# Synthesis of 3,4-alkoxythieno[2,3-*b*]thiophene derivatives. The first block copolymer associating the 3,4-ethylenedioxythieno[2,3-*b*]thiophene (EDOThT) unit with 3,4-ethylenedioxythiophene (EDOT) moieties†‡

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*Received 6th August 2007, Accepted 7th September 2007*
*First published as an Advance Article on the web 26th September 2007*
**DOI: 10.1039/b712052d**

The synthesis of 3,4-alkoxythieno[2,3-*b*]thiophene derivatives has been developed from the readily accessible dimethyl or diethyl 3,4-dihydroxythieno[2,3-*b*]thiophenedicarboxylates. The yields for the dialkoxy derivatives were strongly dependent both on the base and the alkylating agent used for the nucleophilic substitutions. A trimer associating the new 3,4-ethylenedioxy-thieno[2,3-*b*]thiophene unit with 3,4-ethylenedioxythiophene moieties has been synthesized and electropolymerized.

## Introduction

The considerable research activity developed around functional polymeric π-conjugated systems is motivated by the high current interest in these materials in the field of plastic electronics.[1] In this area, polythiophenes have been widely investigated as the most significant class of conjugated polymers[2,3] and, in particular poly(3,4-ethylenedioxythiophene) (PEDOT) which has acquired a prominent position among conducting polymers.[4–6] PEDOT presents a unique combination of moderate band gap, low redox potential, optical transparency in the visible spectral region for the stable conducting oxidized state.[4,7] Much effort has been devoted to the derivatization of 3,4-ethylenedioxythiophene (EDOT) and also to the design of new molecules involving the modification of the chemical structure of the EDOT in order to develop new functional polymers. Thus, structural changes to the EDOT core have been achieved and consist of i) the replacement of the oxygen by sulfur[8–12] or selenium atoms,[13] ii) modifications of the ethylenedioxy group by grafting various functional groups or its replacement by another alkylenedioxy bridge,[5,7] iii) the substitution of the ethylene bridge by a vinylene unit[14] or benzene core.[15–17]

We have recently shown that 3,6-dimethoxythieno[3,2-*b*]thiophene **DMThT** also led to a polymer presenting low oxidation potential and moderate band gap.[18] As for PEDOT, this result is due to the synergistic association of electronic and structural effects of the alkoxy groups. In addition to their strong electron-donor properties, the oxygen atoms have the propensity to give rise to non covalent S–O intramolecular interactions that stabilize the planar conformation of the conjugated chain. Thus for poly-DMThT, the self-rigidification between intrinsically rigid thienothiophene units leads to a strong rigid character of the polymeric chain.

As a further step in our work concerning alkoxy-thienothiophene derivatives, we report here on the synthesis of a new rigid building block based on 3,4-alkoxythieno[2,3-*b*]thiophene and we present the first example of a block copolymer associating EDOT with 3,4-ethylenedioxythieno[2,3-*b*]thiophene (EDOThT) units (Chart 1). Thieno[2,3-*b*]thiophene is a highly stable heterocycle which presents a central cross-conjugated double bond. As recently demonstrated, the conjugation length of polythiophenes can be controlled by the insertion of the non conjugated thieno-[2,3-*b*]thiophene units, a fact that improves the stability of the polymers towards atmospheric oxygen.[19] The combination of alkoxythieno[2,3-*b*]thiophene with EDOT is thus expected to give a self-rigidified polymer due to the multiplication of S–O intramolecular interactions giving the neutral state a higher stability in air than that for PEDOT.

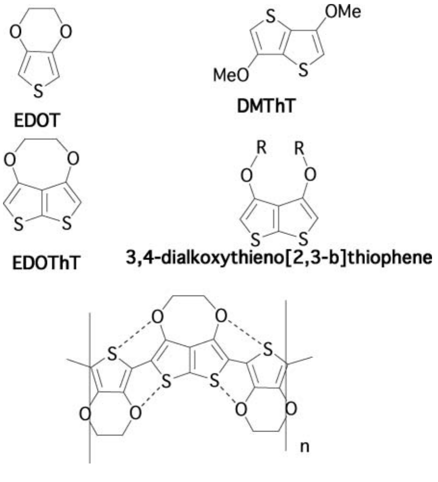

**Chart 1**

## Results and discussion

### Synthesis

The 3,4-dialkoxythieno[2,3-*b*]thiophene derivatives were prepared according to Scheme 1 from the readily accessible diethyl

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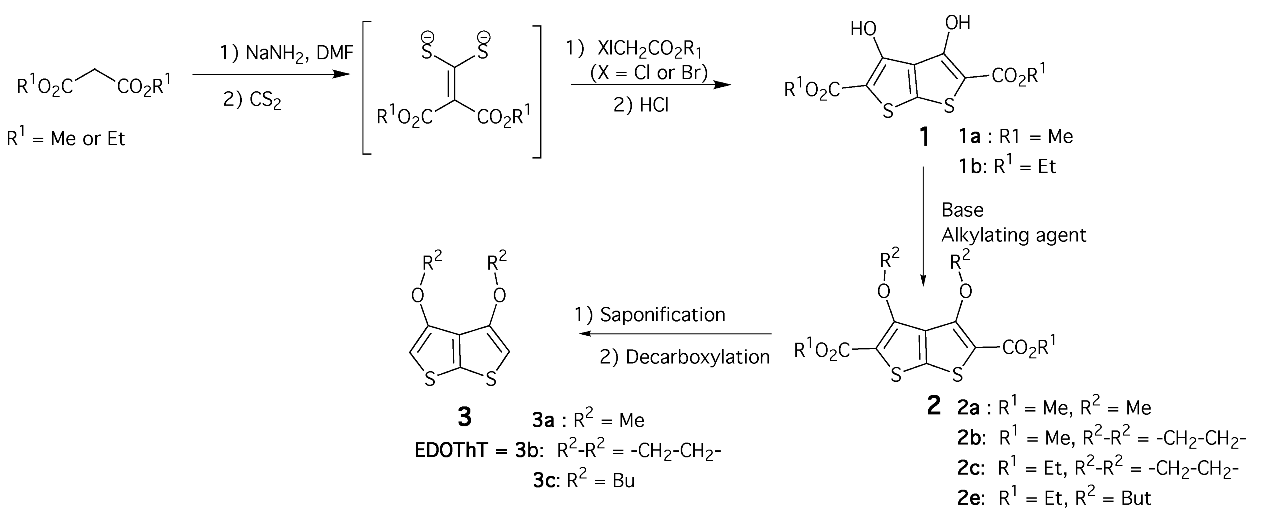
† Electronic supplementary information (ESI) available: Copies of $^{1}$H NMR and $^{13}$C NMR of the new compounds and structure and refinement of **2c**. See DOI: 10.1039/b712052d

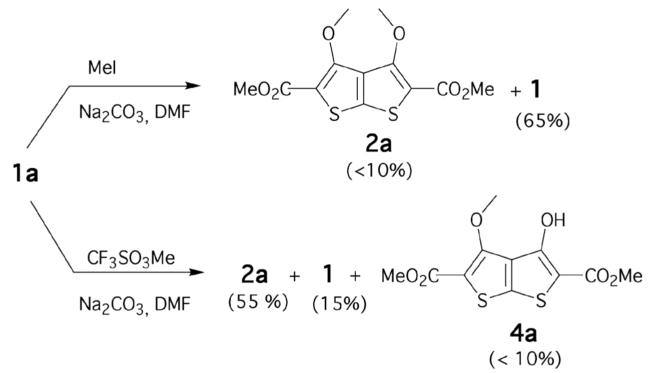
‡ CCDC reference number 656589. For crystallographic data in CIF or other electronic format see DOI: 10.1039/b712052d



**Scheme 1** Synthetic route to 3,4-dialkoxythieno[2,3-*b*]thiophene.

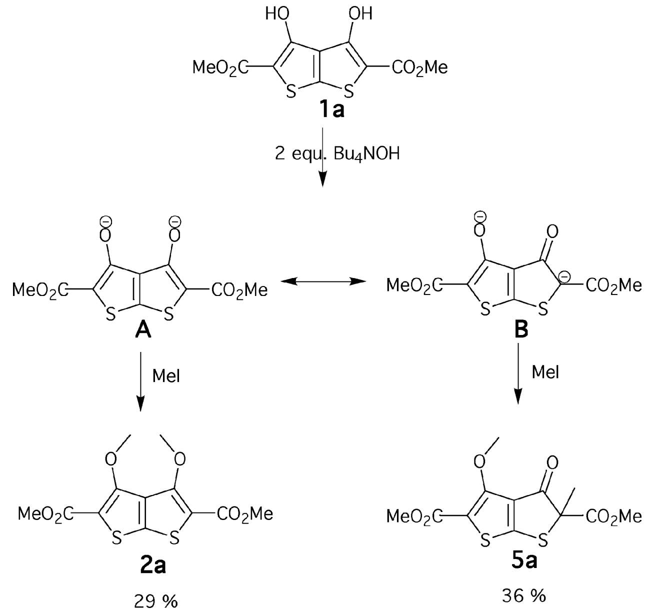
or dimethyl 3,4-dihydroxythieno[2,3-*b*]thiophenedicarboxylates **1**.[20,21] The condensation of $CS_2$ on the anion of dimethyl or diethyl malonate followed by the addition of chloromethylacetate or bromoethylacetate gave **1** in 40–45% yield after acidification. The direct bis O-alkylation of the dianion of **1** with a double Williamson reaction followed by classical saponification and decarboxylation steps led to the target molecules. However, the yields of O-alkylation of compounds **1** for obtaining dialkoxy derivatives **2** were strongly dependent both on the base and the alkylating agent used for the nucleophilic substitutions.

Treating **1** with an excess of methyl iodide (4 equivalents) in the presence of carbonate as base in DMF at 80 °C for 8 h led to **2a** in very low yield (less than 5%) while the starting material was recovered in 65% yield after acidification (Scheme 2). Increasing the time or the temperature of the reaction did not enhance the yield and even decreased the quantity of recycled starting material probably due to its slow degradation. Using the more reactive trifluoromethylsulfonate alkylating agent in similar conditions increased the yield of pure **2a** to 55%. It can be noted that mono O-alkylated derivative **4a** and starting material were also observed.



**Scheme 2**

The dianion of **1** was also generated by addition of two equivalents of $Bu_4NOH$. The following nucleophilic substitution on methyl iodide led to a mixture of **2a** and a product identified as compound **5a** in 29% and 36% yield respectively (Scheme 3).



**Scheme 3**

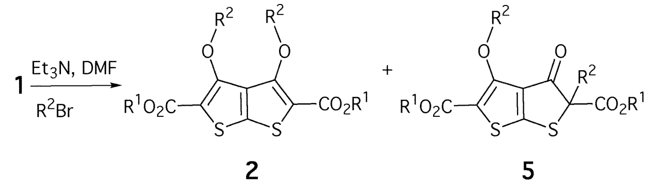
The dianion of **1** can be regarded as an ambident enolate anion present in two mesomeric forms A and B. The O-alkylation of A leads to derivative **2a** whereas the C-alkylation of B affords **5a**.

The procedure recently described for 3,4-dialkoxythiophene derivatives using 3 equivalents of triethylamine instead of carbonate anion as base in the presence of a slight excess of brominated derivatives in DMF[22] led to double O-alkylation reactions in better yields (Scheme 4 and Table 1). Hence the treatment of **1a** or **1b** with two equivalents of 1,2-dibromoethane at 80 °C for 3 hours gave compounds **2b** and **2c** in 63% and 70% yield respectively (entry 1–2 in Table 1). When the brominated derivative is limited to 1 equivalent, the time of reaction to observe the complete disappearance of the starting material is longer and the yields are lower due to the slow degradation of the anion of **1**. Under similar conditions, in presence of 4 equivalents of bromobutane (entry 3) as alkylating agent, compound **2d** was obtained in 61% yield and derivative **5d** was isolated in 9% yield. The reaction is more effective

**Table 1** Preparation of **2** by treatment of **1** with $Et_3N$ and alkyl bromide in DMF

| Entry | **1** | Alkyl bromide (*n* equiv.) | **2**[a] (% yield) | **5**[a] (% yield) |
|---|---|---|---|---|
| 1 | **1a** ($R^1$ = Me) | Dibromoethane (2 equiv.) | **2b** (63%) | — |
| 2 | **1b** ($R^1$ = Et) | Dibromoethane (2 equiv.) | **2c** (71%) | — |
| 3 | **1b** | Bromobutane (4 equiv.) | **2d** (61%) | **5d** (9%) |

[a] Isolated compound.



Scheme 4

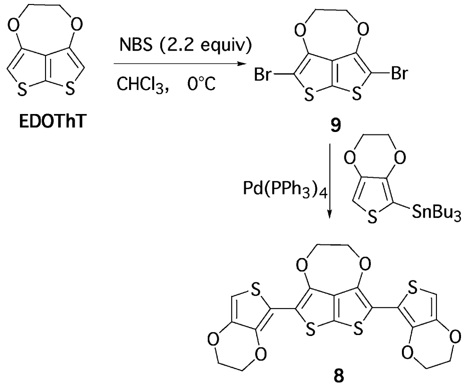
with dibromoethane than with bromobutane because the second O-alkylation reaction involves a faster intramolecular reaction and thus no side product **5** was obtained. For the same reason, in spite of the excess of dibromoethane, the substitution with two bromoethane groups was not observed.

The carboxylic acids resulting from the saponification of compounds **2** were decarboxylated at 200 °C in quinoline under microwave irradiation in presence of copper chromite leading to the target molecules in 65–70% yields for the two steps (Scheme 5).

In order to develop a block copolymer associating EDOThT with EDOT moieties, the trimer **8** was prepared according to Scheme 6. A two-fold Stille coupling between mono stannyl-EDOT and 2,5-dibromo-3,4-ethylenedioxythieno[2,3-*b*]thiophene **9**, obtained in 80% yield by action of a slight excess of NBS on **EDOThT** in DMF at 0 °C, led to trimer **8** in 18% yield. Trimer **8** must be handled under nitrogen to avoid degradation.

## Crystal structure of 2c

The crystallographic structure of single crystals of **2c** obtained from slow evaporation of chloroform–ethanol solutions has been analyzed by X-ray diffraction. **2c** crystallizes in the monoclinic *P*21/*c* space group and the structure is defined from a molecule. The structure of **2c** (Fig. 1) reveals that the molecule is planar except for the ethyl and ethylenedioxy groups. The ethylenedioxy bridge presents a half-boat conformation with no disorder at the methylene carbons. The molecules stack along the *c* axis with intermolecular distances of 3.73 Å. Between two stacks of molecules presenting a face to face orientation along the *b* direction, close S–S contacts less than 3.65 Å are observed as indicated in Fig. 1.



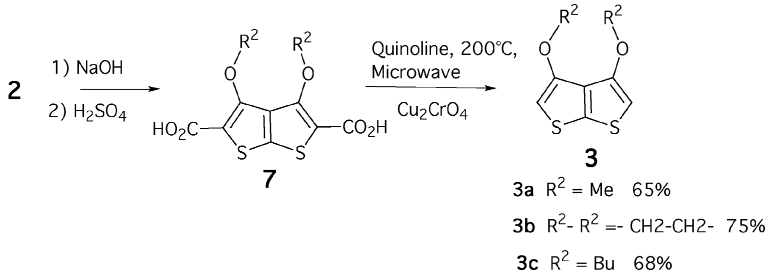
Scheme 6

## Electronic properties

Cyclic voltammetry (CV) of compounds **3** was carried out in dry acetonitrile using tetrabutylammonium hexafluorophosphate as the supporting electrolyte. All the CV traces present an irreversible oxidation peak over the potential range 1.28–1.31 V corresponding to the formation of radical cations (Table 2). The oxidation potential of **3b** is lower than that of EDOT (1.5 V) measured under the same conditions while close values are obtained between **3a** and DMThT (Table 2), thus indicating that the HOMO level of **3b** is higher than that of EDOT while similar HOMO levels are expected for **3a** and DMThT.[18] These results are confirmed by theoretical calculations.

Electrooxidation of compounds **3** did not lead to the formation of electroactive polymer films on the anode. With 3,4-ethylenedioxythieno[2,3-*b*]thiophene **EDOThT** (**3b**), recurrent potential scans quickly led to the passivation of the anode (see ESI†) probably due to the deposition of a thin insulating film.

The electronic properties of trimer **8** have been compared to that of ter-EDOT and their molecular structures were investigated



Scheme 5

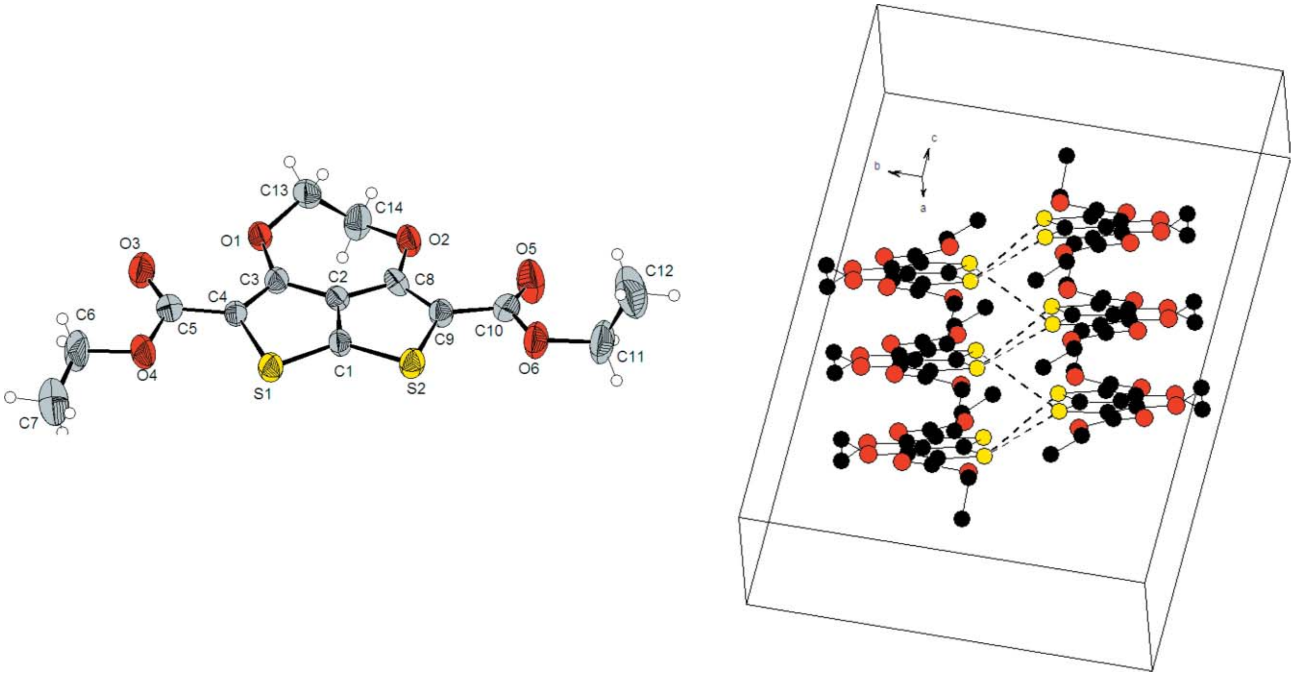


**Fig. 1** Molecular structure (left) and packing mode (right) of **2c** in a single crystal.

**Table 2** Anodic peak potential[a], calculated HOMO and LUMO[b] for compounds **3a–c**, EDOT and (DMThT)

| Compound | $E_{pa}$/V | HOMO/eV | LUMO/eV |
|---|---|---|---|
| **3a** | 1.31 | −5.30 | −0.16 |
| **EDOThT = 3b** | 1.28 | −5.60 | −0.68 |
| **3c** | 1.30 | — | — |
| **EDOT** | 1.50 | −5.80 | −0.05 |
| **DMThT** | 1.35 | −5.33 | −0.43 |

[a] $5 \times 10^{-3}$ M in 0.1 M $Bu_4NPF_6$ in $CH_3CN$, reference Ag/AgCl, $v = 100$ mV $s^{-1}$. [b] HOMO/LUMO energy levels calculated by DFT method (B3LYP/6-31 g(d,p).

theoretically by DFT calculations at the B3LYP/6-31G(d,p) level. Table 3 lists the energy values of the HOMO and LUMO levels and the main UV-vis and electrochemical data of trimer **8** and ter-EDOT.

The UV-vis absorption spectrum of **8** presents a vibronic fine structure with a $\lambda_{max}$ at 332 nm. Such a fine structure has already been observed for oligo-EDOT[23,24] and the dimer of DMThT[18] and is characteristic of a self-rigidification of the conjugated chain due to non covalent S–O intramolecular interactions. Compared to ter-EDOT[25] the absorption band of **8** is blue shifted by 68 nm indicating a decrease of the effective conjugation of the backbone due to the central cross-conjugated double bond.

The optimized structure of trimer **8** leads to a fully planar conformation. The coplanarity of the external EDOT moieties with the median thienothiophene unit is associated with short intramolecular S–O distances (2.91 Å) less than the sum of the van der Waals radii of sulfur and oxygen atoms (3.35 Å). Such short distances, already observed for optimized structures and confirmed by X-ray structures of oligomers based on EDOT units, are an indication of the establishment of non covalent intramolecular interactions which stabilize the planar conformation of the molecule. The highest occupied molecular HOMO orbital and HOMO − 1 orbital are very close in energy and can be considered as almost two degenerate levels. As shown in Fig. 2, the molecular orbital analysis reveals the strong π-character of the two degenerate HOMO and HOMO − 1 orbitals. The oxygen atoms of the EDOThT unit and the inner oxygen atoms of the EDOT moieties present a significant contribution of the atomic orbital coefficients to the HOMO and HOMO − 1 levels of trimer **8**, which indicates their participation in raising the HOMO and HOMO − 1 levels by their electron releasing mesomeric effect.

Compared to ter-EDOT, the significantly higher HOMO–LUMO gap, corresponding both to a decrease of the HOMO and an increase of the LUMO energy levels, is actually associated

**Table 3** UV-vis[a], electrochemical data[b] and calculated HOMO/LUMO energy levels[c] and gap Δ$E$[d] for trimer **8** and ter-EDOT

| Compound | $\lambda_{max}$ | $E_{ox}$ | HOMO − 1 | HOMO | LUMO | LUMO + 1 | Δ$E$ |
|---|---|---|---|---|---|---|---|
| **8** | 332 nm | $E_{ox1} = 0.8$ V<br>$E_{ox2} = 1.1$ V | −4.84 eV | −4.73 eV | −0.87 eV | −0.76 eV | 3.86 eV |
| **Ter-EDOT** | 400 nm[25] | $E_{ox} = 0.65$ V[26] | −5.58 eV | −4.40 eV | −1.10 eV | +0.11 eV | 3.30 eV |

[a] $10^{-5}$ M in $CH_2Cl_2$. [b] $10^{-3}$ M in 0.1 M $Bu_4NPF_6$ in $CH_2Cl_2$, reference Ag/AgCl, $v = 100$ mV $s^{-1}$. [c] HOMO/LUMO energy levels and gap are calculated by DFT method (B3LYP/6-31g(d,p)). [d] $\Delta E = E_{LUMO} - E_{HOMO}$.

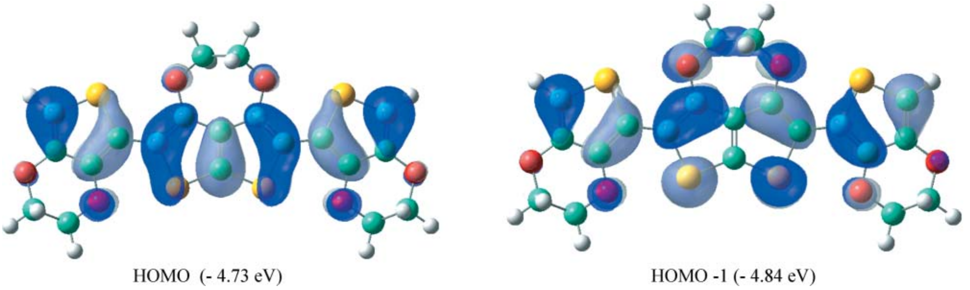


**Fig. 2** Electron density contours (0.04 e bohr$^{-1}$) and energies calculated for HOMO and HOMO -1 orbitals of **8**.

with the disruption of the conjugation due to the planar cross conjugated thieno[2,3-*b*]thiophene unit.

The CV of **8** performed in $CH_2Cl_2$ presents two irreversible oxidation peaks at 0.81 V and 1.13V (*vs.* Ag/AgCl). Compared to ter-EDOT[25,27] the +150 mV anodic shift of the first oxidation potential of **8** reflects the lower HOMO level due to a smaller conjugation length. Application of recurrent potential scans with a positive limit set at the second oxidation potential led to the emergence of new redox systems at lower potentials characteristic of straightforward electropolymerization (Fig. 3 left). By contrast when the potential scan is limited to the first oxidation potential, the growth of the polymers on the anode is more difficult and the quality of the films is mediocre. Interestingly, this result suggests the formation of a bis-cation radical state from the second oxidation peak that enhances the electropolymerization process (Scheme 7).

To gain a deeper insight into the charge distribution of the dication and taking into account that the HOMO and HOMO − 1 of **8** are close in energy, calculations for the dication state were done with the same B3LYP functional as for the neutral state and also with the U-B3LYP method by considering singlet and triplet states respectively. Geometric optimization with the two methods led to fully planar systems. The open-shell triplet dication is computed to be 11.1 kcal mol$^{-1}$ more stable than the close-shell singlet dication in $CH_2Cl_2$ (10.8 kcal mol$^{-1}$ in gas phase). This result indicates that the second oxidation process leads preferentially to a biradical structure for **8**, thus supporting the results of electropolymerization.

The CV trace of the resulting polymer recorded in a monomer-free electrolytic medium exhibits clearly two reversible oxidation peaks at 0.55 V and 0.84 V associated with the p doping of the polymer (Fig. 3 right).

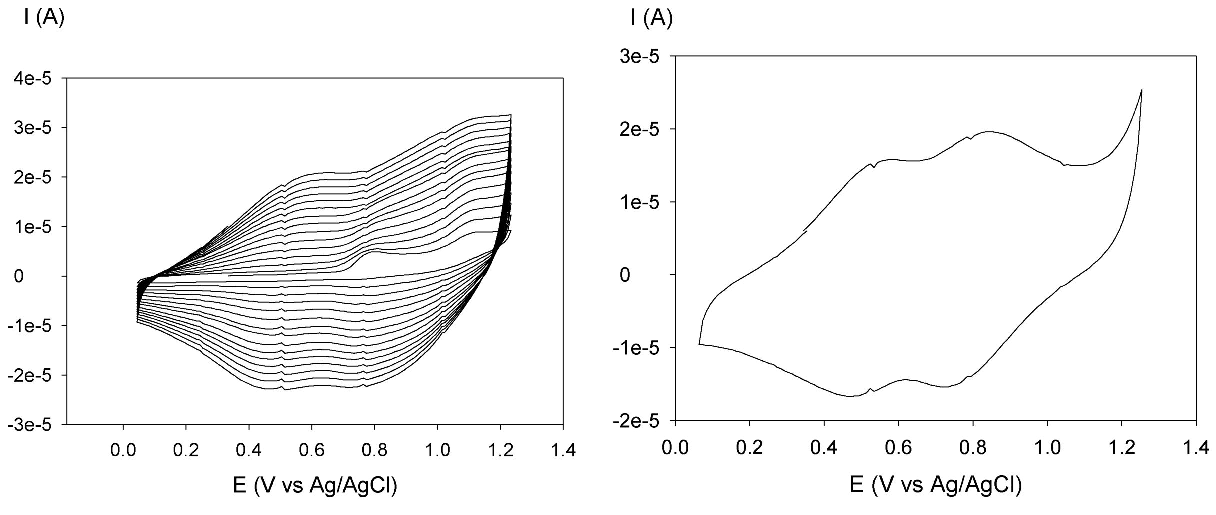
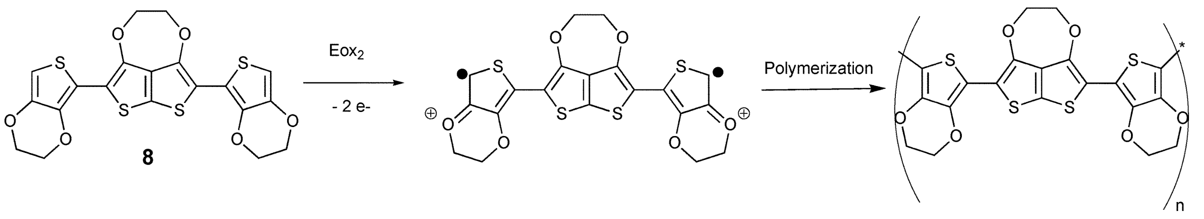


**Fig. 3** Electropolymerization of compound **8** at $10^{-3}$ M in 0.1 M $Bu_4NPF_6$ in $CH_2Cl_2$, reference Ag/AgCl, $v = 100$ mV s$^{-1}$ (left). CV of film of poly-**8** deposited on a Pt disk ($d = 1$ mm) in 0.1 M $Bu_4NPF_6$ in $CH_3CN$, reference Ag/AgCl, $v = 100$ mV s$^{-1}$ (right).



**Scheme 7**

The optical properties of the polymer have been analyzed on a thin film electrodeposited on ITO electrodes. Fig. 4 shows the spectral series for **poly-8** while changing from the neutral state to the fully oxidized states. The spectrum of the neutral polymer presents a fine structure, which is an indication of the formation of a rigid backbone with a $\lambda_{\max}$ at 457 nm and a shoulder at 492 nm. The band gap of the polymer estimated from the onset of the absorption band is 2.25 eV. The spectrum of **poly-8** remains unchanged after several hours in ambient conditions indicating a good stability of the polymer in the neutral state.

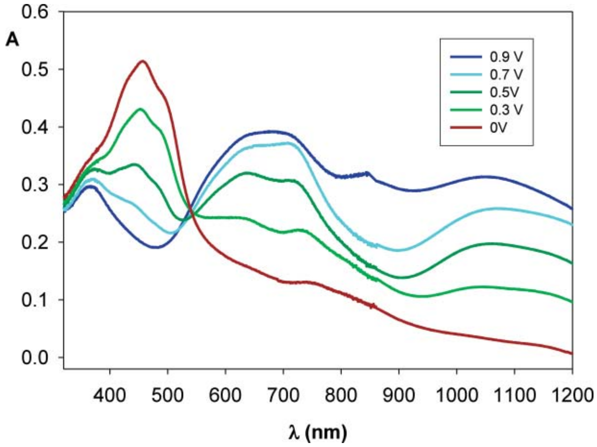


**Fig. 4** Electronic absorption spectra of **poly-8** deposited on ITO.

Oxidation of the polymer leads to a color change from red–orange to deep blue with the appearance of two close bands at 640 nm and 715 nm and a broad band at 1065 nm when the oxidation is limited to the first oxidation potential (0.5 V). After the second oxidation potential (0.9 V), the spectrum presents broad bands at 680 nm and 1045 nm. Consistent with the electrochemical properties of the polymer, these optical features should be attributed to polaron and bipolaron states. However, further studies are required for an unequivocal assignment of these transitions.

## Conclusions

To summarize, an efficient synthesis of 3,4-alkoxythieno[2,3-*b*]thiophenes has been developed from the readily accessible diethyl or dimethyl 3,4-dihydroxythieno[2,3-*b*]thiophenedicarboxylates. The key step corresponding to the bis O-alkylation by a double nucleophilic substitution is strongly improved by using triethylamine as base and bromine derivatives as alkylating agents. A trimer associating the new building block EDOThT with EDOT moieties has been synthesized and electropolymerized. It is shown that the grown of the polymer is favored from a bis-radical cation structure after extraction of two electrons. Due to the disruption of the conjugation through the thieno[2,3-*b*]thiophene units, the polymer is more difficult to oxidize than PEDOT and presents a good stability in the neutral state in ambient conditions. Oligomers and polymers based on structures combining EDOThT and thiophene units are potentially interesting for controlling the electronic properties of the π-conjugated systems in view of realizing field effect transistors or solar cells.

## Experimental

### General

NMR spectra were recorded with a Bruker Avance DRX 500 ($^1$H, 500.13 MHz and $^{13}$C, 125.75 MHz) or a JEOL GSX 270 WB ($^1$H, 270 MHz) instrument. Chemical shifts are given in ppm relative to TMS. Cyclic voltammetry was performed in dichloromethane solutions purchased from SDS (HPLC grade). Tetrabutylammonium hexafluorophosphate (0.1 M as supporting electrolyte) were purchased from Fluka and used without purification. Solutions were deaerated by nitrogen bubbling prior to each experiment which was run under a nitrogen atmosphere. Experiments were done in a one-compartment cell equipped with a platinum working microelectrode ($\Phi = 1$ mm) and a platinum wire counter electrode. An Ag/AgCl electrode checked against the ferrocene/ferricinium couple (Fc/Fc$^+$) before and after each experiment was used as reference. Electrochemical experiments were carried out with a PAR 273 potentiostat with positive feedback.

### Synthetic procedures

**Diethyl and dimethyl 3,4-dihydroxythieno[2,3-*b*]thiophenedicarboxylates 1a and 1b.** These compounds have been synthesized by adapting procedure described by Gompper *et al.*[20]

Dimethyl malonate (0.1 mol, 11.72 mL) was added dropwise to a solution of 8 g of $NaNH_2$ (0.2 mol) in 120 mL of DMF at 0 °C under inert atmosphere. After allowing to warm to room temperature, 6 mL of $CS_2$ then 18 mL of methyl chloroacetate (0.2 mol) were added dropwise and the mixture was warmed at 80 °C for 15 min before adding dropwise 24 g of sodium methanolate in 100 mL of MeOH. The mixture was heated at 80 °C for 30 min, then after cooling at room temperature, addition of 250 mL of HCl (3 M) allowed the precipitation of a crude product. The solid is filtered and dried to give 13.8 g of **1a** as a brown solid (47% yield).

**1a**: Mp = 222 °C (decomp.). $^1$H NMR ($CDCl_3$): $\delta = 3.93$ (s, 6H), 10.15 (s, 2H). MS (EI) 288 [M+$^\bullet$].

Compound **1b** was prepared by using the same synthetic procedure with diethyl malonate and ethyl bromoacetate. **1b** was obtained as a brown solid (45% yield).

**1b**: Mp = 158 °C (decomp.). $^1$H NMR ($CDCl_3$): $\delta = 1.35$ (t, $^3J = 7.3$ Hz, 6H), 4.33 (q, $^3J = 7.3$ Hz, 4H), 10.05 (s, 2H, OH). MS (EI) 316 [M$^{+\bullet}$].

**Dimethyl 3,4-dimethoxythieno[2,3-*b*]thiophenedicarboxylate 2a.**

*Method A.* From sodium carbonate as base and $CF_3SO_3Me$ as alkylating agent.

16.65 g of $Na_2CO_3$ (0.157 mol) were added to a solution of 4.53 g (15.7 mmol) of **1a** in 150 mL of DMF. After 15 min of stirring at room temperature, 8 mL of $CF_3SO_3Me$ (70.7 mmol) were added and the mixture was stirred overnight at room temperature. The mixture was poured into 400 mL of a solution of HCl (2 M) to give a white precipitate. The solid was filtered and then was washed twice with water. The crude product was purified by recrystallization in MeOH to give 2.75 g of **2a** (55% yield).

*Method B.* from $Bu_4NOH$ as base and methyl iodide as alkylating agent.

To a solution of 288 mg of **1a** (1 mmol) in 3 mL of DMF, 2 mL of a solution of $Bu_4NOH$ 1 M (2 mmol) in MeOH were added dropwise. After 5 min stirring 0.3 mL of methyl iodide was added then the mixture was stirred at 60 °C overnight. 10 mL of a solution of $H_2SO_4$ (10%) were added then the aqueous phase was extracted with ethyl acetate (2 × 20 mL) and the organic phase was dried over $MgSO_4$. Removal of the solvent at reduced pressure and purification by chromatography on silica gel (eluent: $CH_2Cl_2$) afforded 90 mg of compound **2a** (29% yield) and 114 mg of compound **5a** (36% yield).

**2a**: White solid. Mp = 178 °C. $^1$H NMR ($CDCl_3$): $\delta = 3.89$ (s, 6H), 4.09 (s, 6H). $^{13}$C NMR ($CDCl_3$): $\delta = 52.26$, 63.26, 118.85, 133.43, 143.09, 155.21, 161.30. MS (EI) 316 [$M^{+\bullet}$]. $C_{12}H_{12}O_6S_2$.

**5a**: Brown oil. $^1$H NMR ($CDCl_3$): $\delta = 1.88$ (s, 3H), 3.75 (s, 3H), 3.86 (s, 3H), 4.21 (s, 3H). $^{13}$C NMR ($CDCl_3$): $\delta = 21.61$, 52.22, 53.74, 63.24, 69.33, 116.01, 128.22, 157.39, 160.95, 168.74, 169.15, 188.96. MS (EI) 316 [$M^{+\bullet}$].

**Dimethyl 3,4-ethylenedioxythieno[2,3-*b*]thiophenedicarboxylate 2b.** To a suspension of 1.9 g (6.59 mmol) of **1a** in 40 mL of DMF were successively added 2.75 mL of $Et_3N$ (19.8 mmol) then 1.14 mL of dibromoethane (13.2 mmol). The mixture was stirred for 8 h at 80 °C. After cooling at room temperature, 100 mL of a solution of HCl (4 M) were added and a precipitate appeared. The solid was filtered, washed twice with water then with MeOH to give 1.31 g of **2b** (63% yield).

**2b**: White solid. Mp > 260 °C. $^1$H NMR ($CDCl_3$): $\delta = 3.89$ (s, 6H), 4.72 (s, 6H). The solubility is too low to do $^{13}$C NMR. MS (EI) 314 [$M^{+\bullet}$].

**Diethyl 3,4-ethylenedioxythieno[2,3-*b*]thiophenedicarboxylate 2c.** To a suspension of 1.5 g (4.74 mmol) of **1b** in 30 mL of DMF were successively added 2.0 mL of $Et_3N$ (14.2 mmol) then 0. 83 mL of dibromoethane (9.2 mmol). The mixture was stirred 8 h. at 80 °C. After cooling at room temperature, 100 mL of a solution of HCl (4 M) were added and a precipitate appeared. The solid was filtered, washed twice with water then with MeOH to give 1.16 g of **2c** (70% yield).

**2c**: White solid. Mp >260 °C. $^1$H NMR ($CDCl_3$): $\delta = 1.35$ (t, $^3J = 7.15$ Hz, 6H), 4.33 (q, $^3J = 7.15$ Hz, 4H), 4.72 (s, 4H). $^{13}$C NMR ($CDCl_3$): $\delta = 14.39$, 61.06, 74.20, 110.31, 129.20, 143.29, 153.49, 161.10. MS (EI) 342 [$M^{+\bullet}$].

**Diethyl 3,4-dibutoxythieno[2,3-*b*]thiophenedicarboxylate 2d.** To a suspension of 0.5 g (1.58 mmol) of **1b** in 10 mL of DMF were successively added 0.7 mL of $Et_3N$ (5 mmol) and 0.7 mL of bromobutane (6.3 mmol). The mixture was stirred 12 h. at 80 °C. After cooling at room temperature, 80 mL of a solution of HCl (4 M) were added then the aqueous phase was extracted with ethyl acetate (2 × 20 mL) and the organic phase was dried over $MgSO_4$. Removal of the solvent at reduced pressure and purification by chromatography on silica gel (eluent: $CH_2Cl_2$–PE, 2 : 1) afforded 410 mg of compound **2d** (61% yield) and 60 mg of compound **5d** (9% yield).

**2d**: White solid. Mp = 155 °C. $^1$H NMR ($CDCl_3$): $\delta = 0.96$ (t, $^3J = 7.5$ Hz, 6H), 1.38 (t, $^3J = 7.15$ Hz, 6H), 1.48 (m, $^3J = 7.5$ Hz, 4H), 1.81 (dt, $^3J = 7.5$ Hz, $^3J = 6.5$ Hz 4H), 4.26 (t, $^3J = 6.75$ Hz, 4H), 4.35 (m, $^3J = 7.15$ Hz, 4H). $^{13}$C NMR ($CDCl_3$): $\delta = 13.96$, 14.36, 19.02, 32.07, 61.20, 76.58, 119.22, 134.03, 142.99, 154.49, 161.12. MS (EI) 428 [$M^{+\bullet}$].

**5d**: Pale yellow oil. $^1$H NMR ($CDCl_3$): $\delta = 0.88$ (t, $^3J = 7.0$ Hz, 3H), 0.94 (t, $^3J = 7.5$ Hz, 3H), 1.22 (t, $^3J = 7.0$ Hz, 3H), 1.34 (t, $^3J = 7.0$ Hz, 3H), 1.39–1.51 (m, 6H), 1.75 (m, 2H), 2.25 (m, 2H), 4.20 (m, 2H), 4.33 (m, 2H), 4.42 (m, 2H). MS (EI) 428 [$M^{+\bullet}$].

### General procedure for the saponification of derivatives 2 and decarboxylation of the resulting diacid

**Saponification reaction.** To a suspension of diester derivatives **2** (5.5 mmol) in 30 mL of EtOH was added a solution of NaOH (40 mmol) in 30 mL of water and the mixture was heated at 80 °C overnight. The mixture was cooled in an ice bath and acidified to pH = 1–2 with conc. $H_2SO_4$ to give a precipitate. The solid was filtered and washed with water, MeOH then $Et_2O$. Compounds were characterized by mass spectroscopy (M − $CO_2$ and M − 2$CO_2$) then the compounds were employed directly in the subsequent decarboxylation reaction.

**Decarboxylation reaction.** $Cr_2Cu_2O_5$ (100 mg) was added to a mixture of 250 mg of diacid in 1 mL of quinoline in a microwave reaction vessel. The reaction was irradiated for 3 min in a CEM microwave ($T = 200$ °C, $P = 13$ bar, power = 250 W). The mixture was poured into 20 mL of a solution of $H_2SO_4$ (2 M) and was extracted with $Et_2O$ (2 × 15 mL). The organic phase was washed twice with 20 mL of water and dried over $MgSO_4$. After removing the solvent at reduced pressure, the crude solid was purified by chromatography on silica gel (eluent: $CH_2Cl_2$–PE, 2 : 1).

3,4-Dimethoxythieno[2,3-*b*]thiophene **3a**: 65% yield. White solid. Mp = 141 °C. $^1$H NMR ($CDCl_3$): $\delta = 3.92$ (s, 6H), 6.15 (s, 2H). $^{13}$C NMR ($CDCl_3$): $\delta = 57.70$, 97.72, 129.20, 136.03, 150.56. MS (EI) 200 ($M^{+\bullet}$). Anal. Calc. for $C_8H_8O_2S_2$: C, 47.98, H, 4.03; found: C, 47.59, H, 3.92.

3,4-Ethylenedioxythieno[2,3-*b*]thiophene (EDOThT): **3b**: 75% yield. White solid. Mp = 174 °C. $^1$H NMR ($CDCl_3$): $\delta = 4.47$ (s, 4H), 6.35 (s, 2H). $^{13}$C NMR ($CDCl_3$): $\delta = 73.80$, 101.97, 130.09, 135.30, 148.03. MS (EI) 198 ($M^{+\bullet}$). Anal. Calc. for $C_8H_6O_2S_2$: C, 48.46, H, 3.05; found: C, 48.18, H, 2.98.

3,4-Dibutoxythieno[2,3-*b*]thiophene: **3c**: 63% yield. White solid. Mp = 78 °C. $^1$H NMR ($CDCl_3$): $\delta = 0.98$ (t, $^3J = 7.55$ Hz, 6H), 1.53 (m, 4H, $^3J = 7.55$ Hz, $^3J = 7.15$ Hz), 1.81 (m, 4H, $^3J = 7.15$ Hz, $^3J = 6.36$ Hz), 4.01 (t, 4H, $OCH_2$, $^3J = 6.36$ Hz), 6.12 (s, 2H). $^{13}$C NMR ($CDCl_3$): $\delta = 13.86$, 19.22, 31.20, 70.03, 98.21, 130.14, 135.41, 150.09. MS (EI) 284 ($M^{+\bullet}$). Anal. Calc. for $C_{14}H_{20}O_2S_2$: C, 59.12, H, 7.09; found: C, 58.67, H, 6.85.

### 2,5-Dibromo-3,4-diethylenedioxythieno[2,3-*b*]thiophene 9

Under nitrogen atmosphere, 215 mg of NBS (1.2 mmol) were added in portions to a solution of 120 mg (0.6 mmol) of **EDOThT** in 7 mL of DMF at 0 °C. The mixture was allowed to warm to room temperature and was stirred for 12 h in the dark. The mixture was poured into 70 mL of water and the aqueous phase was extracted with $Et_2O$ (2 × 25 mL) and the organic phase was dried over $MgSO_4$. After removing the solvent at reduced pressure, the crude solid was purified by flash chromatography on silica gel (eluent: $CH_2Cl_2$) to give 169 mg of **9** (80% yield).

**9**: Pale yellow solid. Mp decomposition from 170 °C. $^1$H NMR ($CDCl_3$): $\delta = 4.75$ (s, 4H), $^{13}$C NMR ($CDCl_3$): $\delta = 73.73$, 88.19, 127.43, 130.31, 145.66. MS (EI) 356 ($M^{+\bullet}$).

### 2,5-Bis(3,4-ethylenedioxythiophene)-3,4-diethylenedioxy-thieno[2,3-*b*]thiophene 8

Brominated derivative **9** (50 mg, 0.14 mmol), 2-tributylstannyl-3,4-ethylenedioxythiophene (0.35 mmol) and 16 mg of $Pd(PPh_3)_4$ were dissolved in 3 mL of toluene and degassed several times. The mixture was heated to 100 °C for 4 h. After cooling at room temperature the mixture was filtered on hyflosupercel and eluted with $CH_2Cl_2$. The organic phase was washed twice with water then dried over $MgSO_4$. After removing the solvent at reduced pressure, the crude product was purified by flash-chromatography ($PE–CH_2Cl_2$, 2 : 1) to give a pale yellow solid (12 mg, 18% yield).

**8**: Pale yellow solid. Mp = decomposition from 150 °C. $^1H$ NMR ($CH_2Cl_2$): $\delta = 4.21$ (m, 4H), 4.31 (m, 4H), 4.62 (s, 4H), 6.25 (s, 2H). Solubility and stability are too low to do $^{13}C$ NMR. HRSM calc. for $C_{20}H_{14}O_6S_4$ 477.96677, found 477.96769.

### Crystal data and structure refinement for compound 2c

Data collections were performed at 293 K on an Enraf-Nonius MACH3 four circle diffractometer equipped with a graphite monochromator utilizing Mo-Kα radiation ($\lambda$ = 0.71073 Å). The structure was solved by direct methods (SIR) and refined on $F^2$ by full-matrix least-squares method, using SHELXL97 (G.M. Sheldrick, 1997). Non-hydrogen atoms were refined anisotropically. The positions of hydrogen atoms were calculated.

$C_{14}H_{14}O_6S_2$, $M_w = 342.37$, white prism, $0.44 \times 0.07 \times 0.01$ mm$^3$, monoclinic, $P12_1/c$, $a$ = 5.098(1) Å, $b$ = 14.076(2) Å, $c$ = 20.831(7) Å, $\beta$ = 92.82 (2)° $V$ = 1493(1) Å$^3$, $Z$ = 4, $\rho_{calc}$ = 1.52 g cm$^{-3}$, 23362 reflections collected in the 3–26° $\theta$ range, 2905 independent reflections from which 1522 with $I > 2\sigma(I)$ converged to $R = 0.0851$ and w$R$2 (all data) = 0.1718 with 201 parameters, GOF = 1.064.

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