



# 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 N<sup>1</sup>,N<sup>3</sup>,N<sup>5</sup>-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<sup>-8</sup> to 10<sup>-9</sup> 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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