



# Novel multielectrochromic and fast-switching copolymers based on methoxybenzene and thiophene via electrochemical copolymerization in boron trifluoride diethyl etherate

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## ABSTRACT

A series of conducting copolymers based on methoxybenzene and thiophene are prepared via direct anodic oxidation of the mixtures of methoxybenzene and thiophene in boron trifluoride diethyl etherate (BFEE). Feed ratio of methoxybenzene/thiophene plays great effect on the electrochromic performance of the copolymers, which can exhibit multicolor and tunable electrochromism. The copolymer prepared with methoxybenzene/thiophene feed ratio of 1/8 exhibits excellent electrochromic properties which presents golden color, yellow green, green blue and dark blue under various applied potentials. The optical contrast and response time (monitored at the absorption peak of 474 nm) are 15.1% and 0.6s, respectively. The corresponding coloration efficiency is calculated as 307 cm<sup>2</sup>/C. In addition, the copolymer shows decent optical stability which only loses optical contrast of 1.4% at 474 nm after 200 steps. All of these indicate that high-performance electrochromic materials can be prepared via simply commercial available monomers such as thiophene and methoxybenzene.

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## 1. Introduction

During the past decades, electrochromism has attracted a great deal of interest because of the broad applications on smart windows [1–4], optical displays [5–7], adaptive camouflage [8–10], etc. Electrochromic conducting polymers have been envisioned as the favored electrochromics because of their superior properties such as fine-tuning of the band gap (and the color) through chemical structure [11–17], outstanding coloration efficiency [18–21], fast-switching response [22–24], and high stability [25–27].

Among electrochromic conducting polymers, polythiophene and its derivatives have occupied the prime position due to their numerous advantages in electrochromic materials [28–32]. However, most of them can not present more than two color change. One important desired goal of electrochromics is that a single electrochromic electrode can exhibit colors as much as possible

[33,34]. It is obvious that one conducting polymer has more than two chromophores in the polymer chain that could possibly induce multicolor electrochromism under applying various potentials. Compared with the laborious chemical synthesis approach, copolymerization supplies as a facile way to combine two different units into single polymer [35,36]. Some literature have reported about the electrochemical copolymerization about 3,4-ethylenedioxythiophene (EDOT), and the derived copolymers exhibit desired multicolor electrochromism, fast switching behaviors and good stability [37–40]. While preparation of high-performance electrochromic materials via commercially available and low-cost raw materials are still of particular interest in industrial field [41–43].

Usually, commercial monomers for electrochemical polymerization possess high oxidation potential due to their small conjugated backbone, which may lead to poor polymer film or even unsuccessful polymerization. To obtain high-performance copolymers via electrocopolymerization based on commercial monomers, the crucial factor is to lower the oxidation potential. According to previous reported literature, boron trifluoride diethyl etherate (BFEE) is an electrolyte-solvent system for polymerization of monomers, its main characteristic is considerable lowering of

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onset potential which is important for successful electro-polymerization [44]. High-quality polythiophene films have been prepared in BFEE [45–47]. However, there is still rare report about the electrochemical copolymerization in BFEE based on two easily accessible or commercially available monomers.

In this work, a series of copolymers based on very simple and commercially available thiophene and methoxybenzene are successfully prepared in BFEE. To the best of our knowledge, such copolymer formations and their electrochromic properties have not been reported to date. The resultant copolymers present desired multicolor electrochromism, fast switching ability, and decent stability. This copolymerization strategy may endeavor a new door in order to obtain high-quality electrochromic materials via simple and commercially available monomers.

## 2. Experimental

### 2.1. Materials

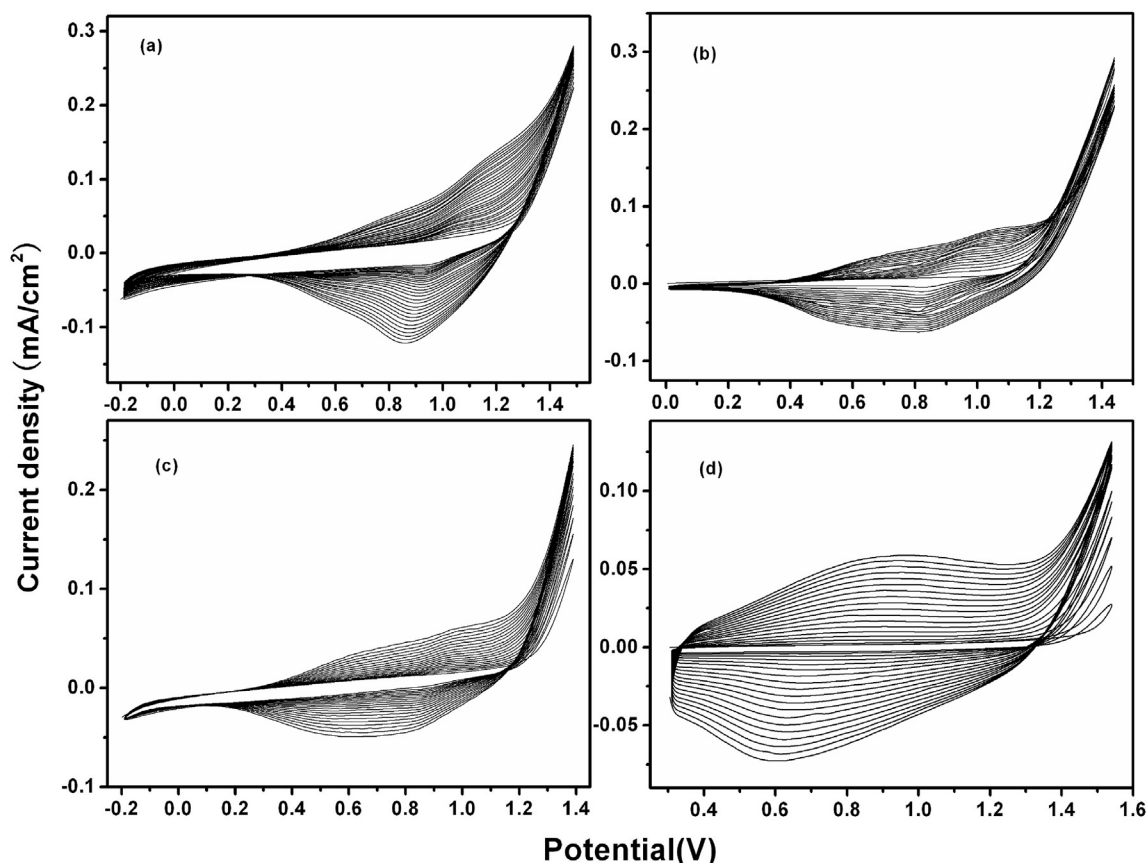
Thiophene, methoxybenzene, BFEE, lithium perchlorate ( $\text{LiClO}_4$ ), and propylene carbonate (PC), are purchased from Chemical Reagent Tianjin institute, and are of analytical grade. Thiophene, methoxybenzene and BFEE are distilled before use, other chemicals are used as received. Indium tin oxide (ITO) coated glass ( $8\text{--}9\Omega/\square$ ) is a product of Zhuhai Kaivo Electronic Components Co., Ltd. Stainless steel sheet (wire) and Ag/AgCl electrode are self-produced. Before usage, ITO, Stainless steel sheet (wire) are rinsed in deionized water, ethanol, acetone and deionized water successively under ultrasonic. The Ag/AgCl reference electrode is calibrated against the ferrocene/ferrocenium redox couple.

### 2.2. Instruments

Electrochemical polymerization and measurements are performed on a CHI660D working station. FT-IR spectra are recorded on a Nicolet IS10 FTIR spectrometer with KBr pellets. XPS spectra are measured by using a Thermo Fisher Scientific K-Alpha1063. The optical images of the copolymer films are taken by a Canon EOS 500D digital camera. UV–vis spectra are recorded on a Shimadzu UV-1800 UV–vis–NIR spectrophotometer.

### 2.3. Preparations of copolymers with methoxybenzene and thiophene

ITO glass, stainless steel sheet and Ag/AgCl are used as working electrode, counter electrode and reference electrode, respectively. Electrochemical copolymerization is carried out in pure BFEE containing methoxybenzene and thiophene with the feed ratio at 1/2, 1/4 and 1/8 as the comonomers (corresponding copolymers are marked as P(MOB-Th-1), P(MOB-Th-2) and P(MOB-Th-3)), the concentration of thiophene in pure BFEE is fixed as 20 mM. For comparison, the homopolymers of methoxybenzene and thiophene are prepared under the same polymerization parameters. For structural, electrochemical and spectroelectrochemical characterizations, poly(methoxybenzene), poly(thiophene) and copolymer films are potentiostatically deposited at 1.35 V, 1.55 V and 1.30 V. After polymerization, the obtained films are rinsed in pure PC for several times to remove the residual monomers/oligomers and BFEE. The electrochemical and spectroelectrochemical measurements are performed in 0.2M  $\text{LiClO}_4/\text{PC}$  solution under  $\text{N}_2$  atmosphere.



**Fig. 1.** Cyclic voltammograms of: (a) 20 mM methoxybenzene, (b) 10 mM methoxybenzene + 20 mM thiophene (feed ratio at 1/2), (c) 2.5 mM methoxybenzene + 20 mM thiophene (feed ratio at 1/8), and (d) 20 mM thiophene in pure BFEE at a scan rate of 100 mV/s on ITO working electrode.

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