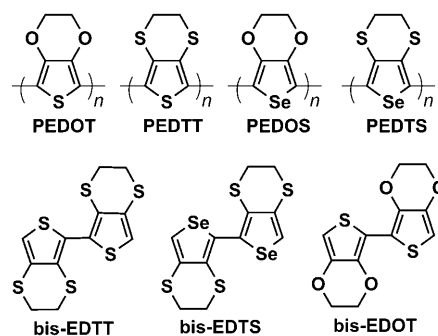


Controlling Rigidity and Planarity in Conjugated Polymers: Poly(3,4-ethylenedithioselenophene)**

Yair H. Wijsboom, Asit Patra, Sanjio S. Zade, Yana Sheynin, Mao Li, Linda J. W. Shimon, and Michael Bendikov*

Conjugated oligomers and polymers^[1,2] attract considerable interest owing to their application in photovoltaic cells,^[3,4] organic light-emitting diodes (OLEDs),^[5,6] organic field-effect transistors (OFETs),^[7] and electrochromic devices.^[8] Generally, planarity and good conjugation are required so that organic materials can achieve band gaps in the semiconductor region, high conductivity, high mobility, and an electrooptical response. Polythiophenes are among the most promising and best-studied conducting polymers.^[1,2] However, even parent bithiophene is not planar in the gas phase (according to both experiment and theory),^[9] and crystal packing forces are responsible for the planarity of oligothiophenes in the solid state.^[10] Various small substituents (such as two adjacent alkyl chains on the same or neighboring rings: 3,4 or 3,3'-substitution) cause oligothiophene to become nonplanar, and the availability of oligo- and polythiophenes with substituents that do not disturb planarity is very limited (for example, poly(3-hexylthiophene) is planar).^[10,11] Although twisting of the oligothiophene backbone requires very little energy, it results in a significant increase in the HOMO–LUMO gap.^[12] The fact that small conformational changes to conjugated polymers may produce large band-gap effects has been utilized in the development of polythiophene-based sensors.^[13,14]

Poly(3,4-ethylenedioxythiophene) (PEDOT)^[15] has many advantages over other conducting polymers in organic electronics applications. However, it cannot be applied as a light-absorbing donor in organic solar cells, for example,



owing to its very low oxidation potential and, consequently, very low work function. PEDOT is believed to be planar; however, its analogue, poly(3,4-ethylenedithiothiophene) (PEDTT),^[16–20] in which oxygen atoms are replaced by sulfur atoms, is assumed to be twisted, as manifested by its significantly wider band gap (2.2 eV for PEDTT vs. 1.6 eV for PEDOT).^[18,21] Indeed, the dimer of 3,4-ethylenedithiothiophene (bis-EDTT) has an inter-ring twist angle of 45°,^[18] whereas bis-EDOT has a planar structure in the solid state.^[17,18,20,22,23]

Recently, we obtained the first conductive polyselenophene, poly(3,4-ethylenedioxysephenophene) (PEDOS), which has a relatively narrow band gap and excellent electrochromic properties.^[24,25] Synthesis of stable and conductive PEDOS enables the development of applications of polyselenophenes as organic electronic materials. Designing such materials demands the identification of more rigid conjugated systems capable of bearing various substituents on their backbone whilst retaining their planarity. Herein, we report that the range of substituents that polyselenophenes can bear whilst still maintaining their planarity is wider than that of polythiophenes, and is mostly due to the more rigid backbone of the polyselenophenes. Poly(3,4-ethylenedithiosephenophene) (PEDTS) has a significantly narrower optical band gap (0.6–0.8 eV) than PEDTT, which can be attributed to its planarity. Moreover, PEDTS is a conducting polymer that is not as electron-rich as PEDOS and PEDOT. The top of the valence band of PEDTS is about 0.7 eV (0.64 eV experimental, 0.81 eV calculated) lower than that of PEDOT, which makes PEDTS a very attractive material for organic solar cell applications.

The energy required to twist around inter-ring bonds in decaselephenene is small; however, it is notably greater (by a factor of 1.2–1.8; Supporting Information, Figure S7)^[26] than in decathiophene. Twisting to a 60° inter-ring dihedral angle requires only 2.6 kcal mol^{–1} per inter-ring bond for decaselephenene (2.1 kcal mol^{–1} for decathiophene) and twisting to a

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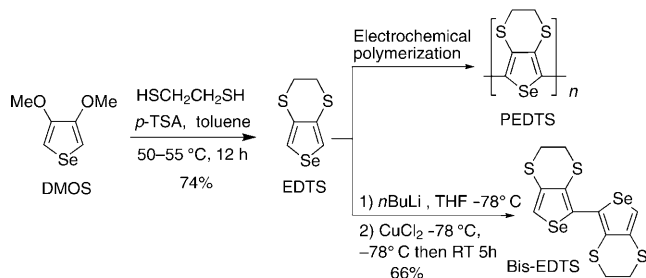
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30° inter-ring angle requires only 0.5 kcal mol⁻¹ per inter-ring bond for decaselenophene (0.3 kcal mol⁻¹ for decathio-phenene).^[12] These calculations suggest that twisting of oligoselenophenes and polyselenophenes requires more energy than for their thiophene analogues, and they should maintain planarity with a wider range of substituents.^[26,27] We decided to test this computational prediction by synthesizing bis-EDTS and PEDTS and comparing them to their sulfur analogues, bis-EDTT and PEDTT.

The synthesis of EDTS (Scheme 1) was accomplished in 74% yield by transesterification of 3,4-dimethoxyselenophene (DMOS)^[24] with an excess of 1,2-ethanedithiol at 55 °C



Scheme 1. Synthesis of EDTS, PEDTS, and bis-EDTS. *p*-TSA = *p*-toluenesulfonic acid.

in the presence of a catalytic amount of *p*-toluenesulfonic acid (*p*-TSA).^[28] Bis-EDTS was obtained in 67% yield by lithiation of EDTS followed by an oxidative coupling reaction with CuCl₂ (Scheme 1). Bis-EDTS crystals were grown from chloroform; examination of the crystal structure of bis-EDTS (Figure 1) revealed that it has a planar structure around the inter-ring C–C bond. This result is in agreement with our calculations, but in complete contrast to the crystal structure of bis-EDTT,^[18] which is strongly twisted by 45° around the inter-ring C–C bond.^[29]

The differences in planarity observed between the dimers are emphasized even more strongly in the polymers. Electrochemical polymerization of EDTS was performed by

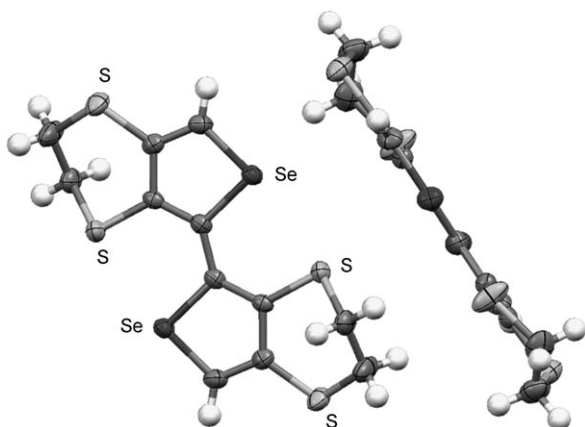


Figure 1. Crystal structure of bis-EDTS, showing two independent molecules in the unit cell; both are planar. Thermal ellipsoids are set at 50% probability.

repeated cyclic voltammetry scans in anhydrous acetonitrile solution with 0.1 M tetra-*n*-butylammonium perchlorate (TBAPC) electrolyte at 50 mV s⁻¹ on either Pt or ITO (indium tin oxide) electrodes (Figure 2, and Supporting Information, Figure S2) to produce an insoluble film.^[30] The

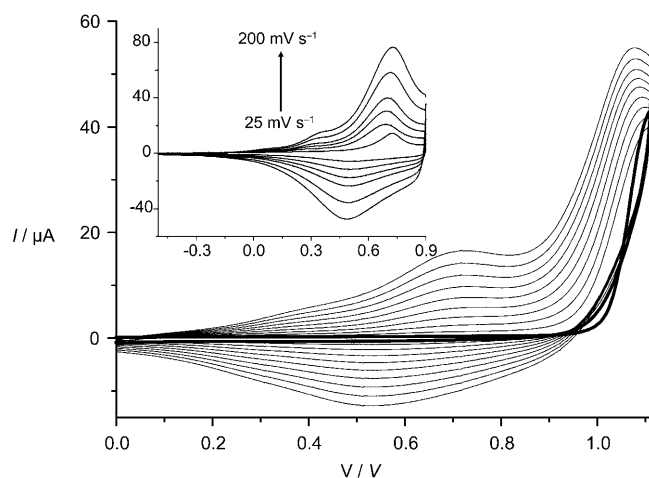


Figure 2. Cyclic voltammograms of the electropolymerization of EDTS on a Pt working electrode in acetonitrile, with 0.1 M TBAPC, 0 to 1.12 V, at 50 mV s⁻¹ for 10 cycles (first cycle shown bold). Inset: Cyclic voltammogram of PEDTS in monomer-free acetonitrile solution at sweep rates of 25, 50, 75, 100, 150, and 200 mV s⁻¹ (vs. Ag|AgCl wire, Fc/Fc⁺ = 0.37 V).

polymer obtained on the Pt electrode has a redox potential of 0.65 V, with an on-set at 0.20 V vs. Ag|AgCl wire calibrated using Fc/Fc⁺ = 0.37 V (Table 1). PEDTT was obtained by

Table 1: Experimental and calculated data for polymers.^[a]

Polymer	Polymer onset [V]	Polymer λ_{max} [nm]	Optical E_g [eV]	HOCO ^[b] [eV]	LUCO ^[c] [eV]	E_g calcd [eV]
PEDTS	0.20	ca. 610 ^[d]	1.4	−4.33 ^[e]	−2.50 ^[e]	1.83 ^[e]
PEDTT	0.43	341, 426	2.0	−4.10 ^[e] −4.91 ^[f]	−2.05 ^[e] −1.78 ^[f]	2.06 ^[e] 3.13 ^[f]
PEDOS	−0.64	673	1.4	−3.44	−1.79	1.66
PEDOT	−0.44	635	1.6	−3.52	−1.68	1.84

[a] Calculated at the PBC/B3LYP/6-31G(d) level. Data for PEDOS and PEDOT are taken from Ref. [24]. E_g = band-gap energy. [b] Highest occupied crystal orbital from PBC calculations. [c] Lowest unoccupied crystal orbital. [d] Broad peak from 500 to 700 nm. [e] Planar, 180°. [f] Twisted, 111.6°.

electropolymerization of EDTT under similar conditions (Supporting Information, Figures S3–S5). The electrochemically determined HOMO energies for PEDOT, PEDOS, and PEDTS (obtained from the on-set of their oxidation potentials from Table 1 by assuming that a zero potential in electrochemical measurements corresponds to a HOMO level of −4.8 eV) are −4.0, −3.8, and −4.6 eV, respectively.

Spectroelectrochemical data for PEDTS and PEDTT obtained on an ITO electrode are shown in Figure 3 and in the Supporting Information, Figure S6, respectively. PEDTS has

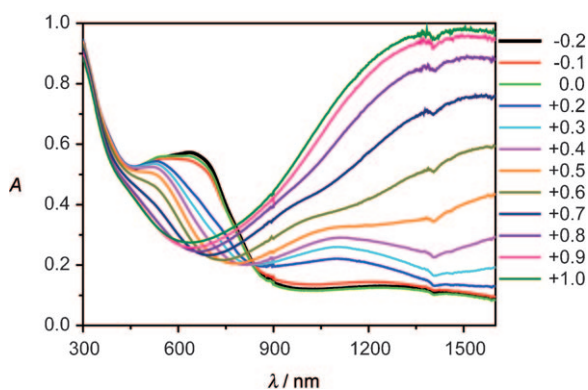
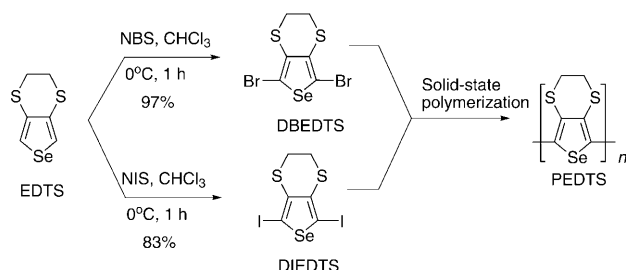


Figure 3. Spectroelectrochemistry of a PEDTS thin film, prepared on ITO-coated glass, as a function of applied potential between -0.2 to 1.0 V in propylene carbonate (vs. $\text{Ag}|\text{AgCl}$ wire, $\text{Fc}/\text{Fc}^+ = 0.34$ V).

a very broad and shallow peak between 500 to 700 nm, which is in contrast to the sharp peak with a well-defined λ_{max} of PEDOS.^[24] This result can be explained by the superposition of several absorption peaks resulting from planar and twisted fragments of the polymer chain. The spectroelectrochemically measured band gap of PEDTS (assigned as the onset of the π – π^* transition) is 1.43 eV (870 nm), and λ_{max} is (610 ± 30) nm. The spectroelectrochemically measured band gap of PEDTT (Supporting Information, Figure S6)^[26] is 2.0 eV, which is somewhat smaller than the previously reported value of 2.2 eV,^[18] and which is significantly larger than that of PEDTS.

Chemical polymerization of EDTS was performed using the solid-state polymerization method,^[24,31] which requires mild polymerization conditions. 2,5-Dibromo-3,4-ethylenedithioselenophene (DBEDTS) was easily polymerized within 24 h under slight heating at 50 °C (Scheme 2). The resulting



Scheme 2. Synthesis of DBEDTS and DIEDTS and their solid-state polymerization. NBS = *N*-bromosuccinimide, NIS = *N*-iodosuccinimide.

bromine-doped PEDTS is completely insoluble in common organic solvents. Similarly, 2,5-diiodo-3,4-ethylenedioxysele-nophene (DIEDTS) polymerized within 3 days at 110 °C. White crystals of DBEDTS slowly transformed to black crystals with a metallic luster that retained the morphology of the starting material. However, SEM analysis of solid-state polymerized PEDTS showed that the structure of the crystal was destroyed by the release of bromine or iodide (Figure 4). Moreover, the surface of solid-state polymerized PEDTS shows a granulated surface, rather than the flattened cauliflower or spiked surface obtained from PEDOT^[31] and PEDOS,^[24] respectively. Interestingly, PEDTS obtained

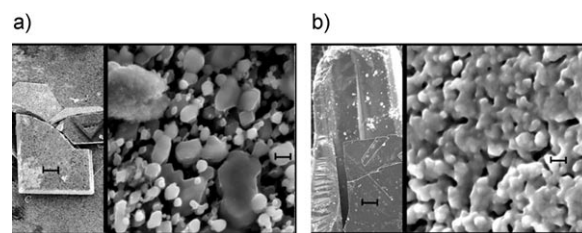


Figure 4. SEM images of the surface of PEDTS obtained by solid-state polymerization of a) DBEDTS and b) DIEDTS. Scale bars in each pair of images: left, 20 μm ; right, 200 nm.

from the bromine derivative (Figure 4a) is more granulated than the iodine product (Figure 4b). The as-obtained powder from PEDTS has a high conductivity of about 3 Scm^{-1} measured with a two-probe pressed-pellet setup, which is similar to the conductivity of PEDOS^[24] measured under similar conditions.^[32] For comparison, chemically prepared PEDTT has a significantly lower conductivity of 0.1 Scm^{-1} .^[16] The as-prepared polymer from DIEDTS (which includes iodine as a dopant) has a conductivity (measured in a pressed pellet) of about $3\text{--}4 \text{ Scm}^{-1}$.

The greater degree of planarity for EDTS derivatives compared to EDTT derivatives is further supported by DFT calculations.^[33] The B3LYP/6-31G(d) calculated structure of bis-EDTT includes an 80–83° twist around the central C–C bond, which depends on the conformation of the ethylenedithio ring.^[26,34] The symmetry-constrained planar structure (C_i symmetry) of bis-EDTT is not a minimum, but rather a first-order saddle point lying above the twisted structure by 3.6–4.2 kcal mol^{-1} , depending on the conformation of the ethylenedithio ring. Replacing the two thiophene rings with selenophene rings results in major conformational changes. The B3LYP/6-31G(d) calculated structure of bis-EDTS is planar around the central C–C bond. Other conformations of bis-EDTS also exist, with energies of -1.9 and $+0.1 \text{ kcal mol}^{-1}$ and twisting angles of 52° and 66°.^[26] This energy difference between the twisted and planar conformations of bis-EDTS is in the order of magnitude of crystal packing energy. Therefore, our calculations support the experimental finding that bis-EDTS packs in the planar conformation in the solid state, whereas bis-EDTT is heavily twisted in the crystalline state (see above).^[35]

The energy of the planar conformation of PEDTT lies higher than the twisted one by 2.33 kcal mol^{-1} per ring, or 4.66 kcal mol^{-1} per unit cell.^[36] The band gap of the twisted conformation is significantly wider (by 1.07 eV) than that of the planar conformation. The energy difference between the planar and twisted PEDTS conformers is only 0.27 kcal mol^{-1} per ring (0.54 kcal mol^{-1} per unit cell), which is in the range of crystal-packing forces. Therefore, polymer chains of PEDTS should exhibit flexible behavior. However, the band-gap difference between these planar and twisted structures is 1.09 eV. In the solid state, PEDTS should prefer the planar structure (although some nonplanar backbone fragments are also observed, as evidenced by broad absorption peak in UV/Vis spectrum), whereas PEDTT will remain twisted. As the planarization energy for PEDTT is already close to the range of crystal-packing forces, polymer regions with planar and

twisted fragments are expected, and PEDTT may also exhibit flexible behavior. Indeed, the additional, and previously unreported, shoulder at around 613 nm^[26] observed in the absorption spectra of PEDTT might originate from polymer fragments having a planar structure (see the Supporting Information, Figure S6, and the discussion therein). The calculated band gap E_g of planar PEDTS (Table 1; 1.83 eV) is somewhat wider than that of PEDOS (1.66 eV).^[24] However, performing a similar comparison between the calculated band gaps of PEDOT and PEDTT^[22] yields a much larger difference between their band gaps, which are 1.83 eV for PEDOT and 3.13 eV for twisted PEDTT (2.06 eV for planar PEDTT).^[37] The calculated HOCO (highest-occupied crystal orbital) values for PEDOT, PEDOS, and PEDTS (in its lowest energy planar conformation) are -3.52, -3.44, and -4.33 eV, respectively; these values are in agreement with the electrochemically determined HOMO energies. Therefore, based on both experimental and calculated results, the work function of PEDTS is expected to be about 0.6–0.8 eV lower than that of PEDOT, which makes PEDTS derivatives attractive polymers for organic solar cells.

Herein we have shown that oligo- and polyselenophenes can maintain planarity and a low band gap with substituents that cause their oligo- and polythiophene analogues to adopt a strongly twisted conformation. Polyselenophenes may be an excellent choice for controlling planarity in conjugated polymers; more substituents can be introduced onto their backbones than onto those of their thiophene analogues without reducing the extent of conjugation. Although PEDTS obtained herein is analogous to PEDTT, PEDOS, and PEDOT that were previously reported, it has a unique combination of relatively low band gap, conductivity, planarity, and relatively high oxidation potential. Additional work is underway to explore the advantages bestowed by the planarity of polyselenophenes and to obtain soluble derivatives of PEDTS for solar-cell applications.

Experimental Section

Detailed experimental procedures for monomer syntheses and their characterization are given in the Supporting Information.

All electrochemical measurements were performed in a standard three-electrode setup in anhydrous acetonitrile solution with 0.1M tetra-*n*-butylammonium perchlorate (TBAPC) as the supporting electrolyte. All results, under these conditions, were calibrated to $\text{Fc}/\text{Fc}^+ = 0.37$ V.

Spectroscopic data were recorded with a JASCO V-570 UV/Vis-NIR spectrophotometer. Monomers were polymerized on ITO-coated glass ($5\text{--}12\ \Omega\ \square^{-1}$), which served as the working electrode ($\text{Fc}/\text{Fc}^+ = 0.34$ V).

EDTS: A solution of 3,4-dimethoxyselenophene (250 mg, 1.30 mmol) with 5 equivalents of 1,2-ethylenedithiol (610 mg, 6.5 mmol) and a catalytic amount of *p*-TSA (50 mg) in dry toluene (60 mL) was stirred for 12 h at 55–60 °C. The completion of the reaction was monitored by thin-layer chromatography (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) gave EDTS (200 mg, 74%) as a low-melting white crystalline solid. M.p.

47–48 °C; ^1H NMR (250 MHz, CDCl_3): $\delta = 7.62$ (s, 2H), 3.18 ppm (s, 4H); ^{13}C NMR (62.5 MHz, CDCl_3): $\delta = 127.3$, 122.3, 28.6 ppm; ^{77}Se NMR (CDCl_3): $\delta = 586.9$ ppm. HRMS for $\text{C}_6\text{H}_6\text{S}_2\text{Se}$ [M^+] calcd 221.9076, found 221.9076.

bis-EDTS: *n*-Butyllithium (1.6M in hexane, 0.28 mL, 0.45 mmol) was added over a period of 5 min to a stirred solution of 3,4-ethylenedisulfanylselenophene (EDTS; 90 mg, 0.4 mmol) in THF (10 mL) at -78 °C under a dry N_2 atmosphere. The reaction mixture was then slowly warmed to room temperature. After additional stirring for 30 min at room temperature, the solution was cooled to -78 °C, CuCl_2 (65 mg, 0.48 mmol) was added, and stirring was continued overnight. The reaction mixture was quenched with H_2O (40 mL) and the resulting aqueous layer was extracted with chloroform (3 × 20 mL). The combined organic extracts were washed with brine, dried (MgSO_4), and concentrated. The crude product was purified by column chromatography on silica gel (4% ethyl acetate/hexane) to provide bis-EDTS (60 mg, 66%) as a light yellow crystalline solid. M.p. > 200 °C; ^1H NMR (250 MHz, CDCl_3): $\delta = 7.74$ (s, 2H), 3.19 ppm (s, 8H); ^{13}C NMR (125 MHz, CDCl_3): $\delta = 131.8$, 128.2, 128.2, 124.1, 28.8, 28.1 ppm; ^{77}Se NMR (CDCl_3): $\delta = 636.1$ ppm. X-ray-quality crystals were obtained from a CHCl_3 solution.^[26] CCDC 714899 contains the supplementary crystallographic data for this paper. These data can be obtained free of charge from the Cambridge Crystallographic Data Centre via www.ccdc.cam.ac.uk/data_request/cif.

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- [35] It was suggested that attractive S···O interactions are responsible for the planar structure of bis-EDOT, whereas repulsive S···S interactions are responsible for twisting in bis-EDTT.^[18] It is very difficult to differentiate between steric effects (which result from the larger radius of sulfur vs. oxygen) and electronic effects, and we did not find any evidence from NBO analyses of significant S···O or Se···S interactions in bis-EDOT and bis-EDTS, respectively.
- [36] All calculations for polymers were performed at the PBC/B3LYP/6-31G(d) level of theory.
- [37] The PBC/B3LYP/6-31G(d) calculations overestimate the band gap for PEDOT and PEDOS derivatives by 0.2–0.4 eV.