Flat conjugated polymers combining a relatively low HOMO energy level and band gap: polyselenophenes versus polythiophenes†

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In this work, we prepared a series of new conjugated polyselenophenes that, in the 3,4-positions of the selenophene ring, have oxygen or sulfur substituents bridged by a phenylene moiety. Such substitution of a conjugated backbone produces a skeleton that has only planar units, does not have stereo centers, and offers the potential to structurally modify the polymer without impairing its conjugation. The reported polyselenophenes exhibit significantly different properties as a function of the heteroatom. The selenophene backbone combined with a phenylene periphery creates the rare combination of a low-band gap, low HOMO energy level, and a flat skeleton, which is desired for many optoelectronic applications. The properties of the phenylene-bridged polyselenophenes were compared with those of their polythiophene analogs. The polyselenophenes obtained in this work have a lower band gap and higher planarity than polythiophenes and their monomers electropolymerize more easily. Theoretical studies support the experimental findings about rigidity and band gap changes.

Introduction

Conducting polymers† and other organic semiconducting materials‡ have found application in organic light emitting diodes (OLEDs), organic field effect transistors (OFETs), chemical sensors, microelectronic actuators, and solar cells. However, new advanced π-conjugated polymers are still required to increase the applicability and performance of these materials. The development of a methodology that enables the properties of the material to be adjusted by rational modifications of its chemical structure is highly desired. For instance, control of polymer frontier orbitals and band gap is required for many optoelectronic applications. A low HOMO energy level is important for polymer stability, while a low band gap is reflected in more efficient solar spectrum absorption capabilities. However, stable conjugated materials that combine both a low band gap and a low HOMO energy are rare.

It is usually necessary to introduce substituents onto the conjugated polymer backbone to achieve solubility and other desired properties. However, such substitution often causes the polymer to twist significantly, which affects conjugation and consequently increases the band gap. The incorporation of a flat phenylene ring into the monomer unit may provide a potential solution to this problem. Such incorporation eliminates the problems of out-of-plane substituents and stereoisomers and potentially enables better ordering and packing. However, this approach has received little attention.

Poly(3,4-phenylene-enedioxyselenophene) (PPheDOT), a phenylene-extended analog of poly(3,4-ethylenedioxythiophene), PEDOT (Scheme 1), has been reported previously. A long alkyl chain substituted PPheDOT-(C12)n, an electroactive soluble polymer with a regioisometric structure that possesses a high degree of inter- and intrachain order, was also reported.

Recently, we have developed a new type of conjugated polymer based on 3,4-ethylenedioxyxelenophene (EDOS). Poly(3,4-ethylenedioxyxelenophene) (PEDOS) and its derivatives benefit from a low band gap (1.4 eV), excellent electrochromic properties, high planarity, and good stability. Our theoretical studies confirmed by experimental
and a lower band gap. All the polyselenophenes studied in this paper are comprehensively compared with the corresponding polythiophenes, P2a–d (Scheme 1), which, with the exception of PheDOT (P2a), are reported for the first time here.

**Experimental**

All chemicals were purchased from the Sigma-Aldrich or ABCR chemical companies. The reported melting points were taken from the onset of the melting peak at DSC measurements. Electrochemical and spectroelectrochemical studies were carried out in CH2Cl2 with 0.1 M of tetrabutylammonium hexafluorophosphate (TBAPF6) as a supporting electrolyte, using indium tin oxide (ITO)-coated glass slides (7 × 50 × 0.7 mm, Rg = 8–12 Ω−1, Delta Technologies Inc.) as the working electrode, a platinum wire as the counter electrode, and a AgCl coated Ag wire (which was directly dipped in the electrolyte solution) as the quasi-reference electrode. The results obtained in other solvents, such as propylene carbonate and acetonitrile, are given in the ESI†. Electrochemical studies were carried out with a Princeton Applied Research 263A potentiostat. All the electrochemical potentials are given in volts vs. SCE and were calibrated to the Fe/Fe⁺ internal standard, which is 0.46 V vs. SCE under these conditions (CH2Cl2/TBAPF6). Monomer concentration was ~0.01 M. The reaction solution was bubbled with N2 before use to remove any incipient oxygen. The polymer films were prepared by electrodeposition onto an ITO anode from monomer solutions under potentiodynamic conditions by repeated cyclic voltammetry (CV) scanning at rates of 50–100 mV s⁻¹. Before examining the polymer’s optical properties, ITO slides with electrodeposited polymer films were rinsed with acetonitrile. UV-vis-NIR spectra were recorded on a JASCO V-570 UV-vis-NIR spectrophotometer in a quartz cell. Spectroelectrochemical measurements of the polymer films deposited on the ITO electrode were performed in CH2Cl2 with 0.1 M TBAPF6 as a supporting electrolyte at various potentials applied in situ.

Scanning electron microscope (SEM) images were taken with a Leo Ultra 55 FEG SEM operating at 5 keV power and at a working distance of 3 mm. HRMS were measured using a Waters Micromass GCT Premier Mass Spectrometer (Water-Micromass, Milford, USA) operating in FD mode using a Carbotec 10 Micron Tungsten FD Emitter with an extraction voltage of 12 000 V.

The experimental values of the HOMO energy levels were obtained from the onset of the oxidation peak in CV scans of each polymer film in monomer free solution using the Koopmann approximation for the ionization energy: $E_{\text{HOMO}} = E_{\text{onset}} + 4.4$ (eV), where 4.4 eV is the energy level of SCE below the vacuum level. Experimental values for the LUMO energy levels were obtained using $E_{\text{LUMO}} = E_{\text{HOMO}} + E_{\text{gap}}$, where $E_{\text{gap}}$ is a band gap obtained from the red edge of the absorption peak of a neutral polymer.

Computational studies were carried out using density functional theory (DFT) with the Gaussian 09 series of programs. The geometries of the polymers were fully optimized using the periodic boundary conditions (PBC) formalism and hybrid DFT with Becke’s three-parameter exchange functional combined with the LYP correlation functional (B3LYP) and the 6-31G(d) basis set (PBC/B3LYP/6-31G(d)). The PBC/B3LYP/6-31G(d) level generally gives a good estimate of the band gaps of
conjugated polymers. The methodology described in ref. 11 was used for twisting studies (up-down twisting was applied). The density of states (DOS) diagrams were obtained by convoluting the calculated crystal orbital energies (at PBC/B3LYP/6-31G(d)) using Gaussian curves ($\sigma = 0.1$ eV).

Synthesis

Benzo[e]thieno[3,4-b]/[1,4]dioxine (PheDOT, 2a). Benzo[e]thieno[3,4-b]/[1,4]dioxine (PheDOT, 2a) was obtained by the previously reported procedure.

General procedure for the synthesis of selenophene monomers (1a–1c). 3,4-Dimethoxyselenophene, with catechol, 2-hydroxythiophenol or 1,2-benzenedithiol and p-toluenesulfonic acid were dissolved in dry toluene (50 mL) and heated at 65 °C for 5–7 hours (monitoring by TLC). After cooling to room temperature, water (20 mL) was added and the mixture was extracted with diethyl ether (3 x 40 mL). The combined organic layers were washed with diluted aqueous NaHCO$_3$ solution and brine, dried over magnesium sulfate, filtered, and the filtrate was evaporated. Purification of the residue by flash chromatography on silica gel (elution with hexane) afforded the desired products.

Benzo[e]seleneno[3,4-b]/[1,4]dioxine (PheDOT, 1a). 3,4-Dimethoxyselenophene (0.50 g, 2.62 mmol), catechol (1.154 g, 10 mmol) and p-toluenesulfonic acid (74 mg, 0.39 mmol) afforded the title product 1a (20 mg, 0.084 mmol) with 32% yield. $^1$H NMR (CDCl$_3$, 300 MHz): $\delta$ 6.90 (m, 4H, phenylene), 6.89 (s, 2H, selenophene). $^{13}$C NMR (CDCl$_3$, 75.5 MHz): $\delta$ 106.79, 118.18, 118.76, 119.40, 123.81, 126.66, 127.28. FD HRMS for C$_{10}$H$_6$O$_2$Se $[M+]^+$ calcd 237.9533, found 237.9529. M.p. 100 °C.

Benzo[e]seleneno[3,4-b]/[1,4]dithiine (PheDTS, 1b). 3,4-Dimethoxyselenophene (0.35 g, 2.42 mmol), 1,2-benzenedithiol (0.80 g, 6.24 mmol), and p-toluenesulfonic acid (59 mg, 15 mol%) afforded the title product 2b (0.33 g, 1.6 mmol) with 76% yield. $^1$H NMR (CDCl$_3$, 400 MHz): $\delta$ 7.03–7.10 (m, 2H, phenylene), 6.93–6.97 (m, 2H, phenylene), 6.74 (d, $J = 3.4$ Hz, 1H, thiophene), 6.61 (d, $J = 3.4$ Hz, 1H, thiophene). $^{13}$C NMR (CDCl$_3$, 100 MHz): $\delta$ 103.66, 115.34, 116.76, 116.90, 118.04, 123.92, 126.86, 127.34, 147.79, 150.85. FD HRMS for C$_{10}$H$_6$OS$_2$ $[M+]^+$ calcd 205.9860, found 205.9854. M.p. 29 °C.

Benzo[e]seleneno[3,4-b]/[1,4]dioxine (PhedOTS, 1c). 3,4-Dimethoxyselenophene (0.30 g, 1.75 mmol), 2-hydroxythiophenol (0.81 g, 6.3 mmol), and p-toluenesulfonic acid (45 mg, 0.23 mmol) afforded the title product 1b (0.22 g, 0.87 mmol) with 2.8% yield. $^1$H NMR (CDCl$_3$, 300 MHz): $\delta$ 7.39 (dd, $J = 4.4$ Hz, $J = 3.6$ Hz, 2H, phenylene), 7.17 (dd, $J = 4.4$ Hz, $J = 3.6$ Hz, 2H, phenylene-2), 7.14 (s, 2H, thiophene). $^{13}$C NMR (CDCl$_3$, 100 MHz): $\delta$ 119.62, 127.41, 128.90, 132.29, 134.94. FD HRMS for C$_{10}$H$_6$S$_3$ $[M+]^+$ calcd 221.9632, found 221.9624. M.p. 124 °C.

Naphtho[2,3-e]seleneno[3,4-b]/[1,4]dioxine (NaphDOS, 1d). A solution of 3,4-dimethoxyselenophene (0.30 g, 2.08 mmol), 3,4-dimethoxythiophene (0.80 g, 6.24 mmol), and p-toluenesulfonic acid (59 mg, 15 mol%) was dissolved in dry toluene (50 mL) and heated at 65 °C for 5–7 hours (monitoring by TLC). After cooling to room temperature, water (20 mL) was added and the mixture was extracted with diethyl ether (3 x 40 mL). The combined organic layers were washed with diluted aqueous NaHCO$_3$ solution and brine, dried over magnesium sulfate, filtered, and the filtrate was evaporated. Purification of the residue by flash chromatography on silica gel (elution with hexane) afforded the desired products.

General procedure for the synthesis of thiophene monomers (2b–2c). A solution of 3,4-dimethoxythiophene with 3 equivalents of the corresponding dihydroxothiophenol, and p-toluenesulfonic acid in dry toluene (25 mL) was stirred for 72 h at 90 °C. The completion of the reaction was monitored by TLC. If, after 72 h, 3,4-dimethoxythiophene had not been consumed, an additional amount of p-toluenesulfonic acid (ca. 4 mol%) was added, and the reaction was continued until completion (for about 5 hours). The reaction mixture was diluted with water (20 mL), the organic layer was separated, and the aqueous phase was extracted with diethyl ether (3 x 40 mL). The combined organic layers were washed with diluted aqueous NaHCO$_3$ solution and brine, dried over magnesium sulfate, filtered, and the filtrate was evaporated. Purification of the residue by flash chromatography on silica gel (elution with hexane) afforded the desired products.

Naphtho[2,3-e]seleneno[3,4-b]/[1,4]dithiine (NaphDTS, 2d). A solution of 3,4-dimethoxythiophene (0.50 g, 3.5 mmol) with 3 equivalents of 2,3-dihydroxythiophenol (1.67 g, 10.5 mmol) and
p-toluenesulfonic acid (130 mg, 20 mol%) in dry toluene (50 mL) was stirred for 96 h at 100 °C. Reaction completion was monitored by TLC. If, after 96 h, 3,4-dimethoxythiophene was not consumed, an additional amount of p-toluenesulfonic acid (5 mol %) was added, and the reaction was continued until completion (about 7 hours). The reaction mixture was diluted with water (30 mL), the organic layer was separated, and the aqueous phase was extracted with ether (3 × 40 mL). The combined organic layers were washed with diluted aqueous NaHCO₃ solution and brine, dried over magnesium sulfate, filtered, and then the filtrate was evaporated. Purification of the residue by flash chromatography on silica gel (elution with hexane) afforded the title product. Yield 3.6% (30 mg, 0.12 mmol). 1H NMR (CDCl₃, 400 MHz): δ 7.55 (dd, J = 6.4 Hz, J = 3.6 Hz, 2H, naphthalene-6,7), 7.34 (dd, J = 6 Hz, J = 3.2 Hz, 2H, naphthalene-5,8), 7.30 (s, 2H, thiophene), 7.26 (s, 2H, thiophene). 13C NMR (CDCl₃, 100 MHz): δ 101.05, 112.57, 125.32, 126.79, 130.46, 138.72, 140.60.

Results and discussion

Monomer synthesis and single crystal X-ray studies

A series of phenylene- and naphthalene-bridged selenophenes and thiophenes was prepared by Mitsunobu reaction⁹ of a 3,4-dimethoxyselenophene/thiophene with catechol/2-hydroxy-thiophenol/1,2-benzenedithiol in the presence of p-toluene-sulfonic acid (Scheme 2). The synthesis of 3,4-phenylenedioxythiophene (2a) was reported previously.¹² 3,4-Phenylendioxselenophene (PheDOS, 1a) was obtained with a low yield of 3.2% (compared to the 21% yield reported for 2a¹²). Interestingly, incorporation of sulfur atoms instead of oxygen at the 3,4-positions of the heterocyclic ring resulted in a significant increase in yields to 14% and 70%, for PheDTS (1c) and PhedTT (2c), respectively. Especially high yields for both the selenophene and thiophene series were observed for the preparation of asymmetric PheOTS (1b) (55%) and PheOTT (2b) (76%) monomers. This might be explained by the higher nucleophilicity of thiophenols compared to phenols. The high yields for O/S asymmetric PheOTS (1b) and symmetric PheOTT (2b) indicate that the second intramolecular substitution/cyclization is a relatively fast process.

Colorless plates of PheDOS (1a), suitable for single-crystal X-ray analysis, were obtained from hexane–ethyl acetate solution. The molecule is nearly planar, having an inter-plane torsion angle of 6° (Fig. 1).¹¹ Such coplanarity was also observed in the X-ray structure of 2,5-dibromosubstituted 2a.¹² The crystal structure shows an interesting packing mode. The unit cell consists of 4 molecules. Two pairs of nearly parallel molecules (having an inter-plane angle of ~6.5° and inter-plane distance of 3.6 Å) lie almost perpendicularly (inter-plane angle of 79°) to each other and the π-system interacts with the Se atoms in a herringbone fashion. Se–(phenyl ring) interactions are notably strong, with

Fig. 1 (a) An ORTEP of a molecule of PheDOS (1a) at the 50% probability level (grey, carbon; red, oxygen; and magenta, selenium).¹¹ (b) Packing of 1a crystals. Hydrogen atoms are omitted for clarity.
a Se–(phenyl) distance of 3.4–3.5 Å. Perhaps, these interactions between Se atoms and the \( \pi \)-electrons of the phenyl ring dictate the crystal packing.

**Electrochemical polymerization**

Electrochemical polymerization of the monomers was performed under potentiodynamic conditions by repeated cyclic voltammetry (CV) in CH\(_2\)Cl\(_2\) with 0.1 M TBAPF\(_6\) as a supporting electrolyte to produce insoluble films on the ITO electrode (used as an anode) (see Fig. 2 for electropolymerization of selenophene-based monomers and Fig. S1† for electropolymerization of thiophene-based monomers). Interestingly, phenylene-bridged 3,4-\( X \),\( Y \)-selenophenes \( 1a–d \) undergo polymerization relatively smoothly, unlike their thiophene analogs \( 2a–d \) (see below). We also found that polymerization of sulfur-containing phenylene-bridged selenophenes, PheOTS \( 1b \) and PheDTS \( 1c \), proceeds more easily than that of the only-oxygen-containing derivative PheDOS \( 1a \) (Table 1). This is in contrast to ethylene-bridged analogs, where EDOS and EDOT (Scheme 1) are polymerized more easily than 3,4-ethylenedithioselenophene (EDTS) and 3,4-ethylenedithiophene (EDTT).\(^{18,32}\)

**Table 1** Electrochemical and spectroelectrochemical data for polymers \( P1 \) and \( P2 \) prepared in CH\(_2\)Cl\(_2\) with TBAPF\(_6\) (0.1 M) as a supporting electrolyte. All data are given vs. SCE and were calibrated to the Fc/Fc\(^+\) standard, which is 0.46 V vs. SCE under these conditions

<table>
<thead>
<tr>
<th>Polymer</th>
<th>( E^{\text{onset}} ) (V vs. SCE)</th>
<th>( \lambda_{\text{max}}^{\text{a}} ) (nm)</th>
<th>FWHM(^b) (nm)</th>
<th>( E_{\text{g,opt}}^{\text{c}} ) (eV)</th>
<th>( E_{\text{g,DFT}}^{\text{d}} ) (eV)</th>
</tr>
</thead>
<tbody>
<tr>
<td>PEDOS(^e)</td>
<td>–0.41</td>
<td>600</td>
<td>230 [0.73]</td>
<td>1.41</td>
<td>1.66</td>
</tr>
<tr>
<td>PPhedOS, P1a</td>
<td>–0.14</td>
<td>562/625/695</td>
<td>205 [0.65]</td>
<td>1.57</td>
<td>1.97</td>
</tr>
<tr>
<td>PPhedOTS, P1b</td>
<td>0.05</td>
<td>660</td>
<td>199 [0.64]</td>
<td>1.49</td>
<td>1.88</td>
</tr>
<tr>
<td>PPhedTDS, P1c</td>
<td>0.20</td>
<td>612</td>
<td>203 [0.64]</td>
<td>1.49</td>
<td>1.89</td>
</tr>
<tr>
<td>PPhedNOS, P1d</td>
<td>–0.10</td>
<td>634/703</td>
<td>204 [0.65]</td>
<td>1.55</td>
<td>1.85</td>
</tr>
<tr>
<td>PPhedDOT, P2a</td>
<td>–0.07</td>
<td>510/562/620</td>
<td>190 [0.60]</td>
<td>1.5</td>
<td>2.13</td>
</tr>
<tr>
<td>PPhedOTT, P2b</td>
<td>0.12</td>
<td>583</td>
<td>180 [0.57]</td>
<td>1.65</td>
<td>2.07</td>
</tr>
<tr>
<td>PPhedDTT, P2c</td>
<td>–</td>
<td>583</td>
<td>180 [0.57]</td>
<td>1.65</td>
<td>2.07</td>
</tr>
<tr>
<td>PPhedNODT, P2d</td>
<td>0.04</td>
<td>522/620</td>
<td>185 [0.59]</td>
<td>1.8</td>
<td>2.02</td>
</tr>
</tbody>
</table>

\(^{a}\) Absorption maxima of the polymers in the neutral (undoped) states. \(^{b}\) Full width at half maximum of the absorption peak(s). Values in eV are given in parentheses. \(^{c}\) The experimental optical band gap obtained from the onset of the longest UV-vis absorption peak. \(^{d}\) The band gap calculated at the PBC/B3LYP/6-31G(d) level of theory. \(^{e}\) See ESI† for electropolymerization of EDOS. \(^{f}\) Polymerization attempts did not lead to film formation.
The onset potentials of phenylene-bridged polyselenophenes \( P1a-d \) are positively shifted by 0.27–0.61 V (Table 1) compared to those of ethylene-bridged PEDOS (−0.41 V vs SCE), which indicates that they have lower HOMO energy levels. A relatively low-lying HOMO energy level might be very important. For instance, it is required to improve the open-circuit voltage \((V_{oc})\) of polymer-based organic solar cells, which is closely related to the offset between the HOMO of the donor and the LUMO of the acceptor\(^{53}\). While the HOMO levels of phenylene-bridged polyselenophenes \( P1a-d \) are lower than those of PEDOS and PEDOT, they are still too high to obtain a relatively large \( V_{oc} \). In order to apply these polymers as donors in organic solar cells, additional lowering of the HOMO energy should be achieved by chemical modification. In addition, a low HOMO energy level improves the oxidation resistance of air-exposed polymers and so improves their handling and processing characteristics.

3,4-Substituents have an important effect on polymer properties. This effect is observed in their electrochemical properties and will be further demonstrated in the spectroelectrochemical and computational studies. The CV of PPhedOS \(( P1a) \) shows a broad peak with an onset of \(-0.14 \) V vs SCE. The onsets of the polymers that contain a sulfur substituent are even more positively shifted, to the value of \(+0.05 \) V vs SCE for PPhFeOTS \(( P1b) \) and to \(+0.20 \) V vs SCE for PPhFeDTS \(( P1c) \), which is the most positive value achieved in this study. These results correlate well with ethylene-bridged polyselenophenes, for which a positive shift of the onset potentials was also observed upon incorporation of sulfur atoms at the 3,4-positions.\(^{58}\) Naphthalene-bridged PNaphDOS \(( 1d) \) shows very similar electrochemical properties to its phenylene-bridged analog \( P1a \) (Fig. 2a and d), so the effect of an additional benzene ring on the phenylene bridge is rather small.

To evaluate the effect of the selenium heteroatom in the polymer backbone \(( P1a-d) \), thiophene-based polymers \( P2a-d \) were also studied in this work. Polymerization of thiophene analogs was more difficult and led to good quality polymer films only in the cases of PPhFeDOT \(( P2a) \), PPhFeOTT \(( P2b) \), and PNaphDOT \(( P2d) \) (see ESI, Fig. S1†, for electrochemical polymerization of \( 2a-2d)\).\(^{54}\) Similarly to the selenophene analogs, substitution of oxygen with a sulfur heteroatom at the 3-position led to a positive shift of the polymer oxidation peak in thiophene derivative \(( P2b) \). We were not able to polymerize PheDTT \(( 2c) \), which has two sulfur atoms in the bridge, most probably because of the steric effect of the sulfur atom compared to an oxygen atom. This observation is in contrast to polymerization of its selenophene analog, \( 1c \) (see above), and suggests that selenophenes are more easily electrochemically polymerized than their thiophene analogs.

### Spectroelectrochemistry

The spectroelectrochemically measured optical band gaps \(( E_{g(\text{opt})} \), assigned as the onset of the \( \pi–\pi^* \) transition of the neutral state of the polymer) of phenylene- and naphthalene-bridged polyselenophenes \( P1a-d \) vary only slightly as a function of the heteroatom substituent at the 3,4-position (Fig. 3 and Table 1). The band gap of PPhedOS \(( P1a) \), which has oxygen substituents at both the 3 and 4 positions, is 1.57 eV, which is somewhat higher than that of parent PEDOS \(( 1.41 \) eV, see Fig. S2 in the ESI†). Incorporation of a sulfur substituent in place of one or both of the oxygen atoms slightly decreases the band gap in PPhFeOTS \(( P1b) \) (1.49 eV) and PPhFeDTS \(( P1c) \) (1.49 eV). The spectroelectrochemically measured band gap of PNaphDOS \(( P1d) \) (1.55 eV) is very close to that of PPhedOS \(( P1a) \) (1.57 eV). Thus, while the oxidation potentials of \( P1a-d \) (i.e. the HOMOs of the polymers) vary in the range of 0.34 eV, variations in their band gaps are much smaller \((0.08 \) eV, Table 1).

The absorption spectrum of PPhedOS \(( P1a) \) exhibits a shouldered pattern with \( \lambda_{\text{max}} \) at 562/625/695 nm (Fig. 4). The presence of such vibronic shoulders is usually an indication of a rather rigid backbone structure. Since the absorption spectrum of the parent analog, PEDOS, shows no or very weakly defined vibronic peaks, such rigidity is, perhaps, caused by incorporation of the planar sp\(^2\) phenylene moiety. Unlike oxygen-substituted \( P1a \), the absorption spectra of the sulfur substituted polyselenophenes \( P1b \) and \( P1c \) in the neutral state do not show defined vibronic shoulders, which is consistent with the decreased rigidity of sulfur substituted polyselenophenes and polythiophenes observed previously\(^{18,19}\) and is in good agreement with the calculated twisting potentials (see below). Spectroelectrochemical data show that oxygen-substituted \( P1a \), the absorption spectra of the sulfur substituted polyselenophenes \( P1b \) and \( P1c \) in the neutral state do not show defined vibronic shoulders, which is consistent with the decreased rigidity of sulfur substituted polyselenophenes and polythiophenes observed previously\(^{18,19}\) and is in good agreement with the calculated twisting potentials (see below). These spectroelectrochemical data show that oxygen-substituted PPhedOS \(( P1a) \) is a rigid polymer, while a more flexible backbone is formed upon sulfur substitution in PPhedOTS \(( P1c) \) and PPhFeOTS \(( P1b) \).

Similarly to its selenophene analogs, 3,4-oxygen-substituted polymer PPhFeDOT \(( P2a) \), demonstrates an absorption spectrum with vibronic features and \( \lambda_{\text{max}} \) at 510/562/620 nm (Fig. 5a, Table 1). The absorption spectrum of PPhFeOTT \(( P2b) \) is blue-shifted compared to its selenophene analog PPhedOTS \(( P1b) \) and exhibits a non-split pattern with \( \lambda_{\text{max}} \) at 583 nm. The spectroelectrochemically measured band gaps \(( E_{g(\text{opt})} \) of all thio- phene-based polymers (in an undoped state) are somewhat higher than those for their selenophene analogs (Table 1). For example, the band gaps of PPhedDOT \(( P2a) \), and PPhedOTT \(( P2b) \), are 1.80 and 1.65 eV, respectively \textit{versus} 1.57 and 1.49 eV for PPhedOS \(( P1a) \) and PPhedOTS \(( P1b) \). PPhedDOT \(( P2d) \) shows a band gap identical to that of PPhedDOT \(( P2a) \) (1.80 eV), so that additional extension of fused benzene rings does not affect the polymer band gap. The substitution of sulfur with polythiophenes \(( P2b \textit{versus} P2a) \) has a similar effect on polymer properties as was observed in the polyselenophene series \(( P1b \textit{versus} P1a) \).

It is interesting to note that the widths of the absorption peaks of the polymers studied here in the undoped state are not significantly affected by substituents at the 3,4-positions (O or S heteroatoms). The peak widths at half maxima (FWHM) for polyselenophenes \( P1a-d \) are 0.64–0.65 eV, while related phenylene-bridged polythiophenes \( P2a,b,d \) show somewhat lower values of 0.57–0.60 eV, again with only a small effect observed for the different heteroatoms in the bridge. This is in contrast to ethylene-bridged polymers,\(^{18,19}\) where sulfur atoms at the 3,4-position cause very significant broadening of the absorption peak. In phenylene-bridged polymers, the benzene ring, which has only non-flexible sp\(^2\) carbon atom arrangements, provides the molecule with additional stiffness. Therefore, the loss of rigidity upon the replacement of the oxygen heteroatom at the 3,4-position is not significant in polymers \( P1 \) and \( P2 \).
Computational studies

(a) Electronic structure. Our experimental findings regarding the energy levels, rigidity, and band gaps of phenylene-bridged polyselenophenes are supported by calculations of orbital energies and twisting potentials. Polymers P1a–d and P2a–d, as well as PEDOS and PEDOT were fully optimized at the PBC/B3LYP/6-31G(d) level of theory. In general, the PBC/B3LYP/6-31G(d) level proves to provide a reasonably good estimation of the optical band gaps (obtained from the onset at the long wavelength of the absorption spectra) of conjugated polymers. It was found that replacement of the ethylenedioxy-bridge in PEDOS and PEDOT with an arylendioxy-oxythio/dithio-bridge causes a significant decrease of 0.85 eV in the highest occupied crystal orbital (HOCO) energy levels (Table 2). A higher level of conjugation in the side chain (in the case of naphthylendioxy-bridged polymers P1d and P2d) leads to an insignificant additional reduction in the HOCO energy level (Table 2 and Fig. 6). Thus, the HOCO energy of PEDOS is ~3.45 eV, while in PEDOS (P1a) it is lowered to ~3.30 eV, which is nearly the same value (~3.43 eV) as for PEDOT (P1d). The same tendency is observed in polythiophenes: ~3.32 eV in PEDOT, ~4.37 eV in PEDOTS (P1b), and ~4.39 eV in PEDOT (P2d). Notably, replacing oxygen with sulfur atom(s) at the 3,4-positions of the selenophene or thiophene rings in P1a and P2a, as occurs in P1b, P1c, P2b, and P2c, further lowers the HOCO energy level (Table 2 and Fig. 6). The HOCO energy levels are found to be ~4.44 eV and ~4.60 eV for phenylene-bridged polyselenophenes PPheOTS (P1b) and PPheDTS (P1c), respectively, and ~4.52 eV and ~4.67 eV for phenylene-bridged polythiophenes PPheOTT (P2b) and PPheDTT (P2c), respectively. Experimental HOMO energy values (taken from the onsets of the oxidation peaks in CV measurements) correlate well with the theoretical data for polymers P1a–d and P2a–d (Table 2, Fig. 6 and Fig. S9a in the ESI†).

Density of states diagrams for P1a–c and PEDOS are shown in Fig. 7. There is a good dispersion of frontier orbitals as experimentally obtained optical band gaps (which is partially due to the point of comparison being the onset at the long wavelength, which corresponds to the lowest experimental estimation of the band gap). It was found that replacement of the arylendioxy-bridge in PEDOS and PEDOT with an arylendioxy-oxythio-dithio-bridge causes a significant decrease of 0.85 eV in the highest occupied crystal orbital (HOCO) energy levels (Table 2). A higher level of conjugation in the side chain (in the case of naphthylendioxy-bridged polymers P1d and P2d) leads to an insignificant additional reduction in the HOCO energy level (Table 2 and Fig. 6). Thus, the HOCO energy of PEDOS is ~3.45 eV, while in PEDOS (P1a) it is lowered to ~3.30 eV, which is nearly the same value (~3.43 eV) as for PEDOT (P1d). The same tendency is observed in polythiophenes: ~3.32 eV in PEDOT, ~4.37 eV in PEDOTS (P1b), and ~4.39 eV in PEDOT (P2d). Notably, replacing oxygen with sulfur atom(s) at the 3,4-positions of the selenophene or thiophene rings in P1a and P2a, as occurs in P1b, P1c, P2b, and P2c, further lowers the HOCO energy level (Table 2 and Fig. 6). The HOCO energy levels are found to be ~4.44 eV and ~4.60 eV for phenylene-bridged polyselenophenes PPheOTS (P1b) and PPheDTS (P1c), respectively, and ~4.52 eV and ~4.67 eV for phenylene-bridged polythiophenes PPheOTT (P2b) and PPheDTT (P2c), respectively. Experimental HOMO energy values (taken from the onsets of the oxidation peaks in CV measurements) correlate well with the theoretical data for polymers P1a–d and P2a–d (Table 2, Fig. 6 and Fig. S9a in the ESI†).

Density of states diagrams for P1a–c and PEDOS are shown in Fig. 7. There is a good dispersion of frontier orbitals as...
evidenced by broad peaks that reveal a strong intermolecular interaction within the polymer backbone. The energies of the frontier orbitals are affected by the identity of the heteroatom substituents. The sharp peaks located at around −7.0 eV and −0.5 eV correspond to the π and π* orbitals of the benzene ring, which do not interact with the polymer backbone. These orbitals are not affected by polymerization. The peaks at around −5.5 eV and 0.5 eV include states with interaction between the benzene and dioxy/dithio/xythio-selenophene moieties. The energies of these orbitals are also affected by the nature of heteroatoms at the 3,4-positions.

Incorporating the aromatic ring as a fused substituent on the conjugated polymer backbone leads to delocalization of electron density between the benzene ring and the polymer backbone (Fig. 7b) resulting in the formation of less electron rich materials. This delocalization lowers the HOCO energy level (located mostly on the polymer backbone). In organic solar cells, decreasing the HOCO energy level of the donor polymer while retaining its low band gap can significantly improve the open circuit voltage (which directly relates to the difference between the HOMO of the donor and LUMO of the acceptor). This should increase the efficiency of organic photovoltaic (OPV) devices, given that their efficiency is a function of the difference between the LUMO energies of the donor and the acceptor and considering that [6,6]-phenyl-C61-butyric acid methyl ester (PCBM)—a commonly used acceptor in OPV devices—has a rather low-lying LUMO energy level.

(b) Rigidity and twisting of the polymer backbone. All the minimal energy structures of the arylene-bridged polymers

![Table 2](Image) Calculated energies (eV) of the frontier orbitals (HOCO and LUMO) and band gaps for phenylene-bridged selenophene- and thiophene-based polymers at the PBC/B3LYP/6-31G(d) level of theory, together with experimental data from cyclic voltammetric and optical measurements.

<table>
<thead>
<tr>
<th>Polymer</th>
<th>HOCO (eV) calc.</th>
<th>LUMO (eV) calc.</th>
<th>(E_{g(DFT)}^a) (eV) calc.</th>
<th>HOMO(b) exp.</th>
<th>LUMO(e) exp.</th>
<th>(E_{g(opt)}^d) (eV) exp.</th>
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<tr>
<td>PEDOS</td>
<td>−3.45</td>
<td>−1.79</td>
<td>1.66</td>
<td>−3.99</td>
<td>−2.58</td>
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<td>−1.68</td>
<td>1.83</td>
<td>−3.95</td>
<td>−2.35</td>
<td>1.60</td>
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<tr>
<td>PPhedOS, P1a</td>
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<td>−2.32</td>
<td>1.98</td>
<td>−4.26</td>
<td>−2.69</td>
<td>1.57</td>
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<td>PPhedOTS, P1b</td>
<td>−4.44</td>
<td>−2.56</td>
<td>1.88</td>
<td>−4.45</td>
<td>−2.96</td>
<td>1.49</td>
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<tr>
<td>PPhedTTS, P1c</td>
<td>−4.60</td>
<td>−2.71</td>
<td>1.89</td>
<td>−4.60</td>
<td>−3.11</td>
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<td>PNaPhedOS, P1d</td>
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<td>1.85</td>
<td>−4.30</td>
<td>−2.75</td>
<td>1.55</td>
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<td>PPhedOT, P2a</td>
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<td>2.06</td>
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<td>1.80</td>
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<tr>
<td>PNaPhedOT, P2d</td>
<td>−4.39</td>
<td>−2.37</td>
<td>2.03</td>
<td>−4.44</td>
<td>−2.64</td>
<td>1.80</td>
</tr>
</tbody>
</table>

\(a\) Energy band gap from DFT calculations, \(E_{g(DFT)} = E(LUMO) − E(HOCO)\). \(b\) Experimental HOMO energy levels were obtained from the onsets of the oxidation peaks in CV scans of the polymer films in monomer free solution using the Koopmann approximation for the ionization energy: \(HOMO = E(onset) + 4.4\) (eV), where 4.4 eV is the energy level of SCE below the vacuum level. \(c\) Experimental values for the LUMO energy levels, deduced from HOMO (experimental, from CV onsets) and optical band gaps using LUMO = HOMO + \(E_{g(opt)}\) (eV). \(d\) Optical band gaps obtained from the onsets of the polymers π-π* vis absorption peaks in the neutral state. \(e\) Polymerization attempts did not lead to good quality films.

Fig. 5 Spectroelectrochemical measurements of polymer films P2a,b,d on an ITO electrode performed in CH2Cl2/TBAPF6 (0.1 M). (a) PPhedOT (P2a); (b) PPhedOTT (P2b); (c) PNaPhedOT (P2d). Various potentials were applied in situ.
studied here, P1a–d and P2a–d, have a planar conformation, in contrast to the analogous ethylene-bridged structures, some of which have non-planar minimal energy structures.\textsuperscript{18,19} Importantly, the twisting potentials of the studied polymers demonstrate significant differences (Fig. 8 and Table S1 in the ESI\textsuperscript{†}; see ref. 11 for methodology used to calculate twisting

![Image](https://via.placeholder.com/150)

**Fig. 6** Band gaps of P1a–d, P2a–d, PEDOS, and PEDOT (black numbers) calculated at the PBC/B3LYP/6-31G(d) level of theory as well as comparison with experimental band gaps (red numbers) obtained from the onsets of the polymers’ π–π* vis absorption peaks in the neutral state. Experimental HOMO energy levels were obtained from the onsets of the oxidation peaks in CV scans of the polymer films in monomer-free CH\textsubscript{2}Cl\textsubscript{2}/TBAPF\textsubscript{6} (0.1 M) solution using the Koopmann approximation for the ionization energy by $E(\text{HOMO}) = E_{\text{onset}} + 4.4$ (eV), where 4.4 eV is the energy level of SCE below the vacuum level.\textsuperscript{24}

![Image](https://via.placeholder.com/150)

**Fig. 7** (a) Density of states (DOS) diagram of P1a–c and PEDOS. (b) DOS diagram of PPhedOS, P1a, with orbital shape drawings of the sharp peaks in the DOS diagram. Calculated at the PBC/B3LYP/6-31G(d) level of theory (convoluted with $\sigma = 0.1$ eV).

![Image](https://via.placeholder.com/150)

**Fig. 8** Twisting energy (kcal mol$^{-1}$) of polymers as a function of interring angle ($\phi$) calculated at the PBC/B3LYP/6-31G(d) level of theory. For PPhedOTS (P1b) and PPhedOTT (P2b), a head-to-tail assignment was used. (a) P1a, P1d, P2a, P2d, PEDOS, and PEDOT. (b) Polyselenophenes P1a–c and polythiophenes P2a–c. The methodology described in ref. 11 was used to calculate twisting energy.
energy in polymers). Twisting to 30° is relatively easy for all the studied polymers and requires only 0–2 kcal mol⁻¹. Additional twisting is more energy consuming: 0–5.5 kcal mol⁻¹ for 60° and 1.2–8.3 kcal mol⁻¹ for 90°. PPheDOS (P1a) is slightly less rigid than PEDOS, and PPheDOT (P2a) is slightly less rigid than PEDOT (Fig. 8a). While twisting potential depends only slightly on the nature of the bridging group (phenylene or naphthalene versus ethylene), for each type of bridging the polyselenophenes require more energy to twist and demonstrate a more rigid backbone than the polythiophenes (Fig. 8). This observation correlates well with our previous theoretical and experimental studies, which suggested that polyselenophenes have a more rigid backbone than polythiophenes.

In contrast to the effect of the bridging group, the nature of the heteroatoms at the 3,4-positions causes significant variations in the rigidity of the polymers. Sulfur substitution leads to a more flexible backbone compared to the oxygen-containing analogs. As seen in Fig. 8b, twisting all-oxygen substituted polymers PPheDOS (P1a) and PPheDOT (P2a) requires more energy (5.4 and 3.5 kcal mol⁻¹ for a 60° twist, respectively) than twisting asymmetric polymers with one sulfur atom (4.3 and 2.0 kcal mol⁻¹ to twist PPheOTS (P1b) and PPheOTT (P2b), respectively, calculated for head-to-tail type polymers). A significant decrease in twisting energy is observed for all-sulfur substituted polymers (0.5 and 0.01 kcal mol⁻¹ to twist PPheDTS (P1c) and PPheDTT (P2c), respectively, by 60°).

The theoretical data given above correlate well with the electron absorption spectra (Table 1), which demonstrate a non-split absorption band for sulfur-containing polymers PPheDTS (P1c), PPheOTS (P1b) and PPheOTT (P2b), while absorption bands for PPheDOS (P1a), and PPheDOT (P2a) show some vibronic features indicative of a more rigid structure. Thus, the substitution of different heteroatoms offers a means of tuning the rigidity of the polymer backbone, as we showed earlier.

Conclusions

In this work, a series of new polyselenophenes that bear aromatic ring bridging substituents having all sp² carbons was prepared and studied. The introduction of an aromatic ring into the periphery of PEDOS/PEDOT type polymers causes a decrease in the HOMO energies and results in the formation of less-electron-rich polymers making their undoped states more environmentally stable. In addition, the planar aromatic ring provides the resultant polymers with a flatter conformation. This opens up the opportunity for further functionalization on the side of the arylene fragments to increase the solubility and processability of the polymers without disturbing the planarity of the backbone and the interplanar distance between the polymer chains.

The reported polyselenophenes P1a–d have different heteroatoms attached at the 3,4-positions of the selenophene ring. We found that the electrochemical properties of such polymers vary significantly depending on the nature of the heteroatoms. Using a sulfur atom as the linker leads to a slight decrease in the band gap and a lower HOMO energy level, while oxygen atoms in the 3,4-positions result in a more rigid polymer backbone. Interestingly, unlike PEDOS and other polyselenophenes with sp³ hybridized carbons in an ethylene bridge, sp² phenylene-bridged polyselenophenes do not demonstrate broadening of the absorption peak upon substitution of oxygen(s) at the 3,4-positions by sulfur(s). This has been attributed to their higher rigidity. Comparison of the phenylene-bridged polyselenophenes P1a–d with their thiophene analogs P2a–d shows that polyselenophenes benefit from a lower band gap and greater rigidity, and that, overall, they create better quality polymer films under electrochemical polymerization.

Acknowledgements

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28 With respect to polymers, we use the term HOMO for the energy of the top of the valence band. This also corresponds to the calculated HOCl (highest occupied crystal orbital) level using PBC formalism.

29 While we used uniform names for the compounds as derivatives of arylene-X-Y-selenophenes (-thiophenes) throughout the text for the convenience of readers, in the experimental section the names of synthesized compounds are given according to IUPAC nomenclature.


31 The structure is disordered and, as such, the molecule has been refined in two alternate orientations with occupancies of approximately 55% and 45%. Because of the twinned structure (disordered structure), we do not discuss the structural parameters of the molecule (bond lengths, bond angles, etc.).

32 The selection of an appropriate solvent is crucial for polymer quality. In this work, dichloromethane, acetonitrile, and propylene carbonate were tested (see Fig. 2 and S3–S7 in the ESI†). PhedOTS (1b) and PhedTTS (1c) can be polymerized in various solvents to good quality films prepared in dichloromethane and propylene carbonate) and at different scan rates. Conditions for the formation of “double oxygen” substituted PPheDOS (Pla) are more restricted. Attempts to produce Pla polymer film in propylene carbonate were unsuccessful, polymerization in acetonitrile results in low-quality films, and only the use of dichloromethane as a solvent led to high-quality films of polymer Pla. In addition, a relatively slow (50 mV s⁻¹) scan rate is required to obtain high-quality films of Pla. Since dichloromethane is a good solvent for all the polymers reported in this paper, subsequent discussions relate to polymers prepared in dichloromethane with TBAPF₆ as a supporting electrolyte.


34 Similarly to previous report, electropolymerization of PhedDOT (2a) proved difficult and required proper choice of the solvent (no polymerization was observed in acetonitrile, while electropolymerization in dichloromethane was observed at high concentrations of PhedDOT). PhedDOT (P2a) was obtained by applying a scan rate of 50 mV s⁻¹ and using a potential range of −0.4 to 1.6 V. PhedOTT (2b) smoothly undergoes electropolymerization to yield a good quality film of PhedOTT (P2b), while electrochemical polymerization of PhedDTT (2c) to obtain PhedDTT (P2c) was problematic and did not lead to a reasonably good polymer film (Fig. S1†).

35 Our calculated values for PPheDODT correlate well with previously estimated values for PPheDODT based on extrapolation of PPheDOT oligomers (band gap = 2.12 eV (ref. 12b)).


37 Indeed, these theoretical data also correlate well with previously observed experimental results that showed very significant broadening of the absorption spectrum upon incorporation of a sulfur atom into PEDOS-type structures (ref. 18).