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Characterization and Electrochemical Synthesize from Selenophene-Substituted Poly(Triphenylamine)S as Anodically Materials for Electrochromic Devices

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Tris[4-(selen-2-yl)phenyl]amine (TSePA), which contains triphenylamine unit and selenophene unit, was successfully synthesized via Suzuki coupling reaction. Poly(tris[4-(selen-2-yl)phenyl]amine) (PTSePA) was successfully electrochemically synthesized. Characterizations of the resulting polymer PTSePA performed by cyclic voltammetry (CV) and UV–vis. Furthermore, the spectroelectrochemical and electrochromic property of the polymer film was investigated in detail. The resulting polymer film exhibited three different colors under various potentials (yellow color at 0 V, green color at 0.80 V and blue color at 1.20 V). Moreover, the PTSePA film showed satisfactory optical contrast (38.2% at 850 nm and 15.2% at 440 nm), response time (2.11 s at 440 nm and 2.60 s at 850 nm), and reasonable coloration efficiency (248.5 cm^2 C^{-1} at 440 nm and 205.4 cm^2 C^{-1} at 850 nm). An electrochromic device (ECD) based on PTSePA and poly(3,4-ethylenedioxythiophene) (PEDOT) was also constructed and characterized. This ECD was found to have good switching times, reasonable contrast, and satisfactory optical memories and redox stability.

Keywords: Conducting polymer; Spectroelectrochemistry; Electrochromic device; Tris[4-(selen-2-yl)phenyl]amine; Electropolymerization.

1. INTRODUCTION

Electrochromism is a phenomenon related to a reversible optical change in absorption or transmittance occurring in materials by a reversible electrochemical process [1]. There are many intrinsically electrochromic materials, such as transiton-metal oxides, inorganic coordination complexes, conjugated polymers, and organic molecules [2–4]. Among them, the conjugated polymers have several advantages, such as easy processability, high coloration efficiency, fast switching ability, and multiple colors within the same material [5]. Possessing those advantages, conjugated polymers have become one of the main research topics and have quite a number of applications in thin-film transistors [6], sensors [7], polymer light-emitting diodes [8], photovoltaics [9], and electrochromic devices [10–11]. The electrochromism of conjugated polymers related to the doping-dedoping process, the doping process modifies the polymer electronic structure, producing new electronic states in the band gap, causing color changes [12]. Thus, the electrochromic properties of conducting polymers can be varied over a wide range by controlling the band gap of the polymer via proper choice of heteroaromatic ring and substituents [13].

Among electrochromic conjugated polymers, thiophene [14], pyrrole [15] and their derivatives [3] are widely studied for electrochromic applications. However, rarely attention was given to polymers of selenophenes in electrochromic applications [16–20], even though selenophene has lower oxidation potential in compare to its sulfur or oxygen analogs [16,21]. The reason is the higher electron donating character of selenium atom [22]. Lower oxidation potential generates high quality polymer films during electrochemical polymerization since high potential cause damage to the process of polymerization (such as degradation of the polymer through over oxidation) [23]. Additionally, aromatic polyamides are considered to be high-performance polymeric materials because of their excellent physical and chemical properties, thermal and oxidative stability, flame resistance, and superior mechanical properties [24,25]. The electron-rich triphenylamine (TPA) derivatives materials can be easily oxidized to form polarons (radical cations), and the oxidation process is always associated with a noticeable change of the coloration [26,27]. Although TPA has many advantages, Adams and coworkers [28,29] reported that TPA could be easily dimerized to form tetraphenylbenzidine during the anodic oxidation pathway. For electrochromic materials, this dimerization could be considered as an undesired side reaction, which might cause irreversible defect after several redox switches. To avoid such behavior, incorporating electron-donating substituents at the para-position of TPA group could prevent the coupling reactions and afford stable cationic radicals with lower potential [27,30].

According to above consideration, in this article, tris[4-(selen-2-yl)phenyl]amine (TSePA) monomer was synthesized via Suzuki coupling reaction. Electrochemical polymerization of TSePA monomer was successfully performed in 0.2 M $NaClO_4/CH_3CN$ solution. The spectroelectrochemical and electrochromic properties of the PTSePA film were investigated in detail. The PTSePA film shows different colors (yellow, green, and blue colors) with the variation of the applied potentials. In addition, we constructed and characterized dual type electrochromic devices based on PTSePA and PEDOT in detail. Neutral state of device shows grayish green color, while oxidized state reveals blue color.

2. EXPERIMENTAL

2.1. Materials

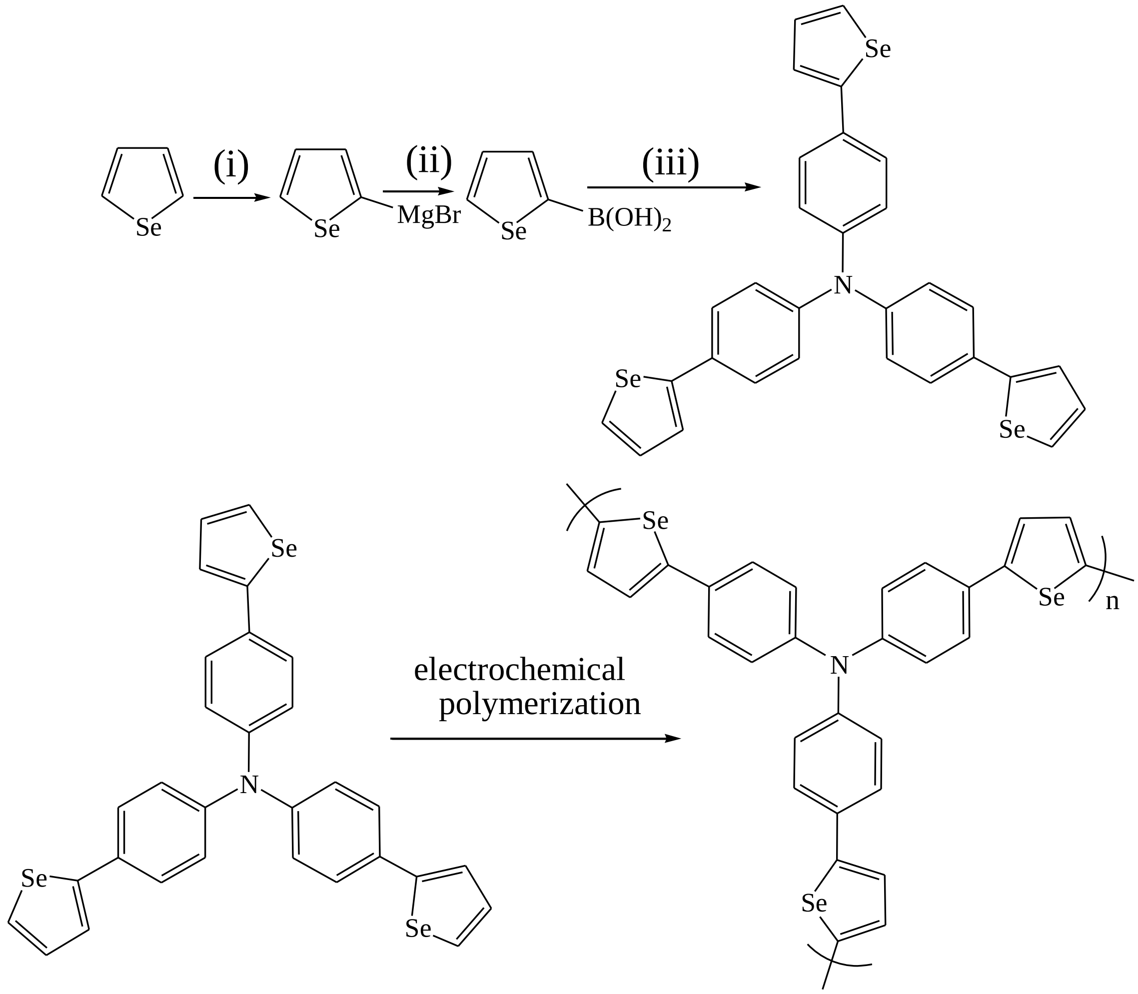
Tris(4-bromophenyl)amine, selenophene, trimethylborate ($B(OMe)_3$), tetrakis(triphenylphosphine)palladium(0) ($Pd(PPh_3)_4$) and 3,4-ethylenedioxythiophene (EDOT, 98%) were all purchased from Aldrich Chemical and used as received. Commercial high-performance liquid chromatography grade acetonitrile (ACN, Tedia Company, INC., USA) was used as received. Poly(methyl methacrylate) (PMMA), propylene carbonate (PC), n-butyllithium (n-BuLi) and lithium perchlorate ($LiClO_4$, 99.9%) were purchased from Shanghai Chemical Reagent Company and used directly without further purification. Tetrahydrofuran (THF, J&K Chemical Co. Beijing China) was distilled over Na/benzophenone prior to been used, sodium perchlorate ($NaClO_4$, Shanghai Chemical Reagent Company, 98%) was dried in vacuum at 60 ºC for 24 h before use. Other reagents were all used as received without further treatment. Indium-tin-oxide-coated (ITO) glass (sheet resistance : $< 10\ \Omega\ \square^{-1}$, purchased from Shenzhen CSG Display Technologies, China) was successively washed with ethanol, acetone and deionized water in an ultrasonic bath and then dried by a constant stream of N_2 flow.

2.2. Instrumentation

^1H NMR spectroscopy studies were carried out on a Varian AMX 400 spectrometer (Varian Co., Santa Clara, USA) and tetramethylsilane (TMS) was used as the internal standard for ^1H NMR. UV–vis spectra were performed on a Perkin-Elmer Lambda 900 UV–vis spectrophotometer (PerkinElmer Inc., Massachusetts, USA). A Canon Power Shot A3000 IS digital camera performed digital photographs of the device and polymer films.

2.3. Synthesis of tris[4-(selen-2-yl)phenyl]amine (TSePA)

Tris[4-(selen-2-yl)phenyl]amine (TSePA) was synthesized via Suzuki coupling reaction [31]. As shown in Scheme 1, 2-bromoselenophene in a dry ethylether (Et_2O) was added dropwise to a stirred suspension of magnesium powder in anhydrous Et_2O at room temperature. The obtained Grignard reagent was reacted with trimethylborate ($B(OMe)_3$) in dry tetrahydrofuran (THF) to afford (2-selenyl)boronic acid, which was then cross-coupled to triphenylamine in the presence of catalytic tetrakis(triphenylphosphine)palladium(0) ($Pd(PPh_3)_4$). The solvent was evaporated the crude product was purified by flash chromatography. The purified product was a yellow solid. Fig 1 shows the ^1H NMR ($CDCl_3$, 400 M Hz, ppm): δ= 7.12 (d, 6H), 7.31 (t, 3H), 7.40 (d, 3H), 7.49 (d, 6H), 7.91 (d, 3H).



Scheme 1. Synthetic routes of the monomer and polymer. Reagents: (i) Mg, Et_2O; (ii) $B(OMe)_3$, THF; (iii) tris(4-bromophenyl)amine, $Pd(PPh_3)_4$, THF.

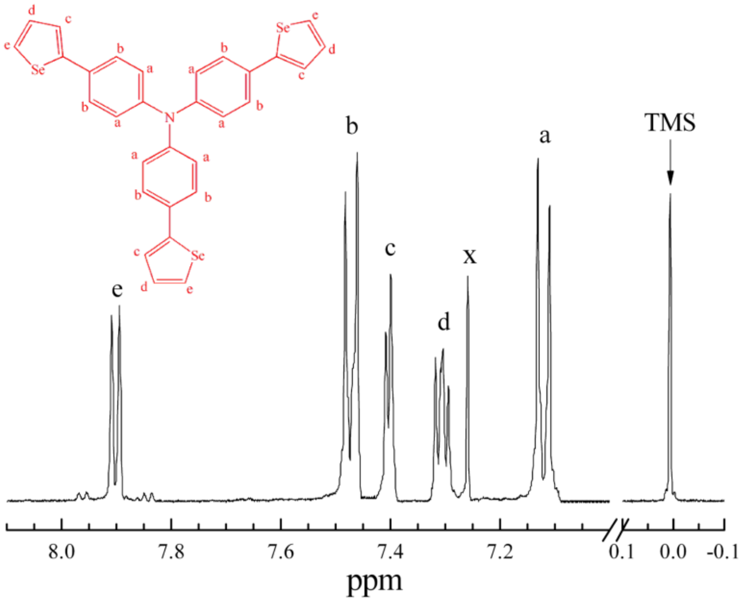


Figure 1. ^{1}H NMR spectrum of TSePA monomer in $CDCl_3$. Solvent peak located at δ=7.26 ppm is marked ‘x’.

2.4. Electrochemistry

Electrochemical synthesis and experiments were performed in a one-compartment cell with a CHI 760 C Electrochemical Analyzer (Shanghai Chenhua Instrument Co., China) under the control of a computer, employing a platinum wire with a diameter of 0.5 mm as working electrode, a platinum ring as counter electrode, and a silver wire (Ag wire) as pseudo reference electrode. The working and counter electrodes for cyclic voltammetric (CV) experiments were placed 0.5 cm apart during the experiments. All electrochemical polymerization and CV tests were performed in 0.2 M $NaClO_4$/ACN solution. The pseudo reference electrode was calibrated externally using a 5 mM solution of ferrocene (Fc/Fc^+) in the electrolyte ($E_{1/2}(Fc/Fc^+) = 0.20$ V vs. Ag wire in 0.2 M $NaClO_4$/ACN solution) [32]. All the potentials mentioned follow were *vs*. Ag wire electrode. The half-wave potential ($E_{1/2}$) of Fc/Fc^+ measured in 0.2 M $NaClO_4$/ACN solution was 0.28 V *vs*. SCE. Thus, the potential of Ag wire was assumed to 0.08 V vs. SCE [33]. All of the electrochemical experiments were carried out at room temperature under nitrogen atmosphere.

2.5. Preparation for measurements

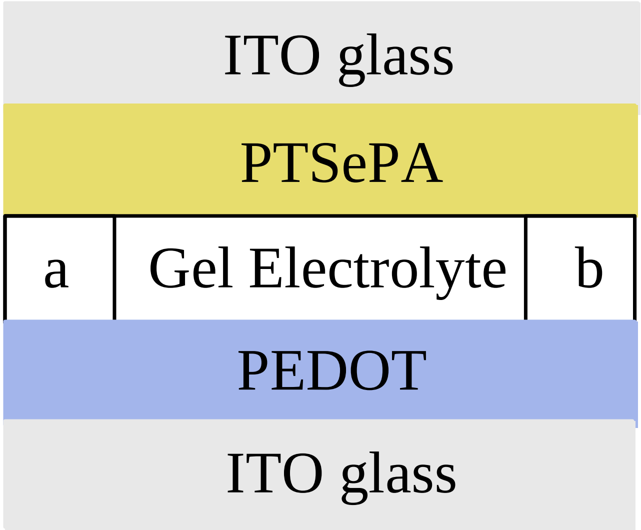
All electrochemical polymerization and CV tests were taken in 0.2 M $NaClO_4$/ACN solution. The amount of polymers deposited on platinum electrode was controlled by the integrated charge passed through the cell for electrochemical tests. After polymerization, electrochemical dedoping process was carried out in 0.2 M $NaClO_4$/ACN solution for 15 minutes, then washed with ACN for 3 times to remove the supporting electrolyte and oligomers/monomers. The spectroelectrochemical data were recorded on Perkin-Elmer Lambda 900 UV–vis spectrophotometer connected to a computer. A three-electrode cell assembly was used where the working electrode was an ITO glass, the counter electrode was a stainless steel wire, and an Ag wire was used as the pseudo reference electrode.

2.6. Preparation of the gel electrolyte

A gel electrolyte based on poly(methyl methacrylate) (PMMA) (MW: 350,000) and $LiClO_4$ was plasticized with propylene carbonate (PC) to form a highly transparent and conductive gel, ACN was also included as a low-boiling point solvent to allow easy mixing of the gel components. The composition of the casting solution by weight ratio of ACN:PC:PMMA:$LiClO_4$ is 70:20:7:3. The gel electrolyte was used for fabrication of the electrochromic device cell [34].

2.7. Fabrication of electrochromic devices (ECDs)

Electrochromic devices (ECDs) were fabricated with the two complementary polymers, where the PTSePA polymer and PEDOT functioned as the anodically and cathodically coloring material, respectively (Scheme 2). The PTSePA and PEDOT films were electrochemically deposited on ITO glass electrodes (active area: 1.8 cm×2.5 cm) at 1.2 V and 1.4 V, respectively. ECDs were fabricated by arranging the two polymer films (one oxidized, the other reduced) facing each other separated by the gel electrolyte, which supported by two pieces of plastic sheet functioned as the spacer (the structure of the ECD is shown in Scheme 2) [35,36].



Scheme 2. Multi-layers structure of ECD, a, b represents two plastic sheets with a 0.3 mm thickness, which functioned as the spacer.

3. RESULTS AND DISCUSSION

3.1. Electrochemical polymerization and characterization of PTSePA films

3.1.1. Electrochemical polymerization

The successive CV curves of 0.004 M TSePA in 0.2 M $NaClO_4$/ACN were illustrated in Fig. 2. The onset oxidation potential (E_{onset}) of TSePA in the solution was 0.70 V. Beginning with the second cycle, the onset of the anodic process is progressively shifted towards lower potentials, coherently with the growth of progressively longer oligomers. As the CV scan continued, PTSePA film is formed on the working electrode surface. The increases in the redox wave current densities imply that the amount of conducting polymers deposited on the electrode are increasing [37]. The CV curves of TSePA showed an anodic peak at 0.83 V and a cathodic peak at 0.65 V, respectively. The redox wave between 0 and 0.9 V is attributed to the radical cation formation of the amine moiety, and the oxidation at around 1.2 V is attributed to the formation of the radical cation of the selenophene group, which is lower than that of structurally similar monomer tris[4-(2-thienyl)phenyl]amine (TTPA) [38]. This is because of the higher electron donating character of selenium atom than that of sulfur atom [22]. The polymerization takes place at around 1.2 V because the radical cation formed by the oxidation of the selenophene unit is the active species for the polymerization. The polymerization proceeds through the oxidative coupling of the selenophene rings (the synthetic route is shown in Scheme 1).

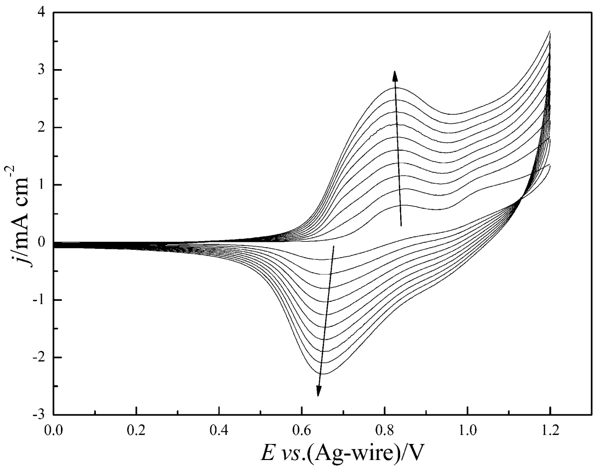


Figure 2. Cyclic voltammogram curves of 0.004 M TSePA in 0.2 M $NaClO_4$/ACN solution at a scan rate of 100 mV s^{-1}. *j* denotes the current density, *E* denotes the potential.

3.1.2. Electrochemistry of the PTSePA film

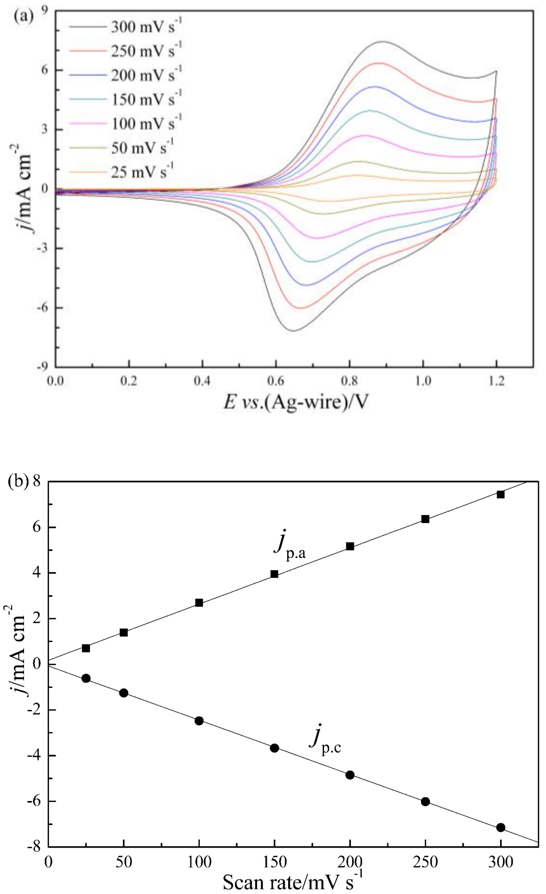


Figure 3. (a) CV curves of the PTSePA film at different scan rates between 25 and 300 mV s^{-1} in the monomer-free 0.2 M $NaClO_4$/ACN, *j* denotes the current density, *E* denotes the potential. (b) Scan rate dependence of the PTSePA, j_{pa} and j_{pc} denote the anodic and cathodic peak current densities, respectively.

Fig. 3 shows the electrochemical behavior of the PTSePA film (prepared on platinum wires by sweeping the potentials from 0 to 1.2 V for three cycles) at different scan rates between 25 and 300 mV s^{-1} in monomer-free 0.2 M $NaClO_4$/ACN solution. As can be seen from Fig. 3a, the PTSePA film exhibited a couple of redox peaks located at 0.89 V and 0.64 V, respectively. The current density (j) response was directly proportional to the scan rate, indicating that the polymer film was electroactive and adhered well to the electrode [39]. The scan rate dependence of the anodic and cathodic peak current densities showed a linear dependence on the scan rate as illustrated in Fig. 3b, which demonstrated that the electrochemical processes of the polymer were reversible and not diffusion limited [12].

3.1.3. Optical properties of TSePA monomer and PTSePA film

Fig. 4 displays the UV–vis spectra of TSePA monomer in CH_2Cl_2 and PTSePA film deposited on ITO electrode. The absorption maximum (λ_{max}) of the monomer TSePA is centered at 354 nm, the UV–vis spectra of the neutral state PTSePA film shows a maximum absorption at 363 nm and a shoulder at 434 nm, which due to the π-π* transition of the polymer backbone. The difference between the absorption of the monomer and the polymer is owing to the increased conjugation length in the polymer [40]. Compare to the λ_{max} of the structurally similar monomers reported, the λ_{max} of TSePA monomer exhibits a 55 nm red shift compare to that of triphenylamine (TPA, 299 nm), a 40 nm blue shift to that of tris[4-(5-phenylthiophen-2-yl)phenyl]amine (TPTPA, 394 nm) [41].

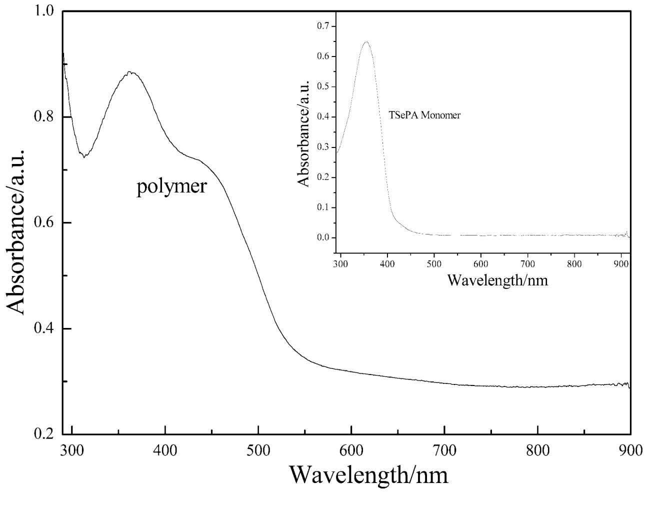


Figure 4. UV–vis spectrum: (a) TSePA monomer dissolved in DCM; (b) PTSePA film deposited on ITO electrode at the dedoped state.

In addition, the optical band gap (E_g) of polymer was calculated from its low energy absorption edges (λ_{onset}) ($E_g = 1241/\lambda_{onset}$). The E_g of the PTSePA film was calculated as 2.30 eV, which was lower than that of monomer TSePA (3.06 eV), clearly due to the extended conjugation length.

Meanwhile, not only TSePA but also TTPA and TPTPA have a reduced E_g when compared with that of TPA, indicating a greater π-delocalization along the molecule when selenophene, thiophene or 2-phenylthiophene was inserted as terminal ring in the arms. Table 1 clearly summarizes the onset oxidation potential (E_{onset}), maximum absorption wavelength (λ_{max}) and the optical band gap (E_g) of the TSePA, TTPA, TPA, TPTPA and PTSePA. HOMO energy levels of them were calculated by using the formula $E_{HOMO} = -e(E_{onset} + 4.4)$ (E_{onset} vs. SCE) and LUMO energy levels (E_{LUMO}) of them were calculated by the subtraction of the optical band gap from the HOMO levels [42].

Table 1. The onset oxidation potential (E_{onset}), maximum absorption wavelength (λ_{max}), HOMO and LUMO energy levels and optical band gap (E_g) of TSePA, TTPA, TPA, TPTPA and PTSePA.

Compounds	E_{onset}, vs.(Ag-wire) (V)	λ_{max} (nm)	E_g [a](eV)	HOMO (eV)	LUMO[b] (eV)
TSePA	0.70	354	3.06	–5.18	–2.12
TPA[c]	—	299	3.50	–5.77	–2.27
TTPA[d]	0.72	355	3.10	–5.15	–2.05
TPTPA[c]	—	394,314	2.82	–5.57	–2.75
PTSePA	0.62	363,434	2.30	–5.10	–2.80

[a] Calculated from the low energy absorption edge: $E_g = 1241/\lambda_{onset}$.

[b] Calculated by the subtraction of the optical band gap from the HOMO level.

[c] Data were taken from Ref. [41].

[d] Data were taken from Ref. [38].

3.2. Electrochromic properties of PTSePA film

3.2.1. Spectroelectrochemical properties of PTSePA film

Spectroelectrochemistry is a useful method for studying the changes in the absorption spectra and the information about the electronic structures of conjugated polymers as a function of the applied potential difference [43]. The PTSePA film was electrodeposited onto ITO electrode (the active area was 0.9 cm × 2.0 cm) with the polymerization charge of 3.2×10^{-2} C at 1.2 V. It switched between 0 and 1.2 V in monomer-free 0.2 M $NaClO_4$/ACN solution in order to obtain the in situ UV–vis spectra (Fig. 5). At the neutral state, the polymer film exhibited an absorption peak at 363 nm with a shoulder located at around 434 nm due to the π–π* transition. Upon increase of the applied potential, the intensity of the PTSePA π–π* electron transition absorption decreased while two charge carrier absorption bands located at around 750 nm and longer than 900 nm increased dramatically. The appearance of charge carrier bands could be attributed to the evolution of polaron and bipolaron bands.

Furthermore, the PTSePA film showed different colors under various potentials. The film at neutral state (0 V) showed yellow color which turned into green color at 0.80 V. With the increase of the potential, the film turned into blue color at fully doped state (1.20 V) (see inserts of Fig. 5), respectively. This electrochromic property possesses significant potential applications in smart windows or displays.

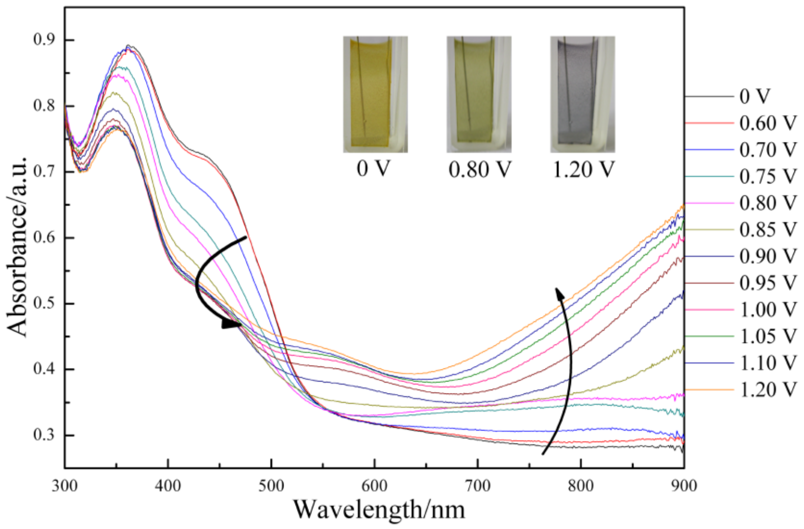


Figure 5. Spectroelectrochemical spectra of PTSePA with applied potentials between 0 V and 1.2 V in 0.2 M $NaClO_4$/ACN solution. The inset shows the various colors at different potentials

3.2.2. Electrochromic switching of PTSePA film in solution

It is important that conjugated polymers can switch rapidly and exhibit a noteworthy color change for electrochromic applications [44]. For this purpose, double potential step chronoamperometry technique was used to investigate the switching ability of PTSePA film. The dynamic electrochromic experiment for PTSePA film (coated on ITO electrode (the active area was 0.9 cm × 2.0 cm) with the polymerization charge of 3.2×10^{-2} C) was carried out at 440 nm and 850 nm in 0.2 M $NaClO_4$/ACN solution. The potential was interchanged between 0 V (the neutral state) and 1.20 V (the oxidized state) at regular intervals of 5 s for 440 nm and 850 nm, respectively. One important characteristic of electrochromic materials is the optical contrast ($\Delta T\%$), which can be defined as the transmittance difference between the redox states. As shown in Fig. 6, the optical contrasts of the PTSePA at 440 and 850 nm found to be 15.2% and 38.2%, respectively. Response time, one of the most important characteristics of electrochromic materials, is the necessary time for 95% of the full optical switch (after which the naked eye could not sense the color change) [45]. The optical response times of PTSePA were found to be 2.11 s from the reduced to the oxidized state, 0.32 s from the oxidized to the reduced state at 440 nm, 2.60 s from the reduced to the oxidized state, 0.80 s from the reduced to the oxidized state at 850 nm. Moreover, the polymer film shows similar response time when compared with that of the structurally similar polymer, poly(tris[4-(2-thienyl)phenyl]amine) (PTTPA) [38]. The satisfactory optical contrast and reasonable response time make this polymer a promising material for electrochromic devices.

The coloration efficiency (CE) is also an important parameter for the electrochromic materials. It is defined as the change in the optical density (ΔOD) for the charge consumed per unit electrode area (ΔQ) [44]. CE can be calculated by using the equations as follows:

$$\Delta OD = \lg\left(\frac{T_b}{T_c}\right) \quad \text{and} \quad \eta = \frac{\Delta OD}{\Delta Q}$$

where T_b and T_c are the transmittances before and after coloration, respectively, and η denotes the coloration efficiency (CE). CE of PTSePA film was measured as 248.5 $cm^2\ C^{-1}$ (at 440 nm), 205.4 $cm^2\ C^{-1}$ (at 850 nm), which had reasonable coloration efficiency. The PTSePA film shows a larger CE when compared with that of the structurally similar polymer PTTPA, indicating the PTSePA is easy deposited onto the ITO glass.

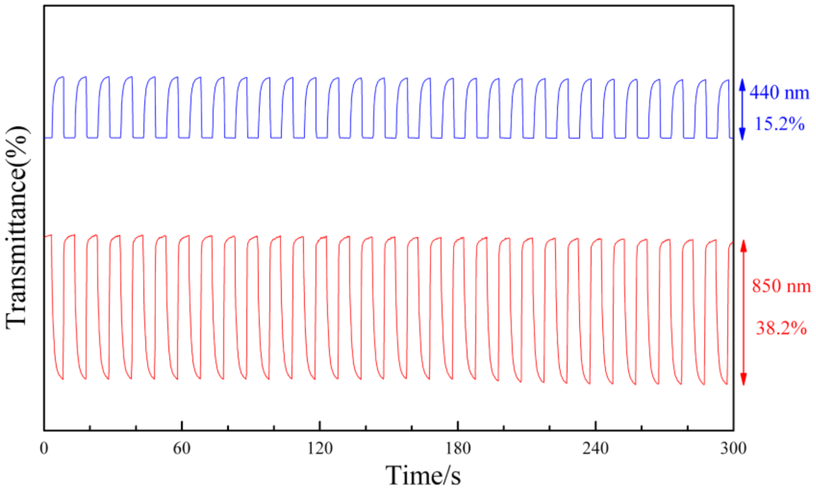


Figure 6. Electrochromic switching response for the PTSePA film monitored at different wavelengths in 0.2 M $NaClO_4$/ACN solution between 0 V and 1.20 V with residence time of 5 s for 440, 850 nm, respectively.

3.3. Spectroelectrochemistry of electrochromic devices (ECDs)

3.3.1. Spectroelectrochemical properties of ECDs

A dual type ECD consisting PTSePA and PEDOT was fabricated, after which, its spectroelectrochemical behavior was also studied. Before composing the ECD, the anodically coloring polymer film PTSePA was in fully reduced state, while the cathodically coloring polymer PEDOT was in fully oxidized state. Fig. 7 shows the spectroelectrochemical spectra of the PTSePA/PEDOT device as a function of applied potential (between 0 V and 1.35 V). The PTSePA layer was in its neutral state at 0 V. At that state, the device revealed grayish green color due to electrochromic device fabricated based on yellow PTSePA and light blue PEDOT upon the basis of color mixing theory (see inserts of Fig. 7). As the applied potential increased, the PTSePA layer started to be oxidized and the intensity of the peak due to the π–π^* transition decreased. Concurrently, the PEDOT layer was in its reduced state, which leaded to a new absorption at around 610 nm due to the reduction of PEDOT, and the dominated color of the device was blue at 1.4 V (Fig. 7).

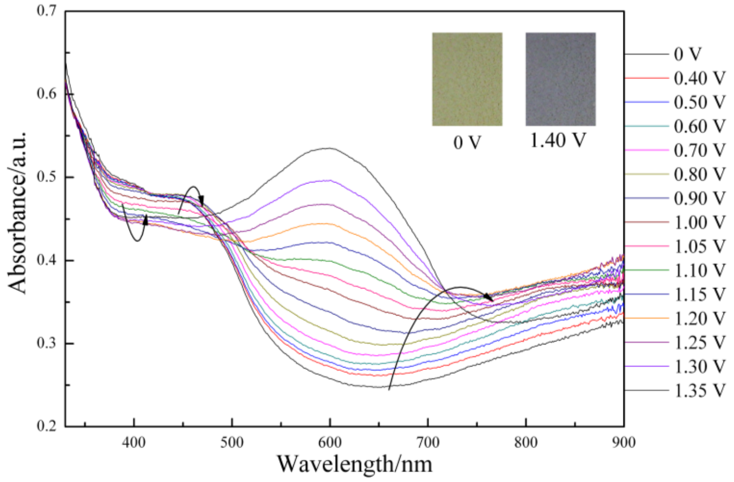


Figure 7. Spectroelectrochemical spectra of the PTSePA/PEDOT device at various applied potentials from 0 to 1.35 V, the inserts show the colors of the device at 0 V (the neutral state) and 1.4 V (the oxidized state).

3.3.2. Switching of ECD

Kinetic studies were also performed to test the percent transmittance changes and the response time of the PTSePA/PEDOT ECD. Under a potential input of 0 and 1.3 V at regular intervals of 5 s, the optical response at 610 nm was illustrated in Fig. 8. The optical contrast (Δ*T*%) was calculated to be 20.1%. The response time was found to be 1.71 s at 95% of the maximum transmittance difference from the neutral state to oxidized state and 0.64 s from the oxidized state to the neutral state. The device (active of area is 1.8 cm × 1.8 cm) also has a high coloration efficiency (CE), which was calculated to be 498.4 cm^2 C^{-1} at 610 nm. Indicating this PTSePA/PEDOT ECD has reasonable optical contrast, satisfactory response time, and high coloration efficiency.

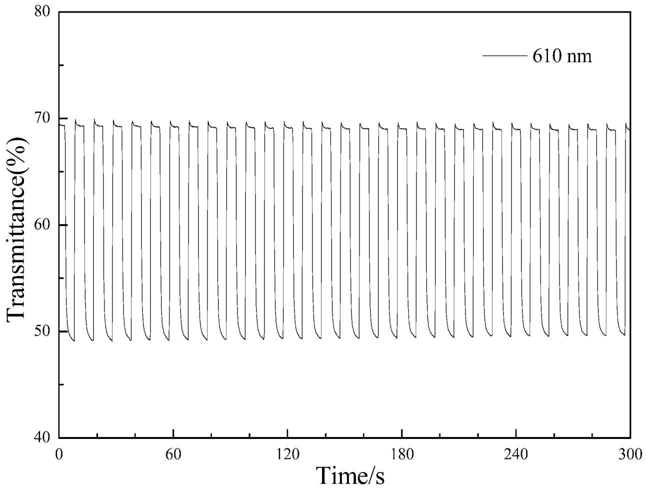


Figure 8. Electrochromic switching monitored at 610 nm for the PTSePA/PEDOT device between 0 V and 1.3 V with a residence time of 5 s.

3.3.3. Open circuit memory of ECD

The color persistence in the electrochromic devices is another important characteristic because it is directly related to its application and energy consumption during the use of ECDs [14]. The optical memory of an electrochromic material is defined as the time during which this material retains its color without applying a potential. The optical spectrum for the PTSePA/PEDOT device was monitored at 610 nm as a function of time at 0 V and 1.30 V by applying the potential for 1 s for each 100 s time interval. As shown in Fig. 9, in grayish green colored state, the device showed a true permanent memory effect since there was almost no transmittance change under the applied potential or open circuit conditions. In blue colored state, the device was rather less stable in terms of color persistence. However, this matter can be overcome by applying current pulses to freshen the fully colored states. Thus, this device shows a good optical memory. Based on this discussion, the PTSePA/PEDOT ECD is well performing under open circuit conditions, indicating this ECD has potential applications.

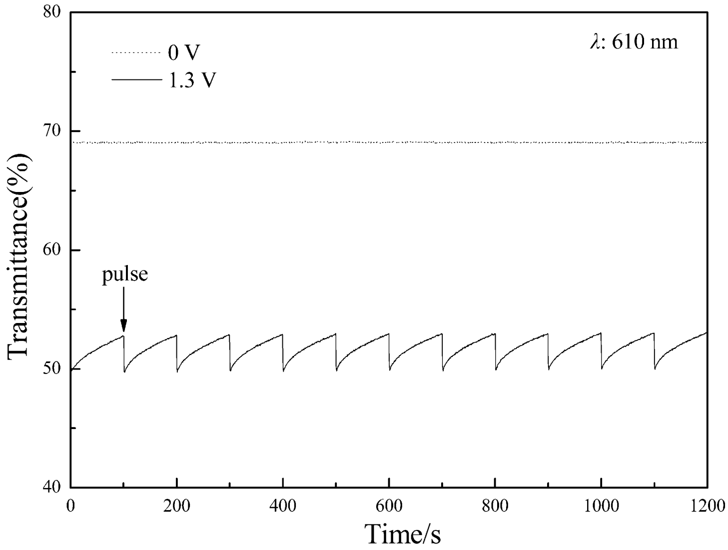


Figure 9. Open circuit stability of the PTSePA/PEDOT device monitored at 610 nm.

3.3.4. Stability of ECD

The stability of the ECD for long-term multiple redox switching between oxidized and neutral states is important for practical applications. Therefore, redox stability is another important parameter for ECD [45]. For this reason, the PTSePA/PEDOT device have been tested by cyclic voltammetry of the applied potential between −0.4 and 1.3 V with 500 mV s^{-1} to evaluate the stability of the device (Fig. 10). After 1000 cycles, 81.9% of its original electroactivity was retained accompanied by unperturbed color change from grayish green to blue, which indicates that this device has reasonable redox stability, makes this ECD a good candidate for electrochromic applications.

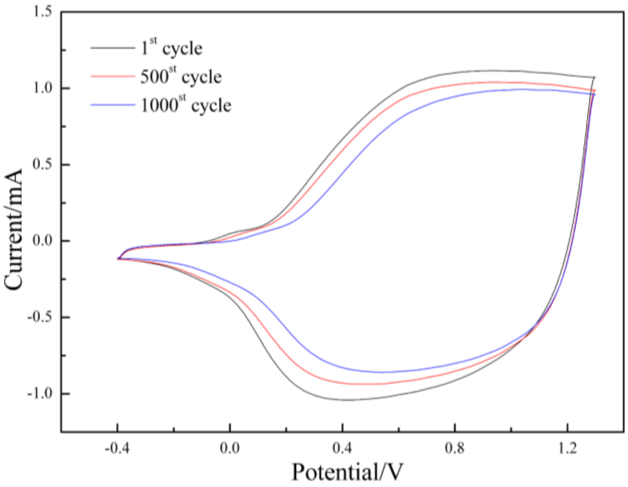


Figure 10. Cyclic voltammogram of PTSePA/PEDOT device as a function of repeated with a scan rate of 500 mV s^{-1}.

4. CONCLUSIONS

Tris[4-(selen-2-yl)phenyl]amine monomer was synthesized by Suzuki coupling reaction and then its polymer was successfully synthesized by electrochemical oxidation of the monomer in 0.2 M $NaClO_4$/ACN solution. The obtained polymer film was studied by cyclic voltammetry, UV–vis spectra. Spectroelectrochemistry reveals that PTSePA film has distinct electrochromic properties and shows three different colors (yellow, green, blue) under various potentials. Maximum contrast (ΔT%) and response time of the PTSePA film were measured as 15.2% and 2.11 s at 440 nm, 38.2% and 2.60 s at 850 nm, respectively. The dual type ECD based on PTSePA and PEDOT was constructed and characterized. Electrochromic switching study shows that optical contrast (ΔT%) and response time are 20.1% and 1.71 s at 610 nm, respectively. The CE of the ECD was calculated to be 498.4 cm^2 C^{-1}. This ECD also shows reasonable redox stability with unperturbed color change from grayish green to blue. In light of the excellent features above, the selenophene substituted TPA-based poly(tris[4-(selen-2-yl)phenyl]amine) (PTSePA) could be a good candidate as an anodic electrochromic material.

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