Supporting Information

Columnar hexa-*peri*-hexabenzocoronene-diketopyrrolopyrrole organic dyes

Wallace W. H. Wong,[†] Jegadesan Subbiah,[†] Sreenivasa R. Puniredd,[§] Balaji Purushothaman,[†] Wojciech Pisula,[§] Klaus Müllen,[§] David J. Jones,[†] and Andrew B. Holmes[†]*

School of Chemistry, Bio21 Institute, University of Melbourne, 30 Flemington Road,
Parkville, Victoria 3010, Australia and Max Planck Institute for Polymer Research,
Ackermannweg 10, D-55128 Mainz, Germany.

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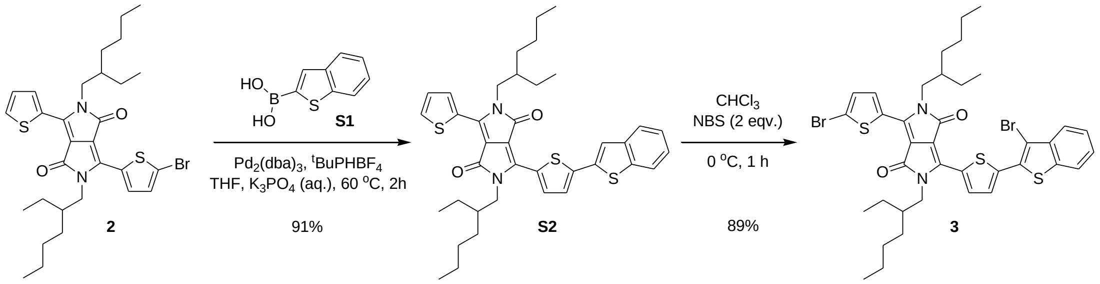
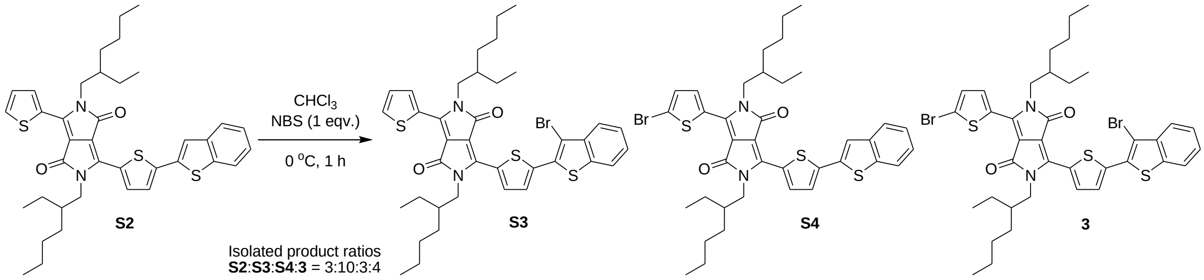
Experimental Procedures

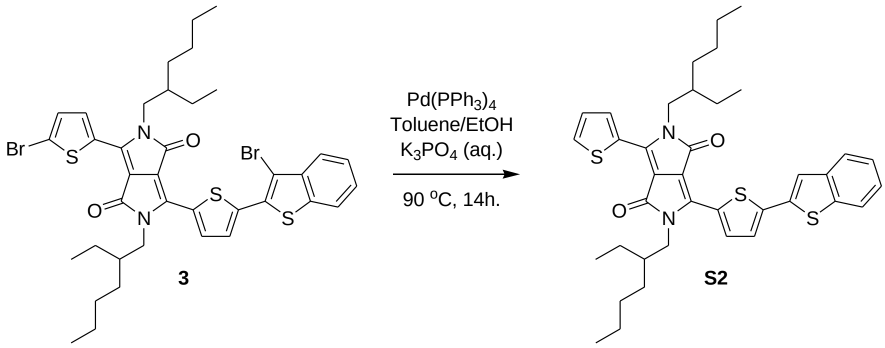
All reactions were performed using anhydrous solvent under an inert atmosphere unless stated otherwise. Silica gel (Merck 9385 Kieselgel 60) was used for flash chromatography. Thin layer chromatography was performed on Merck Kieselgel 60 silica gel on glass (0.25 mm thick). ^{1}H and ^{13}C NMR spectroscopy were carried out using either the Varian Inova-400 (400 MHz) or the Varian Inova-500 (500 MHz). Electrospray (ESI) high resolution mass spectra (HRMS) were recorded with a Thermo-Finnigan 7T LTQ-FTMS spectrometer and matrix-assisted laser desorption/ionization time-of-flight (MALDI-TOF) mass spectra were recorded on a Bruker Reflex 2 (DCTB as matrix). IR spectra were obtained on a Perkin Elmer Spectrum One FT-IR spectrometer while UV-vis spectra were recorded using a Cary 50 UV-vis spectrometer. Photoluminescence was measured with a Varian Cary Eclipse fluorimeter. Melting points were determined on a Büchi 510 melting point apparatus. Elemental analyses were obtained commercially through Chemical & Analytical Services Pty. Ltd. (Australia) an Exeter Analytical CE–440 elemental analyzer. Thermal gravimetric analysis (TGA) experiments were carried out with a Mettler Toledo TGA/SDTA851e and differential scanning calorimetry (DSC) experiments were performed on a Perkin-Elmer Sapphire DSC. Electrochemical measurements were recorded on a Solartron 1287A Potentiostat/Galvanostat. Compound **1** has been reported in the literature.[1] Diketopyrrolopyrrole (DPP) dye precursor **2** was purchased from Luminescence Technology Corporation, Taiwan. All other compounds and reagents are widely available commercially.



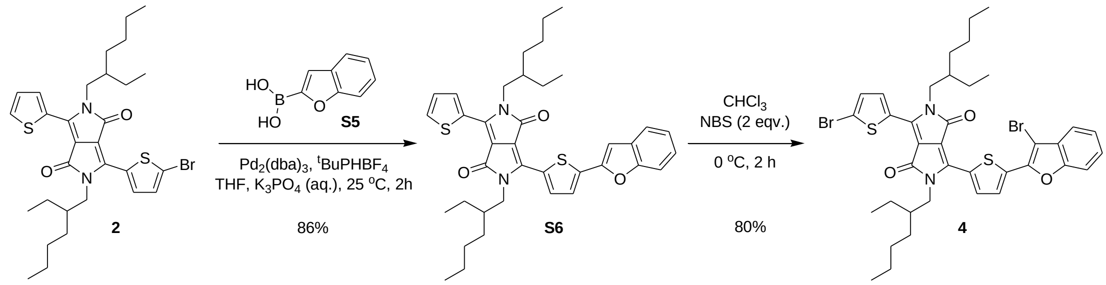
Scheme S1. Synthesis of DPP dye precursor **3** from commercially available compound **2**.



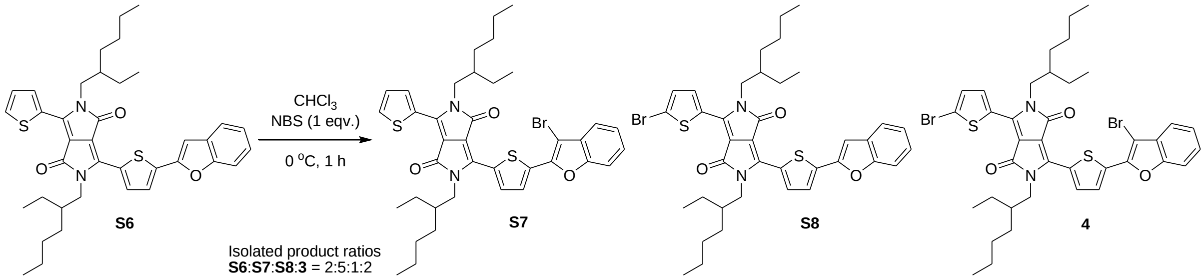
Scheme S2. Bromination of compound **S2** with 1 equivalent of *N*-bromosuccinimide giving a mixture of brominated products.



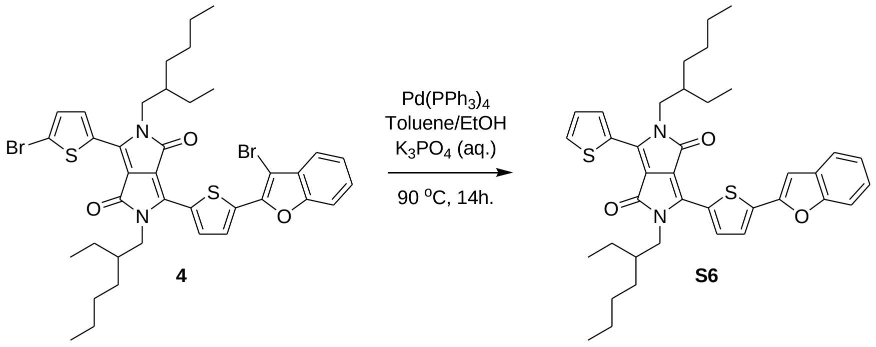
Scheme S3. Palladium-catalysed de-bromination of dibromo compound **3** to compound **S2** with ethanol as the hydrogen source.



Scheme S4. Synthesis of DPP dye precursor **4** from commercially available compound **2**.



Scheme S5. Bromination of compound **S6** with 1 equivalent of *N*-bromosuccinimide giving a mixture of brominated products.



Scheme S6. Palladium-catalysed de-bromination of dibromo compound **4** to compound **S6** with ethanol as the hydrogen source.

3-(5-Benzothienylthiophen-2-yl)-2,5-bis(2-ethylhexyl)-6-(thiophen-2-yl)pyrrolo[3,4-c]pyrrole-1,4(2H,5H)-dione (Compound S2)

3-(5-Bromothiophen-2-yl)-2,5-bis(2-ethylhexyl)-6-(thiophen-2-yl)pyrrolo[3,4-c]pyrrole-1,4(2H,5H)-dione **2** (604 mg, 1 mmol) and 2-benzothiopheneboronic acid **S1** (180 mg, 1 mmol) was dissolved in THF (25 mL) and potassium phosphate tribasic (2 M aq., 5 mL) was added. The mixture was degassed by bubbling nitrogen gas for 15 min and $Pd_2(dba)_3$ (50 mg, 0.05 mmol) and tri-tert-butylphosphonium tetrafluoroborate (50 mg, 0.17 mmol) was added. The reaction was heated at 60 °C for 2 h and cooled to 25 °C. The product was extracted with toluene, washed with water and the organic extract was dried with $MgSO_4$. After solvent removal, the residue was purified by column chromatography (SiO_2, toluene, R_f 0.4) and a dark amorphous solid (600 mg, 91% yield) was collected by filtration after precipitation from methanol.

m.p. 100-105 °C. ^{1}H NMR (500 MHz, $CDCl_3$, 20 °C, δ): 0.88 (m, 12H, $-CH_3$), 1.2-1.3 (m, 16H, $-CH_2-$), 1.88 (m, 2H, -CH-), 4.04 (m, 4H, $-CH_2N-$), 7.27 (m, 1H, Ar-H), 7.36 (m, 2H, ArH), 7.42 (d, *J* 4 Hz, 1H, Ar-H), 7.54 (s, 1H, Ar-H), 7.63 (m, 1H, Ar-H), 7.79 (d, *J* 7.5 Hz, 2H, Ar-H), 8.91 (d, *J* 4 Hz, 1H,Ar-H), 8.93 (d, *J* 4 Hz, 1H, Ar-H). ^{13}C NMR (125 MHz, $CDCl_3$, 20 °C, δ): 10.5, 10.6, 14.0, 14.1, 23.1 (2), 23.6, 23.7, 28.4, 28.6, 29.7, 30.2 (2), 30.4 (2), 39.1, 39.2, 45.9 (2), 108.1, 108.5, 121.3, 122.2, 123.8, 125.0, 125.2, 125.3, 126.0, 128.2, 128.4 (2), 129.0, 129.2, 129.9, 130.6, 135.2, 135.3, 135.8, 136.4, 139.6, 140.1, 140.3, 142.4, 161.6, 161.7 (2). FT-IR (neat, cm^{-1}): 2958, 2929, 2858, 1664 (C=O), 1557, 1457, 1403, 1231, 1101, 857, 811, 735. HRMS-ESI (*m/z*), calcd. for $C_{38}H_{44}N_2O_2S_3$: M^+ 656.25594, found 656.25591. Elemental analysis: calcd. for $C_{38}H_{44}N_2O_2S_3$, C 69.47, H 6.75, N 4.26; found C 69.54, H 6.83, N 4.24.

3-(5-(3-Bromobenzothienyl)thiophen-2-yl)-2,5-bis(2-ethylhexyl)-6-(5-bromothiophen-2-yl)pyrrolo[3,4-c]pyrrole-1,4(2H,5H)-dione (Compound 3)

Compound **S2** (500 mg, 0.76 mmol) was dissolved in chloroform (25 mL) and cooled to 0 °C. *N*-Bromosuccinimide (280 mg, 1.57 mmol) was added and the reaction was stirred for 1 h at 0 °C. Water was added to the reaction and the product was extracted with chloroform and the organic extract was dried with $MgSO_4$. After solvent removal, the residue was purified by column chromatography (SiO_2, toluene, R_f 0.5) and a dark amorphous solid (500 mg, 89% yield) was collected by filtration after precipitation from methanol.

m.p. 125-130 °C. ^{1}H NMR (500 MHz, $CDCl_3$, 20 °C, δ): 0.89 (m, 12H, $-CH_3$), 1.2-1.3 (m, 16H, $-CH_2-$), 1.85 (m, 2H, -CH-), 3.9-4.1 (m, 4H, $-CH_2N-$), 7.20 (d, *J* 4 Hz, 1H, Ar-H), 7.40 (t, *J* 7Hz, 1H, ArH), 7.46 (t, *J* 7Hz, 1H, ArH), 7.67 (d, *J* 4 Hz, 1H, Ar-H), 7.75 (d, *J* 8 Hz, 1H, Ar-H), 7.82 (d, *J* 8 Hz, 1H, Ar-H), 8.66 (d, *J* 4 Hz, 1H,Ar-H), 9.07 (d, *J* 4 Hz, 1H, Ar-H). ^{13}C NMR (125 MHz, $CDCl_3$, 20 °C, δ): 10.5 (2), 14.0, 14.1, 23.0, 23.2, 23.6 (2), 28.3 (2), 28.5, 30.2, 30.3 (2), 39.1, 39.5, 46.0, 46.2, 106.6, 108.4, 108.5, 118.8, 122.0, 123.8, 125.7, 126.5, 128.8, 130.5, 131.2, 131.3, 131.4, 135.3, 135.9, 137.0, 138.9, 139.2, 139.9, 140.1, 161.4, 161.5. FT-IR (neat, cm^{-1}): 2959, 2931, 2859, 1665 (C=O), 1554, 1400, 1229, 1105, 808, 748. HRMS-ESI (*m/z*), calcd. for $C_{38}H_{42}Br_2N_2O_2S_3$: M$^+$ 812.07697, found 812.07784. Elemental analysis: calcd. for $C_{38}H_{42}Br_2N_2O_2S_3$, C 56.02, H 5.20, N 3.44; found C 57.41, H 5.59, N 3.22.

Bromination experiment for compound S2 (Scheme S2)

N-Bromosuccinimide (1 eqv., 54 mg, 0.3 mmol) was added to a solution of compound **S2** (200 mg, 0.3 mmol) in chloroform (10 mL) at 0 °C. The reaction was stirred at 0 °C for 1 h and the solvent was removed. Thin layer chromatography analysis of the reaction mixture revealed a mixture of brominated products including starting material **S2**, two mono-brominated products **S3** and **S4**, and dibromo product **3**. The compounds were separated by column chromatography (SiO_2, toluene) and each compound isolated (**S2**, 20 mg, R_f = 0.3; **S3**, 60 mg, R_f = 0.35; **S4**, 20 mg, R_f = 0.45; **3**, 30 mg, R_f = 0.5).

Characterisation for compound **S3**: ^{1}H NMR (400 MHz, $CDCl_3$, 20 °C, δ): 0.87 (m, 12H, $-CH_3$), 1.27-1.37 (m, 16H, $-CH_2-$), 1.87-1.96 (m, 2H, -CH-), 4.05 (m, 4H, $-CH_2N-$), 7.27 (t, *J* 4 Hz, 1H, ArH), 7.41 (t, *J* 8 Hz, 1H, ArH), 7.47 (t, *J* 8 Hz, 1H, ArH), 7.63 (d, *J* 4 Hz, 1H, ArH), 7.69 (d, *J* 4 Hz, 1H, ArH), 7.77 (d, *J* 8 Hz, 1H, ArH), 7.83 (d, *J* 8 Hz, 1H, Ar-H), 8.92 (d, *J* 4 Hz, 1H, ArH), 9.06 (d, *J* 4 Hz, 1H, ArH). ^{13}C NMR (125 MHz, $CDCl_3$, 20 °C, δ): 10.48, 10.52, 14.02, 14.10, 23.06, 23.20, 23.55, 28.34, 30.21, 30.32, 30.34, 39.09, 39.48, 45.92, 46.08, 106.50, 108.17, 108.69, 122.04, 123.77, 125.68, 126.42, 128.47, 128.76, 129.82, 130.61, 130.67, 131.23, 135.48, 136.95, 139.25, 139.55, 140.46, 161.64. FT-IR (neat, cm^{-1}): 2958, 2929, 2859, 1663 (C=O), 1556, 1456, 1403, 1317, 1231, 1103, 1026, 734. HRMS-ESI (*m/z*), calcd. for $C_{38}H_{43}BrN_2O_2S_3$: M$^+$ 734.16645, found 734.16694.

Characterisation data for compound **S4**: ^{1}H NMR (500 MHz, $CDCl_3$, 20 °C, δ): 0.90 (m, 12H, $-CH_3$), 1.27-1.37 (m, 16H, $-CH_2-$), 1.85 (m, 2H, -CH-), 3.9-4.1 (m, 4H, $-CH_2N-$), 7.20 (d, *J* 4 Hz, 1H, Ar-H), 7.36 (m, 2H, ArH), 7.40 (d, *J* 4 Hz, 1H, ArH), 7.53 (s, 1H, ArH), 7.75-7.81

(m, 2H, Ar-H), 8.64 (d, *J* 4 Hz, 1H, ArH), 8.94 (d, *J* 4 Hz, 1H, ArH). ^{13}C NMR (125 MHz, $CDCl_3$, 20 °C, δ): 10.48, 10.55, 14.02, 14.08, 23.04, 23.11, 23.56, 23.69, 28.32, 28.54, 30.16, 30.18, 30.35, 39.11, 39.26, 46.00, 108.25, 118.25, 121.43, 122.21, 123.86, 125.02, 125.30, 126.00, 129.01, 131.25, 131.39, 135.17, 135.74, 136.76, 138.72, 139.63, 140.03, 140.09, 142.78, 161.32, 161.57. FT-IR (neat, cm^{-1}): 2959, 2929, 2859, 1664 (C=O), 1552, 1400, 1228, 1103, 1026, 809, 733. HRMS-ESI (*m/z*), calcd. for $C_{38}H_{43}BrN_2O_2S_3$: M$^+$ 734.16645, found 734.16686.

Palladium-catalysed de-bromination of compound 3 (Scheme S3)

Compound **3** (100 mg, 0.12 mmol) was dissolved in toluene (10 mL) and ethanol (2 mL) and potassium phosphate tribasic (2 M aq., 2 mL) was added. The mixture was degassed by bubbling nitrogen gas for 15 min and $Pd(PPh_3)_4$ (5 mg, 3 mol%) was added. The reaction was heated at 90 °C for 14 h and cooled to 25 °C. The product was extracted with toluene and the organic extract was dried with $MgSO_4$. The solution was filtered through a silica plug and the solvent was removed to give a purple solid (60 mg, 76% yield). The product was revealed to be compound **S2** via chromatographic and ^{1}H NMR analysis.

3-(5-Benzofurylthiophen-2-yl)-2,5-bis(2-ethylhexyl)-6-(thiophen-2-yl)pyrrolo[3,4-c]pyrrole-1,4(2H,5H)-dione (Compound S4)

3-(5-Bromothiophen-2-yl)-2,5-bis(2-ethylhexyl)-6-(thiophen-2-yl)pyrrolo[3,4-c]pyrrole-1,4(2H,5H)-dione **2** (1.208 g, 2 mmol) and 2-benzofuranboronic acid **S3** (324 mg, 2 mmol) was dissolved in THF (50 mL) and potassium phosphate tribasic (2 M aq., 10 mL) was added. The mixture was degassed by bubbling nitrogen gas for 15 min and $Pd_2(dba)_3$ (100 mg, 0.1 mmol) and tri-tert-butylphosphonium tetrafluoroborate (100 mg, 0.34 mmol) was added. The reaction was stirred at 25 °C for 2 h. The product was extracted with toluene, washed with water and the organic extract was dried with $MgSO_4$. After solvent removal, the residue was purified by column chromatography (SiO_2, toluene, R_f 0.4) and a dark amorphous solid (1.1 g, 86% yield) was collected by filtration after precipitation from methanol.

m.p. 115-120 °C. ^{1}H NMR (500 MHz, $CDCl_3$, 20 °C, δ): 0.89 (m, 12H, $-CH_3$), 1.3-1.4 (m, 16H, $-CH_2-$), 1.9 (m, 2H, -CH-), 4.03 (m, 4H, $-CH_2N-$), 7.07 (s, 1H, ArH), 7.27 (m, 2H, Ar-H), 7.34 (m, 1H, ArH), 7.52 (d, *J* 11 Hz, 1H, Ar-H), 7.6 (m, 2H, Ar-H), 7.65 (d, *J* 7.5 Hz, 1H, Ar-H), 8.91 (d, *J* 5 Hz, 1H,Ar-H), 8.97 (d, *J* 5 Hz, 1H, Ar-H). ^{13}C NMR (125 MHz, $CDCl_3$, 20 °C, δ): 10.5 (2), 14.0, 14.1, 23.1 (2), 23.6, 23.7, 28.4, 28.5, 30.2, 30.3, 39.1, 39.2, 46.0 (2), 103.6, 111.3, 121.2, 123.5, 125.3, 125.4, 128.5, 128.8, 129.5, 129.8, 130.6, 135.4, 136.4, 137.8, 139.8, 140.3, 150.0, 155.0, 161.7 (2). FT-IR (neat, cm^{-1}): 2959, 2931, 2859, 1664 (C=O), 1555, 1451, 1404, 1233, 1101, 858, 735. HRMS-ESI (*m/z*), calcd. for $C_{38}H_{44}N_2O_3S_2$: M$^+$ 640.27879, found 640.27886. Elemental analysis: calcd. for $C_{38}H_{44}N_2O_3S_2$, C 71.21, H 6.92, N 4.37; found C 71.29, H 6.94, N 4.32.

3-(5-(3-Bromobenzofuryl)thiophen-2-yl)-2,5-bis(2-ethylhexyl)-6-(5-bromothiophen-2-yl)pyrrolo[3,4-c]pyrrole-1,4(2H,5H)-dione (Compound 4)

Compound **S4** (500 mg, 0.78 mmol) was dissolved in chloroform (25 mL) and cooled to 0 °C. *N*-Bromosuccinimide (178 mg 1 mmol) was added and the reaction was stirred for 1 h at 0 °C. Additional *N*-bromosuccinimide (178 mg 1 mmol) was added and the reaction was stirred for a further 1 h at 0 °C. Water was added to the reaction and the product was extracted with chloroform and the organic extract was dried with $MgSO_4$. After solvent removal, the residue was purified by column chromatography (SiO_2, toluene, R_f 0.6) and a dark amorphous solid (450 mg, 80% yield) was collected by filtration after precipitation from methanol.

m.p. 145-150 °C. ^{1}H NMR (500 MHz, $CDCl_3$, 20 °C, δ): 0.89 (m, 12H, -CH_3), 1.3-1.4 (m, 16H, -CH_2-), 1.85 (m, 2H, -CH-), 3.9-4.1 (m, 4H, -CH_2N-), 7.21 (d, *J* 4 Hz, 1H, Ar-H), 7.33 (t, *J* 7Hz, 1H, ArH), 7.39 (t, *J* 7Hz, 1H, ArH), 7.49 (d, *J* 10 Hz, 1H, Ar-H), 7.52 (d, *J* 10 Hz, 1H, Ar-H), 7.92 (d, *J* 5.5 Hz, 1H, Ar-H), 8.67 (d, *J* 5 Hz, 1H,Ar-H), 9.09 (d, *J* 5 Hz, 1H, Ar-H). ^{13}C NMR (125 MHz, $CDCl_3$, 20 °C, δ): 10.5, 14.0, 14.1, 23.0, 23.2, 23.6, 28.3, 28.5, 30.2, 30.3, 39.1, 39.4, 46.0, 46.1, 95.9, 108.4, 108.6, 111.4, 118.8, 119.9, 124.0, 126.6, 127.3, 129.1, 130.4, 131.2, 131.4, 135.3, 135.9, 136.3, 138.9, 140.1, 146.3, 153.5, 161.4, 161.5. FT-IR (neat, cm^{-1}): 2958, 2930, 2872, 1667 (C=O), 1553, 1401, 1259, 1104, 819, 733. HRMS-ESI (*m/z*), calcd. for $C_{38}H_{42}Br_2N_2O_3S_2$: [M-H]$^+$ 796.10036, found 796.10533. Elemental analysis: calcd. for $C_{38}H_{42}Br_2N_2O_3S_2$, C 57.14, H 5.30, N 3.51; found C 56.60, H 6.01, N 2.96.

Bromination experiment for compound S6 (Scheme S5)

N-Bromosuccinimide (1 eqv., 26 mg, 0.15 mmol) was added to a solution of compound **S6** (100 mg, 0.15 mmol) in chloroform (10 mL) at 0 °C. The reaction was stirred at 0 °C for 1 h and the solvent was removed. Thin layer chromatography analysis of the reaction mixture revealed a mixture of brominated products including starting material **S6**, two mono-brominated products **S7** and **S8**, and dibromo product **4**. The compounds were separated by column chromatography (SiO_2, toluene) and each compound isolated (**S6**, 20 mg, R_f = 0.3; **S7**, 50 mg, R_f = 0.35; **S8**, 10 mg, R_f = 0.45; **4**, 20 mg, R_f = 0.5).

Characterisation for compound **S7**: ^{1}H NMR (400 MHz, $CDCl_3$, 20 °C, δ): 0.89 (m, 12H, -CH_3), 1.28-1.39 (m, 16H, -CH_2-), 1.88-1.94 (m, 2H, -CH-), 4.04-4.09 (m, 4H, -CH_2N-), 7.27 (m, 1H, ArH), 7.32 (t, *J* 8 Hz, 1H, ArH), 7.39 (t, *J* 8 Hz, 1H, ArH), 7.49-7.54 (m, 1H, ArH), 7.63 (d, *J* 5 Hz, 1H, ArH), 7.93 (d, *J* 4 Hz, 1H, ArH), 8.93 (d, *J* 5 Hz, 1H, ArH), 9.08 (d, *J* 4 Hz, 1H, ArH). ^{13}C NMR (125 MHz, $CDCl_3$, 20 °C, δ): 10.49, 10.51, 14.02, 14.10, 23.06, 23.17, 23.54, 23.57, 28.35, 28.54, 30.20, 30.21, 30.34, 39.09, 39.44, 46.04, 95.73, 108.17, 108.76, 111.35, 119.89, 123.98, 126.49, 127.26, 128.47, 129.09, 129.82, 130.47, 130.68, 135.50, 135.54, 136.00, 139.64, 140.45, 146.36, 153.45, 161.63, 161.65. FT-IR (neat, cm^{-1}): 2956, 2928, 2858, 1659 (C=O), 1551, 1402, 1232, 1104, 1023, 732. HRMS-ESI (*m/z*), calcd. for $C_{38}H_{43}BrN_2O_3S_2$: M^+ 718.18930, found 718.18971.

Characterisation data for compound **S8**: ^{1}H NMR (500 MHz, $CDCl_3$, 20 °C, δ): 0.88 (m, 12H, -CH_3), 1.20-1.40 (m, 16H, -CH_2-), 1.83-1.93 (m, 2H, -CH-), 3.94-4.08 (m, 4H, -CH_2N-), 7.06 (s, 1H, furan-H), 7.23-7.33 (m, 3H, ArH), 7.48-7.61 (m, 3H, ArH), 8.65 (m, 1H, ArH), 8.98 (m, 1H, ArH). ^{13}C NMR (125 MHz, $CDCl_3$, 20 °C, δ): 10.51, 14.01, 14.06, 23.03, 23.07, 23.58, 23.63, 28.33, 28.48, 29.69, 30.19, 30.29, 39.12, 39.22, 46.03, 103.74, 108.35, 111.26, 121.19, 123.53, 125.39, 125.44, 128.80, 129.38, 131.24, 131.42, 135.18, 136.65, 138.15, 138.80, 140.18, 149.92, 154.96, 161.62. FT-IR (neat, cm^{-1}): 2958, 2927, 2858, 1663 (C=O), 1553, 1402, 1258, 1101, 1027, 797, 733. HRMS-ESI (*m/z*), calcd. for $C_{38}H_{43}BrN_2O_3S_2$: M^+ 718.18930, found 718.18978.

Palladium-catalysed de-bromination of compound 4 (Scheme S6)

Compound **4** (65 mg, 0.08 mmol) was dissolved in toluene (10 mL) and ethanol (2 mL) and potassium phosphate tribasic (2 M aq., 2 mL) was added. The mixture was degassed by bubbling nitrogen gas for 15 min and $Pd(PPh_3)_4$ (5 mg, 5 mol%) was added. The reaction was heated at 90 °C for 14 h and cooled to 25 °C. The product was extracted with toluene and the organic extract was dried with $MgSO_4$. The solution was filtered through a silica plug and the solvent was removed to give a purple solid (45 mg, 88% yield). The product was revealed to be compound **S6** via chromatographic and ^{1}H NMR analysis.

FHBC-DPP dye 5

Compound **1** (0.5 g, 0.32 mmol) and 3-(5-bromothiophen-2-yl)-2,5-bis(2-ethylhexyl)-6-(thiophen-2-yl)pyrrolo[3,4-c]pyrrole-1,4(2H,5H)-dione **2** (0.4 g, 0.66 mmol) was dissolved in THF (25 mL) and potassium phosphate tribasic (2 M, 5 mL) was added. The mixture was degassed by bubbling nitrogen gas for 15 min and $Pd(PPh_3)_4$ (5 mg, 1 mol%) was added. The reaction was heated at 60 °C for 14 h and cooled to 25 °C . The product was extracted with toluene and the organic extract was dried with $MgSO_4$. After solvent removal, the residue was purified using size exclusion chromatography (BioRad BioBeads SX-1) with toluene as eluent. The high molecular weight purple fraction was collected and passed through a plug of silica. A dark amorphous solid (0.55 g, 73% yield) was collected by filtration after precipitation from methanol.

TGA, T_{decomp} (5% mass loss) = 408 °C. DSC, T_g = 130 °C. UV-vis: λ_{max} nm (ε, $M^{-1}cm^{-1}$) = 365 (1.6×10^5), 580 (1.0×10^5). ^{1}H NMR (500 MHz, 20 mM, $CDCl_3$, 20 °C, δ): 0.83 (m, 12H, $-CH_3$), 0.94 (m, 12H, $-CH_3$), 0.96 (m, 12H, $-CH_3$), 1.0-1.3 (m, 80H, $-CH_2-$), 1.88 (br m, 2H, -CH-), 2.01 (br m, 2H, -CH-), 2.40 (br m, 8H, $-CH_2-$), 4.03 (br m, 8H, $-NCH_2-$), 7.23 (br, 2H, Ar-H), 7.35 (br, 4H, HBC-H), 7.60 (br m, 4H, ArH), 7.7-7.9 (m, 24H, Ar-H), 8.81 (br, 4H, HBC-H), 8.37 (br, 4H, HBC-H), 8.84 (br s, 2H, thiophene-H), 9.01 (br s, 2H, thiophene-H). ^{13}C NMR (125 MHz, 60 mM, $CDCl_3$, 20 °C, δ): 10.5, 10.6, 14.0, 14.2, 22.7, 23.1, 23.2, 23.6, 23.8, 24.4, 28.4, 28.6, 29.5, 29.6, 30.2, 30.3, 30.5, 31.9, 39.1, 39.3, 40.6, 45.8, 55.6, 107.9, 108.0, 118.3, 118.5, 118.9, 120.2, 120.6, 121.9, 122.5, 123.2, 124.3, 124.8, 125.5, 126.9, 128.3, 128.5, 128.9, 129.9, 130.2, 132.1, 135.1, 137.1, 139.5, 139.7, 140.1, 141.4, 142.0, 150.6, 152.0, 152.3, 161.5, 161.7. FT-IR (neat, cm^{-1}): 2924, 2854, 1661 (C=O), 1557, 1456, 1232 1084, 813, 759. MALDI-TOF MS (*m/z*): M^+ 2343.3. Elemental analysis: calcd. for $C_{160}H_{174}N_4O_4S_4$, C 81.94, H 7.48, N 2.39; found C 81.90, H 7.57, N 2.34.

FHBC-DPP dye 6

Compound **1** (0.4 g, 0.26 mmol) and 3-(5-benzothienylthiophen-2-yl)-2,5-bis(2-ethylhexyl)-6-(5-bromothiophen-2-yl)pyrrolo[3,4-c]pyrrole-1,4(2H,5H)-dione **3** (0.4 g, 0.54 mmol) was dissolved in toluene (50 mL) and ethanol (5 mL) and potassium phosphate tribasic (2 M aq., 2 mL) was added. The mixture was degassed by bubbling nitrogen gas for 15 min and $Pd(PPh_3)_4$ (5 mg, 1 mol%) was added. The reaction was heated at 90 °C for 14 h and cooled to 25 °C. The product was extracted with toluene and the organic extract was dried with $MgSO_4$. After solvent removal, the residue was purified using size exclusion chromatography

(BioRad BioBeads SX-1) with toluene as eluent. The high molecular weight blue fraction was collected and passed through a plug of silica. A dark amorphous solid (0.50 g, 74% yield) was collected by filtration after precipitation from methanol.

TGA, T_{decomp} (5% mass loss) = 378 °C. DSC, T_g = 130 °C. UV-vis: λ_{max} nm (ε, $M^{-1}cm^{-1}$) = 365 (2.2×10^5), 620 (1.2×10^5). ^{1}H NMR (500 MHz, 20 mM, $CDCl_3$, 20 °C, δ): 0.90 (br m, 36H, $-CH_3$), 1.0-1.4 (m, 80H, $-CH_2-$), 2.0 (br m, 4H, -CH-), 2.40 (br m, 8H, $-CH_2-$), 3.96 (br m, 8H, $-NCH_2-$), 6.8-7.0 (br, Ar-H), 7.55 (br m, ArH), 7.84 (br m, Ar-H), 7.94 (br m, Ar-H), 8.06 (m, Ar-H), 8.22 (br, Ar-H), 8.36 (br, Ar-H), 8.55 (br, Ar-H), 8.97 (br, Ar-H). NOTE: NMR spectrum is very broad as a result of strong molecular aggregation in solution. ^{13}C NMR (125 MHz, 50 mM, $CDCl_3$, 20 °C, δ): 10.5, 10.7, 14.2, 22.7, 22.8, 23.1, 23.2, 23.6, 24.6, 28.5, 28.7, 29.5, 29.6, 29.7, 30.5, 31.9, 32.0, 39.2, 40.5, 45.8, 55.6, 108.0, 119.1, 120.6, 122.0, 123.7, 124.2, 125.1, 127.1, 128.5, 129.0, 129.4, 132.2, 135.5, 138.4, 139.4, 139.7, 139.9, 141.4, 141.9, 150.3, 152.1, 152.5, 161.0. FT-IR (neat, cm^{-1}): 2925, 2855, 1663 (C=O), 1555, 1457, 1101, 813, 761. MALDI-TOF MS (*m/z*): M^+ 2607.3. Elemental analysis: calcd. for $C_{176}H_{182}N_4O_4S_6$, C 81.00, H 7.03, N 2.15; found C 81.06, H 7.11, N 2.19.

FHBC-DPP dye 7

Compound **1** (0.4 g, 0.26 mmol) and 3-(5-benzofurylthiophen-2-yl)-2,5-bis(2-ethylhexyl)-6-(5-bromothiophen-2-yl)pyrrolo[3,4-c]pyrrole-1,4(2H,5H)-dione **4** (0.373 g, 0.52 mmol) was dissolved in toluene (50 mL) and ethanol (5 mL) and potassium phosphate tribasic (2 M aq., 2 mL) was added. The mixture was degassed by bubbling nitrogen gas for 15 min and $Pd(PPh_3)_4$ (5 mg, 1 mol%) was added. The reaction was heated at 90 °C for 14 h and cooled to 25 °C . The product was extracted with $CHCl_3$ and the organic extract was dried with $MgSO_4$. After solvent removal, the residue was purified using size exclusion chromatography (BioRad BioBeads SX-1) with $CHCl_3$ as eluent. The high molecular weight blue fraction was collected and passed through a plug of silica. A dark green solid (0.55 g, 82% yield) was collected by filtration after precipitation from methanol.

TGA, T_{decomp} (5% mass loss) = 343 °C. DSC, T_g = 130 °C. UV-vis: λ_{max} nm (ε, $M^{-1}cm^{-1}$) = 365 (1.4×10^5), 625 (3.5×10^4). ^{1}H NMR (500 MHz, $CDCl_3$, 20 °C, δ): 0.82 (br, CH_3), 0.94 (br, CH_3), 1.37 (br, $-CH_2-$), 2.39-2.54 (br, $-CH_2-$), 3.93 (br, $-CH_2-$), 6.55 (br, ArH), 6.98 (br, ArH), 7.32-7.58 (br, ArH), 7.86-8.08 (br, ArH), 8.48 (br, ArH), 8.95 (br, ArH). NOTE: NMR spectrum is extremely broad as a result of strong molecular aggregation in solution. ^{13}C NMR (125 MHz, $CDCl_3$, 20 °C, δ): 10.5, 10.7, 14.0, 14.2, 14.3, 22.8, 23.7, 24.6, 28.4, 28.7, 29.6, 30.5, 32.0, 39.2, 40.6, 45.7, 55.7, 103.0, 108.0, 108.1, 111.1, 119.1, 120.5, 120.9, 125.0, 129.0, 132.2, 137.0, 138.5, 139.4, 141.5, 141.9, 149.7, 150.4, 152.5, 154.7, 161.0. FT-IR (neat, cm^{-1}): 2924, 2854, 2249, 1656 (C=O), 1549.9, 1432, 1103, 906, 812, 729. MALDI-TOF MS (*m/z*): M$^+$ 2575.3. Elemental analysis: calcd. for $C_{176}H_{182}N_4O_6S_4$, C 82.01, H 7.12, N 2.17; found C 81.95, H 7.20, N 2.09.

NMR Data – Compound **S2**

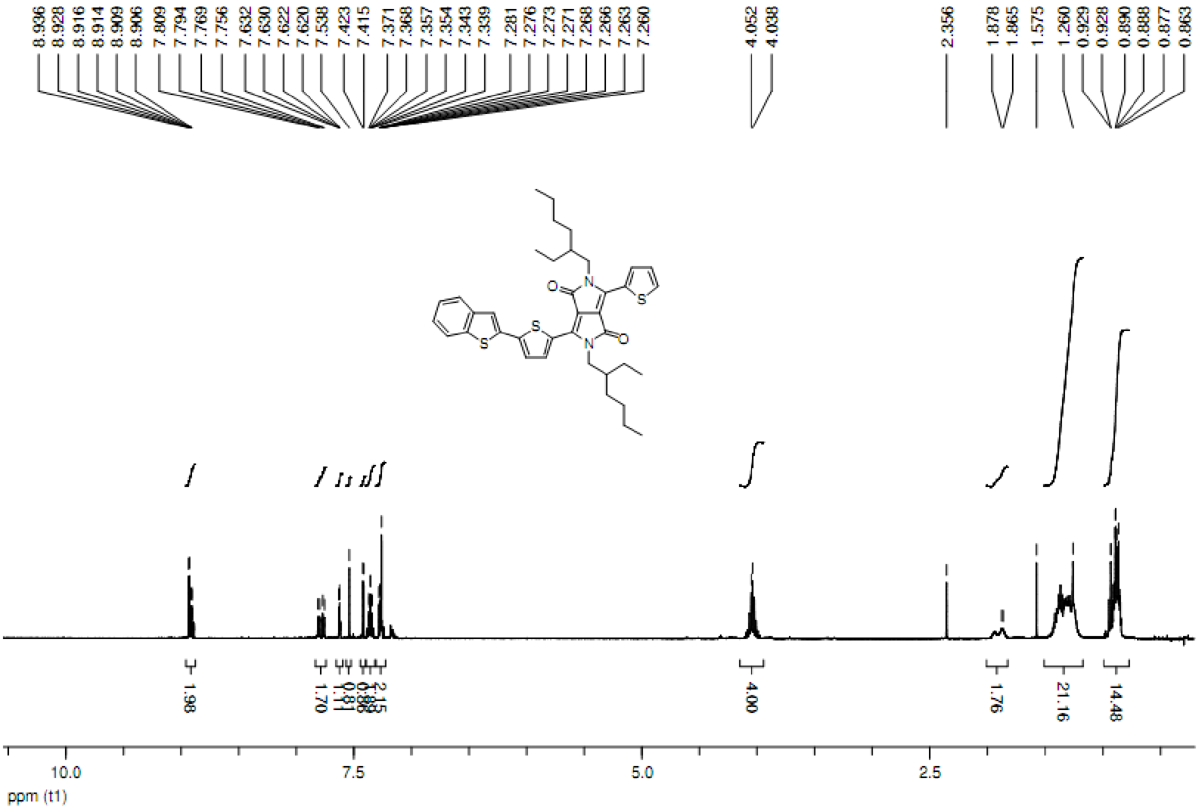


Figure S1. ^{1}H NMR (500 MHz) spectrum of compound **S2** in CDCl$_3$.

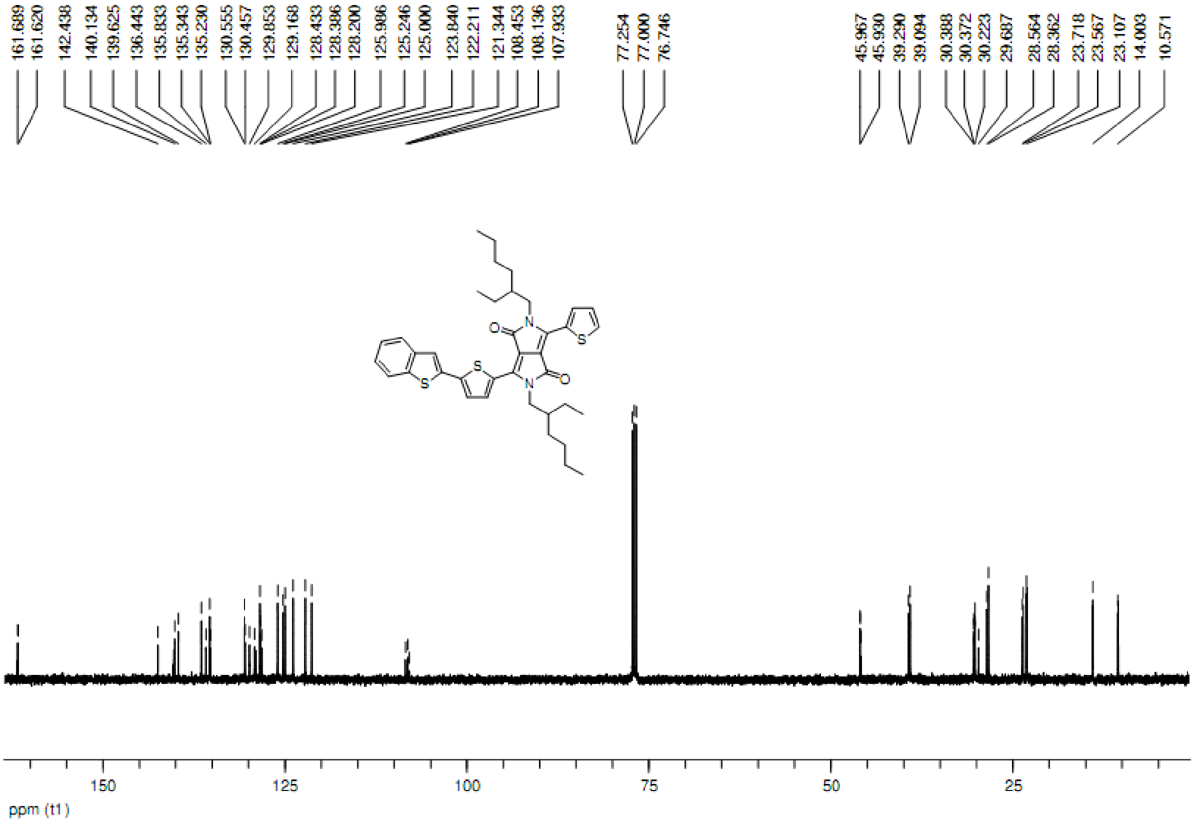


Figure S2. ^{13}C NMR (125 MHz) spectrum of compound **S2** in CDCl$_3$.

NMR Data – Compound **3**

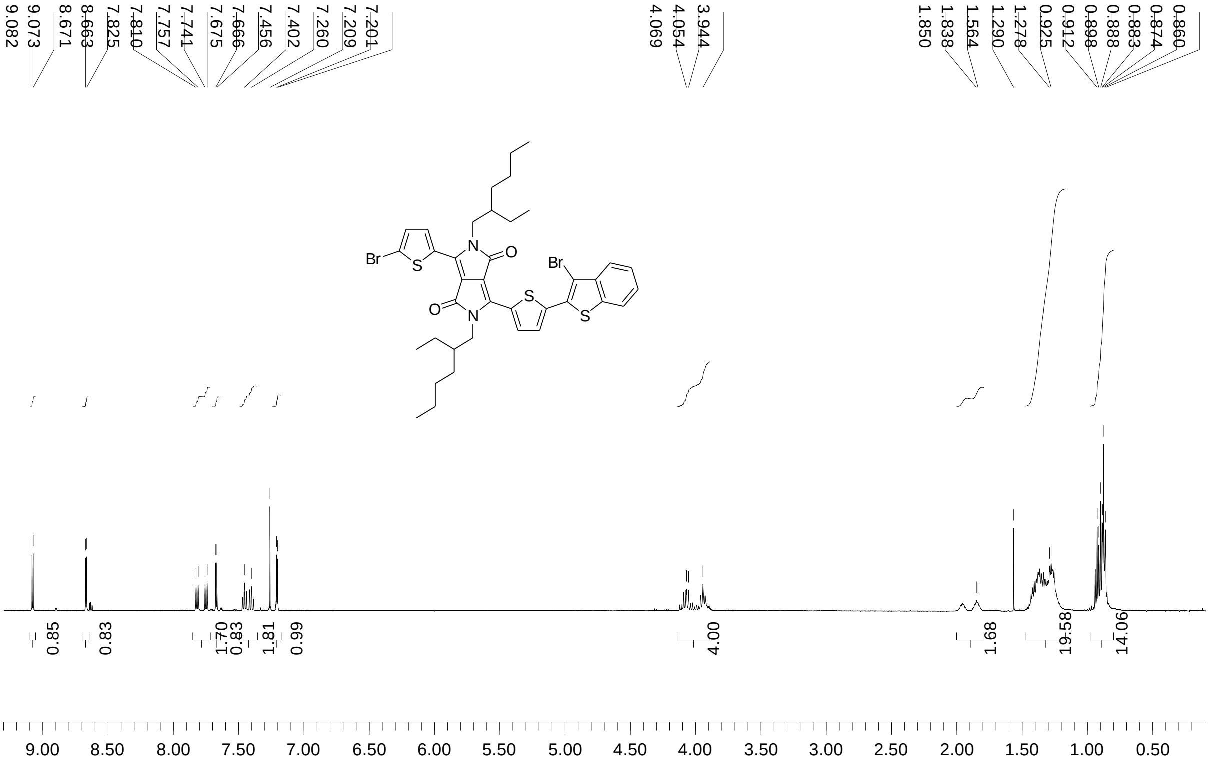


Figure S3. ^{1}H NMR (500 MHz) spectrum of compound **3** in $CDCl_3$.

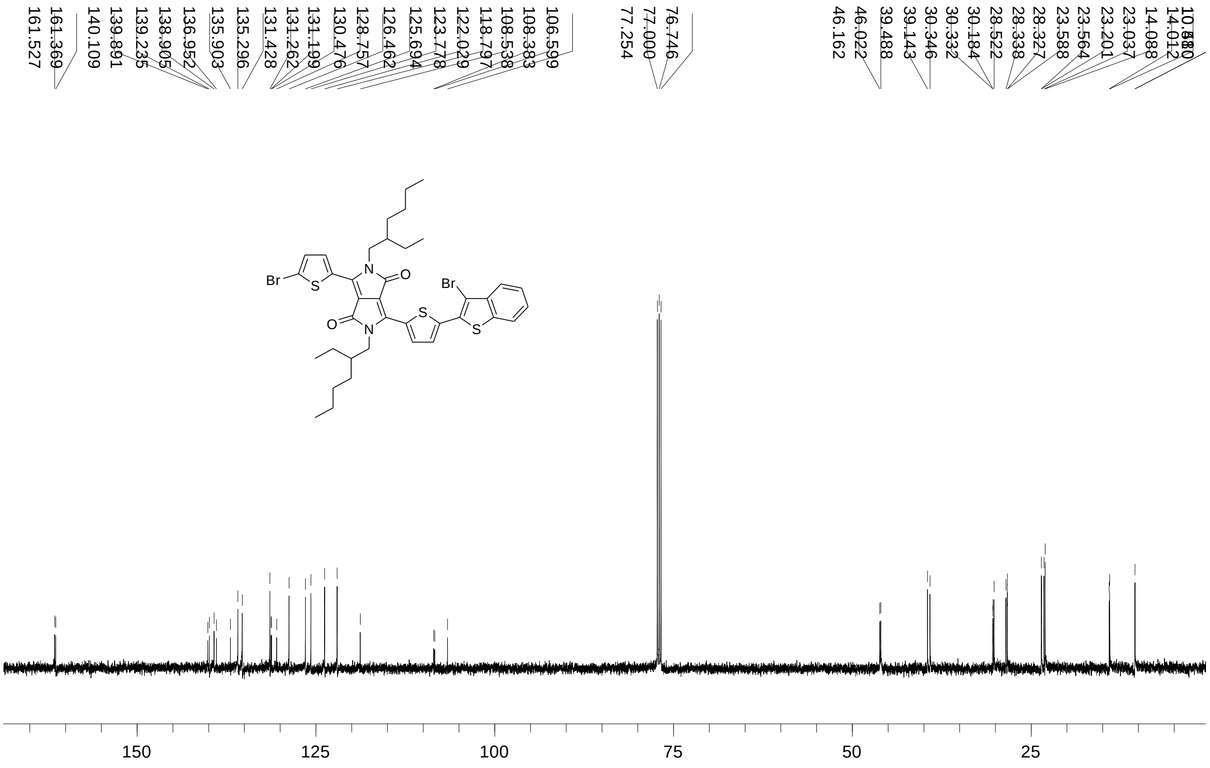


Figure S4. ^{13}C NMR (125 MHz) spectrum of compound **3** in $CDCl_3$.

NMR Data – Compound **S3**

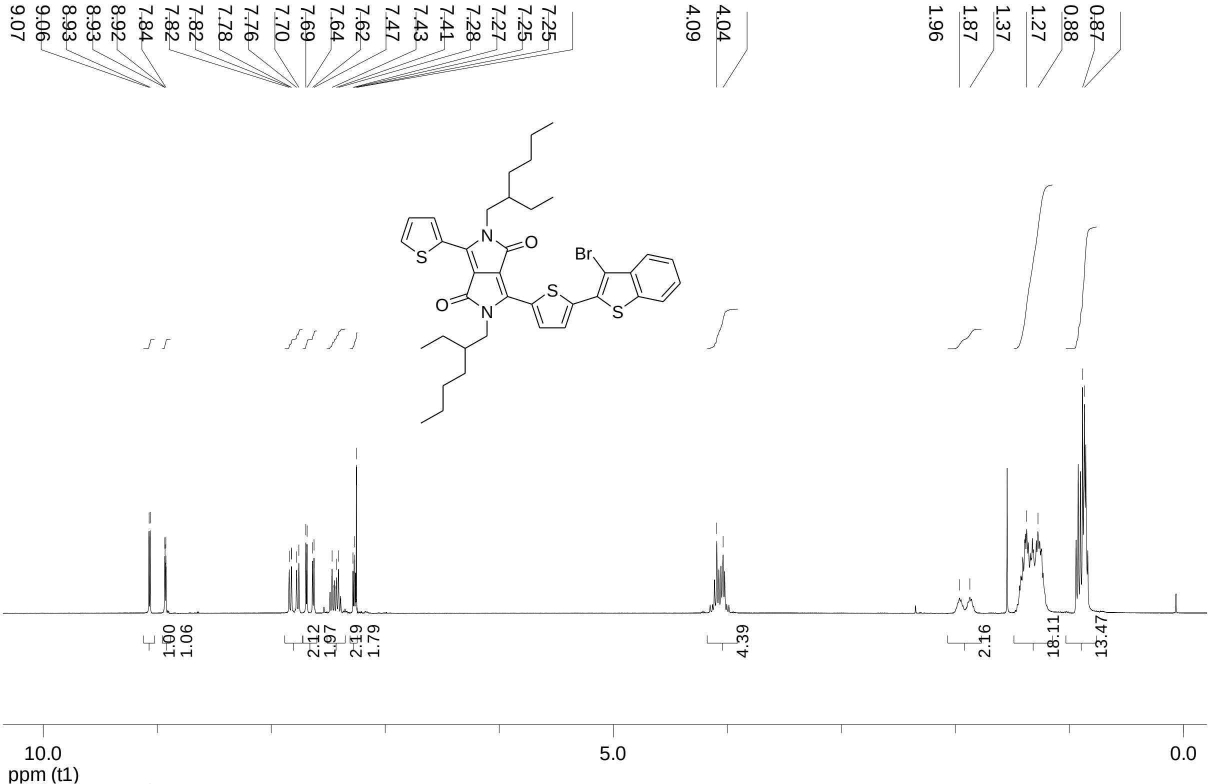


Figure S5. ^{1}H NMR (400 MHz) spectrum of compound **S3** in $CDCl_3$.

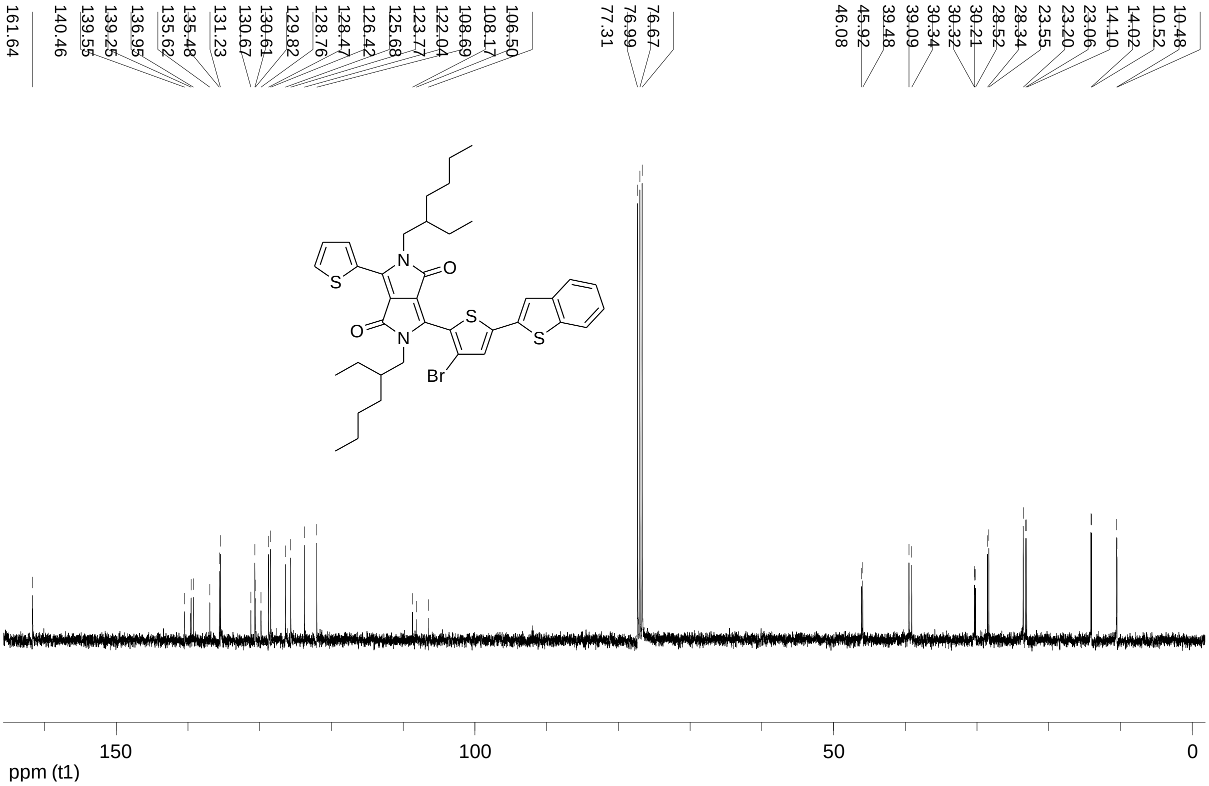


Figure S6. ^{13}C NMR (100 MHz) spectrum of compound **S3** in $CDCl_3$.

NMR Data – Compound **S4**

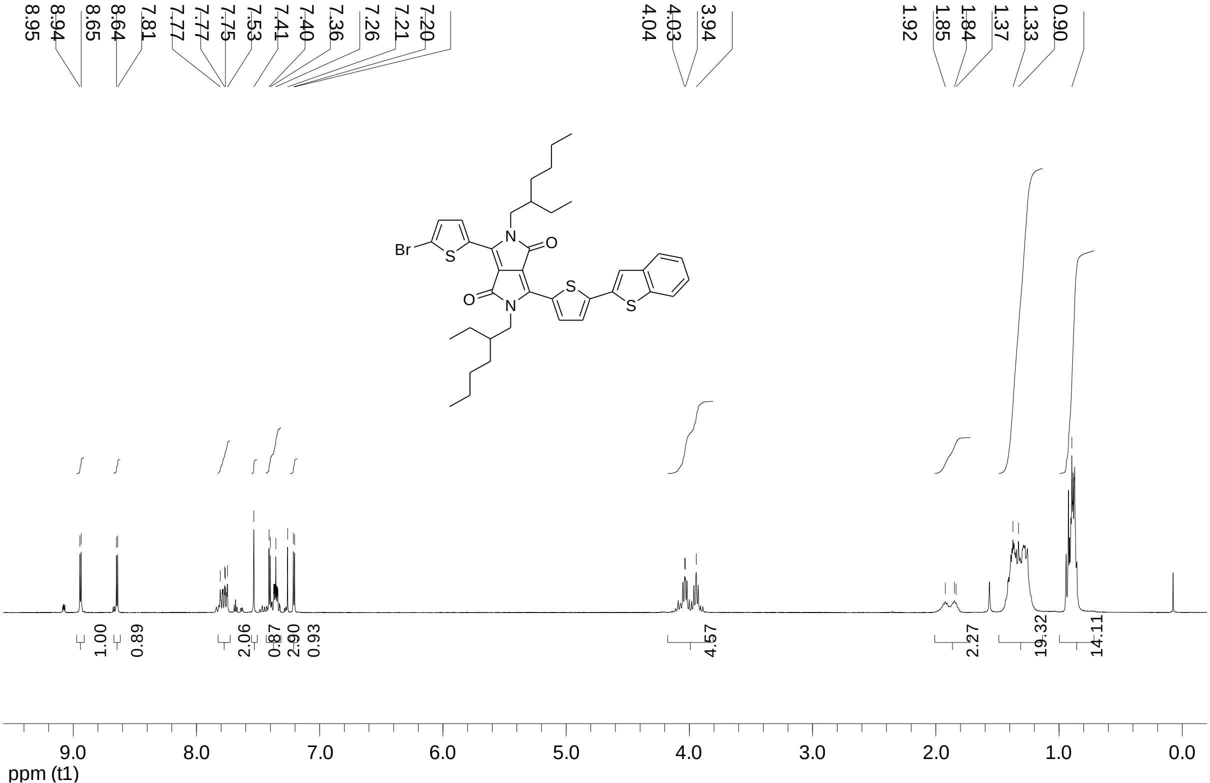


Figure S7. ^{1}H NMR (400 MHz) spectrum of compound **S4** in $CDCl_3$.

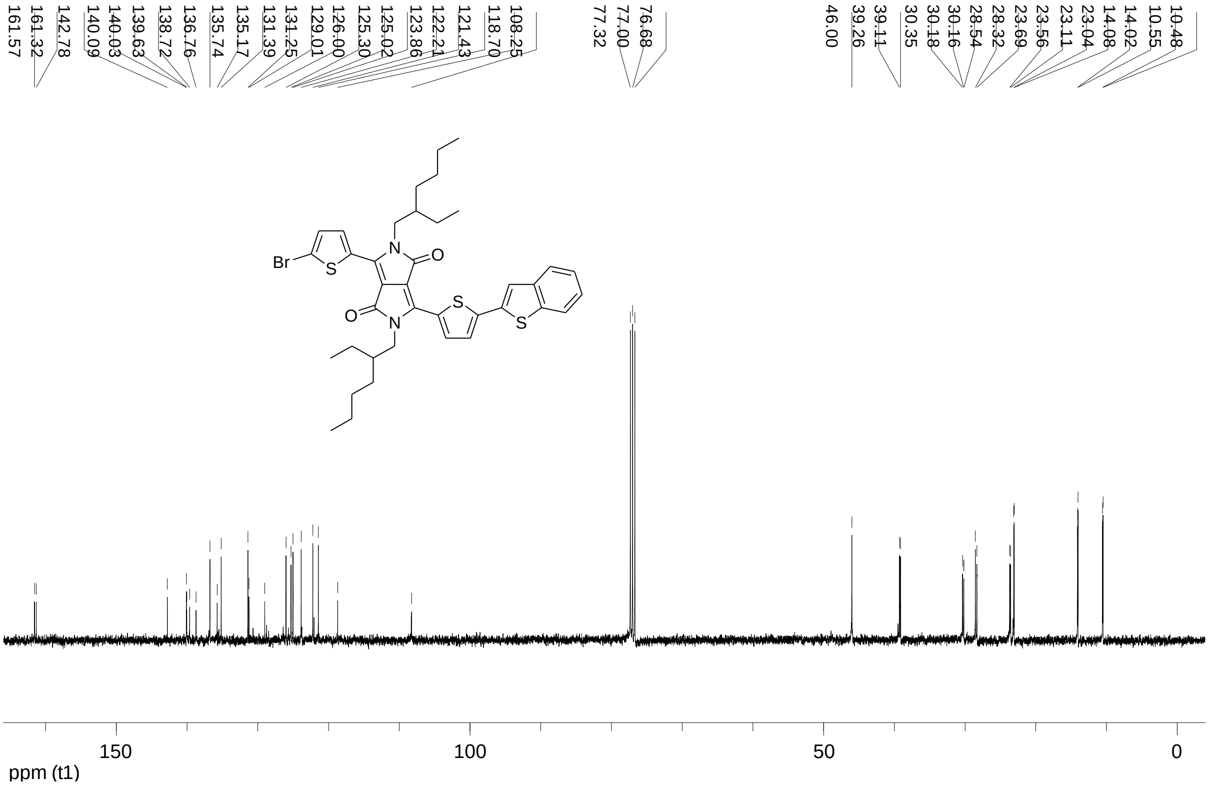


Figure S8. ^{13}C NMR (100 MHz) spectrum of compound **S4** in $CDCl_3$.

NMR Data – Compound **S6**

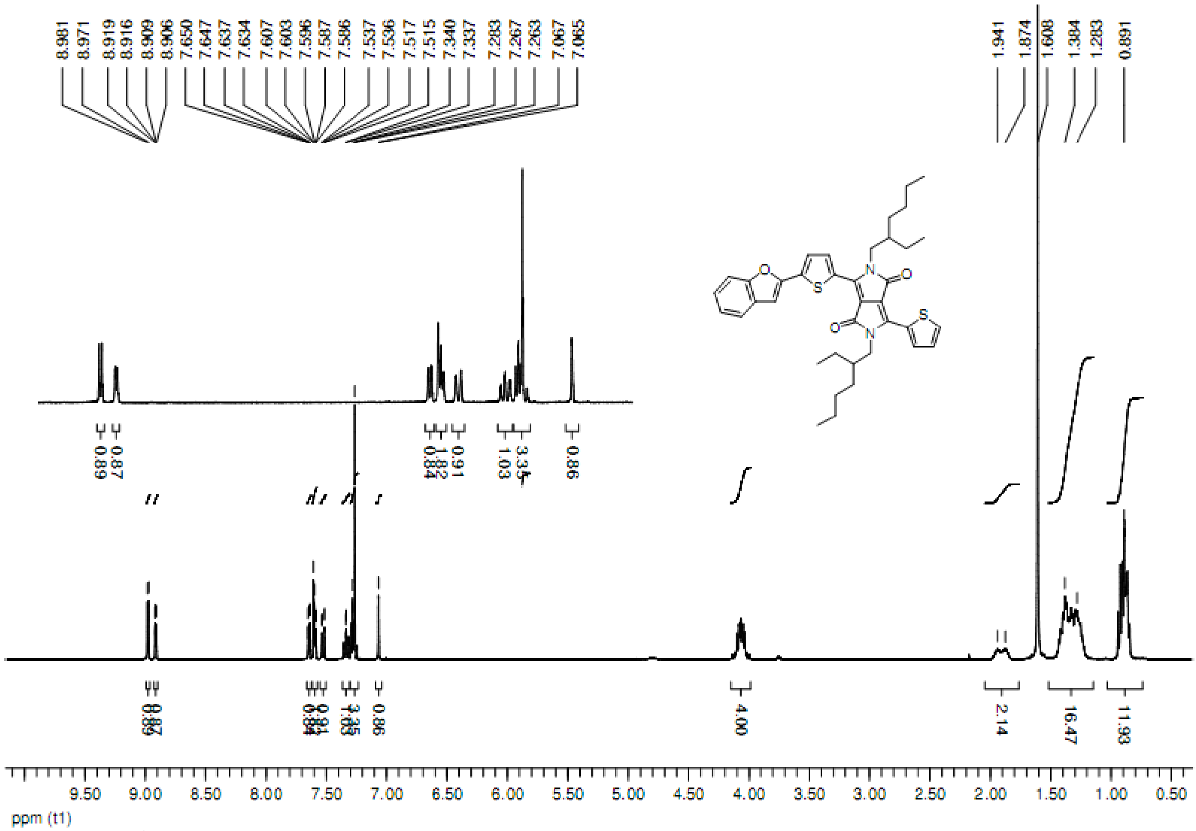


Figure S9. ^{1}H NMR (500 MHz) spectrum of compound **S6** in $CDCl_3$.

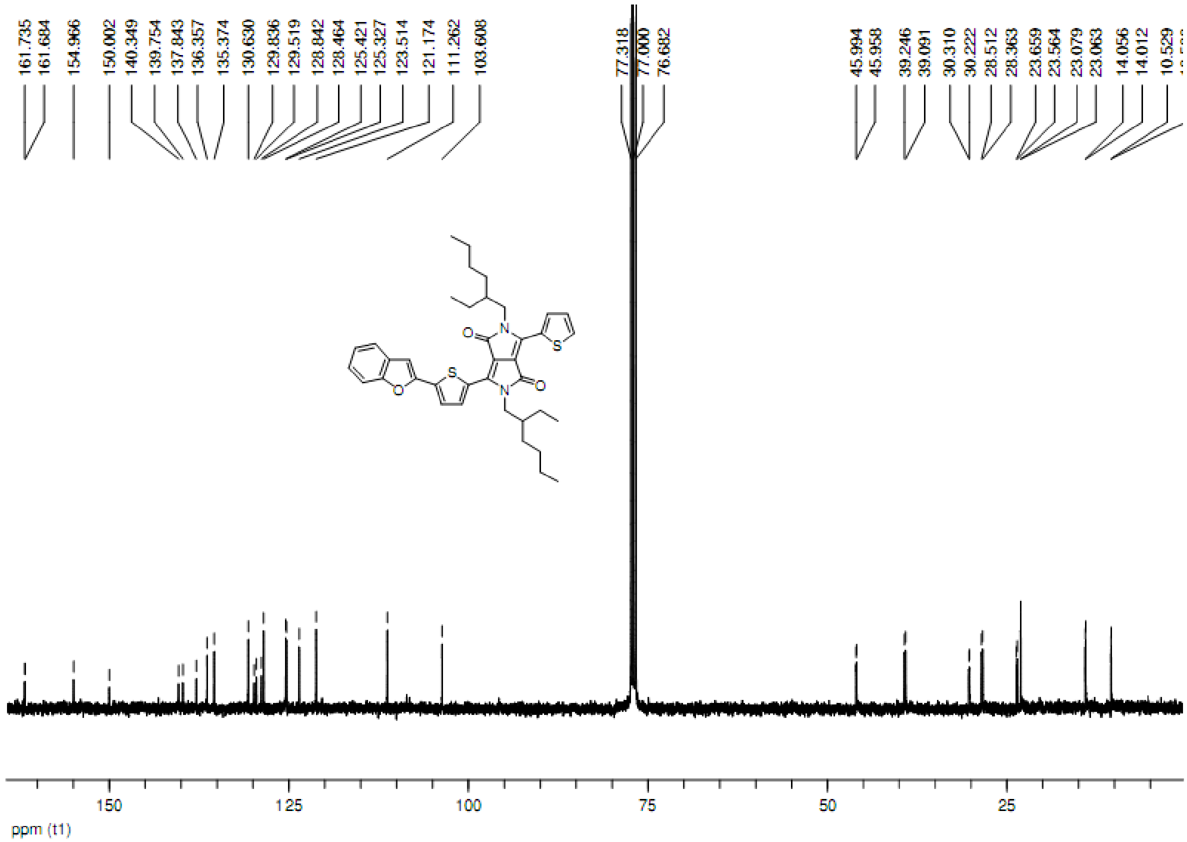


Figure S10. ^{13}C NMR (125 MHz) spectrum of compound **S6** in $CDCl_3$.

NMR Data – Compound **4**

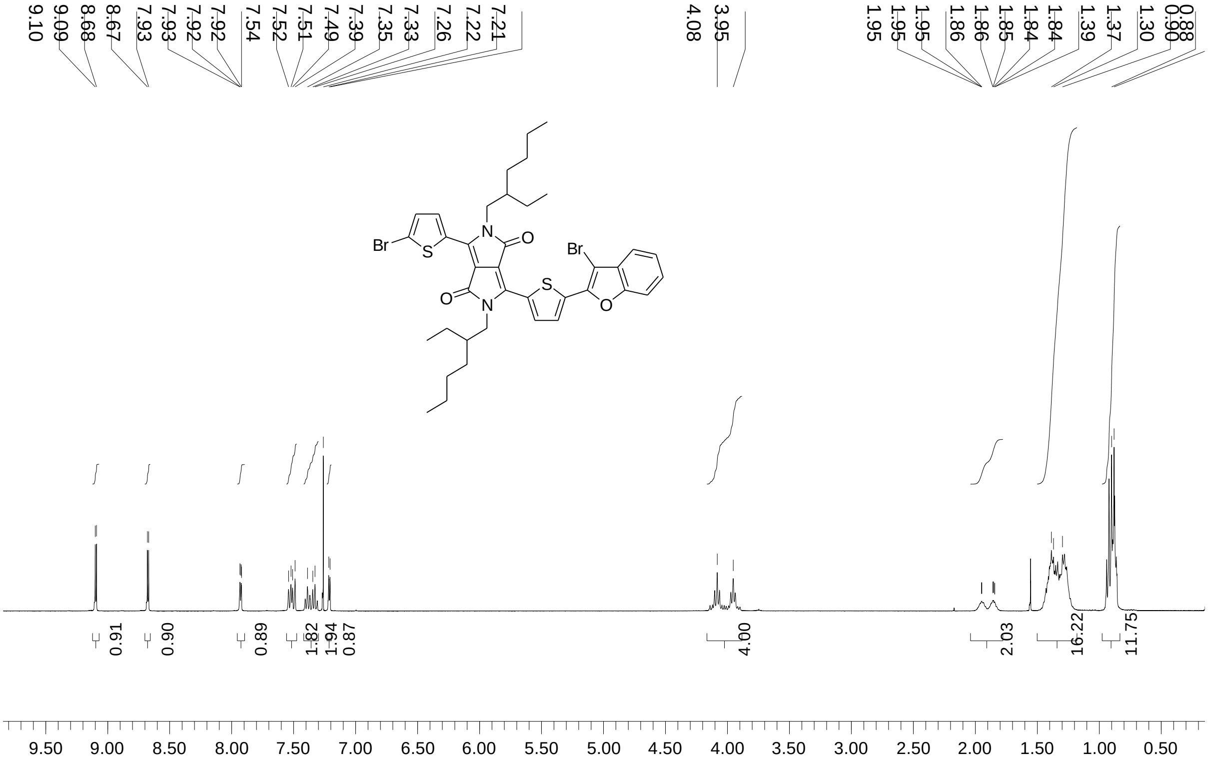


Figure S11. ^{1}H NMR (500 MHz) spectrum of compound **4** in $CDCl_3$.

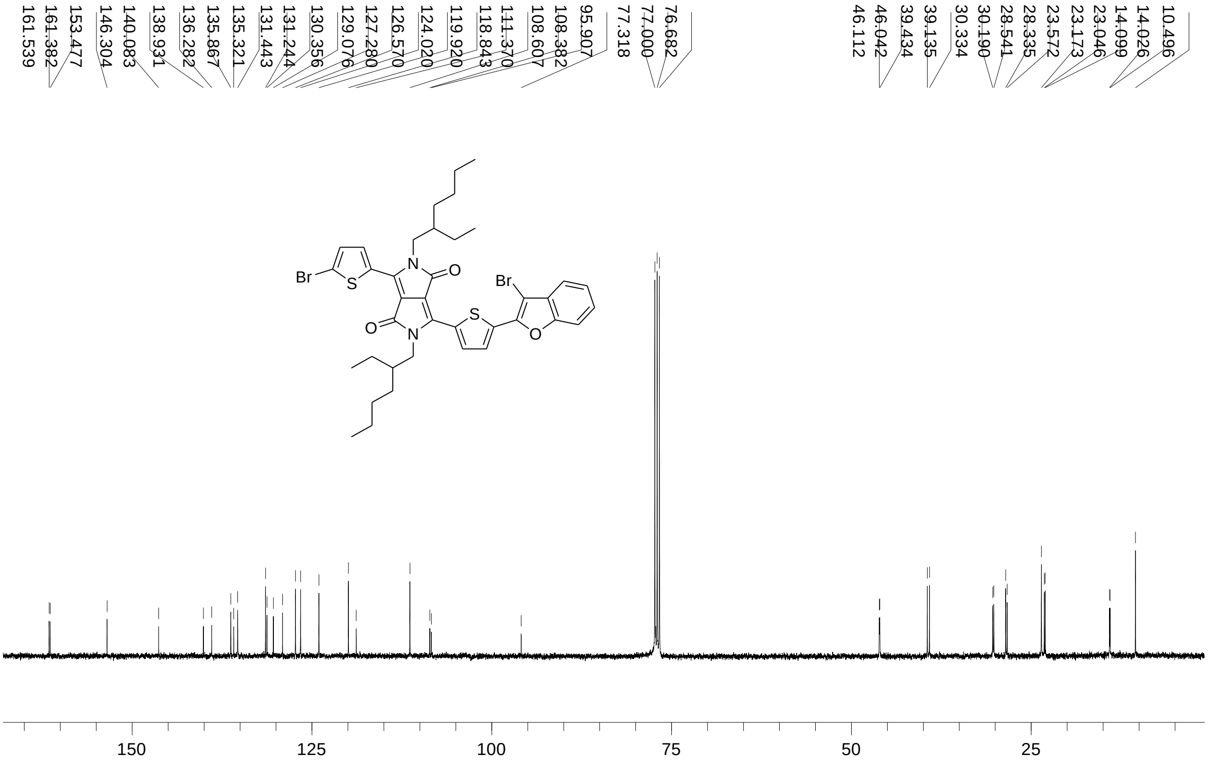


Figure S12. ^{13}C NMR (125 MHz) spectrum of compound **4** in $CDCl_3$.

NMR Data – Compound **S7**

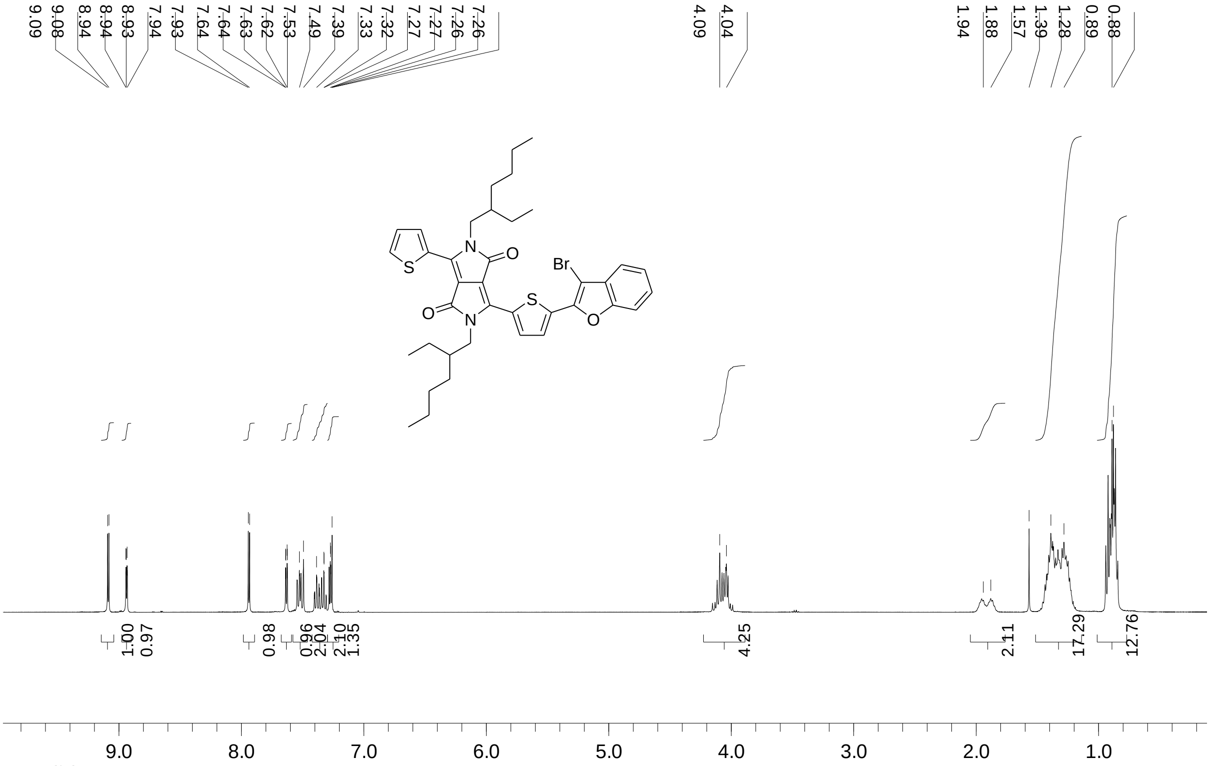


Figure S13. ^{1}H NMR (400 MHz) spectrum of compound **S7** in $CDCl_3$.

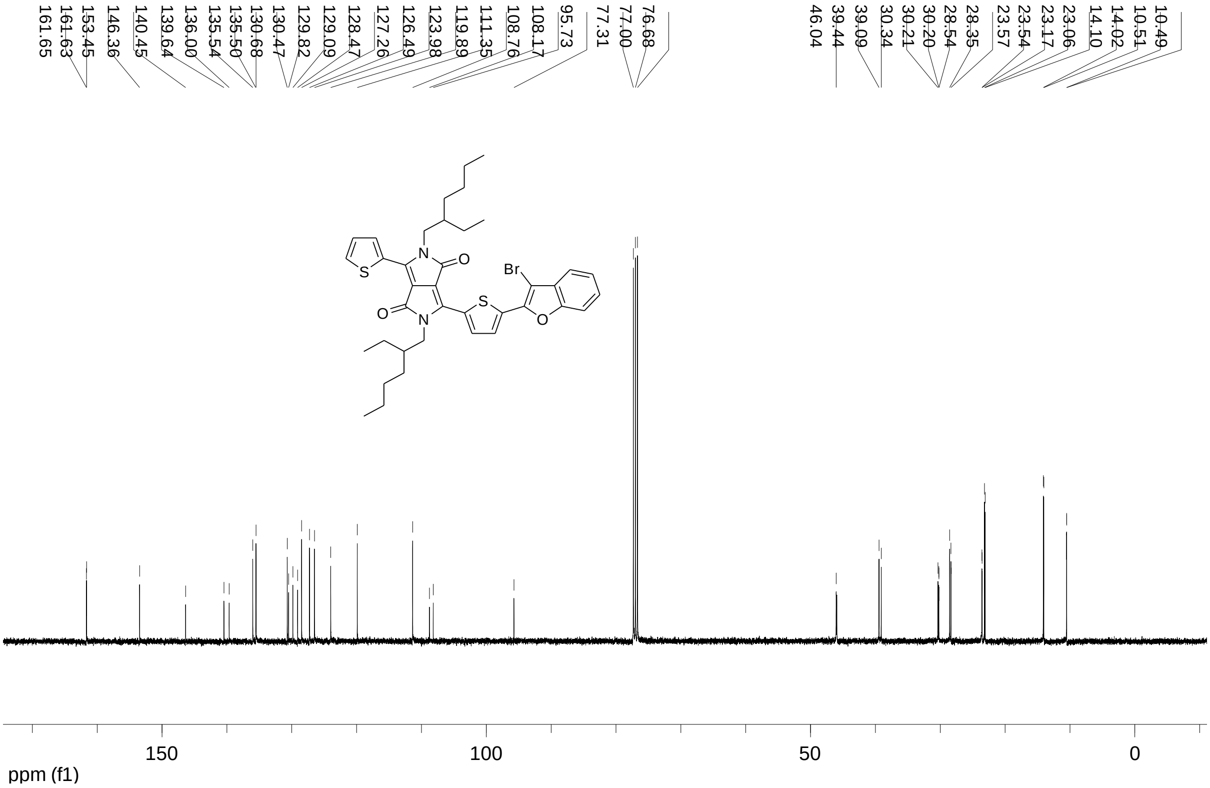


Figure S14. ^{13}C NMR (100 MHz) spectrum of compound **S7** in $CDCl_3$.

NMR Data – Compound **S8**

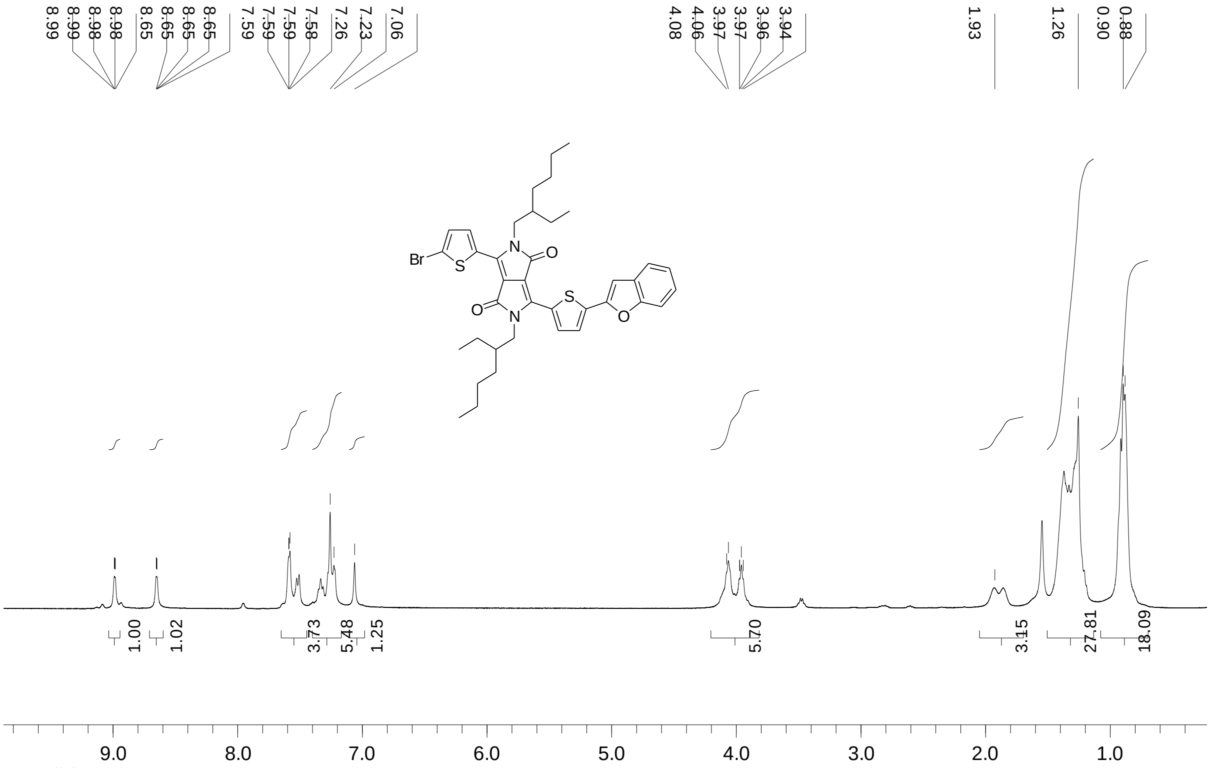


Figure S15. ^{1}H NMR (400 MHz) spectrum of compound **S8** in $CDCl_3$.

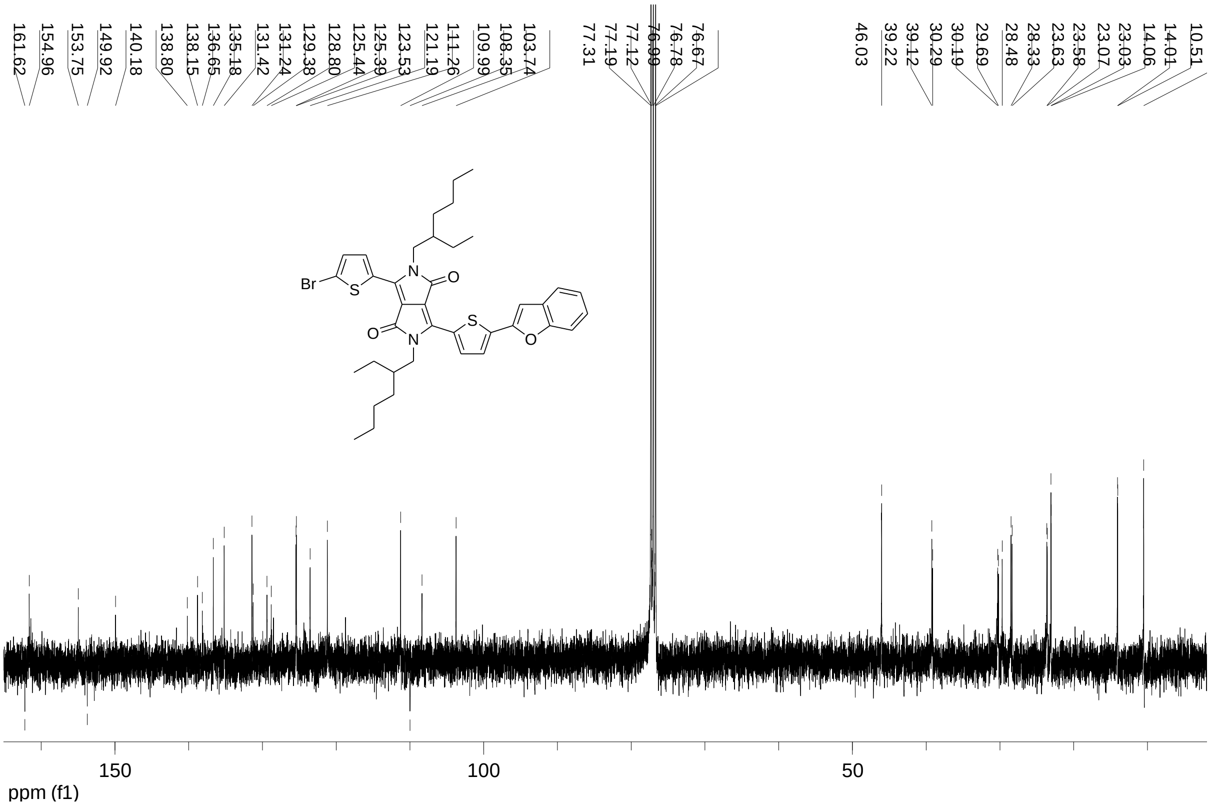


Figure S16. ^{13}C NMR (100 MHz) spectrum of compound **S8** in $CDCl_3$.

NMR Data – Compound **5**

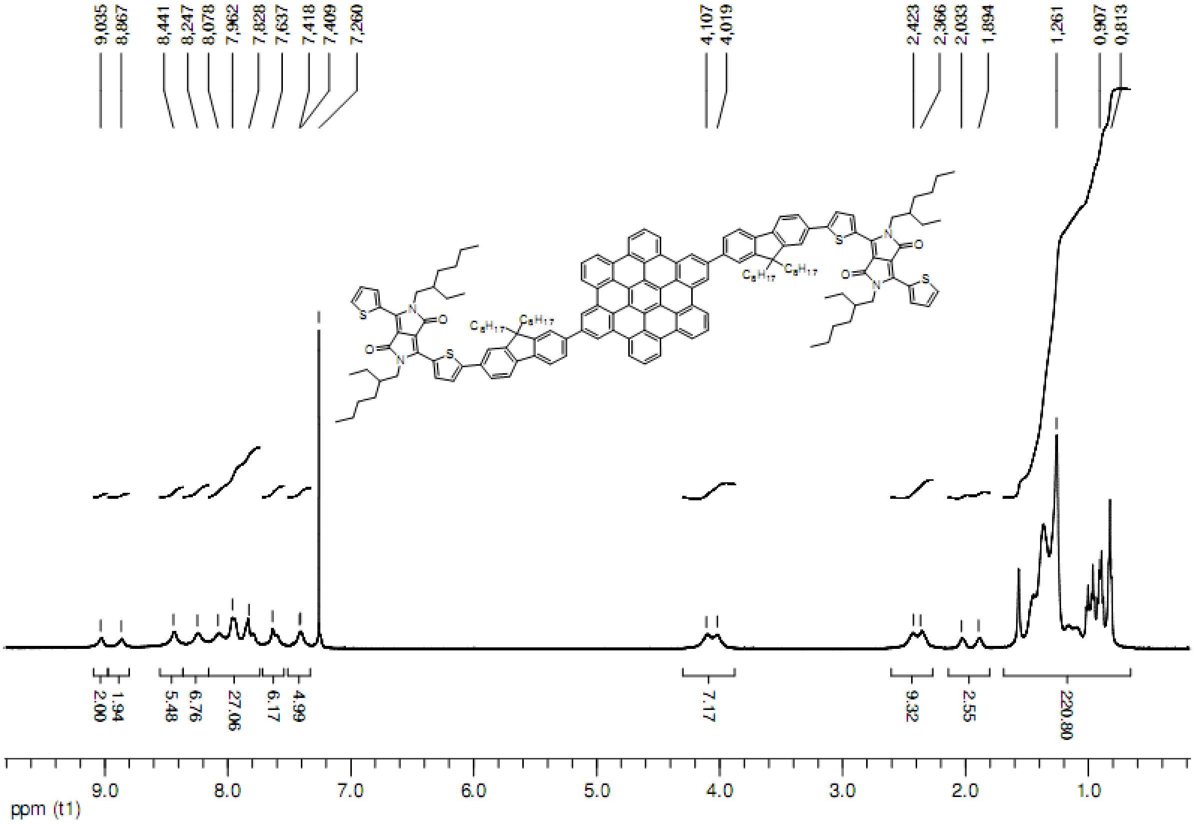


Figure S17. ^{1}H NMR (500 MHz) spectrum of FHBC-DPP **5** in $CDCl_3$.

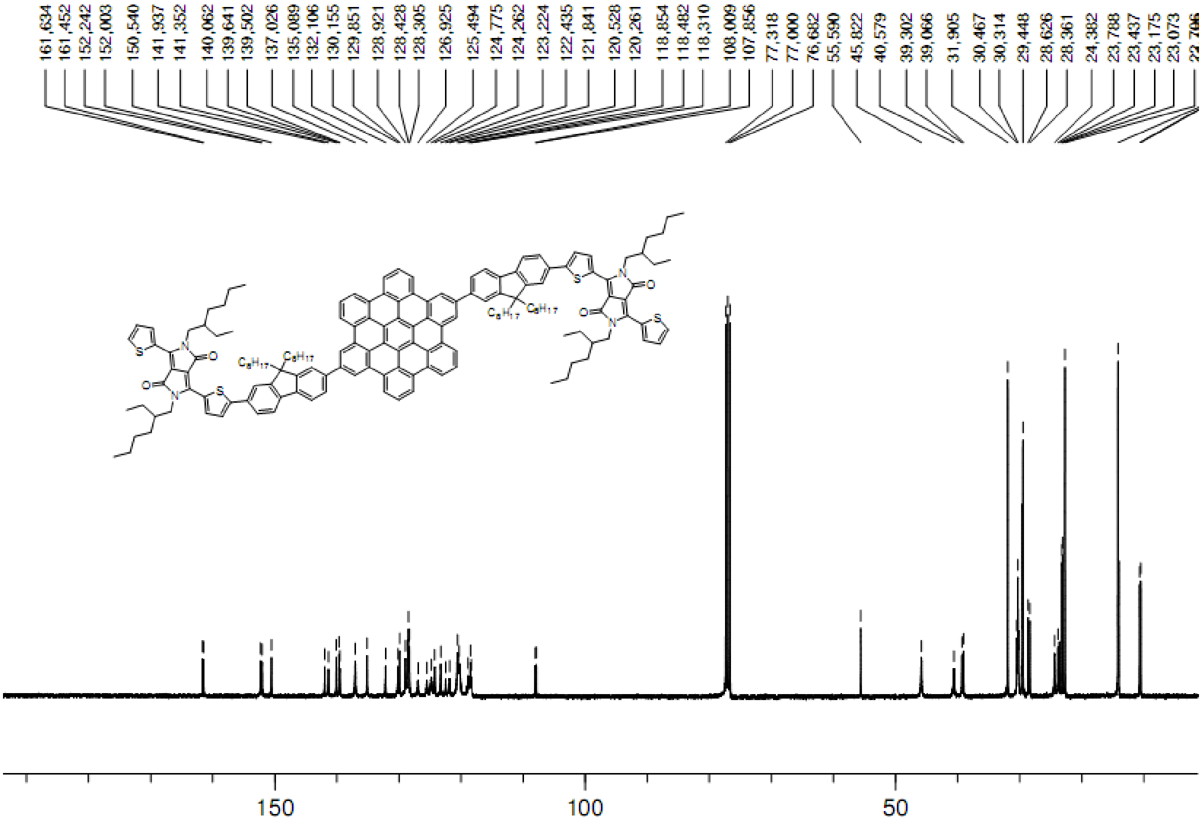


Figure S18. ^{13}C NMR (125 MHz) spectrum of FHBC-DPP **5** in $CDCl_3$.

NMR Data – Compound **6**

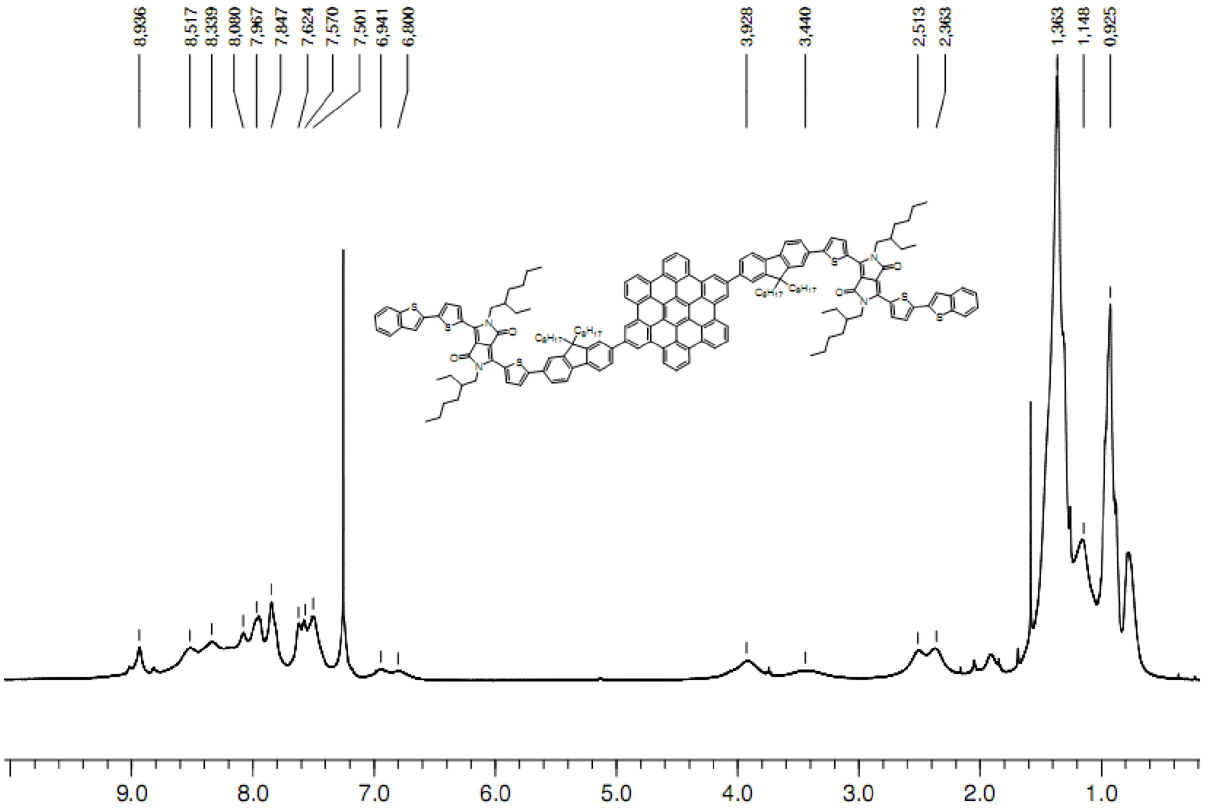


Figure S19. ^{1}H NMR (500 MHz) spectrum of compound **6** in $CDCl_3$.

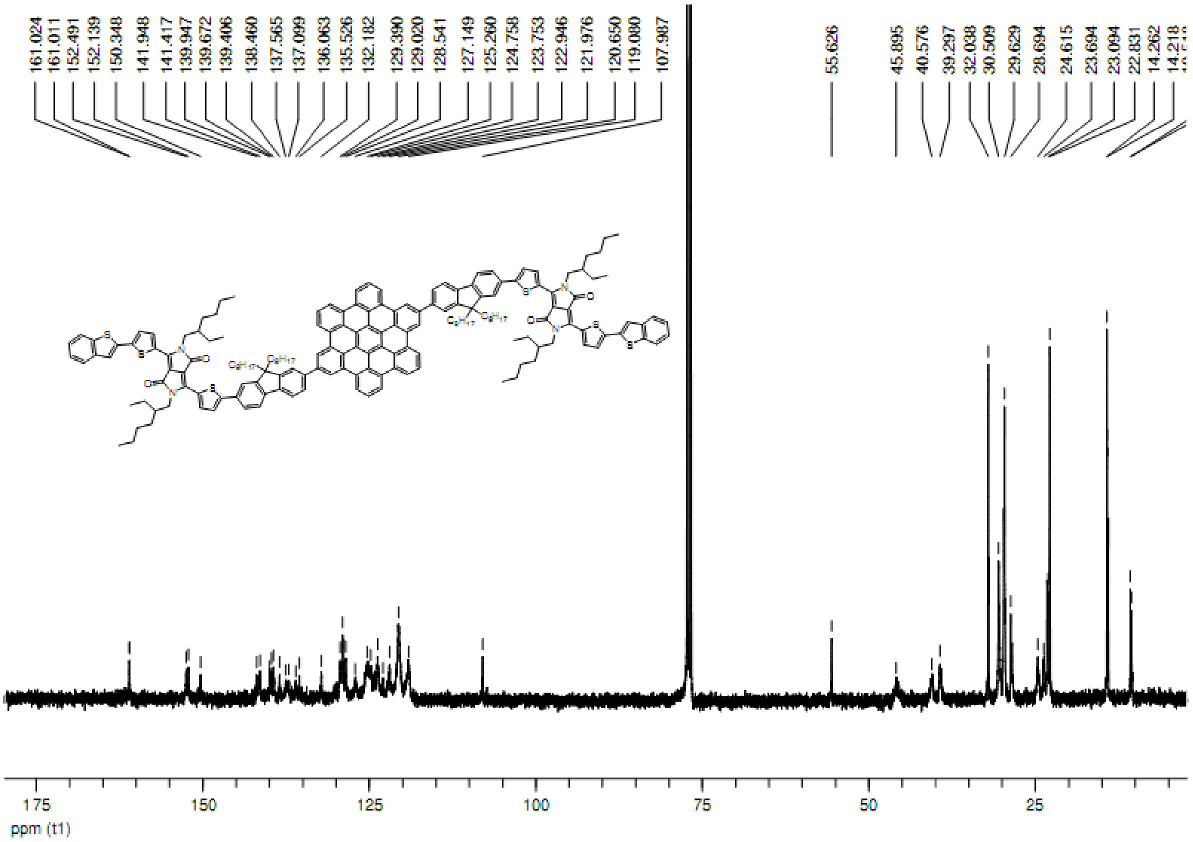


Figure S20. ^{13}C NMR (125 MHz) spectrum of compound **6** in $CDCl_3$.

NMR Data – Compound **7**

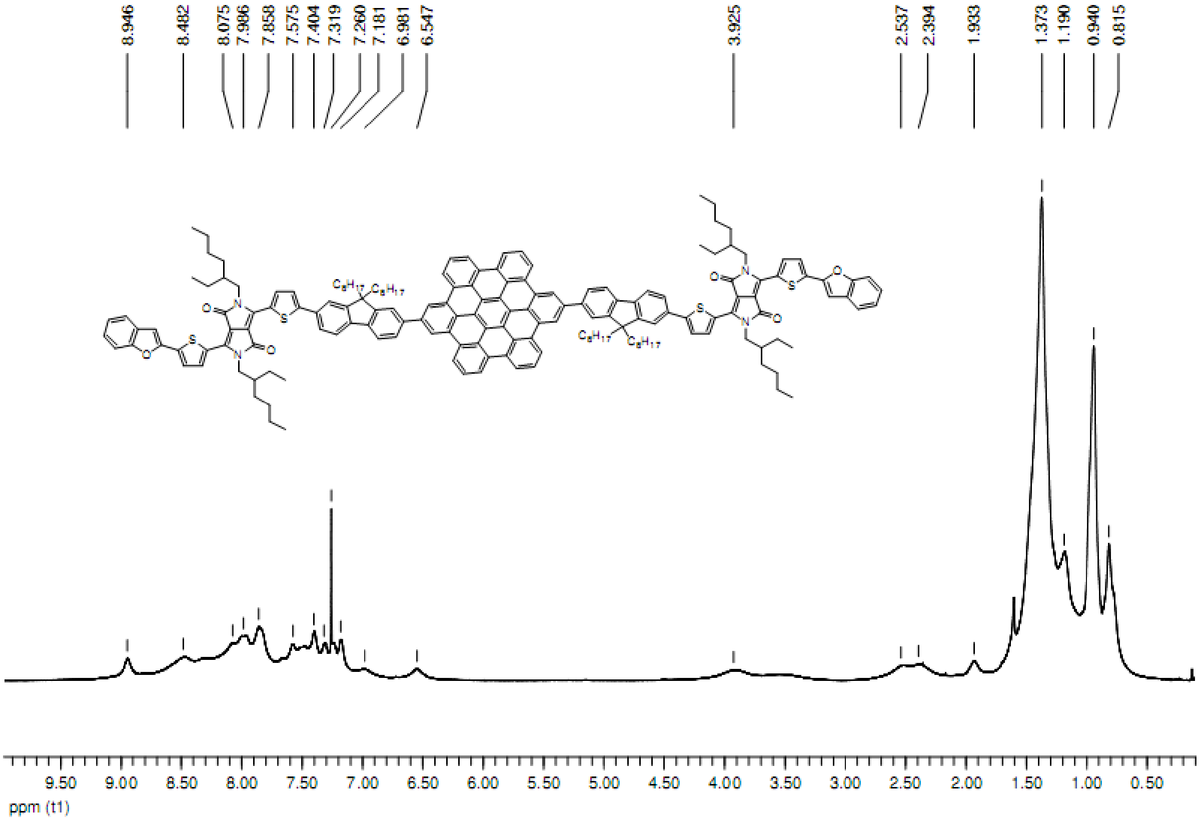


Figure S21. ^{1}H NMR (500 MHz) spectrum of compound **7** in $CDCl_3$.

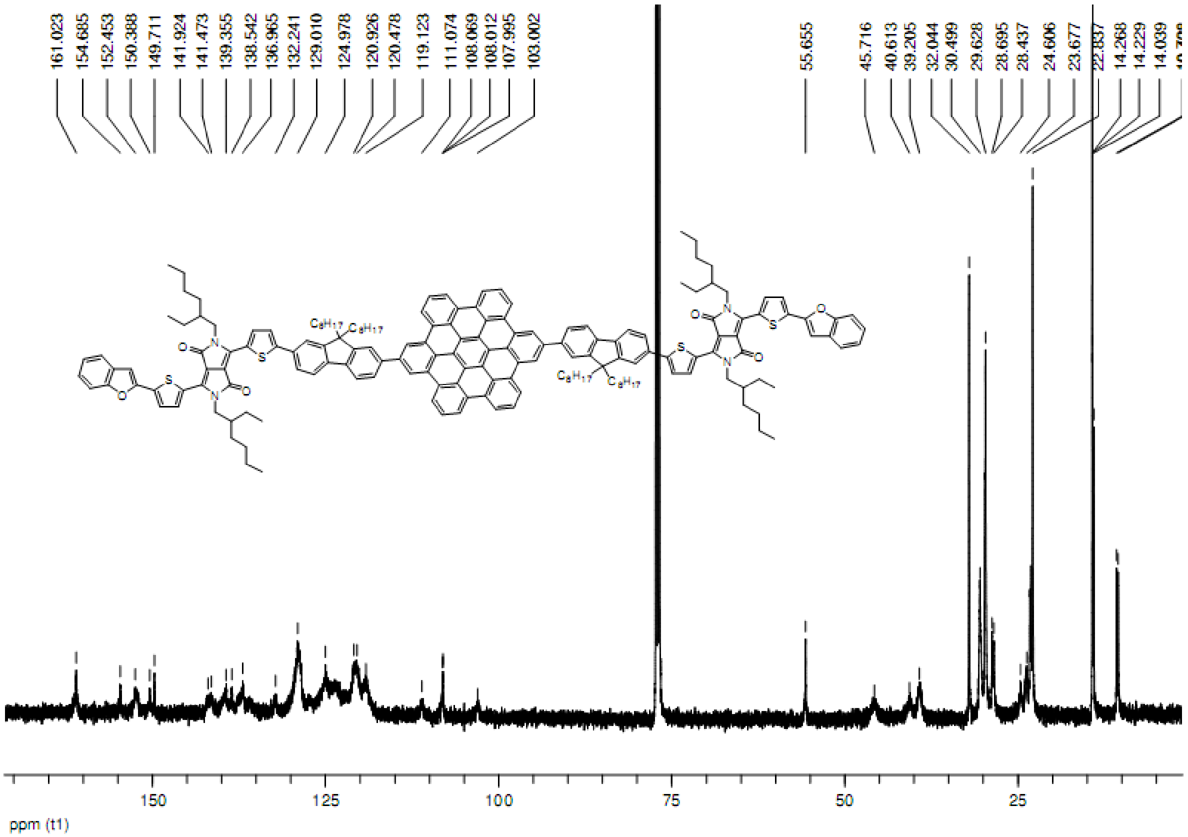


Figure S22. ^{13}C NMR (125 MHz) spectrum of compound **7** in $CDCl_3$.

Thermal properties of FHBC-DPP dyes

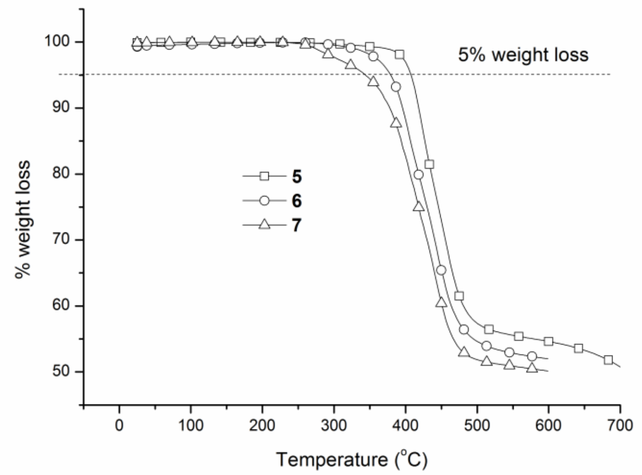


Figure S23. Thermal gravimetric analysis plots of FHBC-DPP compounds showing percentage weight loss.

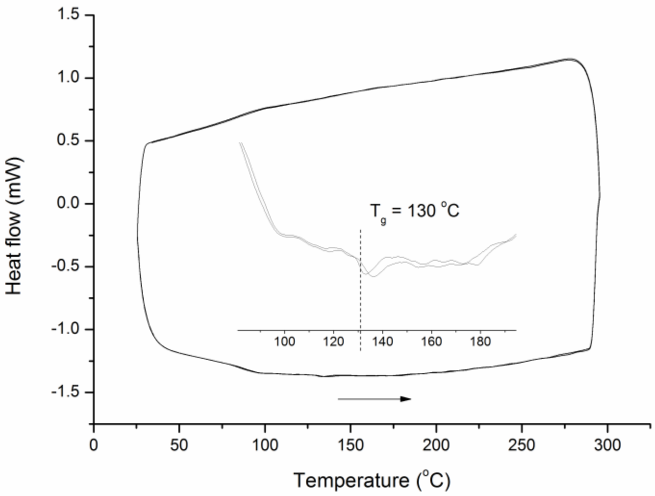


Figure S24. Differential scanning calorimetry data for FHBC-DPP dye **5** showing the second and third heat-cool cycles (20 °C/min). Insert shows the expansion between 100 °C and 180 °C.

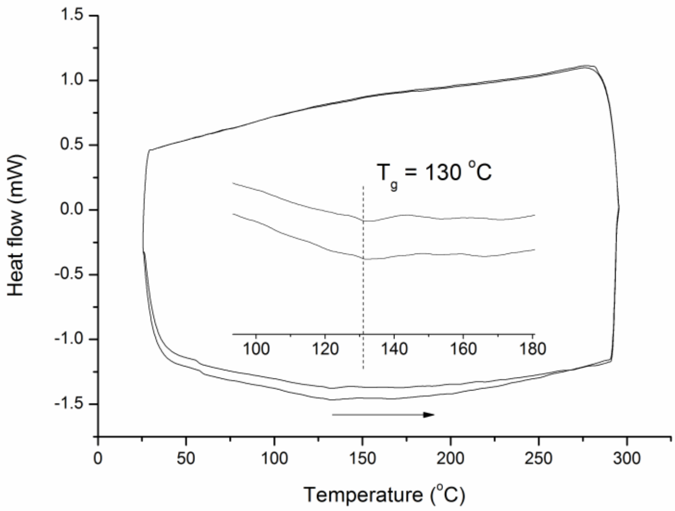


Figure S25. Differential scanning calorimetry data for FHBC-DPP dye **6** showing the second and third heat-cool cycles (20 °C/min). Insert shows the expansion between 100 °C and 180 °C.

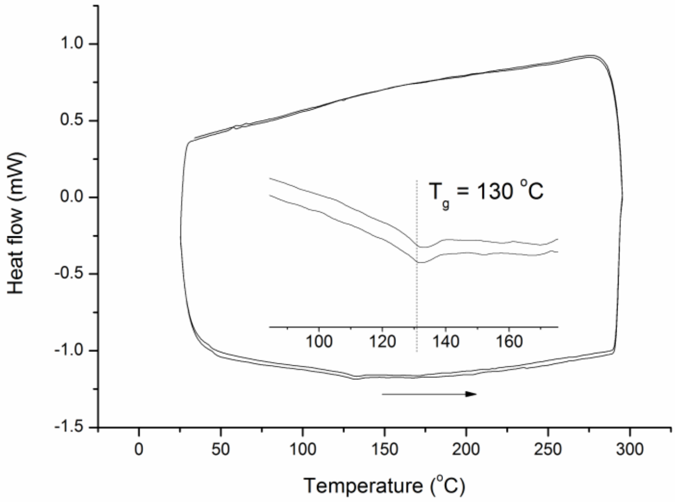


Figure S26. Differential scanning calorimetry data for FHBC-DPP dye **7** showing the second and third heat-cool cycles (20 °C/min). Insert shows the expansion between 100 °C and 180 °C.

UV-vis and fluorescence spectral data

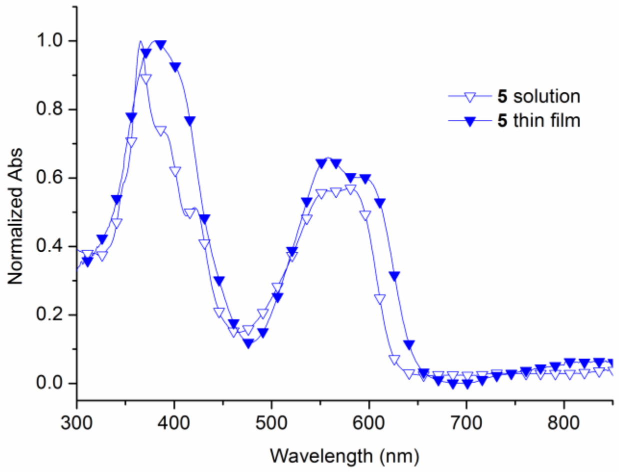


Figure S27. Normalized UV-vis spectrum of FHBC-DPP dye **5** in solution and in solid state.

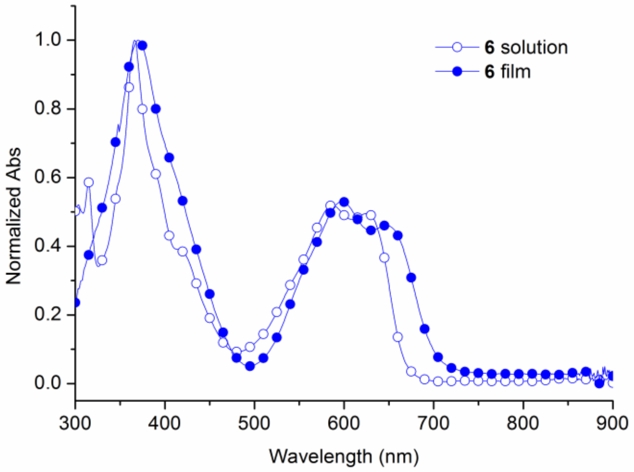


Figure S28. Normalized UV-vis spectrum of FHBC-DPP dye **6** in solution and in solid state.

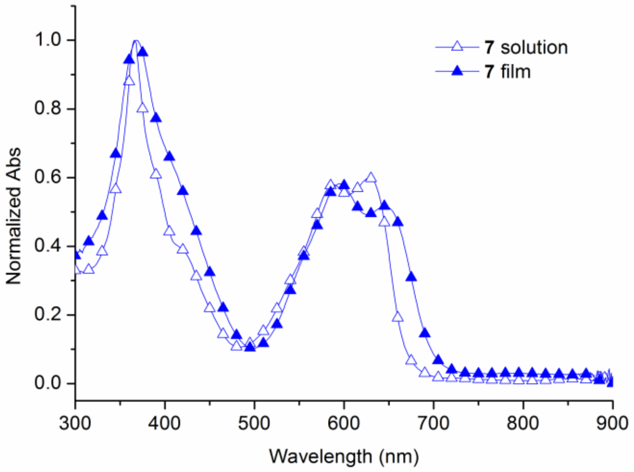


Figure S29. Normalized UV-vis spectrum of FHBC-DPP dye **7** in solution and in solid state.

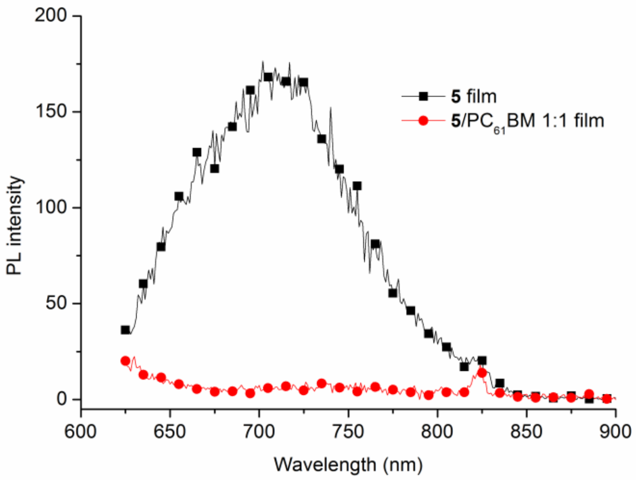


Figure S30. PL spectrum of FHBC-DPP dye **5** and a blend of **5** and $PC_{61}BM$ 1:1 in solid state.

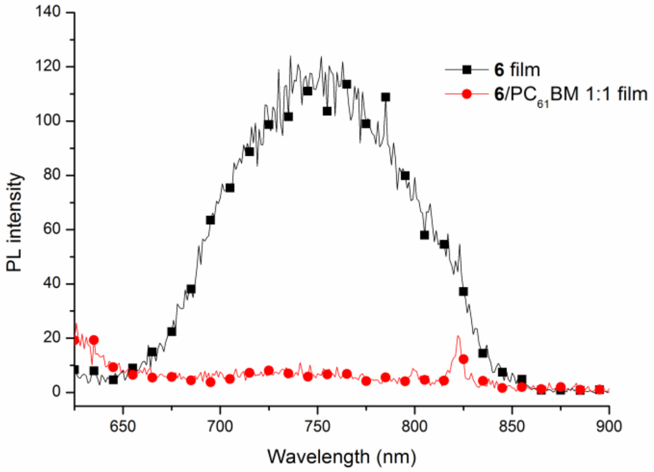


Figure S31. PL spectrum of FHBC-DPP dye **6** and a blend of **6** and $PC_{61}BM$ 1:1 in solid state.

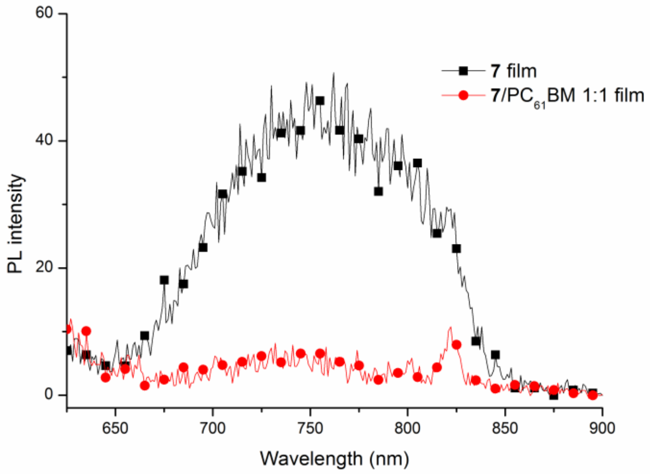


Figure S32. PL spectrum of FHBC-DPP dye **7** and a blend of **7** and $PC_{61}BM$ 1:1 in solid state.

Electrochemistry of FHBC-DPP dyes

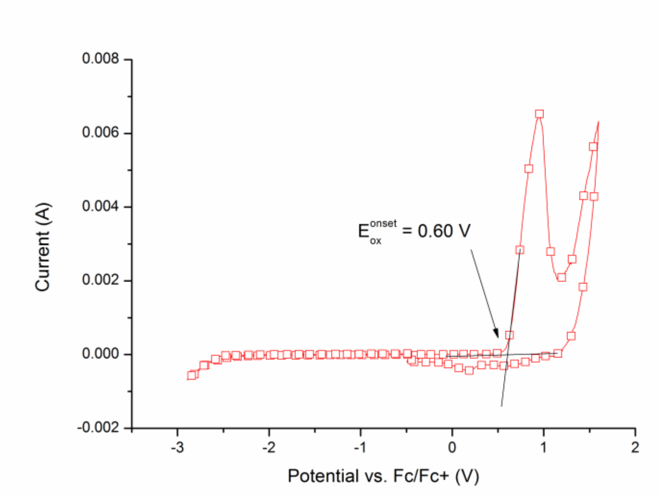


Figure S33. CV curve of **5** in CH_2Cl_2, 1 × 10^{-3} M, Bu_4NPF_6 (0.1 M), 295 K, scan rate = 100 mV·s^{-1}, versus Fc/Fc^+;

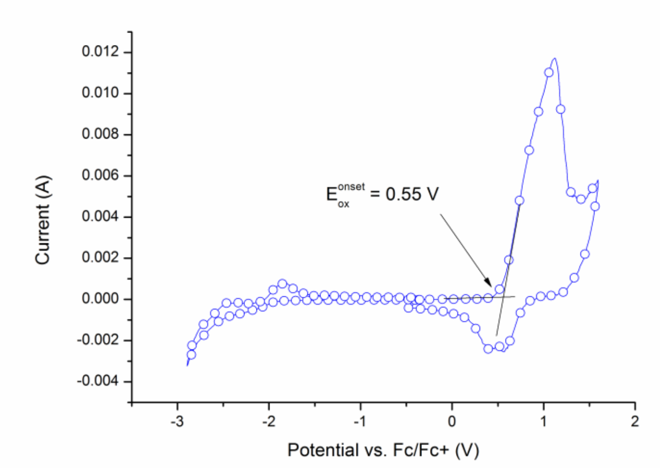


Figure S34. CV curve of **6** in CH_2Cl_2, 1 × 10^{-3} M, Bu_4NPF_6 (0.1 M), 295 K, scan rate = 100 mV·s^{-1}, versus Fc/Fc^+.

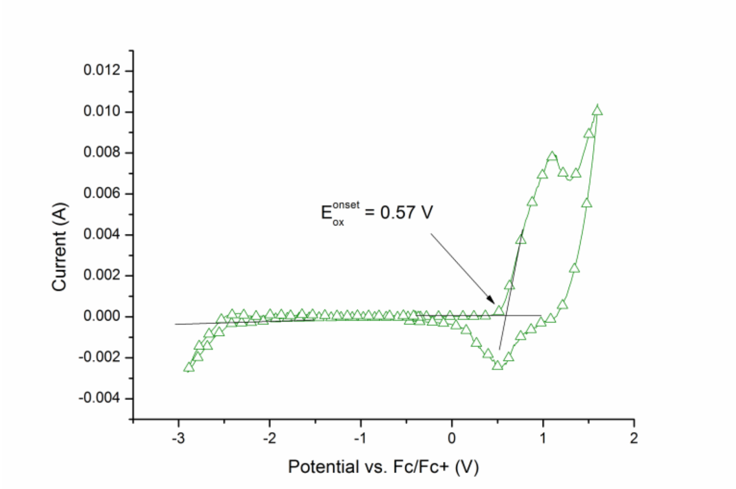


Figure S35. CV curve of **7** in CH_2Cl_2, 1 × 10^{-3} M, Bu_4NPF_6 (0.1 M), 295 K, scan rate = 100 mV·s^{-1}, versus Fc/Fc^+.

Two-dimensional wide-angle X-ray scattering (2D-WAXS)

2D-WAXS measurements were performed using a custom setup consisting of the Siemens Kristalloflex X-ray source (copper anode X-ray tube, operated at 35 kV/20 mA), Osmic confocal MaxFlux optics, two collimating pinholes (1.0 and 0.5 mm – Owis, Germany) and an antiscattering pinhole (0.7 mm – Owis, Germany). The patterns were recorded on a MAR345 image plate detector (Marresearch, Germany). The samples were prepared by filament extrusion using a home-built mini-extruder. Therein, if necessary, the material is heated up to a phase at which it becomes plastically deformable and is extruded as 0.7 mm thin fiber by a constant-rate motion of the piston along the cylinder.

Grazing incidence wide-angle X-ray scattering (GI-WAXS)

Thin films for GI-WAXS experiments were prepared in a similar manner to the solar cell devices. Blends of the dyes and $PC_{71}BM$ (1:2) were prepared in chlorobenzene solution (25 mg/mL). These solutions were spin coated onto PEDOT:PSS covered ITO on glass substrates. The films were annealed at 150 °C for 30 s.

2D-WAXS data was measured on the Australian Synchrotron SAXS/WAXS beamline at a wavelength of 0.6888 Å. The spot size on the sample was 250 (H) x 80 (V) µm FWHM. The height and zero incident angle was calibrated for each individual sample, then data collected at an incident angle of 0.18 ° using a MAR165 CCD detector at a distance of 391 mm from the sample with a vacuum path between the sample and detector.

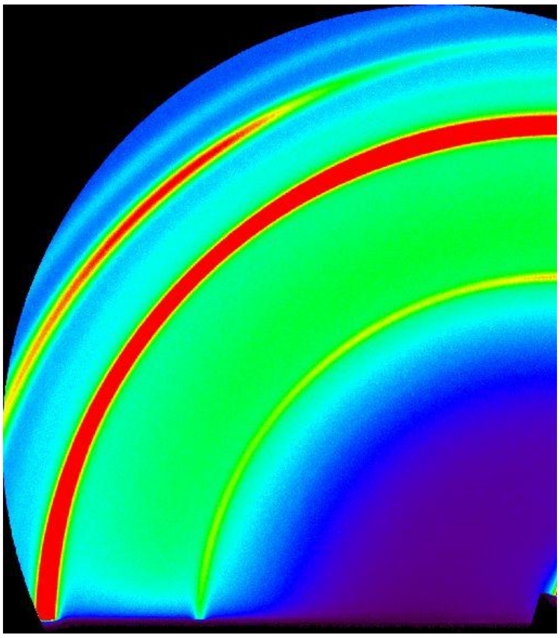


Figure S36. GIWAXS of ITO|PEDOT:PSS|FHBC-DPP **6**:$PC_{71}BM$ (1:2 w/w) thin film.

Field-effect transistors

For all the devices fabricated and studied, highly doped silicon was used as the gate electrode, while a 200 nm thick SiO2 oxide film was used as the dielectric. Bottom contact (channel lengths L = 5-100 µm and widths W = 0.35 to 7.0 mm, W/L = 70) FETs were prepared by spin coating, 25 mg/ml in chlorobenzene solution on top of the SiO_2 dielectric modified with self-assembled monolayers (SAMs) of HMDS (by vapor deposition). The electrical characterization by using a Keithley SCS 4200 was performed inside a nitrogen filled glovebox (oxygen and humidity < 0.1 ppm, pressure ~ 1120 Pa) at room temperature (~ 25°C). Devices were measured before and after thermal annealing (150 °C, 45 min). However, no significant changes in charge mobility was observed.

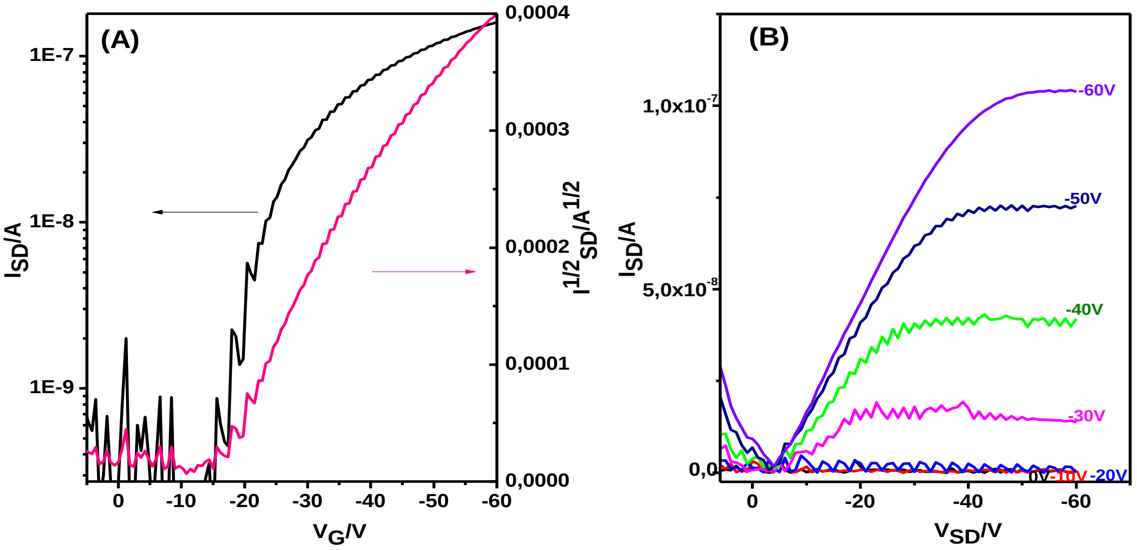


Figure S37. a) Transfer (at V_{SD} = -60 V) and b) output curves at different gate voltages of **5**.

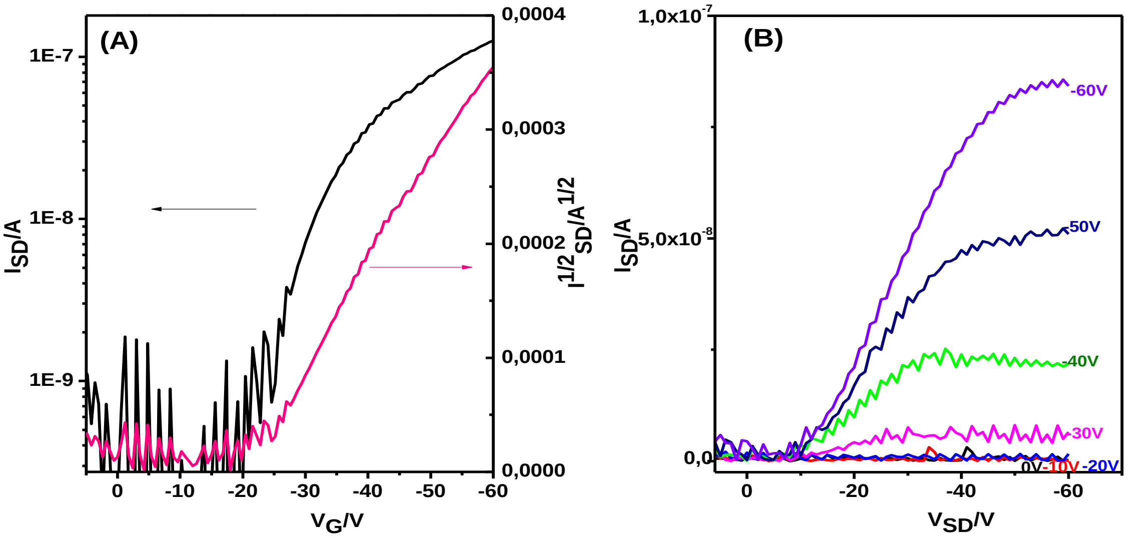


Figure S38. a) Transfer (at V_{SD} = -60 V) and b) output curves at different gate voltages of **7**.

Space-charge limited current experiments:

The space charge limited current (SCLC) in the organic dyes (5, 6 & 7) were studied using hole-only devices to find the charge-transport properties. The hole-only devices, consisting of a organic dye (5/6/7) sandwiched between a PEDOT:PSS coated ITO electrode and MoO_3/Au counter-electrode as the electron-blocking contact, were fabricated as shown in figure S31. From the current density as a function of voltage data, the hole mobility in the trap-free space-charge limited current (SCLC) region can be estimated using the Mott-Gurney equation for trap-free SCLC $J = {}^{9}\!/_{8}\,\mu\varepsilon\frac{V^2}{d^3}$, where ε is the dielectric constant, μ is the chargecarrier mobility, d is the sample thickness. Using this expression, the hole mobility of the pristine dye molecules (5, 6 & 7) were calculated.

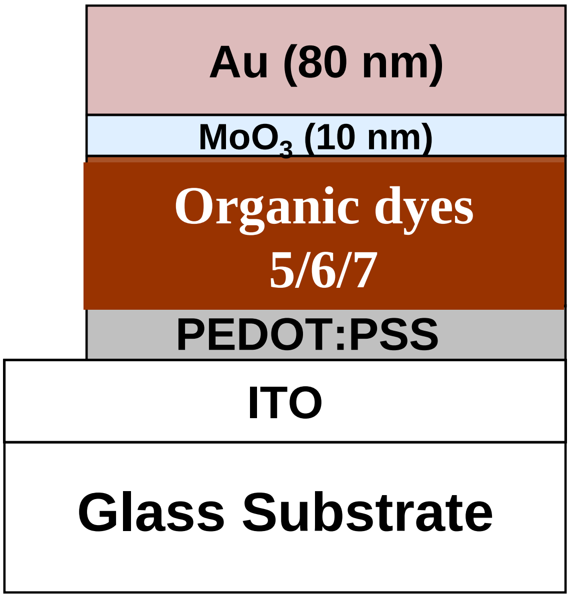


Figure S39: The schematic diagram of hole-only device geometry.

Bulk heterojunction solar cell fabrication

Poly(3,4-ethylenedioxythiophene): poly(styrenesulfonate) (PEDOT:PSS, Baytron P AI 4083) was spin-coated (5000 rpm) on patterned ITO glasses which were washed by detergent, deionized water, methanol, acetone and 2-propanol in ultrasonication bath and UV/ozone treated. The films were baked at 150 °C for 5 min in air. Solutions of dye/fullerene blends were prepared in chlorobenzene (25 mg/mL). The resulting solutions were spin coated on the PEDOT:PSS films. TiO_x precursor solution (1:200 in methanol) was deposited on the active layer by spin coating (2000 rpm) to form ~10 nm of TiOx layer.[2] The films were exposed to air for about 20 min at room temperature for hydrolysis. The films were transferred to a metal evaporation chamber and aluminum (100 nm) were deposited through a shadow mask (active area was 0.20 cm^2) at approximately 1×10^{-6} torr. Film thickness was determined by Veeco Dektak 150+ Surface Profiler. The thickness of the photoactive layers was optimised for each of the donor-acceptor blends and was typically around 80 nm. The solar cells were illuminated at 100 mW cm^{-2} using 1 kW Oriel solar simulator with an AM 1.5G filter in air and *J-V* curves were measured using a Keithley 2400 source measurement unit. For accurate measurement, the light intensity was calibrated using a reference silicon solar cell (PVmeasurements Inc.) certified by the National Renewable Energy Laboratory. Spectral response was measured with a Keithley 2400 source meter, using monochromatic light from a Xe lamp in combination with monochromator (Oriel, Cornerstone 130). A calibrated Si cell was used as reference.

Morphology of active layer blend

Atomic force microscopy (NanoScope II, Dimension, Digital Instrument Inc.) was carried out with commercially available tapping mode tips. The scanning area is between $10\times10\mu m^2$ and $1\times1\ \mu m^2$. The AFM samples were prepared by spin casting the material of interest (25 mg/mL in chlorobenzene, 2000 rpm) on silicon substrate.

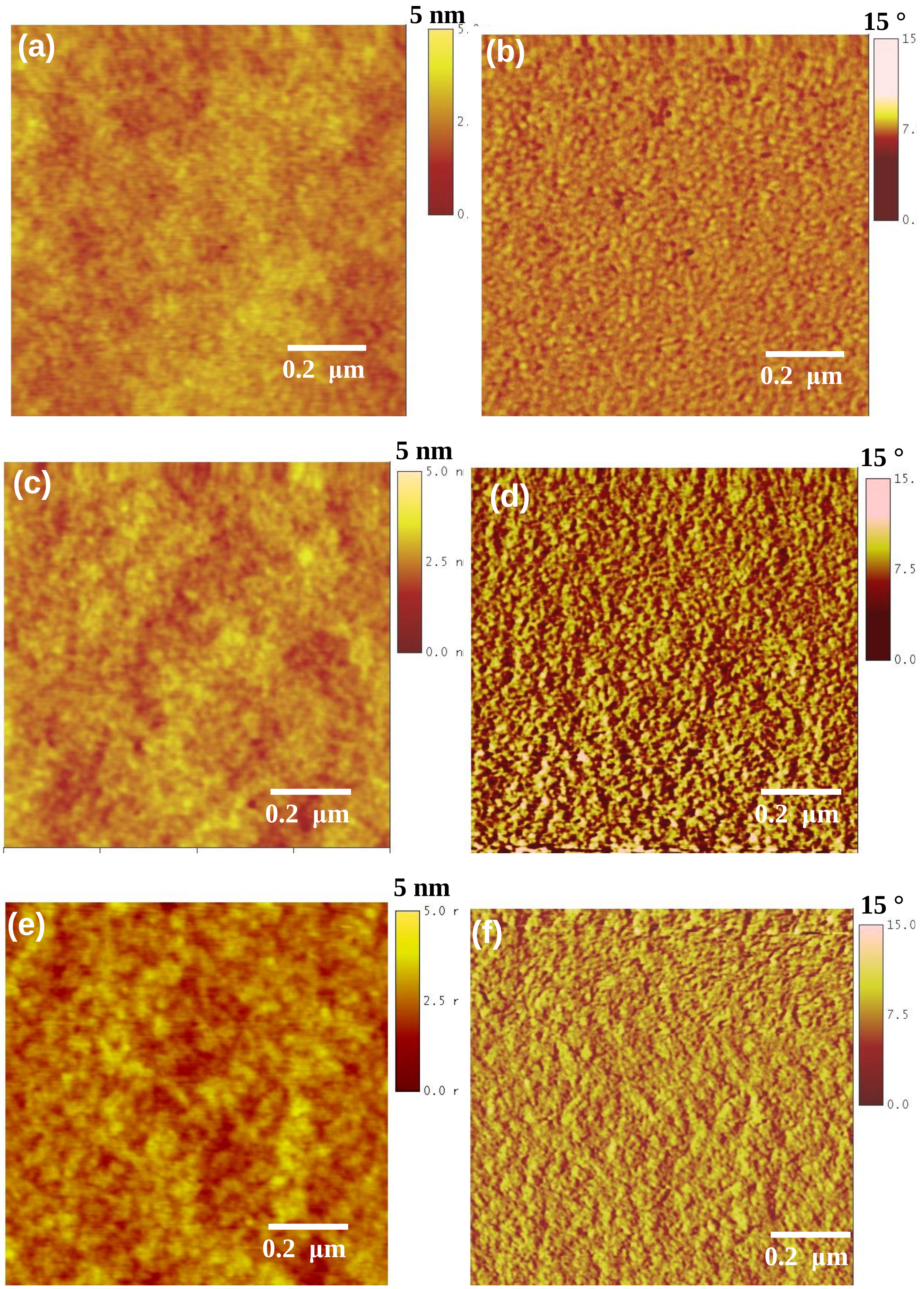


Figure S40: AFM Height images of active layer from the blends of (a) dye5:$PC_{70}BM$, (c) dye6:$PC_{70}BM$ (e) dye7:$PC_{70}BM$ and corresponding phase image are shown in (b), (d) and (f).

References

1. W. W. H. Wong, T. Khoury, D. Vak, C. Yan, D. J. Jones, M. J. Crossley and A. B. Holmes, *J. Mater. Chem.*, 2010, **20**, 7005-7014.
2. J. Y. Kim, S. H. Kim, H.-H. Lee, K. Lee , W. Ma, X. Gong, A. J. Heeger,
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