

# Fast switching soluble electrochromic polymers obtained from a 4,9-Dihydro-s-indaceno[1,2-b:5,6-b']dithiophene-embedded system



Yongqiang Pang<sup>a,b,d</sup>, Yijie Tao<sup>c,d,\*</sup>, Chaoyang Zhang<sup>d,\*\*</sup>, Haifeng Cheng<sup>d</sup>

<sup>a</sup> School of Electronics and Information Engineering, Xi'an Jiaotong University, Xi'an, Shanxi 710049, People's Republic of China

<sup>b</sup> Air Force Engineering University, Xi'an, Shanxi 710051, People's Republic of China

<sup>c</sup> College of Material Science and Chemical Engineering, Harbin Engineering University, Harbin, 150001, People's Republic of China

<sup>d</sup> Science and Technology on Advanced Ceramic Fibers and Composites Laboratory, National University of Defense Technology, Changsha 410073, People's Republic of China

## ARTICLE INFO

### Keywords:

Electrochromism  
4,9-Dihydro-s-indaceno[1,2-b:5,6-b']  
dithiophene  
EDOT  
Solution-processable

## ABSTRACT

A series of conjugated polymers containing 4,9-dihydro-s-indaceno[1,2-b:5,6-b']dithiophene (IDT) and 3,4-ethylenedioxythiophene (EDOT) or benzo[c][1,2,5]thiadiazole (Tz) are successfully synthesized via Stille coupling polymerization with reasonable yields as well as high molecular weights. The synthesized polymers can dissolve in chloroform, toluene, THF, etc. Additionally, the physical, optical and electrochemical properties of these synthesized polymers are fully characterized. After a film is spin-coated on the ITO electrode, the prepared polymer films present remarkable electrochromic behaviors. Increasing the composition of electron-rich EDOT along with the conjugated backbone of the synthesized D-A polymer is shown to induce red-shift of the short-wavelength absorption band and blue-shift of the long-wavelength counterpart. On the other hand, as the strong electron-deficient benzo[c][1,2,5]thiadiazole (Tz) incorporates into all-donor polymer mainchain, a new low-energy absorption band due to the intramolecular charge transfer of D-A interaction emerges and the corresponding intensity intensifies with the composition of electron-deficient moieties increasing. In addition, the prepared IDT-based polymers also exhibit fast switching response and good stability.

## 1. Introduction

Electrochromism, defined as the properties of the reversible optical transmittance/absorbance change in response to an externally applied potential, has gained considerable interest due to the broad applications in smart windows, displays, military camouflage, etc. [1–9]. In comparison with the inorganic metal oxide (such as WO<sub>3</sub>, V<sub>2</sub>O<sub>5</sub>, NiO, etc.), electrochromic conjugated polymers (ECPs) present several advantages such as ease of structural modification, high optical contrast, fast switching response, and good stability [10–16].

As one of the regular methods for preparation of conjugated polymer, electropolymerization technique can directly deposit an insoluble polymer film on the conducting substrate, even though the shape of the substrate is complex [17,18]. However, the resulting insoluble polymer film is difficult to process after deposition, which is detrimental for large-scale fabrication of time- and cost-effective electrochromic devices. Thus, solution-processable ECPs exhibit unique advantages for the commercial usage in the field of electrochromism

[19–23].

Incorporation of long alkyl side chains into the polymer backbone inducing solubility has been considered as the main strategy for preparing soluble ECPs [24–28]. During the past few years, 4,9-Dihydro-s-indaceno[1,2-b:5,6-b']dithiophene (IDT) has appeared as one of the important donor block for high-performance organic electronic materials [29–31]. It is easy to attach long alkyl side chain on the IDT units due to the presence of sp<sup>3</sup>-hybridized carbon atoms on the heterocycles [32]. In addition, the IDT-based polymers present high charge transfer properties and tunable HOMO level, which have been broadly applied as the donor part in organic solar cells [33–36]. Therefore, the IDT unit may act as an excellent building block for preparing of solution-processable ECPs. Recently, several IDT-based ECPs have been prepared and exhibit good electrochromic properties with high coloration efficiency and fast switching rate [37,38]. However, more researches on IDT-based ECPs especially designation, preparation and characterization of novel IDT-based ECPs is still needed and necessary for providing deep guidelines for the IDT-based polymer design optimization.

\* Corresponding author at: Science and Technology on Advanced Ceramic Fibers and Composites Laboratory, National University of Defense Technology, Changsha 410073, People's Republic of China.

\*\* Corresponding author.

E-mail addresses: [taoyijie112@163.com](mailto:taoyijie112@163.com) (Y. Tao), [zhangcy\\_nudt@163.com](mailto:zhangcy_nudt@163.com) (C. Zhang).

On the other hand, donor-acceptor (D-A) strategy has been confirmed as a valuable approach for synthesizing ECPs, which can obtain unique green or black electrochromism with fast switching response and high stability [39–42], etc. Among the several well-known donors and acceptors, 3,4-ethylenedioxythiophene (EDOT) and benzo[1,2,5]thiadiazole (Tz) are extensively investigated as building blocks in preparation of ECPs due to the excellent properties of their derived polymers [43–45]. Synthesizing novel and high-performance ECPs with these units are still attractive, and researches on the electrochromic polymers with IDT and EDOT or Tz units are still uncommon.

All of the forementioned observations motivated our group to do more detailed studies on synthesizing ECPs containing IDT and EDOT or Tz units with good EC performance. Consequently, in this work, we report the synthesis, characterizations and electrochromic properties of four soluble IDT-embedded polymers. Among these synthesized polymers, EDOT units are mainly used as block units for tuning the optical properties and investigating the increasing electron-rich character effect. With the incorporation of Tz unit (acceptor moiety) into the polymer backbone, the prepared D-A polymers present superior EC properties in comparison with the all donor polymer containing IDT and EDOT units.

## 2. Experimental

### 2.1. Synthesis

The attached supporting information gives detail information of the monomers and polymer synthesis. Scheme 1 gives the chemical structure of the synthesized polymers.

### 2.2. Characterizations

A Varian AMX 400 spectrometer was used to record the  $^1\text{H}$ NMR spectra of the monomers and polymers in  $\text{CDCl}_3$  at 400 MHz and chemical shifts ( $\delta$ ) were reported relative to tetramethylsilane as the internal standard. Mass spectrometry (MS) analysis of the synthesized monomers was performed on a GCT Premier spectrometer (Waters, USA). Molecules of the prepared polymers were obtained by Waters 2690D gel permeation chromatography (GPC), and chloroform was used as the mobile phase at the flow rate of 1.0 mL/min at 30 °C.

Thermogravimetric analyses were performed on a Q500IR. Experiments were carried out on samples of approximately 10 mg in flowing nitrogen heated at the rate of 20 °C/min. SEM images including the surface morphology and thickness of the spin-coated films were taken by a Hitachi S4800 scanning electron microscopy. AFM images were taken by an Ambios QScope 250 instrument at room temperature and ambient conditions.

Electrochemical and spectroelectrochemical characterizations were performed on a CHI660D electrochemical workstation and Shimadzu UV-1800 UV-vis-NIR spectrophotometer with the supporting electrolyte system of 0.2 M  $\text{LiClO}_4/\text{acetonitrile}$  (ACN). Before the measurement, the potentials were calibrated by the ferrocene redox couple. For cyclic voltammetry tests and spectroelectrochemical measurements, the polymer films were spin-coated on the ITO glass at 2000 r/min for 30 s from 10 mg/mL solutions in chloroform. The optical images of the electrochromic films were taken by a canon EOS 500D digital camera.

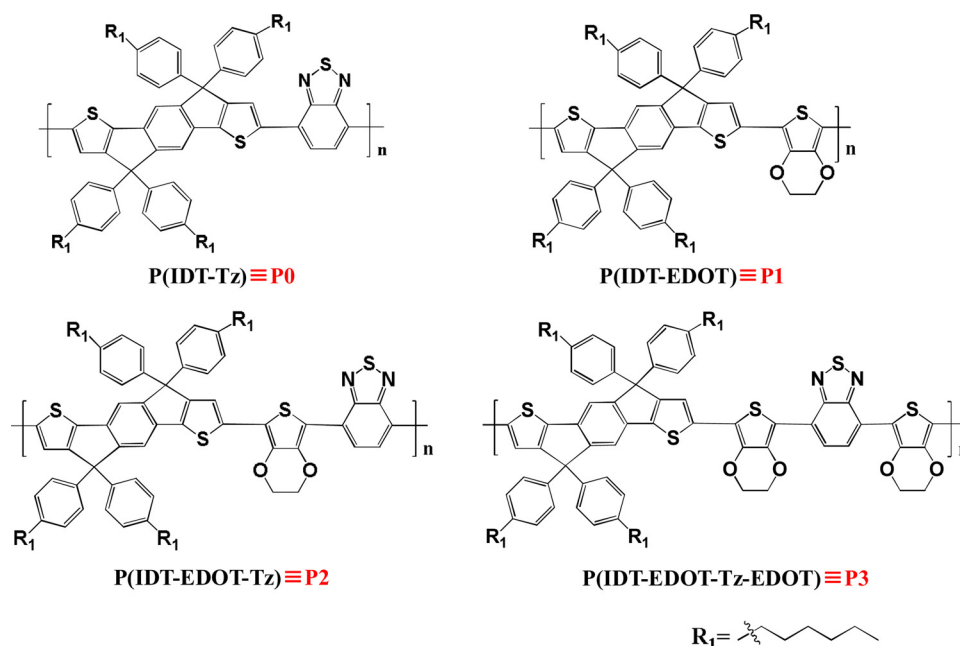
## 3. Results and discussion

### 3.1. Synthesis

The synthesis of monomers and IDT-based polymers were outlined in Scheme S1 and Scheme S2 (Supporting information). All monomers were synthesized except for 5,7-dibromo-2,3-dihydrothieno[3,4-b]-[1,4]dioxine (M1), which was a product of Sigma Aldrich. Previously published procedures were used for the synthesis of brominated benzothiadiazole derivatives, stannylated EDOT and IDT [37,46]. After synthesized via Stille coupling reaction, the derived polymers (Scheme 1) were firstly precipitated in cold methanol, and then purified using Soxhlet extraction with methanol, hexane, and chloroform. The concentrated parts were collected from chloroform and reprecipitated in cold methanol to obtain the final polymer products.

All these four polymers are highly soluble in common organic solvents such as toluene, chloroform, tetrahydrofuran, etc, which can be attributed to the existence of bulky pendants in IDT moieties.  $^1\text{H}$ NMR spectra of the prepared polymers are given in Fig. S2, which confirm the formation of the polymers.

In the  $^1\text{H}$ NMR spectra of P2, it should be noted that the appearance of the peak at 7.81 originating from the hydrogen of center benzene of (IDT-EDOT-Tz)-(IDT-Tz-EDOT) and (IDT-Tz-EDOT)-(IDT-Tz-EDOT)



Scheme 1. Chemical structure of the synthesized polymers.

Download English Version:

<https://daneshyari.com/en/article/7873445>

Download Persian Version:

<https://daneshyari.com/article/7873445>

[Daneshyari.com](https://daneshyari.com)