Spintronics across molecular spin chains using solvent-free nanojunction processing

K. Katcko1,*, E. Urbain1, L. Kandpal1, B. Chowrina1,2, U. Halisdemir1, F. Ngassamnyakam1, D. Mertz1, B. Leconte1, N. Beyer1, D. Spor1, P. Panissod1, A. Boulard1, J. Arabisski1, C. Kieber1, E. Sternitsky1, V. Da Costa1, M. Alouani1, M. Hehn3, F. Montaigne3, A. Bahouka4, W. Weber1, E. Beaurepaire1,11, D. Lacour3, S. Boukari1, M. Bowen1@

1 Institut de Physique et Chimie des Matériaux de Strasbourg, UMR 7504 CNRS, Université de Strasbourg, 23 Rue du Léaas, BP 43, 67034 Strasbourg, France.
2 Synchrotron SOLEIL, L’Orme des Merisiers, Saint-Aubin, BP 48, 91192 Gif-sur-Yvette, France.
3 IREPA LASER, Institut Carnot MICA, Parc d’innovation - Pole API, 67400 Illkirch, France.

* These authors contributed equally.
† Deceased April 24th, 2018.
@ e-mail: bowen@unistra.fr

Abstract [234 words]

The quantum properties of nano-objects, such as atoms or molecules, are typically manipulated using scanning tunnelling microscopes1–3 and lateral break junctions4. The resulting nanotransport path is well established in these model devices. Societal applications require transposing this knowledge to nano-objects embedded within vertical solid-state junctions, which advantageously can harness spintronics to addressing these quantum properties thanks to ferromagnetic electrodes and high-quality interfaces5. Here, one challenge is to ascertain the device’s effective, buried nanotransport path6,7. Another is to achieve a nanojunction comparing a molecular layer with high-quality interfaces. We’ve developed a low-tech, resist- and solvent-free technological process that can craft nanopillar devices from in-situ grown heterostructures, and use it to study magnetotransport between two Fe and Co ferromagnetic electrodes across a CoPc functional magnetic molecular layer. By identifying three magnetic units along the effective nanotransport path thanks to a macropin model of magnetotransport, our experiments show how spin-flip transport across CoPc molecular spin chains promotes a specific magnetoresistance effect, and alters the nanojunction’s magnetism through spintronic anisotropy8. Our work elegantly connects the until now loosely associated concepts of spin-flip spectroscopy2,3, magnetic exchange bias9,10 and magnetotransport11,12 due to molecular spin chains. We notably measure a 5.9meV energy barrier for magnetic decoupling between the Fe layer’s buried atoms and those in contact with the CoPc layer forming the so-called ‘spinterface’13. This provides a first insight into the experimental energetics of this promising low-power information encoding unit14.

Main Text [~2850 words without captions]

Recent research has unraveled how two electronic spins may interact with one another in the presence of an electric current between them2,3. This interaction may be tuned thanks to the positional control of a scanning tunnelling microscope (STM), but also through molecular design. For example, metal-organic phthalocyanines can form molecular columns such that superexchange interactions between the central atom of neighboring molecules can promote magnetic order. The nature of the metal atom and the molecular stacking geometry determines whether this order is ferromagnetic or antiferromagnetic and can exceed room temperature15. STM experiments have evidenced conductance jumps as a spectroscopic signature of electrically manipulating antiferromagnetic (AF) spin correlations along the chain (e.g. CoPc with spin S=1/2) from a ground state to well-characterized excited states1. However, in such experiments, setting a spin referential thanks to an external magnetic field16 or using metallic ferromagnetic (FM) electrodes17 is cumbersome. This has prevented the direct observation of the magnetoresistance
due to this spin-flip current, or any insight into how this spin-flip current interacts with the magnetic properties of the FM/molecule interface.

Conversely, limited experiments on macroscale shadow-mask and nanoindented solid-state junctions that integrate FM electrodes and molecular layers reveal novel but so-far disjointed effects that conceptually overlap only loosely with STM-based reports, and with magnetometry at the FM/molecule interface. According to transport experiments, molecular adsorption onto a FM layer not only generates a highly spin-polarized interface\(^\text{18}\) at room temperature\(^\text{19}\) (nicknamed a ‘spinterface’), but can attenuate the otherwise strong FM coupling between the FM layer’s topmost and remaining monolayers\(^\text{20}\). According to magnetometry\(^\text{9,10}\), this ‘magnetic hardening’ effect can complement the magnetic exchange coupling between a FM metal and AF-coupled molecular spin chains (MSCs). This effective magnetic exchange bias, and spin chain excitations, both appear to qualitatively alter magnetotransport\(^\text{11,12}\), but the link has so far remained indirect and speculative.

Overall, this differing level of maturity between these STM-assembled and solid-state junctions reflects not only a technological bottleneck to designing high-quality vertical nanojunctions without damaging the molecular layer, but also a challenge to precisely determine the effective nanotransport path\(^\text{6,21}\) within a solid-state device. In this Letter, we bridge these technological and knowledge gaps through spectroscopic temperature-dependent magnetotransport experiments. Herein, we craft solid-state nanojunctions from full \textit{in-situ} grown FM/CoPc/FM heterostructures using a low-tech nanojunction process that does not structurally degrade the active organic layer, or expose it to resist, solvents or air. By fitting our magnetotransport data using a three-macrospin model, we find that the magnetoresistance generated upon flipping the magnetic orientation of the two FM electrodes tracks the increase in junction conductance resulting from excitations along spin chains in the intervening CoPc molecular magnetic layer. Magnetic hardening at, and MSCs coupled to, the spinterface combine to define a central magnetic unit with a unidirectional anisotropy. According to the model, its strength at 17K nearly doubles with spin excitations to effectively reach 18T at $|V|>100mV$, while its temperature dependence mimicks that of exchange bias seen in magnetometry\(^\text{9,10}\). The magnetic coupling between this unit and the bottom FM layer abruptly drops with increasing $T$ at $\sim$70K, which pegs a 5.9+0.3meV anisotropic energy barrier of the magnetic hardening effect at the Fe/CoPc interface. We find that spin excitations dynamically induce a mutual magnetic coupling of all magnetic units, and alter their magnetic anisotropy as direct experimental evidence of spintronic anisotropy\(^\text{8}\) due to this transport mechanism.

Figure 1: Organic nanojunctions: processing and magnetics. (a-d) Processing steps to transform entire heterostructure stacks into vertical nanopillars with dielectrically separated bottom and top contacts, without using resists/solvents. See text for details. (e) Schematic of the Fe/CoPc/Co junction’s effective nanotransport path across
three magnetic units (green boxes): a bottom Fe layer, the junction’s lower interface forming a spinterface that is coupled to MSCs, and a top Co layer that is coupled to a MSC without a spinterface due to interdiffusion at the top interface. Not all molecular layers are shown (semi-transparent zone). The macrospin model’s coupling terms ECTop and MHBott between the central and outer units are shown. See text for details. (f) Major and minor R(H) loops at T=60K and V=58mV reveal three R levels due to the magnetization reversal of the three magnetic units, which are schematized by green arrows.

Our junctions are crafted from entire in-situ grown FM/molecular layer/FM stacks, thereby preserving nominal structural/magnetic properties, especially at interfaces, using a novel, solvent-and resist-free processing technique inspired by nanosphere lithography (see Methods for growth and processing details). After depositing the entire heterostructure through a shadow mask to define the lower electrode, 500nm-diameter SiO$_2$ nanobeads synthesized using a surfactant-mediated sol-gel reaction are randomly distributed on the surface (Fig. 1a). Once Ar atom milling to the organic layer is complete (Fig. 1b), the sample is encapsulated in sputtered SiO$_2$ and the beads are blown off, leaving a sub-diameter access (not shown) to the nanopillar (Fig. 1c). In a final step, top metallic contacts are deposited through a shadow mask (Fig. 1d).

The nanotransport path across our 20nm-thick CoPc nanojunctions is schematized in Fig. 1e. Consistently with our magnetic model, the effective nanotransport path proceeds across three magnetic units. The energy density $E$ of the nanotransport path is that of the top (i=t), central (i=c) and bottom (i=b) units and can be written as:

$$E = -\mu_0 \sum_{i=t,b} H \cdot M_i + \frac{1}{2} \sum_{i=t,b} K_i \sin^2(\theta_{M_i} - \theta_{K_i}) - \sum_{i=t,b} C_{ci} m_c \cdot m_i .$$

where $H$ is the applied magnetic field and, for each unit, $M_i$ is the magnetization, $m_i$ the reduced magnetization, $\theta_{M_i}$ the magnetization angle, $K_i$ its uniaxial anisotropy with an easy axis angle $\theta_{K_i}$. Finally, $C_{ci}$ is the coupling strength between the central (c) and outer (b,t) magnetic units, such that $C_{ct} = ECTop$ and $C_{cb}=MHBott$. For each H step, the energy of all three magnetic units is minimized to yield, for each magnetic unit, the magnetization’s in-plane orientation and the anisotropy strength/orientation.

The adsorption of Pc molecules onto a FM surface induces a change in sign of spin polarization, as well as a magnetic hardening for temperatures lower than ~70K of the FM’s top monolayer, which can rotate independently of the buried FM monolayers thanks to a weakened FM coupling that we call MHBott. The term ‘spinterface’ encompasses these interfacial properties, and sets the magnetic referential of the central magnetic unit, including that of MSCs that extend away from the interface and are formed by CoPc molecules with AF interactions. Magnetometry confirms that these spin chains also contribute to the anisotropy below 100K. In the following, we remain above the ~15K standalogue ordering temperature for these chains inferred from magnetotransport measurements (Suppl. Fig. S1). The remainder of the bottom FM forms a lower magnetic unit that is modelled as a free layer, i.e. with a reduced anisotropy $K/M=5mT$. As we will see, the top magnetic unit is comprised of the Co layer directly coupled to a MSC. The absence of a spinterface at the top interface presumably reflects metal interdiffusion during top electrode deposition. The presence in the nanotransport path of disjointed chains across the film thickness is expected from both structural and magnetic studies, such that a weak AF exchange term ECTop is present between the top and central magnetic units.

We first examine magnetotransport at 60K and 58mV, i.e at the temperature onset of the magnetic hardening effect, and with MSCs already promoting exchange bias. Fig. 1 shows R(H) loops following a cooldown at H=−1T. As the positive maximum H is increased, one notices a 1$^{st}$ reversible resistance jump near H=0, and a 2$^{nd}$ resistance change centered around H=1.17T that is reversible as long as the resistance baseline at H=−2T isn’t exceeded. For higher positive field sweeps, a third resistance change is observed and the R(H) loop becomes field-symmetric.

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3 Only at the (V=80mV,17K) and (V=100mV, 72K) critical points does the modelled anisotropy strength of the bottom FM layer strongly increase, as expected in an exchange bias system near criticality [xxx ref].
We are able to fit this unusual R(H) using our 3-unit macrospin model, thanks to which we identify the sequential magnetization reversal of the top, bottom and central magnetic units (see green arrows in Fig. 1f). Despite its low anisotropy, the bottom magnetic unit reverses at |H|>1T due to the FM coupling term \( M_{HBott} \) arising from magnetic hardening.

To accomplish this fitting of magnetotransport using the macrospin model, the resistance \( R \) due to non-collinear magnetizations \( M_t, M_b \) and \( M_c \) is:

\[
R = R_0 \left[ 1 - \frac{MRTop}{2} \cdot (m_t \cdot m_c - 1) - \frac{SpinFlipMR}{2} \cdot (m_c \cdot m_b - 1) \right].
\]

\( MRTop \) refers to the impact on nanojunction resistance of flipping the magnetization of the top magnetic unit relative to that of harder magnetic units, i.e. to the central magnetic unit. \( SpinFlipMR \) considers the MR due to flipping both the top and bottom magnetic units. We experimentally define \( MRTop = R(2T)/R(-2T) - 1 \) and \( SpinFlipMR = R(1T)/R(2T) - 1 \) and schematize these MR contributions in the R(H) at 80mV and \( T = 17K \) (see Fig. 2a), for which the magnetic states within |H|<2T are better defined. Due to our experimental \( |H|<2T \), when comparing the model with experiment, we make the approximation that \( R_0 = R(-2T) \), while small deviations between experimental and modelled values of \( MRTop \) and \( SpinFlipMR \) can occur because full magnetization reversal of the bottom magnetic unit can be incomplete within |H|<2T. Nevertheless, dataset consistency criteria and the shape of the R(H) data strongly limit possible errors. See SI for details. The \( EC_{Top} \) and \( MH_{Bott} \) coupling terms are also shown in Fig. 2a next to the reversal process for the top and bottom magnetic units, respectively.

**Figure 2: Current-induced alterations to magnetotransport.** (a-e) R(H) loops at 17K for 20 < V(mV) < 80 and associated fits, also represented in panel f for ±20T. (g) Bias dependence of \( dI/dV \), and of \( MRTop / SpinFlipMR \) inferred from \( I(V) \) and R(H) data. Bias dependencies of the strength and angle of the reduced anisotropy K/M for the (h-i) top and (j-k) central magnetic units. Bias dependencies of the (l) MH Bott and (m) EC Top coupling terms. The \( SpinFlipMR \) term tracks the \( dI/dV \) increase due to spin excitations. At the \( dI/dV \) peak, coupling between the MSCs of the top and central unit causes strong changes to their anisotropy parameters (panels h-k) and to the coupling parameters (panels l-m), which distorts the R(H) at 73mV (panel b). In the absence of the spin-flip conduction channel, flipping the bottom FM magnetization does not induce any MR (panel e) because the spininterface-stabilized MSC’s AF ground state degrades spin-conserved transport.

We now examine magnetotransport at 17K. For 43 ≤ V(mV) ≤ 150, only two magnetization reversals are observed, as illustrated for R(H) loops in Fig. 2a-e. According to the model’s fits (black lines of Fig. 2a-e), also shown in Fig. 2f for a larger field sweep, the central unit flips at \( H>2T \), i.e. beyond our experimental limit. At 20mV, the R(H) loop (Fig. 2f) exhibits only one resistance change, even though the model’s fit indicates that the bottom FM electrode has flipped.
during the sweep (data not shown). This implies that, at 20mV, SpinFlipMR=0. We will discuss this effect in what follows. Similar effects are observed for V<0 (data not shown).

Varying the in-plane orientation angle θ of the applied magnetic field for |V|<35mV causes MRTop to smoothly switch sign between 0° and 180° (Suppl. Fig. S2). This unidirectional response points to an origin in terms of tunnelling anisotropic magnetoresistance (TAMR)\textsuperscript{11}. It is difficult to draw a similar conclusion regarding SpinFlipMR since the 1T resistance level becomes undefined at intermediate angles. Nevertheless, we observe (see SI) that the R(H) at 17K after cooling at H=-1T and θ =0 is flipped along H between θ = 0° and 180°, and that the R(H) at 17K and θ =0 is flipped along H when field cooling at θ=0 is switched from H=-1T to H=1T. Finally, cooling at H=0+ and H=1T yield the same R(H). We thus infer that the device’s magnetic state during cooling defines a unidirectional axis for magnetotransport. As we will see, this unidirectional character arises from the coupling of the outer magnetic units to the central magnetic unit with very high anisotropy strength.

We show in the SI that this effect doesn’t depend on the bias voltage applied during cooldown. While magnetometry on FM/MPc bilayers revealed a fatigue effect upon repeatedly sweeping the external magnetic field\textsuperscript{9,10}, no such fatigue effect was seen in magnetotransport. This, and the ability to reproduce magnetotransport data using a macrospin model (see Fig. 1f, Fig. 2a-e and Fig. 3a-e), suggest that the nanotransport path within the 500nm-nominal diameter is proceeding through a reduced number of grains.

Referring to Fig. 2g, the bias dependence of dI/dV reveals a mostly constant amplitude for |V|<35mV, and large increases for |V|>35mV, punctuated by peaks at |V|≈70mV. The dI/dV amplitude further increases at higher bias. In line with previous literature\textsuperscript{12,12} on STM-assembled and solid-state-based transport across spin chains, we interpret these dI/dV features as the signature of spin excitations. Although the different amplitudes in the dI/dV peaks for V>0 and V<0 might be interpreted as a signature of spin-polarized transport\textsuperscript{7}, we note that the near-elastic transport regime across our nominally 20 nm-thick CoPc film, and the likely presence of magnetic disorder across the molecular layer (see hereafter), could also account for this asymmetry.

We observe that SpinFlipMR spectroscopically tracks dI/dV, both from R(H) and l(V) data (see Fig. 2g). To the best of our knowledge, this is the first observation of a MR signal that is driven to appear due to bias voltage, and whose amplitude tracks junction conductance. Given the above interpretation of dI/dV, this means that we have successfully measured MR between the two FM electrodes due to opening of spin-flip channels of transport across MSCs. The opposite signs of MRTop and SpinFlipMR are consistent with the change in sign of the spin-polarized current due to the spin-flip process.

The modelling of the bias-dependent R(H) data reveals that the reduced anisotropy strength K/M of the top magnetic unit is \( \approx 0.2T \), \textit{i.e.} over an order of magnitude stronger than that of a free layer (see Fig. 2h). We infer that it contains not only the top Co FM electrode, but also MSCs (see Fig. 1g). The weak, mostly bias-independent coupling term ECTop is then attributed to AF coupling between two MSCs belonging to the top two magnetic units along the nanotransport path.

With K/M\textsuperscript{=}10-20T, the central magnetic unit is magnetically very hard at 17K, and is coupled by \( MH\text{Bott} \approx 1T \) to the bottom magnetic unit. With an almost always constant K/M\textsuperscript{=}5mT, we infer that the bottom magnetic unit corresponds to the sub-interface atoms of the lower Fe electrode. \( MH\text{Bott} \) describes the FM coupling expected between these layers and the spinterface owing to magnetic hardening. Comparing Figs. 2g and 2j, we see that the central unit’s K/M tracks the spin excitations. We thus infer that the central magnetic unit’s spin referential is set by the spinterface and the MSC that is coupled to it. Our model indicates that, for V<35mV, the molecular layer’s anisotropy must be at least \( \approx 10T \) in order not to witness a symmetric R(H).

Now that the nanotransport path’s three magnetic units and couplings are identified and summarized in Fig. 1g, we examine how they are affected by spin excitations. While the R(H) loop for V=65mV (Fig. 2c) resembles that of
V=80mV (Fig. 2a), reaching the dI/dV peak at 73mV results in a strongly distorted $R(H)$ (Fig. 2b). To the best of our knowledge, this is the first evidence of how small bias changes can so drastically alter magnetotransport. This can be modelled only though a strong deviation in the angle of the central unit’s anisotropy. We also witness strong deviations in the anisotropy strength/angle of the top and bottom magnetic units, while the AF coupling $ECTop$ jumps by one order of magnitude. Meanwhile, the FM coupling $MHBott$ jumps from 1.2T to 1.4T. We propose that spin excitations drive a dynamical magnetic coupling of the two otherwise disjointed MSCs. This would explain, for $V>$73mV, not only the increase in $MHBott$ due to an effectively longer single MSC, but also how the top magnetic unit’s anisotropy increases while its angle jumps and further increases in order to dynamically accommodate the geometrical requirements of the 90deg super-exchange interaction between the two MSCs.

Overall, this strong impact on all three magnetic units at the bias voltage corresponding to maximum spin-flip conductance (see dI/dV peak at 73mV) can be interpreted as a mutual magnetic coupling between all three units that is induced by spin excitations. This constitutes direct evidence in magnetotransport of spintronic anisotropy, i.e. a change in magnetic anisotropy caused by a spin-polarized current\(^8\).

In light of these observations, we now discuss the absence of any MR due to flipping the bottom FM layer for $|V|\leq35mV$. Since $SpinFlipMR$ does not abruptly reach a saturated value at a threshold bias voltage, we conclude that the spin-flip transport channel is not altering the magnetic anisotropy of the bottom FM layer such that it can abruptly switch orientations. This is in line with the model’s treatment of the bottom FM layer as a free layer subject to the strong FM coupling $MHBott$ by the central unit’s spininterface. We propose that, in the $|V|\leq35mV$ bias range, the MSC that is coupled to the spininterface impedes spin-polarized transport because it is in its AFM ground state and is structurally of high quality (high K/M). In that case, only the spin flip channel can reveal MR due to flipping the bottom FM layer’s magnetization. We presume that this doesn’t occur at the top interface because of structural imperfections that are embodied by the top magnetic unit’s much lower K/M.
Figure 3: Temperature weakens spin chain coupling and magnetic hardening. (a-e) R(H) loops at 100mV for 17 < T(K) < 80. Data are in blue, while the modelled fits are in black and are also shown in panel f for ±20T. Temperature dependencies of (g) ECTop, (h) MHBott, (i) K/M of the central magnetic unit and (j) of the SpinFlipMR and MRTop. The gray data in panel i for T≥80K are the minimum values required to obtain R(-2T)=R(2T).

Increasing temperature causes the nanojunction magnetics, and thus magnetotransport, to strongly change, as illustrated by the R(H) loops at 100mV for 17 < T(K) < 80 of Fig. 3a-e. The increasing noise despite the R decrease suggests that thermal excitations are destabilizing magnetism along the nanotransport path. For 17 < T(K) < 55, the same flipping of the top and bottom magnetic units is observed for |H|≤2T (data at 55K not shown). For 60 ≤ T(K) ≤ 72, a symmetric R(H) is observed (see also Fig. 1f). For T≥80K, the R(H) loop has collapsed, and only low-field MR is observed until 100K. Thus, only a 5-8K temperature increase around 55K and 75K can promote remarkable changes in the R(H) loop shape.

Modelling these R(H) loops (black lines of Fig. 3a-e and Fig. 3f) reveals that, while ECTop remains mostly constant, weak and negative (i.e. AFM coupling, see Fig. 3g), MHBott decreases only moderately up to 65K, and then abruptly decreases for T>65K (Fig. 3h). We thus peg a $E_{\text{MIF}}=5.9±0.3\text{meV}$ energy barrier for the magnetic hardening effect at the $\text{bcc Fe(110)}/\text{CoPc}$ interface, which constitutes a first experimental energetic benchmark toward encoding information using the spinterface$^{14}$. Once this barrier is overcome though thermal fluctuations, the spinterface and bottom FM electrode can no longer rotate independently, which explains the collapse for T>72K of the R(H) loop (Fig. 4e).

According to the model, the central unit’s anisotropy decreases steadily from ≈18T at 17K to ≈4.4T at 65K, and then to under 3T for T>70K (Fig. 4i). This anisotropy term is thus dominated by a MSC contribution, but also comprises a contribution due to magnetic hardening, in line with the model’s description of the molecular layer (see Fig. 1a). This term, combined with MHBott, cause SpinFlipMR and MRTop to concurrently decrease with increasing T, and disappear at T=100K, thereby mimicking the effective exchange bias effect seen in magnetometry data$^{9,10}$.

To conclude, our work transposes progress in transport across spin chains using STM techniques to the domain of solid-state devices, in which FM layers can magnetically interact with molecular spin chains (MSCs) while fixing a spin referential for transport. This nanotechnological progress is enabled by an innovative, low-tech, solvent- and resist-free processing technique that works with entire heterostructure stacks and can be further rationalized (e.g. using nanobead positioning techniques) toward industrial applications. By using FM electrodes, and thanks to a phenomenological macrospin model of transport across three coupled magnetic units, the MR contribution arising from electrically exciting the MSC was isolated, and spintronic anisotropy due to spin excitations was directly evidenced. This enabled the nanotransport path’s three magnetic units to be identified. Temperature-dependent studies reveal the energy barrier for magnetic decoupling of the spinterface, and the complementary impact on magnetotransport of both the MSC and of the magnetic hardening effect, beyond magnetometry data on FM/molecule bilayers$^{9,10}$. This level of insight into the bias- and temperature-dependent magnetotransport properties of the nanotransport path across the solid-state junction should, thanks to novel organic-compatible nanojunction processing techniques such as ours, promote accelerated research into deploying the quantum physical properties of nano-objects within solid-state devices. It also establishes an experimental benchmark into the energetics of encoding information using the spinterface$^{14}$.

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References

1. Chen, X. et al. Probing Superexchange Interaction in Molecular Magnets by Spin-Flip Spectroscopy and Microscopy. *Physical Review Letters* **101**, 197208 (2008).

2. Muenks, M., Jacobson, P., Ternes, M. & Kern, K. Correlation-driven transport asymmetries through coupled spins in a tunnel junction. *Nature Communications* **8**, 14119 (2017).

3.Ormaza, M. et al. Controlled spin switching in a metallocene molecular junction. *Nature Communications* **8**, 1974 (2017).

4. Gaudenzi, R., Misiorny, M., Burzurí, E., Wegewijs, M. R. & van der Zant, H. S. J. Transport mirages in single-molecule devices. *The Journal of Chemical Physics* **146**, 092330 (2017).

5. Miao, G.-X., Münzenberg, M. & Moodera, J. S. Tunneling path toward spintronics. *Rep. Prog. Phys.* **74**, 036501–036519 (2011).

6. Studniarek, M. et al. Probing a Device’s Active Atoms. *Advanced Materials* 1606578 (2017) doi:10.1002/adma.201606578.

7. Schleicher, F. et al. Consolidated picture of tunnelling spintronics across oxygen vacancy states in MgO. *J. Phys. D: Appl. Phys.* **52**, 305302 (2019).

8. Misiorny, M., Hell, M. & Wegewijs, M. R. Spintronic magnetic anisotropy. *Nat Phys* **9**, 801–805 (2013).

9. Gruber, M. et al. Exchange bias and room-temperature magnetic order in molecular layers. *Nat Mater.* **14**, 981–984 (2015).

10. Boukari, S. et al. Disentangling Magnetic Hardening and Molecular Spin Chain Contributions to Exchange Bias in Ferromagnet/Molecule Bilayers. *Nano Letters* **18**, 4659 (2018).

11. Barraud, C. et al. Unidirectional Spin-Dependent Molecule-Ferromagnet Hybridized States Anisotropy in Cobalt Phthalocyanine Based Magnetic Tunnel Junctions. *Phys. Rev. Lett.* **114**, 206603 (2015).

12. Barraud, C. et al. Phthalocyanine based molecular spintronic devices. *Dalton Trans.* **45**, 16694–16699 (2016).

13. Delprat, S. et al. Molecular spintronics: the role of spin-dependent hybridization. *J. Phys. D: Appl. Phys.* **51**, 473001 (2018).

14. Cinchetti, M., Dediu, V. A. & Hueso, L. E. Activating the molecular spinterface. *Nat Mater* **16**, 507–515 (2017).
15. Serri, M. et al. High-temperature antiferromagnetism in molecular semiconductor thin films and nanostructures. *Nat Commun* **5**, 3079–3087 (2014).

16. Khajetoorians, A. A. et al. Atom-by-atom engineering and magnetometry of tailored nanomagnets. *Nature Physics* **8**, 497–503 (2012).

17. Schmaus, S. et al. Giant magnetoresistance through a single molecule. *Nature Nanotechnology* **6**, 185–189 (2011).

18. Barraud, C. et al. Unravelling the role of the interface for spin injection into organic semiconductors. *Nature Physics* **6**, 615–620 (2010).

19. Katcko, K. et al. Spin-driven electrical power generation at room temperature. *Communications Physics* **2**, 116 (2019).

20. Raman, K. V. et al. Interface-engineered templates for molecular spin memory devices. *Nature* **493**, 509–513 (2013).

21. Schleicher, F. Linking Electronic Transport through a Spin Crossover Thin Film to the Molecular Spin State Using X-ray Absorption Spectroscopy Operando Techniques. *ACS Appl. Mater. Interfaces* **10**, 31580 (2018).

22. Wang, W. G. et al. Parallel fabrication of magnetic tunnel junction nanopillars by nanosphere lithography. *Scientific Reports* **3**, 1948 (2013).

23. He, Q., Cui, X., Cui, F., Guo, L. & Shi, J. Size-controlled synthesis of monodispersed mesoporous silica nanoparticles under a neutral condition. *Microporous and Mesoporous Materials* **117**, 609–616 (2009).

24. Djeghloul, F. et al. High Spin Polarization at Ferromagnetic Metal-Organic Interfaces: a Generic Property. *J. Phys. Chem. Lett.* **7**, 2310–2315 (2016).

25. Raman, K. V. Interface-assisted molecular spintronics. *Applied Physics Reviews* **1**, 031101 (2014).