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Synthesis and electrochromic properties of star-shaped oligomers with phenyl cores

Jinming Zeng[a], Xiaoyuan Zhang[a], Xiaoting Zhu[a], Ping Liu*[a]

Abstract: A series of star-shaped conjugated oligomers, 1,3,5-tri(2'-thienyl) benzene (3TB), 1,3,5-tri(3',4'-ethylenedioxythienyl) benzene (3EB), 1,3,5-tri[5',2''-(3'',4''-ethylenedioxy-thienyl)-2'-thienyl] benzene (3ETB), and 1,3,5-tri[5',2''-(3'',4''-ethylenedioxy-thienyl)-2'-thienyl]-4-(3',4'-ethylenedioxythienyl)benzene (3TB-4EDOT), were synthesized. The star-shaped polymer, poly(1,3,5-tri[5',2''-(3'',4''-ethylenedioxythineyl)-2'-thienyl]benzene) (P3ETB), was also prepared. The electrochemical and electrochromic properties of these conjugated oligomers and polymer were investigated. These oligomer and polymer films showed reversible, clear color changes upon electrochemical doping and dedoping. The color of the P3ETB film reversibly changed from orange to blue under doping and dedoping. The switching times for doping and dedoping were 1.2 and 0.9 s, respectively.

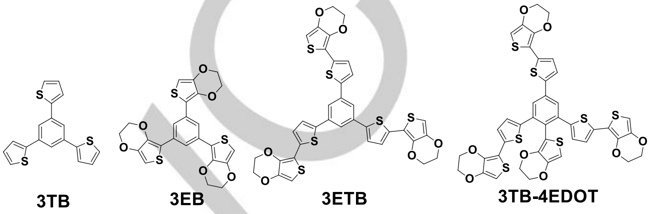
Electrochromism is a phenomenon in which the optical characteristics of a material can be tuned by applying voltage.[1] In recent decades, electrochromic materials have attracted considerable attention because of their potential application in smart windows, antiglare rearview mirrors, and displays.[2]

Electrochromic materials include inorganic compounds and conjugated organic compounds.[3] Compared with inorganic electrochromic materials such as tungsten trioxide,[4] conjugated organic compounds are perhaps more promising as electrochromic materials because of the ability to fine-tune their molecular structure, and their high optical contrast and fast switching times.[5]

Research on organic thin-film electrochromic materials has largely focused on line-shaped conjugated polymers,[6] such as polythiophene, polypyrrole, polyaniline, and poly(3,4-ethylenedioxythiophene) (PEDOT). In our previous work,[7] a series of line-shaped conjugated oligothiophene derivatives were synthesized. Solid films of these line-shaped oligothiophene derivatives showed reversible, clear color changes upon electrochemical doping and dedoping. We have also synthesized star-shaped conjugated oligothiophene derivatives,[8] and studied their electrochromic properties. In general, the color stability of organic electrochromic materials depends on the stability of the ion radical. Thus, the stability of the ion radical of organic electrochromic materials is very important. Star-shaped oligomers can offer advantages in terms of higher stability of the ion radical, compared with line-shaped oligomers.

Many star-shaped conjugated oligomers have recently been synthesized, and their electrochemical and optical properties have been well studied. However, their electrochromic properties have received little attention.

In this study, a series of star-shaped conjugated oligomers, 1,3,5-tri(2'-thienyl)benzene (3TB), 1,3,5-tri(3',4'-ethylenedioxythineyl) benzene (3EB), 1,3,5-tri[5',2''-(3'',4''-ethylenedioxythineyl)-2'-thienyl] benzene (3ETB), and 1,3,5-tri[5',2''-(3'',4''-ethylenedioxythineyl)-2'-thienyl]-4-(3',4'-ethylenedioxythineyl)benzene (3TB-4EDOT) (Scheme 1) were synthesized, and their electrochromic properties were investigated.



Scheme 1 Molecular structures of 3TB, 3EB, 3ETB, and 3TB-4EDOT.

The electronic absorption spectra and fluorescence emission spectra are important parameters for conjugated compounds. Figure 1a shows the electronic absorption spectra of 3TB, 3EB, 3ETB, and 3TB-4EDOT in DCM. They all absorbed in the wavelength range of 235-428 nm. The maximum absorption peaks of 3TB, 3EB, 3ETB, and 3TB-4EDOT were located at 293, 302, 369, and 367 nm, respectively. The band edge wavelengths (λ_{edge}) of 3TB, 3EB, 3ETB, and 3TB-4EDOT were located at 330, 345 426, and 426 nm, respectively. From the formula $E = 1240 / \lambda_{edge}$, the optical band gaps (E_g^{opt}) of 3TB, 3EB, 3ETB, and 3TB-4EDOT were calculated to be 3.76, 3.54, 2.91, and 2.91 eV, respectively. Figure 1b shows the fluorescence emission spectra of 3TB, 3EB, 3ETB, and 3TB-4EDOT in DCM. The maximum emission peaks of 3TB, 3EB, 3ETB, and 3TB-4EDOT were located at 370, 378, 423, and 448 nm, respectively. The electronic absorption spectra and fluorescence spectra indicated that these oligomers all possessed semiconductor properties.

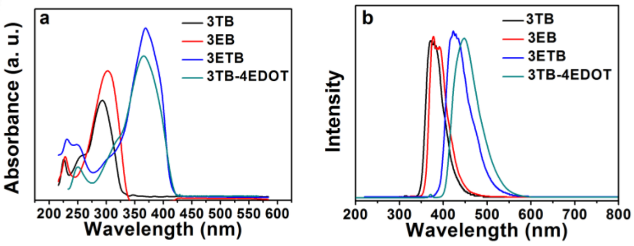


Figure 1 (a) Electronic absorption spectra and (b) fluorescence emission spectra of 3TB, 3EB, 3ETB, and 3TB-4EDOT.

Electrochemical cyclic voltammetry (CV) experiments were performed to determine the energy levels of the highest occupied molecular orbital and lowest unoccupied molecular orbital of the conjugated compounds. The cyclic voltammograms of 3TB, 3EB, 3ETB, and 3TB-4EDOT were carried out in DCM solution containing 0.1 M TBAP. A saturated calomel electrode, platinum wire, and glassy carbon were used as the reference, counter, and working electrodes, respectively. The initial oxidation potentials (E_{ox}^{onset}) of 3TB, 3EB, 3ETB, and 3TB-4EDOT were located at 1.50, 0.85, 0.65, and 0.66 V verses SCE, respectively. The initial reduction potentials (E_{red}^{onset}) of 3TB, 3EB, 3ETB, and 3TB-4EDOT were located at –0.85, –0.75, –0.80, and –0.75 V verses SCE, respectively. This indicated that

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electrochromic devices containing these star-shaped oligomers as active layers might have low driving voltages. Table 1 shows photoelectric properties of 3TB, 3EB, 3ETB, and 3TB-4EDOT. The CV results also indicated that these oligomers possessed semiconductor properties.

Table 1 Photoelectric properties data of 3TB, 3EB, 3ETB, and 3TB-4EDOT

Compound	λ_{max}/nm (absorption)	λ_{edge} /nm	λ_{max}/nm (emission)	$E_g^{opt\,[a]}$ /eV	E_{ox}^{onset} /V*vs.*SCE	E_{red}^{onset} /V*vs.*SCE	$E_g^{electro\,[b]}$ /eV
3TB	293	330	370	3.76	1.5	-0.85	2.35
3EB	302	345	378	3.54	0.85	-0.75	1.60
3ETB	369	426	423	2.91	0.65	-0.80	1.45
3TB-4EDOT	367	426	448	2.91	0.66	-0.75	1.41

[a] E_g^{opt} *(eV)= 1240/*λ_{edge}; E_g^{opt} : the optical band gap. [b] $E_g^{electro}$ (*eV*): the electrochemical band gap.

Electrochromic devices were fabricated to investigate the electrochromic properties of the star-shaped oligomers. The device structure was an indium tin oxide (ITO) glass slide (or ITO PET slide)/electrochromic active layer/gel electrolyte/ITO glass slide (or ITO PET slide). Figure 2 shows a schematic of the structure of the electrochromic device.

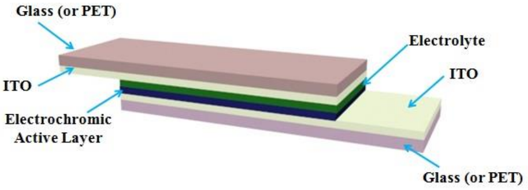

Figure 2 Schematic of the electrochromic device.

3TB, 3EB, 3ETB, and 3TB-4EDOT were deposited on ITO glass slides by vacuum deposition. In the devices, ITO glass slides were used as the electrode, and the conducting gel was used as the semi-solid state electrolyte. The gel electrolyte consisted of PMMA, TBAP, ACN, and PC (7:3:70:20, mass ratio). Electrochemical doping and dedoping were performed using the electrochromic cycling tester.

Figure 3 shows electronic absorption spectra and digital photographs of devices containing 3TB, 3EB, 3ETB, and 3TB-4EDOT, upon electrochemical doping and dedoping. Table 2 shows the colors of 3TB, 3EB, 3ETB, and 3TB-4EDOT solid state films under neutral conditions, and their colors upon electrochemical doping and dedoping. The color of the 3TB solid state film changed from colorless to light green upon applying +2.8 V, and then from light green to yellow-brown upon applying –2.0 V. The change in color from light green to yellow-brown is reversible. The color of the 3EB solid state film changed from colorless to red upon applying +2.2 V, and then from red to yellow upon applying –1.2 V. The change in color from red to yellow is reversible. The color of the 3ETB solid state film changed from light yellow to blue upon applying +1.5 V, and then from blue to orange upon applying –0.8 V. The change in color from blue to orange is reversible. The color of the 3TB-4EDOT solid state film changed from colorless to blue upon applying +2.0 V, and then from blue to orange upon applying –1.5 V. The change in color from blue to orange is reversible. However the solid state films of 3TB, 3EB, 3ETB, and 3TB-4EDOT could not change back to their intrinsic colors (colorless, colorless, light yellow, and colorless, respectively) upon electrochemical dedoping. One possible reason for this was that they electropolymerized to their corresponding polymers P3TB, P3EB, P3ETB, and P(3TB-4EDOT)) upon electrochemical doping, respectively.[9] The results indicated that P3TB, P3EB, P3ETB, and P(3TB-4EDOT) had clear, reversible color changes upon electrochemical doping and dedoping.

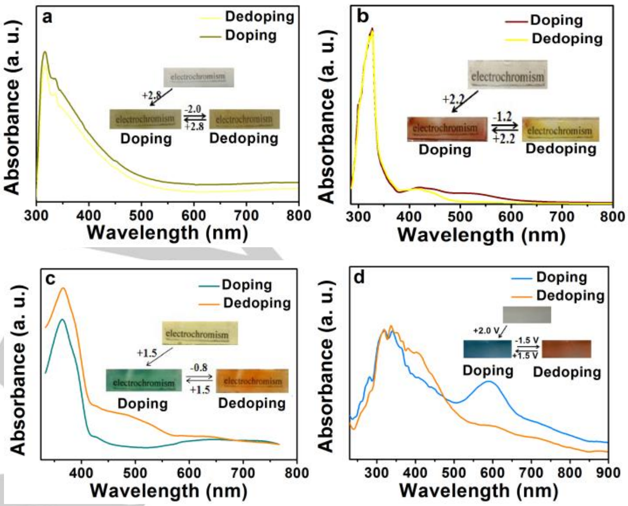

Figure 3 Electronic absorption spectra and digital photographs of the (a) 3TB, (b) 3EB, (c) 3ETB, and (d) 3TB-4EDOT, upon electrochemical doping and dedoping.

Table 2 Colors of 3TB, 3EB, 3ETB, and 3TB-4EDOT films upon electrochemical doping and dedoping.

Eletrochromic active layer	intrinsic color	Doping state	Dedoping state	Doping voltage/V	Dedoping voltage/V
3TB	colorless	light green	yellow-brown	+2.8	-2.0
3EB	colorless	red	yellow	+2.2	-1.2
3ETB	light yellow	blue	orange	+1.5	-0.8
3TB-4EDOT	colorless	blue	orange	+1.5	-1.5

In order to confirm whether the oligomers have been polymerized upon electrochemical doping, the polymer based on the 3ETB was prepared by electropolymerization. The electropolymerization of 3ETB was carried out in ACN solution containing 0.1 M TBAP. ITO glass, platinum wire, and a saturated calomel electrode were used as the working, counter, and reference electrodes, respectively. The electrolyte was purged with N_2 for 10 min to eliminate oxygen.

Figure 4 shows cyclic voltammograms of the electro-polymerization of 3ETB. 3ETB was electropolymerized on the ITO glass (or pET) substrates, when the potential was scanned between 0 V and +1.0 V versus SCE at a scan rate of 50 mV/s. In the first cycle, the initial oxidation potential of the 3ETB monomer was located at 0.46 V versus SCE. As cycling progressed, the initial oxidation potential decreased and the current density increased. This indicated that P3ETB was deposited on the ITO glass (or ITO PET) substrate electrode.[10] After a great many cycles, no appreciable change was observed in the redox response of P3ETB, which indicated that it was highly stable.

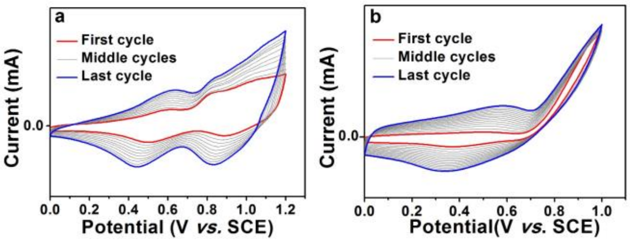

Figure 4 Electropolymerization of 3ETB in ACN solution containing 0.1 M TBAP on (a) ITO glass and (b) ITO PET substrates.

Figure 5 shows spectroelectrochemical properties of the P3ETB film on the ITO glass substrate at different potentials. The orange P3ETB film gradually transformed to gray, when the potential changed from 0 V to +1.0 V versus SCE, and then transformed to blue when the potential was further increased to +1.5 V versus SCE. The electronic absorption spectra showed that the intensity of the absorption peak at 480 nm decreased, and that a new absorption peak gradually appeared at 550–800 nm, upon electrochemical doping. This was attributed to the formation of polarons. [11] This results was consistent with electrochromic properties of device based on 3ETB, which confirmed that the oligomers have been polymerized in electrochromic devices upon electrochemical doping.

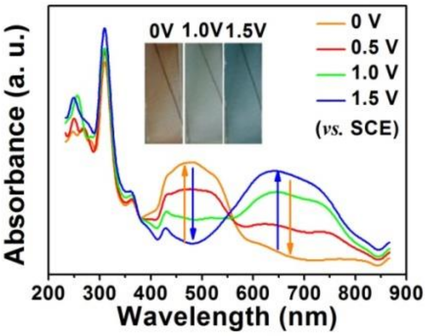

Figure 5 Spectroelectrochemistry of the P3ETB film on an ITO glass substrate in ACN solution containing 0.1 M TBAP.

The response time is an important parameter for evaluating electrochromic materials. The response time of the P3ETB film was measured by chronoamperometry, in a typical three-electrode system. Figure 6a and 6b show voltage-time and current-time curves of the P3ETB film on ITO glass and ITO PET substrates, respectively. Figure 6c and 6d show magnified views of single cycles on ITO glass and ITO PET substrates, respectively. Figure 6c shows that the doping and dedoping times of the P3ETB film on the ITO glass substrate were 1.2 and 0.9 s, respectively. Figure 6d shows that the doping and dedoping times of the P3ETB film on the ITO PET substrate were 16 and 7.5 s, respectively. The doping and dedoping times of the P3ETB film coated on the ITO PET substrate were longer than those on the ITO glass substrate. One reason for this was the lower conductivity of ITO PET compared to ITO glass.

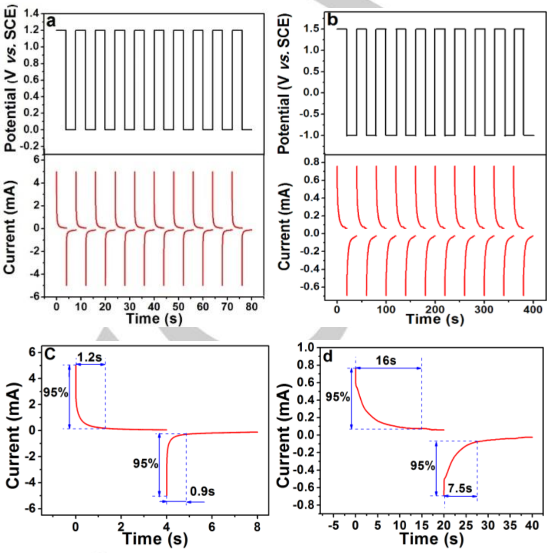

Figure 6 Voltage-time and current-time curves of P3ETB films on (a) ITO glass and (b) ITO PET substrates. Magnified view of a single current-time curve on (c) ITO glass and (d) ITO PET substrates.

The stabilities of P3ETB films on ITO glass and ITO PET substrates were measured by cyclic voltammetry, in ACN solution containing 0.05 M TBAP (Figure 7). The potential was scanned between 0 V and +1.3 V versus SCE, at a scan rate of 50 mV/s. After 500 cycles, the electric charge loss of the P3ETB film on the ITO glass substrate was 19.2%. The corresponding electric charge loss of the P3ETB film on the ITO PET substrate was 19.8%. This result indicated that the P3ETB film had good electrochemical and electrochromic stability.

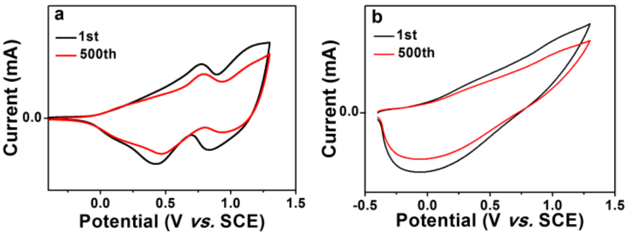

Figure 7 1st and 500th cyclic voltammograms of P3ETB films on (a) ITO glass and (b) ITO PET substrates, in ACN containing 0.05 M TBAP.

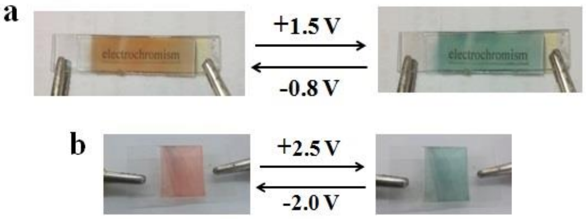

Figure 8 Digital photographs of changes in the colors of devices based on P3ETB films on (a) ITO glass and (b) ITO PET substrates, upon electrochemical doping and dedoping.

The structure of the electrochromic devices was ITO glass (or ITO PET)/P3ETB film/electrolyte/ITO glass (or ITO PET). The conducting gel was used as the semi-solid state electrolyte. The gel electrolyte consisted of PMMA, TBAP, ACN, and PC (7:3:70:20, mass ratio).The color changes of the device upon electrochemical doping and dedoping are shown in Figure 8. The device based on the ITO glass substrate exhibited reversible color changes from orange to blue, upon electrochemical doping and dedoping. The doping and dedoping response times of the device based on the P3ETB film on the ITO glass substrate were 1.9 and 1.3 s, respectively. The device based on the ITO PET substrate exhibited reversible color changes from orange to blue, upon electrochemical doping and dedoping. The doping and dedoping times of the device based on the P3ETB film on the ITO PET substrate were 18 and 9.2 s, respectively. Therefore, the rigid and flexible electrochromic devices based on P3ETB both showed clear and reversible color changes. This results was consistent with electrochromic properties of device based on 3ETB, which further confirmed that the oligomers have been polymerized in electrochromic devices upon electrochemical doping.

In summary, a series of star-shaped oligomers, 3TB, 3EB, 3ETB, and 3TB-4EDOT, was synthesized. Their electrochromic properties were investigated. These oligomer films showed reversible, clear color changes upon electrochemical doping and dedoping. However, these oligomer films could not change back to their intrinsic colors upon electrochemical dedoping. The P3ETB film changed color reversibly from orange to light green. The P3ETB film had a short response time and good electrochemical stability. The doping and dedoping times of the P3ETB film were 1.2 and 0.9 s, respectively.

Acknowledgements

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Keywords: star-shaped oligomers • thin films • spectroelectrochemistry• electrochromic devices • electrochromic properties

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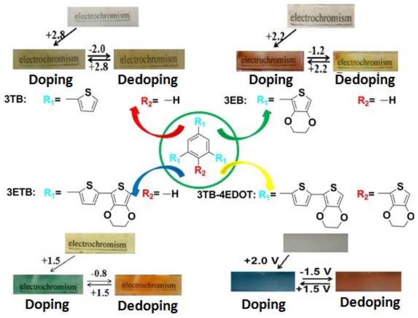

Electrochromic materials: A series of star-shaped oligomers (3TB, 3EB, 3ETB, and 3TB-4EDOT) with phenyl cores were synthesized, and their electrochromic properties were investigated. These oligomer films show reversible and clear color changes upon electrochemical doping and dedoping because of the star-shaped oligomers form stable ion radical upon electrochemical doping and dedoping.

J. M. Zeng, X. Y. Zhang, X. T. Zhu, P. Liu[*]

Synthesis and electrochromic properties of star-shaped oligomers with phenyl cores

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