

Electrosynthesis of Electrochromic Polymeric Films Based on Di(carbazol-9-yl)-substituted Carbazole and Triphenylamine Derivatives

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Abstract

Two carbazole end-capped monomers containing triphenylamine or *N*-phenylcarbazole as an interior core, namely 4,4'-di(carbazol-9-yl)-4'-methoxytriphenylamine (TPA-2Cz) and 3,6-di(carbazol-9-yl)-*N*-(4-methoxyphenyl)carbazole (PhCz-2Cz), were prepared by a well-known chemistry from readily available reagents. The electroactive polymeric films were built onto the ITO glass surface by using electrochemical polymerization process. The electrochemical and optical properties of the monomers and their polymers have been investigated. The electropolymerized films exhibited reversible electrochemical oxidation processes and strong color changes upon electro-oxidation, which can be switched by potential modulation. The remarkable electrochromic behavior of the film was clearly interpreted on the basis of spectroelectrochemical studies.

1. Introduction

Electrochromic materials have been studied for different technological applications,¹ such as anti-glare mirrors, smart windows, and electrochromic displays. Conjugated polymers stand for a family of important electrochromic materials that have recently received much attention due to their several advantages over inorganic compounds. These include high coloration efficiency, fast response speed, multiple colors with the same material, good processability, and fine-tunability of the band gap.² The conjugated polymers can be synthesized by either chemical or electrochemical polymerization. Compared with the chemical routes, electrochemical polymerization can obtain conjugated polymer films on conductive substrates directly. This not only enlarges the scope of candidate polymers, but also avoids the procedure of the film coating.

Carbazole and triarylamine derivatives are well-known for their electroactive and photoactive properties that may find optoelectronic applications as photoconductors, hole-transporters, and light-emitters.³ Carbazole can be substituted or polymerized either at the 3- and 6- positions or 2- and 7- positions and a wide variety of alkyl and aryl chains can be added on the nitrogen atom without altering the planar conformation of the resulting polymers.⁴ Using different synthetic strategies and substitution patterns, the physic-chemical properties of poly(3,6-carbazole)s and poly(2,7-carbazole)s can be fine-tuned, leading to high performance materials for a number electronic applications. As reported by Ambrose and co-workers in their pioneering work⁵ devoted to anodic oxidation of carbazole and various *N*-substituted carbazoles, ring-ring coupling is the predominant decay pathway, the carbazole radical cation yielding 3,3'-bicarbazyls. The resulting 3,3'-bicarbazyls

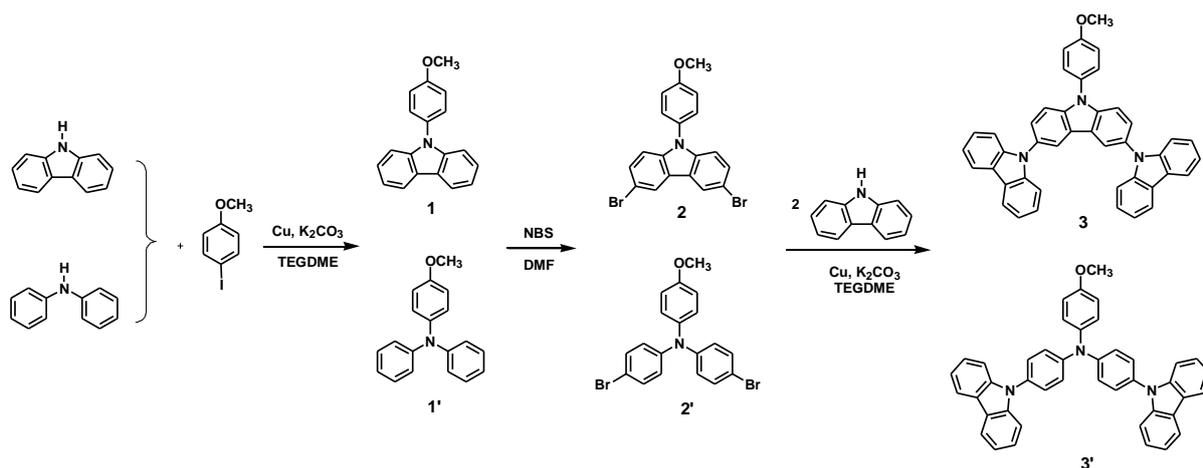
display two successive, reversible, one-electron redox steps to yield quinoid, green-coloured radical cation and blue dications, respectively. Although these bicarbazyls possess a lower first oxidation potential than the corresponding monomers and are therefore, potentially, more suitable for electrochemical polymerization, dimers were cleanly obtained in quantitative yields, due to the high stability of the oxidized states (bicarbazylum cations). Polymerization may occur anodically by using di-carbazoles, *N*-linked by suitable spacers, to produce materials with redox properties characteristic of bicarbazyls.

In recent years, carbazole derivatives have been widely used as effective host materials in phosphorescent light-emitting diodes because of their sufficiently high triplet energy and good hole-transporting ability.⁶ In addition, many condensation-type high-performance polymers (typically, aromatic polyamides and polyimides) carrying the triarylamine unit have been reported as potential electrochromic materials.⁷ However, there is little reports on the electrosynthesis and electrochromic properties of electroactive polymers from triphenylamine or *N*-phenylcarbazole containing carbazole derivatives. According to above considerations, in this work, two carbazole end-capped monomers containing triphenylamine or *N*-phenylcarbazole as an interior core are prepared, and their electrochemistry and electropolymerization are investigated. The electrochromic properties of the electrogenerated films are evaluated by the spectroelectrochemical and electrochromic switching studies.

2. Experimental section

2.1 Monomer synthesis

According to literature methods,^{6(a),8} The *N*-phenylcarbazole-centered dicarbazole PhCz-2Cz (**3**) and triphenylamine-centered dicarbazole TPA-2Cz (**3'**) were synthesized by a three-step reaction sequence (Scheme 1). The first step is to prepare *N*-(4-methoxyphenyl)carbazole (**1**) and 4-methoxytriphenylamine (**1'**) using an Ullmann C-N coupling reaction between 4-iodoanisole with carbazole and diphenylamine, respectively. In the second step, dibromo compounds **2** and **2'** were prepared by bromination of **1** and **1'** by using *N*-bromosuccinimide (NBS) in DMF. The target compounds **3** and **3'** were obtained using the Ullmann coupling again between the carbazole and dibromo compounds **2** and **2'**, respectively. Monomers **3** and **3'** were finally purified by column chromatography. The structures of all the synthesized compounds were confirmed by IR and NMR analyses. Figure 1 illustrates the ¹H NMR spectra of monomers **3** and **3'**. These spectra verify the structures and purity of these two monomers.



Scheme 1. Synthesis of PhCz-2Cz (**3**) and TPA-2Cz (**3'**).

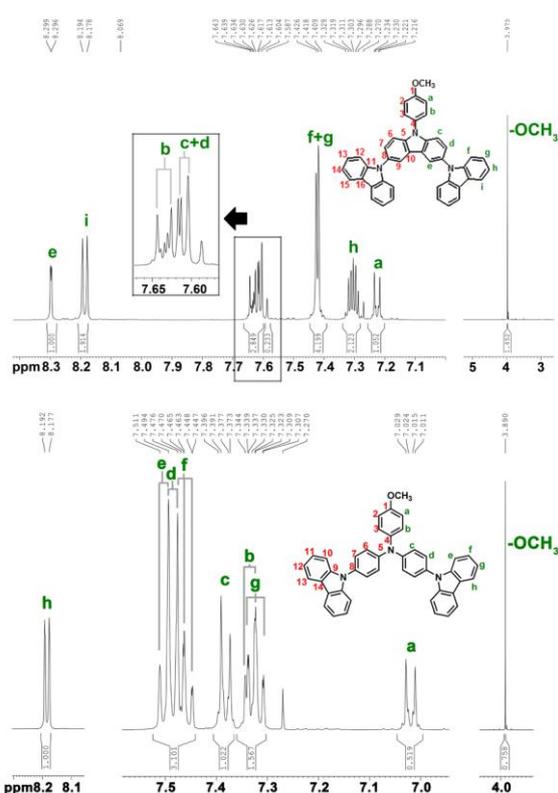


Figure 1. ^1H NMR spectra of PhCz-2Cz (**3**) and TPA-2Cz (**3'**) in CDCl_3 .

2.2 Electrochemical polymerization

Electrochemical polymerization was performed with a CHI 750A Electrochemical Analyzer. The polymers were synthesized from 10^{-4} M monomers and 0.1 M Bu_4NClO_4 in acetonitrile (MeCN) solution via repetitive cyclic voltammetry (CV) between 0 and 1.5 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.

3. Results and discussion

3.1 Electrochemical polymerization

Figure 2(a) and Figure 3(a) display the first and second CV curves of PhCz-2Cz (**3**) and TPA-2Cz (**3'**), respectively.

The first oxidation peak potential ($E_{\text{pa}}^{\text{Ox1}}$) of PhCz-2Cz in the solution is 1.19 V, while that of TPA-2Cz is 0.97 V. The first oxidation process of these two compounds can be assigned to the oxidation of the methoxy-substituted *N*-phenylcarbazole and triphenylamine unit. The higher oxidation potential of the former can be attributed to the fact that the lone pair electrons of the nitrogen atom of a Cz prefer to localize within the coplanar ring, making the oxidation potentials of Cz derivatives normally independent of the nature of the N9 substituent. For the first positive potential scan of TPA-2Cz (Fig. 3a), we observed another strong oxidation peak at about 1.56 V, which can be attributable to the oxidation of terminal Cz units. From the first reverse negative potential scan, we detected three cathodic peaks. After the second scan, a new oxidation peak appeared at 1.29 V. In addition, when the potential was continuously cycled, we observed a progressive growth in all peak currents (Fig. 3b). This behavior suggests that the oxidative coupling of the radical cations of TPA-2Cz produced a continuous buildup of an electroactive and conductive layer on the electrode. Therefore, we attribute the electrochemical processes observed at 1.56 V to the generation of Cz radical cations, which subsequently dimerize to form 3,3'-bicarbazyl moieties.

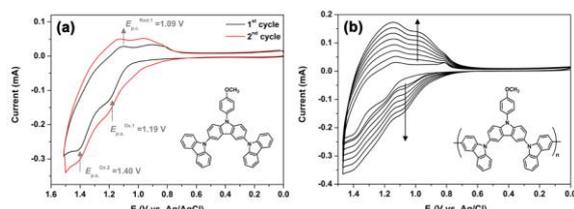


Figure 2. (a) The first and second CV curves and (b) the first ten repeated CV scans of PhCz-2Cz (**3**) with a scan rate of 50 mV/s in 0.1 M $\text{Bu}_4\text{NClO}_4/\text{MeCN}$ solution.

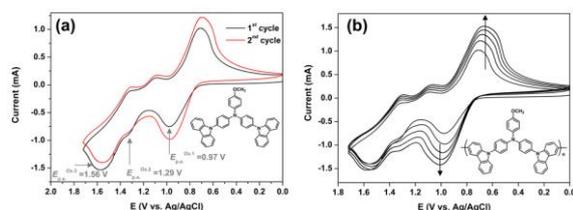


Figure 3. (a) The first and second CV curves and (b) the first ten repeated CV scans of TPA-2Cz (**3'**) with a scan rate of 50 mV/s in 0.1 M $\text{Bu}_4\text{NClO}_4/\text{MeCN}$ solution.

Table 1. Optical and Electrochemical Properties of the Electrosynthesized Polymers

Polymer	UV-vis Absorption (nm) ^a		Oxidation Potential (V) ^b			Optical Bandgap (eV) ^c	HOMO (eV) ^d		LUMO (eV) ^e	
	λ_{\max}	λ_{onset}	Monomer		Polymer		E_{onset}	$E_{1/2}$	E_{onset}	$E_{1/2}$
			$E_{\text{peak}}^{\text{Ox}}$			$E_{\text{g}}^{\text{opt}}$				
Poly-3	309	450	1.19, 1.40	0.88	1.03, 1.23	2.76	5.24	5.39	2.48	2.63
Poly-3'	346	554	0.97, 1.29	0.72	0.85, 1.15	2.24	5.08	5.21	2.84	2.97

^a UV-vis absorption maximum and onset for the polymer films. ^b Calculated from first CV scans, versus Ag/AgCl in acetonitrile at a scan rate of 50 mV/s. ^c Band gaps calculated from absorption edge of the polymer films: Energy gap = $1240/\lambda_{\text{onset}}$. ^d The HOMO energy levels were calculated from $E_{1/2}$ or E_{onset} values of CV curves and were referenced to ferrocene (4.8 eV relative to the vacuum energy level). ^e LUMO = HOMO- E_{g} .

3.2 Electrochemical properties of the polymer films

The electrochemical behavior of the electrodeposited polymer films was investigated by cyclic voltammetry in a monomer-free $\text{Bu}_4\text{NClO}_4/\text{CH}_3\text{CN}$ solution. The quantitative details are summarized in Table 1. There are two reversible oxidation redox couples for **Poly-3**, and three reversible oxidation redox couples for **Poly-3'**, respectively. In comparison, **Poly-3'** exhibited lower first oxidation potentials than the corresponding **Poly-3**. This could be attributed to the fact that the methoxy-substituted triphenylamine center of the **Poly-3'** ($E_{\text{p,a}} = 0.98$ V) is easier to oxidize than *N*-(4-methoxyphenyl)carbazole unit of **Poly-3** ($E_{\text{p,a}} = 1.07$ V). As shown in Scheme 2, these two polymer films showed two reversible redox couples attributed to the radical cation and dication states of biscarbazole, respectively.

The redox potentials of the polymers as well as their respective highest occupied molecular orbital (HOMO) and lowest unoccupied molecular orbital (LUMO) (versus vacuum) are calculated and summarized in Table 1. The HOMO level or called ionization potentials (versus vacuum) of **Poly-3** and **Poly-3'** could be estimated from the onset of their oxidation in CV experiments as 5.08-5.24 eV (on the basis that ferrocene/ferrocenium is 4.8 eV below the vacuum level with $E_{\text{onset}} = 0.36$ V).

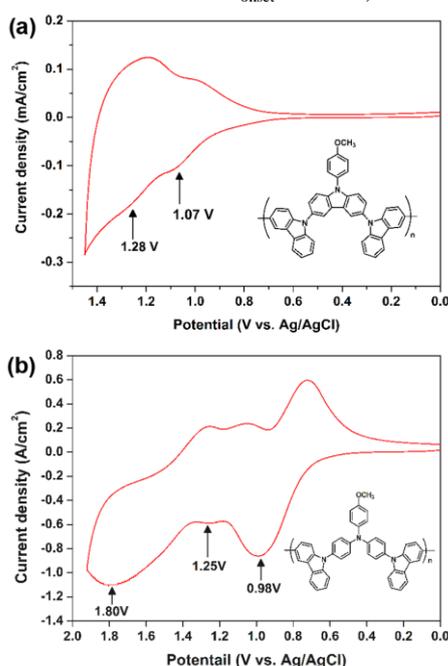


Figure 4. Cyclic voltammograms of the polymer films on the ITO-coated glass slide in 0.1 M $\text{Bu}_4\text{NClO}_4/\text{MeCN}$ solution at scan rate of 50 mV/s.

For the scan rate dependence experiments, the working electrode (ITO-glass) coated by **Poly-3** film was immersed into the monomer free electrolyte solution of 0.1 M $\text{Bu}_4\text{NClO}_4/\text{MeCN}$ solution and then cycled between oxidized and neutral states at various scan rates (Fig. 5). As can be seen in Figure 5, the current response rises as the scan rate increases and this behavior strongly indicates that the polymer film is electroactive and well adhered to the surface of the working electrode.⁹ The oxidation and reduction peak currents show a linear dependence as a function of scan rate as shown in Figure 5. This linearity indicates that the redox processes are reversible and nondiffusional.

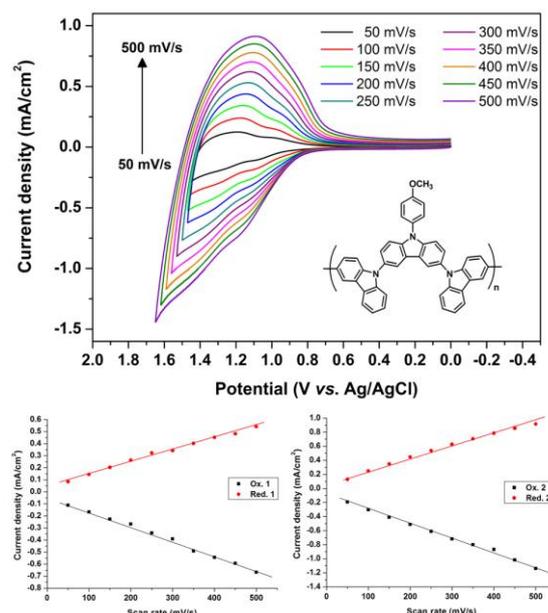


Figure 5. Scan rate dependence of **Poly-3** film on the ITO-coated glass slide in CH_3CN containing 0.1 M Bu_4NClO_4 at different scan rates between 50 and 500 mV/s.

3.3 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. We use **Poly-3** as an example to explain the spectroelectrochemical behavior (Figure 6). In the neutral form, **Poly-3** exhibited strong absorption at 308 nm, characteristic $\pi-\pi^*$ transitions of the biscarbazole, but it was almost transparent in the visible and near-IR regions. The optical band gap of **Poly-3** was estimated to be 2.76 eV from the onset of the $\pi-\pi^*$ transition at 450 nm. Upon incremental oxidative scans from 0.0 to 1.16 V, the valence

conduction band at 434 nm is initially intensified and a broadband that extended to the near-IR range, which we assigned to the formation of biscarbazole radical cations. The absorption band in the near-IR region may be attributed to an intervalance charge transfer (IVCT)¹⁰ between states in which the positive charge is centered at different amino centers (biscarbazole). Upon further oxidation at applied potential to 2.0 V, the dication (bipolaron) band at 741 nm appeared, and the absorption at 434 nm decreased in intensity. The observed spectral changes of the **Poly-3** film were fully reversible upon varying the applied potential. In addition, they were associated with significant color changes (from colorless to yellow, and to green) that were homogeneous across the ITO glass and easy to detect with the naked eye.

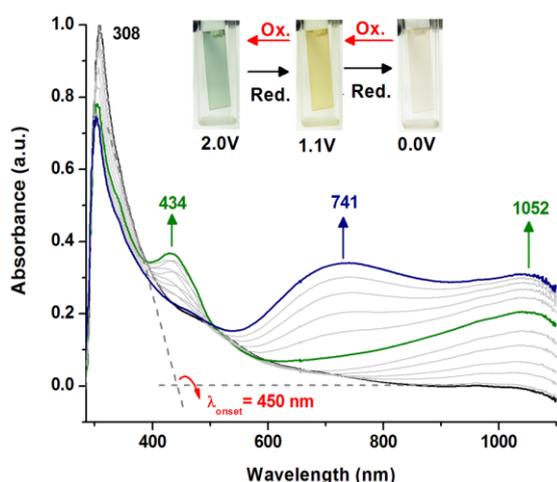


Figure 6. Spectroelectrochemistry of **Poly-3** thin films on the ITO-coated glass substrate in 0.1 M $\text{Bu}_4\text{NClO}_4/\text{MeCN}$ solution at various applied potentials (vs Ag/AgCl). The insets show the color changes of the polymer films at indicated electrode potentials..

4. Conclusions

Two carbazole-endcapped monomers containing triphenylamine or *N*-phenylcarbazole as an interior core were successfully synthesized. Polymer films with biscarbazole groups were successfully electrodeposited onto the ITO electrode surface by electropolymerization of the monomers in $\text{Bu}_4\text{NClO}_4/\text{CH}_3\text{CN}$. 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 yellow and green oxidized forms. These properties make the prepared polymer films good candidates for electrochromic applications.

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