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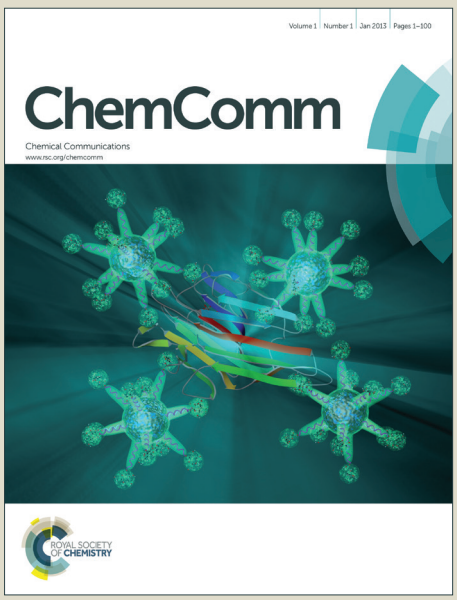

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Well-Defined Star-Shaped Donor-Acceptor Conjugated Molecules for Organic Resistive Memory Devices

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Solution processable star-shaped donor-acceptor (D-A) conjugated molecules (TPA-T-NI and TPA-3T-NI) with an electron-donating triphenylamine (TPA) core, three thienylene or terthienylene spacers, and three 1.8-naphthalimide (NI) electron-withdrawing end-groups are firstly explored as charge storage materials for resistor-type memories owing to the efficient electric charge transfer and trapping.

Resistive memory devices based on organic materials have attracted large research interests recently because of their advantages of light-weight, tunable electrical properties, and capability to fabricate flexible/stretchable electronics.[1-10] The electrical switching behaviors (i.e. resistance changes) are mainly controlled by the organic active materials in the two-terminated memory cell. Well-defined organic small molecules are one of the most promising candidates to be used as the active materials in resistor-type memory devices with the attractive merits of monodispersity, simple purification, and batch-to-batch reproducibility compared to polymeric materials.[11-18] Among various organic molecules in the research community, materials containing donor (D) and acceptor (A) moiety can create at least two different resistance states (i.e. the digital "0" and "1" states of memory bits) due to the D-A intra- and inter-molecular charge transfer. By adjusting the molecular coplanarity, D-A arrangement, spacer linkage, and strength of D or A groups, the electrical switching characteristics can be manipulated directly.

Star-shaped molecule possesses superior solution processability, which is related to its unique chemical architecture, compared to common linear-type materials, and is largely used in optoelectronic devices, such as field-effect transistors[19,20] and solar cells.[20-22] In this communication, star-shaped D-A conjugated molecules (TPA-T-NI and TPA-3T-NI), which consist of an electron-donating triphenylamine (TPA) core, three thienylene or terthienylene spacers, and three 1.8-naphthalimide (NI) electron-withdrawing end-groups, are explored for solution-processable non-volatile resistive memory (Fig. 1). The length of inserted thiophene spacer between TPA donor and NI acceptor can efficiently manage the polarity of such star-shaped molecules, controlling the strength of charge transfer/separation as well as the resistance/conductance switching property. Non-volatile write-once-read-many-times (WORM) memory characteristic with ON/OFF ratio of 10^5 is observed using TPA-3T-NI as active material. More important, this is the first achievement using single-layer star-shaped conjugated small molecules for resistor-type memory application, to the best of our knowledge.

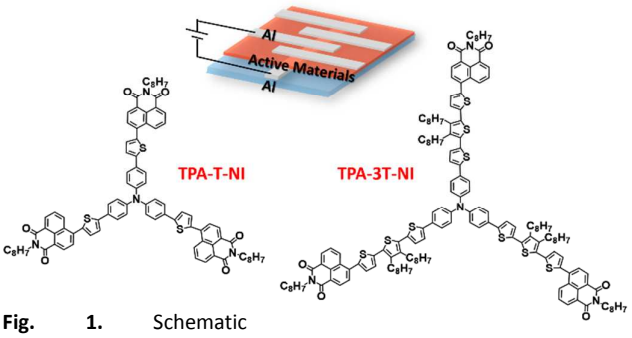

Fig. 1. Schematic illustration of cross-point resistive memory device architecture and chemical structure of the star-shaped D-A active materials.

The studied TPA-T-NI and TPA-3T-NI conjugated molecules possess good thermal stability (with a thermal decomposition temperature over 450 °C) and solubility (soluble in common organic solvents, such as chloroform and *o*-dichlorobenzene) with an optical band gap of approximately 2.2 eV.[20] The chemical structure-electrical switching property relationship is probed using a standard two-terminal resistive memory with cross bar array, which possesses a sandwich configuration of Al/star-shaped molecules/Al on the Si wafer substrate (see Fig. 1). Note that the cross-point memory device is integrated by the logical-organized cells on a joint square of 0.6×0.6 mm^2 with a single bit-line (utilized as the bottom

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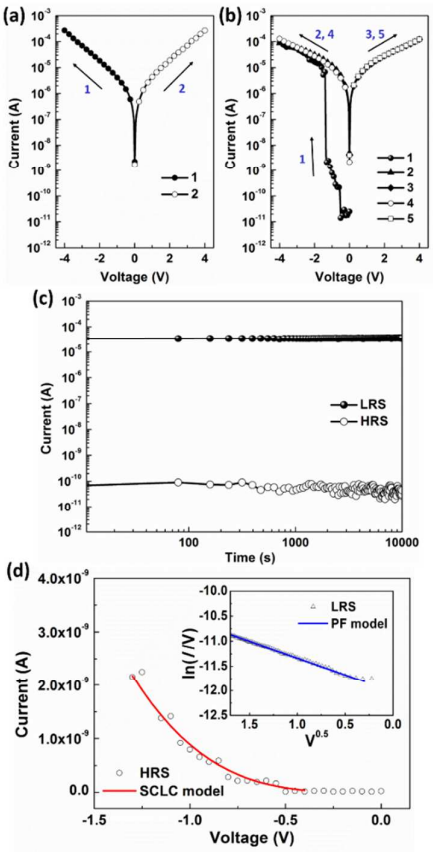

Fig. 2. Electrical *I-V* properties of (a) TPA-T-NI and (b) TPA-3T-NI memory device. (c) Retention endurance and (d) experimental and fitted *I-V* characteristics of TPA-3T-NI-based device in the HRS and LRS.

electrode) and several word-lines (utilized as the top electrode).[23] Accessing the particular memory cell in a square array, the electrical switching transition in the resistance states of the studied D-A materials is measured by applying a direct voltage sweep with the step of 0.05 V, and the voltage bias is applied to the top Al electrode while the bottom Al electrode is grounded. Fig. 2(a) exhibits the current-voltage (*I-V*) curves of TPA-T-NI-based memory cells under a nitrogen atmosphere at room temperature. The curves, however, are stabilized on a low resistance state (LRS; ON state) initially, indicating this device only shows conductor characteristics without any resistance switching phenomena under the positive (0 to 4 V) or negative (0 to -4 V) bias. As the number of thiophene spacer increased from 1 to 3, the star-shaped molecule, TPA-3T-NI, shows the complete *I-V* electrical switching characteristics through five voltage sequences (Fig. 2(b)): 0 to -4 V (sweep 1); 0 to -4 V (sweep 2, 4); 0 to 4 V (sweep 3, 5). The TPA-3T-NI memory cell is initially in the high resistance state (HRS; OFF state) with a current level in the range of 10^{-11}~10^{-9} A as the voltage swept progressively from 0 to -1.4 V. Then, the current switches from the HRS to the LRS abruptly as a threshold voltage is applied at approximately -1.4 V. Note that this operation used to drive HRS to LRS electrical transition is defined as the SET or writing process. Such device is maintained in the LRS for the subsequent negative sweep from 0 to -4 V (sweep 2) and the positive sweep from 0 to 4 V (sweep 3) with an ON/OFF current ratio of 10^5 at -1 V. The TPA-3T-NI-based resistive memory cannot switch back to the original HRS after turning off the power for at least 2 days or even applying a reverse bias (sweep 4 and 5), indicating a non-volatile WORM memory property. Fig. 2(c) exhibits the digital information retention behavior of the TPA-3T-NI-based memory device. The LRS and HRS are maintained for at least 10^4 s at a bias of -1 V, demonstrating that the TPA-3T-NI device has stable WORM characteristics with a high ON/OFF ratio of ~10^5 to distinguish each resistance states. The above electrical switching results explore that the TPA-3T-NI thin film possesses a unipolar WORM memory behavior, while TPA-T-NI only shows conductor characteristics without any resistance state changes. This indicates that the memory digital switching characteristics can be tuned by changing spacer length between donor and acceptor moiety in star-shaped conjugated molecules.

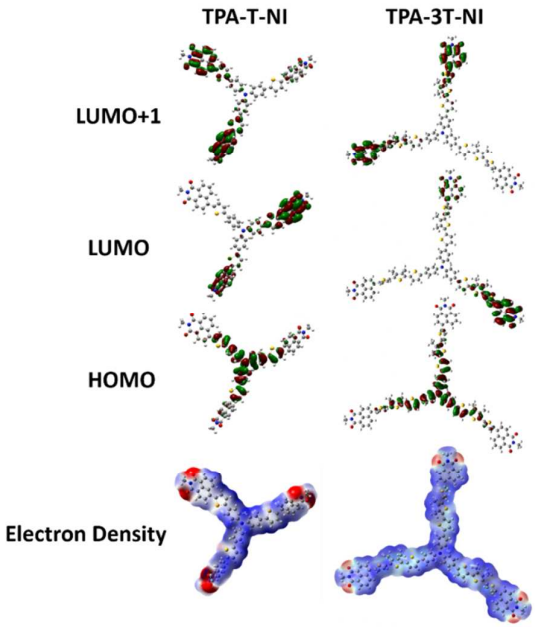

Fig. 3. Optimized chemical geometry, molecular orbitals, and electron density surface of TPA-T-NI and TPA-3T-NI.

Smooth surface was explored on the spin-coated TPA-T-NI and TPA-3T-NI thin film, with a surface roughness below 0.25 nm (see Fig. S1 in ESI†). This suggests that the resistance switching would not be dominated by filament conduction since there is no effective pathway for metal penetration in the uniform and crack-free active layer.[15-17] To elucidate the conduction mechanism of resistive switching in the memory device, the optimized molecular geometry and electronic properties are depicted in Figs. 3 and S2 (ESI†) through density functional theory simulation method.[24] It can be clearly observed that the highest occupied molecular orbital (HOMO) orbitals and lowest unoccupied molecular orbital (LUMO) orbitals are localized at the electron-donating groups (TPA and thiophene) and electron-withdrawing moiety (NI), respectively. The resistance switching mechanism of the studied D-A star-shaped molecules, therefore, can be explained by the electric field-induced charge transfer effect between the electron donors and acceptors.

Electrons can be transferred from the TPA core to the NI end groups under excitations with sufficient energy (i.e. applied voltage), then the charge transfer interaction gives rise to the charge separation state and the effective charge transport channel would be built up in the active layer with reduced charge mobile resistance.[16] In addition, the *I-V* characteristics of TPA-3T-NI-based device are theoretically fitted for both LRS and HRS in the negative voltage regions (Fig. 2(d)). In the HRS, the *I-V* curve in the logarithmic plots exhibit a linear line with the slopes of 4.1 and a critical point between two distinct *I-V* regions (HRS/LRS) is observed. It is worth noting that the slope larger than 2 indicates the switching behavior in the HRS is qualitatively interpreted to match by the trap-associated space-charge-limited-conduction (SCLC) model.[25] Typically, the charges are injected into the active layer of memory cell and captured by the trapping centers, attributed to the donor and acceptor moieties. The induced countering space charge near the electrode, indeed, limits the charge escape from the trapping site. Both donor and acceptor moieties can be served as trapping sites that depended on the polarity of electric field and charge association in our star-shaped molecule thin film. The TPA core and thiophene spacer (i.e. donors) are defined as nucleophilic centers (hole transporters/trapping sites) while the NI end group (i.e. acceptor) acts as an electrophilic center (electron transporter/trapping site). The electron density surface of the studied molecules (Fig. 3) is used to classify the electron distribution on the star-shaped material, and the electrons are mainly located on the NI electron-accepting end groups (red color), demonstrating such region can be acted as an electrophilic site to localize the electrons. In the LRS, the linear relationship is found in the plot of $\log(I\ V^{-1})$ versus $V^{0.5}$, which suggests that the trap-assisted Poole–Frenkel (PF) emission mechanism dominated the ON state. The occurrence of the PF emission is probably owing to the charge transport of the organic materials filled charge traps to form the trap-free junction.[13,14]

The charge trapping/detrapping environment and strength of D-A intramolecular charge transfer (ICT) interaction in the star-shaped molecules significantly affect the memory behaviors. Larger calculated dipole moment is found of TPA-T-NI (5.85 Debye) compared to TPA-3T-NI (2.33 Debye), which suggests a higher polarity as well as stronger ICT interaction in the molecule. Such big dipole moment difference may mainly be attributed to the length of thiophene spacer. Without the influence of conformational distortion of thiophene spacer, TPA-T-NI possesses an extremely efficient ICT process from TPA to the NI moieties and thus forms the channel current flow for the charge conduction. Hence, TPA-T-NI does not exhibit the bistability and resistance switching memory effects. On the contrary, the irreversible WORM-type memory behavior is observed in TPA-3T-NI because (1) the transferred electrons can be delocalized in the NI end group that provides a deep trapping barrier and stable charge transfer state and (2) the twisted conformation between terthienylene spacers can further stabilize the charge transfer and carrier trapping environment after turning off the power.[26] A quasi-permanent conductance in the LRS, as a result, is exhibited of TPA-3T-NI-based non-volatile device.

Compared star-shaped TPA-3T-NI to our previously reported linear-type D-A small molecule, TPA-NI-DCN, which consists of TPA donor and NI/dicyanovinylene (DCN) acceptors.[16] Both D-A materials show non-volatile WORM memory property due to the efficient ICT interaction and stable charge trapping in the conjugated molecules. The thin film fabricated from linear TPA-NI-DCN, however, could only be deposited using thermal evaporation. The star-shaped architecture design in this study successfully improves the solubility of D-A small molecules. Smoother thin film of TPA-3T-NI can be prepared, and more stable memory switching behavior (e.g. larger ON/OFF ratio) is probed. Furthermore, the memory characteristics can be tuned based on the length of spacers between TPA and NI moiety, indicating this D-A star molecular system can be acted as a potential candidate for high performance solution processable resistive memory device.

Herein, resistive memory based on star-shaped D-A conjugated molecules, TPA-T-NI and TPA-3T-NI, is firstly presented. The star-shaped architecture successfully improves the solution processability of the conjugated materials, and the D-A design provides efficient charge transfer and charge-separated state for digital information storage, as demonstrated by theoretical quantum calculation and physical models. Stronger polarity of TPA-T-NI leads to a conductor electrical characteristic while TPA-3T-NI exhibits non-volatile WORM switching behavior as the length of spacer is increased to three thiophene units. Specifically, the star-shaped D-A configuration is a promising material system for high performance resistive memory devices.

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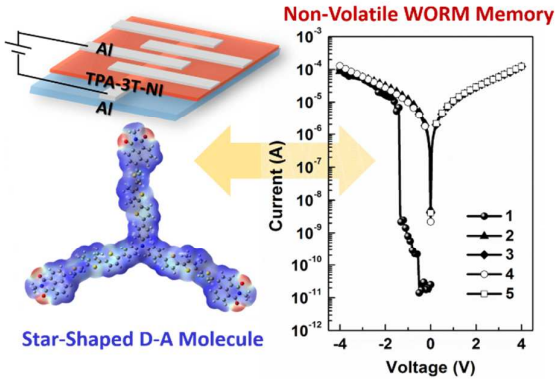

Graphical Abstract. Solution processable star-shaped donor-acceptor conjugated molecules are firstly explored as charge storage materials for high performance resistor-type memories with an electron-donating triphenylamine core, oligothiophene spacers, and three 1.8-naphthalimide electron-withdrawing end-groups.