

# Synthesis and optoelectrochemical properties of dark blue-to-transmissive electrochromic poly(2-methyl-3,4-dihydro-2H-thieno[3,4-b][1,4]dioxepine)

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A new electrochromic polymer poly(2-methyl-3,4-dihydro-2H-thieno[3,4-b][1,4]dioxepine) (PProDOT-as-Me) based on 3,4-propylenedioxythiophene (ProDOT) with asymmetric mono-methyl pendant groups was successfully synthesized through electropolymerization in lithium perchlorate/acetonitrile electrolyte couple. The polymer film displays reversible electrochromic behavior switching between dark blue neutral state (-1V) and transmissive sky blue oxidized state (1V). The electrochemistry, spectroelectrochemistry and electrochromic properties of the polymer film were characterized in details.

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**Keywords:** Dark blue, Transmissive, Electrochromic polymer

## 1. Introduction

Electrochromic materials are a class of smart materials that changing their colors reversibly through redox reactions under the externally applied potentials. Conjugated polymers are one of the most popular candidates in electrochromism research field by means of their good optical contrast, fast switching speed and high coloration efficiency, which make them suitable for use in various applications such as smart windows, nonemissive displays, textiles and camouflage devices [1-3]. An attractive merit of conjugated polymers to be used as effective electrochromes is that the electrochromic properties could be adjusted through modification of conjugated backbones [4] or side chains [5].

Colored-to-transmissive electrochromic polymers are long lived aspirations in electrochromic applications because in most cases materials which switches between a colored state and a transmissive state are required [6]. In the full color palette much effort has been devoted into achieving broadly absorbing electrochromic polymers with intense colored neutral states such as black and dark blue, which would find real-world applications such as information displays and e-papers [7]. Reynolds group reported the pioneering work on this subject and synthesized broadly absorbing black-to-transmissive electrochromic polymers through donor-acceptor approach [8-9] in which propylenedioxythiophene (ProDOT) was employed as the donor unit and 2,1,3-benzothiadiazole (BTD) was used as the acceptor unit. On the other hand dark blue are one of the most often utilized pigments in textile industries [10] which are the potential application field of electrochromic materials. However, to the best of our knowledge, dark blue-to-transmissive electrochromic polymer has not been reported up to date.

To fine tune the electrochromic properties of conjugated polymer, design and prepare new corresponding monomers is an effective approach [11]. Polypropylenedioxythiophene (PProDOT) is a promising blue-to-transmissive electrochromic polymer as it can be symmetrically disubstituted on the central carbon of the propylene bridge for realizing improved electrochromic properties [12-13]. The most successfully developed PProDOT derivative is poly(3,3-dimethyl-3,4-dihydro-2H-thieno[3,4-b][1,4]dioxepine) (PProDOT-Me<sub>2</sub>) which is symmetrically substituted by two methyl groups on the central carbon of the propylene bridge of ProDOT. It shows an outstanding optical contrast of 78% at 578 nm [12]. Sotzing group reported a series of symmetrically substituted derivatives of PProDOT at the 1<sup>st</sup> and 3<sup>rd</sup> carbon atoms of the propylene bridge of ProDOT which produced a single platform for full color realization [14]. However, as in the case of asymmetrically substituted derivatives of PProDOT, to the best of our knowledge, the reports on it in the literatures are still rare to date.

In this contribution the electrochemical synthesis of a homopolymer poly(2-methyl-3,4-dihydro-2H-thieno[3,4-b][1,4]dioxepine) (PProDOT-as-Me) based on ProDOT derivative with asymmetrically mono-substituted methyl group on the 1<sup>st</sup> carbon atom of the propylene bridge was reported.

In our previous studies on electrochromic polymers based on dioxythiophene with symmetrical substituents, such as PProDOTCB-acid [15], PEDOT(MeBr)<sub>2</sub> [16], and PBrPOT [17], we found that their absorption splitting (bimodal absorption peaks) at about 600 nm can be attributed to vibronic coupling concerning the formation of a highly regular polymer backbone with symmetric alkyl chains. Therefore, we hope that introducing asymmetric substituents to the polymer chain will increase the steric

repulsion of side chains and reduce the conjugation length of the polymer, therefore realizing a broadly absorbing electrochromic polymer. The results indicate that PProDOT-as-Me exhibits broadly absorbing behavior at about 516–638 nm in the visible region, therefore, shows a dark blue color in its neutral state. The PProDOT-as-Me film has a reversible electrochromism switching between dark blue and transmissive sky blue under externally applied potentials (-1V and 1V). The electrochemical, spectroelectrochemical and electrochromic properties have been characterized in detail as presented in the following.

## 2. Experimental

### 2.1. Materials

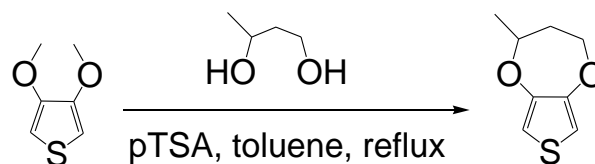
3,4-Di(methoxy)thiophene (DMOT) was synthesized according to the procedure reported by Beaujeu and Reynolds et al [18]. 1,3-butanediol, lithium perchlorate ( $\text{LiClO}_4$ , 99%, anhydrous) was purchased from Aladdin Industrial Inc. Acetonitrile (ACN, HPLC), propylene carbonate (PC, AR) and all other chemicals were bought from Sinopharm Chemical Reagent Co. Ltd. All reagents were used as received.

### 2.2. Instruments

NMR spectra were collected on a 400 MHz Bruker Avance 400 spectrometer in deuteriochloroform ( $\text{CDCl}_3$ ). IR spectra were determined using NICOLET 6700 FTIR spectrometer (Thermo Scientific). Cyclic voltammetry, spectroelectrochemistry and colorimetry studies were performed using a CHI600E electrochemical analyzer (CH Instruments Ins.) and T6 New Happy UV-Vis-NIR spectrometer (Beijing Persee General).

### 2.3. Synthesis of 2-methyl-3,4-dihydro-2H-thieno[3,4-b][1,4]dioxepine (ProDOT-as-Me)

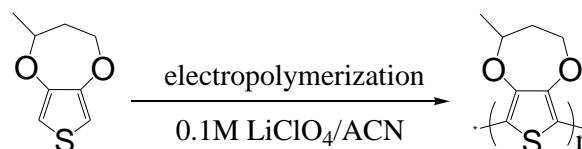
The synthetic route of ProDOT-as-Me is shown in Scheme 1. In a 500 mL round bottom flask with a Soxhlet extractor with type 4 Å molecular sieves the reaction mixture consisting of DMOT (21mmol, 3.03g), 1,3-butanediol (30mmol, 2.7g), p-toluenesulfonic acid monohydrate (pTSA, 2.1mmol, 0.399g) and 250 mL toluene were loaded. The reaction mixture was refluxed for 24 h, and then washed with deionized water for three times. By rotary evaporation under vacuum the solvent was removed. The residue was subjected to column chromatography (petroleum ether/ethyl acetate = 30:1, v/v) to give the final product as a white solid 1.1g (31% yield).  $^1\text{H}$  NMR (400 MHz,  $\text{CDCl}_3$ ,  $\delta$ ): 6.52 (q, 2H), 4.30 (m, 1H), 4.10 (m, 1H), 3.98 (m, 1H), 2.12 (m, 2H), 1.43 (d, 3H).  $^{13}\text{C}$  NMR (100 MHz,  $\text{CDCl}_3$ ,  $\delta$ ): 150.6, 149.1, 106.5, 105.7, 70.1, 40.4, 21.9.



Scheme 1. The synthesis of ProDOT-as-Me

### 2.4. Electrochemical synthesis of the polymer PProDOT-as-Me

The synthetic route is depicted in Scheme 2. Electropolymerization of ProDOT-as-Me was carried out in a one-compartment cell in which Pt wire was used as the counter electrode, Ag wire as the pseudo-reference electrode and an ITO-coated glass slide as the working electrode. The reaction mixture consists of 0.01 M ProDOT-as-Me and 0.1 M  $\text{LiClO}_4/\text{ACN}$  solution. Ag wire pseudo reference electrode was calibrated externally using 5 mM solution of ferrocene ( $\text{Fc}/\text{Fc}^+$ ) in the same electrolyte ( $E_{1/2}(\text{Fc}/\text{Fc}^+) = 0.36$  V versus Ag wire). The reaction mixture was deaerated by pure  $\text{N}_2$  to circumvent the effect of oxygen. The polymer was directly deposited on ITO/glass through repeated cyclic voltammetry scans between 0V and 1.8V for 5 cycles. After the electropolymerization, the polymer film was fully reduced and repeatedly washed with pure ACN to remove the electrolyte, monomers and oligomers.



Scheme 2. The synthesis of PProDOT-as-Me

### 2.5. Electrochemical and spectroelectrochemical characterization

In an electrochemical cell consisting of an ITO/glass (4 cm  $\times$  0.7 cm), a Pt wire and an Ag wire the electrochemical and spectroelectrochemical characterizations were performed. All measurements were carried out in monomer-free  $\text{LiClO}_4/\text{PC}$  electrolyte solution. Following the suggestion of Silva and Ribeiro et al. [19], CIE (Commission Internationale de l'Eclairage) 1931 color coordinates ( $x$ ,  $y$ ) were calculated from UV-Vis-NIR spectroscopy using a Microsoft Excel spreadsheet developed by Mortimer and Varley [20].

### 3. Results and discussion

#### 3.1. Electrochemical polymerization

ProDOT-as-Me (0.01 M) in 0.1 M LiClO<sub>4</sub>/ACN solution was subjected to repeated CV scans between 0 and 1.8 V at a potential scan rate of 100 mV/s for 5 cycles as presented in Fig. 1. In Fig. 1 we can see that when the potential is beyond 1.2 V in the first cycle the current exhibits a sharp increase, indicating the oxidation of the monomer ProDOT-as-Me occurs. Upon repeated CV scans a new redox wave between 0V and 1V can be found which is due to the redox of the polymer PProDOT-as-Me. Concomitantly the current of each cycle increases with the cycle number of CV, suggesting that on the ITO-glass working electrode there was a film of redox-active and conductive polymer and the amount of the polymer increased with the cycle number of CV.

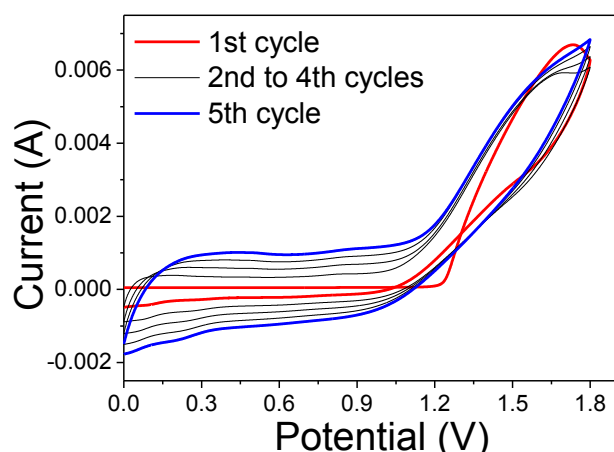


Fig. 1. Repetitive cyclic voltammogram of 0.01M ProDOT-as-Me between 0 and 1.8V at 100mV/s in 0.1M LiClO<sub>4</sub> in ACN.

#### 3.2. Polymer characterization

Fig. 2 (A) and (B) show the FTIR spectra of the monomer ProDOT-as-Me and the polymer PProDOT-as-Me respectively. From Fig.2(A) we can see characteristic absorption peaks of the monomer such as 2939, 2902cm<sup>-1</sup>(CH<sub>2</sub>), 2976cm<sup>-1</sup>(CH<sub>3</sub>), 3112cm<sup>-1</sup>(CH group in the thiophene ring), 1478, 1441, 1367cm<sup>-1</sup>(C=C, C-C in the thiophene ring), 848cm<sup>-1</sup>(C-S) [21-23]. As in the case of IR spectrum of the corresponding polymer we can see in Fig.2 (B) that due to the wide chain dispersity of the polymer the absorption bands were obviously broadened in comparison with the monomer [23]. From Fig.2 (B) it can also be seen that 3112cm<sup>-1</sup> absorption band disappeared in the spectrum of the polymer indicating that the electropolymerization occurred at 2,5-positions of the thiophene ring [21-23].

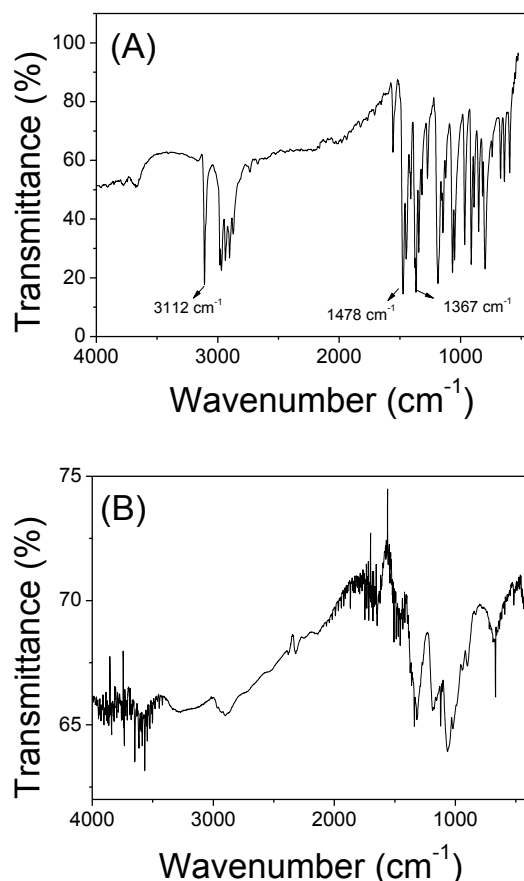


Fig. 2. FTIR spectra of the monomer (A) and the polymer (B)

#### 3.3. Electrochemistry

Cyclic voltammetry studies of the as-prepared PProDOT-as-Me film were performed in the potential range from -1V to 1V in 0.1 M LiClO<sub>4</sub>/PC solution as can be seen in Fig. 3.

It can be seen in Fig.3(A) that PProDOT-as-Me shows an oxidation wave between -0.2V and 1V, no current density peaks are observed in the oxidation process. This may be due to the potential scan rate of CV cycle was too fast for the polymer film to response in a very short time.

A reduction peak at 0.21V can be found when the potential scan rate is 100mV/s in CV experiments. Fig.3(B) shows the scan rate dependence of current density ( $j_{pc}$ ) of the cathodic peak. As the scan rate increases from 50mV/s to 100, 150 and 200mV/s, it can be seen in Fig.3(B) that the cathodic peak current response increases as the scan rate increases and exhibits a linear relationship. It suggests that the redox reaction of the polymer is reversible and not diffusion limited [24].

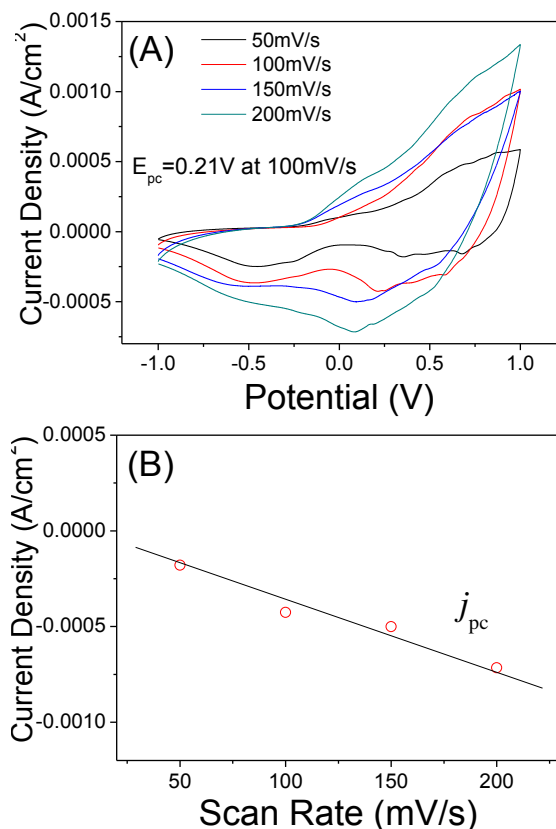


Fig. 3. Cyclic voltammogram of PProDOT-as-Me film ( $2\text{ cm} \times 0.7\text{ cm}$ ) at 50, 100, 150 and 200 mV/s in  $0.1\text{ M LiClO}_4/\text{PC}$ .

### 3.4. Spectroelectrochemistry

Spectroelectrochemistry experiments are very informative in the study on electrochromic materials because the optical and electronic properties of the polymer upon redox reaction can be detected simultaneously [25].

The Vis-NIR absorption spectra of the polymer film were studied under a series of potentials increasing from  $-1\text{ V}$  to  $1\text{ V}$  as presented in Fig. 4. The photos of the polymer at its neutral form and oxidized form are also indicated. And Fig. 5 shows the changes of CIE1931 color coordinates ( $x$ ,  $y$ ) of the PProDOT-as-Me film during the oxidation process. It can be seen from Fig. 4 that PProDOT-as-Me film has a broad absorption band at  $516\text{--}638\text{ nm}$  due to the  $\pi\text{--}\pi^*$  transition and the maximum absorption wavelength is  $559\text{ nm}$ . A dark blue color of the polymer in its neutral form ( $x=0.2215$ ,  $y=0.1073$ ) is achieved as can be seen in Figs. 4 and 5. In our viewpoint introducing asymmetric mono-methyl substituents to the polymer chain will increase the steric repulsion of side chains, reduce the conjugation length of the polymer, and therefore, the blue shift of the absorption occurs, realizing a broadly absorbing neutral form of PProDOT-as-Me. When the potential is raised from  $-1\text{ V}$  to  $1\text{ V}$  PProDOT-as-Me film is progressively oxidized. The absorption bands at  $516\text{--}638\text{ nm}$  decreases and the polymer absorbs at longer wavelength in the near-IR region ( $>900\text{ nm}$ ) because of the polaronic and bipolaronic transition. Upon fully oxidation ( $x=0.3034$ ,

$y=0.3178$ ), the intensity of absorption at  $516\text{--}638\text{ nm}$  decreases significantly and PProDOT-as-Me film exhibits a transmissive sky blue oxidized state.

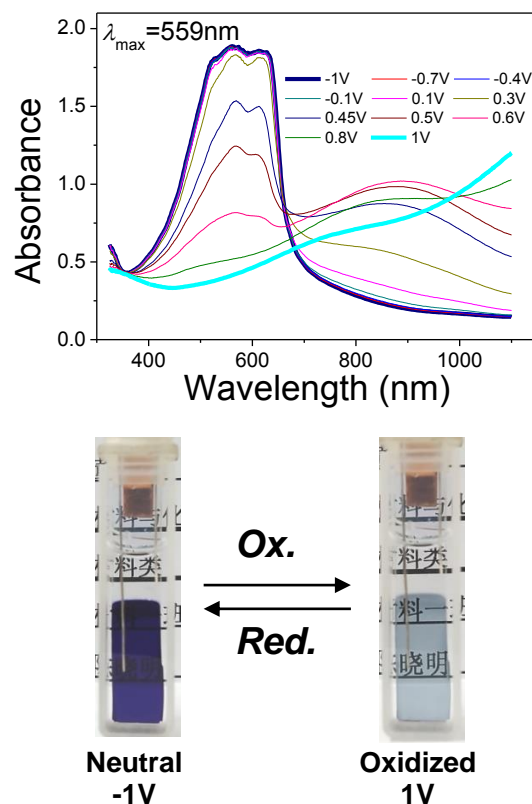


Fig. 4. Spectroelectrochemistry of PProDOT-as-Me film ( $2\text{ cm} \times 0.7\text{ cm}$ ) at externally applied potentials from  $-1\text{ V}$  to  $1\text{ V}$  in  $0.1\text{ M LiClO}_4/\text{PC}$ . Pictures at the bottom show the hues of blue perceived and give an indication of the degree of transmissivity obtained upon complete oxidation.

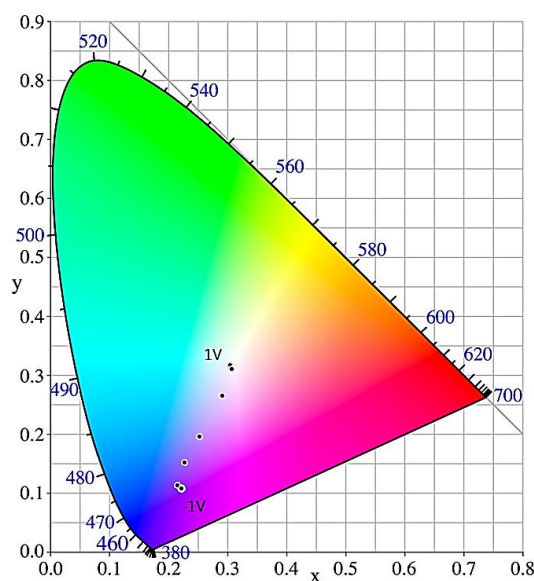


Fig. 5. CIE1931 color coordinates  $x$ ,  $y$  of PProDOT-as-Me film at the potentials increasing from  $-1\text{ V}$  to  $1\text{ V}$  in  $0.1\text{ M LiClO}_4/\text{PC}$ .

### 3.5. Electrochromic switching

Square wave potential step chronoabsorptometry and chronocoulometry were employed to study the electrochromic switching behavior of PProDOT-as-Me film. The results were shown in Fig. 6 (A) and (B). The potential square waves were set as  $-1V$  and  $1V$  with various potential residence time of 30s, 15s and 10s.

It can be seen from Fig. 6 that the transmittance of the neutral state and the fully oxidized state are 10.7% and 45.7% at 559nm respectively. PProDOT-as-Me film exhibits a reasonable optical contrast  $\Delta T_{\max} = 35\%$  at 559nm. However the response time of the polymer during the oxidation process is relatively longer ( $t_{95} = 11s$ ). That implies a relatively lower switching speed of PProDOT-as-Me which could be due to the interaction between methyl pendant groups and  $ClO_4^-$ , making the doping and dedoping of counter-ions be slower.

The coloration efficiency is calculated from the slope of  $\Delta OD$  versus  $Q_d$  plot (Fig. 7) in the oxidation process of the polymer film ( $CE = \Delta OD / Q_d$ ,  $\Delta OD$  is the change of optical density at the monitoring wavelength,  $Q_d$  is the inserted charge per area of the electrode). In the oxidation process PProDOT-as-Me shows a good coloration efficiency of  $199 \text{ cm}^2/\text{C}$ . As in the case of transition metal oxides, they usually show CE values of ranging from 10 to  $100 \text{ cm}^2/\text{C}$  [12].

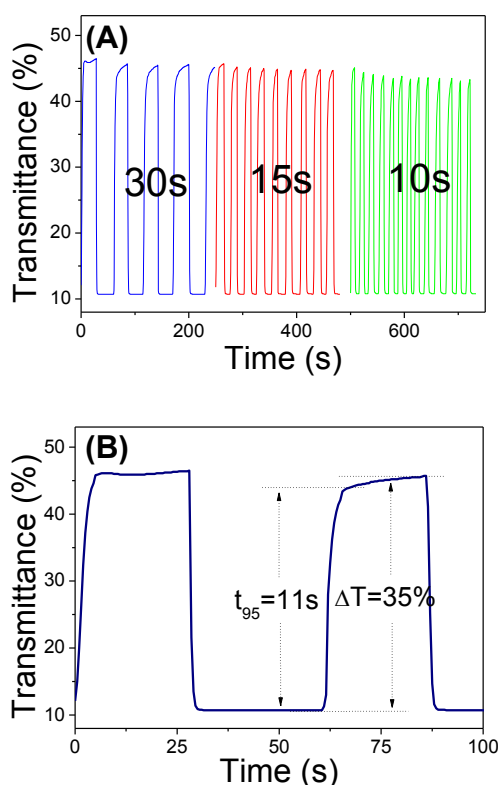


Fig. 6. Square wave potential step chronoabsorptometry (A) and calculation of  $\Delta T$  and response time (B) of PProDOT-as-Me film ( $A = 0.97 \text{ au}$ ) at 559 nm,  $-1V$  to  $1V$  at various potential residence time in  $0.1M \text{ LiClO}_4/\text{PC}$  with a Pt wire counter and Ag wire pseudo reference electrode

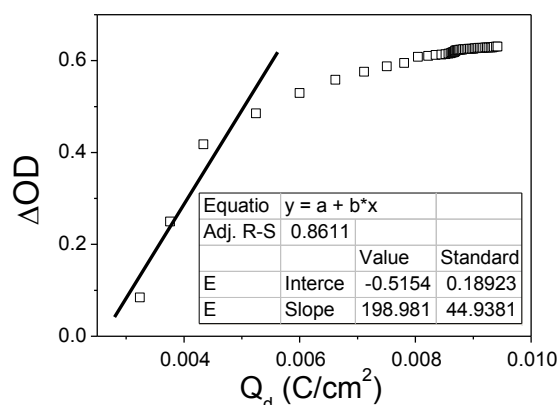


Fig. 7.  $\Delta OD$  versus  $Q_d$  plot of PProDOT-as-Me film at 559 nm,  $-1V$  to  $1V$  at potential residence time of 30s in  $0.1M \text{ LiClO}_4/\text{PC}$  with a Pt wire counter and Ag wire pseudo reference electrode

Square wave potential step chronoabsorptometry scans between  $-1V$  and  $1V$  for total 1000 cycles were employed to study the long term switching property of the PProDOT-as-Me film. The results are shown in Fig. 8. It can be seen in Fig. 8 that after 1000 cycles the contrast ratios do not show any loss, suggesting that PProDOT-as-Me has a promising switching stability and could be used in electrochromic applications.

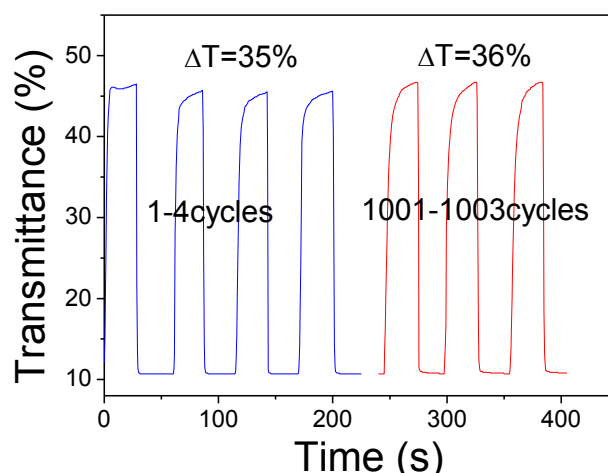


Fig. 8. Square wave potential step chronoabsorptometry of PProDOT-as-Me film between  $-1V$  and  $1V$  at potential residence time of 30s in  $0.1M \text{ LiClO}_4/\text{PC}$

### 4. Conclusions

In summary, in this study a novel electrochromic polymer PProDOT-as-Me with asymmetrically monomethyl substituents was electrochemically synthesized and characterized. The polymer reveals promising electrochromic nature and exhibits a broadly absorbing dark blue neutral state and a transmissive sky blue oxidized state. It exhibits a reasonable optical contrast of 35% at 559 nm, an appropriate coloration efficiency of  $199 \text{ cm}^2/\text{C}$ , a relative

longer switching time  $t_{95}=11$ s during the bleaching process and good long term switching stability.

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