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Electrochromic behavior of PI thin film. The inset shows the photographic images of the film at indicated applied voltages.

# Multicoloured Near-Infrared Electrochromic Polyimides: Synthesis,

# **Electrochemical, and Electrochromic Properties**

Jiwei Cai<sup>a</sup>, Haijun Niu<sup>a</sup>\*, Ping Zhao<sup>b</sup>, Yan Ji<sup>a</sup>, Lina Ma<sup>a</sup>, Cheng Wang<sup>a</sup>, Xuduo Bai<sup>a</sup>, Wen Wang<sup>c</sup>

<sup>a</sup> Key Laboratory of Functional Inorganic Material Chemistry, Ministry of Education, Department of Macromolecular Materials and Engineering, Heilongjiang University, Harbin 150086, P R China

<sup>b</sup>Key Laboratory for Advanced Materials and Institute of Fine Chemicals, East China University of Science and Technology, Shanghai 200237, PR China

<sup>c</sup>School of Material Science and Engineering, Harbin Institute of Technology, Harbin 150080, P R China

<sup>\*</sup>Corresponding author: Tel: 086-13684501571; Fax: 086-0451-86608131;

email: haijunniu@hotmail.com

# Abstract

A novel series of multicoloured near-infrared electrochromic aromatic polyimides have been synthesized by a conventional two-step polymerization process. All polymers displayed outstanding thermal stability, i.e. 20 % wt loss in excess of 593 °C in nitrogen and high char yields (higher than 68% at 750 °C). In addition, the polymer films showed reversible electrochemical oxidation, high coloration efficiency, low switching time, and anodic green electrochromic behaviors. The Highest Occupied Molecular Orbital (HOMO) and Lowest Unoccupied Molecular Orbital (LUMO) energy levels of these polymers were determined in the range of -4.759 - -4.801 and -1.758 - -2.002 eV (vs the vacuum level) by cyclic voltammetry method

consisting with the results of quantum chemical calculation well, respectively. The polymer films revealed excellent stability of electrochromic characteristics for the radical cations generated, changing color from original yellowish to green and blue, with the absorption changing from ultraviolet to near-infrared.

**Key words**: triphenylamine, electrochromism, polyimides, near-infrared, functional dyes, coloration efficiency

#### **1.Introduction**

Aromatic polyimides are well accepted as advanced materials for thin-film applications in microelectronic devices and liquid crystal displays due to their outstanding mechanical, chemical, thermal, and physical properties [1]. However, the technological applications of most polyimides are limited by processing difficulties because of high melting or glass transition temperatures and limited solubility in most organic solvents due to their rigid backbones. A general approach to overcome this drawback was to introduce bulky lateral substituents, flexible linkages, and noncoplanar biphenylene moieties into the polymer [2-9]. The introduction of propeller-shaped triarylamine units into the polyimide backbone as a structural modification to the rigid polyimides has the potential to form an amorphous structure exhibiting excellent solubility and film-forming capabilities.

Electrochromism is known as the alternation of color by the application of a potential [10-12]. Color changes are commonly between a transparent state, where the chromophore only absorbs in the UV region, and a colored state or between two colored states in a given electrolyte solution. The electrochromic material may exhibit several colors and can be termed as polyelectrochromic.

Therefore remarkable effort has been performed for achieving new polymers which meet the criteria for commercial applications. Some key issues such as long-term stability, rapid redox switching, high coloration efficiency (CE), and high optical transmittance change ( $\Delta$ %T) during operation played important roles and are required to be achieved.

As an electrochromic functional moiety, the TPA unit has two basic properties: (1) the easy oxidizability of the nitrogen center and (2) its hole-transporting ability via the radical cation species. Triarylamine derivatives are well known as their photo- and electro-active properties that have potentials for optoelectronic applications, such as photoconductors, hole transporters, light emitters, and memory devices [13].

It also can be easily oxidized to form radical cations, and the oxidation process is always associated with a noticeable change of coloration. In recent years, Liou and coworkers have developed several high-performance polymers such as polyimides[14] and polyamides[15] carrying the triarylamine unit as a redox-chromophore. They found that the polymer based on TPA as core exhibited stable, excellent, multi-color, electrochromic characteristic, furthermore the corporation of electron-donating substituents at the para positions of triarylamines afforded stable radical cations.

On the other hand, near-infrared (NIR)-absorbing electrochromic materials are receiving great attention due to their potential applications in optical communications [16], biomedicine [17], camouflage materials in warfare [18], electro-optic switching in devices [19], thermal control and thermal emission detectors for spacecrafts [20]. However, compared with Uv-visible absorbing materials, few NIR electrochromic materials have been developed to date [21].

In our ongoing effort to develop electrochromic polymeric materials, we have synthesized

and investigated a series of high-performance polymers containing triphenylamine (TPA) [22], which showed good electrochromic reversibility in the visible region. In this contribution, we therefore synthesized the diamine monomer N,N'-bis(4-aminophenyl)-N,N'-di-2- naphthalenyl -1,4-benzenediamine. PIs as thermally stable microelectronic materials have attracted great interest. Thus, we anticipated that the prepared electroactive PIs would reveal multielectrochrmic behaviors, high-electrochemical stability, improved optical response times, and enhanced contrast of optical transmittance in NIR region. Lastly, investigation of the oxidation mechanism for the conjugated polymer was done using theoretical analysis based on molecular orbital theory.

#### 2 Experimental

#### **2.1 Materials**

N, N'-di(2-naphthyl)-1,4-benzenediamine were purchased from TCI Co., 4,4'-oxydiphthalic anhydride, 4,4'-biphthalic anhydride, 3,3',4,4'-benzophenonetetracarboxylic dianhydride, pyromellitic dianhydride, 4,4'-(hexafluoroisopropylidene) diphthalic anhydride were purchased from TCI Co.; Pd/C(10%)were purchased from Acros;. 4-fluoronitrobenzene, N,N-dimethylformamide (DMF) were supplied from Sinopharm Chemical Reagent Co., Ltd., China and used as received.

#### 2.2 Synthesis of Monomers

N,N'-bis(4-aminophenyl)-N,N'-di-2-naphthalenyl-1,4-benzenediamine (3) were synthesized according to the procedure reported [22].

#### 2.3 Synthesis of Polymers

*Preparation of PIs P1-P5 by Two-Step Method via Thermal Imidization Reaction.* The synthesis of PI P1 was used as an example to illustrate the general synthetic route. To a solution of 0.2704 g (0.5 mmol) of diamine **3** in 3.8 mL of N,N-dimethylformamide (DMF), 0.1098 g (0.5 mmol) of

dianhydride (pyromellitic dianhydride a) was added in one portion. Thus, the solid content of the solution is approximately 10 wt%. The mixture was stirred at room temperature for about 6 h to afford a viscous poly (amic acid) solution. The poly (amic acid) film was obtained by casting from the reaction polymer solution onto a glass plate and drying at 90 °C overnight under vacuum. The inherent viscosity of polyamic acid of P1 was 0.74 dL/g in DMF at a concentration of 0.5 g/dL at 30 °C. The polyamic acid in the form of film was converted to PI by successive heating under vacuum at 100 °C for 1 h, 200 °C for 1 h, and then 300 °C for 30 min. All other PIs were synthesized by an analogous procedure as described.

FTIR spectrum ( KBr pellet, polyimide of P1): 1775 cm<sup>-1</sup> (asymmetrical C=O), 1721 cm<sup>-1</sup> (symmetrical C=O), 1650 cm<sup>-1</sup> (amide carbonyl),1377 cm<sup>-1</sup> (C-N), and 739 cm<sup>-1</sup> (imide ring deformation). <sup>1</sup>H NMR (400 MHz, DMSO- $d_6$ , ppm, polyamic acid solid of Pa): 10.44-10.52 (m, the terminal groups of polyamide), 8.30-8.35 (the amide group), 6.99-7.99 (aromatic ring of benzene).

**2.3.1 Polymer P2.** Monomer **3** feed 0.2705 g ( $0.5 \times 10^{-3}$  mol); dianhydride (b) 0.1472g ( $0.5 \times 10^{-3}$  mol); FTIR spectrum (KBr pellet, polyimide): 1777, 1715, 1665, 1596, 1499, 1385. <sup>1</sup>H NMR (400 MHz, DMSO- $d_6$ , ppm, polyamic acid solid of Pa): 10.37-10.42 (m, the terminal groups of polyamide), 8.30-8.35 (the amide group), 6.86-8.13 (aromatic ring of benzene).

**2.3.2 Polymer P3.** monomer **3** feed 0.1370 g ( $2.5 \times 10^{4}$ mol); dianhydride (c) 0.0725g ( $2.5 \times 10^{4}$ mol); FTIR spectrum (KBr pellet, polyimide):1778, 1718, 1659, 1595, 1500, 1383. <sup>1</sup>H NMR (400 MHz, DMSO- $d_6$ , ppm, polyamic acid solid of Pa): 10.37-10.40 (m, the terminal groups of polyamide), 8.31-8.35 (the amide group), 6.89-8.00 (aromatic ring of benzene).

**2.3.3 Polymer P4.** monomer **3** feed 0.1367 g (2.5×10<sup>4</sup>mol); dianhydride (d) 0.0835 g

 $(2.5 \times 10^{-4} \text{mol})$ ; FTIR spectrum (KBr pellet, polyimide):1777, 1718, 1658, 1595, 1492, 1382. <sup>1</sup>H NMR (400 MHz, DMSO-*d*<sub>6</sub>, ppm, polyamic acid solid of Pa): 10.37-10.44 (m, the terminal groups of polyamide), 8.31-8.35 (the amide group), 6.88-8.02 (aromatic ring of benzene).

**2.3.4 Polymer P5.** monomer **3** feed 0.1370 g  $(2.5 \times 10^{-4} \text{ mol})$ ; dianhydride (e) 0.1117 g  $(2.5 \times 10^{-4} \text{ mol})$ ; FTIR spectrum (KBr pellet, polyimide):1776, 1718, 1659, 1596, 1500, 1385. <sup>1</sup>H NMR (400 MHz, DMSO, ppm, polyamic acid solid of Pa): 10.49-10.55 (m, the terminal groups of polyamide), 8.30-8.32 (the amide group), 7.00-7.98 (aromatic ring of benzene).

# Scheme 1 Synthesis of polymers





#### 2.4 Preparation of the PIs Films

A solution of polymer was made by dissolving about 0.5 g of the PIs sample in 10 mL of DMF. The homogeneous solution was poured into a 9 cm glass Petri dish, which was placed in a 90 °C oven for 6 h to remove most of the solvent; then the semidried film was further dried in vacuum at 190 °C for 10 h. The obtained films were about 40-60  $\mu$ m in thickness and were used for solubility tests, and thermal analyses.

#### 2.5 Measurements

FT-IR spectra were recorded on a PerkinElmer Spectrum 100 Model FT-IR spectrometer. <sup>1</sup>H NMR spectra were measured on a Bruker AC-400 MHz spectrometer in DMSO, using tetramethylsilane as an internal reference. SEM measurement was carried out on a S4800 instrument with an accelerating voltage of 2 kV, and the samples were sputtered with Pt prior to observation. Thermogravimetric analysis (TGA) was conducted with a PerkinElmer Pyris 6 TGA. Experiments were carried out on approximately 6~8 mg powder samples heated in flowing nitrogen or air (flow rate =  $20 \text{ cm}^3 / \text{min}$ ) at a heating rate of 10 °C / min. DSC analyses were performed on a PerkinElmer Pyris diamond DSC at a scan rate of 10 °C / min in flowing nitrogen (20 cm<sup>3</sup> / min). UV-vis-NIR absorption spectra were recorded using a SHIMADZU UV-3600 spectrophotometer whereas the photoluminescence solution spectra were registered on a Jasco

FP-6200 spectrometer with 450 W xenon lamp as the light source. The emission spectra of PIs were taken at  $\lambda_{exc}$  being equal to about the wavelength of the absorption maximum.

Cyclic voltammetry (CV) measurements were conducted on a CH Instruments 660A electrochemical analyzer at a scan rate of 50 mV s<sup>-1</sup> with a 0.1 M solution of LiClO<sub>4</sub> as an electrolyte under nitrogen atmosphere in dry acetonitrile (CH<sub>3</sub>CN). The oxidation and reduction potentials of polymer film coated on an ITO disk were measured using a Pt wire and an Ag / AgCl electrode as a counter electrode and a quasi reference electrode, respectively. Under these conditions, the onset of oxidation and reduction potentials of the polymer thin films against the reference Ag/AgCl quasi electrode were measured and calibrated against the ferrocene/ferrocenium (Fc/Fc<sup>+</sup>) redox couple. The HOMO and LUMO levels of the polymers were calculated by assuming the absolute energy level of Fc / Fc<sup>+</sup> as - 4.80 eV to vacuum.

#### **3 Results and discussion**

#### 3.1 Synthesis of monomers

All monomers were synthesized using modified literature procedures. In general, many series of dinitrotriphenylamines are synthesized by the nucleophilic amination of aromatic amine and 4-fluoro-1-nitrobenzene under nucleophilic displacement conditions using NaH as base. Reduction of the dinitro intermediates was carried using 10 % Pd / C in DMF in autoclave with high pressure H<sub>2</sub> and resulted in a near quantitative yield of diaminotriphenylamine derivatives without toxicity to atmosphere by using hydrazine and tedious process by using SnCl<sub>2</sub>. Especially, the H<sub>2</sub> can convert the little raw materials to be soluble in the solution to be got rid of. The monomer structure was verified to be consistent with the object by the NMR and FT-IR characterization.

#### 3.2 Synthesis of polymers

The PIs were synthesized from diamine 3 and five commercially available dianhydrides a-e via a typical two step polymerization method. The structures and codes of the prepared polymers are shown in Scheme 1. In the first step, the viscosities of the reaction mixtures became very high as poly(amic acid)s formed, indicating the formation of high-molecular-weight polymers. The poly(amic acid) precursors could be thermal imine dehydrated to PIs by extended heating at elevated temperatures. The chemical structures of the PIs were characterized with IR analysis, and the formation of poly(amic acid)s was confirmed with NMR spectroscopy. The IR spectra of these PIs exhibited characteristic imide absorption bands at around 1776 (asymmetrical C=O), 1720 (symmetrical C=O), 1360 (C-N), and 745 cm<sup>-1</sup> (imide ring deformation). The microstructures of these poly(amic acid)s were also verified by the NMR spectra (Fig. S1).

#### 3.3 Inherent viscosity and thermal properties

#### Table 1 Thermal properties and inherent viscosity of the PIs

These PIs were obtained in almost quantitative yields, with inherent viscosities in the range of 0.74–0.82 dL/g, as shown in Table 1. As shown in Table 1, compared with the analogous PI, the series of PI did not show clear  $T_g$ , but showed an enhanced thermal stability (Fig. S2) due to the decreased conformational flexibility or free volume caused by the introduction of planar napthalene groups in the repeat unit. All the polymers indicated no clear melting endotherms up to the decomposition temperatures on the DSC thermograms.

The thermal stabilities of PIs were evaluated by TGA in nitrogen atmospheres. The Fig. S2 inset depicts a typical set of TGA curves for Pa-Pe in nitrogen. The decomposition temperatures  $(T_{ds})$  at 5 % and 20 % weight losses in nitrogen were taken from the original TGA thermograms and are given in Table 1. All the prepared PIs exhibited good thermal stability with insignificant

weight loss up to 470 °C under nitrogen atmosphere. The 5% weight loss temperatures of these polymers in nitrogen were recorded in the range of 479 – 580 °C respectively. The amount of carbonized residues (char yield) at 750 °C in nitrogen for all PIs was in the range of 66 – 78 wt %. The high char yields of these polyamides can be attributed to their high aromatic content. The lowest  $T_{ds}$  value of Pc could be explained in terms of the ether bond segment in its backbone. Thus, the thermal analysis results revealed that these PIs exhibited excellent thermal stability, which in turn is beneficial to increase the service time in device application and enhance the morphological stability to the spin-coated film.

Table 2 Optical and electrochemical properties for PIs

Fig. 1 Uv-visible absorption spectra of PIs (films)

#### 3.4 Optical and electrochemistry properties

The optical properties of the TPA-based polymers P1 – P5 were investigated by UV-vis and photoluminescence (PL) spectroscopy, and the relevant data are presented in Table 2. PL quantum yields  $\varphi$ s of the samples in different solvents were measured by using quinine sulfate dissolved in 0.5 M sulfuric acids as reference standard ( $\varphi$  =0.546). The  $\varphi$ s of these PIs after refractive index correction can be calculated according to the following eq[23]:

$$\phi_{unk} = \phi_{std} \left( \frac{I_{unk}}{I_{std}} \right) \left( \frac{A_{std}}{A_{unk}} \right) \left( \frac{\eta_{unk}}{\eta_{std}} \right)^2$$

where  $\phi_{unk}$ ,  $\phi_{std}$ ,  $I_{unk}$ ,  $I_{std}$ ,  $A_{unk}$ ,  $A_{std}$ ,  $\eta_{unk}$ , and  $\eta_{std}$  are the fluorescent quantum yield, integration of the emission intensity, absorbance at the excitation wavelength, and the refractive indices of the corresponding solutions for the samples and the standard, respectively. Here, we use

the refractive indices of the pure solvents as those of the solutions. Their PL spectra in DMF solution showed emission maximum around 504–515 nm (in the yellow-green region), with very low fluorescence quantum yields. These PIs exhibited strong UV–vis absorption bands in the range of 319 – 336 nm for solid film shown in Fig. 1, assignable to the  $\pi$ - $\pi$ \* transitions resulting from the conjugated TPA segment. Optical band gaps (E<sub>g</sub>s) determined from the absorption edge of the solid-state spectra of polymers are found to be 2.77 – 3.00 eV.

The redox behaviors of the PIs were investigated by cyclic voltammetry (CV) conducted for the cast film on an ITO-coated glass substrate as working electrode in anhydrous CH<sub>3</sub>CN containing 0.1 M of LiClO<sub>4</sub> as an electrolyte under nitrogen atmosphere for oxidation and reduction measurements, respectively. The results are summarized in table **2**. Fig. 2 shows representative CV curves for P1 recorded at a scan rate of 50 mV/s. The CV diagram indicates two well-defined redox waves, with half-wave potentials ( $E_{1/2}$ ) of 0.54 and 0.91 V. The first peak, at 0.80 V, can be ascribed to oxidation of the electron-rich nitrogen atom in the TPA core. The second peak, at 1.17 V, can be attributed to the formation of the TPA<sup>2+</sup> dication, causing radical recombination and formation of a quinoid structure. Because of the stability of the films and good adhesion between the polymer and ITO substrate, the P1 exhibited excellent reversibility of electrochromic characteristics by five continuous cyclic scans between 0.0 and 1.60 V, changing color from original colourless to yellow-green. A similar spectral change was observed for other PIs (see the Fig. S3, supporting information).

The energy levels of the highest occupied molecular orbital (HOMO) and the lowest unoccupied molecular orbital (LUMO) of the investigated polymers can be determined from the oxidation onset potentials ( $E_{onset}$ ) or half-wave potentials ( $E_{1/2}$ ) and the onset absorption

wavelengths, and the results are listed in Table 2. In the voltammograms, the redox peaks have been associated with reduction–oxidation process accompanying the double injection/extraction of  $CIO_4^-$  ions and electrons. To obtain accurate redox potentials, the reference electrode was calibrated by the ferrocene/ ferrocenium (Fc/Fc<sup>+</sup>), whose redox potential is assumed to have an absolute energy level of -4.80 eV to vacuum. As a result, the HOMO energy values were calculated using the equation [24].

 $E_{HOMO}$ = -e( $E_{ox vs Ag/AgCl}$  + 4.35)eV

where E<sub>ox</sub> is the onset oxidation potential vs Ag/AgCl.

The LUMO energy levels of the polymers are estimated from the HOMO energy levels and  $E_g$  using the equation

 $E_{LUMO} = E_{HOMO} + Eg^{opt}$ 

 $E_g(eV)=1240/\lambda_{onset}$ 

The HOMO energy values of P2 and P5 were calculated to be in the range from -4.759 to -4.801 eV. Due to the reduction curves could hardly be obtained,  $E_{LUMOS}$  are at between -1.758 (Pc) to -2.00282 (Pa) eV. In the PIs containing the same amine monomer, P5 showed the highest HOMO, and the P2 exhibited the lowest HOMO. The rule is the same as that of Uv-visible absorption. The different dianhydrides play the key role in the electron structure and regulate the  $E_g$  of PIs. The lower ionization potential (IP, about 4.7eV) could suggest an easier hole injection into films from ITO electrodes (4.7eV) in electronic device applications.

Fig. 2 Repetitive CV scanning of the P1 film on the ITO/glass electrode in 0.1 M  $LiClO_4/MeCN$  solution over the potential range from 0 to 1.6 V at a scan rate of 50 mV s<sup>-1</sup>.

**Fig. 3** Electrochromic behavior of P4 thin film (in  $CH_3CN$  with 0.1 M LiClO<sub>4</sub> as the supporting electrolyte) at 0.0, 0.5, 0.6, 0.7, 0.8, 0.9, 1.0, 1.1, 1.2, 1.3 (V vs. Ag/AgCl couple as reference). The inset shows the photographic images of the film at indicated applied voltages.

#### 3.5 Electrochromic properties

The spectroelectrochemistry characteristics of the polymer P4 are also shown in Figure 3. In the neutral form, at 0 V the film exhibited strong absorption at wavelength around 335 nm, characteristic for triarylamine, but it was almost transparent in the visible region. Upon oxidation of the P4 film (increasing applied voltage from 0 to 1.0 V), the intensity of the absorption peak at 335 nm gradually decreased while a new peak at 425 nm and a broad band with maximum absorption wavelength at 1086 nm in the NIR region gradually increased in intensity. We attribute the spectral change in visible range to the formation of a stable monocation radical of the TPA center in diamine 3 moiety. Furthermore, the broad absorption in NIR region was the characteristic result owing to IV-CT (leading an intervalence charge transfer) excitation associated with ET (intramolecular electron transfer) from active neutral nitrogen atom to the cation radical nitrogen center of diamine 3 moiety, which was consistent with the phenomenon classified by Robin and Day [25]. As the applied potential became more anodic to 1.3 V, the absorption bands of the cation radical decreased gradually in intensity, with the formation of a new broadband centered at 832 nm. The disappearance of NIR absorption band can be attributable to the formation of dication by the further oxidation of monocation radical species in the diamine 3 segments. The observed UV-vis absorption changes in the film of P4 at various potentials are fully reversible and are associated with strong color changes. Indeed, they even can be seen

readily by the naked eye. The other PIs showed similar spectral changes to that of P4 (see the Fig S4, supporting information).

The stability, response time, and color efficiency are the key parameters for an electroactive polymer film to be amenable for usage in optical and electrochromic devices, thus the electrochromic switching studies were further measured. The color switching times were estimated by applying a potential step, and the absorbance profiles were followed. The switching time was calculated at 90% of the full switch because it is difficult to perceive any further color change with naked eye beyond this point [26]. The polymer switched rapidly between the highly transmissive neutral state and the colored oxidized state. As depicted in Fig. 4, P4 film revealed switching time of 1.76 s at 1.1V for coloring process at 425 nm and 1.90 s for bleaching. After continuous cyclic scans between 0.0 V and 1.10 V in 100 s, the polymer films still exhibited excellent stability of electrochromic characteristics, indicating that the film was very stable and had good adhesion with the ITO substrate.

After over continuous 190 cyclic switches between 0.00 and 1.10 V, the polymer films still exhibited good stability of electrochromic characteristics (see Fig. 5 and Fig. S5). Because of the apparent high electrochromic contrast, optical switching studies were investigated more deeply to manifest the outstanding electrochromic characteristics of these obtained novel anodically electrochromic materials.

The electrochromic coloration efficiency (CE;  $\eta$ ) is also an important characteristic for the electrochromic materials. CE can be calculated using the equations and given below [27]:

$$\delta_{OD} = lg(T_b/T_c)$$

 $\eta = \delta_{OD}/Q$ 

where  $T_b$  and  $T_c$  are the transmittances before and after coloration, respectively,  $\delta_{OD}$  is the change of the optical density, which is proportional to the amount of created color centers.  $\eta$  denotes the coloration efficiency(CE) and Q (mC / cm<sup>2</sup>) is the amount of injected/ejected charge per unit sample area. CE of P4 film was measured as 111.8 cm<sup>2</sup>/C. (at 425 nm) at full doped state, which had reasonable coloration efficiency (the others were listed in table 3).

Table 3. Optical and Electrochemical Data Collected for Coloration Efficiency Measurements of PIs

**Fig. 4** Current consumption (upper) and potential step absorptometry (lower) of P4 (at 425 nm) (in 0.1 M LiClO<sub>4</sub> / CH<sub>3</sub>CN as the supporting electrolyte) by applying a potential step  $(0.00 \leftrightarrow 1.1 \text{ V})$  with a cycle time of 8 s.

Fig. 5 Current consumption between 0.00 and 1.0 V (vs. Ag/AgCl) of polymer P4 thin film on the ITO-coated glass substrate in a 0.1 M LiClO<sub>4</sub>/CH<sub>3</sub>CN solution with a cycle time of 8 s.

# 3.6 Photoelectrochemical activity

To clarity the flow trend and mechanism of photo-generated electrons, the photocurrent and photo-voltage properties of PIs were investigated.

A steady anodic photocurrent was obtained from the dye monolayer-modified electrode when the PI-ITO electrode was illuminated under white light of 150 mWcm<sup>-2</sup> intensity without any bias voltage in 0.1 M LiClO<sub>4</sub> electrolyte solution (Fig. 6a). A reversible rise/decay of the photocurrent was observed when switching on and off many times, as shown in Fig. 6. For comparison, the bare

ITO did not exhibit the phenomena suggesting that the PI was responsible for photocurrent generation.

Fig. 6b showed typical open-circuit photovoltaic response of electrode on illumination. After the light was turned off, the photovoltage decayed to lowest slowly. On the contrast, after the light was turned on, the photovoltage increased instantly. A similar characteristic was observed for other PIs of this series. Thus, these PIs can act as the photoelectric conversion material for optoelectronic applications.

The observation result can be explained by that there is charge separation and electron transfer in the interface of PI film and electrolyte solution under illumination. The electrons absorb energy from light and jump onto LUMO, followed by the injection of electrons from the LUMO (-1.85 eV) of P1 to the conduction band of ITO surface (-4.7 eV), then the interparticulate hopping of electrons generates photocurrent and photo-voltage. It is to be noted that there is no sacrifice regent in the electrolyte such as  $I_3/I$  ion couple, which can result in the photocurrent and photo-voltage decaying with on/off illumination cycles procedure.

**Fig. 6** A typical photocurrent (A) and photovoltage (B) response for P4 immobilized ITO glass upon exposure to light at room temperature.

#### 3.7 Quantum chemistry calculation

To better understand the evolution of the oxidation and reduction potentials, the electronic

structures of the polymer series (as isolated oligomers) were evaluated by using DFT at the B3LYP/6-31G level of theory. The HOMO energy, LUMO energy and HOMO-LUMO energy gaps ( $E_g$ ) are given in Table 2. Pictorial representations of the frontier molecular orbitals of polymer series are shown in Fig. 7, which illustrate that the electron density distribution of the HOMO state of the basic unit (ground state) was mainly located on diamine moiety, and that of the LUMO state of the basic unit was mainly located on the dianhydride group of PI. The electronic density contours in Fig. 7 obviously show that the lone pair of electron on the nitrogen atoms have little coupling with  $\pi$  electrons.

**Fig. 7** Pictorial representations of the electron density in the frontier molecular orbitals of repetition units for P1 to P5 in the order.

The trend of  $E_g$  for the oligomer series follows in the order: P4 < P1 < P5 < P2 < P3 which basically corresponds with the experimental data in the order:  $P1 \approx P4 < P2 \approx P5 < P3$  (Table 2). The bias may be due to the adjacent ring which plays extra interaction on the energies. It should be noted that the calculated results are based on monomer unit. In fact, the experiment data are obtained from polymer which are influenced by the solvent and electrolyte and more complicated.

### 4. Conclusion

The triarylamine-based aromatic diamine monomer, N, N'- bis( 4- aminophenyl) -N, N'- di-2- naphthalenyl-1, 4- benzenediamine was synthesized in high purity and high yields from readily available reagents. The novel aromatic PIs containing pendent triarylamine groups were prepared by the two- step method starting from diamine with various aromatic tetracarboxylic dianhydrides. All of them exhibit good thermal stability. The multicolor electrochromic behavior of the PIs film

of P1- P5 exhibit from original pale yellowish to green and then to blue color when various potentials were applied. Thus, our novel PIs have a great potential as a new type of hole-transporting and electrochromic materials due to their proper HOMO values and excellent electrochemical and thermal stability.

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#### **Figures Captions**

Table 1 Thermal properties and inherent viscosity of the PIs

Table 2 Optical and electrochemical properties for PIs

Table 3. Optical and electrochemical data collected for coloration efficiency measurements of PIs

Fig. 1 Uv-visible absorption spectra of PIs (film)

**Fig. 2** Cyclic voltammograms for P1 in CH<sub>3</sub>CN/0.1 M LiClO<sub>4</sub> with ferrocene/ferrocenium (Fc/Fc<sup>+</sup>) as an internal standard, at 50 mV s<sup>-1</sup>.

**Fig. 3** Electrochromic behavior of P1 thin film (in CH<sub>3</sub>CN with 0.1 M LiClO<sub>4</sub> as the supporting electrolyte) at 0.0, 0.5, 0.6, 0.7, 0.8, 0.9, 1.0, 1.1, 1.2, 1.3, 1.4, 1.5, 1.6 (V vs. Ag/AgCl couple as reference). The inset shows the photographic images of the film at indicated applied voltages. **Fig. 4** Current consumption (upper) and potential step absorptometry (lower) of P4 (at 425 nm) (in 0.1 M LiClO<sub>4</sub> / CH<sub>3</sub>CN as the supporting electrolyte) by applying a potential step  $(0.00 \leftrightarrow 1.1 \text{ V})$  with a cycle time of 8 s.

**Fig. 5** Current consumption between 0.00 and 1.0 V (vs. Ag/AgCl) of polymer P4 thin film on the ITO-coated glass substrate in a 0.1 M LiClO<sub>4</sub>/CH<sub>3</sub>CN solution with a cycle time of 8 s.

**Fig. 6** A typical photocurrent (A) and photovoltage (B) response for P3 immobilized ITO glass upon exposure to light at room temperature.

**Fig. 7** Pictorial representations of the electron density in the frontier molecular orbitals of repetition units for P1 to P5 in the order.

Table 1 Thermal properties and innerent viscosity of the Pis						
	т <sup>с</sup>	т <sup>с</sup>	т <sup>с</sup>	Char	Poly(amic acid)	
	1 5%	1 20%	1 50%	Yield(%) <sup>b</sup>	$\eta (dL/g)^a$	
P1	580	632	>800	68	0.74	
P2	576	628	>800	67	0.78	
P3	479	593	>800	66	0.82	
P4	528	688	>800	78	0.73	
P5	549	637	>800	74	0.76	

Table 1 Thermal properties and inherent viscosity of the PIs

<sup>a</sup> Measured at a polymer concentration of 0.5 g/dL in DMF at 30 °C.

<sup>b</sup> Measured at 750 °C in nitrogen.

<sup>c</sup> The decomposition temperatures ( $T_{ds}$ ) at 5 %, 20 % and 50 % weight losses in nitrogen.

	$\lambda^{abs}_{film}$	$\lambda^{\scriptscriptstyle PL}_{\scriptscriptstyle solution}$	$\lambda^{abs}_{onset}$	$\phi^{\rm c}{}_{\rm (DMF)}$	$E^{\it peak}$ vs	$E_{\mathit{onset}}^{\mathit{peak}}$	$E_{\rm HOMO}^{\it electro}$	$E_{\it LUMO}^{\it electro}$	$E_g^{\it film}$	$E_{HOMO}^{quntum}$	$E_{LUMOH}^{quntum}$	$E_{g}^{quntum}$
	(nm) <sup>a</sup>	(nm) <sup>a</sup>	(nm) <sup>b</sup>	%	d Ag/AgCl	vs Ag/AgCl	(ev) <sup>f</sup>	(ev) <sup>f</sup>	(ev) <sup>e</sup>	(ev) <sup>g</sup>	(ev) <sup>g</sup>	(ev) <sup>g</sup>
P1	319.6	504	447.3	0.0294	0.547	0.424	-4.774	-2.002	2.772	-5.109	-3.721	1.387
P2	343.9	506	427.7	0.0546	0.534	0.409	-4.759	-1.860	2.899	-5.031	-3.343	1.688
P3	336.1	518	412.5	0.1985	0.552	0.413	-4.763	-1.758	3.006	-5.039	-3.053	1.986
P4	335.6	511	424.8	0.1683	0.540	0.422	-4.772	-1.853	2.919	-5.042	-3.714	1.328
P5	330	515	421.0	0.3566	0.528	0.451	-4.801	-1.856	2.945	-5.047	-3.417	1.630

# Table 2 Optical and electrochemical properties for PIs

<sup>a</sup> UV-vis absorption and PL spectra measurements in DMF at room temperature.

 $^{b}$   $\lambda_{onset}$  of the polymer film.

<sup>c</sup> The quantum yield was calculated with quinine sulfate as the standard ( $\phi$ =54.6 %).

 $^{d}\,E_{1/2}\!\!:$  average potential of the redox couple peaks

 $^{e} E_{gap} = 1240 \; / \lambda_{onset}$ 

<sup>f</sup> The HOMO energy levels were calculated from cyclic voltammetry and were referenced to ferrocene (4.8 eV).

 $E_{LUMO} = E_{HOMO} - E_g; E_{ox/onset (Fc/Fc vs. Ag/AgCl)} = 0.45 V.$ 

<sup>g</sup> Theoretical calculation of the polymers

PIs						
I	Polymer code <sup>a</sup>	$\lambda \left( nm ight) ^{b}$	$\delta_{OD}{}^c$	$Q (mC/cm^2)^d$	$\eta(cm^2/C)^e$	
	P1	428	0.7907	15.24	51.83	
	P2	430	0.7914	2.037	388.2	~
	P3	428	0.9193	6.9	133.23	
	P4	425	0.7990	8.6	111.8	
	P5	425	1.0538	6.89	150.9	

Fable 3 Optical and Electrochemical Data	Collected for Coloration Efficiency Measurements of
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<sup>a</sup> Switching between 0.0 and 1.10 V for P1–P5 (V vs. Ag/AgCl).

<sup>b</sup> The given wavelength where the data were determined.

<sup>c</sup> Optical density change at the given wavelength.

<sup>d</sup> Injected charge, determined from the in situ experiments.

 $^{e}$  Coloration efficiency is derived from the equation  $\eta{=}\delta_{OD}/Q.$ 

















1. The polymer films showed reversible electrochemical oxidation, high coloration efficiency (CE), low switching time.

2. The polyimides revealed multielectrochromic characteristic.

3. The polyimides were the near-infrared (NIR)-absorbing electrochromic materials

# **Supporting information**

# **Multicoloured Near-Infrared Electrochromic Polyimides:**

# Synthesis, Electrochemical, and Electrochromic Properties

Jiwei Cai<sup>a</sup>, Haijun Niu<sup>a</sup>\*, Ping Zhao<sup>b</sup>, Yan Ji<sup>a</sup>, Lina Ma<sup>a</sup>, Cheng Wang<sup>a</sup>, Xuduo Bai<sup>a</sup>, Wen Wang<sup>c</sup>

<sup>a</sup> Key Laboratory of Functional Inorganic Material Chemistry, Ministry of Education, Department of Macromolecular Materials and Engineering, Heilongjiang University, Harbin 150086, P R China

<sup>b</sup>Key Laboratory for Advanced Materials and Institute of Fine Chemicals, East China University

of Science and Technology, Shanghai 200237, PR China

<sup>c</sup>School of Material Science and Engineering, Harbin Institute of Technology, Harbin 150080, P R

China

<sup>\*</sup>Corresponding author: Tel: 086-13684501571; Fax: 086-0451-86608131;email:

haijunniu@hotmail.com



Fig. S1 <sup>1</sup>H NMR spectra of polyamic acids



Fig. S2 Repetitive CV scanning of the P2-P5 film on the ITO/glass electrode in 0.1 mol  $L^{-1}$ LiClO<sub>4</sub>/MeCN solution over the potential range from 0 to 1.6 V at a scan rate of 50 mV s<sup>-1</sup>.



Fig. S4 Electrochromic behavior of P2-P5 thin film (in  $CH_3CN$  with 0.1 mol L<sup>-1</sup> LiClO<sub>4</sub> as the supporting electrolyte) at 0.0 -1.6 (V vs. Ag/AgCl couple as reference). The inset shows the photographic images of the film at indicated applied voltages.



Fig. S5 Current consumption between 0.0 and 1.0 V (vs. Ag/AgCl) of polymer P1, P2, P3, P5, thin film on the ITO-coated glass substrate in a 0.1 mol  $L^{-1}$  LiClO<sub>4</sub>/CH<sub>3</sub>CN solution with a cycle time

of 8 s.