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Supporting Information

Investigated Structure-Property Relationship of Thiadiazoloquinoxaline-Based Copolymer Semiconductors via Molecular Engineering

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Contents

EXPERIMENTAL SECTION

(1) General methods

^{1}H NMR and ^{13}C NMR spectra were recorded in deuterated solvents on a Bruker DPX 250. High Resolution Mass Spectra (HRMS) were carried out by the Microanalytical Laboratory of Johannes Gutenberg-University, Mainz. Elemental analysis was carried out using a Foss Heraeus Vario EL in the Institute of Organic Chemistry at the Johannes Gutenberg-University, Mainz. UV–Vis-NIR absorption spectra were measured on a Perkin-Elmer Lambda 9 spectrophotometer at room temperature. Thermogravimetry analysis (TGA) were carried out on a Mettler 500 Thermogravimetry Analyzer. Cyclic Volatammetry (CV) was carried out on a computer-controlled GSTAT12 in a three-electrode cell in anhydrous solvents solution of Bu_4NPF_6 (0.1 M) with a scan rate of 50 mV/s at room temperature under argon (dichloromethane for both monomers and acetonitrile for both polymers). A Pt wire, a silver wire, and a glassy carbon electrode were used as the counter electrode, the reference electrode, and the working electrode, respectively. For the monomers, the measurements were carried out using a 0.1 mol/L dichloromethane solution of n-Bu_4NPF_6 as electrolyte, while the analyte were dissolved in a concentration of 10^{-3} mol/L. EA were estimated from the onsets of the first reduction peak, while the potentials were determined using ferrocene (Fc) as standard by empirical formulas EA = - (E_{Red}^{onset}- $E_{Fc/Fc+}^{1/2}$+4.8) eV wherein $E_{Fc/Fc+}^{1/2}$ = 0.63 eV.[1] The molecular weights were determined by PSS-WinGPC (PSS) (pump: alliance GPC 2000) GPC equipped with an UV or RI detector running in 1,2,4-trichlorobenzene at 135 °C using a PLgel MIXED-B column (particle size: 10 mm, dimension: 0.8×30 cm) calibrated against polystyrene standards.

(2) OFET device fabrication and measurements

All FETs were fabricated employing the bottom-gate, bottom-contact architecture. The 200 nm thick SiO_2 dielectric covering the highly doped Si which acts as the gate electrode was functionalized with hexamethyldisilazane (HMDS) to minimize interfacial trapping sites. Polymer thin films were deposited by drop-coating 2 mg mL^{-1} chlorobenzene solution on FET substrates in nitrogen atmosphere, followed by annealing at 180 °C for 30 min. The channel length and width are 20 and 1400 μm, respectively. All electrical measurements (using Keithley 4200 SCS) were performed in a glovebox under nitrogen atmosphere.

(3) 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.

(4) Synthetic details

All chemicals and reagents were used as received from commercial sources without further purification unless stated otherwise. Chemical reactions were carried out under ambient atmosphere. Intermediates 4,7-bis(4-dodecylthiophen-2-yl)benzo[c][1,2,5]thiadiazole-5,6-diamine (**1**),[2] 1,2-bis(4-dodecylphenyl)ethane-1,2-dione (**2**),[3] 4,7-di(thiophen-2-yl)benzo[c][1,2,5]thiadiazole-5,6-diamine (**5**),[4] 4,7-bis(4-(2-decyltetradecyl)thiophen-2-yl)-5,6-dinitrobenzo[c][1,2,5]thiadiazole (**8**),[1] 2,5-bis(trimethylstannyl)thiophene (**13**),[5] 2,5-bis(trimethylstannyl)thieno[3,2-b]thiophene (**14**),[6] 2,6-bis(trimethylstannyl)benzo[1,2-b:4,5-b']dithiophene (**15**),[7] 5,5'-bis(trimethylstannyl)-2,2'-bithiophene (**16**),[1] and (3,3'-didodecyl-[2,2'-bithiophene]-5,5'-diyl)bis(trimethylstannane) (**17**)[2] were prepared according to the literature procedures.

6,7-Bis(4-dodecylphenyl)-4,9-bis(4-dodecylthiophen-2-yl)-[1,2,5]thiadiazolo[3,4-g]quinoxaline (3)

A suspension of **1** (0.2 g, 0.30 mmol), **2** (0.164 g, 0.30 mmol) and 20 mL acetic acid were placed into a 50 mL Schlenk tube. The mixture was heated to 55 ºC and stirred overnight. After cooling to room temperature, the product was filtered and washed with methanol. The crude product was purified by column using hexane/dichloromethane as eluent to give 0.328 g of compound **3** (green solid, 93 %). ^{1}H NMR (250 MHz, CD_2Cl_2) δ 8.83 (d, *J* = 2.50 Hz, 2H), 7.73 (s, *J* = 10.0 Hz, 4H), 7.9 (m, 6H), 2.80-2.64 (m, 8H), 1.78-1.63 (br, 8H), 1.28 (br, 72H), 0.90-0.85 (br, 12H). ^{13}C NMR (62.5 MHz, CD_2Cl_2) δ 153.63, 152.27, 145.38, 143.44, 136.09, 135.96, 135.24, 135.02, 130.88, 128.63, 126.86, 121.39, 36.21, 32.34, 31.67, 31.19, 30.99, 30.12, 30.08, 29.98, 29.93, 29.88, 29.78, 29.73, 23.10, 14.29. HRMS (ESI+): m/z calcd 1177.8127, found 1177.8116.

4,9-Bis(5-bromo-4-dodecylthiophen-2-yl)-6,7-bis(4-dodecylphenyl)-[1,2,5]thiadiazolo[3,4-g]quinoxaline (4)

Compound **3** (236 mg, 0.2 mmol) was dissolved in 15 mL THF at the room temperature. NBS (39 mg, 0.22 mmol) was carefully added into the solution in small batches under darkness. The mixture was stirred for 5 h. The solvent was removed under reduced pressure to give crude product, which was purified by column chromatography to give monomer **4** as a green solid (198 mg, 74 %). ^{1}H NMR (250 MHz, CD_2Cl_2) δ 8.70 (s, 2H), 7.53 (d, *J* = 7.50 Hz, 4H), 7.20 (d, *J* = 10.0 Hz, 4H), 2.72-2.58 (m, 8H), 1.69 (br, 8H), 1.31-1.27 (br, 72H), 0.91-084 (br, 12H). ^{13}C NMR (62.5 MHz, CD_2Cl_2) δ 153.78, 151.18, 145.35, 142.03, 135.83, 135.48, 134.46, 134.46, 131.16, 128.46, 119.93, 118.15, 36.26, 32.37, 31.66, 30.26, 30.18, 30.16, 30.12, 30.04, 30.01, 29.99, 29.94, 29.85, 23.13, 14.31. HRMS (ESI+): m/z calcd 1333.6338, found 1333.6329.

6,7-Bis(4-dodecylphenyl)-4,9-di(thiophen-2-yl)-[1,2,5]thiadiazolo[3,4-g]quinoxaline (6)

Compound **6** was prepared from compound **2** (164 mg, 0.3 mmol) and **5** (99 mg, 0.3 mmol) in similar procedure to compound **3**. Compound **6** (green solid, 215 mg, 85 %). ^{1}H NMR (250 MHz, THF-d_8) δ 9.11-9.09 (dd, *J* = 2.50 Hz, *J* = 5.0 Hz, 2H), 7.76-7.69 (m, 6H), 7.27-7.22 (m, 6H), 2.68 (t, *J* = 7.50 Hz, 4H), 1.71-1.63 (br, 4H), 1.38-1.29 (br, 36H), 0.89 (t, *J* = 7.50 Hz, 6H). ^{13}C NMR (62.5 MHz, THF-d_8) δ 154.51,151.57, 145.58, 138.24, 136.04, 134.68, 134.09, 131.63, 130.17, 128.70, 120.88, 120.51, 36.50, 32.72, 32.01, 30.52, 30.47, 30.36, 30.25, 30.17, (overlap with THF-d_8) , 23.40, 14.28. HRMS (ESI+): m/z calcd 841.4371, found 841.4370.

4,9-Bis(4-(2-decyltetradecyl)thiophen-2-yl)-6,7-diphenyl-[1,2,5]thiadiazolo[3,4-g]quinoxaline (11)

Compound **8** (0.5 g, 0.47 mmol) and fine iron powder (311 mg, 5.55 mmol) in acetic acid (15 mL) were stirred for 5 h at 75 °C under Argon. The reaction mixture was cooled to room temperature, precipitated in 5% aqueous NaOH and extracted with diethyl ether. The combined organic layers were washed with brine, dried with $MgSO_4$.The solvent was removed under reduced pressure to give corresponding diamine **9** with deep red oil. This crude product was directly added into acetic acid (15 mL) solution of benzyl **10** (99 mg, 0.47 mmol). The mixture was heated to 80 °C overnight under argon. After cooling down to room temperature, the mixture was poured into 100 mL 5% aqueous NaOH and extracted with dichloromethane. The combined organic phases were dried with $MgSO_4$ and filtered. The filtrate was concentrated and purified by column chromatography eluting with hexane dichloromethane (4:1) to give 0.387 g (green solid, two steps 70%) of compound **11**. ^{1}H NMR (250 MHz, CD_2Cl_2, ppm) δ 8.87 (d, *J* = 2.5 Hz, 2H), 7.82-7.78 (m, 4H), 7.47-7.38 (m, 6H), 7.27 (d, 2H), 2.72 (d, *J* = 5.0 Hz, 4H), 1.80-1.73 (m, 2H), 1.28-1.24 (br, 80H), 0.88-0.83 (m, 12H). ^{13}C NMR (62.5 MHz, CD_2Cl_2, ppm) δ 153.39, 152.32, 142.10, 138.64, 135.85, 135.73, 135.14, 130.98, 129.88, 128.58, 128.15, 121.59, 39.48, 35.29, 33.79, 32.33, 30.50, 30.13, 30.08, 30.07, 29.77, 27.07, 23.10, 14.29. HRMS (ESI+): m/z calc. 1177.8127 found 1177.8153.

4,9-Bis(5-bromothiophen-2-yl)-6,7-bis(4-dodecylphenyl)-[1,2,5]thiadiazolo[3,4-g]quinoxaline(7) and **4,9-bis(5-bromo-4-(2-decyltetradecyl)thiophen-2-yl)-6,7-diphenyl-[1,2,5]thiadiazolo[3,4-g]quinoxaline (12)**

Compound **7** and **12** were prepared from corresponding precursors compound **6** (168 mg, 0.2 mmol) and **11** (235 mg, 0.2 mmol) in similar procedure to compound **4**. For **7** (green solid, 172 mg, 86 %) ^{1}H NMR (250 MHz, THF-d_8) δ 8.90 (d, *J* = 5.0 Hz, 2H), 7.66-7.63 (dd, *J* = 2.5 Hz, *J* = 5.0 Hz, 4H), 7.28-7.25 (dd, *J* = 2.5 Hz, *J* = 5.0 Hz, 4H), 7.21(d, *J* = 5.0 Hz, 2H), 2.71 (t, *J* = 7.50 Hz, 4H), 1.71-1.65 (br, 4H), 1.41-1.25 (br, 36H), 0.89 (t, *J* = 7.50 Hz, 6H). ^{13}C NMR (62.5 MHz, THF-d_8) δ 154.01, 152.40, 145.24, 136.67, 136.64, 135.31, 133.79, 131.89, 131.45, 128.67, 126.90, 121.73, 36.49, 32.70, 32.02, 30.49, 30.45, 30.33, 30.20, 30.15, (overlap with THF-d_8) ,

23.39, 14.26. HRMS (ESI+): m/z calc. 997.2582 found 997.2589; For **12** (green solid , 232 mg, 87 %) ^{1}H NMR (250 MHz, CD_2Cl_2, ppm) δ 8.83 (s, 2H), 7.72-7.67 (m, 4H), 7.75-7.38 (m, 6H), 2.62 (d, *J* = 7.5 Hz, 4H), 1.81 (br, 2H), 1.36-1.22 (br, 80H), 0.88-0.82 (m, 12H). ^{13}C NMR (62.5 MHz, CD_2Cl_2, ppm) δ 153.76, 151.60, 141.34, 138.07, 135.67, 135.40, 134.71, 131.14, 130.05, 128.56, 120.48, 119.14, 38.98, 34.54, 33.81, 32.34, 30.50, 30.15, 30.13, 30.08, 29.78, 26.97, 23.10, 14.30. HRMS (ESI+): m/z calc. 1333.6338 found 1333.6306.

Synthesis of P1

Compound **4** (0.1 mmol), compound **5** (0.1 mmol), chlorobenzene (8 mL) were placed in a 50 mL two-neck flask. The mixture was purged with argon for 5 min, and then 5.5 mg of tris(dibenzylideneacetone)dipalladium(0) ($Pd_2(dba)_3$) and 7.3 mg of tri(*o*-tolyl)phosphine (P(*o*-tolyl)$_3$) were added. Then the mixture was heated up to 110 °C under argon. After 3 days, the polymer was end-capped with tributylphenylstannane and bromobenzene in sequence. After cooling to room temperature, the reaction mixture was added into methanol. The polymer was filtered and subjected to Soxhlet extraction with methanol, acetone, hexane, chloroform and chlorobenzene. The chlorobenzene fraction was collected and added 30 mL of sodium diethyldithiocarbamate aqueous solution (1g/ 100 ml) to remove residual Pd catalyst, the mixture was heated to 60 °C with vigorous stirring for 2 h. The mixture was separated and organic phase was washed with water for 3 times. The polymer was collected from the chlorobenzene fraction and dried in vacuum to afford black solid (103 mg, 81 %). Molecular weight by GPC (135 °C): M_n = 7.0 kDa, PDI = 2.68. Anal. Calcd for C80H112N4S4: C, 76.40; H, 8.97; N, 4.45; S, 10.17. Found: C, 75.44; H, 10.17; N, 4.27; S, 10.13.

Synthesis of P2, P3 and **P4**

P2, **P3** and **P4** were prepared from acceptor **4** and donors **14, 15** and **16** in similar procedure and workup to **P1**.

P2 (black solid, 88 mg, 67 %). Molecular weight by GPC (135 °C): M_n = 5.4 kDa, PDI = 2.15. Anal. Calcd for C82H112N4S5: C, 74.97; H, 8.59; N, 4.26; S, 12.17. Found: C, 74.08; H, 9.42; N, 4.13; S, 11.79.

P3 (black solid, 118 mg, 86 %). Molecular weight by GPC (135 °C): M_n = 8.0 kDa, PDI = 2.34. Anal. Calcd for C86H114N4S5: C, 75.75; H, 8.42; N, 4.11; S, 11.72. Found: C, 74.41; H, 10.02; N, 3.88; S, 11.41.

P4 (black solid, 77 mg, 57 %). Molecular weight by GPC (135 °C): M_n = 9.1 kDa, PDI = 2.33. Anal. Calcd for C84H112N4S5: C, 75.31; H, 8.58; N, 4.18; S, 11.93. Found: C, 74.18; H, 8.94; N, 3.98; S, 11.73.

Synthesis of P5 and **P6**

P5 and **P6** were prepared from acceptors **7** and **12** and donors **17** and **16** in similar procedure to **P1**. Due to good solubility of **P5** and **P6**, both polymer fractions were collected from chloroform.

P5 (black solid, 115 mg, 85 %). Molecular weight by GPC (135 °C): M_n = 12.7 kDa, PDI = 4.05. Anal. Calcd for C84H114N4S5: C, 75.31; H, 8.58; N, 4.18; S, 11.93. Found: C, 74.08; H, 10.00; N, 4.02; S, 11.87.

P6 (black solid, 96 mg, 71 %). Molecular weight by GPC (135 °C): M_n = 18.8 kDa, PDI = 3.48. Anal. Calcd for C84H114N4S5: C, 75.31; H, 8.58; N, 4.18; S, 11.93. Found: C, 74.67; H, 10.29; N, 4.11; S, 11.06.

Table S1 The HOMO and LUMO levels of **PTQ**, **TQ-2T**, **T**, **TT**, **BDT** and **BT**. Calculations were carried out using the DFT//B3LYP/6-31G* level.

	PTQ	**TQ-2T**	**T**	**TT**	**BDT**	**BT**
HOMO (eV)	-6.08	-5.02	-6.34	-6.04	-5.47	-5.54
LUMO (eV)	-3.03	-3.13	-0.21	-0.99	-1.08	-1.18

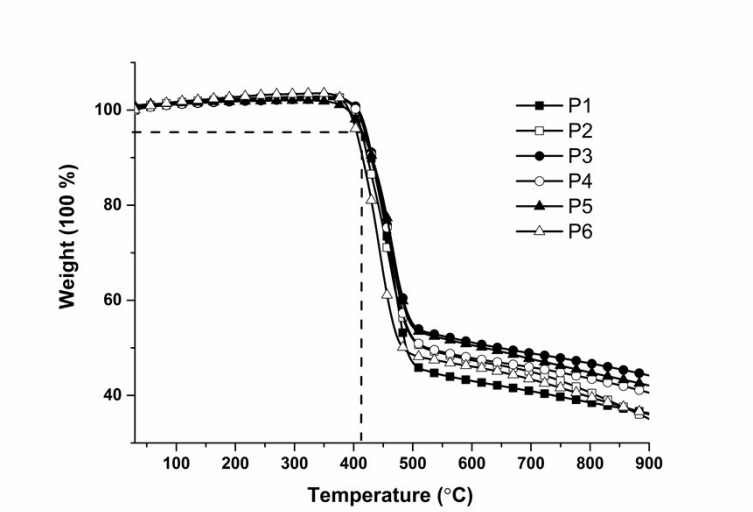

Figure S1. TGA curves for **P1-P6** measured under nitrogen atmosphere at a heating rate of 10 ºC/min.

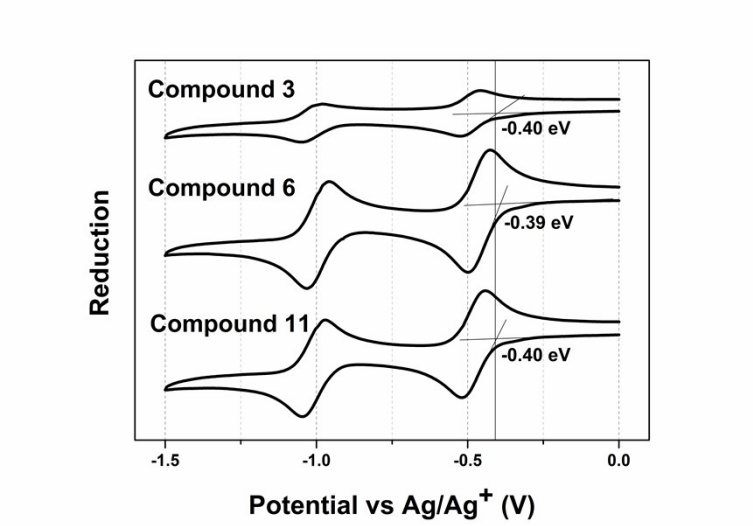

Figure S2. Reduction curves of three compounds (**3**, **6** and **11**) in dichloromethane solution. (The corresponding EA values are -3.77, -3.78 and -3. 77 eV for compound **3, 6** and **11**, respectively.)

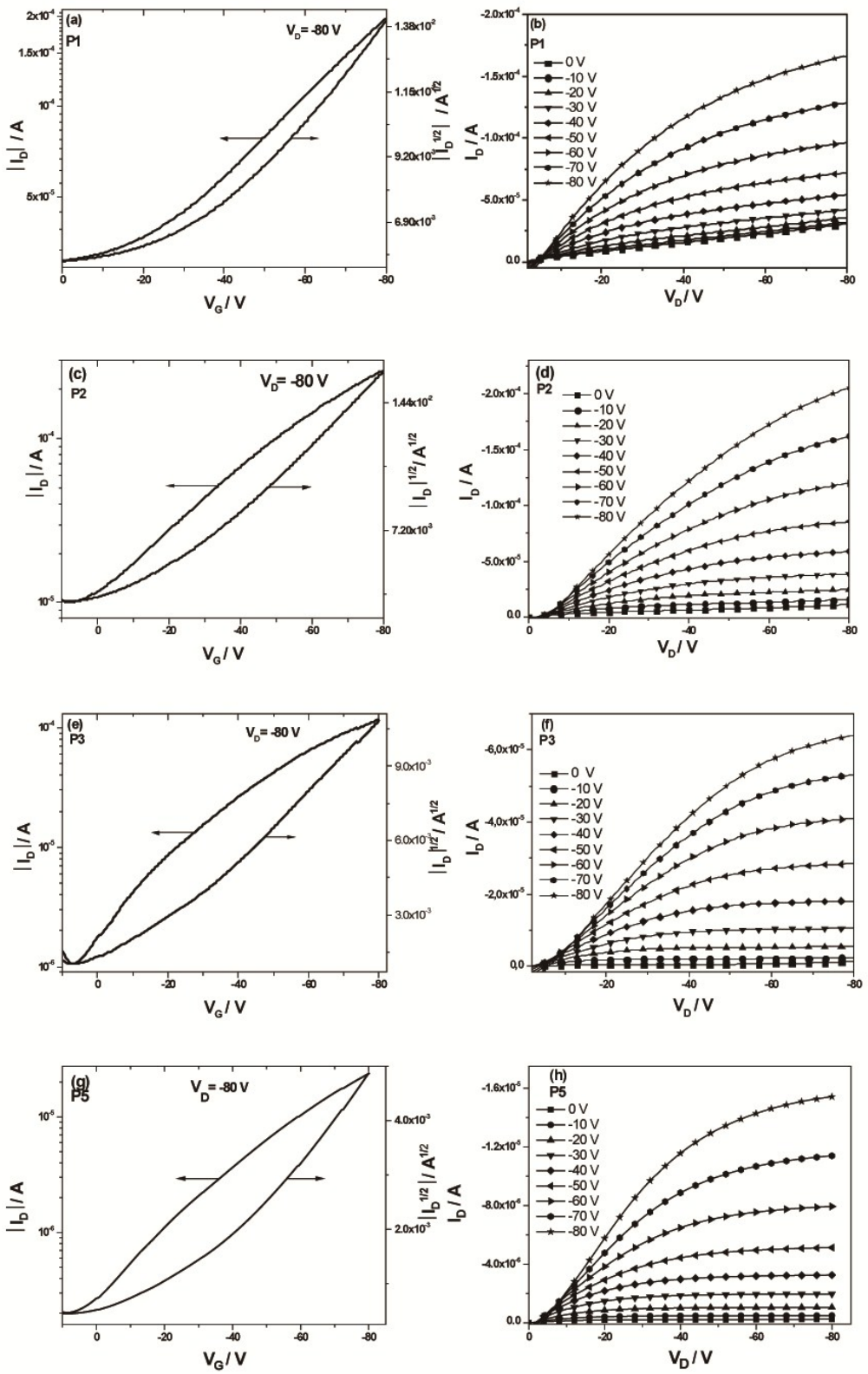

Figure S3. The transfer (a), (c), (e) (g), and output (b), (d), (f), (h) curves of **P1, P2, P3** and **P5**, respectively.

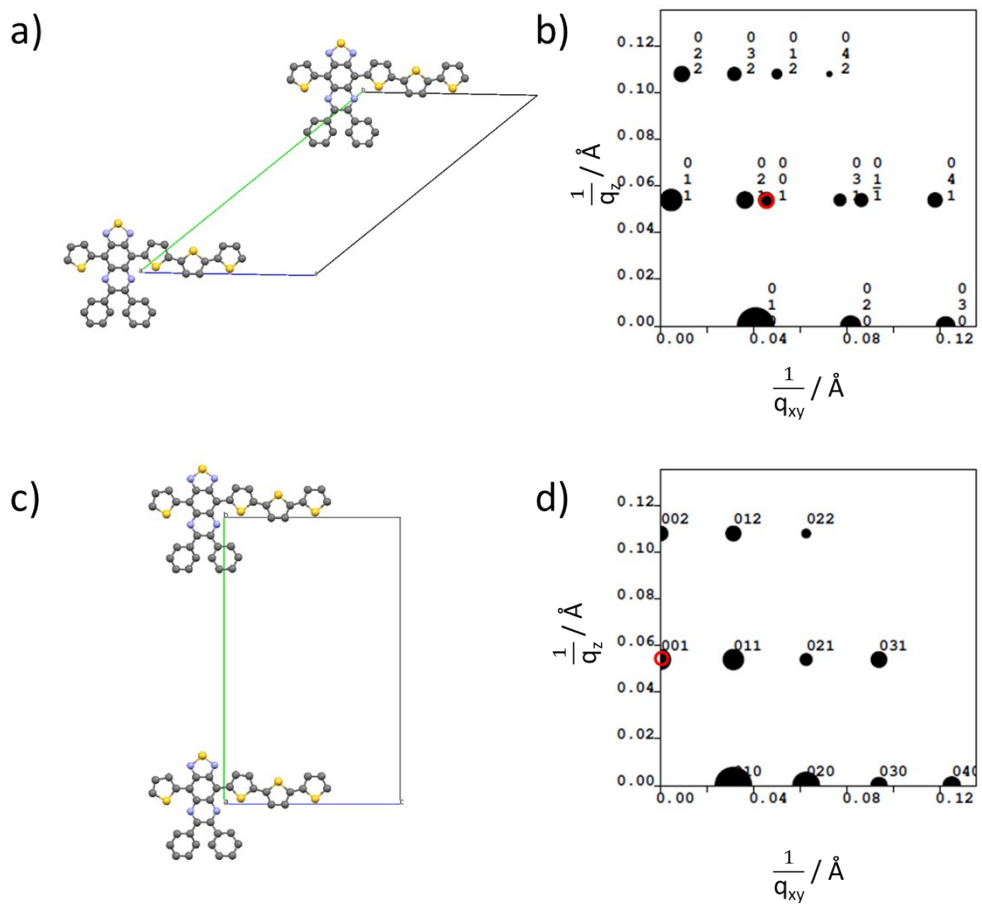

Figure S4. Schematic illustrations of the unit cells with (a) and without (c) polymer shift in neighbouring layers. This shift occurs along the fibre extrusion direction. (b) and (d) simulated 2DWAXS patterns with and without translation. The 001 reflection, which is observed in the experimental patterns and corresponding to the length of a monomeric unit, is indicted by red color. This reflection is shifted in the simulated pattern from meridional to off-meridional position with translation of the polymer backbones towards each other.

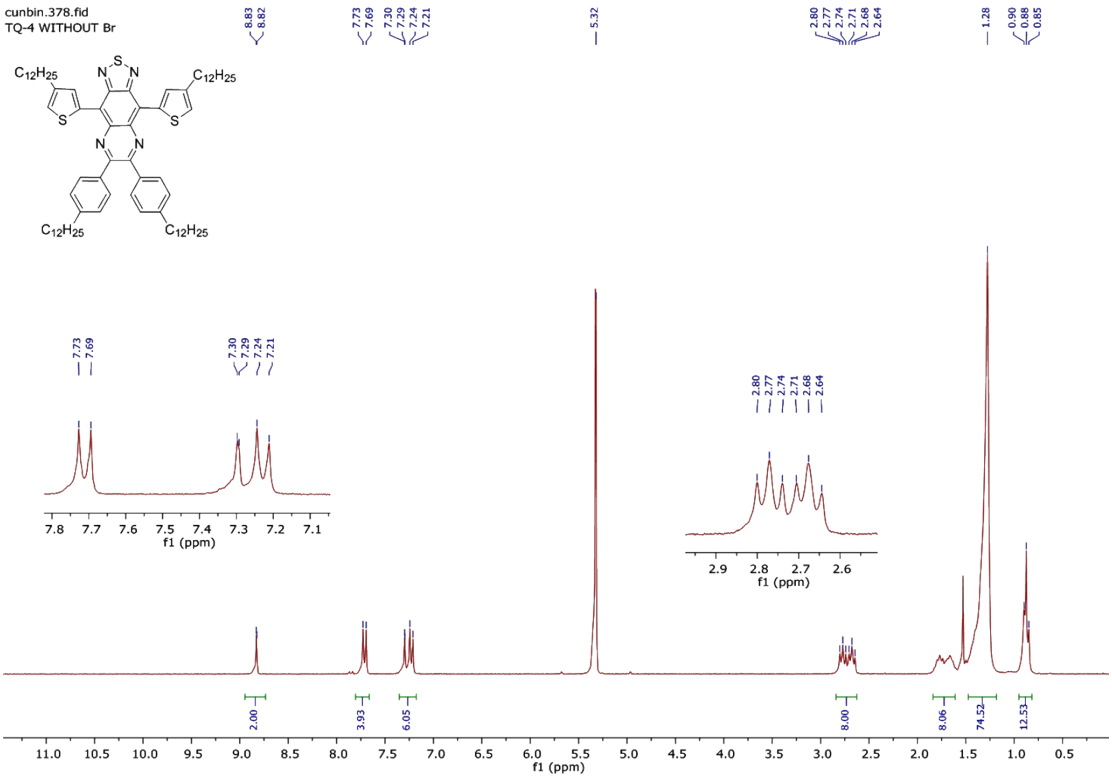

Figure S5. ^{1}H NMR spectrum of compound **3**.

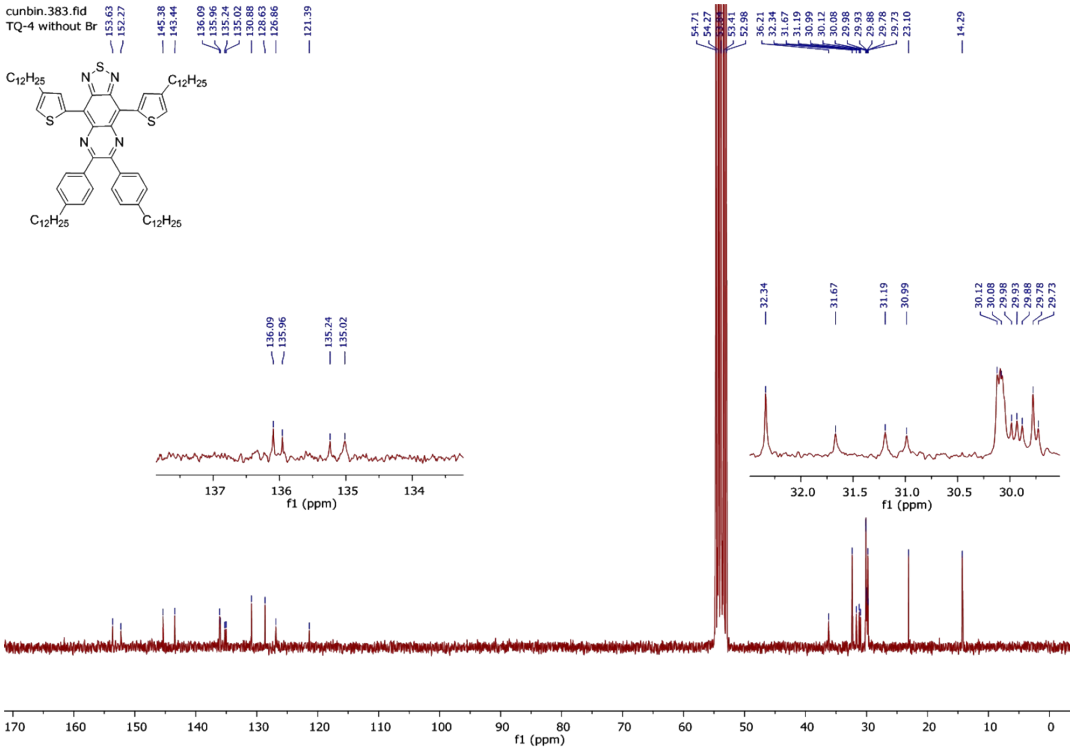

Figure S6. ^{13}C NMR spectrum of compound **3**.

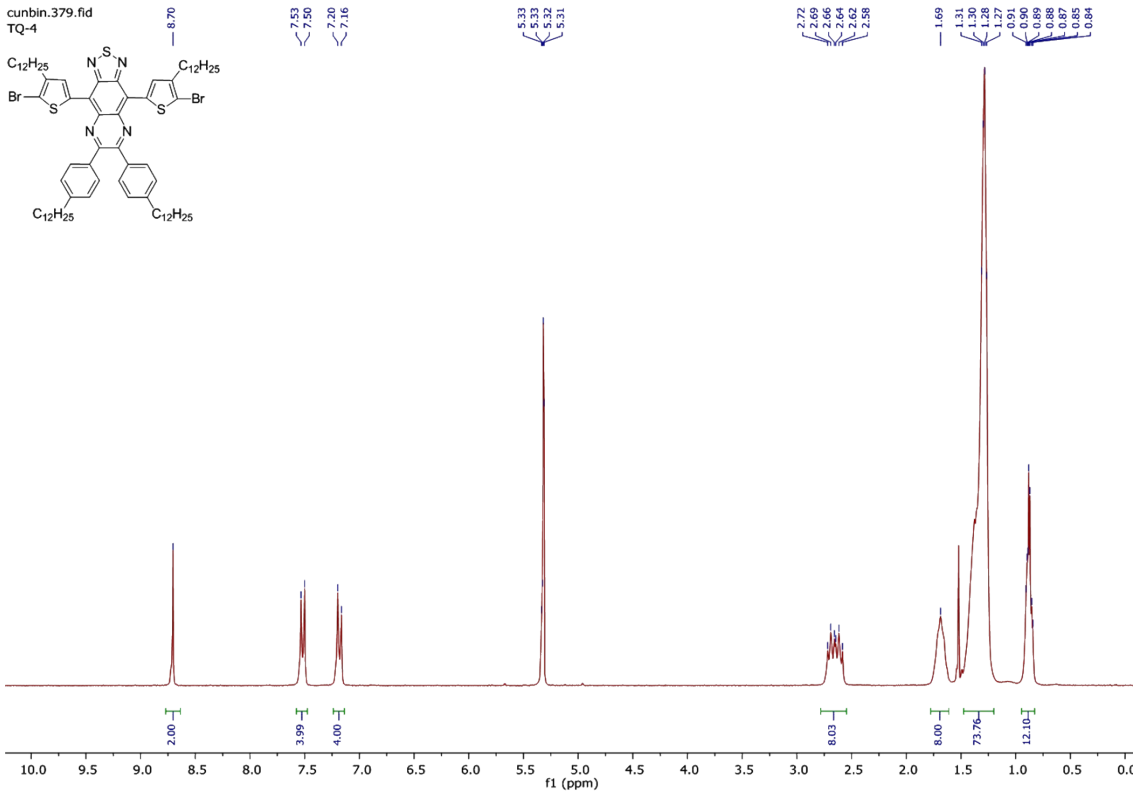

Figure S7. ^{1}H NMR spectrum of compound **4**.

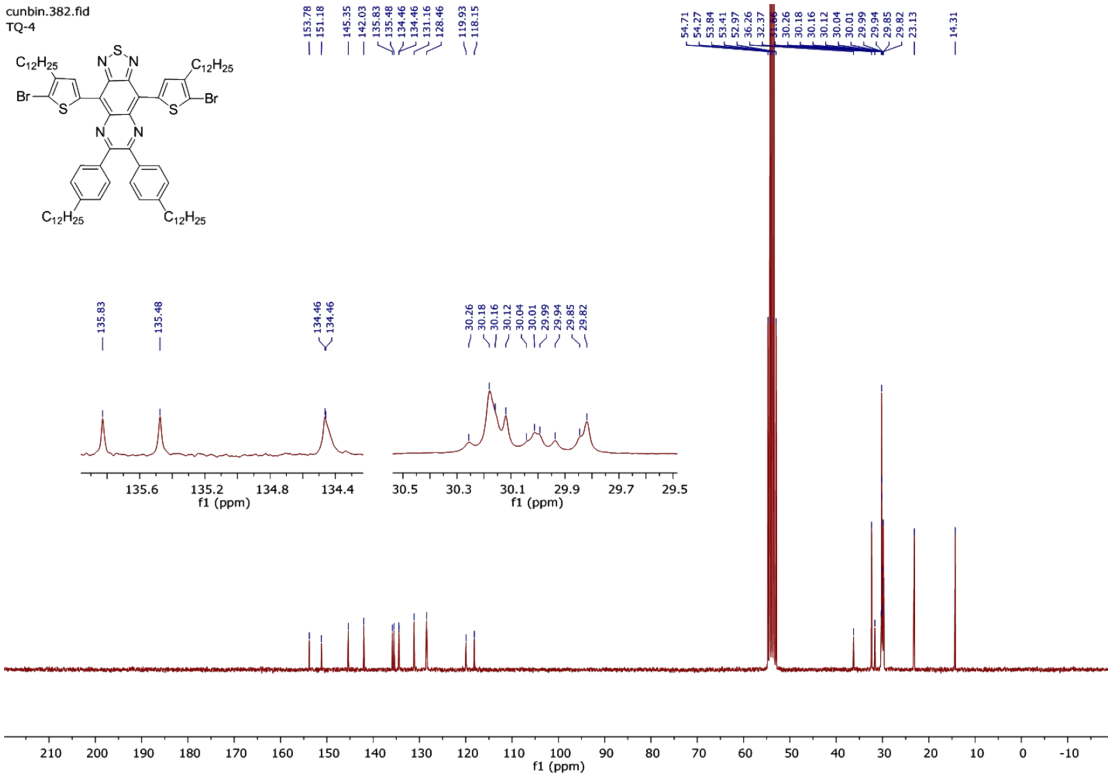

Figure S8. ^{13}C NMR spectrum of compound **4**.

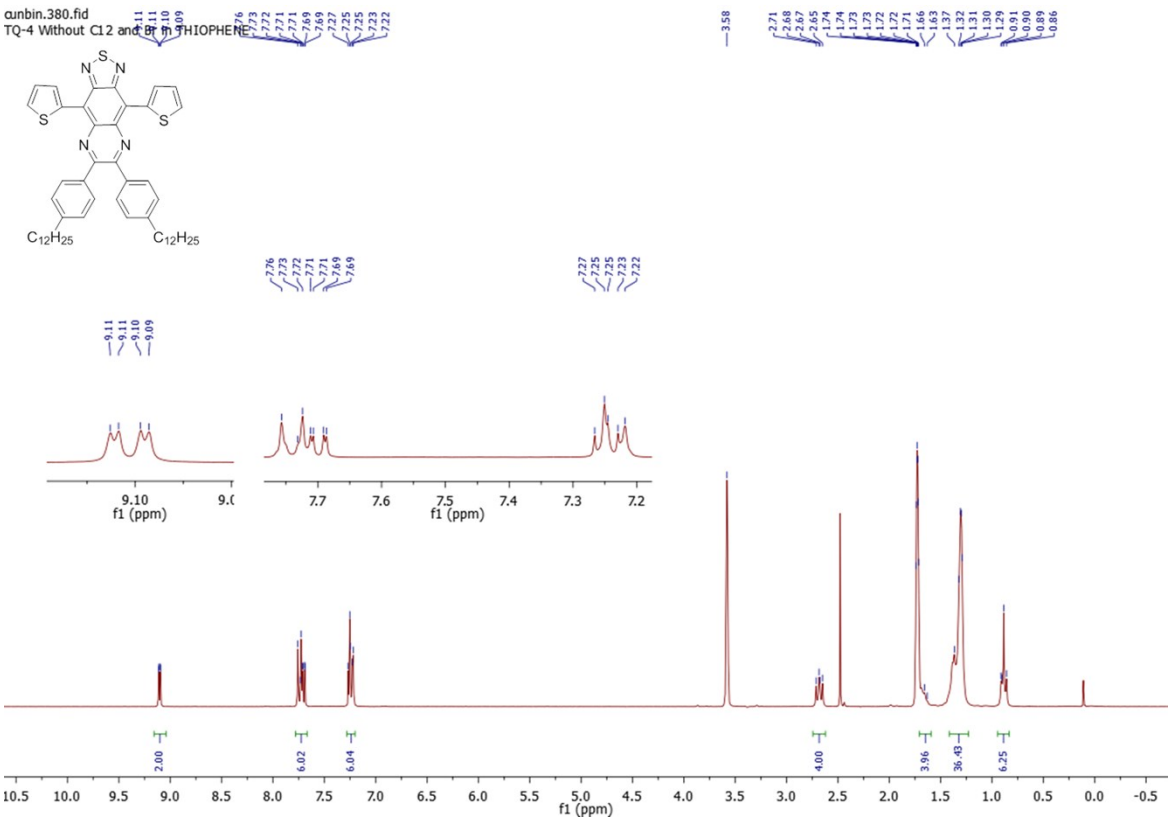

Figure S9. ^{1}H NMR spectrum of compound **6**.

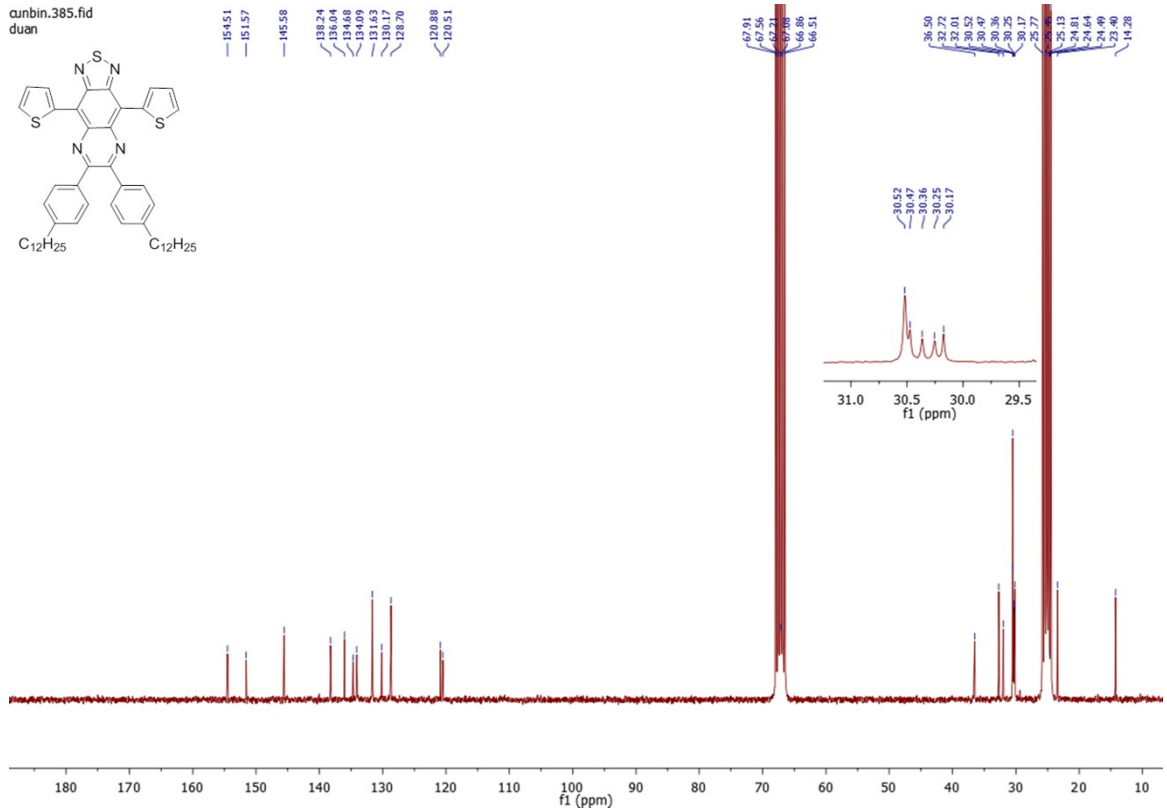

Figure S10. ^{13}C NMR spectrum of compound **6**.

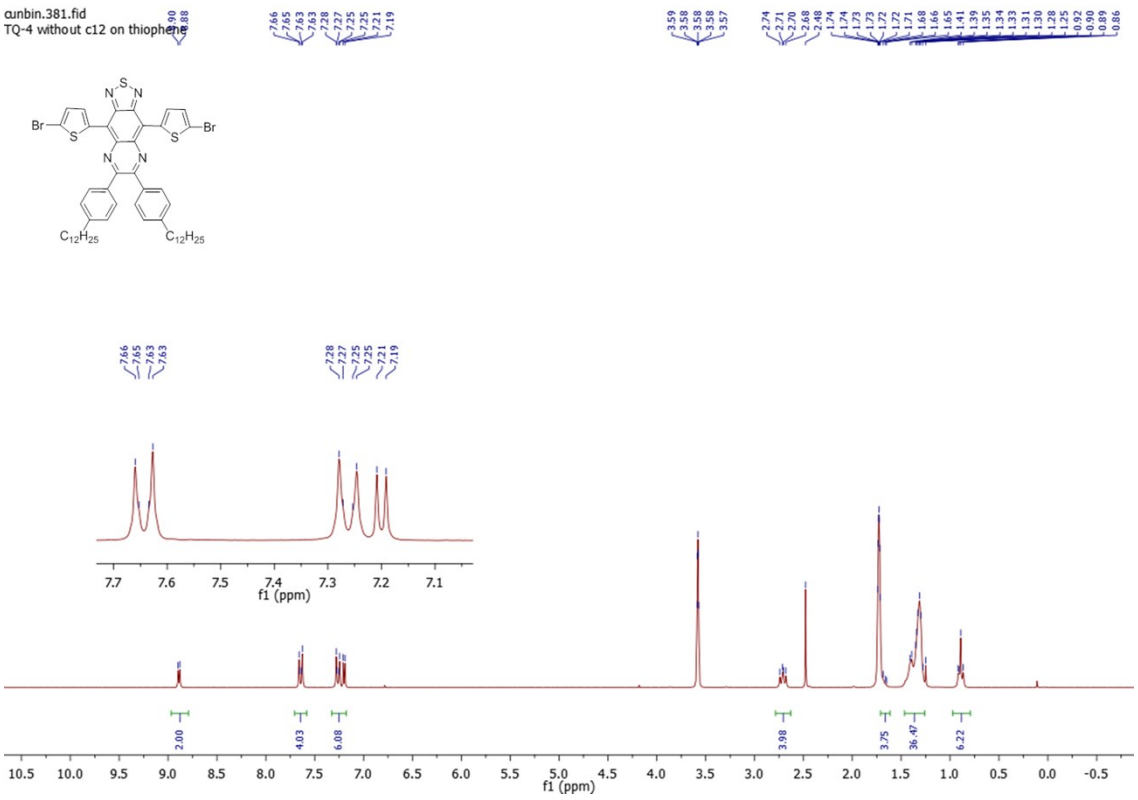

Figure S11. ^{1}H NMR spectrum of compound **7**.

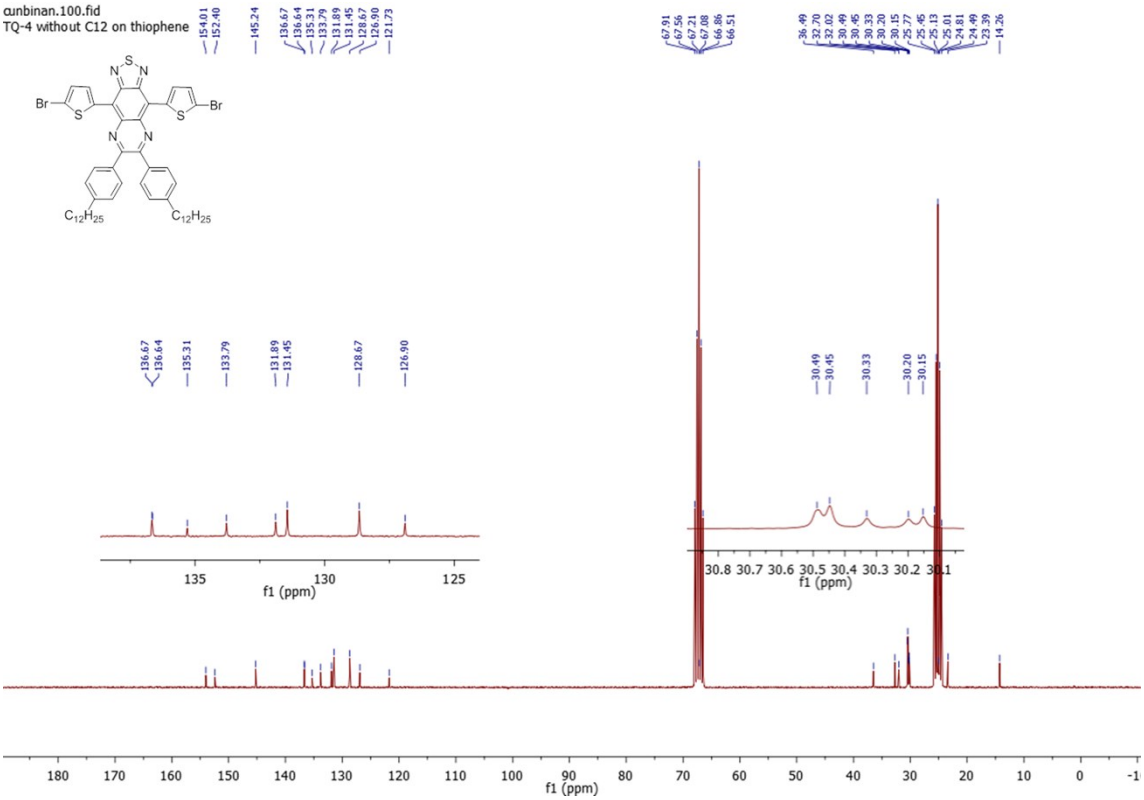

Figure S12. ^{13}C NMR spectrum of compound **7**.

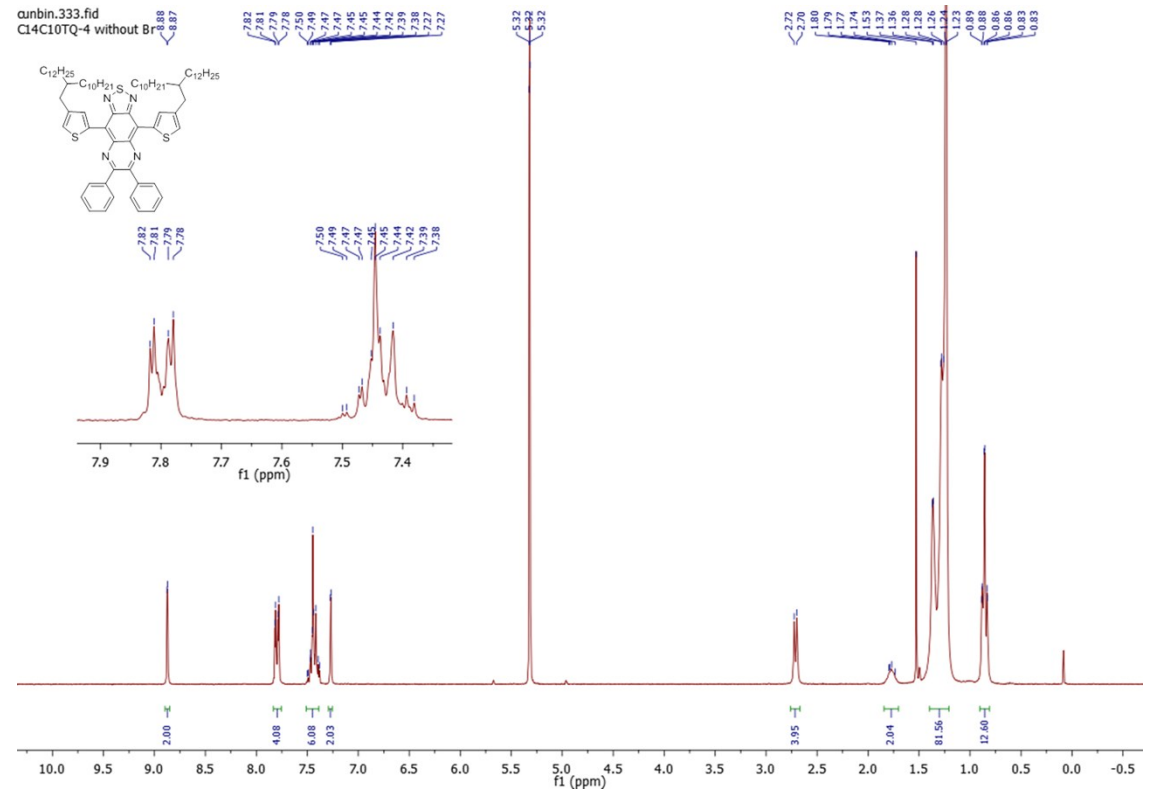

Figure S13. ^{1}H NMR spectrum of compound **11**.

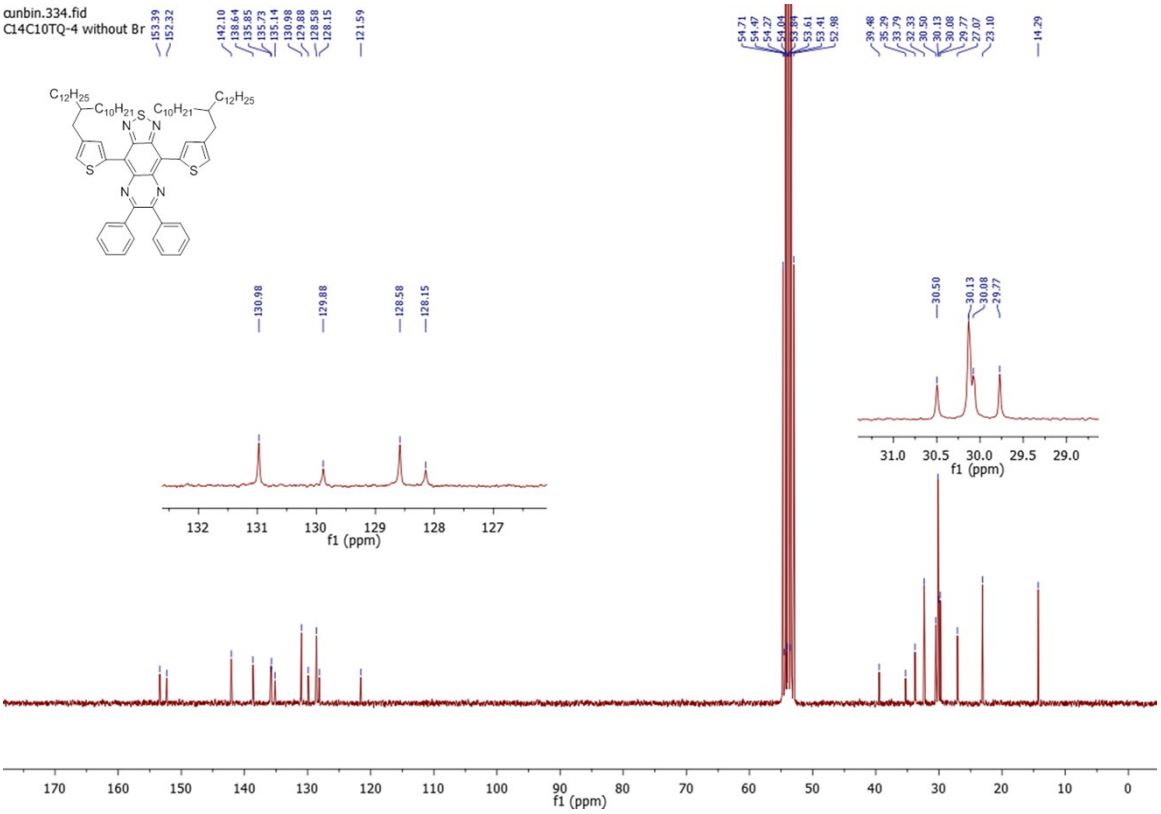

Figure S14. ^{13}C NMR spectrum of compound **11**.

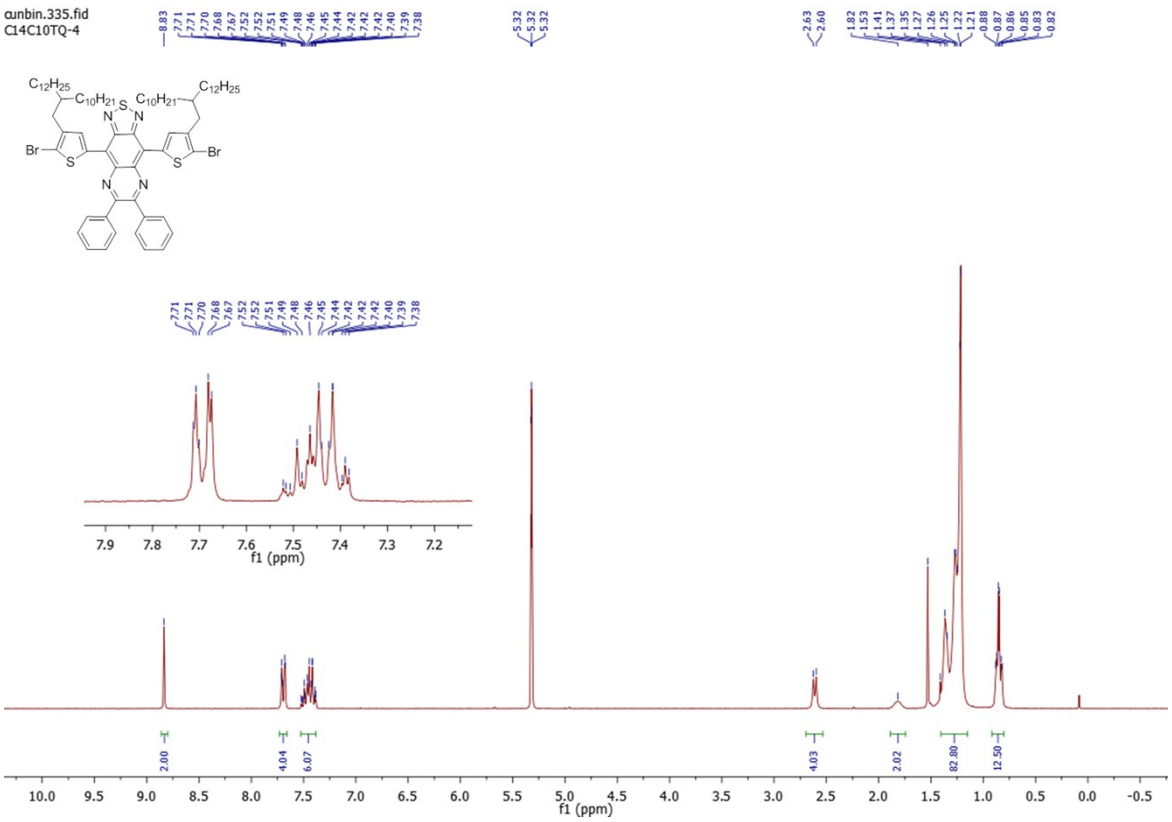

Figure S15. ^{1}H NMR spectrum of compound **12**.

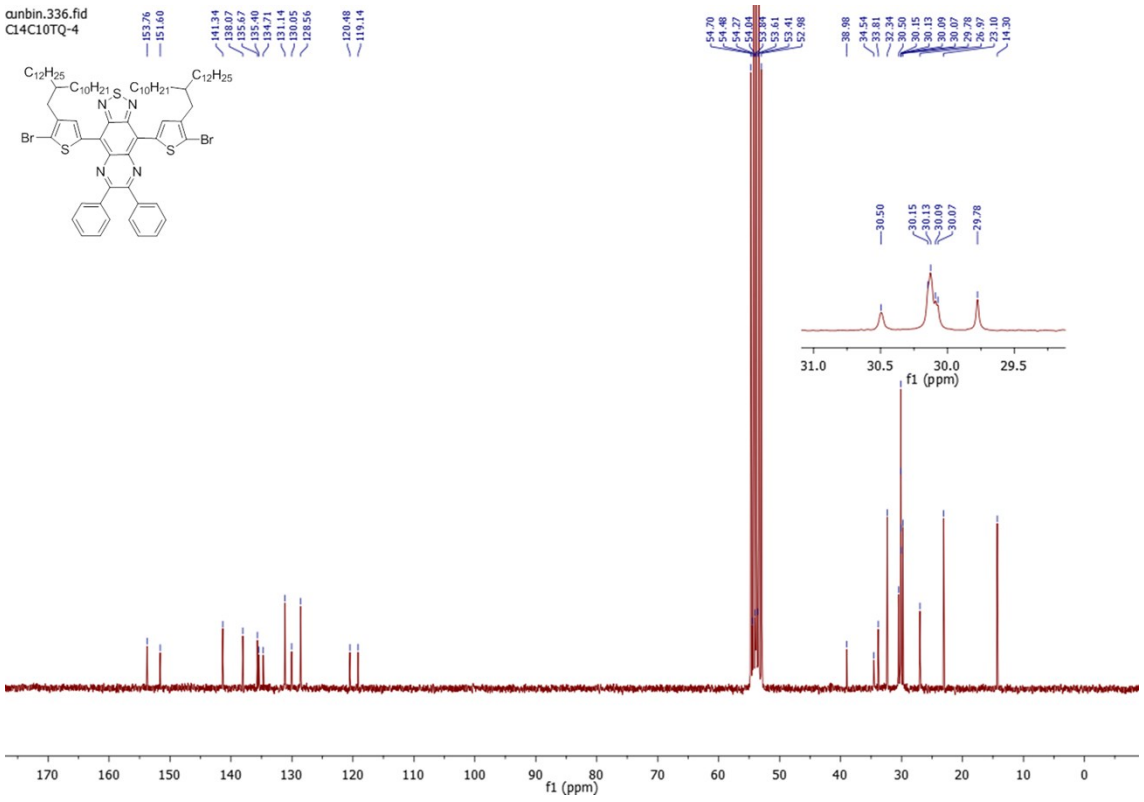

Figure S16. ^{13}C NMR spectrum of compound **12**.

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