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Electrosynthesis and characterization of stable radical-functionalized oligo/polythiophenes†

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A poly(terthiophene) pendant verdazyl radical was prepared via the electrochemical oxidation of either the parent radical or its precursor. Cyclic voltammetry showed 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 application in photovoltaic cells,¹ magnetic materials² and energy storage.³ 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 a polythiophene backbone result in an increase in the electrical conductivity of the polymer.⁴ Chelating agents such as bipyridine have been attached to polythiophenes to form valence tautomeric conducting metallopolymer.⁵ Moreover, the incorporation of such substituents can help to tune the electrical, optical and electrochemical properties of conducting materials.⁶

Other motifs that have been linked to conducting materials such as polythiophene are phenoxyl radicals.⁷ The chemical oxidation of the parent monomer using FeCl₃ affords polythiophene with a pendant phenoxyl radical, which exhibits a high spin ground state and an intramolecular ferromagnetic coupling through the polymeric π system. Other polythiophenes pendant radicals, such as TEMPO⁸ 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 a polythiophene backbone. The presence of the

radical on the polythiophene would provide 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 the electrochemical properties of nitroxide radical derivatives.¹⁰

Despite there being a wide range of complexes with verdazyl radicals,¹¹ few examples of such radicals linked to organic/inorganic oxidative electroactive species have been reported. A verdazyl radical linked to a ferrocene motif has shown interactions between the radical and the ferrocenium (radical cation).¹² Another isolated example is a verdazyl-radical-functionalized tetrathiafulvalene (TTF), which shows an interaction between the 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 a verdazyl radical has also 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 a 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, the verdazyl-radical-functionalized polythiophene can be directly synthesized *via* the electrooxidation of the verdazyl radical precursor. In addition to the presence of the charge of the doped electroactive polymer, the verdazyl radical can host a new

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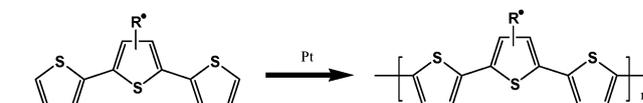
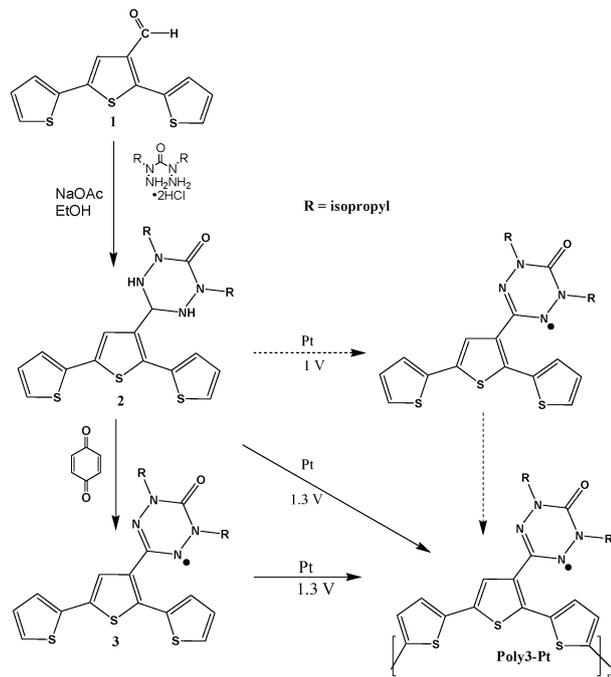


Chart 1 Polyterthiophenes bearing stable radicals.



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

negative charge, which may affect the optical and the electrical properties of the poly(verdazyl radical-terthiophene).

The synthesis of verdazyl-radical-functionalized terthiophene **3** was 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-hydrazine-carboxylate, which 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 radical **3** exhibits hyperfine coupling constants of $a(\text{N}2,4) = 6.5\text{ G (2N)}$,

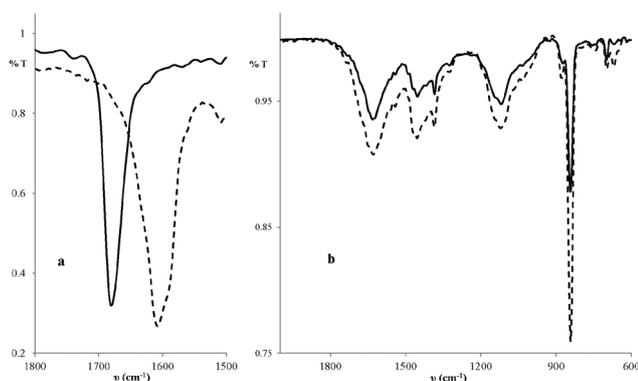


Fig. 1 IR spectra of **2** (a, dashed line), **3** (a, solid line) and their corresponding polymer poly(**2**)-Pt (b, dash line) and poly(**3**)-Pt (b, solid line).

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

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

^a Reversible system. []: potentials vs. Fc/Fc^+ . WE: platinum electrode. Scan rate: 100 mV s^{-1} .

$a(\text{N}1,5) = 5.3\text{ G (2N)}$ and $a(\text{H}) = 1.3\text{ G (2H)}$, which are characteristic of the isopropyl-substituted verdazyl radical reported in the literature (see ESI[†]).

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

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 the verdazyl radical and terthiophene motif, respectively (Fig. 2d). The oxidation potential of the verdazyl radical is in agreement with the value described in the literature (Fig. 3).

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

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

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 a high scan rate of 20 V s^{-1} (Fig. 4), demonstrating the formation of the verdazyl radical at a lower potential of 0.66 V (vs. Ag/AgCl).

Repeated CV scans of **3** on a Pt electrode show an increase of the current for both the verdazyl radical and terthiophene peaks, indicating the formation of poly(radical) and poly(thiophene). The CV of poly(**3**)-Pt exhibits features characteristic of the verdazyl radical and terthiophene at 0.54 V and 1.14 V (vs. Ag/AgCl). A small positive shift ($\sim 120\text{ mV}$) of the oxidation potential of the

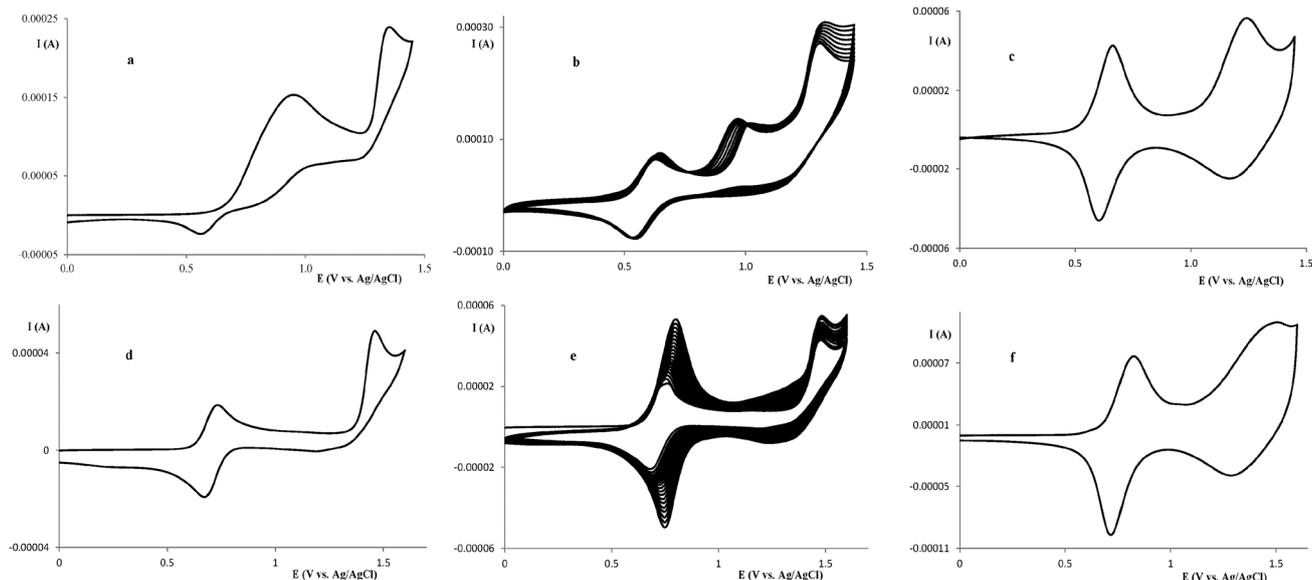


Fig. 2 Electrochemical polymerization of the verdazyl radical **3** and its precursor tetrazane **2**. (a) 1st CV scan of **2**, (b) electropolymerization of **2**, (c) CV of poly(**2**)-Pt, (d) 1st CV scan of **3**, (e) Electropolymerization of **3** and (f) CV of poly(**3**)-Pt.

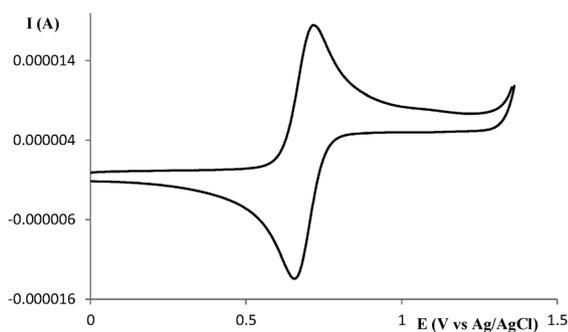


Fig. 3 Reversible mono-electronic cyclic voltammogram of the oxidation of the radical verdazyl **3** on a platinum electrode. Scan rate: 0.1 V s^{-1} .

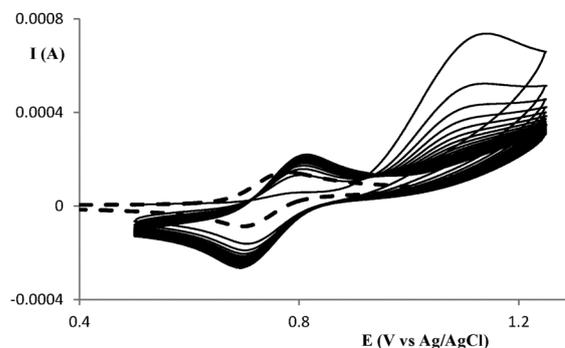
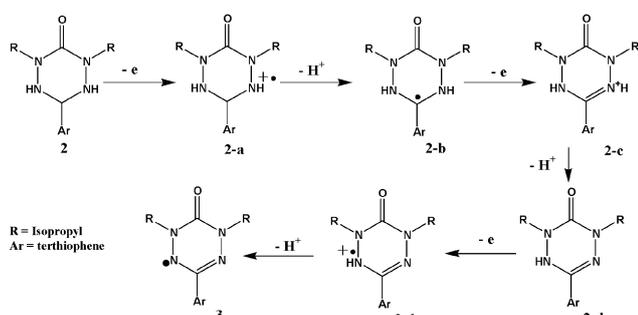


Fig. 4 Electrochemical oxidation of the heterocyclic tetrazane **2** on a platinum electrode at a scan rate of 20 V s^{-1} . Dashed line: CV of the verdazyl radical **3**.



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

verdazyl radical has been observed in poly(**3**)-Pt. The verdazyl radical is a withdrawing component, which positively shifts 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, where the oxidation potential is enhanced by 50–100 mV.²⁰

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 the doped polymer enhances the localization of the spin on the heterocyclic tetrazane, which explains the positive shift of the verdazyl radical in poly(**3**)-Pt.

Orbital molecular calculations are underway to estimate the spin density on the monomers and on the corresponding doped polymer.

The resulting polymer from the electrooxidation 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 electropolymerization of **3**. In the CV, poly(**3**)-Pt shows the same peak as poly(**2**)-Pt (Fig. 2f). To confirm that poly(**2**) and poly(**3**)-Pt have similar properties, infrared spectra were obtained for 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), is shifted by 50 cm^{-1} . This can be explained by the strong interaction (electro-donating behaviour) of the resulting π -conjugated polymer and the verdazyl radical. A similar behaviour was observed when the verdazyl radical was chelated to a redox active metal such as ruthenium (Ru).²¹ In this case, the $\nu(\text{CO})$ of the verdazyl radical was shifted by 25 cm^{-1} , due to the interaction of the $d\pi$ of Ru with the π^* orbital of the verdazyl radical. In our case, the interactions of the π -conjugated system of the polymer and the π^* of the radical are very strong, which explains the 50 cm^{-1} shift. Moreover, no significant shift was observed in the carbonyl of poly(1). Poly(2)-Pt and poly(3)-Pt were prepared by CV-cycling between 0 and 1.50 V vs. Ag/AgCl (oxidation followed by a reduction) of the corresponding monomers, 2 and 3. Therefore, poly(2)-Pt and poly(3)-Pt are in verdazyl radical forms. On the other hand, it was reported that the IR of the carbonyls for the cation and di-cation of the verdazyl are 1688 and 1706 cm^{-1} ,²² which confirms the presence of the verdazyl radical form in both the deposited polymers.

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

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