Electronic Supplementary Information (ESI):

Photo-induced amplification of readout contrast in nanoscale data storage

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Absorption spectrum of DBA molecule

The absorption spectrum of the DBA molecule in dilute chloroform solution (10^{-6} mol L^{-1}) is measured(Figure S1a). The main absorption bands are split into two peaks at about 408 nm and 430 nm with a shoulder peak at 460 m. The other absorption peak is at 580 nm. These absorption peaks showed various molar extinction coefficients and extinction pathways.

Figure S1b shows the absorbance spectra on ITO substrate at ON and OFF states, respectively. The absorbance of the DBA thin film at the ON state increases in the range from 500 nm to 700 nm, compared with its absorbance at the OFF state. The result indicates the intense interaction among molecules, especially intra- or inter-molecular CT.[1,2]

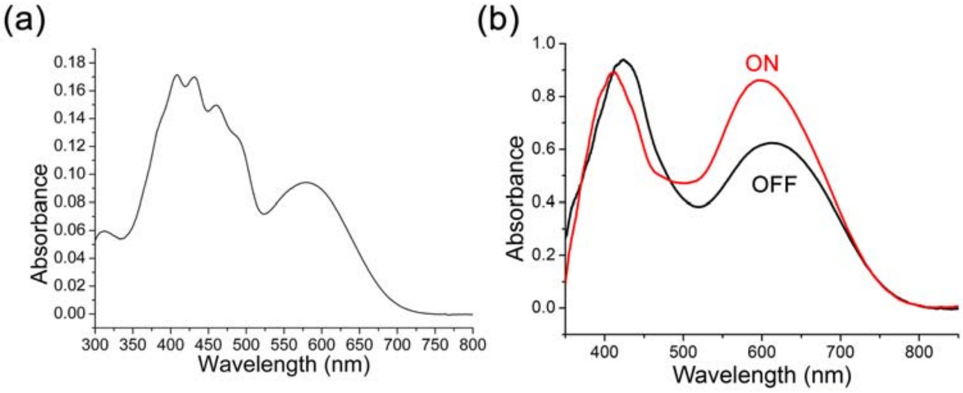

Figure S1 (a) Absorption spectrum in $CHCl_3$ solution (10^{-6} mol L^{-1}); **(b)** The absorbance spectra of the DBA thin film on ITO substrate at ON/OFF states.

Computational Details and Molecular Orbitals

In order to investigate the recording mechanism of the DBA thin film, quantum chemical calculations were performed by using the hybrid Hartree-Fock/density functional theory (HF/DFT) method of B3LYP14with the 6-31G* basis set with the Gaussian 03 program. Orbital pictures were prepared with GaussView 3.07 visual software.[3] The highest occupied molecular orbital (HOMO) and lowest unoccupied molecular orbital (LUMO) levels of DBA molecule are -4.68 eV and -3.37 eV, respectively.

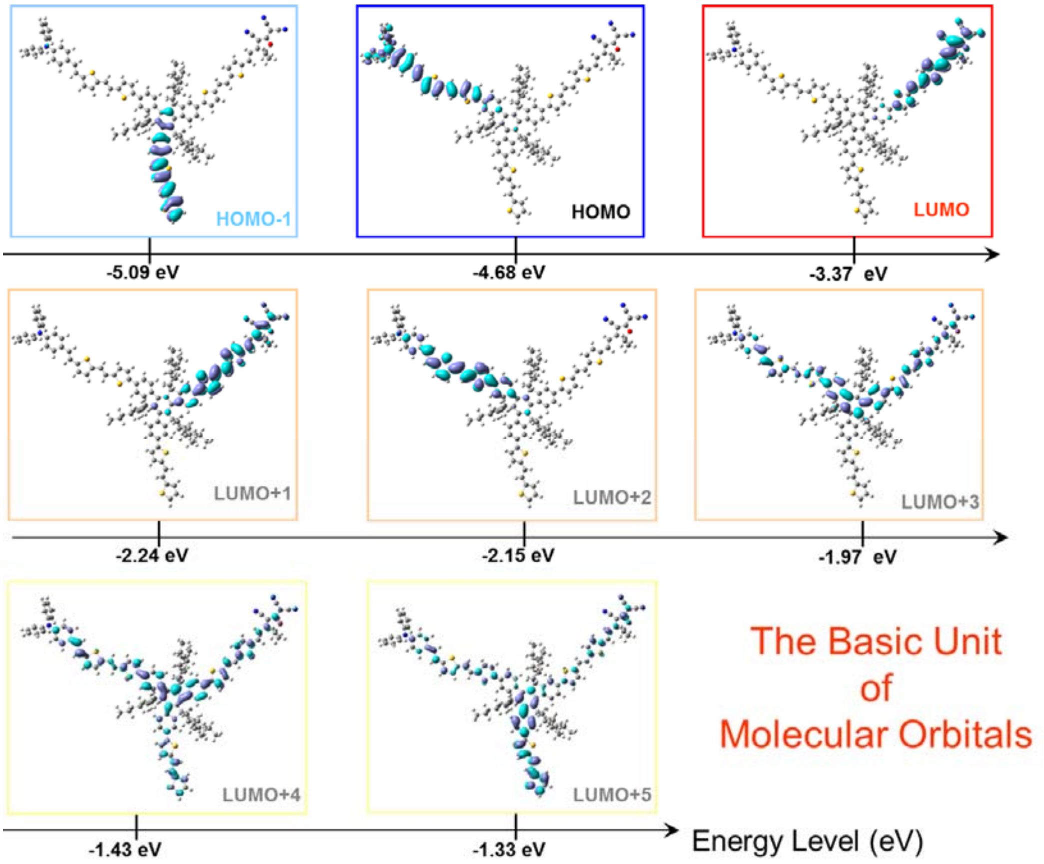

Figure S2 Computational orbital units of the DBA molecule.

The charge density isosurfaces of the basic unit of DBA molecule with the most energetically favorable geometry are shown in Figure S2. The truxene core exhibits good planarity. The HOMO of the molecular are mostly found on the TPA conjugated arm (Donor), and the LUMO mostly exists on the TCF segment (Acceptor). The delocalization of the whole molecule expanded well for other orbitals. For example, LUMO+1, LUMO+2 for DBA molecule suggested slightly distributed on the truxene core. The LUMO+3 isosurfaces tend to appreciable interaction between TPA and TCF.

When the voltage pulse is applied on the thin film, the external electric field can give the molecule enough energy to make the charge-transfer from the donor (TPA) to the acceptor (TCF) between the adjacent molecules. This can lead an increased number of the carriers and a delocalized state, resulting in a higher conductivity at the "on" state. Meantime, because the HOMO and the LUMO were found to be intercepted at the central meta-substituted truxene core, the charges recombination is suppressed and the delocalized state can be stably retained.

Photoelectric cooperation on bistable electrical performance of macroscopic devices

The effect of light radiation on the I-V characteristics of the macroscopic devices is also investigated under both dark condition and UV light irradiation. Figure S3 shows the currents of both ON and OFF states under dark and UV light from 1.1 mW cm^{-2} to 3.0 mW cm^{-2}. The wavelength of the light is set at 405 nm, according to the maximum absorbance of the DBA. The current curves increase under UV light illumination, compared with those in the dark condition. It proves the DBA compound is photoactive and the macroscopic memory device based on the material has photo-electrical responses to the UV light of 405 nm.

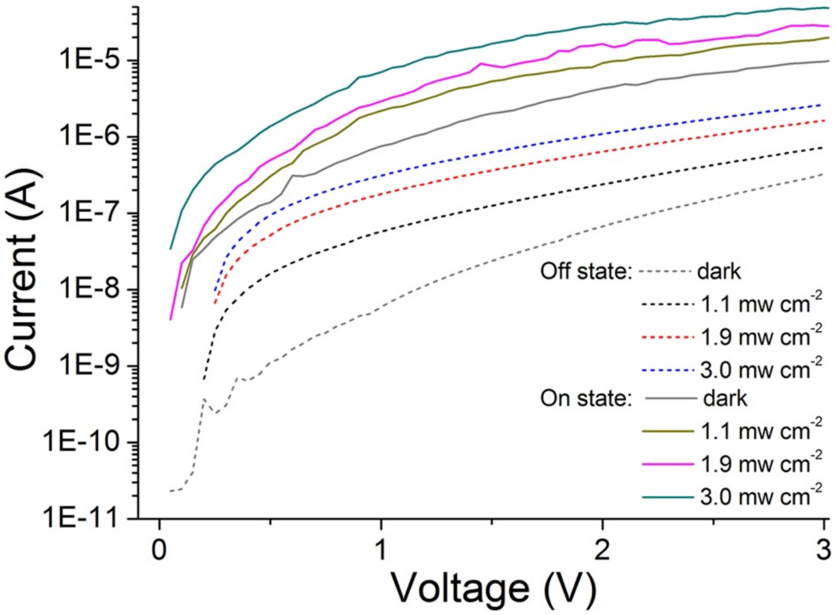

Figure S3 *I-V* characteristics of the memory device at both the ON and the OFF state under dark and various UV light intensities.

Figure S4a shows the net increment of the current (ΔI), comparing the currents under UV light of 1.1 mW cm^{-2} and dark condition. Figure S4b shows the comparison of the ΔI of ON (ΔI_{ON}) and OFF (ΔI_{OFF}) state at 1 V under various light intensities. The ΔI_{ON} is 6.26e-6 A when the light power intensity rises to 3 mW cm^{-2}. At the same power intensity, the ΔI_{OFF} is only 3.05e-7 A. The ΔI_{ON} is more than 20 times larger than ΔI_{OFF}. These results demonstrate that the conductance of both states can be modulated by the UV incident light. The photoelectrical effect amplifies the ON current much larger than the OFF current. This characteristic could make this DBA compound has potential in the photoelectric storage field.

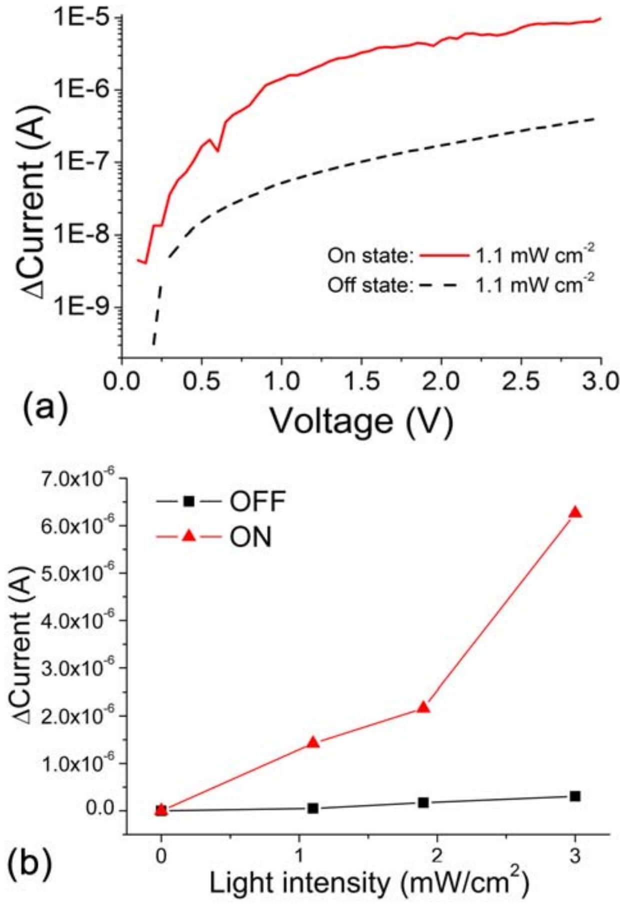

Figure S4 (a) After subtracting the current under dark condition, the net increment of the current of the ON (ΔI_{ON}) and OFF (ΔI_{OFF}) states under UV light illumination (power intensity: 1.1 mW cm^{-2}) are shown. (b) The comparison of the ΔI_{ON} and ΔI_{OFF} at 1V under various light intensities. The ΔI_{ON} is 6.26e-6 A and the ΔI_{OFF} is only 3.05e-7 A, when the light power intensity rises to 3 mW cm^{-2}.

Energy levels calculated from the experiments

Cyclic voltammetry experiment was performed in tetrahydrofuran solution containing 0.1 M n-Bu_4NPF_6 using Ag/AgCl as the reference electrode at a scan rate of 50 mV s^{-1} (Figure S5). The HOMO and LUMO energy levels of DBA molecule can be calculated from the onset oxidation potential (E_{Ox}(onset)) and the onset reduction potential (E_{Red}(onset))

HOMO=-[4.65 V-E_{Ox}(onset)] =-5.45 eV;

LUMO=-[4.65 V-E_{red}(onset)] =-4.35 eV;

E_g=LUMO–HOMO=1.10 eV.

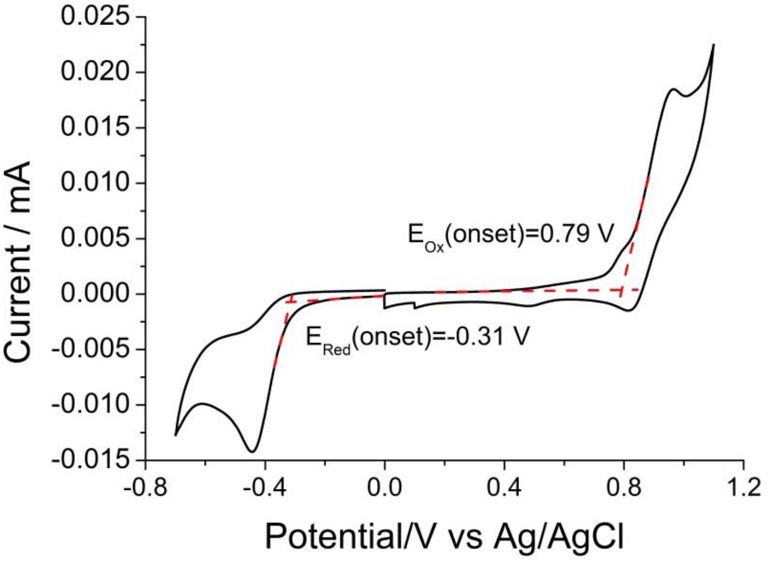

Figure S5 Cyclic voltammetry sweep of DBA in 0.1 M *n*-Bu4NPF6/ tetrahydrofuran (scan rate: 0.1 V/s).

For DBA molecule, the onset of the absorption represents the low-energy edge in solid film absorption spectrum (Figure S6). The observed band gap of the molecules estimated from the onset of the absorption (800 nm) is 1.59 eV. It is larger than the calculated HOMO-LUMO gaps from cyclic voltammetry (1.1 eV). This shows there is no direct transition from the HOMO to the LUMO. Three major absorption peaks of the DBA compound is around 614 nm (i.e. 2.02 eV), 475 nm (i.e. 2.61 eV), and 441 nm (i.e. 2.81 eV). Form the theoretical calculations in Figure S2, the gap between the HOMO and LUMO+1, LUMO+2, and LUMO+3 is 2.44eV, 2.53 eV, 2.71 eV respectively. The UV light irradiation can excite photo-induced electrons into the LUMO+1 and higher orbitals and open additional electron-transfer channels.

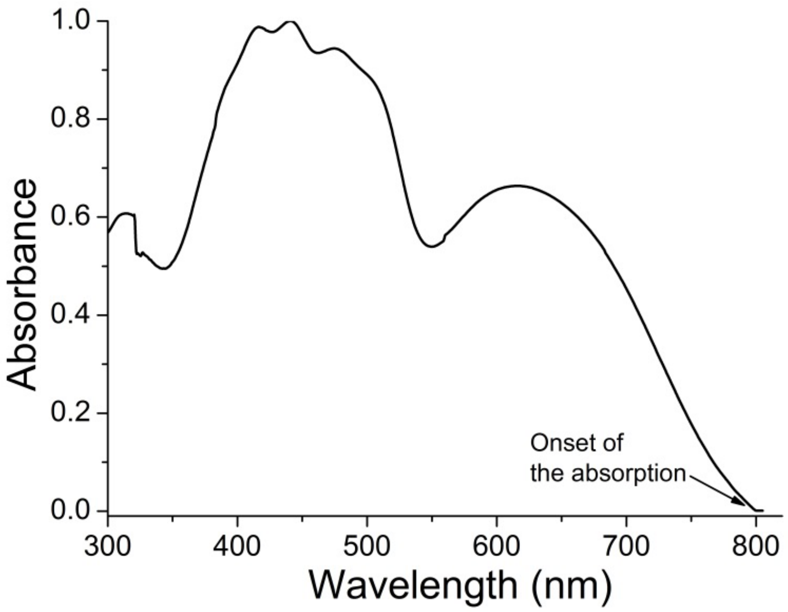

Figure S6 Absorption spectrum of DBA compound in solid film on quartz glass.

Reference

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