Supporting Information

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EXPERIMENTAL

Materials and Characterization

3,4-Dimethoxythiophene (97 %, Aldrich), 1,1,1-Tris(hydroxymethyl)ethane (99 %, Aldrich), p-Toluene-sulfonic acid monohydrate (98 %, Aldrich), N,N'-Dicyclohexylcarbodiimide (DCC, 99 %, Aldrich), 4-(Dimethylamino)pyridine (DMAP, 99 %, Aldrich), 4-vinylbenzoic acid (96 %, TCI), N,N,N',N''. Pentamethyldiethylenetriamine (PMDETA, 99 %, Aldrich), Ethyl α bromoisobutyrate (98 %, Aldrich), tert-Butyl acrylate (98 %, Aldrich), Methyl 2bromopropionate (98 %, Aldrich), Dowex 50WX8-200 ion exchange resin (Aldrich), Toluene (ACS grade, EMD), Ethyl acetate (ACS grade, Macron), Hexanes (ACS grade, EMD), Dichloromethane (ACS grade, EMD), Anisole (99 %, Alfa Aesar), Lithium borohydride (2.0 M in THF, Aldrich), Sodium periodate (SPI), Ruthenium(IV) oxide hydrate (99.5%, SPI) were commercially available and used as received. Copper(I) bromide (98 %) was purchased from Aldrich and purified by stirring in glacial acetic acid, filtering, washing with ethanol and ethyl ether, and drying under vacuum before use. ¹H and ¹³C nuclear magnetic resonance (NMR) spectra were obtained using a Bruker DRX 500 MHz or a BrukerAvance III 400 MHz spectrometer. Chemical shifts are referenced to Me₄Si (δ 0.00 ppm) for ¹H NMR and residual CHCl₃ (δ 77.0 ppm) in CDCl₃ for ¹³C NMR. Size exclusion chromatography (SEC) was performed in a tetrahydrofuran (THF) mobile phase with a Waters 1515 isocratic pump running

three 5- μ m PLgel columns (Polymer Labs, pore size 10⁴, 10³ and 10² Å) at a flow rate of 1 mL/min with a Waters 2414 differential refractometer and a Waters 2487 dual-wavelength UV-vis spectrometer. Molar masses were calculated using the Empower software (Waters), calibrated against low polydispersity linear polystyrene standards. TEM images were obtained on a Phillips CM12 transmission electron microscope (CM12) at 80 kV, using prepared carbon coated grids (Electron Microscopy Sciences, Cu, square, 300 mesh). Image analysis was performed using ImageJ software (Rasband, W.S., National Institutes of Health, http://rsb.info.nih.gov/ij/, 1997-2007)

Experimental Procedures

Synthesis of (1), (3-methyl-3,4-dihydro-2*H*-thieno[3,4-*b*][1,4]dioxepin-3-yl)methanol (ProDOT-OH) according to literature methods.

A 1 L 3-necked round bottom flask equipped with a magnetic stir bar and condenser was loaded a solution of 3,4-dimethoxythiophene (5.0 g, 34.7 mmol) in toluene (850 mL). 1,1,1,-Tris(hydroxyl-methyl)ethane (5.4 g, 45.0 mml) and *p*-toluenesulfonic acid monohydrate (0.7 g, 3.5 mmol) were added sequentially. The resulting mixture was heated at T = 100 °C and stirred at this temperature for 3 days. After cooling to room temperature, the solvent was removed by evaporation and the viscous black residue was dissolved in ethyl acetate (800 mL). Organic layer was washed with deionized water (400 mL) three times, dried over anhydrous MgSO₄, filtered and concentrated under vacuum. The residue was purified by silica gel column chromatography using a gradient elution from 10 % ethyl acetate to 20 % ethyl acetate in hexanes to afford a white solid (5.6 g, 80 % isolated yield). ¹H NMR (500 MHz, CDCl₃) δ 6.47 (s, 2H), 4.07 (d, *J* = 11.95 Hz, 2H), 3.75-3.72 (m, 4H), 1.69 (t, *J* = 5.08 Hz, 1H), 0.95 (s, 3H); ¹³C NMR (125 MHz, CDCl₃) δ 149.6, 105.6, 76.6, 65.8, 43.8, 17.0.

Synthesis of (2), (3-methyl-3,4-dihydro-2*H*-thieno[3,4-*b*][1,4]dioxepin-3-yl)methyl 4-vinylbenzoate (ProDOT-Styrene)

A 1 L 2- necked round bottom flask equipped with a magnetic stir bar was loaded with a solution of 4-vinylbenzoic acid (16.5 g, 111.3 mmol) in dichloromethane (400 mL) and the resulting solution was cooled under an ice bath to T = 0 °C. 4-(Dimethylamino)pyridine (1.4 g, 11.5 mmol) and *N*,*N*'-dicyclohexylcarbodiimide (23.0 g, 111.3 mmol) were added sequentially to the reaction mixture and the resulting mixture was stirred at 0 °C for 15 minutes. A solution of ProDOT-OH (17.5 g, 87.4 mmol) in dichloromethane (450 mL) was added to the reaction mixture over 15 minutes at 0 °C. The reaction mixture was stirred at 0 °C for 1 hour and warmed to room temperature slowly while stirring overnight. The reaction mixture was filtered to remove the urea precipitate and the filtrate was concentrated under vacuum. The residue was purified by silica gel column chromatography using 10 % ethyl acetate in hexanes as an eluent to afford a white solid (24.6 g, 86 % isolated yield)

¹H NMR (400 MHz, CDCl₃) δ 7.99 (dt, J = 8.4, 2.0 Hz, 2H), 7.47 (dt, J = 8.4, 2.0 Hz, 2H), 6.76 (dd, J = 17.6, 10.9 Hz, 1H), 6.50 (s, 1H), 5.87 (dd, J = 17.6, 0.7 Hz, 1H), 5.40 (dd, J = 10.9, 0.7 Hz, 1H), 4.43 (s, 1H), 4.14 (d, J = 12.0 Hz, 1H), 3.83 (d, J = 12.0 Hz, 1H), 1.08 (s, 3H). ¹³C NMR (100 MHz, CDCl₃) δ 166.1, 149.6, 142.2, 136.0, 129.9, 129.0, 126.2 116.7, 105.8, 76.3, 66.8, 42.9, 17.4. HRMS (ESI) m/z calculated for C₁₈H₁₉O₄S (M+H)⁺ 331.0999, observed 331.1000.

ATRP of ProDOT-Sty $([M]_0 : [I]_0 : [L] : [Cu^I] = 100 : 1 : 1 : 1)$

A typical polymerization was conducted as follows: A 10 mL Schlenk flask equipped with a magnetic stir bar was loaded with ProDOT-Sty (2.0 g, 6.1 mmol) and Cu(I)Br (8.7 mg, 6.1 x 10^{-2} mmol). The flask was fitted with a rubber septum, evacuated and back-filled with argon five times. Deoxygenated anisole (5 mL) was added via purged syringe and the resulting mixture was stirred at room temperature until a homogeneous, light yellow solution was formed. PMDETA (12.6 μ L, 6.1 x 10^{-2} mmol) was added via purged syringe and the resulting mixture was stirred for 10 minutes to allow for the formation of the copper catalyst complex, yielding a light green solution. Ethyl α -bromoisobutyrate (8.9 μ L, 6.1 x 10^{-2} mmol) was added via purged syringe to the reaction mixture. The resulting mixture was stirred at 80 °C until desired conversion was achieved after which the reaction was quenched by exposure to air. The copper catalyst was removed from the reaction mixture by stirring over Dowex 50WX8-200 ion exchange resin, followed by filtering the solution through a short plug of activated neutral alumina. The polymer was isolated via precipitation into a 10 fold excess of rapidly stirred methanol, followed by filtration to yield a white powder (0.58 g yield).

Synthesis of poly(tert-butyl acrylate) Macroinitiator

A 25 mL Schlenk flask equipped with a magnetic stir bar was loaded with Cu(I)Br (97.5 mg, 6.8 x 10^{-1} mmol). The flask was fitted with a rubber septum, evacuated and backfilled with argon three times. Deoxygenated *tert*-buty acrylate (20 mL, 136.0 mmol), deoxygenated acetone (5 mL) and deoxygenated PMDETA (0.14 mL, 6.8 x 10^{-1} mmol) were added sequentially via purged syringe. The resulting mixture was stirred at room temperature to form the copper catalyst complex, yielding a light green solution. Methyl 2-bromopropionate (0.15 mL, 1.36 mmol) was added via purged syringe to the reaction mixture and the resulting solution was heated at 60 °C for 6.5 hours after which the reaction was quenched by exposure to air. The copper catalyst was removed from the reaction mixture by stirring over Dowex 50WX8-200 ion exchange resin, followed by filtering the solution through a short plug of activated neutral alumina. The polymer was isolated via precipitation into a 10 fold excess of rapidly stirred a mixture of MeOH and cold H₂O (1:1 = v:v), followed by filtration to give poly(*tert*-butyl acrylate) macroinitiator (3.8 g yield). M_{n SEC} = 9200 g/mol, M_w/M_n = 1.07.

Synthesis of poly(*tert*-butyl acrylate)-*b*-poly(ProDOT-Sty)

A 10 mL Schlenk flask equipped with a magnetic stir bar was loaded with poly(*tert*-butyl acrylate) macroinitiator (570 mg, 1×10^{-2} mmol) and Cu(I)Br (8.7 mg, 6.1 x 10^{-2} mmol). The flask was fitted with a rubber septum, evacuated and back-filled with argon five times. Deoxygenated anisole (5 mL) was added via purged syringe and the resulting mixture was stirred at room temperature until a homogeneous solution was formed. PMDETA (12.6 µL, 6.1 x 10^{-2} mmol) was then added via purged syringe and the resulting mixture was stirred for 10 minutes to allow for the formation of the copper catalyst complex, yielding a light green solution. The mixture was then degassed by three freeze-pump-thaw cycles. The resulting mixture was stirred at 80 °C overnight after which the reaction was quenched by exposure to air. The copper catalyst was removed from the reaction mixture by stirring over Dowex 50WX8-200 ion exchange resin, followed by filtering the solution through a short plug of activated neutral alumina. The polymer was isolated via precipitation into a 10 fold excess of rapidly stirred methanol at 0 °C, followed by filtration to yield a white crystalline powder (1.36 g yield). M_{n SEC} = 19,100 g/mol, M_w/M_n = 1.15.

Electrochemical oxidative polymerization of pendant ProDOT groups

A typical polymerization was conducted as follows: A 100 mL round bottom flask with a magnetic stirbar was loaded with poly(*tert*-butyl acrylate)-*b*-poly(ProDOT-Sty) (100.7 mg, 5 μ mol). Chloroform (25 mL) was added and the mixture was stirred until a homogeneous solution resulted. A solution of FeCl₃ (104 mg, 0.64 mmol) in chloroform (10 mL) was added and the solution was stirred at 50 °C for 5 hours. The resulting dark blue solution was stirred over Dowex 50WX8-200 ion exchange resin for 1 hour and then passed through a short plug of activated basic alumina to remove excess oxidant. The solvent was then removed under vacuum to yield a dark bluish black powder with 85% isolated yield. The product was analyzed by UV-Vis absorption spectroscopy as a solution in CHCl₃ (Figure S1).



Figure S1. Optical absorption spectra of poly(*tert*-butyl acrylate)-b-poly(ProDOT-Sty) (---) and electrochemically polymerized polymer nanoparticles (_____).



Figure S2. ¹H NMR spectra of poly(ProDOT-Sty) over 5 hours of electrochemical oxidative polymerization.

TEM Sample Staining with RuO₄

A solution of RuO_4 was prepared as follows: Sodium periodate (1.00 g, 4.68 mmol) was dissolved in H_2O (25 mL). The solution was cooled in an ice bath and ruthenium(IV) oxide hydrate (150 mg) was added. The mixture was allowed to come to room temperature while stirring for 3 hr.

Samples were then prepared by drop casting a chloroform solution of the material to be imaged onto C coated Cu TEM grids which were then exposed to RuO₄ vapors for 1 hr at room

temperature by placing the TEM grid on a PTFE coated stage in a secondary sealed container along with the RuO_4 solution.

Reduction of Oxidized poly(ProDOT)-Sty to poly(ProDOT-OH) and poly(vinylbenzyl alcohol)

A 10 mL round bottom flask with a magnetic stirbar was loaded with oxidized poly(ProDOT-Sty) that had been subjected to electrochemical oxidation with Fe^{III}Cl₃ as previously described for 4 hours (45 mg, 4 µmol). The flask was then evacuated and backfilled with argon three times and dry THF (1 mL) was added yielding a dark blue solution after stirring. LiBH₄ in THF (2.0 M, 1.0 mL) and MeOH (81 µL, 2.0 mmol) were then added sequentially which rapidly turned the solution a vibrant reddish orange color. The reaction was allowed to proceed with stirring overnight at room temperature. The solution was then added to an excess of H₂O (~50 mL) and carefully acidified with 1 N HCl until ~pH 7.0. The resulting reddish purple precipitate was recovered via centrifugation at 10,000 rpm for 5 min (35.7 mg yield). The mixture of products was analyzed via ¹H NMR (Figure S4) and GPC employing a UV detector set at 350 nm.



Figure S4. ¹H NMR spectrum of poly(ProDOT-OH) and poly(vinylbenzyl alcohol) yielded from the LiBH₄ reduction of oxidized poly(ProDOT-Sty).