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Multilevel Resistance Switching and Enhanced Spin Transition Temperature in Single and Double Molecule Spin Crossover Nanogap Devices

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Abstract

Spin crossover (SCO) molecules are promising bi-stable magnetic switches with applications in molecular spintronics. However, little is known about the switching effects of a single SCO molecule when it is confined between two metal electrodes. Here we examine the switching properties of a [Fe(III)(EtOSalPet)(NCS)] SCO molecule that is specifically tailored for surface deposition and binding to only one gold electrode in a nanogap device. Temperature dependent conductivity measurements on SCO molecule containing electromigrated gold break junctions show voltage independent telegraphic-like switching between two resistance states at temperature below 200 K. The transition temperature is very different from the transition temperature of 83 K that occurs in a bulk film of the same material. This indicates that the bulk, co-operative SCO phenomenon is no longer preserved for a single molecule and that the surface interaction drastically increases the temperature of the SCO phenomenon. Another key finding of this work is that some devices show switching between multiple resistance levels. We propose that in this case, two SCO molecules are present within the nanogap with both participating in the electronic transport and switching.

Introduction

The ability of spin crossover (SCO) compounds to exist in a bi-stable spin configuration makes them an attractive candidate for constructing new spintronic devices. SCO compounds have already been employed in the design of electromechanical actuators,[1] thermochromic displays[2] and data storage.[3] However, there remains a long way to go from current research to the ultimate goal of using these compounds as the building blocks of an electrically addressable memory technology, especially in the case of miniaturising towards the molecular scale and even single molecule devices.[4]

The SCO phenomenon has been known about since the 1930s,[5] where it was discovered that certain compounds can undergo a transition between a high spin (HS) and low spin (LS) state via the application of an external stimulus e.g. the selective wavelength irradiation, pressure or most commonly a change in temperature. In these compounds, a central metal ion is bound to ligands with an octahedral symmetry. The ligand field lifts the degeneracy of the metals ions d orbitals resulting in two sets of energy levels separated by a splitting energy (Δ), as shown in figure 1b.

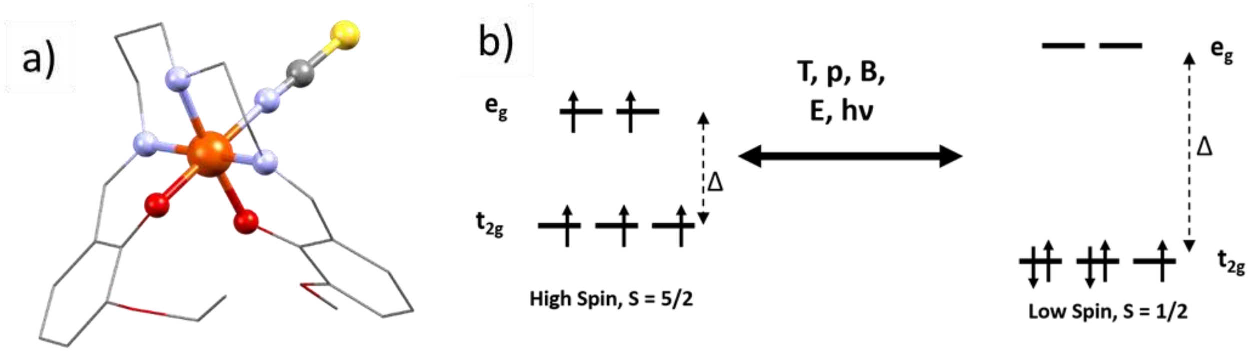

Figure 1 a) Molecular structure of the [Fe(L)NCS] complex. Fe-orange, N-blue, O-red, C-grey, S-yellow. b) Resulting energy levels for the HS and LS states split by energy Δ.

The switching mechanism is caused by a change in the interaction strength between the metal ion and ligands as a result of the external stimulus. At a certain point it becomes energetically favourable for the d electrons of the ion to either populate or depopulate the higher energy e_g orbitals based on the interaction of this external stimulus. For example, an increase in temperature results in a reduced ligand-metal ion field strength due to thermal expansion increasing the bond distances which at a certain temperature results in the spin transition from LS to HS.

In recent years, there has been progress in electrically contacting these compounds at a single molecule level using scanning tunnelling microscopes (STM) and nanogap break junctions. Whilst STM has been successful in studying the underlying physics,[3,6–9] it is not suitable for real-world devices. Nanogap break junctions come in two main types. Flexible substrates that with bending, open and close the nanogap for molecular insertion. These have the advantage of controllable nanogap size,[10,11] but the approach is incompatible with current scaling techniques and with traditional semiconductor fabrication flow processes. In this study we use the electromigration method,[12–14] which has the advantage of scalability and a rigid silicon wafer substrate for better device stability. This is particularly important in the case of magnetic electrodes,[15] where SCO compounds have the potential to be used as highly efficient spin-filters,[16–18] as it can eliminate effects from magnetostriction.[19]

DFT modelling of isolated SCO compounds in contact with metallic electrodes predicts that in general there will be a change in conductance associated with the spin transition. In one case, DFT calculations on SCO compounds between metallic Au electrodes have predicted large conductance changes as much as 3000% between the HS and LS states.[20] However, the greatest challenge concerning the usefulness of these compounds is that the switching properties shown in the bulk material are not always preserved when they are deposited onto a surface in isolation. This is due to the strong surface interaction on the molecules, which can prevent the necessary structural changes needed for the spin transition to occur. Additionally, the cooperative effects of the bulk crystal[21] are no longer present in the case of an isolated molecule and so switching may be less energetically favourable. STM studies have confirmed theoretical predictions that the two spin states can have very different resistances owing to the large electronic and structural rearrangement that occurs during the spin transition. Additionally, they have confirmed the role of the interface on the switching mechanism, demonstrating how challenging the work is at the molecular level with attempts at decoupling surface interactions by placing either a thin insulating layer[3,22] or a secondary layer of SCO molecules[7] to maintain the SCO behaviour. Others have measured the low temperature signature of unpaired spins in gated molecular junctions containing SCO compounds by the presence of a Kondo peak in the I-V characteristics, and were able to control the spin transition by charging the SCO molecule via electrical gating.[23] A zero bias (Kondo) resonance is an indication of unpaired spins and a hallmark of SCO phenomenon in isolated molecules. However, this is a feature that is present only at low temperature.

In this work we investigate a SCO complex with general formula [Fe(L)NCS] compound, where L = N,N'-bis(3-ethoxy-2-hydroxybenzylidene)-1,6-diamino-3-azahexane, as shown in figure 1a. This compound belongs to a group of Schiff base complexes in which the sixth Fe(III) coordination site is taken up by a pseudohalido ligand. In the compound used in this study, this site is occupied by an NCS (isothiocyanate) group allowing the molecule to bind to Au surfaces. In the bulk this compound shows a sharp spin transition around 83 K with a small hysteresis loop of 2K (Supporting Information). The synthesis of [Fe(L)NCS] has been previously reported.[24]

Results here contrasts with recent work that has observed conductance switching in electro-burnt graphene nanogaps containing $[Fe(L')_2](BF_4)_2{\cdot}CH_3CN{\cdot}H_2O$ SCO compound in which they observe a switching process in the I-V characteristics that is random and independent of temperature. The authors aim of reducing molecule – electrode coupling to preserve the SCO behaviour using graphene has the disadvantage that telegraph-like switching has also been observed in clean electro-burnt junctions, which as discussed below, sheds doubt onto the origin of the switching mechanism.[25]

Experimental

Devices are prepared using a two-step bilayer nanoimprint and photolithography process.[4] First, a bilayer resist structure is coated onto oxidised silicon substrates. The top layer is a low molecular weight PMMA (15k M_w) which is coated onto a PMGI layer. Both layers are baked for 10 minutes at 190°C to drive off residual solvent. Nanoimprint lithography is used to pattern the top PMMA layer with a stamp prepared using EBL and RIE. After a brief plasma etch the bottom PMGI layer is partially removed so that an undercut of the PMMA layer is created after development. 15 nm of Au is deposited using e-beam evaporation in a system with a base pressure of $1{\times}10^{-7}$ mbar and lift-off is performed first in acetone and then N-Methyl-2-pyrrolidone. These features are then connected to bonding pads using photolithography. A complete device containing 15 nanojunctions is shown in figure 2a.

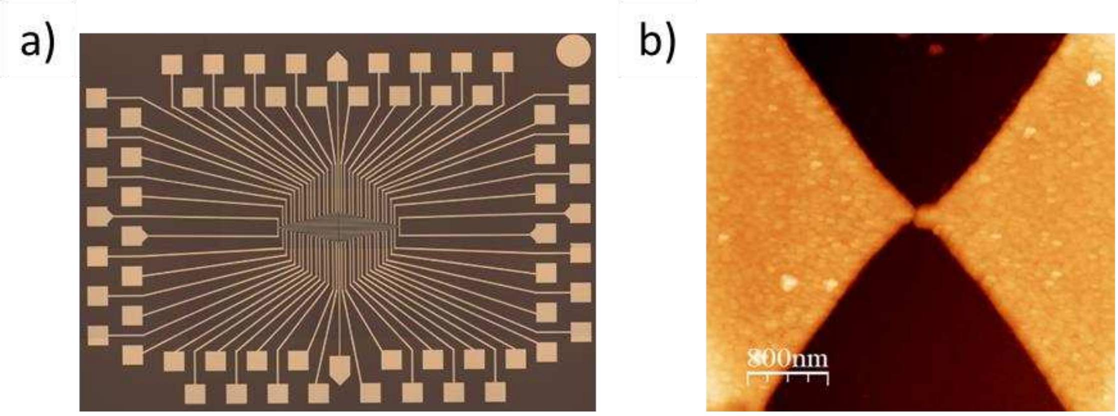

Figure 2 a) Device containing 15 nanojunctions with bonding pads. b) Nanogap after feedback controlled electromigration.

Molecules are deposited onto the nanojunctions by first oxygen plasma cleaning the devices at low power before depositing a solution of 0.01 mM [Fe(L)NCS] (see[24] for details of the [Fe(L)NCS] molecules) dissolved in acetone onto the device. After careful drying with nitrogen the devices are then mounted in a custom-made sample holder within a continuous flow cryostat and the sample space is evacuated to $1{\times}10^{-7}$ mbar before breaking the nanojunction. A feedback controlled electromigration technique (see Supporting

Information) is used to produce a nanoscale gap in the gold nanojunction.[13,14,26] In brief, this process monitors the resistance of the nanojunction using a lock-in technique, a series of pulses of variable length and voltage are applied to the device. Through a combination of joule heating and electron-wind force the junction becomes thinned until a tunnelling gap is formed. This is indicated by a sharp jump in conductance to values well below $G_0 = 2e^2/h$, where G_0 is the quantized unit of electrical conductance that is defined by the elementary charge e and Planck constant h. A feedback mechanism is used to reduce the power applied to the junction so that a thermal runaway is avoided with the results that nanogaps can be produced with high yield, figure 2b.

Nanogaps produced using this technique regularly yield devices with electrode separation below 5 nm, as confirmed by *in situ* TEM measurements.[27] In particular, the great benefit of the feedback-controlled process is that devices can be fabricated with high reliability as it avoids the process of thermal runaway allowing the possibility of very small metallic electrodes to be reproducibly made.[4] We have been able to produce controllable electromigration in over 40 devices with metallic constrictions fabricated from either permalloy, Co or Au. In a study on several electromigrated Au devices identical to those used in this work, the gap size was found to be below 2 nm which was determined by measuring the tunnelling current across empty nanogaps formed *in situ* under high vacuum conditions. Two plots are shown in the supporting information, figure S3a) and 3b), in support of this.

Temperature dependent resistance measurements are performed by allowing the cryostat to warm slowly over the course of 24 hrs. Temperature is measured using a calibrated Pt-100 situated on the sample holder and resistance is monitored every 300 ms using a lock-in technique with 8 mV excitation at 989 Hz.[28]

Results and Discussion

The results in figure 3 show the typical behaviour of an electromigrated Au nanogap junction that contains the SCO complex. Figure 3a shows the resistance vs temperature during cooling from 293 K to 70 K. The SCO phenomenon is evident at temperatures below 200 K, where the resistance of the device shows a clear bi-stable effect with fluctuations in the resistance between two well-defined levels. We ascribe these two resistance levels to the two different spin states of the molecule, which appears to freely switch without being triggered by light or current. We note here that during all measurements the sample was kept in the dark and the current used for measuring, 22 nA, is too small to trigger the switching. Furthermore, the induced switching of SCO complexes has been shown to be an electric field driven process, requiring upwards of 0.5 - 0.75 V in STM and mechanical break-junction devices.[3,29] At 83 K the switching effect is well established, and the lifetime of the states are long-lived with each state existing for a maximum of 167 minutes, as shown in figure 3b. Resistance histograms of the state of the molecule at 83 K and 293 K are shown in figure 3c and 3d, respectively, and clearly shown the two well-defined states at the lower temperature. Analysis of figure 3c shows that on average the molecule is in the low resistance state slightly more of the time (≈53%) than the high resistance state. This was determined by deconvolving the histogram into two Gaussian peaks and integrating the area of each peak. This gave approximately 53% and 47% for the probability of occupation of the low and high resistance states, indicating the molecule slightly favours being in the low resistance state. (see Fig S5 of the Supporting Information for more details)

In contrast, figure 4a shows the situation when multi-level switching behaviour of a device was observed in a device after heating to room temperature a device that previously showed bi-stability. This is likely as a result of a second SCO complex either becoming active or moving into the nanogap after an extended duration at room temperature. This behaviour can be explained if instead of one molecule in the junction, there are two molecules situated in the nanogap region. In this case, the total tunnelling current is influenced by the relative contributions from both molecules. Monitoring the resistance over a long period of time a resistance histogram plot was obtained, as shown in figure 4b. Four narrow peaks are clearly visible. These are expected to be due to the following spin combinations of the two molecules within the gap (LS-LS, HS-LS, LS-HS, HS-HS). Figure 4c shows the resistance histogram of the device before cooling. In this case only a single broad peak is observed, indicating that the molecule is in the HS state due to the temperature dependence of the splitting energy, Δ. We note here that the greater broadness of this peak is due to the larger noise at high temperature arising from intrinsic electronic noise sources as well as thermal motion of the molecule within the junction and electrodes.

In both cases, resistance fluctuations from the structural motion of the electrode can be excluded, as this process is unlikely to present itself as a clear two or four level stability in the conduction. If this were the case, a random evolution in the measured resistance over many values or irreversible jumps in the resistance because of different molecular arrangements on the surface would be instead observed. Moreover, this behaviour would be strongly temperature dependent, being reduced at cryogenic temperatures as atomic motion is reduced. Voltage induced changes in the electrode structures can also be excluded since we limit the measurement to very small applied bias of 8 mV.[30] In devices broken without the deposition of molecules we see only a weak temperature dependence in the tunnelling resistance after cooling of the device to 70 K, as shown in Figure S3c (Supporting Information).

There is only one previous report of similar telegraphic-like switching behaviour reported, albeit at a much lower temperature, in molecular junctions containing SCO compounds. Electro-burnt graphene devices containing a $Fe(L')_2](BF_4)_2 \cdot CH_3CN \cdot H_2O$ compound exhibited telegraphic like conductance switching at 4 K. With the aid of DFT calculations, Burzurí *et al.* were able to show[6] that due to changes in the electronic structure of the compound, the two particular spin states of the compounds manifest as different levels of current suppression in the I-V curves with the LS state corresponding to a large current suppression and HS presenting less.

The structure of the SCO compound used here differs significantly from this previous study based on $[Fe(L')_2](BF_4)_2 \cdot CH_3CN \cdot H_2O$. The complex used in this study, being smaller and lacking the large pyrene end groups and extended linking units do not impart such a high degree of spin-state switching sensitivity on the ligand positions that $[Fe(L')_2](BF_4)_2 \cdot CH_3CN \cdot H_2O$ is known to have.[16] We believe that this structural difference is the key to preserving the temperature induced SCO.

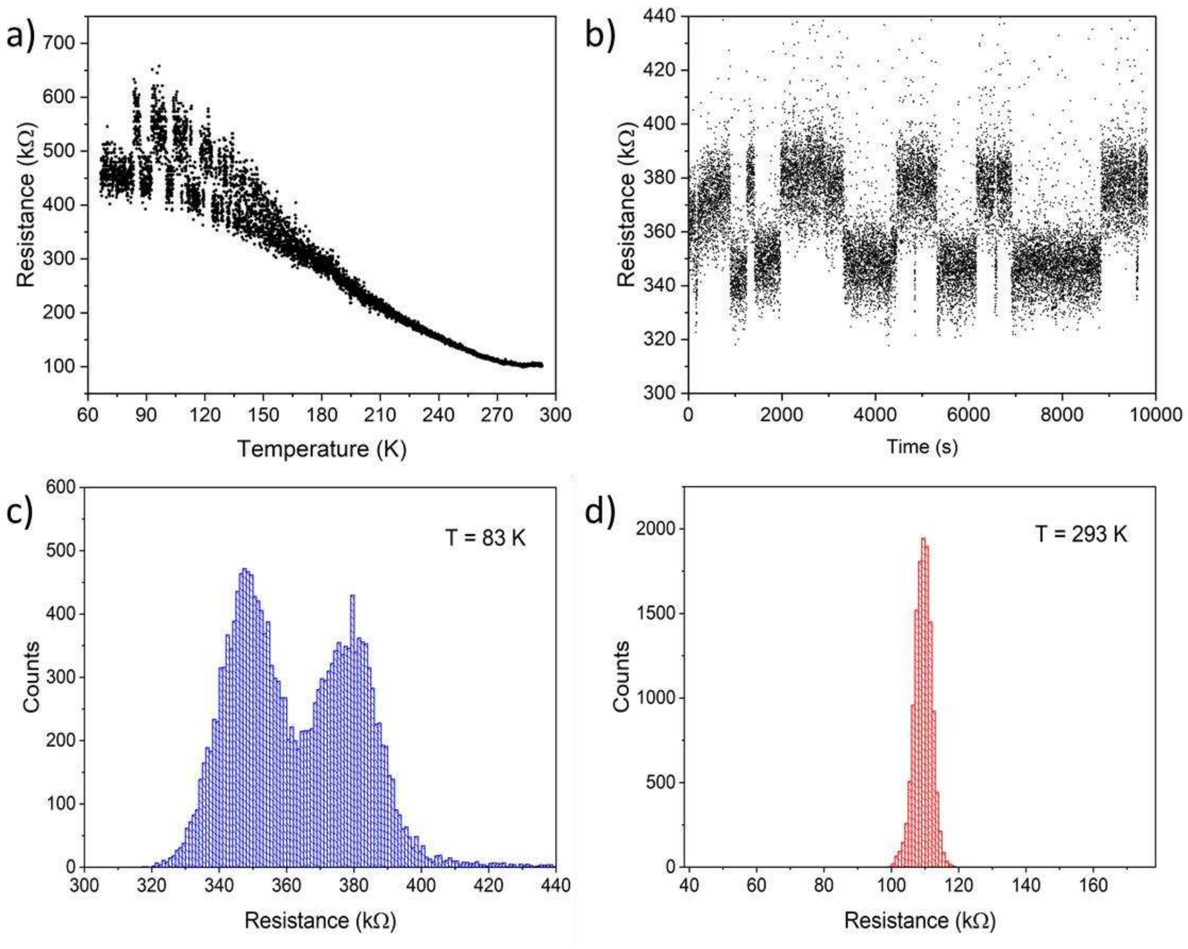

Figure 3. a) Resistance vs temperature during cooling from 293 K to 70 K for an electromigrated Au nanogap containing the SCO compound and showing the appearance of the SCO phenomenon at temperatures below 200 K. b) Resistance vs time of the device at 83 K. Resistance histograms at c) 83 K and d) 293 K. (Note: Bin size is 1 kΩ for each of the histograms with 1.2×10^4 measurements made on a single device at each temperature).

The emergence of the resistance switching fluctuations between two states at temperatures below 200 K in figure 3 shows that the switching behaviour of the isolated molecule is drastically modified compared to that of the bulk and thin-film material, which have transition temperatures during cooling of 68 K and 80 K respectively (see the supporting information Fig. S6). This is not surprising since in a bulk material there is a cooperative switching effect that makes it difficult for a single molecule to switch by itself. Instead, the cooperative effect enforces all molecules to switch at once and they remain locked in that state thereafter (unless heated again above its SCO transition temperature). Furthermore, molecules in bulk films are not strongly influenced by metal surfaces since most of the molecules are not in the direct vicinity of the surface. In contrast, for a single molecule device, the molecule is attached to a metal electrode and experiences a strong coupling with the metal surface and this has been shown to drastically change the molecule's switching properties. In some cases, SCO compounds remain locked in one spin state when deposited on surfaces while other examples show the influence of a nearby surface, which can even induce HS behaviour in compounds which are otherwise fixed in a LS state.[3, 31]

In contrast to a previous report, which reported telegraphic-like switching within I-V sweeps,[16] this work used only a small bias voltage to avoid the effects of voltage triggered conformational changes[29] and resistance switching memory effects from filamentary formation.[32] Additionally, we note that telegraphic-like switching has been observed in empty graphene nanogaps resulting from interfacial defects.[25] In this study we have used clean gold nanojunctions, yet still observe telegraphic-like switching at very low and constant bias (8 mV), which is specifically used to avoid these above effects. In this work, it is more likely that the switching process arises from a reduction in the energy of the ligand field splitting parameter, Δ, as a result of the reduced temperature in conjunction with thermal perturbations of the complex. In the previous report the large extended $Fe(L')_2](BF_4)_2{\cdot}CH_3CN{\cdot}H_2O$ molecule and its extended arrangement across electrodes is potentially more susceptible to thermal perturbations than the far smaller SCO complex used in this work.

In this work, great care was taken to ensure the switching was not induced by the applied field. With such a small bias value it is very unlikely that the field is large enough to induce a switching effect. Electrostatic driven conformational changes have been widely reported in STM measurements and are a known conductance switching mechanism. A variety of molecules have been shown to display this effect and structurally they range from simple phenyl rings to complex macrocyclic complexes. Generally, these types of field driven switches occur for electric field strengths in the GV m^{-1} range. For example, reversible *cis-trans* isomerization has been reported[33] for azobenzene molecules at field strengths of around 2.9 GV m^{-1} and also a phenyl based single molecule switch has been demonstrated[34] which operates with an applied field strength around 0.2 GV m^{-1} . In addition, several porphyrin complexes have been shown to display a switching behaviour[35] between two nonplanar configurations at field strengths in excess of 2 GV m^{-1} or require threshold voltage of 0.5 to 1 V in order to induce a structural change.[36,37]

Previously reported studies on voltage triggered switching has occurred only for complexes which are either specifically tailored heteroleptic metal complexes which have large intrinsic dipole moments[29] and are hence susceptible to a voltage driven distortion of the octahedral structure or in STM studies on specially prepared substrates which decouple the SCO complexes from the strong surface interactions.[38,39] In both types of measurement, switching still occurs at a fairly high bias voltage, typically between 0.5 V and 1 V in MCBJ experiments and up to 1.5 V is reported in STM studies.[7] This is in line with theoretical predictions that a critical field strength upwards of 1 GV m^{-1} is needed in order to electrostatically induce the spin transition[40] when typical electrode – molecule distances are considered.

In comparison to other studies which reported field induced molecular switching, the electric field used in this work is approximately 3 orders of magnitude smaller ($E = V/ d \approx 8\ mV /2\ nm \approx 40\ kV / cm \approx 4\ MV\ m^{-1}$) than that typically used to induce these types of conformational switches. Furthermore, our I-V curves with a single SCO molecules present show no abrupt switching effects or bi-stability features, which would indicate the presence of a field induced switching effect (see Supporting Information S4). Current induced switching effects would similarly be small because of the small power dissipation ($P \approx V^2/R \approx 8\ mV / 360\ k\Omega \approx 1.7\text{x}10^{-10} = 178\ pW$)

Altogether our results confirm that in the bulk material, or thin-film form, the temperature above and below the spin crossover transition temperature serves to stabilize the high spin state or the low spin state respectively. The temperature at which this occurs is as a result of a competition between the electron pairing energy and the field splitting. However, in the case of the single molecule state, when the temperature is reduced, an intermediate regime exists such that random thermal perturbations can cause a switching effect between the two states. In this regime spin fluctuations dominate the electrical resistance, which is observed to switch between the two different states in the single molecule case and four resistance states when two molecules are present. At even lower temperatures, we expect, that the molecules with remain locked in the lower spin state.

Although there is no direct observational proof that two molecules are present in the gap, at this stage, no other scenario could be attributed to the cause of the four-level switching behaviour. We performed many control experiments on nanogap devices containing no molecules both at high and low temperature. We did not observe any consistent and reproducible switching phenomenon that would suggest the switching was due to something else other than the molecules. In particular, resistance fluctuations from the structural motion of the electrode can be excluded, as this process is unlikely to present itself as a clear four level stability in the conduction. If this were the case, a random evolution in the measured resistance over many values or irreversible jumps in the resistance because of different molecular arrangements on the surface would be instead observed. Moreover, this behaviour would be strongly temperature dependent, being reduced at cryogenic temperatures as atomic motion is reduced, and this was not observed.

The only previously reported measurement of multilevel switching (three distinct states) in a SCO complex by Jasper-Toennies *et al.* was attributed to being due to an extrinsic effect due to substrate coupling.[22] The LS state is shown to possess two possible closely spaced conductance values which arise due to a rotation of the complex on the crystalline substrate. In addition to applying a sufficiently large voltage (> 1.8 V), the complexes must also possess a degree of flexibility and be suitably decoupled from the substrate.[41] The authors achieved this via the use of a Cu_xN spacer layer but this is unlikely to occur for the Au-thiol bound complex presented here. Additionally, the molecules in these measurements are unlikely to exist on a flat crystalline surface due to the nature of the electromigration process[27] eliminating this possible mechanism as an explanation of the four level resistance states.

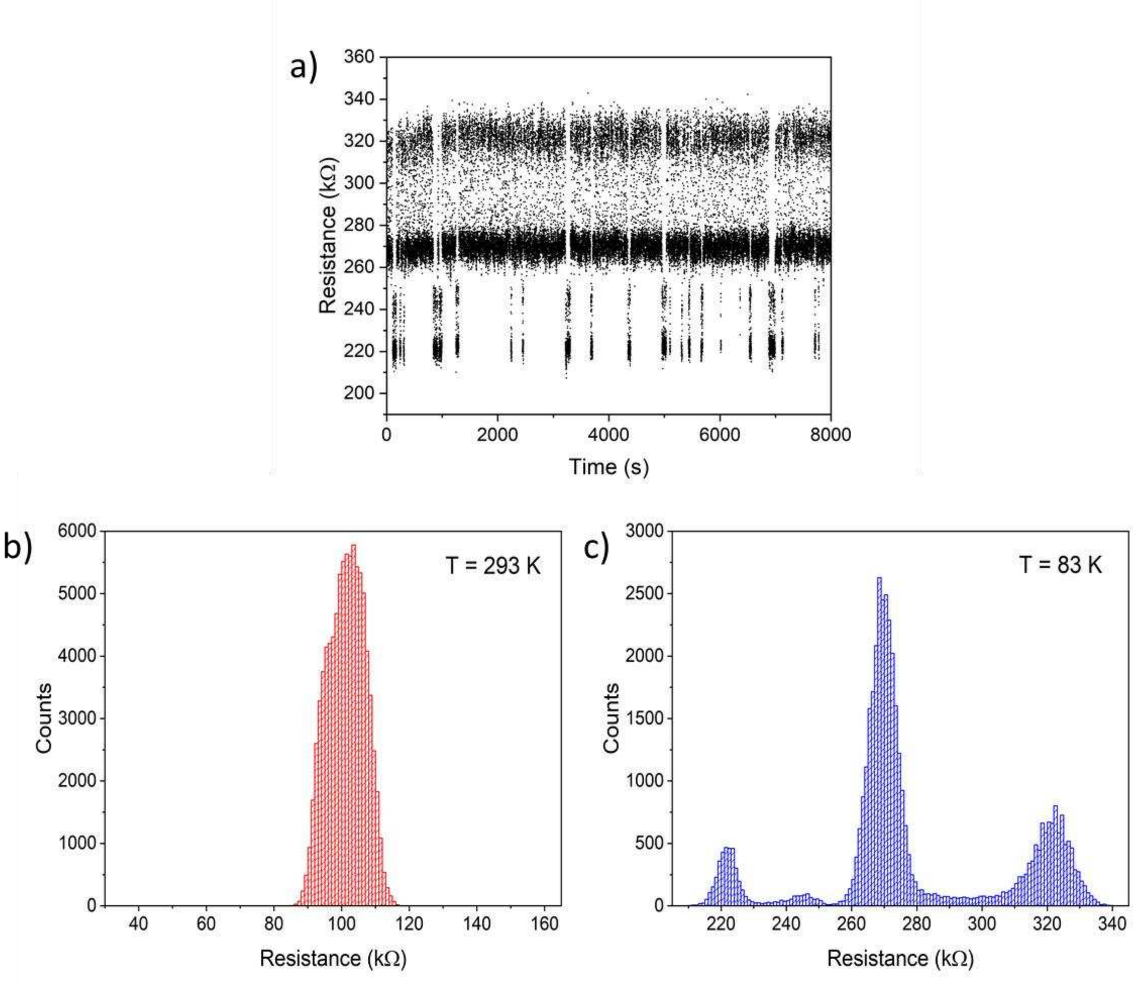

Figure 4. a) Resistance vs time for a device displaying multilevel resistance switching at 83 K. b) Resistance histograms at 83 K showing four individual peaks, which are expected to be due to the following spin combinations that occurs when two molecules are present within the gap (LS-LS, HS-LS, LS-HS, HS-HS). c) Resistance histogram at 293 K and showing only a single broad peak. (Note: Bin size is 1 kΩ for each of the histograms with 4.3×10^4 measurements made on a single device at each temperature).

Conclusion

Using electromigrated gold nanogap break-junction devices, we have electrically detected spin state fluctuations between spin states of a SCO compound at the single molecule level. In contrast to bulk devices containing a thin-film of the SCO molecules, switching behaviour of the single molecule devices occurs at a far higher temperature and without a cooperative switching effect. We measure a strong temperature dependence of the conductivity as well as a temperature induced spin transition that manifests in two well-defined resistance levels at low temperature, while at room temperature, only one resistance state is measured. The two well-defined resistance levels are expected to be due to conformational change in the SCO molecule as a result of thermal perturbations and the reduced energy of the ligand field splitting parameter that occurs at low temperature.

In some cases, switching between four resistance states occurred. In this case, we propose that two SCO molecules are present within the nanogap and are participating in the electron tunnelling and spin-transition process. Behaviour such as this, when controllable, could facilitate multi-level resistance switching and the development of ultra-small memory having more than two binary states.

Supporting Information

Please see the supporting information of this manuscript for further details on the feedback-controlled electromigration approach and experimental setup. Information is also given on the electrical properties of devices containing no molecules. This includes their current-voltage properties and their temperature dependent electrical resistance over the range of 70 K to 300 K. A number of investigations were also made on the magnetic properties of [Fe(L)NCS]. This include temperature dependent magnetometry on powder samples and thin-films of the SCO complex. Lastly, the supporting information gives further details on some minor experimental artefacts that were occasionally observed in the experiments that we associate with movement of the SCO molecule within the gap.

Conflicts of interest

There are no conflicts to declare.

Acknowledgement

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