Electronic Supplementary Material (ESI) for Journal of Materials Chemistry C.

Supporting Information

Bromination of the Benzothioxanthene bloc: Toward New π-Conjugated Systems for Organic Electronic Applications

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General methods

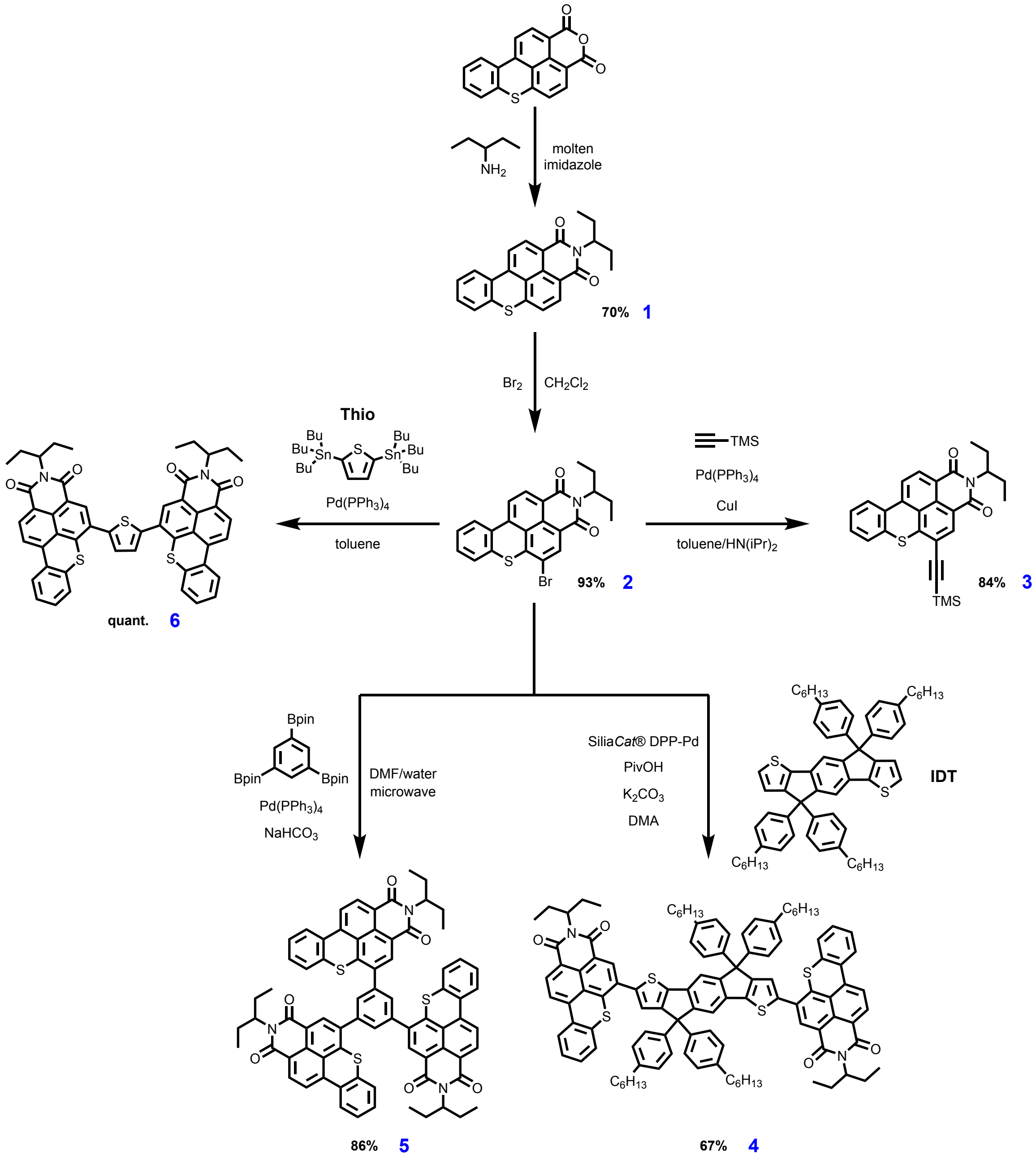
All reagents and solvents were purchased from commercial sources and used without further purification unless otherwise stated. Reactions were carried out under an argon atmosphere unless otherwise stated. Flash chromatography was performed with analytical-grade solvents using Aldrich silica gel (technical grade, pore size 60 Å, 230–400 mesh particle size). Flexible plates ALUGRAM® XtraSIL G UV254 from MACHEREY-NAGEL were used for TLC. Compounds were detected by UV irradiation (Bioblock Scientific) or staining with I_2, unless stated otherwise. ^{1}H and ^{13}C NMR were recorded on a Bruker AVANCE III 300 (^{1}H, 300 MHz ; ^{13}C, 75 MHz) or a Bruker AVANCE DRX500 (^{1}H, 500 MHz ; ^{13}C, 125 MHz). Chemical shifts are given in parts per million (ppm) relative to TMS and coupling contants *J* in Hertz (Hz). High resolution mass spectrometry (HRMS) was performed with a JEOL JMS-700 B/E. UV-visible absorption spectra were recorded with a Shimadzu UV-1800 spectrometer. Electrochemical measurements were performed with a Biologic SP-150 potentiostat with positive feedback compensation using a conventional single-compartment three-electrode cell. The working electrode was a platinum electrode. The auxiliary was a platinum wire and the pseudo-reference electrode was a silver wire calibrated with the ferrocene potential. The supporting electrolyte was 0.1 M Bu_4NPF_6 (tetrabutylammonium hexafluorophosphate) in dichloromethane (DCM) and solutions were purged with argon prior to each experiments. All potentials are quoted relative to Fc/Fc^+. In all the experiments the scan rate was 100 mV/s.

General procedure for purification with recycling preparative HPLC :

Crude compounds were solubilized in HPLC grade chloroform (stabilized with ethanol, 5 mL). Prior to injection, the solution was filtered through a 0.45 μm PTFE filter (VWR 25mm syringe filter w/ 0.45 μm membrane). Purification was performed on a LC-9160NEXT system from the Japan Analytical Industry Co., Ltd. (JAI) equipped with coupled UV-vis 4Ch NEXT and RI-700 II detectors at room temperature through a set of two JAIGEL-2H and 2.5H columns at an elution rate of 10 mL.min^{-1}.

Synthetic Procedures

4,4,9,9-tetrakis(4-hexylphenyl)-4,9-dihydro-s-indaceno[1,2-b:5,6-b']dithiophene (**IDT**)[1] and 2,5-bis(tributylstannyl)thiophene (**Thio**)[2] were synthetized according to reported procedures.



2-(pentan-3-yl)-1H-thioxantheno[2,1,9-def]isoquinoline-1,3(2H)-dione (**1**) : 1H,3H-thioxantheno[2,1,9-def]isochromene-1,3-dione (500 mg, 1.64 mmol), 3-aminopentane (157 mg, 1.81 mmol) and imidazole (5 g) were placed into a 100 mL round bottom flask equipped with a condenser and heated at 100°C for five hours. After cooling down to room temperature, 1M HCl was added and the mixture was extracted with dichloromethane. The organic layers were washed with water and brine, then dried over $MgSO_4$. The solvent was removed by rotary evaporation and the crude was purified by silica gel column chromatography with petroleum ether:dichloromethane (3:7 v/v) as eluent. The product was obtained in 70% yield (434 mg). **^{1}H NMR** (500 MHz, $CDCl_3$) δ = 8.61 (d, *J*=8.2, 1H), 8.41 (d, *J*=8.0, 1H), 8.26 – 8.16 (m, 2H), 7.51 (d, *J*=8.0, 1H), 7.42 – 7.39 (m, 3H), 5.07 (td, *J*=9.6, 4.8, 1H), 2.33 – 2.14 (m, 2H), 1.99 – 1.81 (m, 2H), 0.89 (t, *J*=7.5, 7H). **^{13}C NMR** (125 MHz, $CDCl_3$) δ = 140.25, 136.64, 131.86, 130.77, 130.05, 128.29, 127.73, 126.63, 126.28, 125.72, 120.54, 119.40, 57.50, 25.08, 11.47. **HRMS (CI)** calculated for $C_{23}H_{19}NO_2S$ 373.1136, found 373.1133 (Δ = 0.9 ppm).

5-bromo-2-(pentan-3-yl)-1H-thioxantheno[2,1,9-def]isoquinoline-1,3(2H)-dione (**2**) : To a solution of 2-(pentan-3-yl)-1H-thioxantheno[2,1,9-def]isoquinoline-1,3(2H)-dione (1) (500 mg, 1.34 mmol) in dichloromethane (100 mL) was added dropwise a solution of bromine in dichloromethane (214 mg, 1.34 mmol, 1M). The reaction mixture was stirred at room temperature for 12h before being washed with saturated $Na_2S_2O_3$, water and brine. After drying over $MgSO_4$, the solvent was removed by rotary evaporation and the crude was subjected to silica gel column chromatography using dichloromethane as eluent. The product was obtained in 93% yield (568 mg). **^{1}H NMR** (500 MHz, $CDCl_3$) δ = 8.62 (d, *J*=8.0, 2H), 8.32 – 8.09 (m, 2H), 7.47 (m, 3H), 5.15 – 4.95 (m, 1H), 2.37 – 2.09 (m, 2H), 2.05 – 1.73 (m, 2H), 0.89 (t, *J*=7.5, 6H). **^{13}C NMR** (125 MHz, $CDCl_3$) δ = 140.31, 136.34, 131.86, 130.25, 129.31, 128.19, 127.72, 127.00, 126.06, 120.09, 114.62, 57.74, 25.03, 11.45. **HRMS (EI)** calculated for $C_{23}H_{18}BrNO_2S$ 451.0242, found 451.0240 (Δ = 0.4 ppm).

2-(pentan-3-yl)-5-((trimethylsilyl)ethynyl)-1H-thioxantheno[2,1,9-def]isoquinoline-1,3(2H)-dione (**3**) : 5-bromo-2-(pentan-3-yl)-1H-thioxantheno[2,1,9-def]isoquinoline-1,3(2H)-dione (2) (50 mg, 110.53 µmol), tetrakis-(triphenylphosphine) palladium(0) (6.4 mg, 5.53 µmol) and copper(I) iodide (1.5 mg, 7.74 µmol) were degassed under vacuum in a dry Schlenk tube equipped with a stir bar. A mixture of HPLC grade toluene and diisopropylamine (1:1 ratio v/v, 5 mL, degassed by argon bubbling for 30 min) was added to the powders. Ethynyltrimethylsilane (21.7 mg, 221.06 µmol) was added and the reaction mixture was heated overnight at 50°C under an argon atmosphere. After cooling down to room temperature, the solvent was removed by rotary evaporation and the crude was purified by silica gel column chromatography using dichloromethane as eluent. The product was obtained in 84% yield (44 mg). **^{1}H NMR** (300 MHz, $CDCl_3$) δ = 8.43 (d, *J*=8.2, 1H), 8.35 (s, 1H), 8.00 (d, *J*=8.3, 2H), 7.37 – 7.22 (m, 3H), 5.04 (m, 1H), 2.39 – 2.10 (m, 2H), 2.03 – 1.85 (m, 2H), 0.93 (t, *J*=7.5, 6H), 0.39 (s, 9H). **^{13}C NMR** (75 MHz, $CDCl_3$) δ = 143.06, 136.03, 134.11, 132.38, 131.80, 129.84, 129.49, 127.67, 127.35, 126.77, 125.66, 125.11, 121.47, 119.44, 117.80, 114.38, 106.08, 100.42, 57.48, 29.82, 24.98, 11.51, 0.05. **HRMS (FAB+)** calculated for $C_{28}H_{27}NO_2SSi$ 469.1532, found 469.1532 (Δ = 0 ppm).

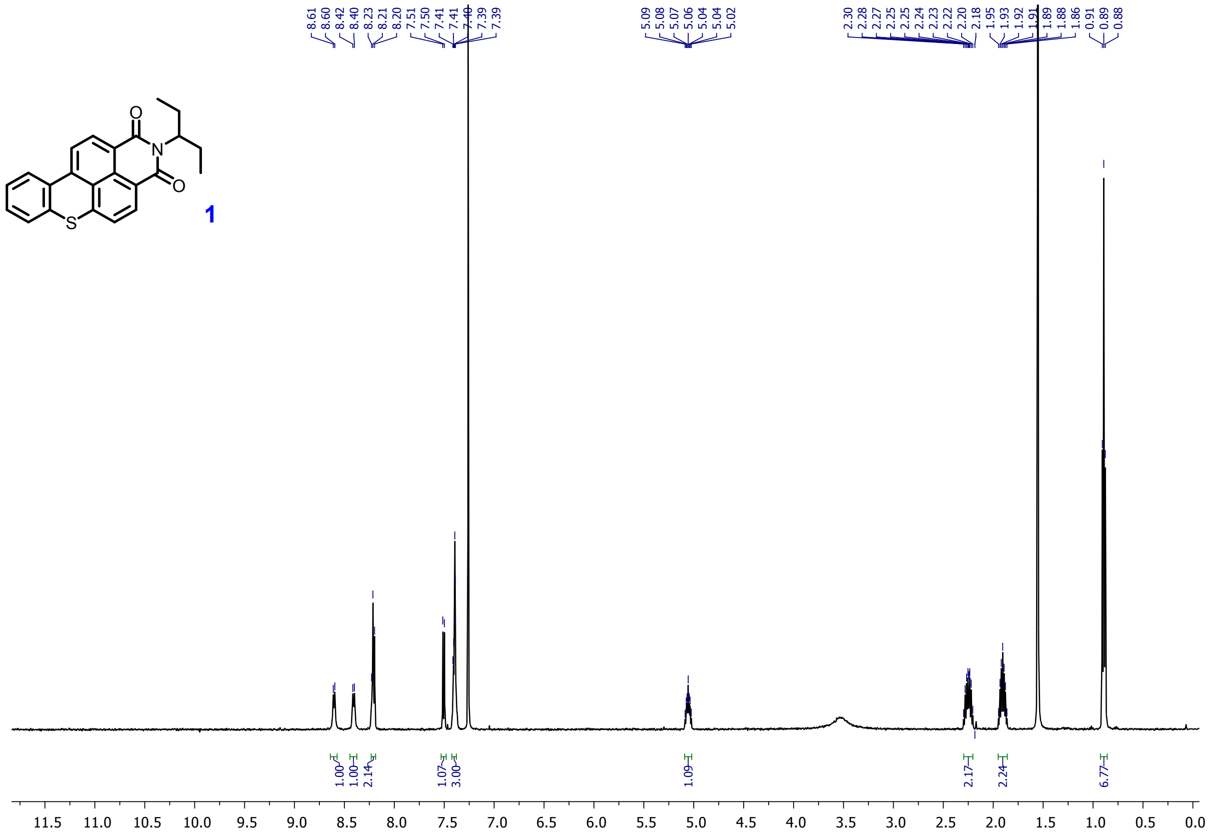
5,5'-(4,4,9,9-tetrakis(4-hexylphenyl)-4,9-dihydro-s-indaceno[1,2-b:5,6-b']dithiophene-2,7-diyl)bis(2-(pentan-3-yl)-1H-thioxantheno[2,1,9-def]isoquinoline-1,3(2H)-dione) (**4**) : 4,4,9,9-tetrakis(4-hexylphenyl)-4,9-dihydro-s-indaceno[1,2-b:5,6-b']dithiophene (**IDT**) (100 mg, 110.20 µmol), 5-bromo-2-(pentan-3-yl)-1H-thioxantheno[2,1,9-def]isoquinoline-1,3(2H)-dione (2) (99.7 mg, 220.41 µmol), Silia*Cat*® DPP-Pd (43 mg, 11.02 µmol, 0.25 mmol/g), potassium carbonate (38 mg, 275.51 µmol) and pivalic acid (3.4 mg, 33.06 µmol) were degassed under vacuum in a dry Schlenk tube equipped with a stir bar. Dry and degassed dimethylacetamide (10 mL, argon bubbling for 30 min) was added to the powders and the reaction mixture was heated overnight at 80°C under an argon atmosphere. After cooling down to room temperature, the crude was dried by rotary evaporation before being solubilized in a minimum amount of $CHCl_3$ and flashed through a short plug of silica to remove the catalyst and baseline impurities. Then, to reach a high degree of purity, the resulting product was injected in a recycling preparative HPLC following the procedure described above. The product was obtained in 67% yield (121 mg). **^{1}H NMR** (300 MHz, $CDCl_3$) δ = 8.62 (d, *J*=8.1, 1H), 8.51 (s, 1H), 8.29 – 8.18 (m, 2H), 7.55 (s, 1H), 7.45 – 7.35 (m, 2H), 7.31 (m, 4H), 7.12 (d, *J*=8.2, 4H), 5.06 (m, 1H), 2.68 – 2.51 (m, 4H), 2.35 – 2.13 (m, 2H), 1.98 – 1.82 (m, 2H), 1.62 (m, 4H), 1.40 – 1.23 (m, 12H), 0.88 (m, 12H). **^{13}C NMR** (75 MHz, $CDCl_3$) δ = 156.33, 153.48, 142.86, 141.79, 141.13, 140.17, 137.02, 135.50, 131.92, 130.01, 129.96, 128.60, 128.06, 127.89, 127.76, 127.23, 126.94, 126.33, 126.03, 124.90, 119.91, 117.96, 63.33, 57.55, 35.75, 31.89, 31.56, 29.32, 25.05, 22.76, 14.27, 11.45. **HRMS (FAB+)** calculated for $C_{110}H_{108}N_2O_4S_4$ 1648.7192, found 1648.7168 (Δ = 1.5 ppm).

5,5',5''-(benzene-1,3,5-triyl)tris(2-(pentan-3-yl)-1H-thioxantheno[2,1,9-def]isoquinoline-1,3(2H)-dione) (5) : 1,3,5-tris(4,4,5,5-tetramethyl-1,3,2-dioxaborolan-2-yl)benzene (50 mg, 109.65 µmol), 5-bromo-2-(pentan-3-yl)-1H-thioxantheno[2,1,9-def]isoquinoline-1,3(2H)-dione (2) (148.8 mg, 328.95 µmol), tetrakis-(triphenylphosphine) palladium(0) (19 mg, 16.45 µmol) and sodium hydrogenocarbonate (82.9 mg, 986.84 µmol) were suspended in a mixture of DMF (8 mL) and H_2O (5 mL) in a 50 mL long single neck flask equipped with a condenser. The mixture was irradiated under microwaves in the cavity of a CEM®-Discover machine for 45 min at a pre-selected temperature of 150°C, using a maximum irradiation power of 150 W. The flask was then cooled to room temperature and chloroform was added. The organic phase was washed with water and brine, dried over $MgSO_4$ and concentrated *in vacuum*. The crude was purified by column chromatography on silica gel using chloroform as eluent to afford the desired compound in 86% yield (112 mg). **^{1}H NMR** (300 MHz, $CDCl_3$) δ = 8.65 (d, *J*=8.1, 1H), 8.57 (s, 1H), 8.28 (d, *J*=8.4, 1H), 8.26 – 8.19 (m, 1H), 7.76 (s, 1H), 7.72 – 7.62 (m, 2H), 7.54 (dd, *J*=7.2, 1.5, 1H), 7.45 (m, 5H), 5.15 – 5.00 (m, 1H), 2.26 (m, 2H), 1.89 (m, 2H), 0.90 (t, *J*=7.4, 6H). **^{13}C NMR** Due to solubility issues, we were unable to obtain a complete ^{13}C NMR spectrum. **HRMS (MALDI-TOF)** calculated for $C_{75}H_{57}N_3O_6S_3$ 1191.3409, found 1191.3393 (Δ = 1.3 ppm).

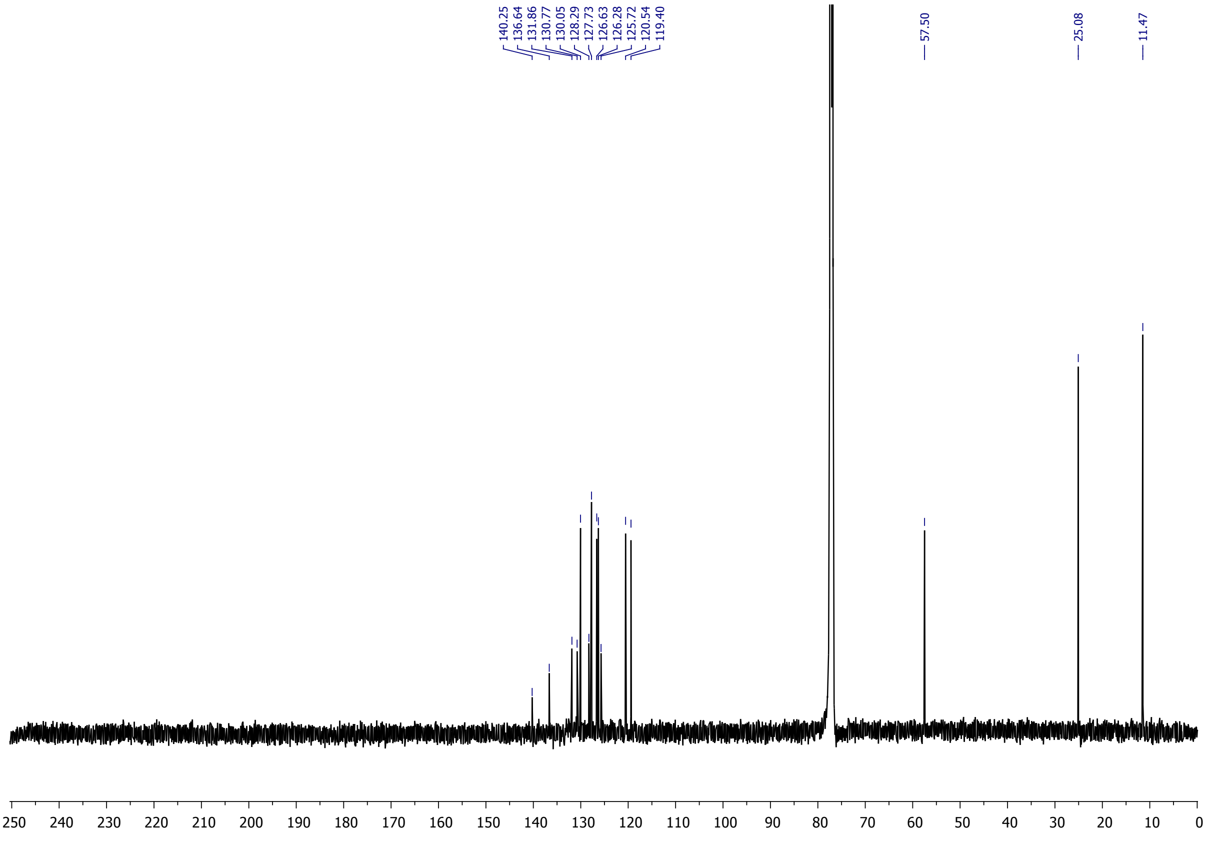
5,5'-(thiophene-2,5-diyl)bis(2-(pentan-3-yl)-1H-thioxantheno[2,1,9-def]isoquinoline-1,3(2H)-dione) (6) : 2,5-bis(tributylstannyl)thiophene (**Thio**) (120 mg, 181.20 µmol), 5-bromo-2-(pentan-3-yl)-1H-thioxantheno[2,1,9-def]isoquinoline-1,3(2H)-dione (2) (163.9 mg, 362.41 µmol) and tetrakis-(triphenylphosphine) palladium(0) (20.9 mg, 18.12 µmol) were degassed under vacuum in a dry Schlenk tube equipped with a stir bar. HPLC grade toluene (5 mL, degassed by argon bubbling for 30 min) was added and the reaction mixture was heated overnight at 120°C under an argon atmosphere. After cooling down to room temperature, the reaction mixture was extracted with chloroform. The organic layers were washed with water, brine and dried over $MgSO_4$. The solvent was removed by rotary evaporation and the crude was subjected to silica gel column chromatography using chloroform as eluent. The product was obtained in a quantitative yield (149 mg). **^{1}H NMR** (300 MHz, $CDCl_3$) δ = 8.65 (d, *J*=8.2, 1H), 8.62 (s, 1H), 8.28 (d, *J*=8.3, 1H), 8.26 – 8.20 (m, 1H), 7.50 – 7.37 (m, 4H), 5.15 – 5.01 (m, 1H), 2.37 – 2.19 (m, 2H), 2.00 – 1.85 (m, 2H), 0.92 (t, *J*=7.4, 6H). **^{13}C NMR** (75 MHz, $CDCl_3$) δ = 140.86, 140.39, 137.08, 131.87, 130.12, 128.91, 127.95, 127.73, 127.05, 126.31, 126.15, 126.03, 122.95, 119.97, 57.63, 25.09, 11.49. **HRMS (FAB+)** calculated for $C_{50}H_{38}N_2O_4S_3$ 826.1994, found 826.2008 (Δ = 1.7 ppm).

NMR Spectra

^{1}H NMR ($CDCl_3$, 500 MHz)

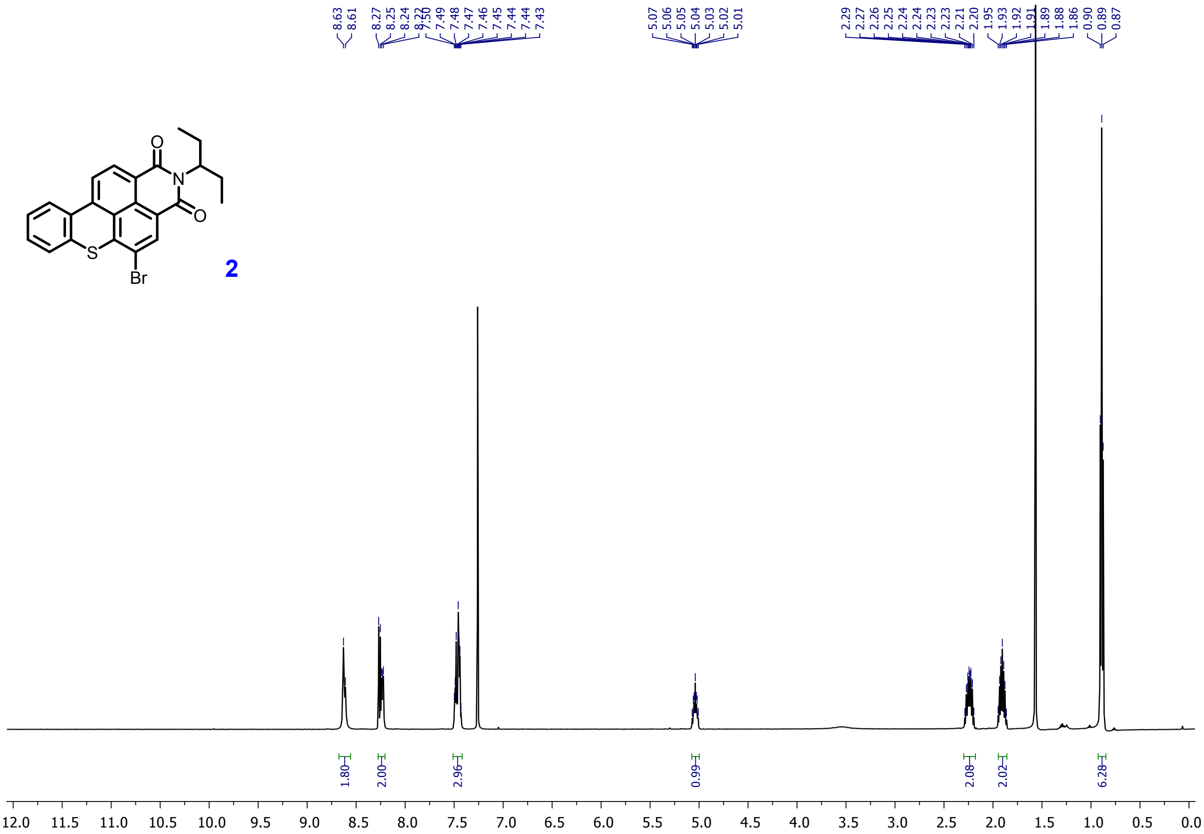


^{13}C NMR ($CDCl_3$, 125 MHz)

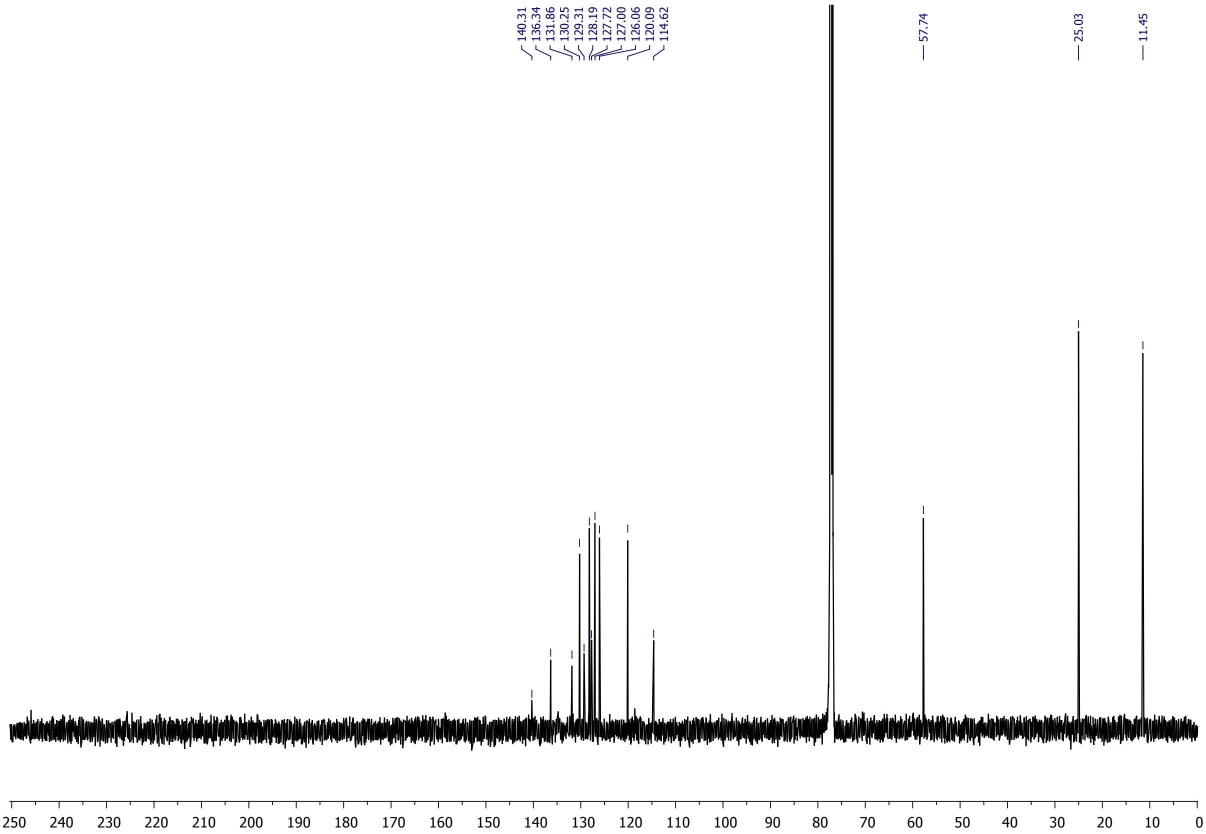


^{1}H NMR (CDCl$_3$, 500 MHz)

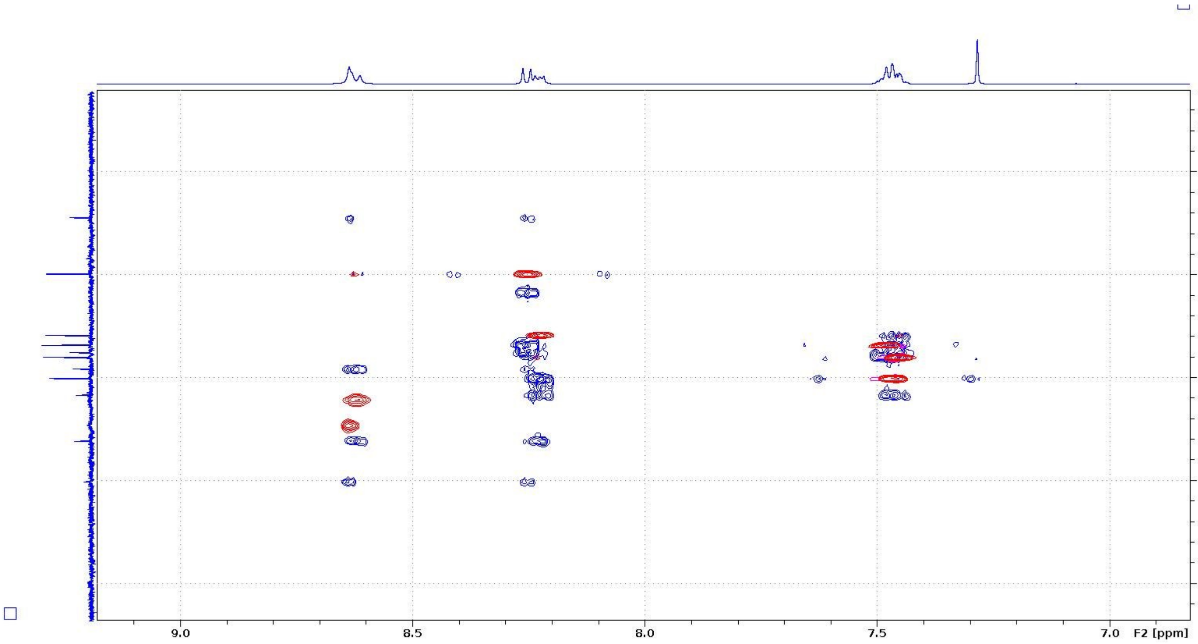
2



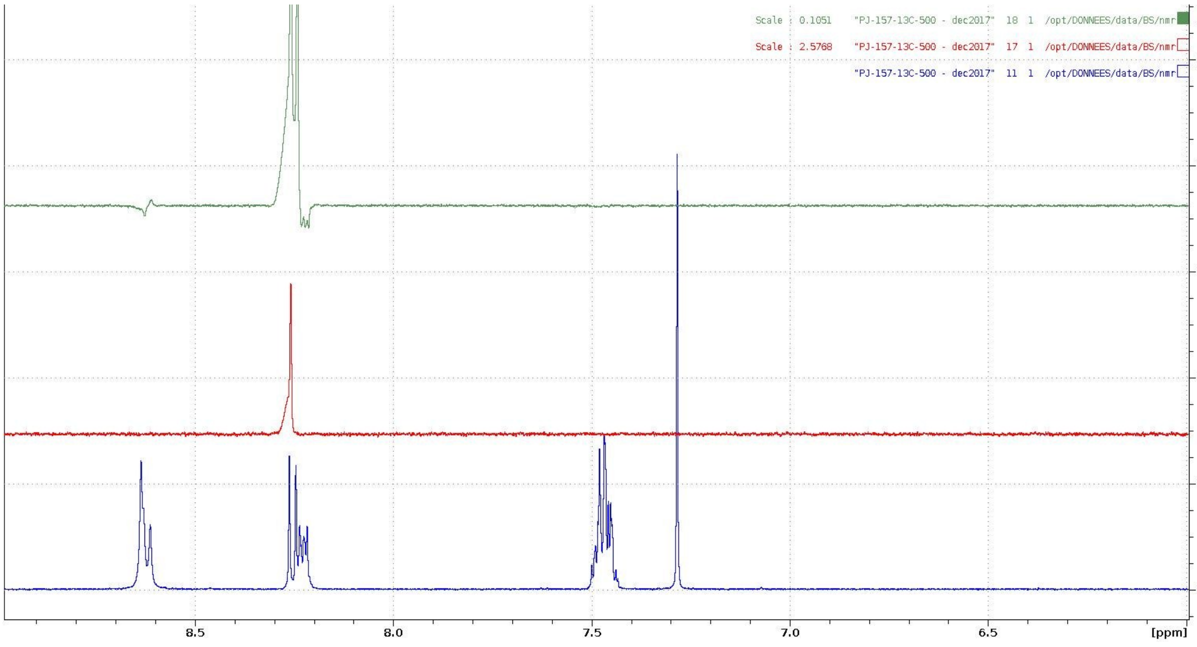
^{13}C NMR (CDCl$_3$, 125 MHz)



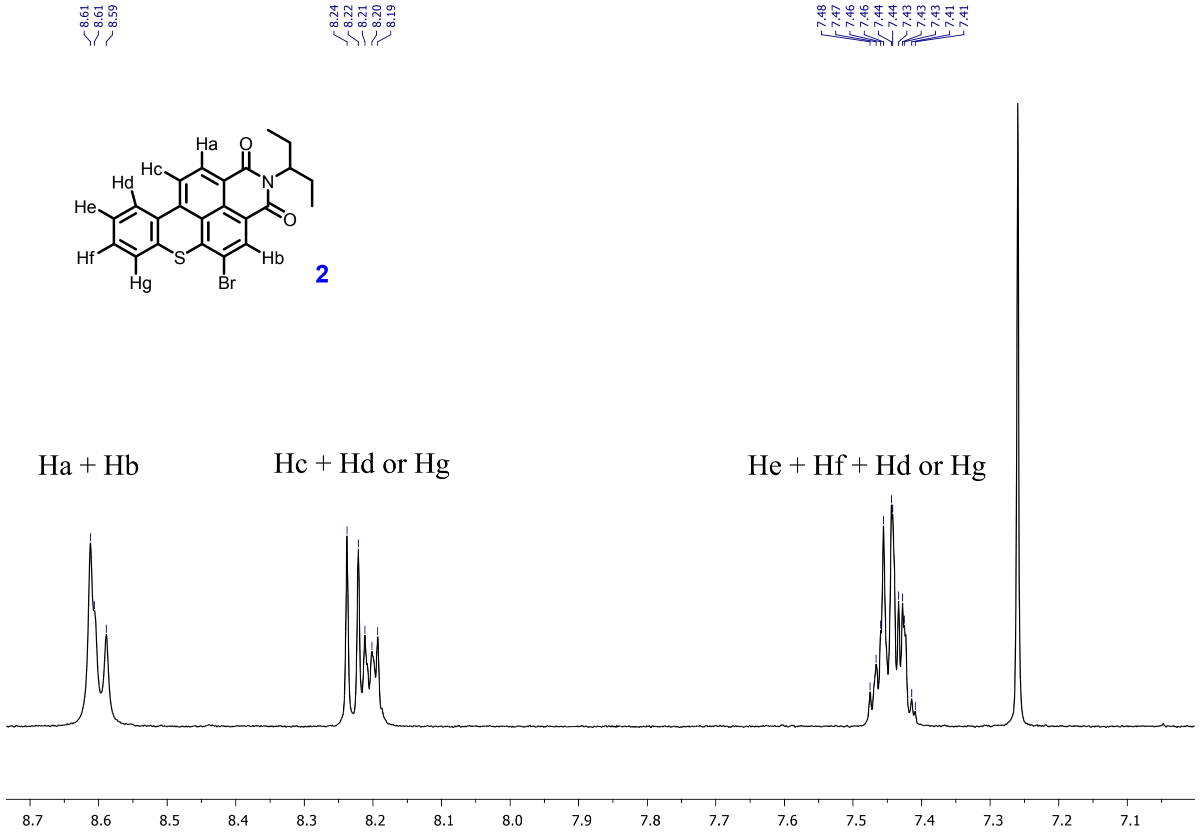
HSQC HMBC NMR ($CDCl_3$, 500 MHz)



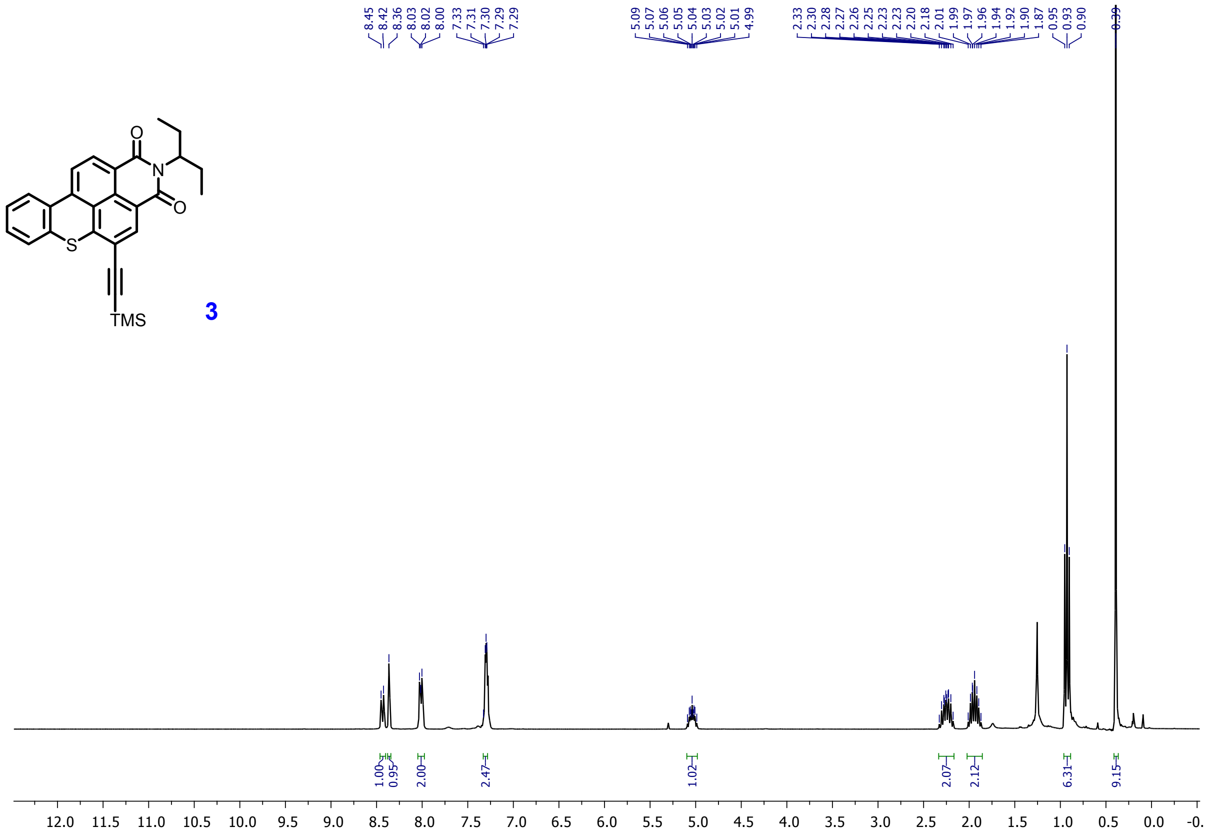
NOE NMR ($CDCl_3$, 500 MHz)



^{1}H NMR ($CDCl_3$, 500 MHz) aromatic zoom

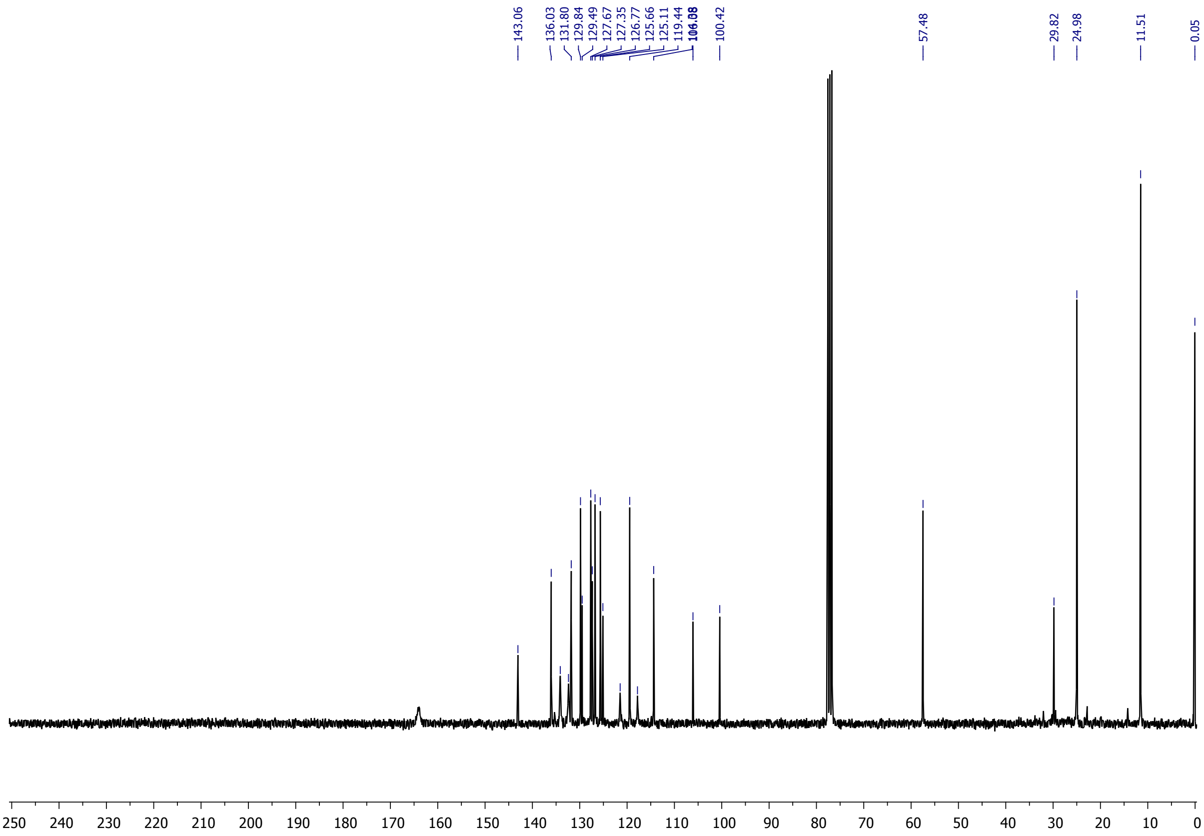


^{1}H NMR ($CDCl_3$, 300 MHz)

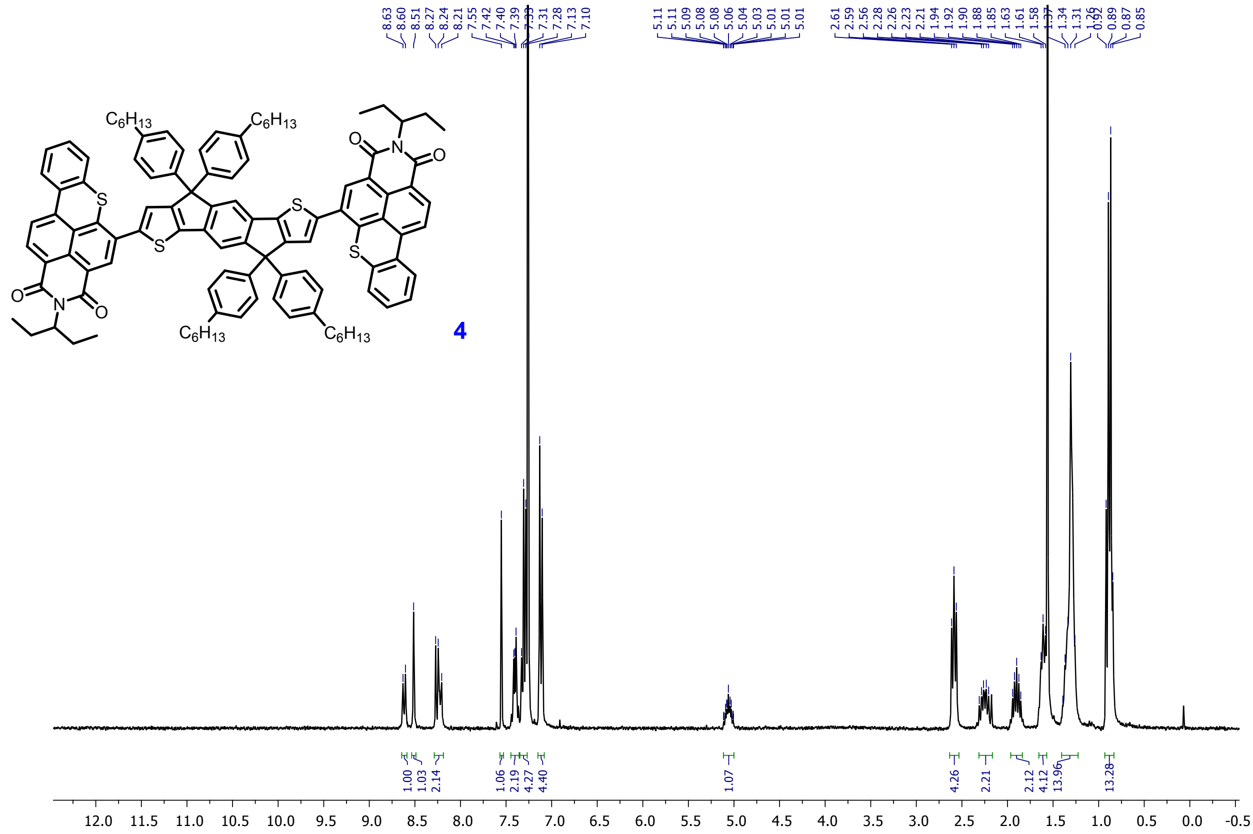


3

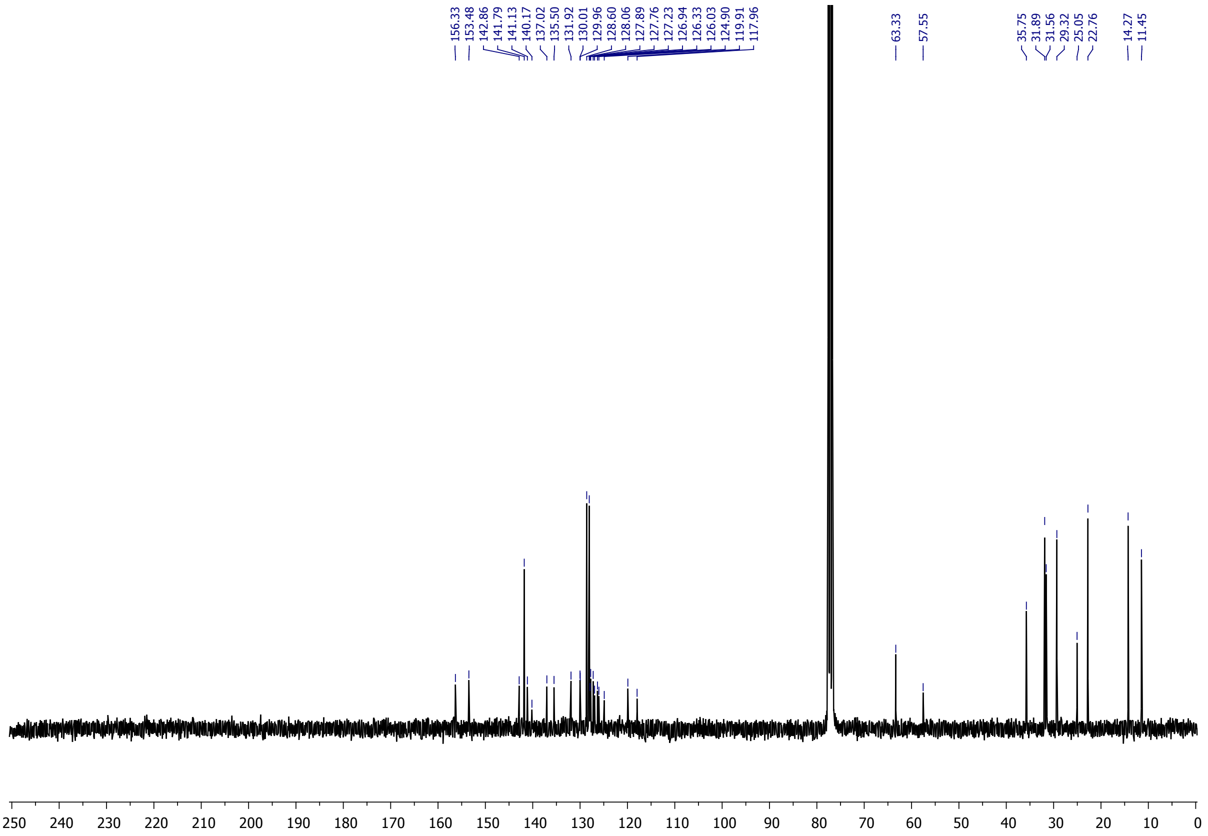
^{13}C NMR ($CDCl_3$, 75 MHz)



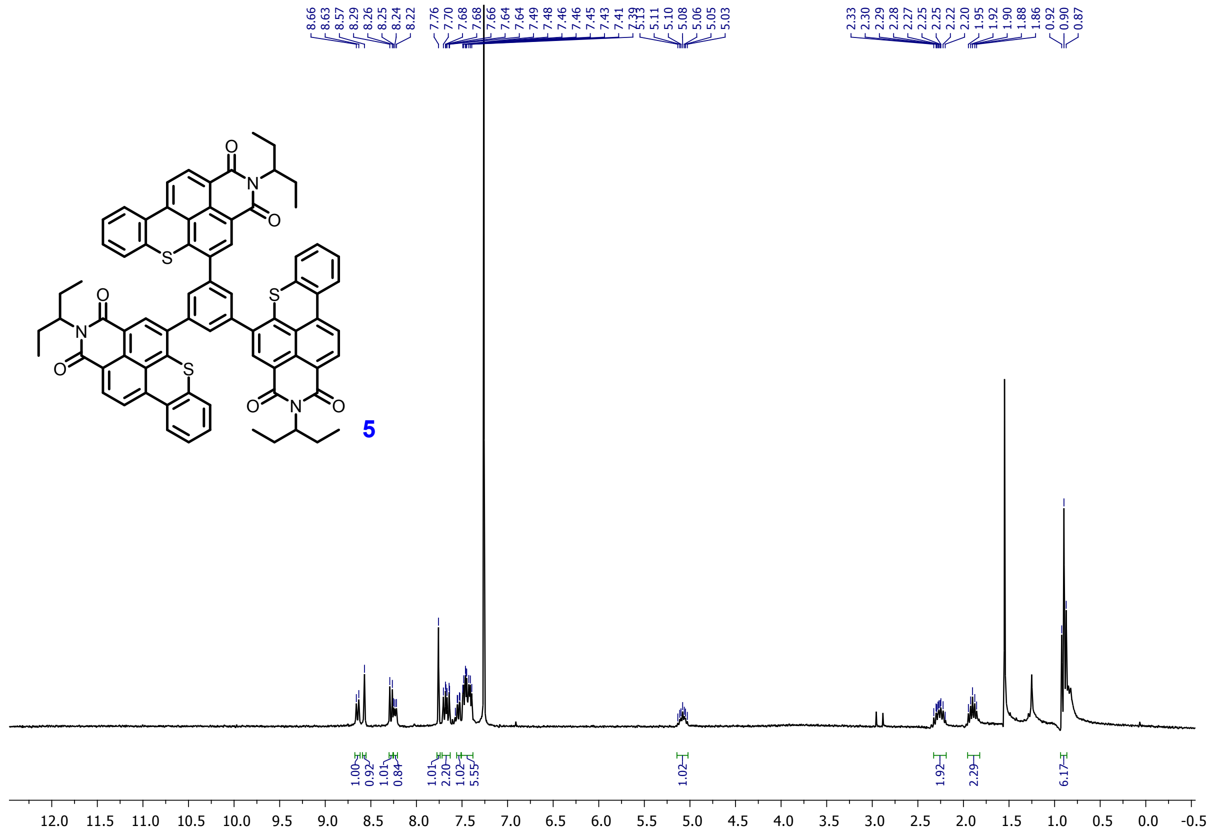
^{1}H NMR ($CDCl_3$, 300 MHz)



^{13}C NMR ($CDCl_3$, 75 MHz)

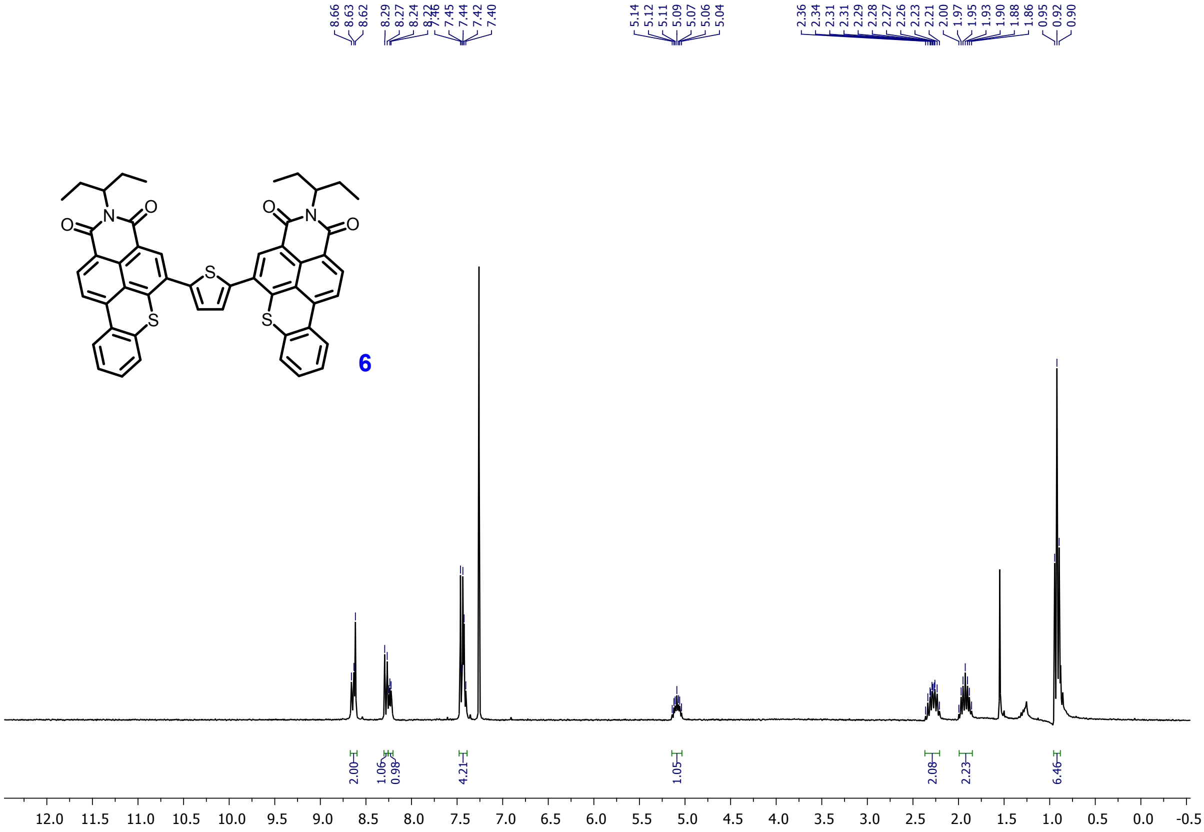


^{1}H NMR (CDCl$_3$, 300 MHz)



^{13}C NMR : Due to solubility issues, we were unable to obtain a complete ^{13}C NMR spectrum.

^{1}H NMR ($CDCl_3$, 300 MHz)



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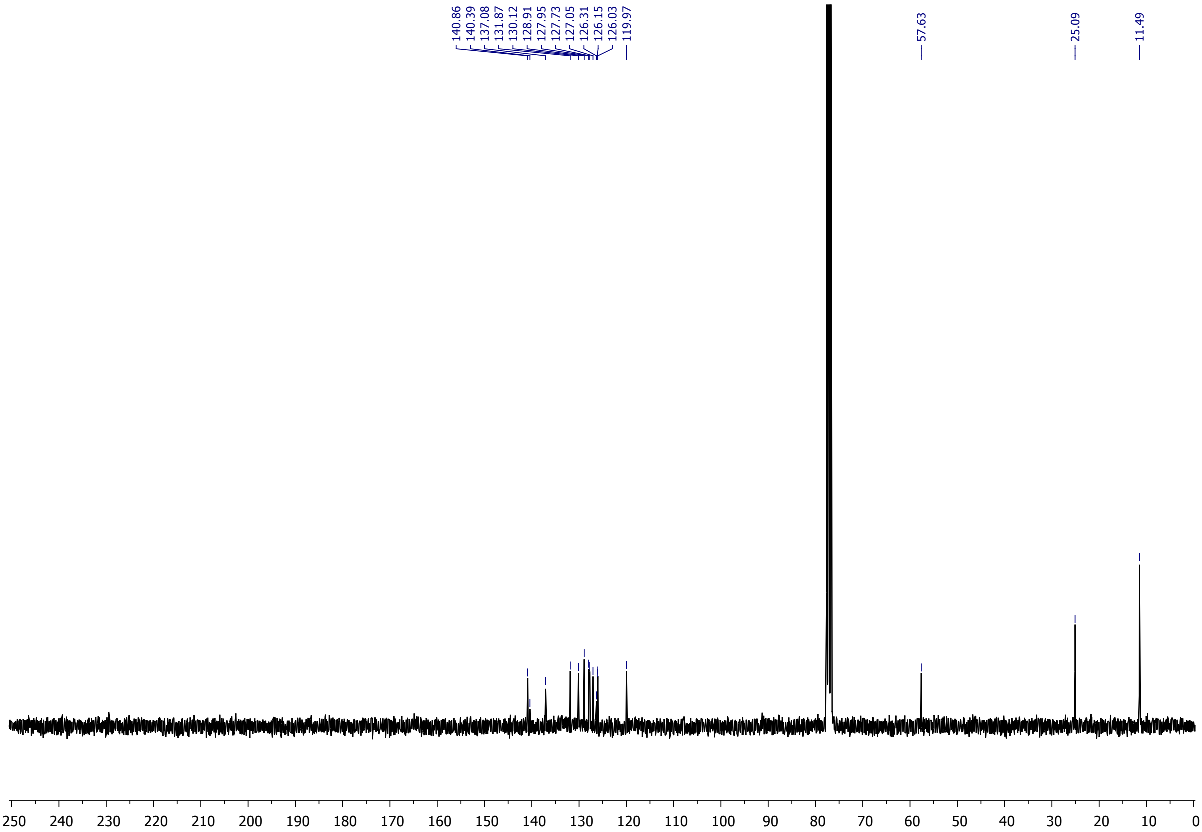
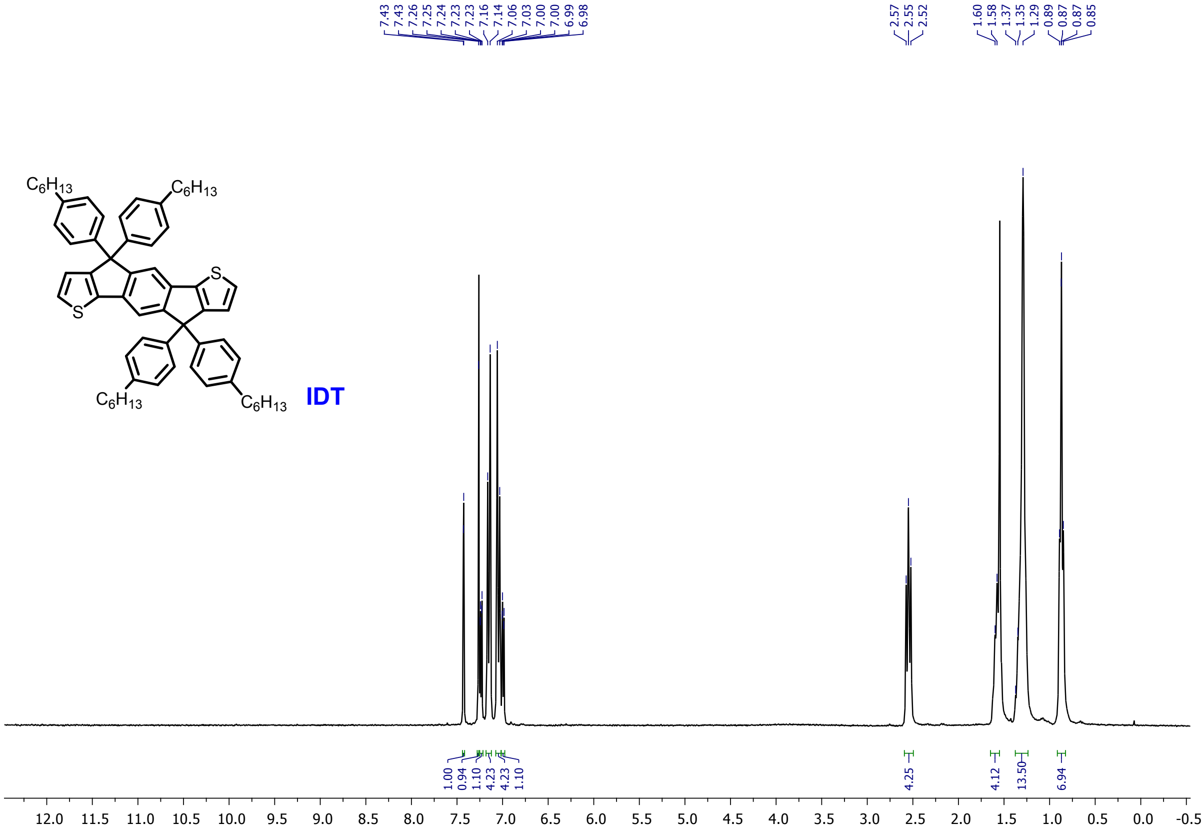
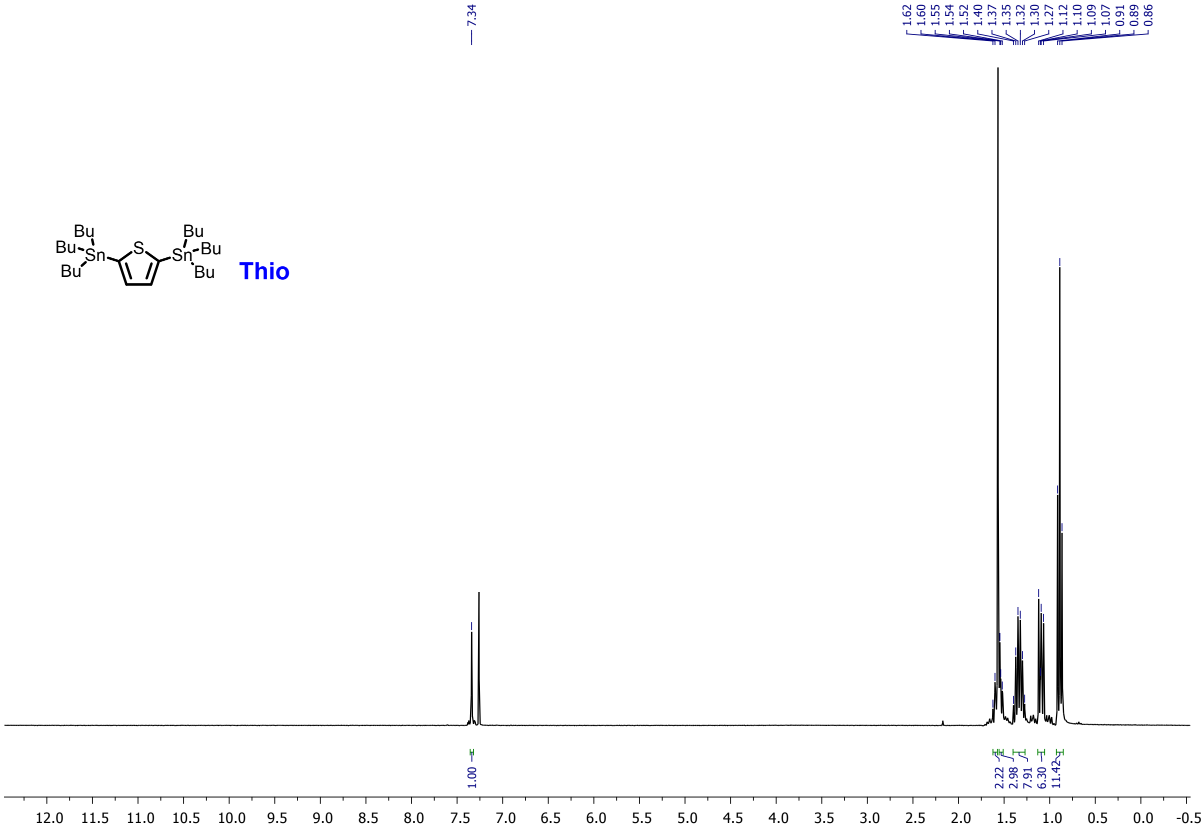
^{13}C NMR ($CDCl_3$, 75 MHz)



^{1}H NMR ($CDCl_3$, 300 MHz)

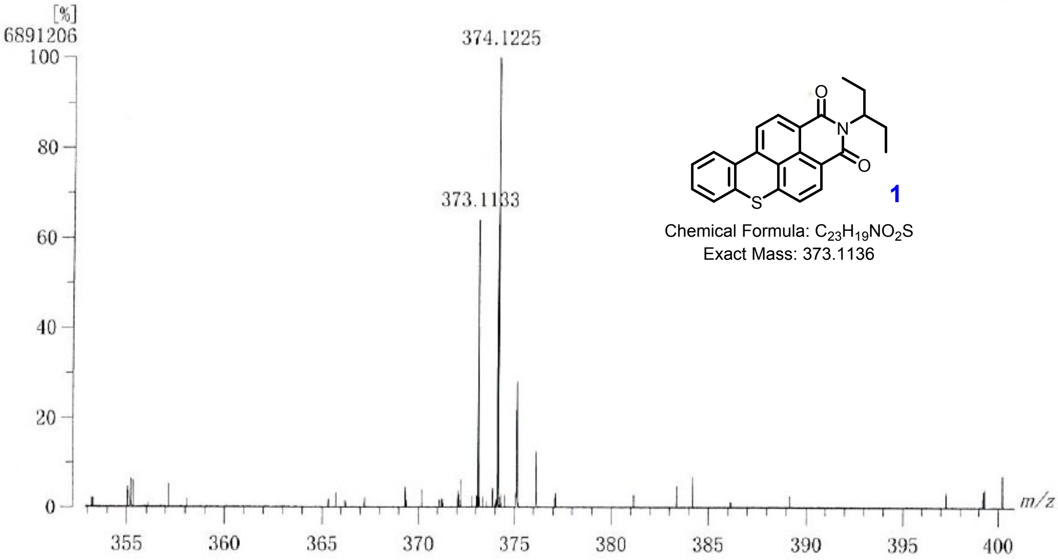


^{1}H NMR ($CDCl_3$, 300 MHz)



HRMS Data

HRMS (CI) calculated for $C_{23}H_{19}NO_2S$ 373.1136, found 373.1133 (Δ = 0.9 ppm).



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  Observed m/z   Int%      Err[ppm / mmu]    U.S.  Composition
1    373.1133    64.05      -0.9 /  -0.4     16.0  C23 H19 N O2 S

2    374.1225   100.00      +2.7 /  +1.0     15.5  C23 H20 N O2 S
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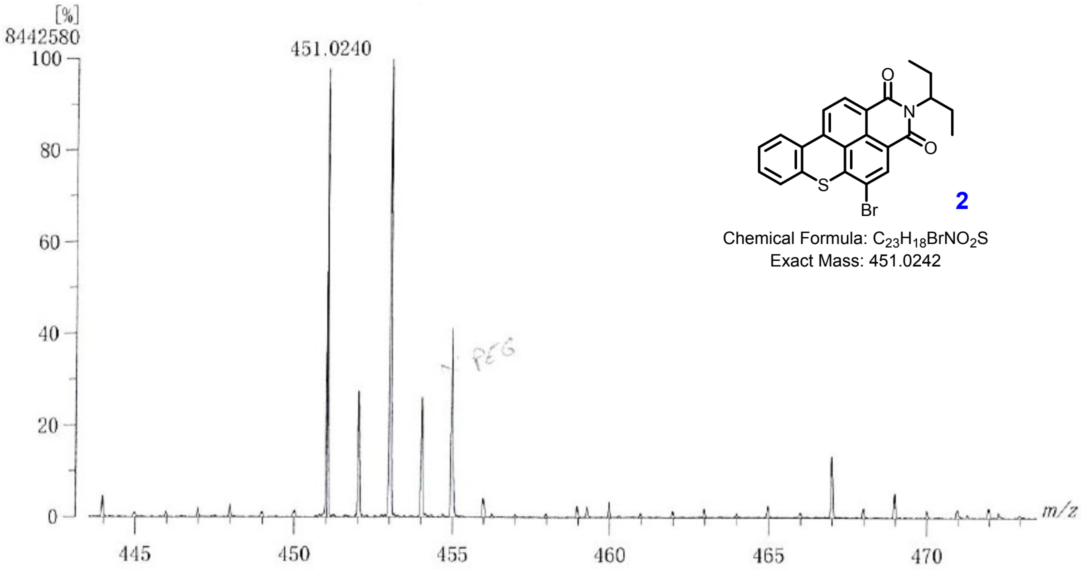
HRMS (EI) calculated for $C_{23}H_{18}BrNO_2S$ 451.0242, found 451.0240 (Δ = 0.4 ppm).



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  Observed m/z   Int%      Err[ppm / mmu]    U.S.  Composition
1    451.0240    97.84      -0.4 /  -0.2     16.0  C23 H18 Br N O2 S
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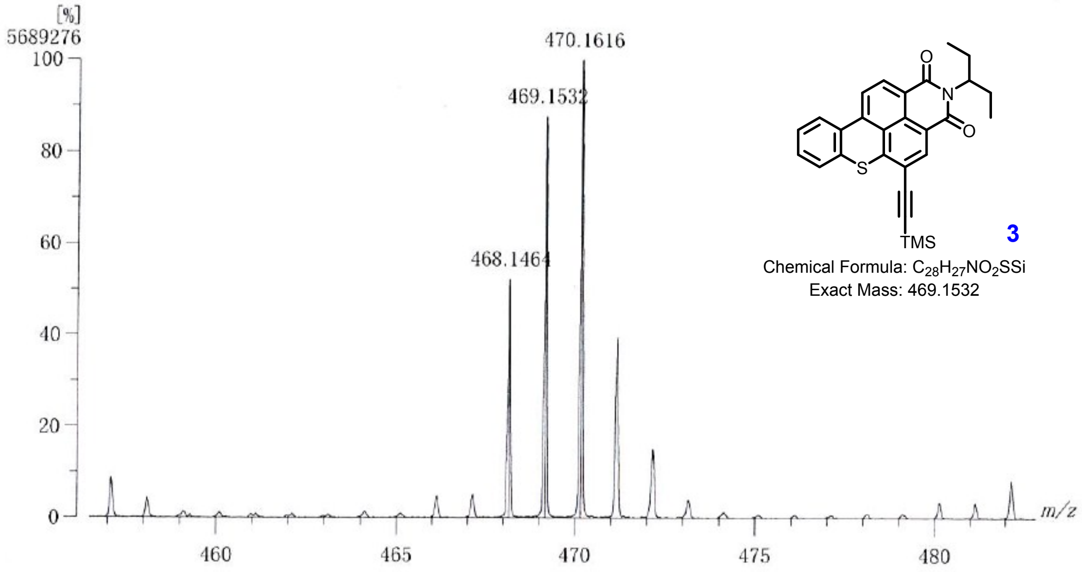
HRMS (FAB+) calculated for $C_{28}H_{27}NO_2SSi$ 469.1532, found 469.1532 (Δ = 0 ppm).



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 Observed m/z   Int%     Err[ppm / mmu]   U.S.  Composition
1   468.1464    52.03     +2.2 /  +1.0    18.5  C28 H26 N O2 S Si

2   469.1532    87.60     +0.0 /  +0.0    18.0  C28 H27 N O2 S Si

3   470.1616   100.00     +1.3 /  +0.6    17.5  C28 H28 N O2 S Si
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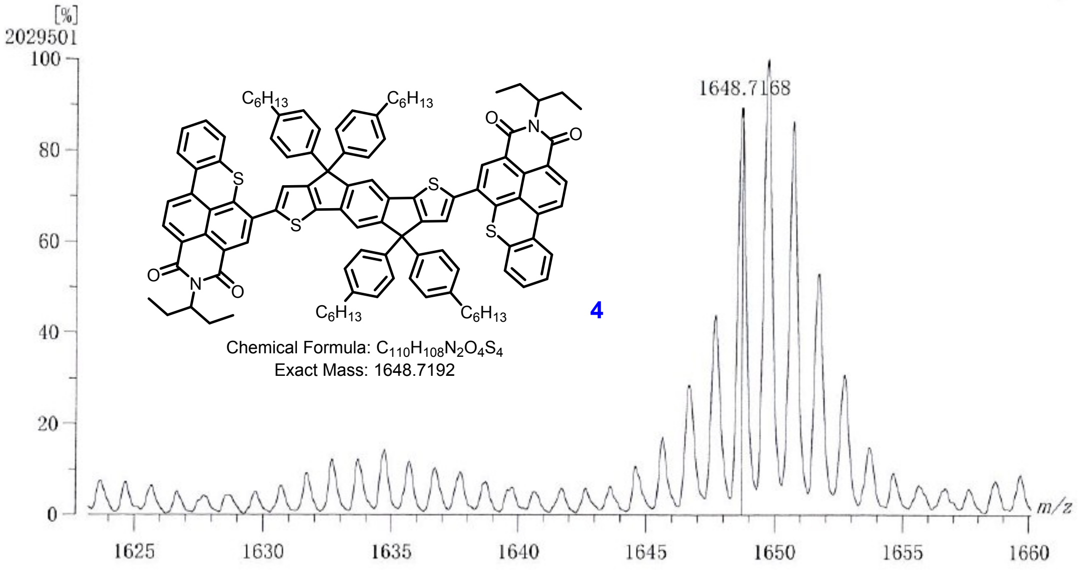
HRMS (FAB+) calculated for $C_{110}H_{108}N_2O_4S_4$ 1648.7192, found 1648.7168 (Δ = 1.5 ppm).



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 Observed m/z   Int%     Err[ppm / mmu]   U.S.  Composition
1  1648.7168    89.29     -1.5 /  -2.4    62.0  C110 H108 N2 O4 S4
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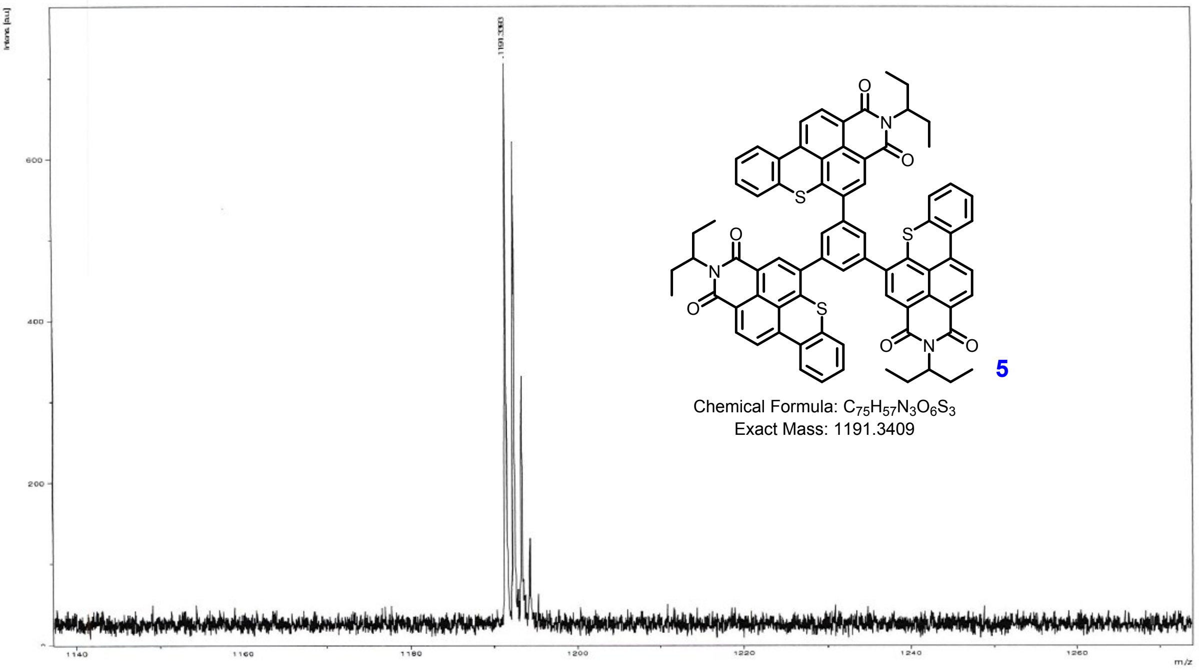
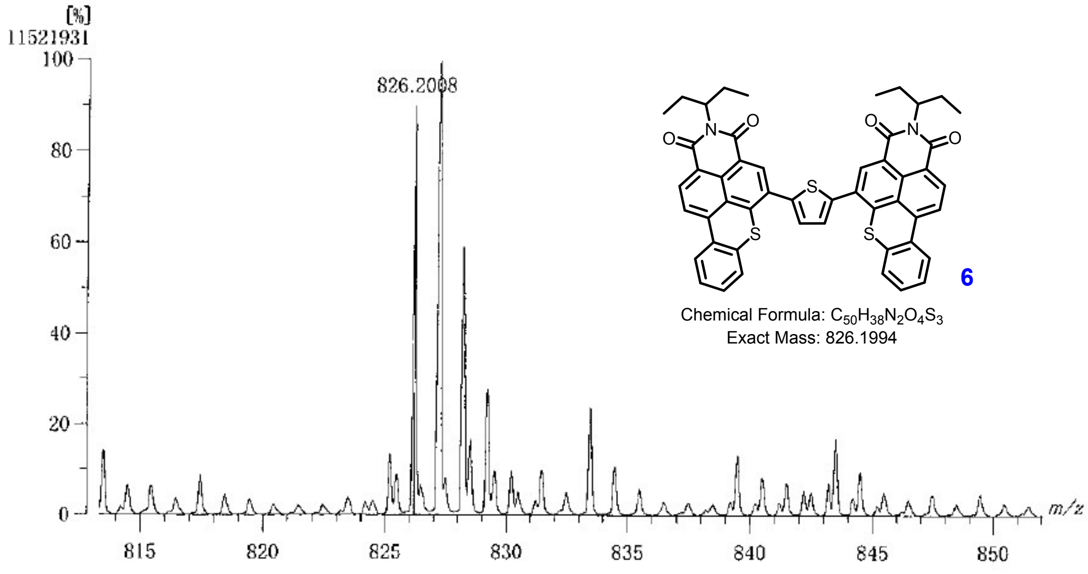
HRMS (MALDI-TOF) calculated for $C_{75}H_{57}N_3O_6S_3$ 1191.3409, found 1191.3393 (Δ = 1.3 ppm)



HRMS (FAB+) calculated for $C_{50}H_{38}N_2O_4S_3$ 826.1994, found 826.2008 (Δ = 1.7 ppm).



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Observed m/z   Int%     Err[ppm / mmu]   U.S.  Composition
1   826.2008   90.00     +1.7 /  +1.4    36.0  C50 H38 N2 O4 S3
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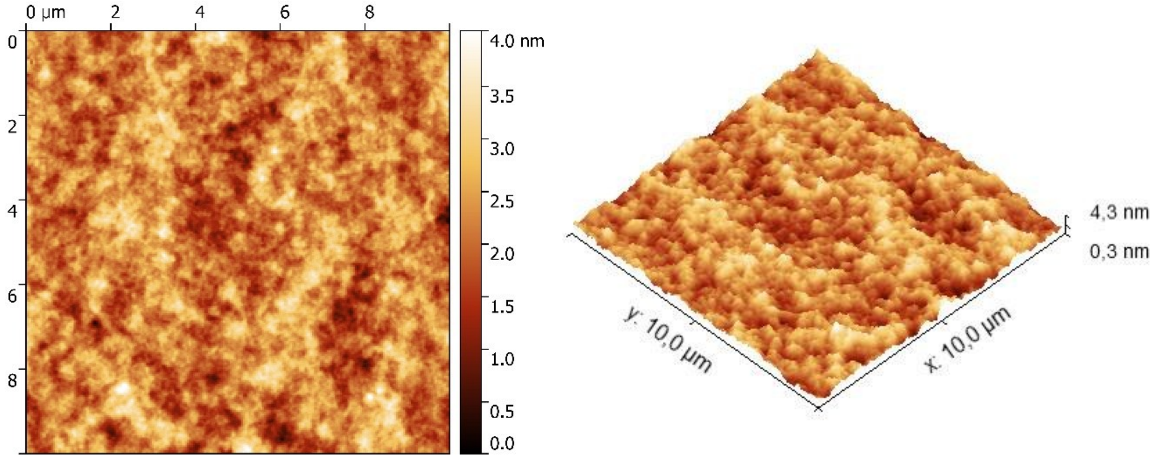
Organic Solar Cells Fabrication

Indium-tin oxide pre-coated glass slides of 24×25×1.1 mm with a sheet resistance of RS = 7 Ω/□ were purchased from Visiontek Systems LTD. The substrates were washed with a diluted Deconex® 12 PA-x solution (2% in water) and scrubbed using dishwashing soap before being cleaned by a series of ultrasonic treatments in distilled water (15.3 MΩ cm-1), acetone and isopropanol for 15 min each. Once dried under a steam of nitrogen, a UV-ozone plasma treatment (UV/Ozone ProCleaner Plus, Bioforce Nanosciences) was performed for 15 min. An aqueous solution of poly(3,4-ethylenedioxy-thiophene)-poly(styrenesulfonate) (PEDOT:PSS; Clevios P VP. AI 4083), filtered through a 0.45 µm RC membrane (Millex®), was spun-cast onto the patterned ITO surface at 5000 rpm for 40 s before being baked at 140°C for 30 min. Then, blends of **4** and **$PC_{61}BM$** at different weight to weight ratios were dissolved in chloroform (10 mg/mL), stirred at 35 °C for 10 minutes and spun-cast at different spin-speeds onto the PEDOT:PSS layer. Finally, devices were completed by the successive thermal deposition of lithium fluoride (1 nm) and aluminum (120 nm) at a pressure of 1.5 x 10-5 Torr through a shadow mask defining six cells of 27 mm2 each (13.5 mm x 2 mm). J vs V curves were recorded using a Keithley 236 source-measure unit and a home-made acquisition program. The light source is an AM1.5 Solar Constant 575 PV simulator (Steuernagel Lichttecknik, equipped with a metal halogen lamp). The light intensity was measured by a broad-band power meter (13PEM001, Melles Griot). EQE were measured under ambient atmosphere using a halogen lamp (Osram) with an Action Spectra Pro 150 monochromator, a lock-in amplifier (Perkin-Elmer 7225) and a S2281 photodiode (Hamamatsu).

Atomic Force Microscopy

Atomic force microscopy (AFM) experiments were performed on the best active layer using a Nano-Observer equipment from CSInstrument. The topographic images were obtained at room temperature in tapping mode. Images were processed with the Gwyddion free SPM data analysis software.



RMS = 0.6 nm

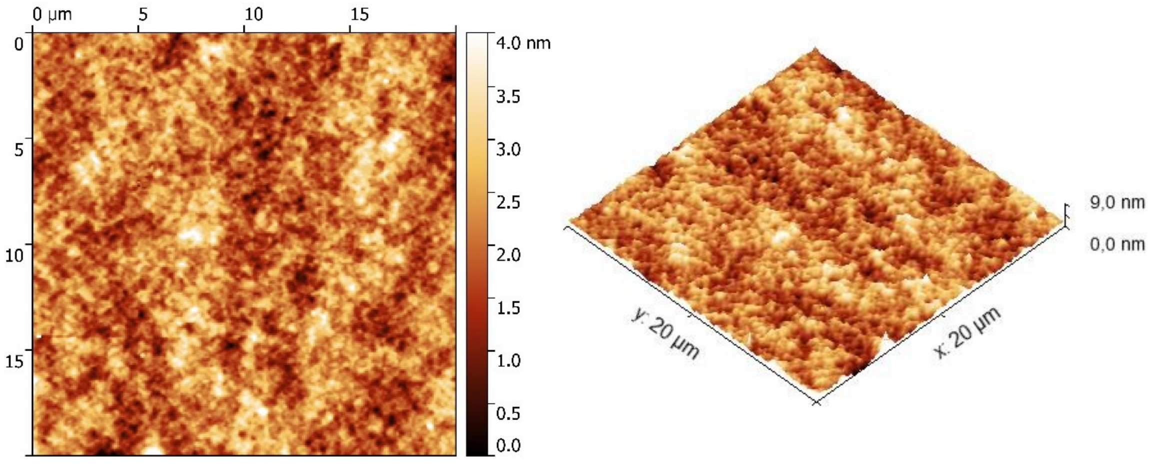


Figure S1. *AFM surface topography images of the best performing active layer (RMS = Root Mean Square)*

Additional Density Functional Theory (DFT) Results

Table S1. Optimized range-separation parameter (ω) as determined via gap fitting at the ωB97X-D/6-31g(d,p) level of theory.

	Range-separation parameter
BTXI	*0.194*
Br-BTXI(1)	*0.164*
Br-BTXI(2)	*0.164*
Br-BTXI(3)	*0.167*
Br-BTXI(4)	*0.167*
Br-BTXI(5)	*0.166*
Br-BTXI(6)	*0.166*
Br-BTXI(7)	*0.165*
Br-BTXI(8)	*0.164*
2Br-BTXI(1, 7)	*0.166*
2Br-BTXI(2, 7)	*0.157*
2Br-BTXI(3, 7)	*0.160*
2Br-BTXI(4, 7)	*0.1607*
2Br-BTXI(5, 7)	*0.159*
2Br-BTXI(6, 7)	*0.159*
2Br-BTXI(7, 8)	*0.158*

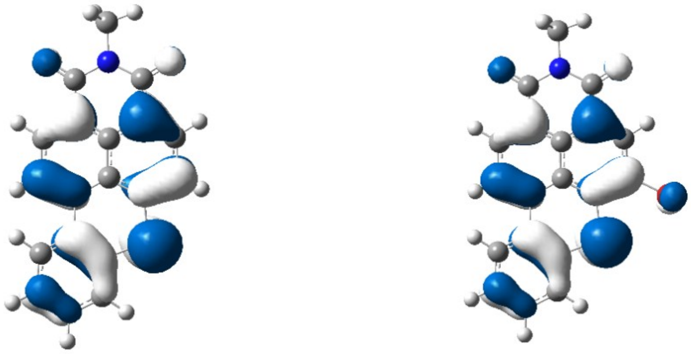


*Figure S2. HOMO of **BTXI** (left) and a monobrominated **Br-BTXI** with the bromine at the β-position with regards to the sulphur atom (right) determined at the OT-ωB97X-D/6-31g(d,p) level of theory.*

*Table S2. Change of enthalpy and Gibbs free energies for the reactions to form monobrominated **Br-BTXI** as determined at the OT-ωB97X-D/6-31g(d,p) level of theory.*

	ΔH (kcal/mol)	*ΔG (kcal/mol)*
Br-BTXI(1)	*-39.95*	*-40.59*
Br-BTXI(2)	*-38.46*	*-37.87*
Br-BTXI(3)	*-35.14*	*-34.72*
Br-BTXI(4)	*-41.91*	*-42.23*
Br-BTXI(5)	*-43.14*	*-43.23*
Br-BTXI(6)	*-42.40*	*-42.60*
Br-BTXI(7)	*-43.79*	*-44.20*
Br-BTXI(8)	*-38.86*	*-39.13*

*Table S3. Change of enthalpy and Gibbs free energies of the reactions to form dibrominated **Br-BTXI** as determined at the OT-ωB97X-D/6-31g(d,p) level of theory.*

	ΔH (kcal/mol)	*ΔG (kcal/mol)*
2Br-BTXI(1, 7)	*-29.45*	*-28.62*
2Br-BTXI(2, 7)	*-27.63*	*-25.80*

2Br-BTXI(3, 7)	*-24.12*	*-22.30*
2Br-BTXI(4, 7)	*-32.45*	*-28.50*
2Br-BTXI(5, 7)	*-32.79*	*-32.17*
2Br-BTXI(6, 7)	*-31.35*	*-30.56*
2Br-BTXI(7, 8)	*-24.25*	*-22.96*

Crystallographic Data

X-ray single-crystal diffraction data for **2** were collected at 150K on an Agilent Technologies SuperNova diffractometer equipped with Atlas CCD detector and mirror monochromated micro-focus Cu-K_α radiation (λ = 1.54184 Å). The structure was solved by direct methods and refined on F^2 by full matrix least-squares techniques using SHELX programs (G.M. Sheldrick, 2013-2016). All non-H atoms were refined anisotropically and the H atoms were included in the calculation without refinement. Multiscan empirical absorption was corrected using CrysAlisPro program (CrysAlisPro, Agilent Technologies, V1.171.38.41r, 2015). One terminal chain of the molecule is statistically disordered and refined on two positions with a final occupation rate of 0.78/0.22. The structure refinement showed disordered electron density which could not be reliably modeled and the program PLATON/SQUEEZE were used to remove the scattering contribution corresponding to chloroform molecules. The assumed solvent composition (1/2 chloroform molecule per asymmetric unit) was used in the calculation of the empirical formula, formula weight, density, linear absorption coefficient and F(000).

Crystallographic data for **$(2)_2$, $CHCl_3$** : $C_{47}H_{37}Br_2Cl_3N_2O_4S_2$, M = 1024.07, orange needle, 0.205 x 0.027 x 0.023 mm^3, monoclinic, space group *P*2/*n*, a = 7.5479(8) Å, b = 16.635(3) Å, c = 16.809(2) Å, β = 94.16(1)°, V = 2105.0(5) $Å^3$, Z = 2, ρcalc = 1.616 g/cm^3, μ(CuKα) = 5.517 mm^{-1}, F(000) = 1036, θmin = 2.656°, θmax = 72.637°, 6506 reflections collected, 3937 unique (R_{int} = 0.0357), parameters / restraints = 258 / 11, R1 = 0.0899 and wR2 = 0.2408 using 2945 reflections with $I>2\sigma(I)$, R1 = 0.1064 and wR2 = 0.2581 using all data, GOF = 1.016, $-1.062 < \Delta\rho < 1.850$ e.$Å^{-3}$. CCDC-1582576 contains the supplementary crystallographic data for this paper.

References

1. Chan, S.-H.; Chen, C.-P.; Chao, T.-C.; Ting, C.; Lin, C.-S.; Ko, B.-T., Synthesis, Characterization, and Photovoltaic Properties of Novel Semiconducting Polymers with Thiophene−Phenylene−Thiophene (TPT) as Coplanar Units. *Macromolecules* **2008,** *41*, 5519-5526.
2. Wei, Y.; Yang, Y.; Yeh, J.-M., Synthesis and Electronic Properties of Aldehyde End-Capped Thiophene Oligomers and Other α,ω-Substituted Sexithiophenes. *Chem. Mater.* **1996,** *8*, 2659-2666.