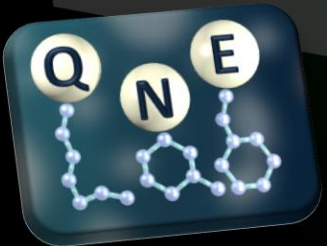


# Magnetic impurities manipulation by chiral spin exchange interactions

Dipole moment



**Yossi Paltiel**  
*Applied Physics,  
Hebrew University  
of Jerusalem*





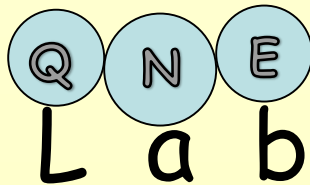
**Our Current Group: Dr. Shira Yochelis**  
**Prof. Yossi Paltiel, Nir Sukenik, Amir Ziv, Tzuriel Metzger,**  
**Hamam Al Bustami, Hen Alpern, Eitan Avigad, Yuval**  
**Koldny, Avi Schneider, Naama Goren, Lior Bezen, Chana**  
**Fridman**  
**Dr. Oren Ben Dor, Dr. Eran Katzir, Dr. Guy Koplovitch**



**Special thanks to:**

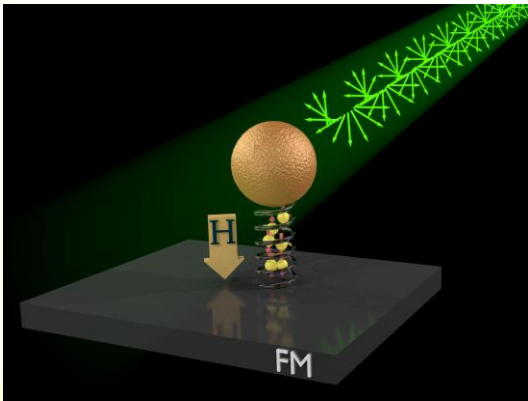
**The Quantum Impurity Meeting organizers**  
Mikhail Zvonarev  
Claire gay  
Universite-paris-saclay

**Collaborators; Ron Naaman, Dave Waldack, Oded Millo, Nir Keren**

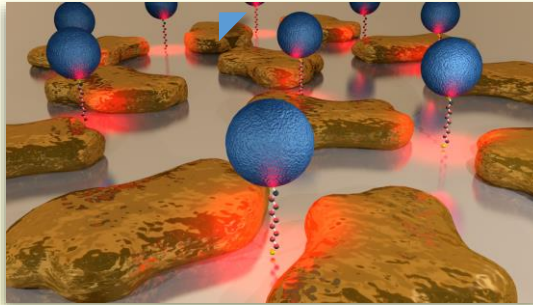


# Quantum Nano Engineering Laboratory

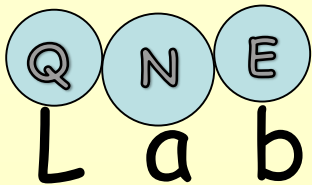
Chiral induced spin selectivity effect



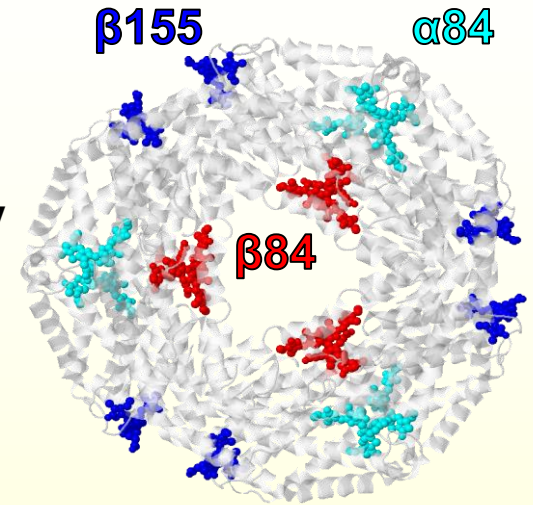
Quantum photon sensors



Surface superconductivity

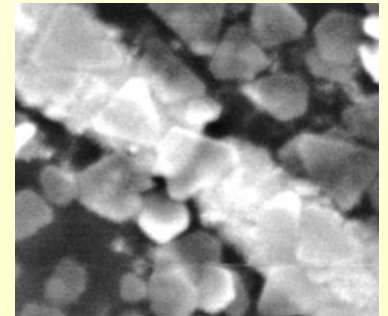


Quantum Biology

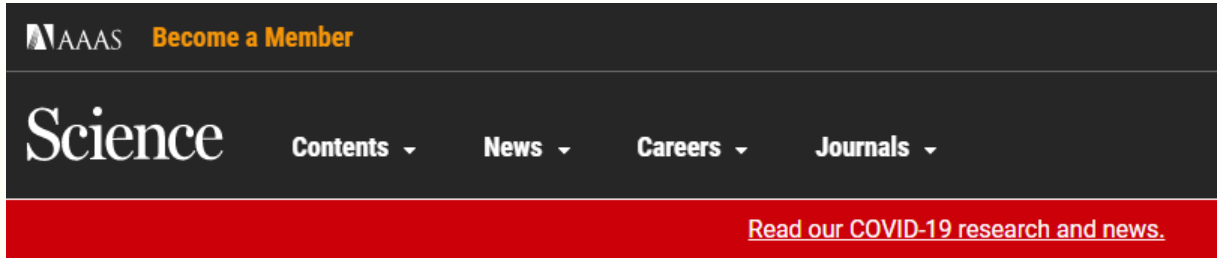


$\beta 155$  is exposed to the environment

Spintronics



# Motivation



SHARE SPECIAL REVIEWS



## Spintronics: A \$ Future

S. A. Wolf<sup>1,2,\*</sup>, D. D. Awschalom<sup>3</sup>,  
+ See all authors and affiliations

Science, 16 Nov 2001



## Spintronics, Magnetoresistive Heads, and the Future of Data Storage

sors b  
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**Spintronics studies the properties of the electron and spin.**

In principle, for spintronics one expects less scattering and higher frequency operation.

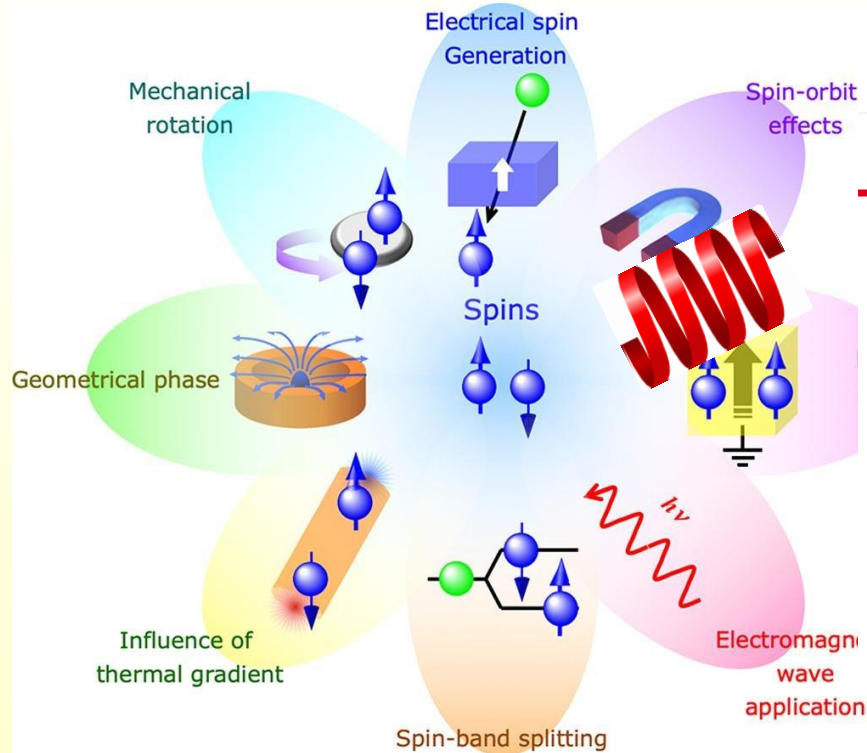


## Spintronics

Spintronics is the area of condensed-matter physics that studies the properties of the electron spin, with a view to improve the efficiency of electronic devices and to enrich them with new functionalities.

Such a broad definition implies that the range of subjects that fall under the umbrella of spintronics is inevitably very wide. In one extreme, researchers explore the control of single localized spins, realized on single atomic sites in crystals — such as nitrogen-vacancy centres in diamond — or in semiconductor quantum dots. These are regarded as spin qubits, ideal for quantum

# Motivation




nature materials

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nature > nature materials > articles > article

Published: 06 March 2005

## Towards molecular spintronics

Alexandre R. Rocha, Víctor M. García-suárez, Steve W. Bailey, Colin J. Lambert, Jaime Ferrer & Stefano Sanvito 

*Nature Materials* **4**, 335–339 (2005) | Cite this article

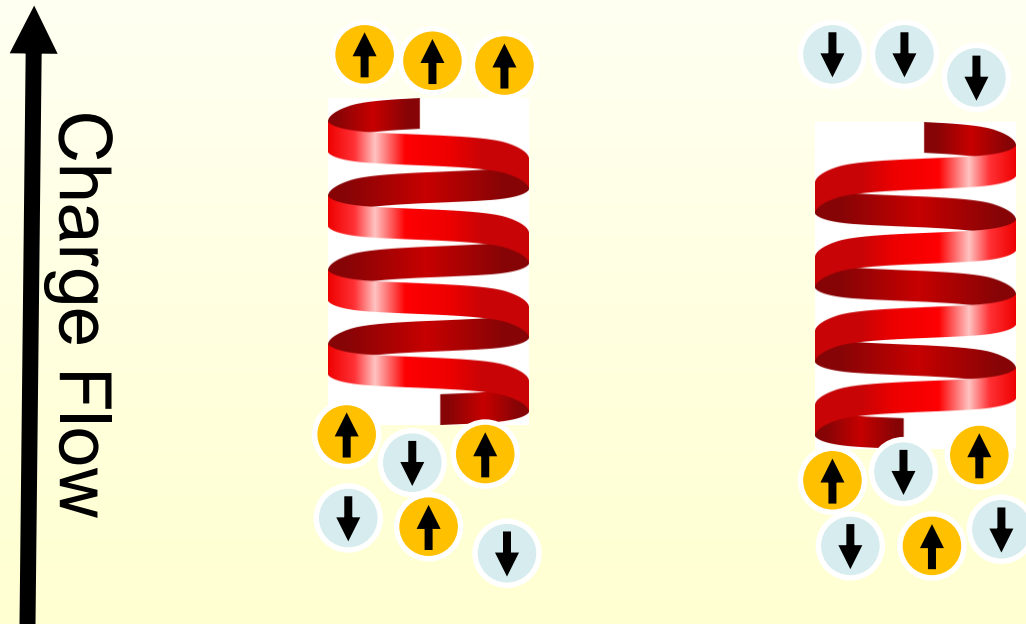
5785 Accesses | 1027 Citations | 12 Altmetric | Metrics

- Easily reproducible
- Inexpensive
- Symmetry breaking in the nano scale

# The CISS Effect

What about the electron spin?

**CISS** – Chiral Induced Spin Selectivity



$$\bar{B}_{eff} = \frac{\bar{E} \times \bar{P}}{mc^2}$$

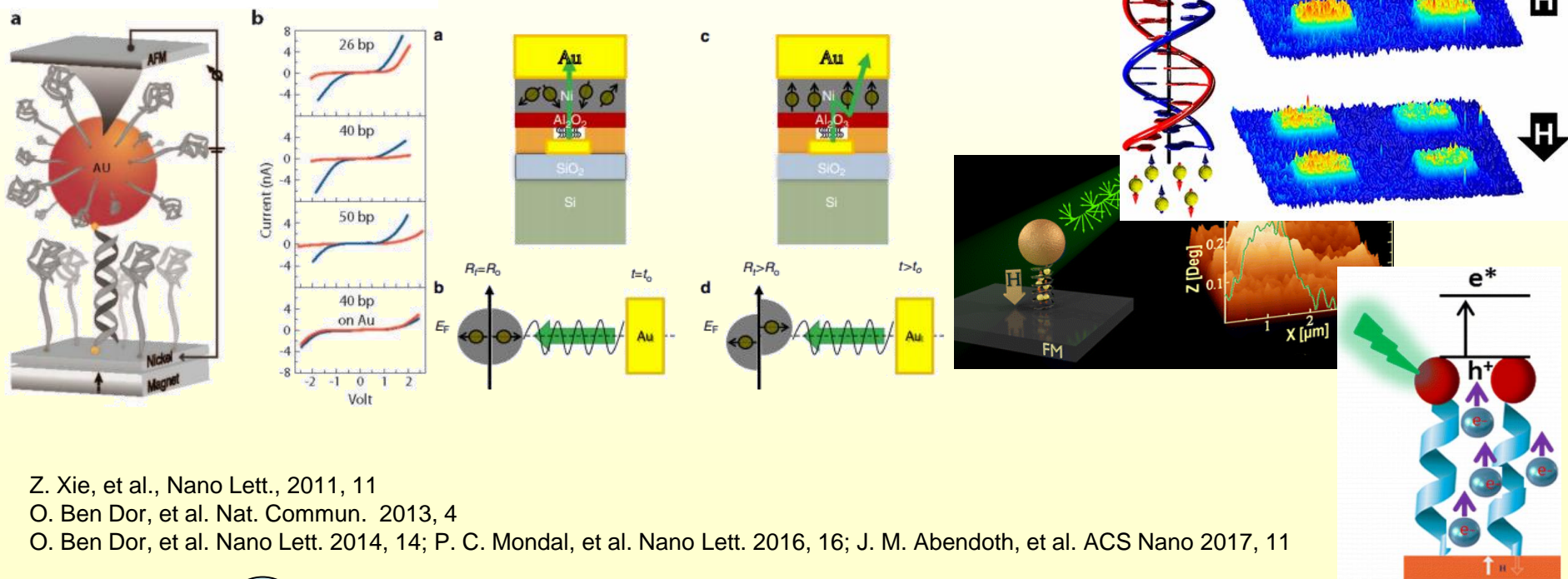
$$H_{SO} = \mu_B \left( \frac{\bar{E} \times \bar{P}}{mc^2} \right) \cdot \bar{\sigma}$$

Chiral molecules as spin filters.

# The CISS Effect

What about the electron spin?

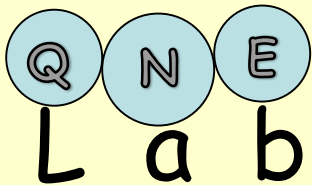
**CISS** – Chiral Induced Spin Selectivity



Z. Xie, et al., Nano Lett., 2011, 11

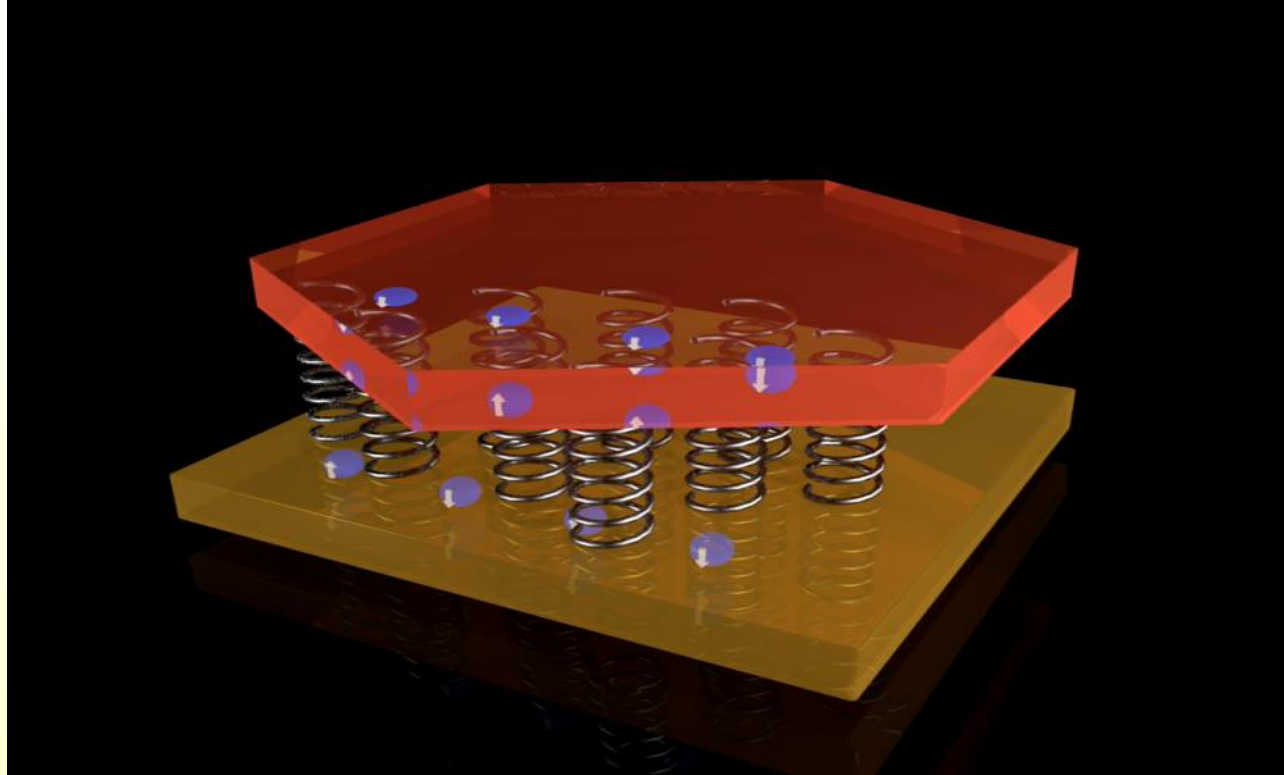
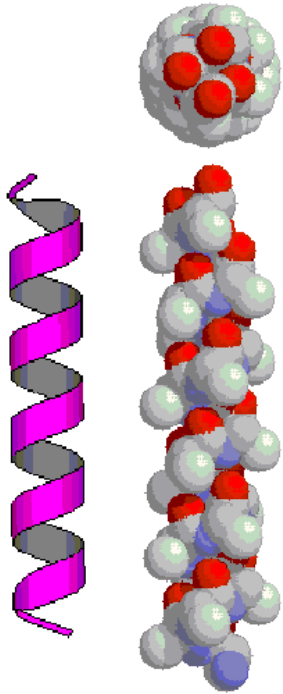
O. Ben Dor, et al. Nat. Commun. 2013, 4

O. Ben Dor, et al. Nano Lett. 2014, 14; P. C. Mondal, et al. Nano Lett. 2016, 16; J. M. Abendoth, et al. ACS Nano 2017, 11

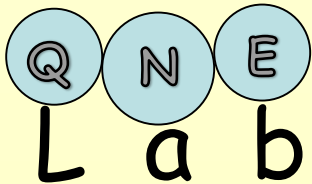


# Electrical CISS Nano Memory

alpha helix

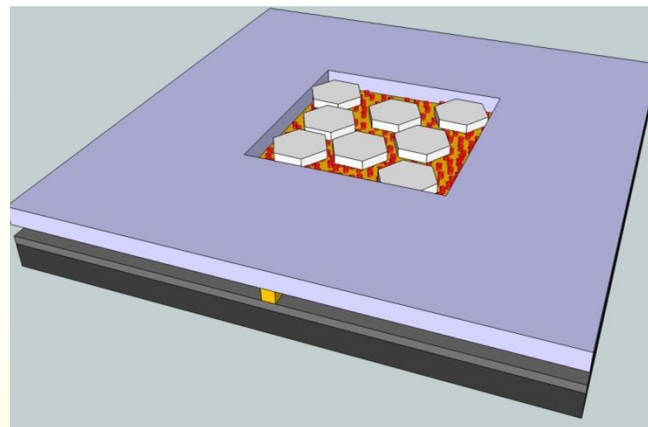
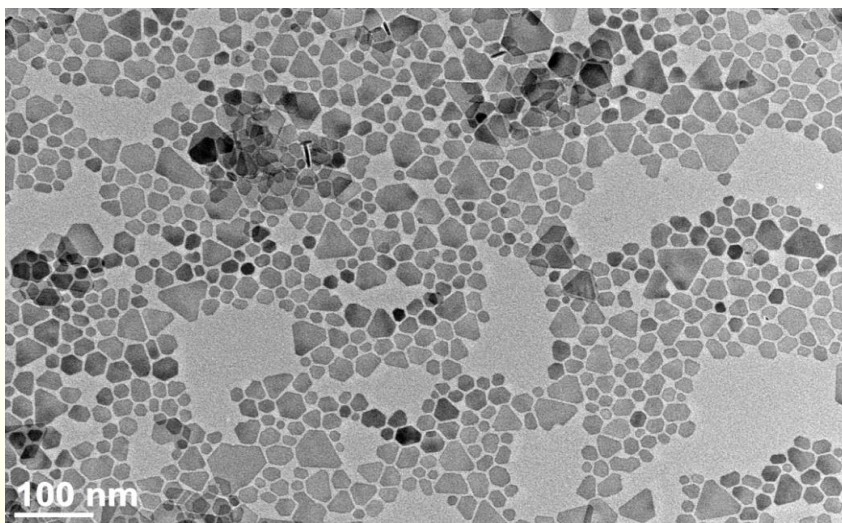


L or D PAL (polyalanine), thiolated  $\alpha$ -helix -  
CAAAKAAAKAAAKAAAKAAAKAAAKAAAK-SH  
C, A, and K represent cysteine, alanine, and lysine





# Vertical Memristor Device

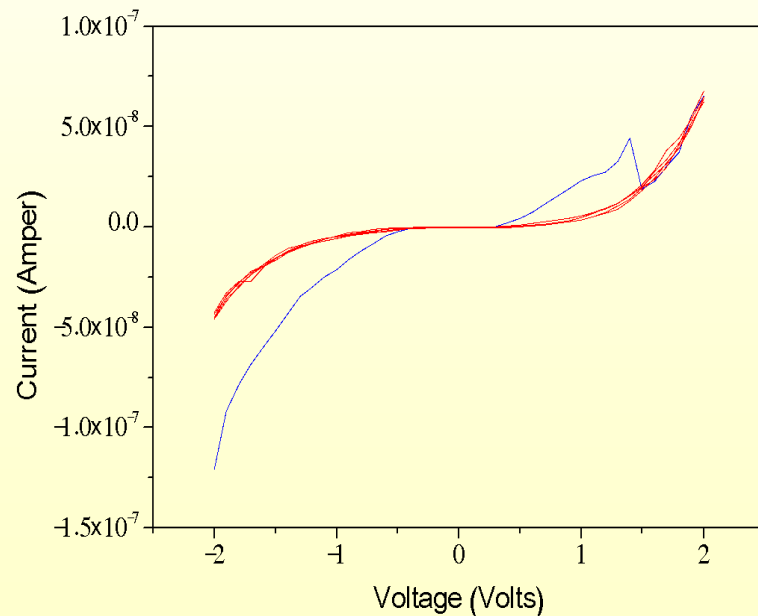
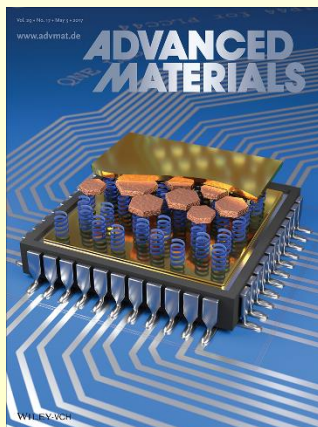


Bottom electrode •

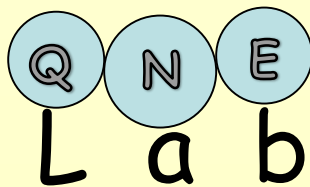
Adsorb AHPA-L or AHPA-D and multiple FMNPs •

Al<sub>2</sub>O<sub>3</sub> tunnel barrier •

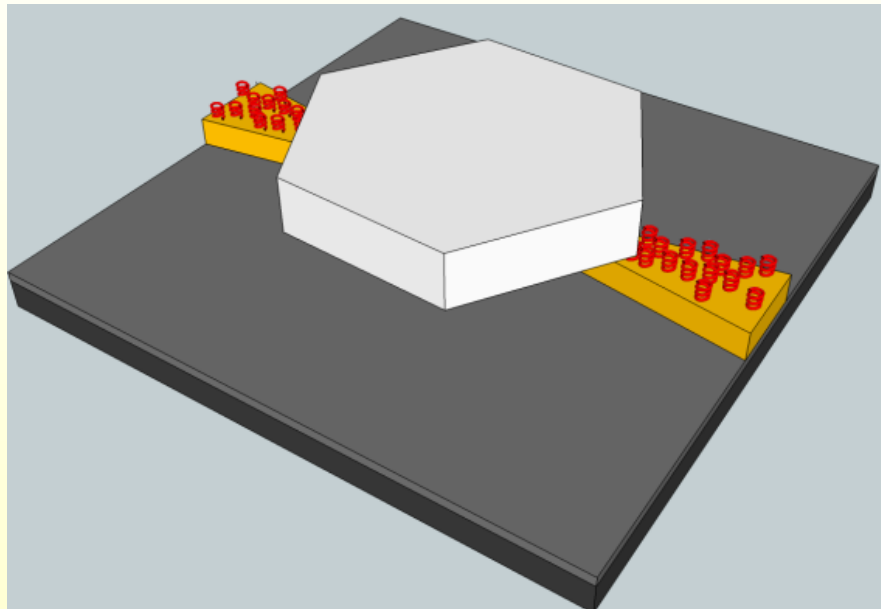
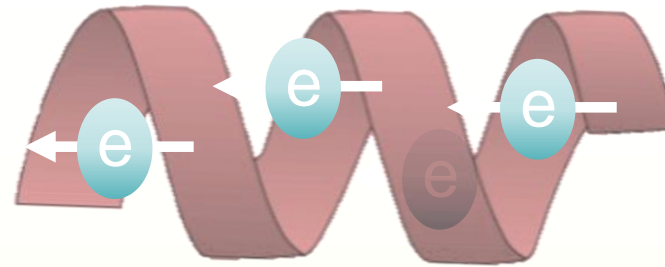
Top electrode •



AHPA chiral molecules-  
[H]-CAAAAKAAAAKAAAAKAAAAKAAAAK  
AAAAKAAAAK-[OH]



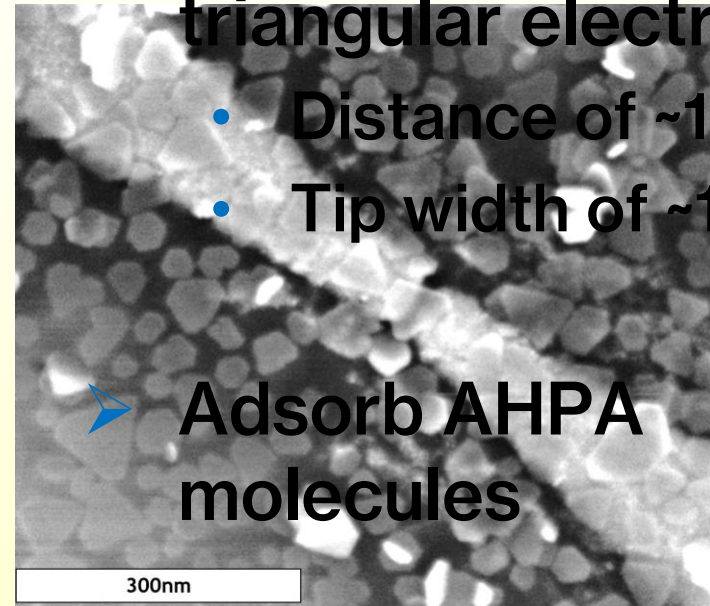
# Single FMNP device



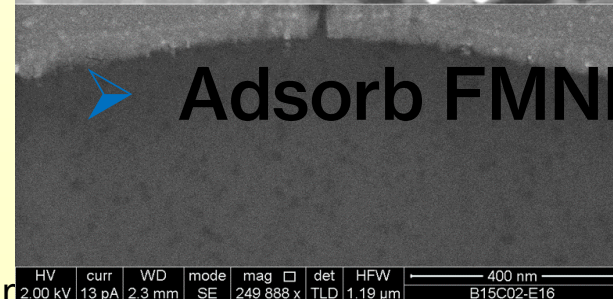
**Single nanoparticle magnetic spin memristor**  
 H. Al Bustami, G. Koplovitz, D. Primc, S. Yochelis,  
 E. Capua, D. Porath, R. Naaman, and Y. Paltiel  
**Small 1801249 (2018).**

## ➤ Fabricating metal triangular electrodes

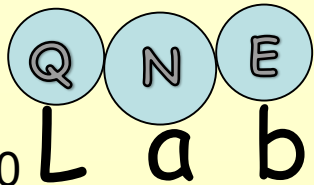
- Distance of ~10nm
- Tip width of ~10nm



## ➤ Adsorb AHPA molecules

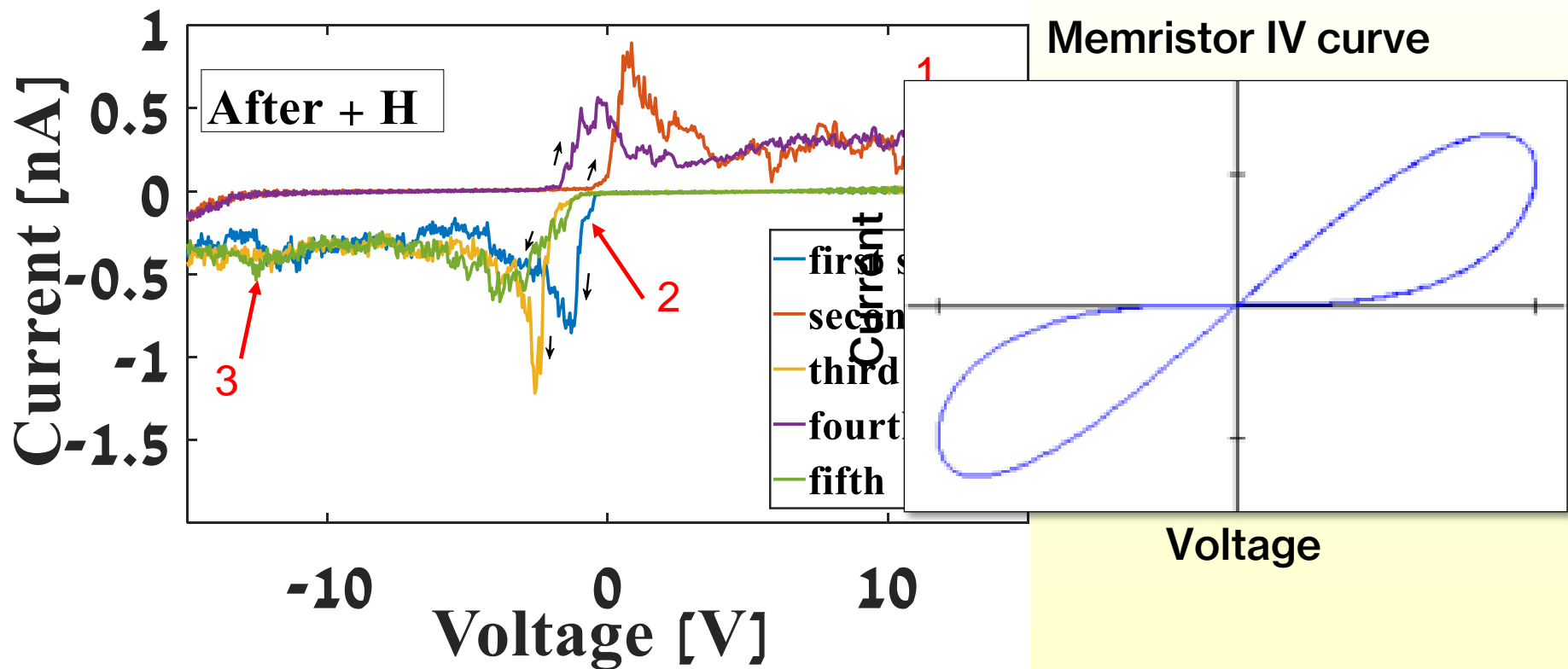


## ➤ Adsorb FMNPs



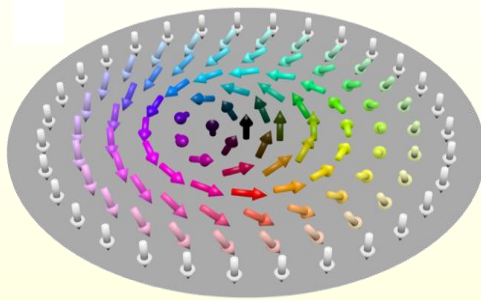
# Single FMNP device

## Results - 2 states logic device



# Magnetic impurities

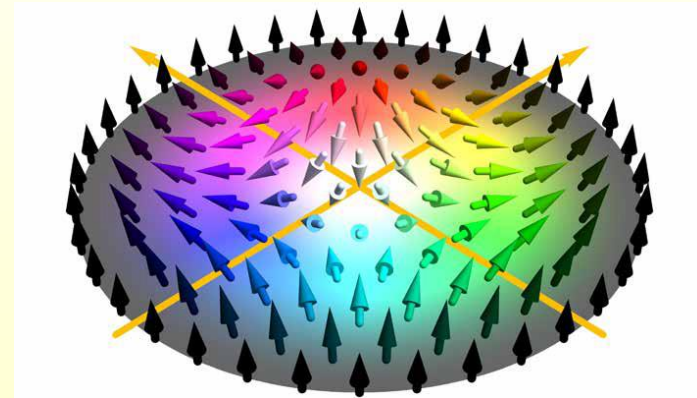
- Skyrmions chiral impurities....



**Sketch of chiral “Bloch skyrmion”**  
*Scientific Reports* **10**, 8657 (2020) .  
*Nature communication* **11**, 1115 (2020) .

## ***Hybrid chiral domain walls and skyrmions in magnetic multilayers***

William Legrand , Jean-Yves Chauleau\*, Davide Maccariello , Nicolas Reyren, Sophie Collin, Karim Bouzehouane, Nicolas Jaouen , Vincent Cros, Albert Fert

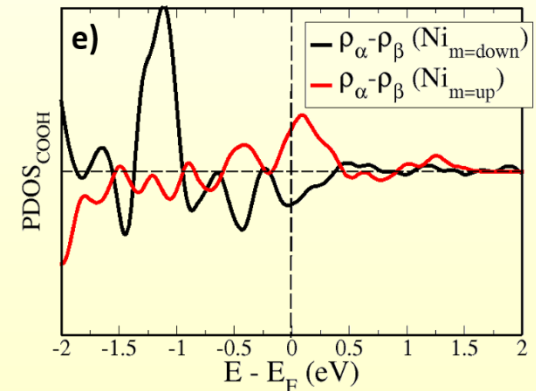
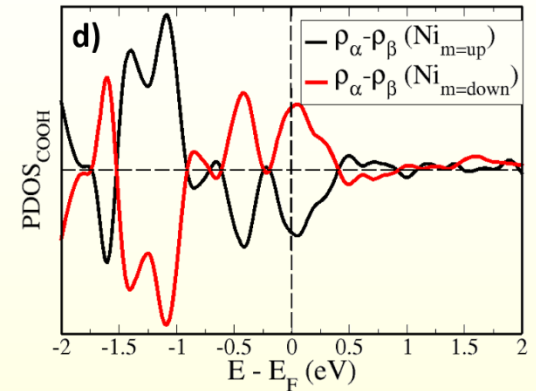
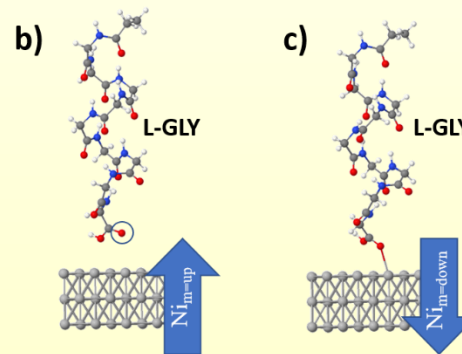
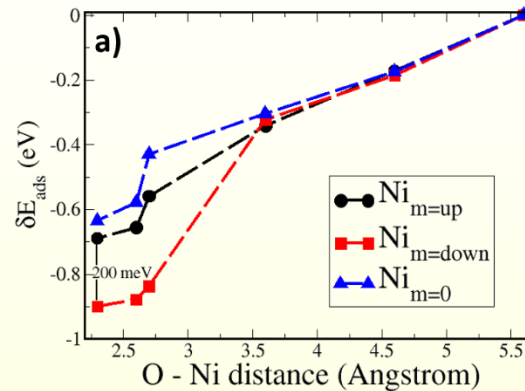
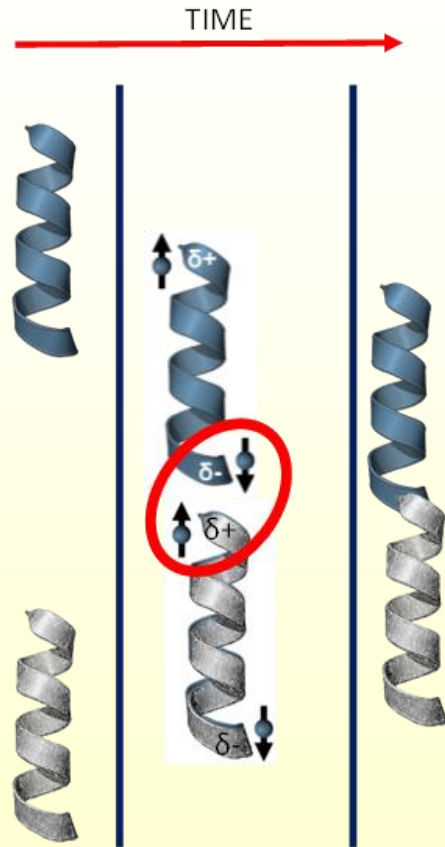


Chiral spintronics S  
*Reviews Physics* , 3

**Can the CISS be utilized  
To control, and manipulate  
magnetic impurities?**

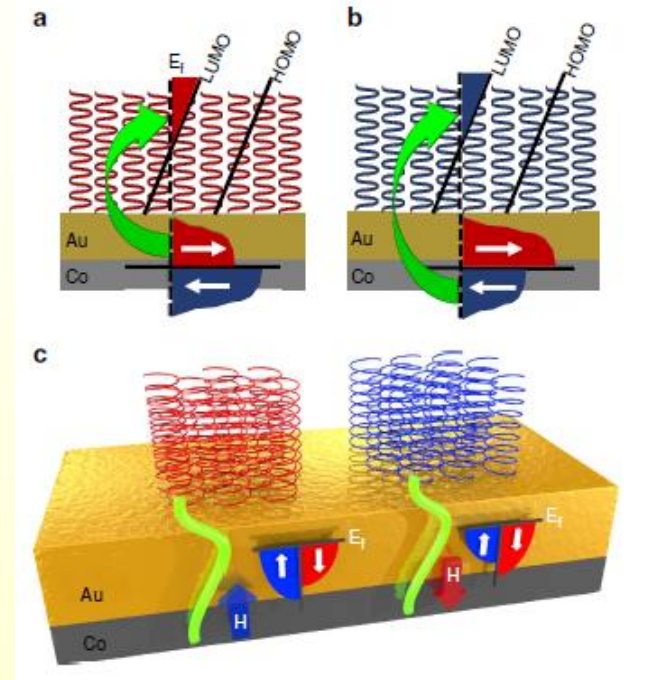
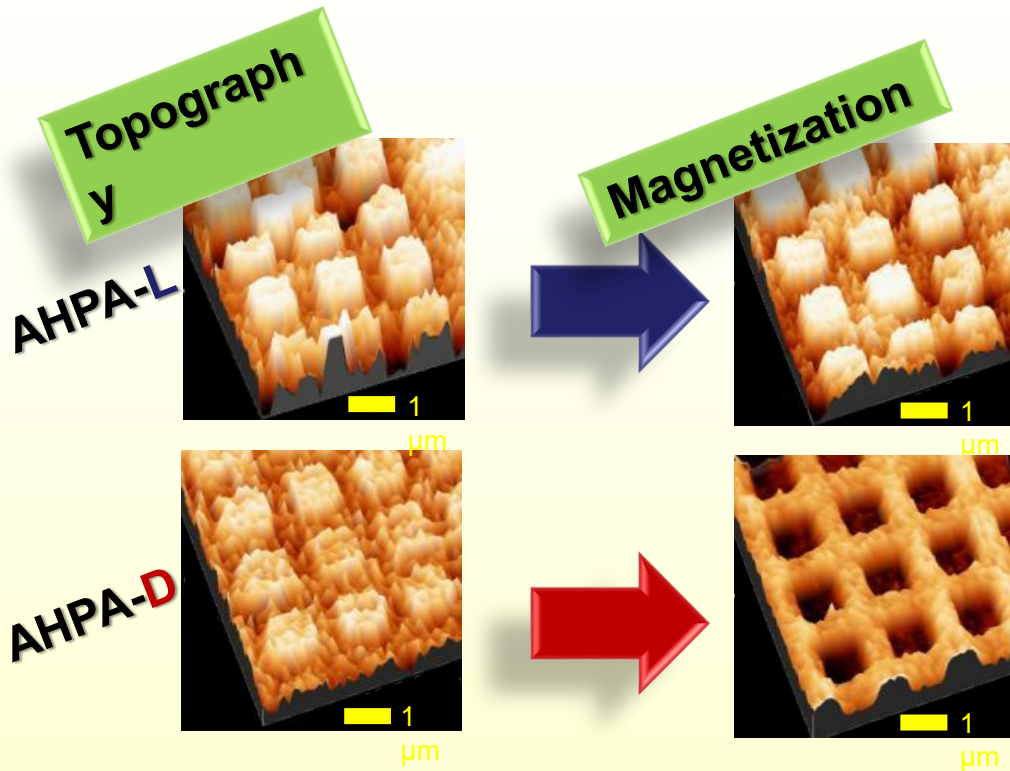
P. Parkin; *Nature*

# Exchange Interactions



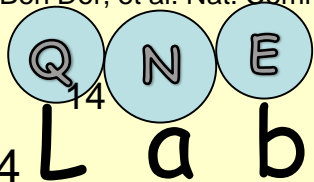
*The Role of Exchange Interactions in the Magnetic Response and Inter-Molecular Recognition of Chiral Molecules, Nano Letters, **10**, 7077–7086 (2020).*

# Selective adsorption -> Selective magnetization



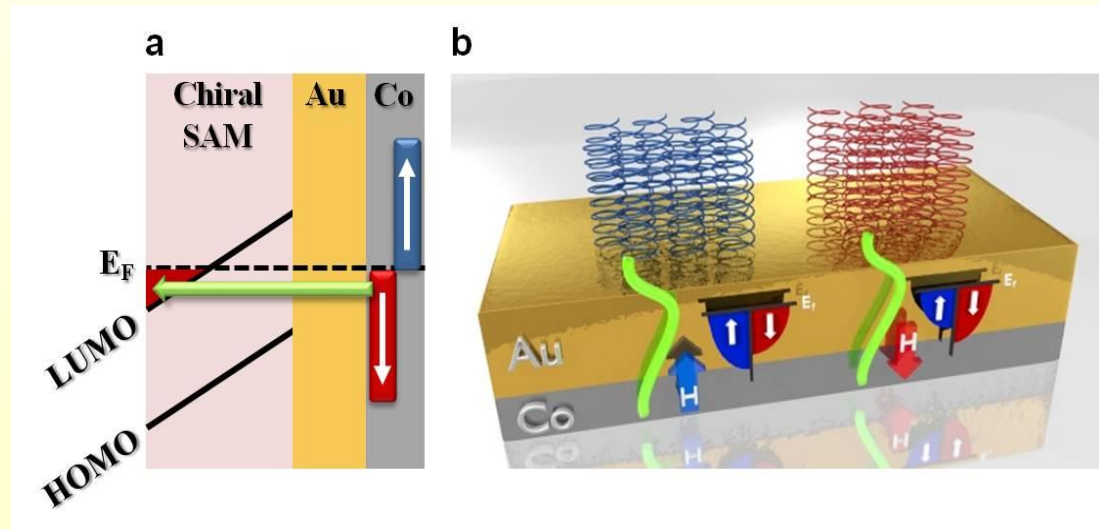
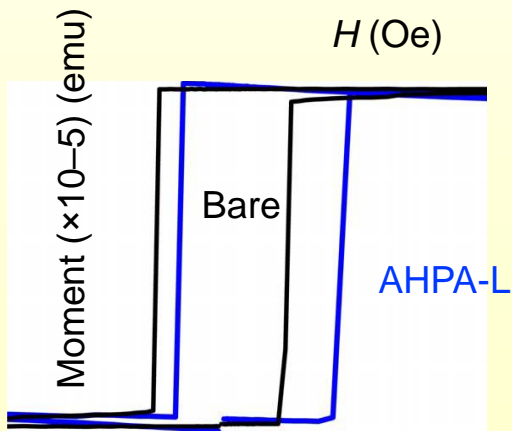
Selective adsorption of  $\alpha$  helix polyaniline results in selective magnetization of a ferromagnet

O. Ben Dor, et al. Nat. Commun. 2017, 8.

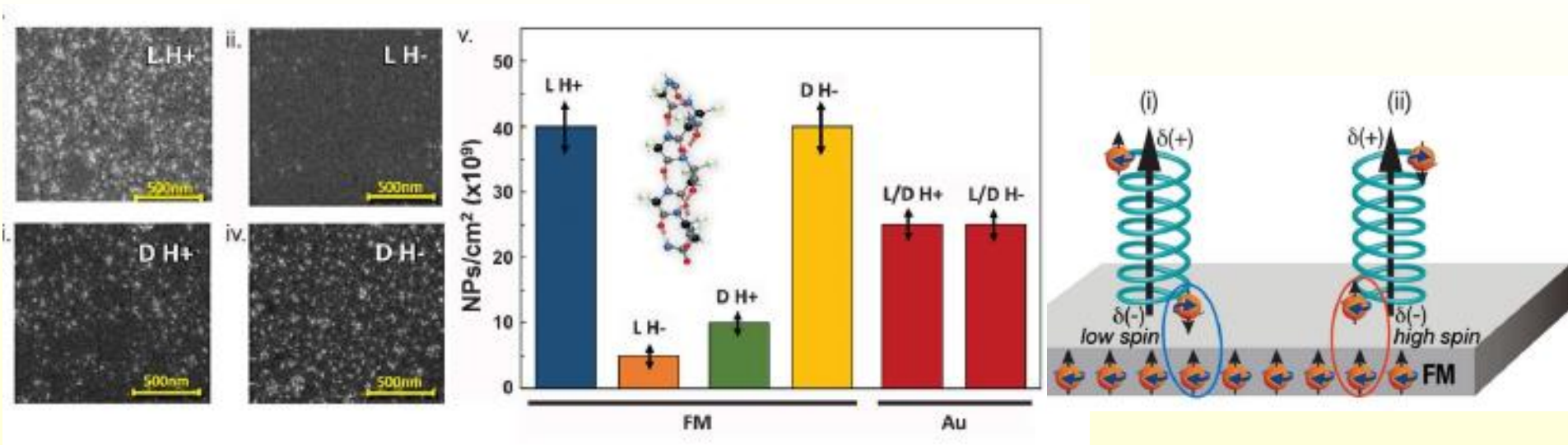


# Magnetization with no current

- The current density required for the spin-transfer torque (STT) is of the order of  $10^6$  A/cm<sup>2</sup>
- STT – current density equals  $10^{25}$  electrons/ s cm<sup>2</sup>
- Adsorption of molecules  $10^{13}$  molecules/cm<sup>2</sup>
- Here if 1 electron is transfer per molecule  $10^{13}$  molecules/cm<sup>2</sup>



# Magnetize substrate enantio-selectivity



Magnetization of a ferromagnet results in selective adsorption of  $\alpha$  helix polyalanine

Banerjee-Ghosh et al. Science. 2018, 360.

**Does this brake time reversal?!**

Q N E  
L a b

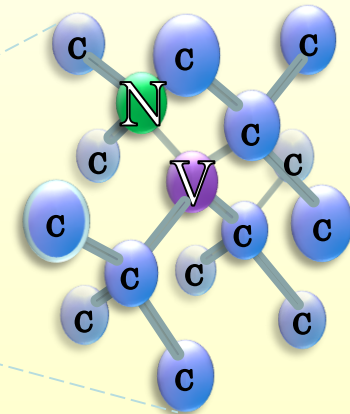
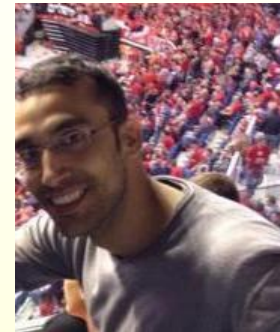


# NV centres

- NV centers- Local highly sensitive magnetic sensor
- Can measure both direction and magnitude
- Consists of a substitutional nitrogen atom and a vacancy on adjacent lattice sites



In collaboration with  
Nir Bar-Gill lab @ HUJI

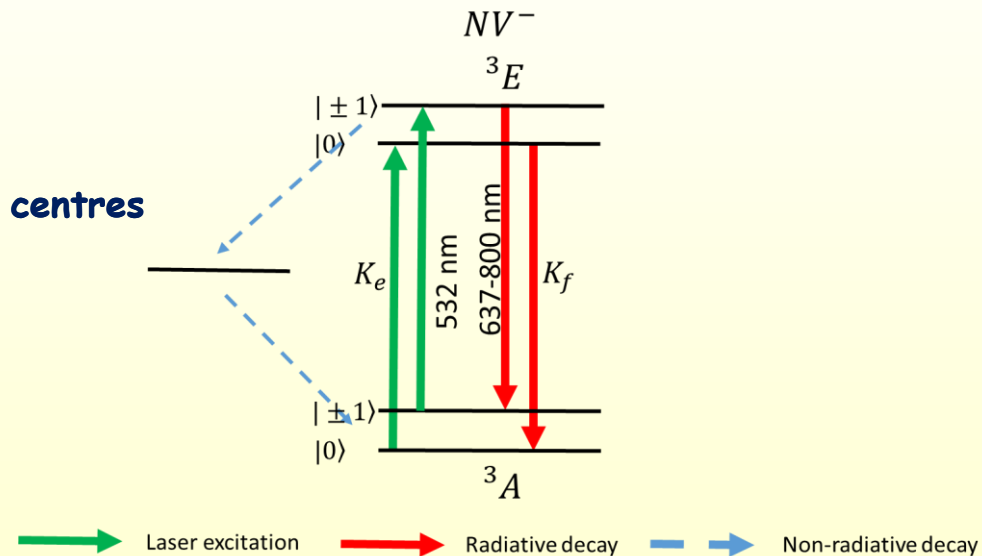


# NV centres manipulation

- Optical absorption (532 nm)
- Fluorescence 600-800 nm
- Spin manipulation with microwave ~3GHz

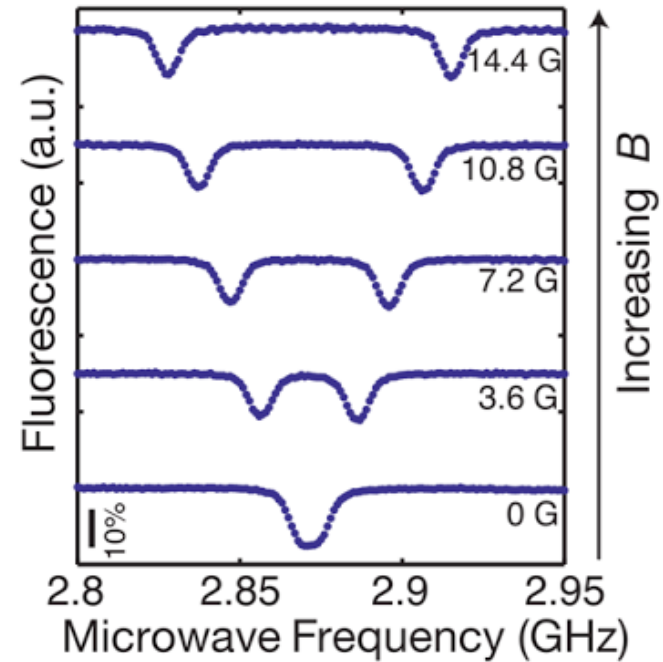
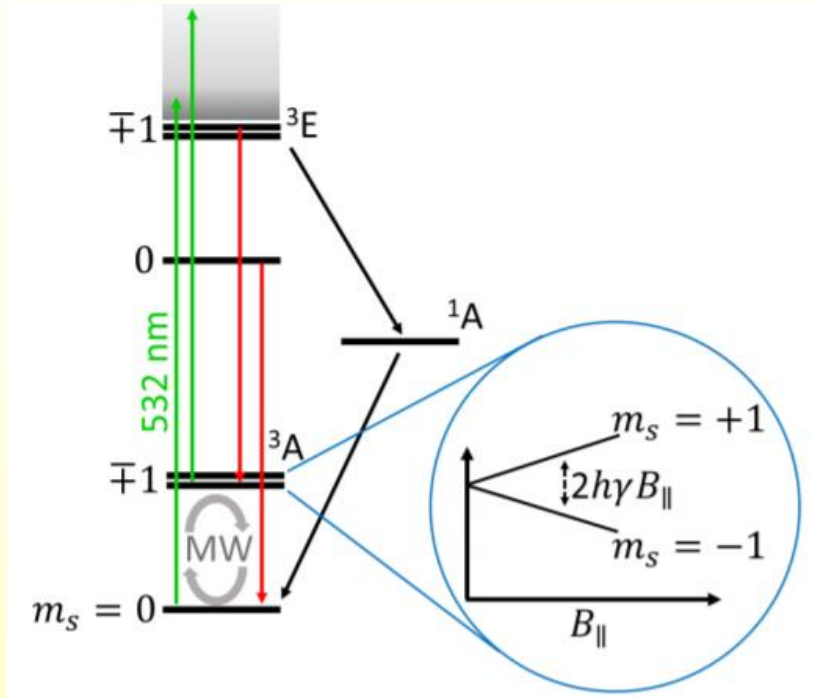
**Initialization in 0 state**

NV centres



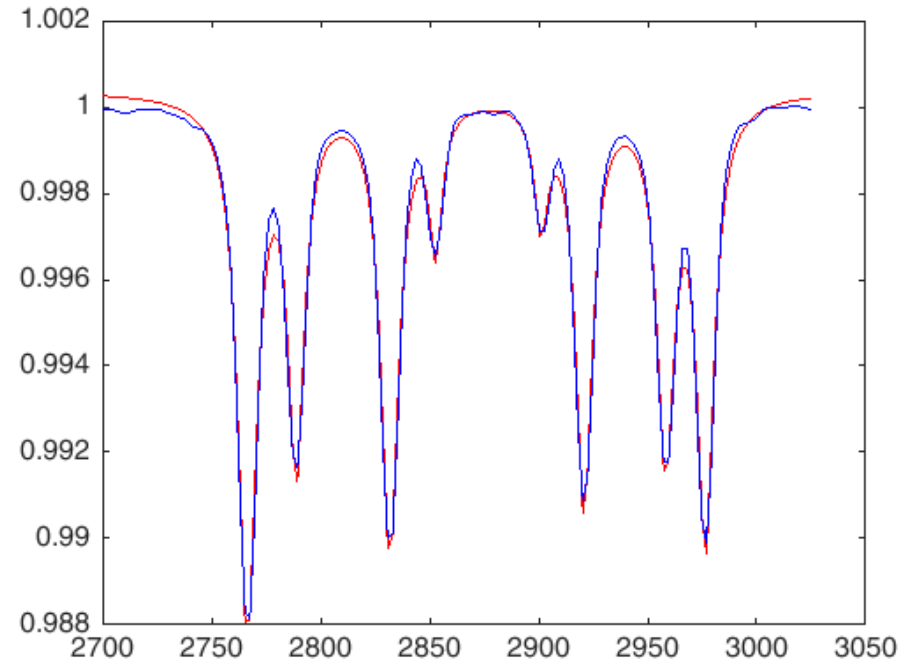
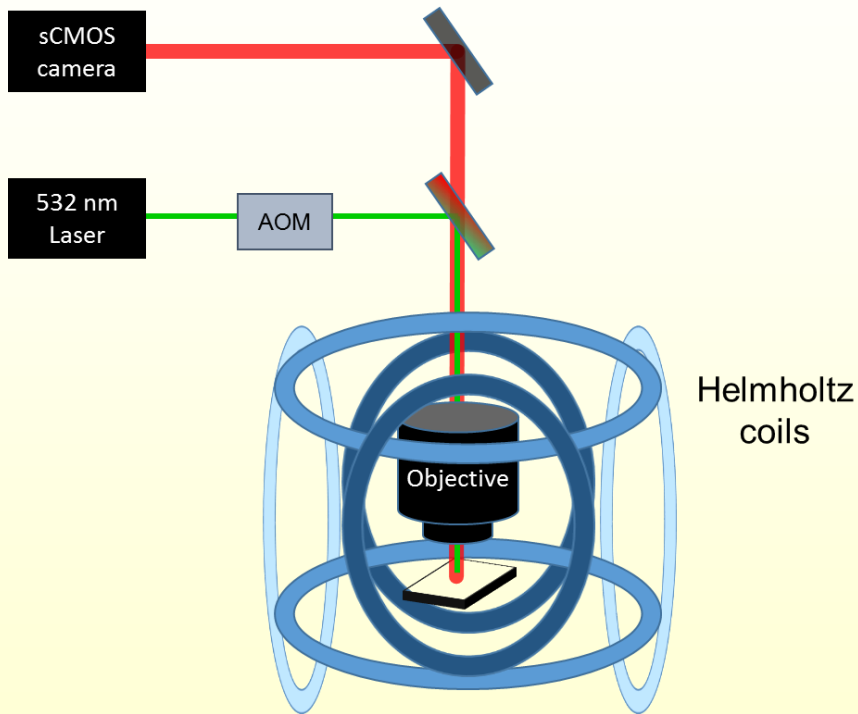
# NV centres magnetization measurement

A decrease in fluorescence in the resonance MW frequency



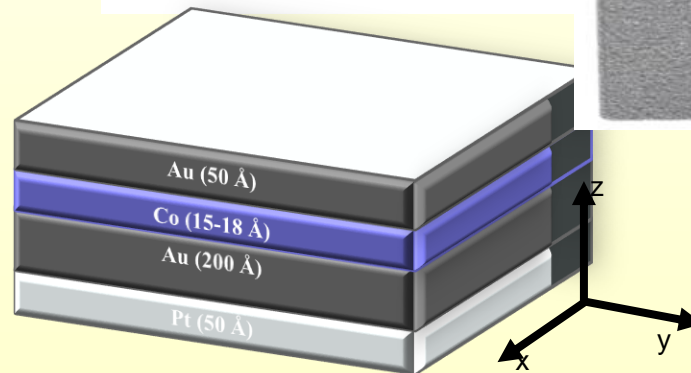
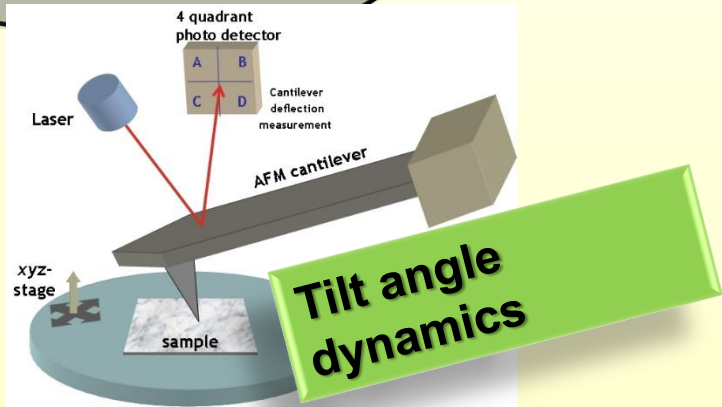
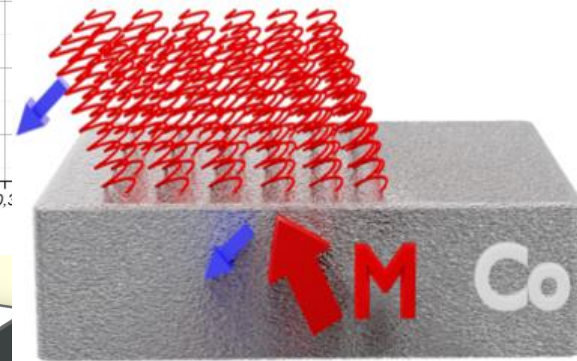
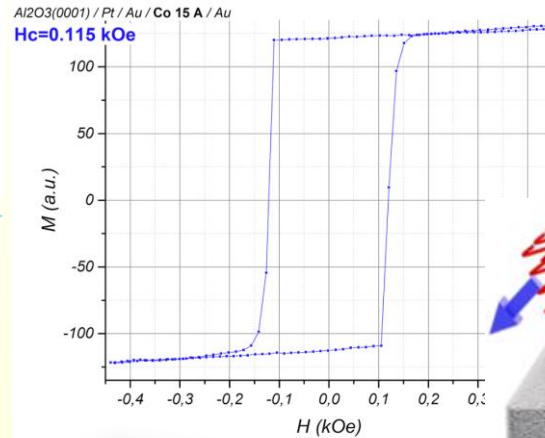
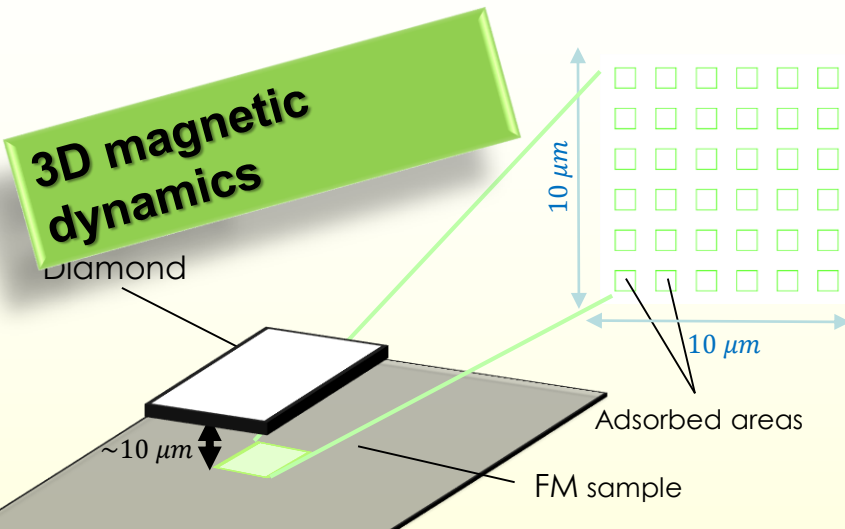
Zeeman Splitting- proportional to external magnetic field

# NV centres magnetization measurement

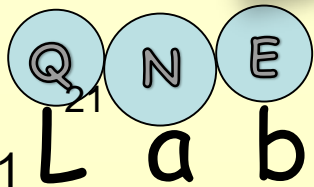


Using NV centers can give us the magnitude & direction of magnetization

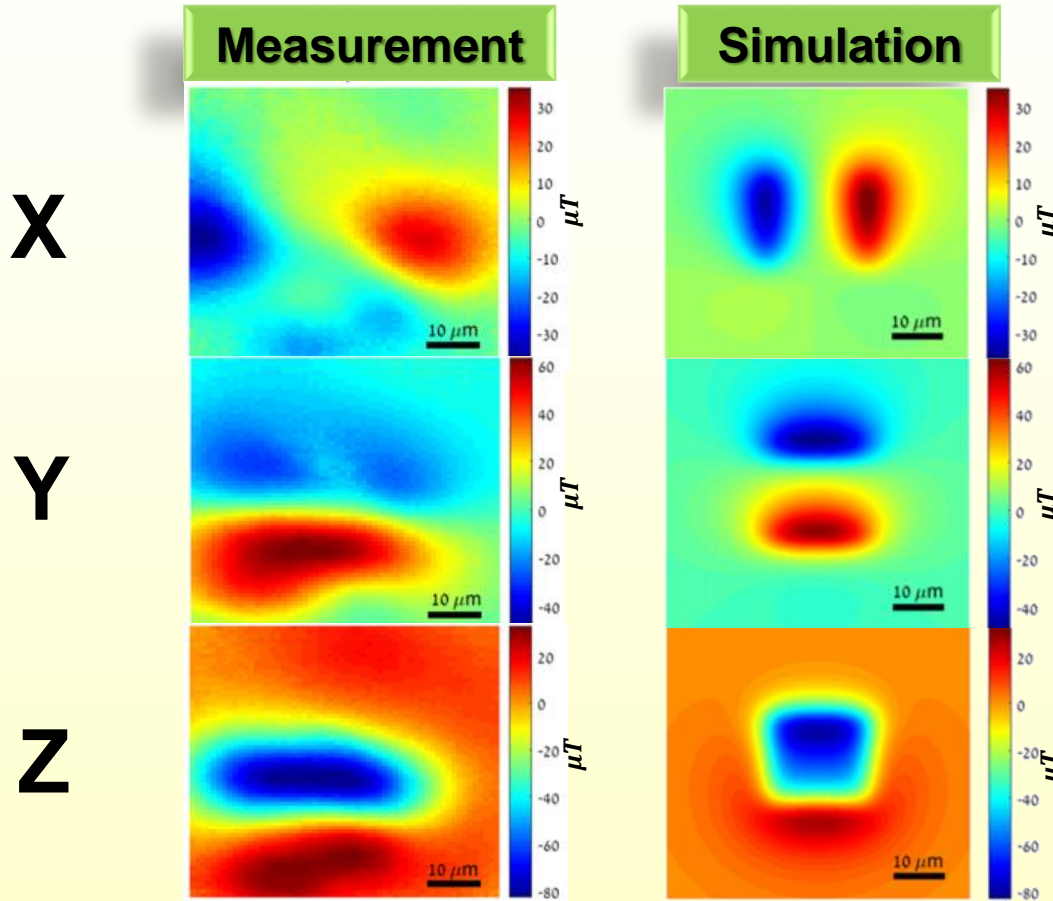
# Time evolution of the magnetization reorientation



I. Meirzada<sup>▽</sup>, N. Sukenik<sup>▽</sup> et al. 'Long-Timescale Magnetization Ordering Induced by an Adsorbed Chiral Monolayer on Ferromagnets' **ACS Nano**. 2021, 15.



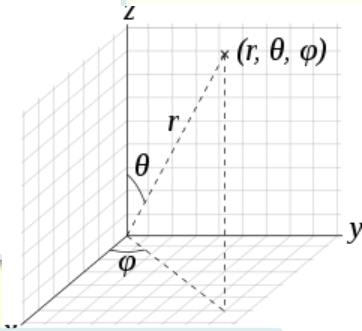
# Time evolution of the magnetization reorientation



Magnetization angles:

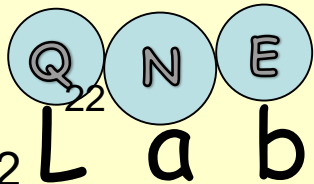
$$\Theta = 40^\circ \pm 10^\circ$$

$$\bar{\phi} = 90^\circ \pm 3^\circ$$



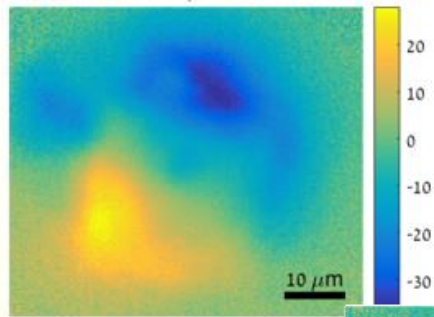
- Magnetization angle compatible with monolayer tilt angle
- $\bar{\phi}$  is not random

I. Meirzada<sup>▽</sup>, N. Sukenik<sup>▽</sup> et al. 'Long-Timescale Magnetization Ordering Induced by an Adsorbed Chiral Monolayer on Ferromagnets' **ACS Nano**. 2021, 15.

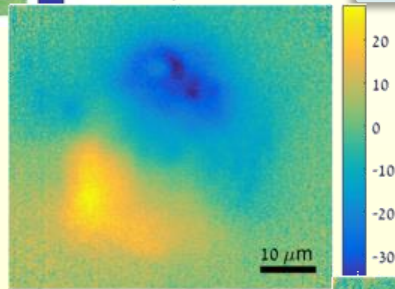


# Magnetization time evolution

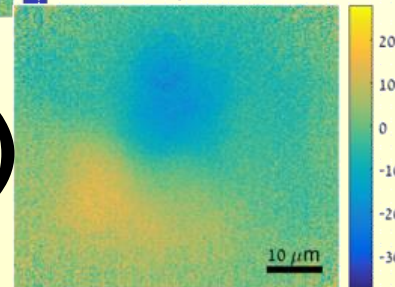
Z  
(t=4hr)



Z  
(t=8hr)



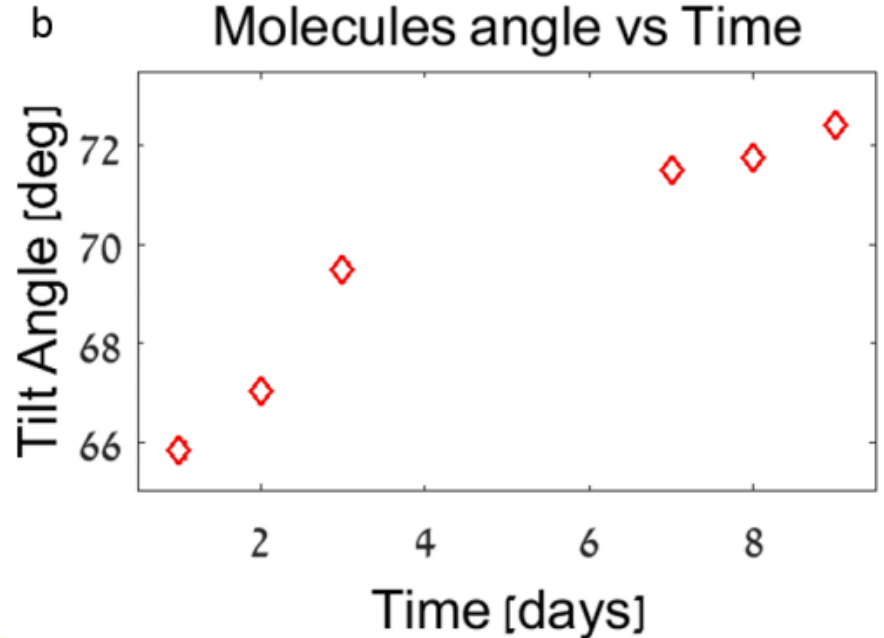
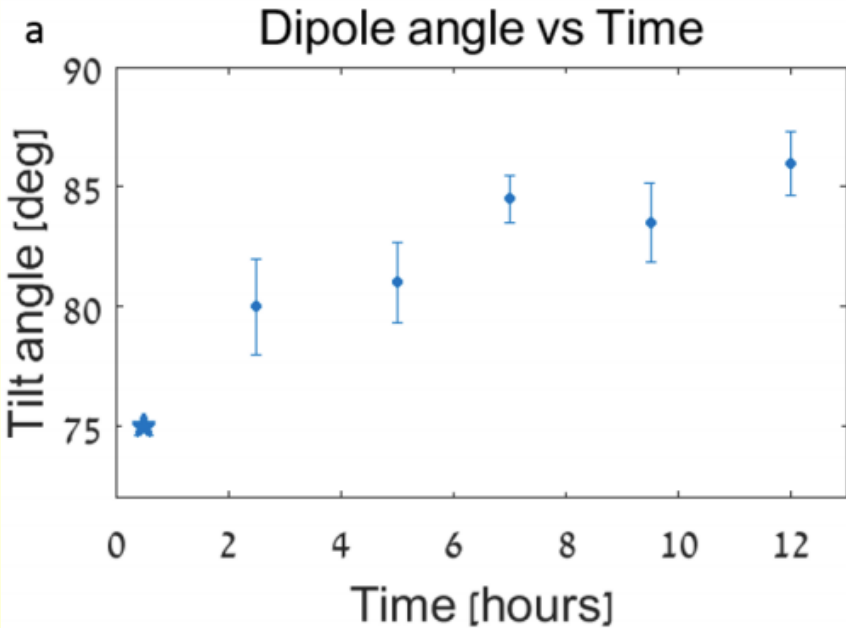
Z (t=12hr)



- Magnetization weakens over time
- Magnetization angle increases over time

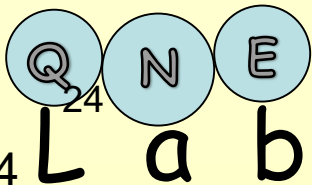
I. Meirzada<sup>▽</sup>, N. Sukenik<sup>▽</sup> et al. 'Long-Timescale Magnetization Ordering Induced by an Adsorbed Chiral Monolayer on Ferromagnets' *ACS Nano*. 2021, 15.

# Time evolution of the magnetization reorientation



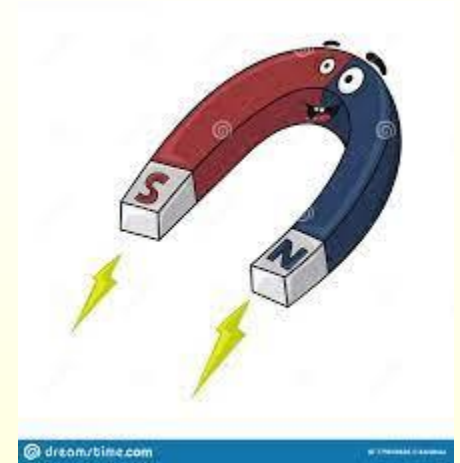
**Both tilt angle and magnetization angle increase over time**

I. Meirzada<sup>▽</sup>, N. Sukenik<sup>▽</sup> et al. 'Long-Timescale Magnetization Ordering Induced by an Adsorbed Chiral Monolayer on Ferromagnets' **ACS Nano**. 2021, 15.



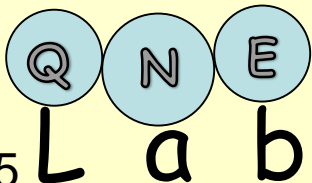


The magnetization is metastable and seems to break T due to thermal fluctuations !!!



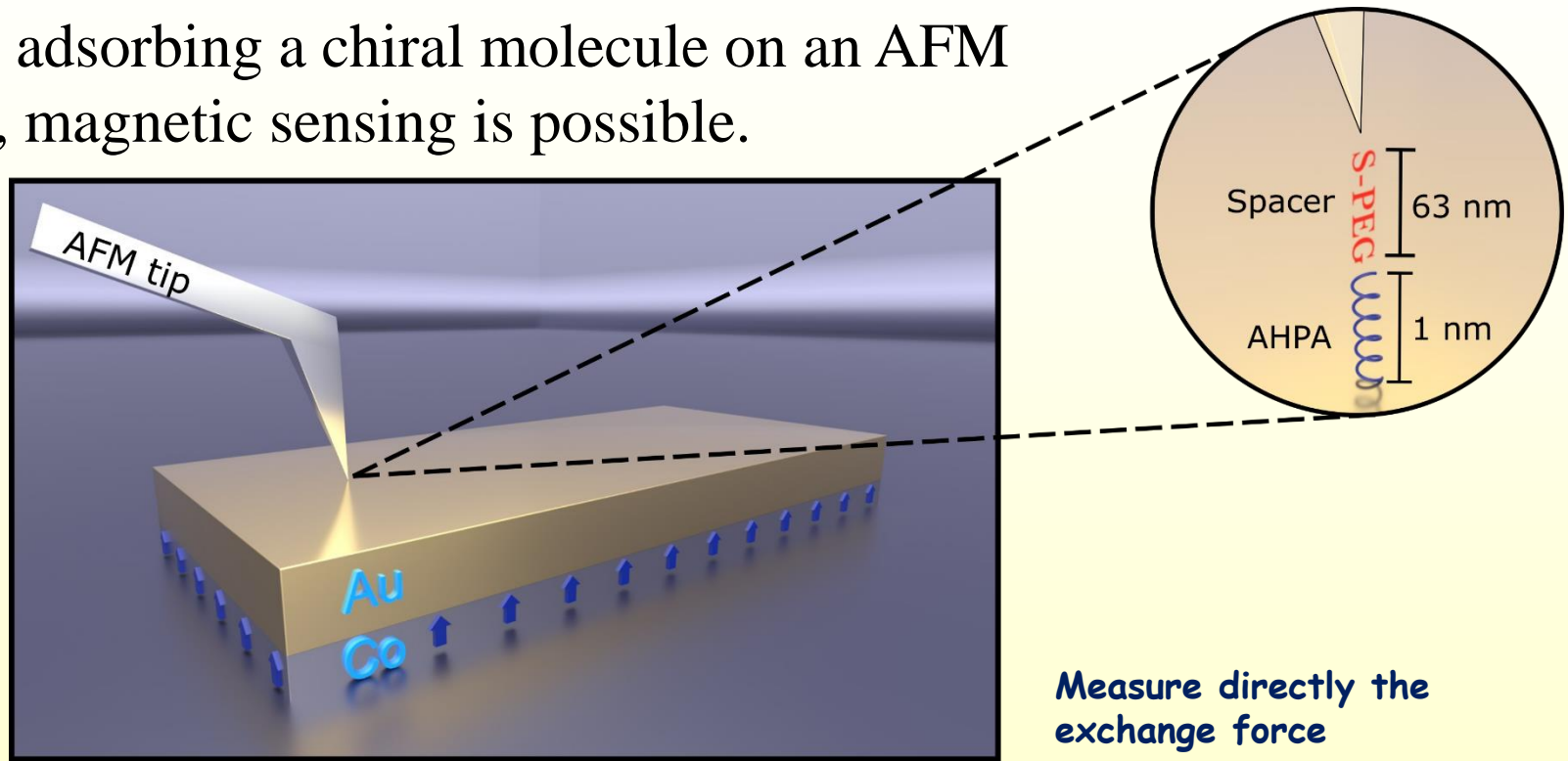
**But we are on a magnet - does break T in any case and we have dissipation**

Artem G. Volosniev, Hen Alpern, Yossi Paltiel, Oded Millo, Mikhail Lemeshko, and Areg Ghazaryan, *Interplay between friction and spin-orbit coupling as a source of spin polarization*; Phys. Rev. B **104**, 024430 (2021).



# AFM-Based Spin-Exchange Microscopy Using Chiral Molecules

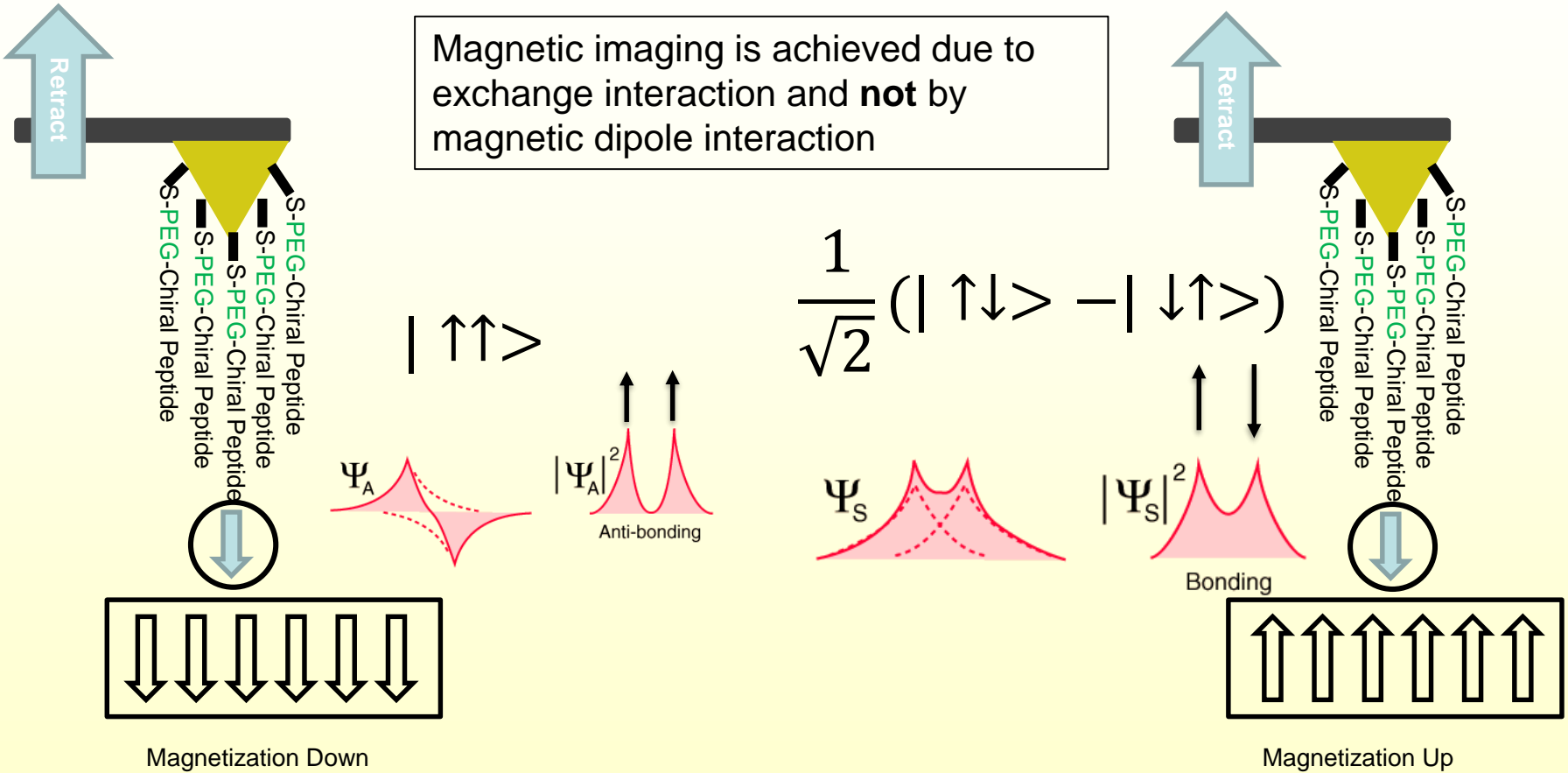
By adsorbing a chiral molecule on an AFM tip, magnetic sensing is possible.



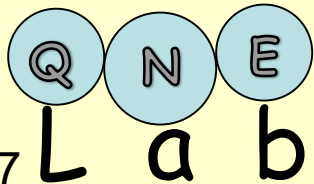
Amir Ziv, Abhijit Saha, Hen Alpern, Nir Sukenik, Lech Tomasz Baczewski, Shira Yochelis, Meital Reches,\* and Yossi Paltiel\*; *AFM-Based Spin Exchange Microscopy Using Chiral Molecules*, Advanced Materials (2019).

# Chiral spin AFM

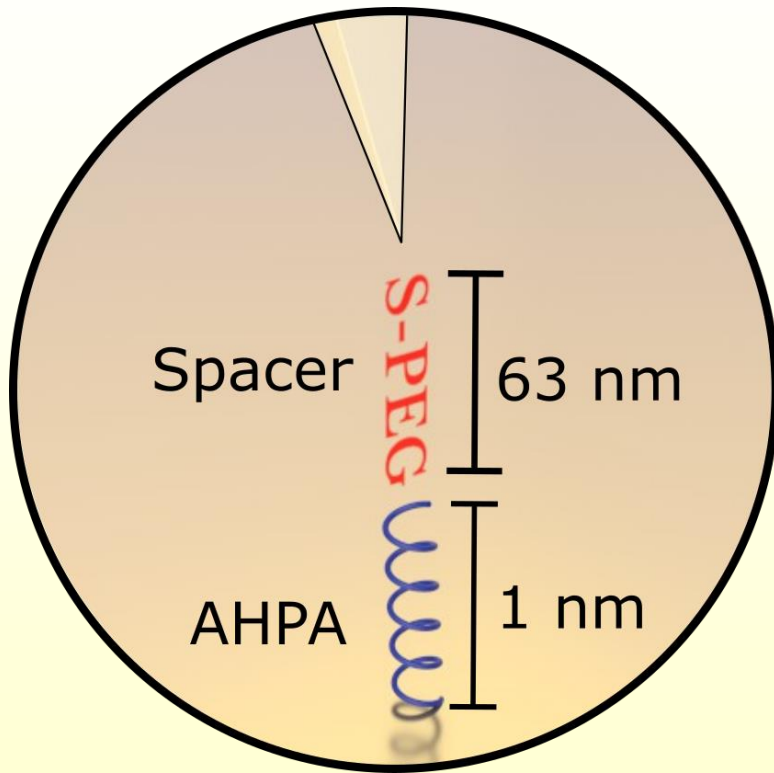
Measure directly the exchange force



Atomic resolution of magnetic mapping!!!!



# CISS on Tip



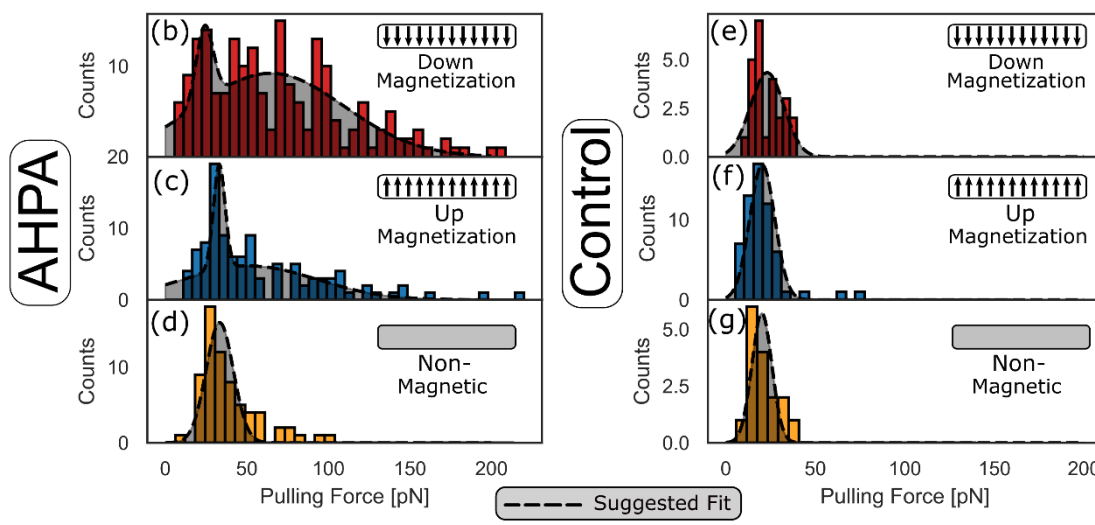
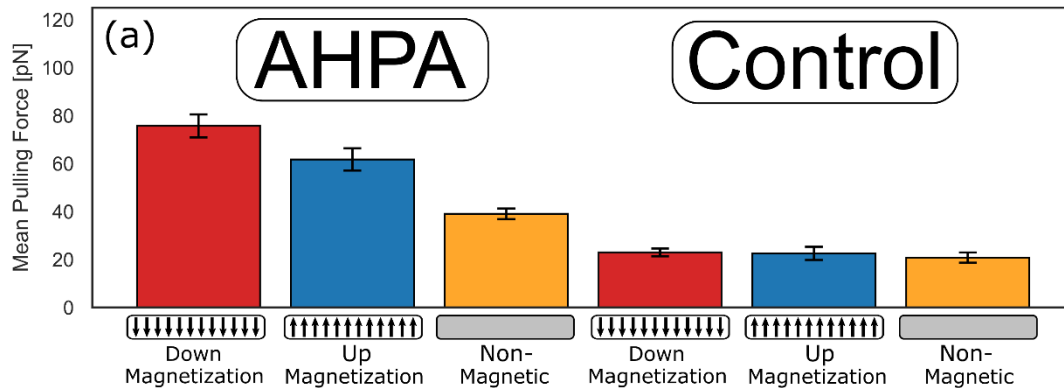
In order to isolate the specific interface-molecule interaction:

- A spacer molecule is placed between the tip and the molecule of interest, to reduce VDW and electrostatic interaction.
- The measurement is performed in a liquid environment to avoid capillary forces
- The measured sample is an MBE grown sample to avoid discrepancies between the composition and topography.

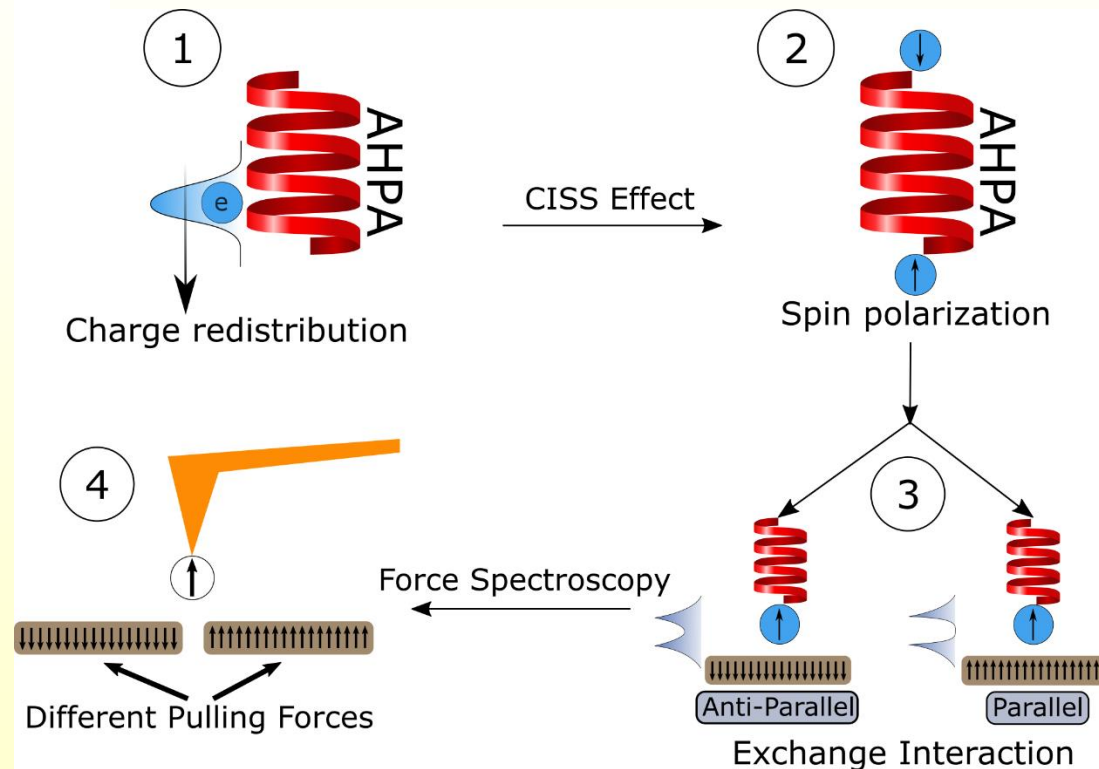
# Results

Control experiments were made with gold alone and with an achiral molecule with the same linkers.

A force difference of  $13.98 \pm 6.67$  [pN] was measured.

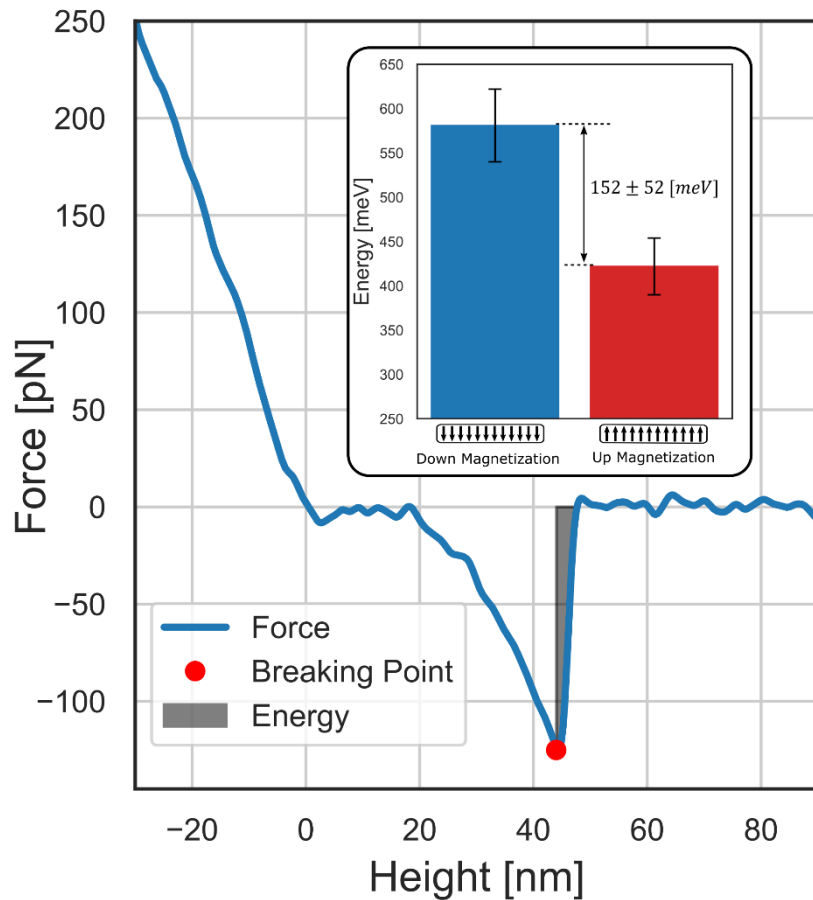


# Suggested Mechanism



Ziv, A, Saha, A. et al. AFM-Based Spin-Exchange Microscopy Using Chiral Molecules. *Advanced Materials* 0, 1904206

# Interaction Energy

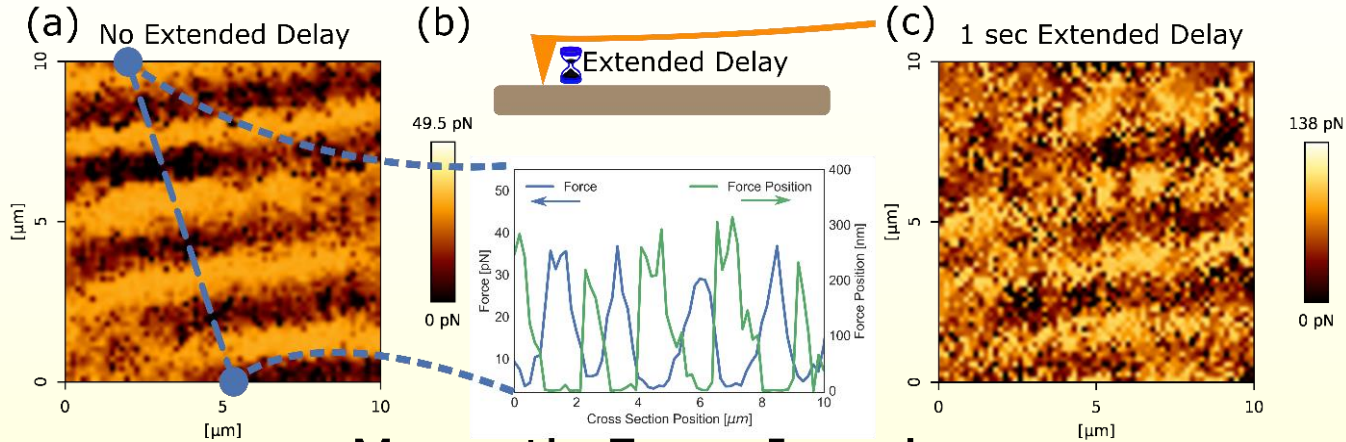


Calculating the energy difference between the down and up magnetization yielded a difference of  $152 \pm 52$  [meV] which corresponds to first principle calculations.

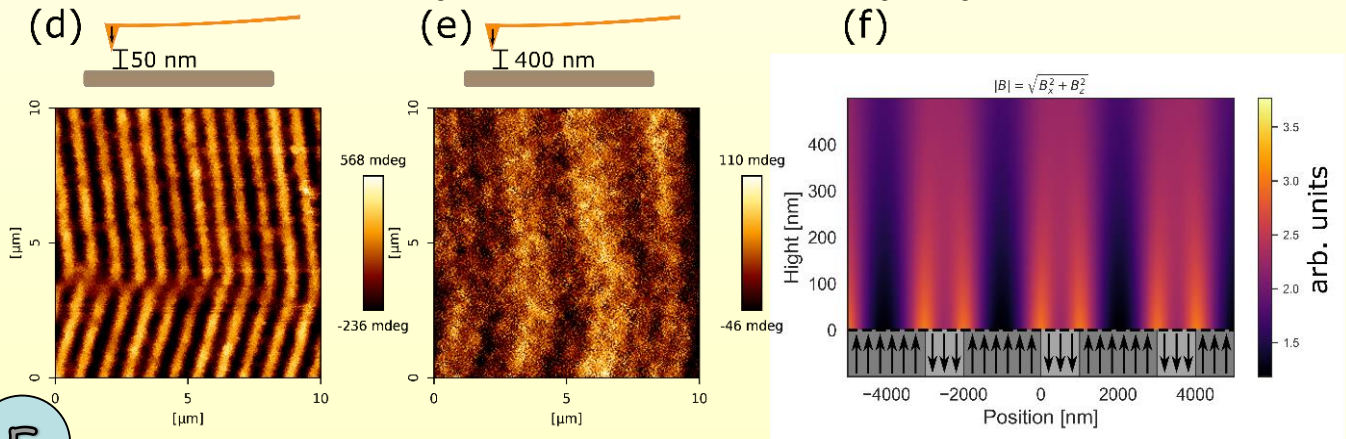
Amir Ziv, Abhijit Saha, Hen Alpern, Nir Sukenik, Lech Tomasz Baczewski, Shira Yochelis, Meital Reches,\* and Yossi Paltiel\*; *AFM-Based Spin Exchange Microscopy Using Chiral Molecules*, Advanced Materials (2019).

# Using Chiral molecules to achieve nano scale magnetic mapping

## Molecular Spin Exchange Imaging



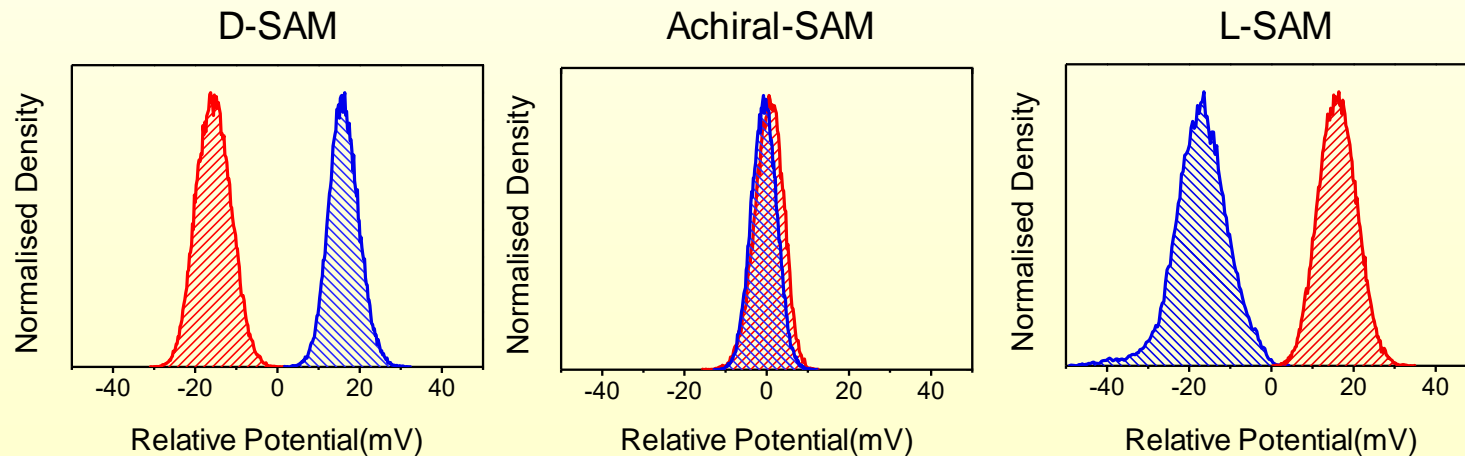
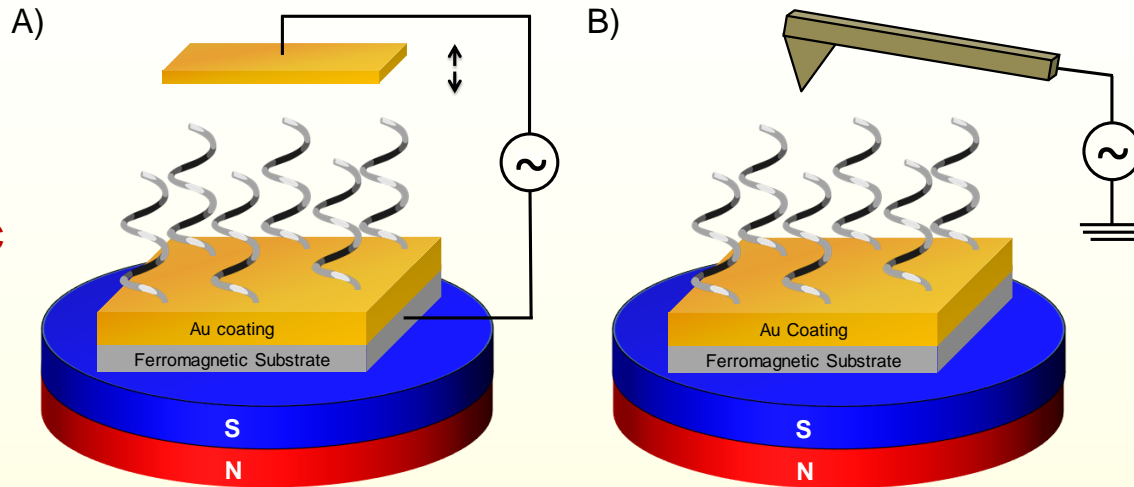
## Magnetic Force Imaging





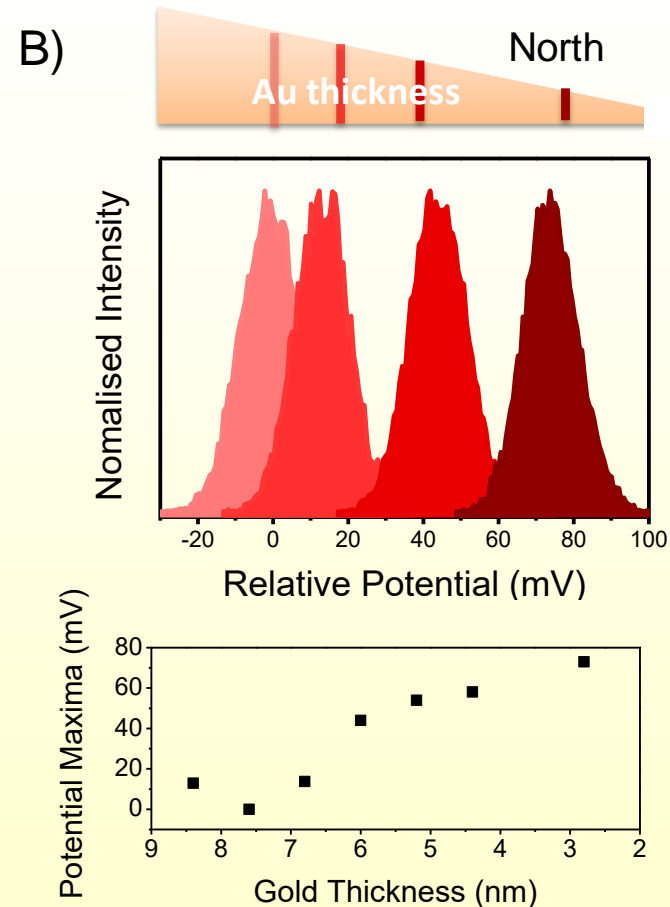
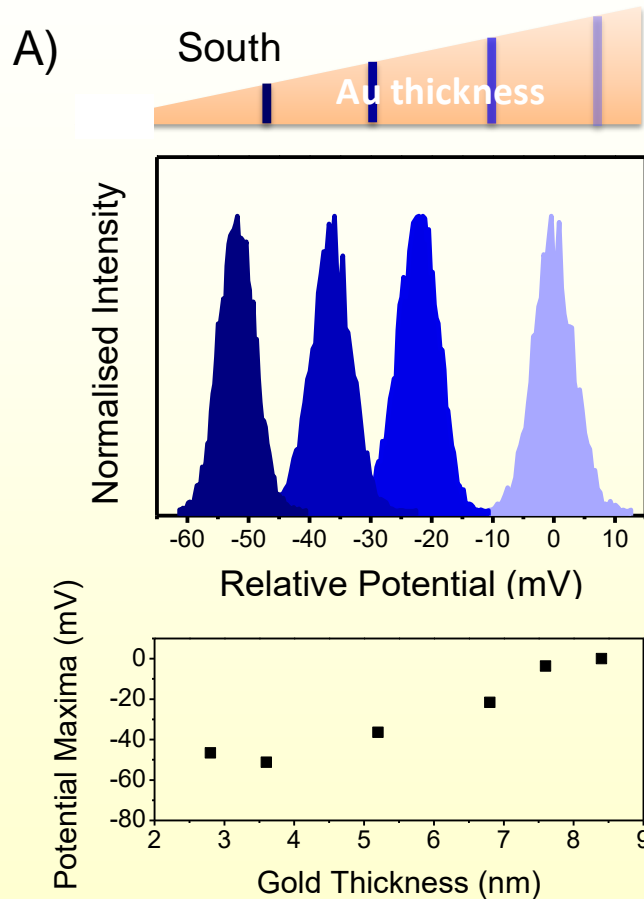
# Work function results

Ni or Co  
Ferromagnetic  
substrate



*Effect of Chiral Molecules on the Electron's Spin Wavefunction at Interfaces,*  
*J. Phys. Chem. Lett., 11, (4), 1550 (2020).*

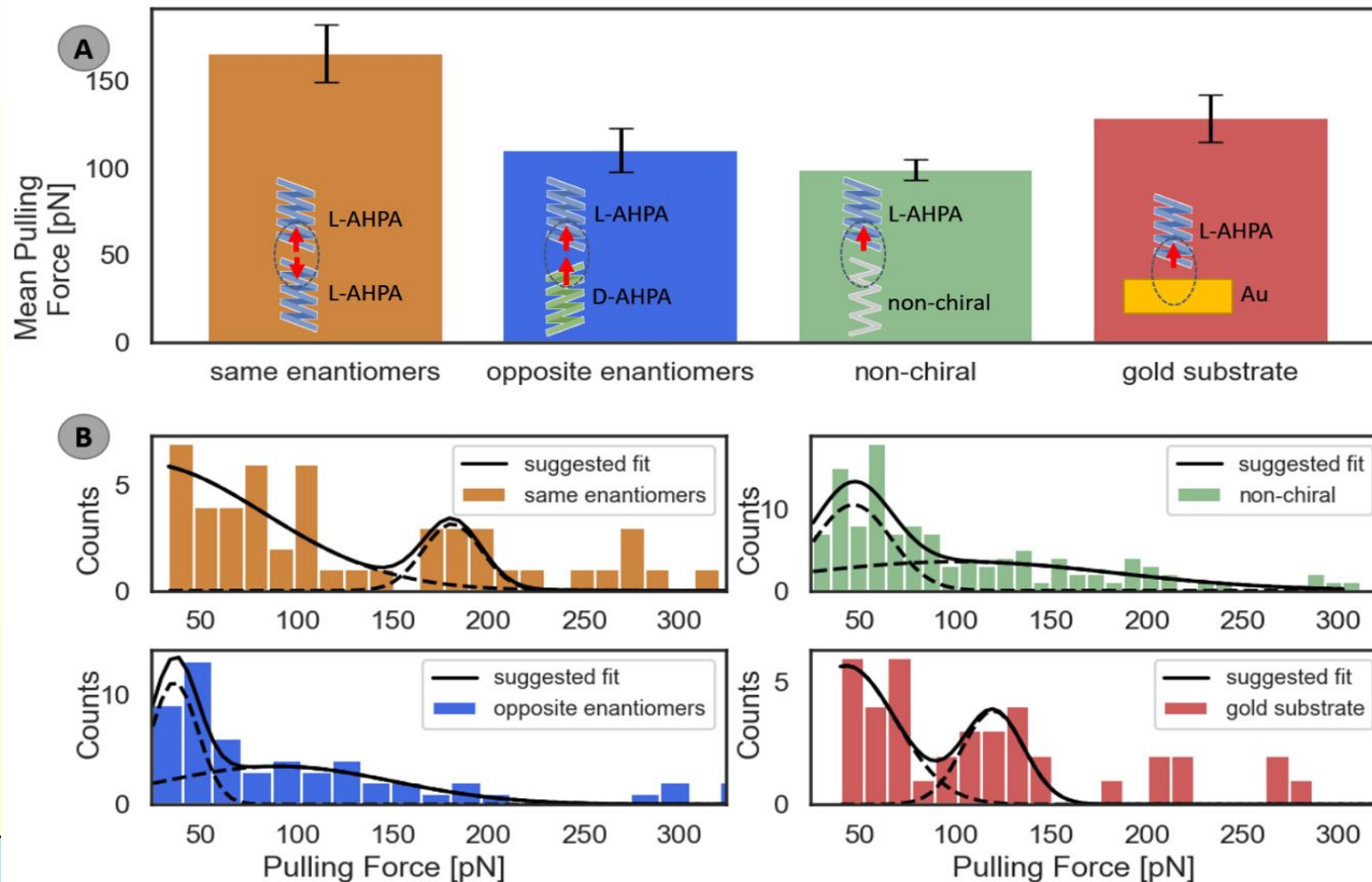
# Spin exchange delocalization



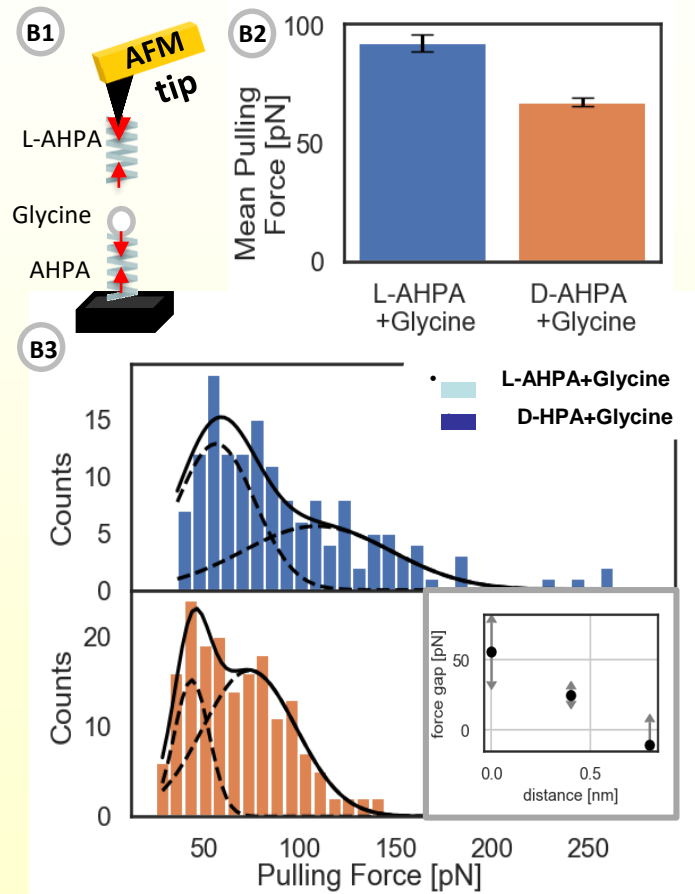
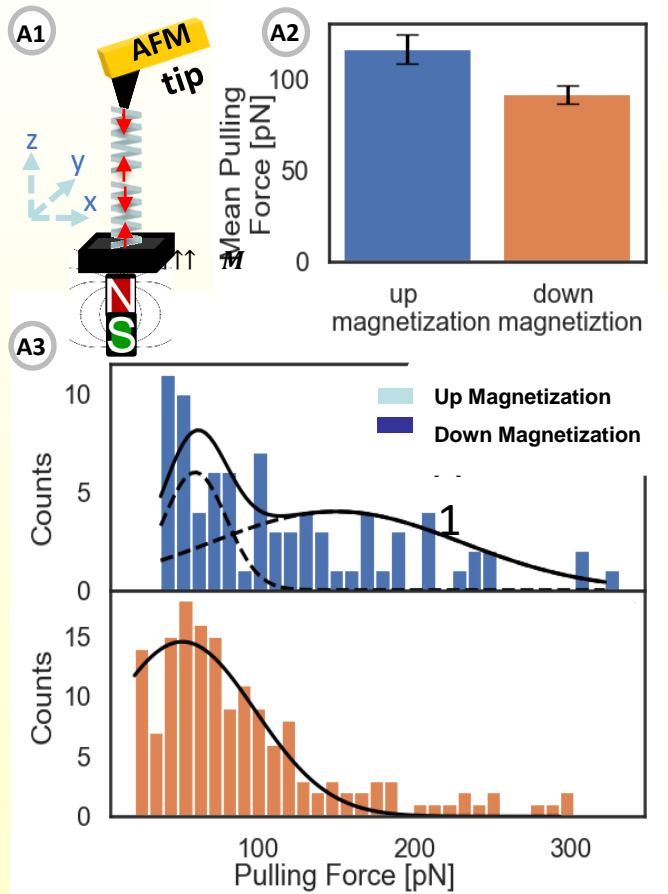
# Bio recognition forces

## Protein folding and bio recognition

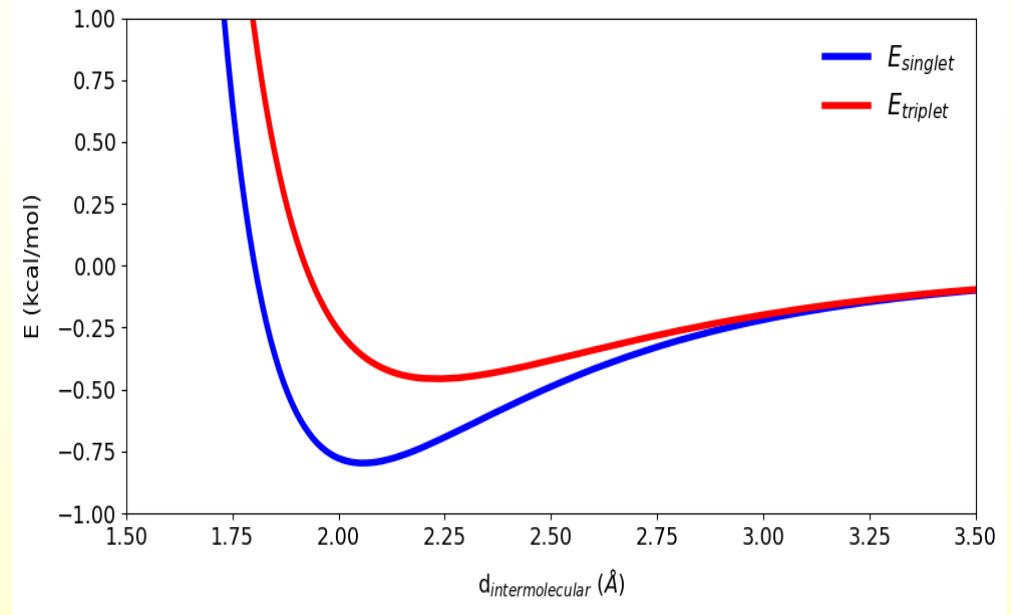
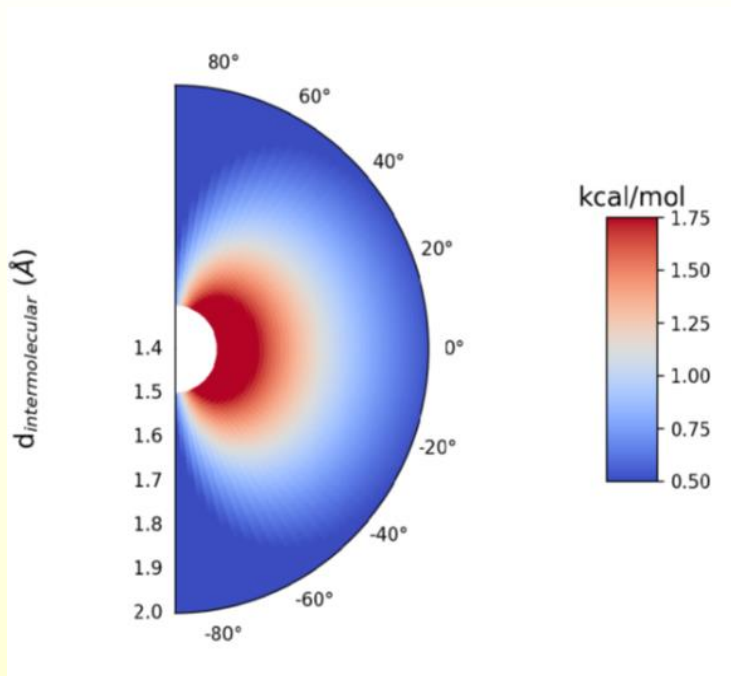
**Evident for New Enantiospecific Interaction Force in Chiral Biomolecules** Yael Kapon,<sup>+</sup> Abhijit Saha,<sup>+</sup> Thijs Stuyver, Amir Ziv, Shira Yochelis, Sason Shaik, Ron Naaman,<sup>\*</sup> Meital Rechtes,<sup>\*</sup> and Yossi Paltiel<sup>\*</sup>



# Relation to spin



# Protein folding and bio recognition

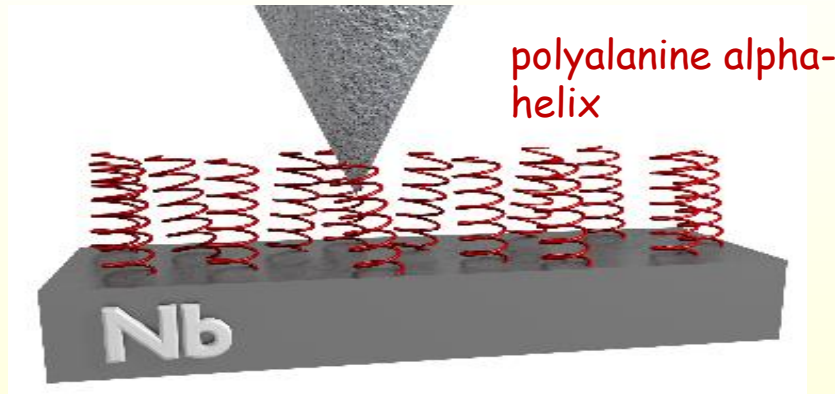


The calculated potential energies from the toy model for interaction of two molecules with spin polarized either antiparallel (blue) or parallel (red) to each other

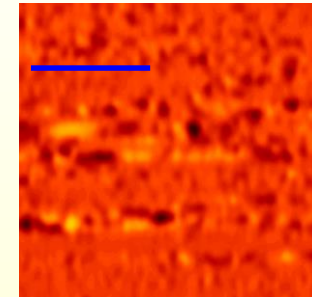
# Can chiral molecules alter an s-wave superconductor

## Not a magnetic system!!!

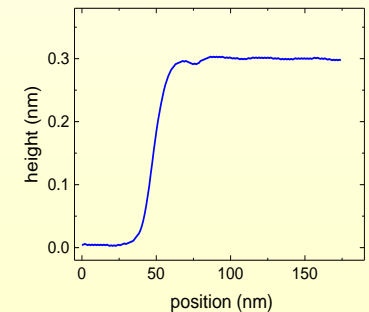
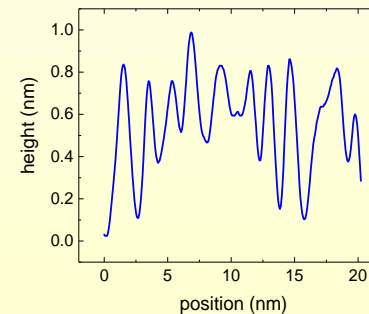
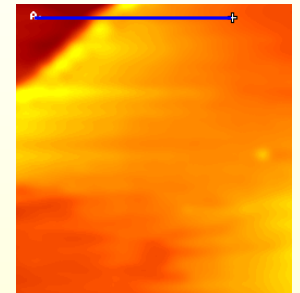
STM tip



molecule-covered area



molecule-free area

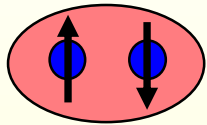


# D wave and P wave spectra

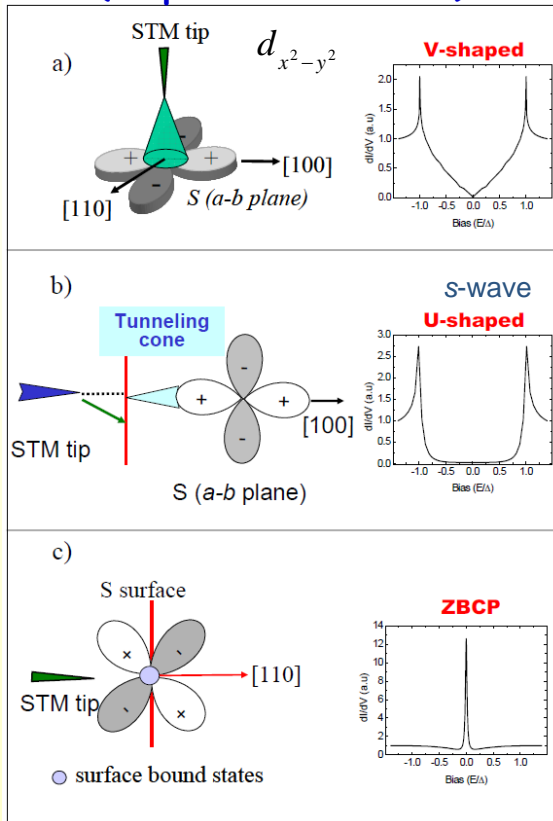
## d-wave (cuprate HTSCs)

## p-wave (triplet superconductors)

Spin Singlet



$$|\uparrow\downarrow\rangle - |\downarrow\uparrow\rangle$$

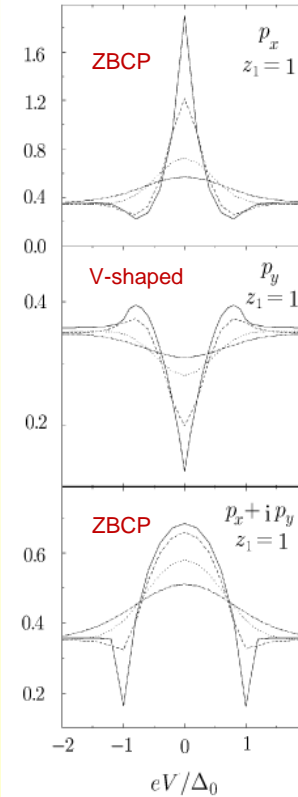


$$d_{x^2-y^2}$$

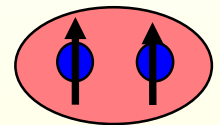
$$\Delta = \Delta_0 \cos(2\phi)$$

Note:

1. (split) ZBCPs
2. V-shaped gaps



Spin triplet



$$\begin{aligned} &|\uparrow\uparrow\rangle \\ &|\uparrow\downarrow\rangle + |\downarrow\uparrow\rangle \\ &|\downarrow\downarrow\rangle \end{aligned}$$

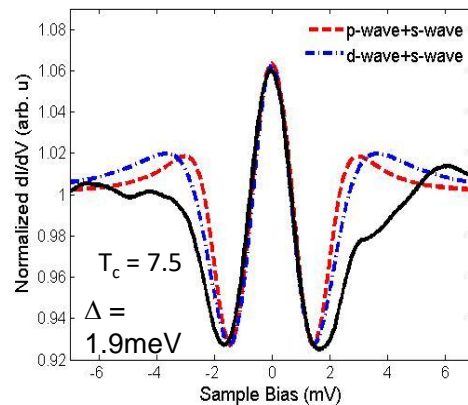
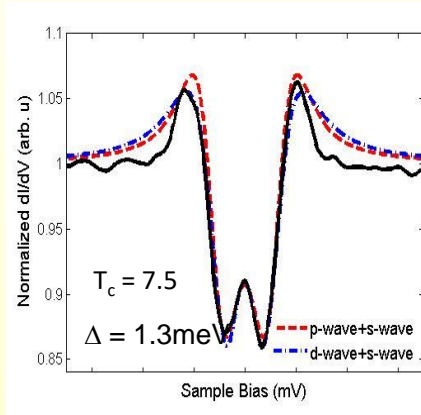
# Fits to the three types of spectra

Combination of *s*-wave, *d*-wave and chiral *p*-wave pairing potentials.

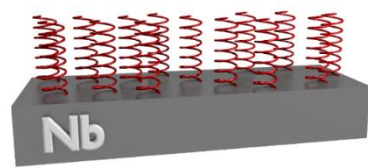
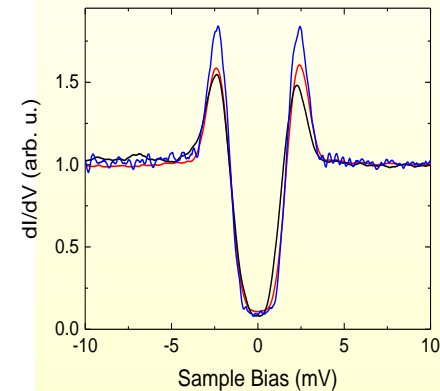
chiral *p*-wave :  $\Delta_{\uparrow\uparrow} = \Delta_0 \sin\theta(\cos\phi + i\sin\phi) \quad (p_x + ip_y, \text{triplet})$

*d*-wave ( $d_{x^2-y^2}$ ) :  $\Delta = \Delta_0 \cos(2\theta) \quad (\text{singlet or odd-frequency triplet})$

After Adsorption



Pristine Sample



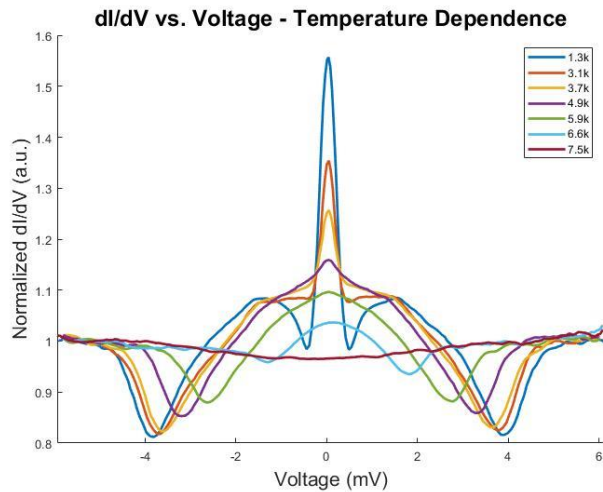
Alpern, et al., *New J. Phys.* 18, 113048 (2016)

Quantum Nano Engineering Lab

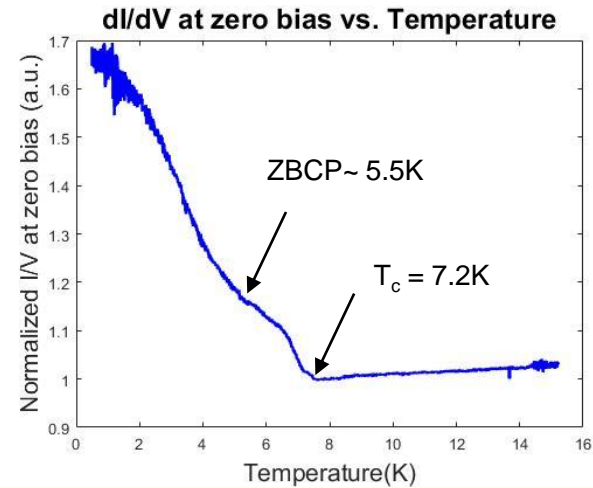
9/2/2021



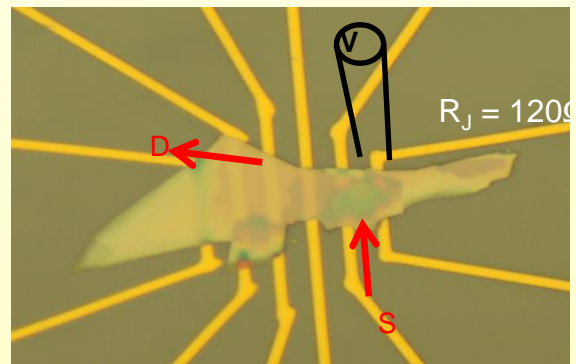
# Non Splitting ZBCP



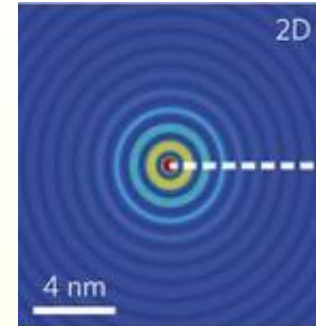
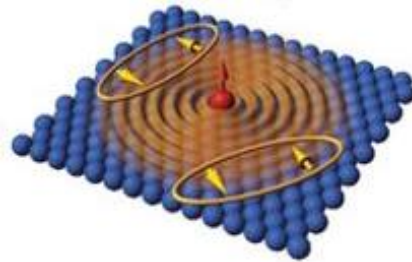
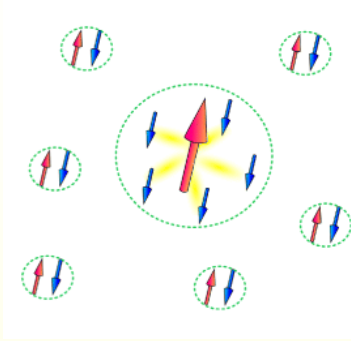
low resistance junction, T-dependence



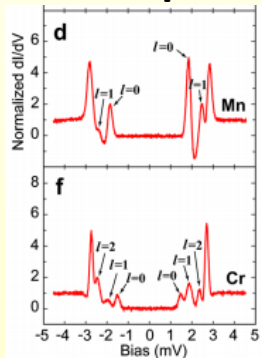
The induced component decreases with temperature.



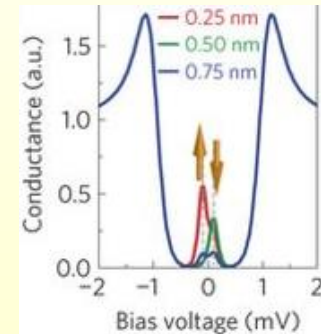
# Yu - Shiba - Rusinov (YSR) States



magnetic impurities form discrete low energy spin-polarized bound states within the superconducting gap



← In-gap states →

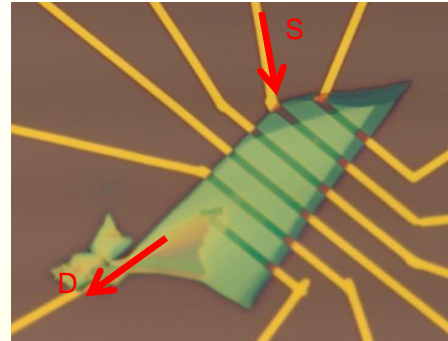
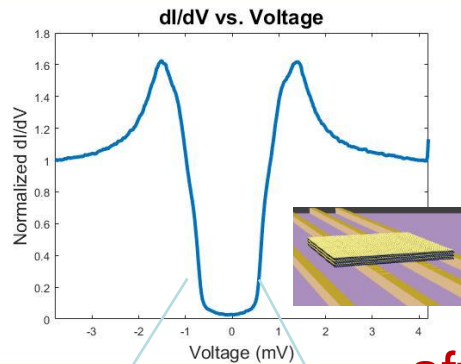


Ménard, G. C. *et al.* Coherent long-range magnetic bound states in a superconductor. *Nat. Phys.* **11**, 1013–1016 (2015).

Ji, S.-H. *et al.* High-Resolution Scanning Tunneling Spectroscopy of Magnetic Impurity Induced Bound States in the Superconducting Gap of Pb Thin Films. *Phys. Rev. Lett.* **100**, 226801 (2008).

# Sub gap states (YSR-like) which diverge with applied magnetic field

Before adsorption



after adsorption

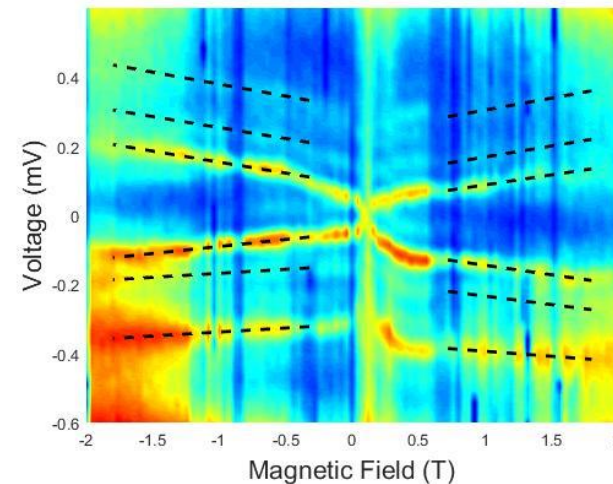
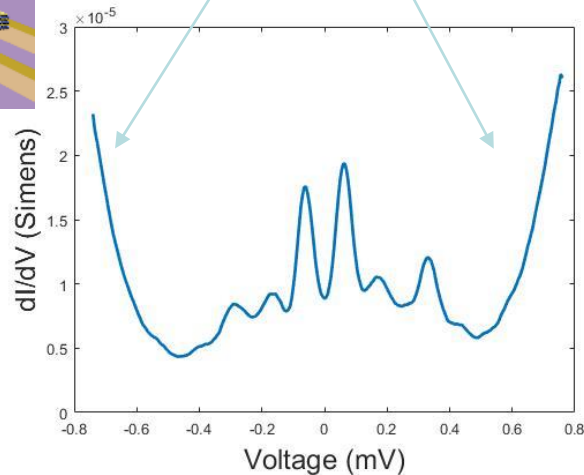
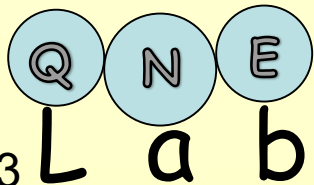
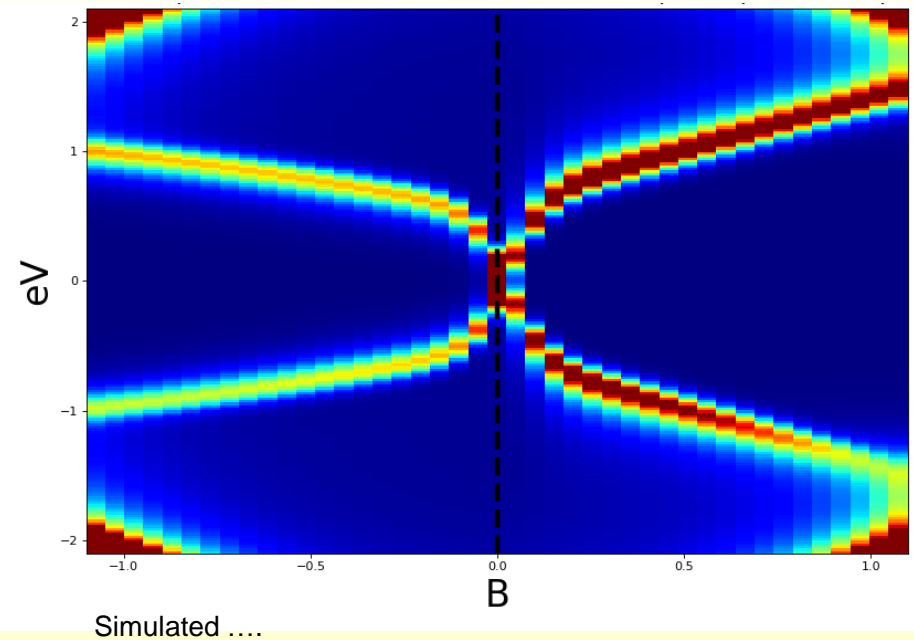
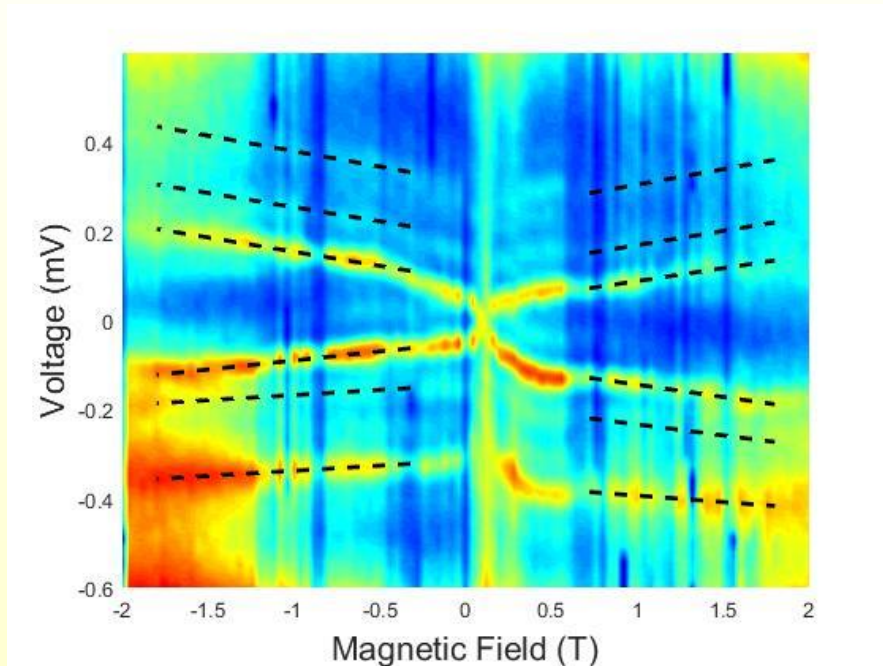


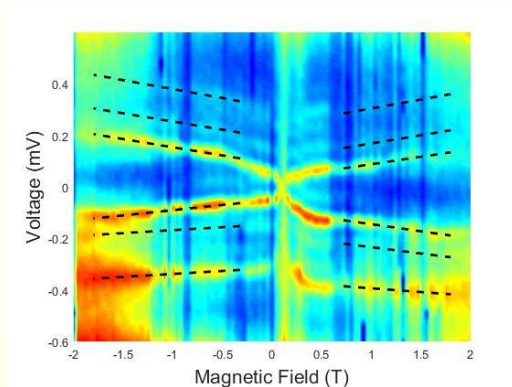
Figure 3: high junction resistance



# Comparison between measurement and simulation of an array of YSR states

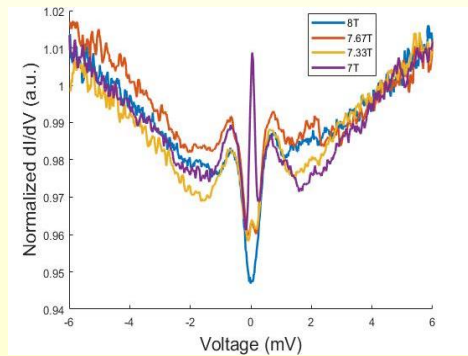


# Possible Scenario



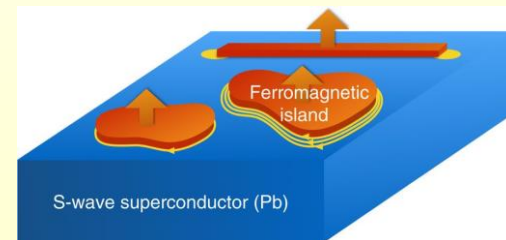
discrete YSR states

Low density adsorption



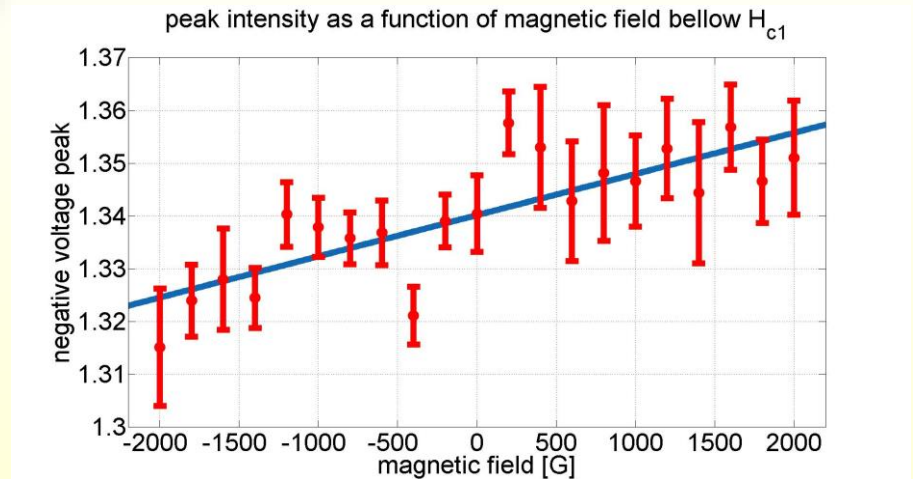
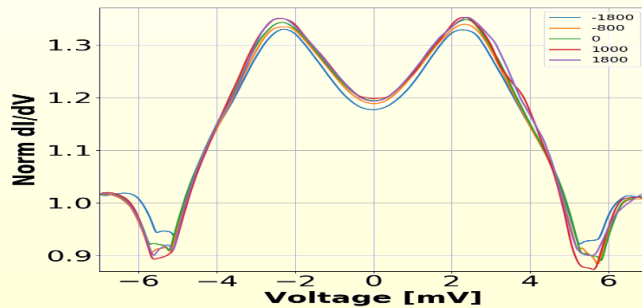
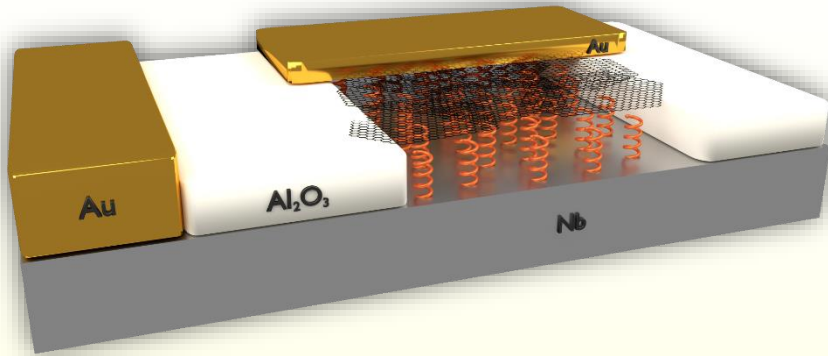
chiral p-wave

High density adsorption



Li, J. et al. *Two-dimensional chiral topological superconductivity in Shiba lattices*. *Nat. Commun.* 7, 12297 (2016).

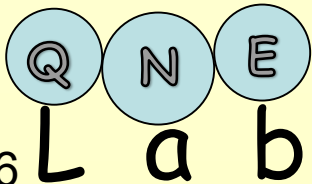
# SC order parameter change by chiral molecules



the junction measured consists of a Nb substrate, chiral polyaniline molecules, conductive graphene flakes and a top gold electrode. The measurement is done between the gold electrodes.

## *Proximity Effect through Chiral Molecules in Nb-Graphene-Based Devices*

Nir Sukenik, Hen Alpern, Eran Katzir, Shira Yochelis, Oded Millo, and Yossi Paltiel  
Adv. Mater. Technol. 2018, 1700300

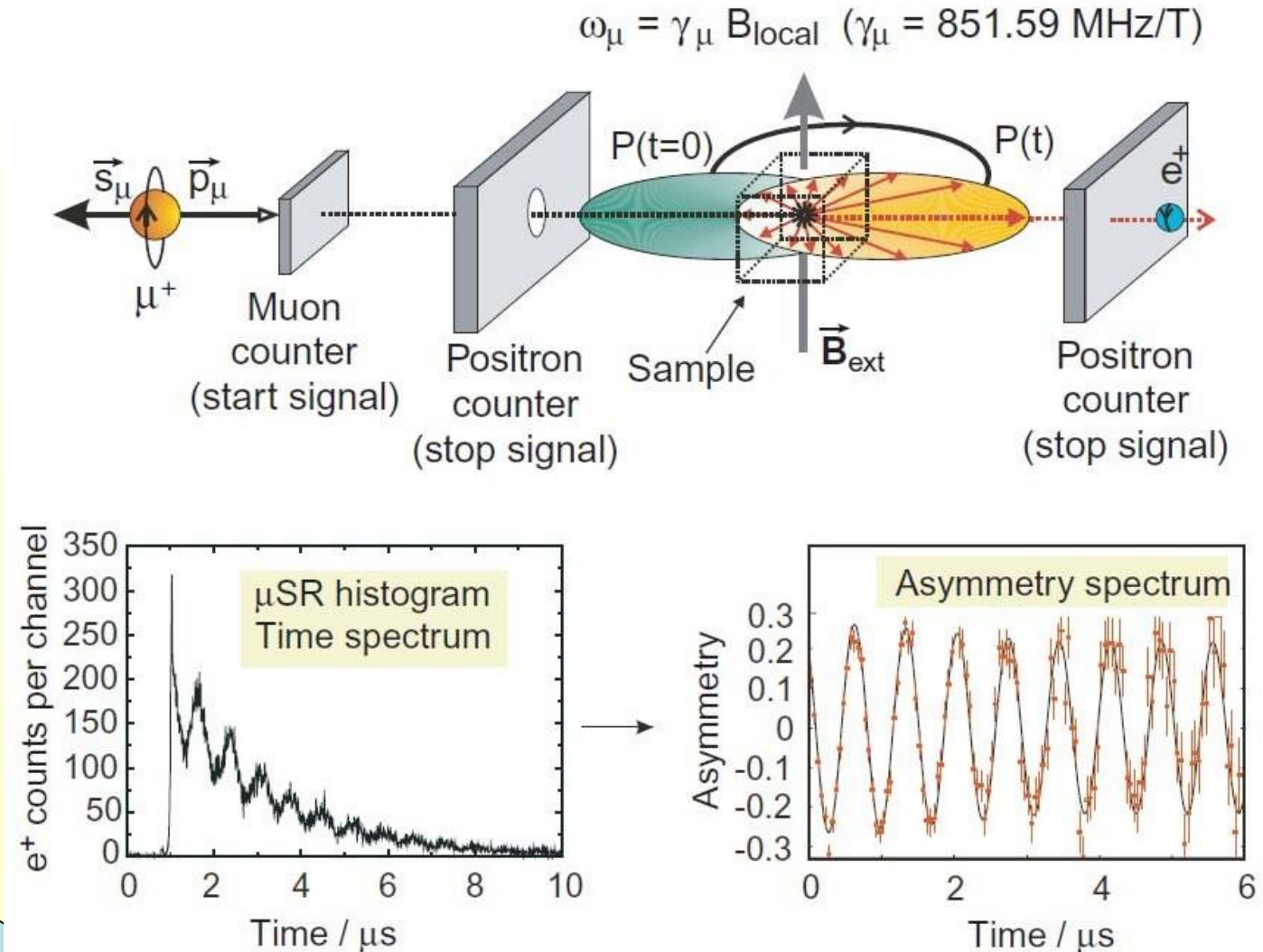


# $\mu$ SR Muon Spin Rotation/Relaxation

Paul Scherrer Institute



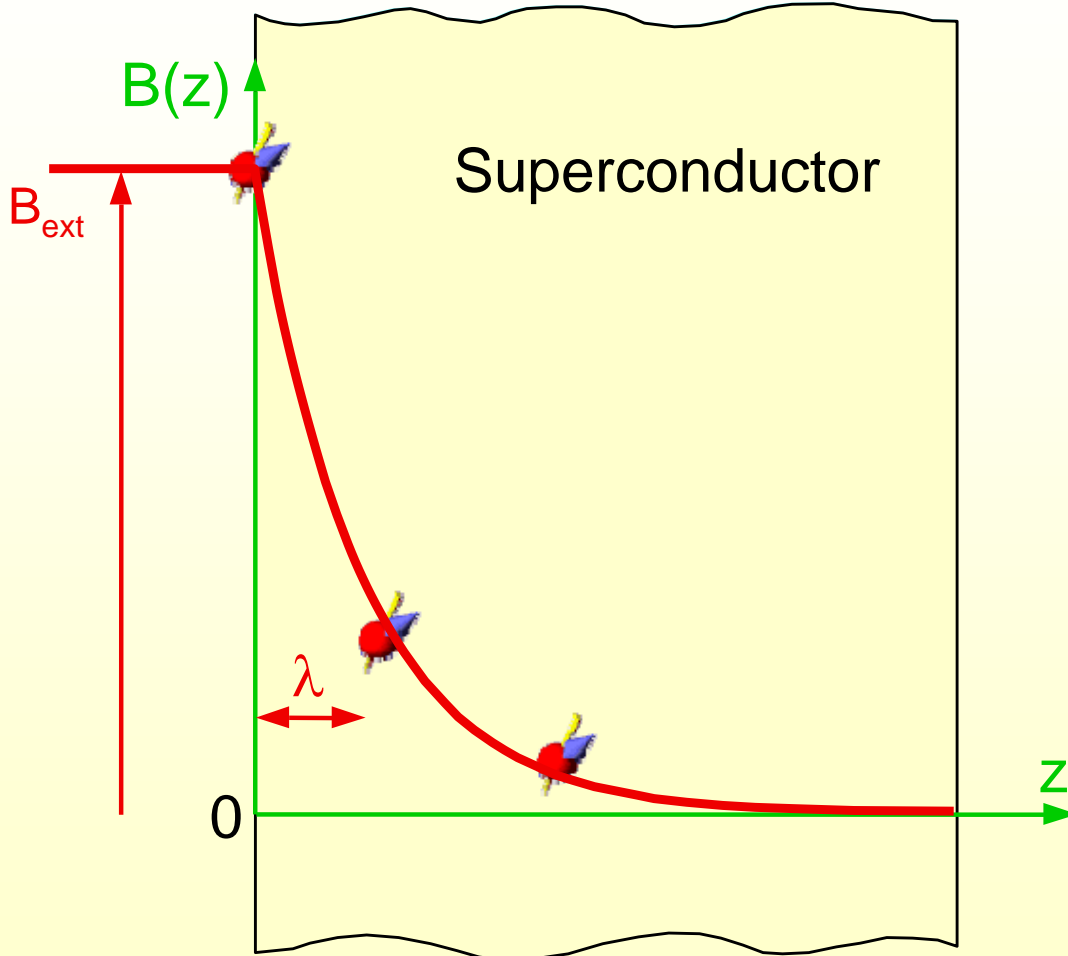
# Principle of a $\mu$ SR experiment



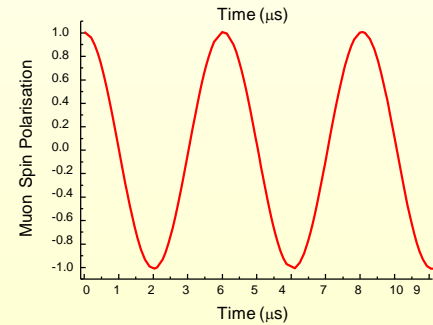
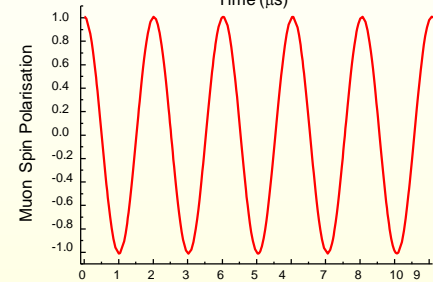
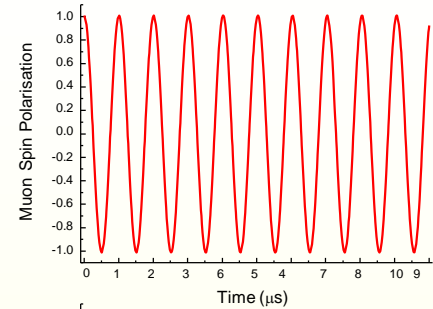


# Depth dependent $\mu$ SR measurements

→ Magnetic field profile  $B(z)$  over nm scale



→ Characteristic lengths of the sc  $\lambda, \xi$

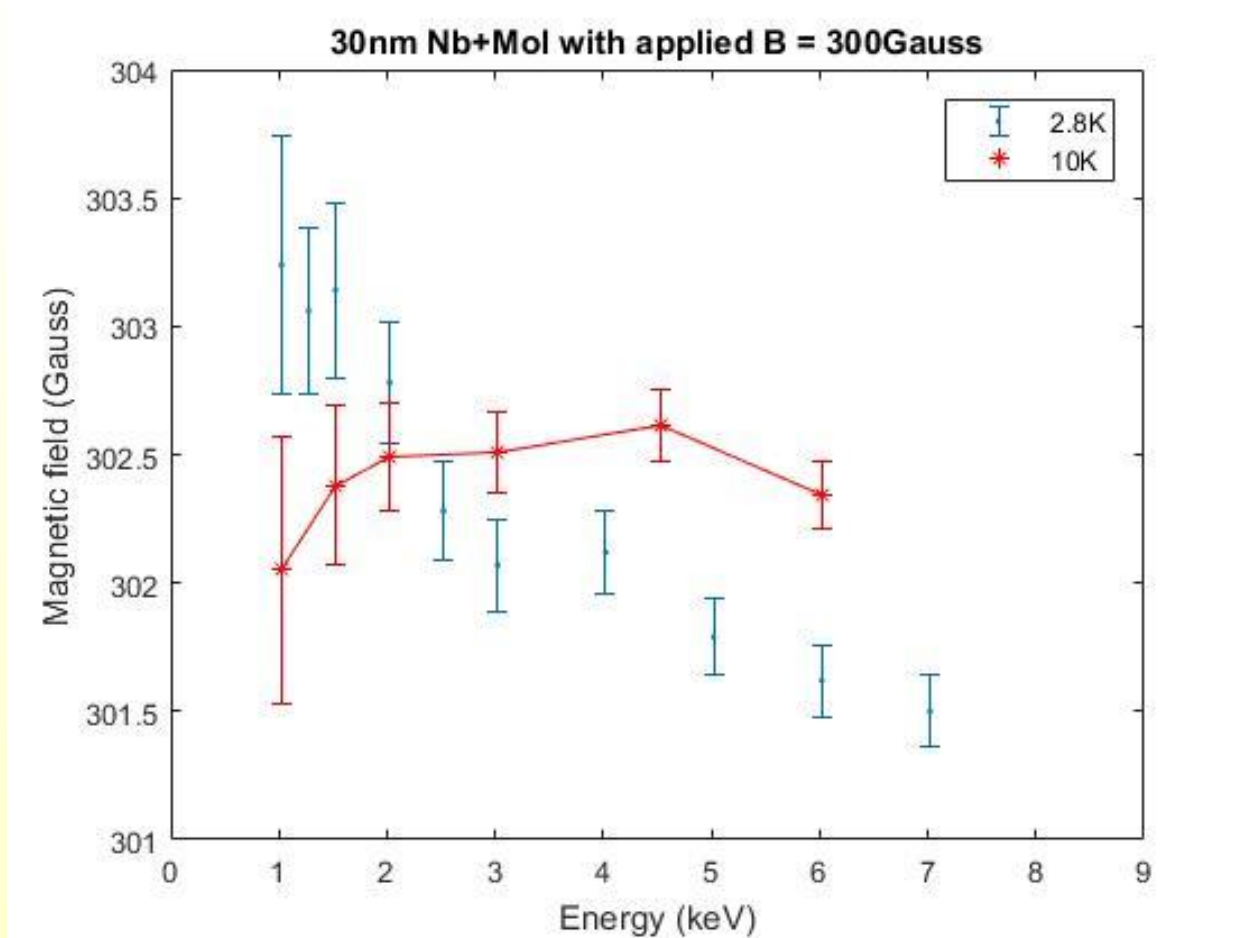


$$\omega_{\mu}(z) = \gamma_{\mu} B_{loc}(z)$$

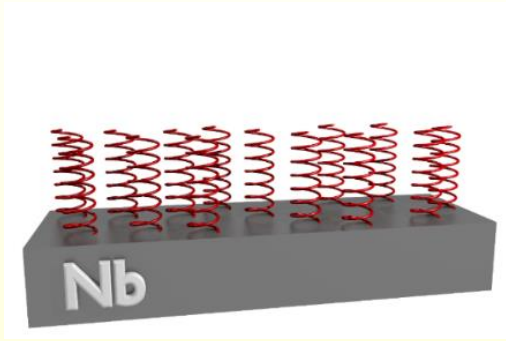
$\langle B \rangle$  vs  $\langle z \rangle \Rightarrow B(z)$

Paul Scherrer Institut • 5232 Villigen PSI

# 30nm Nb sample under 300G

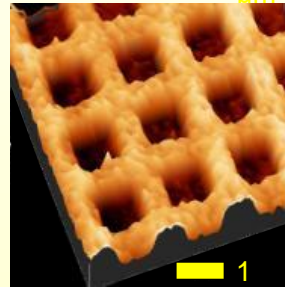


# Inducing magnetic impurities

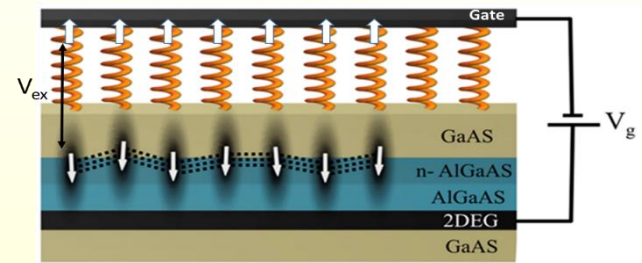


New Journal of Physics 2016

Magnetization



Nature Communication 2017



JPC letters 2019

# Manipulation of Skyrmions

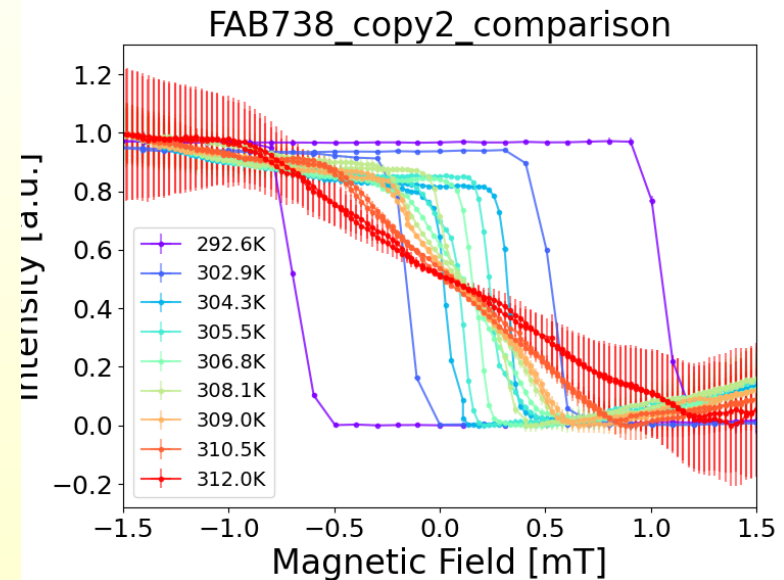
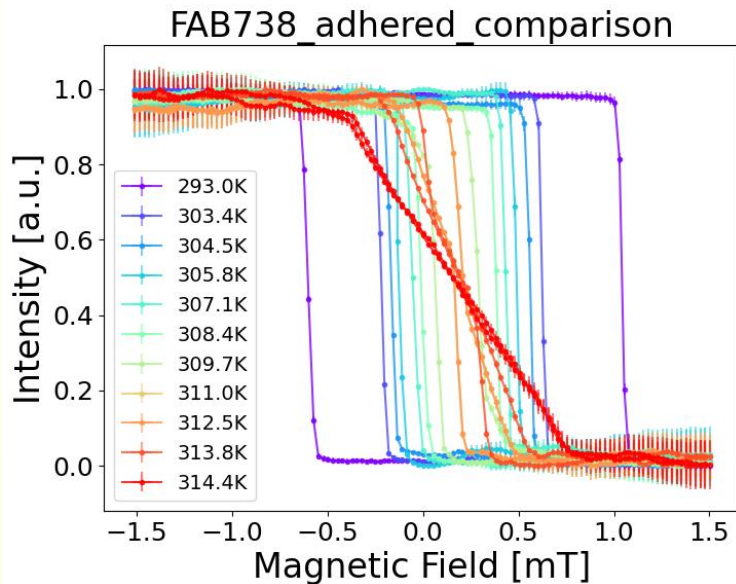
Pt (3) / Au (5)

Ta (2)

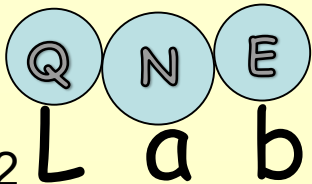
MgO (2)

CoFeB (0.9)

Ta (5)

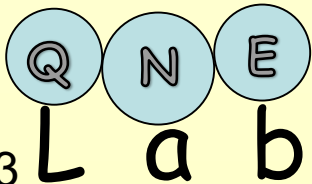
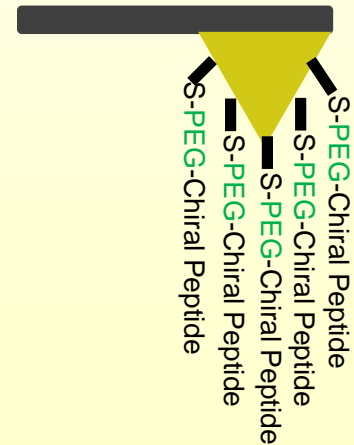
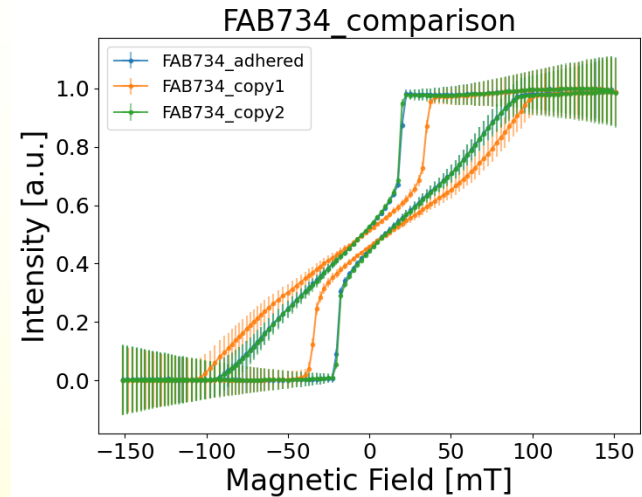


In collaboration with  
Mathias Kläui



# Future ideas

- Paramagnets
- Ferromagnets
- Anti-ferromagnets
- Superconducting and magnetics
- Multi-gated devices



Long Range Spin exchange interactions in chiral molecules can be used to control measure and manipulate quantum magnetic impurities.

Ron Naaman, Yossi Paltiel, David H. Waldeck;  
*Chiral molecules and the electron spin*;  
Nature Review Chemistry  
DOI: 10.1038/s41570-019-0087-1 (2019).

