Article

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Poly(tris(4-carbazoyl-9-ylphenyl)amine)/Three Poly(3,4-ethylenedioxythiophene) Derivatives in Complementary High-Contrast Electrochromic Devices

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Abstract: A carbazole-based polymer (poly(tris(4-carbazoyl-9-ylphenyl)amine) (PtCz)) is electrosynthesized on an indium tin oxide (ITO) electrode. PtCz film displays light yellow at 0.0 V, earthy yellow at 1.3 V, grey at 1.5 V, and dark grey at 1.8 V in 0.2 M LiClO 4 /ACN/DCM (ACN/DCM = 1:3, by volume) solution. The ΔT and coloration efficiency (η) of PtCz film are 30.5% and 54.8 cm 2 ·C −1, respectively, in a solution state. Three dual-type electrochromic devices (ECDs) are fabricated using the PtCz as the anodic layer, poly(3,4-ethylenedioxythiophene) (PEDOT), poly(3,3-dimethyl-3,4-dihydro-thieno[3,4-b][1,4]dioxepine) (PProDOT-Me 2), and poly(3,4-(2,2-diethylpropylenedioxy)thiophene) (PProDOT-Et 2) as the cathodic layers. PtCz/PProDOT-Me 2 ECD shows high ΔT max (36%), high η max (343.4 cm 2 ·C −1), and fast switching speed (0.2 s) at 572 nm. In addition, PtCz/PEDOT, PtCz/PProDOT-Me 2, and PtCz/PProDOT-Et 2 ECDs show satisfactory open circuit memory and long-term stability.

Keywords: electrochemical polymerization; optical contrast; electrochromic switching; coloration efficiency; electrochromic device

1. Introduction

π-conjugated polymers (CPs) and oligomers have attracted a great deal of interest due to their suitability for potential applications in supercapacitors [1,2], catalysts [3–5], actuators [6], polymer light-emitting diodes [7–9], electrochromic devices (ECDs) [10–12], polymer solar cells [13], and sensors [14–16]. The most commonly studied classes of CPs are poly(phenylene vinylene)s (PPV) [17], polycarbazoles (PCz) [18,19], polythiophenes (PT) [20], polypyrroles (PPy) [21], poly(3,4-ethylenedioxythiophene) (PEDOT) [22], and polyanilines (PANI) [23]. Cz-based polymers have been widely used as hole transporting and host materials in optoelectronic devices due to the nitrogen atom of Cz ring shows good hole transporting ability, high thermal stability, and ease of formation of radical cations and dbinations [24]. Polythiophenes and polypyrroles have been extensively used as electrochromic materials due to the fact that they can be easily
synthesized electrochemically or chemically with a wide range of electrochromic properties available through alkyl, alkoxy, and phenyl substitution on polythiophenes and polypyrroles. PEDOT and its derivatives poly(3,3-dimethyl-3,4-dihydro-thieno[3,4-b][1,4]dioxepine) (PProDOT-Me₂) and poly(3,3-diethyl-3,4-dihydro-thieno[3,4-b][1,4]dioxepine) (PProDOT-Et₂) were extensively investigated for many useful properties including low oxidation potential, electron-rich dioxy group, optical transparency in doped state, moderate band gap, and high stability [25,26].

There have been no reports for the applications of poly(tris(4-carbazoyl-9-ylphenyl)amine) as anodic polymer in electrochromic devices. In the present study, a carbazole-based monomer (tris(4-carbazoyl-9-ylphenyl)amine, tCz) was synthesized and its corresponding homopolymer (PtCz) was polymerized electrochemically. The spectroelectrochemistry, electrochromic photographs, optical contrast, and coloration efficiency of PtCz film in solution state were studied. Moreover, dual-type ECDs based on PtCz and PEDOT derivatives were fabricated, the electrochromic behaviors, open circuit memory, and long-term switching stability of PtCz/PEDOT, PtCz/PProDOT-Me₂, and PtCz/PProDOT-Et₂ ECDs were also investigated.

2. Materials and Methods

2.1. Materials

All chemicals were purchased from Sigma-Aldrich, Tokyo Chemical Industry Co., Ltd. (TCI, Tokyo, Japan), Acros (Geel, Belgium), Alfa-Aesar (Ward Hill, MA, USA), and used as received. Tris(4-carbazoyl-9-ylphenyl)amine, 3,3-dimethyl-3,4-dihydro-thieno[3,4-b][1,4]dioxepine (ProDOT-Me₂) and 3,3-diethyl-3,4-dihydro-thieno[3,4-b][1,4]dioxepine (ProDOT-Et₂) were synthesized following previously published procedures [27,28].

2.2. Synthesis of Tris(4-carbazoyl-9-ylphenyl)amine (tCz)

Carbazole (70.22 mg, 0.42 mmol), tris(4-iodophenyl)amine (68.53 mg, 0.11 mmol), K₂CO₃ (165.84 mg, 1.20 mmol), Cu bronze (69.58 mg, 1.095 mmol) and 18-crown-6 (8.72 mg, 0.033 mmol) were stirred in 45 mL 1,2-dichlorobenzene for two days at 190 °C. The crude product is vacuum distilled and the residue is purified by column chromatography using a mixture of hexane and dichloromethane (DCM) (2:1 by volume) as eluent. Yield: 41%. ¹H-NMR (700 MHz, DMSO-d₆): δ 8.26 (d, 6H, Ar-H), 7.69 (dd, 6H, Ar-H), 7.57 (dd, 6H, Ar-H), 7.50–7.46 (m, 12H, Ar-H), 7.32–7.30 (m, 6H, Ar-H). Elem. anal. calcd. for C₅₄H₃₆N₄: C, 87.54%; H, 4.90%; N, 7.56%. Found: C, 87.32%; H, 4.82%; N, 7.57%.

2.3. Electrosynthesis of PtCz, PProDOT-Me₂, and PProDOT-Et₂ Films

The electrosynthesis of PtCz film in an ACN/DCM (1:3, by volume) solution containing 0.2 M LiClO₄ as a supporting electrolyte was carried out by scanning the potential between 0.0 and 1.8 V (vs. Ag/AgCl) potentiodynamically at 100 mV·s⁻¹ for 3 cycles. The electrochemically deposited PtCz film was rinsed with DI water for 5 min and then dried at 105 °C for 3 min. As shown in Table 1, the PEDOT, PProDOT-Me₂, and PProDOT-Et₂ films were deposited from 0.008 M EDOT, 0.010 M ProDOT-Me₂, and 0.017 M ProDOT-Et₂ in a 0.2 M LiClO₄/acetonitrile (ACN) solution, respectively. Electrosynthesis of PEDOT, PProDOT-Me₂, and PProDOT-Et₂ films were performed potentiostatically at 1.7 V (vs. Ag/AgCl) for 50 mC. Polymer thicknesses at the electrode surface obtained from an Alpha-Step profilometer (KLA Tencor D-120, CA, USA) were about 200–300 nm.

Table 1. Feed species of cathodic polymer electrodes (a)–(c).

| Electrodes | Cathodic Polymer | Feed Species | Deposition Amount of Cathode |
|------------|-----------------|-------------|-----------------------------|
| (a)        | PEDOT           | 8 mM EDOT   | 50 mC                       |
| (b)        | PProDOT-Me₂     | 10 mM PProDOT-Me₂ | 50 mC                       |
| (c)        | PProDOT-Et₂     | 17 mM PProDOT-Et₂ | 50 mC                       |
2.4. Electrochromic Characterization

Electrochromic characterization of the polymer films and electrochromic devices were carried out using a CHI660D electrochemical analyzer (CH Instruments, Austin, TX, USA). Cyclic voltammetry (CV) studies were performed using in a three-component cell, which contained an ITO-coated glass plate (area: 1 cm × 1.5 cm) as the working electrode, a platinum wire as the counter electrode, and an Ag/AgCl as the reference electrode. The in situ spectroelectrochemical spectra were recorded using an Aglient Cary 60 UV-Visible spectrophotometer (Varian Inc., Walnut Creek, CA, USA) in time course mode.

2.5. Preparation of Electrochromic Electrolytes

The polymer electrolytes of the ECDs were prepared using the solution-cast method. To prepare the solution, poly(methyl methacrylate) (PMMA), propylene carbonate (PC), and LiClO\(_4\) were dissolved in acetone, and the mixture was stirred magnetically at room temperature for 36 h. The polymer electrolytes were prepared using PMMA:PC:LiClO\(_4\) in a weight ratio of 33:53:14. The final mixture was cast on glass petri dishes. After evaporating the solvent at room temperature for 2 h, the samples were vacuum-dried at 80 °C for 24 h to remove the remaining solvent completely. Finally, the self-standing polymer electrolytes were obtained. The ECDs were fabricated by sandwiching the polymer electrolytes between two electrodes to perform the electrochromic measurements.

2.6. Fabrication of the ECDs

The ECDs were constructed using two complementary polymer layers, PtCz as the anodically coloring layer, PEDOT, PProDOT-Me\(_2\), or PProDOT-Et\(_2\) as the cathodically coloring layer. PtCz, PEDOT, PProDOT-Me\(_2\), and PProDOT-Et\(_2\) films were deposited on ITO substrates (active area: 1 cm × 1.5 cm). The ECDs were fabricated by arranging the oxidized and reduced films to face each other, and they were separated by an electrolyte. The fabrication procedures of ECDs are shown in Figure 1.

![Figure 1. The fabrication procedures of electrochromic devices (ECDs).](image-url)

3. Results and Discussion

3.1. Electrochemistry of tCz and Its Electrochemical Polymerization

The electrosynthesis of PtCz film was implemented using CV with a scan rate of 100 mV s\(^{-1}\). The electropolymerization scheme and mechanism of PtCz are shown in Figure 2 [29]. The successive cyclic voltammograms of 0.002 M neat tCz taken in an ACN/DCM (1:3, by volume) solution containing 0.2 M LiClO\(_4\) as a supporting electrolyte at a scanning rate of 100 mV s\(^{-1}\) are shown in Figure 3. For the first scan of cyclic voltammogram, the onset potential of tCz is 0.86 V vs. Ag/AgCl, two oxidation peaks located at 0.95 and 1.18 V indicate the polaron and bipolaron formation of tCz, the reduction peaks of tCz locate at 1.1 and 0.7 V. The increase in the oxidation and reduction curves wave current
densities indicates that the amount of polymer deposited on the ITO working electrode increases with increasing cycles. The polymerization of tCz shows two quasi-reversible oxidation and reduction processes in Figure 3.

**Figure 2.** (a) The electrochemical polymerization scheme of the carbazole-based polymer (poly(tris(4-carbazoyl-9-ylphenyl)amine) (PtCz)); (b) the electropolymerization mechanism of PtCz.
3.2. Electrochemical Behavior of PtCz Films

The as-prepared PtCz film was swept between 0.0 to 1.8 V at various scan rates between 10 and 200 mV s\(^{-1}\) in 0.2 M LiClO\(_4\)/ACN/DCM solution. As shown in Figure 4, the electrochemical behavior of the PtCz film shows a single well-defined redox process, the anodic and cathodic peak current densities are proportional to the scan rates, implying that PtCz film is electroactive and adheres well to the electrode, and the electrochemical processes of PtCz film are reversible and not dominated by diffusion effects [30].

![Figure 3. Electrochemical synthesis of PtCz in acetonitrile (ACN)/dichloromethane (DCM) (1:3, by volume) solution at 100 mV s\(^{-1}\) on indium tin oxide (ITO) working electrode.](image)

![Figure 4. Cyclic voltammetry (CV) curves of the PtCz film-coated ITO working electrode at different scan rates between 10 and 200 mV s\(^{-1}\) in 0.2 M LiClO\(_4\)/ACN/DCM solution. Inset: Scan rate dependence of the PtCz anodic and cathodic peak current densities, respectively.](image)
3.3. Spectroelectrochemistry of PtCz and PProDOT-Me₂ Films

Spectroelectrochemistry can be used to analyze the changes in the absorption spectra of ECDs at various potentials [31]. Optoelectrochemical spectra of PtCz and PProDOT-Me₂ films are shown in Figure 5. The PtCz film shows a π-π* transition peak at around 360 nm at 0.0 V, and it is light yellow in undoped state. Upon stepwise oxidation, the peak intensity at 360 nm diminishes gradually and new absorption bands at around 800 nm emerge, the PtCz film displays earthy yellow at 1.3 V, grey at 1.5 V, and dark grey at 1.8 V. On the other hand, the PProDOT-Me₂ film shows two significant peaks at 570 and 625 nm at −1.5 V and presents dark blue in its neutral state. Upon oxidation progressively, the peak intensity at 570 and 625 nm diminish gradualy and new absorption bands at more than 1000 nm emerge, the PProDOT-Me₂ film displays grey at −0.8 V and light blue at −1.5 V. The colorimetric values \( (L^*, a^*, b^*) \), CIE chromaticity values \((x, y)\), and CIE chromaticity diagrams of the PtCz and PProDOT-Me₂ films at various potentials were shown in Table 2.

**Figure 5.** UV-Visible spectra of (a) PtCz and (b) PProDOT-Me₂ on ITO in an ACN/DCM (1:3, by volume) solution containing 0.2 M LiClO₄.

**Table 2.** Colorimetric values \((L^*, a^*, b^*)\), CIE chromaticity values \((x, y)\), and CIE chromaticity diagrams of the PtCz and PProDOT-Me₂ at various applied potentials.

| Electrodes | Potential (V) | \( L^* \) | \( a^* \) | \( b^* \) | \( x \) | \( y \) | Diagrams |
|------------|---------------|-----------|-----------|-----------|-------|-------|----------|
| PtCz       | 0.0           | 73.95     | 5.59      | 15.85     | 0.4770| 0.4159|          |
|            | 1.0           | 74.84     | 6.13      | 24.13     | 0.4864| 0.4226|          |
|            | 1.3           | 73.46     | 3.02      | 21.02     | 0.4778| 0.4248|          |
|            | 1.5           | 68.67     | −1.78     | 11.72     | 0.4588| 0.4239|          |
|            | 1.7           | 64.66     | −3.54     | 6.65      | 0.4490| 0.4215|          |
|            | 1.8           | 61.15     | −3.02     | 5.17      | 0.4482| 0.4193|          |
| PProDOT-Me₂| −1.5          | 49.73     | 6.28      | −46.01    | 0.3710| 0.3162|          |
|            | −1.0          | 60.60     | 5.54      | −31.45    | 0.4078| 0.6232|          |
|            | −0.8          | 78.43     | 3.60      | −10.50    | 0.4411| 0.3911|          |
|            | −0.4          | 88.43     | −2.94     | −5.89     | 0.4362| 0.4050|          |
|            | −0.2          | 88.98     | −2.68     | −5.85     | 0.4368| 0.4048|          |
|            | 0.0           | 89.57     | −2.56     | −5.18     | 0.4378| 0.4053|          |

3.4. Electrochemical Switching of PtCz Film

Double potential step techniques can be used to investigate the response time and stability of polymer films during consecutive scans [32]. The double potential step chronoamperometry coupled with spectrophotometer of PtCz film was performed by stepping potentials between 0.0 and 1.8 V with a residence time of 10 s, and the transmittance-time profile of PtCz film is displayed in Figure 6. The coloration switching time \( (\tau_c) \) and bleaching switching time \( (\tau_b) \) were defined as the period
required for achieving 90% of the desired response [33–36]. The \( \tau_c \) and \( \tau_b \) of PtCz film estimated at the third cycle at 760 nm are 5.5 and 5.0 s, respectively. The optical contrast (\( \Delta T \)) is an important property of electrochromic polymer films, which denotes as the transmittance difference between bleaching and coloring states of polymer films in solution state. The optical density (\( \Delta \text{OD} \)) can be calculated using the following formula:

\[
\Delta \text{OD} = \log\left(\frac{T_{\text{ox}}}{T_{\text{red}}}\right)
\]

where \( T_{\text{ox}} \) is the transmittance of anodic material in coloration state and \( T_{\text{red}} \) is the transmittance of anodic material in bleaching state.

As shown in Table 3, the \( \Delta T_{\text{max}} \) and \( \Delta \text{OD} \) values of PtCz film are 30.5% and –0.28, respectively, at 760 nm in 0.2 M LiClO4 / ACN/DCM (ACN/DCM = 1:3, by volume) solution. The \( \Delta T_{\text{max}} \) of PtCz film is larger than those reported for poly(9H-carbazol-9-ylpyrene) (\( \Delta T_{\text{max}} = 29\% \) at 460 nm [37]) and poly(1,3-bis(carbazol-9-yl)benzene) (\( \Delta T_{\text{max}} = 18.6\% \) at 1050 nm [38]) (Table 4). However, the \( \Delta T \) of PtCz film is smaller than those reported for poly(ethyl-4-(3,6-di(thiophen-2-yl)-9H-carbazole-9-yl)-benzoate) (\( \Delta T_{\text{max}} = 36\% \) at 1100 nm [39]), poly(2,5-bis(9-methyl-9H-carbazol-3-yl)-1,3,4-oxadiazole) (\( \Delta T_{\text{max}} = 75\% \) at 660 nm [40]), poly(3,6-di(carbazol-9-yl)-N-(4-nitrophenyl)carbazole) (\( \Delta T_{\text{max}} = 52\% \) at 710 nm [29]), and poly(4,4'-bis(N-carbazolyl)-1,1'-biphenyl) (\( \Delta T_{\text{max}} = 44.1\% \) at 800 nm) [41].

### Table 3. Optical and electrochemical properties investigated at the selected applied wavelength for PtCz film and ECDs.

| PtCz film and ECDs | N | \( T_{\text{ox}} \) (%) | \( T_{\text{red}} \) (%) | \( \Delta T \) (%) | \( \Delta \text{OD} \) | \( \eta \) (cm²-C⁻¹) | \( \tau_c/s \) | \( \tau_b/s \) |
|-------------------|---|----------------|----------------|----------------|----------------|-----------------|---------------|---------------|
| PtCz (760 nm) a   | 3 | 33.0           | 63.5           | 30.5           | –0.28          | 54.8            | 5.5           | 5.0           |
| PtCz / PEDOT (600 nm) a | 50 | 10.4           | 33.0           | 22.2           | –0.49          | 256.5           | 0.2           | 0.2           |
| PtCz / PProDOT-Me₂ (572 nm) a | 3 | 11.6           | 47.6           | 36.0           | –0.61          | 248.4           | 0.2           | 0.6           |
| PtCz / PProDOT-Et₂ (591 nm) a | 50 | 9.3            | 37.3           | 28.0           | –0.59          | 343.4           | 0.2           | 0.2           |

a The selected applied wavelength for PtCz film and ECDs.
The coloration efficiency ($\eta$) of electrochromic materials can be estimated using the following equation [42]:

$$\eta = \frac{\Delta \text{OD}}{Q_d}$$  \hspace{1cm} (2)

where $Q_d$ is the charge density (injected/ejected charges per unit sample area). The $\eta$ value of PtCz film is 54.8 cm$^2$·C$^{-1}$ at 760 nm in 0.2 M LiClO$_4$/ACN/DCM (ACN/DCM = 1:3, by volume) solution. The $\eta$ of PtCz film is larger than that reported for poly(1,3-bis(carbazol-9-yl)benzene) ($\eta = 35$ cm$^2$·C$^{-1}$ [29]). However, the $\Delta T_{\text{max}}$ of PtCz film is smaller than those reported for poly(4,4$^*$-bis(N-carbazolyl)-1,1$'$-biphenyl ($\eta = 98$ cm$^2$·C$^{-1}$ [41]) and poly(1,3-bis(carbazol-9-yl)benzene) ($\eta = 180.3$ cm$^2$·C$^{-1}$ [38]).

3.5. Spectroelectrochemistry of PtCz/PEDOT, PtCz/PProDOT-Me$_2$, and PtCz/PProDOT-Et$_2$ ECDs

Figure 7 shows the UV-Visible spectra of PtCz/PEDOT, PtCz/PProDOT-Me$_2$, and PtCz/PProDOT-Et$_2$ ECDs at various voltages. At 0.0 V, the PtCz/PEDOT, PtCz/PProDOT-Me$_2$, and PtCz/PProDOT-Et$_2$ ECDs show $\pi-\pi^*$ transition peaks of PtCz film at around 360 nm.

Upon increasing the potential gradually, the $\pi-\pi^*$ transition peak of PtCz film diminishes and new absorption band at around 580–650 nm emerges. At 1.7–1.8 V, PEDOT, PProDOT-Me$_2$, and PProDOT-Et$_2$ films exhibit distinct absorption band at around 500–700 nm, and PtCz/PEDOT, PtCz/PProDOT-Me$_2$, and PtCz/PProDOT-Et$_2$ ECDs became dark blue at 1.7–1.8 V. The electrochromic photographs, colorimetric values ($L^*$, $a^*$, and $b^*$), CIE chromaticity values ($x$, $y$), and CIE chromaticity diagram of the PtCz/PProDOT-Me$_2$ ECD at various potentials are summarized in Table 5.
Table 5. Electrochromic photographs, colorimetric values ($L^*$, $a^*$, and $b^*$), CIE chromaticity values ($x$, $y$), and CIE chromaticity diagram of the PtCz/PProDOT-Me2 ECD at various applied potentials.

| ECD          | Potential (V) | Photographs | $L^*$  | $a^*$  | $b^*$  | $x$   | $y$   | Diagram |
|--------------|---------------|-------------|--------|--------|--------|-------|-------|---------|
| PtCz/PProDOT-Me2 | −0.8          |             | 85.06  | −1.40  | 26.92  | 0.472 | 0.434 |         |
|              | 0.0           |             | 80.27  | −0.28  | 19.04  | 0.468 | 0.427 |         |
|              | 0.8           |             | 61.82  | 2.72   | −8.36  | 0.441 | 0.392 |         |
|              | 1.2           |             | 56.30  | 4.46   | −17.66 | 0.428 | 0.374 |         |
|              | 1.5           |             | 54.18  | 5.26   | −21.30 | 0.423 | 0.366 |         |

Figure 8 shows the transmittance-time profiles of PtCz/PEDOT, PtCz/PProDOT-Me2, and PtCz/PProDOT-Et2 ECDs by repeating potentials between 0.0 and 1.8 V with a time interval of 10 s. The $\tau_c$ and $\tau_b$ estimated at various cycles for PtCz/PEDOT, PtCz/PProDOT-Me2, and PtCz/PProDOT-Et2 ECDs are listed in Table 3. The $\tau_c$ and $\tau_b$ of PtCz/PEDOT ECD at 600 nm were 0.2 and 0.2 s, respectively, at the 50th cycle. Under similar conditions, the $\tau_c$ values of PtCz/PProDOT-Me2 ECD at 572 nm and PtCz/PProDOT-Et2 ECD at 591 nm were 0.2 and 0.1 s at the 50th cycle, respectively, and the corresponding $\tau_b$ values were 0.2 and 0.1 s at the 50th cycle, respectively, indicating that PtCz/PEDOT, PtCz/PProDOT-Me2, and PtCz/PProDOT-Et2 ECDs showed fast switching speed when PtCz/PEDOT, PtCz/PProDOT-Me2, and PtCz/PProDOT-Et2 are employed as electrochromic layers. The $\tau_c$ and $\tau_b$ values of PtCz/PEDOT ECD were 0.6 and 1.0 s, respectively, at the third cycle, and 0.2 and 0.2 s, respectively, at the 50th cycle, indicating that switching time shortened with the number of switching cycles. Under similar conditions, PtCz/PProDOT-Me2 and PtCz/PProDOT-Et2 ECDs showed fast switching speed at high switching cycles than those at low switching cycles.

Figure 8. Optical contrast of (a) PtCz/PEDOT (b) PtCz/PProDOT-Me2, and (c) PtCz/PProDOT-Et2 ECDs in an ACN/DCM (1:3, by volume) solution containing 0.2 M LiClO$_4$ between 0.0 V and 1.8 V with a residence time of 10 s.
As summarized in Table 3, the ΔT values of PtCz/PEDOT, PtCz/PProDOT-Me2, and PtCz/PProDOT-Et2 ECDs were 24.0, 36.0, and 28.0% at the 3rd cycle, respectively. The ΔT of PtCz/PProDOT-Me2 and PtCz/PProDOT-Et2 ECDs were larger than that of PtCz/PEDOT, indicating PProDOT derivatives facilitated to increase the transmittance disparity when we employed PProDOT derivatives as cathodic layers in ECDs. PtCz/PProDOT-Me2 ECD shows the highest ΔT among these ECDs, the ΔT of PtCz/PProDOT-Me2 ECD is higher than those reported for poly(4,4′-di(N-carbazolyl)biphenyl)/PEDOT [43], poly(9H-carbazol-9-ylpyrene)/PEDOT [37], poly(3,6-bis(2-(3,4-ethylenedioxy)thienyl)-N-methylcarbazole)/PEDOT [44], poly(carbazole-co-indole-6-carboxylic acid)/PProDOT- Me2 [45], poly(4,4′-di(N-carbazoyl)biphenyl-co-2,2′-bithiophene)/PEDOT [46] and poly(2,5-bis(9-methyl-9H-carbazol-3-yl)-1,3,4-oxadiazole)/PEDOT [40] ECDs (Table 6). However, PtCz/PProDOT-Me2 ECD shows lower ΔT than that reported for poly(4,4′-di(N-carbazoyl)biphenyl-co-4H-cyclopenta[2,1-b:3,4-b′]dithiophene)/PEDOT ECD [47].

Table 6. Optical contrast and coloration efficacies of ECDs.

| ECD configuration                                      | ΔTmax (%) | ηmax (cm²·C⁻¹) | Ref. |
|--------------------------------------------------------|-----------|----------------|------|
| poly(4,4′-di(N-carbazolyl)biphenyl)/PEDOT             | 19 (550 nm) | —              | [43] |
| poly(9H-carbazol-9-ylpyrene)/PEDOT                    | 23 (623 nm) | 290            | [37] |
| poly(3,6-bis(2-(3,4-ethylenedioxy)thienyl)-N-methylcarbazole)/PEDOT | ca. 30 | —              | [44] |
| poly(carbazole-co-indole-6-carboxylic acid)/PProDOT-Me2 | 32 (575 nm) | 372.7          | [45] |
| poly(4,4′-di(N-carbazoyl)biphenyl-co-2,2′-bithiophene)/PEDOT | 28.6 (700 nm) | 234            | [46] |
| poly(4,4′-di(N-carbazolyl)biphenyl-co-4H-cyclopenta[2,1-b:3,4-b′]dithiophene)/PEDOT | 39.8 (628 nm) | 319.98         | [47] |
| poly(2,5-bis(9-methyl-9H-carbazol-3-yl)-1,3,4-oxadiazole)/PEDOT | 35 (620 nm) | —              | [40] |
| PtCz/PProDOT-Me2                                       | 36 (572 nm) | 343.4          | This work |
The change of transmittance in the bleached state, i.e., a durable memory effect. The transmittances of three ECDs in the colored state are less stable than in the bleached state, but the transmittance loss is less than 3%. Both the bleached and colored states were highly stable, and the ECDs kept their color without loss, demonstrating PtCz/PEDOT, PtCz/PProDOT-Me2, and PtCz/PProDOT-Et2 ECDs reveal satisfied open circuit memory.

Figure 9. Open circuit stability of (a) PtCz/PEDOT (b) PtCz/PProDOT-Me2, and (c) PtCz/PProDOT-Et2 ECDs at 0.0 V and 1.8 V. The working electrode is PtCz film-coated ITO glass substrate.

3.7. Long-Term Stability of ECDs

The stability of long-term switching between redox states is important for ECDs’ applications [48,49]. The long-term switching ability between redox states of PtCz/PEDOT, PtCz/PProDOT-Me2, and PtCz/PProDOT-Et2 ECDs were examined using CV at potentials between 0.0 and 1.5 V with a scan rate of 500 mV·s⁻¹ (Figure 10). From the observation of switching between bleaching and coloring states of the ECDs, 93%, 92%, and 93% of their electrical activities are retained after 500 cycles for PtCz/PEDOT, PtCz/PProDOT-Me2, and PtCz/PProDOT-Et2 ECDs, respectively, and 87%, 87%, and 87% of their electrical activities are retained after 1000 cycles for PtCz/PEDOT, PtCz/PProDOT-Me2, and PtCz/PProDOT-Et2 ECDs, respectively, the electrical activities of PtCz/PEDOT, PtCz/PProDOT-Me2, and PtCz/PProDOT-Et2 ECDs at 500th cycle are larger than those reported for P(BTN-co-BT)/PEDOT ECD (stability = 79% at 500th cycle) [50] and PBTBE/PEDOT ECD (stability = 80.2% at 500th cycle) [51], indicating they are good candidates for electrochromic applications.
4. Conclusions

A carbazole-based monomer (tCz) was synthesized, and its corresponding homopolymer (PtCz) was prepared using electrochemical polymerization. The electrochemical processes of PtCz film are reversible, and the PtCz film shows four color variations (light yellow, earthy yellow, grey, and dark grey) from an undoped state to a doped state. Three ECDs based on PtCz as anodic polymer and PEDOT, PProDOT-Me₂, and PProDOT-Et₂ as the cathodic polymers were constructed, and the spectroelectrochemical properties of ECDs were characterized. The colors of constructed PtCz/PProDOT-Me₂ ECD switched from yellowish-grey, light grey, purple, and dark blue upon the application of potential between −0.8 and +1.5 V. Electrochromic switching studies showed that the ΔT_{max} values of PtCz/PEDOT, PtCz/PProDOT-Me₂, and PtCz/PProDOT-Et₂ ECDs were 24.0%, 36.0%, and 28.0%, respectively, and the η_{max} values of PtCz/PEDOT, PtCz/PProDOT-Me₂, and PtCz/PProDOT-Et₂ ECDs were calculated as 256.5, 343.4, and 336.8 cm²·C⁻¹, respectively. Moreover, PtCz/PEDOT, PtCz/PProDOT-Me₂, and PtCz/PProDOT-Et₂ ECDs reveal satisfied open circuit memory and long-term switching ability between redox states. The results show that the PtCz film is a potential anodic material for electrochromic applications in rear-view mirrors and motorcycle helmet-visors.

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