

Electronic Supplementary Information (ESI):

Multi-Level Conductance Switching of Memory Device through Photo-Electric Effect

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1. Molecular structure of model compounds for the calculation

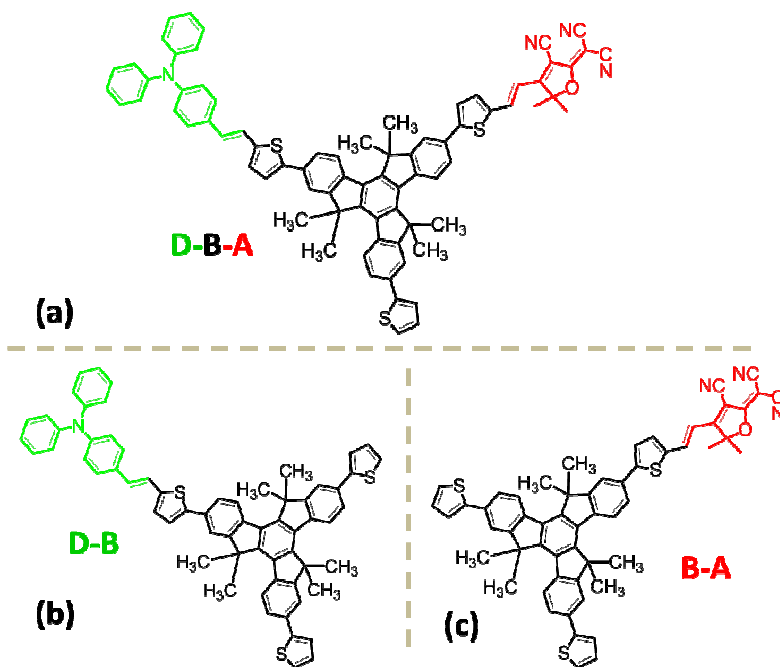


Figure S1. Molecular structures for the calculation: **(a)** the donor-bridge-acceptor (D-B-A) compound. **(b)** Model compound only containing donor unit and truxene core (D-B). **(c)** Model compound only containing acceptor unit and truxene core (B-A).

2. Switching speed of the DBA device among different states

Switching time of the DBA memory device was measured on a SUSS microchamber probe station, with a Keithley 4200-SCS semiconductor system and a Tektronix DPO 2012 digital phosphor oscilloscope. Standard four-probe measurement of I - V characteristics was applied on the device and the oscilloscope was used to capture the switching of the current at the threshold voltage.

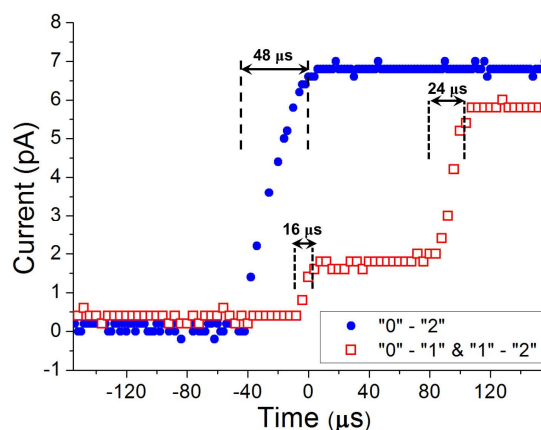


Figure S2. Transient response of current in the DBA memory device shows the switching times of *ca.* 48 μs from the “0” state to “2” state; *ca.* 16 μs from the “0” state to “1” state and *ca.* 24 μs from the “1” state to “2” state under UV light, respectively.

3. The stability and reliability measurement of memory device

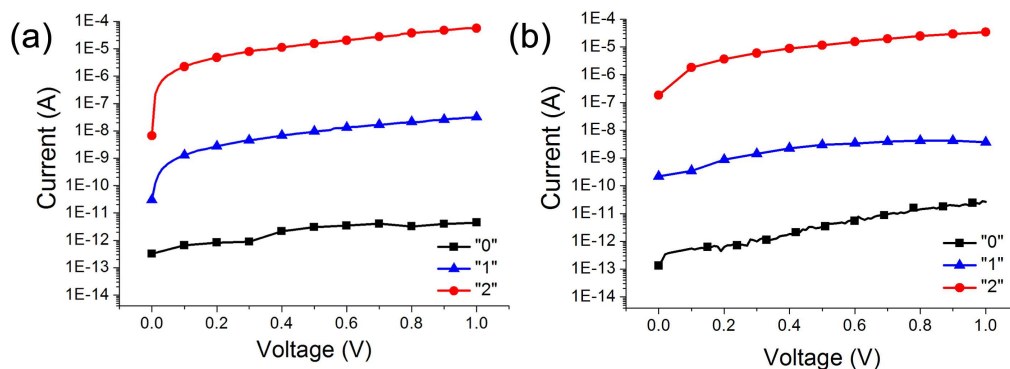


Figure S3 I - V curves of (a) the fresh DBA device and (b) the same device stored after 7 months are compared. The I - V curves at each states show little change in 7 months even without the protection of encapsulation.

4. More details about the quantum chemical calculation.

To explore the photo-electronic switching mechanism of the multi-level memory, the electronic properties of DBA molecule were studied. The relative ordering of the occupied and unoccupied molecular orbitals can give a reasonable indication of the excited properties and charge transport ability. The charge density distributions of the highest occupied molecular orbital (HOMO) and the lowest unoccupied molecular orbital (LUMO) were found to be intercepted at the central meta-conjugated truxene core (Figure S4a, b). Besides, both the HOMO and LUMO+1 isosurfaces tended to locate on TPA arm (donor). The energy gap between the HOMO and LUMO+1 was 2.91 eV. It was close to the energy of the absorbance peak of TPA arm (421 nm, i.e. 2.94 eV) and the UV light used to trigger the “1” state (405 nm, i.e. 3.06 eV). Therefore, UV light with the wavelength of 405 nm can excite electrons' transition within TPA unit.

Figure S4d summarized the energy levels of the HOMO and LUMO, along with the work functions (Φ) of the ITO and Al electrodes. The ITO electrode had a work function of -4.8 eV. The Al electrode had a work function of -4.3 eV. DBA had a LUMO level of -3.35 V and a HOMO level of -4.83 eV. The energy barrier between the Φ_{ITO} and the HOMO (0.05 eV) was much lower than the energy barrier between the LUMO and Φ_{Al} (0.95 eV). The holes injection from ITO into the HOMO of DBA was much easier than electron injection from Al into the LUMO of DBA. Therefore, the DBA was a p-type material and electrons dominated the conduction process in this memory device. There was an energy barrier between the Al electrode and the DBA

layer. So it was easy to understand from the energy levels that the current at “0” state was controlled by thermionic emission process, and the charge injection through the energy barrier dominated the conduction mechanism.

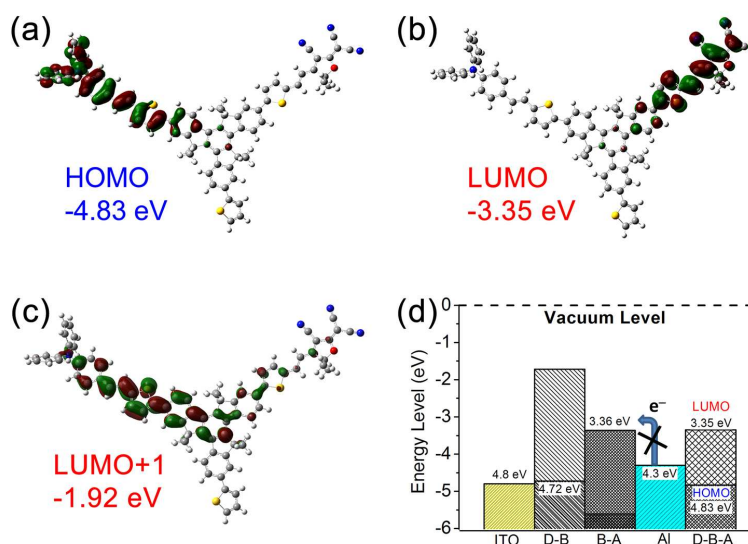
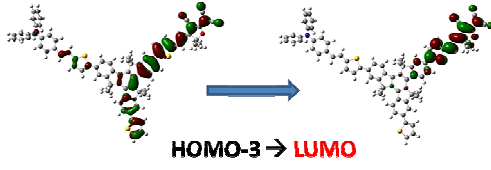
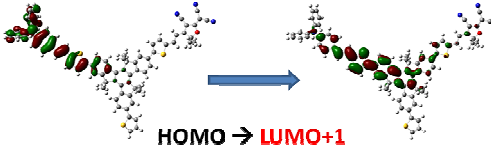
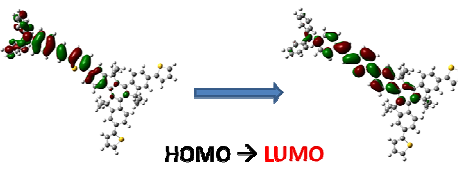
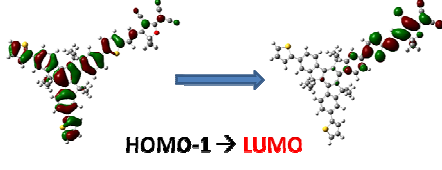
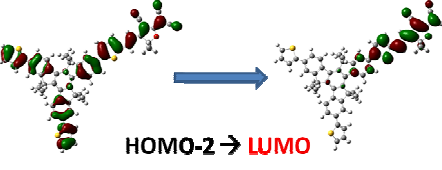


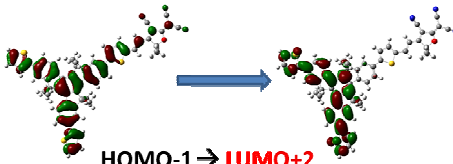
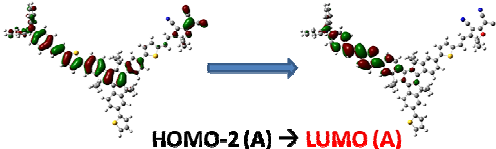
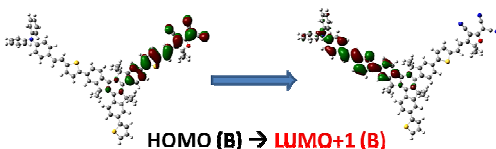
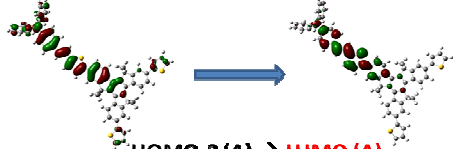
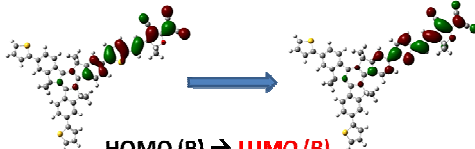
Figure S4. Molecular orbitals of the DBA molecule: (a) HOMO; (b) LUMO; (c) LUMO+1. HOMO and LUMO are found to be intercepted at the central truxene core, which can lead an asymmetric CT behavior. (d) HOMO and LUMO energy levels for the DBA molecule and the functional segments (D-B, B-A) along with the work functions (Φ) of the ITO and Al electrodes. It shows that the HOMO of the DBA come from the HOMO of the D-B segment; the LUMO of the D-B-A come from the LUMO of the B-A segment.

At the optimized geometries of the ground states, the excitation energies and oscillator strengths of the low-lying states are calculated. The selected vertical excitation energies, oscillator strengths and the corresponding main transitions of three compounds in the neutral, anion and cation states were summarized in Table S1. Here, only major excitations with large oscillator strengths and the corresponding main transitions with configuration coefficient larger than 0.5 was selected. The oscillator strength is a dimensionless quantity to express the strength of the transition. Excitation with large oscillator strength can absorb light and more likely undergo a

transition from one quantum state to another. Therefore selected vertical excitation energies with large oscillator strengths could coincide with the major absorbance of the compound.

Table S1. Selected vertical excitation energies with large oscillator strengths, the corresponding transitions and main configurations.

Compound	Transition	Vertical excitation energy	Oscillator strengths	Main Configuration
D-B-A (neutral state)	S0→S4	527.58 nm	1.5707	 <p>HOMO-3 → LUMO</p> <p>Configuration coefficient = 0.68575</p>
	S0→S5	470.13 nm	1.6897	 <p>HOMO → LUMO+1</p> <p>Configuration coefficient = 0.67312</p>
D-B (neutral state)	S0→S1	461.90 nm	2.1759	 <p>HOMO → LUMO</p> <p>Configuration coefficient = 0.69836</p>
B-A (neutral state)	S0→S2	581.39 nm	0.6412	 <p>HOMO-1 → LUMO</p> <p>Configuration coefficient = 0.70225</p>
	S0→S3	509.43 nm	1.3209	 <p>HOMO-2 → LUMO</p> <p>Configuration coefficient = 0.69611</p>

	$S_0 \rightarrow S_{14}$	344.71 nm	0.6369	 <p>HOMO-1 \rightarrow LUMO+2</p> <p>Configuration coefficient = 0.61568</p>
$(D-B-A)^+$ (cation state)	$S_0 \rightarrow S_{11}$	648.52 nm	0.8349	 <p>HOMO-2 (A) \rightarrow LUMO (A)</p> <p>Configuration coefficient = 0.57873</p>
$(D-B-A)^-$ (anion state)	$S_0 \rightarrow S_9$	675.85 nm	0.8353	 <p>HOMO (B) \rightarrow LUMO+1 (B)</p> <p>Configuration coefficient = 0.55705</p>
$(D-B)^+$ (cation state)	$S_0 \rightarrow S_{10}$	653.01 nm	0.9597	 <p>HOMO-2 (A) \rightarrow LUMO (A)</p> <p>Configuration coefficient = 0.69335</p>
$(B-A)^-$ (anion state)	$S_0 \rightarrow S_4$	674.09 nm	0.8760	 <p>HOMO (B) \rightarrow LUMO (B)</p> <p>Configuration coefficient = 0.54541</p>

Electrostatic potentials (ESP) of the **D-B-A** at neutral and charged states verified the charge carriers' transport behaviors at different conductance states (Figure S5). Both surfaces of the **D-B-A** molecule at neutral and cation states had some negative ESP regions which arise from the electron-acceptor groups such as the TCF segment. These negative regions can serve as "traps". At "1" state, the negative regions decreased and the traps were partly filled, compared with the neutral state of the

D-B-A molecule. At the “2” state, The molecular surface of the $(\text{D-B-A})^-$ had a continuous ESP along the conjugated backbone which indicates that charge carriers can more easily migrate through this open channel. Thus the film became highest conductive.

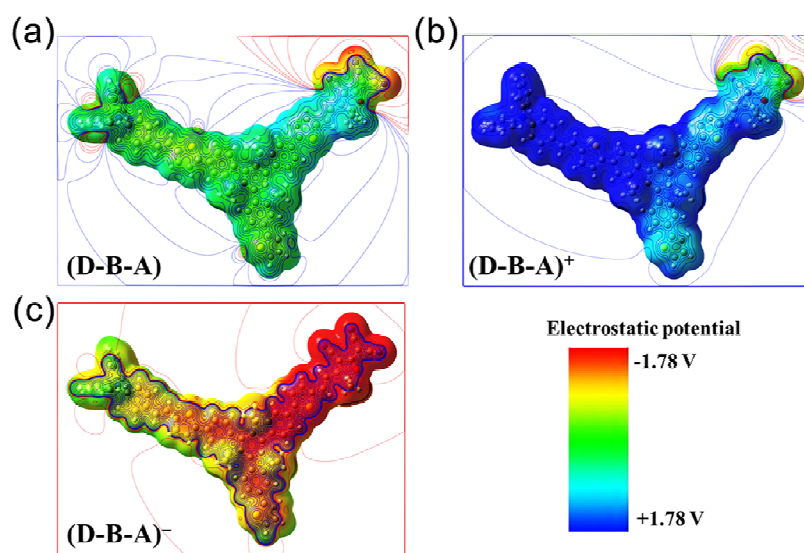


Figure S5. Molecular electrostatic potential (ESP) surfaces of the D-B-A at (a) neutral state; (b) cation state; (c) anion state. The DBA molecule at neutral and cation states had some negative ESP regions which can serve as traps. The molecular surface of the $(\text{D-B-A})^-$ had a continuous ESP along the conjugated backbone which indicated that charge carriers can more easily migrate through this open channel.

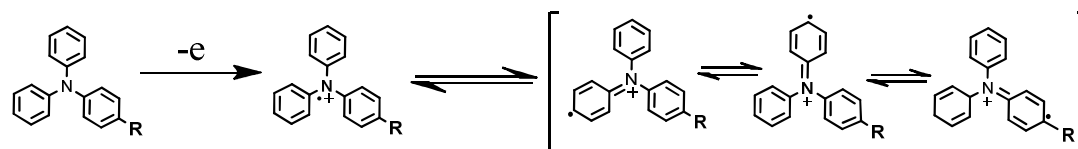


Figure S6. The radical cation of TPA unit can be delocalized over the nitrogen and the three rings, which is resonance or time averaged over the center part of the molecule.^{1,2}

Reference:

- (1) Shacklette, L. W.; Wolf, J. F.; Gould, S.; Baughman, R. H. *J. Chem. Phys.* **1988**, *88*, 3955.
- (2) Wu, X.; Davis, A. P.; Lambert, P. C.; Steffen, L. K.; Toy, O.; Fry, A. J. *Tetrahedron* **2009**, *65*, 2408.