

A warm exchange

Molecular layers show antiferromagnetic ordering up to room temperature and are able to exchange-bias a ferromagnetic electrode, demonstrating that molecules could be much more than a simple vehicle for transporting spin.

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The idea that molecules could play a role in spintronics dates back to 2002, when the group led by Alek Dediu showed that a molecular semiconductor placed between two ferromagnetic electrodes could demonstrate a spin-valve behaviour.¹ Molecular spintronics generated a multitude of new questions and concepts. For example, the states created between the molecular materials and the electrode could change the sign of magnetoresistance.² In tribute to the importance of this interface, the term “spinterface” was coined.³ The spinterface is particularly interesting when the molecules themselves contain a spin-bearing ion, which can interact with the magnetic substrate and can couple either ferro- (parallel) or antiferromagnetically (antiparallel) to it. Now, Manuel Gruber and colleagues show that a *molecular film* can control the interaction and induce exchange bias.⁴ This astonishing discovery rests on the second breakthrough of their work, which is that the molecular film itself is strongly magnetic – even at room temperature, the highest temperature reported so far for such a system.

The molecular materials in question are the phthalocyanines (Pcs), which are one of the early molecular materials shown to have magnetic properties in the crystal phase (in the case of MnPc, the manganese derivative explored here), and belong to a family of well-known molecular semiconductors used for example in solar cells. Using X-ray magnetic circular dichroism (XMCD) – which allows to probe the magnetism of the individual atomic species in a sample – on a range of MnPc film thicknesses, and comparing the polarisations of the molecules at room temperature and low fields with those at low temperatures and high fields, the authors are able to distinguish the molecules that are strongly coupled (to the substrate and to each other) from the free paramagnetic species. They find that the manganese ions in the first layer adopt the same direction of magnetisation as the ferromagnetic cobalt substrate. So far, so unremarkable. However, the second layer almost entirely suppresses the magnetic moment, suggesting strong antiferromagnetic

coupling between molecules, *even at room temperature*. The effect propagates to the third layer before leaving the material mainly paramagnetic, although longer coupled spin chains might be present. Such a strong coupling is more than two orders of magnitude higher than those previously observed in the material,^{5,6} and three times higher than for the most strongly coupled phthalocyanine, CoPc.⁷ The effect could be due to the polarisation of the substrate, a concept which has been exploited in the second part of the work and is a valuable contribution but lack flexibility if the properties of the material are to be exploited in other contexts. The effect could also be intrinsic to the molecular material, and arise due to a new structure which provides alternative paths for magnetic coupling. In this case, clever crystal engineering could enable room temperature magnetism in MnPc and other members of the phthalocyanine family. Density Functional Theory (DFT) calculations confirm the strength of the coupling, and suggest that the strong interaction in the molecular film is not solely due to the interface, as charge transfer and structural modification do not extend beyond the first monolayer, so the signs for robust intrinsic magnetism are promising.

The strong antiferromagnetism is then exploited to control the properties of the substrate through exchange bias as illustrated in Figure 1. Exchange bias occurs due to the magnetic exchange at the interface between a ferromagnet and an antiferromagnet.⁸ This can lead to the shifting of the hysteresis loop of the ferromagnet so that it is centred on a non-zero field. It has been a key property in the development of spin valves in information technology as it controls the coercivity, i.e. the field that needs to be applied to manipulate information. So far, studies in hybrid structures used the inorganic substrate to control the organic layer, and only acted on the molecules in the first layer.⁹ Here, it is the organic layer that acts on the inorganic ferromagnet, shifting its coercivity by 60 mT at 14 K, and persisting up to a temperature of approximately 100 K – which is not quite room temperature, but warm enough to qualify for helium-free operation.

The question arises – why is this a good thing? Arguments on the benefits of molecular materials in (opto)electronics and more recently spintronics abound, and include ease of processing, low cost, flexibility, versatility, *etc.* However, it is really their ability to combine multiple functionalities in a single material that allows them to claim a position as a potentially disruptive concept that should be taken seriously. It appears that in the framework developed by Gruber and colleagues, MnPc films are the elusive room temperature magnetic semiconductor that has been sought for decades. Of course, it remains to be seen whether this effect can be achieved in the absence of an adjoining inorganic ferromagnet so that the full “manufacturing” benefits of molecular-based spintronics can be reaped. But in combination with theoretical studies predicting couplings above room

temperature in CoPc⁷ and experimental observation of strong dependence of magnetism on structure,⁵ the results are certainly suggesting that ambient operation is a distinct possibility.

The study by Gruber and colleagues shows that molecular films can be so much more than a passive spin transport medium. Firstly, they can be magnetic themselves, and could therefore act on the injected spin in a controllable manner, ultimately offering the possibility of foregoing the inorganic spin injector altogether. Second, they can modify the magnetism of a metallic ferromagnet. These new findings certainly suggest that in organic spintronics, the molecules are taking control.

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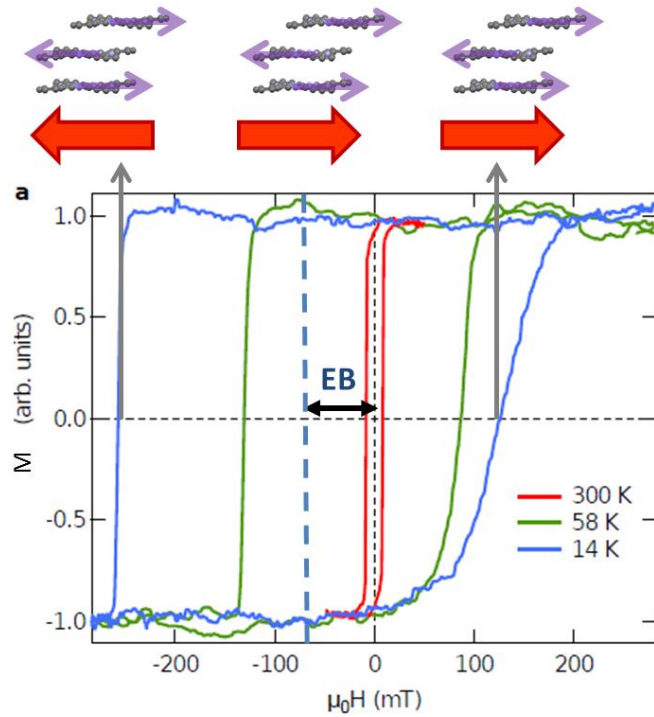


Figure 1 | Illustration of the exchange bias (EB) imparted to the ferromagnetic substrate by the MnPc film at 14 K. The magnetic loops were measured after cooling down the sample under an applied magnetic field of 200 mT. The magnetisation of the substrate is represented by the red arrows, and the spin orientation of the MnPc film by the purple arrows. The blue dashed vertical line corresponds to the centre of the hysteresis curve at 14 K, and the exchange bias is the shift of the field with respect to a standard a zero-shift hysteresis curve (marked with a double arrow). Due to exchange bias, the positive (right-hand) orientation of the magnetism is stabilised down to more negative fields. The exchange bias still occurs at 58 K but has disappeared at 300 K.