

# Side-chain and linkage-mediated effects of anthraquinone moieties on ambipolar poly(triphenylamine)-based volatile polymeric memory devices†

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**Two ambipolar and thermally stable poly(triphenylamine)s with pendent anthraquinone acceptors were readily synthesized and prepared for the investigation of side-chain and linkage-mediated effects on the memory behaviour.**

Over the years, the use of polymeric materials in electronic devices, such as light-emitting devices, transistors, solar cells, and electrochromic devices, has attracted significant attention due to their rich structural flexibility, low-cost, feasibility for solution processing and large area fabrication, and three-dimensional stacking capability.<sup>1</sup> Besides, polymeric memory devices<sup>2</sup> have been paved as a new avenue for design and synthesis of the next generation memory devices with better performance than conventional memory devices, which depend on semiconductor-based integrated circuits. Furthermore, polymeric memory materials have the outstanding properties of higher data storage density, longer data retention time, faster speed, and lower power consumption to confront the challenges of scaling down from the micro- to nano-scale.<sup>3</sup>

The resistive-type memory devices store data based on the high (ON) and low (OFF) current state according to an applied voltage using the simple sandwich device, consisting of a metal electrode/polymer/indium tin oxide (ITO) substrate, where the polymer material is used as a data storage medium. Among the emerging researched polymeric systems, the charge transfer (CT) effect<sup>4</sup> is one of the important mechanisms to induce the RRAM (resistor-type polymer memory) behavior by introducing the electron donor and the electron acceptor moieties into the repeat unit in the main chain or side chain of the polymers. Many precedents using donor-acceptor polymeric systems with electrical memory switching characteristics have been demonstrated, including conjugated

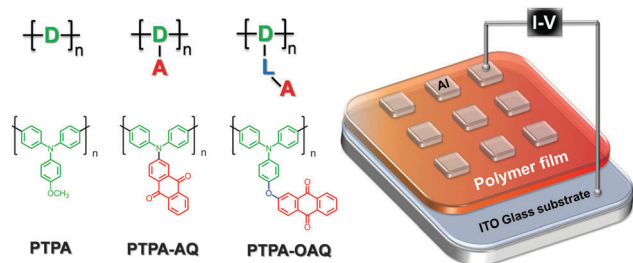
polymers,<sup>5</sup> functional polyimides,<sup>6</sup> non-conjugated polymers with pendent electroactive chromophores,<sup>7</sup> and polymer hybrids.<sup>8</sup>

Meanwhile, a wide range of non-conjugated polymers such as polyethylene or polymethacrylate consisting of a side-chain donor-acceptor, which played the roles in elucidating the mechanism of charge transfer or space charges and traps effect, have been intensively investigated and used for memory applications. Recently, a donor-acceptor (D-A) conjugated polymer with two or more main-chain donors and a side-chain acceptor has been reported by Kang<sup>5a,b</sup> and Chen.<sup>5d</sup> In addition, Chen<sup>5e</sup> also reported tunable electrical switching characteristics of the vinylene-based conjugated polymers using different backbone donors with side chain acceptors, which showed volatile static random-access memory (SRAM) and nonvolatile write once read many (WORM) memory behaviors. The above studies demonstrated the importance of control memory characteristics *via* the donor-acceptor strength and backbone coplanarity. Recently, our group also reported a series of triphenylamine (TPA)-based high performance polymers with different main chain linkages for tunable memory properties.<sup>9</sup> TPA and its derivatives are well-known candidates as hole-transport materials due to their stable radical cation and high hole-mobility.<sup>10</sup> Furthermore, TPA-based polymers could not only be used as the hole-transport layer in electroluminescent devices but are also widely investigated in the field of electrochromic and memory<sup>6d,e</sup> applications. However, the D-A TPA-based conjugated polymers with side chain and linkage effects have not been well studied for resistive type memory devices yet.

In this communication, we therefore synthesized two D-A poly(triphenylamine)s, **PTPA-AQ** and **PTPA-OAQ**, which are adopted for memory device applications and compared with **PTPA** as a pure electron donor system (Fig. 1). Besides, the isolated side chain ether linkage between the TPA donor and the anthraquinone (AQ) acceptor could be expected to affect the backward charge transfer which was also investigated and compared.

Three poly(TPA)s were readily prepared by oxidative coupling polymerization (Schemes S1 and S2, ESI†). The detailed synthetic procedures, structure identification and thermal properties of monomers and polymers are provided in Fig. S1–S8 (ESI†). The molecular weight and solubility behavior of resulting polymers

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 † Electronic supplementary information (ESI) available: Experimental section. Table: inherent viscosity, molecular weights, solubility behavior, and thermal properties. Figure: NMR, and IR of monomers; NMR, TGA, DSC and CV traces of polymers. See DOI: 10.1039/c4cc00639a



**Fig. 1** Chemical structures of poly(triphenylamine)s and the schematic diagram of the memory device consisting of a polymeric active layer sandwiched between an ITO bottom electrode and an Al top electrode. The thickness of the polymeric thin film is about 50 nm and the thickness of the electrode is 300 nm.

**Table 1** Redox potentials and energy levels of the polymers studied

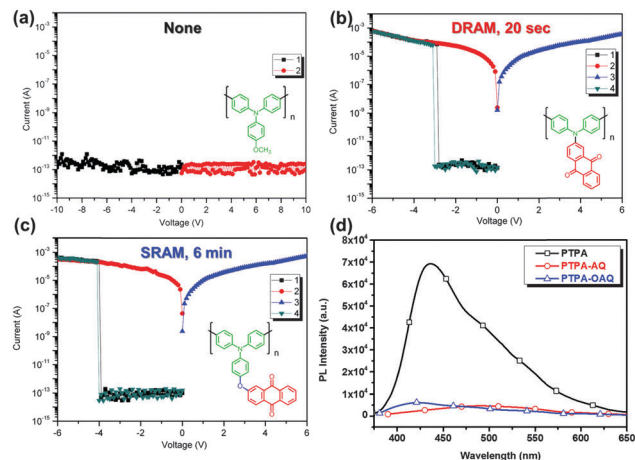
Polymer	Oxidation <sup>a</sup> (V)		Reduction <sup>b</sup> (V)			HOMO <sup>c</sup>	LUMO <sup>d</sup>
	$E_{\text{onset}}$	$E_{1/2}$	$E_{\text{onset}}$	$E_{1/2}$ (re,1)	$E_{1/2}$ (re,2)		
<b>PTPA</b>	0.62	0.85	—	—	—	5.17	2.17 <sup>e</sup>
<b>PTPA-AQ</b>	0.99	1.17	-0.74	-0.77	-1.53	5.49	3.50
<b>PTPA-OAQ</b>	0.83	1.02	-0.65	-0.76	-1.53	5.34	3.51

<sup>a</sup> From cyclic voltammograms *versus* Ag/AgCl in CH<sub>3</sub>CN.  $E_{1/2}$ : average potential of the redox couple peaks. <sup>b</sup> From cyclic voltammograms *versus* Ag/AgCl in DMF. <sup>c</sup> The HOMO energy levels were calculated from cyclic voltammetry and were referenced to ferrocene ( $E_{1/2} = 0.48$  V). <sup>d</sup> The LUMO energy levels were calculated from cyclic voltammetry and were referenced to ferrocene ( $E_{1/2} = 0.53$  V). <sup>e</sup> The LUMO energy levels were calculated from the HOMO-gap (3.00) by the equation:  $\text{gap} = 1240/\lambda_{\text{onset}}^{11}$

were also measured and are summarized in Table S1 (ESI<sup>†</sup>). The degree of polymerization of **PTPA-AQ** and **PTPA-OAQ** was determined to be, respectively, 8 and 6 as an oligomer. The electrochemical properties of these polymers were investigated by cyclic voltammetry (CV, Fig. S9, ESI<sup>†</sup>) and the results are summarized in Table 1. All the polymers exhibit one reversible oxidation redox couple while the lowest oxidation potential of **PTPA** could be attributed to the *para*-position substituted electron-donating methoxyl group. On the other hand, **PTPA-AQ** revealed the highest oxidation potential which resulted from the directly attached electron withdrawing AQ unit on the polymer backbone. These results indicate that the ether linkage in **PTPA-OAQ** can interdict the electron pathway and interrupt the CT between TPA to AQ units.

**PTPA-AQ** and **PTPA-OAQ** (Fig. S9, ESI<sup>†</sup>) both revealed two reversible reduce redox couples ( $E_{1/2}$  around  $-0.76$  V and  $-1.53$  V) corresponding to the redox reaction of AQ moieties. The possible resonance structures and charge delocalization at different reductive stages are shown in Scheme S3 (ESI<sup>†</sup>). The redox potentials of the polymers as well as their respective highest occupied molecular orbital (HOMO) and lowest unoccupied molecular orbital (LUMO) (*versus* vacuum) are calculated and summarized in Table 1.

The memory behaviors of **PTPA-AQ** and **PTPA-OAQ** were investigated based on the current–voltage ( $I$ – $V$ ) characteristics of an ITO/polymer/Al sandwich device as depicted in Fig. 2. The data stored by the memory device defined as the high- and low-conductivity are in response to the external applied voltage. In the case of **PTPA-AQ** (Fig. 2b), the as-fabricated device is initially in the OFF state (defined as “0” signal in digital) with



**Fig. 2** Current–voltage ( $I$ – $V$ ) characteristics of (a) ITO/**PTPA**/Al, (b) ITO/**PTPA-AQ**/Al, (c) ITO/**PTPA-OAQ**/Al memory devices, and (d) photoluminescence spectra of polymers.

the current around  $10^{-13}$  A as the voltage sweeps from 0 to  $-2.8$  V. When the applied voltage was increased to the switch-on voltage at  $-2.9$  V, an abrupt increase in the current could be observed, indicating the transition from the OFF state to the ON state (“1” signal in data storage). In a memory device, this OFF-to-ON transition can be defined as a “writing” process. The ON/OFF current ratio of the memory device is up to  $10^9$ , which could avoid the misreading in digital data storage applications. The device remained in the ON state during the subsequent negative scan (the second sweep) and then positive scan (the third sweep), indicating the reading process. After turning off the power for about 20 seconds, the device can be reprogrammed from the OFF state to the ON state again with a threshold voltage of  $-3.1$  V (the fourth sweep). Thus, the ON state could be relaxed to the OFF state without an erasing process but only removing the external applied bias. The short retention time of the ON state indicates that **PTPA-AQ** exhibits volatile DRAM memory behavior.

$I$ – $V$  curves of **PTPA-OAQ** are shown in Fig. 2c, and the retention time and writing–reading tests are depicted in Fig. S10 and S11 (ESI<sup>†</sup>), respectively. The device can be switched to the ON state with a sharp increase of the current in several orders of magnitude ( $\sim 10^9$ ) as the external applied voltage increased to its threshold voltage of  $-3.9$  V during the first negative sweep. The reading process of the device could be conducted by the subsequent negative (the second sweep) and positive scans (the third sweep), implying the non-erasable characteristic of the device. The fourth sweep with a switch-on voltage of  $-4.0$  V was measured after turning off the power for 6 minutes, revealing that the **PTPA-OAQ**-based memory device remained in the ON state for a longer time than **PTPA-AQ** after turning off the power. The longer retention time in the ON state yet volatile as well as the randomly accessible ON and OFF states is analogous to SRAM memory behavior.

In order to demonstrate the CT process of the polymers, the solid state photoluminescence (PL) spectra of **PTPA**, **PTPA-AQ** and **PTPA-OAQ** excited at the corresponding absorption  $\lambda_{\text{max}}$  were measured and are presented in Fig. 2d. When compared to **PTPA**, the fluorescence of **PTPA-AQ** and **PTPA-OAQ** were both

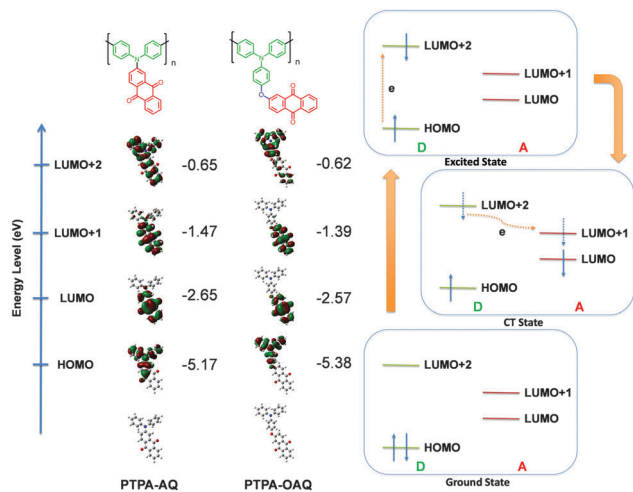


Fig. 3 Calculated molecular orbitals and corresponding energy levels of the basic units (BU) for **PTPA-AQ** and **PTPA-OAQ** (left) and electronic transition from the ground state to the CT state (right).

obviously quenched in intensity, indicating the strong CT from the TPA donor to the AQ acceptor. Thus, once the applied voltage overcomes the energy barrier, the generated carriers and charged moieties would consequently induce the CT phenomenon with a sharp increase in the current.

For gaining valuable insight to the memory behaviors of the polymeric devices, we calculated the molecular orbital and electric density contours of the basic units by molecular simulation. The electrostatic potential surface (ESP) of the basic unit, the most energetically favorable geometry, HOMO and LUMO energy levels of **PTPA-AQ** and **PTPA-OAQ** are depicted in Fig. 3. These two systems with analogous charge density distribution indicated that a similar CT pathway from the TPA donor to the pendent AQ acceptor could occur upon the stimulation of the external applied electrical field. As the applied potential reaches the switching-on voltage, electrons at the HOMO may accumulate energy then overcome the band gap and transit to the LUMO + 2 resulting in an excited state. On the other hand, electrons at the HOMO could also be excited to LUMO + 1 with a lower energy barrier. Therefore, charge transfer could be induced through several routes such as indirectly from the LUMO + 2 through intermediate LUMO + 1 and then to LUMO, or from the intermediate LUMO + 1 to LUMO, and even directly from the HOMO to the LUMO then form the conductive charge transfer complexes. However, during the intra- or intermolecular charge transfer induced by the applied electric field, the generating holes of conjugated TPA moieties could be delocalized to produce a conducting channel within the polymer chain that facilitates the migration of the charge carriers (holes). Therefore, the current increases rapidly and the memory device can be switched to the high conductivity state (ON state). The back charge transfer from the AQ (LUMO) moiety to TPA (HOMO) could occur easily due to the overlapping of these two ESP, resulting in a short life time of the high conductivity state of **PTPA-AQ** and the volatile DRAM behavior. In contrast, the **PTPA-OAQ** device exhibits a higher energy barrier for back CT as opposed to **PTPA-AQ** due to incorporation of the ether group between TPA and AQ units that effectively isolates the D–A system for depressing the

coplanarity, stabilizing the CT complex, and resulting in a longer retention time as SRAM behavior.

In summary, a series of thermally stable and electron-donating poly(triphenylamine)s with pendent electron acceptors have been successfully prepared and investigated systematically. The devices with a sandwich structure of ITO/**PTPA-AQ** or **PTPA-OAQ**/Al exhibited the volatile bistable electrical switching with very high ON/OFF current ratios of  $10^9$ . The **PTPA-OAQ**-based memory device revealed extended retention time in the ON state as opposed to **PTPA-AQ** due to the incorporation of an isolated ether group between the TPA donor and the pendent AQ acceptor. Our results demonstrate the feasibility of tailoring the memory device properties through a facile oxidative coupling reaction of TPA derivatives allowing fine-tuning of the energetics and CT process.

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