

# Enhancement on Redox-Stability and Electrochromic Performance of Aromatic Polyamides by Incorporating with 3,6-Dimethoxycarbazolyl-substituted Triphenylamine Units

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## Abstract

New series aromatic polyamides with main-chain triphenylamine and pendent 3,6-dimethoxycarbazole units were synthesized from 4,4'-diamino-4''-(3,6-dimethoxycarbazol-9-yl)triphenylamine and various aromatic dicarboxylic acids via the phosphorylation polyamidation technique. These polyamides were amorphous with good solubility in many organic solvents and could be solution-cast into flexible and strong films. They showed well-defined and reversible redox couples during oxidative scanning, with a strong color change from colorless neutral form to green and blue oxidized forms at applied potentials scanning from 0.0 to 1.3 V. They exhibited enhanced redox-stability and electrochromic performance as compared to the corresponding analogs without methoxy substituents on the active sites of the carbazole unit.

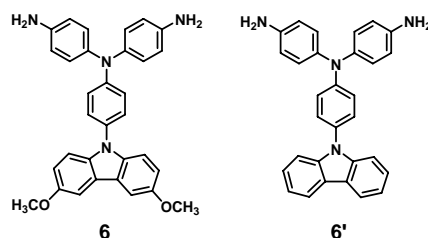
## 1. Introduction

Electrochromism refers to the reversible electromagnetic absorbance/transmittance and color change resulting from the oxidation or the reduction of the material in response to an externally applied potential by electrochemical means.<sup>1</sup> One of the main uses of electrochromic materials is in smart windows for cars and buildings and in antiglare rear-view mirrors. Potential applications in information storage, electrochromic displays, and adaptive camouflages can also be envisioned. Among the different types of electrochromic materials, conjugated polymers such as polyanilines, polypyrroles, polyselenophenes, polythiophenes, and in particular, poly(3,4-ethylenedioxythiophene) (PEDOT) and its derivatives attract increasing interest because of mechanical flexibility, ease in band-gap/color-tuning via structural control, and the potential for low-cost processing for large-area devices. For efficient operation of an electrochromic device, it is necessary to take a number of properties into consideration: electrochromic efficiency, optical contrast, response time, stability and durability.<sup>2</sup> The difficulty in achieving satisfactory values for all these parameters at the same time stimulates the development of new methods of preparation of electrochromic films, new materials and components for the devices.

Triarylamine derivatives are well known as its photo- and electroactive properties have potential for optoelectronic applications, such as photoconductors, hole-transporters, light-emitters, and memory devices. Electron-rich triarylamines can be easily oxidized to form stable radical cations, and the oxidation process is always associated with a noticeable change of coloration. Thus, studies of the synthesis and electrochromism of triarylamine-based polymers have been reported in the literature.<sup>3</sup> Since 2005, Liou's and our groups have initiated the studies on high-performance polymers (e.g., aromatic polyamides and polyimides) bearing the triarylamine unit as an electrochromic functional moiety.<sup>4</sup> It has also been reported in our previous publications<sup>5</sup> that the incorporation of electron-donating substituents such as methoxy and *tert*-butyl groups at the *para*-position of phenyl groups on the electrochemically active sites of the triphenylamine (TPA) unit resulted in stable TPA cationic radicals and decreased oxidation potential, leading to a significant enhancement on redox and electrochromic stability of the prepared polyamides.

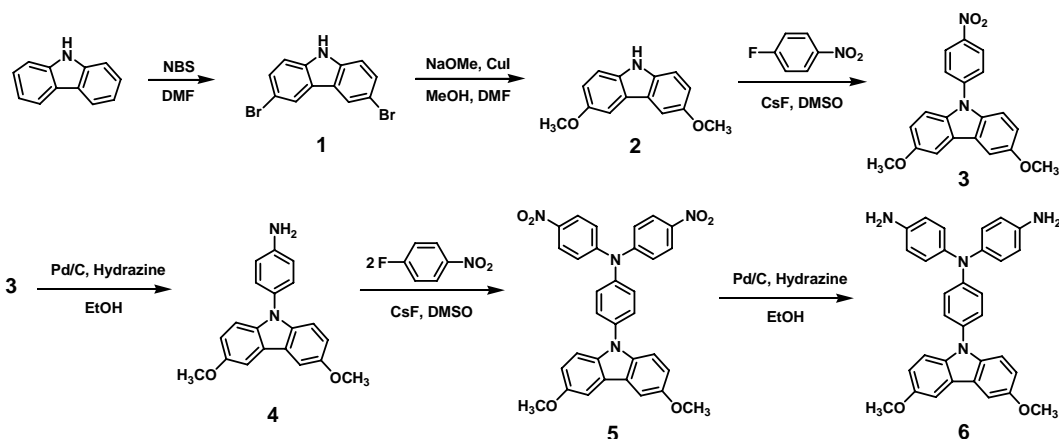
Carbazole is also a well-known hole-transporting and light-emitting unit. Carbazole could be easily functionalized at its

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 pending groups.<sup>6</sup> Polymers containing carbazole moieties in the main chain or side chain have attracted much attention because of their unique properties, which allow various optoelectronic applications such as photoconductive, electroluminescent, electrochromic and photorefractive materials. We recently reported on the polyamides bearing main-chain TPA and pendent carbazole units from the diamine monomer 4,4'-diamino-4''-(carbazol-9-yl)triphenylamine (**6'**).<sup>7</sup> They also reveal good redox stability for the first oxidation state, and the oxidation process is always associated with a noticeable change of the coloration. However, the second oxidation process of these polymers is not reversible, possibly due to the electrochemical coupling of carbazoles through the active C-3 and C-6 sites. Therefore, we synthesized the diamine monomer, 4,4'-diamino-4''-(3,6-dimethoxycarbazol-9-yl)triphenylamine (**6**), and its derived aromatic polyamides with main-chain electroactive TPA units and electron-donating methoxy groups substituted on the C-3 and C-6 positions of pendent carbazole units. The incorporation of electron-donating methoxy substituents is expected to not only reduce the oxidation potential associated with increased electrochemical and electrochromic stability of the result polyamides. For a comparative study, some properties of the present polyamides will be compared with those of structurally related ones based on the previously reported diamine monomer **6'**.

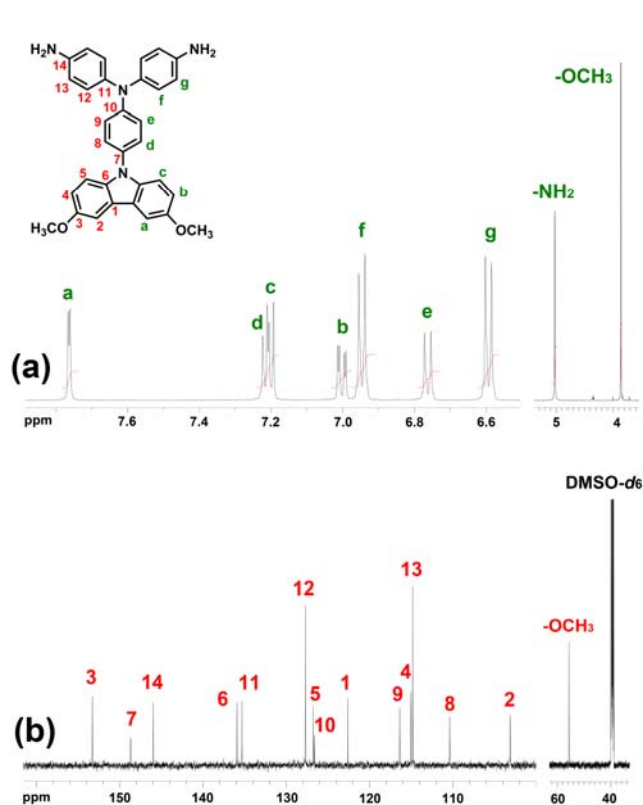


## 2. Monomer synthesis

The new aromatic diamine monomer **6** was synthesized starting from carbazole by a reaction sequence as shown in Scheme 1. First, bromination of carbazole with *N*-bromosuccinimide (NBS) gave 3,6-dibromocarbazole (**1**). Following a procedure published by Kikugawa et. al,<sup>8</sup> synthesis of 3,6-dimethoxycarbazole (**2**) was achieved by direct methoxide displacement of bromine from **1** by using MeONa and CuI in DMF. The intermediate compound, 3,6-dimethoxy-9-(4-nitrophenyl)carbazole (**3**), was synthesized by nucleophilic aromatic fluoro-displacement reaction of *p*-fluoronitrobenzene with compound **2** in the presence of cesium fluoride (CsF). Reduction of the nitro group of compound **3** by means of hydrazine and Pd/C gave 3,6-dimethoxy-9-(4-aminophenyl)carbazole (**4**). The target diamine monomer **6** was prepared by hydrazine Pd/C-catalyzed reduction of dinitro compound **5** resulting from the CsF-assisted *N,N*-diarylation reaction of compound **4** with two equivalent amount of *p*-fluoronitrobenzene. Figure 1 illustrates the <sup>1</sup>H NMR and <sup>13</sup>C NMR spectra of the diamine monomer **6**. These spectra are in good agreement with the proposed molecular structure of **6**.



**Scheme 1.** Synthetic route to target diamine monomer **6**.



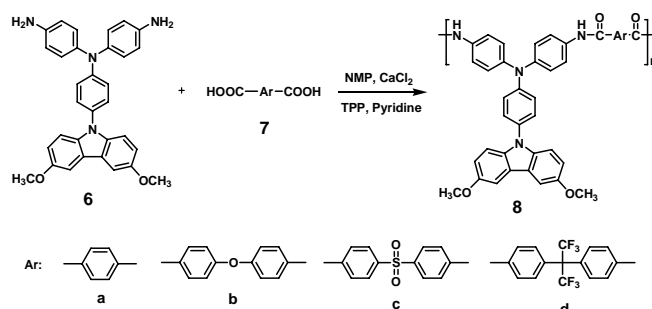
**Figure 1.** (a)  $^1\text{H}$  NMR and (b)  $^{13}\text{C}$  NMR spectra of diamine monomer **6** in  $\text{DMSO-}d_6$ .

### 3. Polymer synthesis

According to the phosphorylation polyamidation technique described by Yamazaki and coworkers,<sup>9</sup> a series of novel polyamides (**8a-8d**) with 3,6-dimethoxycarbazoyl-substituted TPA units were synthesized from the diamine **6** and various dicarboxylic acids **7a-7d** using triphenyl phosphite (TPP) and pyridine as condensing agents (Scheme 2). The obtained polyamides had inherent viscosities in the range of 0.52–0.57 dL/g and could be solution-cast into flexible and tough films, indicating high molecular weight polymers.

### 4. Solubility and film property

The solubility behavior of polyamides was tested qualitatively, and the results are summarized in Table 1. All the polyamides were highly soluble in polar solvents such as NMP, DMAc, DMF, and DMSO, and the high solubility could be attributed to the introduction of bulky, packing-disruptive 3,6-dimethoxycarbazoyl-substituted triphenylamino unit into the repeat unit. Thus, the excellent solubility makes these polymers potential candidates for practical applications by spin-coating or inkjet-printing processes to afford high performance thin films for optoelectronic devices.



**Scheme 2.** Synthesis of polyamides **8a-8d**.

**Table 1.** Inherent viscosity and Solubility Properties of Polyamides

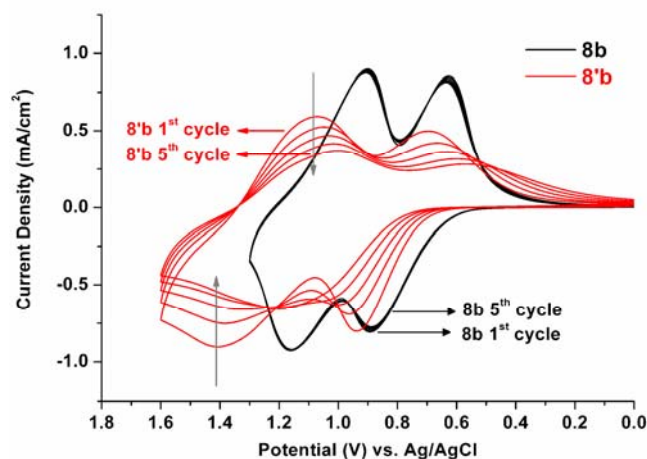
| Code      | $\eta_{\text{inh}}^a$<br>(dL/g) | Solubility in Various Solvents <sup>b</sup> |      |     |      |                  |     |
|-----------|---------------------------------|---|------|-----|------|------------------|-----|
|           |                                 | NMP   | DMAc | DMF | DMSO | <i>m</i> -cresol | THF |
| <b>8a</b> | 0.57                            | ++  | ++   | ++  | ++   | +                | +–  |
| <b>8b</b> | 0.52                            | ++  | ++   | ++  | ++   | +–               | +–  |
| <b>8c</b> | 0.54                            | ++  | ++   | ++  | ++   | +                | +–  |
| <b>8d</b> | 0.56                            | ++  | ++   | ++  | ++   | +                | ++  |

<sup>a</sup> Measured at a polymer concentration of 0.5 g/dL in DMAc-5 wt % LiCl at 30 °C.

<sup>b</sup> The qualitative solubility was tested with 10 mg of a sample in 1 mL of stirred solvent. Notation: ++, soluble at room temperature; +: soluble on heating; + –: partially soluble.

### 5. Electrochemical properties

The electrochemical behavior of the polyamides was investigated by cyclic voltammetry (CV) conducted for the cast film on an ITO-coated glass substrate as working electrode in dry acetonitrile ( $\text{CH}_3\text{CN}$ ) containing 0.1 M of  $\text{Bu}_4\text{NClO}_4$  as an electrolyte under nitrogen atmosphere. The derived oxidation potentials are summarized in Table 2. The representative cyclic voltammograms for polyamides **8b** (with methoxy substituents on the active sites of the carbazole unit) and **8'b** (without the methoxy substituents on its carbazole unit) are illustrated in Figure 2 for comparison. There are two reversible oxidation redox couples with half-wave potentials ( $E_{1/2}$ ) of 0.76 V and 1.04 V for polyamide **8b** and 0.83 and 1.26 V for polyamide **8'b**, respectively. We found that polyamide **8b** is more easily being oxidized than its analogous polyamide **8'b**. Polyamide **8b** also preserved good electroactivity after 5 repetitive scans between 0.0 and 1.3 V at a scan rate of 50 mV/s. In contrast, the corresponding polyamide **8'b** without the methoxy groups on its carbazole unit rapidly lost redox reversibility in five cycles. Thus, the introduction of electron-donating methoxy group not only greatly prevents the coupling reaction but also slightly lowers the oxidation potentials of the present polyamides. According to these results, mechanisms of oxidation reactions for polyamides **8b** and **8'b** are proposed in Scheme 3. For polyamide **8b**, the two oxidation processes observed correspond to successive one electron removal from the TPA and carbazole moieties. These processes are highly reversible due to

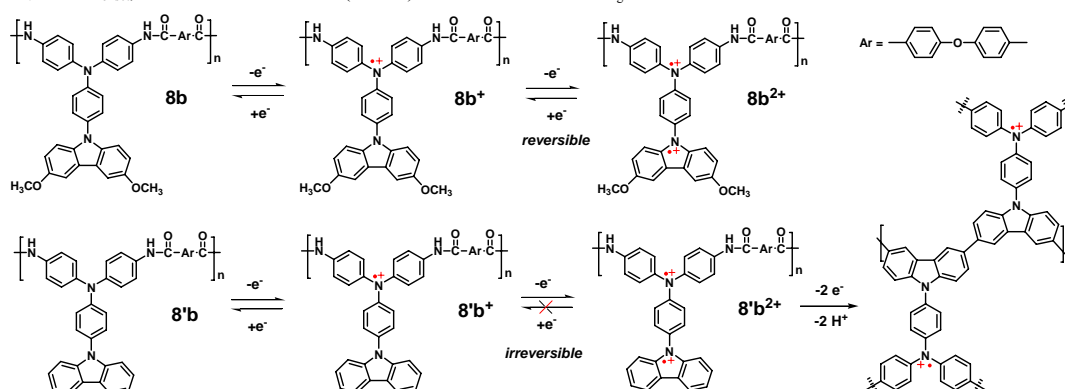


**Figure 2.** Repeated CV diagrams of polyamide **8b** and **8'b** films on the ITO-coated glass substrate in 0.1 M Bu<sub>4</sub>NClO<sub>4</sub>/CH<sub>3</sub>CN at a scan rate of 50 mV/s.

**Table 2.** Redox Potentials and Energy Levels of Polyamides

| Polymer code | thin films (nm) |                   | Oxidation (V) <sup>a</sup> (vs. Ag/AgCl in CH <sub>3</sub> CN) |                 |                 | $E_g^b$ (eV) | HOMO <sup>c</sup> (eV) |                 | LUMO <sup>d</sup> (eV) |                 |
|--------------|-----------------|-------------------|--|-----------------|-----------------|--------------|------------------------|-----------------|------------------------|-----------------|
|              | $\lambda_{max}$ | $\lambda_{onset}$ | $E_{onset}$  | $E_{1/2}^{Ox1}$ | $E_{1/2}^{Ox2}$ |              | $E_{onset}$            | $E_{1/2}^{Ox1}$ | $E_{onset}$            | $E_{1/2}^{Ox1}$ |
| <b>8a</b>    | 312             | 429               | 0.64   | 0.76            | 1.04            | 2.89         | 5.00                   | 5.12            | 2.11                   | 2.23            |
| <b>8b</b>    | 312             | 400               | 0.65   | 0.76            | 1.04            | 3.10         | 5.01                   | 5.12            | 1.91                   | 2.02            |
| <b>8c</b>    | 313             | 466               | 0.65   | 0.77            | 1.05            | 2.72         | 5.01                   | 5.13            | 2.29                   | 2.41            |
| <b>8d</b>    | 312             | 406               | 0.66   | 0.78            | 1.06            | 3.05         | 5.02                   | 5.14            | 1.97                   | 2.09            |
| <b>8'b</b>   | 340             | 400               | 0.76   | 0.83            | 1.26            | 3.10         | 5.12                   | 5.19            | 2.02                   | 2.09            |

<sup>a</sup> Oxidation potentials from cyclic voltammograms (vs. Ag/AgCl in CH<sub>3</sub>CN). <sup>b</sup> Energy gap =  $1240/\lambda_{onset}$  of the polymer film. <sup>c</sup> The HOMO energy levels were calculated from  $E_{1/2}^{Ox1}$  or  $E_{onset}$ , referenced to ferrocene (4.8 eV). <sup>d</sup> LUMO = HOMO -  $E_g$ .



**Scheme 3.** The anodic oxidation pathways of polyamides **8b** and **8'b**.

## 6. Spectroelectrochemical and electrochromic properties

Spectroelectrochemical measurements were performed on films of polymers drop-coated onto ITO-coated glass slides immersed in electrolyte solution. The electrode preparations and solution conditions were identical to those used in the CV experiments. **Figure 3a** presents the UV-vis-NIR absorption spectra of polyamide **8b** film at various applied potentials. In the neutral form, polyamide **8b** exhibited strong absorptions at 312 and 343 nm, characteristic for  $\pi$ - $\pi^*$  transitions, but it was almost transparent in the visible and NIR regions. The band gap of polyamide **8b** was estimated to be 3.10 eV from the onset of the  $\pi$ - $\pi^*$  transition at 400 nm. Upon applying potentials near the  $E_{pa}^1$  of **8b**, the absorption of  $\pi$ - $\pi^*$  transition decreased while a new absorption peak at 424 nm grew up and a broad absorption centered at 800 nm in the visible region together with a broad band from 900 nm extending into the NIR region beyond 1100 nm gradually increased in intensity. Since the potentials examined are similar to the first anodic process, the spectral changes are assigned to the radical cation (polaron) formation arising from the oxidation of TPA unit. The absorption band in the NIR region may be attributed to an intervalence charge transfer (IVCT) between states in which the positive charge is centered at different amino centers (TPA and carbazole). Upon

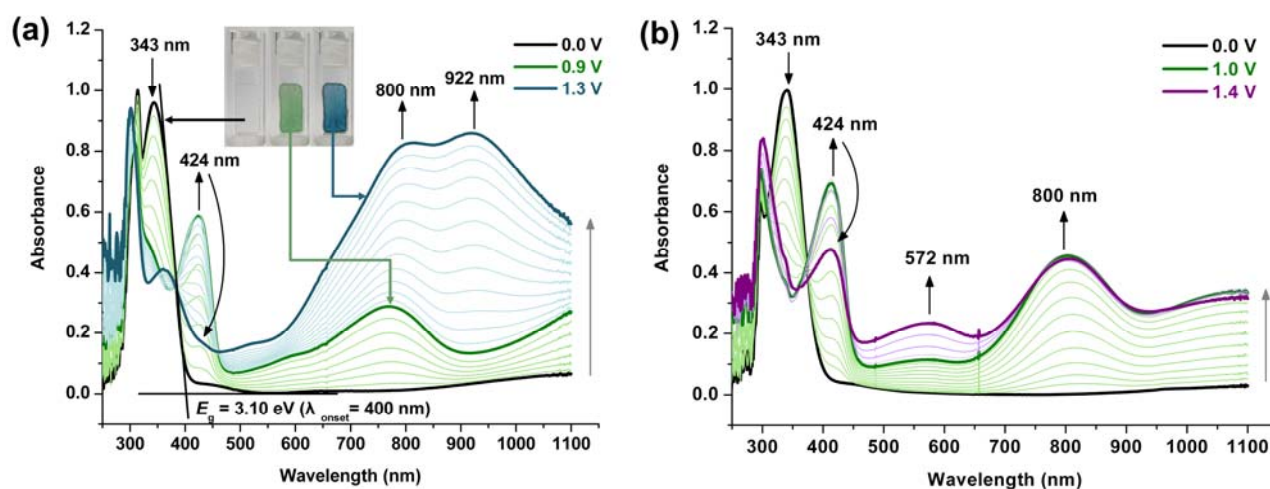
blockage of electrochemically active sites of the carbazole moiety with electron-donating methoxy group. As reported by Ambrose and co-workers in their pioneering work<sup>10</sup> devoted to anodic oxidation of carbazole and various *N*-substituted derivatives, ring-ring coupling is the predominant decay pathway. One possible coupling reaction of carbazylum radical cations to biscarbazylum dications shown in **Scheme 3** can be used to explain the irreversible oxidation process occurring in polyamide **8'b**.

The HOMO (highest occupied molecular orbital) energy levels of the investigated polyamides were calculated from the oxidation onset potentials ( $E_{onset}$ ) or half-wave potentials of the first oxidation wave ( $E_{1/2}^{Ox1}$ ) and by comparison with ferrocene (4.8 eV). These data together with absorption spectra were then used to obtain the LUMO (lowest unoccupied molecular orbital) energy levels (**Table 2**). According to the HOMO and LUMO energy levels obtained, the polyamide in this study appear to be appropriate as hole injection and transport materials.

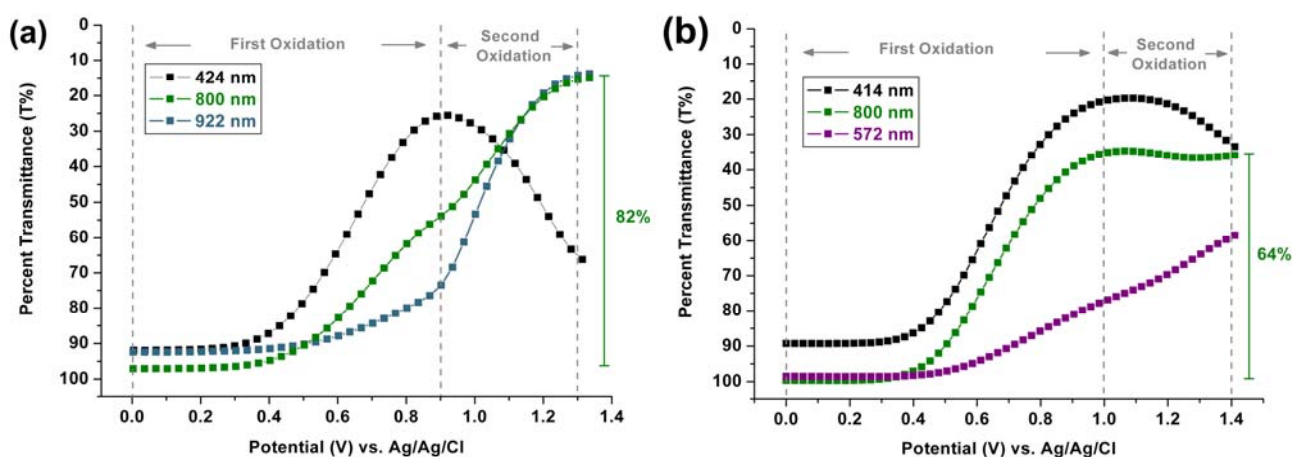
further oxidation at applied voltages to 1.3 V, the intensity of the absorption peak at 424 nm gradually decreased while the absorption peak at 800 nm gradually increased in intensity with a formation of a new strong absorption band centered at about 922 nm. The observed electronic absorption changes in the film of **8b** at various potentials are fully reversible and are associated with strong color changes; indeed, they even can be seen readily by the naked eye. As shown in **Figure 3a** inset, it can be seen that the film of polyamide **8b** switches from a transmissive neutral state (nearly colorless) to a highly absorbing semi-oxidized state (green) and a fully oxidized state (blue). For comparison, the spectroelectrochemical series of polyamide **8'b** was shown in **Figure 3b**. The change of % transmittance for the absorption maxima of polyamides **8b** and **8'b** at various applied electrode potentials are depicted in **Figure 4**. It can be seen that polymer **8b** revealed a higher optical contrast (82%) than the referenced polymer **8'b** (64%) without the methoxy substituents on the carbazole unit at 800 nm when the applied potential was set at 1.3~1.4 V. This result may be explained by the irreversible second oxidation process associated with polyamide **8'b**. Therefore, the introduction of the methoxy group at the active sites of the carbazole unit not only enhances the redox stability but also



improve the electrochromic contrast of these polymers.



**Figure 3.** Spectral changes of the cast films of (a) polyamide **8b** and (b) polyamide **8'b** on an ITO-coated glass in 0.1 M  $\text{Bu}_4\text{NClO}_4/\text{CH}_3\text{CN}$  at various applied potentials (vs Ag/AgCl). The insets show the color changes of the polymer films at indicated electrode potentials



**Figure 4.** Optical change in %T as a function of applied potential for the cast films of (a) polyamide **8b** and (b) polyamide **8'b** on an ITO-coated glass.

## 7. Conclusions

A series of novel carbazole and triphenylamine-functionalized aromatic polyamides were readily prepared from the newly synthesized aromatic diamine monomer 4,4'-diamino-4''-(3,6-dimethoxycarbazol-9-yl)triphenylamine with various aromatic dicarboxylic acids via the phosphorylation polyamidation reaction. Because of the introduction of three-dimensional triphenylamine units and bulky 3,6-dimethoxycarbazole pendent groups in polymer backbone, all the polymers were amorphous, had good solubility in many polar aprotic solvents, and exhibited excellent film-forming ability. All the obtained polyamides revealed good electrochemical and electrochromic stability along with multi-electrochromic behavior. By substitution of the electrochemically active C-3 and C-6 sites of the carbazole unit with electron-donating methoxy groups, the new polyamides exhibit greatly enhanced electrochemical stability and electrochromic performance in comparison with previously reported analogs without methoxy substituents on the carbazole moiety. Such prominent features make these processable polymers amenable for optoelectronic applications such as OLEDs and electrochromic devices.

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