Conjugated Polymers from Napthalene Bisimide

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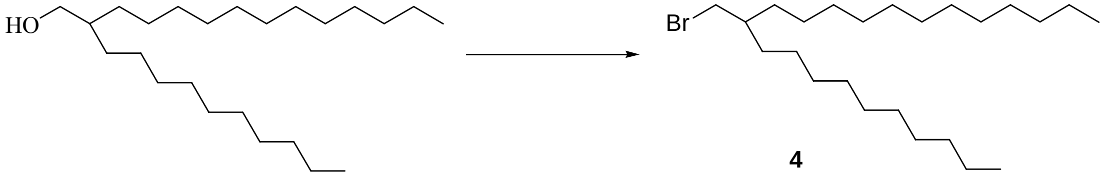
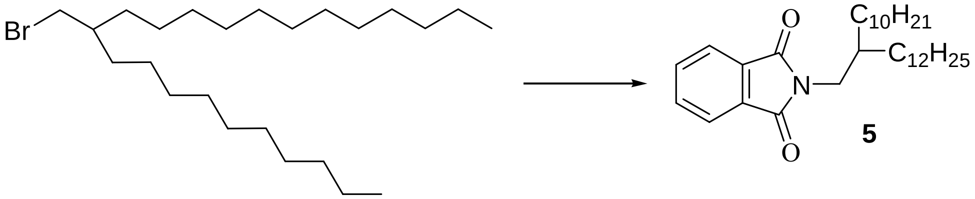
Materials and Methods. THF, diethyl ether, acetonitrile and toluene were distilled from appropriate drying agents and stored over molecular sieves under argon. All other reagents were used as received except where noted. 2,6-Dibromonaphthalene-1,4,5,8-tetracarboxylic acid dianhydride **7** was prepared by a published procedure[1] known to produce a mixture of brominated products and used without purification. 3,3'-Dibromo-2,2'-bithiophene[2] was prepared via published procedure. Unless otherwise stated, all manipulations and reactions were carried out under argon atmosphere using standard Schlenk techniques. ^{1}H and ^{13}C spectra were recorded on a Varian INOVA 400MHz spectrometer (purchased under the CRIF Program of the National Science Foundation, grant CHE-9974810). Chemical shifts were referenced to residual protio-solvent signals. GC-MS data were collected from an Agilent technologies 6890N GC with 5973 MSD. Relative molecular weights of polymers were measured using a Waters 600E HPLC system, driven by Waters Empower Software and equipped with two linear mixed-bed GPC columns (American Polymer Standards Corporation, AM Gel Linear/15) in series. Eluting polymers were detected with both refractive index and photodiode array detectors and the system was calibrated with 11 narrow PDI polystyrene samples in the range 580 to 2 x10^6 Da with THF at a flow rate of 1mL/min. Melting points are reported as the endothermic maxima of 1st order transitions detected by differential scanning calorimetry (Mettler 822^e, heating rate = 10 º C/min, nitrogen purge). UV-vis-NIR data were recorded on an HP8452 B photodiode array spectrophotometer or Varian Cary 1 UV-Visible spectrometer. Photoluminescence data were recorded on a Fluorolog-3 fluorometer. Elemental analysis was performed by Robertson Microlit Laboratories. Cyclic voltammetry measurements of polymers were carried out under nitrogen atmosphere using a BAS-CV-50W voltammetric analyzer with 0.1 M tetra-*n*-butylammonium hexafluorophosphate in acetonitrile as supporting electrolyte. A platinum disk working electrode, a platinum wire counter electrode and silver wire reference electrode were employed and Fc/Fc$^+$ was used as internal reference for all measurements. The scan rate was 50mV/S. Polymer films were produced by drop casting from 0.2 % (w/w) toluene solutions. CV measurement of N,N'-bis(2-ethylhexyl)-naphthalene-1,4,5,8-tetracarboxylic acid diimide (NBI) was carried out in 0.02 % (w/w) dichloromethane. The supporting electrolyte solution was thoroughly purged with N_2 before all CV measurements. WAXD data of polymers were collected on Bruker-Nonius X8 Proteum (purchased under NSF MRI program grant number 0319176) using an area detector and extruded, oriented fibers mounted perpendicular to the incoming beam. The fibers were produced with a home-built, thermally equilibrated piston-actuated extruder (0.5 mm orifice).

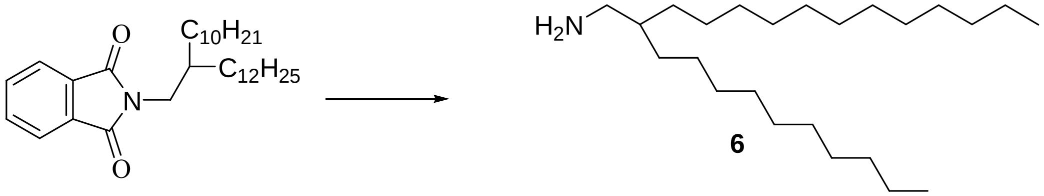
Synthetic Procedures.


4

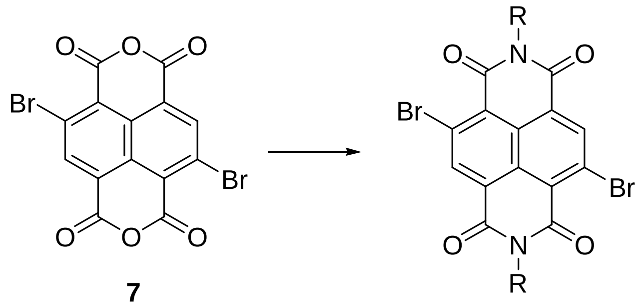
2-decyl-1-tetradecylbromide 4. A solution of triphenylphosphine (50 g, 0.191 mol) in 300 ml dichloromethane was sparged with argon for 15 minutes at 0 ^{0}C, followed by addition of Br_2 (9.77 ml, 0.191 mol) at room temperature. After 2-decyl-1-tetradecanol (80.31 ml, 0.191 mmol) was added dropwise via additional funnel over 30 minutes, the reaction solution was stirred at room temperature overnight under argon. Dichloromethane was evaporated, and the concentrate filtered with pentane wash. The filtrate was concentrated via rotary evaporation and the resulting crude yellow oil was purified via column chromatography (silica gel, 4:1 hexane/dichloromethane). The title compound was isolated as colorless oil (74.97 g, 94 %). ^{1}H NMR (400MHz, $CDCl_3$) δ: 3.43 (d, 2H), 1.57 (m, 1H), 1.24 (m, 40H), 0.86 (m, 6H). ^{13}C NMR (100MHz, $CDCl_3$) δ: 39.95, 39.71, 32.78, 32.16, 30.01, 29.90, 29.87, 29.82, 29.60, 26.78, 22.92, 14.35 (**Note:** some peaks in^{13}C NMR spectrum overlap). GC-MS: m/z: 336 (M-HBr)$^{+}$, 57 (100%).


5

N-(2-decyltetradecyl)phthalimide 5. Potassium phthalimide (7.5 g, 0.0404 mol) was added to a solution of 2-decyl-1-tetradecylbromide (15.7 g, 0.0376 mol) in 45 ml dry DMF. The reaction was stirred for 16 hours at 90 ^{0}C. After cooling to room temperature, the reaction mixture was poured into 150 ml water and extracted with dichloromethane (3 x 100 ml). The combined organic layers were washed with 200 ml 0.2 N KOH, water, saturated ammonium chloride, dried over anhydrous $MgSO_4$, and concentrated under reduced pressure. The resulting crude yellow oil was purified via column chromatography (silica gel: dichloromethane) giving **5** as a pale yellow oil (17.83 g, 98 %). ^{1}H NMR (400MHz, $CDCl_3$) δ: 7.81 (m, 2H), 7.68 (m, 2H), 3.54 (d, 2H), 1.84 (m, 1H), 1.25 (m, 40H), 0.85 (m, 6H). ^{13}C NMR (100MHz, $CDCl_3$) δ: 168.90, 133.99, 132.32, 123.33, 42.50, 37.21, 32.12, 31.66, 30.15, 29.88, 29.87, 29.85, 29.83, 29.80, 29.55, 29.54, 26.48, 22.89, 14.32 (**Note:** some peaks in^{13}C NMR spectrum overlap). GC-MS: m/z: 483 ($C_{32}H_{53}NO_2^{+}$), 161 (100%).


6

2-decyl-1-tetradecylamine 6.[3] N-(2-decyltetradecyl) phthalimide (10 g, 0.021 mol), hydrazine hydrate (hydrazine, 51 %) (4 ml, 0.065 mol) and 100 ml methanol were stirred at 95 ºC and monitored by TLC. After disappearance of the starting imide, the methanol was evaporated under reduced pressure, the residue diluted with 100ml dichloromethane and washed with 10 % KOH (2 x 50 ml). Aqueous layers were combined and extracted with dichloromethane (3 x 20 ml). The combined organic layers were washed with brine (2 x 50 ml) and dried over $MgSO_4$. The removal of dichloromethane afforded a yellow oil as product which was used in NBI synthesis without further purification. ^{1}H NMR (400MHz, $CDCl_3$) δ: 4.44 (br, 2H), 2.65 (d, 2H), 1.45 (m, 1H), 1.22 (br, 40H), 0.84 (m, 6H). ^{13}C NMR (100MHz, $CDCl_3$) 45.33, 41.01, 32.09, 31.71, 30.28, 29.86, 29.54, 26.96, 22.86, 14.26 (**Note:** some peaks in^{13}C NMR spectrum overlap). GC-MS: m/z: 352 (M-H)$^{+}$, 55 (100%).



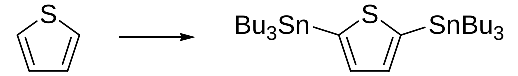
7

3a: R = 2-ethyl-hexyl
3b: R = 2-decyl-tetradecyl

NBI monomers 3: Bromination[1] of commercially available naphthalene-1,4,5,8-tetracarboxylic acid dianhydride (NDA) gave compound **7** as part of a mixture of brominated NDAs which was used without further purification for the synthesis of monomers **3**.

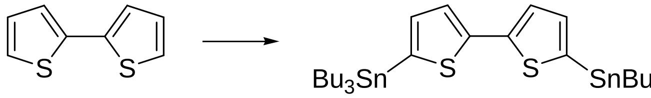
Monomer 3a: A flask was charged with **7** (3.0 g, 7.04 mmol assuming pure **7**), 2-ethyl-hexyl amine (3.64 g, 28.16 mmol) and 80 mL glacial acetic acid and the whole stirred at 120 ºC under argon. When all solids were dissolved, approximately 60 mL of the acetic acid was evaporated, and the concentrate was added to 200 ml methanol. The resulting reddish solid was collected by filtration, washed with methanol, and dried under reduced pressure. The crude product was then purified via column chromatograph (silica gel, dichloromethane). The resulting orange solid was further purified via recrystallization from hexanes to give **3a** as yellow crystals (2.65 g, 58 % assuming pure **7**). ^{1}H NMR ($CDCl_3$, 400 MHz, ppm): δ 8.97 (s, 2H), 4.13 (m, 4H), 1.92 (m, 2H), 1.31 (m, 16H), 0.86 (m, 12H). ^{13}C NMR ($CDCl_3$, 100 MHz, ppm): δ 161.42, 161.25, 139.38, 128.58, 127.96, 125.48, 124.28, 45.35, 37.97, 30.82, 28.74, 24.17, 23.29, 14.30, 10.78. mp: 246 ºC. Anal. Calcd for $C_{30}H_{36}Br_2N_2O_4$: C, 55.57; H, 5.60; N, 4.32. Found: C, 55.72; H, 5.42; N, 4.18.

Monomer **3b:** Prepared isolated using the same procedures as for **3a**, but from **7** and **6**, giving **3b** as a yellow solid (52 % assuming pure **7**). ^{1}H NMR ($CDCl_3$, 400 MHz, ppm): δ 8.97 (s, 2H), 4.12 (d, 4H), 1.97 (m, 2H), 1.21 (m, 80H), 0.85 (m, 12H). ^{13}C NMR ($CDCl_3$, 100 MHz, ppm): δ 161.39, 161.24, 139.38, 128.59, 127.97, 125.50, 124.30, 45.67, 36.68, 32.15, 31.77, 30.25, 29.87, 29.82, 29.67, 29.59, 29.57, 26.55, 22.92, 14.35 (**Note:** some peaks in ^{13}C NMR spectrum overlap). mp: 94 ºC. Anal. Calcd for $C_{62}H_{100}Br_2N_2O_4$: C, 67.86; H, 9.19; N, 2.55. Found: C, 68.10; H, 9.47; N, 2.28.



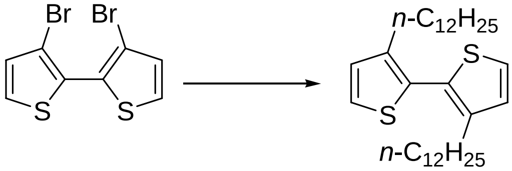
1

2,5-bis(tributylstannyl)thiophene 1:[4] *n*-Butyl lithium (8.8 ml 2.5 M in hexane, 22 mmol) was added dropwise -78 ºC to thiophene (0.84 g, 10 mmol) in 20 ml dry THF and the whole was stirred at -78 ºC for 1 hour, followed by 1 hour at room temperature. After cooling to -78 ºC, tributyltin chloride (7.2 g, 22 mmol) was added in one portion and the whole was warmed to room temperature and stirred for 1 hour. The reaction mixture was diluted with ethyl acetate (50 mL) and washed with water (2 x 20 ml) and brine (2 x 20 ml) and dried over $MgSO_4$. After concentration by rotary evaporation, the residue was purified by column chromatography (alumina, 95:5 hexane:triethyl amine) to give monomer **1** as a colorless liquid (5.8 g, 88 %). ^{1}H NMR ($CDCl_3$, 400 MHz, ppm): δ 7.33 (s, 2H), 1.56 (m, 12H), 1.32 (m, 12H), 1.08 (m, 12H), 0.88 (m, 18H). ^{13}C NMR ($CDCl_3$, 100 MHz, ppm): δ 141.98, 135.94, 29.22, 27.50, 13.90, 11.09. Anal. Calcd for $C_{28}H_{56}SSn_2$: C, 50.78; H, 8.52. Found: C, 51.08; H, 8.47; N, < 0.02.



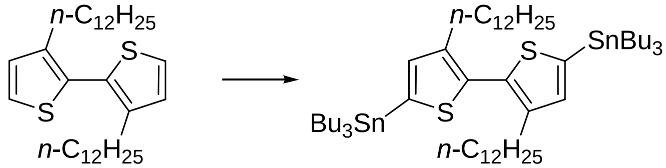
2a

5,5'-bis(tributylstannyl)-2,2'-bithiophene.[5] Monomer **2a** was prepared and isolated as a colorless oil using the same procedure as **1** but from commercially available 2,2'-bithiophene. (86 %). ^{1}H NMR ($CDCl_3$, 400 MHz, ppm): δ 7.27 (d, 2H), 7.03 (d, 2H), 1.56 (m, 12H), 1.33 (m, 12H), 1.09 (m, 12H), 0.88 (m, 18H). ^{13}C NMR ($CDCl_3$, 100 MHz, ppm): δ 143.22, 136.38, 136.27, 124.89, 29.18, 27.48, 13.89, 11.07. Anal. Calcd for $C_{32}H_{58}S_2Sn_2$: C, 51.63; H, 7.85. Found: C, 52.00; H, 8.03; N, < 0.02.



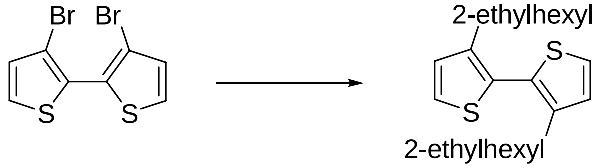
8

3,3’-didodecyl-2,2’-bithiophene 8.[2] Known compound **8** was prepared and isolated via the published procedure (Kumada coupling of dodecyl magnesium bromide and 3,3’-dibromo-2,2’-bithiophene) as a colorless solid (92 %) after column chromatography. ^{1}H NMR ($CDCl_3$, 400 MHz, ppm): δ 7.26 (d, 2H), 6.94 (d, 2H), 2.47 (t, 4H), 1.51 (m, 4H), 1.23 (m, 36H), 0.87 (t, 6H). ^{13}C NMR ($CDCl_3$, 100 MHz, ppm): δ 142.56, 128.93, 128.74, 125.43, 32.15, 30.94, 29.91, 29.89, 29.79, 29.67, 29.65, 29.59, 29.00, 22.92, 14.35 (**Note:** two peaks in ^{13}C NMR spectrum overlap). mp: 52 ºC. GC-MS: m/z: 502 ($C_{32}H_{54}S_2^+$), 502 (100%).



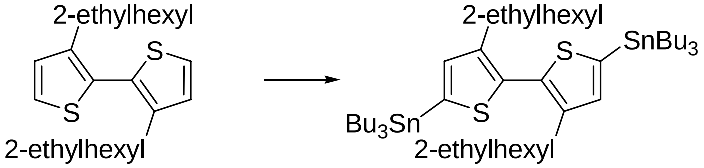
2b

5,5’-bis(tributylstannyl)-3,3’-didodecyl-2,2’-bithiophene 2b. Monomer **2b** was prepared and isolated as a colorless oil using the same procedures employed for monomer **1**. (82 %). ^{1}H NMR ($CDCl_3$, 400 MHz, ppm): δ 6.96 (s, 2H), 2.51(t, 4H), 1.56 (m, 16H), 1.27 (m, 48H), 1.08 (m, 12H), 0.88 (m, 24H). ^{13}C NMR ($CDCl_3$, 100 MHz, ppm): δ 142.78, 137.31, 136.31, 135.38, 32.17, 31.23, 29.96, 29.94, 29.91, 29.89, 29.80, 29.74, 29.62, 29.21, 28.98, 27.49, 22.93, 14.35, 13.92, 11.01. Anal. Calcd for $C_{56}H_{106}S_2Sn_2$: C, 62.22; H, 9.88. Found: C, 62.59; H, 9.84; N, < 0.02.



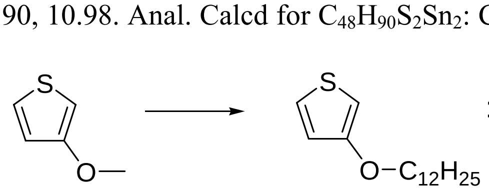
9

3,3’-(2-ethyl-hexyl)-2,2’-bithiophene 9. Compound **9** was prepared as a colorless liquid following the same procedures employed for compound **8**, but using 2-ethylhexyl magnesium bromide (90 %). ^{1}H NMR (CD_2Cl_2, 400 MHz, ppm): δ 7.30 (d, 2H), 6.94 (d, 2H), 2.43 (d, 4H), 1.52 (m, 2H), 1.21 (m, 16H), 0.83 (t, 6H), 0.75 (t, 6H). ^{13}C NMR (CD_2Cl_2, 100 MHz, ppm): δ 142.15, 129.93, 129.58, 125.58, 40.88, 33.56, 33.23, 29.32, 26.35, 23.55, 14.44, 11.08. GC-MS: m/z: 390 ($C_{24}H_{38}S_2^+$), 193 (100%).



2c

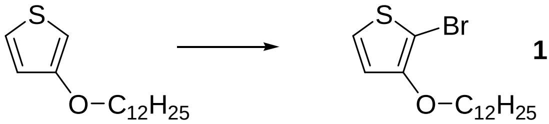
5,5’-bis(tributylstannyl)-3,3’-bis(2-ethylhexyl)-2,2’-bithiophene 2c. 2c was prepared and isolated as a colorless oil using the same procedures as **1**. (92 %). ^{1}H NMR ($CDCl_3$, 400 MHz, ppm): δ 6.90 (s, 2H), 2.44 (d, 4H), 1.56 (m, 14H), 1.32 (m, 12H), 1.12 (m, 28H), 0.88 (t, 18H), 0.81 (t, 6H), 0.72 (t, 6H). ^{13}C NMR ($CDCl_3$, 100 MHz, ppm): δ 141.88, 137.89, 136.01, 135.81, 40.60, 33.07, 32.90, 29.20, 29.00, 27.46, 26.05, 23.23, 14.34, 13.90, 10.98. Anal. Calcd for $C_{48}H_{90}S_2Sn_2$: C, 59.51; H, 9.36. Found: C, 59.73; H, 9.60; N, < 0.02.



10

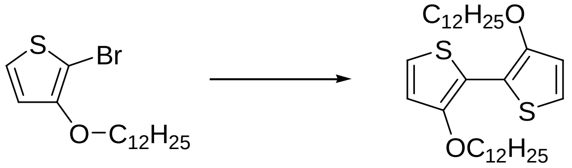
3-dodecyloxythiophene 10. A mixture of 3-methoxythiophene (6.00 g, 52.60 mmol), 1-dodecanol (23.54 ml, 105.2 mmol), p-toluenesulfonic acid monohydrate (1.00 g, 0.1 eq) and 50 ml toluene was heated in a

130 ºC bath for 15 hours under argon. After dichloromethane/water extraction, the organic layer was dried over $MgSO_4$. After solvent evaporation, the residue was purified by column chromatography (silica gel 3:1 hexane:dichloromethane) to give **10** as a colorless solid (8.75 g, 62 %). ^{1}H NMR ($CDCl_3$, 400 MHz, ppm): δ 7.15 (dd, 1H), 6.74 (dd, 1H), 6.21 (dd, 1H), 3.92 (t. 2H), 1.75 (m, 2H), 1.43 (m, 2H), 1.26 (m, 16H), 0.87 (t, 3H). ^{13}C NMR ($CDCl_3$, 100 MHz, ppm): δ 158.29, 124.70, 119.76, 97.16, 70.50, 32.14, 29.88, 29.85, 29.82, 29.79, 29.61, 29.57, 29.49, 26.27, 22.91, 14.34. mp: 35 ºC. GC-MS: m/z: 268 ($C_{16}H_{28}OS^+$), 100 (100%).



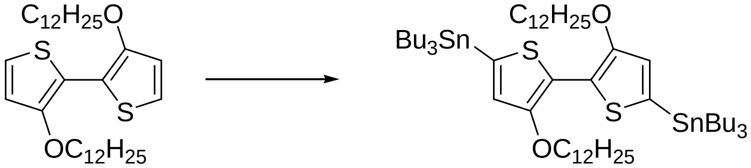
11

2-bromo-3-dodecyloxythiophene 11. NBS (1.78 g, 10 mmol) was added in one portion to **10** (2.69 g, 10 mmol) in 20 ml DMF at 0 ºC and the whole was warmed to room temperature and stirred for 15 hours. The reaction mixture was diluted with ether (50 ml) and washed with water (2 x 20 ml). The organic layer was dried over $MgSO_4$, concentrated under reduced pressure, and the residue subjected to column chromatography (silica gel, pentane) to give **11** as a colorless solid (3.06 g, 88 %). ^{1}H NMR ($CDCl_3$, 400 MHz, ppm): δ 7.16 (d, 1H), 6.72 (d, 1H), 4.01 (t, 2H), 1.73 (m, 2H), 1.43 (m, 2H), 1.25 (m, 16H), 0.86 (t, 3H). ^{13}C NMR ($CDCl_3$, 100 MHz, ppm): δ 154.77, 124.31, 117.71, 91.78, 72.46, 32.13, 29.87, 29.85, 29.79, 29.76, 29.69, 29.56, 29.54, 26.02, 22.90, 14.33. mp: 48 ºC. GC-MS: m/z: 346 ($C_{16}H_{27}BrOS^+$), 180 (100%).



12

3,3'-bis(dodecoxy)-2,2'-bithiophene 12. A mixture of bis(1,5-cyclooctadienyl)nickel (0) (2.0 g, 7.27 mmol), 2,2'-dipyridyl (1.14 g, 7.27 mmol), 1,5-cyclooctadiene (0.59 ml, 4.84 mmol) and 20 ml anhydrous DMF was stirred at 80 ºC for 1 hour under argon. To this solution, **11** (1.68 g, 4.84 mmol) in 30 ml toluene was added slowly via cannula at room temperature. The resulting reaction mixture was stirred at 80 ºC overnight. The reaction mixture was diluted with dichloromethane and washed with 10 % HCl, brine and dried over $MgSO_4$. After concentration under reduced pressure, the residue was subjected to gradient column chromatography (silica gel, 1:0 → 3:1 hexane:DCM) to give **12** as a pale yellow solid (1.06 g, 82 %). ^{1}H NMR ($CDCl_3$, 400 MHz, ppm): δ 7.04 (d, 2H), 6.81 (d, 2H), 4.06 (t, 4H), 1.81 (m, 4H), 1.49 (m, 4H), 1.24 (m, 32H), 0.85 (t, 6H). ^{13}C NMR ($CDCl_3$, 100 MHz, ppm): δ 152.15, 121.81, 116.25, 114.31, 72.20, 32.14, 29.92, 29.89, 29.88, 29.83, 29.79, 29.58, 26.26, 22.92, 14.35 (**Note**: two peaks in ^{13}C NMR overlap). mp: 69 ºC. GC-MS: m/z: 534 ($C_{32}H_{54}O_2S_2^+$), 534 (100%).



2d

5,5'-bis(tributylstannyl)-3,3'-bis(dodecoxy)-2,2'-bithiophene 2d. 2d was prepared and isolated as a pale yellow oil using the same procedures as for monomer **1** (86 %). ^{1}H NMR ($CDCl_3$, 400 MHz, ppm): δ 6.81 (s, 2H), 4.08 (t, 4H), 1.83 (m, 4H), 1.56 (m, 16H), 1.30 (m, 44H), 1.07 (m, 12H), 0.88 (m, 24H). ^{13}C NMR ($CDCl_3$, 100 MHz, ppm): δ 153.94, 132.72, 124.01, 120.44, 72.13, 32.15, 30.10, 29.98, 29.95, 29.91, 29.78, 29.61, 29.19, 27.48, 26.46, 22.92, 14.35, 13.93, 10.96 (**Note**: two peaks in ^{13}C NMR overlap). Anal. Calcd for $C_{56}H_{106}S_2Sn_2$: C, 60.43; H, 9.60. Found: C, 60.06; H, 9.70; N, < 0.02. (**Note**: **2d** is not stable in air at room temperature, but could be stored in a -15 ºC refrigerator under argon.).

General Procedure for Polymerization. To an air-free flask, monomer **1** or **2** (0.2 mmol) and **3a** or **3b** (0.2 mmol) were added under argon followed by tris(dibenzylideneacetone) dipalladium (0) and tri(*o*-

tolyl)phosphine (1:8 molar ratio between $Pd_2(dba)_3$ and $P(o\text{-tolyl})_3$; Pd loading: 0.03 equiv). The flask and its contents were subjected to 3 pump/purge cycles with argon followed by addition of anhydrous, degassed THF (4 ml) via syringe. The sealed reaction mixture was stirred at 80 ºC for two days. After cooling to room temperature, the deeply colored reaction mixture was dripped into 100 ml vigorously stirred methanol (containing 5 ml 12 M hydrochloride acid). After stirring for 4 hours, the precipitated solid was collected by centrifugation and decantation. The solid polymers were redissolved in chloroform and reprecipitated into methanol. After filtration and drying under reduced pressure, the polymers were subjected to sequential Soxhlet extraction. For polymers **P1** and **P2c**, the sequential solvents were methanol, acetone and chloroform; for polymers **P2a, P2b, P2d**, the sequential solvents were methanol, acetone, hexane and chloroform. Finally, the polymer solution in chloroform was concentrated to approximately 20 ml and the polymers precipitated into 100 ml methanol, collected by centrifugation and dried under reduced pressure. See Table 1 in main text for yields, melting points, molecular weights.

P1: Deep violet solid. ^{1}H NMR ($CDCl_3$, 400 MHz, ppm): δ 8.95 (s, 2H), 7.43 (s, 2H), 4.13 (brs, 4H), 2.01 (brs, 2H), 1.20 (m, 80H), 0.83(m, 12H). ^{13}C NMR ($CDCl_3$, 100 MHz, ppm): δ 162.67, 162.60, 143.79, 139.65, 137.02, 129.46, 127.91, 125.81, 123.38, 45.32, 36.73, 32.14, 31.82, 30.36, 29.93, 29.89, 29.58, 26.65, 22.91, 14.34 (**Note**: some peaks in ^{13}C NMR overlap). Anal. Calcd for $C_{66}H_{102}N_2O_4S$ (%): C, 77.75; H, 10.08; N, 2.75. Found (%): C, 77.44; H, 10.55; N, 2.46.
P2a: Deep blue-green solid. ^{1}H NMR ($C_2D_2Cl_4$, 130 ºC, 400 MHz, ppm): δ 8.91 (s, 2H), 7.43 (s, 4H), 4.22 (brs, 4H), 2.13 (brs, 2H), 1.39 (m 80H), 0.94 (m, 12H). Anal. Calcd for $C_{70}H_{104}N_2O_4S_2$ (%): C, 76.31; H, 9.51; N, 2.54. Found (%): C, 76.43; H, 9.80; N, 2.33. **Note**: Due to aggregation, no ^{13}C signals arising from the polymer backbones could be observed after collecting at 130 ºC for 12 hours.
P2b: Deep blue solid. ^{1}H NMR ($CDCl_3$, 400 MHz, ppm): δ 8.85 (s, 2H), 7.27 (s, 2H), 4.14 (brs, 4H), 2.74 (brs, 4H), 1.97 (t, 2H), 1.71 (brs, 4H), 1.31 (m, 52H), 0.92 (m, 18H). ^{13}C NMR ($CDCl_3$, 60 ^{0}C, 100 MHz, ppm): δ 163.02, 162.75, 143.50, 141.10, 140.22, 136.77, 132.07, 130.94, 127.89, 125.82, 123.25, 45.02, 38.42, 38.31, 32.18, 31.30, 31.14, 31.08, 30.00, 29.93, 29.86, 29.69, 29.66, 29.60, 29.08, 24.58, 23.33, 22.90, 14.27, 11.02, 10.96. Aanl. Calcd for $C_{62}H_{88}N_2O_4S_2$ (%): C, 75.26; H, 8.96; N, 2.83. Found (%): C, 74.98; H, 9.11; N, 2.84.
P2c: Deep violet solid. ^{1}H NMR ($CDCl_3$, 400 MHz, ppm): 8.82 (s, 2H), 7.21 (s, 2H), 4.10 (brs, 4H), 2.65 (brs, 4H), 1.94 (m, 2H), 1.67 (m, 2H), 1.28 (m, 32H), 0.86 (m, 24H). ^{13}C NMR ($CDCl_3$, 100 MHz, ppm): δ 163.00, 162.56, 142.66, 140.84, 140.09, 136.71, 132.40, 131.13, 127.76, 125.59, 123.13, 44.88, 40.75, 38.03, 33.68, 33.01, 31.00, 29.21, 28.90, 26.03, 24.25, 23.34, 23.30, 14.40, 14.33, 11.09, 10.88. Anal. Calcd for $C_{54}H_{72}N_2O_4S_2$ (%): C, 73.93; H, 8.27; N, 3.19. Found (%): C, 74.04; H, 8.51; N, 2.96.
P2d: Deep green solid. ^{1}H NMR ($C_2D_2Cl_4$, 130 ºC, 400 MHz, ppm): δ 8.95 (s, 2H), 7.32 (s, 2H), 4.33 (t, 4H), 4.24 (brs, 4H), 2.14 (brs, 2H), 2.05 (m, 4H), 1.67 (m, 4H), 1.40 (m, 112H), 0.94 (m, 18H). Anal. Calcd for $C_{94}H_{152}N_2O_6S_2$ (%): C, 76.78; H, 10.42; N, 1.91. Found (%): C, 76.69; H, 10.70; N, 1.66. **Note**: Due to aggregation, no ^{13}C signals arising from the polymer backbones could be observed after collecting at 130 ºC for 12 hours.

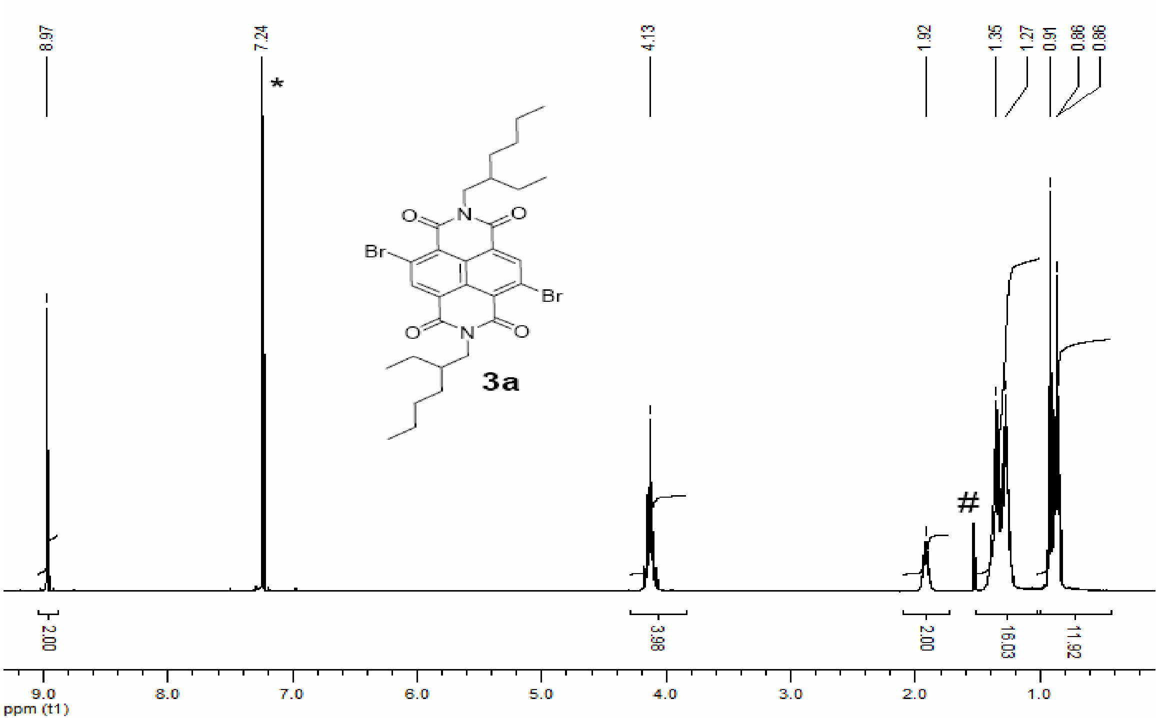


Figure S1. ^{1}H NMR spectrum of **3a** (r.t., in $CDCl_3$, *: solvent, #: H_2O)

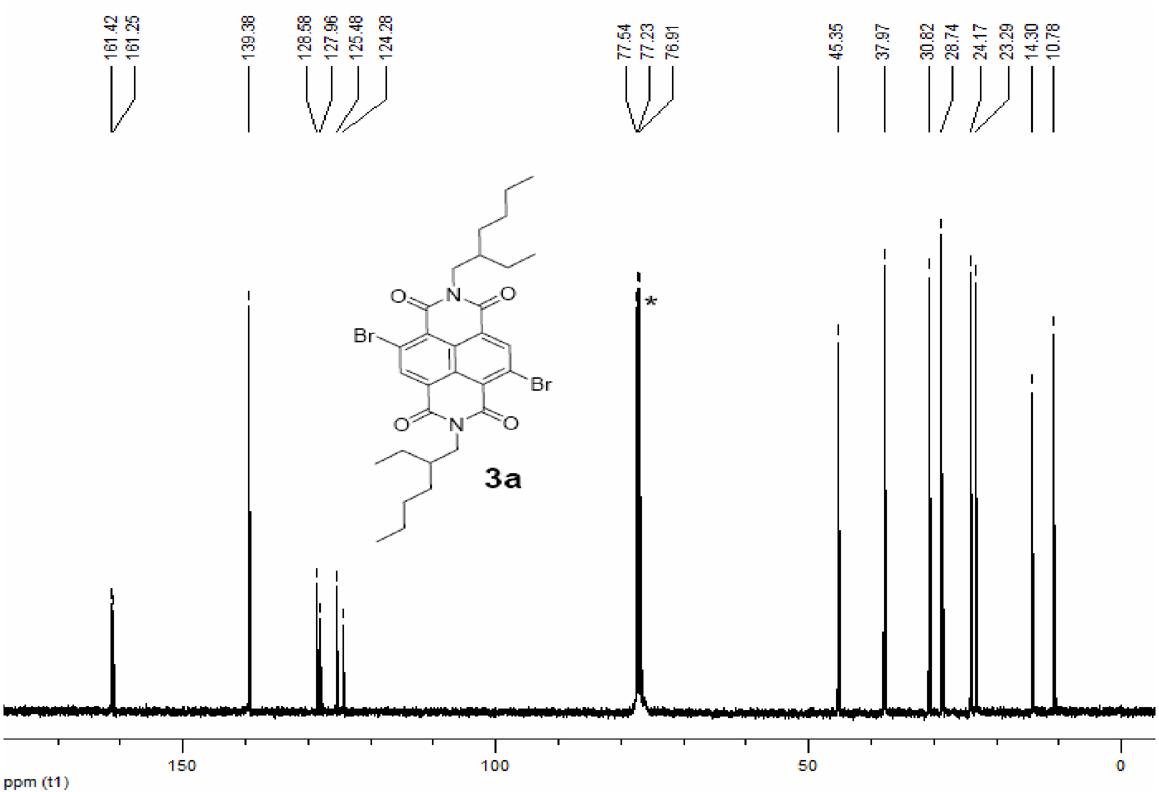


Figure S2. ^{13}C NMR spectrum of **3a** (r.t., in $CDCl_3$, *: solvent)

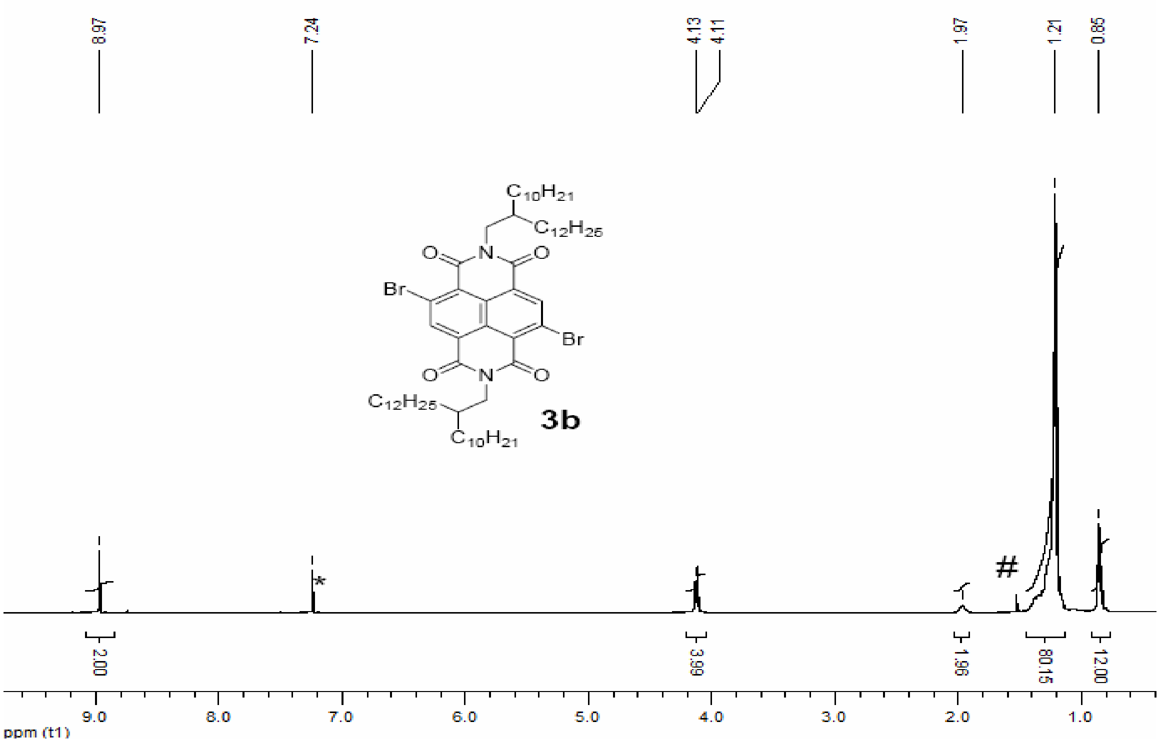


Figure S3. ^{1}H NMR spectrum of **3b** (r.t., in $CDCl_3$, *: solvent, #: H_2O)

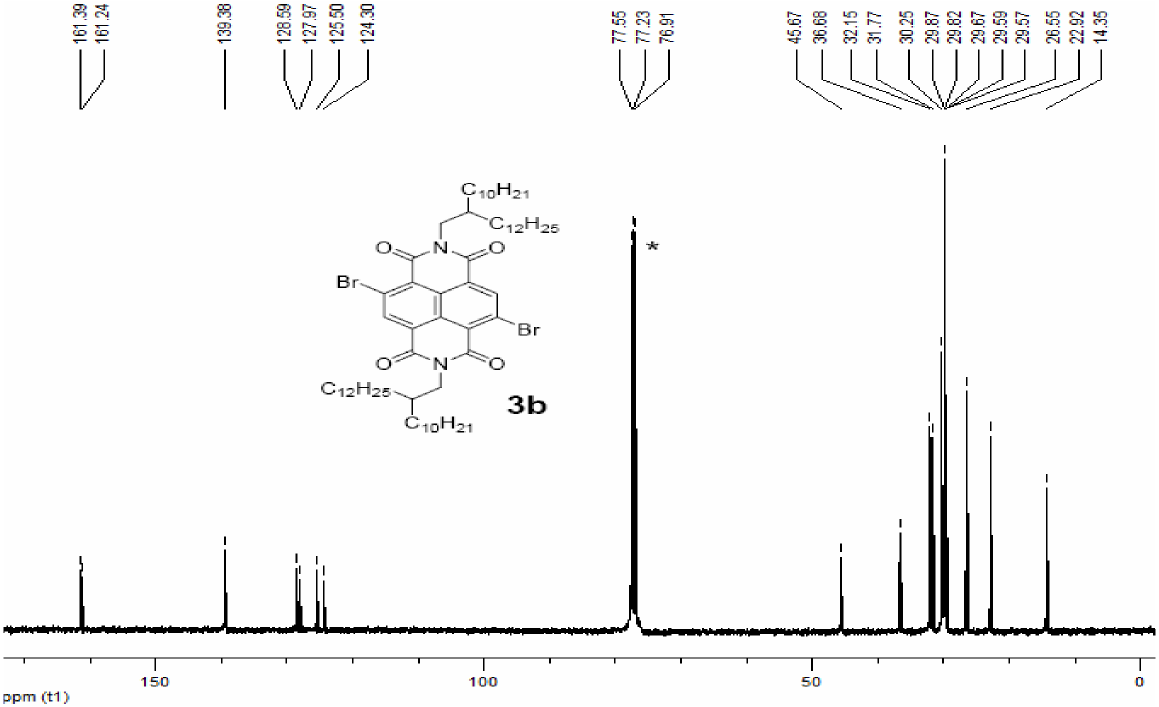


Figure S4. ^{13}C NMR spectrum of **3b** (r.t., in $CDCl_3$, *: solvent)

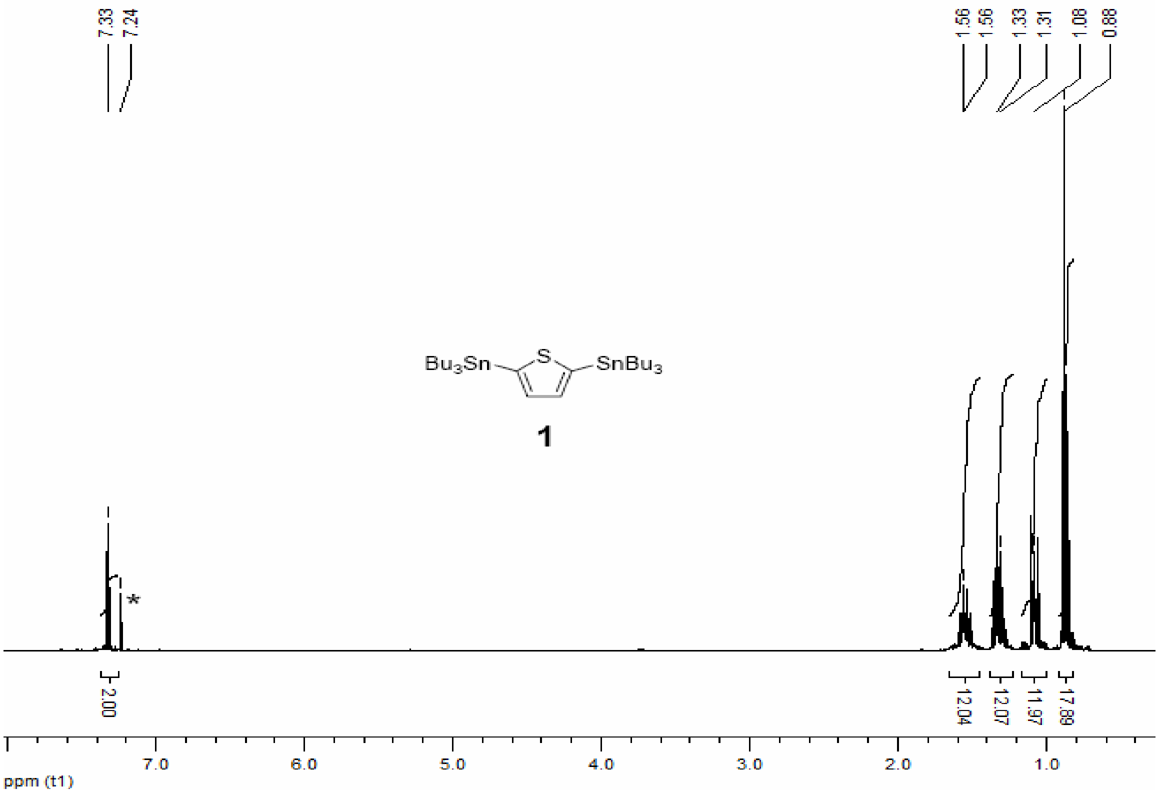


Figure S5. ^{1}H NMR spectrum of **1** (r.t., in CDCl$_3$, *: solvent)

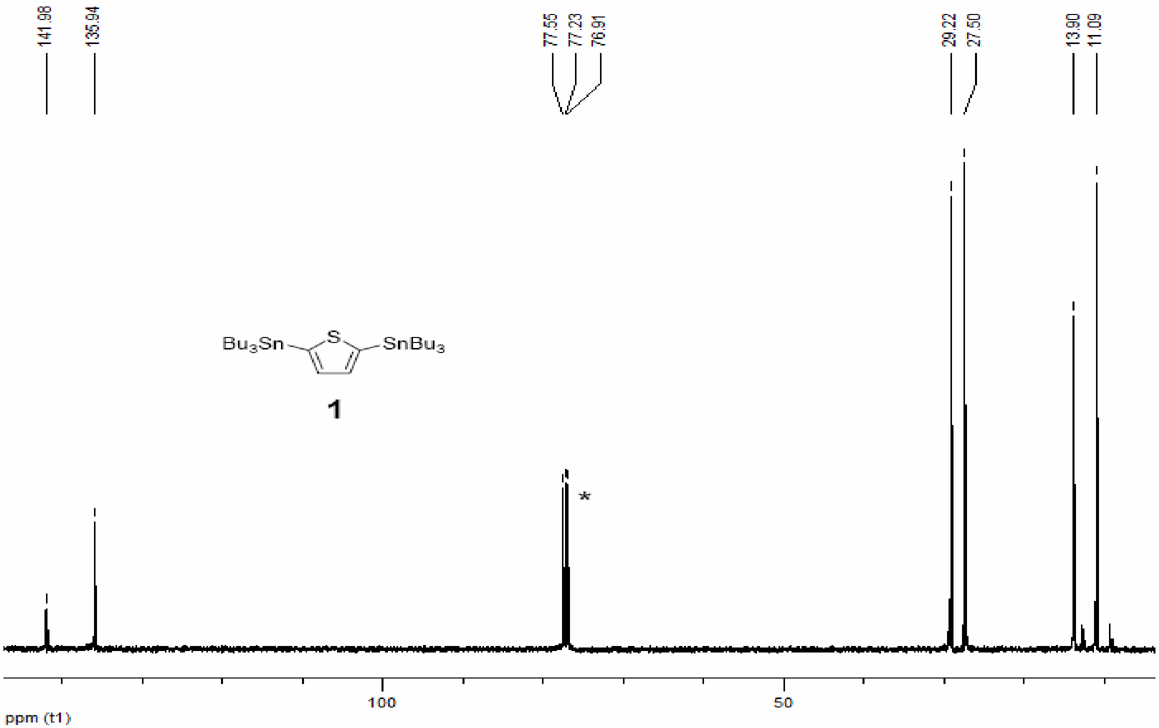


Figure S6. ^{13}C NMR spectrum of **1** (r.t., in CDCl$_3$, *: solvent)

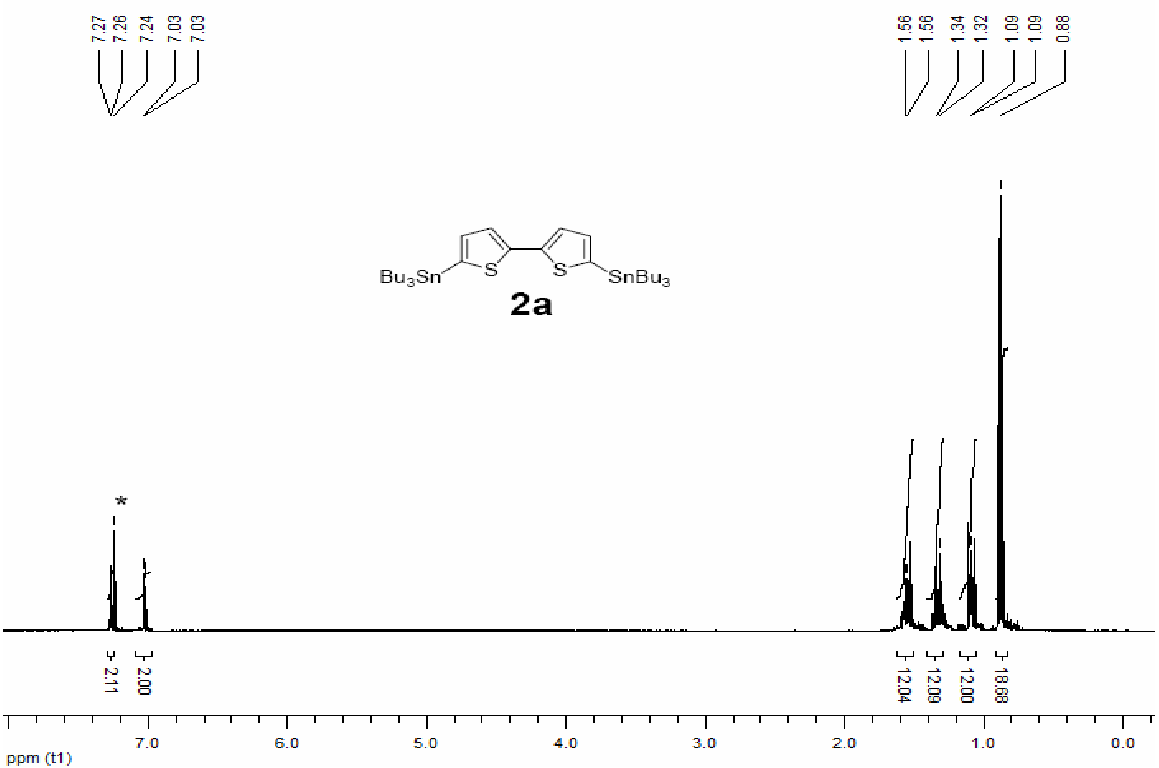


Figure S7. ^{1}H NMR spectrum of **2a** (r.t., in $CDCl_3$, *: solvent)

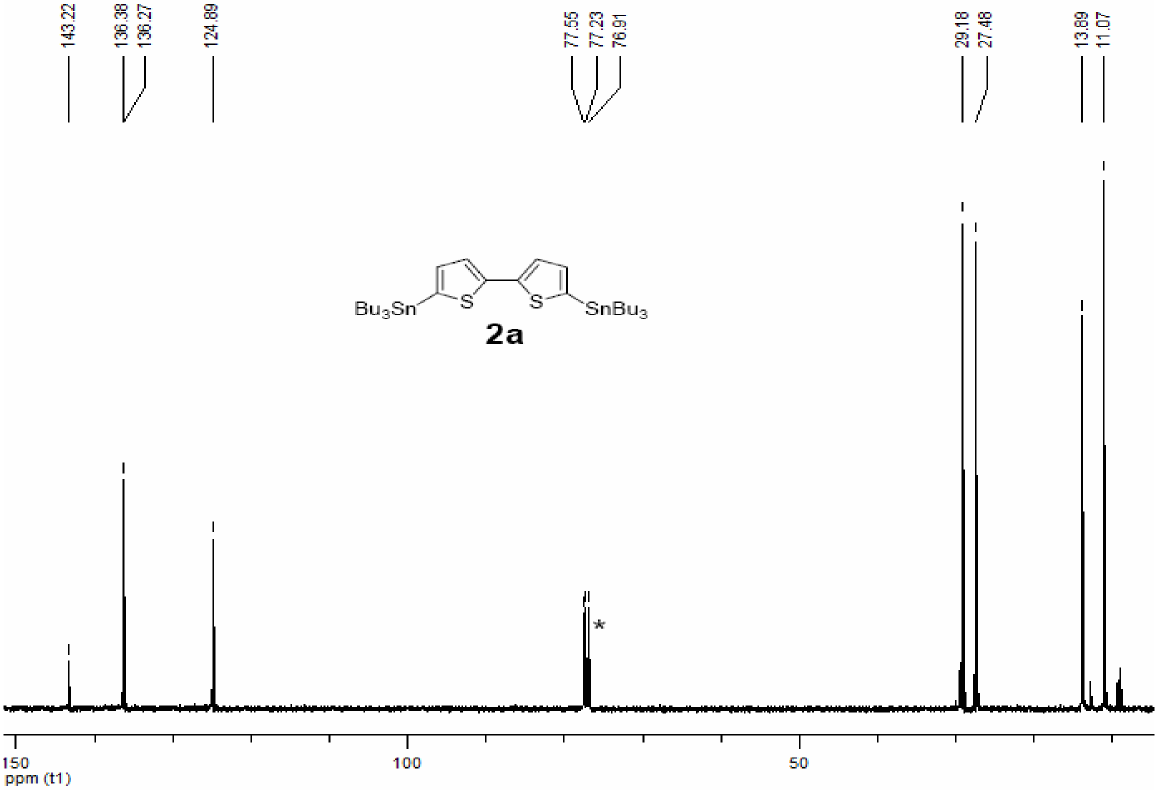


Figure S8. ^{13}C NMR spectrum of **2a** (r.t., in $CDCl_3$, *: solvent)

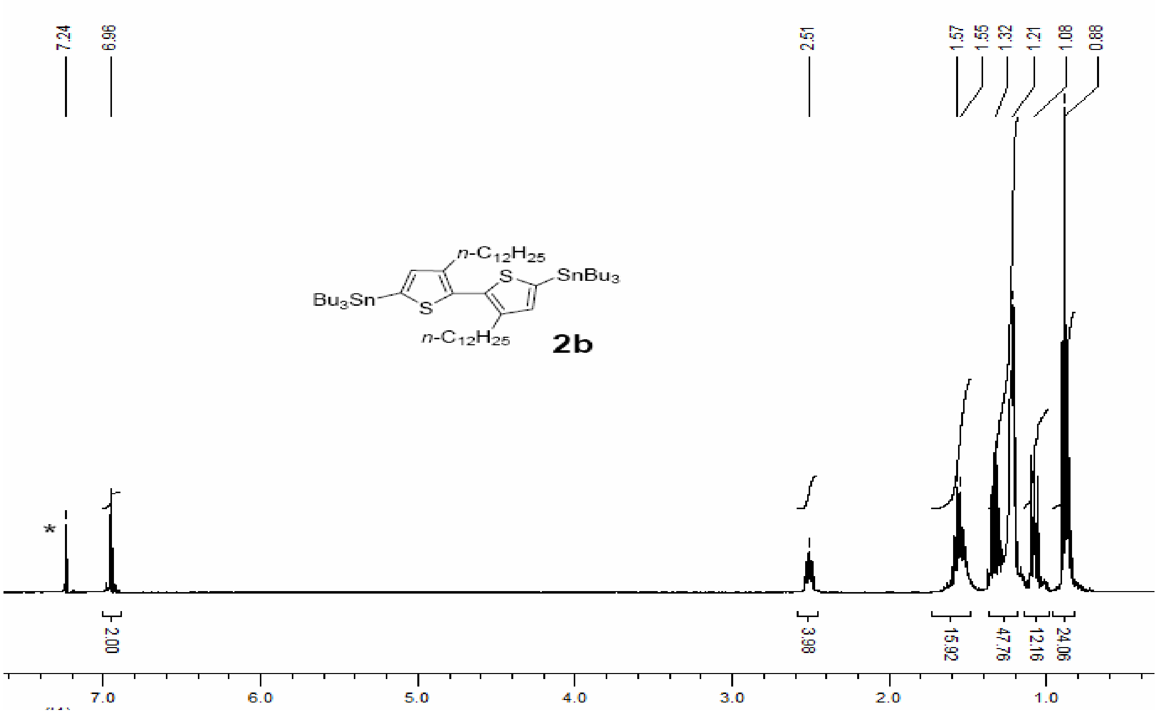


Figure S9. ^{1}H NMR spectrum of **2b** (r.t., in $CDCl_3$, *: solvent)

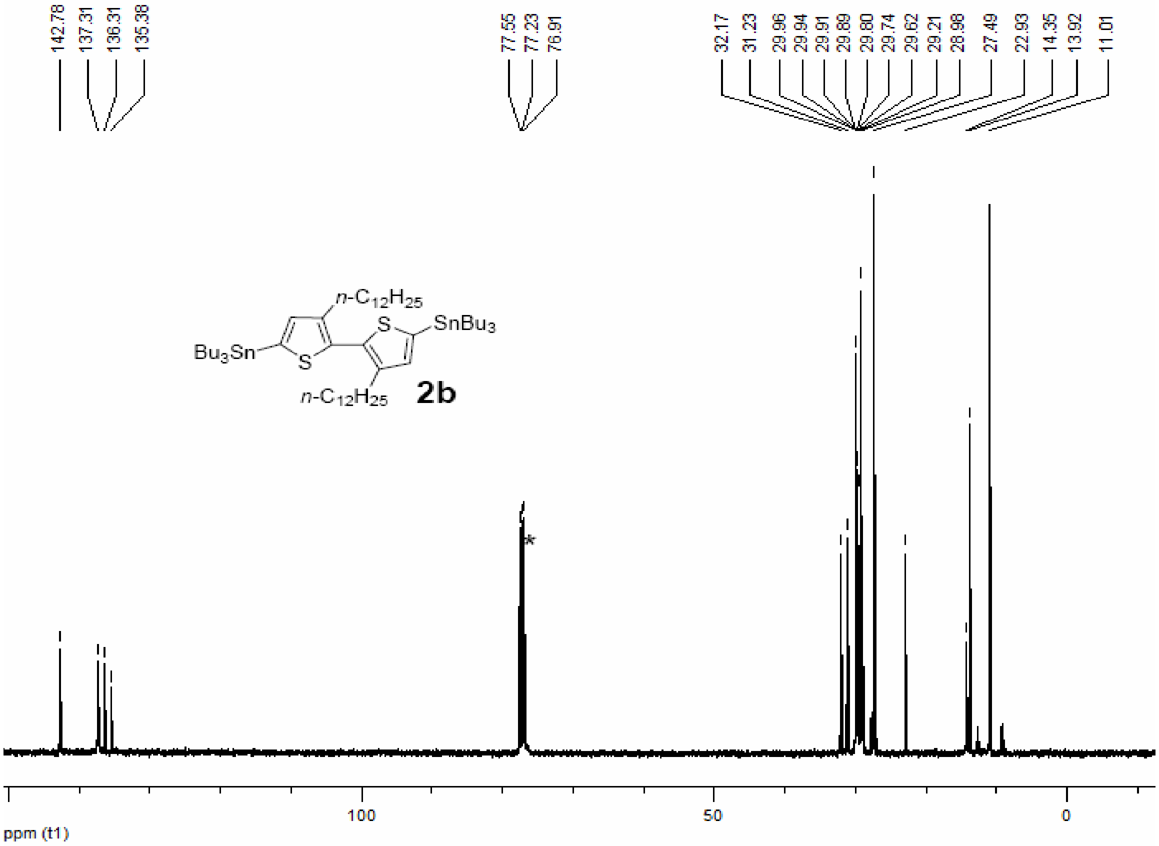


Figure S10. ^{13}C NMR spectrum of **2b** (r.t., in $CDCl_3$, *: solvent)

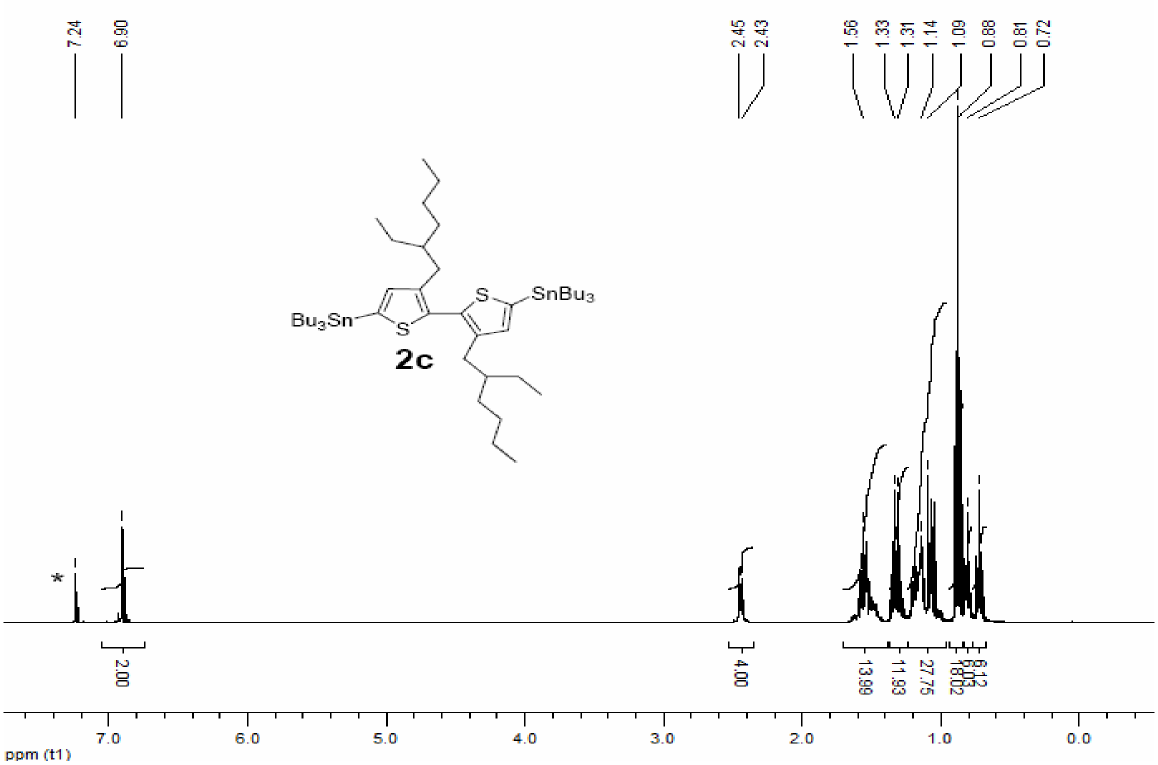


Figure S11. ^{1}H NMR spectrum of **2c** (r.t., in $CDCl_3$, *: solvent)

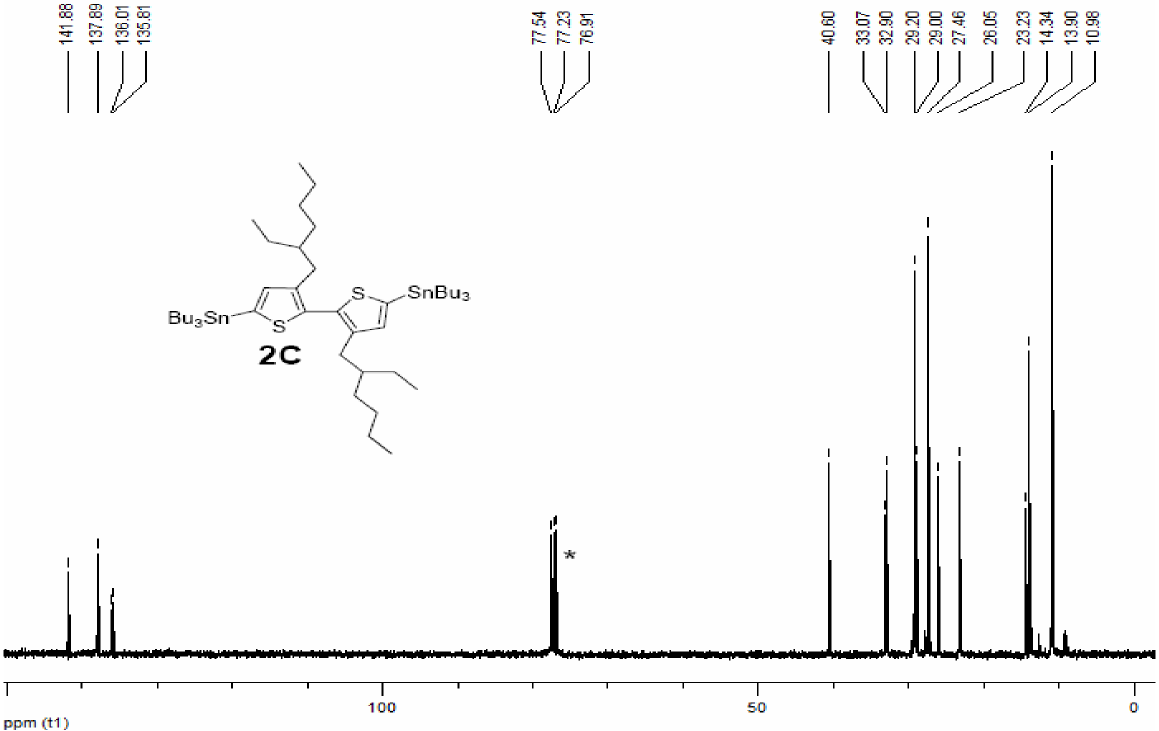


Figure S12. ^{13}C NMR spectrum of **2c** (r.t., in $CDCl_3$, *: solvent)

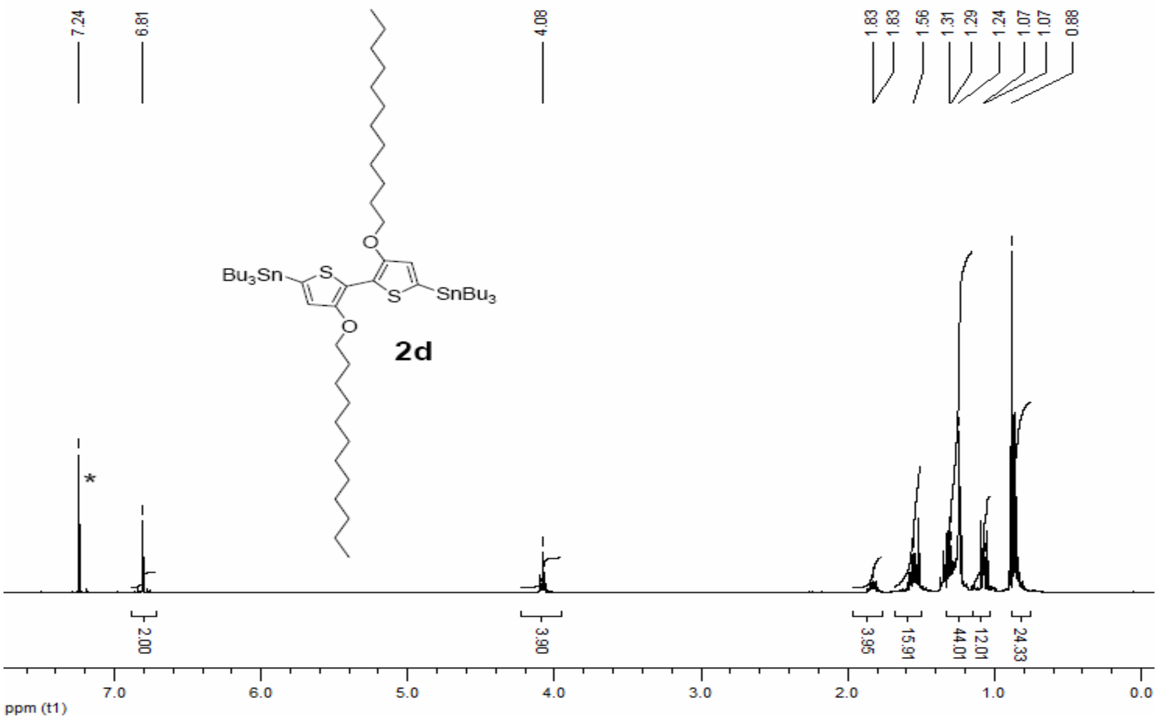


Figure S13. ^{1}H NMR spectrum of **2d** (r.t., in CDCl$_3$, *: solvent)

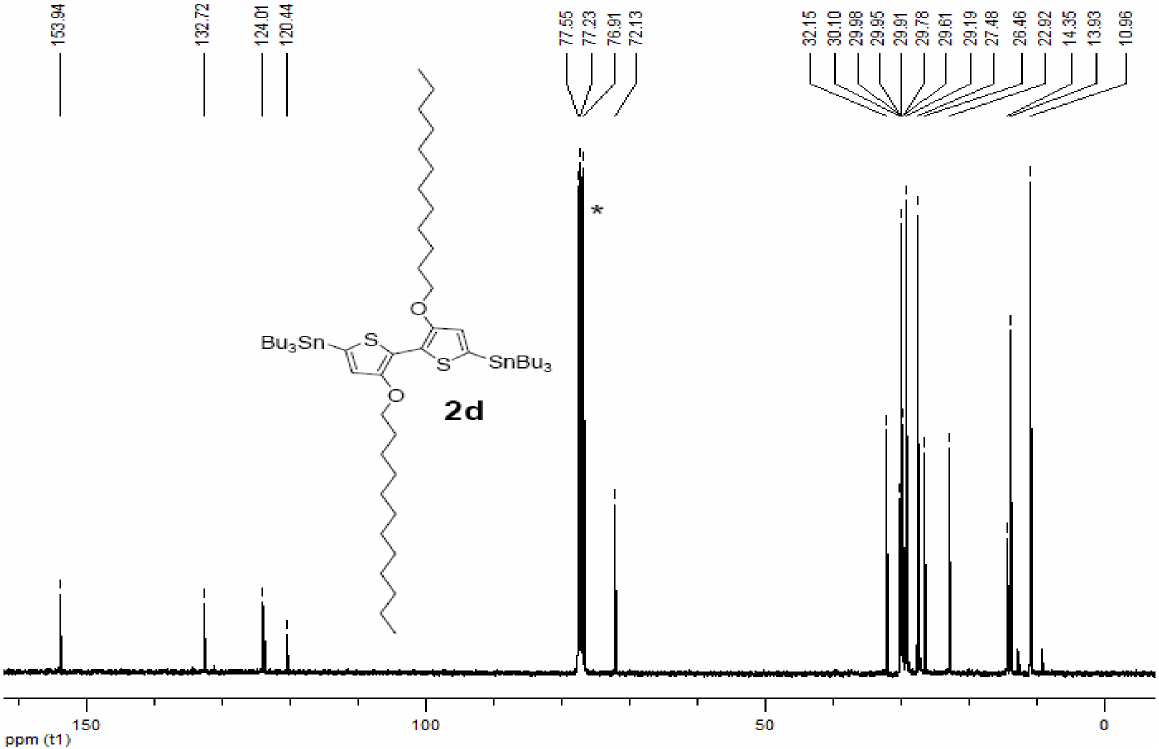


Figure S14. ^{13}C NMR spectrum of **2d** (r.t., in CDCl$_3$, *: solvent)

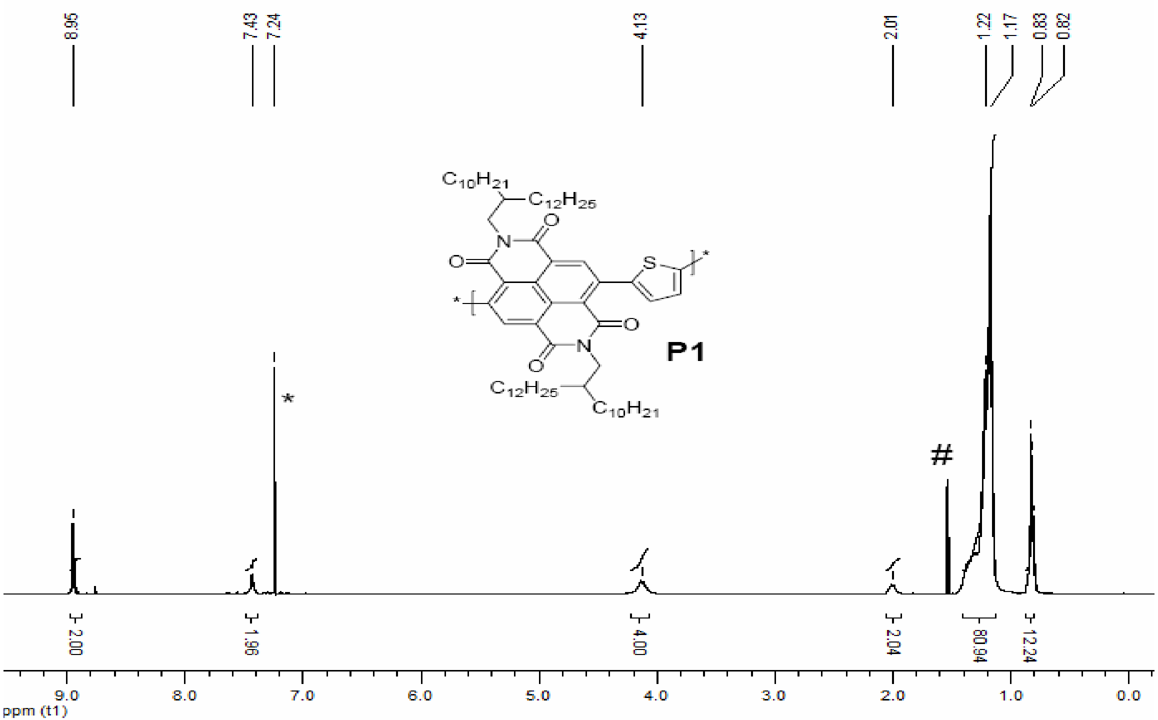


Figure S15. ^{1}H NMR spectrum of **P1** (r.t., in $CDCl_3$, *: solvent, #: H_2O)

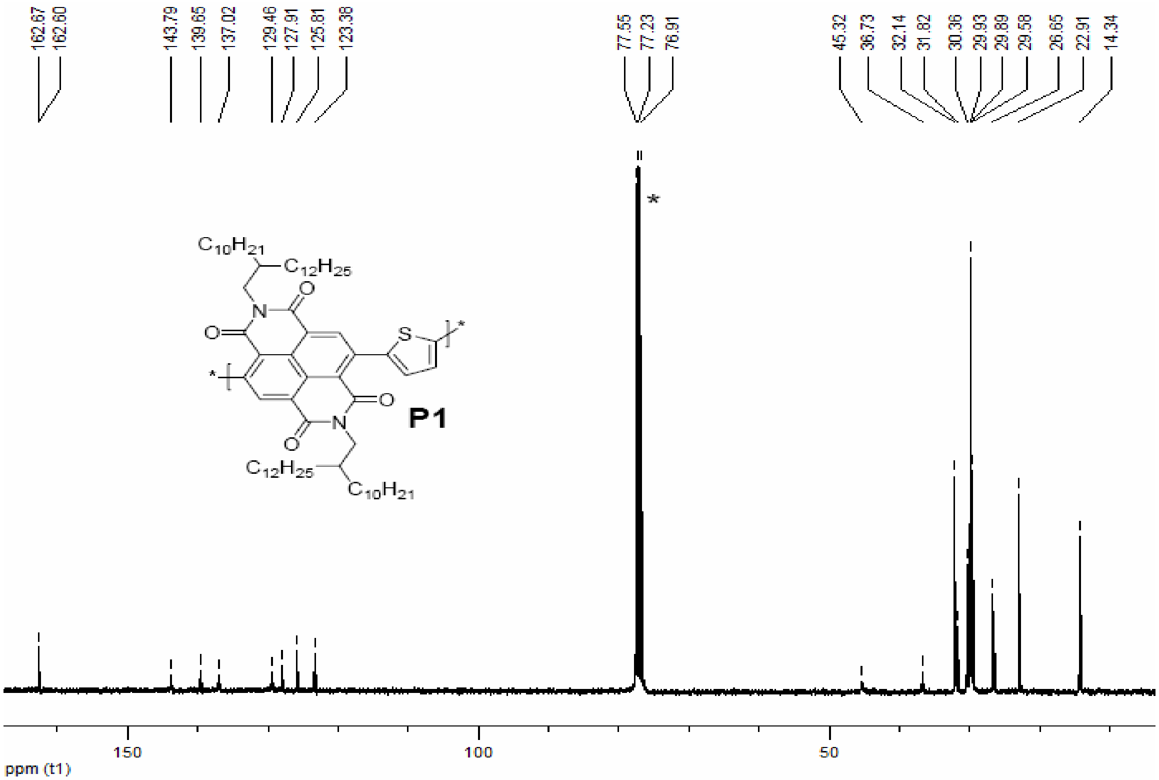


Figure S16. ^{13}C NMR spectrum of **P1** (r.t., in $CDCl_3$, *: solvent)

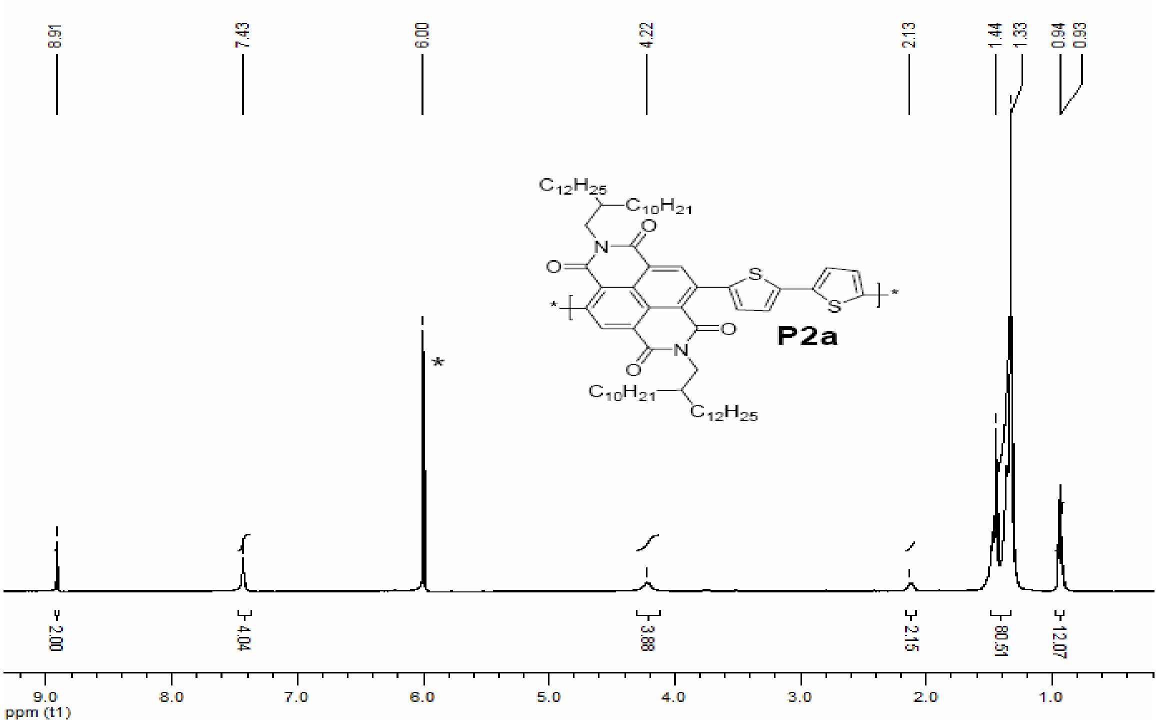


Figure S17. ^{1}H NMR spectrum of **P2a** (130 ºC, in $C_2D_2Cl_4$, *: solvent)

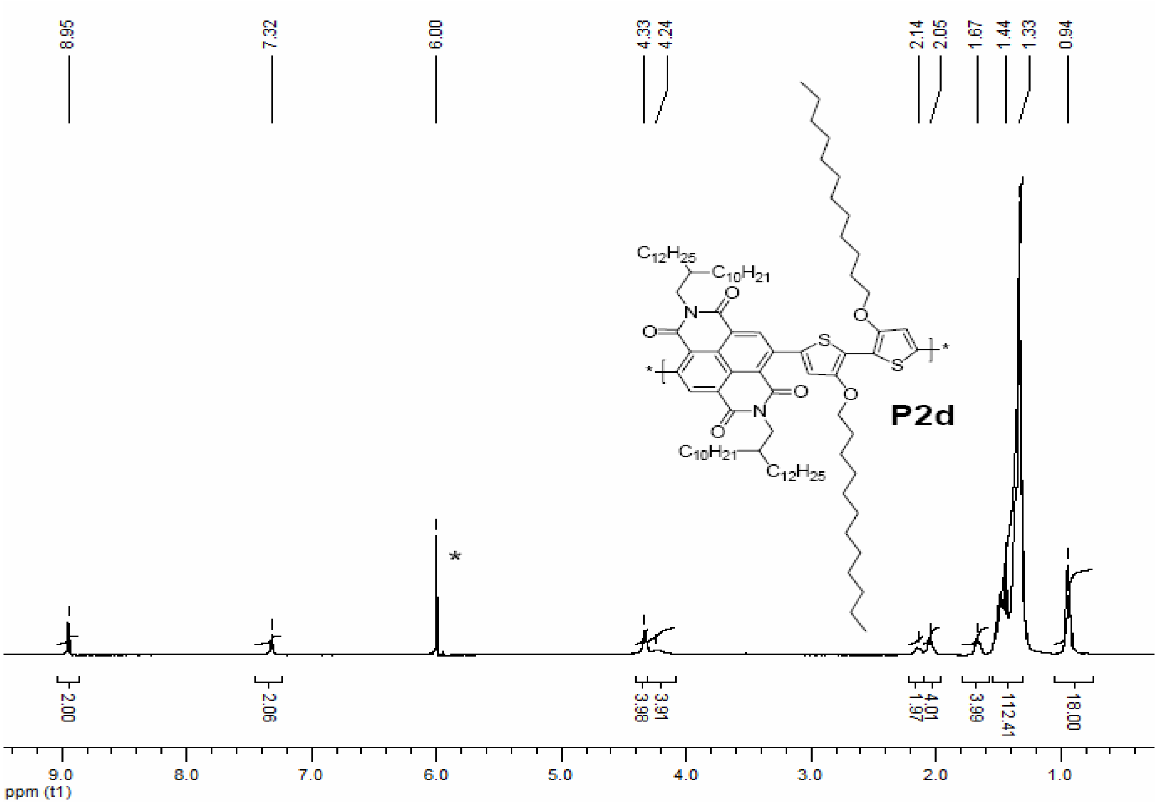


Figure S18. ^{1}H NMR spectrum of **P2d** (130 ºC, in $C_2D_2Cl_4$, *: solvent)

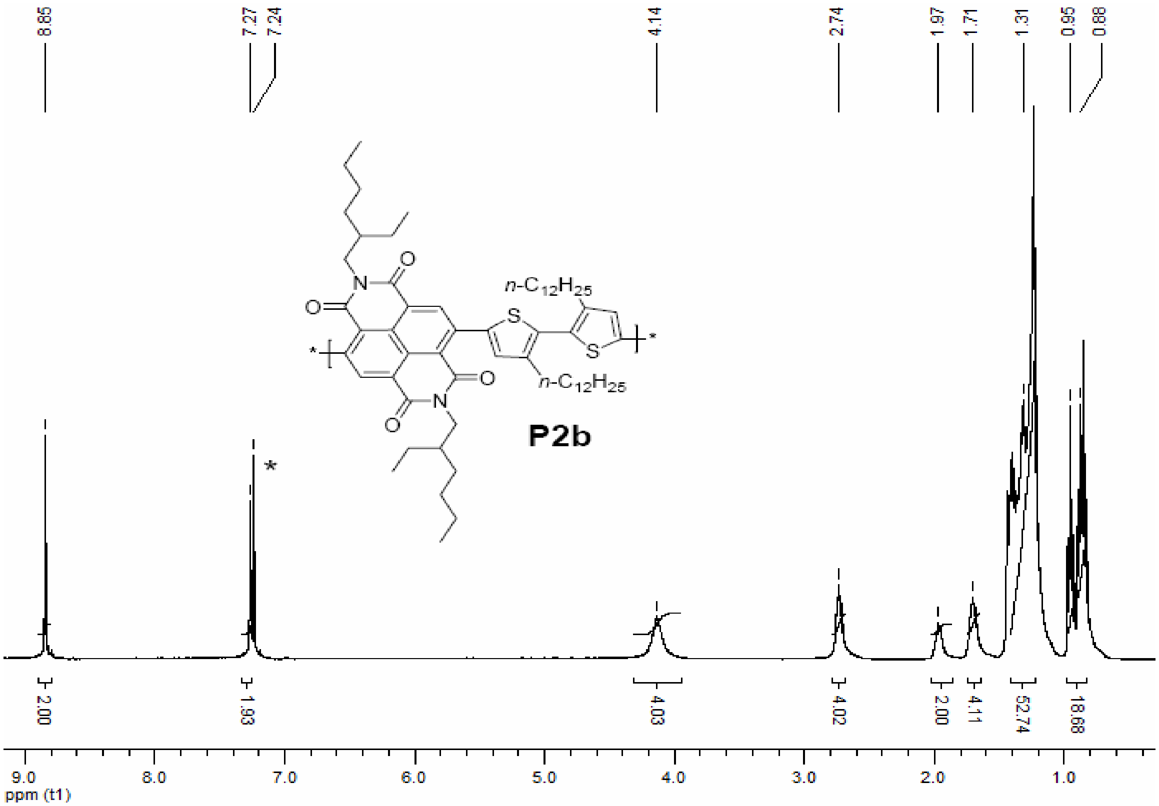


Figure S19. ^{1}H NMR spectrum of **P2b** (r.t., in $CDCl_3$, *: solvent)

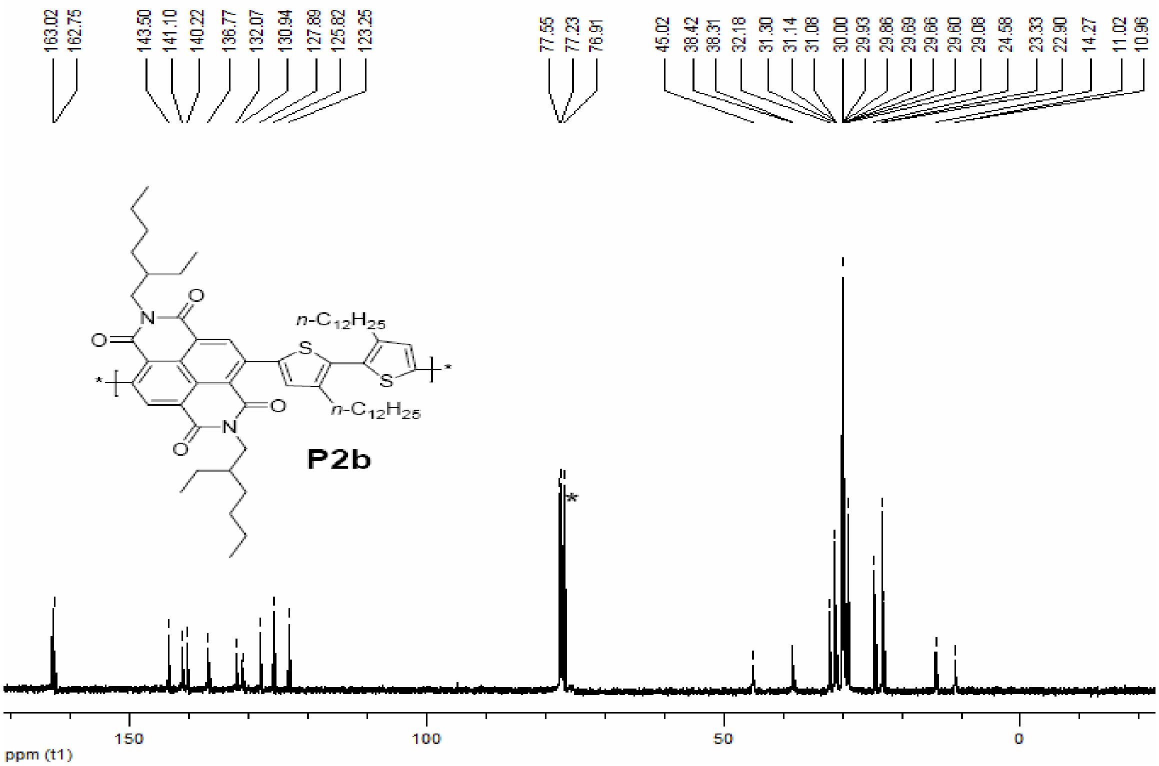


Figure S20. ^{13}C NMR spectrum of **P2b** (r.t., in $CDCl_3$, *: solvent)

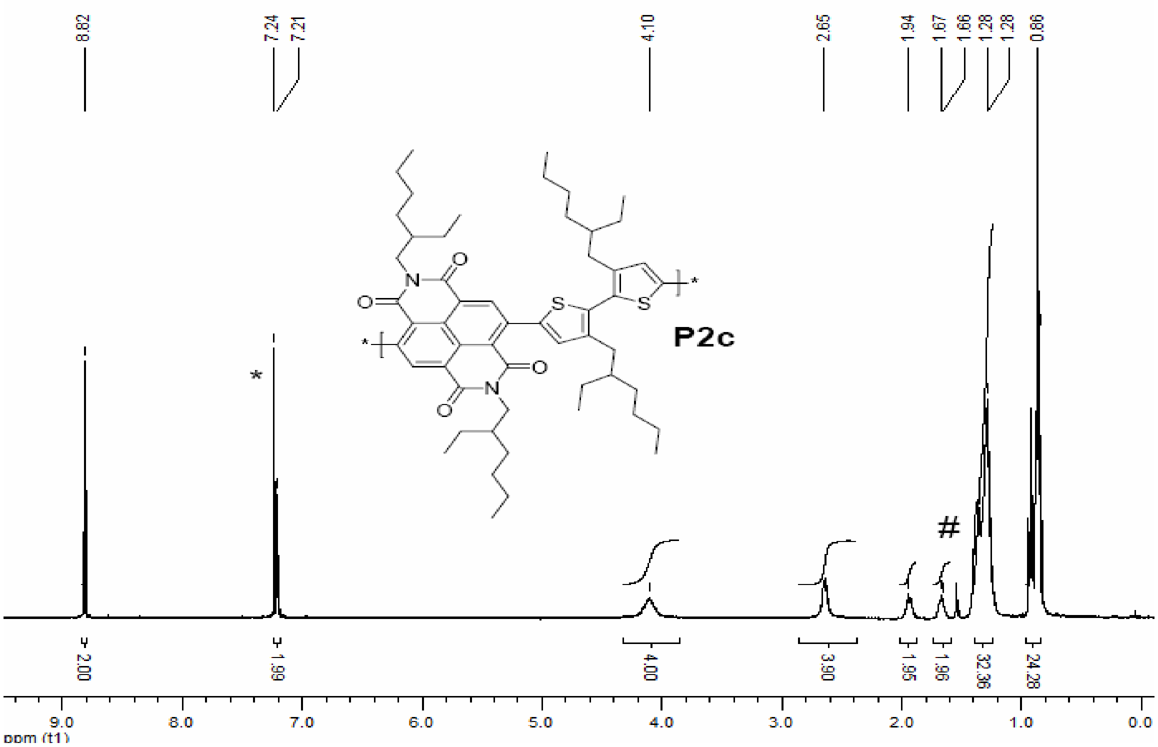


Figure S21. ^{1}H NMR spectrum of **P2c** (r.t., in $CDCl_3$, *: solvent, #: H_2O)

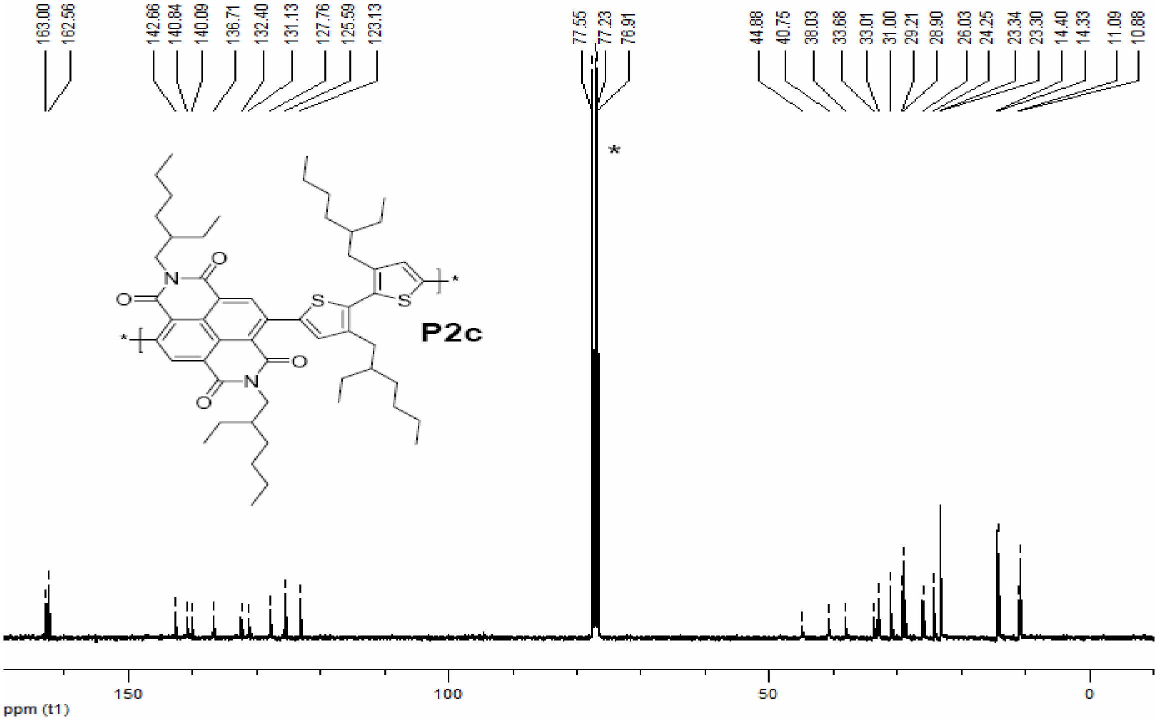


Figure S22. ^{13}C NMR spectrum of **P2c** (r.t., in $CDCl_3$, *: solvent)

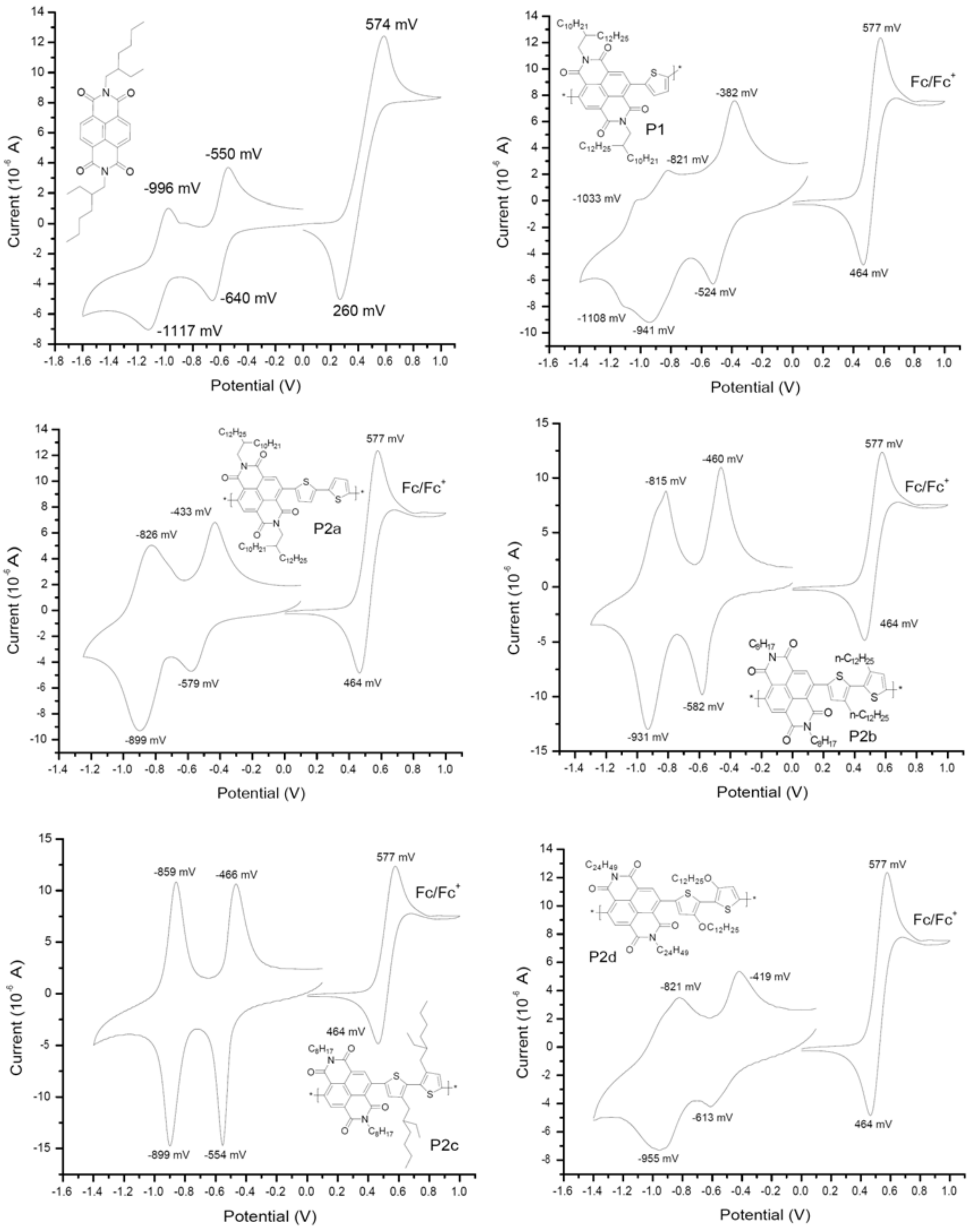


Figure S23. Cyclic Voltammograms of NBI and polymers**.** Conditions: 0.1 M (*n*-Bu)$_4$N·PF$_6$ in dichloromethane (NBI); 0.1 M (*n*-Bu)$_4$N·PF$_6$ in acetonitrile (Polymers); working electrode, Pt; counter electrode, Ag wire; reference electrode, Ag/AgCl; Scanning rate, 50 mV/s.

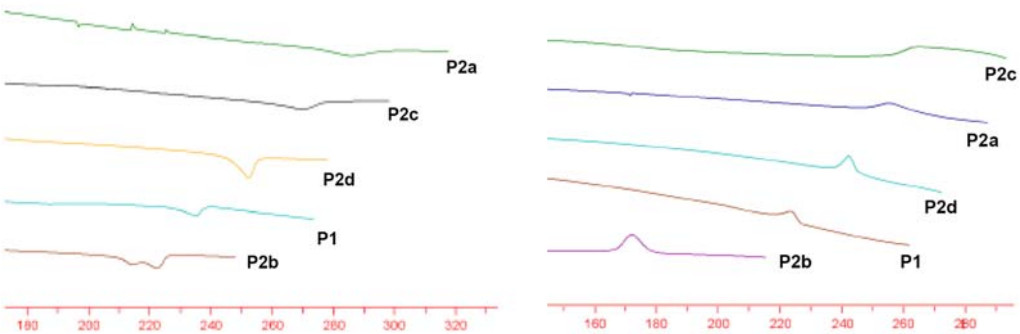


Figure S24. DSC thermograms during second heating run (left) and first cooling run (right) at a rate of 10 ^{0}C/min.

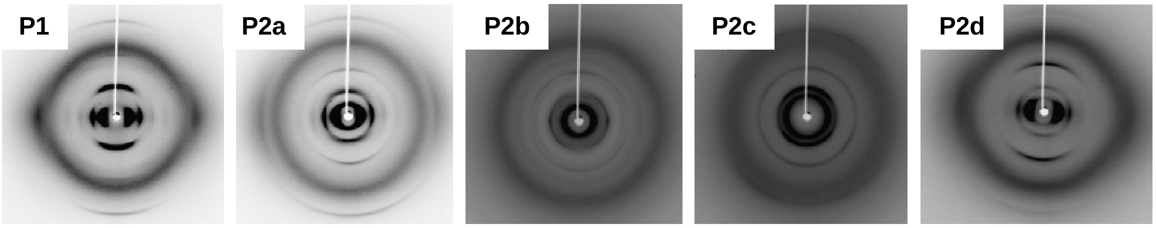


Figure S25. Fiber WAXD diffractograms from polymers **P1** and **P2a-d**. Fiber/polymer backbone axes approx. vertical.

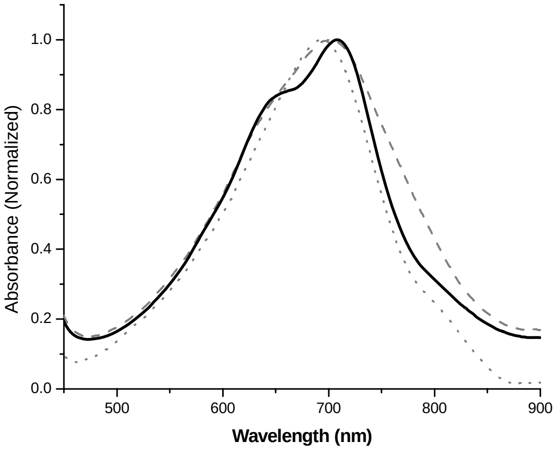


Figure S26. Solution (5 x 10^{-6} M THF, grey dotted line), pristine film (gray dashed line) and thermally annealed thin film (black) absorption spectra from polymer **P2a**.

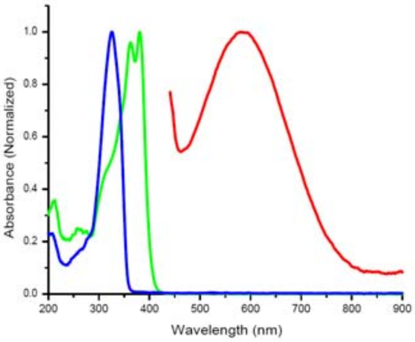


Figure S27. Solution absorption spectra of **12** (blue line), *N,N'*-bis(2-decyltetradecyl)-1,4,5,8-naphthalene bisimide (green line) and their mixture (red line) showing CT band (1.8 x 10^{-2} M in toluene).

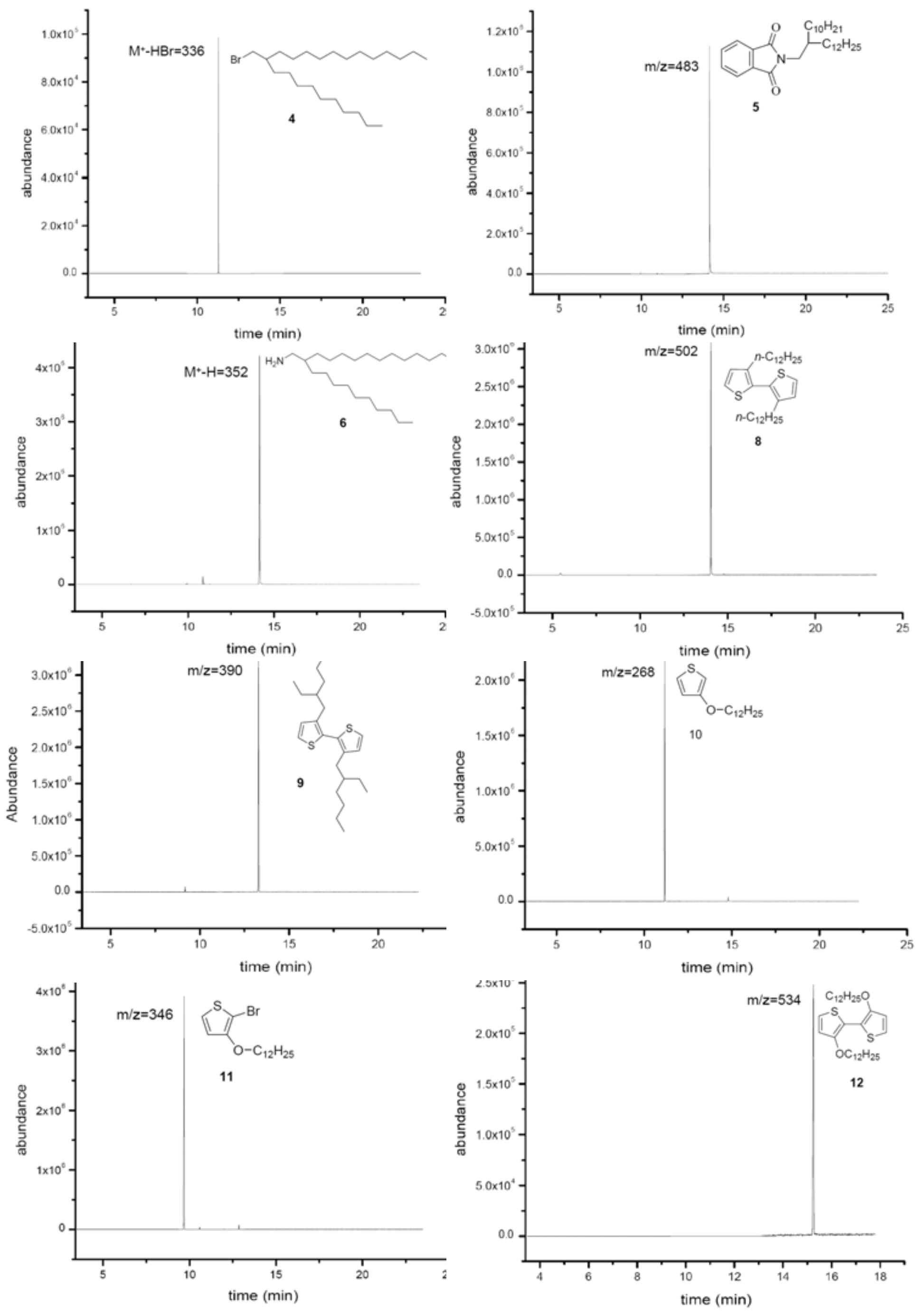


Figure S28. GC chromatograms (total ion count) from GC-MS measurements.

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