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## Mixed $\pi$ -conjugated oligomers of thiophene and 3,4-ethylenedioxythiophene (EDOT)

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### Abstract

Conjugated oligomers based on various combinations of thiophene and 3,4-ethylenedioxythiophene (EDOT) moieties have been synthesised. Comparison of the optical and electrochemical properties shows that the introduction of a bis-EDOT core in the middle of the system produces a decrease of the HOMO–LUMO gap which is attributed to an enhancement of the planarity and rigidity of the  $\pi$ -conjugated system. © 2000 Elsevier Science Ltd. All rights reserved.

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Thiophene-based monodisperse linear  $\pi$ -conjugated oligomers with a well-defined chemical structure are the subject of considerable current interest related to their potential applications as active material in organic electronic and photonic devices and in molecular electronics.<sup>1</sup> Further progress in these various fields implies the molecular engineering of conjugated systems with electronic properties specifically tailored in view of a given application.<sup>1,2</sup> In this context, the past few years have witnessed the emergence of the 3,4-ethylenedioxythiophene (EDOT) as the building block at the forefront of the chemistry of conjugated systems.<sup>3</sup> This rapid development is related to the unique combination of environmental stability, low oxidation potential and moderate bandgap of poly(EDOT).

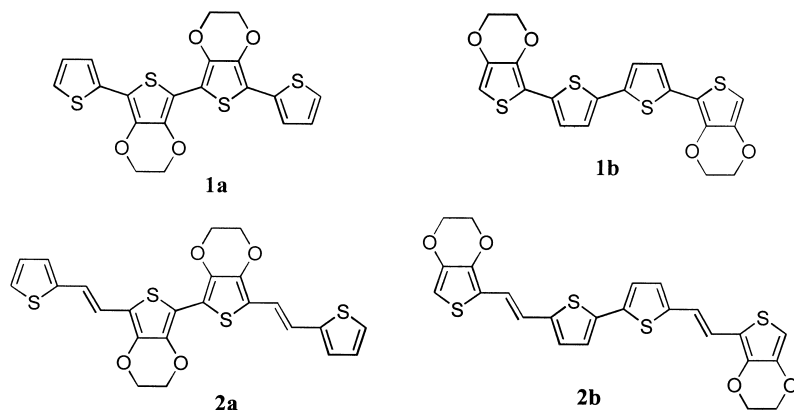
As exemplified in several works, the use of the EDOT building blocks allows the development of new conjugated systems with original properties, such as polymers with improved electrochromic behavior, precursors of electrogenerated functional conjugated polymers with a better aptitude for electropolymerization,<sup>3</sup> polymers with small intrinsic bandgap<sup>4</sup> and extended tetrathiafulvalene analogs with enhanced  $\pi$ -donor ability.<sup>5</sup> However, examples of oligomers incorporating the EDOT system remain scarce. EDOT oligomers have so far been limited to the trimer by stability

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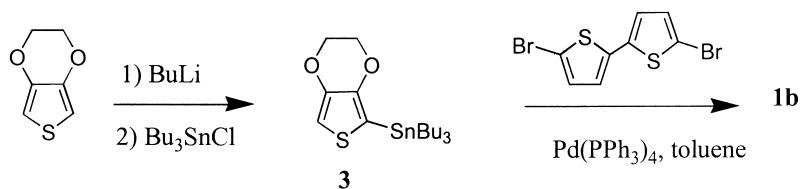
problems.<sup>6</sup> Oligothiophenes containing EDOT have been recently reported but their electronic properties were not investigated.<sup>7</sup>

We report here preliminary results on the synthesis of two series of conjugated oligomers **1** and **2** (Scheme 1) in which EDOT moieties have been inserted either as a median bis-EDOT core (**1a**, **2a**) or as external end groups (**1b**, **2b**). The electronic and electrochemical properties of these compounds have been analyzed by UV-vis spectroscopy and cyclic voltammetry in order to discuss the effects of the position of the EDOT groups on the electronic properties and reactivity of the resulting conjugated systems.

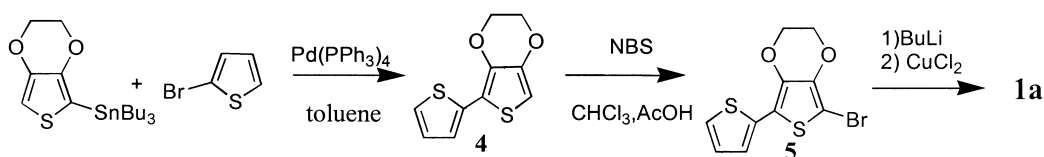


Scheme 1.

Compounds **1a** and **1b** have been recently described.<sup>7</sup> Compound **1a** was obtained in 47% yield by Stille coupling of bis-tributylstannyl bis-EDOT with 2-bromothiophene; **1b** was obtained in 20% yield by coupling of  $\alpha,\alpha'$ -dibromobithiophene with a boronic ester of EDOT. In this work, we have obtained the tetramer **1b** with a better yield (47%) by the reaction of  $\alpha,\alpha'$ -dibromobithiophene with tributylstannyl-EDOT **3** in the presence of  $\text{Pd}(\text{PPh}_3)_4$  (Scheme 2). Tetramer **1a** has been prepared by a new synthetic approach which takes advantage of the different reactivities of thiophene and EDOT (Scheme 3). A Stille coupling between 2-bromothiophene and the tributylstannyl EDOT derivative **3** gave 2-(2-thienyl)-(3,4-ethylenedioxythiophene) **4** in 72% yield. Treatment of **4** by 1 equiv. of NBS under protic conditions gave the bromo-derivative **5** in 90% yield. The selectivity of this reaction results from the electron-donating effect of the ethylenedioxy group which favors electrophilic substitution of the EDOT cycle. Metal-halogen exchange on compound **5**, with 1 equiv. of BuLi, followed by oxidative coupling in the presence of  $\text{CuCl}_2$ , afforded **1a** in 42% yield.

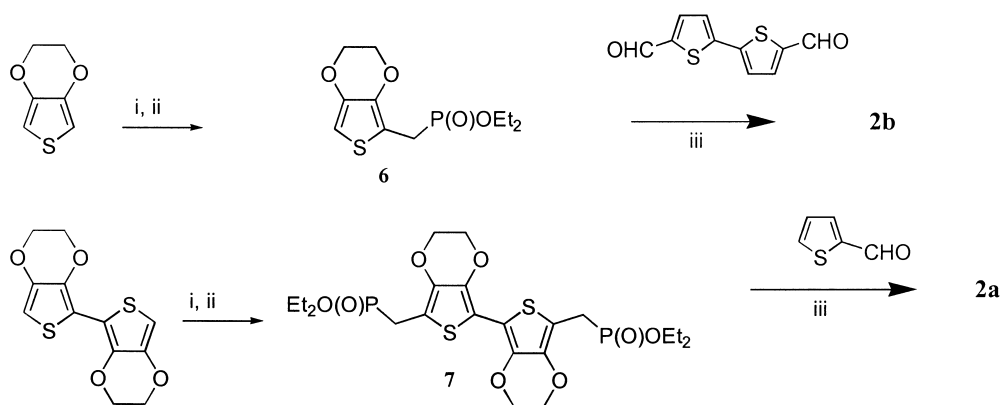


Scheme 2.



Scheme 3.

The bis-olefinated oligomer **2b** is prepared in 68% yield by the Horner–Wadsworth–Emmons reaction between diformyl-bithiophene and the EDOT phosphonate **6**, while **2a** is synthesized in 65% yield from 2-thiophenecarbaldehyde and the bis-phosphonate **7** (Scheme 4). Phosphonates **6** and **7** have been obtained in 55 and 15% yield, respectively, by a one-step reaction between iodomethylphosphonate and the appropriate mono and dilithiated derivatives in the presence of CuI.<sup>8</sup> Attempts to synthesize **2a** by olefination of  $\alpha,\alpha'$ -diformyl bis-EDOT with an excess of thiophene phosphonate remain unsuccessful, presumably because of the poor solubility of the dialdehyde. The <sup>1</sup>H NMR spectra of **2a** and **2b** in C<sub>6</sub>D<sub>6</sub> exhibit the 15.9 Hz coupling of the ethylenic protons expected for an all *trans* configuration.

Scheme 4. (i) BuLi; (ii) ICH<sub>2</sub>P(O)OEt<sub>2</sub>, CuI; (iii) *t*-BuOK

As shown by the cyclic voltammetric (CV) data in Table 1, the position of the EDOT moieties exerts a marked effect on the electrochemical behavior of the oligomers. For both series, moving the EDOT groups from the middle to the end of the molecule produces a positive shift of the first

Table 1  
Optical and cyclic voltammetry data

Compound	E <sub>pa1</sub> (V) <sup>a</sup>	E <sub>pa2</sub> (V) <sup>a</sup>	λ <sub>max</sub> (nm) <sup>c</sup>
<b>1a</b>	0.65	1.10	416
<b>1b</b>	0.75 <sup>b</sup>	-	412
<b>2a</b>	0.59	1.00	461
<b>2b</b>	0.71 <sup>b</sup>	-	454

<sup>a</sup>10<sup>-4</sup> mol.L<sup>-1</sup> in *n*-Bu<sub>4</sub>NPF<sub>6</sub> 0.1 M/CH<sub>2</sub>Cl<sub>2</sub>, Ref. Ag/AgCl, 100 mV.s<sup>-1</sup>

<sup>b</sup> irreversible peak

<sup>c</sup>10<sup>-5</sup> mol.L<sup>-1</sup> in CH<sub>2</sub>Cl<sub>2</sub>

anodic peak potential ( $E_{pa1}$ ) indicative of a decrease in the HOMO level. Moreover, the CV of **1a** and **2a** shows two reversible one-electron oxidation steps corresponding to the successive generation of the cation radical and dication (Fig. 1), whereas compounds **1b** and **2b** undergo an irreversible oxidation process associated with electrochemical polymerization, as already observed for other conjugated systems with EDOT end groups.<sup>9</sup> As in the case of oligomers substituted in the  $\beta$ -position by methoxy groups,<sup>10</sup> the donor effect of ethylenedioxy groups stabilizes the positive charge of the radical cation in the terminal thiophene of **1b** and **2b**, causing a high density spin in the  $\alpha$ -position, which allows the electropolymerization process.

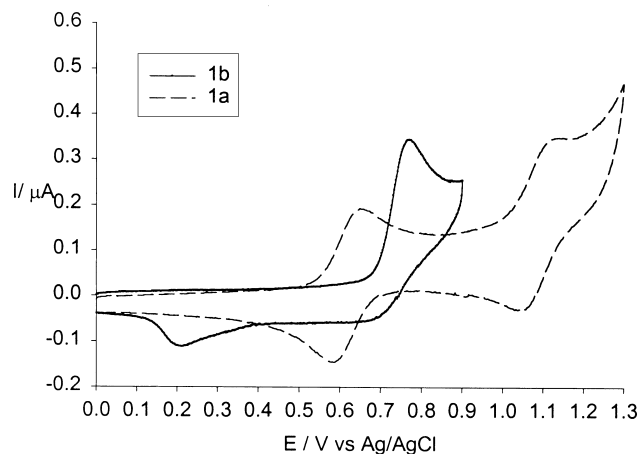


Figure 1. Cyclic voltammograms of **1a** and **1b** (see Table 1 for conditions)

Comparison of the UV–vis spectra shows that oligomers with a central bis-EDOT (**1a** and **2a**) exhibit slightly red shifted  $\lambda_{max}$ , indicative of a smaller HOMO–LUMO gap. Furthermore, as shown in Fig. 2, the electronic spectrum of **1a** and **2a** exhibit a significantly better resolved vibronic structure than **1b** and **2b**. Such behavior, already observed for covalently bridged  $\pi$ -conjugated

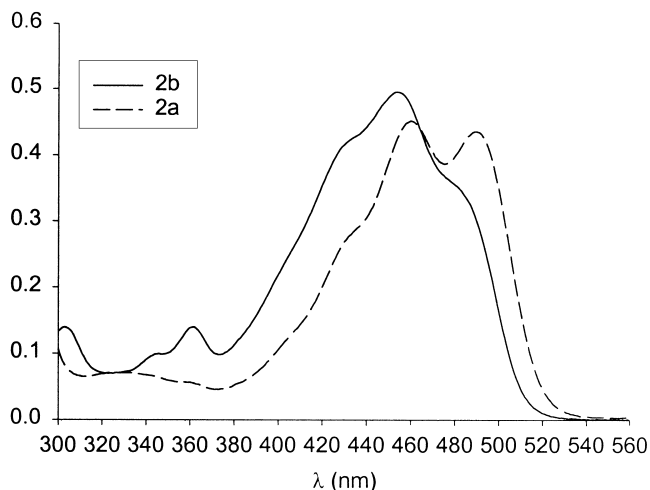


Figure 2. Electronic spectra of **2a** and **2b** in  $\text{CH}_2\text{Cl}_2$

systems,<sup>11</sup> suggests that S...O intramolecular interactions between the two central EDOT groups result in a planarization and rigidification of the conjugated system, and hence in an enhanced  $\pi$ -electron delocalization. A crystallographic analysis of these compounds is now underway and should allow a definitive confirmation of this hypothesis.

To summarize, two series of  $\pi$ -conjugated oligomers incorporating the EDOT moiety have been synthesised.<sup>12</sup> In both cases the electron-donating effect of the ethylenedioxy groups leads to a decrease in the oxidation potential and HOMO–LUMO gap. It also significantly affects the electron distribution in the conjugated system and hence the reactivity of the corresponding cation radical. In view of their original electronic properties these new oligomers could lead to interesting active materials for the realization of electronic devices.

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- All new compounds give satisfactory spectroscopic data. Selected examples: **5**: Pale yellow solid, mp 83°C, HRMS calcd for C<sub>10</sub>H<sub>7</sub>O<sub>2</sub>S<sub>2</sub>Br 301.9071, found 301.9064 <sup>1</sup>H NMR (CDCl<sub>3</sub>) 7.22 (dd, 1H, <sup>3</sup>J=5.0 Hz, <sup>4</sup>J=1.5 Hz), 7.15 (dd, 1H, <sup>3</sup>J=3.5 Hz, <sup>4</sup>J=1.5 Hz), 7.05 (dd, 1H, <sup>3</sup>J=5.0 Hz, <sup>3</sup>J=5.0 Hz), 4.30 (m, 4H). **1a** and **1b** present same characteristics as already described.<sup>7</sup> **2a**: Red powder, mp > 260°C; HRMS calcd for C<sub>24</sub>H<sub>18</sub>O<sub>4</sub>S<sub>4</sub> 498.0088, found 498.0085; <sup>1</sup>H NMR (C<sub>6</sub>D<sub>6</sub>) 7.39 (d, 2H, <sup>3</sup>J=15.9 Hz), 7.20 (d, 2H, <sup>3</sup>J=15.9 Hz), 6.70 (d, 2H, <sup>3</sup>J=3.3 Hz), 6.67 (d, 2H, <sup>3</sup>J=4.9 Hz), 6.63 (dd, 2H, <sup>3</sup>J=4.9 Hz, <sup>3</sup>J=3.3 Hz), 3.48 (m, 4H), 3.33 (m, 4H). **2b**: Orange powder, mp 205°C; HRMS calcd for C<sub>24</sub>H<sub>18</sub>O<sub>4</sub>S<sub>4</sub> 498.0088, found 498.0085; <sup>1</sup>H NMR (C<sub>6</sub>D<sub>6</sub>) 7.22 (d, 2H, <sup>3</sup>J=15.9 Hz), 7.11 (d, 2H, <sup>3</sup>J=15.9 Hz), 6.79 (d, 2H, <sup>3</sup>J=3.8 Hz), 6.52 (d, 2H, <sup>3</sup>J=3.8 Hz), 6.01 (s, 2H), 3.35 (m, 8H).