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### **Electronic materials**



## Anthraquinone-functionalized polyurethane designed for polymer electrochromic and electrical memory applications

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#### ABSTRACT

Novel electroactive functional polyurethane PU(IPDI-AQ-EG) with anthraquinone moiety in the backbone is synthesized and characterized. Due to the stable redox behaviors from spectroelectrochemical tests, PU(IPDI-AQ-EG) film is used to prepare electrochromic device with ITO/PU(IPDI-AQ-EG)/gel electrolyte/ITO structure, which shows well-behaved electrochromic properties with obvious color contrast when applied the external potentials from 0 to - 2.0 V. Moreover, electrical memory devices with configuration of ITO/ PU(IPDI-AQ-EG)/Al are successfully fabricated via convenient spin-coating process. Current-voltage sweeps between the two electrodes indicate this type of device exhibits typical resistive switching performance with the function of flash memory. The devices can operate at low threshold voltages (write voltage of -2.7 V and erase voltage of +2.8 V) with a high ON/OFF current ratio up to  $10^5$ . The retention time of both conductivity states can be maintained as long as 3000 s without obvious deterioration. It has been demonstrated that the anthraquinone group serving as good electron-withdrawing site in the polymer backbone has a strong influence on the resistive switching characteristics. Preliminary results reveal that the obtain polyurethane PU(IPDI-AQ-EG) is a promising multi-functional material that can be applied in both polymeric electrochromic and memory devices.

#### Introduction

The booming development of information technology demands for the electrical memory devices to achieve flexible, light weight, high data storage, fast response, and low cost. The fabrication and application of the traditional silicon- and metal oxide-based semiconductor have met many difficulties [1]. In recent years, polymer nonvolatile memory devices, which not only overcome the disadvantage of silicon-based semiconductor device but also possess the advantages such as flexible, light weight, easy fabrication, and

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most likely breaking potential limiting scaling difficulties, have become the active research topic in new nonvolatile data storage technology [2, 3]. Polymer memory devices can exhibit several different conductivity states at the same applied voltage to fulfill ultrahigh density and ultrahigh-capacity data storage, and thus they are promising candidates for next generation memories. To date, owing to their resistive switching properties, various polymers and composites, such as poly(N-vinylcarbazole) and derivatives [2, 4], non-conjugated and conjugated copolymer containing chelated europium complex [2, 4], polyimides [5–7], polythiophene and their derivatives [8, 9], polyfluorene derivative [10], conjugated-polymer-functionalized graphene oxide [11], have been reported in nonvolatile memory applications. It is worth noting that a number of interpretations have been addressed for the memory effect in electron donor-acceptor (D-A) containing polymers [12–14], in which electric-field-induced charge transfer (CT) can easily occur within the repeating unit of the polymer to develop a CT complex. The stability of a CT complex is essential for the retention of charge in the resistive-type memory device, and it strongly depends on the molecular electronic properties, that can be tuned by electron-donating or electron-withdrawing substituents [15]. Electron-donating moieties containing electron-rich substituents, such as carbazole, arylamine, or dibenzothiophene groups, and electron-withdrawing moieties, such as hexafluoroisopropyl or sulfonyl groups and imide rings, have been widely introduced in the synthesis of D-A polymers, and the impact of various electron-donating/electron-withdrawing moieties on the memory characteristics has been fully addressed [16-18]. Recently, anthraquinone (AQ) group as electronwithdrawing moieties was introduced into some azo molecules [19, 20] and polyimides [21], and memory investigations of these organic or polymeric systems have showed that AQ units were not only suitable receptors but also acted as charge carriers for electronic conductivity in the materials [19, 21]. Besides, AQ unit holds the feature of two-electron reduction/oxidation reactions, which enables an AQ containing molecular wires being invertibly switched by chemical reduction and oxidation between crossconjugated and linear conjugated to cause a conductance change from low ("off") to high ("on") [22]. Interestingly, in the two-electron reduction reactions, the anthraquinone group is reduced to radical

anionic and dianionic forms, and this process is usually involved with a remarkable change of coloration. Several polymers consisting of AQ moieties have been introduced as active materials in electrochromic devices [23, 24]. Therefore, AQ group can be promising chemical components in decorating either the side chain or in the backbone of high-performance polymers, and their roles in the memory and electrochromic characteristics are essential for the development of advanced multi-functional polymers.

Polyurethane (PU), a cheap but superior engineering thermoplastic, has already received considerable attention since it has been synthesized, due to their unique physical and chemical properties, as well as outstanding biological compatibility. The potential application of PUs in photoelectric device has been proposed in some studies [25–29]. Recently, significant research efforts have been devoted to decorating PU with some functional electroactive components to meet the production requirements for nonvolatile memory devices. Mixing PU with some micromolecules or carbon nanotubes forming a continuous network of the conducting composite material has showed the bidirectionally switchable memory characteristics [26, 30]. However, resistive switching behaviors of pure PU material have not been reported yet. The development of highly stable anthraquinone-based polyurethanes as single active polymeric layer for multi-functional applications has become rapidly evolving research fields.

In this work, we attempted to modify PU chain using the electrosensitivity of AQ moieties to obtain a functionalized PU(IPDI-AQ-EG) for high-performance memory devices and electrochromic devices. AQ unit was from an important diol monomer 1,5bis(2-hydroxyethoxy)anthraquinone (BHEA), and isophorone diisocyanate (IPDI) was employed as a non-toxic connecting unit. With a flexible ethoxyl linkage between AQ and the IPDI units, the synthesized material is highly hydrophilic and soluble in common organic solvents and exhibits high thermal stability. The film morphology is measured by AFM technique, and the optical properties and energy levels are analyzed by cyclic voltammetry (CV) accompanied with UV-Vis spectroscopy. As is expected, smooth nanoscale thin films of PU(IPDI-AQ-EG) were readily obtained by conventional spincoating method. Memory device based on this PU(IPDI-AQ-EG) exhibits excellent resistive flash memory characteristics, in which the devices can be operated at low threshold voltages with a high current ratio and retention time of both ON and OFF states. Investigations of the electrochemical and electrochromic properties of PU(IPDI-AQ-EG) are also carried out, and the results suggested that this polyurethane is also a promising candidate for electrochromic application.

#### Experimental

1,5-Dichloroanthraquinone, dibutyltin dilaurate, and isophorone diisocyanate (DBTDL) came from Sigma-Aldrich Chemicals. All the other chemicals and reagents were of high quality and available from reputed suppliers. FTIR spectrum (KBr pellets) was recorded at resolutions of 4 cm<sup>-1</sup> on a Thermo Nicolet 360 spectrometer within the range of 4000–400 cm<sup>-1</sup>. The relative molecular weight  $(M_w)$ and polydispersity  $(M_w/M_p)$  were estimated using a Waters alliance e2695 GPC system. HPLC-grade THF was used as the eluent flowing at 1.0 mL/min at 30 °C. Monodisperse poly(ethylene oxide) were employed as calibration curve standards. The UV-Vis absorption spectrum was measured by a Varian Cary 300 UV-Vis spectrophotometer. TG analyses were performed on TA Q5000IR at a scan rate of 10 °C/min under nitrogen atmosphere. DSC studies were carried out with a NETZSCH 200 F3 at a heating rate of 20 °C/min under nitrogen flow. The rheological properties were measured on a HAAKE MARS II rheometer with 25-mm-diameter parallelplate geometry. Oscillatory shear was applied on the sample at a constant temperature of 160 °C. The chosen gap was 1 mm and the strain amplitude is 1% in all experiments. The morphological characterization of the polymer films was measured on a Bruker Dimension Edge atomic force microscope (AFM) with the tapping mode. Cyclic voltammogram (CV) was measured using a CHI 760E potentiostat by a three-electrode system. ITO substrate with the casting polymer films was used as the working electrode, a saturated Ag/AgCl as the reference electrode, and platinum plate as the counter electrode, respectively. The CV sweeps were performed in a solution of 0.1 M tetrabutylammonium hexafluorophosphate (n-Bu<sub>4</sub>NPF<sub>6</sub>) in anhydrous acetonitrile (ACN) at a scanning rate of 50 mV/s with nitrogen blowing at room temperature. SEM image was taken on a

Hitachi su8010 field emitting scanning electron microscope.

The synthesis procedure of BHEA was as follows. 1,5-Dichloroanthraquinone (5.58 g, 20 mmol), KOH (2.70 g, 48 mmol), and ethylene glycol (80 mL) were mixed together and heated to 120 °C under vigorous stirring until the reaction was completed. After being cooled, the mixture was poured into distilled water (400 mL). The yellow precipitate was filtered, washed with ethanol, and dried at 80 °C for 8 h to yield 4.90 g of the crude product. And then it was purified by repeated recrystallization from N,N-dimethylformamide (DMF)/H<sub>2</sub>O mixture in the presence of charcoal to yield brilliant yellow crystals (2.75 g, a productivity of 42%). M.p. = 182 °C, ref: 185-186 °C [31]. FTIR (KBr, cm<sup>-1</sup>): 3385, 2949, 2875, 1654, 1588, 1440, 1260, 1014, 711. <sup>1</sup>H NMR (δ, DMSO-*d*<sub>6</sub>, ppm): 7.80 (t, J = 7.8 Hz, 1H), 7.71 (dd,  $J_1 = 7.8$  Hz,  $J_2 = 1.2$  Hz, 1H), 7.53(dd,  $J_1 = 8.4$  Hz,  $J_2 = 0.84$  Hz,) 4.84 (t, J = 5.4 Hz, 1H), 4.20 (t, J = 5.4 Hz, 2H), 3.81 (q, J = 5.4 Hz), 3.81 (q, J = 5.4 Hz),*J* = 4.8 Hz, 2H). <sup>13</sup>C NMR: 59.94, 71.5, 119.4, 119.7, 120.9, 135.9, 137.2, 159.3, 182.0.

The synthesis procedure of PU(IPDI-AQ-EG) was as follows. A mixture of IPDI (7.66 mmol, 1.7027 g) and DBTDL (0.1 wt% of total mass of reactants) was dropwise added into a solution of BHEA (1.70 mmol, 0.5587 g) in dewatered DMF (3 mL) in a three-neck flask. The reaction mixture was heated to 80 °C and stirring under nitrogen for 8 h, and then ethylene glycol (6.81 mmol, 0.4226 g) dissolved in 3 mL dewatered DMF was added and maintained at 80 °C for another 12 h. Afterward, the pure polymer was obtained by precipitations from DMF into petroleum ether following by drying under vacuum at room temperature for 24 h to give 1.98 g yellow powder, yield 87.7%. The relative molecular weight (Mw) obtained by GPC was found to be 11014 g/mol with the polydispersity indexes (PDI) of 2.18. FTIR (KBr, cm<sup>-1</sup>): 3339, 2954, 2925, 1709, 1671, 1585, 1531, 1259, 1237, 808, 775, 714, 662.

The synthesis procedure of PU(IPDI-EG) was as follows. Dry ethylene glycol (1 mmol, 0.0621 g) was added in a three-necked flask, and then IPDI (2 mmol, 0.4446 g) and DBTDL (catalyst, 0.1 wt% of the total mass of reactants) dissolved in 1 mL dewatered THF were added dropwise to the flask. After stirring for 1 h of the reaction at 80 °C under nitrogen, the mixture of dry ethylene gylcol (1 mmol, 0.0621 g) and dewatered THF (2 mL) was added dropwise into the flask and stirred for 3 h. During the

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reaction, the THF (2 mL) was added once an hour to control the viscosity. Afterward, the PU(IPDI-EG) was gained by reprecipitating from THF into petroleum ether for several times. Finally, we obtained pure PU(IPDI-EG) of 0.5178 g (91%). FTIR (KBr, cm<sup>-1</sup>): 3339, 2953, 1709, 1531, 1259, 1237, 775.

Electrochromic devices were fabricated on ITO  $(< 10 \Omega/sq)$  substrates, with the configuration of ITO/PU(IPDI-AQ-EG)/gel electrolyte/ITO. The PU(IPDI-AQ-EG) film was fabricated by casting a 5.0 wt% THF solution onto the ITO substrates, then dried under vacuum. A final sample with area of around  $1.0 \times 1.0 \text{ cm}^2$  was obtained after removing the edge of the film. The used gel electrolyte was prepared by dissolving polyethylene oxide (PEO,  $M_{\rm v} \sim 100000$ , 0.32 g) and lithium perchlorate (LiClO<sub>4</sub>, 0.0731 g) in dry ACN (4 mL), followed by adding 1 mL propylene carbonate as plasticizer. Subsequently, sandwiched structure device with the configuration of ITO/PU(IPDI-AQ-EG)/gel electrode/ITO was fabricated by assembling the two ITO/glass substrates. Finally, the device was sealed with a two-component epoxy resin. Electrochromic measurements of the devices were performed on the CHI 760E potentiostat under ambient conditions.

Memory devices with the configuration of ITO/ PU/Al were fabricated as following steps. ITOcoated glass substrates (< 10  $\Omega$ /sq) were sequentially cleaned by ultrasonic treatment in deionized water, acetone and isopropanol and then dried by nitrogen gas blowing. The PU solution in THF (1.0 wt%) was filtered through 0.45-µm PTFE microfilters and then spin-coated on the clean ITO substrates at a rotation speed of 1000 rpm for 60 s. Subsequently, the substrates were transferred to a vacuum oven for solvent removal at room temperature for 16 h. Finally, circle Al top electrode was defined by thermal evaporation through a shadow mask (cell size of  $0.0314 \text{ mm}^2$ ) at a base pressure of about  $10^{-6}$  Torr with an evaporation rate of 1–2 Å/s. All devices without any encapsulation were measured using a Keithley 4200SCS semiconductor characterization system in ambient condition. During the electrical measurements, ITO was stated as the ground electrode and Al was maintained as the top electrode.

#### **Results and discussion**

The synthetic route of anthraquinone-functionalized PU(IPDI-AQ-EG) is shown in detail in Scheme 1. The anthraquinone monomer BHEA was synthesized by the reaction of 1,5-dichlorianthraquinone with ethylene glycol in the presence of potassium hydroxide at 120 °C. And then, PU(IPDI-AQ-EG) was prepared by using a facile approach involving a two-step polymerization. Firstly, NCO-terminated prepolymers were carried out by the polycondensation of IPDI and BHEA at an IPDI/BHEA molar ratio of 4.5:1 in dry DMF by using DBTDL as a catalyst. And then a portion of chain extender ethylene glycol (EG) was added to the mixture, and the reaction was allowed to proceed until the NCO peaks (2260–2280 cm<sup>-1</sup>) in the FTIR spectrum disappeared completely. Similar method was used to synthesize the PU without anthraquinone unit, namely PU(IPDI-EG), which is adopted as a pure urethane system without AQ functionalized component. The synthesized PU(IPDI-AQ-EG) and PU(IPDI-EG) are not soluble in petroleum ether and water, but slightly soluble in solvents such as methanol, diethyl ether, ACN and acetone, and freely soluble in solvents such as ethyl acetate, CH<sub>3</sub>Cl, THF, DMF, and DMSO, producing pale yellow-colored solutions. However, PU(IPDI-EG) only exhibited a good solubility in THF and partially soluble in CH<sub>3</sub>Cl and ACN.

The FTIR spectra of monomer BHEA and polymers confirmed effective formation of polyurethanes are presented in Fig. 1. The FTIR spectrum of BHEA shows strong characteristic bands at 3392, 1654, 1588 and 1260  $\text{cm}^{-1}$  due to the O–H, C=O, C=C of AQ ring and C-O stretching, respectively. While in the FTIR spectrum of PU(IPDI-AQ-EG), the isocyanate characteristic peak at 2270 cm<sup>-1</sup> disappears, suggesting IPDI was completely reacted. A broad band appeared at 3339  $\text{cm}^{-1}$  can be ascribed to the N–H stretching from urethane group. The characteristic band of C=O is split into two peaks: one at 1709  $\text{cm}^{-1}$  caused by urethane carbonyls and the other at  $1655 \text{ cm}^{-1}$ caused by anthraquinone carbonyls. New bands appeared at 1531 and 1237  $\text{cm}^{-1}$  ascribing to the C–N and -C-O-C- stretching imply that polymerization has occurred. Further, when comparing the spectrum of PU(IPDI-AQ-EG) with that of PU(IPDI-EG), bands at 1655 and 1585  $\text{cm}^{-1}$  attributed to the C=O and C=C stretching vibration mode of AQ unit, and bands at 808, 714, and 662  $\text{cm}^{-1}$  due to C–H in-plane and out-





**Scheme 1** Synthetic route of anthraquinone-functionalized polyurethane.



**Figure 1** FTIR spectra of BHEA, PU(IPDI-AQ-EG) and PU(IPDI-EG).

of-plane bending vibrations in AQ ring of PU(IPDI-AQ-EG) are all disappeared in the spectrum of PU(IPDI-EG). These variations also confirm that anthraquinone component has been successfully incorporated into polyurethane chains. Figure 2 shows the <sup>1</sup>H NMR spectra of BHEA and PU(IPDI-AQ-EG) with the chemical shifts assignment. The hydroxyl proton signal of BHEA observed at

4.84 ppm was completely disappeared after polymerization, thereby further confirming the functionalization. And the appearance of the proton from the IPDI moieties ( $\delta$  1.19, 1.70, 2.07, 3.72 ppm) and urethane protons ( $\delta$  5.01 ppm) are in good agreement with those in the Ref. [32]. The characterization results suggest that the target PU(IPDI-AQ-EG) has been prepared successfully.

Thermal properties of both polyurethane samples were analyzed by DSC and TGA. As show in Fig. 3, there is no evidence of crystallization and melting processes from DSC curves, which indicates that both polyurethanes are full amorphous polymers and will contribute to a better stability of active layer in the device [33]. The glass transition temperature ( $T_g$ ) of both polyurethanes were estimated to be around 140 °C from DSC thermograms. However, PU(IPDI-AQ-EG) exhibit better thermal resistance than PU(IPDI-EG) from the TGA curves. The 5% weight loss temperature ( $T_{5\%}$ ) of PU(IPDI-AQ-EG) was determined at 185 °C, while that of PU(IPDI-EG) was observed at 92 °C. The good thermal properties of PU(IPDI-AQ-EG) could be ascribed to the rigid AQ

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Figure 2<sup>1</sup>H NMR spectra of BHEA and PU(IPDI-AQ-EG).



Figure 3 TGA and DSC scans of PU(IPDI-EG) and PU(IPDI-AQ-EG).

units in the backbones and it is adequate for the fabrication of electronic devices.

On the basis of the DSC curves of PU (IPDI-AQ-EG) and PI(IPDI-EG), relatively high molecular weight and backbone chemistry allows energy to be stored elastically. The single bond of C–C and C–O also contribute to the flexibility in polymers at the molecular level. Therefore, the dynamic rheological

behavior of PU(IPDI-AQ-EG) and PU(IPDI-EG) were performed to determine the hard-segment content of the molecular chains. The obtained results are given in Fig. S1 in supporting information. The curves of complex viscosity ( $\eta^*$ ) versus sheared frequency revealed that PU(IPDI-AQ-EG) is less dependent on frequency than PU(IPDI-EG), which imply higher hard-segment content of PU(IPDI-AQ-EG) [34]. Further, from the curves of the plot elastic and loss modulus (G' and G'') against sheared frequency, it can be observed frequency dependence of both G'and G". The G' value of PU(IPDI-AQ-EG) was higher than that of PU(IPDI-EG) as a result of the decrease in chain mobility of PU(IPDI-AQ-EG) [35]. The higher G'' value also demonstrated the better viscosity behavior of PU(IPDI-AQ-EG) because of the decreased chain motion. In short, after introduction of AQ moieties into the PU chain, the elastic modulus and loss modulus can be enhanced, results in the improvement in the strength and mechanical and deformation response capacity PU(IPDI-AQ-EG).

The optical properties of PU(IPDI-AQ-EG) and PU(IPDI-EG) were measured through UV–Vis absorption in diluted THF solution. As depicted in



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**Figure 4 a** Absorption spectra of PU(IPDI-AQ-EG) and PU(IPDI-EG) in dilute THF solution (0.5 mg/mL). **b** CV curves of PU(IPDI-AQ-EG) and PU(IPDI-EG) as films coated on an ITO

Fig. 4a, the maximum absorption wavelengths  $(\lambda_{max})$ of PU(IPDI-EG) exhibit at 236 and 267 nm. While for PU(IPDI-AQ-EG),  $\lambda_{max}$  appear at 254 and 375 nm, which could be ascribed to the  $n-\pi^*$  and  $\pi-\pi^*$  transitions delocalized within the anthraquinone conjugated system of the chain [36]. Additionally, the optical band gap  $(E_g^{opt})$  of the PU(IPDI-AQ-EG) is estimated from the absorption edge by equation  $E_{\rm g}^{\rm opt} = 1240/\lambda_{\rm onset}$ , which is equal to 3.00 eV. The typical reduction cyclic voltammograms of polyurethanes PU(IPDI-EG) and PU(IPDI-AQ-EG) are depicted in Fig. 4b. PU(IPDI-EG) did not show obvious redox peaks during the cyclic scan. While for PU(IPDI-AQ-EG), CV curve revealed two reduce couples ( $E_{1/2}$  around -1.02 and -1.38 V) corresponding to reversible two-electron redox behavior of AQ moieties [7, 21]. Further, from the CV curve, the onset oxidation potential  $(E_{OX})$  can be estimated to be 2.16 V versus Ag/AgCl. The ferrocene/ferrocenium couple (Fc<sup>+</sup>/Fc) was added as external reference, whose oxidation potential is accepted as - 4.8 eV to zero vacuum level. The half-wave potential of the external Fc<sup>+</sup>/Fc standard ( $E_{1/2}$ , ferrocene) was found to be 0.53 V related to Ag/AgCl reference electrode under same condition. Therefore, the HOMO and LUMO levels of PU(IPDI-AQ-EG) were calculated according to the equations [37]:  $E_{\text{HOMO}}$  (eV) = - ( $E_{\text{OX}}$  + 4.80 -  $E_{1/2}$ , ferrocene) and  $E_{\text{LUMO}}$  (eV) =  $E_{\text{HOMO}} - E_{\text{g}}^{\text{opt}}$ . The values are determined to be -6.43 and -3.43 eV, respectively. These results indicate that PU(IPDI-AQ-EG) can be operated as the n-type semiconductors because the



working electrode versus Ag/AgCl in  $0.1 \text{ M Bu}_4\text{NPF}_6/\text{ACN}$  solution at a sweep rate of 50 mV/s.

deep-lying HOMO values would result in large hole injection barriers [38].

An appropriate surface morphology of the active layer is essential to build up the electronic devices. Therefore, a water contact angle experiment was carried out (Fig. 5a), and the result indicates PU(IPDI-AQ-EG) formed a hydrophilic surface with the water contact angle of 65°. Therefore, uniform PU(IPDI-AQ-EG) films can be easily achieved by spin-coating procedure on ITO substrate for the fabrication of the electrical devices. To further investigate the microphase morphology, tapping-mode AFM was used to examine the microstructure of PU(IPDI-AQ-EG) film, which was fabricated by spincoating procedure on a silicon substrate. AFM images of the PU(IPDI-AO-EG) film are presented in Fig. 5b, and the bright and dark regions represented the hard and soft microphase morphology by convention,



**Figure 5 a** Water contact angle for PU(IPDI-AQ-EG) film; **b** AFM image of the PU(IPDI-AQ-EG) film  $(5.0 \times 5.0 \ \mu\text{m}^2)$  on a silicon substrate. The corresponding 3D image is shown as the inset.

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respectively. The bright regions, which are nanocylinders in 3D images, can be attributed to hard-segment (AQ moieties) nanocylinders dispersed within a soft segment (ethylene oxide) [39, 40]. The surface root-mean-square roughness (Rq) is 1.31 nm and the Z rang is 14.7 nm, suggesting its property of film forming is excellent. The smooth surface morphology is beneficial for charge injection from the electrode into the polymer films [38, 41].

During the CV measurements of PU(IPDI-AQ-EG), the remarkable change of film color was observed, therefore the spectroelectrochemical properties of the single PU(IPDI-AQ-EG) film on ITO substrate were investigated to assess the electron-withdrawing capability of AQ unit in this polymer [19]. Figure 6a shows the UV-Vis absorbance spectra of the only PU(IPDI-AQ-EG) film under varying applied potentials in 0.1 M Bu<sub>4</sub>NPF<sub>6</sub>/ACN. The photograph of the film was taken synchronously as shown in Fig. 6a. In the neutral state at 0 V, PU(IPDI-AQ-EG) film was pale yellow and displayed strong absorption at 377 nm, denoting as the  $\pi$ - $\pi$ \* transition. As the applied voltage was set at -1.0 V (the first stage reduction potential of PU(IPDI-AQ-EG) film), the intensity of absorption band was slightly diminished as the film turning to light pink. In this process, an electron was attached to AQ to form a radical anion (as seen in Fig. 6b) [23], and therefore, the film exhibited spectral and color change. As the potential stepped to -1.4 V (the second stage reduction potential of PU(IPDI-AQ-EG) film), a band at about 510 nm intensified apparently, accompanying with the color change to deep red. When decreased the voltage to -2.0 V or lower, the band at 377 nm intensely decreased and split into two peaks at 350 and 390 nm. Meanwhile, the absorption peak at 510 nm increased gradually. Simultaneously, the color varied from pink to pinkish purple. The appearance of peaks at 390 and 510 nm both indicated the anion radical and dianion were the produced within AQ group along the polymer backbone.

Based on the above results, electrochromic characterization can be proposed for this PU(IPDI-AQ-EG) thin film. Rapid switching, stability and optical ratio are important factors in electrochromic applications. To investigate its potential applications in electrochromic device, the PU(IPDI-AQ-EG) film was subjected to switch by repetitive voltage stress between + 2.5 and - 2.0 V at intervals of 15 s, as shown in upper panel of Fig. 7. Electrical current responses and the synchronous changes in optical transmittance at  $\lambda = 510$  nm monitored as a function of time is also illustrated in the middle and lower panel of Fig. 7. As the voltage switched, the PU(IPDI-AQ-EG) film was alternated between the totally oxidized state and reduced state. The response time, worked out by chronocoulometry, is approximately 3 s from the oxidized state to the neutral state and 2 s from the neutral state to the reduced state. In addition, it was found that % transmittance at 510 nm wavelength varied from 26 to 50%; thus an optical ratio,  $\Delta T$ , is equal to 24% between the totally oxidized state and reduction states. Continuous eight cycles between double-potential steps demonstrated good



Figure 6 a In situ UV–vis spectral changes and color variations of PU(IPDI-AQ-EG) film casted on ITO substrate in 0.1 M  $Bu_4NPF_6/ACN$  at several reducing potentials; b postulated redox structures of anthraquinone moiety.





Figure 7 Switching current by applied repetitive potential steps between + 2.5 and - 2.0 V and synchronous optical transmittance changes for PU(IPDI-AQ-EG) film monitored at 510 nm in supporting electrolyte solution.

stability of electrochromic characteristics. The switching time are quantified in terms of a time for achieving 90% of the total absorbance changes [42]. Therefore, it can be found that its coloration and bleaching time was determined to be 5.3 and 2.3 s, respectively, from the analysis of the first cycle as shown in Fig. S2.

Electrochromic device with single polymeric layer was further prepared by assembling a thicker PU(IPDI-AQ-EG) film  $(1 \times 1 \text{ cm}^2)$  with gel conductive electrolyte between ITO substrates. As shown in Fig. 8, the device exhibited clear electrochromic characteristics and different color under various applied potential. Apparently, the color of the film varied from yellow to pink gradually as the applied



**Figure 8** Images of reversible color switching of PU(IPDI-AQ-EG) film as an active layer in sandwich-type of electrochromic device.

voltage set at -1.0 V, owing to the single electron transfer reaction. Subsequently, the pink color faded after the potential reset backward to 0 V. Further, as the applied voltage descended to -1.4 V or lower, the device changed color from yellow to deep red due to the development of double-electron transfer reactions. These phenomena were in coincident with electrochromic behaviors of PU(IPDI-AQ-EG) film in 0.1 M Bu<sub>4</sub>NPF<sub>6</sub>/ACN supporting electrolyte. Therefore, due to its stable electrochemical properties, this novel PU(IPDI-AQ-EG) polymer may find application in electrochromic devices.

Because of the feature of electron withdrawing of AQ moieties, the conductance of PU(IPDI-AQ-EG) could be reversibly switched from low conductivity to high conductivity [19, 22]. Therefore, sandwiched memory devices were fabricated by spin-coating PU(IPDI-AQ-EG) film as the only active layer and then deposited Al electrode onto PU(IPDI-AQ-EG) film through shadow mask. The device configuration is illustrated in Fig. 9a. The PU(IPDI-AQ-EG) film thickness was examined by the cross-sectional SEM image of the substrate before the Al deposition, as shown in Fig. 9b. From bottom to top, the three layers are glass, ITO, and PU(IPDI-AQ-EG) film, where ITO is 187 nm and PU(IPDI-AQ-EG) film is 180 nm, respectively.

The electrical characterizations of memory device were investigated via current-voltage (I-V) and current-time (I-t) curves. Figure 10a shows I-V curves for ITO/PU(IPDI-AQ-EG)/Al device scanned from 0 to  $\pm$  4.0 V with grounding the bottom ITO electrode. As shown in Fig. 10a, during the first negative sweep from 0 to - 4.0 V (sweep 1), ITO/PU(IPDI-AQ-EG)/ Al device initially had a low conductivity (OFF state) with the current ranging from  $10^{-10}$  to  $10^{-6}$  A. However, a sharp increase in current from  $10^{-6}$  to  $10^{-1}$  A occurred at the voltage of around -2.7 V, demonstrating the device switched to high-conductivity state (ON state). The transition from OFF to ON is accepted as a "SET" operation or a "writing" process in data storage device. Upon undergoing the transition, the device can retained the ON state during the following second negative sweep from 0 to -4.0 V (sweep 2), which was corresponding to the reading process. However, in the subsequent sweep from 0 to + 4.0 V (sweep 3), the device switched to the OFF state at about + 2.8 V with the current descending abruptly from  $10^{-1}$  to  $10^{-6}$  A, suggesting the "RESET" or "erasing" process for the ON to OFF

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Figure 10 a Typical *I–V* curves of the memory device with the configuration of ITO/PU(IPDI-AQ-EG)/Al; b data-retention performance for the ITO/PU(IPDI-AQ-EG)/Al memory cell with the

transition. Similarly, the device underwent the OFF state during the following sweep from 0 to + 4.0 V (sweep 4). It is worth noting that both ON and OFF states can achieve non-destructive readout and maintain stable even after removing the power supply. The storage cells in device show repeatable *I*–*V* characteristics in the next sweep cycles (sweeps 5–8). The complete "write–read–erase–read" cycles

applied voltage at -1.0 V; **c** the measured and the fitted data in the OFF state with the Schottky emission model; **d** the measured and the fitted data in the ON state with the ohmic current model.

with the nonvolatile behavior demonstrated a flash memory type of this device. Further, the data retention times for the ITO/PU(IPDI-AQ-EG)/Al memory cell were determined and data are shown in Fig. 10b. Both ON and OFF states maintain stable within 3000 s, and ON/OFF current ratio can be up to 10<sup>5</sup>; this magnitude can meet the requirement of low misreading rates in practical applications [28].

Typical *I–V* curves from a ITO/PU(IPDI-EG)/Al device were tested for comparison, which is shown as Fig. S3 in supporting information. In the case of ITO/PU(IPDI-EG)/Al, the devices was always at small current of around  $10^{-9}$  A with minimal conductance change as the voltage scanning either from 0 to -7.0 V or 0 to +7.0 V, since there is no electrochemical redox reaction. This result also provides an evident that the memory character is associated with AQ units in the backbone.

To get a further insight into the charge transport mechanism in both OFF state and ON state, the previous I-V data were replotted according to the theoretical conduction models [43-49]. As indicated in Fig. 10c, the measured data of the OFF state fits well with Schottky emission model [47] in terms of the plot of logI and  $V^{1/2}$  (voltage from 0 to -2.7 V) found to be linear, implying that Schottky effects dominated the charge injection before the current transition. In this process, electron injection from the Al electrode is probably a controlling step, which can be understandable by the explanation of the energy barriers. The work functions  $(\Phi)$  of traditional ITO substrate and Al electrode are accepted as -4.80 and -4.20 eV, respectively. In the other hand, the LUMO and HOMO levels of PU(IPDI-AQ-EG) obtained from the CV associating with UV-Vis measurements are -3.43 and -6.43 eV, respectively. Therefore, the lowest energy barrier between  $\Phi$  of Al and the LUMO energy level is only 0.77 eV, which is lower than that between  $\Phi$  of ITO and the HOMO energy level (1.63 eV). This result suggests electron injection from Al into the LUMO level of PU(IPDI-AQ-EG) is the favored process, since hole injection from ITO into HOMO level is more difficult. While for the ON state (Fig. 10d), the *I*–*V* relation displays a good linearity, demonstrating that ohmic-type conduction dominated the charge transport just as in metallic conduction in this process. In addition, the ON current magnitude was observed independent of the area of the memory cell, which indicates the existing of the heterogeneous local filament formation in the ON state.

Furthermore, to propose the electronic transition mechanism of this device, quantum chemical calculation was carried out to predict the molecular structure and relevant energy of the optimized geometry associated with charge transfer. The basic unit of PU(IPDI-AQ-EG) was first optimized at level of B3LYP theory with 6-31G(d, p) basis sets by using

the Gaussian 09 program [50], Electrostatic potential (ESP) surface, molecular orbitals of LUMO and LUMO as well as energy levels, were also predicted at the same level. From the ESP surface (Fig. 11a), it can be seen that positive ESP (depicted in red area) was distributed along the whole polymer chain, which can facilitate the migration of charge carriers in this open channel [20]. Meanwhile, an apparent negative ESP region (blue) was allocated at the AQ groups, which can serve as trapping site to localize the charge, leading to charge retention and memory effects [51]. The electronic density contours of LUMO and HOMO energy levels are illustrated in Fig. 11b. From the results of calculation, The HOMO and LUMO energies were found to be -6.48 and - 2.83 eV, respectively, which are in good agreement with those from experimental measurements ((HOMO, LUMO) energy levels of (-6.43, -3.43)eV). The high-lying of LUMO level reveals a high electron affinity of PU(IPDI-AQ-EG), which should results from the strong electron-withdrawing ability of AQ groups in the backbone. In addition, the lowlying HOMO level demonstrates the ethoxy unit, and urethane group can act as a weak electron donor in



Figure 11 a ESP surface of PU(IPDI-AQ-EG) basic unit. b HOMO and LUMO energies and electron density contour of PU(IPDI-AQ-EG) basic unit obtained by simulation.

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this polymer. The HOMO of PU(IPDI-AQ-EG) was localized not only on the carbon atoms having double bonds in the AQ ring, but also on oxygen atom form ethoxy units, while the LUMO was distributed on the carbon atoms having single bonds only in the AQ ring. Upon excitation with sufficient energy, a charge transfer could occur in the nature of HOMO-LUMO transition, in which the electron density located on the donor side (ethoxy unit) could slightly shift to the acceptor side (AQ unit) to form a conductive CT complex. Because of the relatively low-lying HOMO level, CT complex can be sustained steadily for a period of time (retention of ON state) until the reverse potential is applied. Therefore, electric-fieldinduced charge transfer can explain the memory characteristics of this polyurethane. The electron density delocalization mechanism is similar to that of a polyurethane modified by an organic molecular as acceptor under a condition of applied electric field [26].

#### Conclusions

Non-toxic IPDI-based polyurethane PU(IPDI-AQ-EG), containing anthraquinone structure as electronwithdrawing moiety in the polymer chain, has been successfully synthesized and characterized. The PU(IPDI-AQ-EG) film exhibited distinct electrochromic properties. Electrochromic device with ITO/PU(IPDI-AQ-EG)/gel electrolyte/ITO structure showed color variations from pale yellow (neutral state) to deep red (reduction state) with obvious optical contrast. Further, the as-fabricated PU(IPDI-AQ-EG) film in ITO/PU(IPDI-AQ-EG)/Al memory device showed outstanding nonvolatile flash memory performance with low operating voltages less than  $\pm$  3 V. High ON/OFF current ratio up to 10<sup>5</sup> and retention time around 3000 s suggested good memory properties of this polymeric device. The results from theoretical analysis and spectroelectrochemical investigations demonstrated that the anthraquinone unit could be served as a moderate trapping site in the polymer backbone. Electric-field-induced charge transfer mechanism can explain the memory characteristics of this polyurethane. All the obtained results demonstrated that polyurethane PU(IPDI-AQ-EG) is a promising candidate for electrochromic and electrical memory fabrications.

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#### Compliance with ethical standards

**Conflict of interest** The authors declare that they have no conflict of interest.

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#### References

- Ling Q-D, Chang F-C, Song Y, Zhu C-X, Liaw D-J, Chan DS-H, Kang E-T, Neoh K-G (2006) Synthesis and dynamic random access memory behavior of a functional polyimide. J Am Chem Soc 128:8732–8733
- [2] Ling Q-D, Liaw D-J, Zhu C, Chan DS-H, Kang E-T, Neoh K-G (2008) Polymer electronic memories: materials, devices and mechanisms. Prog Polym Sci 33:917–978
- [3] Lin W-P, Liu S-J, Gong T, Zhao Q, Huang W (2014) Polymer-based resistive memory materials and devices. Adv Mater 26:570–606
- [4] Liu C-L, Chen W-C (2011) Donor–acceptor polymers for advanced memory device applications. Polym Chem 2:2169
- [5] Li YQ, Fang RC, Zheng AM, Chu YY, Tao X, Xu HH, Ding SJ, Shen YZ (2011) Nonvolatile memory devices based on polyimides bearing noncoplanar twisted biphenyl units containing carbazole and triphenylamine side-chain groups. J Mater Chem 21:15643–15654
- [6] Li Y, Xu H, Tao X, Qian K, Fu S, Shen Y, Ding S (2011) Synthesis and memory characteristics of highly organo-soluble polyimides bearing a noncoplanar twisted biphenyl unit containing aromatic side-chain groups. J Mater Chem 21:1810–1821
- [7] Li Y, Chu Y, Fang R, Ding S, Wang Y, Shen Y, Zheng A (2012) Synthesis and memory characteristics of polyimides containing noncoplanar aryl pendant groups. Polymer 53:229–240

#### 15612

- [8] Kumar R, Pillai RG, Pekas N, Wu Y, McCreery RL (2012) Spatially resolved Raman spectroelectrochemistry of solidstate polythiophene/viologen memory devices. J Am Chem Soc 134:14869–14876
- [9] Li Y, Song Y, Zhang X, Wu X, Wang F, Wang Z (2015) Programmable polymer memory device based on hydrophilic polythiophene and poly(ionic liquid) electrolyte. Macromol Chem Phys 216:113–121
- [10] Ling Q-D, Song Y, Lim S-L, Teo EY-H, Tan Y-P, Zhu C, Chan DSH, Kwong D-L, Kang E-T, Neoh K-G (2006) A dynamic random access memory based on a conjugated copolymer containing electron-donor and -acceptor moieties. Angew Chem Int Ed 45:2947–2951
- [11] Zhuang X-D, Chen Y, Liu G, Li P-P, Zhu C-X, Kang E-T, Noeh K-G, Zhang B, Zhu J-H, Li Y-X (2010) Conjugatedpolymer-functionalized graphene oxide: synthesis and nonvolatile rewritable memory effect. Adv Mater 22:1731–1735
- [12] Ouyang J, Chu C-W, Szmanda CR, Ma L, Yang Y (2004) Programmable polymer thin film and non-volatile memory device. Nat Mater 3:918–922
- [13] Chu CW, Ouyang J, Tseng HH, Yang Y (2005) Organic donor-acceptor system exhibiting electrical bistability for use in memory devices. Adv Mater 17:1440–1443
- [14] Ling Q, Liaw D, Zhu C, Chan D, Kang E, Neoh K (2008) Polymer electronic memories: materials, devices and mechanisms. Prog Polym Sci 33:917–978
- [15] Li Y, Fang R, Ding S, Shen Y (2011) Rewritable and nonvolatile memory effects based on polyimides containing pendant carbazole and triphenylamine groups. Macromol Chem Phys 212:2360–2370
- [16] Kurosawa T, Higashihara T, Ueda M (2013) Polyimide memory: a pithy guideline for future applications. Polym Chem 4:16–30
- [17] Park S, Kim K, Kim JC, Kwon W, Kim DM, Ree M (2011) Synthesis and nonvolatile memory characteristics of thermally, dimensionally and chemically stable polyimides. Polymer 52:2170–2179
- [18] Lee TJ, Ko Y-G, Yen H-J, Kim K, Kim DM, Kwon W, Hahm SG, Liou G-S, Ree M (2012) Programmable digital nonvolatile memory behaviors of donor–acceptor polyimides bearing triphenylamine derivatives: effects of substituents. Polym Chem 3:1276–1283
- [19] Hu Y-C, Chen C-J, Yen H-J, Lin K-Y, Yeh J-M, Chen W-C, Liou G-S (2012) Novel triphenylamine-containing ambipolar polyimides with pendant anthraquinone moiety for polymeric memory device, electrochromic and gas separation applications. J Mater Chem 22:20394–20402
- [20] Zhang Y, Zhuang H, Yang Y, Xu X, Bao Q, Li N, Li H, Xu Q, Lu J, Wang L (2012) Thermally stable ternary data-

storage device based on twisted anthraquinone molecular design. J Phys Chem C 116:22832-22839

- [21] Wu J-H, Yen H-J, Hu Y-C, Liou G-S (2014) Side-chain and linkage-mediated effects of anthraquinone moieties on ambipolar poly(triphenylamine)-based volatile polymeric memory devices. Chem Commun 50:4915–4917
- [22] van Dijk EH, Myles DJT, van der Veen MH, Hummelen JC (2006) Synthesis and properties of an anthraquinone-based redox switch for molecular electronics. Org Lett 8:2333–2336
- [23] Hsiao S-H, Lin J-Y (2015) Synthesis and electrochromic properties of novel aromatic fluorinated poly(ether-imide)s bearing anthraquinone units. J Fluor Chem 178:115–130
- [24] Zheng Y, Zheng J, Dou L, Qiao W, Wan X (2009) Synthesis and characterization of a novel kind of near-infrared electrochromic polymers containing an anthraquinone imide group and ionic moieties. J Mater Chem 19:8470–8477
- [25] Cabanlit M, Maitland D, Wilson T, Simon S, Wun T, Gershwin ME, Van de Water J (2007) Polyurethane shapememory polymers demonstrate functional biocompatibility in vitro. Macromol Biosci 7:48–55
- [26] Sun Y, Li L, Wen D, Bai X (2015) Bistable electrical switching characteristics and memory effect by mixing of oxadiazole in polyurethane layer. J Phys Chem C 119:19520–19525
- [27] Qiu F, Wang Q, Yang D, Cao G, Guan Y, Zhuang L (2013) Preparation of azo waveguide polyurethane and its analysis of Y-branch and Mach–Zehnder optical switches. Eur Polym J 49:2247–2256
- [28] Lim SL, Li N-J, Lu J-M, Ling Q-D, Zhu CX, Kang E-T, Neoh KG (2009) conductivity switching and electronic memory effect in polymers with pendant azobenzene chromophores. ACS Appl Mater Interfaces 1:60–71
- [29] Wang L-D, Tang J, Li R-Z, Zhang T, Tong L, Tang J (2016) Synthesis and characterization of cross-linkable polyurethane-imide electro-optic waveguide polymer. Appl Phys A 122:38
- [30] Sun Y, Miao F, Li R (2015) Bistable electrical switching and nonvolatile memory effect based on the thin films of polyurethane-carbon nanotubes blends. Sens Actuators A 234:282–289
- [31] Meng Q, Huang D, Wei S, Chen L (2002) Synthesis and application of polymeric dyes containing the anthraquinone structure. J Appl Polym Sci 83:1252–1257
- [32] John JV, Uthaman S, Augustine R, Chen H, Park I-K, Kim I (2017) pH/redox dual stimuli-responsive sheddable nanodaisies for efficient intracellular tumour-triggered drug delivery. J Mater Chem B 5:5027–5036
- [33] Thelakkat M (2002) Star-shaped, dendrimeric and polymeric triarylamines as photoconductors and hole transport

#### Mater Sci (2018) 53:15600-15613

materials for electro-optical applications. Macromol Mater Eng 287:442-461

- [34] Wang LL, Dong X, Liu XG, Xing Q, Huang MM, Hu HQ, Wang DJ (2013) Microstructure and rheological properties of thermoplastic polyurethane and its composites. Acta Polym Sin 3:367–376
- [35] Li RM, Yu W, Zhou CX (2007) Investigation of phase separation in a partially miscible polymer blend by rheology. J Macromol Sci B Phys 46:1051–1062
- [36] Mao H, Yang F, Wang C, Wang Y, Yao D, Yin Y (2015) Anthraquinone chromophore covalently bonded blocked waterborne polyurethanes: synthesis and application. RSC Adv 5:30631–30639
- [37] Song Y, Yao H, Tan H, Zhu S, Dong B, Guan S (2017) Changing the memory behaviors from volatile to nonvolatile via end-capping of hyperbranched polyimides with polycyclic arenes. Dyes Pigments 139:730–736
- [38] Zhao Z, Yin Z, Chen H, Zheng L, Zhu C, Zhang L, Tan S, Wang H, Guo Y, Tang Q, Liu Y (2017) High-performance, air-stable field-effect transistors based on heteroatom-substituted naphthalenediimide–benzothiadiazole copolymers exhibiting ultrahigh electron mobility up to 8.5 cm V<sup>-1</sup> s<sup>-1</sup>. Adv Mater 29:1602410
- [39] Zhou X, Fang C, Lei W, Du J, Huang T, Li Y, Cheng Y (2016) Various nanoparticle morphologies and surface properties of waterborne polyurethane controlled by water. Sci Rep 6:34574
- [40] Fernández-d'Arlas B, Ramos JA, Saralegi A, Corcuera M, Mondragon I, Eceiza A (2012) Molecular engineering of elastic and strong supertough polyurethanes. Macromolecules 45:3436–3443
- [41] Wang M, Li Z, Li H, He J, Li N, Xu Q, Lu J (2017) Different steric-twist-induced ternary memory characteristics in nonconjugated copolymers with pendant naphthalene and 1,8naphthalimide moieties. Chem Asian J 12:2744–2748
- [42] Liou G-S, Hsiao S-H, Su T-H (2005) Synthesis, luminescence and electrochromism of aromatic poly(amine-amide)s with pendent triphenylamine moieties. J Mater Chem 15:1812–1820
- [43] Frenkel J (1938) On pre-breakdown phenomena in insulators and electronic semi-conductors. Phys Rev 54:647–648

- [44] Laurent C, Kay E, Souag N (1988) dielectric breakdown of polymer films containing metal clusters. J Appl Phys 64:336–343
- [45] Li L, Ling Q-D, Lim S-L, Tan Y-P, Zhu C, Chan DSH, Kang E-T, Neoh K-G (2007) A flexible polymer memory device. Org Electron 8:401–406
- [46] Mark P, Helfrich W (1962) J Appl Phys 33:205-215
- [47] Campbell AJ, Bradley DDC, Lidzey DG (1997) Spacecharge limited conduction with traps in poly(phenylene vinylene) light emitting diodes. J Appl Phys 82:6326–6342
- [48] Jensen KL (2003) Electron emission theory and its application: Fowler–Nordheim equation and beyond. J Vac Sci Technol B 21:1528–1544
- [49] Ling Q-D, Wang W, Song Y, Zhu C-X, Chan DS-H, Kang E-T, Neoh K-G (2006) Bistable electrical switching and memory effects in a thin film of copolymer containing electron donor–acceptor moieties and europium complexes. J Phys Chem B 110:23995–24001
- [50] Frisch MJ, Trucks GW, Schlegel HB, Scuseria GE, Robb MA, Cheeseman JR, Scalmani G, Barone V, Mennucci B, Petersson GA, Nakatsuii H, Caricato M, Li X, Hratchian HP. Izmaylov AF, Bloino J, Zheng G, Sonnenberg JL, Hada M, Ehara M, Toyota K, Fukuda R, Hasegawa J, Ishida M, Nakajima T, Honda Y, Kitao O, Nakai H, Vreven T, Montgomery JA, Peralta JE, Ogliaro F, Bearpark M, Heyd JJ, Brothers E, Kudin KN, Staroverov VN, Keith T, Kobayashi R, Normand J, Raghavachari K, Rendell A, Burant JC, Iyengar SS, Tomasi J, Cossi M, Rega N, Millam JM, Klene M, Knox JE, Cross JB, Bakken V, Adamo C, Jaramillo J, Gomperts R, Stratmann RE, Yazyev O, Austin AJ, Cammi R, Pomelli C, Ochterski JW, Martin RL, Morokuma K, Zakrzewski VG, Voth GA, Salvador P, Dannenberg JJ, Dapprich S, Daniels AD, Farkas O, Foresman JB, Ortiz JV, Cioslowski J, Fox DJ (2010) Gaussian 09, Revision B.01. Gaussian Inc., Wallingford
- [51] Lee W-Y, Kurosawa T, Lin S-T, Higashihara T, Ueda M, Chen W-C (2011) New donor–acceptor oligoimides for highperformance nonvolatile memory devices. Chem Mater 23:4487–4497