

# Synthesis and Characterization of Four Random copolymers Containing Fluorene as Electron Donors and Benzotriazole, Benzothiadiazole, Pyrido[3,4-b]pyrazine as Electron Acceptors

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Four copolymers, poly(fluorene-pyrido[3,4-b]pyrazine) (PFPP), poly(benzotriazole-fluorene-pyrido[3,4-b]pyrazine) (PBTFPP), poly(benzotriazole-fluorene-benzothiadiazole) (PBTfBD), poly(benzothiadiazole-fluorene-benzothiadiazole) (PBDFBD) were synthesized successfully. Afterwards, a series of characterization, including cyclic voltammetry (CV), spectroelectrochemistry, kinetics, colorimetry and thermal gravimetric analysis were carried out to fully investigate the properties of the copolymers we got. Their band gaps are 1.87 eV, 1.91 eV, 1.97 eV and 1.98 eV, respectively. From neutral state to oxidized state, PFPP changes from thistle to transparent gray, PBTFPP changes from tan to transparent gray, PBTfBD changes from sienna to light slate gray, and PBDFBD changes from rosy brown to light grey. The coloration efficiencies are  $269.91 \text{ cm}^2 \cdot \text{C}^{-1}$  for PFPP,  $177.45 \text{ cm}^2 \cdot \text{C}^{-1}$  for PBTFPP,  $241.92 \text{ cm}^2 \cdot \text{C}^{-1}$  for PBTfBD, and  $174.67 \text{ cm}^2 \cdot \text{C}^{-1}$  for PBDFBD in near infrared region. Except for PFPP, all the other three copolymers are stable and could be good candidates in electrochromic application.

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**Keywords:** fluorene; pyrido[3,4-b]pyrazine; benzotriazole; benzothiadiazole; conducting polymers.

## 1. INTRODUCTION

The appearance and development of new materials play an important role in promoting the advancement of society. Since the first discovery of conducting polymers by Hideki Shirakawa and his coworkers [1], it has received a lot of attention, because it breaks the traditional opinion that conducting

copolymers are good insulators, and many investigations have been carried out, enriching the content of conducting copolymers. Through doping, no matter chemical doping or electrochemical doping, the conductivity has been rose even to the metal level.

Electrochromic conducting polymers could display at least two different kinds of colors through oxidation and reduction, and could be applied to display devices. The application areas of conducting polymers contain organic light emitting diodes [2], solid-state laser materials [3], polymer image sensors [4], field-effect transistors [5], and so on. During several decades' development, many kinds of polymers containing different blocking units have been successfully synthesized and characterized, including polythiophene, polypyrrole, polyaniline as well as their derivatives [6-10]. The goals of researchers are trying to synthesize new polymers with excellent properties and exploring the mechanisms. We hope the polymers possess low band gap, fast response time and high coloration efficiency [11].

The band gap is defined as the difference between the highest occupied molecular orbital (HOMO) and the lowest unoccupied molecular orbital (LUMO)[12,13]. There are some methods to tune the band gap, including bond-length alternation and creating high planar structure, while donor-acceptor (D-A) approach is the most widely used method in polymer synthesis [14-17]. The push-pull function among donor-acceptor units could promote charge transfer and create electronic delocalization [5]. In detail, the donor blocking unit could enhance the HOMO level and make polymers easy to be oxidized, while the acceptor unit could lower the LUMO energy, facilitating the reduction of polymers [18]. The charge carriers in conducting polymers are polarons and bipolarons. G. M. e Silva and his coworker confirmed that polarons are not stable under strong electric field, while bipolarons are relatively stable when the strength increases [19].

Fluorene-based polymers consist rigid and planar structure and could act as donor units in donor-acceptor copolymers. In addition, polyfluorene and derivatives have a high band gap between 2.8 eV-3.0 eV, so we can lower the band gap by introducing appropriate acceptor units [20]. Benzothiadiazole and benzotriazole have been used as the acceptor units to achieve low band gap polymers [21,22]. Thiophene-2,1,3-benzothiadiazole-thiophene is the most popular building block when combined with different comonomers [20]. Pyrido[3,4-b]pyrazine has a stronger electron-withdrawing ability than quinoxaline, and the band gap is lower than quinoxaline when copolymerized with carbazole [20], so it can be a good electron acceptor because of the presence of pyridine N-atom [23].

In this study, four random copolymers were synthesized, in which fluorene derivatives was used as electron donors, benzothiadiazole, benzotriazole and pyrido[3,4-b]pyrazine derivatives was used as electron acceptors. Afterwards, a series of characterizations, including cyclic voltammetry (CV), spectroelectrochemistry, colorimetry, kinetics and thermal gravity, were carried out. The experiment results demonstrate that all the four copolymers have relatively low band gaps (ranging from 1.87 eV to 1.98 eV) and high coloration efficiency in near infrared region.

## 2. EXPERIMENTAL

### 2.1 Materials

Thiophene (AR), Potassium tert-butoxide (AR), 1-bromododecane (AR), hydrobromic acid (AR), bis-(triphenylphosphine)palladium (II) chloride ( $\text{Pd}(\text{PPh}_3)_2\text{Cl}_2$ , 99 %), bromine (98%), N-

bromosuccinimide (NBS, AR), tetrakis(triphenylphosphine)palladium(0)(Pd[P(C<sub>6</sub>H<sub>5</sub>)<sub>3</sub>]<sub>4</sub>), tetra-n-butylammonium fluoride (TBAF), tetra-n-butylammonium hexafluorophosphate (TBAPF<sub>6</sub>, AR), n-butyllithium, chlorotributyltin (AR), 1H-benzotriazole (AR) were all purchased from Aladdin Industrial Corporation and used without further treatment. Sodium carbonate anhydrous (Na<sub>2</sub>CO<sub>3</sub>, ≥98.8%), sodium sulfite (Na<sub>2</sub>SO<sub>3</sub>) and magnesium sulfate(MgSO<sub>4</sub>, ≥99.0 %) were bought from Tianjin Chemreagent Co., Ltd. and used directly. Acetonitrile (ACN, AR), toluene (AR), dichloromethane(AR), chloroform(AR), acetone(AR),methanol, glacial acetic acid and ethanol (AR) were all bought from Laiyang Fine Chemical Factory without any treatment. 2,2'-(9,9-dioctyl-9H-fluorene-2,7-diyl)bis(4,4,5,5-tetramethyl-1,3,2-dioxaborolane) (M1), 4,7-bis(5-bromo-4-hexylthiophen-2-yl)benzo[c][1,2,5]thiadiazole (M2), 4,7-dibromo-5,6-bis(octyloxy)benzo[c][1,2,5]thiadiazole(M3) and 2,3-bis(4-(decyloxy)phenyl)-5,8-di(thiophen-2-yl)pyrido[3,4-b]pyrazine were purchased from Derthon Optoelectronic Materials Sci.&Tech Co., Ltd.(Shenzhen, China). Indium-tin-oxide (ITO) coated glass (sheet resistance: < 10 Ω·□<sup>-1</sup>) was cleaned with ethanol and water deionized water before use. The electrolyte used in the experiments is 0.1 M TBAPF<sub>6</sub>/ACN. Tetrabutylammonium hexafluorophosphate (TBAPF<sub>6</sub>) was obtained from Tokyo Chemical Industry Co., LTD (TCI, Tokyo, Japan)

## 2.2 Instrumentation

<sup>1</sup>H NMR and <sup>13</sup>C NMR spectra of the products were recorded with a Varian AMX 400 spectrometer, taking CDCl<sub>3</sub> as solvent and tetramethylsilane as internal standard. The cyclic voltammetry (CV) experiments were finished with CHI 760 C Electrochemical Analyzer, where ITO conducting glass was as working electrode, a platinum wire as counter electrode, and an Ag wire as pseudo reference electrode. The scan rate in the CV measurement was 100 mV/s, if no special requirements. Spectroelectrochemistry and colorimetry experiments were both finished with a Varian Cary 5000 spectrophotometer connected with CHI 600 Electrochemical Analyzer. Photos of the copolymer solutions and films were taken with a Canon Power Shot A3000 IS digital camera. To get the copolymer films, spay-casting method was adopted with an airbrush after the copolymers were dissolved in chloroform. The thermal stability was measured by NETZSCH STA 499C TG-DSC in an N<sub>2</sub> atmosphere, with a heating rate of 15 K/min<sup>-1</sup>. The changes in colors were quantitatively measured by colorimetric analysis on the Varian Cary 5000 spectrophotometer with the help a chromaticity software.

## 2.3 Synthesis of the monomers

### 2.3.1 Synthesis of 4,7-bis(5-bromothiophen-2-yl)-2-dodecyl-2H-benzo[d][1,2,3]triazole (M4)

M4 was synthesized according to the previous paper [21,24]. As shown in Scheme 1. 2.0 g of 2-dodecyl-4,7-di(thiophen-2-yl)-2H-benzo[d][1,2,3]triazole and 1.89 g of NBS(2.4 equiv) dissolved in a mixture of 150 mL of CH<sub>2</sub>Cl<sub>2</sub>/glacCH<sub>3</sub>COOH (1:1). The flask containing the mixture was placed in a oil bath, refluxed and stirred magnetically in dark. Then the mixture was poured into 200 mL of deionized water. Then extraction was repeated 4 times with 100 mL of saturated Na<sub>2</sub>SO<sub>3</sub> and dichloromethane. After distilling the solvent, we adopted column chromatograph to purify the crude

product, at last, we got the yellow crystallized solid product.  $^1\text{H}$  NMR(400 MHz,  $\text{CDCl}_3$ ,  $\delta$  ppm) 7.78(d, 2H), 7.48(s, 2H), 7.12(d, 2H), 4.78(t, 2H), 2.17(m, 2H), 1.48-1.15(m, 18H), 0.88(t, 3H).  $^{13}\text{C}$  NMR (101 MHz,  $\text{CDCl}_3$ ,  $\delta$  ppm) 141.62, 141.15, 130.81, 126.88, 122.89, 122.11, 113.10, 56.87, 31.87, 29.99, 29.58, 29.51, 29.40, 29.30, 28.96, 26.52, 22.65, 14.10 (See Supporting Information, Fig. S1).

### 2.3.2 Synthesis of 5,8-bis(5-bromothiophen-2-yl)-2,3-bis(4-(decyloxy)phenyl)pyrido-[3,4-b]pyrazine (M5)

7 g of 2,3-bis(4-(decyloxy)phenyl)-5,8-di(thiophen-2-yl)pyrido[3,4-b]pyrazine, 3.98 g NBS(2.4 equiv) were dissolved in 150 mL mixture of  $\text{CH}_2\text{Cl}_2/\text{glacCH}_3\text{COOH}$  (1:1), then be placed in a flask. After refluxed for 24 hours under stir in dark, the solution was poured into the 200 mL of deionized water and extracted with saturated  $\text{Na}_2\text{SO}_3$  solution and dichloromethane for 3 times, respectively. After the solvent was distilled, column chromatograph was adopted to separate the product and impurity.  $^1\text{H}$  NMR (400 MHz,  $\text{CDCl}_3$ )  $\delta$  9.00 (s, 1H), 8.26 (d, 1H), 7.61 (m, 4H), 7.12 (s, 1H), 7.07 (d, 1H), 6.96-6.8 (m, 5H), 4.00 (m, 4H), 1.82 (m, 4H), 1.6-1.2 (m, 28H), 0.92 (m, 6H).  $^{13}\text{C}$  NMR (101 MHz,  $\text{CDCl}_3$ )  $\delta$  160.77, 160.42, 155.72, 153.16, 151.31, 146.45, 141.55, 140.53, 132.98, 132.52, 131.90, 131.61, 131.22, 130.42, 130.25, 129.91, 122.19, 119.74, 115.21, 114.36, 114.24, 109.50, 68.09, 31.89, 29.58, 29.40, 29.34, 29.26, 29.20, 26.08, 22.69, 14.14 (See Supporting Information, Fig. S2).

## 2.4 Synthesis of the copolymers

### 2.4.1 Synthesis of poly(fluorene-pyrido[3,4-b]pyrazine) (PFPP)

The synthesis process of the four random copolymers was shown in Scheme 1. 0.9179 g of M5 (1 equiv), 0.6426 g of M1 (1 equiv), 90 mL of toluene, 60 mL of  $\text{Na}_2\text{CO}_3$  solution(2 mol/L), 0.015 g of TBAF and 0.04624 g of  $\text{Pd}[\text{P}(\text{C}_6\text{H}_5)_3]_4$  were placed in a 500 mL of flask and the reaction lasted for 72 hours in argon atmosphere. After the reaction, the mixture was extracted with deionized water and chloroform repeatedly. Then chloroform was distilled and methanol was added to the flask. After filtration, the solid was extracted with methanol for 24 hours until the solution in Soxhlet extractor was transparent, then extracted with acetone for 24 hours until the solution in Soxhlet extractor was transparent, too.  $^1\text{H}$  NMR (400 MHz,  $\text{CDCl}_3$ )  $\delta$  7.66 (s, 11H), 6.90 (s, 8H), 4.00 (s, 4H), 1.80 (s, 4H), 1.50-0.60 (m, 68H) (See Supporting Information, Fig. S3).

### 2.4.2 Synthesis of poly (benzotriazole-fluorene-pyrido[3,4-b]pyrazine) (PBTFPP)

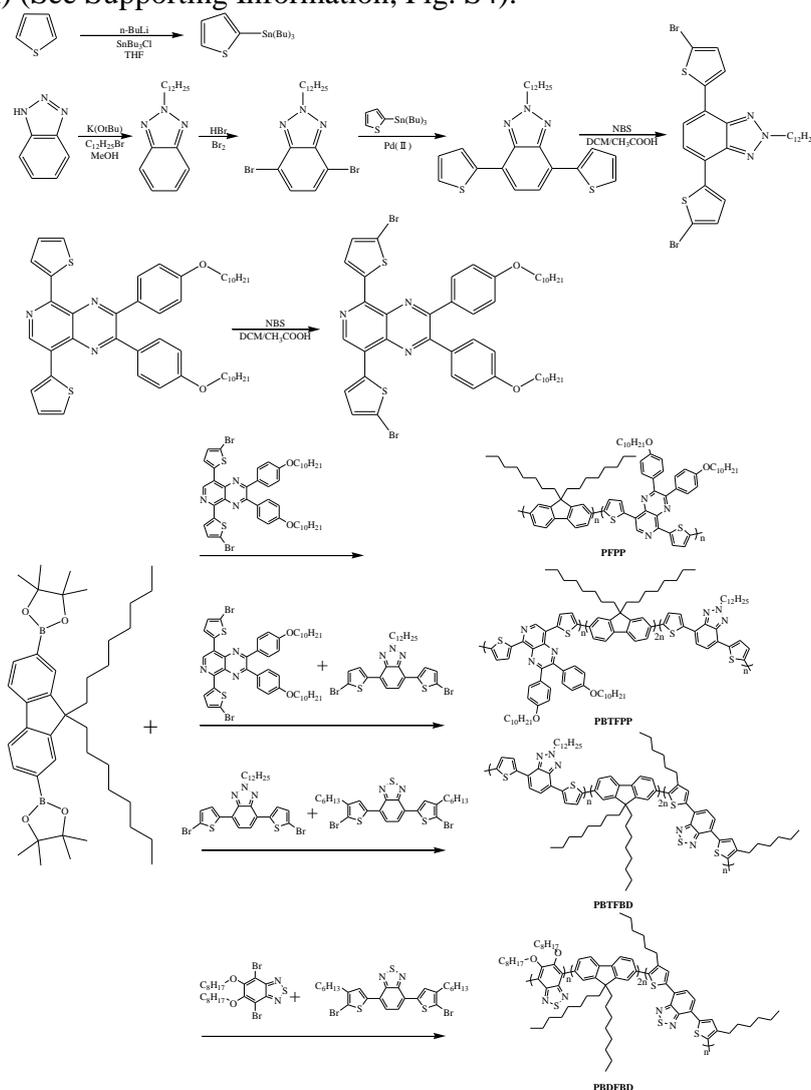
0.4590 g of M5 (1 equiv), 0.3123 g of M4 (1 equiv), 0.6426 g of M1(2 equiv), 0.015 g of TBAF and 0.04624 g of  $\text{Pd}[\text{P}(\text{C}_6\text{H}_5)_3]_4$  were resolved in the mixture of 90 mL of toluene and 60 mL of  $\text{Na}_2\text{CO}_3$  solution(2 mol/L), then added to a 500 mL of flask and the reaction lasted for 72 hours. The treatment process was similar with that of PFPP.

### 2.4.3 Synthesis of poly(benzotriazole-fluorene-benzothiadiazole) (PBTFBFD)

To a 500 mL of flask, 0.3047 g of M4 (1 equiv), 0.3133 g of M2(1 equiv), 0.6426 g of M1(2 equiv), 90 mL of toluene, 60 mL of Na<sub>2</sub>CO<sub>3</sub> solution(2 mol/L), 0.015 g of TBAF and 0.04624 g of Pd[P(C<sub>6</sub>H<sub>5</sub>)<sub>3</sub>]<sub>4</sub> were added, and the reaction lasted for 72 hours. The crude product was treated as above method.

### 2.4.4 Synthesis of poly(benzothiadiazole-fluorene-benzothiadiazole) (PBDFBD)

0.2752 g of M3 (1 equiv), 0.3133 g of M2 (1 equiv), 0.6426 g of M1 (2 equiv), 0.015 g of TBAF, 0.04624 g of Pd[P(C<sub>6</sub>H<sub>5</sub>)<sub>3</sub>]<sub>4</sub>, 90 mL of toluene, 60 mL of Na<sub>2</sub>CO<sub>3</sub> solution(2 mol/L) were added to a 500 mL of flask and reacted for 72 hours. The treatment method was same with above method. <sup>1</sup>H NMR (400 MHz, CDCl<sub>3</sub>) δ 8.30-7.00 (m, 16H), 4.07-3.75 (m, 4H), 2.94-2.68 (m, 4H), 2.22-1.70 (m, 16H), 1.46-0.52 (m, 104H) (See Supporting Information, Fig. S4).

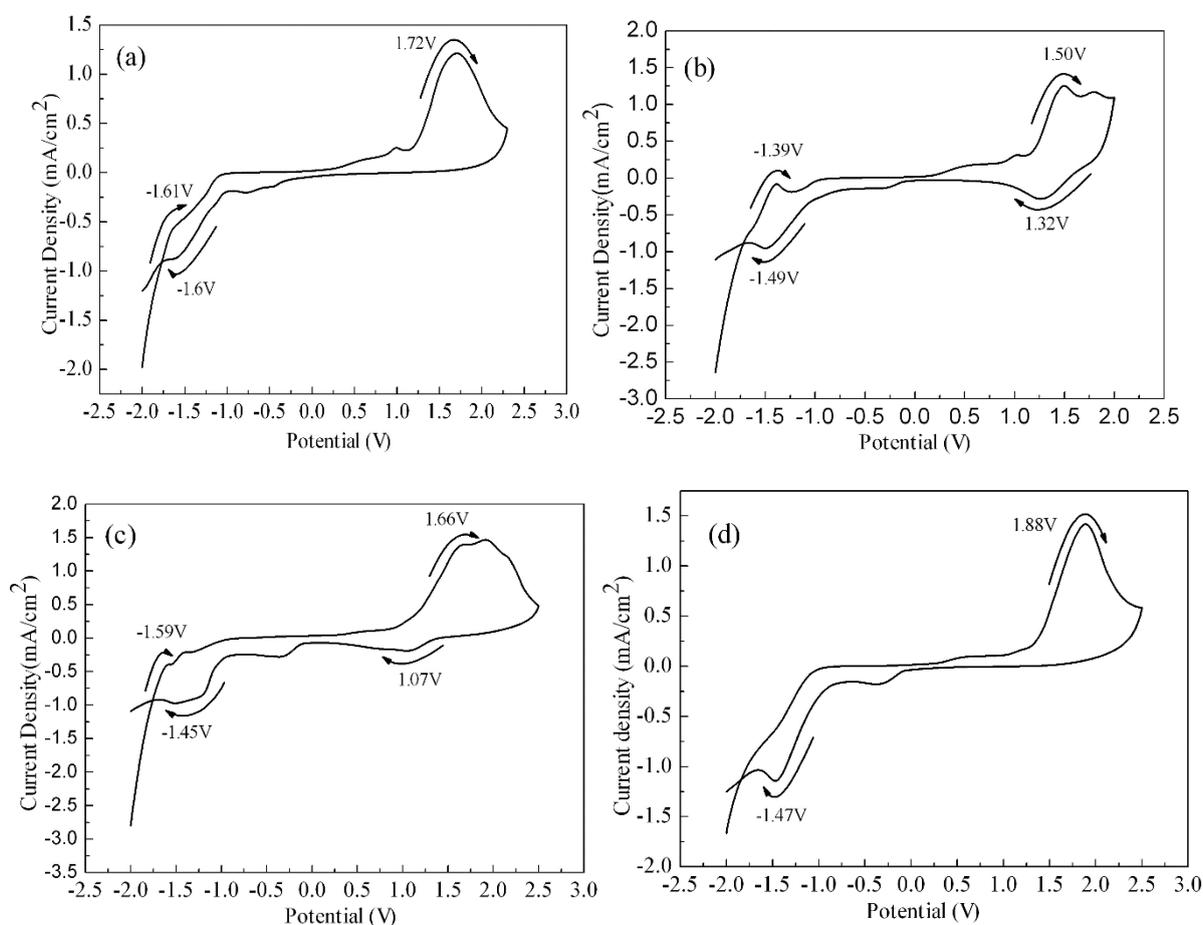


**Scheme 1.** Synthetic routes of monomers and copolymers of PFPP, PBTFBFD and PBDFBD, the synthetic details could be obtained from the Experimental part.

### 3. RESULTS AND DISCUSSION

#### 3.1 Electrochemistry

As shown in Fig. 1, cyclic voltammetry(CV) experiments were carried out to investigate the electrochemical property of the four copolymers. The voltage was swept from -2.0 V to 2.3 V for PFPP, -2.0 V to 2.0 V for PBTFPP, -2.0 V to 2.5 V for PBTFBD and -2.0 V to 2.5 V for PBDFBD. When the voltage is positive, it donates p-doping and p-dedoping, and when the voltage is negative, it means n-doping/n-dedoping. The p-doping peak of PFPP is located at 1.72 V, while PBTFPP has a smaller p-doping peak at 1.50 V owing to the introduction of benzotriazole unit. When the species of the backbone units increases, it's beneficial to lowering the oxidation difficulty. The oxidation peak of PBTFBD is at 1.66 V, higher than PBTFPP, because the pyrido[3,4-b]pyrazine has a more stronger electron accepting ability than that of benzothiadiazole, which has a more efficient electron delocalization. The p-doping peak of PBDFBD is at 1.88 V, because it lacks two thiophene units in each repeating unit compared with PBTFBD, while thiophene is a good electron donor unit.



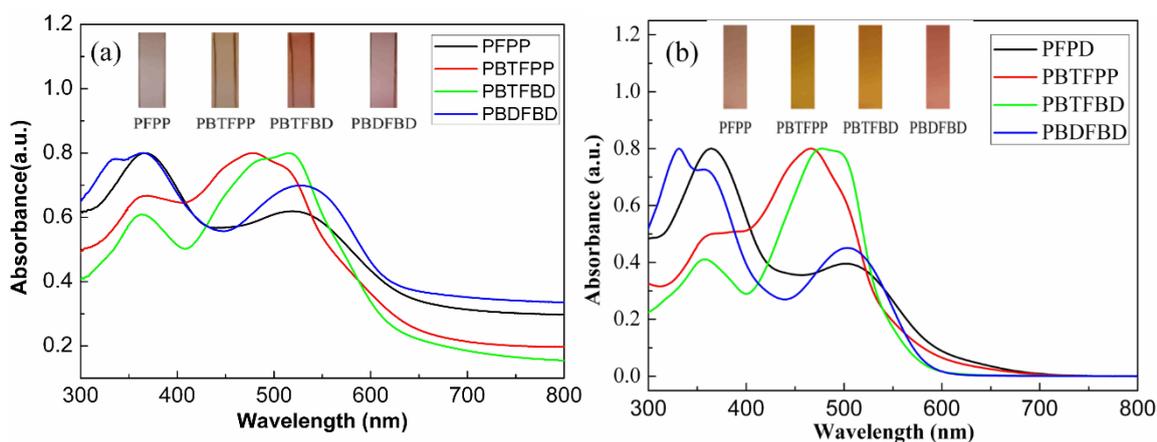
**Figure 1.** Cyclic voltammograms(CV) of PFPP(a), PBTFPP(b), PBTFBD(c), PBDFBD(d). The CV was conducted in 0.2 M TBAPF<sub>6</sub>/ACN with a scan rate of 100 mV/s.

All the four copolymers could be n-doped, and the n-doping peak of PFPP is at -1.60 V, lower than -1.49 V of PBTFPP, -1.45 V of PBTFBD, -1.47 V of PBTFPP. Oxidation onset value is used to

calculate the HOMO level of the copolymers, and can be read from the CV graphs by taking the intersection of the baseline and the tangent line of the p-doping peak [21].

### 3.2 Optical absorption spectra of copolymer solutions and films

The absorption spectra and the photos of the four copolymers in the form of solution and film were shown in Fig. 2. There are two peaks for all the copolymers no matter in solution or in film form, which is due to the  $\pi$ - $\pi^*$  transition and intramolecular charge transfer, respectively [16]. When they exist in films, PFPP has a strong absorption of short wavelength, while has a weak absorption of long wavelength, and the film displays thistle color. For PBTFPP, the absorption peak was located at 478 nm in the visible region, and the film color is tan. Compared with PBTFPP, the peak of PBTFBD has a red shift from 478 nm to 515 nm, and the color of the film is sienna, deeper than PBTFPP. While for PBDFBD, the maximum absorption peak is at 528 nm in the visible region and the color of the film is rosy brown color. Fig. 2(b) demonstrates the color of the four copolymers in the solution. They display dark salmon, dark goldenrod, peru and indianred colors for PFPP, PBTFPP, PBTFBD, PBDFBD solutions, respectively. For the same copolymers, there is a bathochromic shift for the absorption peak of copolymer film compared with corresponding solution in the visible region, from 503 nm to 520 nm for PFPP, 466 nm to 478 nm for PBTFPP, 477 nm to 515 nm for PBTFBD and 504 nm to 528 nm for PBDFBD. The reason is that the structure of the film is more compact than the solution, so it has a better  $\pi$ - $\pi$  stacking, promoting interchain interaction, lowering the energy between the HOMO and LUMO [26].

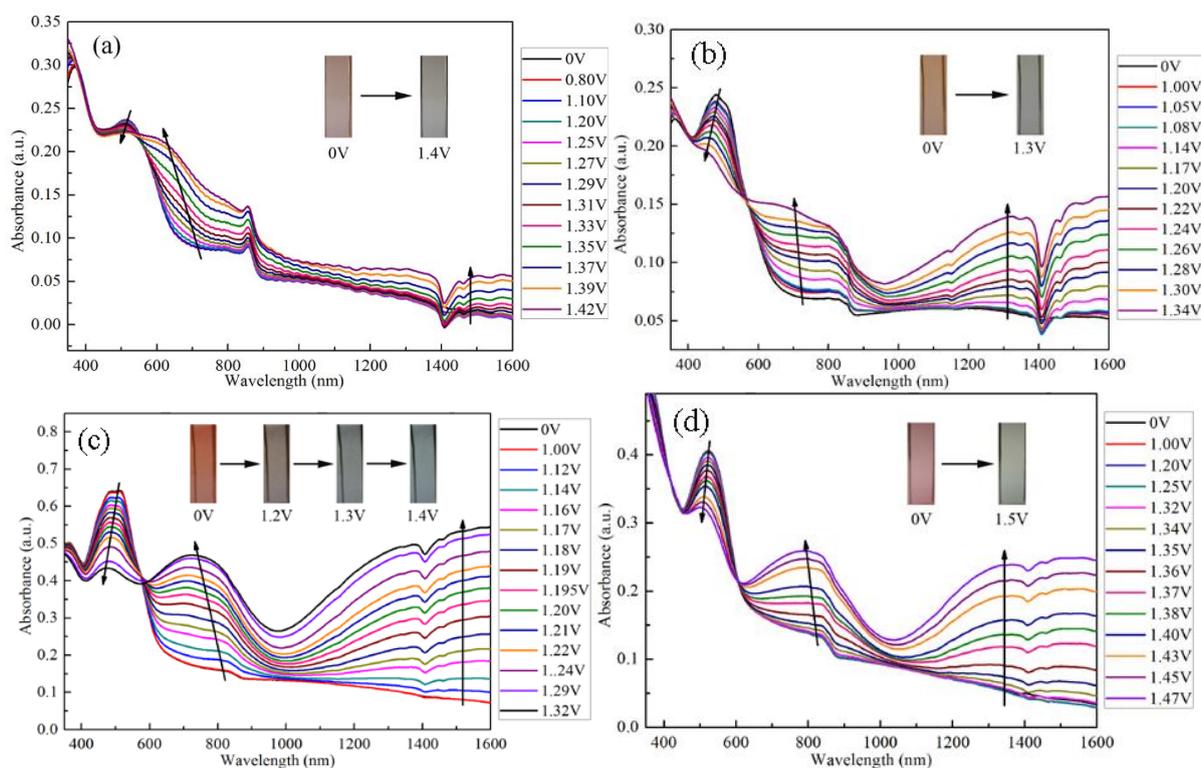


**Figure 2.** The absorption spectra of the four copolymers and their photos in the form of film(a) and chloroform solution(b).

### 3.3 Spectroelectrochemistry

Through spectroelectrochemistry, we can get the absorption spectra at different potentials. The spectroelectrochemistry graphs of the four copolymers are shown in Fig. 3. As for PFPP, when it is in neutral state, there is one peak located at 514 nm, which could be ascribed to the  $\pi$ - $\pi^*$  transition [27,28].

When the voltage raises, the absorption in the visible region decreases, while it increases for the peak located at 856 nm till 1.42 V, because of the formation of polarons. When it is at a longer wavelength, the absorption increases with the increase of voltage, because there exists bipolarons [26,27]. From neutral state to oxidized state, the change of absorbance in visible region isn't very obvious, so the color change isn't obvious, either. When the copolymer is in neutral state, the film is thistle, and when the polymer is in oxidized state, the film displays transparent gray. As for PBTFFP, when it is in neutral state, there is a peak at 479 nm, and when it is in oxidized state, there are two new peaks at 802 nm and 1326 nm due to the formation of polarons and bipolarons. The change of absorbance is more obvious than PFPP due to the introduction of benzotriazole. The color of the film changes from tan in neutral state to transparent grey in oxidized state. PBTFFD is sienna at 0 V and light slategray at 1.4 V. With the potential increasing, the peak of the polarons reached to a maximum when the voltage is 1.32 V, while the peak of bipolarons increases with the intensity of voltage due to the repression of inter-band transition [26, 29]. The isobestic point is at 574 nm where the absorbance doesn't change with the potential. For PBTFFD, there is a peak of  $\pi$ - $\pi^*$  transition at 523 nm in neutral state, and two new peaks at 799 nm and 1364 nm corresponding to the formation of polarons and bipolarons in oxidized state. The color changes from initial rosybrown in neutral state to the final lightgrey in oxidized state. There exists one isobestic point at 605 nm.



**Figure 3.** Spectroelectrochemistry graphs and photos of PFPP(a), PBTFFP(b), PBTFFD(c), PBTFFD(d) under different applied potentials, and the polymer coated ITO electrode was immersed in 0.2 M TBAPF<sub>6</sub>/ACN solution.

We can get the onset of the optical absorption wavelength ( $\lambda_{\text{onset}}$ ) by choosing the intersection of the tangent of the peak of  $\pi$ - $\pi^*$  transition and the baseline in neutral states. The onset oxidation potential

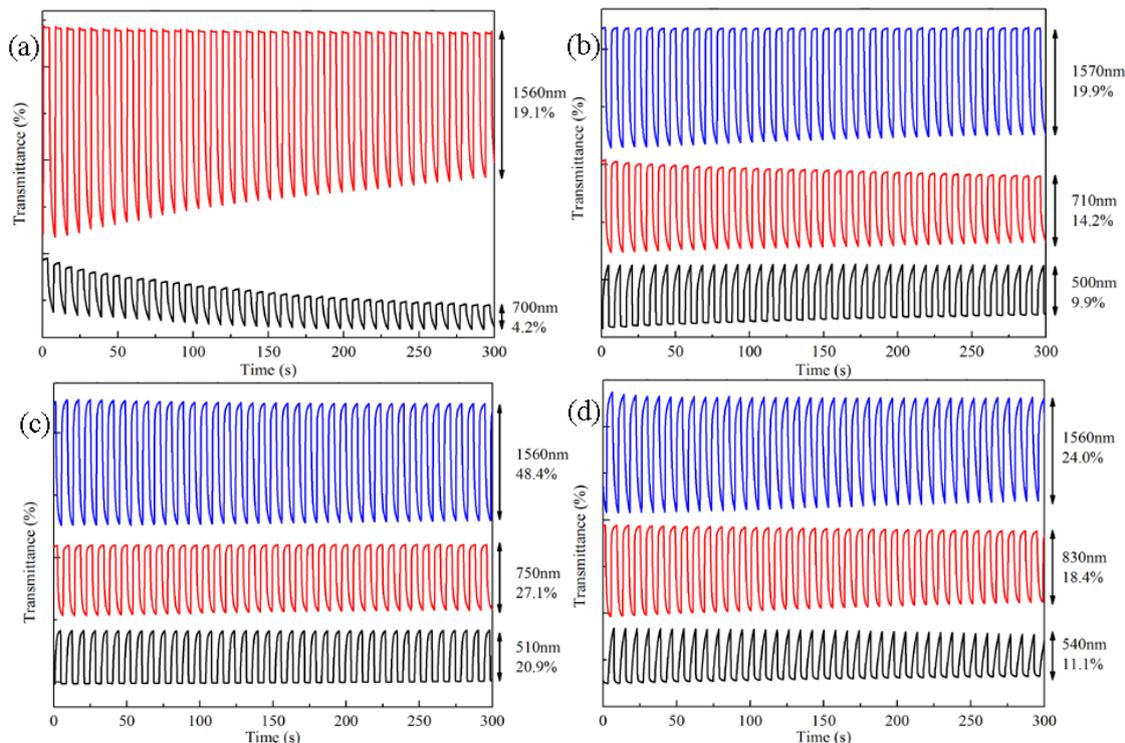
( $E_{\text{onset}}$ ) is calculated from the CV graphs. Based on the  $\lambda_{\text{onset}}$  and  $E_{\text{onset}}$ , we can get the band gap ( $E_g$ ) and the HOMO/LUMO values according to the formula:  $E_g=1241/\lambda_{\text{onset}}$ ,  $E_{\text{HOMO}}=-e(E_{\text{onset}}+4.4)$  and  $E_{\text{LUMO}}=E_{\text{HOMO}}+E_g$ , respectively[30]. Above mentioned parameters and maximum absorption wavelength in the form of solution ( $\lambda_{\text{max, solution}}$ ) and film ( $\lambda_{\text{max, film}}$ ) are summarized in Table 1.

**Table 1.**  $\lambda_{\text{onset}}$ ,  $E_{\text{onset}}$ ,  $\lambda_{\text{max, solution}}$ ,  $\lambda_{\text{max, film}}$ ,  $E_g$  and HOMO/LUMO of PFPP, PBTFFPP, PBTFFBD and PBDFFBD.

copolymers	$\lambda_{\text{onset}}$ nm	$E_{\text{onset}}$ V	$\lambda_{\text{max}}(\text{solution})$ nm	$\lambda_{\text{max}}(\text{film})$ nm	$E_g$ eV	HOMO eV	LUMO eV
PFPP	662	1.19	364	367	1.87	-5.59	-3.72
PBTFFPP	651	1.13	466	478	1.91	-5.53	-3.62
PBTFFBD	630	1.07	477	515	1.97	-5.44	-3.47
PBDFFBD	628	1.35	331	365	1.98	-5.75	-3.77

The band gap of PBTFFPP is larger than PFPP, may be due to that pyrido[3,4-b]pyrazine connecting two benzene has a more sufficient  $\pi$ - $\pi$  localization than benzotriazole. The band gap of PBTFFPP is slightly lower than that of PBTFFBD and PBDFFBD, which may be due to the same reason that pyrido[3,4-b]pyrazine has a larger  $\pi$ - $\pi$  conjugation structure.

### 3.4 Electrochromic switching of the four copolymers



**Figure 4.** Electrochromic switching of PFPP(a), PBTFFPP(b), PBTFFBD(c) and PBDFFBD(d) at different wavelengths. The transmittance ratio was monitored by the UV-vis-IR spectrophotometer, and the polymer coated ITO electrode was switched between its reduced and oxidized state with a resident time of 4 s in the 0.2 M TBAPF<sub>6</sub>/ACN solution.

We hope the copolymers could change color obviously and have a fast color switch, so kinetic experiments were carried out to investigate their switching properties, where the interval is 4 s. Optical contrast ( $\Delta T\%$ ) is defined as the difference of transmittance between neutral state and oxidized state[31]. As shown in Fig.4, when the voltage was interchanged between 0 V and 1.45 V, the optical contrast of PFPP is 4.2 % at 700 nm and 19.1% at 1560 nm. We can find that  $\Delta T\%$  decreases substantially with time, suggesting that the copolymer isn't very stable. In addition, the optical contrast in visible region is very small, so the color change is not very obvious.

When the voltage was interchanged between 0 V and 1.34 V, the optical contrast of PBTFFPP is 9.9 % at 500 nm, 14.2 % at 710 nm and 19.9 % at 1570 nm. The introduction of M4 makes the copolymer more stable. While for PBTFFBD, when the potential interchanged from 0 V to 1.33 V, the optical contrast is much higher than PBTFFPP, 20.9 % at 510 nm, 27.1 % at 750 nm and 48.4 % at 1560 nm, demonstrating that the color change is more obvious, which is corresponding with the spectroelectrochemistry. The optical contrast of PBDFBD is 11.1 % at 540 nm, 18.4 % at 830 nm and 24.0 % at 1560 nm. All the four copolymers have a higher  $\Delta T\%$  in near infrared region than visible region.

**Table 2.** The optical contrast, response time, coloration efficiency of PFPP, PBTFFPP, PBTFFBD and PBDFBD at different wavelengths.

copolymers	$\lambda$	$\Delta T\%$	response time( $t_{95\%}$ )	coloration efficiency ( $\eta$ )
	nm	%	s	$\text{cm}^2 \cdot \text{C}^{-1}$
<b>PFPP</b>	700	4.2	3.56	58.03
	1560	19.1	2.78	269.91
<b>PBTFFPP</b>	500	9.9	3.21	129.63
	710	14.2	2.95	123.52
	1570	19.9	2.68	177.45
<b>PBTFFBD</b>	510	20.9	2.44	112.00
	750	27.1	2.54	227.27
	1560	48.4	2.66	241.92
<b>PBDFBD</b>	540	11.1	3.39	105.18
	830	18.4	2.29	110.95
	1560	24.0	3.06	174.67

Response time ( $t_{95\%}$ ) is another important parameter and defined as the time from neutral state to 95 % of oxidized state [32]. The reason is that human eye isn't so sensitive to the color change of the remaining 5% [33]. The response time of the four copolymers are summarized in Table 2. The response time of the four copolymers is about 3 s, which is relatively high. Coloration efficiency ( $\eta$ ) is defined as the ratio of the change in optical density to the charge density, and calculated as the following equations [32,33]

$$\eta = \Delta OD / \Delta Q$$

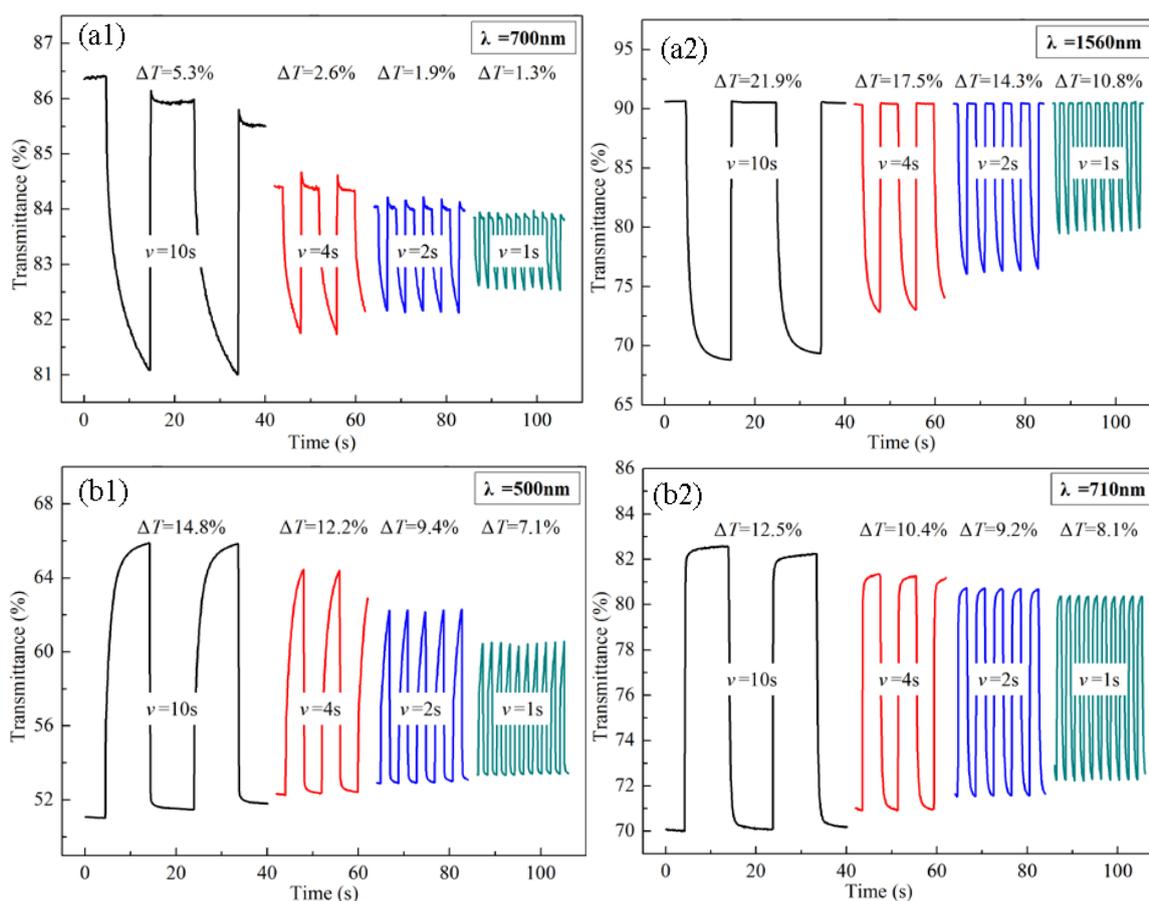
$$\Delta OD = \lg(T_b / T_c)$$

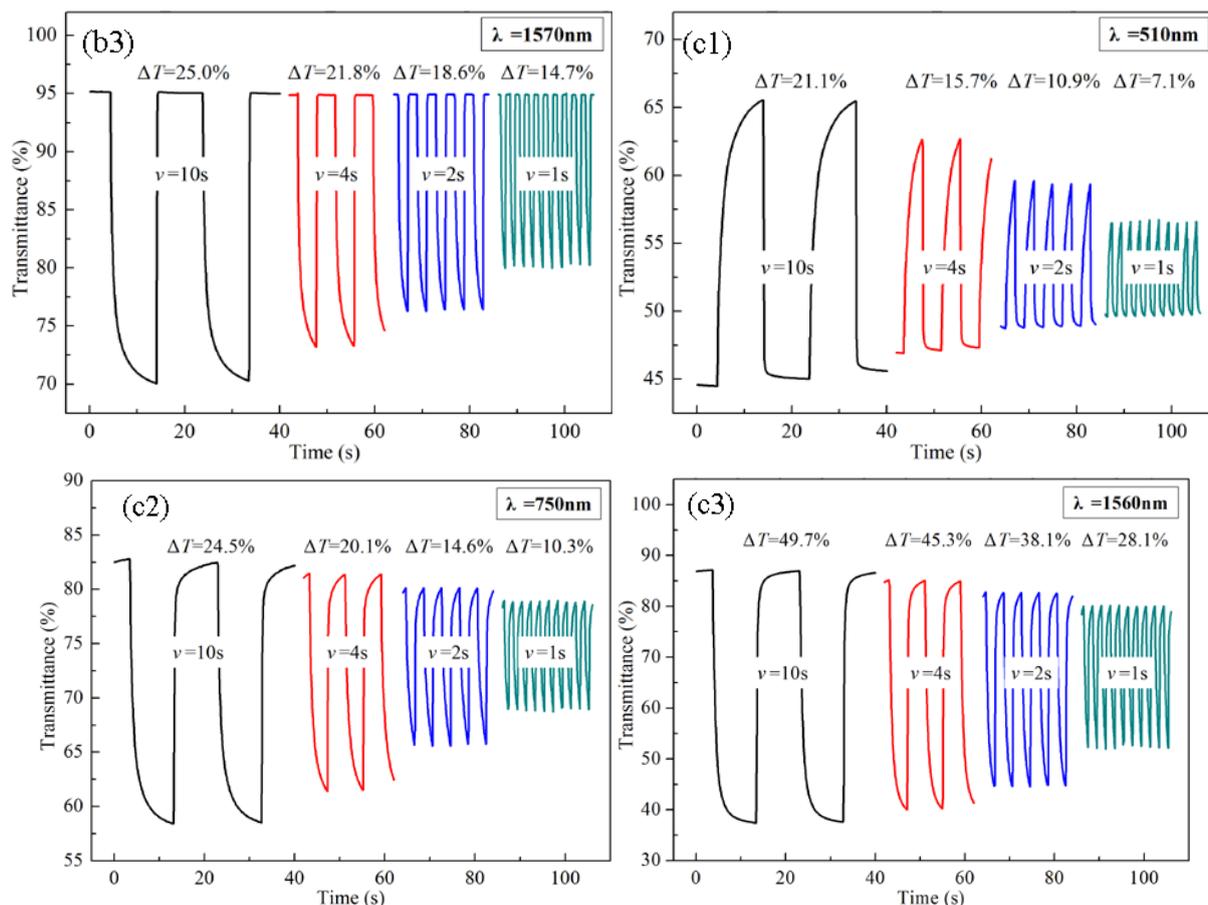
$$\Delta Q = Q / A$$

where  $T_b$ ,  $T_c$  are transmittances in neutral states and oxidized states, respectively.  $\Delta Q$  is the charge injected to the film per unit area.  $Q$  is integrated from the multi-potential steps diagram according to the Electrochemical Analyzer, and  $A$  donates the area of the film. The coloration efficiency of PFPP are  $58.03 \text{ cm}^2 \cdot \text{C}^{-1}$  at 700 nm and  $269.91 \text{ cm}^2 \cdot \text{C}^{-1}$  at 1560 nm. As we can see, the coloration efficiency at

long wavelength is much higher than short wavelength, manifesting that it could have a potential application in near infrared region. The other three copolymers have the same trend and the coloration efficiencies at different wavelengths are summarized in Table 2.

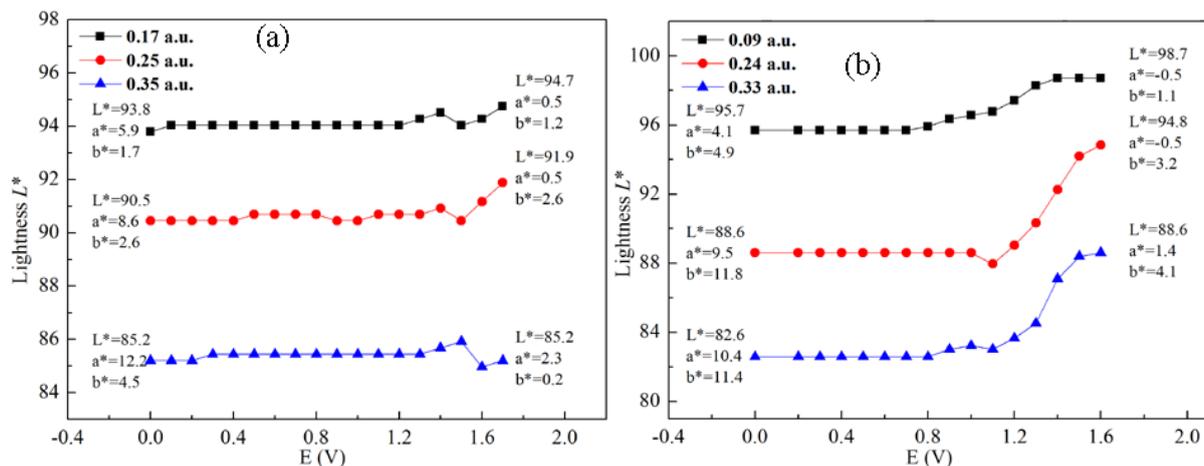
In addition, we also measure the kinetic parameters at different intervals, 10 s, 4 s, 2 s and 1 s. As shown in Fig. 5, for PFPP, when the interval changes from 10 s to 1 s, the optical contrast decreases from 5.3 % to 1.3 % at 700 nm, 21.9 % to 10.8 % at 1560 nm. Besides, when the interval drops from 10 s to 1 s, it declines from 25.0 % to 14.7 % for PBTFFP at 1570 nm, 49.7 % to 28.1 % for PBTFFB at 1560 nm and 30.6 % to 15.4 % for PBTFFB at 1560 nm. The decrease is very significant, indicating that if we want to get a full color change, sufficient interval is necessary. Since the less compact structure is beneficial to promoting the ion-solvent ingress and egress from the film [33], we could conclude that the four copolymers have a compact film structure due to the  $\pi$ - $\pi$  stacking.

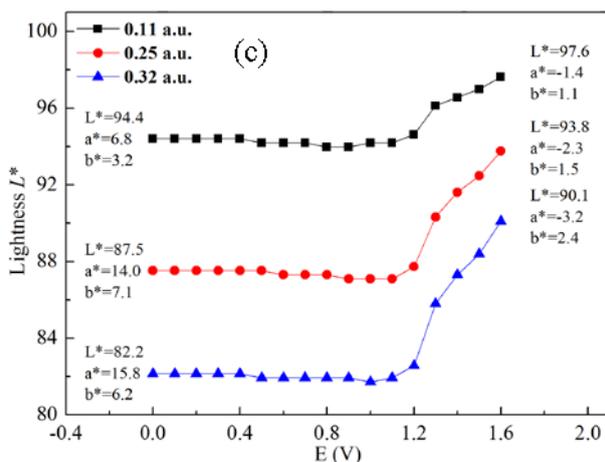




**Figure 5.** Electrochromic switching of PFPP(a<sub>1</sub>, a<sub>2</sub>), PBTFFPP(b<sub>1</sub>, b<sub>2</sub>, b<sub>3</sub>), PBTFFBD(c<sub>1</sub>, c<sub>2</sub>, c<sub>3</sub>) and PBDFBD(d<sub>1</sub>, d<sub>2</sub>, d<sub>3</sub>) with an interval of 10 s, 4 s, 2 s and 1 s. The transmittance ratio was monitored by the UV-vis-IR spectrophotometer, and the polymer coated ITO electrode was switched between its reduced and oxidized state with varied resident times in the 0.2 M TBAPF<sub>6</sub>/ACN solution.

### 3.5 Colorimetry





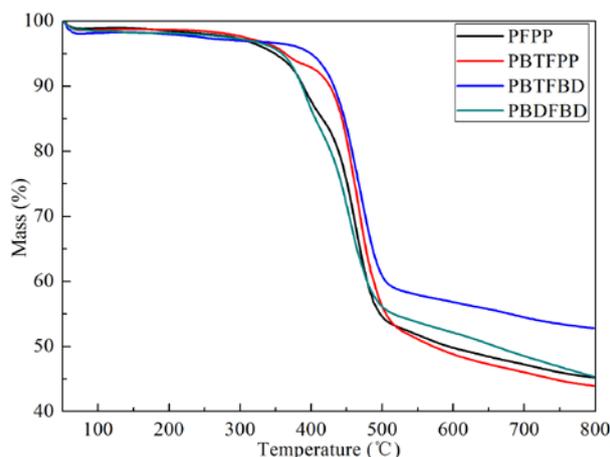
**Figure 6.** Lightness as a function of the applied voltage for PFPP(a), PBTFPP(b), PBTFBD(c) and PBDFBD(d). The polymer coated ITO electrode was applied with different voltages in the 0.2 M TBAPF<sub>6</sub>/ACN solution. And the lightness was monitored with UV-vis-IR spectrophotometer with the aid of a chromaticity analysis software.

To better characterize the change of color, we adopt CIE1976  $L^*a^*b^*$  Color Space to uncover the variation of color at different potential. Where,  $L^*$  represents the lightness from 0 to 100 (black to white),  $a^*$  represents how much red versus green and  $b^*$  represents how much yellow versus blue [34]. The lightness changing with the potential of all the four copolymers is shown in Fig. 6.

For PFPP, we find that the change of lightness is negligible from neutral state to oxidized state, which is corresponding to spectroelectrochemistry. Moreover, the variation of  $a^*$  and  $b^*$  isn't very significant, manifesting that PFPP isn't a good copolymer in display application. Compared with PFPP, the change of lightness of PBTFPP is more obvious. At first, the lightness keeps stable, and when the potential is up to 1.0 V, the lightness begins to have a dramatic increase, finally stays steady again. Similar with PBTFPP, the lightness of PBTFBD and PBDFBD also have the same trend, and the increase of PBTFBD at 1.1 V is more obvious. In addition, we also investigate the effect of the film thickness on the lightness. Based on the dates of the four copolymers, we can find that the thinner the film is, the higher the lightness is. For instance, for PBTFBD, when the film thickness changes from 0.32 a.u. to 0.25 a.u. and to 0.11 a.u., the lightness changes from 82.2, 87.5, 94.4 in neutral state to 90.1, 93.8, 97.6 in oxidized state, respectively. So if we want to get a light film, we could meet it by tuning the film thickness.

### 3.6 Thermal gravimetric analysis

Thermal stability is important if these materials are used at a high temperature. Through thermal gravimetric analysis, we can get the thermal gravimetric graphs shown in Fig. 7. Through choosing the intersection of the baseline and the tangent of the peak, the decomposition temperature could be acquired. The decomposition temperature is 412 °C for PFPP, 425 °C for PBTFPP, 427 °C for PBTFBD and 399 °C for PBDFBD. They are all stable at a high temperature and could meet the demand of thermal stability.



**Figure 7.** Thermal gravimetric graphs of PFPP, PBTFPP, PBTFBD and PBDFBD.

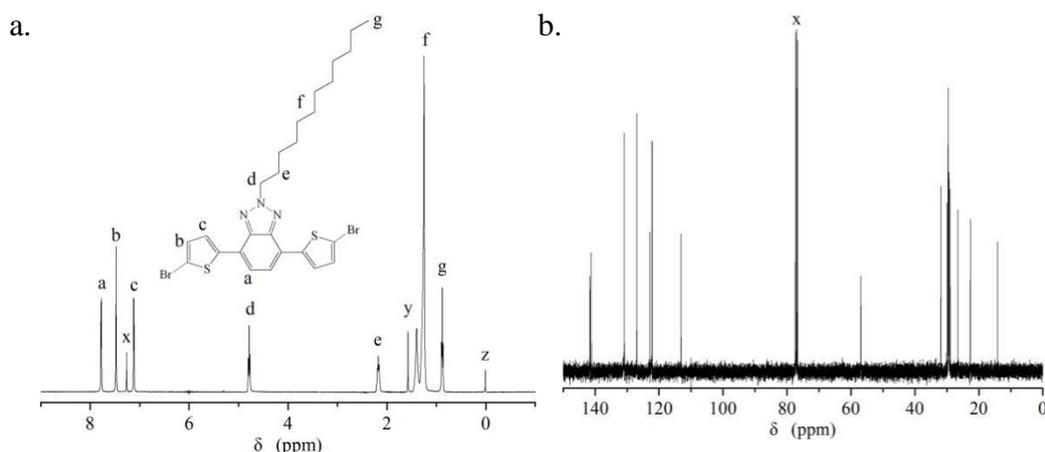
#### 4. CONCLUSION

Four copolymers, PFPP, PBTFPP, PBTFBD and PBDFBD, were synthesized successfully, and their corresponding band gaps are 1.87 eV, 1.91 eV, 1.97 eV and 1.98 eV, respectively. The coloration efficiencies are  $269.91\text{cm}^2\cdot\text{C}^{-1}$  for PFPP at 1560 nm,  $177.45\text{cm}^2\cdot\text{C}^{-1}$  for PBTFPP at 1570 nm,  $241.92\text{cm}^2\cdot\text{C}^{-1}$  for PBTFBD at 1560 nm, and  $174.67\text{cm}^2\cdot\text{C}^{-1}$  for PBDFBD at 1560 nm. When the copolymers change from neutral state to oxidized state, PFPP turns from thistle to transparent gray, PBTFPP turns from tan to transparent gray, PBTFBD turns from sienna to light slategray, and PBDFBD turns from rosy brown to light grey. The main problem we met in the experiments is the poor solubility of the copolymers, making the operation difficult, so researchers can introduce longer alkyl chain to enhance the solubility. In the kinetic experiments, PFPP is not stable, while the other three copolymers are relatively stable. In summary, except for PFPP, all the other copolymers could be candidates in electrochromic application.

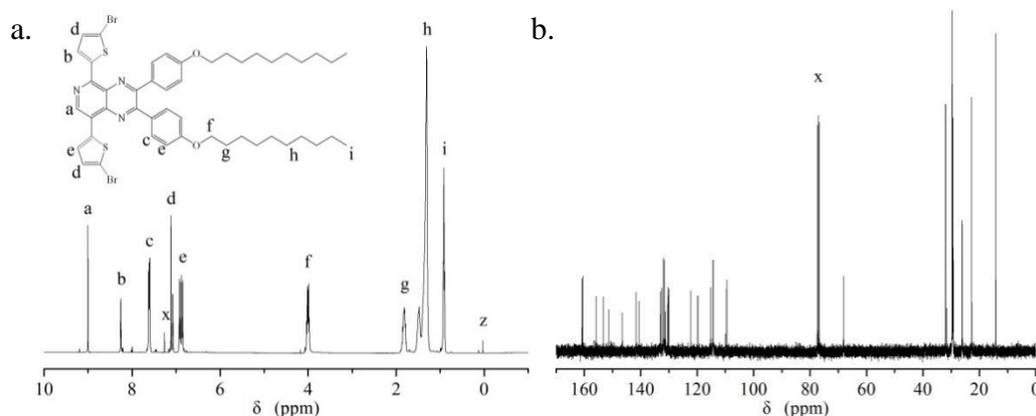
#### ACKNOWLEDGEMENTS

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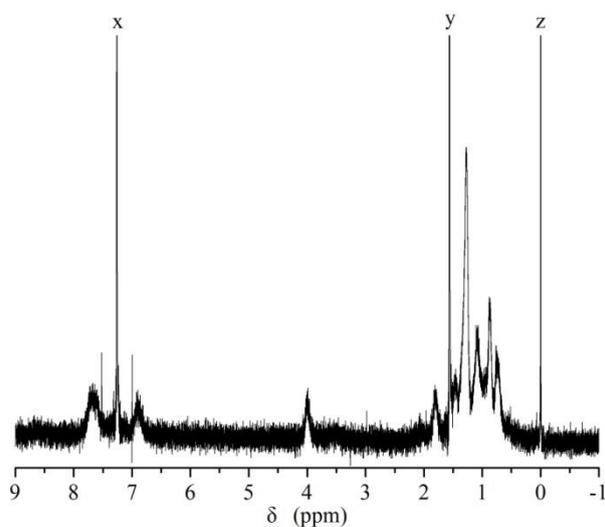
## SUPPORTING INFORMATION



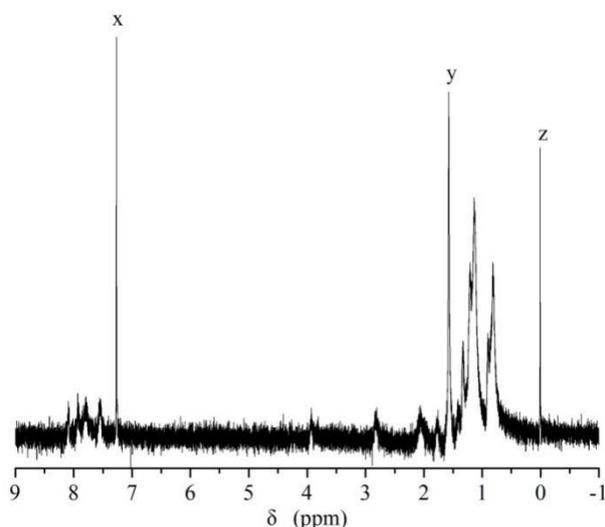
**Fig. S1.** (a) <sup>1</sup>H NMR spectrum and (b) <sup>13</sup>C NMR spectrum of 4,7-bis(5-bromothiophen-2-yl)-2-dodecyl-2H-benzo[d][1,2,3]triazole in CDCl<sub>3</sub>, x, y, z donate the peaks of chloroform, water and tetramethylsilane.



**Fig. S2.** (a) <sup>1</sup>H NMR spectrum and (b) <sup>13</sup>C NMR spectrum of 5,8-bis(5-bromothiophen-2-yl)-2,3-bis(4-(decyloxy)phenyl)pyrido[3,4-b]pyrazine in CDCl<sub>3</sub>, x, y, z donate the peaks of chloroform, H<sub>2</sub>O and tetramethylsilane.



**Fig. S3.** <sup>1</sup>H NMR spectrum of PFPP in CDCl<sub>3</sub>, x, y, z donate the peaks of chloroform, H<sub>2</sub>O and tetramethylsilane.



**Fig. S4.**  $^1\text{H}$  NMR spectrum of **PBDFBD** in  $\text{CDCl}_3$ , x, y, z donate the peaks of chloroform,  $\text{H}_2\text{O}$  and tetramethylsilane.

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