CHEMISTRY AN ASIAN JOURNAL

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Accepted Article

Title: Upgrading Electroresistive Memory from Binary to Ternary Through Single Atom Substitution in Molecular Design

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To be cited as: Chem. Asian J. 10.1002/asia.201601317

Link to VoR: http://dx.doi.org/10.1002/asia.201601317

A Journal of

ACES Asian Chemical Editorial Society A sister journal of Angewandte Chemie and Chemistry – A European Journal

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Upgrading Electroresistive Memory from Binary to Ternary Through Single Atom Substitution in Molecular Design

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Abstract: In this paper, two molecules based on urea and thiourea only differing by a single atom were designed, successfully synthesized and fabricated into resistive random access memory devices (RRAM). Urea-based molecule shows binary WORM storage behavior while thiourea-based molecule demonstrates ternary storage behavior. The atomic force microscopy (AFM) and Xray diffraction (XRD) patterns show that both two molecules have smooth morphology and ordered layer-by-layer lamellar packing, which is be beneficial to charge transportation and in consequence device performance. Meanwhile the optical and electrochemical properties indicate that thiourea-based molecule has lower band-gap and is feasible to be polarized by trapped charges, thus the formation continuous conductive channel and the electric switching occurs under lower bias voltage, result in ternary WORM behavior. This study, together with our previous single atom substitution work, may be useful to tune and improve the device performance in future design of organic memories.

Introduction

With rapid development of modern information technology, the society has already entered into an information explosion time. The traditional optical and magnet storage technology have almost been reaching downscaling limits¹ while they still cannot satisfy the increasing demands for high density data storage. Under this circumstance, resistive random access memory (RRAM)² has received widely attention as one of the most promising candidates for the next generation of high-density storage solution. Of a metal/insulator (or semiconductor)/metal configuration, RRAM is a type of resistive memory with simple structures, layer-by-layer stack capability, low power consumption and capability to store multilevel conductive state. Once RRAMs store more than two states in each cell, the information will increase from 2ⁿ to Xⁿ (X is the state number of each cell) under the original cell density. This dramatic increase of the information density will hopefully solve the high density memory problem. Among the potential materials which could demonstrate resistive memory behavior, organic molecules perform better than others because of low cost, flexibility, easy purification and tunable structures.³

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 Supporting information for this article is given via a link at the end of the document Intensive studies were carried out to investigate the mechanism of the RRAM storage behaviors through tuning the molecular structure. The knowledge obtained could be used to further guide the optimization of memory performance. Zhang et al. changed the conjugated groups in the molecular backbone to adjust the threshold voltages of the devices.⁴ Kang and coworkers obtained different types of memory behavior through substitution of terminal groups.⁵ Chen's group used different bridging bonds to adjusting the planarity of the molecular plane and successfully optimized the memory performance.⁶ However, in the above molecular tuning studies, an intrinsically methodological flaw exists: in most of these work, the structural change of molecule was too large, causing many electronic (donor-acceptor numbers, HOMO-LUMO levels, and gaps), geometric (planarity and conjugation length) and intermolecular (stacking manner and strength) properties simultaneously. These complex variations will cause unnecessary confusion when correlating single structural effect with macroscopic device performances. In this term, substituting the target molecule by a single heteroatom, which only causes infinitesimal change to molecular structure, is a rigorous way to study the structureperformance relationship in RRAMs. Indeed, recently our group successfully applied this single heteroatom substitution method to decrease the threshold voltages⁷ and switch the storage type from DRAM to SRAM⁸. The mechanisms behind these are also studied in depth, thanks to the simple structural variation. However, switching the memory level through single atom substation, for example, from binary to ternary, remains challenging but very interesting.

In this paper, we designed urea and thiourea based molecules TFMCU and TFMCT (**Figure 1**), which only differ by one atom (O versus S). We fabricate organic memory device using these two molecules and successfully tune the devices from binary to ternary memory behavior because of the easy polarizable of sulfur atom and low band-gap of molecule TFMCT. This study, together with our previous single atom substitution work, may be useful to tune and improve the device performance in future design of organic memories.

Results and Discussion

Synthesize and Characterization

TFMCU and TFMCT were successfully synthesized according to **Scheme 1**. Through thermogravimetric analysis (TGA), TFMCU and TFMCT were found exhibiting good thermal stability with decomposition temperature (5% weight-loss) to be about 198 °C and 230 °C, respectively (Supporting Information, **Figure S1**).

10.1002/asia.201601317

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Figure 1. (a) Molecular structures of TFMCU and TFMCT. (b) Scheme of the





 $TBAP/CH_2Cl_2$ solution of (c) TFMCU and (d) TFMCT in thin film on ITO-coated substrate at a sweep rate of 100 mV/s. The insert shows the CV curve of the ferrocene standard swept in the same condition.

	λ_{onset}	TFMŒŢ ^{a)}	HOMO ^{b)}	LUMO ^{c)}	Hole injection ^{d)}	Electron injection ^{e)}
	(nm)	(eV)	(eV)	(eV)	(eV)	(eV)
FMCU	302	4.11	-5.74	-1.63	0.94	2.67
FMCT	345	3.59	-5.78	-2.19	0.98	2.11

a) Estimated from the onset of UV-vis absorption: $E_g = 1240/\lambda_{onset}$; b) HOMO = -[$E^{onset}_{OX} + 4.8 - E_{Ferrocence}$]; c) LUMO = HOMO + E_g ; d) The difference between the work function of ITO and the HOMO level of molecule; e) The difference between the LUMO level of molecule and the work function of AI.

ITO/organic layer/memory device.

Scheme 1. Synthetic routes of TFMCU and TFMCT.

Optical and electrical properties

To understand the optoelectronic properties of the two molecules, UV-vis spectra of their films and solution were recorded. As shown in Figure 2 (a) and (b), the absorption peaks at 280 nm and 290 nm for TFMCU and TFMCT were caused by the $\pi\text{-}\pi^*$ transition of urea and thiourea group. For both TFMCU and TFMCT, compared with that in solution state, the absorption peaks in film state become wider significantly, and the peaks have 2 nm bathochromic-shift. These broadened and red-shift of absorption peaks might be associated with the accumulation of the molecules in the film state, orderly π - π stacking or formation of molecular aggregation and increased polarizability of the film, which will contribute to the improving of the charge carrier mobility in the film⁹. From the UV-visible spectra, λ_{onset} of TFMCU and TFMCT were 302 and 345 nm, and the corresponding bandgap are 4.11 eV and 3.59 eV according to the equation bandgap = $1240 / \lambda_{onset}$, respectively.

Figure 2. UV-vis spectra of (a) TFMCU and (b) TFMCT in dilute CH_2CI_2 solution and in the film on quartz substrates. Cyclic voltammograms in 0.1 M

The electrical properties of TFMCU and TFMCT were characterized by cyclic voltammetry (CV) in 0.1 mol/L tetrabutylammonium hexafluorophosphate dried dichloromethane solution. In Figure 2 (c) and (d), the onset oxidation potentials of TFMCU and TFMCT are 1.35 eV and 1.39 eV. Assuming the absolute redox potential of ferrocene/ferrocenium is -4.8 eV to vacuum. The external ferrocene/ferrocenium redox standard potential measured under the identical condition is 0.41 eV. The energy of the highest occupied molecular orbital (HOMO) and the lowest unoccupied molecular orbital (LUMO) were obtained from the equation HOMO = - [E_{onset}^{OX} + 4.8 - E_{Ferrocence}] and LUMO = HOMO + $E_{g}.^{10}$ As shown in Table 1, the energy of HOMO and LUMO for TFMCU and TFMCT are -5.74 eV, -1.63 eV, -5.78 eV and -2.19 eV, respectively. There are two basic transportation model of the charged species. One is hole injection model, the other one is electron injection model. The hole injection barriers of TFMCU and TFMCT are 0.94 eV and 0.98 eV while the electron injection barriers of TFMCU and TFMCT are found to be 2.67 eV and 2.11 eV. Since the hole injection barriers are smaller than the electron injection barriers for TFMCU and TFMCT, the hole injection is the dominant charge transportation model in the devices and both TFMCU and TFMCT are p-type materials.

 Table 1. Optical and electrochemical properties of the films fabricated with TFMCU and TFMCT

 Morphology and accumulation of the film

In order to explore the molecular stacking in the active layer, we investigated the X-ray diffraction patterns of the deposited film. In Figure 3, three diffraction peaks appear at $2\theta = 9.1^{\circ}$, 13.1° and 18.3° in TFMCU-fabricated film, corresponding to the spacing of 9.7 Å, 6.8 Å and 4.8 Å, respectively. For TFMCT film, diffraction peaks at $2\theta = 8.7^{\circ}$, 13.8° and 17.5° , were observed, indicating ordered stacking with spacing of 10.2 Å, 6.4 Å and 5.1 Å. The primary diffraction peaks of these two molecules can be contributed to the interlayer spacing.11 In TFMCU film, 9.7 Å is approximately twice as 4.8 Å while in TFMCT film, 10.2 Å is a doublet of 5.1 Å. These relationships indicate that both TFMCU and TFMCT molecules form ordered layer-by-layer lamellar packing in the film state while 9.7 Å and 10.2 Å are probably the interlayer distances. This ordered layered stacking was widely reported in both organic memory or solar cells devices, and such construction is beneficial to charge transportation and in consequence device performance.^{9d, 12}

The surface roughness was characterized by atomic force microscopy (AFM), as shown in **Figure 4**. The root-mean-square roughness (RMS) of the films fabricated by TFMCU and TFMCT are 1.59 nm and 2.22 nm, which indicate both films have smooth morphology. TFMCU film has smoother surface and denser accumulation, which are helpful to construct highly efficient charge carrier transmission channel and improve device performance.



Figure 3. X-ray diffraction patterns of TFMCU and TFMCT in evaporated films.



Figure 4. a, b) Tapping-mode (2 μ m × 2 μ m) AFM topography and typical cross-section profile of AFM topography images of TFMCU and TFMCT, respectively.

Current–voltage (I–V) characteristics





device.

Figure 5 shows the current-voltage (I-V) characteristics of ITO/TFMCU or TFMCT/AI sandwich structure devices. For TFMCU, the device initially located at a low conductive state (OFF state). When a voltage sweeps from 0 to -5 V (Sweep 1), an abrupt jump occurred at -3.95 V from OFF state (10⁻⁷ A) to high conductive state (ON state, 10⁻² A). This kind of transformation from the low to high conductive state can be regarded as the "writing" process in memory devices. Such an ON state could be sustained when a negative (Sweep 2, 0 to -5 V) or positive sweeps (Sweep 3, 0 to 5 V). This means the reverse voltage cannot "erase" the data that had been stored. The ITO/TFMCU/AI devices show typical nonvolatile binary property (WORM) with a threshold voltage of -3.95 V and an ON/OFF ratio as high as 10⁵. While for ITO/TFMCT/AI device, the device initially located at a low conductive state (OFF state) as well. When a voltage sweeps from 0 to -5 V (Sweep 1), two significant jump showed at -2.75 V and -4.30 V from OFF state (10⁻⁹ A) to intermediate conductive state (ON1 state, 10⁻⁶ A) and finally jumped to high conductive state (ON2 state, 10⁻² A). Such an ON2 state could be maintained when a negative (Sweep 2, 0 to -5 V) or positive sweeps (Sweep 3, 0 to 5 V). Afterwards, when a voltage sweeps from 0 to -4 V (Sweep 4) on another storage unit, only one jump occurred at -2.55 V from OFF state to ON1 state and such an ON 1 state could be sustained when a negative (Sweep 5, 0 to -4 V) or positive sweeps (Sweep 6, 0 to 4 V) as well. Next, when another sweep from 0 to -5 V (Sweep 7, 0 to -5 V) was applied to this storage unit again, another jump occurred from ON1 state to ON2 state. This ON2 state could also be maintained when a negative (Sweep 8, 0 to -5 V) or positive sweeps (Sweep 9, 0 to 5 V). These experiments mean the reverse voltage cannot "erase" the data neither stored by ON1 state nor ON2 state. ITO/TFMCT/AI devices show typical nonvolatile ternary property (WORM) with a threshold voltage of -2.75 V and 4.30 V, and ON2/ON1/OFF ratio as high as 10³ and 10⁴.

Furthermore, the retention stability of TFMCU and TFMCT based memory devices under a constant voltage of -1 V (Supporting Information, **Figure S5**). No obvious changes in each conducting state for at least 10^3 s.

Proposed mechanism

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Figure 6. (a) Energy level diagram for the ITO/TFMCU and TFMCT/Al devices. (b) DFT-calculated variation in the HOMO-LUMO gap under an electric field along different directions; (c) Molecular geometries of TFMCU, TFMCT and the directions of the electrical field. Electrical field strengths are given in a.u. (1 a.u. = $51.4 \vee Å^{-1}$).

In the previous research, many mechanisms have been applied to explain the performance of organic storage behaviors, such as metal-filament formation¹³, field-induced charge transfer¹⁴, molecular redox¹⁵, conformational change¹⁶ and charge trapping¹⁷. The charge trapping mechanism was originally applied to describe the charge transportation in inorganic insulators¹⁸. In previous study, we extended this theory into the case of organic materials based on the positive-feedback effect from the polarization of organic conjugated molecules. Here the extend theory is invoked to explain the multilevel conductance switching behaviors.

Since organic molecules stacking through relatively weak intermolecular force, there are types of crystalline defects or impurities.¹⁹ They are able to capture and immobilize charges during charge transportations, functionalizing as charge traps. When a charge injected into the active layer from the positive electrode to fill a trap, the molecules around the trap will be polarized due to the electric field. Even though polarization from each trap just distributes in very small region, accumulation of high density of injected charges and the filled traps will allow more and more molecules rounding them be polarized. These polarized molecules become more conductive and more readily accept injected charges, leading to a positive feedback effect to accelerate the polarization effect. Finally, sufficient conductive regions overlap together to form the continuous conductive channel which contributes to the sudden increase in conductivity at specific voltage. Even when the external voltage removed, the charge will mainly remain trapped, because the deep trapping level prevents the detrapping process.^{17a, 20} Therefore the polarized region and the conductive channel still remained. In general preparation process, there are multiple types of traps, including chemical impurities, crystal defects and domain boundaries.^{19, 21} These traps are of distinctly energetic levels, which would be filled sequentially under increasing voltages, leading to multilevel electro-switching behaviors. Despite their unknown nature, the types of traps existing in our organic films were proposed related with the electron-acceptors, could be one, two or three, corresponding to the binary, ternary and quaternary RRAMs.^{17, 22} In our two molecules, the two electron-acceptors: 3,5-bis(trifluoromethyl)phenyl and 4-cyanophenyl groups in the backbones play the roles of traps. According to the DFT calculation, these two groups have different trap depths (in **Figure S4** in Supporting Information). When the external voltage is applied, these two traps will be filled one by one.^{17b, 23} Therefore, theoretically, two sharply jumps should emerge and exhibit ternary memory behaviors for both two molecules. However, triggered by the substitution of "O" by "S", only TFMCT-based devices show ternary memory behaviors whereas TFMCU ones are binary type.

The mechanism behind is attributable to the discrepancies in the band gaps. In order to understand the mechanism of the electric switching in these sandwiched devices, the energy level diagram (Figure 6 (a)) of ITO/TFMCU and TFMCT/AI devices was drawn to provide a visualized relationship between HOMO. LUMO energy levels of TFMCU, TFMCT, and the work functions of ITO and aluminum. The differences between the work function of ITO and HOMO energy level (0.94 eV, 0.98 eV) are smaller than that between LUMO energy and the work function of AI (2.67 eV. 2,11 eV) for both molecules, which indicates that hole injection is the predominant way for the charge transfer under negative bias. As shown in Figure 6 (b), when external electric fields were applied to the two molecules from x, y and z directions, the HOMO-LUMO gaps of TFMCU and TFMCT are narrowed as the increase of electric filed, particularly from the chain direction. The original band-gap of TFMCT is smaller than that of TFMCU. Even though the band-gap of TFMCU is more sensitive to the electric field, its gap is always large than that of TFMCT. With similar crystalline structures, a narrower band-gap of molecule would offer a significantly higher carrier-hopping rate, or namely become more conductive, according to the Marcus transport theory for organic materials.²⁴ Additionally, the molecule TFMCT has smaller dipole moment (1.79 a.u., for TFMCU is 2.24 a.u.). Smaller dipole moment suggests that molecule TFMCT is easier to be polarized, and the continuous conductive channel could be formed under lower voltage which also contributes to the lower threshold voltage of TFMCT based devices. That means compared to TFMCU-based devices, TFMCT-based devices will have lower threshold voltage.

Since the threshold voltage of TFMCU based devices are larger, we just observed one conductivity transition, which current level had already arrived our testing limitation (Maximum compliance current is 0.1 A). In a word, under our present instrument limitation, we found that TFMCU based devices perform binary WORM storage behavior while TFMCT based devices perform ternary WORM storage behavior.

Conclusions

In conclusion, two molecules based on urea and thiourea (TFMCU and TFMCT) were synthesized and the memory devices were fabricated to investigate. For the TFMCT, because

of its lower band-gap and feasibility to be polarized, the formation continuous conductive channel and the electron transition will occur under lower bias voltage, contributing to the ternary WORM behavior of TFMCT based device while under present testing environment. In contrast, TFMCU has a large band gap, even under a polarization field, therefore the as-fabricated device shows binary WORM behavior at limited voltages. Our work demonstrated that a low band gap of organic molecules is critical to achieve multilevel electro-resistive memory and such a low band gap could be tuned by simply substitute the functional groups by a single atom while keep its superior intermolecular stacking and other parameters intact as much as possible. This study, together with our previous single atom substitution work, may be useful to tune and improve the device performance in future design of organic memories.

Experimental Section

Materials

4-isocyanatobenzonitrile, 4-isothiocyanatobenzonitrile, 3,5bis(trifluoromethyl) aniline tetrabutylammonium hexafluorophosphate were purchased from commercial sources (Alfa Aesar and TCI). All other reagents and solvents were used as received without further purification.

Synthesis

Synthetic routes of molecules TFMCU and TFMCT were shown in $\ensuremath{\textbf{Scheme 1}}$.

Synthesis of 1-(3,5-bis(trifluoromethyl)phenyl)-3-(4-cyanophenyl)urea (TFMCU). 3,5-bis(trifluoromethyl)aniline (708.8 mg, 6 mmol) and dry CH₂Cl₂ (60 mL) was added into a 100 mL three-neck round-bottom flask. Then the nitrogen gas was blown into the solution for 20 min to remove dissolved oxygen. After that, 4-isocyanatobenzonitrile (1212 μ L, 6.6 mmol) was added dropwise to the mixture under the protection of nitrogen gas at 0 °C. The reaction mixture was stirred at this temperature for 5 h and at room temperature for two more hours. Then the reaction mixture was extracted with water. Then the solvent in the organic phase was evaporated under reduced pressure and the crude product was purified by column chromatography (PE: EA = 3: 1) to give the target compound TFMCU as white powder with a yield of 52% (1.2801 g, 3.43 mmol). ¹H NMR (400 MHz, DMSO-d₆): δ 9.56 (s, 1H), 9.52 (s, 1H) 8.15 (s, 2H), 7.77 (t, *J*=2.0 Hz, 1H), 7.75 (t, *J*=2.0 Hz, 1H), 7.72 – 7.65 (m, 3H). HRMS: calcd for C₁₆H₉F₆N₃O [M + H] * 374.0683, found 374.0713

Synthesis of 1-(3,5-bis(trifluoromethyl)phenyl)-3-(4-cyanophenyl)thiourea (TFMCT). 3,5-bis(trifluoromethyl)aniline (708.8 mg, 6 mmol) was dissolved in dry CH₂Cl₂ (60 mL) in a 100 mL three-neck round-bottom flask. Blowing of nitrogen gas into the solution was followed to remove the dissolved oxygen for 20 min. Then 4-isothiocyanatobenzonitrile (1212 μ L, 6.6 mmol) was added under nitrogen atmosphere at 0 °C. After that, the reaction mixture was stirred at 0 °C for 5 h and at room temperature for two more hours. After completion of the, deionized water was poured into the reaction system to extract and reserved the organic phase, which was later evaporated. At last, column chromatography (PE: EA = 3: 1) was used to purify the crude product and finally TFMCT was obtained as white powder with a yield of 44% (1.1305 g, 2.90 mmol). ¹H NMR (400 MHz, DMSO-d₆): δ 10.64 (s, 1H), 10.55 (s, 1H), 8.25 (s, 2H), 7.86 – 7.80

(m, 3H), 7.75 (t, J=2.0 Hz, 1H), 7.73 (t, J=2.0 Hz, 1H). HRMS: calcd for $C_{16}H_9F_6N_3S$ [M + H] * 390.0455, found 390.0483

Fabrication of the devices

The indium tin oxide (ITO) glass was cleaned by detergent, and then deionized water, acetone and ethanol were used to wash the glass by ultrasonication for 20 min, respectively. After that, under the vacuum degree of 10^{-6} torr, the organic materials were thermally deposited on the ITO glass substrate by thermal evaporation. Next, a shadow mask was covered on the organic film and Al film was evaporated with 100 nm thickness and 0.2 mm diameter as top electrode. The area of the storage unit is approximately 0.0314 mm².

Measurements and general methods

All NMR spectra of organic molecules were obtained in dimethylsulfoxide-d₆ (DMSO-d₆) solution containing 0.03 % TMS as an internal reference using an Inova 400 MHz FT-NMR spectrometer. Shimadzu UV-3600 spectrometer was used to record UV-visible absorption spectra at room temperature. Cyclic voltammograms was collected by CorrTest CS Electrochemical Workstation analyzer at a sweep rate of 100 mV/s in 0.1 mol/L solution of tetrabutylammonium hexafluorophosphate (TBAPF₆) or in dried dichloromethane. X-ray diffraction patterns were obtained from Shimadzu XRD-6000 spectrometer with a Cu Ka monochromatic radiation source at 40 kV and 30 mA, MFP-3DTM (Digital Instrument/Asylum Research) AFM instrument was applied to characterize the surface morphology of the fabricated film devices. The current-voltage (I-V) characteristics of the memory devices were measured by Keithley 4200-SCS in voltage sweeping mode. Thermogravimetric analysis (TGA) was performed on a Perkin-Elmer Diamond TG/DTA instrument under a nitrogen atmosphere with a heating rate of 10 °C min⁻¹. SEM images were taken on a Hitachi S-4700 scanning electron microscope. High-resolution mass spectra (HRMS) were acquired using a Micro mass GCT-TOF mass spectrometer with an electrospray ionization source.

Acknowledgements

This work was financially supported by the NSF of China (21176164, 21336005, 21603158), Chinese-Singapore Joint Project (2012DFG41900), Suzhou Science and Technology Bureau Project (SYG201524), and the Priority Academic Program Development of Jiangsu Higher Education Institutions (PAPD).

Keywords: Urea and thiourea • Ternary • Single atom substitution • Charge trapping • Resistive random access memory

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