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Fluorescent and electrochromic polymers from 2,8-di(carbazol-9-yl) dibenzothiophene and its *S*,*S*-dioxide derivative

Sheng-Huei Hsiao^{*}, Li-Chu Wu

Department of Chemical Engineering and Biotechnology, National Taipei University of Technology, Taipei 10608, Taiwan

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ABSTRACT

We report the synthesis and characterization of two carbazole-endcapped monomers, namely 2,8di(carbazol-9-yl)dibenzothiophene (SCz) and 2,8-di(carbazol-9-yl)dibenzothiophene *S*,*S*-dioxide (SO₂Cz), and their derived polymers PSCz and PSO₂Cz prepared by both FeCl₃ oxidative coupling and electropolymerization processes. The dilute solutions of PSCz and PSO₂Cz prepared by chemical oxidative coupling exhibited fluorescent and solvatochromic behavior. Thin polymeric films could be robustly electrodeposited onto the surface of the ITO-glass substrate by repetitive cyclic voltammetry scanning of monomers SCz and SO₂Cz in an electrolyte solution between 0 and 1.8 V. The electrochemically generated polymer films exhibited two reversible oxidation redox couples due to successive oxidations of the biscarbazole unit. These polymer films also revealed good electrochemical and electrochromic stability, with coloration change from a colorless neutral state to yellow, green and blue oxidized states. Switching ability of the polymers was evaluated by kinetic studies upon measuring the percent transmittance (%T) at their maximum contrast point, indicating that the polymers exhibit moderate electrochromic performance.

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1. Introduction

Functionalized conjugated polymers have attracted continuing attention since they are potentially useful materials for a broad range of applications such as photovoltaic devices [1], lightemitting diodes (LEDs) [2], organic thin-film transistors [3], sensors [4], and electrochromic devices [5-8]. Electrochromism consists in the formation of new optical transitions in an electroactive species subjected to reversible electrochemical oxidation/reduction process [9]. 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. Optically responsive conjugated polymer systems that reveal electrochromism are particularly required for their potential use in smart window and display technologies. Even though many inorganic materials, especially tungsten oxides, have been utilized over the past decades [10–13], the use of conjugated polymers as active layers in electrochromic devices has received enormous attention because of their high optical contrasts, fast

* Corresponding author. E-mail address: shhsiao@ntut.edu.tw (S.-H. Hsiao). switching times, processability, and fine-tuning of the bandgap by structural modification [14–19].

Carbazole derivatives are well-known hole-transporting and photonic materials for the applications in optoelectronic devices [20,21]. Carbazole can be 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. Carbazole-containing polymers such as poly(N-vinylcarbazole), poly(2,7-carbazole)s, and poly(3,6-carbazole)s are considered as a very important class of electroactive and photoactive materials [22]. For instance, the excellent hole transporting properties of poly(2,7-carbazole) derivatives make them highly promising materials for electroluminescent devices, organic thinfilm transistors and photovoltaic cells [23-25]. It has been demonstrated that poly(3,6-carbazole) derivatives exhibit interesting electrochromic properties because of the conjugation breaks that are present due to the inclusion of a 3,6-linkage [26]. N-Substituted carbazole based polymers are generally colorless or near-colorless at their neutral state and then can change colors at their oxidized states, which is an important property for neutral state colorless electrochromic device applications [27–29]. It has been demonstrated that N-substituted carbazoles can form biscarbazoles upon anodic oxidation [30]. Therefore, various







carbazole-containing electrochomic polymeric films have been prepared via the electrochemical coupling of carbazole units [31–39].

Dibenzothiophene and its S,S-dioxide derivatives containing diarvlamine segments have been reported as potential holetransporting and emitting materials [40-44]. Conjugated copolymers containing electron-deficient dibenzothiophene-S.S-dioxide moiety are of particular interests on account of their high efficiency and excellent spectral stability [45,46]. The synthesis and optical and electrochromic properties of dibenzothiophene (or dibenzothiophen-S,S-dioxide) and 3-hexylthiophene (or EDOT) based conjugated polymers have been reported in literature [47–51]. However, to our knowledge, there is little information about the synthesis and electrochromic properties of electroactive polymers from dibenzothiophene or dibenzothiophene-S,S-dioxide containing carbazole derivatives so far. In this study, two carbazole end-capped monomers containing dibenzothiophene (SCz) or dibenzothiophene-S,S-dioxide (SO₂Cz) 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. Two referenced compounds with tert-butyl blocking groups on their carbazole units, namely 2,8-di(3,6-di-*tert*-butylcarbazol-9-yl) dibenzothiophene (StBCz) and 2,8-di(3,6-di-tert-butylcarbazol-9yl)dibenzothiophene-S,S-dioxide (SO2tBCz), are also synthesized and characterized as a contrast experiment.

2. Experimental details

2.1. Materials

2,8-Dibromodibenzothiophene 2,8-(1), dibromodibenzothiophene-S,S-dioxide (2) and 3,6-di-tert-butyl-9H-carbazole (3) were synthesized according to literature methods [52–54]. Dibenzothiophene (Acros), carbazole (Acros), N-bromosuccinimide (NBS, Acros), N,N-dimethylformamide (DMF, Tedia), hydrogen peroxide 35% (H₂O₂, Shimakyu's Pure Chemicals), acetic acid (Tedia), 2-chloro-2-methylpropane (*tert*-butyl chloride) (Acros), aluminum chloride (Acros), dichloromethane (CH₂Cl₂, Fischer Chemical), potassium carbonate (K₂CO₃, Showa), copper (Cu, Acros), triethylene glycol dimethyl ether (TEGDME, Acros), iron(III) chloride (FeCl₃, Fischer Chemical), nitrobenzene (Acros), 18-crown-6 (TCI), and 1,2-dichlorobenzene (Acros) were used without further purification. Tetrabutylammonium perchlorate (Bu₄NClO₄) (Arcos) was dried in vacuo prior to use. All other reagents were used as received from commercial sources.

2.2. Monomer synthesis

2.2.1. Synthesis of 2,8-di(carbazol-9-yl)dibenzothiophene (SCz)

In a 100-mL three-neck round-bottomed flask equipped with a stirring bar under nitrogen atmosphere, a mixture of 2,8-dibromodibenzothiophene (3.42 g, 0.01 mol), carbazole (4.18 g, 0.025 mol), K₂CO₃ (5.53 g, 0.04 mol), and Cu (1.34 g, 0.021 mol) in TEGDME (15 mL) was heated at 180 °C with stirring for 24 h. The reaction mixture was hot filtered, and the filtrate was poured into 200 mL ethanol. The light yellow crystals (2.68 g, 52% yield; mp = 290–293 °C) was collected by filtration and vacuum dried. ¹H NMR (500 MHz, CDCl₃, δ , ppm): 7.31 (t, *J* = 7.0 Hz, 4H, Hf), 7.42 (t, *J* = 8.0 Hz, 4H, He), 7.43 (d, *J* = 7.0 Hz, 4H, Hd), 7.73 (dd, *J* = 8.5, 2.0 Hz, 2H, Hb), 8.15 (d, *J* = 8.5 Hz, 2H, Ha), 8.17 (d, *J* = 7.5 Hz, 4H, Hg), 8.34 (d, *J* = 2.0 Hz, 2H, Hc). ¹³C NMR (125 MHz, CDCl₃, δ , ppm): 109.54 (C⁸), 120.08 (C¹⁰), 120.38 (C¹¹), 120.59 (C⁵), 123.42 (C¹²), 124.35 (C²), 126.06 (C⁹), 126.58 (C³), 134.94 (C⁶), 136.59 (C¹), 139.24

(C⁴), 141.17 (C⁷). Calcd for C₂₄H₂₂N₂S (370.52): C, 77.80%; H, 5.98%; N, 7.56%. Found: C, 77.68%; H, 5.89%, N, 7.50%.



2.2.2. Synthesis of 2,8-di(carbazol-9-yl)dibenzothiophene-S,Sdioxide (**SO₂Cz**)

In a 100-mL three-neck round-bottomed flask equipped with a stirring bar under nitrogen atmosphere, a mixture of 2,8dibromodibenzothiophene-S,S-dioxide (3.74 g, 0.01 mol), carbazole (4.18 g, 0.025 mol), K₂CO₃ (5.53 g, 0.04 mol), and Cu (1.34 g, 0.021 mol) in TEGDME (15 mL) was heated at 180 °C with stirring for 24 h. The reaction mixture was filtered while hot, and the filtrate was poured into 200 mL methanol. The precipitated product was collected by filtration (1.15 g, 21% yield) and then recrystallized from toluene to give white crystals with a melting point of 392–395 °C. FT-IR (KBr): 1300 and 1162 cm⁻¹ (sulfonyl asymmetric and symmetric stretching). ¹H NMR (500 MHz, CDCl₃, δ , ppm): 7.31 (t, J = 8.0 Hz, 4H, Hf), 7.44 (t, J = 8.0 Hz, 4H, He), 7.58 (d, J = 8.0 Hz, 4H, Hd), 7.96 (dd, *J* = 8.5, 2.0 Hz, 2H, Hb), 8.25 (d, *J* = 8.0 Hz, 4H, Hg), 8.34 (d, J = 8.5 Hz, 2H, Ha), 8.80 (d, J = 2.0 Hz, 2H, Hc). ¹³C NMR (125 Hz, CDCl₃, δ, ppm): 110.11 (C⁸), 120.52 (C¹¹), 120.75 (C¹⁰), 121.91 (C⁵), 123.15 (C¹²), 123.95 (C²), 126.48 (C⁹), 129.01 (C³), 132.94 (C⁶), 135.51 (C¹), 139.53 (C⁷), 142.57 (C⁴). Calcd for C₂₄H₂₂N₂SO₂ (402.52): C, 71.61%; H, 5.51%; N, 6.96%. Found: C, 71.52%; H, 5.45%, N, 6.88%.



2.3. Polymer synthesis

2.3.1. Electrochemical polymerization

Electrochemical polymerization was carried out with a CH Instruments 750A electrochemical analyzer. The polymers were synthesized from 1×10^{-4} M monomer solutions in 0.1 M Bu₄N-ClO₄/CH₂Cl₂ via repetitive cyclic voltammetry (CV) scanning between 0 and 1.8 V at a scan rate of 50 mV s⁻¹ for ten cycles. The polymer was deposited onto the surface of the working electrode (ITO/glass surface, polymer films area about 0.8 cm × 1.25 cm), and the film was rinsed with plenty of acetone for the removal of inorganic salts and other organic impurities formed during the



Scheme 1. Synthetic routes to compounds SCz, SO₂Cz, StBCz and SO₂tBCz.

process.

2.3.2. Chemical oxidative polymerization

PSCz and **PSO₂Cz** could also be prepared by the chemical oxidative polymerization of **SCz** and **SO₂Cz**, respectively, with FeCl₃ as an oxidant. In a 50-mL two-necked round-bottom flask equipped with a stirring bar under nitrogen atmosphere, a mixture of **SCz** (0.514 g, 1 mmol), FeCl₃ (0.404 g, 2.5 mmol) in nitrobenzene (2 mL) was stirred at room temperature for 24 h. The reaction mixture was poured into methanol containing 10% hydrochloric acid. The precipitate was collected and washed thoroughly with aqueous ammonium hydroxide. The crude polymer (0.43 g, 84% yield) was re-dissolved in chloroform. After removing the insoluble fraction by filtration, the filtrate was condensed and poured into methanol. The resulting precipitate was washed with methanol and dried under reduced pressure to yield the desired polymer **PSCz** (0.28 g, 54% yield). **PSO₂Cz** (88% yield for the crude product; 42% for the soluble part) was prepared from monomer **SO₂Cz** by a similar procedure.

2.4. Fabrication of electrochromic device

Electrochromic **PSCz** films were prepared by electropolymerization of **SCz** onto an ITO-coated glass substrate $(20 \times 30 \times 0.7 \text{ mm}, 50-100 \Omega \text{ cm}^{-2})$ by a procedure as described above. A gel electrolyte based on PMMA (Mw: 120000) and LiClO₄ was plasticized with propylene carbonate to form a highly transparent and conductive gel. PMMA (1 g) was dissolved in dry acetonitrile (4 mL), and LiClO₄ (0.1 g) was added to the polymer solution as supporting electrolyte. Then propylene carbonate (1.5 g) was added as plasticizer. The mixture was then gently heated until gelation. The gel electrolyte was spread on the polymer-coated side of the electrode, and the electrodes were sandwiched. Finally, an epoxy resin was used to seal the device.

2.5. Instrumentation and measurements

Infrared (IR) spectra were recorded on a Horiba FT-720 FT-IR spectrometer. ¹H and ¹³C NMR spectra were measured on a Bruker AVANCE 500 FT-NMR system with tetramethylsilane as an internal standard. Elemental analyses were carried out with a Heraeus VarioEL III elemental analyzer. DSC analyses were performed on a Perkin-Elmer DSC 4000 at a scan rate of 20 °C min⁻¹ under nitrogen. Ultraviolet-visible (UV-Vis) spectra of the polymer films were recorded on an Agilent 8453 UV-Visible spectrometer. Gel permeation chromatography (GPC) analysis was carried out on a Waters chromatography unit interfaced with a Waters 2410 refractive index detector. Two Waters 5 µm Styragel HR-2 and HR-4 columns (7.8 mm I.D. \times 300 mm) were connected in series with NMP as the eluent at a flow rate of 0.5 mL min⁻¹ at 40 °C and were calibrated with polystyrene standards. Electrochemistry was performed with a CHI 750A electrochemical analyzer. Voltammograms are presented with the positive potential pointing to the left and with increasing anodic currents pointing downwards. Cvclic voltammetry (CV) was conducted with the use of a three-electrode cell in which ITO (polymer films area about 0.8 cm \times 1.25 cm) was used as a working electrode. A platinum wire was used as an auxiliary electrode. All cell potentials were taken with the use of a homemade Ag/AgCl, KCl (sat.) reference electrode. Ferrocene was used as an external reference for calibration (+0.48 V vs. Ag/AgCl). Spectroelectrochemistry analyses were carried out with an electrolytic cell, which was composed of a 1 cm cuvette, ITO as a working electrode, a platinum wire as an auxiliary electrode, and a Ag/AgCl reference electrode. Absorption spectra in the spectroelectrochemical experiments were measured with an Agilent 8453 UV-Visible photodiode array spectrophotometer. Photoluminescence (PL) spectra were measured with a Varian Cary Eclipse fluorescence spectrophotometer. Fluorescence quantum yields (Φ_F) values of the samples in NMP were measured by using



quinine sulfate in 1 N H₂SO₄ as a reference standard ($\Phi_F = 0.546$).

3. Results and discussion

3.1. Monomer synthesis



Fig. 2. First (in red) and second (in black) CV diagrams of 1×10^{-4} M solutions of (a) SC2 and (b) SO₂C2 in 0.1 M Bu₄NClO₄/CH₂Cl₂ at a scan rate of 50 mV s⁻¹. (For interpretation of the references to colour in this figure legend, the reader is referred to the web version of this article.)

dibromodibenzothiophene (1) was prepared from bromination of dibenzothiophene with N-bromosuccinimide (NBS) in DMF, the oxidation of compound 1 with hydrogen peroxide in acetic acid gave 2,8-dibromodibenzothiophene-S,S-dioxide (2). Friedel-Crafts alkylation of carbazole with *tert*-butyl chloride in the presence of aluminum chloride gave 3.6-di-*tert*-butyl-9H-carbazole (**3**). The target monomers **SCz** and **SO₂Cz** and their *tert*-butyl derivatives **StBCz** and **SO₂tBCz** were synthesized by the Ullmann C–N coupling reactions of dibromo compounds 1 and 2 with carbazole and 3 by using copper powder (Scheme 1). The synthetic details and characterization data of the tert-butyl derivatives are included in the Supplementary Information file. The structures of all the synthesized compounds were confirmed by FTIR, ¹H and ¹³C NMR analyses. Fig. S1 (Supplementary Information) illustrates the FT-IR spectra of the synthesized monomers SCz and SO₂Cz together with their starting materials. The IR spectra of compounds 2 and SO₂Cz gave characteristic bands of sulfonyl groups at around 1300 and 1162 cm⁻¹ ($-SO_2$ - asymmetric and symmetric stretching). The secondary amino group of carbazole showed a sharp N-H stretching absorption at 3419 cm⁻¹, which disappeared after Ullmann coupling reaction. The IR spectra of the referenced compounds StBCz and SO₂tBCz and their starting materials are compiled in Fig. S2. The IR spectra of compounds 2 and SO₂tBCz gave characteristic bands of sulfonyl groups at around 1300 and 1162 cm^{-1} (-SO₂- asymmetric and symmetric stretching). Compounds 3, StBCz and SO₂tBCz showed additional aliphatic C-H stretching absorptions around 2956 cm⁻¹ due to the presence of *tert*-butyl groups. Fig. 1 illustrates the ¹H NMR spectra of SCz and SO₂Cz. ¹³C NMR and two-dimensional (2-D) NMR spectra of SCz, SO₂Cz, StBCz and SO₂tBCz are summarized in the Supplementary Information (Figs. S3–S6). Assignments of all proton and carbon signals were assisted by the 2-D NMR spectra. These spectra agree well with their proposed molecular structures. In the proton NMR spectra, the aromatic protons in the central core (i.e., protons Ha to Hc) of compounds SO₂Cz and SO₂tBCz resonated at a more downfield region than those of compounds SCz and StBCz due to the strong electron-withdrawing nature of the sulfonyl group. The resonance peaks appearing at a high field region (about 1.47 ppm) and their integration values in the proton NMR spectra, together with the resonance signals of the carbon-13 NMR spectra at 31 and 34 ppm confirmed the presence of tert-butyl groups in StBCz and SO₂tBCz. Thus, all the IR and NMR spectra confirmed the successful syntheses of the desired compounds.



Fig. 3. Repetitive CV diagrams of 1 × 10⁻⁴ M solutions of (a) SC₂, (b) SO₂C₂, (c) StBC₂ and (d) SO₂tBC₂ in 0.1 M Bu₄NClO₄/CH₂Cl₂ at a scan rate of 50 mV s⁻¹. The first CV curves are marked in red.

3.2. Polymer synthesis

3.2.1. Electrochemical polymerization

The electrochemical property of the dicarbazole compounds was probed by cyclic voltammetry (CV). Fig. 2 presents the CV diagrams of SCz and SO₂Cz in 0.1 M Bu₄NClO₄/CH₂Cl₂. For the first positive potential scan, an oxidation peak at ca. 1.60 V and 1.70 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 1.17 V and 1.26 V, respectively. 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 and SO₂Cz radical cations were involved in very fast electrochemical reactions that produced a substance that was easier to oxidize than was the parent SCz and SO₂Cz. The additional peak is most likely resulted from coupling reaction of C3 and C6 of the carbazole. Fig. 3(a) displays the successive cyclic voltammograms (CV) of the SCz solution between 0 and 1.8 V at a potential scan rate of 50 mV s⁻¹. In the first anodic half-cycle, one oxidation peak is observed at $E_{pa} = 1.60$ V, which is attributed to the oxidation of carbazole unit, resulting in formation of oligomers/polymer in the vicinity of electrode surface. In the reverse scan, two peaks are detected at $E_{pc} = 0.91$ and 1.20 V, which correspond to reduction of film deposited in the preceding anodic scan. In the second and subsequent voltammetric cycles, the anodic peaks gradually shifted to higher potentials and the cathodic peaks shifted to lower potentials with the increasing intensity of the peaks. 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** (Fig. 3(b)). The electrodeposited **PSCz** and **PSO₂Cz** polymer films are proposed to be formed by the carbazole-carbazole coupling reactions. In contrast, **StBCz** and **SO₂tBCz** showed reversible and almost the same oxidation behavior upon repeated scanning (Fig. 3(c) and (d)). The electrochemical stability and non-polymerizability of these two compounds can be attributed to the blocking of the active sites of carbazole by the *tert*-butyl group.

3.2.2. Chemical oxidative polymerization

PSCz and **PSO₂Cz** could also be readily prepared by chemical oxidative polymerizations of **SCz** and **SO₂Cz** with FeCl₃ as an oxidant. By using the reaction conditions shown in the Experimental details, the reactions generally resulted in a large insoluble fraction. For the chemical polymerization of **SCz**, an 84% yield of the polymer with 35% insoluble fraction was obtained. In the case of **SO₂Cz**, an 88% yield of the polymer with 52% insoluble fraction was obtained. The high yields and the formation of a great amount of an insoluble fraction indicate that these two monomers are highly reactive and more than 3 positions were reacted leading to the gel formation. The solubility of the CHCl₃-insoluble polymers was also tested in highly polar organic solvents such as NMP and DMAc. They were insoluble in all the available organic solvents and even in concentrated sulfuric acid. These results implied that the insoluble



Fig. 4. Absorbance and photoluminescence (PL) spectra of (a) PSC2 and (b) PSO2C2 in solution and solid film. (c) Photographs were taken under illumination of a 365 nm UV light.

polymers exhibited a crosslinked structure. The soluble portions of **PSCz** and **PSO₂Cz** were used for GPC, FT-IR, DSC, and UV–vis absorption measurements. As shown in Table S1, the soluble **PSCz** and **PSO₂Cz** had M_w values of 5000 and 3000, respectively, indicating they are low-molecular-weight oligomers.

Fig. S7 illustrates the FT-IR spectra of polymers PSCz and **PSO₂Cz**. These spectra are essentially very similar to those of their monomers. As compared to PSCz, PSO₂Cz gave additional characteristic bands of sulfonyl groups at around 1309 and 1182 cm⁻¹ (-SO₂- asymmetric and symmetric stretching). The DSC thermograms of the monomers and the polymers prepared by the chemical oxidative polymerization method are shown in Fig. S8. Monomers SCz and SO₂Cz showed a sharp melting endotherm at 291 and 293 °C, respectively. The polymers PSCz and PSO₂Cz displayed glass transition at 301 and 302 °C, respectively. No melting endotherms were observed in their DSC curves up to 450 °C. The UV-Vis absorption spectra of monomers SCz and SO₂Cz and polymers PSCz and PSO₂Cz in CH₂Cl₂ and as solid films on the ITOglass are shown in Fig. S9. The monomers showed absorption maxima at 293 and 289 nm, with absorption onsets at 309 and 317 nm, respectively. The polymers showed absorption maxima at 294 and 290 nm and absorption onsets at 366 and 411 nm, respectively. The red-shift of absorption maxima and onsets of the polymer films might be attributed to higher conjugation length in comparison with the monomers and/or the aggregation of the polymer chains and enhanced inter-chain $\pi - \pi^*$ stacking interaction in the film state.

3.3. Optical properties

All the monomers and polymers were examined by UV-Vis absorption and photoluminescence (PL) spectroscopy. Fig. 4 shows the absorption and emission profiles of the monomers and polymers, together with their PL images on exposure to an UV light. The relevant absorption and PL data are collected in Table S2. Compounds **SCz** and **SO₂Cz** and their derived polymers exhibited strong UV-Vis absorption bands at 289-294 nm in CH₂Cl₂ solutions, assignable to the $\pi - \pi^*$ and $n - \pi^*$ transitions of the **SCz** and **SO₂Cz** moieties. Solid film absorption spectra of PSCz and PSO₂Cz were similar to those in solution, with a slight red-shift of ca. 15 nm. The monomer SCz and polymer PSCz exhibited blue PL emission with PL quantum yield of 0.48% and 1.54% at the maximum peaks of 386 and 426 nm, and the monomer SO₂Cz and polymer PSO₂Cz exhibited bright blue and yellowish green PL emission with a PL quantum yield of 7.77% and 4.05% at the maximum peaks of 471 and 528 nm, respectively. The monomer **SO₂Cz** and polymer **PSO₂Cz** with the electron-withdrawing sulfonyl group exhibited 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 has been demonstrated to be beneficial for increasing electron affinity and PL efficiency [55].

It is well known that dibenzothiophene-S,S-dioxide derivatives exhibited environment sensitive solvatochromic behavior in which the relative intensity of emission bands is dependent on the solvent polarity. In order to further investigate the solvatochromic properties, we investigated the absorption and fluorescence of **PSCz** and **PSO₂Cz** in some organic solvents with different polarity. Fig. 5



Fig. 5. Normalized PL spectra the dilute solutions of (a) **PSCz** (b) **PSO₂Cz** (*ca.* 1×10^{-5} M) in toluene and DMSO. Photographs were taken under illumination of a 365 nm UV light.

shows the normalized PL spectra of PSCz and PSO2Cz of dilute solutions in toluene and DMSO, together with fluorescence images of their solutions. The absorption and PL emission data of PSCz and PSO₂Cz in various solvents are summarized in Table S3. The solution absorption spectra of PSCz are similar, with little shift in the peak maximum (absorption $\lambda_{max} \sim 294$ nm). This clearly indicates that the solvent polarity exerts little effect on its ground-state electronic transition. In contrast, the PL emission spectra of PSCz show strong solvent-polarity dependence, revealing a dominant broad emission band that undergoes a remarkable bathochromic shift in highly polar DMSO. The emission color changes from purple-blue in toluene (PL $\lambda_{max} = 402 \text{ nm})$ to bright blue in DMSO (PL $\lambda_{max} = 458$ nm). **PSO₂Cz** showed a similar solvatochromic phenomenon, with emission color changing from blue in toluene (PL $\lambda_{max} = 460 \text{ nm}$) to yellow-green in DMSO (PL $\lambda_{max} = 528 \text{ nm}$). It was also found that PSO₂Cz exhibited a larger solvatochromic effect in emission when compared to PSCz because the former has a stronger donor (carbazole)-acceptor (sulfone) pair. The solvatochromic effect could be attributed to the fast intramolecular charge-transfer (ICT) process resulting in a large change of dipole moment in the excited state. Such solvatochromic behavior is associated with the stabilization of the polar emissive excited states by the polar solvents.

We also investigated the absorption and fluorescence of small molecules **SCz**, **SO₂Cz**, **StBCz** and **SO₂tBCz** in solvents with different polarity. Fig. S10 shows the normalized PL spectra of **SCz** and **StBCz**

in dilute solution in various solvents, together with PL images of their solutions. The absorption and PL emission data of SCz and StBCz are summarized in Table S4. The solution absorption spectra of **SCz** in various solvents are very similar (absorption λ_{max} : ca 294 nm), and its emission wavelengths are not very sensitive to the solvent polarity (382 nm in toluene; 392 nm in DMSO). The solutions of **StBCz** in various solvents shows absorption peaks at around 298 nm and PL emission maxima from 390 nm in toluene to 409 nm in DMSO. The variation of emission wavelengths between toluene and DMSO is in within 20 nm, indicating low polar character of these two compounds. Fig. 6 shows the normalized PL spectra of SO₂Cz and SO₂tBCz in dilute solution in various solvents, together with fluorescence images of their solutions. The absorption and PL emission data of SO₂Cz and SO₂tBCz are also listed in Table S4. Their solution absorption spectra in different solvents are similar, with little shift in the peak maximum (absorption λ_{max} : 290–294 nm). This clearly indicates that the solvent polarity exerts little effect on their ground-state electronic transitions. In contrast, the PL emission spectra of these two compounds show strong solvent-polarity dependence, revealing a dominant broad emission band that undergoes remarkable bathochromic shifts with an increase of the solvent polarity. The emission color changes from purple-blue in toluene (PL $\lambda_{max} = 425-443$ nm) to yellow-green in DMSO (PL $\lambda_{max} = 508-530$ nm). The emission wavelength increases as the solvent polarity increases. This clearly indicates that these two molecules permit strong intramolecular charge transfer from the donor (carbazole) to acceptor (dibenzothiophene-S.S-dioxide) unit. It is obvious that the compounds stabilized in the excited state by the polar solvent molecules will display red-shifted emission.

3.4. Electrochemical properties

Cyclic voltammetry (CV) experiments were conducted to investigate the electrochemical behavior of the monomers. The oxidation and reduction cycles of the monomers were measured in dichloromethane (CH₂Cl₂) containing 0.1 M of Bu₄NClO₄ as the supporting electrolyte and saturated Ag/AgCl as the reference electrode under a nitrogen atmosphere. The CV curves of SCz, StBCz, SO₂Cz and SO₂tBCz are shown in Fig. 7. SO₂Cz and SO₂tBCz display a quasi-reversible reduction wave ($E_{pc} \sim -1.93$ V vs. ferrocene) due to the electron-deficient dibenzothiophene-S,S-dioxide segment. SCz and SO₂Cz exhibit a quasi-reversible oxidation wave (Epa ~1.60 and 1.70 V, respectively, vs. ferrocene). SO₂Cz shows a slightly higher oxidation potential than that of SCz due to the electron-withdrawing sulfonyl group. The reverse negative potential scans of these two compounds show two cathodic peaks attributed to the in-situ coupling reaction of C-3 and C-6 of the carbazole. StBCz and SO2tBCz reveal a reversible oxidative wave at lower potentials (E_{pa} ~1.37 and 1.53 V, respectively, vs. ferrocene) attributable to the tert-butyl substitution on the C-3 and C-6 positions of the carbazole. The reverse negative potential scans of these two compounds show only one corresponding cathodic peak at 1.12 and 1.28 V because the active sites of their carbazole units are blocked with bulky tert-butyl groups. The derived oxidation and reduction potentials of the monomers as well as their respective highest occupied molecular orbital (HOMO) and lowest unoccupied molecular orbital (LUMO) (vs. vacuum) are summarized in Table 1.

The electrochemical behavior of the electrodeposited polymer films was investigated by CV in a monomer-free Bu₄NClO₄/CH₃CN solution. The quantitative details are also summarized in Table 1. As shown in Fig. 8, 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 1.07 V and 1.30 V for **PSCz** and at 1.17 V and 1.42 V for **PSO₂Cz**. The slightly higher oxidation voltages of the latter one could be



Fig. 6. Normalized PL spectra the dilute solutions of (a) **SO₂Cz** and (b) **SO₂tBCz** (*ca.* 1×10^{-5} M) in solvents of various polarities. Photographs were taken under illumination of a 365 nm UV light.



Fig. 7. Cyclic voltammograms of (a) SCz, (b) SO₂Cz, (c) StBCz and (d) SO₂tBCz (1 × 10⁻⁴ M) in 0.1 M Bu₄NClO₄/CH₂Cl₂ solutions at a scan rate of 50 mV s⁻¹.

Table 1	
Redox potentials and energy levels of monomers and the electrodeposited polymer films.	

Polymer code (as film)	Absorpti	on (nm)	Oxidation	ı potential (V) ^a	Reduction potential (V) ^a		Bandgap (eV) ^{b,c}		Energy level (eV) ^d	
	λ_{max}	λ_{onset}	Eonset	$E_{1/2}^{\text{ox}}$	Eonset	$E_{1/2}^{\rm red}$	$E_{\rm g}^{\rm opt}$	$E_{\rm g}^{\rm ec}$	НОМО	LUMO
PSCz	319	381	0.90	1.07, 1.30	_	_	3.26	_	5.43	2.17
PSO ₂ Cz	306	421	0.98	1.17, 1.42	-1.54	-1.69	2.95	2.86	5.53	2.58
Monomer code (in CH ₂ Cl ₂)										
SCz	293	309	1.32	1.38	_	_	_	_	5.74	_
SO ₂ Cz	289	317	1.49	1.49	-1.55	-1.75	-	3.21	5.85	2.61 ^e
StBCz	297	307	1.25	1.13	-	-	_	-	5.61	_
SO ₂ tBCz	294	311	1.30	1.41	-1.54	-1.75	_	3.05	5.66	2.61 ^e

^a vs. Ag/AgCl in CH₃CN. $E_{1/2}$ = average potential of the redox couple peaks.

^b The data were calculated from polymer films by the equation: $E_g^{opt} = 1240/\lambda_{onset}$ (optical energy gap between HOMO and LUMO).

^c E_{g}^{ec} , electrochemical band gap is derived from the difference between first $E_{1/2}^{ox}$ and $E_{1/2}^{red}$ values.

^d The HOMO energy levels were calculated from first $E_{1/2}^{ox}$ values and were referenced to ferrocene (4.8 eV relative to the vacuum energy level; $E_{1/2}^{ox} = 0.44$ V in CH₃CN): HOMO = first $E_{1/2}^{ox} + 4.8 - 0.44$ (eV); LUMO = HOMO $- E_{g}^{opt}$.

^e LUMO = HOMO - E_{g}^{ec} .

explained by the strong electron-withdrawing nature of the sulfone group. The reduction of the dibenzothiophene-S,S-dioxide core of **PSO₂Cz** occurs at a notably negative potential ($E_{pc} \sim -1.95$ V) relative to ferrocene/ferrocenium (Fc/Fc⁺). The energy levels of HOMO and LUMO of these two polymers were estimated from the $E_{1/2}$ values. Assuming that the HOMO energy level for the Fc/Fc⁺ standard is 4.80 eV with respect to the zero vacuum level, the HOMO levels for **PSC₂** and **PSO₂Cz** were calculated to be 5.43 and 5.53 eV (relative to the vacuum energy level), whereas the values for the LUMO levels lay at about 2.17 and 2.58 eV. Redox reactions for **PSCz** shown in Scheme S1 represent a possible distribution of electron density for the oxidized forms and describe by other resonance forms, which contribute to the charge delocalization.

3.5. 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 Fig. 9. Their spectroelectrochemical behaviors are very similar. We use **PSCz** as an example to explain the spectroelectrochemical behavior of these two polymers. In the neutral form,

polymer **PSCz** exhibited strong absorption at 319 nm corresponding to π - π ^{*} transitions in the polymer backbone, 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 381 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 (polarons). The absorption band in the near-IR region may be attributed to an intervalence charge transfer (IV-CT) between states in which the positive charge is centered at different amino centers (biscarbazole). The IV-CT phenomenon of the family of triarylamines with multiple amino centers has been reported in literature [56]. 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 blue) that were homogeneous across the ITO glass and easy to detect with the naked eye (Fig. 9 insets). Fig. S11 illustrates the spectral and coloration changes of PSO₂Cz upon electro-reduction. When the applied potential was decreased to about -1.93 V, the spectra displayed the absorption peaks at 538, 819 and 904 nm. Meanwhile, the color of the film changes from



Fig. 8. Cyclic voltammograms of electrochemically synthesized (a) PSC2 and (b) PSO2C2 polymer films on the ITO-coated glass slide in 0.1 M Bu₄NCIO₄/CH₃CN at a scan rate of 50 mV s⁻¹.



Fig. 9. Spectral changes of the polymer films (a) **PSCz** and (b) **PSO₂Cz** on an ITO-coated glass in 0.1 M Bu₄NClO₄/CH₃CN at various applied potentials (vs. Ag/AgCl).

colorless to pink.

3.6. Electrochromic switching studies

Electrochromic switching studies for the polymer film were

performed to monitor the percent transmittance changes (Δ %T) as a function of time at their absorption maximum and to determine the response time by stepping potential repeatedly between the neutral and oxidized states. The active area of the polymer film on ITO glass is about 2 cm^2 . Fig. 10 depicts the optical transmittance as a function of time, current densities monitored and the optical transmittance changes for the **PSCz** film at 427 and 762 nm by applying square-wave potential steps between 0 and 1.15 V for a pulse width of 13 s and between 0 and 1.43 V for a pulse width of 14 s. The response time was calculated at 90% of the fulltransmittance change, because it is difficult to perceive any further color change with naked eye beyond this point. As shown in Fig. 11, the PSCz film attained 90% of a complete greenish-yellow coloring and bleaching in 5.5 and 1.3 s, respectively. The optical contrast measured as $\Delta \% T$ of **PSCz** between neutral colorless and oxidized greenish-yellow states was found to be 44% at 427 nm. The PSCz film attained 90% of a complete blue coloring and bleaching in 7.3 and 1.5 s, respectively. The optical contrast measured as $\Delta \% T$ of PSCz between neutral colorless and oxidized blue states was found to be 61% at 762 nm. The electrochromic coloring efficiency (CE) for the greenish-yellow coloring ($\eta = \Delta OD_{427}/Q$) was estimated to be 122 cm² C⁻¹, and that for the blue coloring ($\eta = \Delta OD_{762}/Q$) of the **PSCz** film was estimated to be 45 cm² C^{-1} (Table 2).

Fig. S12 depicts the optical transmittance as a function of time, current densities monitored and the optical transmittance changes for the **PSO₂Cz** film at 425 and 747 nm by applying square-wave potential steps between 0 and 1.28 V for a resident time of 13 s and between 0 and 1.60 V for a resident time of 15 s. As shown in Fig. S13, the **PSO₂Cz** film attained 90% of a complete greenishyellow coloring and bleaching in 4.7 and 1.0 s, respectively. The optical contrast measured as $\Delta \% T$ of **PSO₂Cz** between neutral colorless and oxidized greenish-yellow states was found to be 39% at 425 nm. The PSO₂Cz film attained 90% of a complete green coloring and bleaching in 7.7 and 1.5 s, respectively. The optical contrast measured as $\Delta \% T$ of **PSO₂Cz** between neutral colorless and oxidized green states was found to be 53% at 747 nm. The electrochromic coloring efficiency (CE) for the greenish-yellow coloring $(\eta = \Delta OD_{425}/Q)$ was estimated to be 116 cm² C⁻¹, and that for the green coloring ($\eta = \Delta OD_{747}/Q$) of the **PSO₂Cz** film was estimated to be 38 cm² C^{-1} (Table 2).



Fig. 10. Electrochromic switching of PSCz (a) 427 nm and (b) 762 nm thin films on the ITO-coated glass substrate in 0.1 M Bu₄NClO₄/CH₃CN for 10 cycles.



Fig. 11. Current densities monitored and optical transmittance changes for polymer PSCz on the ITO-glass slide in 0.1 M Bu₄NCIO₄/CH₃CN while the potential was switched (a) between 0.0 V and 1.15 V at 427 nm with a pulse width of 13 s and (b) between 0.0 V and 1.43 V at 762 nm with a pulse width of 14 s.

3.7. Electrochromic device of PSCz

Using the schematic diagram illustrated in Fig. 12, a simple electrochromic sandwich cell using **PSCz** as the electroactive layer was constructed. The polymer film was electrodeposited onto ITO-coated glass and then dried. Afterwards, the gel electrolyte was spread on the polymer-deposited side of the electrode and the electrodes were sandwiched under atmospheric condition. To prevent leakage, an epoxy resin was applied to seal the device. The color changes of the electrochromic device upon oxidation are illustrated in Fig. 12. The polymer film is colorless in neutral form. When the voltage was increased (to a maximum of 3.20 V), the color changed to yellowish green and green due to electrooxidation. When the potential was subsequently set back at 0 V, the polymer film turned back to original colorless. We believe that optimization could further improve the device performance and fully explore the potential of these electrochromic polymers.

4. Conclusions

	Two	carbazole-endcapped	dibenzothiophene	and
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dibenzothiophene-S,S-dioxide monomers SCz and SO₂Cz were synthesized and used as the building blocks of fluorescent and electrochromic polymers via oxidative polymerization using FeCl₃ as catalyst or electrochemical polymerization onto the ITO/glass substrate. The polymeric thin films were successfully deposited onto the surface of the working electrode by repetitive cyclic voltammetry (CV) scanning of compounds SCz and SO₂Cz in Bu₄NClO₄/ CH₃CN solution between 0 and 1.8 V. However, the compounds **StBCz** and **SO₂tBCz** with *tert*-butyl groups attached on the reactive sites of the carbazole units did not give any polymer films on the electrode upon repetitive CV scanning, indicating the electrochemical polymerization occurred through the coupling reaction between the carbazole units at the 3- or 6-position. The electrochemically generated PSCz and PSO2Cz 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, blue and green oxidized forms. These properties make the prepared PSCz and **PSO₂Cz** films promising materials for electrochromic devices.

Table 2

Table 2			
Electrochromic	properties	of poly	ne

Polymer	$\lambda_{max}^{a}(nm)$	$\Delta \% T$	Response time ^b		ΔOD^c	Q_d^d (mC cm ⁻²)	$CE^{e} (cm^{2} C^{-1})$
			$t_{\rm c}({\rm s})$	$t_{\rm b}({\rm s})$			
PSCZ	427	44	5.5	1.3	0.280	2.29	122
	762	61	7.3	1.5	0.459	10.2	45
PSO ₂ CZ	425	39	4.7	1.0	0.320	2.74	116
	747	53	7.7	1.5	0.344	9.05	38

^a Wavelength of absorption maximum.

^b Time for 90% of the full-transmittance change.

^c Optical Density (ΔOD) = log[$T_{bleached}/T_{colored}$], where $T_{colored}$ and $T_{bleached}$ are the maximum transmittance in the oxidized and neutral states, respectively.

 d_{Q_d} is ejected charge, determined from the *in situ* experiments.

^e Coloration efficiency (CE) = $\Delta OD/Q_d$.



Fig. 12. (a) Photos of single-layer ITO-coated glass electrochromic device, using polymer PSCz as active layer. (b) Schematic diagram of polymer ECD sandwich cell.

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Appendix A. Supplementary data

Supplementary data related to this article can be found at http://dx.doi.org/10.1016/j.dyepig.2016.06.043.

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