

Novel electroactive polyamides containing bis(diphenylamine)-fluorene units with highly stable electrochromic and electrofluorescent properties

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Abstract

Two kinds of electroactive polyamides with bis(diphenylamine)-fluorene units acting as electroactive fluorophores were prepared via a condensation polymerization from a novel diamine, *N,N'*-Bis(4-aminophenyl)-*N,N'*-bis(4-methoxyphenyl)-2,7-diamine-9,9-dimethylfluorene, with two dicarboxylic acids. Cyclic voltammograms of the polyamide films revealed two reversible redox couples with half-wave potentials at 0.54-0.56 and 0.75-0.78 V, respectively. The polyamide films showed excellent reversible stability of multicolor electrochromic characteristics (colorless-red-blue) after over 1000 cyclic switches. The polyamide derived from cycloaliphatic dicarboxylic acids exhibited strong fluorescence with quantum yield up to 50.2%. Furthermore, the fluorescence could be reversibly modulated by electrochemical redox with superior stability and a high contrast ratio of 152.

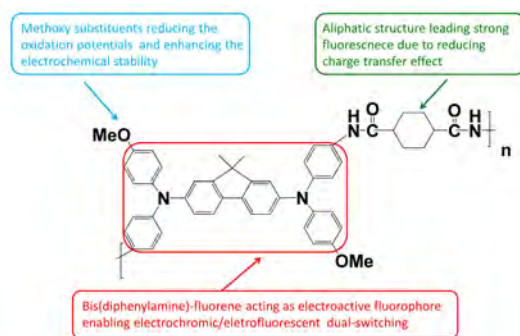
Introduction

Recently, stimuli-responsive fluorescence materials have attracted great interest owing to their promising applications in bio-analysis, sensors and displays [1-3]. Specifically, fluorescence materials modulated by electrical triggers are receiving more and more attentions as the electrical stimuli could be applied reversibly, rapidly and remotely. While the electrofluorescent materials still remain at the laboratory research stage, the electrochromic materials have been successfully commercialized in the fields of smart windows and displays [4-5]. Definitely, electrochromic materials exhibit reversible changes in absorption upon electrochemical oxidation and reduction. Thus, the electrochromic-displays greatly rely on a back light when used in dark conditions. To achieve high visibility in either bright or dark environment, dual-mode displays with both tunable coloration and emission will be promising candidates, and these novel displays could be obtained by combining electrochromic and electrofluorescent technologies. Up to now, a few examples of dual-switching materials have been reported [6-7]. However, most of the emerged materials usually lack long-term stability, rapid response time and high-contrast of optical response. For better satisfaction of the future applications, more appropriate materials with dual-switching of both coloration and emission need to be further exploited.

4-methoxy triphenylamine derivatives exhibited lower oxidation potential and superiorly stable electroactivity, which could act as an effective modulator in electro-switching system [8]. While the photoluminescence of triphenylamine is poor, fluorene-triphenylamine derivatives exhibit strong fluorescence [9]. Thus, fluorophores consist of triphenylamine and fluorene are promising candidates for dual-switching coloration/emission materials.

In this contribution, we herein described a new diamine monomer, *N,N'*-bis(4-aminophenyl)-*N,N'*-bis(4-methoxyphenyl)-2,7-diamine-9,9-dimethylfluorene, and its facile incorporation into polymer backbones, yielding two polyamides. Introducing electro-donating methoxy substituents is expected to reduce the oxidation potential associated with enhanced electrochemical stability of the resulting polyamides. We anticipate that the semi-aromatic polyamide will exhibit electrochromic/electrofluorescent

dual-switching properties with low trigger voltage and high stability.



Results and discussion

Monomer and polyamide synthesis

As shown in Scheme 1, the new diamine 3 bearing bis(diphenylamine)-fluorene group was synthesized via a multistep route. 4-Methoxyaniline, on reaction with 4-fluoronitrobenzene yielded 2,7-dibromo-9,9-dimethylfluorene. The diamine 3 was successfully synthesized by Pd/C-catalyzed reduction of the dinitro 2 resulting from the Ullmann reaction of 2,7-dibromo-9,9-dimethylfluorene and 4-methoxy-4'-nitrodiphenylamine. Two kinds of polyamides were prepared from the diamine 3 with two different dicarboxylic acids through the phosphorylation technique (Scheme 2).

Scheme 1 Synthetic route to the diamine 3.

Scheme 2 Synthesis of the polyamides with bis(diphenylamine)-fluorene units.

Optical and electrochemical properties

The optical and electrochemical properties of these polyamides were investigated by UV-vis, PL spectroscopy and CV, with the results summarized in Table 2. The absorption maxima of these polyamides are located at 389-391 nm for NMP solutions and 370-378 nm in solid films, respectively, which are ascribed to the π - π^* transition of bis(diphenylamine)-fluorene moieties. As shown in Fig. 3, these polyamides in NMP solutions exhibited fluorescence emission maxima at 442-505 nm with Φ_{FS} ranging from 1.9 to 50.2. It is interesting to note that the Φ_{F} of the polyamide 5a is much higher than that of polyamide 5b, which could be attributed to the effectively reduced conjugation and capability of charge

transfer complex formation by aliphatic diacids with the electro-donating diamine moiety in comparison with that of the strong electro-accepting aromatic diacid.

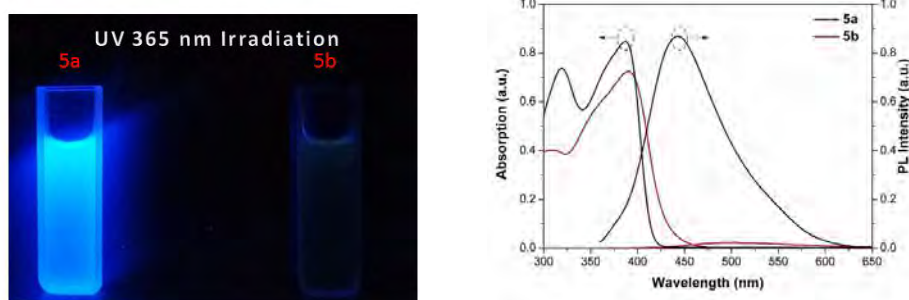


Fig. 1 UV-vis absorption and PL spectra of the polyamides in NMP solutions (1×10^{-5} M). Photographs were taken under illumination of a 365 nm UV light.

The electrochemical properties of these polyamides were investigated by CV using 0.1 M TBAP as the supporting electrolyte and Ag/AgCl as the reference electrode in anhydrous CH_3CN solution. The polyamide 5a and 5b all revealed two reversible oxidation redox couples with low onset potential of 0.41 and 0.42, respectively. Due to the high electrochemical stability of the polymer film and nice adhesion between the polymer film and ITO substrate, polyamide 5a exhibited excellent reversibility of electrochemical characteristic in 200 continuous cyclic scans, which is of great benefit in electro-switching system.

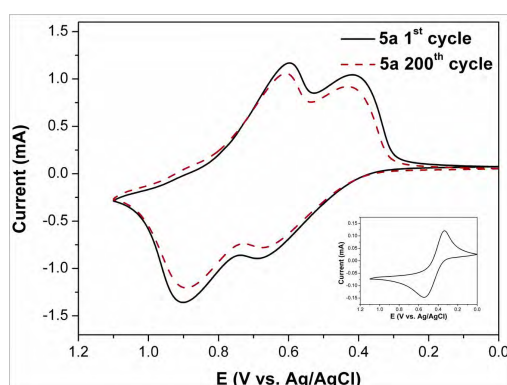


Fig. 3 Cyclic voltammograms of polyamide 5a film on ITO-coated glass substrates over cyclic scans in CH_3CN containing 0.1M TBAP at scan rate of 50 mV s^{-1} .

Electrochromic and switching properties

During CV scans, the polyamide films were observed to switch their colors obviously. Therefore, the spectroelectrochemical techniques were performed to evaluate their electrochromic properties. These two polyamides exhibited similar electrochromic properties, and typical absorption spectra changes of polyamide 5a at different applied potentials are depicted in Fig. 2. Upon the electro-oxidation steadily arising from 0 V to 0.7 V, the intensity of the characteristic absorption peak at 320 and 375 nm for the neutral form of the polyamide decreased gradually, while two new peaks at 485 and 1400 nm grew up ascribed to the formation of a monocation radical in the first stage oxidation. The broad NIR absorption at 1400 nm was the characteristic result of the intervalence charge transfer band, which was similar to the phenomenon reported earlier []. With the potential further increased to 1.0 V, the absorptions at 485 and 1400 nm gradually decreased accompanying the appearance of a new peak at around 900 nm. The disappearance of NIR absorption band could be attributable to the further oxidation of monocation radical to dication of the polyamide 5a. From the inset photos shown in Fig. 2, the color of the polyamide 5a film

changed from nearly colorless to red (semioxidation stage), and finally to blue (fully oxidation state).

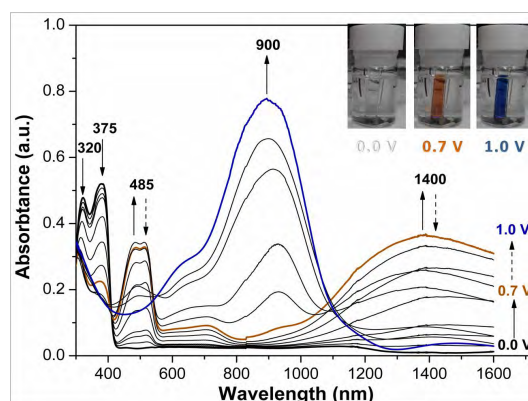


Fig. 2 Absorption spectra of polyamide 5a thin film coated on an ITO-coated glass substrate (in CH₃CN with 0.1M TBAP as supporting electrolyte) at different applied potentials (0.0-1.0 V). The insets show the color changes.

Optical switching studies were carried out to investigate the electrochromic properties more deeply with the transmittance monitored at the given wavelength as a function of time by stepping potential between neutral and oxidation states. The switching behaviors of polyamide 5a were depicted in Fig. 3. The switching time is defined as 90% of the time taken for the full switch. As shown in Fig. 3C, when the switched potentials were set between 0 and 0.7 V for the first oxidation stage, the switching time for coloration and bleaching were 4.8 s and 2.1s, respectively. When the potentials were switched between 0 and 1.0 V (Fig. 3D), the polyamide film required 4.6 s for coloration and 2.6 s for bleaching. The polyamide 5a film exhibited a high CE up to 257 cm² C⁻¹ at 1400 nm in the first cycle and could remain 94 % after switching 1000 cycles between 0 and 0.7 V. After the applied switching potential increased to 1.0 V, the CE is 278 cm² C⁻¹ and showed only 12.2% decay after 1000 cycles. The high values of CE indicate that the polyamide film could provide large optical modulation with a small intercalation charge density, which meet the requirement of energy-saving in smart windows.

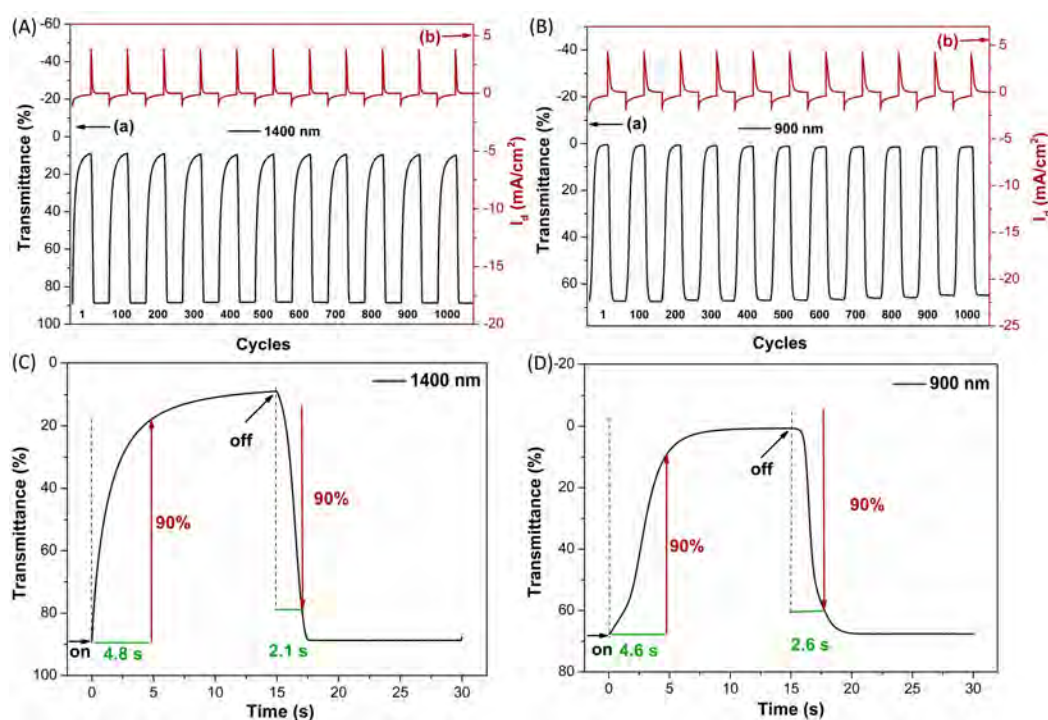


Fig. 3 Optical switching between (A) 0 and 0.7 V and (B) 0 and 1.0 V of polyamide 5a thin film on the ITO-coated glass substrate (coated area: $\sim 1\text{cm}^2$) in 0.1 M TBAP/ CH_3CN with a cycle time of 30 s. (a) Transmittance changes and (b) current consumptions monitored at the given wavelength of 1400 nm and 900 nm. Optical switching time at (C) 1400 nm and (D) 900 nm.

Electrofluorescent properties

In light of the strong fluorescence as well as the excellent electrochemical stability of polyamide 5a, its electrofluorescent switching performance was examined by monitoring the photoluminescent intensity at different applied potentials. In the neutral state, the polyamide film showed vivid blue fluorescence (Fig. 4a). Upon application of positive potentials from 0 to 0.7 V, the fluorescence of the polymer film became weak and finally extinguished to dark, which ascribed to the quench effect of the cation radical of polyamide 5a with strong absorption at 420-580 nm. When the reverse potential was applied, the quenched fluorescence could be recovered, and thus the oxidative quenching offered a high contrast ratio up to 152. In addition, no shift of spectral band was observed during the changes of the fluorescence intensity, which indicates that the fluorescence quenching originated from the electrochemical oxidation of the neutral polyamide 5a to its cation radical form, without the production of side product. Furthermore, the response behavior of the fluorescence switching was also investigated by repetitive cycling between -0.7 and 0.7 V. As shown in Fig. 4b, the switching progress was quite reversible and reproducible between the fluorescent state and non-fluorescent state. It was found that the contrast ratio greatly depended on the duration time with the ratio changed from 152 to 31 by reducing the duration time from 360 to 10 s. When the duration time was set as 10s, no noticeable fluorescence changes in either “on” or “off” states were observed in 100 cycles, indicating the excellent long-term stability of electrofluorescent switching. Thus, the highly stable electrochromic/electrofluorescent material of polyamide 5a will actively promote the development of dual-switch displays in the near future.

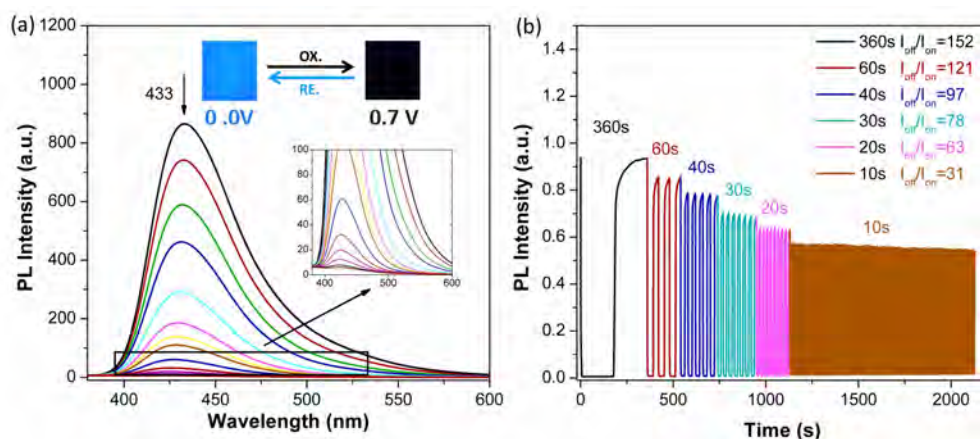


Fig. 4 (a) Fluorescence spectra changes of polyamide 5a film upon different applied potentials from 0 to 0.7 V. (b) Fluorescence switching response of polyamide 5a film under applied step potential between -0.7 and 0.7 V with a step duration time for 360, 60, 40, 30, 20, 10 s at each potential.

Conclusion

In this report, we have readily synthesized two kinds of polyamides with bis(diphenylamine)-fluorene units, which exhibited excellent solubility and thermal stability. Introducing electron-donating methoxy substituents at the *para*-position of diphenylamine effectively reduce the oxidation potentials and increase the electrochemical stability of the resulting polyamides. These polyamides revealed multicolor electrochromic behaviors with amazing characteristics such as low switching times, high coloration efficiency and highly durable switching reversibility. Furthermore, the strong fluorescence of the polyamide

5a could be effectively modulated between fluorescent state and non-fluorescent state by electrochemical redox with high contrast and superior stability. Thus, the reported properties prove that the polyamide 5a will contribute to the development of electrochromic/electrofluorescent dual-switching materials in the future. Further studies on the stimuli-responsive aspects of these materials for flexible devices are currently carried out in our laboratories.

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