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Title: New random copolymers with pendant carbazole donor and 1,3,4-oxadiazole acceptor for high performance memory device applications

Non-conjugated random copolymers with pendant carbazole donor and oxadiazole acceptor exhibit electrical characteristics of diode, volatile memory and insulator depending on donor/acceptor ratio and acceptor strength. The excellent memory effects make them promising candidates for low-cost reproducible SRAM memory devices.



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# PAPER

# New random copolymers with pendant carbazole donor and 1,3,4-oxadiazole acceptor for high performance memory device applications<sup>†</sup>

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New non-conjugated random copolymers containing pendent electron-donating 9-(4vinylphenyl)carbazole (VPK) and electron-accepting 2-phenyl-5-(4-vinylphenyl)-1,3,4-oxadiazole (OXD) or 2-(4-vinylbiphenyl)-5-(4-phenyl)-1,3,4-oxadiazole (BOXD) were successfully synthesized by nitroxide-mediated free radical polymerization (NMRP) method. The prepared random copolymers are denoted as  $P(VPK_xOXD_y)$  or  $P(VPK_xBOXD_y)$  with three different electron donor/acceptor (x/y) ratios of 8/2, 5/5, and 2/8. The electrical switching behavior based on the ITO/polymer/Al device configuration could be tuned through the donor/acceptor ratio or acceptor trapping ability. Both experimental and theoretical results indicated that the charge transfer between the pendant donor and acceptor was relatively weak without significant orbital hybridization. In addition, the low-lying HOMO energy level of **OXD** or **BOXD** units as compared to **VPK** units created the trapping environment. Therefore, distinct electrical current-voltage (I-V) characteristics changed between the diode, the volatile memory, and the insulator depending on the relative donor/acceptor ratios of 10/0, 8/ 2, and (5/5, 2/8 and 0/10), respectively. The memory device based on  $P(VPK_8OXD_2)$  or P(VPK<sub>8</sub>BOXD<sub>2</sub>) copolymers exhibited volatile static random access memory (SRAM) behavior with an ON/OFF current ratio of approximately  $10^4$ - $10^5$ , up to  $10^7$  read pulses, and retention time of more than 1 h. The unstable ON state in the device was due to the shallow trapped holes with spontaneously back transferring of charge carriers when the electric field was removed and thus exhibited a volatile nature. The slightly lower HOMO level of OXD moieties than that of BOXD led to the P(VPK<sub>8</sub>OXD<sub>2</sub>) device storing the charge for a longer period of time. The present study suggested the high performance polymer memory devices could be achieved by changing the donor/acceptor ratio or chemical structure.

# Introduction

Donor–acceptor (D–A) type polymers have been widely explored for electronic and optoelectronic device applications, including light emitting diodes,<sup>1–3</sup> photovoltaic cells,<sup>4–10</sup> field-effect transistors,<sup>10–18</sup> and polymer memory devices.<sup>19–41</sup> In particular, D–A polymer-based memory devices with electrically bistable behavior attracted significant scientific interest recently due to the advantages of rich structure flexibility, low cost, solution processability, and three-dimensional stacking capability.<sup>19–22</sup>

The reported D-A polymeric materials for memory device applications included conjugated polymers,23-26 non-conjugated polymers with donor/acceptor chromophores (main chain polymers<sup>27-29</sup> or pendent polymers<sup>30-35</sup>) and polymer nanocomposites (metal nanoparticle,36,37 fullerene,38 carbon nanotube39 or graphene oxide<sup>40</sup> embedded). The reported polymer memory types included non-volatile memory (write-once-read-many times (WORM) memory,<sup>26,33–35,39</sup> flash (rewritable) memory<sup>25,28,30–34,37–40</sup> or negative differential resistance (NDR) behavior<sup>36,41</sup>) and volatile memory (dynamic random access memory (DRAM)<sup>24,27,29</sup> or static random access memory (SRAM)<sup>29</sup>). The memory devices with two different states of conductance were realized through several proposed mechanisms such as charge effect,<sup>7-33,35-38,40</sup> transfer trapping/de-trapping of charges,<sup>24,26,34,39,41</sup> and filamentary conduction.<sup>25</sup> It was believed that the polymer structure and morphology significantly affected the origin of the switching mode.

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<sup>&</sup>lt;sup>†</sup> Electronic supplementary information (ESI) available: <sup>1</sup>H NMR spectra of **P(VPK<sub>5</sub>BOXD<sub>5</sub>)**, **P(VPK<sub>2</sub>BOXD<sub>8</sub>)**, **P(VPK<sub>8</sub>OXD<sub>2</sub>)**, **P(VPK<sub>5</sub>OXD<sub>5</sub>)** and **P(VPK<sub>2</sub>OXD<sub>8</sub>)** in CD<sub>2</sub>Cl<sub>2</sub>. DSC and TGA thermograms of all homopolymers and copolymers. Retention time test on the ON and OFF states of the ITO/P(VPK<sub>8</sub>OXD<sub>2</sub>)/Al device under a continuous readout voltage. Stimulus effect of read pulses on the ON and OFF states of the ITO/P(VPK<sub>8</sub>OXD<sub>2</sub>)/Al device. See DOI: 10.1039/c0jm02535f

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Electronic resistive-type memory devices using organic polymers as active elements were shown to efficiently store the data based on the high- and low-conductance response to an applied voltage. Non-conjugated polymers with specific pendent chromospheres were widely used in the fabrications of memory device to obtain the switching characteristics.<sup>30–35,42–48</sup> Polymers with side chain carbazole-containing units exhibited hole-transporting ability that dominated the conduction. Conformation-induced electrical bistability in the pendant polymers with carbazole units exhibited the WORM and SRAM switching effect.44,45 The carbazole moieties as electron donors were expected to enhance charge transfer ability with suitable strong acceptors such as organic acceptors, 31,35,43 Eu complex, 30,31 or C<sub>60</sub>. 32 Therefore, the devices showed two distinguished conductivity states through the formation of the charge transfer complex when the voltage bias was applied. However, the effects of pendant donor/acceptor ratios or chemical structure on the non-conjugated polymer based memory devices have not been explored yet, to the best of our knowledge.

In this work, we report the synthesis and memory device characteristics of new non-conjugated random copolymers with pendant electron-donating 9-(4-vinylphenyl)carbazole (VPK) and electron-withdrawing 2-phenyl-5-(4-vinylphenyl)-1,3,4-oxadiazole (OXD) or 2-(4-vinylbiphenyl)-5-(4-phenyl)-1,3,4-oxadiazole (BOXD) moieties. The random copolymers are denoted as  $P(VPK_xOXD_y)$  and  $P(VPK_xBOXD_y)$ , in which the x/y is the donor/acceptor ratio as shown in Scheme 1. Copolymers with three different donor/acceptor (x/y) ratios of 8/2, 5/5, and 2/8were synthesized through the nitroxide-mediated free radical polymerization (NMRP) method. The thermal, optical, and electrochemical properties of the prepared copolymers were characterized. The low-lying HOMO energy level of OXD or BOXD electron acceptors can block the transport of charge carriers. The ITO/polymer/Al sandwiched device configuration was employed to explore the energy levels on the memory characteristics and the volatility of the memory effect was determined by the ability of charge trapping/back transferring of trapped charges. The experimental results suggested that the electrical switching could be efficiently tuned by donor/acceptor ratio or acceptor ability in the prepared copolymers as compared to the homopolymers.

Scheme 1 Synthesis of  $P(VPK_xOXD_y)$  and  $P(VPK_xBOXD_y)$  random copolymers.

## **Experimental section**

#### Materials

4-Vinylphenylboronic acid, sodium carbonate and Pd(PPh<sub>3</sub>)<sub>4</sub> were purchased from Aldrich (Milwaukee, WI), Showa (Tokyo, Japan), and Strem Chemicals (Newburyport, MA), respectively. Benzoyl peroxide (BPO) and 2,2,6,6-tetramethylpiperidine-1oxyl (TEMPO) was obtained from Acros (Geel, Begium). Anhydrous toluene and dimethyl formamide (DMF) were purchased from TEDIA (Fairfield, CT). All the chemicals were used as received and without further purification. Tetrabutylammonium perchlorate (TBAP, TCI) was recrystallized twice from ethyl acetate and then dried under vacuum prior to use. The monomers of 9-(4-vinylphenyl)carbazole (VPK) and 2-phenyl-5-(4-vinvlphenvl)-1.3.4-oxadiazole (OXD) were synthesized according to the literature method.49 The synthesis routes of 2-(4vinylbiphenyl)-5-(4-phenyl)-1,3,4-oxadiazole (BOXD) monomer and PVPK, POXD and PBOXD homopolymers are described in the ESI<sup>†</sup>.

#### General polymerization procedure of random copolymers

The random copolymers, poly(9-(4-vinylphenyl)carbazole- $\gamma$ -2-phenyl-5-(4-vinylphenyl)-1,3,4-oxadiazole) **P(VPK\_xOXD\_y)** and poly (9-(4-vinylphenyl)-carbazole- $\gamma$ -2-(4-vinylbiphenyl)-5-(4-phenyl)-1,3,4-oxadiazole) **P(VPK\_xBOXD\_y)** with three different **VPK/OXD** or **BOXD** ratios (8/2, 5/5, 2/8), were synthesized *via* nitroxide-mediated free radical polymerization (NMRP) and further purified by Soxhlet extractor in acetone, as illustrated in Scheme 1. The copolymers were finally dried under vacuum at 60 °C overnight. The weight-average molecular weights ( $M_w$ ) of the copolymers, obtained by GPC using THF as the eluent and polystyrene as standards, were 12 300–22 300 g mol<sup>-1</sup> with the polydispersity index (PDI) of 1.19–1.43, and the relative ratio of electron donor/acceptor segments in the random copolymers were estimated from elemental analysis.

**P(VPK<sub>8</sub>OXD<sub>2</sub>). VPK** (539 mg, 2.0 mmol), 124 mg of **OXD** (0.5 mmol), 6.0 mg of BPO (0.025 mmol), 5.1 mg of TEMPO (0.0325 mmol), and DMF (1 mL) were used to afford 273 mg yellow solid (41.2%). <sup>1</sup>H NMR (300 MHz, CDCl<sub>3</sub>) δ 1.99–1.49 (br, 3H, –CH<sub>2</sub>–CH–), 6.33–8.17 (br, 21H, Ar–H); anal. calcd. for  $[(C_{20}H_{15}N)_{0.8}+(C_{16}H_{12}N_2O)_{0.2}]$ : C 86.90, H 5.43, N 6.34; found C 84.87, H 5.46, N 6.21. Weight-average molecular weight ( $M_w$ ) and polydispersity index (PDI) estimated from gel permeation chromatographic (GPC) are 12 300 and 1.19, respectively.

**P**(**VPK<sub>5</sub>OXD<sub>5</sub>**). **VPK** (337 mg, 1.25 mmol), 310 mg of **OXD** (1.25 mmol), 6.0 mg of BPO (0.025 mmol), 5.1 mg of TEMPO (0.0325 mmol), and DMF (1 mL) were used to afford 325 mg white solid (50.2%). <sup>1</sup>H NMR (300 MHz, CDCl<sub>3</sub>)  $\delta$  1.35–2.08 (br, 3H, –CH<sub>2</sub>–CH–), 6.37–8.21 (br, 21H, Ar–H); anal. calcd. for [(C<sub>20</sub>H<sub>15</sub>N)<sub>0.5</sub>+(C<sub>16</sub>H<sub>12</sub>N<sub>2</sub>O)<sub>0.5</sub>]: C 83.46, H 5.22, N 8.11; found C 82.14, H 5.70, N 8.68. *M*<sub>w</sub> and PDI estimated from GPC are 12 400 and 1.21, respectively.

**P**(**VPK<sub>2</sub>OXD<sub>8</sub>**). **VPK** (135 mg, 0.5 mmol), 310 mg of **OXD** (2.0 mmol), 6.0 mg of BPO (0.025 mmol), 5.1 mg of TEMPO (0.0325 mmol), and DMF (1 mL) were used to afford 382 mg white solid (60.5%). <sup>1</sup>H NMR (300 MHz, CDCl<sub>3</sub>) δ 1.31–2.09 (br, 3H, –CH<sub>2</sub>–CH–), 6.30–8.24 (br, 21H, Ar–H); anal. calcd. for [( $C_{20}H_{15}N$ )<sub>0.2</sub>+( $C_{16}H_{12}N_{2}O$ )<sub>0.8</sub>]: C 79.84, H 4.99, N 9.98; found:



C 78.79, H 5.27, N 10.05.  $M_{\rm w}$  and PDI estimated from GPC are 12 600 and 1.30, respectively.

**P(VPK<sub>8</sub>BOXD<sub>2</sub>)**. **VPK** (539 mg, 2.0 mmol), 162 mg of **OXD** (0.5 mmol), 6.0 mg of BPO (0.025 mmol), 5.1 mg of TEMPO (0.0325 mmol), and DMF (1 mL) were used to afford 219 mg yellow solid (31.3%). <sup>1</sup>H NMR (300 MHz, CDCl<sub>3</sub>) δ 1.38–2.08 (br, 3H, –CH<sub>2</sub>–CH–), 6.39–8.21 (br, 25H, Ar–H); anal. calcd. for  $[(C_{20}H_{15}N)_{0.8}+(C_{22}H_{16}N_2O)_{0.2}]$ : C 87.32, H 5.42, N 5.99; found: C 86.09, H 5.60, N 6.18. *M*<sub>w</sub> and PDI estimated from GPC are 21 100 and 1.43, respectively.

**P(VPK<sub>5</sub>BOXD<sub>5</sub>)**. **VPK** (337 mg, 1.25 mmol), 405 mg of **OXD** (1.25 mmol), 6.0 mg of BPO (0.025 mmol), 5.1 mg of TEMPO (0.0325 mmol), and DMF (1 mL) were used to afford 299 mg white solid (40.3%). <sup>1</sup>H NMR (300 MHz, CDCl<sub>3</sub>) δ 1.38–2.03 (3H,  $-CH_2-CH$ –), 6.41–8.22 (br, 25H, Ar–H); anal. calcd. for [(C<sub>20</sub>H<sub>15</sub>N)<sub>0.5</sub>+(C<sub>22</sub>H<sub>16</sub>N<sub>2</sub>O)<sub>0.5</sub>]: C 84.89, H 5.22, N 7.07; found: C 83.91, H 5.35, N 7.28. *M*<sub>w</sub> and PDI estimated from GPC are 22 300 and 1.40, respectively.

**P(VPK<sub>2</sub>BOXD<sub>8</sub>). VPK** (135 mg, 0.5 mmol), 657 mg of **OXD** (2.0 mmol), 6.0 mg of BPO (0.025 mmol), 5.1 mg of TEMPO (0.0325 mmol), and DMF (1 mL) were used to afford 390 mg white solid (49.3%). <sup>1</sup>H NMR (300 MHz, CDCl<sub>3</sub>) δ 1.35–2.06 (3H,  $-CH_2-CH-$ ), 6.35–8.18 (br, 25H, Ar–H).  $M_w$  and PDI estimated from GPC are 16 800 and 1.30, respectively.

#### Characterization

<sup>1</sup>H NMR spectra were measured on a Bruker Avance 300 MHz FT-NMR and Bruker Avance DRX 500 MHz FT-NMR spectrometer. Gel permeation chromatographic (GPC) analysis was performed on a Lab Alliance RI2000 instrument (one column, MIXED-D from Polymer Laboratories) connected with one refractive index detector from Schambeck SFD Gmbh. All GPC analyses were performed on polymer/THF solution at a flow rate of 1 mL min<sup>-1</sup> at 40 °C and calibrated with polystyrene standards. Elemental analyses were performed with a Heraeus VarioEL-III-NCSH instrument.

Thermogravimetric analysis (TGA) was conducted with a PerkinElmer Pyris 1 TGA at a heating rate of 20 °C min<sup>-1</sup>. Differential scanning calorimetry (DSC) measurements were performed under a nitrogen atmosphere at a heating rate of 20 °C min<sup>-1</sup> from -50 to 250 °C using a TA instrument DSC-Q100. Electrochemistry was performed with a CHI 611B electrochemical analyzer. Voltammograms are presented with the positive potential pointing to the left and with increasing anodic currents pointing downwards. Cyclic voltammetry was performed by a three-electrode cell in which ITO (polymer films area about  $0.7 \times 0.5$  cm<sup>2</sup>) was used as a working electrode. A platinum wire was used as an auxiliary electrode. All cell potentials were taken with the use of a homemade Ag/AgCl, KCl (sat.) reference electrode. Absorption spectra were measured with a Hitachi U4100 UV-Vis-NIR spectrophotometer. The thickness of the polymer film was measured with a Microfigure Measuring Instrument (Surfcorder ET3000, Kosaka Laboratory Ltd).

#### Fabrication and characterization of polymer memory devices

The memory devices were fabricated on the indium-tin oxide (ITO) coated glass, with the configuration of ITO/polymer/Al.

Before the fabrication of the polymer layer, the glass was precleaned by ultrasonication with water, isopropanol, and acetone each for 15 min, respectively. Then, 20 mg mL<sup>-1</sup> of polymer solution in chlorobenzene was first filtered through 0.45 µm pore size of a PTFE membrane syringe filter. The filtered solution was spin-coated onto the pre-cleaned ITO glass at a speed rate of 1000 rpm for 60 s and annealed at 100 °C for 10 min under vacuum. The polymer film thickness was determined to be around 70 nm. Finally, a 300 nm thick Al top electrode (recorded device units of  $0.5 \times 0.5 \text{ mm}^2$  in size) was thermally evaporated through the shadow mask at a pressure of 10<sup>-7</sup> torr with a uniform depositing rate of  $3-5 \text{ \AA s}^{-1}$ . The electrical characterization of the memory device was performed by a Keithley 4200-SCS semiconductor parameter analyzer equipped with a Keithely 4205-PG2 arbitrary waveform pulse generator. ITO was used as the anode and Al was set as the cathode (maintained as common) during the voltage sweep with a step of 0.1 V. The probe tip used 10 µm diameter tungsten wire attached to a tinned copper shaft with a point radius  $< 0.1 \,\mu m$  (GGB Industries, Inc.). All of the electronic measurements were performed in a glove hox

#### Computational methodology

Molecular calculations studied in this work have been performed with Gaussian 03 program package.<sup>50</sup> Equilibrium ground state geometry and electronic properties were optimized by means of the density functional theory (DFT) method at the B3LYP level of theory (Beckes-style three-parameter density functional theory using the Lee–Yang–Parr correlation functional) with the 6-31G(d) basic set.

#### **Results and discussion**

#### **Polymer structure**

The chemical structures of the synthesized homopolymers and random copolymers were confirmed by <sup>1</sup>H NMR and elemental analysis. Fig. 1 shows the <sup>1</sup>H NMR spectra of PVPK, PBOXD and P(VPK<sub>8</sub>BOXD<sub>2</sub>) in CD<sub>2</sub>Cl<sub>2</sub>, respectively. P(VPK<sub>8</sub>BOXD<sub>2</sub>) random copolymer has vinyl protons (1.3 to 2.1 ppm) and aromatic protons (6.3 to 8.3 ppm), similar to those of the homopolymers, **PVPK** and **PBOXD**. The <sup>1</sup>H NMR spectra of the other copolymers also show similar peak signals and are consistent with the proposed structure, as shown in Fig. S1 and S2 of the ESI<sup>†</sup>. Due to the mixed proton signals of the random copolymers, it is difficult to estimate the relative ratio of donor (VPK)/acceptor (OXD or BOXD) from the peak integration of NMR spectra. Therefore, the pendent donor/acceptor ratios of the prepared copolymers are further confirmed by elemental analysis. As described in the synthesis part of the experimental section, the carbon, hydrogen, and nitrogen experimental contents of the synthesized copolymers are all in a good agreement with the theoretical contents. It suggests that the pendent donor/acceptor ratios of the synthesized random copolymers are close to the original design. The weight-average molecular weights  $(M_w)$  of the copolymers are from 12 300 to 22 300 with the polydispersity index (PDI) in the range of 1.19-1.43, determined by GPC analysis with polystyrene as standards. All the polymers were readily soluble in several common organic



Fig. 1 <sup>1</sup>H NMR spectra of (a) **PVPK**, (b) **PBOXD** and (c)  $P(VPK_8BOXD_2)$  in CD<sub>2</sub>Cl<sub>2</sub>.

solvents such as tetrahydrofuran (THF), chlorobenzene and chloroform. Thus, uniform thin films could be obtained by spin-coating for electronic device applications.

#### **Optical properties**

UV-Vis absorption spectra of the synthesized polymer films are shown in Fig. 2 and the corresponding absorption maxima ( $\lambda_{max}^{abs}$ ) in thin film state are summarized in Table 1. The PVPK film shows three strong absorption bands at 294, 330 and 342 nm, which is consistent with spectral features of the poly(N-vinylcarbazole) (PVK) film.<sup>32</sup> The spectra of POXD or PBOXD film has one main absorption peak at 293 or 311 nm, respectively, due to the  $\pi$ - $\pi$ \* transition of the aromatic ring. The slightly redshifted spectrum of PBOXD compared to that of POXD is probably due to the additional conjugated phenylene ring of the former. For the synthesized random copolymers of  $P(VPK_xOXD_y)$  (or  $P(VPK_xBOXD_y)$ ), the absorption band reveals a superposition rule of PVPK and POXD (or PBOXD) spectra. For example, the maximum peak of  $P(VPK_8BOXD_2)$ shows two bands centered at around 294 and 311 nm, which are mainly contributed to from the  $\pi$ - $\pi$ \* transition of **PVPK** and **PBOXD**, respectively. The optical band gaps of **PVPK**, **POXD**, **PBOXD**,  $P(VPK_xOXD_y)$ , and  $P(VPK_xBOXD_y)$  estimated from the absorption edges are 3.48, 3.68 and 3.40, 3.44-3.52, and 3.42-3.47 eV, respectively. Besides, the copolymers with different pendent donor/acceptor ratios exhibit no obvious significant shift to a lower energy transition. It suggests that the intramolecular charge transfer between the pendent carbazole donor and the 1,3,4-oxadiazole acceptor is relatively weak.



Fig. 2 Normalized UV–Vis absorption spectra of the polymer films on quartz plate: (a) PVPK, POXD and P(VPK<sub>x</sub>OXD<sub>y</sub>) and (b) PVPK, PBOXD and P(VPK<sub>x</sub>BOXD<sub>y</sub>).

## **Electrochemical properties**

The electrochemical properties of the polymers were investigated by cyclic voltammetry (CV), as shown in Fig. 3 and summarized in Table 1. The oxidation and reduction behaviors of the prepared film were measured on an ITO-coated glass substrate in dry acetonitrile or DMF containing 0.1 M of TBAP under nitrogen. The HOMO and LUMO energy levels of the random copolymers were estimated from CV with reference to ferrocene (4.8 eV) by the following equations:  $LUMO = (E_{red}^{onset} vs. Ag/AgCl$ + 4.8 eV –  $E_{1/2}$ , ferrocene); HOMO = ( $E_{red}^{onset}$  vs. Ag/AgCl + 4.8  $eV - E_{1/2}$ , ferrocene). In the CV, the **PVPK** and **POXD** (or PBOXD) homopolymer only show quasi-reversible anodic and cathodic peaks at 1.23 and -1.89 V (or -1.74 V), respectively, which corresponds to the HOMO level of -5.55 eV and LUMO level of -6.08 eV (or -5.95 eV), respectively. The cathodic peak is not detected in the CV of PVPK and thus the LUMO level of -2.07 eV is determined from the difference between the HOMO level and the optical band gap. Similar estimation is used to determine the HOMO levels of **POXD** and **PBOXD**, which are -6.08 eV and -5.95 eV, respectively. The LUMO energy level of **PBOXD** (-2.55 eV) is lower than that of **POXD** (-2.40 eV), which is attributed to the incorporation of one more conjugated phenyl moieties. The CV of  $P(VPK_xOXD_v)$  or  $P(VPK_xBOXD_v)$ random copolymers show both p-doping and n-doping behavior.

Table 1 Thermal, optical and electrochemical properties of the synthesized homopolymers and random copolymers

Index	T <sub>g</sub> (°C)	$T_{\rm d}  (^{\circ}{ m C})^a$	film $\lambda_{\max}$	$E_g^{\ b}$ (eV)	E/V ( <i>vs.</i> Ag/AgCl in MeCN or DMF) <sup>c</sup>			
					Eox	$E_{\rm red}$	$HOMO^{d}$ (eV)	$LUMO^{d}$ (eV)
РVРК	206	405	294, 330, 342	3.48	1.23	NA	-5.55	-2.07
POXD	173	367	293	3.68	NA	-1.89	-6.08	-2.40
PBOXD	192	381	311	3.40	NA	-1.74	-5.95	-2.55
P(VPK <sub>8</sub> OXD <sub>2</sub> )	193	376	295, 342	3.44	1.24	-1.88	-5.56	-2.41
P(VPK <sub>5</sub> OXD <sub>5</sub> )	187	373	294	3.48	1.25	-1.91	-5.57	-2.38
P(VPK <sub>2</sub> OXD <sub>8</sub> )	177	379	292	3.52	1.22	-1.90	-5.54	-2.39
P(VPK <sub>8</sub> BOXD <sub>2</sub> )	202	386	294, 311	3.42	1.23	-1.72	-5.55	-2.57
P(VPK <sub>5</sub> BOXD <sub>5</sub> )	197	404	311	3.44	1.25	-1.75	-5.57	-2.54
P(VPK <sub>2</sub> BOXD <sub>8</sub> )	193	406	311	3.47	1.22	-1.76	-5.54	-2.53

<sup>*a*</sup> Thermal decomposition temperature (5% weight-loss). <sup>*b*</sup> The data were calculated by the equation:  $gap = 1240/\lambda_{onset}$  of monomer and polymer film. <sup>*c*</sup> vs. Ag/AgCl in CH<sub>3</sub>CN (oxidation), vs. Ag/AgCl in DMF (reduction). <sup>*d*</sup> The HOMO energy levels were calculated from cyclic voltammetry and were referenced to ferrocene (4.8 eV).



**Fig. 3** Cyclic voltammograms of the homopolymer and copolymer thin films spin-coated onto an indium-tin oxide (ITO)-coated glass substrate in CH<sub>3</sub>CN (oxidation) and DMF (reduction) containing 0.1 M TBAP. Scan rate = 0.1 V s<sup>-1</sup>. The inset shows HOMO and LUMO energy level of **PVPK**, **POXD**, **PBOXD**, **P(VPK<sub>x</sub>OXD<sub>y</sub>)** and **P(VPK<sub>x</sub>BOXD<sub>y</sub>)** and work function of Al and ITO.

The HOMO energy levels of the copolymers with different donor/acceptor ratio are almost located at -5.55 eV from the electron-donating tendency of **PVPK**, whereas the LUMO energy levels are located at -2.40 (or 2.55 eV) from the electron-accepting tendency of **POXD** (or **PBOXD**). The HOMO and LUMO energy levels of the random copolymers are similar to their corresponding donor and acceptor moieties, indicating the relatively weak interaction between them.

#### Memory device characteristics of random copolymers

The effects of donor/acceptor ratio and acceptor moieties of the random polymers on memory device performance were systematically investigated. The memory behavior on  $P(VPK_xOXD_y)$  and  $P(VPK_xBOXD_y)$  random copolymers were tested by the current–voltage (*I–V*) characteristics of ITO/polymer/Al device structures. ITO was used as the anode and Al was set as the cathode (maintained as common) in all electrical measurements. The polymer memory devices store data based on the high- (ON) and low-conductivity (OFF) response to the external applied voltages. Fig. 4 shows the typical I-V characteristics of the memory devices fabricated with  $P(VPK_8BOXD_2)$  and



Fig. 4 Current–volatge (I-V) characteristics of (a)  $P(VPK_8BOXD_2)$ , (b)  $P(VPK_8OXD_2)$  memory device.

P(VPK<sub>8</sub>OXD<sub>2</sub>) in steps of 0.1 V. In the case of P(VPK<sub>8</sub>BOXD<sub>2</sub>) (see Fig. 4(a)), the device is initially in the OFF state ("0" signal in data storage) with a current in the range of  $10^{-11}$ - $10^{-12}$  A as the voltage sweeps from 0 to 6 V. When the voltage increases further, an abrupt current jump occurs at a threshold voltage of about 6 V indicating that the transition from low-conductivity OFF state to the high-conductivity ON state ("1" signal in data storage). This electronic transition from the OFF state to ON state in the first sweep serves as the "writing" process. The electrical switching of the  $P(VPK_8BOXD_2)$  device shows the distinctly bistable conductance state with the ON/OFF current ratio up to  $10^5$ . In the second sweep, the memory device can be kept in the ON state during a subsequent sweep from 0 to 8.0 V. The third sweep is conducted after turning off the power for about 8 min. The device can be reprogrammed from OFF state to ON state when the voltage bias increases to 6.1 V and the current is kept in the ON state (the third and fourth sweeps). From the continuous repeated sweep cycle, it indicates that the ON state could be maintained for approximately a period of 5-10 min after the removal of power and would gradually relax back to the OFF state. This electrical switching concludes that the P(VPK<sub>8</sub>BOXD<sub>2</sub>) memory device still exhibits the volatile nature of a static random access memory (SRAM) because the stored data are finally lost. It is also found that the transition to the ON state is reversible with a variation on threshold voltage, probably due to the delay on conformation change of the pendent aromatic ring under the voltage bias. Moreover, the volatile **P(VPK<sub>8</sub>BOXD<sub>2</sub>)** device can be repeated many times for at least 10 different devices with reproducible data. The unstable ON state of the volatile memory device can also be retained by a refreshing voltage pulse of 1 V within 1 ms duration every 30 s (named the rf trace). Further increase in the BOXD content, P(VPK5BOXD5) or P(VPK<sub>2</sub>BOXD<sub>8</sub>) shows almost an insulating state in a low current variation of  $10^{-11}$ - $10^{-12}$  A, as shown in Fig. 5(a).

The electrical behavior of the P(VPK<sub>8</sub>OXD<sub>2</sub>) device was also studied, as shown in Fig. 4(b). The I-V characteristics define the two electrical conductance state of P(VPK<sub>8</sub>OXD<sub>2</sub>) device and also reveal the volatile nature of the memory effect. As compared to the  $P(VPK_8BOXD_2)$  device, the  $P(VPK_8OXD_2)$  memory device performance shows a slightly longer period for the retained ON state. The transition from the OFF  $(10^{-11}-10^{-12} \text{ A})$ state to the ON  $(10^{-6}-10^{-7}A)$  state is observed with an abrupt current increase (the first and third sweep). Besides, the ON/OFF current ratios are about 104 with a threshold voltage of 6.3 V. The third sweep is performed after turning off the power, whereas the device returns back to the OFF state after more than 10 min (usually 15 min). The OFF state can be further recovered to a stored state again with a re-applied switching voltage bias indicating that this device is also rewritable. Thus, the P(VPK<sub>8</sub>OXD<sub>2</sub>) device still reveals the common characteristics as a SRAM feature since it exhibits a temporary data remanence behavior. However, for the higher content of POXD moieties, the I-V curves of P(VPK5OXD5) and P(VPK2OXD8) device display the insulator behavior (Fig. 5(a)) which is similar to the P(VPK<sub>5</sub>BOXD<sub>5</sub>) and P(VPK<sub>2</sub>BOXD<sub>8</sub>) devices. Besides, testing on the device based on homopolymers (PVPK, POXD and **PBOXD**) was also carried out as a reference (Fig. 5(b)). The device fabricated with PVPK material as the active memory layer shows only single moderately high conductance state without



Fig. 5 Current-volatge (I-V) characteristics of the memory device: (a)  $P(VPK_5OXD_5)$ ,  $P(VPK_2OXD_8)$ ,  $(P(VPK_5BOXD_5)$  and  $P(VPK_2BOXD_8)$ , and (b) PVPK, POXD and PBOXD.

a conductance switching behavior whereas the **POXD** or **PBOXD** device maintains in a low conductance state even if the voltage across the device is swept from 0 to 8 V.

The stability of the memory effect was also evaluated under the same atmosphere. Fig. 6 shows the retention time tests under a constant stress of 1 V for both the ON and OFF states of the **P(VPK<sub>8</sub>BOXD<sub>2</sub>)** device, respectively. As shown in the figure, an ON/OFF current ratio of  $10^4$ – $10^5$  can be maintained and no obvious degradation in current is observed for both the ON and OFF states after periods of at least 1 h. In addition, the stimulus effect of read pulse on the ON and OFF state was also investigated as shown in Fig. 7. The insert shows the pulse generation used in the measurement with a pulse period and width of 3 and 2  $\mu$ s, respectively. The **P(VPK<sub>8</sub>BOXD<sub>2</sub>)** memory device is quite stable for over  $10^7$  continuous read pluses of 1 V. Therefore, both ON and OFF states are conducted under the voltage stress and continuous pulse cycles.

#### Operating mechanism of random copolymers memory device

The volatile memory behavior can be rationalized by evaluating the electronic structures of basic units and random copolymers.



Fig. 6 Retention time test on the ON and OFF states of the ITO/ P(VPK<sub>8</sub>BOXD<sub>2</sub>)/Al device under a continuous readout voltage.



Fig. 7 Stimulus effect of read pulses on the ON and OFF states of the  $ITO/P(VPK_8BOXD_2)/Al$  device. The insert shows the pulse shapes in the measurement.

Molecular simulation on the VPK, OXD and BOXD moieties and basic units of  $P(VPK_xOXD_y)$  and  $P(VPK_xBOXD_y)$  were carried out by DFT/B3LYP/6-31G(d) with Gaussian 03 software. The results of optical absorption and CV indicate that there is no obvious charge transfer interaction between the pendent donor (VPK) and acceptor (OXD or BOXD) moieties, which is also verified by theoretical calculation. The relative energy diagram is summarized in Fig. 8. The electronic structures of the basic units through the simulation give a reasonable qualitative result and are consistent with our trend of experimental data. In the random copolymers, the HOMO energy level is associated with **PVPK** units whereas the LUMO energy level is associated with the corresponding POXD or PBOXD units. With а configuration of  $ITO/P(VPK_xOXD_y)$ or P(VPK<sub>x</sub>BOXD<sub>y</sub>)/Al device, the barrier height of the ITO/polymer (HOMO level) contact (0.74–0.76 eV) is quite smaller than that of Al/polymer (LUMO level) contact (1.73-1.92 eV) when the polymers are at the ground state. It suggests that the hole injection from ITO into the HOMO level of random copolymers is the dominated process and all the random copolymers can be served as hole-transporting materials. However, due to the lowlying HOMO level of OXD or BOXD moieties embedded in the polymer thin film layer, a poor (or limited) charge transport occurred through the neighboring VPK moieties. As a result, the incorporation of the electron-accepting OXD or BOXD moieties could serve as the hole-blocking layer in the active memory layer. For the case of the larger acceptor content in the copolymers, the I-V characteristic curves of P(VPK5OXD5), P(VPK5BOXD5),  $P(VPK_2OXD_8)$ , and  $P(VPK_2BOXD_8)$  devices exhibit a low current state between  $10^{-12}$  to  $10^{-11}$  A as shown in Fig. 5(a). This insulating behavior is almost the same as the pure POXD or PBOXD device (Fig. 5(b)). On the other hand, the PVPK homopolymer is a hole transport material and the formation of pathways for hole hopping with neighboring carbazole units under the electric field contribute to the ON state conductance (Fig. 5(b)).<sup>31,32,44,45</sup> Therefore, the electrical switching between the top and bottom electrodes depends on the trapping amounts of **POXD** or **PBOXD** moieties in the random copolymers. The higher electron acceptor ratio (5/5 or 2/8) of random copolymers may prevent the positive charge from the direct hopping process and maintain the OFF state.

For the case of a device with relatively higher donor ratio of the copolymers, P(VPK<sub>8</sub>OXD<sub>2</sub>) and P(VPK<sub>8</sub>BOXD<sub>2</sub>), the electrical switching exhibits the volatile memory behavior. Under a low voltage bias (0-6 V), holes do not have sufficient energy to overcome the charge injection barrier between VPK/OXD or VPK/BOXD moieties and are blocked by the electron-accepting OXD or BOXD moieties in the film. Thus, the device is on the low conductance state (OFF state). As sweeping up to the threshold voltage, the generated amounts of holes with sufficient activation energy inject into memory layer and fill the charge trapping environment. The holes are able to flow continuously and more effectively in the copolymer film, switching the device from the OFF to ON state. The increase of current probably results from the efficient interchain hopping of the charge carriers in the neighboring carbazole chain. The ON state can not be maintained without a continuous voltage bias and it returns to the original state after the removal of the applied electric field for a short period of time. This is probably due to the shallow depth of trap, which is 0.59 eV for P(VPK<sub>8</sub>BOXD<sub>2</sub>) and 0.74 eV for  $P(VPK_8OXD_2)$ , respectively. Note that the depth is calculated from the difference of HOMO level of VPK and BOXD or OXD units in Fig. 8. The shallow traps contribute to the unstable ON state of the volatile nature.<sup>24</sup> The reported **PVK-C<sub>60</sub>** copolymer memory device exhibited a non-volatile memory characteristic since the formed charge transfer complex switching to ON state could be retained, due to the strong dipole moment.32 However, our synthesized P(VPK<sub>8</sub>OXD<sub>2</sub>) or P(VPK<sub>8</sub>BOXD<sub>2</sub>) copolymers show no obvious interaction between donor and acceptor moieties and the spontaneously back transferring of shallow trapped charges lead to the volatile memory performance as the electric field is removed.<sup>24</sup>

Besides, the higher HOMO energy level of  $P(VPK_8BOXD_2)$ relative to that of  $P(VPK_8OXD_2)$  allows a shorter holding period of the ON state, due to the relative rapid back transferring of shallow trapped holes process. The slightly smaller threshold voltage of  $P(VPK_8BOXD_2)$  as compared to  $P(VPK_8OXD_2)$ may attribute to the lower hole injection barrier between ITO/polymer interface. However, poly(9-(2-((4-vinylbenzyl) oxy)ethyl)-9*H*-carbazole) (PVBCz) reported in the literature<sup>45</sup> exhibited a much smaller threshold voltage (-2 V) since the  $P(VPK_8OXD_2)$  and  $P(VPK_8BOXD_2)$  devices need to overcome



Fig. 8 Molecular simulation of HOMO and LUMO energy levels for VPK, OXD and BOXD segments and basic units of P(VPK<sub>x</sub>OXD<sub>y</sub>) and P(VPK<sub>x</sub>BOXD<sub>y</sub>) along with the work function of the electrodes.

the percolation threshold of the trapping site for effective charge carrier transport. It concludes that electric-field induced memory switching based on  $P(VPK_8OXD_2)$  or  $P(VPK_8BOXD_2)$  random copolymers depend on the charge hopping conduction between the carbazole units with coexisting charge trapping environment and the volatility of the memory effect is determined from the ability of charge trapping/back transferring of trapped charge.

# Conclusions

We have successfully synthesized new non-conjugated random copolymers containing pendant electron-donating carbazole and electron-accepting 1,3,4-oxadiazole by nitroxide-mediated free radical polymerization. The random copolymers exhibited good solubility in common organic solvents and good thermal stability. The optical band gaps of PVPK, POXD, PBOXD,  $P(VPK_xOXD_v)$  and  $P(VPK_xBOXD_v)$  estimated from the absorption edges were 3.48, 3.68, 3.40, 3.44-3.52, 3.42-3.47 eV, respectively, indicating that there is no strong electronic interaction between donor and acceptor segments. The low-lying HOMO energy level of OXD or BOXD compared to VPK could serve as hole-blocking moieties and provide the charge trapping environment. Thus, the switching effect of the ITO/random polymers/Al device was found to be dependent on the donor/ acceptor ratio or acceptor ability. The  $P(VPK_8OXD_2)$  or P(VPK<sub>8</sub>BOXD<sub>2</sub>) memory device exhibited volatile SRAM features, and ON/OFF current ratio reached up to 104-105. Both ON and OFF states could endure 10<sup>7</sup> cycles under a pulse read voltage and be stable for at least 1 h under a constant voltage stress. The electrical volatile nature is mainly attributed to the back transferring of shallow trapped charges in the pendent functional moieties. Our results provided the strategies to manipulate the memory characteristics on non-conjugated copolymers with pendent donor/acceptor moieties.

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