



# Electrochemical synthesis and capacitance properties of a novel poly(3,4-ethylenedioxythiophene bis-substituted bithiophene) electrode material



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## ABSTRACT

A novel EDOT-bithiophene-EDOT based comonomer, 5,5'-bis(2,3-dihydrothieno[3,4-b][1,4]dioxin-5-yl)-2,2'-bithiophene (BEDOT-BT), was synthesized, and further, it was electrodeposited into PBEDOT-BT on platinum electrode as an active electrode material for supercapacitor. As-formed PBEDOT-BT film was characterized by FTIR, SEM and thermal analysis. The electrochemical performances of the PEDOT-BT electrode with good thermal stability were also investigated by cyclic voltammetry, galvanostatic charge–discharge and electrochemical impedance spectroscopy techniques. The electrochemical results showed that PBEDOT-BT electrode afforded a specific capacitance of 171 F g<sup>-1</sup> at a current density of 1 A g<sup>-1</sup> and good cycling stability in ACN-Bu<sub>4</sub>NPF<sub>6</sub> electrolyte solution. The specific energy of the PEDOT-BT electrode reached 23.76 Wh/kg at a specific power of 0.49 kW/kg. These results indicated that the PBEDOT-BT is a promising electrode material for supercapacitor applications.

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## 1. Introduction

Supercapacitor has recently attracted considerable attention because of its fast energy delivery, short charging time, high power capability, long cycle life, and environment-friendly features [1–3]. Currently, the studied electrode materials for the supercapacitor mainly are carbon materials, metal oxides, and conducting polymers. Carbon materials as supercapacitor electrode are attractive materials because of their high electronic conductivity and large specific surface area [4], but with limited capacitance values (15–200 F/g) [5]. Among the available metal oxides, RuO<sub>2</sub> shows the best performance [6]. But its high cost and toxic nature significantly limit commercial application [7]. Alternative the cheaper metal oxides NiO, cannot be used at potential windows above 0.6 V; furthermore, most of them are poorly conductive [8]. Conducting polymers (CPs), such as polypyrrole (PPy), polyaniline (PANI) and polythiophene (PTh) and their derivatives [9], have been considered as the promising candidates because of their high theoretical specific capacitances, low cost, facile synthesis, fast charge/discharge electron-transfer kinetics, and high conductivity

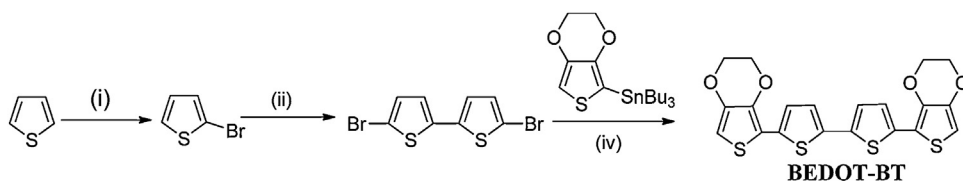
in the doped state [10]. However, the practical specific capacitances obtained in the experiments are lower relative to their theoretical specific capacitances and the cyclic stability is poor. In order to improve the performance of CPs, several approaches have been explored, such as the micro-structure and morphology of CPs [11], composites with carbon and transition metal oxides [12,13], and novel electrolytes with wide electrochemical windows [14].

Among CPs, poly(3,4-ethylenedioxythiophene) (PEDOT) is considered to be a prospective electrode material due to its high conductivity (up to 500 S/cm.), fast charge/discharge ability, wide potential window, and good environmental stability [14–17]. Moreover, PEDOT has its high ability to store charge, which plays an important role in supercapacitors [18–20]. In addition, the distinctive feature of PEDOT with positive (p-) and negative (n-) doping privilege has made it become the most common used electrode material in many supercapacitors [12,21]. However, the low specific capacitance of PEDOT compared with those of other CPs suggests the necessity of exploring new alternatives [22]. The molecular engineering for synthesizing new PEDOT derivative or modifying the structure of EDOT unit is extremely urgent to achieve better supercapacitive performances. Encouragingly, Güllü and collaborators recently reported the supercapacitive performance of a series of PEDOT derivatives [23], which showed better supercapacitive performances than PEDOT and can be explored for supercapacitors applications. However, in contrast to the direct

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(i)  $\text{CHCl}_3$ :  $\text{CH}_3\text{COOH}$  = 1:1, NBS; (ii)  $\text{Pd}(\text{OAc})_2$  (3 mol%),  $\text{AgNO}_3$ , KF, DMSO, 60 °C, 24 h; (iii)  $\text{Pd}(\text{PPh}_3)_4$ , DMF, 24 h, 100 °C

**Scheme 1.** The synthetic route for BEDOT-BT.

modification of the EDOT units, the research to the capacitance performance of the comonomers based on the combination of EDOT moieties with other functional compounds is insufficient. Recently, bis(3,4-ethylenedioxythiophene)-(4,4'-dinyonyl-2,2'-bithiazole) comonomer [24] and 6,6'-bis(ethylene-3,4-dioxythien-2-yl)-N,N'-dialkylisindigo comonomers [25] were synthesized and the corresponding polymers were incorporated as an electroactive material into electrochemical supercapacitors. These PEDOT based copolymers showed moderate capacitance values and excellent stability.

Herein, a novel 3,4-ethylenedioxythiophene bis-substituted bithiophene comonomer was synthesized according to the synthetic route given in Scheme 1, namely, 5,5'-bis(2,3-dihydrothieno[3,4-b][1,4]dioxin-5-yl)-2,2'-bithiophene (BEDOT-BT). The comonomer has several advantages as below. First, the bithiophene-bridged copolymers expand the choice of optoelectronic materials due to the formation of alternating  $\pi$ -conjugated chain [26]. Second, the conducting polymer based BEDOT-BT (PBEDOT-BT) will further possibly improve the properties of PEDOT because PTh has higher specific capacitance compared to PEDOT [22]. Third, the external EDOT units will not only function as donor groups, increasing the HOMO level of polymer [27], but also lower the oxidation potential, avoiding any side reactions during the electrochemical polymerization [28]. Thus, it is very significant and necessary to study the synthesis and characterization of PBEDOT-BT. In this text, the capacitive behaviors and performances of as-prepared PBEDOT-BT were tested by cyclic voltammetry, galvanostatic charge-discharge and electrochemical impedance spectroscopy techniques, which were compared with those of PEDOT. Besides, the structural characterization and other properties of the as-formed PBEDOT-BT film, such as morphology and thermal stability, were also investigated in detail.

## 2. Experimental

### 2.1. Materials

All materials were reagent grade and were used directly without further purification unless otherwise noted. 3,4-Ethylenedioxythiophene (EDOT), thiophene, N-bromosuccinimide (NBS), tetrakis(triphenylphosphine)palladium(0) ( $\text{Pd}(\text{PPh}_3)_4$ ), *n*-butyl lithium (*n*-BuLi), tributyltin chloride (*n*-Bu<sub>3</sub>SnCl), silver nitrate ( $\text{AgNO}_3$ ), and potassium fluoride (KF) were purchased from Energy Chemical (Shanghai, China) and used as received. Acetonitrile (ACN), dichloromethane (DCM), chloroform ( $\text{CHCl}_3$ ), tetrahydrofuran (THF), N,N-dimethylformamide (DMF), diethyl ether ( $\text{Et}_2\text{O}$ ), and dimethyl sulfoxide (DMSO) were purchased from Beijing Chemical Plant, China and used after reflux distillation. Palladium acetate ( $\text{Pd}(\text{C}_2\text{H}_3\text{O}_2)_2$ ) was purchased from Sinopharm Chemical Reagent (Shanghai, China). Tetrabutylammonium hexafluorophosphate ( $\text{Bu}_4\text{NPF}_6$ , 98%; Acros Organics) was dried under vacuum at 60 °C for 24 h before use.

### 2.2. Characterization

Melting points were measured with a WRS-1B melting point apparatus.  $^1\text{H}$  and  $^{13}\text{C}$ NMR spectra were recorded on a Bruker AV-400NMR spectrometer at room temperature and chemical shifts were given relative to tetramethylsilane as the internal standard. Infrared spectra were recorded with a Bruker Vertex 70 Fourier transform infrared (FT-IR) spectrometer with samples in KBr pellets. Thermogravimetric analysis (TGA) was performed with a Pyris Diamond TG/DTA thermal analyzer (Perkin-Elmer) under a nitrogen stream from 290 to 1100 K at a heating rate of 10 K min<sup>-1</sup>. Scanning electron microscope (SEM) measurements were carried out by using scanning electron microscope (JSM-5600, JEOL) with the polymer deposited on the indium-tin-oxide (ITO) coated glass.

All the electrochemical experiments were carried out using a CHI 660B potentiostat/galvanostat (Shanghai Chenhua Instrumental Co., Ltd., China) at room temperature, in a one-compartment cell with a three-electrode configuration. With the Ag/AgCl wire (ferrocene  $E_{1/2}$  = 0.07 V) as the reference electrode and two Pt wires (1.0 mm diameter) as counter and working electrodes, respectively. The areas of the counter and working electrodes immersed into the electrolyte were 0.1 cm<sup>2</sup>, respectively. The capacitance performances of the PEDOT-BT electrode was evaluated by using cyclic voltammetry (CV) measurement, galvanostatic charge/discharge cycling and electrochemical impedance spectroscopy in 5 mL ACN containing 0.1 M  $\text{Bu}_4\text{NPF}_6$  solution.

### 2.3. 2.3. Synthesis

#### 2.3.1. Synthesis of 2-bromothiophene

The 2-bromothiophene was synthesized according to literature procedures [29]. Yield: 59%, yellowish transparent liquid.  $^1\text{H}$  NMR (400 MHz,  $\text{CDCl}_3$ ,  $\delta$ ): 7.24 (d,  $J$  = 5.6 Hz, 1H), 7.06 (d,  $J$  = 3.2 Hz, 1H), 6.88 (d,  $J$  = 5.2 Hz, 1H).  $^{13}\text{C}$  NMR (100 MHz,  $\text{CDCl}_3$ ,  $\delta$ ): 131.3, 129.6, 129.5, 111.5. IR (ATR)  $\nu/\text{cm}^{-1}$ : 3095, 2924 (C-H stretching), 1517, 1487, 1409 (C=C stretching), 975 (Br sensitive vibrational modes), 840, 819, 785 (C-H out-of-plane bending), 688 (C-S stretching).

#### 2.3.2. Synthesis of 5,5'-Dibromo-2,2'-bithiophene

To a 50 mL two-neck round bottom flask equipped with a magnetic stirring bar, 2-bromothiophene (2 g, 12.27 mmol),  $\text{Pd}(\text{OAc})_2$  (82 mg, 0.37 mmol),  $\text{AgNO}_3$  (8.34 g, 49.08 mmol), KF (2.84 g, 49.08 mmol), and DMSO (25 mL) were added successively, the resulting mixture was stirred at 60 °C for 24 h [30]. After cooling to the room temperature, the reaction mixture was filtered through a Celite pad to remove a solid residue and the cake was washed repeatedly with diethyl ether. The filtrate was washed with water twice (50 mL  $\times$  2) and the organic layer was dried over anhydrous magnesium sulfate and concentrated under reduced pressure to leave a crude solid, which was purified by column chromatography on silica gel to afford 1.18 g of the product. Yield: 60%, light yellow solid, melting point 144–145 °C (literature melting point 146–146.5 °C [31]).  $^1\text{H}$  NMR (400 MHz,  $\text{CDCl}_3$ ,  $\delta$ ): 6.84 (d,

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