

Electrosynthesis and Characterization of Aminomethyl Functionalized PEDOT with Electrochromic Property*

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Abstract We herein report the electrosynthesis of an aminomethyl functionalized poly(3,4-ethylenedioxythiophene) (PEDOT) derivative, poly(2'-aminomethyl-3,4-ethylenedioxythiophene) (PEDOT-MeNH₂), in CH₂Cl₂-Bu₄NPF₆ (0.1 mol·L⁻¹) system containing 2% boron trifluoride diethyl etherate (BFEE). The electrochemical behavior, structure characterization, thermal properties and surface morphology of this novel polymer were systematically investigated by cyclic voltammetry (CV), Fourier-transform infrared spectroscopy (FTIR), thermogravimetry (TG) and scanning electron microscopy (SEM), respectively. Electrochemistry results demonstrated that PEDOT-MeNH₂ film displayed good redox properties and high electrochemical stability. Besides, PEDOT-MeNH₂ films exhibited the electrochromic nature with obvious color changing from purple in the reduced form to blue upon oxidation. By further investigation, kinetic studies revealed that PEDOT-MeNH₂ film had decent contrast ratio (41.8%), favorable coloration efficiency (152.1 cm²·C⁻¹), low switching voltages and moderate response time (2.4 s). Satisfactory results implied that the obtained PEDOT-MeNH₂ film is a promising optoelectronic material and holds promise for electrochromic devices and display applications.

Keywords: Conducting polymers; Poly(3,4-ethylenedioxythiophene) derivatives; Aminomethyl group; Electrochemical polymerization; Electrochromics.

INTRODUCTION

Of all polythiophenes which have received much attention in recent years for their unique electrical properties^[1], one of the most studied is poly(3,4-ethylenedioxythiophene) (PEDOT)^[2–4]. Owing to its high stability, moderate band gap, low oxidation potential, and good optical transparency in the visible spectral region, PEDOT is one of the most industrially important conjugated polymers. Based on these properties, many applications of PEDOT have been rapidly developed including electrochromic materials^[5], electrode materials in organic electronics^[3], ion sensing^[6], biosensors^[7], and most recently thermoelectricity^[8, 9].

In its well-known studies, the one of the most attractive properties of PEDOT is that its properties can be tuned by grafting various functional groups. Therefore, different functionalized PEDOT derivatives have been successfully synthesized and presented^[3, 4, 10, 11]. The grafting of pendant side groups onto the PEDOT backbone such as flexible hydroxyl^[12, 13] and carboxylic acid^[14] functional groups was investigated in order to provide the

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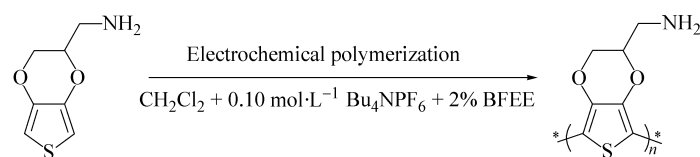
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bioconjugation function. Ethylene glycol groups provided hydrophilic surfaces for preventing the nonspecific binding^[15]. Yu's and Guittard's groups fabricated alkyl and perfluorocarbon substituted PEDOT to create a superhydrophobic and self-cleaning surface^[16,17]. There were also some reports of chemo/bio-sensors based on functionalized PEDOT derivatives, such as tetrathiafulvalene, nucleobase and sulfonates functionalization^[18–21]. These methods provide a simple mean of processing functionalized and modified PEDOT derivatives. However, there are few reports on amino group functionalized PEDOT derivatives.

The chemistry of amino groups is one of the cornerstones of organic chemistry. The amino group as a functionalized group in polymer chemistry has very profound value of research and application because of its water-solubility and excellent biocompatibility. It is well known that some attractive properties could be tuned by grafting amino groups. (1) Amino group can increase the band gap of corresponding conducting polymers by the increase of LUMO energy level as an electron-donating group substitution. (2) Amino group has an effect on the properties of the corresponding conducting polymers because these polymers can be further modified by functional molecules, which is popular in the electrosynthesis of functional conducting polymers^[22–24]. (3) It is also a biocompatible and relatively friendly environment for further immobilization of biomolecules, and plays an important role in DNA detection^[25–29]. However, to the best of our knowledge, there have been no reports on the electrochemical polymerization of 3,4-ethylenedioxythiophene (EDOT) with an aminomethyl group. Hence, we introduced the aminomethyl group into EDOT to form the monomer of 2'-aminomethyl-3,4-ethylenedioxythiophene (EDOT-MeNH₂) and the corresponding polymer (PEDOT-MeNH₂) was synthesized *via* electrochemical polymerization (Scheme 1).

The electrochemical polymerization of EDOT-MeNH₂ was studied in detail. Furthermore, the properties of the resulting polymer, such as electrochemical behavior, structural information and electrochromic properties were investigated, and the electrochromic performance was emphasized in particular.



Scheme 1 The chemical structure of EDOT-MeNH₂ and its electrochemical polymerization

EXPERIMENTAL

Chemicals

2'-Aminomethyl-3,4-ethylenedioxythiophene (EDOT-MeNH₂) was synthesized as previously described^[30]. Dimethyl sulfoxide (DMSO, AR) was purchased from Tianjin Bodi Chemicals Co. Ltd. Dichloromethane (CH₂Cl₂, AR; Tianjin Damao Chemical Reagent Factory) was purified by distillation over calcium hydride before use. Tetrabutylammonium hexafluorophosphate (Bu₄NPF₆, 99%; Acros Organics) was dried under vacuum at 60 °C for 24 h before use. BFEE (1.12–1.14 × 10³ g·L⁻¹, BF₃ = 48.24%; Beijing Changyang Chemical Plant, Beijing, China) was distilled and stored at 0 °C before use.

Electrochemical Polymerization

Electrochemical polymerization and examinations were performed in a one-compartment cell with a model 263A potentiostat/galvanostat (EG&G Princeton Applied Research) under computer control. For electrochemical examinations, the working and counter electrodes were typically both Pt wires of 1 mm diameter. They were placed 5 mm apart during the tests. To obtain a sufficient amount of the polymer films for characterization, a Pt sheet or an ITO-coated glass with a surface area of 3 cm² was employed as the working electrode, and another Pt sheet (3 cm × 2 cm) was used as the counter electrode. These electrodes were carefully polished with 1500 mesh abrasive paper (for ITO, they were immersed in ethanol for 6 h and then cleaned by ultrasonic wave for 15 min), cleaned successively by water and acetone, and dried in air before each experiment. An Ag/AgCl electrode

directly immersed in the solution served as the reference electrode, and it revealed sufficient stability during the experiments.

The typical electrolytic solution was $\text{CH}_2\text{Cl}_2\text{-Bu}_4\text{NPF}_6$ ($0.1 \text{ mol}\cdot\text{L}^{-1}$) containing 2% BFEE. BFEE, which serves not only as the solvent but also as the supporting electrolyte, is electrochemically stable over a wide potential range and has been proven to be an excellent medium for the electrochemical polymerization of aromatic compounds. All solutions were de-aerated by a dry nitrogen stream (more than 15 min) and maintained under a slight overpressure through all the experiments. The PEDOT-MeNH₂ film was grown potentiostatically and its amount of polymer film deposited on the electrode was controlled by the integrated current passed through the cell, which could be read directly from the current-time ($I-t$) curves by the computer. In order to remove the electrolyte and monomer/oligomer, the electropolymerized films were rinsed with CH_2Cl_2 . For spectral analyses, the polymer films were dedoped with 25% ammonia for 3 days (chemical dedoping), and then washed repeatedly with pure water, or dedoped electrochemically at -0.30 V to exclude the dopants until the current passed through the cell became equal to zero (electrochemical dedoping), and then washed with anhydrous diethyl ether. Finally, the polymer films were dried at 60°C under vacuum for 24 h.

Characterization

Electrochemical, spectroelectrochemical and kinetic studies were carried out on a Model 263 potentiostat-galvanostat (EG&G Princeton Applied Research) and a Perkin-Elmer Lambda 900 Ultraviolet-Visible Near-infrared spectrophotometer under computer control. Infrared spectra were measured by a Bruker Vertex 70 Fourier-transform infrared (FTIR) spectrometer with samples in KBr pellets. With an F-4500 fluorescence spectrophotometer (Hitachi), the fluorescence spectra were determined. Scanning electron microscopy (SEM) measurements were taken with a VEGA\\LSU scanning electron microscope (Tescan). Thermogravimetric (TG) analysis and differential thermogravimetric (DTG) analysis were performed with a Pyris Diamond TG/DTA thermal analyzer (Perkin Elmer) under a nitrogen stream from 290 to 1070 K with a heating rate of $10 \text{ K}\cdot\text{min}^{-1}$.

Spectroelectrochemical measurements were carried out to investigate the absorption spectra of the polymer films under an applied potential. The spectroelectrochemical cell consisted of a quartz cell, an Ag/AgCl wire (RE), a Pt wire (CE), and an ITO/glass as the transparent working electrode (WE). All measurements were carried out in monomer-free $\text{CH}_2\text{Cl}_2\text{-Bu}_4\text{NPF}_6$ ($0.1 \text{ mol}\cdot\text{L}^{-1}$). The quartz cell filled with monomer-free $\text{CH}_2\text{Cl}_2\text{-Bu}_4\text{NPF}_6$ ($0.1 \text{ mol}\cdot\text{L}^{-1}$) and ITO-coated glass without a deposited film was used as the background for spectroelectrochemical measurements.

The change in optical density (ΔOD) at a specific wavelength (λ_{max}) is determined by the % T values of electrochemically oxidized and neutral films using equation (1)^[31]:

$$\Delta\text{OD} = \lg(T_{\text{ox}}/T_{\text{red}}) \quad (1)$$

The coloration efficiency (CE) is defined as the relation between the injected/ejected charge as a function of electrode area (Q_d) and the change in optical density (ΔOD) at a specific dominant wavelength (λ_{max}), as illustrated by equation (2)^[32]:

$$\text{CE} = \Delta\text{OD}/Q_d \quad (2)$$

RESULTS AND DISCUSSION

Electrochemical Polymerization of EDOT-MeNH₂

Cyclic voltammogram (CV) is a very useful method which qualitatively reveals the reversibility of electron transfer during the electropolymerization, and also examines the electroactivity of the polymer films because the oxidation and reduction processes can be monitored in the form of a current-potential diagram^[33]. The electrochemical performance of the monomer was first examined by CV in $\text{CH}_2\text{Cl}_2\text{-Bu}_4\text{NPF}_6$ ($0.1 \text{ mol}\cdot\text{L}^{-1}$) solution, as shown in Fig. 1(a). From the first cycle (the red line), the onset oxidation potential of EDOT-MeNH₂ in $\text{CH}_2\text{Cl}_2\text{-Bu}_4\text{NPF}_6$ ($0.1 \text{ mol}\cdot\text{L}^{-1}$) was approximately at 1.25 V versus Ag/AgCl. It could be seen that the current density of cyclic voltammograms (CVs) was very small, and after successive potential scans, no polymer film

was formed on the electrode at all. It indicated that the electropolymerization of the monomer was not successful in $\text{CH}_2\text{Cl}_2\text{-Bu}_4\text{NPF}_6$ ($0.1 \text{ mol}\cdot\text{L}^{-1}$).

Simultaneously, CV of the monomer was also investigated in $\text{CH}_2\text{Cl}_2\text{-Bu}_4\text{NPF}_6$ ($0.1 \text{ mol}\cdot\text{L}^{-1}$) containing 2% BFEE. BFEE is an excellent electrolyte^[34, 35] and a good solvent^[36–38] in which many fused-ring compounds have been electropolymerized successfully^[39–42]. The onset oxidation potential of EDOT-MeNH₂ was 0.75 V versus Ag/AgCl (the red line of Fig. 1b), which was lower than that in $\text{CH}_2\text{Cl}_2\text{-Bu}_4\text{NPF}_6$ ($0.1 \text{ mol}\cdot\text{L}^{-1}$) 1.25 V. As we all know, high oxidation potential might make the electropolymerization of monomer much difficult and even result in some side reactions. The reason why onset oxidation potential reduced was that BFEE could interact with the thiophene ring of EDOT-MeNH₂, which could decrease the resonance stability of the corresponding monomer through the formation of π -complexes between the monomer and BFEE, and make electron loss much easier from the monomer. So, the lower onset oxidation potential was beneficial to prepare high-quality PEDOT-MeNH₂. From this point of view, the solution of $\text{CH}_2\text{Cl}_2\text{-Bu}_4\text{NPF}_6$ ($0.1 \text{ mol}\cdot\text{L}^{-1}$) containing 2% BFEE was a better choice for the electropolymerization of EDOT-MeNH₂.

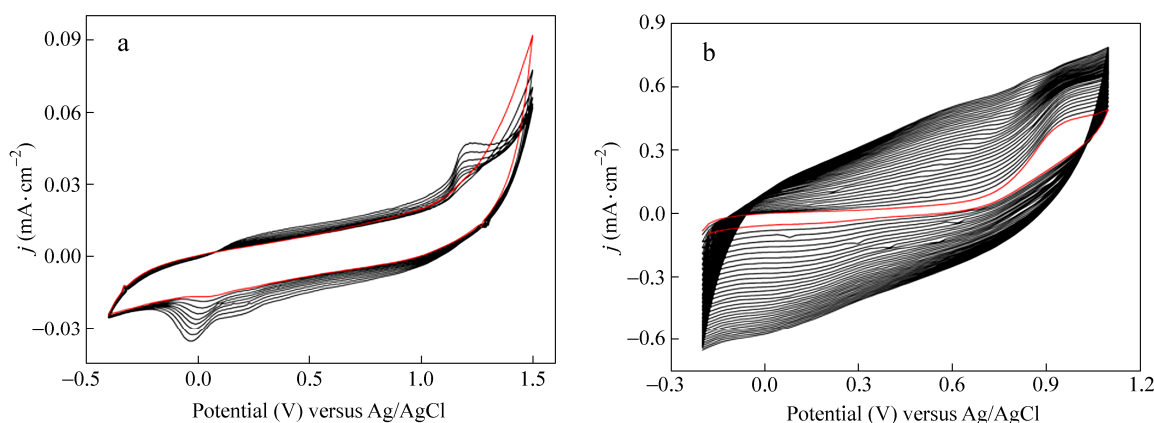


Fig. 1 CVs of $0.01 \text{ mol}\cdot\text{L}^{-1}$ EDOT-MeNH₂ in $\text{CH}_2\text{Cl}_2\text{-Bu}_4\text{NPF}_6$ ($0.1 \text{ mol}\cdot\text{L}^{-1}$) (a) and $\text{CH}_2\text{Cl}_2\text{-Bu}_4\text{NPF}_6$ ($0.1 \text{ mol}\cdot\text{L}^{-1}$) containing 2% BFEE (b) (Potential scan rate: $100 \text{ mV}\cdot\text{s}^{-1}$.)

Consecutive CVs of EDOT-MeNH₂ were shown in Fig. 1(b). In the first cycle, the anodic current began to increase at 0.75 V, and there was a current loop between 0.75 V and 1.10 V. The formation of this loop could be explained as the characteristics of nucleation process, as reported in literature^[43]. Upon sequential cycles, redox currents increased, implying that the amount of the polymer film increased on the electrode surface. The broad redox peaks of the as-formed PEDOT-MeNH₂ film could be ascribed to the wide distribution of the polymer chain length or the conversion of conductive species on the polymer main chain from the neutral state to the metallic state^[44]. The potential shift of current density peaks provided information about the increase in the electrical resistance of the polymer film and the overpotential needed to overcome this resistance.

Optimization of Electrical Conditions and Preparation of PEDOT-MeNH₂

Potentiostatic synthesis was employed to prepare the polymer films for characterization. To optimize the applied potential for polymerization, a set of current transients during the electropolymerization of EDOT-MeNH₂ at different applied potentials in $\text{CH}_2\text{Cl}_2\text{-Bu}_4\text{NPF}_6$ ($0.1 \text{ mol}\cdot\text{L}^{-1}$) containing 2% BFEE were recorded, as exhibited in Fig. 2. Typically, at applied potentials below the onset oxidation potential, no polymer film is found on the electrode, indicating that polymerization does not occur on the electrode surface due to the low current density. Once the applied potential reaches the threshold value, all the electrosynthetic current densities experience an initial sharp increase followed by a slow decrease. The current density eventually becomes constant as a result of the uniform deposition of the polymer film on the electrode surface. At relatively high potentials, however, the surfaces of the polymer films become rough, discontinuous, and heterogeneous. Even worse, some films even

fell into the solution from the electrode surface during/after the experiments. This phenomenon is mainly due to significant overoxidation at higher potentials, which leads to poor quality films. Considering the overall factors affecting the quality of the as-formed polymer films, such as moderate polymerization rate, negligible overoxidation, regular morphology, and good adherence against the working electrode, the optimized applied potential was 1.05 V versus Ag/AgCl. Therefore, PEDOT-MeNH₂ films used for all the characterizations mentioned below were prepared by the chronoamperometry method at the constant potential of 1.05 V versus Ag/AgCl in CH₂Cl₂-Bu₄NPF₆ (0.1 mol·L⁻¹) containing 2% BFEE.

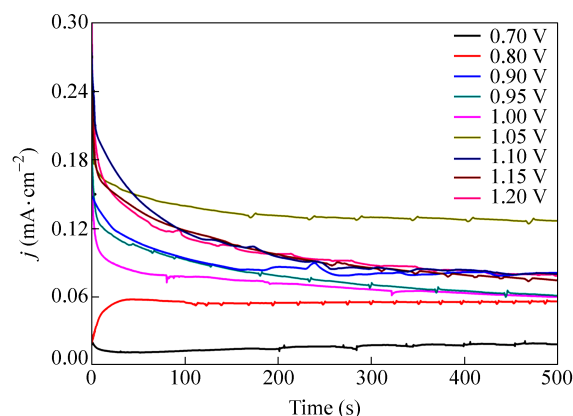


Fig. 2 Chronoamperometric curves of 0.01 mol·L⁻¹ EDOT-MeNH₂ in CH₂Cl₂-Bu₄NPF₆ (0.1 mol·L⁻¹) containing 2% BFEE at different applied potentials for 500 s

Electrochemistry of PEDOT-MeNH₂ Films

In order to get a deeper insight into the electroactivity and stability of the obtained polymer films, the electrochemical behaviors of PEDOT-MeNH₂ films were investigated carefully by CV in monomer-free CH₂Cl₂-Bu₄NPF₆ (0.1 mol·L⁻¹) (Fig. 3). Similar to previous results^[45, 46], the steady-state CVs displayed broad anodic and cathodic peaks (Fig. 3a) and peak current densities were proportional to potential scan rates (Fig. 3b), indicating that the redox process was non-diffusional and the electroactive material was well adhered to the working electrode surface. With the increase of the scan rate, the potentials of anodic and cathodic peak current densities showed positive and negative shifts, which meant a quasi-reversible redox processes at high scan rates. The PEDOT-MeNH₂ film could be oxidized and reduced from 0.45 (anodic peak potential, E_a) to -0.07 V (cathodic peak potential, E_c).

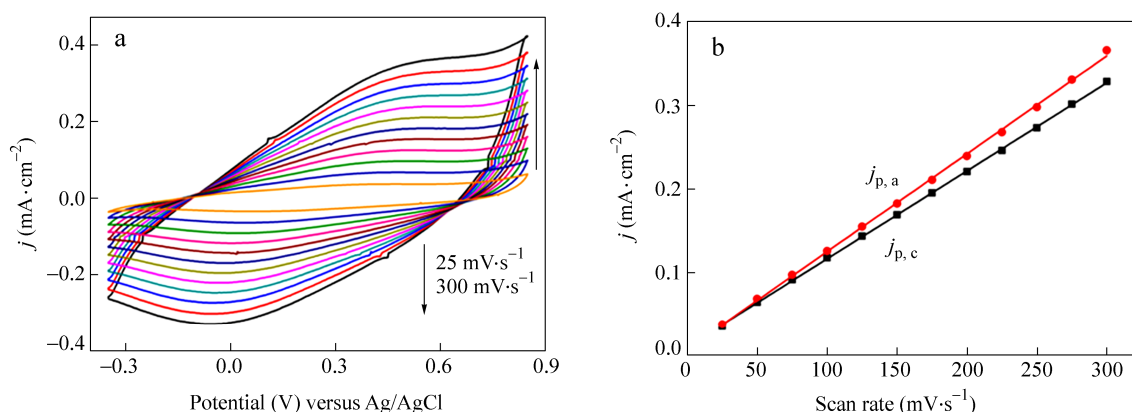


Fig. 3 (a) CVs of PEDOT-MeNH₂ in CH₂Cl₂-Bu₄NPF₆ (0.1 mol·L⁻¹) at potential scan rates of 300, 275, 250, 225, 200, 175, 150, 125, 100, 75, 50, and 25 mV·s⁻¹; (b) Plots of redox peak current densities versus potential scan rates (j_p is the peak current densities, $j_{p,a}$ and $j_{p,c}$ denote the anodic and cathodic peak current densities, respectively.)

It is well known that the good stability of conducting polymers is critical for their applications in electronic devices^[47, 48]. For example, the long-term stability upon switching and/or cycling plays a key role in the electrochromic performance of electronic devices and smart windows. For that reason, the long-term stability of the redox activity of PEDOT-MeNH₂ films deposited on the Pt electrode was investigated by potential scanning between neutral and oxidized states in monomer-free CH₂Cl₂-Bu₄NPF₆ (0.1 mol·L⁻¹), as illustrated in Fig. 4. The number of scanning cycles was 3000 between -0.25 and 0.60 V at the potential scan rate of 150 mV·s⁻¹. According to Fig. 4, the polymer could be cycled repeatedly between the conducting (oxidized) and insulating (neutral) states without significant decomposition, indicating good redox stability of this material. The amount of charge exchange was remaining 73% after 500 cycles, and even after 3000 cycles PEDOT-MeNH₂ still had about 43% of electrochemical activity.

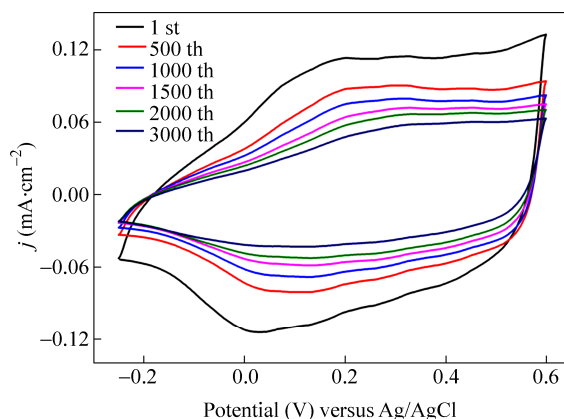


Fig. 4 Long-term redox stability of PEDOT-MeNH₂ upon repeated cycling in monomer-free CH₂Cl₂-Bu₄NPF₆ (0.1 mol·L⁻¹) solution at the scan rate of 150 mV·s⁻¹

Structural Characterization

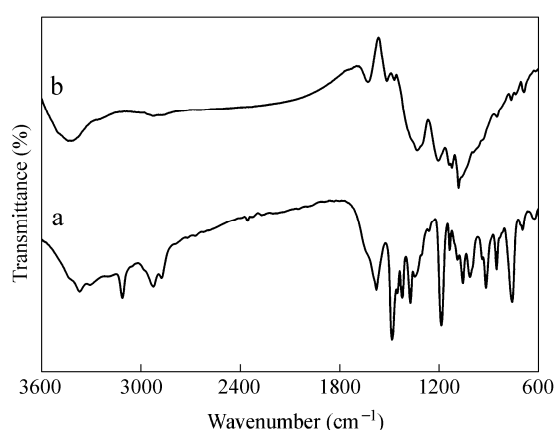
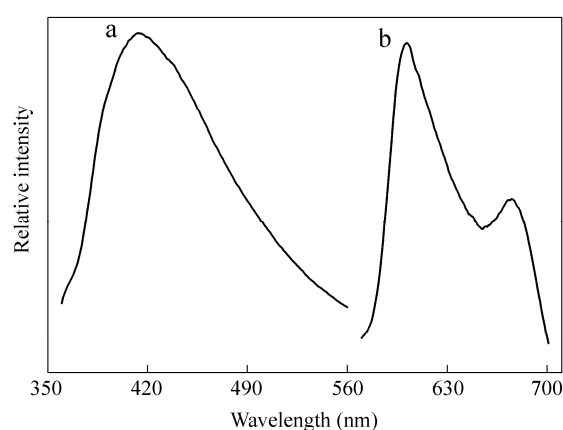
FTIR can provide much structural information for newly obtained polymers, especially for insoluble and infusible polymers. A comparison of the evolution of the vibrational modes appearing in conducting polymers and in some simple molecules acting as references usually facilitates the interpretation of the experimental absorption spectra. In order to interpret the polymerization mechanism and elucidate the structure of PEDOT-MeNH₂, FTIR spectra of EDOT-MeNH₂ and dedoped PEDOT-MeNH₂ were recorded (Fig. 5). The details of the band assignments of the monomer and the dedoped polymer are given in Table 1. As can be seen from Fig. 5, the absorption bands of the polymer were obviously broadened in comparison with those of the monomer. This was mainly due to the wide chain dispersity of the resulting product composed of oligomers/polymers. The strong and broad peak at 3368 cm⁻¹ observed in the spectrum of EDOT-MeNH₂ was the characteristic absorption of the NH₂ in-plane vibration mode, which was broader and shifted to 3437 cm⁻¹ in the spectrum of the dedoped PEDOT-MeNH₂ film. The peak at 3112 cm⁻¹ for EDOT-MeNH₂ was produced by C—H vibration of 2,5-positions in the thiophene ring. This peak of the monomer disappeared in the electrochemical polymerized sample. This indicated that the electropolymerization mainly occurred at the 2,5-positions of the thiophene ring^[49].

Fluorescence Spectra

Figure 6 shows the fluorescence emission spectra of the monomer dissolved in DMSO and the dedoped polymer film on ITO-coated glass. It was observed that the emission peaks for the monomer emerged at 413 nm whereas the maximum emission at 602 nm characterized the spectrum of the dedoped polymer film. The red shift between the monomer and the polymer could be clearly seen from Fig. 6, which was mainly attributable to the elongation of the polymer delocalized π -electron chain sequence.

Table 1. Assignments of FTIR spectra of the monomer and dedoped PEDOT-MeNH₂

Band (cm ⁻¹)		Assignments
EDOT-MeNH ₂	PEDOT-MeNH ₂	
917	852	C—S—C deformation
1485	1517	C=C stretching
1188	1205	C—O—C stretching
1376	1332	C—C stretching
2928	2922	CH ₂ vibration
3368	3437	NH ₂ in-plane vibration
3112	Absent	C—H vibration

**Fig. 5** FTIR spectra of EDOT-MeNH₂ monomer (a) and the dedoped PEDOT-MeNH₂ (b)**Fig. 6** Fluorescence spectra of EDOT-MeNH₂ monomer (a) in DMSO and dedoped PEDOT-MeNH₂ films (b) electrodeposited on the ITO-coated glass

Spectroelectrochemistry

Spectroelectrochemical study of the electrochemically produced polymer, PEDOT-MeNH₂, as shown in Fig. 7, was performed to evaluate the electronic properties and band gaps and, consequently, to elucidate the effect of amino substitution on the electronic properties of PEDOT. The electro-optical properties of the polymer films were investigated using the changes in electronic absorption spectra at various applied voltages. PEDOT-MeNH₂ film was cast on an ITO-coated glass slide, and a home-made electrochemical cell was built from a commercial UV-Vis cuvette. The cell was placed in the optical path of the sample light beam in a UV-Vis-NIR spectrophotometer, which allowed us to acquire electronic absorption spectra under potential control in CH₂Cl₂-Bu₄NPF₆ (0.1 mol·L⁻¹) solution. As each potential was stepped, the absorption in the visible regime began to decrease, whereas that in the NIR regime increased, indicating the creation of lower energy charge carriers at the expense of π - π^* transition^[50].

The spectroelectrochemistry of PEDOT-MeNH₂ films upon oxidation is presented in Fig. 7 as a series of UV-Vis-NIR absorbance curves and the corresponding colors of electrochemically prepared films correlated with electrode potentials. In view of the overall situation, for PEDOT-MeNH₂, the trend of absorbance curves and the position of absorbance peaks were very similar to PEDOT. Stepwise oxidation of the polymer (increasing applied voltage from -0.6 V to 1.0 V) showed the fading of absorbance at 582 nm and typical evolution of peaks at more than 730 nm^[51]. In the neutral form, the film exhibited strong absorption at the wavelength around 582 nm, approximately the same as that of PEDOT, but it is almost transparent at the wavelength more than 710 nm. The band gap (extracted from the onset of the π - π^* transition) for the dedoped polymer was calculated as 1.7 eV using the absorption band centered at 730 nm, which was slightly higher than the reported optical band gap of parent PEDOT (1.6 eV). This implied that the pendant amino group had little influence on the electronic properties of PEDOT.

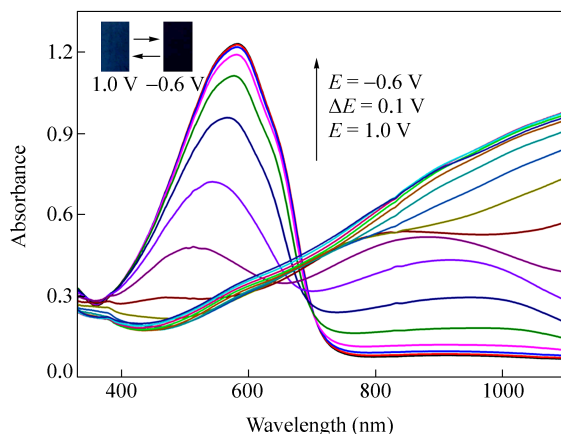


Fig. 7 Spectroelectrochemistry of PEDOT-MeNH₂ film on ITO-coated glass in CH₂Cl₂-Bu₄NPF₆ (0.1 mol·L⁻¹) solution at applied potentials from -0.6 V to 1.0 V

Electrochromic Switching of PEDOT-MeNH₂ Films

The optical switching studies of PEDOT-MeNH₂ films were carried out using a square wave potential step method coupling with optical spectroscopy known as chronoabsorptometry in a monomer free solution. The electrochromic parameters, such as optical contrast ratio ($\Delta T\%$), coloration efficiency (CE) and response time of the polymer films were investigated by increment and decrement in the transmittance with respect to time at the specific absorption wavelength of 582 or 1050 nm, as demonstrated in Fig. 8. The potentials switched stepwise between neutral and oxidized states with a residence time of 10 s. The optical contrast ratio, coloration efficiency and response time of PEDOT-MeNH₂ films are summarized in Table 2.

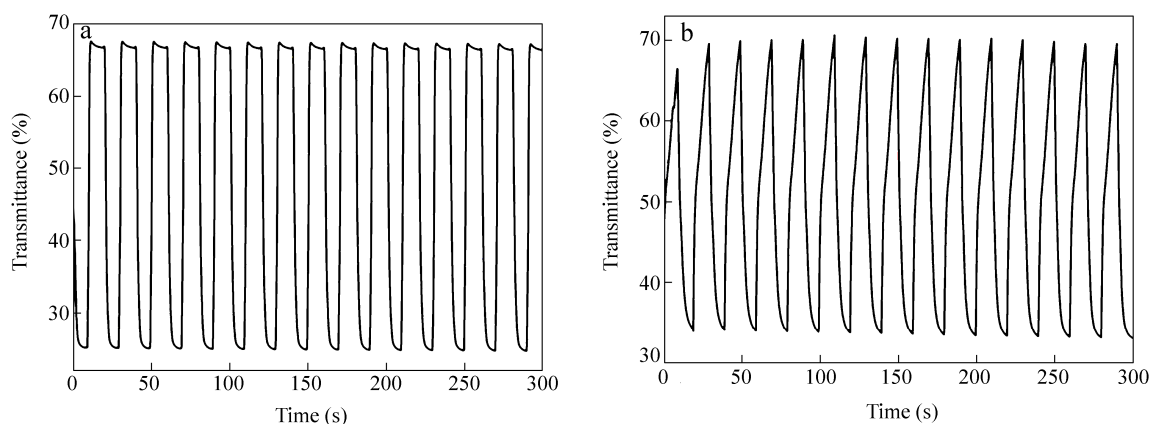


Fig. 8 Electrochromic switching and optical absorbance monitored at 582 nm (a) and 1050 nm (b) profiles of PEDOT-MeNH₂ film recorded during double step spectrochronoamperometry between -0.6 V and 0.6 V for the switching time of 10 s

Table 2. Electrochromic parameters of PEDOT-MeNH₂ film at the wavelength of 582 nm and 1050 nm

Polymers	Wavelength (nm)	T_{red} (%)	T_{ox} (%)	ΔT (%)	Response time (s)		Coloration efficiency (cm ² ·C ⁻¹)
					Oxidation	Reduction	
PEDOT-MeNH ₂	582	24.8	66.6	41.8	2.4	3.6	152.1
	1050	70.2	33.3	36.9	5.2	9.8	91.0
PEDOT ^[31]	585	24.77	78.50	54	0.36	—	137

The optical contrast ratios of PEDOT-MeNH₂ between the neutral (at -0.6 V) and oxidized states (at 1.0 V) were found to be 41.8% at 582 nm and 36.9% at 1050 nm (Fig. 8), respectively. The $\Delta T\%$ value of PEDOT-

MeNH₂ at 582 nm (41.8%) was lower than that of PEDOT^[31] but approximately the same as the analogous polymer PEDOT-MeOH (41.1% at 590 nm)^[52]. The CE is an important characteristic for electrochromic materials and obtained for a certain amount of the charge injected in the polymer as a function of the change in optical density. In this study, the CE of PEDOT-MeNH₂ was calculated to be 152.1 cm²·C⁻¹ at 582 nm and 91.0 cm²·C⁻¹ at 1050 nm, a little higher than that of PEDOT (137 cm²·C⁻¹)^[31], but lower than poly((2,3-dihydrothieno[3,4-*b*][1,4]dioxin-2-yl)methyl acrylate) (PEDOT-AA) (339 cm²·C⁻¹)^[49] and poly((2,3-dihydrothieno[3,4-*b*][1,4]dioxin-2-yl)methyl methacrylate) (PEDOT-MA) (175 cm²·C⁻¹)^[53]. Response time is also an important parameter for a polymer since it indicates the speed of ions moving into the polymer chains during the doping process. The response time required to attain 95% of total transmittance difference was found to be 2.4 s at 582 nm and 5.2 s at 1050 nm for PEDOT-MeNH₂ from the reduced state to the oxidized state, while from the oxidized state to the reduced state, the response time was 3.6 s at 582 nm and 9.8 s at 1050 nm, respectively.

Morphology and Thermal Analysis

Surface morphology of conducting polymers is closely related to their properties, such as electrical conductivity, redox activity and stability. The surface morphology of PEDOT-MeNH₂ film deposited on the ITO electrodes was investigated by scanning electron microscopy (SEM), as shown in Fig. 9. Macroscopically, the doped PEDOT-MeNH₂ films on the ITO displayed sphere-type growth processes whereby a number of clusters were observed. Microscopically, even at high magnifications, the globular structure of the doped polymer films was more apparent. In contrast, after dedoping electrochemically (the counter anions migrate out of the polymer films), the dedoped PEDOT-MeNH₂ film was rough and resembled coralline algae. This morphology of compact PEDOT-MeNH₂ film was extremely beneficial to improve its electrical conductivity and electron transfer capability, thus making it a good candidate for various applications.

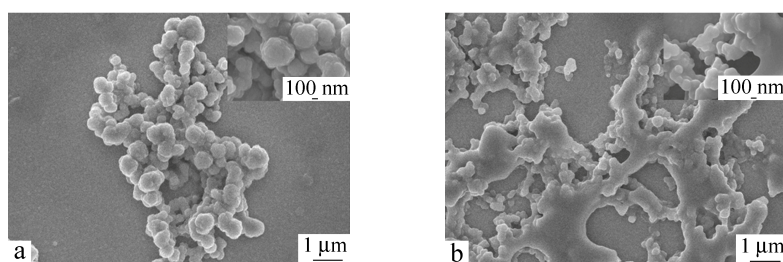


Fig. 9 SEM images of the doped (a) and dedoped (b) PEDOT-MeNH₂ films

Thermal degradation behavior of conducting polymers is very important for their potential applications. To investigate the thermal stability of the newly obtained polymer, Thermogravimetric (TG) analysis and differential thermogravimetric (DTG) analysis experiments were performed under a nitrogen stream, as shown in Fig. 10. At low temperatures ($T < 400$ K), the polymer initially underwent a small weight decrease of about 6.89%. Such a weight loss was closely related to water evaporation and other moisture trapped in the polymer. The following prominent degradation between 400 and 673 K (33.75%) was probably caused by the decomposition of the skeletal chain structure. Simultaneously, the DTG curve showed that the corresponding maximal decomposition occurred at 599 K. Such a weight loss was closely related to the overflow of some oligomers or with short chain structure. Secondly, the degradation between 673 and 1070 K amounting to 15.85% was probably caused by the oxidizing decomposition of the skeletal PEDOT-MeNH₂ backbone chain structure. In addition, when the temperature reached 1100 K, the residual weight was even about 43.51%. Compared with the TG behavior of PEDOT and its derivatives in our previous reports^[52, 54], PEDOT-MeNH₂ films had better thermal stability due to the presence of amino-functional group.

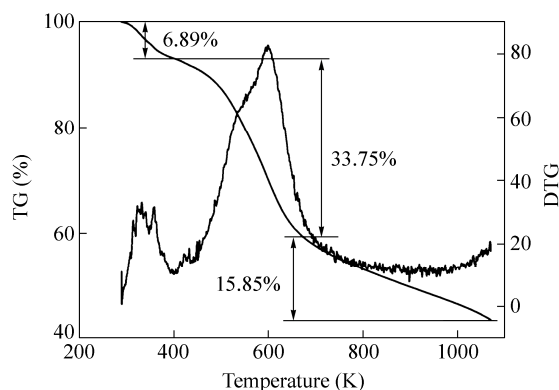


Fig. 10 TG and DTG curves of the doped PEDOT-MeNH₂ film

CONCLUSIONS

In this paper, aminomethyl-functionalized PEDOT (PEDOT-MeNH₂) was electrosynthesized, and then the novel electrochromic PEDOT-MeNH₂ film was deposited by electrochemical polymerization. The as-formed PEDOT-MeNH₂ film was minutely studied by FTIR, fluorescence, SEM and TG. The obtained PEDOT-MeNH₂ films exhibited good redox activity and excellent electrochemical stability. Moreover, PEDOT-MeNH₂ was found to possess electrochromic nature with its color changing from blue to purple with decent contrast ratio of 41.8% and favorable coloration efficiency of 152.1 cm²·C⁻¹ and moderate response time of 2.4 s. Considering all these results, PEDOT-MeNH₂ is very promising as an optoelectronic material, and some prospective applications in organic electronic devices field can be found.

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