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Comparison of Two Strategies to Improve Organic Ternary Memory Performance:

3-hexylthiophene Linkage and Fluorine Substitution

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Abstract

In this paper, two acceptor-donor-acceptor (A-D-A) type organic small molecules, 4,4'-(5,5'-(benzo[c][1,2,5]thiadiazole-4,7-diyl)bis(3-hexylthiophene-5,2-diyl))bis(N-(4-nitrophenyl)-N-phenylaniline) (NTPA₂TBT) and

4,4'-(5,6-difluorobenzo[c][1,2,5]thiadiazole-4,7-diyl)bis(N-(4-nitrophenyl)-N-phenylaniline) (NTPA₂BTF₂), were synthesized and fabricated into resistive random access memory devices. Compared with our previously reported molecule NTPA₂BT, NTPA₂TBT has 3-hexylthiophene linkages bridging its donor and acceptor, while there are two additional fluorine atoms in the benzothiadiazole moiety for NTPA₂BTF₂. Both the fabricated memory devices based on these two new molecules perform nonvolatile ternary memory characteristics with lower threshold voltages, higher reproducibility and better stability. The addition of 3-hexylthiophene bridges significantly promotes the planarity of the conjugation backbone and facilitates the molecular stacking, while

the substitution hydrogen by fluorine improves the intermolecular interaction, and thus also induces an ordered molecular stacking. The insertion of 3-hexylthiophene bridges or fluorine atoms could be an effective strategy of tailoring organic molecules to improve data storage performance with lower power consumption.

Keywords

Ternary memory; conjugated small molecules; 3-hexylthiophene group; fluorine atom; lower power consumption

1. Introduction

Recently, organic conjugated materials have received considerable attention for their potential applications in the field of solar cells [1-3], field effect transistors [4, 5], data-storage devices [6-9] and sensors [10]. Among them, small molecules were focused because of their tunable structures, low costs, simple processing routes and flexibility [11-14]. Especially, organic resistive random access memory (RRAM) has become one of the high-density information storage solutions due to its simple structure, capability of layer-by-layer stacking and fast reading/writing speed [15-18]. Moreover, RRAM devices based on small organic molecules can achieve multilevel conductive states per unit under external voltages by rational molecular design, leading to huge growth of information density compared to traditional binary memories [19-22].

In order to effectively improve RRAM device performance, researchers have explored a series of molecular engineering strategies, such as varying the types and numbers of electron acceptors and/or donors in the molecular backbone, tailoring the molecular conjugated length, and

modulating the length of side alkyl chain [23-26]. In our previous study, we demonstrated that inserting alkynyl group as conjugated linkers could enhance the memory performance [27]. Such an enhancement is attributable to the increase of intramolecular planarity, and in consequence the better intermolecular stacking and facilitation of charge transportation. However, considering that insertion of alkynyl can only be applied to limited categories of conjugated chains, it is necessary to explore more efficient molecular design strategies to further promote storage performance.

Herein, we performed a comparative study to demonstrate two new effective molecular design strategies: incorporation of thiophene ring as conjugation linkage or substitution of hydrogen by fluorine atom. On one hand, inserting thienyl linkage into the conjugated backbone can attenuate molecular torsion, facilitate the intermolecular π - π stacking, and thus optimize the device performance [28-30]. On the other hand, organic molecules containing fluorine atoms possess advantages of hydrophobicity, good solubility and film-forming ability [31-33]. Meanwhile, fluorine atoms usually have influence on inter- or intramolecular interactions. Particularly, it has been found that fluorine substitution on acceptor unit can ameliorate the efficiency of photovoltaic devices dramatically [34-36]. However, such strategy was scarcely reported in RRAM devices application [37].

We demonstrated these two strategies on the basis of our previous synthesized molecule NTPA₂BT with ternary memory performance [27]. Two new A-D-A type small organic conjugated molecules (NTPA₂TBT and NTPA₂BTF₂) were synthesized, respectively (Fig. 1). In NTPA₂TBT, 3-hexylthiophene were inserted between benzothiadiazole and TPA moieties. The hexyl group of thiophene was added to enhance the solubility of molecules. While in NTPA₂BTF₂, two hydrogen atoms of benzothiadiazole group were replaced by fluorine. Both the two new molecule based

devices show typical ternary WORM (Write-Once-Read-Many) memory behaviors. Compared with NTPA₂BT [27], both NTPA₂TBT and NTPA₂BTF₂ based devices exhibit superior ternary memory performance with lower average threshold voltages and higher reproducibility of tri-stable conductance states. However, the mechanisms for memory performance enhancement were distinct, as we discussed below.

2. Experimental section

2.1. Materials

3-hexylthiophene, tributylchlorostannane, triphenylamine, N-bromosuccinimide (NBS), $Cu(NO_3)_2 \cdot 3H_2O$, bis(pinacolato)diboron (B₂pin₂), 4,7-dibromobenzo[c][1,2,5]thiadiazole and 4,7-dibromo-5,6-difluorobenzo[c][1,2,5]thiadiazole were all purchased from commercial sources (Alfa Aesar, Aladdin, Tansoole and TCI). All other related reagents and solvents were used as received without further purification.

2.2. Synthesis and characterization

The synthesis and characterization of the two target molecules (NTPA₂TBT and NTPA₂BTF₂) are shown as following. While the complete synthetic procedures of the intermediates and final products are depicted in Fig. 2 (see the supplementary information for detailed experimental processes).

4,4'-(5,5'-(benzo[c][1,2,5]thiadiazole-4,7-diyl)bis(3-hexylthiophene-5,2-diyl))bis(N-(4-nitrophenyl)-N-phenylaniline) (NTPA₂TBT) [38]. A 100 mL three-neck round-bottom flask was filled with 4-nitro-N-phenyl-N-(4-(4,4,5,5-tetramethyl-1,3,2-dioxaborolan-2-yl)phenyl)aniline (1.2)

mmol, 0.5 g), 4,7-bis(5-bromo-4-hexylthiophen-2-yl)benzo[c][1,2,5]thiadiazole (0.5 mmol, 0.31 g), potassium carbonate (2.17 mmol, 0.3 g), toluene (20 mL), H₂O (20 mL) and ethanol (8 mL). Under N₂ protection, tetrakis (triphenylphosphine) palladium (0.04 mmol, 47 mg) was added to the mixture quickly. The reactants were refluxed at 70 °C for 24 h until water addition. The water phase was extracted with ethyl acetate and the organic phase was washed with water and brine. The extract was dried over sodium sulfate. Column chromatography on silica gel using dichloromethane-petroleum ether as eluent was used to purify the crude product. Purple solid **NTPA₂TBT** was obtained (0.29 g, 56%). ¹H-NMR (400 MHz, CDCl₃) δ (ppm): 8.10 – 8.07 (m, 4H), 8.03 (s, 2H), 7.87 (s, 2H), 7.51 (d, *J* = 8.6 Hz, 4H), 7.41 (t, *J* = 7.8 Hz, 4H), 7.24 (dd, *J* = 8.6, 1.8 Hz, 10H), 7.04 – 7.01 (m, 4H), 2.79 – 2.75 (m, 4H), 1.76 – 1.71 (m, 4H), 1.32 – 1.27 (m, 12H), 0.89 (d, *J* = 2.3 Hz, 6H).

4,4'-(5,6-difluorobenzo[c][1,2,5]thiadiazole-4,7-diyl)bis(N-(4-nitrophenyl)-N-phenylaniline)

(NTPA₂BTF₂) [38]. A 100 mL three-neck round-bottom flask was added with 4-nitro-N-phenyl-N-(4-(4,4,5,5-tetramethyl-1,3,2-dioxaborolan-2-yl)phenyl)aniline (1.2 mmol, 0.5 g), 4,7-dibromo-5,6-difluorobenzo[c][1,2,5]thiadiazole (0.5 mmol, 0.17 g), potassium carbonate (2.17 mmol, 0.3 g), toluene (20 mL), H₂O (20 mL) and ethanol (8 mL). Under N₂ protection, tetrakis (triphenylphosphine) palladium (0.04 mmol, 47 mg) was added quickly to the mixture. The reaction was refluxed at 70 °C for 24 h and then water was added. The water phase was extracted with ethyl acetate before the organic phase was washed with water and brine. The solvent was removed under reduced pressure after the extract dried over sodium sulfate. Purification was done by column chromatography on silica gel using dichloromethane-petroleum ether as eluent. Yellow solid NTPA₂BTF₂ was produced (0.20 g, 53%). ¹H-NMR (400 MHz,

DMSO) δ (ppm): 8.15 (d, *J* = 8.9 Hz, 4H), 7.90 (d, *J* = 8.0 Hz, 4H), 7.52 (t, *J* = 7.5 Hz, 4H), 7.44 (d, *J* = 8.2 Hz, 4H), 7.34 (d, *J* = 7.7 Hz, 6H), 6.99 (d, *J* = 8.9 Hz, 4H).

2.3. Fabrication of the memory devices

Indium-tin-oxide (ITO)-coated glass substrates were ultrasonicated in water for 20 min firstly. Then they were pre-cleaned with detergent water and ultrasonicated in water, acetone, and ethanol for 20 min sequentially. NTPA₂TBT and NTPA₂BTF₂ were dissolved in chlorobenzene at a concentration of 10 mg mL⁻¹ respectively and the solutions were ultrasonicated for complete dissolution. Then the solutions were filtered through syringe filter (pore size: $0.22 \ \mu$ m). The obtained filtrates were spin-coated onto each ITO-coated glass substrate at a speed of 380 RPM (revolutions per minute) for 9 s, followed with 1700 RPM for 20 s. After the substrates were placed into an evaporation chamber which was then pumped to a 1.0×10^{-6} Torr vacuum environment, the top aluminum (Al) electrodes of about 100 nm in thickness were thermally evaporated and deposited onto the active organic layer through a shadow mask. The active area of each memory device cell was 0.0314 mm².

2.4. Measurements and general methods

An Inova 400 MHz FT-NMR spectrometer unless otherwise noted was used to obtain all NMR spectra in chloroform-*d* or dimethylsulfoxide-d6 containing 0.03% TMS as an internal reference. UV-Vis absorption spectra were studied at room temperature with a Shimadzu UV-3600 spectrophotometer. Under the assistance of a reference electrode Ag/AgCl, a Pt wire counter electrode and an ITO working electrode, a CorrTest CS Electrochemical Workstation analyzer at a

100 mV/s sweeping rate collected the cyclic voltammograms of the solution of 0.1 mol/L tetrabutylammonium hexafluorophosphate (TBAPF₆) in anhydrous acetonitrile. A Shimadzu XRD-6000 spectrometer determined X-ray diffraction patterns with a Cu KR monochromatic radiation source at 40 kV and 30 mA. Atomic force microscopy (AFM) measurement was used to record the surface morphology of the spin-coated thin films with a MFP-3DTM (Digital Instruments/Asylum Research) AFM instrument. An HP 4145B semiconductor parameter analyzer was employed to perform the current-voltage (I-V) measurements of the organic memory devices (OMDs) under ambient conditions. Molecular simulations were conducted with the density functional theory (DFT) on the level of GGA-BLYP-DNP using DMol³ code [39]. Scanning Electronic Microscopy (SEM) images were investigated on a Hitachi S-4700 scanning electron microscope.

3. Results

3.1. Optical and electrochemical properties

First, we demonstrate that the two molecules are of intramolecular charge transfer, faciliating the memory switching as previously reported [27]. The UV-visible absorption spectra of the two molecules NTPA₂TBT and NTPA₂BTF₂ were collected in dilute dichloromethane solution and in thin film state on quartz substrates as shown in Fig. 3a and 3b. The high-energy absorption bands around 300 nm can be attributed to an intramolecular charge transfer (ICT) process mainly from triphenylamine (TPA) skeleton to two nitro groups [27, 40]. While the peak in the region of 400-500 nm is associated with a $\pi \rightarrow \pi^*$ transition with a minor part of ICT from the conjugated backbones to the benzothiadiazole core [27, 41]. It is obvious that the CT transition of thin film

shows a red-shift compared to that of the solution state, possibly resulting from the formation of molecular aggregates and/or increased polarity of the thin film [41, 42]. For NTPA₂TBT, the absorption edge of the films is 615 nm while it is 518 nm for NTPA₂BTF₂. Correspondingly, the optical band gaps of the two molecules are 2.02 and 2.39 eV, respectively.

Fig. 3c and 3d show the cyclic voltammograms demonstrating the electrochemical properties of the two molecules. For calibration, the absolute redox potential of ferrocene/ferrocenium (F_c/F_c^+) is supposed to be -4.80 eV to vacuum, while under the identical condition, the external F_c/F_c^+ redox standard potential is tested to be 0.426 eV vs. Ag/AgCl. The onset oxidation potentials (E_{ox}^{onset}) are 0.92 and 1.13 eV vs. Ag/AgCl for NTPA₂TBT and NTPA₂BTF₂ respectively. While the onset reduction potentials (E_{red}^{onset}) are -0.89 and -0.92 eV, respectively. The highest occupied molecular orbital (HOMO) and lowest unoccupied molecular orbital (LUMO) values are calculated according to the following equations: $E_{HOMO} = -[E_{ox}^{onset} + 4.8 - E_{ferrocene}^{1/2}]$ (eV), $E_{LUMO} = -[E_{red}^{onset} + 4.8 - E_{ferrocene}^{1/2}]$ (eV) [43, 44], in which E_{ox}^{onset} is the onset potential of the oxidation process and E_{red}^{onset} is the onset potential of the reduction process. Therefore, as shown in Table 1, the HOMO are calculated to be -5.29 and -5.50 eV, while the LUMO are determined to be -3.48 and -3.45 eV, respectively. For the two molecule-based memory devices, hole injection energy barriers between the work functions of ITO (-4.8 eV) and HOMO of the active layer are found to be 0.49 and 0.70 eV, respectively. While electron injection energy barriers between the work functions of Al (-4.3 eV) and LUMO of the active layer are estimated to be 0.82 and 0.85 eV. As shown in Fig. 4, an energy level diagram was drawn. Compared with the work function of Al to the LUMO energy levels, the work function of ITO is more approaching to the HOMO energy levels of both molecules. Obviously, hole injection from ITO into the HOMO

level is more convenient than electron injection from Al into the LUMO level, thus hole injection will have priority in the charge conduction process [45-47]. On one hand, the low HOMO levels are favorable to make memory devices stable against oxygen oxidation; on the other hand, it is advantageous for the hole transfer from the ITO electrode [48].

3.2. Film crystallinity and morphology

It has been widely reported that the crystallinity of the active materials has influence on the performances of organic electro-resistive memories, such as the device yield and onset voltages [17, 27]. Therefore, X-ray diffraction (XRD) was conducted to investigate the molecular stacking of the two molecules in thin films (ca. 100 nm thickness). Fig. 5 shows the conspicuous diffraction peaks of both thin films, indicating stacking ordering in the solid states. NTPA2TBT exhibits a primary diffraction peak at $2\theta = 6.27^{\circ}$, corresponding to an interlayer spacing of 14.1 Å, which is smaller than that of NTPA₂BT (14.6 Å) [27, 49]. Another diffraction peak appears at $2\theta = 20.41^{\circ}$ (d = 4.3 Å), which likely corresponds to the third order Bragg reflection [50]. For NTPA₂BTF₂, the XRD pattern shows a sharp peak at $2\theta = 8.20^\circ$, which can be attributed to the interlayer spacing peak. The corresponding value d = 10.8 Å is also smaller than that of NTPA₂BT (14.6 Å) [27]. Another two diffraction peaks are observed at $2\theta = 16.45^{\circ}$ (d = 5.4 Å) and 24.78° (d = 3.6 Å). The value d = 5.4 Å is half of d = 10.8 Å, and d = 3.6 Å is exactly one third of d = 10.8 Å. This manifests that NTPA₂BTF₂ based thin films form a more ordered layer-by-layer lamellar packing than NTPA₂BT [27, 51], which is beneficial for achieving highly efficient charge transport and hence better memory properties [17, 42, 52]. Furthermore, the intensity of diffraction peaks for NTPA₂BTF₂ steeply increase, indicating an enhanced degree of crystallinity, which may be

attributed to the promoted intermolecular stacking and the potential intra- and/or intermolecular interactions (e.g., C-H···F interaction) originated from fluorine atoms [53-55].

The morphology surfaces of NTPA₂TBT and NTPA₂BTF₂ films were investigated by atomic force microscopy (AFM) as shown in Fig. 6. As both the NTPA₂TBT and NTPA₂BTF₂ thin films display even height images, they have smooth morphologies and thus good film-forming processability for device fabrication, which are comparable with that of NTPA₂BT ($R_{RMS} = 0.356$ nm) [27]. For NTPA₂TBT, the thin film exhibits a granular-like surface with the root-mean-square roughness (R_{RMS}) of 0.451 nm (Fig. 6a). While NTPA₂BTF₂ shows fibril-like structure with R_{RMS} = 0.332 nm (Fig. 6b). The densely-packed crystallinity and low roughness could lead to form highly efficient pathways for charge carrier transport [39, 56].

3.3. Current-voltage (I-V) characteristics of the memory devices

I-V measurements on ITO/molecule/AI sandwich-structured devices reveal the memory effects of these two molecules as shown in Fig. 7. Originally, all devices stay in a low-conductivity (OFF or "0") state. When one of the cells of the device is swept by a negative voltage from 0 to -4.0 V (Sweep 1), two sharp jumps of the current occur at two threshold voltages, indicating electrical transitions of the cell from the low-conductivity (OFF or "0") state to an intermediate-conductivity (ON1 or "1") state and finally to the high-conductivity (ON2 or "2") state. The "0"-"1" and "1"-"2" transitions can be regarded as the "writing" process for practical memory storage [6, 57]. The following scan from 0 to -4.0 V (Sweep 2) or to 4.0 V (Sweep 3) suggests that the high-conductivity (ON2) state is maintained even after the power supply is removed. As a negative voltage sweeps from 0 to -2.5 V, there is only the transition from OFF state to the ON1

state achieved (Sweep 4). Subsequent sweep from 0 to -2.5 V on the same cell shows that the memory cell stays in the ON1 state (Sweep 5). If a voltage sweep from 0 to 2.5 V is applied, the cell exhibits in an intermediate-conductivity state (Sweep 6). Then, during the 0 to -4.0 V voltage sweep, the cell goes through the ON1-to-ON2 transition (Sweep 7) and remains in the high-conductivity state when the subsequent same voltage is swept (Sweep 8). When positive voltage from 0 to 4.0 V is applied, the cell still retains in the ON2 state (Sweep 9). Thus, both devices based on the two molecules exhibit typical nonvolatile ternary WORM (Write-Once-Read-Many) memory behavior.

3.4. Comparison of memory performances

The molecular arrangements can greatly influence the reproducibility of the switching phenomena, which is a significant parameter to evaluate the applicability of devices for practical use [56, 58]. In order to investigate the reproducibility of ternary behavior, statistical analysis on totally 100 memory cells for each molecule was developed. Table 2 shows that there are 43 out of 100 cells performing electrical ternary behavior (43% yield) for NTPA₂TBT, while the possibility of ternary switching for NTPA₂BTF₂ based device is 44% yield (44 out of 100 cells), which are both higher than that of NTPA₂BT (38% yield). Hence, introducing 3-hexylthiophene bridge or fluorine atom can be effective and encouraged to improve the device yield though current ratio of ternary memory is still low. Moreover, compared with NTPA₂BT, the average ON1 and ON2 threshold voltages of NTPA₂TBT based device (-1.87 and -2.53 V) and NTPA₂BTF₂ based device (-1.76 and -2.58 V) are both lower than those of NTPA₂BT (-2.04 and -2.69 V), as seen in Table 2, which could contribute to lowering the power consumption [41, 59].

4. Discussion

4.1. Proposed storage mechanism

Here, "charge trapping" mechanism which has successfully guided our design of organic molecules to perform ternary memory behaviors is proposed to explain the storage properties [6, 20]. As shown in Fig. 8, for NTPA₂TBT and NTPA₂BTF₂, the calculated HOMO molecular orbitals are mainly localized at the donor side (the triphenylamine moiety), while the LUMOs are mostly localized at the acceptor sides. This suggests that there is intramolecular charge transfer during migration from HOMO to LUMO. In addition, the electrostatic potential (ESP) of the two molecules is also calculated. As shown in Fig. 8, the continuous positive ESP regions of the molecular surface (in red and white) indicate that charge carriers can smoothly transfer throughout the open channels of conjugated backbone. However, the negative ESP regions (in blue) can serve as "charge traps" with distinct depths to block the migration of charge carriers, which are functioned by the electron-deficient groups, such as benzothiadiazole and nitro groups [20, 60]. When there remains a low negative bias, as there is no enough energy for charge carriers to overcome the injection barriers, the device stays in the OFF state [17]. Once an external voltage is applied, because the "charge traps" depth is in accordance with the electron-withdrawing strength of the acceptors, the shallower charge traps caused by the benzothiadiazole moieties will be firstly fully filled, leading to the current transition from the OFF to ON1 state [61, 62]. As external voltage continues to increase, the deeper charge traps from the nitro fragments are fully filled later, realizing the current switching from the ON1 to ON2 state [15]. When the power is turned off or under reverse bias, the separated-charges could not be de-trapped, as the trapped charges can form

a stable charge-separated state due to the intramolecular charge transfer process [62, 63]. Thus, the high-conductivity state can maintain for a long time (Fig. S6) [15]. Therefore, both devices exhibit typical nonvolatile multilevel WORM memory performance.

4.2. The effect of 3-hexylthiophene and fluorine atom

By comparing molecules NTPA₂BT and NTPA₂TBT, their discrepancies on average threshold voltages and ternary memory device yield suggest that 3-hexylthiophene bridges make a contribution to tuning the device performance. From cyclic voltammograms data, it is apparent that the hole injection barriers for NTPA₂TBT (0.49 eV) are lower than that for NTPA₂BT (0.63 eV) [27], partially contributing to the lower threshold voltages of NTPA₂TBT based device [51, 64]. Moreover, the optimized geometry of NTPA₂TBT as shown in Fig. 8 indicates that the torsion angle of benzothiadiazole and triphenylamine groups is about 8° whereas that of NTPA₂BT is 35° [27]. Thus the introduction of 3-hexylthiophene bridges greatly decreases the steric repulsion between these two groups. A better planarity could effectively extend the conjugation length, enhance the conjugation degree, and thus facilitate the charge transport within the molecule. Moreover, the increased planarity can contribute to the intermolecular stacking in thin film as confirmed by the XRD pattern in Fig. 5a. These parameters are beneficial for improving the memory device performance of lower threshold voltages and more reliable reproducibility [65, 66].

Similarly, fluorine atoms substitution also tunes the device performance such as decreasing the average threshold voltages and improving ternary memory yield. However, the role of fluorine is different from that of 3-hexylthiophene. The geometries of NTPA₂BT and NTPA₂BTF₂ molecules

are almost the same and the introduction of fluorine atoms does not increase the steric repulsion between benzothiadiazole group and triphenylamine as revealed from the dihedral angle between benzothiadiazole and TPA planes. However, in the view of molecular stacking, as shown in our XRD pattern, NTPA₂BTF₂ appears in denser intermolecular packing and better crystallinity in thin film than NTPA₂BT, which facilitate the charge transfer [17, 27, 42, 52]. This could be attributed to the highly ordered intermolecular stacking benefiting from the C-H…F interactions [54]. Hence, lower threshold voltages for electrical switching can be achieved due to closer intermolecular stacking, and thus the ternary memory yield is also improved. When the crystallinity is particularly focused on, like in the case of organic electronic field [67], fluorine incorporation is recommended.

5. Conclusion

In summary, two conjugated organic molecules (NTPA₂TBT and NTPA₂BTF₂) were designed and fabricated as the active layer of sandwich-structured RRAM devices. Both molecules contain the same electron-withdrawing (benzothiadiazole and nitro groups) and electron-donating (TPA fragment) moieties. The NTPA₂TBT and NTPA₂BTF₂-based devices are of the lower switching voltages and higher ternary yield than that of NTPA₂BT. On one hand, the addition of 3-hexylthiophene bridges significantly promotes the planarity of the conjugation backbone and facilitates the molecular stacking. On the other hand, the insertion of fluorine atoms also enhances the film crystallinity, and thus induces an ordered molecular stacking. Our results show that both insertion of 3-hexylthiophene bridges or substitution by fluorine atoms are effective strategies in designing conjugated organic molecules to achieve superior organic memory performances.

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Appendix A. Supplementary data

Supplementary data related to this article can be found at

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Fig. 1 Sandwiched ITO/small molecule/Al memory device based on molecule NTPA2BT,

NTPA₂TBT or NTPA₂BTF₂.



Fig. 2 Synthetic route of NTPA₂TBT and NTPA₂BTF₂.



Fig. 3 UV-vis absorption spectra of (a) NTPA₂TBT and (b) NTPA₂BTF₂ in dilute DCM solution and thin film on quartz substrate. Cyclic voltammograms in 0.1 M TBAP/ acetonitrile solution of (c) NTPA₂TBT and (d) NTPA₂BTF₂ in thin film on ITO-coated substrate.



Fig. 4 Energy level diagram for the ITO/ NTPA2BT, NTPA2TBT and NTPA2BTF2/Al memory

devices [27].

Molecule	$E_{\rm ox}({\rm onset})^a$	$E_{red}(onset)^b$	HOMO ^c	LUMO ^d	Injection Barrier
	(eV)	(eV)	(eV)	(eV)	Hole ^{e} (eV) Electron ^{f} (eV)
NTPA ₂ TBT	0.92	-0.89	-5.29	-3.48	0.49 0.82
NTPA ₂ BTF ₂	1.13	-0.92	-5.50	-3.45	0.70 0.85

Table 1. Electrochemical properties of NTPA2TBT and NTPA2BTF2 films

^{*a*,*b*} Vs. Ag/AgCl. ^{*c*} Determined by the onset of the oxidation peak of cyclic voltammograms. ^{*d*} Determined by the onset of the reduction peak of cyclic voltammograms. ^{*e*} The difference between the work functions of ITO and the HOMO energy level. ^{*f*} The difference between the work functions of Al and the LUMO energy level.



Fig. 5 XRD patterns of (a) NTPA₂TBT and (b) NTPA₂BTF₂ films as-spun on ITO substrates.



Fig. 6 AFM topography images of (a) NTPA₂TBT and (b) NTPA₂BTF₂ thin films spin-coated on

ITO substrates. The scan size of both images is 2 μ m \times 2 μ m.



ITO/NTPA2BTF2/A1.

Table 2. Statistic results of the three molecules-based memory devices

Molecule	proportion of	proportion of	ON1 threshold	ON2 threshold
	binary behavior ^a	ternary behavior ^b	voltage ^{c} (V)	voltage d (V)
NTPA ₂ BT ^e	62%	38%	-2.04	-2.69
NTPA ₂ TBT	57%	43%	-1.87	-2.53

ACCED	TED		TTIC	ODIDT	
ACCEP	TED	MAN	JUS	CKIPT	

$NTPA_2BTF_2$	56%	44%	-1.76	-2.58

^{*a, b*} Measured from totally 100 cells for each molecule-based memory device. ^{*c, d*} Average values calculated from the cells of ternary behaviors for each type of device. ^{*e*} Data for NTPA₂BT from reference [27].

Molecule	Molecular conformation	ESP	номо	LUMO
NTPA₂TBT	θ=8°		- Andrew Contractor	
NTPA ₂ BTF ₂			See Gee S	

Fig. 8 Molecular simulation results of NTPA2TBT and NTPA2BTF2: molecular conformation,

ESP, and HOMO and LUMO molecular orbitals (isovalue = 0.03 e/Å^3).

- Two novel A-D-A type small organic conjugated molecules are synthesized.
- The incorporation of 3-hexylthiophene group greatly decreases the steric repulsion.
- The substitution of fluorine atom enhances crystallinity and molecular stacking.
- Both the fabricated devices show better nonvolatile ternary WORM memory behaviors.
- Both the two devices have higher ternary yield and lower threshold voltages.