Supporting Information

Synthesis of tetranitro-oxacalix[4]arene with oligoheteroacene groups and its nonvolatile ternary memory performance

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Experimental

Materials

10% Pd/C and hydrazine monohydrate were purchased from Alfa Aesar. 1,5-Difluoro-2,4-dinitrobenzenen and 2,5-dihydroxy-1,4-benzoquinone were purchased from Tokyo chemical industry (TCI) company. 1,2-Bis(decyloxy)-4,5-diaminobenzene was synthesized according to a reported procedure.[1] Other chemicals and solvents were used directly as received without further purification.

Instrumentation and characterization

Using $CDCl_3$, CF_3COOD (TFA), or DMSO-d_6 as solvent and tetramethylsilane (TMS) as the internal standard, ^1H NMR and ^{13}C NMR spectra were measured on INOVA 300 or 400 MHz NMR spectrometer at ambient temperature. UV/Vis absorption spectra were carried out at room temperature with a Shimadzu UV-3600 spectrophotometer. Cyclic voltammetry (CV) was performed by using a three-electrode cell, in which indium tin oxide (ITO) was used as a working electrode, platinum wire was used as an auxiliary electrode, and Ag/AgCl (KCl saturated) was used as a reference electrode at a sweep rate of 100 mV s^{-1} (CorrTest CS Electrochemical Workstation analyzer). A 0.1 mol L^{-1} solution of tetrabutylammoniumhexafluorophosphate ($TBAPF_6$) in anhydrous acetonitrile solution was used. SEM images were taken on a Hitachi S-4700 scanning electron microscope. Atomic force microscopy (AFM) measurements were performed using a MFP-3DTM (Digital Instruments/Asylum Research) AFM instrument. Thermal properties were estimated from a PE TGA-7 thermogravimetric analysis system (TGA) under a nitrogen atmosphere at a heating rate of 20 ^oC min^{-1}. All electrical measurements of the device were characterized under ambient conditions, without any encapsulation, using a Hachioji B1500A (Agilent Technologies) semiconductor parameter analyzer. The fluorescent quantum yield (QY) in the solution was determined using fluorescein (Φ_F = 79 % in 0.1 M NaOH as standard), whereas that of solid film was measured using a calibrated integrating sphere.

Fabrication and measurements of the memory devices

The indium-tin oxide (ITO) glass was precleaned by sonicating for 15 min with deionized water, acetone and ethanol, sequentially. Then the **4N4OPz** was deposited onto the surface of the ITO under a pressure of 10^{-6} Torr. The thickness of the film was typically ~ 100 nm, which was traced by a calibrated quartz crystal monitor. Finally, aluminum (Al) was thermally evaporated onto the film surface at 5×10^{-6} Torr through a shadow mask to yield top electrodes with thickness around 120 nm and area of 0.0314 mm^2. To confirm memory performance, a 5 nm LiF buffer layer was added between the **4N4OPz** layer and the Al top electrode.

Synthesis

Synthesis of 7,8-bis(decyloxy)phenazine-2,3-diol

A mixture of 1,2-bis(decyloxy)-4,5-diaminobenzene (840 mg, 2 mmol) and 2,5-dihydroxy-1,4-benzoquinone (308 mg, 2.2 mmol) in refluxing ethanol (v = 100 mL) was stirred 24 h under N_2 atmosphere. The mixture was allowed to cool down to ambient temperature and the obtained precipitate was isolated by filtration and washed with cold methanol and small ethyl ether affording 7,8-bis(decyloxy)phenazine-2,3-diol as a yellow solid (650 mg, 1.24 mmol, yield: 62 %)

^{1}H NMR (300 MHz, DMSO-d_6) δ 10.48 (s, 2H), 7.29 (s, 2H), 7.22 (s, 2H), 4.16 (t, J = 6.0 Hz, 4H), 1.89 – 1.69 (m, 4H), 1.59 – 1.42 (m, 4H), 1.42 – 1.16 (m, 24H), 0.84 (t, J = 5.6 Hz, 6H).

HR-MS: Calcd for: $C_{32}H_{48}O_4N_2Na$: 547.3512; Found: 547.3561.

^{13}C NMR spectrum of 7,8-bis(decyloxy)phenazine-2,3-diol could not be recorded because of very poor solubility of the sample in DMSO-d_6.

Synthesis of 4,6,25,27-tetranitro-2,8,23,29-tetraoxacalix[*4*]-36,37-bis(decyloxy)phenazine (4N4OPz)

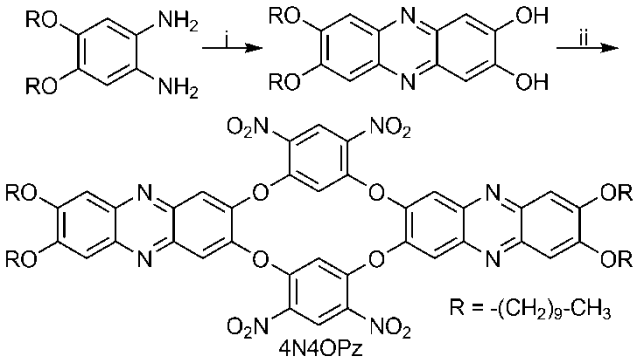
A mixture of 7,8-bis(decyloxy)phenazine-2,3-diol (1.57 g, 3 mmol) and potassium carbonate (4.14 g, 30 mmol) in 50 mL anhydrous DMF was stirred 2 h under N_2 atmosphere. 1,5-difluoro-2,4-dinitrobenzene (612 mg, 3 mmol) was added in 50 mL of anhydrous DMF and the mixture was heated at 80 °C for 3 days. The mixture was allowed to cool down to ambient temperature before pouring into deionised water

(500 mL). The obtained precipitate was isolated by filtration and washed with acetone and small ethyl ether affording 4N4OPz as a yellow powder (248 mg, 0.18 mmol, yield: 12 %).

^{1}H NMR (400 MHz, TFA) δ 7.89 (s, 4H), 7.65 (s, 4H), 7.01 (s, 2H), 4.46 (s, 8H), 2.04 (d, J = 6.5 Hz, 8H), 1.64 (d, J = 7.0 Hz, 8H), 1.48 (s, 8H), 1.32 (d, J = 14.5 Hz, 40H), 0.87 (d, J = 6.6 Hz, 12H).

^{13}C NMR (400 MHz, TFA) δ 160.70, 160.41, 148.28, 136.83, 136.48, 133.03, 105.89, 105.75, 98.99, 72.07, 31.44, 29.04, 29.00, 28.83, 28.66, 27.83, 25.38, 21.99, 12.25.

HR-MS: Calcd for: $C_{76}H_{97}N_8O_{16}$, 1380.6934; Found: 1380.6315.



Scheme 1. Synthetic route of compound 4N4OPz: (i) 1.1 equiv 2,5-dihydroxy-1,4-benzoquinone, CH_3CH_2OH, N_2, reflux, 62 %; (ii) 1 equiv 1,5-difluoro-2,4-dinitrobenzene, 10 equiv K_2CO_3, DMF, 80 °C, 12 %.

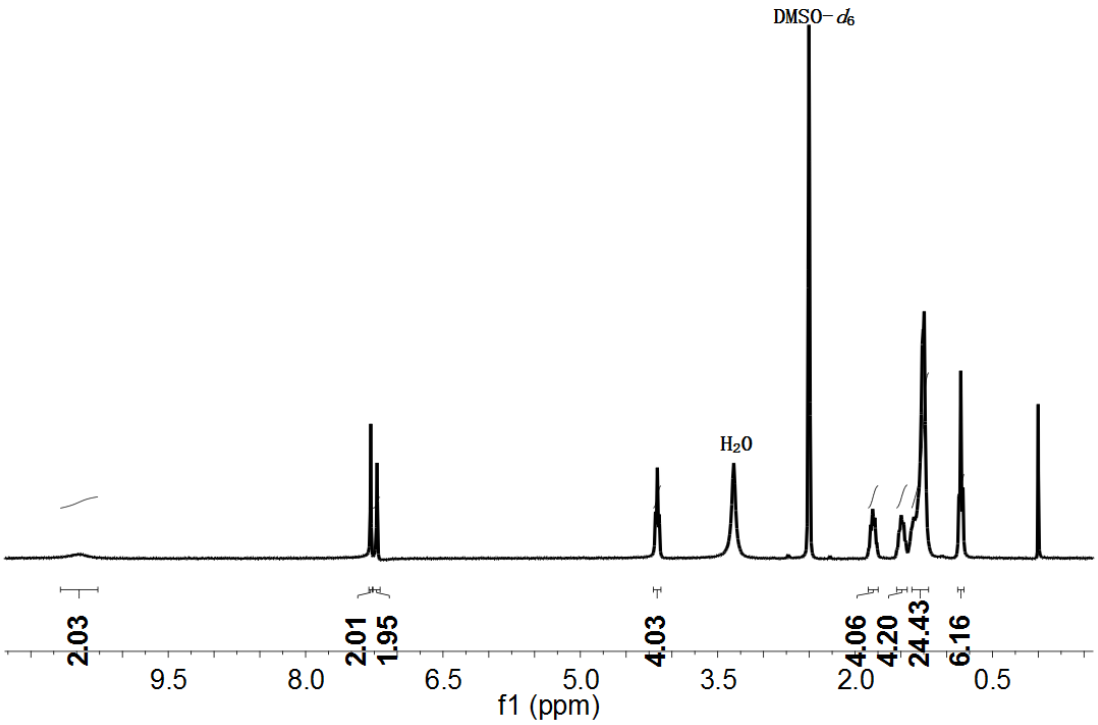


Figure S1. ^{1}H NMR spectrum of 7,8-bis(decyloxy)phenazine-2,3-diol in DMSO-d_6.

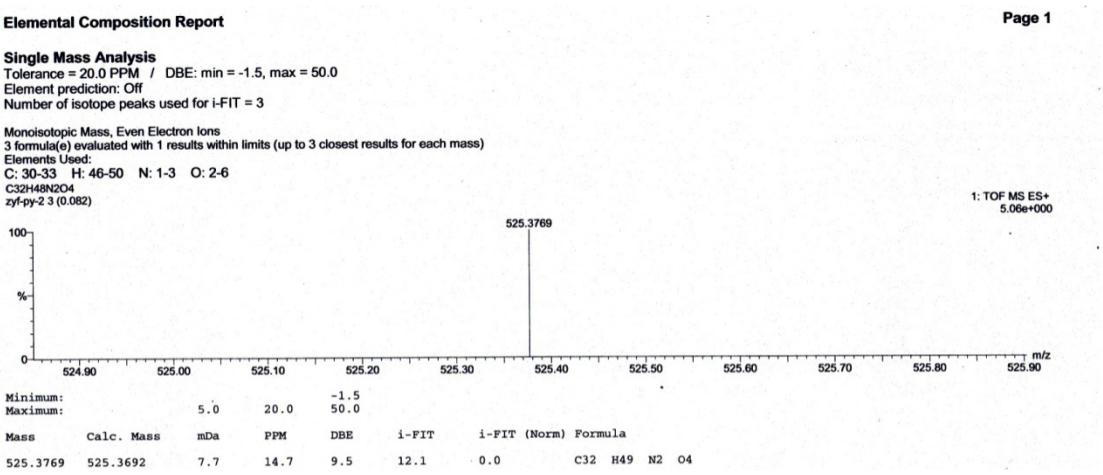


Figure S2. HR-MS spectrum of 7,8-bis(decyloxy)phenazine-2,3-diol.

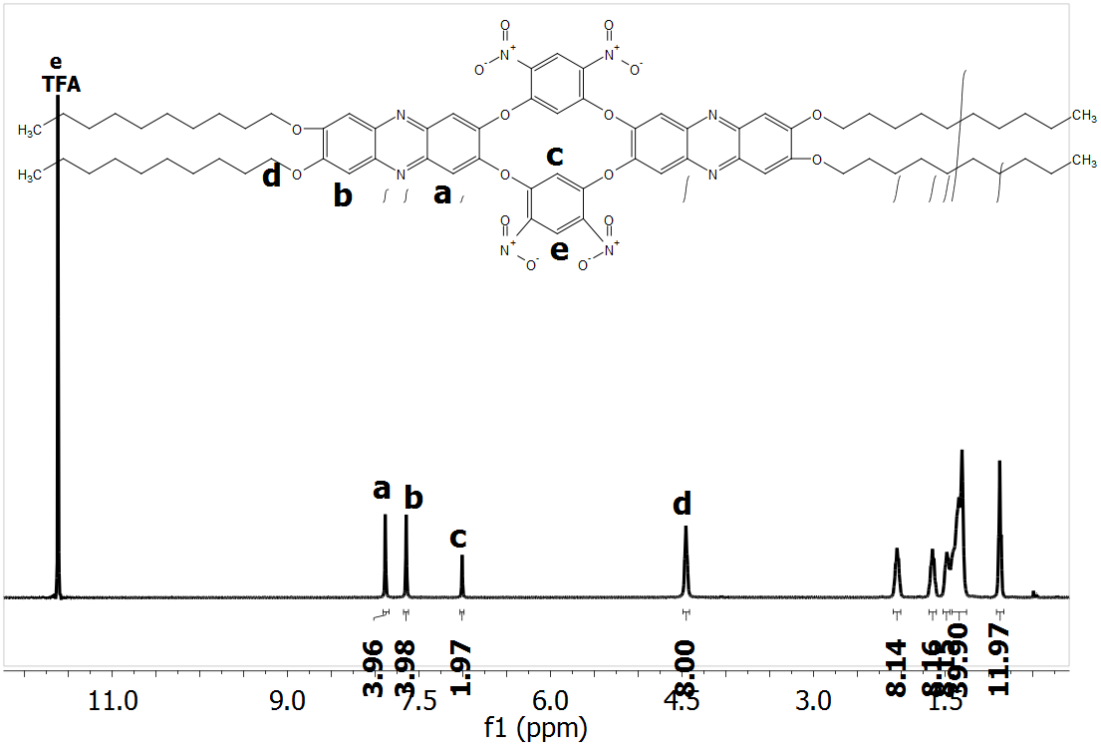


Figure S3. ^{1}H NMR spectrum of 4N4OPz in CF_3COOD (TFA).

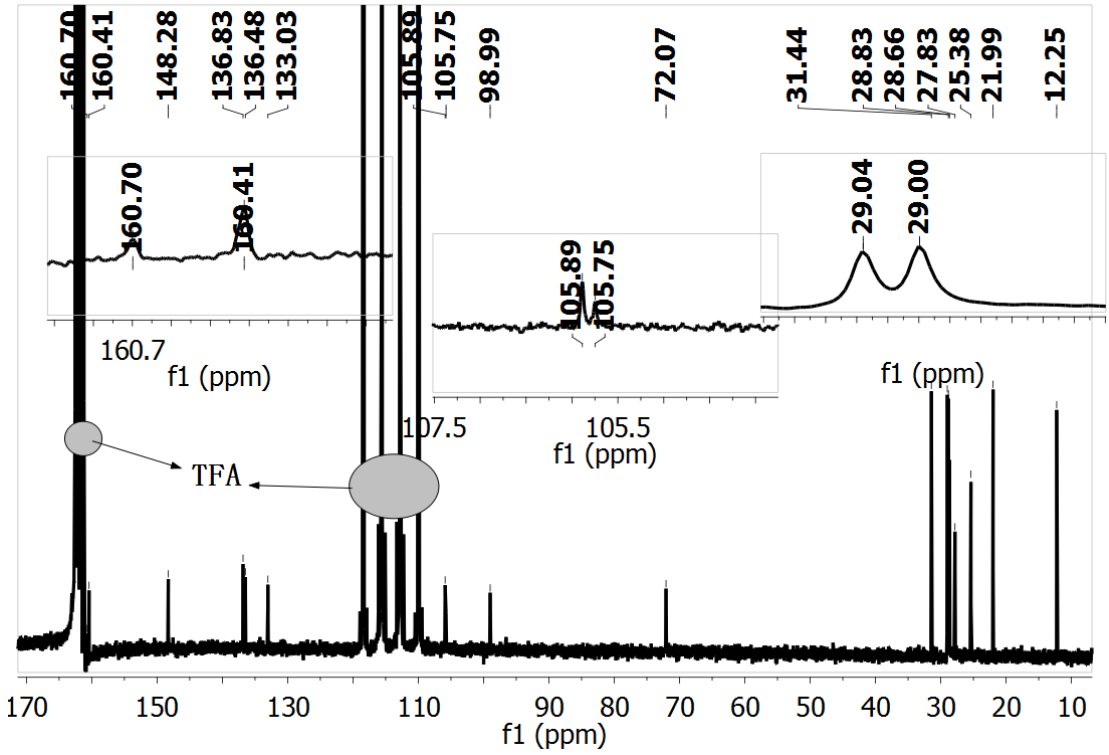


Figure S4. ^{13}C NMR spectrum of 4N4OPz in TFA.

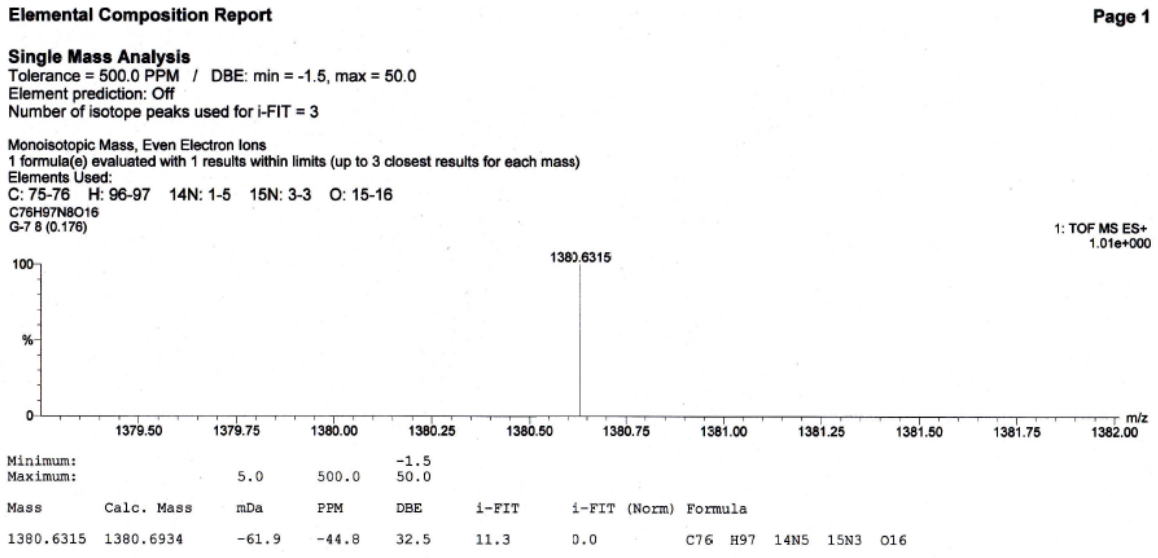


Figure S5. HR-MS spectrum of 4N4OPz.

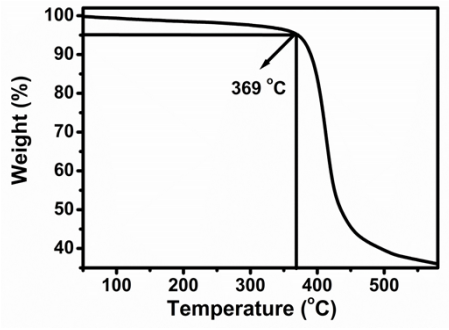


Figure S6. TGA curve of 4N4OPz.

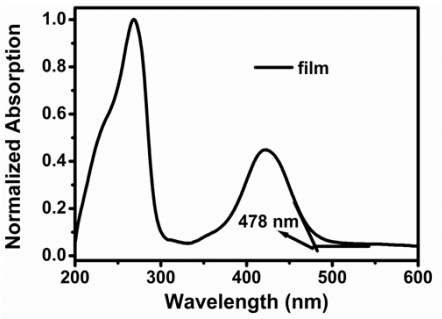


Figure S7. Normalized optical absorption of 4N4OPz at thin film state on a quartz plate.

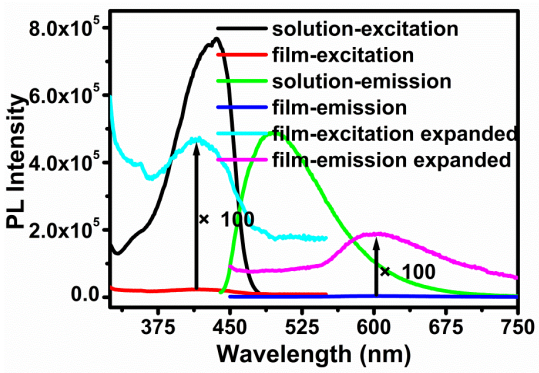


Figure S8. Fluorescence excitation and emission spectra of 4N4OPz in $CHCl_3$ and thin film on a quartz plate (λ_{ex} = 426 nm for solution and 421 nm for film).

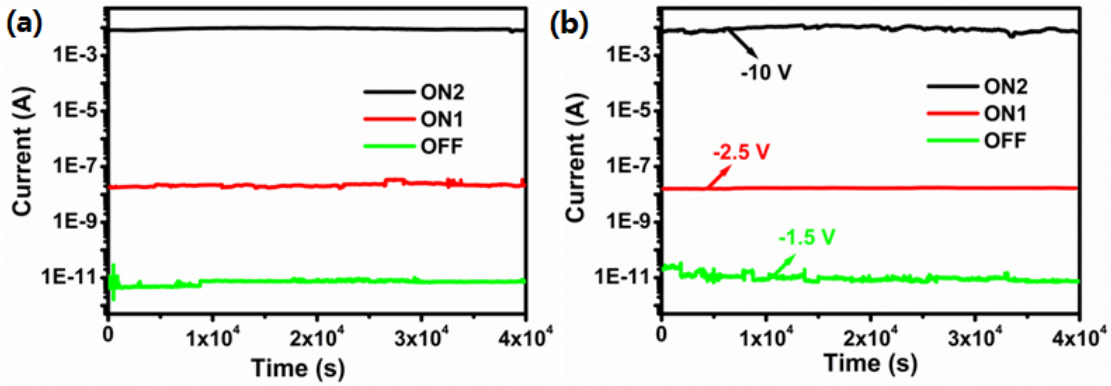


Figure S9. (a) Stability of the memory device (ITO/4N4OPz/Al) in three states under a constant "read" voltage of -1V at 50 °C. (b) Stability of the memory device (ITO/4N4OPz/Al) in three states under a constant "read" voltage of -1.5 V on the OFF state, -2.5 V on the ON1 state, and -10 V on the ON2 state at 25 °C.

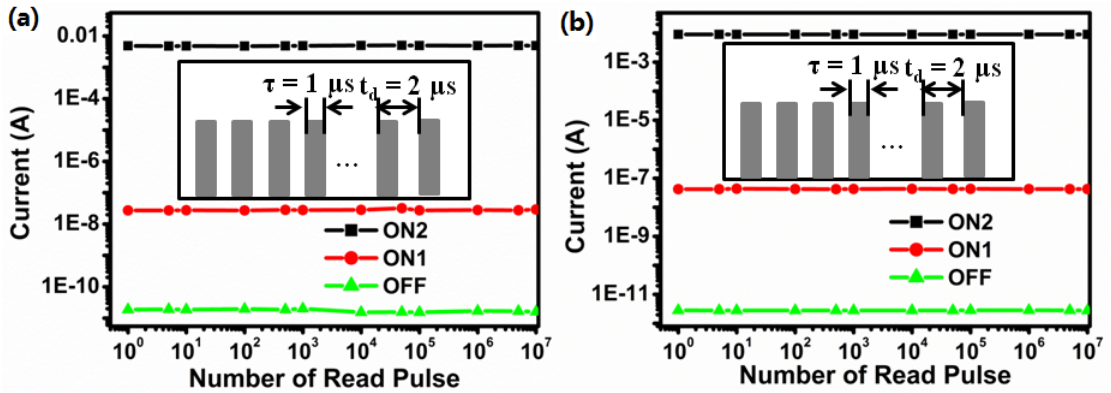


Figure S10. Stimulus effect of read pulse of -1 V on the ON2, ON1 and OFF states (a: ITO/4N4OPz/Al; b: ITO/4N4OPz/LiF/Al). Inset shows the pulse shapes of the measurements.

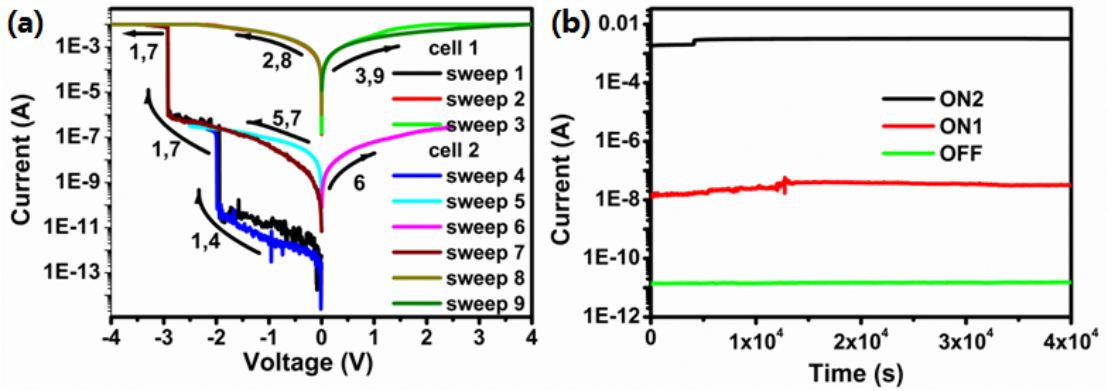


Figure S11. (a) I-V characteristics of the memory device (ITO/4N4OPz/Pt) fabricated with 4N4OPz. (b) Stability of the memory device (ITO/4N4OPz/Pt) in three states under a constant "read" voltage of -1V at 25 ^{o}C.