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Application of unusual on/off electrochemical properties of a molecularly imprinted polymer based on an EDOT–thiophene precursor for the detection of ephedrine

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ABSTRACT

Electrocopolymerization of bithiophene with a monomer combining an EDOT moiety with a thiophene ring on which a carboxylic group is attached at the internal β-position via a sulphide linkage (**1**) has been investigated with the aim of producing a molecularly imprinted polymer. Analysis of the electrochemical behaviour of the film grown under various conditions shows that potentiostatic electrocopolymerization leads to a polymer which can detect ephedrine via an unusual on/off switching of the electrochemical properties of the film in the presence of the target molecule.

1. Introduction

Preparation of molecularly imprinted polymers (MIPs) starts with the formation of a complex between functionalized monomers and a molecular template, followed by a cross-linking step producing a polymer network around the template [1]. Classical functional groups such as alcohols, carboxylic acid and amines are used to interact with the target template. The removal of this template creates binding cavities which retain the shape, size and orientation of the template. This type of polymer has attracted great attention due to their highly selective recognition properties, simple synthesis, high stability and low cost [2,3].

This approach has been extended in the field of conducting polymers by electrocopolymerization of acetic acid thiophene (as functionalized monomer) with ethylenedioxithiophene (EDOT) to produce a polymer that can detect atrazine [4–6]. This strategy (based on acetic acid thiophene as a functionalized monomer) has since been adopted to develop sensors for glucose [7], melphalan [8], taurine [9] and, more recently, adenine [10]. To reduce the oxidation potential of the acetic monomer and promote the formation of an ordered film, acetic acid terthiophene was used [11].

Here, we describe the preparation of a new electrocopolymerized MIP obtained from bithiophene (**BT**) and a monomer combining an EDOT moiety with a thiophene ring on which acetic acid is attached at the internal β-position via a sulphide linkage (**1**) (Scheme 1) [12]. The versatility of these β-substituted EDOT–thiophene precursors has been demonstrated by the facile electropolymerization of derivatives connected to fullerene [13], bipyridyl ligands and metal complexes [14], polyether chains [15], ferrocene [16,17], siderophores [18] and more recently gold nanoparticles [19].

Electrocopolymerization of **1** and **BT** has been investigated in potentiodynamic and potentiostatic conditions in the presence and absence of ephedrine, which can be used as a stimulant, appetite suppressant, concentration aid or medicinal drug for decongestion and hypotension. Analysis of the electrochemical behaviour of imprinted (MIP-**1**-**BT**) and non-imprinted (NIP-**1**-**BT**) polymers obtained with and without ephedrine, respectively, shows that potentiostatic copolymerization leads to a MIP-**1**-**BT** with the capacity to detect ephedrine via an unusual on/off switching of its electrochemical properties depending on whether ephedrine is present or not.

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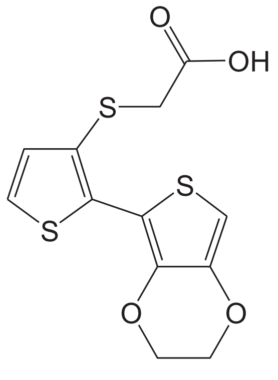

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Scheme 1. Structure of precursor.

2. Experimental section

2.1. Materials

Anhydrous acetonitrile (analytical grade), absolute ethanol and bithiophene were purchased from Sigma Aldrich. Tetrabutylamonium hexafluorophosphate (TBHP) was purchased from Fluka. 2-(3,4-Ethylenedioxythienyl)-3-(carboxymethylsulfanyl)thiophene **1** was prepared according to the literature [13].

2.2. Preparation of modified electrodes

A solution of acetonitrile containing 0.1 M TBHP as supporting electrolyte with 0.01 M **1** and 0.005 M **BT** was used for electrosynthesis of NIP-**1**-**BT**. For MIP-**1**-**BT**, 0.1 M TBHP, 0.01 M **1**, 0.005 M **BT** and 0.01 M ephedrine were used. Monomer **1** and ephedrine were allowed to combine for 10 min. Potentiodynamic and potentiostatic data were acquired using a Biologic VSP-300 electrochemical potentiostat (Biologic Instruments, France). A three-electrode system with an Au working electrode (diameter 1.6 mm), a platinum counter electrode and a SCE reference electrode were used. Potentiodynamic electrocopolymerizations were carried out between −0.2 and 1.3 V vs SCE at 100 mV/s. Films were also grown under potentiostatic conditions, at 1.3 V vs SCE with a charge corresponding to 1 mC·cm^{-2}. All cyclic voltammograms (CV) of the modified electrodes were recorded in acetonitrile with only 0.1 M TBHP as electrolyte support before and after washing, and after rebinding with the target.

To remove ephedrine, the modified MIP-**1**-**BT** electrode was immersed in ethanol solution for 24 h without other treatments. The same protocol was used for NIP-**1**-**BT**-modified electrodes to evaluate the impact of ethanol on the electrochemical properties of the polymers. To rebind ephedrine, the modified electrode was immersed in aqueous solution with 0.01 M ephedrine for 1 to 15 min. The second washing was carried out in ethanol for 3 h without other treatments and the second rebinding took 1 min.

3. Results and discussion

Repetitive potential scans on the monomers **1**–**BT** (ratio 2/1) mixture show a regular increase in the intensity of the reversible redox system, with anodic and cathodic peaks at $E_{pa} = 0.60$ V and $E_{pc} = 0.46$ V respectively, characteristic of formation of the polymer NIP-**1**-**BT** on the electrode surface (Fig. 1A). A difference is observed between the current intensities for each CV, indicating an efficient electrocopolymerization process [12]. The CV of NIP-**1**-**BT** in a free monomer solution shows a reversible redox system (inset to Fig. 1A). In detail, the CV of NIP-**1**-**BT** exhibits three successive oxidation waves peaking at 0.30, 0.53 and 0.94 V, which can be attributed to polymer

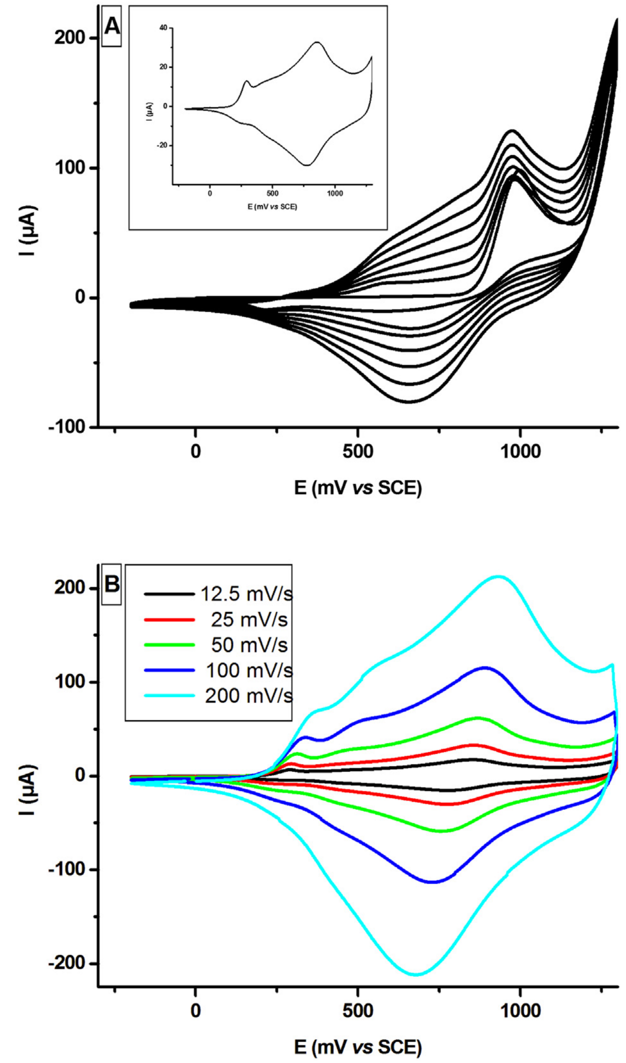

Fig. 1. A: Repetitive CVs of **1**-**BT** in 0.1 M TBHP/CH$_3$CN, v = 100 mV/s; inset: CV of NIP-**1**-**BT** in 0.1 M TBHP/CH$_3$CN, v = 25 mV/s. B: CVs of NIP-**1**-**BT** in 0.1 M TBHP/CH$_3$CN, v = 12.5–200 mV/s.

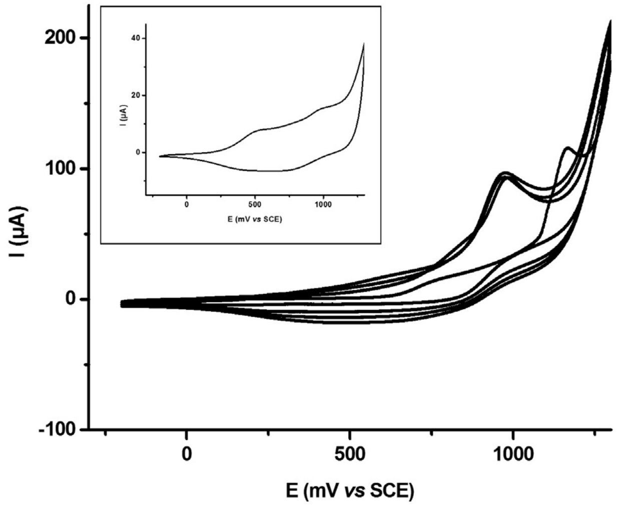

Fig. 2. Repetitive CVs of **1**-**BT** in 0.1 M TBHP/CH$_3$CN and 0.001 M ephedrine, v = 100 mV/s. Inset: CV of MIP-**1**-**BT** in 0.1 M TBHP/CH$_3$CN, v = 25 mV/s.