

SUPPORTING INFORMATION

Improving the Charge Conductance of Elemental Sulfur via Tandem Inverse Vulcanization and Electropolymerization

Philip T. Dirlam,[†] Adam G. Simmonds,[†] R. Clayton Shallcross,[†] Kyle J. Arrington,[†] Woo Jin Chung,[†] Jared J. Griebel,[†] Lawrence J. Hill,[†] Richard S. Glass,[†] Kookheon Char,^{*,‡} and Jeffrey Pyun^{*,†,‡}

[†]Department of Chemistry and Biochemistry, University of Arizona, 1306 East University Boulevard, Tucson, Arizona 85721, United States, [‡]School of Chemical and Biological Engineering, The National Creative Research Initiative Center for Intelligent Hybrids, Seoul 151-744, Korea.

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I. Materials

Sulfur (S_8 , refined, 99.5%, Acros), 3,4-Dimethoxythiophene (97 %, Aldrich), 1,1,1-Tris(hydroxymethyl)ethane (99 %, Aldrich), *p*-Toluenesulfonic acid monohydrate (98 %, Aldrich), *N,N'*-Dicyclohexylcarbodiimide (DCC, 99 %, Aldrich), 4-(Dimethylamino)pyridine (DMAP, 99 %, Aldrich), 4-vinylbenzoic acid (96 %, TCI), Toluene (ACS grade, EMD), Ethyl acetate (ACS grade, Macron), Hexanes (ACS grade, EMD), Dichloromethane (ACS grade, EMD), Chloroform-*d* ($CDCl_3$, 0.01 % v/v TMS Cambridge Isotope Laboratories), Tetrahydrofuran (THF, 99.8%, Fischer), Acetonitrile (anhydrous, 99.8%, EMD) were commercially available and used as received. 1,3-Diisopropenylbenzene (DIB, 97 %, TCI), was passed through a short plug of activated alumina to remove inhibitor prior to use, Tetrabutylammonium hexafluorophosphate (TBAFP, 99 %, Fluka) was recrystallized from absolute ethanol and dried *in vacuo* before use. Indium Tin Oxide coated glass (ITO, Colorado Concepts) was cut into squares ($A = 2\text{ cm}^2$) and cleaned by first scrubbing with an aqueous Triton-X 100 solution using a microfiber cloth followed by successive sonication in deionized water and absolute ethanol for 20 min each changing the solvent after 10 min. Prior to use a fresh ITO surface was produced by etching in a $FeCl_3$ (2M) solution in conc. HCl for 10 s followed by rinsing with excess deionized water three times, and absolute ethanol two times.

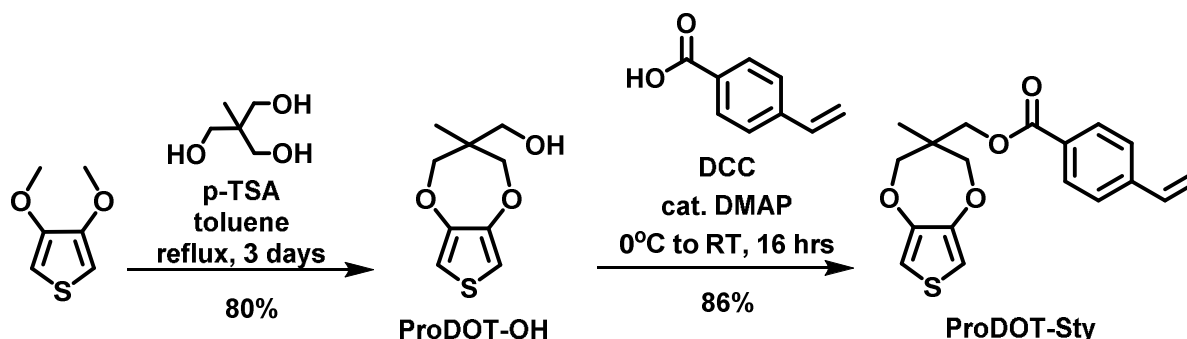
II. Instrumentation and Methods

1H and ^{13}C 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 Me_4Si (δ 0.00 ppm) for 1H NMR and residual $CHCl_3$ (δ 77.0 ppm) in $CDCl_3$ for ^{13}C NMR. Size exclusion chromatography (SEC) was performed in a tetrahydrofuran (THF) mobile phase with a Waters 1515 isocratic pump running three 5- μm PLgel columns (Polymer Labs, pore size 10^4 , 10^3 and 10^2 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. Thermal gravimetric analysis (TGA) was performed with a Q50 TGA (TA instruments) from 25 °C to 600 °C at a rate of 20 °C/min under nitrogen atmosphere and data was analyzed with TA Universal Analysis software. SEM images were taken on a Hitachi 4800 FE-SEM and analyzed with ImageJ software (Rasband, W.S., National Institutes of Health, <http://rsb.info.nih.gov/ij>). Electrochemical measurements (cyclic voltammetry, impedance spectroscopy) were performed with a Zahner Zennium Electrochemical Workstation utilizing a three electrode electrochemical cell with ITO as the working electrode, a platinum mesh counter electrode, and a $Ag/AgNO_3$ reference. Impedance spectroscopy data were fit with ZView software (ver. 2, Scribner Associates).

III. Experimental Procedures

A. **Preparation of ProDOT-Sty** was completed in two steps (Scheme S1) according to previously reported methods.¹

Scheme S1. Synthesis of ProDOT-Sty from 3,4-dimethoxythiophene



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

To a 1 L 3-necked round bottom flask equipped with a magnetic stir bar and reflux condenser was added 3,4-dimethoxythiophene (5.0 g, 34.7 mmol) and toluene (850 mL). 1,1,1-Tris(hydroxyl-methyl)ethane (5.4 g, 45.0 mmol) and *p*-toluenesulfonic acid monohydrate (0.7 g, 3.5 mmol) were then added sequentially. The resulting mixture was heated to 100 °C and stirred at this temperature for 3 days. After cooling to room temperature, the solvent was removed *in vacuo*. The resulting viscous black residue was dissolved in ethyl acetate (800 mL), washed with deionized water (400 mL) three times, dried over anhydrous MgSO₄, filtered and concentrated *in vacuo*. The residue was purified by silica gel column chromatography using a gradient elution from 10 % ethyl acetate to 20 % ethyl acetate in hexanes affording 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.

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

To a 1 L 2-necked round bottom flask equipped with a magnetic stir bar was added 4-vinylbenzoic acid (16.5 g, 111.3 mmol) and dichloromethane (400 mL) and the resulting mixture was stirred until a clear colorless solution resulted and then cooled to 0 °C in an ice bath. 4-(Dimethylamino)pyridine (1.4 g, 11.5 mmol) and *N,N'*-dicyclohexylcarbodiimide (23.0 g, 111.3 mmol) were added sequentially 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 then warmed to room temperature while stirring overnight. The reaction mixture was filtered to remove the urea precipitate and the filtrate was concentrated *in vacuo*. 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). ^{13}C NMR (100 MHz, CDCl_3) 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.

B. Preparation of ProDIBS (poly(ProDOT-Sty-*r*-1,3-diisopropenylbenzene-*r*-sulfur))

1. Inverse Vulcanization of ProDOT-Sty, DIB, and Sulfur (40 : 50 : 10 wt% respectively)

A typical polymerization was conducted as follows: To a 5 mL glass vial equipped with a magnetic stir bar was added elemental sulfur (500 mg, 1.95 mmol as S_8) and ProDOT-Sty (400 mg, 1.21 mmol). The mixture was heated to 180 °C with rapid stirring (500 rpm) for 5 min to facilitate the oligomerization of sulfur and ProDOT-Sty yielding a viscous orange liquid. 1,3-Diisopropenyl benzene (100 mg, 108 μL , 0.63 mmol) was then added and the reaction was allowed to stir at 180 °C until vitrification occurred (ca. 5 additional minutes). Following vitrification the product was maintained at 180 °C for 30 s before being rapidly cooled in a dry ice/acetone bath for 2 min. The vitreous reaction product was extracted by breaking the glass vial yielding a dark red glass (946 mg, 95% isolated yield).

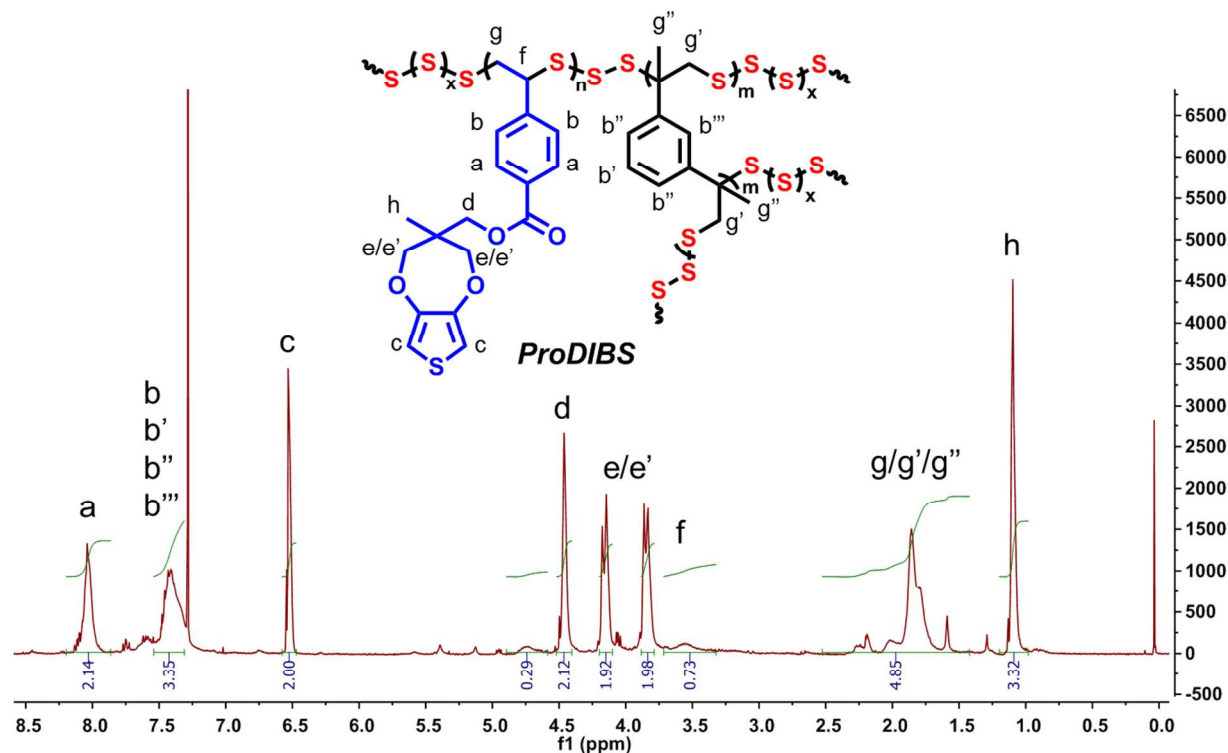


Figure S1. Annotated ^1H NMR (400 MHz, CDCl_3) spectrum of ProDIBS

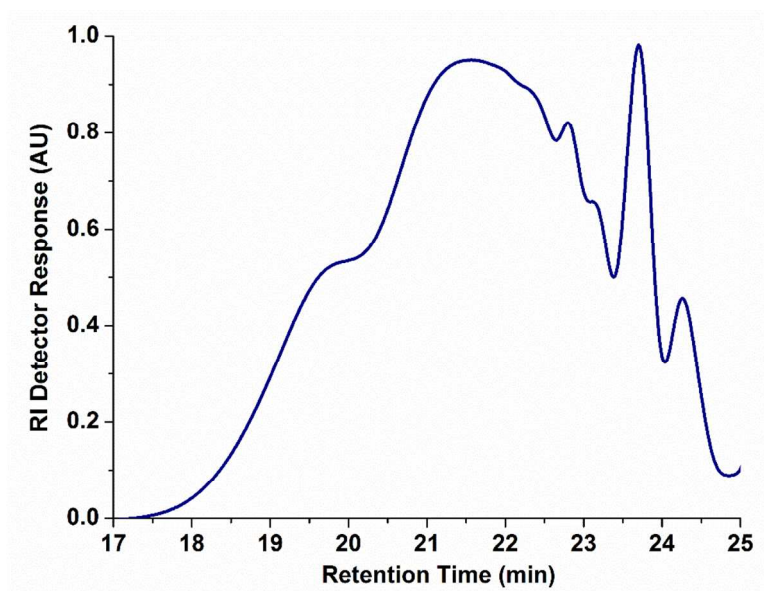


Figure S2. GPC Trace of ProDIBS indicating a $M_{n \text{ apparent}} = 2000 \text{ g/mol}$ and $M_w/M_n = 1.75$.

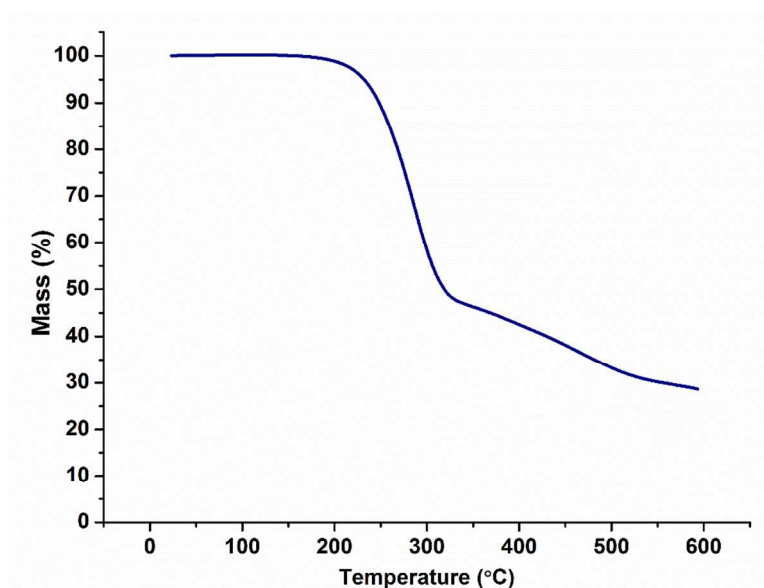


Figure S3. Thermogravimetric curve of ProDIBS indicating a mass loss of ca. 50% with an onset at 225 °C corresponding to sulfur content.

C. Fabrication of ProDIBS thin films on ITO

1. Solution Processing of ProDIBS via Spin Coating

A thin film of ProDIBS (ca. 90 nm thickness) was deposited onto a freshly cleaned ITO coated glass substrate (2 cm x 2 cm) by spin-coating from a solution of ProDIBS (25 mg/mL) in 1:1 by volume toluene:CH₂Cl₂ with a two-step spin-coating protocol (step 1: ramp at 400 rpm/s to 1500 rpm for a total of 15 s, step 2: ramp at 665 rpm/s from 1500 to 3500 rpm for an additional 15 s).

D. Electrochemical Oxidative Polymerization of ProDOT Side Chains

An electrochemical cell was assembled with ProDIBS coated ITO as the working electrode ($A = 1 \text{ cm}^2$), a Pt mesh counter electrode, and a Ag/AgNO₃ reference electrode. A 100 mM tetrabutylammonium hexafluorophosphate (TBAFP) solution in acetonitrile was bubbled with Ar for 30 min and then added to the cell as the supporting electrolyte. The system was then allowed to rest for 5-10 min to allow for swelling of the polymer with the supporting electrolyte solution. Oxidative polymerization of the ProDOT moieties was then carried out by cycling the potential from 0.5 V to 1.2 V vs. Ag/Ag⁺ at a rate of 100 mV/s.

IV. Electrochemical Impedance Spectroscopy (EIS)

A. Impedance Measurement Procedure

The same three-electrode electrochemical cell with TBAFP/MeCN supporting electrolyte previously described for electropolymerization experiments was utilized for EIS measurements. Impedance spectra were recorded between 150 kHz and 0.1 Hz at $E = 0.8 \text{ V}$. Spectra were taken of the ProDIBS film on ITO in its pristine state and after various numbers of potentiodynamic polymerization scans in order to interrogate the effect of increasing conversion of ProDOT side chains to poly(ProDOT) inclusions. The impedance spectra were then imported into ZView 2.0 software and the data fit to a modified Randles equivalent circuit (Figure S5).

B. EIS Spectra Interpretation

Electrochemical impedance spectroscopy has proven an excellent method for interrogating the electronic properties of conducting polymer films as aptly introduced in a tutorial review by Robinson and Kayinamura.² An in-depth discussion of the theory of AC impedance is beyond the scope of this work but a brief explanation of interpreting EIS data represented in a Nyquist plot (Figure S4) modeled with a Randles circuit³ modified with a constant phase element (Figure S5) is presented. Modeling EIS data with an equivalent circuit allows for interpretation of the complex electrochemical processes in terms of common circuit elements (i.e. resistors, capacitors) and therefore extraction of practical values. The Nyquist plot of the real (Z) and imaginary (Z') components of the total impedance as a function of frequency is a useful way to graphically represent complex impedance.

Impedance is measured from the surface of the working electrode to the reference electrode and the various circuit elements account for the different components of the system (electrolyte solution, and polymer film).⁴ The impedance of the supporting electrolyte solution is interpreted in the Randles circuit by a resistor (R_s). The resistance of the electrolyte solution is indicated on a Nyquist plot by the intercept of the high frequency response with the real impedance axis. The polymer film is modeled as a constant phase element (CPE) in parallel with a resistor (R_{CT}) and Warburg element in series. The CPE is frequency dependent element associated with a non-ideal capacitance attributed to film inhomogeneity and is represented in the Nyquist plot by the depression of the semi-circular feature. The Warburg element accounts for the impedance of charge carrier diffusion and is manifested in the Nyquist plot as the positively sloped line at low frequencies. The resistor (R_{CT}) accounts for the impedance of charge

transfer in the polymer film. It is graphically represented in the Nyquist plot as the diameter of the semi-circular feature at high and mid frequencies.

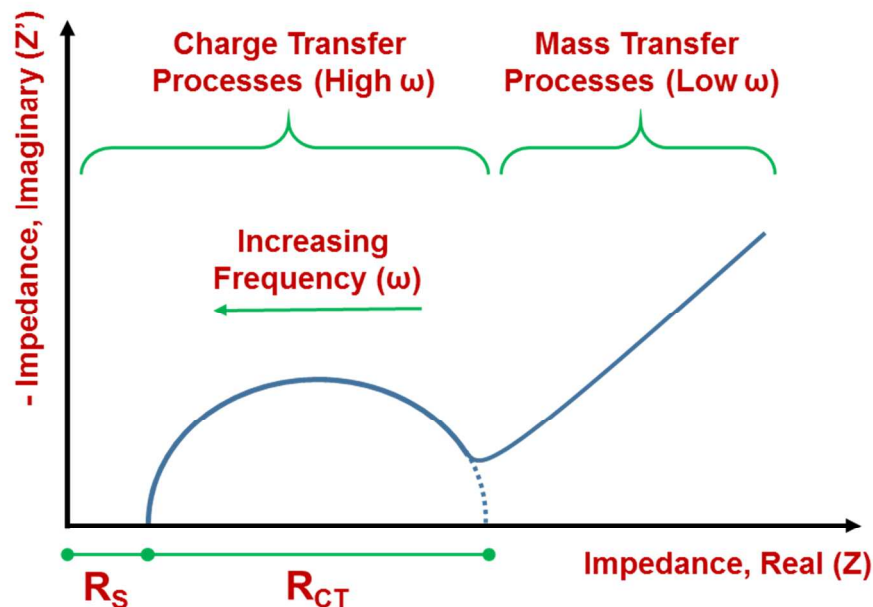


Figure S4. Theoretical Nyquist plot annotated with select parameters relevant to interpretation of the complex impedance in terms of a Randles equivalent circuit.

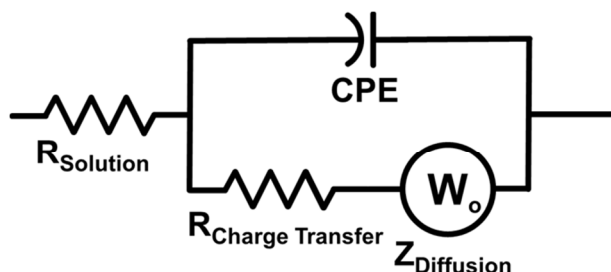


Figure S5. Randles circuit with constant phase element (CPE) in place of an ideal capacitor.

V. References

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