

# Synthesis, spectroscopic and electrochemical characterization of polyurethanes containing triphenylamine derivative

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**Abstract** A series of novel conducting polyurethanes (PUs) with methoxyl triphenylamine (methoxyl-TPA) were synthesized from a new isocyanate with various dihydroxy monomers. The new isocyanate was prepared with *p*-anisidine and 4-fluoronitrobenzene. The structures of the designed polymers had been determined by FT-IR and <sup>1</sup>H NMR. These polymers are amorphous and readily soluble in many polar organic solvents, such as *N,N*-dimethylformamide, dimethylacetamide and dimethyl sulfoxide. Similarly, the optical band gaps of PU-1, PU-2 and PU-3 are found to be 2.41, 2.51 and 2.44 eV, respectively. In addition, the polymers display excellent thermal stability, reversible electrochemical oxidation, high optical contrast ratio and electrochromic behavior from brown to cyan in the range of 0–1.5 V. High coloration efficiency of PU-2 arrives to 94.17 cm<sup>2</sup> C<sup>-1</sup>.

**Keywords** Polyurethanes · Spectroscopic · Electrochromic · Band gap

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## Introduction

Owing to their chemical compositions, electrochromic (EC) materials can be electrochemically oxidized or reduced. Electrochromic materials have huge potential applications for information storage, electrochromic display, photovoltaic cells, transistors, smart windows, antiglare mirrors, and optical switch [1–3]. Generally speaking, the electrochromic materials are classified as transition metal oxides (e.g.,  $\text{WO}_3$  or  $\text{IrO}_2$ ) [4], inorganic coordinating complexes [5], organic small molecules [6] and conjugated organic polymers [7]. Among them, conjugated organic polymers have obtained significant attention in the past decades due to high conductivities, redox properties and optoelectronic properties [8–10]. Recently, researchers have focused on conjugated organic polymers with triphenylamine derivatives up to strong *N* electron-donating ability, and can form stable delocalized radical cation [11–13]. Triphenylamine is a stable bulky three-dimensional propeller group, which is used in the electrochromic and photoconductor field due to the hole transport properties.

Polyurethane is one of the most important polymers which is often widely used in adhesives, plastics, composite materials, coating industry and other fields, due to its broad substrate suitability, outstanding chemical resistance abrasion resistance, mechanical properties and excellent good elasticity [14–16]. However, PU has high melting or softening temperatures and is insoluble in organic solvents owing to the presence of strong intermolecular interactions and the rigidity of the backbone [17]. If a long alkyl group or side chain was imported on the PUs, they could solve this problem. But they would degrade the stability and have no help to change PUs' color [18]. To conquer these disadvantages, the PUs molecular structures should be rational designed for increasing solubility and electrochromic properties [19]. Recently, researchers have synthesized the electrochromic polymers by incorporation TPA segment. Nitrogen atom is an active center in TPA group and could form a stable delocalized radical  $\text{TPA}^+$  by applying a voltage along with electrochromic phenomenon from reduction to oxidation. Even so, the electrogenerated cation radical of TPA is instable and the radical electron could resonance to ortho and para positions. Charge-transfer complexes (CTC) tetraphenyl benzidine (TPB) are formed by two  $\text{TPA}^+$  tail-to-tail coupling and loss of two H per dimer [20]. To prevent coupling, methoxyl was introduced at the para position of triphenylamine and performed a stable radical cation.

In the work, we synthesized a new isocyanate and several polyurethanes with methoxyl triphenylamine group PU-1, PU-2 and PU-3, respectively. We adopted a straightforward synthetic mean via isocyanate and dihydroxys chemical polymerization. All the PUs were tested by approaches of FT-IR,  $^1\text{H-NMR}$ , TGA and SEM. Electrochemical and electrochromic properties of the polymers were conducted with cyclic voltammetry (CV) and UV–Vis absorption spectra by casting solution onto an indium tin oxide (ITO) coated glass substrate. PUs display excellent thermal stability, solubility, reversible electrochemical property and electrochromic stability.

## Experimental

### Materials

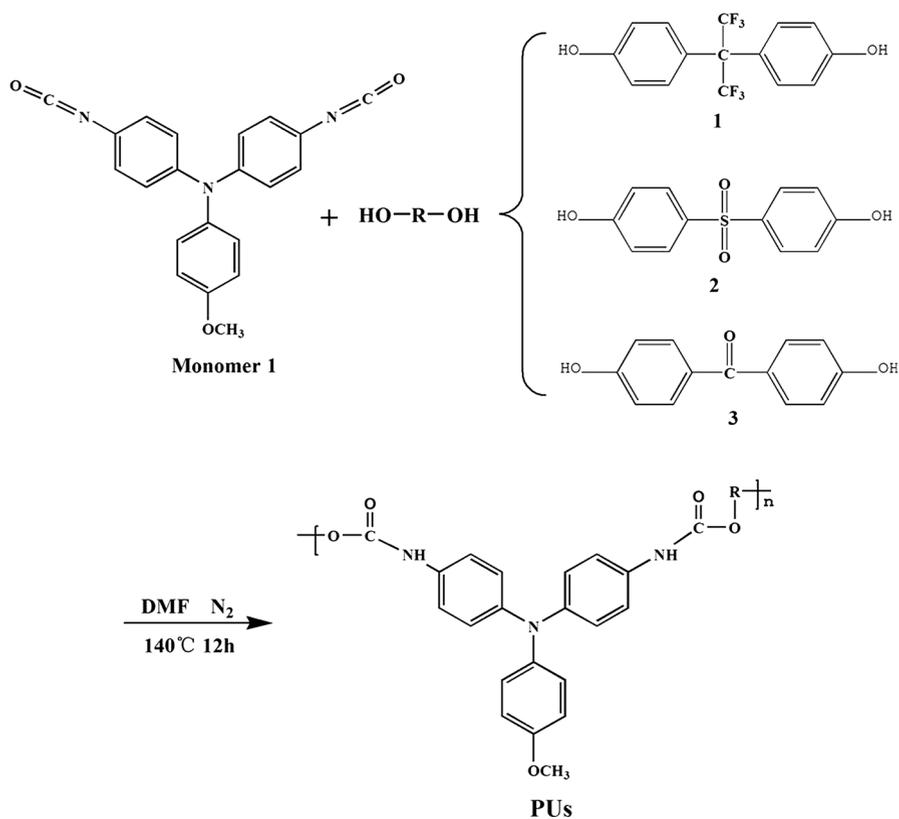
*p*-Anisidine, 4-fluoronitrobenzene, bis(trichloromethyl)carbonate and 5 wt% palladium on activated carbon (Pd C<sup>-1</sup>) were used directly without further purification. Commercial dihydroxy compounds, including 4,4'-(hexafluoroisopropylidene) diphenol (1), 4,4'-sulfonyldiphenol (2) and 4,4'-dihydroxybenzophenone (3) were purchased from Alfa Aesar. Acetonitrile (CH<sub>3</sub>CN) and tetrabutylammonium perchlorate (TBAP) were used with electrochemical tests. *N,N*-dimethylformamide (DMF) (analytical reagent) (AR), dimethylacetamide (DMAC), toluene and dimethyl sulfoxide (DMSO) as the reaction solvents were purified under reduced pressure.

### Synthesis of monomer

Monomer 1 was synthesized by bis (trichloromethyl) carbonate and compound 2 in Scheme S1 referring to Refs. [20, 21]. *p*-Anisidine (0.06 mol), 4-fluoronitrobenzene (0.12 mol) and NaH were mixed in 180 ml DMSO into a three flask glass. Then the mixture was raised to 130 °C for 20 h under N<sub>2</sub>. The obtained compound 1 was collected by filtration and washed with acetone, subsequently. Compound 2 was reduction by compound 1, hydrazine monohydrate and catalyst. 10 ml hydrazine monohydrate was added dropwise to mixture for compound 1 and 5 wt% Pd C<sup>-1</sup> (1 g) for 1 h in ethanol. The reaction mixture was stirred at 70 °C for 15 h. Pure compound 2 was collected until Pd C<sup>-1</sup> was removed by hot filtration. Compound 2 (10 mmol) in dry 20 ml toluene dropped bis (trichloromethyl) carbonate (6.67 mmol) which was added 6 ml toluene in a constant pressure funnel at 0 °C for 1 h. The reaction mixture was stirred at 80 °C for 15 h. Blue Monomer 1 was dried at 60 °C in vacuum. Monomer 1 (FT-IR/cm<sup>-1</sup>): 2260 cm<sup>-1</sup> (N=C=O, stretching). <sup>1</sup>H NMR (400 MHz, DMSO-d<sub>6</sub>, δ ppm): 7.60–6.56 (m, H of benzene), 3.78 (s, H of OCH<sub>3</sub>).

### Polymer synthesis

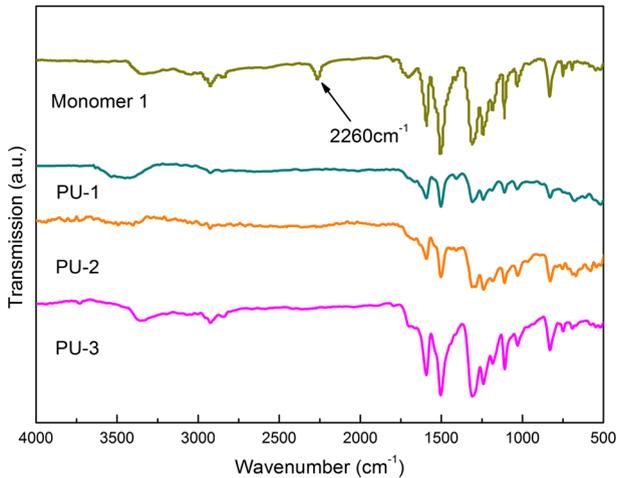
Monomer 1 and dihydroxy compounds were polymerized (the rate of mole was 1:1). The synthesis of PU-1 was given as an example to illustrate the PUs synthetic procedure. Monomer 1 (5 mmol) and dihydroxy compound 1 (5 mmol) were stirred at 140 °C for 12 h in DMF under N<sub>2</sub>. The PU solution was poured slowly into 200 ml of cool water. The solid was collected by filtration. PU was purified with methanol in a Soxhlet extractor. The Synthetic route for Monomer 1 and PUs are shown in Scheme 1 and Scheme S1. FT-IR and <sup>1</sup>H NMR spectra are illustrated in Table 1, Fig. 1, Figs. S1 and S2.



**Scheme 1** Synthetic route for PU-1, PU-2 and PU-3

**Table 1** FT-IR and <sup>1</sup>H NMR characteristic peaks of PUs

	PU-1	PU-2	PU-3
N-H (cm <sup>-1</sup> )	3419	3406	3376
C=O (cm <sup>-1</sup> )	1668	1674	1692
aromatic ring of benzene (cm <sup>-1</sup> )	1596, 1499	1596, 1500	1596, 1503
NH-C=O (cm <sup>-1</sup> )	1108	1113	1107
<i>p</i> -Substituted benzene (cm <sup>-1</sup> )	829	823	830
-HN-C=O (ppm)	8.03	8.04	8.04
H of triphenylamine (ppm)	7.57–6.63	6.62–5.59	7.58–6.64
H of methoxyl (ppm)	3.78	3.78	3.78



**Fig. 1** FT-IR spectra of monomer 1 and PUs

### Preparation of the film

A solution of PU was dissolved in DMF, then coated on a  $1 \times 4 \text{ cm}^2$  ITO-coated glass. The glass substrate was placed into an oven in vacuum at  $100 \text{ }^\circ\text{C}$  for 10 h to remove the DMF. The resulted films were used for the electrochemical performance, morphology and optical analysis.

### Characterization techniques

$^1\text{H}$  NMR spectra of PUs were measured by Bruker AC-400 MHz and advance III Spectrometer, and referenced to  $\text{DMSO-d}_6$ , using tetramethylsilane as an internal reference signals. The peak multiplicity were listed as follows: s, singlet; d, doublet; t, triplet; m, multiplet. The Fourier transform infrared (FT-IR) spectra were determined by Perkin Elmer Spectrum between 400 and  $4000 \text{ cm}^{-1}$ . An ubbelohde viscometer was used to test the viscosities of PUs in DMAC ( $0.5 \text{ g dl}^{-1}$ ) at  $30 \text{ }^\circ\text{C}$ . Thermogravimetric analysis (TGA) was conducted by a PerkinElmer Pyris 6 at a heating rate of  $10 \text{ }^\circ\text{C min}^{-1}$  in  $\text{N}_2$ . The structures of the samples measurements were recorded by X-ray diffraction (Rigaku D/max-rB, Cu  $\text{K}\alpha$  radiation,  $\lambda = 0.1542 \text{ nm}$ , 40 kV, 100 mA). Contact angles were carried out by JY-82 video contact angle measurement. Scanning electron microscopy (SEM) images were presented with Hitachi S-4800 at an acceleration voltage of 20 kV. Geometry optimizations were carried out using the B3LYP functional as implemented in the Gaussian 98 program [22]. Ultraviolet–Visible (UV–Vis) absorption spectra were conducted by Perkin Elmer Lambda 950. Electrochemistry was taken by electrochemical workstation CHI 660E in a three-electrode mode: working electrode with  $1 \times 4 \text{ cm}^2$  ITO, auxiliary electrode with a platinum wire and reference electrode with a  $\text{Ag/AgCl}$  in 0.1 M TBAP/ $\text{CH}_3\text{CN}$ .

## Results and discussion

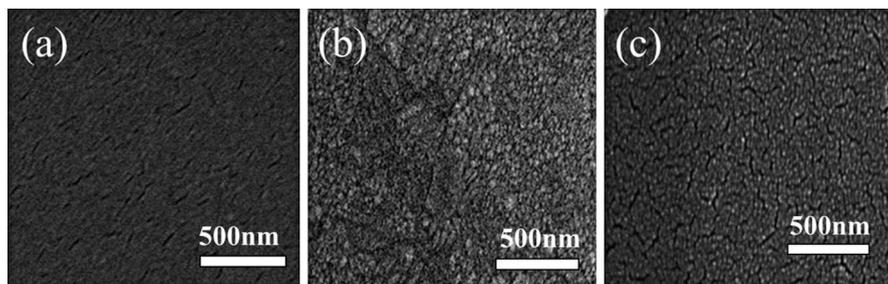
### FT-IR and $^1\text{H}$ NMR analysis of polymers

A series of PUs with pendent methoxyl triphenylamine group were synthesized with Monomer 1 and dihydroxy compounds via solution polycondensation in the atmosphere of  $\text{N}_2$ . The structures of Monomer 1 and PUs were taken with FT-IR spectra and are shown in Fig. 1. A typical FT-IR spectrum for Monomer 1 exhibits an absorption peak at  $2260\text{ cm}^{-1}$  ( $-\text{NCO}$ ), which disappears after polymerization, indicating a completed reaction. There are performed approximate to  $3400$  and  $1680\text{ cm}^{-1}$ , corresponding to stretching vibrations  $\text{N-H}$  and  $\text{C=O}$  unit for PUs. The absorption peaks around  $1110\text{ cm}^{-1}$  is attributed to the vibrations of  $\text{NH-C}$  group in polymer backbone.  $^1\text{H}$  NMR spectra of PUs are shown in Fig. S2. The peak at  $8.04\text{ ppm}$  in DMSO, corresponds to hydrogen in  $\text{NH-COO}$  group. The chemical shifts of the protons on phenylene rings are shown at the range of  $7.6\text{--}6.6\text{ ppm}$ . All the peaks are consistent with the given structures. All polymers are soluble in polar organic solvents, like DMF DMAC, DMSO and NMP, which are beneficial for polymer film formation. The inherent viscosity values were recorded as  $0.42$ ,  $0.45$  and  $0.53\text{ dl g}^{-1}$  by an ubbelohde viscometer, respectively.

### XRD and morphology

XRD patterns for PU-1 to PU-3 are shown in Fig. S3. All the polymers appear steamed bread peak, which show that all the PUs are completely amorphous. The amorphous nature of PUs doses not form a well-packed structure and reflects in their excellent solubility, due to the incorporation of the bulk three-dimensional stable propeller methoxyl-TPA group along the polymer backbone [23].

SEM images of PUs are shown in Fig. 2. It can be seen that PU-1 has the similar morphology with PU-3, which is not only roughness but also has many cracks and pinholes. The resulted porous structure could minimize the diffusion distance and improves the diffusion rate of electron during injection/extraction. SEM image of PU-2 is composed of many granules which could enlarge the contact area with the anions in the electrolyte. These surface morphologies of the polymers are beneficial to improve the transport counter ion speed.



**Fig. 2** The SEM images of **a** PU-1, **b** PU-2 and **c** PU-3

## Thermal properties and interfacial wettability

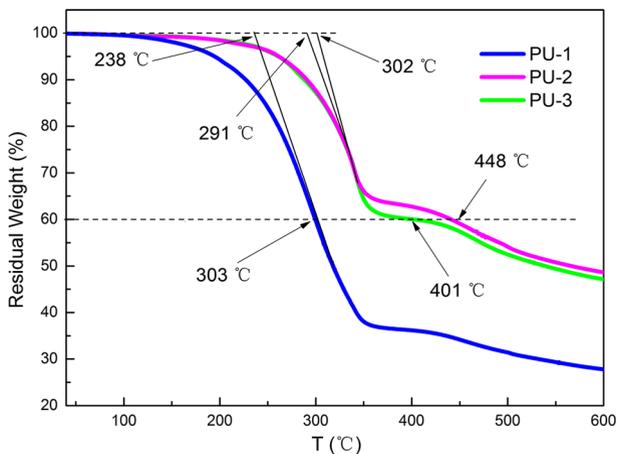
The thermal behaviors of PUs are shown in Fig. 3. The maximum decomposition rates of PU-1, PU-2 and PU-3 are at 238, 292 and 302 °C, respectively. The temperature with 10% weight-loss are in the range of 230–290 °C, attributed to decomposition of the small molecule and the oligomer. The temperature for PU-1 with 60 wt% weight-loss is recorded over 303 °C. Moreover, PU-2 and PU-3 curves are exhibited over 60 wt% loss at 400 °C. Compared to PU-1, the higher weight-loss temperatures of PU-2 and PU-3 can be ascribed to high char yields in the polymer backbone. The TGA curves show that all PUs possess excellent thermal stability, mainly due to the introduction of high aromatic contents of the three-dimensional stable propeller methoxyl-TPA segment in the main chain. The water contact angles of the PUs films are shown in Fig. S4. The contact angles are 71.5°, 71.7° and 70.8°, respectively, less than 90°. All the wetting angles of polymers show a certain of wetting properties of polyurethanes.

## Optical properties and electrochemical properties

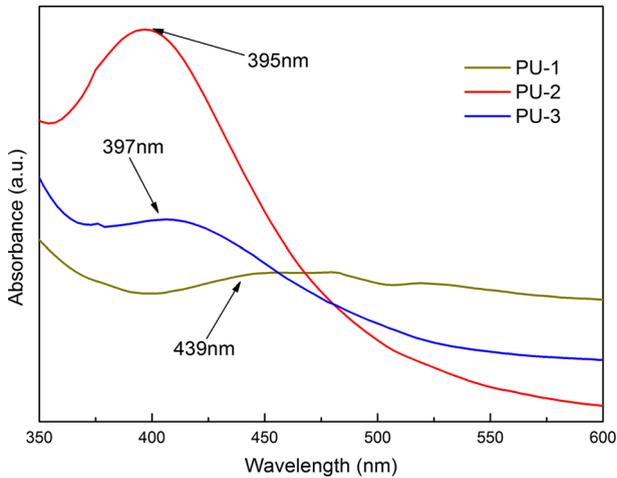
UV–Vis absorption bands are exhibited in Fig. 4, and display strong absorption at 395–439 nm due to  $\pi$ – $\pi^*$  transition resulting from charge-transfer between N atoms from the aromatic rings and methoxyl-TPA group. In addition, different absorption bands for the polymers are assignable to dihydroxy compound. The optical band gaps are calculated from the following equation:

$$E_g = 1240/\lambda_{\text{onset}}^{\text{abs}}, \quad (1)$$

where  $\lambda_{\text{onset}}^{\text{abs}}$  is onset absorption wavelength from UV–Vis spectra of thin films. The relevant data are summarized in Table 2. The values follow the order: PU-1 < PU-3 < PU-2.



**Fig. 3** TGA curves of the PUs



**Fig. 4** UV-Vis spectra of PUs films

**Table 2** Optical and electrochemical properties of the PUs

	$\lambda_{\text{film}}^{\text{abs a}}$ (nm)	$\lambda_{\text{onset}}^{\text{abs b}}$ (nm)	$E_{1/2}^{\text{peak c}}$ vs Ag/AgCl (V)	$E_{\text{onset}}^{\text{peak}}$ vs Ag/ AgCl (V)	$E_{\text{HOMO}}^{\text{electro d}}$ (eV)	$E_{\text{LUMO}}^{\text{electro d}}$ (eV)	$E_{\text{g}}^{\text{e}}$ (eV)	$E_{\text{HOMO}}^{\text{quantum}}$ (eV)	$E_{\text{LUMO}}^{\text{quantum}}$ (eV)	$E_{\text{g}}^{\text{quantum}}$ (eV)
PU-1	439	513	0.94	0.67	5.03	2.62	2.41	-4.99	-1.06	3.93
PU-2	395	494	0.98	0.71	5.07	2.56	2.51	-5.12	-1.48	3.64
PU-3	397	507	0.93	0.65	5.01	2.57	2.44	-4.97	-1.67	3.30

<sup>a</sup>UV-Vis absorption peaks in PUs film

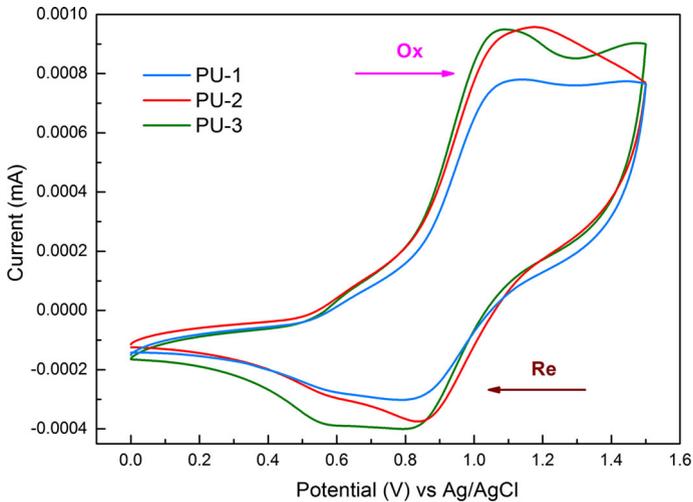
<sup>b</sup>The onset of absorbance for polymer thin film

<sup>c</sup>Average potential of the redox couple peaks

<sup>d</sup>The measured data were calculated

<sup>e</sup>Theoretical data were calculated

The CV curves of polymers are recorded in Fig. 5 at a scan rate of  $50 \text{ mV s}^{-1}$  from 0 to 1.5 V. The curves show one reversible oxidation redox couples for all PUs. The color of PUs changes from brown to cyan with the corresponding oxidation redox peaks. The oxidation state is due to the electron removal from the electron-donating N atom in TPA segment to form a stable delocalized radical mono cation  $\text{TPA}^+$ . The reduction state is owed to the N atom in  $\text{TPA}^+$  to yield neutral TPA group after gaining one electron. The reversible oxidation redox couple at half-wave potentials ( $E_{1/2}$ ) and onset potentials ( $E_{\text{onset}}$ ) is calculated from Fig. 5. In addition, the oxydation peak current of PU-1 is different from those of PU-2 and



**Fig. 5** Cyclic voltammograms of PUs in 0.1 M TBAP/CH<sub>3</sub>CN

PU-3. This phenomenon could be attributed to the strong electrophilic hexafluoroisopropylidene group in the dihydroxy compound. The hexafluoroisopropylidene can interrupt the conjugation of the conjugated  $\pi$  bond and disorder the configuration of polymer molecule. Then this effect may reduce the density of electro-active nitrogen. Oxidation peak current of PUs is determined by the density of electro-active nitrogen. So, the oxidation peak current of PU-1 is smaller than those of PU-2 and PU-3.

To gain exact oxidation reduction potential, the reference electrode is corrected by the Fc/Fc<sup>+</sup>, whose redox potential is assumed to be energy level of  $-4.80$  eV to vacuum. The external ferrocene/ferrocenium (Fc/Fc<sup>+</sup>) redox standard  $E_{Fc/Fc^+}$  is  $0.44$  V versus Ag/AgCl in CH<sub>3</sub>CN. The energy levels of the highest occupied molecular orbital (HOMO) and the lowest unoccupied molecular orbital (LUMO) of the conjugated polymers are calculated from CV curves and formula.

$$\begin{aligned}
 E_{\text{HOMO}}^{\text{electro}} &= -e \left( E_{\text{onset vs Ag/AgCl}}^{\text{OX}} + 4.80 - E_{\text{Fc/Fc}^+} \right) \text{ eV} \\
 &= -e \left( E_{\text{onset vs Ag/AgCl}}^{\text{OX}} + 4.36 \right) \text{ eV},
 \end{aligned}
 \tag{2}$$

$$E_{\text{LUMO}}^{\text{electro}} = E_{\text{HOMO}}^{\text{electro}} + E_g,
 \tag{3}$$

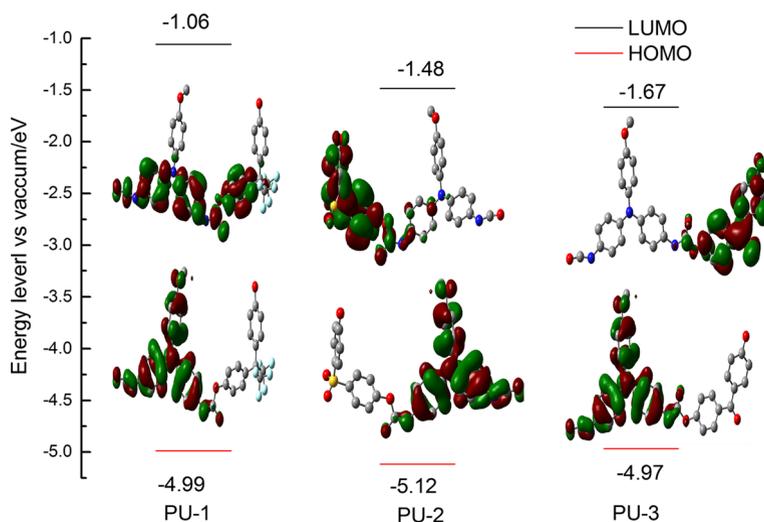
where  $E_{\text{onset}}^{\text{OX}}$  is the onset oxidation potential vs Ag/AgCl,  $E_{\text{HOMO}}^{\text{electro}}$  of PU-1 to PU-3 are calculated in the range from  $-5.07$  to  $-5.01$  eV.  $E_{\text{LUMO}}^{\text{electro}}$  of PU-1 to PU-3 are calculated in the range from  $-2.62$  to  $-2.56$  eV. The  $E_{\text{HOMO}}^{\text{electro}}$  follow the order: PU-3 < PU-1 < PU-2. The results illustrate that diverse dihydroxyphenyl segment play the key role in the electron structure and regulate the gaps of polymers.

## Quantum chemistry calculation

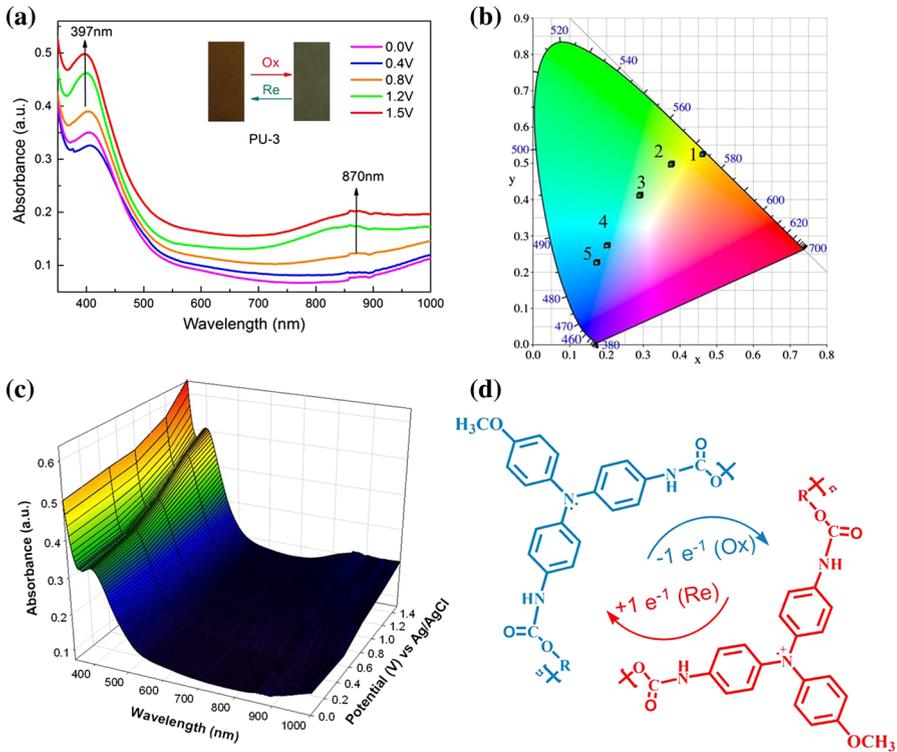
To better observe the geometries and the electron-density distribution, ground-state geometry optimization and calculation of energy levels of repeating structure unit of PUs are illustrated using density functional theory (DFT) based on the Becke's three parameter gradient-corrected functional (B3LYP) with a polarized 6-31G(d) basis in the Gaussian 98 program. Ground-state optimized structures and values of HOMO ( $E_{\text{HOMO}}^{\text{quantum}}$ ) and LUMO ( $E_{\text{LUMO}}^{\text{quantum}}$ ) are evaluated and shown in Fig. 6. The electron-density distribution of HOMO state of the ground-state is fully located on methoxy triphenylamine moiety for electronic state of the oxidation state, which make for receiving higher hole mobility. LUMO state of the basic unit is mainly located on dihydroxyphenyl moiety.  $E_{\text{HOMO}}^{\text{quantum}}$  are given in the range from  $-5.12$  to  $-4.97$  eV, and  $E_{\text{LUMO}}^{\text{quantum}}$  are given in the range from  $-1.67$  to  $-1.06$  eV. HOMO–LUMO energy gaps ( $E_{\text{g}}^{\text{quantum}}$ ) are listed between 3.30 and 3.93 eV. Due to different dihydroxy, energy gaps of the polymers are distinct. The trend of  $E_{\text{g}}^{\text{quantum}}$  follows in the order: PU-3 < PU-2 < PU-1.  $E_{\text{g}}$  follows the order: PU-1 < PU-2 < PU-3. The bias is considered that the calculated results are based on the repeat units of the polymers in vacuum, while the experimental result are based on the polymer films.

## Electrochemical behavior

Electrochromic absorption spectra of the thin polymer films are shown in Fig. 7 and Fig. S5. All the polymers disclose similar electrochromic behaviors, and a representative electrochromic spectrum of PU-3 is exhibited in Fig. 7a. When the applied potential increases positively, the peak intensity of the characteristic



**Fig. 6** Pictorial representations of the electron-density in the frontier molecular orbitals of the repeating units and pictorial energy gaps



**Fig. 7** Electrochromic behaviors of PU-3 thin film: **a** UV–Visible absorption spectra (in CH<sub>3</sub>CN with 0.1 M TBAP as the work electrolyte); **b** the CIE 1931 (x, y) chromaticity diagram; **c** 3D spectrum; **d** proposed simplified redox mechanism of PUs

absorbance at 397 nm increases gradually, owed to the characteristic  $\pi-\pi^*$  transition in TPA. A new absorbance band turns up at 870 nm at 0.8 V, due to the oxidation of the removal from electron. Simultaneously, the color changes from initial brown to cyan. Chromaticity diagram is drawn with the CIE 1931 in Fig. 7b. The five points correspond to five absorption spectra and color from brown (CIE 1931:  $x$  0.4609;  $y$  0.5266) to cyan (CIE 1931:  $x$  0.1783;  $y$  0.2307) in Fig. 7b. The similar electrochromic properties are taken for PU-1 and PU-2 (Fig. S5). Colors of PU-1 range from brown (CIE 1931:  $x$  0.4462;  $y$  0.524) to cyan (CIE1931:  $x$  0.1509;  $y$  0.2463). Colors of PU-2 range from brown (CIE 1931:  $x$  0.4560;  $y$  0.5400) to cyan (CIE 1931:  $x$  0.1442;  $y$  0.1109). The colors of all polymers change from brown (neutral state) to cyan (oxidized state) due to one electron removal from the electroactive N site in TPA moiety to form a stable delocalized mono cation TPA<sup>+</sup>. In addition, inter-valence charge-transfer (IV-CT) also stimulates the formation of radical cation on N atom for TPA excitation. Visually UV–Visible absorption spectrum of PU-3 is depicted with 3D spectrum in different voltage (Fig. 7c). Simplified redox process of PUs is proposed corresponding to electronic transfer process in Fig. 7d. With the applying of voltage, neutral N atom lost an electron to be a N<sup>+</sup>.

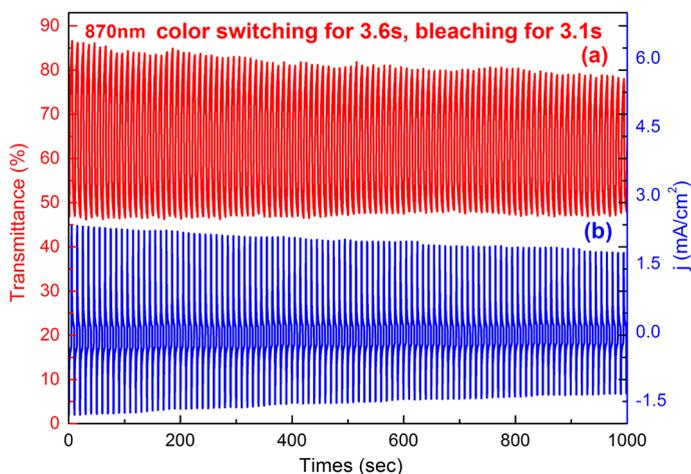
To further research electrochromic characteristics of the PUs, optical switching and coloration efficiency are studied. For optical switching studies, the films are applied potential step from neutral (0.0 V) and oxidized (+ 0.85 V) state and the absorbance profiles are shown in Fig. 8, Figs. S6 and S7. The switching time is defined as the time required for obtaining 90% of the full change in absorbance after switching the potential. The color switching time is 3.6 s and bleaching time is 3.1 s at 870 nm for PU-3 (Fig. 8). Color switching time is slower than the fade switching time, which may be due to the high internal resistance and ion permeation in comparison to those of conducting polymers such as polythiophene or polypyrrole derivatives [24]. Similar electrochromic switching for PU-1 and PU-2 can be seen in Figs. S6 and S7. After continuous 100 cyclic switches between 0.0 and 0.85 V, all polymer films still display high optical contrast ratio.

Coloration efficiency (CE:  $\eta$ ) is another key parameter of the electrochromic materials, which can be calculated according to the following equations:

$$\delta_{(\text{OD})} = \lg(T_b/T_c), \quad (4)$$

$$\eta = \delta_{(\text{OD})}/Q, \quad (5)$$

where  $T_b$  is the transmittances before coloration and  $T_c$  is the transmittances after coloration.  $\delta_{(\text{OD})}$  is the change of the optical density, which is proportional to the amount of created color centers.  $\eta$  denotes the CE ( $\text{cm}^2 \text{C}^{-1}$ ) and  $Q$  ( $\text{mC cm}^{-2}$ ).  $Q$  is the amount of injected/extracted charge in each unit sample area. The calculation data are recorded in Table 3. The highest CE of PU-2 is  $94.17 \text{ cm}^2 \text{C}^{-1}$ , due to the diverse dihydroxyphenyl segment.



**Fig. 8** Optical switching procedures: **a** potential step absorptometry (at 870 nm, upper); **b** current consumption (lower) as a function of time of PU-3 by applying a potential step (0.0–0.85 V) with a cyclic time for 10 s (0.1 M TBAP/CH<sub>3</sub>CN)

**Table 3** Optical and electrochemical data collected for the coloration efficiency measurements of the PUs

	$\lambda$ (nm) <sup>a</sup>	$\delta_{(OD)}^b$	$Q$ (mC cm <sup>-2</sup> ) <sup>c</sup>	$\eta$ (cm <sup>2</sup> C <sup>-1</sup> ) <sup>d</sup>
PU-1	830	0.18	2.14	84.11
PU-2	800	0.21	2.23	94.17
PU-3	870	0.17	2.21	76.92

<sup>a</sup>Wavelength where the data were determined<sup>b</sup>Optical density change at the given wavelength<sup>c</sup>Injected charge which is determined from the in situ experiments<sup>d</sup>Coloration efficiency which is calculated from the equation

## Conclusion

In summary, a series of electrochromic polyurethanes with excellent optical transmittance change have been successfully synthesized from new isocyanate with methoxyl-TPA group and three different dihydroxy compounds. Methoxyl-TPA structure forms the amorphous polymers, which exhibit good solubility in polar organic solvents. PUs possess excellent thermal stability. The PUs display reversible electrochromic property and high optical contrast ratio. PU-2 has highest coloration efficiency. The color changed from initial brown to cyan. Hence, these novel PUs incorporate methoxyl-TPA have great potential in optoelectronics as optical coating, electrochemical energy storage, smart windows, displays, dimming mirrors and sensors.

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