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Exomethylene-3,4-ethylenedioxythiophene (emEDOT): A New Versatile Building Block for Functionalized Electropolymerized Poly(3,4-ethylenedioxythiophenes) (PEDOTs)

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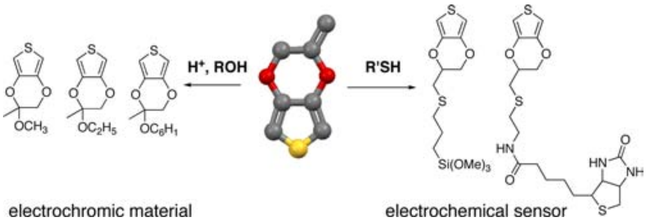
ABSTRACT



A new versatile thiophene derivative exomethylene-3,4-ethylenedioxythiophene (emEDOT) is introduced. The molecule can be straightforwardly prepared in two steps from commercially available derivatives and enables facile further derivatization through both acid catalyzed additions of alcohols and standard thiol–ene click chemistry. The preparation of electrochromic materials and of an electrochemical avidine sensor is shown by the oxidative polymerizations of several functionalized EDOT monomers straightforwardly prepared from emEDOT.

Currently, conjugated polymers represent a key enabling technology in plastic electronics. In particular, poly(3,4-ethylenedioxythiophene) (**PEDOT**)[1] and its derivatives, including those obtained by exchanging the sulfur atom with a selenium one,[2] play a special role in this field.

PEDOT is one of the most extensively explored conducting polymers for use in thin-film conductive coatings and as the electrode material in organic electronics. It is well-known for its environmental stability, conductivity, and solution processability. Its main successful applications include electrochromic materials,[3] electrode material in organic electronics,[4] ion sensing,[5] biosensors,[6] and most recently thermoelectricity.[7] Interest in combining the remarkable characteristics of **PEDOT** with various additional functions, such as contrast tuning[8] and sensing capabilities,[69] has driven research efforts toward the development of new **EDOT** monomers endowed with functional

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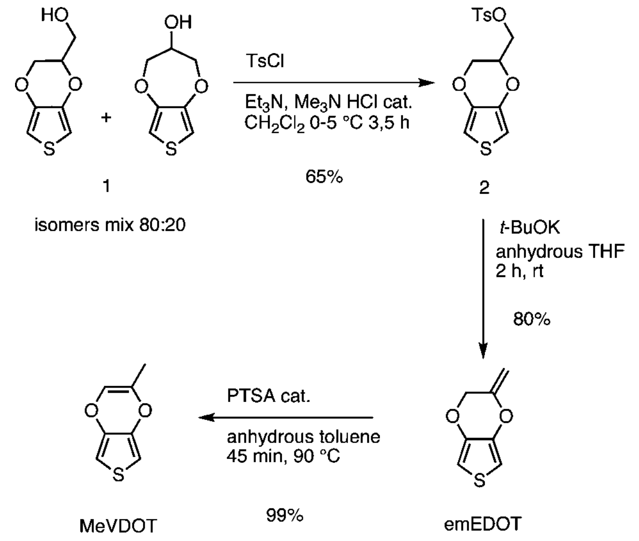
side chains, compatible with the oxidative polymerization process.[10]

All of the functionalization protocols involve elaboration of the ethylenedioxy bridge, often starting from the commercially available hydroxymethyl derivative **EDOT**$-CH_2OH$, leading among others to esters,[11] ethers,[12] and, through 1,3-dipolar cycloaddition, triazole bridged derivatives.[13]

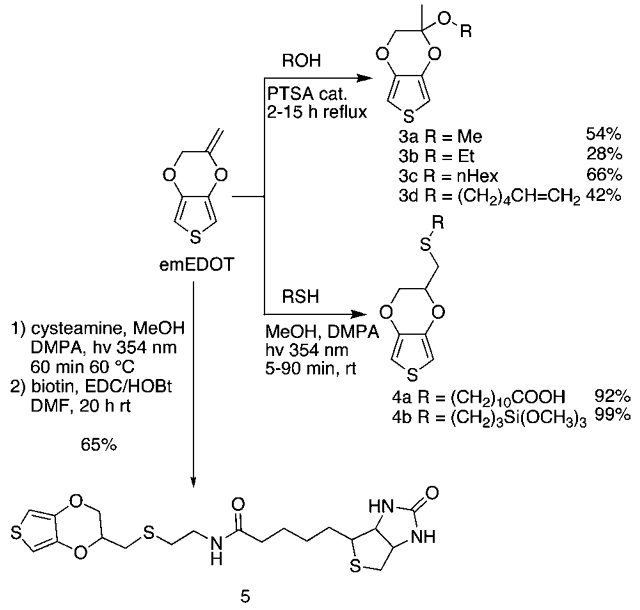
Scheme 1



Aiming at the establishment of a possibly general, versatile, and substituent tolerant **EDOT** functionalization protocol, we here show the synthesis and spectroelectrochemical characterization of a new, easily accessible, **EDOT** derivative, the exomethylene-**EDOT** (**emEDOT**). This new compound features efficient acid catalyzed addition of alcohols and efficient thiol−ene reaction, thus providing an excellent synthone for the preparation of a variety of original **EDOT**-based electropolymerizable monomers.

We show, as a purely demonstrative example, the preparation of acetal and siloxane functionalized derivatives to be employed as electrochromic materials and adhesion promoters in transparent conductive thin layers, as well as a biotine functionalized derivative showing potentials as a building block for electrochemical avidine sensors. Scheme 1 shows the synthesis of **emEDOT**. The reaction of the commercially available mixture **1** (80% **EDOT**−CH_2OH, 20% **ProDOT**−**OH**) with *p*-toluenesulphonyl chloride in the presence of a trimethylamine−triethylamine mixture as a base leads to the corresponding mixture of tosylate esters.

Scheme 2



Crystallization from MeOH affords the pure isomer **2** in 65% overall yield. Reaction of **2** with ^{t}BuOK in THF at rt leads to almost immediate and high yield elimination with the formation of **emEDOT**, isolated as a colorless liquid, after chromatographic purification. **emEDOT** undergoes quantitative, acid catalyzed, thermal isomerization to the methyl-substituted analogue (**MeVDOT**) of 3,4-vinylenedioxythiophene (**VDOT**), a valuable **EDOT** derivative originally reported by Roncali et al.[14] Conversely, while treated at rt and under an excess of alcohols, **emEDOT** undergoes efficient catalyzed alcohol addition with the formation of the corresponding addition products. The reaction takes place smoothly with methanol, ethanol, and hexanol and is also efficient with hex-5-en-1-ol (Compounds **3a**−**d**, Scheme 2).

emEDOT reacts with thiols in the presence of thermal or photochemical radical initiators to give the corresponding anti-Markovnikov addition products (derivatives **4a**−**b**, Scheme 2). This type of hydrothiolation reaction of alkenes has recently received renovated interest from the scientific community as a consequence of its unconventional characteristics. These include high versatility, extreme rapidity, vast functional group tolerance, regioselectivity, high yields, moisture, and oxygen tolerance.[15] All these features

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supported this reaction being considered part of the so-called "click" reactions, following the criteria defined by Sharpless.[16]

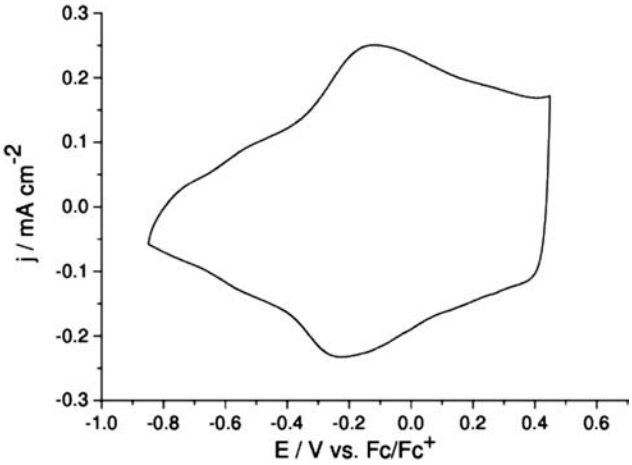

Figure 1. CV of poly(**3a**) in 0.1 M Bu_4NClO_4/MeCN monomer-free solution; scan rate 50 mV s^{-1}. The polymer was deposited galvanostatically at 2.5 mA cm^{-2} with a total charge of 15 mC cm^{-2} on FTO/glass.

We tested the reactivity of **emEDOT** using 11-mercaptoundecanoic acid as a model, functionalized thiol. In the absence of any initiator, simple UV irradiation at 365 nm from an hand-held UV lamp for 3 days of a mixture of **emEDOT** and thiol in methanol leads to 63% conversion, as assessed by the NMR of the reaction mixture (see Figures S1−S2 of the Supporting Information, SI).

Under otherwise identical conditions, the presence of a catalytic amount of 2,2-dimethoxy-2-phenylacetophenone (DMPA) as the photoinitiator drives the reaction to a 92% conversion in 90 min. Remarkably, when the thiol is miscible with **emEDOT**, as in the case of the second functionalized thiol we tested, 3-(trimethoxysilyl)propane-1-thiol, the reaction can be conveniently carried out without solvent. These conditions lead to the desired product with quantitative conversion in < 5 min. Compound **4b** obtained with this method can be used directly, without further purification. To the best of our knowledge, this represents the first example of an **EDOT** monomer functionalized with a trialkoxysilane moiety. Such a feature can in principle enhance the adhesion of the polymer layer to the underlying substrate, which represents a key technological aspect for the lifetime of electronic devices. Finally, **emEDOT** reacts, in the minimum amount of MeOH, with cysteamine in the presence of DMPA to give the corresponding adduct, eventually converted to the biotinilated **EDOT** derivative **5** by hydroxybenzotriazole/EDC promoted condensation with biotine (Scheme 2).

All new derivatives, including **emEDOT** itself, were thus submitted to electrochemical oxidative polymerization.

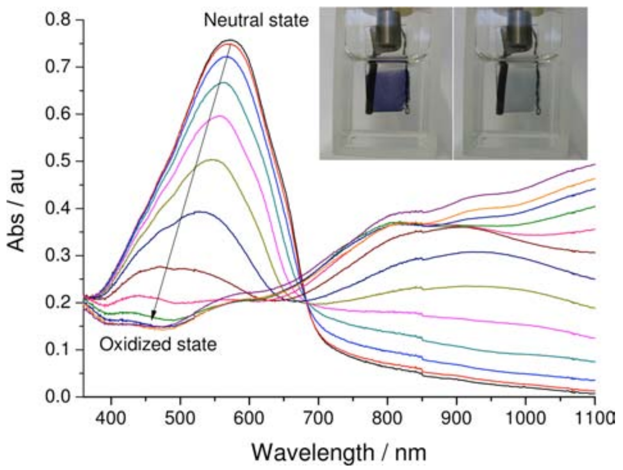

Figure 2. UV−vis−NIR spectra taken at different oxidation potentials of poly(**3a**) in 0.1 M Bu_4NClO_4/MeCN monomer-free solution. Inset: picture of the reduced (purple) and oxidized (light blue) film on an FTO-glass working electrode.

Figure S3 (SI) shows the cyclic voltammetry (CV) of **emEDOT** featuring the onset of an oxidative process at 1.2 V (all potentials reported vs the Fc/Fc$^+$ redox couple). Upon further cycling, current peaks in the region 0.3−0.8 V appear as a consequence of the deposition of electroactive material on the working electrode. However, the polymer growth is inefficient and the redox reversibility of the material deposited is limited (Figure S4, SI).

Similar behavior is observed for the isomer **Me-VDOT**. Despite the presence of an oxidation process with an onset around 0.6 V, the CV of this compound (Figure S5, SI) does not change upon cycling, evidence of a completely hindered polymerization. This is in complete agreement with the results originally observed with the parent compound **VDOT**.[14]

Alcohol functionalized derivatives **3a**−**d** feature remarkably different electrochemical behavior. The CV of **3a** (Figure S6, SI) shows the presence of an oxidation process with an onset at 0.94 V, with the typical nucleation loop on the reverse scan. The current rises quickly upon further cycling. The CV of poly(**3a**) in a monomer-free solution (Figure 1) displays a reversible redox process between −0.8 and 0.4 V, coherent with the values previously reported for electropolymerized **PEDOT**. Poly(**3a**) is also endowed with the typical electrochromic behavior associated with **PEDOT** derivatives (Figure 2). The polymerization becomes less efficient upon elongation of the alkyl chains. In particular, derivative **3b** can still be electropolymerized, although less efficiently than **3a**, while attempts to polymerize **3c** and **3d** lead to passivation of the working electrode attributed to inhomogeneous growth of poorly conductive material.

Conversely, the polymerization of the siloxane derivative **4b** can be efficiently carried out leading to a stable, redox reversible, layer of polymeric material firmly attached to the working electrode (see Figures S7 and S8, SI).

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We believe this to be the consequence of both the efficient polymerization of the **EDOT** residue and the presence of the trialkoxysilane functionalities that enhance the adhesion of the deposited material to the substrate. The result could be of interest for the preparation of covalently linked thin **PEDOT** interlayers, to be employed instead of the popular **PEDOT**-PSS ones.

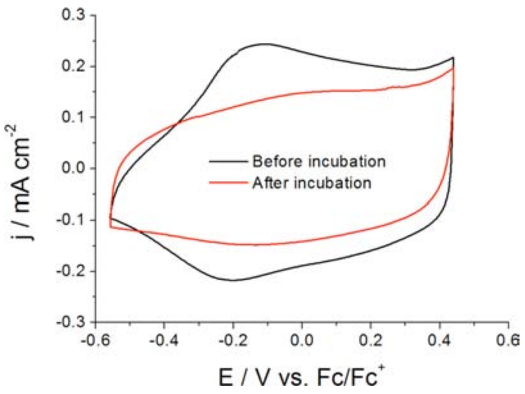

Figure 3. CV of *ran*-poly(**5**-co-**EDOT**) in 0.1 M Bu_4NClO_4/MeCN monomer-free solution before (black) and after (red) incubation with avidine; scan rate 50 mV s^{-1}.

Finally, in order to test the generality of our approach, we polymerized the biotinilated derivative **5** on both glassy carbon and glass-FTO working electrodes aiming at the preparation of an electrochemical avidine sensor. The use of biotinilated **PEDOT**s and polythiophenes was already reported in the literature, demonstrating both high sensitivity and selectivity in the electrochemical sensing of avidine. In particular, Higgins reported the copolymerization of a biotinilated **EDOT** derivative whose structure is similar to that of **5**.[6] Thanks to the optimization of both deposition conditions and electrodes design and miniaturization, the authors were able to easily detect 10^{-16} mol of avidine (working with a 10^{-13} M solution). Such a derivative could only be copolymerized with **EDOT**,[6] as attempts to homopolymerize it were not successful.

Conversely, derivative **5** can be both homopolymerized and copolymerized with **EDOT**. Figures S9 and S10 of the SI show the polymerization and CV plot in monomer free solutions, respectively, for poly(**5**), while Figure S12 shows the CV of *ran*-poly(**5**-co-**EDOT**) on glassy carbon. The two plots are similar and coherent with those obtained with other **EDOT** derivatives.

Indeed, poly(**5**) shows electrochromic behavior similar to that of poly(**3a**) (see Figure S11). Both films where incubated for 15 min in a 10^{-8} M avidine buffer (0.1 M NaCl, 0.01 M NaEDTA) solution, rinsed with deionized water and then cycled again in 0.1 M tetrabutylammonium tetrafluoborate acetonitrile solution. Interestingly, the homopolymer CV does not show any change even at such a relatively high avidine concentration, while the copolymer displays the expected reduction in the current associated with a shielding of the electroactive layer surface by the bulky avidine molecules (Figure 3).[17] We did not further test the minimum detectable avidine concentration, as this study is beyond the scope of the present paper.

In conclusion, we introduced a new functional **EDOT** monomer featuring an easy synthetic access and very versatile reactivity including acid catalyzed alcohols addition and thiol–ene "click" addition. In particular, through thiol–ene coupling we were able to prepare the first siloxane functionalized **EDOT** monomer to date. We successfully electropolymerized such a monomer on a TCO layer to give a robust electroactive film. We also exploited thiol–ene chemistry for the straightforward preparation of a biotinilated **EDOT** derivative whose copolymer with **EDOT** shows potential as an electrochemical biosensor. We believe the derivatives we described and characterized represent valuable examples of several new **EDOT** functionalized monomers accessible through further simple chemical manipulation of **emEDOT**.

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Supporting Information Available. Synthesis of all new compounds. NMR investigation of the thiol–ene addition mechanism. Polymerization CV plots of **emEDOT**, **MeVDOT**, **3a**, **3b**, **4b**, **5**, and **5**-co-**EDOT**. Spectroelectrochemical characterization of poly(**5**). Sensing experiments with poly(**5**) and poly(**5**-co-**EDOT**). This material is available free of charge via the Internet at http://pubs.acs.org.

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The authors declare no competing financial interest.