Electronic Supplementary Information for

Effect of π-spacer between donor and acceptor on small molecule-based data-storage device performance

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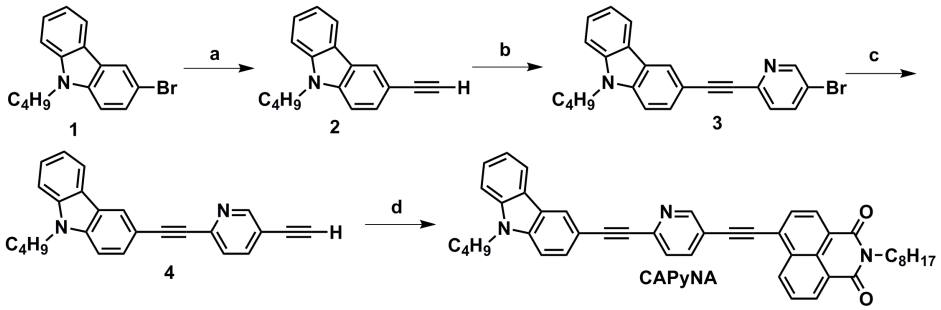
1 Experimental Section

1.1 Materials

Carbazole and PPh_3 (CP, Sinopharm Chemical Reagent Co. Ltd., China), NBS and 1-bromobutane (AR, Sinopharm Chemical Reagent Co. Ltd., China), 4-bromo-1,8-naphthalic anhydride (97%, Liaoning Liangang Dyes Chemical Co. Ltd., China), trimethylsilylacetylene, $Pd(PPh_3)_2Cl_2$, CuI, 5-bromo-2-iodopyridine and octan-1-amine were purchased from commercial sources (TCI and Alfa Aesar), diisopropylamine, diethylamine and triethylamine (AR, Sinopharm Chemical Reagent Co. Ltd., China) were distilled under argon atmosphere prior to use. All other reagents are used as received unless further instruction. The detailed synthesis route of CAPyNA was shown in Scheme S1.[S1]

1.2 Preparation of CAPyNA

Scheme S1. Synthetic routes of CAPyNA



Reaction Conditions:

a) trimethylsilylacetylene, $Pd(PPh_3)_2Cl_2$, CuI , PPh_3, $(i\text{-}Pr)_2NH$, 70 °C, 18h; b) 5-bromo-2-iodopyridine, $Pd(PPh_3)_2Cl_2$, CuI, PPh_3, $(C_2H_5)_2NH$, RT, 18h; c) trimethylsilylacetylene, $Pd(PPh_3)_2Cl_2$, CuI, PPh_3 , $(C_2H_5)_3N$, 70 °C , 18h; d) 6-bromo-2-octyl-1*H*-benzo[*de*]isoquinoline-1,3(2*H*)-dione, $Pd(PPh_3)_2Cl_2$, CuI, PPh_3, $(i\text{-}Pr)_2NH$, 70 °C, 18h.

Synthesis of Compound 1. In a flask, covered with aluminum foil, a stirred solution of 9-butyl-9*H*-carbazole (4.46 g, 20.0 mmol) in $CHCl_3$ (100 mL) was cooled to 0 ^oC. NBS (3.56 g, 20.0 mmol) was added in small portions. The mixture was allowed to warm to room temperature overnight. $CHCl_3$ was evaporated and the crude product was purified by extraction with diethylether and water. After same work up as above, final product was obtained as a yellow oil (5.4 g, 89%). ^1H NMR (400 MHz, CD_3OD) δ (ppm): 8.21 (s, 1H), 8.06 (d, J = 8.0 Hz, 1H), 7.58 – 7.36 (m, 4H), 7.21 (d, J = 6.7 Hz, 1H), 4.35 (t, J = 7.1 Hz, 2H), 1.81 (dd, J = 15.0, 7.4 Hz, 2H), 1.36 (dd, J = 15.3, 7.4 Hz, 2H), 0.94 (t, J = 7.4 Hz, 3H).

Synthesis of Compound 2. A mixture of 3-bromo-9-butyl-9*H*-carbazole (1.21 g, 4 mmol), trimethylsilylacetylene (0.47 g, 4.8 mmol), $Pd(PPh_3)_2Cl_2$ (28 mg, 0.04 mmol), CuI (7.6 mg, 0.04 mmol), triphenylphosphine (21 mg, 0.08 mmol) and diisopropylamine (20 mL) were heat at 70 ^oC for 18 h. The volatiles were removed and the residue dissolved in diethylether and passed through a short silica gel column. The eluant was concentrated to dryness and redissolved in dichloromethane/methanol mixture (1:2). It was treated with sodium hydroxide (0.16 g, 4 mmol) overnight. The reaction was quenched by the addition of water and the organic product was extracted into diethylether. The ethereal extract was dried over anhydrous $MgSO_4$ and evaporated to yield the crude product. It was further purified by column chromatography using hexane/dichloromethane mixture (15:1) as eluent. Yield: 0.5 g (51%), light yellow solid. ^1H NMR (400 MHz, DMSO-d_6) δ (ppm): 8.34 (s, 1H), 8.21 (d, J = 7.7 Hz, 1H), 7.66 – 7.46 (m, 4H), 7.23 (d, J = 7.5 Hz, 1H), 4.40 (t, J = 7.0 Hz, 2H), 4.04 (s, 1H), 1.76 – 1.70 (m, 2H), 1.30 – 1.26 (m, 2H), 0.87 (t, J = 7.4 Hz, 3H).

Synthesis of Compound 3. A mixture of 9-butyl-3-ethynyl-9*H*-carbazole (1.0 g, 4 mmol), 5-bromo-2-iodopyridine (1.59 g, 5.6 mmol), $Pd(PPh_3)_2Cl_2$ (28 mg, 0.04 mmol), CuI (7.6 mg, 0.04 mmol), triphenylphosphine (21 mg, 0.08 mmol) and diethylamine (20 mL) were heat at RT for 18 h. It was further purified by column chromatography using hexane/dichloromethane mixture (1.5:1) as eluent. Yield: 0.68 g (84%), yellow solid. ^1H NMR (400 MHz, $CDCl_3$) δ (ppm): 8.68 (s, 1H), 8.37 (s, 1H), 8.09 (d, J = 1.1 Hz, 1H), 7.82 (dd, J = 8.3, 2.1 Hz, 1H), 7.69 (dd, J = 8.5, 0.9 Hz, 1H), 7.52 – 7.38 (m, 4H), 7.29 – 7.26 (m, 1H), 4.31 (t, J = 7.2 Hz, 2H), 1.92 – 1.80 (m, 2H), 1.48 – 1.35 (m, 2H), 0.96 (t, J = 7.4 Hz, 3H).

Synthesis of Compound 4. A mixture of compound **3** (1.21 g, 3 mmol), trimethylsilylacetylene

(0.36 g, 3.6 mmol), $Pd(PPh_3)_2Cl_2$ (21 mg, 0.03 mmol), CuI (5.7 mg, 0.03 mmol), triphenylphosphine (15.7 mg, 0.06mmol) and triethylamine (20 mL) were heat at 70 ^oC for 18 h. The volatiles were removed and the residue dissolved in diethylether and passed through a short silica gel column. The eluent was concentrated to dryness and re-dissolved in dichloromethane/methanol mixture (1:2). It was treated with sodium hydroxide (0.12 g, 3 mmol) overnight. The reaction was quenched by the addition of water and the organic product was extracted into diethylether. The ethereal extract was dried over anhydrous $MgSO_4$ and evaporated to yield the crude product. It was further purified by column chromatography using petroleum ether/dichloromethane mixture (1:1) as eluent. Yield: 0.6 g (57%), yellow solid. ^1H NMR (400 MHz, $CDCl_3$) δ (ppm): 8.72 (s, 1H), 8.38 (s, 1H), 8.09 (d, J = 7.7 Hz, 1H), 7.77 (d, J = 8.1 Hz, 1H), 7.70(d, J = 8.4 Hz, 1H), 7.55 – 7.35 (m, 4H), 7.33 – 7.19 (m, 1H), 4.31 (t, J = 7.2 Hz, 2H), 3.31 (s, 1H), 2.00 – 1.79 (m, 2H), 1.41 – 1.36 (m, 2H), 0.96 (t, J = 7.3 Hz, 3H).

Synthesis of Compound 5. A mixture of compound **4** (0.348 g, 1 mmol), 6-bromo-2-octyl-1*H*-benzo[*de*]isoquinoline-1,3(2*H*)-dione (0.388 g, 1 mmol), $Pd(PPh_3)_2Cl_2$ (7 mg, 0.01 mmol), CuI (1.9 mg, 0.01 mmol), triphenylphosphine (5.3 mg, 0.02 mmol) and diisopropylamine (5 mL) were heated at 70 ^oC for 18 h. It was further purified by column chromatography using petroleum ether/dichloromethane mixture (1:2) as eluent. Yield: 0.25 g (38%), deep yellow solid. The ^1H NMR spectrum of CAPyNA was shown in Fig. S3. ^1H NMR (400 MHz, $CDCl_3$) δ (ppm): 8.92 (s, 1H), 8.68 (dd, J = 14.8, 7.8 Hz, 2H), 8.57 (d, J = 7.6 Hz, 1H), 8.40 (s, 1H), 8.08 (d, J = 7.7 Hz, 1H), 7.98 (d, J = 7.3 Hz, 1H), 7.88 (t, J = 7.7 Hz, 1H), 7.75 (s, 1H), 7.64 (s, 1H), 7.50 (t, J = 7.6 Hz, 1H), 7.45 – 7.36 (m, 2H), 7.31 – 7.26 (m, 2H), 4.31 (t, J = 7.2 Hz, 2H), 4.22 – 4.14 (m, 2H), 1.91 – 1.82 (m, 2H), 1.74 – 1.72 (m, 2H), 1.45 – 1.26 (m, 12H), 0.96 (t, J = 7.3 Hz, 3H), 0.87 (t, J = 6.5 Hz, 3H). HRMS: calcd for $C_{45}H_{41}N_3O_2$ $[M + H]^+$ 656.3272, found 656.3248.

1.3 Memory Device Fabrication

The memory device was fabricated on the indium-tin oxide (ITO)-coated glass, with the configuration of ITO/CAPyNA/Al. Before the fabrication of the organic layer, the ITO glass was pre-cleaned with deionized water, acetone, and alcohol, in that order, in an ultrasonic bath for 20 min, respectively. A 10 mg mL^{-1} of well-dissolved CAPyNA solution in cyclohexanone was first filter through 0.45 μm pore size of syringe filter. Then, the filtered solution was spin-coated onto

the ITO glass at a speed rate of 1200 rpm for 40 s and the solvent was removed in a vacuum chamber at 10^{-1} Pa and 60 ^{o}C for 12 h. A layer of Al, about 100 nm in thickness and 0.5 mm in diameter, was thermally evaporated and deposited onto the organic film surface at about 10^{-6} Torr through a shadow mask to form the top electrode.

1.4 Measurements

All electrical measurements of the device were characterized under ambient conditions, without any encapsulation, using a Agilent B1500A semiconductor parameter analyzer equipped with HP 8110A pulse generator. NMR spectra were obtained on an Inova 400 MHz FT-NMR spectrometer. High-resolution mass spectra (HRMS) were determined on Micromass GCT-TOF mass spectrometer with ESI resource. UV-vis absorption spectra were carried out at room temperature from 250 to 600 nm with a Shimadzu UV-3600 spectrophotometer. Thermo gravimetric analysis (TGA) was conducted on a TA instrument Dynamic TGA 2950 at a heating rate of 10 ^{o}C·min^{-1} under a nitrogen flow rate of 50 mL min^{-1}. SEM image was taken on a Hitachi S-4700 scanning electron microscope. Atomic force microscopy (AFM) measurements were performed by using a MFP-3DTM (Digital Instruments/Asylum Research) AFM instrument in tapping mode. Cyclic voltammetry was performed at room temperature using an ITO working electrode, a reference electrode Ag/AgCl and a counter electrode (Pt wire) at a sweep rate of 0.1 V/s (CorrTest CS Electrochemical Workstation analyzer). A 0.1 M solution of tetrabutylammonium perchlorate (TBAP) in anhydrous acetonitrile was used as an electrolyte. X-ray diffraction (XRD) analysis was performed on film using a Shimadzu XRD-6000 spectrometer with a Cu KR monochromatic radiation source at 40 kV and 30 mA.

2. Thermal stability

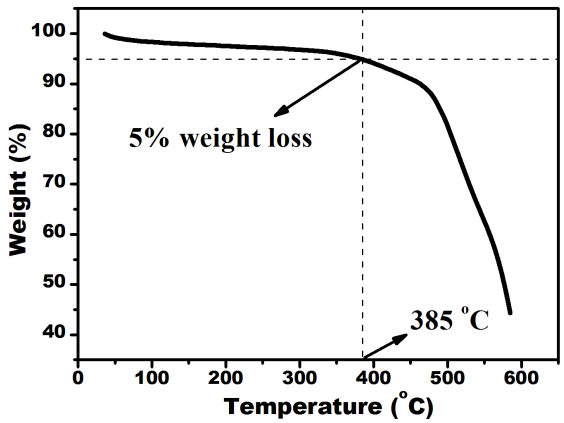


Figure S1. TGA curve of **CAPyNA** at a heating rate of 10 ^{o}C min^{-1} under a nitrogen atmosphere.

3. Device structure and SEM image

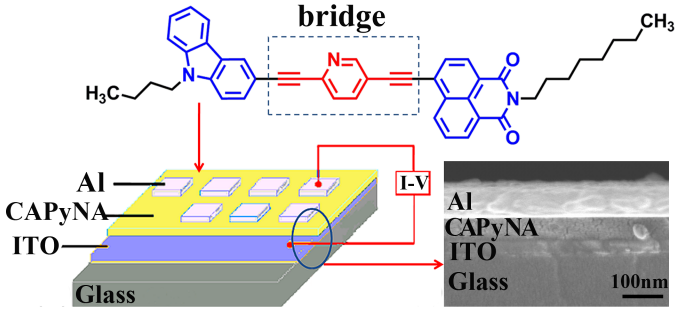


Figure S2. Molecular structure of CAPyNA (top); schematic diagram of the sandwich-structure memory device (bottom-left) and SEM image of its cross-section view (bottom-right).

4. ^{1}H NMR spectrum

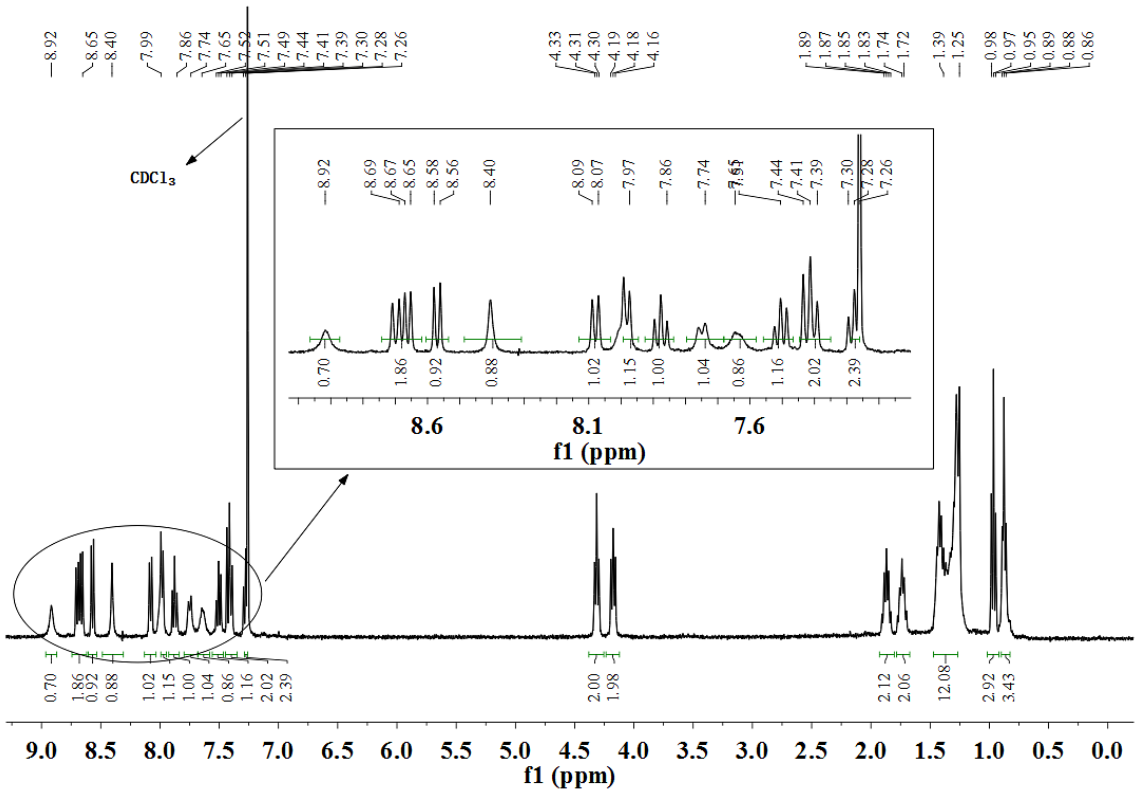


Figure S3. ^{1}H NMR spectrum of **CAPyNA** in $CDCl_3$.

5. UV-vis absorption spectra

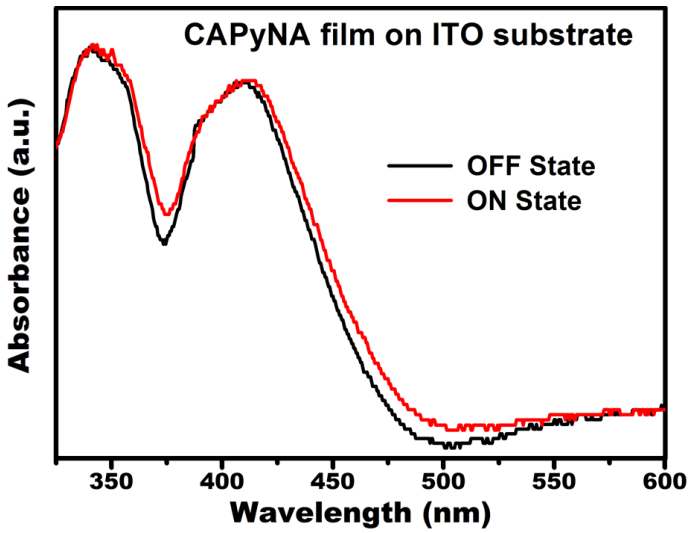


Figure S4. UV-vis absorption spectra of the CAPyNA film onto ITO substrate in the OFF and ON states.

6. *I–V* curves

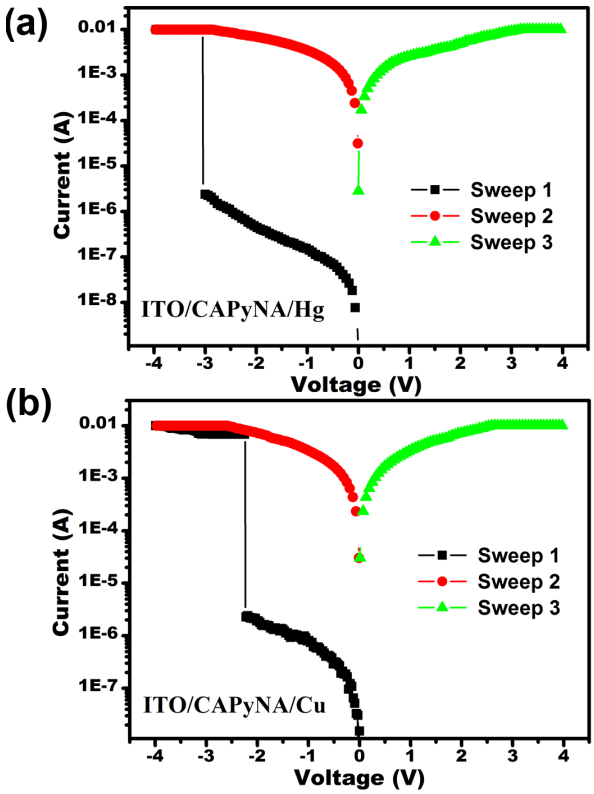


Figure S5. *I–V* characteristics of the CAPyNA memory devices based on ITO-Hg (a) and ITO-Cu electrodes (b), respectively.

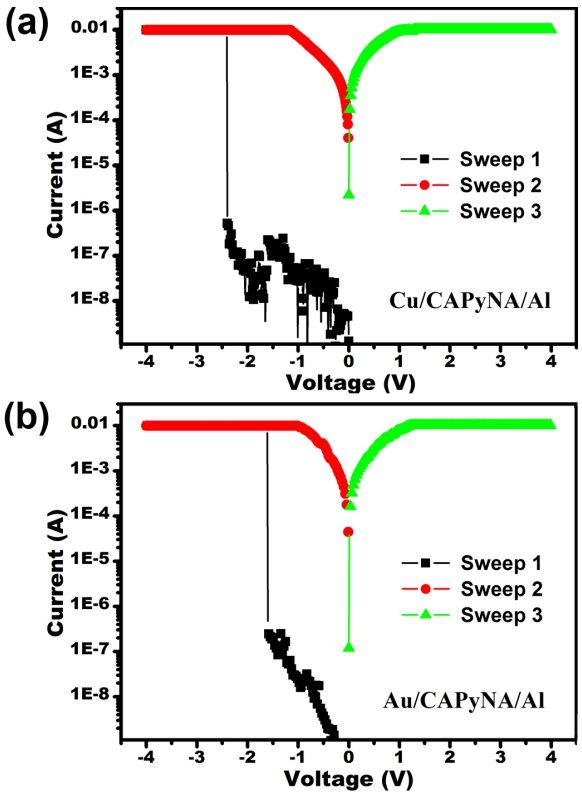


Figure S6. *I–V* characteristics of the CAPyNA memory devices based on Cu-Al (a) and Au-Al electrodes (b), respectively.

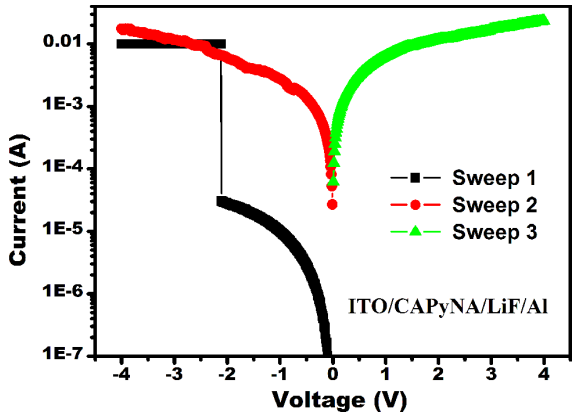


Figure S7. *I–V* characteristics of the CAPyNA memory device based on ITO-Al electrode with LiF (1–2 nm) insulator layer between CAPyNA and Al electrode.

7. Temperature-resistance curve

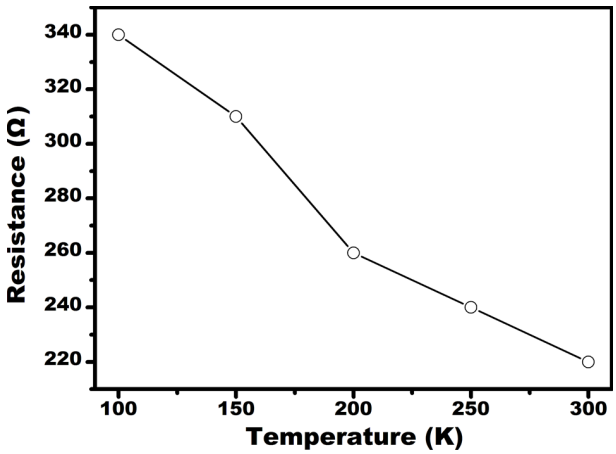


Figure S8. The resistance of the ON state of the ITO/CAPyNA/Al plotted with respect to the temperature.

8. The cross-section SEM

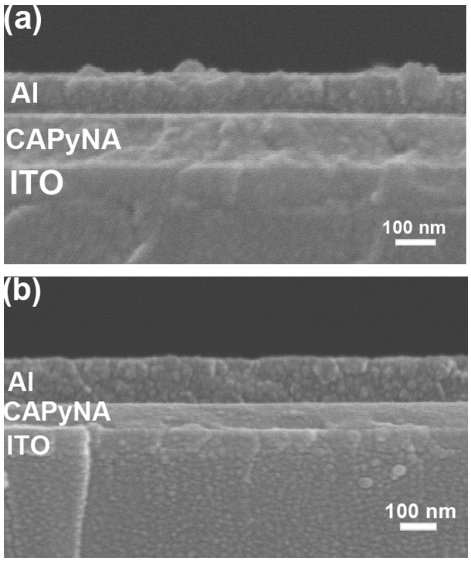


Figure S9. (a) The cross-section SEM of one device with no voltage. (b) The cross-section SEM of one device with an applied voltage.

9. Surface potential AFM image

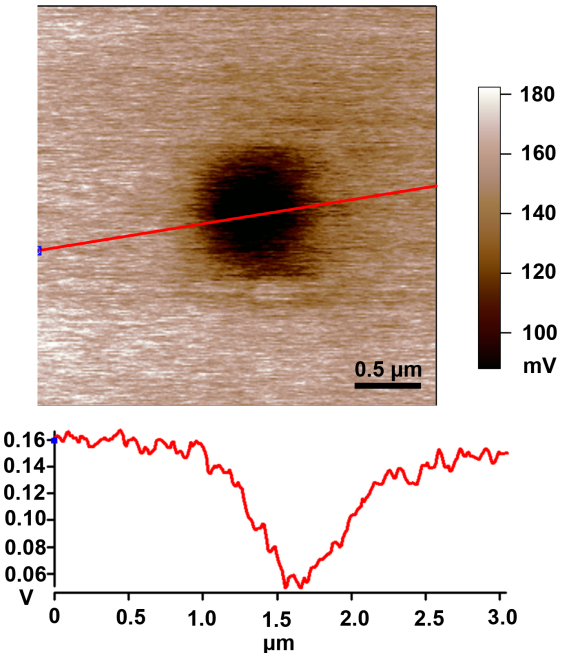


Figure S10. Scanning surface potential AFM image of CAPyNA film with ITO as bottom electrode. The dark region was pre-treated with –5 V.

10. *I–V* curve

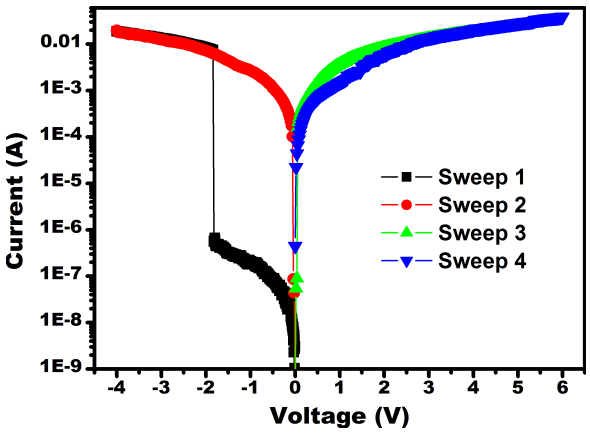


Figure S11. *I–V* characteristic of the CAPyNA memory device.

11. *I–V* curves of different film thickness

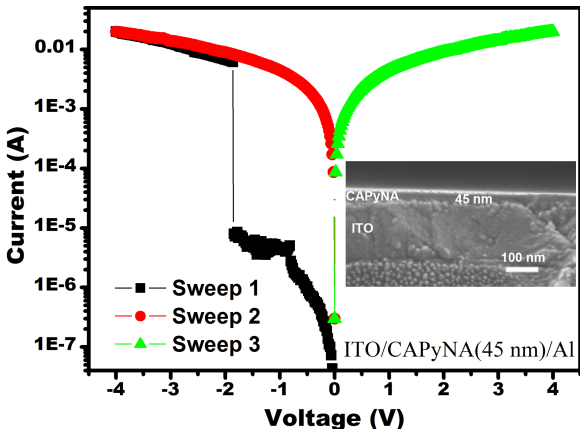


Figure S12. *I–V* curve for the device fabricated with CAPyNA film of 45 nm.

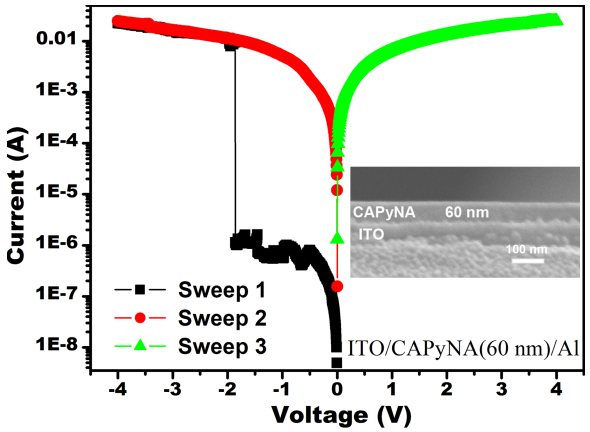


Figure S13. *I–V* curve for the device fabricated with CAPyNA film of 60 nm.

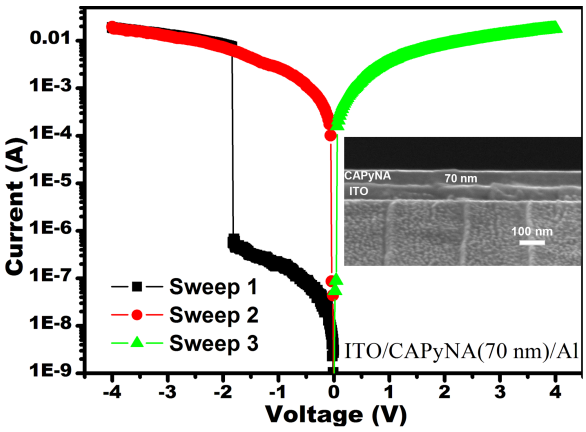


Figure S14. *I–V* curve for the device fabricated with CAPyNA film of 70 nm.

12. Theoretical simulation

Molecular calculations studied in this work have been performed through Gaussian 03 program package.[S2]

13. References

[S1] A. L. Thompson, T. S. Ahn, K. R. J. Thomas, S. Thayumanavan, T. J. Martnez and C. J. Bardeen, *J. Am. Chem. Soc*., 2005, **127**, 16348.

[S2] Gaussian 03, Revision B. 04 Gaussian, Inc., Wallingford, CT 2004.