Supporting Information

Tuning of Electronic Properties and Rigidity in PEDOT Analogs

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Experimental

Toluene was distilled from sodium/benzophenone under an atmosphere of dry argon. In most of the column chromatographic separations, hexane and ethyl acetate were used as eluents. Columns were prepared with silica gel (60-230 mesh). All reagents were purchased from Sigma-Aldrich in reagent grade and used without purification unless noted.

Dry anhydrous acetonitrile (ACN) and propylene carbonate (PC) were purchased from Sigma-Aldrich and used as is. Tetrabutylamonium perchlorate, (TBAPC, Fluka) was dried under vacuum. Ferrocene powder (Fluka) was used as is to establish an electrochemical reference (Fc/Fc+). Ag/AgCl wire was prepared by dipping silver wire in a solution of $FeCl_3$ (0.8 g) and HCl (0.8 ml) in water (total volume, 20 ml).

Melting points were recorded on a hot-coil stage melting point apparatus (and are uncorrected) and also extracted from Differential Scanning Calorimetry (DSC) measurements (using the onset value). ^{1}H NMR and ^{13}C NMR spectra were recorded on Brücker spectrometers as a solution in ^{2}H-Chloroform with TMS as the external standard. Chemical shifts are expressed in δ units, and the ^{1}H-^{1}H coupling constant is in Hz.

Electrochemistry

All electrochemical measurements were performed using PAR Potentiostat model 263A in a standard three-electrode, one compartment configuration equipped with Ag/AgCl wire, Pt wire, and a Pt disk electrode (dia. 1.6 mm from BASi) as the pseudo reference, counter electrode and working electrode, respectively. The cyclic voltammetry (CV) experiments were performed in anhydrous acetonitrile solution with 0.1 M TBAPC as the supporting electrolyte with a scan rate of 50 mV/s. Ferrocene powder was used to establish an electrochemical internal reference at the end of each experiment as a ferrocene/ferrocenium redox couple (Fc/Fc$^+$ = 0.37 V vs saturated calomel electrode (SCE)). All electrochemical solutions were purged with dry N_2 for at least 15 minutes.

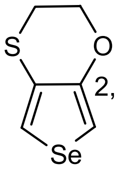
Spectroelectrochemistry

Spectra were taken in a UV-vis-NIR quartz optical cell (100-QX, Hellma) with a JASCO V-570 UV-VIS-NIR spectrophotometer. Monomers were polymerized on indium tin oxide (ITO) (5–15Ω, Delta Technologies, Stillwater) coated glass as a working electrode. Films were electrodeposited in 0.1 M TBAPC in acetonitrile or propylene carbonate (PC) (Aldrich) by CV and terminated at the stable oxidized state. Films were then washed with acetonitrile and stored till needed. Under PC/ TBAPC conditions, the Fc/Fc$^+$ standard was calibrated to be 0.34 V vs SCE.

Details of DFT calculations

All calculations were carried out using the Gaussian 03 program.[1] All molecules and polymers were fully optimized without symmetry constraints using a hybrid density functional method,[2] Becke's three-parameter exchange functional combined with the LYP correlation functional (B3LYP)[3] and with the 6–31G(d) basis set (B3LYP/6–31G(d)). The calculations for polymers were performed using Periodic Boundary Conditions (PBC) as implemented in Gaussian 03.[4] The polymer unit cell consists of two monomer units oriented anti to each other. It has been shown that band gaps predicted for conducting polymers using the hybrid B3LYP functional coupled with PBC are in excellent agreement with the experimental values.[5]

Synthesis

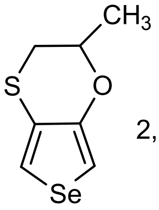


2,3-dihydroselenopheno[3,4-b]-1,4-oxathiane

2,3-dihydroselenopheno[3,4-b]-1,4-oxathiane (EOTS): 3,4-Dimethoxyselenophene[6] (2.5 mmol), 2-mercaptoethanol (15 mmol) and a catalytic amount of *p*-toluensulfonic acid (0.18 mmol) were dissolved in dry toluene (100 mL) and the resulting reaction mixture was heated at 65°C for 5–7 h. The completion of the reaction was monitored by TLC. After cooling to room temperature, the reaction mixture was diluted with 20 mL water and extracted with ether. The combined organic layers were dried over anhydrous $MgSO_4$, and the solvent was removed. The resulting oil was purified by column chromatography (hexane, ethyl acetate). Pale yellow solid (38%). ^{1}H NMR ($CDCl_3$, 500 MHz) δ 2.95-2.99 (m, 2H), 4.32-4.36 (m, 2H), 6.96 (d, 2H, J=3.1Hz, with ^{77}Se satellites, $^2J_{H\text{-}Se}$ 44 Hz), 7.29 (d, 2H, J=3.1Hz, with ^{77}Se satellites, $^2J_{H\text{-}Se}$ 44 Hz).

^{13}C NMR ($CDCl_3$, 126 MHz,) δ 24.36, 66.74, 105.47 (with ^{77}Se satellites, $^1J_{C\text{-}Se}$ 109.4 Hz), 117.95 (with ^{77}Se satellites, $^1J_{C\text{-}Se}$ 113.2 Hz), 118.03, 149.36.

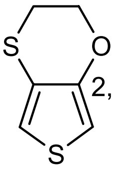
FD HRMS for C_6H_6OSSe [M+] calcd 205.9305, found 205.9294.



2,3-dihydro-2-methylselenopheno[3,4-*b*][1,4]oxathiine

MeEOTS (2Me) was prepared from 3,4-dimethoxyselenophene and 2-mercaptopropanol according to the procedure used for the preparation of **EOTS**, see above. Yield 43.9%. ^{1}H NMR ($CDCl_3$, 250 MHz) δ 1.43 (d, J=6.3 Hz, 3H), 2.72-2.92 (m, 2H), 4.26-4.32 (m, 1H), 6.93 (d, J=3Hz, 1H), 7.28(d, J=3Hz, 1H).

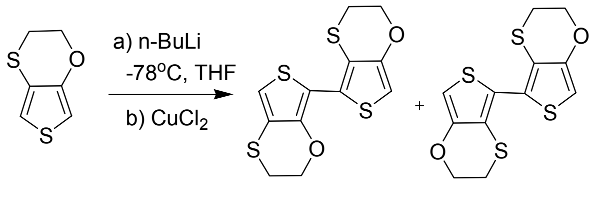
HRMS FD for C_7H_8OSSe [M+] calcd 219.9461, found 219.9453.



2,3-dihydrothieno[3,4-b]-1,4-oxathiane

2,3-dihydrothieno[3,4-b]-1,4-oxathiane (EOTT)[7]: A solution of 3,4-dimethoxythiophene (1.68 g, 11.7 mmol) with 4 equivalents of 1,2-ethylenedithiol (4.39 g, 46.6 mmol) and a catalytic amount of *p*-TSA (100 mg) in dry toluene (100 mL) was stirred for 72 h at 90°C, after which more *p*-TSA (40 mg) was added and the mixture was stirred for another 5 h at 90°C. The completion of the reaction was monitored by TLC. Toluene was removed under reduced pressure and the residue was diluted with water (60 mL). The mixture was extracted with ether (3 ×40 mL). The combined organic layers were washed with dilute $NaHCO_3$ solution and brine and then concentrated. Purification of the crude residue by chromatography on silica gel (hexane: EtOAc = 10:0.05). Yield 72 %. ^{1}H NMR ($CDCl_3$, 250 MHz) δ 2.99–3.02 (m, 2H), 4.35–4.39 (m, 2H), 6.45 (d, J=3.5 Hz, 1H), 6.72 (d, J=3.5 Hz, 1H). ^{1}H NMR spectra match the previously reported[7] data.

bis-2,3-dihydrothieno[3,4-b]-1,4-oxathiane (bis-EOTT)



7a **7b**

To a stirred solution of 1.4 g (8.8 mmol) **EOTT** in 50 mL of THF was added 7.9 mL (12 mmol) *n*-BuLi at -78 °C. The mixture was stirred at -78 °C for 45 min, then copper chloride (1.67g, 12 mmol) was added and stirring continued for 1 h at -78 °C, then for 2h at room temperature. The solution was poured out into water and extracted with dichloromethane (3 × 50 mL). The combined organic layers were dried over magnesium sulfate, filtered and evaporated. Purification of the residue by flash chromatography on silica gel (elution with hexane:ethyl acetate = 10:0.05) afforded **bis-EOTT** as an inseparable mixture of at least two isomers detected by ^{1}H NMR. The third possible isomer (in which the sulfur atoms point outside the inter-ring bond) was not detected by ^{1}H NMR. Yield 4.3% (60 mg). **7a**:**7b** = 77:23.

^{1}H NMR($CDCl_3$, 250 MHz). δ (**7a**) 3.0-3.07 (m, 4H), 4.37-4.40 (m, 2H), 4.48-4.51 (m, 2H), 6.44 (s, 1H), 6.75 (s, 1H). (**7b**) 3.0-3.07 (m, 4H), 4.37-4.40 (m, 4H), 6.52 (s, 2H).

^{13}C NMR ($CDCl_3$, 100.6 MHz) δ (**7a**) 23.46, 24.25, 65.68, 66.34, 101.61, 113.79. (**7b**) 23.93, 65.62, 102.76. Signals of either **7a** or **7b**: 113.77, 116.64, 116.66, 123.44, 123.46, 127.57, 145.55, 148.42, 148.44.

MS (ESI): $[M+H]^+$, 315.22.

We note that because of its disorder, the X-ray structure of **7** can be refined in a centrosymmetrical space group P21(note: 1 in subscript)/c and not in any of the noncentrosymmetrical space groups. This enforces some constraints and does not allow us to distinguish the isomer composition of crystals of **7**.

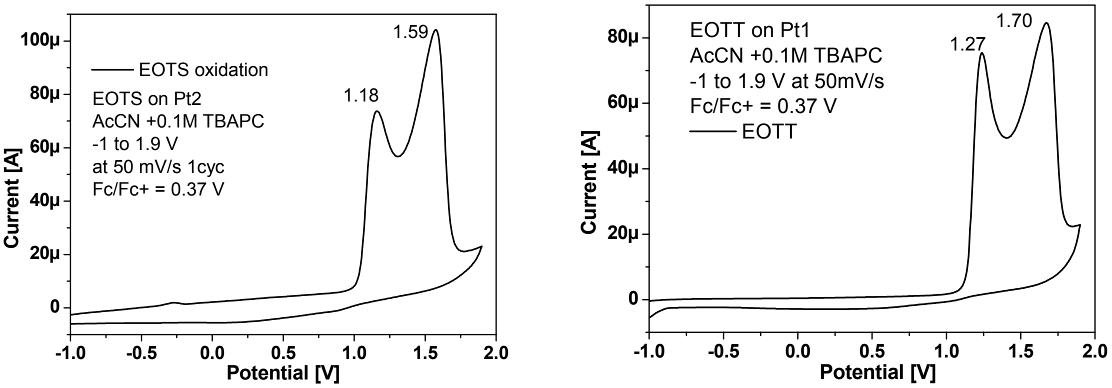


Figure S1. Cyclic voltammetry of monomers **EOTS 2** and **EOTT 5** in acetonitrile with 0.1M TBAPC at 50 mV/s on Pt electrode vs. Ag|AgCl wire, Fc/Fc$^+$ = 0.37 V. Monomer concentration corresponds to 2uL of monomer in 3mL of solvent.

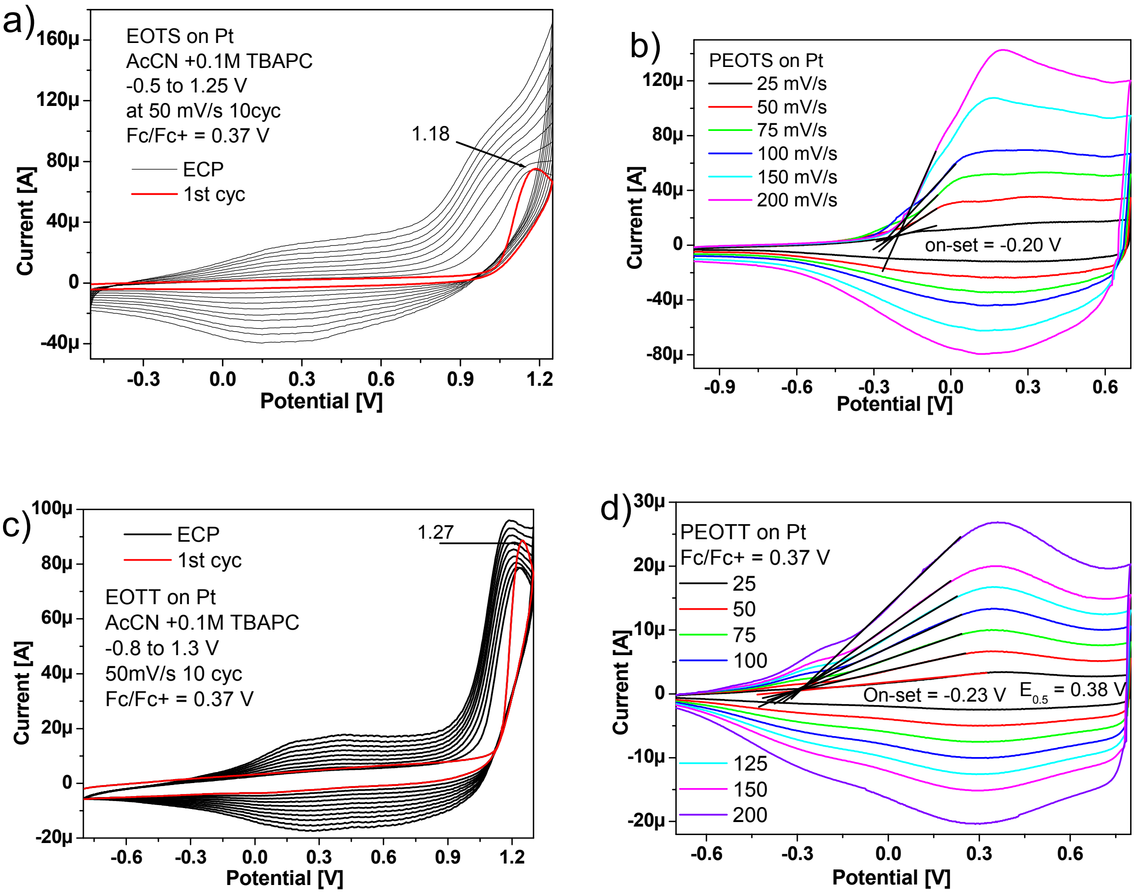


Figure S2. Cyclic voltammograms of (a and b) **EOTS 2** and (c and d) **EOTT 5**. (a and c) Electropolymerization and (b and d) the obtained polymers on Pt electrodes in monomer free solution at ranging scan rates 25-100 mV/s. Performed in ACN +0.1M TBAPC on Pt electrode vs. Ag|AgCl wire, $Fc/Fc^+ = 0.37$ V.

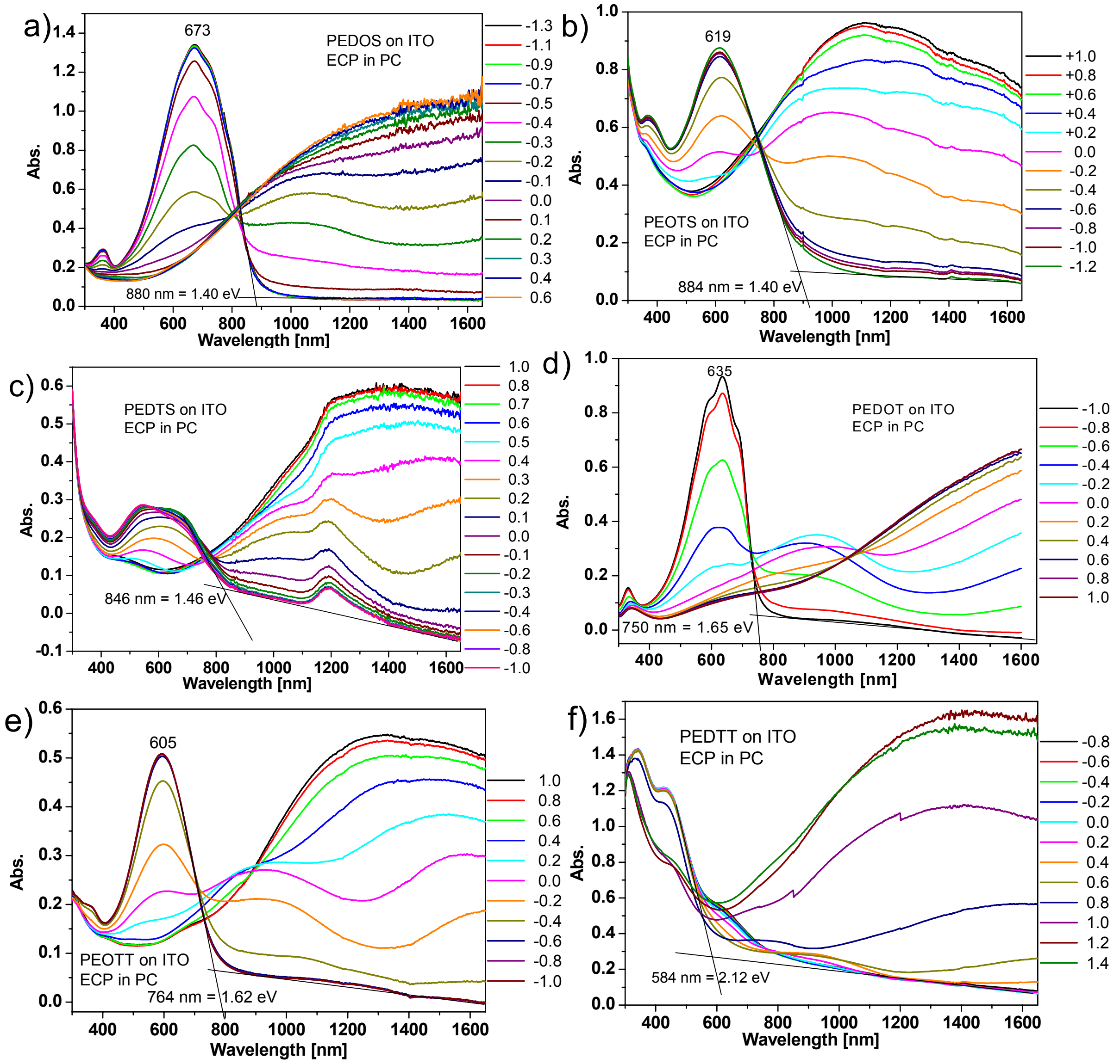


Figure S3. Spectroelectrochemistry of polymers **1–6** electropolymerized in propylene carbonate on ITO glass electrodes, (a) **PEDOS P1**, (b) **PEOTS P2,** (c) **PEDTS P3**, (d) **PEDOT P4**, (e) **PEOTT P5**, (f) **PEDTT P6**. The spectra were recorded under a constant potential and a N_2 atmosphere.

Table S1. Experimental (in PC) HOMO level energies for polymers **1–6** obtained using the Koopmann approximation for the ionization energy by E (HOMO) = E_{onset} + 4.4 (eV), where 4.4 eV is the ionization energy of an SCE electrode. Experimental values for the LUMO levels obtained using $E_{(LUMO)}$ = $E_{(HOMO)}$ + Eg($_{exp.}$). The experimental optical band gap obtained from the onset of the UV-vis absorption peak.

Polymer	HOMO	LUMO	E_g Exp.
PEDOS P1	-3.76	-2.36	1.40
PEOTS P2	-4.20	-2.80	1.40
PEDTS P3	-4.67	-3.21	1.46
PEDOT P4	-4.05	-2.40	1.65
PEOTT P5	-4.17	-2.55	1.62
PEDTT P6	-4.86	-2.74	2.12

Table S2. Absolute energies (per unit cell, which includes 2-monomers) for polymers calculated at PBC/B3LYP/6-31G(d).

Name	Twist Angle	Energy (Hartree)
PEDOT	0	-1559.310538
PEDOT	15	-1559.309280
PEDOT	30	-1559.305914
PEDOT	45	-1559.301572
PEDOT	60	-1559.297522
PEDOT	75	-1559.293996
PEDOT	90	-1559.290652
PEOTT	0	-2205.263528
PEOTT	15	-2205.262771
PEOTT	30	-2205.260937
PEOTT	45	-2205.258623
PEOTT	60	-2205.256358
PEOTT	75	-2205.254009
PEOTT	90	-2205.251398
PEDTT	0	-2851.195656
PEDTT	15	-2851.199392
PEDTT	30	-2851.201549
PEDTT	45	-2851.201830
PEDTT	60	-2851.202920

PEDTT	75	-2851.202983
PEDTT	90	-2851.202145
PEDOS	0	-5561.701690
PEDOS	15	-5561.699739
PEDOS	30	-5561.694714
PEDOS	45	-5561.688157
PEDOS	60	-5561.682490
PEDOS	75	-5561.677565
PEDOS	90	-5561.673061
PEOTS	0	-6207.654566
PEOTS	15	-6207.653141
PEOTS	30	-6207.649459
PEOTS	45	-6207.646052
PEOTS	60	-6207.644074
PEOTS	75	-6207.641298
PEOTS	90	-6207.637437
PEDTS	0	-6853.5946174
PEDTS	15	-6853.5934125
PEDTS	30	-6853.5901472
PEDTS	45	-6853.5932512
PEDTS	60	-6853.5952272
PEDTS	75	-6853.5948146
PEDTS	90	-6853.5922316

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