

# Synthesis and Electropolymerization of 9H-Carbazol-9-ylpyrene and Its Electrochromic Properties and Electrochromic Device Application

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9H-Carbazol-9-ylpyrene monomer was successfully synthesized via coupling reaction. Poly(9H-carbazol-9-ylpyrene) (PMCzP) was electrochemically synthesized and characterized. Characterizations of the resulting polymer PMCzP were performed by cyclic voltammetry (CV), UV-vis spectroscopy, Fourier transform infrared spectroscopy (FT-IR) and scanning electron microscopy (SEM). Moreover, the spectroelectrochemical and electrochromic properties of the polymer film were investigated. The resulting polymer film has distinct electrochromic properties and shows three different colors (light yellow, gray, grayish green) under various potentials. The PMCzP film shows a maximum optical contrast ( $\Delta T\%$ ) of 29% at 460 nm with a response time of 2.18 s. An electrochromic device (ECD) based on PMCzP and poly(3,4-ethylenedioxythiophene) (PEDOT) was also constructed and characterized. The optical contrast ( $\Delta T\%$ ) of the device at 623 nm was found to be 23% and response time was measured as 0.50 s. The CE of the device was calculated to be  $290 \text{ cm}^2 \text{ C}^{-1}$ . This ECD has satisfactory redox stability.

**Keywords:** Conjugated polymer; Spectroelectrochemistry; Electrochemical polymerization; Electrochromic device; 9H-Carbazol-9-ylpyrene.

## 1. INTRODUCTION

With the discovery of conducting polymers, a new era had been started in macromolecular science. It was found that they can be used in many areas, such as organic-based solar cells [1], organic field effect transistors [2], organic light-emitting diodes [3] and electrochromic devices [4–6]. An electrochromic material is one that changes color reversibly by an electrochemical reaction and the phenomenon is called electrochromism [7]. Up to now, many different types of organic and inorganic

electrochromic materials have been developed, such as inorganic metal oxide, mixed-valence metal complexes, organic small molecules and finally conjugated polymers [7]. Recently, electrochromic conjugated polymers have received much attention due to their fine-tunability of the band gap (and the color) [8], outstanding coloration efficiency [9], fast switching times, excellent processability and low cost [10]. For conjugated polymers, the electrochromism is 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 [11].

Conjugated polymers derived from polythiophene, polypyrrole, polyaniline and polycarbazole have been widely investigated. Among them, carbazole-containing polymers deserve a great attention due to their various useful properties such as easily forming relatively stable polarons (radical cations), high charge carrier mobility, photochemical stability [12] and electrochromic properties [13,14]. Recently, carbazole-based polymers have extensively studied in electrochromic devices application [15–18]. On the other hand, pyrene is also an important aromatic monomer, it is interesting to note that fine tuning in the band gap and neutral state color of the polymer can be achieved by the introduction of pyrene units into the polymer backbone [19,20]. The synthesis of new conjugated polymers by functionalizing precursor molecules is an attractive way to tailor the optical and electronic characteristics of electrochromic materials [21].

According to above consideration, in this study, 9H-carbazol-9-ylpyrene (MCzP) monomer was synthesized via coupling reaction according to the report in the literature [22]. Electrochemical polymerization of MCzP monomer was successfully carried out in 0.2 M NaClO<sub>4</sub>/acetonitrile (ACN)/dichloromethane (CH<sub>2</sub>Cl<sub>2</sub>) solution. The spectroelectrochemical and electrochromic properties of the PMCzP film were investigated in detail. The PMCzP film shows light yellow color at neutral state and grayish green color at full doped state. In addition, we constructed and characterized dual type electrochromic devices based on PMCzP and PEDOT in detail. Neutral state of device shows light yellow color, while oxidized state reveals blue color.

## 2. EXPERIMENTAL

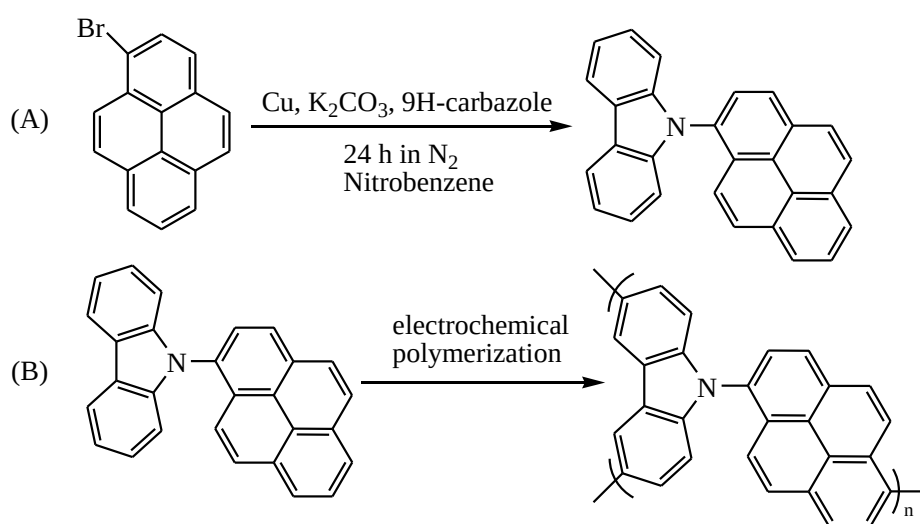
### 2.1. Materials

1-Bromopyrene, 9H-carbazole, potassium carbonate, copper powder, and 3,4-ethylenedioxythiophene (EDOT, 98%) were purchased from Aldrich Chemical and used as received. Commercial high-performance liquid chromatography grade acetonitrile (ACN, Tedia Company, INC., USA), dichloromethane (CH<sub>2</sub>Cl<sub>2</sub>, Sinopharm Chemical Reagent Co., Ltd, China), poly(methyl methacrylate) (PMMA, Shanghai Chemical Reagent Company), propylene carbonate (PC, Shanghai Chemical Reagent Company) and lithium perchlorate (LiClO<sub>4</sub>, Shanghai Chemical Reagent Company, 99.9%) were used directly without further purification. Sodium perchlorate (NaClO<sub>4</sub>, Shanghai Chemical Reagent Company, 98%) was dried in vacuum at 60 °C 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 washed with ethanol, acetone and deionized water successively under ultrasonic, and then dried by  $N_2$  flow.

## 2.2. Synthesis of 9H-carbazol-9-ylpyrene (MCzP)

9H-Carbazol-9-ylpyrene (MCzP) was synthesized according to the procedure reported by Seonju Jeong et al. [22]. As shown in Scheme 1, 1-bromopyrene, 9H-carbazole, potassium carbonate and copper powder were added in a three-neck flask and slowly stirred in nitrobenzene. The resulting solution was refluxed for 24 h at  $180^\circ\text{C}$ . The mixture was allowed to cool to room temperature and extracted with ethyl acetate and deionized water, then dried over  $\text{Na}_2\text{SO}_4$  and concentrated. The residue was purified by silica gel chromatography using 2:1 EtOAc/hexane as an eluent, yielding compound MCzP as a white solid.  $^1\text{H}$  NMR (DMSO, 400 MHz, ppm):  $\delta$ = 8.59 (d, 2H), 8.45 (d, 2H), 8.31 (d, 2H), 8.21 (d, 2H), 7.69 (d, 2H), 7.35 (t, 3H), 7.05 (m, 4H). FT-IR (KBr,  $\text{cm}^{-1}$ ): 1626, 1599, 1491, 1452(C=C, aromatic), 1234 ( $\nu_{\text{C-N}}$ ), 750, 721 ( $\nu_{\text{C-H}}$  carbazole ring out of plane), 750, 695 (out-of-plane vibration of the three adjacent C-H bonds of pyrene ring), 848, 818 (two adjacent C-H bonds of pyrene ring).



**Scheme 1.** Synthetic routes of 9H-carbazol-9-ylpyrene (MCzP) monomer and polymer.

## 2.3. Instrumentation

$^1\text{H}$  NMR spectroscopy studies were carried out on a Varian AMX 400 spectrometer and tetramethylsilane (TMS) was used as the internal standard for  $^1\text{H}$  NMR. FT-IR spectra were recorded on a Nicolet 5700 FT-IR spectrometer, where the samples were dispersed in KBr pellets. Scanning electron microscopy (SEM) measurements were taken using a Hitachi SU-70 thermionic field emission SEM. UV-vis spectra were carried out on a Perkin-Elmer Lambda 900 UV-vis-near-infrared

spectrophotometer. Digital photographs of the polymer film were taken by a Canon Power Shot A3000 IS digital camera.

#### 2.4. Electrochemistry

Electrochemical synthesis and experiments were performed in a one-compartment cell with a CHI 760 C Electrochemical Analyzer under computer control, employing a platinum wire with a diameter of 0.5 mm as the working electrode, a platinum ring as the counter electrode, and a silver wire (Ag wire) as the 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 taken in ACN/CH<sub>2</sub>Cl<sub>2</sub> (1:1) solution containing 0.2 M NaClO<sub>4</sub> as the supporting electrolyte. The pseudo reference electrode was calibrated externally using a 5 mM solution of ferrocene (Fc/Fc<sup>+</sup>) in the electrolyte ( $E_{1/2}(\text{Fc}/\text{Fc}^+) = 0.25 \text{ V vs. Ag wire in } 0.2 \text{ M NaClO}_4/\text{ACN}/\text{CH}_2\text{Cl}_2 (1:1, \text{ by volume}))$  [23]. All of the electrochemical experiments were carried out at room temperature under nitrogen atmosphere.

#### 2.5. Spectroelectrochemistry

Spectroelectrochemical data were recorded on Perkin-Elmer Lambda 900 UV–vis–near-infrared 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. The polymer films for spectroelectrochemistry were prepared by potentiostatically deposition on ITO electrode (the active area: 0.8 cm × 2.0 cm). The measurements were carried out in a 0.2 M NaClO<sub>4</sub>/ACN/CH<sub>2</sub>Cl<sub>2</sub> (1:1, by volume) solution.

#### 2.6. Preparation of the gel electrolyte

A gel electrolyte based on PMMA and LiClO<sub>4</sub> was plasticized with PC to form a highly transparent and conductive gel. ACN was also included as a high vapor pressure solvent to allow an easy mixing of the gel components. The composition of the casting solution by weight ratio of ACN:PC:PMMA:LiClO<sub>4</sub> was 70:20:7:3. The gel electrolyte was used for construction of the polymer electrochromic device cell [9].

#### 2.7. Construction of ECDs

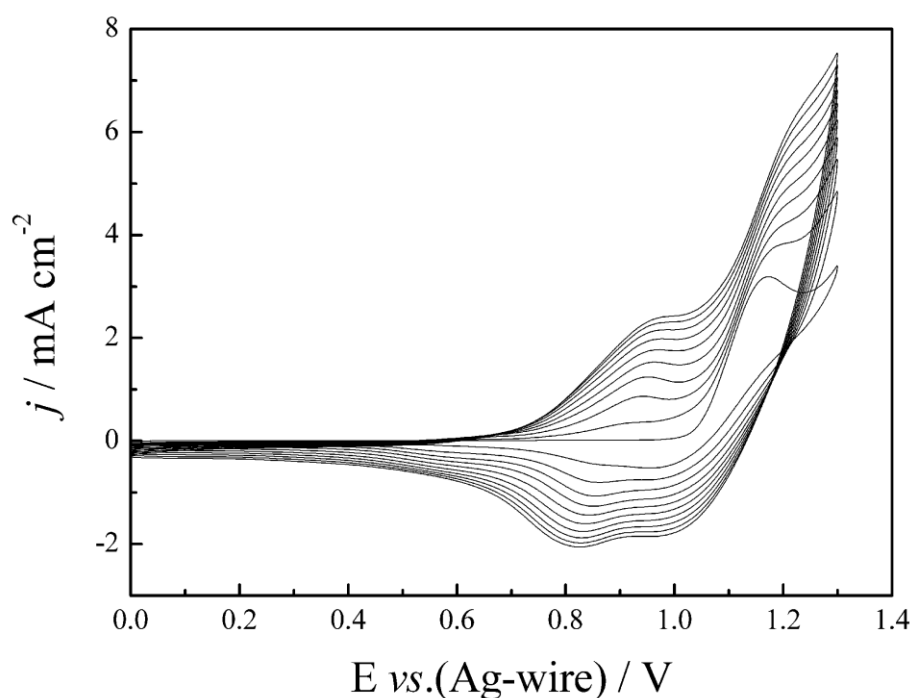
ECDs were constructed using two complementary polymers, namely PMCzP as the anodically coloring material and PEDOT as the cathodically coloring material. The PMCzP and PEDOT films were electrodeposited on two ITO glasses (the active area: 1.8 cm × 2.5 cm) at 1.3 and 1.4 V, respectively. Electrochromic device was built by arranging the two polymer films (one oxidized, the other reduced) facing each other separated by a gel electrolyte.

### 3. RESULTS AND DISCUSSION

#### 3.1. Electrochemical polymerization and characterization of PMCzP films

##### 3.1.1. Electrochemical polymerization

The successive CV curves of 0.005 M MCzP in 0.2 M NaClO<sub>4</sub>/ACN/CH<sub>2</sub>Cl<sub>2</sub> (1:1, by volume) was illustrated in Fig. 1. The onset oxidation potential ( $E_{\text{onset}}$ ) of MCzP in the solution is 1.03 V. As the CV scan continued, PMCzP film was 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 were increasing [24]. The CV curves of MCzP exhibit two redox processes, the oxidation and reduction peaks of the first redox process appear at 0.95 and 0.83 V, respectively. The reduction peak of the second redox process was located at 0.98 V, and the corresponding oxidation peak was overlapped with the oxidation waves of the MCzP monomer [25].

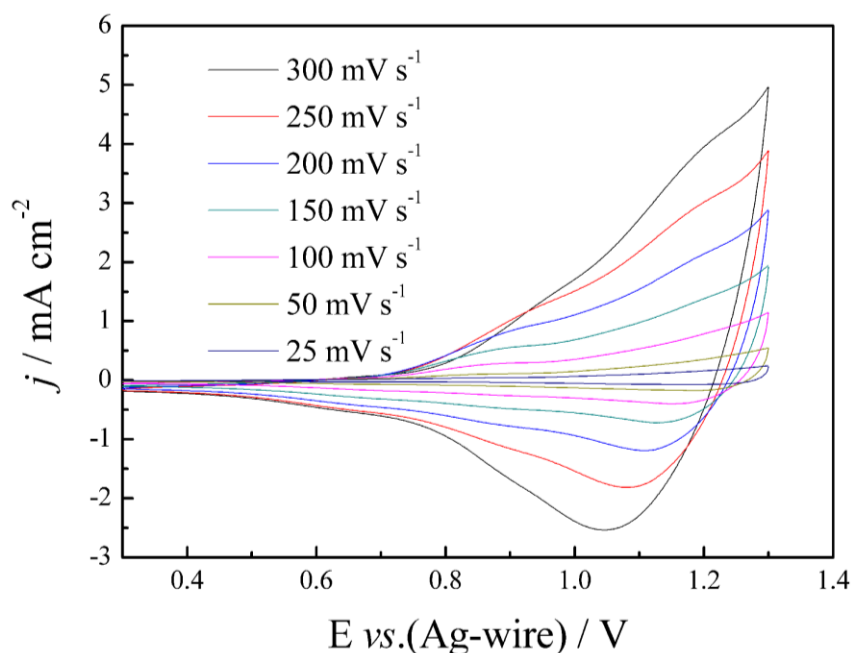


**Figure 1.** Cyclic voltammogram curves of 0.005 M MCzP in 0.2 M NaClO<sub>4</sub>/ACN/CH<sub>2</sub>Cl<sub>2</sub> (1:1, by volume) solutions at a scan rate of 100 mV s<sup>-1</sup>,  $j$  denotes the current density.

##### 3.1.2. Electrochemistry of the PMCzP film

Fig. 2 shows the electrochemical behavior of the PMCzP film (prepared on platinum wires by sweeping the potentials from 0 to 1.3 V for three cycles) at different scan rates between 25 and 300 mV s<sup>-1</sup> in 0.2 M NaClO<sub>4</sub>/ACN/CH<sub>2</sub>Cl<sub>2</sub> (1:1, by volume) solution. As shown in Fig. 2, the peak current

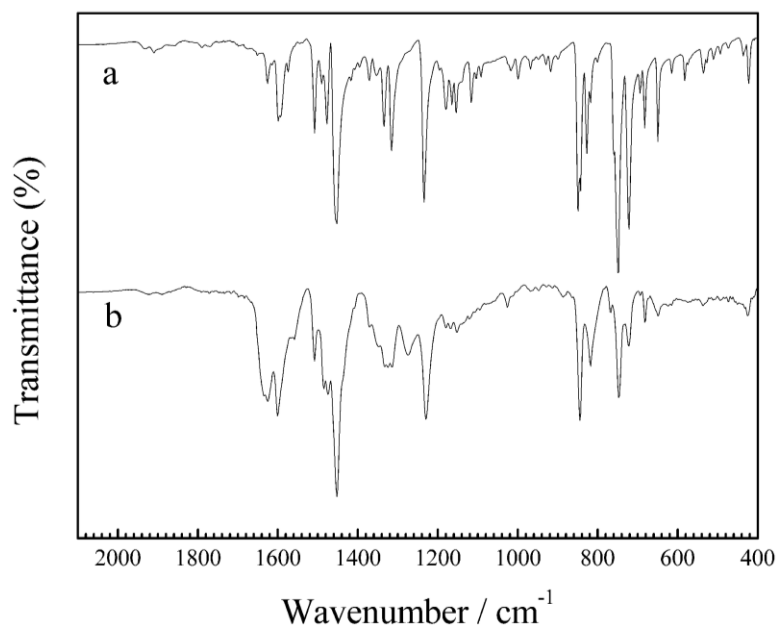
density ( $j$ ) response increases with the increasing of the scan rate, indicating that the polymer film adheres well to the electrode [25].



**Figure 2.** CV curves of the PMCzP film at different scan rates between 25 and 300  $\text{mV s}^{-1}$  in a monomer-free 0.2 M  $\text{NaClO}_4/\text{ACN}/\text{CH}_2\text{Cl}_2$  (1:1, by volume) solution,  $j$  denotes the current density.

### 3.1.3. FT-IR spectrum of PMCzP

To obtain a sufficient amount of PMCzP film for characterization, the ITO glass (the active area:  $1.8 \text{ cm} \times 2.5 \text{ cm}$ ) was employed as the working electrode. The polymer was synthesized at 1.3 V vs. Ag wire potentiostatically in a solution of 0.2 M  $\text{NaClO}_4/\text{ACN}/\text{CH}_2\text{Cl}_2$  (1:1, by volume) containing 0.005 M MCzP. Fig. 3 shows the FT-IR spectra of MCzP monomer and PMCzP film. In the spectrum of MCzP (Fig. 3a), the bands at 1626, 1599, 1491, 1452  $\text{cm}^{-1}$  were assigned to the vibration of the C=C bond of the phenylene ring. The peak at 1234  $\text{cm}^{-1}$  was ascribed to the vibration of C–N bond [15]. The peaks located at 750 and 721  $\text{cm}^{-1}$  were related to the out-of-plane vibration of C–H bonds of carbazole ring. The absorptions at 750 and 695  $\text{cm}^{-1}$  were assigned to the out-of-plane vibration of the three adjacent C–H bonds of pyrene ring, the 848 and 818  $\text{cm}^{-1}$  peaks were due to the two adjacent C–H bonds of pyrene ring [25,26]. Compare to the spectrum of MCzP, in the spectrum of PMCzP (Fig. 3b), the polymer exhibits two new peaks at about 885 and 820  $\text{cm}^{-1}$ , indicating the emergence of 1,2,4-tri-substituted benzene ring. The absorption at 748  $\text{cm}^{-1}$  dramatically decreases and the peak at 695  $\text{cm}^{-1}$  disappears after polymerization. These results imply that the polymerization occurs at the 3,6 positions of carbazole units and 4-position of pyrene rings.



**Figure 3.** The FT-IR spectra of (a) MCzP monomer and (b) PMCzP prepared potentiostatically at 1.3 V.

#### 3.1.4. Morphology

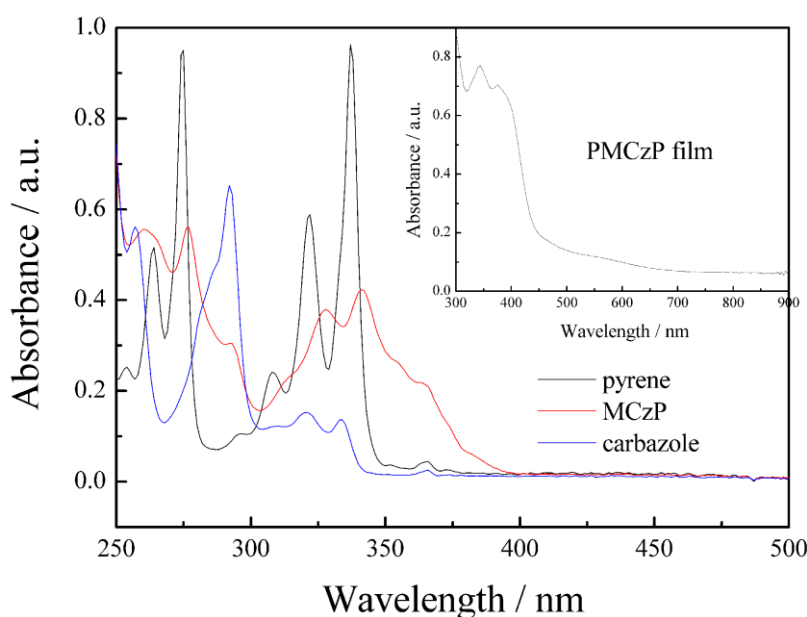
The morphology of PMCzP film was investigated by scanning electron microscopy (SEM). The PMCzP film was prepared by constant potential electrolysis from the solution of 0.2 M NaClO<sub>4</sub>/ACN/CH<sub>2</sub>Cl<sub>2</sub> (1:1, by volume) containing 0.005 M monomer on ITO electrode and dedoped before characterization. As shown in Fig. 4, the PMCzP film exhibits a porous structure with clusters of globules and the approximate diameters of these globules were around 500 nm.



**Figure 4.** SEM image of PMCzP deposited on ITO electrode potentiostatically at 1.3 V.

### 3.1.5. Optical properties of MCzP monomer and PMCzP film

The UV–vis spectra of MCzP, pyrene and carbazole monomers in  $\text{CH}_2\text{Cl}_2$  solution and PMCzP film deposited on ITO electrode were shown in Fig. 5. As seen from Fig. 5, the spectrum of the MCzP monomer shows both the characteristic absorptions of pyrene and carbazole. The neutral state PMCzP film exhibits two absorption bands at 344 and 377 nm. In addition, the optical band gaps ( $E_g$ ) of monomer and polymer were calculated from its low energy absorption edges ( $\lambda_{\text{onset}}$ ) ( $E_g = 1241/\lambda_{\text{onset}}$ ) [27]. The low energy edge of the absorption spectra of MCzP monomer was at 395 nm and the  $E_g$  was calculated as 3.14 eV, which was lower than that of the pyrene (3.60 eV) and carbazole (3.64 eV). The  $E_g$  of the PMCzP film was calculated as 2.73 eV, there was a decrease in the  $E_g$  comparing with that of polypyrene (2.95 eV) and polycarbazole (3.18 eV) [28]. Table 1 summarizes low energy absorption edges ( $\lambda_{\text{onset}}$ ) and the optical band gap ( $E_g$ ) of the MCzP, pyrene, carbazole, PMCzP, polypyrene and polycarbazole quite clearly.



**Figure 5.** UV–vis spectra of MCzP, pyrene and carbazole monomers dissolved in  $\text{CH}_2\text{Cl}_2$  solution. Inset: absorption spectrum of PMCzP film deposited on ITO electrode at the neutral state.

**Table 1.** The low energy absorption edges ( $\lambda_{\text{onset}}$ ) and the optical band gap ( $E_g$ ) of the MCzP, pyrene, carbazole, PMCzP, polypyrene and polycarbazole.

| Compounds                     | MCzP | pyrene | carbazole | PMCzP | polypyrene <sup>a</sup> | polycarbazole <sup>a</sup> |
|-------------------------------|------|--------|-----------|-------|-------------------------|----------------------------|
| $\lambda_{\text{onset}}$ (nm) | 395  | 345    | 341       | 454   | 421                     | 390                        |
| $E_g$ (eV)                    | 3.14 | 3.60   | 3.64      | 2.73  | 2.95                    | 3.18                       |

<sup>a</sup> Data were taken from Ref. [28].

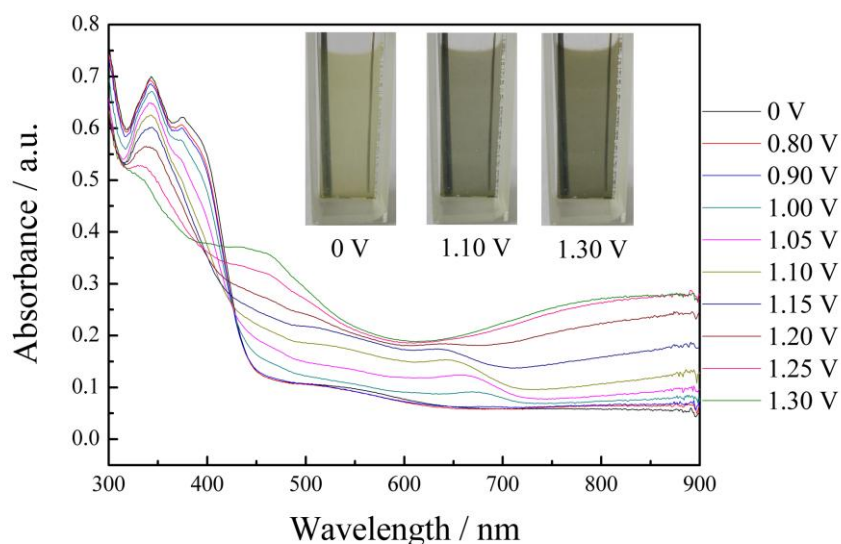


### 3.2. Electrochromic properties of PMCzP film

#### 3.2.1. Spectroelectrochemical properties of PMCzP film

Spectroelectrochemistry was 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 [29]. The PMCzP film (coated on ITO, prepared potentiostatically at 1.3 V in 0.2 M NaClO<sub>4</sub>/ACN/CH<sub>2</sub>Cl<sub>2</sub> (1:1, by volume) solution mixing with 0.005 M MCzP monomer) was switched between 0 and 1.30 V in a monomer-free 0.2 M NaClO<sub>4</sub>/ACN/CH<sub>2</sub>Cl<sub>2</sub> (1:1, by volume) solution in order to obtain the in situ UV-vis spectra (Fig. 6). At the neutral state, the polymer film exhibits a maximum absorption band centered at 344 nm with a shoulder located at around 377 nm were observed, which were due to the  $\pi$ - $\pi^*$  transition. As shown in Fig. 6, the intensity of the PMCzP  $\pi$ - $\pi^*$  electron transition absorption decreases while two charge carrier absorption bands located at around 460 nm and 800 nm increase dramatically upon oxidation. The appearance of charge carrier bands could be attributed to the evolution of polaron and bipolaron bands.

Furthermore, the PMCzP film shows three different colors under various potentials. The light yellow color of the film at neutral state (0 V) turns into gray color at an intermediate doped state (1.10 V), and then into grayish green color at full doped state (1.30 V) (Fig. 6).



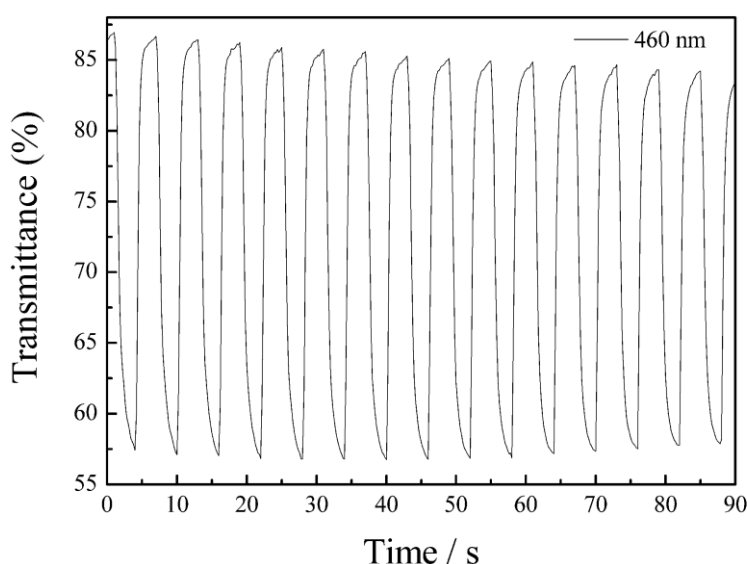
**Figure 6.** Spectroelectrochemical spectra of PMCzP film on ITO electrode with applied potentials between 0 V and 1.30 V in monomer-free 0.2 M NaClO<sub>4</sub>/ACN/CH<sub>2</sub>Cl<sub>2</sub> (1:1, by volume) solutions. Inset: the images of polymer film at 0 V (the neutral state), 1.10 V (the intermediate doped state) and 1.30 V (the full doped state).

#### 3.2.2. Electrochromic switching of PMCzP film in solution

It is important that polymers can switch rapidly and exhibit a noteworthy color change for electrochromic applications [30]. For this purpose, double potential step chronoamperometry technique

was used to investigate the switching ability of PMCzP film between its neutral and full doped states (Fig. 7) [31]. The dynamic electrochromic experiment for PMCzP film was carried out at 460 nm. The potential was switched between 0 V (the neutral state) and 1.30 V (the oxidized state) with regular intervals of 3 s. One important characteristic of electrochromic materials is the optical contrast ( $\Delta T\%$ ), which can be defined as the transmittance difference between the redox states. The  $\Delta T\%$  of the PMCzP was found to be 29% at 460 nm as shown in Fig. 7.

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) [32]. The optical response time of PMCzP was found to be 2.18 s from the reduced to the oxidized state and 1.13 s from the oxidized to the reduced state at 460 nm.



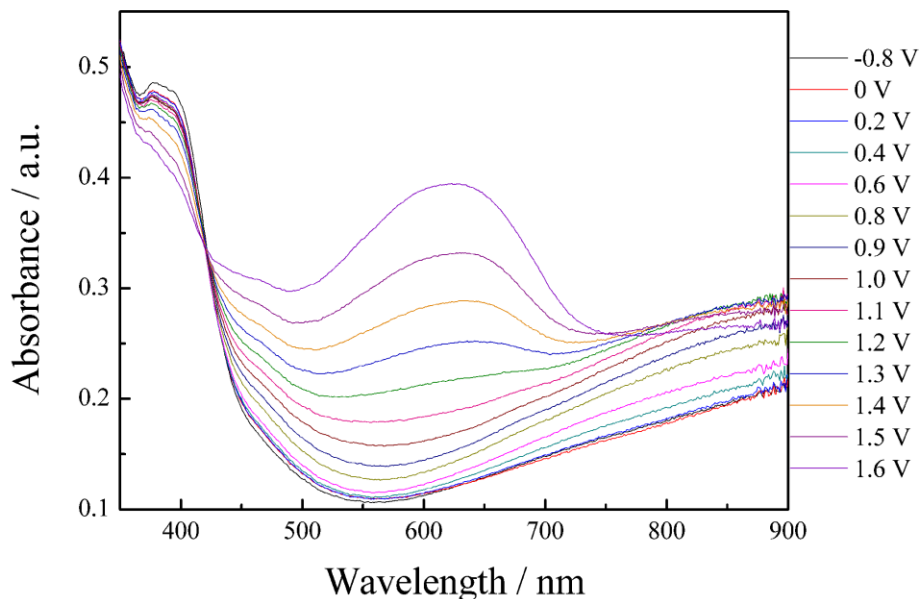
**Figure 7.** Electrochromic switching response for PMCzP film monitored at 460 nm in a 0.2 M NaClO<sub>4</sub>/ACN/CH<sub>2</sub>Cl<sub>2</sub> (1:1, by volume) solution between 0 V and 1.30 V with a residence time of 3 s.

### 3.3. Spectroelectrochemistry of electrochromic devices (ECDs)

#### 3.3.1. Spectroelectrochemical properties of ECDs

A dual type ECD consisting of PMCzP and PEDOT was constructed and its spectroelectrochemical behaviors were studied. Before composing the ECD, the anodically coloring polymer film PMCzP was fully reduced and the cathodically coloring polymer PEDOT was fully oxidized. The spectroelectrochemical spectra of the PMCzP/PEDOT device as a function of applied potential (between -0.8 V and 1.6 V) were given in Fig. 8. The PMCzP layer was in its neutral state at -0.8 V, where the absorption at 378 nm was due to  $\pi$ - $\pi^*$  transition of the PMCzP film. At that state, PEDOT does not reveal an obvious absorption at the UV-vis region of the spectrum and device reveals light yellow color. As the applied potential increases, the PMCzP layer starts to get oxidized and the

intensity of the peak due to the  $\pi$ - $\pi^*$  transition decreased. Meanwhile, PEDOT layer was in its reduced state, which leads to a new absorption at 623 nm due to the reduction of PEDOT, and the dominated color of the device was blue at 1.6 V.



**Figure 8.** Spectroelectrochemical spectra of the PMCzP/PEDOT device at various applied potentials from  $-0.8$  to  $1.6$  V.

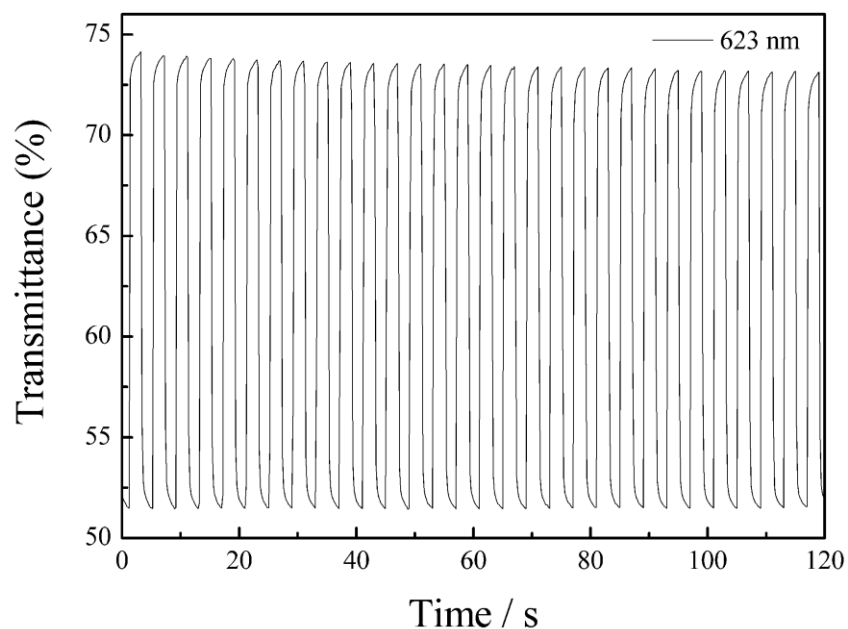
### 3.3.2. Switching of ECD

Kinetic studies were also done to test the response time of PMCzP/PEDOT ECD. Between  $-0.8$  and  $1.6$  V inputs with a regular time interval of  $2$  s, the optical response at  $623$  nm was illustrated in Fig. 9. The response time was found to be  $0.50$  s at 95% of the maximum transmittance difference from the neutral state to oxidized state and  $0.27$  s from the oxidized state to the neutral state, and optical contrast ( $\Delta T\%$ ) was calculated to be 23%.

The coloration efficiency (CE) is also an important characteristic for the electrochromic devices. CE can be calculated by using the equations and given below [33]:

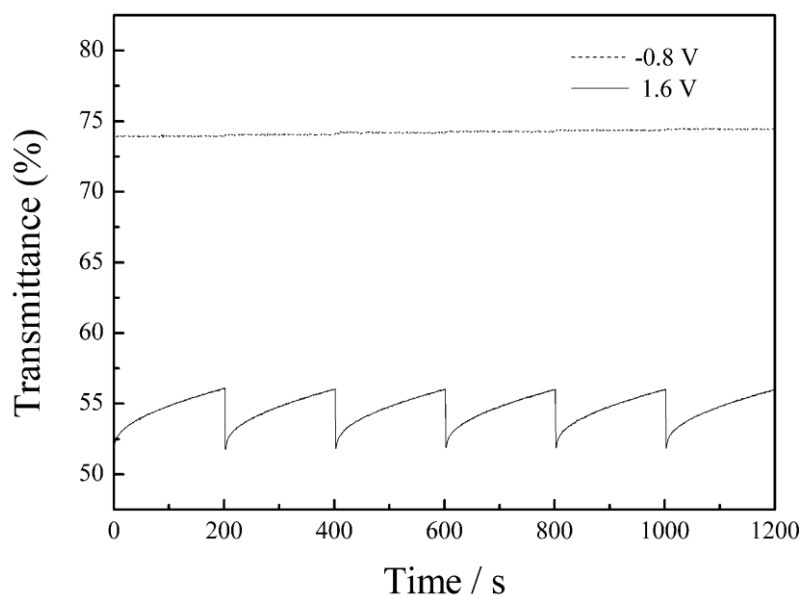
$$\Delta OD = \lg\left(\frac{T_b}{T_c}\right) \quad \text{and} \quad \eta = \frac{\Delta OD}{\Delta Q}$$

where  $T_b$  and  $T_c$  are the transmittances before and after coloration, respectively.  $\Delta OD$  is the change of the optical density, which is proportional to the amount of created color centers.  $\eta$  denotes the coloration efficiency (CE).  $\Delta Q$  is the amount of injected charge per unit sample area. The CE of the device (the active of area:  $1.8 \text{ cm} \times 2.0 \text{ cm}$ ) was calculated to be  $290 \text{ cm}^2 \text{ C}^{-1}$  at  $623 \text{ nm}$ , which had satisfactory coloration efficiency.



**Figure 9.** Electrochromic switching, optical transmittance change monitored at 623 nm for PMCzP/PEDOT device between  $-0.8$  V and  $1.6$  V with a residence time of 2 s.

### 3.3.3. Open circuit memory of ECD



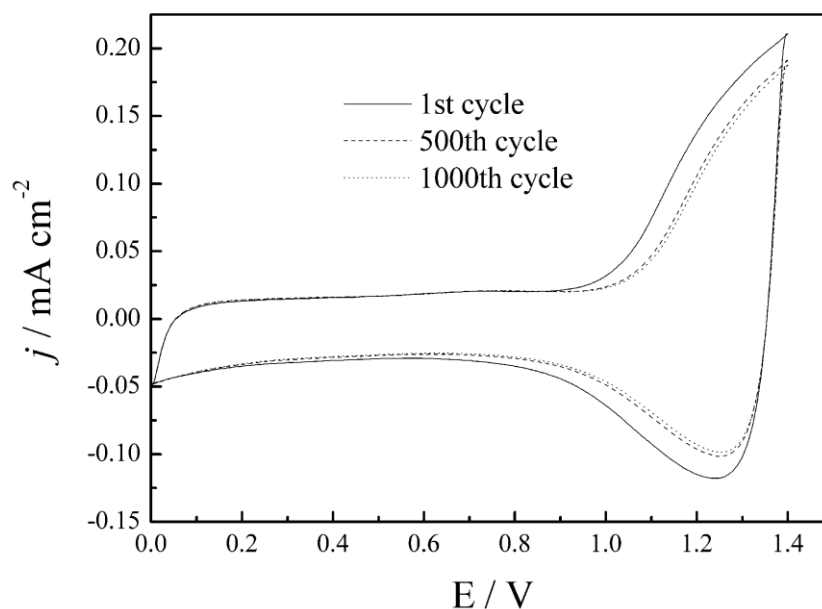
**Figure 10.** Open circuit stability of the PMCzP/PEDOT device monitored at 623 nm.

The optical memory in the electrochromic devices is an important parameter because it is directly related to its application and energy consumption during the use of ECDs [34]. The optical

spectrum for PMCzP/PEDOT device was monitored at 623 nm as a function of time at  $-0.8$  V and  $1.6$  V by applying the potential for  $1$  s for each  $200$  s time interval. As shown in Fig. 10, at light yellow colored state device shows a true permanent memory effect since there was almost no transmittance change under applied potential or open circuit conditions. In blue colored state device was rather less stable in terms of color persistence, however this matter can be overcome by application of current pulses to freshen the fully colored states.

### 3.3.4. Stability of ECD

The stability of the devices toward multiple redox switching usually limits the utility of electrochromic materials in ECD applications. Therefore, redox stability is another important parameter for ECD [35]. For this reason, the PMCzP/PEDOT device was tested with cyclic voltammetry by applying potentials between  $0$  and  $1.4$  V with  $500$   $\text{mV s}^{-1}$  to evaluate the stability of the device (Fig. 11). After  $500$  cycles,  $86\%$  of its electroactivity was retained and there was no obvious decrease of activity between  $500$  cycles and  $1000$  cycles, which indicating that this device has satisfactory redox stability.



**Figure 11.** Cyclic voltammogram of PMCzP/PEDOT device as a function of repeated with a scan rate of  $500$   $\text{mV s}^{-1}$ .

## 4. CONCLUSIONS

9H-Carbazol-9-ylpyrene monomer was synthesized by coupling reaction and then its polymer was successfully synthesized by electrochemical oxidation of the monomer in  $0.2$  M  $\text{NaClO}_4/\text{ACN}/\text{CH}_2\text{Cl}_2$  ( $1:1$ , by volume) solution. The obtained polymer film was studied by cyclic

voltammetry, UV–vis spectra, FT-IR spectra and scanning electron microscopy. Spectroelectrochemistry reveals that PMCzP film has distinct electrochromic properties and shows three different colors under various potentials (light yellow, gray, and grayish green). Maximum contrast ( $\Delta T\%$ ) and response time of the PMCzP film were measured as 29% and 2.18 s at 460 nm. The dual type ECD based on PMCzP and PEDOT was also constructed and characterized. Electrochromic switching study results show that optical contrast ( $\Delta T\%$ ) and response time were 23% and 0.50 s at 623 nm, respectively. The CE of the ECD was calculated to be  $290 \text{ cm}^2 \text{ C}^{-1}$ . This ECD shows light yellow color at neutral state and blue color at oxide state.

#### ACKNOWLEDGEMENTS

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