A comparative study of redox-active, ambipolar electrochromic triphenylamine-based polyimides prepared by electrochemical polymerization and conventional polycondensation methods†

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N,N′-Bis(4-diphenylaminophenyl)pyromellitimide (TPA-PMDI) was synthesized from the condensation reaction of 4-aminotriphenylamine with pyromellitic dianhydride (PMDA). The triphenylamine-diimide TPA-PMDI could be electrochemically polymerized into ambipolar, redox-active polyimide films on the electrode surface in an electrolyte solution via the coupling reactions between triphenylamine radical cations. The electro-generated polyimide films (coded as PI-E) exhibit reversible redox processes and stable color changes upon electro-oxidation, changing from a colorless neutral form to orange-yellowish and blue oxidized states. The film could also display pale green and pink cathodic coloring upon electro-reduction. Electrochromic devices using the electropolymerized film as an active layer were also fabricated as preliminary investigations for electrochromic applications. For a comparative study, a structurally similar polyimide (PI-C) was prepared by a conventional two-step condensation from N,N′-bis(4-aminophenyl)-N,N′-diphenyl-4,4′-biphenyldiamine with PMDA, and its spectroscopic, electrochemical and electrochromic properties were compared with those of the electro-synthesized PI-E.

Introduction

Aromatic polyimides are an important class of high-performance polymers because of their outstanding thermal stability, chemical resistance, dimensional stability and mechanical properties.1–3 They are commercially important materials that are used extensively as dielectric films and coatings in a wide range of high-technology applications. Incorporating a specific functionality into polyimide backbones leads to various functional materials that exhibit certain advantageous properties, such as proton conductivity,4 high refractive index,5 photo-sensitivity,6 gas separation,7 electrochromism,8 and memory characteristics.9 Studies in the field of functionalization of polyimides continue to be actively developed, as evidenced from the appearance of a large number of publications on this subject in the past few years.10

Triphenylamine (TPA) and its derivatives with pseudo-three-dimensional conjugated architecture constitute an attractive class of materials because of their easy oxidizability, good charge transport, and high thermal and morphological stability.11 Owing to their attractive electroactive and photoactive properties, various TPA derivatives and polymers are developed for optoelectronic applications, such as electrophotography, electroluminescent diodes, field-effect transistors, solar cells, memory devices, and electrochromic devices.12 TPAs can be easily oxidized to form stable radical cations as long as the para-position of the phenyl rings is protected,13 and the oxidation process is always associated with a strong color change.14 The synthesis and characterization of polyimides containing TPA units were first reported by the Imai group in 1992.15 However, the electrochromic function associated with the TPA-based polyimides was reported in our work published in 2005.16 Since then, a variety of high-performance polymers (typically, aromatic polyamides and polyimides) carrying the redox-active TPA unit have been developed and became a new and attractive family of anodically electrochromic materials.17

Conventional aromatic polyimides such as that derived from the condensation of pyromellitic dianhydride (PMDA) and 4,4′-oxydianiline (ODA) have been shown to be electrochemically active.18 The redox sites are the diimide functional groups as shown by the electrochemical and spectroscopic results for the polyimides and imide model compounds.19 The reduced forms of some polyimides are stable and exhibit strong absorption in the visible region. Therefore, several aromatic polyimides such as polypyromellitimides and poly-
naphthalimides containing TPA or triarylamine moieties have been reported to be ambipolar electrochromics. In addition to the conventional polycondensation route, it has also been demonstrated that electrochromic polyimides can be facilely prepared from imide ring-preformed compounds with triphenylamine termini via electrochemical oxidative coupling reactions. In this work, we extend our effort to the electrochemical synthesis and characterization of a novel ambipolar TPA-based polyimide (coded as PI-E) from \(N,N'\)-bis(4-diphenylaminophenyl)pyromellitimide (coded TPA-PMDI). In addition, a structurally similar polyimide (coded as PI-C) was prepared from \(N,N'\)-bis(4-aminophenyl)-\(N,N'\)-diphenyl-4,4'-biphenyldiamine and PMDA by a conventional two-step condensation, and its electrochemical and electrochromic properties were compared with those of the electro-synthesized polyimide. It was found that the PI-E sample displays almost the same UV and IR absorption spectra, CV diagrams, spectroelectrograms, and electrochromic color changes upon oxidation and reduction. These results together with the model compound study should yield reliable evidence to prove the structural similarity between PI-E and PI-C. This work is the first that is intended to help alleviate the structural information gap of the electrochemically generated triphenylamine-based polyimides.

**Experimental section**

**Materials**

Diphenylamine (Acros), phthalic anhydride (TCI), \(p\)-fluoronitrobenzene (Acros), sodium hydride (Alpha), hydrazine monohydrate (TCI), and 10% palladium on activated carbon (Pd/C, Fluka) were used as received. \(N,N\)-Dimethylacetamide (DMAc, TEDIA) was dried over calcium hydride for 24 h, distilled under reduced pressure, and stored over 4 Å molecular sieves in a sealed bottle. Pyromellitic dianhydride (PMDA, TCI) was purified by vacuum sublimation before use. Tetrabutylammonium perchlorate (Bu4NClO4, TCI) was recrystallized from ethyl acetate under a nitrogen atmosphere and

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**Scheme 1** Synthesis of TPA-PMDI and its derived polyimide PI-E via electropolymerization.

**Scheme 2** Synthesis of diamine monomer 3 and polyimide PI-C.
then dried in vacuo prior to use. According to a previously described procedure,16 4-aminotriphenylamine (TPA-NH₂) was synthesized by the sodium hydride-mediated condensation of diphenylamine with p-fluoronitrobenzene, followed by a Pd/C-catalyzed hydrazine reduction. N,N′-Bis(4-diphenylaminophenyl)pyromellitimide (TPA-PMDI) could be readily obtained from the condensation of PMDA with two equivalent amount of TPA-NH₂. The synthetic details and characterization data of TPA-PMDI are included in the ESI. Its synthetic details and characterization data are also included in the ESI.† All other reagents and solvents were used as received from commercial sources.

Measurements
Infrared (IR) spectra were recorded on a Horiba FT-720 FT-IR spectrometer. 1H and 13C NMR spectra were recorded on a Bruker Avance III HD-600 MHz NMR spectrometer with tetramethylsilane (TMS) as an internal standard. Electrochemical measurements were performed with a CH Instruments 750A electrochemical analyzer. The polymers were electropolymerized from 1 × 10⁻³ M monomers in a 0.1 M Bu₄NClO₄/dichloromethane (CH₂Cl₂) solution via repetitive cycling at a scan rate of 50 mV s⁻¹. Voltammograms are presented with the positive potential pointing to the left and with increasing anodic currents pointing downwards. Cyclic voltammetry (CV) was conducted with the use of a three-electrode cell in which ITO (polymer film area about 0.7 cm × 3.0 cm) was used as a working electrode. A platinum wire was used as an auxiliary electrode. All cell potentials were obtained with the use of a reference electrode. A home-made Ag/AgCl, KCl (sat.) reference electrode. Ferrocene electrode. All cell potentials were obtained with the use of a three-electrode cell in which ITO (polymer film area about 0.7 cm × 2 cm), and the film was rinsed with plenty of acetone for the removal of the unreacted monomer, inorganic salts and other organic impurities formed during the process.

Conventional synthesis of polyimide PI-C
PI-C was synthesized from N,N′-bis(4-aminophenyl)-N,N′-diphenyl-4,4′-biphenyldiamine (3) and PMDA by using the conventional two-step method via the thermal imidization reaction. The diamine monomer 3 (0.704 g; 1.35 mmol) was dissolved in 9.5 mL of CaH₂-dried DMAc in a 50 mL round bottom flask. Then, PMDA (0.296 g; 1.35 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 6 h to yield a viscous poly(amic acid) solution. The inherent viscosity of the resulting poly(amic acid) was 0.87 dL g⁻¹, measured in DMAc at a concentration of 0.50 g dL⁻¹ at 30 °C. The obtained poly(amic acid) solution was transferred to a 9 cm glass Petri-dish, which was placed in an oven at 90 °C for 3 h. The poly(amic acid) film was subsequently converted to a PI-C film by successive heating under vacuum at 100 °C for 1 h, 200 °C for 1 h, and 300 °C for 1 h. The IR spectrum of PI-C (film) exhibited characteristic imide absorption bands at 1780 and 1717 cm⁻¹ (imide ring C=O stretching).

Electrosynthesis of polyimide PI-E
Electrochemical polymerization was performed with a CH Instruments 750A electrochemical analyzer. The PI-E films were synthesized from a solution of 1 × 10⁻³ M monomer TPA-PMDI and 0.1 M Bu₄NClO₄ in dichloromethane (CH₂Cl₂) via cyclic voltammetry repetitive cycling at a scan rate of 50 mV s⁻¹ for five cycles. The polymer was deposited onto the surface of the working electrode (ITO/glass surface, polymer film area about 0.7 cm × 2 cm), and the film was rinsed with plenty of acetone for the removal of the unreacted monomer, inorganic salts and other organic impurities formed during the process.

Scheme 3  Synthesis of model compounds M₁ and M₂.
Fabrication of electrochromic devices

Electrochromic polymer films were electrodeposited on the ITO-coated glass substrate by using the electropolymerization method described above. A gel electrolyte based on poly (methyl methacrylate) (PMMA) (M_w: 120 000) and TBABF_4 was plasticized with propylene carbonate (PC) to form a highly transparent and conductive gel. PMMA (1.25 g) was dissolved in PC (2.75 g), and TBABF_4 (0.15 g) was added to the polymer solution as a supporting electrolyte. The mixture was then gently heated until gelation. The gel electrolyte was spread on the polymer-coated side of the electrode, and the electrodes were sandwiched. Finally, a Kapton tape (a PMDA/ODA polyimide film) was used to seal the device.

Results and discussion

Synthesis of monomers and model compounds

As shown in Scheme 1, the diimide end-capped with two triphenylamine (TPA) units, TPA-PMDI, could be easily prepared by the condensation of PMDA with two equivalent amount of 4-aminotriphenylamine (TPA-NH_2). The triphenylamine-containing aromatic diamine monomer 3 was synthesized by a two-step reaction sequence as shown in Scheme 2. In the first step, the intermediate dinitro compound N,N,N′-bis(4-nitrophenyl)-N,N′-diphenyl-4,4′-biphenyldiamine (2) was obtained in a 77% yield by the nucleophilic aromatic fluoro-displacement reaction of p-fluoronitrobenzene with the sodium amide of N,N′-diphenyl-4,4′-biphenyldiamine formed in situ by the treatment of sodium hydride (NaH). Then, the target diamine monomer 3 was prepared in an 89% yield by the Pd/C-catalyzed hydrogenation of dinitro compound 2 in DMF. As depicted in Scheme 3, model compounds M_1 and M_2 were readily obtained from the condensation reactions of phthalic anhydride with TPA-NH_2 and compound 3, respectively. The chemical structures of all the target compounds were confirmed by FT-IR and NMR spectroscopic techniques.
The IR spectra of TPA-PMDI (1), M₁ and M₂ exhibited characteristic absorption peaks around 1769–1715 and 1736–1714 cm⁻¹ due to the five-membered imide ring symmetric and asymmetric C═O pair stretching (Fig. S1 and S2) (ESI).† The dinitro compound 2 shows the characteristic absorption of nitro groups at around 1580 and 1320 cm⁻¹ (–NO₂ asymmetric and symmetric stretching). After reduction, the characteristic absorption of nitro groups disappeared and the amino group shows the typical –NH₂ stretching absorption pair at 3460 and 3370 cm⁻¹ as shown in the IR spectrum of diamine monomer 3.

Fig. S3 to S9 (ESI)† illustrate the ¹H and ¹³C NMR spectra of these compounds. The ¹H NMR spectra of compounds 2 and 3 confirm that the nitro groups have been completely trans-

Scheme 4  Proposed structure of PI-E resulting from the electrochemical oxidative coupling of TPA-PMDI.

Fig. 4  Cyclic voltammograms of model compounds (a) M₁ and (b) M₂ in 0.1 M Bu₄NClO₄/CH₂Cl₂ at a scan rate of 50 mV s⁻¹.
formed into amino groups by the high field shift of the protons Hg and the resonance signals at around 5.08 ppm corresponding to the amino protons Hh. Assignments of all proton and carbon signals were assisted by the two-dimensional (2-D) NMR spectra. These spectra agree well with the proposed molecular structures.

### Conventional synthesis of PI-C

Polyimide PI-C was synthesized from diamine monomer 3 and PMDA through a conventional two-step method. The inherent viscosity of the resulting poly(amic acid) precursor was 0.87 dL g$^{-1}$, measured in DMAc at a concentration of 0.50 g dL$^{-1}$ at 30 °C. The molecular weight was sufficiently high to permit the casting of a flexible and tough poly(amic acid) film, which was subsequently converted into a flexible and strong polyimide film (see the photo in Scheme 2) by stage-by-stage heating from 100 °C to 300 °C. The IR spectrum of PI-C (film) exhibited the characteristic imide absorption bands at 1780

Fig. 5 UV-vis absorption spectra of TPA-PMDI in dichloromethane and the PI-E and PI-C films on ITO-glass substrates.

### Table 1: Electrochemical properties of PI-E and PI-C

<table>
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<tr>
<th>Polymer code</th>
<th>λ$_{\text{max}}$ (nm)</th>
<th>λ$_{\text{onset}}$ (nm)</th>
<th>Oxidation potential$^b$ (V)</th>
<th>Reduction potential$^c$ (V)</th>
<th>Optical bandgap$^d$ (eV)</th>
<th>Energy level$^e$ (eV)</th>
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<tr>
<td>PI-E</td>
<td>352</td>
<td>424</td>
<td>$E_{\text{Ox1}}$</td>
<td>$E_{\text{Red1}}$</td>
<td>$E_g$</td>
<td>$E_{\text{HOMO}}$</td>
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<td></td>
<td></td>
<td></td>
<td>$E_{\text{Ox2}}$</td>
<td>$E_{\text{Red2}}$</td>
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<td>$\text{LUMO}$</td>
</tr>
<tr>
<td>PI-C</td>
<td>352</td>
<td>424</td>
<td>0.79</td>
<td>0.87</td>
<td>0.98</td>
<td>2.92</td>
</tr>
</tbody>
</table>

$^a$ UV-vis absorption maximum and onset for the polymer films. $^b$ Calculated from the first CV scan, versus Ag/AgCl in acetonitrile at a scan rate of 50 mV s$^{-1}$. $^c$ Calculated from the first CV scan, versus Ag/AgCl in DMF at a scan rate of 50 mV s$^{-1}$. $^d$ Optical bandgap calculated from the absorption edge of the polymer film: $E_g = \frac{1240}{\lambda_{\text{onset}}}$. $^e$ $E_{\text{HOMO}} = E_{\text{Ox1}1} + 4.8 - 0.44$ (eV); $E_{\text{LUMO}} = E_{\text{HOMO}} - E_g$.

Fig. 6 Cyclic voltammograms of (a) the PI-E film and (b) the PI-C film on the ITO-coated glass substrate in 0.1 M Bu$_4$NClO$_4$/CH$_2$Cl$_2$ (for the anodic process) and DMF (for the cathodic process) at a scan rate of 50 mV s$^{-1}$. 

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and 1724 cm\(^{-1}\) (imide ring C=O stretching), as displayed in Fig. 1. The glass-transition temperature (\(T_g\)) of PI-C was measured at 328 °C by DSC. As shown in Fig. 2, PI-C had no significant weight loss below 600 °C under a nitrogen atmosphere. The decomposition temperature (\(T_d\)) at which a 10% weight loss of PI-C occurred in nitrogen was measured at 660 °C. The thermal analysis results indicate that PI-C exhibits high thermal stability, which in turn is beneficial to increase the service time in device application and enhance the morphological stability of the spin-coated films.

**Electrochemical synthesis of PI-E from TPA-PMDI**

The electrochemical activity of the monomer and model compounds was investigated by cyclic voltammetry (CV) using a \(1 \times 10^{-3}\) M solution in 0.1 M Bu\(_4\)NClO\(_4\)/CH\(_2\)Cl\(_2\) at a scan rate of 50 mV s\(^{-1}\). Fig. 3(a) presents the first two CV scans of TPA-PMDI between 0 and 1.4 V. In the first scan, an oxidation wave at 1.24 V was observed. In the subsequent scan, a new oxidation wave appeared at 0.97 V, which is a typical oxidation wave of the benzidine group, indicating the occurrence of the oxidative coupling between the TPA units. As the CV scan continued [Fig. 3(b)], the current intensity of redox waves increased which indicates the formation of the electrochemically active polymeric film on the electrode surface. After only 5 CV scans, a visible polymer film (coded as PI-E) of TPA-PMDI was deposited on the electrode surface. The oxidative coupling of TPA oxidation produces a tetraphenylbenzidine (TPB) unit that shows more extended \(\pi\)-conjugation (Scheme 4). As a

![Cyclic voltamograms of (a) the PI-E film and (b) the PI-C film on the ITO-coated glass substrate in 0.1 M Bu\(_4\)NClO\(_4\)/DMF.](image)

![Spectroelectrochemistry of (a) the PI-E film (thickness: 200 ± 100 nm) and (b) the PI-C film (thickness: 200 ± 30 nm) on the ITO-coated glass substrate in 0.1 M Bu\(_4\)NClO\(_4\)/CH\(_2\)Cl\(_2\) between 0 V and 1.2 V.](image)
result, TPB has a lower oxidation potential than the original TPA unit. The result is consistent with that reported in the pioneering studies on the anodic oxidation of aromatic amines by Nelson and Adams et al.\textsuperscript{13} In the electrochemical oxidation of triphenylamines in an organic solvent such as acetonitrile, it has been proposed that the initial step is the formation of the cation radical; two of these then couple in solution to form a substituted TPB.\textsuperscript{13}

The CV behaviors of model compounds $M_1$ and $M_2$ are depicted in Fig. 4. In the first scan of $M_1$, only one oxidation peak at 1.25 V was observed [Fig. 4(a)], which is attributed to the oxidation of the TPA unit. Upon the first reverse negative potential scan, two cathodic peaks at ca. 0.99 V and 0.81 V were observed. In the second scan, a new oxidation peak occurred at 0.90 V, which was the complementary anodic process of the cathodic peak at 0.81 V. The observation of a new redox couple in the second and subsequent potential scans implies that the TPA radical cations were involved in a very fast electrochemical reaction that produced a substance that was easier to oxidize than the parent compound. The additional redox peaks most likely resulted from the coupling reaction of the TPA units with a TBP unit. The dimer seems to be the major product during the oxidation process of $M_1$ because no significant increase in redox wave current density was observed as the CV scan continued. This can be further evidenced by the redox behavior of model compound $M_2$ [Fig. 4(b)]. The oxidation and reduction peak potentials of $M_2$ are very similar to those of the product formed after several CV scans of $M_1$. Thus, it is reasonable that the molecular chain of the polymer produced by the electrochemical polymerization of TPA-PMDI is predominantly linear. As illustrated in Fig. 1, the IR spectrum of an electrodeposited thin film of PI-E is essentially identical to that of PI-C.

**Polymer properties**

**Optical properties.** The UV-vis absorption profiles of TPA-PMDI in CH$_2$Cl$_2$ and the PI-E and PI-C films on ITO-glass are illustrated in Fig. 5. In general, the polymer film of PI-E shows a slight red-shift of the absorption maximum and onset compared to the monomer TPA-PMDI because of the increased conjugation length. The spectra of PI-E and PI-C showed the same absorption onsets at 424 nm, corresponding to a band gap of 2.92 eV. They also displayed the same wavelengths at the absorption maxima. This also implies that PI-E and PI-C possess a similar molecular structure.

**Electrochemical properties.** The electrochemical properties of PI-E and PI-C were investigated by cyclic voltammetry (CV) conducted with the cast film on an ITO-coated glass slide as the working electrode in dichloromethane (CH$_2$Cl$_2$), using 0.1 M of tetrabutylammonium perchlorate (TBAP) as a supporting electrolyte. The derived oxidation potentials are summarized in Table 1. The CV diagrams for polyimides PI-C and PI-E are compared in Fig. 6. These polyimides exhibited two reversible oxidation redox peaks, indicating that electrons could be successively removed from the two different redox centers bridged by the 4,4′-biphenylene unit. In addition, the cathodic redox behavior of the PI-E and PI-C films was investigated by CV using a platinum wire as a working electrode in dimethylformamide (DMF) and 0.1 M of TBAP as a supporting electrolyte under a nitrogen atmosphere. The CV curves of PI-E and PI-C also revealed two reversible reduction redox steps at $E_{pc} = -0.73$ and $-1.38$ V, respectively.

Both of these two polyimides showed reversible redox behavior with good cycling stability during the anodic CV scanning. However, upon cathodic scanning, they revealed a little different redox stability. As shown in Fig. 7(a), we can see that the PI-E film is still quite stable in the second CV scan. Conversely, as shown in Fig. 7(b), PI-C greatly lost its electrochemical activity and most of the cast film delaminated/dissolved during the second cathodic scanning. The reason is not very clear for this result; however, it could possibly be related to the firmly adhered PI-E film on the electrode surface during
electropolymerization. It demonstrates that the electro-generated polyimide film seems to be more suitable for the cathodically electrochromic material.

**Spectroelectrochemical and electrochromic properties of the polyimide films.** The electro-optical properties of the polymer films were investigated using the changes in the electronic absorption spectra under the applied potentials. During the test, a three-electrode configuration identical to that used in the CV experiments was used for applying the potential to the PI-C casting film or the electrodeposited PI-E film on the ITO-glass substrates immersed in a 0.1 M Bu$_4$NClO$_4$/CH$_2$Cl$_2$ (oxidation) or 0.1 M Bu$_4$NClO$_4$/DMF (reduction) electrolyte solution. When the films were electrochemically oxidized or reduced, a strong color change was generally observed in them. The results of the PI-E film upon electro-oxidation (p-doping) are presented in Fig. 8(a). The corresponding surface plot diagram for the absorption-wavelength-applied potential correlation of the PI-E film is illustrated in Fig. 9(a). In the neutral form, at 0 V, the film exhibited strong absorption at wavelengths around 320 and 353 nm, characteristic for triarylamine, but it was almost colorless in the visible region. As the applied voltage was raised to 0.95 V, the intensity of the absorption bands around 320 and 353 nm decreased gradually, and the growth of a new peak at 490 nm was observed. At the same time, the film color turned into pale orange. As the potential increased more positively to 1.2 V, the absorbance at 490 nm decreased and a strong absorption band centered at 740 nm appeared. Meanwhile, the film changed its color from orange to blue. As shown in Fig. 8(b) and 9(b), the PI-C film showed similar spectral and color changes as compared to PI-E because of the strong similarity in their chemical structure. Clearly, the spectral and color changes of these films are associated with the oxidation processes occurring on the TPB units.

Fig. 10(a) and 11(a) show the spectral changes of the polymer films of PI-E upon cathodic reduction (n-doping). The redox reactions are believed to occur on the carbonyl groups of the PMDI moieties of the polymer backbones.18 The first one-electron reduction yields the anion radical form followed by a second one-electron step generating the dianion form. Upon doping at −0.9 V, a new absorption band attributed to the anion radical form of the diimide unit appeared at 722 nm where the polymer film changed its color from colorless to pale green. During the second reduction process, the band attributed to the anion radical significantly decreased in intensity, and a new peak at 560 nm appeared as the applied voltage was more negative than −1.4 V. According to this spectral change, the film color turned from pale green to bright pink. It was also found that the PI-C film exhibited almost the same absorption and color changes upon electro-reduction [Fig. 10(b) and 11(b)].
Surface morphology. The morphological properties of the polyimide films were studied by scanning electron microscopy (SEM) and the images are shown in Fig. 12. As shown in Fig. 12(a), the surface of the PI-E film is very rough and exhibits a number of clusters accompanied by lots of micropores. The porous structure might arise from the dissolution of the adhered electrolyte, unreacted monomer, and oligomers. This surface morphology could affect the stability and electrochromic properties of the polymer film. The porous structure might be more favorable for the movement of doping ions into and out of the polymer film, which could be beneficial for the improvement of the switching time. In contrast, the PI-C cast film presents a very smooth surface without visible defects [Fig. 12(b)].

Electrochromic switching. For the electrochromic switching studies, the polymer films were electrodeposited on ITO-coated glass slides in the same manner as described above, and chronoamperometry and absorbance measurements were performed. While the films were switched, the absorbance at selected wavelengths was monitored as a function of time with UV-vis-NIR spectroscopy. Fig. 13 depicts the optical transmittance of the PI-E films at 490 nm and the PI-C films at 485 nm as a function of time by applying square-wave potential steps between 0 and 1.0 V with a pulse time of 30 s (for PI-E) and 40 s (for PI-C).
The electrochromic coloration efficiencies (CE = ΔOD/Qd) after various switching steps of the polyimide films are summarized in Tables S1 and S2 (ESI).† The electrochromic film of PI-C was found to exhibit good coloration efficiencies up to 183 cm² C⁻¹ at 485 nm. It was confirmed that the PI-C film does not lose its electro-optical activity significantly and

### Table 2  Electrochromic properties of PI-E and PI-C

<table>
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<tr>
<th>Polymer code</th>
<th>λ&lt;sub&gt;max&lt;/sub&gt;&lt;sup&gt;a&lt;/sup&gt; (nm)</th>
<th>Δ%T</th>
<th>ΔOD&lt;sup&gt;b&lt;/sup&gt;</th>
<th>Q&lt;sub&gt;d&lt;/sub&gt;&lt;sup&gt;c&lt;/sup&gt; (mC cm&lt;sup&gt;-2&lt;/sup&gt;)</th>
<th>CE&lt;sup&gt;e&lt;/sup&gt; (cm² C⁻¹)</th>
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<tr>
<td>PI-E</td>
<td>490</td>
<td>50</td>
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<td>3.34</td>
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<td>740</td>
<td>87</td>
<td>0.97</td>
<td>7.93</td>
<td>122</td>
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<tr>
<td>PI-C</td>
<td>485</td>
<td>68</td>
<td>0.72</td>
<td>3.93</td>
<td>183</td>
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<tr>
<td></td>
<td>750</td>
<td>69</td>
<td>0.53</td>
<td>9.54</td>
<td>56</td>
</tr>
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</table>

<sup>a</sup>Wavelength of absorption maximum. <sup>b</sup>Time for 90% of the full-transmittance change. <sup>c</sup>Optical density (ΔOD) = log[T<sub>bleached</sub>/T<sub>colored</sub>], where T<sub>colored</sub> and T<sub>bleached</sub> are the maximum transmittance in the oxidized and neutral states, respectively. <sup>d</sup>Q<sub>d</sub> is ejected charge, determined from the in situ experiments. <sup>e</sup>Coloration efficiency (CE) = ΔOD/Qd.

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Fig. 14  CV and electrochromic behaviors of the electrochromic devices based on PI-E (1.25 g PMMA in 2.75 mL DMF with 0.15 g TBABF<sub>4</sub> as the supporting electrolyte) on the ITO-coated glass substrate (thickness: 200 ± 100 nm) at indicated applied potentials: (a) single layer on the anode and (b) double layers on both anode and cathode.
trochromic coloration which might be more favorable for the movement of doping for the 90% oxidized blue states in 21.1 s. The faster response time for the coloring process [Fig. S10(b) and S11(b)] (ESI). In contrast, PI-C attained 90% of the complete coloring in 14.7 s. The optical contrast measured as Δ%T of PI-E between neutral colorless and oxidized orange states was found to be 50% at 490 nm. When the applied voltage was stepped between 0 and 1.3 V, the PI-E exhibited Δ%T up to 87% at 740 nm for oxidized blue states and required 14.6 s for the coloring process [Fig. S10(b) and S11(b)] (ESI). In contrast, PI-C attained 90% oxidized orange states in 22.5 s and reached 90% oxidized blue states in 21.1 s. The faster response time for the PI-E film can be attributed to its porous structure, which might be more favorable for the movement of doping anions into and out of the polymer film. In addition, the electrochromic coloration efficiency (CE; η) can be calculated via optical density using the equation η = ΔOD/Qd, where ΔOD is the optical absorbance change, and Qd (mC cm−2) is the inject/ejected charge during a redox step. Based on this equation, the CE values of PI-E estimated from the data shown in Table 2 were found to be 149 cm2 C−1 at 490 nm and 122 cm2 C−1 at 740 nm. The CE value of PI-C was calculated to be 183 cm2 C−1 at 485 nm and 56 cm2 C−1 at 750 nm by chrononamperometry.

Electrochromic devices

Finally, we fabricated single-layer electrochromic cells as preliminary investigations of the PI film for electrochromic applications. The PI-E films were electrodeposited on ITO-coated glass, thoroughly rinsed, 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, a commercial Kapton PI tape was applied to seal the device. An electrochromic device based on PI-E was fabricated which is shown in Fig. 14(a). The PI-E film is colorless in the neutral form. When the applied voltage was increased to 2.6 V, the color changed to orange. Upon further oxidation at an applied potential of 3.1 V, the color changed to blue due to electro-oxidation. Then, when the applied voltage was reduced to ~2.6 V and ~3.1 V, the color changed to pale green and pink due to electro-reduction. When the potential was subsequently set back at 0.0 V, the polymer film gradually turned back to its original color.

In addition, we also fabricated a dual-layer electrochromic device. The ITO-glass electrodeposited with the PI-E film was employed as both anode and cathode. As shown in Fig. 14(b), the two electrodes exhibited high matched performance. The driving voltage of the device decreased effectively. In the meantime, the device could change to a mixed color of the two electrodes. For example, this device can switch to purple color at a reduced voltage of 2.3 V. This color is a combination from the oxidized TBP units (blue color) and the reduced PMDI moieties (pink color). The decrease in the working voltage of this device may be due to the overall charge balance between the two electrodes; the pyromellitimide segments have the capability to accept electrons from the TBP units and then the resulted inside radical anions or dianions could donate electrons back to TBP radical cations or dications during the reduction process.

Conclusions

Bis(triphenylamine)pyromellitimide, TPA-PMDI, has been successfully synthesized from the condensation reaction of 4-aminophenylamine with pyromellitic dianhydride. A polyimide film with a tetraphenylbenzidine (TPB) segment was successfully electrodeposited onto the ITO electrode surface by the electropolymerization of TPA-PMDI in Bu4NClO4/CH3Cl2. The cyclic voltammograms of the electrodeposited PI-E film exhibit reversible redox processes and stable color changes upon electro-oxidation, changing from a colorless neutral form to orange-yellowish and blue oxidized states. The film could also display pale green and pink cathodic coloring upon electro-reduction. For comparison, a structurally similar polyimide (PI-C) was also synthesized from N,N'-bis(4-aminophenyl)-N,N'-diphenyl-4,4'-biphenyldiamine with PMDA via a conventional two-step route. As compared to PI-E, PI-C exhibited very similar UV-vis and IR absorption profiles, CV diagram, and electrochromic behavior. Electrochromic devices using the PI-E film as an active layer were also fabricated as preliminary investigations for electrochromic applications. A dual polymer electrochromic device fabricated using two electrodes with the electrodeposited PI-E film showed a reduced driving voltage as compared to the single-layer device.

Conflicts of interest

There are no conflicts to declare.

References


