Supporting Information

Room Temperature Conductance Switching in a Molecular

Iron(III) Spin Crossover Junction

Senthil Kumar Karuppannan,¹ Alejandro Martín-Rodríguez,² Eliseo Ruiz,^{2*} Phimphaka Harding,^{3*} David J. Harding,^{3*} Xiaojiang Yu,⁴ Anton Tadich⁵, Bruce Cowie⁵, Dongchen Qi⁶, Christian A. Nijhuis^{1,7*}

¹Department of Chemistry, National University of Singapore, 3 Science Drive, Singapore 117543, Singapore.

²Departament de Química Inorgànica and Institut de Recerca de Química Teòrica i

Computacional, Universitat de Barcelona, Diagonal 645, 08028 Barcelona, Spain.

³Functional Materials and Nanotechnology Center of Excellence, Walailak University,

Thasala, Nakhon Si Thammarat, 80160, Thailand.

⁴Singapore Synchrotron Light Source, National University of Singapore, 5 Research Link,

Singapore 117603, Singapore.

⁵Australian Synchrotron Clayton, Victoria 3168, Australia

⁶School of Chemistry, Physics and Mechanical Engineering, Queensland University of

Technology, Brisbane, Queensland 4001, Australia.

⁷Centre for Advanced 2D Materials & Graphene Research, National University of Singapore,

6 Science Drive 2, Singapore 117546, Singapore.

*Author to whom correspondence should be addressed: chmnca@nus.edu.sg,

hdavid@mail.wu.ac.th, kphimpha@mail.wu.ac.th, eliseo.ruiz@qi.ub.edu

Materials and methods

Sample preparation. The SCO [Fe^{III}(gsal-I)₂]NTf₂ (qsal-I 4-iodo-2-[(8-= quinolylimino)methyl]phenolate molecule was obtained according to the procedure reported in ref¹. The single-layer graphene on Cu foil was prepared using chemical vapor deposition as reported previously.² The Cu foil (99.8%, Alfa Aesar, No. 13382) was loaded in a quartz tube (semiconductor grade, UFO Labglass), and the Cu foil was first annealed in H₂ with a flow rate of 8 standard cubic centimeter per minute (sccm) at 1030 °C for 30 minutes. After annealing, CH₄ was introduced into the quartz tube at a flow rate of 8 sccm for 30 minutes at 1030 °C with a continuous flow of H₂ at a flow rate 16 sccm, after which the Cu//SLG surface was cooled to room temperature at a rate of 30 °C/min with continuous flow of H₂ at a flow rate of 8 sccm. The monolayer of [Fe^{III}(qsal-I)₂]NTf₂ was deposited on the Cu//SLG surface by immersion of the Cu//SLG substrate into a 1.0 mM solution of [Fe^{III}(qsal-I)₂]NTf₂ in CH₂Cl₂ molecule for 12 h after which the samples were rinsed with CH₂Cl₂ to remove excess materials.

Atomic force microscopy (AFM). The AFM images of Cu//SLG with and without $[Fe^{III}(qsal-I)_2]NTf_2$ monolayers were obtained with a Bruker Dimension FastScan AFM in tapping mode with FASTSCAN-A tips. AFM software NanoScope Analysis (version 1.4) was used to analyze the AFM images.

Surface characterization of Cu//SLG//[Fe^{III}(qsal-I)₂]NTf₂. We performed angle-resolved highresolution X-ray photoelectron spectroscopy (ARXPS) of the Cu//SLG//[Fe^{III}(qsal-I)₂]NTf₂ samples at SINS (Surface, interface and Nanostructure Science beamline of Singapore Synchrotron Light Source; SSLS). The measurements and analyses procedures have been reported before.³ All the samples were kept at room temperature under an ultra-high vacuum (~10⁻⁹ mbar) throughout the measurements.

X-ray absorption spectroscopy (XAS). The temperature-dependent Fe $L_{2,3}$ -edge XAS measurements were performed at the soft X-ray beamline of the Australian Synchrotron in TEY (total electron yield) mode following previously reported procedures.⁴ A step size of 0.1 eV was used over the energy range of 700 – 730 eV. We used the Quick AS NEXAFS Tool

(QANT) provided by the beamline⁵ to normalize the spectra to the incident photon flux. We used a linear combination of simulated Fe³⁺ spectra using the CTM4XAS software by Stavitski and de Groot⁶ and followed previously reported procedures.⁷

Electrical measurements. We followed previously reported procedures for the data collection (using cone-shape EGaIn tips⁸ or EGaIn stabilized in through-holes⁹) and analysis of the J(V) curves.¹⁰ We recorded the J(V) curves using a home-written code in LabView (Version 2010) and a Keithley 6430 sub-femtoamp remote source meter. We followed the procedure for statistical analysis of the junction data as reported before.¹¹ We used Matlab code for data analysis and plotted the heat map of current density as a function of applied bias. The Matlab code provided the Gaussian log-standard deviation and the Gaussian log-mean of the value of J, $\langle \log_{10} | J | \rangle_G$, for each applied voltage. These data were used to construct $\langle \log_{10} | J | \rangle_G$ vs. V curves shown in the main text.

Temperature-dependent measurements. The J(V) measurements as a function of temperature *T* were carried out in a probe station (Lakeshore CRX-VF) at a pressure of 1 × 10^{-5} mbar as described elsewhere.⁹ A code written in LabView (version 2010) was used to operate the source meter (Keithley, model 6430) which was used to record the J(V) curves. The change of pressure from ambient to vacuum and solidification of the bulk EGaIn at *T* = 220–240 K did not result in shorts, open circuits, or change the electrical characteristics of the devices, in any other notable way.

Computational details. The DFT calculations to optimize the periodic structures were performed with the fhi-aims code¹² using the PBE exchange-correlation functional¹³ with a numerical basis set using the option "light" due to a large number of atoms. The complex structure of the eutectic GaIn electrode was modeled by starting with the X-ray structure of α -Gallium that has a melting point of 303 K.¹⁴ The optimizations were performed using only the Γ point. During the optimization, the O₂ molecules dissociated resulting in the formation of Ga₂O₃. A similar distribution of the oxygen atoms was included in the first four layers to match the experimental thickness of the GaO_x layer (0.7 nm).¹⁵ The dispersion effects were included using the method proposed by Tkachenko and Scheffler using the Hirschfeld partitioning of the electron density.¹⁶ For the system, a conventional all-electron method was

employed only for the two last structural optimizations (high- and low-spin), while for the whole system a frozen core approach was included for the orbitals below -500 eV. The meta-GGA SCAN functional was employed to calculate the high- and low-spin difference because it is more accurate than GGA functionals such as PBE. Furthermore, the hybrid meta-GGA TPSSh functional was employed as implemented in Gaussian 09 code{Tao, 2003 #13} to calculate the transition metal complex using a TZVP basis set.¹⁷ We have combined the SIESTA code¹⁸ to obtain the electronic structure and the GOLLUM code¹⁹ for the transport properties, respectively. A DZP basis set was employed for all atoms except Cu, Ag, Ga and In in which an SZ basis set was used in order to reduce the computational time (see the details in Section S2). We used the Hubbard correction on the Fe^{III} atom U = 4 eV to improve the position of the metal orbitals with respect to the Fermi level. Γ -point was used to compute the transport properties.

Section S1

Figure S1 shows the angle-resolved high-resolution O 1s, F 1s, I 3d, and S 2p spectra of $[Fe^{III}(qsal-I)_2]NTf_2$ on graphene. In the O 1s spectra (Fig. S1A), the peak at 532.4 eV is assigned to S=O peak (which comes only from the counterion) and the peak 531.2 eV is assigned to Fe-O-C peak (contribution coming from the complex). Figure S1B shows the F 1s spectra which are dominated by a single peak at 688.6 eV and the peak intensity increases at $\theta = 90^{\circ}$ confirming that the counterion is close to the graphene surface. Figure S1C shows the peak at 621.0 eV which corresponds to the C-I bond and a smaller peak at 619.5 eV caused by radiation damage usually observed in iodinated compounds.²⁰ The spin-orbit splitting (SOS) for I 3d is 11.3 eV which is close to the expected 11.5 eV. These two peaks originate only from the SOS of 1.18 eV is maintained here. The peak intensity increases at $\theta = 90^{\circ}$ once again pointing to the counter ion being sandwiched between the complex and the SLG layer. Thus, the counter ion is sandwiched between the graphene and $[Fe^{III}(qsal-I)_2]NTf_2$ which is consistent with the observed peak shifts in the Raman spectra as discussed in the main text.



Figure S1. Angle dependent X-ray photoelectron spectra of A) O 1*s*, B) F 1*s*, C) I 3*d*, and D) S 2*p*. All spectra were recorded at room temperature.



Figure S2. X-ray absorption spectra (XAS) of Fe $L_{2,3}$ edges recorded from a monolayer of $[Fe^{III}(qsal-I)_2]NTf_2$ on SLG at 340 K (black), and the corresponding simulated Fe $L_{2,3}$ edges for octahedral Fe^{II} (red) and Fe^{III} (blue) ions using CTM4XAS software, the spin-orbit splitting (SOS) and crystal field splitting (Δ_{SOC}) are indicated in the figure panels.



Figure S3. A) X-ray absorption spectra of Fe $L_{2,3}$ edges recorded from $[Fe^{III}(qsal-I)_2]NTf_2$ powder at different temperatures. B) $\chi_M T vs. T$ plot of $[Fe^{III}(qsal-I)_2]NTf_2$.

Comparison with previously reported SCO junctions

An exhaustive search of the literature was undertaken with the results shown in Table S1. We find that among the devices reported, our junction is the smallest currently known. It is also the only molecular junction to be fabricated by simple immersion of the electrode into a solution of the complex. This is a significant advantage over the previous molecular junctions where the SCO molecule is sublimed and is likely to be applicable to other SCO systems.

Device structure	Oxidation state	Deposition method	Nature of electrode-molecule contact	Film thickness (nm)	Switching Temperature (K)	Mechanism	On/off ratio	Ref.
Au ^{TS} //[Fe(HB(trz) ₃) ₂]//EGaIn	Fe ^{II} (88% HS ^a)	Thermal	van der Waals	5.6	100-300	Hopping	10 ^b	21
		evaporation	interface					
Au ^{TS} //[Fe(HB(trz) ₃) ₂]//Ga ₂ O ₃ /EGaIn	Fe ^{II} (95% HS)	Thermal	van der Waals	6.7	297-300	Not reported	100	22
		evaporation	interface					
$Au^{TS}/[Fe(HB(trz)_3)_2]/AI$	Fe ^{II} (80% HS)	Thermal	Unknown	100	336	Hopping	8	23
		evaporation						
Glass/ITO/[Fe(H ₂ B(pz) ₂) ₂ (phen)]/Al	Fe ^{II} (NA ^c)	Thermal	Unknown	10	100-250	Coherent	2	24
		evaporation				Tunneling		
Cu/CuN/[Fe(phen) ₂ (NCS) ₂]/STM-tip	Fe ^{II} (46% HS)	Sublimation	Covalent bond	2	4.5	Inelastic	0.06	25
ITO/[Fe(HB(tz)₃)₂]/Al	Fe ^{II} (NA)	Thermal	Unknown	100	336	scattering Hopping	400	26
		evaporation						
Au/[Fe(III)(EtOSalPet)(NCS)]/Au	Fe ^Ⅲ (47% HS)	Drop-casting	Electrostatic	~2	83	Not reported	2	27
			interaction					
Cu/Cu ₂ N/[Fe(pap) ₂]/STM-tip	Fe ^{III} (NA)	Sublimation	Electrostatic	1.9	4.6	Not reported	~1.5	28
			interaction					
Cu//SLG//[Fe(qsal-I) ₂]NTf ₂ //GaO _x /EGaIn	Fe ^{III} (98% HS)	Self-assembly	van der Waals	1.4	310	Coherent	10	This
			interface			Tunneling		work

Table S1. Device characteristics of various SCO junctions.

^aHS means "high spin-state", % refers to the existence of HS after switching event

^bIt is difficult to separate the contribution to the on/off ratio from the gradual SCO and the ordinary thermal activation processes. ^cNA means "not applicable"

Atoms	Expected elemental composition from the empirical formula	Elemental composition from the XPS spectra ^a		
	$(C_{34}H_{20}F_6FeI_2N_5O_6S_2)$			
S	1	1.00		
0	3	3.56 ^b		
Ν	2.5	2.59		
I	1	0.97		
F	3	3.18		
С	17	20.54 ^b		

Table S2. The elemental composition of [Fe^{III}(qsal-I)₂]NTf₂ molecule.

^aThe error of the ratios is about 5% due to fitting errors.

^bThe excess C and O likely orginate from adventitious materials since our samples were prepared *ex situ*.



Figure S4. A) J(V) curves recorded from a Cu/SLG//[Fe^{III}(qsal-I)₂]NTf₂//GaO_x/EGaIn junction as a function of *T* during cooling and heating cycles at intervals of 10 K. B) *J* as a function of *T* at -0.5 V applied bias.



Figure S5. A) J(V) curves recorded from a Cu/SLG//[Fe^{III}(qsal-I)₂]NTf₂//GaO_x/EGaIn junction as a function of *T* during cooling the cycle at intervals of 10 K. B) *J* as a function of *T* at -0.5 V applied bias.

Section S2.

Here, we used the Green functions combined with the DFT methods which are the state-ofart approach to calculate transport properties in junction systems. This approach provides a correct description of coherent tunneling transport, but it has some limitations, for instance Stark effects as a result from large applied electric fields or spin-orbit coupling can induce a state mixing which is ignored by our approach. Nevertheless, Michaeli et al.²⁹ showed recently that such Stark effects likely result in additional conduction channels for coherent charge transport reinforcing our conclusions. The results of the DFT calculations using the PBE functional include dispersion contributions using the many body approach³⁰ proposed by Tkachenko and Scheffler approach (see Computational details section) to analyse the relative stability of the interaction between the surface and the molecule Cu/SLG//[Fe^{III}(qsal-I)₂]NTf₂ in the low spin state and are summarized in Table S3. The many-body approach provides more accurate energies than the two body approach.¹⁶ Similar results are expected for the high-spin state because the coordination sphere of the metal does not affect the molecule-surface contact.

Number of iodines towards the surface	Energy (kcal/mol)
Two	0
One	+9.0
Zero	+7.7

Table S3. Relative DFT energies for the optimized $Cu/SLG//[Fe^{III}(qsal-I)_2]NTf_2$ with different orientations of the molecule and the low-spin state configuration.

The EGaln electrode has not been modelled before, and thus we substituted the EGaln electrode for Ag(111) to check for inconsistencies. We selected silver as it has a similar work function to the EGaln electrode. The zero-voltage approximation mentioned in the main text yields larger conductance value for the HS state ($G = 1.65 \cdot 10^{-3} G_0$) than for the LS state ($G = 6.00 \cdot 10^{-4}G_0$), in agreement with the experimental observations. However, a closer examination of the PDOS of the HS state (see Figure S7B) reveals that the beta d_{xy} orbital is now below the Fermi Level. This suggests charge transfer from the Ag electrode to the [Fe(qsal-I)₂]⁺ moiety leading to a reduction of the Fe^{III} to Fe^{II}. This is not observed in either of the PDOS obtained with the EGaln electrode (Figure 7D), but it is worth noting that the empty beta levels are also very close to the Fermi level and that the EGaln top electrode is important to ensure that the SCO complex remains in the Fe^{III} oxidation state. The orbitals of the Fe(III) complex are protected by the ligands, thus, the influence of the position of the anion should be negligible. To corroborate such assumption, we have repeated the calculation but with the anion in a vertical position perpendicular to the graphene (Fig. S8). The comparison of the two DOS clearly indicates the lack of influence of the anion position.



Figure S6. Representation of the optimized unit cell for A) the high-spin and B) the low-spin systems.



Figure S7. A) A $[Fe(qsal-I)_2]NTf_2$ representation within Cu/graphene and Ag electrodes. Projected density of states (DOS) of $[Fe(qsal-I)_2]NTf_2$ for B) the high spin and D) the low spin states. The transmission spectra of $[Fe(qsal-I)_2]NTf_2$ for C) the high spin and E) the low spin

states. Red and blue colours stand for alpha and beta spin-orbitals. The filled curves are the PDOS of the Fe^{III} ion.



Figure S8. Projected density of states (DOS) of $[Fe(qsal-I)_2]NTf_2$, in which the anion in a A) perpendicular and B) vertical to the graphene surface.

References

- N. Phukkaphan, D. L. Cruickshank, K. S. Murray, W. Phonsri, P. Harding and D. J.
 Harding, *Chemical Communications*, 2017, 53, 9801–9804.
- X. Li, A. Reina, X. Jia, J. Ho, D. Nezich, H. Son, V. Bulovic, M. S. Dresselhaus, J. Kong, W. Cai, J. An, S. Kim, J. Nah, D. Yang, R. Piner, A. Velamakanni, I. Jung, E. Tutuc, S. K. Banerjee, L. Colombo and R. S. Ruoff, *Science*, 2009, **324**, 1312–1314.
- 3 H. Jeong, Y. Jang, D. Kim, W. T. Hwang, J. W. Kim and T. Lee, *Journal of Physical Chemistry C*, 2016, **120**, 3564–3572.
- 4 W. Du, Y. Han, H. Hu, H.-S. Chu, H. V. Annadata, T. Wang, N. Tomczak and C. A. Nijhuis, *Nano Letters*, 2019, **19**, 4634–4640.
- D. Cocco, E. Plönjes and M. Zangrando, *Journal of Synchrotron Radiation*, 2016, 23, 1–
 2.
- 6 E. Stavitski and F. M. F. de Groot, *Micron*, 2010, **41**, 687–694.
- S. Swaraj, P. M. Dietrich and W. E. S. Unger, *Journal of Physics: Conference Series*, 2017, 849, 8–12.
- 8 N. Nerngchamnong, L. Yuan, D. C. Qi, J. Li, D. Thompson and C. A. Nijhuis, *Nature Nanotechnology*, 2013, **8**, 113–118.

- A. Wan, L. Jiang, C. S. S. Sangeeth and C. A. Nijhuis, *Advanced Functional Materials*, 2014, 24, 4442–4456.
- 10 C. A. Nijhuis, W. F. Reus, J. R. Barber and G. M. Whitesides, *The Journal of Physical Chemistry C*, 2012, **116**, 14139–14150.
- 11 W. F. Reus, C. A. Nijhuis, J. R. Barber, M. M. Thuo, S. Tricard and G. M. Whitesides, *The Journal of Physical Chemistry C*, 2012, **116**, 6714–6733.
- 12 V. Blum, R. Gehrke, F. Hanke, P. Havu, V. Havu, X. Ren, K. Reuter and M. Scheffler, *Computer Physics Communications*, 2009, **180**, 2175–2196.
- J. P. Perdew, K. Burke and M. Ernzerhof, *Physical Review Letters*, 1996, 77, 3865– 3868.
- H. G. von Schnering, R. Nesper, S. Bøwadt, T. K. Hansen, K. S. Varma, J. Becher and A.
 E. Underhill, Acta Chemica Scandinavica, 1991, 45, 870–872.
- K. S. Wimbush, R. M. Fratila, D. Wang, D. Qi, C. Liang, L. Yuan, N. Yakovlev, K. P. Loh,
 D. N. Reinhoudt, A. H. Velders and C. A. Nijhuis, *Nanoscale*, 2014, 6, 11246–11258.
- 16 A. Tkatchenko and M. Scheffler, *Physical Review Letters*, 2009, **102**, 073005.
- A. Schäfer, C. Huber and R. Ahlrichs, *The Journal of Chemical Physics*, 1994, **100**, 5829–5835.
- 18 J. M. Soler, E. Artacho, J. D. Gale, A. García, J. Junquera, P. Ordejón and D. Sánchez-Portal, *Journal of Physics Condensed Matter*, 2002, **14**, 2745–2779.
- J. Ferrer, C. J. Lambert, V. M. García-Suárez, D. Z. Manrique, D. Visontai, L. Oroszlany,
 R. Rodríguez-Ferradás, I. Grace, S. W. D. Bailey, K. Gillemot, H. Sadeghi and L. A.
 Algharagholy, *New Journal of Physics*, 2014, **16**, 093029.
- 20 C. C. Perry, N. S. Faradzhev, T. E. Madey and D. H. Fairbrother, *The Journal of Chemical Physics*, 2007, **126**, 204701.
- L. Poggini, M. Gonidec, R. K. C. Balasubramanyam, L. Squillantini, G. Pecastaings, A.
 Caneschi and P. Rosa, *Journal of Materials Chemistry C*, 2019, 7, 5343–5347.
- 22 L. Poggini, M. Gonidec, J. H. González-Estefan, G. Pecastaings, B. Gobaut and P. Rosa, Advanced Electronic Materials, 2018, **4**, 1800204.
- V. Shalabaeva, K. Ridier, S. Rat, M. D. Manrique-Juarez, L. Salmon, I. Séguy, A. Rotaru,
 G. Molnár and A. Bousseksou, *Applied Physics Letters*, 2018, **112**, 013301.
- 24 C. Lefter, S. Rat, J. S. Costa, M. D. Manrique-Juárez, C. M. Quintero, L. Salmon, I. Séguy, T. Leichle, L. Nicu, P. Demont, A. Rotaru, G. Molnár and A. Bousseksou,

Advanced Materials, 2016, 7508–7514.

- T. Miyamachi, M. Gruber, V. Davesne, M. Bowen, S. Boukari, L. Joly, F. Scheurer, G. Rogez, T. K. Yamada, P. Ohresser, E. Beaurepaire and W. Wulfhekel, *Nature Communications*, 2012, 3, 936–938.
- Y. Zhang, I. Séguy, K. Ridier, V. Shalabaeva, M. Piedrahita-Bello, A. Rotaru, L. Salmon,
 G. Molnár and A. Bousseksou, *Journal of Physics: Condensed Matter*, 2020, 32, 214010.
- A. Gee, A. H. Jaafar, B. Brachňaková, J. Massey, C. H. Marrows, I. Šalitroš and N. T.
 Kemp, *The Journal of Physical Chemistry C*, 2020, **124**, 13393–13399.
- 28 T. Jasper-Toennies, M. Gruber, S. Karan, H. Jacob, F. Tuczek and R. Berndt, Nano Letters, 2017, 17, 6613–6619.
- L.M. Malard, M.A. Pimentaa, G. Dresselhaus, M.S. Dresselhaus, *Physics Reports*, 2009, 473, 51-87.
- J. Hermann, R. A. DiStasio and A. Tkatchenko, *Chemical Reviews*, 2017, **117**, 4714–4758.