

Synthesis and Electrochromic Properties of Polyimides with Pendent Benzimidazole and Triphenylamine Units^{*}

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Abstract Five novel near-infrared electrochromic aromatic polyimides (PIs) with pendent benzimidazole group were synthesized from 4,4'-diamino-4''-(1-benzylbenzimidazol-2-yl)triphenylamine (named as DBBT) with five different dianhydrides *via* two-step polymerization process, respectively. The maximum UV-Vis absorption bands of these PIs locate at about 335 nm for solid films due to the π - π^* transitions. A reversible pair of distinct redox peaks, that were associated with a noticeable color change from original yellow to blue, was observed in the cyclic voltammetry (CV) test. A new absorption peak emerged at 847 nm in near-infrared (NIR) region with increasing voltage in UV-Vis-NIR spectrum, which indicates that PI can be used as NIR electrochromic material. These novel PIs have good electrochemical stability, appropriate energy levels for the highest occupied molecular orbital (HOMO) and the lowest unoccupied molecular orbital (LUMO), in the range of -5.17 eV to -5.20 eV and -2.14 eV to -2.26 eV (versus the vacuum level) determined by cyclic voltammetry method. These values basically consisted with the results of quantum chemical calculation. These polyimides can be used as novel electrochromic and hole transportation materials.

Keywords: Triphenylamine; Electrochromic; Benzimidazole; Polyimide; Near-infrared.

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INTRODUCTION

Electrochromism suggested by Platt in 1961 is well known as the reversibly changing color resulted from the redox reaction by applying an external voltage^[1, 2]. As a member of electrochromic materials, conducting polymers possess great advantages because they provide possibility to various chemical design and modifications, which make it easy to control energy gap (E_g) and absorption site, and to realize low driving voltage, short switching time, facile processing and multiple colors changing. So that, a number of high performance polymers were invented and explored for applications in rear-view mirrors, smart windows of building and the digital displays^[3–5]. In addition, PI and polyamide (PA)^[6, 7] have been also widely used as

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electrochromic materials. For examples, PI polymers play an important role in engineering plastics with outstanding mechanical properties, electrical properties, weather resistance, flame resistance and chemical resistance due to their high rigidity of main chain and strong intermolecular forces^[8, 9]. However, the high processing temperature and low solubility in most organic solvents limit their practical applications. Triphenylamine (TPA) has been frequently introduced into rigid PI polymers to improve their processibility for fabricating high performance material^[10]. This is due to the propeller-like TPA can disrupt the coplanarity in PI main chains and increase the internal free volume, which benefit to improve the solubility of PIs in common solvents. Furthermore, the unique twisting TPA, consisting of nitrogen atom in the center, has been developed and applied as functional electrochrome in the formation of stable ionic state in the oxidation procedure^[11–13]. Recently, several series of TPA containing PIs with good multi-electrochromic reversibility were investigated as new electrochromic materials^[14–16]. Thus, rich-electrons TPA has been a noteworthy building block as an electro-donating unit for photoelectronic PIs. Moreover, the combination of TPA unit and imide segment, forming donor (D)-acceptor (A) type PIs, can induce the intramolecular charge transfer to enhance the charge storage, which will stimulate the characteristic PIs for their applications to xerography, photovoltaics and resistor-type memory^[17–20].

Benzimidazole derivatives have been used effectively as electron-transporting capability layer in organic light-emitting diodes (OLEDs) and as sensitizers for dye-sensitized solar cells (DSSCs) due to its relative electron mobility^[21–24]. Recently, Thomas *et al.* have designed three benzimidazole-branched isomeric dyes to study their photoelectric properties, which manifested remarkable variations by replacement of TPA at various nuclear positions of benzimidazole^[25]. Inspired by these studies, we tried to introduce 1-benzylbenzimidazole unit into TPA, with expectation to elongate conjugation between the two units and build a bulky three-dimensional structure that limits the chain packing density to obtain a better solubility. To our knowledge, there are no reports of similar work in electrochromic field.

In this paper, we have introduced benzimidazole unit into diamine monomer, and different PIs were prepared using this benzimidazole-containing monomer to react with five different dianhydrides *via* two-step thermal imidization. The structures of these PIs were studied for optical, electrochemical and electrochromic properties. Further the oxidation mechanism of these PIs was discussed using theoretical analysis based on molecular orbital theory.

EXPERIMENTAL

Materials

O-phenylenediamine, nitrobenzoic acid, pyromellitic dianhydride, 4,4'-bipthalic anhydride, 4,4'-oxydiphthalic anhydride, 3,3',4,4'-benzophenonetetracarboxylic dianhydride, and 4,4'-(hexafluoroisopropylidene) diphthalic anhydride (TCI Development Co., Ltd., Japan), benzyl bromide (Sinopharm Chemical Reagent Co., Ltd., China), 10% palladium on charcoal (Pd/C, Acros), 4-fluoronitrobenzene (Sinopharm Chemical Reagent Co., Ltd., China), were used as received. *N,N*-dimethylformamide (DMF, Sinopharm Chemical Reagent Co., Ltd., China) was dried over and distilled from CaH₂. Polyphosphoric acid (PPA) was obtained by dissolving 75 g of phosphorus pentoxide into 50 mL of phosphoric acid of 85% concentration and heating at 100 °C for 2.5 h.

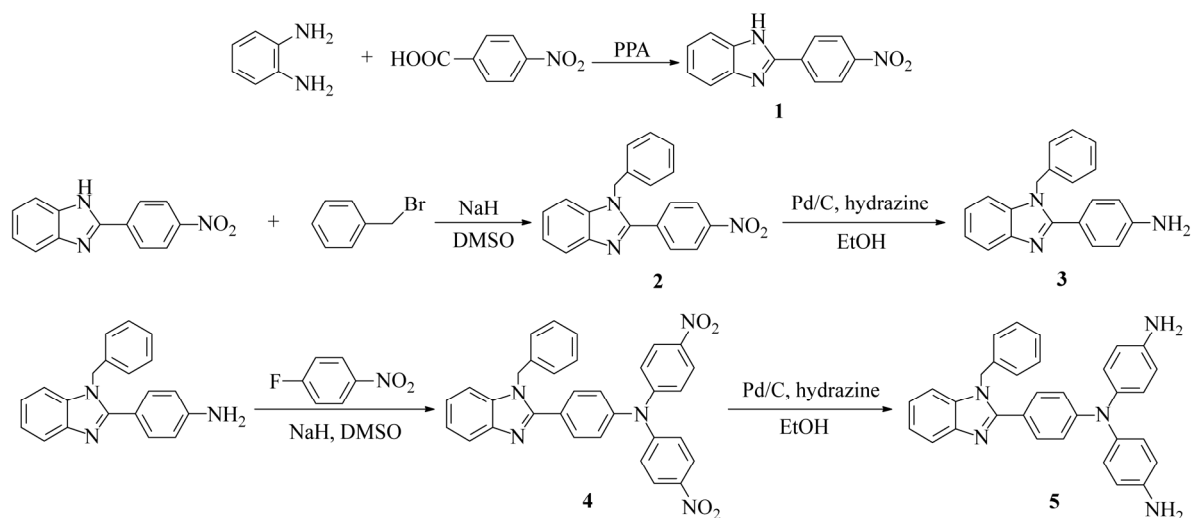
Synthesis of Benzimidazole-based Monomers

Intermediates (1)–(5) were synthesized according to the modified procedures^[26–29], and the synthesis route is shown in Scheme 1.

2-(4-Nitrophenyl)benzimidazole (1)

In a 250 mL three-neck round-bottom flask equipped with a magnetic rotor, 10.7903 g (0.1 mol) of *o*-phenylenediamine and 16.6941 g (0.1 mol) of nitrobenzoic acid were dissolved in 50 mL of PPA under nitrogen atmosphere, the mixture was heated to 135 °C under stirring and kept at that temperature for 5 h. The resulting solution was cooled to approximately 90 °C and was then poured into 200 mL of ice-water to precipitate the crude product, which was collected by filtration, washed with water, and dried in vacuum at 60 °C overnight, followed by purification by recrystallization from ethanol to give 7.9450 g of claybank powder with a

yield of 33.24%. FTIR (KBr, cm^{-1}): 3120 (N—H stretch), 1692 ($\text{C}=\text{N}$), 1606, 1517, 1493 (benzene stretch), 1541, 1350 ($-\text{NO}_2$), 1311, 1279 ($\text{C}-\text{N}$).



Scheme 1 Synthesis route of DBBT

1-Benzyl-2-(4-nitrophenyl)benzimidazole (2)

To a solution of 11.9501 g (0.05 mol) of compound **1** and 10.2665 g (0.072 mol) of benzyl bromide in 70 mL of dried DMSO, 1.200 g (0.05 mol) of NaH was added under stirring. The mixture was heated to 100 °C and kept for 10 h under nitrogen atmosphere. After being poured into 100 mL of water under stirring, white crystal product was collected by filtration and dried under vacuum at 60 °C. The white crystals were recrystallized in ethanol to get 8.6081 g of gray crystals as the target compound **2**: yield, 52.32%; mp, 86.4–87.8 °C.

4-(1-Benzylbenzimidazol-2-yl)aniline (3)

0.5607 g of Pd/C and 6.2032 g of compound **2** were added into 100 mL of ethanol under nitrogen atmosphere in a round-bottom flask of 200 mL capacity, followed by slow addition of 8.1259 g of hydrazine monohydrate. The mixture was refluxed at 70 °C for 10 h, the resulting solution was hot-filtered to remove Pd/C. The crude product was collected by filtration and dried under vacuum at 60 °C to give 4.9557 g of a white solid with a yield of 83.96%. FTIR (KBr, cm^{-1}): 3459, 3358 ($\text{N}-\text{H}$ stretch), 1684 ($\text{C}=\text{N}$), 1601, 1517, 1495 (benzene stretch), 1456 ($\text{C}-\text{H}$ stretch), 1313, 1281 ($\text{C}-\text{N}$). $^1\text{H-NMR}$ (CDCl_3 , δ): 7.87–7.92, 7.25–7.64, 6.62–6.64 (aromatic ring of benzene), 5.32 (2H, CH_2), 4.10 (2H, NH_2).

4,4'-Dinitro-4''-(1-benzylbenzimidazol-2-yl)triphenylamine (4)

A mixture of 4.4994 g (0.015 mol) of compound **3**, 5.3201 g (0.03 mol, 20% excess) of 4-fluoronitrobenzene, 0.7200 g (0.03 mol) of NaH, and 30 mL of DMSO was heated under stirring at 100 °C for 20 h, the reaction solution was poured into a saturated saline solution to precipitate out a yellow product. The raw product was collected by filtration, dried under vacuum at 60 °C, and then recrystallized in acetonitrile to give 7.0014 g of yellow crystals. Yield, 86.00%; mp, 224–228 °C. FTIR (KBr, cm^{-1}): 1712 ($\text{C}=\text{N}$), 1589, 1504, 1492 (benzene stretch), 1452 ($\text{C}-\text{H}$ stretch), 1581, 1340 ($-\text{NO}_2$), 1314, 1266 ($\text{C}-\text{N}$). $^1\text{H-NMR}$ (CDCl_3 , δ): 7.16–8.24 (aromatic ring of benzene), 5.4 (2H, CH_2), (The NMR spectra are given in Fig. S1 in Supporting Information).

4,4'-Diamino-4''-(1-benzylbenzimidazol-2-yl)triphenylamine (DBBT, 5)

DBBT was synthesized according to the synthetic process of compound **3**. In the end, 0.9429 g of khaki crystals was obtained with a yield of 21.10%. FTIR (KBr, cm^{-1}): 3438, 3358 ($\text{N}-\text{H}$ stretch), 1694 ($\text{C}=\text{N}$), 1595, 1505 (benzene stretch), 1454 ($\text{C}-\text{H}$ stretch), 1313, 1268 ($\text{C}-\text{N}$) (The FTIR spectra are shown in Fig. S2). $^1\text{H-NMR}$ (CDCl_3 , δ): 6.5–7.9 (aromatic ring of benzene), 5.3 (2H, CH_2), 3.6 (4H, NH_2). The NMR spectra are shown in Fig. 1.

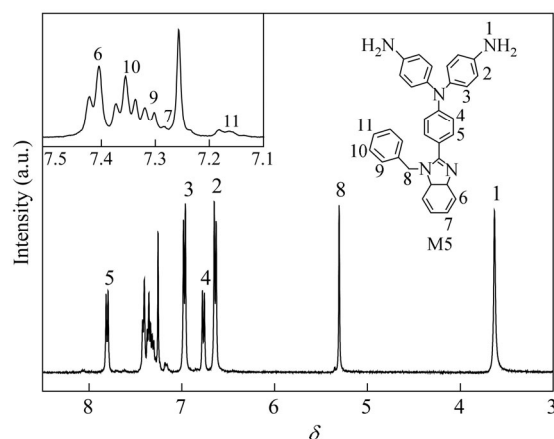


Fig. 1 ^1H -NMR spectra of DBBT

Synthesis of PI Polymers

The preparation of PIs (P_a – P_e) was done by a two-step method *via* a thermal imidization reaction. The synthesis of P_a , as an example, was shown in Scheme 2 to illustrate the general synthetic route. In a round-bottom flask, 0.1216 g (2.5×10^{-4} mol) of DBBT was dissolved in 1.8 mL of DMF, 0.0546 g (2.5×10^{-4} mol) of dianhydride (**a**) (pyromellitic dianhydride) was added in one shot under stirring at room temperature, and the mixture was stirred for 4 h. The resulting solution, a viscous poly(amic acid) solution, was poured on a glass plate. The poly(amic acid) was converted to P_a by successive heating under vacuum at 100 °C for 1 h, 200 °C for 1 h, and at 300 °C for 30 min. A yield of 72% was obtained. The inherent viscosity (η_{inh}) of P_a was $0.51 \text{ dL} \cdot \text{g}^{-1}$ at 30 °C at a concentration of $0.5 \text{ g} \cdot \text{dL}^{-1}$ in DMF. All other PIs were synthesized in the same way.

Polymer P_a

FTIR (KBr, cm^{-1}) spectra showed in Fig. S3: 1779 (asymmetrical C=O), 1721 (symmetrical C=O), 1596, 1504 (benzene stretch), 1315 (C–N), 734 (imide ring deformation), ^1H -NMR spectra shown in Fig. 2 (DMSO- d_6 , δ): 6.59–8.28 (aromatic ring of benzene).

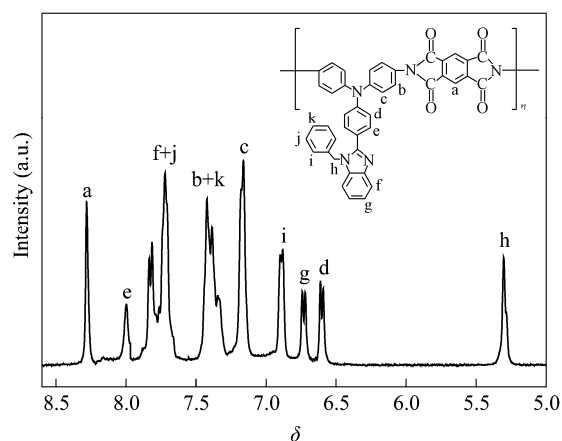
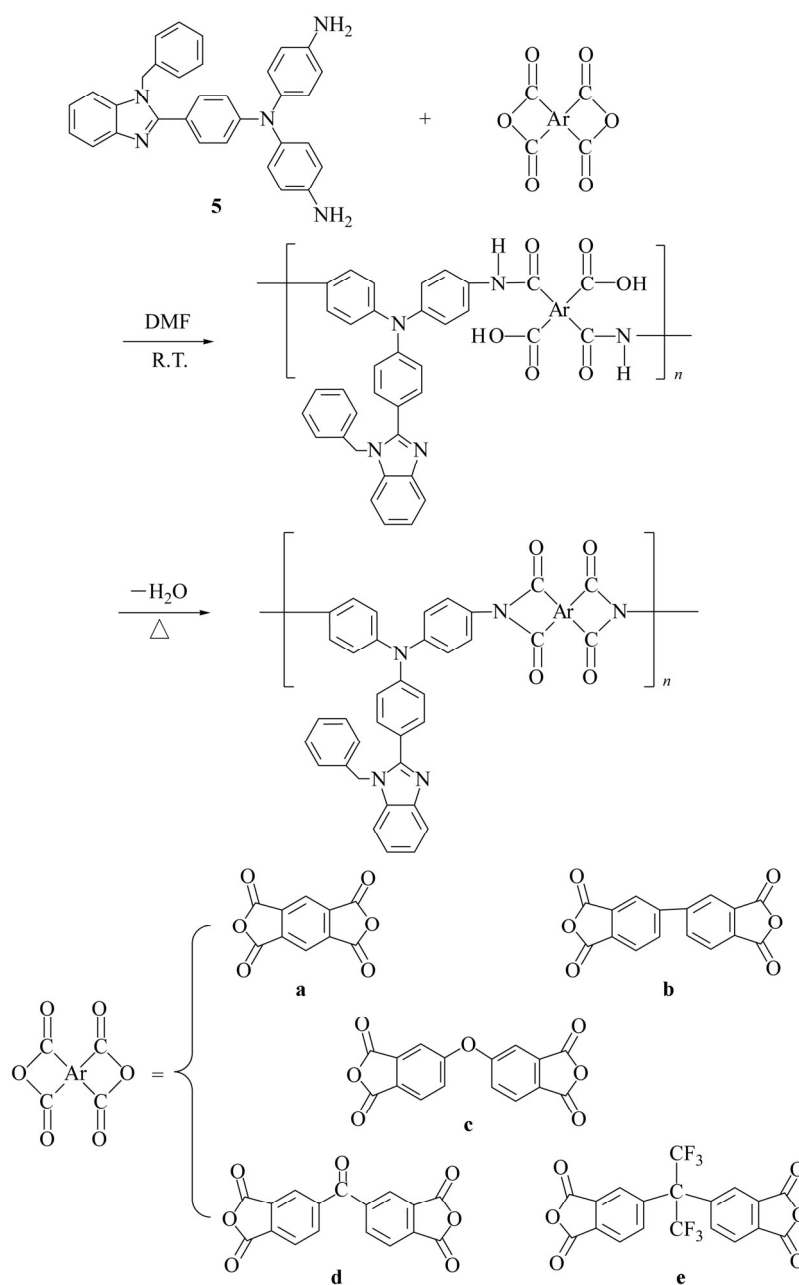


Fig. 2 ^1H -NMR spectrum of P_a

Polymer P_b

0.0595 g (1.25×10^{-4} mol) of DBBT and 0.0371 g (1.25×10^{-4} mol) of dianhydride (**b**) were fed in 1 mL of DMF, with a yield of 69%. The η_{inh} was $0.55 \text{ dL} \cdot \text{g}^{-1}$. FTIR (KBr, cm^{-1}): 1777, 1713, 1657, 1595, 1503, 1313, 734. ^1H -NMR (DMSO- d_6 , δ): 6.80–8.23 (aromatic ring of benzene).

*Polymer P_c*

0.0599 g (1.25×10^{-4} mol) of DBBT and 0.0387 g (1.25×10^{-4} mol) of dianhydride (**c**) were fed in 1 mL of DMF, with a yield of 80%. The η_{inh} was $0.42 \text{ dL} \cdot \text{g}^{-1}$. FTIR (KBr, cm^{-1}): 1777, 1714, 1662, 1597, 1501, 1312. $^1\text{H-NMR}$ (DMSO-d_6 , δ): 6.89–8.52 (aromatic ring of benzene).

Polymer P_d

0.1203 g (2.5×10^{-4} mol) of DBBT and 0.0807 g (2.5×10^{-4} mol) of dianhydride (**d**) were fed in 2.1 mL of DMF, with a yield of 76%. The η_{inh} was $0.37 \text{ dL} \cdot \text{g}^{-1}$. FTIR (KBr, cm^{-1}): 1778, 1714, 1664, 1597, 1505, 1315. $^1\text{H-NMR}$ (DMSO-d_6 , δ): 6.59–8.35 (aromatic ring of benzene).

Polymer P_e

0.0598 g (1.25×10^{-4} mol) of DBBT and 0.0558 g (1.25×10^{-4} mol) of dianhydride (**e**) were fed in 2.1 mL of DMF, with a yield of 75%. The η_{inh} was $0.21 \text{ dL} \cdot \text{g}^{-1}$. FTIR (KBr, cm^{-1}): 1776, 1711, 1668, 1598, 1507, 1315. $^1\text{H-NMR}$ (DMSO-d_6 , δ): 6.56–8.40 (aromatic ring of benzene).

Preparation of PIs Films

The polymers (P_a to P_e) were dissolved in an amount of DMF to form a homogenous solution. Covered with ITO-conductive glass, the solution was placed in a vacuum oven at 100°C for 6 h, the temperature was then raised to and kept 190°C for 10 h to evaporate the solvent.

Instrumentation

Fourier transform infrared (FTIR) spectra were recorded on a spectrometer (Perkin-Elmer Spectrum 100). $^1\text{H-NMR}$ spectra were obtained on a Bruker AC-400 MHz spectrometer with tetramethylsilane as an internal reference. Gel permeation chromatography (GPC) analysis, calibrated with polystyrene standards in DMF solution at 35°C , was performed on Malvern instrument. Thermogravimetric analysis (TGA) was conducted on a Perkin-Elmer (Pyris 6 TGA) in a nitrogen atmosphere with a heating rate of $10 \text{ K} \cdot \text{min}^{-1}$ and the sample weight of about 6–8 mg. UV-Vis absorption spectra were recorded using a Shimadzu UV-3600 spectrophotometer. CV measurements were conducted on a CH Instruments (660A electrochemical analyzer) with a $0.1 \text{ mol} \cdot \text{L}^{-1}$ solution of LiClO_4 in dry acetonitrile (CH_3CN) as an electrolyte at a scan rate of $50 \text{ mV} \cdot \text{s}^{-1}$. The onset of oxidation and reduction potentials of the PIs thin films against the Ag/AgCl quasi reference electrode were measured and calibrated against the ferrocene/ferrocenium (F/Fc^+) redox couple. HOMO and LUMO levels of the PIs were calculated by assuming the absolute energy level of Fc/Fc^+ as -4.80 eV to vacuum.

RESULTS AND DISCUSSION

Basic Characteristics of Monomer and Polymers

In each step of the synthesis, the compounds needed to be purified by recrystallization to obtain a pure compound of high yield in the next step. The structure of DBBT was verified by $^1\text{H-NMR}$ and FTIR spectrometer. The double characteristic absorption bands at 3438 and 3358 cm^{-1} in the FTIR-spectra were attributed to amino group, which was also confirmed by observation of a peak at $\delta = 3.6$ in the $^1\text{H-NMR}$ spectra. Five different PIs (P_a – P_e) with pendent benzimidazole group were synthesized *via* two-step polymerization. The chemical structures of the PIs were characterized with FTIR-spectra, exhibiting obvious characteristic absorption bands at around 1776 cm^{-1} , 1714 cm^{-1} corresponding to the asymmetrical and symmetrical stretching vibration of imide group in the main chain. The molecular weight of PIs was measured by GPC, using DMF as eluent and polystyrenes as standard. The weight-average molecular weight (M_w) and polydispersity (PDI) were in the range of 8400 – 19000 and 1.37 – 2.01 (Table 1), respectively. All the PIs exhibited similar TGA properties with no significant weight loss below 400°C in nitrogen atmosphere, showed in Fig. 3 and Table 1. The temperatures, at which a 20% weight-loss was observed, were determined in the range of 458 – 538°C . The residual weight for all the PIs was more than 45% at 700°C , which could be contributed to the high aromatic content in the polymers. Generally, the higher aromatic content was consistent with the higher residual weight for these analogous polymers, such as P_d (71%) > P_a (47%).

Table 1. Thermal properties and average molecular weights of the PIs

PIs	Temperature at weight loss ($^\circ\text{C}$)			Char yield ^a (wt%)	M_n ^b ($\text{g} \cdot \text{mol}^{-1}$)	M_w ^b ($\text{g} \cdot \text{mol}^{-1}$)	PDI ^c
	5%	10%	20%				
P_a	384	421	458	47	4800	9700	2.01
P_b	390	431	534	62	4500	8400	1.86
P_c	394	420	461	56	7400	10200	1.37
P_d	393	430	538	71	12500	19000	1.52
P_e	378	407	475	52	10900	17300	1.59

^a Residual weight percentage at 700°C in nitrogen; ^b Relative to polystyrene standards using DMF as the eluent at 35°C ; ^c Polydispersity index, M_w/M_n

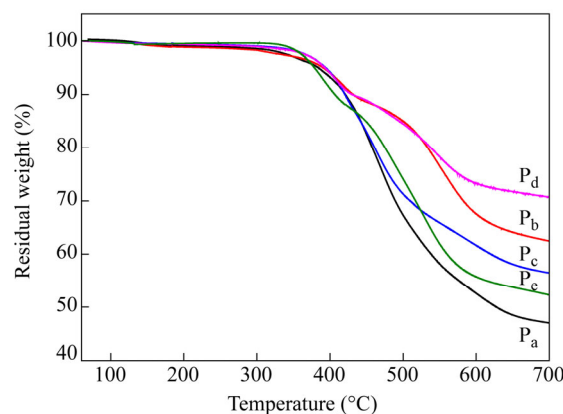


Fig. 3 TGA curves of P_a to P_e

Optical and Electrochemical Properties

Optical properties of the PIs were examined by UV-Vis absorption as depicted in Fig. 4. The maximum UV-Vis absorption bands in the range of 332–339 nm for these PIs were contributed to the π - π^* transitions from the TPA unit. The onset wavelength (λ_{onset}) of polymer was determinant for the E_g value according to the following formula (For details, see Table 2.): $E_g = 1240/\lambda_{\text{onset}}$. The experimental E_g values follows $P_a < P_d < P_b = P_c < P_e$, which was related to the conjugated degree of the analogue PIs. The DBBT, combined with pyromellitic dianhydride, formed the P_a of highest conjugated degree among all the PIs, its E_g value was therefore the lowest. Nevertheless, there is little deviation for the whole series of PIs, which might be caused by the solvent, the different molecular weight and its distribution.

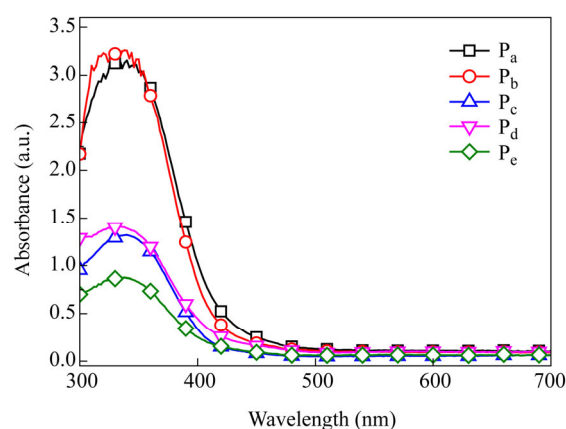


Fig. 4 UV-Visible absorption spectra of the different PIs films

The redox behaviors of the polymers film on the ITO/glass electrode were investigated by CV, and the results are showed in Table 2 and Fig. 5. What we can see from there are the similar changes in these graphs. For example, the graph of P_c exhibited a pair of obvious reversible redox peaks. The emergence of the peaks, at 1.08 V, was attributable to the oxidation of TPA containing rich electrons, which must be easy to be oxidized to TPA^+ , accompanying the color change in P_c film from light yellow to blue between 0.0–1.6 V. The peak, at 0.78 V, was attributed to the reduction of TPA^+ . The reason why the positions of the oxidation peaks of the PIs were different was owing to the structure of different dianhydride units, which played an adjusting role in connecting the polymer.

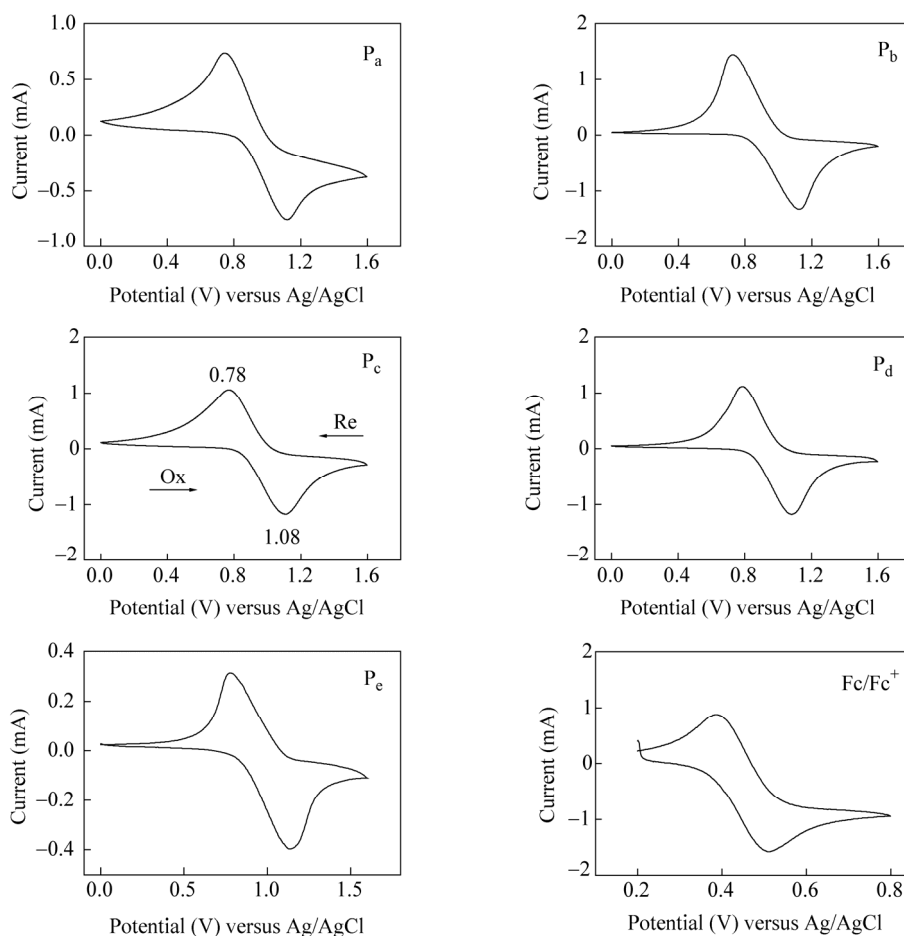


Fig. 5 Repetitive CV scanning of the PIs films on ITO/glass electrode in $0.1 \text{ mol}\cdot\text{L}^{-1} \text{ LiClO}_4/\text{MeCN}$ solution over the potential range from 0 to 1.6 V at a scanning rate of $50 \text{ mV}\cdot\text{s}^{-1}$

The oxidation peak appeared and it showed that the redox reaction occurred in the CV curves, accompanied by injection and extraction process of Li^+ . The ferrocene/ferrocenium (Fc/Fc^+), of which the absolute energy level was 4.80 eV under vacuum, calibrated reference electrode to obtain accurate redox potentials. Using the oxidation onset potentials (E_{ox} versus Ag/AgCl) and the following equation, the energy levels of HOMO and LUMO of the polymers were calculated. The results are listed in Table 2.

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

$$E_{\text{LUMO}} = E_{\text{HOMO}} + E_g$$

The HOMO energy values were in the range from -5.17 eV (P_e) to -5.20 eV (P_a), and the order, $\text{P}_a = \text{P}_d < \text{P}_b = \text{P}_c < \text{P}_e$, was similar to that of E_g values due to the same reasons. Similarly, the results of LUMO energy values were in the range from -2.14 eV (P_e) to -2.26 eV (P_a).

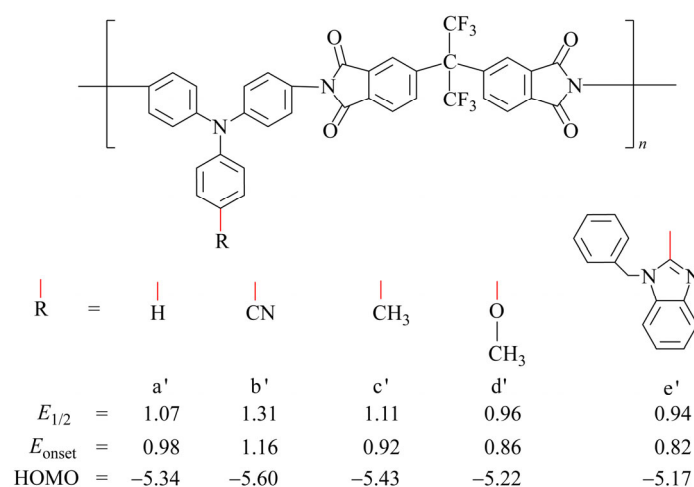
From Fig. 6, it was observed that P_e showed the lowest E_{onset} and HOMO among all the PIs films (a'-hydrogen^[30], b'-cyano^[31], c'-methyl^[32], d'-methoxy^[30]), which indicates that incorporation of electro-donating benzimidazole group into TPA made it easier to be oxidized, as was further proven by the lowest $E_{1/2}$. Significantly, the lower oxidation potential reduced the destruction of the PI containing benzimidazole, which prolonged the cycle life for the electrochromic material in the electrochemical process and decreased energy consumption.

Table 2. Optical and electrochemical properties for PIs

PIs	$\lambda_{\text{film}}^{\text{abs}}$ ^a (nm)	$\lambda_{\text{onset}}^{\text{abs}}$ ^b (nm)	$E_{1/2}$ versus Ag/AgCl ^c (V)	$E_{\text{onset}}^{\text{peak}}$ versus Ag/AgCl ^c (V)	$E_{\text{HOMO}}^{\text{electro}}$ ^d (eV)	$E_{\text{LUMO}}^{\text{electro}}$ ^d (eV)	$E_{\text{g}}^{\text{film}}$ ^e (eV)	$E_{\text{HOMO}}^{\text{quantum}}$ ^f (eV)	$E_{\text{LUMO}}^{\text{quantum}}$ ^f (eV)	$E_{\text{g}}^{\text{quantum}}$ ^f (eV)
P _a	335	421	0.93	0.85	-5.20	-2.26	2.94	-5.31	-3.76	1.54
P _b	338	412	0.92	0.84	-5.19	-2.18	3.01	-5.28	-3.30	1.98
P _c	339	412	0.93	0.84	-5.19	-2.18	3.01	-5.26	-3.04	2.22
P _d	332	416	0.94	0.85	-5.20	-2.22	2.98	-5.28	-3.65	1.63
P _e	336	410	0.94	0.82	-5.17	-2.14	3.02	-5.27	-3.39	1.88

$E_{\text{ox/onset}}(\text{Fc}/\text{Fc}^+ \text{ versus Ag/AgCl}) = 0.45 \text{ V}$

^a UV-Vis absorption spectra in DMF at room temperature; ^b λ_{onset} of the PIs film; ^c $E_{1/2}$ average potential of the redox couple peaks; ^d The HOMO energy levels were calculated from cyclic voltammetry and were referenced to ferrocene (-4.8 eV); ^e $E_{\text{g}} = 1240/\lambda_{\text{onset}}$ (energy gap between HOMO and LUMO); ^f Theoretical calculation of the polymers

**Fig. 6** Effect of different substituents on $E_{1/2}$, E_{onset} and HOMO of PIs films

Quantum Chemistry Calculation

The DFT theory was used to better understand the evolution of redox potentials and electronic structure of the polymer series (dimers). As shown in Fig. 7, the electron cloud distribution, obtained from theoretical calculations, showed that the electrons of HOMOs of PIs were localized on the TPA unit, the donor moiety; while the electrons of LUMOs of PIs were dispersed over the imide unit, the acceptor moiety. This implies that charge transfer between electron-donor and electro-acceptor moieties occurs in the process of the transition from ground state to excited state of the PIs. As shown in Fig. 4, π electrons were slightly coupled with lone pair electrons on nitrogen atom. In this series of oligomers, the theoretical trend of E_{g} is in the order of $P_{\text{a}} < P_{\text{d}} < P_{\text{e}} < P_{\text{b}} < P_{\text{c}}$; and the experimental data is in the order of $P_{\text{a}} < P_{\text{d}} < P_{\text{b}} = P_{\text{c}} < P_{\text{e}}$. The slight deviation may be generated by the reason that the theoretical results were obtained only based on dimers, whereas the experimental data were collected from the test on the polymers^[33].

Electrochromic Properties

The electrochromic behavior of PIs film was investigated by UV-Vis-NIR spectroscopy. As shown in Fig. 8, P_c film exhibited strong absorption at 339 nm at 0 V due to π - π^* transitions of TPA, and there was no significant absorption in the visible light region. The absorption of P_c film was gradually weakened at 339 nm, while new absorptions emerged at 406 nm, 537 nm and 847 nm in NIR region with voltage increasing (from 0 to 1.8 V). These were believed to be due to that TPA in the center of polymer was oxidized to TPA⁺. The color change in P_c film, from original yellow to oxidized blue with the voltage increasing, were observed by UV-Vis-NIR spectrometer. The films made from the other PIs manifested similar changes as shown in Fig. S4.

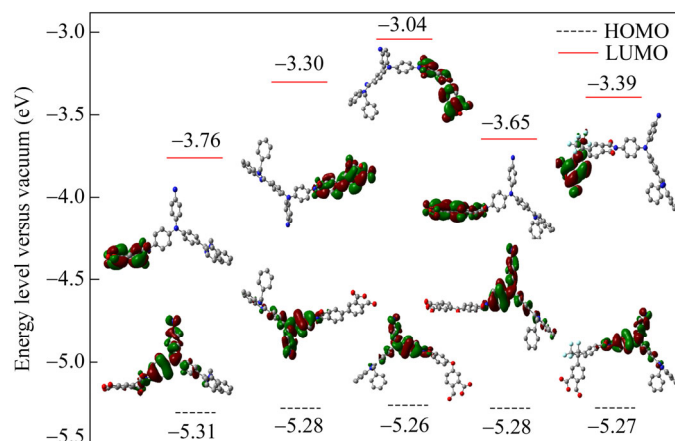


Fig. 7 Pictorial representations of the electron cloud in the frontier molecular orbitals of repetition units for dimer of P_a to dimer of P_e

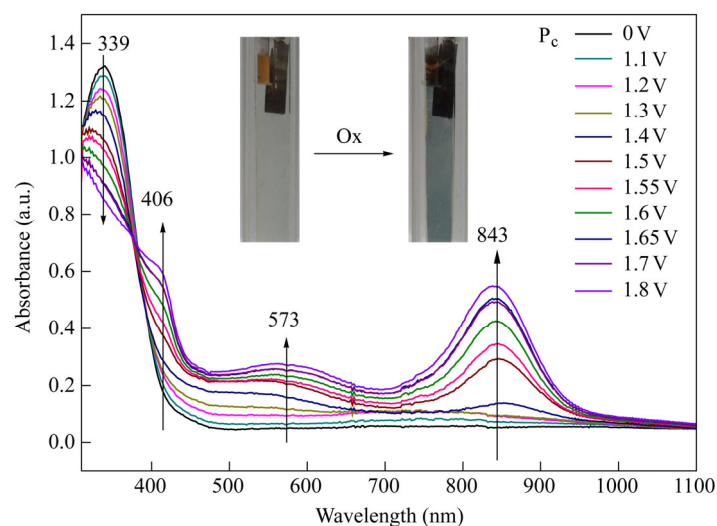


Fig. 8 Electrochromic behavior of P_e thin film (in CH_3CN with $0.1 \text{ mol}\cdot\text{L}^{-1} \text{ LiClO}_4$ as the supporting electrolyte) at 0.0–1.8 V (versus Ag/AgCl)

The stability of the P_a film was estimated through potential step absorptiometry between 0–1.2 V (versus Ag/AgCl) at 605 nm. Its current density and transmittance basically remained unchanged after 30 cycles with a cycle time of 10 s as displayed in Fig. 9, which indicated that P_a possessed good electrochromic reversibility. In order to further prove that, a CV test with 25 cycles was done, and the results are given in Fig. S5. Except for the slightly increased oxidation potential, fair stability and reversibility were observed in P_a material in the measured range. The electrochromic coloration efficiency (CE: η), one of the important characteristics for electrochromic materials, was $43 \text{ cm}^2\cdot\text{C}^{-1}$, calculated using the following equations:

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

$$\eta = \Delta_{\text{OD}}/Q$$

where, Δ_{OD} is the optical density change; T_b , the maximum transmittance in the oxidized state, and T_c , the maximum transmittance in the neutral state, as exhibited in Fig S6. Q is the injected charge per unit electrode area.

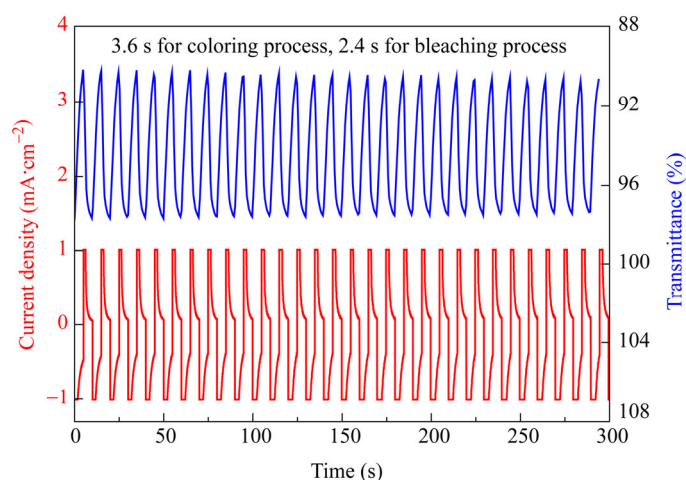


Fig. 9 Potential step absorptiometry between 0 and 1.2 V (versus Ag/AgCl) at 605 nm of polymer P_a thin film on the ITO-coated glass substrate in a 0.1 mol·L⁻¹ LiClO₄/CH₃CN solution with a cycle time of 10 s

CONCLUSIONS

Based on 4,4'-diamino-4''-(1-benzylbenzimidazol-2-yl)triphenylamine, several polyimides (PIs, including P_a, P_b, P_c, P_d and P_e) were successfully synthesized *via* thermal imidization reaction. The structures of the PIs were confirmed using FTIR and ¹H-NMR. The maximum UV-Vis absorption bands appeared in the range of 332–339 nm for the solid films of the PIs. A reversible pair of distinct redox peaks with a noticeable color change from original yellow to blue was observed in the CV test, and a new absorption peak emerged at 847 nm in the UV-Vis-NIR spectrum. In addition, good thermal property and appropriate energy levels of HOMO and LUMO suggest that these PIs are potential candidates as NIR electrochromic materials.

REFERENCES

- 1 Platt, J.R., J. Chem. Phys., 1961, 34: 862
- 2 Monk, P.M.S., Mortimer, R.J. and Rosseinsky, D.R., "Electrochromism: fundamentals and applications", VCH, New York, 1995, p. 3
- 3 Baetens, R., Jelle, B.P. and Gustavsen, A., Sol. Energ. Mat. Sol. C., 2010, 94: 87
- 4 Beaujuge, P.M., Ellinger, S. and Reynolds, J.R., Nat. Mater., 2008, 7: 795
- 5 Beaupré, S., Breton, A.C., Dumas, J. and Leclerc, M., Chem. Mater., 2009, 21: 1504
- 6 Yu, P., Wang, Y., Yu, J.R., Jing, Z. and Hu, Z.M., Chinese J. Polym. Sci., 2016, 34(1): 122
- 7 Aly, K.I. and Hussein, M.A., Chinese J. Polym. Sci., 2015, 33(1): 1
- 8 Li, W.M., Li, S.H., Zhang, Q.Y. and Zhang, S.B., Macromolecules, 2007, 40: 8205
- 9 Liu, C.J., Mei, M., Pei, X.L., Huang, X.H. and Wei, C., Chinese J. Polym. Sci., 2015, 33(8): 1074
- 10 Hsiao, S.H., Liou, G.S., Kung, Y.C., Pan, H.Y. and Kuo, C.H., Eur. Polym. J., 2009, 45: 2234
- 11 Hsiao, S.H. and Cheng, S.L., Polym. Int., 2015, 64: 811
- 12 Yen, H.J., Chen, C.J. and Liou, G.S., Adv. Funct. Mater., 2013, 23: 5307
- 13 Yen, H.J., Guo, S.M., Yeh, J.M. and Liou, G.S., J. Polym. Sci., Part A: Polym. Chem., 2011, 49: 3637
- 14 Wang, H.M. and Hsiao, S.H., J. Mater. Chem. C., 2014, 2: 1553
- 15 Hsiao, S.H., Chang, P.C., Wang, H.M., Kung, Y.R. and Lee, T.M., J. Polym. Sci., Part A: Polym. Chem., 2014, 52: 825
- 16 Wang, H.M. and Hsiao, S.H., J. Polym. Sci., Part A: Polym. Chem., 2014, 52: 1172
- 17 Tian, G.F., Wu, D.Z., Qi, S.L., Wu, Z.P. and Wang, X.D., Macromol. Rapid Commun., 2011, 32: 384
- 18 Liu, Y.L., Wang, K.L., Huang, G.S., Zhu, C.X., Tok, E.S., Neoh, K.G. and Kang, E.T., Chem. Mater., 2009, 21: 3391

- 19 Liu, C.L., Kurosawa, T., Yu, A.D., Higashihara, T., Ueda, M. and Chen, W.C., *J. Phys. Chem. C.*, 2011, 115: 5930
- 20 You, N.H., Chueh, C.C., Liu, C.L., Ueda, M. and Chen, W.C., *Macromolecules*, 2009, 42: 4456
- 21 Tao, Y.T., Wang, Q., Yang, C.L., Zhong, C., Qin, J.G. and Ma, D.G., *Adv. Funct. Mater.*, 2010, 20: 2923
- 22 Wang, F.F., Hu, J., Cao, X.D., Yang, T., Tao, Y.T., Mei, L., Zhang, X.W. and Huang, W., *J. Mater. Chem. C.*, 2015, 3: 5533
- 23 Kumar, D., Thomas, J.K.R., Lee, C.P. and Ho, K.C., *Asian J. Org. Chem.*, 2015, 42: 164
- 24 Bodedla, G.B., Thomas, J.K.R., Lee, C.P. and Ho, K.C., *RSC Adv.*, 2014, 4: 53588
- 25 Bodedla, G.B., Thomas, J.K.R., Fan, M.S. and Ho, K.C., *J. Org. Chem.*, 2016, 81: 640
- 26 Algul, O., Kaessler, A., Apcin, Y., Yilmaz, A. and Jose, J., *Molecules*, 2008, 13: 736
- 27 Niu, H.J., Luo, P.H., Zhang, M.L., Zhang, L., Hao, L.N., Luo, J., Bai, X.D. and Wang, W., *Eur. Polym. J.*, 2009, 45: 3058
- 28 Niu, H.J., Kang, H.Q., Cai, J.W., Wang, C., Bai, X.D. and Wang, W., *Polym. Chem.*, 2011, 2: 2804
- 29 Cai, J.W., Niu, H.J., Wang, C., Ma, L.N., Bai, X.D. and Wang, W., *Electrochim. Acta*, 2012, 76: 229
- 30 Chang, C.W., Yen, H.J., Huang, K.Y., Yeh, J.M. and Liou, G.S., *J. Polym. Sci., Part A: Polym. Chem.*, 2008, 46: 7937
- 31 Chou, Y.H., Yen, H.J., Tsai, C.L., Lee, W.Y., Liou, G.S. and Chen, W.C., *J. Mater. Chem. C.*, 2013, 1: 3235
- 32 Yen, H.J., Guo, S.M., Yeh, J.M. and Liou, G.S., *J. Polym. Sci., Part A: Polym. Chem.*, 2011, 49: 3637
- 33 Cai, J.W., Niu, H.J., Zhao, P., Ji, Y., Ma, L.N., Wang, C., Bai, X.D. and Wang, W., *Dyes Pigments*, 2013, 99: 1124