

## Anodically Electrochromic Aromatic Polyimides Containing Dimethoxy-Activated Triphenylamine Moiety

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**Introduction.** Electrochromism can be defined as the reversible change in optical properties of a material resulting from electrochemically induced redox states [1,2]. 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. Electrochromic anti-glare car rear-view mirrors have already been commercialized, with other proposed applications of electrochromic materials including their use in controllable light-reflective or light-transmissive devices for optical information and storage, sunglasses, protective eyewear for the military, controllable aircraft canopies, and glare-reduction systems for offices and smart windows for use in cars and buildings [1-4].

Triarylamine derivatives have attracted considerable interest as hole transport materials for use in multilayer organic electroluminescence (EL) devices due to their relatively high mobilities and their low ionization potentials [5,6]. The feasibility of utilizing spin-coating and ink-jet printing process for large-area EL devices and possibilities of various chemical modifications (to improve emission efficiencies and allow patterning) make polymeric materials containing triarylamine units very attractive. To enhance the hole injection ability of polymeric emissive materials such as poly(1,4-phenylenevinylene)s (PPV) and polyfluorenes (PF), there have been several reports on PPV and PF derivatives involving hole-transporting units such as triarylamine in the emissive  $\pi$ -conjugated core/main chains or grafting them as side chains in a polymer or attaching them onto the polymer chain-ends or the outer surface of dendritic wedges [7-9].

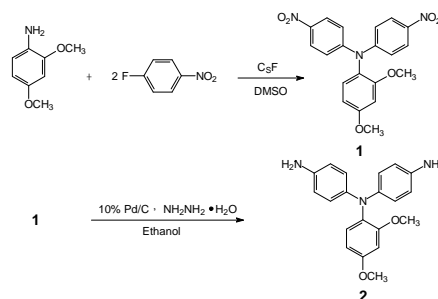
Aromatic polyimides are characterized as highly thermally stable polymers with a favorable balance of physical and chemical properties [10]. However, rigidity of the backbone and strong interchain interactions result in high melting or glass-transition temperatures ( $T_g$ ) and limited solubility in most organic solvents. These properties make them generally intractable or difficult to process, thus restricting their wide-spread applications. To overcome such a difficulty, polymer-structure modification becomes necessary. One of the common approaches for increasing solubility and processability of aromatic polyimides without sacrificing high thermal stability is the introduction of bulky, packing-disruptive groups into the polymer backbone. We have demonstrated that aromatic polyimides containing bulky, propeller-shaped triphenylamine (TPA) unit are amorphous, have increased solubility in organic solvents, and exhibit excellent thin-film-forming capability and high thermal stability [11-13]. Furthermore, these TPA-based polyimides also show interesting electrochromic behavior.

The anodic oxidation pathways of TPA are well studied [14]. The unsubstituted TPA may undergo coupling-deprotonation to form tetraphenylbenzidine after the formation of the initial monocation radical. It has been well established that incorporation of electron-donating substituents such as methoxy group at the para position of TPA prevents the coupling reactions and affords stable radical cations [15-18]. Therefore, we synthesized the diamine monomer, 4,4'-diamino-2,4''-dimethoxytriphenylamine (**2**), and its derived polyimides containing electroactive TPA units with electron-donating methoxy groups *para* and *ortho* substituted on the pendent phenyl ring. We anticipated that the electrochromic films obtained from the present polyimides would exhibit an enhanced stability upon redox switching.

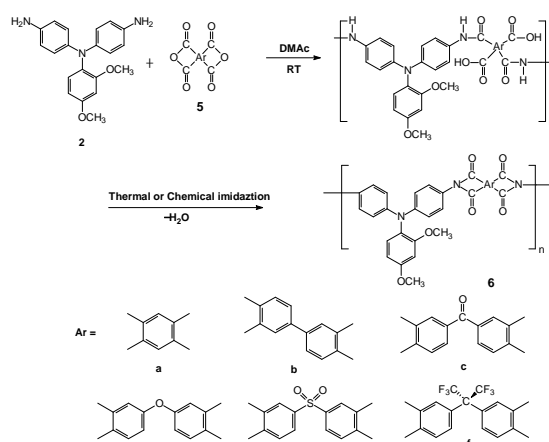
**Synthesis of 2,4-Dimethoxy-4',4''-diaminotriphenylamine (2).** The triphenylamine-containing diamine monomer, 2,4-dimethoxy-4',4''-dinitrotriphenylamine (**2**), was prepared by a two-step reaction sequence outlined in Scheme 1. The target TPA-based diamine monomer **2**, was successfully synthesized by the cesium fluoride (CsF)-mediated double *N*-arylation of 2,4-dimethoxyaniline with two equivalent 4-fluoronitrobenzene followed by catalytic reduction of the intermediate dinitro compound **1** using Pd/C and hydrazine in refluxing ethanol. The proposed molecular structure of **2** was confirmed by elemental analysis, IR and <sup>1</sup>H and <sup>13</sup>C NMR spectroscopy.

**Synthesis of Polyimides.** Polyimides **6a-6f** were prepared through a conventional two-step method by the reactions of equal molar amounts of diamine **2** with various aromatic dianhydrides (**5a** to **5f**) to form poly(amic acid)s, followed by thermal or chemical

cyclodehydration (Scheme 2). The inherent viscosities of the poly(amic acid) precursors were in the range 2.44-2.87 dL/g, indicating the formation of high-molecular-weight polymers. All of these poly(amic acid)s could be cast into flexible and tough films, which were subsequently converted into tough polyimide films by extended heating at elevated temperatures (up to 300°C). The poly(amic acid)s also could be chemically cyclodehydrated to polyimides by treatment with a mixture of pyridine and acetic anhydride.



**Scheme 1.** Synthetic route to the diamine monomer **2**.



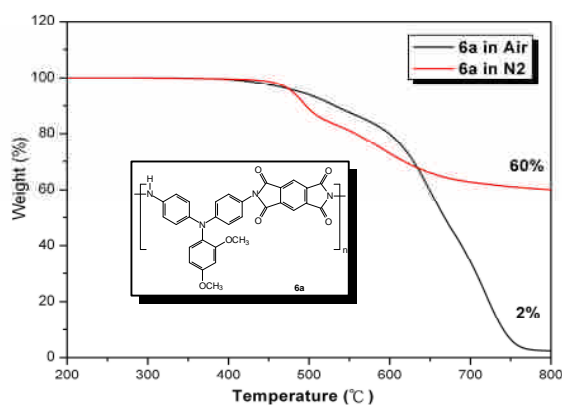
**Scheme 2.** Synthesis of polyimides.

**Thermal Stability.** Thermal properties of all polymers were evaluated by DSC, TMA and TGA. The thermal behavior data of the polyamides are summarized in Table 1.  $T_g$  of these polyamides was obtained from the midpoint temperature of baseline shift on the second DSC heating trace (heating rate = 20°C/min) after rapid cooling from 400°C. All the polyimides except **6a** showed clear  $T_g$  in the range of 269~307°C. The  $T_s$  values of these polymer film samples were also measured with TMA by the penetration method; they were observed in the range 265~308°C. All of the polymers exhibited good thermal stability; the  $T_d$  of polyimides **6a-6f** at a 10% weight loss temperatures were in the range of 470-508 °C in nitrogen and 504-556°C in air, respectively. A typical set of TGA curves of polymer **6a** in air and nitrogen atmospheres are depicted in Fig. 1.

**Table 1.** Thermal Properties of Polyimides

Polymer code	$T_g^a$ (°C)	$T_s^b$ (°C)	$T_d$ at 5 wt % Loss <sup>c</sup> (°C)		$T_d$ at 10 wt % Loss <sup>c</sup> (°C)		Char yield <sup>d</sup> (%)
			In N <sub>2</sub>		In air		
			In N <sub>2</sub>	In air	In N <sub>2</sub>	In air	
<b>6a</b>	— <sup>f</sup>	308	481	488	497	531	60
<b>6b</b>	307	292	478	498	499	552	63
<b>6c</b>	277	274	477	498	500	544	60
<b>6d</b>	269	265	476	508	506	556	50
<b>6e</b>	288	284	454	467	470	504	53
<b>6f</b>	286	280	480	464	508	516	55

<sup>a</sup>The midpoint temperature of baseline shift on the second heating DSC trace (heating rate 20°C/min). <sup>b</sup>Softening temperature measured by TMA using a penetration method at a scan rate of 10°C/min. <sup>c</sup>Decomposition temperature recorded by TGA at a heating rate of 20°C/min. <sup>d</sup>Residual weight percentages at 800°C under nitrogen flow. <sup>e</sup>No discernible transition.



**Figure 1.** TGA thermograms of polyimide **6a** at a heating rate of 20°C/min.

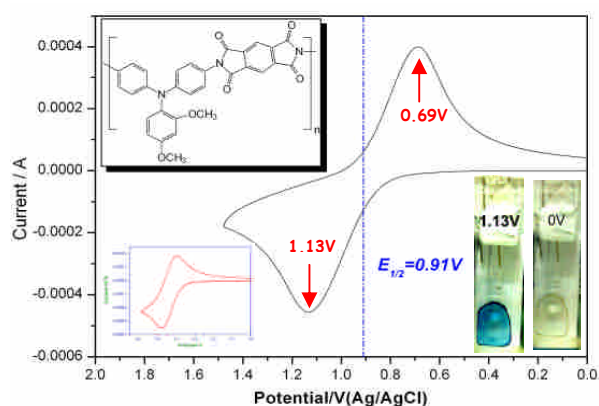
#### Optical, Electrochemical, and Electrochromic Properties.

The optical properties of the polyimides were investigated by UV-vis and PL spectroscopy. As shown in Table 2, these polymers exhibited strong UV-vis absorption bands at 262–322 nm in NMP solutions, which were assignable to the  $\pi$ - $\pi^*$  transition resulting from the conjugation between the aromatic rings and nitrogen atoms. In the solid state, the UV-vis absorption of polyimides **6a-6f** showed absorbance at 328–344 nm. The PL spectra in NMP solution showed maximum bands around 476–489 nm in the blue region. The electrochemical properties of the polyimides **6a-6f** were investigated by cyclic voltammetry (CV) conducted for a cast film on an ITO-coated glass substrate as working electrode in dry acetonitrile ( $\text{CH}_3\text{CN}$ ) containing 0.1 M of tetrabutylammonium perchlorate (TBAP) as supporting electrolyte and saturated Ag/AgCl as reference electrode under nitrogen atmosphere. The typical CV curve for polyimide **6a** is shown in Fig. 2. One reversible redox couple at half-wave potential ( $E_{1/2}$ ) = 0.91 V was observed. After hundreds of cyclic scans, the polymer film still exhibited good redox stability. The polyimide **6a** exhibited excellent reversibility of electrochromic characteristics between 0 and 1.4 V, changing color from pale yellow to blue at electrode potentials over 1.13 V. The other polyimides showed similar CV curves to that of **6a**. The redox potentials of the various polyimides as well as their respective HOMO and LUMO potentials (vs vacuum) are shown in Table 2. It is also worth noting that all the **6** series polyimides reveal a slightly lower  $E_{1/2}$  value than their respective **6'** series polyimides with only one methoxy substituent on the TPA unit.

#### References:

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**Figure 2.** Cyclic voltammograms of the cast film of polyimide **6a** on an ITO-glass substrate in  $\text{CH}_3\text{CN}$  containing 0.1 M  $\text{Bu}_4\text{NOCl}_4$  (TBAP) at a scan rate of 100 mV/s. The inset shows the CV curve of ferrocene as the standard.

**Table 2.** Optical and Electrochemical Properties of Polyimides

Index	Solution (nm) <sup>a</sup>		Film (nm)		$E_{\text{ox}}$ (V) (vs. Ag/AgCl in $\text{CH}_3\text{CN}$ )		$E_{\text{g}}^{\text{b}}$ (eV)	HOMO <sup>c</sup> (eV)		LUMO <sup>d</sup> (eV)	
	$\lambda_{\text{max}}^{\text{Abs}}$	$\lambda_{\text{max}}^{\text{PL}}$	$\lambda_{\text{max}}^{\text{Abs}}$	$\lambda_{\text{onset}}^{\text{Abs}}$	$E_{1/2}$	$E_{\text{onset}}$		$E_{1/2}$	$E_{\text{onset}}$	$E_{1/2}$	$E_{\text{onset}}$
<b>6a</b>	263, 322	476	344	476	0.91 (1.01) <sup>e</sup>	0.85	2.61	5.27	5.21	2.66	2.60
<b>6b</b>	312	475	341	486	0.96 (1.00)	0.87	2.55	5.32	5.23	2.77	2.68
<b>6c</b>	262, 306	480	328	424	0.92 (0.99)	0.80	2.92	5.28	5.16	2.36	2.24
<b>6d</b>	314	476	329	465	1.00 (1.02)	0.82	2.67	5.36	5.18	2.69	2.51
<b>6e</b>	300	486	341	570	0.97 (0.99)	0.89	2.18	5.33	5.25	3.15	3.07
<b>6f</b>	298	489	341	439	0.92 (0.98)	0.80	2.82	5.28	5.16	2.46	2.34

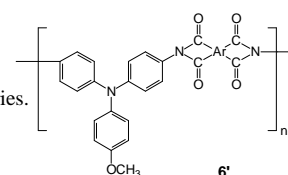
<sup>a</sup> Measured in NMP at a concentration of about  $1 \times 10^{-5}$  mol/L.

<sup>b</sup> The data were calculated by the equation:  $E_{\text{g}} = 1240/\lambda_{\text{onset}}$  of polymer film.

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

<sup>d</sup> LUMO = HOMO -  $E_{\text{g}}$ .

<sup>e</sup> Values in parentheses are data of analogous polyimides **6'** having the corresponding dianhydride residue as in the **6** series.



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## ABSTRACT

A new triphenylamine-containing diamine monomer, 2,4-dimethoxy-4',4''-diaminotriphenylamine (**2**), was synthesized from readily available reagents and was reacted with various dianhydrides to produce one series of polyimides **6a-f** containing 2,4-dimethoxy-activated triphenylamine units. All the resulting polyimides were readily soluble in polar organic solvents and could be solution cast into tough and flexible films. These polymers exhibited good thermal stability with glass-transition temperatures of 269-307°C and softening temperatures of 265-308°C, 10% weight-loss temperatures in excess of 556°C in nitrogen, and char yields at 800°C in nitrogen higher than 50%. The redox behaviors of the polymers were examined using cyclic voltammetry (CV). All poly(amine-imide)s showed one reversible oxidation processes in the first CV scan. The polymers also displayed low ionization potentials as a result of their 2,4-dimethoxy-activated triphenylamine moieties. In addition, the polymers displayed excellent stability of electrochromic characteristics with coloration change from a pale yellowish neutral state to a blue-violet oxidized state. These anodically polymeric electrochromic materials not only showed excellent reversible electrochromic stability with good blue coloration efficiency (CE = 894 cm<sup>2</sup> C<sup>-1</sup>) but also exhibited contrast of optical transmittance change ( $\Delta T\%$ ) up to 52% at 831 nm, 52% at 620 nm and 83% at 378 nm. After over 50 cyclic switches, the polymer films still exhibited excellent stability of electrochromic characteristics.

## INTRODUCTION

Electrochromism can be defined as the reversible change in optical properties of a material resulting from electrochemically induced redox states [1,2]. 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. Electrochromic anti-glare car rear-view mirrors have already been commercialized, with other proposed applications of electrochromic materials including their use in controllable light-reflective or light-transmissive devices for optical information and storage, sunglasses, protective eyewear for the military, controllable aircraft canopies, and glare-reduction systems for offices and smart windows for use in cars and buildings [1-4].

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The anodic oxidation pathways of TPA are well studied [14]. The unsubstituted TPA may undergo coupling-deprotonation to form tetraphenylbenzidine after the formation of the initial monocation radical. It has been well established that incorporation of electron-donating substituents such as methoxy group at the para position of TPA prevents the coupling reactions and affords stable radical cations [15-18]. Therefore, we synthesized the diamine monomer, 4,4''-diamino-2,4''-dimethoxytriphenylamine (**2**), and its derived polyimides containing electroactive TPA units with electron-donating methoxy groups *para* and *ortho* substituted on the pendent phenyl ring. We anticipated that the electrochromic films obtained from the present polyimides would exhibit an enhanced stability upon redox switching.

## MONOMER SYNTHESIS

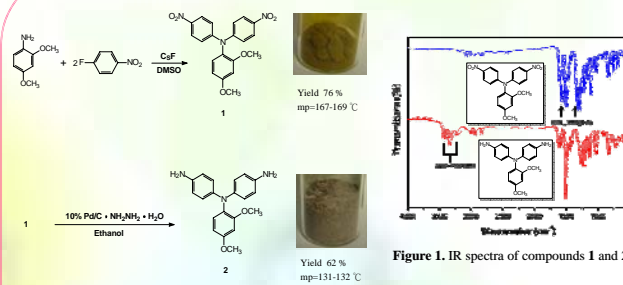


Figure 1. IR spectra of compounds **1** and **2**.

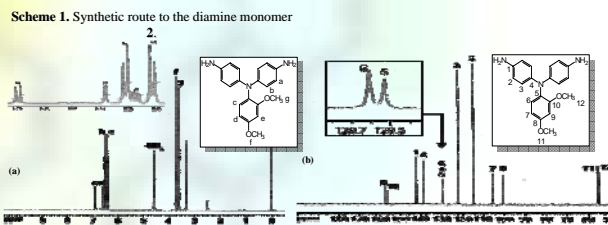
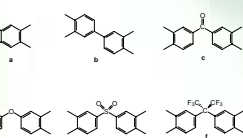
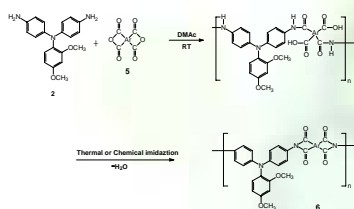


Figure 2. (a) <sup>1</sup>H NMR and (b) <sup>13</sup>C NMR spectra of diamine monomer **2** in DMSO-*d*<sub>6</sub>.

## POLYMER SYNTHESIS AND SOLUBILITY



Scheme 2. Synthesis of polyimides **6a-f**.

Table 1. Inherent viscosities and solubility of the polyimides

Polymer code	FAA	polyimide	Solubility <sup>a</sup>						
			NMP	DMAc	DMF	DMSO	m-Cresol	THF	
6a-T	2.73	—	++	++	++	++	++	++	++
6b-T	2.87	—	++	++	++	++	++	++	++
6c-T	2.69	—	++	++	++	++	++	++	++
6d-T	2.44	—	++	++	++	++	++	++	++
6e-T	2.51	0.44	++	++	++	++	++	++	++
6f-T	2.58	—	++	++	++	++	++	++	++
6a-C	—	—	++	++	++	++	++	++	++
6b-C	—	—	++	++	++	++	++	++	++
6c-C	—	0.77	++	++	++	++	++	++	++
6d-C	—	0.77	++	++	++	++	++	++	++
6e-C	—	0.41	++	++	++	++	++	++	++
6f-C	—	0.62	++	++	++	++	++	++	++

<sup>a</sup> Measured in DMAc containing 5 wt % LiCl at 30 °C on 0.5 g/dL.  
<sup>b</sup> Qualitative solubility was tested with 10 mg sample in 1 mL solvent. Symbol: ++, soluble at room temperature; +, soluble on heating at 100 °C; ++, partially soluble or swelling on heating; —, insoluble even on heating. NMP, *N*-methyl-2-pyrrolidone; DMAc, *N,N*-dimethylacetamide; DMF, *N,N*-dimethylformamide; DMSO, dimethyl sulfoxide; THF, tetrahydrofuran.

## THERMAL PROPERTIES

Table 2. Thermal properties of the polyimides

Polymer code	$T_g^a$ (°C)	$T_c^b$ (°C)	$T_d$ at 5 wt % loss <sup>c</sup> (°C)		$T_d$ at 10 wt % loss <sup>c</sup> (°C)		Char yield <sup>d</sup> (%)
			In N <sub>2</sub>		In air		
			In N <sub>2</sub>	In air	In N <sub>2</sub>	In air	
6a	—	308	481	488	497	531	60
6b	307	292	478	498	499	552	63
6c	277	274	477	498	500	544	60
6d	269	265	476	508	506	556	50
6e	288	284	454	467	470	504	53
6f	286	280	480	464	480	516	55

<sup>a</sup> No discernible transition.  
<sup>b</sup> The sample was heated from 50 to 400 °C at a scan rate of 20 °C/min followed by rapid cooling to 50 °C at 200 °C/min in nitrogen. The midpoint temperature of baseline shift on the subsequent DSC trace (from 50 to 400 °C at heating rate 20 °C/min) was defined as  $T_g$ .  
<sup>c</sup> Softening temperature measured by TMA using a penetration method.  
<sup>d</sup> Decomposition temperature at which a 5% or 10% weight loss was recorded by TGA at a heating rate of 20 °C/min.  
<sup>e</sup> Residual weight percentages at 800 °C under nitrogen flow.

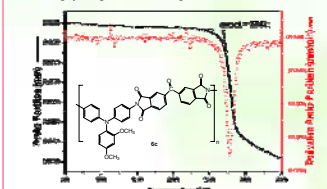


Figure 3. TMA curve of polyimide **6c** with a heating rate of 10 °C/min.

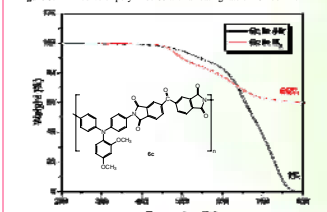


Figure 4. TGA thermograms of polyimide **6c** with heating rate 20 °C/min.

## OPTICAL AND ELECTROCHEMICAL PROPERTIES

Table 3. Optical and electrochemical properties of the polyimides

Index	Solution (nm) <sup>a</sup>		film (nm)		$E_{ox}^b$ (V vs. Ag/AgCl in CH <sub>3</sub> CN)	$E_{red}^b$ (V vs. Ag/AgCl in CH <sub>3</sub> CN)	$E_g^c$ (eV)	HOMO <sup>d</sup> /eV		LUMO <sup>e</sup> /eV			
	$\lambda_{max}$	$\lambda_{min}$	$\lambda_{max}$	$\lambda_{min}$				$E_{1/2}$	$E_{onset}$	$E_{1/2}$	$E_{onset}$		
	6a	263	322	476	300	450	0.91 (1.01) <sup>f</sup>	1.06 <sup>g</sup>	0.85	2.61	5.27	5.21	2.51
6b	312	475	302	410	409	0.96 (1.00)	(1.01)	0.87	2.55	5.32	5.23	2.30	2.21
6c	262	306	480	308	409	0.92 (0.99)	(1.03)	0.80	2.92	5.28	5.16	2.25	2.13
6d	314	476	308	381	410	1.00 (1.02)	(1.01)	0.82	2.67	5.36	5.18	2.11	1.93
6e	300	486	303	418	418	0.97 (0.99)	(1.04)	0.89	2.18	5.33	5.25	2.36	2.28
6f	298	489	305	405	405	0.92 (0.98)	(1.01)	0.80	2.82	5.28	5.16	2.22	2.10

<sup>a</sup> Spectra in NMP (1x10<sup>-5</sup> mol L<sup>-1</sup>).  
<sup>b</sup> Excited at the absorption maximum for both the solid and solution states.  
<sup>c</sup> The data were calculated by the equation:  $E_g = 1240/\lambda_{onset}$  of polymer film.  
<sup>d</sup> The HOMO energy levels were calculated from cyclic voltammetry and were referenced to ferrocene (4.8 eV).  
<sup>e</sup> LUMO = HOMO +  $E_g$ .  
<sup>f</sup> Values in parentheses are data of analogous polyimides **6'** having the corresponding dianhydride residue as in the **6** series.  
<sup>g</sup> Values in parentheses are data of analogous polyimides **6''** having the corresponding dianhydride residue as in the **6** series.

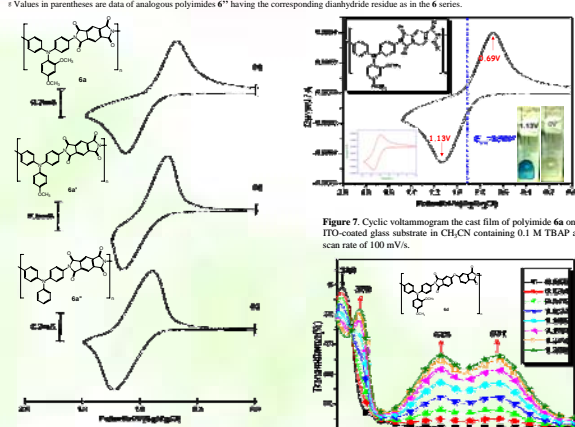


Figure 6. Cyclic voltammograms the cast films of polyimides **6a-f** on an ITO-coated glass substrate in CH<sub>3</sub>CN containing 0.1 M TBAP at a scan rate of 100 mV/s. The inset shows the CV curve of ferrocene as the standard.

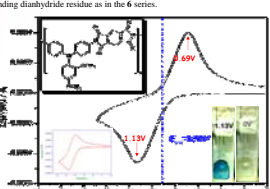


Figure 7. Cyclic voltammogram the cast film of polyimide **6a** on an ITO-coated glass substrate in CH<sub>3</sub>CN containing 0.1 M TBAP at a scan rate of 100 mV/s.

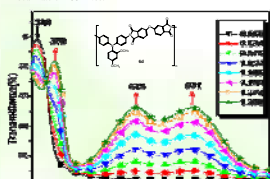


Figure 8. Spectroelectrochemical behavior of polyimide **6d** in CH<sub>3</sub>CN with 0.1 M TBAP as supporting electrolyte at (■) 0.00V, (●) 0.82V, (○) 0.94V, (▼) 1.03V, (◆) 1.10V, (◄) 1.19 V, (□) 1.27 V, (▲) 1.35 V.

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