Supplementary Information

Experimental Section

Chemicals. 3,4-ethylenedioxythiophene (EDOT) was purchased from Agfa. All other reagents and solvents were purchased from either Aldrich or Fisher Scientific. Acetonitrile and propylene carbonate to be used for electrochemical studies were distilled and dried before use. THF was distilled over K/ benzophenone. The starting material, 3,4-dimethoxythiophene was synthesized as previously reported.[1] The supporting electrolyte tetrabutylammonium perchlorate (TBAP) was recrystallized from hot isopropanol and vacuum-dried prior to use.

Electrochemistry. Electrochemistry was performed in a three-electrode electrochemical cell with a 0.02 cm^2 Pt Button working electrode, and a Pt flag counter electrode. For solutions of propylene carbonate, an $Ag/AgClO_4$ (10 mM in TBAP/PC) reference electrode, purchased from Bioanalytical Systems, Inc., was used, and was calibrated to the ferrocene-ferricinium redox couple. For electrochemistry performed in acetonitrile a silver wire pseudoreference electrode was used and was calibrated, after each experiment to the ferrocene-ferricinium redox couple. Unless otherwise mentioned, a 0.2 M concentration of TBAP was used as the supporting electrolyte. All measurements were made with an EG&G PAR model 273A potentiostat/ galvanostat. All cyclic voltammetric polymer deposition was performed in propylene carbonate at a scan rate of 50 mV/sec.

Optical Measurements. Polymer films were potentiostatically deposited onto transparent indium tin oxide (ITO)/glass anodes to a charge of 50 mC/cm^2. Contact to the ITO was made using conductive Cu tape (1131) purchased from 3M. A Pt wire was used as the counter electrode, and an Ag wire was used as a pseudoreference. Spectra were measured with a Cary 500 UV/vis/near IR spectrophotometer and electrochemically switched with an EG&G PAR model 273A potentiostat/ galvanostat. Digital photographs were taken with a Canon PowerShot A75 digital camera.

X-ray experimental. X-ray data were collected at 173 K on a Siemens SMART PLATFORM equipped with A CCD area detector and a graphite monochromator utilizing MoK_α radiation (λ = 0.71073 Å). Cell parameters were refined using up to 8192 reflections. A full sphere of data (1850 frames) was collected using the ω-scan method (0.3° frame width). The first 50 frames were re-measured at the end of data collection to monitor instrument and crystal stability (maximum correction on I was < 1 %). Absorption corrections by integration were applied based on measured indexed crystal faces. The structure was solved by the Direct Methods in *SHELXTL6,*[2] and refined using full-matrix least squares. The non-H atoms were treated anisotropically, whereas the hydrogen atoms were calculated in ideal positions and were riding on their respective carbon atoms. A total of 282 parameters were refined in the final cycle of refinement using 5124 reflections with $I > 2\sigma(I)$ to yield R_1 and wR_2 of 3.47% and 8.70%, respectively. Refinement was done using F^2. ^1H and ^{13}C NMR spectra were recorded on a Gemini 300 FT-NMR, Mercury 300 Ft-NMR, or a VXR 300 FTNMR. HRMS measurements were performed with a Finnigan MAT 95Q mass spectrometer.

(3-methyl-3,4-dihydro-2H-thieno[3,4-b][1,4]dioxepin-3-yl)methanol[3] (1)

To a 500-mL RB flask outfitted with a magnetic stir bar, condenser, and an argon atmosphere was added 3,4-dimethoxythiophene (2.00 g, 13.9 mmol), 1,1,1-

Tris(hydroxymethyl)ethane (2.50 g, 20.8 mmol), *p*-toluenesulfonic acid hydrate (0.26 g, 1.39 mmol), and toluene (200 mL). The reaction was heated to 100 ^{0}C for 12 hours and the pale green solution was cooled to room temperature, washed twice with deionized water, and concentrated via rotary evaporation. The crude mixture was purified via silica gel flash chromatography (1:1 = Hexanes: Et_2O) to yield 2.47 g (89 %) of a white solid. TLC R_f = 0.22 (Silica, 1:1 = Hexanes:Et_2O); mp 61.8 – 62.1 ^{0}C; ^{1}H NMR (300 MHz, $CDCl_3$): δ 6.48 (s, 2H), 3.91 (dd, 4H, J = 115 Hz, J = 13.7 Hz), 3.75 (s, 2H), 1.68 (t, 1H, J = 6.3 Hz), 0.95 (s, 3H); ^{13}C NMR (75 MHz, $CDCl_3$): δ 157.6, 105.9, 76.7, 66.0, 44.0, 17.2; HRMS (EI): Calcd for $C_9H_{12}O_3S$ ($[M]^+$), 200.0507, found *m/z*, 200.0514; Anal. Calcd for $C_9H_{12}O_3S$: C, 53.98; H, 6.04 %, found: C, 54.07; H, 6.13 %.

3-methyl-3-((5-((3-methyl-3,4-dihydro-2H-thieno[3,4-b][1,4]dioxepin-3-yl)methoxy)pentyloxy)methyl)-3,4-dihydro-2H-thieno[3,4-b][1,4]dioxepine (2)

To a 500-mL RB flask outfitted with a magnetic stir bar and an argon atmosphere was added compound **1** (2.00 g , 9.99 mmol), sodium hydride (60% suspension in mineral oil, 0.42 g, 10.5 mmol), and anhydrous DMF (125 mL). The reaction was stirred at room temperature for 1 hour, where evolution of hydrogen appeared to be finished. To the reaction, 1,5-Bis(*p*-toluenesulfonoxy)pentane (2.01 g, 4.87 mmol) was added and the reaction was stirred for 10 hours. DI water (250 mL) was then added and the reaction was extracted with 3x 100 mL of Et_2O. The organic layers were combined and washed with brine, dried over anhydrous sodium sulfate, and concentrated under vacuum. The crude mixture was purified via silica gel flash chromatography (4:1 = Hexanes: Et_2O) to yield 1.61 g (71%) of a clear oil. TLC R_f = 0.55 (Silica, 4:1 = Hexanes: Et_2O); ^{1}H NMR (300 MHz, $CDCl_3$): δ 6.47 (s, 4H), 3.86 (dd, 8H, J = 99.0 Hz, J = 13.0 Hz), 3.45 (s, 4H), 3.43 (t, 4H, J = 7.0 Hz), 1.61 (p, 4H, J = 7.3 Hz), 1.36 – 1.46 (m, 2H), 0.98 (s, 6H) ; ^{13}C NMR (75 MHz, $CDCl_3$): δ 150.1, 105.7, 77.1, 73.5, 71.9, 43.6, 29.6, 23.0, 17.7; HRMS (EI): Calcd for $C_{23}H_{32}O_6S_2$ ($[M]^+$), 468.1640, found *m/z*, 468.1612; Anal. Calcd for $C_{23}H_{32}O_6S_2$: C, 58.95; H, 6.88 %, found: C, 59.14; H, 7.14 %.

Pentyl Bridge Macrocycle (3)

All glassware was flame-dried prior to use. To a 100-mL round bottom flask equipped with a magnetic stir bar, septum, and an argon atmosphere was added compound **2** (0.48 g, 1.02 mmol), and anhydrous THF (50 mL). The reaction was chilled in a CO_2/acetone bath, and a solution of *n*-Butyllithium (2.5M in hexanes, 1.02 mL) was added drop-wise via syringe. The reaction was stirred for 30 minutes and then warmed to room temperature, during which a white precipitate was seen to form and the solution became yellow. The solution was transferred to a pressure equalizing addition funnel, and its contents were added very slowly (over a period of 30 minutes) to a refluxing mixture of iron (III) acetylacetonate (0.90 g, 2.55 mmol). The reaction was stirred for 30 minutes, cooled to room temperature, concentrated *in vacuo*, and purified via gravity column chromatography on silica gel (2:1 = Petroleum Ether: Et_2O) to yield 72 mg (15%) of a white solid. For x-ray analysis, the solid was recrystallized from $CDCl_3$ via petroleum ether vapor diffusion. TLC R_f = 0.60 (Silica, 2:1 = Petroleum Ether: Ether); mp 128.5 – 129.0 ^{0}C; ^{1}H NMR (300 MHz, $CDCl_3$): δ 6.47 (s, 2H), 4.14 (dd, J = 160 Hz, J = 13 Hz), 3.89 (dd, J = 54 Hz, J = 13 Hz), 3.52 – 3.37 (m, 4H), 3.36 (dd, 4H, J = 111 Hz, J = 10 Hz), 1.52 (m, 4H), 1.26 (m, 2H), 1.11 (s, 6H); ^{13}C NMR (75 MHz, $CDCl_3$): δ 150.6, 146.2, 114.6, 104.7, 77.6, 77.1, 74.2, 71.9, 44.1, 29.8, 25.0, 18.2; HRMS (EI): Calcd for $C_{23}H_{30}O_6S_2$ ($[M]^+$), 466.1484, found *m/z*, 466.1496.

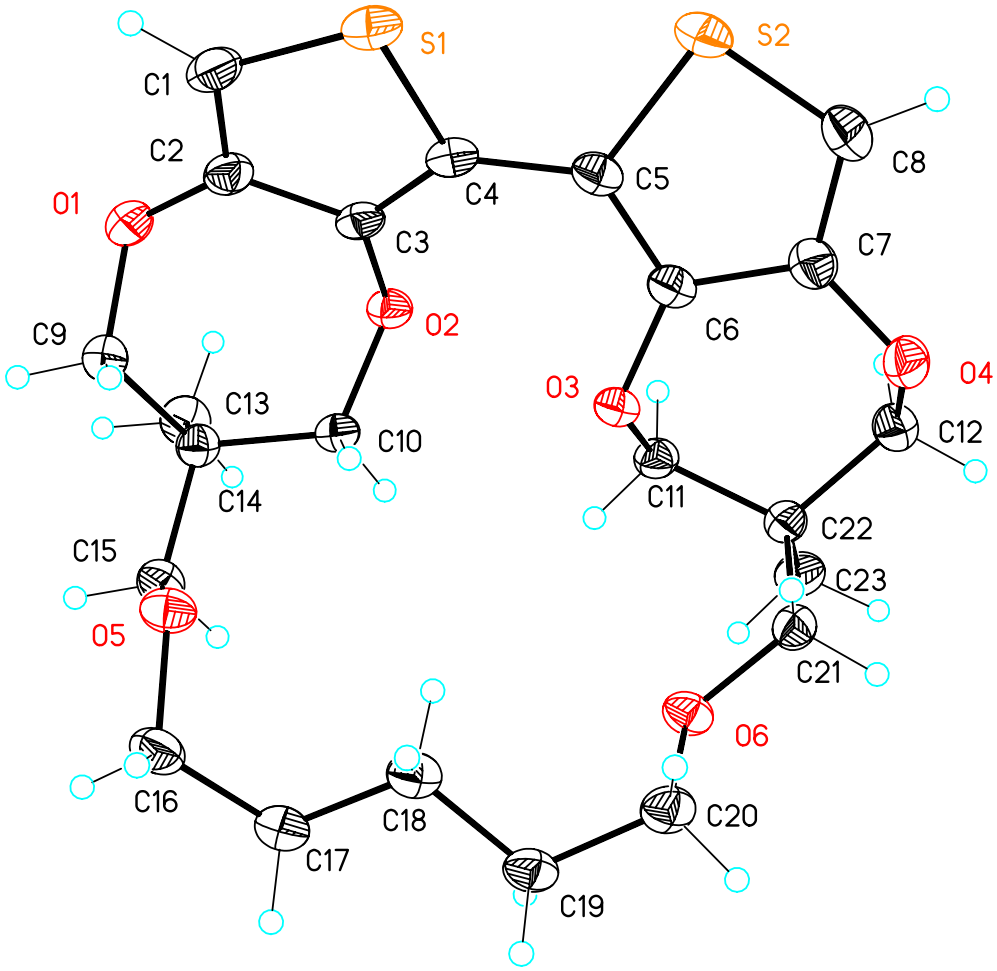

Figure 1: X-ray crystal structure (50% thermal ellipsoids) of compound **3**.

3-Butoxymethyl-3-methyl-3,4-dihydro-2H-thieno[3,4-b][1,4]dioxepine (4)

Into a 50-mL RB flask outfitted with an argon atmosphere, and containing a stir bar, was added compound **1** (1.00 g, 5.00 mmol) and *N*,*N*-Dimethylformamide (25 mL). While solution stirred, NaH (60% suspension in mineral oil, 0.40 g, 10.00 mmol) was slowly added. After 20 minutes of stirring, the flask was chilled in an ice bath, and Toluene-4-sulfonic acid butyl ester (1.37 g, 6.00 mmol) was added. After 1 hour of stirring, NaH suspension (0.25 g, 6.25 mmol) was added, and 2 hours later an additional portion of NaH suspension (0.40 g, 10.00 mmol) was added to the flask. After 30 minutes, an additional portion of Toluene-4-sulfonic acid butyl ester was added to the flask (0.13 g, 0.60 mmol). The reaction stirred for 30 more minutes, and afterwards was quenched with water (100 mL), extracted 3 times with Et_2O, washed once with water, and washed once with brine. Product was purified via flash chromatography on silica gel (9:1 = Hexanes: Et_2O) to yield 0.82 g (63%) of colorless oil TLC R_f = 0.49 (silica gel, 9:1 = Hexanes: Et_2O); ^{1}H NMR (300 MHz, $CDCl_3$): δ 6.47 (s, 2H), 3.86 (dd, 4H, J = 99 Hz, J = 13 Hz), 3.45 (s, 2H), 3.43 (t, 2H, J = 7.3 Hz), 1.54 (p, 2H, J = 7.6 Hz), 1.36 (m, 2H, J = 7.6 Hz), 0.99 (s, 3H), 0.92 (t, 3H, J = 8.0. Hz); ^{13}C NMR (75 MHz, $CDCl_3$): δ 150.1, 105.7, 77.1, 73.5, 71.7, 43.6, 31.9, 19.6, 17.7, 14.1; HRMS (EI): Calcd for $C_{13}H_{20}O_3S$

([M]$^+$), 256.1133, found *m/z*, 256.1125; Anal. Calcd for $C_{13}H_{20}O_3S$: C, 60.91; H, 7.86 %, found: C, 60.93; H, 8.10 %.

3-(butoxymethyl)-6-(3-(butoxymethyl)-3-methyl-3,4-dihydro-2H-thieno[3,4-b][1,4]dioxepin-6-yl)-3-methyl-3,4-dihydro-2H-thieno[3,4-b][1,4]dioxepine (5)

Into a flame-dried 3 neck 100 mL flask outfitted with an argon atmosphere, and equipped with a stir bar, condenser, and 2 stoppers, was added compund **4** (0.328 g, 1.28 mmol) and freshly distilled THF (50 mL). While stirring, the flask was chilled to -78 °C and n-butyllithium (0.66 mL, 1.54 mmol) was added. After 1 hour of stirring, the flask was warmed to room temperature and iron (III) acetylacetonate (0.59 g, 1.66 mmol) was added to the solution. The flask stirred at reflux for 3 hours and was afterwards cooled to room temperature. The product was purified via flash chromatography on silica gel (16:1 = Hexanes: Et_2O) to yield 0.051 g (15 %) of an off-white solid. TLC R_f = 0.16 (silica gel, 16:1 = Hexanes: Et_2O); ^{1}H NMR (see Figures 2 and 3) (300 MHz, $CDCl_3$): δ 6.40 (s, 2H), 3.95 (dd, 4H, J = 105.7 Hz, J = 13.3 Hz), 3.87 (dd, 4H, J = 106.7 Hz, J = 13 Hz), 3.53-3.42 (m, 8H), 1.55 (p, 4H, J = 7.6 Hz), 1.37 (m, 4H, J = 9 Hz), 1.01 (s, 6H), 0.92 (t, 6H, J = 8.3 Hz); ^{13}C NMR (75 MHz, $CDCl_3$): δ 149.5, 145.1, 115.6, 103.3, 77.0, 76.8, 73.3, 71.5, 43.5, 31.6, 19.3, 17.3, 13.9; HRMS (EI): Calcd for $C_{26}H_{38}O_6S_2$ ([M]$^+$), 510.2110, found *m/z*, 510.2109.

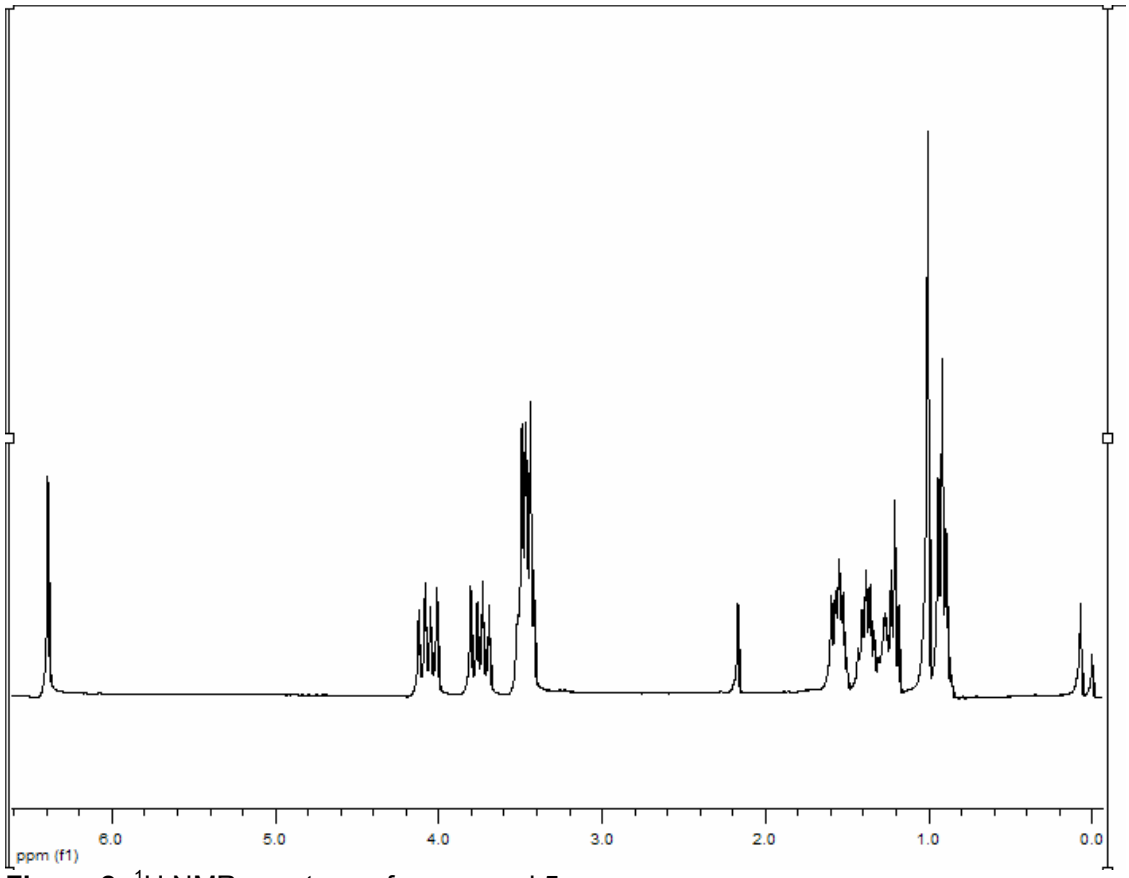

Figure 2: ^{1}H NMR spectrum of compound **5**.

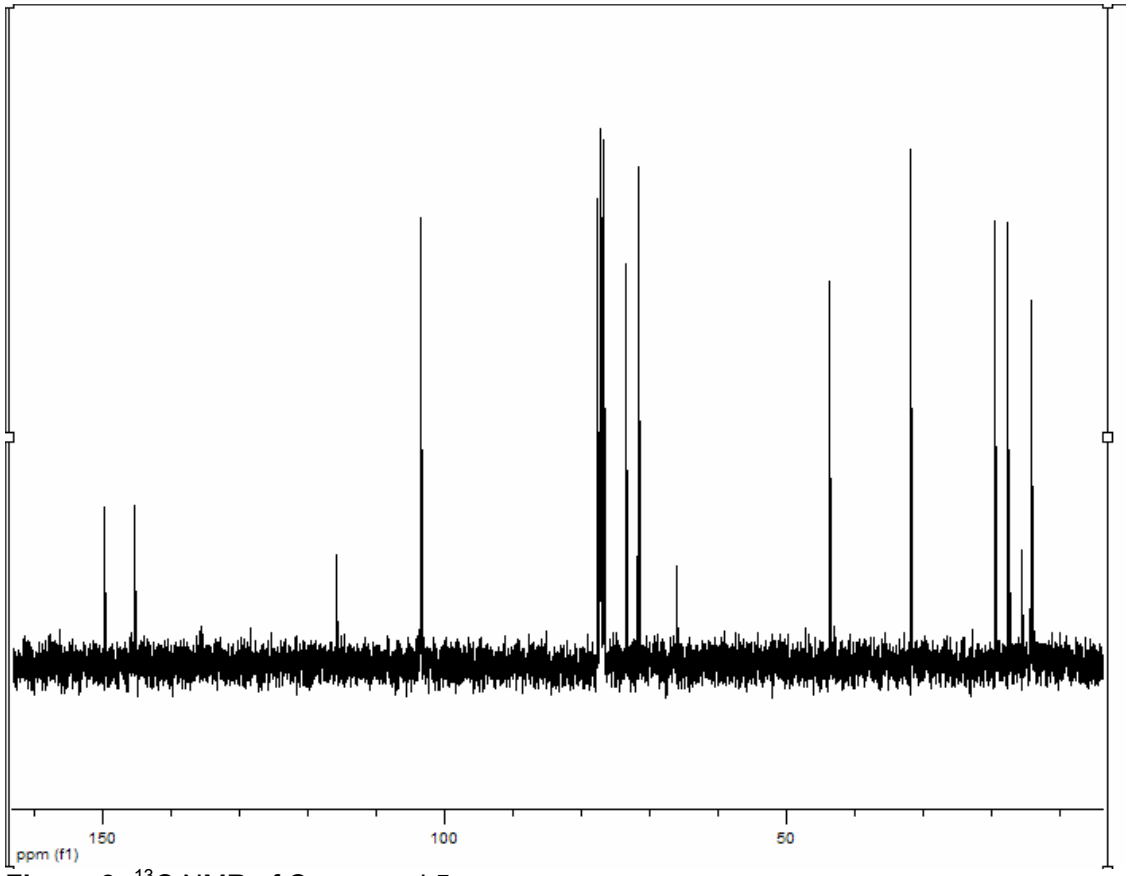

Figure 3: ^{13}C NMR of Compound **5**.

1,5-Bis(*p*-toluenesulfonoxy)pentane

To a 500-mL RB flask outfitted with a magnetic stir bar, addition funnel, and argon atmosphere was added 1,5-pentanediol (10.00 g, 96.0 mmol) and pyridine (20 mL). The flask was cooled to ~0 ^{0}C in an ice bath. A mixture of *p*-toluenesulfonyl chloride (38.44 g, 202 mmol) and pyridine (55 mL) was added to the addition funnel and its contents were added drop-wise over a period of 30 minutes. The reaction was stirred at 0 ^{0}C for two hours, where it became a solid white mass. The mixture was poured into water (400 mL) under vigorous stirring and the resulting white precipitate was vacuum-filtered and recrystallized in hot methanol to yield 30.00 g (76%) of shiny white, flaky crystals. mp = 72.7 – 73.0 ^{0}C; ^{1}H NMR (300 MHz, $CDCl_3$): δ 7.77 (dd, 2H, J = 7.3 Hz, J = 2.0 Hz), 7.35 (dd, 2H, J = 7.3 Hz, J = 2.0 Hz), 3.97 (t, 4H, J = 7.0 Hz), 2.46 (s, 6H), 1.61 (p, 4H, J = 7.6 Hz), 1.40 – 1.32 (m, 2H); ^{13}C NMR (75 MHz, $CDCl_3$): δ 145.1, 133.2, 130.1, 128.1, 70.2, 28.4, 21.9, 21.7; HRMS Calcd. for $C_{19}H_{24}O_6S_2$: 412.1014, Found: 412.1006; Elemental anal. calcd. for $C_{19}H_{24}O_6S_2$: C, 55.32; H, 5.86;, found: C, 55.38; H, 5.75.

Butyl 4-Methylbenzenesulfonate

Into a 100-mL RB flask outfitted with an argon atmosphere, and containing a stir bar was added 1-butanol (5.00 g, 67 mmol) and pyridine (100 mL). The flask was chilled in an ice bath, and after 5 minutes of stirring, p-Toluenesulfonyl chloride (19.30 g, 101 mmol) was added. The solution was stirred for 2 hours and was then poured into a flask of ice

cold 3 M HCl (500 mL). After 10 minutes of vigorous stirring, a thick white precipitate formed. The supernatant liquid was decanted off and the solid melted at room temperature. Product was purified via flash chromatography on silica gel (6:1 = Hexanes: Et_2O) to yield 9.52 g (62%) of a colorless oil. TLC R_f = .2 (silica gel, 6:1 = Hexanes: Et_2O); ^{1}H NMR (300 MHz, $CDCl_3$): δ 7.77 (d, 2H, J = 9.3 Hz), 7.34 (d, 2H, J = 9.3 Hz), 4.02 (t, 2H, J = 7.0 Hz), 2.44 (s, 3H), 1.62 (p, 2H, J = 7.3 Hz), 1.33 (m, 2H, J = 8.0 Hz), 0.85 (t, 3H, J = 8.3 Hz); ^{13}C NMR (75 MHz, $CDCl_3$): δ 144.8, 133.4, 130.0, 128.0, 70.6, 31.0, 21.8, 18.8, 13.5; HRMS (ESI-FTICR-MS): Calcd for $C_{11}H_{16}NaO_3S$ ($[M + Na]^+$), 251.0712, found *m/z*, 251.0705; Anal. Calcd for $C_{11}H_{16}O_3S$: C, 57.87; H, 7.06 %, found: C, 57.60; H, 7.37 %.

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[1] (a) Blockhuys, F.; Rousseau, B.; Peeters, L. D.; Van Alsenoy, C.; Geise, H. J.; Kataeva, O. N.; Van der Veken, B.; Herrebout, W. A. *J. Phys. Chem. A* **2000**, *104*, 8983-8988. (b) Gronowitz, S.; Moses, P.; Hakansson, R. *Ark. Kemi* **1960**, *16*, 267. (c) Langeveld-Voss, B. M. W.; Janssen, R. A. J.; Meijer, E. W. *J. Molec. Struct.* **2000**, *521*, 285-301. (d) Lawesson, S. *Acta Chem. Scand*. **1956**, *10*, 1020. (e) Tour, J. M.; Wu, R. *Macromolecules* **1992**, *25*, 1901-1907.

[2] *SHELXTL6* (2000). Bruker-AXS, Madison, Wisconsin, USA.

[3] Mishra, S. P.; Sahoo, R.; Ambade, A. V.; Contractor, A. Q.; Kumar, A. *J. Mater. Chem.* **2004**, *14*, 1896