

Linkage effect on the memory behavior of sulfonyl-containing aromatic polyether, polyester, polyamide, and polyimide†

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Sulfonyl-containing aromatic polymers DSPE, DSPET, DSPA, and DSPI consisting of a triphenylamine moiety were synthesized and the memory behavior was investigated. By choosing the suitable linkage between the electron donor and acceptor, tunable memory properties (from insulator to different retention time SRAM) could be achieved.

With the rapid growth of information industry, there is an increasing demand for the next generation memory devices with better performance than conventional memory devices which depend on semiconductor-based integrated circuits.¹ Thus, polymeric memory materials have attracted increasing attention over the years since the first one published by Sliva *et al.*² in 1970. Comparing with conventional inorganic memory materials, polymeric materials have advantages in their ease of miniaturization and tailored properties through molecular design. Besides, polymeric memory materials store information in the form of high (ON) and low (OFF) current state in place of the amount of charges stored in a cell of silicon devices and have the advantages of low-cost, solution processability, flexibility, and three-dimensional stacking capability for practical use.³ Hence, they are likely to be the next generation materials for memory devices.

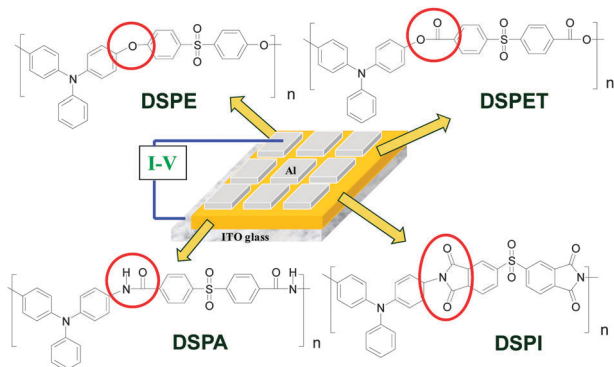
In the starting stage of polymer memory applications, polymers were used as polyelectrolytes or matrices in a doped system.⁴ To advance the function of polymers for memory devices further, the design and synthesis of the polymers with specific structures that can provide the expected memory properties within a single polymer chain is an important and crucial issue. Donor–acceptor type polymers containing both electron donor and acceptor moieties within a repeating unit which could contribute electronic transition between the ground and excited states exhibited resistive memory behavior,⁵ including conjugated polymers,⁶ non-conjugated pendent polymers,⁷ polymer composites,⁸ and functional polyimides.⁹

Among all the studied donor–acceptor systems, aromatic polyimides are promising candidates for memory device applications due to the excellent thermal dimensional stability, chemical resistant, and high ON/OFF current ratio resulting from the low conductivity in the OFF state. In addition, wholly aromatic polyamides were also characterized as highly thermally stable polymers with a favorable balance of physical and chemical properties.¹⁰ In our previous study, triphenylamine (TPA) based polyamide revealed different volatile memory characteristics from polyimide due to the difference of linkage, dipole moment, HOMO, and LUMO energy levels between polyamide and polyimide.¹¹ Besides, the conformational changes of the flexible amide linkage between the donor and acceptor moiety induced by charge transfer increases the torsional displacement and produces a potential energy barrier for the back charge transfer (CT) which results in the longer retention time. It is interesting to get more insight into the relationship between memory properties and linkage groups of functional polymers. Aromatic sulfonyl-containing polyether and polyester are also classified as high performance polymers and exhibit excellent transparency and mechanical property.¹² However, to the best of our knowledge, the memory properties of polyether and polyester have not been reported to date. In this study, we therefore synthesized aromatic sulfonyl-containing polyether (DSPE), polyester (DSPET), polyamide (DSPA), and polyimide (DSPI) to demonstrate the effects of different linkages between donor and acceptor moieties within these TPA-based polymers on the memory behaviors systematically. The different linkage groups of polyether, polyester, polyamide, and polyimide are expected to have different linkage conformation, dipole moment, HOMO, and LUMO energy levels and retention time.

Chemical structures and memory devices of these sulfonyl-containing polymers are illustrated in Scheme 1, and the detailed synthesis procedures are provided in Fig. S1 (ESI†). Inherent viscosities and molecular weights of these four polymers are summarized in Table S1 (ESI†). Besides, the IR spectrum, thermal properties, and solubility behavior of new functional polyester DSPET could be obtained from the ESI.† UV-vis absorption spectra of these polymers are shown in Fig. S4 (ESI†) and the onset wavelengths of optical absorption were utilized to obtain the optical energy band gap (E_g). The electrochemical behavior of

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Scheme 1 Chemical structures and memory device diagram.

these polymers was investigated by cyclic voltammetry conducted by film cast on an ITO-coated glass substrate as the working electrode in dry acetonitrile (CH_3CN) containing 0.1 M of TBAP as an electrolyte.

The typical cyclic voltammograms for these polymers are depicted in Fig. S5 (ESI[†]), and the onset oxidation is used to calculate the HOMO energy level. The optical and electrochemical properties of these four polymers are summarized in Table 1. The LUMO energy levels of these polymers decrease in the order of **DSPE**, **DSPA**, **DSPET**, and **DSPI**.

The memory behavior of these polymers was depicted by the current–voltage (I – V) characteristics of an ITO/polymer/Al sandwich device as shown in Fig. 1, and Al was used as the electrode for applying voltage during the sweep. To exclude the effect of the polymer film thickness on memory properties, a standard thickness (50 nm) was used without specific mention.

The memory devices of **DSPE** retained a low-conductivity (OFF) state during the ambipolar scan without switch capability as shown in Fig. 1(a). Fig. 1(b) reveals I – V characteristics of **DSPET**. The device based on **DSPET** could not be switched to the ON state and stayed in the OFF state with a current range 10^{-12} – 10^{-13} in the positive sweep up to 6 V (not shown). However, a sharp increase in the current could be observed at -3.8 V during the negative sweep, indicating that the device undergoes an electrical transition from the OFF state to the ON state (writing process). The device also remained in the ON state during the subsequent negative (the second sweep) and positive scans (the third sweep). Thus, this **DSPET** memory device could not be reset to the initial OFF state by the introduction of a

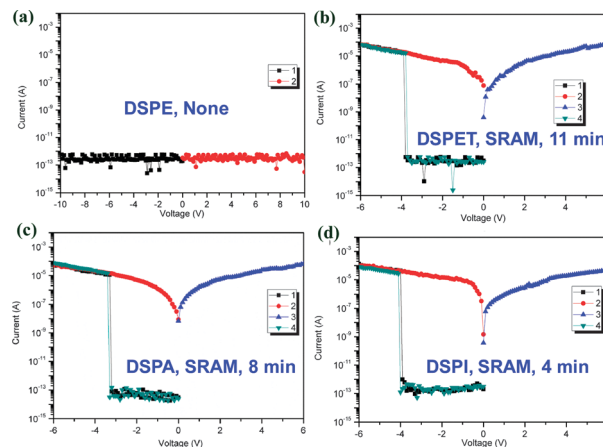


Fig. 1 Current–voltage (I – V) characteristics of the ITO/polymer (50 ± 3 nm)/Al memory device. (a) **DSPE** (b) **DSPET** (c) **DSPA** (d) **DSPI**.

reverse scan and is thus non-erasable. The fourth sweep was conducted after turning off the power for about 11 minutes and it was found that the ON state had relaxed to the steady OFF state without an erasing process. During the fourth sweep, the device could be switched to the ON state again at the threshold voltage of -3.7 V. Thus, the device could open to the ON state again and was rewritable. The longer retention time at the ON state yet volatile as well as the randomly accessible ON and OFF states in each ITO/**DSPET**/Al device are similar to the data remanence behavior of SRAM.¹³ Fig. 1(c) and (d) reveal I – V characteristics of **DSPA** and **DSPI**, which have similar SRAM memory properties with different retention time of 8 minutes and 4 minutes, respectively. The memory devices of **DSPET**, **DSPA**, and **DSPI** have a high ON/OFF current ratio around 10^8 which is advantageous to reduce misreading probability between the ON state and the OFF state.

In order to get more insight into the different memory behavior of the present sulfonate-containing polymers, molecular simulation on the basic unit was carried out by DFT/B3LYP/6-31G(d) with the Gaussian 09 program as shown in Fig. 2. The HOMO and LUMO energy levels calculated by molecular simulation were in agreement with the experimental values tendency and the charge density isosurfaces of the basic unit were summarized.

According to a previous literature,^{5a} when the applied electric field reaches the switching-on voltage, some electrons at the HOMO accumulate energy and transit to the LUMO to form a charge transfer complex (ON state) by different ways. Using **DSPET** as an example, the HOMO is located mainly at the electron-donating TPA moiety, while LUMO is distributed around the electron-withdrawing ester linkage, adjacent phenyl ring, and sulfonyl group. When the applied electric field reaches the switching-on voltage, some electrons at the HOMO accumulate energy and transit to the LUMO5 with the highest probability because of overlapping of the HOMO and LUMO5 resulting in an excited state. Nevertheless, electrons at the HOMO may also be excited to the three intermediate LUMOs with a lower energy barrier belonging to the acceptor units. Thus, CT occurs through several courses to form the conductive CT complexes, including indirectly from the LUMO5 through intermediate LUMOs and then to the LUMO, or from the intermediate LUMOs to the LUMO, and directly from the HOMO to the LUMO.

Table 1 Redox potentials and energy levels of polymers

Polymer	Thin film (nm)	Oxidation potential ^a (V)	E_g^b (eV)	HOMO ^c (eV)	LUMO ^{opt} (eV)
DSPE	361	0.68	3.43	5.12	1.69
DSPET	458	1.01	2.71	5.45	2.74
DSPA	496	0.74	2.50	5.18	2.68
DSPI	567	1.02	2.19	5.46	3.27

^a From cyclic voltammograms versus Ag/AgCl in CH_3CN . ^b The data were calculated from polymer films by the equation: $E_g = 1240/\lambda_{\text{onset}}$ (energy gap between HOMO and LUMO). ^c The HOMO energy levels were calculated from cyclic voltammetry and were referenced to ferrocene (4.8 eV; $E_{\text{onset}} = 0.36$ V). LUMO^{opt} (LUMO energy levels calculated from the optical method): difference between HOMO^{EC} and E_g^{opt} .

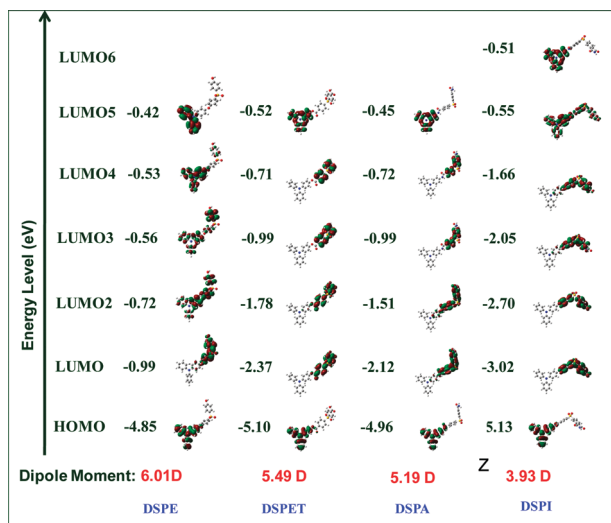


Fig. 2 Calculated molecular orbitals and corresponding energy levels of the basic units (BU) for sulfonyl-containing polymers.

When the intra- or intermolecular CT occurred by the applied electric field, the generating holes can be delocalized to the TPA moieties forming an open channel in the HOMO of polyimides for the charge carriers (holes) to migrate through. Therefore, the current increases rapidly and the memory device can be switched to the high conductivity state (ON state).

Based on this proposed mechanism, when the negative sweep was conducted, the hole injected from the bottom electrode ITO to the HOMO of the polymer due to the lower band gap between ITO (-4.8 eV) and HOMO.^{9,11} In contrast, during the positive sweep, the hole is difficult to be injected from the top electrode Al into the HOMO of these polymers because of the larger energy gap between the work function of Al (-4.2 eV) and HOMO of the polymers, thus the memory device could not be switched to the ON state. Furthermore, the stability of the CT complex is important and is relative to the retention time of the memory device. Therefore, **DSPE** showed only insulator behavior due to the large band gap and weak CT capability. **DSPA** revealed longer retention time than **DSPI** contributing to the conformation effect and higher dipole moment. The conformation of the phenyl ring with amide linkage is not a planar structure as shown in Fig. S6 (ESI[†]) which may block the back CT occurring. Besides, higher dipole moment also facilitates to stabilize the CT complex. **DSPET** having a similar non-planar structure to **DSPA** but higher dipole moment than **DSPA** leads to the longest retention time among all these polymers.

In summary, a new functional aromatic polyester **DSPET** has been successfully synthesized for memory device application. For comparison, **DSPE**, **DSPA**, and **DSPI** were also prepared for systematically investigating the relationship between chemical structure and memory behavior of these sulfonyl-containing polymers. **DSPE** exhibited the insulator behavior, while **DSPET**, **DSPA**, and **DSPI** exhibited SRAM properties with different retention times of 11 min, 8 min, and 4 min, respectively. By choosing the suitable linkage between electron donor and acceptor moieties of high performance polymers, tunable memory

properties (from insulator to different retention time SRAM) could be achieved.

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