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LETTER

Electrosynthesis and characterization of stable radical functionalized oligo/polythiophenes

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Poly(terthiophene) pendant verdazyl radical was prepared via electrochemical oxidation of either the parent radical or its precursor. Cyclic voltammetry shows a positive shift of the verdazyl radical oxidation potential in the corresponding electroactive poly(verdazyl radical-terthiophene).

Materials with multiple properties have attracted great attention for their applications in photovoltaic cells,[1] magnetic materials[2] and energy storage.[3] In order to enhance the properties of conducting materials, several specific groups have been incorporated onto polymer backbones. As an example, electro-donating groups such as methyl and alkoxy groups introduced on polythiophene backbone, result in an increase in the electrical conductivity of the polymer.[4] Chelating agent such as bipyridine have been attached to polythiophenes in order to form valence tautomeric conducting metallopolymers.[5] Moreover, incorporation of such substituents can help tune the electrical, optical and electrochemical properties of conducting materials.[6]

Other motifs that were linked to conducting materials like polythiophene are phenoxyl radicals.[7] The chemical oxidation of the parent monomer using $FeCl_3$ affords polythiophene with pendant phenoxyl radical, which exhibit high spin ground state and an intramolecular ferromagnetic coupling through the polymeric π system. Other polythiophenes pendant radical such as TEMPO[8] and nitroxide[9] have also been described. However, their electropolymerizations have been overlooked.

Our strategy involves the preparation of materials combining both properties (radical and thiophene) in which their redox properties can be switched by applying an external potential.

We are interested in the introduction of a stable radical such as verdazyl on polythiophene backbone. The presence of the radical on polythiophene provides a great opportunity to introduce either an extra negative charge (reduction of the radical) or a positive charge (oxidation of the radical), which may have a significant effect on the optical and electrical properties of the conjugated polymers. Moreover, verdazyls exhibit excellent stability in the presence of organic solvents and moisture comparable to electrochemical properties of nitroxide radical derivatives.

Despite a wide range of complexes with verdazyl radicals,[11] few examples of such radicals linked to organic/inorganic oxidative electroactive species are reported. The verdazyl radical linked to ferrocene motif shows interactions between the radical and the ferrocenium (radical cation).[12] Another isolated example was verdazyl-radical functionalized tetrathiafulvalene (TTF), which shows interaction between TTF radical cation and the verdazyl radical.[13] Recently, verdazyl linked to inorganic redox active species such as ruthenium Ru have been reported.[14]

A monothiophene bearing verdazyl radical has been prepared; however, their polymerization using chemical oxidation was unsuccessful.[15] To the best of our knowledge, no polythiophene bearing verdazyl radical has been prepared or deposited on platinum electrode using electrochemical oxidation.

Herein, we present the synthesis and characterization of a new poly(terthiophene) pendant verdazyl radical via electrochemical oxidation of the parent monomer (Chart 1). Furthermore, verdazyl radical functionalized polythiophene can be directly synthesized via electrooxidation of the verdazyl radical precursor. In addition to the presence of the charge of the doped electro-active polymer, verdazyl radical can host a new negative charge, which may affect the optical and the electrical properties of the poly(verdazyl radical-terthiophene).

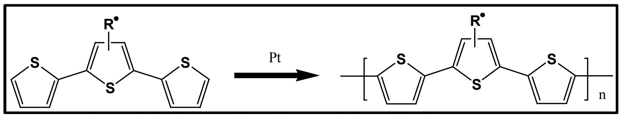
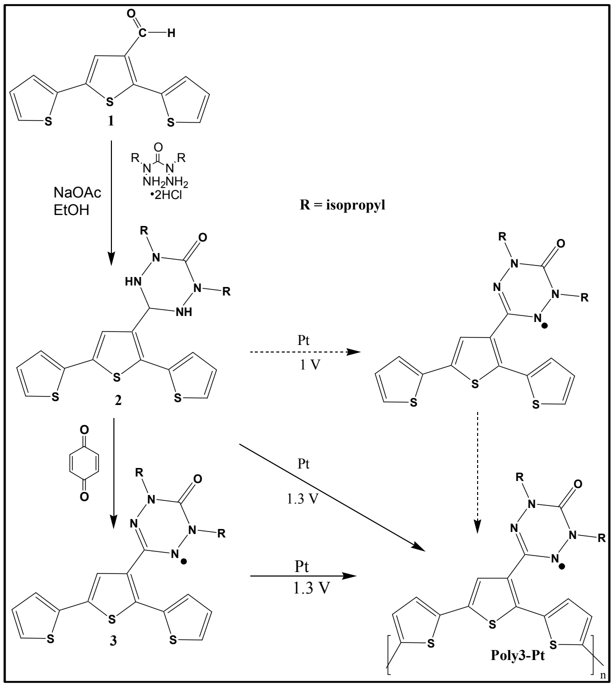


Chart 1. Polyterthiophenes bearing stable radicals

The synthesis of verdazyl radical functionalized terthiophene **3** has been performed in several steps as depicted in Scheme 1. The condensation of terthiophene carboxaldehyde **1** with carbonic acid bis(1-alkylhydrazide)s affords the corresponding heterocyclic tetrazane **2**. The latter was oxidized using 1,4-benzoquinone to the corresponding radical **3**. In our case, the carbonic acid bis(1-alkylhydrazide)s was 2,4-diisopropylcarbonhydrazide bis-hydrazinecarboxylate that was prepared using a procedure described in the literature.[16] Radical **3** was characterized by infrared and ESR. As shown in Fig. 1a, the carbonyl stretch was shifted by 83 cm^{-1} (1690 cm^{-1}) in comparison to the carbonyl of the precursor **2** (1607 cm^{-1}). Moreover, the ESR spectrum of the radical **3** exhibits hyperfine coupling constants of a(N2,4) = 6.5 G (2N), a(N1,5) = 5.3 G (2N) and a(H) = 1.3 G (2H), which are characteristics of isopropyl substituted verdazyl radical reported in the literature (see electronic supplementary information).[17]



Scheme 1. Synthetic pathway of verdazyl radical functionalized oligo/polyterthiophene.

Electrochemical properties of terthiophenes **2** and **3** and their corresponding electro-active polymer have been investigated by cyclic voltammetry (CV) and their peak potentials are summarized in Table 1.

Table 1 Electrochemical properties and carbonyl frequency of verdazyl functionalized oligo/polythiophenes. E_1: peak potential of verdazyl or its precursor. E_2: peak potential of terthiophene. *Reversible system. [ ]: potentials vs Fc/Fc$^+$. WE: Platinum electrode. Scan rate: 100 mV/s

Compound	E_1 (vs. Ag/AgCl)	E_2 (vs. Ag/AgCl)	υ_{co}(cm^{-1})
1	-	1.18 [0.80]	1676
2	0.90 [0.52]	1.26 [0.98]	1607
3	0.54 [0.16]*	1.25 [0.97]	1690
Poly(**1**)-Pt	-	1.01 [0.63]*	1671
Poly(**2**)-Pt	0.53 [0.15]*	1.11 [0.73]*	1640
Poly(**3**)-Pt	0.66 [0.28]*	1.14 [0.76]*	1640

Terthiophene **2** exhibits two irreversible peaks at 0.90 V (vs. Ag/AgCl) and 1.26 V (vs Ag/AgCl), which correspond to the oxidation of the heterocyclic tetrazane and the oxidation of terthiophene, respectively (Fig. 2a). Verdazyl radical-terthiophene **3** displays one reversible monoelectronic peak at 0.54 V (vs. Ag/AgCl) and one monoelectronic irreversible peak at 1.25 V (vs. Ag/AgCl), which correspond to the oxidation of verdazyl radical and terthiophene motif, respectively (Fig. 2d). The oxidation potential the verdazyl radical is in agreement with the value described in the literature (Fig. 3).[17]

The broad peak at 0.90 V observed in heterocyclic tetrazane is due to electrooxidation of the two secondary amines to afford verdazyl radical following an $(EC)_n$ mechanisms.[18] the oxidation of amines have been studied in order to graft amines on carbon electrode by Pinson and co-workers.[19] Every amine oxidation consumes 2 electrons (1 electron oxidation is followed by a deprotonation).

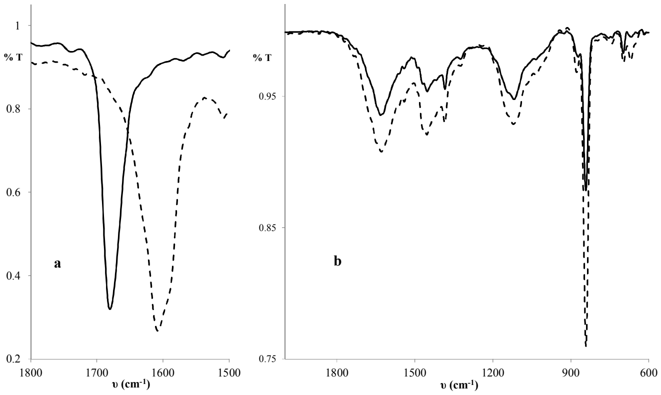
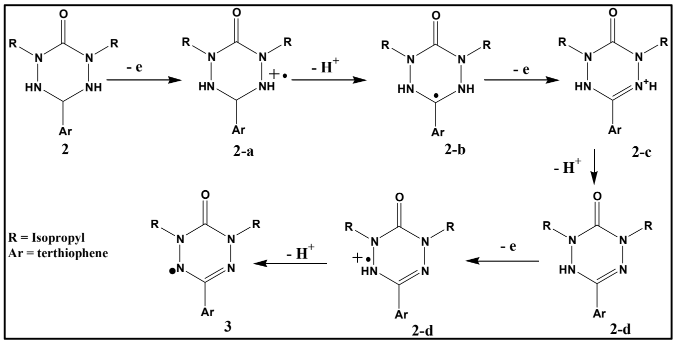


Fig. 1 IR spectra of **2** (**a** dash line), **3** (**a** solid line) and their corresponding polymer poly(**2**)-Pt (**b** dash line) and poly(**3**)-Pt (**b** solid line).

The conversion of the heterocyclic tetrazane **2** to the correspondingverdazyl radical **3** needs 3 electron as described in the proposed mechanism in Scheme 2. To elucidate the mechanism of the electrooxidation of **2**, the variation of oxidation peak potential with the scan rate and with the concentration will be studied using cyclic voltammetry in order to examine the nature of the electron transfers and the chemical reactions.



Scheme 2. Formation of the verdazyl radical via electrooxidation of the tetrazane.

To ascertain the formation of the verdazyl radical **3** from the tetrazane-terthiophene **2**, repeated CV scans were performed beyond the oxidation peak potential of the tetrazane moiety (e.g. 0.90 V) at high scan rate of 20 V/s (Fig. 4) demonstrating the formation of the verdazyl radical at lower potential 0.66 V (vs Ag/AgCl).

Repeated CV scans of **3** on Pt electrode show an increase of the current of both verdazyl radical and terthiophene peaks indicating the formation of poly(radical) and poly(thiophene). The CV of poly(**3**)-Pt exhibits features characteristic of verdazyl radical and terthiophene at 0.54 V and 1.14 V (vs. Ag/AgCl). A small positive shift (~120 mV) of the oxidation potential of verdazyl radical has been observed in poly(**3**)-Pt. Verdazyl radical is a withdrawing component, which shift positively the oxidation potential of the other verdazyl radical present on the corresponding polymer. This behaviour has been observed when two verdazyl radicals are linked with an alkyl group, the oxidation potential is enhanced by 50-100 mV.[20]

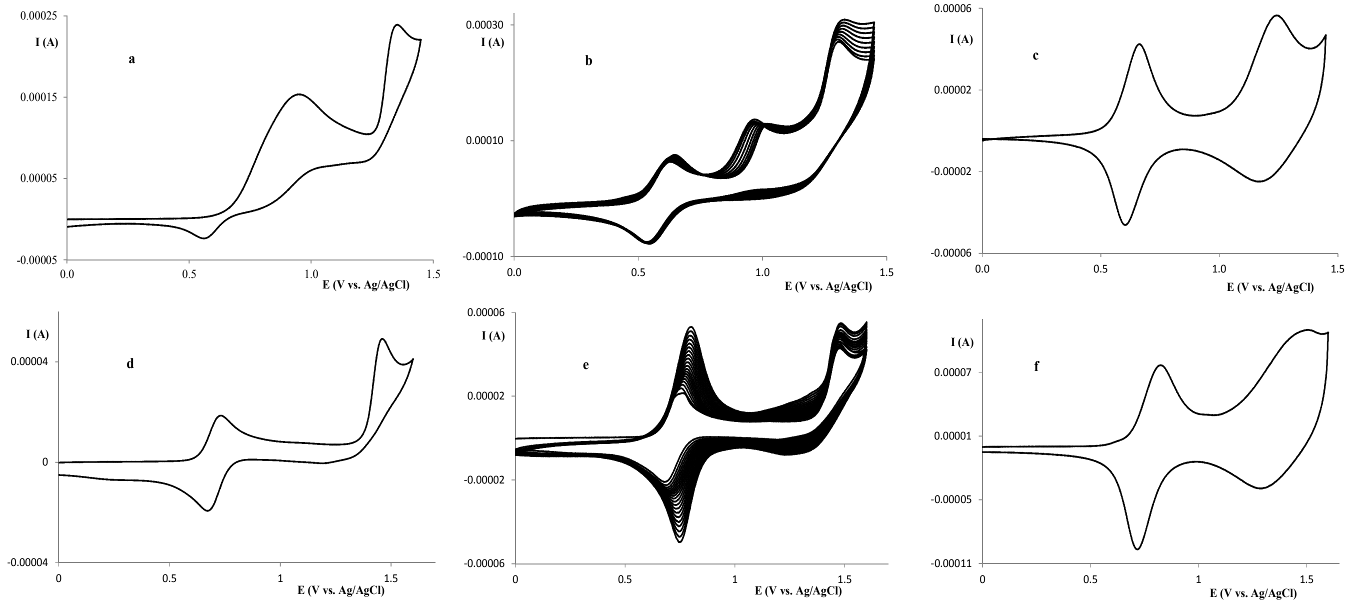


Fig. 2 Electrochemical polymerization of verdazyl radical **3** and its precursor tetrazane **2**. (a) 1st CV scan of **2**, (b) Electropolymerization of **2**, (c) CV of poly(**2**)-Pt, (d) 1st CV scan of **3**, (e) Electropolymerization of **3** and (f) CV of poly(**3**)-Pt.

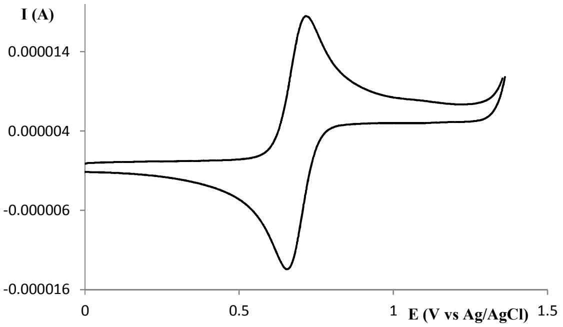


Fig. 3 Reversible monoelectronic cyclic voltammogram of the oxidation of the radical verdazyl **3** on platinum electrode. Scan rate: 0.1 V/s .

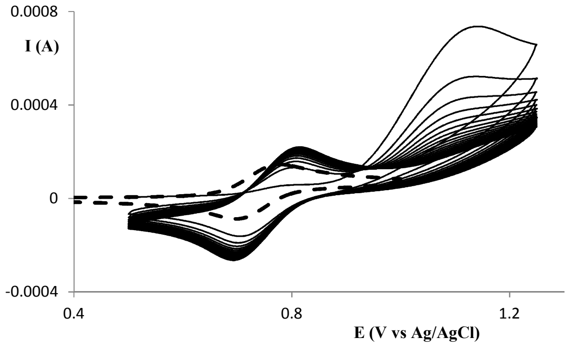


Fig. 4 Electrochemical oxidation of the hetercyclic tetrazane **2** on platinum electrode at scan rate of 20 V/s. Dash line: CV of the verdazyl radical **3**.

Moreover, due to the presence of the verdazyl radical, the geometry of the polythiophene backbone is no longer planar. The loss of the planarity in doped polymer enhances the localization of the spin on the heterocyclic tetrazane, which explain the positive shift of the verdazyl radical in poly(**3**)-Pt. Orbital molecular calculations are underway to estimate the spin density on monomers and on the corresponding doped polymer.

The resulting polymer from the electro-oxidation of **2**, poly(**2**)-Pt displays two reversible peaks at 0.53 and 1.11 V (vs. Ag/AgCl), which correspond to the oxidation of the verdazyl radical and terthiophene, respectively (Fig. 2c). Similar behaviour has been observed for the electro-polymerization of **3**. In CV, poly(**3**)-Pt shows the same peak as poly(**2**)-Pt (Fig 2.f). To confirm that poly(**2**) and poly(**3**)-Pt have similar properties, infrared was performed on both films which are shown in Fig. 1b.

It is clear that both resulting polymers poly(**2**)-Pt and poly(**3**)-Pt have similar IR spectra as depicted in Fig. 1b. The strong stretch at 840 cm^{-1} corresponds to the supporting electrolyte anion PF_6^- incorporated on the polymer during the electropolymerization process (doped polymer). The carbonyl stretch of both polymers, which is shown at 1640 cm^{-1} (Fig. 1b) shifted by 50 cm^{-1}. This can be explained by the strong interaction (electro-donating behaviour) of the resulted π-conjugated polymer and the verdazyl radical. Similar behaviour has been observed when verdazyl radical was chelated to redox active metal such Ruthenium (Ru).[21] In this case the υ(CO) of verdazyl radical was shifted by 25 cm^{-1}, due to the interaction of the dπ of Ru with π* orbital of the verdazyl radical. In our case, the interactions of π-conjugated system of the polymer and the π* of the radical are very strong, which explain the 50 cm^{-1} shift. Moreover, no significant shift has been observed in the carbonyl of poly(**1**). Poly(**2**)-Pt and poly(**3**)-Pt have been pepared by CV-cycling between 0 and 1.50 V vs Ag/AgCl (oxidation followed by the reduction) of the corresponding monomers, **2** and **3,** respectively. Therefore, poly(**2**)-Pt and poly(**3**)-Pt are in verdazyl radical forms. In another hand, it was reported that the IR of the carbonlys of the cation and dication of the verdazyl are 1688 and 1706 cm^{-1},[22] which confirms the presence of the verdazyl radical form in both deposited polymers.

In summary, we have prepared polythiophenes bearing verdazyl radicals using electrochemical oxidation. Moreover, for the first time, the synthesis of verdazyl radical using electrochemical method is presented. Interaction with the spin and the π-conjugated system has been observed by infrared and CV. The measurement of the conductivity and the modelling of poly(radical-terthiophene) are underway.

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Notes and references

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Electronic supplementary information: General synthesis of radical **3** and its precursor **2**, and electrochemical data of **2**.

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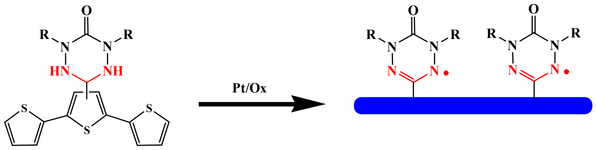
Graphical Abstract



Stable poly(terthiophene) bearing verdazyl radical has been prepared using electrochemical oxidation of either the parent radical or its precursor.