

Supporting Information

Rational design of Ru(II) complex with donor-acceptor-donor structure for organic resistive memory devices

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Part I. Experimental section

Fabrication of memory devices

The Ag/Ru(II) complex/Pt sandwich-structure devices were fabricated on Si wafer by traditional semiconductor process, *e.g.* spin-coating, masking, and physical vapor deposition (PVD). First, the Si wafer was cleaned by ultrasonic in ethanol, deionized water, and acetone for 30 min, respectively. Afterwards, the bottom Pt electrode was deposited onto the wafer by PVD with electron beam assisted sputtering. In order to obtain a good film stack of resistive layers, the Pt/SiO₂/Si was treated by UV-ozone to improve the interface contact between resistive active layer and the bottom electrode. Next, an acetonitrile solution of Ru(II) complex (10 mg/mL) was spin-coated onto the top surface of Pt/SiO₂/Si stack at 1000 rpm for 30 s followed by annealing at 80 °C for half an hour. Finally, about 100-nm-thick top Ag electrode was deposited by DC sputter-deposition at ambient temperature.

Materials and measurements

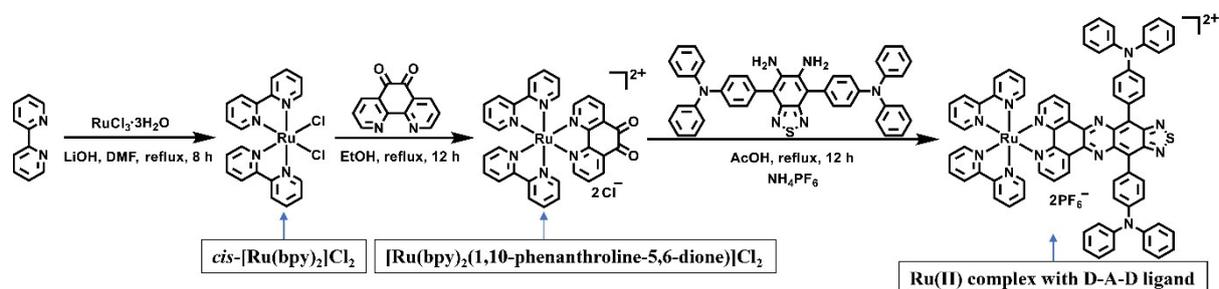
All reagents and chemicals were purchased from commercial sources and used without further purification.

Nuclear magnetic resonance (NMR) spectra were recorded on a Bruker Ultra Shield Plus 400 MHz NMR instrument Avance III-HD 600 MHz spectrometer at 298 K using deuterated solvents (¹H: 600 MHz, ¹³C{¹H}: 150 MHz). Chemical shifts (ppm) were reported relative to tetramethyl-silane. Mass spectrometry was performed using an Agilent 6224 ESI/TOF MS instrument. UV-vis absorption spectra were obtained with a Shimadzu UV-3600 UV-VIS-NIR spectrophotometer. CV curves were performed with a CHI660E electrochemical analyzer by using a glassy carbon as the working electrode, a platinum wire as the auxiliary electrode and an Ag/AgNO₃ as the reference electrode at a scan rate of 100 mV s⁻¹ in acetonitrile solution of 0.1 M Bu₄NPF₆ under a nitrogen atmosphere. It is noted that ferrocene served as the internal standard. SEM experiments were performed on a Hitachi S-4800 FEG Scanning Electron Microscope. Atomic force microscopy (AFM) measurements were carried out by using a Dimension Icon AFM instrument. All electrical measurements of memory devices were performed by using Cascade MPS150 and Keithley 4200A-SCS semiconductor characterization analyzer under ambient conditions. Density functional theory (DFT) was used to optimize the ground-state geometry of the Ru(II) complex at the B3LYP/6-31G(d)/SDD level, and the vibrational frequency calculation was performed to verify the minimum nature of

the optimized structure. The DFT calculation was performed on Gaussian 09 package and the visualization of molecular orbitals was finished by GaussView.

Part II. Synthetic procedures and characterizations

Synthesis of Ru(II) complex with D-A-D ligand



Scheme S1 Synthesis route of Ru(II) complex with D-A-D ligand

Synthesis of *cis*-[Ru(bpy)₂]Cl₂: *cis*-[Ru(bpy)₂]Cl₂ was synthesized according to the literature procedure¹. N, N-dimethylformamide solution (50 mL) of RuCl₃•3H₂O (7.8 g, 29.8 mmol), bipyridine (9.36 g, 60 mmol) and LiCl (8.4 g, 200 mmol) was heated at reflux for 8 h. After the reaction was completed, the mixture was cooled to room temperature, then 250 mL acetone was added, and the resulting mixture was cooled at 0 °C overnight. The purple-red solution was filtered to obtain a dark brown solid, which was washed three times with 25 mL of water and three times with 25 mL of diethyl ether.

Synthesis of [Ru(bpy)₂(1,10-phenanthroline-5,6-dione)]Cl₂: [Ru(bpy)₂(1,10-phenanthroline-5,6-dione)]Cl₂ was synthesized according to the literature procedure². A mixture of *cis*-[Ru(bpy)₂]Cl₂ (2.42 g, 5 mmol) and 1,10-phenanthroline-5,6-dione (1.05 g, 5 mmol) in 120 mL ethanol was stirred at reflux for 12 h under N₂ atmosphere. After the reaction was completed, the mixture was cooled to room temperature, and the solvent was then removed by evaporation under reduced pressure. The crude product was collected and purified using preparative column chromatography (Al₂O₃) to afford the product.

Synthesis of the Ru(II) complex with D-A-D ligand: [Ru(bpy)₂(1,10-phenanthroline-5,6-dione)]Cl₂ (738 mg, 1 mmol) and 4,7-bis[4-(N,N-diphenylamino)phenyl]-5,6-diamino-2,1,3-benzothiadiazole (652 mg, 1 mmol) were added to 100 mL acetic acid, the mixture was heated at reflux for 12 h under N₂ atmosphere. After the reaction was completed, the mixture was cooled to room temperature. The solvent was evaporated, and the residue was purified by neutral alumina column chromatography. The product was dissolved in a saturated aqueous solution of NH₄PF₆ to give a dark green precipitate. The precipitate was filtered, washed with water and dried to obtain the Ru(II) complex. ¹H NMR (600 MHz, DMSO-*d*₆) δ 9.09 (d, *J* = 8.4 Hz, 2H), 8.94 (m, 4H), 8.25 (m, 2H), 8.18 (m, 4H), 7.99 (m, 6H), 7.84 (m, 4H), 7.62 (m, 2H), 7.41 (m, 10H), 7.23 (m, 12H), 7.15 (t, *J* = 7.2 Hz, 2H). ¹³C NMR (150 MHz, DMSO-*d*₆)

δ 100.00, 121.50, 124.27, 125.24, 128.24, 128.45, 129.32, 130.24, 131.04, 133.61, 134.72, 136.69, 138.54, 141.31, 147.30, 148.12, 151.88, 152.35, 153.04, 153.99, 156.99, 157.22. ESI-MS m/z: Calcd. for, 620.1523 ($[(M-2PF_6)/2]^+$); found, 620.15228.

Part III. Supplementary Figs

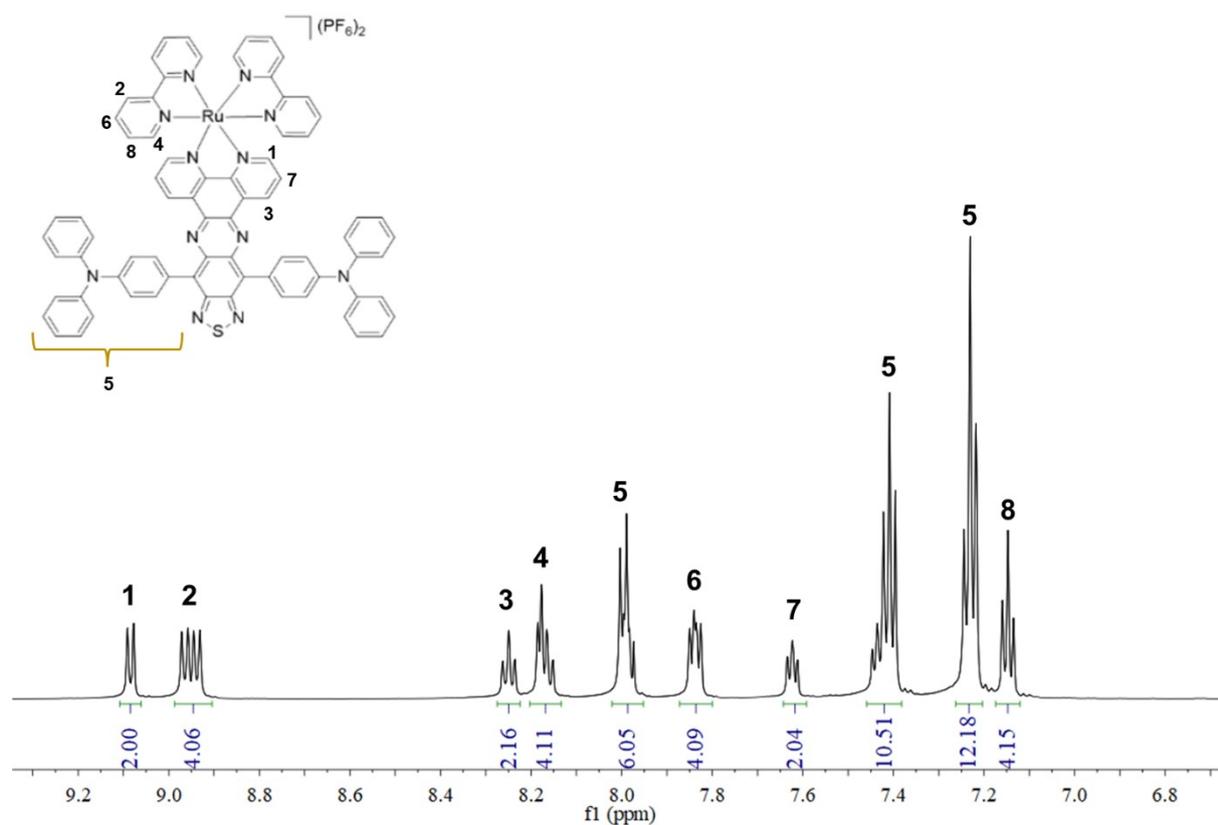


Fig. S1. ¹H NMR spectrum of the Ru(II) complex with D-A-D ligand in DMSO-*d*₆.

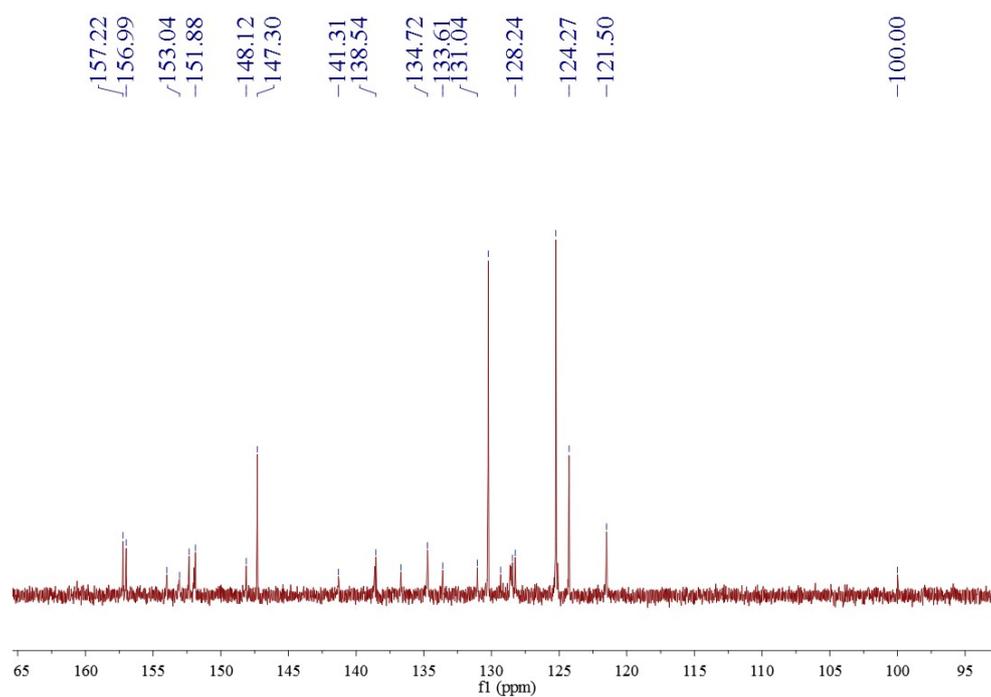


Fig. S2. ¹³C NMR spectrum of the Ru(II) complex with D-A-D ligand in DMSO-*d*₆.

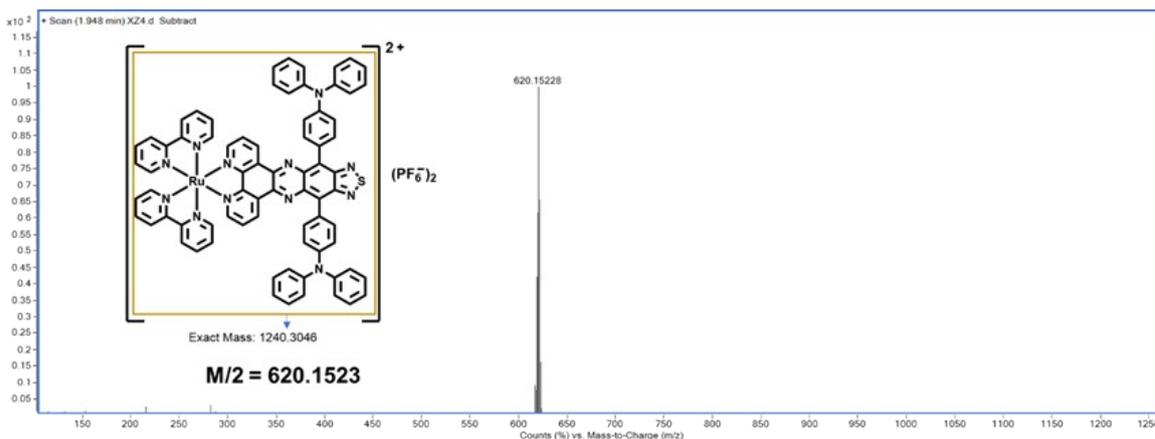


Fig. S3. ESI-MS mass spectrum of the Ru(II) complex with D-A-D ligand.

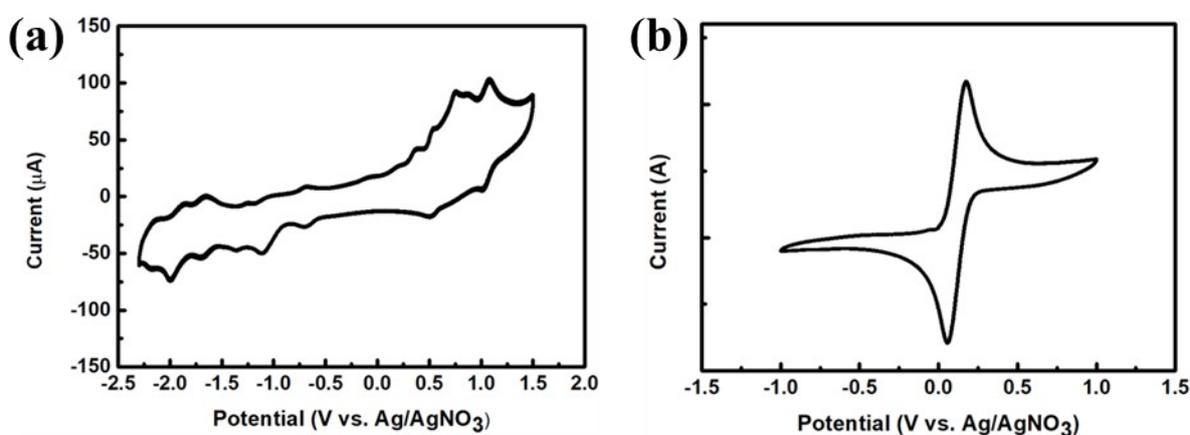


Fig. S4. Cyclic voltammogram of the (a) Ru(II) complex and (b) ferrocene.

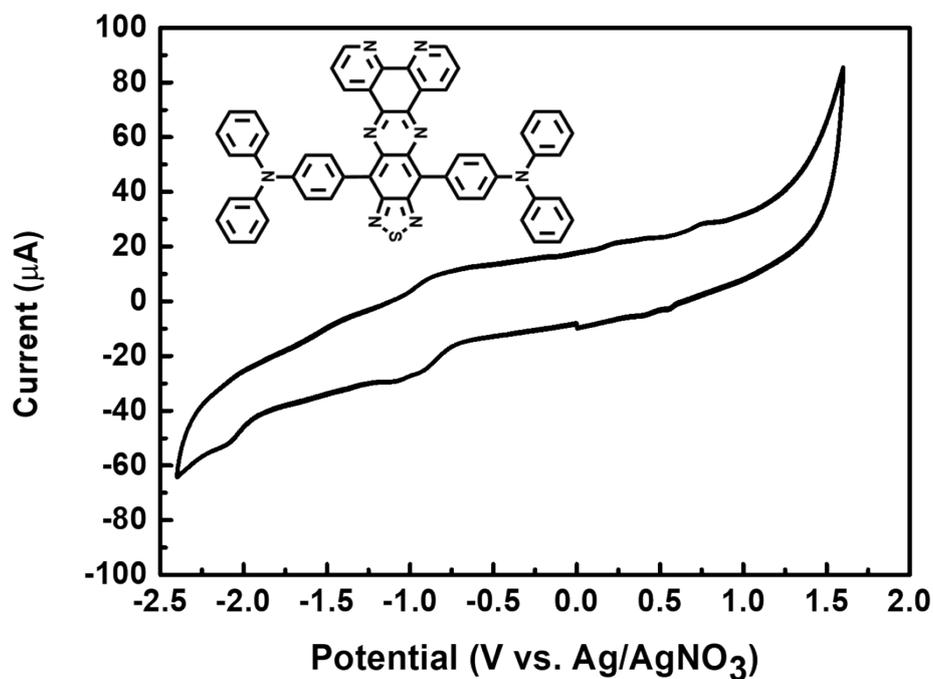


Fig. S5. Cyclic voltammogram of the complex precursors.

Table S1. Electrochemical data of Ru(II) complex with D-A-D ligand.

Complex	Oxidation / V	Reduction / V
Ru(II) complex with D-	+1.04 ^a	-1.12 ^b , -1.67 ^a ,
A-D ligand	+0.63 ^a	-1.94 ^a , -2.16 ^a

^a Quasi-reversible couples. ^b Irreversible wave.

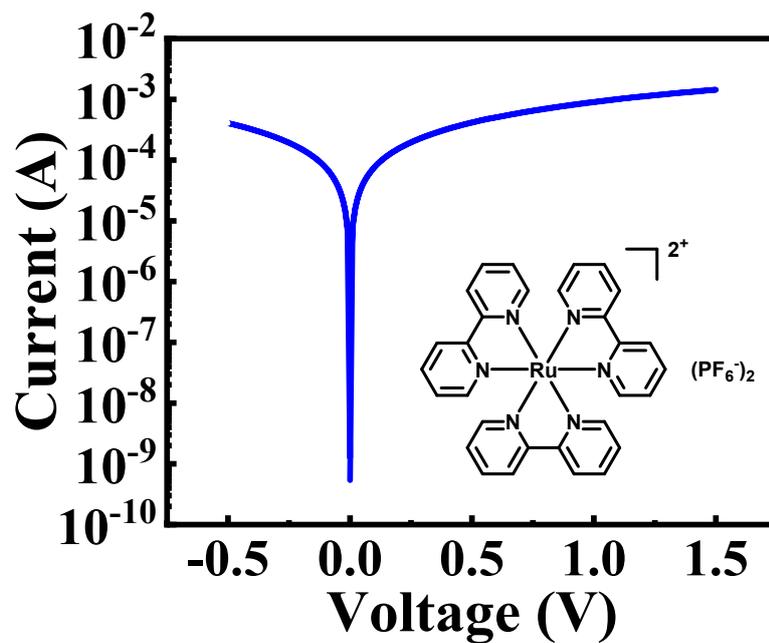


Fig. S6. *I-V* characteristic curve of the contrast compound Ru(bpy)₃(PF₆)₂.

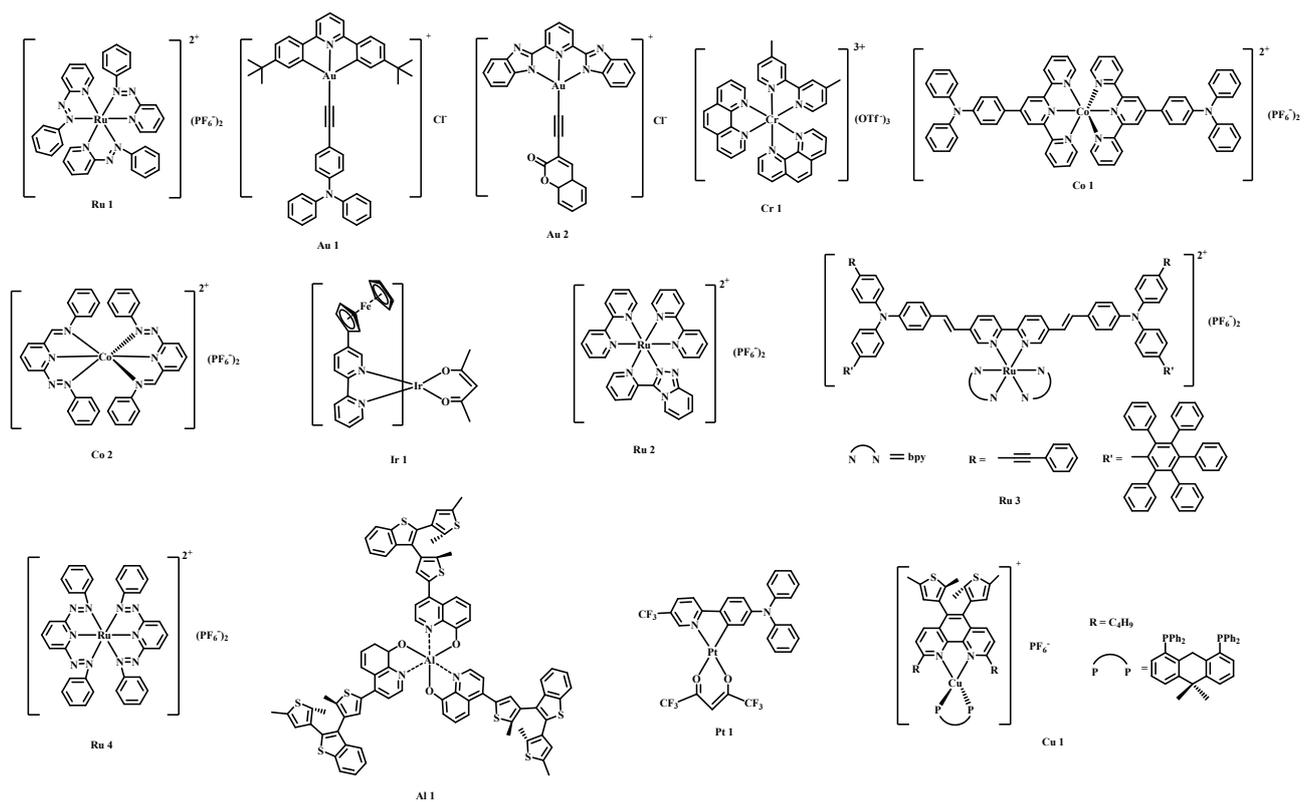


Fig. S7. Molecular structures of the reported metal complexes for organic memory devices.

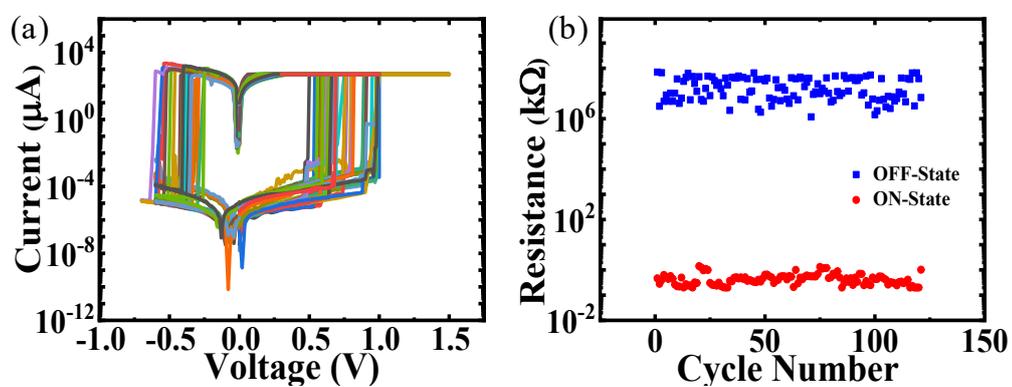


Fig. S8. (a) The I - V curves and (b) cyclic endurance characteristics of the Ag/Ru(II) complex/Ag structured device.

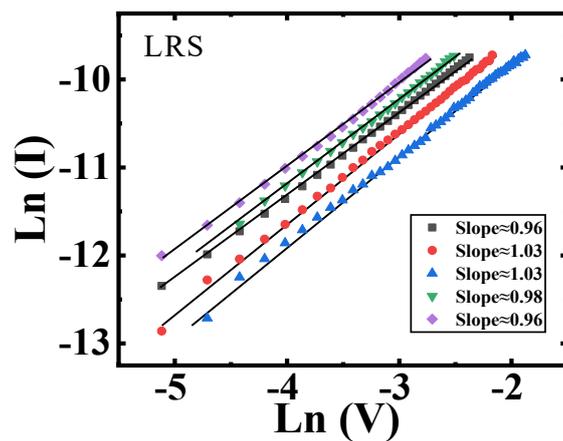


Fig. S9. The fitting results of LRS for Ag/Ru(II) complex/Pt structured device, revealing the ohmic conduction.

Part IV Reference

1. X. Liu, G. Li, M. Xie, S. Guo, W. Zhao, F. Li, S. Liu and Q. Zhao, *Dalton Trans.*, 2020, **49**, 11192-11200.
2. M.-S. Steiner and A. Duerkop, *Analyst*, 2011, **136**, 148.