Electronic Supplementary Material (ESI) for Journal of Materials Chemistry C.

Supporting information

Temperature-induced transport changes in molecular junctions based on a Spin Crossover complex

Lorenzo Poggini,[*ab] Mathieu Gonidec,[*ab] Ram Kumar C.B.,[ab] Lorenzo Squillantini,[abc] Gilles Pecastaing,[d] Andrea Caneschi[c] and Patrick Rosa[ab]

[a] CNRS, ICMCB, UMR 5026, F-33600 Pessac, France
[b] Univ. Bordeaux, ICMCB, UMR 5026, F-33600 Pessac, France
[c] DIEF - Department Industrial Engineering and INSTM Research Unit, University of Florence, Via S. Marta 3, I-50139 Florence, Italy.
[d] LCPO, CNRS UMR 5629, Université de Bordeaux, Bordeaux-INP, Pessac 33607 Cedex, France

E-mail: mathieu.gonidec@icmcb.cnrs.fr; lorenzo.poggini@icmcb.cnrs.fr

Experimental Section

Synthesis: Compound **1** was synthesized as previously described elsewhere.[1]

Chip preparation: Gold micro-patterns (200 nm in thickness) were deposited directly (without adhesion layer) on an ultra-flat Si (100) wafer by masked thermal evaporation at a rate of 2 Å/s using a tungsten boat in a Plassys thermal evaporator dedicated to metal evaporation. To silanize the parts of the wafer that were not covered by the gold patterns, it was placed inside of a desiccator together with a glass slide on which a drop of 1*H*,1*H*,2*H*,2*H*-perfluorooctyltrichlorosilane was deposited. The dessicator was partially evacuated to saturate the chamber with silane vapours, and the functionalization was left under reduced pressure for one hour. Clean glass chips were aligned with the micro-patterns and glued to them with Norland optical adhesive (NOA 61) that was cured under UV light.

EGaIn channel preparation: A standard soft lithography process was used to prepare linear micro-channel in PDMS (Silgard 184) by replica molding of a SU8 mold on a silicon wafer. The final chip Au^{TS}//**1**//EGaIn was realized by the following steps: i) the PDMS micro-channel was deposited on a clean glass covered by ITO; ii) we filled the microchannel with EGaIn by applying reduced pressure to the outlet of the channel with a drop of EGaIn at the inlet of the channel; iii) we positioned the filled PDMS microchannel perpendicularly to the **1**//Au electrodes.

Sample deposition: The evaporations were performed in a Plassys thermal evaporator connected to a glove box system. An alumina crucible was filled with the powder of **1** and once the pressure reached the 10^{-7} mbar range, the temperature was gently raised up to the evaporation temperature. The evaporation rate was followed by a quartz microbalance, and was stabilized in the 0.05 nm/s range at a temperature of 380-385 K. The tooling factor was determined by evaporating a thick film of **1** on an ultra-flat silicon wafer through a soft porous PDMS membrane, and by checking the thickness of that film *ex situ* by AFM (see Figure S1 for details). For a target thickness of 20 nm, we measured an actual film thickness of 22.4 ± 1.6 nm, which corresponds to a tooling factor of 112%. We used this value to correct the thickness of the thin films prepared for physical characterizations.

Electrical measurements: In order to measure the current through the junctions, the microchannels filled with EGaIn were aligned with the sample to form crossbar junctions. The chips were placed inside a Linkam microscope stage equipped with electrical feedthrough connections, and top and bottom electrodes were connected to a Keithley 2635b sourcemeter. The data (Figure 2 in main text and Figure S3) were acquired after a systematic thermalisation time of 5 minutes and are the average of 10 J/V traces acquired in at least 2 different junctions (*i.e.* different crossbar junction). For each measurement, we recorded J−V traces for forward bias 0→-V→V and J−V traces for the reverse bias V→-V. Due to the low magnitude of the currents measured in the junctions (often of the order of 1 to a few pA), the built-in potential contributed to a non-negligible offset of the I/V curves and the data were thus systematically corrected by subtracting the 0 bias current for every junction. We also performed a more extensive series of measurements at room temperature on the 11.2 nm sample in order to have statistical information on the reproducibility of the measurements. To

do so, we made 35 different junctions for which we measured 10 forward and backward J/V traces. The histogram of the log |J| values measured at 1.0 V and -1.0 V are shown on Figure S2.

Theoretical calculations: The orbital energies were estimated by performing single-point DFT calculations using the crystal-structures as input geometries with the B3LYP functional using the specified basis sets as implemented in the Gaussian 09 program.[2] The geometry were first optimized using the 6-31G(d,p) basis set, and single point calculations were then performed using 6-31G++(d,p) basis set.

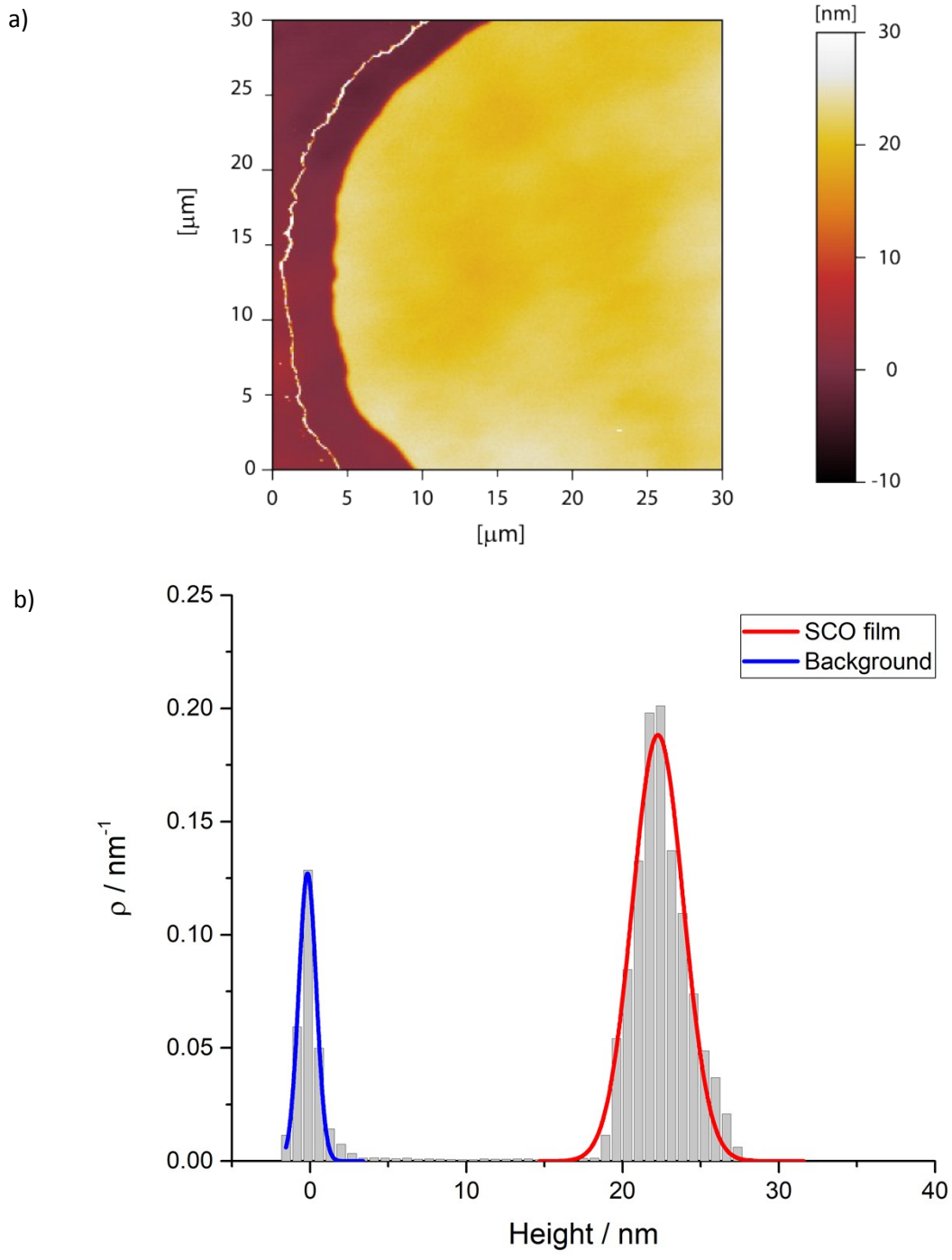

Fig. S1. a) AFM topography image of a film of compound **1** thermally evaporated on a silicon wafer through a porous membrane with a target thickness of 20 nm. b) Height distribution histograms from the AFM topography image showing an actual film thickness of ca. 22.4 ± 1.6 nm. The blue and red lines are Gaussian fits to the height distribution of the background and SCO film, respectively.

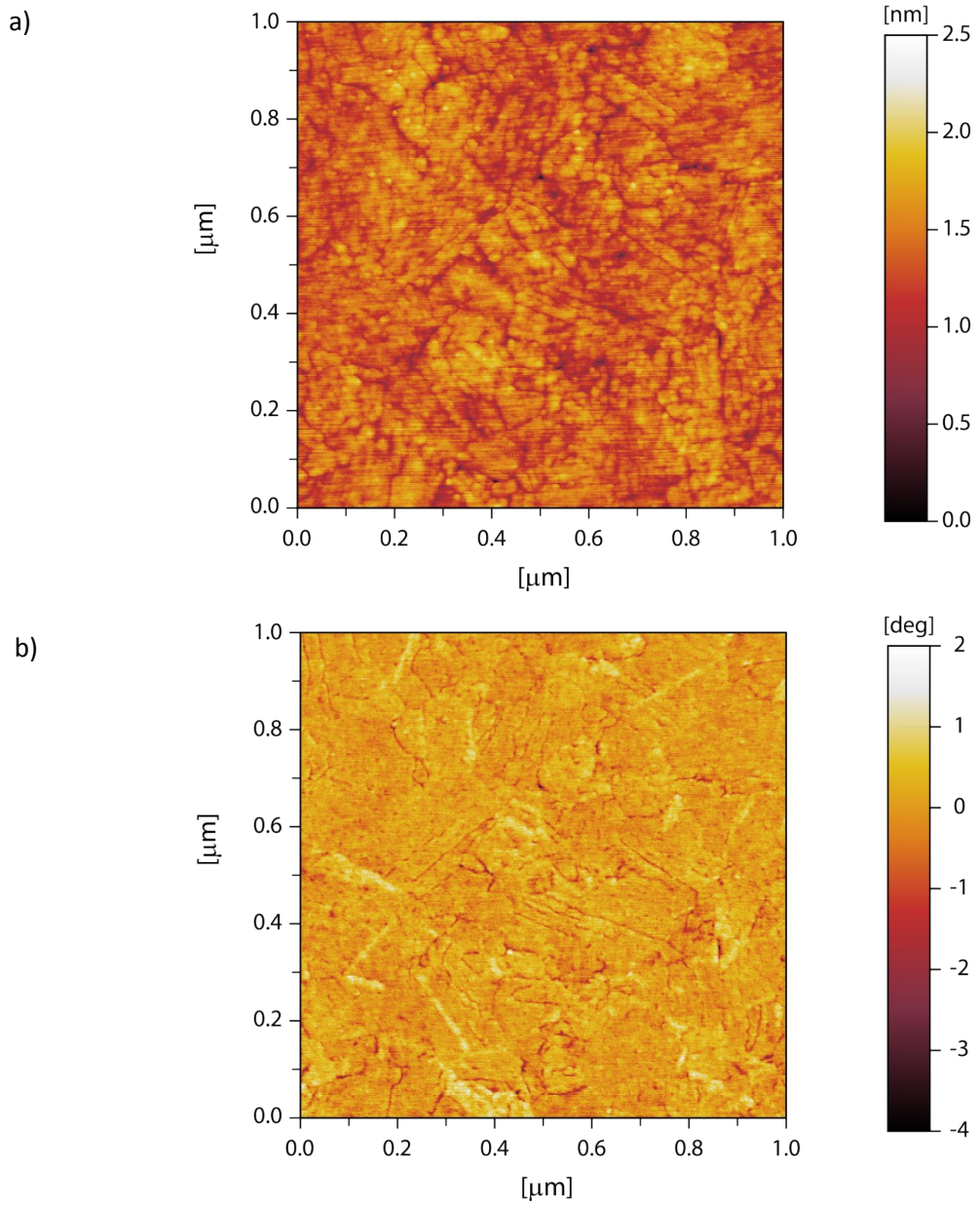

Fig. S2. a) 1×1 µm AFM topography image and b) 1×1 µm AFM phase image of a template-stripped gold substrate.

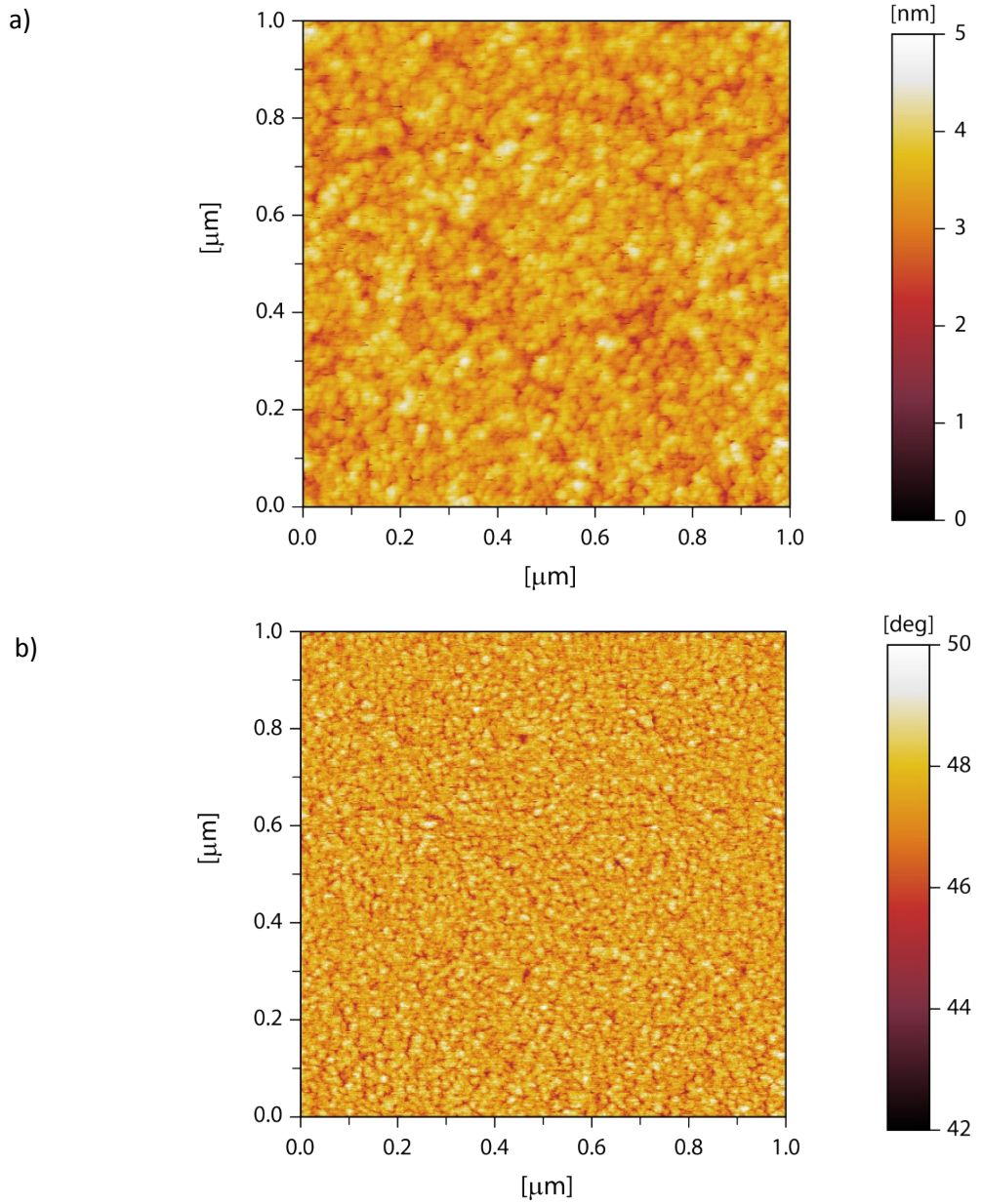

Fig. S3. a) 1×1 µm AFM topography image and b) 1×1 µm AFM phase image of a 10 nm film of **1** evaporated on top of a template-stripped gold substrate.

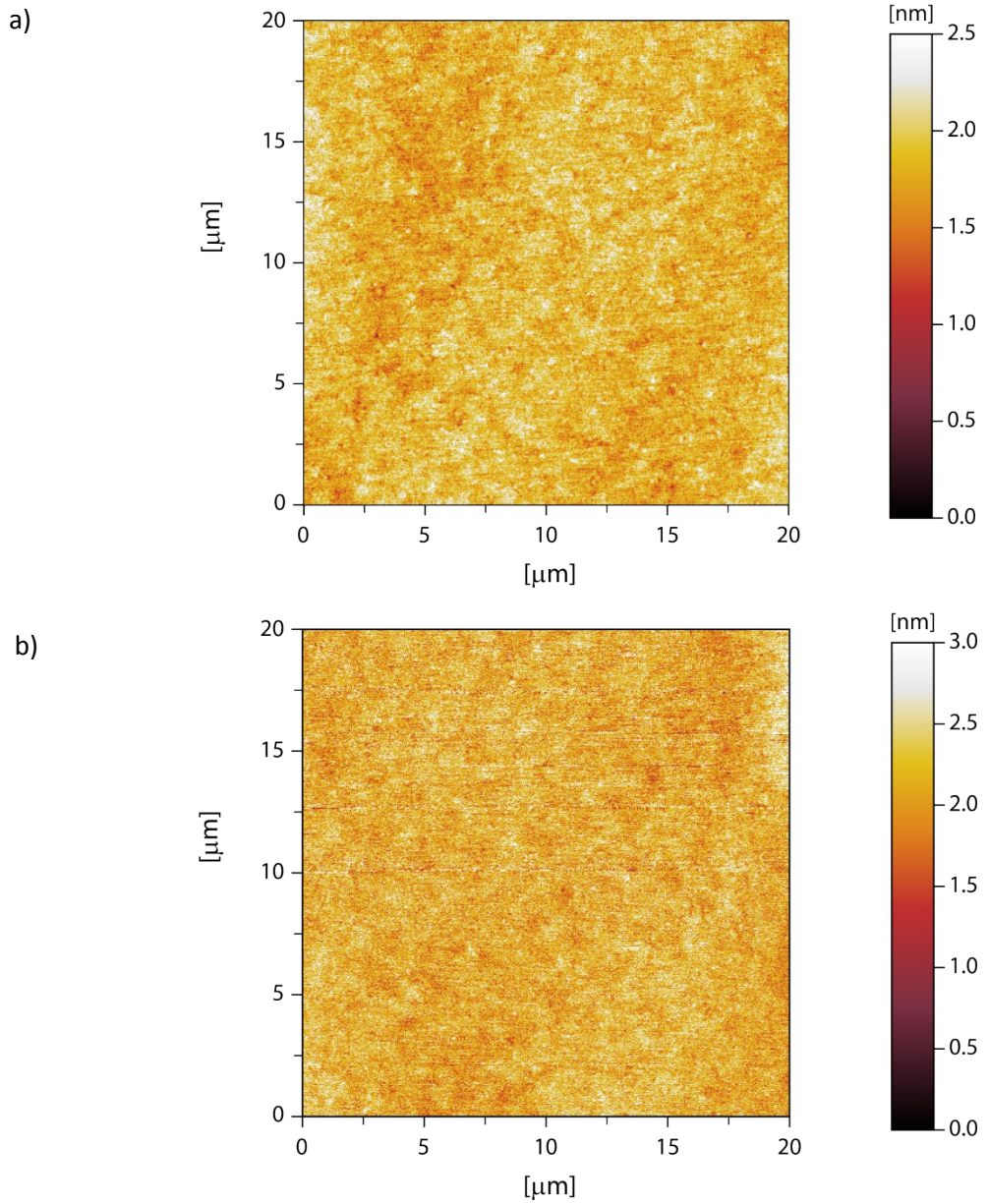

Fig. S4. a) 20×20 µm AFM topography image of a template-stripped gold substrate and b) 20×20 µm AFM topography image of a 10 nm film of **1** evaporated on top of a template-stripped gold substrate.

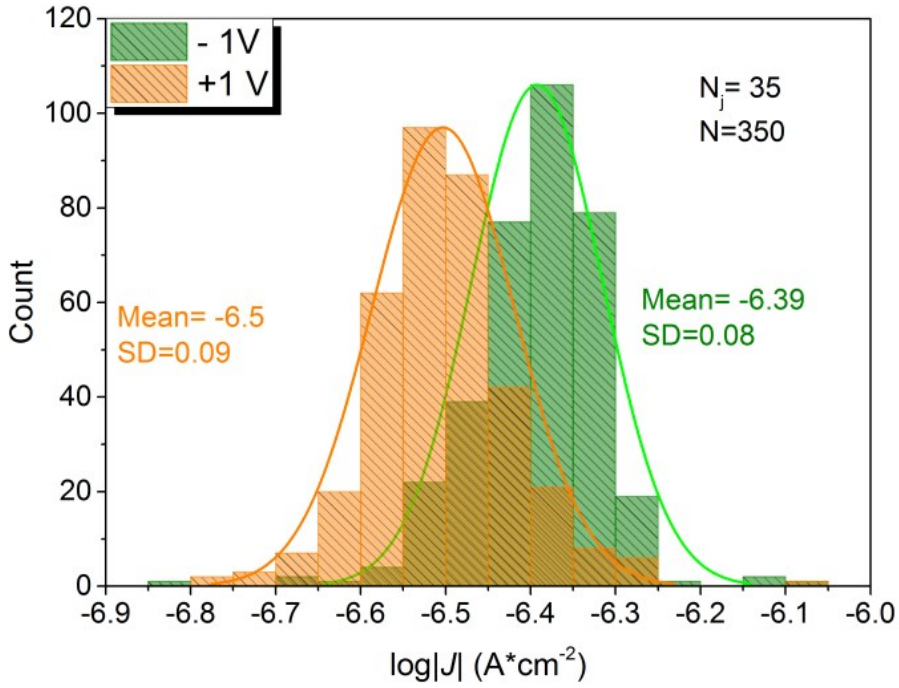

Fig. S5. Histograms showing the distribution of the logarithm of the absolute value of the current density, log |J|, measured on a 11.2 nm film of **1** at room temperature and at applied biases of +1 V (orange) and -1 V (green) for 35 different junctions.

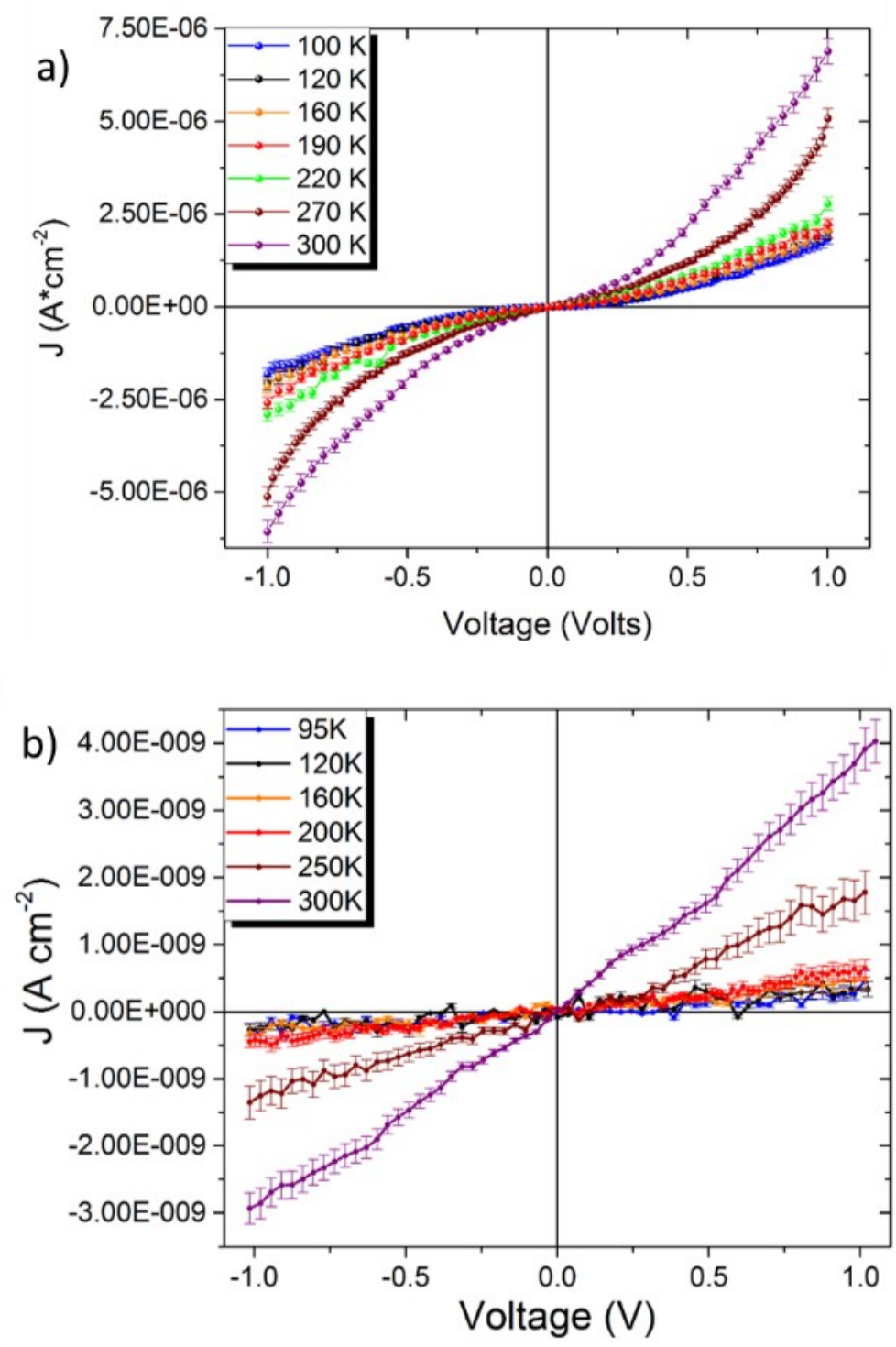

Fig. S3. Evolution of the J/V characteristics with temperature for a) 5.6 nm and b) 16.7 nm thin film junctions of **1**.

References:

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