

Supporting Information for:

**Resistive Memory Based on a Triphenylamine-Decorated
Non-Precious Cobalt(II) Bis-Terpyridine Complex**

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Synthesis of $\mathbf{1}(\text{PF}_6)_2$: A solution of $\text{CoCl}_2 \cdot 6\text{H}_2\text{O}$ (47.6 mg, 0.20 mmol) in 5 mL of CH_3OH was added to a solution of $\mathbf{L1}^1$ (190.6 mg, 0.40 mmol) in 5 mL of CH_2Cl_2 . The mixture was stirred for 5 h at rt, followed by the addition of 5 mL of saturated aq. KPF_6 solution. The mixture was stirred for another 0.5 h. The resulting red precipitate was collected by filtration and washing with water and ether successively. The crude product was purified by reprecipitation from a mixture of acetone and ether to afford 210 mg of $\mathbf{1}(\text{PF}_6)_2$ as a red solid in 81% yield. ^1H NMR (400 MHz, CD_3CN): δ 7.78 (t, $J = 8.0$ Hz, 4H), 8.09 (t, $J = 8.0$ Hz, 8H), 8.40 (d, $J = 8.0$ Hz, 8H), 8.84 (d, $J = 4.0$ Hz, 4H), 9.12 (s, 4H), 14.00 (s, 4H), 31.87 (s, 4H), 43.93 (s, 4H), 54.38 (s, 4H), 91.63 (s, 4H). HR-ESI calcd for $[\text{M} - 2\text{PF}_6]^+$ ($\text{C}_{66}\text{H}_{48}\text{CoN}_8$): 505.6661. Found: 505.6660. Anal. Calcd for $\text{C}_{66}\text{H}_{48}\text{CoF}_{12}\text{N}_8\text{P}_2 \cdot 3\text{H}_2\text{O}$: C, 58.44; H, 3.65; N, 8.21. Found: C, 58.46; H, 4.01; N, 8.26.

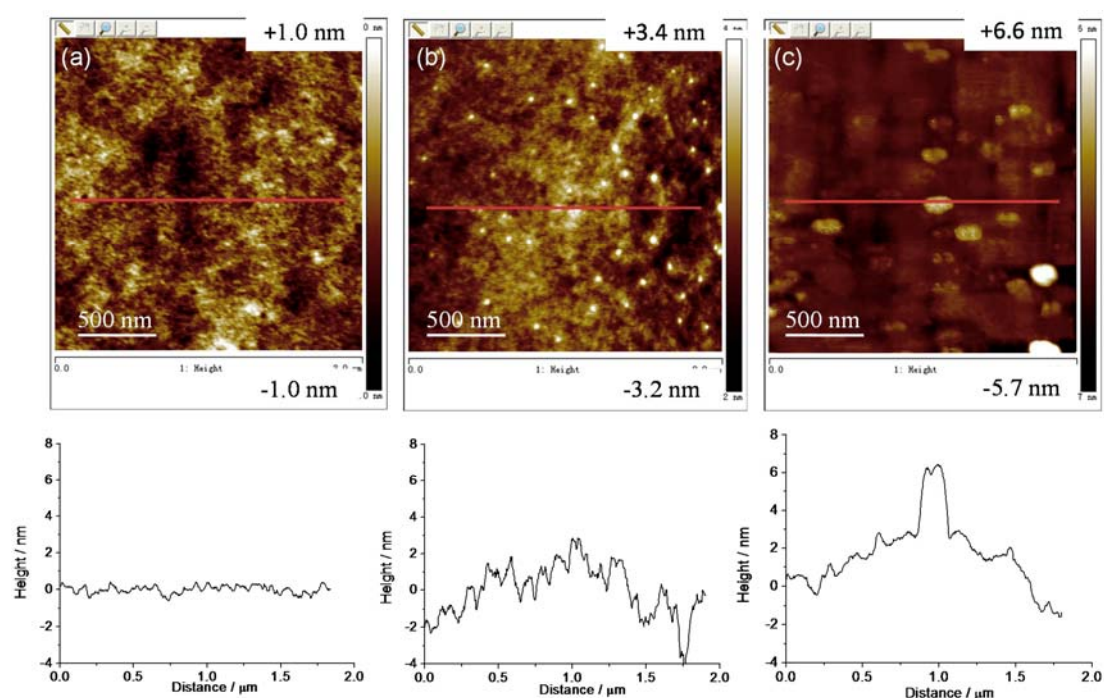


Figure S1. AFM height images of thin films of (a) $\mathbf{1}(\text{PF}_6)_2$ (rms = 0.28 nm), (b) $\mathbf{L1}$ (rms = 0.92 nm), and (c) $[\text{Co}(\text{tpy})_2](\text{PF}_6)_2$ (rms = 1.60 nm) spin-coated on ITO glass (size: $2 \mu\text{m} \times 2 \mu\text{m}$). The bottom figure shows the height variation along the red line across the AFM image. AFM was measured by the Bruker Multimode 8 using the tapping-mode with a scan speed of 1 Hz.

¹ C.-J. Yao, Y.-W. Zhong and J. Yao, *Inorg. Chem.*, 2013, **52**, 10000.

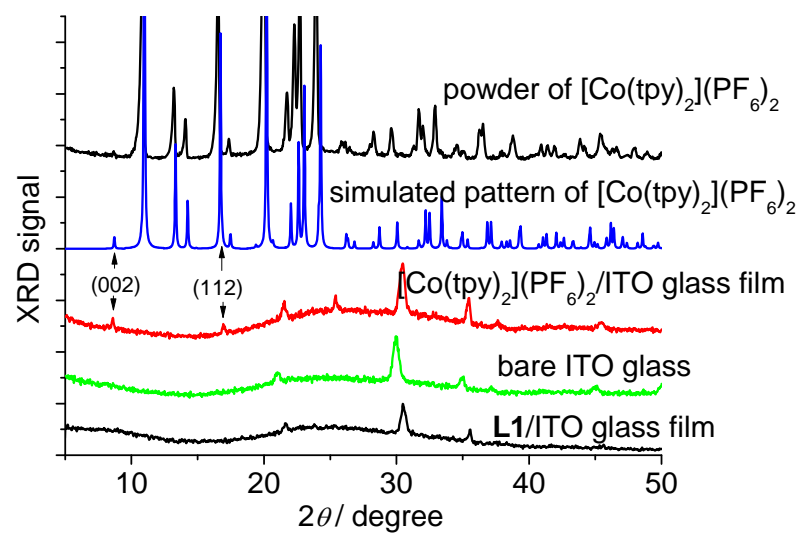


Figure S2. XRD spectra of a bare ITO glass, film of L1 and [Co(tpy)₂](PF₆)₂ on ITO glass, powder sample of [Co(tpy)₂](PF₆)₂, and those simulated by Mercury 3.9 from the single-crystal X-ray data of [Co(tpy)₂](PF₆)₂.²

² S. Aroua, T. K. Todorova, P. Hommes, L.-M. Chamoreau, H.-U. Reissig, V. Mougél and M. Fontecave, *Inorg. Chem.*, 2017, **56**, 5930.

Device Fabrication and Characterization: The ITO-coated glass ($< 10 \Omega/\text{square}$) was cleaned by successive sonication in mild detergent, deionized water, isopropanol and acetone for 10 min each and dried under a N_2 stream. A solution of 20 mg of **L1** in 1 mL of CHCl_3 or 20 mg of cobalt complex in a mixed solvent of CHCl_3 (1 mL) and CH_3CN (0.5 mL) was spin-coated onto the freshly cleaned ITO glass. The top Au electrode ($\sim 100 \text{ nm}$) was thermally evaporated onto the film through a molybdenum shadow mask. The active area of each cell is about 0.5 mm^2 . The current-voltage (I - V) characteristics of the sandwiched device were tested with a Keithley 4200 SCS semiconductor parameter analyzer under ambient condition.

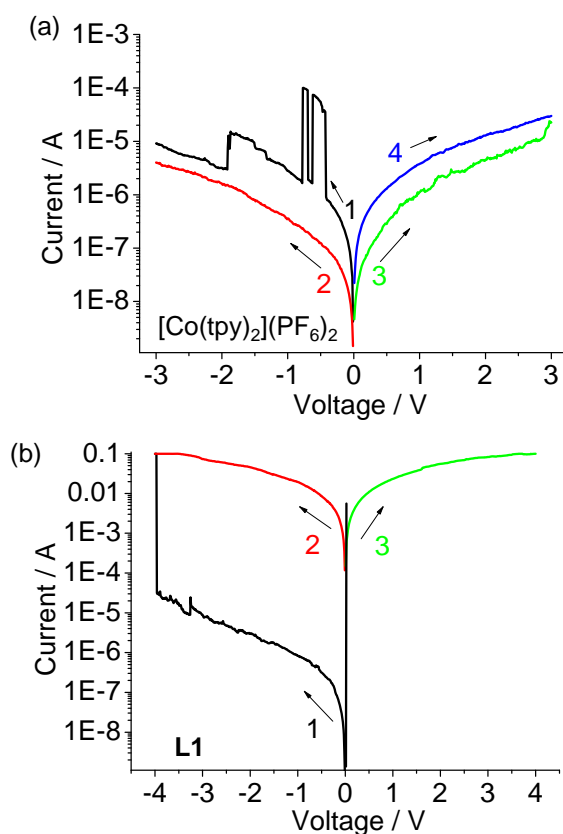


Figure S3. Typical I - V characteristics of the memory device with spin-coated (a) $[\text{Co}(\text{tpy})_2](\text{PF}_6)_2$ or (b) **L1** as the active film. The arrows denote switching order and direction. The y axes are in logarithmic scale.

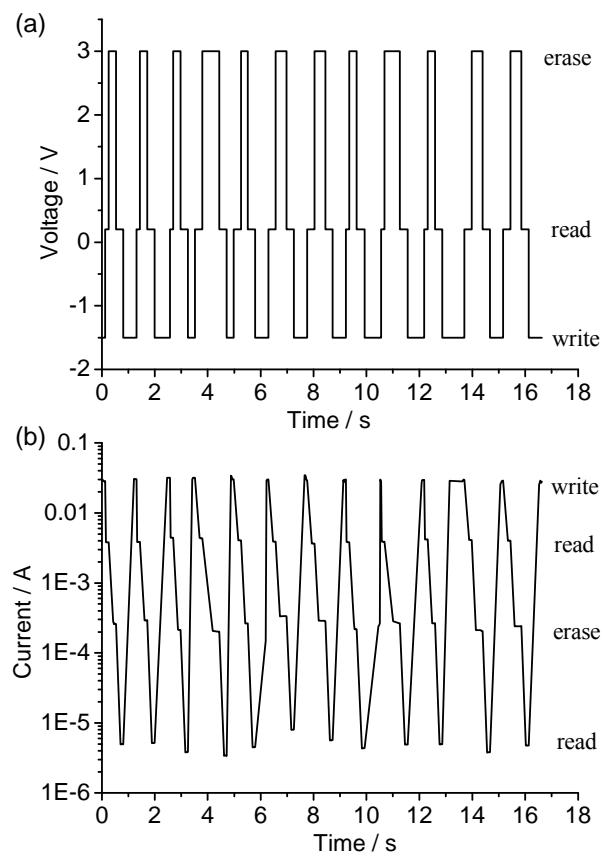


Figure S4. (a) Input applied voltage sequence and (b) output current responses during repeated write/read/erase/read (-1.5 V/+0.2 V/+3 V/+0.2 V) cycles of a ITO/1(PF₆)₂/Au device.

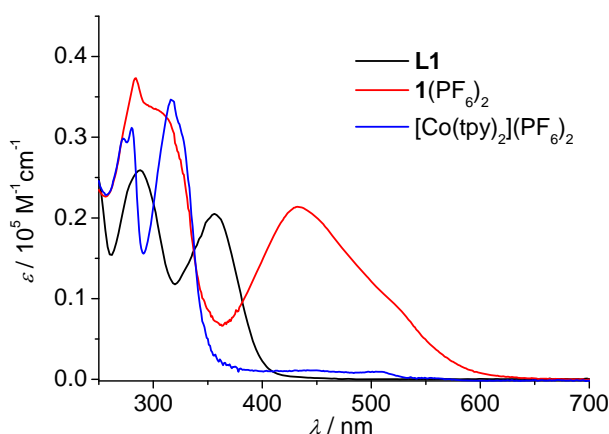


Figure S5. Absorption spectra in CH_3CN . Absorption spectra were recorded at room temperature on a TU-1810DSPC spectrometer from Beijing Purkinje General Instrument Co., Ltd.

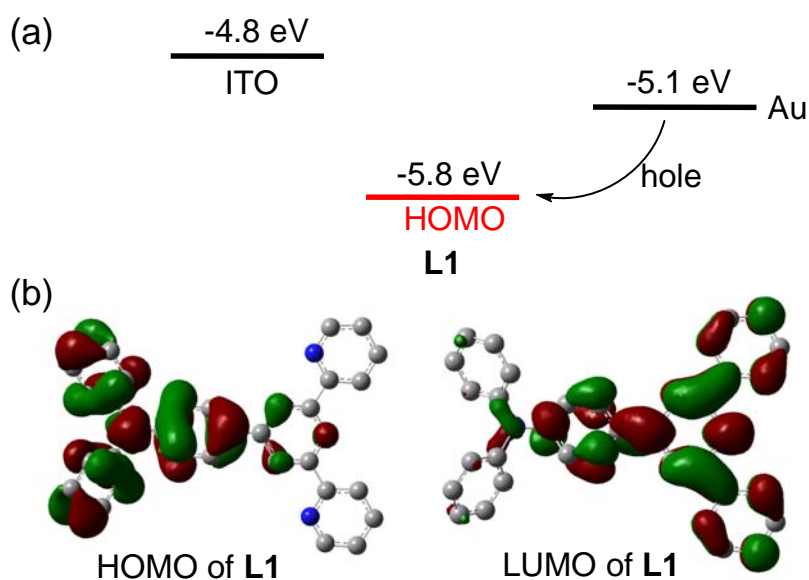


Figure S6 (a) Schematic diagram of the charge injection process and (b) DFT-calculated HOMO and LUMO plots of **L1**.

Electrochemical Measurements: All electrochemical measurements were taken using a CHI 660D potentiostat under an atmosphere of nitrogen. All measurements were carried out in 0.1 M of ${}^n\text{Bu}_4\text{NClO}_4$ in denoted solvents. The potentials are referenced to a Ag/AgCl electrode in saturated aqueous NaCl without compensation for the liquid junction potential. The working electrode was a home-made Pt disk electrode ($d = 2 \text{ mm}$). A large area platinum wire coil was used as the counter electrode.

SEM Measurements: SEM images were obtained using a field-emission microscope (JEOL S-4800) operated at an acceleration voltage of 10 kV. Prior to measurement, an ultrathin conductive Au coating was deposited on the top of the thin films on ITO glass electrodes by low vacuum sputter coating of the sample.

Computational Methods: DFT calculations were carried out using the B3LYP exchange correlation functional³ and implemented in the *Gaussian 09* package. The electronic structures of complexes were determined using a general basis set with the Los Alamos effective core potential LANL2DZ basis set for cobalt and 6-31G* for other atoms.⁴ No symmetry constraints were used in the optimization (nosymm keyword was used). Frequency calculations have been performed with the same level of theory to ensure the optimized geometries to be local minima. All orbitals have been computed at an isovalue of 0.02 e/bohr³.

³ C. Lee, W. Yang and R. G. Parr, *Phys. Rev. B.*, 1988, **37**, 785.

⁴ P. J. Hay, W. R. Wadt, *J. Chem. Phys.*, 1985, **82**, 299.

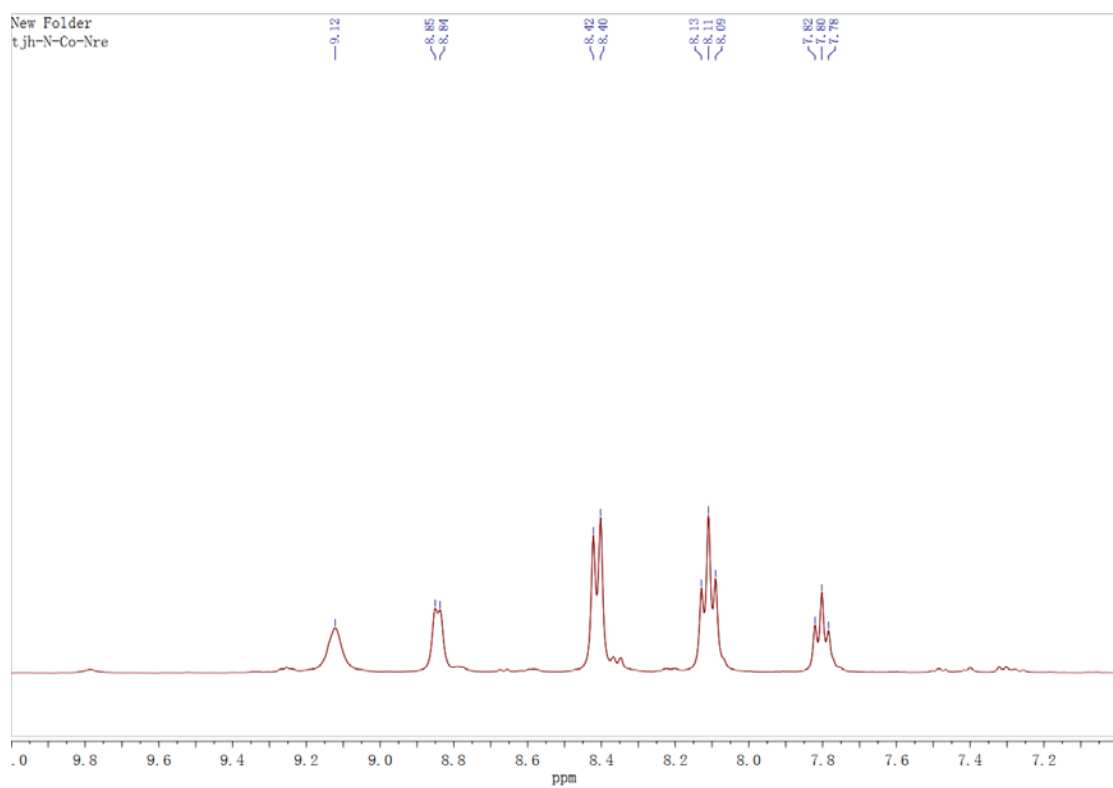
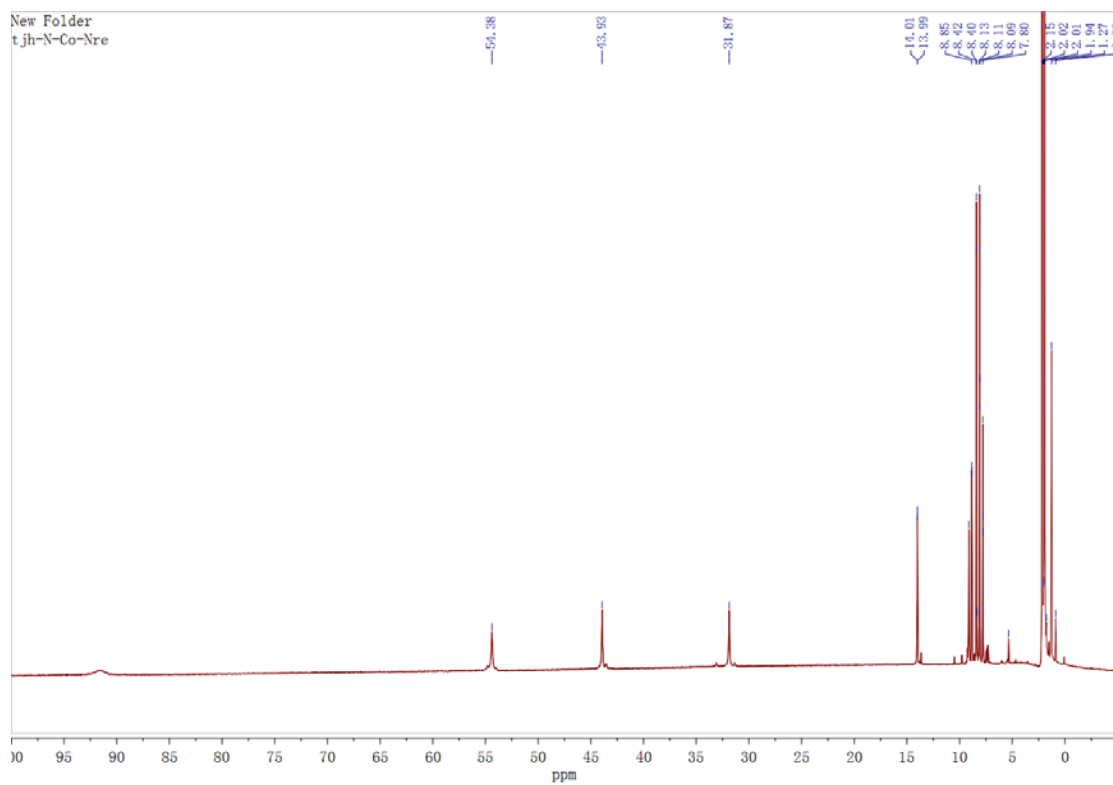


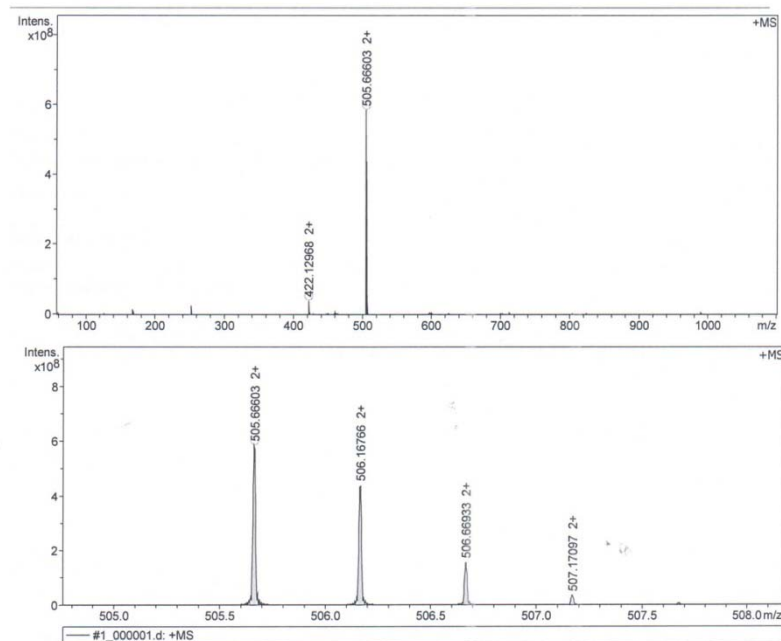
Figure S7. ^1H NMR spectrum of $\mathbf{1}(\text{PF}_6)_2$ in CD_3CN .

ESI(P),#1,20160722

Analysis Info Acquisition Date 7/22/2016 9:57:33 AM
 Analysis Name D:\Data\ESI\2016\2016-07\0722\#1_000001.d
 Sample Name #1 Instrument solarix

Acquisition Parameter

Polarity Positive Acquired Scans 2
 Broadband Low Mass 57.7 m/z Broadband High Mass 1100.0 m/z



Meas. m/z	#	Ion Formula	Score	m/z	err [ppm]	Mean err [ppm]	mSigma	rdb	e ⁻ Conf	N-Rule
422.129684	1	C54H39CoN7	100.00	422.129396	-0.7	-0.9	23.9	39.0	even	-
505.666035	2	C56H41CoN4O	82.18	422.130067	0.9	0.8	30.4	38.5	odd	-
505.666035	1	C66H48CoN8	100.00	505.666146	-0.2	0.1	5.1	47.0	even	-

Figure S8. HR-ESI mass spectrum of **1**(PF₆)₂.