


Article

Applications of Electrochromic Copolymers Based on Tris(4-carbazoyl-9-ylphenyl)amine and Bithiophene Derivatives in Electrochromic Devices

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Abstract: Four copolymers (P(tCz (tris(4-carbazoyl-9-ylphenyl)amine)-co-bTP (2,2'-bithiophene)), P(tCz-co-CPDT (4H-cyclopenta[2,1-b:3,4-b']dithiophene)), P(tCz-co-DTC (3,6-di(2-thienyl)carbazole)), and P(tCz-co-CPDTK (cyclopentadithiophene ketone))) are deposited on indium tin oxide (ITO) surfaces using electrochemical polymerization. Spectroelectrochemical properties of copolymer electrodes reveal that the colors of P(tCz-co-bTP) film are pinkish-orange, light olive green, light grayish blue, and dark blue at 0.0, 0.8, 1.2, and 1.6 V, respectively, whereas the color variations of P(tCz-co-CPDTK) film are light yellow, yellow, and blue at 0.0 V, 0.8 V, and 1.5 V, respectively. The ΔT of P(tCz-co-bTP), P(tCz-co-CPDT), P(tCz-co-DTC), and P(tCz-co-CPDTK) films are estimated to be 43.0% at 967 nm, 28.7% at 864 nm, 43.6% at 870 nm, and 24.5% at 984 nm, respectively. Five electrochromic devices (ECDs) are assembled using the tCz-based homopolymer and copolymers as coloring electrodes, and poly(2,2-dimethyl-3,4-propylenedioxythiophene) (PProDOT-Me₂) as the complementary electrode. P(tCz-co-DTC)/PProDOT-Me₂ ECD reveals high transmittance change (45.9% at 624 nm), P(tCz-co-CPDTK)/PProDOT-Me₂ ECD shows high η (513.0 cm² C⁻¹ at 582 nm), and P(tCz-co-bTP)/PProDOT-Me₂ ECD presents short switching time (less than 0.4 s) at 628 nm. Moreover, these ECDs show satisfactory redox stability and open circuit stability.

Keywords: copolymer; electrochemical polymerization; spectroelectrochemistry; electrochromic device; redox stability

1. Introduction

Electrochromic materials (ECMs) have attracted attention in the scientific communities due to their advantage of low driving voltage and high contrast of transmittance [1]. In around 1960–1970, ECMs have been widely investigated for potential use in automotive rearview mirrors, smart windows, and sunroofs. The most studied electrochromic materials are metal oxides, metal phthalocyanines, metal coordination complexes, viologens, and conjugated polymers [2]. Among these ECMs, conjugated polymers show high coloration efficiency and short response time. The electrochromic behaviors of conjugated polymers can be tuned by proper incorporations of specific substituents in polymer backbones [3].

The commonly used conjugated polymers of ECMs contain polythiophene [4,5], polycarbazole [6,7], polytriphenylamine [8,9], polyaniline [10], polyindole [11,12], and poly(3,4-

ethylenedioxythiophene) (PEDOT) [13]. Polycarbazoles have been extensively studied for various optical and electrochemical devices due to their superior electroactive properties. Polycarbazoles can be functionalized at the 3,6-, 2,7-, and 9-positions of carbazole groups [14,15]. Polythiophene can be easily modified to offer a wide variety of useful optical and electrochemical properties such as tunable band gap, conductivity, and oxidation and reduction activity [16,17]. Jia et al. [18] reported the electrochromic properties of poly(carbazoyltriphenylamine) (poly(CBZ-TPA)) and poly(carbazoyltriphenylaminethiophene) (poly(CBZ-TPA-Th)) films. Poly(CBZ-TPA) film displayed camel gray, light gray, and army green at -0.5 , 0 , and 1.6 V, respectively, whereas poly(CBZ-TPA-Th) film exhibited maize-yellow, milk white, and dark green at -0.5 , 0 , and 1.4 V, respectively. Yigit et al. [19] reported the spectroelectrochemical characterization of azobenzene- and coumarin-containing polymers (poly[9-(2-(4-(phenyldiazenyl) phenoxy) ethyl-3,6-di(thiophen-2-yl)-9H-carbazole)] (PTCbzAz), poly[3,6-bis(2,3-dihydrothieno[3,4-b][1,4]dioxin-5-yl)-9-(2-(4-(phenyldiazenyl)phenoxy) ethyl)-9H-carbazole] (PECbzAz), poly[4-(2-(3,6-di(thiophen-2-yl)-9H-carbazol-9-yl) ethoxy)-2H-chromen-2-one] (PTCbzCo) and poly[3,6-bis(2,3-dihydrothieno[3,4-b][1,4]dioxin-5-yl)-9H-(carbazol-9-yl)ethoxy-2H-chromen-2-one] (PECbzCo)). The spectroelectrochemical studies showed that the incorporations of azobenzene and coumarin units in polymer backbone gave rise to multicolored electrochromisms. Moreover, PProDOT-Me₂ is one of the promising polythiophene derivatives. PProDOT-Me₂ has been employed as the cathodically coloring material of ECDs due to PProDOT-Me₂ film being transparent in the oxidized state and the resulting deep color in the reduced state [20]. Furthermore, copolymerization is a promising way to tune the electrochromic characteristics of polymer films. Copolymerization of various monomers containing specific functional groups can bring about interesting electrochromic behaviors. For this matter, four carbazole- and bithiophene-containing copolymers (P(tCz-co-bTP (2,2'-bithiophene)), P(tCz-co-CPDT), P(tCz-co-DTC (3,6-di(2-thienyl)carbazole)), and P(tCz-co-CPDTK (cyclopentadithiophene ketone))) are copolymerized electrochemically to study their promising applications as ECMs. tCz contains three carbazole units linked by a triphenylamine core. The presence of three oxidizable carbazole and one oxidizable triphenylamine groups in tCz unit facilitates the formations of polaron and bipolaron in the oxidized states of tCz-based polymer films. All of bTP, CPDT, DTC, and CPDTK units comprise two thiophene rings linked by specific groups. The two thiophene rings of bTP and DTC units are linked by a single bond and a carbazole group, respectively. CPDT comprises two thiophene rings linked by a single bond and a methylene bridge at the 2- and 3-positions of thiophene rings. CPDTK contains two thiophene rings linked by a carbonyl group and a single bond at the 2- and 3-positions of thiophene rings. The electron-withdrawing carbonyl group in CPDTK unit can diminish the LUMO level and band gap of polymers, which is useful in electrochromic applications. Moreover, five ECDs comprised of PtCz, P(tCz-co-bTP), P(tCz-co-CPDT), P(tCz-co-DTC), or P(tCz-co-CPDTK) as anodically coloring layer, and PProDOT-Me₂ as cathodically coloring layer were constructed and their spectroelectrochemical behaviors, transmittance variations of electrochromic switching, optical memory, and redox stability were also investigated.

2. Experimental

2.1. Materials

2,2'-bithiophene (bTP), CPDT, and CPDTK were purchased from Luminescence Technology Corp. (Taipei, Taiwan). ProDOT-Me₂, DTC, and tCz were synthesized according to previously published procedures [21–23].

2.2. Electrosynthesis of PtCz, P(tCz-co-bTP), P(tCz-co-CPDT), P(tCz-co-DTC), P(tCz-co-CPDTK), and PProDOT-Me₂ Films

The electrosynthesis of PtCz, P(tCz-co-bTP), P(tCz-co-CPDT), P(tCz-co-DTC), and P(tCz-co-CPDTK) films was carried out in a 0.2 M LiClO₄/acetonitrile (ACN)/dichloromethane

(DCM) solution, and the feed molar ratio of monomers are presented in Table 1. The PtCz, P(tCz-co-bTP), P(tCz-co-CPDT), P(tCz-co-DTC), and P(tCz-co-CPDTK) films were prepared potentiodynamically by scanning the potential between 0.0 V and 1.8 V (vs. Ag/AgCl in 3 M KCl solution) for 3 cycles. The PProDOT-Me₂ film was prepared using 2 mM ProDOT-Me₂ in a 0.2 M LiClO₄-containing ACN solution. PProDOT-Me₂ film was deposited potentiostatically at 1.7 V (vs. Ag/AgCl in 3 M KCl solution).

Table 1. Feed species of anodic polymer electrodes.

Anodic Polymer Electrodes	Feed Species of Anodic Polymers	Feed Molar Ratio of Anodic Polymers
PtCz	2 mM tCz	Neat tCz
P(tCz-co-bTP)	2 mM tCz + 2 mM bTP	tCz:bTP = 1:1
P(tCz-co-CPDT)	2 mM tCz + 2 mM CPDT	tCz:CPDT = 1:1
P(tCz-co-DTC)	2 mM tCz + 2 mM DTC	tCz:DTC = 1:1
P(tCz-co-CPDTK)	2 mM tCz + 2 mM CPDTK	tCz:CPDTK = 1:1

2.3. Electrochemical and Spectroelectrochemical Characterizations

Electrochemical characterizations of PtCz, P(tCz-co-bTP), P(tCz-co-CPDT), P(tCz-co-DTC), P(tCz-co-CPDTK) films and their corresponding ECDs were performed using a CHI627D electrochemical analyzer (CH Instruments, Austin, TX, USA). The active areas of PtCz, P(tCz-co-bTP), P(tCz-co-CPDT), P(tCz-co-DTC), P(tCz-co-CPDTK), and PProDOT-Me₂ films on ITO coated glass plate were 1.5 cm². The characterizations of polymer films in ACN/DCM solution were carried out using Ag/AgCl and platinum wire as the reference and counter electrodes, respectively. Spectroelectrochemical characterizations were performed using an Agilent Cary 60 UV (Ultraviolet)-Visible spectrophotometer (Varian Inc., Walnut Creek, CA, USA) and a CHI627D electrochemical analyzer.

2.4. Construction of Electrochromic Devices

The electrolyte of ECD was prepared using poly(methyl methacrylate) (PMMA), propylene carbonate (PC), and LiClO₄, the weight ratio of PMMA:PC:LiClO₄ is 33:53:14. Electrochromic devices were fabricated using PtCz, P(tCz-co-bTP), P(tCz-co-CPDT), P(tCz-co-DTC), or P(tCz-co-CPDTK) as the anodic coloring layer and PProDOT-Me₂ as the cathodic coloring layer. Both anodic coloring and cathodic coloring materials were electrodeposited on ITO glasses, respectively. The ECDs were constructed by arranging the anodic and cathodic coloring layers to face each other, and they were separated by the PMMA/PC/LiClO₄ electrolyte.

3. Results and Discussion

3.1. Electrochemical Polymerization

Figure 1 showed the electrooxidation of 2 mM tCz, 2 mM bTP, 2 mM CPDT, 2 mM DTC, and 2 mM CPDTK in 0.2 M LiClO₄/ACN/DCM solution. The onset potential of oxidation for tCz, bTP, CPDT, DTC, and CPDTK were 0.78, 0.83, 0.89, 0.79, and 0.93 V, respectively. CPDTK showed higher onset potential of oxidation than those of bTP and CPDT, indicating the incorporation of electron withdrawing ketone group in CPDTK increasing the onset potential of oxidation significantly. The discrepancies between tCz vs. bTP, tCz vs. CPDT, tCz vs. DTC, and tCz vs. CPDTK were less than 0.15 V, implying that the copolymerizations of tCz vs. bTP, tCz vs. CPDT, tCz vs. DTC, and tCz vs. CPDTK are workable [24].

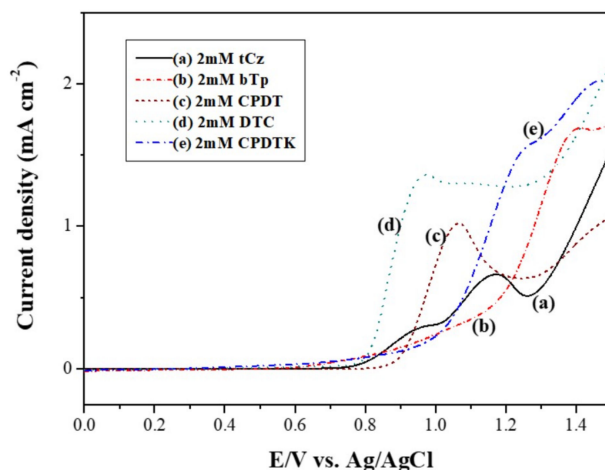


Figure 1. Electrooxidation of (a) 2 mM tCz; (b) 2 mM bTP; (c) 2 mM CPDT; (d) 2 mM DTC; and (e) 2 mM CPDTK at a scan rate of 100 mV s^{-1} .

Figure 2 shows the electrochemical synthesis of copolymer films in a solution. The redox peak current densities increased with the increasing number of cycles, indicating the formation of polymer films on ITO substrates [25]. The oxidation peaks of P(tCz-co-bTP), P(tCz-co-CPDT), P(tCz-co-DTC), and P(tCz-co-CPDTK) located at around 1.10, 1.35, 1.45, and 1.10 V, respectively, and the reduction peaks of P(tCz-co-bTP), P(tCz-co-CPDT), P(tCz-co-DTC), and P(tCz-co-CPDTK) located at around 0.65, 0.73, 0.70, and 0.60 V, respectively. The polymerization schemes of P(tCz-co-bTP), P(tCz-co-CPDT), P(tCz-co-DTC), and P(tCz-co-CPDTK) are displayed in Figure 3.

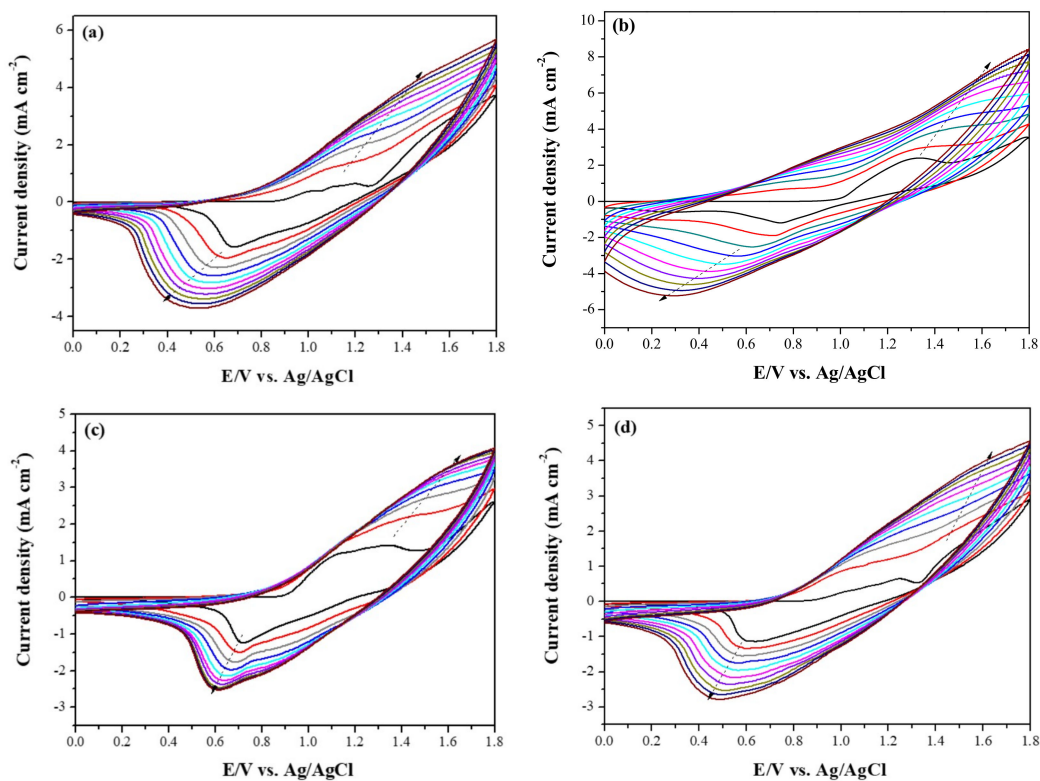


Figure 2. Electrochemical synthesis of (a) P(tCz-co-bTP); (b) P(tCz-co-CPDT); (c) P(tCz-co-DTC); and (d) P(tCz-co-CPDTK) in $0.2 \text{ M LiClO}_4 / \text{ACN/DCM}$ solution.

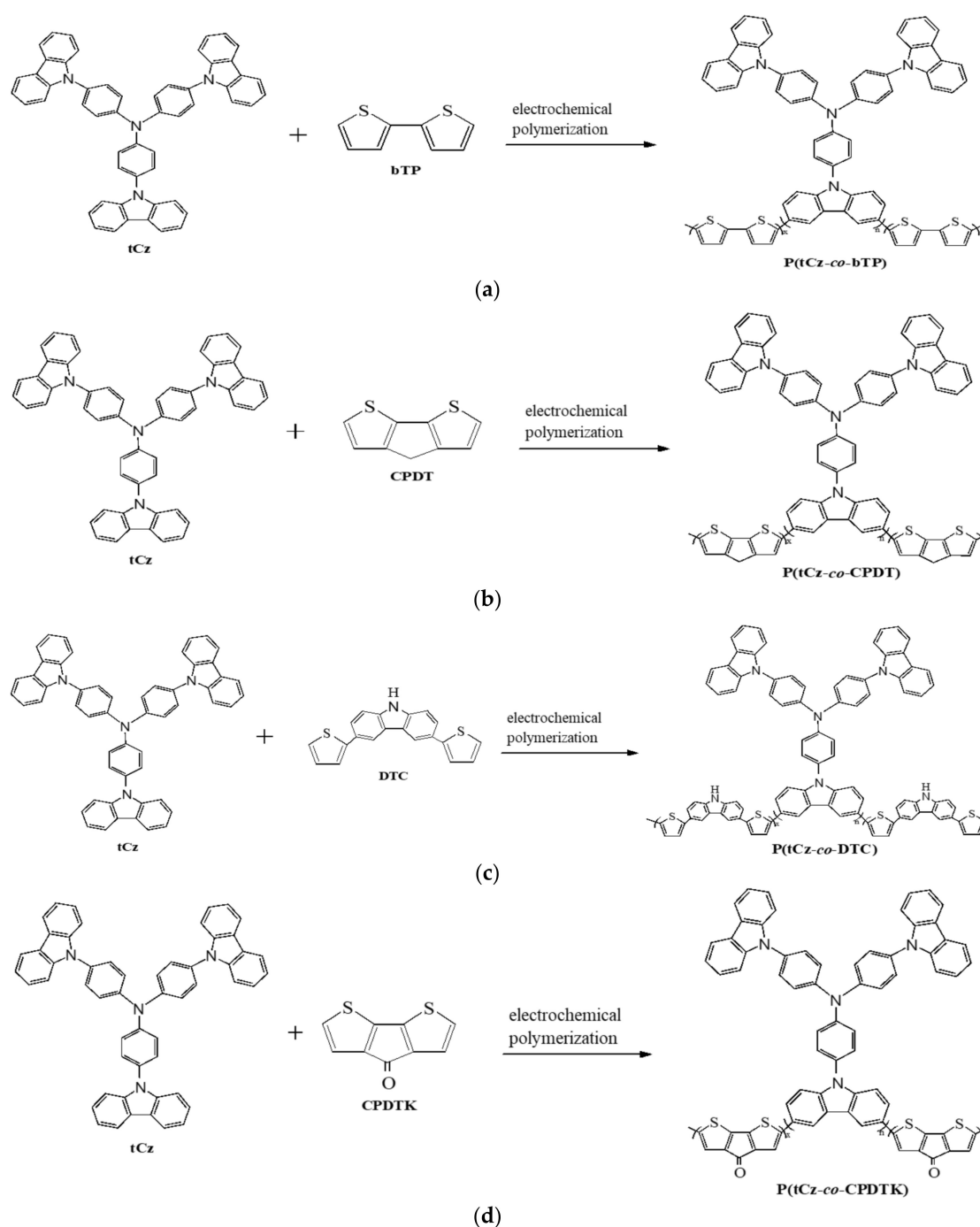


Figure 3. The polymerization schemes of (a) P(tCz-co-bTP); (b) P(tCz-co-CPDT); (c) P(tCz-co-DTC); and (d) P(tCz-co-CPDTK).

3.2. Electrochemical Behavior of P(tCz-co-DTC) Film

The P(tCz-co-DTC) film was synthesized using the electropolymerization of tCz and DTC monomers were scanned at different scan rate in 0.2 M LiClO₄/ACN/DCM solution. As shown in Figure 4, cyclic voltammogram (CV) curves of P(tCz-co-DTC) film showed well-defined redox peaks and the peak current densities increased linearly with the increasing scan rates (inset in Figure 4), demonstrating that the redox process is electroactively non-diffusional limited and P(tCz-co-DTC) film has adhered well to the ITO electrode [26].

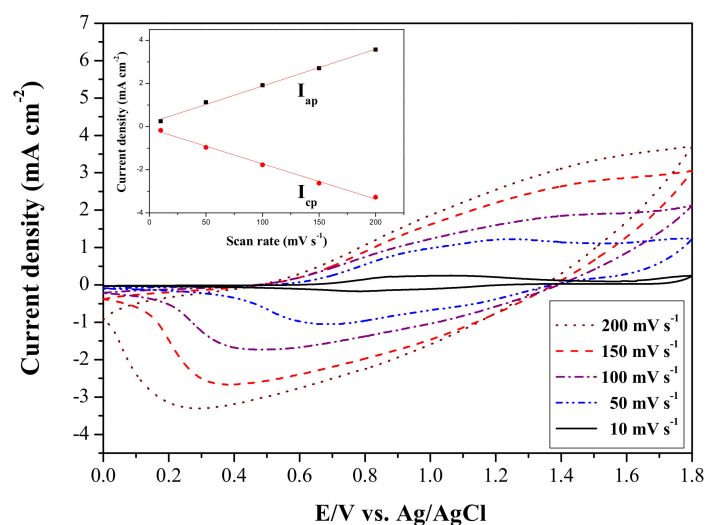


Figure 4. CV curves of the P(tCz-co-DTC) film at different scan rates. Inset: Scan rate dependence of the peak current densities of P(tCz-co-DTC) film.

3.3. Spectroelectrochemical Studies of Polymer Films

P(tCz-co-bTP), P(tCz-co-CPDT), P(tCz-co-DTC), and P(tCz-co-CPDTK) films were coated on ITO substrate and the spectral variations at various voltages were monitored using a UV-Vis spectrophotometer. As shown in Figure 5a, P(tCz-co-bTP) film has an absorption peak at 450 nm in the neutral state at 0.0 V, which can be referred to the π - π^* transition of P(tCz-co-bTP), and P(tCz-co-bTP) film being light orange in the neutral state.

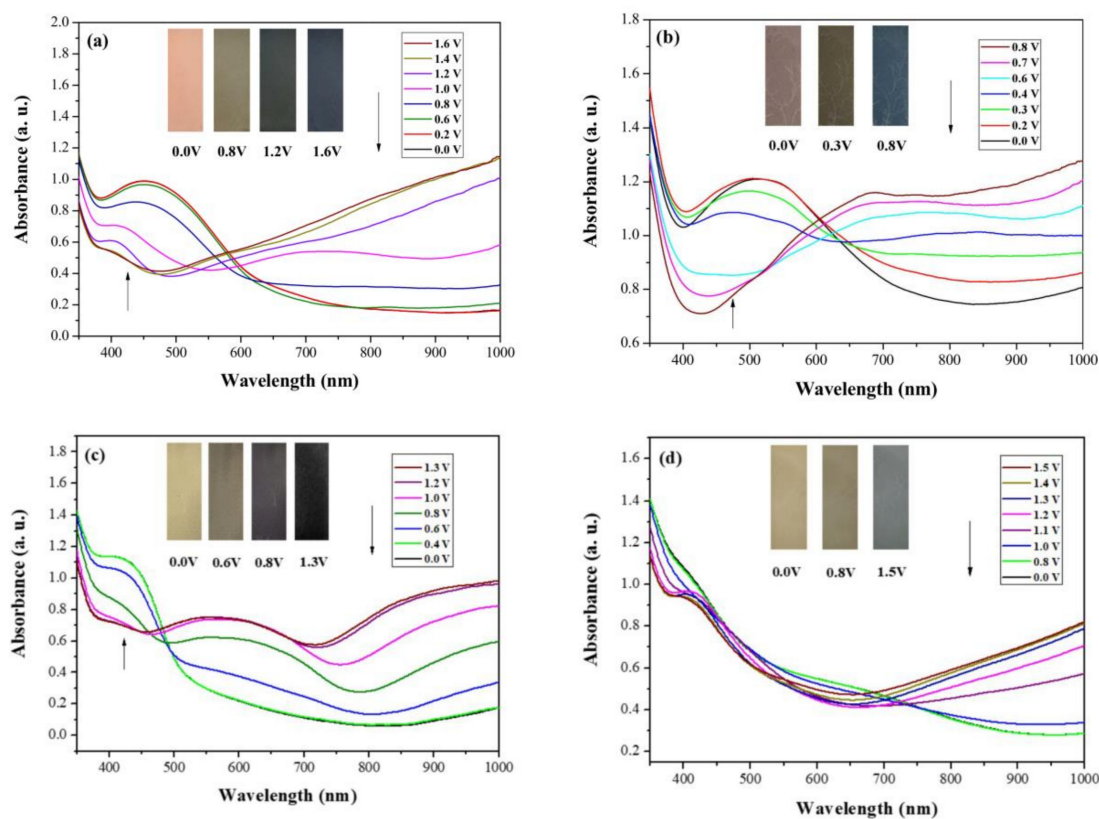


Figure 5. UV-Visible spectra of (a) P(tCz-co-bTP); (b) P(tCz-co-CPDT); (c) P(tCz-co-DTC); and (d) P(tCz-co-CPDTK) electrodes in 0.2 M LiClO₄/ACN/DCM solution.

Table 2. Colorimetric values of (a) P(tCz-co-bTP); (b) P(tCz-co-CPDT); (c) P(tCz-co-DTC); and (d) P(tCz-co-CPDTK) at various potentials.

(a)						
Potentials (V)	L*	a*	b*	x	y	Diagram
0.0	59.71	25.70	35.21	0.5478	0.3972	
0.6	61.13	26.79	35.94	0.5491	0.3962	
0.8	64.73	17.19	32.72	0.5227	0.4117	
1.0	66.51	-5.10	13.39	0.4541	0.4317	
1.2	65.02	-9.35	-3.89	0.4221	0.4168	
1.4	62.61	-8.10	-9.70	0.4154	0.4066	
1.6	61.80	-8.19	-9.45	0.4152	0.4071	
(b)						
Potentials (V)	L*	a*	b*	x	y	Diagram
0.0	33.23	9.79	2.26	0.4864	0.3867	
0.2	33.04	8.76	3.17	0.4851	0.3909	
0.3	34.63	7.31	3.78	0.4804	0.3962	
0.4	36.96	3.80	3.85	0.4679	0.4053	
0.6	40.41	-5.99	-6.39	0.4160	0.4082	
0.7	39.46	-7.88	-13.21	0.3945	0.3971	
0.8	38.68	-8.05	-17.92	0.3822	0.3862	
(c)						
Potentials (V)	L*	a*	b*	x	y	Diagram
0.0	78.67	10.33	56.32	0.5184	0.4378	
0.4	78.54	10.66	55.83	0.5177	0.4380	
0.6	69.27	5.59	36.01	0.4992	0.4343	
0.8	56.67	0.98	5.35	0.4580	0.4130	
1.0	50.67	1.78	-5.50	0.4426	0.3955	
1.2	50.04	2.84	-5.54	0.4452	0.3934	
1.3	50.17	2.77	-5.43	0.4452	0.3937	
(d)						
Potentials (V)	L*	a*	b*	x	y	Diagram
0.0	58.60	4.72	20.92	0.4870	0.4244	
0.8	58.60	4.78	20.73	0.4869	0.4240	
1.1	62.27	8.94	26.46	0.5007	0.4214	
1.3	63.43	6.43	24.90	0.4929	0.4244	
1.4	62.67	5.38	22.10	0.4879	0.4237	
1.5	63.53	7.92	27.59	0.4990	0.4241	

Upon increasing the voltage in the positive direction, the new absorption band at 967 nm emerged gradually, which are assigned to the formation of polaron and bipolaron absorption bands [27]. The colors of P(tCz-co-bTP) film were dark yellow, light blue and dark blue at 0.8, 1.2, and 1.6 V, respectively. In similar condition, P(tCz-co-CPDT), P(tCz-co-DTC), and P(tCz-co-CPDTK) films showed the maximum absorption at 500, 420, and 410 nm in the neutral state, respectively. This may be

attributed to the effective conjugation of the polymer chains [28]. The colors of P(tCz-co-CPDT) film were light purple at 0.0 V, green at 0.3 V, and dark blue at 0.8 V, whereas the color variations of P(tCz-co-DTC) film were light yellow at 0.0 V, yellow at 0.6 V, blue at 0.8 V, and black at 1.3 V, the color variations of P(tCz-co-CPDTK) film were light yellow at 0.0 V, yellow at 0.8 V, and blue at 1.5 V. Table 2 shows the colorimetric values of P(tCz-co-bTP), P(tCz-co-CPDT), P(tCz-co-DTC), and P(tCz-co-CPDTK) at various applied potentials.

3.4. Electrochemical Switching of Polymer Films

Figure 6 shows the electrochromic switching properties of PtCz, P(tCz-co-bTP), P(tCz-co-CPDT), P(tCz-co-DTC), and P(tCz-co-CPDTK) films in a 0.2 M LiClO₄/ACN/DCM solution, and the optical contrast ($\Delta T\%$) and ΔOD of polymer films were listed in Table 3. The polymer films were switched by potentials between 0.0 and 1.5 V with a time interval of 10 s. The ΔT of PtCz, P(tCz-co-bTP), P(tCz-co-CPDT), P(tCz-co-DTC), and P(tCz-co-CPDTK) films were estimated to be 30.5% at 760 nm, 43.0% at 967 nm, 28.7% at 864 nm, 43.6% at 870 nm, and 24.5% at 984 nm, respectively. P(tCz-co-bTP) and P(tCz-co-DTC) films showed a higher ΔT than those of PtCz, P(tCz-co-CPDT), and P(tCz-co-CPDTK) films, implying the incorporation of bTP and DTC units in the copolymer backbone enhances ΔT significantly. The response time required to reach 90% of entire transmittance change were determined to be 3.5–6.5 s for these polymer films.

The η can be determined using the formula [29]:

$$\eta = \frac{\Delta OD}{Q_d} \quad (1)$$

where Q_d refers to the amount of injected/ejected charge per unit active area. The η values of PtCz, P(tCz-co-bTP), P(tCz-co-CPDT), P(tCz-co-DTC), and P(tCz-co-CPDTK) films are calculated to be 42.6 cm² C⁻¹ at 760 nm, 67.6 cm² C⁻¹ at 967 nm, 76.7 cm² C⁻¹ at 864 nm, 78.3 cm² C⁻¹ at 870 nm, and 62.5 cm² C⁻¹ at 984 nm, respectively. Copolymer films show higher η values than that of PtCz film in a solution.

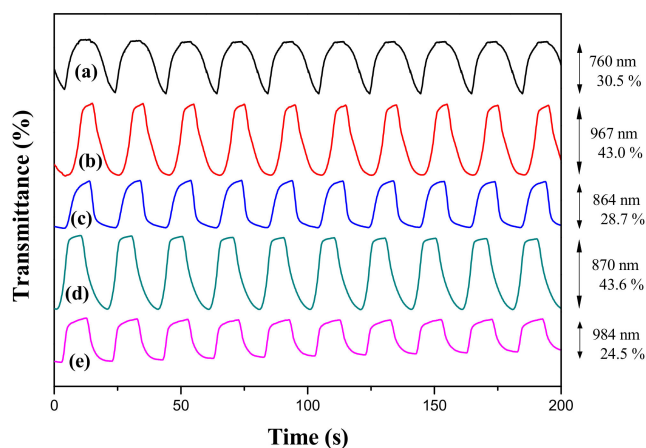


Figure 6. Transmittance-time profiles of (a) PtCz; (b) P(tCz-co-bTP); (c) P(tCz-co-CPDT); (d) P(tCz-co-DTC); and (e) P(tCz-co-CPDTK) electrodes in a solution.

Table 3. Electrochromic switching properties of the electrodes.

Electrodes	λ (nm)	T_{ox}	T_{red}	ΔT	ΔOD	Q_d (mC cm ⁻²)	η (cm ² C ⁻¹)	τ_c (s)	τ_b (s)
PtCz	760	33.0	63.5	30.5	0.284	6.660	42.6	6.0	5.0
P(tCz-co-bTP)	967	9.5	52.5	43.0	0.742	10.986	67.6	6.5	5.0
P(tCz-co-CPDT)	864	13.5	42.2	28.7	0.494	6.453	76.7	6.5	5.5
P(tCz-co-DTC)	870	10.0	53.6	43.6	0.729	9.310	78.3	6.5	4.5
P(tCz-co-CPDTK)	984	19.5	44.0	24.5	0.353	5.653	62.5	5.5	3.5

As shown in Table 4, P(tCz-co-DTC) film showed higher transmittance change than those reported for poly(ethyl-4-(3,6-di(thiophen-2-yl)-9H-carbazole-9-yl)-benzoate) (PETCB) film at 1100 nm [15], poly(9H-carbazol-9-ylpyrene) (PMCzP) film at 460 nm [30], and poly(1,3-bis(carbazol-9-yl)benzene) (PBCz) film at 1050 nm [31]. However, P(tCz-co-DTC) film showed a lower transmittance change than those reported for P(NO₂-3Cz) film at 710 nm [14]. On the other hand, P(tCz-co-DTC) film revealed higher η than that reported for P(NO₂-3Cz) [14], whereas P(tCz-co-DTC) film presented lower η than that reported for PBCz [31].

Table 4. Transmittance changes and colouration efficiencies of carbazole-based polymer films.

Polymer Films	ΔT_{\max} (%)	η (cm ² C ⁻¹)	Ref.
PETCB	36 (1100 nm)	-	[15]
PMCzP	29 (460 nm)	-	[30]
PBCz	18.6 (1050 nm)	180.3	[31]
P(NO ₂ -3Cz)	52 (710 nm)	35	[14]
P(tCz-co-DTC)	43.6 (870 nm)	78.3	This work

3.5. Spectroelectrochemistry of ECDs

Figure 7 shows the UV-Vis spectra of dual-type PtCz/PProDOT-Me₂, P(tCz-co-bTP)/PProDOT-Me₂, and P(tCz-co-DTC)/PProDOT-Me₂ ECDs at various applied potentials. At 0.0 V, PtCz, P(tCz-co-bTP), and P(tCz-co-DTC) films showed a bleached color in their neutral state and PProDOT-Me₂ was transparent in its oxidized state.

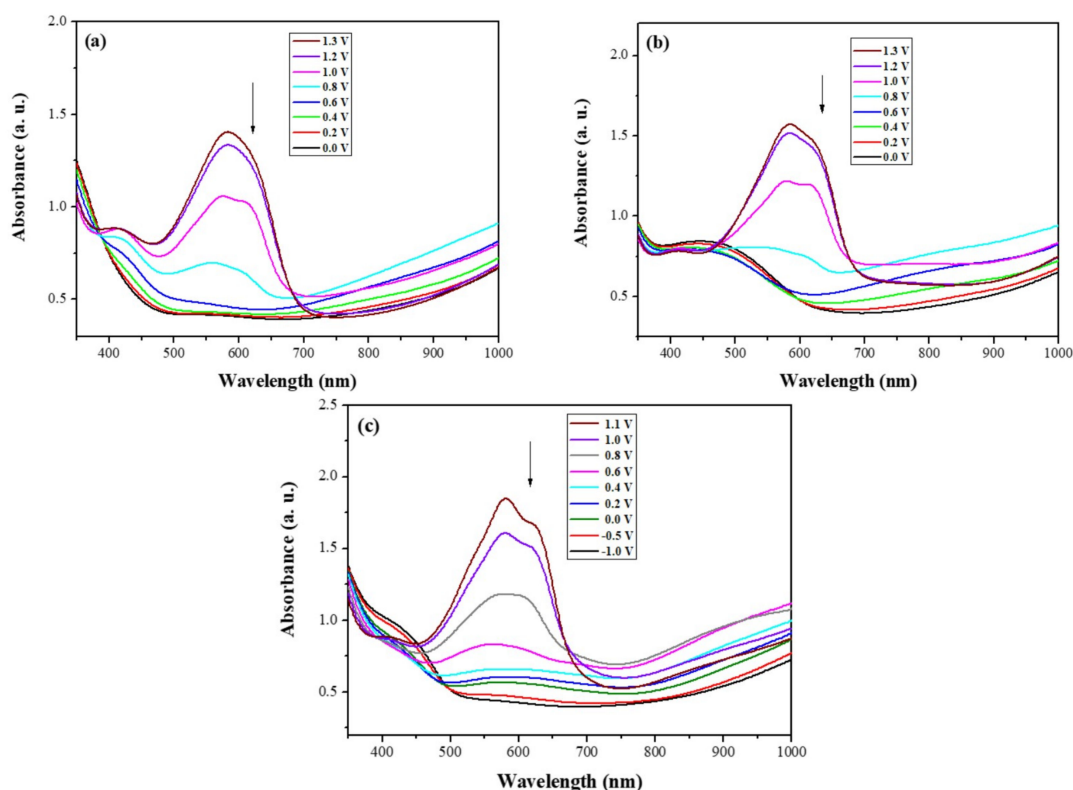


Figure 7. UV-Visible spectra of (a) PtCz/PProDOT-Me₂; (b) P(tCz-co-bTP)/PProDOT-Me₂; and (c) P(tCz-co-DTC)/PProDOT-Me₂ ECDs.

Accordingly, PtCz/PProDOT-Me₂, P(tCz-co-bTP)/PProDOT-Me₂, and P(tCz-co-DTC)/PProDOT-Me₂ ECDs revealed a bleached color at 0.0 V. Upon increasing the applied voltage from 0 to 1.3 V gradually, the absorption bands at 583–628 nm were emerged due to the

absorption of PtCz, P(tCz-co-bTP), and P(tCz-co-DTC) films in their oxidized state and PProDOT-Me₂ film in its neutral state. The colors of PtCz/PProDOT-Me₂, P(tCz-co-bTP)/PProDOT-Me₂, and P(tCz-co-DTC)/PProDOT-Me₂ ECDs were dark blue at 1.3 V. Table 5 showed the photographs and colorimetric values of P(tCz-co-bTP)/PProDOT-Me₂ and P(tCz-co-DTC)/PProDOT-Me₂ ECDs at various potentials. P(tCz-co-bTP)/PProDOT-Me₂ ECD revealed light tan, light brown, purple, blue, and dark blue at 0.0, 0.4, 0.6, 0.8, and 1.3 V, respectively, whereas P(tCz-co-DTC)/PProDOT-Me₂ ECD displayed light beige, grey, light grey, blue, and dark blue at −1.0, 0.0, 0.4, 0.6, and 1.1 V, respectively.

3.6. Electrochemical Switching of ECDs

The double-potential-step chronoamperometry experiments of PtCz/PProDOT-Me₂, P(tCz-co-bTP)/PProDOT-Me₂, and P(tCz-co-DTC)/PProDOT-Me₂ ECDs were implemented by stepping potentials between bleached and colored states, the time interval being 10 s. Figure 8 showed the transmittance-time profiles of PtCz/PProDOT-Me₂, P(tCz-co-bTP)/PProDOT-Me₂, and P(tCz-co-DTC)/PProDOT-Me₂ ECDs, and the ΔT , η , and the switching time of PtCz/PProDOT-Me₂, P(tCz-co-bTP)/PProDOT-Me₂, P(tCz-co-CPDT)/PProDOT-Me₂, P(tCz-co-DTC)/PProDOT-Me₂ and P(tCz-co-CPDTK)/PProDOT-Me₂ ECDs were presented in Table 6. The ΔT of PtCz/PProDOT-Me₂, P(tCz-co-bTP)/PProDOT-Me₂, P(tCz-co-CPDT)/PProDOT-Me₂, P(tCz-co-DTC)/PProDOT-Me₂ and P(tCz-co-CPDTK)/PProDOT-Me₂ ECDs were estimated to be 30.9% at 583 nm, 32.0% at 628 nm, 19.7% at 582 nm, 45.9% at 624 nm, and 29.5% at 582 nm, respectively. P(tCz-co-DTC)/PProDOT-Me₂ ECD showed the highest ΔT , and P(tCz-co-bTP)/PProDOT-Me₂ ECD showed higher ΔT than that of PtCz/PProDOT-Me₂ ECD, indicating that the incorporation of copolymers (P(tCz-co-bTP) and P(tCz-co-DTC)) as the anodically coloring layers leading to a higher ΔT than that of the homopolymer (PtCz). In similar situation, P(tCz-co-bTP)/PProDOT-Me₂ and P(tCz-co-DTC)/PProDOT-Me₂ ECDs showed higher ΔOD than that of PtCz/PProDOT-Me₂ ECD. On the other side, the η of dual-type PtCz/PProDOT-Me₂, P(tCz-co-bTP)/PProDOT-Me₂, P(tCz-co-CPDT)/PProDOT-Me₂, P(tCz-co-DTC)/PProDOT-Me₂ and P(tCz-co-CPDTK)/PProDOT-Me₂ ECDs were 437.4 cm² C⁻¹ at 583 nm, 387.0 cm² C⁻¹ at 628 nm, 419.7 cm² C⁻¹ at 582 nm, 400.5 cm² C⁻¹ at 624 nm, and 513.0 cm² C⁻¹ at 582 nm, respectively. P(tCz-co-CPDTK)/PProDOT-Me₂ ECD showed the highest η among these ECDs. The τ_c and τ_b estimated for dual-type PtCz/PProDOT-Me₂, P(tCz-co-bTP)/PProDOT-Me₂, P(tCz-co-CPDT)/PProDOT-Me₂, P(tCz-co-DTC)/PProDOT-Me₂, and P(tCz-co-CPDTK)/PProDOT-Me₂ ECDs are also shown in Table 6. The τ_s of dual-type ECDs were shorter than those of their corresponding anodic polymer films, indicating that the dual-type ECDs revealed a short distance between the two electrodes. P(tCz-co-bTP)/PProDOT-Me₂ ECD showed the shortest τ among these ECDs.

Table 5. Photographs and colorimetric values of ECDs at different potentials.

ECDs	Potentials(V)	Photographs	L*	a*	b*	x	y	Diagrams
P(tCz-co-bTP)/ PProDOT-Me ₂	0.0		59.28	17.14	23.93	0.5180	0.4040	
	0.4		60.06	11.55	21.45	0.5022	0.4120	
	0.6		58.60	8.09	18.02	0.4912	0.4150	
	0.8		48.18	6.06	1.66	0.4666	0.3980	
	1.3		25.92	0.87	-35.37	0.3387	0.3039	
P(tCz-co-DTC)/ PProDOT-Me ₂	-1.0		66.76	1.24	29.12	0.4848	0.4368	
	0.0		59.60	-1.10	10.31	0.4597	0.4228	
	0.4		54.42	-0.90	2.01	0.4485	0.4120	
	0.6		46.72	2.84	-6.41	0.4434	0.3912	
	1.1		20.49	5.63	-38.24	0.3299	0.2703	

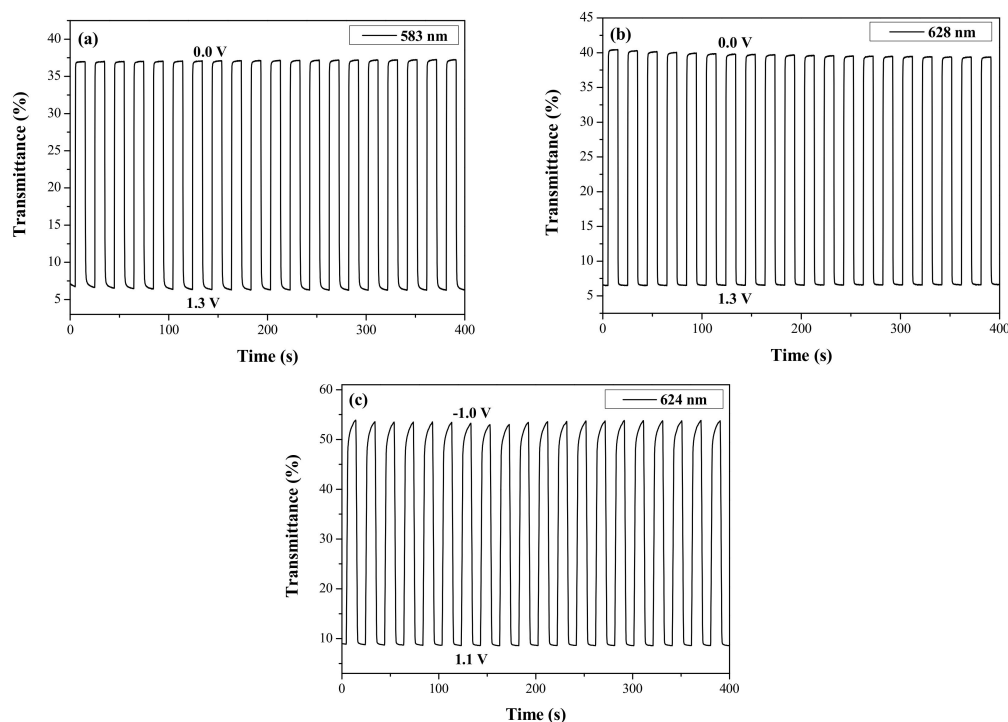


Figure 8. Transmittance-time profiles of (a) PtCz/PProDOT-Me₂; (b) P(tCz-co-bTP)/PProDOT-Me₂; and (c) P(tCz-co-DTC)/PProDOT-Me₂ ECDs carried out by stepping potentials between bleached and colored states with a residence time of 10 s.

Table 6. Electrochromic properties of the devices.

Devices	λ (nm)	T_{ox}	T_{red}	ΔT	ΔOD	Q_d (mC cm ⁻²)	η (cm ² C ⁻¹)	τ_c (s)	τ_b (s)
PtCz/PProDOT-Me ₂	583	6.6	37.5	30.9	0.754	1.724	437.4	0.9	0.4
P(tCz-co-bTP)/PProDOT-Me ₂	628	6.7	38.7	32.0	0.761	1.968	387.0	0.4	0.2
P(tCz-co-CPDT)/PProDOT-Me ₂	582	7.4	27.1	19.7	0.563	1.343	419.7	0.3	0.5
P(tCz-co-DTC)/PProDOT-Me ₂	624	8.6	54.5	45.9	0.801	2.001	400.5	1.2	1.6
P(tCz-co-CPDTK)/PProDOT-Me ₂	582	7.6	37.1	29.5	0.688	1.342	513.0	0.6	0.2

Table 7 shows the comparisons of ΔT_{max} and η_{max} with reported ECDs. P(tCz-co-DTC)/PProDOT-Me₂ ECD shows higher ΔT_{max} than those reported for P(dcbp-co-cpdt)/PEDOT [32], P(dcbp)/PEDOT [33], P(dcbp-co-bt)/PEDOT [34], P(bmco)/PEDOT [35], P(BCz-co-ProD)/tri-l poly(3,4-ethylenedioxythiophene)-poly(styrene sulfonic acid) (PEDOT-PSS) [31], and P(BCz-co-In)/PProDOT-Et₂ ECDs [36].

Table 7. ΔT and η of ECDs.

ECD Configurations	ΔT_{max} (%)	η_{max} (cm ² C ⁻¹)	Ref.
P(dcbp-co-cpdt)/PEDOT	39.8 (628 nm)	319.98 (628 nm)	[32]
P(dcbp)/PEDOT	19 (550 nm)	-	[33]
P(dcbp-co-bt)/PEDOT	28.6 (700 nm)	234 (700 nm)	[34]
P(bmco)/PEDOT	35 (620 nm)	-	[35]
P(BCz-co-ProD)/tri-l PEDOT-PSS	41 (642 nm)	417 (642 nm)	[31]
P(BCz-co-In)/PProDOT-Et ₂	42.0 (587 nm)	634 (587 nm)	[36]
P(tCz-co-DTC)/PProDOT-Me ₂	45.9 (624 nm)	401 (624 nm)	This work

Moreover, the comparison of η_{\max} with reported ECDs revealed that P(tCz-co-DTC)/PProDOT-Me₂ ECD showed higher η_{\max} than those reported for P(dcbp-co-cpdt)/PEDOT [32] and P(dcbp-co-bt)/PEDOT ECDs [34]. However, P(tCz-co-DTC)/PProDOT-Me₂ ECD showed lower η_{\max} than those reported for P(BCz-co-ProD)/tri-l PEDOT-PSS [31] and P(BCz-co-In)/PProDOT-Et₂ ECDs [36].

3.7. Open Circuit Memory

The open circuit memory of ECDs is a crucial property due to it is related to the energy-saving of ECDs [37,38]. The open circuit stability of PtCz/PProDOT-Me₂, P(tCz-co-bTP)/PProDOT-Me₂, and P(tCz-co-DTC)/PProDOT-Me₂ ECDs as shown in Figure 9a–c was detected at 583, 628, and 624 nm, respectively, by applying potentials at bleached and colored states for 1 s at each 100 s time interval. PtCz/PProDOT-Me₂, P(tCz-co-bTP)/PProDOT-Me₂, and P(tCz-co-DTC)/PProDOT-Me₂ ECDs were nearly no transmittance change at bleached state. However, the open circuit stability of PtCz/PProDOT-Me₂, P(tCz-co-bTP)/PProDOT-Me₂, and P(tCz-co-DTC)/PProDOT-Me₂ ECDs at colored state were less stable than that at bleached state. The transmittance changes of these ECDs were less than 5% at the colored state, indicating that PtCz/PProDOT-Me₂, P(tCz-co-bTP)/PProDOT-Me₂, and P(tCz-co-DTC)/PProDOT-Me₂ ECDs would not need a refreshing current for retaining their colors in bleached and colored states.

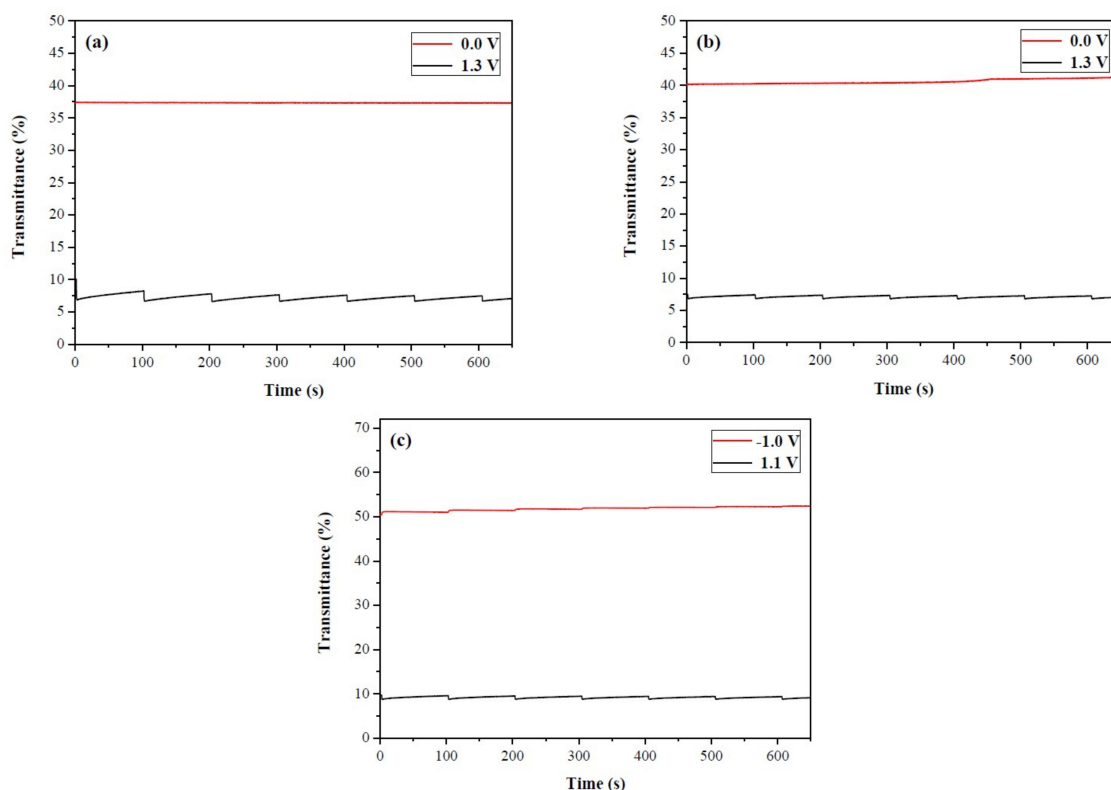


Figure 9. Open circuit stability of (a) PtCz/PProDOT-Me₂; (b) P(tCz-co-bTP)/PProDOT-Me₂; and (c) P(tCz-co-DTC)/PProDOT-Me₂ ECDs.

3.8. Stability

The redox stabilities of PtCz/PProDOT-Me₂, P(tCz-co-bTP)/PProDOT-Me₂, and P(tCz-co-DTC)/PProDOT-Me₂ ECDs were monitored by CV at 1st, 500th and 1000th cycles [39,40], the scan rate was 500 mV s⁻¹. As shown in Figure 10, 96.0%, 93.6%, and 96.7% of their electroactivities were maintained after the 500th cycle for PtCz/PProDOT-Me₂, P(tCz-co-bTP)/PProDOT-Me₂, and P(tCz-co-DTC)/PProDOT-Me₂ ECDs, respectively, and 95.5%,

90.3%, and 96.0% of their electroactivities were maintained after the 1000th cycle for PtCz/PProDOT-Me₂, P(tCz-co-bTP)/PProDOT-Me₂, and P(tCz-co-DTC)/PProDOT-Me₂ ECDs, respectively. Considering these results, ECDs employ P(tCz-co-bTP) and P(tCz-co-DTC) as anodic polymer films show potential for use in auto-dimming car mirror and motorcycle helmet-visors.

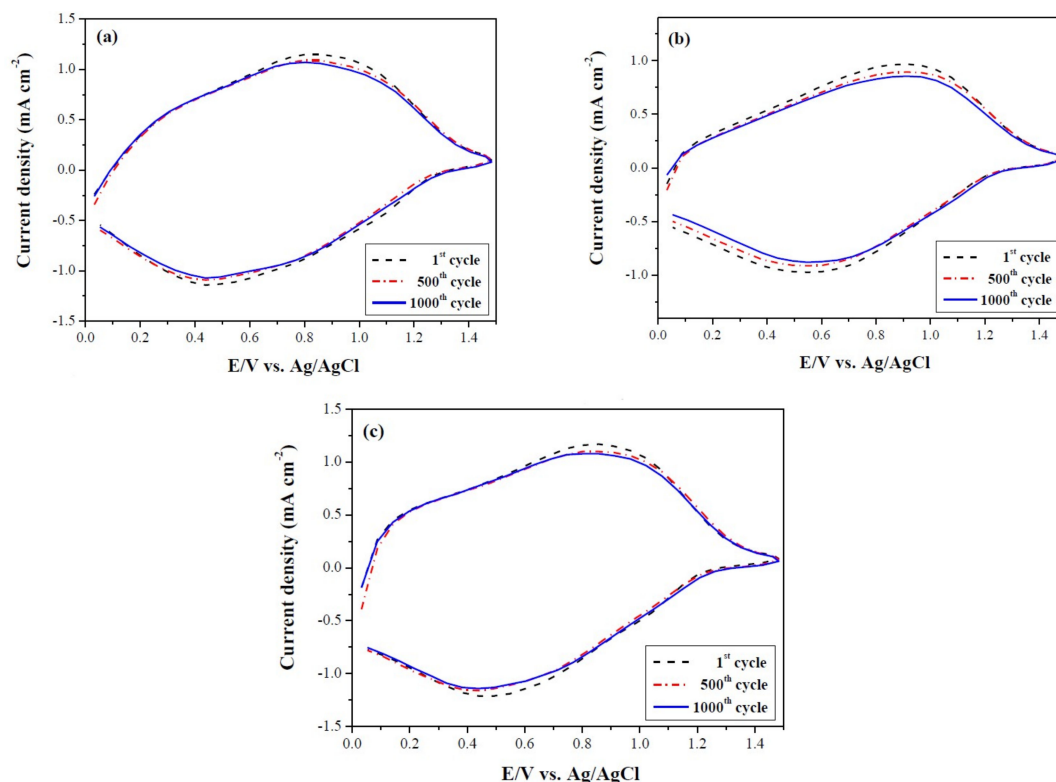


Figure 10. Cyclic voltammograms of (a) PtCz/PProDOT-Me₂; (b) P(tCz-co-bTP)/PProDOT-Me₂; and (c) P(tCz-co-DTC)/PProDOT-Me₂ ECDs at the first, 500th, and 1000th cycles.

4. Conclusions

Copolymers (P(tCz-co-bTP), P(tCz-co-CPDT), P(tCz-co-DTC), and P(tCz-co-CPDTK)) were copolymerized electrochemically. Spectroelectrochemical investigations showed that P(tCz-co-CPDT) film revealed three different colors (light grey, green, and dark blue) at various voltages, whereas the color variations of P(tCz-co-DTC) film were light yellow at 0.0 V, yellow at 0.6 V, blue at 0.8 V, and black at 1.3 V. Five dual-type ECDs based on PtCz, P(tCz-co-bTP), P(tCz-co-CPDT), P(tCz-co-DTC), and P(tCz-co-CPDTK) films as anodic polymers and PProDOT-Me₂ as the cathodic polymer were constructed and their electrochromic properties were characterized. P(tCz-co-bTP)/PProDOT-Me₂ ECD showed high ΔT_{\max} (32% at 628 nm) and fast switching time (less than 0.4 s), whereas P(tCz-co-DTC)/PProDOT-Me₂ ECD revealed high ΔT_{\max} (45.9% at 624 nm), high open circuit stability, and high redox stability after 1000 cycles, which makes P(tCz-co-bTP) and P(tCz-co-DTC) promising anodic copolymer films for ECDs' applications.

Author Contributions: P.-Y.L. and C.-W.K. implemented the experiments. T.-Y.W., C.-W.K., J.-C.C., and Y.-C.H. analyzed the electrochromic properties.

Conflicts of Interest: The authors declare no conflict of interest.

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