Electronic Supplementary Information

Multibranched aliphatic side chains for π-conjugated polymers with a high density of 'unshielded' aromatics

Simeng Wang,[a] Jessica Shaw,[a] Yang Han,[b] Zhuping Fei,[c] Florian Glöcklhofer*[a] and Martin Heeney*[a]

[a] Department of Chemistry and Centre for Plastic Electronics, Imperial College London, Molecular Sciences Research Hub, 80 Wood Lane, London W12 0BZ, United Kingdom

[b] School of Materials Science and Engineering, Tianjin University, Tianjin 300072, P. R. China

[c] Institute of Molecular Plus, Tianjin Key Laboratory of Molecular Optoelectronic Science, Tianjin University, Tianjin 300072, P. R. China

* E-mail: f.glocklhofer@imperial.ac.uk, m.heeney@imperial.ac.uk

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1 Synthetic details

All starting materials, reagents, and solvents were purchased from commercial suppliers (and used as received), with the exception of alkyl bromide **1** and monomer **M4**, which were obtained following published procedures.[1-2] The polymerisations were carried out in a Biotage Initiator microwave reactor. Other reactions requiring inert condition were performed using Schlenk technique.

NMR spectra were recorded at 400 MHz for ^{1}H and 101 MHz for ^{13}C on a Bruker AV-400 spectrometer. The small molecules were measured at room temperature in $CDCl_3$, the polymers at 73 °C in 1,1,2,2-tetrachloroethane-d_2 to avoid peak broadening. The spectra were analysed using MestReNova 14.1.0. High-resolution mass spectrometry (HRMS) data was obtained via Atmospheric Pressure Chemical Ionisation (APCI) on a Thermo Scientific Q-Exactive system.

The molecular weight and dispersity of the polymers were measured in dichlorobenzene at 80 °C against polystyrene standard, using Agilent Technologies 1260 Infinity Gel Permeation Chromatograph (GPC) system with 1260 RID attachment. Polymer solutions of 1 mg mL^{-1} in dichlorobenzene were used for the measurements.

1.1 Synthesis of multibranched aliphatic amine 3

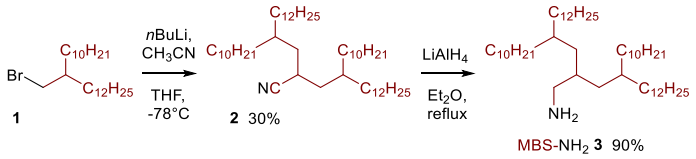

Figure S1. Synthetic route to multibranched aliphatic amine **3**.

4-Decyl-2-(2-decyltetradecyl)hexadecanenitrile 2. Synthesis adapting a protocol previously used for the monoalkylation of acetonitrile.[3] Dry acetonitrile (2.95 g, 3.75 mL, 71.8 mmol, 2.5 equiv.) was dissolved in dry THF (200 mL) under argon and cooled to -78 °C. *n*-Butyllithium solution (44.9 mL, 71.8 mmol, 2.5 equiv., 1.6 M in hexanes) was then slowly added to the reaction and stirred for 2 hours at -78 °C. In a separate flask, 1-bromo-2-decyltetradecane **1** (12.0 g, 28.7 mmol, 1.0 equiv.) was dissolved indry THF (100 mL) under argon and cooled in a dry ice/acetone bath. The flask was removed from the bath when 1-bromo-2-decyltetradecane **1** started to form a white precipitate. The mixture was allowed to warm up until a cold homogeneous solution was formed, which was then immediately transferred to the reaction solution via a cannula. The reaction was kept at -78 °C for an additional 5 hours before left to warm up to room temperature and stirred for another 12 hours before being quenched with 50 mL of water. The aqueous fraction was separated and extracted with 3 x 50 mL of hexane. All organic phases were combined, dried over $MgSO_4$ and concentrated *in vacuo* to yield an orange oil. The oil was purified using column chromatography (silica gel, 95:5 hexane/diethyl ether, R_F

0.8) and the product was obtained as a viscose colourless oil (3.10 g, 4.34 mmol, 30 %). ^{1}H NMR (400 MHz, $CDCl_3$): δ = 2.65 – 2.53 (m, 1H), 1.66 – 1.51 (m, 4H), 1.44 – 1.08 (m, 82H), 0.93 – 0.81 (m, 12H); ^{13}C NMR (101 MHz, $CDCl_3$) δ = 122.9, 37.6, 35.6, 33.8, 33.0, 32.1, 30.2, 30.1, 29.9, 29.84, 29.81, 29.5, 27.6, 26.6, 26.1, 22.9, 14.3 (note: several peaks overlap); HRMS (APCI): *m*/*z* calcd for $C_{50}H_{99}N+H^+$: 714.7850 $[M+H]^+$; found: 714.7869.

4-Decyl-2-(2-decyltetradecyl)hexadecyl-1-amine 3. To a solution of compound **2** (1.00 g, 1.40 mmol) in dry diethyl ether (100 mL) under argon at 0 °C, a $LiAlH_4$ solution (2.86 mL, 2.86 mmol, 2.04 equiv., 1 M in diethyl ether) was added slowly. The reaction was then heated to reflux for 2 hours, cooled to 0 °C again and quenched with 5 mL of water. The reaction mixture was washed with 50 mL of water and the aqueous fraction was extracted with 3 x 50 mL of hexane. The combined organic phases were dried over $MgSO_4$ and concentrated *in vacuo* to yield the multibranched aliphatic amine **3** as a colourless oil (0.91 g, 1.27 mmol, 90 %), which was used for the synthesis of **M1** without further purification. ^{1}H NMR (400 MHz, $CDCl_3$): δ = 2.57 (d, *J* = 5.1 Hz, 2H), 1.46 – 1.36 (m, 2H), 1.36 – 1.00 (m, 87H), 0.92 – 0.84 (m, 12H); ^{13}C NMR (101 MHz, $CDCl_3$) δ = 45.9, 37.3, 35.0, 34.3, 34.0, 32.1, 30.38, 30.35, 29.91, 29.85, 29.6, 26.9, 26.5, 22.9, 14.3 (note: several peaks overlap); HRMS (APCI): *m*/*z* calcd for $C_{50}H_{103}N+H^+$: 718.8163 $[M+H]^+$; found: 718.8140.

1.2 Synthesis of monomers M1-3

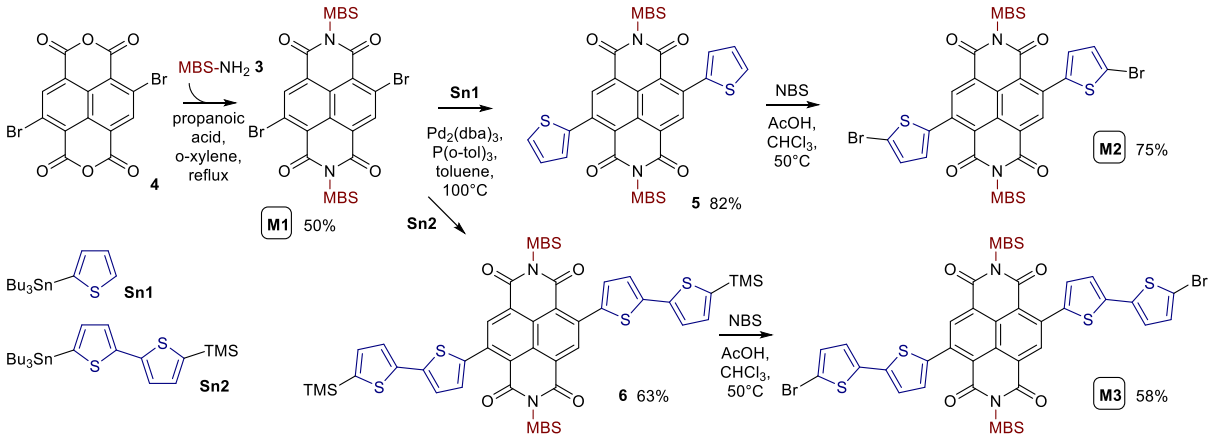

Figure S2. Synthetic route to monomers **M1-3**.

Monomer M1. Synthesis adapting a protocol previously used for the introduction of monobranched aliphatic side chains.[4] Multibranched aliphatic amine **3** (0.90 g, 1.25 mmol, 2.5 equiv.) and 2,6-dibromonaphthalene-1,4,5,8-tetracarboxylic dianhydride **4** (213 mg, 0.50 mmol, 1.0 equiv) were added to a dry round bottom flask under argon. 4 mL propionic acid and 12 mL o-xylene were added and the reaction mixture was heated to reflux for 12 hours. The reaction mixture was diluted with 50 mL of dichloromethane and extracted with 50 mL water. The aqueous phase was extracted twice with 20 mL

of dichloromethane and all organic phases were combined, washed with aqueous saturated potassium carbonate solution and brine and dried over $MgSO_4$. The solvents were removed *in vacuo* to yield a viscous red oil, which was purified by column chromatography (silica gel, 1:2 dichloromethane/petroleum ether) to yield monomer **M1** as an orange oil (455 mg, 0.25 mmol, 50 %). ^{1}H NMR (400 MHz, $CDCl_3$): δ = 9.00 (s, 2H), 4.10 (d, *J* = 7.3 Hz, 4H), 2.17 – 2.06 (m, 2H), 1.43 – 1.01 (m, 172H), 0.92 – 0.83 (m, 24H); ^{13}C NMR (101 MHz, $CDCl_3$): δ = 161.3, 161.2, 139.3, 128.5, 127.8, 125.4, 124.2, 46.4, 38.1, 35.1, 34.1, 34.0, 32.1, 31.8, 30.3, 29.93, 29.90, 29.88, 29.86, 29.6, 26.64, 26.58, 22.9, 14.3 (note: several aliphatic peaks overlap); HRMS (APCI): *m*/*z* calcd for $C_{114}H_{204}Br_2N_2O_4^+$: 1826.4196 $[M]^+$; found: 1826.4157.

Compound 5. Monomer **M1** (330 mg, 0.18 mmol, 1.0 equiv.), **Sn1** (150 mg, 0.40 mmol, 2.2 equiv.), $Pd_2(dba)_3$ (8.2 mg, 0.009 mmol, 0.05 equiv.) and tri(*o*-tolyl)phosphine (5.5 mg, 0.018 mmol, 0.1 equiv.) were added to a vial, which was equipped with a stirrer and flushed with argon. Subsequently, 10 mL anhydrous toluene was added and the reaction was heated to 100 °C for 12 hours. After cooling to room temperature, the reaction mixture was passed through a layer of KF on silica gel with dichloromethane as the eluent. The resultant solution was concentrated *in vacuo* and the crude product was further purified by column chromatography (silica gel, 1:4 dichloromethane/ petroleum ether) to yield compound **5** as a viscous red oil (270 mg, 0.15 mmol, 82%). ^{1}H NMR (400 MHz, $CDCl_3$): δ = 8.77 (s, 2H), 7.54 (dd, *J* = 5.1, 1.1 Hz, 2H), 7.30 (dd, *J* = 3.6, 1.2 Hz, 2H), 7.18 (dd, *J* = 5.1, 3.6 Hz, 2H), 4.02 (d, *J* = 7.2 Hz, 4H), 2.07 (hept, *J* = 6.7 Hz, 2H), 1.45 – 1.00 (m, 172H), 0.93 – 0.82 (m, 24H); ^{13}C NMR (101 MHz, $CDCl_3$): δ = 162.7, 162.6, 141.0, 140.3, 136.7, 128.4, 128.2, 127.6, 127.5, 125.6, 123.4, 45.7 38.0, 35.0, 34.1, 34.0, 32.1, 31.9, 30.4, 30.3, 30.0, 29.92, 29.87, 29.83, 29.6, 29.5, 26.7, 26.6, 22.9, 14.3 (note: several aliphatic peaks overlap); HRMS (APCI): *m*/*z* calcd for $C_{122}H_{210}N_2O_4S_2+H^+$: 1833.5839 $[M+H]^+$; found: 1833.5798.

Monomer M2. Synthesis adapting a previously reported bromination protocol.[5] Compound **5** (183 mg, 0.10 mmol, 1.0 equiv.) was dissolved in 20 mL chloroform, followed by the addition of 5 mL glacial acetic acid. N-bromosuccinimide (44.5 mg, 0.25 mmol, 2.0 equiv.) was then added to the stirred solution and the reaction was heated to 50 °C for 12 hours. After cooling to room temperature, the reaction mixture was washed with water and aqueous saturated potassium carbonate solution before being concentrated *in vacuo* to yield a red viscous oil. The crude product was subsequently purified by column chromatography (silica gel, 1:4 dichloromethane/petroleum ether) to yield monomer **M2** as a red oil (150 mg, 0.075 mmol, 75%). ^{1}H NMR (400 MHz, $CDCl_3$): δ = 8.73 (s, 2H), 7.13 (d, *J* = 3.9 Hz, 2H), 7.09 (d, *J* = 3.8 Hz, 2H), 4.03 (d, *J* = 7.2 Hz, 4H), 2.13 – 2.01 (m, 2H), 1.45 – 1.03 (m, 172H), 0.93 – 0.81 (m, 24H); ^{13}C NMR (101 MHz, $CDCl_3$): δ = 162.5, 162.4, 142.3, 139.1, 136.5, 130.3, 129.0, 127.6, 125.8, 123.1, 115.8, 45.8, 38.0, 35.0, 34.1, 34.0, 32.1, 31.9, 30.4, 30.3, 29.95, 29.91, 29.88, 29.86,

29.83, 29.6, 26.7, 26.6, 22.9, 14.3 (note: several aliphatic peaks overlap); HRMS (APCI): *m*/*z* calcd for $C_{122}H_{208}Br_2N_2O_4S_2^+$: 1990.3950 $[M]^+$; found: 1990.3937.

Compound 6. *n*-Butyllithium solution (0.2 mL, 0.315 mmol, 2.73 equiv., 1.6 M in hexane) was added to a solution of 2,2'-bithiophene (50 mg, 0.30 mmol, 2.6 equiv.) in 5 mL of anhydrous THF at -78 °C and stirred for 30 minutes. At the same temperature, trimethylsilyl (TMS) chloride (39 µL, 34 mg, 0.31 mmol, 2.7 equiv.) was added and the reaction stirred for another 30 minutes. Another portion of *n*-butyllithium solution (0.2 mL, 0.315 mmol, 2.73 equiv., 1.6 M in hexane) was then added, followed by 30 minutes stirring at -78 °C. Tributylstannyl chloride (84 µL, 101 mg, 0.31 mmol, 2.7 equiv.) was then added and the reaction was allowed to warm to room temperature and stirred for 30 minutes. The reaction was diluted with 30 mL diethyl ether and washed with water and brine. The organic phase was dried over Na_2SO_4, concentrated under reduced pressure and further dried under vacuum to yield crude **Sn2** (146 mg, 0.276 mmol, 2.4 equiv.) as a pale brown oil. To this oil, monomer **M1** (211 mg, 0.115 mmol, 1.0 equiv.), $Pd_2(dba)_3$ (5.5 mg, 0.006 mmol, 0.05 equiv.) and tri(o-tolyl)phosphine (3.7 mg, 0.012 mmol, 0.1 equiv.) were added in a vial. The reaction was equipped with a stirrer and flushed with argon. Subsequently, 10 mL of anhydrous toluene was added and the reaction was heated to 100 °C for 12 hours. After cooling to room temperature, the reaction mixture was passed through a layer of KF on silica gel with dichloromethane as the eluent. The resultant solution was concentrated *in vacuo* and the crude product was further purified by column chromatography (silica gel, 1:9 dichloromethane/petroleum ether) to obtain compound **6** as an impure viscous dark blue oil (155 mg, 0.072 mmol, 63 %), which was used for the next step without further purification. ^{1}H NMR (400 MHz, $CDCl_3$): δ = 8.81 (s, 2H), 7.30 (d, *J* = 3.8 Hz, 2H), 7.29 (d, *J* = 3.4 Hz, 2H), 7.24 (d, *J* = 3.7 Hz, 2H), 7.15 (d, *J* = 3.5 Hz, 2H), 4.05 (d, *J* = 7.1 Hz, 4H), 2.17 – 2.04 (m, 2H), 1.45 – 1.02 (m, 172H), 0.92 – 0.81 (m, 24H), 0.35 (s, 18H); ^{13}C NMR (101 MHz, $CDCl_3$): δ = 162.8, 162.7, 141.9, 141.1, 141.0, 139.53, 139.47, 136.6, 134.9, 130.2, 127.6, 125.8, 125.5, 124.1, 122.6, 45.8, 38.0, 35.1, 34.1, 34.0, 32.1, 32.0, 30.4, 30.3, 29.97, 29.94, 29.91, 29.88, 29.84, 29.6, 26.7, 26.6, 22.9, 14.3, 0.0 (note: several aliphatic peaks overlap); HRMS (APCI): *m*/*z* calcd for $C_{136}H_{230}N_2O_4S_4Si_2^+$: 2140.6306 $[M]^+$; found: 2140.6240.

Monomer M3. Synthesis adapting a previously reported bromination procedure.[5] Compound **6** (122 mg, 0.057 mmol, 1.0 equiv) was dissolved in 10 mL chloroform, followed by the addition of 3 mL of glacial acetic acid. N-bromosuccinimide (25.5 mg, 0.143 mmol, 2.5 equiv.) was then added to the stirred solution and the reaction was heated to 50 °C for 12 hours. After cooling to room temperature, the reaction mixture was diluted with chloroform and washed with water and aqueous saturated potassium carbonate solution before being concentrated *in vacuo* to yield a purple viscous oil. The crude product was subsequently purified by column chromatography (silica gel, 5% dichloromethane in petroleum ether) to yield monomer **M3** (71.0 mg, 0.033 mmol, 58%). ^{1}H NMR (400 MHz, $CDCl_3$): δ =

8.79 (s, 2H), 7.28 (d, J = 3.8 Hz, 2H), 7.17 (d, J = 3.8 Hz, 2H), 7.01 – 6.97 (m, 4H), 4.05 (d, J = 7.1 Hz, 4H), 2.17 – 2.03 (m, 2H), 1.47 – 1.02 (m, 172H), 0.92 – 0.80 (m, 24H); ^{13}C NMR (101 MHz, $CDCl_3$): δ = 162.7, 162.6, 140.0, 139.7, 139.4, 138.4, 136.5, 130.9, 130.0, 127.7, 125.6, 124.6, 124.3, 122.8, 112.1, 45.8, 38.0, 35.1, 34.1, 34.0, 32.1, 31.9, 30.4, 30.3, 29.98, 29.95, 29.90, 29.87, 29.85, 29.6, 26.7, 26.6, 22.9, 14.3 (note: several aliphatic peaks overlap); HRMS (APCI): m/z calcd for $C_{130}H_{212}Br_2N_2O_4S_4^+$: 2154.3705 $[M]^+$; found: 2154.3619.

1.3 Polymerisations

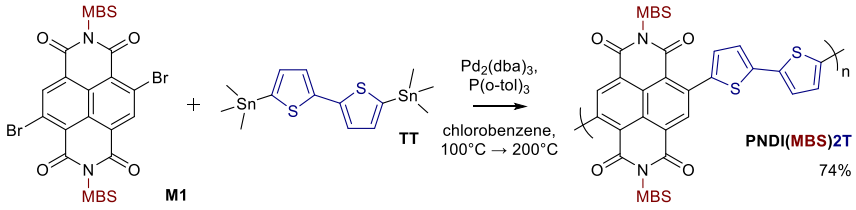

Figure S3. Synthesis of polymer **PNDI(MBS)2T**.

PNDI(MBS)2T. Monomer **M1** (140.8 mg, 0.0771 mmol, 1.0 equiv.), 5,5′-bis(trimethylstannyl)-2,2′-bithiophene **TT** (37.9 mg, 0.0771 mmol, 1.0 equiv.), $Pd_2(dba)_3$ (1.41 mg, 0.0015 mmol, 0.02 equiv.) and tri(o-tolyl)phosphine (1.88 mg, 0.0062 mmol, 0.08 equiv.) was added to a dry microwave vial. The vial was sealed and flushed with argon. 0.5 mL dry chlorobenzene was added and the reaction mixture was purged with argon for 15 minutes. The reaction was then heated to 100 °C in a microwave oven and the temperature was further increased in steps of 20 °C every 2 minutes, before it was kept at 180 °C and 200 °C for 20 minutes each. The reaction was poured into methanol, the precipitated polymer was filtered off and treated with methanol (12 hour) and acetone (12 hours) in a Soxhlet extractor. Final treatment with hexane (4 hours) dissolved the polymer. After removing the solvent *in vacuo*, the polymer was redissolved in boiling chloroform and precipitated into methanol. The mixture was filtered to yield **PNDI(MBS)2T** as a dark blue sticky solid (105 mg, 74%). M_n = 24 kDa, M_w = 29 kDa, Đ = 1.2; ^{1}H NMR (400 MHz, 1,1,2,2-tetrachloroethane-d_2 , 73 °C): δ = 8.89 (s, 2H), 7.46 – 7.32 (m, 4H), 4.15 (bs, 4H), 2.22 (bs, 2H), 1.60 – 1.14 (m, 172H), 0.97 – 0.87 (m, 24H).

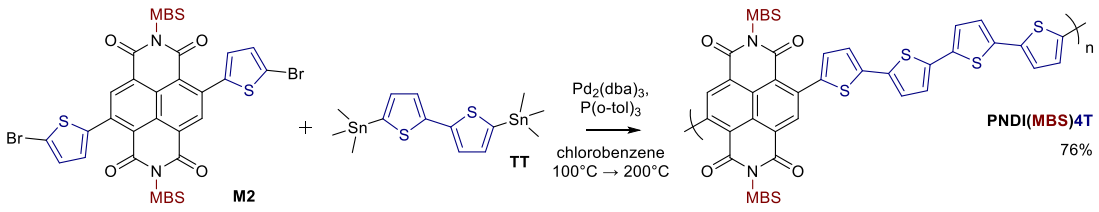

Figure S4. Synthesis of polymer **PNDI(MBS)4T**.

PNDI(MBS)4T. Synthesis and purification following the procedure of **PNDI(MBS)2T** using monomer **M2** (122.8 mg, 0.0617 mmol, 1.0 equiv), bithiophene **TT** (30.3 mg, 0.0617 mmol, 1.0 equiv.) and

accordingly adapted amounts of catalyst, ligand, and solvent. Polymer **PNDI(MBS)4T** was obtained as an elastic dark green solid (93 mg, 76%). M_n = 51 kDa, M_w = 72 kDa, Đ = 1.4; ^{1}H NMR (400 MHz, 1,1,2,2-tetrachloroethane-d_2, 73 °C): δ = 8.89 – 8.84 (m, 2H), 7.48 – 7.08 (m, 8H), 4.13 (bs, 4H), 2.20 (bs, 2H), 1.43 – 1.10 (m, 172H), 0.99 – 0.84 (m, 24H).

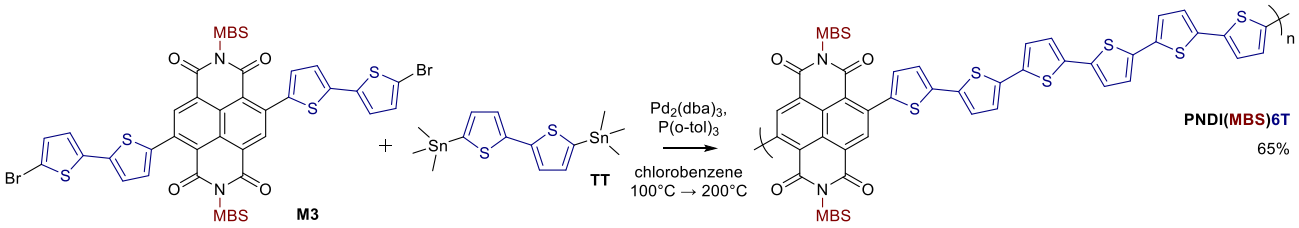

Figure S5. Synthesis of polymer **PNDI(MBS)6T**.

PNDI(MBS)6T. Synthesis following the procedure of **PNDI(MBS)2T** using monomer **M3** (69.5 mg, 0.0322 mmol, 1.0 equiv.), bithiophene **TT** (15.9 mg, 0.0322 mmol, 1.0 equiv.) and accordingly adapted amounts of catalyst, ligand, and solvent. For the purification, the reaction was poured into methanol and the precipitated polymer was filtered off and treated with methanol (12 hour), acetone (12 hours) and hexane (12 hours) in a Soxhlet extractor. Final treatment with chloroform (4 hours) dissolved the polymer. After removing the solvent *in vacuo*, the polymer was redissolved in boiling chloroform and precipitated into methanol. The mixture was filtered to yield polymer **PNDI(MBS)6T** as an elastic dark green solid (45.5 mg, 65%). M_n = 61 kDa, M_w = 119 kDa, Đ = 2.0; ^{1}H NMR (400 MHz, 1,1,2,2-tetrachloroethane-d_2, 73 °C): δ = 8.87 – 8.82 (m, 2H), 7.58 – 6.92 (m, 12H), 4.13 (bs, 4H), 2.20 (s, 2H), 1.40 – 1.10 (m, 172H), 0.96 – 0.88 (m, 24H).

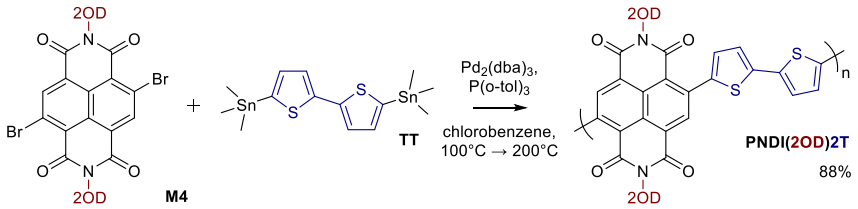

Figure S6. Synthesis of polymer **PNDI(2OD)2T**.

PNDI(2OD)2T. Synthesis following the procedure of **PNDI(MBS)2T** using monomer **M4** (268 mg, 0.272 mmol, 1.0 equiv), bithiophene **TT** (134 mg, 0.272 mmol, 1.0 equiv.) and accordingly adapted amounts of catalyst, ligand, and solvent. For the purification, the reaction was poured into methanol and the precipitated polymer was filtered off and treated with methanol (12 hour), acetone (12 hours) and hexane (12 hours) in a Soxhlet extractor. Final treatment with chloroform (4 hours) dissolved the polymer. After removing the solvent *in vacuo*, the polymer **PNDI(2OD)2T** was obtained as shiny sheets of dark blue solid (237 mg, 88%). M_n = 88 kDa, M_w = 207 kDa, Đ = 2.35; ^{1}H NMR (400 MHz, 1,1,2,2-tetrachloroethane-d_2, 73 °C): δ = 8.88 (s, 2H), 7.46 – 7.33 (m, 4H), 4.18 (bs, 4H), 2.08 (bs, 2H), 1.47 – 1.23 (m, 64H), 0.95 – 0.85 (m, 12H).

2 Thermal analysis

2.1 Thermogravimetric analysis (TGA)

Thermogravimetric analysis (TGA) was performed under nitrogen on a Mettler Toledo TGA/DSC 1LF/UMX instrument, from 25 °C to 800 °C at a heating rate of 10 °C min^{-1}.

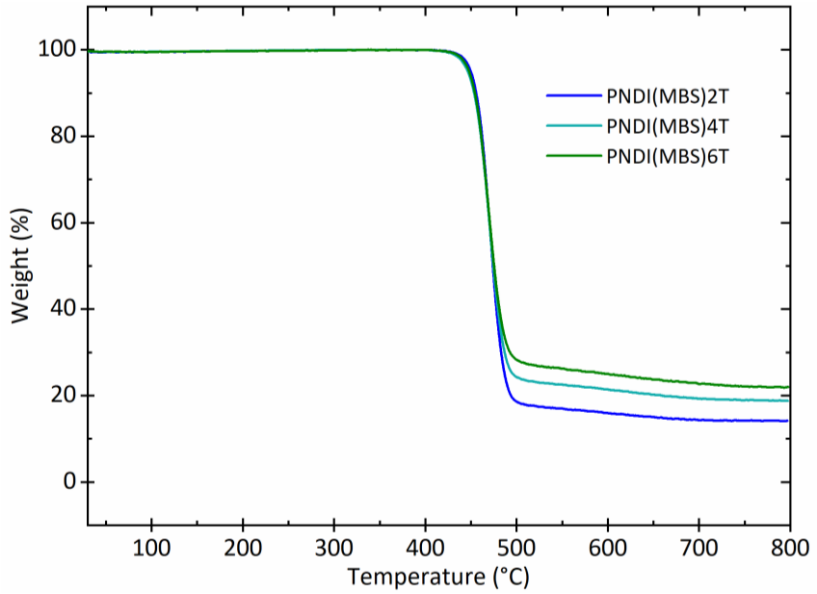

Figure S7. TGA measurements of polymers **PNDI(MBS)2T**, **PNDI(MBS)4T**, and **PNDI(MBS)6T**, showing a 5% mass loss at 450 °C, 447 °C, and 448 °C respectively.

2.2 Differential scanning calorimetry (DSC)

Differential Scanning Calorimetry (DSC) measurements were conducted under nitrogen on a TA Instruments DSC TZero Q20 v24.10, from -30 °C to 300 °C at a heating rate of 20 °C min^{-1}.

In contrast to **PNDI(MBS)4T** and **PNDI(MBS)6T**, neither endothermic nor exothermic transitions were observed for **PNDI(MBS)2T**.

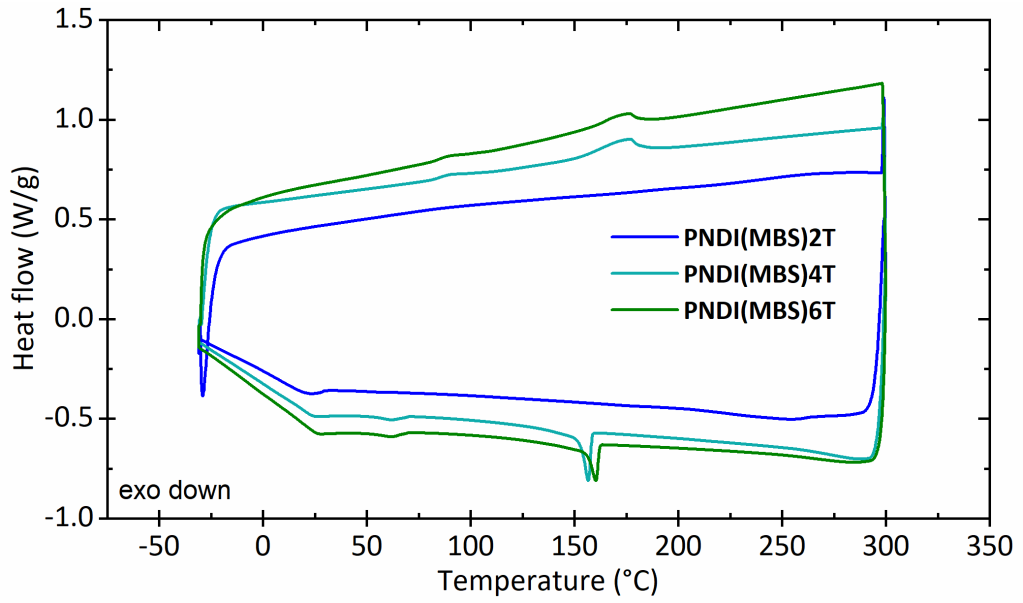

Figure S8. DSC measurements of polymers **PNDI(MBS)4T-6** (second cycle shown).

3 Solubility tests

For testing the solubility in chlorobenzene, 0.10 mL of solvent was added to 20 mg of polymer (10 mg in the case of **PNDI(2OD)2T**) and the mixture was gently heated. If the added amount of solvent was insufficient to dissolve the polymer, further solvent was added in 0.05 mL increments until the polymer was fully dissolved (with prolonged stirring between additions). The solution was then cooled to room temperature and left to stand for 1 h to confirm that no precipitation or gelation occurs. If precipitation or gelation was observed, more solvent was added, and the mixture was gently heated again. The procedure was repeated until the polymer remained in solution upon cooling to room temperature.

The same procedure was applied for testing the solubility in *n*-hexane, but only 2 mg of polymer were used for these tests.

Table 1. Solvent amounts needed to dissolve 20 mg of polymer (10 mg in the case of **PNDI(2OD)2T**) in chlorobenzene or 2 mg of polymer in *n*-hexane, as well as the corresponding solubility range. 0.10 mL of solvent was added initially, with further solvent added in 0.05 mL increments.

Polymer	Chlorobenzene	Solubility	*n*-Hexane	Solubility
PNDI(MBS)2T	0.00-0.10 mL	>200 g L^{-1}	0.00-0.10 mL	>20 g L^{-1}
PNDI(MBS)4T	0.15-0.20 mL	100-133 g L^{-1}	0.20-0.25 mL	8-10 g L^{-1}
PNDI(MBS)6T	0.25-0.30 mL	67-80 g L^{-1}	-	
PNDI(2OD)2T	0.35-0.40 mL	25-29 g L^{-1}	-	

4 UV-vis absorption

Solution and thin-film UV-vis absorption spectra were recorded on a UV-1800 Shimadzu UV-vis spectrophotometer. The solutions were prepared by dissolving the polymers in chlorobenzene (CB) or chloronaphthalene (CN) at a concentration of 0.10 or 0.01 g L^{-1}. The thin films were prepared by spin-casting polymer solutions (10 g L^{-1} in chlorobenzene) onto glass substrates at 2000 rpm for 1 minute. The films were annealed at 200 °C for 30 minutes and gradually cooled to room temperature. Absorption onsets were determined using the tangent method.

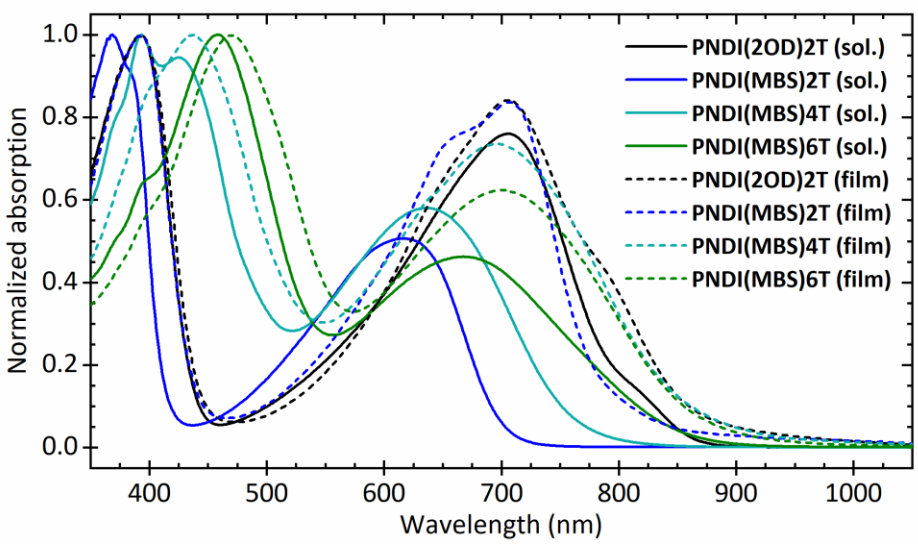

Figure S9. Normalized UV-vis absorption spectra of polymers **PNDI(2OD)2T**, **PNDI(MBS)2T**, **PNDI(MBS)4T**, and **PNDI(MBS)6T** in chlorobenzene (0.1 g L^{-1}) and as spin-cast annealed films.

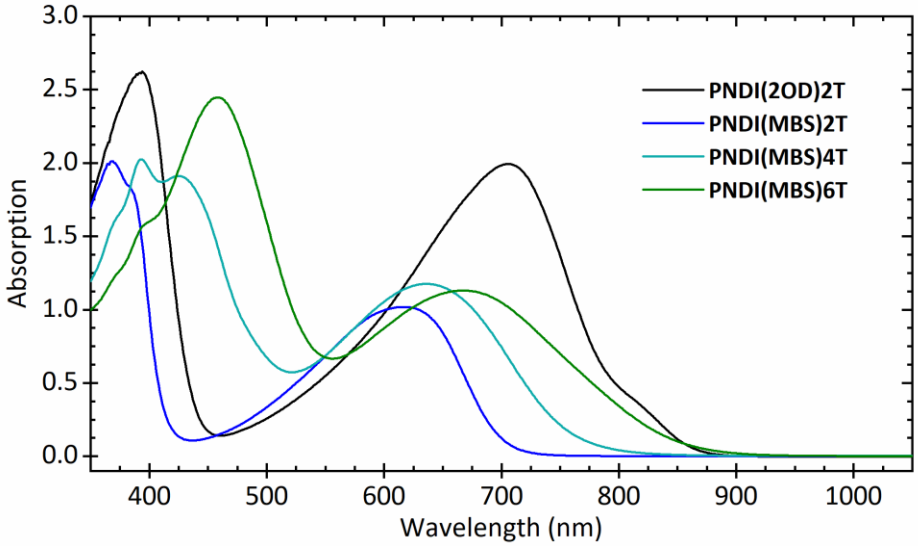

Figure S10. UV-vis absorption spectra of polymers **PNDI(2OD)2T**, **PNDI(MBS)2T**, **PNDI(MBS)4T**, and **PNDI(MBS)6T** in chlorobenzene (0.1 g L^{-1}).

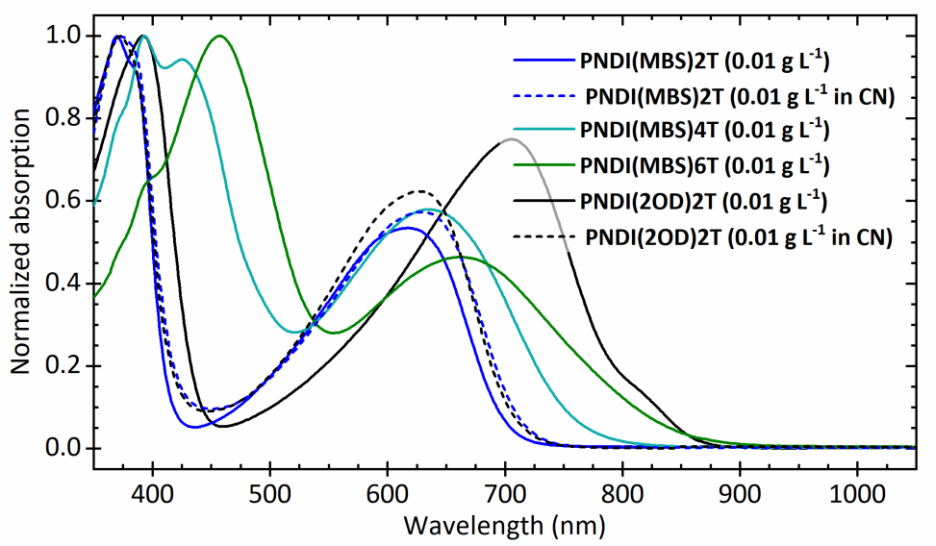

Figure S11. Normalized UV-vis absorption spectra of polymers **PNDI(2OD)2T**, **PNDI(MBS)2T**, **PNDI(MBS)4T**, and **PNDI(MBS)6T** in chlorobenzene (solid lines) and chloronaphthalene (dashed lines) at a lower concentration of 0.01 g L^{-1}.

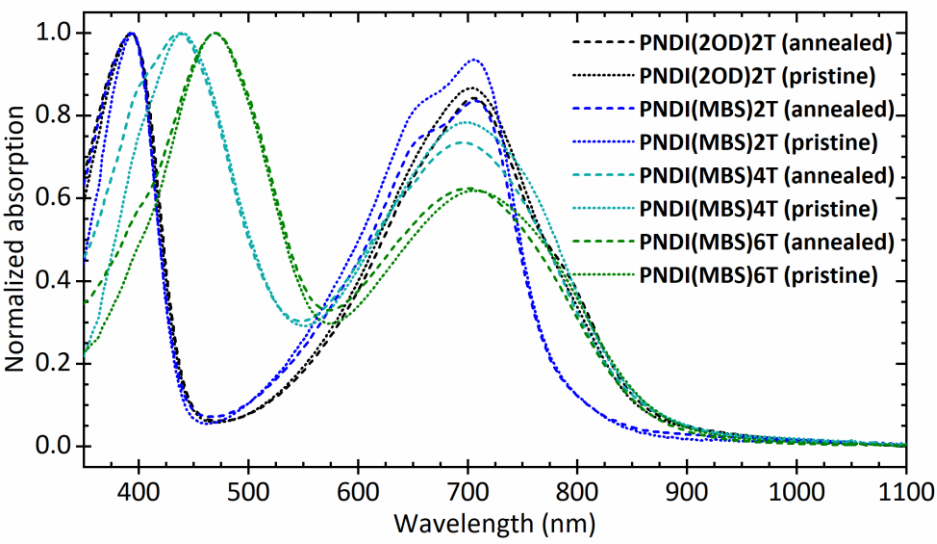

Figure S12. Normalized UV-vis absorption spectra of spin-cast annealed films (dashed lines) and spin-cast pristine films (dotted lines) of polymers **PNDI(2OD)2T**, **PNDI(MBS)2T**, **PNDI(MBS)4T**, and **PNDI(MBS)6T**.

5 Photoluminescence

Photoluminescence spectra in solution were recorded on an Agilent Cary Eclipse fluorescence spectrophotometer. The solutions were prepared by dissolving the polymers in chlorobenzene (CB) or chloronaphthalene (CN) at a concentration of 0.1 or 0.01 g L^{-1}. The excitation wavelengths are provided in the figures. Ex. slit: 10 nm, em. slit: 5 nm.

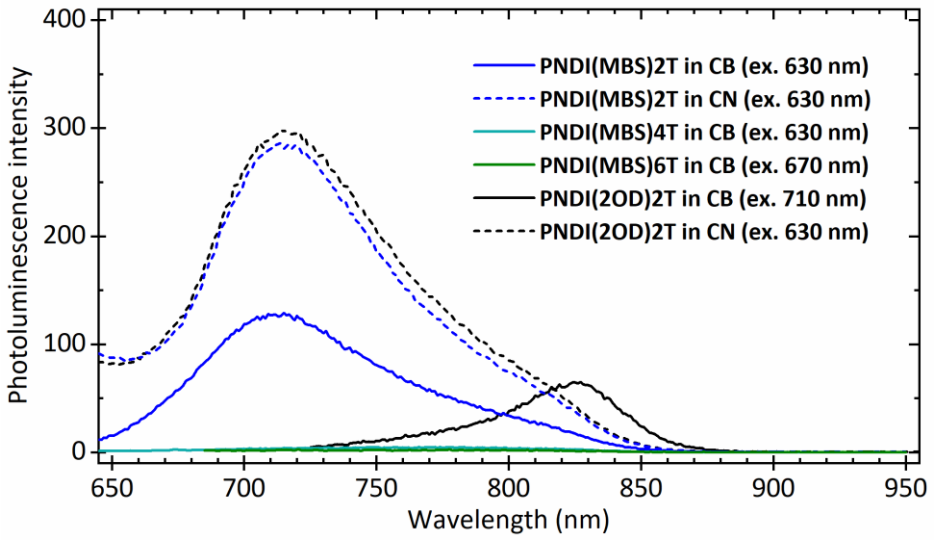

Figure S13. Photoluminescence spectra of polymers **PNDI(MBS)2T-6T** and **PNDI(2OD)2T** in chlorobenzene (CB) and chloronaphthalene (CN). Conc.: 0.01 g L^{-1}.

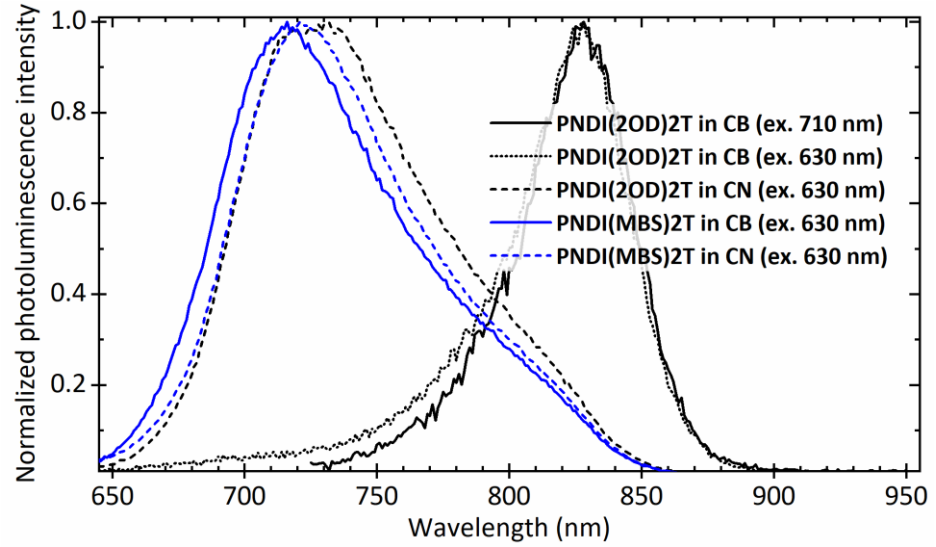

Figure S14. Normalized photoluminescence spectra of polymers **PNDI(MBS)2T** and **PNDI(2OD)2T** in chlorobenzene (CB) and chloronaphthalene (CN). Conc.: 0.1 g L^{-1}.

6 Cyclic voltammetry (CV)

Cyclic voltammetry (CV) measurements of polymer thin films were performed at a scan rate of 100 mV s^{-1} using a standard three-electrode setup and an Autolab potentiostat. ITO-coated glass slides were used as the working electrode, a platinum mesh as the counter electrode, and a Ag/AgCl wire as the quasi-reference electrode. The polymers were drop cast onto the ITO-coated glass slides from chloroform solution. The measurements were then performed using 0.1 M tetrabutylammonium

hexafluorophosphate (Bu_4NPF_6) in acetonitrile as the electrolyte, which was prepared using anhydrous acetonitrile and degassed by purging with nitrogen for 30 minutes. Following the measurements, an arbitrary amount of ferrocene was added to the solution and measured as a reference to evaluate the redox potentials of the compounds.

In line with best practice,[6] the HOMO and LUMO energy levels of the polymers were estimated from the half-wave potential $E^{1/2}$ (where reversibility was observed) or from the inflection-point potential E^{i} (when irreversibility was observed): HOMO = -($E^{1/2 \text{ or } i}$ + 4.8) eV and LUMO = -($E^{1/2 \text{ or } i}$ + 4.8) eV for oxidation and reduction respectively, with the ferrocene/ferrocenium (Fc/Fc^{+}) reference redox system at 4.8 eV below the vacuum level.

7 ^{1}H and ^{13}C NMR spectra

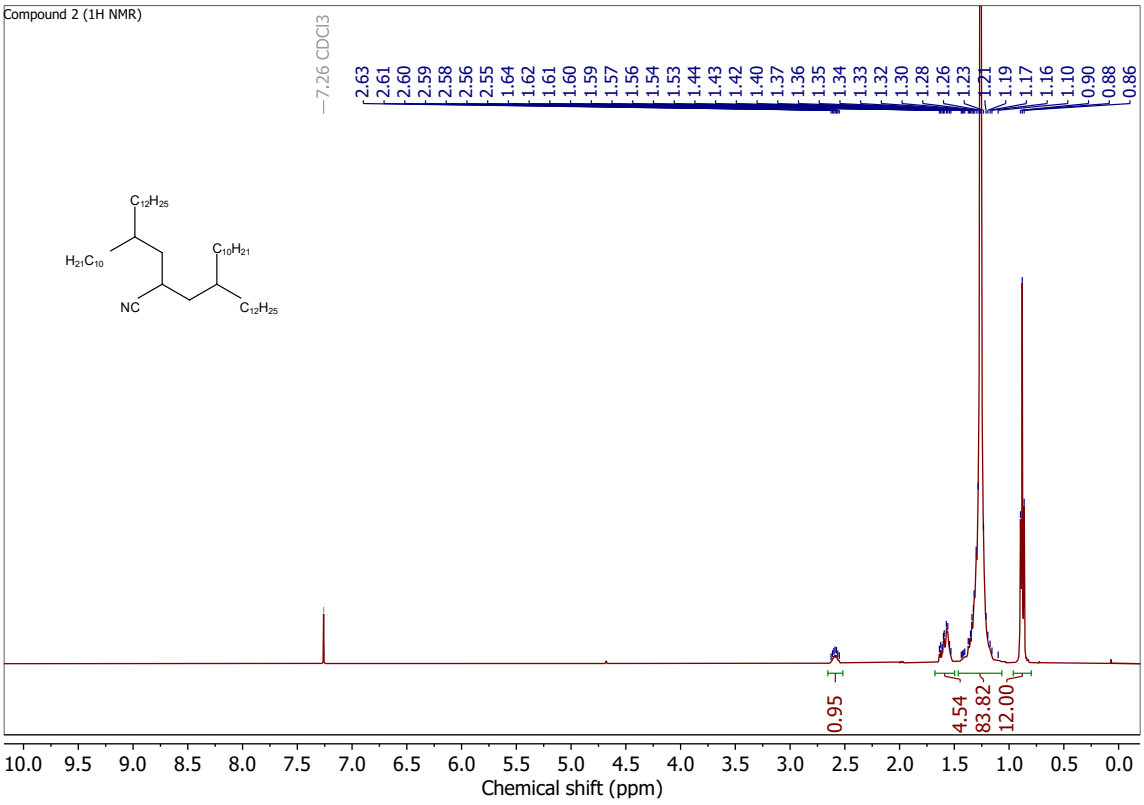

Figure S15. ^{1}H NMR (400 MHz, $CDCl_3$) of compound **2**.

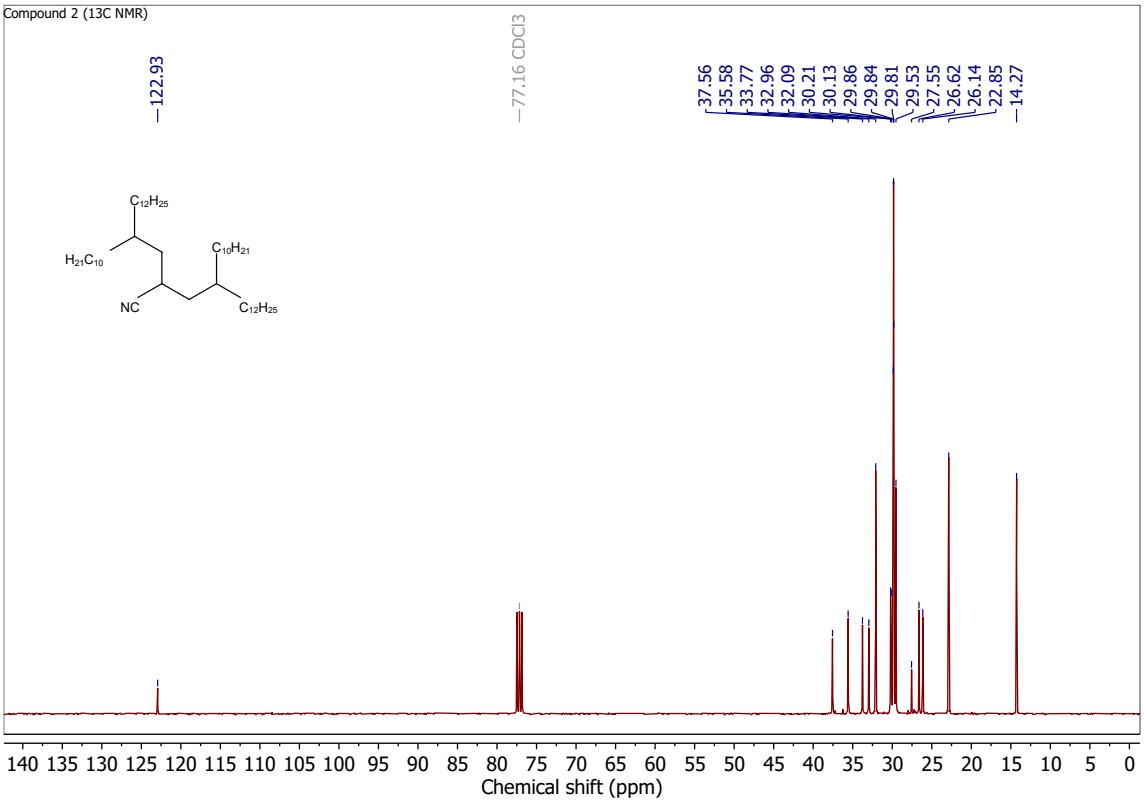

Figure S16. ^{13}C NMR (101 MHz, $CDCl_3$) of compound **2**.

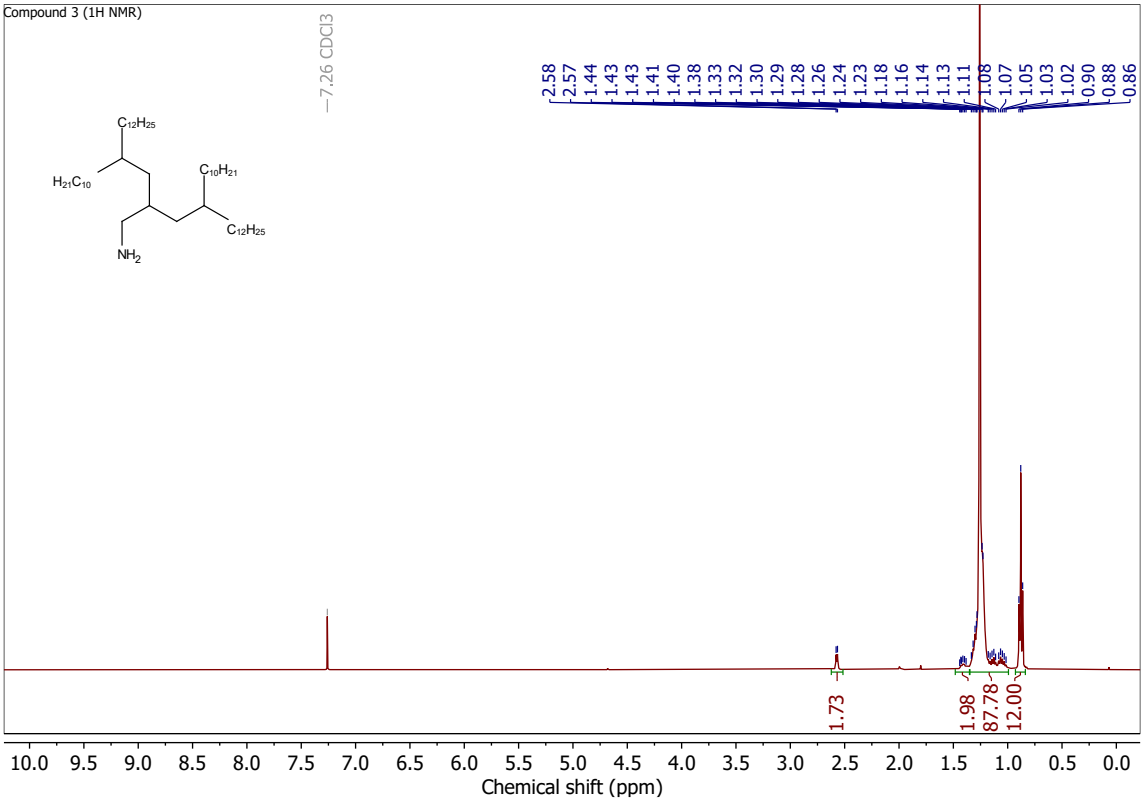

Figure S17. ^{1}H NMR (400 MHz, $CDCl_3$) of compound **3**.

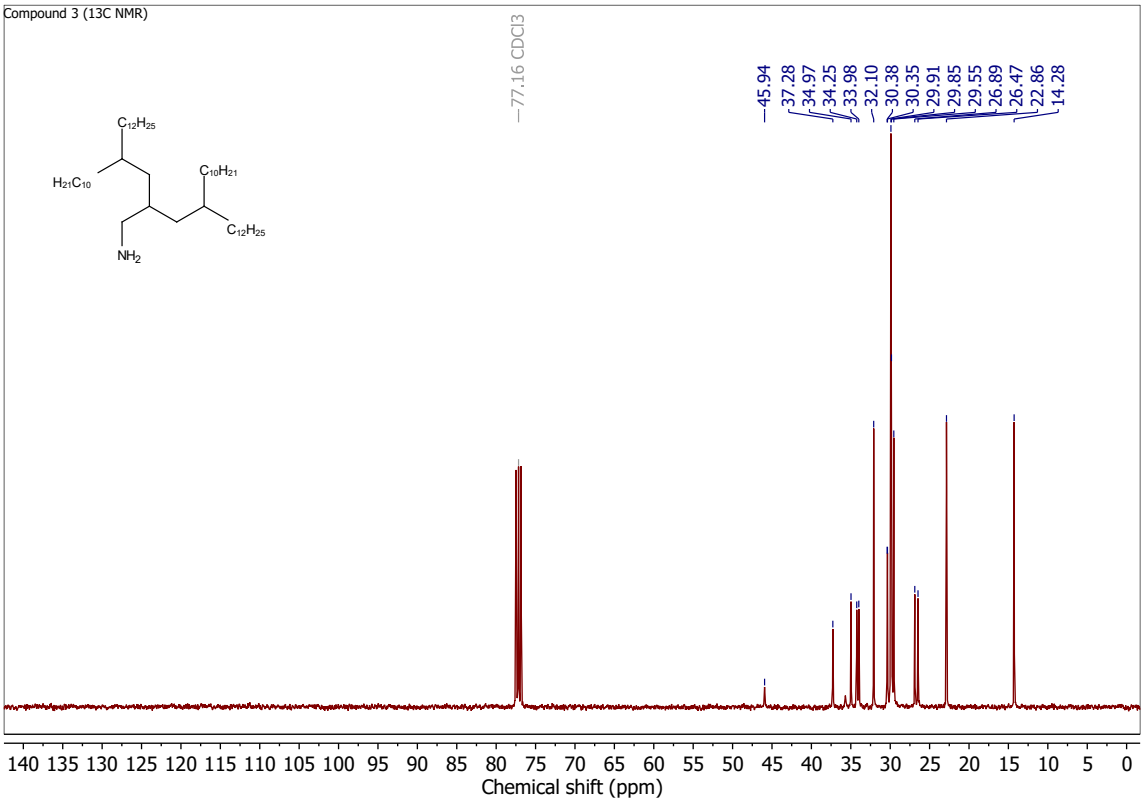

Figure S18. ^{13}C NMR (101 MHz, $CDCl_3$) of compound **3**.

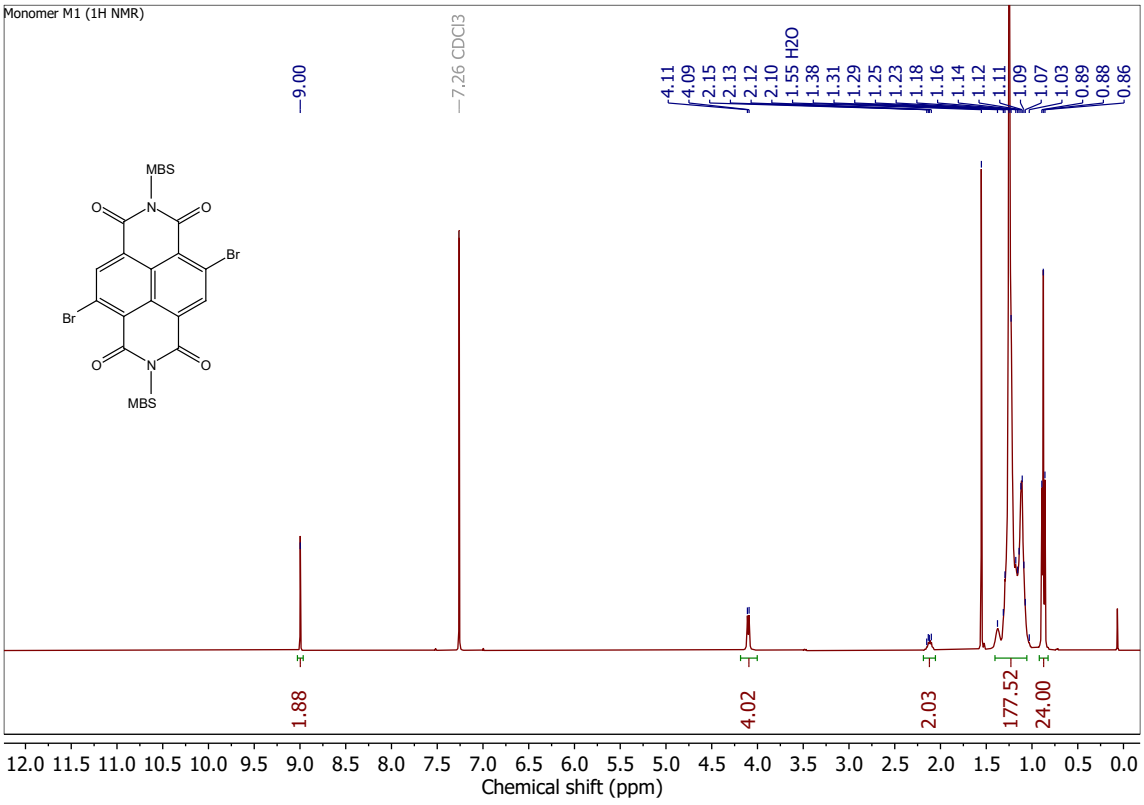

Figure S19. ^{1}H NMR (400 MHz, $CDCl_3$) of monomer **M1**.

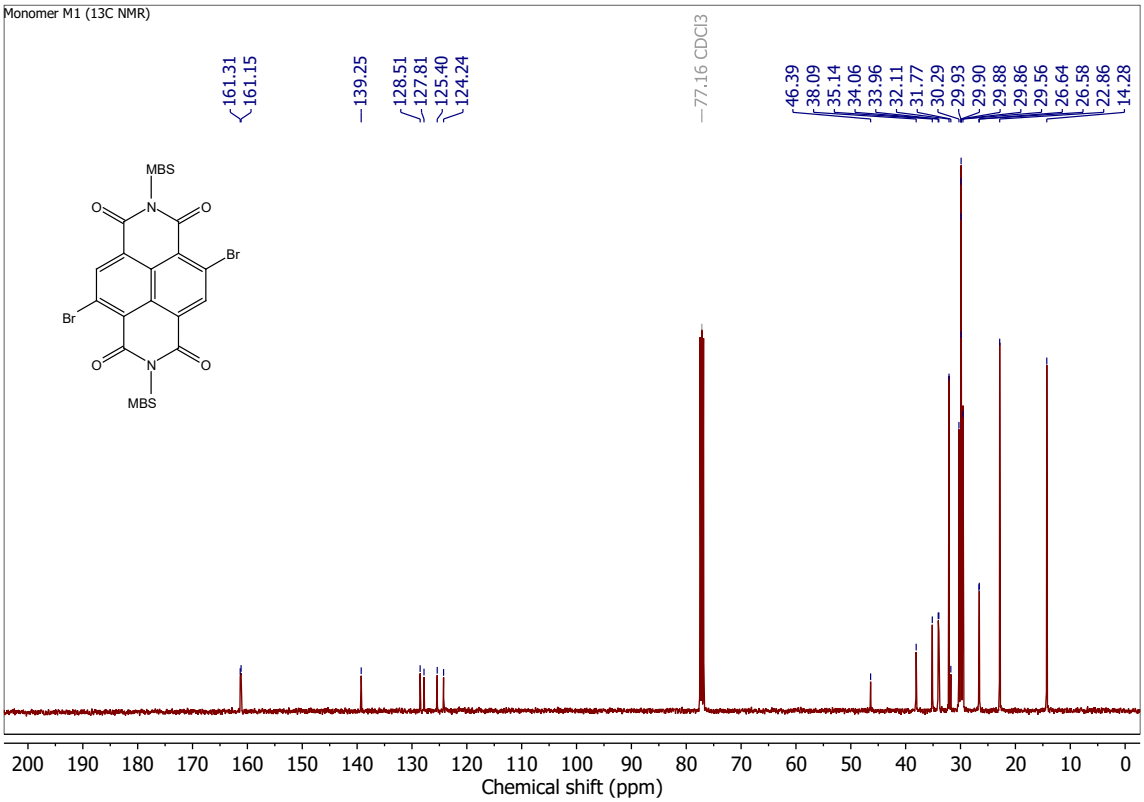

Figure S20. ^{13}C NMR (101 MHz, $CDCl_3$) of monomer **M1**.

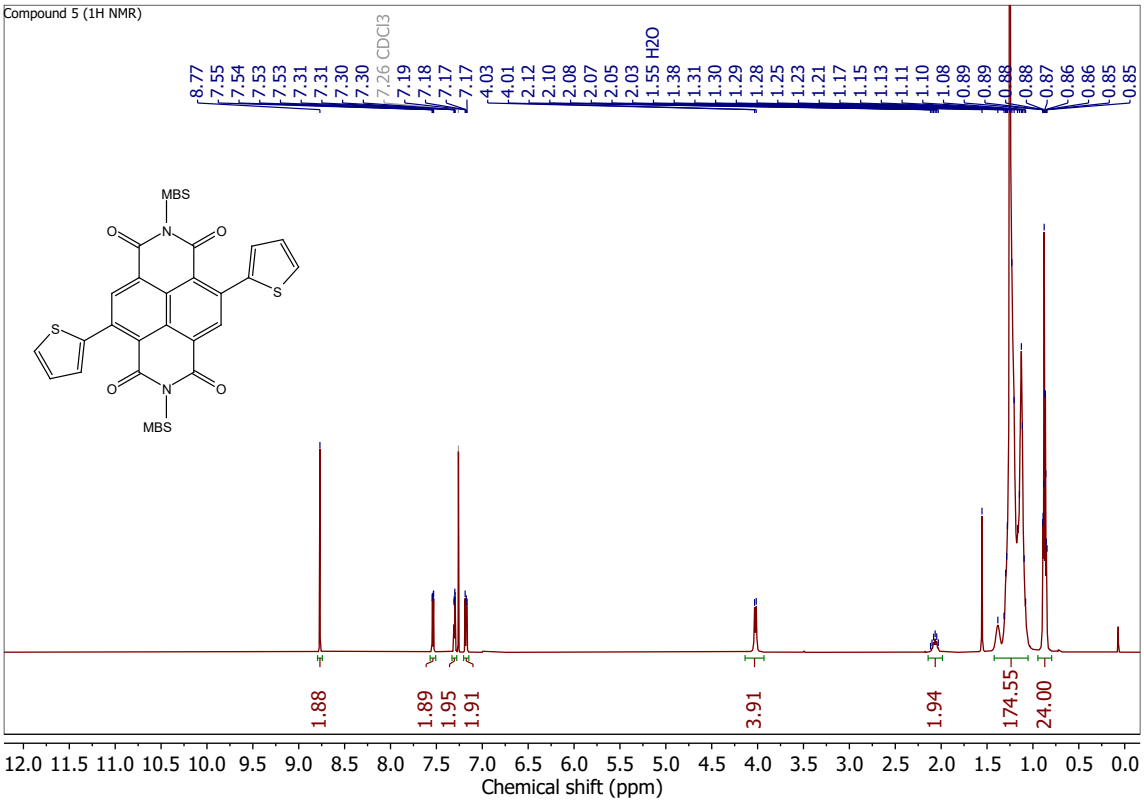

Figure S21. ^{1}H NMR (400 MHz, $CDCl_3$) of compound **5**.

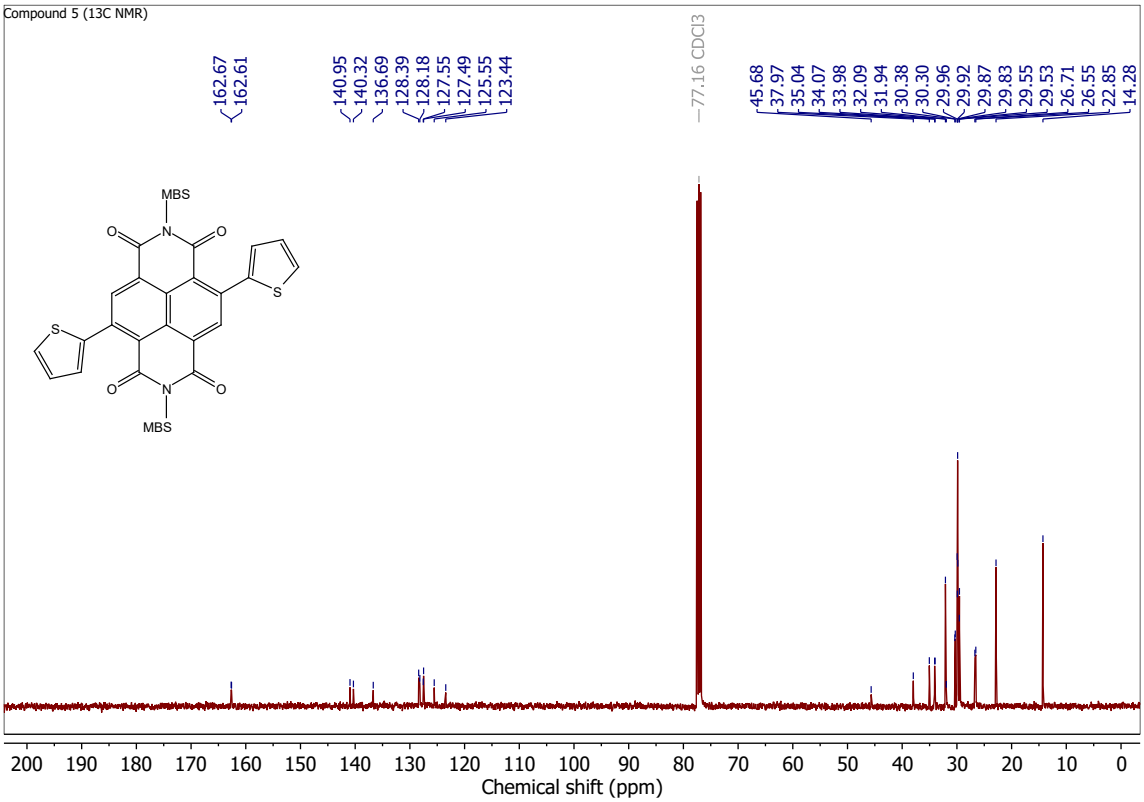

Figure S22. ^{13}C NMR (101 MHz, $CDCl_3$) of compound **5**.

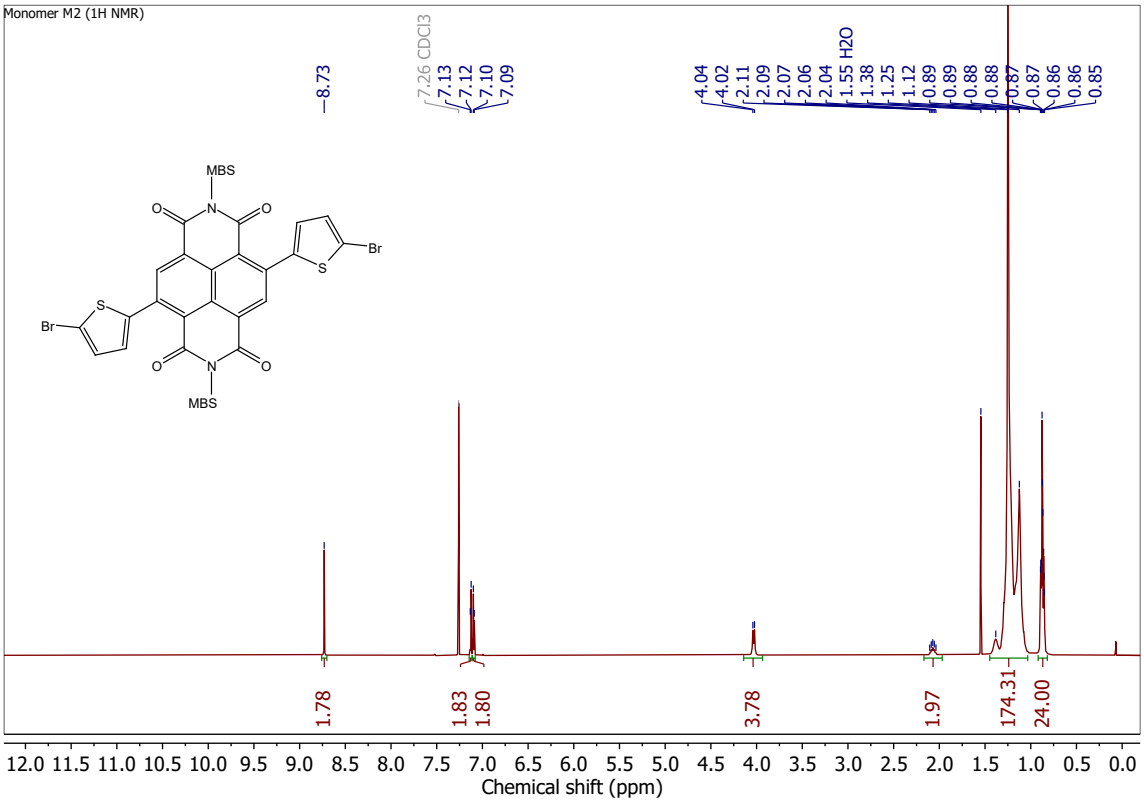

Figure S23. ^{1}H NMR (400 MHz, $CDCl_3$) of monomer **M2**.

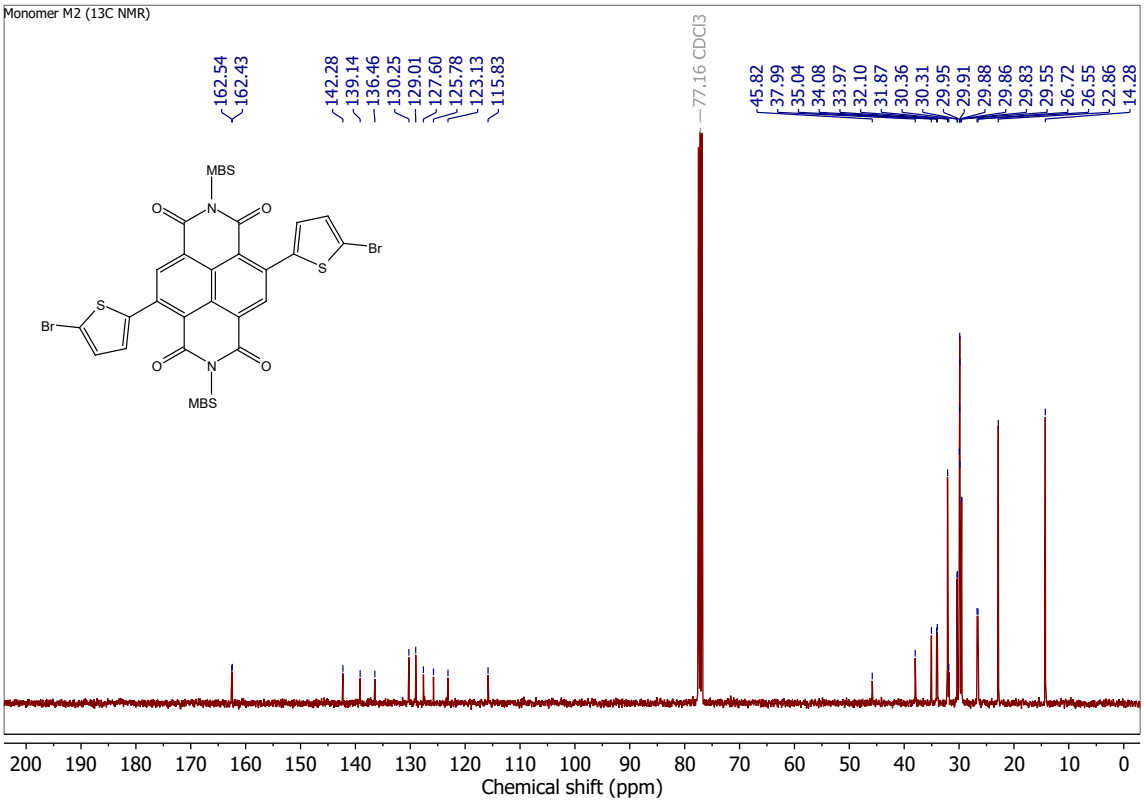

Figure S24. ^{13}C NMR (101 MHz, $CDCl_3$) of monomer **M2**.

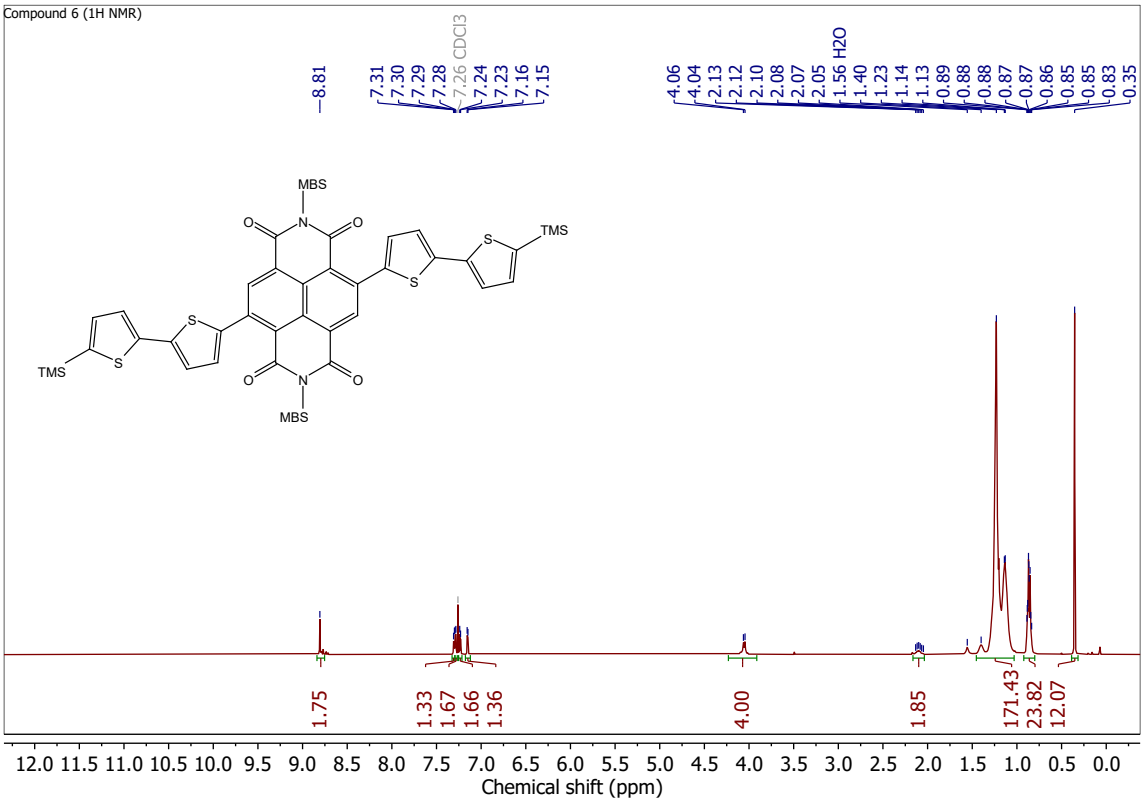

Figure S25. ^{1}H NMR (400 MHz, $CDCl_3$) of compound **6** (impure).

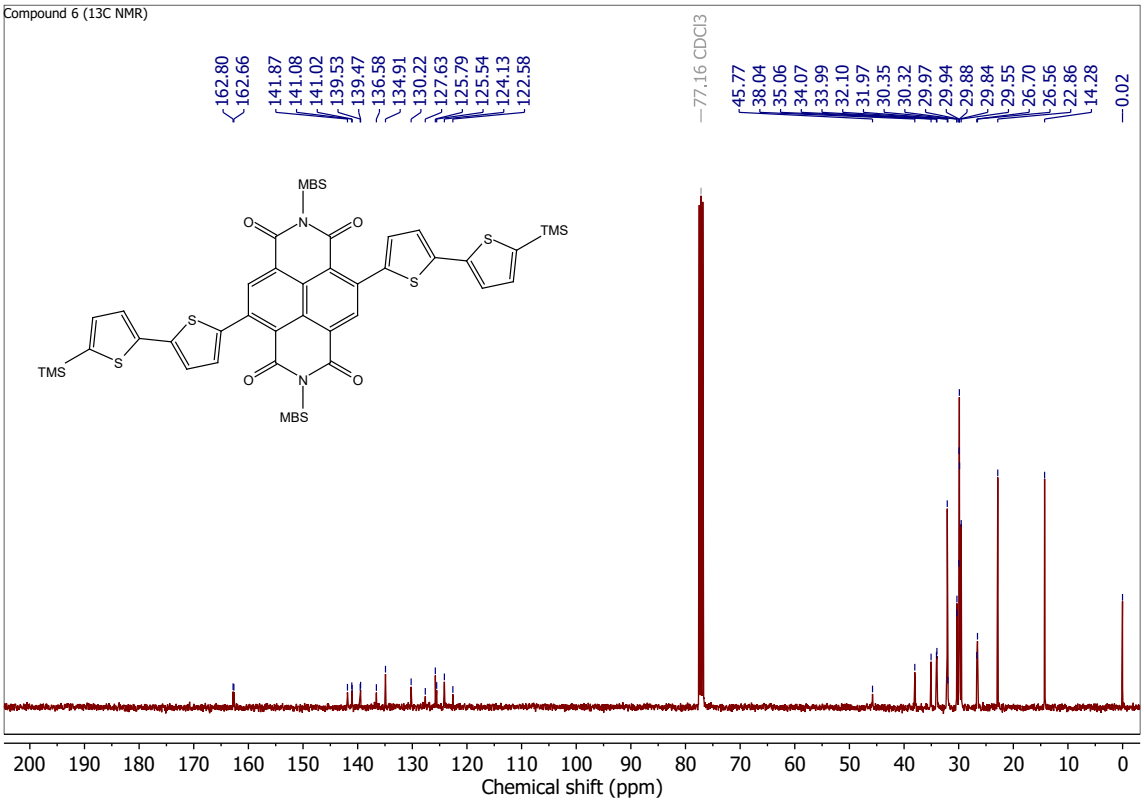

Figure S26. ^{13}C NMR (101 MHz, $CDCl_3$) of compound **6** (impure).

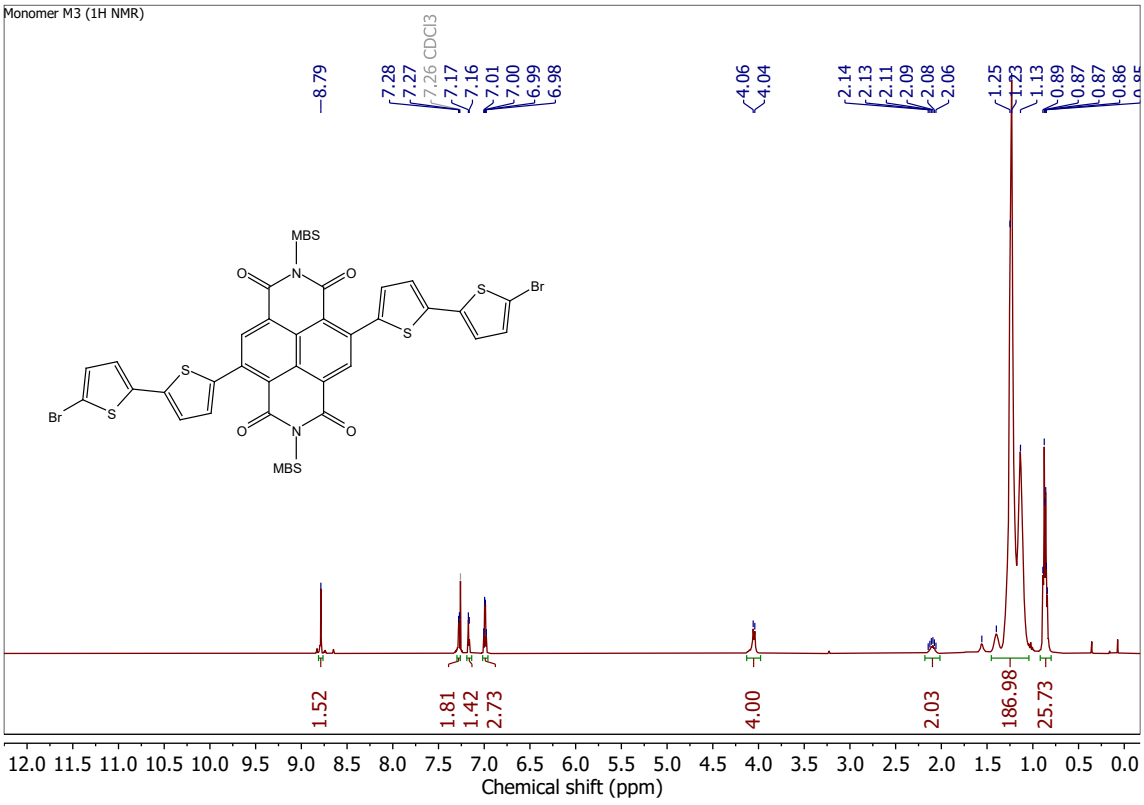

Figure S27. ^{1}H NMR (400 MHz, $CDCl_3$) of monomer **M3**.

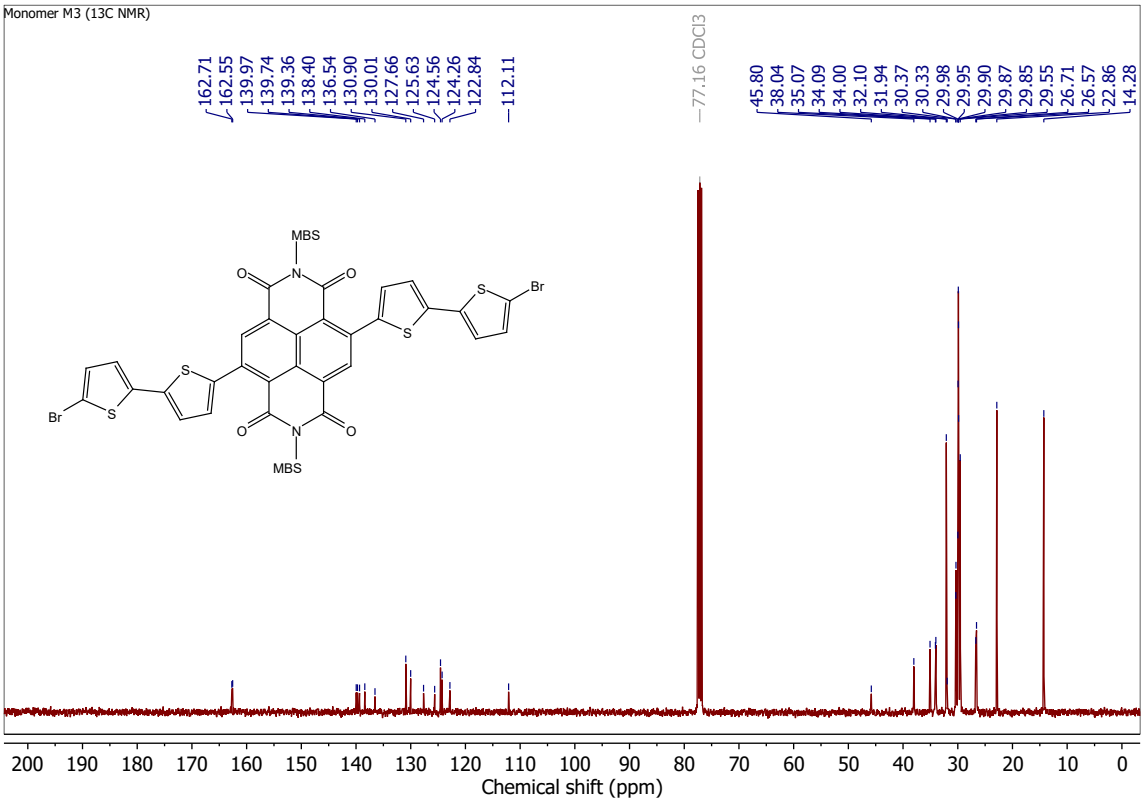

Figure S28. ^{13}C NMR (101 MHz, $CDCl_3$) of monomer **M3**.

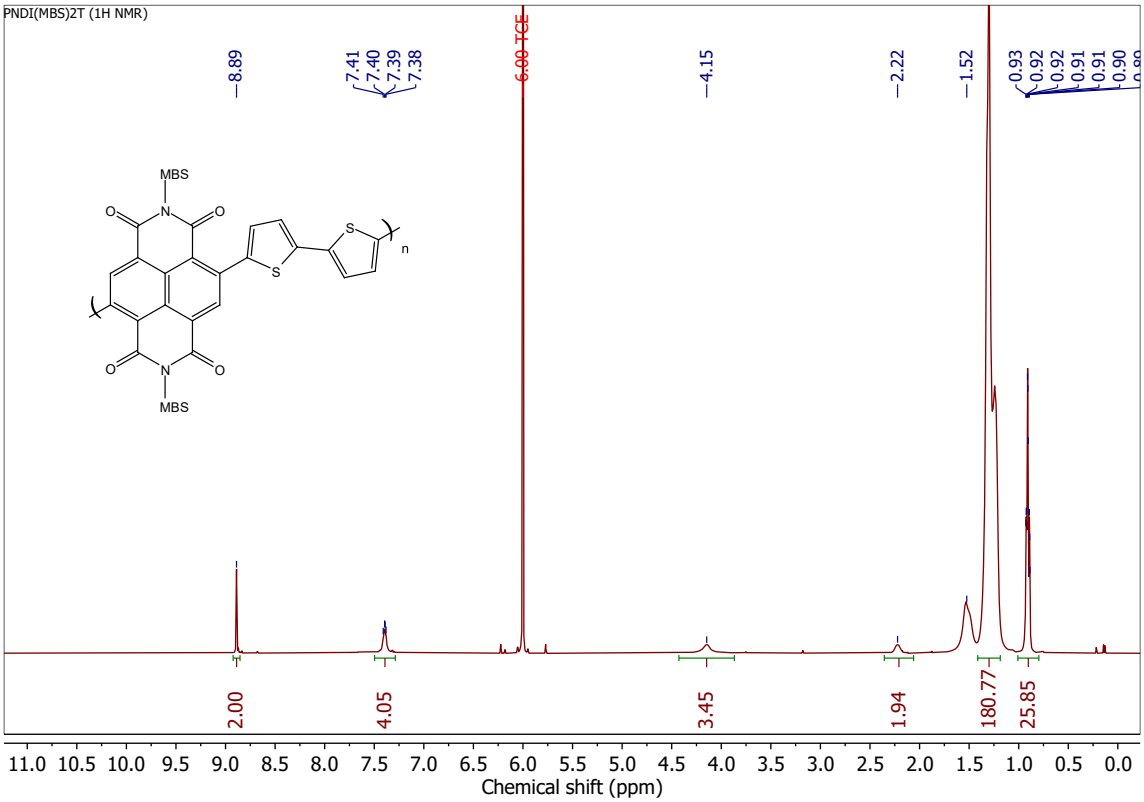

Figure S29. ^{1}H NMR (400 MHz, 1,1,2,2-tetrachloroethane-d_2, 73 °C) of polymer **PNDI(MBS)2T**.

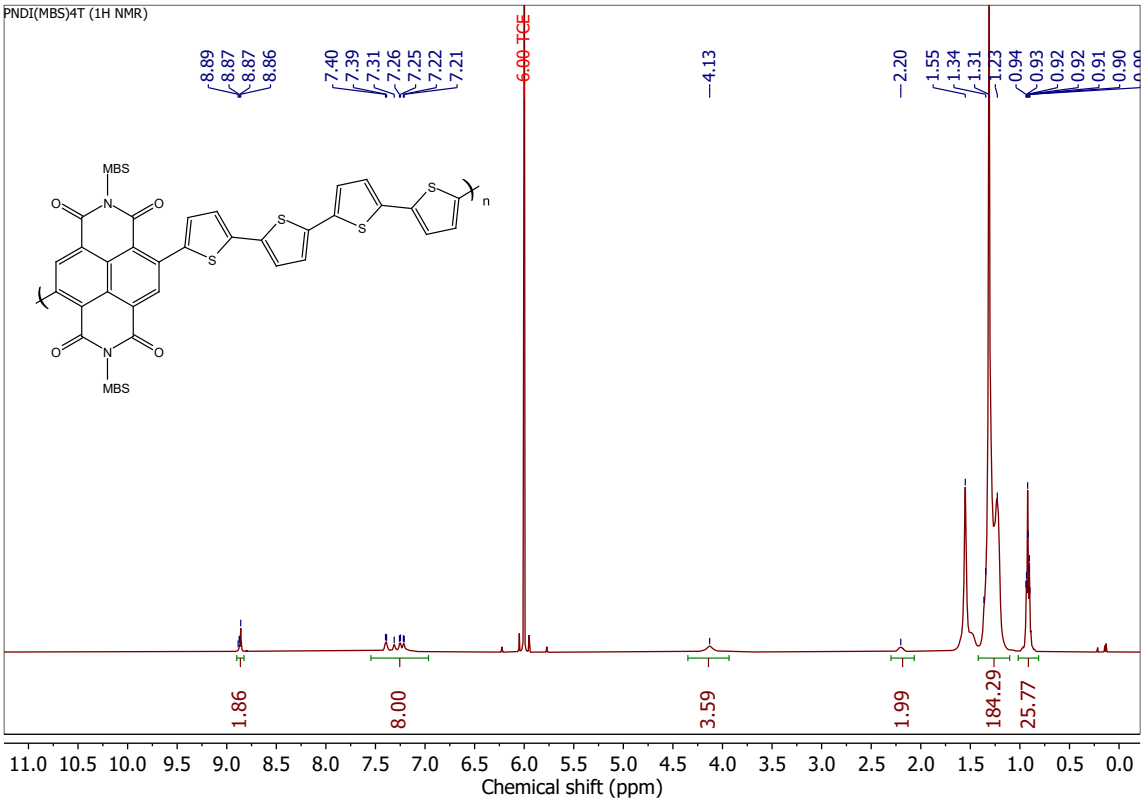

Figure S30. ^{1}H NMR (400 MHz, 1,1,2,2-tetrachloroethane-d_2, 73 °C) of polymer **PNDI(MBS)4T**.

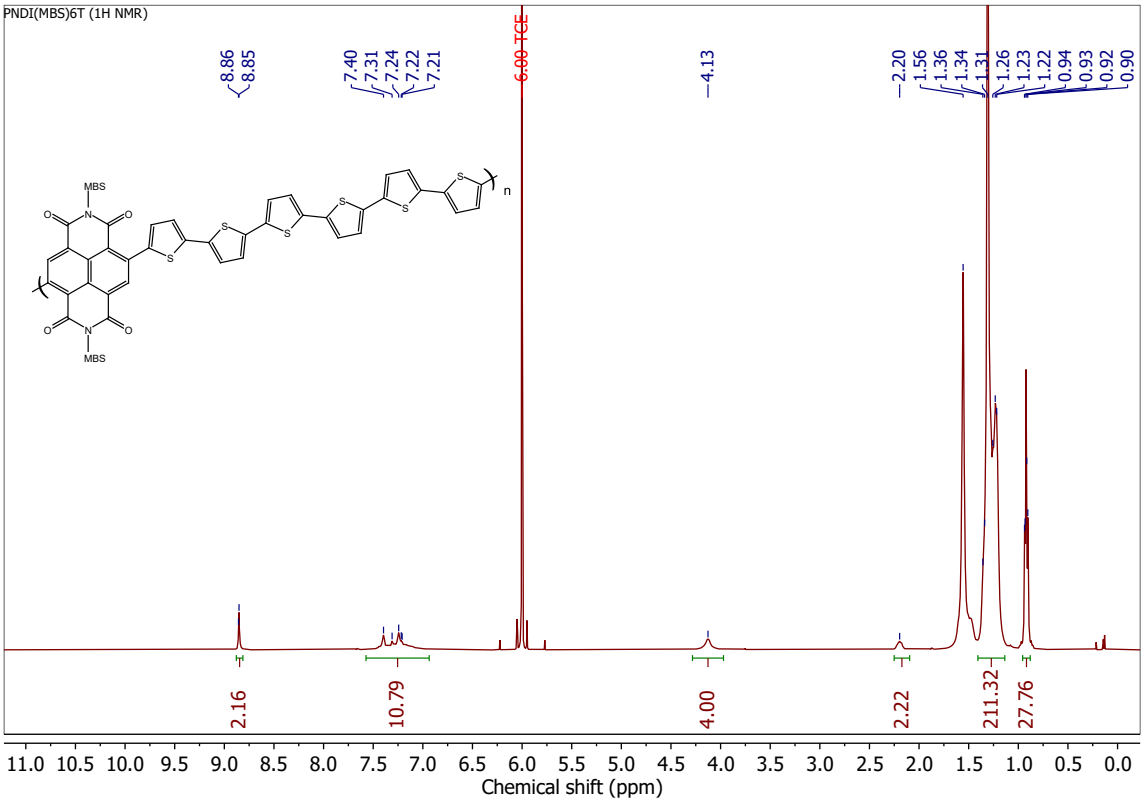

Figure S31. ^{1}H NMR (400 MHz, 1,1,2,2-tetrachloroethane-d_2, 73 °C) of polymer **PNDI(MBS)6T**.

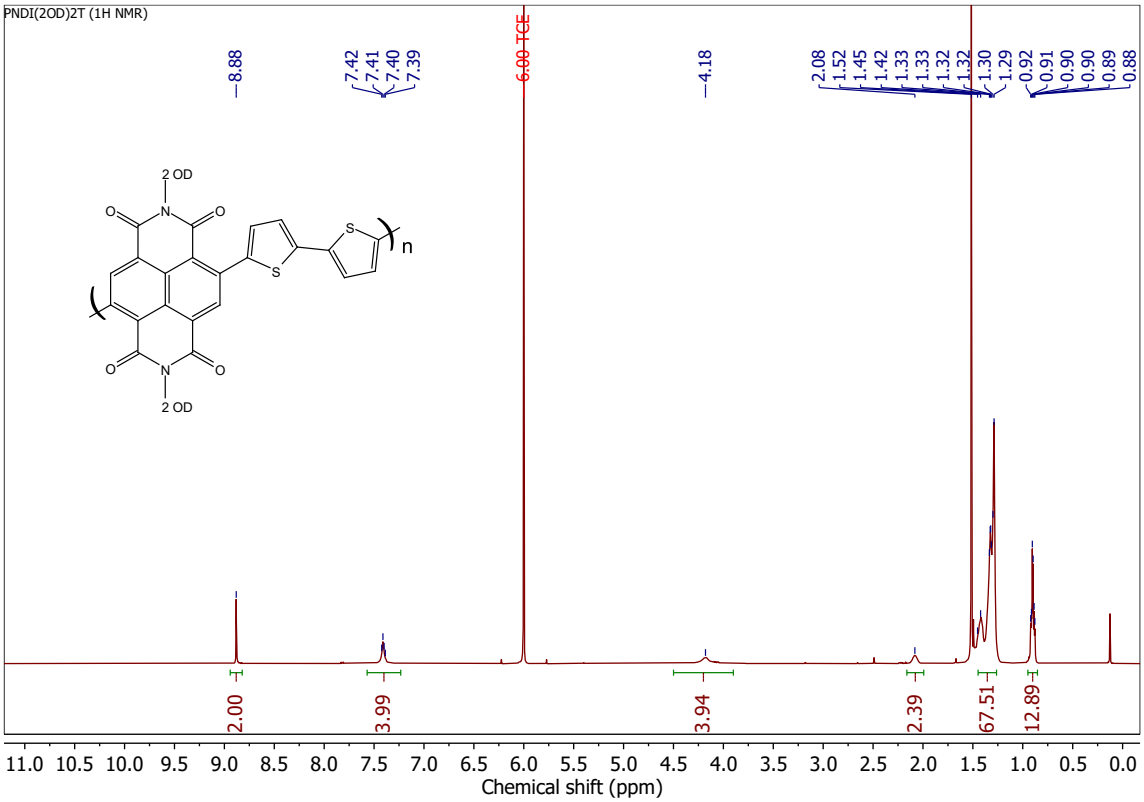

Figure S32. ^{1}H NMR (400 MHz, 1,1,2,2-tetrachloroethane-d_2, 73 °C) of polymer **PNDI(2OD)2T**.

8 References

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