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Rigid oligomers based on the combination of 3,6-dimethoxythieno[3,2-*b*]thiophene and 3,4-ethylenedioxythiophene

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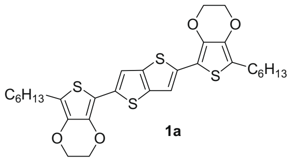
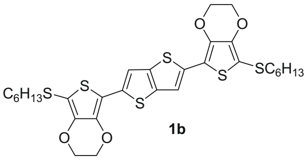
New oligomers based on the combination of the 3,6-dimethoxythieno[3,2-*b*]thiophene and 3,4-ethylenedioxythiophene (EDOT) moieties have been prepared and studied by UV–vis spectroscopy and cyclic voltammetry. The use of the intrinsically rigid thienothiophene units in addition to the S···O intramolecular interactions leads to planar conformation of the conjugated chains. While the radical cations of oligomers end capped by *n*-hexyl chains show a tendency to the dimerization, those substituted by *n*-hexylsulfanyl chains present a high stability.

Thiophene-based conjugated oligomers represent one of the most widely investigated class of functional π-conjugated systems, motivated by their potential technological applications as organic semi-conducting materials for the fabrication of (opto)electronic devices such as field-effect transistors (OFET), electroluminescent diodes (OLED) and photovoltaic cells.[1–3] Careful modifications on the oligothiophene backbone allow to control the energy levels of the HOMO and LUMO frontier orbitals and thus to tune crucial electronic properties such as ionization potential, electron affinity, absorption and emission properties.[4] For example, structural modifications, consisting of rigidifying planar-conjugated frameworks, have been developed to limit the rotational disorder between the thiophene rings which affects the band gap in the solid state.[4,5] Recently many works based on the incorporation of the intrinsically rigid thieno[3,2-*b*]thiophene units in conjugated oligomers or polymers have been developed to improve their electronic properties and optimize the performances of the corresponding devices.[6–11] However, the extension of the conjugated systems is always limited by the twist from planarity between adjacent thienothiophene units. Substitution on the β-position with alkyl chain for enhancing the solubility increases steric hindrances leading to the materials with higher gap.[10,11] Fully fused oligothiophene derivatives have recently been described but the lengthening of the conjugated chain is rapidly limited by the synthetic pathways.[12–15] An alternative consists in associating rigid units by sigma bonds and additionally in limiting the rotational disorder by intramolecular interactions which rigidify the conjugated backbone. In this context, we have shown that poly-3,6-dimethoxythieno[3,2-*b*]thiophene presents a self-rigidification through S···O intramolecular interactions of the conjugated chain.[16] Electropolymerized or chemically generated poly-3,6-dialkoxythieno[3,2-*b*]thiophenes present a moderate band gap around 1.7–1.8 eV.[16,17]

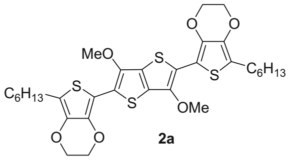
We report here on the synthesis and the characterization of hybrid EDOT–thienothiophene oligomers **1** and **2** (Chart) in which thieno[3,2-*b*]thiophene and 3,6-dimethoxythieno[3,2-*b*]thiophene units have been inserted between the two EDOT moieties.



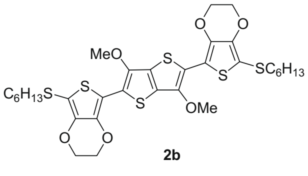
1a



1b



2a



2b

The comparison of the electronic properties of these two series of oligomers shows the role of the methoxy groups both for strengthening the rigidification of the conjugated systems and for increasing the donor character of the molecules.

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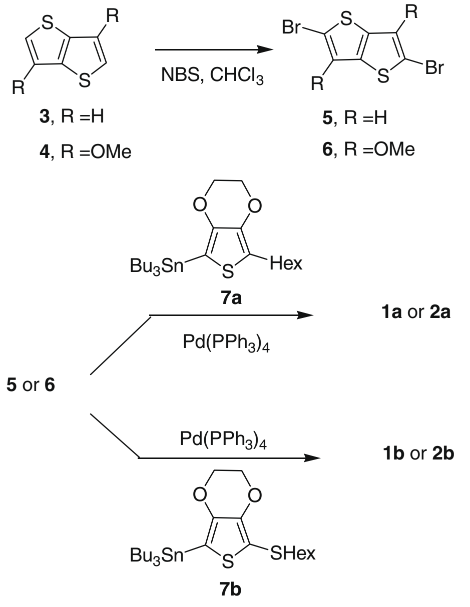
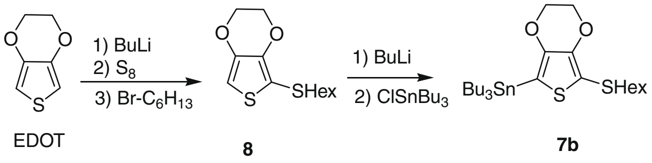
The syntheses of compounds **1** and **2** are based on a twofold Stille coupling reaction between the dibromo-thienothiophene units **5** or **6** and the tributylstannyl-EDOT derivatives **7** (Scheme 1). Treatment of thienothiophene cores **3** or **4** with 2 equiv of *N*-bromosuccinimide (NBS) in $CHCl_3$ at −20 °C afforded dibromo derivatives **5** or **6** in 95% or 90% yields, respectively. Then the coupling reactions of **5** and **6** with a slight excess of stannyl derivative **7a**[18] in the presence of $Pd(PPh_3)_4$ led to oligomers **1a** and **2a** in 54% and 25% yields, respectively.[19] The substitution of the EDOT core by the hexylsulfanyl chains has been achieved by the sequence $BuLi/S_8$ leading to thiolato-EDOT derivative which was immediately treated with bromohexane to give compound **8** in 78% yield (Scheme 2). The stannyl derivative **7b**, obtained by the sequence $BuLi/Bu_3SnCl$ on **8**, was coupled with **5** or **6** to lead to oligomers **1b** and **2b** in 45% and 30% yields, respectively.[19]

The optical and electrochemical properties of **1** and **2** are gathered in Table 1 and compared to their analogues **9**[20,21] incorporating a 2,2′-bithiophene core in the median position (Scheme 3).

The comparison of the UV–vis absorption spectra of oligomers **1** and **2** shows the role of the methoxy group for strengthening the self-rigidification of the conjugated chain (Fig. 1). Compared to compounds **9**, the spectra of compounds **1** present a blue shift of the absorption band as expected for shorter oligomers. For **1**, the shape of the band is narrowed and the vibronic fine structure is more accentuated with the apparition of second maxima (λ_{0-0}). Such effects are the indication of a higher rigidification of the conjugated chain due to the intrinsically rigid thienothiophene core in the median position. Additionally, the insertion of the methoxy groups in oligomers **2** provokes a refinement of the fine structure and a slight bathochromic shift of the absorption band. The first effect suggests that the methoxy groups increase the self-rigidification of the



Scheme 1. Synthesis of oligomers.



Scheme 2. Synthesis of 2-hexylsulfanyl-3,4-ethylenedioxythiophene.

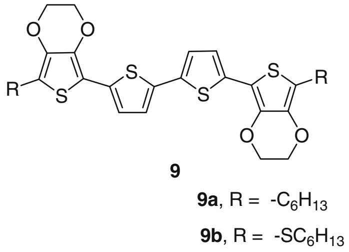
Table 1

Electrochemical and UV–vis spectroscopic data of compounds **1**, **2** and **9**

Compounds	λ_{max}[a] (nm)	λ_{0-0}[a] (nm)	E_1[b] (V)	E_2[b] (V)	ΔE (mV)
1a	398	418	0.65	1.02	370
2a	402	426	0.45	0.80	350
9a[20]	422	446	0.57	0.84	270
1b	410	430	0.74	0.85	110
2b	414	438	0.56	0.66	100
9b	431	455	0.65	0.68	30

[a] λ_{max} (main absorption band) and λ_{0-0} (lowest energy band) in CH_2Cl_2 10^{-5} M.

[b] Versus Ag/AgCl, 100 mV s^{-1}.



Scheme 3. Structure of compounds **9**.

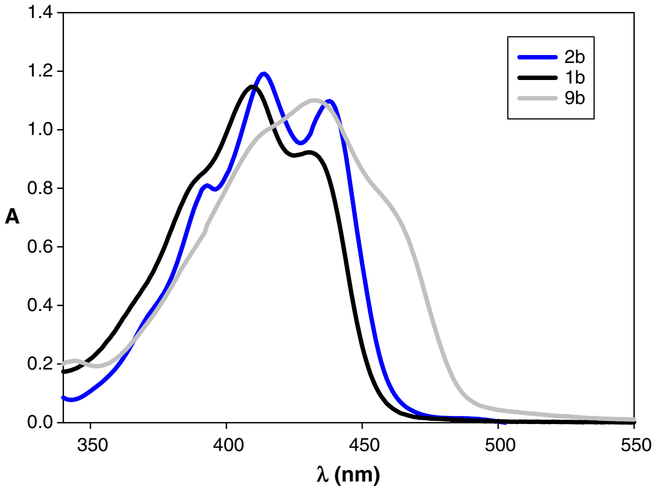


Figure 1. UV–vis spectra of compounds **1b, 2b** and **9b** in CH_2Cl_2.

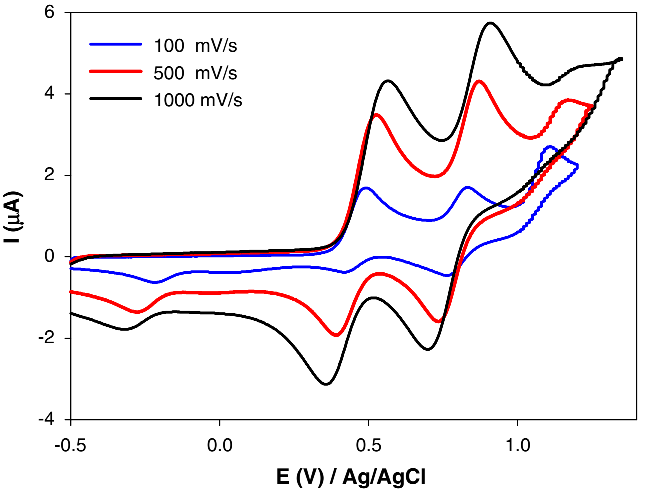
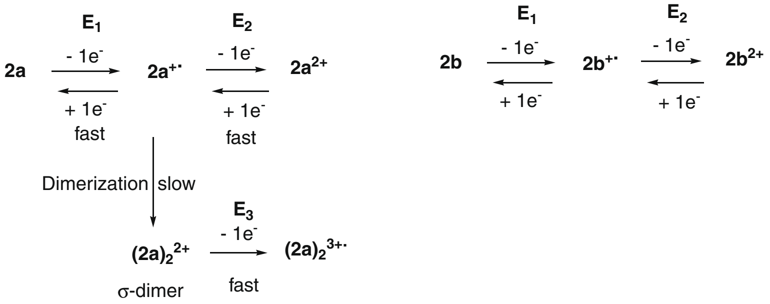


Figure 2. CV of **2a** in 0.1 M Bu_4NPF_6/CH_2Cl_2.



Scheme 4.

conjugated chains by the multiplication of S···O intramolecular interactions between the median thienothiophene unit and the external EDOT moieties.[22] Thus, the synergy of the structural and electronic effects of the methoxy groups leads to a higher rigidity of the conjugated systems and to a lower HOMO–LUMO gap.

The electrochemical properties of oligomers have been analyzed by cyclic voltammetry (CV) and the oxidation potentials are gathered in Table 1. The CV traces of oligomers **1a** and **2a** are strongly dependent on the scan rates (Fig. 2 for **2a**). Thus at 100 mV s^{-1} scan rate, the CV of **1a** and **2a** shows a first partially reversible oxidation peak followed by a second reversible peak and then by a third irreversible peak. By increasing the rate of the scan in potential, the reversibility of the first peak increases while the intensity of the third peak strongly decreases. From scan rate of 1 V s^{-1}, the two first oxidation waves are fully reversible while the third oxidation peak is quasi vanished. At high scan rate the CV corresponds to the subsequent formation of the radical cation $\mathbf{1a}^{+\cdot}$ or $\mathbf{2a}^{+\cdot}$ at potential E_1 and then a dication $\mathbf{1a}^{2+}$ or $\mathbf{2a}^{2+}$ at potential E_2. At lower scan rate the CV data can be interpreted by the formation of a dimeric dication $(\mathbf{1a})_2{}^{2+}$ or $(\mathbf{2a})_2{}^{2+}$, named σ-dimer, by coupling of the radical cation (Scheme 4). Such dimerization processes have already been described for bithiophene derivatives.[23,24]

The kinetic of the dimerization process of the radical is not very fast and an amount of radical cation is not dimerized when the potential reaches E_2 allowing the formation of dication $\mathbf{1a}^{2+}$ or $\mathbf{2a}^{2+}$. The third oxidation potential (E_3) corresponds to the oxidation step of the σ-dimer involving the transfer of one electron followed by another chemical reaction. The intensity of this oxidation step allows evidencing the formation of the σ-dimer. By increasing the scan rate, the time scale allowing the coupling reaction becomes shorter, thus limiting the formation of σ-dimer and by consequence decreasing the intensity of the third oxidation peak.

The CV of compounds **1b** and **2b** end capped by hexylsulfanyl chains shows two reversible close oxidation waves, even for scan rate inferior to 100 mV s^{-1}, corresponding to the successive formation of radical cation and dication. Thus the presence of the sulfur atoms on the external positions strongly stabilizes the radical cation which does not present the dimerization process.[25,26]

Compared to tetrathiophene derivatives **9a** and **9b**, the first oxidation potential of **1a** and **1b** is positively shifted as expected by the shortening of the conjugated chain. Moreover, the higher difference $\Delta E = E_2 - E_1$ observed for **1a** and **1b** corresponds to an increase of the coulombic repulsion between the two positive charges in the dication state. It can be noted that the lower difference ΔE observed for **9b**, **1b** and **2b** compared to **9a**, **1a** and **2a** is an indication of the strong participation of the terminal sulfur atoms of the hexylsulfanyl chains for stabilizing the positive charge of the dication in the external position. Finally, by comparison with **1a** and **1b**, the introduction of the methoxy group on the central thienothiophene unit provokes a negative shift of the oxidation potentials for **2a** and **2b** due to the mesomeric donor effect of the ether groups.

In conclusion, we have synthesized a series of hybrid oligomers combining EDOT and thienothiophene units. These oligomers present a planar conformation due to the association of the intrinsically rigid thieno[3,2-*b*]thiophene unit together with the self-rigidification of the conjugated chain by S···O intramolecular interactions. The radical cations of oligomers substituted with *n*-hexyl chains present a tendency to dimerize while with hexylsulfanyl group as substituent the stability of the radical cations is strongly improved.

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19. All new compounds exhibited spectral properties consistent with the assigned structures: Compound **1a**: orange solid, mp 142 °C, ^1H NMR (500 MHz) 0.89 (t, ^3J = 6.8 Hz, 6H), 1.33 (m, 12H), 1.61 (m, 4H), 2.64 (m, 4H, ^3J = 7.2 Hz), 4.23 (m, 4H), 4.32 (m, 4H), 7.28 (s, 2H). ^{13}C NMR (125.7 Hz) 14.1, 22.6, 25.7, 28.8, 30.3, 31.5, 64.5, 65.1, 108.4, 114.1, 116.6, 136.0, 137.5, 137.6, 137.7. MS Maldi-tof calcd for $C_{30}H_{36}O_4S_4$: 588.15; found: 588.14. Compound **2a**: orange solid, mp 202 °C, ^1H NMR (500 MHz) 0.89 (t, ^3J = 6.8 Hz, 6H), 1.33 (m, 12H), 1.63 (m, 4H), 2.65 (m, 4H, ^3J = 7.1 Hz), 4.09 (s, 6H), 4.23 (m, 4H), 4.33 (m, 4H). ^{13}C NMR (125.7 Hz) 14.1, 22.5, 25.8, 28.8, 30.4, 31.5, 59.4, 64.5, 65.2, 106.1, 117.3, 126.2, 136.8, 136.9, 144.7. MS Maldi-tof Calcd for $C_{32}H_{40}O_6S_4$: 648.17; found: 648.09. Compound **1b**: orange solid, mp 140 °C, ^1H NMR (500 MHz) 0.90 (t, ^3J = 6.8 Hz, 6H), 1.28 (m, 8H), 1.40 (m, 4H), 1.62 (m, 4H), 2.73 (t, 4H, ^3J = 7.5 Hz), 4.34 (m, 8H), 7.34 (s, 2H). ^{13}C NMR (125.7 Hz) 13.9, 22.5, 28.1, 29.3, 31.3, 38.5, 64.7, 64.9, 109.3, 115.1, 118.6, 136.5, 138.5, 139.0, 140.6. MS Maldi-tof calcd for $C_{30}H_{36}O_4S_6$: 652.09; found: 652.14. Compound **2b**: orange solid, mp 136 °C, ^1H NMR (500 MHz) 0.88 (t, ^3J = 7.0 Hz, 6H), 1.25 (m, 8H), 1.41 (m, 4H), 1.63 (m, 4H), 2.75 (t, 4H, ^3J = 7.5 Hz), 4.11 (s, 6H), 4.25 (m, 4H), 4.36 (m, 4H). ^{13}C NMR (125.7 Hz) 14.1, 22.4, 28.0, 29.5, 32.3, 38.9, 59.9, 64.7, 64.9, 109.3, 115.1, 118.6, 136.5, 138.5, 140.6, 146.3. MS Maldi-tof calcd for $C_{32}H_{40}O_6S_6$: 712.12; found: 712.08.
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21. Compound **9b** has been synthesized by Stille coupling between dibromobithiophene and 2.5 equiv of **7b**. Orange solid, mp = 118 °C, ^1H NMR (500 MHz) 0.90 (t, ^3J = 6.8 Hz, 6H), 1.28 (m, 8H), 1.40 (m, 4H), 1.62 (m, 4H), 2.73

(t, 4H, $^3J = 7.5$ Hz), 4.34 (m, 8H),7.05 (d, $^3J = 3.8$ Hz, 2H), 7.10 (d, $^3J = 3.8$ Hz, 2H). ^{13}C NMR (125.7 Hz) 14.0, 22.5, 28.1, 29.4, 31.3, 38.0, 64.7, 64.9, 105.0, 114.4, 123.4, 123.7, 133.0, 135.8, 137.0, 143.9. MS Maldi-tof calcd for $C_{32}H_{38}O_4S_6$: 678.11; found: 677.96.

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