Cite this: J. Mater. Chem., 2012, 22, 19957

Memory devices based on functionalized copolymers exhibiting a linear dependence of switch threshold voltage with the pendant nitro-azobenzene moiety content change

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Received 28th May 2012, Accepted 13th August 2012 DOI: 10.1039/c2jm33426g

A nonvolatile nanoscale memory device based on pendent copolymer exhibits write-once-read-manytimes (WORM) characteristics with the highest ON/OFF current ratio up to 10⁴ and a long retention time. Moreover, it was observed that switch threshold voltages of the device varied almost linearly with the functional moiety content in the copolymer. The cyclic voltammetry (CV) curves and UV-vis spectra of the copolymer's nanofilms were investigated and the obtained results associated with the linear decreasing memory behavior. The mechanisms of the device exhibiting WORM characteristics were elucidated from molecular simulation results showing that the electron density transition from the HOMO to LUMO surfaces is permanently under electric field and would not revert to the original state after the external voltage was removed.

Introduction

In recent years, memory devices based on nanoscale thin films have been widely investigated by scientists.¹⁻⁴ Currently, there is increasing interest in the use of organic and polymeric materials as novel memory elements.⁵⁻⁹ Compared with organic small molecule materials, polymeric materials show rapid, easy and cost effective processing of the thin layers required in devices.¹⁰⁻¹⁹ The pendant polymers containing donor-acceptor structures in the side-chains have been precisely studied and could achieve different memory performance through adjusting the push-pull ability of electron donors and acceptors.²⁰⁻²⁴ Whereas, there are other important factors that may influence devices' performance, such as the film thickness, the content of functional moieties in the copolymer and the energy barrier between the film and the electrode's surface. In this paper, we mainly investigate how the varied functional moiety content in the copolymer would affect the performance of the fabricated sandwiched devices.

Carbazole, containing a large conjugated planar structure, has good hole transport capability for optoelectronic applications.¹⁴ The nitro-benzene has the advantages of a simple synthesis route and low cost, and thus is frequently incorporated as an electron acceptor in organic semiconductors.¹⁹ Herein, one azobenzene derivative was prepared as shown in Scheme 1, where the carbazole acts as an electron donor and the nitro-azobenzene as an electron acceptor. The pull–push electron groups would undergo charge transfer under the electric field,^{23,24} which is important for the device to achieve OFF to ON state switching. A simple and accessible free radical polymerization was adopted in this paper to prepare PAzo-*co*-St (P(Azo)_x(St)_y) in which the monomer styrene was introduced to enhance both the material's solubility and scalability. The memory devices based on copolymers with different contents of functional moieties exhibited excellent write-once-read-many times (WORM) performances with their ON/ OFF current ratio up to 10⁴ and the switch threshold voltages of the device varied almost linearly with functional moiety content in the copolymer. This is important information for the design of pendent polymer structures to obtain good electronic performance.

Experimental section

Materials

1-Chloro-6-hydroxyhexane, tetrahydrofuran (THF), azobisisobutyronitrile (AIBN) (99%), carbazole (99%), cyclohexanone (99%), potassium hydroxide (KOH) (99%) and other solvents were all purchased from Shanghai Chemical Reagent Co. Ltd. Cyclohexanone and Styrene were purified by reduced pressure distillation. AIBN was recrystallized from methanol before use. Other reagents were used as received without any further purification.

Preparation of $P(Azo)_x(St)_y$

Synthesis of CZ. Potassium hydroxide (5.0 g, 88.9 mmol) was added into 120 mL *N*,*N*-dimethylacetamide (DMF). After

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Scheme 1 The synthesis route and molecular structure of the copolymers.



Fig. 1 ¹H-NMR spectrum of $P(Azo)_1(St)_1$ in CDCl₃.

Table 1 Characterization data of $P(Azo)_x(St)_y$

$P(Azo)_x(St)_y$	GPC result				
	$M_{\rm n}$	$M_{\rm w}/M_{\rm n}$	Wt% ^a	TGA (°C)	$T_{\rm g}(^{\circ}{ m C})$
PAzo	3682	1.71	100	308	129
$P(Azo)_1(St)_1$	3447	1.40	80	304	126
$P(Azo)_1(St)_5$	3899	1.73	67	301	123
$P(Azo)_1(St)_{10}$	4582	1.49	36	298	119
$P(Azo)_1(St)_{20}$	6344	1.62	26	293	117

^{*a*} The weight percentage of Azo moiety in the copolymers were measured by UV-vis absorption standard curve.

stirring for 10 min, carbazole (3.34 g, 20 mmol) was added to the mixture and continued stirring for 45 min. Then, 1-chloro-6-hydroxyhexane (2.85 g, 21 mmol) was added slowly to the mixture and the reaction kept at 50 °C for 24 hours. The resulting mixture was poured into a large amount of water and the precipitate was collected by filtration. Then, the final white product CZ was dried and purified *via* silica gel column with chloroform and petroleum ether (petroleum ether boiling point range 60–90 °C) (volume ratio = 2 : 1), yield 69%. ¹H-NMR

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(CDCl₃, δ , ppm): 8.12 (d, 2H), 7.46–7.41 (m, 4H), 7.23–7.20 (m, 2H), 4.32 (t, 2H), 3.61–3.59 (t, 2H), 1.91–1.89 (m, 2H), 1.55 (m, 2H), 1.41 (m, 4H), 1.30 (s, 1H). Elemental analysis calculated for C₁₈H₂₁NO (wt%): C, 80.86; H, 7.92; N, 5.24; found: C, 80.80; H, 7.87; N, 5.28.

Synthesis of CA. A mixed solution of 4-nitroaniline (1.38 g, 10 mmol), concentrated hydrochloric acid (4 g, 37%) and deionized water (4 g) was stirred below 4 °C in an ice bath. Then, sodium nitrite (0.83 g, 12 mmol) dissolved in deionized water (4 g) was slowly added dropwise to the above solution and stirring continued for an hour at 0-4 °C. After the solution had become transparent, the mixture was filtered and the filtrate (diazonium salt solution) was kept in the ice bath. Sodium dodecyl sulfate (107 mg) was added into the filtrate. CZ (2.67 g, 10 mmol) was dissolved in methylene chloride (100 mL), and then added dropwise to the above filtrate under intense stirring at room temperature for 48 hours. Dichloromethane was removed under reduced pressure, the mixture was filtered to get a red precipitate and this was rinsed with plenty of water. The crude product was purified through silica gel column with chloroform and petroleum ether (volume ratio = 5 : 1), yield 50%.¹H-NMR (d₆-DMSO, δ, ppm): 8.85 (s, 1H), 8.43 (d, 2H), 8.34 (d, 1H), 8.12 (d, 1H), 8.07 (d, 2H), 7.80 (d, 1H), 7.71–7.68 (t, 1H), 7.56–7.54 (t, 1H), 7.31 (t, 1H), 4.50–4.46 (t, 2H), 4.32–4.29 (t, 2H), 1.82–1.79 (m, 2H), 1.32–1.29 (m, 6H). Elemental analysis calculated for C₂₄H₂₄N₄O₃ (wt%): C, 69.21; H, 5.81; N, 13.45; found: C, 69.25; H, 5.87; N, 13.38.

Synthesis of Azo. A mixture of CA (1.04 g, 2.5 mmol), tetrahydrofuran (10 mL) and triethylamine (0.5 mL) was kept in the ice bath. Then, methacryloyl chloride (0.36 g, 3.45 mmol) diluted in 5 mL of THF was added dropwise to the mixture and the reaction continued for 10 hours in the ice bath. The reaction solution was concentrated and added into 50 mL chloroform and then washed with 1% hydrochloric acid solution and 3% sodium hydroxide solution. Finally, the solution was washed with deionized water to neutral pH and chloroform was removed to get red product, yield 99%. ¹H-NMR (d₆-DMSO, δ , ppm): 8.85



Fig. 2 UV-visible absorption spectra of $P(Azo)_x(St)_y$ with different Azo moiety content (a) in THF solution and (b) nanofilms spin-coated on ITO glasses; (c) fluorescence intensity spectra of the nanofilms of $P(Azo)_x(St)_y$ with different Azo moiety content at the excitation wavelength $\lambda_{ex} = 327$ nm.

(s, 1H), 8.43–8.41 (d, 2H), 8.32 (d, 1H), 8.06–8.04 (m, 3H), 7.78 (d, 1H), 7.70 (d, 1H), 7.54 (t, 1H), 7.30 (t, 1H), 5.97 (s, 1H), 5.62 (s, 1H), 4.45 (t, 2H), 4.02 (t, 2H), 2.02 (s, 3H), 1.81 (m, 4H), 1.33–1.31 (m, 4H). Elemental analysis calculated for $C_{28}H_{28}N_4O_4$ (wt %): C, 69.41; H, 5.82; N, 11.56; found: C, 69.37; H, 5.86; N, 11.60.

Synthesis of $P(Azo)_x(St)_y$. The free radical copolymerization of Azo with styrene was carried out in cyclohexanone solution, a typical procedure is as follows: styrene (0.52 g, 5 mmol), Azo (0.242 g, 0.5 mmol), 2,2'-azobis(isobutyronitrile) (AIBN, 4.1 mg, 0.025 mmol) and 1 mL cyclohexanone were added to a dry glass tube under N₂ atmosphere and the reaction temperature was kept at 90 °C. After 20 hours, the mixture was cooled, diluted with a little tetrahydrofuran and precipitated in a large amount of methanol. The precipitated product was filtrated and further purified by extraction with methanol in a Soxhlet apparatus to remove small molecules to give the red product.

Instruments

¹H-NMR spectra were obtained on an Inova 400 MHz FT-NMR spectrometer (Fig. 1). The elemental analysis was performed by Italian 1106 FT analyzer. UV-vis absorption spectra were recorded by a PerkinElmer Lambda-17 spectrophotometer at room temperature. Thermogravimetric analysis (TGA) was conducted on a TA instrument Dynamic TGA 2950 at a heating rate of 10 °C min⁻¹ under a N₂ flow rate of 50 mL min⁻¹. Cyclic voltammetry was performed at room temperature using an ITO working electrode, a reference electrode Ag/AgCl, and a counter electrode (Pt wire) at a sweep rate of 20 mV s⁻¹ (CorrTest CS Electrochemical Workstation analyzer) in a solution of tetrabutylammonium hexafluorophosphate (n-Bu₄NPF₆) in acetonitrile (0.1 M). SEM images were taken on a Hitachi S-4700 scanning electron microscope. Molecular weights (M_n) and polydispersity (M_w/M_p) was measured by gel permeation chromatography (GPC) utilizing a Waters 1515 pump and a differential refractometer, THF was used as a mobile phase at a flow rate of 1.0 mL min⁻¹. Differential scanning calorimetry (DSC) analyses were performed on a Shimadzu DSC-60A Instrument.

Device fabrication

The indium tin oxide (ITO) glass substrate was carefully precleaned sequentially with deionized water, acetone and alcohol by ultrasonic bath for 20 minutes, respectively. The copolymer solution was prepared in cyclohexanone (10 mg mL⁻¹) and filtered through micro filters with a pinhole size of $0.22 \,\mu\text{m}$, after then the solutions were spin-coated onto ITO controlled at 2000 rpm and the solvent was removed in a vacuum chamber at 10^{-1} Pa and 50 °C for 12 h. The thickness of the polymer nano-layer was about 100 nm (Fig. 3b). Finally, the top metal electrode was obtained by a 100 nm thick nanofilm of Al, which was thermally evaporated at about 10^{-6} torr through a shadow mask. The active area of the fabricated device was 0.126 mm^2 (a nummular point with a radius of 0.2 mm). All electrical measurements of the device were characterized under ambient conditions, without any encapsulation, using a HP 4145B semiconductor parameter analyzer.

Results and discussion

The synthetic route and molecular structures of monomers and copolymers are shown in Scheme 1. The weight percentages of azobenzene moieties in the copolymers were determined by UV-vis absorption standard curve. The Mn, PDIs, Azo moiety content and the onset decomposition temperatures of the copolymers for different monomer ratios are summarized in Table 1. The Azo moiety content in the copolymers decreases from 100% to 26% with the decreasing proportion of Azo monomer. All the polymers exhibit good thermal stability, with an onset decomposition temperature of about 300 °C and T_g of about 120 °C, which promise good heat deterioration endurance for the material in the memory devices.

Fig. 2 shows the UV-vis spectra of $P(Azo)_x(St)_y$ with different Azo moiety content in THF solution and in solid nanofilms. In THF, the peak maxima are almost the same for all copolymers with different Azo content (Fig. 2a), this result indicates that the polymer backbones are flexible and the arrangement of Azo



Fig. 3 (a) A schematic diagram of the ITO/polymer/Al nano device; (b) a SEM image of a cross section of ITO/PAzo/Al nano device; (c) current–voltage (I-V) characteristics of the memory device based on PAzo nanofilm; (d) the effect of retention time on the ON and OFF states of the memory device under a constant stress of -1.0 V, and the inset is the effect of read cycles on the ON and OFF state under a read pulse voltage of -1.0 V.



Fig. 4 HOMO, LUMO and Electrostatic Potential (ESP) surfaces of the Azo monomer units of $P(Azo)_x(St)_y$ obtained by molecular simulation.

moieties in the side chains are irregular in the solution so that the steric influence of the side chain is negligible. For nanofilms of $P(Azo)_x(St)_y$ on ITO substrate, both the UV-vis spectra and the fluorescence spectra show the largest absorbance peak or emitting peak red shifted as the Azo moiety content in the copolymer increased from 26% to 100% (Fig. 2b and c), which indicated that the functional moieties in the copolymer side-chains stacked more orderly and more closely as the functional moieties content increasing.

Nano memory devices of an ITO/copolymer/Al sandwich structure were fabricated using nanofilms of the copolymers mentioned above. The device structure is shown schematically in Fig. 3a. Fig. 3b is the scanning electronic microscopic (SEM) image of one storage cell from the direction of a cross-section view, from the top to bottom is aluminum electrode,

(a) -7 ((VII-)goJ OFF State Experimental Date Fitted Date 0.6 0.8 1.0 1.2 0.0 0.2 0.4 1.4 Voltage ((-V)^{1/2}) (b) 0.01 0.014 (mA) 0.01 0.01 Current ON State 0.00 Experimental Date Fitted Date 0.004 -3.3 -3.0 -3.6 -39 -24 .27 Voltage (V)

Fig. 5 Experimental and fitted data of I-V curves for the ITO/PAzo/Al nano device in the OFF and ON states; (a) is the OFF state with the Poole–Frenkel model (-0.19 to -2.30 V); (b) is the ON state with the Ohmic current model.

 $P(Azo)_x(St)_y$ nanofilm, and ITO glass, respectively. Electrical transitions in the ITO/copolymer/Al devices were investigated in the measurements of the current regarding to an external applied voltage. ITO was maintained as the ground electrode in all electrical measurements. The current–voltage (*I–V*) characteristics of the ITO/P(Azo)_x(St)_y/Al nano device in Fig. 3c showed two distinct conductivity states (herein, Azo content in the copolymer is 100%). In the first round scan from 0 to -4 V, the current increased dramatically at a threshold voltage around -2.31 V, indicating a transition from a low-conductivity state (OFF state) to a high-conductivity state (ON state). The device remained in this ON state during a subsequent scan from 0 to



Fig. 6 Current–voltage (I-V) curves of several nano devices based on $P(Azo)_x(St)_v$ nanofilms with different Azo moiety content.



Fig. 7 (a) A UV-visible absorption spectrum of $P(Azo)_1(St)_5$ nanofilm; (b) cyclic voltammetry (CV) curves of $P(Azo)_1(St)_5$ nanofilm on an ITO substrate in acetonitrile with 0.1 M *n*-Bu₄NPF₆ as the supporting electrolyte. The inset is the CV curves of the ferrocene standard, swept in the same conditions as for $P(Azo)_1(St)_5$.

-4 V (sweep 2). The distinct bi-electrical states in the voltage range of about 0 to -2.31 V, where the ON/OFF current ratio is up to 10^4 , allowed a voltage (*e.g.*, -1.0 V) to read the "0" or "OFF" signal (before writing) and "1" or "ON" signal (after writing) of the nano memory device. However, the nano device also remained in the ON state when scanning from 0 to 4 V (sweep 3) and could not return to the original OFF state. It is shown that the nano device fabricated with PAzo exhibits WORM memory behavior. The ON and OFF states of the

devices are stable for up to 10^7 continuous read pulses of -1 V without any resistance degradation. The high ON/OFF current ratios of the devices promise a low misreading rate by precise control over the OFF and ON states. The retention ability of the OFF and ON states of a device was investigated under a constant voltage stress of -1 V, recording the current passing through the device at regular intervals. Fig. 3d shows that the device has both stable OFF and ON state currents within a 300 min time frame, with a high ON/OFF current ratio sustained. Thus, both states are insensitive to read pulses and are stable under voltage stress.

Further information about the charge transport mechanism can be obtained from I-V curves in the OFF and ON states according to various theoretical models. As shown in Fig. 5a, the OFF states for the ITO/P(Azo)_x(St)_y/Al nano device can be elucidated as Poole-Frenkel (PF)²⁵ emission in terms of the plots of $\log(-I/V)$ versus $(-V)^{1/2}$, which were found to be linear in a range from -0.32 V to -2.31 V. In order to investigate the reason why the $\log(-I/V)$ and $(-V)^{1/2}$ didn't have a strictly linear relationship in the whole OFF state, calculation of electrostatic potentials (ESP) for the functional groups of Azo was further carried out at the B3LYP/6-31G(d) level with the Gaussian03 program package to understand the charge carriers' migration through the polymer nanofilm (Fig. 4). We found that carbazole acted as an electron donor and nitro-azobenzene groups as the electron acceptor in the functional monomer. The molecular surface with the continuous positive ESP (Fig. 4) in red areas along with the side-chain of the copolymer indicates that charge carriers can migrate through this open channel. However, there are some negative ESP regions (blue), which arise from the nitro groups, ester groups and the azo groups. These negative regions can serve as "traps" to block the mobility of charge carriers. Thus, the low current level in the OFF-state was due to the PF emission models and the "traps" lying in the conjugated backbone of the side-chains. On the other hand, the currents in the ON states are almost linearly dependent on the applied voltage, just as in metallic conduction (Fig. 5b), this indicates that the charge transport is dominated by the Ohmic model in the ON states. Therefore, the change of the current conduction from the OFF-state to the ON-state for both types of devices is attributed to the PF emission model and "traps limited" model, and to the Ohmic model.

Under a low bias, the ITO/P(Azo)_x(St)_y/Al nano device is in a low conductivity state (OFF state) for the unfilled traps. As the applied voltage increases, the traps are filled by charge carriers and the device would be activated to the ON-state when the transition voltage is reached. However, trapped charges are stabilized by intramolecular charge transfer to form a charge separated state, which can be illustrated by the molecular simulation (Fig. 4). The HOMO surface represents that the electron density is primarily located on the electron donor group (carbazole); upon undergoing the HOMO to LUMO transition, the electron density obviously underwent a transition from the carbazole (electron donor) side to the nitro-azobenzene (electron acceptor) side, so a charge-separated state occurred when the copolymer film was activated by an electrical field. Therefore the filled traps could hardly be detrapped and the device showed WORM type characteristics.²³

The relationship between the memory performance and the functional moieties content in the copolymers was investigated

Table 2 Characterization data of the $P(Azo)_x(St)_y$ nanofilms

$P(Azo)_x(St)_y$	λ_{Edge} (nm)	$E_{\rm g}~({\rm eV})$	E _{ox} (onset) (eV)	HOMO (eV)	LUMO (eV)	$\Delta E_{\rm p}^{\ a} ({\rm eV})$	$\Delta E_{\rm n}^{\ b} ~({\rm eV})$
PAzo	576	2.15	0.92	-5.38	-3.23	0.58	1.07
$P(Azo)_1(St)_1$	563	2.20	0.85	-5.31	-3.11	0.51	1.19
$P(Azo)_1(St)_5$	554	2.24	0.79	-5.25	-3.01	0.45	1.29
$P(Azo)_1(St)_{10}$	543	2.28	0.65	-5.11	-2.83	0.31	1.47
$P(Azo)_1(St)_{20}$	537	2.31	0.57	-5.03	-2.72	0.23	1.58



Fig. 8 (A) ΔE_p (the energy barrier between the HOMO of copolymer nanofilms and the ITO work function) and (B) switch threshold voltages of several devices based on P(Azo)_x(St)_y with different Azo moiety content.



Fig. 9 Current–voltage (I-V) curves for the devices fabricated with PAzo nano-films of various thicknesses (20–80 nm).

(as shown in Fig. 6). The functional monomer Azo contents have nothing to do with the device storage type, all of the fabricated devices are WORM type. The switching threshold voltage varied approximately linearly with the nitrobenzene moiety content in a range from 100% to 26% in the inter-medium copolymer. In order to figure out why the switching threshold voltage varied approximately linearly with the decreasing azobenzene moieties content, the experimental values of the highest occupied molecular orbital (HOMO) and lowest unoccupied molecular orbital (LUMO) and UV-vis spectra of all copolymer nanofilms were further investigated (Fig. 7, herein, azobenzene content in the copolymer is 67%). The HOMO and LUMO energy levels can be calculated from the onset oxidation potential and UV-vis spectra of all copolymers, according to the following equations:

> HOMO (eV) = $-[(E_{ox}(onset) - E_{Foc}) + 4.80]$ LUMO (eV) = HOMO + E_g $E_g = hc/\lambda_{Edge}$

where $E_{\rm ox}$ is the onset oxidation potential, $E_{\rm Foc}$ is the external standard potential of the ferrocene/ferricenium ion couple, 4.80 is the reference energy level of ferrocene, $E_{\rm g}$ is the energy bandgap of the copolymer nanofilms, *h* is the Planck constant (6.63 × 10⁻³⁴ m² kg s⁻¹), *c* is the speed of light (3 × 10⁸ m s⁻¹) and $\lambda_{\rm Edge}$ is the optical absorbance band edge of the copolymer nanofilms. Therefore, the $\lambda_{\rm Edge}$, $E_{\rm g}$, $E_{\rm ox}({\rm onset})$, $\Delta E_{\rm p}$, $\Delta E_{\rm n}$, HOMO and LUMO energy levels of the P(Azo)_x(St)_y nanofilms were determined and are summarized in Table 2.

It can be seen from Table 2 that the energy barrier between the work function of the ITO bottom electrode (-4.8 eV) and the HOMO level of P(Azo)_x(St)_y is smaller than that between the LUMO level of P(Azo)_x(St)_y and the work function of the Al (-4.3 eV) top electrode. The hole injection from ITO into the HOMO level of P(Azo)_x(St)_y is more favorable than electron injection from the Al top electrode into the LUMO level of P(Azo)_x(St)_y. Thus, P(Azo)_x(St)_y is a p-type material and holes dominate the conduction process. Meanwhile, the measured HOMO of the corresponding copolymer nanofilm reduced gradually as the azobenzene moiety content decreased in the nanofilms, and the energy barrier between the HOMO of the copolymer film and the ITO work function also reduced, which illustrated the turn-on voltage showing a linear decline (as showed in Fig. 8).

The device's performance based on different film thickness, such as 20, 40, 60, 80 nm, is also investigated (Fig. 9). The devices fabricated with 80–40 nm thick films revealed WORM memory characteristics, as observed for the 100 nm thick films device. However, the OFF-state current level increases as the film thickness decreases; the ON-state current level is almost the same and is independent of the film thickness. The 20 nm thick film never shows electrical switching behavior and always stays in the ON state, which maybe arising from the top Al electrode penetrating through the whole film during the vacuum deposition process. Meanwhile, the turn-ON voltage does not change with

the thickness decreasing from 80 to 40 nm, with all about -2.3 V. This phenomenon is also consistent with the conclusion that the transition voltage is determined by the energy barrier between the work function of the ITO bottom electrode and the HOMO level of P(Azo)_x(St)_y.

Conclusions

In summary, we have demonstrated that uniform $P(Azo)_{y}(St)_{y}$ nanofilms prepared by simple spin-coating can be successfully utilized in a novel nonvolatile nano memory device. This device exhibited WORM behavior with high ON/OFF ratios up to 10⁴. It was found that the switching threshold voltage varied almost linearly with the functional moiety content, which was attributed to the reduced energy barrier between the HOMO of copolymer nanofilm and the ITO work function. The mechanism of the WORM behavior was further elucidated from the molecular simulations of electron density from the HOMO to LUMO surfaces, and the obviously electron density shifting from donor to acceptor side indicates that the charge separated state could remain permanently and wouldn't revert to its original state even after applying a reverse voltage scan. Overall, the nano memory devices fabricated with $P(Azo)_x(St)_v$ copolymers have potential applications in the future.

Acknowledgements

This work was supported by the Chinese Natural Science Foundation (NSFC 21076134, 21176164), the Natural Science Foundation of Jiangsu Province (BK2010208), and the Doctoral Program of Higher Education of China (Grant no. 20113201130003), and a project funded by the Priority Academic Program Development (PAPD) of Jiangsu Higher Education Institutions.

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