

Electrochemical synthesis, characterization and capacitive properties of novel thiophene based conjugated polymer



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ABSTRACT

In this paper, a novel thiophene based monomer, 1-(pyren-1-yl)-2,5-di(thiophen-2-yl)-1H-pyrrole, PThP, was synthesized and characterized by ¹H NMR and ¹³C NMR spectroscopic methods. The electrochemical behavior and electropolymerization of this novel monomer were performed on pencil graphite electrode (PGE) by cyclic voltammetry. The effect of solvent, dopant, scan number and scan rate on the electropolymerization and properties of the conjugated polymer films were investigated. The capacitive properties of the poly(PThP) films were tested by electrochemical impedance spectroscopy (EIS). The highest specific capacitance value was calculated for the conjugated polymer modified PGE that was obtained in 0.1 M tetrabutylammonium perchlorate/dichloromethane solution for 30 cycles at 25 mV/s scan rate as 25.45 mF cm⁻². The surface morphologies of the conjugated polymer modified electrodes were determined by scanning electron microscopy (SEM).

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1. Introduction

Electrochemical capacitors, often called supercapacitors, electrical double-layer capacitors, pseudocapacitances or ultracapacitors have attracted worldwide research interest because of their potential applications as energy storage devices in many fields [1]. The enormous progress in supercapacitor technology, resulting in electrode materials with higher and higher specific capacitance values, has led to extension of their application [2]. Supercapacitors can store more energy than a conventional capacitor because: (i) charge separation takes place across a very small distance in the electrical double layer that constitutes the inter phase between electrode and electrolyte; and (ii) an increased amount of charge can be stored on the highly extended electrode surface area created by a large number of pores within an electrode material. The mechanism of energy storage is naturally rapid because it simply involves movement of ions to and from electrode surfaces [3].

On the basis of electrode materials used and the charge storage mechanisms, electrochemical supercapacitors are classified as: (a) electrical double-layer capacitors which employ carbon or other similar materials as blocking electrodes and (b) redox supercapaci-

tors in which electroactive materials are used such as insertion type compounds (e.g. RuO₂, NiO, etc.) or conjugated polymers (CPs) [4].

These organic polymers possess conductive chain structures and electrical conductivity [5]. The conjugated polymers of unique properties such as mechanical strength, electrical conductivity, remarkable stability and possibility of both chemical and electrochemical synthesis and low bandgap, have received great attention. Therefore, they are used in potential applications in various emerging fields such as transparent electrodes, OLEDs, rechargeable batteries, electrochromic displays and smart windows, light emitting diodes, sensors, corrosion inhibitors, field effect transistors (FETs), electromagnetic interference (EMI) shielding and electrochemical supercapacitors, etc. [6–9]. CPs are promising materials for the realization of high performance supercapacitors, as they are characterized by high specific capacitances and by high conductivities in the charged states. Furthermore, their charge–discharge processes are generally fast. These features suggest the possibility to develop devices with low equivalent series resistance (ESR) and high specific energy and power [10].

Electrochemical synthesis of conjugated polymers has some advantages. For instance, it permits the synthesis without using oxidizing agent together with doping with different organic and inorganic ions. In addition, it is a simple and relatively inexpensive method. By adjusting the conditions, both powders and films can be obtained and also this allows controlling thickness [11,12]. In

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the electropolymerization process of the conducting polymers, two oxidation reactions occur simultaneously. The oxidation of monomers and oligomers and the oxidation of a polymer form on the electrode surface producing positive charges (polarons and/or bipolarons). The positive charges are compensated by the anions such as chloride, perchlorate, sulfonate, in the electrolyte solution which is called doping process [13]. In this process, it is possible to control the electrical conductivity of polymer over the range from insulating to highly conducting state. In addition simple modifications of the experimental parameters, e.g. changing the electrode material or solvent, result in changes in the electropolymerization process and in the properties of the final film [14].

Pyrrole, aniline, thiophene and their derivatives can be polymerized to get conjugated polymers by electrochemical synthesis [15]. Electrodeposition of conductive polythiophene (PTh) films by electrochemical oxidation of thiophene and its derivatives has been widely described in recent years [16]. Polythiophenes and their derivatives present an important class of conjugated polymers that form some of the most environmentally and thermally stable materials in both doped and undoped states. These polymers have various useful properties like having high-charge carrier mobilities and high thermal and photochemical stability. In addition, they easily form relatively stable radical cations (holes) [17,18]. PTh and its derivatives are one of the most promising supercapacitor materials and has received a significant amount of attention in applications [19].

Carbon in its dispersed and conducting form is the most widely used commercial material for electrochemical supercapacitors applications as an electrode material. Among carbon based materials, PGE can be seen an important electrode material due to its large active electrode surface area, high electrochemical reactivity, good mechanical rigidity, low cost, disposable and wide potential window. It can be also easily modified and miniaturized. A combination of conjugated polymers and carbon for positive and negative electrodes in supercapacitors is both scientifically and commercially applicable due to the low cost of the two materials [20–22].

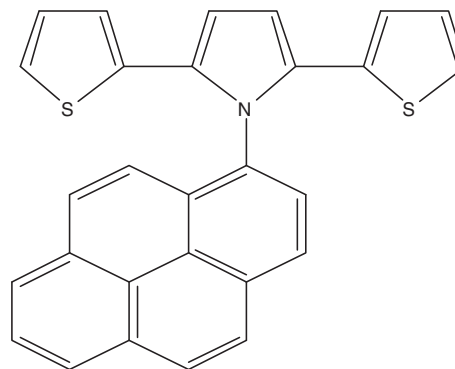
EIS is an attractive method to study the electrical behavior of coated and uncoated neutral prosthetic devices. It involves measuring the electrode impedance over a spectrum of frequencies. By using magnitude and phase information data, one can obtain qualitative and quantitative information about the electrical properties of the coated and uncoated electrodes. Interesting information can be obtained concerning potential distribution across the interface, doping level, solution resistance, carrier recombination and generation at the surface and in the space region. To determine the magnitude of the resistive and capacitive response, their performance can be examined in a wide range of frequencies [23,24].

In this work, a novel thiophene derivative, 1-(pyren-1-yl)-2,5-di(thiophen-2-yl)-1H-pyrrole, PThP, (Scheme 1) was synthesized by a chemical method and electropolymerized on PGE as an electrode material for supercapacitor applications for the first time in this work. The effect of solvent, dopant ions, scan rate and scan number on electropreparation and properties of the poly(PThP) films were investigated. ^1H NMR and ^{13}C NMR spectroscopic methods were used to characterize the PThP. The properties of the polymer were studied in detail using cyclic voltammetry. The capacitive properties of the modified poly(PThP)/PGEs were tested by electrochemical impedance spectroscopy. The surface morphology of conjugated poly(PThP) films was investigated by SEM.

2. Experimental

2.1. Materials

Glassware was routinely oven-dried at 110 °C for a minimum of 4 h. Column chromatography was performed on silica-gel 70–230



Scheme 1. The chemical structure of 1-(pyren-1-yl)-2,5-di(thiophen-2-yl)-1H-pyrrole.

mesh. Dichloromethane (HPLC grade, 99.9%) and acetonitrile (HPLC grade, 99.9%) were purchased from Sigma–Aldrich. All chemicals were analytical grade reagents and were used without further purification. Tetrabutylammonium tetrafluoroborate (TBABF₄) (>99%), tetrabutylammonium perchlorate (TBAP) (>99%) and tetrabutylammonium hexafluorophosphate (TBAPF₆) (>99%) were obtained from Fluka.

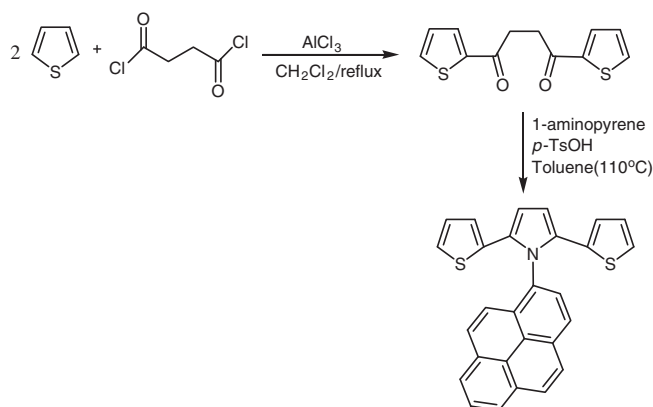
2.2. Synthesis of PThP

1,4-di(thiophene-2-yl)butane-1,4-dione was synthesized according to literature procedure [25]. A solution of 500 mg (2 mmol) 1,4-di(thiophene-2-yl)butane-1,4-dione, 434 mg (2 mmol) 1-aminopyrene and catalytic amount of *p*-toluenesulfonic acid (*p*-TsOH) in dry toluene were refluxed in a Dean–Stark apparatus until all the starting materials were disappeared on TLC. The flask was cooled and the solvent was removed under reduced pressure. The residue was placed in a silica-gel column with dichloromethane (CH₂Cl₂) to give the pure PThP monomer. Synthesis route of the PThP is shown in Scheme 2.

NMR spectra were recorded on a Bruker Advance 500 DPX spectrometer (^1H at 500 MHz and ^{13}C at 125 MHz) in chloroform-*d* (CDCl₃) with tetramethylsilane (TMS) as the internal standard.

2.2.1. 1-(pyrene-6-yl)-2,5-di(thiophen-2-yl)-1H-pyrrole

Yield 64%; Orange solid; Mp = 244–246 C. ^1H NMR (500 MHz, CDCl₃): δ 6.39 (s, 2H), 6.58 (s, 2H), 6.80 (br, s, 4H), 7.61 (d, *J* = 8.5, 1H), 8.06 (m, 3H), 8.21 (m, 3H), 8.28 (t, *J* = 9.5, 2H), ^{13}C NMR (125 MHz, CDCl₃): δ 109.75, 122.10, 123.64, 123.68, 124.40, 124.90, 125.05, 125.92, 126.52, 126.73, 127.28, 128.06, 128.59, 129.34, 130.75, 130.96, 131.10, 131.48, 132.07, 132.11.



Scheme 2. The synthesis route of the PThP.

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