Robust resistive memory devices using solution-processable metal-coordinated azo aromatics

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Non-volatile memories will play a decisive role in the next generation of digital technology. Flash memories are currently the key player in the field, yet they fail to meet the commercial demands of scalability and endurance. Resistive memory devices, and in particular memories based on low-cost, solution-processable and chemically tunable organic materials, are promising alternatives explored by the industry. However, to date, they have been lacking the performance and mechanistic understanding required for commercial translation. Here we report a resistive memory device based on a spin-coated active layer of a transition-metal complex, which shows high reproducibility (\sim 350 devices), fast switching (\leq 30 ns), excellent endurance (\sim 10¹² cycles), stability (>10⁶ s) and scalability (down to \sim 60 nm²). *In situ* Raman and ultravioletvisible spectroscopy alongside spectroelectrochemistry and quantum chemical calculations demonstrate that the redox state of the ligands determines the switching states of the device whereas the counterions control the hysteresis. This insight may accelerate the technological deployment of organic resistive memories.

ince the seminal work by Williams and Strukov in 2008¹, the field of resistive memory devices has progressed rapidly² and applications in next-generation computing such as neuromorphic³ architectures are now being evaluated for commercial potential. A wide range of materials have been explored as active components of resistive memory devices, including inorganic oxides^{1,2,4-6}, two-dimensional materials^{7,8}, polymers⁹⁻¹¹, and various molecular systems¹²⁻¹⁵. Oxide devices have so far evolved as the most promising candidates in terms of application potential, although high forming voltage/current and large set/reset voltage still remain as challenges to realize high-density memories¹⁶. Among other genres, organic devices have been of interest to the research community because of their solution processability (leading to cheap manufacturing) and chemically tunable functionalities^{12,17}. In fact, some of the organic devices have made inroads into display technologies (OLED based¹⁸) and a few others seem attractive for emerging applications such as flexible electronics9,12. However, when compared to the enormous research effort spent, the overall commercial translation of organic devices has been poor¹⁹ and the area of resistive memory exemplifies too many such cases^{12,17}. The problems arise from insufficient reproducibility, endurance, stability, scalability and low switching speed¹⁷. To address the issue of reproducibility, systematic

statistical analysis of device characteristics is essential²⁰ but rarely shown for organic resistive memory devices9. Furthermore, most devices show endurances of $< 10^3$ cycles and stability of a few hours (see Supplementary Tables 1 and 2), which are lower by orders of magnitude compared to the commercial flash memories (endurance $\sim 10^6$ cycles²¹, stability \sim years²) and as a result are insufficient for any real-world application. Additionally, because of the inherent structural complexities of the molecules in such systems, the understanding of the switching mechanism tends to be poor¹⁷, rendering further device optimization difficult. In most devices, switching behaviour is attributed to field-driven polarization^{22,23}, structural changes (for example, *cis-trans* isomerization¹⁷) or redox transitions^{10,11}, but such assignments lack direct evidence. Singling out the primary driving mechanism from several possibilities is a challenge and requires in situ molecular characterization which has so far been scant for such devices^{12,17}. In this report, we introduce a memristive device based on a ruthenium (Ru) complex with an azo-aromatic ligand which, in terms of performance, exceeds all previous reports in organic memory devices (see Supplementary Table 3) and shows potential comparable to the oxide-based memories (see Supplementary Table 2). Also, these devices allow us to study the switching mechanism via in situ Raman and ultraviolet-visible (UV-vis)

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Figure 1 | **Structure and device characteristics. a**, Molecular view of the compound *mer*-[Ru(L)₃](PF₆)₂ (hydrogen atoms are omitted for clarity; crystal structure deposited to Cambridge Crystallographic Data Centre with the deposition number: CCDC 1556448). **b**, Schematic of our device with the molecular film sandwiched between two electrodes. **c**, AFM-image of the topography of a planar ITO-bottom electrode (top panel) and an ITO electrode covered with sputtered Au NPs (bottom panel). **d**,**e**, Current-voltage characteristics, *J*(*V*), for 321 devices with planar electrodes (**d**), and 50 devices with NP electrodes (**e**) (details listed in Supplementary Table 3): the clouds contain the *J* values of all devices while the blue lines indicate the mean values of *J* at each point. There is a low-current plateau near 0 V, but note that here the device remains in the on state (for retention test, see Supplementary Fig. 1). **f**, Device structure where a c-AFM tip is used a top electrode. **g**, The current *I* and *J*(*V*) measured with the device structure shown in Fig. 1f. Orange cloud shows data from 50 different measurements performed at five different locations (for details see Supplementary Section 1).

spectroscopy supported by quantum chemical calculations, establishing the unambiguous role of ligand redox in device conductance.

Device structure and characteristics

Figure 1a shows a molecular view of our model system, *mer*-[Ru(L)₃](PF₆)₂ complex²⁴, with three bidentate ligands (L = 2(phenylazo)pyridine) each containing one azo (N = N) functional group. The molecule has a charge of +2 which is balanced by two PF₆⁻ counterions. The full preparation details, characterization of this molecule, and details of device fabrication are provided in the Methods. Our basic device (type A) structure is shown in Fig. 1b, where a film of [Ru(L)₃](PF₆)₂ is spin-coated on epitaxially grown indium tin oxide (ITO) above which top electrodes are evaporated using a shadow mask. We also prepared a second device (type B) where Au nanoparticles (NPs) are sputtered at the ITO–organic layer interface. NPs are used for interface engineering to reduce the charge injection barrier (and/or the potential drop at the interface) via several mechanisms, including local electric field enhancement²⁵, provision of mid-gap states^{26,27}, charge trapping^{28,29} and domain de-pinning³⁰ (for example, ferroelectrics). The atomic force microscopy (AFM) images of both types of bottom electrodes with and without NPs are shown in Fig. 1c (top and bottom panel).

Figure 1d shows the typical current density-voltage characteristics, J(V), for device A while Fig. 1e shows J(V) for device B. We have measured 321 samples of varied sizes for device A and 50 samples for device B. All the measured data are contained in the orange cloud shown in Fig. 1d,e and the device details are listed in Supplementary Table 3. Beginning at zero bias, device A starts in the off state until reaching (3.95 ± 0.21) V, where the conductance suddenly increases by four orders of magnitude. When exceeding the switching voltage, the device remains in the on state, which is, in fact, retained while reversing the voltage sweep until it is switched off at (-4.14 ± 0.19) V. The off state is then maintained until the maximal negative bias and during the return to 0 V, after



Figure 2 | **Device statistics. a**, Histogram of the current measured at +2 V in on and off states for 321 samples of device A. **b**, Distribution of on and off voltage of device A. **c**, Histogram of the current measured at +0.3 V in on and off states for 50 samples (10 measurements on each sample) of device B. **d**, Distribution of on and off current measured at +0.3 V in on and off current measured at +0.05 V in on and off states for 50 different *J*(*V*) of the c-AFM device (Fig. 1e). **f**, Distribution of on and off voltages of the c-AFM device. The black lines are Gaussian fits to the histograms.

which the cycle repeats. During reverse voltage sweep, near 0 V, a non-conducting plateau is observed, but notably in this regime the device is not turned off, as illustrated in Supplementary Fig. 1. These devices, although robust and reproducible, suffer from high switching voltage values compared to the International Technology Roadmap for Semiconductors (ITRS) specifications for resistive random access memory (ReRAM) devices. Additionally, the low current-density values constrain their scaling to smaller dimensions. These shortcomings are addressed by device B with gold NPs at the ITO/film interface. To address this, we use a modified device structure (device B) with NPs sputtered at the ITO/film interface. The presence of NPs in device B improves the following two device characteristics substantially: the switching bias window reduces by 90%, enabling switching on and off at $(519 \pm 30) \,\mathrm{mV}$ and (-547 ± 37) mV respectively, and the current densities increase by four orders of magnitude compared to device A. To demonstrate scalability of device B, we created a nanoscale test device using a conductive-AFM (c-AFM) tip as the top electrode and a NP on ITO as the bottom electrode, as shown in Fig. 1f (see Supplementary Section 1 for measurement details). The contact area to the c-AFM tip is estimated to be $\sim 60 \text{ nm}^2$ (see Supplementary Section 1 for calculation). The I(V) and J(V) characteristics of this device are shown in Fig. 1g, where we achieve a switching voltage of 100 mV along with the on- and off-state current of $(0.8 \pm 0.1) \mu A$, and

 (0.6 ± 0.1) nA, respectively (implying on- and off-state device resistance of 62 k Ω and 83 M Ω for a ~60 nm² device area), at a reading voltage of 50 mV. This switching voltage together with the read voltage and current values exceed the ITRS-2015 specifications for current sensing, which makes this device a promising candidate for high-density memory applications via integration with CMOS¹⁶, with further scope for scaling down.

Device statistics

To address the issue of device-to-device reproducibility, we analysed the distribution of currents and switching voltages obtained by measuring 321 samples of device A, 50 samples of device B (10 measurements per sample) and 50 measurements on five distinct locations with the c-AFM top electrode on the NPs. Figure 2a shows the statistical distribution of current densities (on and off) for device A and Fig. 2b shows the histogram of switch-on and off voltage for the same device. Figure 2c,d shows the same for device B, while for the c-AFM device the statistical distribution is shown in Fig. 2e,f. Evidently, the $(\Delta J (2\sigma)/J_{mean})$ values for on and off states are about 31% and 16% for device A, while the same for device B are around 46% and 50% (see Supplementary Fig. 2 for on/off ratio of devices of various sizes). Even when scaled down to ~60 nm² these values for the c-AFM device come out to be 20% and 50%. All these values of current spread are much smaller compared to the current-density on/off ratio



Figure 3 | **Device performance. a**, Read-write pulse sequence for device A: $V_{write-on} = 5 V$, $V_{reset-off} = -5 V$, $V_{read-on/off} = \pm 2 V$ (acronyms: W, Write; R1, R2, Read; E, Erase). **b**, Read/write pulse sequence for device B. $V_{write-on} = 0.65 V$, $V_{reset-off} = -0.7 V$, $V_{read-on/off} = 0.3 V$. The switching time is estimated to be less than 30 ns. (Note that the size of the device used for this measurement is $3 \mu m \times 3 \mu m$, for which the off-state resistance ~900 M\Omega. This resistance value might look too high for devices where off-state current assists the filament formation but it is irrelevant for our device. In our device, the electrostatic conditions drive the switching, and hence in spite of having a high off-state resistance we do observe a switching time as low as 30 ns.) **c**, **d**, The endurance of device A (**c**) and device B (**d**) over 10^{12} cycles probed with the respective pulse pattern shown in **a** and **b**. Microsecond pulses are used for planar devices and are measured over 230 days. Device B was driven with ~100 ns pulses over a period of about two days. **e**, **f**, The stability of on and off currents measured on (**e**) device A and (**f**) device B. For both, twin devices were fabricated on the same chip: we put one device in the on state, the other one in the off state. Both devices were measured simultaneously with constant application of read voltage (+2 V for device A, +0.2 V for device B) at 350 K.

of ~10⁴, eliminating the possibility of any overlap between the current readings in the on and off states. The variation $(\Delta V (2\sigma)/V_{mean})$ in the switch-on and switch-off voltages of all of these devices is <10%, which is much smaller compared to other device reports with even smaller sample sizes^{31,32}. These data demonstrate a great control over device-to-device as well as cycle-to-cycle consistency, even at nanodimensions, which has been a major concern of the community, as emphasized in several recent review articles^{2,9,12}.

Device performance

Now we discuss the dynamical and temporal characteristics of the devices. The read–write sequences for devices A and B are shown in

Fig. 3a,b. Device B is operated at a write-voltage as low as 650 mV and a readout voltage of 300 mV, and the on-state current density becomes as high as 10⁴ A cm⁻². Based on the measured resistance (R) and capacitance (C), an RC time constant (τ_{RC}) = 1.37 ps is estimated for this device. Here we demonstrate (Fig. 3b) a switching speed of about 30 ns, limited by our measurement system. Notably, even with a 30 ns switching time, the estimated switching energy per bit comes down to ~1.5 fJ (for this calculation, see Supplementary Section 1) for a 60 nm² device area—comparable to TaO_x-based RRAM devices which are in the process of commercialization³³.

The endurance (cycles) of devices A and B are demonstrated in Fig. 3c,d. No visible degradation is observed for either of these



Figure 4 | **Detection of redox states by** *in situ* **spectroscopy. a**, Cyclic voltammetry (CV) of $[Ru(L)_3](PF_6)_2$ (2 mM) with Ag/AgNO₃ reference electrode in anhydrous acetonitrile solvent with 0.1 M $[Et_4N]PF_6$. The formal potentials for the six redox events are -0.35, -0.66, -1.14, -1.42, -1.78, -2.09 V versus Ag/AgNO₃. **b**, Gas phase DFT-calculated HOMO, LUMO+1, LUMO+2 and LUMO+3. The acceptor orbitals (LUMO-LUMO+2) are localized on individual ligands. **c**, Spectroelectrochemical (UV-vis spectroscopy coupled to CV) data for the first four redox states. **d**, UV-vis spectra measured for thin-film devices at indicated values of applied bias. The film spectra are matched with the spectroelectrochemical spectrum with which it best agrees. **e**, Raman spectra measured for thin-film devices at indicated values of applied bias (same values as **d**). We have shown the spectra between 1,100 cm⁻¹ and 1,500 cm⁻¹ since this range includes the region of our interest capturing the dynamics of the peaks at 1,365 cm⁻¹, 1,313 cm⁻¹ and 1,275 cm⁻¹. Other peaks show relatively insignificant sensitivity to applied bias.

devices even after about 10^{12} write-read-erase-read pulse cycles. This endurance is exceptional compared to typical read-write cycles of 10^5 - 10^6 in commercial flash memories²¹. Device A was measured continuously over 230 days with microsecond write-read pulses (Fig. 3a), while device B was driven with 100 ns pulses (Fig. 3b) over two days. These data match the performance of the best endurance data reported so far in a RRAM device⁶.

To estimate stability, two devices of each type were placed into on and off states at time zero and current was sampled at 350 K, which is the typical semiconductor-device test temperature. During measurement, the readout voltage (indicated in Fig. 3e,f) was sustained. Device A was measured for two months and device B for one month without degradation. Accelerated lifetime tests are being conducted to determine the upper limit of the stability of the devices. For now, however, it is clear that these devices exceed by far any report on (metal) organic devices (see Supplementary Tables 1 and 2) in terms of every performance parameter, rendering them competitive to metal-oxide devices.

In situ spectroscopy

To relate the transport phenomena to the electronic structure of the molecules, in situ Raman and ultraviolet-visible-nearinfrared (UV-vis-NIR) spectroscopy for the thin-film devices was performed. We compared these film-state spectra to spectroelectrochemistry data where UV-vis-NIR absorption spectra were measured simultaneously with cyclic voltammograms (CVs). Figure 4a shows the CV with six well-resolved reduction peaks. With the help of density functional theory (DFT) calculations, these redox peaks were assigned to the population of three closely spaced, low-lying lowest unoccupied molecular orbitals (LUMOs) of $[Ru(L)_3](PF_6)_2$, each localized to a single ligand (Fig. 4b). The spectroelectrochemistry of the constituent $[Ru(L)_3]^{2+}$ complexes in solution during the first four redox events are shown in Fig. 4c. Figure 4d shows in situ UV-vis-NIR absorption spectra measured for device A at different bias voltages, as indicated in the figure. Evidently, spectral transitions during reduction events in solution show a very close match to the spectra of the thin-film

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Figure 5 | **Correlation between Raman peaks and film conductance. a**, Pseudo-colour plot of voltage-resolved Raman spectra measured for device A during forward voltage sweep (voltage sweep from -4.2 V to +4.2 V). **b**, Top panel: J(V) response for forward voltage sweep. Bottom panel: the extracted values of intensity (normalized to produce an average sum of ~100) of the Raman peaks at 1,365 cm⁻¹, 1,313 cm⁻¹, 1,275 cm⁻¹ for individual applied biases during forward voltage sweep. **c**, Pseudo-colour plot of voltage-resolved Raman spectra measured for device A during reverse voltage sweep (voltage sweep from +4.2 V to -4.2 V). **d**, Top panel: J(V) response of device A for reverse voltage sweep. Bottom panel: the extracted values (normalized) of intensity of the Raman peaks at 1,365 cm⁻¹, 1,215 cm⁻¹ for individual applied biases during reverse voltage sweep. **e-h**, Corresponding measurements and data analysis for device B; voltage range ~(-0.8 V to +0.8 V and vice versa).

devices for specific voltage ranges. These observations imply that the applied bias voltage triggers a ligand redox process within the molecules in the film^{34,35}. To confirm that redox processes are important, we characterized the devices with in situ Raman spectroscopy as a function of applied voltage. Figure 4e shows the Raman spectra of device A measured at the same voltage values as in the UV-vis spectroscopy (Fig. 4d). Notably, the applied voltage induces prominent changes in only three Raman modes, those at $1,275\,cm^{-1},\,1,313\,cm^{-1}$ and $1,363\,cm^{-1}.$ DFT calculations indicate that these modes correspond to the azo (N = N) stretching mode, which changes for different redox states (Supplementary Fig. 3a-c). These are the most sensitive modes in the Raman spectra because the acceptor orbitals are localized on the azo-groups of specific ligands (see Fig. 4b), consistent with previous studies³⁶⁻³⁹. The Raman peak at $1,363 \text{ cm}^{-1}$ (E_1) corresponds to the neutral azogroup. After single-electron reduction, an azo-anion is produced and the corresponding Raman peak shifts to $1,313 \text{ cm}^{-1}$ (E_2). The peak at $1,275 \text{ cm}^{-1}$ (E_3) corresponds to a doubly reduced species (hydrazido di-anion). The oscillator strength of the azomodes in all three redox states are almost the same, as observed in the Raman measurement (see Supplementary Section 2), and as a result the spectral weight of each peak is a measure of the amount

of each ligand redox state present within the bulk of the molecular thin film.

Figure 5a shows a pseudo-colour map of the voltage-resolved Raman spectra for device A in the forward voltage sweep (-4.2 V to)+4.2 V, off state) while Fig. 5c shows the same in the reverse voltage sweep (+4.2 V to -4.2 V, on state). The spectral weight of the three peaks of our interest $(E_1, E_2 \text{ and } E_3)$ and their sum is plotted for forward and backward voltage sweeps in Figs 5b and 5d, respectively. It is observed that the sum is constant within the measurement uncertainty, which is consistent with our hypothesis. The number of molecules (and hence the number of ligands) in the film remains the same in this process, and since they have almost the same oscillator strength, the sum of the Raman intensities is conserved. Figure 5e-h shows the results of the same experiment on device B. Clearly, molecular changes in both devices are overall practically identical with the exception of the voltage windows in which they occur. Therefore, the presence of the NPs does not change the operation mechanisms of the devices, but merely reduces the charge injection barriers. In fact, in the 60 nm² devices measured with c-AFM tip as the top electrode, the charge injection barrier further reduces. A detailed model of the device's electrostatic condition and its effect on device performance is currently under investigation.

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Figure 6 | **Effect of counterion. a**, Isosurfaces (isovalue = 0.035) of LUMO of $[Ru(L)_3]^{2+}$ as structurally optimized in the presence of one PF₆⁻ counterion in four different pockets. **b**, Variation in HOMO and LUMO energy levels for the four counterion positions of $[Ru(L)_3](PF_6)^+$ (shown in **a**) and their combinations in $[Ru(L)_3](PF_6)_2$ (pairs illustrate the effect of two counterions). **c**, Effect of counterions in device A. **d**, Effect of counterions in device B.

Discussing the Raman maps in more detail, we notice that they are clearly different for forward and reverse voltage sweeps, reflecting the hysteresis observed in the J(V) plots. We identify a clear correlation between the molecular redox states and film conductance: in the on state, almost all molecular ligands are in the same redox state (90 \pm 6%: device A, 87 \pm 7%: device B), while in the off state they are in mixed redox states. The on state at positive bias is dominated only by the E_1 mode (that is, all ligands neutral in the bulk of the film), while the on state at negative bias is dominated only by E_2 (indicating ligands reduced by one electron dominate). This observation is consistent with the trend in the UV-vis-NIR spectra during a reverse voltage sweep, where only minor changes are observed between +4 V and +1 V as well as between -1 V and -4 V (Supplementary Fig. 4a–l). Note that during this operation, the film becomes charged, which is balanced by image charges formed in the metal electrodes (see Supplementary Section 2).

Role of counterions

While the bias-induced redox-state switching explains the origin of the on and off states, it does not explain the origin of the hysteresis. In the solution state, the six redox events are fully reversible, which is not true in the film. In existing literature, ionic drift-diffusion models are often used to explain current hysteresis observed in thin-film devices⁴⁰. Hence, we propose that the displacement of counterions in the film plays a key role here. DFT calculations show that the counterions can reside in several pockets around the molecule and we anticipate that the applied electric field in the device can displace them from one pocket to another, travelling sub-nanometre distances. Figure 6a shows the LUMO for four different representative positions (or pockets) of PF_6^- , as optimized with DFT (for highest occupied molecular orbital (HOMO), LUMO+1, LUMO+2, see Supplementary Fig. 5). Clearly, depending on the placement of PF_6^- , the energy order

of the three closely spaced ligand-centred LUMOs changes, as well as the degree of inter-ligand delocalization. Figure 6b shows the calculated orbital energies for these four pockets and their combinations (to emulate the presence of two counterions). It should be noted that the HOMO-LUMO gap is unchanged upon addition of a second counterion. The second anion moves both these levels equally towards the vacuum level due to a decreased total system charge, falling closer to those obtained from CV measurements. When an electric field on the order of 100 MV m⁻¹ is applied across the film, the relative position of counterions with respect to the molecule is likely to change due to fieldassisted reorientation. To move the counterions back to their original position, an electric field of opposite polarity would be required, resulting in I(V) hysteresis. Given this hypothesis, one would expect to observe a steric effect of the counterions on the current hysteresis. To verify this, we prepared additional devices with counterions of various van der Waals (vdW) volumes⁴¹. With planar ITO electrodes, BPh_4^- (vdW-volume = 187.7 Å³) devices show a much less robust on state when compared to the PF_6^- (vdW-volume = 69 \pm 0.3 Å³) devices while those with $Cl^{-}(vdW-volume = 22.4 \text{ Å}^{3})$ show slightly increased hysteresis (Fig. 6c), all of which is consistent with our hypothesis. In fact, this field-assisted counterion displacement appears to play a decisive role in devices with NPs as well. Figure 6d shows I(V) of devices (with NP) with different counterions, where we observe that bulkier counterions such as BPh4- require a larger switching voltage and yield weaker currents compared to smaller ions such as PF₆⁻ or Cl⁻. We reason that, in our film, the spatial separation between molecule and counterion results in the formation of dipoles (supported by DFT, see Supplementary Fig. 6) and the dipole-dipole interaction brings forth the bulk changes which are initiated at the NP-film interface by the locally enhanced field, similar to the case in ferroelectric films⁴². This hypothesis is substantiated by the correspondence between the size of counterions and the effect of NPs observed in the bulk film (Fig. 6d). Clearly, counterion mobility facilitates the bulk change in the film and it is consistent with the larger switching voltages observed in devices with heavier counterions.

Overall, a combination of molecular redox processes in conjugation with counterion displacement is what brings forth the resistive memory effect. The ligand we have chosen here is one of the strongest π -acceptor ligands, which when coordinated to the metal centre brings down the acceptor orbitals⁴³ to even lower energies (compared to most other complexes10,11,44,45, see Supplementary Table 2). This results in stable redox states which impart stability to the molecules over a large number of redox cycles. Also, the ligand-centred LUMO orbitals are of π character, enhancing intermolecular coupling, which in turn facilitates intermolecular electron transfer, essential for this kind of charge transport. Notably, the molecule we are considering here has three redox-active azo-centres, which give rise to two sets of redox combinations: either all ligands in the same redox state (either neutral or single-electron reduced) or two of them in one state while the third in a different state. These two possibilities give rise to two different film-conductance states, resulting in a binary switching. In principle, if these ligands could be replaced with other species with a higher number of redox-active sites, it could potentially lead to more than two conductance levels. In addition, unusual phenomena may be possible when ruthenium is replaced with other transition-metal centres. From a fundamental scientific point of view this class of systems is exceptionally promising.

In summary, our devices shift the paradigm in organic resistive memories both in terms of performance and understanding, both of which have been long-standing roadblocks in this community. This class of devices has the potential for further optimization and commercial translation.

Methods

Methods, including statements of data availability and any associated accession codes and references, are available in the online version of this paper.

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Author contributions

Sreetosh Goswami devised the project, fabricated the devices, and did the J(V) measurements and the *in situ* spectroscopies. S.Saha helped Sreetosh Goswami with the *in situ* Raman measurement technique and data analysis. A.J.M. and S.H. built the theoretical models and performed the DFT calculations. S.P.R. and D.S. synthesized and characterized the compounds in solution. M.A. did the c-AFM measurements and analysis. A.P. did the AFM measurement, analysis and strategic discussions. H.J., S.Sarkar helped Sreetosh Goswami, to fabricate NP devices. M.R.M. conducted the Rutherford Back Scattering (RBS) measurements. J.M. analysed the transport data and guided Sreetosh Goswami for experimental planning and data interpretation. C.A.N. provided guidance in experimental designs and understanding the phenomena. V.S.B. supervised the theoretical contributions. Sreebrata Goswami introduced the materials and supervised their synthesis and characterization. T.V. supervised the entire research programme. All the authors participated in manuscript writing.

Additional information

Supplementary information is available in the online version of the paper. Reprints and permissions information is available online at www.nature.com/reprints. Publisher's note: Springer Nature remains neutral with regard to jurisdictional claims in published maps and institutional affiliations. Correspondence and requests for materials should be addressed to Sreebrata Goswami, V.S.B. or T.V.

Competing financial interests

The authors declare no competing financial interests.

Methods

Synthesis of materials. The ligand L was synthesized as previously reported^{46,47}. *mer*-[Ru(L)₃](PF₆)₂ was synthesized via the double decomposition of the corresponding perchlorate salt of the complex by NH₄PF₆. The precursor complex *mer*-[Ru(L)₃](ClO₄)₂ was synthesized as previously reported²⁴. The calculated elemental analysis percentages for $C_{33}H_{27}F_{12}N_9P_2Ru$ were C,42.14; H,2.89; N,13.40 while the experimentally measured numbers were C,42.28; H,2.93; N,13.32.

Electrochemical characterization. Cyclic voltammetric (CV) experiments of mer-[Ru(L)₃](PF₆)₂ were carried out in dried acetonitrile using tetraethylammonium hexafluorophosphate as the supporting electrolyte; the reported potentials are all referenced to the Ag/AgNO₃ electrode. All electrochemical measurements were performed using a PC-controlled PAR model 273A electrochemistry system, keeping the CV-cell assembly inside a glove box maintained at an O₂ level of <1 ppm and a moisture level of <1 ppm. We used a three-electrode cell where the working electrode is glassy carbon (area = 3.14 mm²), the reference electrode is Ag/AgNO₃, the electrolyte is acctonitrile containing 0.1 M [Et₄N]PF₆ and the counter electrode is a Pt-wire (area = 220.69 mm²) dipped in a glass compartment having solution of 0.1 M [Et₄N]PF₆ in acetonitrile separated by a Vycor frit from the main solution.

NMR, ESI-MS spectroscopy and elemental analysis. NMR spectra were obtained using a Bruker Avance 500 MHz spectrometer. A Perkin-Elmer 240C elemental analyser was used to collect microanalytical data (C, H, N). ESI mass spectra were recorded on a Micromass Q-TOF mass spectrometer (Model No. YA263). Supplementary Fig. 7a–c summarizes the results.

Device preparation and characterization. Indium tin oxide (ITO) grown on annealed yttria-stabilized zirconia (YSZ) was used as the bottom electrode for all the devices. Freshly grown ITO electrodes were used for device preparation, which ensures a much higher surface coverage and better reproducibility. Treatment of the electrode with oxygen plasma just before film preparation was found to be favourable to device performance. Au NPs on the bottom electrode were obtained by annealing ultrathin Au-film sputtered on ITO substrate following the well-established methods⁴⁸.

The solution of precursor molecules in acetonitrile was deposited on ITO by off-centred spin coating (OCSC)⁴⁹. The solution concentration and substrate position in the spin coater with respect to the centre and the rotor speed can both be varied to get various film thicknesses. After deposition, the samples were stored in a vacuum chamber with a pressure of ~10⁻⁸ torr for 12 h. Subsequently, we deposited Au/ ITO using shadow masks of numerous sizes. Au-electrodes were fabricated using electron beam evaporation. ITO top electrodes were deposited by the pulsed laser deposition (PLD) technique.

Rutherford backscattering spectroscopy of the film (RBS). Rutherford backscattering spectroscopy was used to measure the ruthenium areal density. A silicon surface barrier detector (energy resolution of 15 keV) was used in a 160-degree scattering angle geometry to collect the RBS spectra by probing with 2 MeV He⁺ ions. We chose beryllium as the substrate to quantify the lighter elements in the molecule. The SIMNRA⁵⁰ software was used to fit the experimental data. The ruthenium areal density was found to be 3×10^{14} atoms cm² for a film thickness of 80 nm, resulting in a volumetric density of ruthenium (and hence the molecule) of 3.75×10^{19} cm⁻³.

Notably, the molecular stoichiometry is not retained in the RBS data since elements of low atomic weight are likely to escape due to high-energy ion irradiation⁵¹. For our film, ruthenium is the heaviest element and, since it is too heavy to be evaporated via irradiation we take the ruthenium count as a reliable measure of the molecular density (each molecule contains 1 Ru-atom so the Ru-count represents the molecular density). Refer to Supplementary Fig. 7e for the RBS spectrum.

J(*V*) **measurements**. The devices were characterized using a standard Keithley and Agilent Measurement Systems. The characterizations were performed in probe stations and a Physical Property Measurement System (PPMS, Quantum Design). The measurements performed in air and in vacuum show almost similar characteristics, eliminating any possibility of effect of moisture in the device response.

ITO/film/ITO devices display very similar J(V)s to ITO/film/Au devices. Notably, even in the ITO/film/ITO configuration, the bottom electrode–film interface is different from the film-top electrode interface owing to the preparation methods of the two electrodes. The fact that the work function of the top electrode does not change the J(V) excludes a Schottky barrier. Devices without a bonding pad for top electrode were measured with a micro-manipulated probe station where the contact between the spring-loaded probes and the electrode is controlled by an automated sensor ensuring minimum mechanical damage to the devices.

In situ Raman spectroscopy. A JY Horiba LabRAM Evolution Raman spectrometer with an air-cooled charge-coupled device (CCD) detector was used for all measurements. A Lexel SHG 95 Argon Ion laser was used for the excitation. Excitation wavelengths of 514.5 nm, 488 nm and 633 nm were used to identify the Raman modes. However, for all voltage-resolved measurements we used the 514.5 nm laser excitation. The measurements were performed in reflection geometry. Since we needed to probe the signal from the film, we used transparent ITO as the top electrode while the rest of the device geometry was the same as described in Supplementary Fig. 8a. As shown in figure, the measurement set-up includes a confocal microscope to focus the laser at a desired spot of $\sim 1 \,\mu\text{m}^2$. We used a 514.5 nm continuous laser with $20\,\mu\text{W}$ power incident on the sample. The voltage was applied on the sample using a Keithley-2400 source meter. The voltage loop was programmed to stay for 300 s at each voltage point during which we measured the Raman spectrum. In between each pair of measurements, the Si-peak at 520 cm⁻¹ was calibrated to avoid any measurement artefacts. The spectra were measured with an average integration time of 15 s.

In situ UV-visible-NIR spectroscopy. We used a Shimadzu (Japan)

Solidspec-3700 spectrophotometer for this *in situ* measurement. The device structure was ITO/film/ITO/YSZ. We measured the spectra in transmission mode where the sample was mounted between the lamp and the detector as shown in Supplementary Fig. 8b. The voltage was applied using a similar instrumentation and interface as described above. Each voltage point was held for 500 s when the UV-vis spectra were recorded and between each pair of UV-vis we corrected background to eliminate artefacts.

Computational methods. Density functional theory (DFT) calculations were performed using the hybrid B3LYP (ref. 52) exchange–correlation functional and def2svp (ref. 53) basis set with unrestricted Kohn–Sham wave functions as implemented in the Gaussian 09 package⁵⁴.

Calculated vibrational frequencies were scaled by 0.96, a scaling factor for the B3LYP functional with this basis set as calculated by the Computational Chemistry Comparison and Benchmark Database. *Ab initio* calculations of vibrational frequencies need to be scaled to match experimental frequencies to accommodate for two factors, the fact that the electronic structure calculation is approximate (no full configuration interaction, no relativity, and so on) and because the potential energy surface is assumed to be harmonic. Since the calculated frequencies seem from the second derivative of the potential energy surface, treating the PES as harmonic rather than a Morse potential results in energy level spacings which are further apart than in reality.

Data availability. The data sets generated and/or analysed during the current study are available from the corresponding authors upon reasonable request.

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Corrigendum: Robust resistive memory devices using solution-processable metal-coordinated azo aromatics

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In the version of this Article originally published, the *x*-axis units of Fig. 3a were incorrectly given as ms, and should have read µs. This has now been corrected. Two places in the text also needed amending to reflect this change: the penultimate sentence of Fig. 3c,d caption now starts 'Microsecond pulses are used', and the penultimate sentence of the second paragraph of 'Device performance' has been changed to begin 'Device A was measured continuously over 230 days with microsecond write–read pulses'. All have now been corrected in the online versions of the Article.