



Novel electrochromic copolymers based on thiophene-anthracene derivatives via electrochemical polymerization in boron trifluoride diethyl etherate



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ABSTRACT

Two monomers named 5-(10-(thiophen-2-yl)anthracen-9-yl)-2,2'-bithiophene (TABT) and 9,10-di([2,2'-bithiophen]-5-yl)anthracene (DBTA) were synthesized via Stille coupling reaction. Electrochemical polymerization for preparation of their homopolymers was failed in boron trifluoride diethyl etherate (BFEE) and acetonitrile (ACN) systems. However, the copolymers of these compounds with thiophene (Th) and 3,4-ethylenedioxythiophene (EDOT) were synthesized and coated onto indium tin oxide (ITO) surface via low-potential electrochemical polymerization in BFEE. Structural and morphological characterizations of these prepared copolymers were taken by FT-IR, X-ray Photoelectron Spectroscopy (XPS) and Scanning Electron Microscopy (SEM). Additionally, spectroelectrochemical and electrochromic properties of these copolymers were also investigated, red-shift effect can be observed on the absorption spectra of the neutral copolymers via substituting EDOT for thiophene as the comonomers and the increase of anthracene content in the copolymer backbone. Switching and electrochemical measurements indicate the prepared copolymers present fast switching rate and good stability.

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1. Introduction

Conjugated polymers have been widely used in organic electronics such as organic solar cells (OSCs) [1–3], organic field-effect transistors (OFETs) [4], organic light-emitting diodes (OLEDs) [5], supercapacitors [6], and electrochromics [7,8] during last decades. Among these applications, electrochromic has been extensively investigated in smart windows [9], flexible displays [10], military camouflage [11], etc. In comparison with their inorganic counterparts, conjugated polymers present the superior advantages in electrochromic field toward high color efficiency, fast switching rate, good stability, and ease of structural modification [12,13]. More importantly, many polymers can exhibit more than two redox states and display multiple colors [14–16].

Nowadays, a large amount of efforts have been invested into the designing and synthesizing novel electrochromic conjugated polymers (ECPs) for achieving excellent electrochromic properties, since the

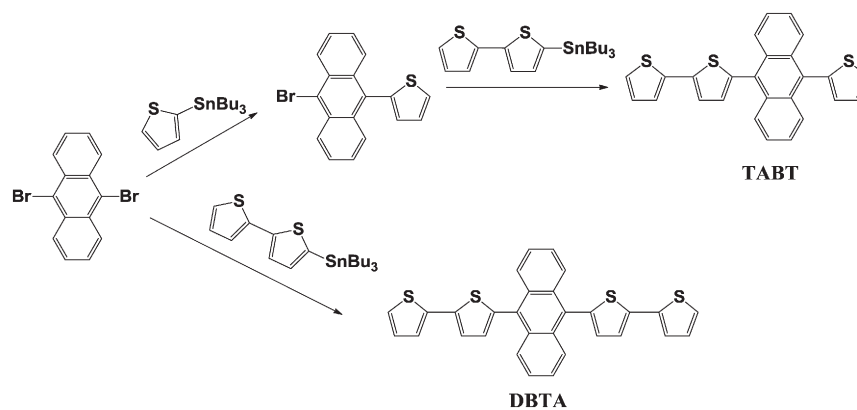
band gap and optical absorption of the neutral polymers can be greatly tuned through the rational structure design and modification [17–20]. For example, combination of electron-deficient and electron-rich moieties in one polymer backbone can induce dual-absorption bands and broad absorption for generating green and black electrochromics [21–26]. In addition, the introduction of other π -conjugated units such as benzene, carbazole, anthracene, etc. into the polythiophene mainchain will certainly tune the band gap and optical absorption [27–31].

Besides the chemical synthesis of novel ECPs, electrochemical copolymerization supplies another promising and facile method to obtain ECPs with fascinating properties [32]. Especially, the random alternation of different moieties connected in the polymer backbone always leads to multielectrochromic properties [25,33]. Therefore, many researches have investigated the electrochemical copolymerization between two commercial available monomers such as EDOT, thiophene or pyrrole [34,35]. To attached successful copolymerization, the applied monomers should possess close and low onset oxidation potentials [36]. Recently, boron trifluoride diethyl etherate (BFEE) has been used as an electrolyte-solvent system for preparation of heterocyclic polymers, which can considerable lower the oxidation potential of the monomers [37,38]. High quality conjugated polymer films have been prepared in BFEE because of the low polymerization potential [39,40]. On the other hand, electrochemical copolymerization can

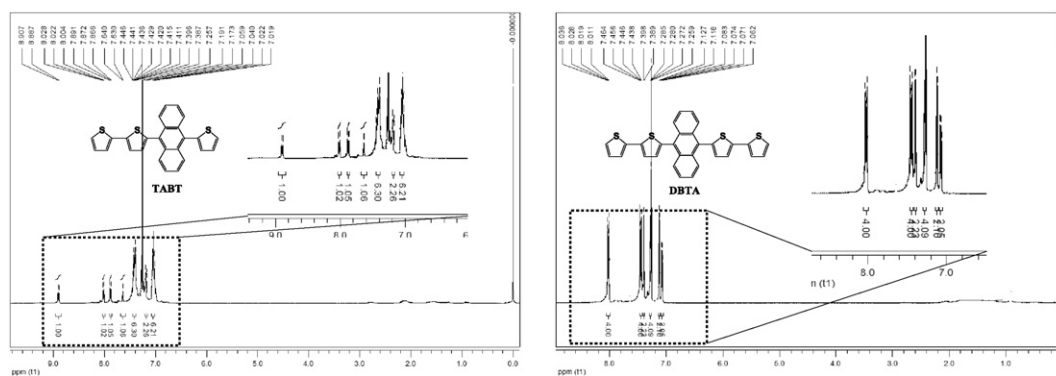
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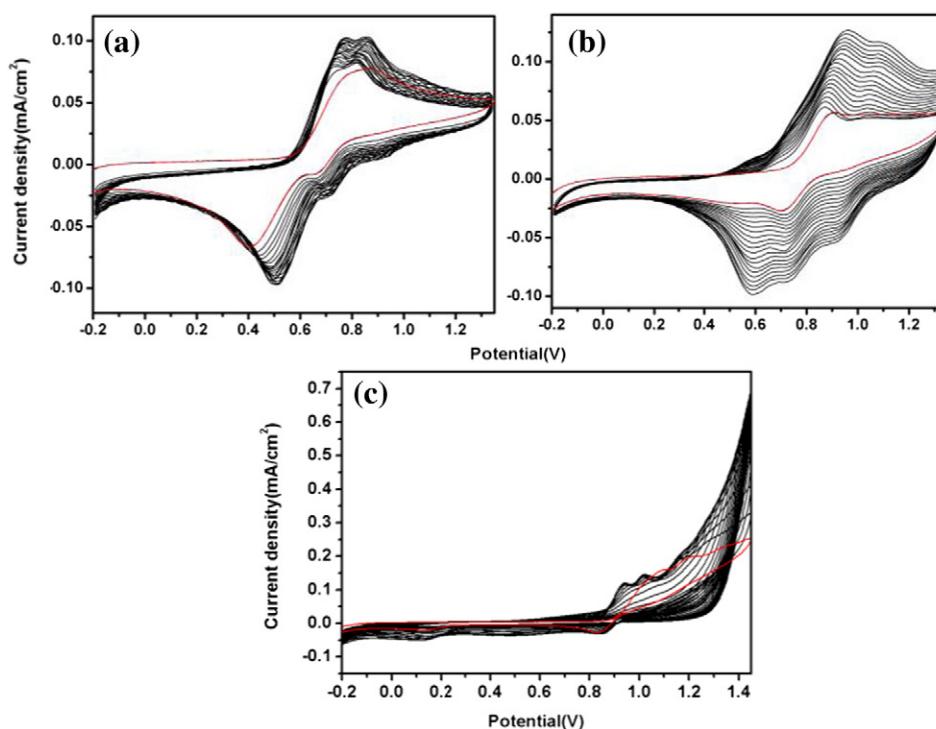


Scheme 1. Synthesis routes of the monomer TABT and DBTA.

Fig. 1. ^1H NMR spectra of TABT and DBTA.

also be successfully carried out in BFEE system for many monomers, which cannot be used as comonomers in acetonitrile (ACN) or aqueous systems.

Anthracene is a promising block for building high-quality conjugated polymers, and many researches have been focused on the synthesis of new polymers based on anthracene with good properties [41,42].

Fig. 2. Cyclic voltammograms of 2 mM TABT in (a) BFEE, (c) 0.2 M $\text{LiClO}_4/\text{ACN}$, and (b) 2 mM DBTA in BFEE at a scanning rate of 100 mV/s (red line: CV curves for the first cycle sweep).

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