Supporting Information

Conjugated Zwitterion-inspired Flexible Ternary Resistive Memory from Rhodamine Dyes

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Materials: Rh B was purchased from Alfa Aesar and R 6G was purchased from TCI Shanghai Co., Ltd. Sulfuric acid was purchased from Chinasun Specialty Products Co., Ltd. 30% H_2O_2 solution was purchased from Tokyo Chemical Industry. Triethylamine was purchased from Shanghai Titan Scientific Co., Ltd. Ethanol was purchased from Shanghai LingFeng Chemical Reagent Co., Ltd. The octyl phosphoric acid was purchased from Shanghai yuanye Bio-Technology Co., Ltd. All reagents and solvents were used without further purification.

Memory Fabrication: ITO substrates were cleaned by detergents and were sonicated by deionized water, acetone, and ethanol for 10 minutes, respectively. Then the cleaned substrates were dried with N_2 gas. The dried ITO substrates were treated with oxygen plasma for 10 min. Rh B and R 6G solutions were spin-coated on ITO substrates with a speed of 500 rpm for 5 s, followed by 2000 rpm for 20 s in a glove box. Then an array of Al top electrodes was deposited through thermal evaporation of Al under a vacuum of 1×10^6 Torr.

Modification of ITO substrates with OPA: The cleaned ITO substrates were treated with piranha solution for 3 s and cleaned with deionized water, then dried with N_2 gas. The treated ITO substrates were immersed in anhydrous ethanol solution with octyl phosphoric acid (OPA 1 mmol/L) for one night. After that, ITO substrates were cleaned by anhydrous ethanol, and dried with N_2 gas. Then the dried ITO substrates were annealed under vacuum at 65 ^{o}C for 8 h. The annealed ITO substrates were sonicated again in a trimethylamine / ethanol solution with a volume ratio of 1/20 for 30 minutes. Finally, the ITO substrates were washed by absolute ethanol and dried with N_2 gas.

Measurements and Characterizations methods: Fourier Transform infrared spectroscopy (FT-IR) tested by VERTEX70 from Bruker. The thickness and roughness tested by atomic force microscopy (AFM) from an MFP-3D (Digital Instruments/Asylum Research) AFM instrument. The cross-section was tested by SEM Hitachi S-4700. Cyclic voltammograms (CVs) tested redox potential by a CorrTest CS Electrochemical Workstation Analyzer. The UV-visible absorption spectra were tested by a Shimadzu UV-3600 spectrometer at room temperature. The thermogravimetric analysis tested with a heating rate of 10 °C min^{-1} by PerkinElmer Diamond thermogravimetry/differential thermal analysis instrument. The I–V and I-T curve of memristors tested by 4200-SCS semiconductor characteristic analysis system from Keithley. Flexible substrates were bent by homemade bending instrument.

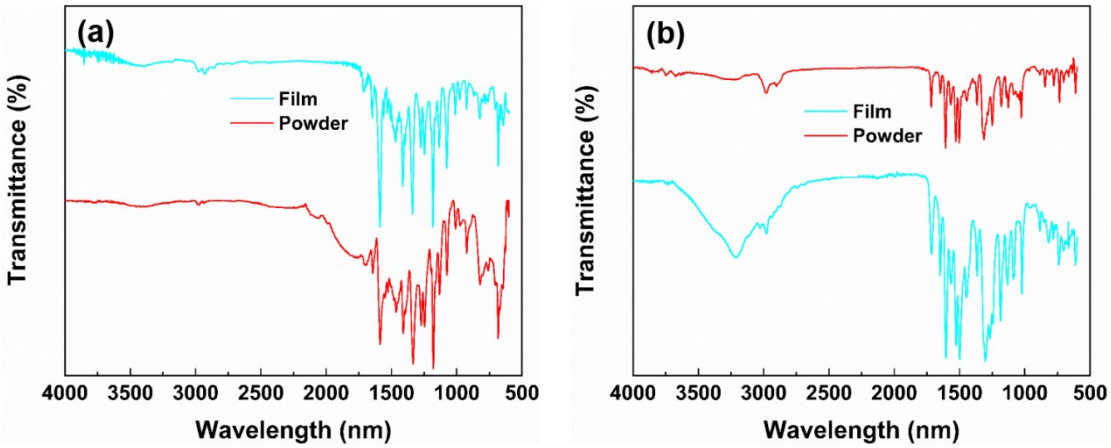

Figure S1. FT-IR measurements of raw material and film: (a) Rh B and (b) R 6G.

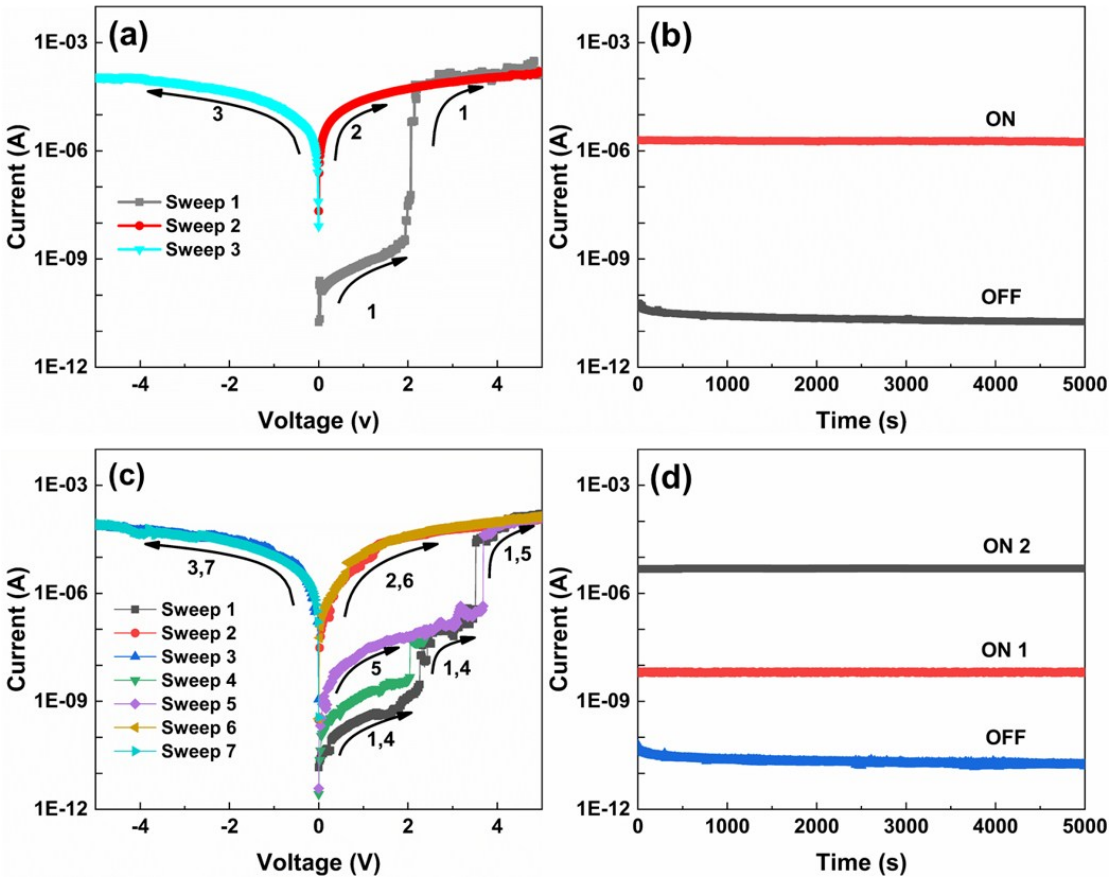

Figure S2. Typical (a) binary and (c) ternary memory behaviors of R 6G-based devices. (b, d) Retention stability of each state under continuous 0.1 V stress.

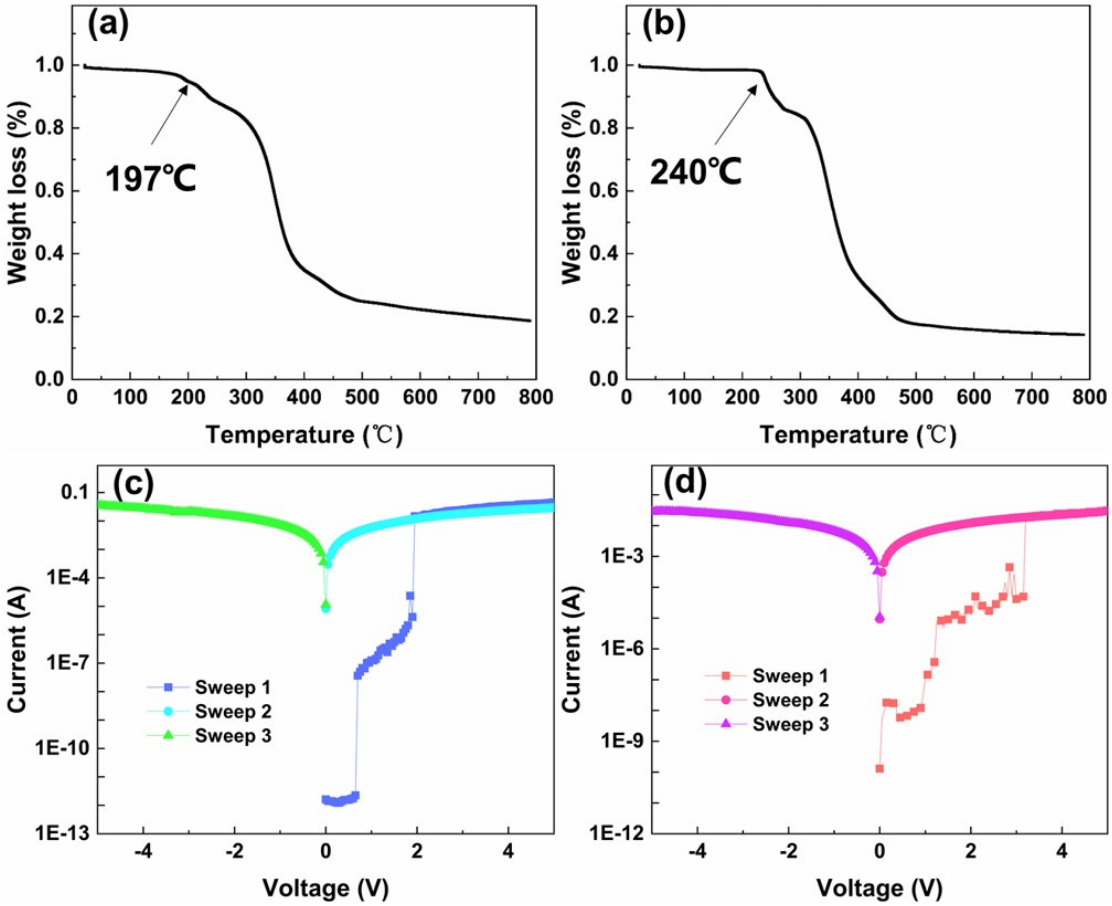

Figure S3. The Thermogravimetric analysis (TGA) measurement of Rh B (a) and R 6G (b) The typical ternary I – V curve of Rh B (c) and R 6G (d) at 80 °C.

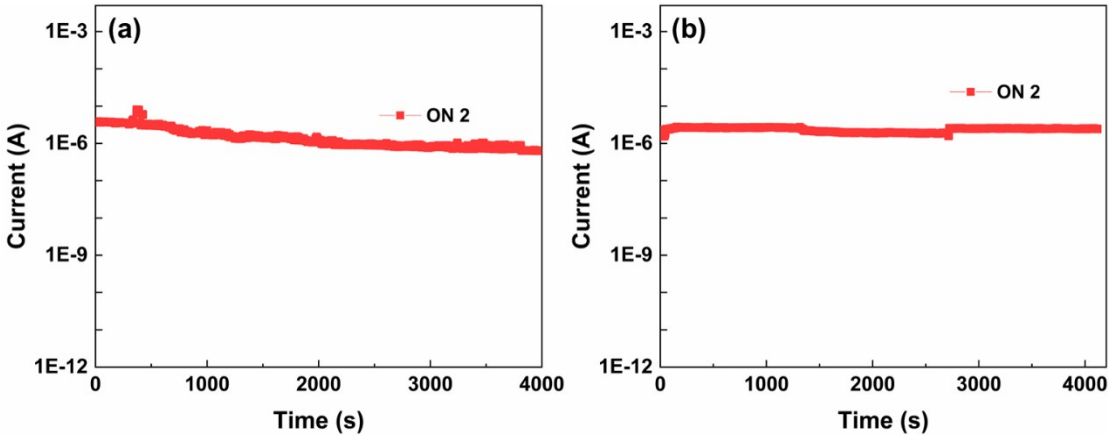

Figure S4. Retention stability of ON2 state under continuous 0.1 V stress of (a) Rh B- and (b) R 6G-based devices.

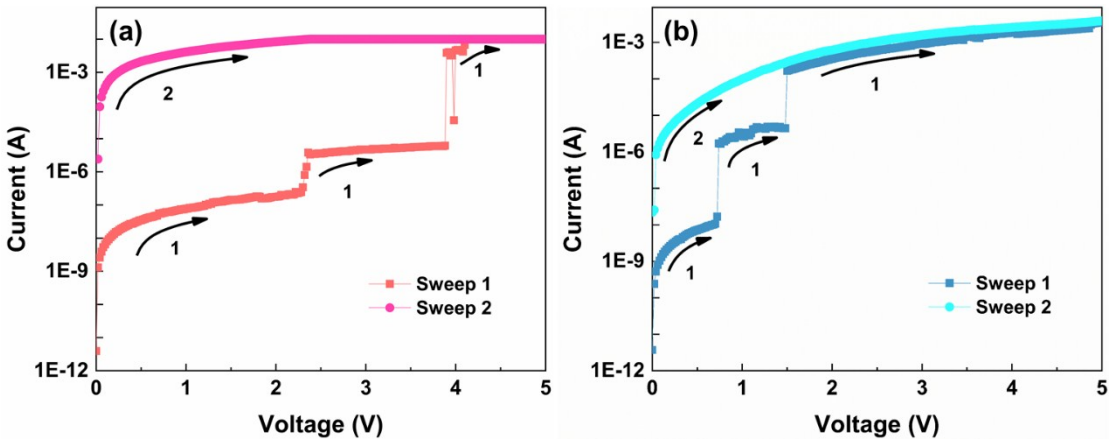

Figure S5. Memory behaviors of (a) Rh B- and (b) R 6G-based devices in pure oxygen environments.

Table S1. Summary of performances of some typical one-time programming memories.

Structure	Switch voltage (V)	Programming current (A)	Switch speed (ns)	Retention time (s)	Operation temperature (°C)	Cell area (mm^2)	Cell thickness (nm)	Physical security level	Ref
ITO/MH-b-PI/Al	-1.91±0.65	(2.63±1.22)×10^{-4}	-	10^4	RT	0.04	50–55	flexibility	1
ITO/PTSi-alt-PDISi/ Au	1.7	10^4	-	4×10^3	RT	0.0225	45	-	2
r-rGO/ PVK/Al	1.1	10^4	-	1.2×10^4	RT-45	0.04	-	30% Stretching	3
Al/PECIC/ITO	-2.28	10^4	-	2.88×10^4	RT	0.3	100	annealing at 130 °C	4
ITO/d-poly(Bb-A)/Al	2.2–3.2	10^4	-	10^4	RT	-	-	-	5
Al/P(INDISi-alt-CzSi)/ ITO/PET6	0.5/1	3.3–5.6×10^5	121/115	2.34×10^4	RT	-	100	flexibility	6
Al/boron(III)-based/ ITO	1.6-2.2 2.6-3.4	1:10^3:10^6	-	>10^4	RT	-	123	-	7
ITO/Spiro-OMeTAD/Al	-	1:10^{-4}:10^{-7}	-	10^4	RT	0.78	325	flexibility	8
Au/TPAPAM-GOQDs/ITO	-1.31, -1.02	10^{-5}	-	10^{-2}	RT	-	130	-	9
ITO/MHPI/Al	2.1/2.8	1:10^5:10^6	-	10^4	RT	0.36	50–60	inert atmosphere	10
Al/ Rhodamine/ITO	2.0/3.4 average	10^6:10^4:6	-	>5×10^3	RT-100	0.78	47	pure oxygen / flexibility	This work

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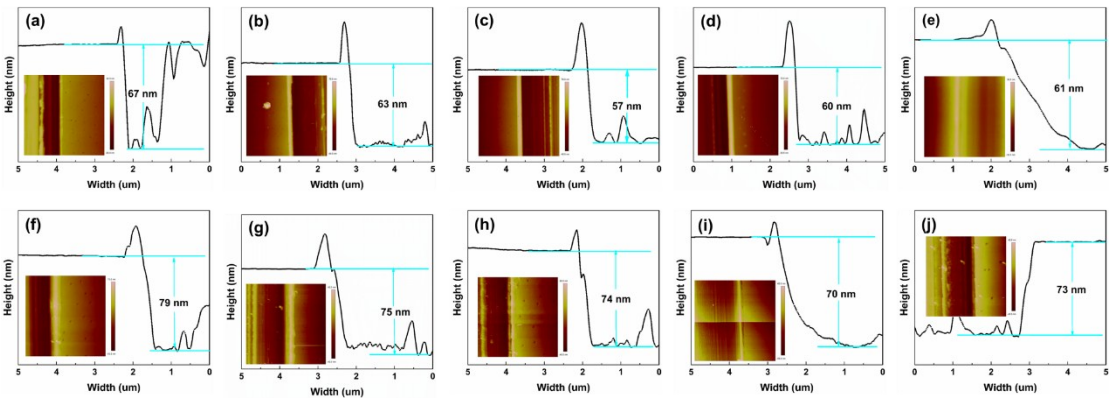

Figure S6. The cross-section images show the thickness with different spin coating speeds by the measurement of AFM, R 6G films (a) 1000; (b) 2000; (c) 3000; (d) 4000; (e) 5000 r/min; Rh B films (f) 1000; (g) 2000; (h) 3000; (i) 4000; (j) 5000 r/min.

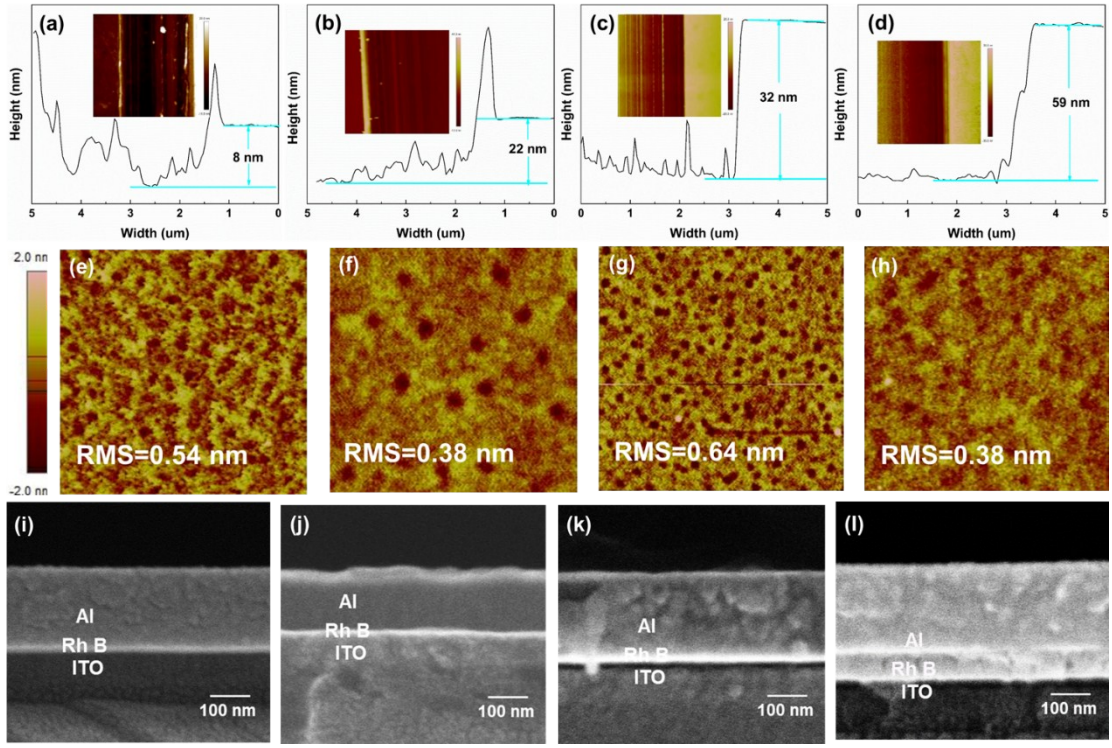

Figure S7. The thickness and roughness images of the Rh B film fabricated at different solubility by the measurement of AFM (a) and (e) 2;(b) and (f) 4;(c) and (g) 6;(d) and (h) 10 mg/ml. The cross-section images show Rh B film different thickness corresponding to the above different solubility by the measurement of SEM (i) 2;(j) 4;(k) 6;(l) 10 mg/ml**.**

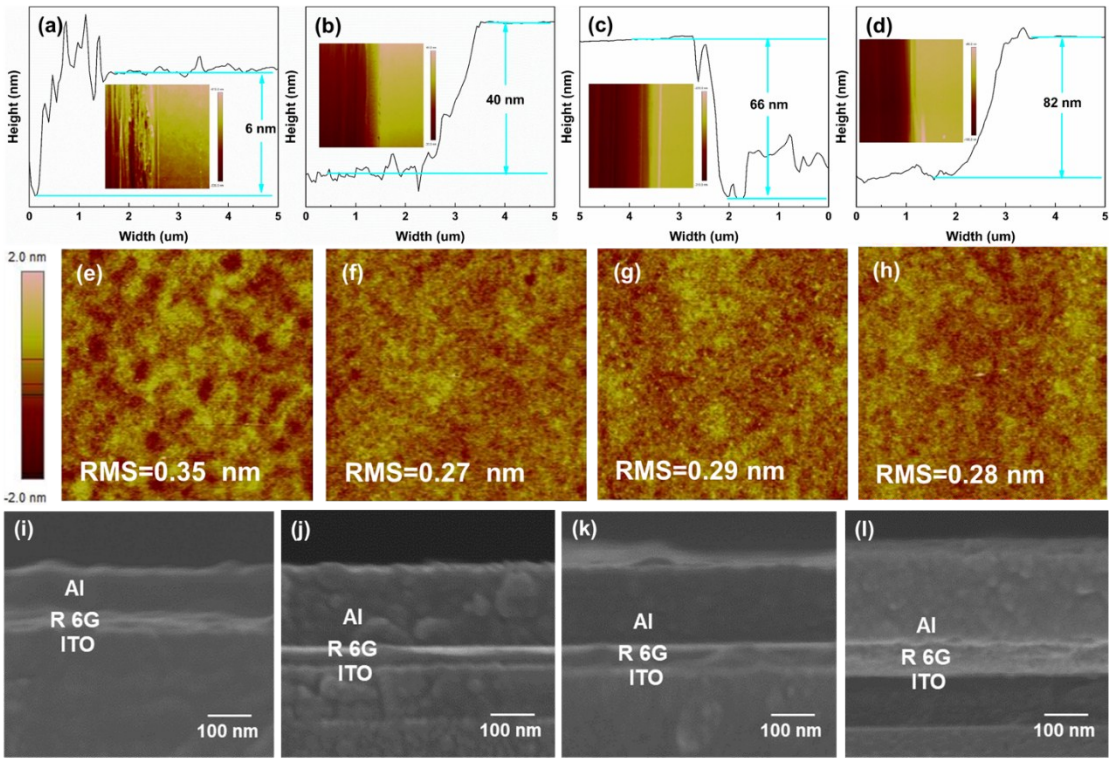

Figure S8. The thickness and roughness images of the R 6G film fabricated at different solubility by the measurement of AFM (a) and (e) 2;(b) and (f) 6;(c) and (g) 8;(d) and (h) 10 mg/ml. The cross-section images show R 6G film different thickness corresponding to the above different solubility by the measurement of SEM (i) 2;(j) 6;(k) 8;(l) 10 mg/ml.

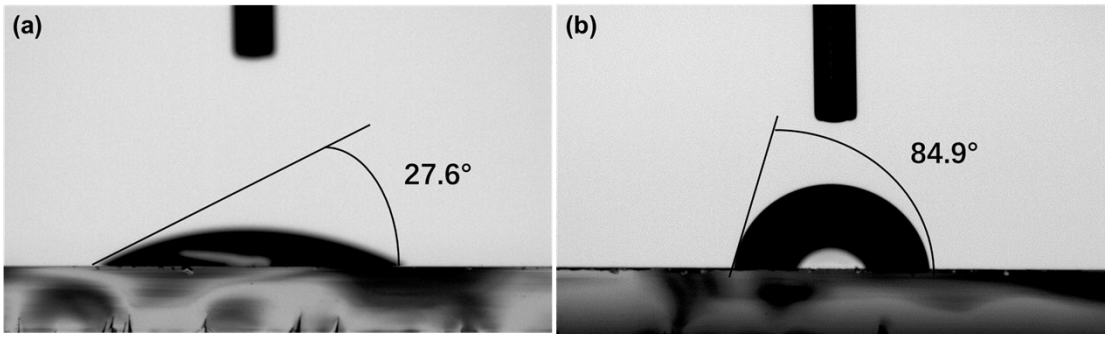

Figure S9. Contact angle test with water on (a) ITO substrates and (b) OPA modified ITO substrates in air, respectively.

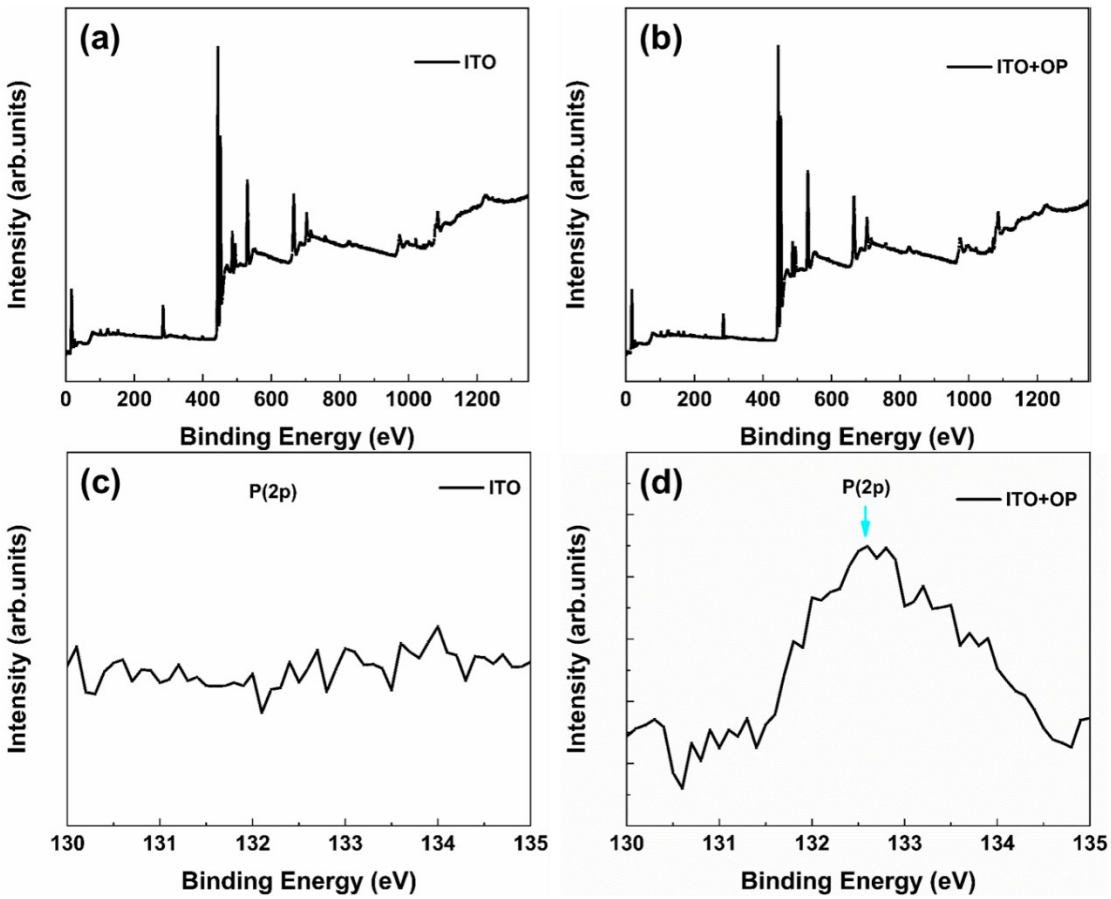

Figure S10. The XPS measurements ITO substrate (a) and (c), OPA modified ITO substrate (b) and (d).

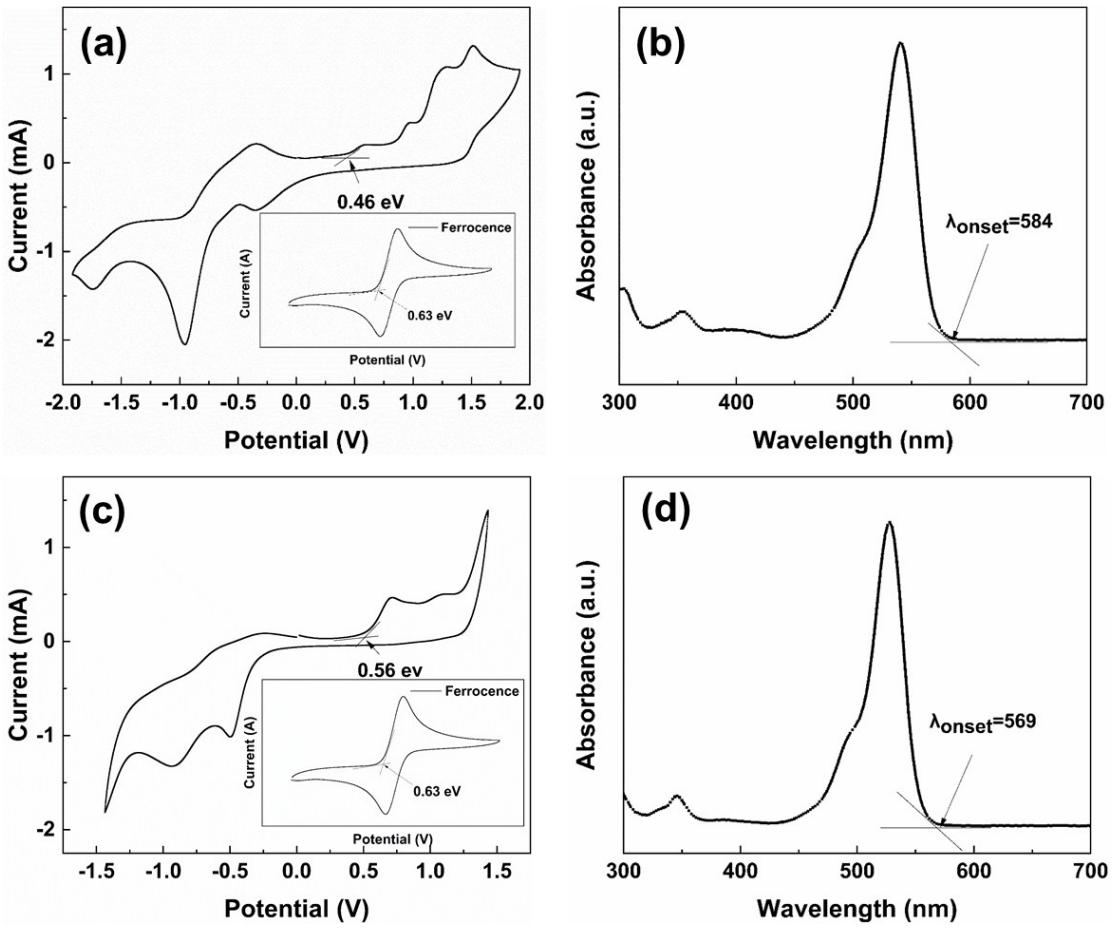

Figure S11. The redox potential of Rh B (a) and R 6G (c) was measured by cyclic voltammetry and the inset shows the cyclic voltammetry of ferrocene as the reference. The UV-visible absorption spectra of Rh B solution (b) and R 6G solution (d).

Table S2. Optical and electronic properties of Rh B and R 6G.

Molecule	E_{onset} (nm)	λ_{onset} (nm)	E_g (eV)	HOMO (eV)	LUMO (eV)	Hole injection barrier (eV)	Electron injection barrier (eV)
Rh B	0.46	584	2.12	-4.83	-2.51	0.17	1.79
R 6G	0.56	569	2.18	-4.73	-2.55	0.07	1.75

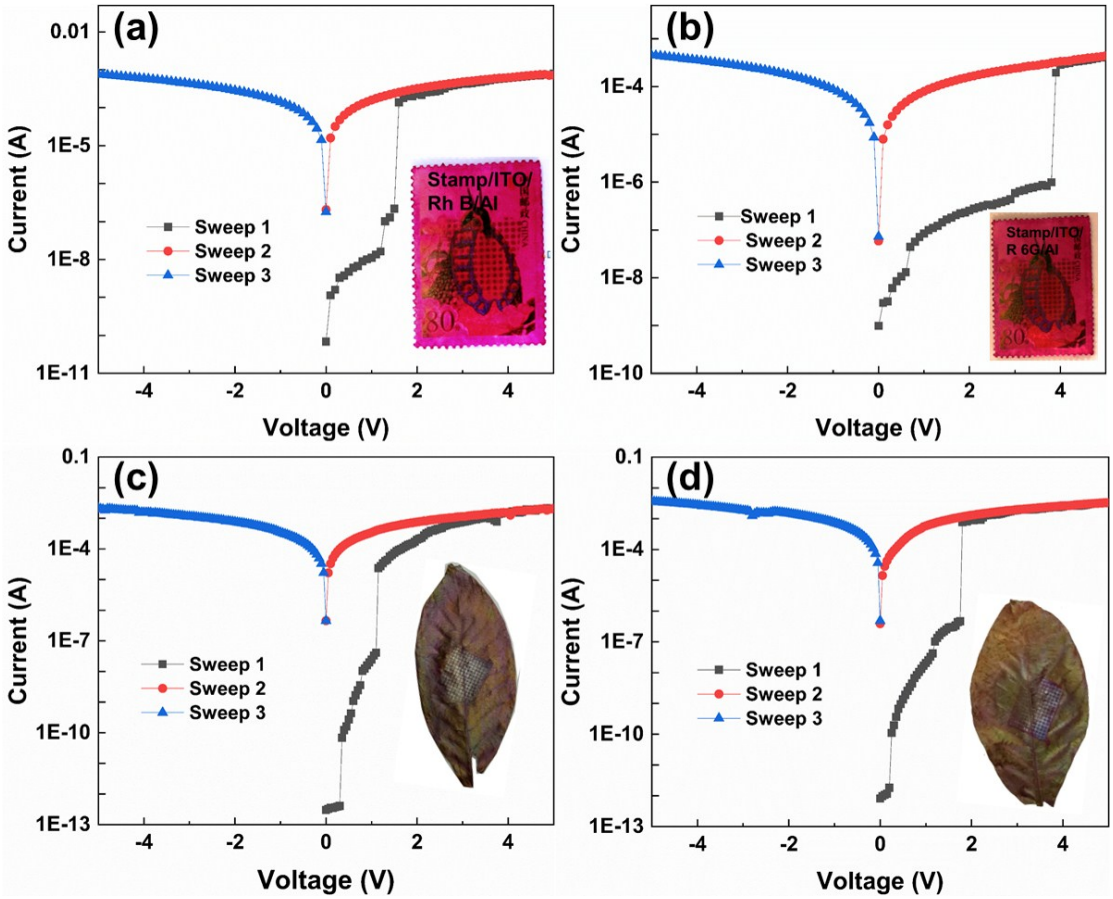

Figure S12. Typical ternary memory behavior Rh B (a) and R 6G (b) on stamps. Typical ternary memory behavior Rh B (c) and R 6G (d) on leaves.

Table S3. R_{square} value of fitting process. Fittings 1~4 refer to four segments in the I-V curves.

R_{square} value	Fitting 1	Fitting 2	Fitting 3	Fitting 4
Rh B	0.99	0.98	0.90	0.94
R 6G	0.99	0.95	0.95	0.99

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