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Functionalized 3,4-ethylenedithiathiophenes (EDTTs) as building blocks for poly (3,4-ethylenedithiathiophene) (PEDTT) derivatives

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Abstract

A convenient and straightforward procedure has been developed for the preparation of functionalized 3,4-ethylenedithiathiophene (EDTT) derivatives by using a new bromomethyl–EDTT derivative as a versatile synthon. Based on this procedure a novel EDTT derivative endowed with 9,10-anthraquinone moieties has been synthesized and electrochemically polymerized to yield a donor–acceptor PEDTT derivative.

A great deal of interest has been received by functionalized polythiophenes (PT) due to their key role as active materials in the development of electrochromic and electronic devices, such as OLEDs, OFETs, and organic solar cells.[1] They have also found application as sensors as a consequence of their ability to detect, transduce, and amplify different physical and chemical information.[2]

Among polythiophenes, poly(3,4-ethylenedioxythiophene) (PEDOT) has received much attention owing to its high electrical conductivity, chemical stability, good film forming ability, low bandgap, outstanding environmental stability, and compatibility with aqueous media.[3] Introduction of a hydroxymethyl group at the ethylene bridge of EDOT like in **1** (Fig. 1) has represented a practical approach for the functionalization of EDOT.[4] More recently, we synthesized an EDOT derivative with a chloromethyl functionality (**2**, Fig. 1) which allowed us to synthesize a number of PEDOT derivatives endowed with electroactive moieties.[5]

Our research group is interested in the development of functionalized semiconducting polymers that display interesting properties (electrochemical stability, low band gap, recognition properties) to be used in different applications including optoelectronic devices and electrochemical sensors. Among them, 3,4-ethylenedithiathiophene (**EDTT**,

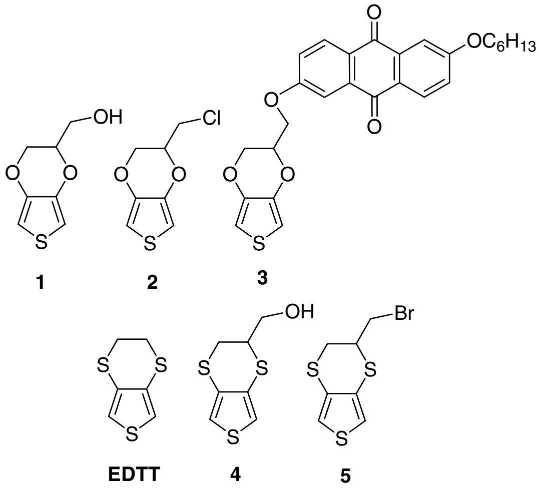

Fig. 1. Structures of functionalized EDOT derivatives (**1**–**3**), ethylenedithiathiophene (**EDTT**), and the novel functionalized EDTT derivatives **4** and **5**.

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Fig. 1),[6] which is the sulfur analog of EDOT, is of interest, to investigate the influence of the substituent bridges on the behavior of the polymer. In contrast to the great number of studies carried out with EDOT derivatives, the EDTT system is relatively unexplored[7] and, to the best of our knowledge, there have been very few reports on functionalized PEDTT derivatives.[8] In this regard, the synthetic methodology developed by Blanchard et al. is relevant for the synthesis of 3,4-dialkylsulfanylthiophenes.[9] In this Letter, we report a straightforward synthesis of functionalized **EDTT** derivatives (**4**, **5**, Scheme 1) bearing functionalities which pave the way for the synthesis of a variety of substituted PEDTT derivatives. To explore the use of this strategy to incorporate electroactive moieties to the PEDTT system we have carried out the synthesis of a PEDTT derivative endowed with 9,10-anthraquinone (AQ) moieties (**9**, Scheme 1) and investigated its electrochemical behavior in comparison with our previously reported AQ–EDOT analog (**3**, Fig. 1).[5b]

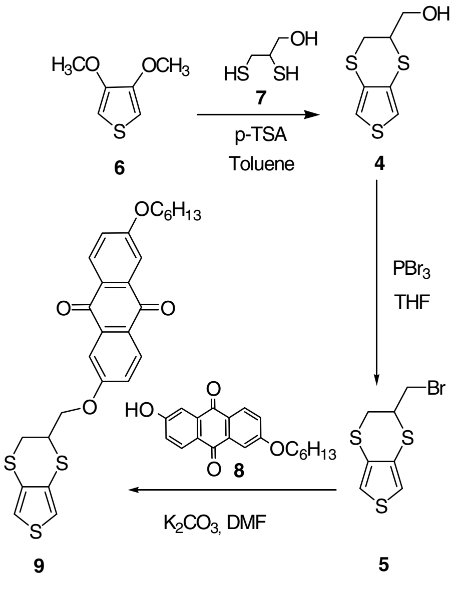
In 2004 Bäuerle and co-workers reported the acid catalyzed transetherification reaction as an efficient route for the synthesis of EDOT derivatives from 3,4-dimethoxythiophene (**6**).[10] On the other hand, Meijer and co-workers reported a convenient synthesis of 3,4-bis(alkylthio)thiophenes by the acid catalyzed nucleophilic substitution of 3,4-dimethoxythiophene (**6**) with suitable thiols.[11]

In this Letter, we wish to extend this strategy to the synthesis of functionalized EDTT derivatives by following the synthetic strategy depicted in Scheme 1. Thus, the reaction of 3,4-dimethoxythiophene (**6**)[12] with 2,3-dimercapto-1-propanol (**7**) in toluene in the presence of *p*-toluenesulfonic acid monohydrate under standard conditions afforded hydroxymethyl–EDTT (**4**) in moderate yield. Reaction of **4** with phosphorus tribromide in THF allows obtaining bromomethyl–EDTT (**5**), which is a reactive synthon against nucleophiles. Further reaction of **5** with 2-hexyloxy-6-hydroxy-9,10-anthraquionone (**8**)[5b] under basic conditions yielded the target AQ–EDTT ensemble (**9**).[13]

The electrochemical behavior of the novel AQ–EDTT system (**9**) was investigated by cyclic voltammetry (CV) in dichloromethane (DCM) and tetrabutylammonium hexafluorophosphate (TBAHFP) as electrolyte (black solid line, Fig. 2). Reduction and oxidation potentials were measured relative to the internal standard ferrocene–ferricenium (Fc/Fc$^+$). In the positive potential regime, CV of **9** shows a typical irreversible oxidation peak at 1.01 V corresponding to the formation of the EDTT radical cations. The value is comparable to that observed for **EDTT** itself, which exhibits an irreversible anodic peak at 0.98 V under identical conditions. The higher oxidation potential of AQ–EDTT (**9**) with respect to that of **EDTT** is due to the close vicinity of the acceptor AQ moiety to the EDTT system, thus decreasing the electron density within the latter. It is also worth mentioning that the anodic peak potential of AQ–EDTT at 1.01 V is lower than that observed for the parent AQ–EDOT system (1.16 V)[5b] (Fig. 2, blue dashed line) due to the higher electron-donating effect of S atoms compared to O atoms in the bridge substituent of the monomer.[7a–c]

A potential scan toward negative potentials (Fig. 2) reveals the reduction waves due to the anthraquinone moiety. AQ–EDTT **9** shows reduction potentials of $E^1_{1/2} = -1.48$ V and $E^2_{1/2} = -1.88$ V. The reduction potentials are similar to that observed for the analogous AQ–EDOT **3** ($E^1_{1/2} = -1.49$ V) and slightly more negative than that corresponding to the reference 2,6-dihexyloxy-9,10-anthraquinone ($E^1_{1/2} = -1.38$ V) which shows the electron-donating ability of the EDTT and EDOT system.

Oxidative polymerization of **9** (Scheme 2) was carried out by potentiodynamic cycling in the potential range of −0.3 to 1.1 V. Similarly to EDOT derivatives, for EDTT



Scheme 1. Synthesis of the AQ–EDTT system **9**.

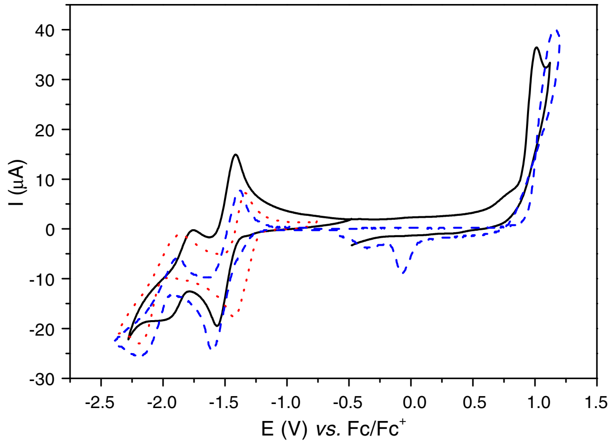
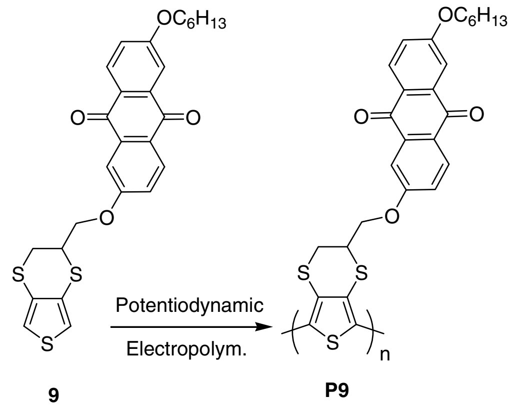


Fig. 2. Cyclic voltammogram of **9** (black solid line), 2,6-dihexyloxy-9,10-anthraquinone (red dotted line) and **3** (blue dashed line) in dichloromethane/TBAHPF (0.1 M) at rt, scan rate of 100 mV/s, Pt disk working electrode, potentials versus Fc/Fc$^+$.



Scheme 2. Potentiodynamic electropolymerization of the AQ–EDTT system **9**.

the growth of polymer chains occurs exclusively via α–α coupling, because the β or β′ positions are blocked by the bridge group. The growth of a conducting polymer is reflected by gradually increasing currents in subsequent potential cycles whose thickness regularly increases with the number of cycles. It has recently been reported that the mechanism of the electrodeposition process is different for PEDOT and PEDTT.[7b] Together with a three-dimensional growth, a certain contribution of a two-dimensional growth is observed for PEDOT and it is not observed for PEDTT. The absence of a two-dimensional mechanism during the electrochemical deposition of PEDTT is due to the large dihedral angle between the bis(ethylenesulfanyl)thiophenes as a consequence of the steric hindrance to coplanarity,[14] which contrasts with the planar structure observed for oligoEDOT derivatives.[15] Introduction of the bulky anthraquinone moiety in every EDTT unit will probably increase the dihedral angle between consecutive EDTT units in the polymer even more. Thus, in comparison with the PEDOT analog (**P3**), a more porous structure should be formed for poly(AQ–EDTT) (**P9**) which will favor its solubility. Thus, while **P3** strongly adhered to the working electrode after polymerization[5b] polymer **P9** tends to separate from the electrode after several cycles.

Poly(AQ–EDTT) (**P9**) was electrochemically characterized in an electrolyte free of monomer (Fig. 3, black solid line). The CV exhibits an anodic peak at 0.55 V. The value of the anodic potential is consistent with the published data[7b,c] as well as with the oxidation potential determined for unsubstituted poly-EDTT (0.56 V) polymerized under identical conditions. The oxidation peak potential of poly(AQ–PEDTT) (**P9**) is more positive than that observed for poly(AQ–PEDOT) (**P3**) (−0.03 V). Thus, despite the lower oxidation potential of the AQ–EDTT system (**9**) in comparison with the parent AQ–EDOT analog (**3**), the peak potential of poly(AQ–PEDTT) (**P9**) becomes higher than that of poly(AQ–PEDOT) (**P3**). This behavior was previously observed for PEDOT and PEDTT[7a,c] and indicates that the twisted structure of the PEDTT skeleton is not appropriate for π-conjugation between EDTT rings which therefore leave the HOMO energy level nearly unchanged under polymerization.

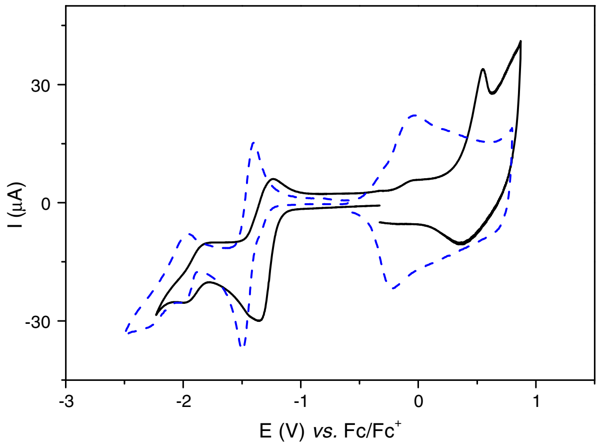


Fig. 3. Electrochemical characterization of polymers **P9** (black solid line) and **P3** (blue dashed line) in acetonitrile/TBAHPF (0.1 M) at rt, scan rate of 100 mV/s, Pt disk working electrode, potentials versus Fc/Fc$^+$.

In the negative potential regime two reduction waves were observed for **P9** with reduction potentials at $E^1_{1/2} = -1.30$ V and $E^2_{1/2} = -1.90$ V. The reduction potentials are slightly less negative for **P9** in comparison with that observed for poly(AQ–PEDOT) (**P3**, $E^1_{1/2} = -1.45$ V and $E^2_{1/2} = -1.99$ V). This behavior reflects the higher electron-donating ability of the PEDOT backbone in comparison with PEDTT. It is also worth mentioning that the ambipolar behavior observed for **P3** indicates that the anthraquinone moieties are electroactive within the polymer film. This behavior is similar to that observed for the PEDOT analog and contrasts with that observed in normal polythiophene. Thus, in polythiophene derivatives bearing pendant electroactive units a direct charge transfer from the electrode surface to the pendant electroactive units is rather unlikely.[16]

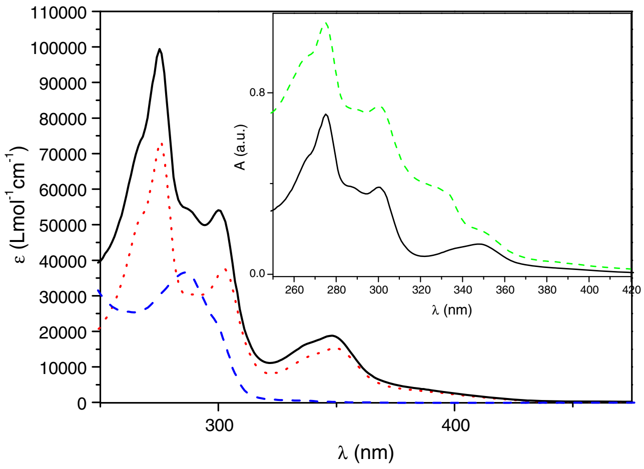


Fig. 4. UV–vis spectra of **9** (black solid line), **EDTT** (blue dashed line), and 2,6-dihexyloxy-9,10-anthraquinone (red dotted line) in dichloromethane solution. Inset: UV–vis spectra of monomer **9** (black solid line) and **P9** (green dashed line) in dichloromethane solution.

The absorption spectrum of AQ–EDTT (**9**, Fig. 4, black solid line) in dichloromethane corresponds approximately to a superposition of the absorption bands belonging to the anthraquinone (red dotted line) and EDTT (blue dashed line) systems. Thus, this indicates a minimal interaction between both moieties in the ground state, which is in agreement with that observed in the electrochemical characterization of the monomers. On the other hand, polymer films of **P9** were soluble enough in dichloromethane to allow obtaining absorption spectrum in solution. On the inset of Figure 4 are depicted the UV–vis spectra of monomer **9** (black solid line) together with that corresponding to polymer **P9** (green dashed line). A new band at ca. 330 nm can be observed for **P9** which can be assigned to the π–π^* transition of the PEDTT backbone. This value is blue shifted in comparison to that reported for unsubstituted PEDTT measured in the solid state (ca. 440 nm)[7a,c] and also to the values obtained in solution (ca. 410 nm).[6] These values indicate a greater degree of planarity of the PEDTT system in the solid state than in solution. Incorporation of the anthraquinone moiety will probably increase the twist angle between consecutive EDTT units, thus blue shifting the absorption band corresponding to the π–π^* transition.

In conclusion, we have developed a straightforward procedure for the preparation of versatile EDTT derivatives which provides easy access to functionalized EDTTs and their corresponding PEDTTs endowed with functional systems such as redox active units. Thus, we have synthesized the first ambipolar PEDTT derivative endowed with anthraquinone functionalities. Full spectroscopic and electrochemical characterization of the new D-A ensemble has been carried out confirming its ambipolar character. The new polymer has been compared with a parent PEDOT analog showing the influence of the substituent bridges on the behavior of the polymer.

Acknowledgments

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13. *Selected data for* **9**: ^{1}H NMR (CDCl$_3$, 200 MHz). δ 8.24 (d, $J = 8.6$ Hz, 1H, *Ant*), 8.22 (d, $J = 8.6$ Hz, 1H, *Ant*), 7.72 (d, $J = 2.7$ Hz, 1H, *Ant*), 7.69 (d, $J = 2.7$ Hz, 1H, *Ant*), 7.28–7.19 (m, 2H, *Ant*), 7.04 (AB system, $J = 3.4$ Hz, 2H, *Th*), 4.53 (dd, $J = 9.5$ Hz, $J = 9.4$ Hz, 1H, O–CH$_2$–CH), 4.31 (dd, $J = 9.5$ Hz, $J = 5.3$ Hz, 1H, O–CH$_2$–CH), 4.14 (t, $J = 6.4$ Hz, 2H, –OCH$_2$–R), 3.93–3.81 (m, 1H, –CH–), 3.44 (dd, $J = 13.7$ Hz, $J = 3.2$ Hz, 1H, CH$_2$–S), 3.33 (dd, $J = 13.7$ Hz, $J = 5.3$ Hz, 1H, CH$_2$–S), 1.89–1.78 (m, 2H, –CH$_2$–), 1.39–1.25 (m, 6H, –CH$_2$–), 0.92 (t, $J = 7.9$ Hz, 3H, –CH$_3$); ^{13}C NMR (CDCl$_3$, 125 MHz). δ 182.22 (C=O), 182.01 (C=O), 164.13 (C$_{Ar}$–O), 162.97 (C$_{Ar}$–O), 135.90, 135.73, 129.79, 129.73, 127.64, 126.88, 125.07, 123.55, 121.01, 120.75, 118.99, 118.62, 110.85, 110.60, 69.26, 68.84, 38.22, 31.50, 29.95, 28.97, 25.62, 22.57, 14.01; FT-IR (KBr). $v = 3094$, 2924, 2853, 1731, 1669, 1590, 1466, 1327, 1304, 1230, 746 cm^{-1}; MS (EI) (*m*/*z*): 510 (M$^+$), 187 (M$^+$-*Ant*); Anal. Calcd for C$_{27}$H$_{26}$O$_4$S$_3$: C, 63.50; H, 5.13; S, 18.84. Found C, 63.83; H, 5.37; S, 18.97.
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