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PAPER

Efficient synthesis of 3,6-dialkoxythieno[3,2-*b*]thiophenes as precursors of electrogenerated conjugated polymers†

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A series of 3,6-dialkoxythieno[3,2-*b*]thiophenes have been synthesized through three synthetic pathways. Symmetrical derivatives have been obtained from 3,6-dibromothieno[3,2-*b*]thiophene or by trans-etherification of 3,6-dimethoxythieno[3,2-*b*]thiophene while unsymmetrical derivatives have been easily prepared from the readily accessible dimethyl 3-hydroxythiophene-2,5-dicarboxylate. These compounds have been used as precursors for electropolymerisation and a first characterisation of the electronic properties of the resulting polymers is presented.

Introduction

The control of the electronic properties of thiophene-based polymers remains at the forefront of research on π-conjugated systems.[1–3] Motivated by their potential technological applications in the field of plastic electronics, a major goal consists of the control of the energy of the HOMO and LUMO frontier orbitals in order to tune crucial electronic properties such as absorption and emission properties, ionization potential and electron affinity.

In this context, synthetic approaches aiming at the rigidification and planarization of the conjugated backbone have been developed in order to minimize the limitations imposed to π-electron delocalization by the rotational disorder between thiophene rings.[2,4] Recently, several groups have reported on the incorporation of the intrinsically rigid thieno[3,2-*b*]thiophene (TT) block in π-conjugated oligomers or polymers in order to improve their electronic properties and optimize the performances of electronic devices such as field-effect transistors or solar cells based on these materials.[5–17] Despite some significant improvement in hole mobility, the use of the TT unit does not suppress rotational freedom between adjacent units. Furthermore, the introduction of solubilizing alkyl chains at the β position of the TT unit leads to steric interactions and thus to distortions of conjugated chains that enlarge the energy gap.[10,14] Rigidified oligothiophene derivatives have been described but the lengthening of the conjugated chain is rapidly limited by synthetic difficulties.[18–25] In the past few years 3,4-ethylenedioxythiophene (EDOT) has progressively emerged as an important versatile building block for the molecular engineering of functional π-conjugated systems with tailored electronic properties.[26,27] The strong electron-donor effect of the ethylenedioxy group raises the HOMO level and thus decreases the oxidation potential of the resulting oligomers or polymers and enhances the stability of the conducting oxidized state. Furthermore, the alkoxy groups at the β-position of thiophene units induce the planarization and rigidification of the π-conjugated system by means of non-covalent intramolecular S---O interactions between adjacent thiophene units.[26–29]

As a further step, one can envision developing a synergistic combination of the two approaches by combining intrinsically rigid TT units with constructive non-covalent intramolecular S---O interactions. Recently, the combination of EDOT and TT moieties has been reported to favour the planarity of conjugated systems.[30,31] On the other hand, we have shown that 3,6-dimethoxythieno[3,2-*b*]thiophene[32] and 3,4-ethylenedioxythieno[2,3-*b*]thiophene[33] are efficient building blocks for the development of self-rigidified conjugated systems. On this basis, soluble poly(3,6-dialkoxythieno[3,2-*b*]thiophene)s have recently been reported to lead to highly conjugated rigid, rod-like structures in solution.[9]

As part of our research aimed at the development of new synthetic routes to substituted thiophenes, we are developing the access to alkoxythiophene derivatives from easily available starting materials. We have recently reported the synthesis of 3,4-dialkoxythieno[2,3-*b*]thiophenes[33] and 3-substituted thieno[3,2-*b*]furanes[34] from 3-hydroxythiophene derivatives. As a further step, we report here on different synthetic pathways leading to various dialkoxythieno[3,2-*b*]thiophenes (Scheme 1). Symmetrical derivatives **3** have been first synthesized from 3,6-dibromothieno[3,2-*b*]thiophene or 3,6-dimethoxythieno[3,2-*b*]thiophene, and we show that alkoxythienothiophenes can be easily prepared from the readily available dimethyl 3-hydroxythiophene-2,5-dicarboxylate. Moreover this new synthetic pathway gives access to unsymmetrical derivatives **4**, difficult to obtain by already known methods.

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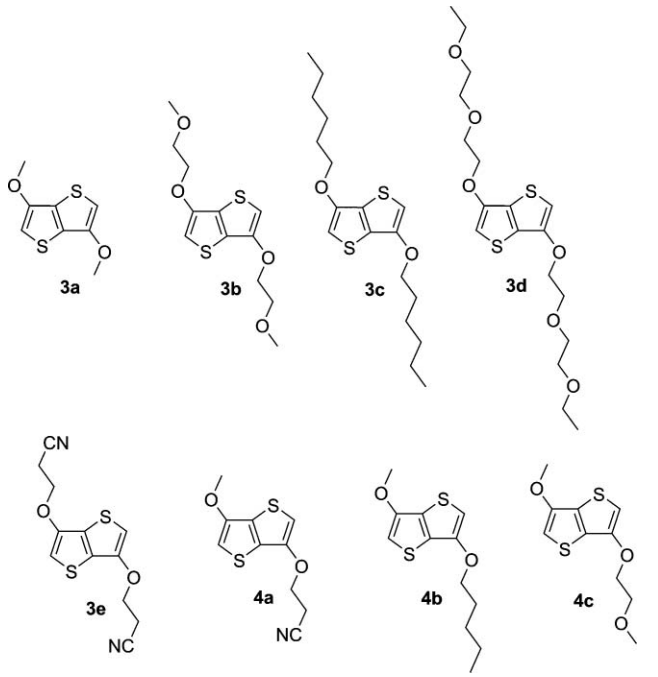


Scheme 1 Symmetrical **3** and unsymmetrical **4** 3,6-dialkoxythieno-[3,2-*b*]thiophenes.

Finally a first analysis of the potential of the dialkoxythienothiophenes as precursors of electrogenerated conjugated polymers is presented.

Results and discussion

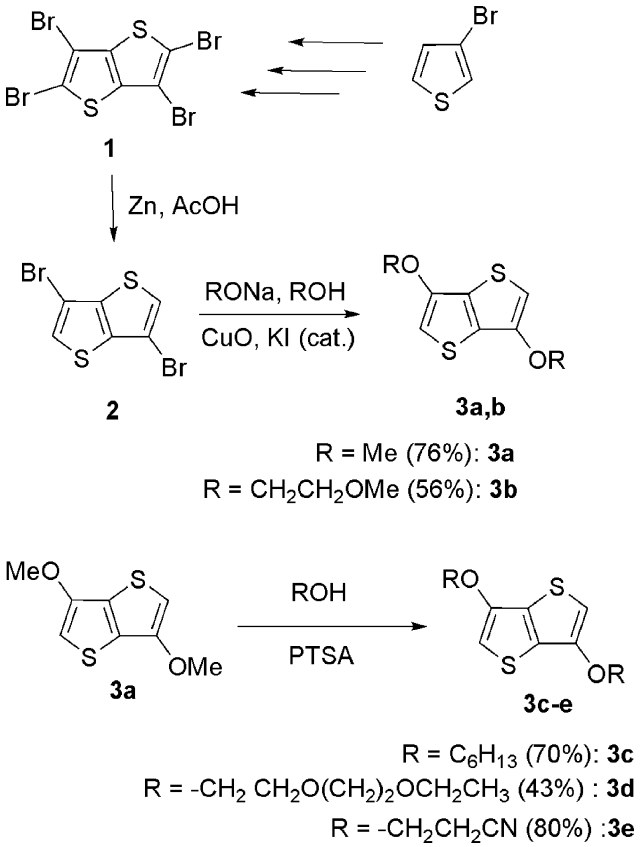
Synthesis

The synthesis of dialkoxy-TT derivatives has been envisaged along three routes. The first involves a nucleophilic substitution of 3,6-dibromothienothiophene **2** using a concentrated solution of alcoholate (Scheme 2). Bromination of TT or thienothiophene-2-carboxylic acid (prepared in two or four steps from 3-bromothiophene),[16,35,36] leads to tetrabromothienothiophene **1** which is reduced to the dibromo derivative **2** by treatment with zinc in acetic acid under microwave activation. Treatment of **2** by sodium methanolate (4 M in MeOH) in the presence of CuO and KI gives 3,6-dimethoxy-TT **3a** in 76% yield.[32]

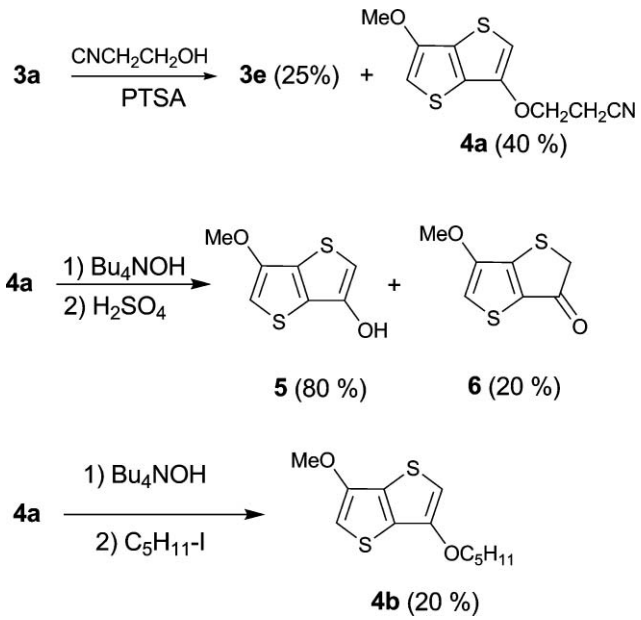
This procedure is less efficient with longer alcoholates, thus 2-methoxyethanol leads to the corresponding TT derivative **3b** in 56% yield while with 2-(2-ethoxyethoxy)ethanol the reaction fails.

An alternative method involves the transetherification of dimethoxy-TT **3a** in the presence of *para*-toluenesulfonic acid (PTSA) and a slight excess of alcohol to afford dialkoxy-TT **3c–e** in 43–80% yield.

The dissymmetrical derivative bearing methoxy and 2-cyanoethoxy groups (**4a**) was prepared by the transetherification of TT **3a** using 1 eq. of 3-hydroxypropionitrile (Scheme 3). The reaction also gives compound **3e** as a side-product, the mixture is easily separated by flash chromatography to give **4a** and **3e** in 40% and 25% yields respectively. The cyanoethoxy group is known to give alcoholate anions by reaction with a hydroxide anion.[37] Thus, reaction of **4a** with 1 equivalent of Bu_4NOH followed by acidification leads to a mixture of **5** and **6**. ^1H NMR in DMSO

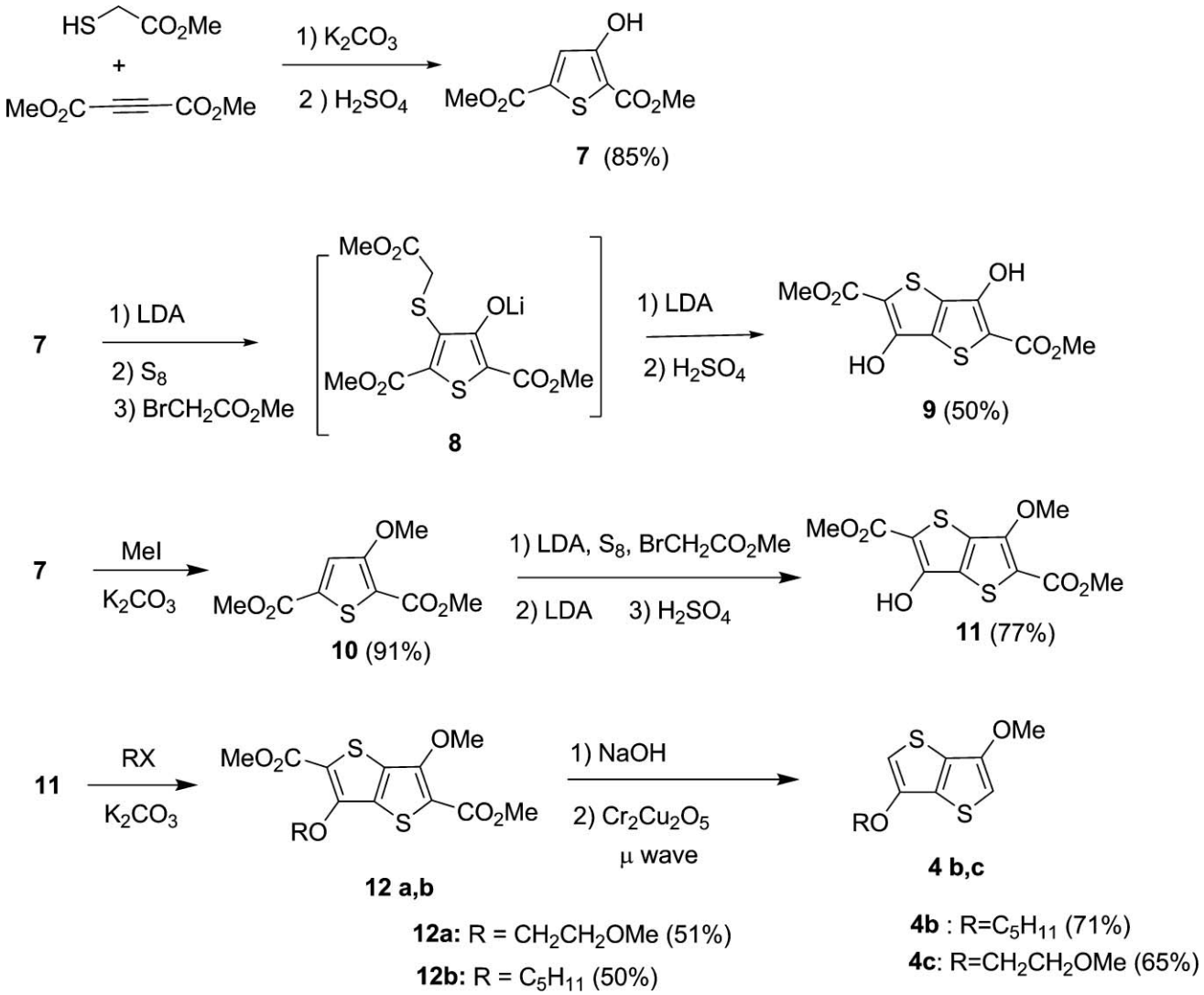


Scheme 2 Synthesis of symmetrical derivatives **3**



Scheme 3 First approach for the synthesis of unsymmetrical derivatives **4**

indicates the presence of 67% of the hydroxy form **5** and 33% of ketone **6** in equilibrium. However, addition of iodopentane to a basic solution of **4a** gives derivative **4b** in only 20% yield, indicating that this procedure is not the most efficient for the synthesis of new dialkoxy TT derivatives.



Scheme 4 General synthesis of unsymmetrical derivatives **4**

The third synthetic route proceeds *via* the easily available dimethyl 3-hydroxythiophene-2,5-dicarboxylate **7** synthesized in 85% yield by a Michael reaction of the thiolate of methyl thioglycolate and the dimethyl acetylenedicarboxylate followed by intramolecular cyclization (Scheme 4).[34,38] Compound **7** is easily purified in large quantities by precipitation after acidification. Treatment of **7** by 2 equivalents of LDA followed by the successive addition of sulfur and methyl bromoacetate leads to compound **8** which is not isolated. Further addition of a slight excess of LDA (1.5 eq.) produces a second intramolecular cyclization to give **9** in 50% yield after acidification. If the low solubility of **9** limits the interest of this route for the synthesis of symmetrical TT, this synthetic pathway appears promising for the development of unsymmetrical dialkoxy derivatives difficult to obtain by the first route. Application of this procedure to the methoxy derivative **10**, obtained in 91% yield from the reaction of **7** with methyl iodide in DMF in the presence of K_2CO_3, leads to compound **11** in 77% yield. Reaction of compound **11** with various alkylating reagents in the presence of K_2CO_3 in DMF gives compounds **12** in 50% yield. Finally, decarboxylation of the acids resulting from the saponification of compounds **12** at 200 °C in quinoline under microwave irradiation in presence of copper chromite affords the target molecules **4b**,**c** in 65–71% yields for the two steps.

Electronic properties

The optical and electrochemical properties of compounds **3a–e** and **4a–c** have been analysed by UV-Vis absorption spectroscopy and cyclic voltammetry (CV). The resulting data are listed in Table 1. The absorption spectrum of the monomers presents a well-resolved vibrational fine structure with two maxima as expected for rigid TT systems. Comparison of the data for unsubstituted TT and 3,6–dialkylthienothiophenes,[14] shows that the introduction of the donor alkoxy groups provokes a bathochromic shift of 17 nm and 10 nm respectively.

The CV of compounds **3** and **4** were recorded in acetonitrile in the presence of tetrabutylammonium perchlorate as the supporting electrolyte. The CV of all compounds presents an irreversible anodic peak (E_{pa}) around 1.30 V *vs.* Ag/AgCl corresponding to the formation of the radical cation. The slight positive shift of E_{pa} to 1.34 V and 1.37 V for compounds **4a** and **3e** is probably due to the long distance electron-withdrawing effect of the cyano group.

Table 1 UV-Vis Absorption and cyclic voltammetric data for compounds **3** and **4**

Compound	λ_{max}/nm[a]	Epa/V[b]
3a	286, 297	1.31
3b	286, 297	1.30
3c	285, 296	1.29
3d	286, 296	1.30
3e	285, 295	1.37
4a	285, 296	1.34
4b	286, 297	1.29
4c	286, 297	1.29

[a] 10^{-5} M in CH_2Cl_2. [b] 10^{-3} M in 0.1 M Bu_4NClO_4 in CH_3CN, ref. Ag/AgCl, v = 100 mV s^{-1}.

Application of recurrent potential scans between –0.5 V and +1.30 V to a solution of compound **3a** (1×10^{-3} M) in acetonitrile, leads to the progressive development of a new redox systems at lower potential associated with the electrodeposition of a polymer (Fig. 1 top). The CV of poly(**3a**) recorded in monomer-free electrolytic medium presents a first anodic wave of weak intensity at –0.18 V followed by a main oxidation wave peaking at + 0.34 V associated with the p-doping process of the polymer. The narrowness of the main oxidation wave is consistent with the formation of a relatively homogenous polymer chain. Compound **3b** with two short diether groups was also electropolymerized but the monomer concentration had to be increased to 5×10^{-2} M. The CV of poly(**3b**) also presents a broad redox-system with two distinct oxidation waves at –0.050 V and 0.82 V. For compounds bearing longer alkoxy groups, no coherent polymer film could deposited on the electrode, presumably because of the excessive solubility of the coupled products.

In the same conditions, the electropolymerization of dissymmetrical compound **4c** leads to a thin film of the polymer (Fig. 1 bottom). Unlike poly(**3a**), the CV of films of poly(**4c**) shows a broad redox system extending from –0.12 V to 1.00 V suggesting the formation of a polymer with higher polydispersity. The dissymmetry introduced in the structure of the monomer probably leads to the formation of a regio-random polymer.

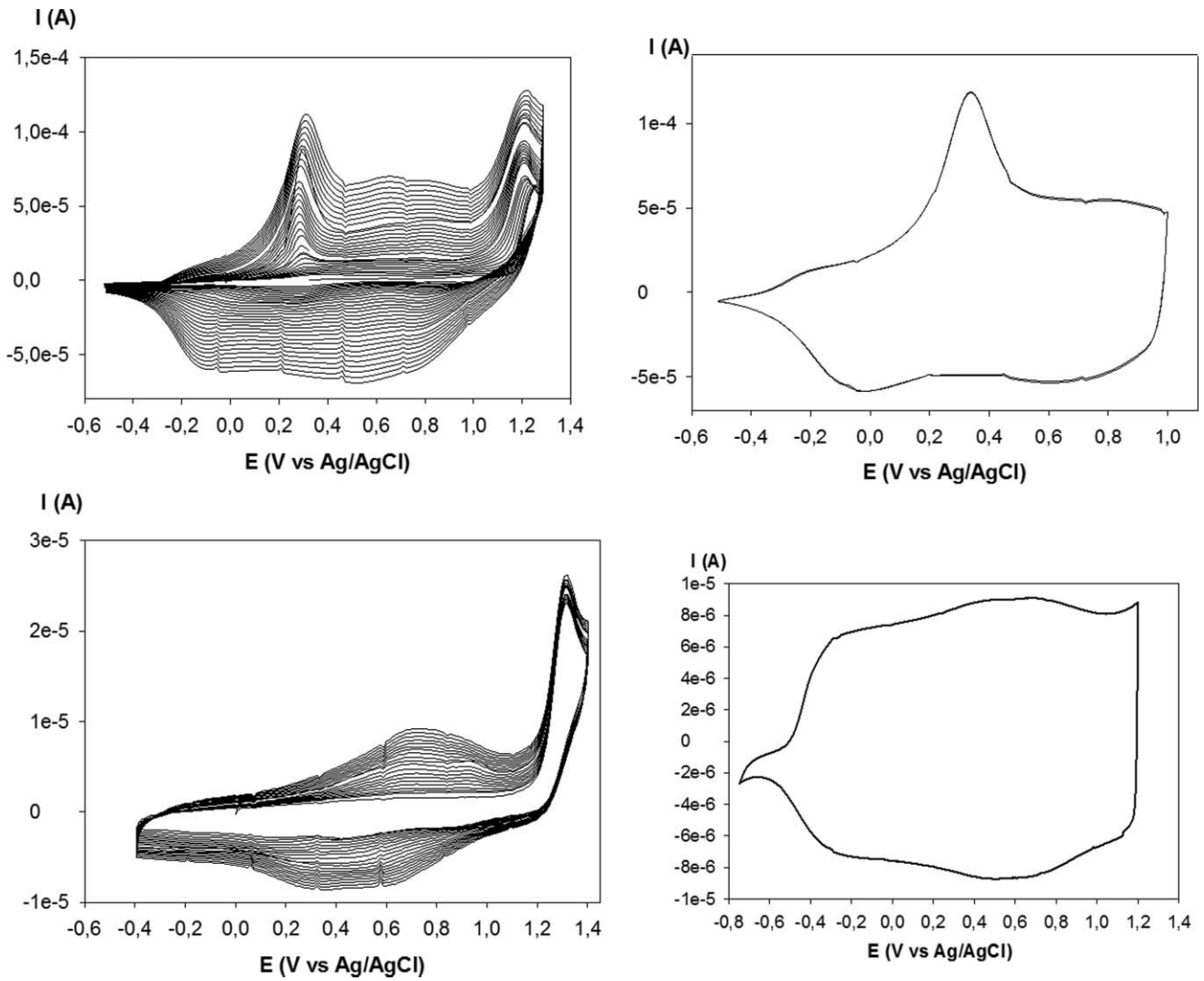


Fig. 1 Left: electropolymerization of compound **3a** (top) and **4c** (bottom) at 1×10^{-3} mol L^{-1} in 0.1 M Bu_4NClO_4 in CH_3CN, ref. Ag/AgCl, v = 100 mV s^{-1}. Right: CV of the resulting electrodeposited materials poly(**3a**) (top) and poly(**4c**) (bottom) in 0.1 M Bu_4NClO_4 in CH_3CN, ref. Ag/AgCl, v = 100 mV s^{-1}.

Table 2 Electrochemical and optical data of electrodeposited polymer films

Polymer	E_{pa}/V[a]		λ_{max}/nm[b]	E_g/eV[c]
Poly(**3a**)	–0.18	0.34	586	1.60
Poly(**3b**)	–0.05	0.82	580	1.69
Poly(**4c**)	–0.12	0.70	541	1.68

[a] Film deposited on Pt electrode, 0.1 M Bu_4NClO_4 in CH_3CN, v = 50 mV s^{-1}. [b] Film deposited on ITO electrode. [c] Calculated from the foot of the absorption band.

The optical properties of the polymers have been analyzed on thin films electrodeposited on ITO electrodes and the optical data are gathered in Table 2. As shown in Fig. 2, the absorption spectrum of poly(**3a**) (top) shows a λ_{max} at 586 nm and presents a fine structure consistent with a rigid backbone. A band gap of 1.60 eV has been estimated from the onset of the absorption band. The lengthening of the alkoxy groups in poly(**3b**) leads to a slight blue shift of λ_{max} to 580 nm with a band gap of 1.70 eV. With the unsymmetrical unit **4c**, the polymer presents a broad absorption band with a 39 nm blue shift of λ_{max} while the width of the band gap remains unchanged at 1.70 eV, which is consistent with a larger polydispersity (Fig. 2 bottom).

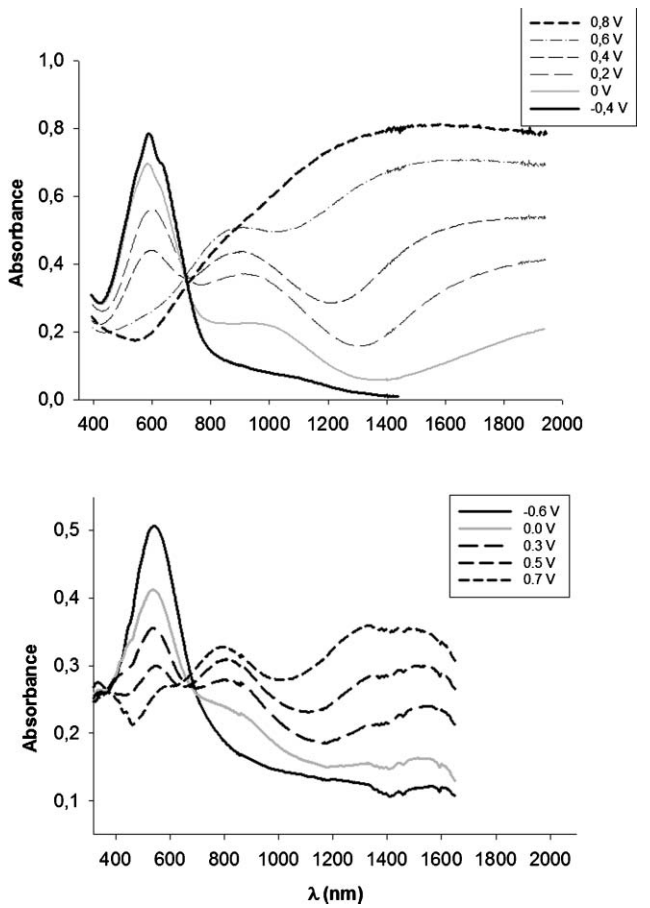


Fig. 2 Electronic absorption spectra of thin films of poly(**3a**) (top) and poly(**4b**) (bottom) on ITO.

Oxidation of the three polymers leads to a similar change in the optical spectrum. When the applied potential reaches the first oxidation wave at *ca* 0.30 V, the main absorption band decreases and two bands around 800 and 1600 nm emerge which is attributed to the polaron state. For higher applied potentials, the spectrum presents a very large band with maxima at 1600 nm for poly(**3a**) and poly(**3b**) and 1200 nm for poly(**4c**) which should correspond to the bipolaronic state. Visually the color of the polymers change from violet to pale blue for poly(**3a**) and poly(**3b**) and dark blue for poly(**4c**) during the oxidation process.

Conclusion

In summary, we have presented herein three methods for the synthesis of dialkoxythieno[3,2-*b*]thiophenes. The first two, inspired from already known procedures, lead easily to symmetrical derivatives. The last one, previously unknown, is promising due to its synthetic pathway which allows the formation of both symmetrical and unsymmetrical systems. This route proceeds from the easily available dimethyl 3-hydroxythiophene-2,5-dicarboxylate which leads to 3-hydroxythienothiophene derivatives *via* a sequence of one-pot reactions.

Electroactive conjugated polymers have been obtained by electrochemical polymerization. The polymers present broad oxidation waves extending from –0.2 V to +1.0 V and moderate band gaps of 1.60–1.70 eV depending on the size and composition of the side substituents.

Experimental

3,6-Dimethoxythieno[3,2-*b*]thiophene (3a). To a solution of methanolate in methanol (4 M, 15 mL) under nitrogen atmosphere were added 1 g of 3,6-dibromothienothiophene **2** (3.35 mmol), 0.56 g of CuO (7.1 mmol) and 30 mg of KI (0.1 mmol) and the mixture was refluxed for 15 h. After cooling at room temperature, the mixture was poured into 20 mL of water and the copper salts were eliminated by filtration on a hyflosupercell then the aqueous phase was extracted with CH_2Cl_2. The organic phase was dried over $MgSO_4$ and the solvent was removed at reduced pressure. A purification by chromatography on silica gel (CH_2Cl_2 : PE, 1 : 2) afforded 0.51 g of compound **3a** (76%).

3a: white solid. Mp = 145 °C. ^{1}H NMR ($CDCl_3$): 3.93 (s, 6H), 6.24 (s, 2H). ^{13}C NMR ($CDCl_3$): 57.5, 97.3, 128.4, 150.8. HRMS (EI): calcd for $C_8H_8O_2S_2$: 199.9966; found: 199.9969. Elemental analysis for $C_8H_8O_2S_2$, calcd: C 47.98, H 4.03, O 15.98; found: C 48.03, H 4.05, O 15.91.

3,6-Bis(2-methoxyethoxy)thieno[3,2-*b*]thiophene (3b). Under nitrogen atmosphere, 0.78 g of sodium (33.8 mmol) was added to 11 mL of 2-methoxyethanol (0.13 mol) and the mixture was stirred at room temperature. After the full reaction of sodium, 360 mg of 3,6-dibromothienothiophene **2** (1.20 mmol), 205 mg of CuO (2.6 mmol) and 11 mg of KI (0.04 mmol) were added and the mixture was refluxed for 15 h. After cooling at room temperature, the mixture was poured into 20 mL of water and the copper salts were eliminated by filtration on a hyflosupercell then the aqueous phase was extracted with CH_2Cl_2. The organic phase was dried over $MgSO_4$ and the solvent was removed at reduced pressure. A purification by chromatography on silica gel (CH_2Cl_2 : PE, 1 : 2) afforded 0.20 g of compound **3b** (56%).

3b: white solid. Mp = 144 °C. ^{1}H NMR ($CDCl_3$): 3.45 (s, 6H), 3.77 (t, 4H, ^{3}J = 4.77 Hz), 4.21 (t, 4H, ^{3}J = 4.77 Hz), 6.29 (s, 2H). ^{13}C NMR ($CDCl_3$): 59.2, 69.8, 70.8, 98.5, 128.6, 149.7. HRMS (EI): calcd for $C_{12}H_{16}O_4S_2$: 288.049; found: 288.0485. Elemental analysis for $C_{12}H_{16}O_4S_2$, calcd: C 49.98, H 5.59, O 22.19; found: C 50.06, H 5.66, O 22.07.

3,6-Bis(2-hexyloxy)thieno[3,2-*b*]thiophene (3c). Under nitrogen atmosphere, a solution of 0.20 g of **3a** (1 mmol), 630 µL of hexanol (5 mmol) and 40 mg of PTSA (0.20 mmol) in 20 mL of toluene was refluxed for 20 h. The solvent was removed at reduce pressure then the crude product was purified by chromatography on silica gel (CH_2Cl_2 : PE, 2 : 1) to afford 0.24 g of compound **3c** (70%).

3c: white solid. Mp = 95 °C. ^{1}H NMR ($CDCl_3$): 0.91 (t, 6H, ^{3}J = 6.80 Hz), 1.35 (m, 8H), 1.45 (m, 4H) 4.05 (t, 4H, ^{3}J = 6.50 Hz), 6.23 (s, 2H). ^{13}C NMR ($CDCl_3$): 14.8, 22.5, 28.1, 28.8, 29.6, 70.8, 98.2, 128.7, 150.1. MS MALDI-TOF: calcd for $C_{18}H_{28}O_2S_2$ 340.15; found 340.1. Elemental analysis for $C_{18}H_{28}O_2S_2$, calcd C 63.48, H 8.29, O 9.40; found C 63.36, H 8.32, O 9.26.

3,6-Bis(1,4,7-trioxanoylthieno[3,2-*b*]thiophene (3d). Under nitrogen atmosphere, a solution of 0.30 g of **3a** (1.48 mmol), 2 mL of 2-(2-ethoxy)ethoxyethanol (14.5 mmol) and 60 mg of PTSA (0.30 mmol) in 10 mL of benzene was heated at 60 °C for 20 h. After cooling at room temperature, the solution was poured on a solution of $NaHCO_3$ (2 M), extracted with CH_2Cl_2 then washed with water. The organic layer was dried over anhydrous $MgSO_4$, the solvent was removed at reduce pressure then the crude product was purified by chromatography on silica gel (CH_2Cl_2 : AcOEt, 9 : 1) to afford 0.26 g of compound **3d** (43%).

3d: white solid presenting decomposition from 80 °C. ^{1}H NMR ($CDCl_3$): 1.22 (t, 6H, ^{3}J = 7.15 Hz), 3.54 (q, 4H, ^{3}J = 7.15 Hz), 3.62 (t, 4H, ^{3}J = 4.77 Hz), 3.73 (t, 4H, ^{3}J = 4.77 Hz), 3.89 (t, 4H, ^{3}J = 4.77 Hz), 4.23 (t, 4H, ^{3}J = 4.77 Hz), 6.28 (s, 2H). ^{13}C NMR ($CDCl_3$): 15.2, 66.7, 69.5, 69.9, 70.0, 71.0, 98.4, 128.6, 149.7. MALDI-TOF: calcd for $C_{18}H_{28}O_6S_2$ 404.13; found 404.19. HRMS (ESI): calcd for $C_{18}H_{18}O_6S_2 + Na^+$ 427.1250; found 427.1219. Elemental analysis for $C_{18}H_{28}O_6S_2$, calcd C 53.44, H 6.98, O 23.73; found C 53.81, H 7.06, O 23.74.

3,6-Bis(2-cyanoethoxy)thieno[3,2-*b*]thiophene (3e). Compound **3e** was obtained from **3a** (0.31 g, 1.5 mmol), 525 µl of 3-hydroxypropionitrile (7.7 mmol) and 2 mg of PTSA in 25 mL of toluene following the procedure described for **3c**. The crude product was purified by chromatography on silica gel (CH_2Cl_2) to afford 0.34 g of compound **3e** (80%).

3e: white solid, Mp = 189 °C. ^{1}H NMR ($CDCl_3$): 2.90 (t, 4H, ^{3}J = 6.0 Hz), 4.30 (t, 4H, ^{3}J = 6.0 Hz), 6.35 (s, 2H). ^{13}C NMR ($CDCl_3$): 18.5, 64.8, 99.8, 116.7, 128.6, 148.5. IR (KBr): ν_{CN} = 2240 cm^{-1}. HRMS (EI): calcd for $C_{12}H_{16}O_4S_2$ 288.049; found 288.0485. Elemental analysis for $C_{12}H_{10}N_2O_2S_2$, calcd C 51.78, H 3.62, O 11.50; found C 51.43, H 3.63, O 11.86.

3-Cyanoethoxy-6-methoxythieno[3,2-*b*]thiophene (4a). Compound **4a** was obtained by following the same procedure described for **3e** from 0.25 g of **3a** (1.25 mmol) and 225 µl of 3-hydroxypropionitrile (3.2 mmol) in presence of 6 mg of PTSA in 20 mL of toluene. The crude product was purified by chromatography on silica gel (CH_2Cl_2 : EP, 2 : 1) to afford 120 mg of **4a** (40%) and 90 mg of **3e** (25%).

4a: white solid, Mp = 82–84 °C. ^{1}H NMR ($CDCl_3$): 2.89 (t, 2H, ^{3}J = 6.5 Hz), 3.92 (s, 3H) 4.29 (t, 2H, ^{3}J = 6.5 Hz), 6.29 (d, 1H, ^{6}J = 1.35 Hz), 6.33 (d, 1H, ^{6}J = 1.35 Hz. ^{13}C NMR ($CDCl_3$): 18.4, 57.5, 64.6, 97.7, 99.4, 116.7, 128.1, 128.8, 148.5, 150.7. IR (KBr): ν_{CN} = 2235 cm^{-1}.MS (EI): 239 (M^+). Elemental analysis for $C_{10}H_9NO_2S_2$, calcd C 50.19, H 3.79 found C 50.26, H 3.73.

3-Methoxy-6-hydroxythieno[3,2-*b*]thiophene (5) and 3-methoxy-6-oxo-5H-dihydrothieno[3,2-*b*]thiophene (6). To a solution of 90 mg of **4a** (0.37 mmol) in 5 mL of freshly distilled THF under nitrogen atmosphere, was added 520 µL of tetrabutylammonium 1 M in methanol (0.414 mmol). After 30 min of stirring at room temperature, the solution was poured on 15 mL of HCl (2 M) and extracted with CH_2Cl_2. The organic phase was washed with water then dried over anhydrous $MgSO_4$. The solvent was removed at reduced pressure to give 60 mg of a pink pale solid (86%). The ^{1}H NMR reveals an equilibrium between compounds **5** and **6** with proportions of 2/3 and 1/3 respectively.

^{1}H NMR (DMSO): compound **5**: 3.86 (s, 3H), 6.39 (s, 1H), 6.68 (s, 1H), 10.28 (s, 1H); compound **6**: 3.86 (s, 3H), 4.31 (s, 2H), 7.49 (s, 1H). IR (KBr): $\nu_{C=O}$ = 1669 cm^{-1}, ν (OH) = 3400 cm^{-1}. MS (EI): 186 ($M^{+\cdot}$).

Dimethyl 3-hydroxythiophene-2,5-dicarboxylate (7). To a stirred solution of dimethylacetylenedicarboxylate (10 mL, 81 mmol) and methyl thioglycolate (7.3 mL, 81 mmol) in 200 mL of dry methanol was added in small portion 22.6 g of K_2CO_3 (163 mmol). Caution the reaction is highly exothermic and the temperature of the mixture should not exceed 80 °C. The mixture was maintained at 80 °C for 2 h leading to an abundant yellow precipitate. After treatment with H_2SO_4 at 10%, the precipitate turned white, it was filtered, washed twice with water and twice with methanol then dried in a desiccator to give 14.88 g of compound **7** (85%).

7: white solid, Mp = 111 °C. ^{1}H NMR ($CDCl_3$): 3.77 (s, 3H), 3.82 (s, 3H), 7.32 (s, 1H), 10.90 (s,1H). ^{13}C NMR ($CDCl_3$): 51.8, 62.7, 111.1, 125.3, 134.5, 159.2, 161.2, 161.8. IR (KBr) $\nu_{C=O}$ = 1676 cm^{-1} and 1718 cm^{-1}.MS (EI): 216 ($M^{+\cdot}$).

Dimethyl 3-methoxythiophene-2,5-dicarboxylate (10). To a stirred solution of compound **7** (6.92 g, 32 mmol) in 60 mL of DMF at room temperature were added 6.63 g of K_2CO_3 (48 mmol) followed by 2 mL of methyl iodide (46 mmol). The mixture was stirred for 6 h at 80 °C and 200 mL of water was added. The suspension was filtered and washed with 50 mL of H_2SO_4 at 10% then twice with 50 mL of water. The solid was dried in a desiccator to give 6.74 g of compound **10** (91% yield).

10: white solid, Mp = 120 °C. ^{1}H NMR ($CDCl_3$): 3.86 (s, 3H), 3.91 (s, 3H), 3.99 (s, 3H), 7.50 (s, 1H). ^{13}C NMR ($CDCl_3$): 52.1, 52.7, 59.2, 115.0, 120.6, 135.3, 160.7, 161.6, 161.8. IR (KBr) $\nu_{C=O}$ = 1720 cm^{-1}. MS (EI): 230 ($M^{+\cdot}$).

Dimethyl 3-hydroxy-6-methoxythieno[3,2-*b*]thiophene-2,5-dicarboxylate (11). To a stirred solution of compound **10** (2.0 g, 8.68 mmol) in 130 mL of dry THF at −78 °C under nitrogen atmosphere was added 1.5 equivalent of LDA. After 30 min of stirring, 0.53 g of sulfur (16.4 mmol) was added and the mixture was stirred for 1 h and the temperature was allowed to rise to −50 °C. Then 1.6 equivalents of methyl bromoacetate were added and the mixture was stirred for 1 h. Finally 1.5 equivalents of LDA were added and the temperature was allowed to rise to

room temperature. The mixture was poured on 250 mL of H_2SO_4 (2 M) to give a precipitate. The solid was filtered, washed twice with water and dried in a desiccator to give 2.0 g of compound **11** (77% yield).

11: beige solid, decomposition from 217 °C. ^{1}H NMR ($CDCl_3$): 3.89 (s, 3H), 3.95 (s, 3H), 4.26 (s, 3H), 9.88 (s, 1H). ^{13}C NMR ($CDCl_3$): 52.2, 52.4, 60.1, 106.9, 129.9 (2 C), 154.7, 156.9, 161.9, 166.7. IR (KBr) $\nu_{C=O}$ = 1686 and 1718 cm^{-1}. MS (EI): 302 ($M^{+\cdot}$).

Dimethyl 3-methoxy-6-(2-methoxyethoxy)thieno[3,2-*b*]thiophene-2,5-dicarboxylate (12a). To a suspension of 400 mg of **11** (1.3 mmol) in 10 mL of DMF were added 1.8 g of K_2CO_3 and 2 equivalents of 1-bromo-2-ethoxyethane. The mixture was stirred for 16 h at 80 °C. After cooling to room temperature, the mixture was acidified with a solution of H_2SO_4 (2 M) and the obtained precipitate was filtered, washed with water and dried in a desiccator to give 244 mg of compound **12a** (51% yield).

12a: yellow pale solid, Mp = 131 °C. ^{1}H NMR ($CDCl_3$): 3.45 (s, 3H), 3.76 (t, 2H, ^{3}J = 4.5 Hz), 3.87 and 3.88 (2 s, 6H), 4.27 (s, 3H), 4.55 (t, 2H, ^{3}J = 4.5 Hz). ^{13}C NMR ($CDCl_3$): 52.1, 52.2, 59.3, 60.2, 71.3, 73.2, 115.0, 117.5, 129.5, 132.3, 153.8, 154.6, 161.6, 161.9. IR (KBr) $\nu_{C=O}$ = 1706 and 1720 cm^{-1}. MS (EI): 360 ($M^{+\cdot}$).

3-Methoxy-6-(2-methoxyethoxy)thieno[3,2-*b*]thiophene 4c. To a suspension of 200 mg of **12a** (0.55 mmol) in 5 mL of ethanol was added a solution of 0.9 g of NaOH in 15 mL of water. The mixture was refluxed for 3 h. After cooling to room temperature, the mixture was acidified with H_2SO_4 to pH = 1 and the obtained precipitate was filtered, washed with water and dried in a desiccator to give 170 mg of carboxylic acid.

Yellow pale solid, Mp >260 °C. ^{1}H NMR (DMSO): 3.28 (s, 3H), 3.63 (t, 2H, ^{3}J = 4.5 Hz), 4.17 (s, 3H), 4.48 (t, 2H, ^{3}J = 4.5 Hz), 13.28 (s, 2H). ^{13}C NMR (DMSO): 58.2, 60.1, 70.7, 73.0, 116.0, 118.6, 129.9, 131.6, 152.7, 153.5, 161.9, 162.1. MS (EI): 288 ($M^{+\cdot}$ – CO_2).

A 10 mL tube equipped with a magnetic stirring bar was filled with 170 mg (0.51 mmol) of carboxylic acid dissolved in 2 mL of quinoline and 60 mg of $Cr_2Cu_2O_5$ (0.20 mmol). The tube was sealed with a rubber cap and irradiated for 3 min at 200 °C with a reactor power of 200 W. The mixture was cooled to room temperature, poured on 20 mL of H_2SO_4 solution (2 M), extracted twice with pentane (2 × 20 mL) and the organic phase was dried on $MgSO_4$. After evaporation of the solvent the residue was purified by a flash chromatography on silica gel (pentane, CH_2Cl_2, 2/1) to give 87 mg of compound **4c** (65% yield for the two steps).

4c: Yellow pale solid, Mp = 104 °C. ^{1}H NMR ($CDCl_3$): 3.46 (s, 3H), 3.78 (t, 2H, ^{3}J = 4.7 Hz), 3.91 (s, 3H), 4.22 (t, 2H, ^{3}J = 4.7 Hz), 6.26 (d, 1H, ^{6}J = 1.6 Hz), 6.29 (d, 1H, ^{6}J = 1.6 Hz). ^{13}C NMR ($CDCl_3$): 57.6, 57.9, 69.9, 70.9, 97.4, 98.5, 128.4, 128.7, 149.9, 150.8. HRMS (EI): calcd for $C_{10}H_{12}O_3S_2$ 244.0228; found 244.0224. Elemental analysis for $C_{10}H_{12}O_3S_2$, calcd C 49.16, H 4.95; found C 49.56, H 4.92.

Dimethyl 3-methoxy-6-(pentyloxy)thieno[3,2-*b*]thiophene-2,5-dicarboxylate 12b. This compound has been prepared by using the same protocol described for **12a** from 300 mg of compound **10** (1 mmol), 276 mg of K_2CO_3 (2 mmol) and 0.2 mL of iodopentane (1.6 mmol) in 10 mL of DMF. After acidification with H_2SO_4 the obtained precipitate was filtered, washed with water and dried in a desiccator to give 330 mg of compound **12b** (50% yield).

12b: white solid, Mp = 104 °C. ^{1}H NMR ($CDCl_3$): 0.93 (t, 3H, ^{3}J = 7.0 Hz), 1.39 (m, 4H), 1.83 (m, 4H), 3.88 (s, 6H), 4.27 (s, 3H), 4.47(t, 2H, ^{3}J = 6.8 Hz). MS (EI): 288 ($M^{+\cdot}$).

3-Methoxy-6-(pentyloxy)thieno[3,2-*b*]thiophene 4b. This compound has been prepared by using the same protocol described for **4c** from 190 mg of **12b** (0.51 mmol) and 0.8 g of NaOH. The intermediate carboxylic acid was not characterized and it was directly engaged for the decarboxylation reaction with 150 mg of $Cr_2Cu_2O_5$ in 2 mL of quinoline. The compound was purified by chromatography on silca gel (pentane : CH_2Cl_2, 5 : 1) to give 93 mg of compound **4b** (71% yield for the two steps).

4b: white solid, Mp = 59 °C. NMR ($CDCl_3$): 0.94 (t, 3H, ^{3}J = 7.1 Hz), 1.42 (m, 4H), 1.83 (q, 2H, ^{3}J = 6.9 Hz), 3.91 (s, 3H), 4.05 (t, 2H, ^{3}J = 6.5 Hz), 6.24 (s, 1H), 6.26 (s, 1H). ^{13}C NMR ($CDCl_3$): 14.0, 22.4, 28.1, 28.8, 57.5, 70.5, 97.2, 97.7, 128.1, 128.7, 150.1, 150.8. HRMS (EI): calcd for $C_{12}H_{16}O_2S_2$ 256.0592; found 256.0591. Elemental analysis for $C_{12}H_{16}O_2S_2$, calcd C 56.22, H 6.29; found C 56.36, H 6.22.

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