# Ambipolar Aromatic Polyimide Electrochromics with Pyrenylamine Moiety

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**ABSTRACT**: Two new pyrenylamine-based polyimides were prepared from the polycondensation reaction of *N,N*-di(4-aminophenyl)-1-aminopyrene with pyromellitic dianhydride (PMDA) and 1,4,5,8-naphthalene-tetracarboxylic dianhydride (NTDA), respectively. The polyimide derived from PMDA is soluble at least in hot *N*-methyl-2-pyrrolidone and can be solution-cast into a flexible and strong film. The polyimides showed high glass transition temperatures ($T_g$ > 364 $^o$C) and high thermal stability. Cyclic voltammetry studies revealed that these two polyimides were ambipolar; they showed well-defined and reversible redox couples during both p- and n-doping processes, together with multi-electrochromic behaviors. The polymer films also exhibited high coloration efficiency, high redox stability, and fast response time.

*Keywords*:  polyimide, electrochromism, pyrenylamine.

## 1. Introduction

Electrochromism consists in the formation of new optical transitions in an electroactive surface film or an electroactive solute as the result of electrochemical oxidation or reduction.[1] This is an intriguing phenomenon for which there might be a wide range of applications, including smart windows, memory elements, large-area information panels, electronic papers (e-papers), and chameleon materials.[2] In general, four major classes of materials are used to construct electrochromic devices (ECDs), including metal oxides, inorganic coordination complexes, molecular dyes, and conjugated polymers.[1,3] Among the available electrochromic materials, π-conjugated polymers represented by polypyrroles and poly(3,4-ethylenedioxythiophene) (PEDOT) and their derivatives have received a great deal of attention because they combine several advantages such as fast response times, high optical contrast ratios, long-term redox stability and color tunability through structural control as well as mechanical deformability, a requirement for flexible electronic applications.[4] Despite the attractive electrochromic performance of many conjugated polymers, some of them were prepared by electrochemical polymerization and were insoluble after deposition on the electrode surface which may hamper their applications for large area devices. Although a great deal of success has already been made in the recent years when it comes to design and prepare solution-processable conjugated polymers for electrochromics, less thermally stable substituents such as alkyl and alkoxy groups are usually needed to be introduced onto the polymer backbone. This leads to a decrease in thermal stability of the material. In addition, long-term stability of conjugated polymers remains a problem. For example, PEDOT degrades over time if exposed to light or heat. Therefore, there remains a great need to develop polymeric electrochromics with useful electrochromic properties as well as good processability and high thermal stability.

Aromatic polyimides are commercially important materials used extensively in a wide range of optoelectronic applications due to their excellent chemical, thermal, and dielectric properties.[5] Despite their outstanding properties, most of the conventional aromatic polyimides have high melting or glass-transition temperatures ($T_g$) and limited solubility in most organic solvents because of their rigid backbones and strong interchain interactions. Thus, polyimide processing is generally carried out via poly(amic acid) precursor, and then converted to polyimide by vigorous thermal or chemical cyclodehydration. However, this process has inherent problems such as emission of volatile by-products and storage instability of poly(amic acid) solution. To overcome these problems, many attempts have been made to the synthesis of soluble and processable polyimides in fully imidized form while maintaining their excellent properties.[6] The majority of methods used for improving the solubility while maintaining the high-temperature performance of polyimides have involved the structural modifications of dianhydride and diamine monomers.[7] Incorporation of three-dimensional, packing-disruptive triarylamine units into the polyimide backbone not only resulted in enhanced solubility but also led to new electronic functionality of polyimides, such as electrochromic[8] and memory[9] characteristics, due to the redox-activity of the triarylamino core.

Aromatic imide dyes, especially perylenediimides, have been used as n-type semiconductors and electron acceptors in many fundamental studies of organic electronics including molecular switches and wires,[10] solar energy conversion devices,[11] n-channel thin film transistors,[12] and electrochromic or light-emitting devices.[13] These molecules have been used in electron-transfer studies because they undergo reversible one-electron reduction at modest potentials to form stable anion radicals localized on the electron deficient units. The electrochemical and spectroscopic properties of different imides, diimides and polyimides have been extensively studied.[14] The most important electrochemical property of aromatic diimide-based compounds, such as pyromellitimides, naphthalenediimides and perylenediimides, is the existence of a stable anion radical and dianion reduced states. Thin layers of polyimides with the above-mentioned diimide units on electrodes are known to be electrochromic and undergo electrically reversible color change between the three redox states (neutral, radical anion, and dianion).[14] Recently, it has been demonstrated that polyimides were proposed as a new class of redox polymers with a charge storage capability if suitably constructing polyimide/carbon nanocomposite

layers on electrode surfaces.[15] Very recently, we have reported the synthesis and fluorescent and electrochromic properties of pyrenylamine-containing polyamides.[16] The polyamides displayed reversible oxidation and reduction processes, indicating their high electrochemical stability for both p and n-doping of the diphenylpyrenylamine core. In this work, we describe the synthesis of two new triarylamine-containing polyimides, **3a** and **3b**, which contains two types of electroactive groups, a pyromellitimide or naphthalenediimide group and a diphenylpyrenylamine group. We could reduce the polymers by one electron to form the imide radical anion or by two electrons to form the imide dianion. We also could further reduce the pyrene ring to form the radical trianion or oxidize the pyrenylamine to a radical cation. The electrochemistry of the polyimides and their model compounds and the ultraviolet-visible-near infrared (UV-vis-NIR) spectroelectrochemistry and electrochromic properties of the polyimides will be investigated.

## 2. Experimental
### 2.1 Synthesis of Polyimides
**Polyimide 3a.** The polyimide **3a** was synthesized from diamine **1** and PMDA by the conventional two-step method via thermal and chemical imidization reaction. The diamine monomer 1 (0.647 g, 1.62 mmol) was dissolved in 9.5 mL of CaH$_2$-dried DMAc in a 50-mL round-bottom flask. Then PMDA (0.353 g, 1.62 mmol) was added to the diamine solution in one portion. Thus, the solid content of the solution is approximately 10 wt %. The mixture was stirred at room temperature for about 12 h to yield a highly viscous poly(amic acid) solution. The inherent viscosity of the resulting poly(amic acid) was 2.02 dL/g, measured in DMAc at a concentration of 0.5 g/dL at 30 $^o$C. For the thermal imidization process, about 5 g of the obtained poly(amic acid) solution was transferred to a 9-cm glass Petri dish, which was placed overnight in a 90 $^o$C oven for the slow release of the casting solvent. The poly(amic acid) in the form of solid film was converted to polyimide **3a** by successive heating under vacuum at 150 $^o$C for 30 min, 200 $^o$C for 30 min, and then 300 $^o$C for 1 h. For the chemical imidization method, 2 mL of acetic anhydride and 1 mL of pyridine were added to the remaining poly(amic acid) solution, and the mixture was heated at 100 $^o$C for 1 h to effect a complete imidization. The homogenous polymer solution was poured slowly into 200 mL of stirring methanol giving rise to a reddish brown precipitate that was collected by filtration, washed thoroughly with hot water and methanol, and dried.

**Polyimide 3b.** Into a 50-mL round-bottom flask were added 0.268 g (1.0 mmol) of NTDA, 0.400 g (1.0 mmol) of the diamine **1**, and 5 mL of m-cresol. The reaction mixture was heated at 80 $^o$C for 2 h and then about three drops of isoquinoline was added to it. Next, the mixture was further heated at 180 $^o$C for 5 h. After the reaction mixture was cooled to 80 $^o$C, an additional 5 mL of *m*-cresol was added to dilute the viscous solution. The polymer solution was cooled to room temperature and precipitated into a large excess of methanol. A gray fibrous precipitate was washed thoroughly with hot water and methanol, collected by filtration, and dried in vacuum at 100 $^o$C for 6 h.

## 3. Results and discussion
### 3.1 Synthesis and Basic Characterization
Polyimide **3a** was prepared by the polycondensation of diamine **1** and pyromellitic dianhydride (PMDA; **2a**) via a conventional two-step process, that is, the formation of a poly(amic acid) and subsequent thermal or chemical imidization (Scheme 1). The poly(amic acid) precursor of **3a** exhibited a very high inherent viscosity of 2.02 dL/g in DMAc and could be cast into a flexible and tough poly(amic acid) film, which could be subsequently converted into a tough polyimide film by extended heating at elevated temperatures. The poly(amic acid) precursor also could be chemically dehydrated to the polyimide **3a** by treatment with acetic anhydride and pyridine. The chemically imidized polyimide **3a** showed a better solubility in organic solvents as compared to the thermally imidized one, and it was soluble at least in hot NMP and partially soluble in DMAc, DMF, and DMSO. Therefore, polyimide **3a** could be cast from solution in the fully imidized state to form flexible film. Polyimide **3b** was prepared by a one-pot, high-temperature solution polymerization of diamine **1** and 1,4,5,8-naphthalene-tetracarboxylic dianhydride (NTDA; **2b**) in *m*-cresol at 180 $^o$C in the presence of isoquinoline as catalyst. In comparison with **3a**, polyimide **3b** revealed a less solubility in organic solvents due to the rigid naphthalenediimide moiety. The polyimides have very high thermal stability. Polyimide **3a** exhibited a very high glass-transition temperature ($T_g$) of 364 $^o$C by differential scanning calorimetry (DSC); with thermogravimetic analysis (heating rate 20 $^o$C/min) showing < 5% weight loss up to 600 $^o$C under flowing nitrogen and up to 550 $^o$C in air.
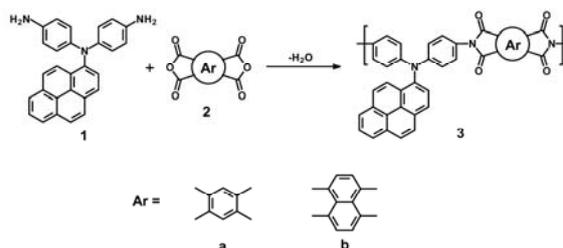


**Scheme 1.** Synthesis and structures of polyimides **3a** and **3b**.

### 3.2 Electrochemical Properties.
The CV of polyimide **3a** (Fig. 1a) shows that the pyromellitimide groups undergo two quasi-reversible one-electron reductions, which occurred at $E_{pc}$ = $-1.00$ and $-1.48$ V. The first reduction corresponds to formation of radical anions, and the second reduction relates to formation of dianions.[14b] The electrochemical behavior of a NTDA-polyimide (**3b**) film shown in Fig. 1b has two redox couples at more positive potentials than that for PMDA-polyimide (**3a**). The results are similar to that reported by Viehbeck et al.[14b] The extended aromatic fused ring will increase the resonance energy and delocalize the negative charge more effectively. Therefore, the first one-electron reduction potential of polyimide **3b** is less negative than that of **3a**. Both of these two polyimides show a third redox couple at more negative potentials due to reduction of the pyrene group. The redox waves observed during the anodic sweep can be attributed to the formation of radical cation originated from the oxidation of the triarylamine core. The dianion form of polyimide **3b** is represented by reduced *cis*-carbonyls. It can also be represented by reduced *trans*-carbonyls, but this requires the loss of aromaticity in the naphthalene unit.[13]
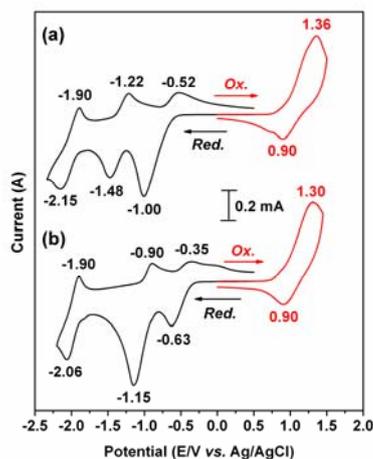
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**Fig. 1** Cyclic voltammograms of the cast films of polyimides (a) **3a** and (b) **3b** on an ITO-coated glass substrate in acetonitrile (for the oxidation process) and DMF (for the reduction process) containing 0.1 M $Bu_4NClO_4$, scan rate = 50 mV/s.

## 3.2 Spectroelectrochemical and Electrochromic Properties

The electro-optical properties of the polymer films were investigated using the changes in electronic absorption spectra at various applied voltages. For these investigations, the polyimide film was cast on an ITO-coated glass slide (a piece that fit in the UV-vis cuvette), and a homemade electrochemical cell was built from a commercial UV-vis cuvette. The cell was placed in the optical path of the sample light beam in a commercial diode array spectrophotometer. This procedure allowed us to obtain electronic absorption spectra under potential control in a 0.1 M $Bu_4NClO_4$/acetonitrile or DMF solution. The result of the **3a** film upon oxidation and reduction is presented in Fig. 2 as a series of UV-vis-NIR absorption curves correlated to electrode potentials. In the neutral form the film exhibits a strong band at 319 nm with a shoulder at 362 nm, due to the π-π* transitions, but it is almost transparent at longer than 450 nm. Upon oxidation of the **3a** film (increasing electrode potential from 0 to 1.35 V), the intensity of the absorption bands at 319 and 362 nm gradually decreased while new peaks at 547 and 589 nm in the visible region together with a broad band from 600 nm extending out into the NIR region beyond 1100 nm gradually increased in intensity (Fig. 2a). Meanwhile, the color of the film changed from pale yellow to purplish blue. We attribute these spectral changes to the formation of a stable radical cation of the diphenylpyrenylamine moiety. Figs. 2b to 2d show the spectral changes of the **3a** film upon reduction. The radical anion **3a**⁻, which appears at potentials between −0.70 and −1.00 V vs. Ag/AgCl, exhibits a strong band at 331 nm and two peaks in the visible region (a stronger band at 723 nm with a shoulder at 657 nm). As shown in the inset of Fig. 2b, the radical anion form of polyimide **3a** is pale green in color. Further reduction at potentials negative to −1.50 V results in the two-electron reduced (dianion) state with new peak at 563 nm and shoulder at 526 nm, and the film turns to a red-violet color during the second reduction (Fig. 2c). The spectral changes associated with the reduction reactions of the pyromellitimde unit are very similar to that of standard PMDA-ODA polyimide (ODA: 4,4'-oxydianiline) reported

by Mazur *et. al.*[14a] This result reconfirms that the diamine residue has very little direct influence on the reduction of the diimide moiety as reported by Mazur *et. al.*[14a] The spectrum at −2.15 V (Fig. 2d) has a strongly intensified peak at 563 nm with slightly intensified shoulders at 509 and 526 nm and a concurrent drop of the absorption intensity at 653 and 723 nm. Since the potential examined is similar to the third cathodic process, the spectral change is assigned to the radical anion formation arising from the reduction of the pyrene unit. At this stage, the polymer film appears as a bright pink color.
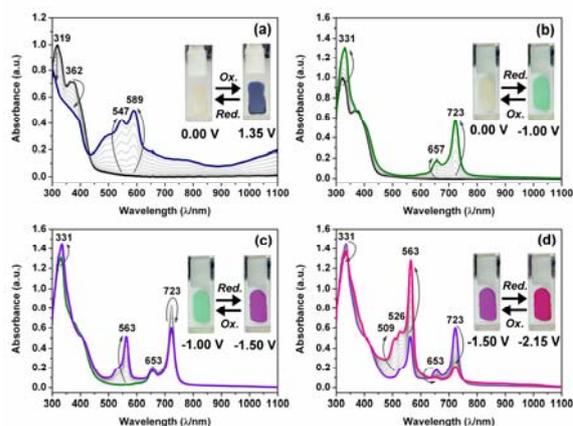


**Fig. 2** Spectroelectrohemistry of polyimide **3a** thin film (~0.2 μm thick) on an ITO-coated glass substrate (in CH3CN or DMF with 0.1 M $Bu_4NClO_4$ as the supporting electrolyte *vs.* Ag/AgCl couple as reference) along with increasing of the applied voltage to +1.35 V (for the oxidation process in acetonitrile) and decreasing to −2.15 V (for the reduction process in DMF). The potential was varied in 50 to 150 mV intervals. The inset shows the color change of the polymer film at indicated potentials.

### 3.3 Electrochromic Switching and Stability

Electrochromic switching studies for the polyimides were performed to monitor the percent transmittance changes (Δ%T) as a function of time at their absorption maximum (λmax) 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 1 cm². Fig. 3 depicts the optical transmittance as a function of time at 547 and 589 nm by applying square-wave potential steps of 4 s between −0.5 and +1.35 V. The response time was calculated at 90% of the full-transmittance change because it is difficult to perceive any further color change with naked eye beyond this point. Polyimide **3a** attained 90% of a complete coloring and bleaching in less than 4 and 1 s, respectively. The optical contrast measured as Δ%T of polyimide **3a** between neutral pale yellow and oxidized blue states was found to be 54% at 547 nm and 62% at 589 nm. As shown in Table 1, the coloration efficiency of **3a** film at 547 and 589 nm was calculated to be 155 and 180 cm²/C, respectively. As mentioned earlier, the polyimide films also exhibited a strong coloration change upon electrochemical reduction. In general, the cathodically coloring polyimide film displayed a fast response time, high optical contrast, and high coloration efficiency at its longer wavelength absorption maximum during each n-doping process. The stability studies of the polyimide films for n-type doping were also achieved using potential square-wave absorptometry. During n-doping, the polyimide films

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showed a moderate optical contrast loss after 10 full switches. It is believed that a little unwanted delaminating or dissolution of the anionic products in the DMF/electrolyte solution is the main cause of the unstable switching behavior.
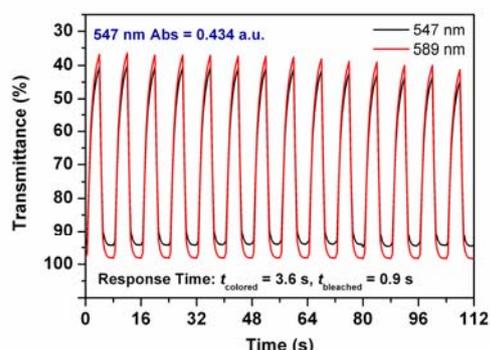


**Fig. 3** Optical transmittance change for polyimide **3a** film (with an optical density of 0.434 a.u.) monitored at 547 nm and 589 nm while switching between its pale yellow (neutral) and purplish blue (oxidized) states in 0.1 M $Bu_4NClO_4/CH_3CN$ by applying a potential step $-0.5$ /+1.35 V (*vs.* Ag/AgCl) and cycle time 8 s.

Finally, we fabricated as preliminary investigations single layer electrochromic cells (Fig. 4). The polyimide films were spray-coated onto ITO-glass and then dried. Afterwards, the gel electrolyte was spread on the polymer-coated side of the electrode and the electrodes were sandwiched. To prevent leakage, an epoxy resin was applied to seal the device. As a typical example, an electrochromic cell based on polyimide **3a** was fabricated. The polymer film is pale yellow in neutral form. When the voltage was increased (to a maximum of 2.7 V), the color changed to purplish blue due to electro-oxidation, the same as was already observed for the solution spectroelectrochemistry experiments. When the potential was subsequently set back at 0 V, the polymer film turned back to original pale yellow. We believe that optimization could further improve the device performance and fully explore the potential of these electrochromic polyimides.
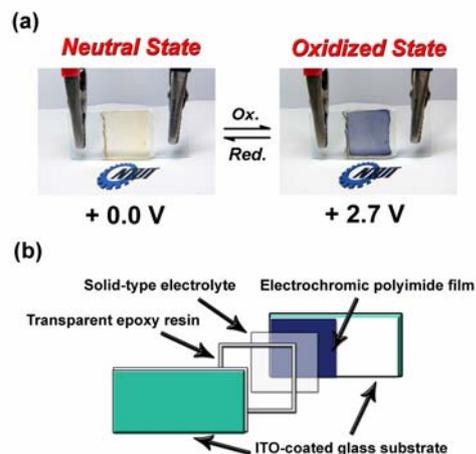


**Fig. 4** (a) Photos of single-layer ITO-coated glass electrochromic device, using polyimide **3a** as active layer. (b) Schematic diagram of polyimide ECD sandwich cell.

## 4. Conclusions

We have successfully prepared two new pyrenylamine-bearing redox-active polyimides and demonstrated that these polymers show modest solubility in organic solvents, high $T_g$, and ambipolar and multicolored electrochromic behavior. Electrochemical and spectral results showed that these polymers can be employed as potential anodically and cathodically coloring materials in the development of electrochromic devices. Further development of materials of this type would seem to be warranted by the encouraging initial results presented here.

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