

Fluorescent and Electrochromic Polymers from 2,8-Di(carbazol-9-yl)dibenzothiophene and Its *S,S*-Dioxide Derivative

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Abstract

Two new polymers from 2,8-di(carbazol-9-yl)-dibenzothiophene and its *S,S*-dioxide derivative were synthesized by using both chemically oxidative in the presence of FeCl₃ and electrochemically oxidative process. The electrogenerated films showed two reversible oxidation redox couple on their cyclic voltammograms. They exhibited reversible electrochemical processes and stable color changes upon electro-oxidation, which can be switched by potential modulation. The remarkable electrochromic behavior of the film is clearly interpreted on the basis of spectroelectrochemical studies.

1. Introduction

A great deal of attention has been focused on conjugated polymers since they are potentially useful materials for a broad range of applications like photovoltaic devices,¹ lightemitting diodes (LEDs),² field effect transistors,³ sensors,⁴ and electrochromic devices.⁵ Electrochromism consists in the formation of new optical transitions in an electroactive species subjected to reversible electrochemical oxidation/reduction process.⁶ There are three general classes of electrochromic materials; inorganic materials such as transition metal oxides and Prussian Blue, molecular electrochromes such as viologens, and conjugated polymers. In particular, optically responsive conjugated polymer systems that reveal electrochromism are particularly required for their potential use in data storage and display technologies. Even though many inorganic materials, especially tungsten oxides, have been utilized over the past three decades,⁷ the use of conjugated polymers as active layers in electrochromic devices has received enormous attention because of their high optical contrasts, fast switching times, processability, and fine-tuning of the bandgap by structural modification.

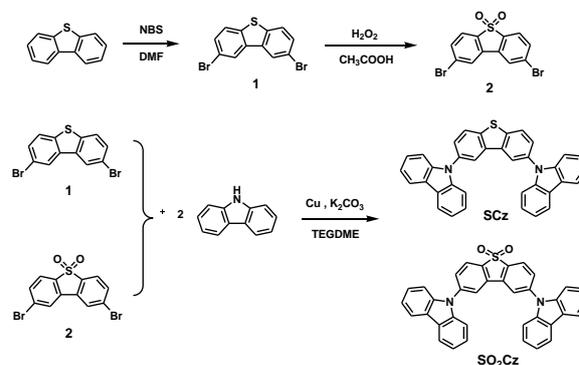
Carbazole-based polymers have various advantages such as a strong electron-donating (p-type) chromophore, and also easily functionalized at its (3,6-), (2,7-), or *N*-positions, and then covalently linked into polymeric systems, both in the main chain as building blocks and in a side chain as subunit.⁸ On the other hand, carbazole-based compounds are well-known as a good hole transport and photonic material for optoelectronic devices. Furthermore, poly(3,6-carbazole)s exhibit interesting electrochromic properties because of the conjugation breaks that are present due to the inclusion of a 3,6-linkage. Reynolds et al. suggested that one of the interesting multicolored system is that based upon the 3,6-linked carbazole moiety.⁹ Owing to broken conjugation lengths, these polymers generate radical cations which are separated from one another and do not combine. Upon further oxidation at higher potentials, another electron is removed, giving dications. Because of these properties, 3,6-linked carbazole-based electrochromic materials have multiple colors with separate colors present

for the neutral, polaronic, and bipolaronic species at various oxidation states. It has been demonstrated that *N*-substituted carbazoles can form extremely stable biscarbazoles upon anodic oxidation.¹⁰ Therefore, various carbazole-containing electrochromic polymeric films have been prepared via the electrochemical dimerization of carbazole units.¹¹ Dibenzothiophene and its *S,S*-dioxide derivatives containing diarylamine segments have been reported as potential hole-transporting and emitting materials.^{12,13} However, to our best knowledge, there are still no reports about the electrosynthesis and electrochromic properties of electroactive polymers from dibenzothiophene or dibenzothiophene *S,S*-dioxide containing carbazole derivatives.

In this study, two carbazole end-capped monomers containing dibenzothiophene or dibenzothiophene-*S,S*-dioxide as the core unit are synthesized and their polymers are successfully synthesized from both chemically oxidative polymerization and electrochemical polymerization techniques. The electrochemical, electrochromic, and luminescent properties of these polymers are also described herein.

2. Monomer synthesis

According to the literature methods, 2,8-dibromo-dibenzothiophene-*S,S*-dioxide¹³ (**2**) was prepared by oxidization of 2,8-dibromodibenzothiophene¹² (**1**) resulting from bromination of dibenzothiophene with *N*-bromo-succinimide (NBS) in DMF. The target monomers 2,8-di(carbazol-9-yl)dibenzothiophene (**SCz**) and 2,8-di(carbazol-9-yl)dibenzothiophene-*S,S*-dioxide¹⁵ (**SO₂Cz**) were synthesized by Ullmann C-N coupling reaction of dibromo compound **1** and **2** with carbazole by using copper powder (Scheme 1). The structures of all the synthesized compounds were confirmed by IR and NMR analyses. Figure 1 illustrates the ¹H NMR spectra of **SCz** and **SO₂Cz**. These spectra are in good agreement with their proposed molecular structures.



Scheme 1. Synthetic routes to monomers **SCz** and **SO₂Cz**.

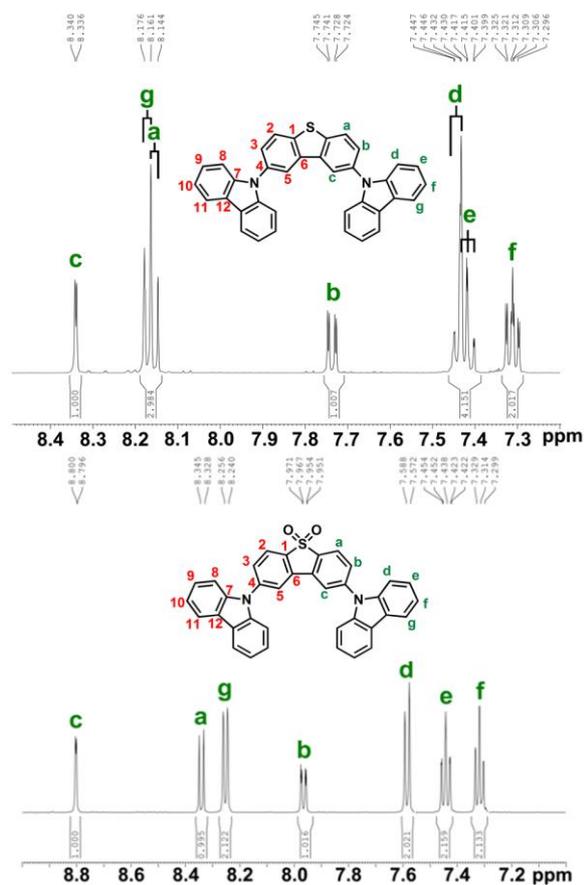


Figure 1. ^1H NMR spectra of (a) **SCz** and (b) **SO₂Cz** in CDCl_3 .

3. Polymer synthesis

3.1 Electrochemical polymerization

Electrochemical polymerization was performed with a CH Instruments 750A electrochemical analyzer. The polymers were synthesized from 10^{-4} M monomers and 0.1 M Bu_4NClO_4 in CH_2Cl_2 solution via cyclic voltammetry (CV) repetitive cycling between 0 and 1.8 V at a scan rate of 50 mV/s for ten cycles. The polymer was deposited onto the surface of the working electrode (platinum disc or ITO/glass surface, polymer films area about $0.8 \text{ cm} \times 1.25 \text{ cm}$), and the film was rinsed with plenty of acetone for the removal of inorganic salts and other organic impurities formed during the process.

Figure 2 displays the successive CV diagrams of 10^{-4} M monomers in 0.1 M $\text{Bu}_4\text{NClO}_4/\text{CH}_2\text{Cl}_2$ solutions between 0 and 1.8 V at a potential scan rate of 50 mV/s. As the CV scan continued, polymer film was formed on the working electrode surface. The increase in the redox wave current densities implied that the amount of conducting polymers deposited on the electrode was increasing. As shown in **Figure 2**, the polymerizations of these monomers showed two oxidation peaks, which are attributed to their polaronic and bipolaronic states, respectively.

For the first positive potential scan of **SCz**, an oxidation peak at ca. 1.6 V was observed. From the first reverse negative potential scan, two cathodic peaks were detected. In the second scan, a new oxidation peak appeared at 1.2 V that was the complementary anodic process of the cathodic peak at a lower potential. The observation of a new oxidation couple in the second potential scan implies that the **SCz** radical cations were involved in very fast electrochemical reactions that produced a substance that

was easier to oxidize than was the parent **SCz**. In addition, when the potential was continuously cycled, we observed a progressive growth in all peak currents (**Figure 2**). This behavior suggests that the oxidative coupling of the radical cations of **SCz** produced a continuous build up of an electroactive and conductive layer on the electrode. Similar results were observed for **SO₂Cz**.

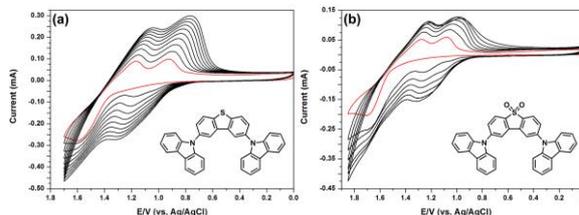
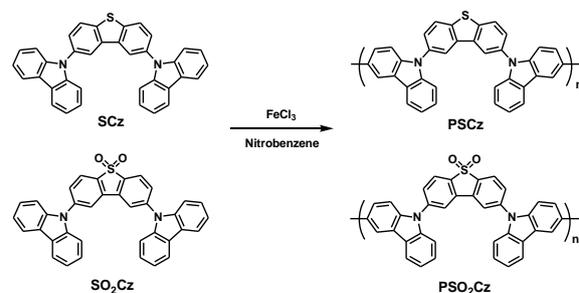


Figure 2. Repetitive cyclic voltammograms of 10^{-4} M (a) **SCz** and (b) **SO₂Cz** in 0.1 M $\text{Bu}_4\text{NClO}_4/\text{CH}_2\text{Cl}_2$ solutions at a scan rate of 50 mV/s. The first CV curves were marked in red.

3.2 Oxidative coupling polymerization

PSCz and **PSO₂Cz** could be readily prepared by the oxidative coupling polymerization of **SCz** and **SO₂Cz** with FeCl_3 as an oxidant, respectively (**Scheme 2**).



Scheme 2. Synthesis of polymers **PSCz** and **PSO₂Cz**.

4. Optical properties

All the monomers and polymers were examined by UV-Vis absorption and photoluminescence (PL) spectroscopy in both solution and solid state. **Figure 3** shows the absorption and emission profiles of the monomers and polymers, together with their PL images on exposure to an UV light in both solution and solid states. The relevant absorption and PL data are collected in **Table 1**. These compounds and their derived polymers exhibited strong UV-vis absorption bands at 289–294 nm in CH_2Cl_2 solutions, assignable to the $\pi-\pi^*$ and $n-\pi^*$ transitions of the **SCz** and **SO₂Cz** moieties in the polymer backbone. Solid film absorption spectra of these polymers were similar to those in solution, with a very slight red-shift of ca. 15 nm. The monomer **SCz** and polymer **PSCz** exhibited purple and blue PL emission with PL quantum yield of 0.57 % and 1.57 % at the maximum peaks of 386 and 426 nm, and the monomer **SO₂Cz** and polymer **PSO₂Cz** exhibited green and yellow PL emission with PL quantum yield of 6.72 % and 2.69 % at the maximum peaks of 471 and 528 nm, respectively. The red-shift of PL maxima of the polymers means higher conjugation backbone in comparison with the monomers. The monomer **SO₂Cz** and polymer **PSO₂Cz** with the electron-withdrawing sulfone group exhibited slightly higher fluorescence quantum yields in comparison to **SCz** and **PSCz**. This can be attributed to the dipolar nature of the former ones. The dibenzothiophene-*S,S*-dioxide moiety was demonstrated to be beneficial for increasing electron affinity and PL efficiency.¹⁶

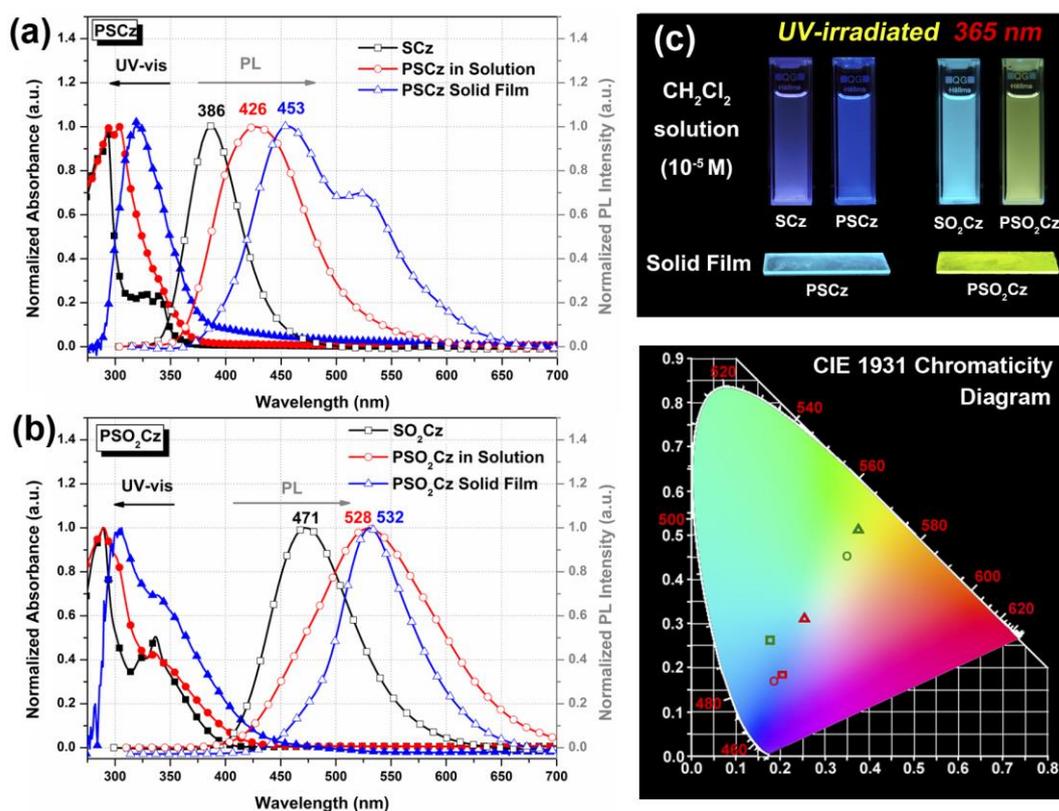


Figure 3. Absorbance and photoluminescence (PL) spectra of (a) **PSCz** and (b) **PSO₂Cz** in solution and solid film. (c) Photographs were taken under illumination of a 365 nm UV light.

Table 1. Optical Properties of Monomers and Polymers

Index	CH ₂ Cl ₂ (1 × 10 ⁻⁵ M) Solution			Solid Film (nm)		
	λ _{abs}	λ _{em} ^a	Φ _{PL} (%) ^b	λ _{max}	λ _{onset}	λ _{em}
SCz	293	386	0.57	—	—	—
SO₂Cz	289	471	6.72	—	—	—
PSCz	294	426	1.54	374	319	453
PSO₂Cz	289	528	2.69	418	304	532

Index	CIE 1931 coordinates			
	CH ₂ Cl ₂ Solution		Solid Film	
	x	y	x	y
SCz	0.211	0.183	—	—
SO₂Cz	0.187	0.265	—	—
PSCz	0.191	0.169	0.278	0.318
PSO₂Cz	0.348	0.456	0.379	0.523

^a They were excited at λ_{abs} for solid and solution states. ^b The quantum yield was measured by using quinine sulfate (dissolved in 1 N H₂SO₄ with a concentration of 1 × 10⁻⁵ M, assuming photoluminescence quantum efficiency of 0.546) as a standard.

5. Electrochemical properties

The electrochemical behavior of the electrodeposited polymer films was investigated by CV in a monomer-free Bu₄NClO₄/CH₃CN solution. The quantitative details are summarized in Table 2. As shown in Figure 4, these two polymer films showed two oxidation peaks attributed to their polaronic and bipolaronic states, respectively. The half-wave oxidation potentials ($E_{1/2}$) were recorded at 1.06 V and 1.29 V for **PSCz** and at 1.16 V and 1.42 V for **PSO₂Cz**. The slightly higher oxidation voltages of the latter ones may be caused by the strong electron-withdrawing nature of the sulfone group. The energy levels of the highest occupied molecular orbital (HOMO) and lowest unoccupied molecular orbital (LUMO) of the corresponding polymers were estimated from the $E_{1/2}$ values. Assuming that the HOMO energy

level for the ferrocene/ferrocenium (Fc/Fc⁺) standard is 4.80 eV with respect to the zero vacuum level, the HOMO levels for **PSCz** and **PSO₂Cz** were calculated to be 5.26-5.32 eV (relative to the vacuum energy level), whereas the values for the LUMO levels lay at about 2.00-2.39 eV.

Table 2. Electrochemical Properties of the Polymer Films

Polymer Code	Oxidation potential (V) ^a		Bandgap (eV) ^b	Energy levels (eV) ^c	
	E_{onset}	$E_{1/2}$	E_g^{opt}	HOMO	LUMO
PSCz	0.90	1.06, 1.29	3.26	5.26	2.00
PSO₂Cz	0.98	1.16, 1.42	2.95	5.34	2.39

^a vs. Ag/AgCl in CH₃CN. ^b Optical band gap, derived from the observed optical edge; $E_g^{opt} = 1240/\lambda_{onset}$. ^c $E_{HOMO} = -(E_{onset} + 4.8)$ (eV); $E_{LUMO} = E_{HOMO} - E_g^{opt}$

6. Spectroelectrochemical properties

Spectroelectrochemistry was used to study the changes in the absorption spectra and the information about the electronic structures of the polymers as a function of the applied potential. The electrogenerated polymer films on ITO glass were switched between 0 and 1.43 V (for **PSCz**) or 1.60 V (for **PSO₂Cz**). The spectral changes of all the polymer films upon potential variation are compiled in Figure 5. Their spectroelectrochemical behaviors are very similar. We use **PSCz** as an example to explain the spectroelectrochemical behavior of these polymers. In the neutral form, polymer **PSCz** exhibited strong absorption at 319 nm, characteristic π - π^* transitions of the biscarbazole, but it was almost transparent in the visible and near-IR regions. Consequently, the film is almost colorless. The optical band gap of polymer **PSCz** was estimated to be 3.26 eV from the onset of the π - π^* transition at 380 nm. When the applied potential was increased to about 1.15 V,

the spectra displayed an absorption peak at ca. 427 nm and a broadband that extended to the near-IR region, which we assigned to the formation of biscarbazole radical cations. The absorption band in the near-IR region may be attributed to an intervalence charge transfer (IVCT) between states in which the positive charge is centered at different amino centers (biscarbazole). The IVCT phenomenon of the family of triarylaminines with multiple amino centers has been reported in literature.¹⁷ Upon further oxidation at applied potential to 1.43 V, the dication (bipolaron) band at 762 nm appeared, and the absorption at 427 nm decreased in intensity. The observed spectral changes of the **PSCz** film were fully reversible upon varying the applied potential. In addition, they were associated with significant color changes (from colorless to greenish-yellow and to green) that were homogeneous across the ITO glass and easy to detect with the naked eye (**Figure 5** insets).

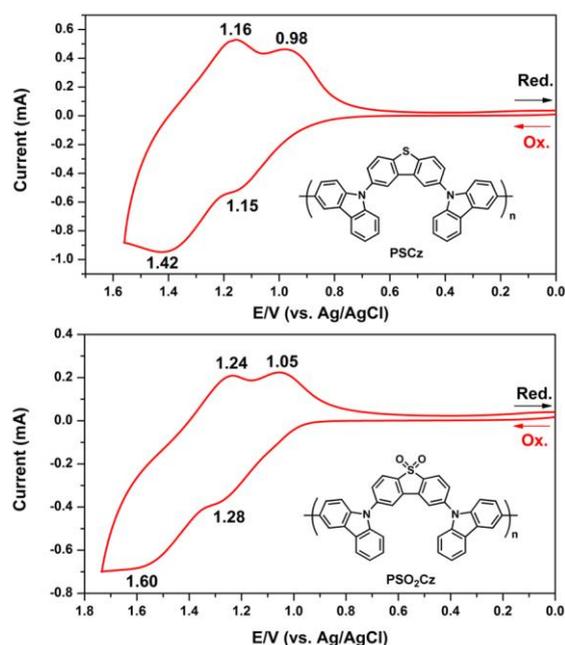


Figure 4. Cyclic voltammograms of (a) **PSCz** and (b) **PSO₂Cz** polymer films on the ITO-coated glass slide in 0.1 M Bu₄NClO₄/CH₃CN at a scan rate of 50 mV/s.

7. Conclusions

The synthesis and polymerization of two carbazole-endcapped dibenzothiophene and dibenzothiophene-*S,S*-dioxide monomers both oxidative polymerization using FeCl₃ as catalyst and also the electrochemical oxidative polymerization in scanning CV conditions is reported. The electrochemically generated polymer films exhibited two reversible oxidation redox couples due to successive oxidations of the biscarbazole unit. These polymer films also revealed excellent electrochemical and electrochromic stability, with coloration change from a colorless neutral state to greenish-yellow and green oxidized forms. These properties make the prepared **PSCz** and **PSO₂Cz** films good candidates for electrochromic applications.

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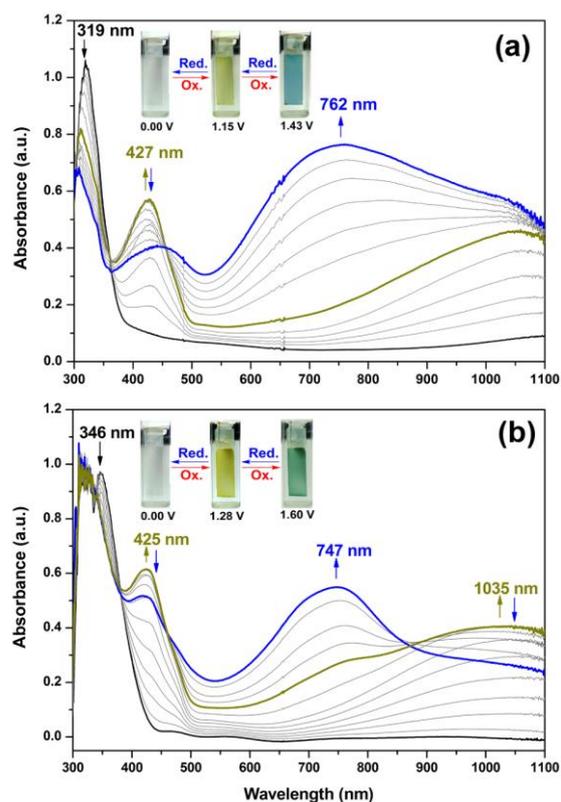


Figure 5. Spectral changes of the cast films of (a) **PSCz** and (b) **PSO₂Cz** on an ITO-coated glass in 0.1 M Bu₄NClO₄/CH₃CN at various applied potentials (vs Ag/AgCl). The insets show the color changes of the polymer films at indicated electrode potentials.

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