

Evolution of Chain Dynamics and Oxidation States with Increasing Chain Length for a Donor-Acceptor Conjugated Oligomer Series

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Supporting Information

Table of Contents

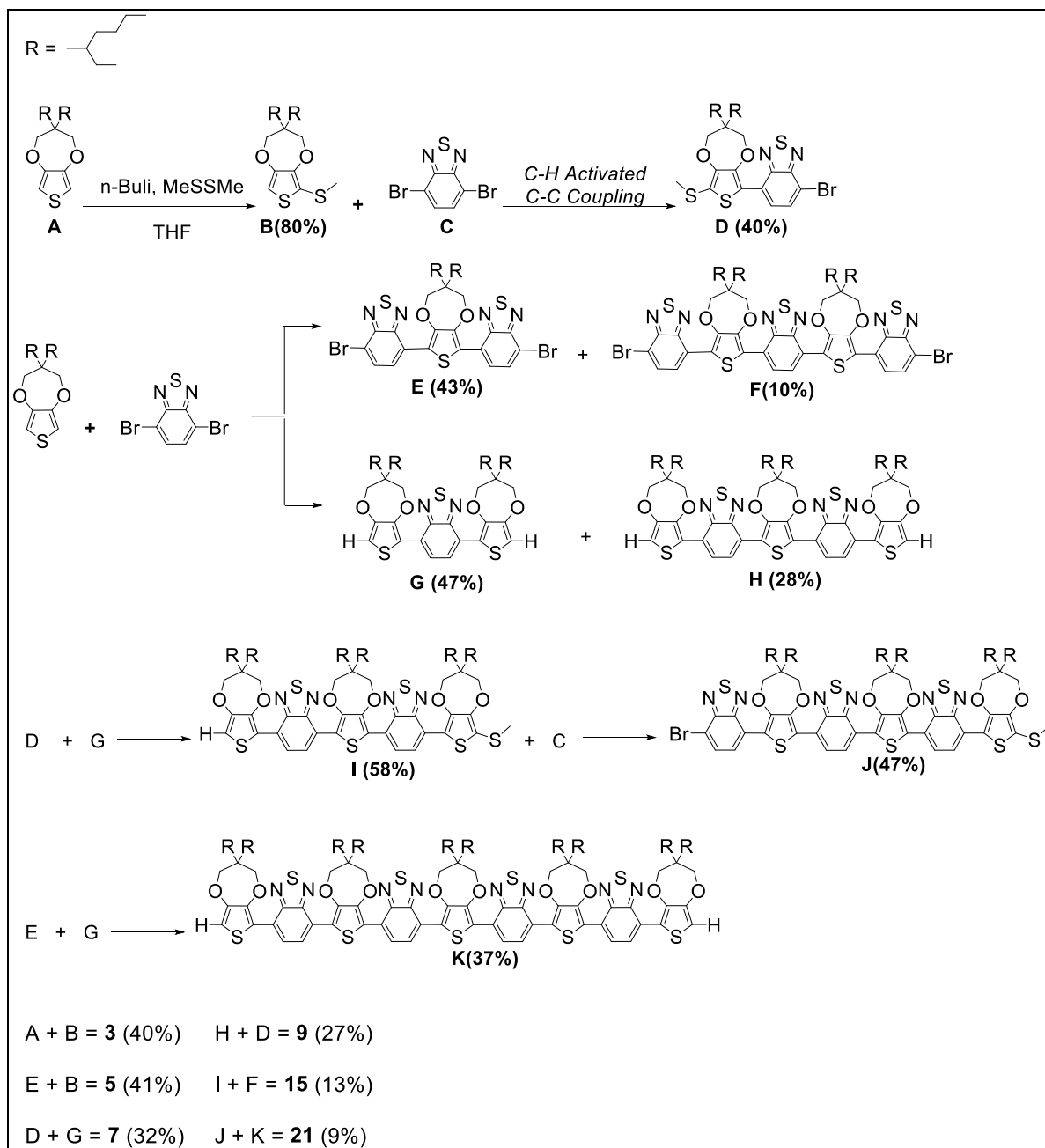
1. GENERAL INFORMATION.....	2
2. SYNTHESIS.....	3
Compound B.....	4
Compound D	4
Compounds E and F	5
Compound G and H.....	5
Compound I.....	6
Compound J.....	7
Compound K	7
Oligomer n=3	8
Oligomer n=5	8
Oligomer n=7	9
Oligomer n=9	9
Oligomer n=15.....	10
Oligomer n=21.....	10
Recycling Preparative HPLC Chromatograms for Polymers	12
3. PHYSICAL CHARACTERIZATIONS	13
Gel Permeation Chromatography (GPC)	13
Electrochemistry.....	16
Voltammetry	16
Spectroelectrochemistry	18
Atomic Force Microscopy (AFM)	18
Small Angle Neutron Scattering (SANS).....	19
Theoretical Calculations.....	21
Nuclear Magnetic Resonance (NMR) Spectra	26

1. GENERAL INFORMATION

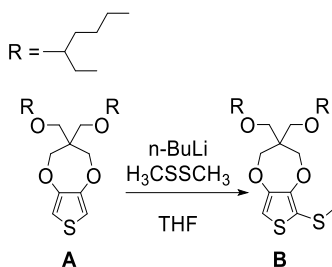
General Considerations. All syntheses were carried out using standard Schlenk or glovebox techniques under an atmosphere of N₂. Solvents were dried and degassed by passing through a column of activated alumina, sparging with N₂ gas, and, storing over dry 3 Å molecular sieves for at least 72 h before use. Deuterated solvent was purchased from Cambridge Isotope Laboratories, Inc. All reagents and starting materials were purchased from commercial vendors and used without further purification unless otherwise noted.

Physical Methods. ¹H NMR spectra were collected at room temperature on Bruker 400 MHz, 500 MHz, or 800 MHz spectrometers. ¹H and ¹³C NMR spectra are reported in parts per million relative to tetramethylsilane, using the residual solvent resonances as an internal standard. High resolution mass data were obtained using an Agilent 6320 LC-MS/MS for HR-APCI and an Applied Biosystems Voyager System 6270 for MALDI. Sample dispersity and polymer molecular weights were obtained using a TOSOH GPC with THF solvent vs. polystyrene standards at 40°C. UV-vis-NIR measurements were acquired on an Agilent Technologies Cary 6000i spectrophotometer (350-2850 nm) using a 1-cm two-window quartz cuvette. Electrochemistry was performed using a BioLogic SP-150 and CHI-660.

Abbreviations. 3,4-propylenedioxythiophene (ProDOT), benzothiadiazole (BTD), dichloromethane (DCM), tetrahydrofuran (THF).

2. SYNTHESIS

Scheme S1. Synthesis of the **nPB** oligomers. a) n-BuLi, CH₃SSCH₃, b) C-H Activation Conditions: Pd(OAc)₂, (o-MeOPh)₃P, pivalic acid, Cs₂CO₃.



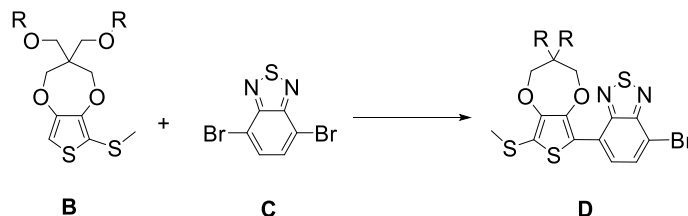
Compound B

To a THF solution (75 mL) of **A** (9.90 g, 22.5 mmol, 1.0 equiv) was added 9.88 mL of n-butyllithium (2.5 M, 24.7 mmol, 1.1 equiv) in hexane at -78°C under N_2 . After stirring for 120 min at 0°C , dimethyldisulfide (2.22 mL, 24.7 mmol, 1.1 equiv) was added dropwise to the reaction mixture and then allowed to warm to room temperature. After stirring overnight, the reaction mixture was quenched with water, extracted with hexane, and dried over Na_2SO_4 . The crude product was concentrated under vacuum and passed through a short alumina column using hexanes:ethyl acetate (75:1). After solvent evaporation, the residue was separated by preparative HPLC (polystyrene/divinylbenzene stationary phase) with CHCl_3 to give **B** as a light-yellow oil (8.76 g, 80% yield).

- ^1H NMR (300 MHz, CDCl_3 , ppm) δ : 6.44 (s, 1H), 4.09 (s, 2H), 4.00 (s, 2H), 3.47 (s, 4H), 3.27 (d, $J = 5.7$ Hz, 4H), 2.37 (s, 3H), 1.35 – 1.23 (m, 20H), 0.90 – 0.84 (m, 13H).
- ^{13}C NMR (101 MHz, CDCl_3 , ppm) δ 150.63, 149.15, 106.15, 74.18, 73.93, 73.61, 69.73, 47.83, 39.51, 30.57, 29.03, 23.89, 23.00, 21.12, 14.02, 11.06.
- HRMS (ESI), $[\text{M}+\text{H}]^+$ m/z calcd. for $\text{C}_{26}\text{H}_{47}\text{O}_4\text{S}_2$: 487.2910; found 487.2902.

General C-H Activation Conditions

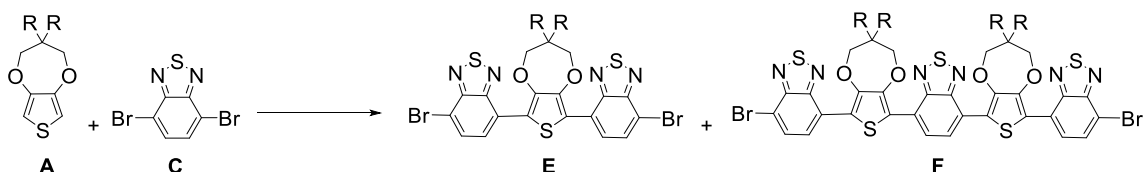
In a 25 mL Schlenk tube, $\text{Pd}(\text{OAc})_2$ (4–8 mol %), $(o\text{-MeOPh})_3\text{P}$ (8–16 mol %), pivalic acid (0.5 per C–H monomer equivalence) and Cs_2CO_3 (1.5 per C–H monomer equivalence) were added, vacuumed for 30 minutes, and then subjected to N_2 purge cycles three times. Anhydrous toluene (0.1 M–0.5 M) was added via needle and syringe. The reaction was heated at 110°C in an oil bath, or until the limiting reagent was consumed per TLC analysis. Upon completion, the reaction mixture was quenched with water and extracted with dichloromethane. The organic layer was washed with water twice, then once with brine. The organic layer was separated and dried over MgSO_4 or Na_2SO_4 , then filtered and concentrated under reduced pressure. The crude product was purified by SiO_2 column chromatography concentrated, and further purified by recycling preparative HPLC (polystyrene/divinylbenzene stationary phase) with CHCl_3 . In cases where an excess of a compound is used, the unreacted portion is retrieved during column chromatography as its r_f value is generally higher than the generated product.



Compound D

The reaction was conducted according to the general procedure without modification using **compound B** (3.0 g, 6.16 mmol, 1.0 equiv), **compound C** (5.44 g, 18.49 mmol, 3.0 equiv) $\text{Pd}(\text{OAc})_2$ (4 mol %, 55.3 mg), $(o\text{-MeOPh})_3\text{P}$ (8 mol %, 173.6 mg), pivalic acid (314.6 mg, 3.08 mmol, 0.5 equiv) and Cs_2CO_3 (3.01 g, 9.24 mmol, 1.5 equiv) in 35 mL of anhydrous toluene. The product was filtered by column chromatography (CH_2Cl_2 :hexanes, gradient of 1:1 to 2:1) and purified by preparative HPLC to provide **compound D** (1.72 g, 40% yield) as an orange oil. Unreacted compound **C** and oligomer **3** was recovered in ~20% yield.

- ^1H NMR (400 MHz, CDCl_3) δ 8.11 (d, $J = 7.9$ Hz, 1H), 7.79 (d, $J = 7.9$ Hz, 1H), 4.18 (d, $J = 6.8$ Hz, 4H), 3.54 (s, 4H), 3.30 (d, $J = 5.7$ Hz, 4H), 2.47 (s, 3H), 1.48 (dt, $J = 11.6, 5.7$ Hz, 2H), 1.41 – 1.23 (m, 18H), 0.90 – 0.84 (m, 13H).
- ^{13}C NMR (101 MHz, CDCl_3) δ 147.79, 132.40, 127.07, 125.25, 111.26, 74.21, 74.18, 73.95, 73.77, 69.84, 47.81, 39.53, 30.59, 30.56, 29.03, 23.92, 23.00, 20.33, 14.03, 11.08.
- HRMS (APCI), $[\text{M}+\text{H}]^+$ m/z calcd. for $\text{C}_{32}\text{H}_{48}\text{BrN}_2\text{O}_4\text{S}_3$: 699.1954; found 699.1944.



Compounds E and F

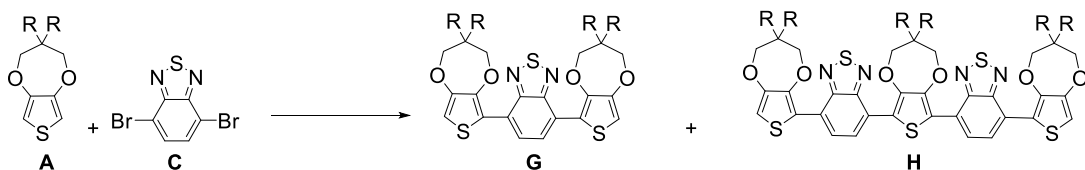
The reaction was conducted according to the general procedure using **compound A** (2.0 g, 4.55 mmol, 1.0 equiv), **compound C** (6.67 g, 22.7 mmol, 5.0 equiv) $\text{Pd}(\text{OAc})_2$ (4 mol %, 40.77 mg), $(o\text{-MeOPh})_3\text{P}$ (8 mol %, 127.98 mg), pivalic acid (927.34 mg, 9.08 mmol, 2.0 equiv) and Cs_2CO_3 (4.59 g, 14.07 mmol, 3.1 equiv) in 130 ml anhydrous toluene. After work-up, the crude material was dissolved in hexane to precipitate out and recover excess **compound C** from the mixture and the filtrate was concentrated. The two products were purified by column chromatography (CH_2Cl_2 :hexanes, gradient of 1:1 to 3:1) to sequentially provide **compound E** as a dark red solid (1.69 g, 43% yield) and **compound F** as a dark purple solid (624 mg, 10% yield).

Compound E

- ^1H NMR (400 MHz, CDCl_3) δ 8.19 (d, $J = 7.8$ Hz, 2H), 7.85 (d, $J = 7.9$ Hz, 2H), 4.28 (s, 4H), 3.60 (s, 4H), 3.34 (d, $J = 5.7$ Hz, 4H), 1.56 – 1.46 (m, 1H), 1.44 – 1.22 (m, 17H), 0.93 – 0.84 (m, 12H).
- ^{13}C NMR (101 MHz, CDCl_3) δ 153.42, 152.03, 148.14, 132.37, 127.77, 125.47, 118.54, 111.85, 74.24, 73.88, 69.94, 47.78, 39.53, 30.57, 29.03, 23.92, 23.02, 14.04, 11.08.
- HRMS (APCI), $[\text{M}+\text{H}]^+$ m/z calcd. for $\text{C}_{37}\text{H}_{47}\text{Br}_2\text{N}_2\text{O}_4\text{S}_3$: 865.1121; found 865.1186.

Compound F

- ^1H NMR (400 MHz, CDCl_3) δ 8.43 (s, 2H), 8.21 (d, $J = 7.9$ Hz, 2H), 7.87 (d, $J = 7.9$ Hz, 2H), 4.31 (d, $J = 7.7$ Hz, 8H), 3.62 (s, 8H), 3.35 (d, $J = 5.7$ Hz, 8H), 1.53 (dt, $J = 12.0, 5.6$ Hz, 6H), 1.42 – 1.24 (m, 38H), 0.93 – 0.87 (m, 24H).
- ^{13}C NMR (101 MHz, CDCl_3) δ 153.46, 152.51, 152.13, 148.25, 132.40, 127.77, 127.65, 124.10, 119.74, 111.56, 74.24, 73.87, 69.99, 47.79, 39.56, 30.58, 29.60, 29.04, 23.95, 23.03, 14.05, 11.10.
- HRMS (APCI), $[\text{M}+\text{H}]^+$ m/z calcd. for $\text{C}_{68}\text{H}_{91}\text{Br}_2\text{N}_6\text{O}_8\text{S}_5$: 1437.3863; found 1437.3866.



Compound G and H

The reaction was conducted according to the general procedure without modification using **compound A** (10.3 g, 23.46 mmol, 6.0 equiv), **compound C** (1.15 g, 3.91 mmol, 1.0 equiv), $\text{Pd}(\text{OAc})_2$ (2 mol %, 17.56 mg), $(o\text{-MeOPh})_3\text{P}$ (8 mol %, 127.98 mg), pivalic acid (927.34 mg, 9.08 mmol, 2.0 equiv) and Cs_2CO_3 (4.59 g, 14.07 mmol, 3.1 equiv) in 130 ml anhydrous toluene. After work-up, the crude material was dissolved in hexane to precipitate out and recover excess **compound C** from the mixture and the filtrate was concentrated. The two products were purified by column chromatography (CH_2Cl_2 :hexanes, gradient of 1:1 to 3:1) to sequentially provide **compound G** as a dark red solid (1.69 g, 43% yield) and **compound H** as a dark purple solid (624 mg, 10% yield).

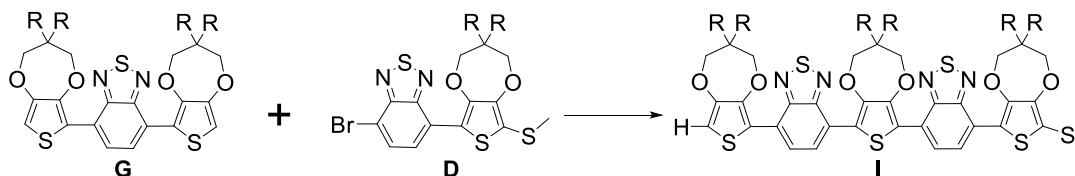
MeOPh)₃P (4 mol %, 55.1 mg), pivalic acid (400 mg, 3.91 mmol, 1.0 equiv), and Cs₂CO₃ (3.7 g, 11.73 mmol, 3.0 equiv) in 75 ml anhydrous toluene. The two products were purified by column chromatography (CH₂Cl₂:hexanes, gradient of 1:2 to 2:1) to sequentially provide **compound G** as an orange oil (1.86 g, 47% yield) and **compound H** as a sticky, magenta solid (1.74 g, 28% yield).

Compound G

- ¹H NMR (400 MHz, CDCl₃) δ 8.29 (s, 2H), 6.66 (s, 2H), 4.20 (s, 4H), 4.10 (s, 4H), 3.54 (s, 8H), 3.31 (d, *J* = 5.5 Hz, 8H), 1.56 – 1.45 (m, 7H), 1.40 – 1.23 (m, 42H), 0.95 – 0.84 (m, 30H).
- ¹³C NMR (101 MHz, CDCl₃) δ 152.56, 149.66, 147.75, 127.47, 124.11, 117.49, 106.38, 74.23, 73.74, 69.87, 47.81, 39.54, 30.57, 29.03, 23.92, 23.01, 14.02, 11.07.
- HRMS (APCI), [M+H]⁺ *m/z* calcd. for C₅₆H₈₈N₂O₈S₃: 1013.5776; found 1013.5771.

Compound H

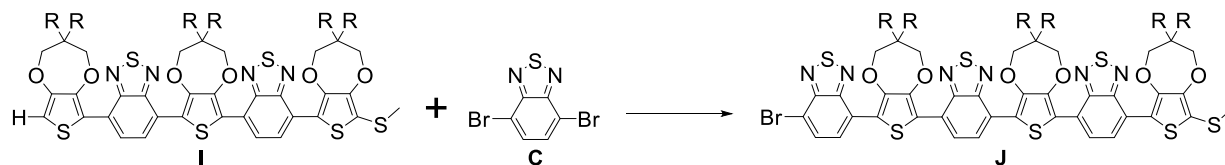
- ¹H NMR (400 MHz, CDCl₃) δ 8.32 (q, *J* = 8.0 Hz, 4H), 6.64 (s, 2H), 4.38 – 4.03 (m, 12H), 3.59 (d, *J* = 40.8 Hz, 12H), 3.35 (dd, *J* = 21.8, 5.6 Hz, 12H), 1.53 (tq, *J* = 14.5, 8.5, 7.0 Hz, 7H), 1.47 – 1.24 (m, 51H), 1.00 – 0.83 (m, 38H).
- ¹³C NMR (101 MHz, CDCl₃) δ 152.45, 152.41, 149.57, 147.89, 147.74, 127.27, 127.10, 124.00, 123.95, 119.20, 117.63, 106.53, 77.28, 74.19, 74.13, 73.59, 69.97, 69.81, 47.80, 39.64, 39.60, 30.65, 29.08, 24.05, 24.00, 23.10, 23.07, 14.10, 11.17, 11.13.
- HRMS (APCI), [M+H]⁺ *m/z* calcd. for C₈₇H₁₃₂N₄O₁₂S₅: 1585.8518; found 1585.8509.



Compound I

The reaction was conducted according to the general procedure without modification using **compound G** (761.3 mg, 0.75 mmol, 2.7 equiv), **compound D** (194.7 mg, 0.28 mmol, 1.0 equiv), Pd(OAc)₂ (8 mol %, 5.0 mg), (o-MeOPh)₃P (16 mol %, 15.7 mg), pivalic acid (14.3 mg, 0.14 mmol, 0.5 equiv), and Cs₂CO₃ (135.9 mg, 0.42 mmol, 1.5 equiv) in 7 ml anhydrous toluene. The product was purified by column chromatography (CH₂Cl₂:hexanes, gradient of 1:3 to 1:1) to provide **compound I** as a sticky, magenta solid (265 mg, 58% yield).

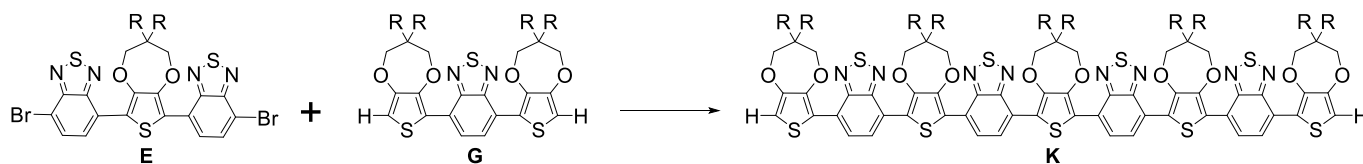
- ¹H NMR (400 MHz, CDCl₃) δ 8.40 – 8.31 (m, 4H), 6.66 (s, 1H), 4.32 (s, 5H), 4.27 – 4.17 (m, 6H), 4.10 (s, 2H), 3.69 – 3.51 (m, 13H), 3.35 (dd, *J* = 16.2, 5.7 Hz, 13H), 2.49 (s, 3H), 1.52 (dt, *J* = 11.7, 5.9 Hz, 7H), 1.46 – 1.22 (m, 56H), 0.91 (m, 40H).
- ¹³C NMR (101 MHz, CDCl₃) δ 152.47, 150.00, 149.63, 148.00, 147.94, 147.80, 147.46, 127.52, 127.26, 127.16, 124.16, 124.03, 123.96, 123.57, 119.21, 119.06, 118.27, 117.58, 116.42, 106.55, 74.22, 74.16, 73.94, 73.68, 70.00, 69.85, 47.82, 39.59, 30.62, 29.06, 23.98, 23.05, 20.51, 14.07, 11.13.
- HRMS (APCI), [M+H]⁺ *m/z* calcd. for C₈₈H₁₃₅N₄O₁₂S₆: 1631.8395; found 1631.8355.



Compound J

The reaction was conducted according to the general procedure using **compound I** (177.1 mg, 0.108 mmol, 1.0 equiv), **compound C** (127.5 mg, 0.434 mmol, 4.0 equiv) Pd(OAc)₂ (8 mol %, 2 mg), (o-MeOPh)₃P (16 mol %, 6.1 mg), pivalic acid (5.5 mg, 0.054 mmol, 0.5 equiv), and Cs₂CO₃ (54.6 mg, 0.173 mmol, 1.6 equiv) in 3 ml anhydrous toluene. After work-up, the crude material was dissolved in hexane to precipitate out and recover excess **compound C** from the mixture and the filtrate was concentrated. The product was purified by column chromatography (CH₂Cl₂:hexanes, gradient of 1:1 to 3:1) to provide **compound J** as a dark purple solid (93.9 mg, 47% yield).

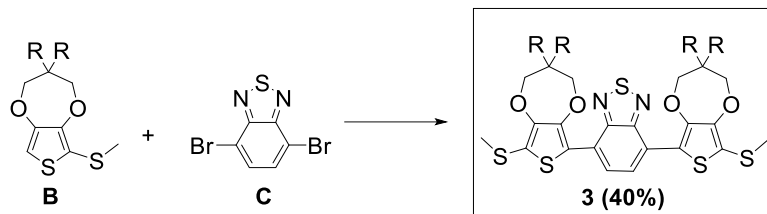
- ¹H NMR (400 MHz, CDCl₃) δ 8.43 – 8.31 (m, 4H), 8.18 (d, J = 7.9 Hz, 1H), 7.83 (d, J = 7.9 Hz, 1H), 4.38 – 4.25 (m, 8H), 4.21 (d, J = 13.5 Hz, 4H), 3.69 – 3.51 (m, 12H), 3.42 – 3.28 (m, 12H), 2.49 (s, 3H), 1.57 – 1.47 (m, 7H), 1.43 – 1.24 (m, 57H), 0.96 – 0.84 (m, 39H).
- ¹³C NMR (101 MHz, CDCl₃) δ 153.51, 152.58, 152.51, 152.19, 150.08, 148.30, 148.17, 148.06, 147.98, 147.55, 132.44, 127.91, 127.81, 127.69, 127.28, 125.81, 124.45, 124.05, 123.89, 123.79, 119.90, 119.30, 118.25, 117.95, 116.51, 111.57, 74.28, 74.23, 74.03, 73.90, 73.80, 70.06, 69.94, 53.34, 47.87, 47.84, 39.62, 39.60, 30.62, 29.64, 29.07, 23.98, 23.96, 23.06, 20.57, 14.08, 11.13.
- HRMS (APCI), [M+H]⁺ *m/z* calcd. for C₉₄H₁₃₆BrN₆O₁₂S₇: 1843.7439; found 1843.7404.



Compound K

The reaction was conducted according to the general procedure using **compound E** (950.6 mg, 0.938 mmol, 4.0 equiv), **compound G** (203.2 mg, 0.234 mmol, 1.0 equiv) Pd(OAc)₂ (8 mol %, 4.2 mg), (o-MeOPh)₃P (16 mol %, 13.2 mg), pivalic acid (24 mg, 0.234 mmol, 1.0 equiv) and Cs₂CO₃ (229.1 mg, 0.725 mmol, 3.1 equiv) in 3 ml anhydrous toluene. The product was purified by column chromatography (CH₂Cl₂:hexanes, gradient of 1:2 to 2:1) to provide **compound K** as a dark blue solid (233 mg, 37% yield).

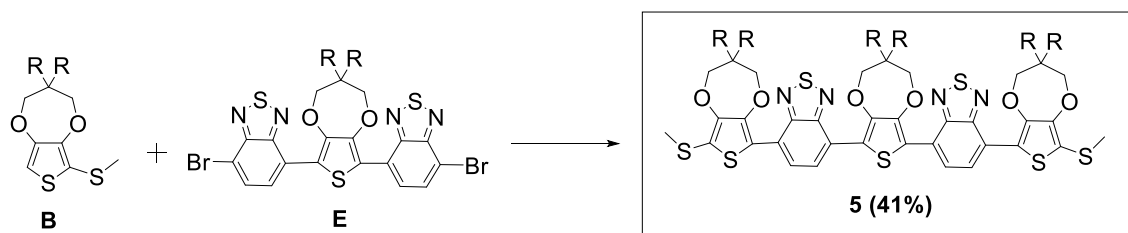
- ¹H NMR (500 MHz, CDCl₃, ppm) δ 8.48 (s, 4H), 8.45 (d, J = 7.9 Hz, 2H), 8.40 (d, J = 7.9 Hz, 2H), 6.74 (s, 2H), 4.40 (d, J = 3.9 Hz, 13H), 4.28 (s, 4H), 4.17 (s, 4H), 3.71 (s, 13H), 3.61 (s, 9H), 3.43 (d, J = 5.7 Hz, 12H), 3.38 (d, J = 5.6 Hz, 8H), 1.60 (dt, J = 19.2, 6.0 Hz, 12H), 1.53 – 1.29 (m, 91H), 1.04 – 0.91 (m, 67H).
- ¹³C NMR (126 MHz, CDCl₃, ppm) δ 152.74, 152.70, 149.81, 148.19, 148.14, 147.95, 127.74, 127.67, 127.49, 124.32, 124.30, 124.23, 119.45, 119.38, 119.34, 117.76, 106.65, 74.40, 74.34, 73.94, 73.85, 70.17, 69.99, 47.96, 39.76, 39.72, 30.77, 30.74, 29.21, 24.15, 24.10, 23.20, 23.18, 14.22, 14.19, 11.28, 11.24.
- HRMS (APCI), [M+H]⁺ *m/z* calcd. for C₁₄₉H₂₂₁N₈O₂₀S₉: 2730.4003; found 2730.3894.



Oligomer n=3

The reaction was conducted according to the general procedure without modification using **compound B** (1.95 g, 4.01 mmol, 2.1 equiv) and **compound C** (560.8 mg, 1.907 mmol, 1.0 equiv), Pd(OAc)₂ (5 mol %, 5.0 mg), (o-MeOPh)₃P (10 mol %, 67.2 mg), pivalic acid (97.4 mg, 0.95 mmol, 0.5 equiv) and Cs₂CO₃ (932 mg, 2.86 mmol, 1.5 equiv) in 5 ml anhydrous toluene. The product was purified by column chromatography (CH₂Cl₂:hexanes, 1:3) and further purified by preparative HPLC to provide oligomer **n=3** as an orange viscous oil (886 mg, 42% yield).

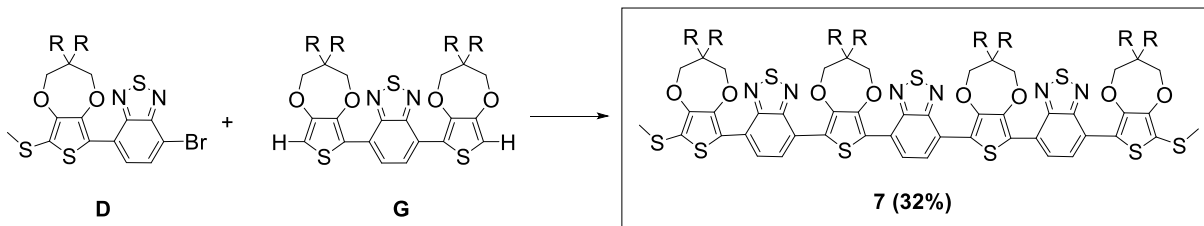
- ¹H NMR (500 MHz, CD₂Cl₂, ppm) δ 8.33 (s, 2H), 4.21 (s, 4H), 4.15 (s, 4H), 3.54 (s, 8H), 3.32 (dd, J = 5.0 Hz, 8H), 2.45 (s, 6H), 1.43 – 1.27 (m, 34H), 0.87 (m, 22H).
- ¹³C NMR (126 MHz, CD₂Cl₂, ppm) δ 151.92, 149.69, 147.47, 126.69, 122.98, 117.32, 115.89, 109.21, 73.48, 73.38, 73.20, 69.04, 54.33, 54.11, 53.89, 53.68, 53.46, 47.58, 39.24, 30.32, 28.91, 23.60, 23.55, 23.26, 20.32, 14.23, 10.94.
- HRMS (ESI), [M+H]⁺ m/z calcd. for C₅₈H₉₂N₂O₈S₅: 1104.5458; found 1104.5441.



Oligomer n=5

The reaction was conducted according to the general procedure without modification using **compound B** (288 mg, 0.592 mmol, 2.2 equiv) and **compound E** (233.2 mg, 0.269 mmol, 1.0 equiv), Pd(OAc)₂ (8 mol %, 6.3 mg), (o-MeOPh)₃P (16 mol %, 15.2 mg), pivalic acid (13.7 mg, 0.135 mmol, 0.5 equiv), and Cs₂CO₃ (131.5 mg, 0.404 mmol, 1.5 equiv) in 2 ml anhydrous toluene. The product was purified by column chromatography (CH₂Cl₂:hexanes, 1:1) and further purified by preparative HPLC to provide oligomer **n=5** as a magenta wax-like solid (185 mg, 41% yield).

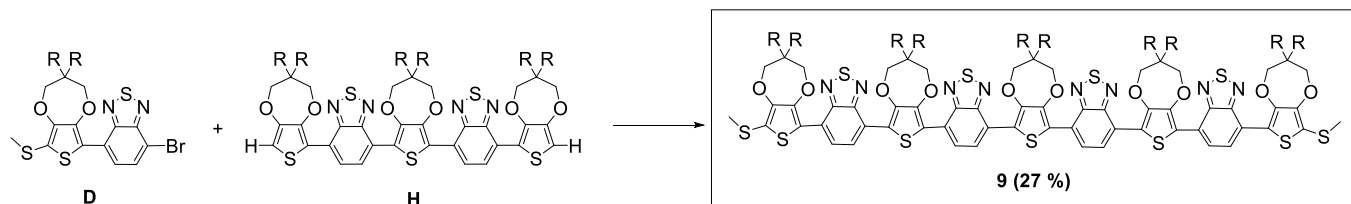
- ¹H NMR (400 MHz, CDCl₃, ppm) δ 8.37 (q, J = 8.0 Hz, 4H), 4.31 (s, 4H), 4.21 (d, J = 12.6 Hz, 8H), 3.63 (s, 4H), 3.57 (d, J = 2.4 Hz, 9H), 3.34 (dd, J = 11.8, 5.6 Hz, 12H), 2.49 (s, 6H), 1.58 – 1.46 (m, 7H), 1.46 – 1.37 (m, 5H), 1.37 – 1.32 (m, 13H), 1.32 – 1.23 (m, 36H), 0.90 (dd, J = 7.3, 4.9 Hz, 39H).
- ¹³C NMR (101 MHz, CDCl₃, ppm) δ 150.04, 148.01, 147.49, 127.70, 127.23, 123.69, 119.09, 74.23, 73.99, 73.74, 70.01, 69.89, 47.83, 39.57, 30.59, 29.04, 23.95, 23.03, 20.54, 14.05, 11.11.
- HRMS (APCI), [M+H]⁺ m/z calcd. for C₈₉H₁₃₇N₄O₁₂S₇: 1677.8272; found 1677.8253.



Oligomer n=7

The reaction was conducted according to the general procedure without modification using **compound D** (445.9 mg, 0.637 mmol, 2.7 equiv) and **compound G** (239.2 mg, 0.236 mmol, 1.0 equiv), Pd(OAc)₂ (4 mol %, 2.7 mg), (o-MeOPh)₃P (8 mol %, 6.7 mg), pivalic acid (24.1 mg, 0.236 mmol, 1.0 equiv) and Cs₂CO₃ (238.4 mg, 0.732 mmol, 3.1 equiv) in 3 ml anhydrous toluene. The product was purified by column chromatography (CH₂Cl₂:hexanes, gradient of 1:1 to 2:1) and further purified by preparative HPLC to provide **oligomer 7-A** as a purple solid (170 mg, 32 % yield).

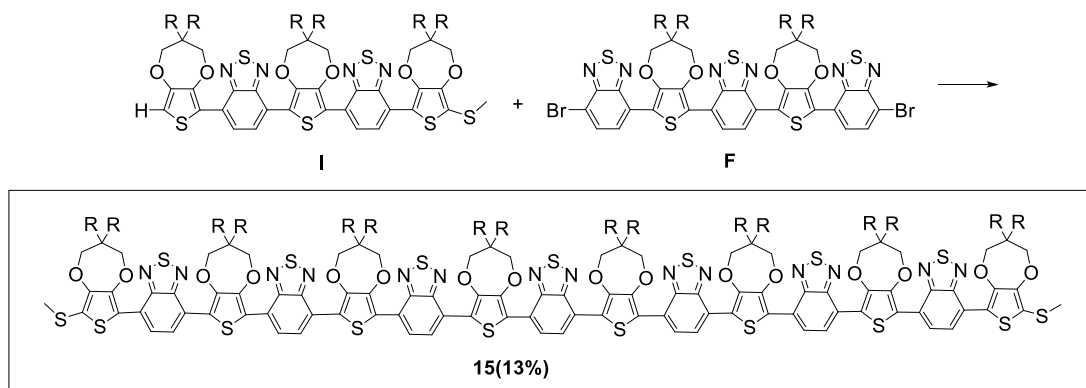
- ¹H NMR (500 MHz, CDCl₃, ppm) δ 8.40 (s, 3H), 8.40 – 8.32 (m, 4H), 4.33 (s, 8H), 4.21 (d, *J* = 17.4 Hz, 8H), 3.57 (s, 8H), 3.37 (d, *J* = 5.7 Hz, 8H), 3.32 (d, *J* = 5.8 Hz, 8H), 2.50 (s, 6H), 1.53 (s, 8H), 1.42 – 1.27 (m, 67H), 0.95 – 0.87 (m, 52H).
- ¹³C NMR (201 MHz, CDCl₃, ppm) δ 152.47, 152.43, 150.04, 148.05, 148.01, 147.46, 127.21, 124.12, 124.01, 123.49, 119.39, 119.17, 118.32, 116.35, 74.25, 74.18, 73.89, 73.71, 69.97, 69.77, 47.85, 47.82, 39.66, 39.62, 30.66, 30.64, 29.10, 24.05, 24.01, 23.99, 23.11, 23.08, 20.56, 14.14, 14.11, 11.19, 11.16.
- HRMS (APCI), [M+H]⁺ *m/z* calcd. for C₁₂₀H₁₈₁N₆O₁₆S₉: 2250.1015; found 2250.1029.



Oligomer n=9

The reaction was conducted according to the general procedure without modification using **compound D** (135 mg, 0.277 mmol, 2.2 equiv) and **compound H** (200 mg, 0.126 mmol, 1.0 equiv), Pd(OAc)₂ (8 mol %, 3.0 mg), (o-MeOPh)₃P (16 mol %, 7.1 mg), pivalic acid (12.9 mg, 0.158 mmol, 1.0 equiv) and Cs₂CO₃ (127.4 mg, 0.391 mmol, 3.1 equiv) in 2 ml anhydrous toluene. The product was purified by column chromatography (CH₂Cl₂:hexanes, gradient of 2:1 to 4:1) to provide oligomer **n=9** as a blue solid (96 mg, 27 % yield).

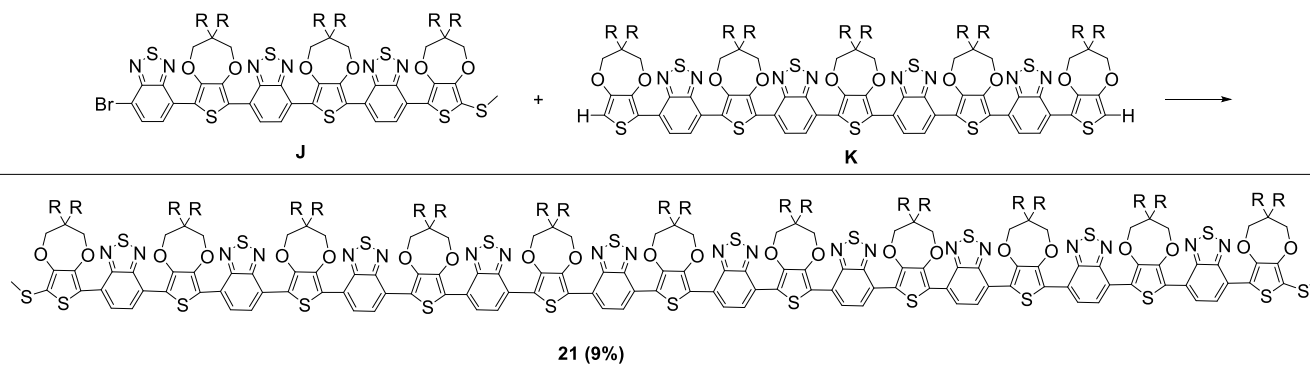
- ¹H NMR (800 MHz, CDCl₃, ppm) δ 8.45 – 8.39 (m, 6H), 8.36 (d, *J* = 7.7 Hz, 2H), 4.35 (s, 10H), 4.24 (s, 4H), 4.21 (s, 4H), 3.67 (s, 11H), 3.58 (s, 8H), 3.39 (s, 12H), 3.34 (s, 8H), 2.52 (s, 6H), 1.55 (dd, *J* = 38.4, 5.9 Hz, 12H), 1.33 (d, *J* = 20.7 Hz, 88H), 0.97 – 0.89 (m, 70H).
- ¹³C NMR (201 MHz, CDCl₃, ppm) δ 152.59, 152.53, 152.48, 150.07, 148.08, 148.05, 147.49, 127.53, 127.26, 124.18, 124.14, 124.07, 123.61, 119.37, 119.34, 119.17, 118.32, 116.40, 74.26, 74.21, 73.96, 73.81, 73.70, 70.03, 69.98, 69.86, 47.86, 47.83, 39.65, 39.61, 34.61, 31.53, 30.65, 30.63, 29.10, 25.22, 24.03, 24.00, 23.98, 23.10, 23.07, 22.60, 20.57, 14.12, 14.09, 14.06, 11.17, 11.14.
- HRMS (APCI), [M+H]⁺ *m/z* calcd. for C₁₅₁H₂₂₅N₈O₂₀S₁₁: 2822.3757; found 2822.3812.



Oligomer n=15

The reaction was conducted according to the general procedure without modification using **compound I** (264.9 mg, 0.162 mmol, 2.3 equiv) and **compound F** (101.5 mg, 0.071 mmol, 1.0 equiv), Pd(OAc)₂ (20 mol %, 4.2 mg), (o-MeOPh)₃P (40 mol %, 10 mg), pivalic acid (8.0 mg, 0.078 mmol, 1.1 equiv), and Cs₂CO₃ (71.7 mg, 0.220 mmol, 3.1 equiv) in 3 ml anhydrous toluene. The product was purified by column chromatography (CH₂Cl₂:hexanes, gradient of 1:1 to 5:1) and further purified by preparative HPLC to provide oligomer **n=15** as a blue solid (42 mg, 13% yield).

- ¹H NMR (800 MHz, CDCl₃, ppm) δ 8.47 (d, *J* = 8.6 Hz, 10H), 8.43 – 8.36 (m, 4H), 4.36 (t, *J* = 8.0 Hz, 24H), 4.25 (s, 4H), 4.22 (s, 4H), 3.67 (d, *J* = 10.4 Hz, 24H), 3.60 (s, 8H), 3.40 – 3.38 (m, 24H), 3.34 (d, *J* = 5.6 Hz, 8H), 2.51 (s, 6H), 1.59 – 1.51 (m, 20H), 1.45 – 1.28 (m, 160H), 0.96 – 0.89 (m, 118H).
- ¹³C NMR (201 MHz, CDCl₃, ppm) δ 152.66, 152.58, 152.51, 150.08, 148.11, 148.08, 147.51, 127.68, 127.30, 124.21, 124.13, 123.71, 119.35, 119.31, 119.14, 118.30, 116.43, 74.28, 74.23, 74.03, 73.89, 73.78, 70.08, 69.93, 47.88, 47.85, 39.63, 39.60, 30.64, 29.09, 24.01, 23.97, 23.09, 23.06, 20.59, 14.11, 14.08, 11.16, 11.13.
- MS (MALDI+), [M+H] *m/z* calcd. for C₂₄₄H₃₅₆N₁₄O₃₂S₁₇: 4541.20; found 4536.57.



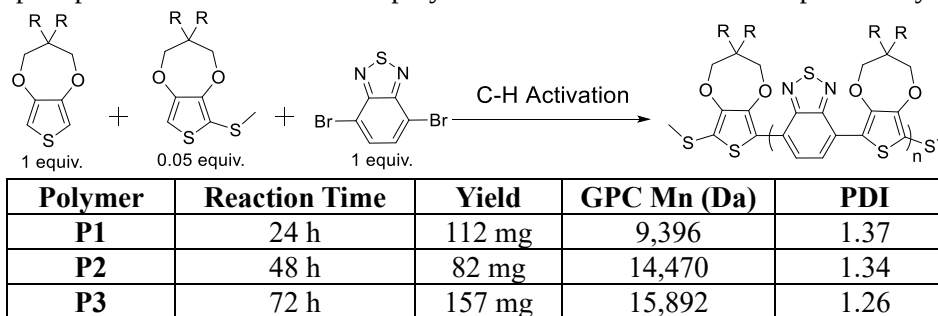
Oligomer n=21

The reaction was conducted according to the general procedure without modification using **compound 10** (93.9 mg, 0.051 mmol, 2.2 equiv) and **compound 11** (63.2 mg, 0.023 mmol, 1.0 equiv), Pd(OAc)₂ (40 mol %, 2.7 mg), (o-MeOPh)₃P (80 mol %, 6.5 mg), pivalic acid (2.3 mg, 0.023 mmol, 1.0 equiv) and Cs₂CO₃ (23.4 mg, 0.072 mmol, 3.1 equiv) in 2 ml anhydrous toluene. The product was purified by column chromatography (CH₂Cl₂:hexanes, gradient of 1:1 to 5:1) and further purified by preparative HPLC to provide **oligomer 21-A** as a blue solid (37 mg, 26% yield).

- ^1H NMR (800 MHz, CDCl_3) δ 8.47 (s, 16H), 8.42 – 8.35 (m, 4H), 4.39 (s, 46H), 4.24 (d, J = 25.9 Hz, 8H), 3.70 (s, 48H), 3.60 (s, 14H), 3.41 (s, 52H), 3.35 (s, 16H), 2.51 (d, J = 7.5 Hz, 6H), 1.56 (d, J = 42.1 Hz, 39H), 1.35 (s, 309H), 0.94 (d, J = 8.0 Hz, 229H).
- ^{13}C NMR (201 MHz, CDCl_3) δ 152.57, 150.03, 148.02, 147.45, 127.56, 124.12, 119.36, 119.12, 118.30, 116.42, 74.27, 74.23, 73.90, 70.14, 69.94, 47.83, 39.65, 39.61, 30.65, 29.64, 29.10, 24.03, 23.99, 23.97, 23.10, 23.07, 20.58, 14.11, 14.09, 11.16, 11.13.
- MS (MALDI+), $[\text{M}+\text{H}]$ m/z calcd. for $\text{C}_{337}\text{H}_{488}\text{N}_{20}\text{O}_{44}\text{S}_{23}$: 6261.09; found 6260.57.

General Polymerization Condition

To a Schlenk tube charged with a stir bar, **compound A** (1.0 equiv), **compound B** (0.05 equiv.), **compound C** (1.0 equiv), $\text{Pd}(\text{OAc})_2$ (2 mol %), $(o\text{-MeOPh})_3\text{P}$ (4 mol %), pivalic acid (1.1 equiv) and Cs_2CO_3 (3.1 equiv) were added, vacuumed for 30 minutes, and then subjected to N_2 purge cycles three times. Anhydrous toluene (3 ml) was added via needle and syringe. The reaction was heated at 110°C in an oil bath until completion. After polymerization was complete, the mixture was precipitated into methanol. The solids were collected by a Soxhlet thimble and purified by Soxhlet extraction successively with methanol, acetone, hexane, dichloromethane and chloroform. 3 separate reaction were carried out with variations in heating time; 24 h (P1, extracted from DCM fraction), 48 h (P2, extracted from chloroform extract), and 72 h (P3, extracted from chloroform extract). The fractions were concentrated and precipitated into methanol. The polymer was collected and further purified by recycling HPLC.



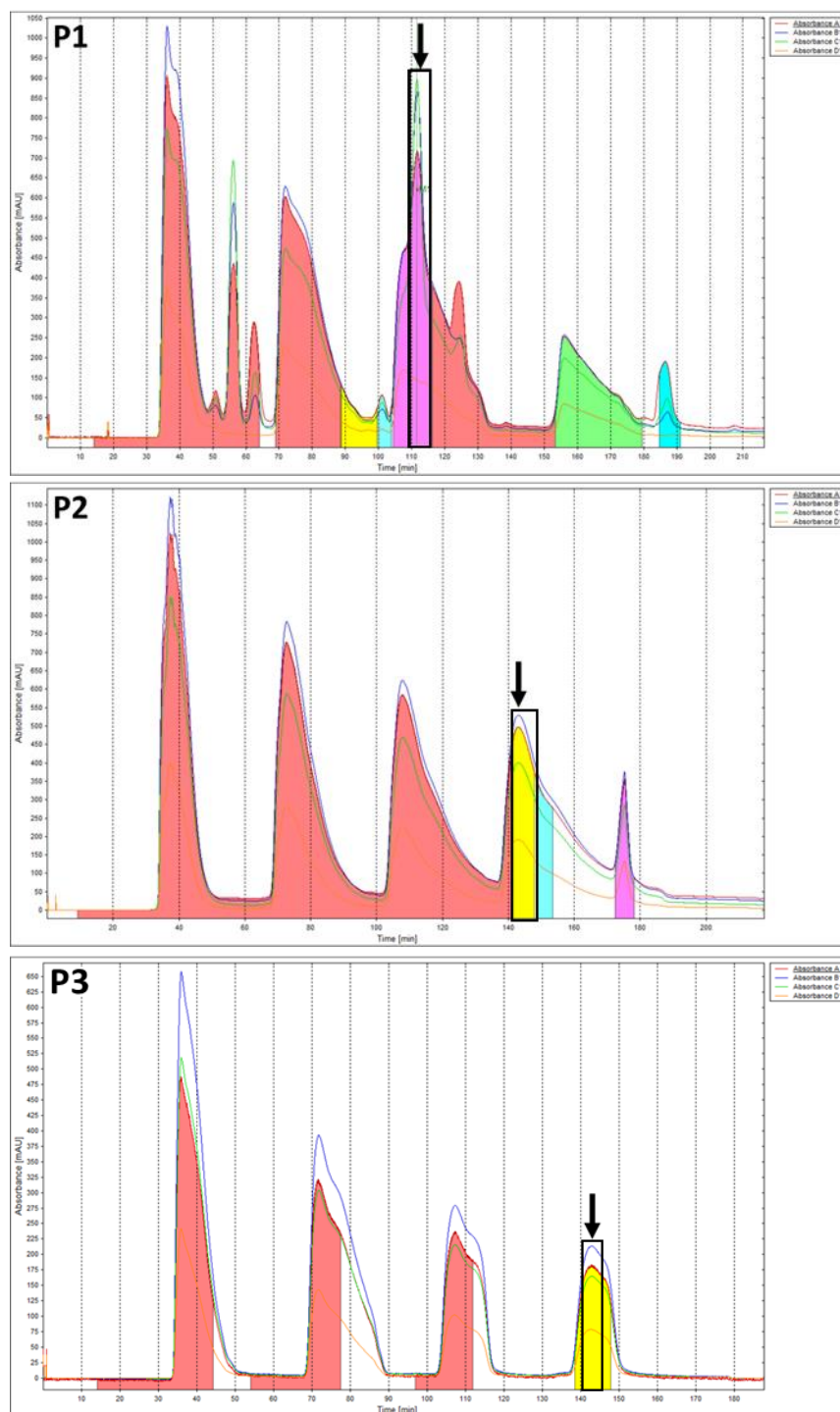
Recycling Preparative HPLC Chromatograms for Polymers

Figure S1. Preparative HPLC chromatograms of P1, P2, and P3.

3. PHYSICAL CHARACTERIZATIONS

Gel Permeation Chromatography (GPC)

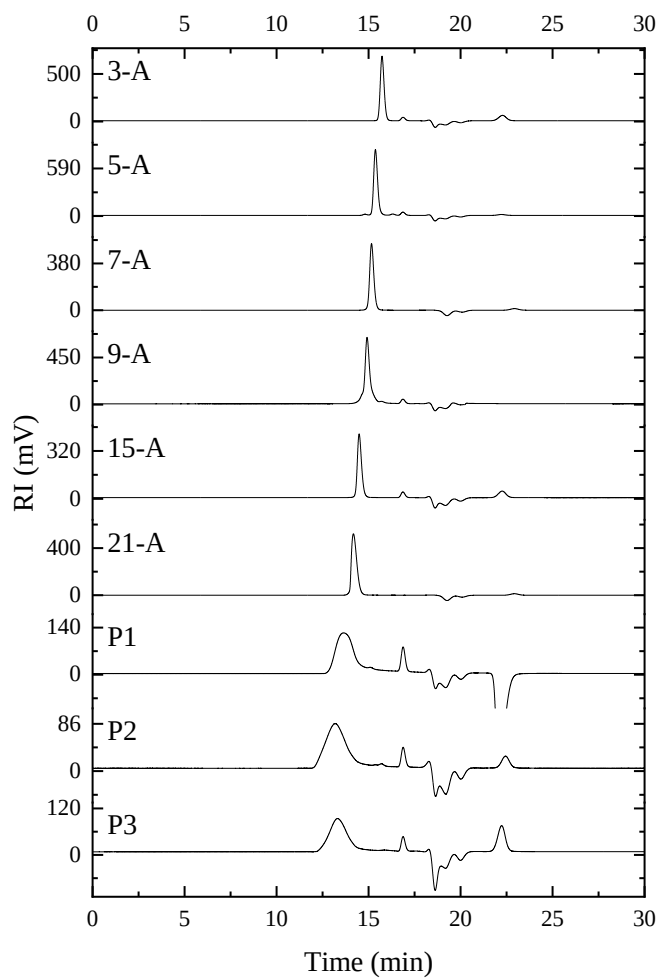
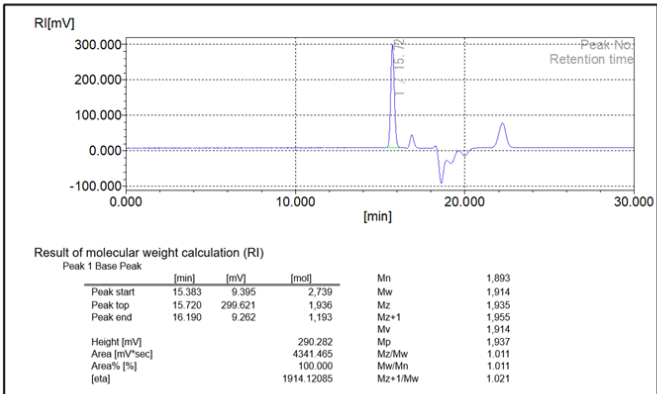
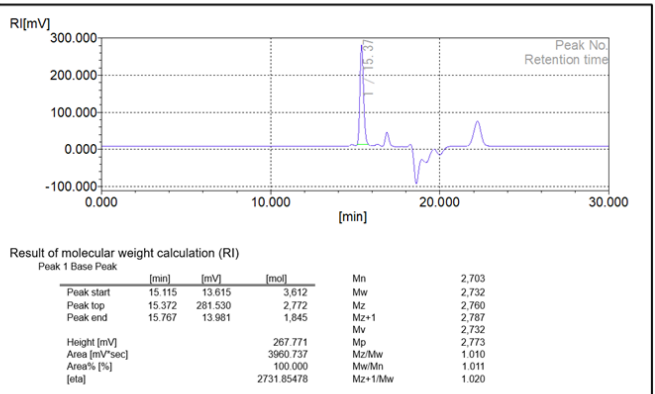


Figure S2. Raw GPC chromatogram for *nPB* series.

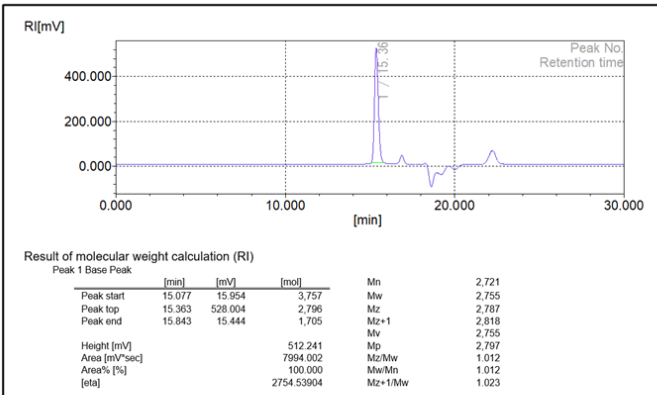
Oligomer n=3



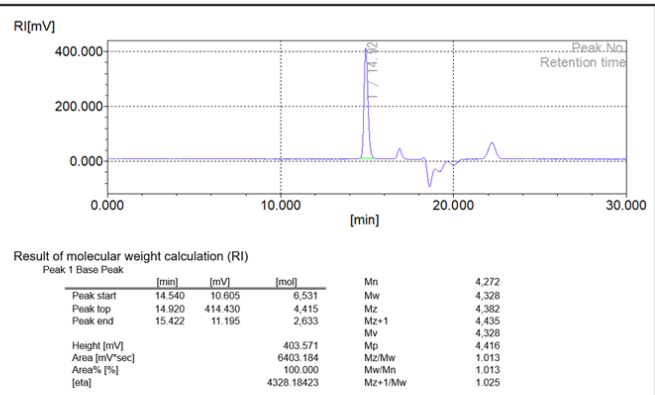
Oligomer n=5



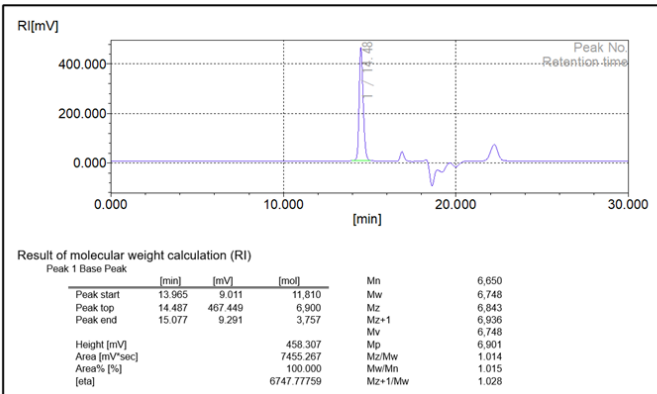
Oligomer n=7



Oligomer n=9



Oligomer n=15



Oligomer n=21

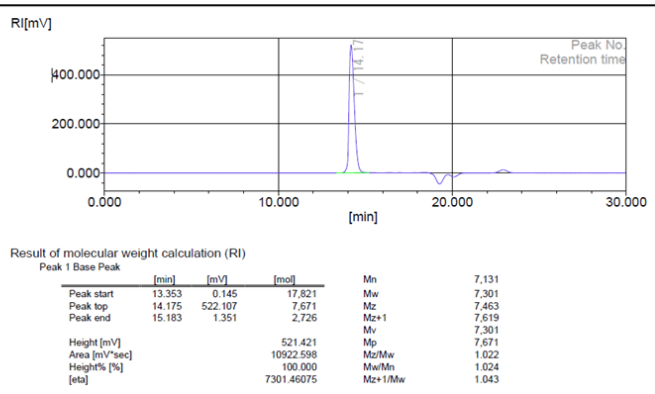


Figure S3. Raw GPC chromatograms for nPB oligomers.

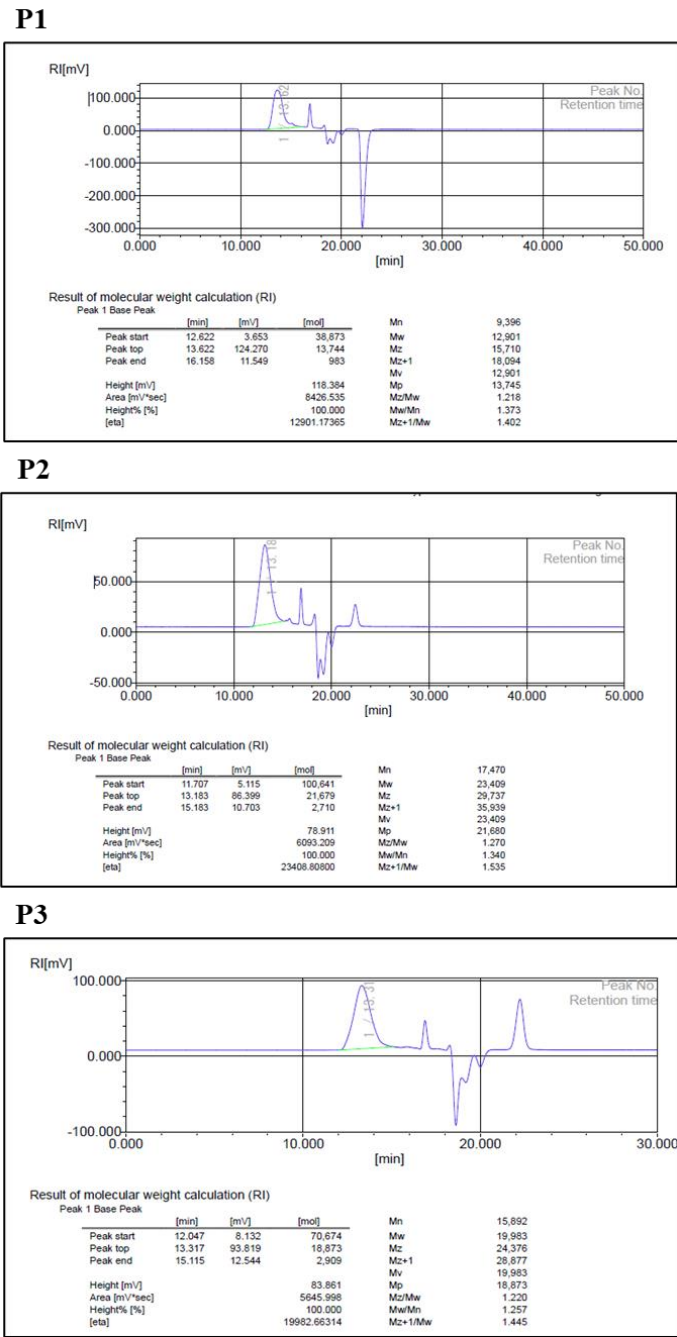


Figure S3. (continued) Raw GPC chromatograms for *n*PB polymers.

Electrochemistry

Electrochemical window stability

0.2 M TBAPF₆ – Dichloromethane electrolyte system at a Pt wire ultramicroelectrode vs. Ag/AgCl under nitrogen. Degradation of electrolyte begins to occur at 2.2 V. All voltammetry was conducted under 2.1 V.

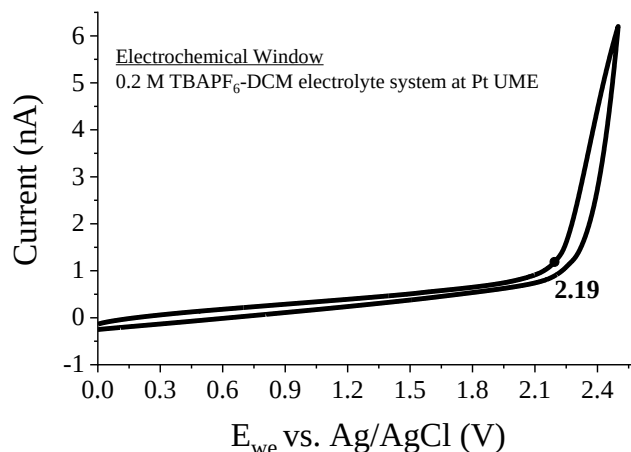


Figure S4. Electrochemical window stability of 0.2 M TBAPF₆ – CH₂Cl₂ at 25 mm Pt ultramicroelectrode vs. Ag/AgCl from 0 to 2.2 V under nitrogen atmosphere.

Voltammetry

Solution CV and DPV of the oligomer series dissolved at ~1 mM in 0.2 M TBAPF₆/ CH₂Cl₂ was conducted under a nitrogen atmosphere on a ultramicroelectrode (25 mm) platinum button electrode and a platinum wire counter electrode. An Ag/AgCl wire was used as the pseudoreference electrode which was calibrated against a ferrocene/ferrocenium as an internal standard ($E_{1/2} = 0.51$ V). For CV, the voltage was scanned from 0 to 2.1 V vs. Ag/AgCl, at a 10 mV/s scan rate. The second cycle is reported in the main text figure. For DPV, the voltage was scanned from 0 to 2.1 V vs. Ag/AgCl in 0.004 V increments, at 0.05 V amplitude, with a 0.05 sec pulse width, a 0.0167 sec sample width, and a 0.5 sec pulse period. For NDPV, all DPV parameters were kept the same with the exception of a 0.2 sec pulse period. DPV deconvolution was achieved by calculating semi-derivatives of the current-voltage voltammograms via the CHI 660 potentiostat software.

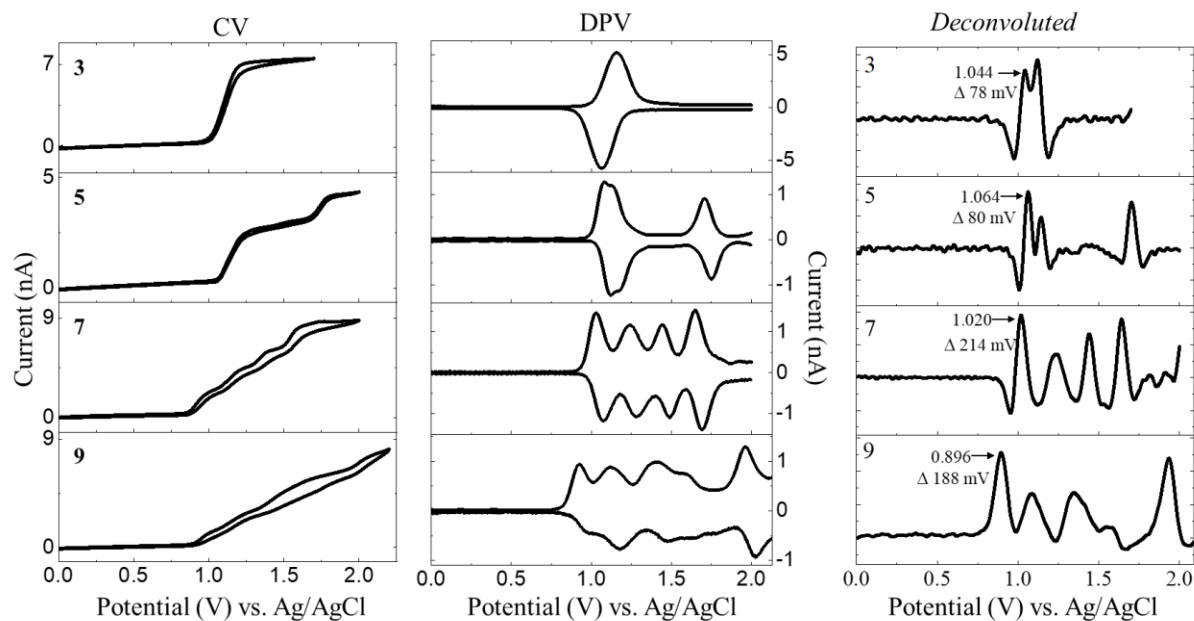


Figure S5. Raw and deconvoluted CV and DPV voltammograms for $n=3-9$.

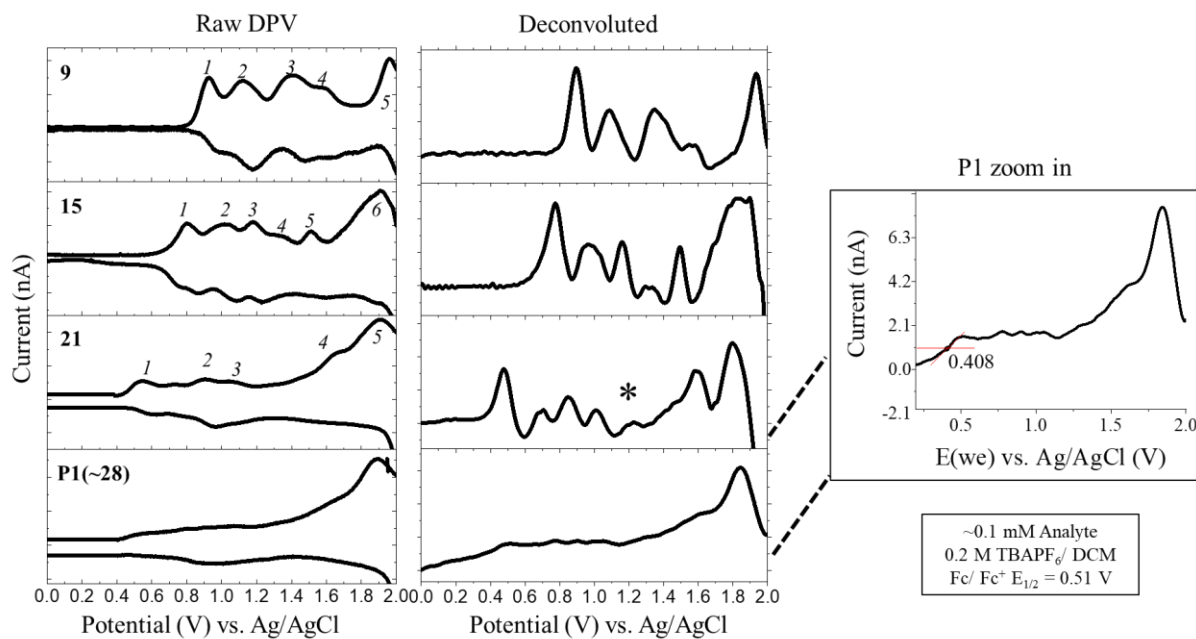


Figure S6. Raw and deconvoluted CV and DPV voltammograms for $n=9-21$ and $P1$.

Spectroelectrochemistry

Solution spectroelectrochemistry was done in a three electrode honeycomb electrochemical cell supplied by Pine Research. A 12.5 x 12.5 x 45.0 mm³ quartz cuvette with a 1.7 mm path length was used as the cell, equipped with a polished platinum honeycomb electrode (working and counter) and Ag/AgCl pseudoreference electrode calibrated against a ferrocene/ferrocenium standard for which the $E_{1/2}$ is taken to be 0.51 V vs. Ag/AgCl. A homemade teflon cap was specially designed to keep the cell sealed from solvent evaporation and air contamination. In a nitrogen filled glove box, 4 x 10⁻⁴ M solution of **PBP** was prepared with 0.2 M TBAPF₆ in anhydrous DCM and transferred and sealed in the electrochemical quartz cell and sealed with teflon tape. During electrochemical oxidation, the voltage is increased from 0 to 1.2 V in 50 mV increments by linear scan voltammetry (LSV) at a 25 mV/s scan rate.

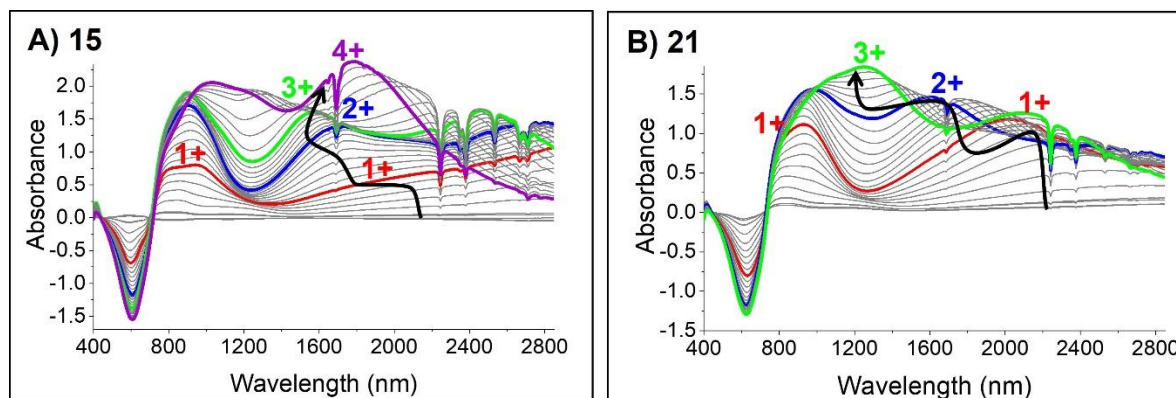


Figure S7: Spectroelectrochemistry of A) 15 and B) 21 in 0.2 M TBAPF₆/CH₂Cl₂. This experiment was conducted in an air-tight optically transparent thin-layer quartz cuvette equipped with a Pt honeycomb electrode under nitrogen.

n	+3 (eV, nm)		+4 (eV, nm)	
3	--	--	--	--
5	NR	NR	--	--
7	0.94	1314	NR	NR
9	0.76/0.90	1636/1375	0.90	1375
15	1.32/0.85/0.62-0.44 ^(b)	940/1465/2000-2800 (b)	1.23/0.70	1010/1778
21	0.98/0.58	1260/2140	NR	NR
P1	NR	NR	NR	NR
(b) = broad				
NR = not resolvable				

Table S1. Photophysical properties ($\lambda_{\max}$) of the +3 and +4 oxidation states of the **nPB** series by spectroelectrochemistry in solution.

Atomic Force Microscopy (AFM)

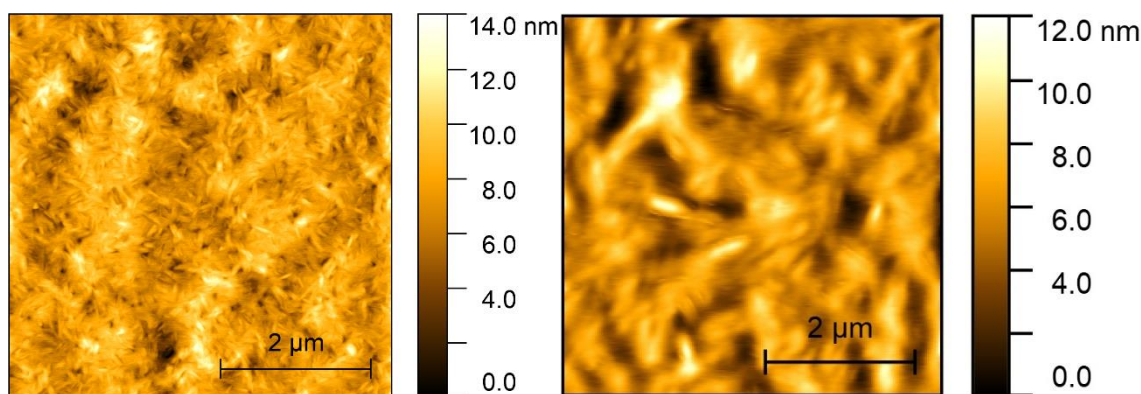


Figure S8. AFM image showing crystallite formation of solution cast n=5 from chloroform as a thin film.

Small Angle Neutron Scattering (SANS)

Dilute solutions of oligomers and polymers were prepared (5 mg/mL) in chlorobenzene-d₅. Chlorobenzene-d₅ (D > 99%) and was purchased from Cambridge Isotopes (Tewksbury, MA) and used as received. SANS measurements were carried out using the Extended Q-Range Small-Angle Neutron Scattering Diffractometer (EQ-SANS) at the Spallation Neutron Source (SNS), ORNL. The scattering wavevector q ranged from 0.003 to 0.8 Å⁻¹, by using two different configurations (4m 12 Å and 2.5m 2.5 Å). The samples were contained in Hellma quartz cells with a 2 mm path length. Measurements were performed at 75 °C. The absolute intensity was obtained through data reduction and correction. Reduced data was later fitted to a flexible cylinder model in SasView.²⁴

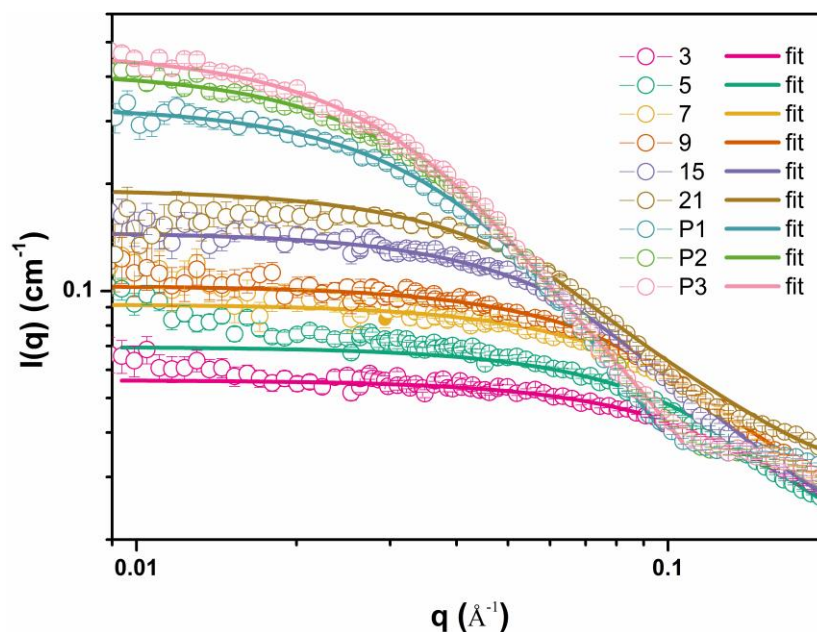


Figure S9. Comparison of scattering profiles for oligomers and polymers with different molecular weights at a concentration of 5 mg/mL.

n	Persistence Length (nm)	Contour Length (nm)	Radius (nm)
3	1.28 ± 0.2	2.10 ± 0.1	1.24 ± 0.02
5	1.77 ± 0.4	3.19 ± 0.1	1.24 ± 0.02
7	2.30 ± 0.4	4.04 ± 0.1	1.24 ± 0.02
9	2.37 ± 0.2	4.97 ± 0.1	1.24 ± 0.02
15	2.56 ± 0.1	7.83 ± 0.2	1.24 ± 0.02
21	2.61 ± 0.2	11.37 ± 0.2	1.24 ± 0.02
P1 (~28)	2.70 ± 0.2	20.04 ± 0.1	1.24 ± 0.02
P2 (~40)	2.89 ± 0.1	23.08 ± 0.2	1.24 ± 0.02
P3 (~48)	3.12 ± 0.2	24.92 ± 0.1	1.24 ± 0.02

Table S2. Parameters obtained from fits to SANS data with the flexible cylinder model. And contour length dispersities are 1.

Theoretical Calculations

	5	7	9	15	19
IP	5.00	4.88	4.84	4.82	4.82
E_{HL}	4.64	4.34	4.12	3.88	3.94
ω	0.1112	0.1067	0.0974	0.0931	0.0985

Table S3. Adiabatic ionization potential (IP), HOMO-LUMO gap (E_{HL}), and optimally tuned long-range correction parameter for $n = 5-19$ as determined at the OT- ω B97X-D/6-31G(d,p) level of theory.

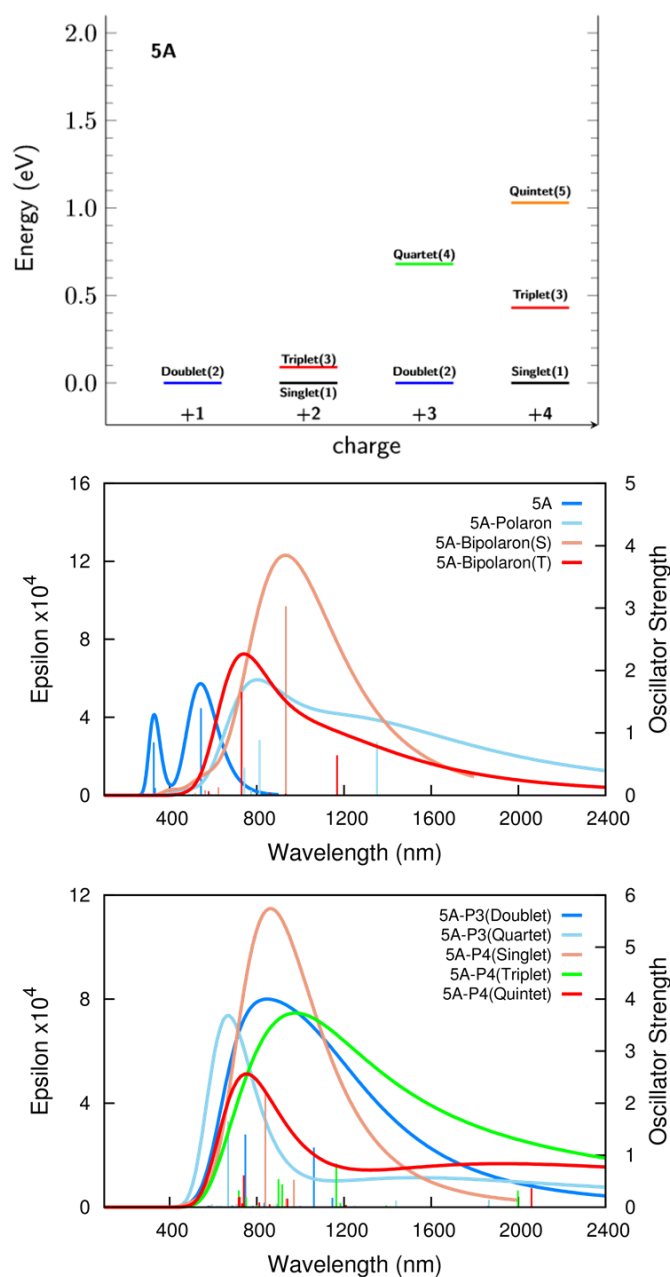


Figure S10. (top) DFT-determined energies of select spin states as a function of oxidation, and (middle, bottom) TDDFT simulated optical absorption profiles [via Gaussian convolution using a FWHM=0.3 eV] for select spin states for $n = 5$ as determined at the OT- ω B97X-D/6-31G(d,p) level of theory.

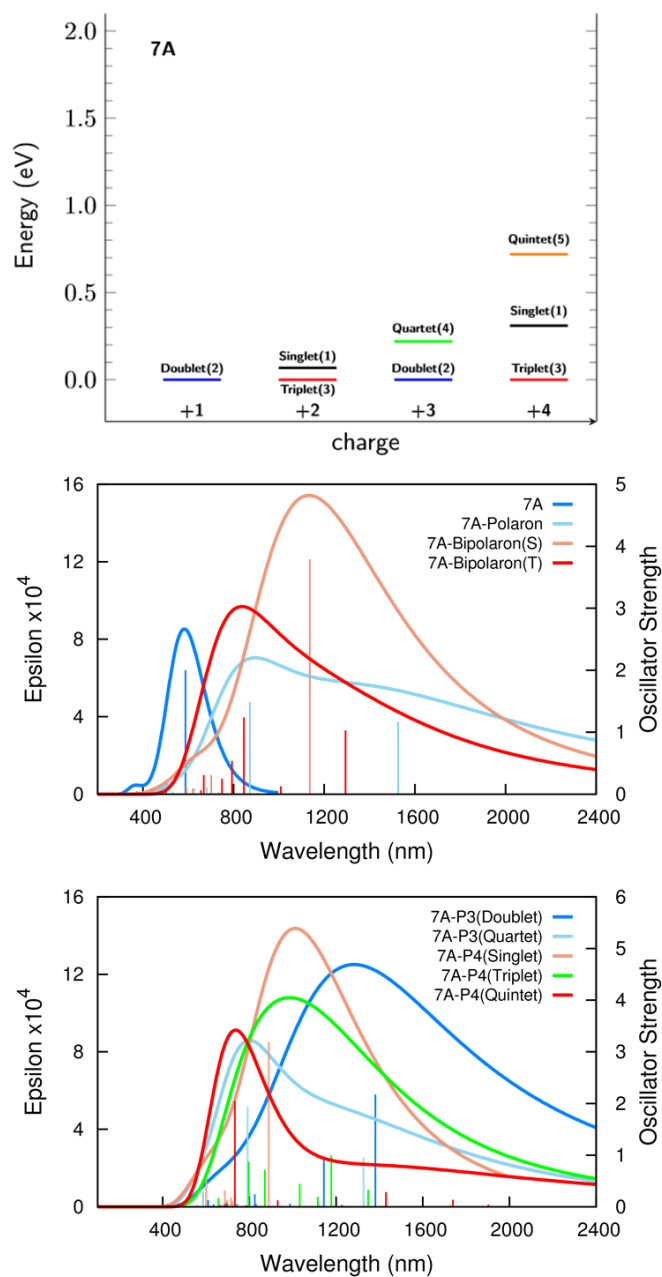


Figure S11. (top) DFT-determined energies of select spin states as a function of oxidation, and (middle, bottom) TDDFT simulated optical absorption profiles [via Gaussian convolution using a FWHM=0.3 eV] for select spin states for $n = 7$ as determined at the OT- ω B97X-D/6-31G(d,p) level of theory.

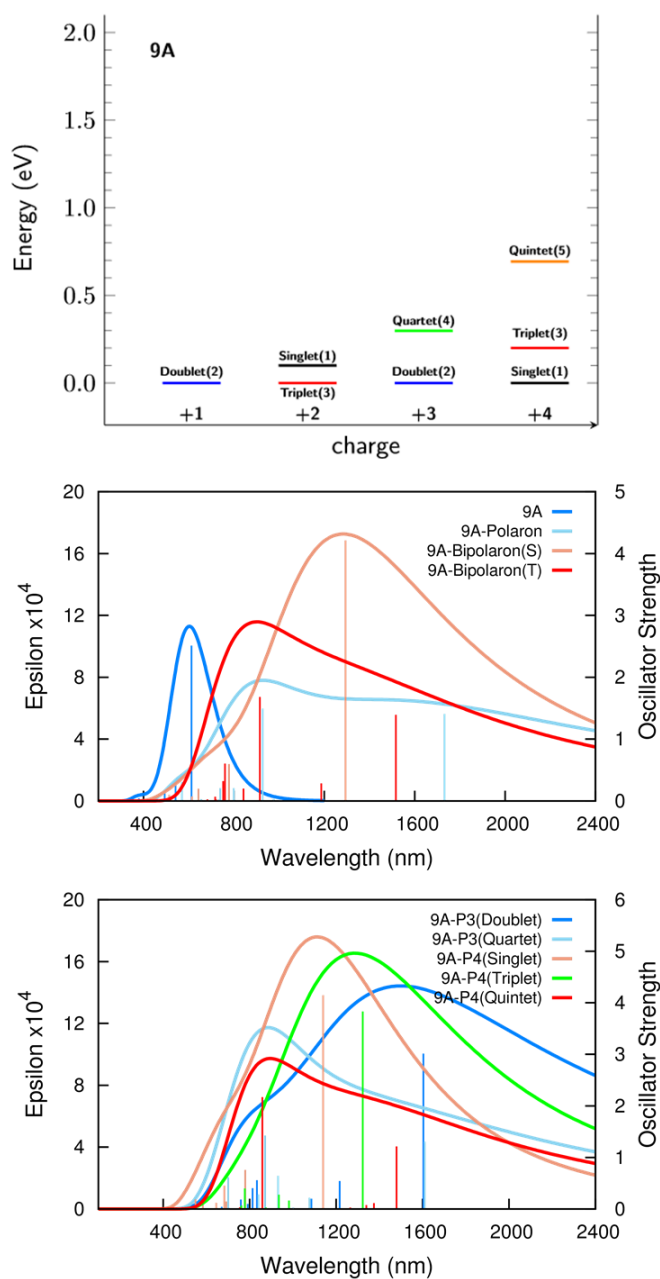


Figure S12. (top) DFT-determined energies of select spin states as a function of oxidation, and (middle, bottom) TDDFT simulated optical absorption profiles [via Gaussian convolution using a FWHM=0.3 eV] for select spin states for $n = 9$ as determined at the OT- ω B97X-D/6-31G(d,p) level of theory.

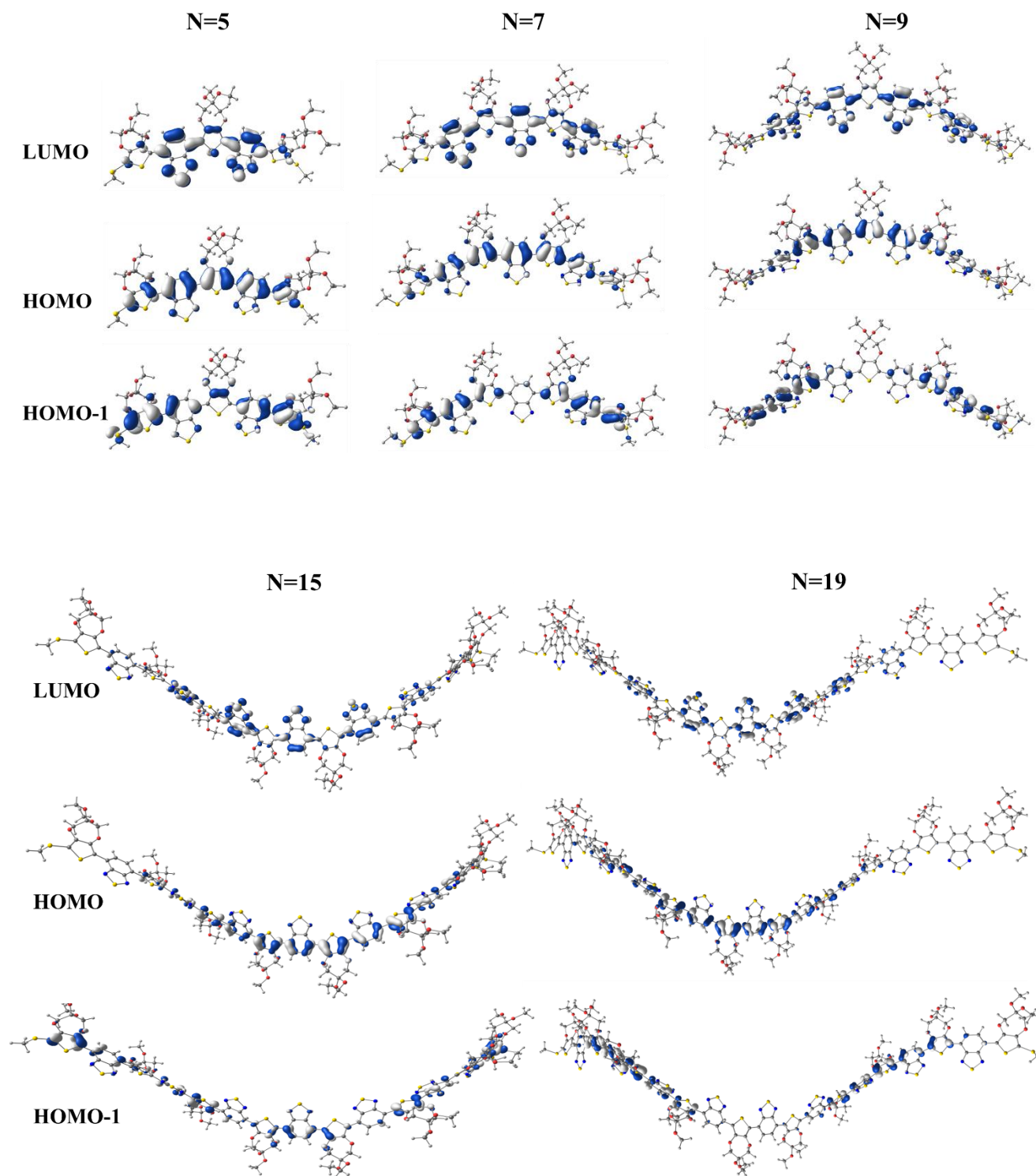


Figure S13: LUMO, HOMO, and HOMO-1 orbitals of $n=5, 7, 9, 15,$ and 19 .

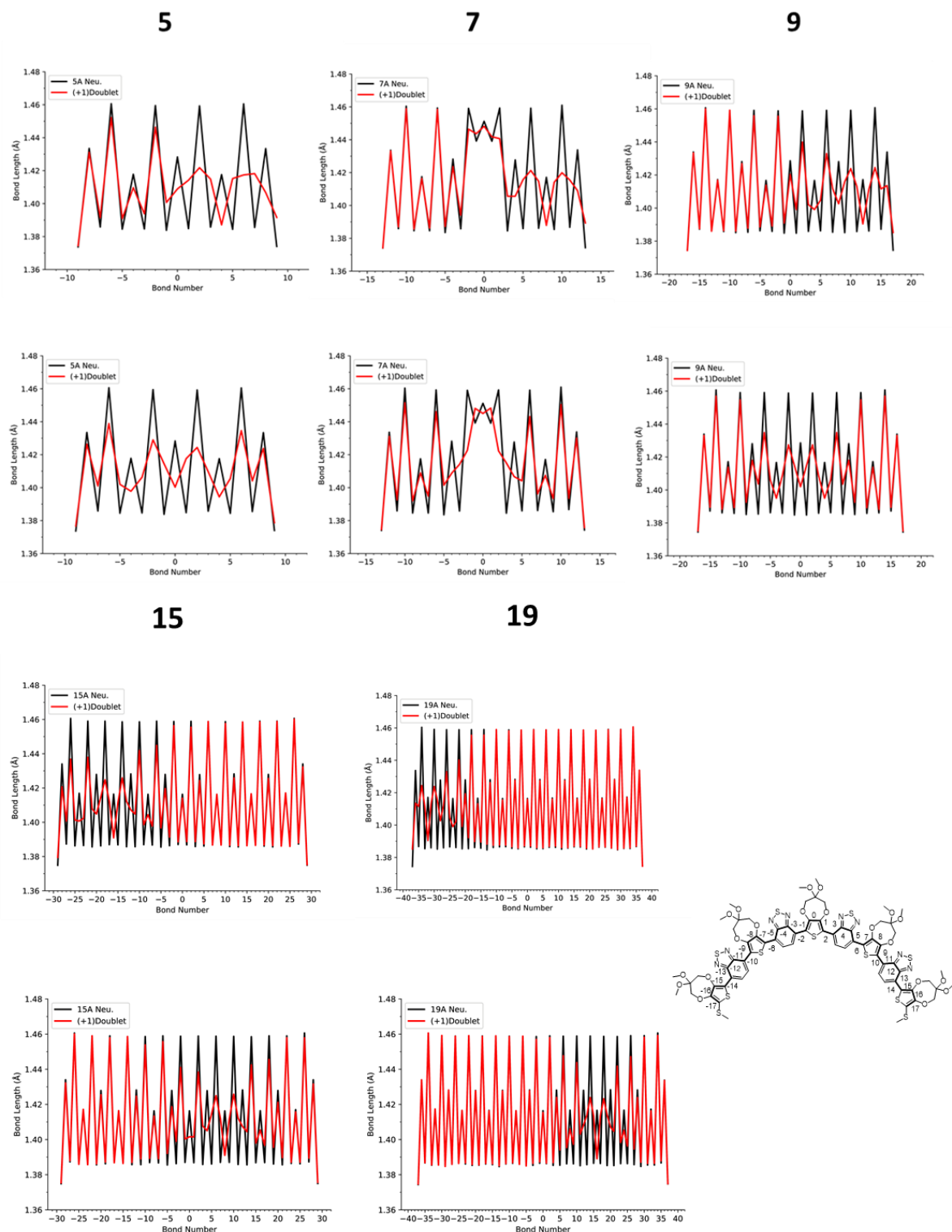
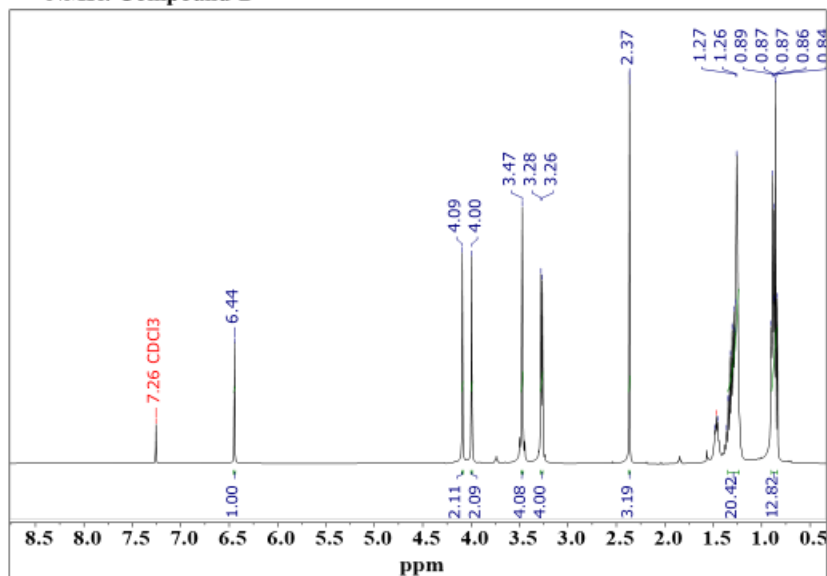
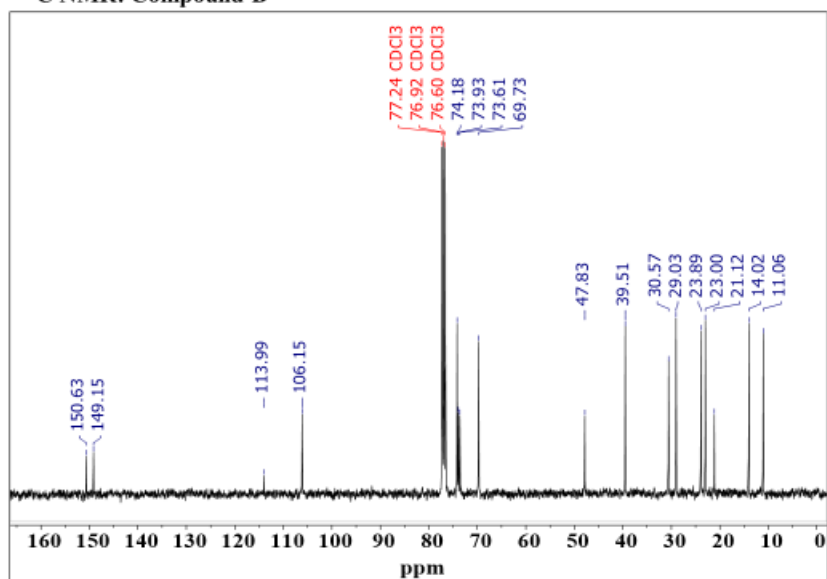


Figure S14. Bond lengths across the C-C π -conjugated backbones of $n=5, 7, 9, 15,$ and 19 for the neutral (black) and radical-cation (red) states as determined at the $\text{OT-}\omega\text{B97X-D/6-31G(d,p)}$ level of theory. Note that for each oligomer, the top image is for the symmetry-broken solution (obtained by twisting the methylthiol group as described in the main text), while the bottom is for the symmetric geometric orientation. The bond numbering scheme for $n=9$ is provided as an example.

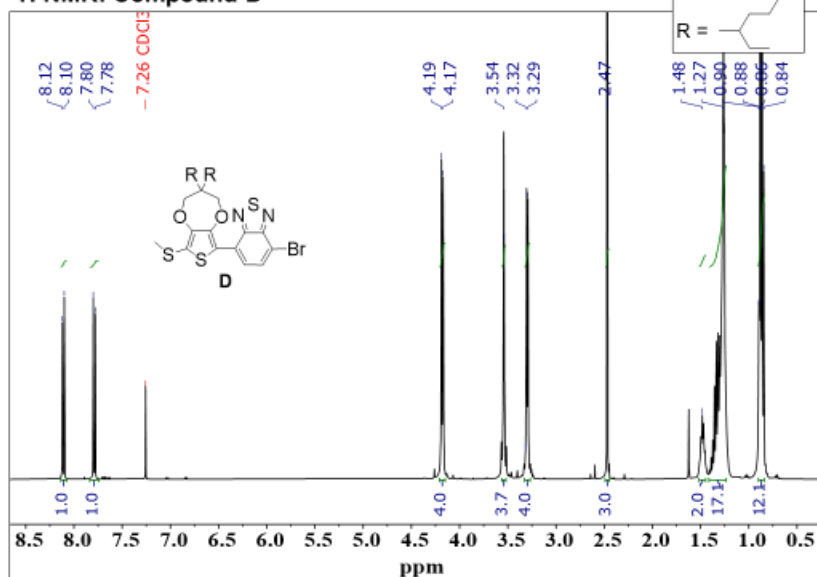
Nuclear Magnetic Resonance (NMR) Spectra

¹H NMR: Compound B

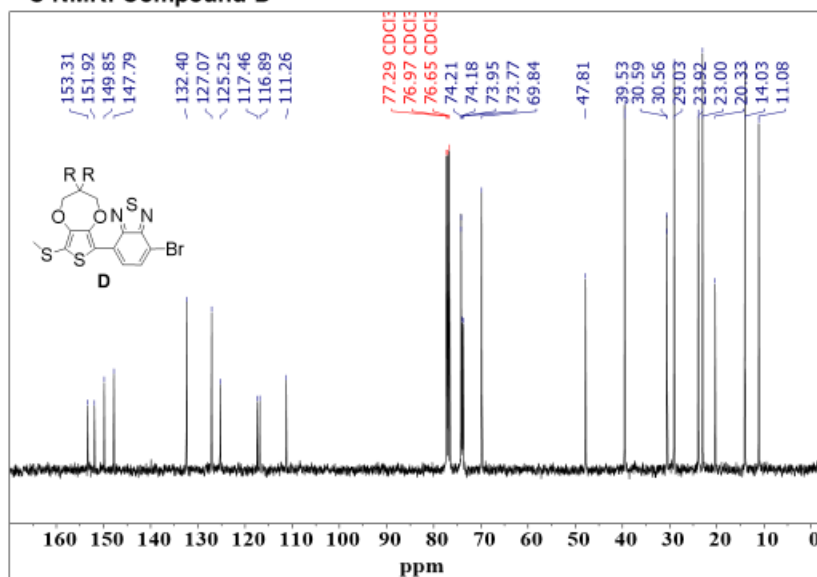
3,3-bis(((2-ethylhexyl)oxy)methyl)-6-(methylthio)-3,4-dihydro-2H-thieno[3,4-b][1,4]dioxepine (¹H NMR, CDCl₃, 300MHz)

¹³C NMR: Compound B

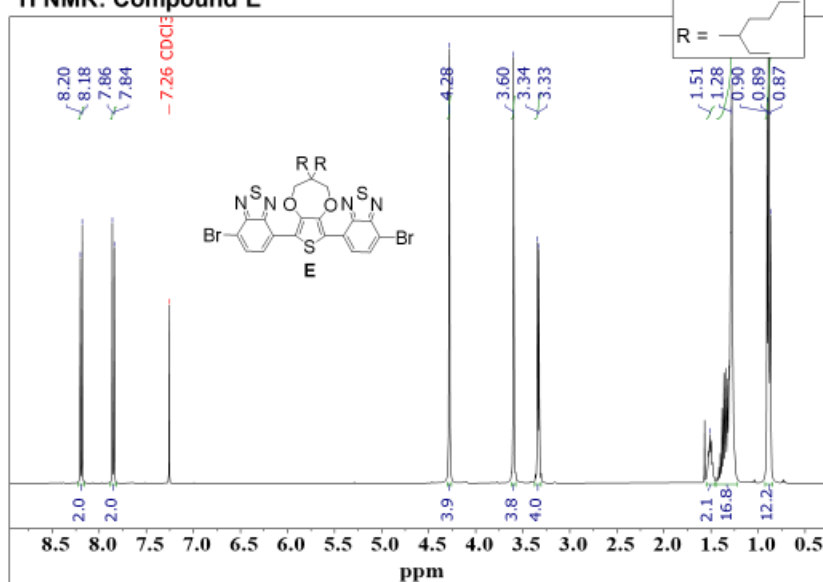
3,3-bis(((2-ethylhexyl)oxy)methyl)-6-(methylthio)-3,4-dihydro-2H-thieno[3,4-b][1,4]dioxepine (¹³C NMR, CDCl₃, 101MHz)

¹H NMR: Compound D

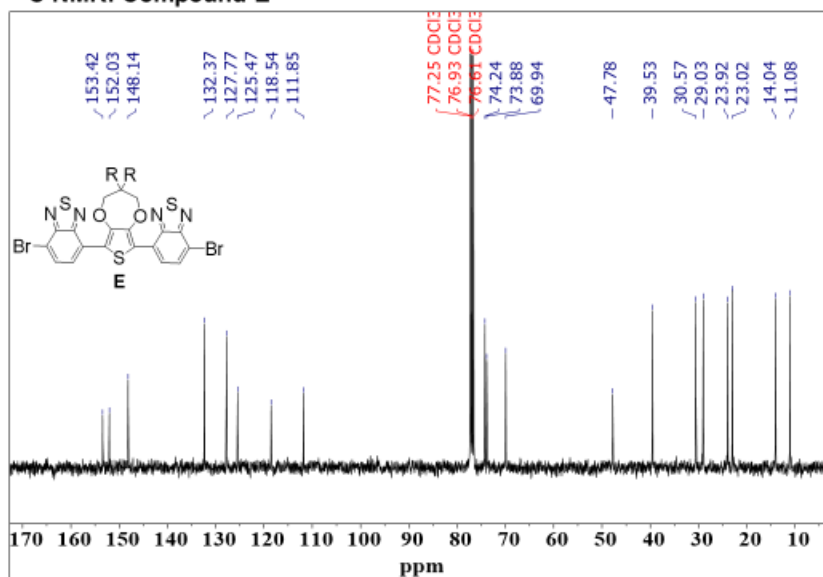
4-(3,3-bis(((2-ethylhexyl)oxy)methyl)-8-(methylthio)-3,4-dihydro-2H-thieno[3,4-b][1,4]dioxepin-6-yl)-7-bromobenzo[c][1,2,5]thiadiazole (¹H NMR, CDCl₃, 400MHz)

¹³C NMR: Compound D

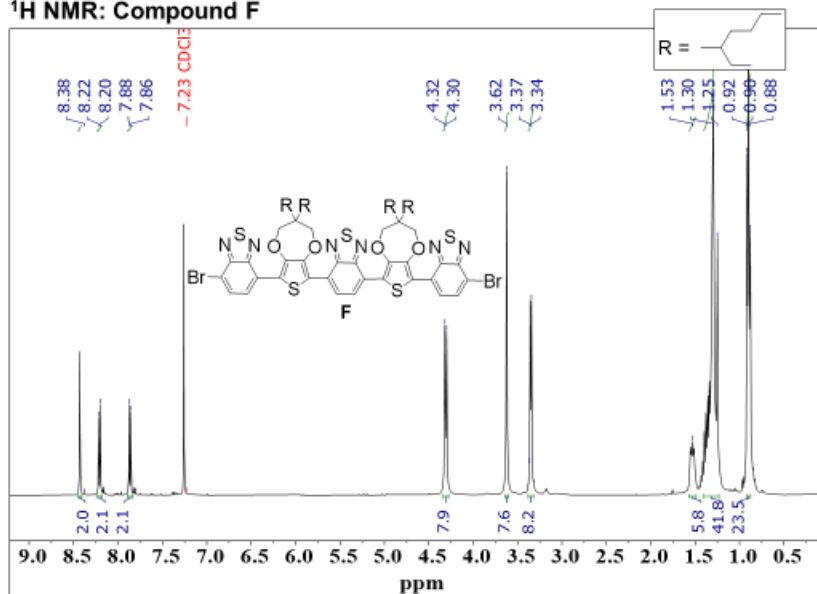
4-(3,3-bis(((2-ethylhexyl)oxy)methyl)-8-(methylthio)-3,4-dihydro-2H-thieno[3,4-b][1,4]dioxepin-6-yl)-7-bromobenzo[c][1,2,5]thiadiazole (¹³C NMR, CDCl₃, 101MHz)

¹H NMR: Compound E

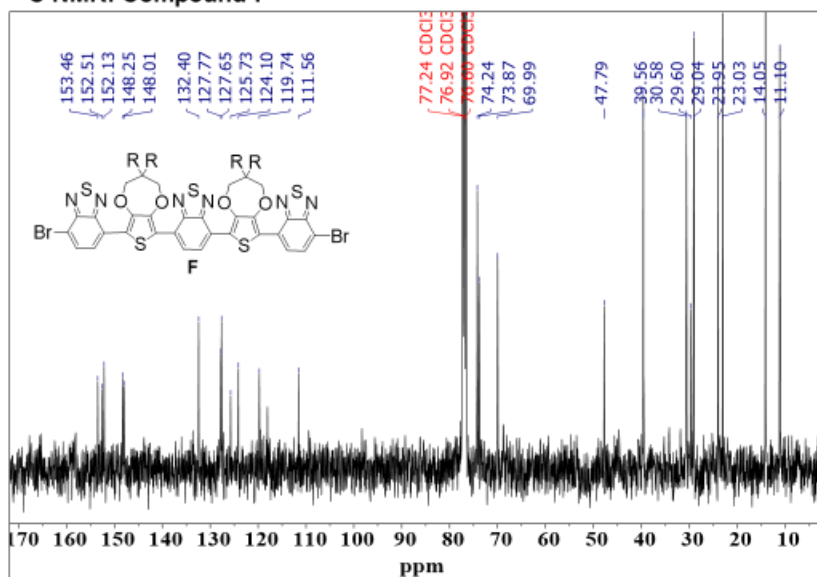
7,7'-((3,3-bis(((2-ethylhexyl)oxy)methyl)-3,4-dihydro-2H-thieno[3,4-b][1,4]dioxepine-6,8-diyl)bis(4-bromobenzo[c][1,2,5]thiadiazole) (¹H NMR, CDCl₃, 400MHz)

¹³C NMR: Compound E

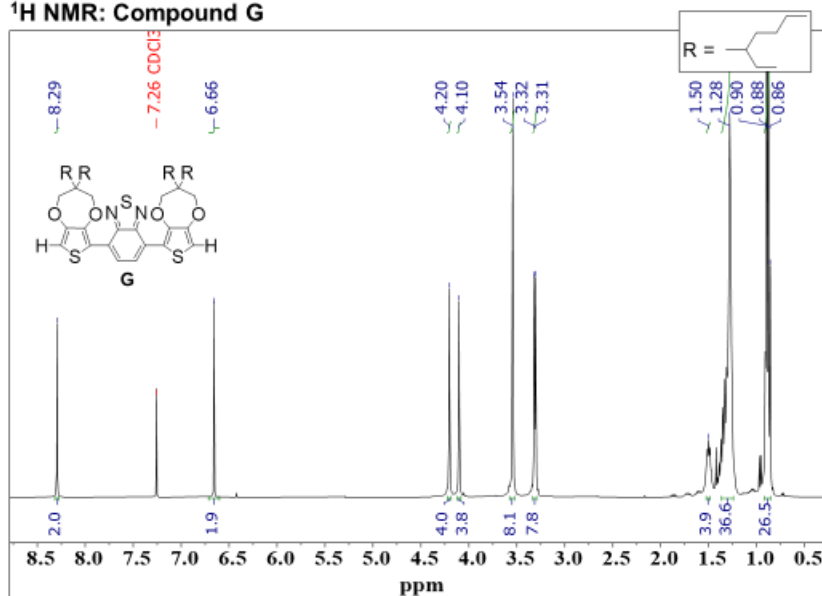
7,7'-((3,3-bis(((2-ethylhexyl)oxy)methyl)-3,4-dihydro-2H-thieno[3,4-b][1,4]dioxepine-6,8-diyl)bis(4-bromobenzo[c][1,2,5]thiadiazole) (¹³C NMR, CDCl₃, 101MHz)

¹H NMR: Compound F

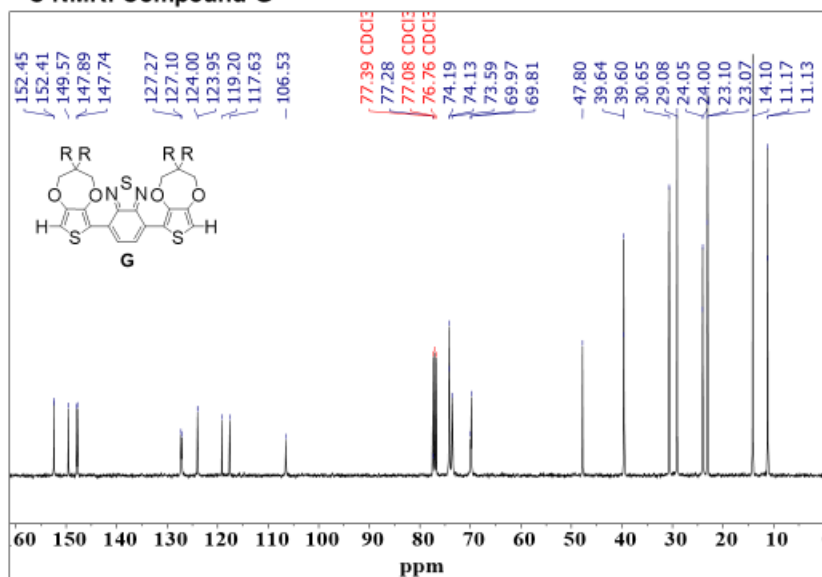
4,7-bis(8-(7-bromobenzo[c][1,2,5]thiadiazol-4-yl)-3,3-bis(((2-ethylhexyl)oxy)methyl)-3,4-dihydro-2H-thieno[3,4-b][1,4]dioxepin-6-yl)benzo[c][1,2,5]thiadiazole (¹H NMR, CDCl₃, 400MHz)

¹³C NMR: Compound F

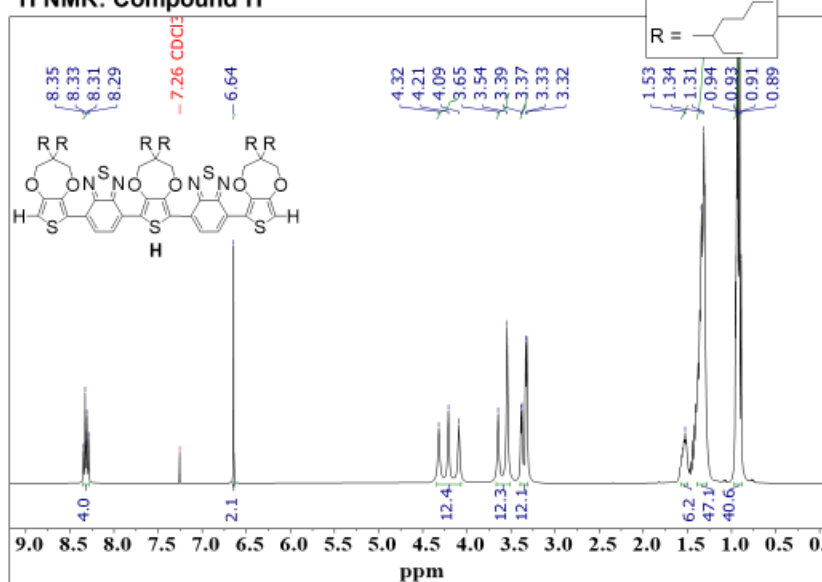
4,7-bis(8-(7-bromobenzo[c][1,2,5]thiadiazol-4-yl)-3,3-bis(((2-ethylhexyl)oxy)methyl)-3,4-dihydro-2H-thieno[3,4-b][1,4]dioxepin-6-yl)benzo[c][1,2,5]thiadiazole (¹³C NMR, CDCl₃, 101MHz)

¹H NMR: Compound G

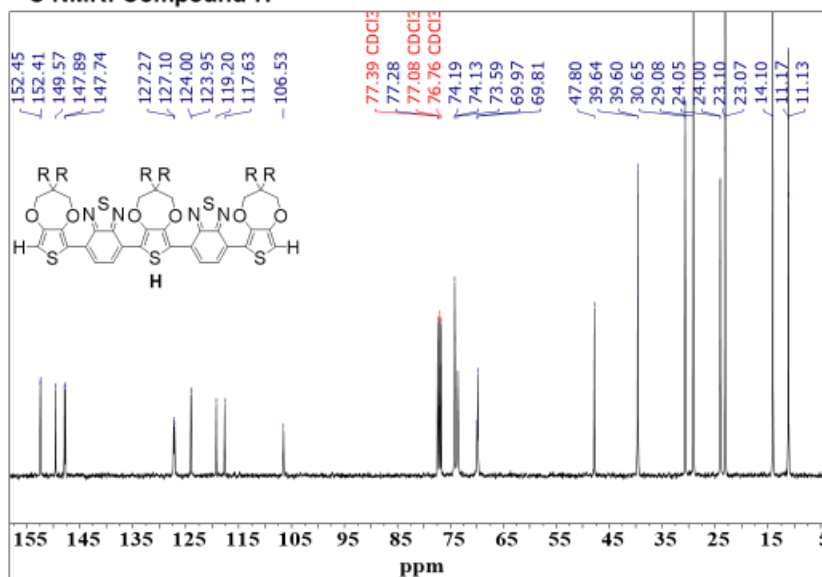
4,7-bis(3,3-bis(((2-ethylhexyl)oxy)methyl)-3,4-dihydro-2H-thieno[3,4-b][1,4]dioxepin-6-yl)benzo[c][1,2,5]thiadiazole (¹H NMR, CDCl₃, 400MHz)

¹³C NMR: Compound G

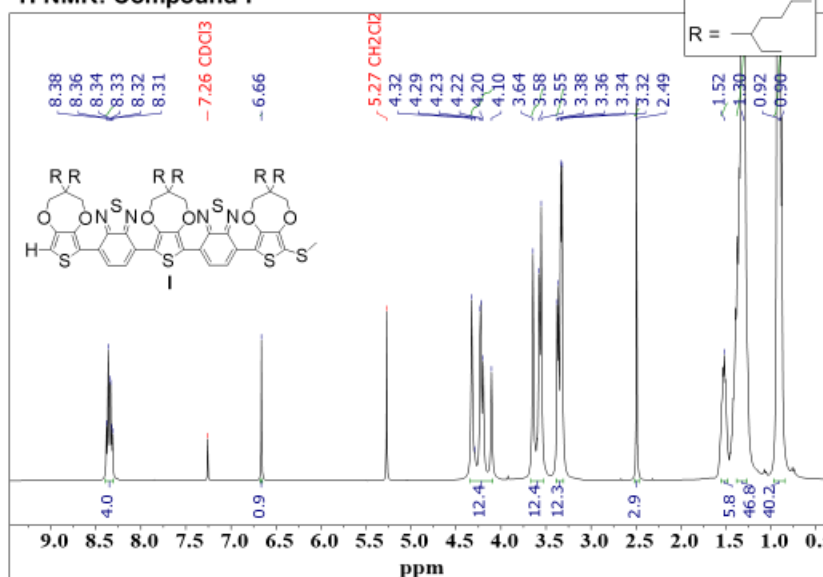
4,7-bis(3,3-bis(((2-ethylhexyl)oxy)methyl)-3,4-dihydro-2H-thieno[3,4-b][1,4]dioxepin-6-yl)benzo[c][1,2,5]thiadiazole (¹³C NMR, CDCl₃, 101MHz)

¹H NMR: Compound H

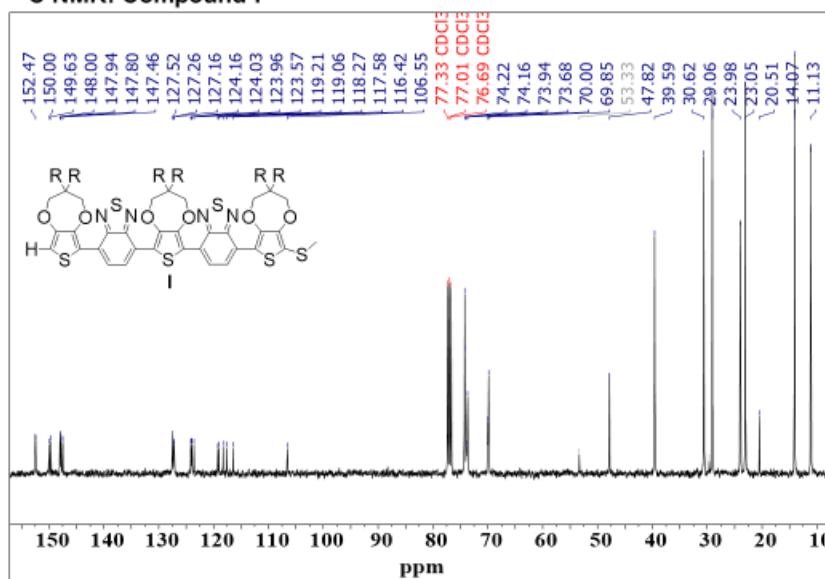
7,7'-bis-((3,3-bis(((2-ethylhexyl)oxy)methyl)-3,4-dihydro-2H-thieno[3,4-b][1,4]dioxepine-6,8-diyl))bis(4-(3,3-bis(((2-ethylhexyl)oxy)methyl)-3,4-dihydro-2H-thieno[3,4-b][1,4]dioxepin-6-yl))benzo[c][1,2,5]thiadiazole) (¹H NMR, CDCl₃, 400MHz)

¹³C NMR: Compound H

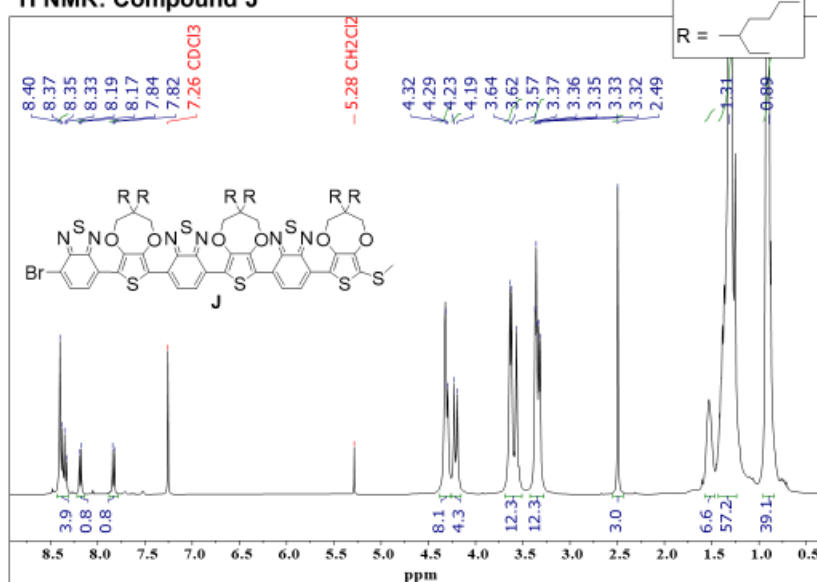
7,7'-bis-((3,3-bis(((2-ethylhexyl)oxy)methyl)-3,4-dihydro-2H-thieno[3,4-b][1,4]dioxepine-6,8-diyl))bis(4-(3,3-bis(((2-ethylhexyl)oxy)methyl)-3,4-dihydro-2H-thieno[3,4-b][1,4]dioxepin-6-yl))benzo[c][1,2,5]thiadiazole) (¹³C NMR, CDCl₃, 101MHz)

¹H NMR: Compound I

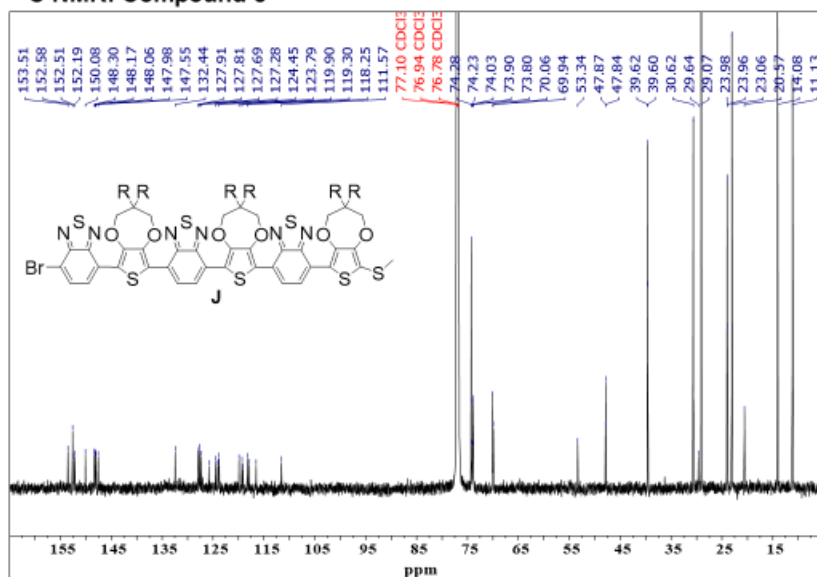
4-(3,3-bis(((2-ethylhexyl)oxy)methyl)-3,4-dihydro-2H-thieno[3,4-b][1,4]dioxepin-6-yl)-7-(8-(7-(3,3-bis(((2-ethylhexyl)oxy)methyl)-8-(methylthio)-3,4-dihydro-2H-thieno[3,4-b][1,4]dioxepin-6-yl)benzo[c][1,2,5]thiadiazol-4-yl)-3,3-bis(((2-ethylhexyl)oxy)methyl)-3,4-dihydro-2H-thieno[3,4-b][1,4]dioxepin-6-yl)benzo[c][1,2,5]thiadiazole (¹H NMR, CDCl₃, 400MHz)

¹³C NMR: Compound I

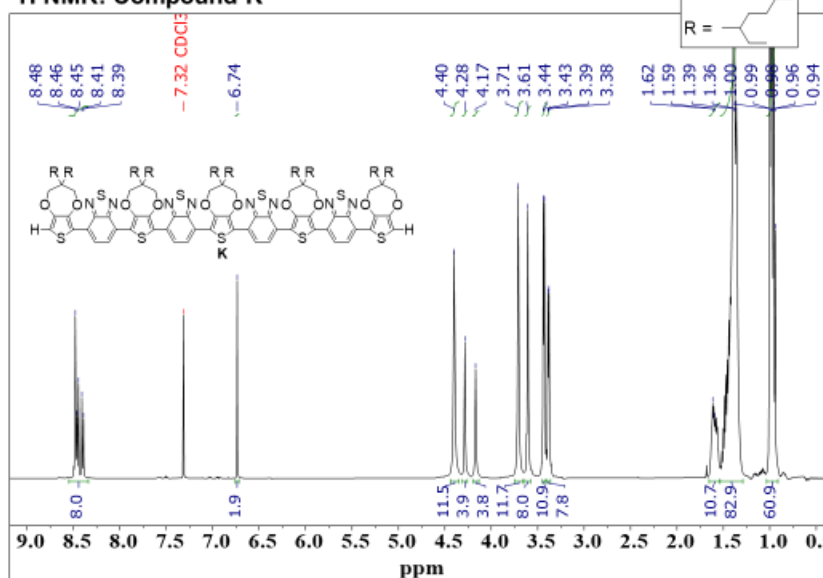
4-(3,3-bis(((2-ethylhexyl)oxy)methyl)-3,4-dihydro-2H-thieno[3,4-b][1,4]dioxepin-6-yl)-7-(8-(7-(3,3-bis(((2-ethylhexyl)oxy)methyl)-8-(methylthio)-3,4-dihydro-2H-thieno[3,4-b][1,4]dioxepin-6-yl)benzo[c][1,2,5]thiadiazol-4-yl)-3,3-bis(((2-ethylhexyl)oxy)methyl)-3,4-dihydro-2H-thieno[3,4-b][1,4]dioxepin-6-yl)benzo[c][1,2,5]thiadiazole (¹³C NMR, CDCl₃, 101MHz)

¹H NMR: Compound J

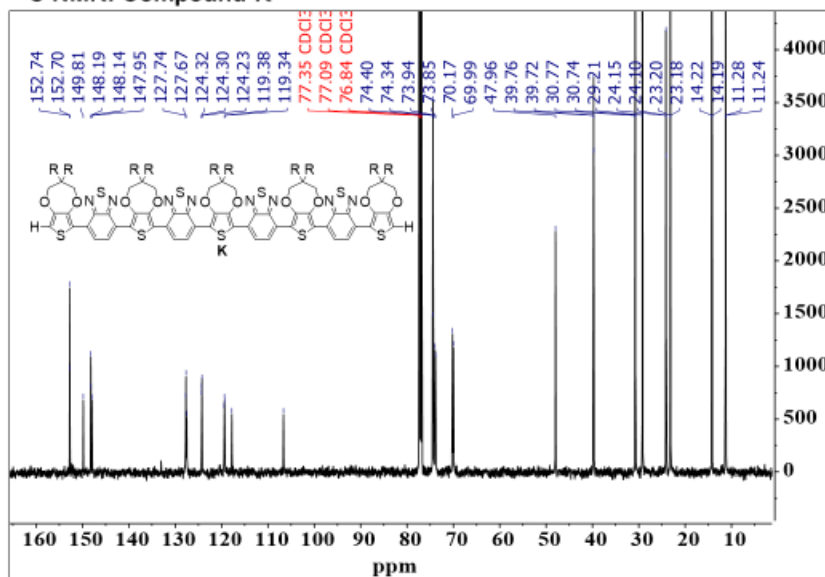
7,7'-bis-((3,3-bis-((2-ethylhexyl)oxy)methyl)-3,4-dihydro-2H-thieno[3,4-b][1,4]dioxepine-6,8-diyl)bis(4-(3,3-bis-((2-ethylhexyl)oxy)methyl)-3,4-dihydro-2H-thieno[3,4-b][1,4]dioxepin-6-yl)benzo[c][1,2,5]thiadiazole (¹H NMR, CDCl₃, 400MHz)

¹³C NMR: Compound J

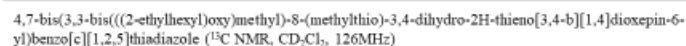
7,7'-bis-((3,3-bis-((2-ethylhexyl)oxy)methyl)-3,4-dihydro-2H-thieno[3,4-b][1,4]dioxepine-6,8-diyl)bis(4-(3,3-bis-((2-ethylhexyl)oxy)methyl)-3,4-dihydro-2H-thieno[3,4-b][1,4]dioxepin-6-yl)benzo[c][1,2,5]thiadiazole (¹³C NMR, CDCl₃, 101MHz)

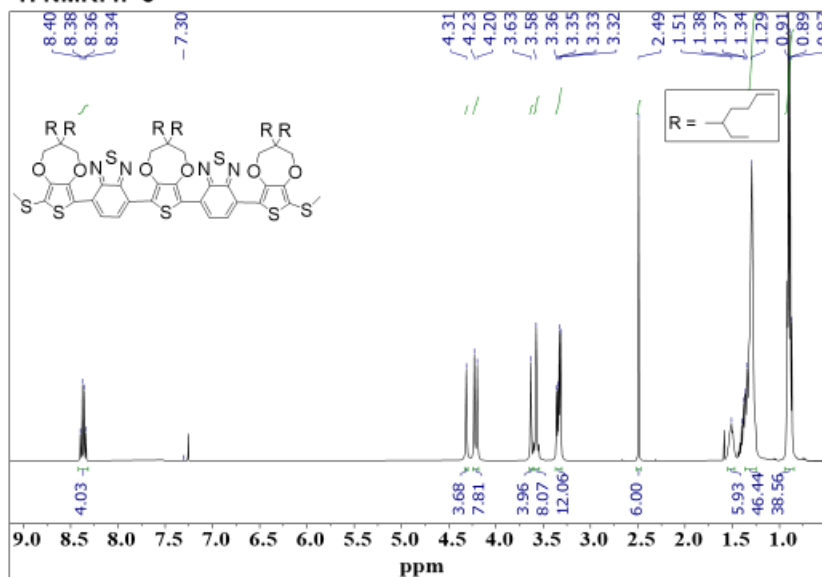
¹H NMR: Compound K

7,7'-(3,3-bis(((2-ethylhexyloxy)methyl)-3,4-dihydro-2H-thieno[3,4-b][1,4]dioxepine-6,8-diyl)bis(4-(8-(7-(3,3-bis(((2-ethylhexyloxy)methyl)-3,4-dihydro-2H-thieno[3,4-b][1,4]dioxepin-6-yl)benzo[c][1,2,5]thiadiazol-4-yl)-3,3-bis(((2-ethylhexyloxy)methyl)-3,4-dihydro-2H-thieno[3,4-b][1,4]dioxepin-6-yl)benzo[c][1,2,5]thiadiazole)) (1H NMR, CDCl₃, 500MHz)

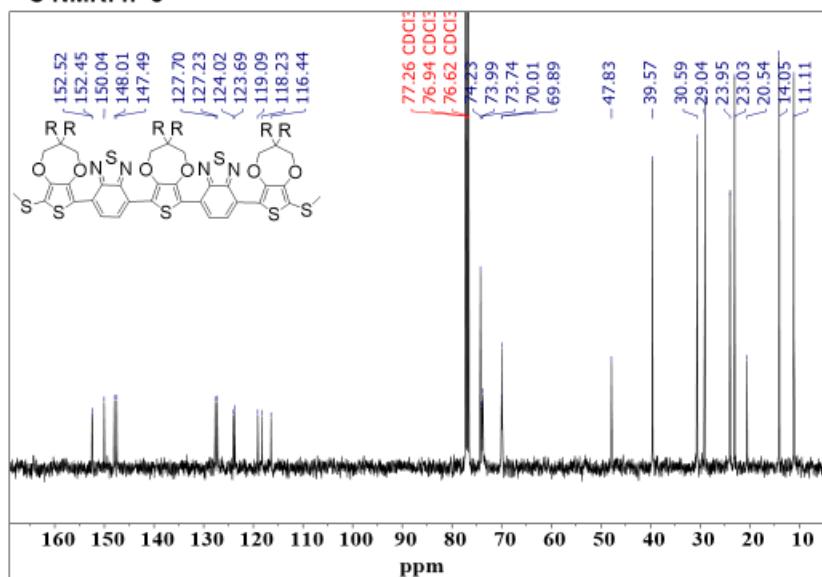
¹³C NMR: Compound K

7,7'-(3,3-bis(((2-ethylhexyloxy)methyl)-3,4-dihydro-2H-thieno[3,4-b][1,4]dioxepine-6,8-diyl)bis(4-(8-(7-(3,3-bis(((2-ethylhexyloxy)methyl)-3,4-dihydro-2H-thieno[3,4-b][1,4]dioxepin-6-yl)benzo[c][1,2,5]thiadiazol-4-yl)-3,3-bis(((2-ethylhexyloxy)methyl)-3,4-dihydro-2H-thieno[3,4-b][1,4]dioxepin-6-yl)benzo[c][1,2,5]thiadiazole)) (13C NMR, CDCl₃, 126MHz)

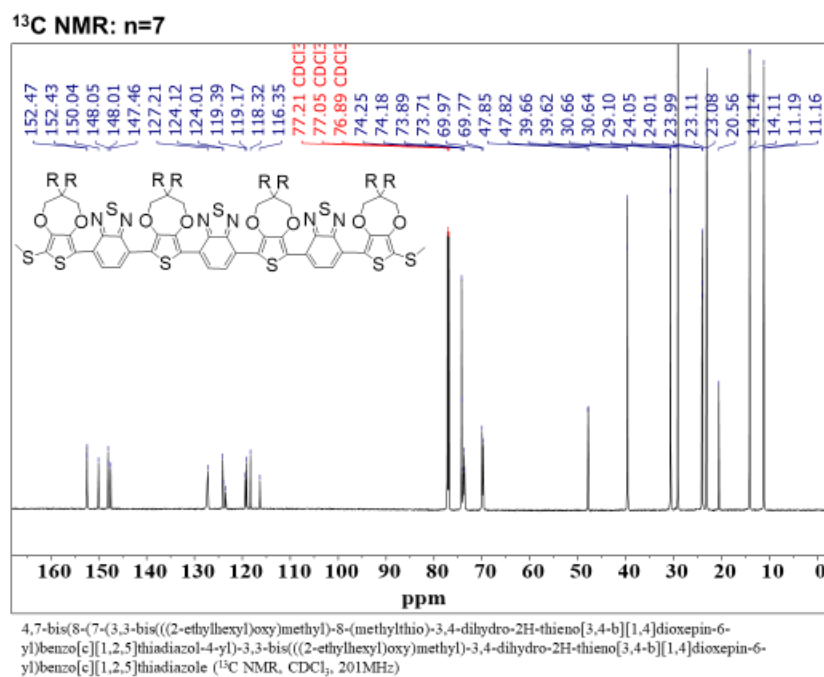


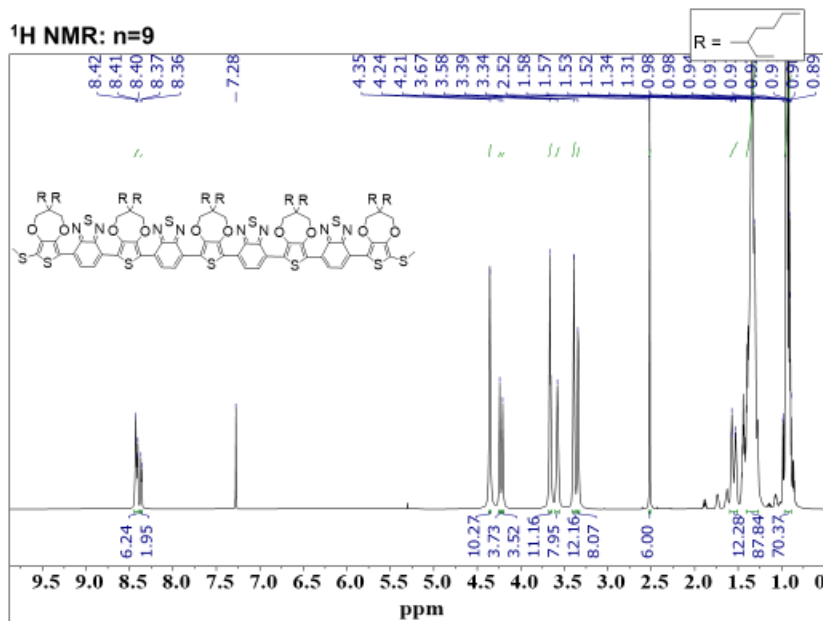
¹H NMR: n=5

7,7'-(3,3-bis(((2-ethylhexyl)oxy)methyl)-3,4-dihydro-2H-thieno[3,4-b][1,4]dioxepine-6,8-diyl)bis(4-(3,3-bis(((2-ethylhexyl)oxy)methyl)-8-(methylthio)-3,4-dihydro-2H-thieno[3,4-b][1,4]dioxepin-6-yl)benzo[c][1,2,5]thiadiazole) (¹H NMR, CDCl₃, 400MHz)

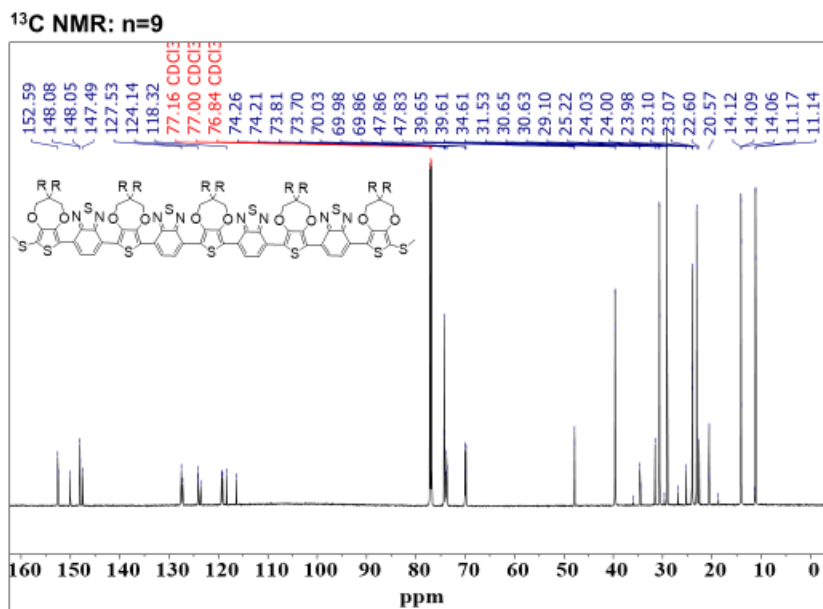
¹³C NMR: n=5

7,7'-(3,3-bis(((2-ethylhexyl)oxy)methyl)-3,4-dihydro-2H-thieno[3,4-b][1,4]dioxepine-6,8-diyl)bis(4-(3,3-bis(((2-ethylhexyl)oxy)methyl)-8-(methylthio)-3,4-dihydro-2H-thieno[3,4-b][1,4]dioxepin-6-yl)benzo[c][1,2,5]thiadiazole) (¹³C NMR, CDCl₃, 101MHz)

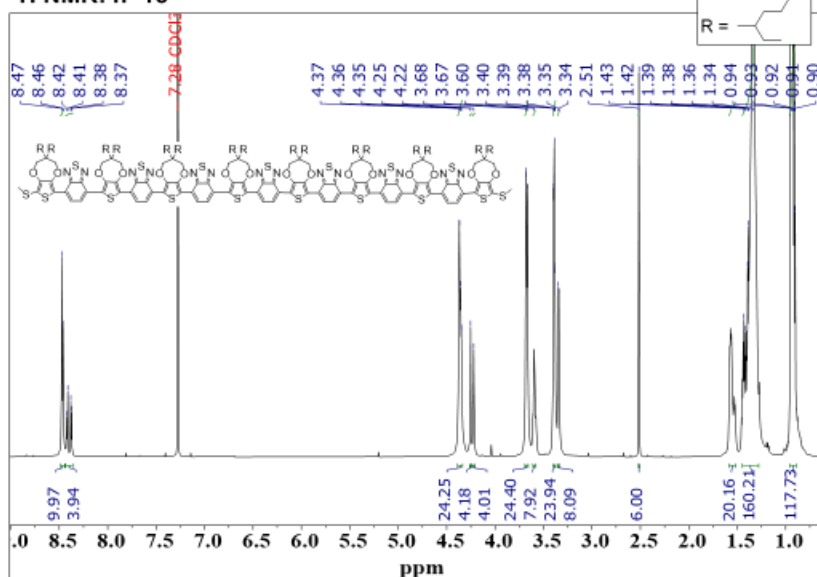




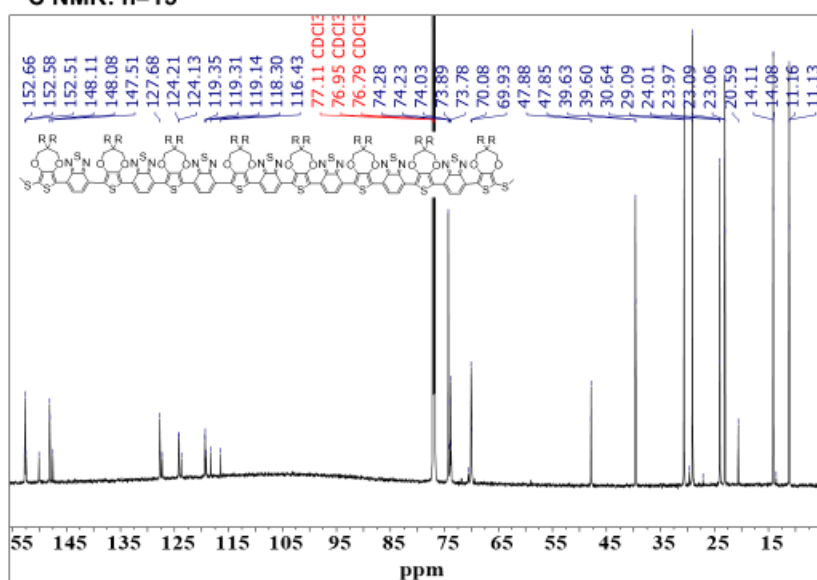
7,7'-(3,3-bis(((2-ethylhexyl)oxy)methyl)-3,4-dihydro-2H-thieno[3,4-b][1,4]dioxepine-6,8-diyl)bis(4-(8-(7-(3,3-bis(((2-ethylhexyl)oxy)methyl)-8-(methylthio)-3,4-dihydro-2H-thieno[3,4-b][1,4]dioxepin-6-yl)benzo[c][1,2,5]thiadiazol-4-yl)-3,3-bis(((2-ethylhexyl)oxy)methyl)-3,4-dihydro-2H-thieno[3,4-b][1,4]dioxepin-6-yl)benzo[c][1,2,5]thiadiazole) (¹H NMR, CDCl₃, 800MHz)



7,7'-(3,3-bis(((2-ethylhexyl)oxy)methyl)-3,4-dihydro-2H-thieno[3,4-b][1,4]dioxepine-6,8-diyl)bis(4-(8-(7-(3,3-bis(((2-ethylhexyl)oxy)methyl)-8-(methylthio)-3,4-dihydro-2H-thieno[3,4-b][1,4]dioxepin-6-yl)benzo[c][1,2,5]thiadiazol-4-yl)-3,3-bis(((2-ethylhexyl)oxy)methyl)-3,4-dihydro-2H-thieno[3,4-b][1,4]dioxepin-6-yl)benzo[c][1,2,5]thiadiazole) (¹³C NMR, CDCl₃, 201MHz)

¹H NMR: n=15

4,7-bis(8-(7-(8-(7-(3,3-bis(((2-ethylhexyl)oxy)methyl)-8-(methylthio)-3,4-dihydro-2H-thieno[3,4-b][1,4]dioxepin-6-yl)benzo[c][1,2,5]thiadiazol-4-yl)-3,3-bis(((2-ethylhexyl)oxy)methyl)-3,4-dihydro-2H-thieno[3,4-b][1,4]dioxepin-6-yl)benzo[c][1,2,5]thiadiazol-4-yl)-3,3-bis(((2-ethylhexyl)oxy)methyl)-3,4-dihydro-2H-thieno[3,4-b][1,4]dioxepin-6-yl)benzo[c][1,2,5]thiadiazole (¹H NMR, CDCl₃, 800MHz)

¹³C NMR: n=15

4,7-bis(8-(7-(8-(7-(3,3-bis(((2-ethylhexyl)oxy)methyl)-8-(methylthio)-3,4-dihydro-2H-thieno[3,4-b][1,4]dioxepin-6-yl)benzo[c][1,2,5]thiadiazol-4-yl)-3,3-bis(((2-ethylhexyl)oxy)methyl)-3,4-dihydro-2H-thieno[3,4-b][1,4]dioxepin-6-yl)benzo[c][1,2,5]thiadiazol-4-yl)-3,3-bis(((2-ethylhexyl)oxy)methyl)-3,4-dihydro-2H-thieno[3,4-b][1,4]dioxepin-6-yl)benzo[c][1,2,5]thiadiazole (¹³C NMR, CDCl₃, 201MHz)

