Electronic Supplementary Material (ESI) for Polymer Chemistry.

supporting information for

π-Expanded Diketopyrrolopyrroles as Acceptor Building Blocks for the Formation of Novel Donor-Acceptor Copolymers

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1. Materials and instruments:

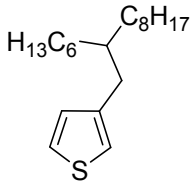
All chemicals and solvents were purchased from suppliers (Sigma Aldrich, VWR, Fisher Scientific etc.) and used without further purification, if not mentioned separately. The EDPPF-derivative **8** was synthesized according to a literature procedure.[1]

^{1}H- and ^{13}C-NMR spectra were recorded on Bruker Avance 400 (basis frequencies: ^{1}H: 400 MHz; ^{13}C: 101 MHz) or Bruker Avance III 600 (basis frequencies: ^{1}H: 600 MHz; ^{13}C: 151 MHz) with tetramethylsilane (TMS) as an internal standard. Measurements were performed at 300 °K for deuterated chloroform and at 353 °K for deuterated tetrachloroethane. In the ^{13}C-NMR spectra only those signals were listed, differing from the background significantly. Due to the strong π-π interactions of the EDPPT-based copolmyers and their poor solubility in organic solvents no ^{13}C-NMR spectra could be recorded for those polymers. The coupling constants (*J*) are given in Hz and the multiplicity of signals is described as s (singlet), d (doublet), t (triplet), and m (multiplet). The measurement of the m/z ratios were carried out with three different setups. GC-MS-spectra were recorded on a Shimadzu GC 17A QP 5050 with Optima-1 Accent-0,25-column. High resolution APCI (atmospheric pressure chemical ionisation) mass spectra were measured on a Bruker Daltronic micrOTOF. High resolution FD (field desorption) mass spectra were recorded on a Jeol AccuTOF GCX. HOMO energy levels were determined by atmospheric pressure photoelectron spectroscopy using a RIKKEN KEIKI AC2 machine. The optical band gap was estimated from the onset of the absorption in solid state and correct by adding 0.3 eV for the exciton binding energy. LUMO levels were determined by subtracting HOMO and band gap energy. PL emission spectra were recorded on a HORIBA Scientific FluroMax-4 equipped with a Quanta-Phi integration sphere (used for photoluminescence quantum yield (PLQY) measurements in solution) and UV/VIS absorption spectra were determined on a JASCO V-670 spectrometer. The excitation wavelength is given as λ_{exc}. in nanometer. Wavelength in brackets correspond to shoulders of absorption/emission bands. Films of the polymers were spin coated from an 8 mg/ml solution in chloroform on a SÜSS MicroTec spin coater. Molecular weight distributions were determined by size exclusion chromatography (SEC) with a PSS SDV pre-column and two PSS SDV linear M columns in series with THF as eluent.

The thermographic analysis (TGA) were carried out on a TGA/DSC1 STAR System from METTLER TOLEDO

2. Synthetic pathway to EDPP monomers 7a and 7b

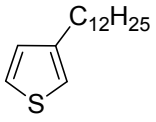
3-(2-Hexyldecyl)thiophene[2]



1a

A mixture of manganese (14.83 g, 270 mmol), cobalt(II)bromide (2.95 g, 13.5 mmol) and tri(p-tolyl)phosphine (4.11 g, 13.5 mmol) was dissolved in DMAc (90 ml) and pyridine (22.5 ml) under an argon atmosphere. 3-bromothiophene (6.3 ml, 67.5 mmol) and 7-(iodomethyl)-pentadecane (26.1 g, 74.2 mmol) were added and stirred at room temperature for 5 minutes. Afterwards a catalytic amount of trifluoroacetic acid TFA (0.3 ml) was added dropwise and the solution was heated to 70 °C for 24 h. The solution was cooled down to room temperature and passed through a celite-pad using ethylacetate as the eluent. The filtrate was stirred with saturated aqueous NH_4Cl solution for another 15 min. The phases were separated and the aqueous phase was extracted three times with ethylacetate. The combined organic layers were washed with water, saturated aqueous NaCl and dried over $MgSO_4$. The solvent was removed under reduced pressure and the crude product was purified by column chromatography (stationary phase: silica, eluent: hexane) to afford desired product **1a** (11.60 g, 38 mmol, 56 %) as a colorless liquid. ^{1}H-NMR (400 MHz, $CDCl_3$): δ [ppm] = 7.23 (dd, *J* = 4.9, 2.9 Hz, 1H), 6.93 – 6.88 (m, 2H), 2.57 (d, *J* = 6.7 Hz, 2H), 1.36 – 1.19 (m, 40H), 0.94 – 0.87 (t, 10H). ^{13}C-NMR (101 MHz, $CDCl_3$): δ [ppm] = 141.9, 128.8, 124.7, 120.6, 38.9, 37.1, 34.8, 33.4, 33.4, 31.9, 31.9, 30.0, 29.7, 29.3, 26.6, 26.6, 22.7, 19.7, 14.1, 14.1. GC-MS: calcd for *m/z* [M^+] 308.25, found *m/z* [M^+] 308.10

3-Dodecylthiophene



1b

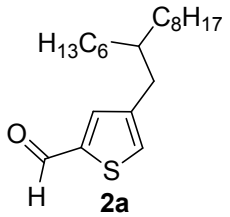
In a flame dried three-neck round-bottom flask equipped with a dropping funnel 3-bromothiophene (20 g, 123 mmol) and [1,3- bis(diphenylphosphino)propane]

dichloronickel(II) (0.507 g, 0.673 mmol) were dissolved in a mixture of heptane (100 ml) and THF (60 ml) under an argon atmosphere. The solution was cooled to 0 °C and a dodecylmagnesium bromide solution (172 ml, 1M in diethyl ether) was slowly added *via* the dropping funnel. Afterwards the solution was heated to reflux at overnight, cooled down and the excess of Grignard reagent was quenched with aqueous 1M HCl solution. The phases were separated and the organic layer was washed with water, dried over $MgSO_4$ and the solvent evaporated under reduced pressure. The yellow oil was passed through a stationary phase: silica pad with hexane as the eluent and the solvents removed in vacuo. The crude product was purified *via* vacuum destillation to obtain **1b** (22 g, 77 mmol, 71 %) as a colorless liquid. ^{1}H-NMR (400 MHz, $CDCl_3$) δ [ppm] = 7.31 – 7.23 (m, 1H), 7.01 – 6.91 (m, 2H), 2.67 (t, *J* = 7.4 Hz, 2H), 1.63 (m, 2H), 1.48 – 1.28 (m, 18H), 0.96 (t, *J* = 6.7 Hz 3H). ^{13}C-NMR (101 MHz, $CDCl_3$) δ [ppm] = 143.3, 128.3, 124.9, 119.7, 31.9, 30.6, 30.3, 29.7, 29.7, 29.7, 29.6, 29.5, 29.4, 22.7, 14.1.GC-MS: calcd for *m/z* [M^+] 252.19, found *m/z* [M^+] 252.20

General procedure for the preparation of 4-alkylthiophene-2-carbaldehydes[3]

A solution of DIPA (2.5 eq) in THF (0.4 M) was cooled to -78 °C under an argon atmosphere. A 1.6 M n-butyllithium solution (2.1 eq) in hexane was added slowly and stirred for 1 h at constant temperature. Then the alkylthiophene (1 eq) in THF (10 ml) was added and stirred for another 30 min at -78 °C. Subsequently, DMF (5 eq) was injected, the solution was stirred overnight and allowed to warm up to room temperature. The excess of base was quenched with 2M aqueous HCl solution (150 ml) and the phases separated. The aqueous phase was extracted three times with ethylacetate and the combined organic layers washed with saturated aqueous NaCl solution, dried with $MgSO_4$ and the solvents were evaporated. The product was purified by column chromatography.

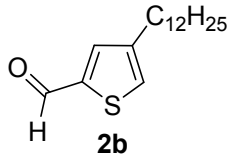
4-(2-Hexyldecyl)thiophene-2-carbaldehyde



2a

According to the general procedure the reaction was carried out with **1a** (11.60 g, 37.6 mmol). The product was purified by column chromatography (stationary phase: stationary phase: silica, eluent: hexane/ethyl acetate, 95:5) and **2a** (8.37 g, 24.8 mmol, 66 %) was obtained as a yellow liquid. ^{1}H-NMR (400 MHz, $CDCl_3$): δ [ppm] = 9.90 (d, *J* = 1.3 Hz, 1H), 7.59 (d, *J* = 1.5 Hz, 1H), 7.39 – 7.33 (m, 1H), 2.60 (d, *J* = 6.8 Hz, 2H), 1.35 – 1.20 (m, 19H), 0.93 – 0.87 (m, 6H). ^{13}C-NMR (151 MHz, $CDCl_3$): δ [ppm] = 182.9, 143.6, 143.5, 137.6, 131.2, 38.9, 34.7, 33.3, 33.3, 31.9, 31.9, 29.9, 29.6, 29.6, 29.3, 26.6, 26.6, 22.7, 22.6, 14.1, 14.1. GC-MS: calcd for *m/z* [M^+] 336.30, found *m/z* [M^+] 336.25

4-Dodecylthiophene-2-carbaldehyde



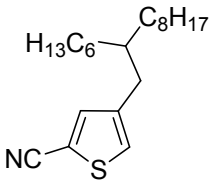
2b

Prepared from **1b** (17.4 g, 68.9 mmol) according to the general procedure. The crude product was cleaned by column chromatography (stationary phase: silica, eluent: hexane/ethyl acetate 95:5). The product **2b** (17.5 g, 62.5 mmol, 71 %) was obtained as yellow oil. ^{1}H-NMR (400 MHz, CDCl3): δ [ppm] = 9.90 (d, *J* = 1.2 Hz, 1H), 7.63 (d, *J* = 1.5 Hz, 1H), 7.39 (dd, *J* = 1.5, 1.2 Hz, 1H), 2.71 – 2.62 (t, *J* = 7.6 Hz 2H), 1.75 – 1.56 (m, 2H), 1.43 – 1.23 (m, 18H), 0.90 (t, *J* = 6.9 Hz, 3H). ^{13}C-NMR (101 MHz, CDCl3): δ [ppm] = 181.8, 144.8, 143.6, 137.0, 130.3, 31.9, 29.7, 29.6, 29.6, 29.6, 29.5, 29.5, 29.4, 29.3, 29.1, 22.7, 14.1. GC-MS: calcd for *m/z* [M^+] 280.16, found *m/z* [M^+] 280.10

General procedure for the preparation of alkylthiophene-2-carbonitriles[4]

The alkylthiophene-2-carbaldehyde (1 eq) was solved in a mixture of THF (0.4 M) and concentrated aqueous ammonia solution (0.08 M). Then, iodine (3.0 eq) was added and the solution was stirred at room temperature overnight. Subsequently, the reaction is stopped by addition of saturated aqueous $NaHSO_4$ solution. The Layers were separated and the aqueous layer was extracted three times with ethylacetate. The combined organic layers were dried over $MgSO_4$, concentrated in vacuo and purified by column chromatography (stationary phase: silica, eluent: eluent: hexane/toluene, 9:1).

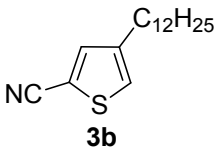
4-(2-Hexyldecyl)thiophene-2-carbonitrile



3a

Prepared from **2a** (8.37 g, 24.9 mmol) and purified *via* column chromatography (stationary phase: silica, eluent: hexane/toluene, 9:1). Product **3a** (6.70 g, 20.1 mmol, 81 %) was obtained as a colorless liquid. ^{1}H-NMR (600 MHz, $CDCl_3$): δ [ppm] = 7.44 (d, *J* = 1.4 Hz, 1H), 7.18 (s, 1H), 2.58 (d, *J* = 6.8 Hz, 2H), 1.65 – 1.56 (m, 1H), 1.28 (s, 24H), 0.91 (t, *J* = 7.1, 6H). ^{13}C-NMR (151 MHz, $CDCl_3$): δ [ppm] = 142.9, 138.8, 128.2, 114.5, 109.3, 38.9, 34.5, 33.2, 33.2, 31.9, 31.8, 29.9, 29.6, 29.3, 26.9, 26.6, 26.6, 22.7, 22.6, 14.1, 14.1. GC-MS: calcd for *m/z* [M^+] 322.25, found *m/z* [M^+] 322.20

4-Dodecylthiophene-2-carbonitrile



3b

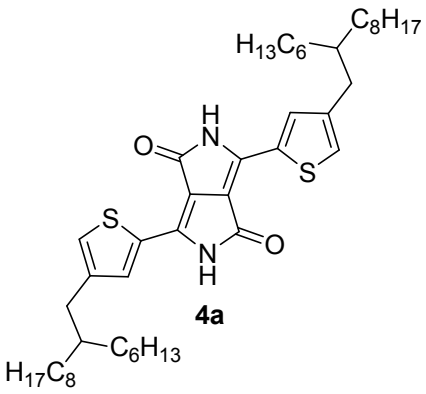
Following the general procedure the reaction was carried out with **2b** (17.3 g, 61.7 mmol). Product **3b** (13.4 g, 48.3 mmol, 78%) was obtained as a slightly yellow liquid. ^{1}H-NMR (600 MHz, $CDCl_3$): δ [ppm] 7.46 (d, *J* = 1.4 Hz, 1H), 7.21 (d, *J* = 1.4 Hz, 1H), 2.63 (t , *J* = 7.7 Hz, 2H), 1.70 – 1.55 (m, 2H), 1.36 – 1.24 (m, 18H), 0.91 (t, *J* = 7.1 Hz, 3H). 13C-NMR (151 MHz, $CDCl_3$) δ [ppm] = 144.1, 138.3, 127.4, 114.5, 109.4, 31.9, 30.3, 29.9, 29.7, 29.6, 29.6, 29.6, 29.5, 29.3, 29.1, 22.7, 14.1. GC-MS: calcd for *m/z* [M^+] 277.19, found *m/z* [M^+] 277.30

General procedure for the preparation of diketopyrrolopyrroles[5]

In a flame dried two-neck round-bottom flask sodium (2.2 eq) was dissolved in amyl alcohol (0.6 M) under generation of the alcoholate. A catalytic amount of iron(III)chlorid was added and the solution was refluxed for 1 h. After cooling down to 90 °C the thiophene-2-carbonitrile (1 eq) was added in one portion. The solution was heated to reflux again and diisopropyl succinate (0.5 eq) was added dropwise over 30 min. The mixture was refluxed for 16 h, cooled down to room temperature and

diluted with a (1:1:1) mixture of water, acetic acid and methanol. A red solid precipitated from the solution and the dispersion was heated to reflux for a further few minutes. After cooling down to room temperature the precipitate was filtered off and washed with methanol for several times.

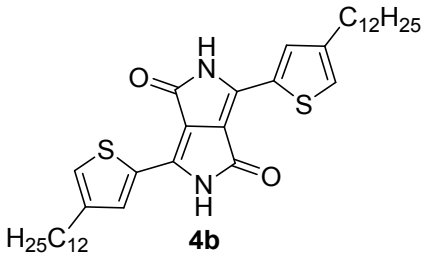
3,6-Bis(4-(2-hexyldecyl)thiophene-2-yl)pyrrolo[3,4-c]pyrrole-1,4(2*H*,5*H*)-dione



4a

Following the general reaction procedure **3a** (6.6 g, 19.8 mmol) was used for the formation of the DPP derivative. The product **4a** (6.0 g, 8.0 mmol, 81%) was isolated as a brick red solid. ^{1}H-NMR (600 MHz, TFA-d/$CDCl_3$ 1:4): δ [ppm] = 8.06 (s, 2H), 7.45 (s, 2H), 2.70 (d, *J* = 6.2 Hz, 4H), 1.73 (s, 2H), 1.37 – 1.20 (m, 48 H), 0.88 (t, *J* = 6.9, Hz, 12H). APCI: calcd for *m/z* [M+H$^+$] 749.5108, found *m/z* [M+H$^+$] 749.5103

3,6-Bis(4-dodecylthiophene-2-yl)pyrrolo[3,4-c]pyrrole-1,4(2*H*,5*H*)-dione



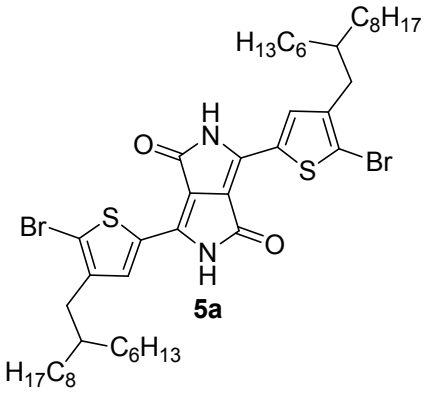
4b

According to the general reaction procedure **3b** (13.2 g, 47.6 mmol) was used for the formation of the DPP derivative. The product **4b** (12.7 g, 19.9 mmol, 84%) was isolated as a brick red solid. ^{1}H-NMR (600 MHz, TFA-d/$CDCl_3$ 1:4): δ [ppm] = 8.01 (s, 2H), 7.43 (s, 2H), 2.71 (s, 4H), 1.69 (s, 4H), 1.40 – 1.23 (m, 36H), 0.88 (t, *J* = 6.8 Hz, 6H). FD-MS: calcd for *m/z* [M+H$^+$] 636.3783, found *m/z* [M+H$^+$] 636.3744

General procedure for the bromination of DPP-derivatives 4a and 4b

In a round-bottom flask the DPP derivative (1 eq) was dissolved in a (1:2) mixture (0.03 M) of TFA and chloroform. NBS (2.1 eq) was added portionwise and the mixture was stirred at ambient temperature and in the absence of light for 24 h. The solution was diluted with chloroform and washed with water several times. The organic layer was separated, the solvent removed and the product dried under reduced pressure.

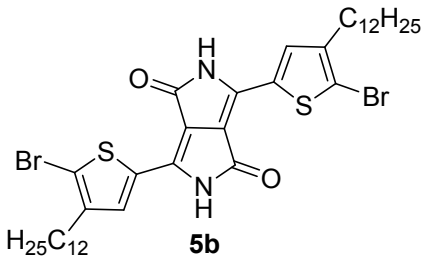
3,6-Bis(5-bromo-4-(2-hexyldecyl)thiophene-2-yl)pyrrolo[3,4-c]pyrrole-1,4(2*H*,5*H*)-dione



5a

The bromination was carried out with **4a** (3.0 g, 4.0 mmol) according to the general procedure to generate **5a** (2.84 g, 3.13 mmol, 78 %) as a purple solid. ^{1}H-NMR (600 MHz, TFA-d/$CDCl_3$ 1:4): δ [ppm] = 7.81 (s, 2H), 2.61 (d, *J* = 4.8 Hz, 4H), 1.85 – 1.66 (m, 2H), 1.52 – 1.07 (m, 48H), 0.88 (t, *J* = 6.8, 3.6 Hz, 12H). APCI: calcd for *m/z* [M+H$^+$] 907.3302, found *m/z* [M+H$^+$] 907.3303

3,6-Bis(5-bromo-4dodecylthiophene-2-yl)pyrrolo[3,4-c]pyrrole-1,4(2*H*,5*H*)-dione



5b

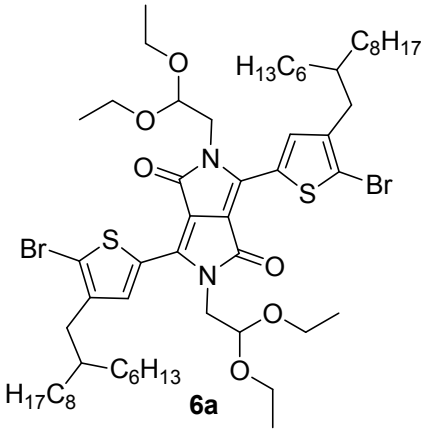
Prepared from **4b** (6.0 g, 9.40 mmol) according to the general procedure. The product **5b** (7.2 g, 9.04 mmol, 94 %) was obtained as a purple solid. ^{1}H-NMR (600

MHz, TFA-d/$CDCl_3$ 1:4) δ [ppm] 7.84 (s, 2H), 2.68 (s, 4H), 1.40 – 1.23 (m, 40H), 0.90 (t, *J* = 6.3 Hz, 6H). APCI: calcd for *m/z* [M+H$^+$] 795.2248, found *m/z* [M+H$^+$] 795.2250

General procedure for the N-alkylation of DPP-derivatives 5a and 5b[5]

In a flame dried, two-neck round-bottom flask containing a magnetic stir bar were placed: the brominated DPP derivative (1 eq), tetrabutylammonium bisulfate (0.05 eq) and K_2CO_3 (9.8 eq) under an argon atmosphere. The mixture was dissolved in DMF (0.03 M) and heated to 120 °C. Then bromoacetaldehyde diethyl acetal (8.9 eq) was added *via* a syringe over 30 min, the reaction mixture stirred under constant temperature for 16 h and raised to 130°C for another 2 h. Afterwards the solution was cooled down to room temperature, diluted with water and methylene chloride. After phase separation, the aqueous layer was extracted with methylene chloride three times. The combined organic layers were washed with water and saturated aqueous NaCl solution and dried over $MgSO_4$. The solvents were evaporated in vacuo and the crude product was purified by column chromatography.

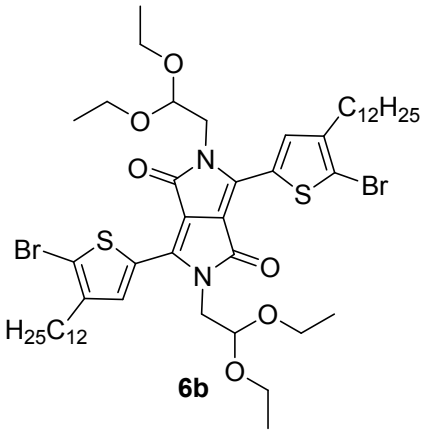
3,6-Bis(5-bromo-4-(2-hexyldecyl)thiophene-2-yl)-2,5-bis(2,2-diethoxyethyl)pyrrolo[3,4-c]pyrrole-1,4(2*H*,5*H*)-dione



6a

Prepared from **5a** (3.0 g, 3.31 mmol) according to the general procedure. Purified by column chromatography (stationary phase: silica, eluent: methylene chloride/hexane 8:2) to obtain **6a** (3.1 g, 2.72 mmol, 82 %) ^{1}H-NMR (600 MHz, $CDCl_3$): δ [ppm] = 8.39 (s, 2H), 4.81 (t, *J* = 5.5 Hz, 2H), 4.07 (d, *J* = 5.7 Hz, 4H), 3.76 (dq, *J* = 9.1, 7.0 Hz, 4H), 3.54 (dq, *J* = 9.1, 7.0 Hz, 4H), 2.26 (d, *J* = 7.0 Hz, 2H), 1.40 – 1.08 (m, 48+12H), 0.91 – 0.80 (m, 12H). APCI: calcd for *m/z* [M+H$^+$] 1139.4966, found *m/z* [M+H$^+$] 1139.4980

3,6-Bis(5-bromo-4-dodecylthiophene-2-yl)-2,5-bis(2,2-diethoxyethyl)pyrrolo[3,4-c]pyrrole-1,4(2*H*,5*H*)-dione



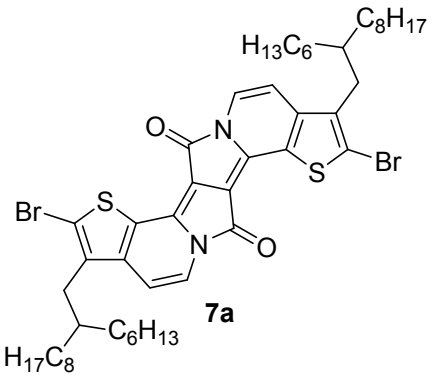
6b

Prepared from **5b** (7.2 g, 9.04 mmol) according to the general procedure. The crude product was purified by column chromatography (stationary phase: silica, eluent: hexane/ethyl acetate 5:1). The product **6b** (8.2 g, 7.98 mmol, 88 %) was obtained as purple solid. ^{1}H-NMR (600 MHz, $CDCl_3$) δ [ppm] = 8.38 (s, 2H), 4.85 (t, *J* = 5.6 Hz, 2H), 4.09 (d, *J* = 5.6 Hz, 4H), 3.81 (dq, *J* = 9.1, 7.0 Hz, 4H), 3.57 (dq, *J* = 9.1, 7.0 Hz, 4H), 2.65 (t, *J* = 7.6 Hz, 4H), 1.70 – 1.64 (m, 4H), 1.42 – 1.16 (m, 36+12H), 0.97 – 0.84 (m, 6H). FD-MS: calcd for *m/z* [M+H$^+$] 1024.3668, found *m/z* [M+H$^+$] 1024.4454

General procedure for the cyclization of acetals 6a and 6b[5]

In a round-bottom flask, the N-alkylated compound (1 eq) was dissolved in chloroform (0.04 M) under an argon atmosphere. Afterwards trifluoromethanesulfonic acid (50 eq) was rapidly added in one portion and the solution was heated at 60°C for 1 h. During this time the solutions color changed from deep purple to green. Subsequently, the solution was cooled to room temperature and the mixture was slowly neutralized by the addition of triethylamine (60 eq). The reaction solution was poured into a beaker containing methanol (500 ml). The blue precipitate was filtered off and dried in vacuo. The crude product was purified by column chromatography.

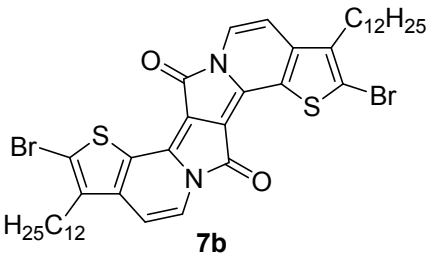
2,9-Dibromo-3,10-bis(2-hexyldecyl)thieno[3',2':7,8]indolizino[2,1-*a*]thieno[3,2-*g*]indolizine-7,14-dione



7a

The cyclization was carried out with acetal **6a** (1.5 g, 1.32 mmol) according to the general procedure. After purification by column chromatography (stationary phase: silica, eluent: methylene chloride) the product **7a** (1.1 g, 1.15 mmol, 88 %) was obtained as a blue solid. ^{1}H-NMR (600 MHz, $CDCl_3$): δ [ppm] = 7.86 (d, *J* = 7.3 Hz, 2H), 6.73 (d, *J* = 7.3 Hz, 2H), 2.62 (d, *J* = 7.3 Hz, 4H), 1.76 – 1.60 (m, 2H), 1.43 – 1.13 (m, 48H), 0.86 (t, *J* = 6.7 Hz, 12H). APCI: calcd for *m/z* [M+H$^+$] 955.3303, found *m/z* [M+H$^+$] 955.3349

2,9-Dibromo-3,10-bisdodecylthieno[3',2':7,8]indolizino[2,1-*a*]thieno[3,2-*g*]indolizine-7,14-dione



7b

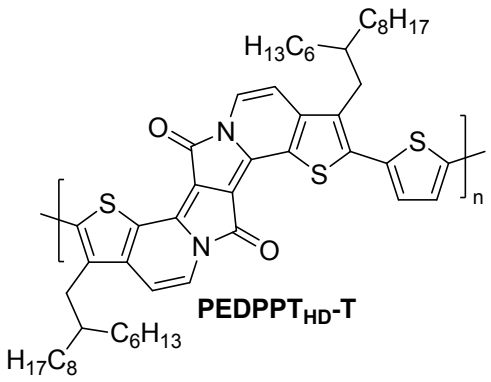
The cyclization was carried out with acetal **6b** (5.6 g, 5.45 mmol) according to the general procedure. Product **7b** (2.8 g, 3.32 mmol, 61 %) was obtained as a blue solid and used for polymerization without further purification. ^{1}H-NMR (400 MHz, $CDCl_3$) δ [ppm] = 7.89 (d, *J* = 7.2 Hz, 2H), 6.78 (d, *J* = 7.2 Hz, 2H), 3.19 (t, *J* = 7.0 Hz, 4H), 2.79 – 2.68 (m, 4H), 1.60 – 1.54 (m, 4H), 1.45 – 1.21 (m, 32H), 0.90 (t, *J* = 6.2 Hz, 6H). FD-MS: calcd for *m/z* [M+H$^+$] 840.1194, found *m/z* [M+H$^+$] 840.1181

3. Polymer synthesis

General procedure for the copolymerization of EDPP-derivatives 7a or 7b with bisstannylderivatives[6]

A mixture of the dibrominated EDPP-derivative (1.0 eq), the bisstanyl-derivative (1.0 eq) and tetrakis(triphenylphosphine)palladium(0) (0.05 eq) were dissolved in a given solvent (0.075 M) under an argon atmosphere. The solution was heated at a given temperature for 72 h. Afterwards the solution was cooled down, diluted with chloroform and washed with aqueous 2M HCl solution, water, saturated aqueous EDTA solution and brine. The solvents were removed under reduced pressure and the polymer was dissolved in 150 ml of chloroform. The solution was poured in a round bottom flask and a cation exchanger resin was added. The suspension was heated at 60 °C for 48 h to remove catalyst traces from the polymer. Subsequently, the resin was filtered off and the polymer dried in vacuo. The crude polymer was dissolved in a small amount of chloroform, precipitated into cold methanol and purified by Soxhlet extraction (methanol, acetone, ethyl acetate, hexane, chloroform).

$PEDPPT_{HD}$-T

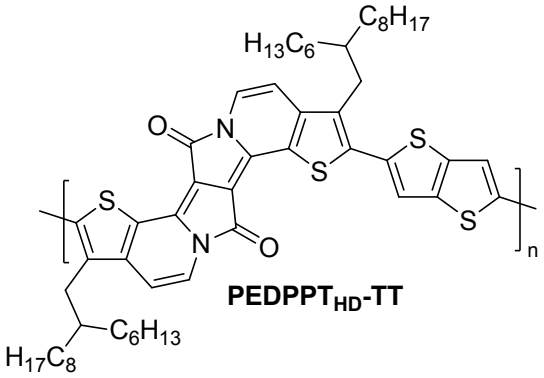


$PEDPPT_{HD}$-T

$PEDPPT_{HD}$-T was prepared from **7a** (0.4 g, 0.42 mmol) and 2,5-bis(tributylstannyl)thiophene (0.26 g, 0.42 mmol) in chlorobenzene at 145 °C according to the general procedure and obtained as a green solid. ^{1}H-NMR (600 MHz, $C_2D_2Cl_4$): δ [ppm] = 7.80 (s, 2H), 7.38 (s, 2H), 6.63 (s, 2H) 3.02 (s, 4H), 1.83 (s, 2H), 1.59 – 0.98 (m, 48H), 0.92 (s, 12H). UV/Vis $\lambda_{max.abs.}$ [nm] = 776, (724), (477), 399. PL $\lambda_{max.em.}$ [nm] ($\lambda_{exc.}$ = 670 nm) = (851), 764. E_{HOMO} [eV] = - 5.00; E_{LUMO} [eV] = - 3.31; E_g [eV] = 1.69.

Fraction	M_n [g/mol]	M_w [g/mol]	M_w/M_n	Yield [mg]	Yield [%]
Chloroform	23,100	49,600	2.15	190	50

PEDPPT$_{HD}$-TT

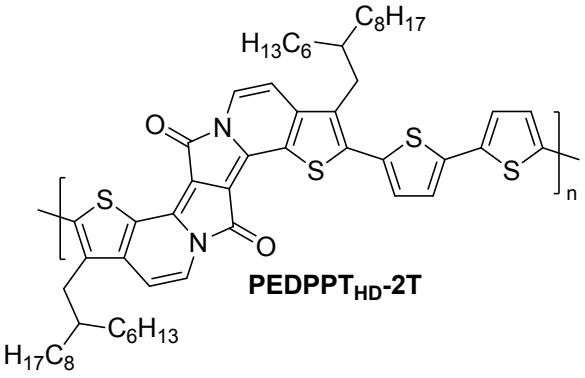


PEDPPT$_{HD}$-TT

PEDPPT$_{HD}$-TT was prepared from **7a** (0.43 g, 0.45 mmol) and 2,5-bis(trimethylstannyl)thieno[3,2-*b*]thiophene (0.21 g, 0.45 mmol) in chlorobenzene at 145 °C according to the general procedure and obtained as a green solid. ^{1}H-NMR (600 MHz, $C_2D_2Cl_4$): δ [ppm] = 8.08 – 6.98 (m, 6H), 3.36 – 2.30 (m, 4H), 1.77 (s, 2H), 1.44 – 1.05 (m, 48H), 0.87 (m, 12H). UV/Vis $\lambda_{max.abs.}$ [nm] = (837), 721, (475), 400. PL $\lambda_{max.em.}$ [nm] ($\lambda_{exc.}$ = 640 nm) = (824), 739. E_{HOMO} [eV] = - 4.83; E_{LUMO} [eV] = - 3.18; E_g [eV] = 1.65.

Fraction	M_n [g/mol]	M_w [g/mol]	M_w/M_n	Yield [mg]	Yield [%]
Chloroform	10,400	18,200	1.75	136	31

PEDPPT$_{HD}$-2T



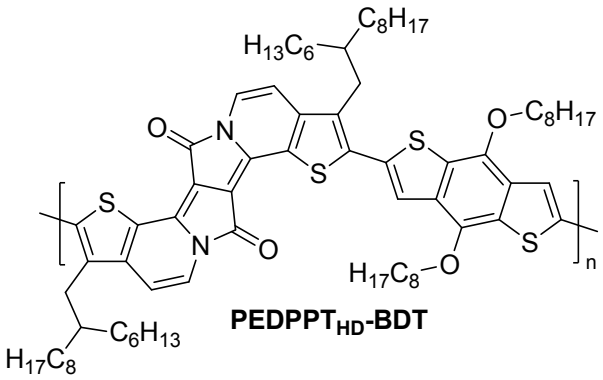
PEDPPT$_{HD}$-2T

PEDPPT$_{HD}$-2T was prepared from **7a** (0.262 g, 0.45 mmol) and 5,5'-bis(trimethylstannyl)-2,2'-bithiophene (0.135 g, 0.45 mmol) in chlorobenzene at

145 °C according to the general procedure and obtained as a green solid. ^{1}H-NMR (600 MHz, $C_2D_2Cl_4$) δ = [ppm] 7.87 (s, 2H), 7.41 – 6.97 (m, 4H), 6.74 (s, 2H), 2.93 (s, 4H), 2.55 (s, 2H), 1.81 (s, 8H), 1.39 (m, 40H), 0.88 (s, 12H). UV/Vis $\lambda_{max.abs.}$ [nm] = (783), 710, 431. PL $\lambda_{max.em.}$ [nm] ($\lambda_{exc.}$ = 650 nm) = (804), 731. E_{HOMO} [eV] = - 5.08; E_{LUMO} [eV] = - 3.35; E_g [eV] = 1.73.

Fraction	M_n [g/mol]	M_w [g/mol]	M_w/M_n	Yield [mg]	Yield [%]
Chloroform	14,600	30,000	2.05	156	58

PEDPPT$_{HD}$-BDT

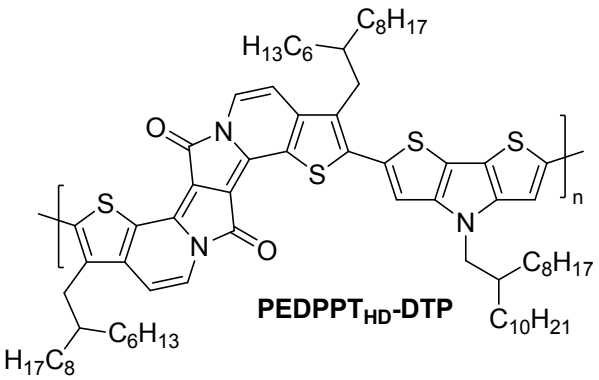


PEDPPT$_{HD}$-BDT

PEDPPT$_{HD}$-BDT was prepared from **7a** (0.239 g, 0.45 mmol) and 2,6-bis(trimethylstannyl)-4,8-bisoctylbenzo[1,2-*b*:4,5-*b'*]dithiophene (0.135 g, 0.45 mmol) in chlorobenzene at 145 °C according to the general procedure and obtained as a green solid. ^{1}H-NMR (400 MHz, $C_2D_2Cl_4$) δ [ppm] = 8.07 – 7.33 (m, 4H), 7.01 – 6.52 (m, 2H), 4.44 (s, 4H), 3.11 (s, 4H), 2.29 – 0.54 (m, 86H). UV/Vis $\lambda_{max.abs.}$ [nm] = (735), 683, (487) 393. PL $\lambda_{max.em.}$ [nm] ($\lambda_{exc.}$ = 630 nm) = (795), 723. E_{HOMO} [eV] = - 5.21; E_{LUMO} [eV] = - 3.40; E_g [eV] = 1.81.

Fraction	M_n [g/mol]	M_w [g/mol]	M_w/M_n	Yield [mg]	Yield [%]
Chloroform	23,300	63,500	2.05	215	68

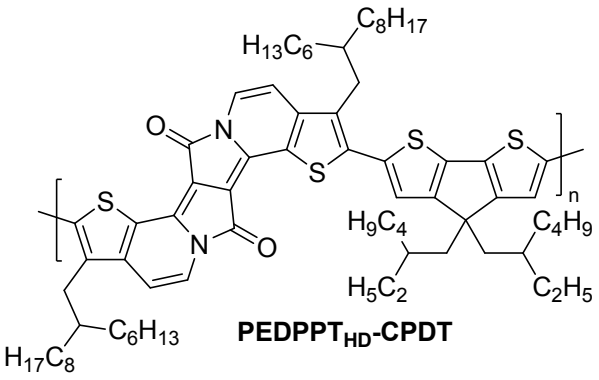
PEDPPT$_{HD}$-DTP



PEDPPT$_{HD}$-DTP was prepared from **7a** (0.420 g, 0.44 mmol) and 2,6-bis(trimethylstannyl)-4-(2-octyldodecyl)-4*H*-dithieno[3,2-*b*:2',3'-*d*]pyrrole (0.345 g, 0.44 mmol) in chlorobenzene at 145 °C according to the general procedure and obtained as a green solid. ^{1}H-NMR (600 MHz, $C_2D_2Cl_4$): δ [ppm] = 7.98 – 7.85 (m, 2H), 7.39 – 7.31 (m, 1H), 7.26 – 7.21 (m, 1H), 7.04 – 6.99 (m, 1H), 6.90 – 6.72 (m, 2H), 4.12 (s, 2H), 3.03 (s, 4H), 2.73 – 2.45 (m, 4H), 1.61 – 1.00 (m, 80H), 1.00 – 0.69 (m, 18H). UV/Vis $\lambda_{max.abs.}$ [nm] = 679, (658), 497. PL $\lambda_{max.em.}$ [nm] ($\lambda_{exc.}$ = 550 nm) = (750), 690, 662.

Fraction	M_n [g/mol]	M_w [g/mol]	M_w/M_n	Yield [mg]	Yield [%]
Ethyl acetate	2,700	3,200	1.17	155	27

PEDPPT$_{HD}$-CPDT

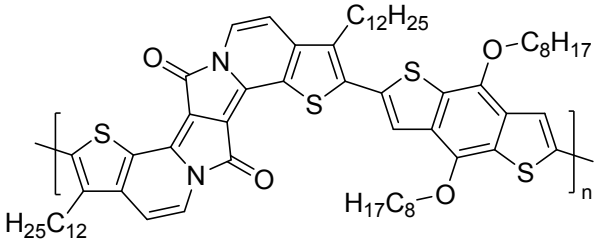


PEDPPT$_{HD}$-CPDT was prepared from **7a** (0.426 g, 0.47 mmol) and 4,4-bis(2-ethylhexyl)-2,6-bis(trimethylstannyl)-4*H*-cyclopenta[1,2-*b*:5,4-*b*']dithiophene (0.437 g, 0.47 mmol) in chlorobenzene at 145 °C according to the general procedure and obtained as a green solid. ^{1}H-NMR (600 MHz, $C_2D_2Cl_4$): δ [ppm] = 8.79 – 6.59 (m,

6H), 3.23 – 2.68 (m, 4H), 2.24 – 1.72 (m, 6H), 1.49 – 0.97 (m, 64H), 0.97 – 0.64 (m, 24H). UV/Vis $\lambda_{max.abs.}$ [nm] = 671, 430. PL $\lambda_{max.em.}$ [nm] ($\lambda_{exc.}$ = 550 nm) = 775.

Fraction	M_n [g/mol]	M_w [g/mol]	M_w/M_n	Yield [mg]	Yield [%]
Ethyl acetate	5,600	8,100	1.44	229	42

PEDPPT$_{Do}$-BDT

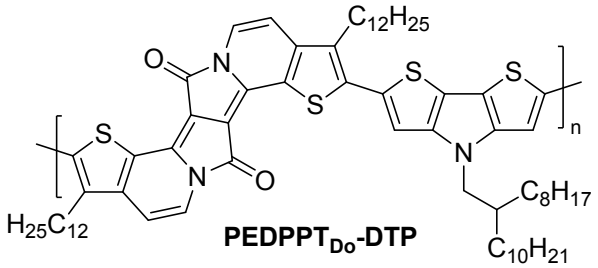


PEDPPT$_{Do}$-BDT

PEDPPT$_{Do}$-BDT was prepared from **7b** (0.50 g, 0.59 mmol) and 2,6-bis(trimethylstannyl)-4,8-bisoctylbenzo[1,2-*b*:4,5-*b'*]dithiophene (0.458 g, 0.59 mmol) in chlorobenzene at 145 °C according to the general procedure and obtained as a green solid. ^{1}H-NMR (600 MHz, $C_2D_2Cl_4$) δ [ppm] = 8.06 – 7.31 (m, 4H), 6.94 – 6.72 (m, 2H), 4.51 – 4.21 (m, 4H), 3.24 – 2.85 (m, 4H), 2.10 – 0.68 (m, 76H). UV/Vis $\lambda_{max.abs.}$ [nm] = 692, 392. PL $\lambda_{max.em.}$ [nm] ($\lambda_{exc.}$ = 730 nm) = (794), 734.

Fraction	M_n [g/mol]	M_w [g/mol]	M_w/M_n	Yield [mg]	Yield [%]
Chloroform	6,600	13,500	2.05	235	34

PEDPPT$_{Do}$-DTP



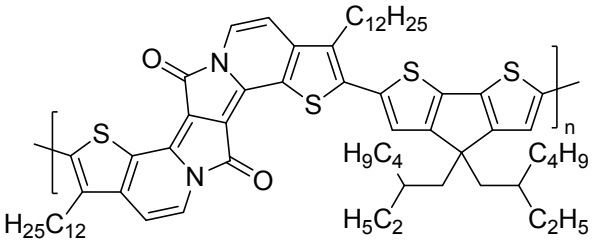
PEDPPT$_{Do}$-DTP

PEDPPT$_{Do}$-DTP was prepared from **7a** (0.30 g, 0.36 mmol) and 2,6-bis(trimethylstannyl)-4-(2-octyldodecyl)-4H-dithieno[3,2-*b*:2',3'-*d*]pyrrole (0.28 g, 0.36 mmol) in chlorobenzene at 145 °C according to the general procedure and obtained as a green solid. ^{1}H-NMR (600 MHz, $C_2D_2Cl_4$) δ [ppm] = 8.01 – 7.69 (m, 2H), 7.39 –

6.55 (m, 4H), 4.18 – 3.86 (m, 4H), 3.11 – 2.50 (m, 4H), 2.15 – 1.93 (m, 2H), 1.89 – 0.63 (m, 74H). UV/Vis $\lambda_{max.abs.}$ [nm] = (803), 740, (507), 414. PL $\lambda_{max.em.}$ [nm] ($\lambda_{exc.}$ = 670 nm) = (907), 759. E_{HOMO} [eV] = - 5.18; E_{LUMO} [eV] = - 3.58; E_g [eV] = 1.60

Fraction	M_n [g/mol]	M_w [g/mol]	M_w/M_n	Yield [mg]	Yield [%]
Chloroform	7,400	10,300	1.38	260	62

PEDPPT$_{Do}$-CPDT

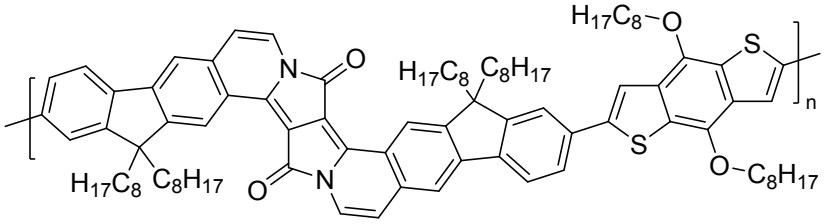


PEDPPT$_{Do}$-CPDT

PEDPPT$_{Do}$-CPDT was prepared from **7b** (0.38 g, 0.45 mmol) and 4,4-bis(2-ethylhexyl)-2,6-bis(trimethylstannyl)-4*H*-cyclopenta[1,2-*b*:5,4-*b*']dithiophene (0.442 g, 0.45 mmol) in chlorobenzene at 145 °C according to the general procedure and obtained as a green solid. ^{1}H-NMR (600 MHz, $C_2D_2Cl_4$) δ [ppm] = 8.11 – 7.78 (m, 2H), 7.57 – 7.12 (m, 2H), 7.03 – 6.64 (m, 2H), 3.14 – 2.74 (m, 8H), 2.21 – 1.82 (m, 10H), 1.82 – 0.38 (m, 60H). UV/Vis $\lambda_{max.abs.}$ [nm] = 730, (489), 427. PL $\lambda_{max.em.}$ [nm] ($\lambda_{exc.}$ = 650 nm) = (892), 800. E_{HOMO} [eV] = - 5.19; E_{LUMO} [eV] = - 3.47; E_g [eV] = 1.72

Fraction	M_n [g/mol]	M_w [g/mol]	M_w/M_n	Yield [mg]	Yield [%]
Chloroform	12,000	20,400	1.71	202	40

PEDPPF-BDT



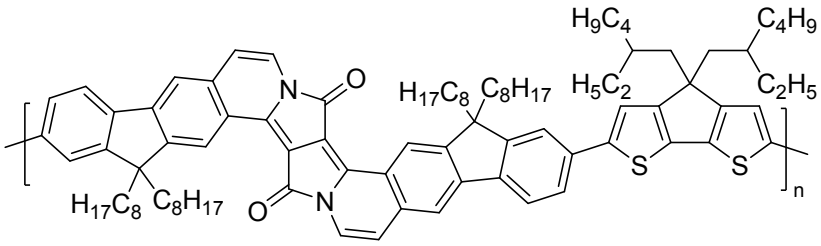
PEDPPF-BDT

Polymer **PEDPPF-BDT** was prepared from **8** (0.50 g, 0.59 mmol) and 2,6-bis(trimethylstannyl)-4,8-bisoctylbenzo[1,2-*b*:4,5-*b*']dithiophene (0.458 g, 0.59 mmol)

in toluene at 120 °C according to the general procedure and obtained as a green solid. ^{1}H-NMR (600 MHz, $C_2D_2Cl_4$) δ [ppm] = 9.26 (s, 2H), 8.02 – 7.67 (m, 12H), 6.91 (s, 2H), 4.42 (s, 4H), 2.33 (m, 4H), 2.21 (m, 4H), 2.03 (m, 8H), 1.66 (s, 8H), 1.58 - 1.33 (m, 16H), 1.32 – 1.02 (m, 28H), 0.99 – 0.68 (m, 20H). ^{13}C-NMR (151 MHz, $C_2D_2Cl_4$) δ [ppm] = 156.1, 153.7, 152.7, 144.7, 141.6, 134.5, 133.3, 129.9, 129.2, 126.9, 126.2, 124.4, 123.4, 122.6, 121.6, 117.4, 116.7, 112.4, 101.7, 99.9, 55.9, 40.5, 39.2, 32.0, 31.9, 31.9, 30.9, 30.2, 29.7, 29.5, 29.3, 29.3, 26.4, 24.3, 22.8, 22.7, 17.2, 14.2, 14.1, 9.4. UV/Vis $\lambda_{max.abs.}$ [nm] = 652, (593), (544), (480), (445) 387. PL $\lambda_{max.em.}$ [nm] ($\lambda_{exc.}$ = 400 nm) = (722), 662. E_{HOMO} [eV] = - 5.41; E_{LUMO} [eV] = - 3.33; E_g [eV] = 2.08

Fraction	M_n [g/mol]	M_w [g/mol]	M_w/M_n	Yield [mg]	Yield [%]
Chloroform	23,400	111,000	4.11	410	56

PEDPPF-CPDT



PEDPPF-CPDT

Polymer **PEDPPF-CPDT** was prepared from **8** (0.425 g, 0.38 mmol) and 4,4-bis(2-ethylhexyl)-2,6-bis(trimethylstannyl)-4H-cyclopenta[1,2-*b*:5,4-*b*']dithiophene (0.372 g, 0.38 mmol) in toluene at 120 °C according to the general procedure and obtained as a green solid. ^{1}H-NMR (600 MHz, $CDCl_3$) δ [ppm] = 9.28 (s, 2H), 7.96 (s, 4H), 7.87 (s, 4H), 7.69 (s, 4H), 7.34 (s, 2H), 6.91 (s, 2H), 2.46 – 1.94 (m, 24H), 1.55 – 0.70 (m, 82H). ^{13}C-NMR (151 MHz, $CDCl_3$) δ [ppm] = 206.0, 158.7, 156.0, 153.4, 152.3, 145.9, 144.8, 141.4, 138.6, 137.1, 136.4, 134.3, 125.4, 124.6, 123.9, 123.0, 122.3, 121.3, 119.7, 118.9, 116.7, 112.2, 101.4, 55.6, 54.3, 43.5, 40.4, 35.6, 34.4, 31.7, 30.6, 30.4, 29.9, 29.1, 28.8, 27.7, 24.0, 22.8, 22.7, 22.5, 22.5, 13.9, 13.9, 13.8, 13.8, 10.7. UV/Vis $\lambda_{max.abs.}$ [nm] = 665, (601), (549), (500), (421). PL $\lambda_{max.em.}$ [nm] ($\lambda_{exc.}$ = 630 nm) = (735), 675. E_{HOMO} [eV] = - 5.26; E_{LUMO} [eV] = - 3.20; E_g [eV] = 2.06

Fraction	M_n [g/mol]	M_w [g/mol]	M_w/M_n	Yield [mg]	Yield [%]
Chloroform	16,200	21,700	1.34	234	44

4. Literature

(1) Grzybowski, M.; Hugues, V.; Blanchard-Desce, M.; Gryko, D. T. Two-photon-induced fluorescence in new pi-expanded diketopyrrolopyrroles. *Chemistry* **2014**, *20*, 12493–12501.

(2) Cai, D.-J.; Lin, P.-H.; Liu, C.-Y. Cobalt-Catalyzed Reductive Alkylation of Heteroaryl Bromides: One-Pot Access to Alkylthiophenes, -furans, -selenophenes, and -pyrroles. *Eur. J. Org. Chem.* **2015**, *2015*, 5448–5452.

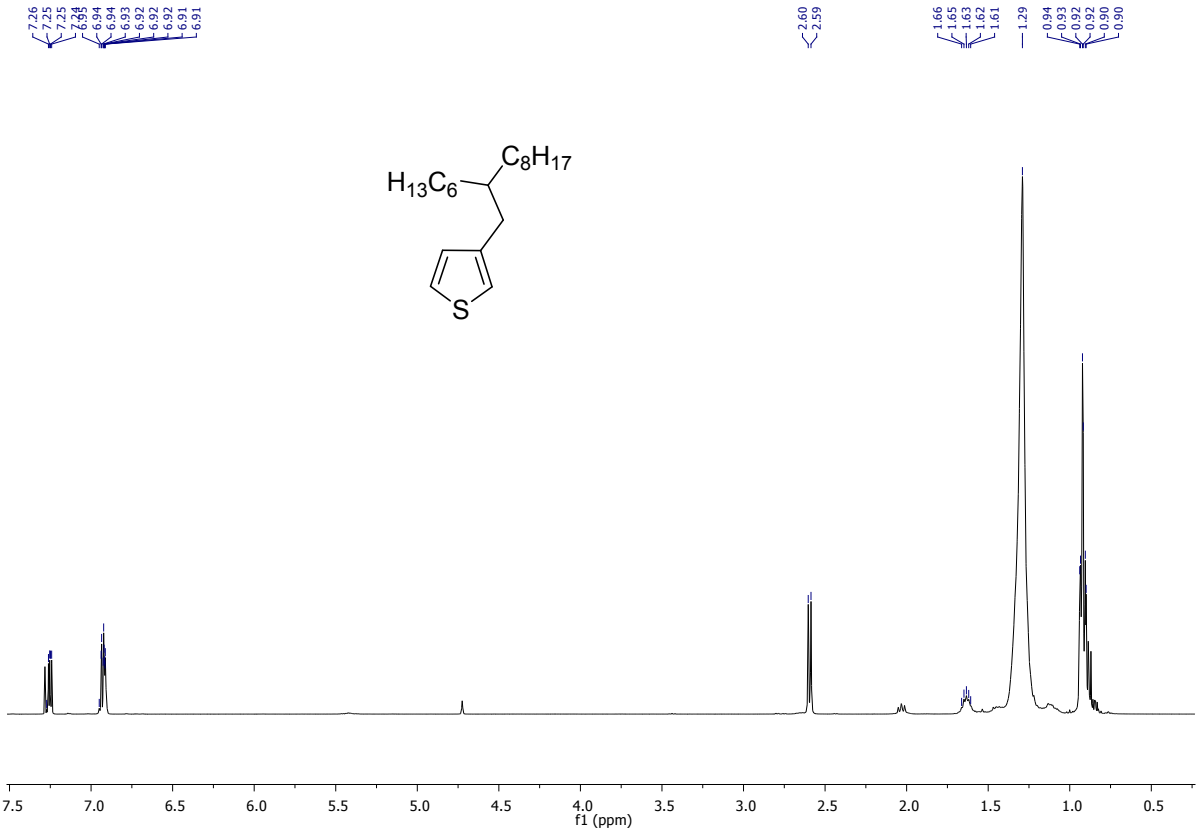
(3) Innocenti, P.; Cheung, K.-M. J.; Solanki, S.; Mas-Droux, C.; Rowan, F.; Yeoh, S.; Boxall, K.; Westlake, M.; Pickard, L.; Hardy, T. *et al.* Design of potent and selective hybrid inhibitors of the mitotic kinase Nek2: Structure-activity relationship, structural biology, and cellular activity. *J. med. chem.* **2012**, *55*, 3228–3241.

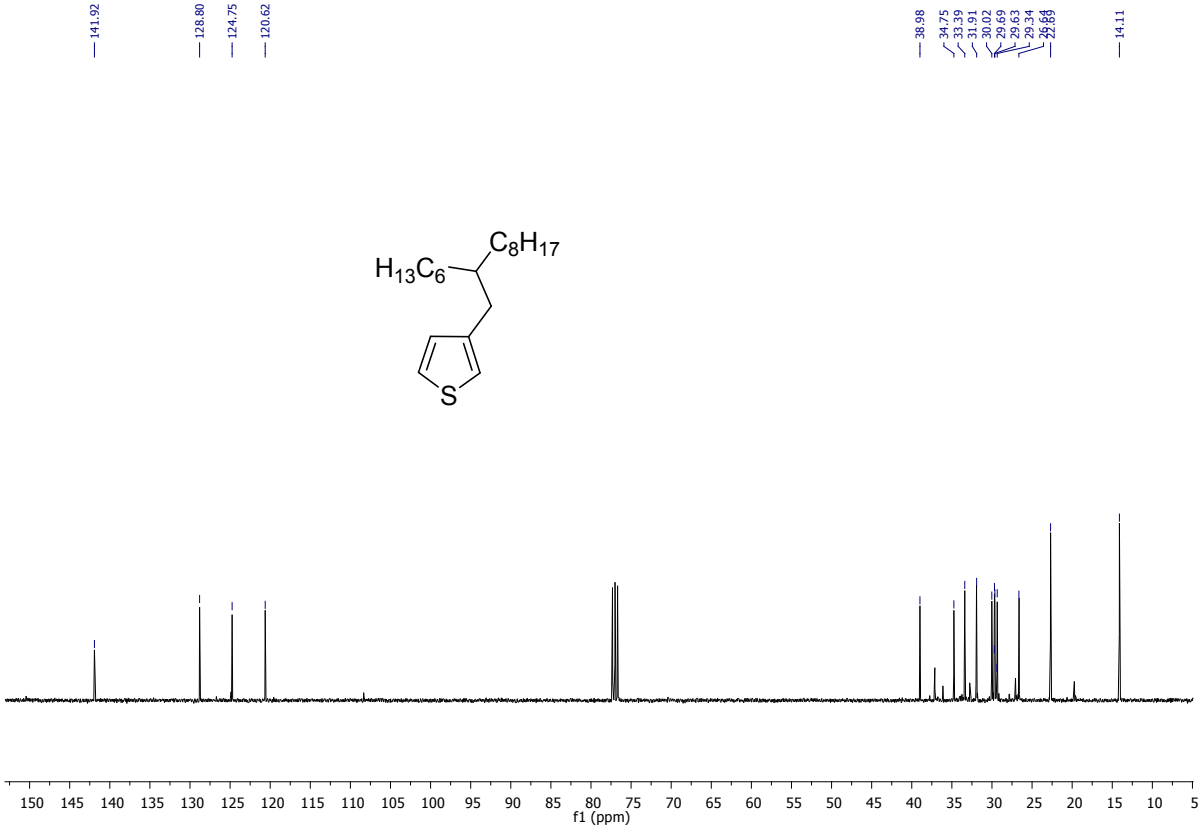
(4) Quinton, C.; Alain-Rizzo, V.; Dumas-Verdes, C.; Clavier, G.; Vignau, L.; Audebert, P. Triphenylamine/tetrazine based π-conjugated systems as molecular donors for organic solar cells. *New J. Chem.* **2015**, *39*, 9700–9713.

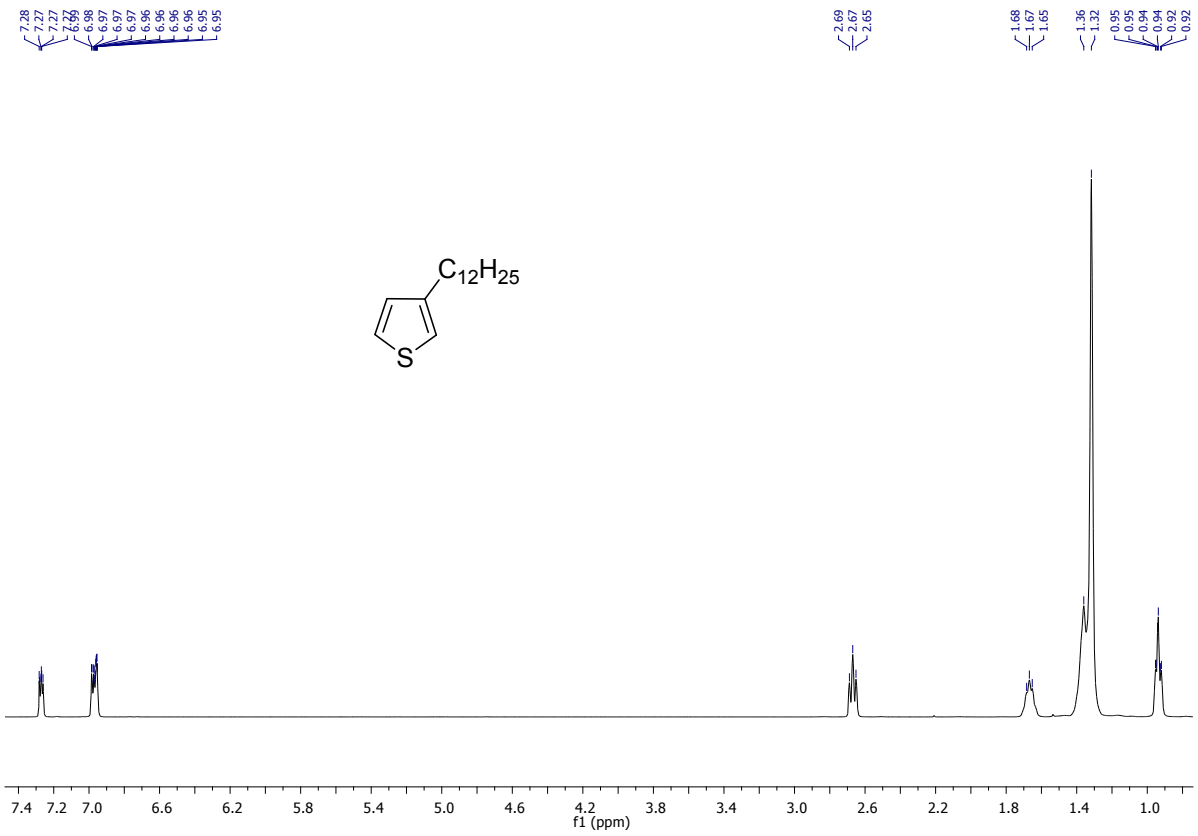
(5) Grzybowski, M.; Glodkowska-Mrowka, E.; Stoklosa, T.; Gryko, D. T. Bright, color-tunable fluorescent dyes based on pi-expanded diketopyrrolopyrroles. *Org. lett.* **2012**, *14*, 2670–2673.

(6) Zhu, Z.; Waller, D.; Gaudiana, R.; Morana, M.; Mühlbacher, D.; Scharber, M.; Brabec, C. Panchromatic Conjugated Polymers Containing Alternating Donor/Acceptor Units for Photovoltaic Applications. *Macromolecules* **2007**, *40*, 1981–1986.

5. Spectral data






7.28
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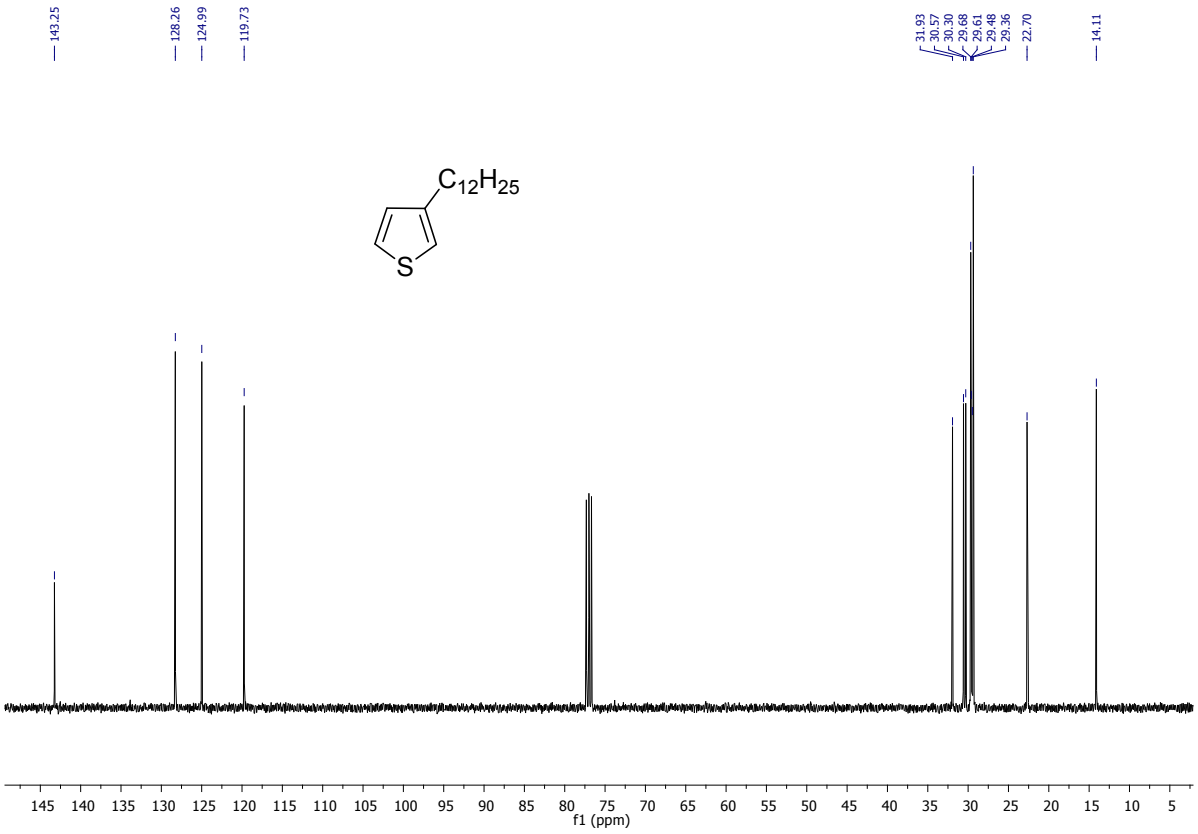
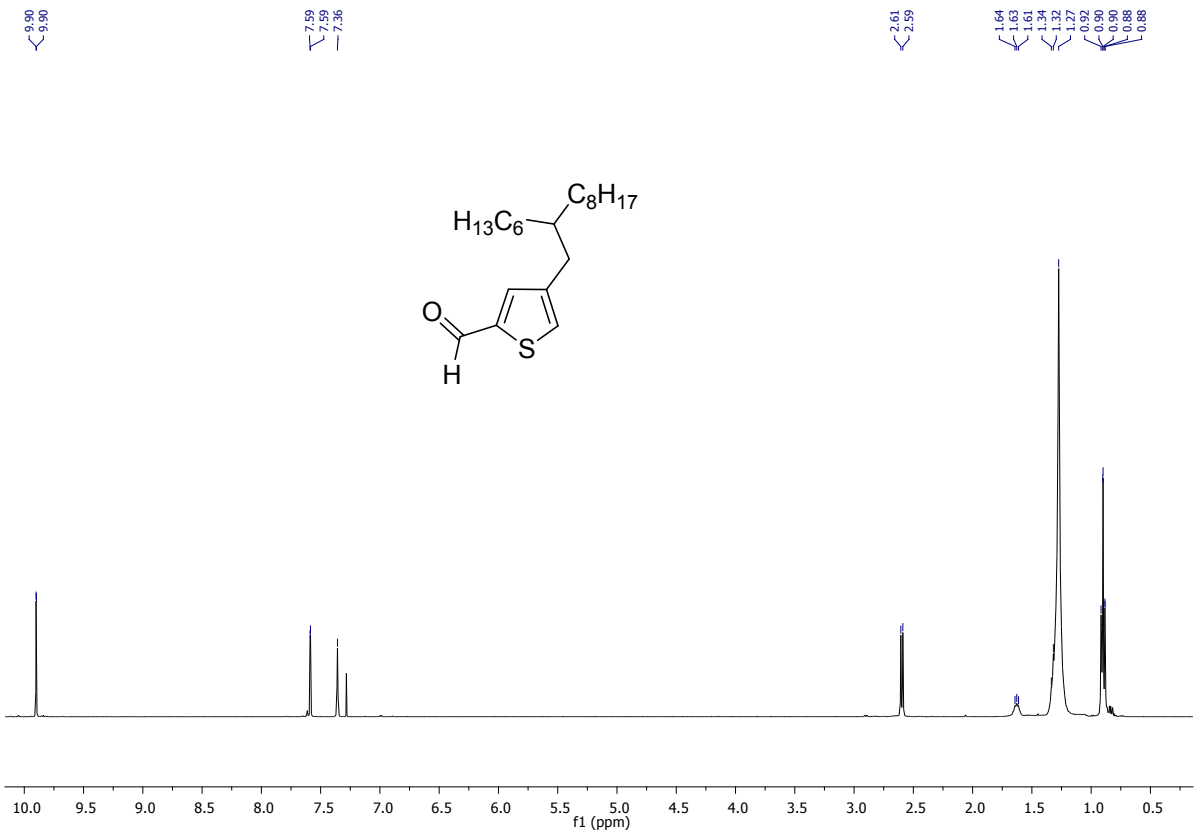
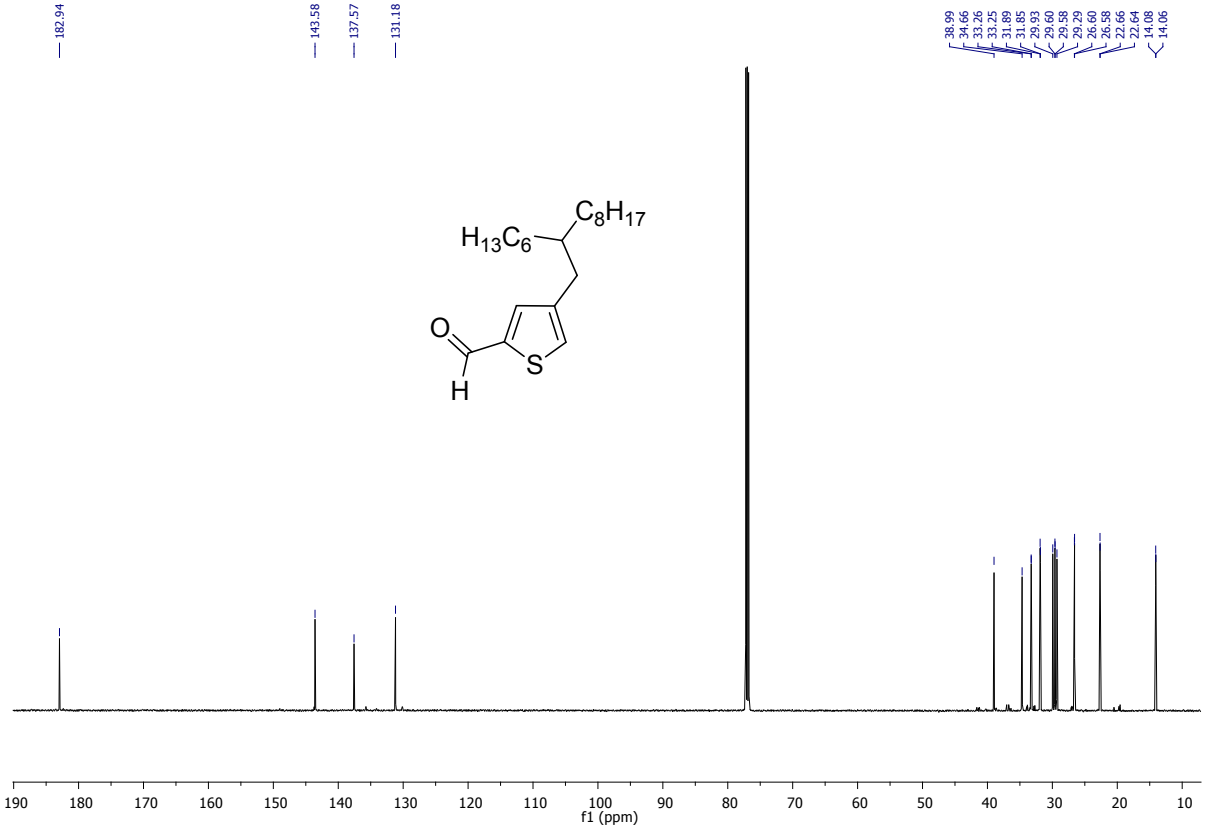
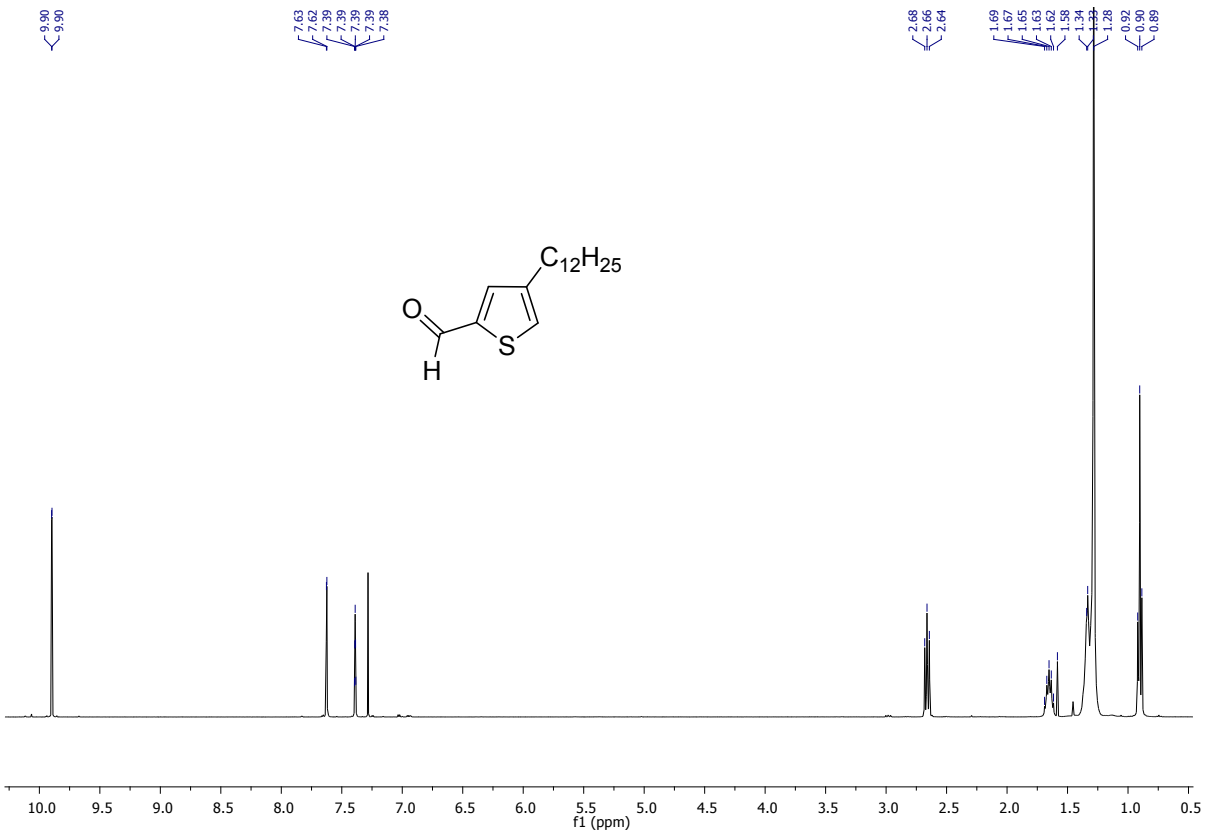
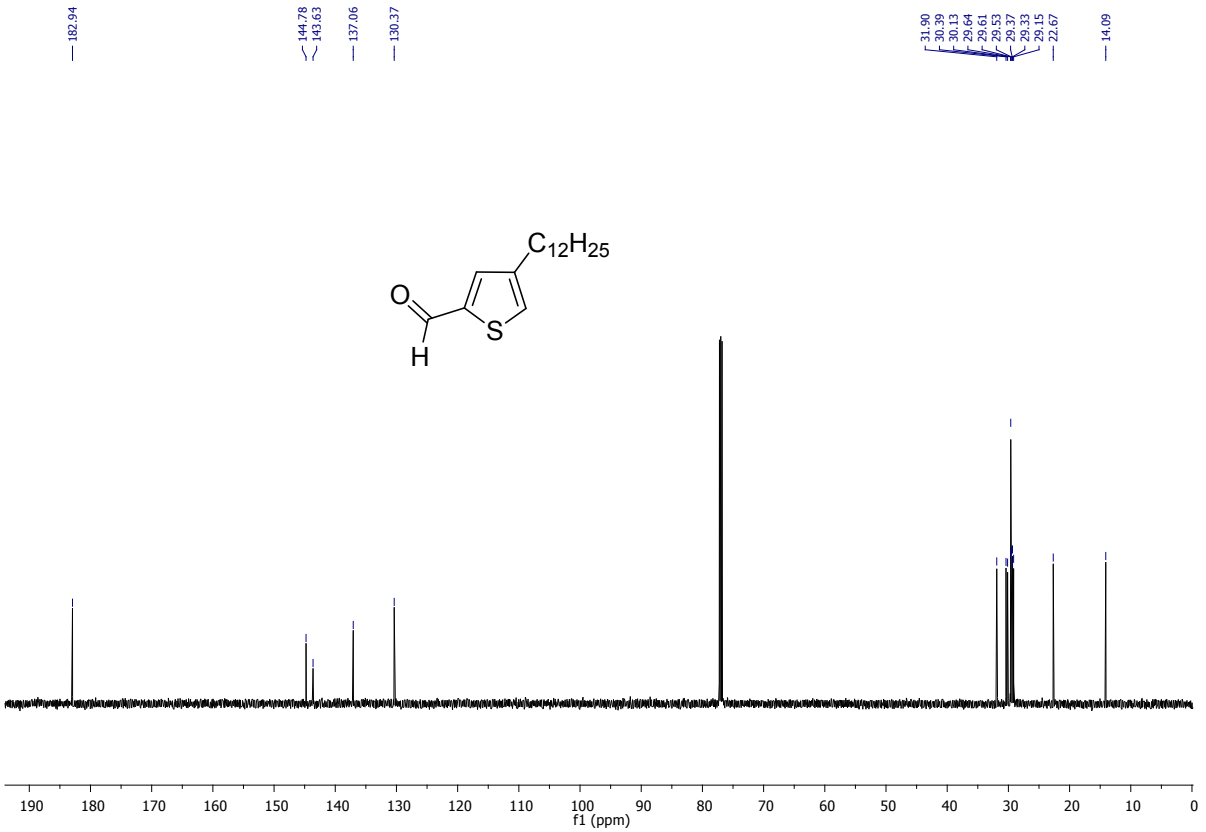
6.99
6.98
6.97
6.97
6.97
6.97
6.96
6.96
6.96
6.96
6.96
6.95
6.95
2.69
2.67
2.65
1.68
1.67
1.65
1.36
1.32
0.95
0.95
0.94
0.94
0.92
0.92
C12H25
S
7.4 7.2 7.0 6.6 6.2 5.8 5.4 5.0 4.6 4.2 3.8 3.4 3.0 2.6 2.2 1.8 1.4 1.0
f1 (ppm)

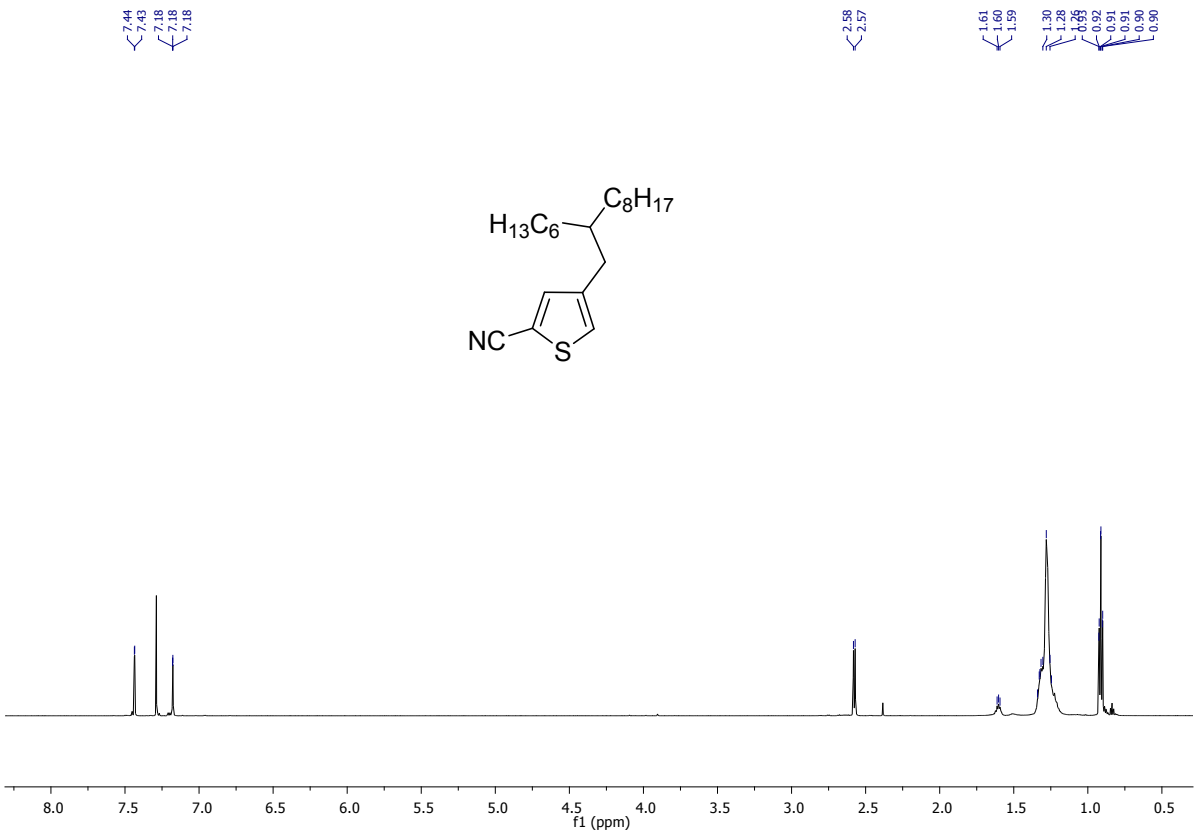

143.25
128.26
124.99
119.73
31.93
30.57
30.30
29.68
29.61
29.48
29.36
22.70
14.11
C12H25
S
145 140 135 130 125 120 115 110 105 100 95 90 85 80 75 70 65 60 55 50 45 40 35 30 25 20 15 10 5
f1 (ppm)

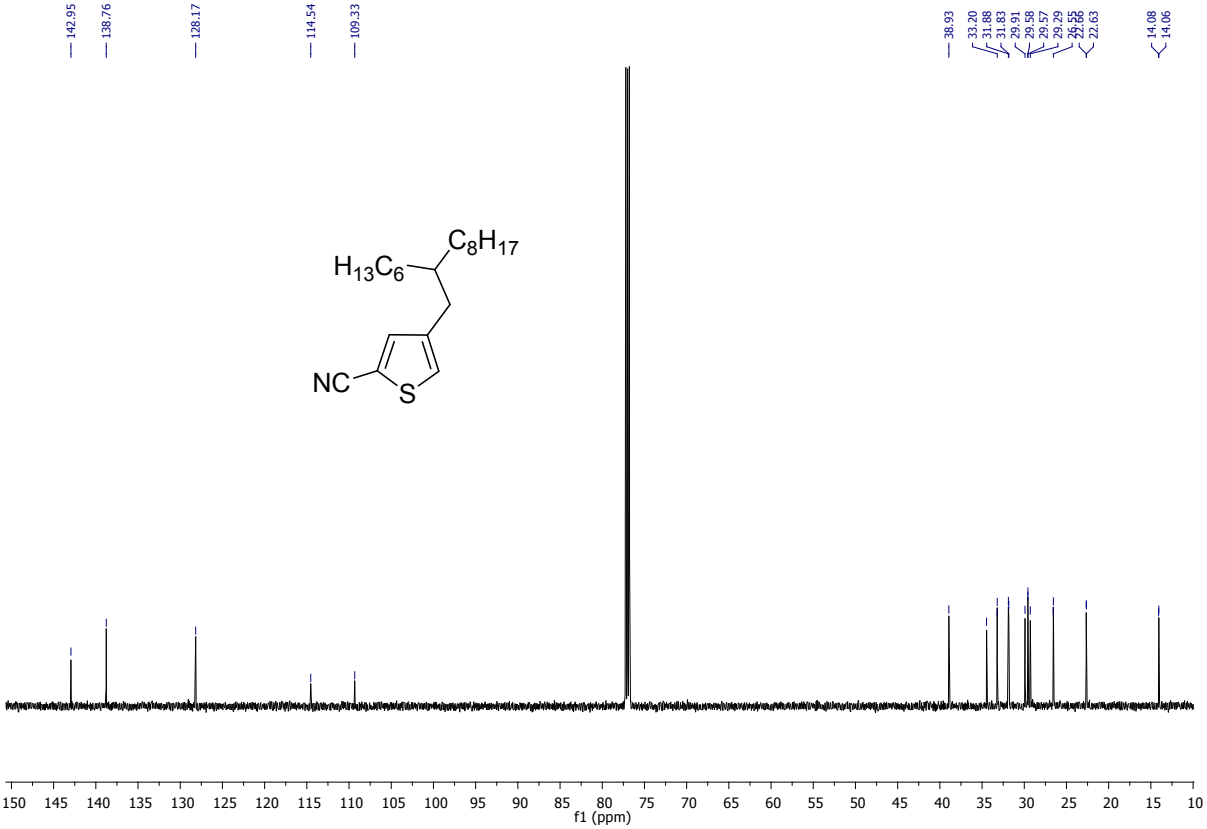

9.90
9.90
7.59
7.59
7.36
2.61
2.59
1.64
1.63
1.61
1.34
1.32
1.27
0.92
0.90
0.90
0.88
0.88
C_8H_{17}
$H_{13}C_6$
O
S
H
10.0 9.5 9.0 8.5 8.0 7.5 7.0 6.5 6.0 5.5 5.0 4.5 4.0 3.5 3.0 2.5 2.0 1.5 1.0 0.5
f1 (ppm)

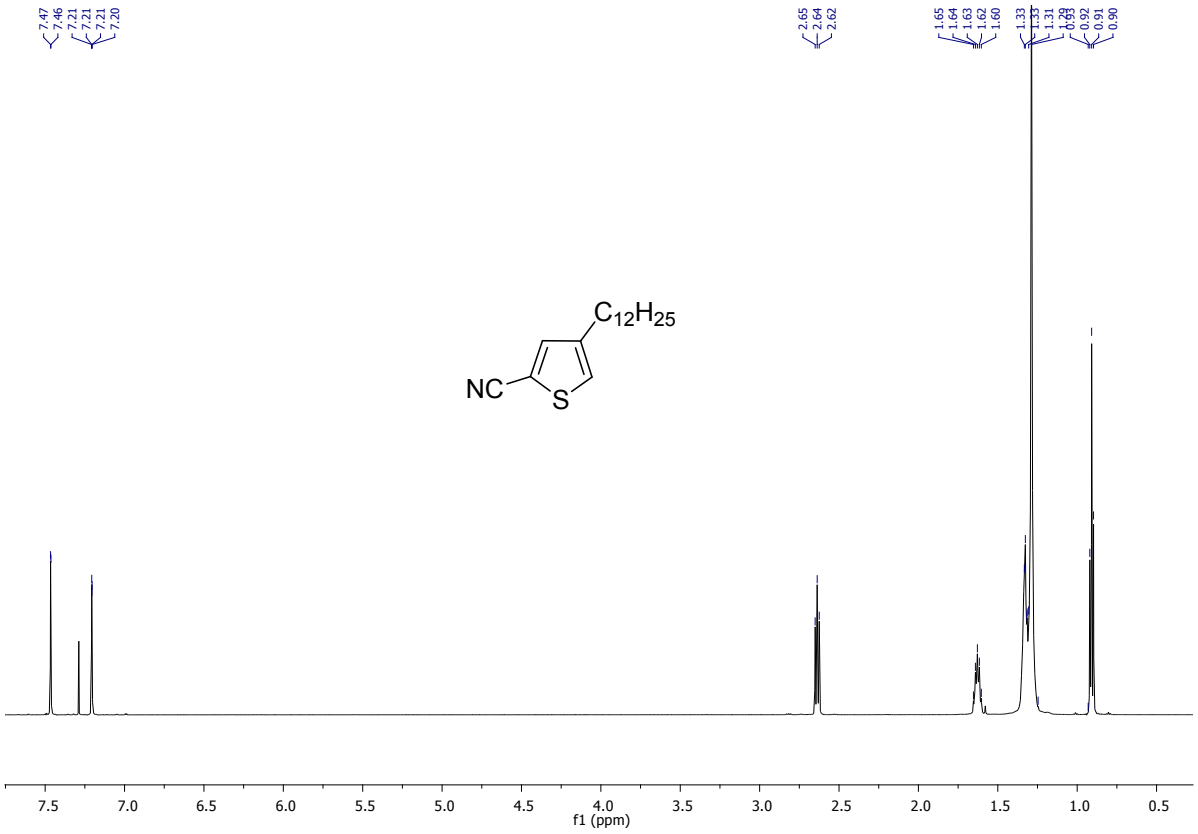

182.94
143.58
137.57
131.18
38.99
34.66
33.26
33.25
31.89
31.85
29.93
29.60
29.58
29.29
26.60
26.58
22.66
22.64
14.08
14.06
C_8H_{17}
$H_{13}C_6$
O
S
H
190 180 170 160 150 140 130 120 110 100 90 80 70 60 50 40 30 20 10
f1 (ppm)

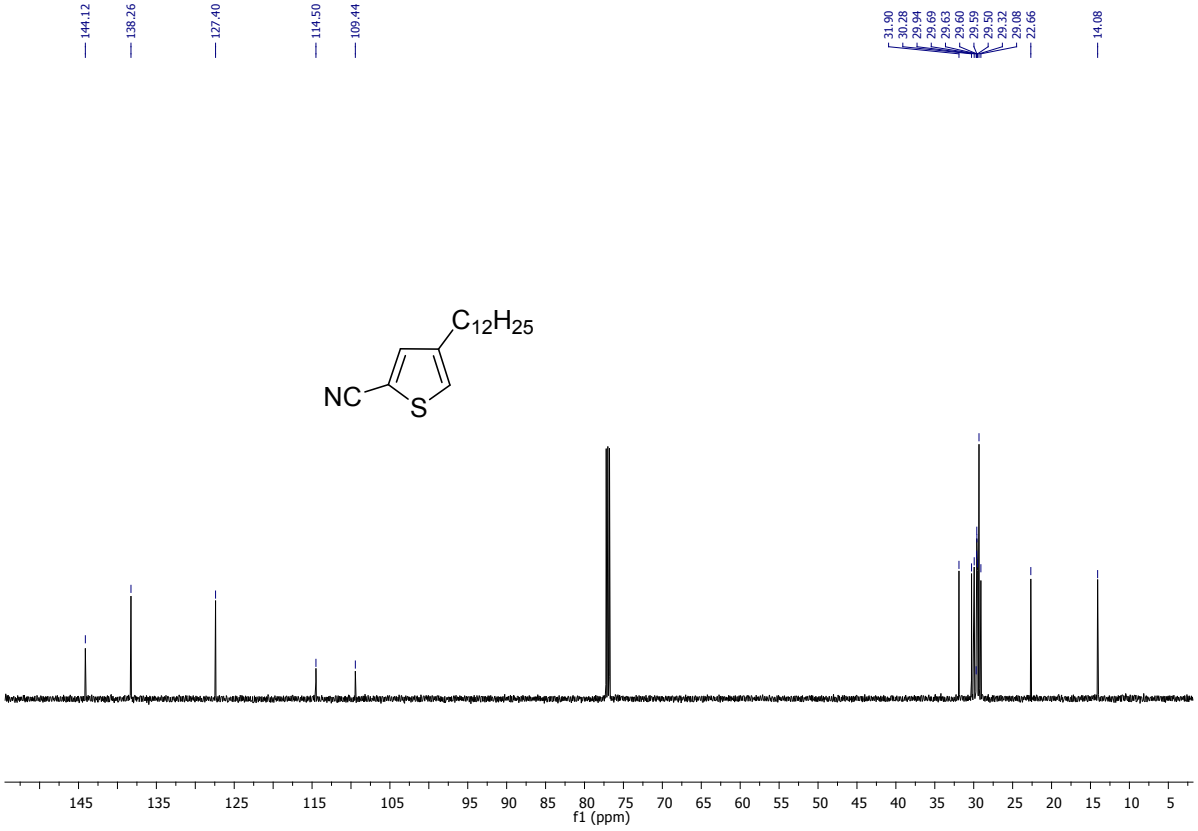

9.90
9.90
7.63
7.62
7.39
7.39
7.39
7.39
7.38
2.68
2.66
2.64
1.69
1.67
1.65
1.63
1.62
1.58
1.34
1.33
1.28
0.92
0.90
0.89
C12H25
O
S
H
10.0
9.5
9.0
8.5
8.0
7.5
7.0
6.5
6.0
5.5
5.0
4.5
4.0
3.5
3.0
2.5
2.0
1.5
1.0
0.5
f1 (ppm)

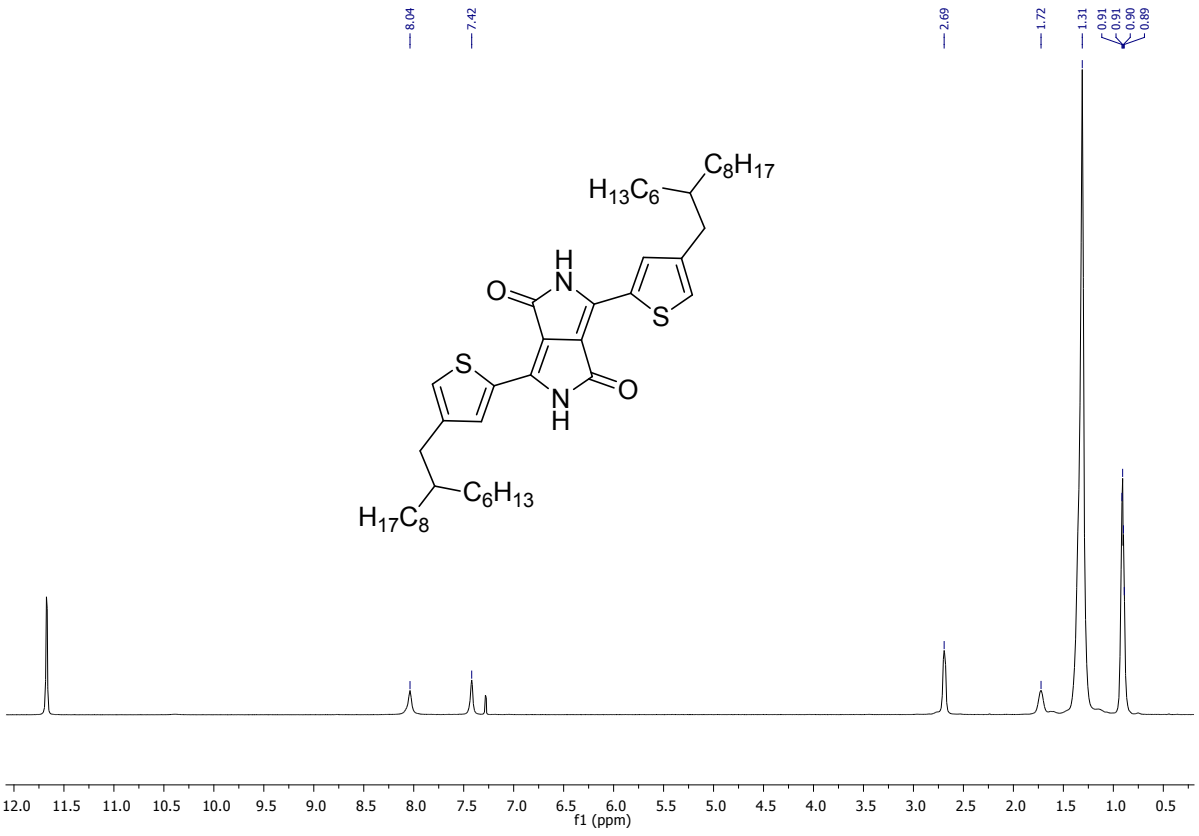

182.94
144.78
143.63
137.06
130.37
31.90
30.39
30.13
29.64
29.61
29.53
29.37
29.33
29.15
22.67
14.09
C12H25
O
S
H
190
180
170
160
150
140
130
120
110
100
90
80
70
60
50
40
30
20
10
0
f1 (ppm)

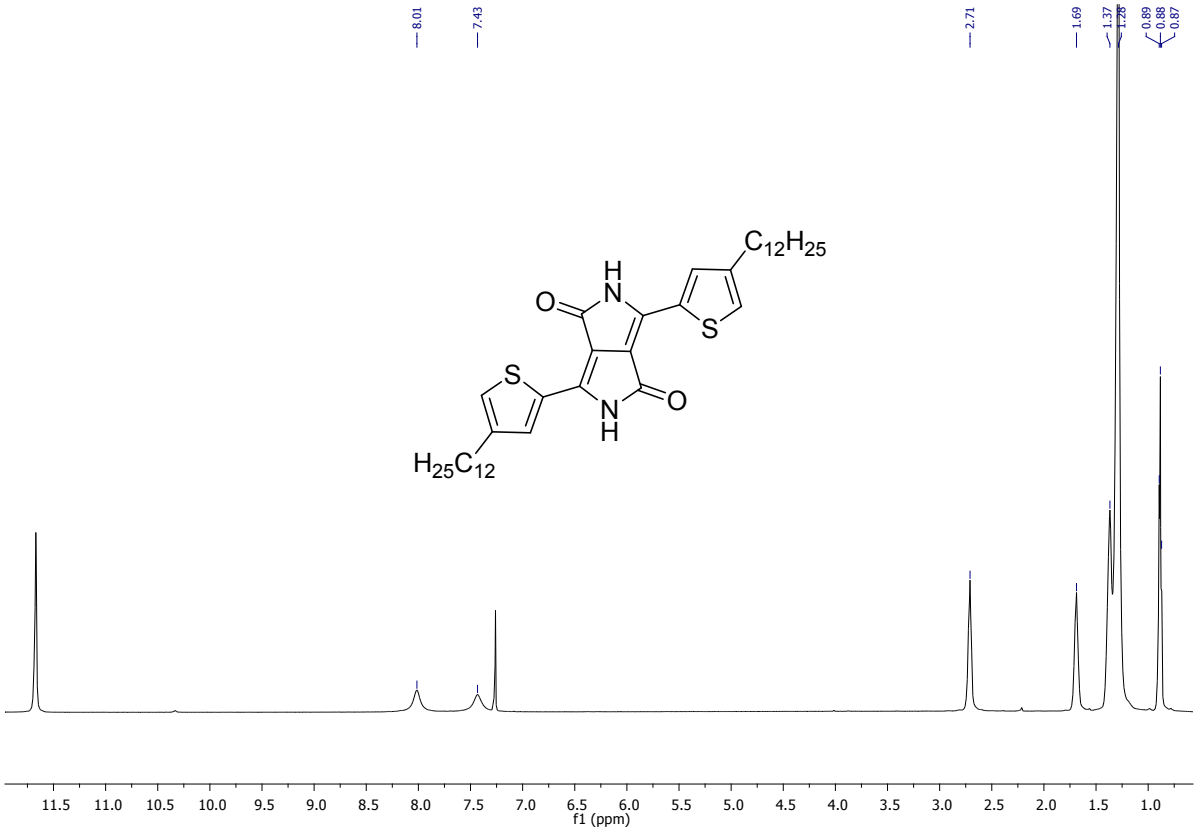

7.44
7.43
7.18
7.18
7.18
2.58
2.57
1.61
1.60
1.59
1.30
1.28
0.93
0.92
0.91
0.91
0.90
0.90
C_8H_{17}
$H_{13}C_6$
NC
S
8.0
7.5
7.0
6.5
6.0
5.5
5.0
4.5
4.0
3.5
3.0
2.5
2.0
1.5
1.0
0.5
f1 (ppm)

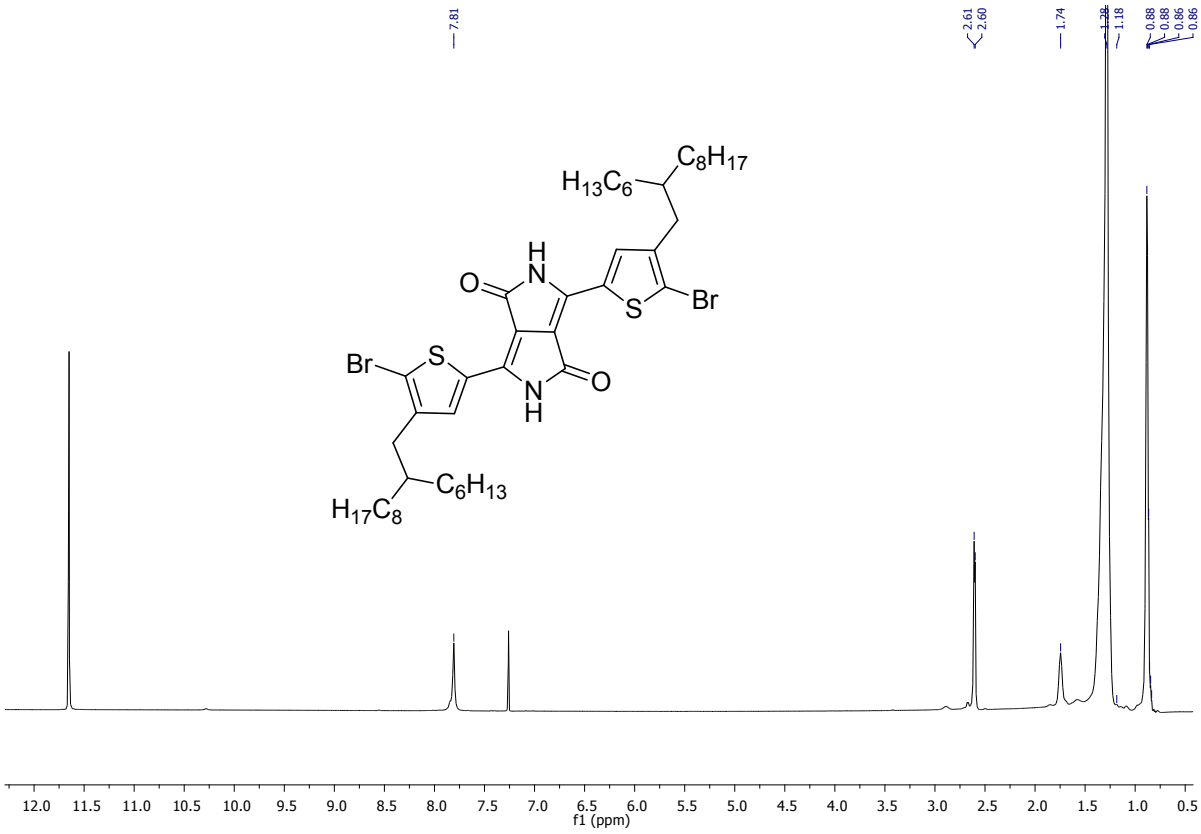

142.95
138.76
128.17
114.54
109.33
38.93
33.20
31.88
31.83
29.91
29.58
29.57
29.29
25.55
25.66
22.63
14.08
14.06
C_8H_{17}
$H_{13}C_6$
NC
S
150
145
140
135
130
125
120
115
110
105
100
95
90
85
80
75
70
65
60
55
50
45
40
35
30
25
20
15
10
f1 (ppm)

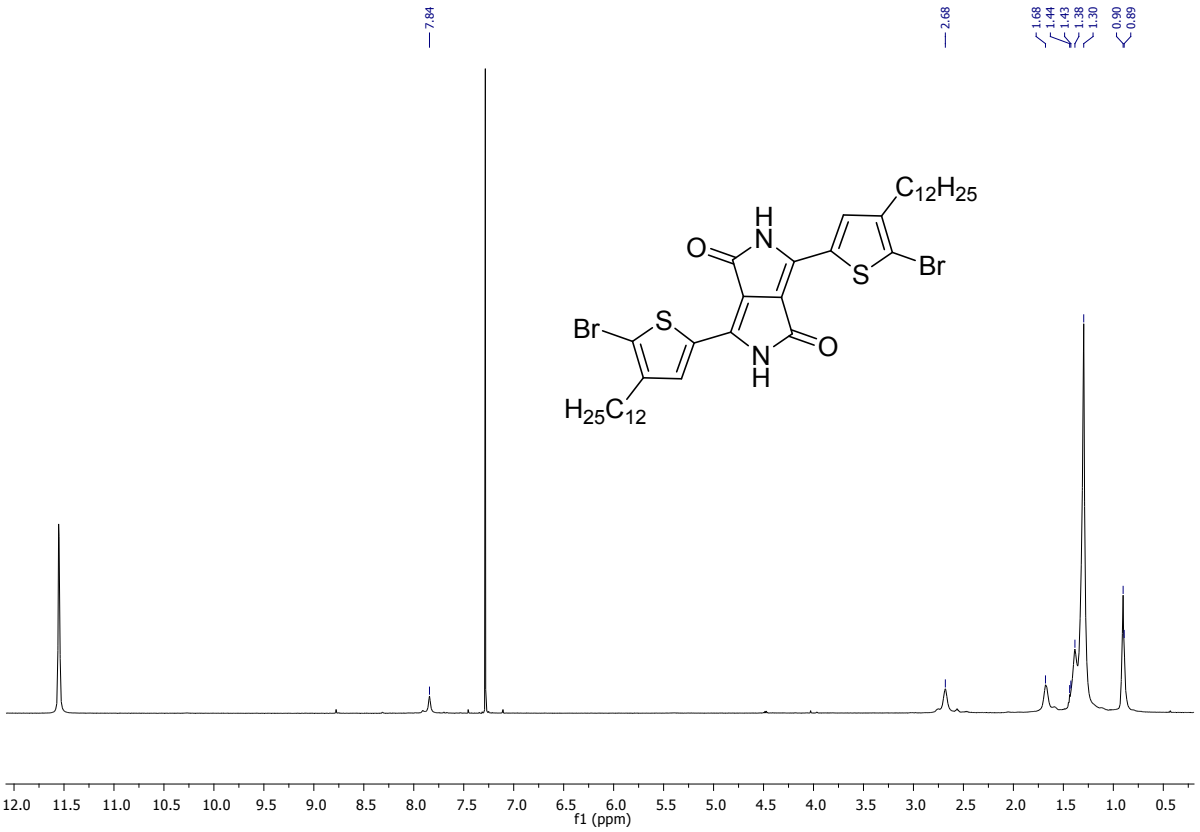

7.47
7.46
7.21
7.21
7.21
7.20
2.65
2.64
2.62
1.65
1.64
1.63
1.62
1.60
1.33
1.31
0.92
0.91
0.90
$C_{12}H_{25}$
NC
S
7.5
7.0
6.5
6.0
5.5
5.0
4.5
4.0
3.5
3.0
2.5
2.0
1.5
1.0
0.5
f1 (ppm)

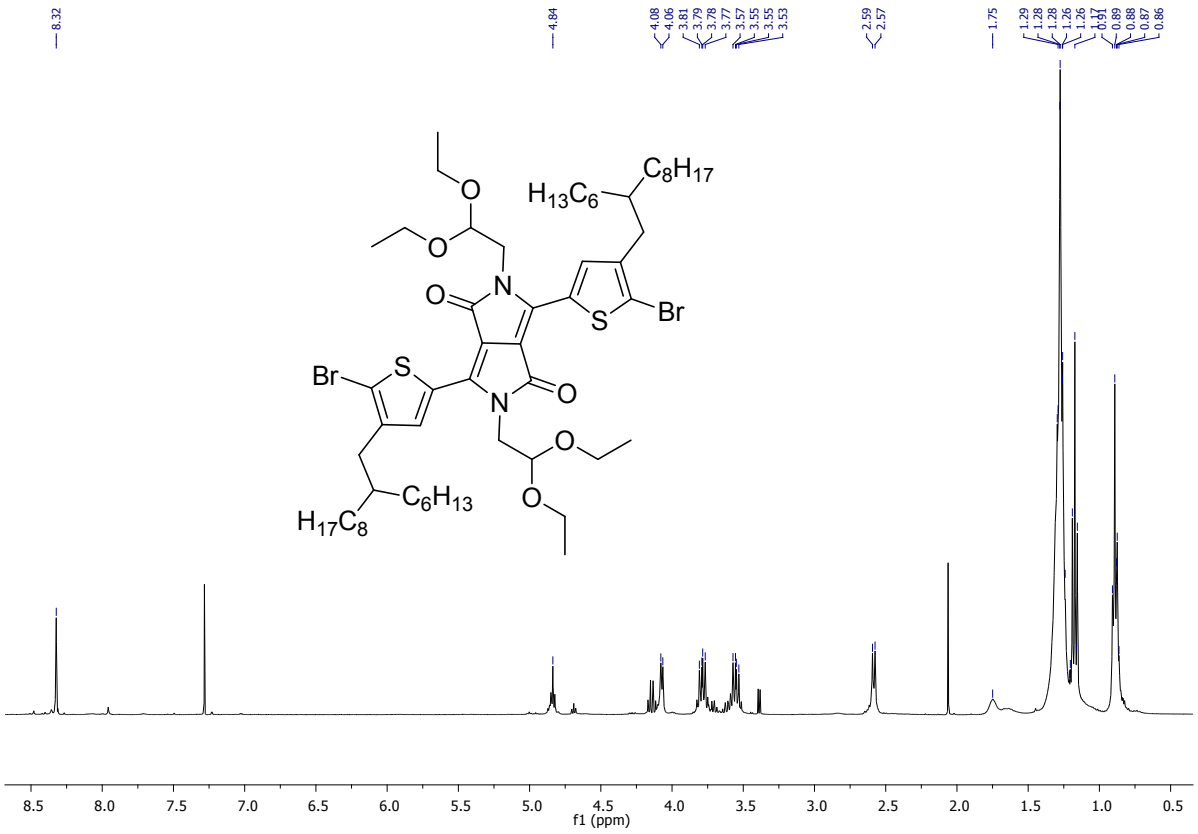

144.12
138.26
127.40
114.50
109.44
31.90
30.28
29.94
29.69
29.63
29.60
29.59
29.50
29.32
29.08
22.66
14.08
$C_{12}H_{25}$
NC
S
145
135
125
115
105
95
90
85
80
75
70
65
60
55
50
45
40
35
30
25
20
15
10
5
f1 (ppm)

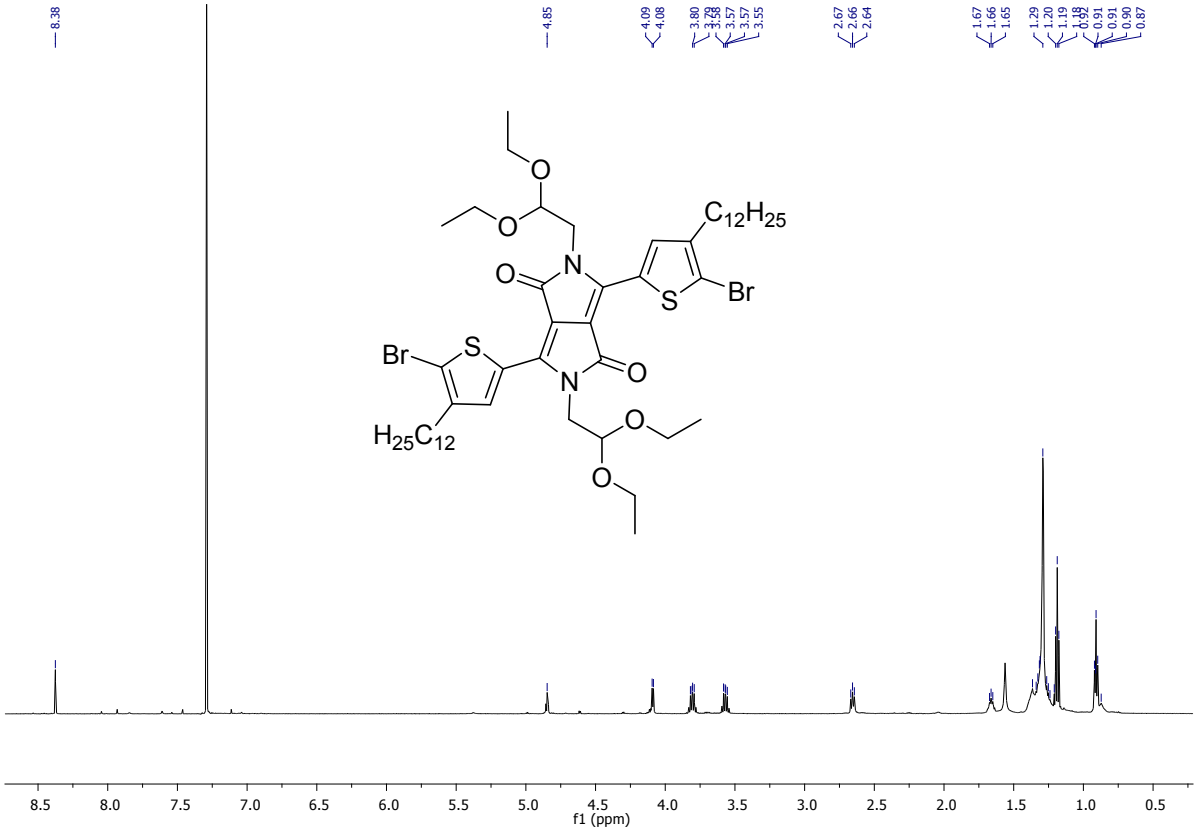

8.04
7.42
2.69
1.72
1.31
0.91
0.91
0.90
0.89
C8H17
H13C6
H
N
O
S
S
N
H
O
C6H13
H17C8
12.0 11.5 11.0 10.5 10.0 9.5 9.0 8.5 8.0 7.5 7.0 6.5 6.0 5.5 5.0 4.5 4.0 3.5 3.0 2.5 2.0 1.5 1.0 0.5
f1 (ppm)

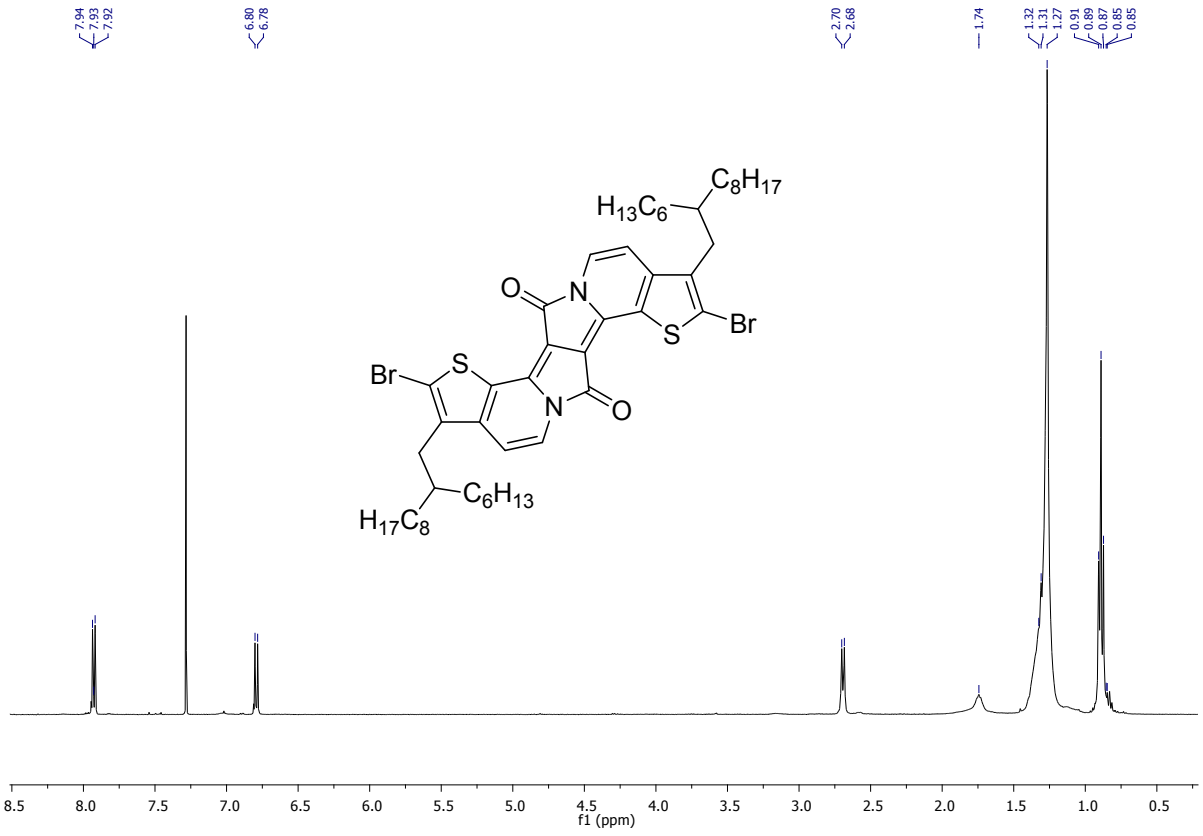

8.01
7.43
2.71
1.69
1.37
1.28
0.89
0.88
0.87
C12H25
H
N
O
S
S
N
H
O
H25C12
11.5 11.0 10.5 10.0 9.5 9.0 8.5 8.0 7.5 7.0 6.5 6.0 5.5 5.0 4.5 4.0 3.5 3.0 2.5 2.0 1.5 1.0
f1 (ppm)

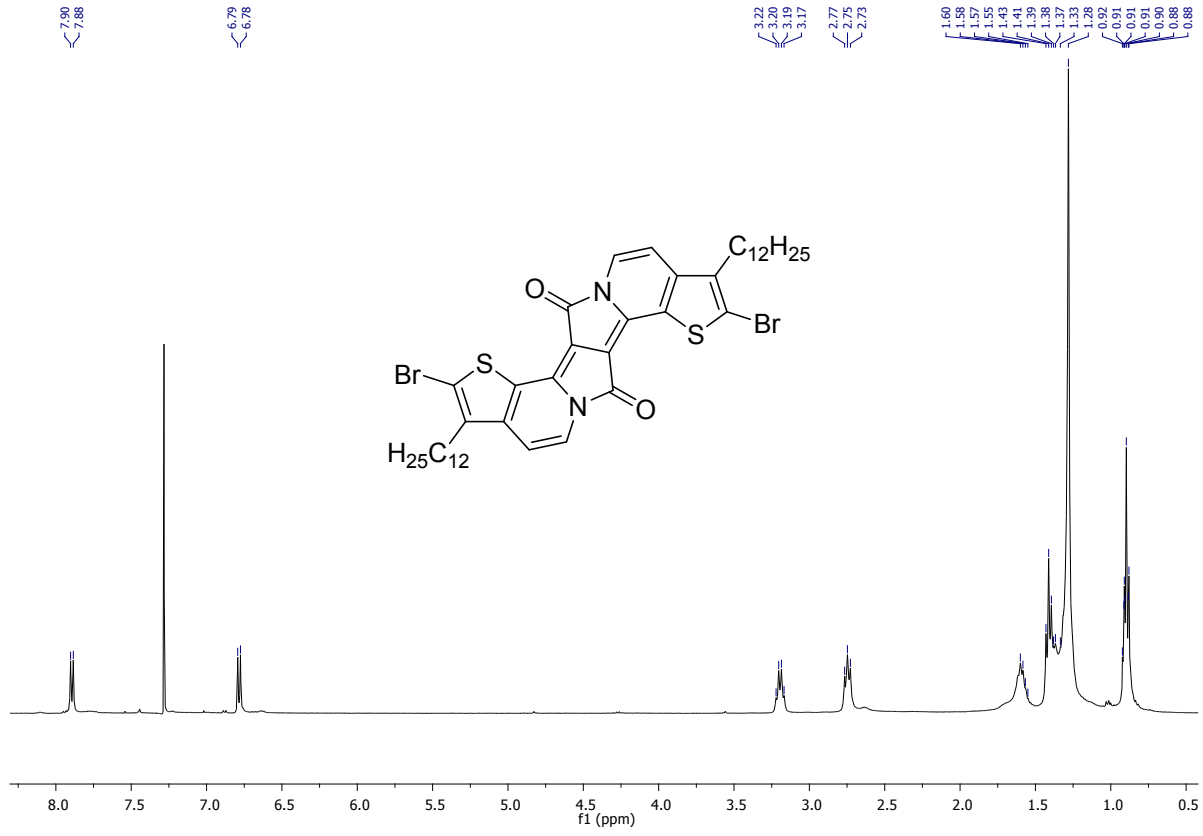

7.81
2.61
2.60
1.74
1.18
0.88
0.88
0.86
0.86
C8H17
H13C6
H
N
O
S
Br
Br
S
O
N
H
C6H13
H17C8
12.0 11.5 11.0 10.5 10.0 9.5 9.0 8.5 8.0 7.5 7.0 6.5 6.0 5.5 5.0 4.5 4.0 3.5 3.0 2.5 2.0 1.5 1.0 0.5
f1 (ppm)

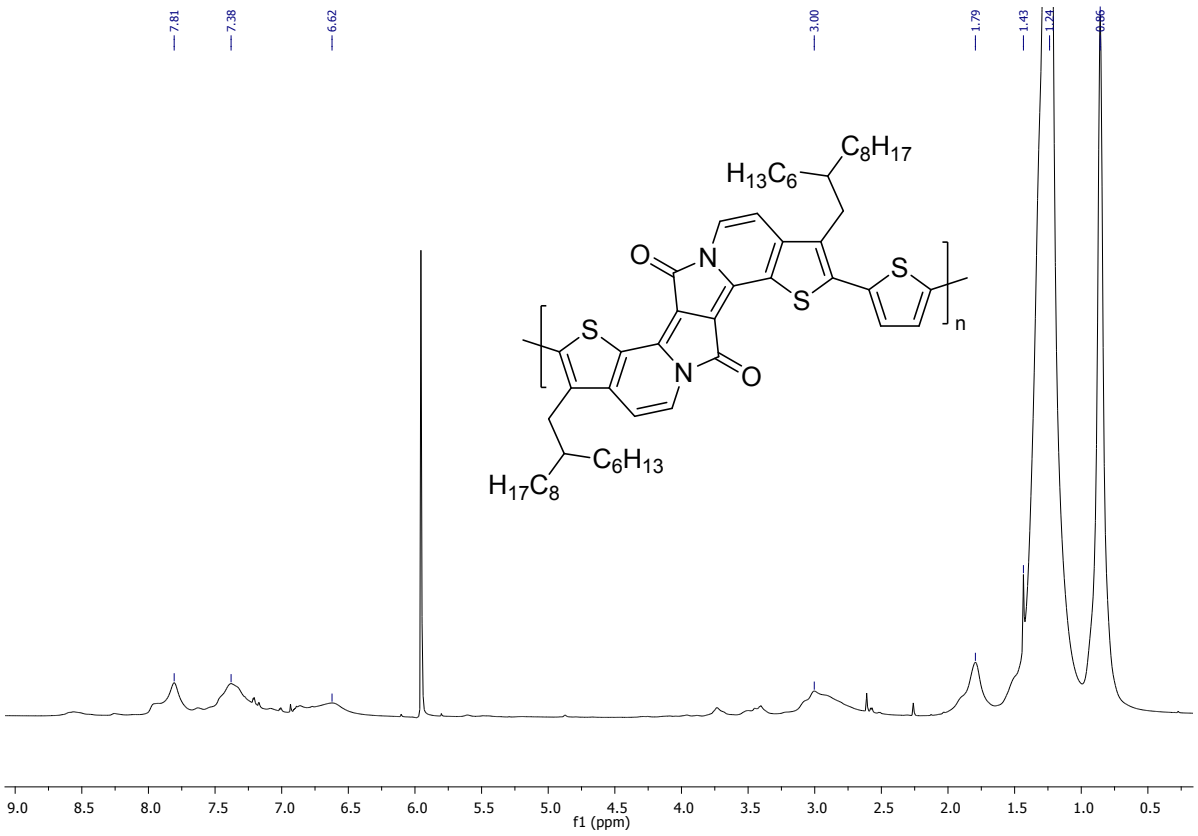

7.84
2.68
1.68
1.44
1.43
1.38
1.30
0.90
0.89
C12H25
H
N
O
S
Br
Br
S
O
N
H
H25C12
12.0 11.5 11.0 10.5 10.0 9.5 9.0 8.5 8.0 7.5 7.0 6.5 6.0 5.5 5.0 4.5 4.0 3.5 3.0 2.5 2.0 1.5 1.0 0.5
f1 (ppm)

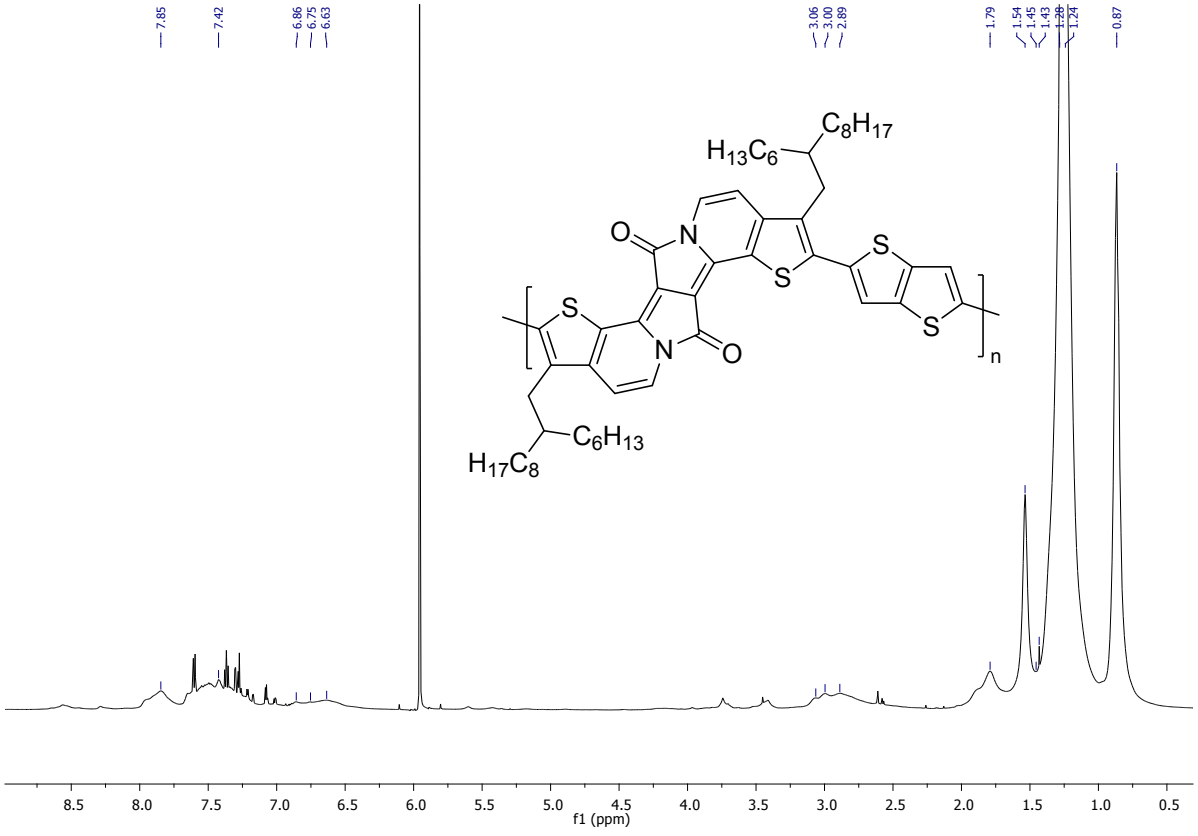

8.32
4.84
4.08
4.06
3.81
3.79
3.78
3.77
3.57
3.55
3.55
3.53
2.59
2.57
1.75
1.29
1.28
1.28
1.26
1.26
0.91
0.89
0.88
0.87
0.86
O
O
N
O
S
Br
Br
S
N
O
O
O
O
$H_{13}C_6$
C_8H_{17}
C_6H_{13}
$H_{17}C_8$
8.5
8.0
7.5
7.0
6.5
6.0
5.5
5.0
4.5
4.0
3.5
3.0
2.5
2.0
1.5
1.0
0.5
f1 (ppm)

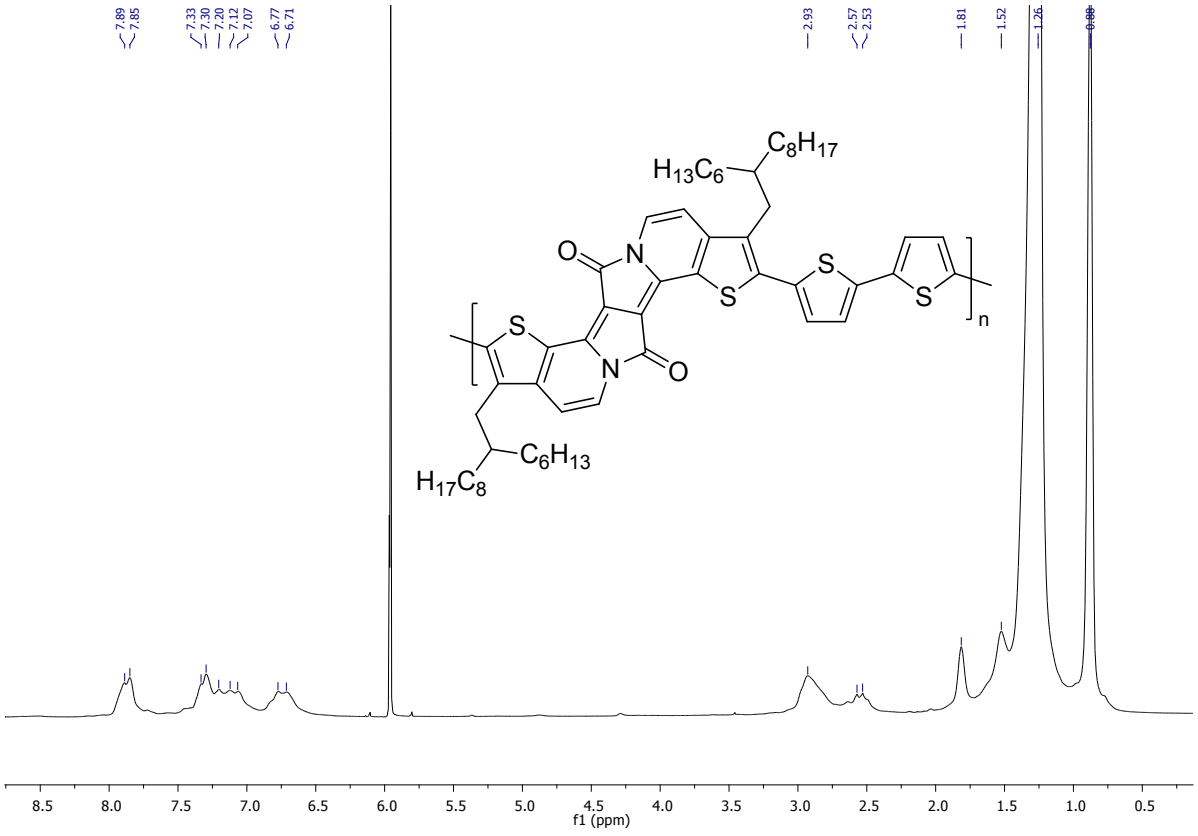

8.38
4.85
4.09
4.08
3.80
3.57
3.57
3.55
2.67
2.66
2.64
1.67
1.66
1.65
1.29
1.20
1.19
0.91
0.91
0.90
0.87
O
O
N
O
S
Br
Br
S
N
O
O
O
$C_{12}H_{25}$
$H_{25}C_{12}$
8.5
8.0
7.5
7.0
6.5
6.0
5.5
5.0
4.5
4.0
3.5
3.0
2.5
2.0
1.5
1.0
0.5
f1 (ppm)

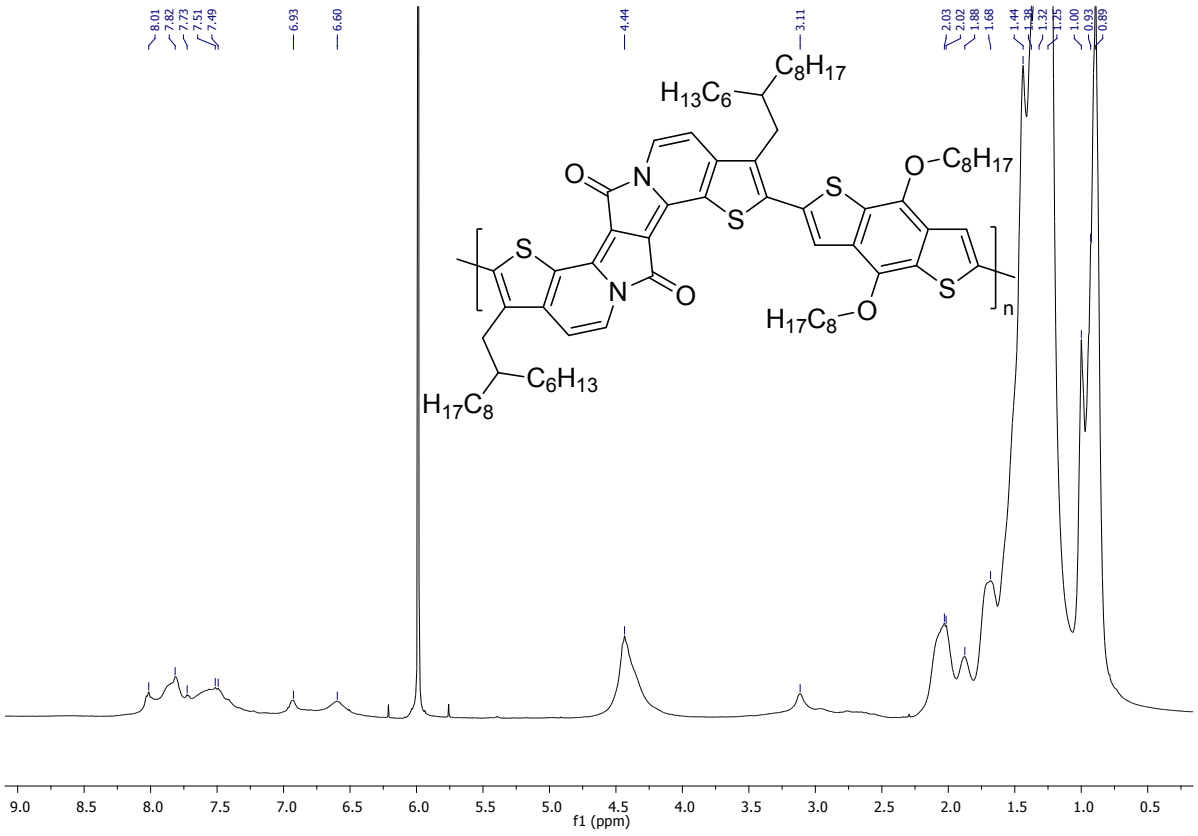

7.94
7.93
7.92
6.80
6.78
2.70
2.68
1.74
1.32
1.31
1.27
0.91
0.89
0.87
0.85
0.85
C8H17
H13C6
O
N
S
Br
Br
S
N
O
C6H13
H17C8
8.5
8.0
7.5
7.0
6.5
6.0
5.5
5.0
4.5
4.0
3.5
3.0
2.5
2.0
1.5
1.0
0.5
f1 (ppm)

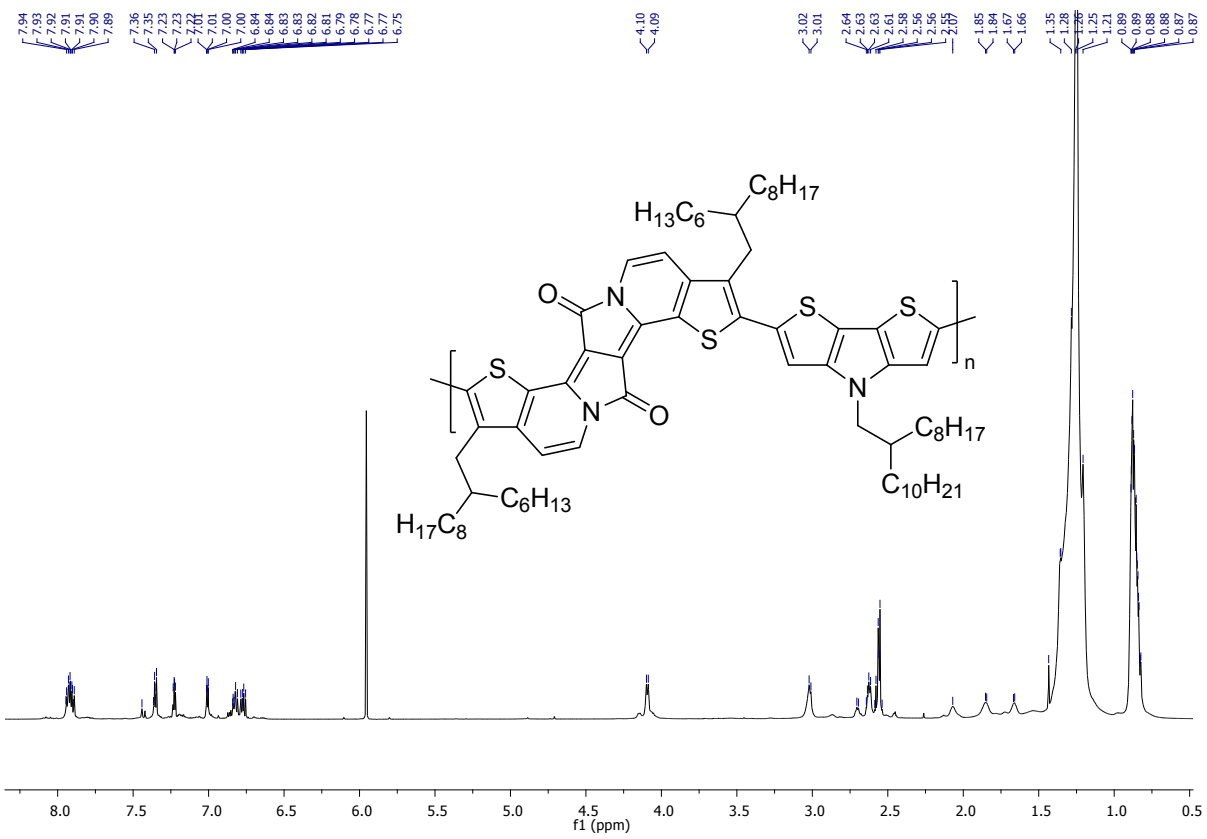

7.90
7.88
6.79
6.78
3.22
3.20
3.19
3.17
2.77
2.75
2.73
1.60
1.58
1.57
1.55
1.43
1.41
1.39
1.38
1.37
1.33
1.28
0.92
0.91
0.91
0.91
0.90
0.88
0.88
C12H25
O
N
S
Br
Br
S
N
O
H25C12
8.0
7.5
7.0
6.5
6.0
5.5
5.0
4.5
4.0
3.5
3.0
2.5
2.0
1.5
1.0
0.5
f1 (ppm)

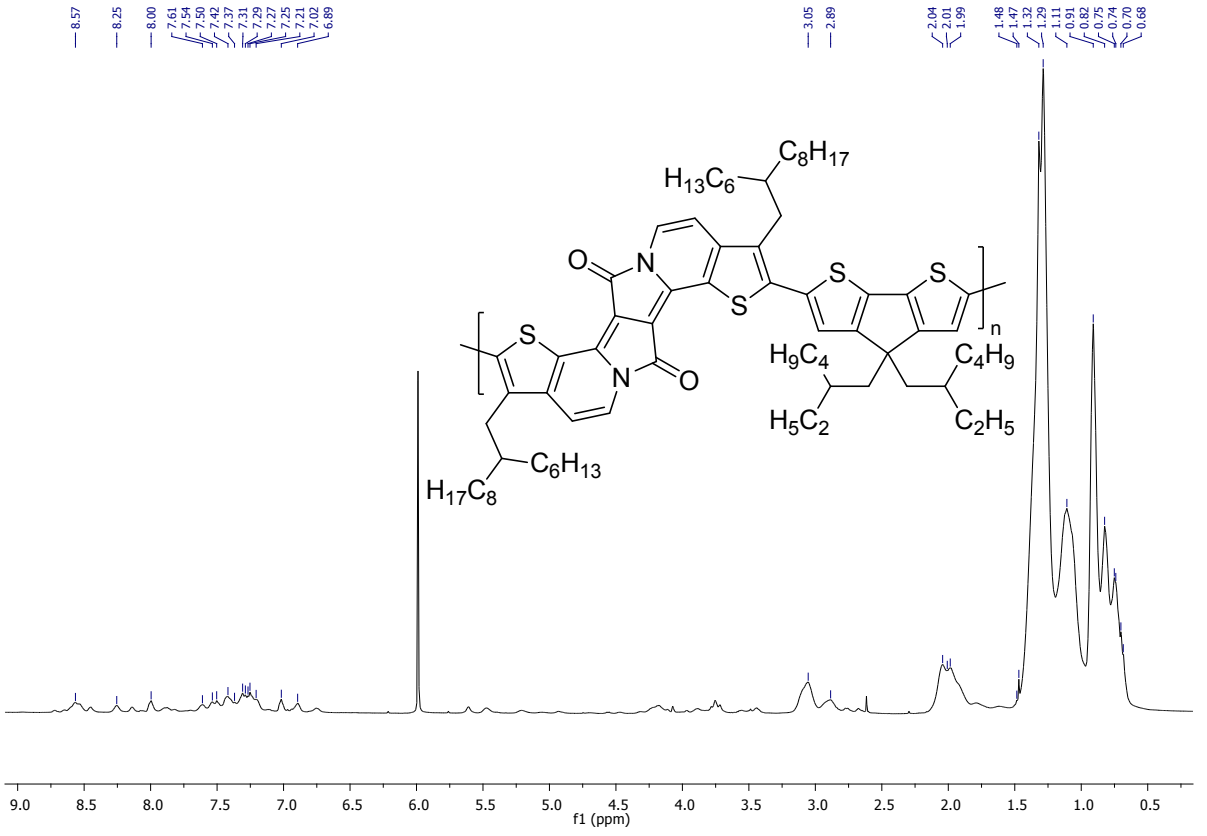

7.81
7.38
6.62
3.00
1.79
1.43
1.24
0.86
$H_{13}C_6$
C_8H_{17}
O
N
S
S
n
S
N
O
$H_{17}C_8$
C_6H_{13}
9.0 8.5 8.0 7.5 7.0 6.5 6.0 5.5 5.0 4.5 4.0 3.5 3.0 2.5 2.0 1.5 1.0 0.5
f1 (ppm)

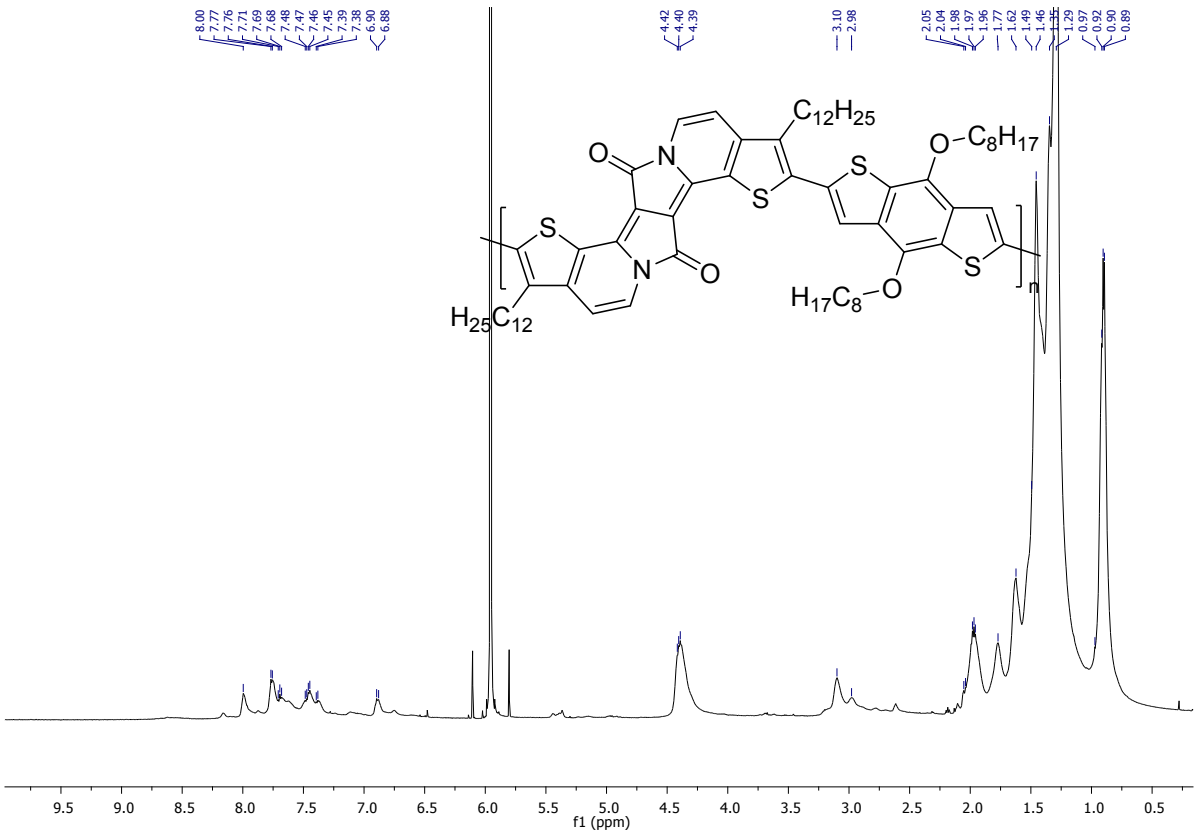

7.85
7.42
6.86
6.75
6.63
3.06
3.00
2.89
1.79
1.54
1.45
1.43
1.28
1.24
0.87
$H_{13}C_6$
C_8H_{17}
O
N
S
S
S
S
n
N
O
$H_{17}C_8$
C_6H_{13}
8.5 8.0 7.5 7.0 6.5 6.0 5.5 5.0 4.5 4.0 3.5 3.0 2.5 2.0 1.5 1.0 0.5
f1 (ppm)

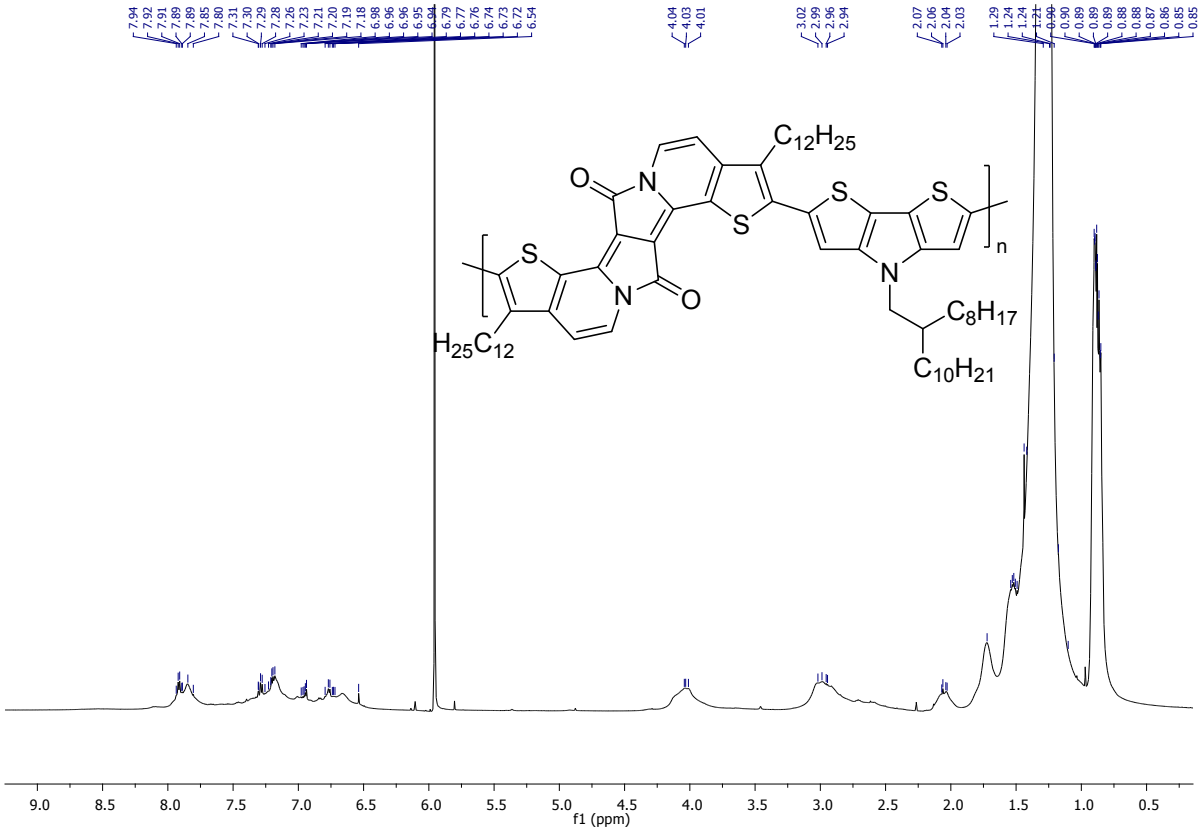

7.89
7.85
7.33
7.30
7.20
7.12
7.07
6.77
6.71
2.93
2.57
2.53
1.81
1.52
1.26
0.88
0.86
C8H17
H13C6
O
N
S
S
S
n
S
N
O
C6H13
H17C8
8.5
8.0
7.5
7.0
6.5
6.0
5.5
5.0
4.5
4.0
3.5
3.0
2.5
2.0
1.5
1.0
0.5
f1 (ppm)

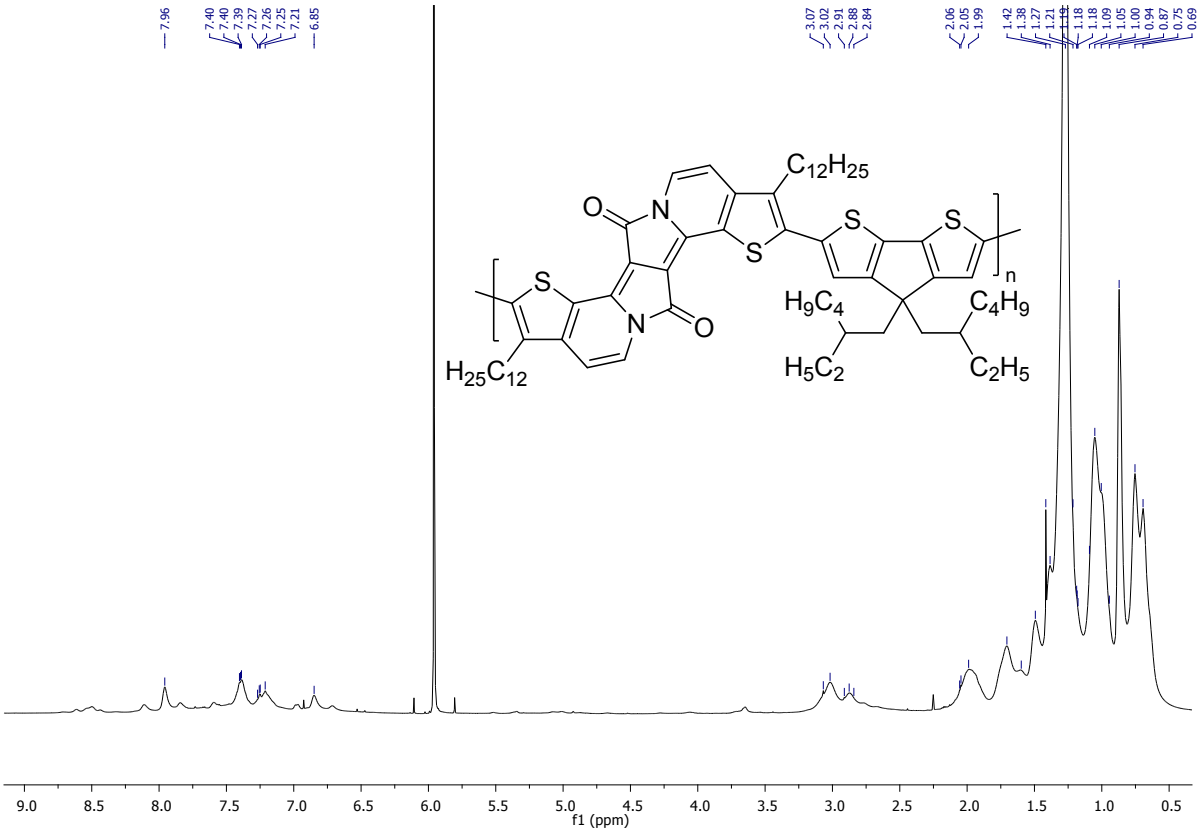

8.01
7.82
7.73
7.51
7.49
6.93
6.60
4.44
3.11
2.03
2.02
1.88
1.68
1.44
1.32
1.25
1.00
0.93
0.89
C8H17
H13C6
O
N
S
S
S
O-C8H17
n
S
N
O
H17C8-O
C6H13
H17C8
9.0
8.5
8.0
7.5
7.0
6.5
6.0
5.5
5.0
4.5
4.0
3.5
3.0
2.5
2.0
1.5
1.0
0.5
f1 (ppm)

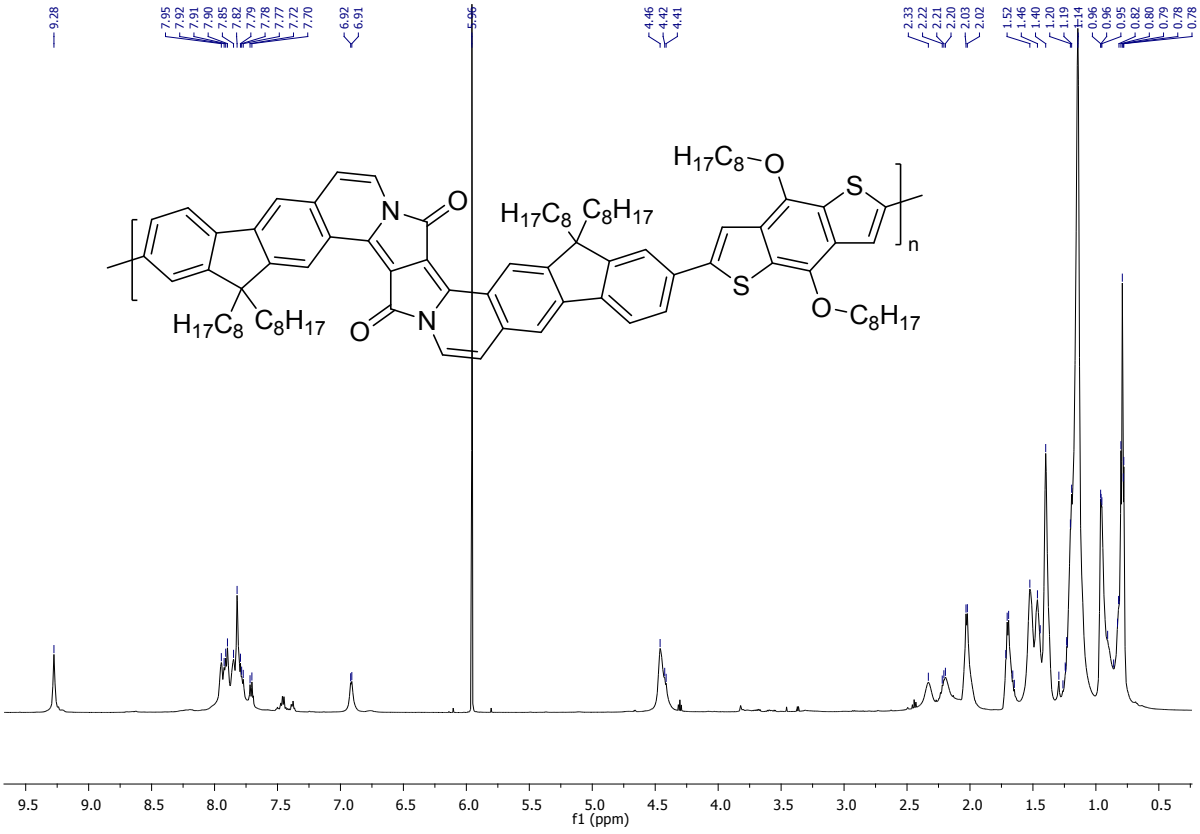

7.94 7.93 7.92 7.91 7.91 7.90 7.89
7.36 7.35 7.23 7.23 7.22 7.01 7.01 7.00 7.00 6.84 6.84 6.83 6.83 6.82 6.81 6.79 6.78 6.77 6.77 6.75
4.10 4.09
3.02 3.01
2.64 2.63 2.63 2.61 2.58 2.56 2.56 2.55 2.07
1.85 1.84 1.67 1.66
1.35 1.28 1.25 1.21
0.89 0.89 0.88 0.88 0.87 0.87
C8H17
H13C6
O
N
S
S
S
n
N
C8H17
C10H21
S
N
O
C6H13
H17C8
8.0 7.5 7.0 6.5 6.0 5.5 5.0 4.5 4.0 3.5 3.0 2.5 2.0 1.5 1.0 0.5
f1 (ppm)

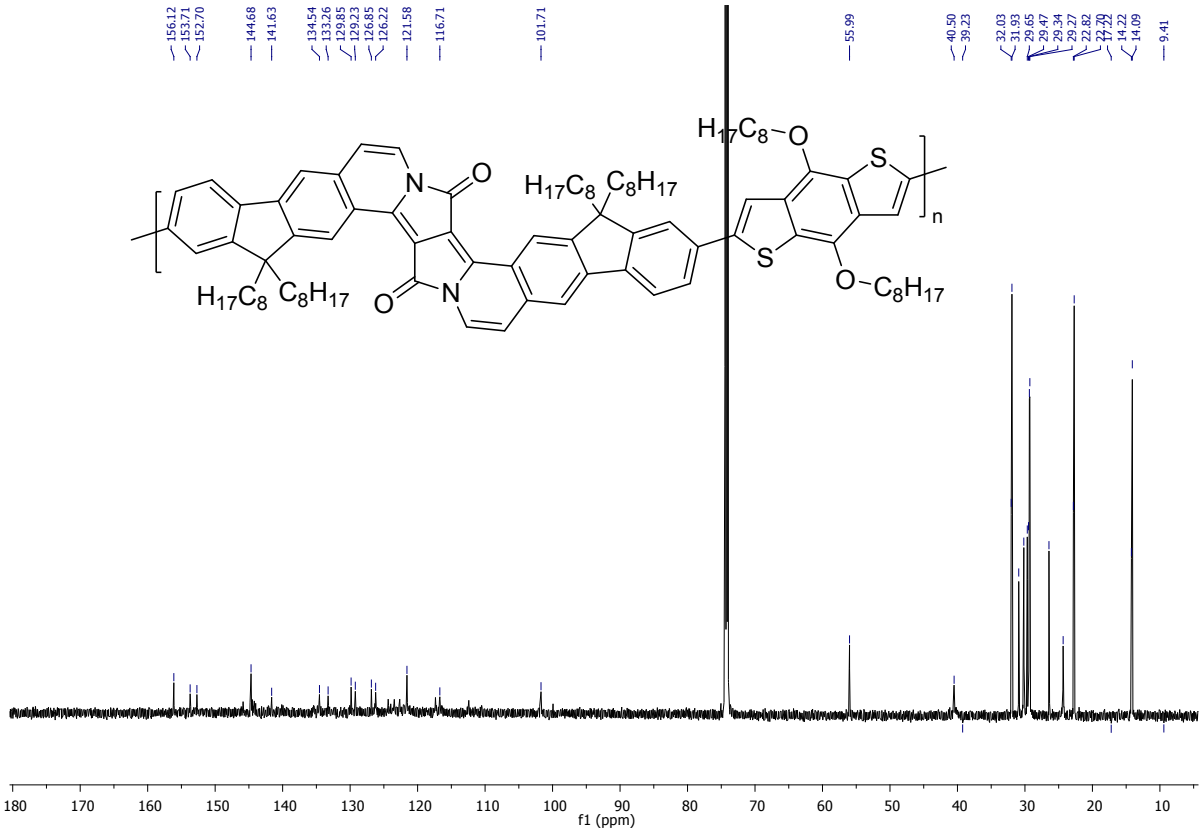

8.57
8.25
8.00
7.61 7.54 7.50 7.42 7.37 7.31 7.29 7.27 7.25 7.21 7.02 6.89
3.05
2.89
2.04 2.01 1.99
1.48 1.47 1.32 1.29 1.11 0.91 0.82 0.75 0.74 0.70 0.68
C8H17
H13C6
O
N
S
S
S
n
H9C4
C4H9
H5C2
C2H5
S
N
O
C6H13
H17C8
9.0 8.5 8.0 7.5 7.0 6.5 6.0 5.5 5.0 4.5 4.0 3.5 3.0 2.5 2.0 1.5 1.0 0.5
f1 (ppm)

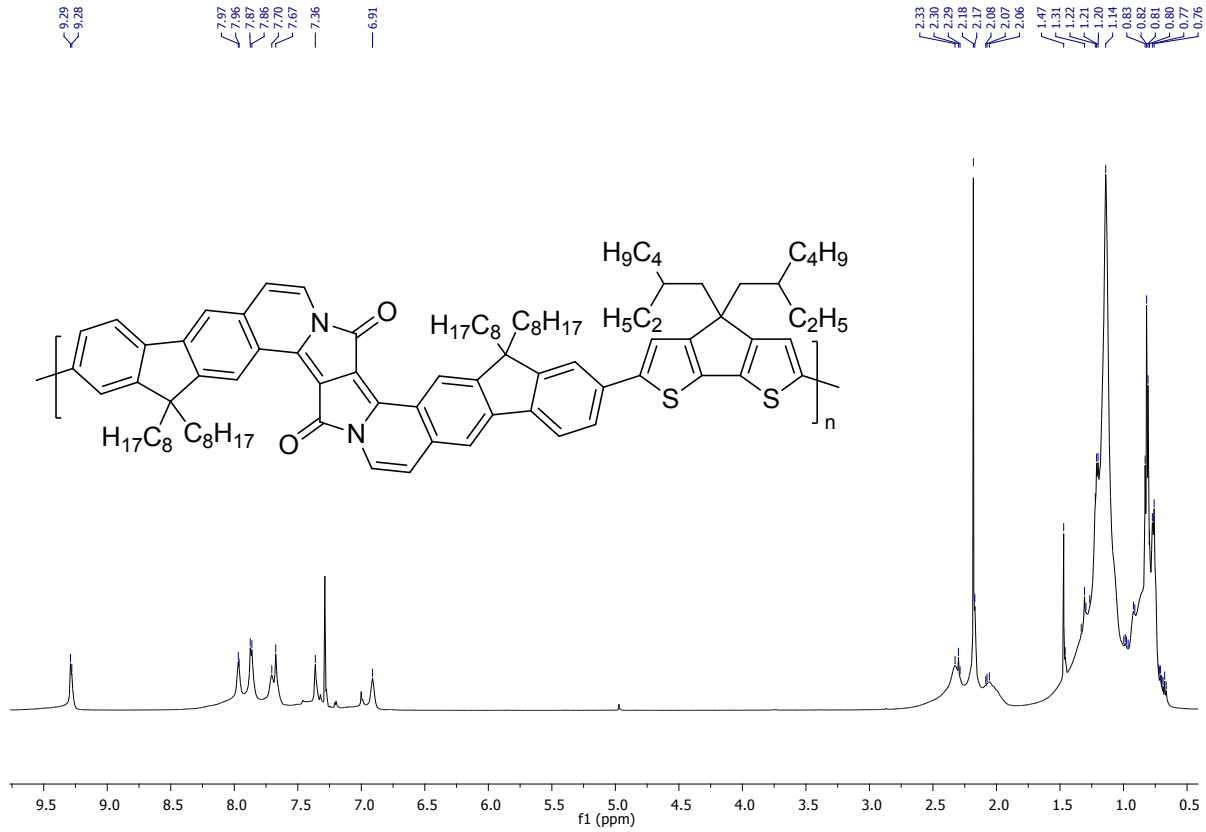

8.00
7.77
7.76
7.71
7.69
7.68
7.48
7.47
7.46
7.45
7.39
7.38
6.90
6.88
4.42
4.40
4.39
3.10
2.98
2.05
2.04
1.98
1.97
1.96
1.77
1.62
1.49
1.46
1.29
0.97
0.92
0.90
0.89
C12H25
O
N
S
O-C8H17
H17C8-O
H25C12
n
9.5
9.0
8.5
8.0
7.5
7.0
6.5
6.0
5.5
5.0
4.5
4.0
3.5
3.0
2.5
2.0
1.5
1.0
0.5
f1 (ppm)

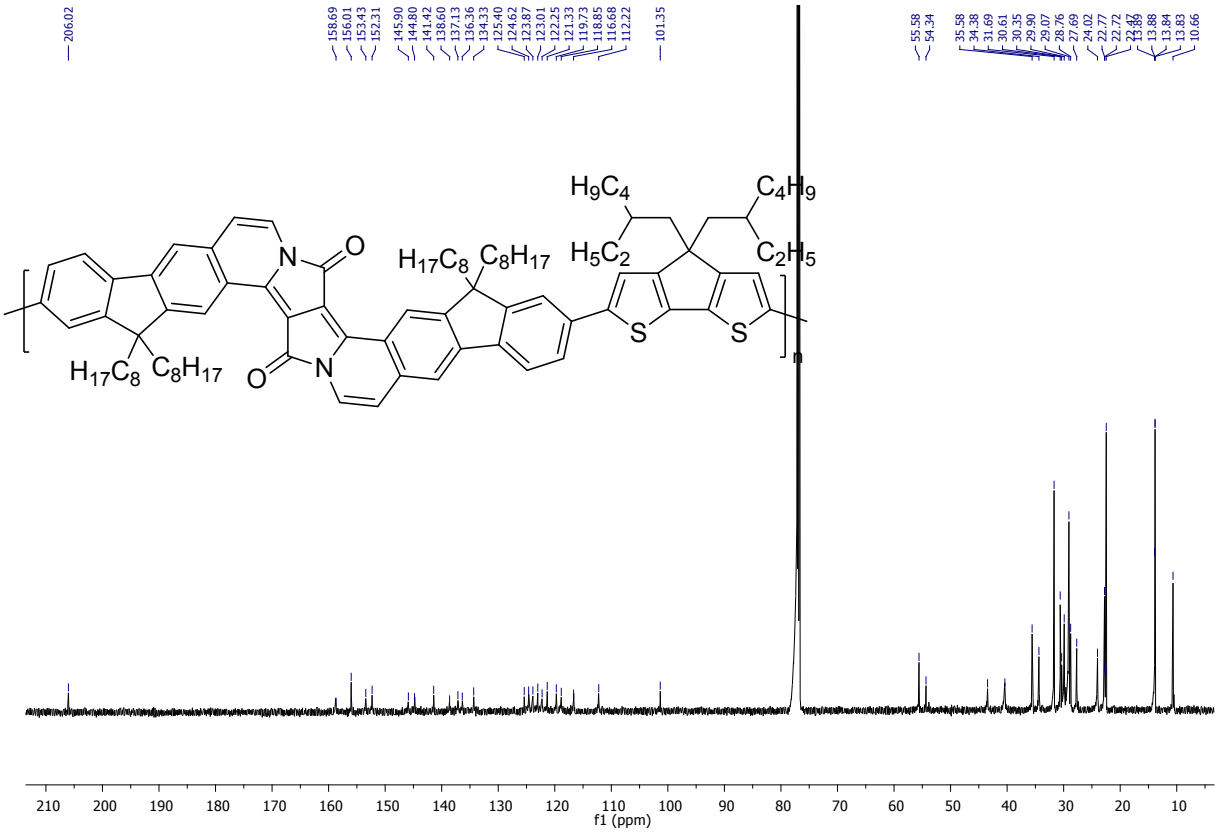

7.94
7.92
7.91
7.89
7.89
7.85
7.80
7.31
7.30
7.29
7.28
7.26
7.23
7.21
7.20
7.19
7.18
6.98
6.96
6.96
6.95
6.94
6.79
6.77
6.76
6.74
6.73
6.72
6.54
4.04
4.03
4.01
3.02
2.99
2.96
2.94
2.07
2.06
2.04
2.03
1.29
1.24
1.24
1.21
0.90
0.89
0.89
0.89
0.88
0.88
0.87
0.86
0.85
0.85
C12H25
O
N
S
n
C8H17
C10H21
H25C12
9.0
8.5
8.0
7.5
7.0
6.5
6.0
5.5
5.0
4.5
4.0
3.5
3.0
2.5
2.0
1.5
1.0
0.5
f1 (ppm)


7.96
7.40
7.40
7.39
7.27
7.26
7.25
7.21
6.85
3.07
3.02
2.91
2.88
2.84
2.06
2.05
1.99
1.42
1.38
1.27
1.21
1.18
1.18
1.09
1.05
1.00
0.94
0.87
0.75
0.69
C12H25
O
N
S
S
S
n
S
N
O
H9C4
C4H9
H25C12
H5C2
C2H5
9.0
8.5
8.0
7.5
7.0
6.5
6.0
5.5
5.0
4.5
4.0
3.5
3.0
2.5
2.0
1.5
1.0
0.5
f1 (ppm)


9.28
7.95
7.92
7.91
7.90
7.85
7.82
7.79
7.78
7.77
7.72
7.70
6.92
6.91
5.96
4.46
4.42
4.41
2.33
2.22
2.21
2.20
2.03
2.02
1.52
1.46
1.40
1.20
1.19
1.14
0.96
0.96
0.95
0.82
0.80
0.79
0.78
0.78
H17C8
O
N
O
H17C8 C8H17
H17C8 C8H17
O
S
n
S
O
C8H17
9.5
9.0
8.5
8.0
7.5
7.0
6.5
6.0
5.5
5.0
4.5
4.0
3.5
3.0
2.5
2.0
1.5
1.0
0.5
f1 (ppm)


156.12
153.71
152.70
144.68
141.63
134.54
133.26
129.85
129.23
126.85
126.22
121.58
116.71
101.71
55.99
40.50
39.23
32.03
31.93
29.65
29.47
29.34
29.27
22.82
14.22
14.09
9.41
H17C8–O
S
n
N
O
H17C8 C8H17
S
O–C8H17
O
N
H17C8 C8H17
180 170 160 150 140 130 120 110 100 90 80 70 60 50 40 30 20 10
f1 (ppm)


9.29
9.28
7.97
7.96
7.87
7.86
7.70
7.67
7.36
6.91
2.33
2.30
2.29
2.18
2.17
2.08
2.07
2.06
1.47
1.31
1.22
1.21
1.20
1.14
0.83
0.82
0.81
0.80
0.77
0.76
H9C4
C4H9
H5C2
C2H5
N
O
H17C8 C8H17
S
S
n
H17C8 C8H17
O
N
9.5 9.0 8.5 8.0 7.5 7.0 6.5 6.0 5.5 5.0 4.5 4.0 3.5 3.0 2.5 2.0 1.5 1.0 0.5
f1 (ppm)


206.02
158.69
156.01
153.43
152.31
145.90
144.80
141.42
138.60
137.13
136.36
134.33
125.40
124.62
123.87
123.01
122.25
121.33
119.73
118.85
116.68
112.22
101.35
55.58
54.34
35.58
34.38
31.69
30.61
30.35
29.90
29.07
28.76
27.69
24.02
22.77
22.72
13.88
13.84
13.83
10.66
H9C4
C4H9
H17C8
C8H17
H5C2
C2H5
N
O
S
n
210
200
190
180
170
160
150
140
130
120
110
100
90
80
70
60
50
40
30
20
10
f1 (ppm)