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# Magnetoresistive Single-Molecule Junctions: the role of the Spinterface and the CISS effect.

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| **Abstract:** | This review is an effort in putting together the latest results about room-temperature magnetoresistive (MR) effects in nanoscale/single-molecule electronic devices consisting of one (few) molecule(s) placed in electrical contact between two nanoscale electrodes. The capability to control at room temperature and under bespoke electrodes' magnetization the MR response of a single-molecule (SM) device has been a longstanding quest. The work carried out so far in this field has identified two key components directly involved in the MR response of a single(few)-molecule(s) device: (i) The molecule\|electrode spinterface, defining the interplay between interfacial electrostatics and spin density. (ii) Two aspects of the molecular structure involved in the spin-dependent conduction mechanism: (1) the presence of paramagnetic metal centres in the molecular structure and (2), the degree of chirality within the molecular wire. |
| **Response to Reviewers:** | Reviewer #1: The manuscript "Magnetoresitive Single-Molecule Junctions: the role of Spinterface and the CISS effect" by Argones et a. is a brief review article giving a brief overview of magnetoresttance measurements on single/few molecule junctions. The total experiments in this space is still relatively small, and the authors cover it well, and point out the main functioning mechanisms behind magnetoresistance effects in molecular junctions. The review is well-written, and I am in favor of publication, with the small caveats noted below.<br><br>- We thank the Reviewer for the general very positive evaluation.<br><br>The authors often discuss the "spin-source" and "spin-drain" I take these to mean the "source" of injected carriers, and the "ending point" of the spin carrier - not the source and drain from a current perspective, but this is not clearly laid out for the reader, especially with the applied biases, and could make Fig. 4 much more readable.<br><br>- We thank the Reviewer pointing out the relevant aspect of "spin-source" and "spin-drain". For the described setups spin drain/source is not different that the drain/source from the current perspective, since both electrodes have a relevant spintronic role for the devices, namely, the top electrode is the ferromagnetic source of spin-polarized |

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| | electrons, and the bottom diamagnetic electrode (drain) is displays active Spinterface. We have modified Fig. 4 and its caption accordingly to make concepts "spin-source" and "spin-drain" clearer for the reader.<br><br>“Figure 4. Two possible MR SM-devices scenarios where the spin-source electrode (labelled in figure) and molecule present matching (a) or mismatching (b) between spin orientation preferences. The spin-drain electrode (purple arrow) has been assigned to have a fixed spin orientation imposed by the Spinterface —enhanced Rashba effect—. The binary traffic lights indicate the preferences of each subsystem, spin-source electrode (top light) and molecule (bottom light), for the injected spin-polarisation direction, where green means match and red means mismatch. Note that the of spin polarisation molecule and top electrode (spin-source) are aligned due to the Zeeman effect.”<br><br>On page 4 the authors discuss that MR can be observed using diamagnetic molecules connected to ferromagnetic electrodes, and the effect is due to the electrodes and the "spinterface". Then, on page 6 they discuss diamagnetic molecules showing MR through the CISS Effect. However, there is a disconnect between these two sections. Why must chirality play a role in the second discussion, how is the effect due to the electrodes and spinterface ruled out when dealing with CISS to identify the underlying mechanism for experiments like these? It would be good to have the authors clearly delineate the two cases for the readers.<br><br>- We thank the reviewer to point us towards the need to stress the differences between “spinterface” and CISS effects. Essentially, what it has been observed is that both effects are independent sources of electron spin-polarization in the molecular device, whose effects can be additive or even synergistic; accordingly, we modified the following text in page 10 and added a relevant reference:<br><br>“The spinterface imposes a spin preference to the transmitted electrical current crossing the SM device, making it an independent spin-selective element in a MR SM device. The Spinterface has been suggested to have an additive role to the CISS effect in diamagnetic molecules, as represented in previous rationalisation of the spin-dependent transport in chiral peptides (Figure 7), or to have a more synergistic role acting as an “enhancer” and necessary ingredient to observe CISS effect (Dubi, 2022)”<br><br>A couple of typos:<br>Page 4 warantee -> guarantee<br><br>- We have corrected the typo, many thanks.<br>pin-splitted -> Spin-split<br><br>- We have amended the typo, many thanks. |
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# Magnetoresistive Single-Molecule Junctions: the role of the *Spinterface* and the *CISS* effect.

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## Abstract

This review is an effort in putting together the latest results about room-temperature magnetoresistive (MR) effects in nanoscale/single-molecule electronic devices consisting of one (few) molecule(s) placed in electrical contact between two nanoscale electrodes. Molecules represent powerful building blocks for developing state-of-the-art MR devices, as they bring long spin relaxation timescales, low cost and high tunability of their electrical and magnetic properties via chemical modifications. The capability to control at room temperature and under bespoke electrodes' magnetization the MR response of a single-molecule (SM) device has been a longstanding quest. Such SM platforms could serve as fundamental tools to understand what the main mechanistic ingredients of MR effects in a molecular device are, leading to their use as building-blocks for miniaturization in spintronic applications. The work carried out so far in this field has identified two key components directly involved in the MR response of a single(few)-molecule(s) device: (i) The molecule|electrode spinterface, defining the interplay between interfacial electrostatics and spin density, has been proven to play a fundamental role in the interpretation of the observed single-molecule junction's MR effects, which is governed by the electrode material and the electrode-molecule chemistry. (ii) Two aspects of the molecular structure have been demonstrated to be involved in the spin-dependent conduction mechanism: (1) the presence of paramagnetic metal centres in the molecular structure and how their orbitals bearing the unpaired electrons couple with the device electrodes, and (2), the degree of chirality within the molecular wire. This contribution will focus on the above points (i-ii) by making use of specific examples in the literature.

## 1. Introduction: A Magnetoresistive Single-Molecule Device:Basic Concepts and Architecture.

The cornerstone of a magnetoresistive single-molecule (MR SM) device is the ability to inject a particular spin (charge) carrier from the device's electrodes to the wired molecule in the junction or *vice versa* while measuring the overall conductance of the molecular device (Figure 1a). This is achieved by using an electron spin-source[1] and/or -drain[2] electrode as part of the design of the MR SM junction. Spin-polarisable (ferromagnetic) electrodes, such as Fe or Ni,[3,4] have been typically used in MR SM junction experiments to act as both electron spin-drain and/or -source.[1,3] The ferromagnetic electrode in the SM junction experiment defines the population of electron spin orientation of the current that flows through the MR SM-device, which in turn modulates the device conductance (Figure 1a). An extensively used approach for the design of MR SM junction experiments is the scanning tunneling microscope-based break-junction technique (STMBJ).[2,3,5] The STM's spin-polarisable tip electrode is driven to the surface and retracted again in successive cycles using a 2-point feedback loop on the tunneling current flowing between the two STM electrodes, the tip and the substrate, under a constant bias voltage. The current decay traces during the retraction cycles (current traces) are recorded and, when a molecule is trapped between the two electrodes, a plateau appears in the current trace (see Figure 1b inset), which allows the determination of the molecular quantum conductance. Commonly the current decay traces are accumulated in 1D conductance histograms, providing an averaged single-molecule conductance value as a peak above the tunnelling background baseline (see Figure 1b). The injected spin-polarised current that flows through the molecular junction results in MR response of the quantum conductance measurement of the molecular wire. Another approach exploited in the characterization of MR response in nanoscale molecular junctions is the conductive atomic force microscope (c-AFM).[6] Similar to the STMBJ approach, the current flowing between the two AFM-based junction electrodes, namely, a conductive AFM tip and an electron spin polarisable substrate, is measured. In this approach, the target molecules are typically self-assembled on the spin-polarized electrode substrate (bottom) and contacted by the conductive AFM tip (see Figure 1c). The measurement is performed under AFM's contact mode maintaining a constant force between the tip and the surface by means of the cantilever deflection feedback loop. The magnetization of the spin-polarized electrode can be done either *ex-situ* or *in-situ* by placing a permanent magnet in close proximity to the ferromagnetic electrode.[7,8]

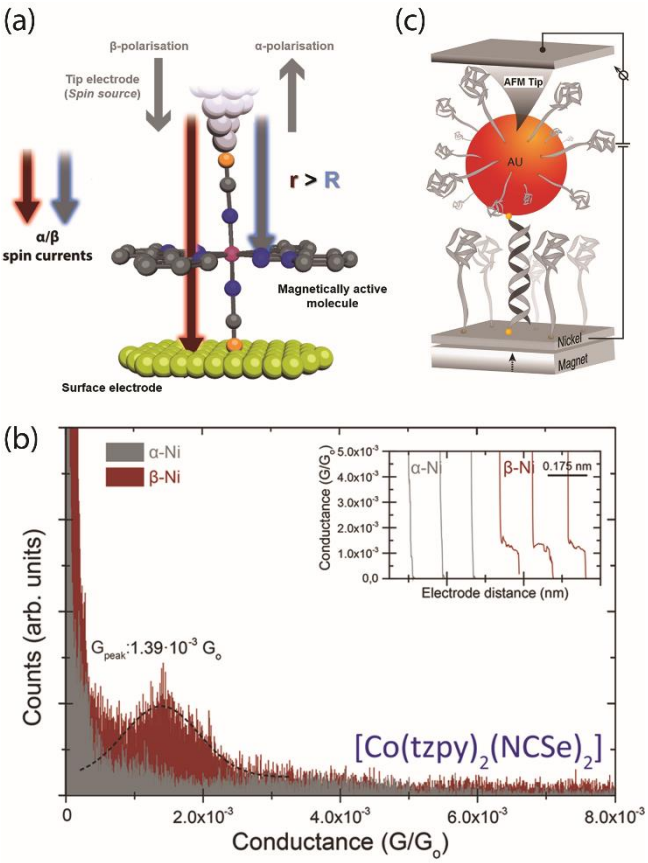


***Figure 1.*** *(a) Schematic diagram of a MR SM device. The device exhibits low (high resistance, R) or high (low resistance r) transmission of the spin polarized electric current injected from the spin polarised tip electrode.(b) Conductance histograms of MR SM junction experiments of a* $Co^{II}$ *complex device under α-(grey) and β- (maroon) spin-polarisations of the top Ni electrode using a STMBJ approach. Inset shows representative individual current traces for the α-polarised (grey traces) and the β-polarised (crimson traces) Ni electrodes. Reprinted with permission from Aragonès et al.*[7] *(c) Experimental setup for the measurement of AFM-based molecular junctions based on double-stranded DNA functionalised with Au nanoparticles. Reprinted with permission from Xie et al.*[6]

## 2. Molecular properties in a Magnetoresistive Single-Molecule Device.

In MR SM junctions, the chemical and transport properties of the contacted molecule play an essential role. The ability of the molecule to discriminate between charge carriers of different spin orientation, due to the interplay of spin-orbit coupling, coulombic interactions, correlation effects, electron-phonon coupling, and symmetry constraints imposed by the molecular chirality on electron transport, is exploited to build MR SM devices.

### *Molecules with Paramagnetic centres*

Magnetically active molecules typically allow spin polarization of the electrical current flowing through a SM junction. Magnetically active molecules are paramagnetic systems owing to their open-shell electronic structure inherent to the presence of metal atoms[2,4,9] or organic radicals.[10,11] Such molecular systems provide energetically available α- or β-polarised spin-orbital channels for charge transport in the SM junction, unlike diamagnetic ones. It is assumed here that these spin channels

correspond to spins aligned parallel or anti-parallel to the direction of charge transport. The existence of these channels was shown in the work by Aragones *et al*[2,7] employing a spin polarised STMBJ approach. Here, a family of paramagnetic metal complexes with varying metal centres were trapped in a spin-polarized SM junction between an *ex-situ* magnetized Ni electrode and a Au electrode.[2] Large MR values were observed (R >> r in Figure 1a), which resulted in molecular conductance modulation of up to two orders of magnitude between opposite spin-polarisations. In the above-mentioned experiments, the relevance of the open-shell electronic structure for spin discrimination in measuring the conductance of a SM was demonstrated by tuning the working temperature of the SM device built with a spin-crossover (SCO) molecule. The transition from a paramagnetic *high-spin* state, at room temperature (RT), to a diamagnetic *low-spin* state, at low temperature (LT), of the SCO compound is induced by decreasing the temperature of the STM chamber under ultrahigh vacuum conditions. When the transition temperature of the SCO molecule is reached, the SM device loses its MR properties, thus evidencing the central role of the molecular magnetism. Similar switchable MR SM devices has been also achieved via redox active molecules, where the spin state varies as a function of molecular oxidation.[12]

Paramagnetism is just a general requirement to generate MR response in a SM device. However, the presence of unpaired electrons does not guarantee an efficient spin filtering. To achieve efficient spin selectivity via paramagnetic centres in the molecular wire structure, we need: (i) large energy spin splitting between the α- and β-polarised orbital channels, and (ii), spin-split frontier spin-orbitals close in energy to the Fermi level of the device electrodes. This has been found experimentally by Aragonès *et al* comparing the conductance of paramagnetic metal ions such as $Mn^{II}$, $Co^{II}$, $Fe^{II}$ and $Ni^{II}$ in SM devices based on mononuclear metal complexes[7] and metalloporphyrins[4]. Only spin-split molecular orbitals close to the Fermi level[13] become relevant and, therefore, contribute significantly to charge transport, allowing efficient spin filtering of the current transmitted through the SM device. $Fe^{II}$ and $Co^{II}$ complexes showed large magnetoresistance due to the unfilled beta $t_{2g}$ orbitals close to the Fermi level of electrodes. In contrast, $Mn^{II}$ and $Ni^{II}$ systems showed negligible spin selectivity since their unpaired electrons/holes were located in orbitals with energies far from the Fermi level of electrodes. It should be noted that if the molecular paramagnetism in an SM device is due to spin-uncompensated open-shell metallic centres, only electron pathways involving the paramagnetic metal centre in the molecular wire will undergo spin discrimination. This has been recently shown in paramagnetic supramolecular junctions[14,15] based on metalloporphyrins.[4] Metalloporphyrin-based SM junctions display different pathways for the transmitted electrons, which are tuned by the final supramolecular structures in the SM junction.[15] Different supramolecular interactions are promoted at different electrode-electrode gap separations of the nanoscale junction, resulting in specific electron pathways, some of them not involving the paramagnetic metal centre (Figure 2a). Out of all the probed electron pathways, only those involving the paramagnetic metal centre, *i.e.* $Co^{II}$, featured spin-dependent conductance (see Figure 2b).[4] In this vein, Yang et al[9] developed the opposite approach. By varying the direction of an external magnetic field, they were able to adjust the electron pathway through an iron phthalocyanine along with the MR response of the device. This was made possible by the induced reorientation of the magnetic moment of the metal centre, which modifies the electron distribution of the d-orbitals.

Alternatively, MR properties in SM devices have been also observed using diamagnetic molecules connected to ferromagnetic electrodes.[3,8,16–18] In such scenario, the wired molecule plays no role in the MR response[8] acting as a mere conductor, leaving the control of the MR effect to the relative magnetization orientation of both the spin-drain and spin-source electrodes, which, in turn, is controlled by spinterface effects generated at the molecule/electrodes interface. The latter MR SM junctions are regarded as a molecular approach of giant magnetoresistance "GMR".[16] Similarly, Pal *et al*,[19] also achieved spin filtering capabilities in a SM device of magnetically inactive molecules by means of quantum interference, a mechanism that can also lead to marked energetically separated α- and β-polarised charge transport channels.

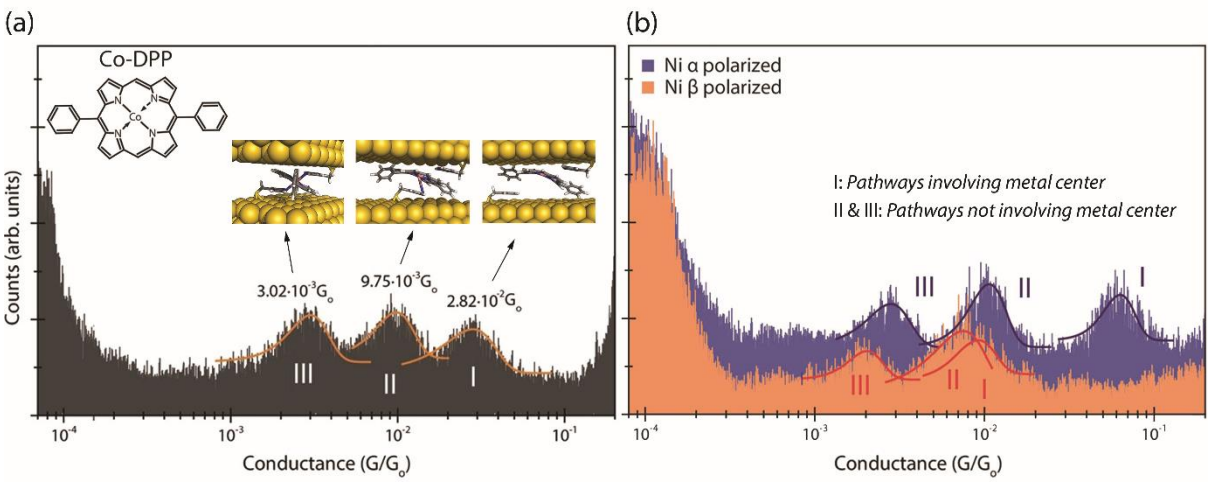


***Figure 2.*** *Conductance measurements of MR-SM-devices based in supramolecular junctions employing a paramagnetic $Co^{II}$ metalloporphyrin. 1D histograms of measurements under non- (a), and α- and β-polarised Ni electrodes (b),. Note that, of the three different paths for transmitted electrons I, II and III (labelled in the figure), only I displays spin-dependent conductance due to the participation of the paramagnetic metal centre. Reprinted with permission from Aragonès et al.*[4,15]

### *Chiral Molecules and the CISS effect*

The molecular ability to discriminate between spin carriers has been commonly associated with the magnetic character of metal or stabilized radical centres embedded within the molecular structure. However, diamagnetic (closed-shell) molecules can also provide spin selectivity if they possess chiral symmetry.[20] This effect is known as the Chiral-Induced Spin Selectivity (CISS) and can be understood as a spin polarization or spin selectivity that occurs in the absence of external magnetic fields, implying that any magnetic interaction is due to the molecular potential. The main idea behind the CISS effect is that chirality breaks the space inversion symmetry and that in a molecular junction where the molecule is an open system, *i.e.* where time reversal is broken, transport becomes spin-dependent.[21] When charge carriers are injected along the chiral structure, spin polarization arises, a phenomenon that, in the tunneling regime, can be simply understood as arising from different transmission barriers associated with different energy penalties favouring one spin component over the other. As proposed in the first theoretical studies addressing the CISS effect,[20,21] intrinsic spin-orbit interaction is crucial in providing a first qualitative insight into the CISS effect. In fact, spin-orbit coupling (SOC) has remained a key ingredient in the vast majority of subsequent theoretical investigations.[22] Besides molecular spin-orbit interactions, it is quite clear that the onset of spin polarization requires the breaking of space inversion (associated with chirality) and time reversal. The role of electron-vibration coupling,[23–25] electronic correlations,[26] influence of (photo)excited states,[27] and interfacial effects[28,29] have been recently highlighted. Still, despite strong theoretical progress, involving both model studies[30–32] as well as first-principle based approaches,[33–35] a fully consistent picture of the CISS effect is still lacking,[30] and a consistent physical description of CISS, studied and reviewed several times,[36,37] is still under strong debate.

Chiral (diamagnetic) molecules, such as peptides, DNA, helicenes or even chiral inorganic materials such as perovskites manifest CISS in a variety of different molecular-based devices.[1,20,38,39] However, only few studies have explored CISS as a molecular spin filtering mechanism in MR nanoscale (SM) devices. In these studies, a spin carrier is injected by a spin-source electrode, where the CISS generated by the (chiral) wired molecule in the device (Figure 3) induces a change in the SM junction conductance which directly depends on the electron spin orientation of the injected spin-polarized current. Xie *et*

*al*[6] performed pioneering charge transport measurements of molecular contacts based on double-stranded DNA functionalised with Au nanoparticles using a conductive AFM setup (Figure 3a). They observed pronounced MR effects in such nanoscale molecular contacts, with large conductance changes upon inversion of electron spin orientation, which were especially visible at large voltage biases >1V. Later on, Aragonès *et al*[1] performed one of the first measurements of the CISS in a SM junction (Figure 3b). In this work, the authors quantified the effect of spin-polarised currents for the two enantiomers (levo- and dextro-rotatory) of an individual α-helical peptide sequence composed of 22 amino acids. As discussed above, when charge carriers with a particular spin-polarization direction are transported through the peptide barrel, each of the two enantiomers shows a preference for the opposite spin orientations resulting in the generation of an enantiospecific electrical current. This study constitutes the first reported case of current asymmetries observed in chiral SM-devices. The above work attests that spin selective transport based on CISS is feasible for few or even individual molecules, thus corroborating that the CISS effect might not be arising from a cooperative effect of the molecular ensemble. Recently, Ghosh *et al*[37] analysed the surface potential differences generated in Au surface-modified electrodes with L- and D-isomers of the same peptide sequence. Measuring the potential difference across the different isomers for different spin orientations allows quantifying the spin penetration ability of each spin carrier in the adsorbed chiral molecular structure, *i.e.,* the spin discrimination efficiency of the chiral molecules. The authors found a dependence of the potential difference in the direction of magnetisation of the spin-source electrode with respect to the chirality of the peptide layer, which correlated with the degree of penetration of the spin-polarized orbitals into the organic layer. This result shows an independent assessment of the CISS effect from previous charge transport characterization methods.

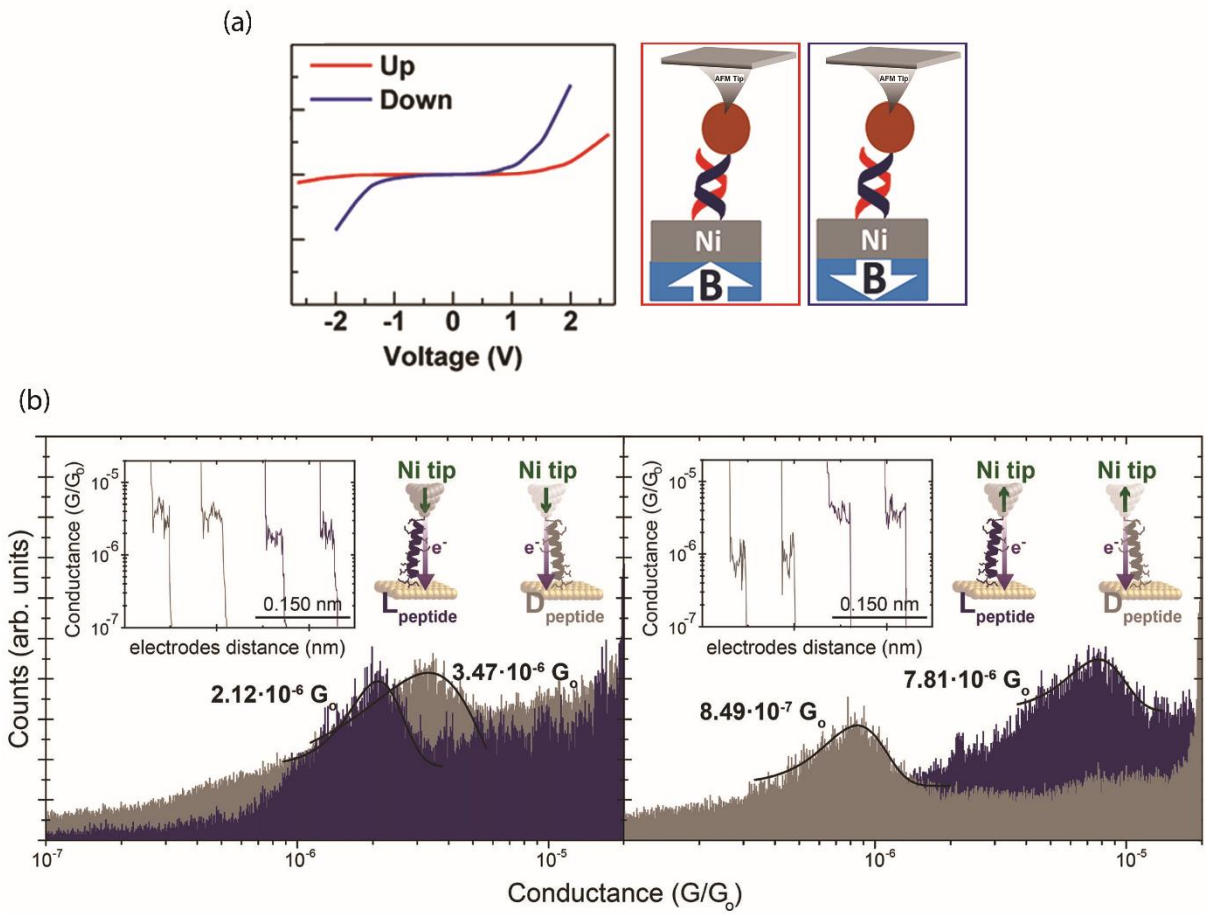


***Figure 3.*** *(a) Current versus voltage characteristics obtained under spin-up (red) and spin-down (blue) magnetic polarisation of bottom Ni electrode in a DNA-based molecular junction (right panel showing the schematic*

*representation of the AFM device). Reprinted with permission from Xie et al.[6] (b) Semilog conductance histograms for the measured SMJBJ-based SM conductance measurements of two enantiomers of an ∝-helical peptide under spin-up and spin-down current polarisation. The short green arrows indicate the spin-source (Ni) electrode's magnetic moment orientation parallel (left) or antiparallel (right), and the violet arrows indicate the current flow direction. Inset: Representative individual current versus pulling traces along with the sketch of the setup. Reprinted with permission from Aragonès et al.[1]*

## 3. The Electron Spin Injection in a Single-Molecule Device

### *Charge carriers' spin population*

Control over the population of the charge carriers' spin in a polarised current., *i.e.,* minority or majority spin carriers, is an indispensable ingredient to achieve MR effects. Minority or majority spin carriers can be transmitted or blocked in the different spin selective components of the MR SM-device, *i.e.*, spin-source and/or spin-drain electrodes, spin-sensitive molecular wire, and spin-polarized interfaces or spinterfaces (see next section). Ferromagnetic electrodes are widely employed in MR devices to control electron spin-polarization in an electric current as they present a particular spin imbalance around the Fermi energy, which depends on the type of material. Ni, for example, a common electrode material for spintronics and magnetism studies,[4,40] displays a large energy difference for injecting or emitting majority electron spin (unfavoured) as compared to the minority spin (favoured).[41] The latter spin preference of the device drain/source electrode needs to be placed in contrast with the spin selectivity of the wired molecule in the MR SM-device. For example, Aravena *et al*[42] studied how $Fe^{II}$ SCO complexes favour the transport of minority spin carriers via low-lying energy molecular orbitals. The differences in the spin preference of each component of the MR SM-device will determine the final MR efficiency of the device. Aragonès *et al*,[4] have shown that the mismatch in the spin preference between the spin-drain device terminal and the wired molecular component severely decreases the MR efficiency of the SM-device (Figure 4a). The spin of the molecule is aligned by the Zeeman effect with the magnetisation of the ferromagnetic electrode. Moreover, the bottom Au substrate is not magnetically innocent as its large SOC induces surface Rashba effect, thus inducing spin imbalance at the surface of the material, which is enhanced by the interaction with molecular orbitals bearing unpaired electrons (see also discussion in section 4). Hence, junctions with Au substrates display magnetoresistance while equivalent systems with copper or platinum do not. In the case of copper, the weak SOC does not meet the previous requirement, while in platinum the interaction of energy levels near the Fermi energy with molecular orbitals containing unpaired electrons is much less efficient than in the case of Au.[7]

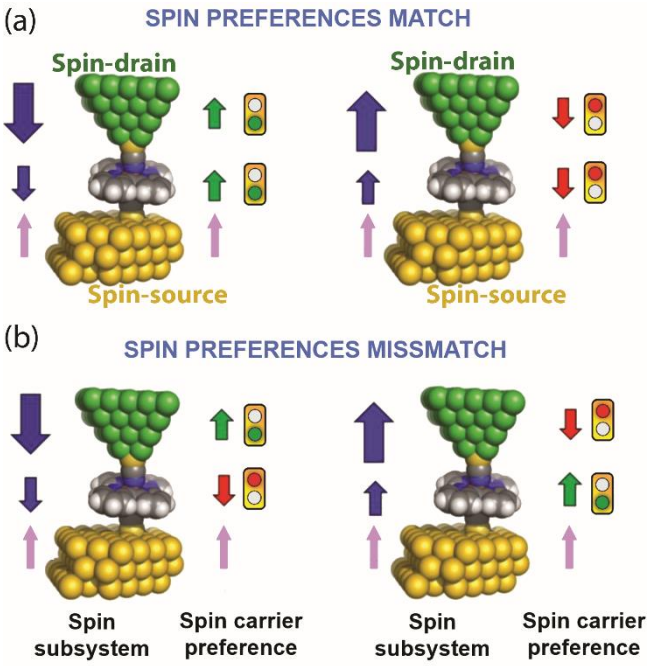


***Figure 4.*** *Two possible MR SM-devices scenarios where the spin-source electrode (labelled in figure) and molecule present matching (a) or mismatching (b) between spin orientation preferences. The spin-drain electrode (purple arrow) has been assigned to have a fixed spin orientation imposed by the Spinterface —enhanced Rashba effect—. The binary traffic lights indicate the preferences of each subsystem, spin-source electrode (top light) and molecule (bottom light), for the injected spin-polarisation direction, where green means match and red means mismatch. Note that the of spin polarisation molecule and top electrode (spin-source) are aligned due to the Zeeman effect.*

### *The orientation of the electrode magnetisation*

The orientation of the magnetic field with respect to the electron flow has been also employed as a mechanism to tune the conductance response in SM junctions (Figure 5). [3,4,9,43–45] The origin lies on the phenomenon called anisotropic magnetoresistance (AMR). Relevant AMR studies display very different scenarios and effects because they have been based in MR devices with different architectures. In two different works based on diamagnetic molecules by Yamada *et al*[44] and Li *et al*[3], they demonstrated the perpendicular magnetisation of the ferromagnetic electrodes with respect to the direction of the current flow increases the conductance of both monolayer-based and SM devices, respectively. On the contrary, in the presence of molecular paramagnetic systems,[4] the MR efficiency is significantly increased for a perpendicular magnetisation to the current flow of the FM spin-drain electrode, which greatly suppresses the conductance of the SM-device below the limit of detection of the STM setup. Interestingly, Xie *et al*,[44] studied MR interfacial effects of the Au-S bond (see also section 4) in molecular contacts employing non-magnetic electrodes. The authors determined a negligible difference between parallel and perpendicular orientations of an external magnetic field with respect to the electric current.[44]

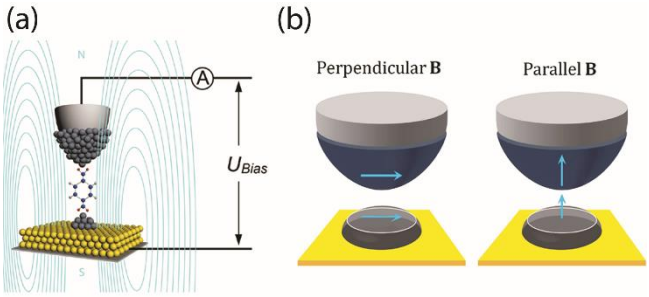


***Figure 5**. (a) Sketch of a MR SM-device formed in between Pt/Ir-Au electrodes with ferromagnetic Fe clusters with a representation of the magnetic field. (b) Schematic illustration of the MR SM-device with the magnetic moment perpendicular (left) and parallel (right) to the direction of current flow. The blue arrows represent the electrodes' magnetisation direction. Reprinted with permission from Li et al.[3]*

## 4. Molecule|Electrode Spinterface

In MR SM devices, the magnetic exchange interaction between the magnetized ferromagnetic electrode and the wired paramagnetic molecule causes the coupling of the magnetic moments of the wired molecule with the electrodes' one,[46] thus preventing asymmetric charge transport between both opposite electronic spin injections in the SM-devices, leading to MR response suppression. The magnetic coupling between both elements prevents any sort of spin carrier discrimination in the SM device. However, spinterface effects,[47] which arise from an asymmetric hybridization of the molecular orbitals at the molecule|electrode interface[47,48], can provide the symmetry breaking necessary for the SM-device's spin discrimination. The spinterface is a consequence of the amplification of the Rashba spin-splitting (Figure 6a) at the metal surface,[49] due to a strong SOC interaction when a paramagnetic molecule strongly binds to a heavy metal electrode surface presenting Rashba splitting. As a result, spin unbalance is created at the molecule|electrode (bond) interface, that results in the generation of spin-texture.[50] The latter occurs when the metal orbitals hybridize with the molecular levels leading to the symmetric surface spin-polarisation of the standard Au Rashba splitting becoming strongly asymmetric. The latter, results in a net spin-polarization at the molecule|electrode interface (Figure 6b,c). As mentioned earlier, the spinterface effect arises then as a subtle interplay between the electronic structure of the paramagnetic molecule and the Rashba diamagnetic metal substrate. Such characteristic interfacial spin-polarisation can be suppressed by using a light Cu metal substrate displaying poor SOC (Figure 6d), or Pt –which lacks well-defined spin-texture. The latter is attested by Aragonès and co-workers[7] who observed the suppression of the MR character of SM-devices based on Co complexes by replacing the Au bottom electrodes substrate by Cu.

It should be noted that DFT (or NEGF-DFT) including SOC, can only give qualitative insights into the spin polarization of the current. Despite these calculations can predict significant spin filtering for paramagnetic molecules, they fail to capture the change in the MR response associated with the choice of the spin injection, as observed experimentally.[4]

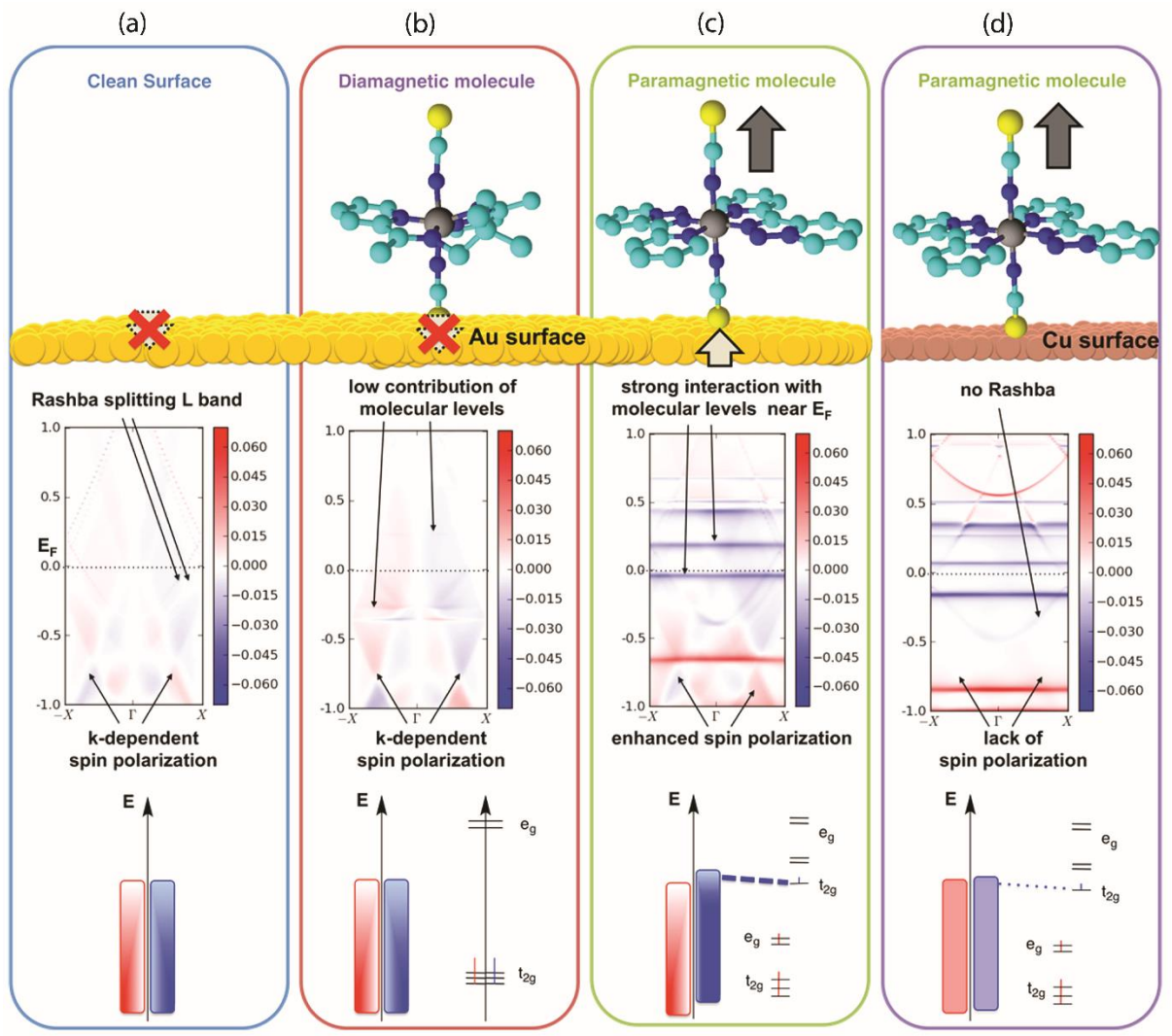


*Figure 6. Calculated out of plane spin texture for bare and functionalised Au(111) surface: DFT calculated logarithm of the z-component for the α- and β-magnetisation density of states (DOS) difference (central panel) and a schematic DOS representation (bottom panel). The usual splitting of L-band and a k-dependent spin-polarisation (Rashba effect) is found in the DFT calculations for the Au surface systems (a–c), also indicated with a nonuniform filling in the schematic DOS of the surface bands as opposed to the copper surface in (d). Horizontal lines correspond to the hybridized molecular levels for the high-spin $Fe^{II}$ complex adsorbed onto the metal surfaces (c,d). Note the high spin-polarisation of the Au surface (k-dependent spin-polarisation) occurs when a high-spin $Fe^{II}$ complex is strongly adsorbed (c). This effect is small when absorbed on the copper surface (d). Reprinted with permission from Aragonès et al.[2]*

The spinterface of an Au-based MR SM device has an inherent spin polarisation that depends on the molecule-electrode interaction and is insensitive to external magnetic fields [45] such as that imposed by the device's ferromagnetic electrode. The spinterface imposes a spin preference to the transmitted electrical current crossing the SM device, making it an independent spin-selective element in a MR SM device. The Spinterface has been suggested to have an additive role to the CISS effect in diamagnetic molecules, as represented in previous rationalisation of the spin-dependent transport in chiral peptides (Figure 7), or to have a more synergistic role acting as an "enhancer" and necessary ingredient to observe CISS effect.[51] The interaction between the inherent polarisation of the spinterface (acting as a spin-source or -drain) and the magnetic moment orientation of a

ferromagnetic electrode (acting as a spin-drain or -source) is a suitable mechanism for tuning the MR response of SM-devices at RT.[1,4,7,14]

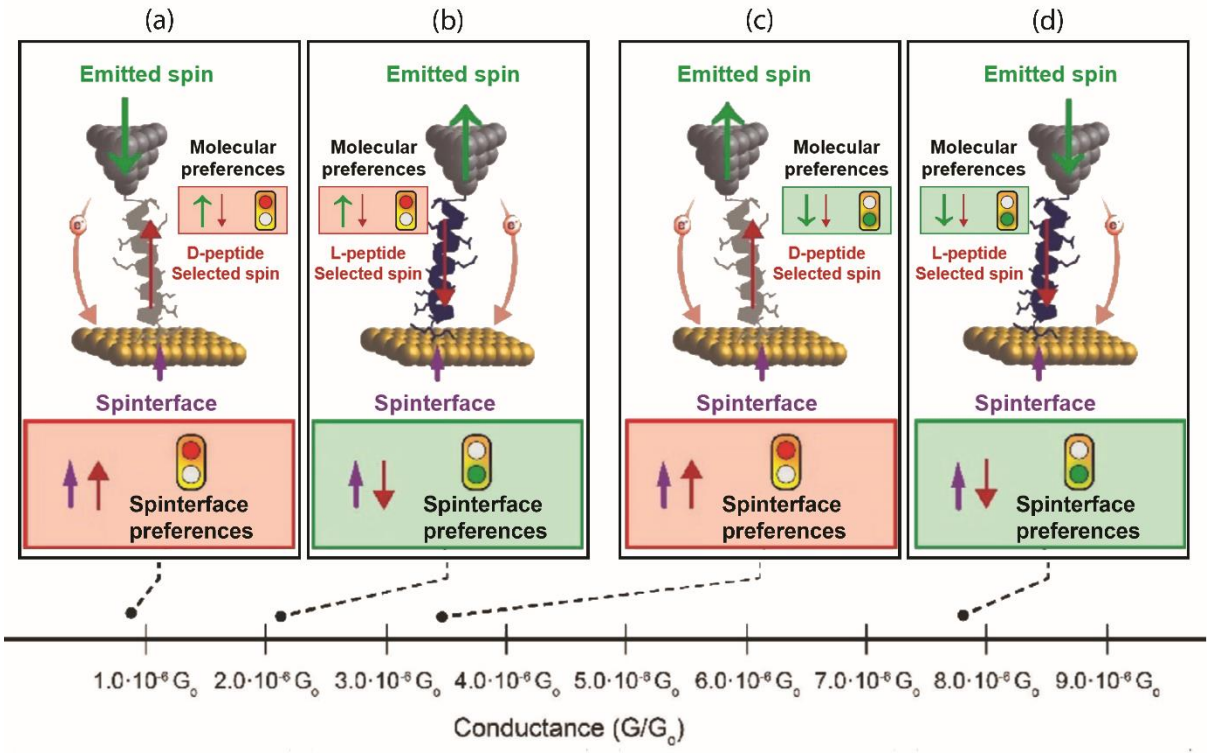


*Figure 7. Schematic representation of two single-molecule devices based on chiral helical peptides and the spinterface as main ingredients. Experimental conductance values on the x-axis are ordered according to increasing values from left to right. Electron transport is defined from tip (current's spin-polarisation indicated with green arrow) to substrate electrode. The binary traffic lights indicate the preferences of each subsystem; molecule (central lights) and spinterface (bottom lights), for the injected spin-polarisation direction, where green means match and red means mismatch. D-Peptide supports spin-up current polarisation and L-peptide supports spin-down polarisation. The spinterface, always spin-up polarised (purple arrow), supports spin-down polarisation versus spin-up polarisation when injected into Au. Reprinted with permission from Aragonès et al.[1]*

## Conclusions and outlook

In this review, we have summarised the latest advances in MR nanodevices at RT with either one or few molecule(s) contacted between two nanoscale electrodes. We have identified three key-components for their development which deserve careful consideration and further research: the molecular structure, the spin injection mechanism, and the molecule|electrode (spin)interface. On the one hand, paramagnetism has been effectively provided in SM junctions by the spin-uncompensated open-shell electronic structure of metal complexes and by organic radicals. On the other hand, CISS has been successfully exploited in SM devices using short peptide and DNA molecules. Spin injection far beyond the selection of spin-up or -down charge carriers, can determine the MR capabilities depending on the spin's population and orientation. The combination of spin preferences of the SM device's subsystems, namely, the molecule and drain/source electrodes, notably affects the device MR efficiency. Also, the details on the spin orientation in the injected electrons has been lately revealed as a mechanism to tailor the MR response in SM junctions. Finally, the molecule|electrode spinterface, governed by the electrode material and electrode-molecule chemistry, has been shown to play a key role in the MR effects of single molecule junctions. The

spinterface showed inherent spin polarisation and spin discrimination capabilities, demonstrating its potential to be used as a spin drain and source in MR SM devices.

Molecular MR SM devices have great potential in spintronic applications and, although still in their infancy, we strongly believe that breakthroughs will occur in the coming years, as the high tunability of the electrical and magnetic properties of molecules opens the door to new device architectures. For instance, a recent study exploring the coupling of CISS with paramagnetism, [50] has demonstrated the potential for observing large MR effects in devices with mix different sources of spin polarization.

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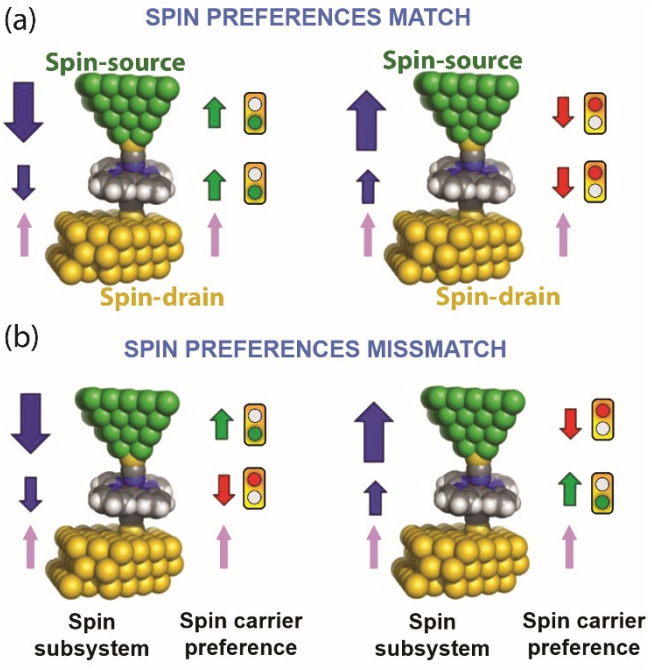
Reviewer #1: The manuscript "Magnetoresitive Single-Molecule Junctions: the role of Spinterface and the CISS effect" by Argones et a. is a brief review article giving a brief overview of magnetoresttance measurements on single/few molecule junctions. The total experiments in this space is still relatively small, and the authors cover it well, and point out the main functioning mechanisms behind magnetoresistance effects in molecular junctions. The review is well-written, and I am in favor of publication, with the small caveats noted below.

- We thank the Reviewer for the general very positive evaluation.

The authors often discuss the "spin-source" and "spin-drain" I take these to mean the "source" of injected carriers, and the "ending point" of the spin carrier - not the source and drain from a current perspective, but this is not clearly laid out for the reader, especially with the applied biases, and could make Fig. 4 much more readable.

- We thank the Reviewer pointing out the relevant aspect of "spin-source" and "spin-drain". For the described setups spin drain/source is not different that the drain/source from the current perspective, since both electrodes have a relevant spintronic role for the devices, namely, the top electrode is the ferromagnetic source of spin-polarized electrons, and the bottom diamagnetic electrode (drain) is displays active Spinterface. We have modified Fig. 4 and its caption accordingly to make concepts "spin-source" and "spin-drain" clearer for the reader.




*"**Figure 4.** Two possible MR SM-devices scenarios where the spin-source electrode (labelled in figure) and molecule present matching (a) or mismatching (b) between spin orientation preferences. The spin-drain electrode (purple arrow) has been assigned to have a fixed spin orientation imposed by the Spinterface —enhanced Rashba effect—. The binary traffic lights indicate the preferences of each subsystem, spin-source electrode (top light) and molecule (bottom light), for the injected spin-polarisation direction, where green means match and red means mismatch. Note that the of spin polarisation molecule and top electrode (spin-source) are aligned due to the Zeeman effect."*

On page 4 the authors discuss that MR can be observed using diamagnetic molecules connected to ferromagnetic electrodes, and the effect is due to the electrodes and the "spinterface". Then, on page 6 they discuss diamagnetic molecules showing MR through the CISS Effect. However, there is a disconnect between these two sections. Why must chirality play a role in the second discussion, how is the effect due to the electrodes and spinterface ruled out when dealing with CISS to identify the underlying mechanism for experiments like these? It would be good to have the authors clearly delineate the two cases for the readers.

- We thank the reviewer to point us towards the need to stress the differences between “spinterface” and CISS effects. Essentially, what it has been observed is that both effects are independent sources of electron spin-polarization in the molecular device, whose effects can be additive or even synergistic; accordingly, we modified the following text in page 10 and added a relevant reference:

“*The spinterface imposes a spin preference to the transmitted electrical current crossing the SM device, making it an independent spin-selective element in a MR SM device. The Spinterface has been suggested to have an additive role to the CISS effect in diamagnetic molecules, as represented in previous rationalisation of the spin-dependent transport in chiral peptides (Figure 7), or to have a more synergistic role acting as an “enhancer” and necessary ingredient to observe CISS effect (Dubi, 2022)”*

A couple of typos:

Page 4 warantee -> guarantee

- We have corrected the typo, many thanks.

pin-splitted -> Spin-split

- We have amended the typo, many thanks.