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Synthesis and Electrochromic Properties of Star-Shaped Oligothiophene Derivatives with Triphenylamine as Core

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Two star-shaped oligothiophene derivatives with triphenylamine as core, Tris[4-(2-thienyl)-phenyl]amine (3TPA) and Tris[4-(5-cyano-2-thienyl)-phenyl]amine (3TPA-3CN) were synthesized and characterized for photophysical, electrochemical and electrochromic properties. The results show that introduction of cyano group to the α-position of thiophene unit of 3TPA-3CN makes the maximum absorption red-shifted in comparison with those of 3TPA, but leads the oxidation potentials shift to positive value. Two electrochromic devices were fabricated using 3TPA and 3TPA-3CN as electroactive layer, and the electrochromic properties of both compounds were studied. 3TPA-3CN exhibits reversible, clear color change from yellow to orange on electrochemical doping and dedoping. 3TPA is electropolymerized firstly, and then switches the colors when the applied potential changes.

Keywords: Oligothiophene Derivative, Triphenylamine, Cyano Group, Electrochromism.

1. INTRODUCTION

Electrochromic (EC) materials exhibit a reversible change in optical absorption or transmittance upon electrochemical redox. Ever since the discovery of the EC effect, great efforts have been made with inorganic compounds, organic molecules, and π-conjugated polymers[1,2] for different technological applications, such as construction of smart windows, rear-view mirrors, optical displays, light-emitting diodes, camouflage materials and other electrochromic devices (ECDs).[3–7] Studies on ECDs began with inorganic compounds such as tungsten trioxide (WO_3) and iridium dioxide (IrO_2). In recent years, organic materials (viologens, metal phtalocyanines, conjugated oligomers and polymers) have received much attention for electrochromic applications[8] because of the different colors observed during switching among their different redox states. Conjugated oligomers and polymers are used as electroactive layers due to their ease of color tuning properties, faster switching speeds, high contrast and flexible chemical-structure modification.[9–11]

The triphenylamine (TPA) unit possesses a three-dimensional structure owing to the noncoplanarity of the three phenyl substituents, which makes molecules containing TPA unit exhibit good solubility. Furthermore, TPA derivatives have high hole mobility and are widely used as hole-transporting materials in organic light-emitting diodes.[12] Many star-shaped molecules consisting of a TPA core substituted by oligophenylenes, 2-phenylthiophene, or fluorene have been designed and synthesized for the applications as organic field-effect transistors (OFETs), light-emitting diodes (LEDs) and organic photovoltaic devices.[13–22] However, the use of TPA-based materials for electrochromic devices has been scarcely considered.

In our previous work, we have synthesized several star-shaped oligothiophene derivatives such as X-5T, X-5T-2CN, et al.[23,24] It was found that these compounds showed reversible and clear color changes on electrochromic doping and dedoping. We report herein the synthesis and properties of two star-shaped triphenylamine oligothiophenes, which are 3TPA and 3TPA-3CN, and their application in electrochromic devices.

2. EXPERIMENTAL DETAILS

2.1. Materials

Tris[4-(2-bromo)-phenyl]amine, 2-thiopheneboronic acid, *bis*(triphenylphosphine)palladium dichloride ($Pd(PPh_3)_2Cl_2$), *N*-chlorosulfonyl isocyanate (CSI) and *N*,*N*-dimethylformamide (DMF) were used as received from the suppliers. Dichloromethane for electrochemistry measurements

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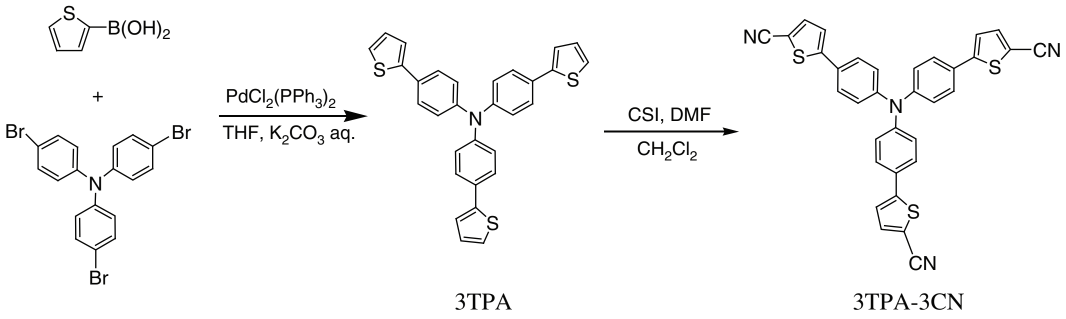


Scheme 1. Sythetic route of the star-shaped oligothiophenes.

was dried over calcium oxide and freshly distilled prior to use. All other chemicals were used as received.

2.2. Synthesis

The synthetic routes for the target products 3TPA and 3TPA-3CN are described in Scheme 1. Both of two compounds were characterized by IR, ^{1}HNMR and mass spectrometry.

Tris[4-(2-thienyl)-phenyl]amine (3TPA) was prepared by Suzuki coupling reactions according to the methods described in the literature.[25] To a solution of tris[4-(2-bromo)-phenyl]amine (1.45 g, 3 mmol) and 2-thiopheneboronic acid (1.92 g, 15 mmol) in 200 mL of tetrahydrofuran (THF), were added $Pd(PPh_3)_2Cl_2$ (90 mg) and 150 mL of 2 M aqueous K_2CO_3 solution. The mixture was heated to reflux for 48 h and then poured into a saturated solution of ammonium chloride and extracted with dichloromethane three times. The combined organic phase was then washed with brine and dried over anhydrous sodium sulfate, filtered and the solvent removed in *vacuo*. The solid residue was purified by silica-gel column chromatography to give a pale yellow crystalline solid. Yield: 0.88 g (59%). ^{1}HNMR (400 MHz, $CDCl_3$, ppm): 7.61 (d, 6H, PhH), 7.45 (d, 3H, ArH), 7.43 (d, 3H, ArH), 7.12 (t, 3H, ArH), 7.09 (d, 6H, PhH). ^{13}C NMR (400 MHz, $CDCl_3$, ppm), δ: 145.9, 143.0, 128.7, 128.4, 126.6, 125.0, 124.1, 123.0. MS (APCI): $m/z = 492.1$ (M^+). $\nu_{\max}$ (KBr) (cm^{-1}): 3105, 3024, 2924, 2853, 1596, 1531, 1495.

Tris[4-(5-cyano-2-thienyl)-phenyl]amine (3TPA-3CN) was prepared by the reaction of TPA (0.4 g, 0.81 mmol) with CSI (0.7 mL, 8 mmol) in methylene chloride at room temperature under a nitrogen atmosphere for 4 h, and then DMF (0.62 mL, 8 mmol) was added. The solution was stirred for 15 h and then hydrolyzed with water. The aqueous solution was extracted with dichloromethane and washed with brine and water. The solvent was removed under reduced pressure to give 3TPA-3CN. The product was purified by silica gel column chromatography. Yield: 0.27 g (59%). ^{1}H NMR (400 MHz, $CDCl_3$, ppm), δ: 7.60 (d, 3H, ArH), 7. 54 (d, 6H, PhH), 7.24 (d, 3H, ArH), 7.18 (d, 6H, PhH). ^{13}C-NMR (400 MHz, $CDCl_3$, ppm), δ: 151.3, 147.5, 138.5, 127.7, 127.6, 124.7, 122.8, 114.3, 107.8. MS (APCI): $m/z = 566.2$ (M^+). IR (KBr, cm^{-1}): 2212 (ν_{CN}).

2.3. Measurements

The ^{1}H NMR and ^{13}C NMR spectra (Bruker AVANCE 400) were recorded at 25 °C in deuterated chloroform and TMS as internal standard. IR spectra were recorded by a Bruker VECTOR33 IR spectrum. Mass spectra were obtained using a Shimadzu GCMS-QP2010 mass spectrometer. The UV-vis spectra were taken as solutions in dichloromethane on a Helio-λ spectrophotometer (Thermo Electron Corporation). Cyclic voltammetry experiments were performed on an electrochemical analyzer (model CHI750A). A carbon working electrode, a platinum wire auxiliary (counter) electrode and a saturated Ag/Ag$^+$ reference electrode were utilized with a scan rate of 50 mV s^{-1}. The solvent used in the experiments was dichloromethane and the supporting electrolyte was 0.1 M tetrabutylammonium pechlorate. Atomic force microscopy (AFM) experiments were carried out using a SEIKO SPI3800N in tapping mode. Thermal transition behaviors of 3TPA and its polymer were investigated by DSC (NETZSCH DSC 204F1 Phoenix.

3. RESULTS AND DISCUSSION

3.1. Optical Properties

The UV-vis absorption spectra recorded for 3TPA and 3TPA-3CN in dichloromethane solutions are showed in Figure 1(a). The $\lambda_{\max}$ for the π to π^* transition is found at 366 nm for 3TPA, and 396 nm for 3TPA-3CN, respectively. The maximum absorption of 3TPA-3CN is red-shifted in comparison with that of 3TPA, which can be assigned to the extension of the conjugated π-system due to the terminal electron-withdrawing cyano groups.

The solid-state UV-vis spectras for both 3TPA and 3TPA-3CN are shown in Figure 1(b). As expected and are common in many conjugated oligomers, the absorption spectra of thin films show red-shifts (3TPA at 381 nm and 3TPA-3CN at 490 nm) and slight band broadening as compared to those of the solution spectra, which could be ascribe to a more extended structure with fewer conformational defects because of the presence of interchain interactions in the solid state through π–π stacking.

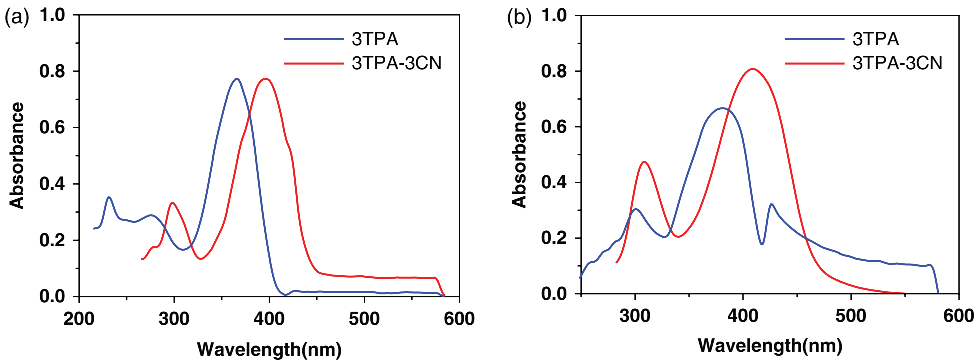


Figure 1. UV-vis absorption spectra of 3TPA and 3TPA-3CN: a, in CH_2Cl_2; b, in film.

3.2. Electrochemical Properties

The electrochemical properties of these compounds were investigated by cyclic voltammetry, and the results show in Figure 2. 3TPA exhibits two oxidation waves with the onset of potential E_{ox}^{onset} at 0.72 V versus Ag/Ag$^+$ and 1.25 V versus Ag/Ag$^+$ and a reduction wave with E_{red}^{onset} at −0.68 V. 3TPA-3CN exhibits two oxidation waves with E_{ox}^{onset} at 0.85 V versus Ag/Ag$^+$ and 1.51 V versus Ag/Ag$^+$ and one reduction wave with E_{red}^{onset} at −0.61 V versus Ag/Ag$^+$. The results suggest that the electron-withdrawing cyano group induces an increase of the oxidation potential and a decrease of the reduction potential compared to compound 3TPA. As we reported in our previous work, only when the substance could be oxided or reduced under the applied voltage will the electrochromism happen. Therefore, the two compounds could be used as electrochromic materials. Compared with 3TPA, the oxidation potential of 3TPA-3CN is shifted to somewhat positive value due to the electron-drawing effect of cyano group.

3.3. Surface Morphology

The morphology of film surface of 3TPA-3CN was studied by AFM, and the result is shown in Figure 3. The AFM image indicates that there are many rod-like aggregations on the surface of the active layer. These aggregations are in nanoscale size, and arrange in a certain order. However, the influence of the morphology to its electrochromic property remains to be further studied.

3.4. Electrochromic Properties

In order to study the electrochromic properties of 3TPA and 3TPA-3CN, two electrochromic devices were fabricated (the structure of device showed in Fig. 4). 3TPA and 3TPA-3CN were deposited by vacuum deposition on indium-tin-oxide (ITO)-coated glass substrate, respectively. The thicknesses of these films were about 80–100 nm. The ITO-coated glass and a platinum wire were serviced as the electrode. A 0.1 M solution of tetra-*n*-butylammonium perchlorate in acetonitrile was used as the supporting electrolyte. Electrochemical doping and dedoping were carried out by applying a voltage to the electrode. The color changes were monitored by a Model Helios-γ spectrophotometer (Thermo, Ltd.).

The results show that quickly reversible, clear color change have occurred in both electrochromic systems (Fig. 5). When the applied external potential is raised from 0 to 2.6 V, the color of 3TPA-3CN film changes from yellow to orange. When the potential is decreased to −1.4 V, the color changes from orange to yellow. The corresponding absorption spectral change of 3TPA-3CN is shown in Figure 5(b). The absorbance changes were noted as the potential was changed. When the 3TPA-3CN

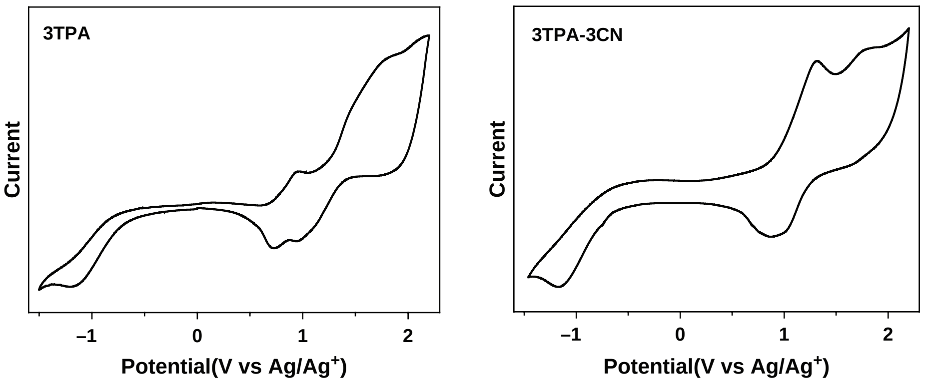


Figure 2. Cyclic voltammograms of 3TPA and 3TPA-3CN in CH_2Cl_2.

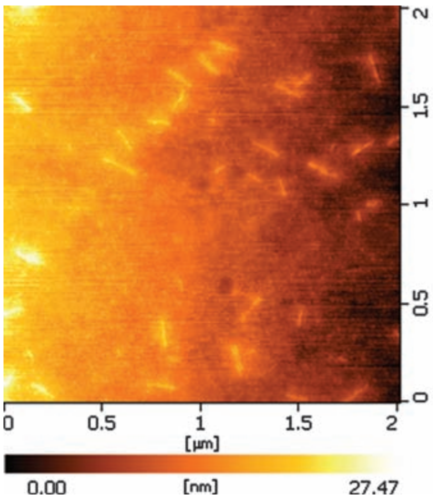


Figure 3. AFM image of 3TPA-3CN onto ITO/glass surface.

is oxidized, two peaks appear at about 308 nm and 406 nm in its absorption spectrum. Upon reduction, the absorption band at 308 nm decreases whereas the absorption bands at 406 nm starts to intensify simultaneously. The results show that 3TPA-3CN is an anode electrochromic material, and its possible electrochromic mechanism is described in Scheme 2. As the potential is increased to 2.6 V, electrons are lost and cation radicals of 3TPA-3CN formed. At the same time, 3TPA-3CN film changes its color from yellow to orange. When electrochemical dedoping is carried out, cation radicals of 3TPA-3CN obtain electrons to become neutral molecules, which corresponding color change from orange to yellow.

Meanwhile, the 3TPA exhibits different electrochromic characters from 3TPA-3CN. The color of 3TPA films is pale yellow. When the applied potential is raised from 0 to 2.6 V, the color of 3TPA film changes from pale yellow to navy blue [Fig. 6(a)]. By further applying potential down to −0.8 V, the color of the film changes from navy blue to yellow [Fig. 6(b)]. During the progress of oxidation and reduction, the film changes color between navy blue and yellow, but the original color of 3TPA could not be observed. Enlightened by the electropolymerization of oligothiophene reported, we deduce that 3TPA firstly electropolymerizes (formed polymer P3TPA) and then dopes when the potential (2.6 V) is applied continually between the ITO electrode and the counter electrode. The neutral P3TPA film is yellow. When the applied potential switches between 2.6 and −0.8 V, the polymer film of P3TPA changes its color between navy blue and yellow. The UV-vis spectrum change of P3TPA with different applied potentials is shown in Figure 5(c). Two new absorption

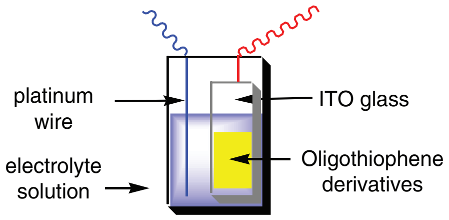


Figure 4. Schematic diagram of electrochromic devices: ITO/electrochromic active layer/electrolyte solution/Pt.

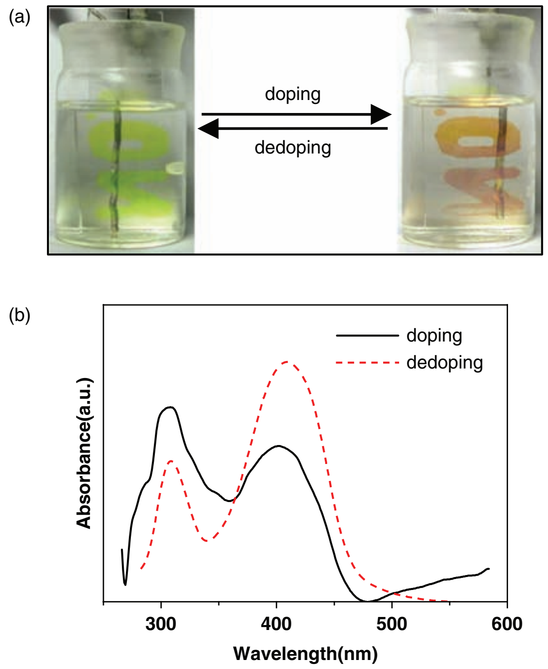
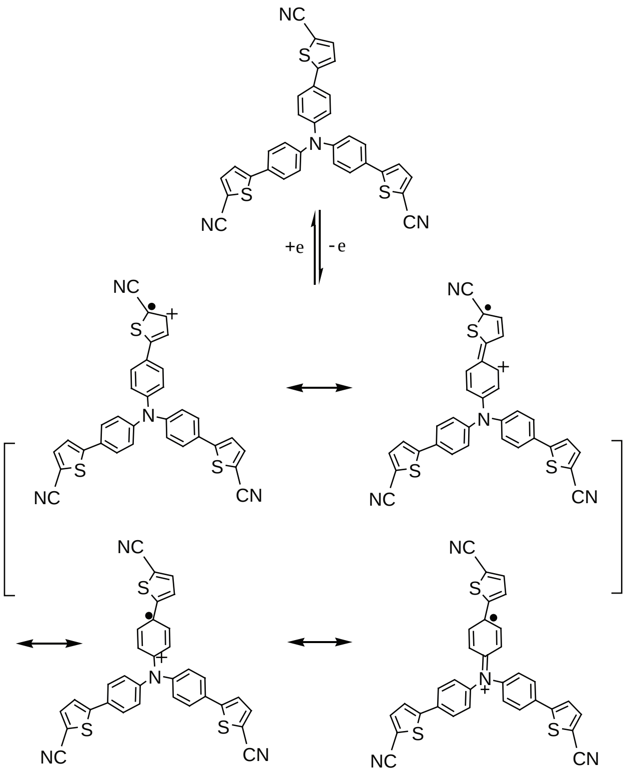


Figure 5. Electrochromism of 3TPA-3CN (a) and UV-vis absorption spectra on electrochemical doping and dedoping (b).



Scheme 2. Electrochromic mechanism of 3TPA-3CN.

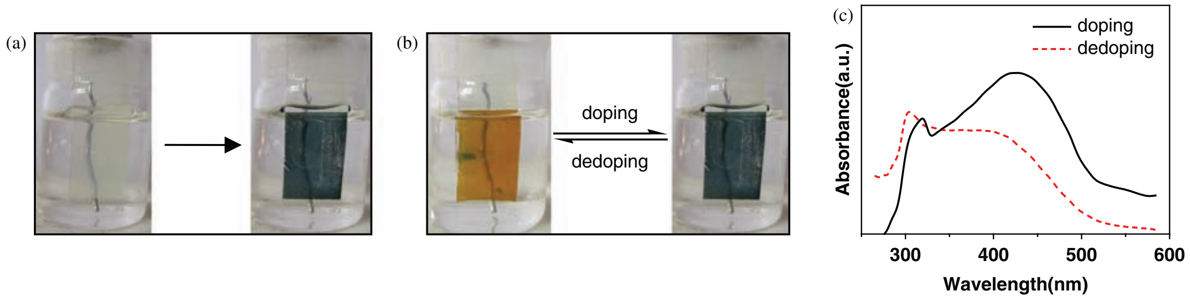
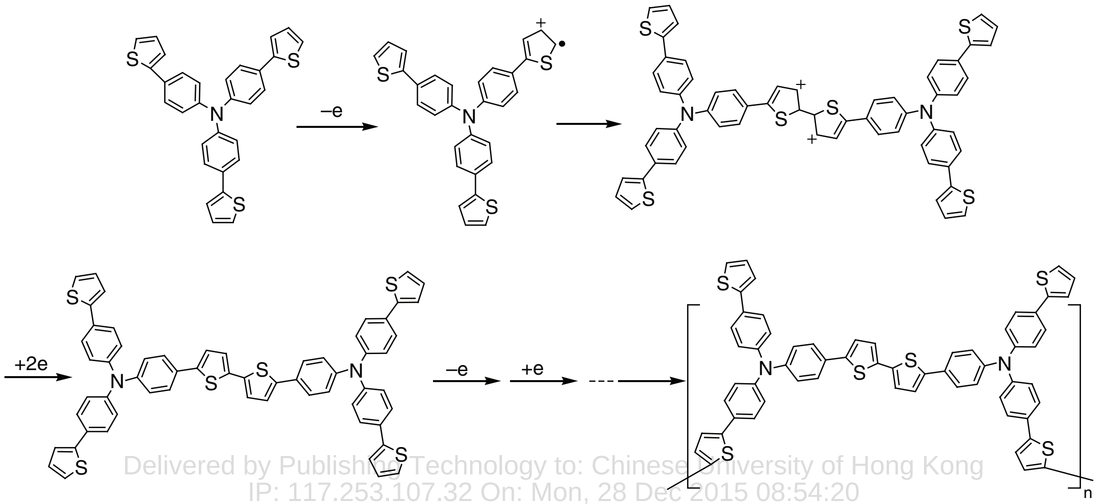
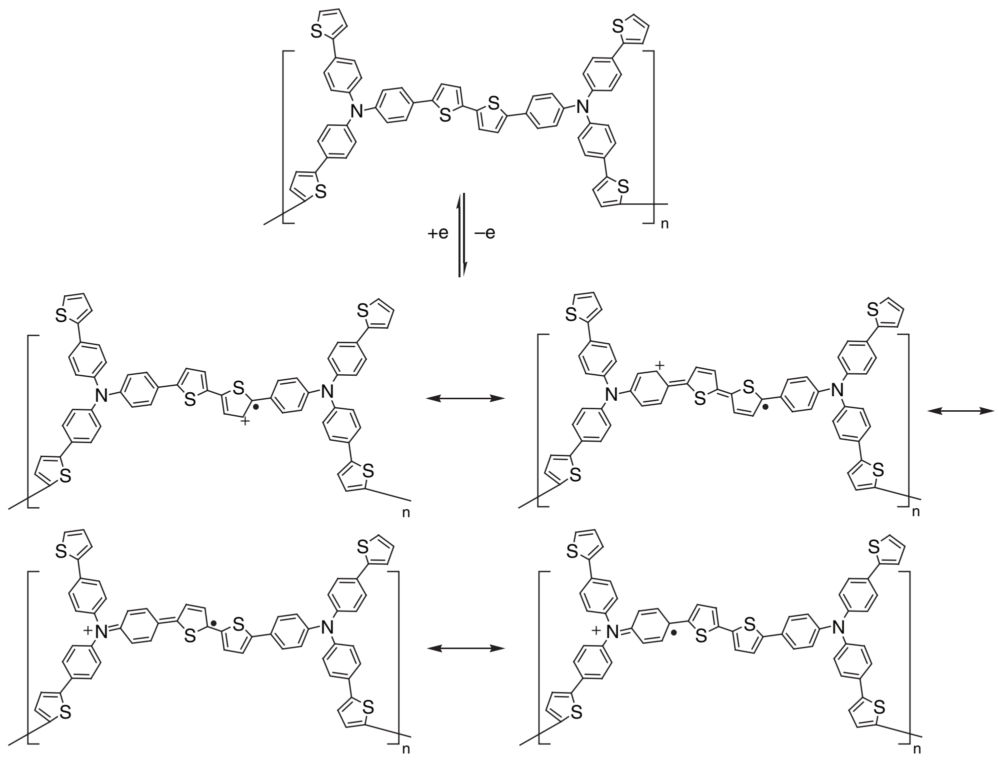


Figure 6. Electrochromism of 3TPA. (a): Irreversibale change; (b): Reversibale change; (c): UV-vis absorption spectra on electrochemical doping and dedoping.



Scheme 3. Electropolymerized mechanism of 3TPA.



Scheme 4. Electrochromic mechanism of poly(3TPA).

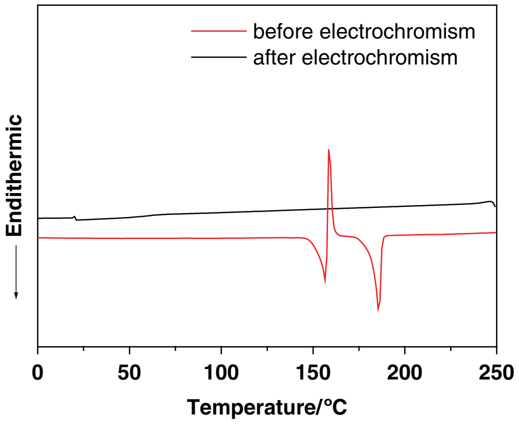


Figure 7. DSC curves of 3TPA before and after electrochromism.

peaks at 319 nm and 425 nm occur upon applying positive potentials for P3TPA. As the potential is decreased to −0.8 V, the absorption peak at 319 nm blue-shifts to 304 nm, while the other peak weakens. We describe possible electropolymerized mechanism of 3TPA in Scheme 3. When a positive voltage is applied, 3TPA loses electrons to form cation radicals, and then cation radicals react with each other to generate dications, which rapidly obtain electrons to form dimers. The dimers can also lose electrons to generate cation radicals on positive potential. These reactions are repeated continuously when the potential is maintained until a polymer is formed. Upon oxidation, the color of the polymer is navy blue at −0.8 V (reduction form), and the color is yellow. The electrochromic mechanism is showed in Scheme 4. We can speculate from above results that oligothiophenes without α-subtitution are easily electropolymerized when a potential is applied.

In order to prove the polymerization of 3TPA during electrochromic process, DSC testing for P3TPA (compound collected from the ITO slide after electrochromic test) and 3TPA were studied, and the results are showed in Figure 7. There are two endothermic peaks at 148 °C and 180 °C and one exothermic peak at 158 °C observed for 3TPA, while no any endothermic or exothermic peak for P3TPA. The results in some way prove our speculation about the polymerization of 3TPA.

4. CONCLUSION

Two star-shaped oligothiophene derivatives with phenylamine core, 3TPA and 3TPA-3CN, have been synthesized and investigated in term of their electronic and optical properties. Introduction of electron-drawing cyano group to the α-position of thiophene unit makes the maximum absorption of 3TPA-3CN red-shift in comparison with that of 3TPA, but leads the oxidation potentials shift to a little positive value. Both oligothiophene derivatives reveals valuable electrochromic characteristics. 3TPA-3CN is found to undergo reversible, clear colour change on electro-chemical doping and dedoping. Whereas 3TPA is electropolymerized firstly, and then switches the colors when the applied potential changed. These two star-shape compounds based on thiophene and triphenylamine will be the multipurpose materials attracted increasing attention.

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