Supporting Information

Synthesis of Poly(3,4-propylenedioxythiophene) (PProDOT) Analogues via Mechanochemical Oxidative Polymerization

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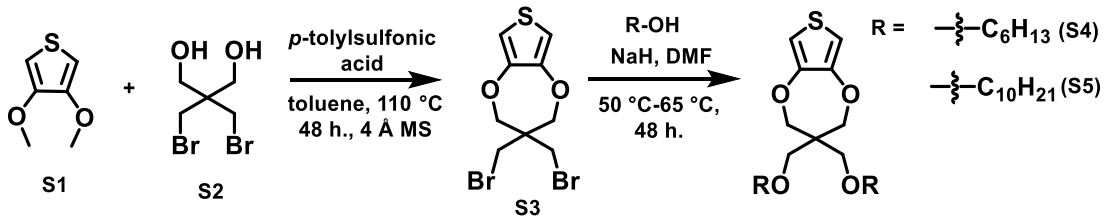
1. General.

All reactions were performed under dry N_2 in oven dried glassware, unless otherwise noted. All reagents and solvents were purchased and used as received from commercial sources: Fisher Scientific, VWR, Ambeed, and Sigma Aldrich. Mechanochemical polymerizations were performed using a Retsch MM-400 mixer mill using 10 mL zirconia lined jars (cat.# 014620234) and 10 mm diameter zirconia grinding balls (cat.# 053680094) under ambient conditions. Ethyl acetate (EtOAc) used for the solvent based oxidative polymerization was dried by storing over activated 3 Å molecular sieves overnight.

NMR were recorded at 25 °C using $CDCl_3$ on a Bruker Avance III 400 MHz. All spectra were referenced to $CHCl_3$ (7.26 ppm). Number average molecular weight (M_n) and polydispersity ($Đ$) were determined by gel-permeation chromatography (GPC) using an EcoSEC Elite HLC-8420GPC with HPLC grade $CHCl_3$ (40 °C) as the eluent. The instrument was calibrated vs. polystyrene standards (589−2,110,000 g/mol). GPC samples were prepared by first dissolving in HPLC grade chloroform at a concentration of 1 mg ml^{-1}, heating at 40 °C until fully dissolved, cooling to room temperature, and filtering through a 0.2 μm PTFE filter prior to measurement. Molecular weight distributions were calculated using Tosoh SECview software where the entire peak range was included in the calculation following baseline correction.

2. Monomer Synthesis.



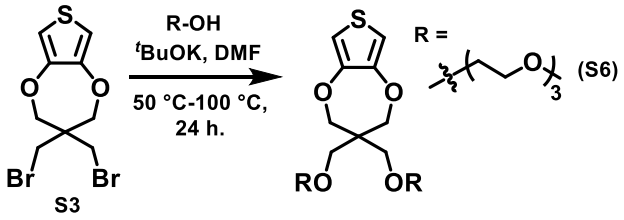
Scheme S1. Synthesis of monomers S4-S5.

3,3-Bis(bromomethyl)-3,4-dihydro-2H-thieno[3,4-b][1,4]- dioxepine (S3). S1 (2.0 g, 13.9 mmol, 1 equiv.), **S2** (7.28 g, 27.8 mmol, 2 equiv.), and p-toluenesulfonic acid (478 mg, 2.78 mmol, 0.2 equiv.) were dissolved in 140 mL toluene and heated for 48 hours at 110 °C under a nitrogen atmosphere. A solvent bulb filled with 4 Å molecular sieves was placed on-top of the condenser during the assembly of the reaction apparatus. The reaction mixture was then cooled to room temperature. The toluene was removed via rotovap, DI-H_2O(50 mL) was added and it was extracted with diethyl ether (3x50 mL). The organic portion was washed with brine three times. Then it was dried over $MgSO_4$ with activated charcoal. After stirring for 20 min. the crude reaction mixture was filtered and concentrated via rotovap. The crude material was then purified by column chromatography on silica gel using 40% DCM/hexanes (v:v) to afford a white crystalline product in 49% yield. ^{1}H-NMR (400 MHz, $CDCl_3$): δ (ppm) 6.48 (s, 2H), 4.09 (s, 4H), 3.60 (s, 4H). Consistent with literature.[1]

3,3-Bis(1-hexyloxymethyl)-3,4-dihydro-2H-thieno-[3,4-b][1,4]dioxepine (S4). A 100 mL oven dried round-bottom flask filled equipped with a stirbar was cooled under nitrogen and vacuum-backfilled with nitrogen 3x. NaH (419.52 mg,17.52 mmol, 6 equiv.) was dissolved in 58 mL of anhydrous DMF, and 1-Hexanol (895 mg, 8.76 mmol, 3 equiv.) was then slowly added to the flask. The mixture was then heated at 50 °C for 16 h. **S3** (1 g**,** 2.9 mmol, 1 equiv.) was then quickly added in a single portion and the reaction temperature increased to 65 °C. After an additional 24 h of heating, the flask was cooled to room temperature and DI-H_2O (50 mL) was added. The crude mixture was then extracted three times with diethyl ether (50 mL). The organic layer was then washed three times with brine, dried over magnesium sulfate, and the solvent was removed by

rotary evaporation. The resulting crude product was purified by column chromatography using 30% DCM/hexanes (v:v) to afford a yellow oil in 75% yield. ^{1}H-NMR (400 MHz, $CDCl_3$): δ (ppm) 6.44 (s, 2H), 4.01 (s, 4H), 3.48 (s, 4H), 3.40 (t, J = 8.0 Hz , 4H), 1.54 (m, 4H), 1.2-1.52 (m, 12H), 0.89(t, J = 4.0 Hz, 6H). ^{13}C-NMR (100 MHz, $CDCl_3$): δ (ppm) 149.7, 105.1, 73.8, 71.7, 69.6, 47.2, 31.7, 29.6, 25.5, 22.6, 14.1. Consistent with literature.[2]

3,3-Bis(1-decyloxymethyl)-3,4-dihydro-2H-thieno-[3,4-b][1,4]dioxepine (S5). Identical to the synthesis of **S4** above, but with 1-decanol(1.38 g, 8.76 mmol, 3 equiv.) in place of 1-hexanol to afford a pale yellow oil in 53% yield. ^{1}H-NMR (400 MHz, $CDCl_3$): δ (ppm) 6.44 (s, 2H), 4.01(s, 4H), 3.48 (s, 4H), 3.40 (t, J = 4.0 Hz, 4H), 1.57-1.50 (m, 4H), 1.26 (m, 28H), 0.88 (t, J = 8.0 Hz, 6H). ^{13}C NMR): δ (ppm) 149.7, 105.0, 73.8, 71.7, 69.6, 47.7, 31.9, 29.64, 29.59, 29.53, 29.47, 26.1, 26.4, 22.7, 14.1.



Scheme S2. Synthesis of monomer S6.

2-(2-(2-Methoxyethoxy)ethoxy)ethoxymethyl-3,4-dihydro-2*H*-thieno[3,4-*b*][1,4]dioxepine (S6). In an oven dried 50 mL three-necked round bottom flask, potassium tert-butoxide (984.17 mg, 8.77mmol, 6 equiv.), 2-(2-methoxyethoxy)ethan-1-ol (959.03 mg,5.84 mmol, 4 equiv.) and 19 mL of anhydrous dimethylformamide (DMF) were added and stirred under nitrogen for 1.5 hours at 50 °C. Then compound **S3** (500 mg, 1.46 mmol, 1 equiv.) was added and the reaction mixture was heated at 100 °C for 24 hours after which it was cooled to room temperature. The cooled mixture was extracted 3x with 50 mL diethyl ether and the combined organic layer was subsequently washed with DI-H_2O (3x20mL), brine and dried over $MgSO_4$ and activated charcoal. The crude reaction mixture was then concentrated under reduced pressure. The residue was then purified by column chromatography on silica gel using 3% Methanol/DCM (v:v) to obtain a pale-brown oil (52%).^{1}H-NMR (400 MHz, $CDCl_3$): δ (ppm) δ 6.44 (s, 2H), 4.01 (s, 4H), 3.65–3.59 (m,

20H), 3.56-3.53 (m, 8H), 3.37 (s, 6H). ^{13}C-NMR (100 MHz, $CDCl_3$) δ 149.7, 105.2, 73.5, 71.9, 71.1, 70.65, 70.61, 70.5, 70.3, 70.1, 59.0, 47.7. Consistent with literature.[1]

3. Monomer NMR.

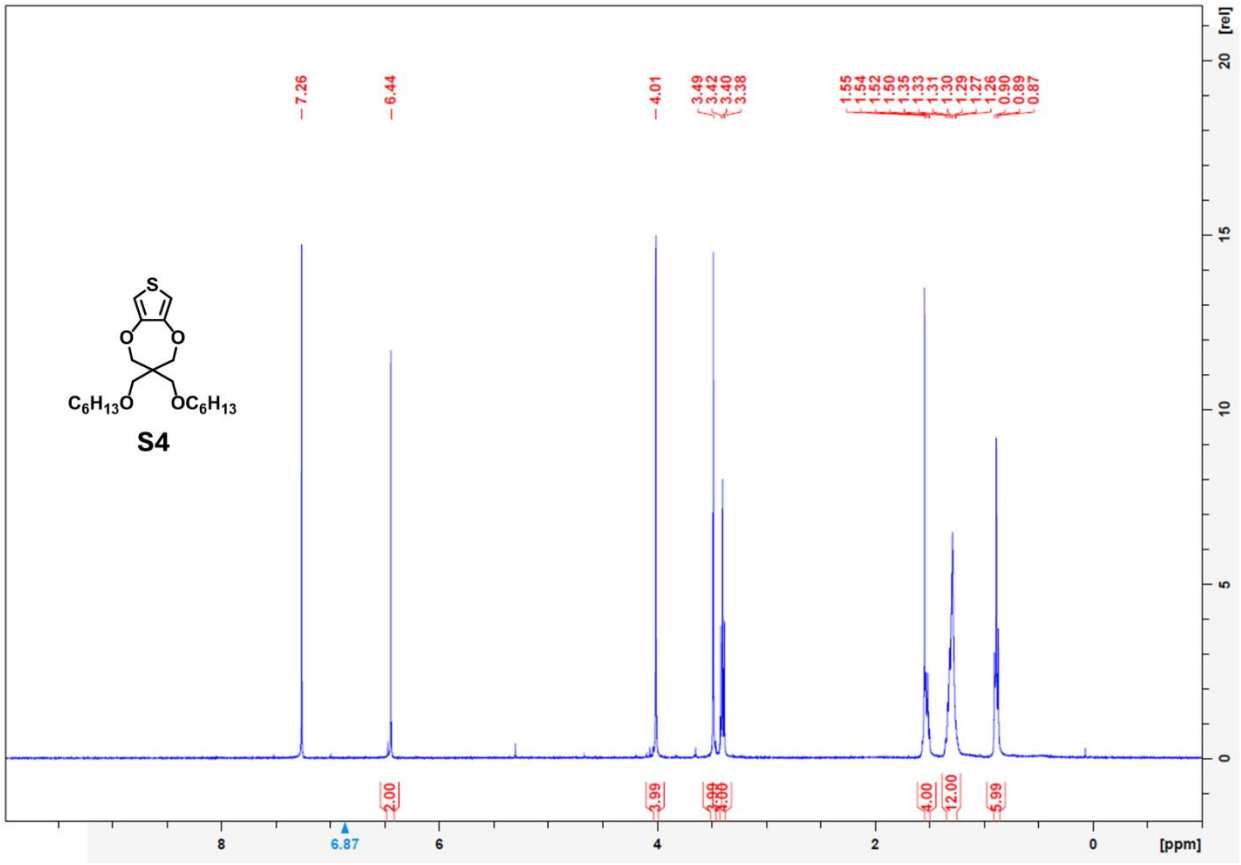


Figure S1. ^{1}H-NMR of S4 collected in $CDCl_3$ at 25 °C and 400 MHz.

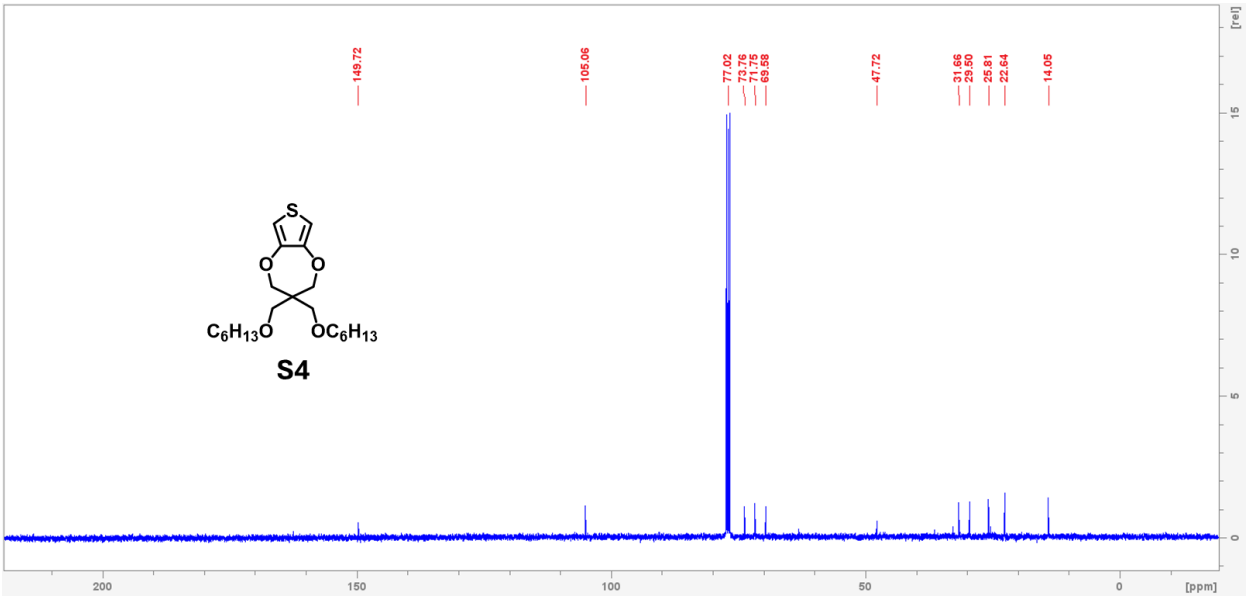


Figure S2. ^{13}C-NMR of S4 collected in $CDCl_3$ at 25 °C and 100 MHz.

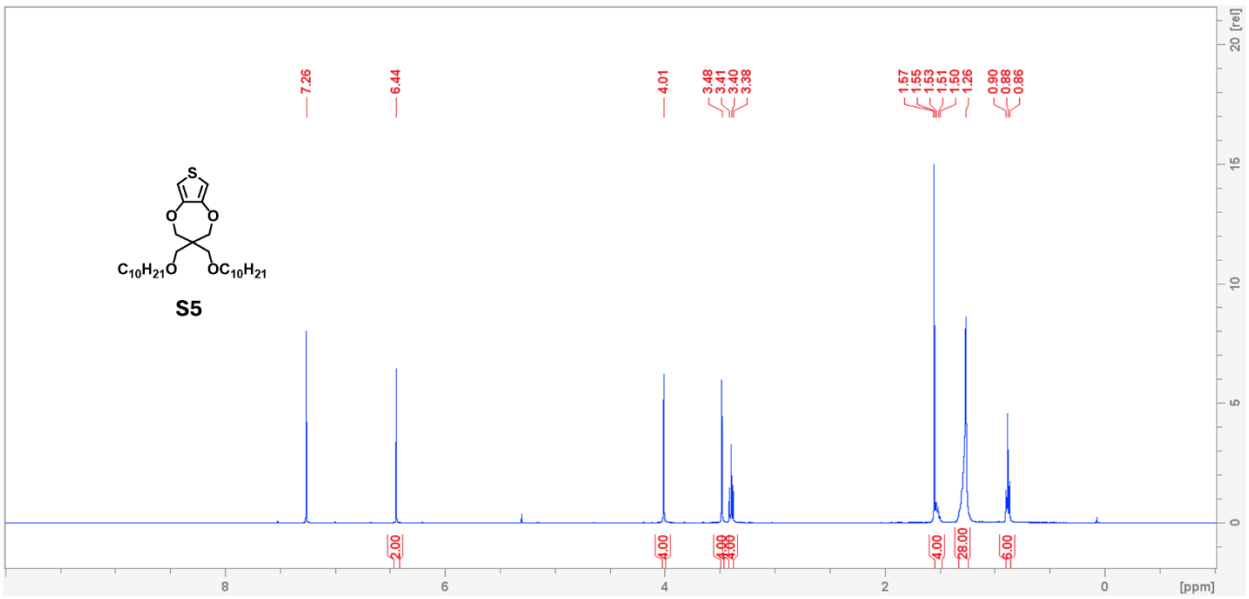


Figure S3. ^{1}H-NMR of S5 collected in $CDCl_3$ at 25 °C and 400 MHz.

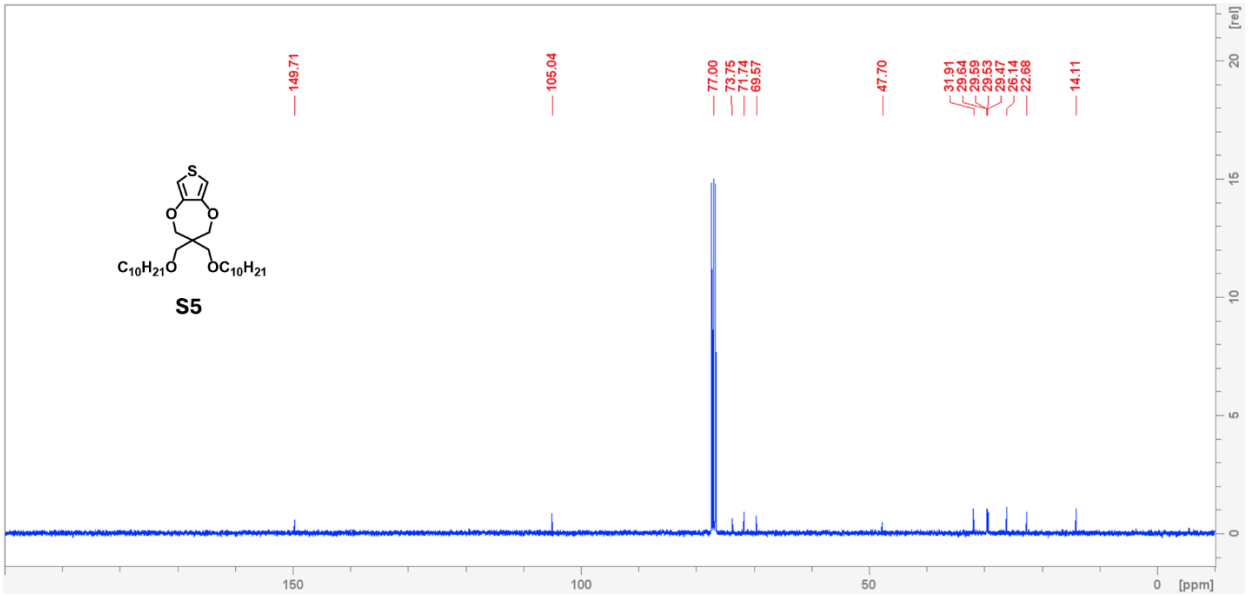


Figure S4. ^{13}C-NMR of S5 collected in $CDCl_3$ at 25 °C and 100 MHz.

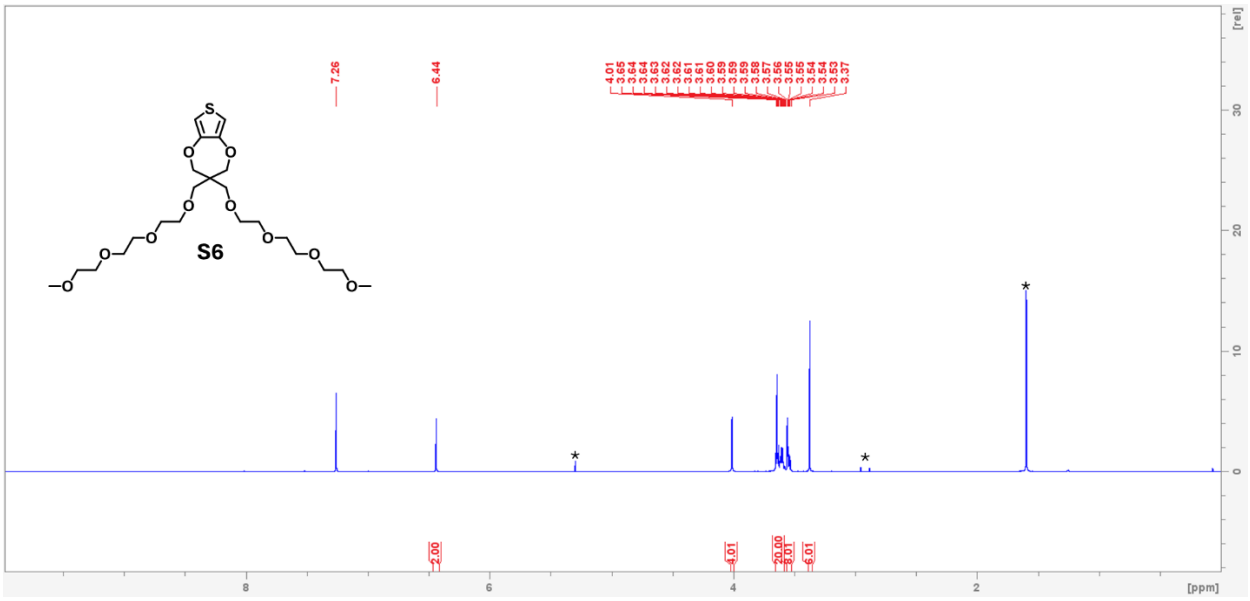


Figure S5. ^{1}H-NMR of S6 collected in $CDCl_3$ at 25 °C and 400 MHz. *Denotes trace solvent and H_2O from $CDCl_3$ supply.

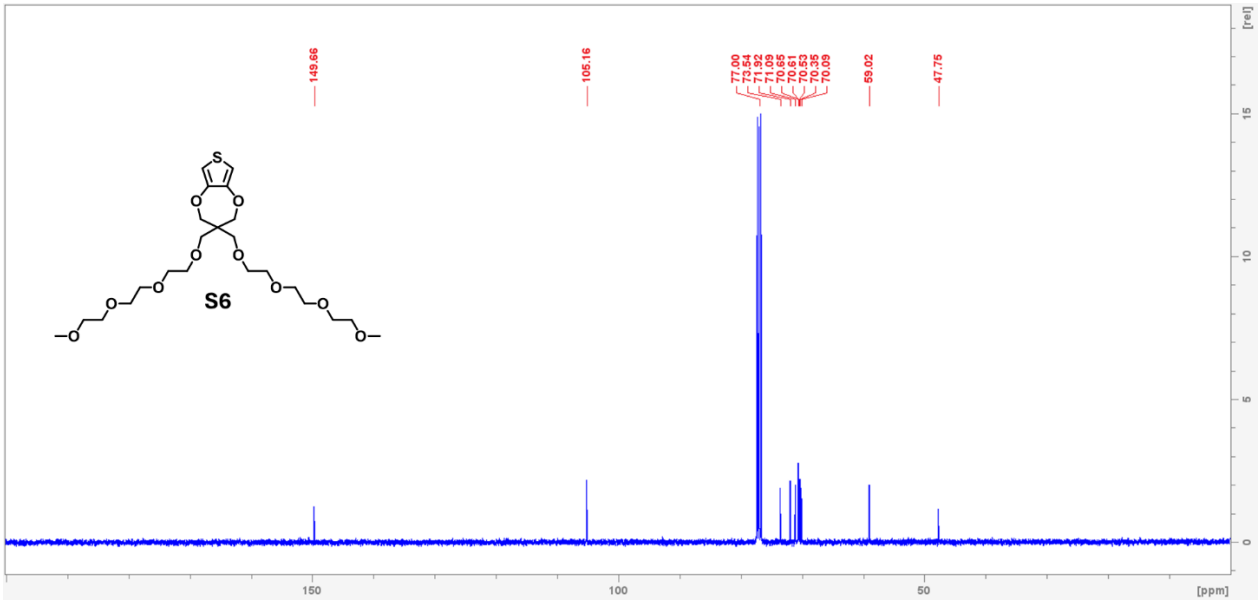
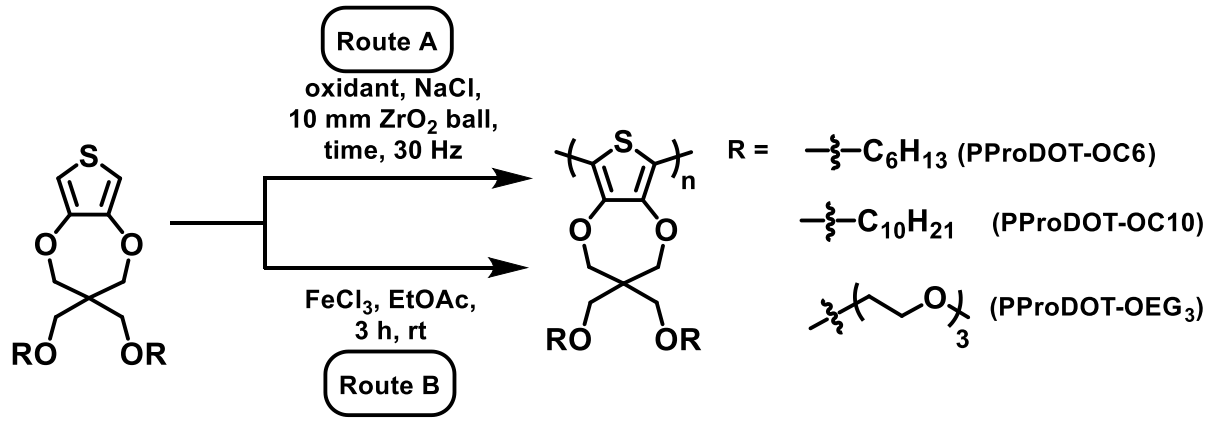


Figure S6. ^{13}C-NMR of S6 collected in $CDCl_3$ at 25 °C and 100 MHz.

4. Polymer Synthesis.



Scheme S3. General routes for polymer synthesis via mechanochemical (Route A) or solvent based (Route B) oxidative polymerization.

General Procedure for Mechanochemical Oxidative Polymerization. A 10 mL stainless steel jar lined with zirconia was charged with 0.52 mmol (1 equiv.) of monomer (**S4-S6**), $FeCl_3$ (506.1 mg, 3.12 mmol, 6 equiv.), NaCl (1.00 g, 17.1 mmol, 32.9 equiv.), and a 10 mm diameter zirconia ball. The jar was then sealed with a screw-cap and subjected to 1 h. of mixing at 30 Hz. Next, to purify the crude polymer product it was first dissolved in toluene (20 mL) and washed with DI-H_2O (30 mL). The toluene layer was collected, and 5 mL hydrazine hydrate was then added to reduce the oxidized polymer. This mixture was allowed to stir at room temperature for 1 h. A noticeable color change occurred during this time from green to bright red. The mixture was then washed with DI-H_2O (20 mL), the toluene layer was collected, and the solvent evaporated via rotovap. The solid was then dissolved in a minimal amount of toluene (2 mL) and this was slowly precipitated into chilled methanol with rapid stirring. After stirring for 20 min. the precipitate was collected via filtration onto a nylon membrane. The precipitate was washed with methanol (5x10 mL) and hexane (5x10 mL). The polymer was dried overnight under vacuum prior to analysis.

Representative Procedure for Solvent Based Oxidative Polymerization. Adapted from literature[4]. Monomer **S4** (200mg, 0.52 mmol, 1 equiv.) and anhydrous EtOAc (2.5 mL) were added to a one-neck round bottom flask equipped with a stir bar. The solution was stirred and degassed via bubbling with nitrogen for 45 minutes. In a separate round bottom flask, $FeCl_3$ (421. 72 mg, 2.6 mmol, 5 equiv.) was dissolved in anhydrous EtOAc (1 mL), and this solution was purged with nitrogen for 5 min. The monomer solution was then added drop wise in $FeCl_3$ solution. The mixture

was stirred vigorously while being continuously bubbled with nitrogen for 3 h. after which the green suspension was poured into methanol (100 mL) . The green precipitate was stirred for 45 minutes, filtered onto a nylon membrane, and washed with methanol (50 mL). The precipitate was then dissolved using toluene (4 mL), treated with hydrazine (5 mL), and then stirred for one hour. The pink toluene solution was poured into a separatory funnel and washed with water (50 mL) three times. The toluene fraction was then collected, and the volume was reduced to ~2 mL under reduced pressure. The concentrated toluene fraction was then precipitated into methanol (150 mL) and stirred for 45 minutes. The purple precipitate was then filtered onto a nylon membrane, and polymer was washed with methanol (5x 10 mL) and hexane (5x 10 mL) to afford the polymer as a purple solid. The polymer was dried overnight under vacuum prior to analysis.

Poly(3,3-bis[(hexyloxy)methyl]-3,4-dihydro-2*H*-thieno[3,4-*b*][1,4]dioxepine) (PProDOT-OC6). Purple solid. ^{1}H-NMR (400 MHz, $CDCl_3$): δ (ppm) 4.15 (b, 4H), 3.61-3.43 (b, 8H), 1.57 (b, 4H), 1.30 (b, 12H), 0.88 (b, 6H).

Poly(3,3-bis[(decyloxy)methyl)-3,4-dihydro-2H-thieno-[3,4-b][1,4]dioxepine) (PProDOT-OC10). Dark purple solid**.** ^{1}H-NMR (400 MHz, $CDCl_3$): δ (ppm) 4.13 (b, 4H), 3.60-3.41 (b, 8H), 1.54 (b, 4H), 1.25 (b, 28H), 0.86 (b, 6H).

Poly(2-(2-(2-methoxyethoxy)ethoxy)ethoxymethyl]-3,4-dihydro-2*H*-thieno[3,4-*b*][1,4]dioxepine) (PProDOT-OEG$_3$). Dark purple solid.^{1}H-NMR (400 MHz, $CDCl_3$): δ (ppm) 4.18 (b, 8H), 3.64-3.34 (b, 34H).

5. Polymer NMR.

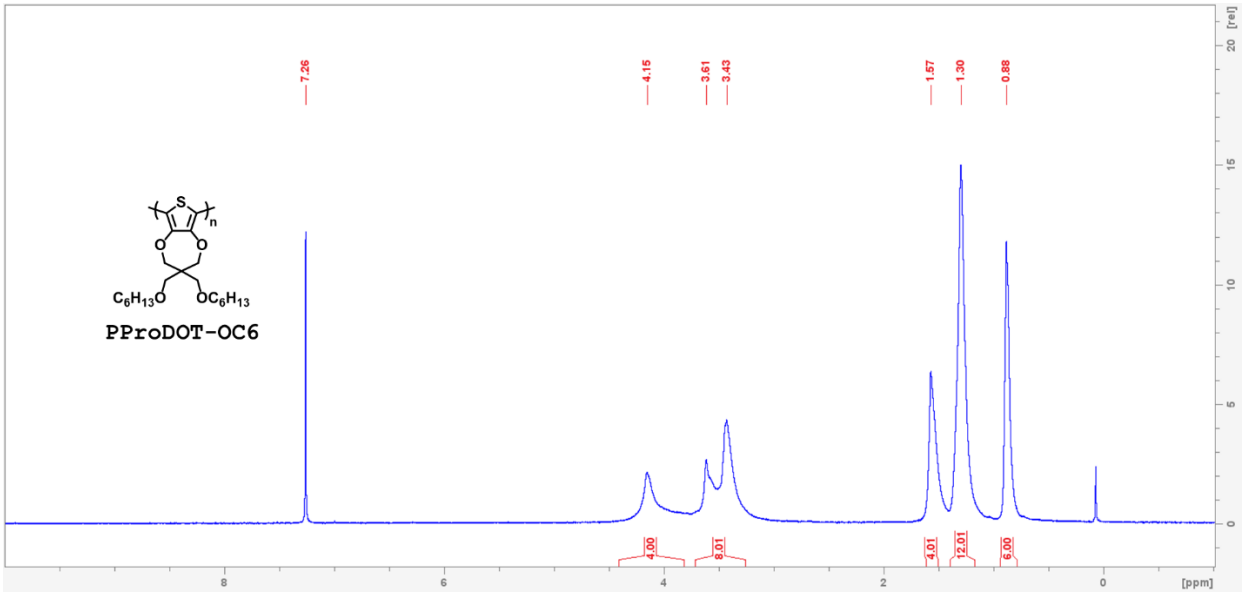


Figure S7. ^{1}H-NMR of PProDOT-OC6 (Entry 1 of Table 1) collected in $CDCl_3$ at 25 °C and 400 MHz.

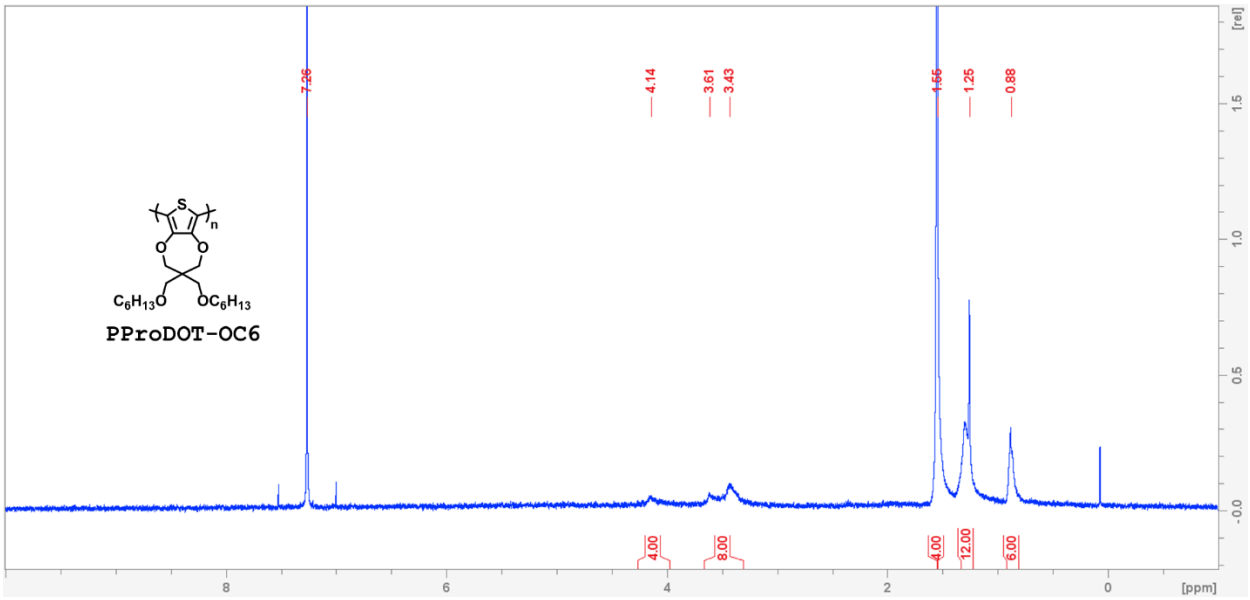


Figure S8. ^{1}H-NMR of PProDOT-OC6 synthesized using $Fe(OTs)_3$ as the oxidant (Entry 4 of Table 1). Collected in $CDCl_3$ at 25 °C and 400 MHz.

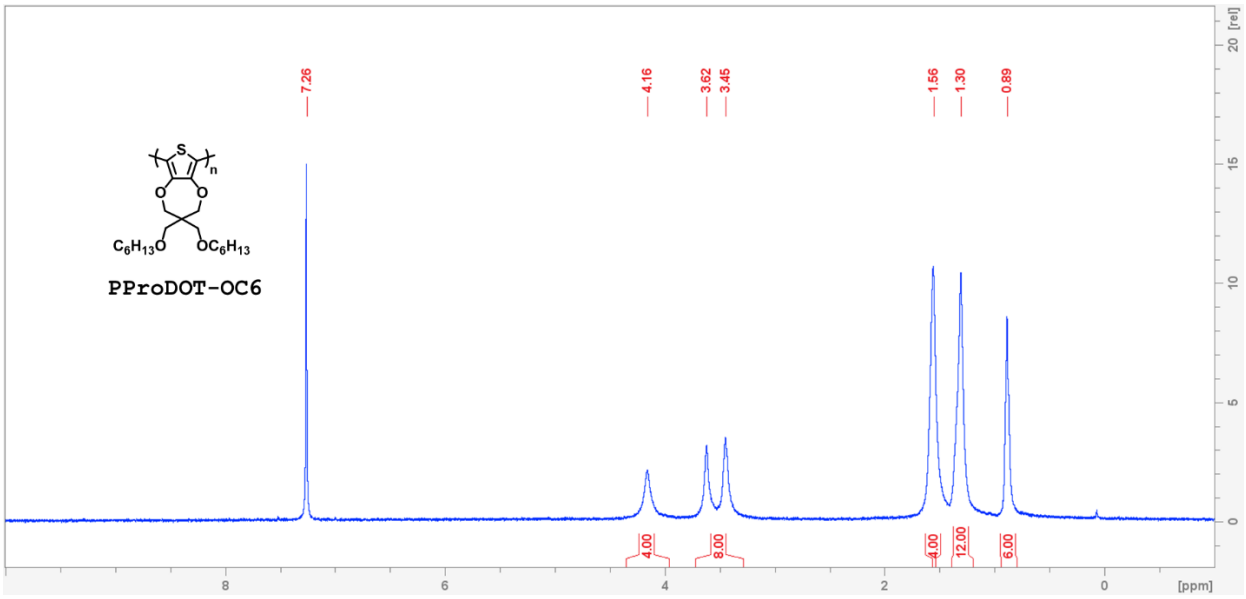


Figure S9. ^{1}H-NMR of PProDOT-OC6 (Entry 5 of Table 1) collected in $CDCl_3$ at 25 °C and 400 MHz.

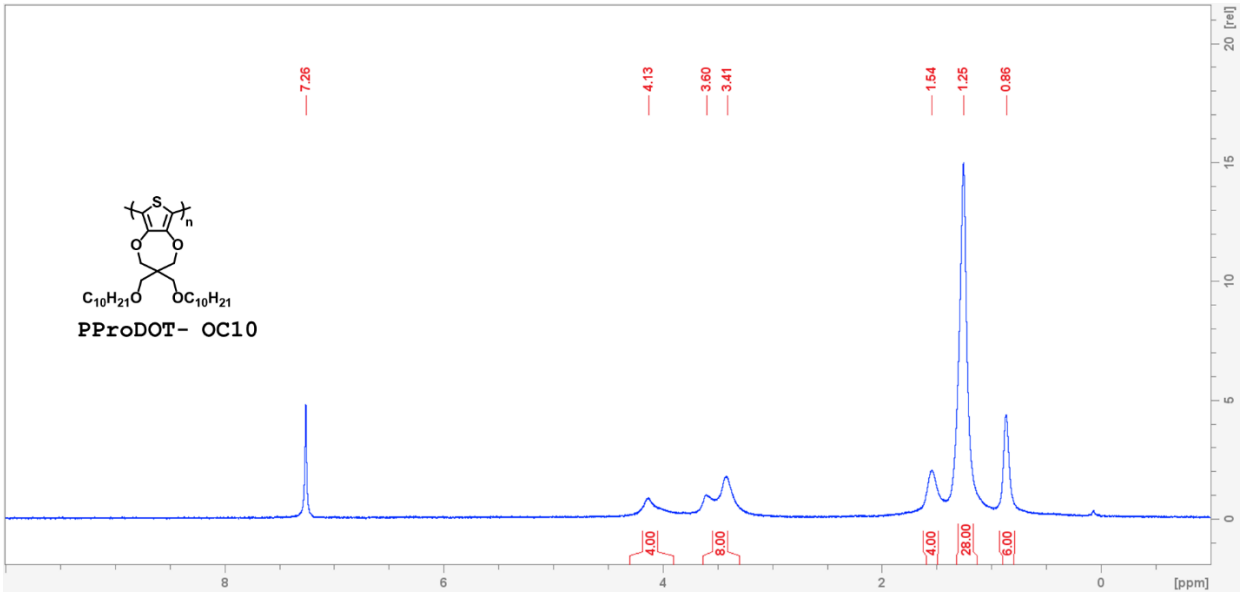


Figure S10. ^{1}H-NMR of PProDOT-OC10 (Entry 8 of Table 1) collected in $CDCl_3$ at 25 °C and 400 MHz.

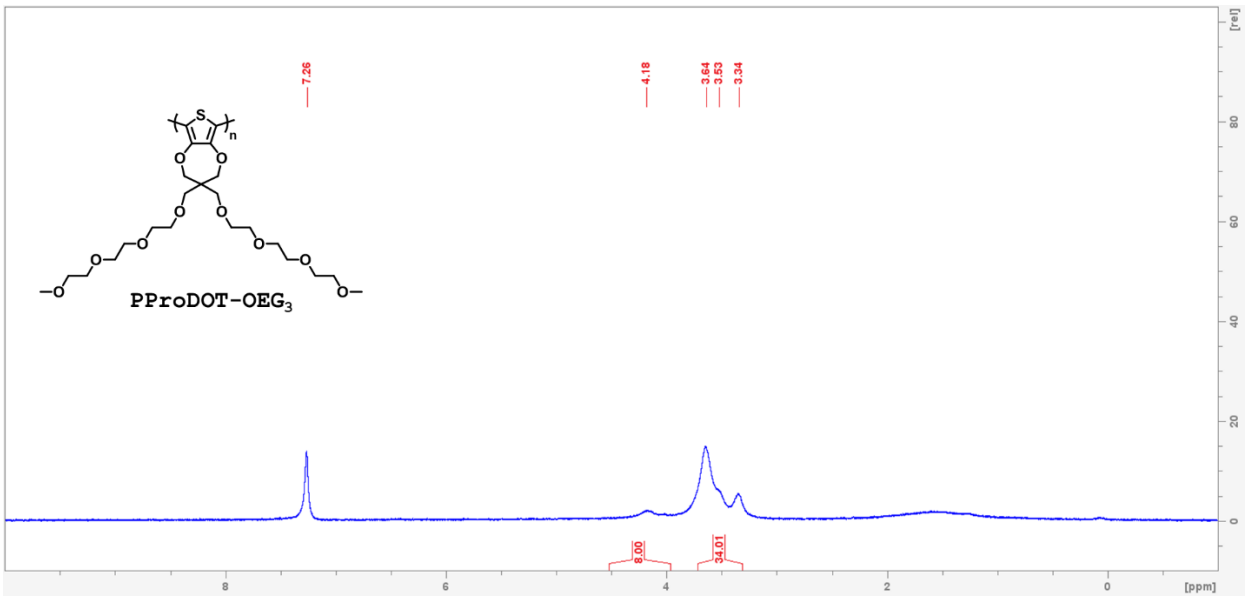


Figure S11. ^{1}H-NMR of PProDOT-OEG$_3$ (Entry 9 of Table 1) collected in $CDCl_3$ at 25 °C and 400 MHz.

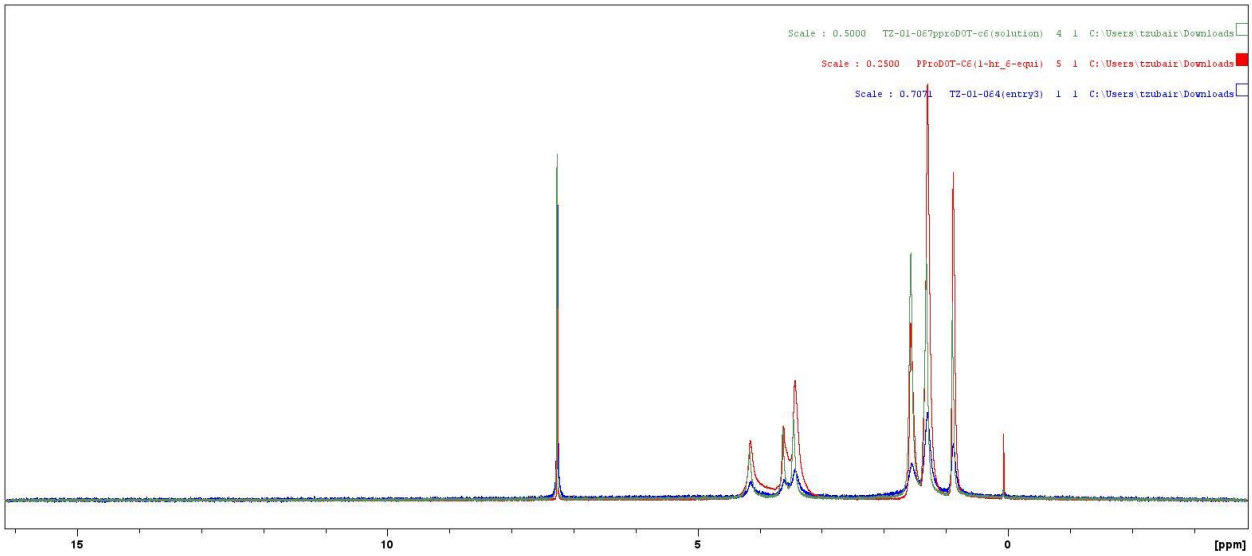


Figure S12. Overlay of ^{1}H-NMR spectra for PProDOT-OC6 Entries 1 (red trace), 3 (blue trace) and 5 (green trace) of Table 1. Collected in $CDCl_3$ at 25 °C and 400 MHz.

6. Polymer Gel Permeation Chromatography (GPC).

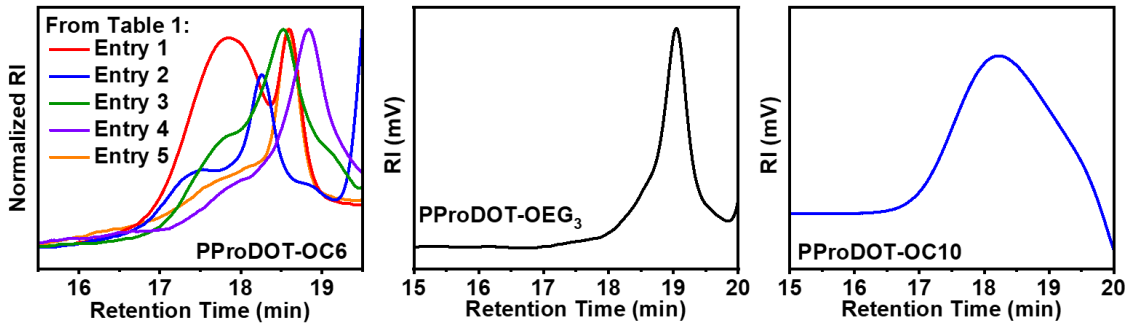


Figure S13. GPC traces for PProDOT-OC6 (Entries 1-5 from Table 1), PProDOT-OEG_3, and PProDOT-OC10. Collected using HPLC $CHCl_3$ at 40 °C and calibrated versus polystyrene standard

7. Optical Absorption and Cyclic-Voltammetry.

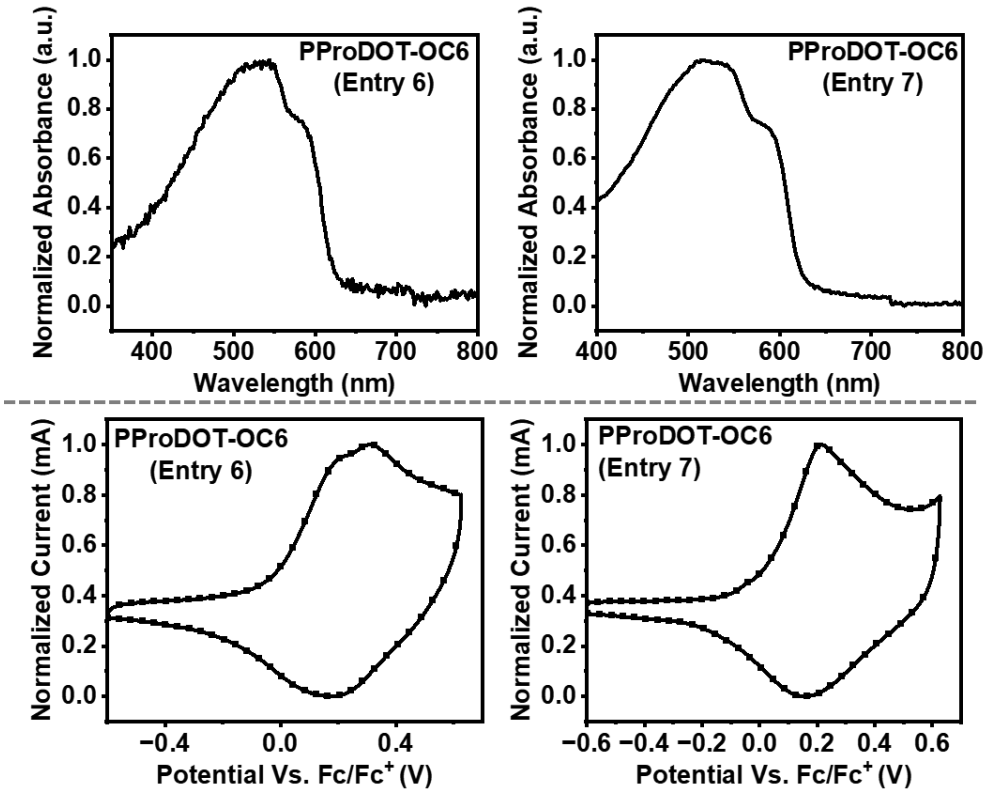


Figure S14. Optical absorption spectra (top) and voltammograms (bottom) for PProDOT-OC6 (Entries 6 and 7 of Table 1).

8. References.

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