Supporting Information

Electrosynthesis of Molecular Memory Elements

Pradeep Sachan^{a,†}, Anwesha Mahapatra^{a,†}, Lalith Adithya Sai Channapragada^b, Rajwinder Kaur^a, Shubham Sahay^b, Prakash Chandra Mondal^{a,*}

^aDepartment of Chemistry, Indian Institute of Technology Kanpur, Uttar Pradesh-208016, India

^bDepartment of Electrical Engineering, Indian Institute of Technology Kanpur, Uttar Pradesh-208016, India

[†]These two authors equally contributed to this work.

E-mail: pcmondal@iitk.ac.in (P.C.M.)

Contents

S5
S6
S11
S11
S12
S12
S13
S14
S15
S16
S18
S20
S20
S22
S22
S24
S25
S27
S28

1. Materials and Instrumentation:

1a. Materials:

Ruthenium (III) chloride trihydrate (RuCl₃·3H₂O, purity 99.99%), 4-Bromo-1,8 naphthalic anhydride (95%), potassium bromide (KBr, 99.999), 4-nitrobenzaldehyde (98%), ammonium acetate (NH₄CH₃COO, \geq 97%), 2-Acetylpyridine (\geq 99%), sodium sulfide (Na₂SO₄, \geq 99%), ammonium hexafluorophosphate (NH₄PF₆, 99.98%), 10% Palladium on carbon (10% Pd/C), silver nitrate (AgNO₃, 99.9995%), and t-butyl nitrite (\geq 90%) was purchased from Sigma-Aldrich (India) and used without further purification. Hydrochloric acid (HCl, 37 wt % in water, 12.1 M), chloroform (CHCl₃, 99.8%), glacial acetic acid (99.7%), ethylene glycol (99.8%), hydrogen peroxide (H₂O₂, 30 wt % in water 9.8 M), ether (Et₂O, 98%), dimethyl formamide (DMF, 99.5%), acetone (99.5%), ethanol (EtOH, 99.9%), Acetonitrile (CH₃CN, 99.9%), and toluene (99.5%), neutral alumina (>90%), were purchased from Finar Chemical (Mumbai, India), and used without further purification. All the glassware was purchased from Borosil Technology (Mumbai, India) and used after cleaning with chromic acid and base bath, followed by washing with DI water and drying in an oven at 70 °C for 5 hrs. Indium tin oxide (ITO)-coated glass substrates were purchased from Nanoshel UK Ltd (sheet resistance of 14–16 Ohm sq⁻¹, with 1.1 mm thickness and transmittance \sim 83% in the visible regime). The substrate was cleaned by Ultra-sonication, 15 min each in n-hexane, acetone, and isopropyl alcohol (IPA), followed by drying with a nitrogen gun. It was then placed in the oven at 100 °C for 30 min and further cleaned with a nitrogen gun. The activated ITO-coated glass substrate was then used for the experiment.

1b. Instrumentation:

4-aminophenyl terpyridine (tpy-ph-NH₂), 2-[4-(2,2':6'2"-terpyridine)-4'-yl] phenyl](6-bromo-1H benzo-(de) isquinoline-1-3(2H)-dione) or (naptpy), [Ru(tpy-ph-NH₂)Cl₃], and [Ru(tpy-ph-NH₂)₂(naptpy)](PF₆)₂ was Synthesized and characterized with ¹H NMR spectra recorded on a JEOLECX 500 FT (500 MHz) at 298 K and the NMR peak positions are listed with reference to TMS and NMR spectra solve through Mestre Nova software. The compound's molecular masses were determined using a WATERS Q–Tof PremierTM API Quadrupole-Time of Flight mass spectrometer equipped with HPLC Autosampler control and electrospray ionization (ESI) capability. This instrument features ESCI ionization, enabling both ESI and Atmospheric pressure chemical ionization (APCI) to be conducted in a single experiment using the same ionization source. It offers a resolution of 3 parts per million (ppm) across the 150-900 Da range. FT-IR spectra were recorded in the ATR-FT-IR unit equipped with ZnSe crystal using the Bruker Alpha II spectrometer with Opus software over a spectral range of 4000-600 cm⁻¹ and a maximum resolution of 0.5 cm⁻¹. The spectra were recorded in the presence of the KBr pallet and solved through Origin 2022b. UV-vis spectra were recorded on a JASCO UV-Visible-NIR double-beam spectrophotometer (V-770, software

Spectramanager) with its single monochromator designed for different types of samples over a range of wavelength from 190 to 2700 nm having deuterium and halogen lamp as a light source equipped with a PMT detector and a Peltier-cooled PbS detector for the NIR region. It has a facility to acquire data at variable temperature conditions. Raman spectra were recorded using a confocal Raman microscope equipped with an air-cooled solid-state laser ($\lambda = 532$ nm) and a CCD camera. The excitation laser radiation was coupled into a microscope through a single-mode optical fiber with a 40 mm diameter. XPS analyses were performed on a modified ITO substrate using a monochromatic Al K α X-ray (h ν = 1486.6 eV) radiation source and a magnetic lens, which increases the electron acceptance angle and the sensitivity. The spectra were acquired in the constant analyzer energy mode with pass energies of 150 and 40 eV for the survey and the narrow regions, respectively. Charge compensation was achieved with an electron flood gun combined with an argon ion gun. Software, data processing, and surface composition determination by Origin software. Electrochemical measurements and EIS data were recorded by using a Gamry Instrument (Model 600+) equipped with a frequency response analyzer (FRA). Current-voltage (I–V) measurements and hysteresis loop were recorded using a Keithley 2604B Source meter unit at room temperature.

2. Synthesis procedure:

Synthesis of tpy-ph-NH₂:

The tpy-ph-NH₂ was prepared following the literature reports.^{1,2} In brief, solid 4-nitrophenyl terpyridine (375 mg, 1.06 mmol) was added to the stirring solution of hot EtOH (50 ml), and stirred until it dissolved entirely. Then 10% Pd/C (160 mg) was added in catalytic amount followed by dropwise addition of 1.3 mL (excess) hydrazine hydrate for over 30 min. After refluxing for 8 hours, the hot solution was filtered through a celite pad to remove the Pd/C from the solution and cooled at room temperature. Yellow-colored needle-like crystals were obtained after three days, which were washed through cold ethanol and dried under vacuum (Yield = 60%). ¹H-NMR (500 MHz, DMSO-*d*₆): δ 8.71 (dd, J= 4.3, 1.4 Hz, 2H), 8.60 (d, J= 7.9 Hz, 2H), 8.59 (s, 2H), 7.79 (td, J= 7.7, 1.8 Hz, 2H), 7.63 (d, J=8.6 Hz, 2H), 7.46 (ddd, J= 7.4, 4.7, 1.0 Hz, 2H), 6.71 (d, J=8.6 Hz, 2H), 5,56 (s, 2H). **Synthesis of 2-[4-(2,2':6'2"-terpyridine)-4'-yl] phenyl](6-bromo-1H benzo-(de) isquinoline-1-3(2H)-dione) or (naptpy):**

The naptpy ligand was prepared by following previously reported literature.³ 4-Bromo-1,8 naphthalic anhydride (1eq. 213.54 mg, 0.77 mmol) and tpy-ph-NH₂ (1eq. 250 mg, 0.77 mmol) in ethanol (30 mL) were refluxed for 24h. The solvent was evaporated through rotavapor, and the residue was washed with water. The crude product was collected and recrystallized with glaycial acetic acid, producing a Yield of 90.74%. ¹H NMR (400 MHz, CHLOROFORM-D) δ 8.72 (t, *J* = 5.4 Hz, 2H), 8.67 (d, *J* = 3.8 Hz, 1H), 8.66 (s, 2H), 8.64 (d, *J* = 7.8 Hz, 2H), 8.42 (d, *J* = 7.8 Hz, 1H), 8.12 – 8.05

(m, 1H), 7.90 (dd, *J* = 6.5, 2.0 Hz, 1H), 7.88 – 7.86 (m, 1H), 7.84 (dd, *J* = 7.7, 1.7 Hz, 2H), 7.79 – 7.73 (m, 2H), 7.32 (ddd, *J* = 7.2, 4.9, 0.9 Hz, 2H), 6.82 – 6.75 (m, 2H).

Synthesis of [Ru(tpy-ph-NH₂)₂] (PF₆)₂(1):

A solution of ligand (tpy-ph-NH₂) and ruthenium (III) trichloride (RuCl₃.3H₂O) in ethylene glycol was heated at 110 °C for 21 hours. Then the solution was then diluted with water and filtered through a celite pad and the product was precipitated with ammonium hexafluorophosphate. The solid was collected by centrifugation, washed with water, and recrystallized using an acetonitrile/diethyl ether mixture. It was then filtered, washed with acetonitrile, and obtained with a yield of 72.34%. In the ¹H NMR (500 MHz, DMSO-*d*₆) spectrum, the signals appeared at d (ppm) δ 9.26 (s, 4H), 9.02 (d, *J* = 8.1 Hz, 4H), 8.18 (d, *J* = 8.6 Hz, 4H), 8.09 – 7.91 (m, 4H), 7.47 (d, *J* = 4.8 Hz, 4H), 7.21 (s, 4H), 6.83 (d, *J* = 8.6 Hz, 4H). In the ¹³C{¹H} NMR (500 MHz, DMSO-*d*₆) spectrum, the signals appeared at d (ppm) 114.62, 119.43, 124.98, 128.06, 129.24, 138.32, 138.51, 152.67, 152.78, 155.31, 158.9, 162.86.

Synthesis of [Ru(tpy-ph-NH₂)Cl₃]:

RuCl₃.3H₂O (1 eq, 91 mg, 0.43 mmol) and tpy-ph-NH₂ (0.8 eq, 113.85 mg, 0.35 mmol) were taken in the solution of ethanol (20 mL) and refluxed for 3 hours at 80 °C, then cooled down to room temperature. The solution was filtered out through vacuum filtration and washed successively with ethanol and diethyl ether. A dark brown crystalline product was obtained with a yield of 66.09 %. ¹H NMR (400 MHz, DMSO-*d*₆) δ 8.91 (d, *J* = 7.5 Hz, 2H), 8.87 – 8.81 (m, 2H), 8.80 (d, *J* = 8.8 Hz, 2H), 8.30 (s, 2H), 7.97 (d, *J* = 8.1 Hz, 2H), 7.75 (s, 2H), 7.11 (d, *J* = 7.5 Hz, 2H), 5.66 (s, 2H).

Synthesis of [Ru(tpy-ph-NH₂)(naptpy)](PF₆)₂ (2):

An amount of 120 mg (1eq. 0.22 mmol,) [Ru(tpy-ph-NH₂)Cl₃] (1 eq. 131.65 mg, 0.22 mmol) was taken in ethylene glycol solution (20 mL), which was refluxed for 21 hours under inert atmosphere. The solution was further diluted with 150 mL of water and filtered through a celite pad. The collected solution was precipitated with the help of ammonium hexafluorophosphate. The solid was collected by centrifugation and then washed with water. The compound was further purified using column chromatography with an acetonitrile-to-toluene ratio of 3:1, yielding 81.13%. In the ¹H NMR (400 MHz, DMSO-*d*₆) spectrum, the signals appeared at d (ppm) δ 9.61 (s, 1H), 9.54 – 9.43 (m, 1H), 9.38 – 9.33 (m, 2H), 9.17 – 9.07 (m, 4H), 8.73 (s, 1H), 8.64 (s, 1H), 8.56 – 8.38 (m, 2H), 8.26 (d, *J* = 8.6 Hz, 2H), 8.13 – 8.04 (m, 4H), 7.96 – 7.86 (m, 1H), 7.56 (dt, *J* = 11.1, 5.6 Hz, 4H), 7.28 (dd, *J* = 10.3, 4.6 Hz, 4H), 7.19 (dd, *J* = 15.5, 7.4 Hz, 4H), 6.91 (d, *J* = 8.5 Hz, 2H), 5.92 (s, 2H). In the ¹³C{¹H} NMR (500 MHz, DMSO-*d*₆) spectrum, the signals appeared at d (ppm) 111.89, 114.61, 119.36,122.86, 125.03, 125.84, 128.06, 128.73, 129.23, 129.42, 130.66, 138.34, 138.48, 147.95, 151.89, 152.51, 155.05, 155.23, 155.65, 158.62, 158.87, 175.22, 207.33.



NH₂)(naptpy)](2PF₆) (**2**).



3. NMR and Mass spectra:

Fig. S1. ¹H NMR spectrum of naptpy ligand (400 MHz, CDCl₃).



Fig. S2. ¹H NMR spectrum of 1 (500 MHz, DMSO-*d*6).



Fig. S3. ¹³C{¹H} NMR spectrum of **1** recorded in DMSO- d_6 . Peak positions in the spectrum were assigned relative to the TMS reference.



Fig. S4. ¹H NMR spectrum of **1** (400 MHz, DMSO-*d*₆).



Fig. S5. ¹H NMR spectrum of **2** (400 MHz, DMSO-*d*₆).



Fig. S6. ¹³C{¹H} NMR spectrum of **2** recorded in DMSO- d_6 . Peak positions in the spectrum were assigned relative to the TMS reference.



Fig. S7. (a) HRMS (ESI-MS, positive mode) was performed on **1**. The isotope pattern at 895.14 (m/z) matches well with theoretical data containing **1** with PF₆, (b) HRMS of **2**. The isotope pattern at 1063.09 (m/z) matches well with theoretical data which contains **2**, Cl⁻, and H₂O.

4. TGA spectrum of 1 and 2: The thermogravimetric analysis of the **1** and **2** was conducted from room temperature to 1000 °C under a nitrogen atmosphere at a heating rate of 10 °C/min. The TGA curve shows three distinct weight loss events. For **1** the first weight loss of 3.32% between 50 °C and 150 °C corresponds to the evaporation of adsorbed moisture and residual solvents (**Fig. S8a**). The second weight loss of approximately 15.48% observed between 200 °C and 450 °C likely indicates

the decomposition of the organic ligand in the metal-organic framework. Finally, a major weight loss above 500 °C corresponds to the thermal degradation of the remaining organic components. This analysis suggests that the **1** has good thermal stability up to 200 °C, with significant decomposition occurring at higher temperatures. For **2** the first weight loss of 11.3% between 50 °C and 255 °C corresponds to the evaporation of adsorbed moisture and residual solvents (**Fig. S8b**). The second weight loss of approximately 24.3 % observed between 250 °C and 650 °C likely indicates the decomposition of the organic ligand in the metal-organic framework. Finally, a major weight loss above 650 °C corresponds to the thermal degradation of the remaining organic component. This analysis suggests that the **2** has good thermal stability up to 250 °C, with significant decomposition occurring at higher temperatures. TGA spectrum of complexes 2 of three different batches, in terms of % of weight loss by increasing temperature up to 1000 °C shown in the bottom **Fig. S8c**.



Fig. S8. TGA spectrum of (a) **1** and (b) **2** complexes in terms of % of weight loss by increasing temperature up to 1000 °C. (c) TGA spectrum of complexes **2** of three different batches, in terms of % of weight loss by increasing temperature up to 1000 °C shown in the bottom

5. FT-IR spectrum of 1 and 2:



Fig. S9. Normalized FT-IR spectrum of 1 and 2.

6. UV-vis absorption spectrum of 1 and 2 complexes:



Fig. S10. Comparison of UV-vis absorption spectrum of 1 and 2 complexes and recorded in acetonitrile solution.

7. Cyclic voltammograms of 1 and 2:



Fig. S11. (a) Cyclic voltammograms of 1 recorded in an acetonitrile solution containing 1 mM of 1 and 100 mM TBAPF₆ as supporting electrolyte, at a scan rate of 100 mV/s. ITO, Pt wire, and Ag wire served as the working, counter, and reference electrodes, respectively. (b) Cyclic voltammograms of 2.

8. Fabrication of patterned ITO: Before deposition, glass substrates were cleaned with piranha solution (i.e., a 3:1 mixture of sulfuric acid and hydrogen peroxide), followed by washing with deionized water (DI) three times then drying with an N₂ gun. Then, all glass substrates were dried inside an oven at 100 °C for 30 minutes to eliminate any solvents present. These cleaned substrates were then mounted onto the sample holder of a Pulsed DC Magnetron sputtering system. A custommade shadow mask, with dimensions of 20 mm length, 15 mm breadth, 0.5 mm line width, and 1 mm line spacing, was placed on each glass substrate. Using Magnetron sputtering at a pressure of 1.6×10^{-3} mbar, approximately 100 nm of indium tin oxide (ITO) was deposited. Argon gas flow was regulated at 15 standard cubic centimeters per minute (SCCM) using a mass flow controller to control the chamber pressure, while the sputtering gun power was set at 30 W. **Fig. S12** illustrates the deposited patterns of ITO electrode on a glass substrate.



Fig. S12. A patterned ITO electrode (20 mm), deposited on a glass substrate, served as both the working electrode for electrochemical grafting and the bottom electrode in device preparation.

9. E-Chem grafting of 2 and 1 complexes on ITO electrode:



Fig. S13. (a-b) CVs of electrochemical grafting of 2 mM complex of **1** and **2** in acetonitrile with 100 mM TBAPF₆ as supporting electrolyte at various potential window ranges and number of CV scans, where ITO, Pt wire, and Ag/AgNO₃ were used as a working, counter, and reference electrodes, respectively.



Fig. S14. Schematic representation of a thin film on an ITO electrode surface grown via electrochemical grafting method. (a) Complex **1** forming aryl diazonium salts by adding 'butylnitrite under 0-5 °C that were electrochemically reduced at ITO working electrode surface, generating aryl radicals. Such reactive radicals form covalent bond between molecules and ITO electrode surfaces, and (b) for Complex **2**.

10. UV-vis spectra of ITO/1 and ITO/2:



Fig. S15. (a) UV-vis absorption spectrum of ITO/1 thin film compared with solution phase UV-vis absorption spectra, (b) thickness-dependent UV-vis spectra of ITO/1, (c) UV-vis absorption spectrum of ITO/2 thin film compared with solution phase UV-vis absorption spectra, and (d) thickness-dependent UV-vis spectra of, ITO/2.



Fig. S16. (a-b) The chemical structure of **1** and **2** with the molecular length of 18.24 Å and 24.67 Å, respectively, determined by Mercury software version 4.1.3.



Fig. S17. (a) UV-vis absorption spectra of ITO/1 exhibit an increase in absorbance at $\lambda_{max} = 338$ nm and 502 nm as the film thickness and the number of molecular layers on the ITO electrode increase, and (b) UV-vis absorption spectra of ITO/2 exhibit an increase in absorbance at $\lambda_{max} = 334$ nm and 499 nm as the film thickness and the number of molecular layers on the ITO electrode increase.





Fig. S18. (a-b) Cyclic voltammograms (CVs) of ITO/1 and ITO/2 were recorded in acetonitrile containing 0.1 M TBAPF₆ as the supporting electrolyte, within a potential window of 0 to +1.5 V at a scan rate of 50 mV/s, and (c-d) CVs of ITO/1 and ITO/2 thin film were recorded in acetonitrile containing 0.1 M TBAPF₆ as the supporting electrolyte, within a potential window of +1.3 to -1.8 V at a scan rate of 100 mV/s, In these measurements, ITO/1 and ITO/2 served as the working electrodes, a Pt wire was used as the counter electrode, and an Ag wire acted as the reference electrode.

12. Stability of ITO/1 and ITO/2



Fig. S19. (a-b) Temperature-dependent UV-vis absorption spectrum of 1, and 2, and (c-d) UV-vis absorption spectrum of 1, and 2 at 500 nm and 503 nm, respectively.



Fig. S20. Analysis of stability of thin films from UV-vis absorption spectra. (a) 1, and (b) 2 after exposure to sunlight for 2 h.



Fig. S21. The adhesive stability of the thin films was assessed by subjecting them to sonication for up to 60 min, followed by recording UV-vis absorption spectra to evaluate their stability. The UV-vis absorption spectra were recorded for (a) **1**, and (b) **2**.



Fig. S22. Analysis of stability of thin films from UV-vis absorption spectra after recording with an interval of 5 days. UV-vis absorption spectrum of (a) **1**, and (b) **2**.



Fig. S23. Analysis of Thin Film Stability via Cyclic Voltammetry. (a-b) Cyclic voltammograms (CVs) of ITO/1 and ITO/2 were recorded in acetonitrile with 0.1 M TBAPF6 as the supporting electrolyte, within a potential range of 0 to +1.5 V at a scan rate of 100 mV/s, under continuous sonication for up to 60 minutes, and (c-d) Stability assessment of ITO/1 and ITO/2 thin films after 2 hours of sunlight exposure. In these experiments, ITO/1 and ITO/2 functioned as working electrodes, with a Pt wire as the counter electrode and an Ag wire as the reference electrode.

13. Atomic force microscopy for morphology and thickness analysis:

The thickness of the **1** and **2** molecular layers was measured using atomic force microscopy (AFM), with bare ITO serving as the reference electrode. Initially, the ITO substrate was etched with hydrochloric acid and zinc dust, and its thickness was determined using an AFM line profile. First, the thickness of the bare ITO was measured (**Fig. S24a-c**). Next, **1** molecular film was grown on the same ITO reference sample via a potential-driven electrochemical reduction method (**Fig. S25a-c**). The increase in thickness observed on the bare ITO indicates the thickness of the **1** molecular film (**Fig. S25d**). Similarly, the **2** molecular layer was grown on bare ITO, with 2-D and 3-D topography images showing the increase in thickness due to the molecular layer (**Fig. S25 e-h**).



Fig. S24. (a-b) 2-D and 3-D cross-section AFM images of chemically etched blank ITO-coated glass, and (c) respective height profile plots for the elucidation of the average thickness of ITO.



Fig. S25. (a-c) 2-D and 3-D topography of the surface $20 \times 20 \ \mu m^2$, cross-section AFM image of E-Chem grafted 1 film on reference ITO electrode corresponding to the thickness measurement, (d) respective height profile plots for the elucidation of the average thickness of ITO/1, (e-h) 2D and 3D cross-section AFM image of E-Chem grafted 2 films on reference ITO sample and their respective height line profile. AFM measurements showcased the formation of nanometric thin films on the ITO substrate.

Table S1: E-chem grafting parameters and thickness of molecular films on ITO electrode at 1 mM concentration of **1** and **2**, 100 mM TBAPF₆ in acetonitrile. The thickness of the molecular layer was calculated by subtracting the thickness of bare ITO (105.72 nm) from the grafted sample (ITO + (**1** or **2**) layer).

S.	Sample	Potential (V)	No. of	Scan	Thickness (nm)	
No.		vs. Ag/AgNO3	Cycles	Rate	ITO/1	ITO/2
				(mV/s)		
1.	Sample 1	0-(-0.7) V	5	100		
2.	Sample 2	0-(-0.8) V	10	100	5.88 <u>+</u> 2.09	6.02 <u>+</u> 1.3
3.	Sample 3	0-(-0.9) V	15	100	10.64 <u>+</u> 0.82	11.27 <u>+</u> 2.39
4.	Sample 4	0-(-1.0) V	20	100	18.9 <u>+</u> 0.73	16.83 <u>+</u> 1.98
5.	Sample 5	0-(-1.0) V	30	100	27.36 <u>+</u> 0.76	23.8 <u>+</u> 0.56

14. FE-SEM for morphology and thickness analysis:

Fig. S26. FE-SEM image of (a) surface morphology of ITO/2 thin film, and (b) Cross-sectional FE-SEM images to deduce the thickness of electrochemically grafted ITO/2.

Table S2: The thicknesses from three different measurements and the average thicknesses are provided in the table for the respective layers.

S.	Sample	Thickness	Thickness	Thickness	Average Thickness
No		(T 1, nm)	(T2, nm)	(T3, nm)	(T _A , nm)
1.	Bare ITO	126.19	123.23	126.15	125.19 ± 1.69
2.	2	24.8	24.61	25.37	25.59 ± 0.92

15. Raman spectra of ITO thin films: The Raman spectrum was recorded for the blank ITO-coated glass substrate, which shows a broad peak at 1088.6 cm⁻¹ corresponding to the symmetric stretching mode of the Sn–O bond (**Fig. S27**). Raman spectra of **1** and **2** films were shown in (**Fig. S28**), which reveals characteristic peaks indicative of the complex's coordination environment and ligand structure.⁴ A strong peak at around 1600 cm⁻¹ corresponds to C=N stretching vibrations in the ligand,

suggesting the presence of aromatic or imine groups often coordinated to the Ru centre. Additionally, a peak near 500 cm⁻¹ is observed, which is typically associated with Ru–N stretching, confirming metal-ligand coordination. The peaks observed at 2142, 2236, and 2425 cm⁻¹ can be associated with the enhancement of CN modes caused by the transition to an MLCT excited state. Furthermore, the Raman spectrum lacks a significant fluorescence background, indicating a relatively pure sample. The sharpness and symmetry of these peaks imply a well-ordered structure, and the positions of these vibrational modes align with similar Ru complexes reported in the literature, confirming the expected coordination environment around the ruthenium center.

Fig. S27. Raman spectrum of blank ITO-coated glass substrate used as a reference.

Fig. S28. Raman spectrum of (a) ITO/1 and (b) ITO/2 films.

Fig. S29. The contact angle measurement after adding a drop of water (2 μ L) on ITO/1 and calculation of the average contact angle value of left and right angle by dropping the drop of water on ITO electrode at different places.

17. Determination of HOMO and LUMO for 2:

HOMO-LUMO energy and band gap were calculated by using the reported procedure.^{5[1]} Firstly, we took the UV-vis spectra of the ITO/1 complex and converted them into the tauc plot to obtain the band gap (2.29 eV) (**Fig. S30a**). In addition, we performed the cyclic voltammetry on the thin film with respect to ferrocene to obtain the E_{LUMO} and E_{HOMO} values. We recorded the CV in acetonitrile by using 100 mM TBAPF₆ and 0.05 mM of ferrocene, ITO/1 as a working electrode, Pt wire as a counter electrode, and Ag/AgNO₃ as a reference electrode in a three-electrode conventional electrochemical setup (**Fig. S30b**). The cyclic voltammogram (CV) of the ITO/1electrode indicates an $E_{1/2}^{Fc/Fc^+}$ redox couple of +0.05 V, and the onset of the first reduction potential (E_{red}^{onset}) at -1.22 V. From these values, the estimated E_{HOMO} and E_{LUMO} energy levels are -5.82 eV and -3.53 eV, respectively. Similarly, band gap and E_{HOMO} and E_{LUMO} energy were calculated with the help of tauc plot and CV with respect to ferrocene. The tauc plot suggested a band gap of 2.21 eV and the CV of the ITO/2 electrode indicates an $E_{1/2}^{Fc/Fc^+}$ redox couple of +0.36 V. Based on these values, the calculated E_{HOMO} and E_{LUMO} energy levels are -5.53 eV, and the GV of the ITO/2 electrode indicates an $E_{1/2}^{Fc/Fc^+}$ redox couple of +0.21 V, and the onset of the first reduction potential (E_{red}^{onset}) at -1.36 V. Based on these values, the calculated E_{HOMO} and E_{LUMO} energy levels are -5.53 eV and -3.32 eV, respectively (**Fig. S30c-d**).

 $E_{LUMO} = -[(E_{red} - E_{1/2(ferrocene)} + 4.8) eV]$

Еномо = Elumo - band gap

Fig. S30. (a) Tauc plot of ITO/1 thin film, (b) CVs of ITO/1 thin film recorded at 50 mV/s scan rate in 0.1M of TBAPF₆ supporting electrolyte in acetonitrile solution, (c) Tauc plot of ITO/1 thin film, and (d) CVs of ITO/2 thin film recorded at 50 mV/s scan rate in 0.1M of TBAPF₆ supporting electrolyte in acetonitrile solution. The data were employed to determine the optical band gap and energy levels of HOMO and LUMO.

Fig. S31. Optical band gap and HOMO and LUMO value, the fermi energy level of the ITO electrode. (a) **1**, and (b) **2**.

18. Density functional theory study: The frontier molecular orbitals of 1^{2+} and 2^{2+} were optimized using density functional theory (DFT) calculations with the help of B3LYP level, 6-31G** basis set for the ligand (C, H, N) and SDD basis set for Ru(II). The frontier orbitals (HOMO-2 to LUMO+2) are plotted using Chemcraft software shown in **Fig. S32**. Energy levels of 1^{2+} and 2^{2+} complexes from HOMO-3 to LUMO+3 are shown in **Table S3**.

Fig. S32. The frontier orbitals (HOMO-2 to LUMO+2) of the 2 complexes.

Table S3: Energies	of the frontier orbitals	(HOMO-3 to LUMO+3)	of 1 and 2 complexes.
Lable Set Energies	or the monther orontally		

S. No.	Orbital	Energ	y in eV
		1	2
1.	HOMO-3	-7.31	-6.91
2.	HOMO-2	-6.19	-6.22
3.	HOMO-1	-6.19	-6.20
4.	НОМО	-6.18	-6.19
5.	LUMO	-2.88	-3.15
6.	LUMO+1	-2.87	-2.91
7.	LUMO+2	-2.72	-2.88
8.	LUMO+3	-2.62	-2.73
9.	Band gap HOMO - LUMO	3.3	3.04

Fig. S33. Comparison of UV-vis spectra of 1 and 2 complex through theoretical (red colour) and experimental (blue colour).

Fig. S34. Molecular electrostatic potential (ESP) mapped on the isodensity surface for (a) **1**, and (b) **2** in their ground states within the range of -0.212 a.u. (red) to +0.212 a.u. (blue) for both **1** and **2** complexes.

19. X-ray photoelectron spectra:

Fig S35. The XPS survey spectra of (a) ITO/1 and (b) ITO/2 confirm the presence of all the elements.

Fig S36. (a-b) C 1s and Ru 3d XPS spectra of the ITO/1, and (b) XPS spectra of N 1s correspond to nitrogen coordinated (N_c) with the Ru metal center.

Fig S37. XPS signals of electrochemically grafted molecular films on ITO electrode surface. (a) C 1s and Ru 3d XPS spectra of the ITO/2/Al interface, (b) N 1s XPS spectra identifying nitrogen signals from the metal-coordinating site (N_c) and bridging nitrogen in the terpyridine and naphthalene groups, and (c, d) O 1s and Br 3d XPS spectra, indicating the presence of bromine associated with the naphthalene component. Solid lines represent fitted data, while open circles show the experimental data points.

S. No.	Material	Elements	State/Term	Binding Energy (eV)
1.		С	1s	284.60
				285.33
	ITO/ 1	Ru	3d _{5/2}	280.67
			3d _{3/2}	284.87
		Ν	1s	399.25
2.		С	1s	284.76
				285.65
				286.47
				287.55
	ITO/ 2	Ru	3d _{5/2}	281.03
			3d _{3/2}	285.14
		Ν	1s	400.06
				399.51
		Br	3d	71.87
		0	1s	532.02

 Table S4: XPS analysis of ITO/1 and ITO/2 complexes.

20. Fabrication of large-area molecular junctions: After successfully attaching a ruthenium complex **1** and **2** onto a patterned ITO substrate, large-area molecular junctions were created by depositing a top electrode of aluminium (Al). Approximately 70.5 ± 0.33 nm of Al was deposited in a crossbar configuration using a thermal evaporator (Hind High Vac. HVV BC 300) and a shadow mask with seven parallel lines of 0.5 mm. The chamber pressure during deposition was kept at 5×10^{-6} mbar.

Fig. S38. Image of ITO/molecule/Al MJs after Al top electrode deposition.

Fig. S39. (a-b) 2-D and 3-D topography of the surface $10 \times 10 \ \mu m^2$, cross-section AFM image of aluminium layer on top of the ITO/1 and ITO/2 electrode corresponding to the thickness of aluminium, (c) respective height profile plots for the elucidation of the average thickness of the Aluminium, and (d) average thickness of the aluminium electrode at three different thicknesses.

21. Electrical measurement of ITO/1/Al and ITO/2/Al molecular junctions:

21a. Device structure and I-V measurement setup:

Fig. S40. (a) Two probe I-V measurement setup of the ITO/molecule/Al based device. (b) Zoomed image to show the bottom ITO and top Al electrode.

Fig. S41. Typical j-V plot of ITO/2/Al device.

Fig. S42. (a-b) j-V Hysteresis and semi-log plot of ITO/2/Al MJ with different devices.

Fig. S43. (a, b) j-V and semi-log plot of the ITO/2/Al MJ at different junction areas.

Fig. S44. (a-b) Distribution of SET and RESET voltage for ITO/2/Al in three batches of devices with eighteen molecular junctions.

Fig. S45. (a) j-V Hysteresis of ITO/2/Al MJ, and (b) semi-log j-V plot of ITO/2/Al MJ at different scan rates 2, 1, and 0.5 V/s, respectively.

Fig. S46. (a) Current density vs. number of cycles plot of ITO/2/Al MJ up to 110 cycles at a read voltage of +0.5 V, with write pulse +5.0 V and erase pulse -3.5 V, and (b) Current density with respect to time output response of cyclic stability up to 82 sec under same condition.

Fig. S47. (a-b) j-V and semi-log plot of the ITO/Al molecular junction, active area of 0.5×0.5 mm².

Fig. S48. (a) Schematic representation of ITO/1/Al MJ with an active area of $0.5 \times 0.5 \text{ mm}^2$, (b) j-V plot of the ITO/1/Al MJ, (c) semi-log plot of the ITO/1/Al MJ, and (d) semi-log lot of Log j vs. time.

S.	Device structure	No. of	No. of	Yield	Switching threshold		On/off ratio		
No.		devices tested	devices working	%	(V)				
			0		SET	RESET	SET	RESET	
1.	ITO/ 1 /Al	6	4	66	+3.52	-2.72	152	10.7	
2.	ITO/2/Al	20	13	65	2.87	-1. 79	1024	59	

Table S5: Device parameters of RRAM from j-V curve.

Table S6: Performance and yield chart of ITO/2/Al for resistive switching devices.

S. No.	Batches	No. of devices tested	No. of devices working	Yield %	Switching threshold (V)		On/off ratio		
			8		SET	RESET	SET	RESET	
1.	1 st	12	9	66.6	+2.9	-1.8	705	175	
2.	2 rd	14	7	50	+2.25	-2.08	93	442	
3.	3 nd	20	13	65	2.87	-1.79	1024	59	

Table S7: Device parameters based on the statistical data for ITO/1/Al and ITO/2/Al MJs.

S.	Device results	SET/RESET			
No.		ITO/ 1 /Al	ITO/ 2 /Al		
1.	Energy Consumption (<i>m</i> J)	25.5/6280	25.5/75000		
2.	Switching time (ms)	66/70	56/24		
3.	Cyclic stability	4	23		
4.	Conductance (µS)	32.03/2.9	2450/0.40		

S.	Device Configuration	Device Configuration Set and Reset		Current	Switching	Refs.
No		Volta	ge (V)	ON/OFF	Mechanism	
•		VSET	VRESET	ratio		
1.	Al/[Cr(bpy) ₂ (Br ₂ bpy)](OTf) ₃ /Al	+1.2	-	150		[5]
2.	Al/[Cr(bpy) ₂ (COOMebpy)](OTf) ₃ /Al	+2.6	-	20		[5]
3.	ITO/[RuII(bpy) ₂ (L)] ²⁺ /Al	-1.3	+1	10 ³	MLCT	[6]
4.	$ITO/[Ru(L)_3]^{2+}/Au$	+3.95	-4.14	~10 ⁵		[7]
5.	$Au/[Rh^{III}(L^{-})_2(L)]CF_3SO_3/Au$	+2.75	-2.05	~10 ³		[8]
6.	ITO [Co(tpy)2](PF6) 2/Al	-0.6	+2.6	10 ³	MLCT	[9]
7.	Au/[Au(Et-thiazdt) ₂]/Au	+16.5	_	10 ²	Electronic	[10]
					avalanche	
8.	ITO/[Au(^t BuC^N^C ^t Bu)(C=C-	2.5	-2.6	10 ⁵	LLCT	[11]
	$C_{6}H_{4}N(C_{6}H_{5})_{2}-p)]/Al$					
9.	ITO/[Au(C^N^C)(C≡CPh]/Al	1.54	2.64	1/10 ³ /10 ⁷	MLCT	[12]
10.	ITO/[Tritetradecyltriindole{(C≡C)Au	+1.5	-	10 ⁵	Charge	[13]
	$(C \equiv N C_6 H_3(OMe) 2-2,6)_3]/Al$				Trapping	
11.	ITO/Co ^{II} L/Al	-1.5	1.5	10	СТ	[14]
12	ITO/[Ni/Ma_dtaa)]/Ou	15	15	2	Daday	[15]
12.	110/[NI(Me4ddaa)]/Cu	1.3	-1.5	Z	induced CE	
12		15		1.06	Induced CF	[16]
13.		1.5	-	10		[17]
14.	$\frac{\text{Ag/[Zn L_2]/110_2/F10}}{\text{Ag/[Ru(II) complex/Ag}}$	0.5	-1	10	СТ	[18]
15.	Ag/Ru(II) complex/Ag	-1.15	-1	10	CI	[19]
10	$\frac{110}{[Co_2^{-1}(L^2)_2]/Cu}$	-1	1	10 ³	Change	[20]
1/.	Au/Cu ₃ (HH1P) ₂ /110	-0.3	-1	10	Tranning	
18	An/SAM SUBMOE/An	0.7	1	106	Chargo	[21]
10.	Au/SAM-SORMOF/Au	0.7	-1	10	Trapping	
10	$ITO/[B_{11}, T_2]/A1$	13.52	2 72	152	Trapping	Prosont
17.		<i>⊤3.3</i> ∠	-2.12	132		work
20	$ITO/2/\Delta 1$	+2 87	-1 79	1076		Present
		12.07	1.17	10/0		work

Table S8: Performance Comparison of ITO/1/Al and ITO/2/Al memory device with previous literature reports on metal-complex-based memory results.

*MLCT = Metal-Ligand Charge Transport, LLCT = Ligand-Ligand Charge Transport, CT= Charge Transport.

22. Electrical impedance measurements of ITO/2/Al:

S.	Elements	Devices ITO/2/Al					
No.		0 mV	5 mV	10 mV	20 mV	50 mV	100 mV
1.	$\mathbf{R}_{\mathrm{C}}\left(\mathbf{\Omega} ight)$	103	106	108	110	111	111
2.	$\mathbf{R}_{\mathrm{ct}}\left(\Omega ight)$	431	438	424	388	377	386
3.	Y ₀ -1 (S*s^a)	29×10 ⁻⁹	23.9×10 ⁻⁹	21.6×10 ⁻⁹	17.3×10 ⁻⁹	15.6×10 ⁻⁹	16.1×10 ⁻⁹
4.	a-1	0.948	0.965	0.974	0.995	1	1
5.	R-1 (Ω)	26.5×10^3	28×10^{3}	31.2×10^{3}	33.1×10 ³	35.4×10^{3}	37×10 ³
6.	Y ₀ -2 (S*s^a)	113×10 ⁻⁹	105×10 ⁻⁹	99×10 ⁻⁹	98.9×10 ⁻⁹	95.1×10 ⁻⁹	87.9×10 ⁻⁹
7.	a-2	0.839	0.84	0.842	0.838	0.84	0.846
8.	GOF (χ^2)	4.3×10 ⁻³	2.8×10 ⁻³	4.0×10 ⁻³	9.5×10 ⁻³	9.2×10 ⁻³	6.9×10 ⁻³

Table S9. Electrical component obtained from EIS data at 100 mV AC amplitude and variable DC potential from 0 to 100 mV for ITO/2/Al MJs.

23. References:

- [1] A. Shafiee, M. M. Salleh, M. Yahaya, *Sains. Malays.* **2011**, *40*, 173.
- [2] A. Kumatani, Y. Li, P. Darmawan, T. Minari, K. Tsukagoshi, Sci. Rep. 2013, 3, 1026.
- [3] Q. Zhang, D. Wu, Y. Fu, J. Li, Y. Chen, B. Zhang, ACS Appl. Mater. Interfaces 2024, 16, 22217.
- [4] C. Lutz, T. Hasegawa, T. Chikyow, *Nanoscale* **2016**, *8*, 14031.
- [5] B. Kandasamy, G. Ramar, L. Zhou, S.-T. Han, S. Venkatesh, S.-C. Cheng, Z. Xu, C.-C. Ko,
 V. A. L. Roy, *J. Mater. Chem. C* 2018, *6*, 1445.
- [6] B. Pradhan, S. Das, *Chem. Mater.* **2008**, *20*, 1209.
- S. Goswami, A. J. Matula, S. P. Rath, S. Hedström, S. Saha, M. Annamalai, D. Sengupta, A. Patra, S. Ghosh, H. Jani, S. Sarkar, M. R. Motapothula, C. A. Nijhuis, J. Martin, S. Goswami, V. S. Batista, T. Venkatesan, *Nat. Mater.* 2017, *16*, 1216.
- [8] N. D. Paul, U. Rana, S. Goswami, T. K. Mondal, S. Goswami, J. Am. Chem. Soc. 2012, 134, 6520.
- [9] J.-H. Tang, T.-G. Sun, J.-Y. Shao, Z.-L. Gong, Y.-W. Zhong, *Chem. Commun.* 2017, 53, 11925.

- P. Stoliar, P. Diener, J. Tranchant, B. Corraze, B. Brière, V. Ta-Phuoc, N. Bellec, M. Fourmigué, D. Lorcy, E. Janod, L. Cario, *J. Phys. Chem. C* 2015, *119*, 2983.
- [11] V. K.-M. Au, D. Wu, V. W.-W. Yam, J. Am. Chem. Soc. 2015, 137, 4654.
- [12] E. Y.-H. Hong, C.-T. Poon, V. W.-W. Yam, J. Am. Chem. Soc. 2016, 138, 6368.
- [13] E. Y.-H. Hong, V. W.-W. Yam, ACS Appl. Mater. Interfaces 2017, 9, 2616.
- [14] N. Kamboj, A. Betal, M. Majumder, S. Sahu, R. K. Metre, *Inorg. Chem.* 2023, 62, 4170.
- [15] A. Sławek, L. Alluhaibi, E. Kowalewska, G. Abdi, T. Mazur, A. Podborska, K. Mech, M. Marciszko-Wiąckowska, A. Maximenko, K. Szaciłowski, *Adv. Electron. Mater.* 2024, 2300818.
- [16] Y. Xu, M.-Y. Leung, L. Yan, Z. Chen, P. Li, Y.-H. Cheng, M. H.-Y. Chan, V. W.-W. Yam, J. Am. Chem. Soc. 2024, 146, 13226.
- [17] S. Birara, S. Saini, M. Majumder, P. Lama, S. P. Tiwari, R. K. Metre, *Dalt. Trans.* 2023, 52, 18429.
- [18] M. Wang, N. He, R. Tang, F. Li, S. Liu, F. Xu, J. Zhao, Y. Tong, Q. Zhao, *Dalt. Trans.* 2023, 52, 7620.
- [19] S. Sinha, M. Sahad E, R. Mondal, S. Das, L. T. Manamel, P. Brandão, B. de Bruin, B. C. Das, N. D. Paul, *J. Am. Chem. Soc.* 2022, *144*, 20442.
- [20] L. Liu, J. Dong, J. Liu, Q. Liang, Y. Song, W. Li, S. Lei, W. Hu, Small Struct. 2021, 2, 2000077.
- [21] L. G. S. Albano, T. P. Vello, D. H. S. de Camargo, R. M. L. da Silva, A. C. M. Padilha, A. Fazzio, C. C. B. Bufon, *Nano Lett.* 2020, 20, 1080.