

Synthesis of highly branched conducting polymer architecture for electrochromic applications

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ABSTRACT

Electrochromic materials have attracted enormous attention due to their potential applications, such as low-power displays, smart windows for energy efficient buildings, electrochromic e-skins, self-dimming rear mirrors for automobiles and so on. Synthetic strategies of new materials for electrochromic are believed to be the key factors that will help to significantly improve the electrochromic performance and extend their application areas. In this account, we designed and synthesized a novel star shape dithienylpyrrole derivative, namely N¹,N³,N⁵-tris(2,5-di(thiophen-2-yl)-1H-pyrrol-1-yl)benzene-1,3,5-tricarboxamide (TCA), to obtain high optical and electrical performance as functional electrochromic material. After electrochemical polymerization of the TCA, the polymer shows superior optical and electrical properties due to its more conjugated unique three-dimensional shape and highly-branched structure in comparison with its linear counterparts. It has been determined that optical properties and long term electrochromic stability of pTCA are the best among the PSNS derivatives in the literature after evaluating its electrochemical, spectroelectrochemical and EQCM experiment results.

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1. Introduction

Recently, electrochromic polymers (ECP), which exhibit reversible absorption spectral changes by changing the applied potentials, have gained much significance [1] [2] [3] [4]. Among ECP, conjugated polymers (CPs) is considered as a promising materials due to their unique physicochemical properties [5] [6] [7] [8] [9] [10] [11]. Currently, researchers have made an effort to obtain novel, simple and effective functional and solution processable polymeric materials [12] [13], [14]. Among electrochromic CPs, dithienylpyrroles (SNS) as new hybrid conducting polymer materials, possess hybrid photoelectrochemical properties of polythiophene and polypyrrole [15] [16] [17] [18].

To explain that the effect of substitution through the pyrrole units of PSNS, a number of SNS derivatives such as substituted phenyl derivatives [19–21], aryl derivatives [22], alkyl derivatives [23], ferrocene derivatives [24,25], carbazole derivatives [26] are gained to literature. These polymers are reported to have satisfactory electrochromic ability. However, there is no studies on hydrazide-substituted dithienyl pyrrole derivatives which have

better optical and electrical properties other than our group in the literature [27–31].

In addition, star-shaped polymers have approved a considerable interest in the last decade due to their unique three-dimensional shape [32,33]. Compared to linear structures, due to the more stable of structures, they have many advantages such as applicability [34].

Besides, electrochemical quartz crystal microbalance (EQCM) technique is a precise in-situ piezoelectric tool which is capable of controlling mass changes in nano-gram range (10^{-8} to 10^{-9} g) [35–37]. It is particularly useful in predicting the polymerization efficiency, as well as the solvent and ion exchange between the polymer and the solution upon redox cycling. The change in resonance frequency of this device, which uses the piezoelectric properties of quartz crystals to measure bound mass (up to nanograms) on the surface of the electrode, depends on the change in mass according to the Sauerbrey equation [38].

Because of three main purposes, EQCM is extensively used to study the properties of CPs such as PPY [39–41], PEDOT [42–44] and PANI [45]. First of all this technique can be used to follow up deposition of the CPs on the working area surface. Secondly, this technique can be used to monitor the intercalation of dopant ions into the deposited CP layer. Finally, this technique can be used to

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determine the specific capacitance values of the conducting polymer.

Herein we reported the hydrazide group into SNS structure to form the hydrazide bridged-SNS (TCA) and its star-shape polymer (pTCA) is presented (Scheme 1). In this unique combination, SNS unit provides low oxidation potential as well as electrochromic features whereas three hydrazide appendage contributes to generate the cross-linked polymer structure.

Through this strategy, star shaped hydrazide substituted dithienyl pyrrole derivative has been investigated for the first time. After electrochemical synthesis of TCA star-shaped conducting polymer was obtained Scheme 2. The spectroelectrochemical properties and electrochromic behavior of the film was systematically and comprehensively studied. More importantly, the polymer, pTCA, had a favorable optical band gap (2.14 eV) to reflect and/or transmit the yellowish brown color in the neutral state, and it could be switched to blue colors upon oxidation. The favorable electrochromic colors of resulting polymer film show that, it has been utilizable in various applications such as electrochromic devices.

2. Experimental details

2.1. General procedure for the synthesis of the star shape SNS derivative (TCA)

TCA was synthesized by three steps as illustrated in Scheme 1. The first step is synthesis of 1,4-di(2-thienyl)-butane-1,4-dione (1) via Friedel–Crafts reaction; The second step is synthesis of benzene-1,3,5-tricarbohydrazide and the third step is dehydrative cyclization between 1,4-di(2-thienyl)-butane-1,4-dione and benzene-1,3,5-tricarbohydrazide via Knorr–Paal reaction [46,47]. A round-bottomed flask equipped with 2.5 g (10 mmol) 1,4-di(2-thienyl)-1,4-butanedione, 0.831 g (3.3 mmol) benzene-1,3,5-tricarbohydrazide, 0.2 g (1.2 mmol) PTSA, 5 ml DMSO and 50 ml toluene. The resulting mixture was stirred and refluxed for 72 h. After various purification processes, the product have obtained, yield 1.9 g, 64% (mp 211–213 °C). The structure of the monomer was elucidated by ¹H NMR and ¹³C NMR spectral analyses (Fig. 1a and b).

2.2. Electrochemical, spectroelectrochemical and EQCM experiment

Electrochemical polymerization was performed with an Ivium compactstat instrument. The polymerization was actualized in an electrolysis cell equipped with an indium tin oxide (ITO)-coated

glass plate as working, Pt wire and Ag wire as counter and reference electrodes respectively. The polymer have synthesized in an acetonitrile (ACN) solution using 1 mM TCA and 0.1 M lithium perchlorate via cyclic voltammetry at 250 mV/s scanrate. The polymer was deposited onto the ITO surface, and the film was rinsed in acetonitrile to remove unreacted monomer and inorganic salts.

Spectroelectrochemical properties of the polymer were investigated by UV-Vis absorption spectroscopy. Spectroelectrochemical behavior of the polymer was utilized by monitoring absorption changes of the polymer thin films upon a simultaneous change of applied external bias across the films.

The optical density (ΔOD) was determined using %T value of electrochemically oxidized and reduced polymeric film at the specified wavelength by the following equation [48].

$$\Delta OD = \log \left(\frac{T_{ox}}{T_{ble}} \right)$$

The coloration efficiency (CE) is calculated depending on the change of the charge of electrode area (Q_d), wavelength (λ_{max}) and the optical density (ΔOD) by the following equation [49].

$$CE = \Delta OD / Q_d$$

Beside this, microbalance experiment was carried out using a QCM unit (Gamry Instrument eQCM 10M) combined with the potentiostat (Gamry Reference 600). The experimental setup consisted of platinum counter electrode and Ag wire reference electrode and working electrode as Au deposited on 10 MHz quartz crystals (Reference Chemistry Limited, TURKEY).

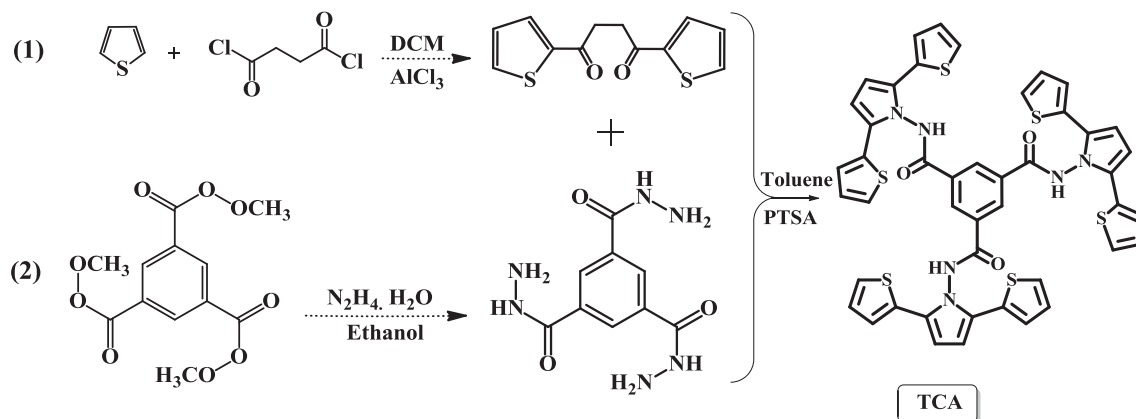
2.3. Fabrication of electrochromic device

Electrochromic polymer film was electrodeposited on the ITO-coated glass substrate by the electrochemical method described above. A gel electrolyte based on poly(methyl methacrylate) (PMMA) (Mw: 120 000), LiClO₄ and propylene carbonate have prepared as in literature [50]. The gel electrolyte was spread on the polymer-coated side of the electrodes, and the electrodes were sandwiched.

3. Result and discussion

3.1. Characterization of TCA

¹H and ¹³C NMR spectra were measured on a Bruker-



Scheme 1. Synthesis scheme of N¹,N³,N⁵-tris(2,5-di(thiophen-2-yl)-1H-pyrrol-1-yl)benzene-1,3,5-tricarboxamide (TCA).

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