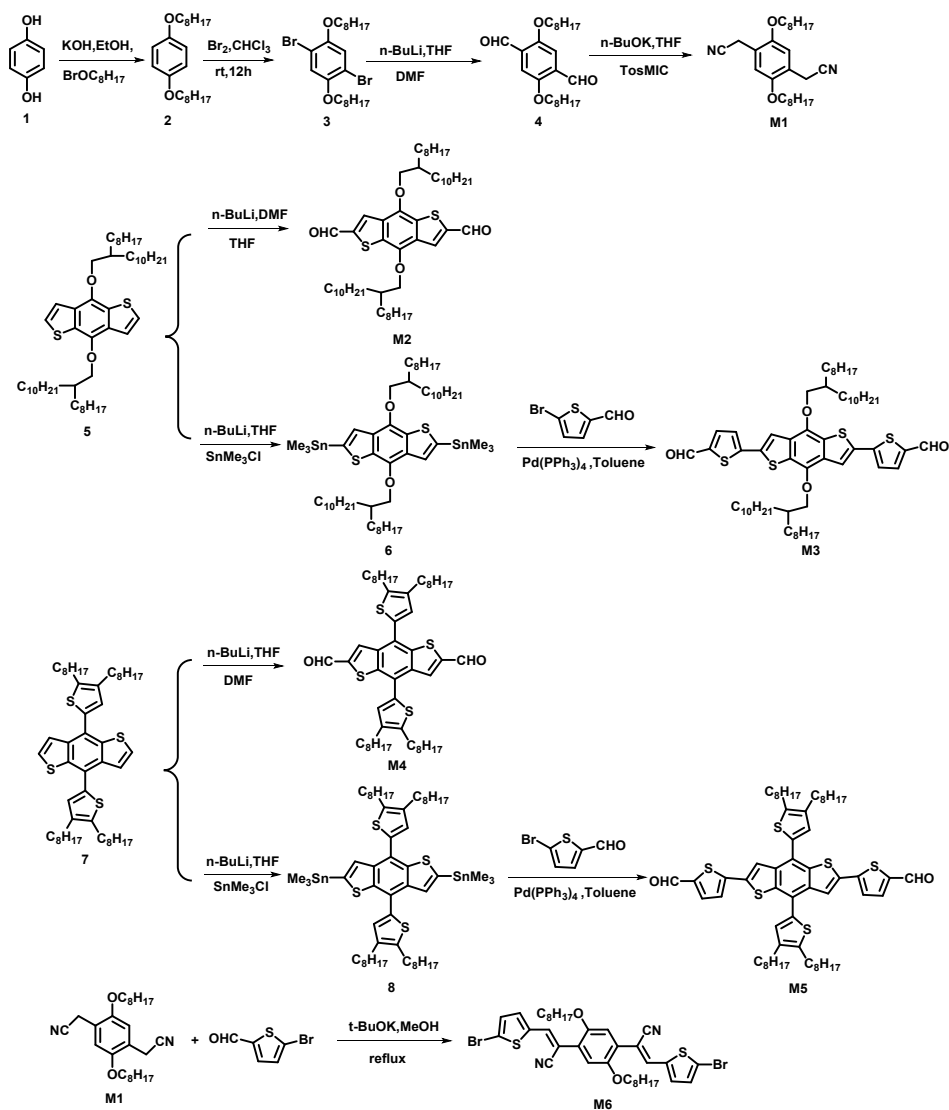
Measurements ¹H NMR and ¹³C NMR spectra were measured on a Bruker AV-500 MHz spectrometer with

tetramethylsilane (TMS) as the internal reference. Molecular weights of the copolymers were obtained on an Agilent Technologies PL-GPC 220 high-temperature chromatograph in 150 °C and 1,2,4-trichlorobenzene using a calibration curve of polystyrene standards. Thermogravimetric (TGA) measurements were carried out with a NETZSCH (TG209F3) apparatus at a heating rate of 20 °C min⁻¹ under a nitrogen atmosphere. Differential scanning calorimetry (DSC) analysis was performed on a NETZSCH (DSC200F3) apparatus at a heating or cooling rate of 10 °C min⁻¹ under a nitrogen atmosphere. UV-vis absorption spectra were recorded on a SHIMADZU UV-3600 spectrophotometer. Cyclic voltammetry (CV) was measured on a CHI660A Electrochemical Workstation equipped with a glass carbon working electrode, a platinum wire counter electrode, and a Ag/Ag⁺ reference electrodes with nitrogen-saturated solution of 0.1 M tetrabutylammonium hexafluorophosphate in dry acetonitrile at a scan rate of 100 mV s⁻¹. Potentials of the saturated calomel reference electrode were internally calibrated using the ferrocene/ferrocenium redox couple (F_c/F_c^+), which has a known reduction potential of -4.8 eV. The deposition of a copolymer on the working electrode was done by the evaporation of a chloroform solution. Photoluminescence was measured with a SHIMADZU RF-5301PC fluorimeter. Tapping-mode atomic force microscopy (AFM) images were obtained using a NanoScope NS3A system (Digital Instrument). Transmission electron microscopy (TEM) images were obtained using a JEM-2100F instrument.

PSCs Fabrication and Characterization. The PSCs structure were ITO/PEDOT:PSS/active layer/PFN-Br/Ag. Indium tin oxide (ITO) glass was washed with acetone, detergent, deionized water and isopropyl alcohol in turn, and then dried in an oven at 80 °C overnight and used as a hole collecting electrode. The PEDOT:PSS solution (mixture of poly (3,4-vinyl dioxathiophene) and polysulfonic acid styrene) was spin coated onto the ITO glass at 3000 rpm for 30 s, annealed at 140 °C on a hot plate in air for 20 min to obtain a thin layer of about 40 nm, and then the device was transferred to a nitrogen filled glove box. Then the active layer of the blend of copolymer:PC₇₁BM or copolymer: ITIC was spin-coated onto the PEDOT: PSS layer. Then the PFN-Br (0.5 mg ml⁻¹) was spin coating on the active layer. Followed by evaporation of about 80 nm Ag as the cathode at the vacuum of 3 × 10⁻⁴ Pa, the effective surface of the device was 0.04 cm². The effective device area of the final device was covered by epoxy resin and cured in an ultraviolet curing oven for 5 min to encapsulate the device to isolate moisture and oxygen from the device. Power conversion efficiency (PCE) was measured under a computer-controlled Keithley 2400 sourcemeter under 1 sun, AM 1.5 G solar simulator (Taiwan, Enlitech SS-F5). The current density-voltage (*J*-*V*) curve of the device was recorded by the Keithley 2400 Source Measure Unit. The EQE spectra were measured by a commercial EQE measurement system (Taiwan, Enlitech, QE-R).

Synthesis of Monomers. 2,6-Bis(thiophene-2-carbaldehyde)-4,8-bis(2,4-dioctylthiophene-5-yl) benzo[1,2-b;4,5-b'] dithiophene (M3)

To a 100ml two-neck round bottom equipped with a condenser was added 6 (2.216 g, 2 mmol), 5-bromo-2-thiophenecarboxaldehyde (764.2 mg, 4 mmol), Pd(PPh₃)₄ (116 mg, 0.1 mmol). After exchange gas three times, 30 ml toluene was added to the mixture. Then the suspension was refluxed at 110 °C overnight under N₂. After cooling to room temperature, 100 ml water was added and the reaction mixture was extracted with dichloromethane (DCM) and washed with water and brine. The organic layer was dried over Na₂SO₄, and then filtered and concentrated. Then the residue was purified with silica gel chromatography to provide pure product as orange solid. (1.1g, yield 55%). ¹H NMR (500 MHz, CDCl₃) δ 9.91 (s, 2H), 7.72 (d, *J* = 3.9 Hz, 2H), 7.68 (s, 2H), 7.38 (d, *J* = 3.9 Hz, 2H), 4.19 (d, *J* = 5.3 Hz, 4H), 1.89 (dt, *J* = 11.9, 5.9 Hz, 2H), 1.56 - 1.21 (m, 64H), 0.87 (m, 12H). ¹³C NMR (125 MHz, CDCl₃) δ 182.40, 146.55, 144.72, 142.93, 136.94, 135.69, 132.72, 129.71, 125.82, 118.93, 39.20, 31.95, 31.94, 31.29, 30.15, 30.14, 29.77, 29.76, 29.73, 29.70, 29.42, 29.39, 27.04, 22.71.



Scheme S1. Synthetic route of the monomers.

2,6-Bis(carbaldehyde)-4,8-bis(2,4-dioctylthiophene-5-yl) benzo[1,2-b:3,4-b']dithiophene (M4)

At $-78\text{ }^{\circ}\text{C}$, 3.6 mL 2.5 M *n*-butyllithium (9 mmol, 3.0 equiv) was added dropwise to a solution of 2.41 g (3 mmol, 1.0 equiv) of 7 in 160 mL dry THF. The solution was then stirred at $-78\text{ }^{\circ}\text{C}$ for 2 h, after which 2.31 mL (30 mmol, 10.0 equiv) dry DMF was added dropwise. After stirring for 1h at this temperature, the resulting solution was warmed to room temperature and stirred overnight. The reaction was then poured into 100 ml ice water and extracted with DCM. The organic layer was then washed with water and brine, and then dried with Na_2SO_4 . Then the residue was purified with silica gel chromatography to provide pure product as orange oil. (1.29 g, yield 50%). ^1H NMR (500 MHz, CDCl_3) δ 10.10 (s, 2H), 8.40 (s, 2H), 7.26 (s, 2H), 2.86 - 2.82 (m, 4H), 2.64 - 2.60 (m, 4H), 1.77 - 1.70 (m, 4H), 1.68 - 1.62 (m, 4H), 1.47 - 1.24 (m, 40H), 0.87 (m, 12H). ^{13}C NMR (125 MHz, CDCl_3) δ 184.80, 145.12, 142.04, 141.22, 138.90, 137.77, 134.44, 132.88, 130.70, 127.73, 31.92, 31.89, 31.83, 30.84, 29.58, 29.51, 29.50, 29.39, 29.35, 29.27, 28.34, 28.08, 22.69, 14.13.

2,6-Bis(thiophene-2-carbaldehyde)-4,8-bis(2,4-dioctylthiophene-5-yl) benzo[1,2-b;4,5-b'] dithiophene (M5)

To a 100 ml two-neck round bottom equipped with a condenser was added 8 (1 g, 0.89 mmol), 5-bromo-2-

thiophenecarboxaldehyde (600 mg, 3.14 mmol), Pd(PPh₃)₄ (51mg, 0.0445 mmol). After exchange gas three times, 16 ml toluene was added to the mixture. Then the suspension was refluxed at 110 °C overnight under N₂. After cooling to room temperature, 100 ml water was added and the reaction mixture was extracted with DCM and washed with water and brine. The organic layer was dried over Na₂SO₄, filtered and concentrated. Then the residue was purified with silica gel chromatography to provide pure product as orange solid. (729 mg, yield 80%). ¹H NMR (500 MHz, CDCl₃) δ 9.88 (s, 2H), 7.90 (s, 2H), 7.69 (d, J = 4.0 Hz, 2H), 7.36 (d, J = 3.9 Hz, 2H), 7.23 (s, 2H), 2.88 - 2.83 (m, 4H), 2.67 - 2.62 (m, 4H), 1.77 - 1.73 (m, 4H), 1.72 - 1.65 (m, 4H) 1.52 - 1.25 (m, 40H), 0.89 (m, 12H). ¹³C NMR (125 MHz, CDCl₃) δ 182.47, 146.81, 142.89, 141.20, 139.37, 138.56, 137.40, 136.96, 136.88, 133.89, 130.20, 125.82, 124.51, 122.34, 31.94, 31.90, 31.83, 30.79, 29.57, 29.56, 29.41, 29.39, 29.32, 28.34, 28.10, 22.70, 14.14.

Synthesis of Copolymers. POD To a 25 ml two-neck round bottom equipped with a con-denser, M1 (41.3 mg, 0.1 mmol), M2 (84.0 mg, 0.1 mmol) was added. After exchange gas three times, 2 ml dry THF and, t-BuOK (11.22 mg, 0.1 mmol) in 0.4 ml t-BuOK was added to the reaction. The solution was heated to 70 °C for 2h. After cooling to room temperature, 5 ml chloroform was added to the reaction mixture and the solution was dropped into 200 ml methanol. The polymer was precipitated and then collected by filtration. The polymer was subjected to Soxhlet extraction with methanol, hexane, DCM and chloroform. The product obtained by chloroform extraction was dried under vacuum. After removal of the solvent, 93.5 mg (75 %) of a dark red solid was isolated. ¹H NMR (500 MHz, CDCl₃) δ 8.92 - 8.56 (m, 2H), 8.20 - 7.46 (m, 2H), 6.91 - 6.78 (m,2H), 4.14 (m, 4H), 4.39 - 4.04 (m, 4H), 1.83(m, 2H), 1.60 - 1.32 (m, 88H), 0.88 (m, 18H). GPC: $M_n = 75.2$ kDa, $M_w = 121.0$ kDa, PDI = 1.6. $T_d = 345$ °C.

PODDT To a 25 ml two-neck round bottom equipped with a condenser, M1 (41.3 mg,0.1 mmol), M3 (100.3 mg,0.1 mmol) was added. After exchange gas three times, 2 ml dry THF and, t-BuOK (11.22 mg, 0.1 mmol) in 0.4 ml t-BuOK was added to the reaction. The solution was heated to 70 °C for 1h. After cooling to room temperature, 5 ml chloroform was added to the reaction mixture and the solution was dropped into 200 ml methanol. The polymer was precipitated and then collected by filtration. The polymer was subjected to Soxhlet extraction with methanol, hexane, DCM and chloroform. The product obtained by chloroform extraction was dried under vacuum. After removal of the solvent, 112.8 mg (yield 80%) of a dark red solid was isolated. ¹H NMR (500 MHz, CDCl₃) δ 8.92 - 8.24 (m, 4H), 8.14 - 7.93 (m, 2H), 7.66 - 7.35 (m, 2H), 7.04 - 6.78 (m,2H), 4.50 - 4.27 (m, 4H), 4.08 (m, 4H), 2.34(m, 2H), 1.43 - 1.26 (m, 88H), 0.86 (m, 18H). GPC: $M_n = 25.5$ kDa, $M_w = 43.2$ kDa, PDI = 1.7. $T_d = 340$ °C.

PdC8Th To a 25 ml two-neck round bottom equipped with a con-denser, M1 (41.3 mg,0.1 mmol), M4 (85.9 mg,0.1 mmol) was added. After exchange gas three times, 2 ml dry THF and, t-BuOK (11.22 mg,0.1 mmol) in 0.4ml t-BuOK was added to the reaction. The solution was heated to 70°C for 2h. After cooling to room temperature, 5 ml chloroform was added to the reaction mixture and the solution was dropped into 200 ml methanol. The polymer was precipitated and then collected by filtration. The polymer was subjected to Soxhlet extraction with methanol, hexane, DCM and chloroform. The product obtained by chloroform extraction was dried under vacuum. After removal of the solvent, 95.0mg (yield 75%) of a dark purple solid was isolated. ¹H NMR (500 MHz, CDCl₃) δ 8.6 (m, 2H), 8.05 (m, 2H), 7.31 (m, 2H), 7.15(m, 2H), 4.10 (m, 4H), 2.84 (m, 4H), 2.63(m, 4H) 1.82- 1.25 (m, 72H), 1.08 - 0.88 (m, 18H). GPC: $M_n = 30.4$ kDa, $M_w = 51.9$ kDa, PDI = 1.7. $T_d = 345$ °C.

PdC8ThDT To a 25 ml two-neck round bottom equipped with a con-denser, M1 (41.3 mg, 0.1 mmol), M2 (115.7 mg, 0.1 mmol) was added. After exchange gas three times, 2 ml dry THF and, t-BuOK (11.22 mg, 0.1 mmol) in 0.4 ml t-BuOK was added to the reaction. The solution was heated to 70 °C for 1h. After cooling to room temperature, 5 ml chloroform was added to the reaction mixture and the solution was dropped into 200 ml methanol. The

polymer was precipitated and then collected by filtration. The polymer was subjected to Soxhlet extraction with methanol, hexane, DCM and chloroform. The product obtained by chloroform extraction was dried under vacuum. After removal of the solvent, 115.7 mg (yield 80%) of a dark purple solid was isolated. ^1H NMR (500 MHz, CDCl_3) δ 8.15 - 7.95 (m, 2H), 7.82 - 7.54 (m, 4H), 7.40 - 7.32 (m, 2H), 7.19 - 7.12 (m, 2H), 6.84(m, 2H), 4.00 (m, 4H), 2.91 (m, 4H), 2.72(m, 4H), 2.01 - 1.25 (m, 72H), 1.08 - 0.88 (m, 18H). GPC: M_n = 35.5 kDa, M_w = 60.9 kDa, PDI = 1.7. T_g = 405 $^\circ\text{C}$.

PdC8ThDT-S To a 25 ml two-neck round bottom equipped with a con-denser, compound 6 (112.9 mg, 0.1mmol), M6 (75.9 mg, 0.1 mmol) and $\text{Pd}(\text{PPh}_3)_4$ (2.9 mg, 0.0025mmol) was added. After exchange gas three times, 6 ml toluene was added to the reaction. The solution was heated to 110 $^\circ\text{C}$ for 4 h. After cooling to room temperature, 5 ml chloroform was added to the reaction mixture and the solution was dropped into 200 ml methanol. The polymer was precipitated and then collected by filtration. The polymer was subjected to Soxhlet extraction with methanol, hexane, DCM and chloroform. The product obtained by chloroform extraction was dried under vacuum. After removal of the solvent, 118.7 mg (83 %) of a dark red solid was isolated. ^1H NMR (500 MHz, CDCl_3) δ 8.15 - 7.95 (m, 2H), 7.82 - 7.54 (m, 4H), 7.40 - 7.32 (m, 2H), 7.19 - 7.12 (m, 2H), 6.84(m, 2H), 4.00 (m, 4H), 2.91 (m, 4H), 2.72(m, 4H), 1.82- 1.25 (m, 72H), 1.08 - 0.88 (m, 18H). GPC: M_n = 26.7 kDa, M_w = 56.0 kDa, PDI = 2.1. T_g = 410 $^\circ\text{C}$.

Analytical Characterization of Materials

^1H and ^{13}C NMR Spectroscopy

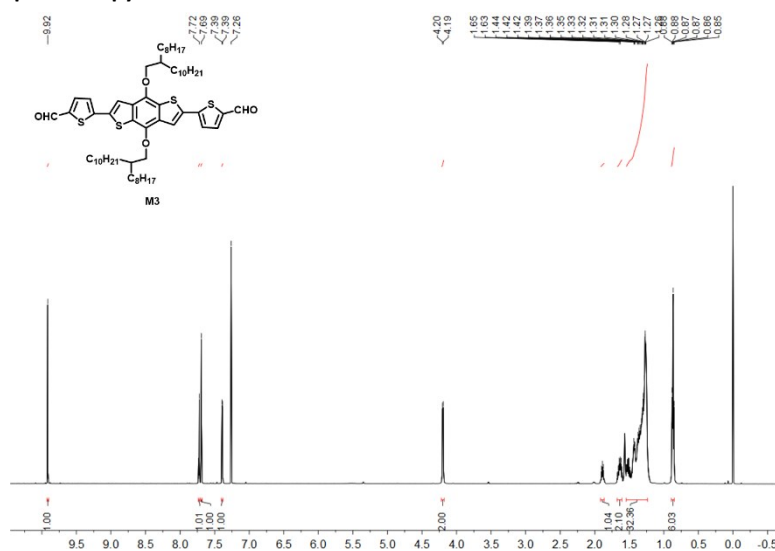


Figure S1. ^1H -NMR spectrum of M3.

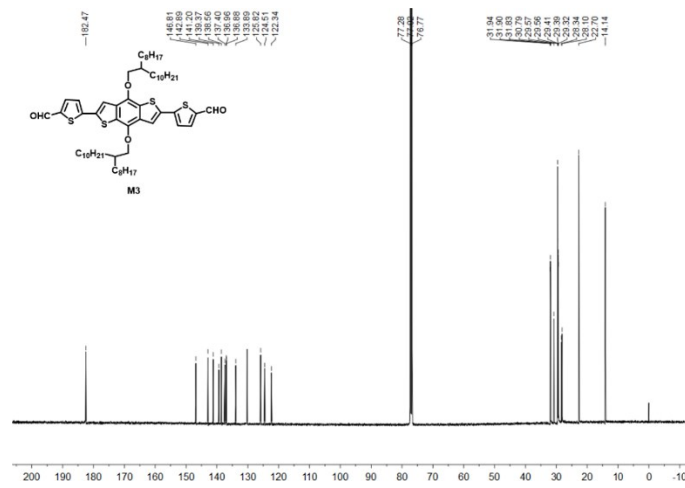


Figure S2. $^{13}\text{C-NMR}$ spectrum of M3.

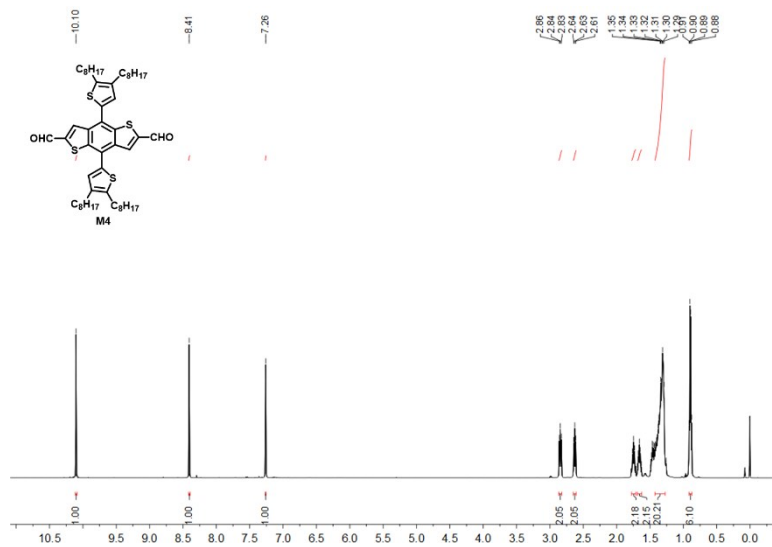


Figure S3. $^1\text{H-NMR}$ spectrum of M4.

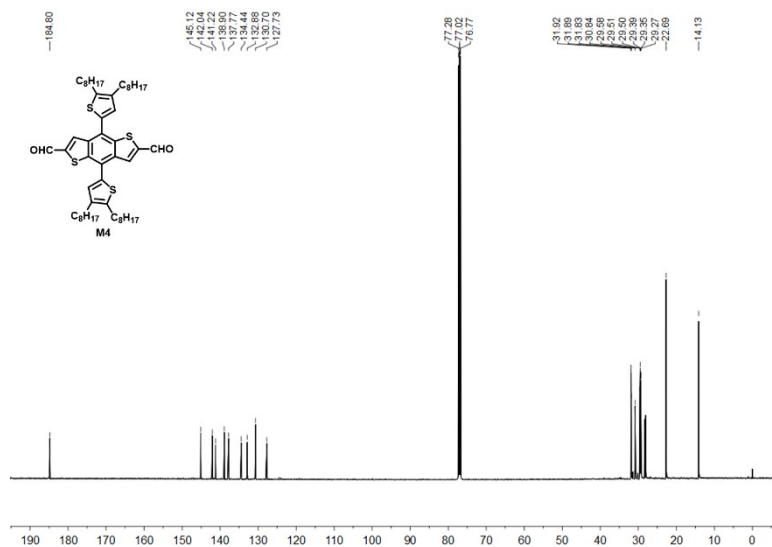


Figure S4. $^{13}\text{C-NMR}$ spectrum of M4.

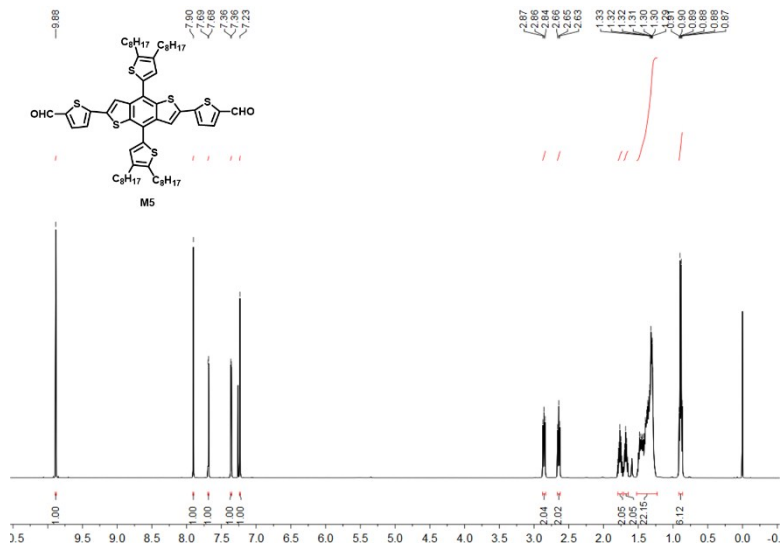


Figure S5. ¹H-NMR spectrum of M5.

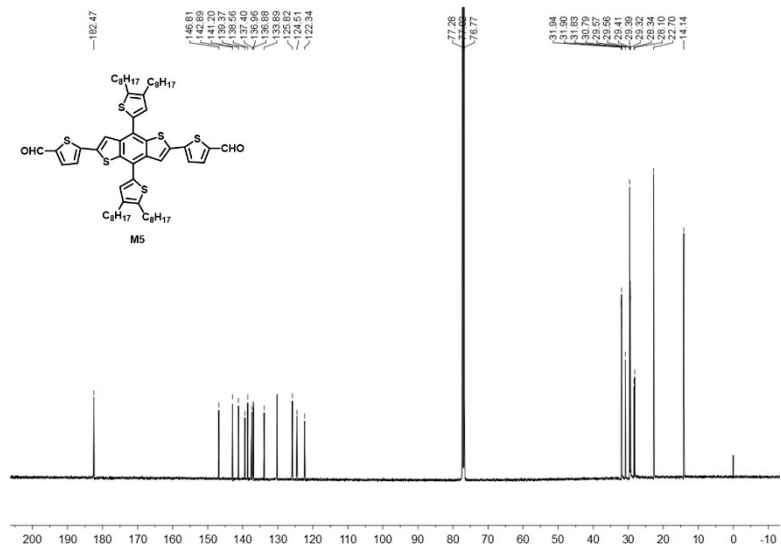


Figure S6. ¹³C-NMR spectrum of M5.

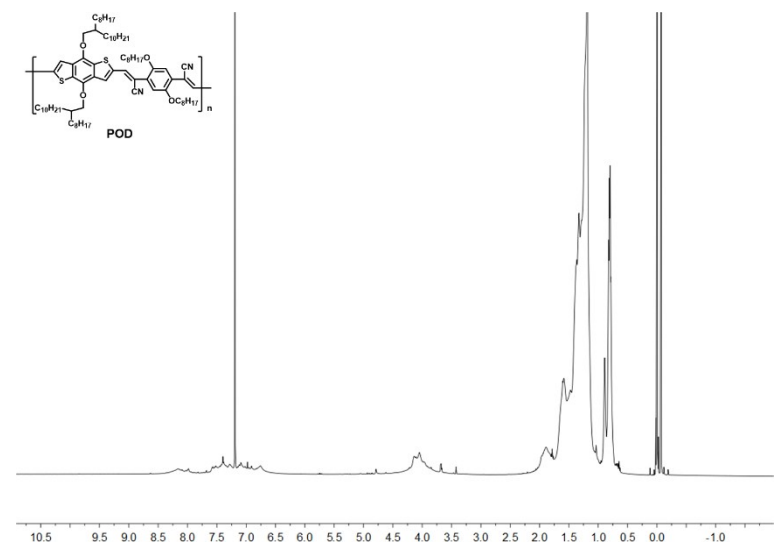
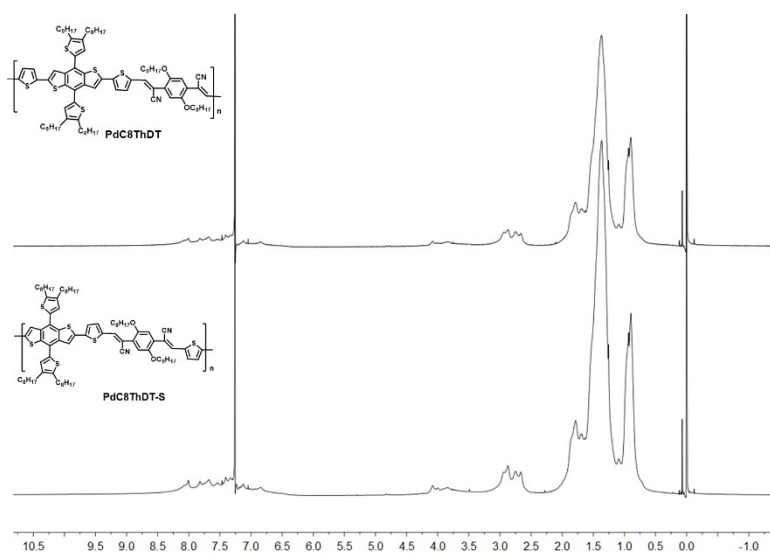
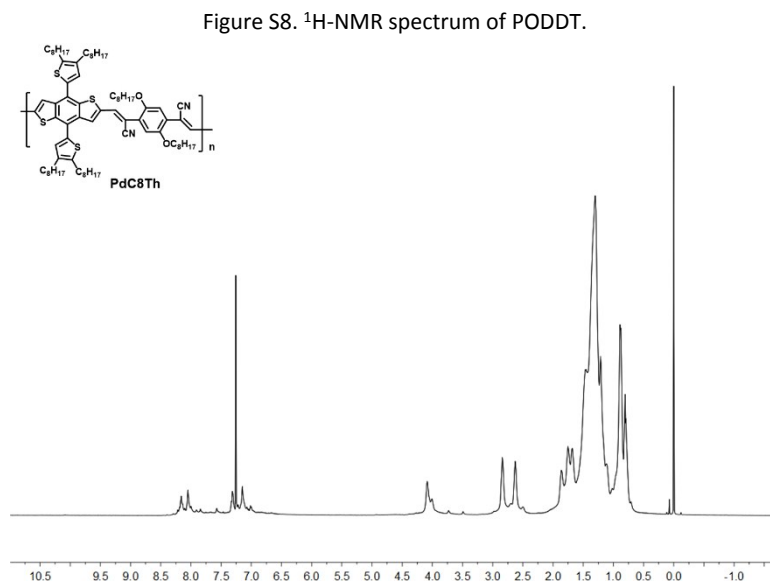
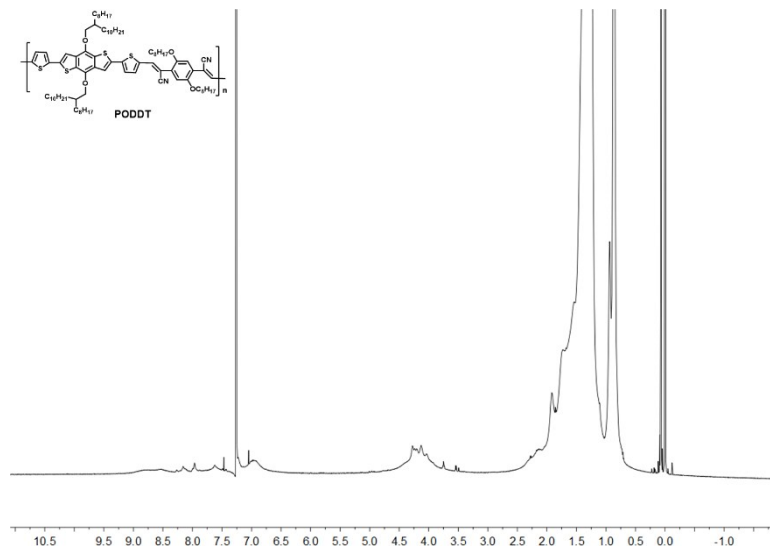


Figure S7. ¹H-NMR spectrum of POD.



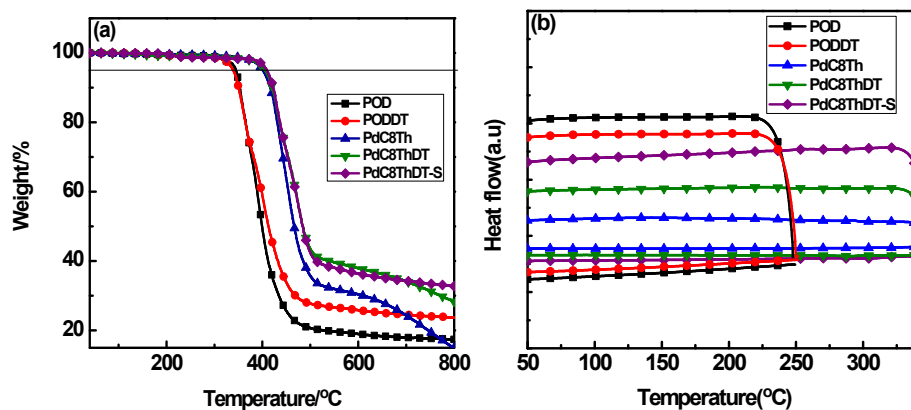
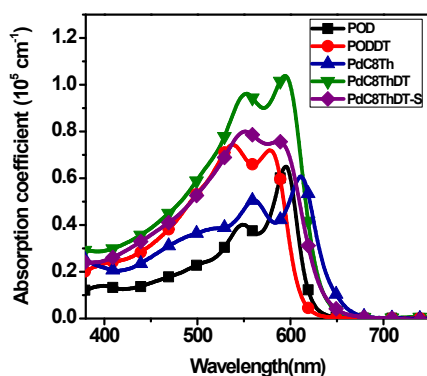


Figure S11. (a) TGA plots of copolymers at a heating rate of 20 °C/min under a nitrogen atmosphere. (b) DSC plot of polymers at a heating or cooling rate of 10 °C /min under a nitrogen atmosphere.



FigureS12. Solution absorption coefficient spectra of copolymers.

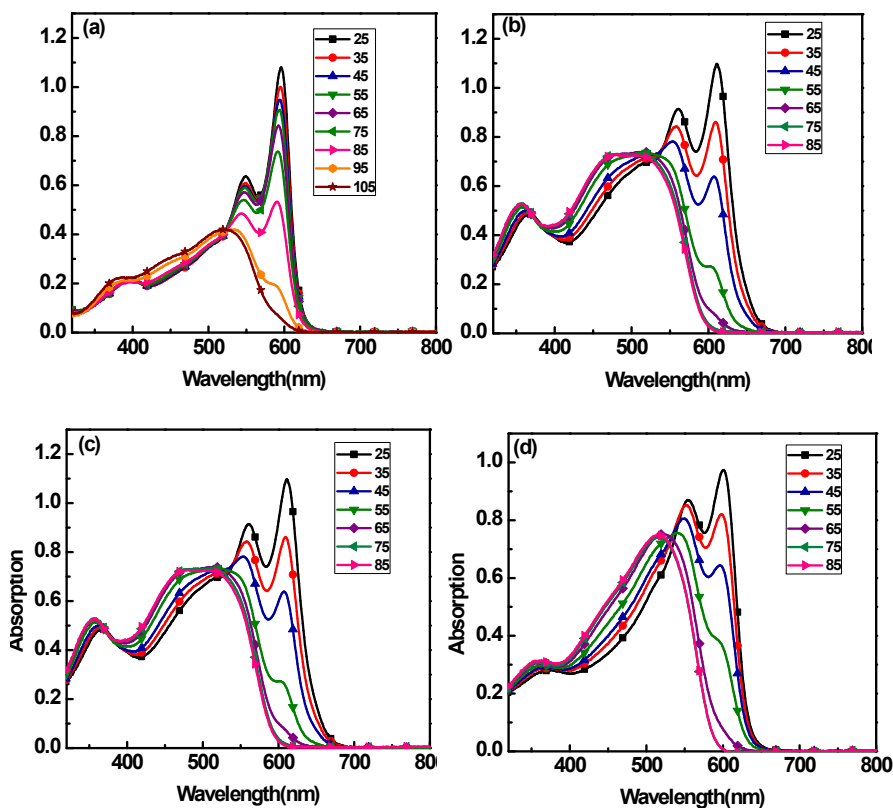


Figure S13. Temperature-dependent absorption spectra of copolymers in chlorobenzene solution. POD (a); PODDT (b); PdC8Th (c); PdC8ThDT (d).

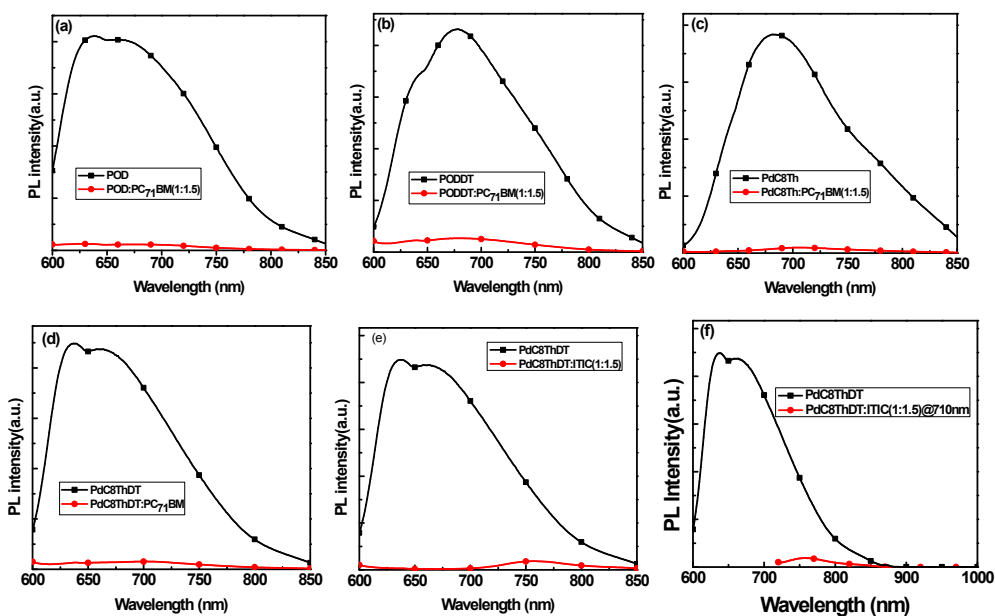


Figure S14. The photoluminescence (PL) quenching spectra of pure copolymers and copolymers: acceptor blends in the thin films. POD: PC₇₁BM(@580nm) (a); PODDT: PC₇₁BM(@580nm) (b); PdC8Th: PC₇₁BM(@580nm) (c); PdC8ThDT: PC₇₁BM(@580nm) (d); PdC8ThDT: ITIC(@580nm) (e); PdC8ThDT: ITIC(@710nm) (f).

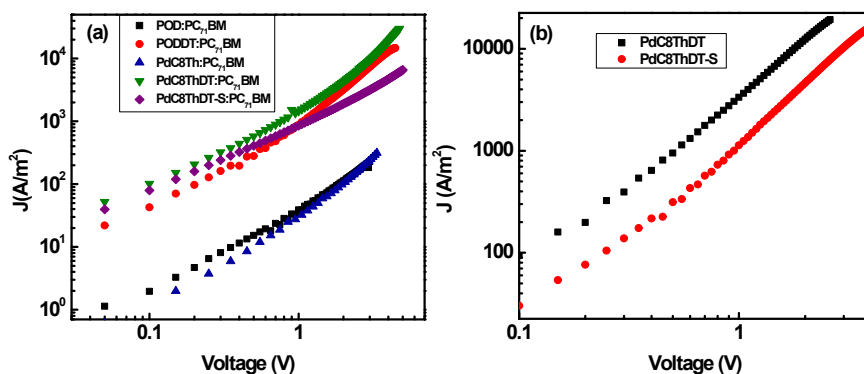


Figure S15. (a) J-V curves of hole-only devices with a structure of ITO/PEDOT:PSS/Copolymer:PC₇₁BM/MoO₃/Al; (b) J-V curves of hole-only devices with a structure of ITO/PEDOT:PSS/Copolymer:ITIC/MoO₃/Al.

Table S1. Photovoltaic performance of devices with structure of ITO/PEDOT:PSS/Copolymer: PC₇₁BM/PFN-Br/Ag (D/A=1:2, w: w; CB) without any post-processing conditions under AM 1.5G, 100 mW cm⁻² illumination.

Polymer	Voc (V)	Jsc (mA cm ⁻²)	FF	PCE (%)
POD	0.96	1.83	41.61	0.73[0.70]
PODDT	0.92	3.99	61.48	2.27[2.18]
PdC8Th	1.05	2.18	38.78	0.89[0.82]

PdC8ThDT	0.94	6.03	53.78	3.06[2.99]
PdC8ThDT-S	0.93	5.07	46.50	2.19[2.08]

Table S2. Effect of the additive on the photovoltaic performance of the PSCs based on PdC8ThDT: PC₇₁BM (1:2, w/w).

Additive	Voc (V)	Jsc (mA cm ⁻²)	FF	PCE (%)
CB	0.94	6.03	53.78	3.06[2.98]
CB+1%DIO	0.89	8.70	62.93	4.89[4.77]
CB+2%DIO	0.87	11.18	64.55	6.29[6.15]
CB+3%DIO	0.86	11.04	66.76	6.35[6.21]
CB+4%DIO	0.86	11.54	61.59	6.09[5.96]
CB+5%DIO	0.86	11.15	62.55	5.97[5.87]

Table S3. Effect of the D: A weight ratio on the photovoltaic performance of the PSCs based on PdC8ThDT: PC₇₁BM (3% DIO).

PdC8ThDT:PC ₇₁ BM (w/w)	Voc (V)	Jsc (mA cm ⁻²)	FF	PCE (%)
1:1	0.89	9.89	69.07	6.06[5.89]
1:1.5	0.89	11.58	73.47	7.76[7.43]
1:2	0.88	11.50	72.32	7.32[7.17]
1:3	0.88	9.72	70.50	6.00[5.85]

Table S4. Effect of the solvent on the photovoltaic performance of the PSCs based on PdC8ThDT: ITIC (1:1.5, w/w).

Solvent	Voc (V)	Jsc (mA cm ⁻²)	FF	PCE (%)
CB	0.97	15.63	56.12	8.54[8.36]
DCB	0.97	13.97	55.48	7.51[7.37]
CF	0.99	14.22	50.47	7.11[6.98]

Table S5. Effect of the additive on the photovoltaic performance of the PSCs based on PdC8ThDT: ITIC (1:1.5, w/w).

Additive	Voc (V)	Jsc (mA cm ⁻²)	FF	PCE (%)
CB	0.97	15.63	56.12	8.54[8.26]
CB+0.5%DIO	0.95	13.41	46.09	5.86[5.57]
CB+1%DIO	0.86	10.37	34.01	3.03[2.85]
CB+0.5%CN	0.92	13.73	54.42	7.27[7.03]
CB+1%CN	0.97	13.33	56.65	7.32[7.11]
CB+3%CN	0.98	10.38	55.13	5.62[5.42]
CB+0.5%DPE	0.94	14.71	58.87	8.18[7.96]
CB+1%DPE	0.94	15.13	59.14	8.37[8.15]

3%DPE 0.93 6.03 37.07 2.07[1.87]

Reference

1. B. C. Thompson, Y. -G. Kim, T. D. McCarley, J. R. Reynolds, *J. Am. Chem. Soc.*, 2006, **128**, 12714.
2. T. Yamamoto, T. Ikai, M. Kuzuba, T. Kuwabara, K. Maeda, K. Takahashi, S. Kanoh, *Macromolecules*, 2011, **44**, 6659.
3. H. Yao, L. Ye, B. Fan, L. Huo, J. Hou, *Sci. China. Mater.*, 2015, **58**, 213.
4. J. -M. Park, S. K. Park, W. S. Yoon, J. H. Kim, D. W. Kim, T. -L. Choi, S. Y. Park, *Macromolecules*, 2016, **49**, 2985.
5. J. -M. Park, D. W. Kim, H. Y. Chung, J. E. Kwon, S. H. Hong, T. -L. Choi, S. Y. Park, *J. Mater. Chem. A*, 2017, **5**, 16681.