Supporting Information

A Versatile Synthetic Strategy for Non-Symmetric Isoindigo Polymers *via* Modular Sidechain Engineering

Rachael J. Warner,[1] P. Blake J. St. Onge,[1] Alyssa Shaw,[2] Tiago C. Gomes,[1] Xiaodan Gu[2] and Simon Rondeau-Gagné [1,*]

[1] Department of Chemistry and Biochemistry, University of Windsor, Ontario, Canada N9B 3P4

[2] School of Polymer Science and Engineering, The University of Southern Mississippi, Hattiesburg, Mississippi 39406, United States

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General Procedure and Materials

Materials. Chemical reagents were purchased from Oakwood Products Inc., Sigma-Aldrich Canada Co., or Tokyo Chemical Industry Co. Ltd. and were used as without further purification unless stated otherwise. Solvents used for organic synthesis were obtained from Sigma-Aldrich, with dry solvents purified using a Solvent Purifier System (SPS) (Swagelok, Solon, Ohio, USA). Tris(dibenzylideneacetone)dipalladium(0)-chloroform adduct ($Pd_2(dba)_3$•$CHCl_3$) and 2,5-Bis(trimethylstannyl)thieno[3,2-b]thiophene were purchased from Sigma-Aldrich and recrystallized following reported procedures.[1,2]

Instrumentation. NMR Spectra were recorded at room temperature in $CDCl_3$ solutions with either a Bruker 300 MHz or 500 MHz spectrometer. Chemical shifts are reported in ppm, relative to external standards. High-resolution mass spectrometry (HRMS) was performed on an Agilent 6550 (ESI-CE/LCMS QToF) instrument using APPI or ESI MS Orbitrap Velos Pro under positive mode. FTIR spectroscopy was performed on a Bruker ALPHA FTIR spectrometer using Platinum ATR sampling module. UV-visible spectroscopy was performed on a Varian UV/Visible Cary 50 spectrophotometer. All electrical measurements for OFET devices were conducted using a Keithley 4200 semiconductor parameter analyzer (Keithley Instruments Inc.) under dry N_2 (glovebox). The surface structure of the polymer film was obtained using a Multimode atomic force microscope (AFM, Digital Instruments) operated in the tapping mode at room temperature. Images were collected using the Nanoscope 6 software and processed using the WSxM 5.0 Develop 8.0 software. The surface mechanical properties (elastic moduli) were characterized using PeakForce™ in tapping mode (Dimension Icon, Bruker). Number average molecular weight (Mn), weight average molecular weight (Mw), and polydispersity index (PDI) were evaluated by high temperature size exclusion chromatography (SEC) using 1,2,4-trichlorobenzene and performed on

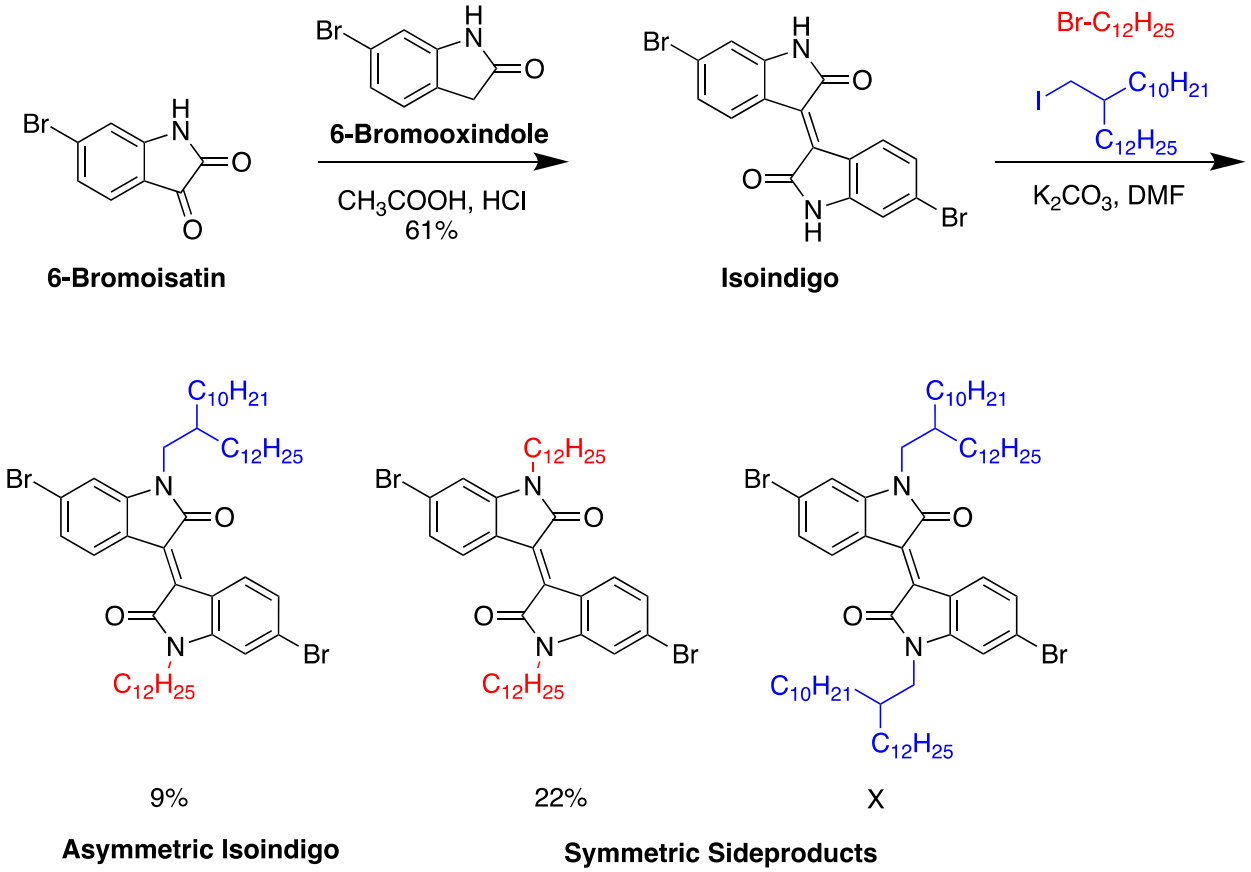
an EcoSEC HLC-8321GPC/HT (Tosoh Bioscience) equipped with a single TSKgel GPC column (GMHHR-H; 300 mm × 7.8 mm) calibrated with monodisperse polystyrene standards. The samples were prepared using 1 mg/mL of sample in trichlorobenzene (TCB), which were allowed to stir at 80 ºC for 12 h prior to injection. The analysis of the samples was performed at 180 ºC with a flow rate of 1.0 mL/min with injection quantities of 300 μL. The data was collected and integrated using EcoSEC 8321GPC HT software suite. Absorption spectra were recorded on an Agilent Technologies 8453 Diode Array UV-Vis spectrometer, with a spectral resolution of 1 nm in a 1 cm quartz cuvette. The error on the measurement was obtained from the standard deviation provided by the instrument.

Grazing incidence wide angle X-ray scattering (GIWAXS): Grazing Incidence Wide Angle X-ray scattering of films was performed by a Xenocs Xeuss 2.0 SAXS/WAXS 2-10 m beamline equipped with a rotating GeniX 3D copper (Cu) anode X-ray source with a wavelength of 1.54 Å at 8.0 keV and 1.2 mm beam size, equipped with a Pilatus 1M 2-D area detector. Silver behenate was used as the calibrant and referenced to determine the sample to detector distance. The sample to detector distance was 154 mm, and the exposure time of each sample was 1.5 hours, using plasma etched silicon as the substrate.

OFET Device Fabrication: Bottom-gate top-contact OFET devices were fabricated on highly doped *n*-type Si(100) wafer with a 300 nm-thick SiO_2 dielectric layer. The wafers were first functionalized with a phenyltrimethoxysilane (PTS) self-assembled monolayer, according to a reported method.[3] The PTS-treated substrate was washed with toluene, acetone, and isopropanol, then dried with nitrogen before use. Thin films of the polymers were spin-coated at 1000 rpm for 1 min onto PTS-treated substrates from prepared polymer solutions (5 mg mL^{-1}, chlorobenzene), giving films approximately 40 nm thick. Gold source and drain contacts were then deposited

through a shadow mask via e-beam physical vapour deposition (2 Å s^{-1}). 50 nm of Au were deposited on top of the polymer films, yielding devices with channel length, L, and width, W, defined as 150 and 1000 µm, respectively. Thermal annealing was carried out using a hot plate at 150 °C inside the glove box under N_2 atmosphere for 60 min. Measurements of the device characteristics were conducted at room temperature using a Keithley 4200-SCS semiconductor parameter analyzer (Keithley Instruments Inc., Cleveland, OH, USA) inside a N_2-purged glovebox. To study the electrical performance of the OFET, the V_{th} and μ were extracted and averaged from the transfer curves of at least 10 devices per polymer.

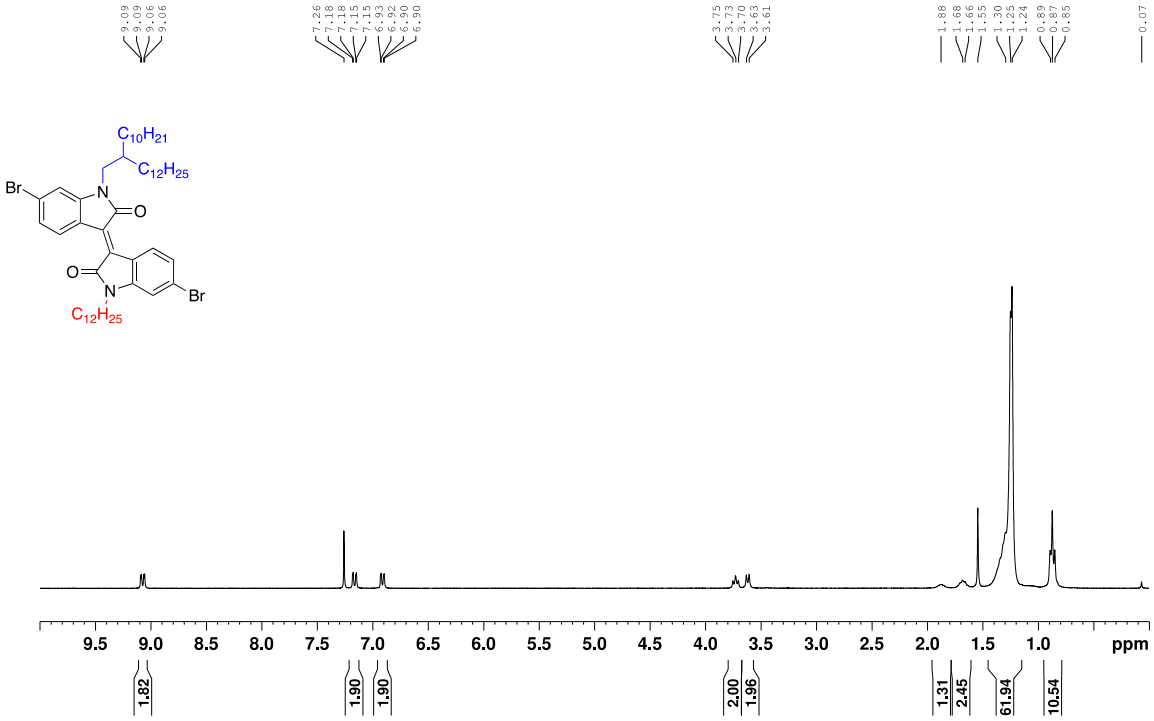
Experimental Procedure



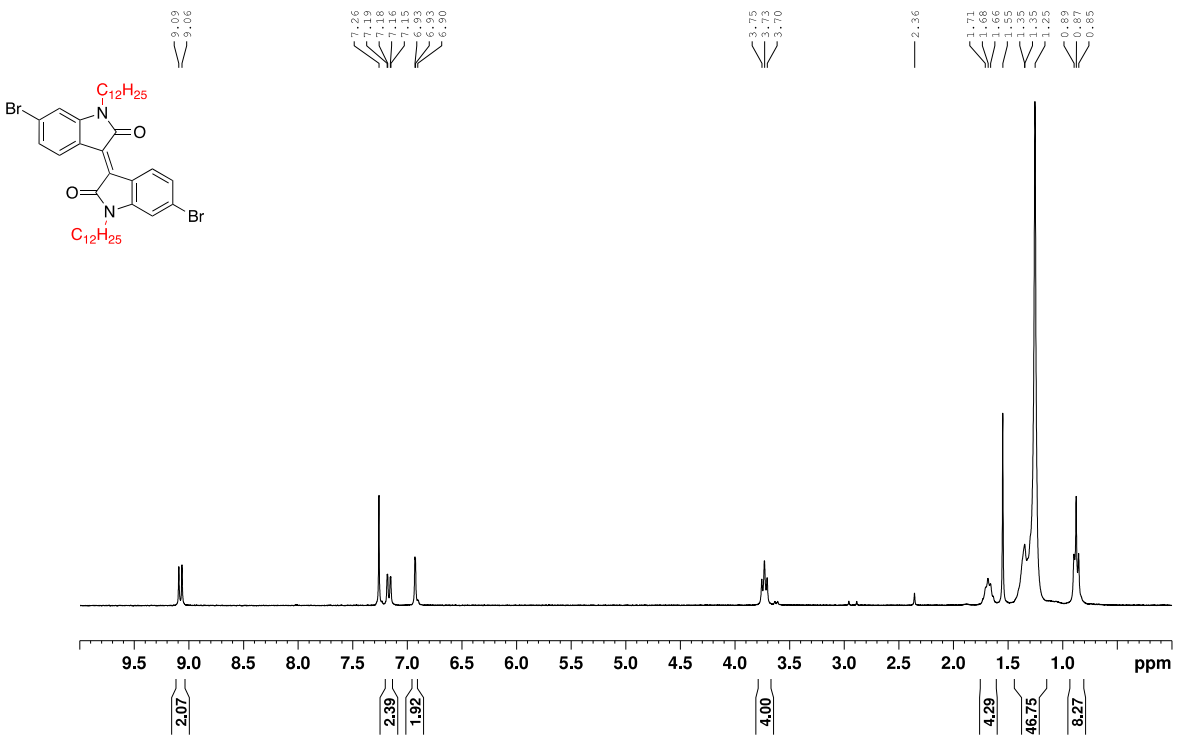
Scheme S1. Representative synthetic pathway to asymmetric isoindigo monomers through one-pot basic alkylation.

Procedure for the one-pot alkylation method.

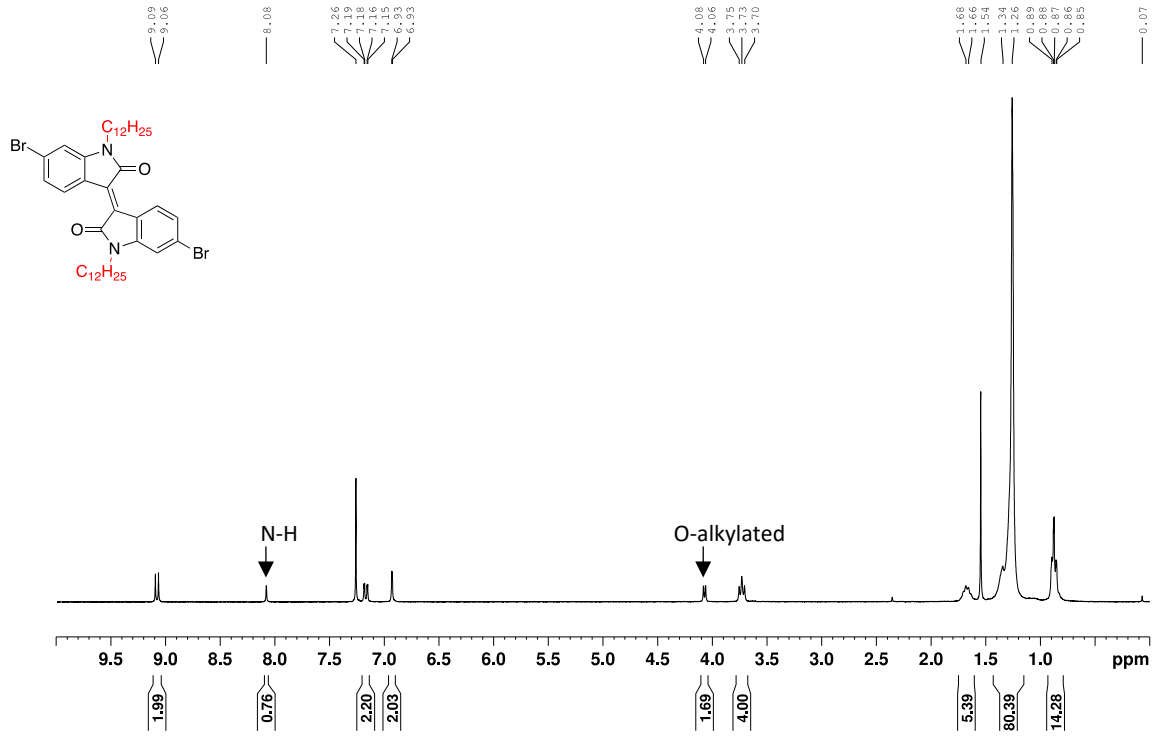
To a purged flame dried 25ml round bottom flask, isoindigo (40mg, 0.095mmol) and potassium carbonate (30mg, 0.23mmol) was added to DMF (2mL). The reaction mixture was then heated to 100ºC and stirred for 30 minutes under nitrogen atmosphere. 1-Bromododecane (30mg, 0.12 mmol) and 1-iodo-2-decyltetradecane (56mg, 0.12 mmol) was then added dropwise, and the reaction was stirred overnight. The compound was then extracted with $CHCl_3$, then washed with H_2O and brine, and dried with Na_2SO_4, and reduced under pressure. The compound was then purified by preparatory thin layer chromatography using hexanes and toluene (1:1) to yield the asymmetric monomer (compound **8**) (7.4mg, 9% yield). Upon NMR characterization it was determined that the symmetric isoindigo; iI-$C_{12}H_{25}$ (17.9mg, 22% yield) was obtained, additionally a crude mixture containing the symmetric isoindigo; iI-$C_{12}H_{25}$, was isolated (4.7mg, 6% yield). The symmetric branched chain isoindigo; iI-$C_1C_{10}C_{12}$, was not isolated.



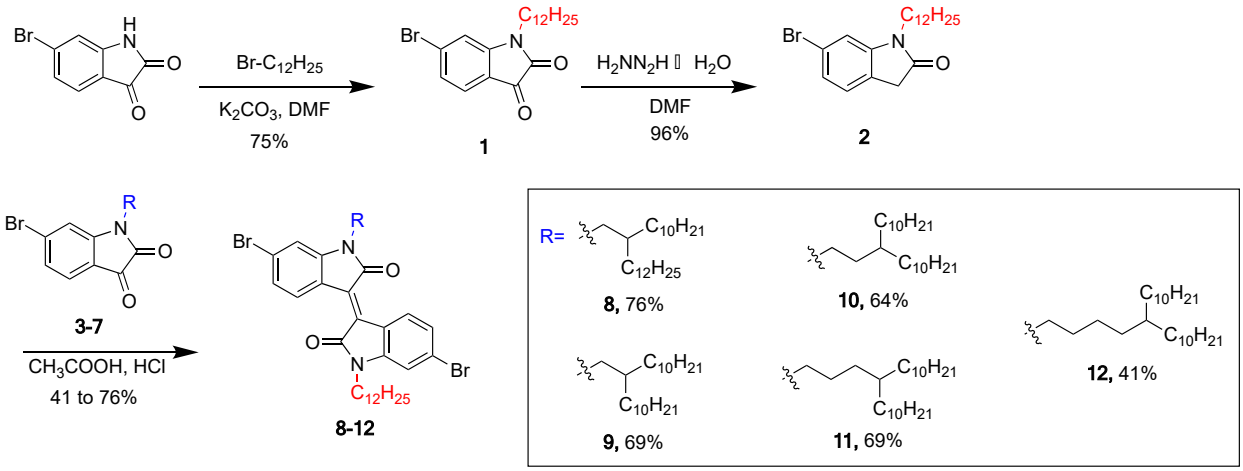
^{1}H NMR of the asymmetric isoindigo monomer (Compound **8)** in $CDCl_3$



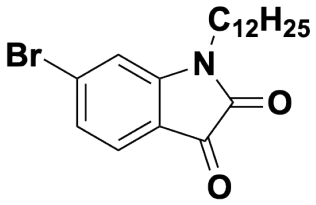
^{1}H NMR of the symmetric isoindigo monomer (iI-$C_{12}H_{25}$) in $CDCl_3$



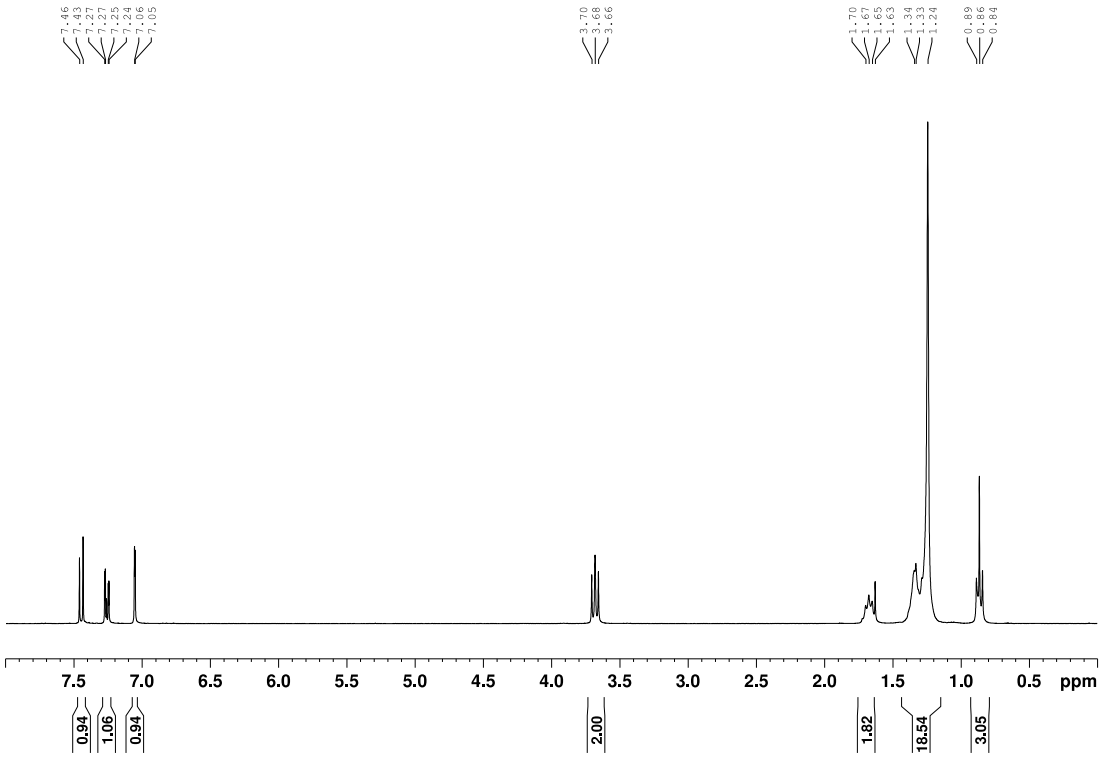
Crude ^{1}H NMR of the symmetric isoindigo monomer (iI-$C_{12}H_{25}$) in $CDCl_3$



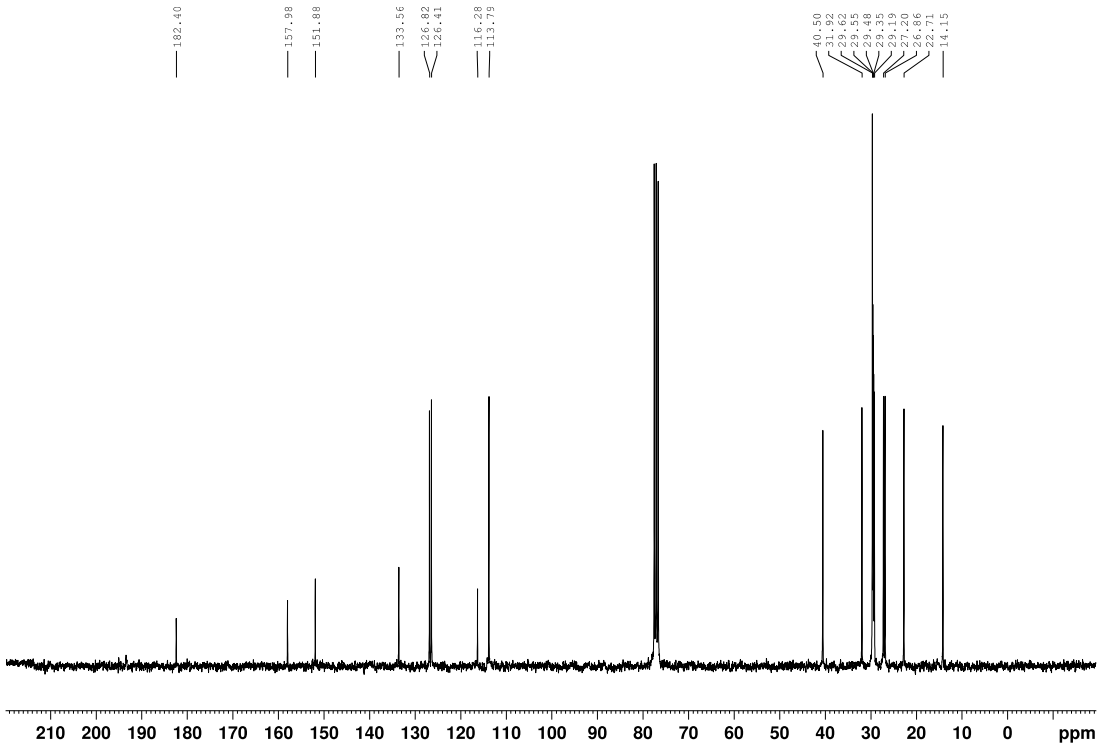
Scheme S2. Synthetic pathway towards 'lego-like' asymmetric monomer formation.



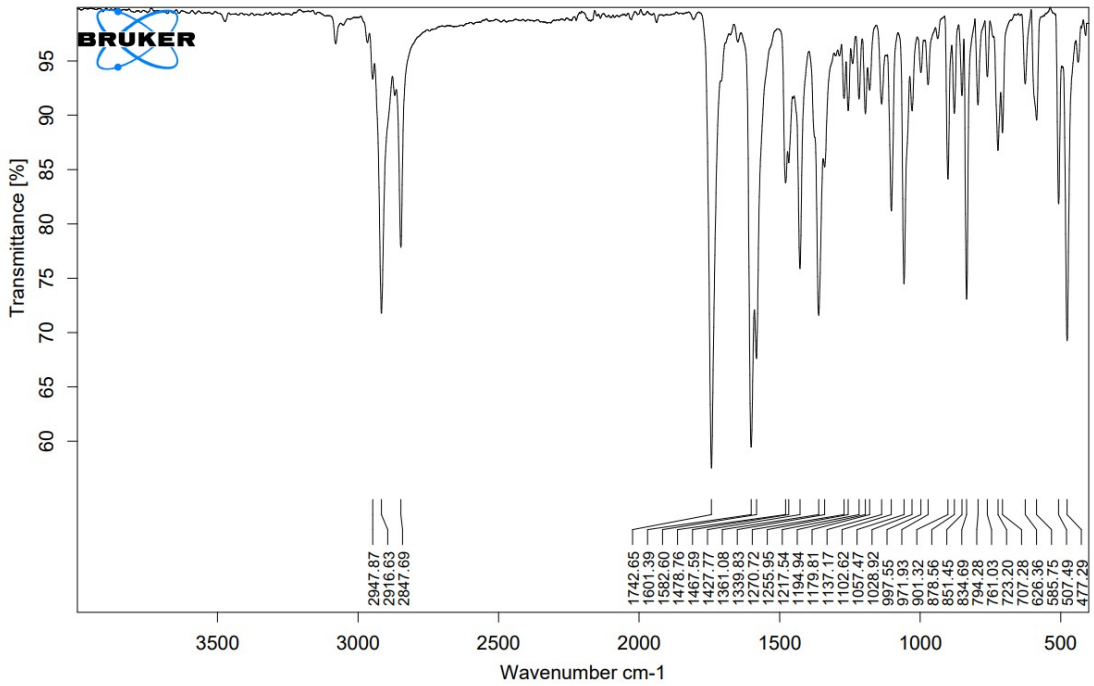
Compound 1. *6-bromo-1-dodecylindolin-2,3-dione*. To a purged flame dried 250 mL round-bottom flask, 6-Bromoisatin (0.5 g, 2.2 mmol) and potassium carbonate (0.37 g, 2.7 mmol) was added to DMF (22 mL). The reaction mixture was then heated to 100 ºC and stirred for 30 minutes under nitrogen atmosphere. 1-Bromododecane (29mg, 0.12 mmol) and was then added dropwise, and the reaction was allowed to stir for 2 hours. The compound was then extracted with CH_2Cl_2, then washed with H_2O and brine, and dried with Na_2SO_4, and reduced under pressure. The compound was then purified by column chromatography using hexanes and CH_2Cl_2 (1:3) to yield compound **1** as orange crystals. Yield: 0.66 g **(75%).** ^{1}H NMR ($CDCl_3$) δ: 7.43 (d, 1H, *J* = 8.1 Hz), 7.23 (m, 1H, *J* = 6.6 Hz), 7.03 (d, 1H, *J* = 1.5 Hz), 3.66 (t, 2H, *J* = 7.2 Hz), 1.66 (p, 2H, *J* = 6 Hz, 7 Hz), 1.230 (s, 18H), 0.852 (t, 3H, *J* = 6.3 Hz, 13.5 Hz). ^{13}C NMR ($CDCl_3$) δ: 182.4, 157.9, 151.8, 133.5, 126.8, 126.4, 116.2, 113.7, 40.5, 31.9, 29.6, 29.5, 29.4, 29.3, 29.1, 27.2, 26.8, 22.7, 14.1. HRMS: *m/z* Calculated for $C_{20}H_{28}BrNO_2$ $[M+H]^+$ 393.1303; found 394.1407.



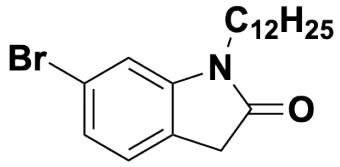
^{1}H NMR of Compound **1** in $CDCl_3$



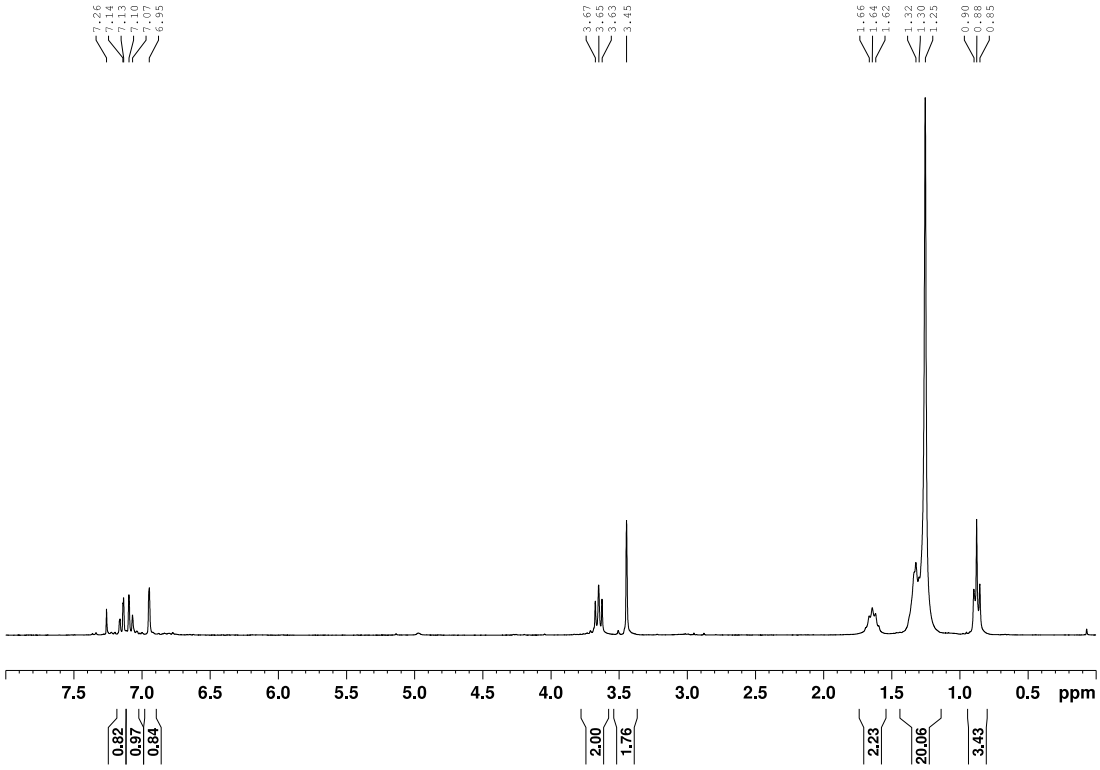
^{13}C NMR of Compound **1** in $CDCl_3$



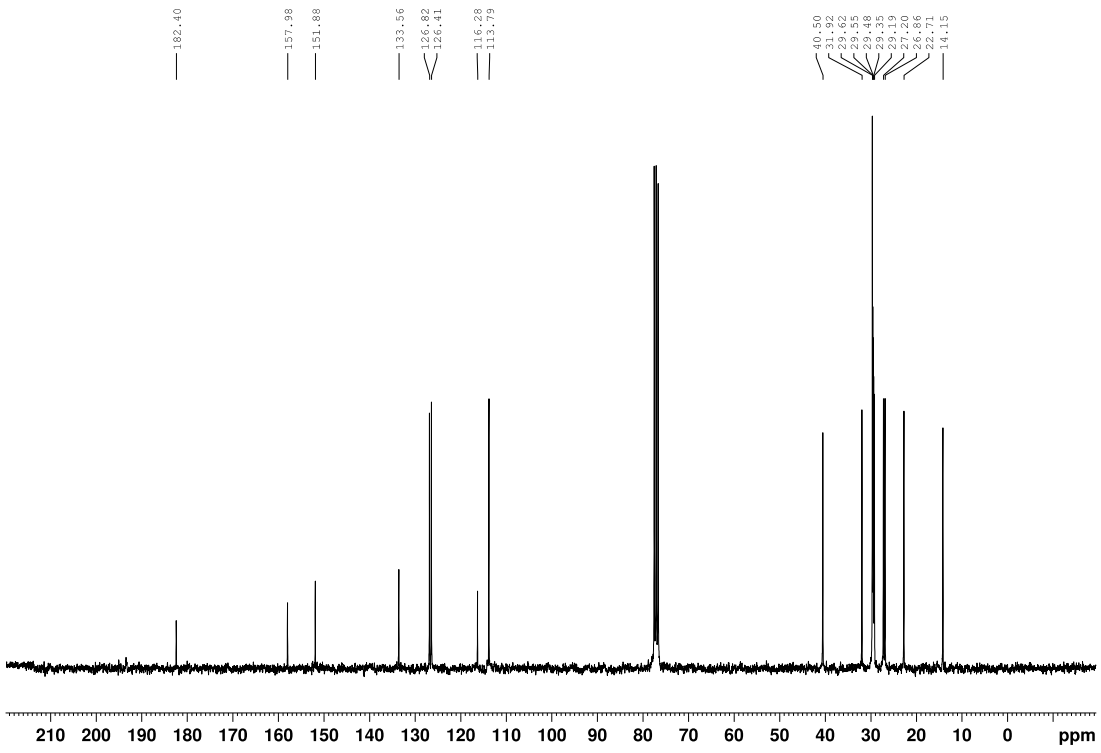
FTIR spectrum of Compound **1**.



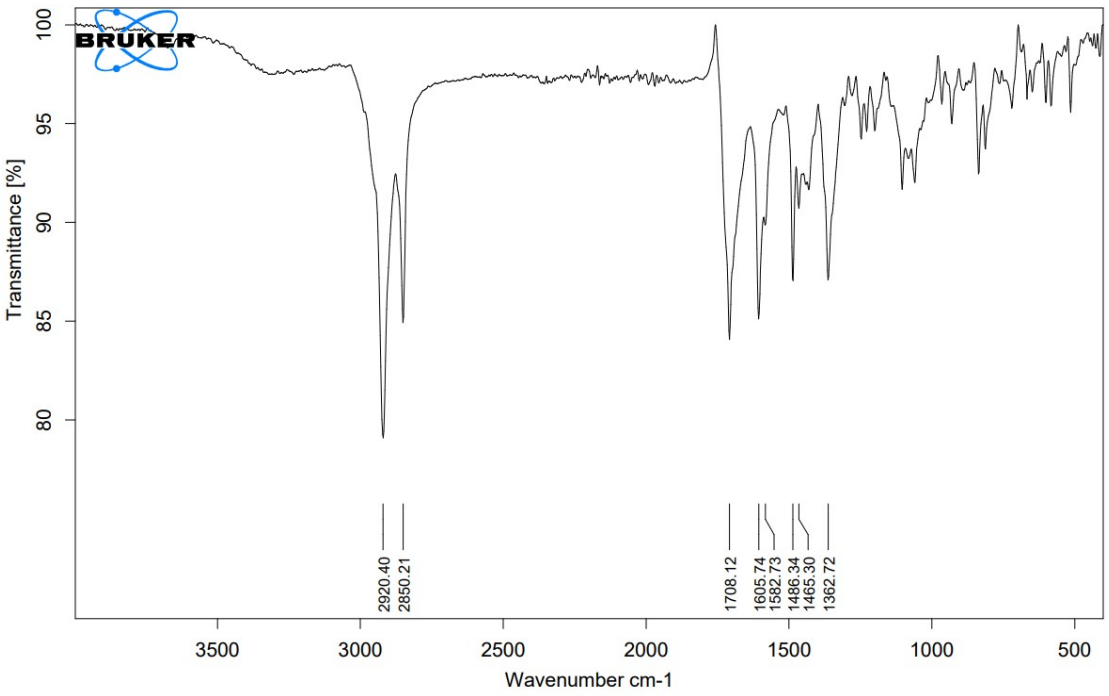
Compound 2. *6-bromo-1-dodecylindolin-2-one*. To a 50 mL round bottom flask, compound **1** (0.5 g, 1.27 mmol) and Hydrazine hydrate 50% (5 mL) is added to DMF (5 mL) is then added. The reaction is allowed to stir for 24 hrs at 130°C under nitrogen atmosphere. The compound is then extracted in CH_2Cl_2, dried with Na_2SO_4, and concentrated under reduced pressure, resulting in light brown crystals. Yield: 0.46 g (96 %). ^{1}H NMR ($CDCl_3$) δ: 7.13 (dt, 2H, J = 1.5 Hz, 7.8 Hz), 6.94 (s, 1H), 3.650 (t, 2H, J = 7.5 Hz, 14.5 Hz), 3.44 (s, 2H), 1.64 (m, 2H), 1.28 (m, 17H), 0.87 (t, 3H, J = 6.3 Hz, 13.2 Hz). ^{13}C NMR ($CDCl_3$) δ: 174.6, 146.1, 125.6, 124.8, 123.5, 121.4, 111.7, 40.2, 35.4, 31.9, 29.7, 29.6, 29.5, 29.3, 29.2, 27.3, 26.9, 22.7, 14.1. HRMS: *m/z* Calculated for $C_{20}H_{30}BrNO_2$ $[M+H]^+$ 379.1511; found 380.1555.



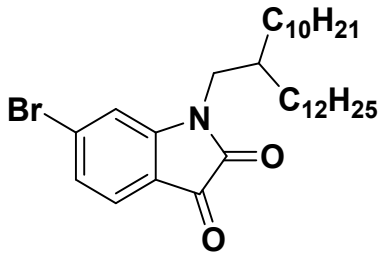
^{1}H NMR of Compound **2** in $CDCl_3$.



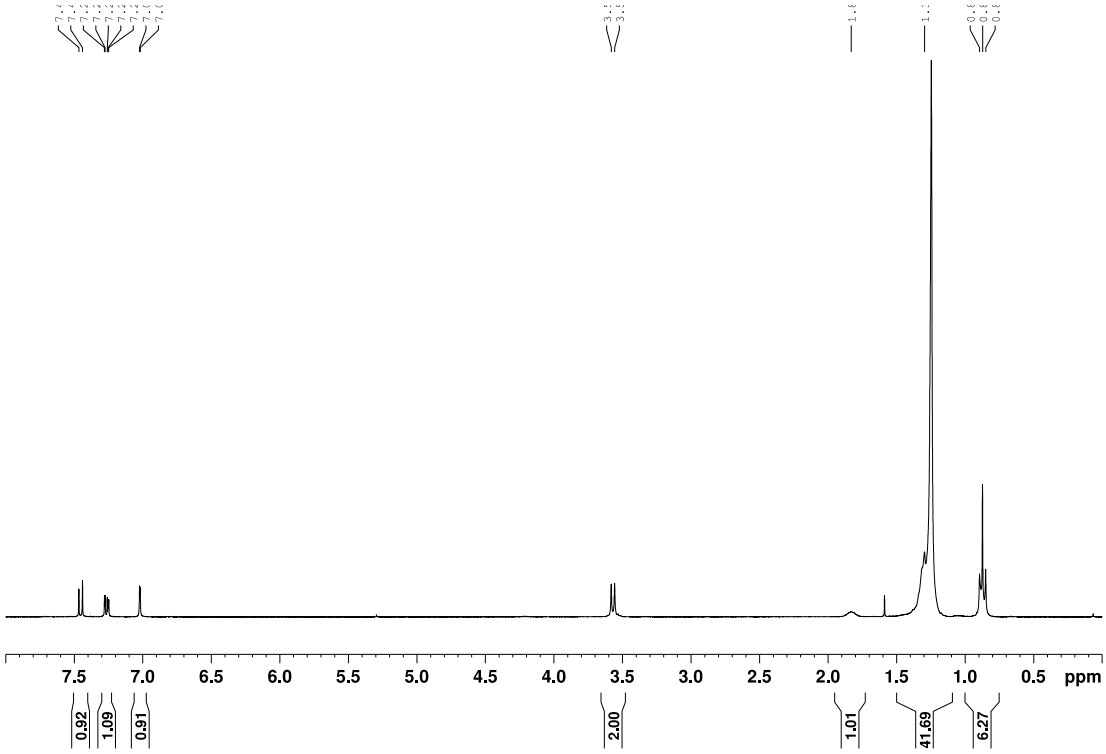
^{13}C NMR of Compound **2** in $CDCl_3$.



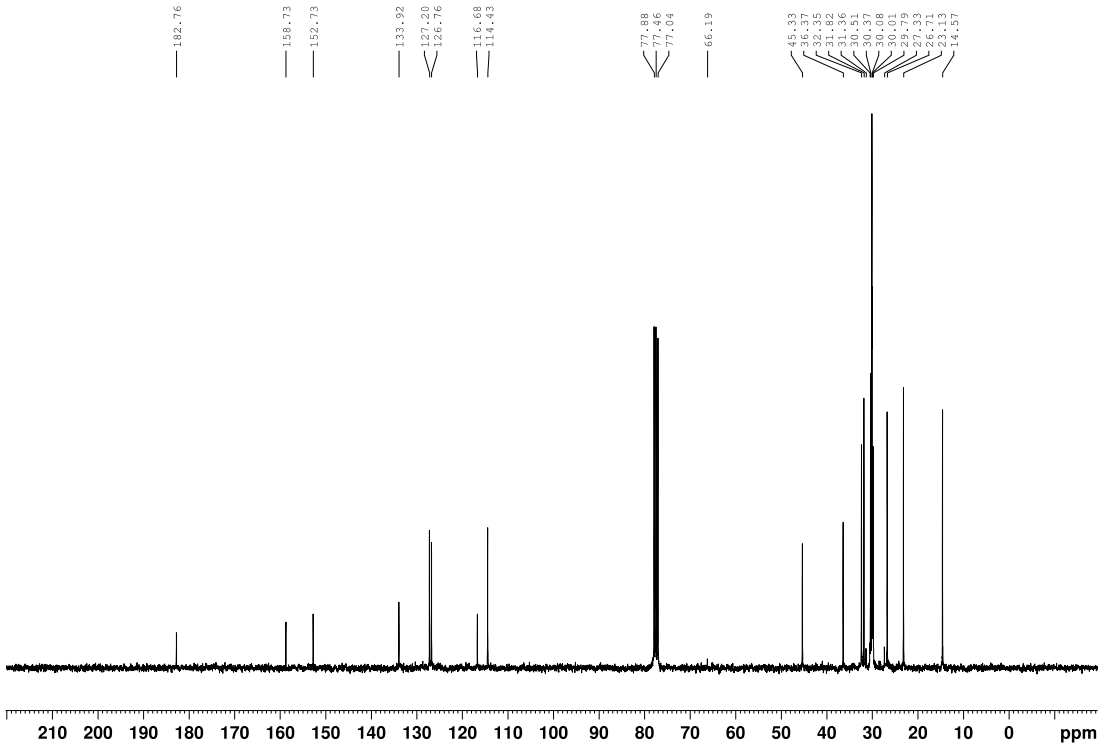
FTIR spectrum of Compound **2**.



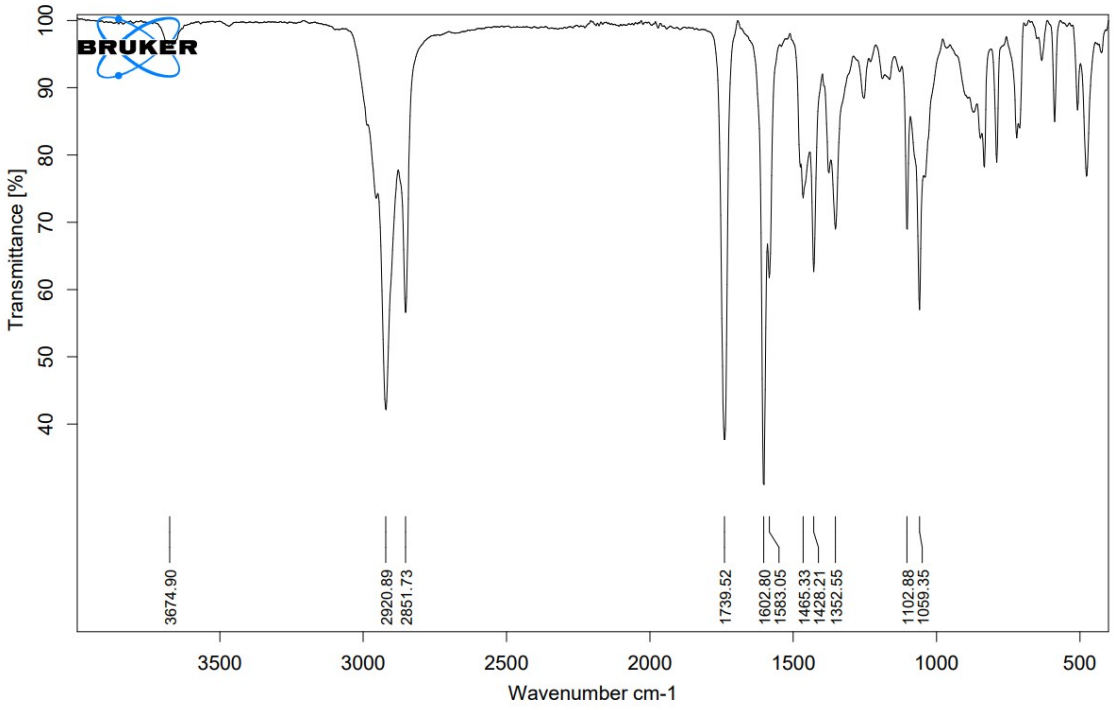
Compound 3. *6-bromo-1-(2-decyltetradecyl)indoline-2,3-dione*. To a purged flame dried 250 mL round-bottom flask, 6-Bromoisatin (0.5 g, 2.2 mmol) and potassium carbonate (0.46 g, 9.6 mmol) was added to a solution of DMF (12 mL) and THF (12 mL). 2-decyl-1-tetradecyl iodide (1.8 g, 3.9 mmol) was added dropwise, and the solution was refluxed at 70˚C under nitrogen atmosphere for 2 hours. The solution is then extracted CH_2Cl_2 and 10% HCl solution, dried with Na_2SO_4, and reduced under pressure. The product is then purified by column chromatography using hexanes and CH_2Cl_2 (2:1) to obtain compound **3** as an orange oil. Yield: 0.74 g (60%). ^{1}H NMR ($CDCl_3$) δ: 7.45 (d, 1H, *J* = 7.43 Hz) 7.27 (m, 1H), 7.02 (d, 1H, *J* = 0.9 Hz), 3.55 (d, 2H, *J* = 9 Hz), 1.83 (m, 1H), 1.24 (m, 41H), 0.87 (t, 6H, *J* = 6.3 Hz, 13.5 Hz). ^{13}C NMR ($CDCl_3$) δ: 182.7, 158.7, 152.7, 133.9, 127.2, 126.7, 116.6, 114.4, 45.3, 36.3, 32.3, 31.8, 31.3, 30.5, 30.3, 30.0, 29.7, 27.3, 26.7, 23.1, 14.5. HRMS: *m/z* Calculated for $C_{32}H_{52}BrNO_2$ $[M+H]^+$ 561.3181; found 581.3462.



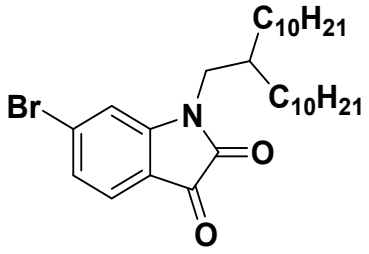
^{1}H NMR of Compound **3** in $CDCl_3$.



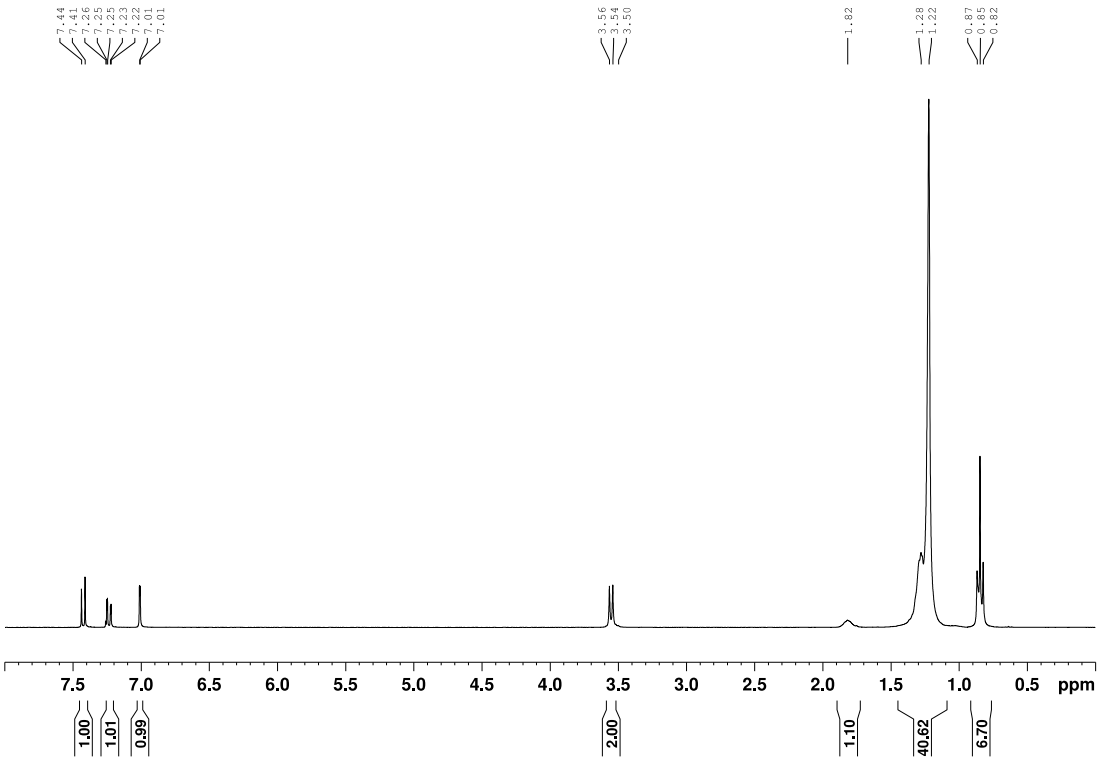
^{13}C NMR of Compound **3** in $CDCl_3$.



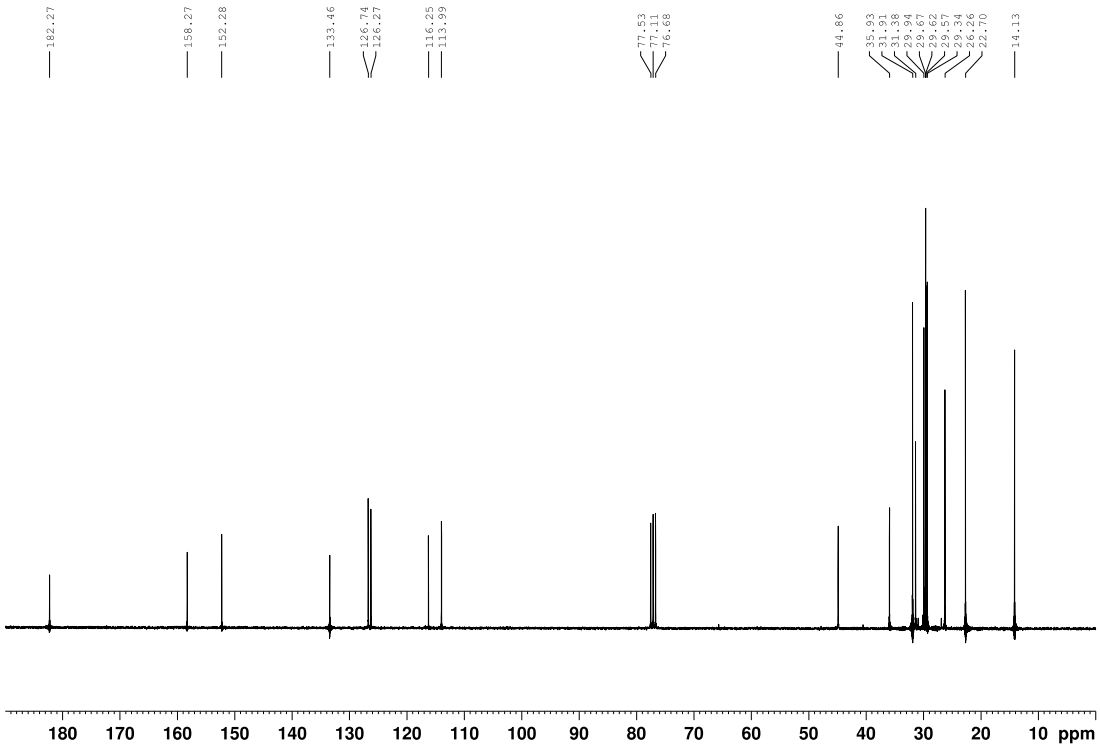
FTIR spectrum of Compound **3.**



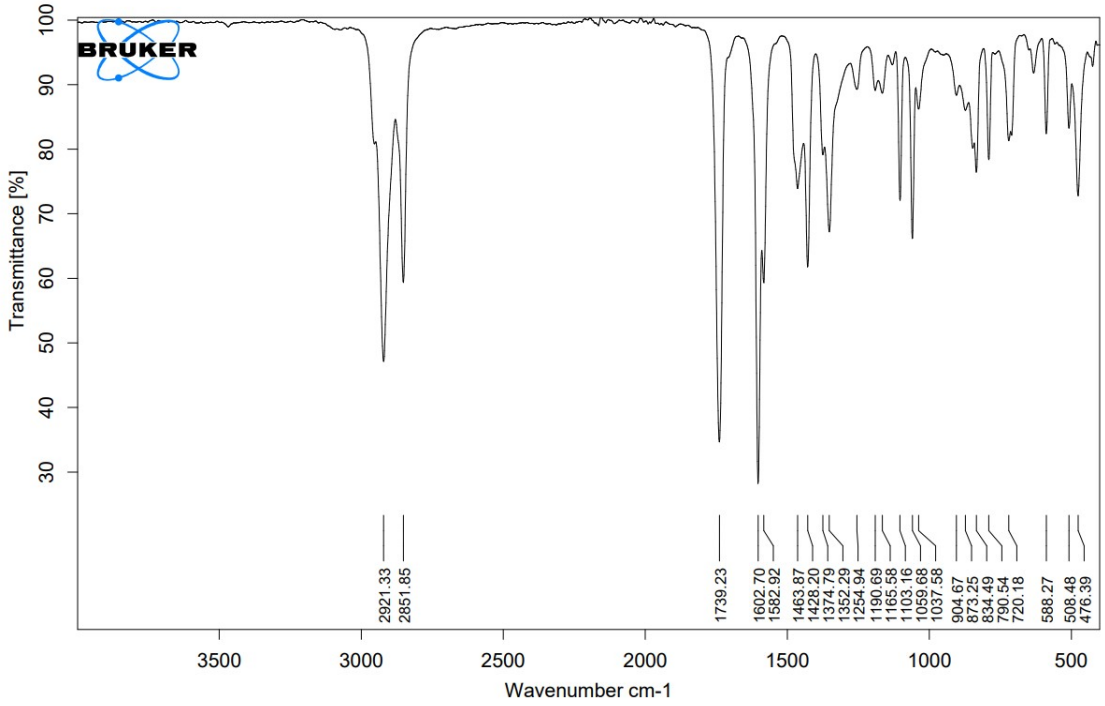
Compound 4. *6-bromo-1-(2-decyldodecyl)indoline-2,3-dione*. To a purged flame dried 250 mL round-bottom flask, 6-Bromoisatin (0.5 g, 2.2 mmol) and potassium carbonate (0.46 g, 3.3 mmol) was added to a solution of DMF (11 mL) and THF (11 mL). 11-(iodomethyl)henicosane (1.2 g, 2.7 mmol) was added dropwise, and the solution was refluxed at 70˚C under nitrogen atmosphere for 2 hours. The solution is then extracted CH_2Cl_2 and 10% HCl solution, dried with Na_2SO_4, and reduced under pressure. The product is then purified by column chromatography using hexanes and CH_2Cl_2 (1:2) to obtain compound **4** as an orange oil. Yield: 0.56 g (47%). ^{1}H NMR ($CDCl_3$) δ: 7.46 (d, 1H, *J* = 6 Hz), 7.27 (m, 1H, *J* = 6 Hz), 7.03 (d, 1H, *J* = 3 Hz), 3.57 (d, 2H, *J* = 9 Hz), 1.84 (b, 1H), 1.30 (m, 36H), 0.88 (t, 6H, *J* = 6 Hz, 12Hz). ^{13}C NMR ($CDCl_3$) δ: 158.3, 152.4, 133.9, 126.8, 126.3, 114.3, 114.0, 45.0, 36.0, 31.9, 31.5, 29.9, 29.7, 29.6, 29.3, 22.7, 14.1. HRMS: *m/z* Calculated for $C_{30}H_{48}BrNO_2$ $[M+H]^+$ 533.2868; found 534.2933.



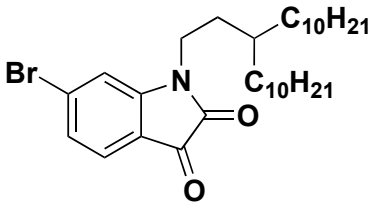
^{1}H NMR of Compound **4** in $CDCl_3$.



^{13}C NMR of Compound **4** in $CDCl_3$.

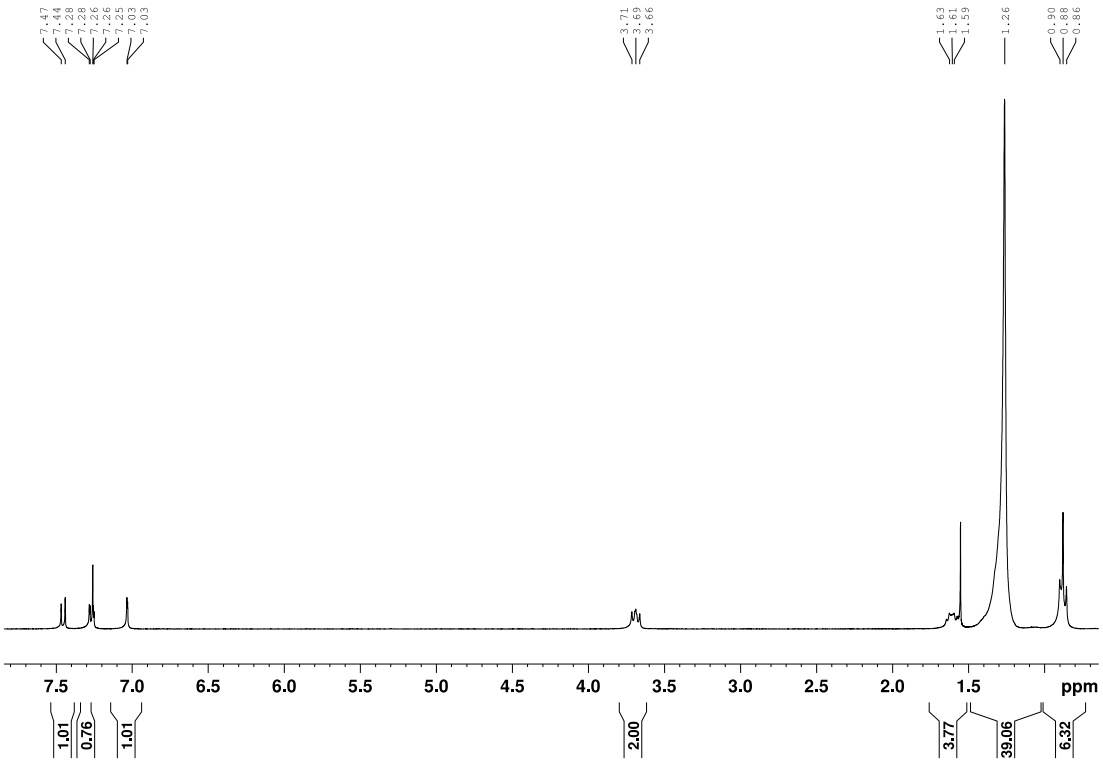


FTIR spectrum of Compound **4**.

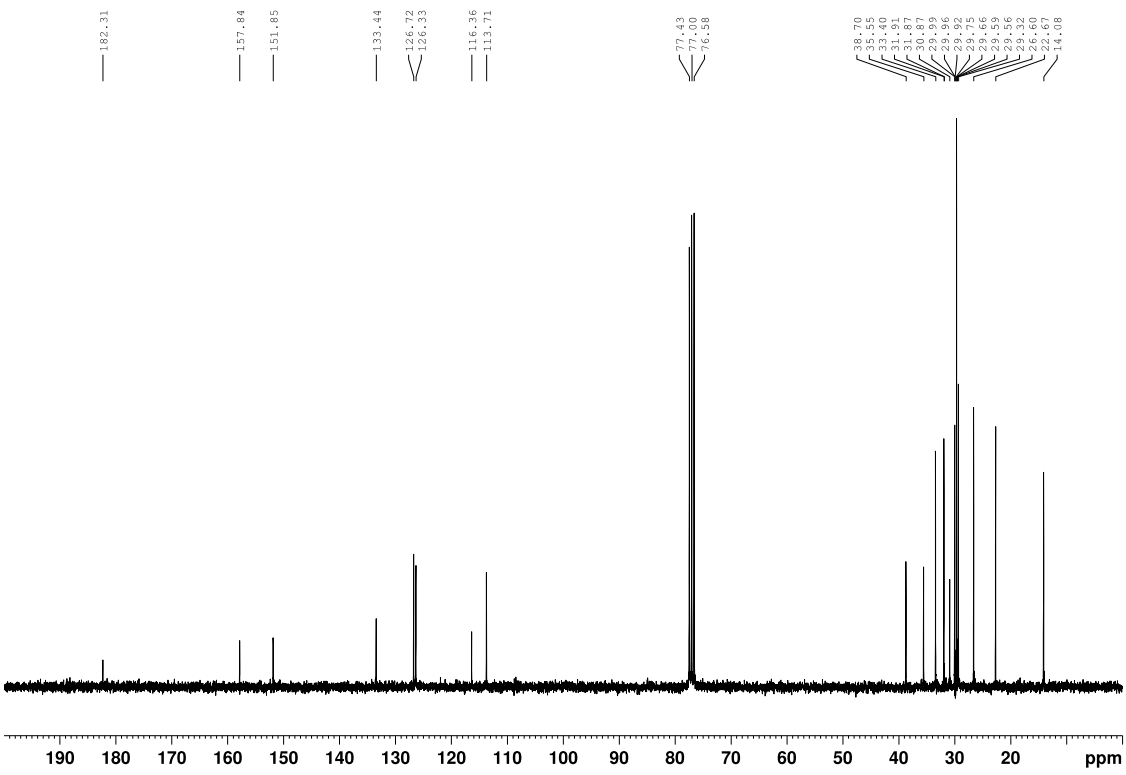


Compound 5. *6-bromo-1-(3-decyltridecyl)indoline-2,3-dione*. To a purged flame dried 250 mL round-bottom flask, 6-Bromoisatin (0.5 g, 2.2 mmol) and potassium carbonate (0.46 g, 3.3 mmol) was added to a solution of DMF (11 mL) and THF (11 mL). 11-(2-iodoethyl)henicosane (1.2 g, 2.7 mmol) was added dropwise, and the solution was refluxed at 70˚C under nitrogen atmosphere for 2 hours. The solution is then extracted CH_2Cl_2 and 10% HCl solution, dried with Na_2SO_4, and reduced under pressure. The product is then purified by column chromatography using hexanes and CH_2Cl_2 (1:2) to obtain compound **5** as an orange oil. Yield: 1.1 g (92%). ^1H

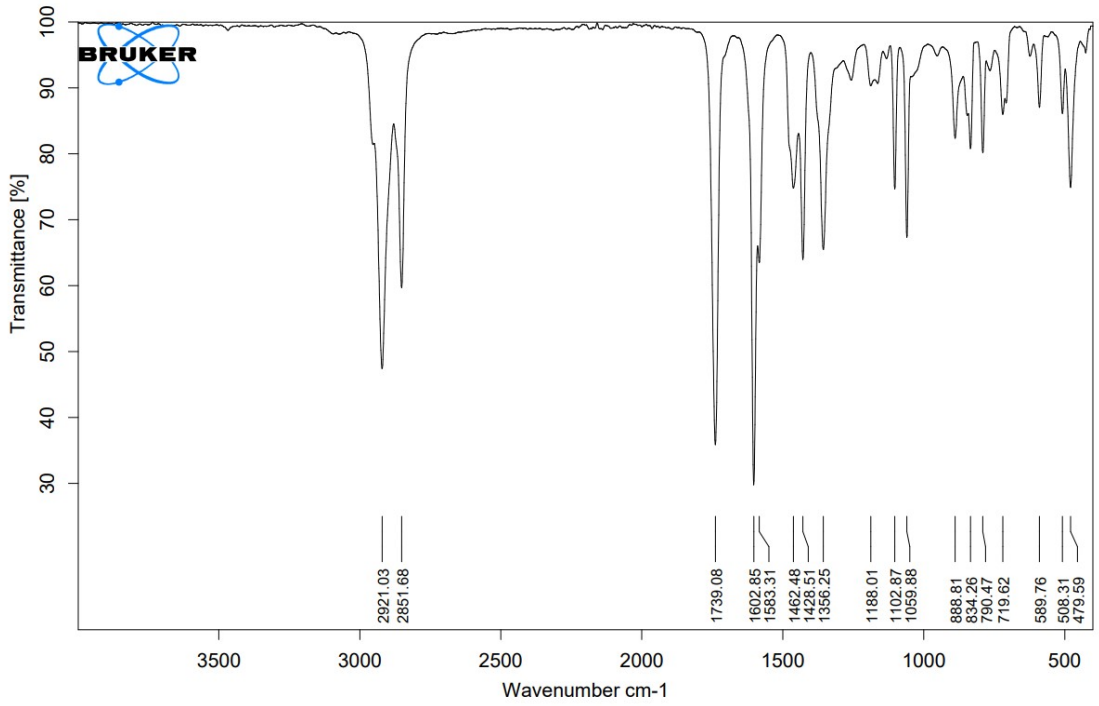
NMR ($CDCl_3$) δ: 7.45 (d, 1H, *J* = 7.9 Hz), 7.27 (m, 1H), 7.03 (d, 1H, *J* = 1.5 Hz), 3.69 (m, 2H), 1.61 (m, 3H), 1.26 (d, 40H), 0.88 (t, 6H, *J* = 6.9 Hz, 5.1Hz). ^{13}C NMR ($CDCl_3$) δ: 182.31, 157.84, 151.85, 133.44, 126.72, 126.33, 116.36, 113.71, 38.70, 35.55, 33.40, 31.91, 31.87, 30.87, 29.99, 29.96, 29.92, 29.75, 29.66, 29.59, 29.56, 29.32, 26.60, 22.67, 14.08. HRMS: *m/z* Calculated for $C_{31}H_{50}BrNO_2$ $[M+H]^+$ 547.3025; found 550.310.



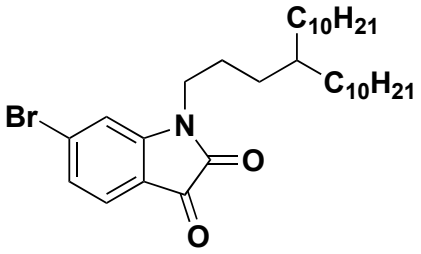
^1H NMR of Compound **5** in $CDCl_3$



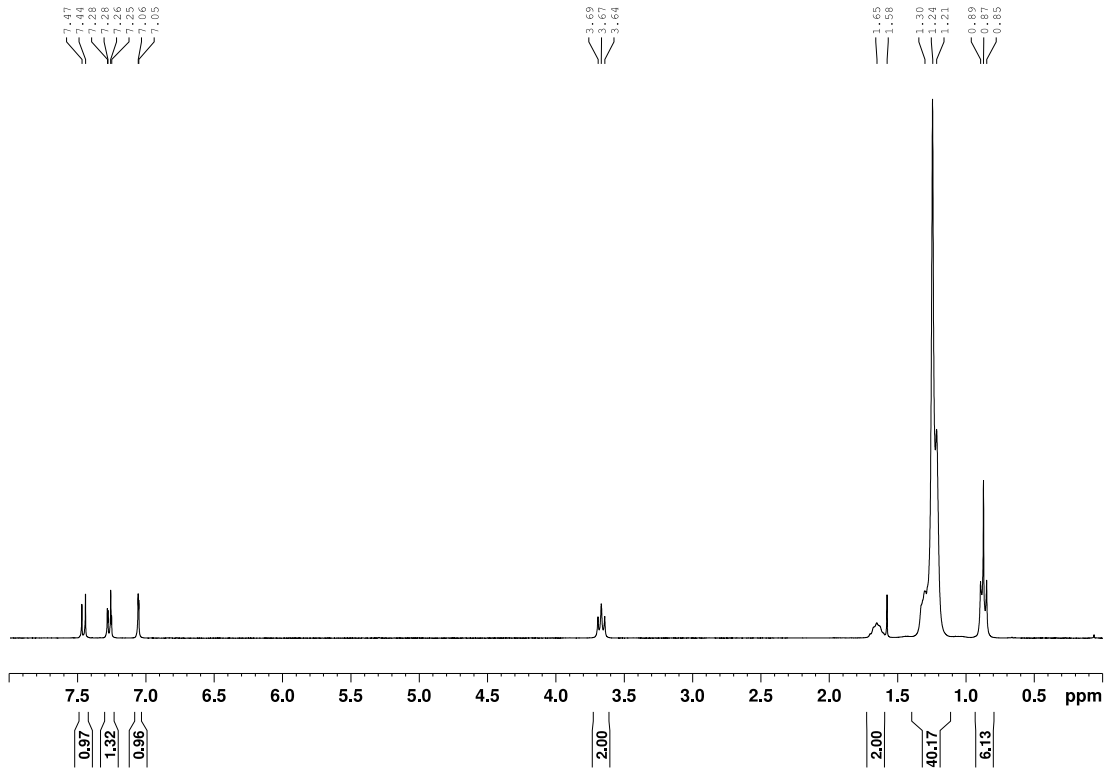
^{13}C NMR of Compound **5** in $CDCl_3$



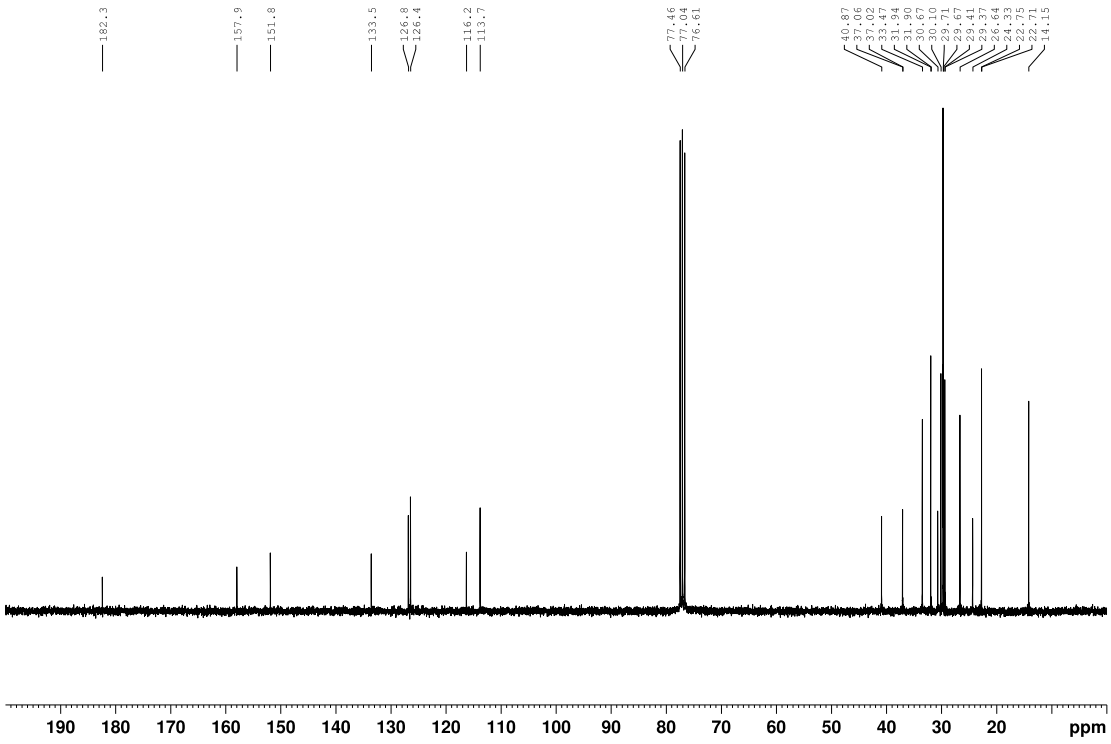
FTIR spectrum of Compound **5.**



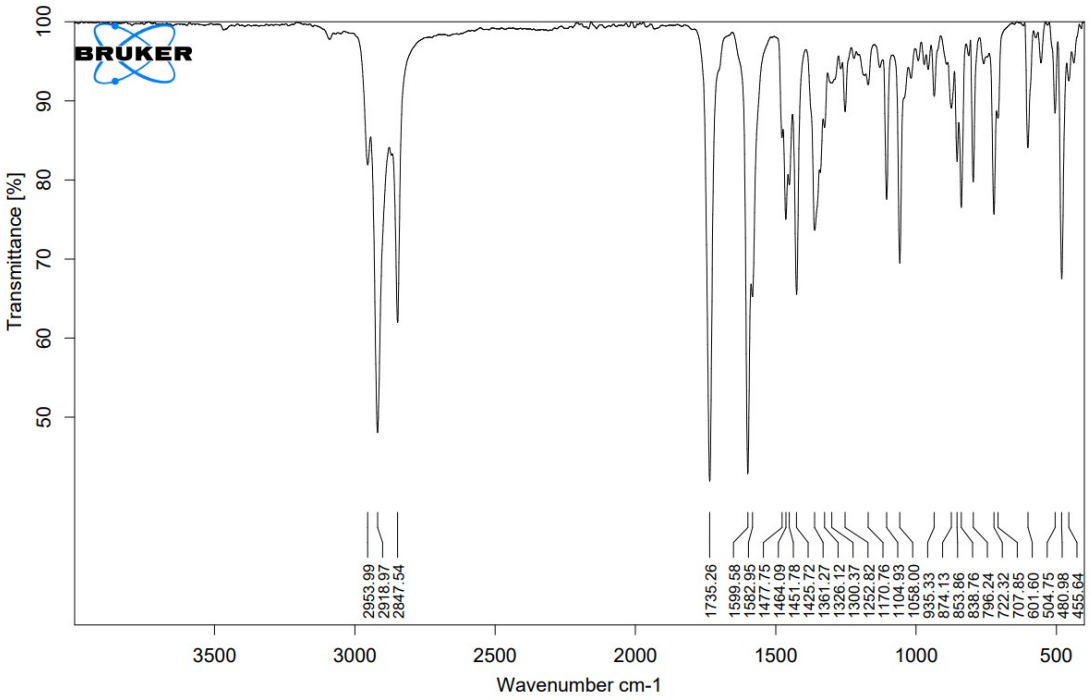
Compound 6. *6-bromo-1-(4-decyltetradecyl)indoline-2,3-dione.* To a purged flame dried 250 mL round-bottom flask, 6-Bromoisatin (0.5 g, 2.2 mmol) and potassium carbonate (0.46 g, 3.3 mmol) was added to a solution of DMF (11 mL) and THF (11 mL). 11-(3-iodopropyl)henicosane (1.2 g, 2.7 mmol) was added dropwise, and the solution was refluxed at 70˚C under nitrogen atmosphere for 2 hours. The solution is then extracted CH_2Cl_2 and 10% HCl solution, dried with Na_2SO_4, and reduced under pressure. The product is then purified by column chromatography using hexanes and CH_2Cl_2 (1:2) to obtain compound **6** as an orange solid. Yield: 0.88 g (71%). ^{1}H NMR ($CDCl_3$) δ: 7.45 (d, 1H, *J* = 7.9 Hz), 7.27 (m, 1H), 7.05 (d, 1H, *J* = 1.7 Hz), 3.67 (t, 2H, *J* = 7.4 Hz), 1.67 (m, 2H), 1.23 (m, *J* = 9.4, 40H), 0.87 (t, 6H). ^{13}C NMR (76 MHz, CDCl3) δ 182.39, 157.97, 151.88, 133.56, 126.83, 126.42, 116.28, 113.79, 77.47, 77.05, 76.62, 40.88, 37.07, 33.47, 31.95, 30.68, 30.11, 29.72, 29.67, 29.38, 26.65, 24.34, 22.72, 14.16. HRMS: *m/z* Calculated for $C_{32}H_{52}BrNO_2$ $[M+H]^+$ 561.3181; found 562.3272.



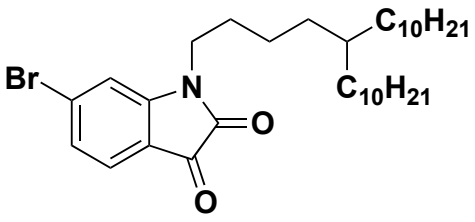
^{1}H NMR of Compound **6** in $CDCl_3$



^{13}C NMR of Compound **6** in $CDCl_3$

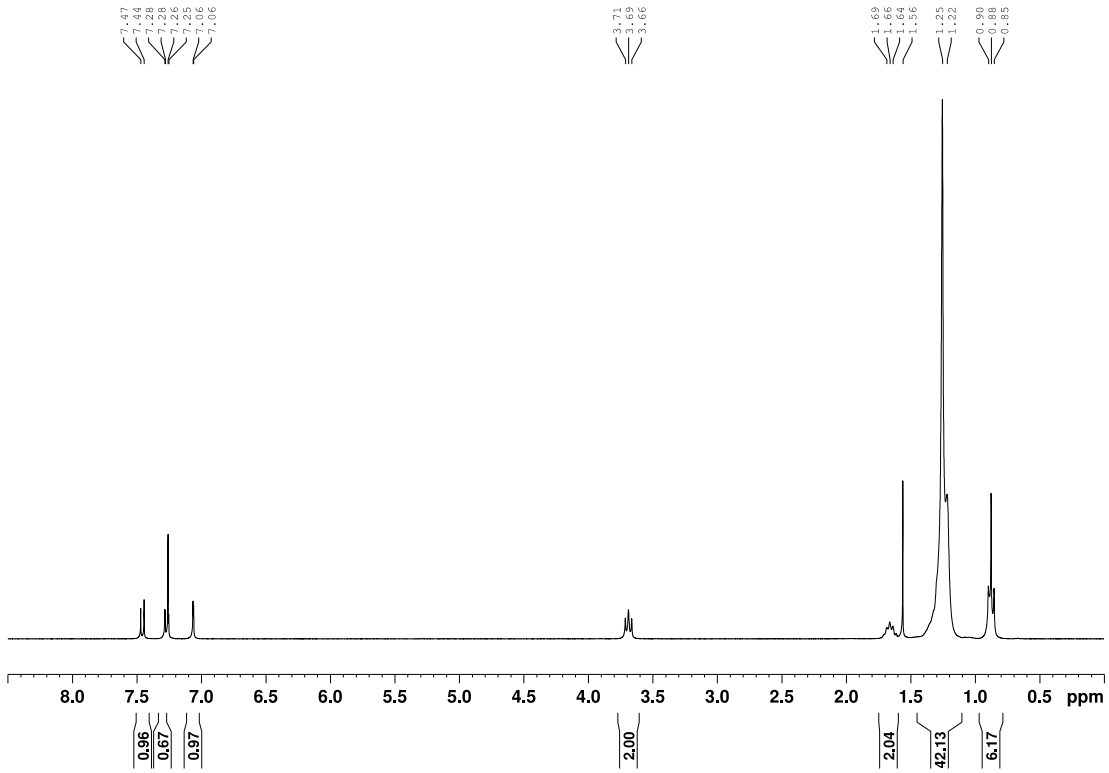


FTIR spectrum of Compound **6.**

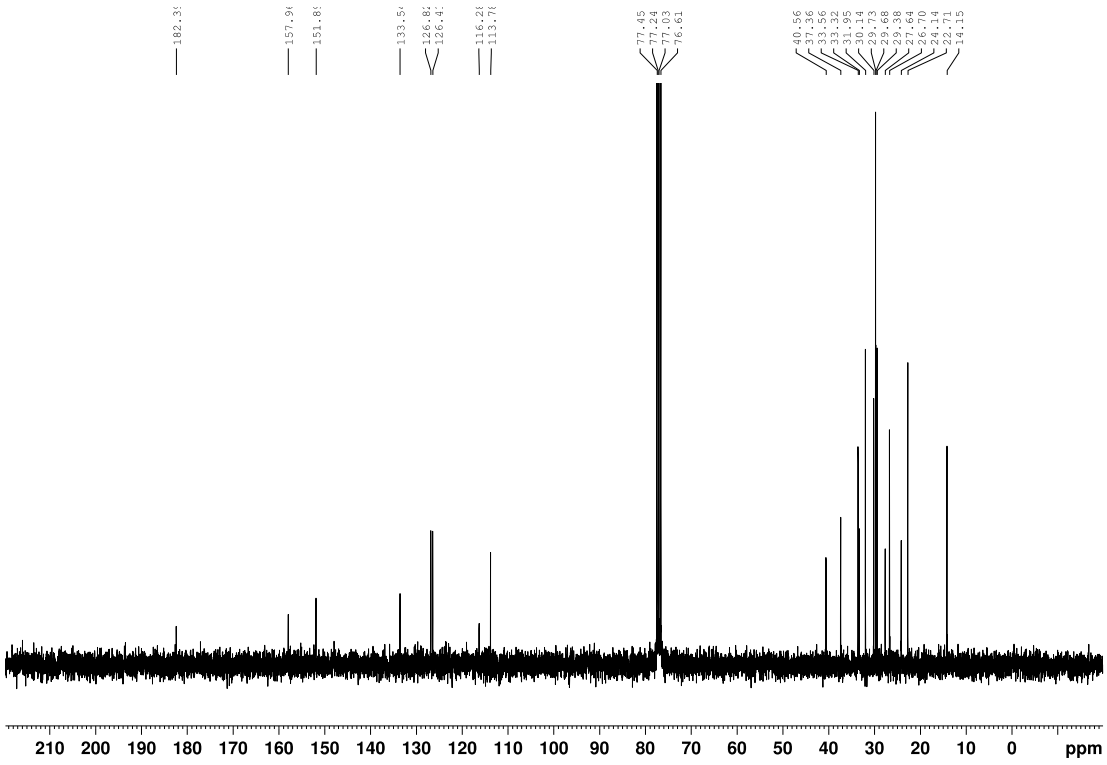


Compound 7. *6-bromo-1-(5-decylpentadecyl)indoline-2,3-dione.* To a purged flame dried 250 mL round-bottom flask, 6-Bromoisatin (0.5 g, 2.2 mmol) and potassium carbonate (0.46 g, 3.3 mmol) was added to a solution of DMF (11 mL) and THF (11 mL). 11-(4-iodobutyl)henicosane (1.3 g, 2.7 mmol) was added dropwise, and the solution was refluxed at 70˚C under nitrogen atmosphere for 2 hours. The solution is then extracted CH_2Cl_2 and 10% HCl solution, dried with Na_2SO_4, and reduced under pressure. The product is then purified by column chromatography using hexanes and CH_2Cl_2 (2:1) to obtain compound **7** as an orange oil. Yield: 0.89 g (70%). ^{1}H NMR ($CDCl_3$) δ 7.46 (d, J = 7.9 Hz, 1H), 7.32 – 7.20 (m, 2H), 7.06 (d, J = 1.6 Hz, 1H), 3.69 (t, J = 7.5 Hz, 2H), 1.66 (p, J = 7.2 Hz, 2H), 1.23 (d, J = 11.5 Hz, 42H), 0.97 – 0.76 (m, 6H).^{13}C NMR (CDCl3) δ 157.97, 151.89, 133.55, 126.83, 126.42, 116.29, 113.79, 77.46, 77.04, 76.62, 40.56, 37.36, 33.57,

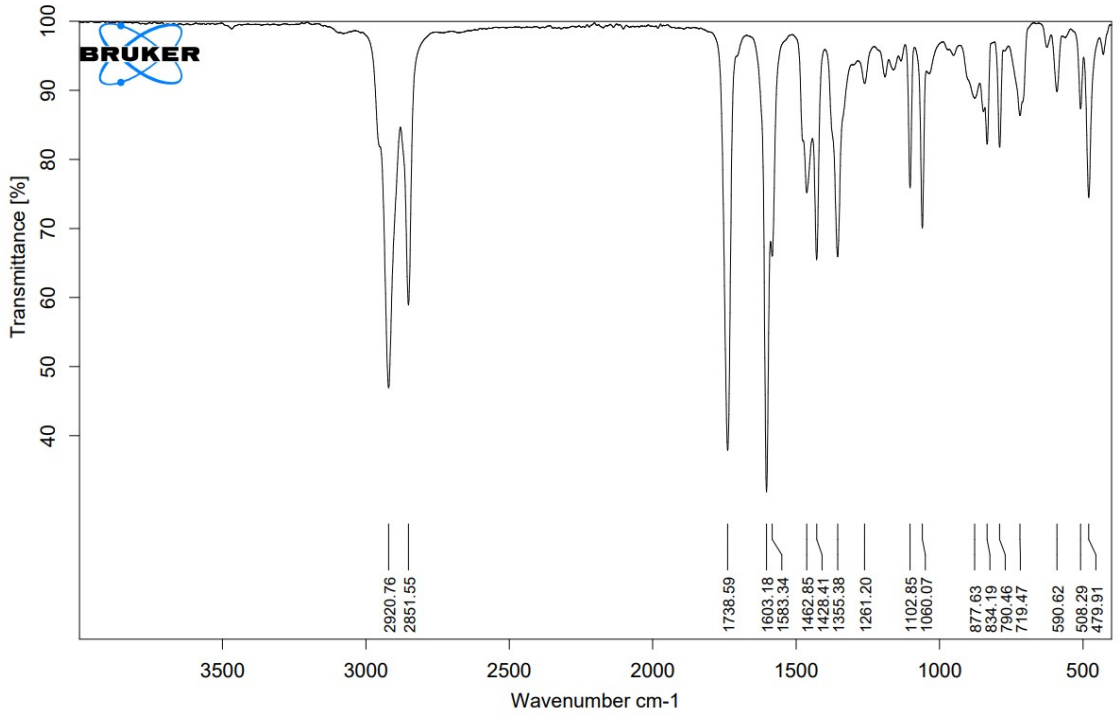
33.32, 31.95, 30.15, 29.74, 29.68, 29.39, 27.64, 26.71, 24.15, 22.72, 14.15. HRMS: *m/z* Calculated for $C_{33}H_{54}BrNO_2$ $[M+H]^+$ 575.3338; found 578.3392.



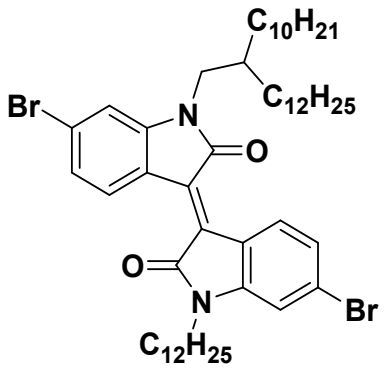
^{1}H NMR of Compound **7** in $CDCl_3$



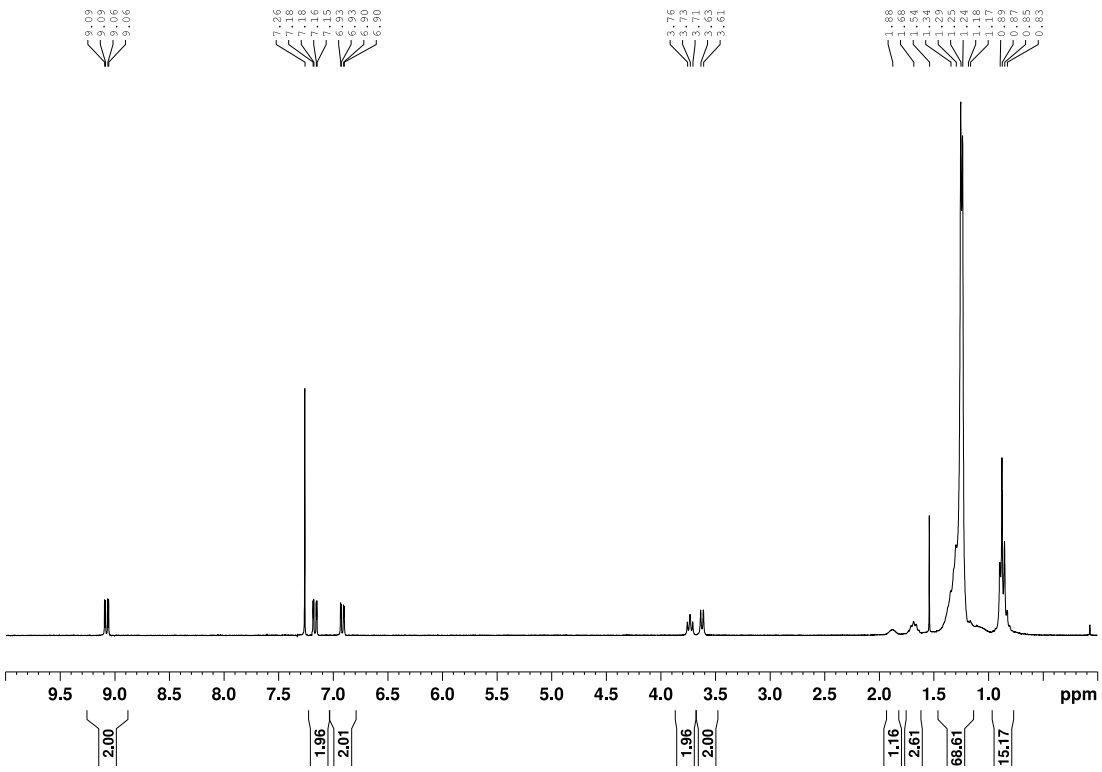
^{13}C NMR of Compound **7** in $CDCl_3$



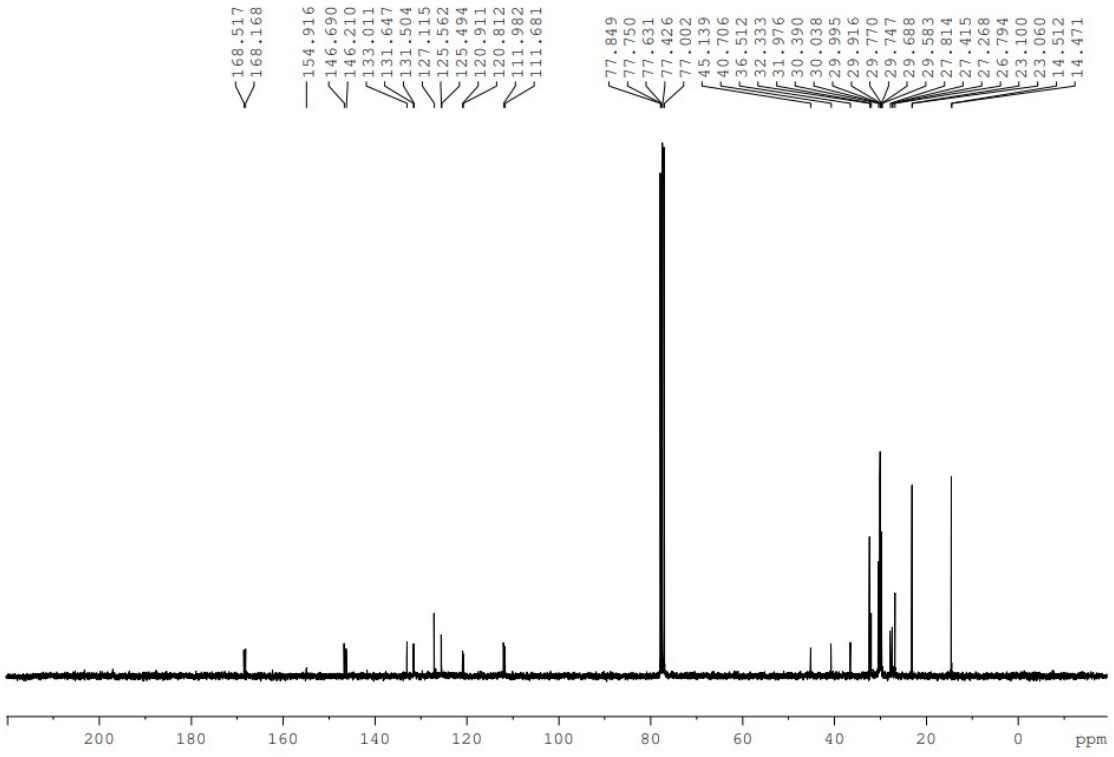
FTIR spectrum of Compound **7.**



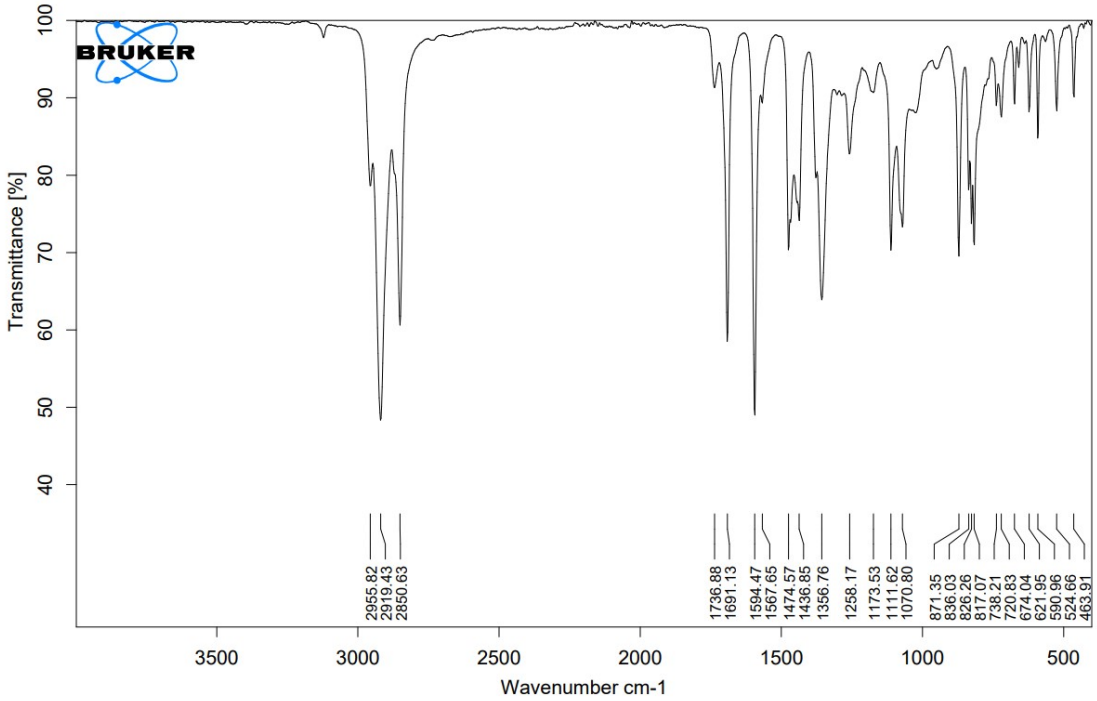
Compound 8. Compound **3** (35 mg, 0.088 mmol) and compound **2** (49 mg, 0.088 mmol) is added to a 250 mL round bottom flask. 0.90 mL acetic acid and a drop of concentrated HCl is then added, and the reaction is allowed to stir for 24 hrs at 120 ℃. The compound is then extracted in CH_2Cl_2 and dried with Na_2SO_4 and concentrated under reduced pressure. The resulting red liquid is then purified by column chromatography using hexanes and toluene (4:1), and the recrystallized in isopropyl alcohol to obtain compound **8** as a dark red powder. Yield: 54 mg (76%). ^{1}H NMR ($CDCl_3$) δ: 9.07 (dd, 2H, *J* = 2.4 Hz, 8.4 Hz), 7.16 (dd, 2H, *J* = 1.8 Hz, 8.7 Hz), 6.91 (dd, 2H, *J* = 8.1 Hz, 8.7 Hz), 3.7 (t, 2H, *J* = 7.2 Hz), 3.61 (d, 2H, *J* = 7.5 Hz), 1.88 (bs, 1H), 1.68 (p, 2H, *J* = 6.6 Hz), 1.24 (bs, 60H), 0.86 (q, 9H, *J* = 6.3 Hz, 13.5 Hz). ^{13}C NMR ($CDCl_3$) δ: 168.5, 168.1, 154.9, 146.7, 133.0, 131.6, 131.5, 127.1, 125.5, 125.4, 120.9, 120.8, 111.9, 111.6, 45.1, 40.7, 36.5, 32.3, 31.9, 30.3, 30.0, 29.9, 29.9, 29.7, 29.7, 29.6, 29.5, 27.8, 27.4, 27.2, 26.7, 23.1, 23.0, 14.5, 14.4. HRMS: *m/z* Calculated for $C_{52}H_{80}Br_2N_2O_2$ $[M+H]^+$ 924.4930; found 925.4636.



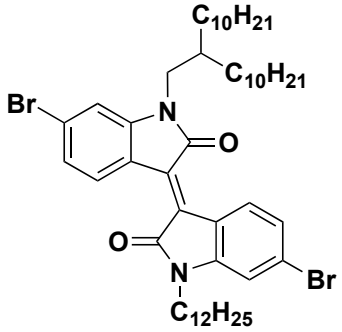
^{1}H NMR of Compound **8** in $CDCl_3$.



^{13}C NMR of Compound **8** in $CDCl_3$

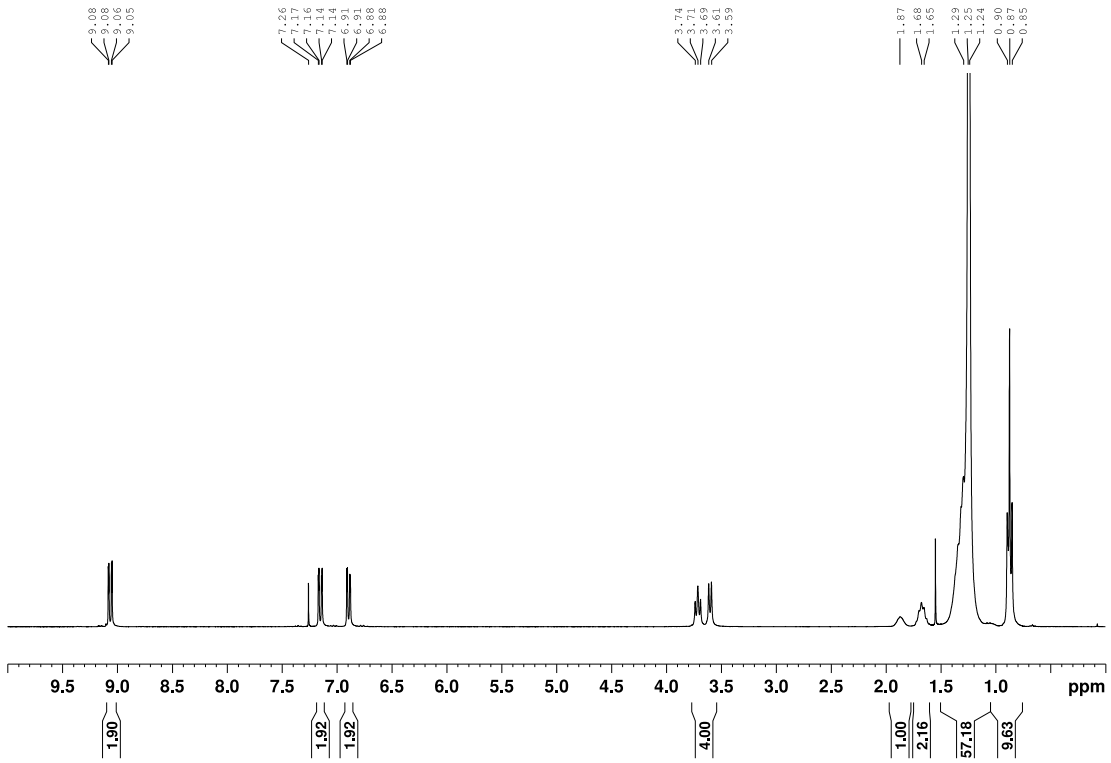


FTIR spectrum of Compound **8**

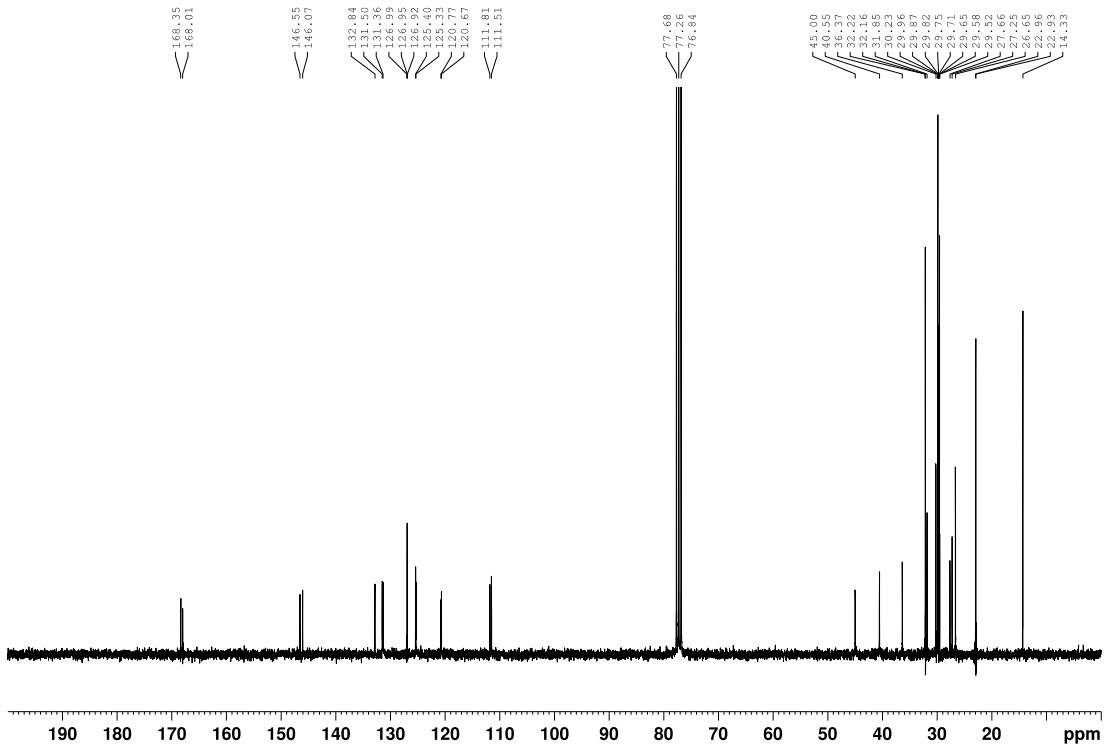


Compound **9**. *(E)-6,6'-dibromo-1-(2-decyldodecyl)-1'-dodecyl-[3,3'-biindolinylidene]-2,2'-dione*. Compound **4** (0.48 g, 0.89 mmol) and compound **2** (0.34 g, 0.89 mmol) is added to a 50 mL round bottom flask. 8 mL acetic acid and a drop of concentrated HCl is then added, and the reaction is allowed to stir for 24 hrs at 120 °C. The compound is then extracted in $CHCl_3$ and dried with Na_2SO_4 and concentrated under reduced pressure. The compound is then purified via column chromatography CH_2Cl_2 and hexanes (4:1). The compound is then recrystallized in isopropyl alcohol to yield a compound **9** as a red solid. Yield: 82 mg (69%). ^{1}H NMR ($CDCl_3$) δ: 9.07 (dd, 2H, J = 3 Hz, 6Hz), 7.15 (dd, 2H, J = 3 Hz), 6.99 (dd, 2H, J = 9 Hz), 3.73 (t, 2H, J = 9 Hz, 15 Hz), 3.60 (d, 2H, J = 6 Hz), 1.87 (s, 1H), 1.67 (m, 2H), 1.25 (m, 54H), 0.87 (t, 9H, J = 6 Hz, 15 Hz). ^{13}C NMR ($CDCl_3$) δ: 168.3, 168.0, 146.5, 146.0, 132.8, 131.5, 131.3, 127.0, 126.9, 126.9, 125.4,

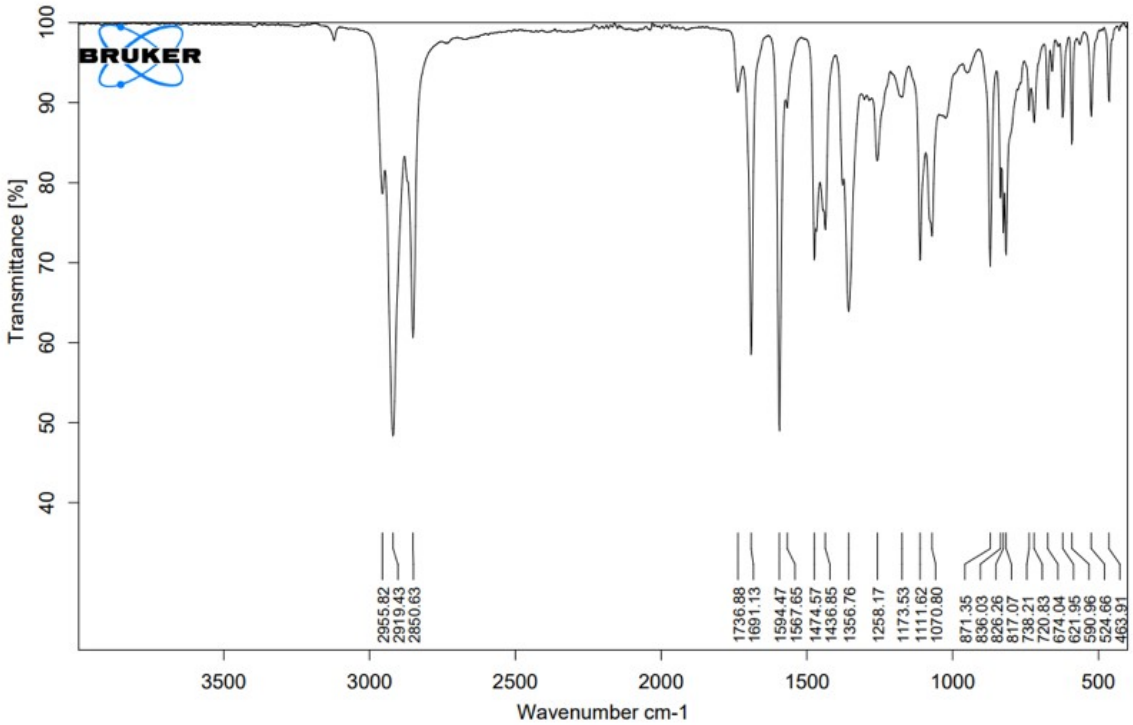
125.3, 120.7, 120.6, 111.8, 111.5, 45.0, 40.5, 36.3, 32.2, 32.1, 31.8, 30.2, 29.9, 29.8, 29.8, 29.7, 29.7, 29.6, 29.6, 29.5, 27.6, 27.2, 26.6, 23.0, 22.9, 14.3. HRMS: *m/z* Calculated for $C_{50}H_{76}Br_2N_2O_2$ $[M+H]^+$ 896.4617; found 896.4259.



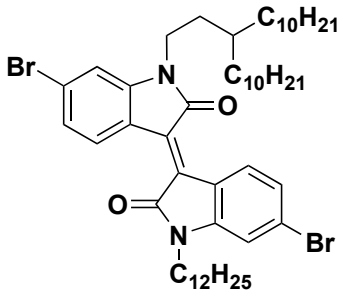
^{1}H NMR of Compound **9** in $CDCl_3$



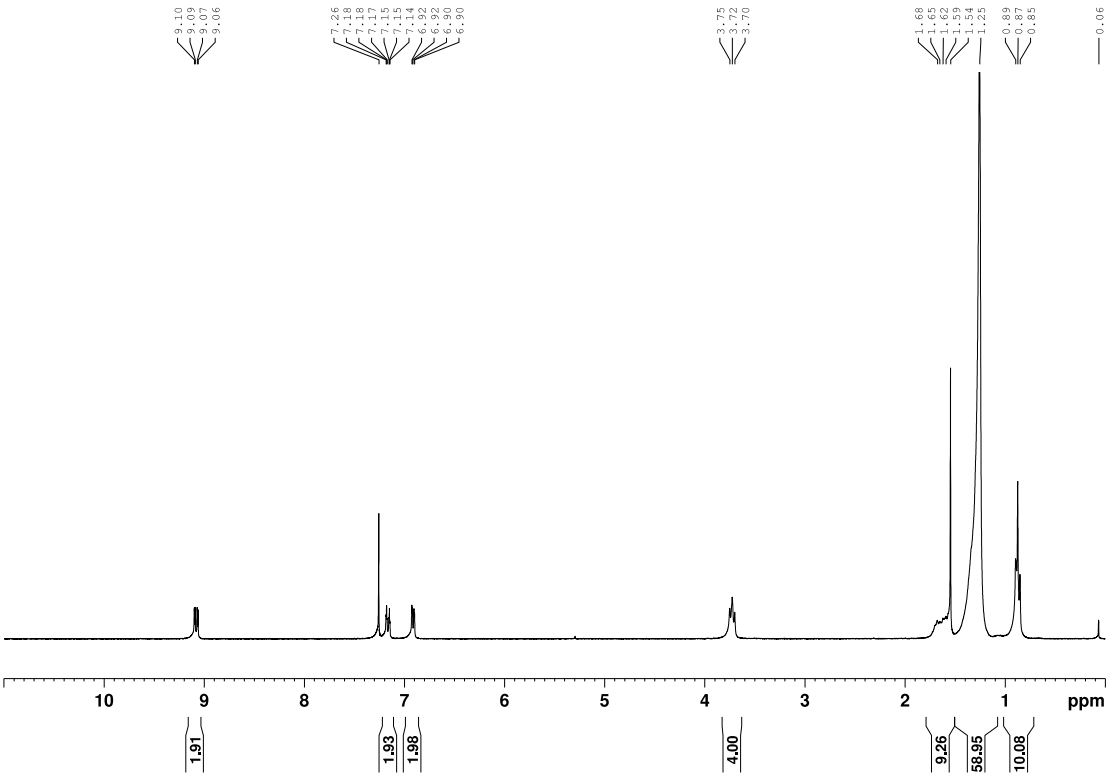
^{13}C NMR of Compound **9** in $CDCl_3$



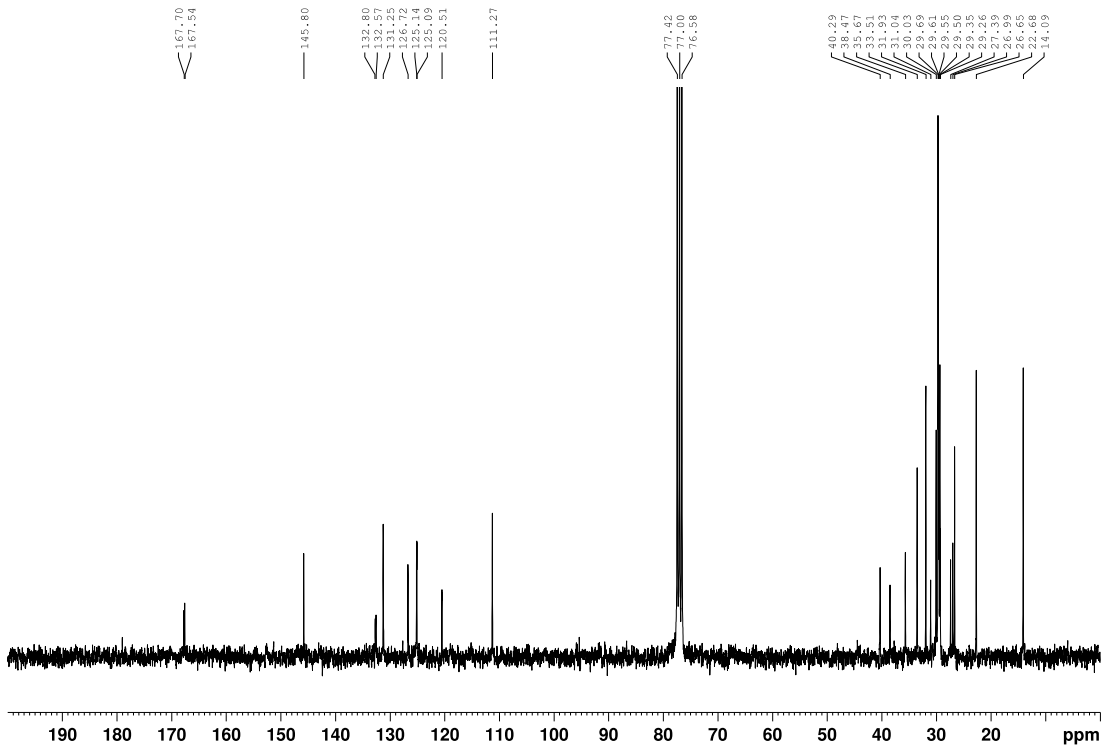
FTIR spectrum of Compound **9.**



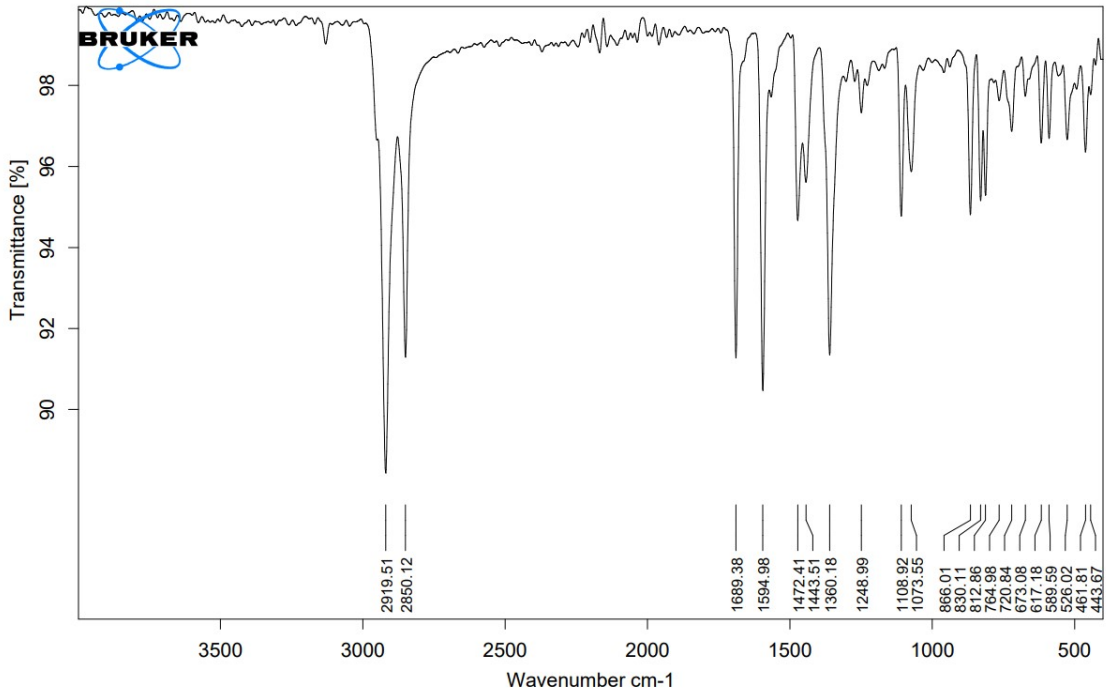
Compound **10.** *(E)-6,6'dibromo-1-(3-decyltridecyl)-1'-dodecyl-[3,3'-biindolinylidene]-2,2' dione.* Compound **5** (0.14 g, 0.26 mmol) and compound **2** (0.1 g, 0.89 mmol) is added to a 50 mL round bottom flask. 3 mL acetic acid and a drop of concentrated HCl is then added, and the reaction is allowed to stir for 24 hrs at 120 ℃. The compound is then extracted in $CHCl_3$ and dried with Na_2SO_4 and concentrated under reduced pressure. The compound is then purified via column chromatography CH_2Cl_2 and hexanes (4:1), and then recrystallized in isopropyl alcohol to yield Compound **10** as a red solid. Yield: 0.14 g (64%). ^{1}H NMR ($CDCl_3$) δ 9.08 (dd, J = 8.6, 2.6 Hz, 2H), 7.16 (dt, J = 8.5, 1.8 Hz, 2H), 6.91 (dd, J = 6.3, 1.9 Hz, 2H), 3.72 (t, J = 7.6 Hz, 4H), 1.63 (d, J = 26.2 Hz, 5H), 1.50 – 1.13 (m, 55H), 0.87 (t, J = 6.5 Hz, 9H). ^{13}C NMR ($CDCl_3$) δ: 167.70, 167.54, 145.80, 132.80, 132.57, 131.25, 126.72, 125.14, 125.09, 120.51, 111.27, 40.29, 48.47, 35.67, 33.51, 31.93, 31.04, 30.03, 29.69, 29.61, 29.55, 29.50, 29.35, 29.26, 27.39, 26.99, 29.65, 22.68, 14.09. HRMS: *m/z* Calculated for $C_{51}H_{78}Br_2N_2O_2$ M^*+ 910.4410; found 910.4402.



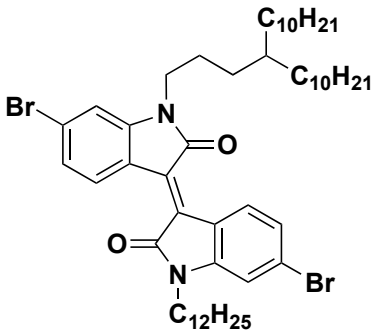
^{1}H NMR of Compound **10** in $CDCl_3$



^{13}C NMR of Compound **10** in $CDCl_3$

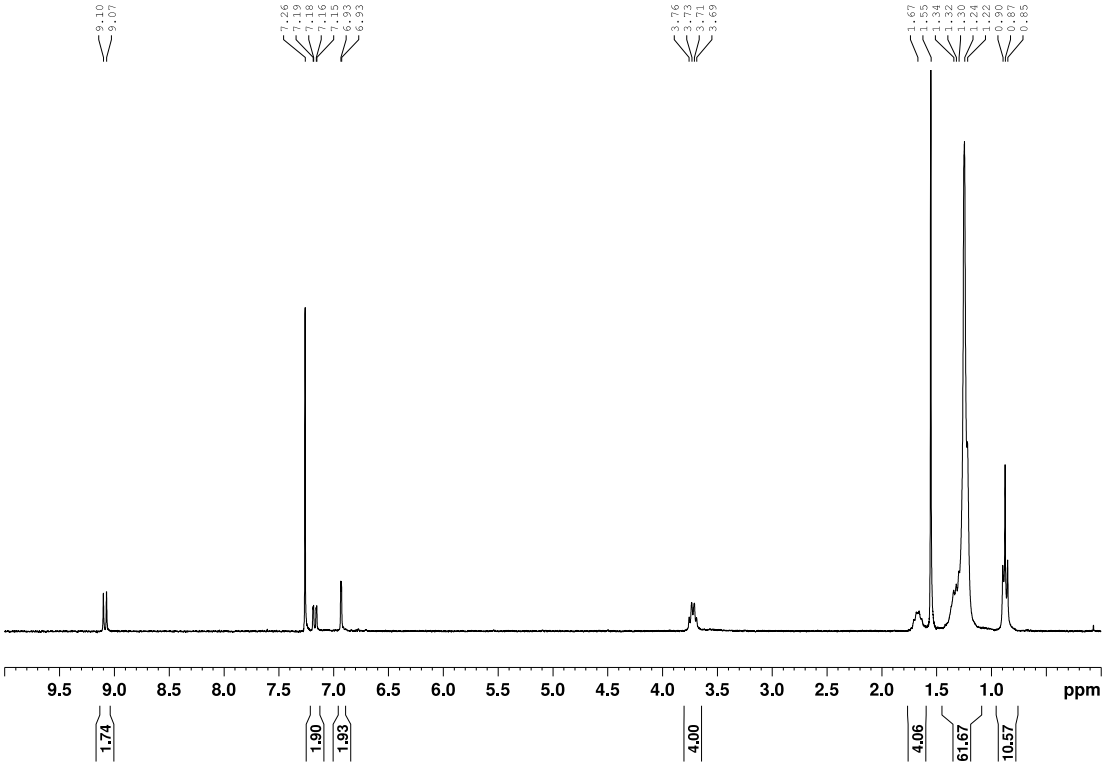


FTIR spectrum of Compound **10**

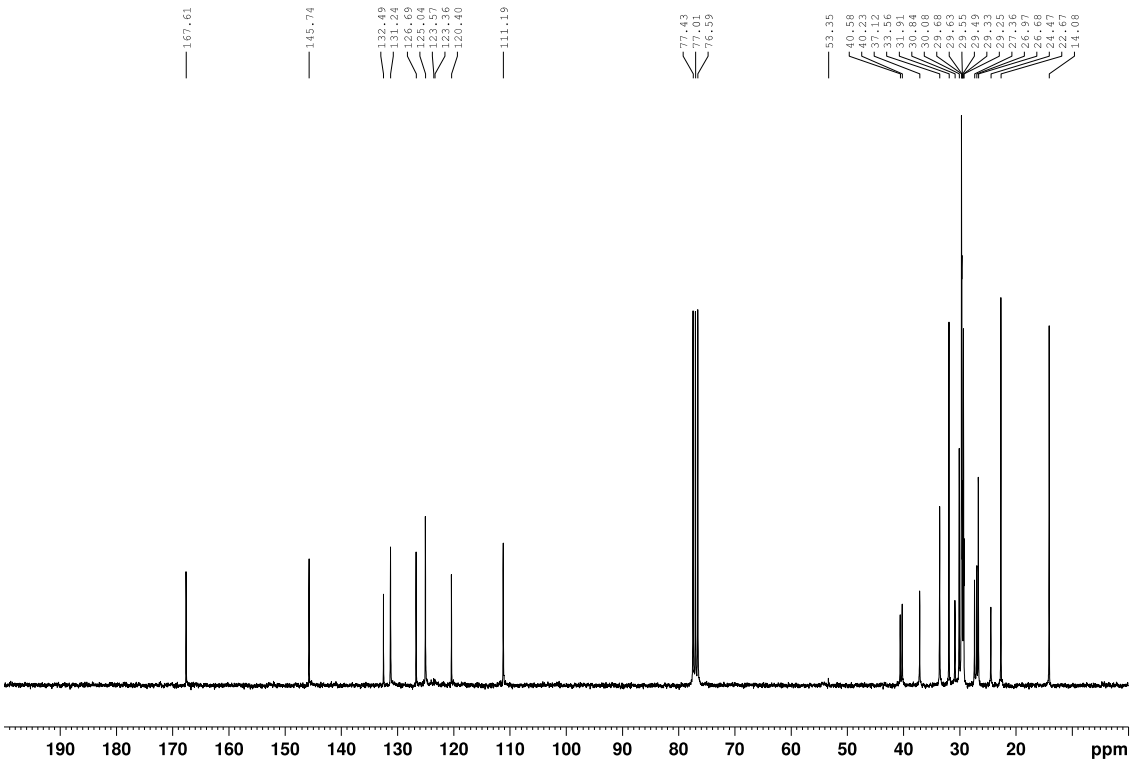


Compound **11.** (E)-6,6'dibromo-1-(4-decyltetradecyl)-1'-dodecyl-[3,3'-biindolinylidene-2,2'-dione. Compound **6** (70.0 mg, 0.13 mmol) and compound **2** (50.0 mg, 0.13 mmol) is added to a 50 mL round bottom flask. 1 mL acetic acid and a drop of concentrated HCl is then added, and the reaction is allowed to stir for 24 hrs at 120 °C under nitrogen atmosphere. The compound is then extracted in CH_2Cl_2 and dried with Na_2SO_4 and concentrated under reduced pressure. The compound is then purified via column chromatography CH_2Cl_2 and hexanes (4:1) and then recrystallized in isopropyl alcohol to yield Compound **11** as a red solid. Yield: 82 mg (69%). ^1H NMR ($CDCl_3$) δ 9.09 (d, J = 8.6 Hz, 2H), 7.17 (dd, J = 8.6, 1.9 Hz, 2H), 6.93 (d, J = 1.9 Hz, 2H),

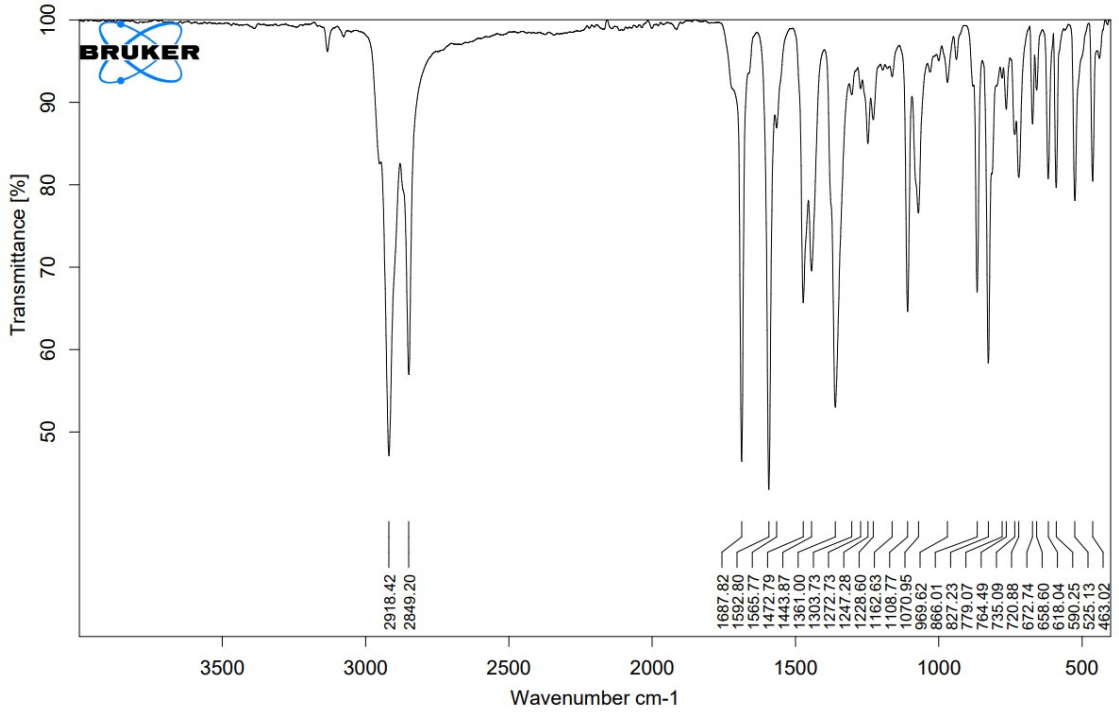
3.72 (q, J = 6.7 Hz, 4H), 1.66 (s, 4H), 1.43 – 1.10 (m, 61H), 0.95 – 0.80 (m, 10H). ^{13}C NMR ($CDCl_3$) δ:167.61, 145.74, 132.49, 131.24, 126.69, 125.04, 123.57, 123.36, 120.40, 111.19, 53.35, 40.58, 40.23, 37.12, 33.56, 31.91, 30.84, 30.08, 29.68, 29.63, 29.55, 29.49, 29.33, 29.25, 27.36, 26.97, 26.68, 24.47, 22.67, 14.08. HRMS: *m/z* Calculated for $C_{52}H_{80}Br_2N_2O_2$ M^{*}+ 924.4566; found 924.4535



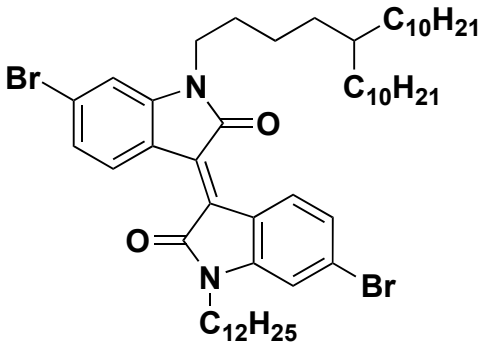
^{1}H NMR of Compound **11** in $CDCl_3$



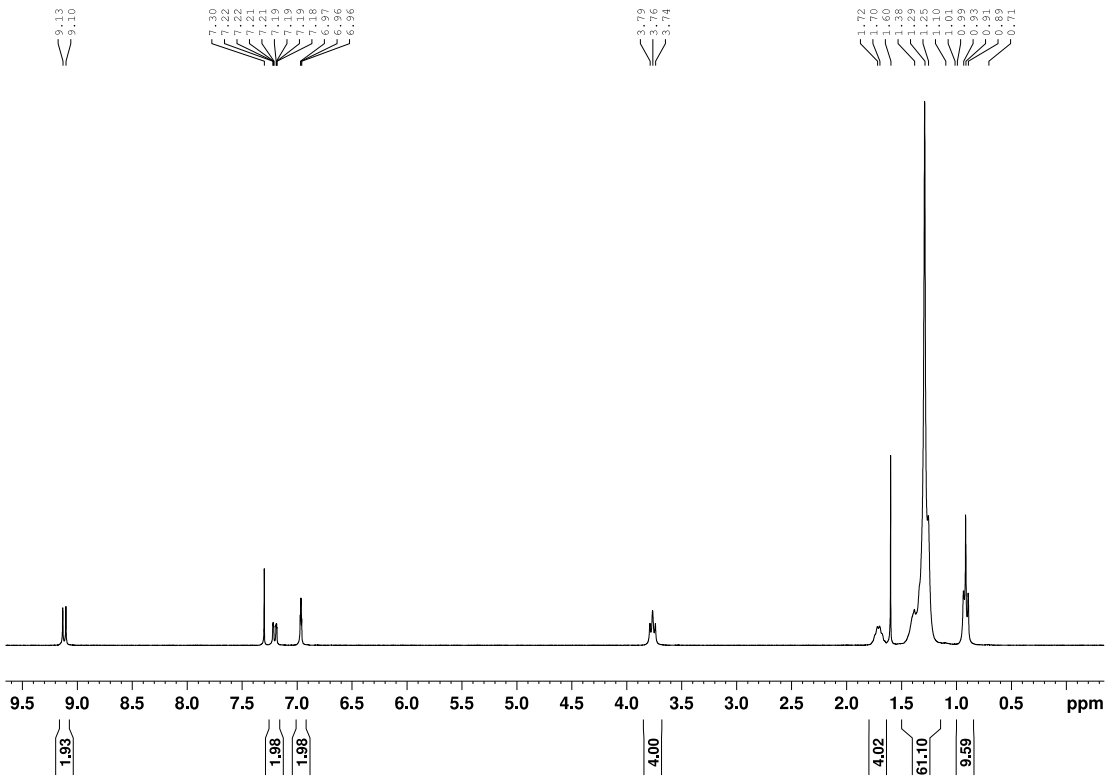
^{13}C NMR of Compound **11** in $CDCl_3$



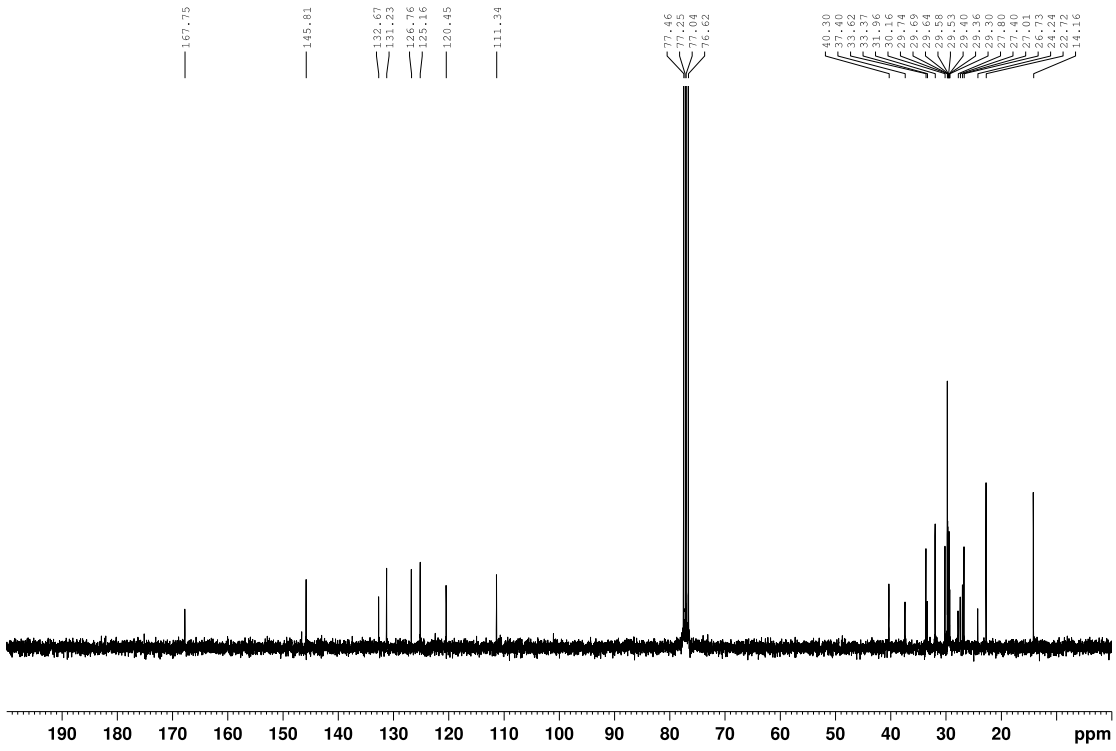
FTIR spectrum of Compound **11**



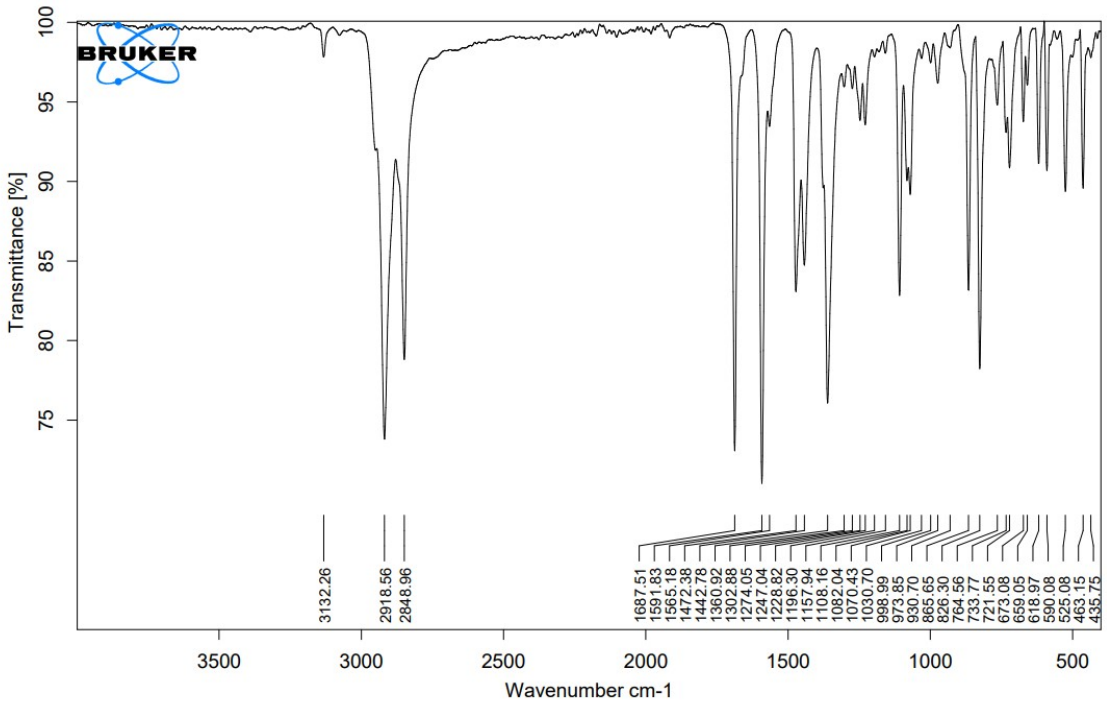
Compound **12.** *(E)-6,6'-dibromo-1-(5-decylpentadecyl)-1'-dodecyl-[3,3'-biindolinylidene]-2,2'-dione.* Compound **7** (74.0 mg, 0.13 mmol) and compound **2** (49.0 mg, 0.13 mmol) is added to a 50 mL round bottom flask. 12 mL acetic acid and a drop of concentrated HCl is then added, and the reaction is allowed to stir for 24 hrs at 120 °C under nitrogen atmosphere. The compound is then extracted in CH_2Cl_2 and dried with Na_2SO_4 and concentrated under reduced pressure. The compound is then purified via column chromatography CH_2Cl_2 and hexanes (1:2), and then recrystallized in isopropyl alcohol to yield Compound **12** as a red solid. Yield: 50 mg (41%). δ 9.12 (d, J = 8.6 Hz, 2H), 7.20 (dt, J = 8.4, 1.7 Hz, 2H), 3.76 (t, J = 7.4 Hz, 4H), 1.71 (q, J = 7.1 Hz, 4H), 1.27 (d, J = 10.8 Hz, 62H), 0.99 – 0.82 (m, 10H). ^{13}C NMR ($CDCl_3$) δ: 167.7, 145.8, 132.6, 131.2, 126.7, 125.1, 120.4, 11.3, 40.3, 37.4, 33.6, 33.3, 31.9, 30.1, 29.7, 29.6, 29.6, 29.5, 29.4, 29.3, 29.3, 27.8, 27.4, 27.0, 26.7, 24.2, 22.7, 14.1. HRMS: *m/z* Calculated for $C_{53}H_{82}Br_2N_2O_2$ M^*+ 938.4723; found 939.4788.



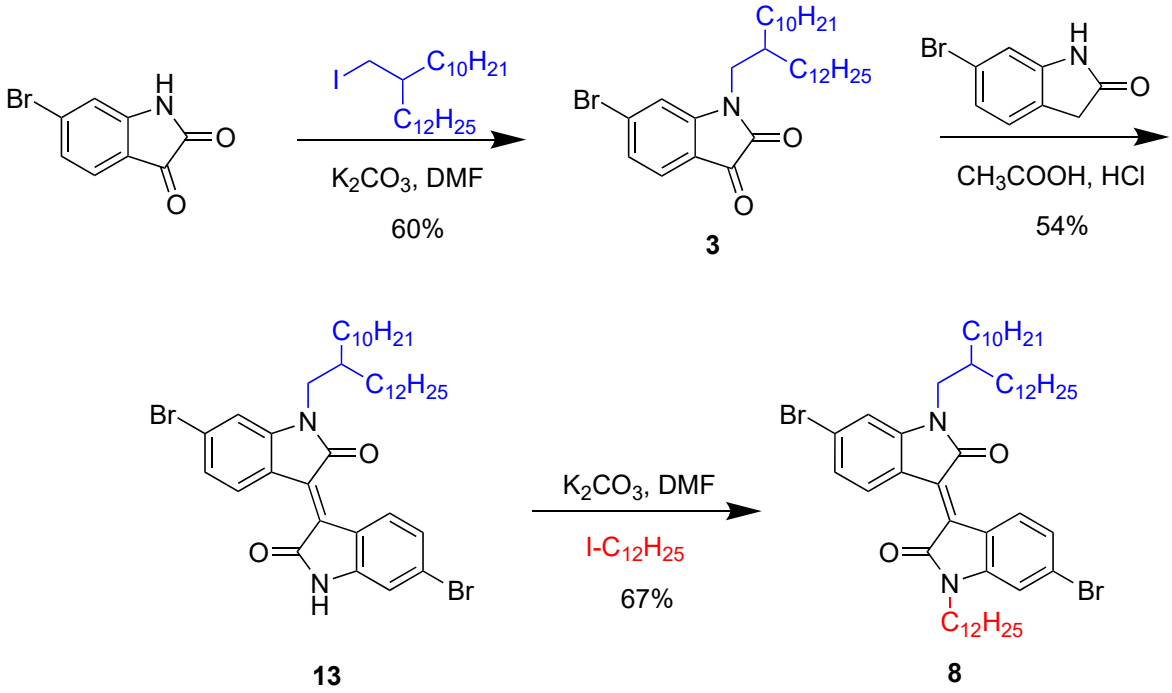
^{1}H NMR of Compound **12** in $CDCl_3$



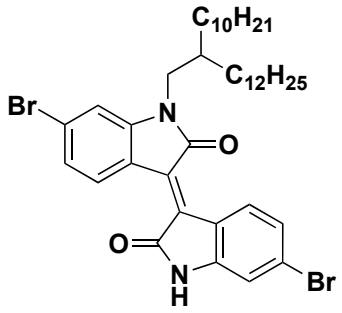
^{13}C NMR of Compound **12** in $CDCl_3$



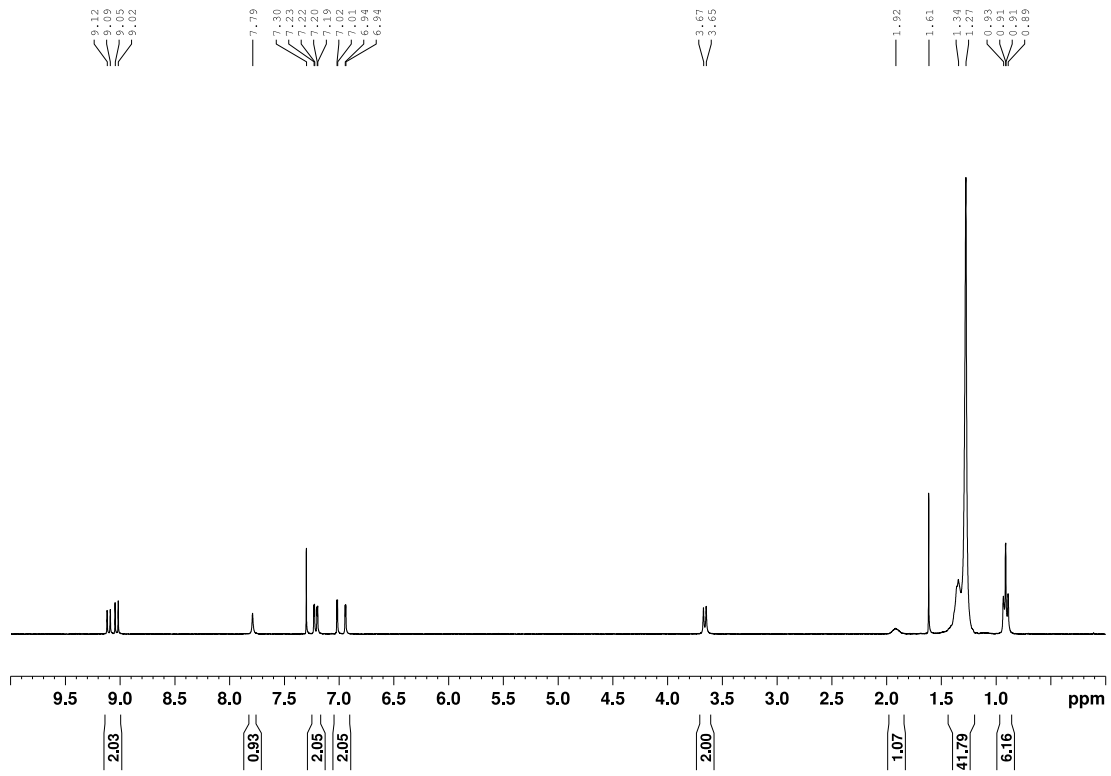
FTIR spectrum of Compound **12**



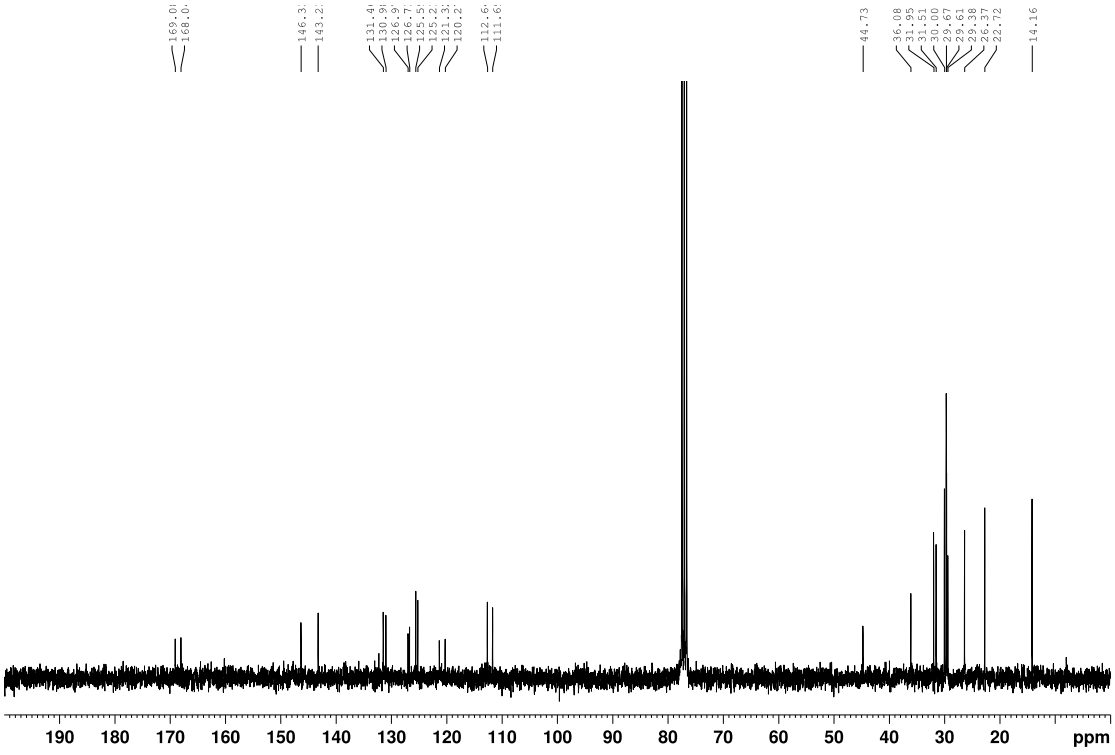
Scheme S3. Alternate synthetic pathway towards non-symmetric monomer Compound **8**.



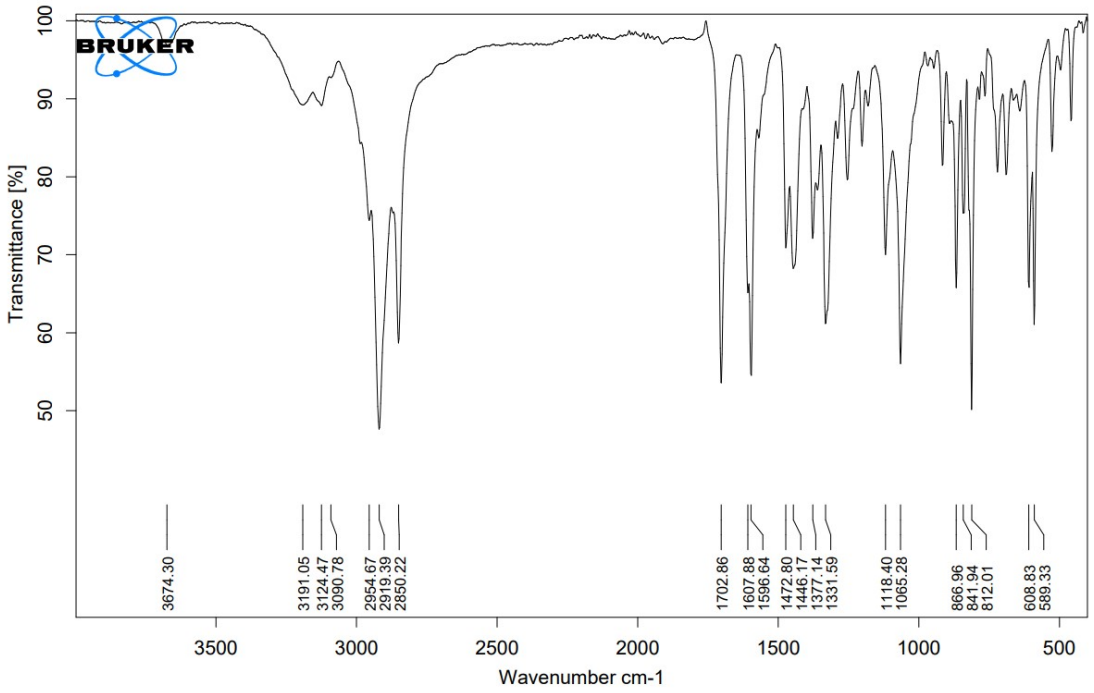
Compound 13. *(E)-6,6'-dibromo-1-(2-decyltetradecyl)-[3,3'-biindolinylidene]-2,2'-dione*. Compound **3** (0.70 g, 1.2 mmol) and 6-Bromooxindole (0.26g, 1.2 mmol) is added to a purged 250 mL round-bottom flask. Acetic acid (12 mL) and a drop of concentrated HCl is then added, and refluxed at 120˚C for 24hrs. The solution is then extracted $CHCl_3$ and H_2O, dried with Na_2SO_4 and reduced under pressure. The resulting dark red product is then purified via column chromatography in pure $CHCl_3$ and then precipitated in methanol to obtain compound **13** as a dark red solid. Yield: 51 g (54%). ^{1}H NMR ($CDCl_3$) δ: 9.07 (d, 1H, *J* = 8.7 Hz), 8.99 (d, 1H, *J* = 8.7 Hz), 7.22 (m, 2H), 6.98 (d, 1H, *J* = 1.8 Hz), 6.90 (d, 1H, *J* = 1.8 Hz), 3.62 (d, 2H, *J* = 7.5 Hz), 1.88 (s, 1H), 1.27 (m, 42H), 0.87 (t, 6H, *J* = 6.3 Hz, 13.5 Hz). ^{13}C NMR ($CDCl_3$) δ: 169.0, 168.0, 146.3, 143.2, 131.4, 130.9, 126.9, 126.7, 125.5, 125.2, 121.3, 120.2, 112.6, 111.6, 44.7, 36.0, 31.9, 31.5, 30.0, 29.7, 29.6, 29.3, 26.3, 22.7, 14.1. HRMS: *m/z* Calculated for $C_{40}H_{56}Br_2N_2O_2$ $[M+H]^+$ 756.2688; found 755.2665.



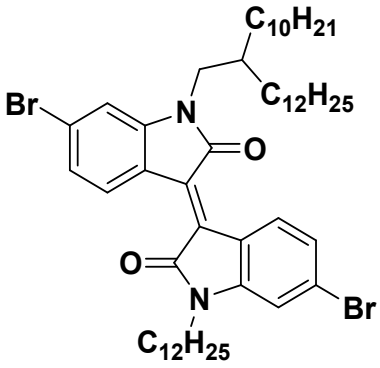
^{1}H NMR of Compound **13** in $CDCl_3$.



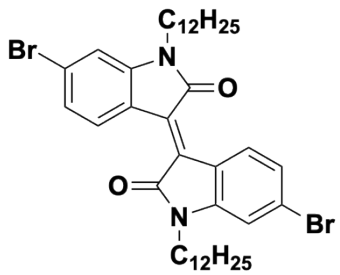
^{13}C NMR of Compound **13** in $CDCl_3$.



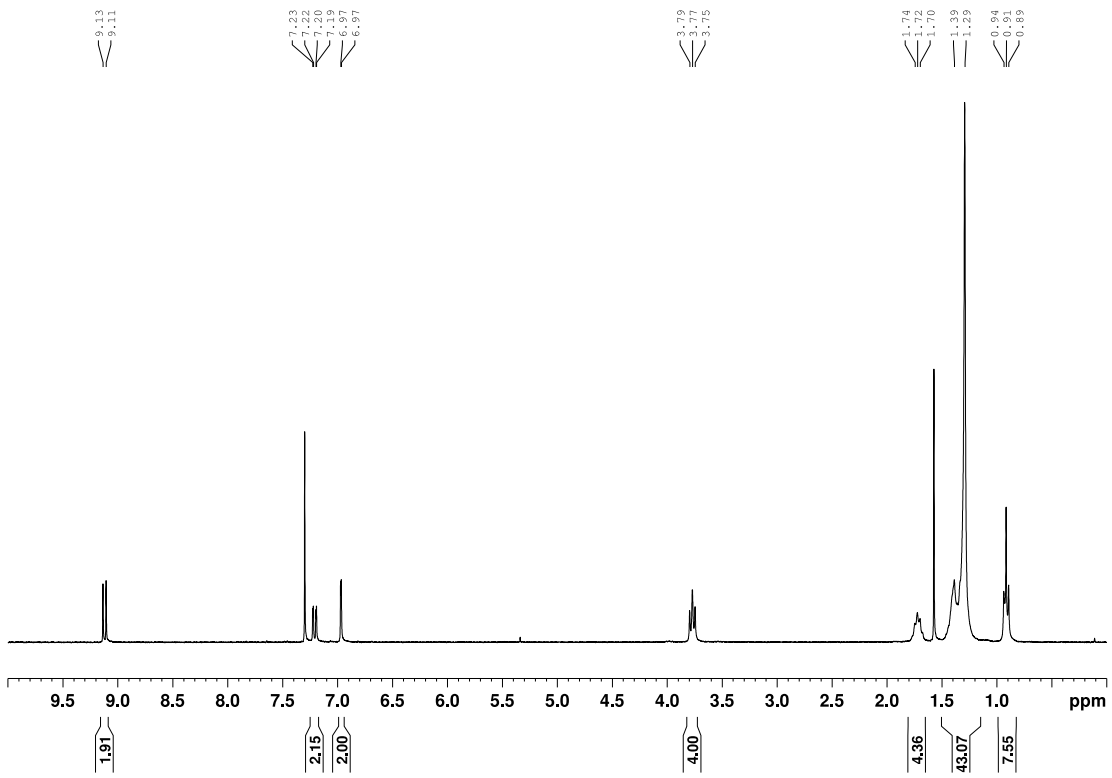
FTIR spectrum of Compound **13.**



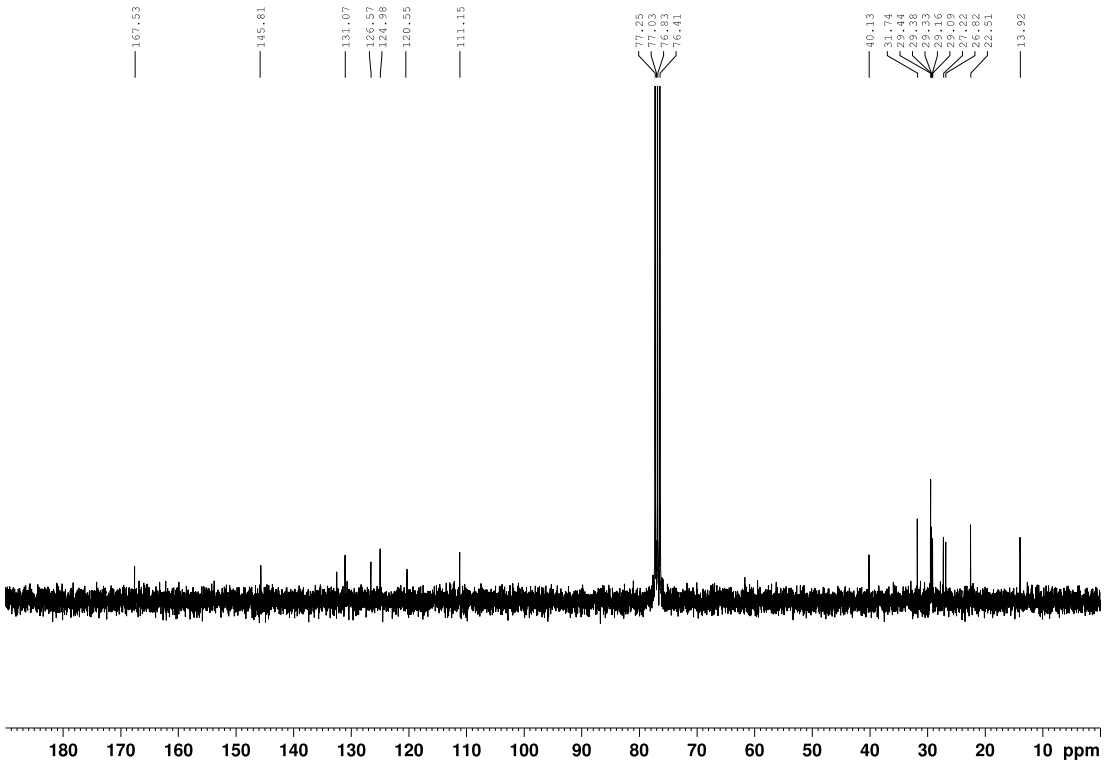
Compound 8. *(E)-6,6'-dibromo-1-(2-decyltetradecyl)-1'-dodecyl-[3,3'-biindolinylidene]-2,2'-dione*. To a purged and flame dried 250 mL round-bottom flask K_2CO_3 (0.88 g, 0.64 mmol) and Compound **8** is added (0.25 g, 0.43 mmol). DMF (4 mL) is then added and the solution is allowed to stir for 30 minutes at 90 ˚C under nitrogen atmosphere. 1-Iodododecane (0.24 g, 0.51 mmol) is then added dropwise, and continued to stir for 12hrs. The solution is then extracted $CHCl_3$ and H_2O, dried with Na_2SO_4 and reduced under pressure. The resulting red liquid is then purified by column chromatography using hexanes and toluene (4:1), and the recrystallized in isopropyl alcohol to obtain compound **9** as a dark red powder. Yield: 132 mg (67%).



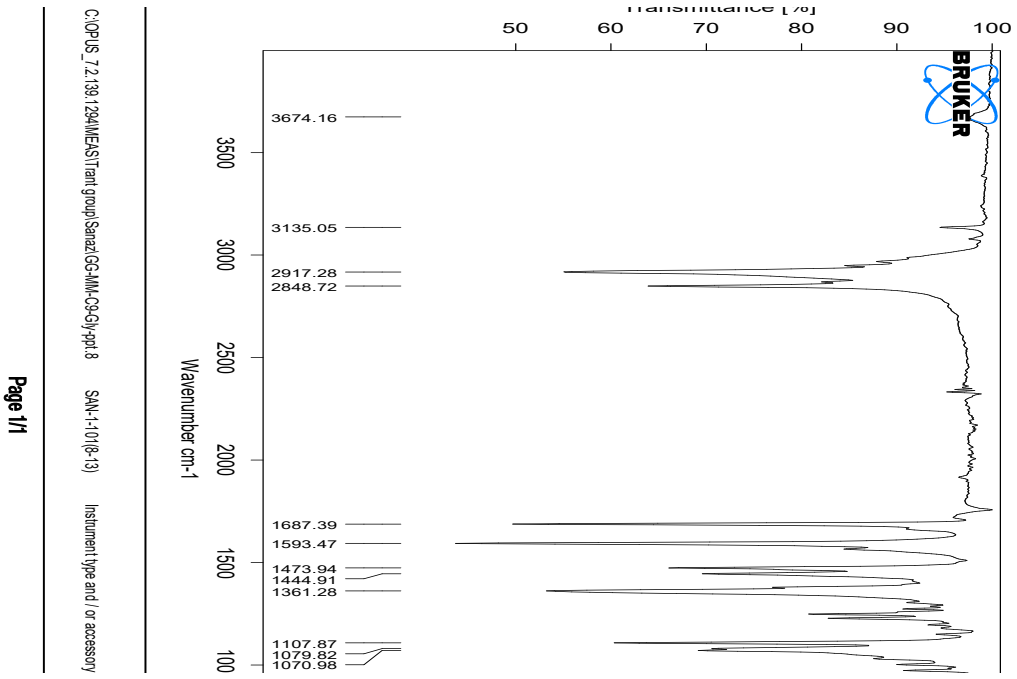
Compound **14.** *(E)-6,6'-dibromo-1,1'-didodecyl-[3,3'-biindolinylidene]-2,2'-dione*. To a 250 mL round bottom flask, 6-bromooxindole (0.50 g, 2.4 mmol) and K_2CO_3 (0.49 g, 3.5 mmol) is added. DMF (22 mL) is then added, and the reaction is allowed to stir for 30 minutes at 80 ℃. 1-Bromododecane (0.88 g, 3.5 mmol) is added dropwise, and continued to stir for 3 hrs. The compound is then extracted in $CHCl_3$ and 10% HCl solution, dried with Na_2SO_4, and concentrated under reduced pressure. The resulting red product is then precipitated in methanol to obtain compound **14** as a bright red solid. Yield: 54 mg (6%). ^{1}H NMR ($CDCl_3$) δ: 9.08 (d, 1H, J = 9Hz), 7.17 (dd, 1H, J = 1.8 Hz, 8.4 Hz), 6.93 (d, 1H, J = 3 Hz), 3.73 (t, 2H, J = 6 Hz), 1.67 (m, 2H, J = 6.6 Hz, 14 Hz), 1.34 (m, 18H), 0.87 (t, 3H, J = 6.6 Hz). ^{13}C NMR ($CDCl_3$) δ: 167.5, 145.8, 131.0, 126.5, 124.9, 120.5, 111.1, 40.1, 31.7, 29.4, 29.4, 29.3, 29.1, 29.0, 27.2, 26.8, 22.5, 13.9.



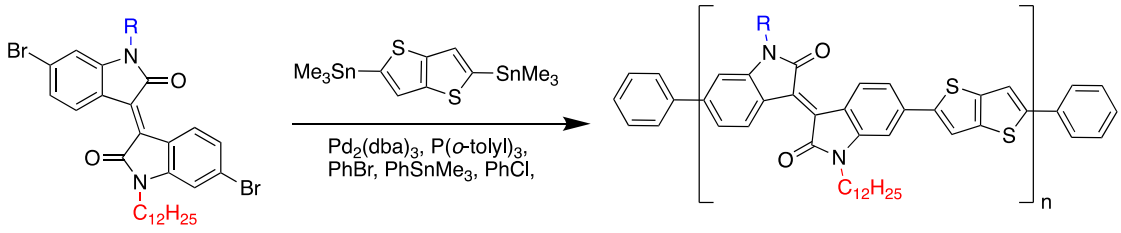
^{1}H NMR of Compound **14** in $CDCl_3$



^{13}C NMR of Compound **14** in $CDCl_3$

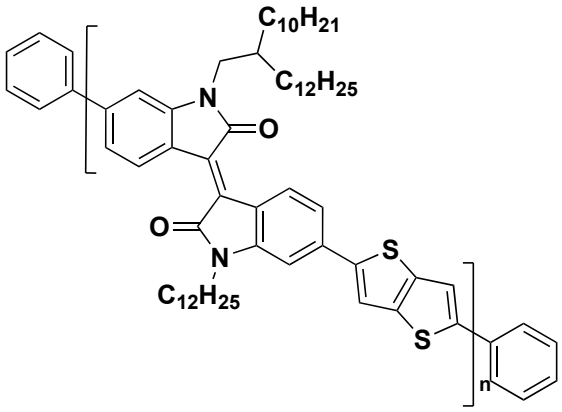


FTIR spectrum of Compound **14.**

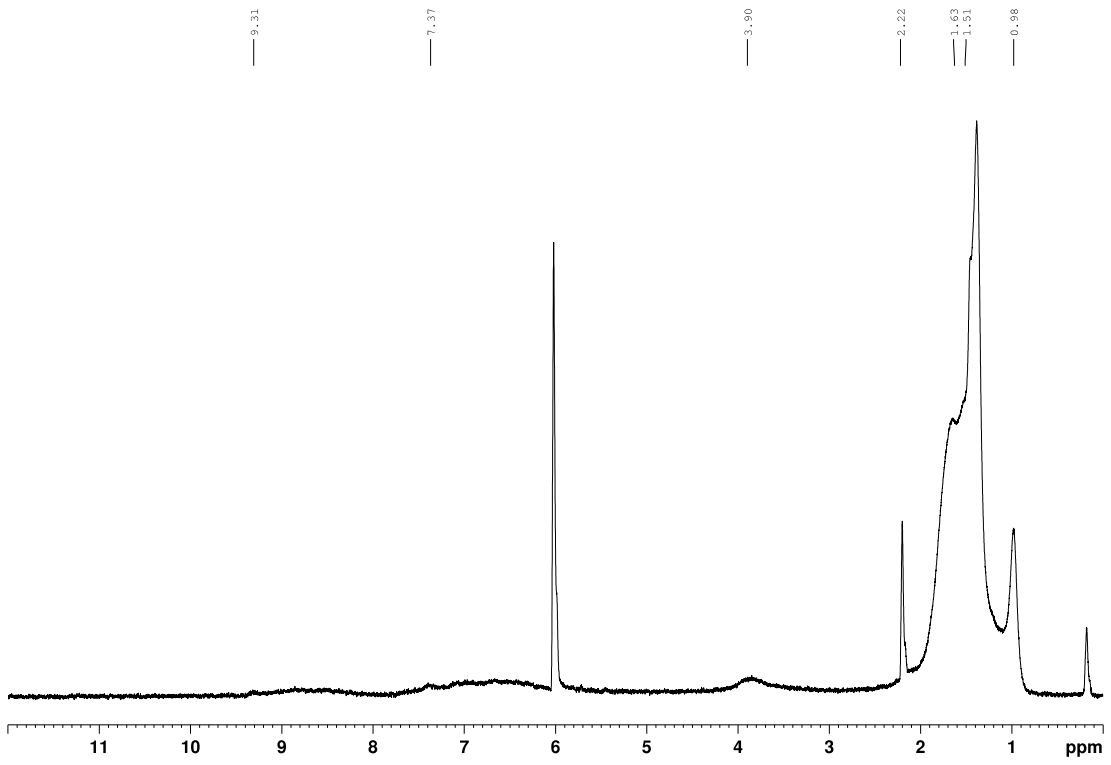


iI($C_nC_xC_y$)(C_{12}) **P[iITT($C_nC_xC_y$)(C_{12})]**

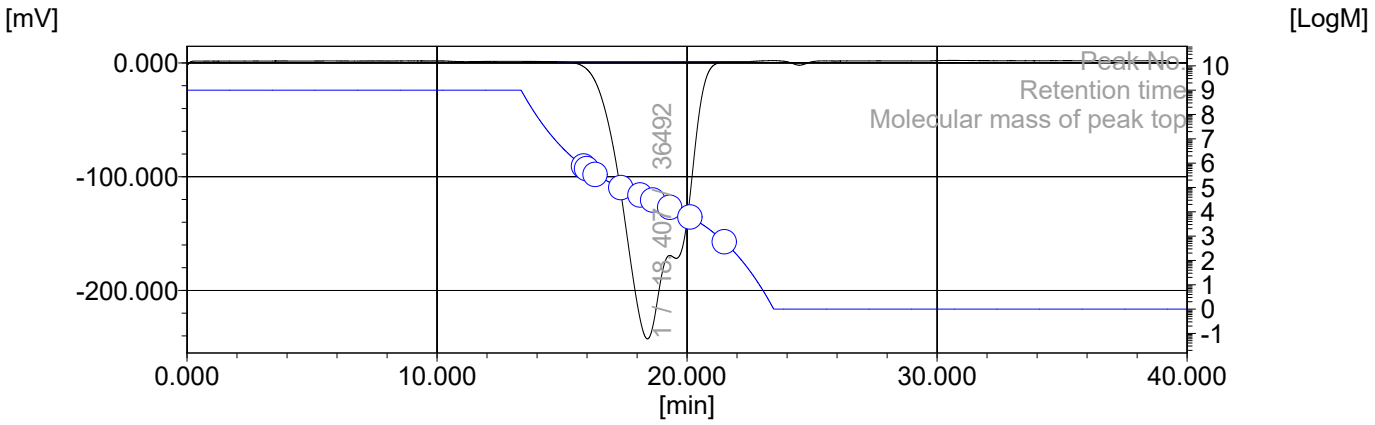
Scheme S4. Synthesis of **P[(iITT)($C_nC_xC_y$)(C_{12})]** polymers through Stille polycondensation.



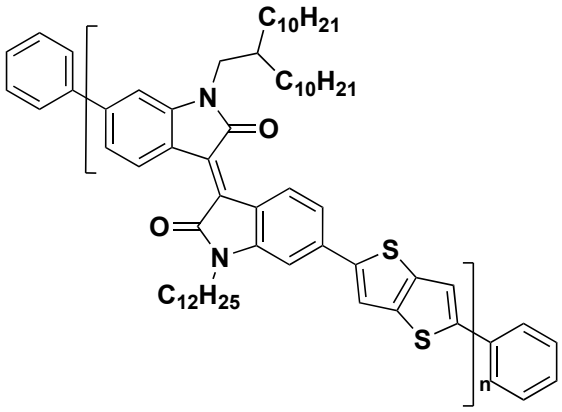
P[(iITT)($C_1C_{10}C_{12}$)(C_{12})]. To a microwave vessel, compound **9** (49.6 mg, 0.0537 mmol), and 2,5-Bis(trimethylstannyl)thieno[3,2-b]thiophene (25.0 mg, 0.0537 mmol) were added. Chlorobenzene (2 mL) was charged to the microwave vessel and the solution was degassed for 40 minutes. $Pd_2(dba)_3$ (0.983 mg, 0.00107 mmol) and P(o-tolyl)$_3$ (1.47 mg, 0.00483 mmol) were added to the microwave vessel. The polymerization reaction was carried out using the microwave at 300W, 180˚C for 1 hour. The reaction mixture became dark-blue in color. $SnMe_3Ph$ (0.01 mL, 0.0537 mmol) was added to the vessel and was reacted again for 7 minutes at 300W, 160˚C. Final end-capping was carried out using the microwave, to where bromobenzene (0.01 mL, 0.0537 mmol) was added to the microwave vessel utilizing the same conditions listed at 160˚C. Upon polymerization, the materials were precipitated in methanol and purified by Soxhlet extraction successively in methanol, acetone, hexanes and chloroform. The materials were collected with chloroform, precipitated in methanol and dried under vacuum. HT-GPC was performed on the material which yielded a Mn, Mw, and PDI of 17.1 kDa, 50.2 kDa and 2.9 respectively. Yield: 45 mg (79%).



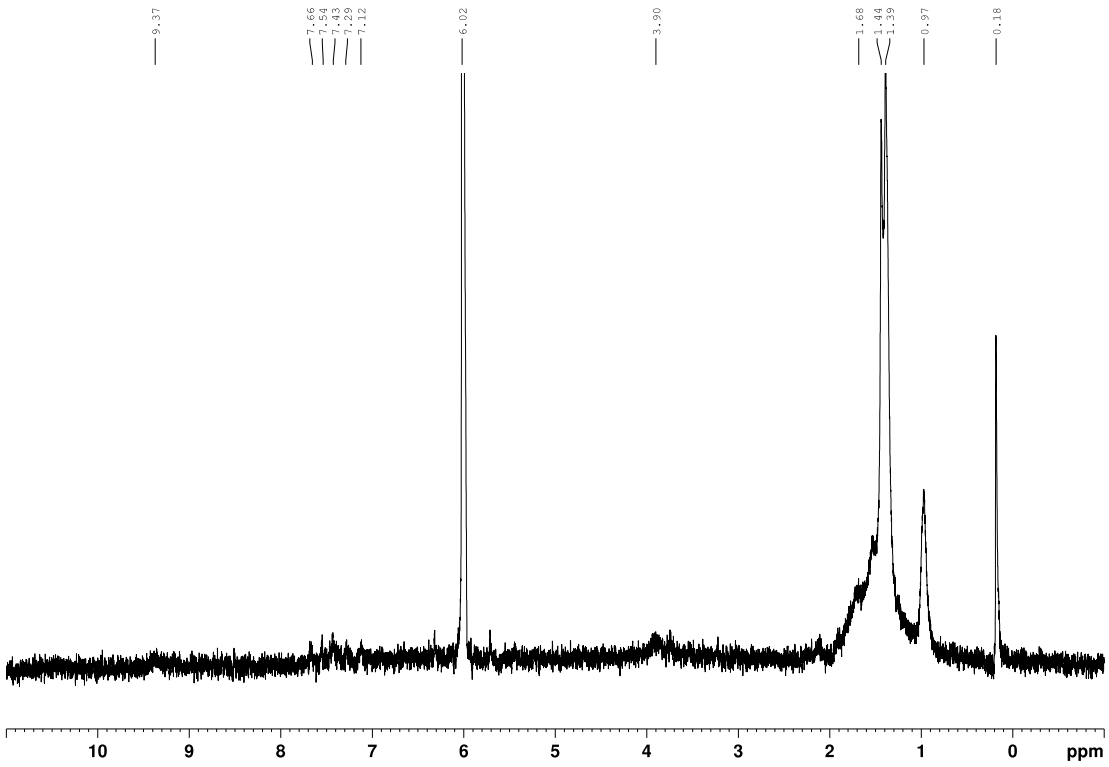
^{1}H NMR of **P[(iITT)($C_1C_{10}C_{12}$)(C_{12})]** in 1,1,2,2,tetrachloroethane-d_2.



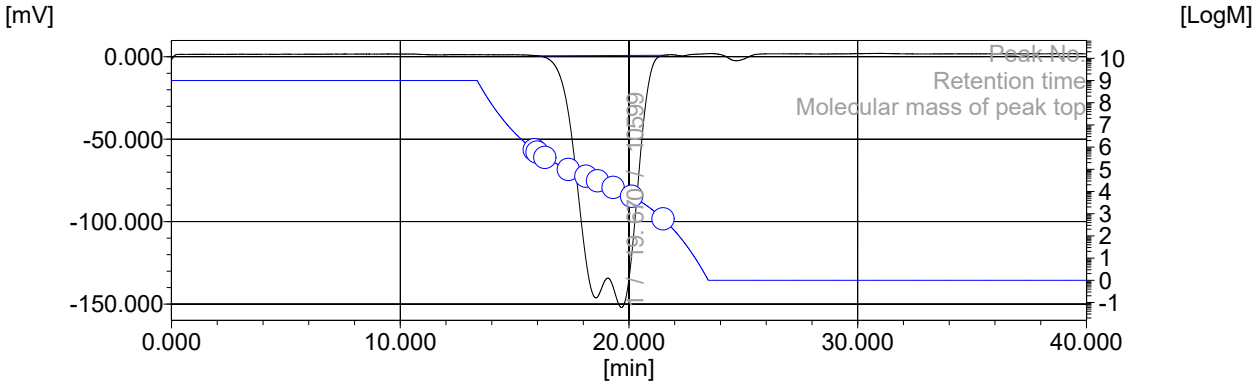
High temperature GPC of compound **P[(iITT)($C_1C_{10}C_{12}$)(C_{12})]** using polystyrene standards.



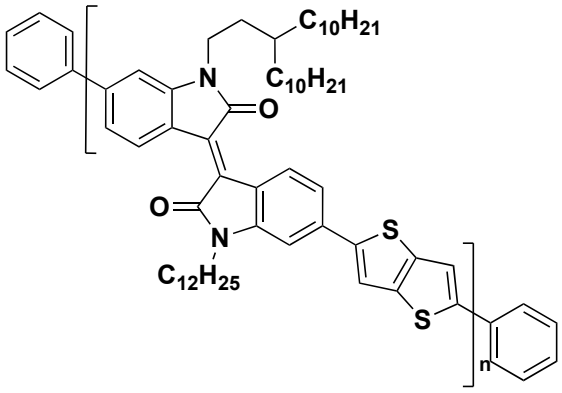
P[(iITT)($C_1C_{10}C_{10}$)(C_{12})]. To a microwave vessel, compound **10** (50.1 mg, 0.0558 mmol), and 2,5-Bis(trimethylstannyl)thieno[3,2-b]thiophene (26.0 mg, 0.0558 mmol) were added. Chlorobenzene (2 mL) was charged to the microwave vessel and the solution was degassed for 40 minutes. $Pd_2(dba)_3$ (1.02 mg, 0.00112 mmol) and $P(o\text{-}tolyl)_3$ (1.53 mg, 0.00502 mmol) were added to the microwave vessel. The polymerization reaction was carried out using the microwave at 300W, 180˚C for 1 hour. The reaction mixture became dark-blue in color. $SnMe_3Ph$ (0.01 mL, 0.0558 mmol) was added to the vessel and was reacted again for 7 minutes at 300W, 160˚C. Final end-capping was carried out using the microwave, to where bromobenzene (0.01 mL, 0.0558 mmol) was added to the microwave vessel utilizing the same conditions listed at 160˚C. Upon polymerization, the materials were precipitated in methanol and purified by Soxhlet extraction successively in methanol, acetone, hexanes and chloroform. The materials were collected with chloroform, precipitated in methanol and dried under vacuum. HT-GPC was performed on the material which yielded a Mn, Mw, and PDI of 12.2 kDa, 29.0 kDa and 2.4 respectively. Yield: 39.5 mg (78%).



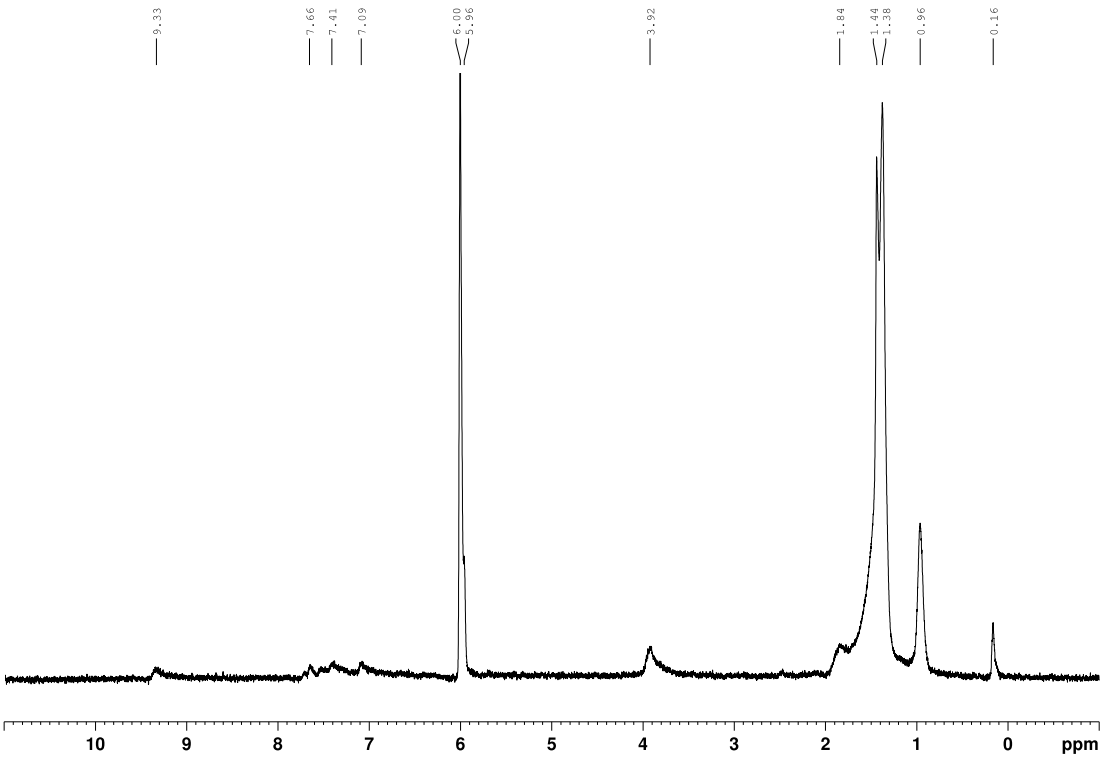
^{1}H NMR of **P[(iITT)($C_1C_{10}C_{10}$)(C_{12})].** in 1,1,2,2,tetrachloroethane-d_2.



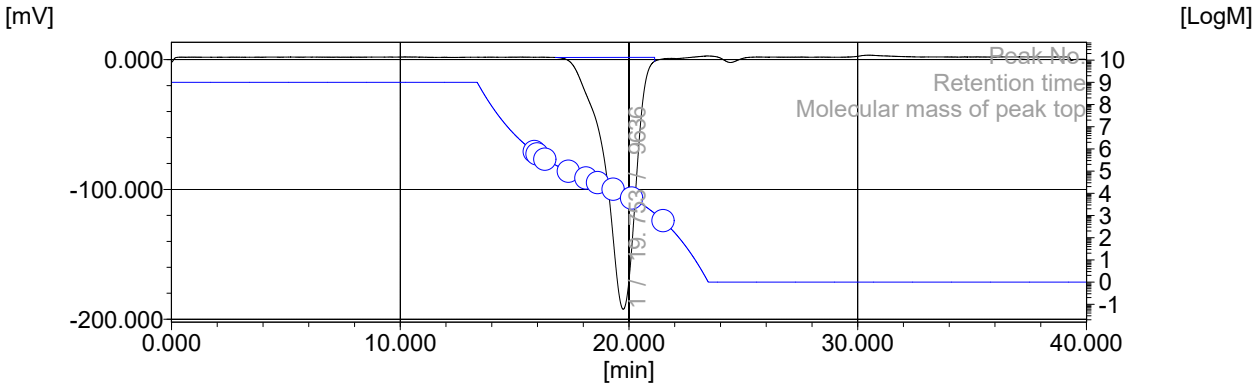
High temperature GPC of compound **P[(iITT)($C_1C_{10}C_{10}$)(C_{12})]** using polystyrene standards.



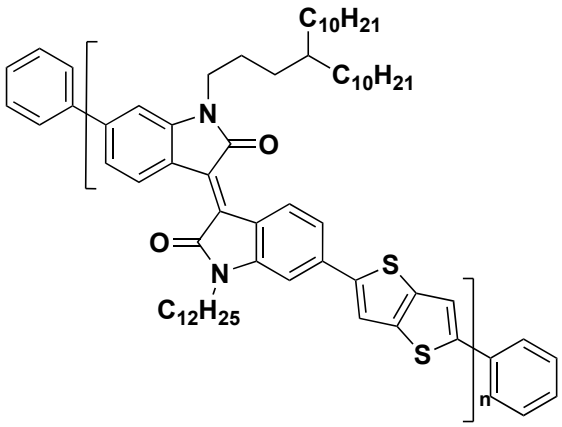
P[(iITT)($C_2C_{10}C_{10}$)(C_{12})]. To a microwave vessel, compound **11** (48.9 mg, 0.0537 mmol), and 2,5-Bis(trimethylstannyl)thieno[3,2-b]thiophene (25.0 mg, 0.0537 mmol) were added. Chlorobenzene (2 mL) was charged to the microwave vessel and the solution was degassed for 40 minutes. $Pd_2(dba)_3$ (0.983 mg, 0.00107 mmol) and P(o-tolyl)$_3$ (1.47 mg, 0.00483 mmol) were added to the microwave vessel. The polymerization reaction was carried out using the microwave at 300W, 180˚C for 1 hour. The reaction mixture became dark-blue in color. $SnMe_3Ph$ (0.01 mL, 0.0537 mmol) was added to the vessel and was reacted again for 7 minutes at 300W, 160˚C. Final end-capping was carried out using the microwave, to where bromobenzene (0.01 mL, 0.0537 mmol) was added to the microwave vessel utilizing the same conditions listed at 160˚C. Upon polymerization, the materials were precipitated in methanol and purified by Soxhlet extraction successively in methanol, acetone, hexanes and chloroform. The materials were collected with chloroform, precipitated in methanol and dried under vacuum. HT-GPC was performed on the material which yielded a Mn, Mw, and PDI of 9.2 kDa, 15.4 kDa and 1.7 respectively. Yield: 30 mg (54%).



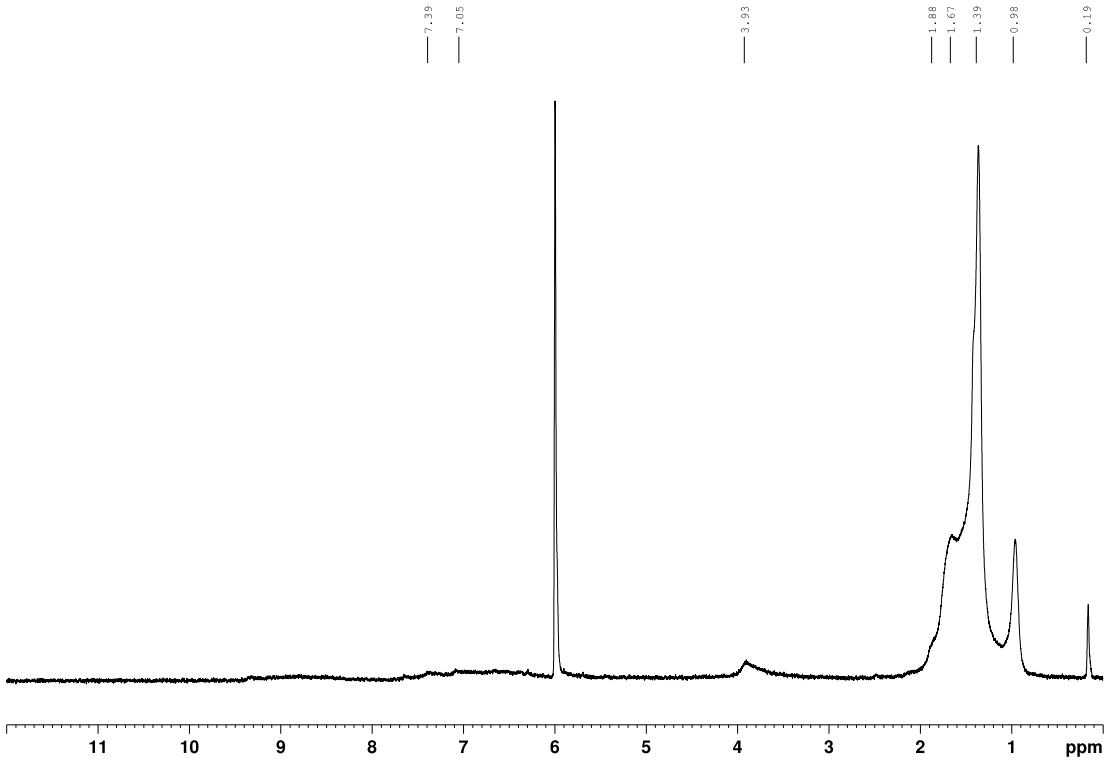
^{1}H NMR of **P[(iITT)($C_2C_{10}C_{10}$)(C_{12})].** in 1,1,2,2,tetrachloroethane-d_2



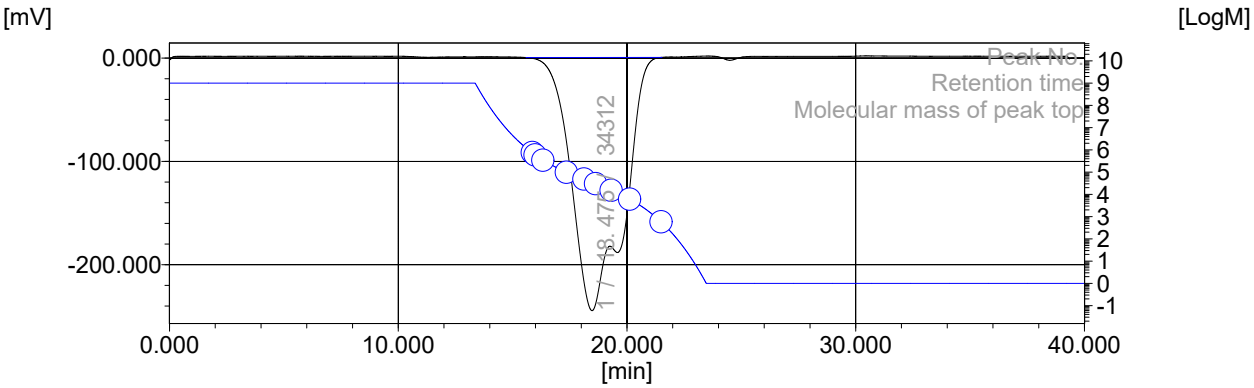
High temperature GPC of compound **P[(iITT)($C_2C_{10}C_{10}$)(C_{12})]** using polystyrene standards.



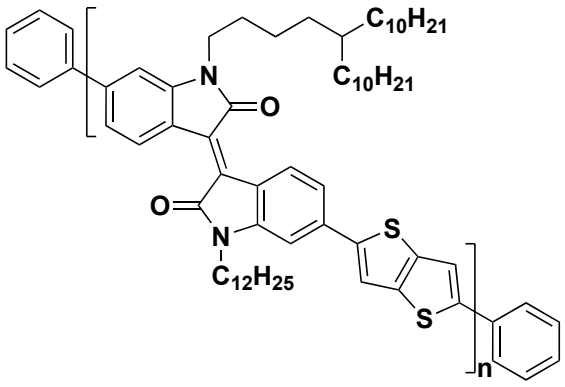
P[(iITT)($C_3C_{10}C_{10}$)(C_{12})]. To a microwave vessel, compound **12** (49.7 mg, 0.0537 mmol), and 2,5-Bis(trimethylstannyl)thieno[3,2-b]thiophene (25.0 mg, 0.0537 mmol) were added. Chlorobenzene (2 mL) was charged to the microwave vessel and the solution was degassed for 40 minutes. $Pd_2(dba)_3$ (0.98 mg, 0.00107 mmol) and P(o-tolyl)$_3$ (1.47 mg, 0.00483 mmol) were added to the microwave vessel. The polymerization reaction was carried out using the microwave at 300W, 180˚C for 1 hour. The reaction mixture became dark-blue in color. $SnMe_3Ph$ (0.01 mL, 0.0537 mmol) was added to the vessel and was reacted again for 7 minutes at 300W, 160˚C. Final end-capping was carried out using the microwave, to where bromobenzene (0.01 mL, 0.0537 mmol) was added to the microwave vessel utilizing the same conditions listed at 160˚C. Upon polymerization, the materials were precipitated in methanol and purified by Soxhlet extraction successively in methanol, acetone, hexanes and chloroform. The materials were collected with chloroform, precipitated in methanol and dried under vacuum. HT-GPC was performed on the material which yielded a Mn, Mw, and PDI of 16.0 kDa, 37.5 kDa and 2.3 respectively. Yield: 39 mg (69%).



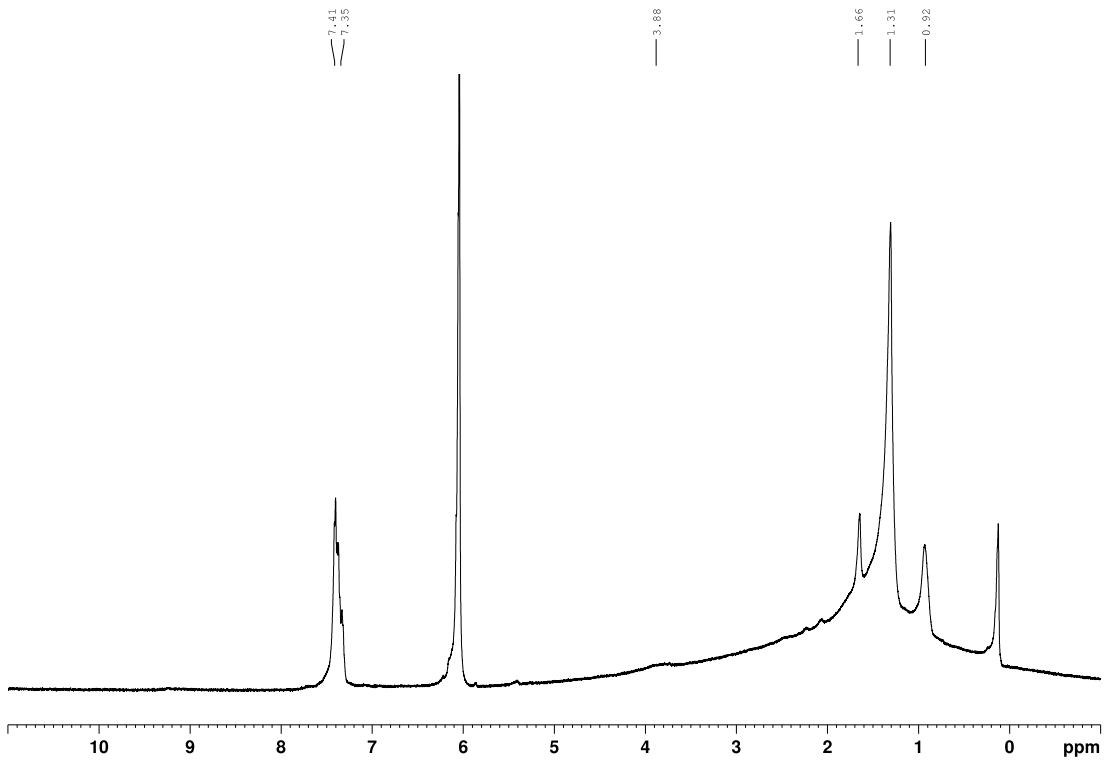
^{1}H NMR of **P[(iITT)($C_3C_{10}C_{10}$)(C_{12})].** in 1,1,2,2,tetrachloroethane-d_2



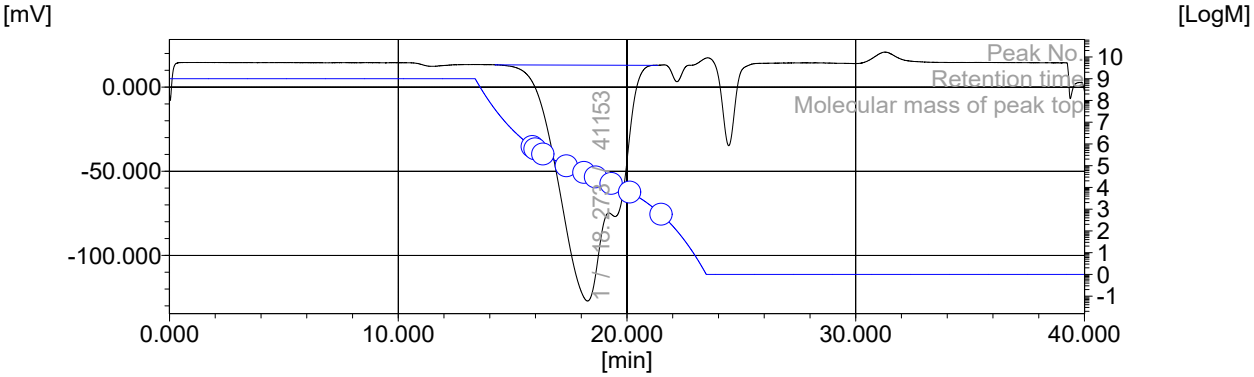
High temperature GPC of compound **P[(iITT)($C_3C_{10}C_{10}$)(C_{12})]** using polystyrene standards.



P[(iITT)($C_4C_{10}C_{10}$)(C_{12})]. To a microwave vessel, compound **13** (100 mg, 0.107 mmol), and 2,5-Bis(trimethylstannyl)thieno[3,2-b]thiophene (50.0 mg, 0.107 mmol) were added. Chlorobenzene (3 mL) was charged to the microwave vessel and the solution was degassed for 40 minutes. $Pd_2(dba)_3$ (1.96 mg, 0.00214 mmol) and P(o-tolyl)$_3$ (2.94 mg, 0.00966 mmol) were added to the microwave vessel. The polymerization reaction was carried out using the microwave at 300W, 180˚C for 1 hour. The reaction mixture became dark-blue in color. $SnMe_3Ph$ (0.02 mL, 0.107 mmol) was added to the vessel and was reacted again for 7 minutes at 300W, 160˚C. Final end-capping was carried out using the microwave, to where bromobenzene (0.01 mL, 0.0113 mmol) was added to the microwave vessel utilizing the same conditions listed at 160˚C. Upon polymerization, the materials were precipitated in methanol and purified by Soxhlet extraction successively in methanol, acetone, hexanes and chloroform. The materials were collected with chloroform, precipitated in methanol and dried under vacuum. HT-GPC was performed on the material which yielded a Mn, Mw, and PDI of 24.6 kDa, 88.1 kDa and 3.6 respectively. Yield: 39mg (34%)



500 MHz ^{1}H NMR of **P[(iITT)($C_4$$C_{10}$$C_{10}$)($C_{12}$)]** in 1,1,2,2,tetrachloroethane-d_2.



High temperature GPC of compound **P[(iITT)($C_4$$C_{10}$$C_{10}$)($C_{12}$)]** using polystyrene standards.

Materials and Device Characterization

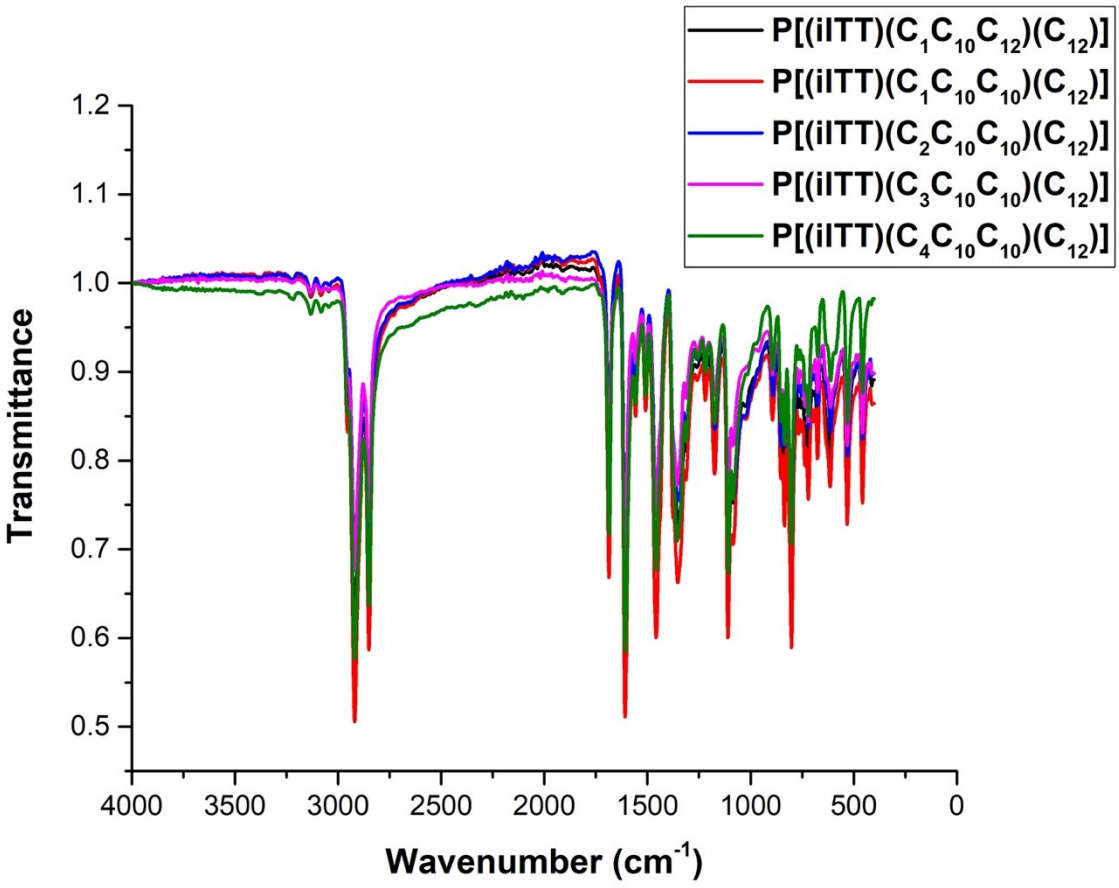


Figure S1. Fourier-Transform Infrared Spectroscopy (FTIR) spectrum of the **P[(iITT)($C_nC_xC_y$)(C_{12})]** polymers.

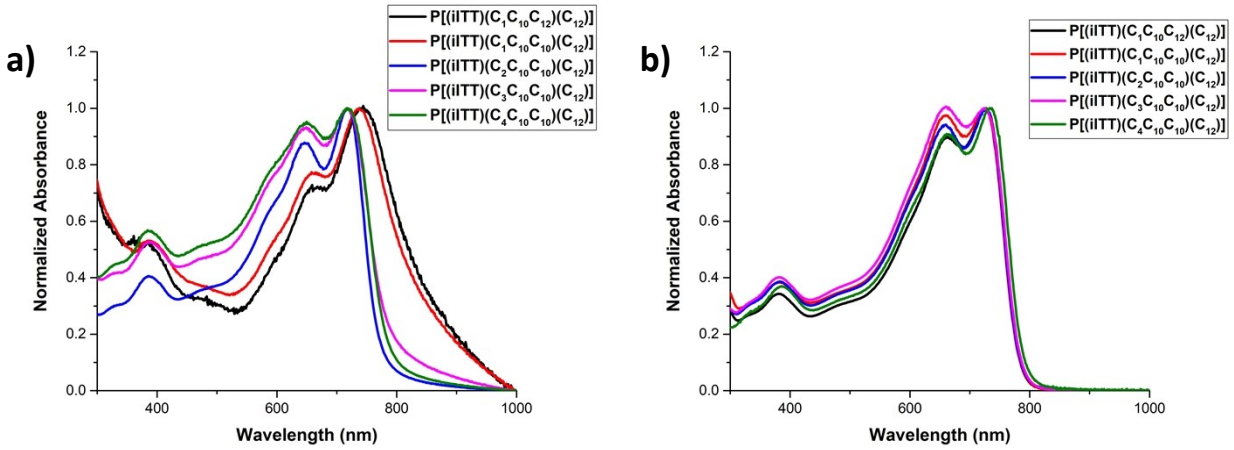


Figure S2. Comparative UV-Vis spectra of **P[(iITT)($C_nC_xC_y$)(C_{12})]** polymers a) solution in $CHCl_3$, and b) drop-casted thin film.

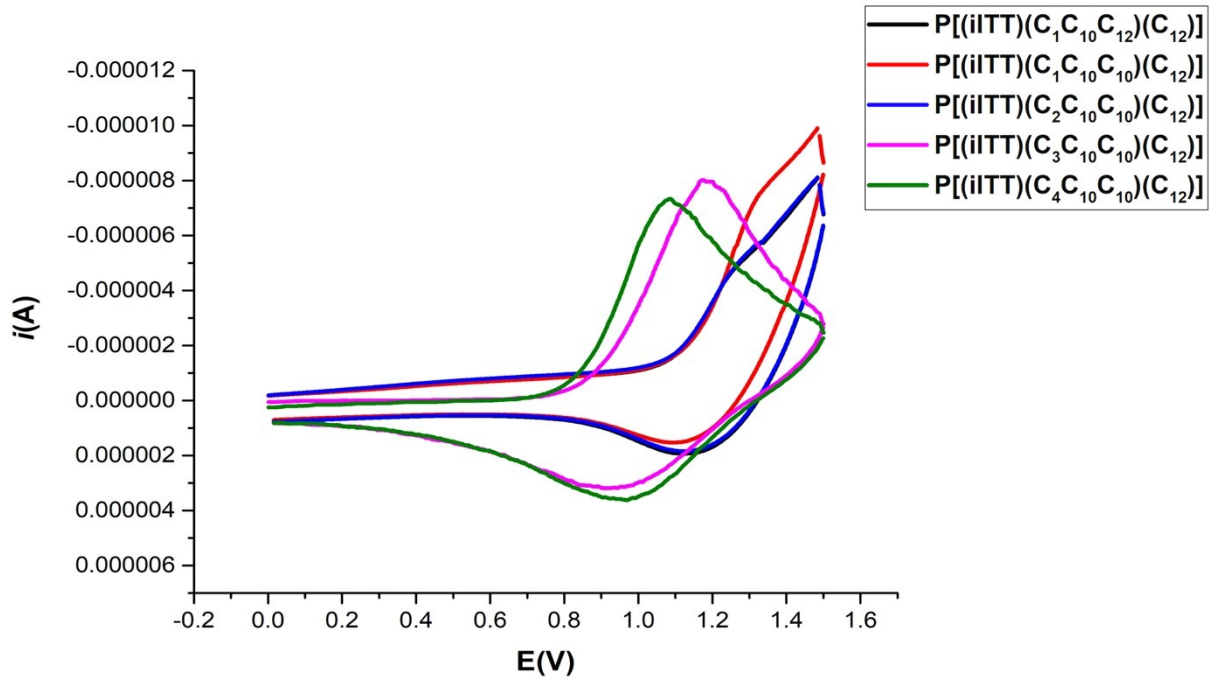


Figure S3. Cyclic voltammetry (CV) of **P[(iITT)($C_nC_xC_y$)(C_{12})]** polymers vs Fc/Fc^+ using 0.1M $TBAPF_6$ in CH_3CN as the electrolyte.

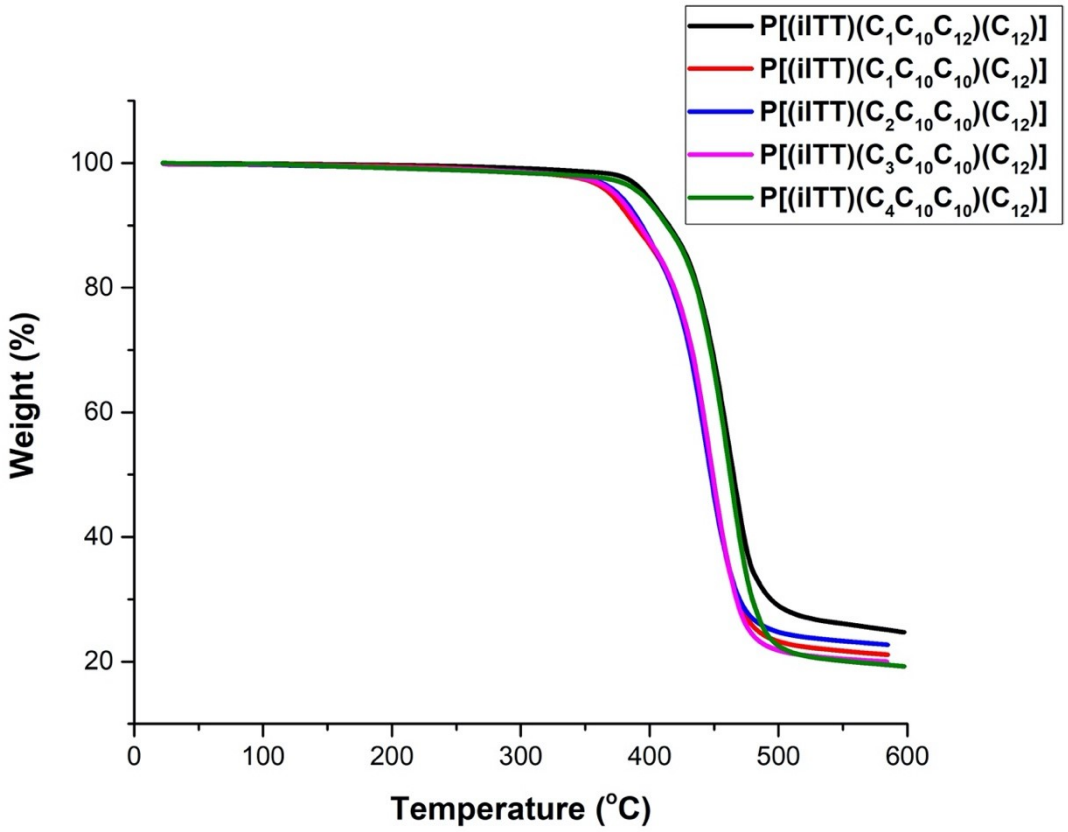


Figure S4. Thermogravimetric analysis (TGA) of **P[(iITT)($C_nC_xC_y$)(C_{12})]** polymers.

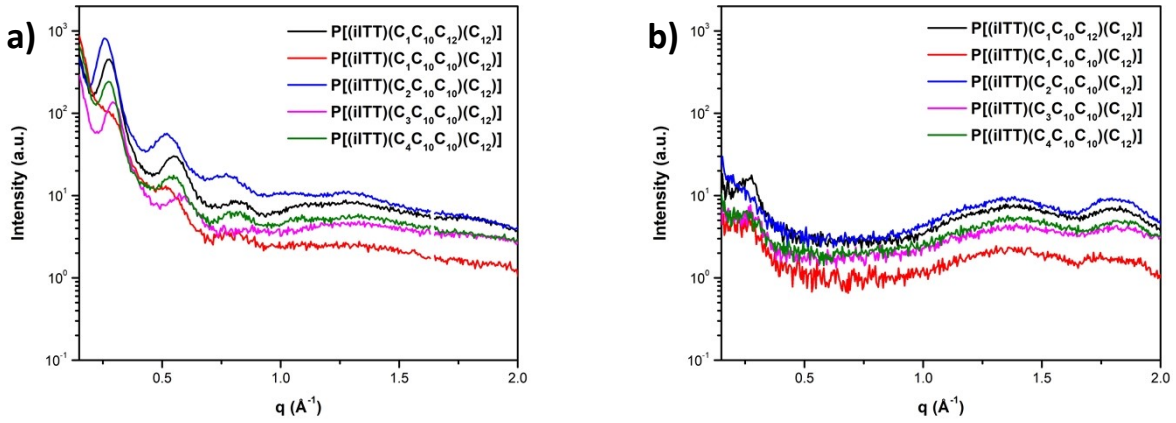


Figure S5. 1D GIWAXS analysis data of **P[(iITT)($C_nC_xC_y$)(C_{12})]** polymers a) out of plane b) in plane.

Table S1. Crystallographic peak assignment of **P[(iITT)($C_nC_xC_y$)(C_{12})]** polymers.

Peak Assignment`	q ($Å^{-1}$) P[iITT($C_1C_{10}C_{12}$) (C_{12})]	q ($Å^{-1}$) P[iITT($C_1C_{10}C_{10}$) (C_{12})]	q ($Å^{-1}$) P[iITT($C_2C_{10}C_{10}$) (C_{12})]	q ($Å^{-1}$) P[iITT($C_3C_{10}C_{10}$) (C_{12})]	q ($Å^{-1}$) P[iITT($C_4C_{10}C_{10}$) (C_{12})]
(100)	0.27	0.28	0.27	0.26	0.27
(200)	0.54	0.55	0.53	0.52	0.54
(300)	0.80	0.82	0.80	0.78	0.79
(400)	1.11	1.13	1.09	1.07	1.06
(010)	1.81	1.81	1.81	1.80	1.82
Lamellar packing distance	23.09	22.51	23.26	23.88	23.00
$\pi-\pi$ Stacking distance	3.47	3.46	3.47	3.49	3.44

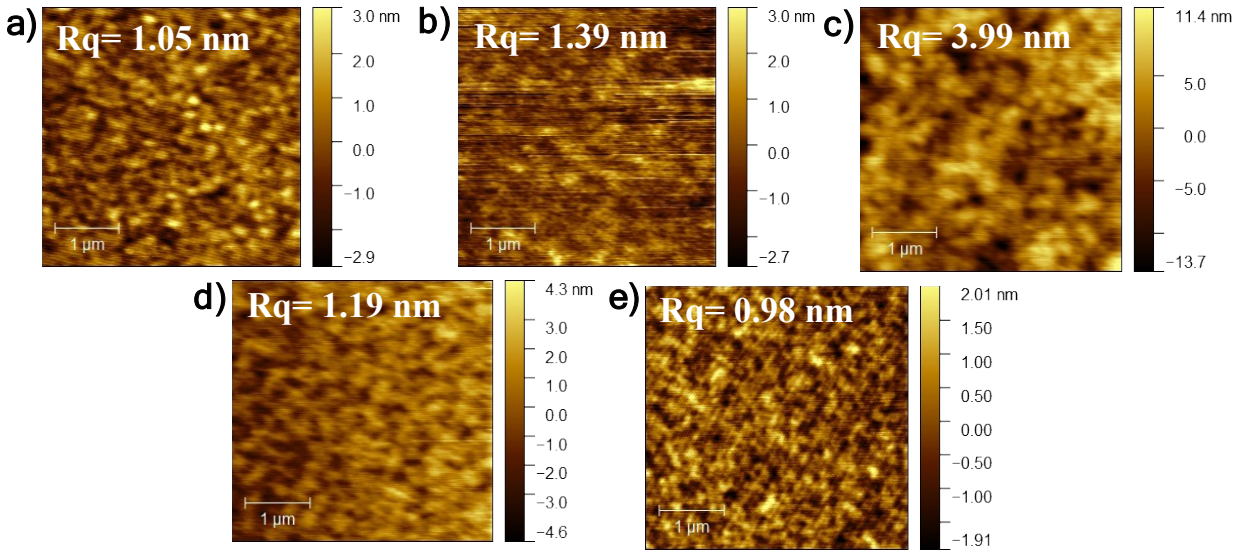


Figure S6. Atomic force microscopy images (height) of thin films of a) **P[(iITT)($C_1C_{10}C_{12}$)(C_{12})]**; b) **P[(iITT)($C_1C_{10}C_{10}$)(C_{12})]**; c) **P[(iITT)($C_2C_{10}C_{10}$)(C_{12})]**, d) **P[(iITT)($C_3C_{10}C_{10}$)(C_{12})]** and e) **P[(iITT)($C_4C_{10}C_{10}$)(C_{12})]** on SiO_2. Scale bar is 1 µm.

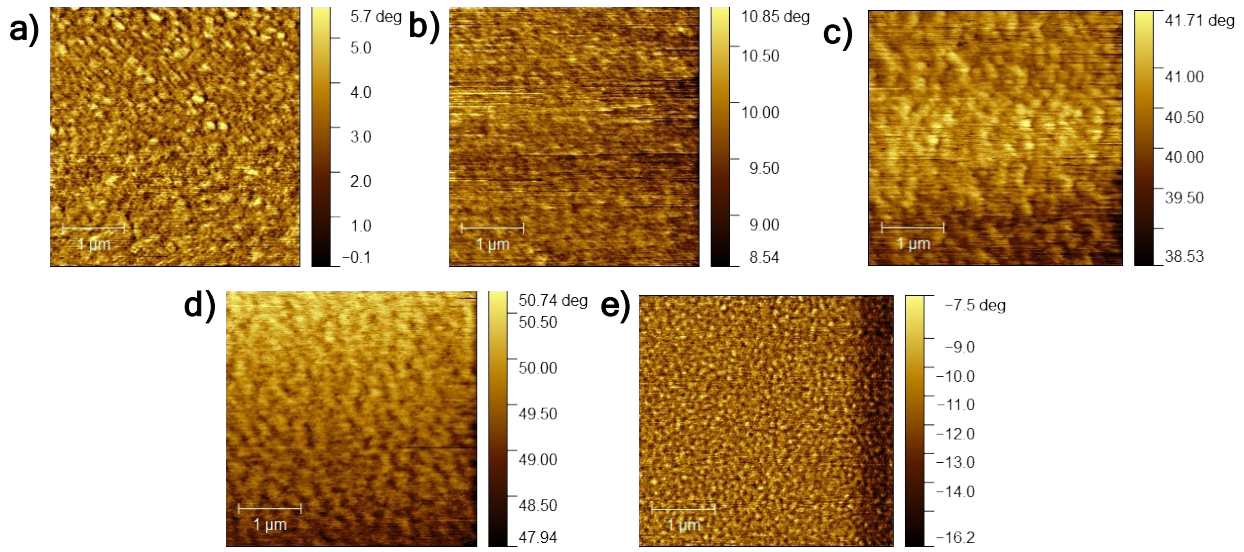


Figure S7. Atomic force microscopy images (phase) of thin films of a) **P[(iITT)($C_1C_{10}C_{12}$)(C_{12})]**; b) **P[(iITT)($C_1C_{10}C_{10}$)(C_{12})]**; c) **P[(iITT)($C_2C_{10}C_{10}$)(C_{12})]**, d) **P[(iITT)($C_3C_{10}C_{10}$)(C_{12})]** and e) **P[(iITT)($C_4C_{10}C_{10}$)(C_{12})]** on SiO_2. Scale bar is 1 µm.

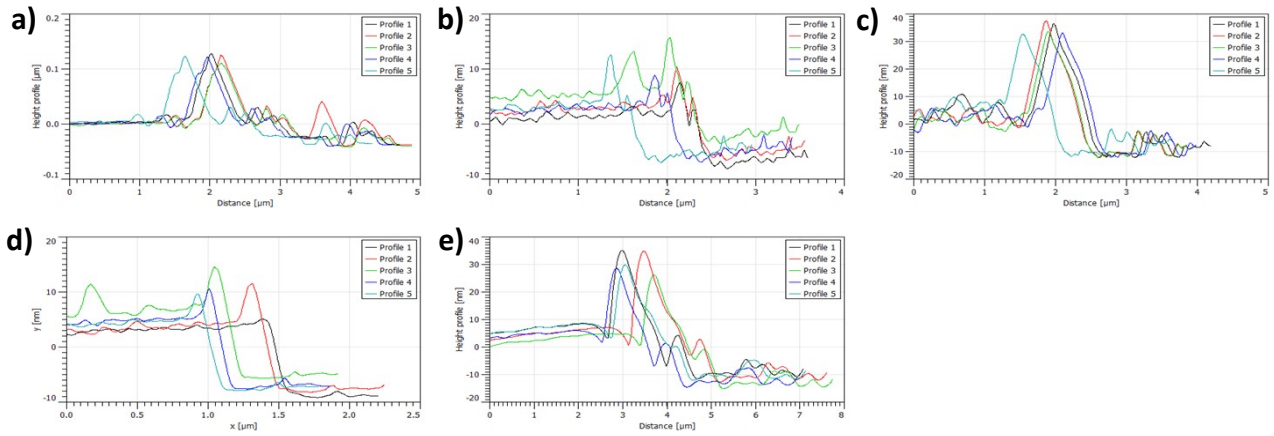


Figure S8. Height profile images of a) **P[(iITT)($C_1C_{10}C_{12}$)(C_{12})]**; b) **P[(iITT)($C_1C_{10}C_{10}$)(C_{12})]**; c) **P[(iITT)($C_2C_{10}C_{10}$)(C_{12})]**, d) **P[(iITT)($C_3C_{10}C_{10}$)(C_{12})]** and e) **P[(iITT)($C_4C_{10}C_{10}$)(C_{12})]** on SiO_2. Scale bar is 1 µm.

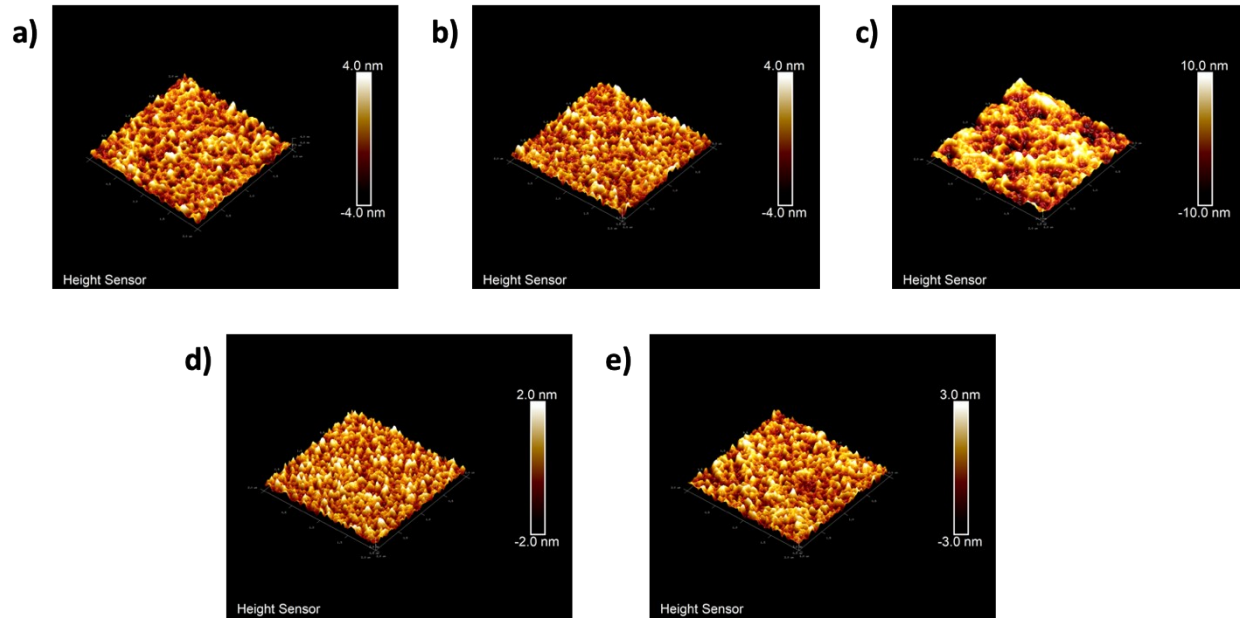


Figure S9. Atomic force microscopy images (3D height) of thin films of a) **P[(iITT)($C_1C_{10}C_{12}$)(C_{12})]**; b) **P[(iITT)($C_1C_{10}C_{10}$)(C_{12})]**; c) **P[(iITT)($C_2C_{10}C_{10}$)(C_{12})]**, d) **P[(iITT)($C_3C_{10}C_{10}$)(C_{12})]** and e) **P[(iITT)($C_4C_{10}C_{10}$)(C_{12})]** on SiO_2. Scale bar is 1 µm.

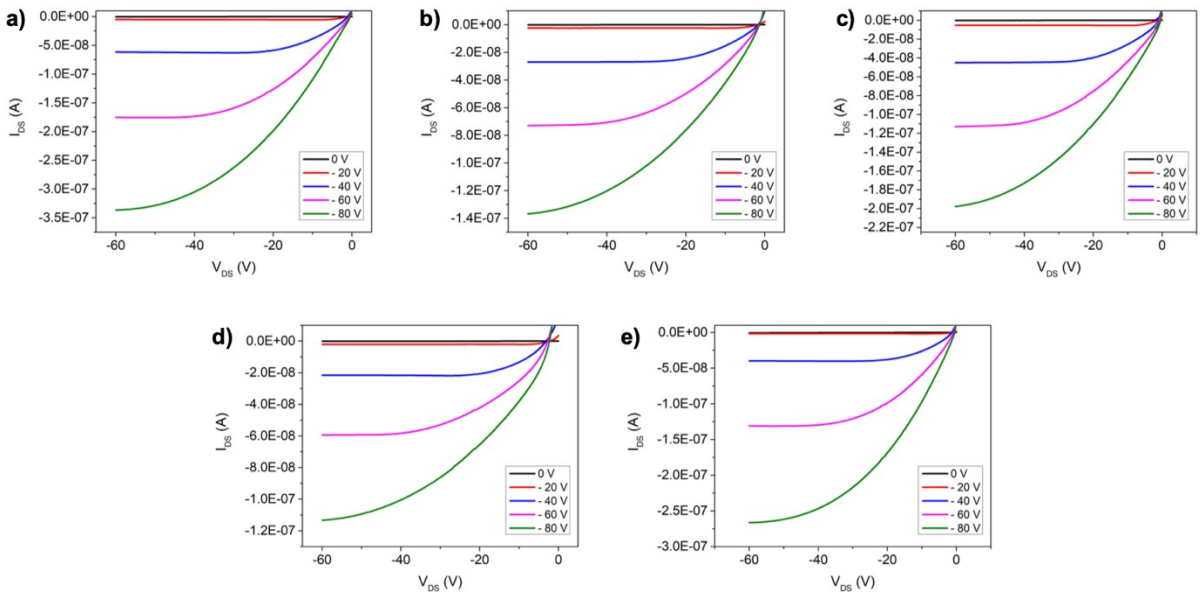


Figure S10. Representative output characteristics of **P[(iITT)($C_nC_xC_y$)(C_{12})]** series. Films spin coated in chlorobenzene at 5mg/ml, OFET devices fabricated after thermal annealing for 1 hour at hour at 150˚C, V_{DS}=-80V. a) **P[(iITT)($C_1C_{10}C_{12}$)(C_{12})]**, b) **P[(iITT)($C_1C_{10}C_{10}$)(C_{12})]**, c) **P[(iITT)($C_2C_{10}C_{10}$)(C_{12})]**, d) **P[(iITT)($C_3C_{10}C_{10}$)(C_{12})],** and e) **P[(iITT)($C_4C_{10}C_{10}$)(C_{12})]**.

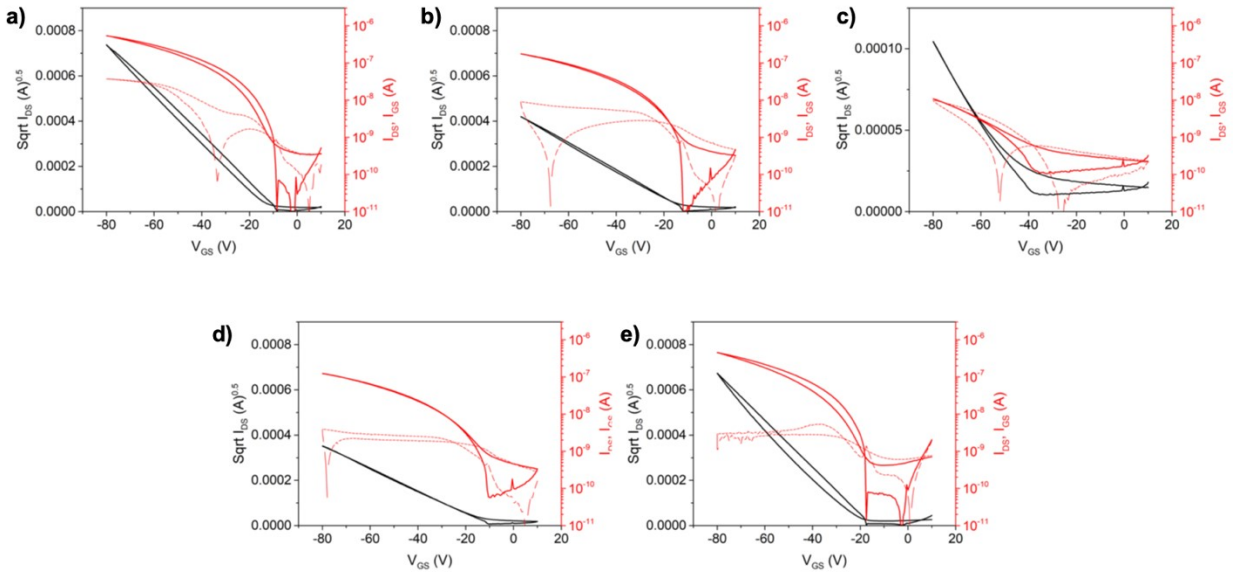


Figure S11. Transfer characteristics of **P[(iITT)($C_nC_xC_y$)(C_{12})]** series. Films spin coated in chlorobenzene at 5mg/ml, OFET devices fabricated after thermal annealing for 1 hour at hour at 150˚C. a) **P[(iITT)($C_1C_{10}C_{12}$)(C_{12})]**, b) **P[(iITT)($C_1C_{10}C_{10}$)(C_{12})]**, c) **P[(iITT)($C_2C_{10}C_{10}$)(C_{12})]**, d) **P[(iITT)($C_3C_{10}C_{10}$)(C_{12})],** and e) **P[(iITT)($C_4C_{10}C_{10}$)(C_{12})]**.

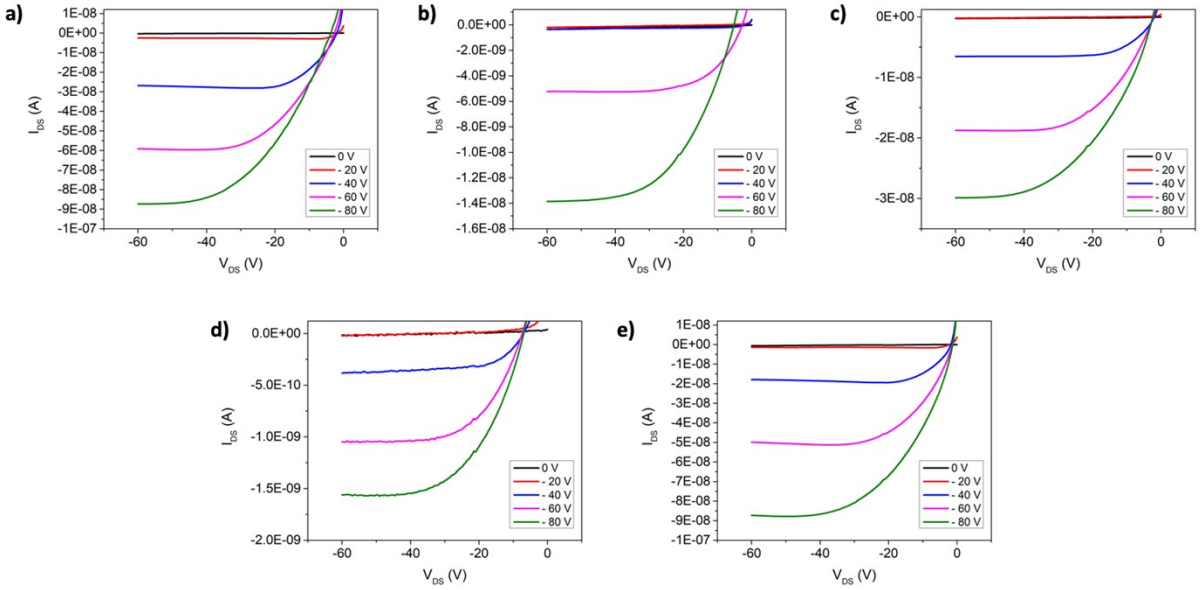


Figure S12. Representative output characteristics of **P[(iITT)($C_nC_xC_y$)(C_{12})]** series. Films spin coated in chloroform at 5mg/ml, OFET devices fabricated after thermal annealing for 1 hour at

hour at 150˚C, V_{DS}= -80V. a) **P[(iITT)($C_1C_{10}C_{12}$)(C_{12})]**, b) **P[(iITT)($C_1C_{10}C_{10}$)(C_{12})]**, c) **P[(iITT)($C_2C_{10}C_{10}$)(C_{12})]**, d) **P[(iITT)($C_3C_{10}C_{10}$)(C_{12})],** and e) **P[(iITT)($C_4C_{10}C_{10}$)(C_{12})]**.

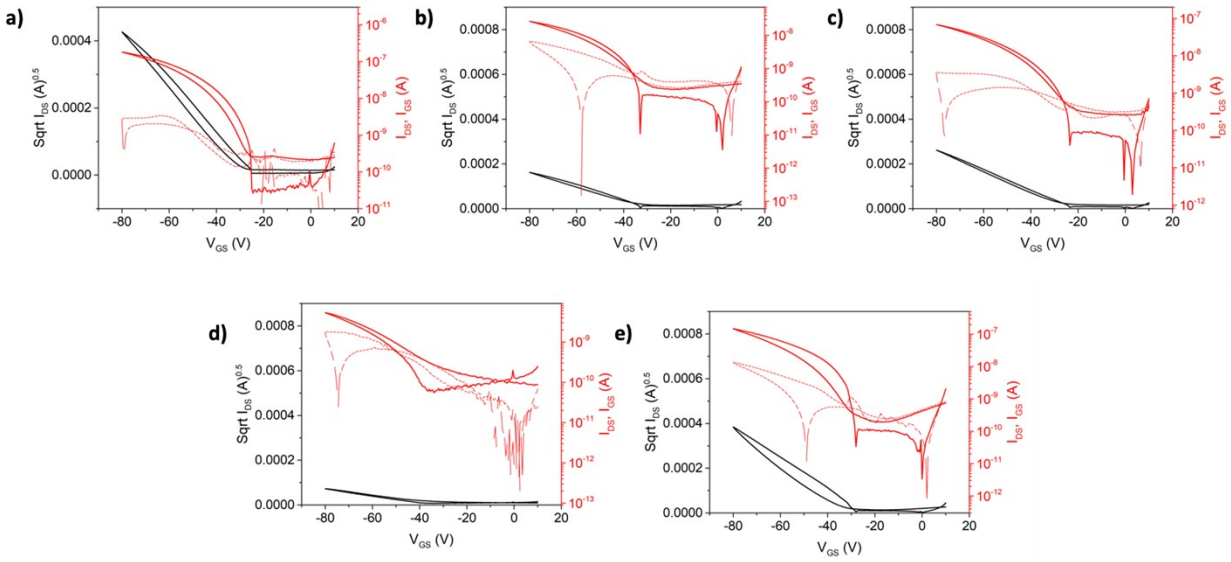


Figure S13. Transfer characteristics of **P[(iITT)($C_nC_xC_y$)(C_{12})]** series. Films spin coated in chloroform at 5mg/ml, OFET devices fabricated after thermal annealing for 1 hour at hour at 150˚C. a) **P[(iITT)($C_1C_{10}C_{12}$)(C_{12})]**, b) **P[(iITT)($C_1C_{10}C_{10}$)(C_{12})]**, c) **P[(iITT)($C_2C_{10}C_{10}$)(C_{12})]**, d) **P[(iITT)($C_3C_{10}C_{10}$)(C_{12})],** and e) **P[(iITT)($C_4C_{10}C_{10}$)(C_{12})]**.

Table S2. Average and maximum hole mobily (μ_h^{ave} / μ_h^{max}), I_{ON}/I_{OFF} current ratios, and threshold voltages (V_{th}) for OFET devices after thermal annealing for 1 hour at 150˚C, processed in chloroform. Results averaged from 10 devices.

Polymer	Thickness (nm)[a]	W/L	μ_h^{ave}/μ_h^{max} [$cm^2V^{-1}s^{-1}$]	I_{ON}/I_{OFF}^{ave}	V_{th}^{ave} [V]
P(iITT)($C_1C_{10}C_{12}$)(C_{12})	10-50	1000/150	0.062 ± 0.0068/ 0.076	10^2	-25
P(iITT)($C_1C_{10}C_{10}$)(C_{12})	10-50	1000/150	0.010 ± 0.0019/ 0.012	10^1	-34
P(iITT)($C_2C_{10}C_{10}$)(C_{12})	10-50	1000/150	0.018 ± 0.0036/ 0.060	10^2	-28
P(iITT)($C_3C_{10}C_{10}$)(C_{12})	10-50	1000/150	0.0015 ± 0.00090/ 0.0032	10^1	-39
P(iITT)($C_4C_{10}C_{10}$)(C_{12})	10-50	1000/150	0.050 ± 0.014/ 0.066	10^2	-27

[a] Thickness verified by AFM

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