Electrochimica Acta 151 (2015) 477–488

Contents lists available at ScienceDirect

Electrochimica Acta

journal homepage: www.elsevier.com/locate/electacta

Alkyl functionalized bithiophene end-capped with 3,4-ethylenedioxythiophene units: synthesis, electropolymerization and the capacitive properties of their polymers

Daize Mo [a,1], Weiqiang Zhou [a,1], Xiumei Ma [a], Jingkun Xu [a,*], Fengxing Jiang [b], Danhua Zhu [a]

[a] Jiangxi Key Laboratory of Organic Chemistry, Jiangxi Science and Technology Normal University, Nanchang 330013, PR China
[b] Department of Physics, Jiangxi Science and Technology Normal University, Nanchang 330013, PR China

ARTICLE INFO

Article history:
Received 14 October 2014
Accepted 5 November 2014
Available online 7 November 2014

Keywords:
Supercapacitors
Poly(3,4-ethylenedioxythiophene)
Electrodeposition
Electrically conducting polymers
Galvanostatic charge/discharge

ABSTRACT

Here, three new 3,4-ethylenedioxythiophene bis-substituted bithiophene containing alkyl side chain groups (alkyl = hexyl, octyl, and dodecyl) comonomers, 5,5′-(4,4′-dihexyl-[2,2′-bithiophene]-5,5′-diyl) bis(2,3-dihydrothieno[3,4-b][1,4]dioxine (BEDOT-BT-BH), 5,5′-(4,4′-dioctyl-[2,2′-bithiophene]-5,5′-diyl) bis(2,3-dihydrothieno[3,4-b][1,4]dioxine (BEDOT-BT-BO), and 5,5′-(4,4′-di dodecyl -[2,2′-bithiophene]-5,5′-diyl) bis(2,3-dihydrothieno[3,4-b][1,4]dioxine (BEDOT-BT-BD) were synthesized, and the three comonomers were facilely formed into PBEDOT-BT-BH, PBEDOT-BT-BO, and PBEDOT-BT-BD polymers on platinum electrode by direct anodic oxidation, respectively. The structure and morphology of the polymers were characterized by Fourier transform infrared (FTIR) spectroscopy, scanning electron microscopy (SEM), and thermal analysis. Electrochemical performances of the polymers were also studied by galvanostatic charge–discharge, cyclic voltammetry and electrochemical impedance spectroscopy. The electrochemical results showed that three polymers showed good cycle ability and favorable capacitive performance, namely, for PBEDOT-BT-BH, PBEDOT-BT-BO, and PBEDOT-BT-BD, the specific capacitance was 132.5 F/g, 135.4 F/g, and 129.3 F/g (three electrode configurations) at 1 A/g, respectively, the capacitance retention was nearly 50.1%, 84.6% and 77.1% after 1000 cycles. The energy density of the symmetric full cell based on two PBEDOT-BT-BO electrodes was 9.5 Wh/kg^{-1} at a power density of 13.8 kW/kg^{-1}. These results implied that the three conducting polymers will be a kind of promising electrode material for supercapacitors.

1. Introduction

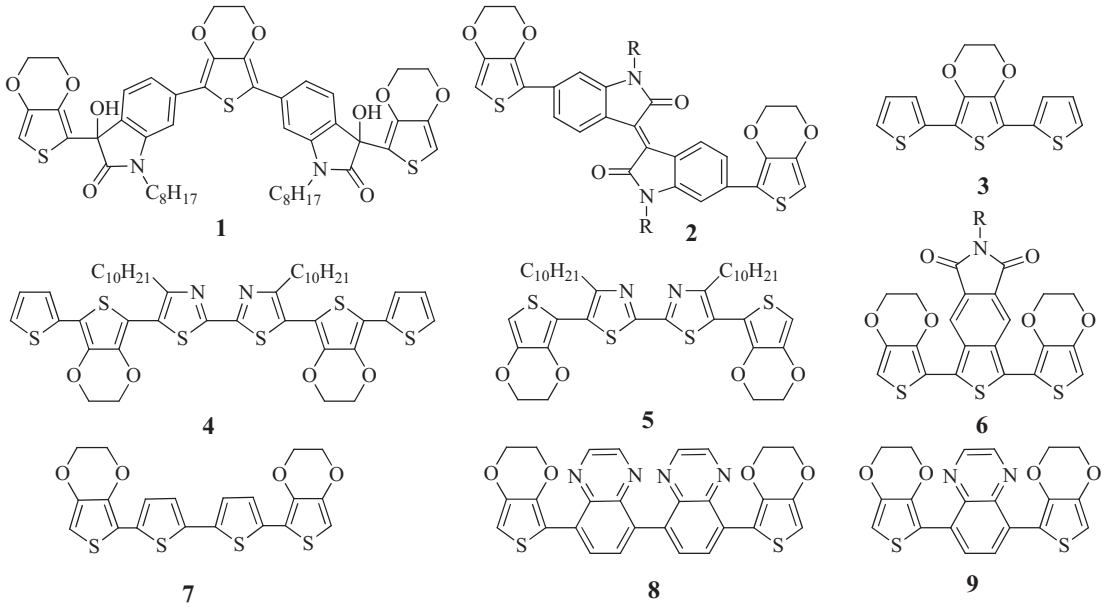
Supercapacitors, which possess higher energy density than dielectric capacitors and higher power density than batteries, have attracted the world′ wide attentions over the last decades due to the high demand for high performing and long lasting energy devices [1–3]. According to charge-discharge mechanisms, supercapacitors can be divided into two categories, namely, electrochemical double layer capacitors which used carbon-based materials as the electrode materials, and pseudocapacitors used metal oxides or electrically conducting polymers (ECPs) [4].

ECPs are interesting candidates as an electrode material for supercapacitor applications because of their combined advantages of low cost, ease of processing, light weight and mechanical flexibility, good compatibility, fast electrochemical charge/discharge rate, large capacitance and high conductivity [5–8]. Among the ECPs, poly(3,4-ethylenedioxythiophene) (PEDOT) is a good candidate for supercapacitor due to its good environmental and thermal stability, high conductivity, and excellent electrochemical stability at broader voltage window relative to polyaniline and polypyrrole [9,10]. Compared with other ECPs, however, its moderate specific capacitance suggests that there is a need to develop new alternatives [11]. Therefore, many efforts focus on improving the capacitive performance of PEDOT through the formation of composites with nanostructured carbon or metal oxides, microstructure modification, novel dopant schemes, and developing asymmetric devices [12–16]. While these efforts continue to advance the field, the need to develop new ECPs with improved Faradaic charge storage still exists.

The past few decades have also witnessed the rapid increase attentions to the 3,4-ethylenedioxythiophene (EDOT) to be used as

* Corresponding author. Tel.: +86 791 88537967; fax: +86 791 83823320.
E-mail address: xujingkun@tsinghua.org.cn (J. Xu).
[1] These authors contributed equally to this work.

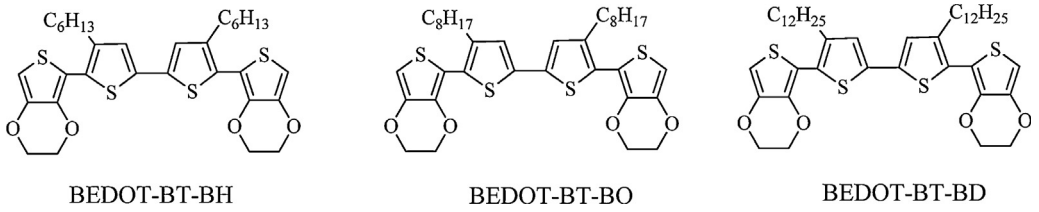
http://dx.doi.org/10.1016/j.electacta.2014.11.033
0013-4686/



Scheme 1. Some representative comonomers based on the combination of EDOT moieties with various heterocycles for supercapacitors applications.

building block for the synthesis of functional π-conjugated systems. Some comonomers based on the combination of EDOT moieties with various heterocycles have been developed (Scheme 1), such as indophenine (**1**) [17], N,N'-dialkylisoindigo (**2**) [18], thiophene (**3**) [19] and bithiophene (BEDOT-BT) (**7**) [20], 4,4′-dinonyl-2,2′-bithiazole (**4** and **5**) [7,21], benzo[c]-thiophene-N-2′-ethylhexyl-4,5-dicarboximide (BEDOT-ITNIm) (**6**) [22], and quinoxaline (DEQ) (**8** and **9**) [23] and these corresponding polymers as the active material were incorporated into supercapacitors. These polymers showed some valuable properties, such as moderate capacitance values (P1, Two-electrode cell, 140 F g^{-1} at 25 mV s^{-1}) and good stability (P1, 90% retention after 1000 cycles; P2, 80% retention after 10,000 cycles). Especially, the high charge storage capacity of P(BEDOT-ITNIm) films (550 C/g) [22] making it become a good candidate for charge storage purposes. Encouragingly, Dwight S. Seferos and co-workers [23] recently constructed a high performance supercapacitors device based on the donor–acceptor conjugated polymers (PDEQ), and achieved specific energy and specific power as high as 11 Wh/kg (at 0.5 A g^{-1}) and 20 kW/kg (at 50 A g^{-1} with a specific energy of 3.6 Wh/kg), which are some of the highest values achieved to date. Very recently, we also synthesized 3,4-ethylenedioxythiophene bis-substituted bithiophene based comonomer, 5,5′-bis(2,3-dihydrothieno[3,4-b][1,4]dioxin-5-yl)-2,2′-bithiophene (BEDOT-BT), and studied the capacitance performance about its polymer (PBEDOT-BT) [20]. It was found that the PBEDOT-BT afforded a higher specific capacitance (171 F g^{-1} at 1 A g^{-1}) and specific energy (23.8 Wh/kg) than PEDOT (120 F g^{-1}, and 16.7 Wh/kg, respectively) at the same conditions. On the other hand, it was well-known that polythiophene with alkyl side chain groups has been most extensively investigated due to their large charge carrier mobility, low band gap in the visible region of the spectrum, environmental stability, solution processability, and synthetic versatility [24–26]. The length of the alkyl chain affects slightly the polymerization reaction but produces important modifications on the structure and properties of the polymers [27–29]. Based on above consideration, one question should be asked: how about the capacitive performance of resultant polymers for the introducing the alkyl chain into bithiophene rings on 3,4-ethylenedioxythiophene bis-substituted bithiophene units?

With curiosity, we firstly synthesized three new 3,4-ethylenedioxythiophene bis-substituted bithiophene containing long alkyl side chain groups (alkyl = hexyl, octyl, and dodecyl) comonomers, which employed alkyl-bithiophene unit as the core and EDOT unit as the terminals (Scheme 2), namely, 5,5′-(4,4′-dihexyl-[2,2′-bithiophene]-5,5′-diyl) bis(2,3-dihydrothieno[3,4-b][1,4] dioxine (BEDOT-BT-BH), 5,5′-(4,4′-dioctyl-[2,2′-bithiophene]-5,5′-diyl) bis(2,3-dihydrothieno[3,4-b][1,4]dioxine (BEDOT-BT-BO), and 5,5′-(4,4′-di dodecyl -[2,2′-bithiophene]-5,5′-diyl) bis (2,3-dihydrothieno[3,4-b][1,4]dioxine (BEDOT-BT-BD) and then electrochemically prepared into PBEDOT-BT-BH, PBEDOT-BT-BO, and PBEDOT-BT-BD on platinum electrode by direct anodic oxidation. The capacitive behaviors and performances of as-prepared polymers were investigated by cyclic voltammetry, galvanostatic charge-discharge, and electrochemical impedance spectroscopy techniques. Furthermore, the structural characterization, morphology and thermal stability of the as-formed copolymer films were minutely investigated.



Scheme 2. Molecular structures of the target molecules.