Supporting Information

Synthesis and Charge Transport Properties of Conjugated Polymers Incorporating Difluorothiophene as a Building Block

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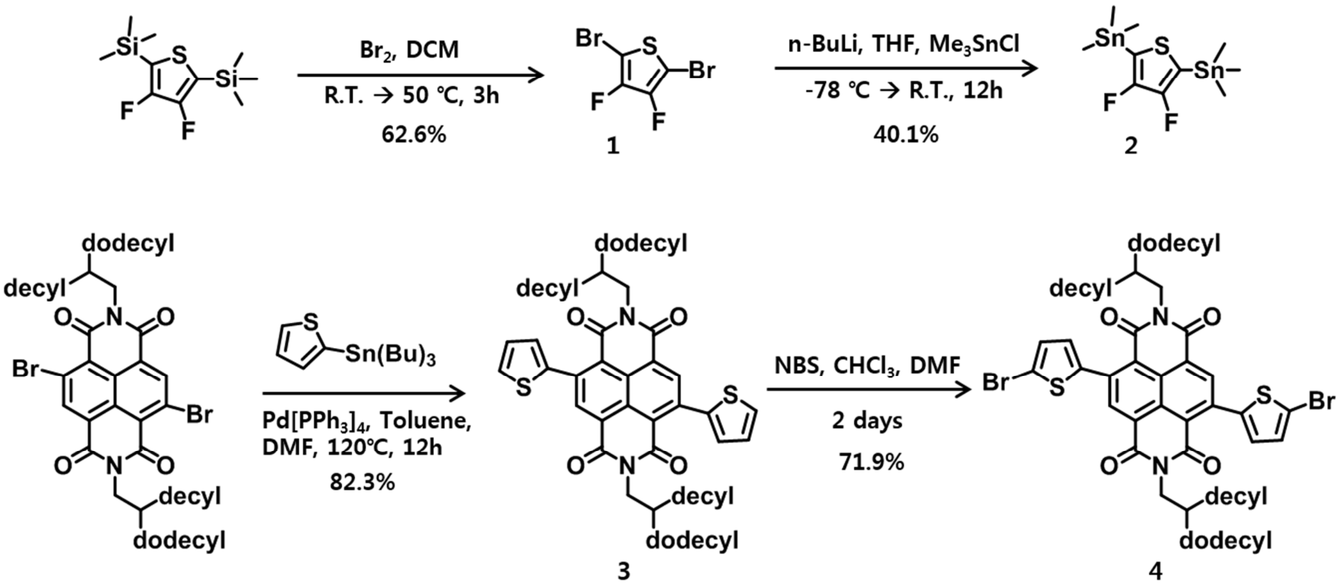
General: Unless stated otherwise, all of the chemicals and solvents were purchased from Sigma-Aldrich and were used without further purification. 3,4-difluoro-2,5-bis(trimethylsilyl)thiophene was purchased from TCI Co., Ltd. Tetrahydrofuran (THF) and toluene were distilled from blue or purple sodium benzophenone ketyl. *N,N′*-bis(2-decyltetradecyl)-2,6-dibomo-naphthalene-1,4,5,8-bis(dicarboximde) and 3,6-Bis(5-bromothiophen-2-yl)-2,5-bis(2-decyltetradecyl)pyrrolo[3,4-c]pyrrole-1,4(2H,5H)-dione were synthesized according to the procedures reported in the literature.[1,2] All the synthesized products were confirmed by a nuclear magnetic resonance (NMR) spectroscopy. ^{1}H NMR (400 MHz) and ^{13}C NMR (100 MHz) spectra were recorded on a Bruker Ascend 400 spectrometer using $CDCl_3$ as a solvent. The ^{1}H NMR spectra for polymers were obtained in $C_2D_2Cl_4$ at 60 ℃. The NMR data were reported as splitting patterns and chemical shifts (δ: ppm) relative to tetramethylsilane (^{1}H NMR), $C_2D_2Cl_4$ (^{1}H NMR; 5.91 ppm) and $CDCl_3$ (^{13}C NMR). The number-average molecular weights (M_n) and distribution (PDI) of the polymers were determined using a Waters Gel-Permeation Chromatography (GPC) system at 80 ℃. The GPC system consists of the 1515 isocratic pump and the 2414 refractive index detector. 1,2-Dichlorobenzene (ODCB) was used as the eluent (flow rate: 1 mL/min) and polystyrene as the standard. The optical absorption spectra were measured by a PerkinElmer Lambda 35 UV/vis spectrometer. The thermal properties of the polymers were measured by a thermogravimetric analysis (TGA, TA instruments Q50 thermal analysis).



Scheme S1. Synthesis of monomers

Synthesis of Monomers

2,5-Dibromo-3,4-difluoro-thiophene (1) Bromine (0.97 mL, 18.96 mmol) was added dropwise into the solution of 3,4-difluoro-2,5-bis(trimethylsilyl)thiophene (2.28 g, 8.62 mmol) in dichloromethane (10 mL) at 0 ℃. After addition, the reaction flask was heated to 50 ℃ and stirred for 3 h. And then, the residue of the bromine was quenched with the aqueous solution of sodium bisulfite. The crude product was extracted with dichloromethane, dried by a rotary evaporator and anhydrous $MgSO_4$. The product was obtained by silica gel column chromatography using hexane. (1.5 g, 62.6%). ^{13}C NMR (100 MHz, $CDCl_3$) δ 143.95, 90.33.

3,4-Difluoro-2,5-bis(trimethylstannyl)-thiophene (2) A solution of the compound **1** (1.22 g, 4.39 mmol) in anhydrous tetrahydrofuran (18 mL) was cooled down to –78 ℃ using an acetone/dry ice bath and *n*-BuLi (1.6 M in Hexanes, 5.77 mL, 9.23 mmol) was added dropwise into the reaction flask at the same temperature. After 40 min, a solution of trimethyltin chloride (1.0 M in tetrahydrofuran, 21.98 mL, 21.98 mmol) was injected at the temperature and the resulting solution was kept with stirring at room temperature for 12 h. The reaction was quenched by injection of water and the crude product was extracted with dichloromethane. The solution was dried over anhydrous $MgSO_4$ and the solvent was removed by a rotary evaporator. The product was obtained by recrystallization in methanol at a decreased temperature. (786.2 mg, 40.1 %) ^{1}H NMR (400 MHz, $CDCl_3$) δ 0.39 (s, 18H), ^{13}C NMR (100 MHz, $CDCl_3$) δ 151.75, 119.84, -8.57.

***N,N′*-bis(2-decyltetradecyl)-2,6-di(thiophene-2-yl)naphthalene-1,4,5,8-bis(dicarboximde) (3)** *N,N′*-bis(2-decyltetradecyl)-2,6-dibomo-naphthalene-1,4,5,8-bis(dicarboximde) (302.2 mg, 0.275 mmol), 2-(tributylstannyl)thiophene (0.26 mL, 0.818 mmol) and tetrakis(triphenylphosphine)palladium(0) (15.9 mg, 0.014 mmol) were put into a flask. 4.8 mL of degassed toluene and 1.2 mL of degassed dimethlyformamide were added into the reaction flask. The reaction mixture were heated to 120 ℃ for 12 h under an argon atmosphere. After cooling the flask to room temperature, the crude product was diluted with dichloromethane and washed with brine. The solvent was dried over anhydrous $MgSO_4$ and removed by rotary evaporator. The product was obtained by silica gel column chromatography using dichloromethane:hexane=1:1. (249.8 mg, 82.3%) ^{1}H NMR (400 MHz, $CDCl_3$) δ 8.75 (s, 2H), 7.60 (d, 2H), 7.31 (d, 2H), 7.20 (d, 2H), 4.07 (d, 4H), 2.10-1.83 (br, 2H), 1.45-1.10 (m, 80H), 0.89-0.82 (m, 12H). ^{13}C NMR (100 MHz, $CDCl_3$) δ 162.33, 162.17, 140.65, 140.06, 136.48, 128.22, 127.95, 127.28, 125.22, 123.14, 44.68, 36.31, 31.80, 31.43, 29.93, 29.53, 29.23, 26.25, 22.57, 14.01.

***N,N′*-bis(2-decyltetradecyl)-2,6-bis(5-bromothiophen-2-yl)naphthalene-1,4,5,8-bis(dicarboximide) (4)** The compound **3** was put into a flask and dissolved in 8 mL of chloroform and 2 mL of dimethylformamide. A solution of *N*-bromosuccinimide (96.7 mg, 0.543 mmol) in 2 mL of chloroform and 3 mL of dimethylformamide was added dropwise into the reaction flask. The mixture was stirred for 2 days at room temperature under dark condition by aluminum foil wrapping. The solvent was removed by rotary evaporator and the crude product was purified by silica gel column chromatography using dichloromethane:hexane=1:2 to obtained the product. (205 mg, 71.9%) ^{1}H NMR (400 MHz, $CDCl_3$) δ 8.71 (s, 2H), 7.14 (d, 2H), 7.08 (d, 2H), 4.06 (d, 4H), 2.01-1.83 (m, 2H), 1.43-1.10 (m, 80H), 0.92-0.79 (m, 12H). ^{13}C NMR (100 MHz, $CDCl_3$) δ 162.34, 142.19, 139.08, 136.49, 130.20, 128.80, 127.50, 125.63, 123.15, 115.55, 44.98, 36.51, 31.94, 31.61, 30.08, 29.67, 29.38, 26.35, 22.69, 14.03.

Synthesis of polymers

PNDIFT(L): 3,4-Difluoro-2,5-bis(trimethylstannyl)-thiophene **(2)** (35.7 mg, 0.08 mmol), *N,N′*-bis(2-decyltetradecyl)-2,6-bis(5-bromothiophen-2-yl)naphthalene-1,4,5,8-bis(dicarboximide) **(4)** (101 mg, 0.08 mmol) and tetrakis(triphenylphosphine)palladium(0) (3.9 mg, 3.44 μmol) was put into a flask. 1.3 mL of degassed toluene and 0.3 mL of dimethylformamide was added into the flask and dissolved the mixture. The reaction flask was heated to 120 ℃ for 36 h under argon protection. After cooling the flask to room temperature, the crude product was precipitated into methanol (50 mL) and collected by filteration. The polymer was washed with hexane, methanol by Soxhlet extraction and collected with chloroform. The collected solution was filtered with celite, condensed by rotary evaporator and precipitated into methanol. The polymer was obtained by filteration and vacuum drying. (62 mg, 63.5%) GPC(*o*-DCB, 80 ℃): M_n = 13.5 kg/mol; PDI = 1.53.

PNDIFT(H): 3,4-Difluoro-2,5-bis(trimethylstannyl)-thiophene **(2)** (35.5 mg, 0.08 mmol), *N,N′*-bis(2-decyltetradecyl)-2,6-bis(5-bromothiophen-2-yl)naphthalene-1,4,5,8-bis(dicarboximide) **(4)** (100.4 mg, 0.08 mmol), Tris(dibenzylideneacetone)dipalladium(0) (1.5 mg, 1.6 μmol) and Tri(*o*-tolyl)phosphine (1.9 mg, 6.4 μmol) were put into a flask. 1.6 mL of degassed chlorobenzene was added into the flask and dissolved the mixture. The reaction flask was heated to 120 ℃ for 36 h under argon protection. After cooling the flask to room temperature, the crude product was precipitated into methanol (50 mL) and collected by filteration. The polymer was washed with hexane, methanol by Soxhlet extraction and collected with chloroform. The collected solution was filtered with celite, condensed by rotary evaporator and precipitated into methanol. The polymer was obtained by filteration and vacuum drying. (82.5 mg, 85.0%) GPC(*o*-DCB, 80 ℃): M_n = 24.7 kg/mol; PDI = 1.83.

PDPPFT(L): PDPPFT(L) was synthesized according to the similar procedure to that for **PNDIFT(L)** at 120 ℃ for 36 h, with 3,4-Difluoro-2,5-bis(trimethylstannyl)-thiophene **(2)** (53.6 mg, 0.12 mmol), 3,6-Bis(5-bromothiophen-2-yl)-2,5-bis(2-decyltetradecyl)pyrrolo[3,4-c]pyrrole-1,4(2H,5H)-dione (136.1 mg, 0.12 mmol) and tetrakis(triphenylphosphine)palladium(0) (6.0 mg, 5.17 μmol). The polymer was washed with methanol, acetone, ethyl acetate by Soxhlet extraction and collected with chloroform. (90 mg, 68.8%) GPC(*o*-DCB, 80 ℃): M_n = 26.8 kg/mol; PDI = 2.98.

PDPPFT(H): PDPPFT(H) was synthesized according to the similar procedure to that for **PNDIFT(H)** at 120 ℃ for 36 h, with 3,4-Difluoro-2,5-bis(trimethylstannyl)-thiophene **(2)** (50.8 mg, 0.114 mmol), 3,6-Bis(5-bromothiophen-2-yl)-2,5-bis(2-decyltetradecyl)pyrrolo[3,4-c]pyrrole-1,4(2H,5H)-dione (129.0 mg, 0.114 mmol), Tris(dibenzylideneacetone)dipalladium(0) (2.1 mg, 2.3 μmol) and Tri(*o*-tolyl)phosphine (2.8 mg, 9.1 μmol). The polymer was washed with methanol, ethyl acetate by Soxhlet extraction and collected with chloroform. (108.9 mg, 87.7%) GPC(*o*-DCB, 80 ℃): M_n = 39.8 kg/mol; PDI = 2.76.

PNDI3T(L): PNDI3T(L) was synthesized according to the similar procedure to that for **PNDIFT(L)** at 120 ℃ for 36 h, with 2,5-bis(trimethylstannyl)-thiophene (77.1 mg, 0.19 mmol), *N,N′*-bis(2-

decyltetradecyl)-2,6-bis(5-bromothiophen-2-yl)naphthalene-1,4,5,8-bis(dicarboximide) **(4)** (237.4 mg, 0.19 mmol) and tetrakis(triphenylphosphine)palladium(0) (9.4 mg, 8.1 μmol) in toluene(3.1 mL) and DMF(0.8 mL). The polymer was washed with methanol, hexane, cyclohexane and collected with dichloromethane. (211 mg, 94.8%) GPC(*o*-DCB, 80 ℃): M_n = 42.6 kg/mol; PDI = 1.81.

PNDI3T(H): PNDI3T(H) was synthesized according to the similar procedure to that for **PNDIFT(L)** at 90 ℃ for 21 h, with 2,5-bis(trimethylstannyl)-thiophene (41.3 mg, 0.1 mmol, 1.25 eq.), *N,N′*-bis(2-decyltetradecyl)-2,6-bis(5-bromothiophen-2-yl)naphthalene-1,4,5,8-bis(dicarboximide) **(4)** (101.8 mg, 0.08 mmol, 1eq.) and tetrakis(triphenylphosphine)palladium(0) (5.0 mg, 4.3 μmol) in toluene(1.8 mL) and DMF (0.2 mL). The polymer was washed with methanol, ethyl acetate, hexane, cyclohexane, dichloromethane and collected with chloroform. (48 mg, 50.2%) GPC(*o*-DCB, 80 ℃): M_n = 80.7 kg/mol; PDI = 1.79.

PDPP3T(L): PDPP3T(L) was synthesized according to the similar procedure to that for **PNDIFT(L)** at 90 ℃ for 21 h, with 2,5-bis(trimethylstannyl)-thiophene (45.7 mg, 0.11 mmol, 1.25 eq.), 3,6-Bis(5-bromothiophen-2-yl)-2,5-bis(2-decyltetradecyl)pyrrolo[3,4-c]pyrrole-1,4(2H,5H)-dione (101.0 mg, 0.09 mmol, 1 eq.) and tetrakis(triphenylphosphine)palladium(0) (5.5 mg, 4.8 μmol) in toluene (1.8 mL) and DMF (0.2 mL). The polymer was washed with methanol, ethyl acetate, hexane by Soxhlet extraction and collected with cyclohexane. (84 mg, 89.3%) GPC(*o*-DCB, 80 ℃): M_n = 90.3 kg/mol; PDI = 2.06.

PDPP3T(H): PDPP3T(H) was synthesized according to the similar procedure to that for **PNDIFT(L)** at 120 ℃ for 36 h, with 2,5-bis(trimethylstannyl)-thiophene (82.4 mg, 0.20 mmol), 3,6-Bis(5-bromothiophen-2-yl)-2,5-bis(2-decyltetradecyl)pyrrolo[3,4-c]pyrrole-1,4(2H,5H)-dione (227.6 mg, 0.20

mmol) and tetrakis(triphenylphosphine)palladium(0) (10.0 mg, 8.65 μmol) in toluene (3.2 mL) and DMF (0.8 mL). The polymer was washed with methanol, hexane, cyclohexane, dichlorobenzene by Soxhlet extraction and collected with chloroform. (169 mg, 79.7%) GPC(*o*-DCB, 80 ℃): M_n = 217.1 kg/mol; PDI = 2.19.

Electrochemical Properties

To study electrochemical properties of the polymers, the cyclicvoltammetry (CV) was carried out by using a CH instruments electrochemical analyzer. Each polymer film was coated on a glassy carbon electrode and used as a working electrode. A platinum (Pt) wire was employed as a counter electrode and an Ag/Ag+ electrode was used as a reference electrode. All of the measurements were performed using a 0.1M deoxygenated tetrabutylammoniumhexafluorophosphate (Bu_4NPF_6) solution in acetonitrile as an electrolyte with a 50 mV/s potential sweep rate. The redox potential of ferrocene/ferrocenium (Fc/Fc^+) was measured under the same conditions for calibration, and located at 0.108 eV vs. Ag/Ag^+ electrode.[3] The HOMO and LUMO energy levels were then estimated according to the following equations, where φ_{ox} is the onset oxidation potential vs. Ag/Ag^+ and φ_{red} is the onset reduction potential vs. Ag/Ag^+.

$$E_{HOMO} = -4.8 - (\varphi_{ox} - 0.108)\ (eV)$$

$$E_{LUMO} = -4.8 - (\varphi_{red} - 0.108)\ (eV)$$

Device fabrication

Top-contact OFETs were prepared on a common gate of highly n-doped silicon with a thermally grown SiO_2 dielectric layer (300 nm) modified by OTS self assembled monolayer. Capacitance of the dielectric layer was measured by using an SR 720 LCR meter at frequencies ranging from 100 Hz to 100 kHz (MIM device structure was used.). The capacitance value measured at 100-120 Hz and 11 nF/cm^2 was used to extract the charge carrier mobility. Solutions including the polymer semiconductors were spin-coated at 2000 rpm from 3 wt% chloroform solutions to form thin films with a nominal thickness of 40 nm, as confirmed using a surface profiler (Alpha Step 500, Tencor). Gold source and drain electrodes were evaporated on top of the semiconductor layers (60 nm). For all measurements, typical channel widths (*W*) and lengths (*L*) were 1000 µm and 50 µm, respectively.

Device characterization

Electrical characteristics of fabricated devices were measured under an air condition by using both Keithley 236 and Keithley 2400 source/measure units combined with home-built Labview program. GIXD studies were performed in the 3C beamline at the Pohang Accelerator Laboratory (PAL). The measurements were carried out with a sample-to-detector distance of 214.111 mm. Data were collected for thirty seconds using an Xray radiation source of 1.1785 nm with a 2D charge-coupled detector (CCD) (Roper Scientific, Trenton, NJ, USA) The incidence angle for the X-ray beam was set to 0.17º, which was intermediate between the critical angles of the films and the substrate.

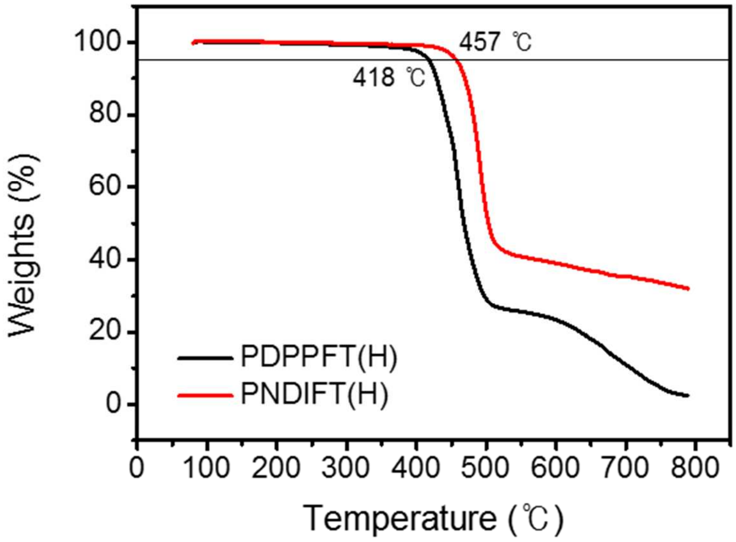


Figure S1. Thermorgravimetric analysis of PDPPFT(H) and PNDIFT(H)

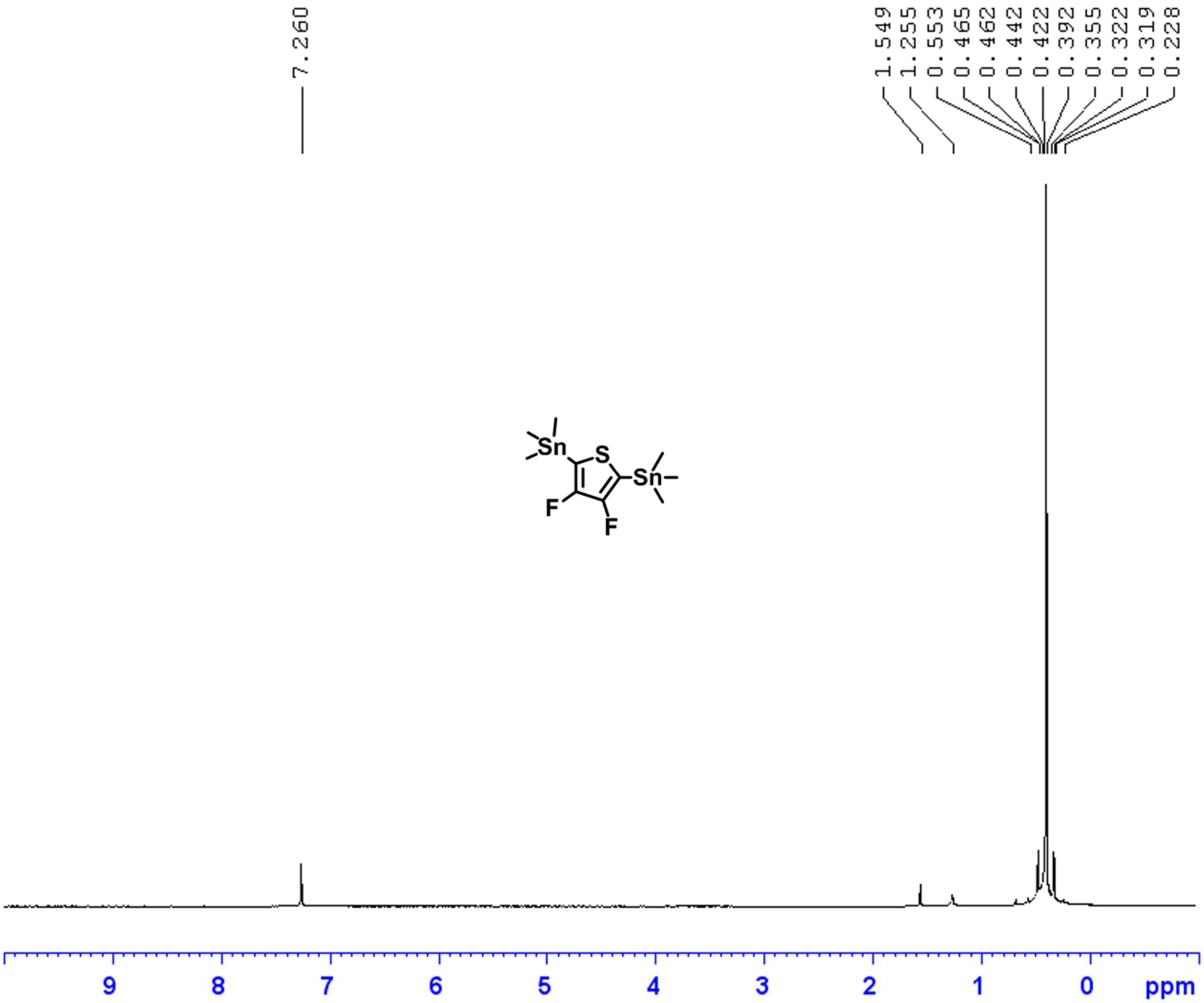


Figure S2. ^{1}H NMR spectrum of compound **2** in $CDCl_3$

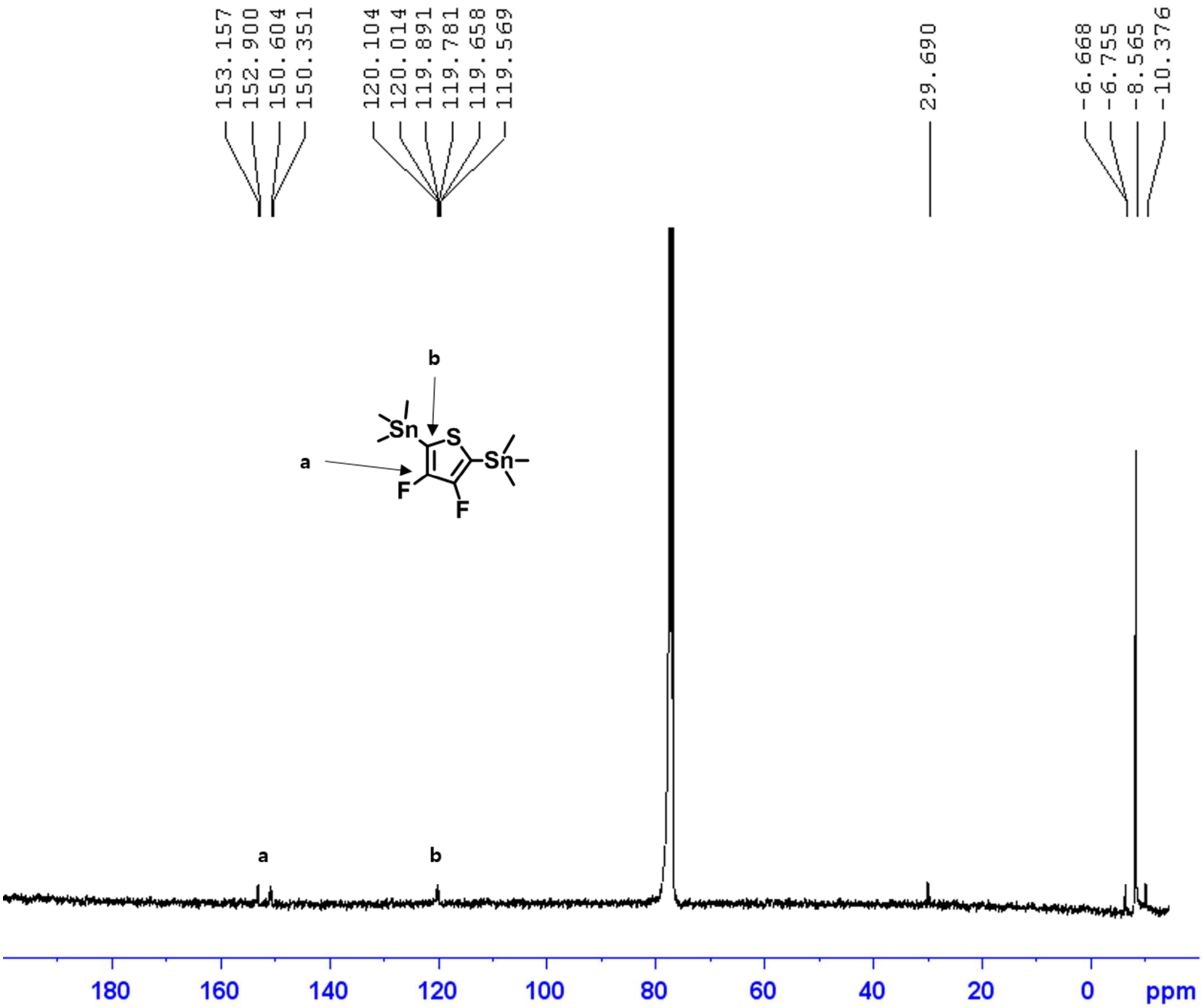


Figure S3. ^{13}C NMR spectrum of compound **2** in CDCl$_3$

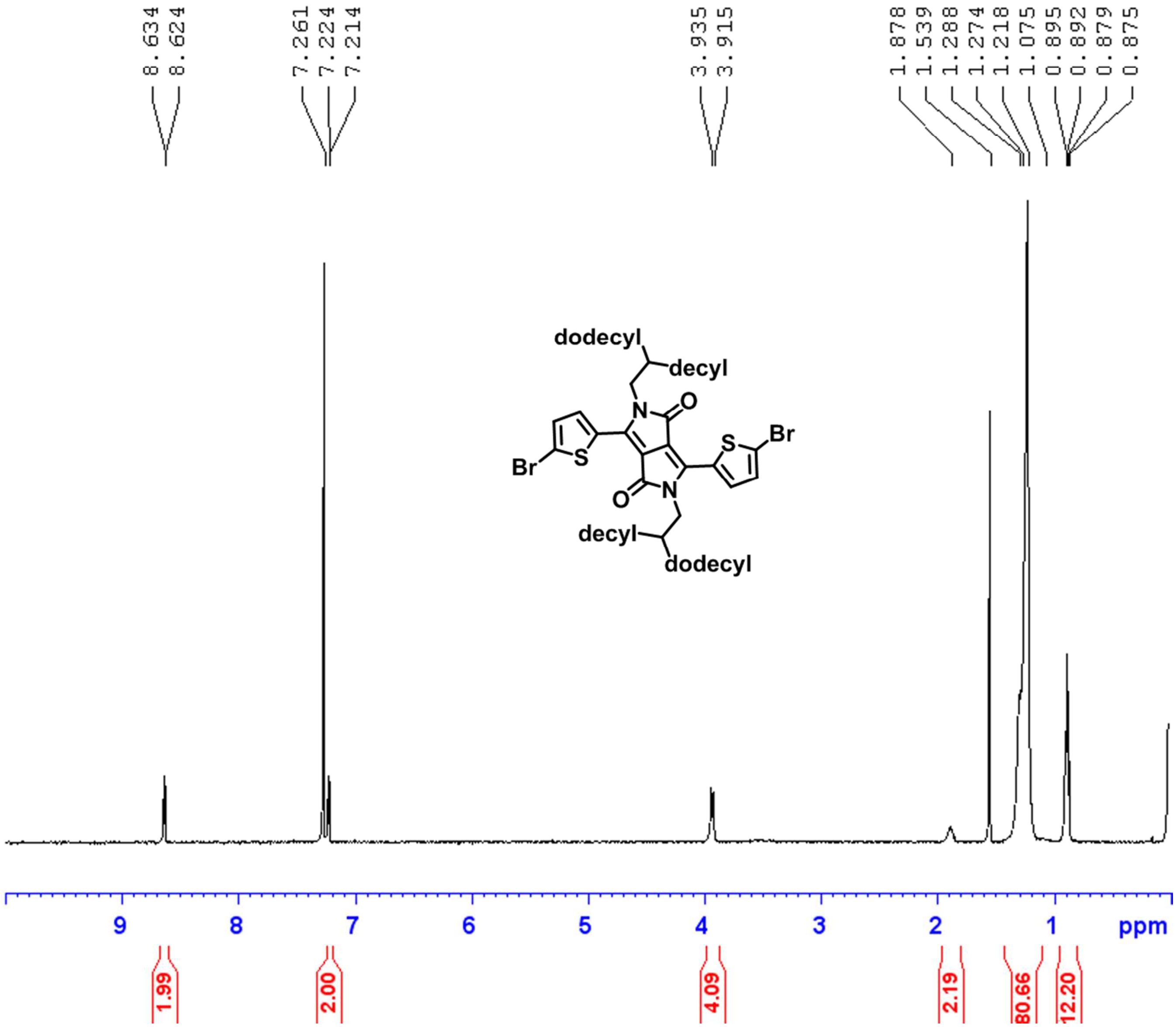


Figure S4. ^{1}H NMR of 3,6-Bis(5-bromothiophen-2-yl)-2,5-bis(2-decyltetradecyl)pyrrolo[3,4-*c*]pyrrole-1,4(2H,5H)-dione in $CDCl_3$

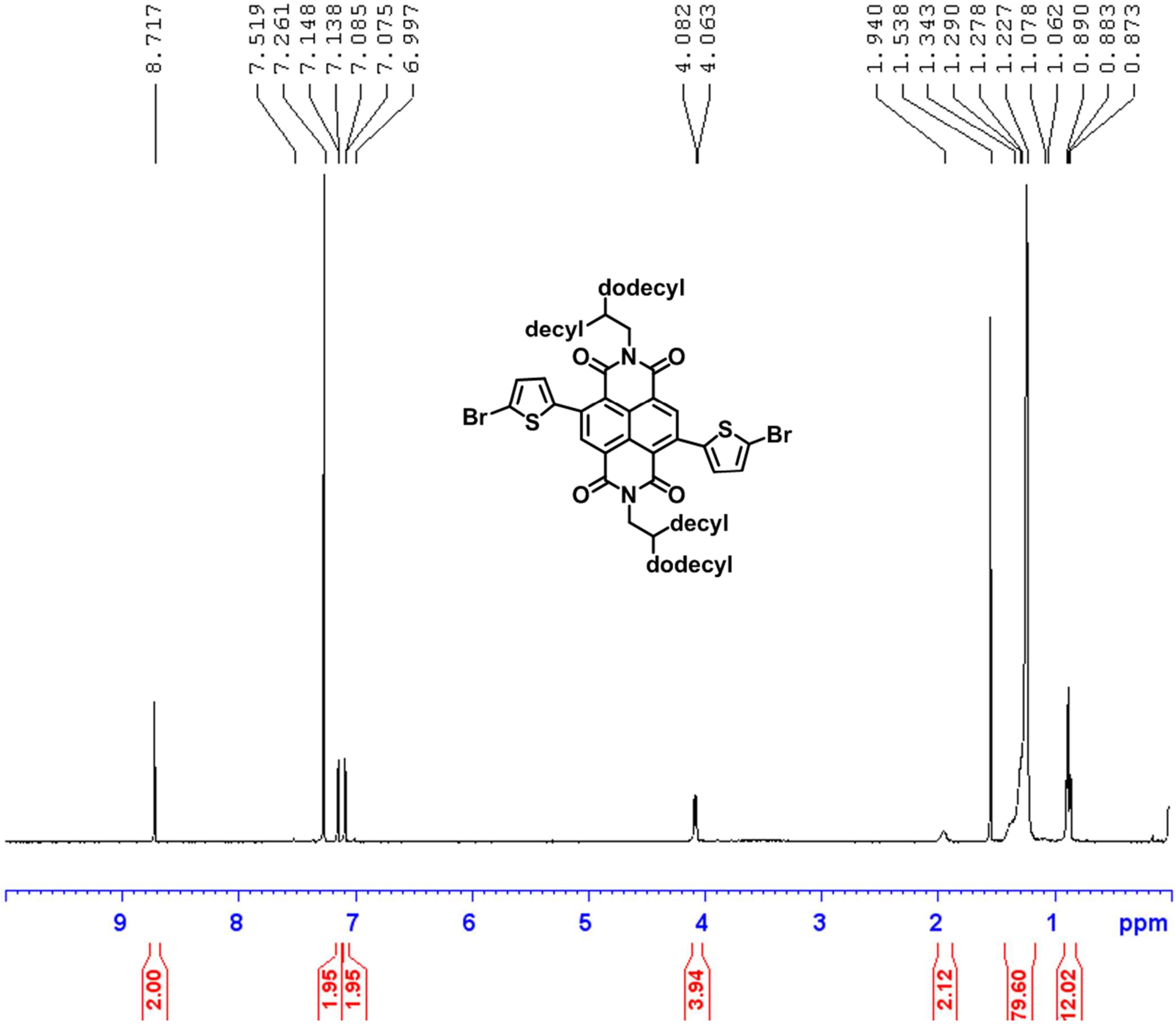


Figure S5. ^{1}H NMR spectrum of compound **4** in $CDCl_3$

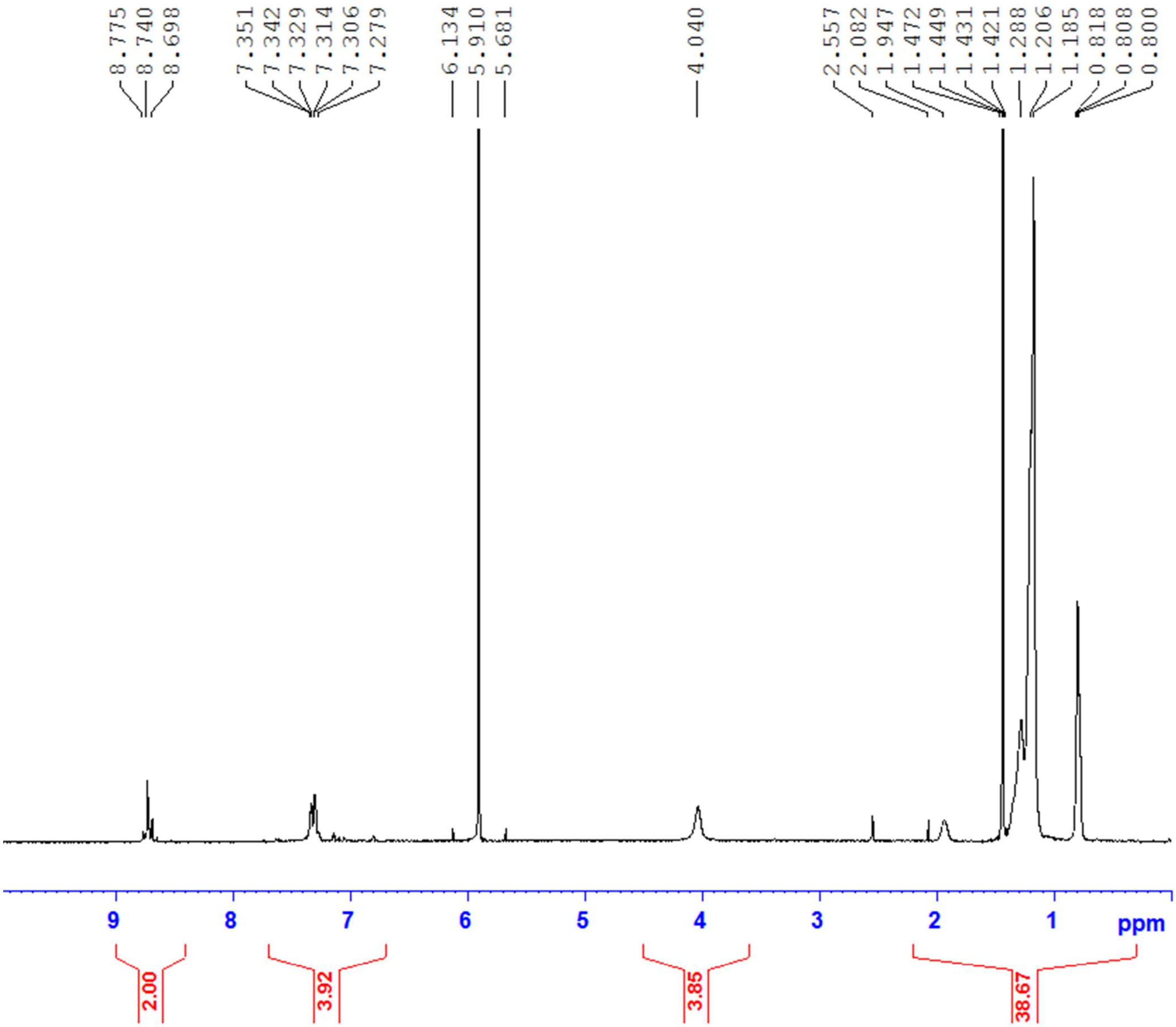


Figure S6. ^{1}H NMR spectrum of **PNDIFT(L)** in $C_2D_2Cl_4$ at 60 ℃

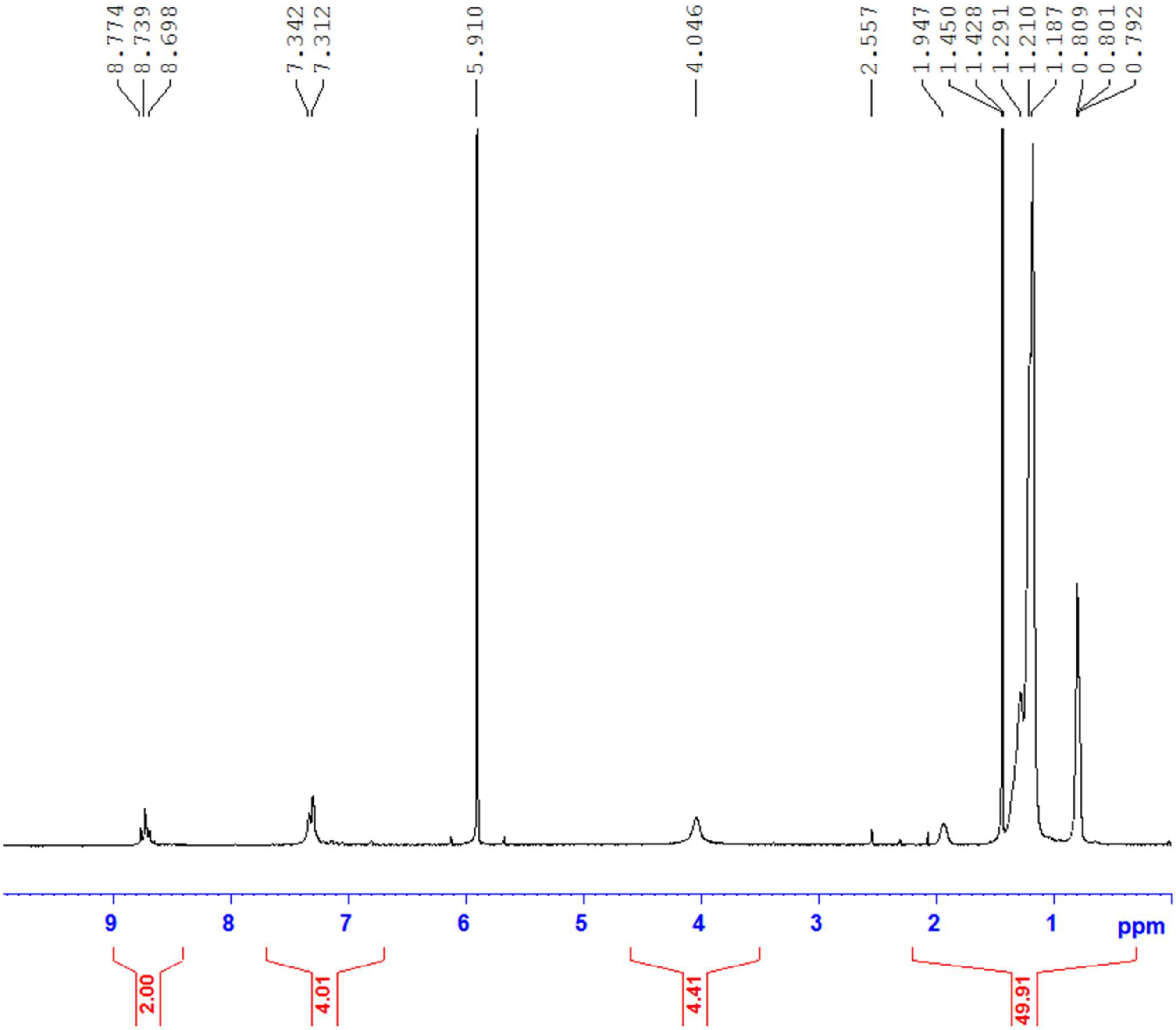


Figure S7. ^{1}H NMR spectrum of **PNDIFT(H)** in $C_2D_2Cl_4$ at 60 ℃

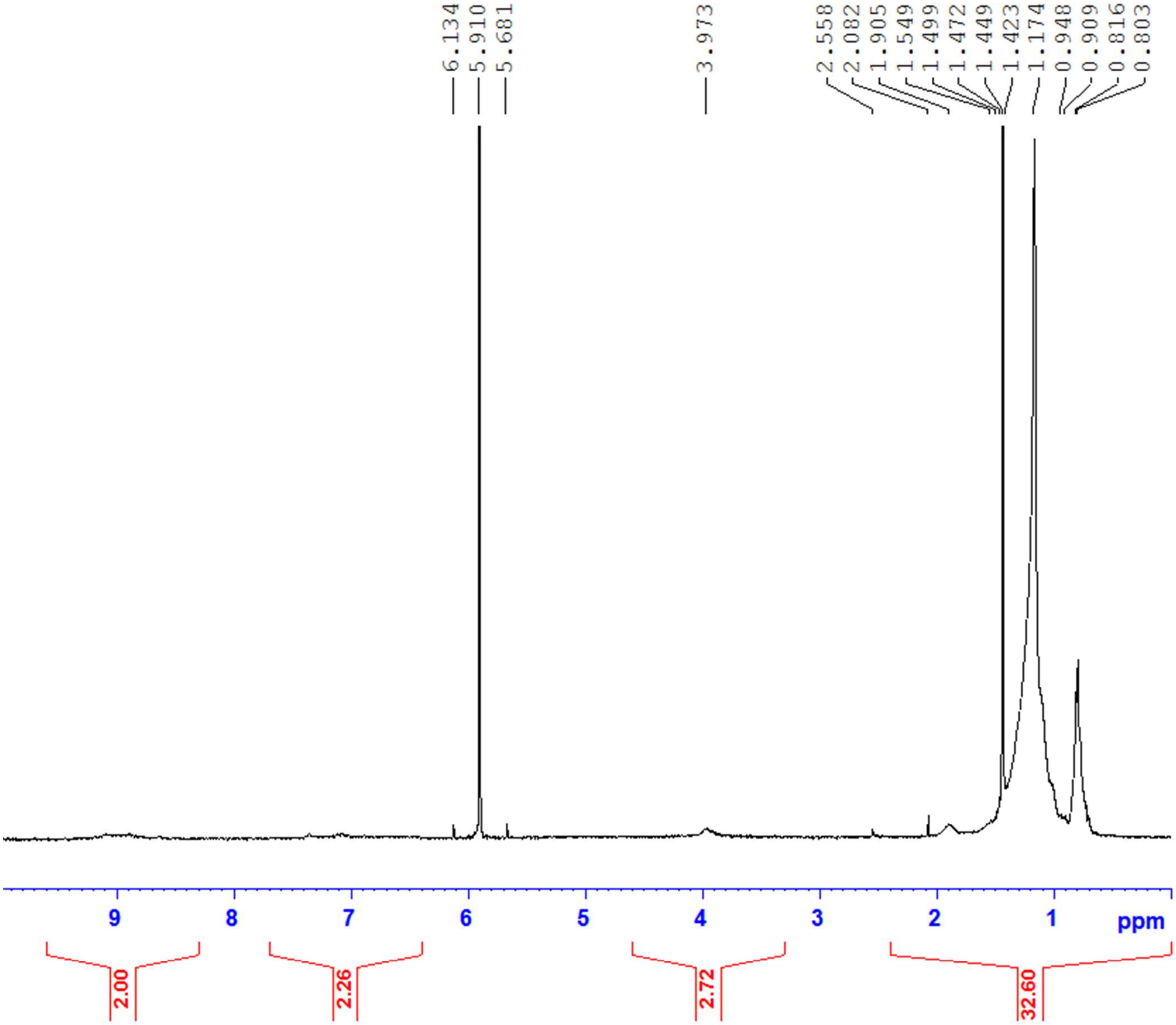


Figure S8. ^{1}H NMR spectrum of **PDPPFT(L)** in $C_2D_2Cl_4$ at 60 ℃

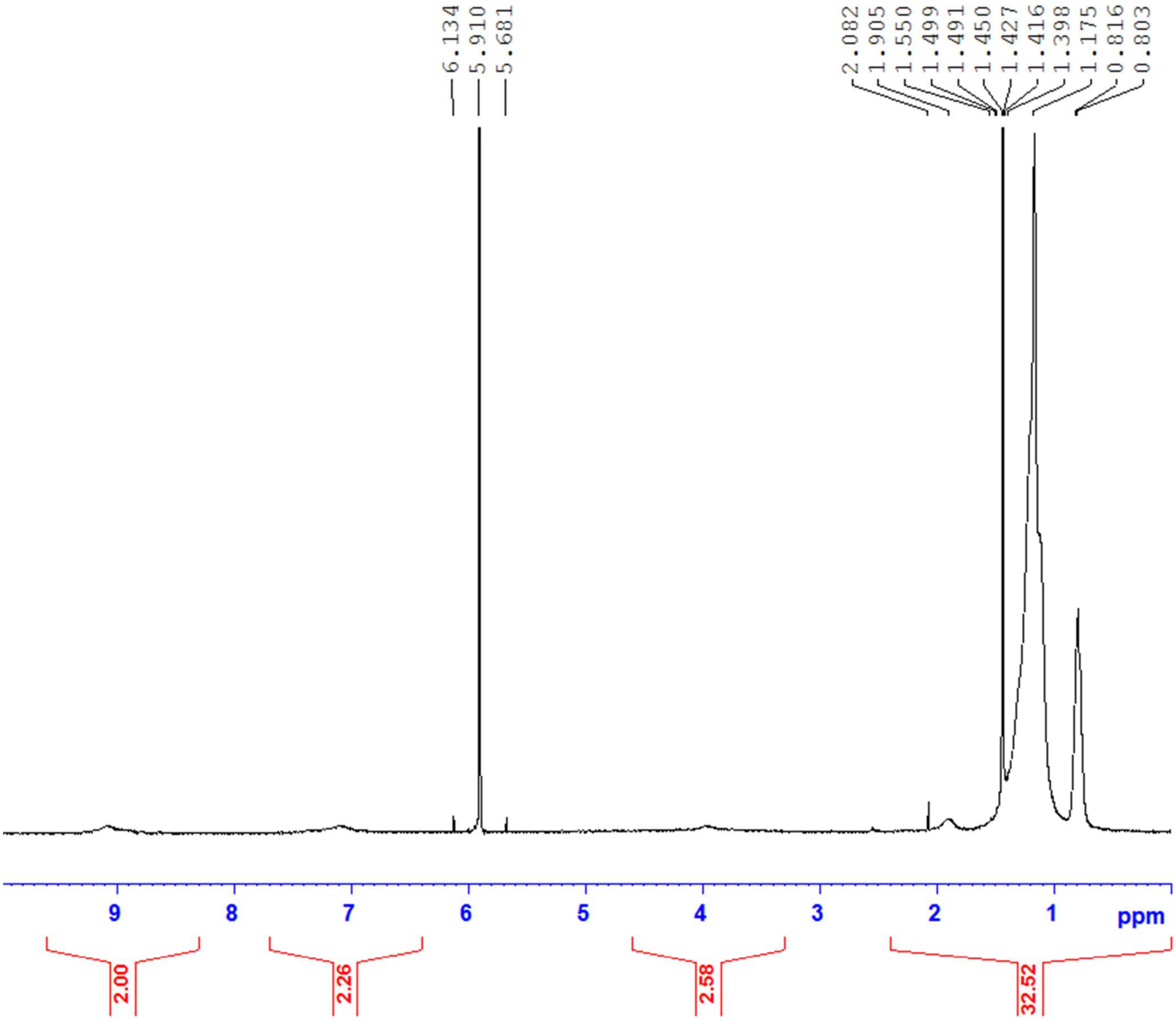


Figure S9. ^{1}H NMR spectrum of **PDPPFT(H)** in $C_2D_2Cl_4$ at 60 ℃

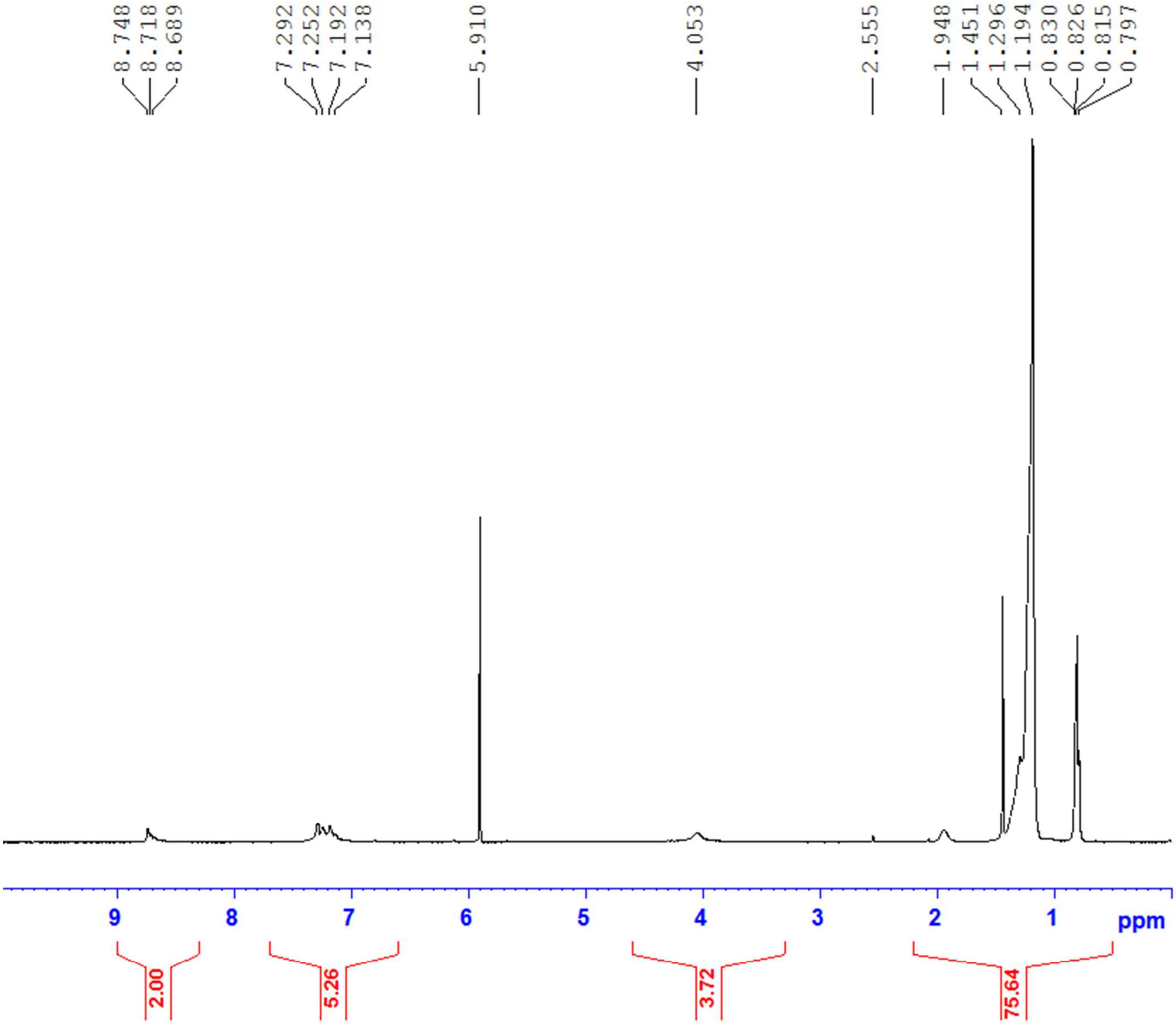


Figure S10. ^{1}H NMR spectrum of **PNDI3T(L)** in $C_2D_2Cl_4$ at 60 ℃

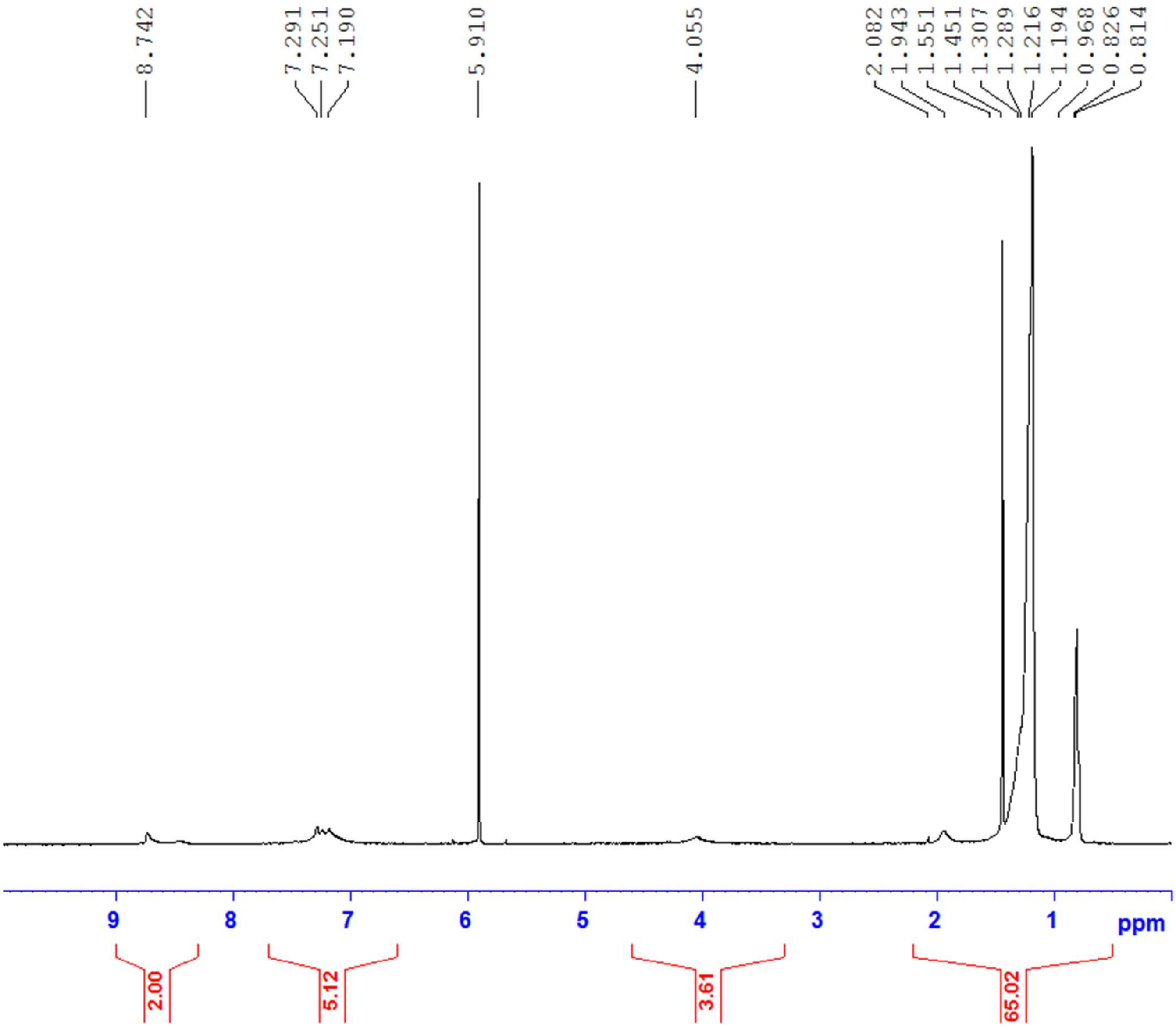


Figure S11. ^{1}H NMR spectrum of **PNDI3T(H)** in $C_2D_2Cl_4$ at 60 ℃

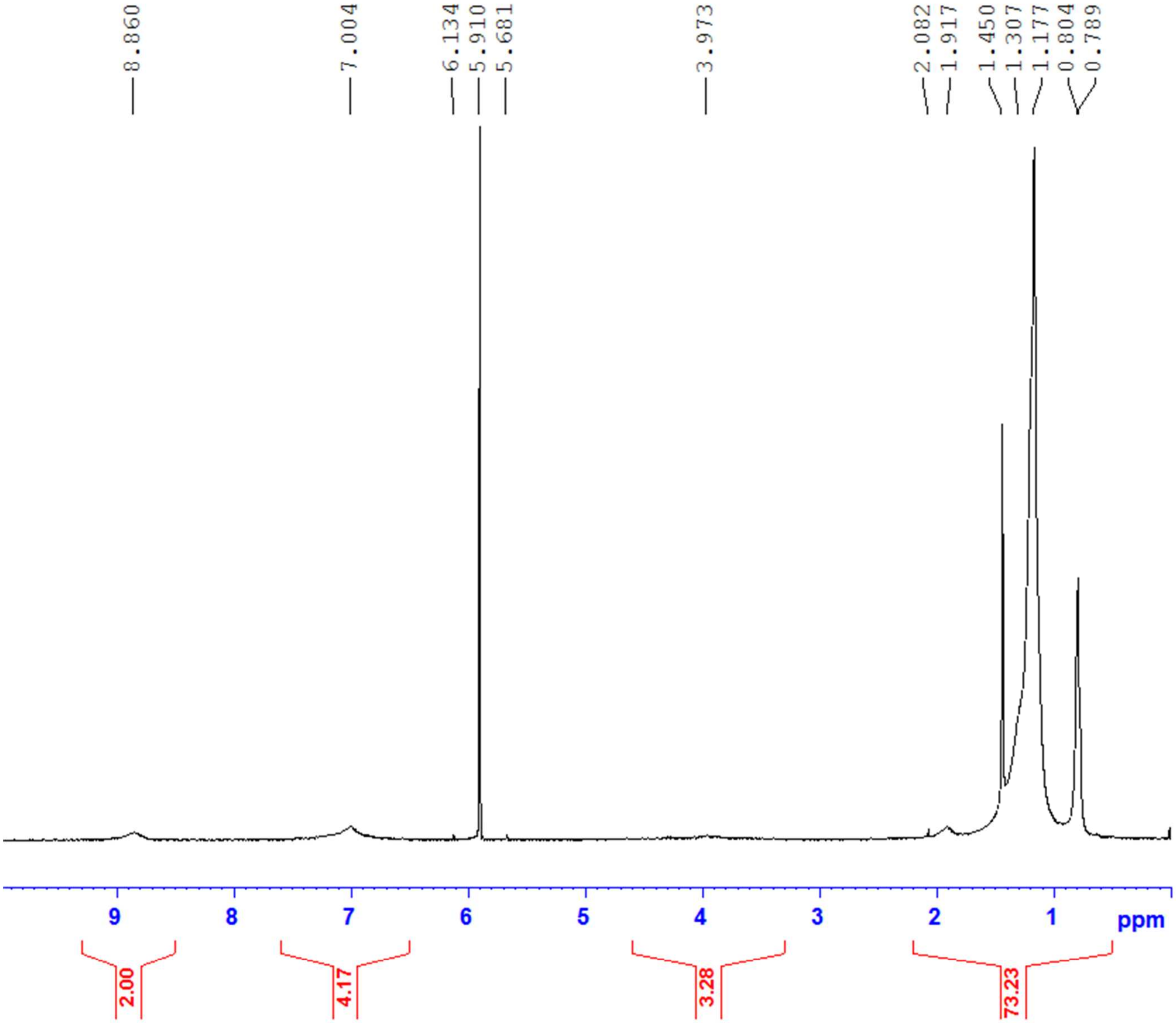


Figure S12. ^{1}H NMR spectrum of **PDPP3T(L)** in $C_2D_2Cl_4$ at 60 ℃

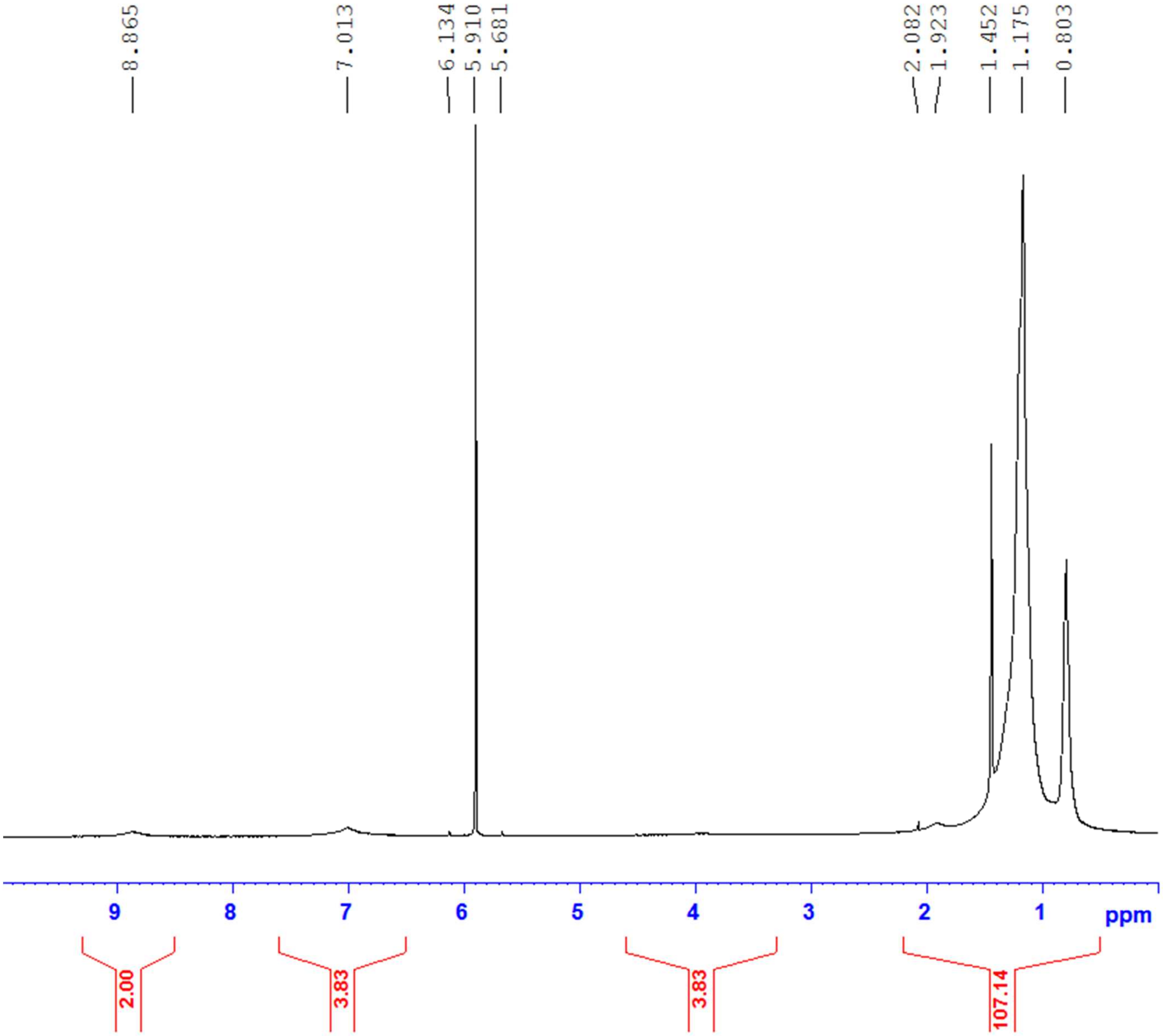


Figure S13. ^{1}H NMR spectrum of **PDPP3T(H)** in $C_2D_2Cl_4$ at 60 ℃

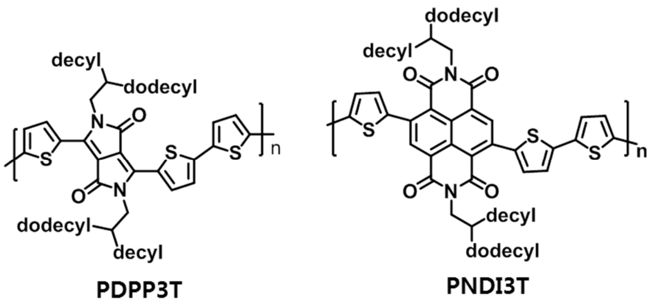


Figure S14. Polymer structures of PDPP3T and PNDI3T

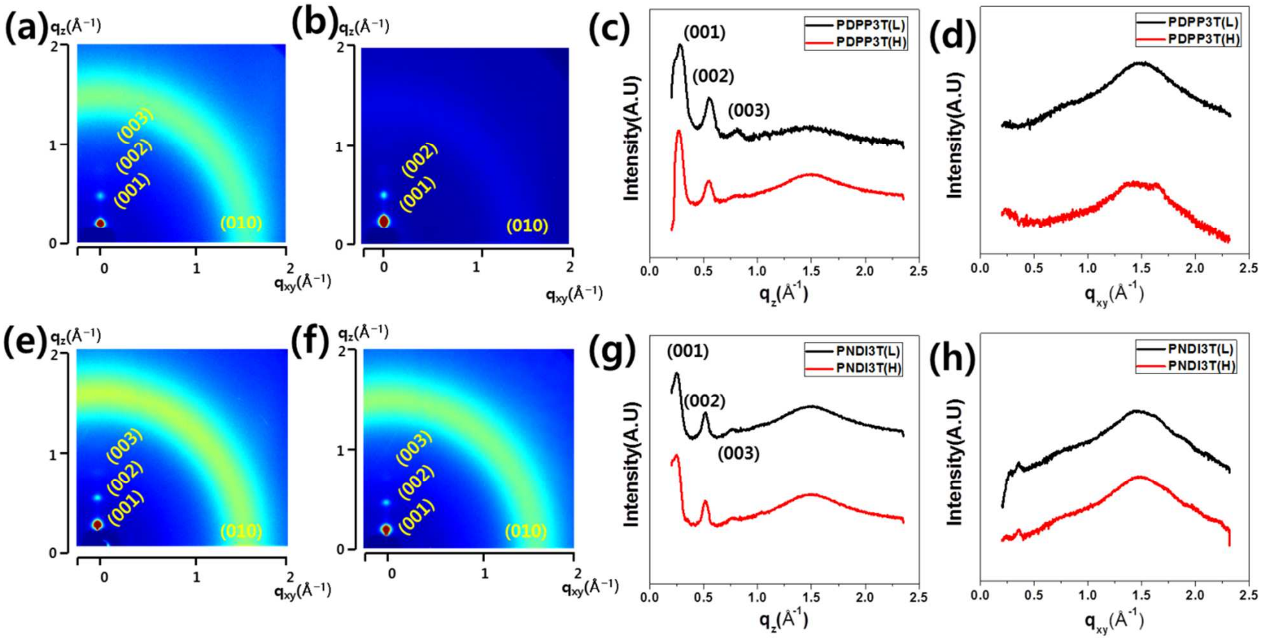


Figure S15. 2D GIXD patterns for annealed (a) PDPP3T(L), (b) PDPP3T(H), (e) PNDI3T(L), and (f) PNDI3T(H) thin films. (c, g) and (d, h) show corresponding out-of-plane and in-plane profiles, respectively, extracted from 2D GIXD patterns.

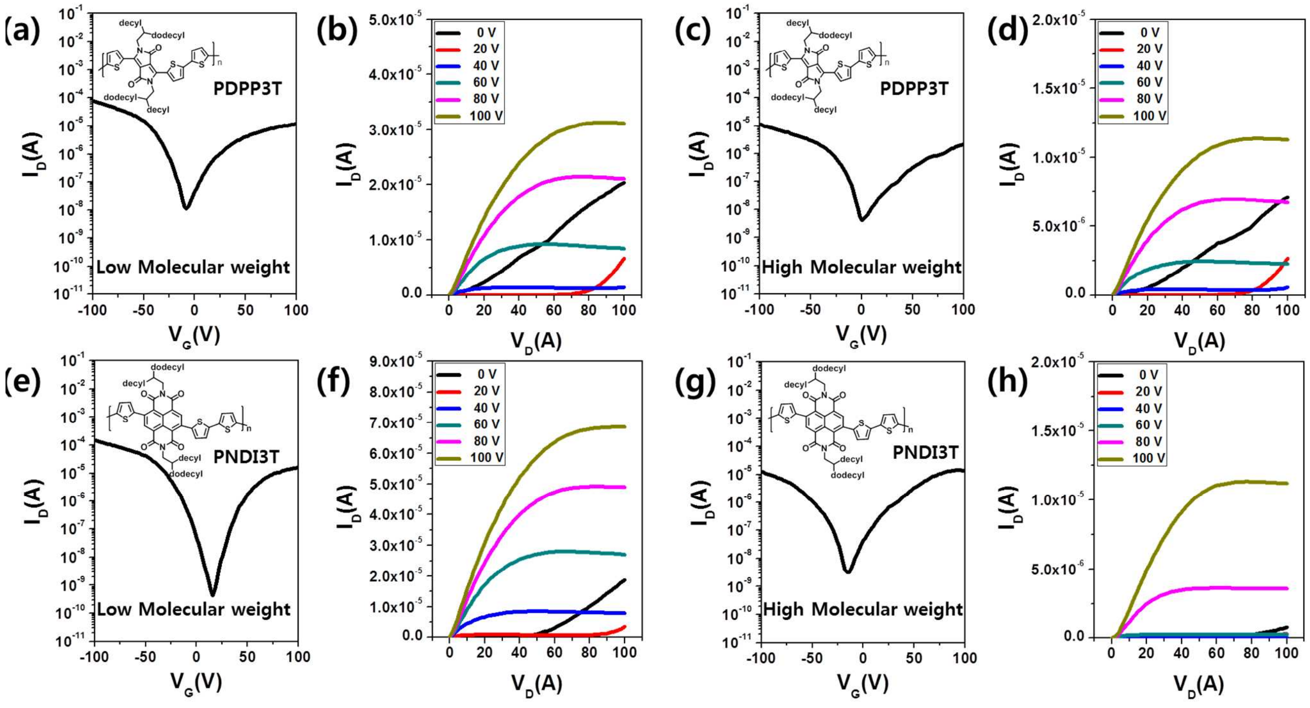


Figure S16. Representative transfer and output curves of OFETs from (a-d) PDPP3T and (e-h) PNDI3T with respect of molecular weights.

Table S1. The summary of mobility values measured at saturation regime.

polymer	μ_{electron} (cm^2/Vs)	μ_{hole} (cm^2/Vs)
PDPP3T(L)	0.077±0.015	0.409±0.027
PDPP3T(H)	0.033±0.001	0.079±0.0007
PNDI3T(L)	0.060±0.005	0.543±0.042
PNDI3T(H)	0.014±0.002	0.041±0.001

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