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Effect of Structural Factor on the Electropolymerization of Bithiophenic Precursors Containing a 3,4-Ethylenedisulfanylthiophene Unit

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ABSTRACT: A series of bithiophenes based on bis(3,4-alkylenedisulfanylthiophene) and hybrid systems associating 3,4-ethylenedisulfanylthiophene (EDST) with thiophene or 3,4-ethylenedioxythiophene (EDOT) moieties have been synthesized. The molecular structures of these systems are characterized by X-ray diffraction and theoretical geometric optimization. Although bis(alkylenesulfanylthiophenes) present a large dihedral angle between the thiophene cycles, for the hybrid systems the steric hindrance to coplanarity is counterbalanced by the development of intramolecular S⋯S and S⋯O interactions. Dramatic structural change from twisted to planar conformation of bis(3,4-ethylenedisulfanylthiophene) is observed when the dimer is associated with TCNQ. The electronic properties of the dimers, analyzed by UV−vis spectroscopy, cyclic voltammetry, and theoretical calculations, are discussed in relation with the molecular structure of the bithiophenes. Finally, the analysis of the electrogenerated polymers confirm the key role of the electronic and self-structuring effects for enhancing the planarity of the conjugated systems and for controlling the gap of the polymers. Thus, the precursor combining EDST and EDOT units shows the lowest oxidation potential and leads to a polymer presenting a lower band gap than those of the two polymers derived from the pure EDOT or EDST dimers.

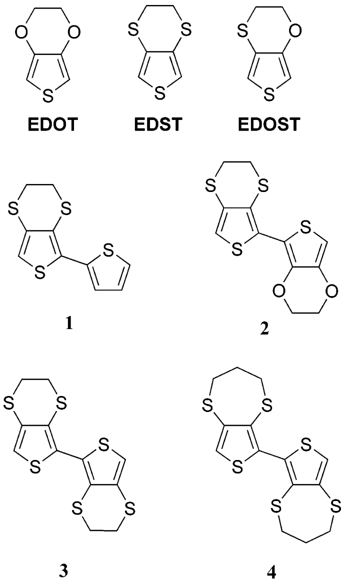
Introduction

The considerable research activity developed around functional polymeric and molecular π-conjugated systems based on 3,4-ethylenedioxythiophene (EDOT)[1,2] has generated a strong interest for the chemistry of conjugated systems based on 3,4-disubstituted heterocycles.[1−7] Among them 3,4-ethylenedisulfanylthiophene (EDST), namely the sulfur analogue of EDOT, presents some interesting features such as a lower oxidation potential than EDOT combined with the well-known propensity of sulfur to contribute to 3D organization of the materials through intermolecular interactions.[7]

The synthesis of poly(EDST) by electropolymerization or chemical oxidation has been reported 10 years ago by Kanatzidis et al.[8] More recently, Skabara et al. described the formation of poly(EDST) by heating crystal of 2,5-dibromo-3,4-ethylenedisulfanylthiophene.[9] Although EDST is oxidized at a lower potential than EDOT, this difference is no longer observed for the polymers and poly(EDST) presents a higher oxidation potential and larger band gap than PEDOT due to the distortion of the π-conjugated chain caused by steric interactions between adjacent EDST moieties.

As already shown by our group, a first possible solution to reduce this steric hindrance to planarity involves replacement of one sulfur atom by oxygen in thieno[3,4-*b*]-1,4-oxathiane EDOST.[10] In fact, the resulting polymer, poly(EDOST), shows oxidation potential and band gap intermediate between those of poly(EDST) and poly(EDOT). Another possible solution involves the synthesis of hybrid systems in which EDST is associated with less sterically demanding building blocks. Thus, Skabara and co-workers have synthesized a terthiophene with a median EDST ring and shown that the resulting polymer has lower oxidation potential and smaller band gap than poly(EDST).[11]

Chart 1



We have shown already that in addition to strong electron-donor properties EDOT possess a strong propensity to give rise to noncovalent intramolecular sulfur−oxygen interactions which result in a self-rigidification of the conjugated structure in which it is incorporated.[2,12] To investigate the interplay of steric interactions and constructive intramolecular interactions on the structure and properties of EDST-based conjugated systems, we report here the synthesis of the bithiophene systems **1**−**4** (Chart 1) and the analysis of their potential use as precursors of electrogenerated conjugated polymers.

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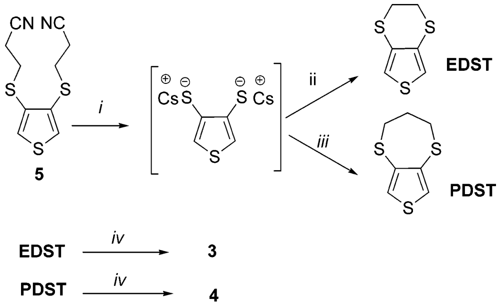
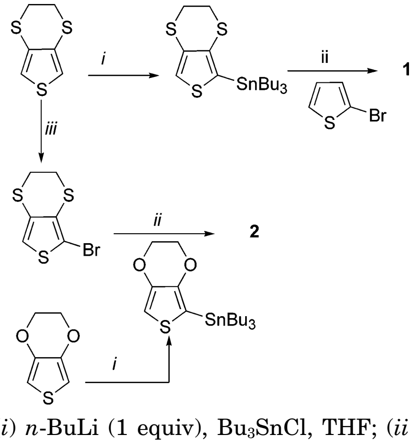
Scheme 1. Synthesis of Edstand PDST and Their Symmetrical Dimers 3 and 4[a]



[a] Key: (*i*) CsOH,H_2O (2 equiv), MeOH; (*ii*) $BrCH_2CH_2Br$ (1 equiv); (*iii*) $BrCH_2CH_2CH_2Br$ (1 equiv); (*iv*) *n*-BuLi (1 equiv), $CuCl_2$.

Scheme 2. Synthesis of the Unsymmetrical Dimers 1 and 2[a]



[a] Key: (*i*) *n*-BuLi (1 equiv), Bu_3SnCl, THF; (*ii*) $Pd(PPh_3)_4$ (5% mol), toluene; (*iii*) NBS (1 equiv), $CHCl_3$.

Results and Discussion

EDST and 3,4-propylenedisulfanylthiophene (PDST) have been synthesized from 3,4-bis(2-cyanoethylsulfanyl)thiophene, **5** (Scheme 1).[13] Alkylation of 3,4-thiophenedithiolate, readily obtained by treatment of **5** with CsOH, and 1,2-dibromoethane or 1,3-dibromopropane led to EDST and PDST in 70% and 60% yield, respectively. Then bis-EDST (**3**) and bis-PDST (**4**) were obtained in 50% and 60% yields, respectively by oxidative coupling of the lithiated derivatives in the presence of $CuCl_2$.

The unsymmetrical compounds **1** and **2** were synthesized by Stille coupling (Scheme 2). The stannic derivative of EDST obtained by the sequence BuLi/$ClSnBu_3$, was reacted with 2-bromothiophene in the presence of $Pd(PPh_3)_4$ to afford **1** in 65% yield. The monobrominated derivatives of EDOT and EDST being difficult to obtain, the stannic derivative of EDOT was reacted with a mixture of mono and dibromo-EDST obtained by treatment of EDST with 1 equiv of NBS. The target molecule **2** was then obtained in 30% yield and it is noteworthy that no tricyclic system has been isolated.

Crystallographic Structures. Single crystals of **2**, **3**, and **4**, obtained by slow evaporation of chloroform-ethanol solutions, have been analyzed by X-ray diffraction. Bis-PDST (**4**) crystallizes in the orthorhombic *Fdd*2 space group, and the structure defined from a half molecule is presented in Figure 1. The two thiophene rings form a dihedral angle of 73° and the length of the thiophene−thiophene single bond (1.48 Å) is larger than for bis-EDOT (1.44 Å) in which the two thiophene are coplanar. The S(1)−S(2) distance (3.63 Å) corresponds to twice the van der Waals radius of sulfur atoms (3.60 Å).

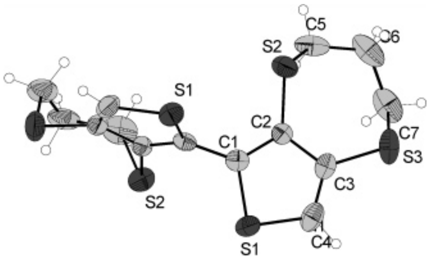


Figure 1. ORTEP view of bis-PDST (**4**).

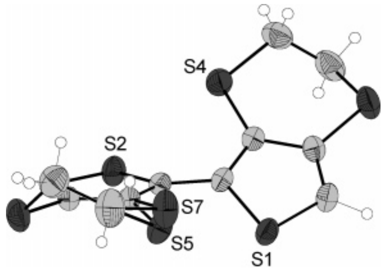


Figure 2. ORTEP view of bis-EDST (**3**).

Bis-EDST (**3**) crystallizes in the orthorhombic *Pbca* space group. As shown in Figure 2, a sulfur atom of the ethylenedisulfanyl groups adopts two different positions, each with a 50% occupancy. The dihedral angle between the two thiophene rings (45°) is smaller than for compound **4** while the intercycle single bond is shorter (1.46 Å). The S(2)−S(4) and S(1)−S(5) distances (3.23 and 3.26 Å respectively) are slightly shorter than twice the van der Waals radius of sulfur suggesting weak S- - -S interactions.

These results show that, as expected, the smaller overall dimensions of the ethylenedisulfanyl group compared to the propylenedisulfanyl one limits steric interactions, thus allowing a better effective conjugation and the development of weak intramolecular interactions.

Compound **2** crystallizes in the monoclinic P1a1 space group and presents cell parameters close to those observed for bis-EDOT.[14] However, the bulkier sulfur atoms result in a larger cell volume (657.1(4) vs (589.1(5) Å^3 for bis-EDOT). Although the low quality of the crystal of **2** did not allow a high degree of resolution, the analysis of the structure was precise enough to show that the two thiophene rings adopt a planar anti conformation.

Compounds **2** and **3** give dark blue complexes with tetracyanoquinodimethane (TCNQ) whereas no complex formation was observed with **1** and **4**. Single crystals of **3-TCNQ** crystallize in the P-1 triclinic space group, the structure defined from half molecules of **3** and TCNQ is presented in Figure 3. Bis-EDST (**3**) adopts a planar conformation in the complex and the distances d_{S---S} = 2.96 Å indicates the occurrence S- - -S intramolecular interactions. The length of the bond linking the two thiophene rings (1.44 Å) is similar to that found for bis-EDOT. The planar donor and acceptor molecules form uniform face-to-face mixed stacks along the *c* axis with interplanar distances of 3.8 Å. A degree of charge transfer (δ) of only ca. 10% was estimated on the basis of the change in the bond lengths of the TCNQ molecule between the neutral and the anion radical state.[15]

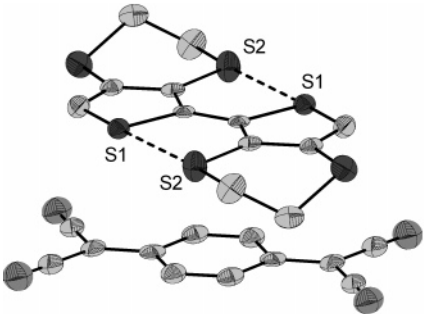


Figure 3. ORTEP view of the complex **3-TCNQ**. Intramolecular interactions are indicated by dotted lines.

This dramatic geometric change for compound **3** is an indication that the weak steric interactions between the ethylenedisulfanyl groups which impose the twisted structure can be counter balanced by the S- - -S intramolecular interactions leading to planar conformation.

Theoretical Calculations. Theoretical calculations have been performed at the ab initio density functional level with the Gaussian 98 package. Becke's three parameter gradient corrected functional (B3LYP) with a polarized 6-31G(d,p) basis was used for full geometry optimization of the bithiophenes. Recently various calculations methods have been tested on dimers including bis-EDST (**3**) and bis-EDOT and concluded on the suitability of the B3LYP methods for geometrical optimization.[16] The optimized structures are presented in Figure 4 and Table 1 lists the energy values of the HOMO and LUMO levels and their gap (ΔE). The structure of bis-PDST (**4**) is in good agreement with the X-ray data. The similarity of the dihedral angle α between the two thiophenes calculated for the gas phase (68°) and that found in the crystal (73°) is an indication that steric S- - -S repulsions represent the major limitation to the conjugation of the two cycles.

Table 1. HOMO/LUMO Energy Levels and Gap Calculated by DFT Method (B3LYP/6-31G*)

compound	α^a/deg	HOMO/eV	LUMO/eV	ΔE/eV
1	37	−5.38	−1.11	4.27
2	7	−4.97	−1.03	3.94
3	77	−5.58	−0.79	4.79
3	45^b	−5.28	−1.08	4.20
4	68	−5.60	−1.08	4.52
bis-EDOT	0	−4.84	−0.79	4.05

[a] Optimized dihedral angle. [b] Fixed dihedral angle.

For bis-EDST (**3**), calculations give a α value of 77° much larger than the 45° found in the crystal in the solid phase. This difference can be imputed to the fact that calculations do not take into account intramolecular S- - -S interactions and thus tend to overestimate the repulsion between the sulfur atoms. Calculations have also been done for an imposed value of α of 45° in order to evaluate the impact of the dihedral angle on the HOMO and LUMO energy levels. As seen in Table 1, reducing α from 77 to 45° results in a ca. 0.59 eV decrease of the HOMO−LUMO gap.

As expected, the removal of a ethylenedisulfanyl cycle on one thiophene ring in compound **1** reduces the dihedral angle between the two thiophenes to 37°. On the other hand, the data for compound **2** show that replacement of one ethylenedisulfanyl group by an ethylenedioxy one induces a reduction of the twist angle to 15° while the S- - -O and S- - -S distances become smaller than the sum of the van der Waals radii. These results show in good agreement with the planar geometry indicated by the X-ray structure that strong S- - -O intramolecular interactions and moderate S- - -S steric repulsions lead to a stabilization of a quasi-planar conformation.

As appears in Table 1, the HOMO and LUMO levels and ΔE strongly depend on the value of α. As expected planarization of the molecule leads simultaneously to an increase of the HOMO level and to a decrease of ΔE. Interestingly, the data for the mixed EDOT-EDST **2** indicate that in spite the nonzero value of α, compound **2** should presents a slightly smaller gap than bis-EDOT.

UV—Vis Spectroscopy. The UV−vis absorption data for compounds **1**−**4** are listed in Table 2. The λ_{max} values show a good agreement with theoretical calcula-

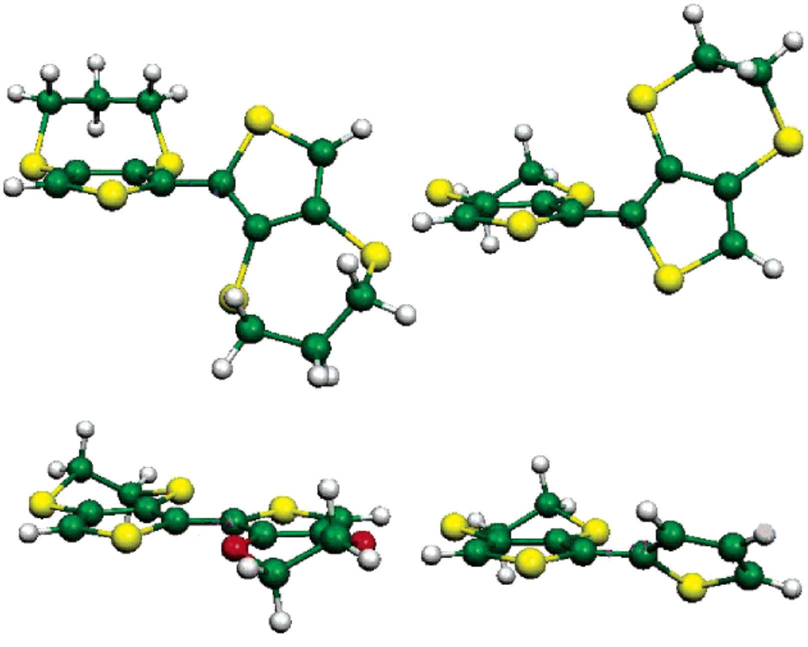


Figure 4. Structure of the calculated gas phase conformation of various bithiophenes. Top: **4** (left); **3** (right). Bottom: **2** (left); **1** (right).

Table 2. UV−vis[a] and Electrochemical[b] Data for Dimers 1−4, Bis-EDOT,[17] and the Corresponding Monomers

compound	λ_{max}/nm	E_{pa}/V
PDST	249	1.53
EDST	283	1.38
EDOT	261	1.56
1	320	1.25
2	336	1.02
3	308	1.13
4	257	1.34
bis-EDOT	322	0.95

[a] 10^{-4} mol L^{-1} in CH_2Cl_2. [b] 10^{-3} mol L^{-1} in 0.1 M Bu_4NPF_6 in CH_3CN, reference Ag/AgCl, v = 100 mV.s^{-1}.

tions and confirm the predominant effect of the twist angle α on the effective conjugation. Thus, the similarity of λ_{max} for compound **4** and its monomer PDST (254 and 249 nm respectively) confirms that a severe torsion of the molecule fully suppress the conjugation. Replacement of the propylenedisulfanyl (**4**) by ethylenedisulfanyl groups (**3**) leads to a 30 nm bathochromic shift of λ_{max} reflecting the reduction of the twist angle. The same trend is observed for the hybrid thiophene-EDST **1**. Finally, comparison of the absorption spectra of EDOT−EDST (**2**) and bis-EDOT shows that although the spectrum of compound **2** exhibits a less resolved vibronic fine structure than that of bis-EDOT, the band maxima are slightly red shifted. These results suggest that whereas the stronger donor effect of the sulfur atoms results in a decrease of ΔE, the partial replacement of strong S···O by moderate S···S interactions decreases the rigidity of the conjugated structure.

Electrochemistry. The cyclic voltammogram (CV) of all compounds presents an irreversible anodic peak corresponding to the oxidation of the compounds into the corresponding radical cation. The less positive anodic peak potential (E_{pa}) of EDST compared to EDOT reflects a higher HOMO level due to the stronger donor effect of the sulfanyl groups (Table 2). The sequence between the oxidation potential of compounds **1**−**4** (**2** < **3** < **1** < **4**) follows well the one obtained with the calculated HOMO levels (Table 1). Thus, the most twisted compound **4** shows the highest E_{pa} value while bis-EDST (**3**) oxidizes at a lower potential than **1** indicating that the lack of the planarity is compensated by the donor effects of the ethylenedisulfanyl groups. As expected, compound **2** shows the lowest E_{pa} value of the series. However, this value is slightly higher than that of bis-EDOT, in agreement with the calculated HOMO levels. Except for compound **4** which does not show any propensity to polymerize, application of recurrent potentials scans to acetonitrile solutions of compounds **1**−**3** using Bu_4NPF_6 as supporting electrolyte leads to the progressive development of a new redox system at lower potential associated with the electrodeposition of the polymers (Figure 6). The lack of polymerization of compound **4** can be attributed to the severely twisted structure of the molecule and presumably of its radical cation which does not allow charge propagation along the chain during the chain growth process. Comparison of the electropolymerization curves for the various compounds reveals noticeable differences related to the structure of the precursor. The CVs of each polymer recorded in a monomer-free electrolytic medium show that the polymers are stable upon cycling and no decrease of the amount of exchanged charge was observed after 1000 charging-discharging cycles.

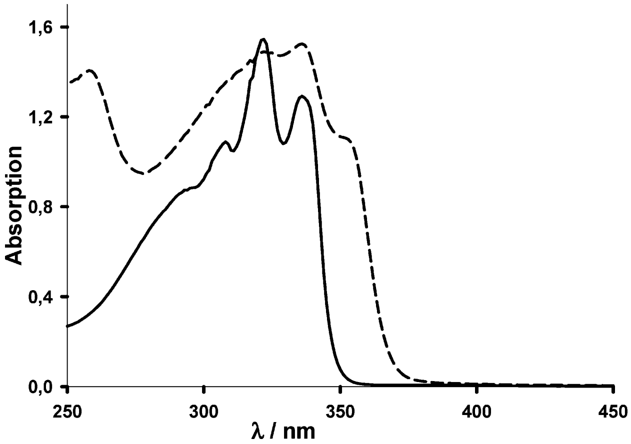


Figure 5. UV−vis absorption spectra of **2** (dotted line) and bis-EDOT (solid line) 10^{-4} M in CH_2Cl_2.

The CV of poly(**3**) presents a first anodic wave of weak intensity at 0.54V followed by a main oxidation peak at 0.84 V (Table 3). The symmetry and narrowness of the main oxidation wave are consistent with the formation of relatively homogeneous polymer chains. It is worth noting that these CV features are quite similar to those reported by Kanatzidis and co-workers for PDST.[8] In contrast, the CV of poly(**1**) presents a broad redox system extending from 0.40 to 1.10 V suggesting the formation of a polymer with higher polydispersity. The similarity of the E_{pa} values for poly(**3**) and poly(**1**) (0.84 V) suggests that for poly(**1**), the decrease of the overall number of electron-releasing ethylenedisulfanyl groups is compensated by a better planarity of the polymer chain and thus enhanced effective conjugation length. The dissymmetry introduced in the electronic structure of radical cation $\mathbf{1}^{\bullet+}$ should result in a different reactivity of the two free α-positions. Thus, the polymer has probably a regularly alternated polymeric structure, but the very low solubility of the electrodeposited film did not allow one to characterize the structure of the polymers.

Finally, the CV of poly(**2**) shows a weak oxidation peak at −0.39 V followed by a main wave with a maximum at 0.44 V. As expected the E_{pa} value is intermediate between those of poly(**3**) and poly(bis-EDOT). This result shows that replacement of an ethylenedisulfanyl group by an ethylenedioxy one leads to a decrease of the steric hindrance to planarity and hence to a better effective conjugation. However, in that case the polymer has probably a regio-random structure since the difference in the electronic effects of the ethylenedisulfanyl and ethylenedioxy groups are too small to induce a large difference in the reactivity of the terminal α-positions.

The optical properties of the polymers have been analyzed on thin films electrodeposited on ITO electrodes. As shown in Table 3, poly(**3**) absorbs at relatively short wavelength (λ_{max} = 440 nm) which is consistent with a twisted structure. This value is slightly red shifted compared to that of a solution-cast film of poly(EDST) (434 nm). Decreasing steric interactions as done in poly(**1**) results in a red shift of λ_{max} to 495 nm associated with a narrowing of the band gap to 1.90 eV.

As could be expected, the spectrum of poly(**2**) (Figure 7) shows the most red shifted λ_{max} (562 nm) and the smallest band gap among the series (1.55 eV). It is noteworthy that these values represent a 30 nm red shift of λ_{max} and a 0.10 eV decrease of the band gap

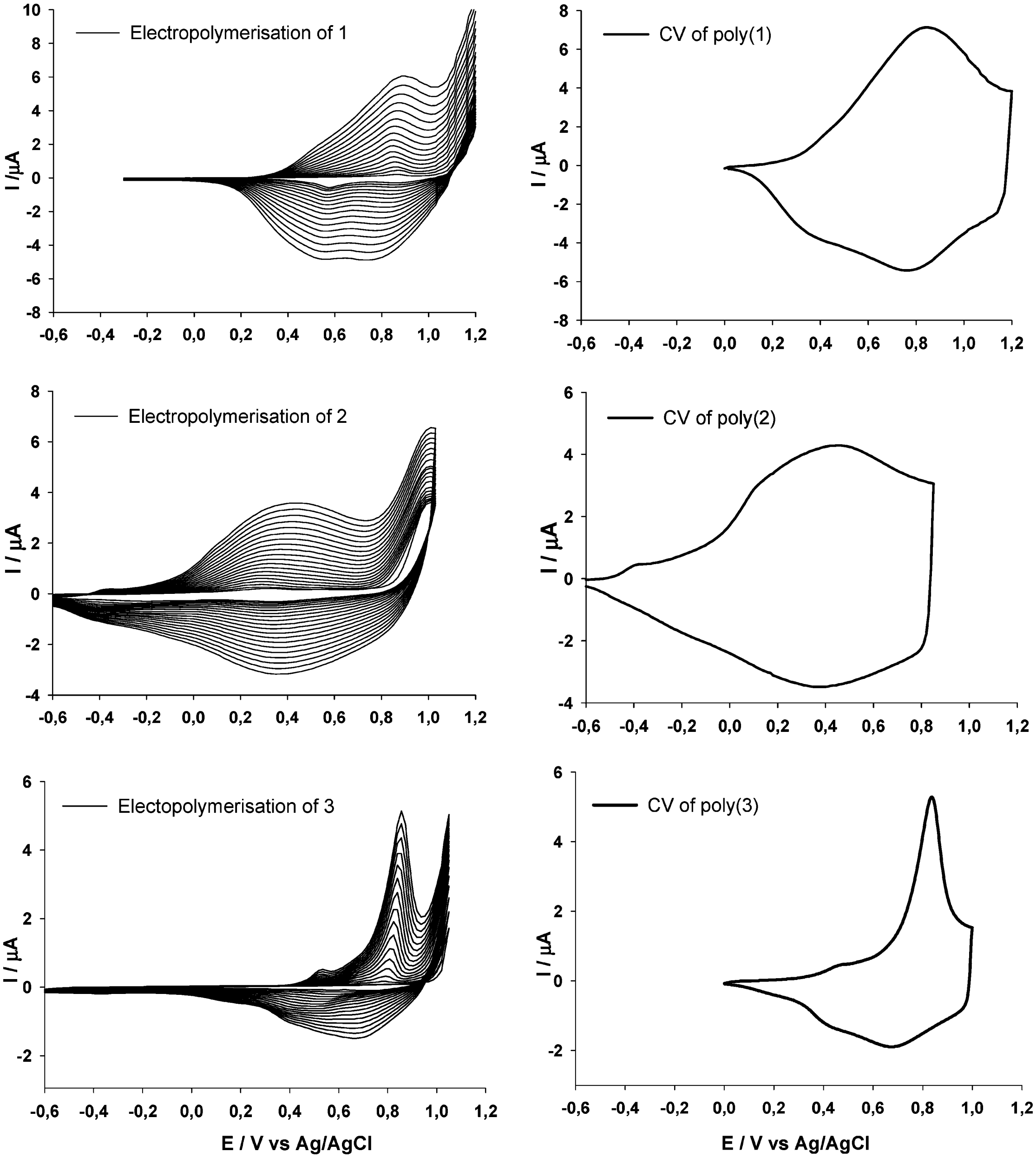


Figure 6. Left: electropolymerization of compounds **1**, **2**, and **3** at 10^{-3} mol L^{-1} in 0.1 M Bu_4NPF_6 in CH_3CN, reference Ag/AgCl, $v = 100$ mV·s^{-1}. Right: CV of polymers deposited on Pt disk ($d = 1$ mm) in 0.1 M Bu_4NPF_6 in CH_3CN, reference Ag/AgCl, $v = 100$ mV·s^{-1}.

Table 3. Optical[a] and Electrochemical[b] Data of the Polymers

polymer	E_{pa}/V	λ_{max}/nm	gap/eV
poly(**1**)	0.84	495	1.90
poly(**2**)	0.44	562	1.55
poly(**3**)	0.84	440	2.10
poly(BisEDOT)[17]	0.11	535	1.65
poly(EDST)[8]	0.86	434	2.19

[a] Film of polymer deposited on ITO. [b] Film of polymer deposited on Pt disk ($d = 1$ mm) in 0.1 M Bu_4NPF_6 in CH_3CN, reference Ag/AgCl, $v = 100$ mV·s^{-1}.

compared to poly(bisEDOT).[17] The spectrum poly(**2**) remains unchanged after several days storage in ambient atmosphere indicating a high stability of the polymer in the neutral sate. Oxidation of the polymer produces a decrease of the absorption in the visible range with the development of a broad absorption band in the near-IR region while the color of the polymer changes from the deep purple to pale blue. Further examination of the spectrum of the oxidized polymer reveals bands around 900 and 1900 nm after oxidation at +0.40 V and a broad band with a λ_{max} around 1500 nm for oxidation at potentials higher than +0.60 V. These optical features can be attributed to the polaron (transitions at ~0.70 and 1.40 eV) and bipolaron states (transition at ~ 0.82 eV). However, further spectroelectrochemical studies are required for an unequivocal assignment of these various transitions.

Conclusion

To summarize, a series of bicyclic systems containing 3,4-alkylenedisulfanylthiophenes has been synthesized. The analysis of the structure and electronic properties of these systems by X-ray diffraction, cyclic voltammetry, UV—vis spectroscopy, and theoretical calculations has shown that whereas steric hindrance is predominant in EDST and PDST dimers, the synthesis of hybrid systems combining EDST with thiophene or EDOT

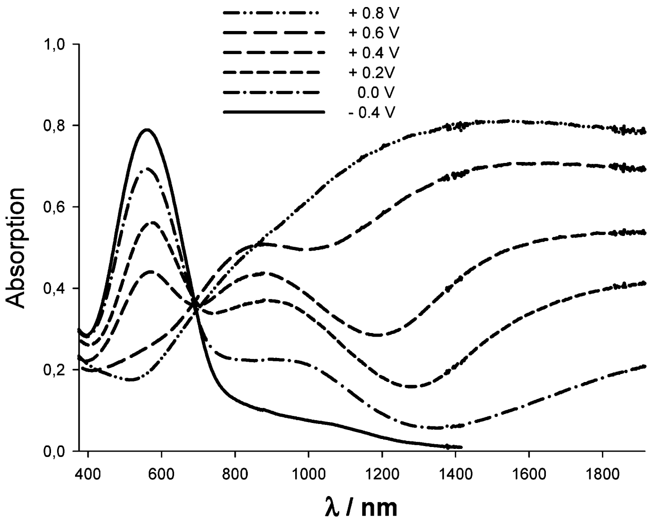


Figure 7. Electronic absorption spectra of a film of poly(**2**) electrodeposited on ITO.

allows one to restore acceptable effective conjugation through an interplay of electronic and self-structuring effects.

The analysis of the electrochemical and optical properties of the polymers electrogenerated from these various precursors confirms the above conclusions and shows that a precursor based on the association of EDST with EDOT leads to a polymer combining a band gap smaller than that of the two homopolymers with an intermediate oxidation potential. This original combination of low band gap and stability of the neutral state suggests that conjugated oligomers and polymers built around this basic structure can be potentially interesting for the realization of organic semiconductors for field-effects transistors or solar cells.

Experimental Part

^{1}H NMR and ^{13}C NMR spectra were recorded on a Bruker AVANCE DRX 500 spectrometer operating at 500.13 and 125.7 MHz; δ values are given in ppm (relative to TMS) and coupling constants (J) in hertz. Mass spectra were recorded under EI mode on a VG-Autospec mass spectrometer or under MALDI−TOF mode on a MALDI−TOF-MS BIFLEX III Bruker Daltonics spectrometer. UV−visible optical data were recorded with a Perkin-Elmer Lambda 19 spectrophotometer. Melting points were obtained from a Reichert-Jung Thermovar hot-stage microscope apparatus and are uncorrected. Electrochemical experiments were performed with a EG&G 273 potentiostat in a standard three-electrode cell using an Ag/AgCl reference electrode. The solutions were degassed by argon bubbling and experiments were carried under an argon blanket. The working electrode was a 1 mm Pt disk sealed in glass. Tetrabutylammonium hexafluorophosphate (Fluka puriss) was used as received.

3,4-Bis(2-cyanoethylsulfanyl)thiophene **5** and 3,4-ethylenedisulfanylethiophene (**EDST**) were synthesized as described in ref 13.

3,4-Propylenedisulfanylthiophene (PDST). Under nitrogen atmosphere, a solution of CsOH,H_2O (1.43 g, 2.2 equiv) in nitrogen degassed MeOH was dropwise added over a period of 5 min to a nitrogen degassed solution of compound **5** (1.0 g, 3.95 mmol) in DMF (30 mL) at 0 °C. After 5 min stirring at 0 °C, 1,3-dibromopropane (0.4 mL, 1 equiv) was added dropwise to the reaction mixture. The solution was stirred 20 min at 0 °C then 1 h at room temperature. After evaporation of the solvents in vacuo and subsequent addition of CH_2Cl_2 (100 mL), the solution was washed with water, dried over $MgSO_4$, and concentrated under reduced pressure. Purification by chromatography on silica gel (eluent, cyclohexane/CH_2Cl_2 7:3) led to a pale green oil (60% yield).

^{1}H NMR ($CDCl_3$): 7.39 (s, 2H); 2.76 (s, 4H); 2.40 (s, 2H). MS EI $M^{\bullet+}$188.

Thiophene-EDST (1). EDST (0.26 g, 1.5 mmol) was dissolved in 10 mL of dry THF under nitrogen atmosphere and cooled to −78 °C. After addition of 1 equiv of *n*-BuLi the mixture was stirred for 1 h at −78 °C, and tributyltin chloride was added dropwise. The mixture was stirred at the same temperature for $^1/_2$ h before allowing it to warm at room temperature. After dilution with diethyl ether, the organic phase was successively washed by a saturated solution of $NaHCO_3$ and then with water. After drying on $MgSO_4$, the solvent was evaporated off, and the product was used without other purification for the coupling reaction.

A mixture of the stannic derivative of EDST, 2-bromothiophene (1.2 equiv), and catalyst ($Pd(PPh_3)_4$ (5% mol) was refluxed in toluene (50 mL) during 12 h under inert atmosphere (N_2). After concentration, the residue was dissolved in CH_2Cl_2, and then the organic phase was washed twice with a saturated solution of $NaHCO_3$ and then with water. After drying on $MgSO_4$ and evaporation of solvent, the product was purified by chromatography on silica gel (eluent, petroleum ether/CH_2Cl_2 1:1) to give compound **1** as a pale green oil (65% yield).

^{1}H NMR ($CDCl_3$): 7.32 (dd, 1H, ^3J = 5.1 Hz, ^3J = 1.1 Hz); 7.28 (dd, 1H, ^3J = 3.7 Hz, ^3J = 1.1 Hz); 7.07 (dd, 1H, ^3J = 5.1 Hz, ^3J = 3.7 Hz); 6.91 (s, 1H); 3.23−3.26 (m, 4H). MS TOF: 255.91 (calcd 255.95). Anal. Calcd for $C_{10}H_8S_4$: C, 46.84; H, 3.14; S, 50.02; Found: C, 46.77; H, 3.04; S, 50.21

EDOT—EDST (2). Under nitrogen atmosphere, 0.38 g of NBS (2.1 mmol) was added by portion to a solution of 0.38 g of EDST (2.1 mmol) in 50 mL of $CHCl_3$ at −20 °C, and the mixture was stirred 2 h at this temperature. The mixture was washed with a saturated solution of $NaHCO_3$ and then twice with water. After drying on $MgSO_4$, the solvent was evaporated off, and the product was used without other purification for the coupling reaction.

A mixture of the brominated derivative of EDST, 2-tributylstannyl-3,4-ethylenedioxythiophene (1.5 equiv), and catalyst ($Pd(PPh_3)_4$ (5% mol) was refluxed in toluene (50 mL) during 12 h under inert atmosphere (N_2). After concentration, the residue was dissolved in CH_2Cl_2 and then the organic phase was washed twice with a saturated solution of $NaHCO_3$ and then with water. After drying on $MgSO_4$ and evaporation of solvent, the product was purified by chromatography on silica gel (eluent, petroleum ether/CH_2Cl_2 1:1) to give compound **2** as a yellow solid (30% yield).

Mp: 163 °C. ^{1}H NMR ($CDCl_3$): 6.98 (s, 1H); 6.40 (s, 1H); 4.32 (m, 2H); 4.24 (m, 2H); 3.23 (s, 4H). ^{13}C NMR ($CDCl_3$): 141.3; 138.5; 126.4; 125.7; 122.8; 117.6; 109.5; 99.4; 64.9; 64.4 28.6; 27.7. MS TOF: 313.98 (calcd 313.96). Anal. Calcd for $C_{12}H_{10}O_2S_4$: C, 45.83; H, 3.21; O, 10.18; Found: C, 45.67; H, 3.18; O, 10.04.

Bis-EDST (3). EDST (0.35 g, 2 mmol) was dissolved in 50 mL of dry diethyl ether under nitrogen atmosphere and cooled to −78 °C. After addition of 1 equiv of *n*-BuLi, the mixture was stirred 1 h at − 78 °C, and copper chloride (1.2 equiv) was added in one portion. After one night of stirring at room temperature, the mixture was washed with water and dried on $MgSO_4$. After evaporation of the solvent, the residue was purified by chromatography on silica gel (eluent, petroleum ether/CH_2Cl_2 2:1) to give compound **3** as a pale yellow powder (50% yield).

Mp: 178 °C. ^{1}H NMR ($CDCl_3$): 7.07 (s, 2H); 3.23 (s, 8H). ^{13}C NMR ($CDCl_3$): 122.3; 122.0; 121.1; 115.3; 24.1; 23.4. MS TOF: 345.97 (calcd 345.91).

Bis-PDST (4). PDST (0.2 g, 1.06 mmol) was dissolved in 50 mL of dry diethyl ether under nitrogen atmosphere and cooled to −78 °C. After addition of 1 equiv of *n*-BuLi, the mixture was stirred for 1 h at 78 °C, and copper chloride (1.2 equiv) was added in one portion. After one night of stirring at room temperature, the mixture was washed with water and dried on $MgSO_4$. After evaporation of the solvent, the residue was purified by chromatography on silica gel (eluent, petroleum ether/CH_2Cl_2 2:1) to give compound **4** as a white powder (60% yield).

Mp: 205 °C. ^{1}H NMR ($CDCl_3$): 7.52 (s, 2H); 2.76 (s, 8H); 2.41 (m, 4H). MS TOF: 373.92 (calcd 373.94).

X-ray structures. Data collection was performed at 293 K on an Enraf-Nonius MACH3 four-circles diffractometer for compounds **3**, **4**, and **3-TCNQ** and on a STOE-IPDS diffractometer for **2**, both equipped with a graphite monochromator utilizing Mo Kα radiation ($\lambda = 0.71073$ Å). The structures were solved by direct methods (SIR) and refined on F by full matrix least-squares techniques using MolEN package programs for **3**, **4**, and **3-TCNQ** and by full-matrix least- squares on F^2 with SHELXL97 for **2**.

Crystal Data and Structure Refinement for Compound 3. $C_{12}H_{10}S_6$, $M_w = 346.60$, yellow prism, 0.57 × 0.49 × 0.14 mm^3, orthorhombic, $Pbca$, $a = 14.343(2)$ Å, $b = 13.027(1)$ Å, $c = 14.805(2)$ Å, $V = 2766(1)$ Å^3, $Z = 8$, $\rho_{calc} = 1.67$ g/cm^3, 2764 reflections collected in the 2.5−25° θ range, 2764 independent reflections from which 1644 with $I > 3\sigma(I)$ converged to $R = 0.030$ and w$R2 = 0.044$ with 180 parameters, GOF = 0.938. S and C atoms were refined anisotropically, and the H atoms were included in the calculation without refinement; absorption was corrected by a ψ-scan technique.

Crystal Data and Structure Refinement for Compound 4. $C_{14}H_{14}S_6$, $M_w = 374.65$, colorless plate, 0.54 × 0.38 × 0.06 mm^3, orthorhombic, $Fdd2$, $a = 40.322(3)$ Å, $b = 13.471(1)$ Å, $c = 5.9582(6)$ Å, $V = 3236.3(8)$ Å^3, $Z = 8$, $\rho_{calc} = 1.53$ g/cm^3, 2325 reflections collected in the 2.5−22° θ range, 2325 independent reflections from which 458 with $I > 3\sigma(I)$ converged to $R = 0.038$ and w$R2 = 0.050$ with 90 parameters, GOF = 1.078. S and C atoms were refined anisotropically and the H atoms were included in the calculation without refinement; absorption was corrected by DIFABS.

Crystal Data and Structure Refinement for 3-TCNQ. $C_{24}H_{14}N_4S_6$, $M_w = 550.79$, black plate, 1.00 × 0.18 × 0.02 mm^3, triclinic, $P\bar{1}$, $a = 6.8401(5)$ Å, $b = 8.0960(6)$ Å, $c = 10.8868(7)$ Å, $\alpha = 102.523(5)°$, $\beta = 100.983(6)°$, $\gamma = 91.136(6)$, $V = 576.6(2)$ Å^3, $Z = 1$, $\rho_{calc} = 1.59$ g/cm^3, 1978 reflections collected in the 2.5−24° θ range, 1805 independent reflections from which 1487 with $I > 3\sigma(I)$ converged to $R = 0.033$ and w$R2 = 0.048$ with 182 parameters, GOF = 1.040. S, N, and C atoms were refined anisotropically, and the H atoms were found from Fourier difference synthesis; absorption was corrected by DIFABS.

Crystal Data and Structure Refinement for Compound 2. $C_{12}H_{10}O_2S_4$, $M_w = 314.44$, orange plate, 0.50 × 0.46 × 0.04 mm^3, monoclinic, $P\ a$, $a = 8.175(3)$ Å, $b = 8.374(2)$ Å, $c = 9.598(4)$ Å, $\beta = 90.11(4)°$, $V = 657.1(4)$ Å^3, $Z = 2$, $\rho_{calc} = 1.589$ g/cm^3, 4936 reflections collected in the 2.5−26° θ range, 2438 independent reflections from which 939 with $I > 2\sigma(I)$ converged to $R = 0.172$ and w$R2 = 0.421$ with 165 parameters, GOF = 1.339. S, O, and C atoms were refined anisotropically, and the H atoms were included in the calculation without refinement; absorption was corrected by the Gaussian technique.

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Supporting Information Available: X-ray structures of **3**, **4**, and **3-TCNQ** in .cif format. This material is available free of charge via the Internet at http://pubs.acs.org.

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