

Electronic supplementary information *for*

**Spacer Length Effect of Tributylsilyl-Terminated Side Chains on the Properties of
Poly(diketopyrrolopyrrole-*alt*-terthiophene)s**

Zhongli Wang, Chenhui Xu, Ziqi Liang, Weijia Dong, Yunfeng Deng, Yang Han*,
Yanhou Geng*

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S1. General methods and experimental details

^1H NMR and ^{13}C NMR spectra were measured by using a Bruker AVANCE III (400 MHz for ^1H NMR and 100 MHz for ^{13}C NMR) spectrometer in chloroform-*d* (CDCl_3) with tetramethylsilane as internal standard at 25 °C. Elemental analysis was conducted on a FlashEA1112 elemental analyzer. High temperature gel permeation chromatography (GPC) analysis of the polymers was performed on a PL-GPC 220 system at 150 °C with 1,2,4-trichlorobenzene as the eluent and polystyrene as the standard. Thermogravimetric analysis (TGA) was measured on a TA Q50 thermogravimetric analyzer with a heating rate of 10 °C min^{-1} under nitrogen flow. Differential scanning calorimetry (DSC) was carried out on a TA Q25 instrument with a heating/cooling rate of 10 °C min^{-1} under nitrogen flow. UV-*vis*-NIR absorption spectra were conducted on Shimadzu UV-3600Plus spectrometer. The optical bandgap was calculated according to film absorption onset ($E_g^{\text{opt}} = 1240/\lambda_{\text{onset}}$ eV). Film cyclic voltammetry (CV) measurement was carried out on a CHI660E electrochemical analyzer with a three-electrode cell at a scan rate of 100 mV s^{-1} in anhydrous acetonitrile. A glassy carbon electrode with a diameter of 10 mm, a Pt wire, and a saturated calomel electrode (SCE) were used as the working, counter, and reference electrodes, respectively. Tetrabutylammonium hexafluorophosphate (Bu_4NPF_6 , 0.1 mol L^{-1}) was used as the supporting electrolyte. Grazing incidence X-ray diffraction (GIXRD) spectra of the thin films were measured on a Rigaku Smart Lab with Cu K_α source ($\lambda = 1.54056 \text{ \AA}$) in air. Atomic force microscopy (AFM) measurement was performed on a Bruker MultiMode 8 instrument with tapping mode in air. The wire bar with a wet film

thickness of about 6 microns was purchased from RK PrintCoat Instruments Ltd (KHC.11.1 K Bar).

S2. Synthetic procedures and characterization

All air and water sensitive reactions were performed under a nitrogen atmosphere. All chemical reagents were purchased from Sigma-Aldrich, Meryer or Heowns and used as received unless otherwise noted. N,N-Dimethylformamide (DMF), dichloromethane and toluene were all distilled in the standard method prior to use. Other solvents were used without further purification. **1** and M1 were prepared according to literature procedures.^{1,2}

Synthesis of 2,5-Di(2-propenyl)-3,6-dithiophen-2-yl-pyrrolo[3,4-c]pyrrole-1,4-dione (2): A mixture of 3,6-dithienyl-2,5-diketopyrrolo[3,4-c]pyrrole (**1**) (0.90 g, 3.00 mmol), anhydrous potassium carbonate (0.91 g, 6.60 mmol), 3-bromopropene (0.83 g, 6.90 mmol) and anhydrous DMF (27 mL) were added to a three-neck roundbottom flask. Then the mixture was stirred at 120 °C for about 12 h, and subsequently cooled to room temperature. The DMF was removed under vacuum, then the residue was dissolved in chloroform, washed with brine and dried with magnesium sulfate. After the solvent was removed, the organic phase was purified by chromatography (silica gel, dichloromethane) to give a dark red solid (0.82 g, yield: 72%). ¹H NMR (400 MHz, CDCl₃, δ): 8.80 (d, *J* = 3.6 Hz, 2H), 7.65 (d, *J* = 4.8 Hz, 2H), 7.29-7.27 (m, 2H), 6.08-5.99 (m, 2H), 5.27-5.23 (m, 4H), 4.78-4.76 (m, 4H).

Synthesis of 2,5-Di(3-(tributylsilyl)propyl)-3,6-dithiophen-2-yl-pyrrolo[3,4-c]pyrrole-1,4-dione (SiC3-DPP): A mixture of **2** (0.76 g, 2.00 mmol), tributylsilane

(1.00 g, 5.00 mmol) and anhydrous toluene (23 mL) were added to a roundbottom Schlenk flask, followed by the addition of a drop of Karstedt's catalyst (Platinum(0)-1,3-divinyl-1,1,3,3-tetramethyldisiloxane, 2% Pt in xylene). The mixture was stirred at 70 °C for about 12 h and the toluene was removed under vacuum. Then the residue was purified by chromatography (silica gel, dichloromethane: petroleum ether = 1:1) to give a bright red solid (1.05 g, yield: 67%). ¹H NMR (400 MHz, CDCl₃, δ): 8.92 (d, *J* = 3.6 Hz, 2H), 7.63 (d, *J* = 4.8 Hz, 2H), 7.30-7.26 (t, *J* = 4.4 Hz, 2H), 4.05 (t, *J* = 8.0 Hz, 4H), 1.75-1.66 (m, 4H), 1.30-1.20 (m, 24H), 0.86 (t, *J* = 6.4 Hz, 18H), 0.62-0.57 (m, 4H), 0.50-0.46 (m, 12H).

General Synthetic procedure of SiC_m-Br (m = 4-8 and 10): A mixture of n-bromo-1-alkene (24.00 mmol), tributylsilane (4.00 g, 20.00 mmol), chloro(1,5-cyclooctadiene)iridium(I) dimer (0.26 g, 0.40 mmol), 1,5-cyclooctadiene (246 μL) and anhydrous dichloromethane (24 mL) were added to a Schlenk tube. The mixture was stirred at room temperature and then the dichloromethane was removed under vacuum. Subsequently, the residue was purified by chromatography (silica gel, petroleum ether) to give a colourless liquid.

(4-Bromobutyl)tributylsilane (SiC₄-Br): 5.24 g, yield: 78%. ¹H NMR (400 MHz, CDCl₃, δ): 3.49 (t, *J* = 6.8 Hz, 2H), 1.97-1.90 (m, 2H), 1.53-1.45 (m, 2H), 1.41-1.27 (m, 12H), 0.95 (t, *J* = 7.2 Hz, 9H), 0.59-0.54 (m, 8H).

(5-Bromopentyl)tributylsilane (SiC₅-Br): 5.18 g, yield: 74%. ¹H NMR (400 MHz, CDCl₃, δ): 3.40 (t, *J* = 6.8 Hz, 2H), 1.90-1.83 (m, 2H), 1.48-1.40 (m, 2H), 1.36-1.21 (m, 14H), 0.88 (t, *J* = 6.8 Hz, 9H), 0.52-0.47 (m, 8H).

(6-Bromohexyl)tributylsilane (SiC6-Br): 6.10 g, yield: 84%. ¹H NMR (400 MHz, CDCl₃, δ): 3.40 (t, *J* = 7.2 Hz, 2H), 1.90-1.83 (m, 2H), 1.48-1.41 (m, 2H), 1.34-1.21 (m, 16H), 0.95 (t, *J* = 6.8 Hz, 9H), 0.52-0.47 (m, 8H).

(7-Bromoheptyl)tributylsilane (SiC7-Br): 5.88 g, yield: 78%. ¹H NMR (400 MHz, CDCl₃, δ): 3.41 (t, *J* = 6.8 Hz, 2H), 1.89-1.82 (m, 2H), 1.45-1.40 (m, 2H), 1.36-1.20 (m, 18H), 0.88 (t, *J* = 6.8 Hz, 9H), 0.51-0.46 (m, 8H).

(8-Bromooctyl)tributylsilane (SiC8-Br): 5.80 g, yield: 74%. ¹H NMR (400 MHz, CDCl₃, δ): 3.41 (t, *J* = 6.8 Hz, 2H), 1.89-1.82 (m, 2H), 1.44-1.41 (m, 2H), 1.34-1.20 (m, 20H), 0.88 (t, *J* = 6.8 Hz, 9H), 0.51-0.46 (m, 8H).

(10-Bromodecyl)tributylsilane (SiC10-Br): 6.66 g, yield: 76%. ¹H NMR (400 MHz, CDCl₃, δ): 3.41 (t, *J* = 7.2 Hz, 2H), 1.89-1.82 (m, 2H), 1.44-1.41 (m, 2H), 1.36-1.20 (m, 24H), 0.88 (t, *J* = 6.8 Hz, 9H), 0.50-0.46 (m, 8H).

General Synthetic procedure of SiC_m-DPP (m = 4-8 and 10): A mixture of **1** (1.50 g, 5.00 mmol), anhydrous potassium carbonate (2.08 g, 15.0 mmol), 18-crown-6-ether (about 15 mg), SiC_m-Br (15.0 mmol) and anhydrous DMF (49 mL) were added to a three-neck roundbottom flask. Then the mixture was stirred at 100 °C for about 12 h, and subsequently cooled to room temperature. The DMF was removed under vacuum, then the residue was dissolved in dichloromethane, washed with brine and dried with magnesium sulfate. After the solvent was removed, the organic phase was purified by chromatography (silica gel, dichloromethane: petroleum ether = 1:1) to give a dark red solid.

*2,5-Dis(4-(tributylsilyl)butyl)-3,6-dithiophen-2-yl-pyrrolo[3,4-*c*]pyrrole-1,4-dione*

(*SiC4-DPP*): 2.31 g, yield: 57%. ¹H NMR (400 MHz, CDCl₃, δ): 8.94 (d, *J* = 3.6 Hz, 2H), 7.64 (d, *J* = 4.8 Hz, 2H), 7.28 (t, *J* = 4.8 Hz, 2H), 4.08 (t, *J* = 8.0 Hz, 4H), 1.80-1.72 (m, 4H), 1.45-1.37 (m, 4H), 1.34-1.20 (m, 24H), 0.87 (t, *J* = 6.8 Hz, 18H), 0.58-0.54 (m, 4H), 0.51-0.47 (m, 12H).

2,5-Di(5-(tributylsilyl)pentyl)-3,6-dithiophen-2-yl-pyrrolo[3,4-c]pyrrole-1,4-dione

(*SiC5-DPP*): 1.63 g, yield: 39%. ¹H NMR (400 MHz, CDCl₃, δ): 8.95 (d, *J* = 4.0 Hz, 2H), 7.65 (d, *J* = 4.8 Hz, 2H), 7.28 (dd, *J*₁ = 5.2 Hz, *J*₂ = 4.0 Hz, 2H), 4.07 (t, *J* = 7.6 Hz, 4H), 1.79-1.71 (m, 4H), 1.47-1.40 (m, 4H), 1.36-1.18 (m, 28H), 0.87 (t, *J* = 6.8 Hz, 18H), 0.49-0.45 (m, 16H).

2,5-Di(6-(tributylsilyl)hexyl)-3,6-dithiophen-2-yl-pyrrolo[3,4-c]pyrrole-1,4-dione

(*SiC6-DPP*): 1.90 g, yield: 44%. ¹H NMR (400 MHz, CDCl₃, δ): 8.95 (d, *J* = 3.6 Hz, 2H), 7.64 (d, *J* = 4.8 Hz, 2H), 7.29 (t, *J* = 4.4 Hz, 2H), 4.07 (t, *J* = 8.0 Hz, 4H), 1.78-1.70 (m, 4H), 1.44-1.19 (m, 36H), 0.87 (t, *J* = 6.8 Hz, 18H), 0.49-0.45 (m, 16H).

2,5-Di(7-(tributylsilyl)heptyl)-3,6-dithiophen-2-yl-pyrrolo[3,4-c]pyrrole-1,4-dione

(*SiC7-DPP*): 1.70 g, yield: 44%. ¹H NMR (400 MHz, CDCl₃, δ): 8.94 (d, *J* = 4.0 Hz, 2H), 7.64 (dd, *J*₁ = 5.2 Hz, *J*₂ = 1.2 Hz, 2H), 7.29 (dd, *J*₁ = 5.2 Hz, *J*₂ = 4.0 Hz, 2H), 4.07 (t, *J* = 8.0 Hz, 4H), 1.79-1.71 (m, 4H), 1.38-1.20 (m, 40H), 0.88 (t, *J* = 6.8 Hz, 18H), 0.50-0.45 (m, 16H).

2,5-Di(8-(tributylsilyl)octyl)-3,6-dithiophen-2-yl-pyrrolo[3,4-c]pyrrole-1,4-dione

(*SiC8-DPP*): 1.38 g, yield: 30%. ¹H NMR (400 MHz, CDCl₃, δ): 8.94 (d, *J* = 4.0 Hz, 2H), 7.64 (d, *J* = 4.8 Hz, 2H), 7.29 (t, *J* = 4.4 Hz, 2H), 4.07 (t, *J* = 8.0 Hz, 4H), 1.78-1.71 (m, 4H), 1.42-1.38 (m, 4H), 1.35-1.20 (m, 40H), 0.88 (t, *J* = 6.8 Hz, 18H), 0.50-

0.45 (m, 16H).

2,5-Diis(10-(tributylsilyl)decyl)-3,6-dithiophen-2-yl-pyrrolo[3,4-c]pyrrole-1,4-dione

(*SiC10-DPP*): 1.22 g, yield: 25%. ¹H NMR (400 MHz, CDCl₃, δ): 8.93 (dd, *J*₁ = 4.0 Hz, *J*₂ = 1.2 Hz, 2H), 7.64 (dd, *J*₁ = 5.2 Hz, *J*₂ = 1.2 Hz, 2H), 7.29 (dd, *J*₁ = 4.8 Hz, *J*₂ = 3.6 Hz, 2H), 4.07 (t, *J* = 8.0 Hz, 4H), 1.78-1.71 (m, 4H), 1.43-1.40 (m, 4H), 1.35-1.20 (m, 48H), 0.88 (t, *J* = 6.8 Hz, 18H), 0.50-0.46 (m, 16H).

General Synthetic procedure of SiCm-DPPBr (m = 3-8 and 10): A solution of SiCm-DPP (2.00 mmol) in chloroform (54 mL) were added to a Schlenk flask, and N-bromosuccinimide (0.89 g, 5.00 mmol) was added slowly at 0 °C. Then the mixture was gradually raised to room temperature and stirred for about 3 h in the absence of light. After the solvent was removed, the organic phase was purified by chromatography (silica gel, dichloromethane: petroleum ether = 1:2) to obtain a dark purple solid.

3,6-Bis(5-bromo-2-thienyl)-2,5-bis(3-(tributylsilyl)propyl)-2,5-dihydro-pyrrolo[3,4-c]

pyrrole-1,4-dione (SiC3-DPPBr): 1.22 g, yield: 65%. ¹H NMR (400 MHz, CDCl₃, δ): 8.61 (d, *J* = 4.4 Hz, 2H), 7.16 (d, *J* = 4.4 Hz, 2H), 3.86 (t, *J* = 8.0 Hz, 4H), 1.64-1.56 (m, 4H), 1.26-1.12 (m, 24H), 0.78 (t, *J* = 6.8 Hz, 18H), 0.54-0.49 (m, 4H), 0.43-0.39 (m, 12H); ¹³C NMR (100 MHz, CDCl₃, δ): 160.91, 138.93, 135.43, 131.63, 131.11, 119.13, 107.72, 45.32, 26.80, 26.11, 24.72, 13.80, 12.23, 11.97, 11.72, 9.54. Elemental Anal. calcd. for C₄₄H₇₀Br₂N₂O₂S₂Si₂: C 56.27, H 7.51, N 2.98, S 6.83; Found: C 55.98, H 7.26, N 2.89, S 7.01.

3,6-Bis(5-bromo-2-thienyl)-2,5-bis(4-(tributylsilyl)butyl)-2,5-dihydro-pyrrolo[3,4-c]

pyrrole-1,4-dione (SiC4-DPPBr): 1.20 g, yield: 62%. ¹H NMR (400 MHz, CDCl₃, δ):

8.68 (d, $J = 4.4$ Hz, 2H), 7.23 (d, $J = 4.4$ Hz, 2H), 3.98 (t, $J = 7.6$ Hz, 4H), 1.76-1.69 (m, 4H), 1.44-1.38 (m, 4H), 1.34-1.22 (m, 24H), 0.88 (t, $J = 6.8$ Hz, 18H), 0.59-0.54 (m, 4H), 0.51-0.47 (m, 12H); ^{13}C NMR (100 MHz, CDCl_3 , δ): 160.97, 138.98, 135.38, 131.60, 131.14, 119.13, 107.77, 41.97, 33.87, 26.85, 26.18, 21.40, 13.84, 12.22, 11.85. Elemental Anal. calcd. for $\text{C}_{46}\text{H}_{74}\text{Br}_2\text{N}_2\text{O}_2\text{S}_2\text{Si}_2$: C 57.12, H 7.71, N 2.90, S 6.63; Found: C 57.34, H 7.82, N 3.01, S 6.24.

*3,6-Bis(5-bromo-2-thienyl)-2,5-bis(5-(tributylsilyl)pentyl)-2,5-dihydro-pyrrolo[3,4-*c*]pyrrole-1,4-dione (SiC5-DPPBr)*: 1.31 g, yield: 66%. ^1H NMR (400 MHz, CDCl_3 , δ): 8.62 (d, $J = 4.0$ Hz, 2H), 7.16 (d, $J = 4.0$ Hz, 2H), 3.91 (t, $J = 7.6$ Hz, 4H), 1.68-1.60 (m, 4H), 1.39-1.34 (m, 4H), 1.27-1.12 (m, 28H), 0.80 (t, $J = 7.2$ Hz, 18H), 0.45-0.39 (m, 16H); ^{13}C NMR (100 MHz, CDCl_3 , δ): 161.01, 138.98, 135.42, 131.64, 131.13, 119.18, 107.76, 42.34, 31.10, 26.87, 26.19, 23.74, 13.83, 12.58, 12.40, 12.15. Elemental Anal. calcd. for $\text{C}_{48}\text{H}_{78}\text{Br}_2\text{N}_2\text{O}_2\text{S}_2\text{Si}_2$: C 57.93, H 7.90, N 2.81, S 6.44; Found: C 57.45, H 7.71, N 2.97, S 6.57.

*3,6-Bis(5-bromo-2-thienyl)-2,5-bis(6-(tributylsilyl)hexyl)-2,5-dihydro-pyrrolo[3,4-*c*]pyrrole-1,4-dione (SiC6-DPPBr)*: 1.29 g, yield: 63%. ^1H NMR (400 MHz, CDCl_3 , δ): 8.61 (d, $J = 4.4$ Hz, 2H), 7.15 (d, $J = 4.4$ Hz, 2H), 3.90 (t, $J = 7.2$ Hz, 4H), 1.66-1.59 (m, 4H), 1.34-1.12 (m, 36H), 0.80 (t, $J = 7.2$ Hz, 18H), 0.43-0.39 (m, 16H); ^{13}C NMR (100 MHz, CDCl_3 , δ): 160.98, 138.95, 135.39, 131.64, 131.12, 119.16, 107.75, 42.32, 33.47, 29.98, 26.88, 26.52, 26.20, 23.84, 13.84, 12.46, 12.17, 11.92. Elemental Anal. calcd. for $\text{C}_{50}\text{H}_{82}\text{Br}_2\text{N}_2\text{O}_2\text{S}_2\text{Si}_2$: C 58.69, H 8.08, N 2.74, S 6.27; Found: C 58.87, H 8.31, N 2.68, S 5.93.

3,6-Bis(5-bromo-2-thienyl)-2,5-bis(7-(tributylsilyl)heptyl)-2,5-dihydro-pyrrolo[3,4-c]pyrrole-1,4-dione (SiC7-DPPBr): 1.30 g, yield: 62%. ¹H NMR (400 MHz, CDCl₃, δ): 8.61 (d, *J* = 4.0 Hz, 2H), 7.16 (d, *J* = 4.0 Hz, 2H), 3.91 (t, *J* = 7.6 Hz, 4H), 1.68-1.60 (m, 4H), 1.33-1.13 (m, 40H), 0.81 (t, *J* = 7.2 Hz, 18H), 0.43-0.39 (m, 16H); ¹³C NMR (100 MHz, CDCl₃, δ): 161.02, 138.99, 135.39, 131.65, 131.11, 119.17, 107.78, 42.31, 33.88, 30.07, 30.00, 29.20, 28.92, 26.88, 26.21, 23.91, 13.84, 12.49, 12.19. Elemental Anal. calcd. for C₅₂H₈₆Br₂N₂O₂S₂Si₂: C 59.41, H 8.25, N 2.66, S 6.10; Found: C 59.89, H 7.93, N 2.71, S 6.27.

3,6-Bis(5-bromo-2-thienyl)-2,5-bis(8-(tributylsilyl)octyl)-2,5-dihydro-pyrrolo[3,4-c]pyrrole-1,4-dione (SiC8-DPPBr): 1.30 g, yield: 60%. ¹H NMR (400 MHz, CDCl₃, δ): 8.61 (d, *J* = 4.0 Hz, 2H), 7.16 (d, *J* = 4.4 Hz, 2H), 3.90 (t, *J* = 7.6 Hz, 4H), 1.67-1.60 (m, 4H), 1.34-1.13 (m, 44H), 0.80 (t, *J* = 7.2 Hz, 18H), 0.43-0.39 (m, 16H); ¹³C NMR (100 MHz, CDCl₃, δ): 161.00, 138.97, 135.39, 131.64, 131.11, 119.18, 107.76, 42.31, 33.88, 30.00, 29.21, 26.89, 26.21, 23.93, 13.84, 12.51, 12.19. Elemental Anal. calcd. for C₅₄H₉₀Br₂N₂O₂S₂Si₂: C 60.09, H 8.40, N 2.60, S 5.94; Found: C 59.87, H 8.20, N 2.39, S 6.27.

3,6-Bis(5-bromo-2-thienyl)-2,5-bis(10-(tributylsilyl)decyl)-2,5-dihydro-pyrrolo[3,4-c]pyrrole-1,4-dione (SiC10-DPPBr): 1.36 g, yield: 60%. ¹H NMR (400 MHz, CDCl₃, δ): 8.61 (d, *J* = 4.0 Hz, 2H), 7.16 (d, *J* = 4.0 Hz, 2H), 3.90 (t, *J* = 7.2 Hz, 4H), 1.64-1.62 (m, 4H), 1.33-1.19 (m, 52H), 0.81 (t, *J* = 6.8 Hz, 18H), 0.43-0.39 (m, 16H); ¹³C NMR (100 MHz, CDCl₃, δ): 161.00, 138.98, 135.39, 131.65, 131.11, 119.18, 42.30, 33.97, 29.99, 29.56, 29.31, 29.23, 26.89, 26.22, 23.94, 13.85, 12.50, 12.21. Elemental Anal.

calcd. for $C_{58}H_{98}Br_2N_2O_2S_2Si_2$: C 61.35, H 8.70, N 2.47, S 5.65; Found: C 61.78, H 9.35, N 2.68, S 5.23.

General Synthetic procedure of SiCm (m = 3-8 and 10): SiCm-DPPBr (0.20 mmol), 2,5-bis(trimethylstannyl)thiophene (M1) (82.8 mg, 0.20 mmol), tris(dibenzylideneacetene)dipalladium(0) (1.8 mg, 1.00 mol%), tri(*o*-tolyl)phosphine (1.2 mg, 2.00 mol%) and anhydrous toluene (4.0 mL) were added to a Schlenk tube under argon. The mixture was stirred for a certain time at 95 °C in the absence of light. 2-Bromobenzene (0.5 mL) was then added as end-capper, and the reaction was stirred for another 12 h. After cooling to room temperature, the mixture was added dropwise to 200 mL methanol. The solid was collected and Soxhlet-extracted with ethanol, acetone, and hexane. Polymer was then obtained as a black solid after vacuum drying.

SiC3: polymerization time 0.6 h, weight 159 mg, yield 92%. Elemental Anal. calcd. for $(C_{48}H_{74}N_2O_2S_3Si_2)_n$: C 66.77, H 8.64, N 3.24, S 11.14; Found: C 67.17, H 8.95, N 3.45, S 10.49.

SiC4: polymerization time 2.5 h, weight 168 mg, yield 94%. Elemental Anal. calcd. for $(C_{50}H_{78}N_2O_2S_3Si_2)_n$: C 67.36, H 8.82, N 3.14, S 10.79; Found: C 67.21, H 8.73, N 2.98, S 11.02.

SiC5: polymerization time 2.3 h, weight 171 mg, yield 93%. Elemental Anal. calcd. for $(C_{52}H_{82}N_2O_2S_3Si_2)_n$: C 67.92, H 8.99, N 3.05, S 10.46; Found: C 68.51, H 8.56, N 3.11, S 10.51.

SiC6: polymerization time 2.0 h, weight 172 mg, yield 91%. Elemental Anal. calcd. for $(C_{54}H_{86}N_2O_2S_3Si_2)_n$: C 68.44, H 9.15, N 2.96, S 10.15; Found: C 69.24, H 9.47, N 3.16,

S 9.57.

SiC7: polymerization time 1.2 h, weight 172 mg, yield 89%. Elemental Anal. calcd. for $(C_{56}H_{90}N_2O_2S_3Si_2)_n$: C 68.94, H 9.30, N 2.87, S 9.86; Found: C 68.59, H 9.13, N 2.69, S 10.23.

SiC8: polymerization time 1.3 h, weight 183 mg, yield 91%. Elemental Anal. calcd. for $(C_{58}H_{94}N_2O_2S_3Si_2)_n$: C 69.40, H 9.44, N 2.79, S 9.58; Found: C 70.27, H 9.18, N 2.85, S 9.70.

SiC10: polymerization time 1.3 h, weight 184 mg, yield 87%. Elemental Anal. calcd. for $(C_{62}H_{102}N_2O_2S_3Si_2)_n$: C 70.26, H 9.70, N 2.64, S 9.07; Found: C 70.35, H 10.05, N 2.84, S 8.87.

S3. Fabrication and characterization of organic thin-film transistors (OTFTs)

Top gate/bottom contact OTFTs were fabricated on highly n-doped silicon wafers covered with a 300 nm thick thermally grown SiO₂ layer. The deionized water, acetone, and isopropanol were used to clean the substrates by an ultrasonic cleaner, and then the substrates were dried under a nitrogen flow. Au (about 30 nm) was vacuum-evaporated on the silicon substrates as source and drain electrodes with an interdigitated electrode pattern ($W/L = 70$, $W = 5.6$ mm, $L = 80$ μm). The interfaces were subsequently treated with UV-ozone for 1 min. The semiconductor layers were then deposited either by spin- or bar-coating. All the films were fabricated from *o*-xylene solutions (4.0 mg mL⁻¹) at 70 °C by spin-coating at 2000 rpm for 2 min or bar-coating with a substrate temperature of 90 °C and then annealed for 5 min at 120 °C. Afterwards, CYTOP (Asahi Glass, type CTL-809M) dielectric layer with a thickness of about 900 nm was spin-coated atop at

2000 rpm for 2 min and annealed at 100 °C for 40 min. Finally, Al was vacuum-evaporated as gate electrodes with a thickness of 80 nm. All the spin- and bar-coating processes were conducted in a glovebox and the devices were measured in ambient conditions with Keysight B1500A analyzer. Saturation and linear mobilities were calculated according to equations (1) and (2), respectively:

$$\mu_{sat}(V_G) = \frac{\partial I_{D,sat}}{\partial V_G} \cdot \frac{L}{WC_i} \cdot \frac{1}{(V_G - V_T)} \quad (1)$$

and

$$\mu_{lin} = \frac{\partial I_D}{\partial V_G} \cdot \frac{L}{WC_i V_D} \quad (2)$$

where μ is the field-effect mobility, I_D is the drain-source current, W/L is the channel width/length, C_i is the capacitance per unit area of the gate dielectric layer, V_G , V_D and V_T are the gate voltage, drain voltage and threshold voltage, respectively.

S4. Supplementary data

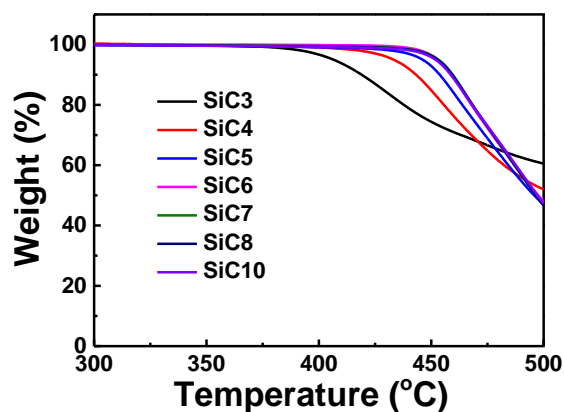


Figure S1. TGA curves of the polymers.

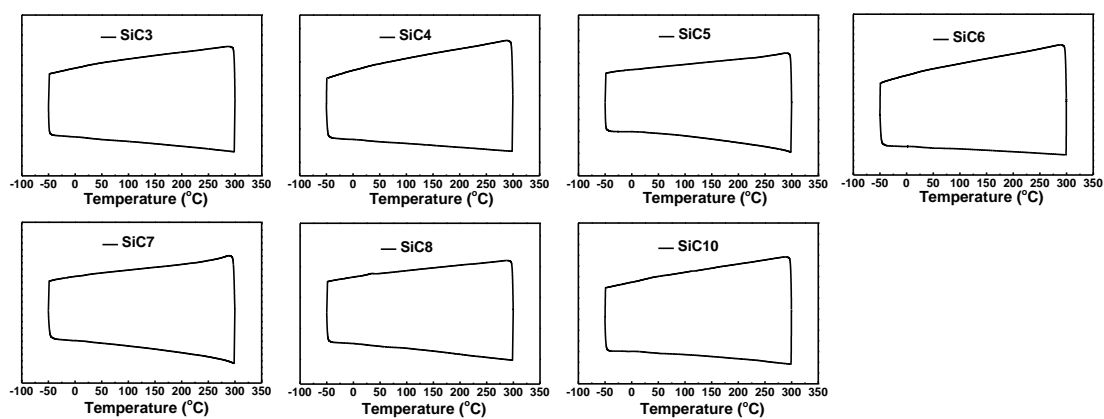


Figure S2. DSC curves of the polymers.

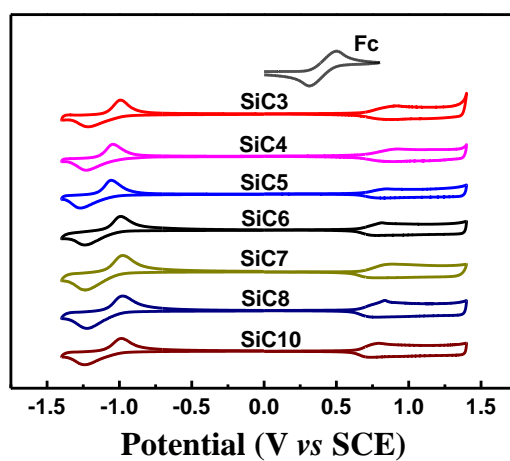


Figure S3. Film cyclic voltammograms of the polymers.

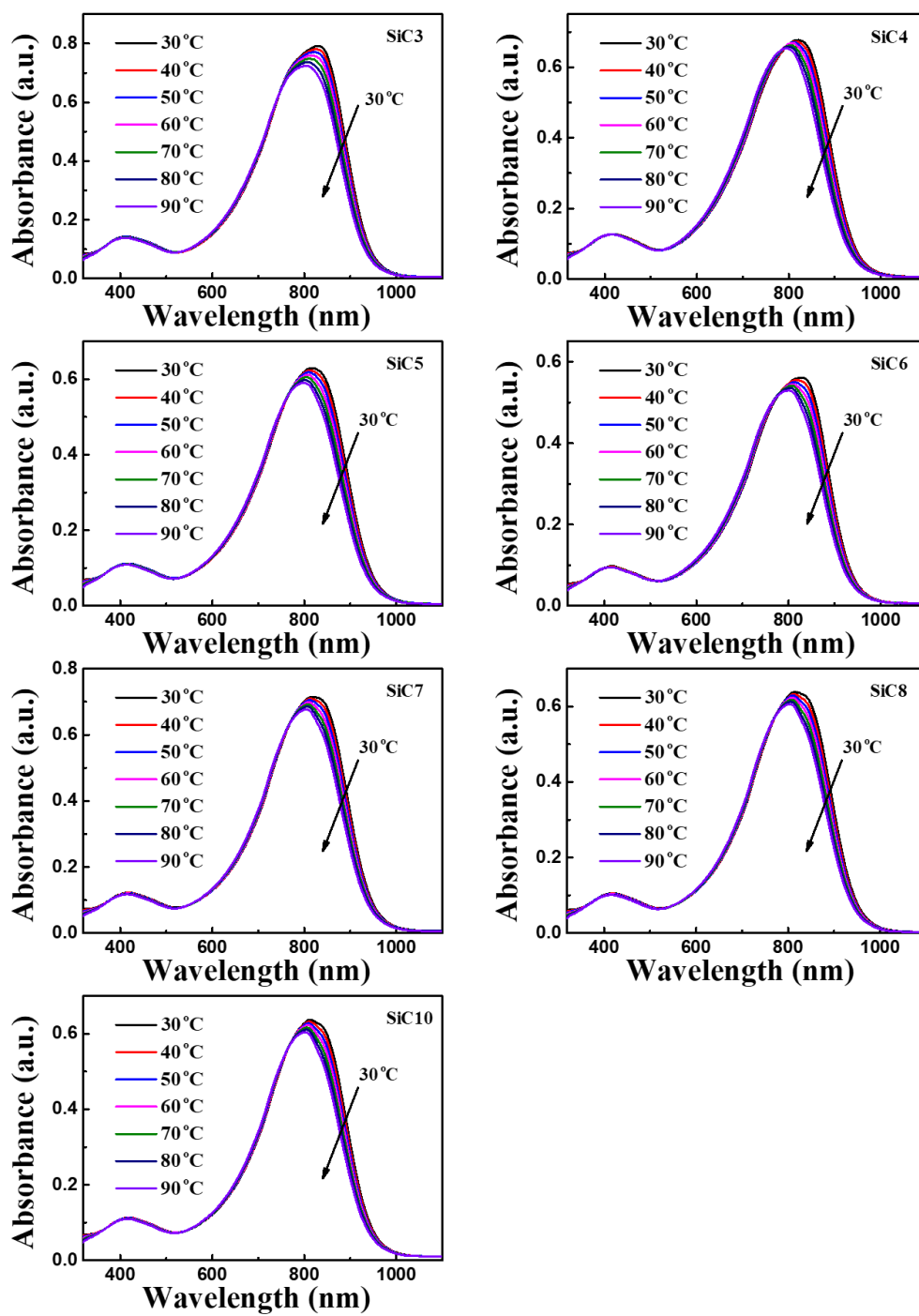


Figure S4. Temperature-dependent UV-vis-NIR absorption spectra of the polymers in solution (10^{-5} mol L $^{-1}$ in *o*-xylene).

Table S1. Summary of parameters characterized by GIXRD for the drop-cast polymer films from *o*-xylene solution.

Polymer		SiC3	SiC4	SiC5	SiC6	SiC7	SiC8	SiC10
q_{xy}	Lamellar stacking distance (d_{100}) [Å]	--	23.44	--	26.99	--	--	--
direction	L_c of Lamellar-stacking ($L_{c(100)}$) [Å] ^{a)}	--	131.10	--	123.65	--	--	--
	π - π stacking distance (d_{010}) [Å]	3.74	3.67	3.66	3.63	3.63	3.62	3.62
	L_c of π -stacking ($L_{c(010)}$) [Å]	25.56	39.43	49.00	58.06	52.71	49.15	48.22
q_z	Lamellar stacking distance (d_{100}) [Å]	19.50	21.41	22.81	24.12	25.10	25.77	27.45
direction	L_c of Lamellar-stacking ($L_{c(100)}$) [Å]	94.79	94.40	121.95	121.45	114.78	110.77	111.06
	π - π stacking distance (d_{010}) [Å]	--	3.60	3.62	3.60	--	--	--
	L_c of π -stacking ($L_{c(010)}$) [Å]	--	38.76	46.58	47.03	--	--	--

^{a)}The coherence length (L_c) was calculated according to $L_c = 2\pi \cdot 0.9 / \Delta q$, where Δq represents the full width at half-maximum of a diffraction peak.

Table S2. Summary of parameters characterized by GIXRD for the bar-coated polymer films from *o*-xylene solution in parallel direction.

Polymer		SiC3	SiC4	SiC5	SiC6	SiC7	SiC8	SiC10
q_z	Lamellar stacking distance (d_{100}) [Å]	19.41	21.55	22.69	23.98	25.04	25.63	27.66
direction	L_c of Lamellar-stacking ($L_{c(100)}$) [Å] ^{a)}	100.99	108.80	127.93	132.60	116.31	111.77	112.13

^{a)}The coherence length (L_c) was calculated according to $L_c = 2\pi \cdot 0.9 / \Delta q$, where Δq represents the full width at half-maximum of a diffraction peak.

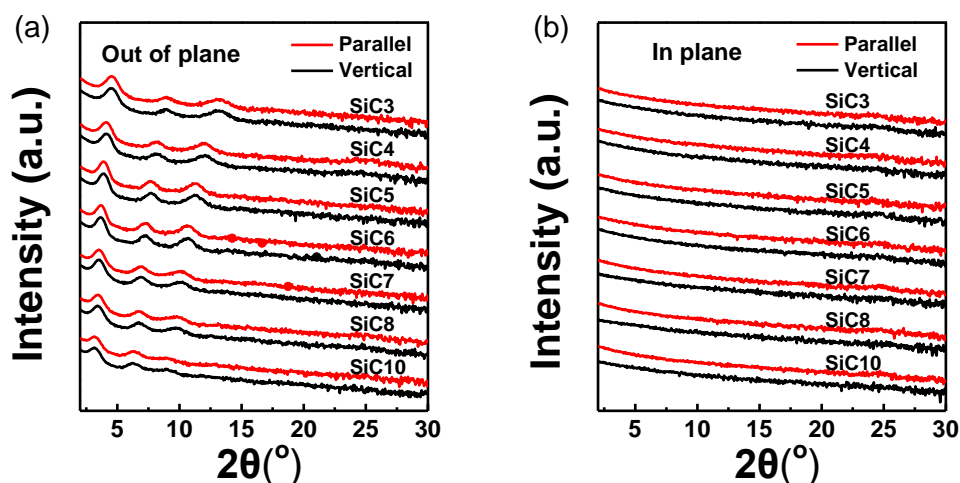


Figure S5. (a) Out-of-plane and (b) in-plane GIXRD profiles of the bar-coated polymer films from *o*-xylene solution.

Table S3. Device performance data of OTFTs based on spin-coated SiCm (m = 3-8 and 10) films processed from *o*-xylene solution.

Polymer	$\mu_{\text{sat,avg}} (\mu_{\text{sat,max}})^{\text{a}}$ [cm ² V ⁻¹ s ⁻¹]	$V_{\text{T}} [\text{V}]^{\text{b}}$	$I_{\text{on}}/I_{\text{off}}^{\text{c}}$	$\mu_{\text{lin,avg}} (\mu_{\text{lin,max}})^{\text{d}}$ [cm ² V ⁻¹ s ⁻¹]
SiC3	0.62±0.05 (0.70)	-3 to 0	10 ⁵ -10 ⁷	0.53±0.03 (0.59)
SiC4	0.73±0.04 (0.78)	-2 to 0	10 ⁵ -10 ⁷	0.59±0.01 (0.60)
SiC5	1.19±0.07 (1.29)	-5 to -2	10 ⁵ -10 ⁷	0.91±0.04 (0.97)
SiC6	1.41±0.09 (1.50)	-4 to 0	10 ⁵ -10 ⁷	1.02±0.04 (1.06)
SiC7	1.34±0.07 (1.45)	-5 to -2	10 ⁵ -10 ⁷	0.95±0.10 (1.12)
SiC8	1.26±0.07 (1.38)	-4 to -1	10 ⁵ -10 ⁶	0.89±0.05 (0.93)
SiC10	1.07±0.14 (1.30)	-6 to -3	10 ⁵ -10 ⁷	0.78±0.10 (0.88)

^a)Average and maximum (in brackets) saturation mobilities. ^b)Threshold voltage.

^c)Current on/off ratio. ^d)Average and maximum (in brackets) linear mobilities.

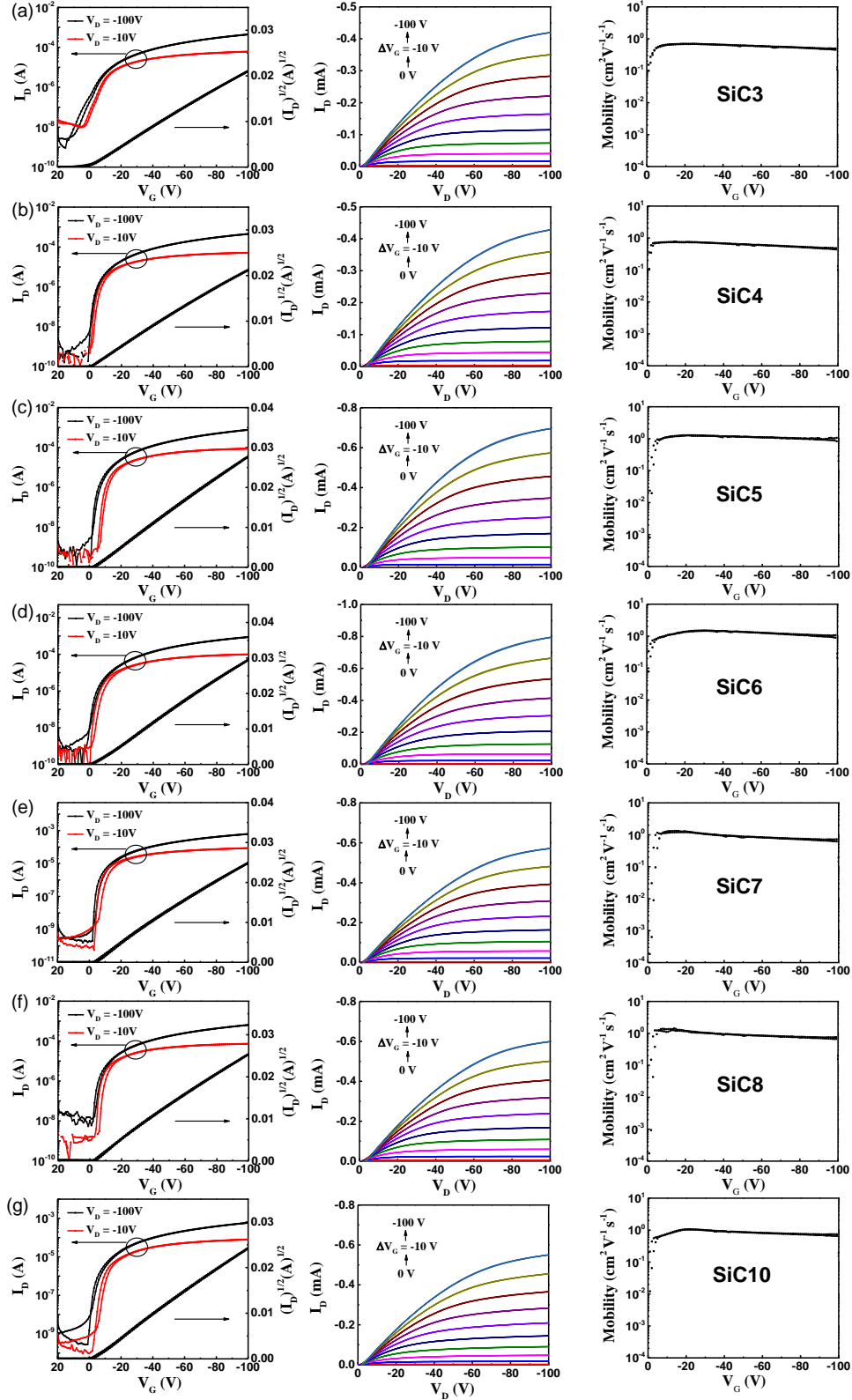


Figure S6. (left) The typical transfer and (middle) output characteristics, and (right) saturation mobility versus V_G of SiC m -based ($m = 3-8$ and 10) OTFTs spin-coated from *o*-xylene solution.

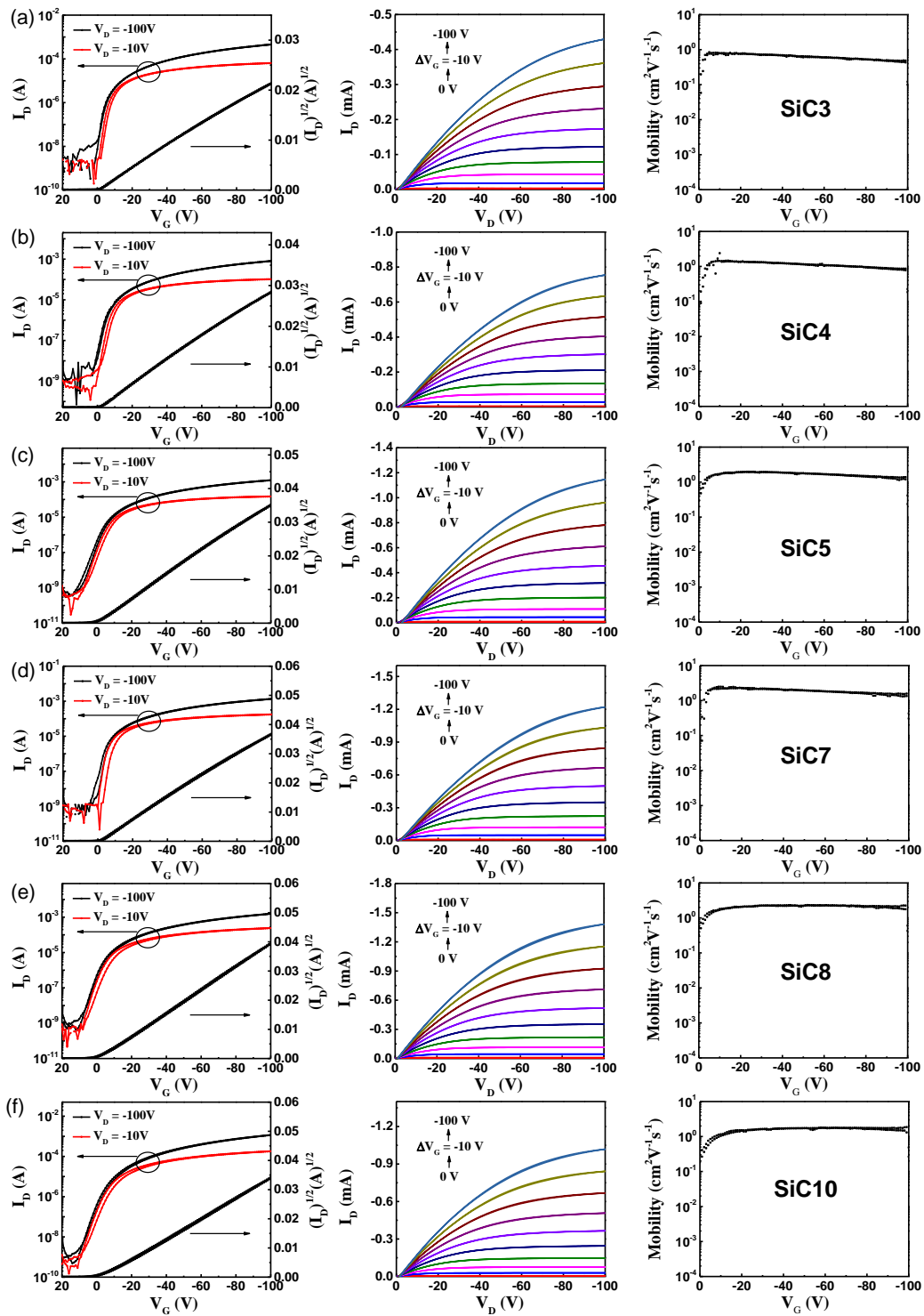


Figure S7. (left) The typical transfer and (middle) output characteristics, and (right) saturation mobility versus V_G of SiC m -based ($m = 3-5, 7, 8, 10$) OTFTs bar-coated from *o*-xylene solution in parallel direction.

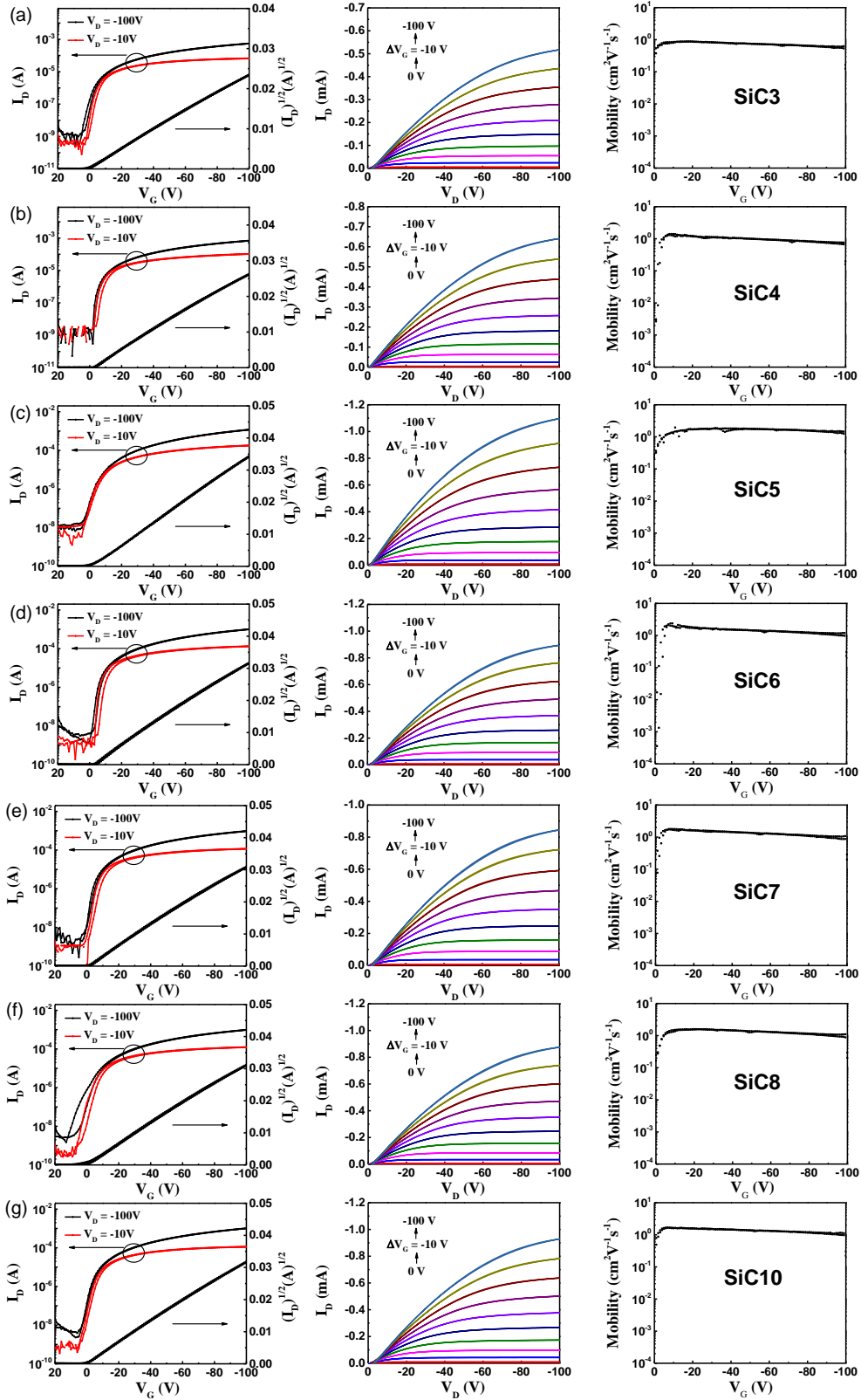


Figure S8. (left) The typical transfer and (middle) output characteristics, and (right) saturation mobility versus V_G of SiC m -based ($m = 3-8$ and 10) OTFTs bar-coated from *o*-xylene solution in vertical direction.

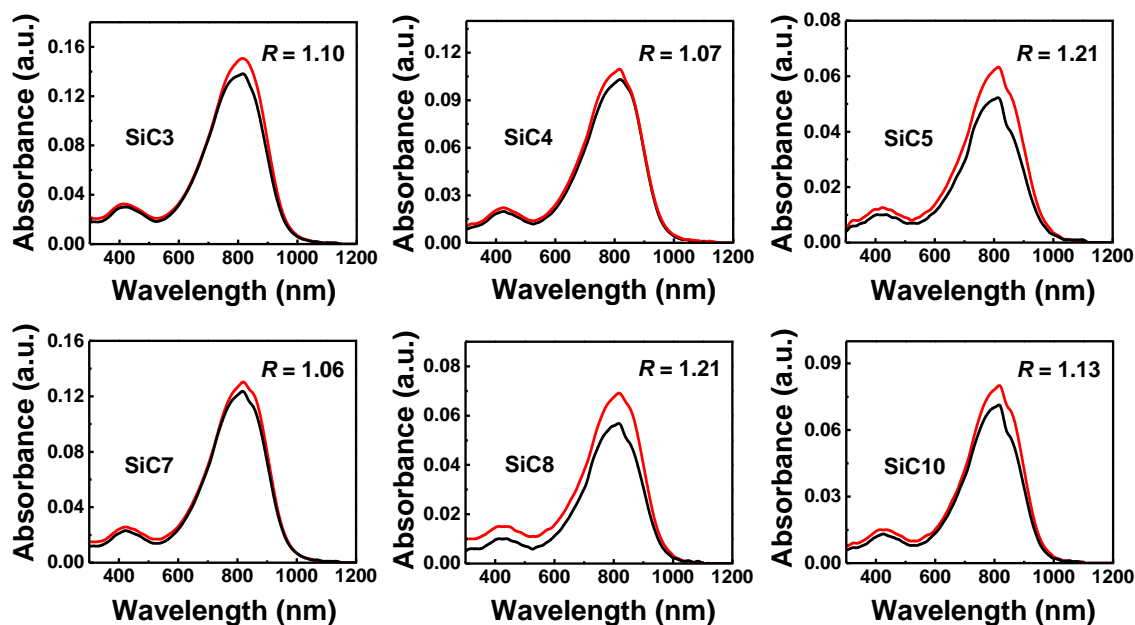


Figure S9. Polarized optical absorption of bar-coated polymer films from *o*-xylene solution with red line in parallel direction and black line in vertical direction.

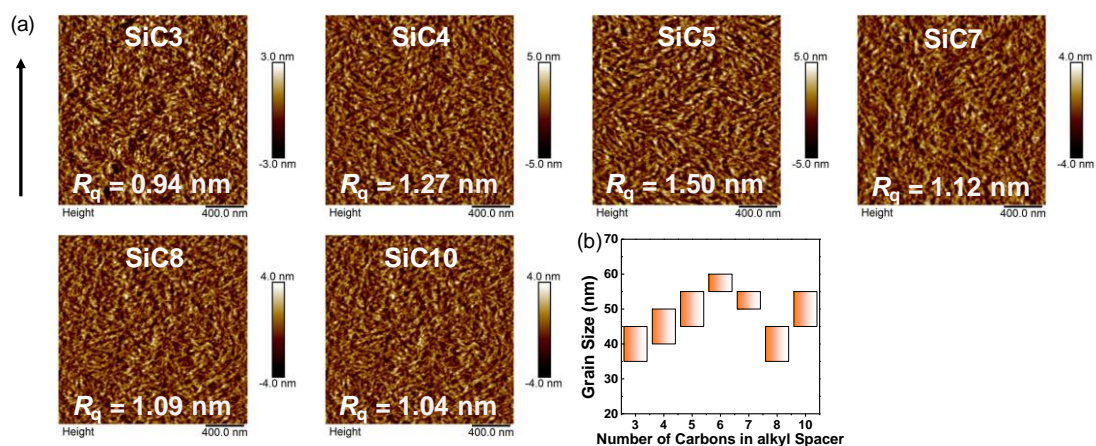


Figure S10. (a) AFM topography images ($2\ \mu\text{m} \times 2\ \mu\text{m}$) of bar-coated SiC $_m$ ($m = 3-8$ and 10) films from *o*-xylene solution (the arrow indicates coating direction) and (b) the corresponding grain size of SiC $_m$ as a function of the number of carbons (m) in alkyl spacer.

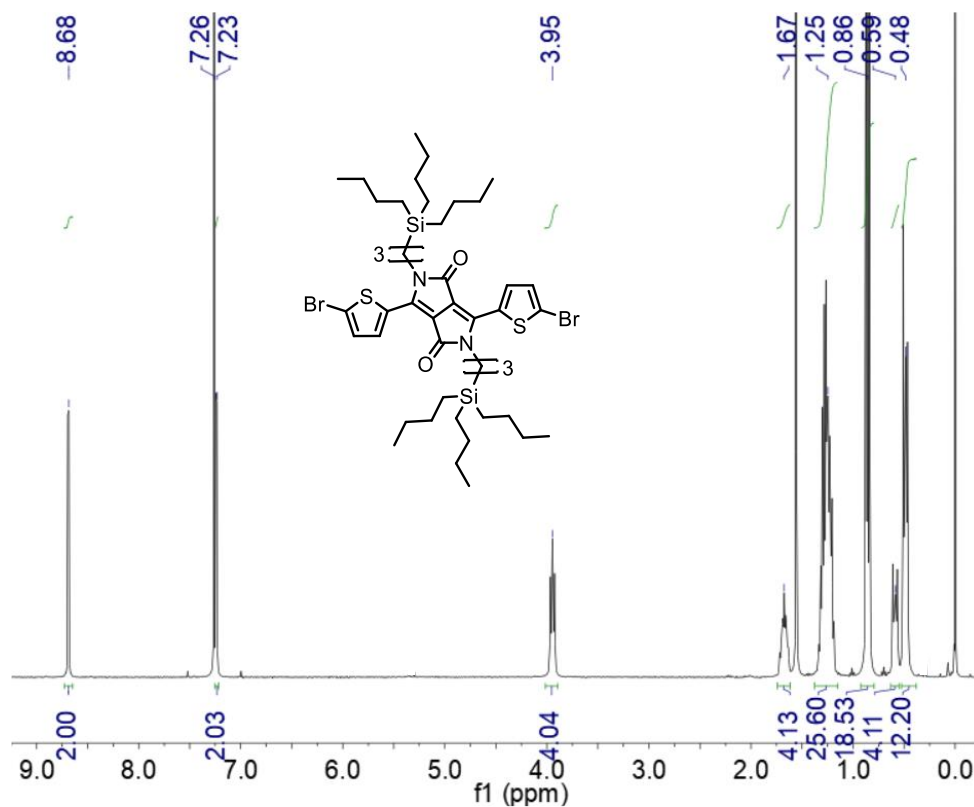


Figure S11. ^1H NMR spectrum (400 MHz, CDCl_3 , 25 °C) of SiC3-DPPBr.

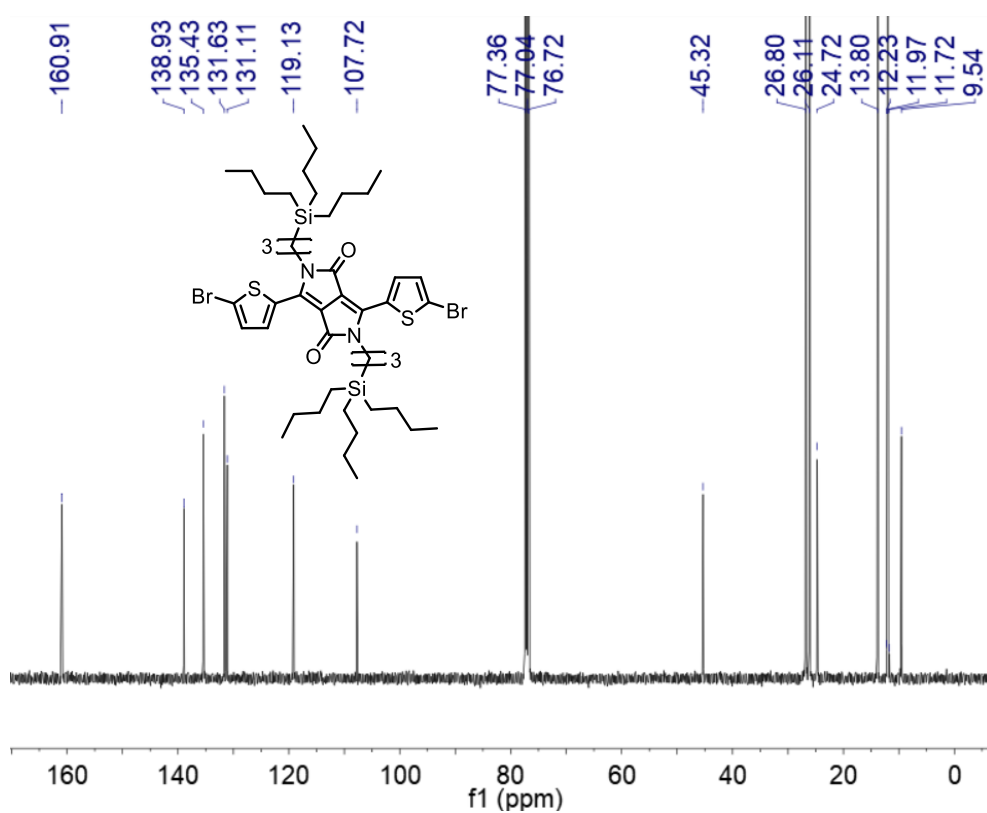


Figure S12. ^{13}C NMR spectrum (100 MHz, CDCl_3 , 25 °C) of SiC3-DPPBr.

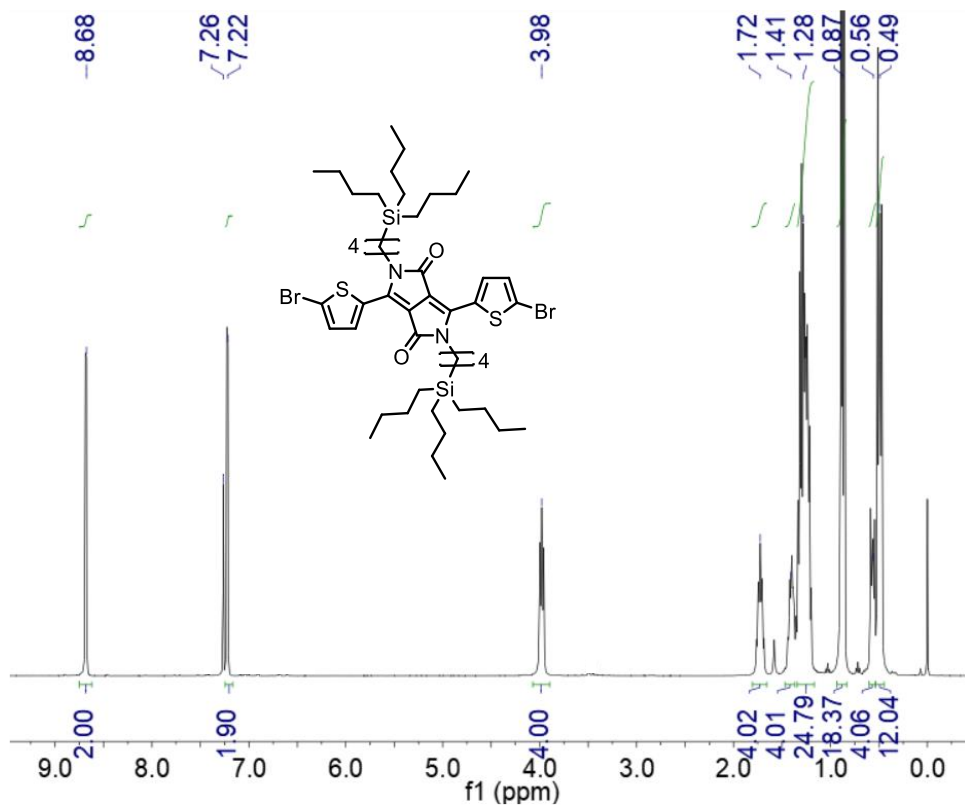


Figure S13. ^1H NMR spectrum (400 MHz, CDCl_3 , 25 °C) of SiC4-DPPBr.

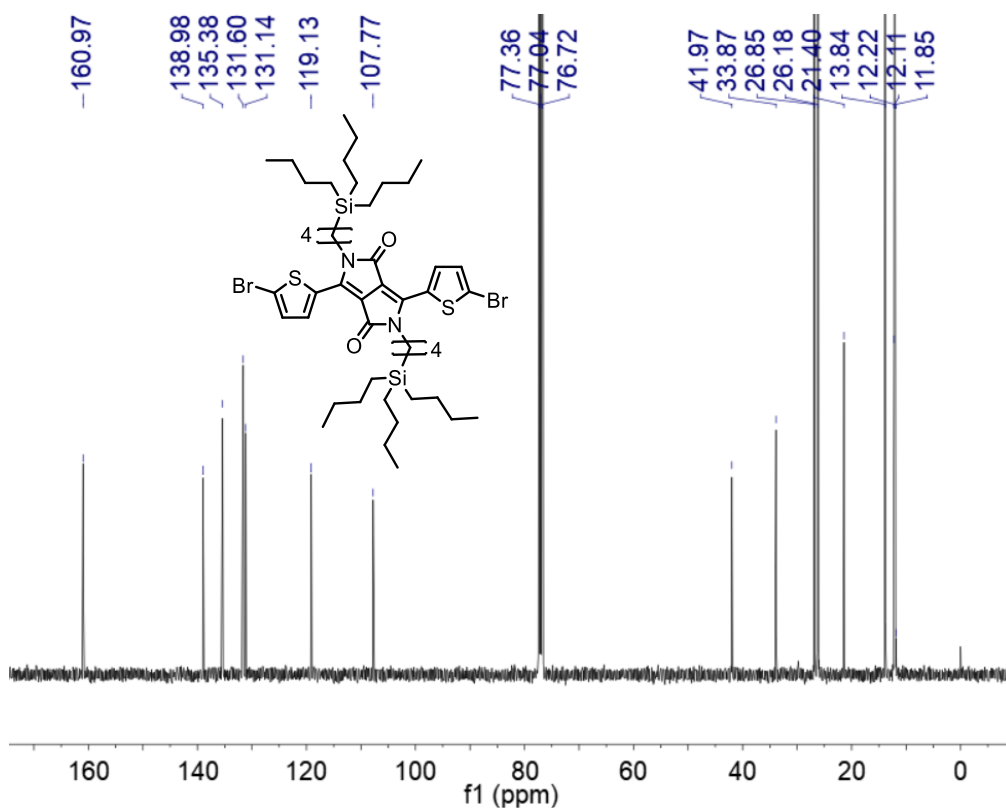


Figure S14. ^{13}C NMR spectrum (100 MHz, CDCl_3 , 25 °C) of SiC4-DPPBr.

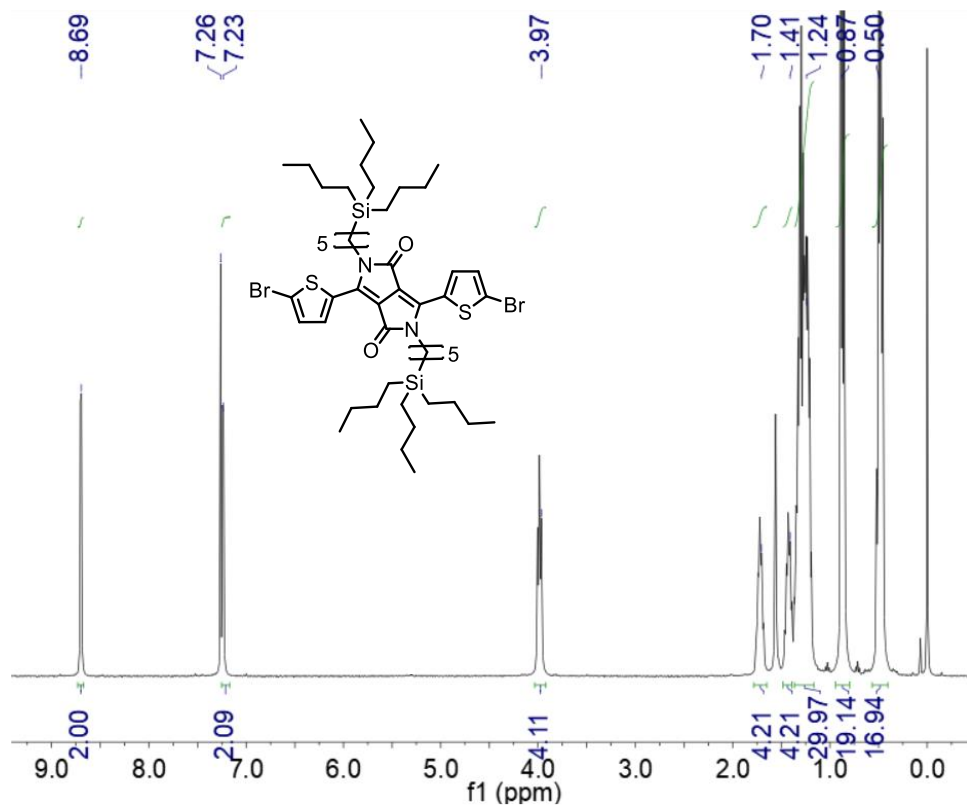


Figure S15. ^1H NMR spectrum (400 MHz, CDCl_3 , 25 °C) of SiC5-DPPBr.

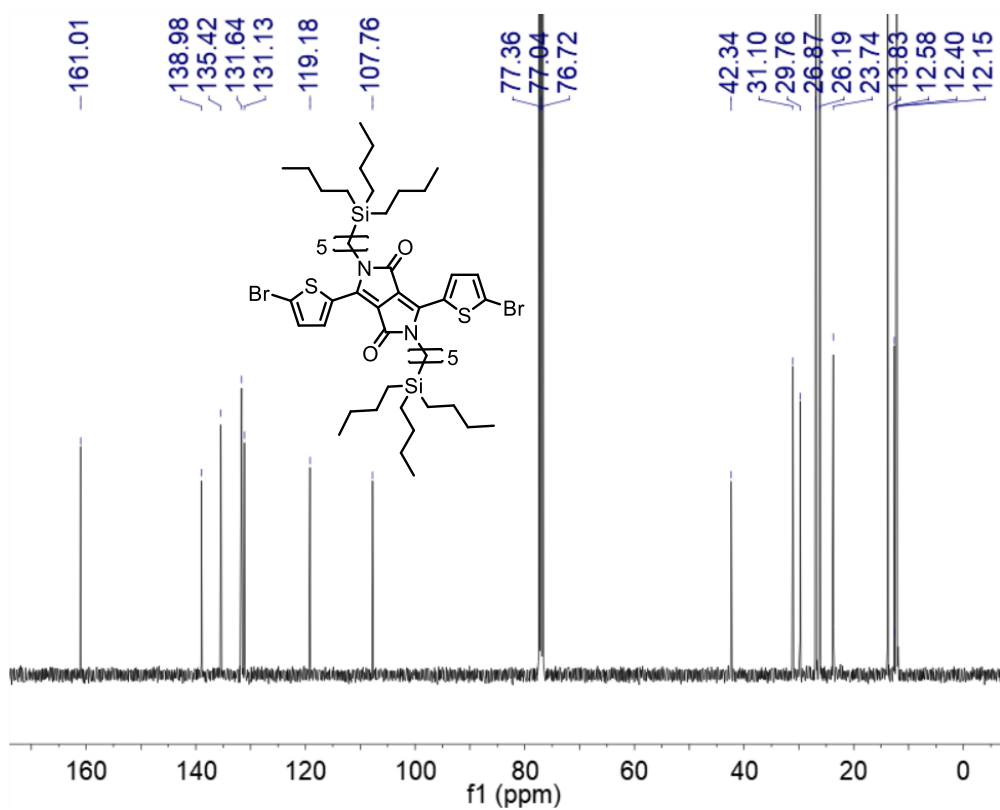


Figure S16. ^{13}C NMR spectrum (100 MHz, CDCl_3 , 25 °C) of SiC5-DPPBr.

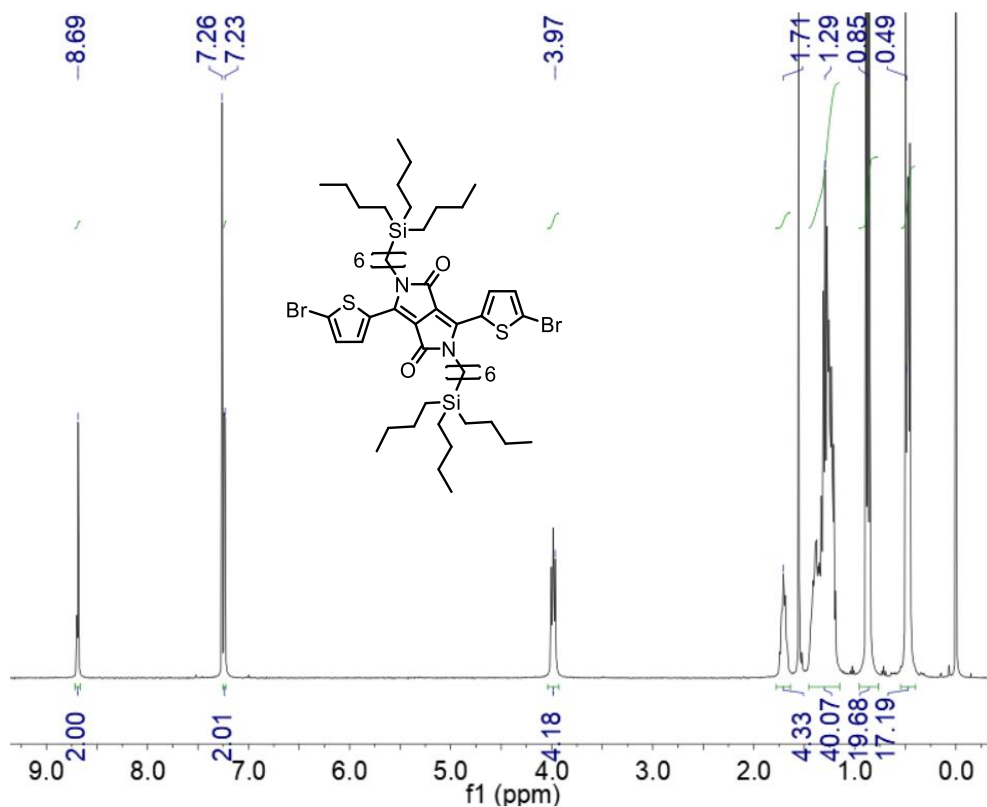


Figure S17. ^1H NMR spectrum (400 MHz, CDCl_3 , 25 °C) of SiC6-DPPBr.

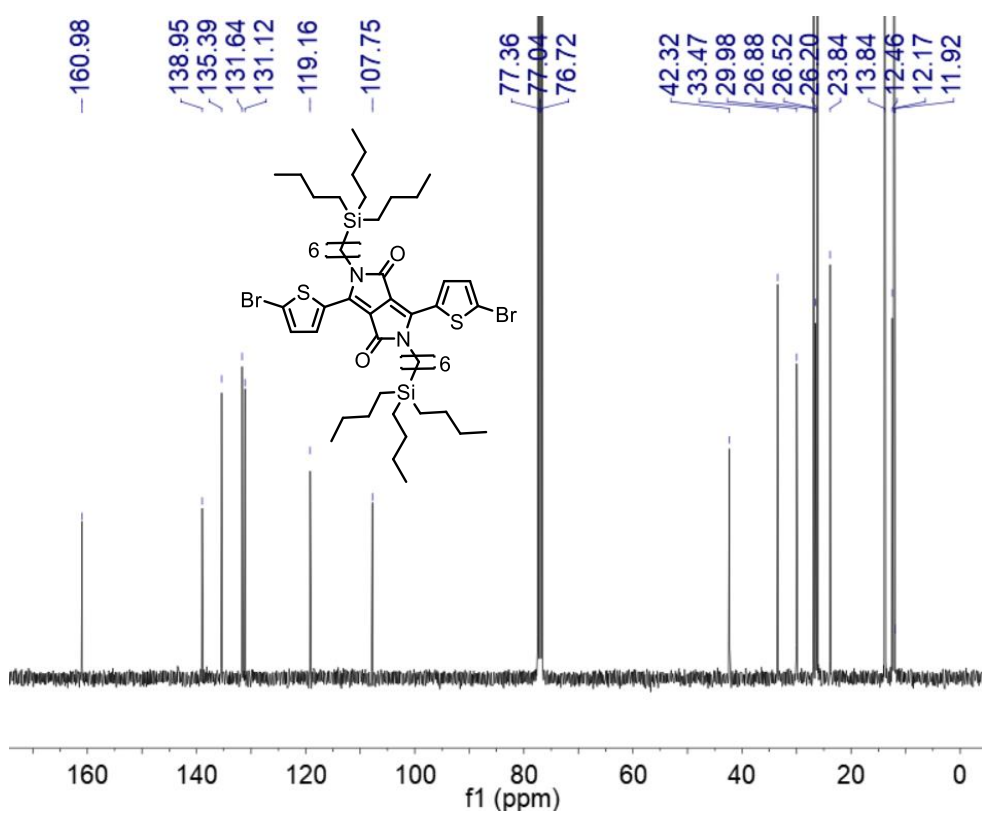


Figure S18. ^{13}C NMR spectrum (100 MHz, CDCl_3 , 25 °C) of SiC6-DPPBr.

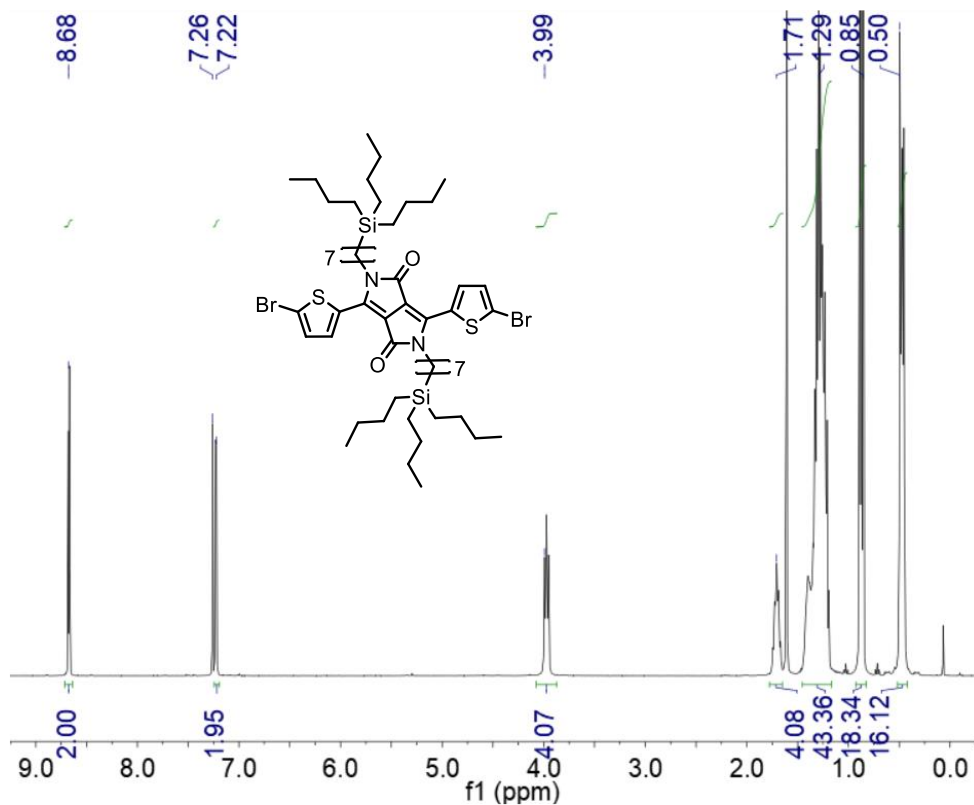


Figure S19. ^1H NMR spectrum (400 MHz, CDCl_3 , 25 °C) of SiC7-DPPBr.

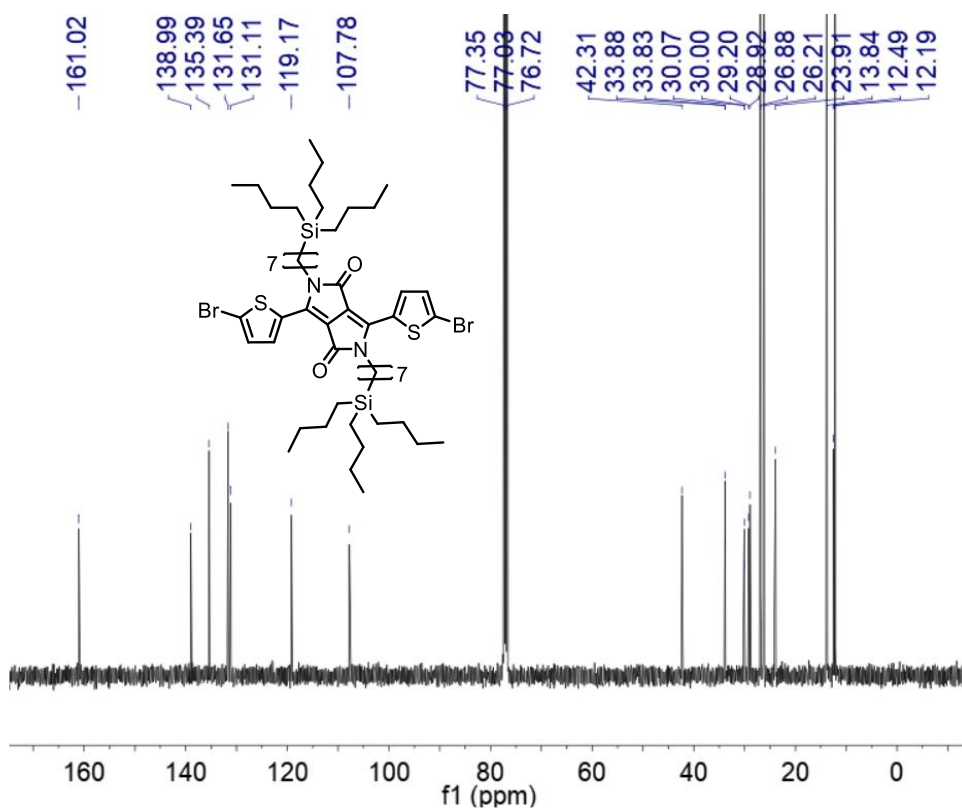


Figure S20. ^{13}C NMR spectrum (100 MHz, CDCl_3 , 25 °C) of SiC7-DPPBr.

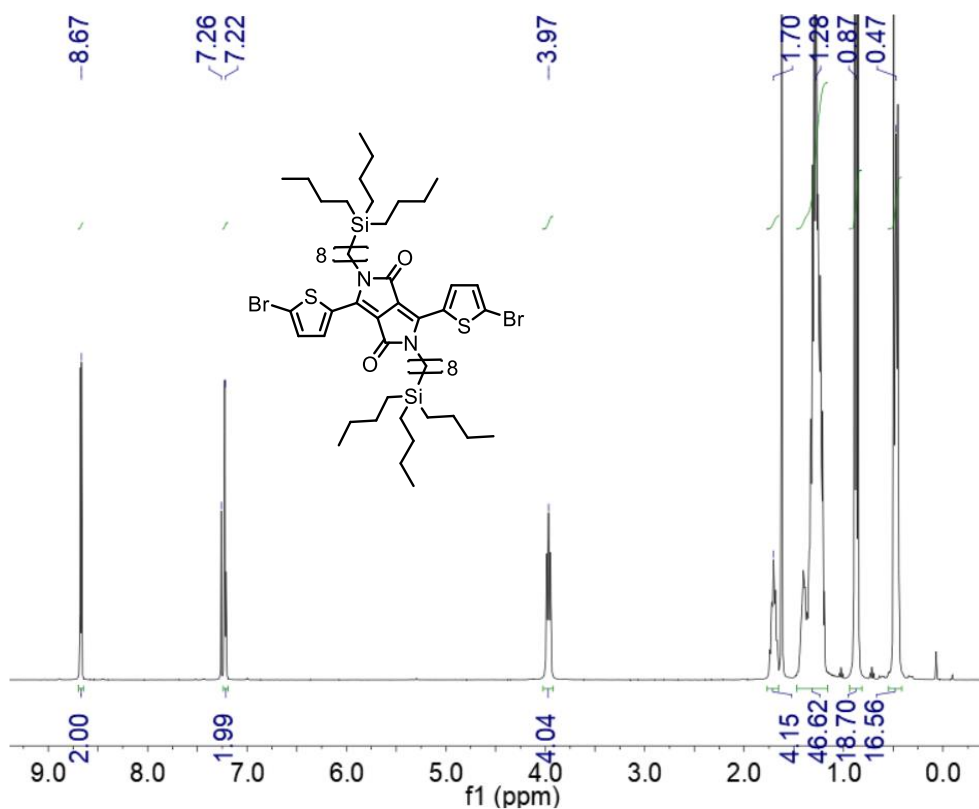


Figure S21. ^1H NMR spectrum (400 MHz, CDCl_3 , 25 °C) of SiC8-DPPBr.

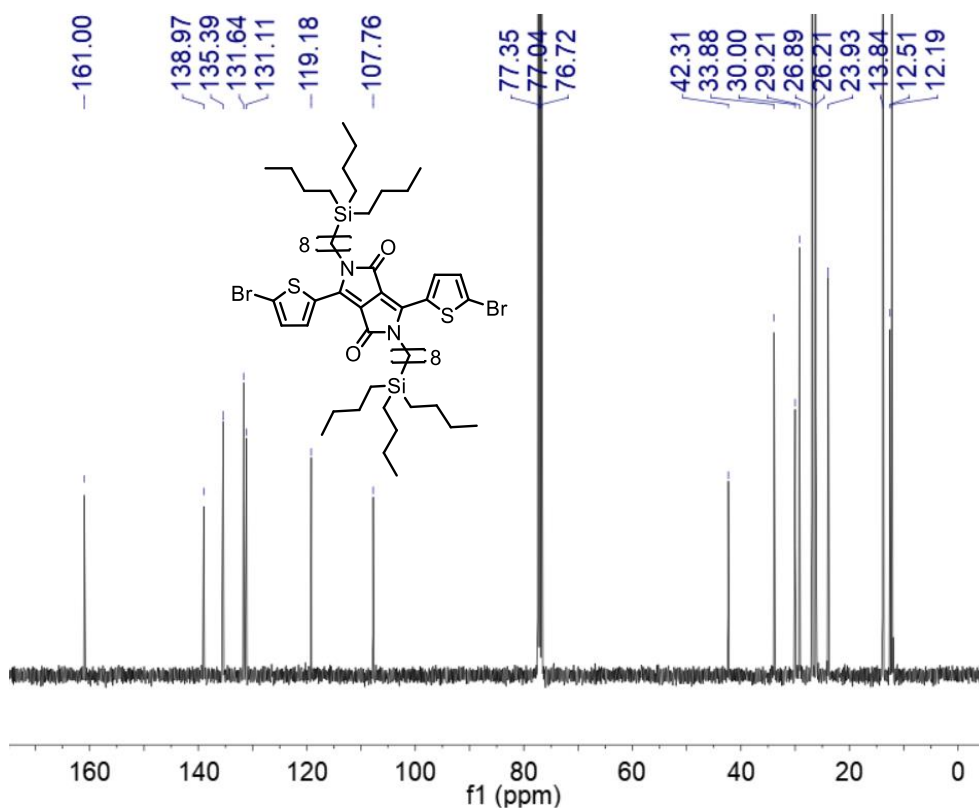


Figure S22. ^{13}C NMR spectrum (100 MHz, CDCl_3 , 25 °C) of SiC8-DPPBr.

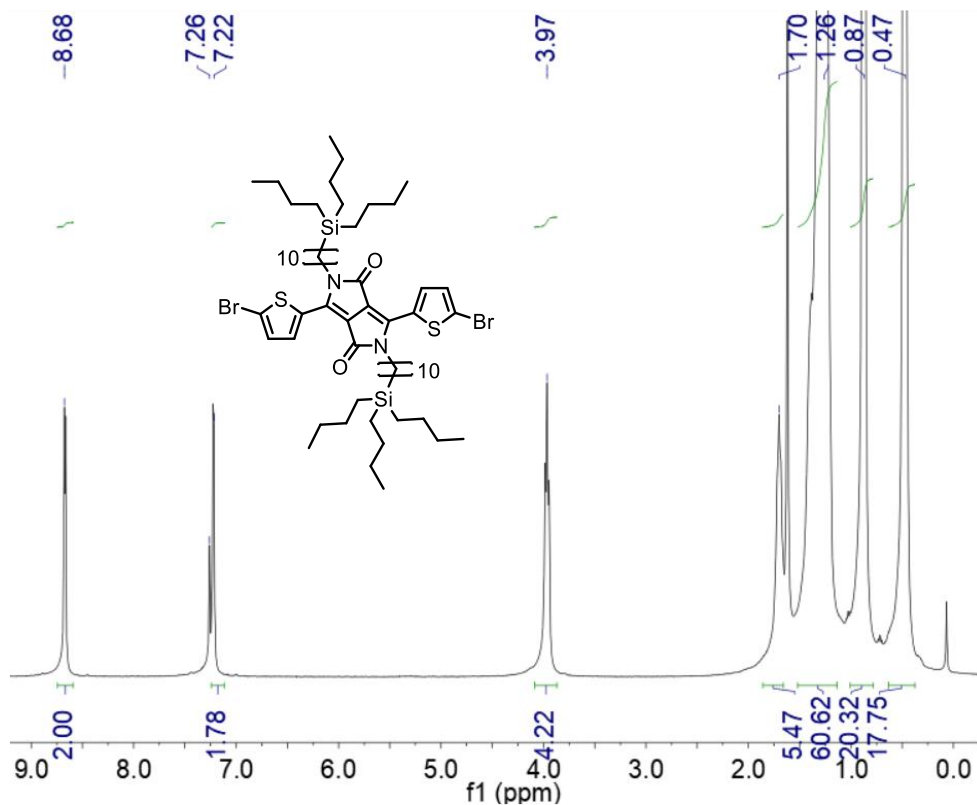


Figure S23. ^1H NMR spectrum (400 MHz, CDCl_3 , 25 °C) of SiC10-DPPBr.

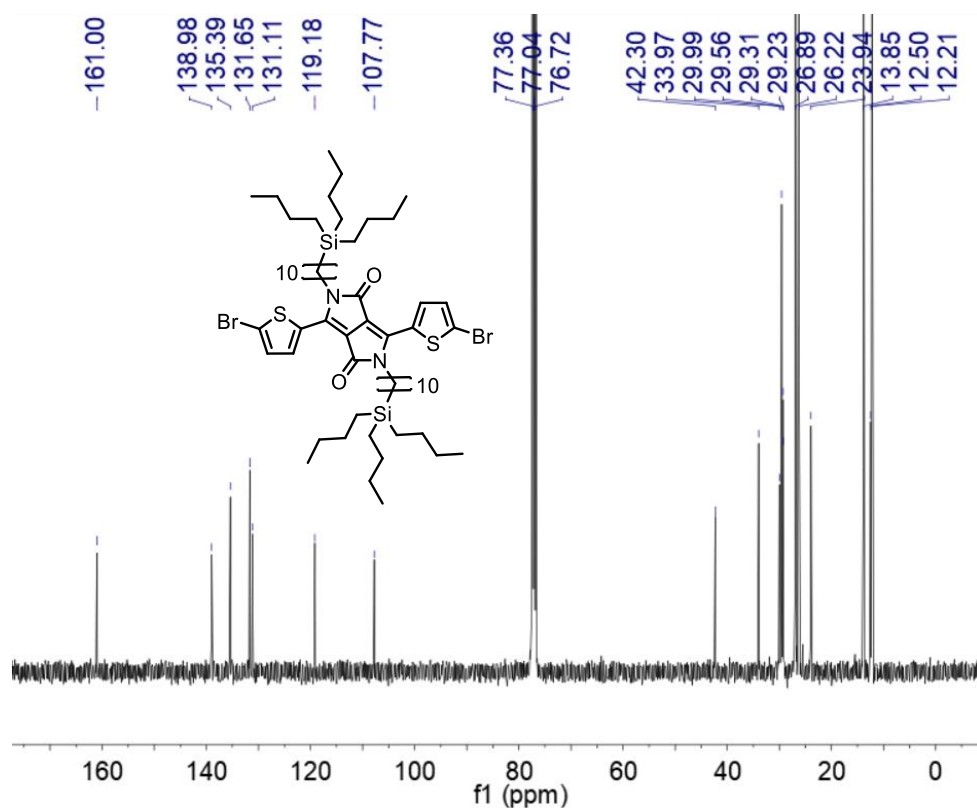


Figure S24. ^{13}C NMR spectrum (100 MHz, CDCl_3 , 25 °C) of SiC10-DPPBr.

S5. References

1. Y. Li, P. Sonar, S. P. Singh, W. Zeng and M. S. Soh, *J. Mater. Chem.*, 2011, **21**, 10829-10835.
2. G. Conboy, R. G. D. Taylor, N. J. Findlay, A. L. Kanibolotsky, A. R. Inigo, S. S. Ghosh, B. Ebenhoch, L. Krishnan Jagadamma, G. K. V. V. Thalluri, M. T. Sajjad, I. D. W. Samuel and P. J. Skabara, *J. Mater. Chem. C*, 2017, **5**, 11927-11936.