Supporting Information

N-type Polymer Semiconductors Incorporating Heteroannulated Benzothiadiazole

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Materials.

All chemicals and solvents were used without further purification unless otherwise stated. 2-Decyl-1-tetradecanol, 3-bromothiophene, 5,5'-bis(trimethylstannyl)-2,2'-bithiophene, 2,5-bis(trimethylstannyl)thieno[3,2-b]thiophene, (3,3'-difluoro-[2,2'-bithiophene]-5,5'-diyl)bis(trimethylstannane), and (4,8-bis(5-(2-ethylhexyl)thiophen-2-yl)benzo[1,2-b:4,5-b']dithiophene-2,6-diyl)bis(trimethylstannane) were purchased from TCI Chemical and Sigma-Aldrich. Sodium 2,2-dicyanoethene-1,1-bis(thiolate) was synthesized according to a reported procedure.[1]

Measurements. ^{1}H NMR, ^{13}C NMR, and ^{19}F NMR spectra were recorded on a Bruker AV-400 spectrometer at room temperature using $CDCl_3$ as solvent. ^{1}H and ^{13}C chemical shift data were references to a residual solvent internal standard (^{1}H: $CHCl_3$ at 7.26 ppm; ^{13}C: $CDCl_3$ at 77.36 ppm). Gas chromatography–mass spectrometry (GC-MS) was performed on an Agilent GC 7890A and MS 5975C. Matrix-assisted laser desorption/ionization time-of-flight (MALDI-TOF) mass spectrometry was carried on a Bruker ultrafleXtreme MALDI-TOF analyzer. The number average molecular weights (M_n), weight average molecular weights (M_w), and dispersities (Đ) (against polystyrene standards) of polymers dissolved in high-performance liquid chromatography (HPLC) grade chloroform were determined using an Agilent 1260 Infinity GPC instrument fitted with a guard column and two PLgel 10 μm mixed-B 7.5 × 300 mm columns running at a temperature of 40 °C and flow rate of 1.0 mL min^{-1}. Computational studies were conducted with Gaussian 16 Revision C.01 and GaussView 6.1.1 software using either Møller-Plesset second-order perturbation theory (MP2) with cc-pvdz basis set, or density functional theory (DFT) with a B3LYP level of theory and 6-31G (d, p) basis set, as outlined in the text. Geometry optimizations were performed with full relaxation of all atoms in gas phase without solvent effects. Potential energy scans were calculated using the redundant coordinate editor, running a 360° scan of the dihedral angle in 72 steps of 5° increments. All theoretical computations were conducted with alkyl side chains replaced by a methyl group for simplification. Thermogravimetric analysis (TGA) measurements were run on a Mettler Toledo TGA/DSC 1LF/UMX instrument from 25 to 600 °C at 10 °C min^{-1} under nitrogen. Differential scanning calorimetry (DSC) measurements were performed on a Mettler Toledo DSC1 at a scan rate of 10 °C min^{-1}. Ultra-violet-visible absorption (UV-vis) spectra were measured on a UV-1601 Shimadzu UV-vis spectrometer. Electrochemical measurements were

carried out under nitrogen with a deoxygenated solution of tetra-n-butylammonium hexafluorophosphate (0.1 mol L^{-1}) in CH_3CN using a computer-controlled CHI660C electrochemical workstation, a platinum rod working electrode (Bioanalytical Systems Inc, 1.6 mm diameter) coated with samples, a platinum-wire auxiliary electrode, and an Ag/AgCl reference electrode. Potentials were referenced to the ferrocenium/ferrocene ($Fc^{0/+}_{P2}$) couple by using ferrocene as an internal standard. X-ray diffraction (XRD) analysis was performed using a Bruker D2 Phaser diffractometer with parallel beam optics equipped with a Lynx-Eye detector. X-rays were generated using a Cu source with Cu $K_{\alpha 1}$ (λ = 1.54056 Å) and Cu $K_{\alpha 2}$ (λ = 1.54439 Å) radiation emitted with an intensity ratio of 2:1. Patterns were collected between 5° – 40° with a step size of 0.01° for a collection time of 1s per step. Films were prepared by spin-coating followed by annealing at 120 °C. Atomic force microscopy (AFM) images were obtained with an Agilent Technologies 5500 AFM in tapping mode. Images were analysed using Gwyddion software with the same processing procedures applied to all images.

Device fabrication

Organic field-effect transistors (OFETs) were fabricated with a top-gate, bottom-contact (TG-BC) architecture onto large (2.54 × 2.54 cm^2) large glass substrates. The source and drain electrodes (Al (5 nm) and Au (35 nm), respectively) were vapor deposited using a shadow mask on the glass substrates. The semiconducting polymer layers were deposited using blade coating from 10 mg ml^{-1} solutions in chlorobenzene at a speed of 30 mm s^{-1} and substrate temperature of 60 °C. The films where then subjected to an additional annealing step at 120 °C for 5 min. A ~900 nm-thick CYTOP film dielectric layer was deposited on top of the blend semiconductor by spin-coating at 2000 rpm followed by annealing at 50 °C for 1 h in nitrogen atmosphere. The geometrical capacitance of the CYTOP layers was measured to be ~ 2.1 nF cm^{-2}. Finally, a 50 nm-thick Al layer was vapor deposited on top serving as the gate electrode. A KEYSIGHT B2912A Precision Source/Measure Unit was used to do the current-voltage measurements for the OFETs.

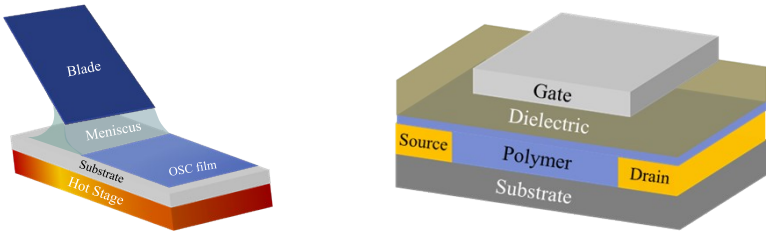

Figure S1. OFET device structure.

Synthesis

11-(Bromomethyl)tricosane (1). To a solution of 2-decyl-1-tetradecanol (10 g, 28.2 mmol) and triphenylphosphine (7.4 g, 28.2 mmol) in anhydrous dichloromethane (30 ml) under nitrogen at 0 °C was added N-bromosuccinimide (5.1 g, 28.6 mmol) in portions. The reaction mixture was warmed to room temperature and stirred for 16 h. After removing the solvent under reduced pressure, the crude product was diluted with petroleum ether and flushed through a silica plug and isolated as a clear oil (10.72 g, yield: 91%). ^{1}H NMR (400 MHz, $CDCl_3$) δ 3.53 (d, J = 5.4 Hz, 2H), 1.49 – 1.41 (m, 1H), 1.37 – 1.15 (m, 40H), 0.88 (t, J = 6.8 Hz, 6H).

3-(2-Decyltetradecyl)thiophene (2). Zn powder was activated as follows: a mixture of Zn powder (1.31 g, 20 mmol) and aqueous HCl (1 M, 6 ml) was combined in a flask, sonicated vigorously for 10 min, and then filtered. The solid was washed with water (300 ml), acetone (300 ml), diethyl ether (300 ml) successively before drying to obtain the activated Zn powder.

A mixture of freshly prepared activated Zn powder (1.25 g, 19.23 mmol), potassium iodide (604.24 mg, 3.64 mmol) and compound **1** (7.6 g, 18.2 mmol) in N,N-dimethylacetamide (20 ml) was heated at 80 ℃ for 16 h. The solution was allowed to cool to room temperature, and any unreacted Zn powder allowed to settle. The resulting freshly prepared Zn reagent was decanted by syringe and used directly in the next step.

To a solution of 3-bromothiophene (2.96 g, 18.16 mmol) and Pd(dppf)Cl_2.DCM (147 mg, 0.18 mmol) in DMA (20 ml) under nitrogen was injected the freshly prepared Zn reagent dropwise. The reaction mixture was stirred at 80 ℃ for 16 h. After cooling to room temperature, the mixture was diluted with 50 ml hexane and 50 ml saturated ammonium chloride solution, and stirred for another 30 min before passing through a pad of celite. The crude product was washed with 1 M HCl (100 ml), extracted with hexane and dried with magnesium sulfate. After removing the solvent under reduced pressure, the crude product was further purified using silica gel column chromatography with hexane as the eluent, yielding a colourless oil (2.43 g, yield: 32%). ^{1}H NMR (400 MHz, $CDCl_3$) δ 7.28 (dd, *J* = 4, 2 Hz,1H), 6.97 (m, 2H), 2.66 (d, *J* = 6.5 Hz, 2H), 1.75 – 1.64 (m, 1H), 1.57 – 1.11 (m, 40H), 0.98 (t, *J* = 6.8 Hz, 6H). ^{13}C NMR (101 MHz, $CDCl_3$) δ 141.62, 128.54, 124.55, 120.44, 38.82, 34.58, 33.22, 31.85, 29.91, 29.60, 29.29, 26.52, 22.60, 13.99.

Tributyl(4-(2-decyltetradecyl)thiophen-2-yl)stannane (3). To a solution of compound **2** (500 mg, 1.19 mmol), N,N,N′,N′-tetramethylethylenediamine (TMEDA, 0.2 ml, 1.33 mmol) in anhydrous THF (35 ml) at 0 ℃ was added *n*-BuLi (2.5 M, 0.53 ml, 1.33 mmol) dropwise. The reaction mixture was stirred at room temperature for 30 min before injecting tributyltin chloride (1 M in hexane, 1.31 mL, 1.31 mmol) at 0 ℃. After keeping the reaction at room temperature for 2 h, the reaction mixture was poured into water (100 ml), extracted with diethyl ether (300 ml) and dried with magnesium sulfate. The solvent was removed under reduced pressure, yielding a yellow oil (659.75 mg, yield: 78%). The crude product was directly used for the next step without further purification. ^{1}H NMR (400 MHz, $CDCl_3$) δ 7.15 (s, 1H), 6.94 (s, 1H), 2.61 (d, *J* = 6.7 Hz, 2H), 1.89 – 1.80 (m, 1H), 1.66 – 1.53 (m, 12H), 1.30 – 1.24 (m, 40H), 0.95 – 0.87 (m, 15H). ^{13}C NMR (101 MHz, $CDCl_3$) δ 142.89, 137.45, 135.64, 126.43, 67.94, 57.72, 45.84, 39.16, 34.38, 33.53, 32.06, 30.16, 29.84, 29.80, 29.50, 29.06, 28.30, 27.37, 27.32, 26.79, 22.81, 16.44, 14.19, 13.72, 10.78.

4,7-Bis(4-(2-decyltetradecyl)thiophen-2-yl)-5,6-difluorobenzo[c][1,2,5]thiadiazole (4). A solution of 4,7-dibromo-5,6-difluoro[2,1,3]benzothiadiazole (244 mg, 0.74 mmol), compound **3** (1.14 g, 1.6 mmol), and Pd(PPh_3)$_2Cl_2$ (26 mg, 0.037 mmol) in anhydrous toluene (50 ml) under nitrogen was stirred at 110 ℃ for 16 h. After cooling to room temperature, the reaction mixture was quenched with water (100 ml), extracted with dichloromethane (300 ml) and dried with magnesium sulfate. After removing the solvent under reduced pressure, the crude product was further purified using silica gel column chromatography with petroleum ether as eluent, yielding a yellow solid (400 mg, yield: 54%). ^{1}H NMR (400 MHz, $CDCl_3$) δ 8.10 (s, 2H), 7.18 (s, 2H), 2.65 (d, *J* = 6.7 Hz, 4H), 1.74 – 1.64 (m, 2H), 1.38 – 1.22 (m, 80H), 0.87 (t, *J* = 6.0 Hz, 12H). ^{19}F NMR (377 MHz, $CDCl_3$) δ -128.23. ^{13}C NMR (101 MHz, $CDCl_3$) δ 149.11, 148.30, 142.52, 132.99, 131.17, 125.00, 39.14, 35.04, 33.51, 32.11, 31.77, 30.21, 29.88, 29.85, 29.55, 26.82, 22.87, 22.83, 14.28 (not all peaks resolved)

2-(4,8-Bis(4-(2-decyltetradecyl)thiophen-2-yl)-[1,3]dithiolo[4',5':4,5]benzo[1,2 c][1,2,5]thiadiazol-6-ylidene)malononitrile (5). A solution of compound **4** (200 mg, 0.2 mmol) and sodium 2,2-dicyanoethene-1,1-bis(thiolate) (55.8 mg, 0.3 mmol) in anhydrous DMF (50 ml) under N_2 was heated at 90 ℃ for 24 h. After cooling to room temperature, the reaction mixture was quenched with water (30 ml), extracted with DCM (3 x 30 ml) and dried with $MgSO_4$. After removing the solvent under reduced pressure, the crude product was further purified using silica gel column chromatography with petroleum ether/dichloromethane (3:1, v/v) as the eluent, yielding a red solid (0.2 g, 90%). ^{1}H NMR (400 MHz, $CDCl_3$) δ 7.50 (s, 2H), 7.25 (s, 2H), 2.68 (d, *J* = 6.7 Hz, 4H), 1.74 – 1.64 (m, 2H), 1.33 – 1.20 (m, 80H), 0.88 (t, *J* = 4.8 Hz, 12H). ^{13}C NMR (101 MHz, $CDCl_3$) δ 177.10, 152.72, 143.11,

137.06, 134.76, 132.37, 125.42, 122.32, 112.30, 68.01, 39.12, 35.01, 34.82, 33.48, 32.09, 31.75, 30.18, 29.86, 29.83, 29.53, 27.07, 26.82, 25.43, 22.85, 22.81, 14.27 (not all peaks resolved).

2-(4,8-Bis(5-bromo-4-(2-decyltetradecyl)thiophen-2-yl)-[1,3]dithiolo[4',5':4,5]benzo[1,2-c][1,2,5]thiadiazol-6-ylidene)malononitrile (6). To a solution of compound **5** (244 mg, 0.22 mmol) in anhydrous THF (50 ml) at room temperature under N_2 was added N-bromosuccinimide (84.5 mg, 0.48 mmol) in portions with the exclusion of light, and the reaction mixture was stirred at room temperature for 16 h. After removing the solvent under reduced pressure, the crude product was purified using silica gel column chromatography with petroleum ether/dichloromethane (3:1, v/v) as the eluent, yielding a red solid (122 mg, yield: 44%). ^{1}H NMR (400 MHz, $CDCl_3$) δ 7.37 (s, 2H), 2.63 (d, J = 7.0 Hz, 4H), 1.80 – 1.67 (m, 2H), 1.31 – 1.19 (m, 80H), 0.96 – 0.84 (m, 12H). ^{13}C NMR (101 MHz, $CDCl_3$) δ 176.22, 152.62, 142.74, 137.08, 134.95, 132.23, 121.72, 115.95, 112.32, 69.19, 39.06, 35.15, 34.73, 33.87, 32.43, 32.09, 30.50, 30.22, 30.18, 29.88, 27.40, 27.06, 25.76, 23.19, 23.15, 14.58. MS (m/z): [M+] calcd. for $C_{66}H_{100}Br_2N_4S_5$: 1269.66, Found: 1269.2 (MALDI-TOF). FTIR (ν cm^{-1}): 2211.2 {ν(CN) stretching}, 1466.7 {ν(C=C) absorption band}, 887.1 {ν(C-S) band}.

Polymer P1. A solution of compound **6** (122 mg, 0.096 mmol), 5,5'-bis(trimethylstannyl)-2,2'-bithiophene (47.2 mg, 0.096 mmol), $Pd_2(dba)_3$ (1.76 mg, 0.002 mmol), and tri(o-tolyl)-phosphine (2.34 mg, 0.007 mmol) in anhydrous chlorobenzene (10 ml) in a sealed microwave vial under N_2 was heated at 110 ℃ for 72 h. After cooling to room temperature, the reaction mixture was precipitated into methanol (100 ml), filtered, and subjected to Soxhlet extraction with methanol, acetone, hexane, chloroform. The chloroform fraction was collected and dried under reduced pressure to yield a dark blue solid (99.84 mg, yield: 82%). ^{1}H NMR (400 MHz, $CDCl_3$) δ 7.57 (s, 2H), 7.22 (s, 4H), 2.98 – 2.69 (m, 4H), 1.90 – 1.69 (m, 2H), 1.31 – 1.11 (m, 80H), 0.85 (t, J = 6.6 Hz, 12H). GPC ($CHCl_3$, 313K): M_n = 41 KDa, M_w = 74 KDa, PDI = 1.80.

Polymers **P2**, **P3**, and **P4** were synthesized using similar procedures as polymer **P1**.

Polymer P2. ^{1}H NMR (400 MHz, $CDCl_3$) δ 7.52 (br s, 2H)), 7.30 (s, 2H), 3.06 – 2.68 (m, 4H), 1.91 – 1.70 (m, 2H), 1.34 – 1.17 (m, 80H), 0.85 (t, J = 6.6 Hz, 12H). GPC ($CHCl_3$, 313K): M_n = 42 KDa, M_w = 83 KDa, PDI = 1.98.

Polymer P3. ^{1}H NMR (400 MHz, $CDCl_3$) δ 7.59 (s, 2H), 7.04 (s, 2H), 2.86 (d, J = 9.3 Hz, 4H), 1.86 – 1.75 (m, 2H), 1.44 – 1.14 (m, 80H), 0.86 (t, J = 6.9 Hz, 12H). ^{19}F NMR (377 MHz, $CDCl_3$) δ -123.40. GPC ($CHCl_3$, 313K): M_n = 35 KDa, M_w = 72 KDa, PDI = 2.14.

Polymer P4. ^{1}H NMR (400 MHz, $CDCl_3$) δ 7.82 – 6.93 (s, 8H), 2.91 – 2.87 (m, 8H), 1.82 – 1.65 (m, 4H), 1.50 – 1.18 (m, 96H), 1.02 – 0.75 (m, 24H). GPC ($CHCl_3$, 313K): M_n = 17 KDa, M_w = 48 KDa, PDI = 2.82.

Table S1. Molecular weight of the polymers **P1-4**.

Polymer	M_n [Kg/mol]	M_w [Kg/mol]	$Đ$
P1	41	74	1.80
P2	42	83	1.98
P3	35	72	2.14
P4	17	48	2.82

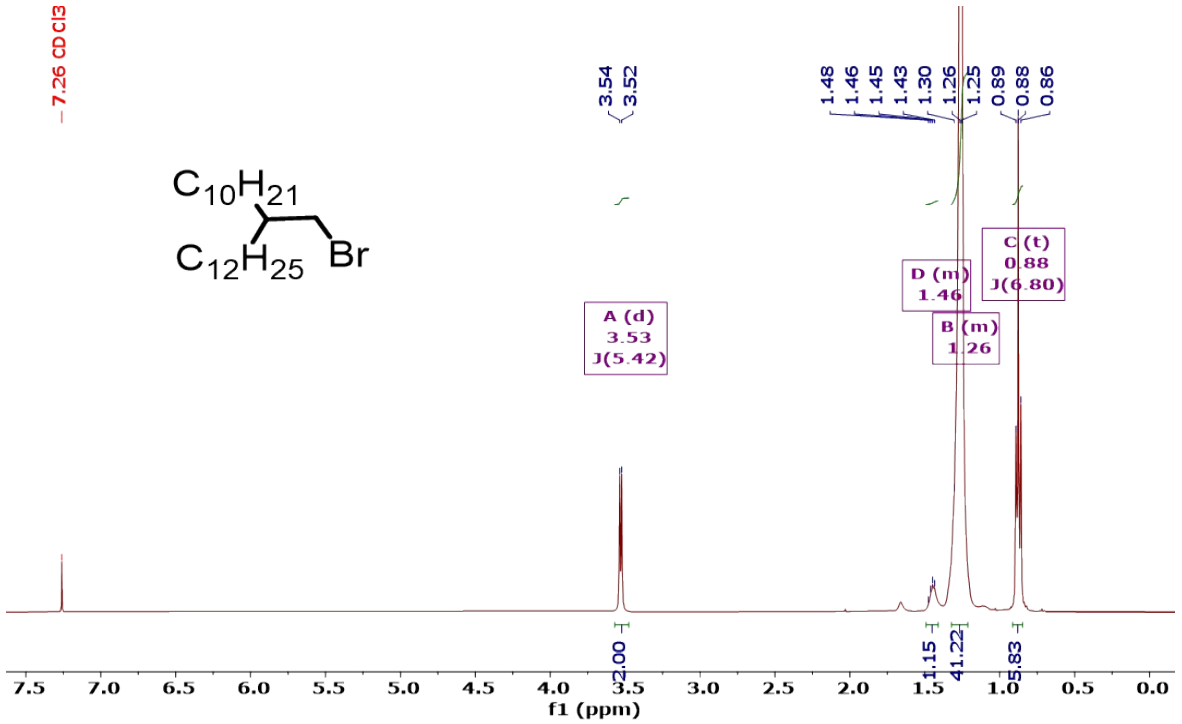

Figure S2. ^{1}H NMR spectrum of compound **1**.

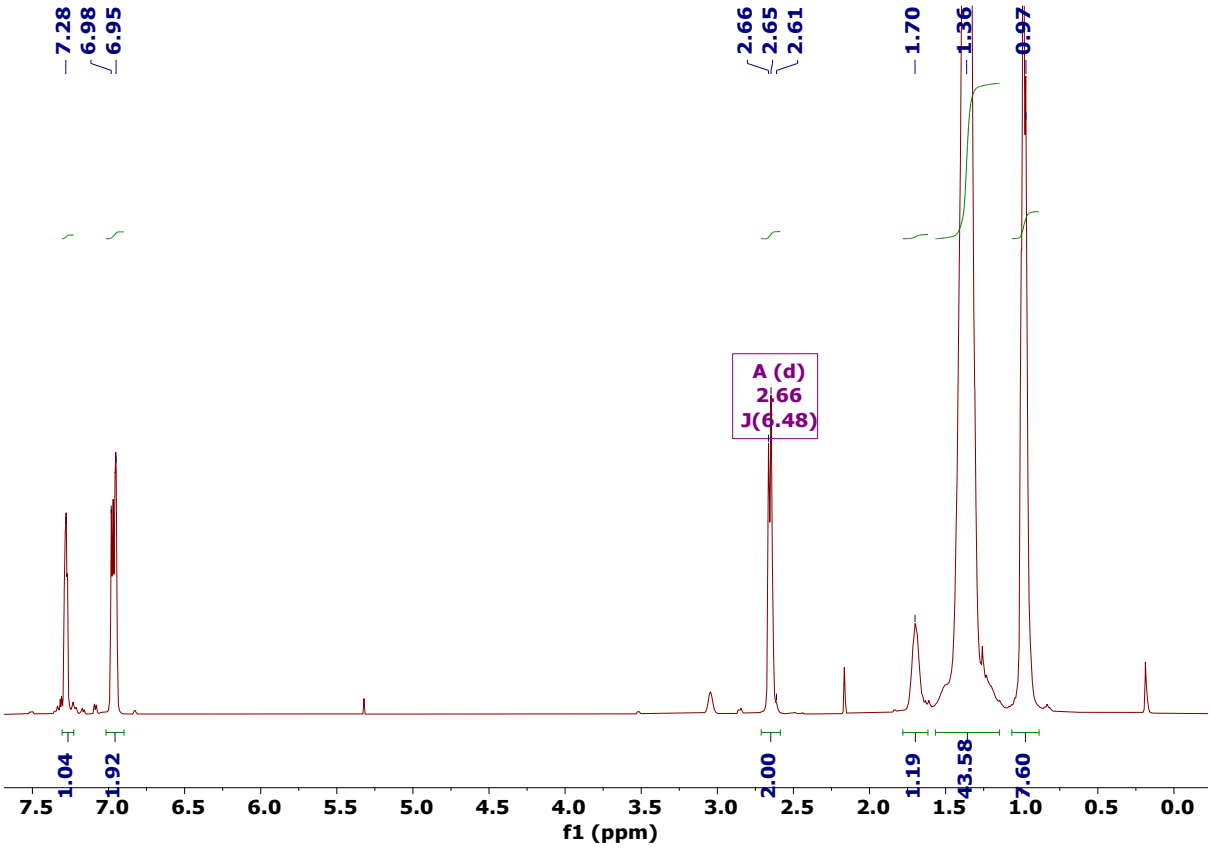

Figure S3. ^{1}H NMR spectrum of compound **2**.

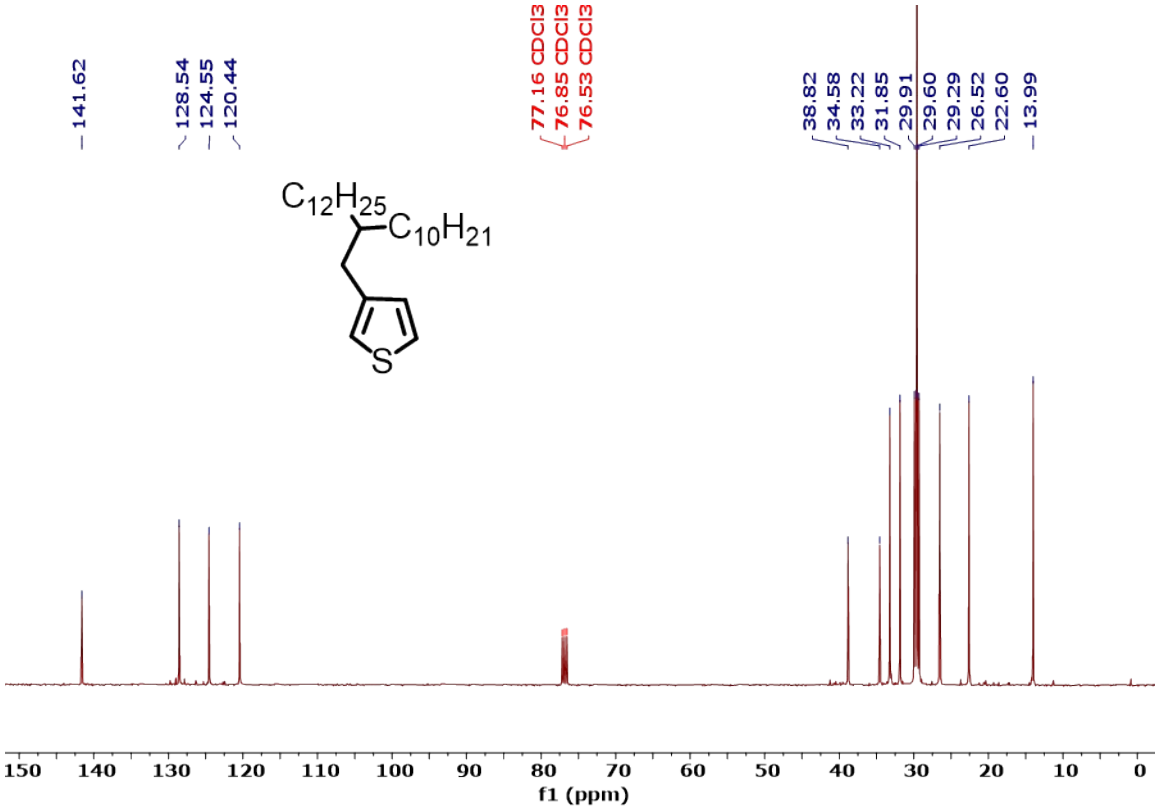

Figure S4. ^{13}C NMR spectrum of compound **2**.

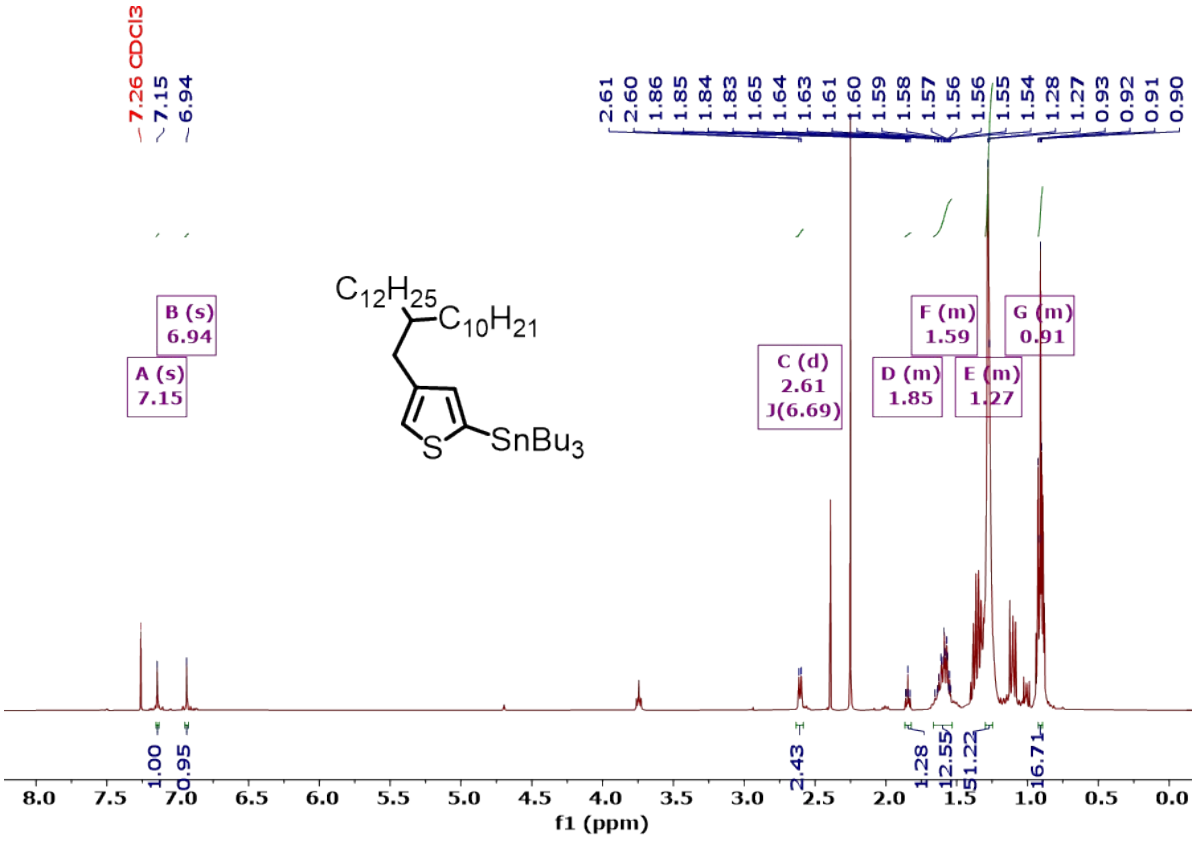

Figure S5. ^{1}H NMR spectrum of compound **3**.

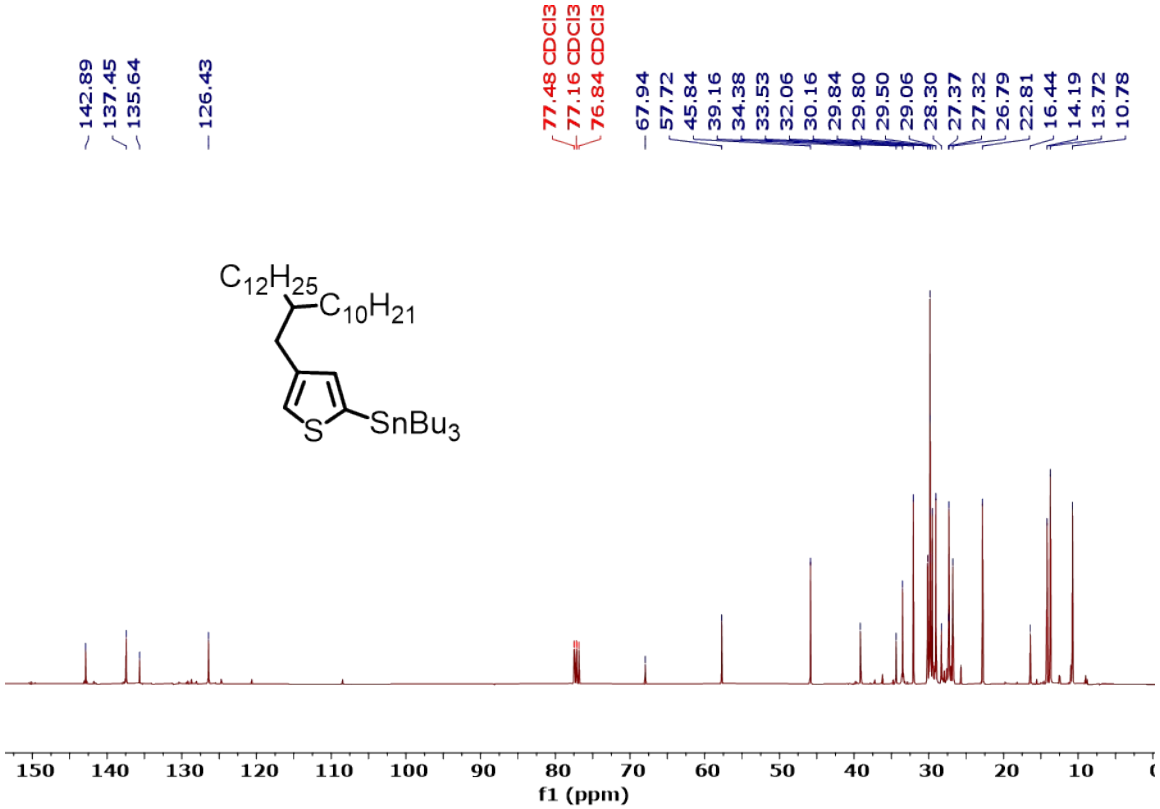

Figure S6. ^{13}C NMR spectrum of compound **3**.

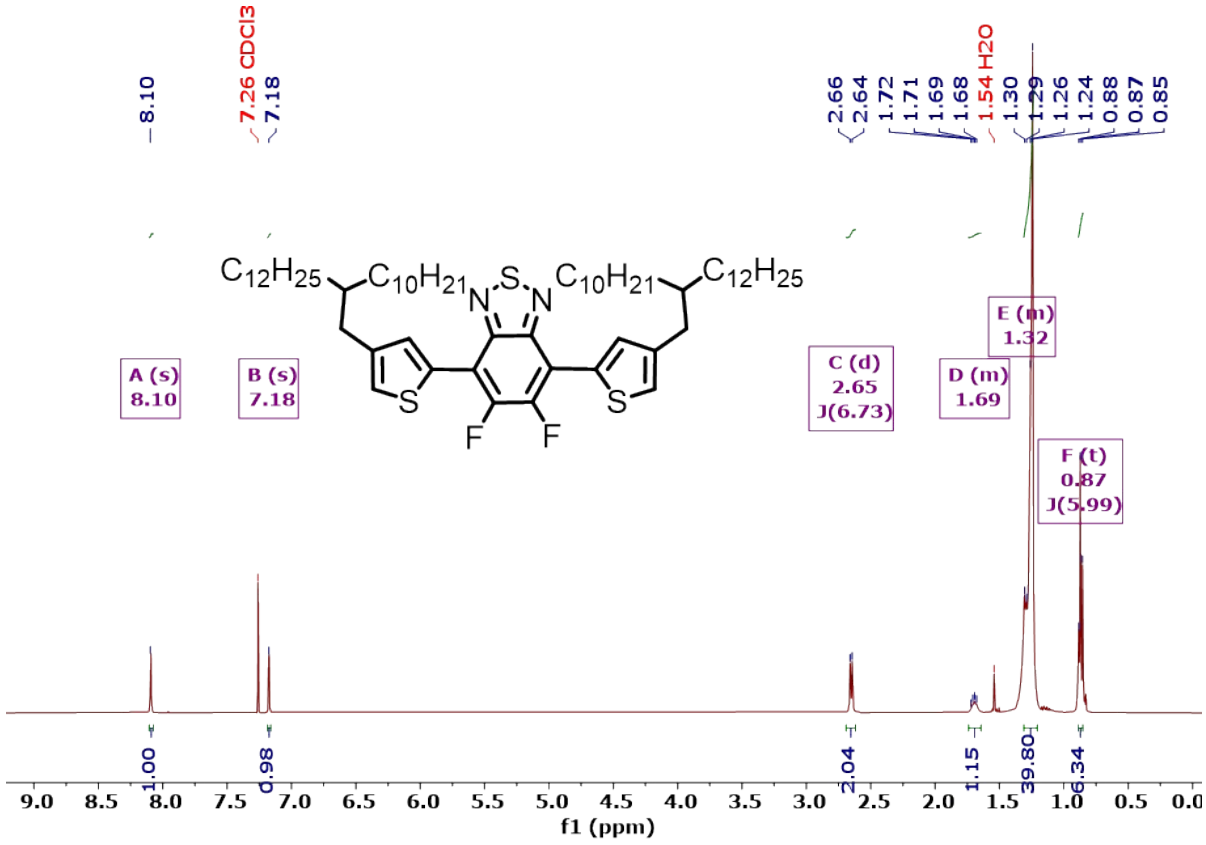

Figure S7. ^{1}H NMR spectrum of compound **4**.

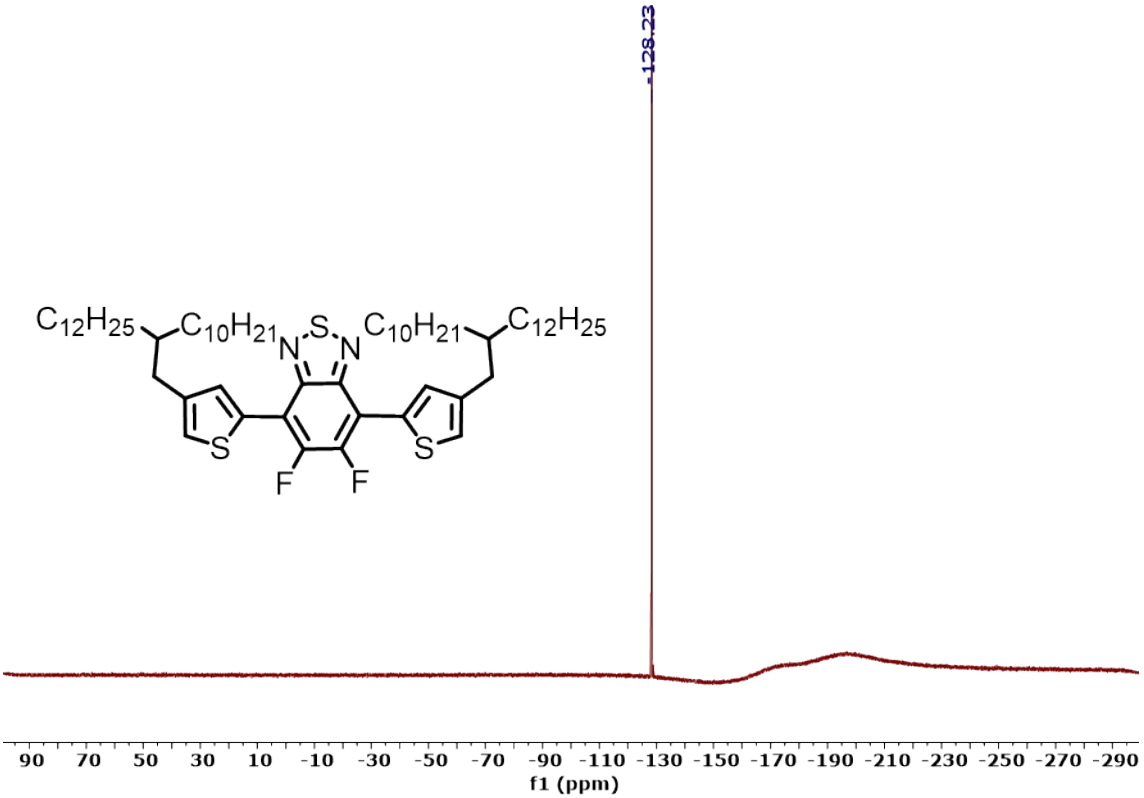

Figure S8. ^{19}F NMR spectrum of compound **4**.

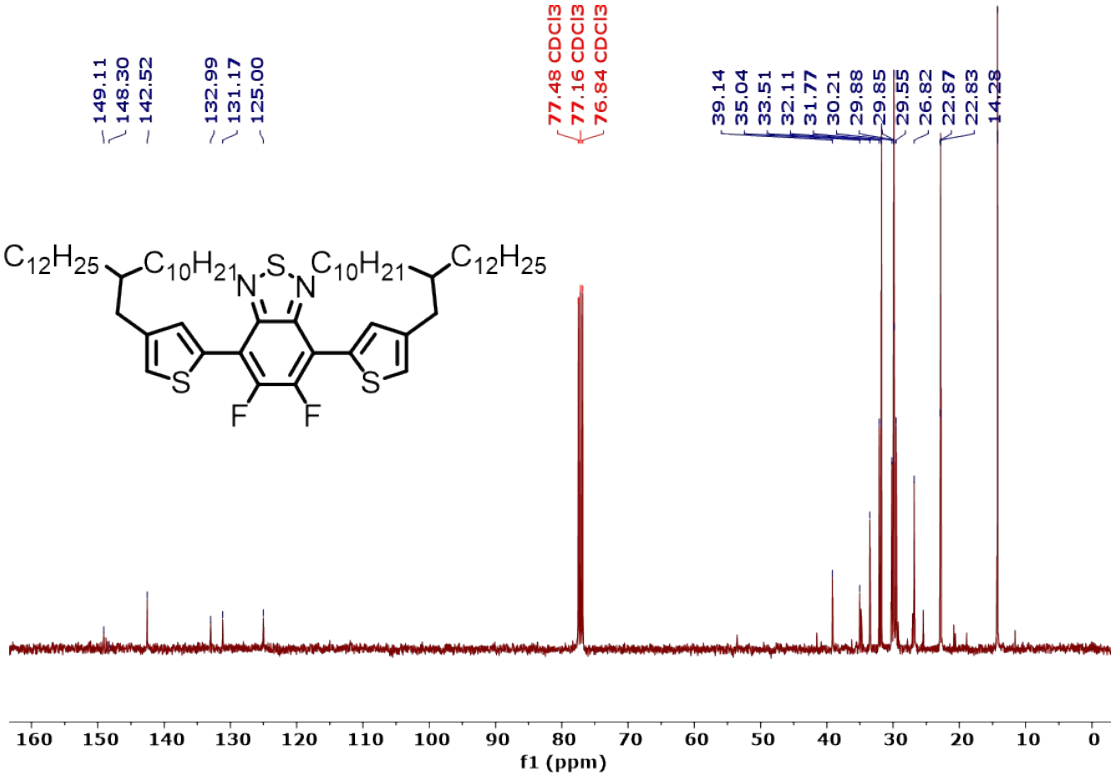

Figure S9. ^{13}C NMR spectrum of compound **4**.

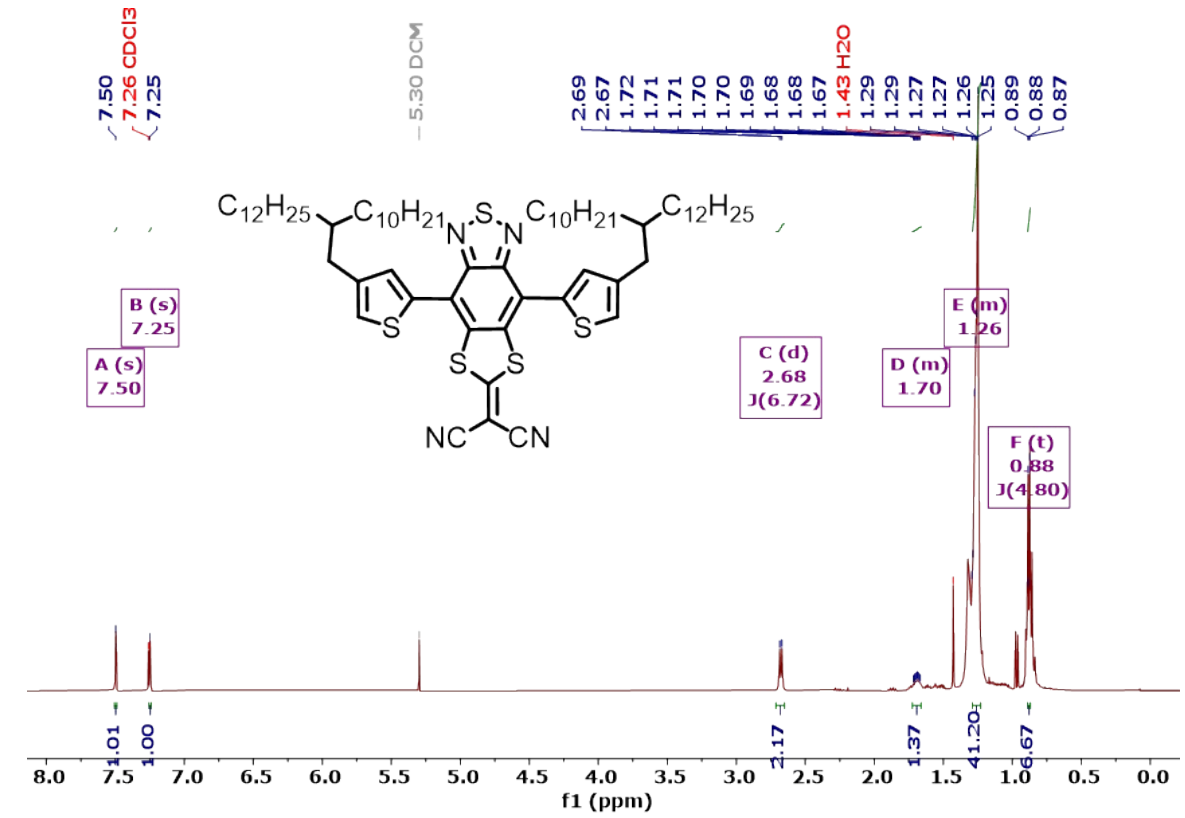

Figure S10. [1]H NMR spectrum of compound **5**.

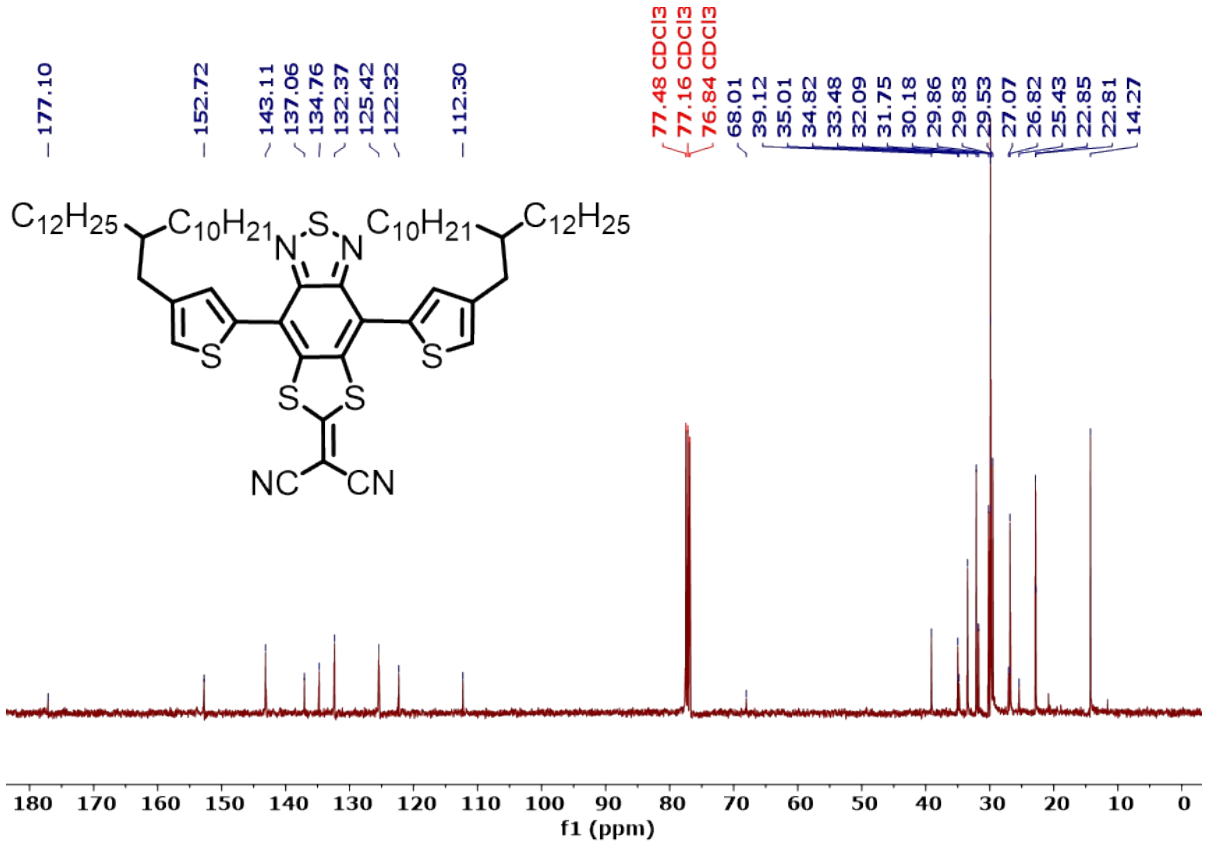

Figure S11. [13]C NMR spectrum of compound **5**.

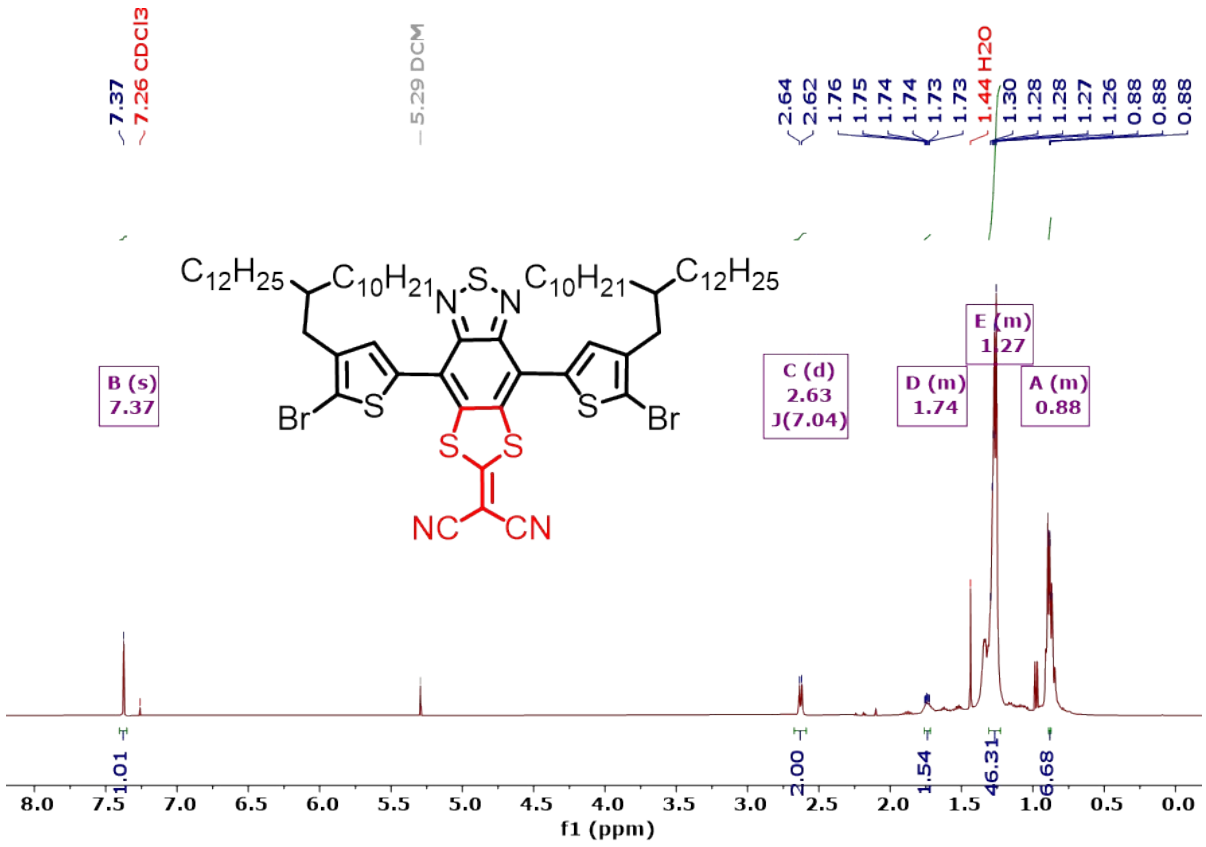

Figure S12. ^{1}H NMR spectrum of compound **6**.

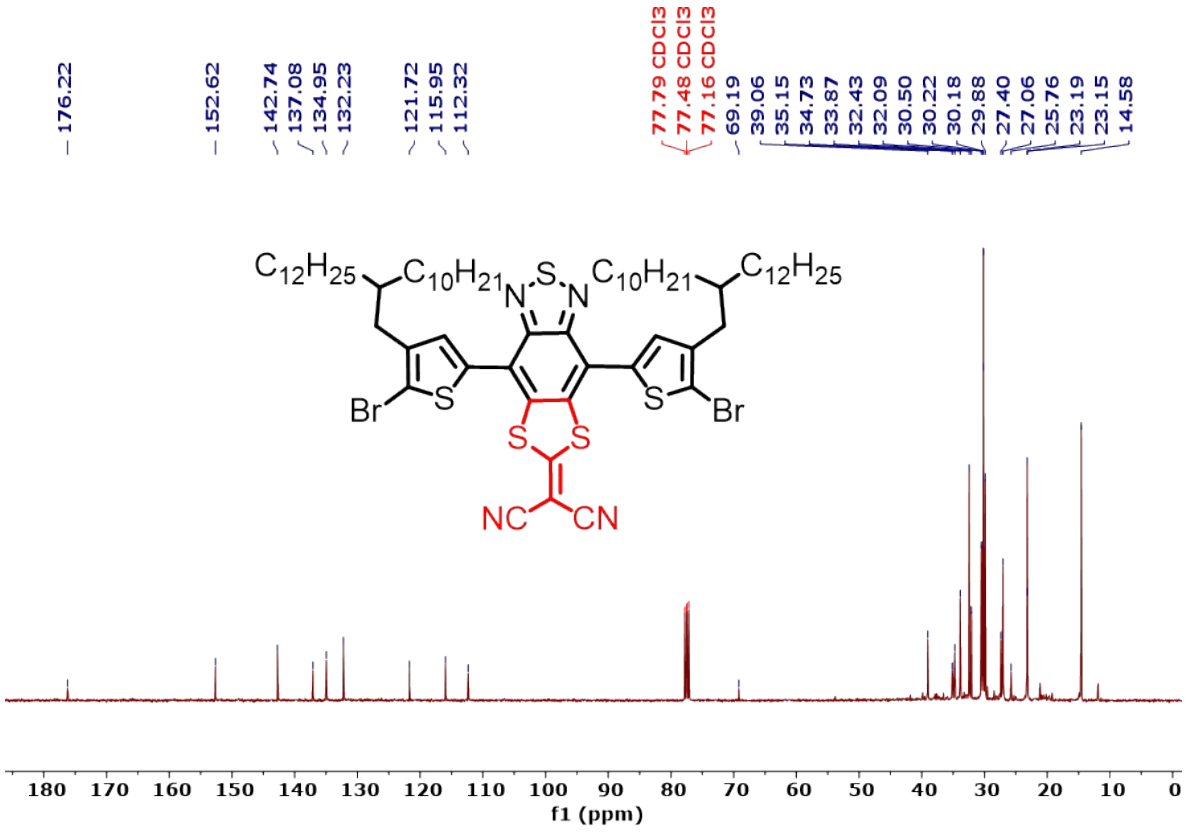

Figure S13. ^{13}C NMR spectrum of compound **6**.

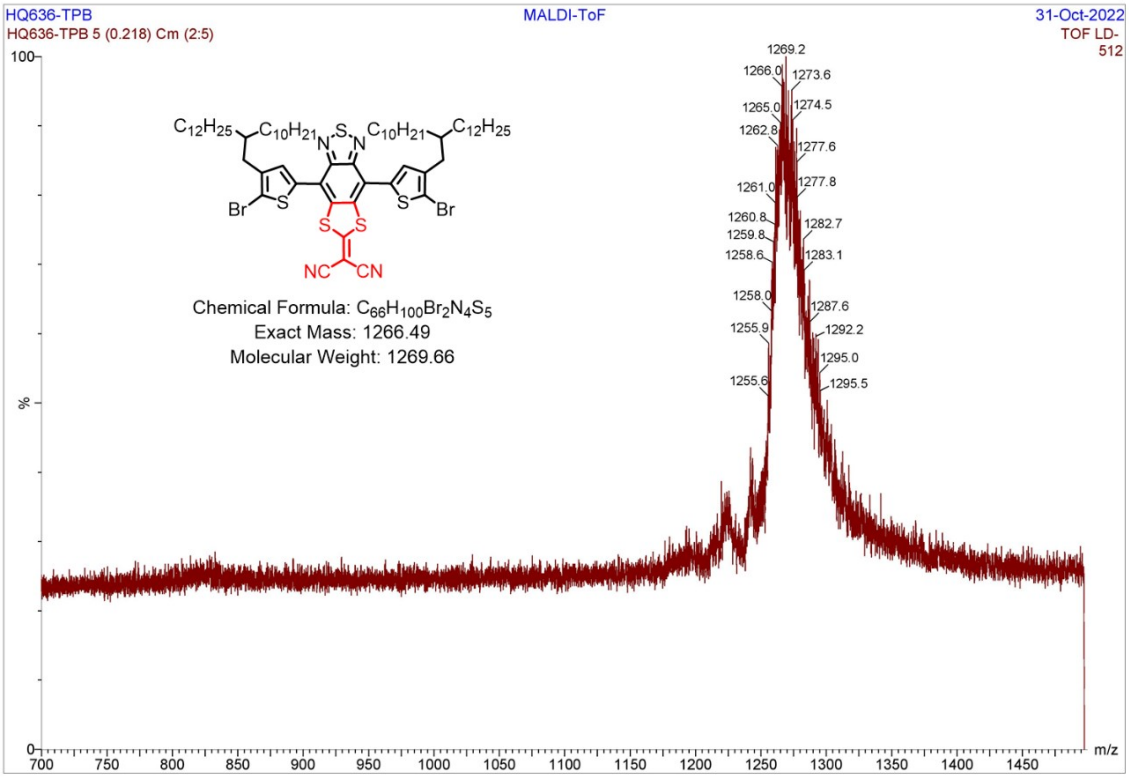

Figure S14. Mass spectrum of compound 6.

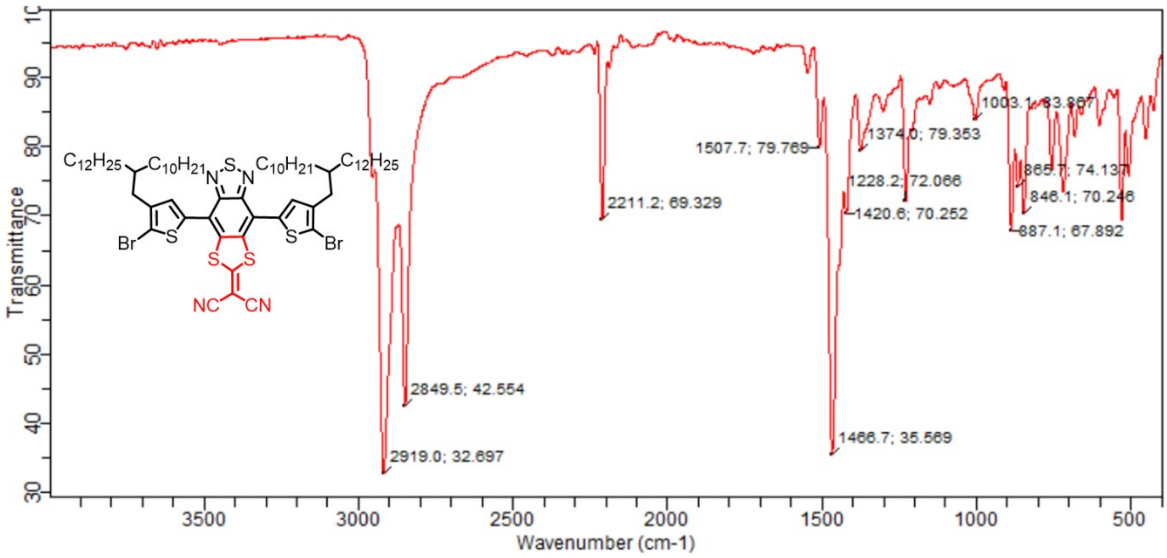

Figure S15. FTIR of compound 6.

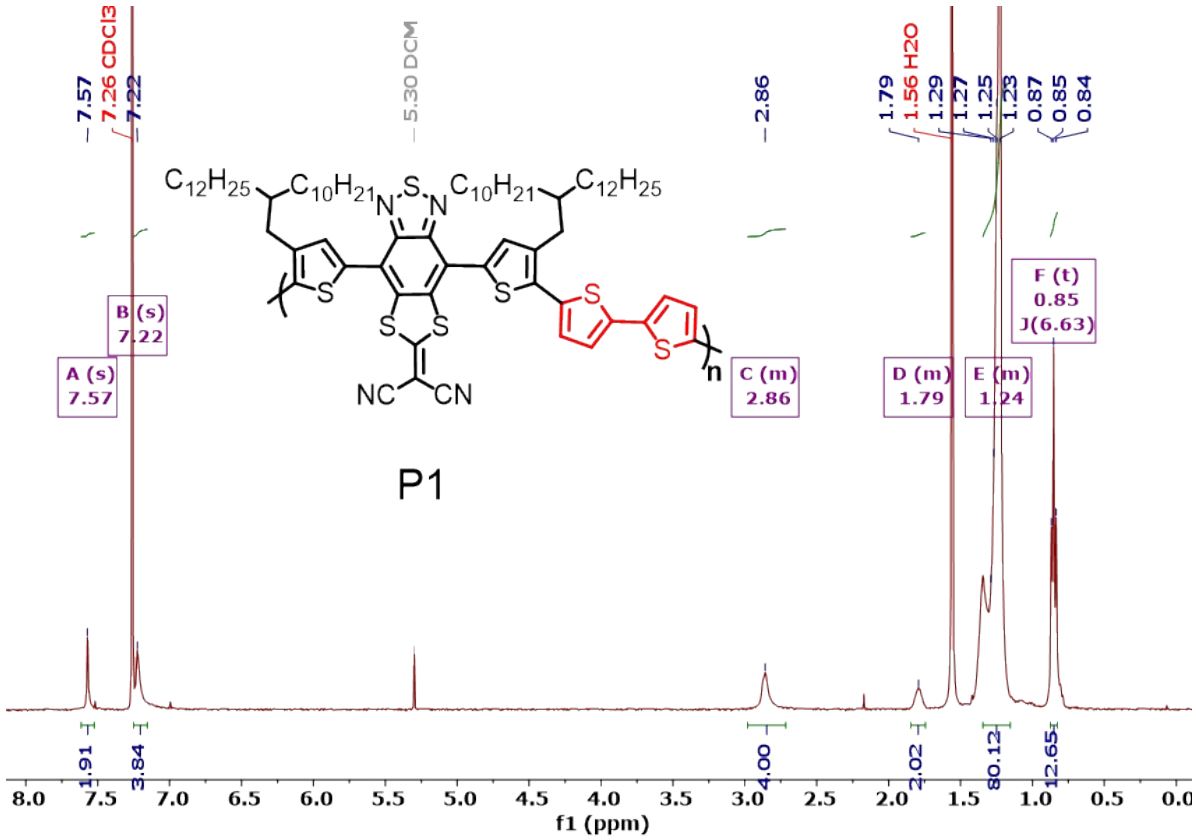

Figure S16. ^{1}H NMR spectrum of polymer **P1**.

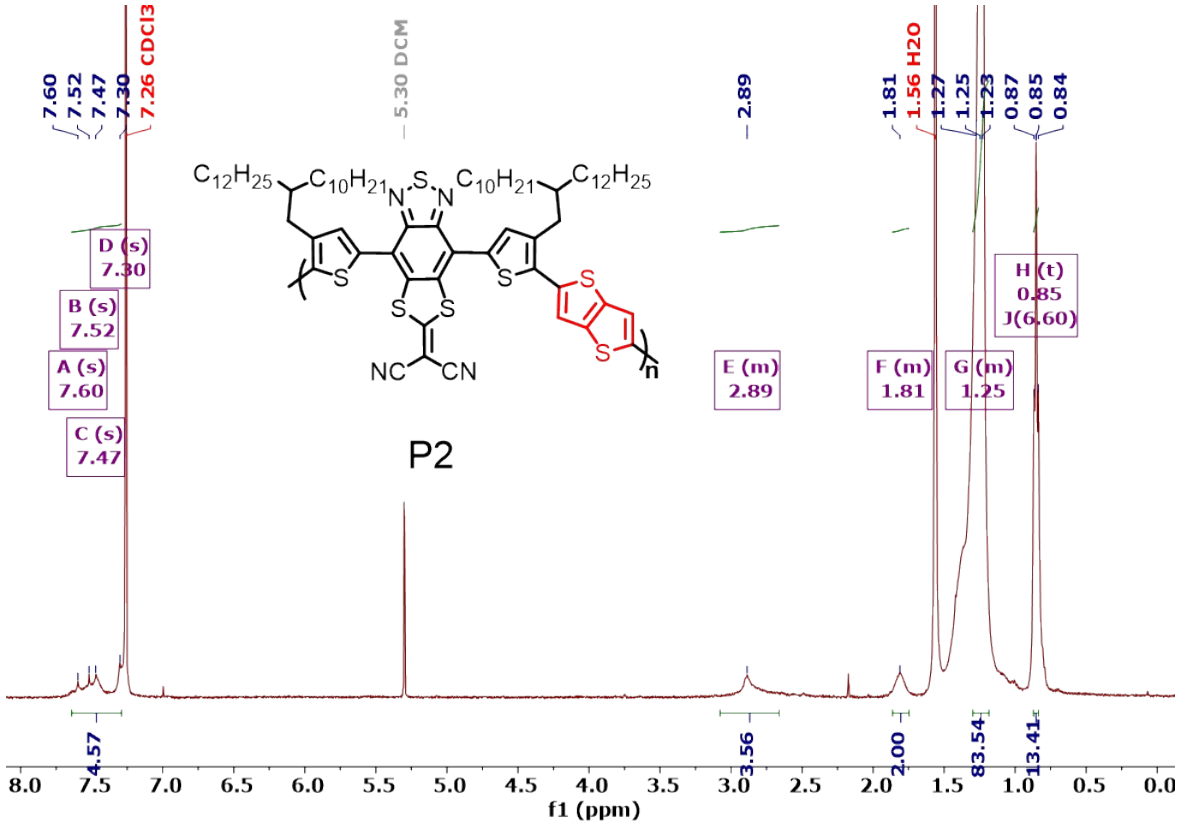

Figure S17. ^{1}H NMR spectrum of polymer **P2**.

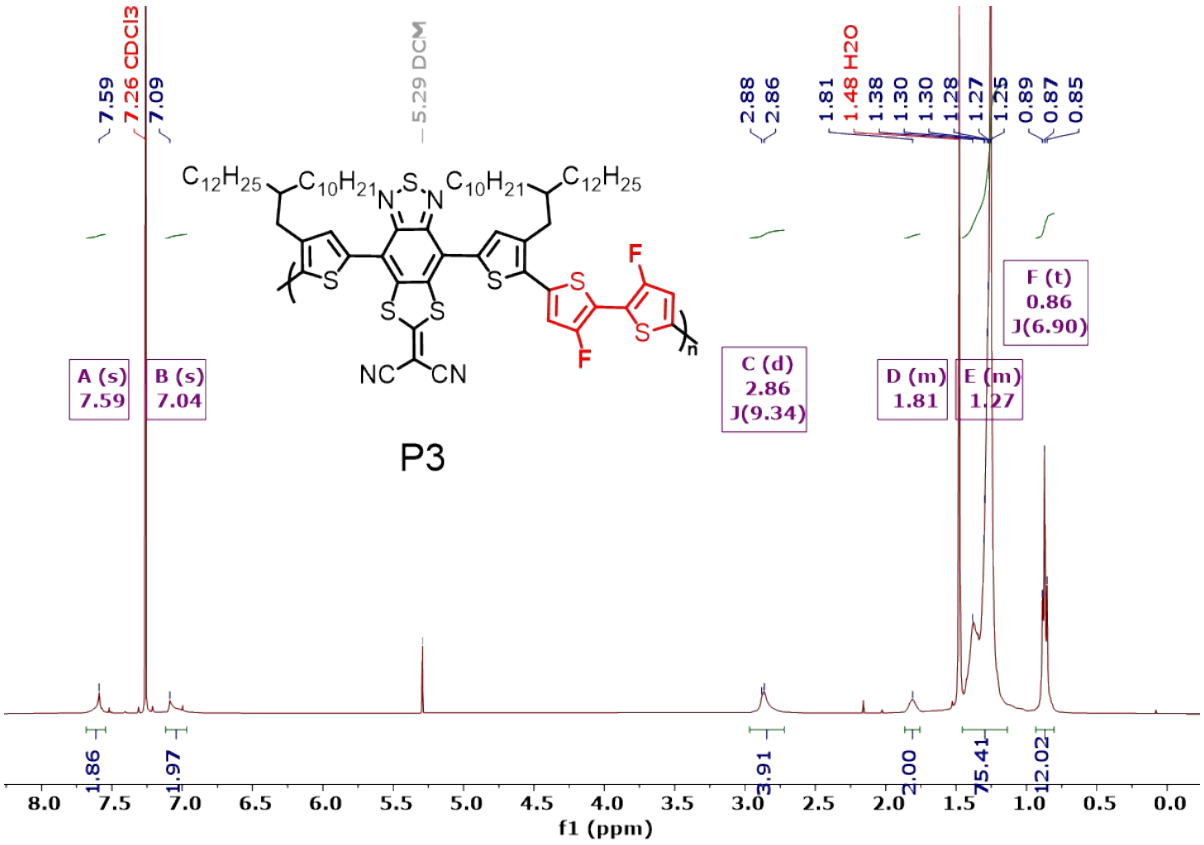

Figure S18. ^{1}H NMR spectrum of polymer **P3**.

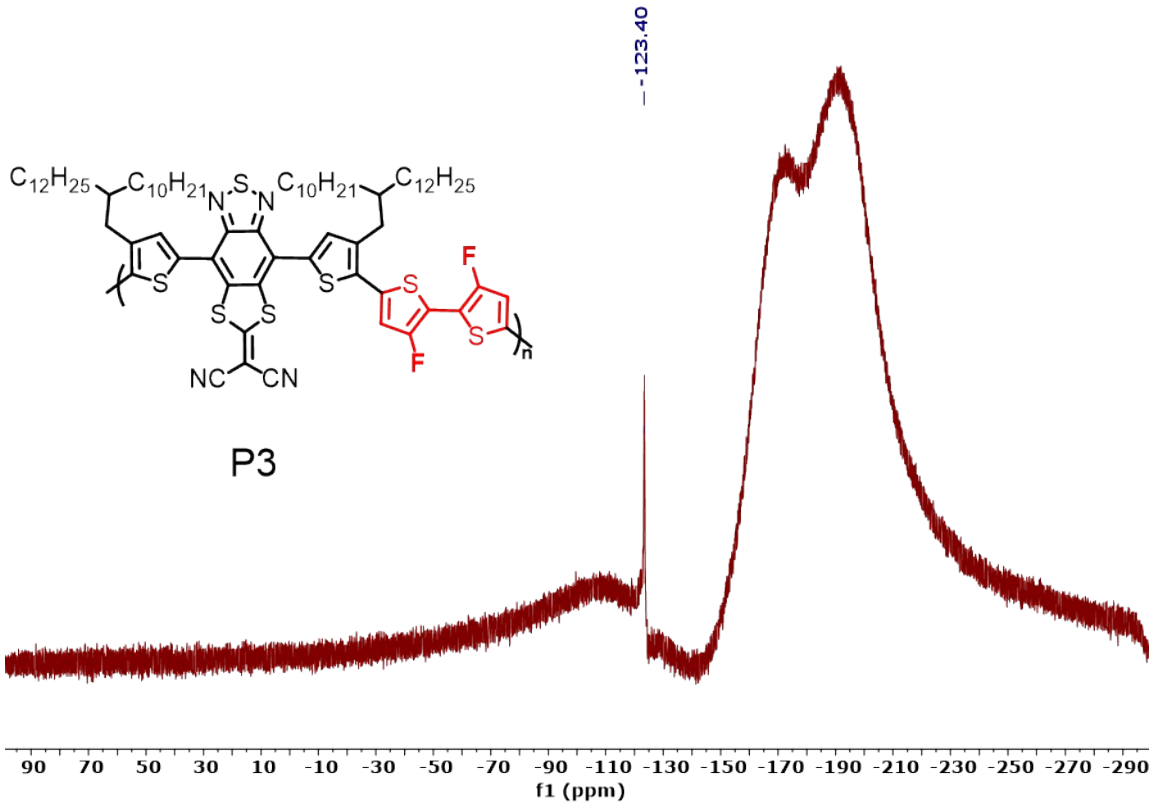

Figure S19. ^{19}F NMR spectrum of polymer **P3**.

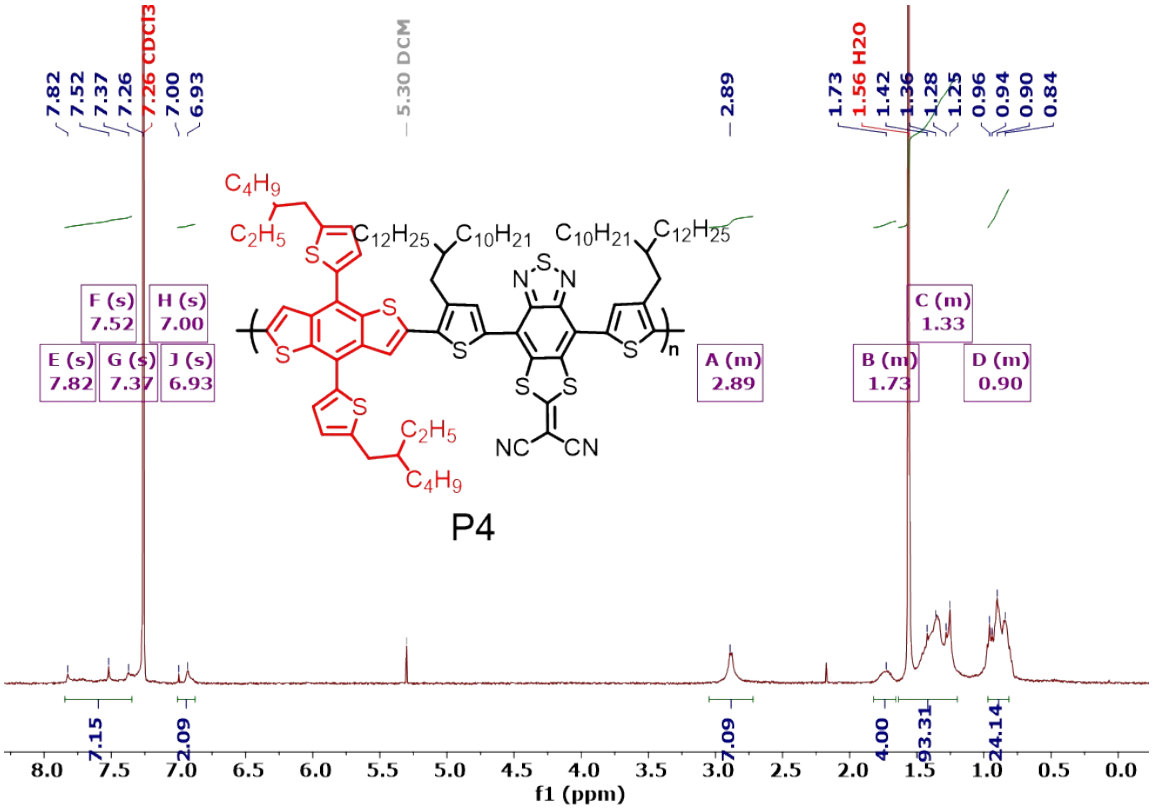

Figure S20. ^{1}H NMR spectrum of polymer **P4**.

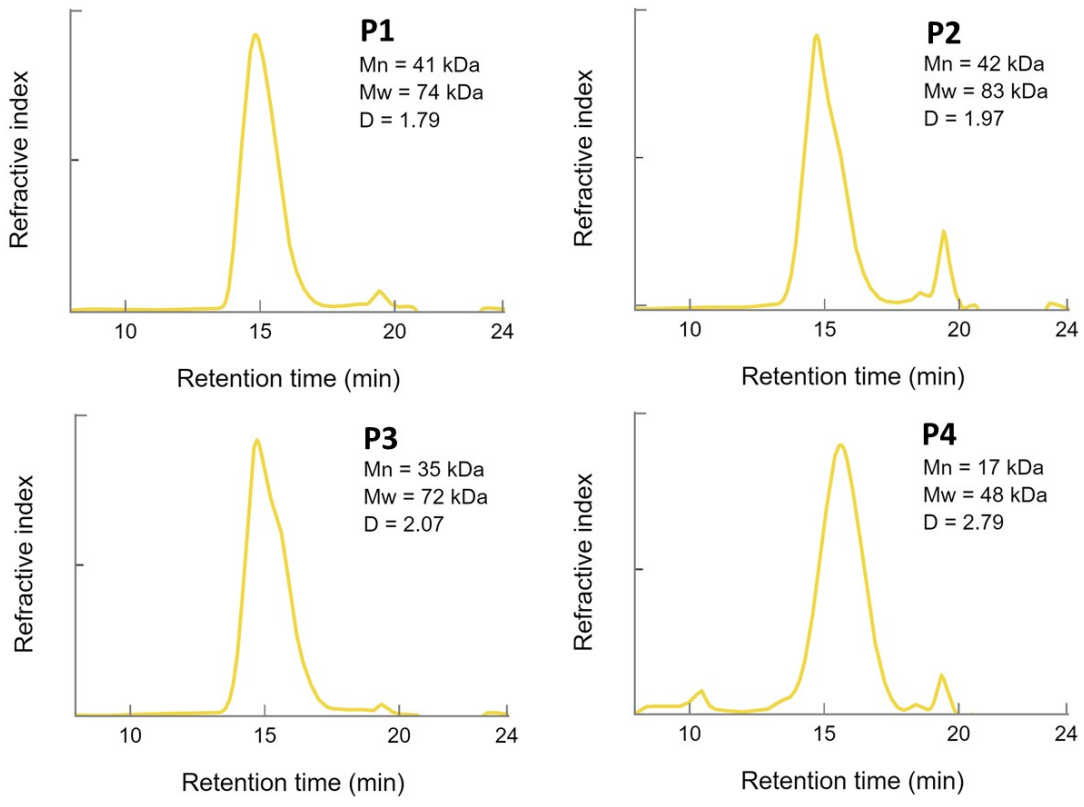

Figure S21. GPC analysis of polymers **P1**-**P4**.

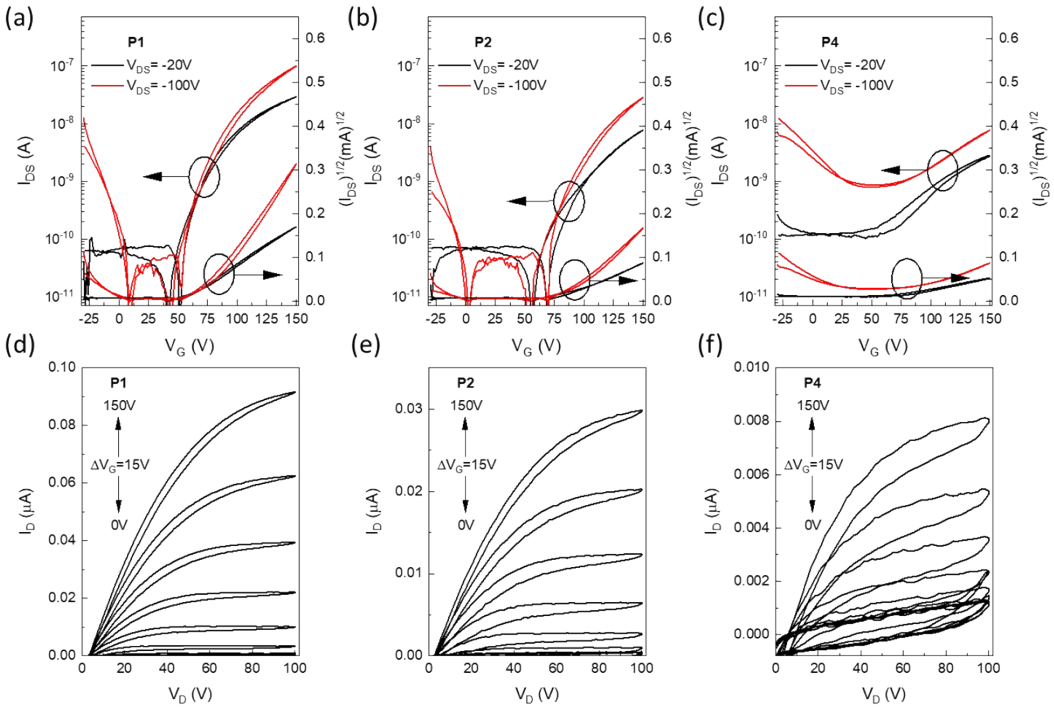

Figure S22. Transfer and output curves of OFET devices using polymers **P1**, **P2**, **P4**.

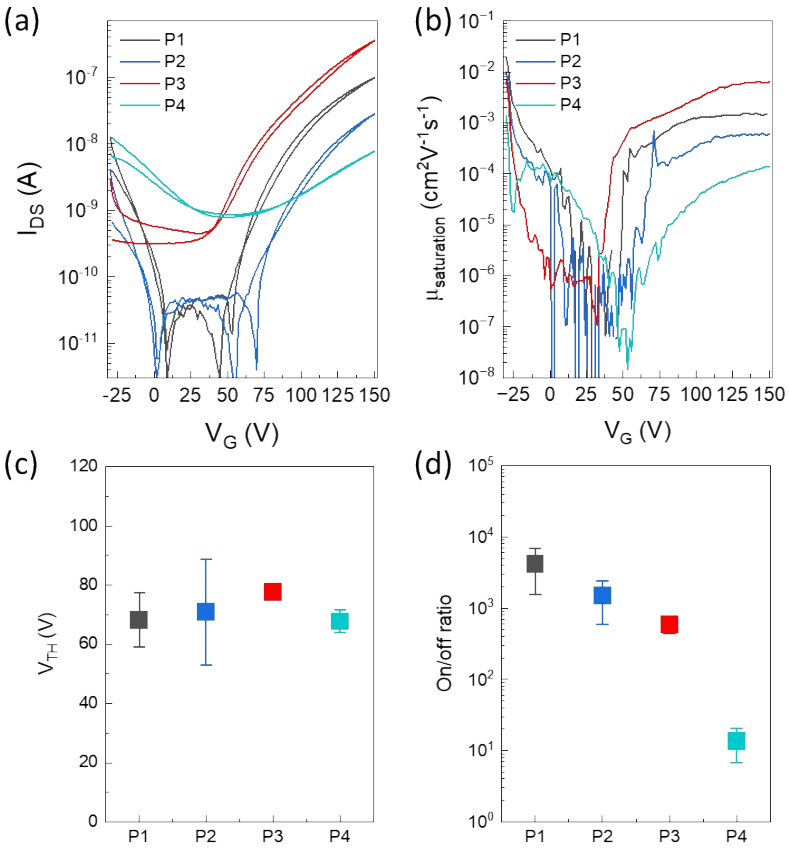

Figure S23. Comparison of the OFET performance of polymer **P1**-**P4**. (a) Transfer curves in the saturation region. (b) Gate dependent mobility curves. (c) Average threshold voltage. (d) Average on/off ratio of the devices.

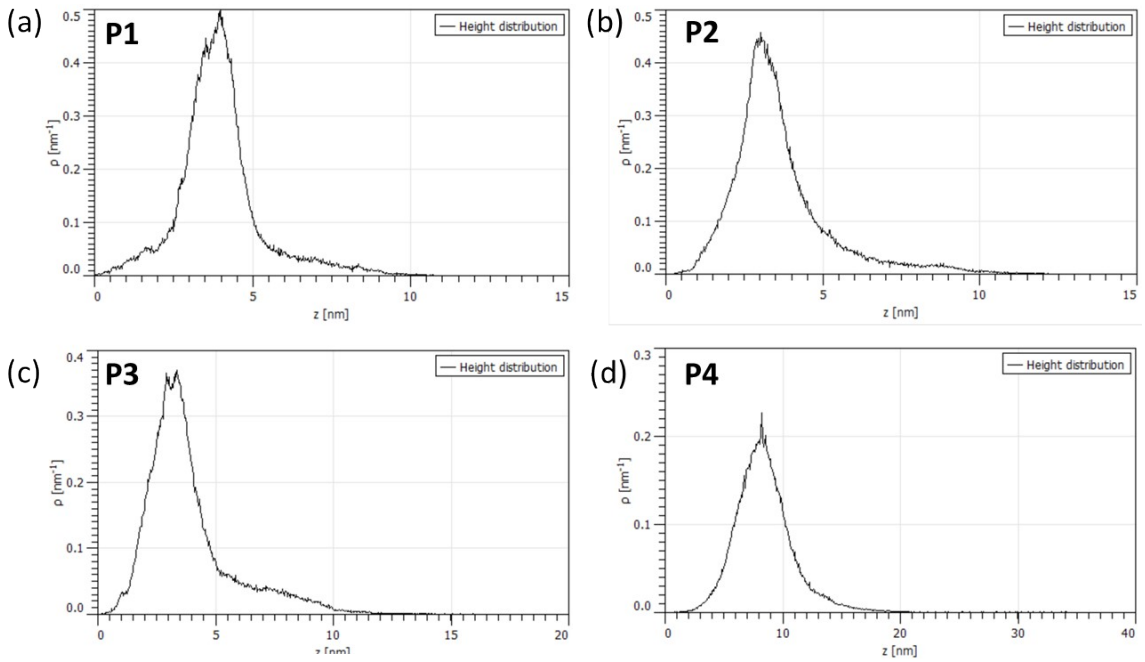

Figure S24. Height distribution extracted from AFM images of polymers **P1**-**P4**.

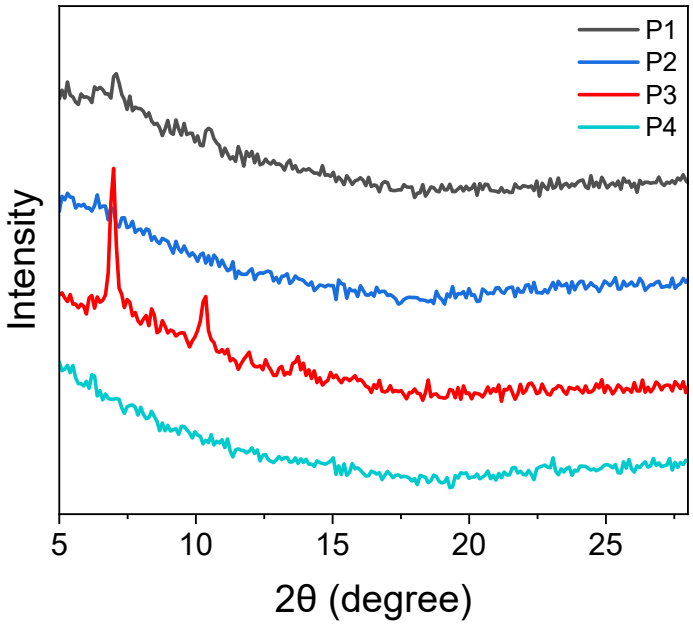

Figure S25. XRD patterns of polymers **P1**-**P4** thin films.

1 X. Hu, R. Datt, Q. He, P. Kafourou, H. Ka Hin Lee, A. J. P. White, W. C. Tsoi and M. Heeney, *Journal of Materials Chemistry C*, 2022, **10**, 9249-9256.