Dual-band modulation of visible and near-infrared light independently with electrochromic poly(3-methyl-3,4-dihydro-2H-thieno[3,4-b][1,4]dioxepine)

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Poly(3-methyl-3,4-dihydro-2H-thieno[3,4-b][1,4]dioxepine) (PProDOT-s-Me) was synthesized through electrochemical polymerization. The surprising feature of the electrodeposited PProDOT-s-Me film is that it can tune absorption in visible region (380-780 nm) and near-infrared (780-1100 nm) independently under different applied potentials: Vis absorbable / NIR transmissive (-1.5 V), Vis absorbable / NIR absorbable (0.1 V) and Vis transmissive / NIR absorbable (1.4 V). It is interesting because PProDOT-s-Me could be potential candidate in smart windows for thermal and light control in buildings in three modes: weak light / warm (-1.5 V), weak light / cool (0.1 V) and strong light / cool (1.4 V).

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1. Introduction

Electrochromic (EC) materials exhibit color or optical changes reversibly and persistently induced by electrochemical redox reactions and the phenomenon is called electrochromism [1]. Due to high optical contrast, fast switching speed and high coloration efficiency, conjugated polymers are one of the most promising candidates for real-world EC applications such as windows and displays [1-5].

EC windows (ECW) can switch reversibly between transparent and colored states and across different degrees of opacity by applying different potentials, therefore, the external light, glare and solar radiation (hence heat from outside) entering through the window can be modulated conveniently. This, in turn, leads to potential energy and cost savings as the reliance of indoor lighting and temperature (e.g. air conditioning) control is reduced [6]. One of the most famous applications of ECW is portholes of the Boeing 787 Dreamliner [6].

Compared with EC materials working in the visible region, the ones which functionalize in the near-infrared region (780-2500 nm) have been paid more and more attention due to their various possibilities in military and civilian applications, such as telecommunications, biomedicines, and particularly thermal control for buildings or airplanes [7]. Additionally, dual-band modulation of visible and near-infrared light is very important, as nearly 50% of solar energy lies in the NIR region [8].

Generally electrochromic polymers (ECP) exhibit absorption in the visible region because they intrinsically have delocalization of π electrons along conjugated chains, therefore, colored neutral states will be displayed [9]. The oxidation of conjugated polymers (i.e. the removal of π electrons from the valence band) creates half-filled polaron levels which are symmetrical about the bandgap centre, leading new electronic transitions at lower energies and a shift of the absorption to higher wavelengths (NIR region), that is the reason for their electrochromism [10]. When the conjugated polymer is oxidized continuously, a bipolaron forms which has two cations coupled to one another, and delocalized over the same polymer segment. On the other hand the absorption of oxidative conjugated polymers in the NIR region has attracted more and more attention due to their potential applications in NIR electrochromism.

Propylenedioxythiophene (ProDOT) is a famous star platform in electrochromic polymers because it can be symmetrically di-substituted on the central carbon atom of the propylene bridge for realizing improved electrochromic properties. For ECP based on ProDOT such as PProDOT-Me$_2$ [11] or PProDOT-Et$_2$ [12] which has two methyl groups or ethyl groups substituted at the central carbon of the propylene bridge reported by Reynolds et al, the decrease of absorption in visible region in the oxidation process and the increase of absorption in NIR region are always occurring simultaneously. Thus the employment of ECP based on PProDOT in smart windows for thermal / light control of buildings still has some problems to be addressed because the modulation of light in Vis and NIR region could not be realized independently.

In our opinion, as for ECPs, lowering the band gap will result in an absorption shift to the longer wavelength or even into the NIR region [13], therefore increase the co-planarity of the conjugated polymer may produce new ECPs functionalizing in NIR region. This may be realized by introducing as little as possible small substituents symmetrically on the central carbon of the propylene bridge to the poly(propylenedioxythiophene) based ECP.

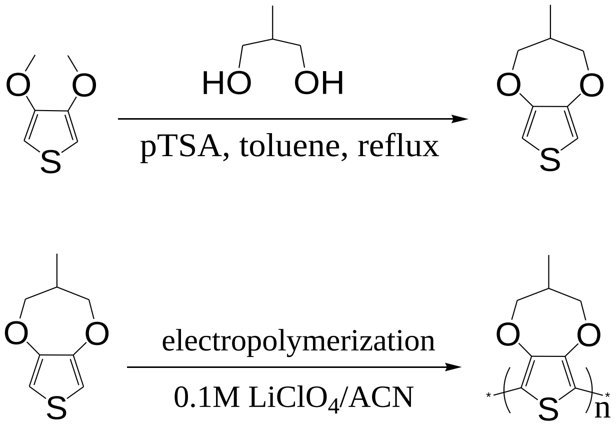
In this letter, an electrochromic polymer, Poly(3-methyl-3,4-dihydro-2H-thieno[3,4-b][1,4]dioxepine) (PProDOT-s-Me), is reported. The surprising feature of the electrodeposited PProDOT-s-Me film is that it can tune absorption in visible region (380-780 nm) and near-infrared region (780-1100 nm) independently in three modes under different applied potentials: Vis absorbable / NIR transmissive (-1.5 V), Vis absorbable / NIR absorbable (0.1 V) and Vis transmissive / NIR absorbable (1.4 V).

2. Experimental

Synthesis of PProDOT-s-Me was initiated by the transetherification reaction of 3,4-dimethoxythiophene and 2-methyl-1,3-propanol. The synthetic routes and conditions of the monomer and its electropolymerization are depicted 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), 2-methyl-1,3-propanol (30 mmol, 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). 1H NMR (400 MHz, CDCl3, δ): 6.53 (s, 2H), 4.17 (m, 2H), 3.72 (m, 2H), 2.40 (m, 1H), 1.02 (d, 3H). 13C NMR (100 MHz, CDCl3, δ): 150.2, 106.0, 76.2, 37.6, 13.1.

Electropolymerization of ProDOT-s-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-s-Me and 0.1 M $LiClO_4$/ACN solution. Ag wire pseudo reference electrode was calibrated externally using 5 mM solution of ferrocene (Fc/Fc+) in the same electrolyte ($E_{1/2}$(Fc/Fc+) = 0.36 V versus Ag wire). The reaction mixture was deaerated by pure 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 1. Synthesis of the monomer ProDOT-s-Me and its electropolymerization.

3. Results and discussion

3.1. Electrochemistry of PProDOT-s-Me

Cyclic voltammetry studies of the as-prepared PProDOT-s-Me film were performed in the potential range between -1.5 V and 1.4 V in 0.1 M $LiClO_4$/PC electrolyte-solvent couple. The results are shown in Fig. 1.

From Fig. 1 we can see that PProDOT-s-Me film shows three distinct redox waves with different anodic and cathodic peak potentials. Those are E_{a1} = -0.39 V, E_{c1} = -0.64 V; E_{a2} = 0.34 V, E_{c2} = -0.20 V; E_{a3} = 1.03 V, E_{c3} = 0.86 V. This is quite different from our previous studies in electrochromic polymers based on propylenedioxythiophene which often show only one redox wave [14, 15]. The possible reason is that three redox waves of PProDOT-s-Me may correspond to redox processes of the polymers with different molecular weights. Polymers with higher molecular weight may have relatively lower oxidation potential because of their increased conjugated chain length. Compared with ProDOT-Me_2 and ProDOT-Et_2 reported by Reynolds et al. [11, 12], ProDOT-s-Me would be easier to be polymerized to produce polymers with higher molecular weight because it only has one methyl group substituted at the central carbon of the propylene bridge, reducing the hinderance of the side groups during the polymerization.

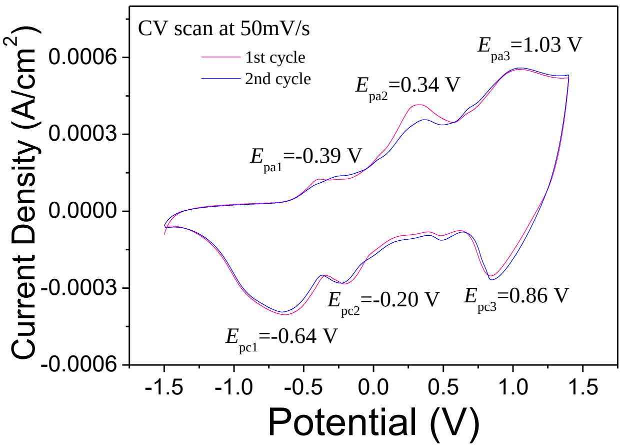


Fig. 1. Cyclic voltammetry of PProDOT-s-Me film between -1.5 V and 1.4 V at scan rate of 50 mV/s in 0.1 M LiClO$_4$/PC with a Pt wire counter and Ag wire pseudo reference electrode (color online)

3.2. Spectroelectrochemistry of PProDOT-s-Me

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 [16].

It can be seen in Fig. 2 (A) that from -1.5 V to 0.1 V, during the oxidation of the polymer film, the absorption in the visible region show very little change, but the absorption in NIR region displays a sharp increase with a maximum wavelength of 961 nm. When the applied potential is forwardly increasing from 0.1 V to 1.4 V as shown in Fig. 2 (B), the absorption in the visible region decreases significantly with the maximum wavelength of 562 nm and the absorption in NIR region does not change much. PProDOT-s-Me film can tune absorption in visible region (380-780 nm) and near-infrared (780-1100 nm) independently under different applied potentials in three modes: Vis absorbable / NIR transmissive (-1.5 V), Vis absorbable / NIR absorbable (0.1 V) and Vis transmissive / NIR absorbable (1.4 V).

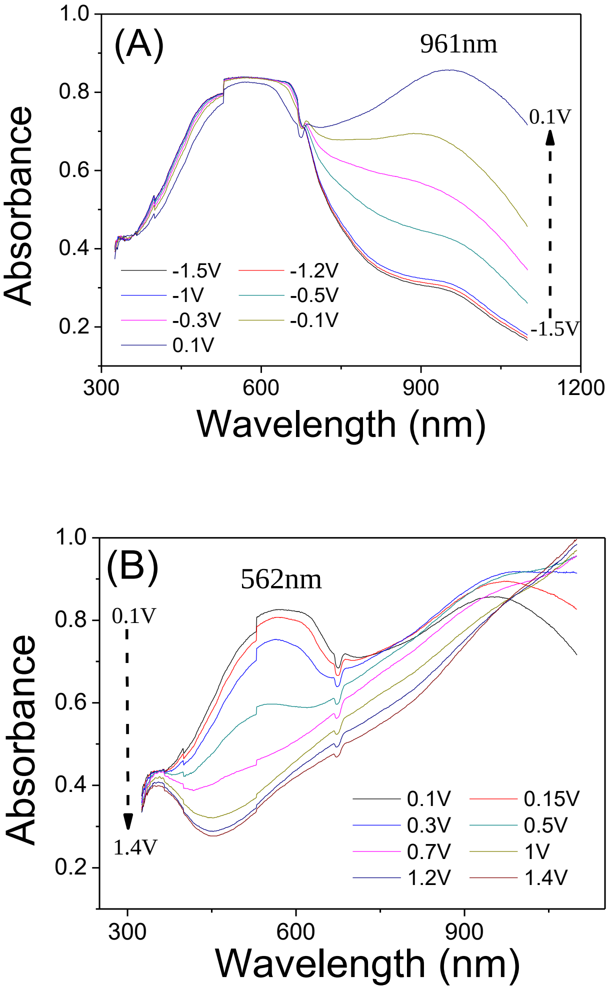


Fig. 2. Spectroelectrochemistry of PProDOT-s-Me film from -1.5 V to 1.4 V. Measurements were performed in 0.1 M LiClO$_4$/PC with a Pt wire counter and Ag wire pseudo reference electrode (color online)

3.3. Colorimetry of PProDOT-s-Me

The colorimetry results are shown in Fig. 3. The successive changes of the CIE1931 color coordinates (x, y) of the polymer film during the oxidation process are displayed. From Fig. 3 we can only see five obvious data points because -1.5V(x=0.305, y=0.2883), -1.2V(x=0.3047, y=0.288), -1V(x=0.3046, y=0.2879), -0.5V(x=0.3033, y=0.2862), -0.3V(x=0.3019, y=0.2842), -0.1V(x=0.3003, y=0.2818), 0.1V(x=0.2975, y=0.277) points overlap to one point, and 1V(x=0.3025, y=0.3157), 1.2V(x=0.3011, y=0.3136), 1.4V(x=0.3026, y=0.3137) points overlap to one point.

From -1.5 V to 0.1 V the color coordinates of the polymer film are almost the same. That verifies the result that PProDOT-s-Me has the Vis / NIR independent light-modulation feature.

It is interesting because PProDOT-s-Me could be potential candidate in smart windows for thermal and light control in buildings in three modes: weak light / warm (-1.5 V), weak light / cool (0.1 V) and strong light / cool (1.4 V) as schematic illustration in Scheme 2.

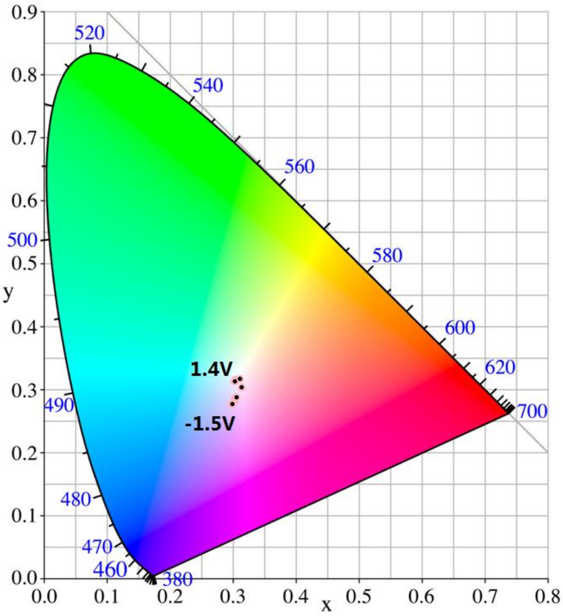
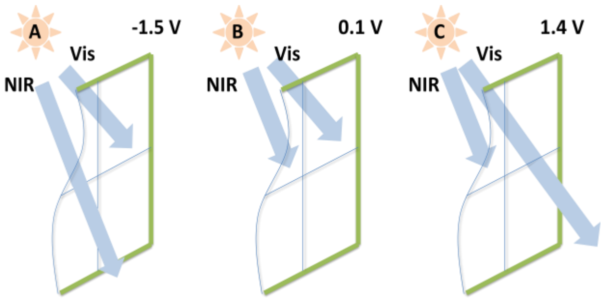


Fig. 3. CIE1931 color coordinates x, y of PProDOT-s-Me film during the oxidation process from -1.5 V to 1.4 V (color online)



Scheme 2. Schematic illustration of dual-band modulation of visible and near-infrared light independently by PProDOT-s-Me (color online)

3.4. Electrochromic switching of PProDOT-s-Me

The electrochromic switching behavior of PProDOT-s-Me film was studied using square wave potential step chronoabsorptometry technique as shown in Fig. 4. The potential square waves were set as (−1.5 V, 1.4 V) at 562 nm and (−1.5 V, 0.1 V) at 961 nm with potential residence time of 30s.

From Fig. 4 we can see that the transmittance changes between the neutral state and the oxidized state are 24% at 562 nm and 36% at 961 nm. The switching time t_{95} (the time required for the polymer to reach 95% of the contrast when switched from the neutral state and the oxidized state) are 7 s at 562 nm and 4 s at 961 nm. After 1000 switching cycles the contrast ratios at 562 nm and 961 nm do not show any loss, suggesting that PProDOT-s-Me has a good switching stability and could be used in electrochromic applications.

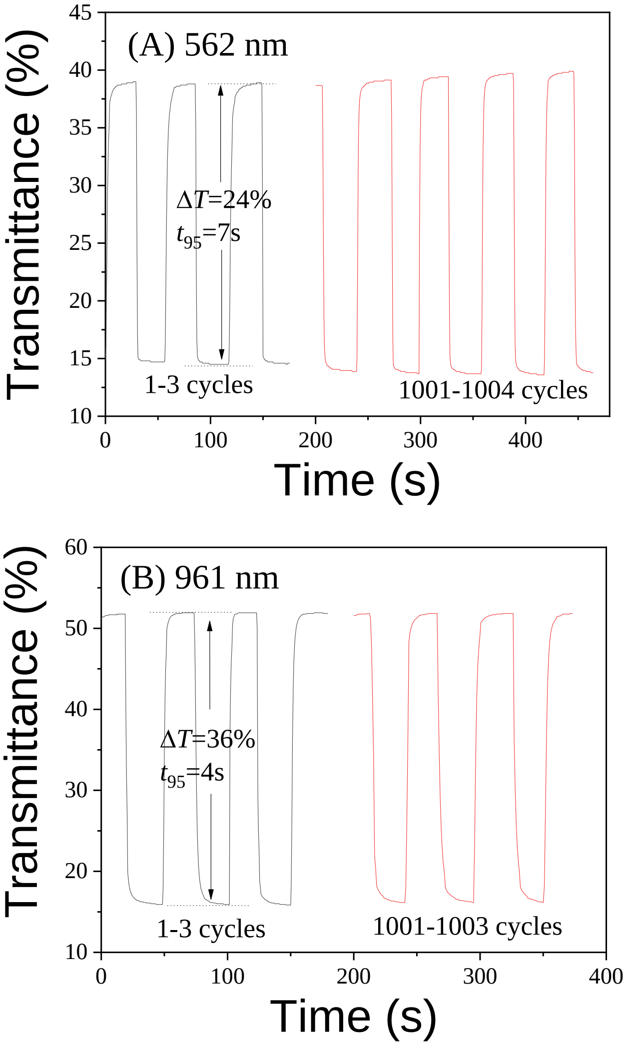


Fig. 4. Square wave potential step chronoabsorptometry at potential residence time 30s at (A) 562 nm, -1.5 V to 1.4 V and (B) 961 nm, -1.5 V to 0.1 V in 0.1 M $LiClO_4$/PC with a Pt wire counter and Ag wire pseudo reference electrode (color online)

4. Conclusions

In conclusion, in this letter the synthesis of a novel Vis / NIR dual band electrochromic polymer PProDOT-s-Me was reported. The electrodeposited PProDOT-s-Me film possesses the salient feature that it can tune absorption in visible region (380-780 nm) and near-infrared (780-1100 nm) independently under different applied potentials in three modes: Vis absorbable / NIR transmissive (-1.5 V), Vis absorbable / NIR absorbable (0.1 V) and Vis transmissive / NIR absorbable (1.4 V).

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