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Electrochemical synthesis of copolymers based on 2-(anthracen-9-yl) thiophene: A facile and efficient route to a series of multicolor electrochromic polymers

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ABSTRACT

A monomer named 2-(Anthracen-9-yl)thiophene (An-Th) has been synthesized via Stille coupling reaction, while its homopolymer is difficult to prepare on the conducting electrode via electrochemical methods. However, it can be a good comonomer to obtain copolymers with other monomers such as thiophene (Th), selenophone (SePh), 3-methylthiophene (MeTh) and 3,4-ethylenethiophene (EDOT) via electrochemical copolymerization. The structures of the prepared copolymers are characterized via FTIR and XPS analysis. In addition, the spectroelectrochemical and electrochromic properties of these copolymers are also investigated. The derived copolymers present multicolor electrochromism, which can be tuned by the applied comonomer and polymerization solvent. Moreover, the copolymers have reasonable switching response and stability. All of these indicate that the synthesized Th-An can be applied as a good comonomer for preparation of electrochromic copolymers.

1. Introduction

Conjugated polymers (CPs) are promising for a variety of applications on span sensors, photovoltaic cells, electrochromic devices [1]. Especially, CPs show significant advantages over their inorganic analogs in electrochromic field, namely multiple colors and fine-tuning of color through modification of chemical structure, high coloration efficiency, fast switching response and enhanced stability [2–4]. The electrochromic mechanism of CPs is that, upon oxidation, CPs are "doped" with counter ions and their π-electron band structure become delocalized, then the optical properties change [5–7].

It is well known that the intrinsic optical properties of CPs are determined by the energy gap (Eg), which can be tuned by structural modifications [8,9]. Two routes have been applied to tune the Eg: (1) design and synthesis of novel monomers for polymerization; (2) copolymerization with different monomers [10]. The main advantage of first route is that the synthesized polymers display designed and prescient properties [11–14]. For example, long alkyl side chain incorporation can improve the solubility of prepared polymers in organic solvent, and donor-acceptor type materials can always possess two absorption peaks in the neutral state, which is necessary for displaying green color [15–19].

In comparison with the first approach, copolymerization is a facile and promising way to obtain desired electrochromic polymers [20–22]. The strategy enables the fine-tuning of the neutral-state hue of several conducting polymers, without further synthetic effort at the monomer level [23]. To attach successful copolymerization, similar and low oxidation potentials of the monomers are necessary [24,25]. On the other hand, boron trifluoride etherate (BFEE) has been proved as a good solvent-electrolyte for electrochemical copolymerization even for thiophene and selenophene, which possesses high oxidation potential in general organic solvents or aqueous solution [26–29]. Many copolymers prepared in BFEE have performed fascinating electrochromic properties, especially based on anthracene and thiophenes [30–32].

In this work, a monomer named 2-(anthracen-9-yl)thiophene (An-Th) has been synthesized by Stille coupling reaction. And it is difficult to obtain its homopolymer via electrochemical

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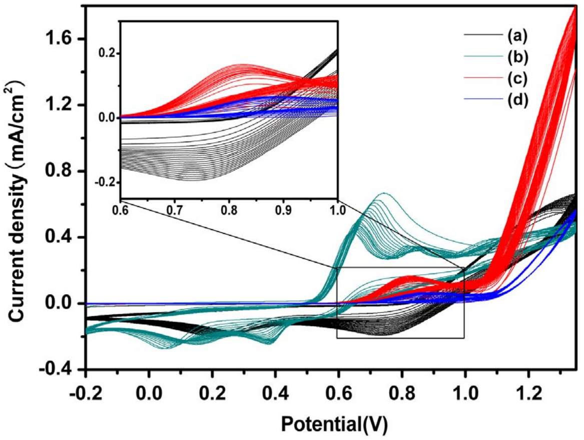

Fig. 1. Cyclic voltammogram curves of 2 mM An-Th in (a) BFEE, (b) BFEE+20% CF_3COOH, (c) 0.2 M $LiClO_4$/ACN, (d) 0.2 M $LiClO_4$/PC solution at a scan rate of 100 mV/s.

polymerization in different solvents, or by the method of an inside assembled solid-state device [33,34]. However, it can be a good choice as a co-monomer to copolymerize with thiophene (Th), 3-methylthiophene (MeTh), 3,4-ethylenedioxythiophene (EDOT) and selenophone (SePh) in BFEE. The derived copolymers present excellent electrochromic properties, which can be tuned by the polymerization conditions such as polymerization solvent and feed ratio.

2. Experimental

2.1. Materials

All chemicals are purchased from Aldrich and J&K Scientific LTD. Indium-tin-oxide-coated (ITO) glass (8–9 Ω/□) is a product of Zhuhai Kaivo Electronic Components Co., Ltd. THF is dried and distilled over benzophenone-sodium under nitrogen before use. 2-Tributylstannyl-thiophene is synthesized by previous literature [35].

2.2. Equipments

^{1}HNMR spectra and mass spectrometry (MS) analysis of the synthesized product are performed on a Bruker AVANCE III 500 MHz instrument (Bruker, Switzerland) and A GCT Premier spectrometer (Waters, USA), respectively. FT-IR spectra are recorded on a Nicolet IS10 FTIR spectrometer. XPS spectra are recorded by using a Thermo Fisher Scientific K-Alpha1063. Electrochemical polymerization and measurements are performed on a CHI660D working station. UV–vis spectra are recorded on a Shimadzu UV-1800 UV–vis spectrophotometer. Optical images are obtained from a canon EOS 500D digital camera.

2.3. Synthesis of 2-(anthracen-9-yl)thiophene (An-Th)

2-Tributylstannyl-thiophene (3.6 g, 9.1 mmol), 9-bromo-anthracene (2.13 g, 8.3 mmol) and $Pd(PPh_3)_2Cl_2$ (200 mg, 0.26 mmol) are dissolved in DMF (100 mL), and the solution is refluxed for 24 h under nitrogen. After purified by column chromatography (DCM: Hexane 1:2), the product is a yellowish-green powder (1.2 g, 52%): ^{1}HNMR ($CDCl_3$) 8.51 (1H), 8.04 (2H), 7.84 (2H), 7.62 (1H), 7.45 (4H), 7.30 (1H), 7.17 (1H) ^{13}C NMR ($CDCl_3$) δ_c 138.8, 131.9, 131.2, 129.4, 128.8, 128.3, 127.9, 127.2, 126.7, 125.9, 125.3. FTIR (KBr, cm^{-1}) 3052, 1578, 1441, 1302, 1013, 831, 744, 683. HRMS m/z calcd for $C_{18}H_{12}S$ 260.3538 found 260.3246.

2.4. Fabrication of assembled solid device

An assembled solid device has been constructed as the previous literature [34]. The gel electrolyte is prepared as described in reference [36]. A 2 wt% ratio of An-Th is added into the casting solution for gel electrolyte. With the increasing viscosity of the solution, the solution is spin-cast onto the ITO substrate, and another ITO electrode is used as counter electrode. Potentiostatic 2.4 V is applied to complete the polymerization of An-Th in the solid device.

2.5. Preparation of copolymers based on An-Th and Th, SePh, MeTh, and EDOT

Electrochemical polymerization is performed in a one-compartment cell with ITO glass as the working electrode. The typical electrolyte for electrochemical synthesis is BFEE containing 2 mM An-Th and 8 mM Th, SePh, 3-methylthiophene (MeTh), or EDOT, respectively. And the corresponding copolymers marked as **P1**, **P2**, **P3**, and **P4** are prepared by potentiostatic 1.35 V with the charge density of 75 mC/cm^2. Additionally, the copolymers marked as **P5** and **P6** are prepared with the feed ratio of An-Th/EDOT at 1/4 in 0.2 M $LiClO_4$/ACN and 0.2 M $LiClO_4$/PC, respectively. All electrochemical polymerization and measurements are performed under nitrogen atmosphere. The spectroelectrochemical tests are taken in 0.2 M $LiClO_4$/PC.

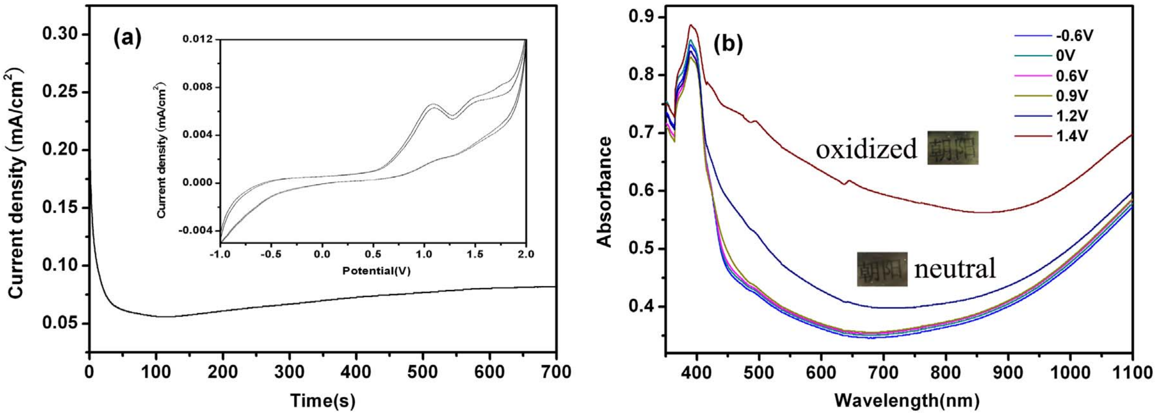

Fig. 2. (a) Chronoamperometric response of An-Th electropolymerization in gel electrolyte containing 2 wt% An-Th at 2.4 V, (b) spectroelectrochemical spectra and optical images of the device after polymerization as a function of applied potential. Inset: CV curves of the assembled solid device after polymerization. (For interpretation of the references to color in this figure, the reader is referred to the web version of this article).