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# Structural effect on controllable resistive memory switching in donor–acceptor polymer systems





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#### ABSTRACT

Controllable bistable electrical conductivity switching behavior and resistive memory effects have been demonstrated in Al/polymer/indium-tin oxide (ITO) sandwich structure devices, constructed from non-conjugated vinyl copolymers of **PTPA<sub>n</sub>OXD<sub>m</sub>** with pendant donor–acceptor chromophores. The observed electrical bistability can be attributed to the field-induced intra- and intermolecular charge transfer interaction between triphenyl-amine electron donor (D) and oxadiazole electron acceptor (A) entities, and is highly dependent on the chemical structure of the copolymers. The vinyl copolymers showed different memory behaviors, which depended on the loading of D/A ratios. The polymers containing only donor or acceptor moieties showed as insulators, the polymers containing both donor and acceptor moieties showed as WORM, flash and DRAM as D/A ratio increased. The structural effect on the physicochemical and electronic properties of the **PTPA<sub>n</sub>OXD<sub>m</sub>** copolymers, *viz* surface morphology, thermal stability, optical absorbance and photoluminescence, and molecular orbital energy levels, were investigated systematically to study the factors that influence the memory characteristics of the devices.

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#### 1. Introduction

With the rapid development of information technology in the 21st century, electronic products such as smart phones and tablet personal computers have become an essential part of our lives [1]. As the performance of the digital gadgets advances, the complexity of data storage device increases, with the concomitant reduction in device dimension. In order to achieve greater density of data storage and faster access to information, more components are deliberately packed onto a single chip. Existing memory technologies may survive another few generations, but are likely to approach the limit of 16 nm in 2018 [2,3], beyond which a single silicon-based memory cell becomes

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less stable or reliable when storing individual bits. To maintain the Moore's Law of the cost learning curve, the potential application of molecular computation, using resistive memory switching materials made of polymers and polymer-based composites as the data storage medium, has resulted in worldwide research campaign in developing novel information storage materials and de-vices [4–6].

Due to the possibility of storing more data in less space and with less energy consumption, and the unique advantages of mechanical flexibility, solution processability and printability, various polymer resistive memory devices have been demonstrated recently [1,5,7–9]. In particular, donor–acceptor (D–A) polymer systems receive great attention due to their simple charge trapping/detrapping or charge transfer (CT) switching mechanism [10–14]. Moreover, the electrical function and memory characteristics of the D–A polymers can be fine-tuned over a wide

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range *via* versatile molecular-cum-synthesis strategy [8]. By regulating the strength of the D/A unities, the interfacial energy barrier for charge transfer and separation will be effectively adjusted, leading to electrical conductance switching phenomena in a controllable manner [13]. The loading ratio of D/A unities, which modulates the degree and stability of charge transfer interaction, defines the volatility and reversibility of the resistive memory switching in donor-acceptor polymers [12]. The packing mode of the polymer chains as well as the morphology on the interface between the D/A unities also significantly influence the charge transport behavior of the memory devices [14,15].

In this work, we demonstrated controllable resistive memory switching phenomena in donor–acceptor polymer systems and investigated the structure–property relationship to better understand the bistable electronic transition and memory effects. A series of non-conjugated homopolymers and random copolymers containing triphenylamine (**TPA**) moiety as the electron-donor and (2,5-biphenyl)-1,3,4-oxadiazole (**OXD**) moiety as the acceptor, which are connected to the vinyl backbone through amide linkage, were synthesized and employed as model materials to construct donor–acceptor polymer systems (Scheme 1). The morphological, thermal, optical and electrochemical properties of the as-synthesized polymers show strong dependence on the chemical structure of the donor-acceptor systems. With continuous adjusting of the D/A loading ratios, the PTPA/POXD homopolymers and PTPA<sub>n</sub>OXD<sub>m</sub> random copolymers demonstrate insulating, volatile switching and non-volatile memory switching behaviors. Computation chemistry using Gaussian were performed to explore the local electronic interaction of the donor-acceptor pentamers, that are responsible for the controllable memory characteristics of the D-A polymers. The present work provides a comprehensive description on the structure-dependent electronic transition and charge transport scenario of the donor-acceptor polymer systems, and serves as guidelines for designing novel D-A polymers for high performance data storage applications and exploring the operating mechanisms of the electronic memories.

#### 2. Experimental section

#### 2.1. Materials

4-Nitrofluorobenzene (Acros), sodium hydride (Acros), benzonitrile (Acros), 2,2'-azobis(2-methylpropionitrile) (AIBN, Sigma–Aldrich), diphenylamine (Sigma–Aldrich), pyridine (Sigma–Aldrich), sodium carbonate (Sigma–Aldrich),



Scheme 1. Synthetic scheme of monomers and PTPAnOXDm copolymers.

ammonium chloride (Showa), sodium azide (Showa), 4-nitrobenzoyl chloride (Alfa Aesar), acryloyl chloride (Alfa Aesar), hydrazine monohydrate (Alfa Aesar), 10% palladium on activated carbon (Merck) were used as received. The AR grade solvents, dichromethane, dioxane, ethyl acetate, methanol, ethanol, toluene, acetonitrile, chloroform, *N*-methyl-2-pyrrolidinone (NMP), *N*,*N*-dimethylacetamide (DMAc) and dimethyl sulfoxide (DMSO) were purchased from TEDIA. Tetrahydrofuran (THF) and *N*,*N*-dimethylformamide (DMF) were purchased from ECHO. These solvents were distilled after drying with appropriate drying agents and stored over 4 Å molecular sieves.

#### 2.2. Instrumentation

NMR spectra were measured on a Bruker Advance 500 NMR spectrometer with  $d_6$ -dimethyl sulfoxide (DMSO) as the solvent and tetramethylsilane as the internal standard (<sup>1</sup>H at 500 MHz and <sup>13</sup>C at 125 MHz). Weight-average  $(M_w)$  and number-average molecular weights  $(M_n)$  were determined by gel permeation chromatography (GPC). Four (Jordi) columns ( $250 \times 10 \text{ mm}^2$ , Gel DVB,  $10^5$ ,  $10^4$ ,  $10^3$ , and  $5 \times 10^2$  Å pore size gel in series) were used for GPC analysis with N,N-dimethyl formamide (DMF, 1 mL/min) as the eluent. The eluents were monitored by a RI detector (JASCO Systems, RI-2031, Japan). Monodispersed polystyrene samples were used as the molecular weight standards. Elemental microanalysis (for C, H, and N) was performed on a Perkin-Elmer 2400 elemental analyzer. Fourier transform infrared (FT-IR) spectra were measured on a Perkin-Elmer GX FTIR spectrometer by dispersing the samples in KBr pellets. Differential scanning calorimetry (DSC) analysis were performed on a Perkin-Elmer Pyris DSC 6 system under a nitrogen flow rate of 20 mL/min and at a heating rate of 10 °C/min. Thermogravimetric analysis (TGA) was conducted on a Perkin-Elmer Pyris 6 TGA thermogravimetric analyzer at a heating rate of 10 °C/min and under a nitrogen or air flow rate of 20 mL/min. Fluorescence spectra were recorded on a Shimadzu RF-5301 PC spectrofluorophotometer. UV-visible absorption spectra were measured on a Shimadzu UV-NIR 1601 spectrophotometer. Cylic voltammetry (CV) measurement was performed on an Autolab potentiostat/galvanostat system using a three-electrode cell under an argon atmosphere. The polymer film coated on a Pt disk electrode (working electrode) was scanned (scan rate: 50 mV/s) anodically and cathodically in a solution of tetrabutylammonium hexafluorophosphate  $(n-Bu_4NPF_6)$  in acetonitrile (0.1 M), with Ag/AgCl and a platinum wire as the reference and counter electrode, respectively.

#### 2.3. Synthesis of monomers and polymers

The synthesized procedures for all the monomers are shown in Scheme 1.

#### 2.3.1. 5-Phenyl-2H-tetrazole (**BTAZ**)

A flask was charged with a mixture of benzonitrile (20.00 g, 0.144 mol), ammonium chloride (13.40 g, 0.25 mol), sodium azide (16.42 g, 0.25 mol), and DMF (300 mL). The mixture was refluxed for 3 days before

cooling to room temperature and precipitating in dilute hydrochloric acid solution. The precipitate was filtered and washed thoroughly with de-ionized water. The crude product was re-crystallized from ethanol to afford white solid. The appearing solid was collected by filtration, and dried under vacuum to give white 5-phenyl-2*H*-tetrazole (**BTAZ**), 18.60 g, 88%), m.p. = 213 °C by DSC. FT-IR (KBr, cm<sup>-1</sup>): 2606, 2839, 2975, 3125 (-NH- stretch), 1563, 1607 (-N=N-). <sup>1</sup>H NMR (DMSO-*d*<sub>6</sub>, ppm):  $\delta$  7.08 (t, 3H, ArH, *J* = 4.9 Hz),  $\delta$  8.0 (t, 2H, ArH, *J* = 3.9 Hz). Anal. calcd. for C<sub>7</sub>H<sub>6</sub>N<sub>4</sub> (wt%): C: 57.53, H: 4.14, and N: 38.34; found: C: 57.43, H: 4.17, and N: 38.35.

#### 2.3.2. 2-(4-Nitrophenyl)-5-phenyl-1,3,4-oxadiazole (NOXD)

A mixture of 5-phenyl-2*H*-tetrazole (**BTAZ**, 15.00 g, 0.103 mol), 4-nitrobenzoyl chloride (22.80 g, 0.123 mol), and pyridine (170 mL) was refluxed for 36 h under nitrogen atmosphere. It was subsequently cooled to room temperature and yellow crystal was obtained. The crude crystal was washed with acetone several times, collected and dried under vacuum to give 16.50 g (60%) of light yellow 2-(4-nitrophenyl)-5-phenyl-1,3,4-oxadiazole (**NOXD**), m.p. = 213 °C by DSC. FT-IR (KBr, cm<sup>-1</sup>): 1515, 1339 (-NO<sub>2</sub> stretch), 1607 (—C=N—). <sup>1</sup>H NMR (DMSO-*d*<sub>6</sub>, ppm):  $\delta$  7.65 (m, 3H, ArH, *J* = 4.8 Hz),  $\delta$  8.15 (t, 2H, ArH, *J* = 4.0 Hz),  $\delta$  8.30 (d, 2H, ArH, *J* = 9.0 Hz),  $\delta$  8.40 (d, 2H, ArH, *J* = 8.8 Hz). Anal. calcd. for C<sub>14</sub>H<sub>9</sub>N<sub>3</sub>O<sub>3</sub> (wt%): C: 62.92, H: 3.39, and N: 15.72; found: C: 62.83, H: 3.37, and N: 15.85.

# 2.3.3. 4-(5-Phenyl-1,3,4-oxadiazole-2-yl)benzenamine (AOXD)

In a 250 mL three-necked flask, a mixture of 2-(4-nitrophenyl)-5-phenyl-1,3,4-oxadiazole (NOXD) (10 g, 37 mmol), 0.50 g 10% Pd/C catalyst, hydrazine monohydrate (9.00 g, 0.18 mol), and 150 mL ethanol was refluxed with vigorous stirring for 16 h. The mixture was then filtered to remove Pd/C and dried by using rotation vapor to afford the pure product. The crude product was re-crystallized from ethanol, and dried under vacuum to give light-purple 4-(5-phenyl-1,3,4-oxadiazole-2-yl)benzenamine (AOXD) (6.66 g, 75%), m.p. = 197 °C by DSC. FT-IR (KBr,  $cm^{-1}$ ): 3406, 3323, 3213 (-NH<sub>2</sub> stretch), 1603 (-C=N-). <sup>1</sup>H NMR (DMSO-*d*<sub>6</sub>, ppm): δ 5.90 (s, 2H, NH), δ 6.70 (d, 2H, ArH, *I* = 8.5 Hz), δ 7.50 (m, 3H, ArH, *I* = 2.6 Hz), δ 7.70 (d, 2H, ArH, *I* = 8.5 Hz), δ 7.70 (m, 2H, ArH, *I* = 3.1 Hz). Anal. calcd. for C<sub>14</sub>H<sub>11</sub>N<sub>3</sub>O (wt%): C: 70.87, H: 4.67, and N: 17.71; found: C: 70.83, H: 4.61, and N: 17.80.

# 2.3.4. N-(4-(5-Phenyl-1,3,4-oxadiazole-2-yl)phenyl) acrylamide (**VOXD**)

An ice-cold solution of acryloyl chloride (2.26 g, 25 mmol) in dry tetrahydrofuran (10 mL) was added drop-wise to a cold solution of 4-(5-phenyl-1,3,4-oxadiaz-ole-2-yl)benzenamine (**AOXD**) (6.00 g, 25 mmol) in dry tetrahydrofuran (40 mL). The reaction temperature was kept in the range from 0 to  $-5 \,^{\circ}$ C for 2 h. The mixture was neutralized with a saturated solution of sodium carbonate to give white solid. The solid product was purified by column chromatography with dichromethane/methanol = 60/1 as an eluent to give 6.30 g (85%) of white *N*-(4-(5-phenyl-1,3,4-oxadiazole-2-ylphenyl)acrylamide (**VOXD**),

m.p. = 144 °C by DSC. FT-IR (KBr, cm<sup>-1</sup>): 1337, 1490 (–NO<sub>2</sub>). <sup>1</sup>H NMR (DMSO- $d_6$ , ppm): δ 5.70–5.90 (m, 1H, vinyl), δ 6.20–6.40 (m, 1H, vinyl), δ 6.40–6.60 (m, 1H, vinyl), δ 7.50–7.70 (m, 3H, ArH), δ 7.70–8.00 (d, 2H, ArH, *J* = 8.5 Hz), δ 8.00–8.20 (m, 4H, ArH), δ 10.49 (s, 1H, amide). <sup>13</sup>C NMR (DMSO- $d_6$ , ppm): δ 118.01, 119.54, 123.41, 126.57, 127.64, 127.74, 129.38, 131.50, 142.28, 163.55, 163.65, 163.84. Anal. calcd. for C<sub>17</sub>H<sub>13</sub>N<sub>3</sub>O<sub>2</sub> (wt%): C: 70.09, H: 4.50, and N: 14.42; found: C: 70.03, H: 4.47, and N: 14.48.

#### 2.3.5. N-(4-(Diphenylamino)phenyl)acrylamide (VTPA)

An ice-cold solution of acryloyl chloride (2.08 g, 23 mmol) in dry tetrahydrofuran (10 mL) was added drop-wise to a cold solution of 4-aminotriphenylamine (ATPA) (6.00 g, 21 mmol) in dry tetrahydrofuran (40 mL). The reaction temperature was kept in the range from 0 to -5 °C for 2 h. The mixture was neutralized with a saturated solution of sodium carbonate to give white crude solid. The crude product was purified by re-crystallization from ethyl acetate to afford 5.87 g (82%) of white N-(4-(diphenyl-amino)phenyl)acrylamide (VTPA), m.p. = 179 °C by DSC. FT-IR (KBr, cm<sup>-1</sup>): 1337, 1490 (-NO<sub>2</sub>). <sup>1</sup>H NMR (DMSO-*d*<sub>6</sub>, ppm): δ 5.70–5.80 (m, 1H, vinyl), δ 6.20–6.30 (m, 1H, vinyl), δ 6.30–6.50 (m, 1H, vinyl), δ 6.90–7.10 (m, 8H, ArH), δ 7.20-7.30 (m, 1H, ArH), δ 7.50-7.70 (d, 2H, ArH, J = 8.0 Hz),  $\delta$  10.11 (s, 1H, amide). <sup>13</sup>C NMR (DMSO*d*<sub>6</sub>, ppm): δ 120.66, 122.40, 123.03, 125.05, 126.56, 129.37, 131.85, 134.71, 142.61, 147.34, 162.88. Anal. calcd. for C<sub>21</sub>H<sub>18</sub>N<sub>2</sub>O (wt%): C: 80.23, H: 5.77, and N: 8.91; found: C: 80.13, H: 5.72, and N: 8.95.

#### 2.3.6. Polymerization procedure of random copolymers

The procedure of homopolymers and random copolymers based on the donor (**VTPA**) and acceptor (**VOXD**) monomers using free radical polymerization is shown in Scheme 1. The reaction process comprises a mixture of **VTPA** and **VOXD** monomers, free radical initiator (AIBN), and NMP in glass tube with a magnetic stirring bar. The mixture was degassed and backfilled with nitrogen three times, sealed under nitrogen flow, and placed in 70 °C oil bath for 24 h. After cooling, the polymer was reprecipitated from methanol. The polymers were used for further purification by Soxhlet extraction in methanol. The copolymers were finally dried under vacuum at 60 °C overnight.

#### 2.4. Device fabrication and characterization

The electrical properties of the **PTPA/POXD** homopolymers and **PTPA<sub>n</sub>OXD<sub>m</sub>** random copolymers were evaluated in Al/polymer/ITO sandwich structures. The indium tin oxide-coated glass (ITO) substrates were pre-cleaned in ultrasonic bath for 15 min each in detergent, de-ionized water, acetone, and isopropyl alcohol. A 50 µL of polymer solution (10 mg/mL) in toluene, chloroform or tetrahydrofuran was spin-coated onto the pre-cleaned ITO substrate. The resultant film thickness is around 100–200 nm as measured by a step-profiler. After drying the film under reduced pressure ( $10^{-5}$  Torr) and at room temperature overnight, Al top electrodes were deposited onto the film surface *via* thermal evaporation at  $10^{-7}$  Torr through a shadow mask. The top electrodes are  $0.4 \times 0.4$  mm<sup>2</sup>,  $0.2 \times 0.2$  mm<sup>2</sup>,  $0.15 \times 0.15 \ mm^2$  in area and about 300 nm in thickness. The devices were characterized under ambient conditions, using a Hewlett–Packard 4155B semiconductor parameter analyzer with an Agilent 16440A SMU/pulse generator. Al was used as the anode subjected to the applied voltage while ITO was grounded and used as the common cathode during all the electrical measurements.

The scanning electron microscopy (SEM) images of the surface morphology of the thin films of **PTPA/POXD** homopolymers and **PTPA<sub>n</sub>OXD**<sub>m</sub> random copolymers on ITO substrates were recorded on a JEOL 6320 scanning electron microscope, with all the samples coated with a thin layer of platinum. Atomic force microscopy (AFM) images of the samples were obtained on a Nanoscope IIIa AFM system from Digital Instrument Inc.

#### 2.5. Molecular computation

Calculations of the optimized geometry and electronic properties, including the dipole moment, electrostatic potential (ESP) surface, highest occupied molecular orbital (HOMO) and lowest unoccupied molecular orbital (LUMO) of the pentamer unit of the **PTPA/POXD** homopolymers and **PTPA<sub>n</sub>OXD<sub>m</sub>** random copolymers, were carried out on a Compaq ES40 supercomputer using the Gaussian 09 program package and the density functional theory (DFT) at the B3LYP/6-31G(d) level [16].

#### 3. Results and discussion

#### 3.1. Polymer synthesis and characterization

Triphenylamine (TPA) was chosen as the electron donor due to its good electron donating and hole transporting properties [17-20], while (2,5-biphenyl)-1,3,4-oxadiazole (OXD) moiety was used as the acceptor with high electron affinity and thermal stability [21,22]. Two homopolymers (PTPA and POXD) and four random copolymers PTPAnOXD<sub>m</sub> with varying donor/acceptor ratios were prepared by free radical polymerization, based on the electron-donor (VTPA) and electron-acceptor (VOXD) vinyl monomers as shown in Scheme 1. The subscripts (n and m) indicate the molar ratio of donor and acceptor moiety. The vinyl monomers were prepared by acylation from analogous amino compounds, 4-aminotriphenylamine (ATPA) [23,24] and 4-(5-phenyl-1,3,4-oxadiazole-2-yl) benzenamine (AOXD) with acryloyl chloride. The amino compounds were prepared as shown in Scheme 1. The chemical structures of the PTPA/POXD homopolymers, PTPAnOXD<sub>m</sub> random copolymers, and monomers were confirmed by <sup>1</sup>H NMR spectra, FTIR, and elemental analysis. The relative ratios of D/A segments in the as-synthesized copolymers, estimated form <sup>1</sup>H NMR spectra (Fig. 1), are in good agreement with the feed ratio (n/m).

The solubility of prepared polymers is summarized in Table 1. Both the **PTPA/POXD** homopolymers and **PTPA\_nOXD\_m** random copolymers show good solubility in polar organic solvents such as tetrahydrofuran (THF), dimethylformamide (DMF), dimethyl sulfoxide (DMSO) and pyridine. Except for the rigid homopolymer of **POXD** 



Fig. 1. <sup>1</sup>H NMR spectra of the PTPA<sub>n</sub>OXD<sub>m</sub> random copolymers.

Table 1	
Solubility of $\ensuremath{\text{PTPA}}\xspace/\ensuremath{\text{POXD}}\xspace$ homopolymers and $\ensuremath{\text{PTPA}}\xspace_{m}\xspace$ random	om copolymers in organic solvents

	Solubility <sup>a</sup>									
	DMAc	DMF	DMSO	NMP	Pyridine	THF	Dioxane	$CH_2Cl_2$	CHCl <sub>3</sub>	Toluene
POXD	++	++	++	++	++	++	-	-	-	-
PTPA2OXD8	++	++	++	++	++	++	+_	-	-	-
PTPA <sub>4</sub> OXD <sub>6</sub>	++	++	++	++	++	++	++	++	++	-
PTPA <sub>6</sub> OXD <sub>4</sub>	++	++	++	++	++	++	++	++	++	-
PTPA <sub>8</sub> OXD <sub>2</sub>	++	++	++	++	++	++	++	++	++	-
PTPA	++	++	++	++	++	++	++	++	++	++

<sup>a</sup> The solubility was tested with 1 mg of sample in 1 ml of the solvent. ++: soluble at room temperature; +-: partially soluble on heating; -: insoluble even heating.

and copolymer of **PTPA<sub>2</sub>OXD<sub>8</sub>**, the copolymers with other **VTPA/VOXD** ratios are soluble in chloroform and dichloromethane at room temperature. Since the solvent plays a key role in controlling the morphology of the spin-casted polymer thin films [25], for the ease of constructing homogeneous films with high quality and therefore better device performance, proper solvent systems were selected carefully for the present **PTPA/POXD** homopolymers and **PTPA<sub>n</sub>OXD<sub>m</sub>** random copolymers.

With no or only low content of triphenylamine species present in the chemical structures, **POXD** and **PTPA<sub>2</sub>OXD**<sub>8</sub> are only soluble in polar solvents through the large dipole–dipole interaction. Thus, tetrahydrofuran (THF) and dimethyl sulfoxide (DMSO) have been used to prepare polymer solutions. The physical parameters of several solvents are summarized in Table 2 [26]. The rheological properties of the flowing solution, especially the volatility and viscosity of the solvent, the compatibility of the polymersolvent system, as well as the changes in these properties during solvent evaporation, have a profound effect on the final film morphologies [25,27]. When the polymer solution is spin-cast onto a substrate, the solvent evaporates so fast that the polymer chains are frozen before reaching the ther-

## Table 2Physical properties of several organic solvents [26].

	Formula	v <sub>p</sub> (kPa)	μ (Debye)	η (mPa s)	γ (mN/m)
DMSO	C <sub>2</sub> H <sub>6</sub> OS	0.031	3.96	2.00	43.54
THF	C <sub>4</sub> H <sub>8</sub> O	10.65	1.63	0.48	26.40
Chloroform	CHCl <sub>3</sub>	11.92	1.01	0.58	27.14
Toluene	C <sub>7</sub> H <sub>8</sub>	1.64	0.36	0.59	28.50

 $v_p$ : Vapor pressure at 20 °C;  $\mu$ : dipole moment in the gas phase;  $\eta$ : viscosity at 20 °C;  $\gamma$ : liquid–air surface tension at 20 °C.

modynamic equilibrium state. This effect can be intensified by employing solvents with higher vapor pressure or volatility, where the fast evaporation of the solvent causes rapid increasing of the solution viscosity that impedes liquid flow and results in non-uniformities in the fast-dried film topography. In contrast, when a solvent with smaller vapor pressure and lower volatility is used, the solution behaves as a Newtonian liquid without introducing hydrodynamic instabilities, and the polymer diffusion will be sufficiently high to smooth out any possible irregularities and therefore enable homogenous surfaces. However, as the vapor pressure of DMSO is extremely low, it was unable to prepare thin films from DMSO solutions with regular spinningcoating technique and most of the solution was swept out from the substrate during spinning. When spin-cast from highly volatile THF solution onto ITO substrates, both polymers form well-like surface structures as shown in Figs. S1(a), S2(a), 2(a), and 3(a), respectively. As discussed above, the featured surface morphology of the **POXD** and PTPA<sub>2</sub>OXD<sub>8</sub> films can be attributed to the fast evaporation of THF which confines the polymer chains rapidly and readily during spin-coating. Since OXD unities are more compatible with THF, higher content of the electron donor will be distributed on the surface of PTPA<sub>2</sub>OXD<sub>8</sub> copolymer film (light part of Fig. 3(a)), while the TPA donors will be found primarily at the bottom of the copolymer well (dark part of Fig. 3(a)) [28].

On the other hand, the use of good solvents will release the confinement of the polymer chains in the solution, dissipating the morphological irregularities during spincoating and leading to rich content of the component of the copolymer that is more compatible with the solvent on the surface [28]. Increase in the **TPA** content in the **PTPA**<sub>n</sub>**OXD**<sub>m</sub> copolymers leads to enhanced compatibility with solvents of lower polarity, and copolymers of **PTPA**<sub>4</sub>**OXD**<sub>6</sub>, **PTPA**<sub>6</sub>**OXD**<sub>4</sub>, **PTPA**<sub>8</sub>**OXD**<sub>2</sub> and homopolymer of **PTPA** can be readily dissolved by chloroform. Even though the vapor pressure of chloroform is higher than that of THF, the relatively larger viscosity and surface tension of the solvent and the better polymer–solvent compatibility promise uniform spreading of the polymers and formation of homogeneous thin films on ITO substrates (Figs. S1(b), S1(c), 2(b), S2(b), S2(c) and 3(b), respectively). Without any **OXD** moieties in **PTPA**, the homopolymer can be readily dissolved in toluene of lower polarity and smaller volatility, and gives rise to featureless thin film on ITO substrate (Figs. S1(d) and S2(d)). Therefore, the solubility and morphology of the **PTPA/POXD** homopolymers and **PTPA<sub>n</sub>OXD<sub>m</sub>** random copolymers show strong dependence on the chemical structures, and their effect on the optical and electrical properties of the devices will discussed later.

The thermal properties, together with other physical properties of the **PTPA/POXD** homopolymers and **PTPA<sub>n</sub>OXD**<sub>m</sub> random copolymers, are summazrized in Table 3. The homopolymer of **PTPA** shows the lowest glass transition temperature (180 °C) while the other homopolymer of **POXA** shows the highest one (225 °C). The glass transition temperatures of the random copolymers increase propotionally to the increase of the **OXD** moities in the chemical strucutes, and idealy fit the Fox equation of copolymers (Table S1) [29]. Both the homopolymers and random copolymers do not decompose until the high temperature of 350 °C. Therefore, the thermal stability of the present pendant donor-acceptor copolymers promises good resistance to the thermal aging effect that is induced



Fig. 2. Scanning electron microscopy images of (a) PTPA<sub>2</sub>OXD<sub>8</sub> and (b) PTPA<sub>8</sub>OXD<sub>2</sub>.



Fig. 3. Atomic force microscopy images of (a) PTPA<sub>2</sub>OXD<sub>8</sub> and (b) PTPA<sub>8</sub>OXD<sub>2</sub>.

	DSC	TGA	UV-visibl	e	Fluorescence		Cyclic voltammetry	
	$T_g$ (°C)	<i>T</i> <sub>d</sub> (°C)	$\lambda_{max}$ (nm)	$\lambda_{edge}$ (nm)	E <sub>g</sub> (eV)	$\lambda_{em}$ (nm)	E <sub>ox</sub> (onset) (V)	HOMO (eV)
POXD	225	362	303.5	344.5	3.614	385.4	0.937	-5.373
PTPA <sub>2</sub> OXD <sub>8</sub>	209	359	304.0	346.1	3.593	380.2/471.8	0.678	-5.114
PTPA <sub>4</sub> OXD <sub>6</sub>	200	353	306.5	349.7	3.552	488.1	0.698	-5.134
PTPA <sub>6</sub> OXD <sub>4</sub>	195	356	307.0	352.1	3.532	484.9	0.738	-5.174
PTPA8OXD2	187	357	308.0	354.8	3.502	478.6	0.832	-5.268
PTPA	180	352	310.5	356.0	3.492	373.1	0.843	-5.279

Т

Thermal decomposition: 5% weight loss in nitrogen atmosphere.



Fig. 4. UV-visible absorption spectra of the PTPA/POXD homopolymer and PTPA<sub>n</sub>OXD<sub>m</sub> random copolymer (a) solutions and (b) films on quartz substrates. (c) Fluorescence spectra of the PTPA/POXD homopolymers and PTPA<sub>n</sub>OXD<sub>m</sub> random copolymers. POXD: 1.2 µg/mL in THF; PTPA<sub>2</sub>OXD<sub>8</sub>: 5 µg/mL in THF; PTPA4OXD6, PTPA6OXD4 and PTPA8OXD2: 0.15 mg/mL in chloroform; PTPA: 0.15 mg/mL in toluene. (d) Anodic scans of the cyclic voltammogram of the PTPA/POXD homopolymers and PTPAnOXDm random copolymers. The inset of (d) shows the oxidation scan of the ferrocene.

by the high electric field ( $\sim 20 \text{ MV/m}$ ) during device characterization.

The UV-visible absorption spectra of the polymers in solutions and films are shown in Fig. 4(a) and (b). The optical spectra of all the homopolymer and random copolymer solutions show absorption in the UV and visible region of 280 to 350 nm originated from the pendant donor-acceptor systems (Fig. 3(a)) [12,13]. The absorption maximum of the POXD homopolymer at 303.5 nm can be assigned to the  $n-\pi^*$  transition while the absorption shoulder at 330 nm is attributed to the inter-chain interaction of the pendant oxadiazole (OXD) aromatic rings [30,31]. The incorporation of triphenylamine donor moieties into the pendant structures of PTPAnOXDm copolymers leads to an observable red-shift of the absorption spectra due to the weak ground state charge transfer (CT) interaction between the D-A pairs. With increase in the TPA content in the copolymers and therefore the degree of ground state CT interaction, the optical absorption spectra red-shift continuously from 304 nm of

LUMO (eV) -1.759 -1.521-1.582-1642-1.766-1.787 **PTPA<sub>2</sub>OXD<sub>8</sub>** to 308 nm of **PTPA<sub>8</sub>OXD<sub>2</sub>**. The intensities of the absorption shoulder at 330 nm also decrease as the **TPA** content increases, possibly due to the hindered inter-chain interaction by the twisted triphenylamine structures. The homopolymer of **PTPA** exhibits absorption maximum at 310.5 nm, corresponding to the  $n-\pi^*$  transition of the pendant triphenylamine donors.

The red-shift of the optical absorption of the copolymers was also observed in thin film samples prepared on quartz substrates (Fig. 4(b)). Due to the aggregation of D/A unities in the solid state, both the homopolymers and copolymers exhibit absorption tails in the visible region of longer wavelength. As demonstrated by the SEM and AFM images, PTPA2OXD8 and POXD films cast from highly volatile THF solutions show featured surface structures rather than smooth surfaces. The surface morphology largely influences the optical properties of the polymer films [32], and PTPA<sub>2</sub>OXD<sub>8</sub> and POXD films on quartz substrates exhibit heavily red-shifted and broadened absorption peaks. The energy band gaps of the homopolymers and copolymers were also derived from the absorption edges of the solution samples and are summarized in Table 3. Due to the electron delocalization in the pendant triphenylamine moieties, PTPA shows energy bandgap of 3.492 eV which is smaller than that of **POXD** (3.614 eV). The optical energy gaps of the random copolymers are between the PTPA/POXD homopolymers, and decrease with increase in the TPA content of the copolymers.

The structure-dependent optical properties of the PTPA/POXD homopolymers and PTPAnOXD<sub>m</sub> random copolymers are also demonstrated by the fluorescence spectra of Fig. 4(c). When excited at 310 nm, the **POXD** homopolymer exhibits strong characteristic emission of the oxadiazole unities at 386 nm [33], while PTPA homopolymer exhibits characteristic emission of the triphenylamine moieties at 373 nm. Upon the introduction of TPA unities into the chemical structure of PTPA<sub>2</sub>OXD<sub>8</sub>, the oxadiazole emission at ~380 nm decreases dramatically with the simultaneous appearance of new emission peak at  $\sim$ 472 nm. The quenching of the oxadiazole emission and the appearance of the new peak at longer wavelength region indicate the occurrence of charge transfer or energy transfer interaction between the D-A pairs [34,35]. However, the possibility of fluorescence quenching via energy transfer can be ruled out by the poor matching between the emission spectrum of **POXD** homopolymer and the absorption spectrum of PTPA homopolymer [36]. Therefore, the occurrence of ground state charge transfer interaction between the TPA donor and OXD acceptor entities can be confirmed by the changes in the lineshapes of the fluorescence spectra of the PTPA/POXD homopolymers and **PTPA<sub>n</sub>OXD<sub>m</sub>** random copolymers. With further increase in the TPA content and decrease in the OXD content in PTPA4OXD6, PTPA6OXD4 and PTPA8OXD2, the emission peak of the oxadiazole unities disappears completely. Because of the changes in the concentration of CT species in the solution, the optical excitation energy is further quenched via charge transfer interaction, and the emission peak in longer wavelength region decreases gradually.

The electrochemical properties of the PTPA/POXD homopolymers and **PTPA<sub>n</sub>OXD<sub>m</sub>** random copolymers are explored in the oxidation scans of the cyclic voltammetry spectra as plotted in Fig. 4(d). Due to the difference in the chemical structures, the six polymers exhibit different oxidation profiles, with their onset oxidation potential ranging from 0.678 V to 0.937 V, respectively. Rich in triphenylamine electron donors, PTPA, PTPA<sub>8</sub>OXD<sub>2</sub>, PTPA<sub>6</sub>OXD<sub>4</sub> and PTPA<sub>4</sub>OXD<sub>6</sub> show reversible oxidation behaviors, while PTPA<sub>2</sub>OXD<sub>8</sub> and POXD with deficient donor content show irreversible oxidation behaviors. The molecular orbital energy levels, in particular the highest occupied molecular orbital (HOMO) levels of the homoand copolymers, can be directly deducted from the equation  $HOMO = -(E_{ox}(onset) + 4.8 - E_{FOC})$ , where 4.8 is the reference energy level of ferrocene (FOC) and  $E_{FOC}$  is the onset oxidation potential of FOC vs. Ag/AgCl reference electrode (0.364 V, as measured by cyclic voltammetry). The electron withdrawing OXD moieties can lower the HOMO levels of the D-A copolymers, and the HOMO levels shift from -5.114 eV of PTPA2OXD8 to -5.268 eV of PTPA<sub>8</sub>OXD<sub>2</sub>. The lowest unoccupied molecular orbital (LUMO) energy levels are calculated from the difference between the HOMO levels and energy band gaps derived from optical absorption spectra (Table 3), according to the equations  $E_g = hc/\lambda_{edge}$  and LUMO = HOMO +  $E_g$ , where *h* is the Planck constant  $(6.63 \times 10^{-34} \text{ m}^2\text{kg/s})$  and c is the speed of light  $(3 \times 10^8 \text{ m/s})$ .

#### 3.2. Simulated electronic properties

To gain insights into the molecular geometry and electronic structures of the PTPA/POXD homopolymers and **PTPA<sub>n</sub>OXD<sub>m</sub>** random copolymers, computational studies have been performed using density functional theory (DFT) method at B3LYP/6-31G(d) level to calculate the HOMO, LUMO, ESP surfaces and dipole moments of the polymers with the Gaussian 09 program package (Table 4) [16]. In order to accelerate the calculation, pentamers with the fewest possible numbers of VTPA and/or VOXD monomers that still represent the ratio of the D/A unities in the homopolymers and copolymers, have been built in the molecular simulation. The molecular geometry and electronic structures of the single VTPA and VOXD monomer units are also simulated for comparative purpose (Table S2). As shown by the geometries of the pentamers optimized to the lowest energy configuration, the pendant donor and acceptor chromophores linked by the flexible vinyl backbone are curled randomly into coils. Thus, the bending of the polymer chains leads to amorphous phase rather than crystalline structures in the thin films. It is found that the pendant chromophores with the same electron donating or accepting nature have the tendency to pack closely to form domains, which may lead to phase separation in the bulk of the film and influence the charge transport behavior of the copolymers [37]. Both VTPA and **VOXD** monomers show positive electrostatic potential channel (blue) throughout the entire molecules, with the nitrogen and oxygen atoms bearing negative ESP spots (yellow-red) (Table S2). Compared with the amide linkage oxygen and nitrogen atoms in both VTPA and VOXD

#### Table 4

HOMO, LUMO, ESP surfaces and dipole moments of the pentamers of **PTPA/POXD** homopolymers and **PTPA<sub>n</sub>OXD<sub>m</sub>** random copolymers.



monomers, the nitrogen atoms associated with the oxadiazole unities serve as the major electron acceptors and charge traps in the molecular structure of VOXD, while the triphenvlamine unities serve as the electron donors in VTPA molecule. As visualized by the electrostatic potential (ESP) surface of the monomers, the continuous positive ESP surface and therefore an effective charge delocalization in the triphenylamine unity leads to a small dipole moment of 3.1110 Debye in VTPA, as compared to the relatively larger dipole moment of 6.5616 Debye in VOXD arising from the asymmetric distribution of the electrons (related to the negative ESP spot associated with OXD moiety in the pendant (2,5-biphenyl)-1,3,4-oxadiazole group). When extended into pentamers (Table 4), the dipole moments in both VOXD<sub>5</sub> and VTPA<sub>5</sub> pentamers are significantly increased, due to the enhancement in the electron withdrawing ability of the oxadiazole acceptors by forming aggregation in coils and the intensified asymmetric distribution of the electron cloud along the pendant groups. With increase in **OXD** content in the pentamers, the dipole moments increase from 3.1422 Debye of VTPA<sub>4</sub>OXD<sub>1</sub> to 21.3451 Debye of **VTPA<sub>1</sub>OXD<sub>4</sub>**. The increase in the dipole moments of the ground state homo- and copolymers favors the occurrence of charge transfer between D-A pairs under electric fields.

The distribution of the molecular orbitals, viz, HOMOs and LUMOs of the pentamers, are directly dependent on the chemical structures of the molecules. Though the HOMOs and LUMOs of VOXD<sub>5</sub> and VTPA<sub>5</sub> are allocated on specific oxadiazole and triphenylamine pendant chains in the pentamer structures respectively, in real homopolymer structures, they should be distributed almost randomly along the polymer chains (but to some extent dependent on the chain lengths of the macromolecules) due to the structure similarity of the repeating units. When both OXD acceptors and TPA donors are present in the chemical structures of the pentamers, the molecular orbitals are aligned distinctively, with the HOMOs residing on the triphenylamine chromophores and the LUMOs residing on the oxadiazole chromophores. For pentamers of VTPA1OXD4, VTPA2OXD3 and VTPA3OXD2, the HOMOS are preferentially located on the first triphenylamine moiety while the LUMOs are located on the oxadiazole moiety next to the D-A interfaces at which charge transfer interaction occurs. With decrease in the OXD contents, the LUMOs shift from the second monomer unit of VTPA1OXD4 to the fourth monomer unit of VTPA<sub>3</sub>OXD<sub>2</sub>. The increase in the intramolecular distance between the chromophores carrying HOMO and LUMO leads to a more asymmetric electron distribution in the molecular orbitals of the ground state pentamers, and is energetically more favorable for the occurrence of the field-induced charge transfer interaction between the TPA donor-OXD acceptor push-pull configurations. The electronic properties of VTPA<sub>4</sub>OXD<sub>1</sub> pentamer are different from those of the other pentamers, with its HOMO primarily located on the second monomer unit of triphenylamine donor. The dipole moment of VTPA<sub>4</sub>OXD<sub>1</sub> is relatively small, which is only 3.1422 Debye, a little larger than that of the VTPA monomer unit. Furthermore, as demonstrated in the electrochemistry analysis, the oxidation peak of **VTPA<sub>4</sub>OXD<sub>1</sub>** pentamer is much higher than



**Fig. 5.** HOMO and LUMO energy levels calculated from molecular simulation for the **VTPA/VOXD** and **VTPA\_nOXD\_m** pentamers, and obtained from optical and electrochemical analysis for the **PTPA/POXD** homopolymers and **PTPA\_nOXD\_m** random copolymers, with the work functions of Al and ITO electrodes.

the other homo- and copolymers. The unexpected electronic and electrochemical properties may be ascribed to the incorporation of the single oxadiazole acceptor into the VTPA<sub>4</sub>OXD<sub>1</sub> pentamer structure, which affect the effective  $\pi$ -conjugation of the aggregated triphenylamine donors, but are not vet to be further understood. The HOMO and LUMO energy levels of the pentamers calculated from simulation, which are consistent with the experimental values obtained by electrochemical (cyclic voltammetry) and optical spectroscopic measurements, are also plotted in Fig. 5. The calculated HOMO energy levels of the VTPA<sub>n</sub>OXD<sub>m</sub> pentamers are distributed in a narrow range close to that of **VTPA<sub>5</sub>** while the LUMO energy levels of the pentamers are within a narrow range close to that of VOXD<sub>5</sub>. Therefore, the respective origins of the HOMOs from the TPA chromophores and LUMOs from the OXD chromophores suggest that if present, only weak interaction between the pendant electron donors and acceptors exists in the ground state VTPAnOXDm pentamers.

#### 3.3. Resistive switching and memory characteristics

The controllable resistive memory switching phenomena in the **PTPA<sub>n</sub>OXD<sub>m</sub>** donor-acceptor polymer systems are demonstrated in the current density vs. voltage (I-V) characteristics (Fig. 6) of the Al (anode)/polymer/ITO (cathode) sandwiched structures. The electrical properties of the devices can be deliberately tuned by varying the D/A composition of the homo- and copolymers. Due to the amorphous nature and the lack of D-A interface of the homopolymer, the Al/POXD/ITO structure exhibits only an insulating state with current density in the range of  $10^{-10}$ - $10^{-5}$  A/cm<sup>2</sup> when swept between ±4 V (Fig. 6(a)), exhibiting a resistance of  $1.4 \times 10^{10} \Omega$ , or a resistivity of  $1.1\times 10^{10}\,\Omega$  m for a 200 nm thin film device when measured at -1 V. The current minima at non-zero voltage are probably due to the interfacial charge trapping in the thin film devices.

When triphenylamine donor moieties are incorporated into the **PTPA<sub>n</sub>OXD<sub>m</sub>** copolymers, bistable resistive



Fig. 6. Current-voltage characteristics of the (a) POXD, (b) PTPA<sub>2</sub>OXD<sub>8</sub>, (c) PTPA<sub>4</sub>OXD<sub>6</sub>, (d) PTPA<sub>6</sub>OXD<sub>4</sub>, (e) PTPA<sub>8</sub>OXD<sub>2</sub> and (f) PTPA homo- and copolymers in the Al/polymer/ITO structures.

switching behaviors are demonstrated. The I-V characteristics of devices constructed from PTPA2OXD8 and PTPA<sub>4</sub>OXD<sub>6</sub> are similar, and both display distinctly bistable electrical conductivity states and non-volatile memory effect. Starting with the low conductivity (OFF) state in the device of **PTPA<sub>2</sub>OXD<sub>8</sub>** (Fig. 6(b)), the current density increases gradually with increase in the applied positive voltage. Due to the low conductivity of the device, the sweeping rate is relatively slow in the initial state. The current density remains low, e.g.  $\sim 4 \times 10^{-6} \text{ A/cm}^2$  at 1 V (corresponding to a resistivity of  $1.1 \times 10^8 \Omega$  m), until the threshold voltage (turn-on voltage) of about 2.4 V is reached. At the turn-on voltage, the current density increases abruptly from  $4 \times 10^{-5}$  to  $3 \times 10^{-2}$  A/cm<sup>2</sup>, indicating device transition from the OFF to the ON state. Thus, the digital data can be encoded binarily as "0" and "1" in respect to the conductivity response of the memory device to the external electric field upon OFF-ON transition ("writing process"). Theoretically, a negative sweep with sufficient magnitude should also be capable to switch the device from the OFF to the ON state. However, such a phenomenon was not observed in our work and deserves further investigation. Once switched into the ON state. the voltage sweep becomes faster with higher conductivity of the device, leading to a higher access rate to the stored information. In the subsequent sweeps, the ON state of the bistable device is well maintained with an ON/OFF state current ratio of about  $1.7 \times 10^3$  at 1 V. Reversing or removing the sweeps does not change the high conductivity state significantly, thereby suggesting the write-once read-many-times (WORM) memory behavior for the PTPA<sub>2</sub>OXD<sub>8</sub> device. With increase in the TPA content in PTPA<sub>4</sub>OXD<sub>6</sub> copolymer, the respective device exhibits a reduced OFF state resistivity of  $6.1 \times 10^6 \,\Omega$  m, a smaller

turn-on voltage of 1.6 V and a slightly higher ON/OFF state current ratio of about  $2 \times 10^3$  with similar **WORM** memory switching behavior (Fig. 6(c)).

The device with **PTPA<sub>6</sub>OXD<sub>4</sub>** also exhibits non-volatile bistable electrical switching behavior, as illustrated by the *I–V* characteristics of Fig. 6(d). With the increasing **TPA** content in the copolymer, the device exhibits an even lower turn-on voltage of 1.4 V and an ON/OFF state current ratio of  $1 \times 10^3$ . However, after reading the ON state in the positive sweep, a reversely biased sweep can erase the ON state back to the initial OFF state at -2.7 V. The OFF state of the device can be read and re-programmed to the ON state again in the subsequent positive sweep, thus completing the "write-read-erase-read-rewrite" cycle. The non-volatile and re-programmable switching behavior of the device based on **PTPA<sub>6</sub>OXD<sub>4</sub>** copolymer is characteristic of that of a rewritable (**Flash**) memory.

Further increase in the TPA content results in a significant change in the volatility of the switching behavior of PTPA<sub>8</sub>OXD<sub>2</sub> device (Fig. 6(e)). The device initially exhibits a low current density of  $10^{-10}$ – $10^{-7}$  A/cm<sup>2</sup> representing the OFF state with a resistivity of  $3.4 \times 10^{10} \Omega$  m read at 1 V. When swept positively, the current density increases abruptly at  $\sim 3.5$  V, from  $2 \times 10^{-4}$  A to  $5 \times 10^{-4}$  A/cm<sup>2</sup>, to switch the device from the OFF to the ON state. However, once the voltage sweep is removed, the device immediately returns to the initial low conductivity state. The subsequent positive sweeps can re-program the device repeatedly, with the threshold voltage varying between narrow ranges of 3.5-3.7 V. The present Al/polymer/ITO devices were characterized in ambient environment, where the absorption and adsorption of air and moisture might have affected the electrical properties of the polymer and the polymer/metal interface [38]. The electrical stress might also have an influence on the inherent electrical relaxation of the polymer materials [1]. Thus, a minor shift or fluctuation in switching voltages might be expected. The extremely short retention ability and volatile nature of the PTPA<sub>8</sub>OXD<sub>2</sub> device is characteristics of a dynamic random access memory (DRAM). In order to sustain the electrical bistability, a refreshing voltage pulse with peak value higher than the switching threshold voltage and period less than the time of ON-OFF back transition should be applied to retain the high conductivity state.

Similar to the homopolymer of **POXD**, the Al/**PTPA**/ITO device also exhibits a single insulating state with a resistivity of  $1.1 \times 10^{12} \Omega$  m when measured at 1 V (Fig. 6(f)). It has been reported that the use of Al as top electrode on polymer devices may lead to conductivity switching arising from the native or electrically oxidized aluminum oxide layer [9,39]. However, the switching behaviors observed in the present bistable devices are less likely to originate from any interfacial phenomena at the Al/polymer contact, as the *I*-*V* characteristics of the **PTPA**/**POXD** and **PTPA**\_**NOXD**\_m devices are strongly dependent on the chemical structure or D/A composition of the polymers, and must be intrinsic to the changes in the physicochemical properties of the polymer materials.

For understanding the different effect of chemical linkage and blending of electron donor (D) and electron acceptor (A) in the polymer systems on memory behavior, the IV characteristics of vary blending systems containing different ratio of PTPA and POXD were tested. For the blend samples, all of them exhibit extremely high current density (please refer to the Supporting information Fig. S3) which will definitely not possible to be arising from the CT effect. Indeed, they should be due to the leaking current that runs along the phase boundaries between the two components. As reported (Ref. [37]), the pendant chromophores with the same electron donating or accepting nature have the tendency to pack closely to form domains, which may lead to phase separation in the bulk of the film and influence the charge transport behavior of the copolymers. In the blend samples, the phase separation occurs more severely, leading to large domains of the donor or acceptor polymers respectively. As a result, a lot of phase boundaries exist throughout the entire polymer film and provide high leakage pathways via these "film defects". Consequently, all the samples show very low resistance. Similar phenomena are also observed in polycrystalline oxide thin films (Rep. Prog. Phys. 2012-75-076502).

The stabilities of the memory devices in the ON and OFF states are also evaluated under ambient conditions. Fig. S4 shows the retention test results of the PTPA<sub>2</sub>OXD<sub>8</sub>, PTPA<sub>4</sub>OXD<sub>6</sub> and PTPA<sub>6</sub>OXD<sub>4</sub> non-volatile devices under constant voltage stresses of 1 V and after being read for cycles with continuous pulses of 1 V, respectively. Before switching to the high conductivity state, the OFF state of the PTPA<sub>2</sub>OXD<sub>8</sub> WORM device can be persisted for at least  $4 \times 10^4$  s without obvious or sudden degradation (Fig. S3(a)). Upon switching, the ON state of the same device can be sustained for about 3 h before decayed to a lower conductivity state at  $2 \times 10^4$  s. The degradation of the ON state may be due to the device failure at the Al/polymer contact with rough polymer surface as shown in Figs. S1(a) and S2(a), and will be discussed later. Both the ON and OFF states of the PTPA2OXD8 WORM device (Fig. S3(b)) are stable for up to  $10^8$  continuous read pulses of 1 V to maintain the ON/OFF ratio of  $\sim 1.7 \times 10^3$  (pulse period = 2  $\mu$ s, pulse width = 1  $\mu$ s). With homogeneous morphologies of the polymer thin films, the electrical bistabilities of the PTPA4OXD6 WORM and PTPA6OXD4 rewritable devices are stable both under constant voltage stresses for more than twelve hours and after being read for one hundred million continuous cycles. The performance of the memory devices is expected to be improved further upon proper encapsulation of the Al/polymer/ITO to avoid the environmental influence. The lack of long-term stability may result from the hygroscopic properties of amide linkage in the polymer.

#### 3.4. Operating mechanism discussion

The conduction and switching mechanism of the **PTPA**/ **POXD** homopolymer and **PTPA<sub>n</sub>OXD<sub>m</sub>** random copolymer devices can be rationalized by studying the local interaction between the electron donor and acceptor moieties. As shown by the energy band diagram in Fig. 5, the energy barriers for hole injection from ITO (with ITO set as grounded) into the highest occupied molecular orbitals (HOMOs) of the polymers are smaller than those for electron injection from aluminum into the lowest unoccupied molecular orbitals (LUMOs) [30]. Thus, hole injection from the electrode into the polymer layer is energetically more favorable than electron injection. Due to the lack of conjugated polymer chains, the injected charge carriers probably do not migrate along the vinvl backbone, but hop between the neighboring biphenyl oxadiazole and/or triphenylamine moieties (either through intra- or intermolecular hopping) and get trapped by the negative electrostatic potential regions associated with the nitrogen or oxygen atoms. Without D-A interface to promote the occurrence of charge transfer interaction, the concentrations of effective (free) charge carriers are low in both homopolymers, leading to small current density and insulating behavior in the sandwich devices. Cast from highly volatile THF solution, the featured surface morphology of POXD thin film results in poor Al/polymer contact which may lead to increased current leakage [40]. Under high electric field (4 V/200 nm, or 20 MV/m), the natural or electricallyformed aluminum oxide or Al atoms in the interfacial region of the poor Al/polymer contact may also provide additional charge transport pathways in the polymer film [9,39]. Thus, even though the energy barrier is less favorable for hole injection at ITO/POXD contact, the conductivity of the **POXD** device is still higher than that of the PTPA device.

By introducing donor–acceptor pair into the **PTPA**<sub>n</sub> **OXD**<sub>m</sub> random copolymers, charge transfer interaction can probably occur both in the ground state and under the stimuli of external electric field. The plausible electronic transition of the **VTPA**<sub>1</sub>**OXD**<sub>4</sub> pentamer is proposed in Fig. 7. The optical absorption spectroscopy of **PTPA**<sub>2</sub>**OXD**<sub>8</sub> copolymer shows absorption maximum at 304 nm corresponding to excitation energy of 4.089 eV. The experimental excitation energy is in good agreement with the energy difference (4.073 eV) between HOMO–1 and LUMO+2 of **VTPA**<sub>1</sub>**OXD**<sub>4</sub> as calculated from Gaussian simulation, thus indicating that the most possible electronic transition in the pentamer of **VTPA**<sub>1</sub>**OXD**<sub>4</sub> is that between the HOMO-1 and LUMO+2. In the initial ground state, the minor charge transfer effect between the TPA donors and **OXD** acceptors leads to a slight larger OFF state current density in PTPA<sub>2</sub>OXD<sub>8</sub> as compared to those of the PTPA/POXD devices. Under high electric field (switching threshold voltage), electrons in the HOMO-1 of the pentamer accumulate sufficient energy and transit into the LUMO+2 to give an excited state. Since LUMO, LUMO+1 and LUMO+2 are all distributed in the oxadiazole domain of the pentamer, the electrons excited from HOMO-1 can be further stabilized by delocalization along the four VOXD moieties via intramolecular hopping, and relax to a lower excited state. The vacancy in the HOMO-1 can be partially compensated by electrons in the HOMO (or the triphenylamine donor unity) through energy-decay transition. Consequently, a charge transfer (CT) state of the **VTPA<sub>1</sub>OXD<sub>4</sub>** pentamer with more asymmetric distribution of the electron cloud has been established. Driven along the direction of the external electric field, the increased amount of effective (free) charge carriers leads to an enhancement in the current flowing through the polymer thin film and switches the device from a low conductivity (OFF) state to a high (ON) conductivity state. The CT process is supported by the quenching of fluorescence of the OXD chromophores and the appearance of a new emission peak with lower energy in **PTPA<sub>2</sub>OXD<sub>8</sub>** in Fig. 4(c), where the excited **OXD** chromophores have been relaxed by forming charge transfer species with the neighboring TPA donors. Due to the increase in charge separation upon electronic transition, a larger dipole moment in the ON state polymer film can be expected. The asymmetric distribution of the electron density in the molecular orbitals and the large dipole moment of the polymer favor the holding of the separated charge carriers, leading to the non-volatile non-erasable WORM memory behavior of the Al/PTPA<sub>2</sub>OXD<sub>8</sub>/ITO device under non-degrading electric fields. However, the uneven topography of the PTPA<sub>2</sub>OXD<sub>8</sub> thin film (Figs. 2(a) and 3(a)) may lead to device failure by Al/polymer contact



Fig. 7. Plausible electric field-induced electronic transition in the pentamer of VTPA1OXD4.

degradation under voltage stresses, and the ON state conductivity of the **PTPA<sub>s</sub>OXD<sub>8</sub> WORM** device decay to a lower value after prolonged operation (Fig. S3(a)).

The electronic transition processes of the other PTPA<sub>n</sub>- $OXD_m$  copolymers, all involving electron excitation and charge transfer steps, are summarized in Table S3 and Figs. S5–S7, respectively. The electronic process of VTPA<sub>2</sub> **OXD**<sub>3</sub> involves molecular orbitals from HOMO-1 to LUMO+4 (Fig. S5). As demonstrated by the UV-visible absorption and fluorescence spectroscopy, increase in the triphenylamine donor content gives rise to an enhanced ground state charge transfer interaction in the copolymer; therefore PTPA<sub>4</sub>OXD<sub>6</sub> exhibits an even larger OFF state conductivity in the Al/polymer/ITO structure. The increase in the TPA contents also leads to decrease of the energy band gap and increase in the intramolecular distance between the chromophores carrying HOMO and LUMO. Assisted by the more asymmetric electron distribution in the molecular orbitals of the pentamers, charge transfer interaction between the TPA donors and OXD acceptors occurs easier and earlier in **PTPA<sub>4</sub>OXD**<sub>6</sub>, with more charge carriers being generated upon the occurrence of CT interaction. Consequently, the Al/PTPA<sub>4</sub>OXD<sub>6</sub>/ITO device exhibits a smaller switching threshold voltage of 1.6 V and a larger ON/OFF state current ratio of  $2 \times 10^3$ . With a more uniform polymer surface when cast from the chloroform solution and thus the better Al/polymer contact, the Al/PTPA4OXD<sub>6</sub>/ITO device shows good retention ability of the electrical bistability either under constant or pulsed voltage stresses for long operation periods. Further increase in the TPA content results in a smaller switching threshold voltage of 1.4 V in **PTPA<sub>6</sub>OXD<sub>4</sub>** bistable devices. Consequently, as the dipole moment of the copolymer also decreases with the increased TPA content, PTPA<sub>6</sub>OXD<sub>4</sub> is unable to hold the separated charge carriers permanently. Under a reverse electric field, the back transfer and recombination of the charge carriers erase the device from the ON to the OFF state.

It is reported that the differences in the structural symmetry play an important role in governing the reversibility of the memory devices [15]. The volatility of the memory effect is also determined by the ability of charge trapping in polymer films [12,13]. When a single oxadiazole acceptor is incorporated into the pentamer structure, VTPA<sub>4</sub>OXD<sub>1</sub> exhibits significantly different electronic properties. In particular, the dipole moment is much smaller (3.1422 Debye) than those of the other pentamers, indicating the weak push-pull interaction between the TPA donors and OXD acceptor of VTPA<sub>4</sub>OXD<sub>1</sub>. Due to the relatively smaller electron withdrawing ability of the single **OXD** acceptor, charge transfer is only possible to occur with the assist of higher electric field, and the **PTPA<sub>8</sub>OXD<sub>2</sub>** device only transits to the high conductivity state at the threshold voltage of 3.5-3.7 V which is much larger than those for the other copolymer memory devices. With more **TPA** content in the pentamer, more electrons are donated upon the occurrence of CT interaction, leading to a larger "ON/OFF" state current ratio when calculating the conductivity change at the switching threshold voltage. The relatively "weak" electron withdrawing ability of the single **OXD** acceptor does not allow the stable storing of the separated charge carriers, and the **PTPA<sub>8</sub>OXD<sub>2</sub>** device returns to the initial low conductivity state immediately after removing the external electric field. Therefore, variation in the D/A ratio, which has a profound influence on the electronic properties of the copolymers, leads to controllable memory switching behavior in the donor–acceptor polymer systems.

#### 4. Conclusion

In this work, a series of homopolymers and random copolymers, containing triphenylamine (TPA) moiety as the electron-donor and (2,5-biphenyl)-1,3,4-oxadiazole (OXD) moiety as the acceptor, have been synthesized to construct donor-acceptor polymer systems. Controllable resistive memory switching phenomena in the PTPAn OXD<sub>m</sub> donor-acceptor polymer systems were demonstrated and investigated by studying the structure-property relationships. Both the physicochemical and electronic properties of the as-synthesized polymers show strong dependence on the chemical structure of the donor-acceptor systems, and play an important role on the electrical and memory characteristics of the Al/**PTPA<sub>n</sub>OXD<sub>m</sub>**/ITO sandwiched structures. The blending systems of donor polymer (PTPA) and acceptor polymer (POXD) do not show memory behavior, which is very different from the donor-acceptor systems via chemical linkage. The current work is meaningful for a comprehensive understanding of the structure-dependent electronic transition of the donor-acceptor polymer systems, and provides useful guidelines for designing novel D-A polymers for high performance data storage applications.

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#### Appendix A. Supplementary material

Supplementary data associated with this article can be found, in the online version, at http://dx.doi.org/10.1016/j.orgel.2013.11.013.

#### References

- Q.D. Ling, D.J. Liaw, C. Zhu, D.S.H. Chan, E.T. Kang, K.G. Neoh, Prog. Polym. Sci. (Oxford) 33 (2008) 917–978.
- [2] ICT Recults (2007, December 23). Next-Generation RAM: Remembering the Future. *Science Daily*. <a href="http://www.sciencedaily.com/releases/2007/12/071221174912.htm">http://www.sciencedaily.com/releases/2007/12/071221174912.htm</a>>.
- [3] Executive summary, in: The International Technology Roadmap for Semiconductors (ITRS). 2009 ed. Austin, TX: Semiconductor Industry Association, International Sematech, 2009. <a href="http://www.itrs.net/Links/2009ITRS/Home2009.htm">http://www.itrs.net/Links/2009ITRS/Home2009.htm</a>.
- [4] R. Waser, Nanoelectronics and Information Technology: Advanced Electronic Materials and Novel Devices, third ed., Wiley-VCH, Weinheim, 2012. ISBN 978-3-527-40927-3.

- [5] R.F. Service, Science 302 (2003) 556-557.
- [6] R. Compañó, Nanotechnology 12 (2001) 85–88.
- [7] Y. Yang, L. Ma, J. Wu, MRS Bull. 29 (2004) 833-837.
- [8] C.L. Liu, W.C. Chen, Polym. Chem. 2 (2011) 2169-2174.
- [9] M. Cölle, M. Büchel, D.M. de Leeuw, Org. Electron. 7 (2006) 305–312.
- [10] S.G. Hahm, S. Choi, S.H. Hong, T.J. Lee, S. Park, D.M. Kim, W.S. Kwon, K. Kim, O. Kim, M. Ree, Adv. Funct. Mater. 18 (2008) 3276–3282.
- [11] K.L. Wang, Y.L. Liu, J.W. Lee, K.G. Neoh, E.T. Kang, Macromolecules 43 (2010) 7159–7164.
- [12] Y.K. Fang, C.L. Liu, W.C. Chen, J. Mater. Chem. 21 (2011) 4778-4786.
- [13] Y.K. Fang, C.L. Liu, G.Y. Yang, P.C. Chen, W.C. Chen, Macromolecules 44 (2011) 2604–2612.
- [14] N.G. Kang, B. Cho, B.G. Kang, S. Song, T. Lee, J.S. Lee, Adv. Mater. 24 (2012) 385–390.
- [15] Y. Ma, X. Cao, G. Li, Y. Wen, Y. Yang, J. Wang, S. Du, L. Yang, H. Gao, Y. Song, Adv. Funct. Mater. 20 (2010) 803–810.
- [16] M.J. Frisch, G.W. Trucks, H.B. Schlegel, G.E. Scuseria, M.A. Robb, J.R. Cheeseman, Gaussian 09 (Revision A.02), Gaussian Inc., Wallingford CT, 2009.
- [17] A. Iwan, D. Sek, Prog. Polym. Sci. (Oxford) 36 (2011) 1277-1325.
- [18] Y.W. Chuang, H.J. Yen, G.S. Liou, Chem. Comm. 49 (2013) 9812-9814.
- [19] C.J. Chen, Y.C. Hu, G.S. Liou, Polym. Chem. 4 (2013) 4162–4171.
- [20] G. Liu, Q.D. Ling, E.T. Kang, K.G. Neoh, D.J. Liaw, F.C. Chang, C.X. Zhu, D.S.H. Chan, J. Appl. Phys. 102 (2007).
- [21] A. Zarghi, Z. Hajimahdi, Expert Opin. Ther. Pat. 23 (2013) 1209–1232.
- [22] Y.L. Liu, K.L. Wang, G.S. Huang, C.X. Zhu, E.S. Tok, K.G. Neoh, E.T. Kang, Chem. Mater. 21 (2009) 3391–3399.
- [23] K.L. Wang, Y.L. Liu, I.H. Shih, K.G. Neoh, E.T. Kang, J. Polym. Sci., Part A: Polym. Chem. 48 (2010) 5790–5800.
- [24] K.L. Wang, T.Y. Tseng, H.L. Tsai, S.C. Wu, J. Polym. Sci., Part A: Polym. Chem. 46 (2008) 6861–6871.
- [25] L.L. Spangler, J.M. Torkelson, J.S. Royal, Polym. Eng. Sci. 30 (1990) 644–653.

- [26] R.C. Weast, M.J. Astle, CRC Hand Book of Chemistry and Physics, 63rd ed., CRC Press, Inc., Boca Raton, Florida, 1982–1983. ISBN 0-8393-0463-6.
- [27] P. Müller-Buschbaum, J.S. Gutmann, M. Wolkenhauer, J. Kraus, M. Stamm, D. Smilgies, W. Petry, Macromolecules 34 (2001) 1369– 1375.
- [28] P.F. Green, T.M. Christensen, T.P. Russell, R. Jerome, J. Chem. Phys. 92 (1990) 1478–1482.
- [29] H. Paul, T. Lodge, Polymer Chemistry, CRC Press, Inc., Boca Raton, Florida, 2007. ISBN 1-57444-779-3.
- [30] Y. Tao, Q. Wang, Y. Shang, C. Yang, L. Ao, J. Qin, D. Ma, Z. Shuai, Chem. Commun. (2009) 77–79.
- [31] P.J. Brown, D.S. Thomas, A. Köhler, J.S. Wilson, J.S. Kim, C.M. Ramsdale, H. Sirringhaus, R.H. Friend, Phys. Rev. B 67 (2003) 642031–6420316.
- [32] Y. Yang, Y.J. Shi, J. Liu, T.F. Guo, In: Electronic and Optical Properties of Conjugated Molecular Systems in Condensed Phases, 2003, ISBN 81-7736-083-3.
- [33] C. Wang, L.-O. Pålsson, A.S. Batsanov, M.R. Bryce, J. Am. Chem. Soc. 128 (2006) 3789–3799.
- [34] A.S. Lukas, Y. Zhao, S.E. Miller, M.R. Wasielewski, J. Phys. Chem. B 106 (2002) 1299–1306.
- [35] Y. Shibano, T. Umeyama, Y. Matano, N.V. Tkachenko, H. Lemmetyinen, H. Imahori, Org. Lett. 8 (2006) 4425–4428.
- [36] R. Gómez, J.L. Segura, N. Martín, Org. Lett. 7 (2005) 717-720.
- [37] C.R. McNeill, S. Westenhoff, C. Groves, R.H. Friend, N.C. Greenham, J. Phys. Chem. C 111 (2007) 19153–19160.
- [38] N. Hiroshiba, K. Tanigaki, R. Kumashiro, H. Ohashi, T. Wakahara, T. Akasaka, Chem. Phys. Lett. 400 (2004) 235–238.
- [39] F. Verbakel, S.C.J. Meskers, R.A.J. Janssen, H.L. Gomes, M. Cölle, M. Büchel, D.M. De Leeuw, Appl. Phys. Lett. 91 (2007) 192103.
- [40] K. Suemori, M. Yokoyama, M. Hiramoto, J. Appl. Phys. 99 (2006) 036109.