Poly(3,6-dimethoxy-thieno[3,2-*b*]thiophene): a possible alternative to poly(3,4-ethylenedioxythiophene) (PEDOT)†

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Electropolymerization of the title compound leads to a conjugated polymer with redox potential, band gap, optical tranparency in the doped state and stability similar to those of PEDOT.

Poly(3,4-ethylenedioxythiophene) (PEDOT) is a focus of high current interest motivated by a unique combination of stability, moderate band gap, low redox potential and optical transparency in the visible spectral region.[1]

These properties result from the synergistic association of the strong donor effect of the ethylenedioxy groups with the propensity of EDOT to develop non covalent intramolecular S–O interactions with adjacent EDOT or thiophene groups in linear π-conjugated structures.[2–5] As shown in various classes of functional π-conjugated systems such as extended tetrathiafulvalene analogs,[2] NLO-phores,[3] low gap systems,[4] or oligomers,[5] these interactions induce a self-rigidification of the conjugated chain thus improving π-electron delocalization.

Whereas much efforts are devoted to the derivatization of EDOT in order to develop functional polymers with new properties such as solubility,[1a,b] enhanced optical contrast,[1c] cation recognition, or hydrophilicity,[6] the synthesis of polymers representing possible alternatives to PEDOT in terms of optical and electrochemical properties has attracted less attention.

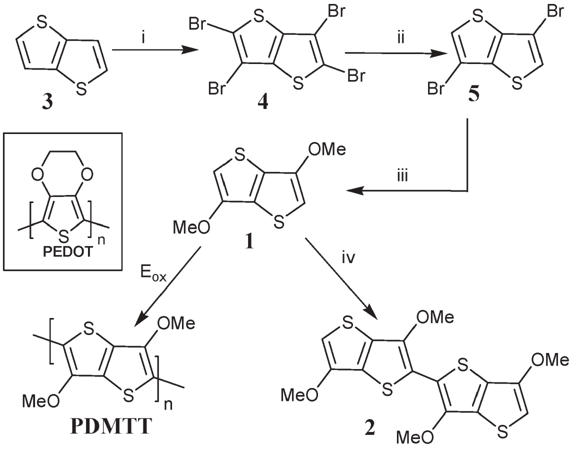
Some years ago, it was shown that poly(4,4′-dimethoxybithiophene) which combines low redox potential, moderate band gap (1.60 eV) and high stability in the conducting state,[7] could advantageously replace PEDOT as hole injection layer in light-emitting devices.[8]

As a further example we report here preliminary results on a novel conjugated polymer obtained by electropolymerization of 3,6-dimethoxy-thieno[3,2-*b*]thiophene (**1**). The analysis of the electrochemical and optical properties of this polymer, named **PDMTT**, reveals electronic properties very close to those of PEDOT with, however, some inherent potential advantages in terms of further derivatization.

Electropolymerization of thieno[3,2-*b*]thiophene (**3**) has already been reported,[9] as well as that of some β-substituted alkyl derivatives.[10] However in that case, steric interactions between substituents produce a distortion of the polymer chain thus severely limiting the effective conjugation.[10a]

Compound **1** was synthesized in three steps from **3**[11] in a 55% overall yield (Scheme 1). Bromination of **3** with Br_2 gave the tetrabromo derivative **4** which was reduced to the dibromo compound **5** using zinc in acetic acid.[12] Reaction of sodium methanolate on **5** in the presence of CuO and KI afforded the target compound in 76% yield.‡ The dimer **2**, synthesized as a model compound for structural analysis, was obtained in 70% yield by homocoupling of the stannic derivative of **1** in the presence of $CuCl_2$ and palladium catalyst.[13]

Whereas the UV-vis spectra of the dimers of 3,6-dialkyl-thieno[3,2-b]thiophenes present a structureless absorption band with λ_{max} around 300 nm,[10,14] the spectrum of **2** exhibits a well resolved vibronic fine structure with a λ_{max} at 360 nm. These marked differences suggest that replacing alkyl chains such as methyl or nonyl groups by methoxy groups allows the conjugated system to adopt a more planar and a more rigid structure. Optimization of the geometry of **2** (density functional theory at the B3LYP/6-31G* level) shows that the two thienothiophene units are nearly coplanar with a median dihedral angle inferior to 5°. This conclusion is supported by the structure of a single crystal of **2** determined by X-ray diffraction.§ As shown in Fig. 1, the two thienothiophene blocks adopt an *anti* conformation with a dihedral angle inferior to 7°. The non bonded S–O distances d_1 = 2.80 Å and d_2 = 2.83 Å, are considerably shorter than the sum of the van der Waals radii of sulfur and oxygen (3.35 Å), thus confirming the occurrence of non covalent S–O intramolecular interactions, as observed for many EDOT-based π-conjugated systems.[2–5] Noteworthy the S…O distances in **2** are even shorter than those observed in bis-EDOT (~2.90 Å)[3] presumably because of the higher flexibility of the methoxy groups compared to the ethylenedioxy ones.



Scheme 1 *Reagents and conditions*: (i) Br_2 – $CHCl_3$; (ii) Zn – AcOH; (iii) MeONa (1 M) in MeOH, CuO (1eq) + KI (5% mol.); (iv) (1)BuLi, (2) Bu_3SnCl, (3) $CuCl_2$ + $Pd(OAc)_2$ (5% mol).

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† Electronic supplementary information (ESI) available: Electronic absorption spectra of a film of poly(1) and picture of the film in oxidized and neutral states. See http://www.rsc.org/suppdata/cc/b4/b414822c/

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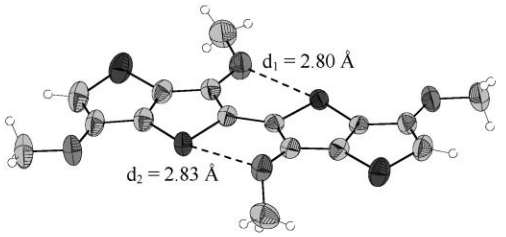

Fig. 1 ORTEP view of the structure of compound **2**. Intramolecular interactions are indicated by dotted lines.

The cyclic voltammograms (CV) of compounds **1** and **2** show an irreversible oxidation peak at 1.35 V and 0.75 V *vs.* Ag/AgCl, respectively. These potentials are significantly lower than those measured for EDOT and bis-EDOT under the same conditions (1.50 and 0.90 V respectively). Application of recurrent potential scans with a positive limit set at the foot of the oxidation wave of compound **1** leads to the emergence of a new redox system at lower potential associated with the electrodeposition of **PDMTT** (Fig. 2). The CV of **PDMTT** in a monomer-free medium shows an anodic peak at +0.20 V associated with the p-doping process, while the corresponding catholic peak is observed at −0.35 V. The asymmetry between the doping-dedoping peaks is also observed for film of PEDOT and is attributed to the heterogeneity in the structure of the polymers.[15] The response of **PDMTT** remains unchanged after several dozens of doping–dedoping cycles. The small positive shift of the potentials of **PDMTT** compared to those of PEDOT can be attributed to the lower ratio of the number of electron donor ether group per sp^2 carbon atom in the conjugated backbone which decreases from 1 : 2 for PEDOT to 1 : 3 for **PDMTT**.

Films of **PDMTT** electrodeposited on indium-tin oxide (ITO) coated glass electrodes are pale blue with a good optical transparency in the visible range (Fig. 3). The spectrum of the as-grown oxidized polymer remains unchanged after one week storage in ambient atmosphere, thus indicating a highly stable semi-transparent conducting state. The spectrum of the neutral polymer shows a discernible vibronic fine structure, a $\lambda_{\max}$ at 592 nm and a band gap of 1.65 eV. These optical data as well as the optical contrast expressed by the absorbance change at $\lambda_{\max}$ between the neutral and oxidized forms are quite similar to those of PEDOT.[1c]

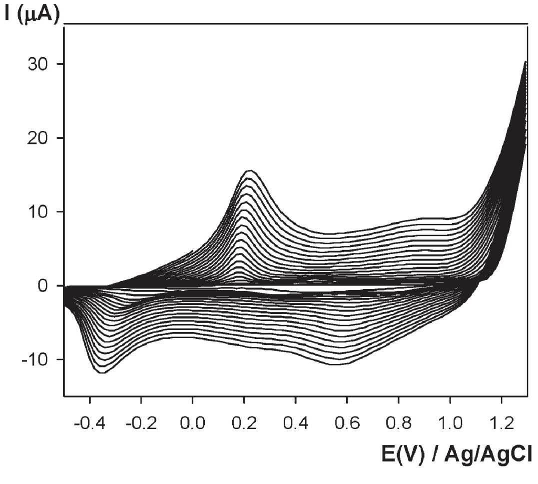

Fig. 2 Potentiodynamic electropolymerization of **1**, 10 mM in 0.10 M Bu$_4$NPF$_6$/CH$_2$Cl$_2$, scan rate 50 mV s^{-1}.

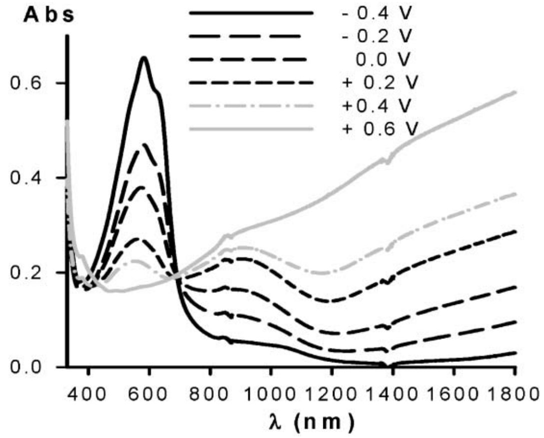

Fig. 3 Electronic absorption spectra of **PDMTT** electrodeposited on ITO.

Electrosynthesis in galvanostatic conditions (10 mM of **1** in 0.1 M Bu$_4$NPF$_6$/CH$_2$Cl$_2$, stainless steel anode 3 cm^2, 2.2 mA cm^{-2}) gave a powdery deposit with a conductivity of 10^{-2} S cm^{-1}. Since no attempt was made to optimize the electropolymerization, the definition of experimental conditions allowing the preparation of free-standing films can be expected to lead to higher conductivities.

To summarize we have shown that 3,6-dimethoxy-thieno[3,2-*b*]-thiophene can be readily electropolymerized at low potential to produce a polymer with redox potential, band gap, optical transparency in the doped state and stability comparable to those of PEDOT. Theoretical and crystallographic results on a model compound indicate that as for EDOT-based π-conjugated systems, the alkoxy substituents give rise to a self-rigidification of the conjugated structure through intramolecular S…O interactions.

This new system is noteworthy because it presents the advantage of allowing derivatization preventing the formation of multiple regio- and stereo-isomers and the weak inter-chain interactions caused by substitution of EDOT on the ethylene bridge of EDOT moieties.[16]

Work aiming at the development of chemically synthesized processable analogs of **PDMTT** and of longer well-defined oligomers is now underway and will be reported in future publications.

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Notes and references

‡ Spectroscopic data for **1** and **2**.

1: white solid; mp 145 °C; ^{1}H NMR (CDCl$_3$) : 6.27 (s, 2 H), 3.93 (s, 6H);^{13}C NMR (CDCl$_3$) 150.81, 128.40, 97.30, 57;52; HRMS calcd for $C_8H_8O_2S_2$: 199.9966; found: 199.9969.

2: orange solid; mp 274 °C; ^{1}H NMR (CDCl$_3$); 6.24 (s, 2 H), 4.10 (s, 6H), 3.94 (s, 6H); HRMS calcd for $C_{16}H_{14}O_4S_4$: 397.9775; found: 397.9765.

§ Crystal data for **2**: $C_{16}H_{14}O_4S_4$, M = 397.98, Monoclinic, $P2_1/c$, a = 8.5263(7)Å, b = 15.1627(16)Å, c = 13.1507(11)Å, α = 90°, β = 98.217(10)°, γ = 90°, V = 1682.7(3)Å^3, Z = 4, μ(MoKα) = 0.583 mm^{-1}, 12464 reflections collected ($2 < \theta < 26$) from which 3180 were independent, 2033 reflections with $I > 2\sigma(I)$, 217 refined parameters, $R_1 = 0.047$, wR_2 (all data) = 0.11. Data were collected on a STOE-IPDS diffractometer at 293 K. 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. CCDC 251832. See http://www.rsc.org/suppdata/cc/b4/b414822c/ for crystallographic data in .cif or other electronic format.

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