

MolNanoSpin: Spintronique moléculaire avec des molécules-aimants

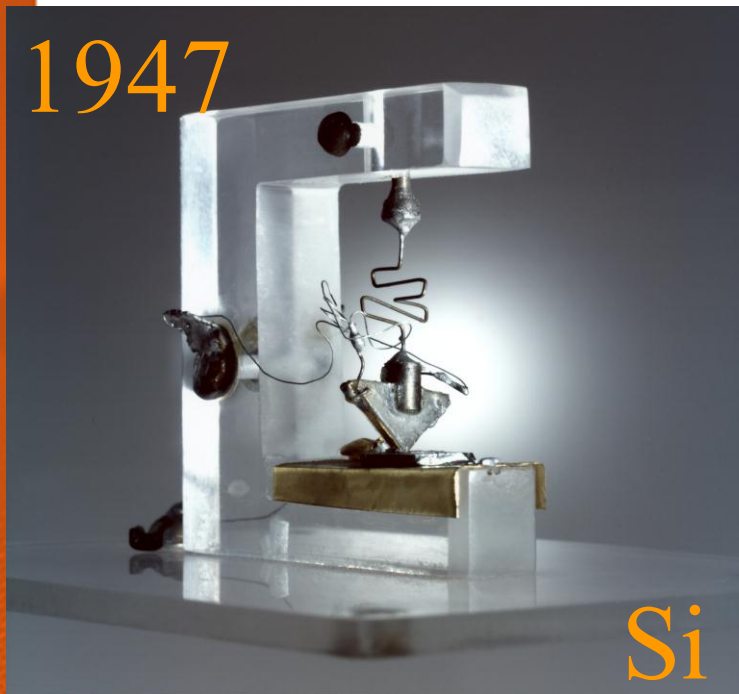


W. Wernsdorfer : Institut Néel
T. Mallah : Institut de Chimie
Moléculaire et
des Matériaux d'Orsay
P. Mialane : Institut
Lavoisier
Journées Nationales Nanosciences et
Nanotechnologies 2012

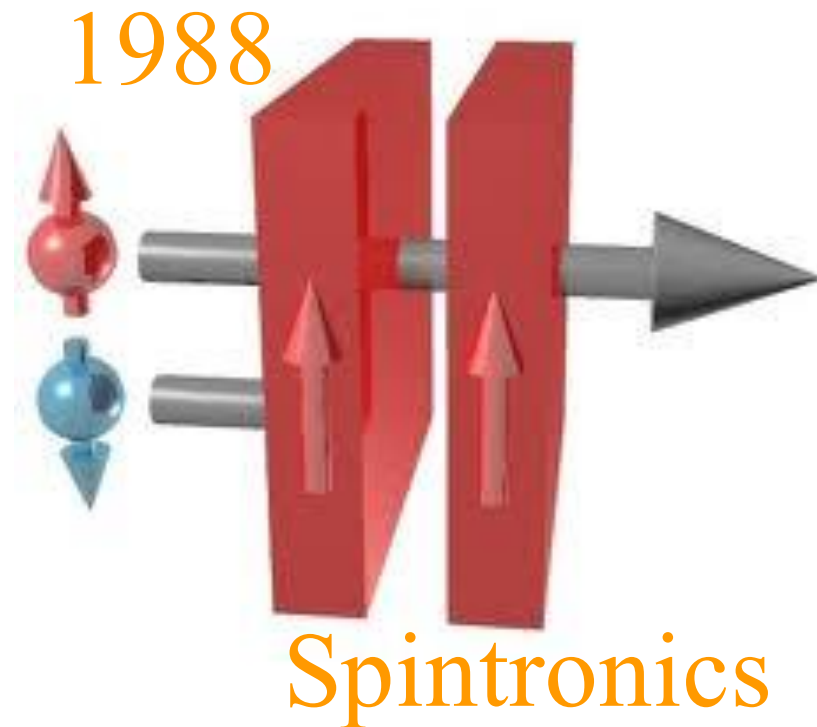
Content

- - remise en contexte du projet
- - description des objectifs
- - stratégie suivie
- - résultats marquants et récents
- - quelques indicateurs d'impact
(production scientifique, brevets,
recrutements...)

Electronic revolutions

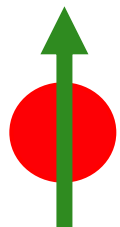


J. Bardeen, W. Shockley, W. Brattain: Nobel - 1956



A. Fert, P. Grünberg: Nobel - 1987

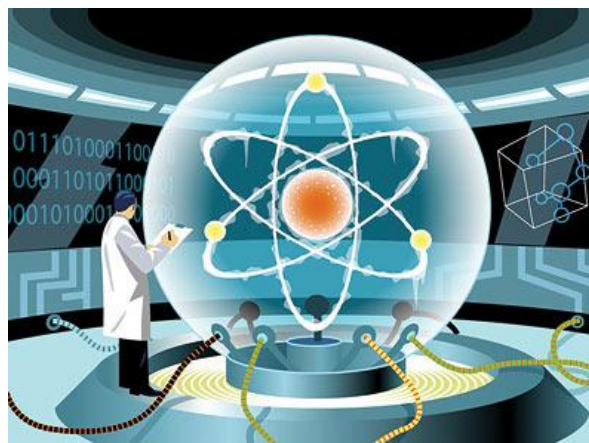
Electron:



spin

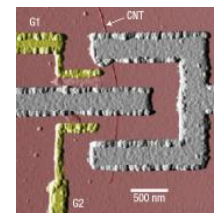
charge

phase



Quantum
electronics

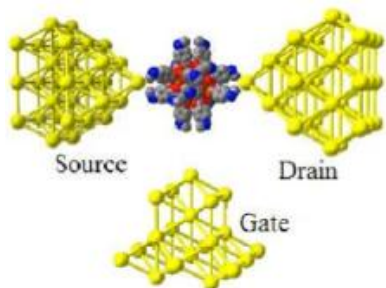
Molecular quantum spintronics



- Linking the ideas of three disciplines:
spintronics, molecular electronics, and quantum computing
- Manipulating spins and charges in electronic devices containing one or more molecules to **perform basic quantum operations**

L. Bogani & W. Wernsdorfer, *Nature Mat.* 7, 179 (2008)

Scheme I



direct
coupling

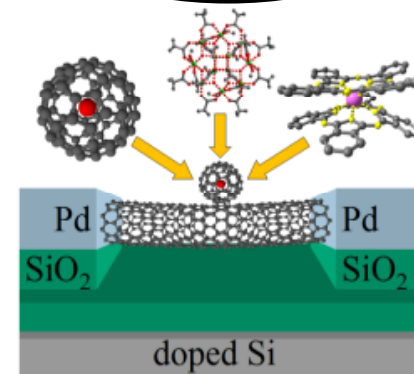
Project: Fabrication, characterization and study of molecular devices

- molecular spin-transistor
- molecular spin-valve and spin filter
- molecular double-dot devices
- carbon nanotube nano-SQUIDs
 etc.

Nature Mat. 10, 502 (2011)
Nature 488, 357 (2012)

Wernsdorfer - MolNanoSpin

Scheme II



indirect
coupling

Stratégie suivie

Livrables et jalons	Partenaires concernés
Tâche 1 : Synthesis and characterization of molecules, fabrication of devices, characterization of devices, instrumentation	
Tâche 1.1 : Synthesis of new molecular spin clusters and functionalisation of SWNT	2, 3
Tâche 1.2 : Characterization of the physical properties of new spin clusters	1, 2, 3
Tâche 1.3 : Deposition of molecular nanomagnets to form devices	1, 2
Tâche 1.4 : Characterization of molecular devices using Raman spectroscopy, HRTEM, STEM and EELS	1, 2

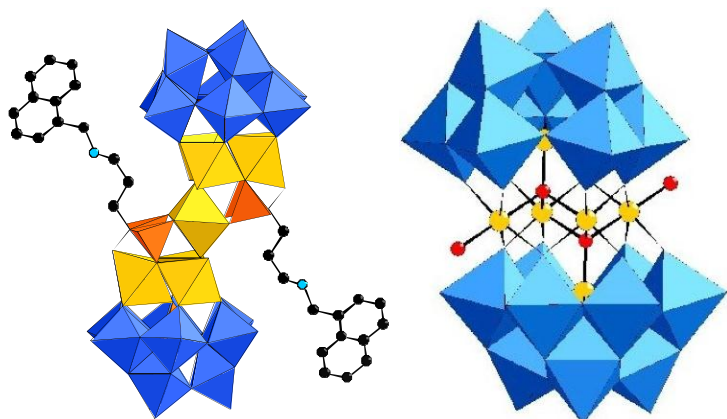
Livrables et jalons	Partenaires concernés
Tâche 2 : Molecular devices	
Tâche 2.1 : Molecular spin-transistor, spin-valve, and spin filter	1
Tâche 2.2 : Molecular double dot (MDD) devices	1
Tâche 2.3 : Carbon nanotube nano-SQUIDs	1
Tâche 2.4 : Theory and modelling of the devices	1
Tâche 3 : Quantum manipulation of molecular spin states	
Tâche 3.1 : Microwave on-chip coil development	1
Tâche 3.2 : Pump probe technique	1
Tâche 3.3 : Electrically detected EPR	1
Tâche 3.4 : Decoherence	1

N°1 : Institute Néel

N°2 : Institut de Chimie Moléculaire et des Matériaux d'Orsay

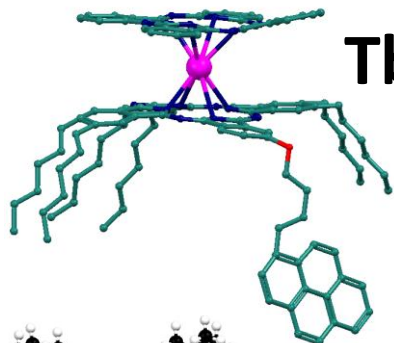
N°3 : Institut Lavoisier

Molecule Grafting

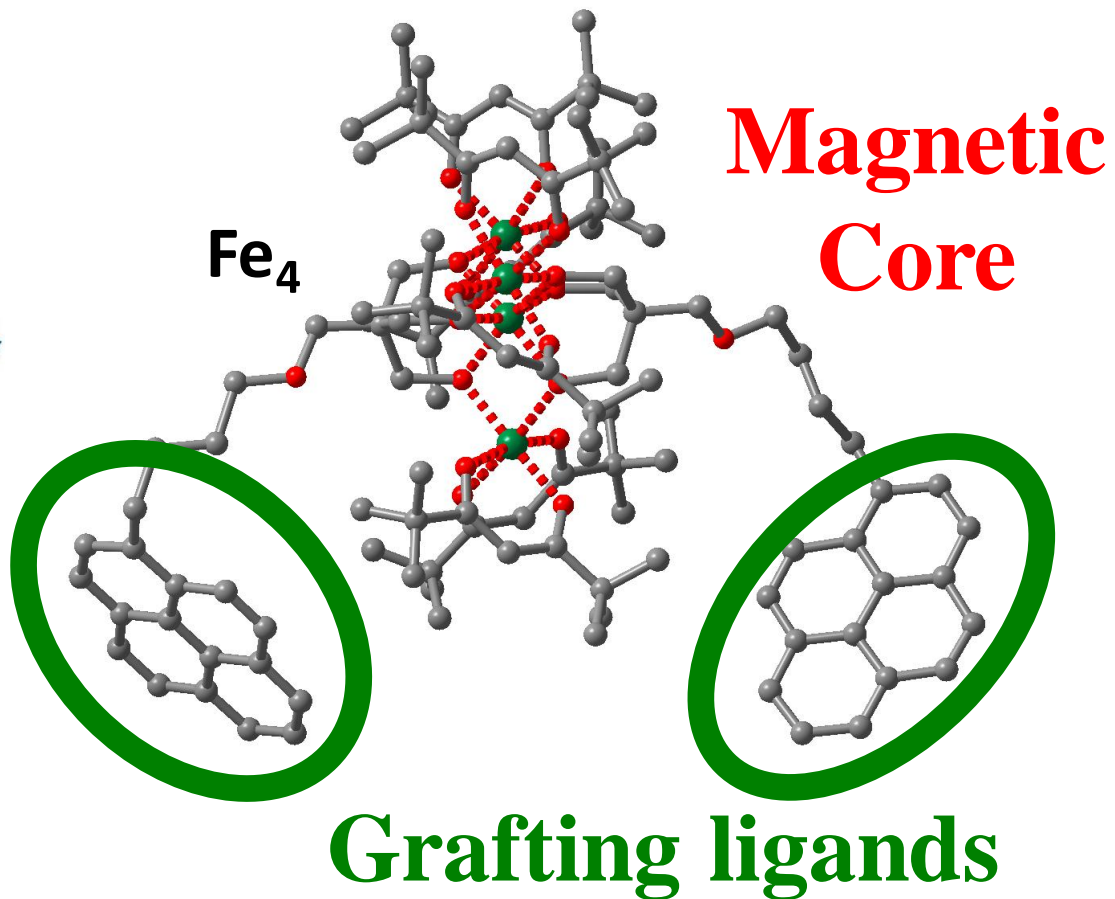
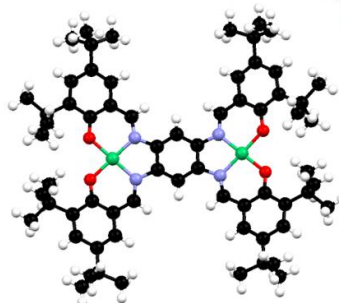


Co_7

Fe_6



TbPC_2



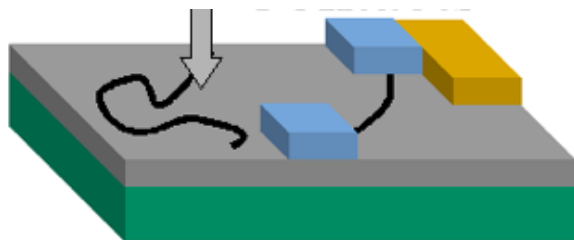
Aromatic rings



π -stacking

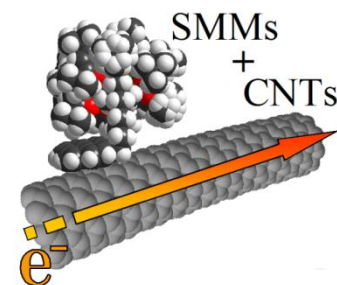
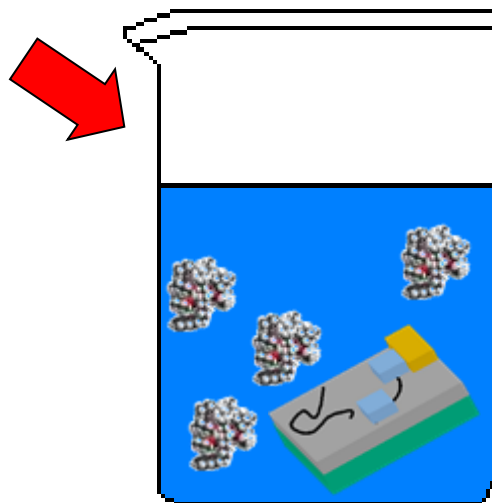
- L. Bogani *et al.*, *Angew. Chem. Int. Ed.* **48**, 746 (2009)
 S. Klyatskaya, *et al.*, *J. Am. Chem. Soc.* **131**, 15143 (2009)
 A. Giusti, *et al.*, *Angew. Chem. Int. Ed.* **48**, 4949 (2009)

Molecule Grafting on Carbon Nanotubes

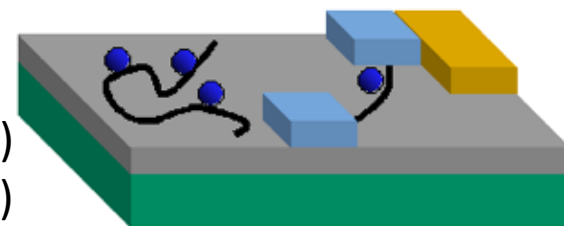


CNT device

Dipping the device into
the solution of molecule



Grafted molecules
on the CNT device

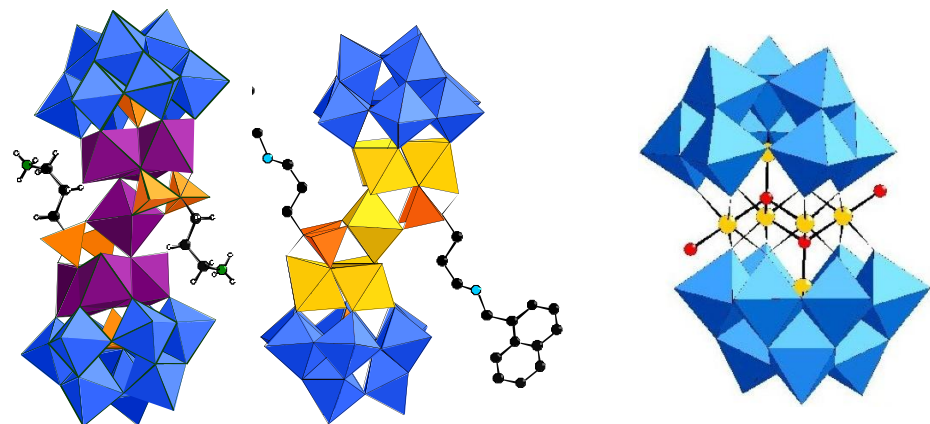


- L. Bogani *et al.*, *Angew. Chem. Int. Ed.* **48**, 746 (2009)
 S. Klyatskaya, *et al.*, *J. Am. Chem. Soc.* **131**, 15143 (2009)
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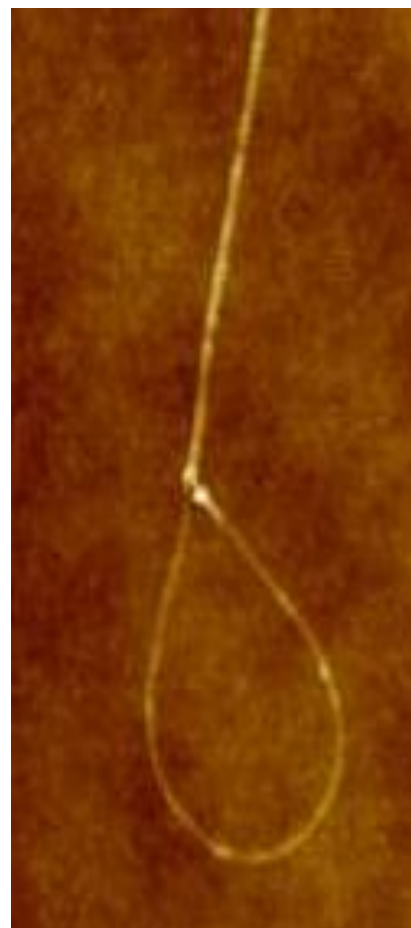
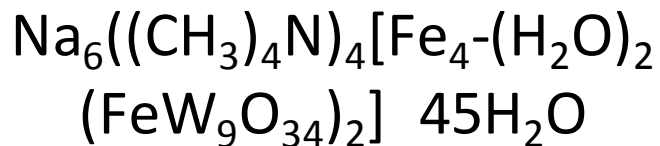
Grafting of SMMs

Co₇

Fe₆



polyoxometalate (POM)

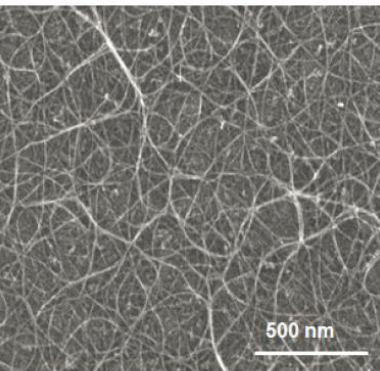


200 nm

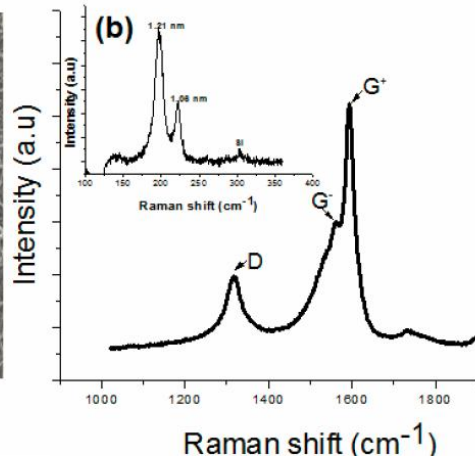
A. Giusti, et al., *Angew. Chem. Int. Ed.* **48**, 4949 (2009)

CNTFET building for transport measurements

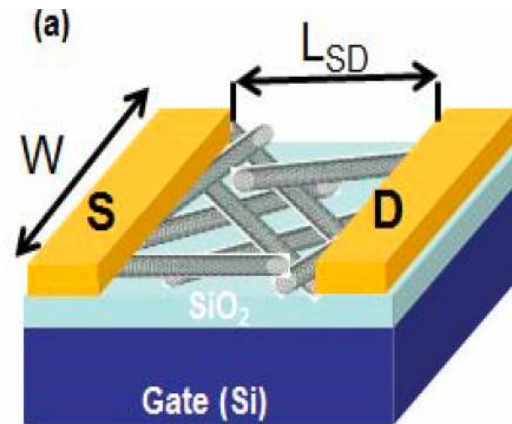
- HFCVD using SAM strategy
- networks of SWNT (few dozens)
- Source-drain palladium contacts
- UV lithography, e-beam evaporation and lift-off processes
- Burning of the metallic SWNT



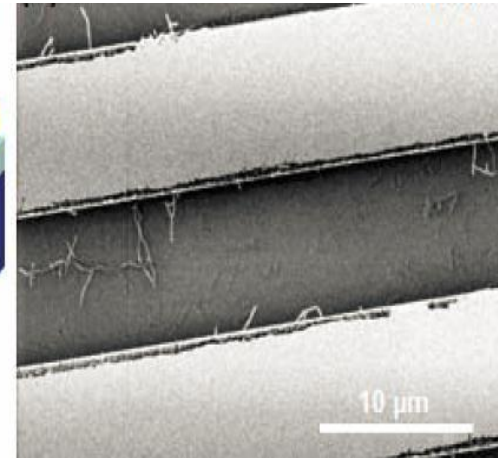
SEM image of grown SWNT



Raman spectrum of grown SWNT

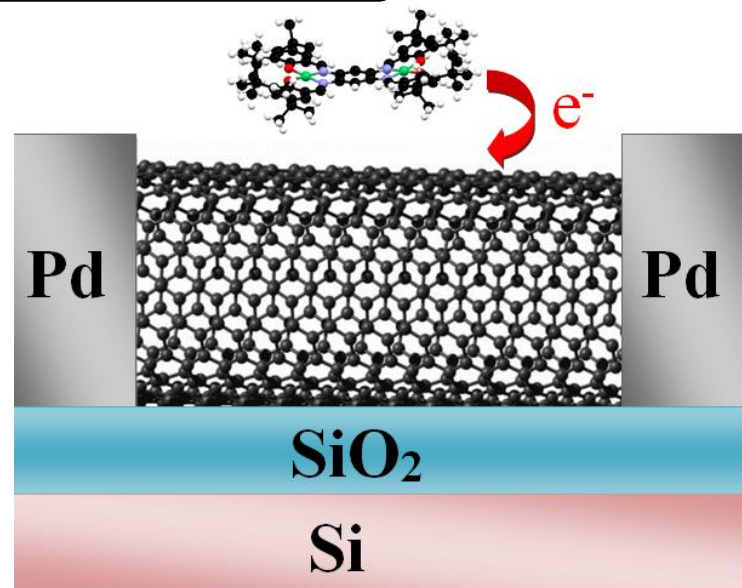
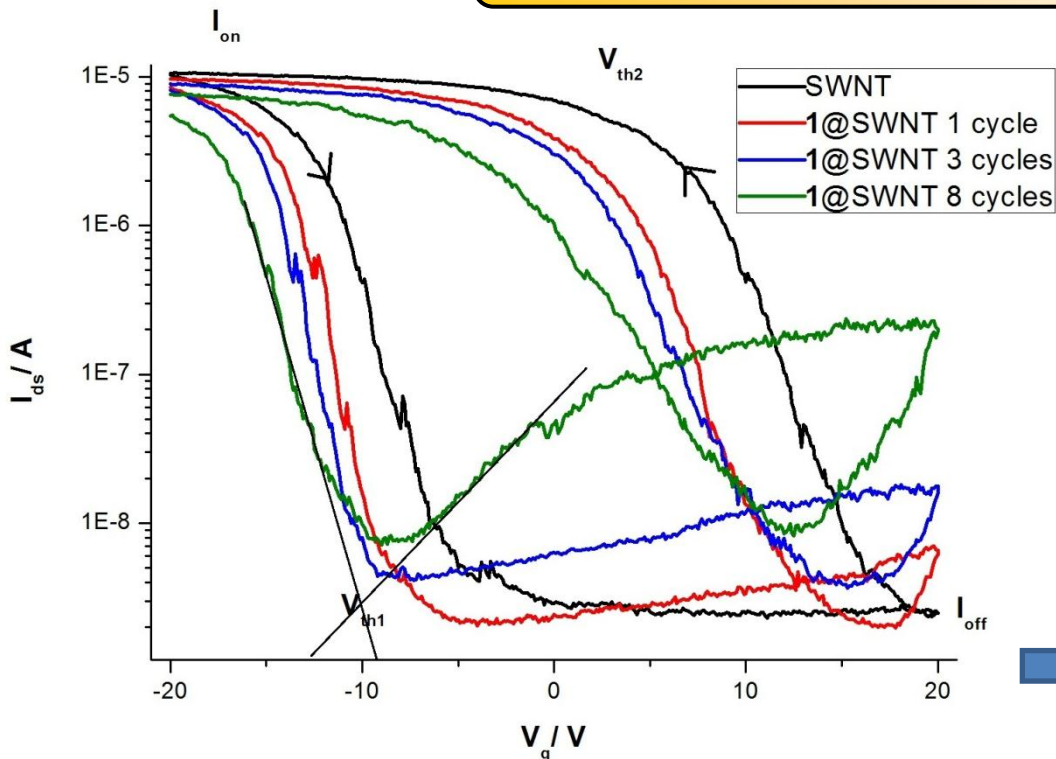


Schematic view of the SWNT-FET



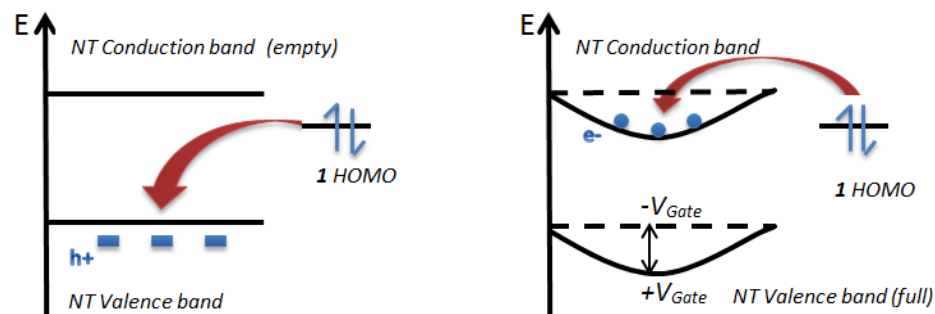
SEM image showing the gate region of a device (large number of SWNTs)

Transport properties at 300 K

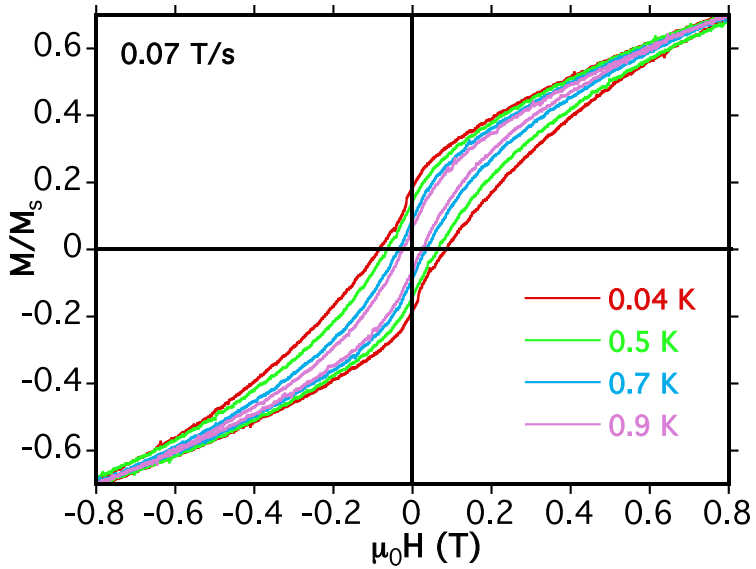


Electron transfer from 1 to the NT

Band theory explanation:



- Repeated grafting cycles
- Gate Potential shifts toward low values
- Increasing ambipolar effect (transition from p to n-type transistor)



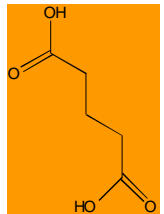
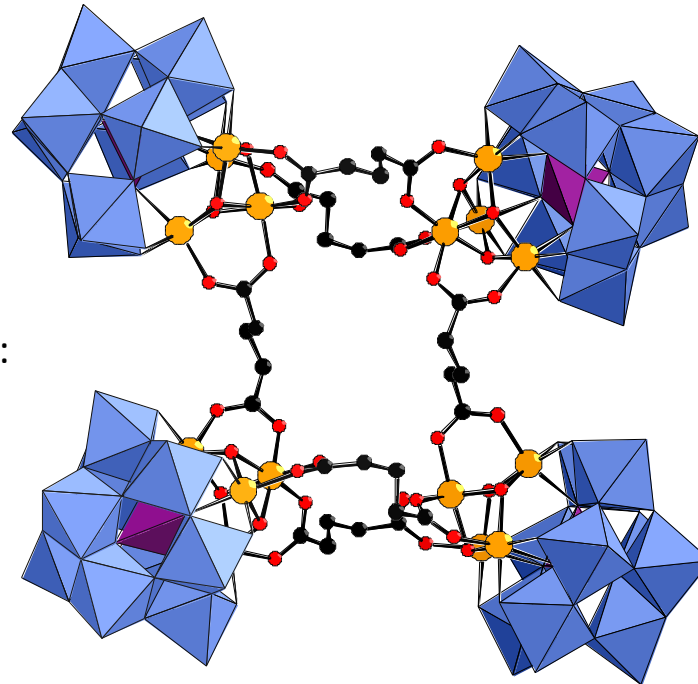
→ Individual molecules present slow relaxation of magnetization

Hybrid magnetic POMs?

- Reinforcement and/or control of the molecule/substrate interactions
- Introduction of functional groups (RAMAN active, etc...)

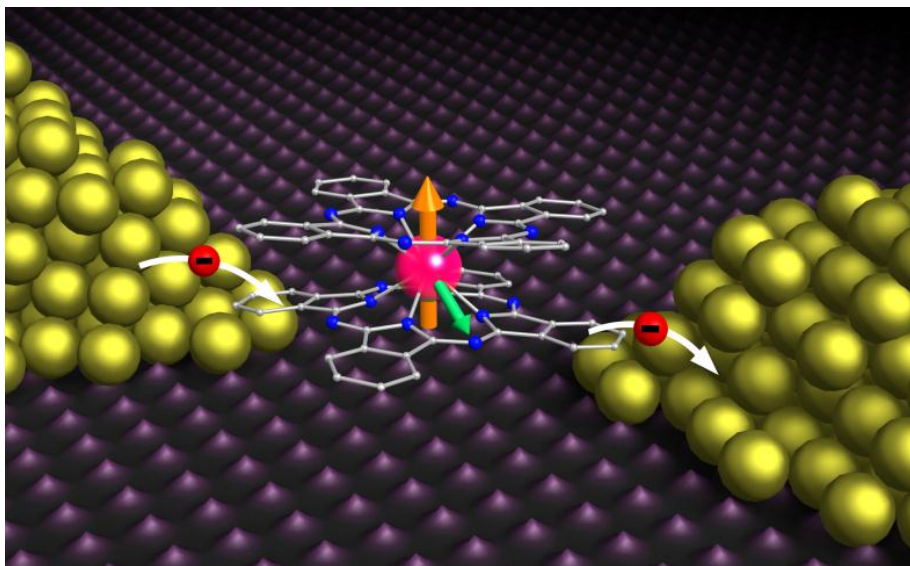
→ Elaboration of a whole family of carboxylato magnetic POM species

An example : a $\{Ni_{16}\}$ glutarate POM :



Résultats marquants et récents

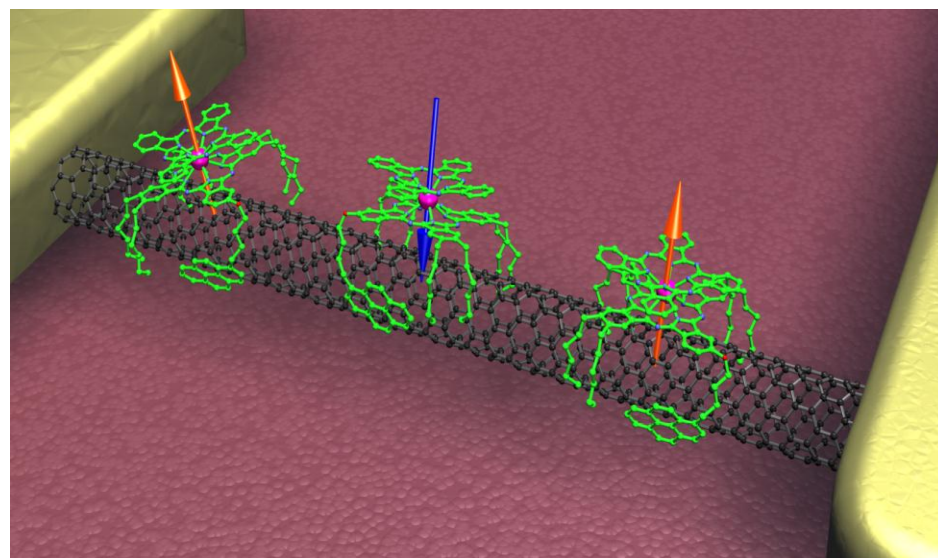
Molecular spin-transistor



Electronic read-out of a single nuclear spin using a molecular spin-transistor

R. Vincent, S. Klyatskaya, M. Ruben, W. Wernsdorfer & F. Balestro, *Nature* 488, 357 (2012)

Molecular spin-valve



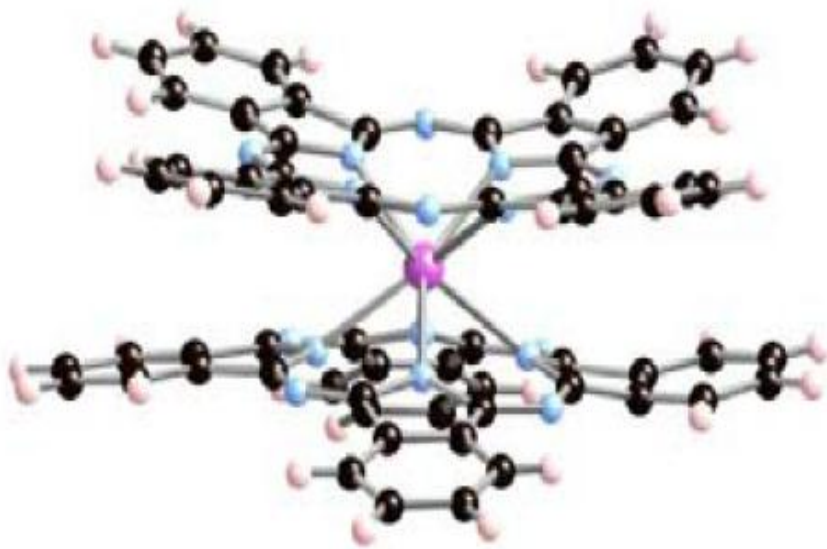
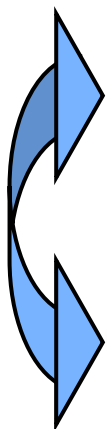
Supramolecular Spin Valves

M. Urdampilleta, S. Klyatskaya, J.-P. Cleuziou, M. Ruben & W. Wernsdorfer
Nature Mat. 10, 502 (2011)

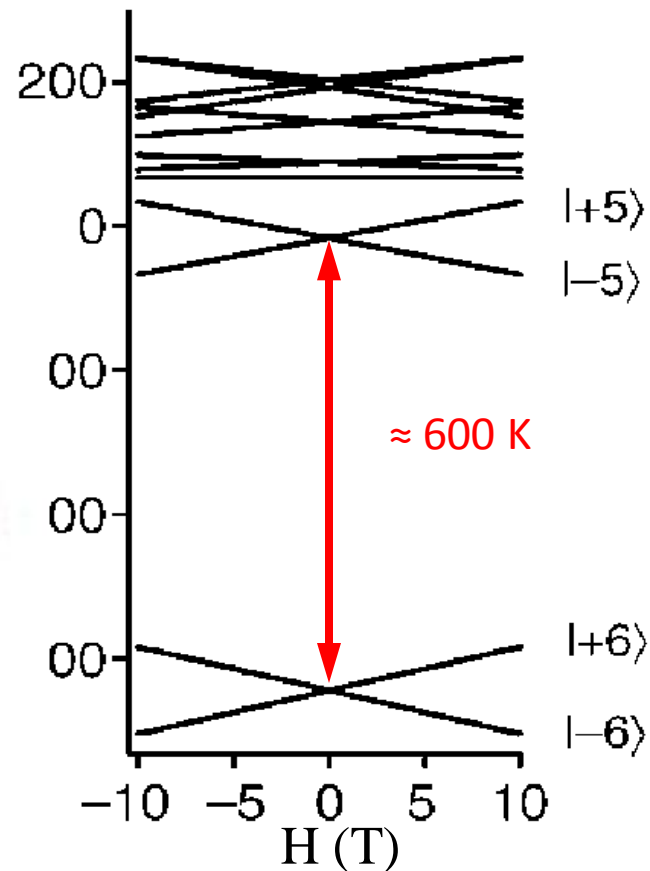
Lanthanide Single-Molecule Magnets

Bis(phthalocyaninato)terbium

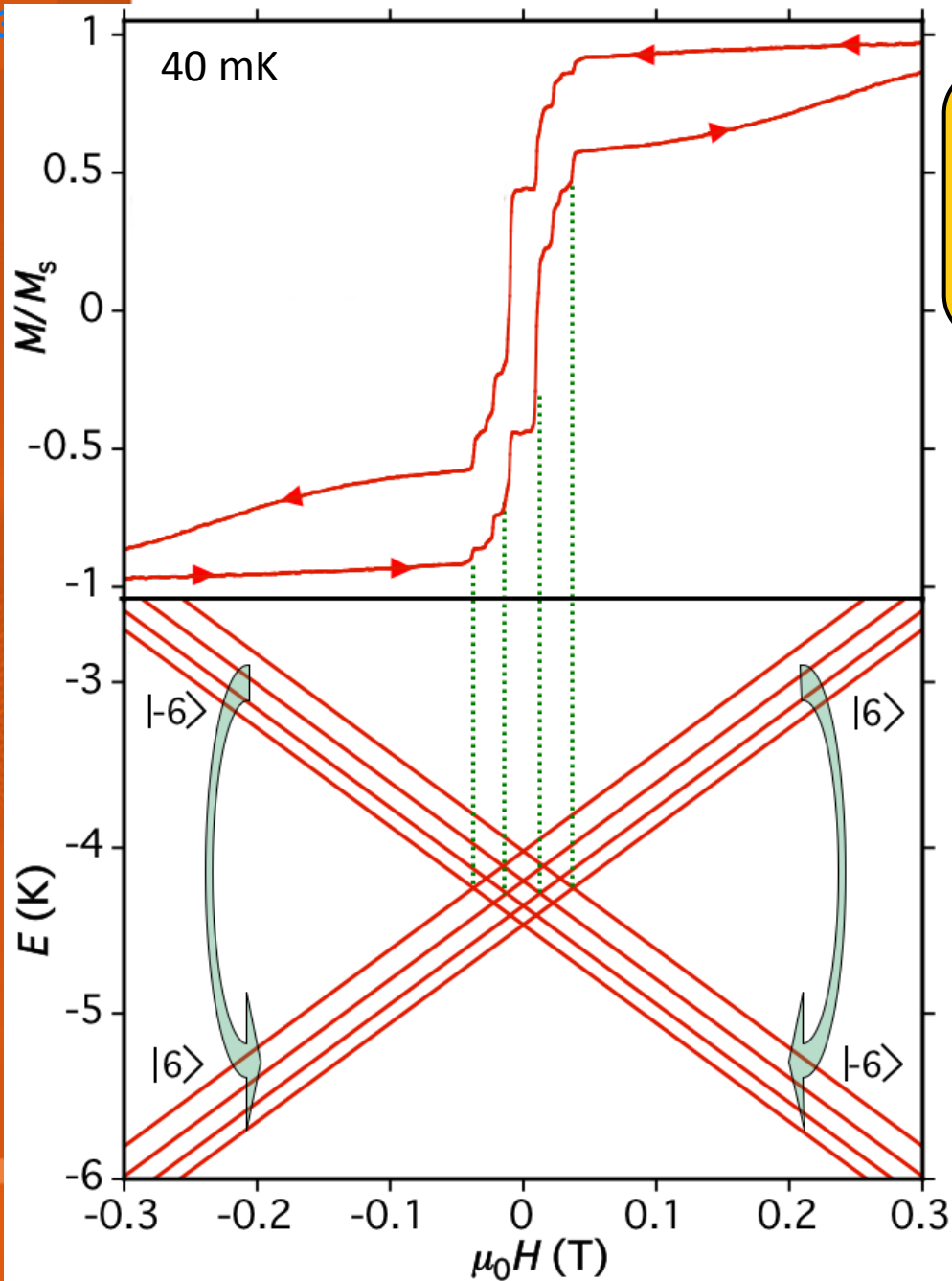
$S = 1/2$
radical



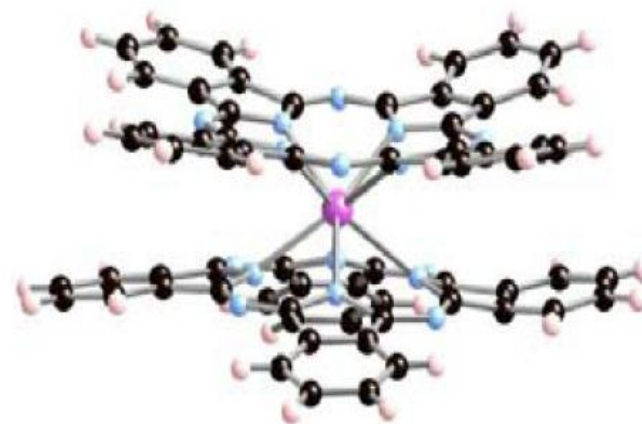
Tb^{3+} anisotropic spin $J = 6$



N. Ishikawa, M. Sugita, W. Wernsdorfer,
Angew. Chem. Int. Ed. 44, 2 (2005), J. Am. Chem. Soc. 127, 3650 (2005)

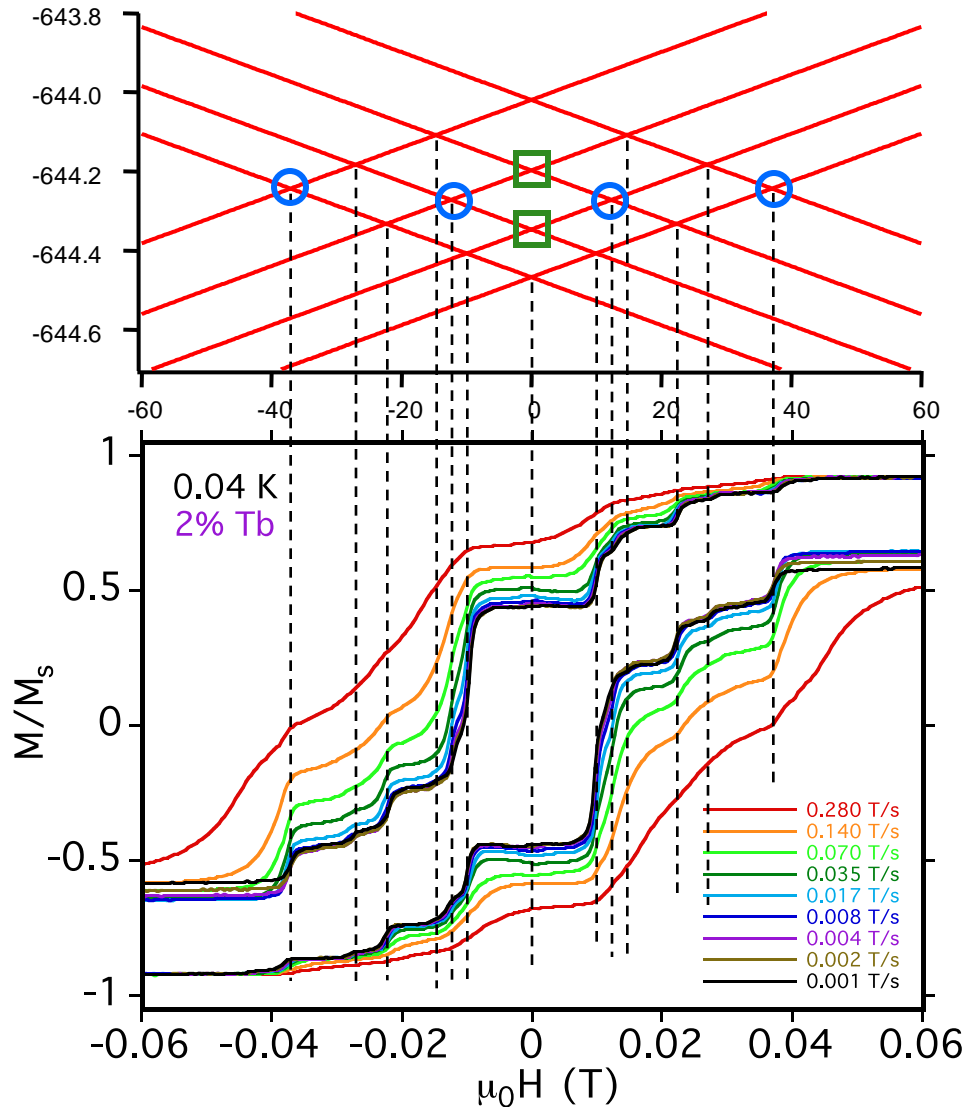


Quantum Tunneling of Magnetization in Lanthanide SMMs



N. Ishikawa, M. Sugita,
W. Wernsdorfer, *Angew.
Chem. Int. Ed.* 44, 2 (2005)

$$H = \text{Zeeman} + \text{LF term} + A_{\text{hf}}\mathbf{J}\cdot\mathbf{I} + P_{\text{quad}}\{I_z^2 + (1/3)\mathbf{I}(\mathbf{I}+1)\}$$



$$A_{\text{hf}} = 0.0173 \text{ cm}^{-1}$$

$$P_{\text{quad}} = 0.010 \text{ cm}^{-1}$$

○ : avoided crossing occurs by off-diagonal LF term

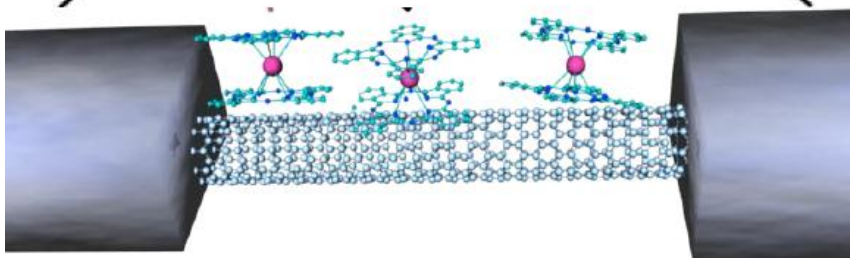
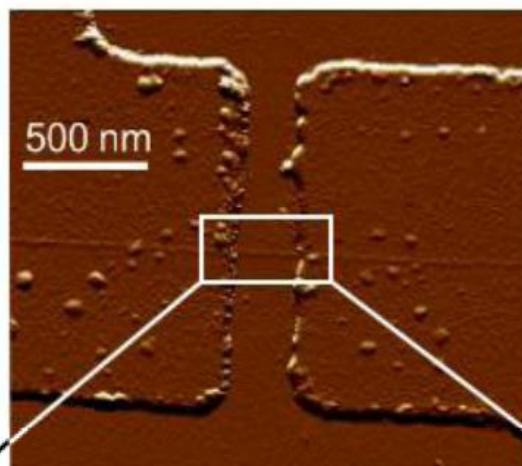
□ : avoided crossing occurs by transverse field

Others: avoided crossing does not occur by either LF terms nor transverse field

N. Ishikawa, M. Sugita,
W. Wernsdorfer, *Angew. Chem. Int. Ed.* 44, 2 (2005)
and *J. Am. Chem. Soc.* 127,
3650 (2005)

Devices

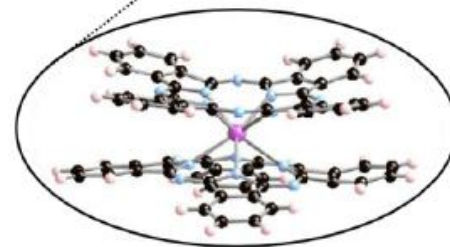
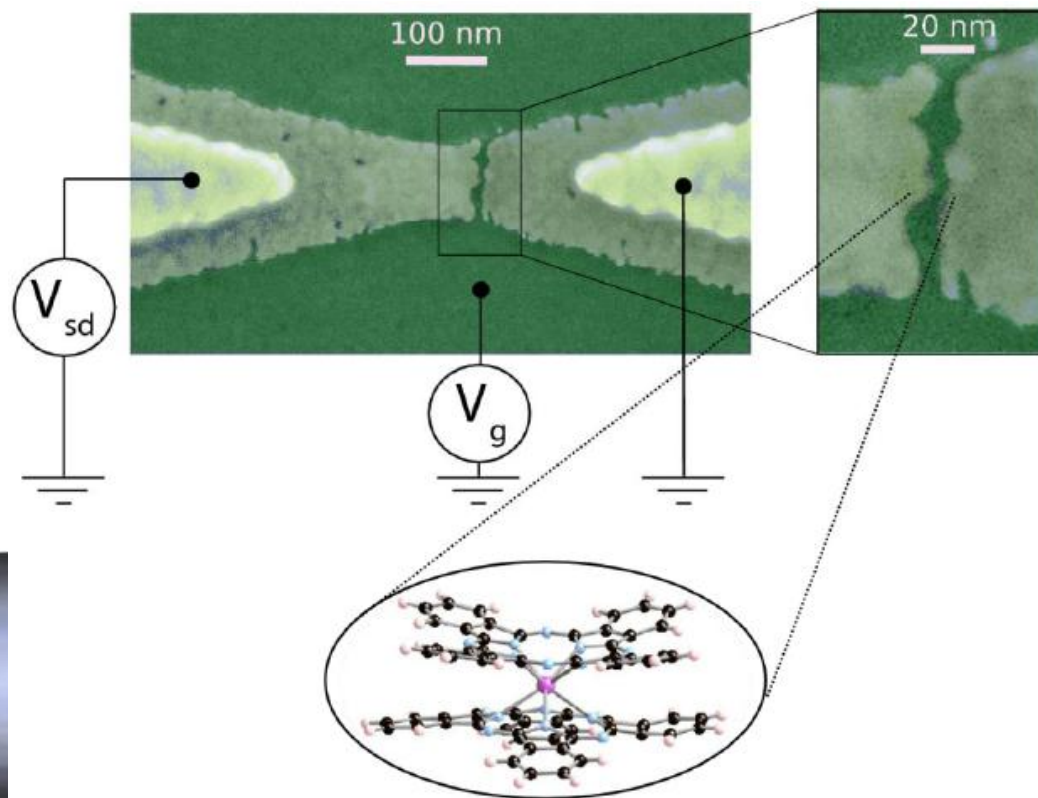
Molecular spin-valve



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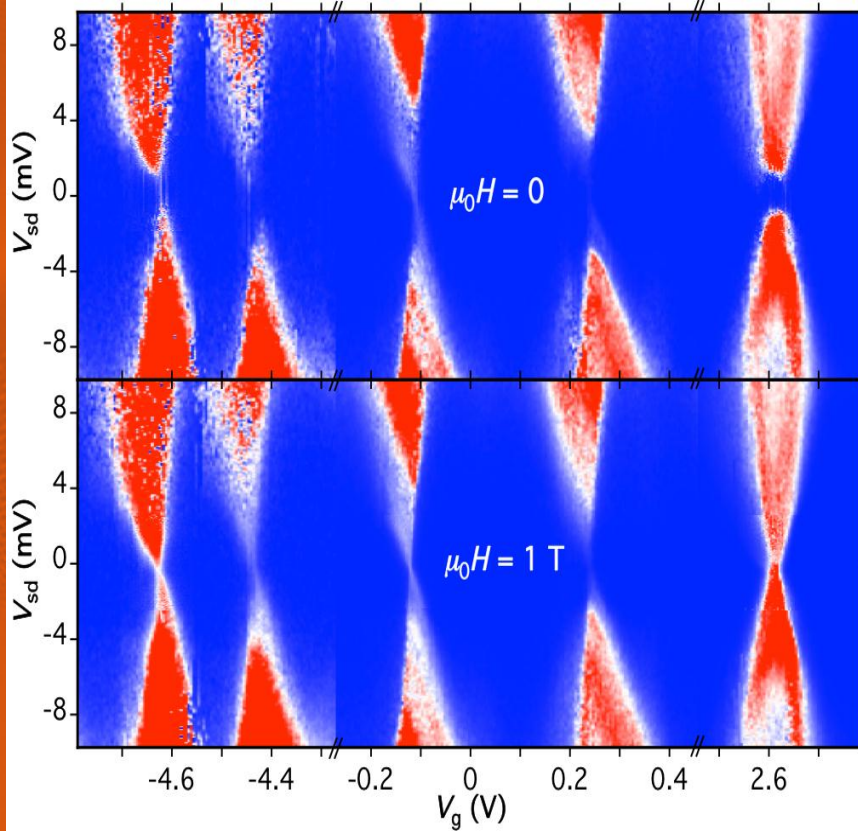
Molecular spin-transistor



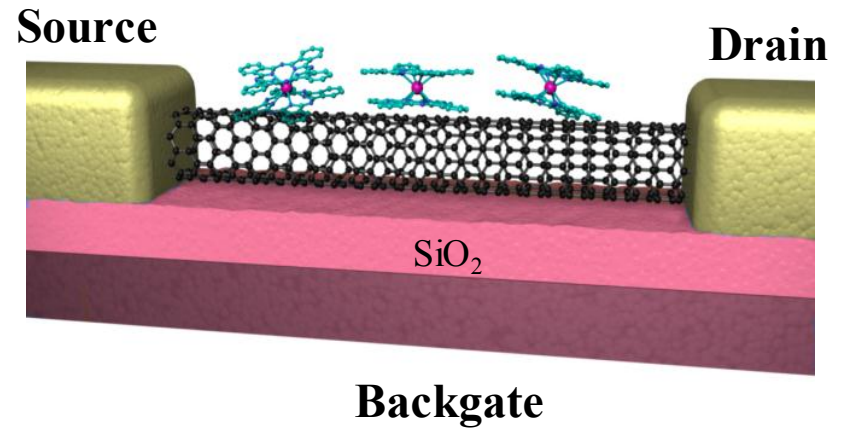
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Device characteristics



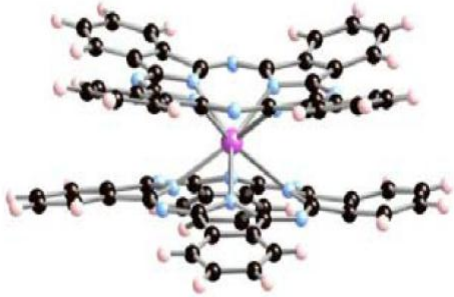
$T = 40$ mK



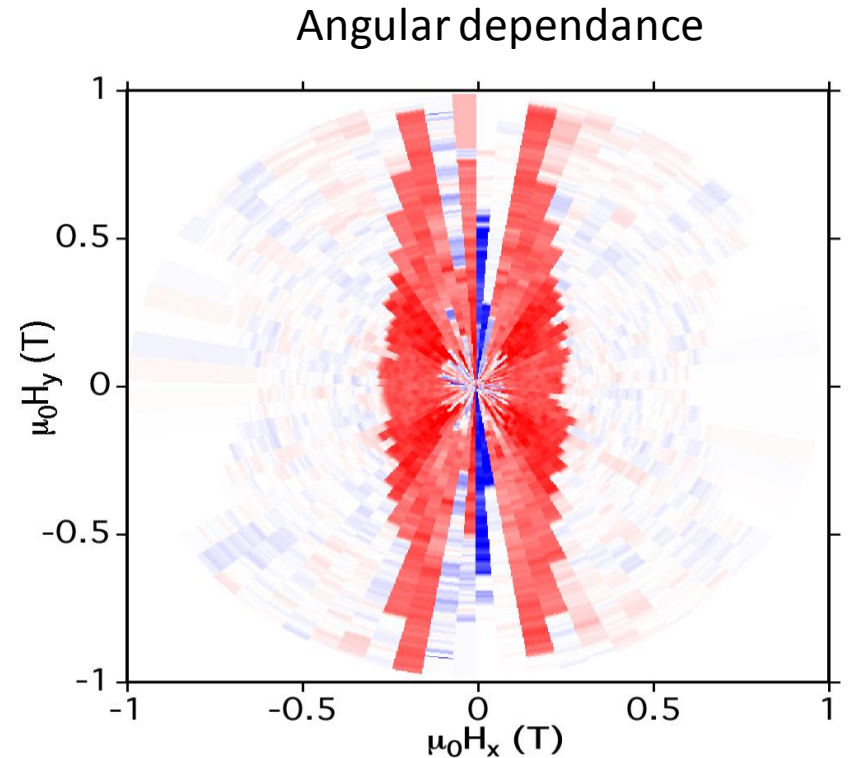
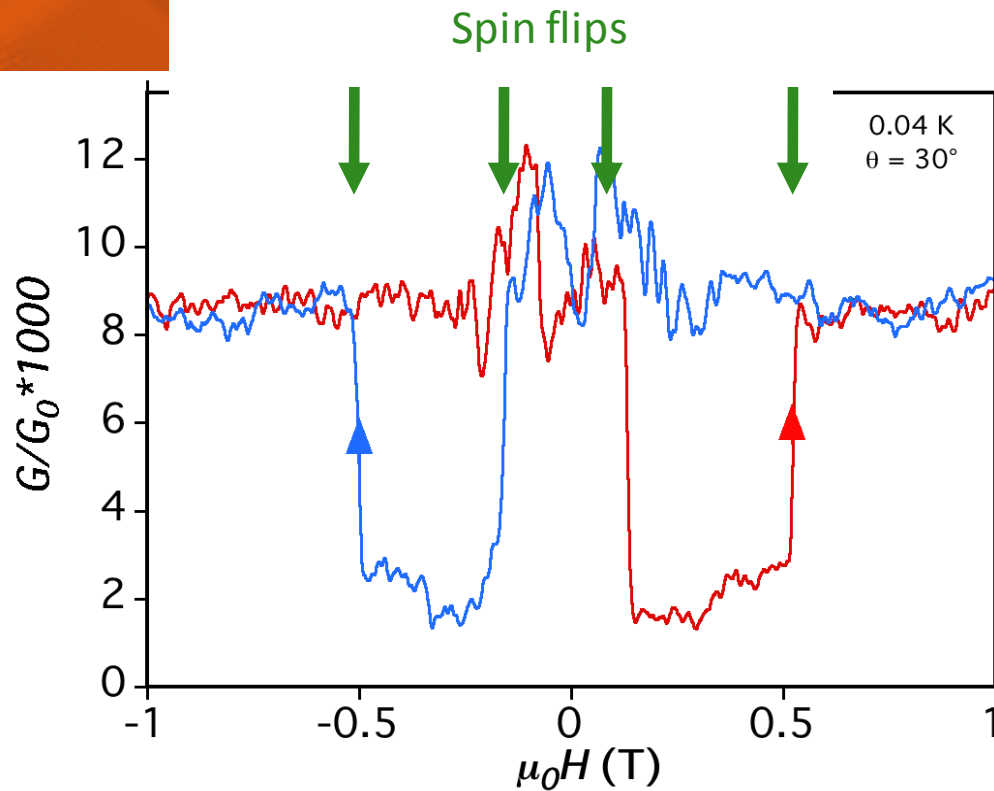
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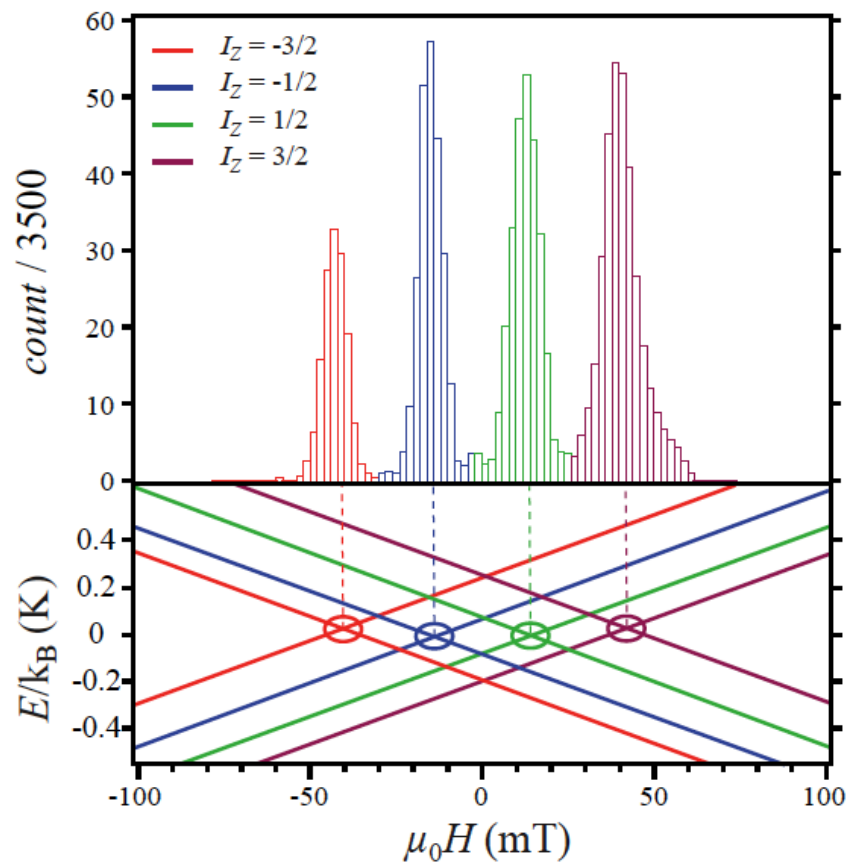
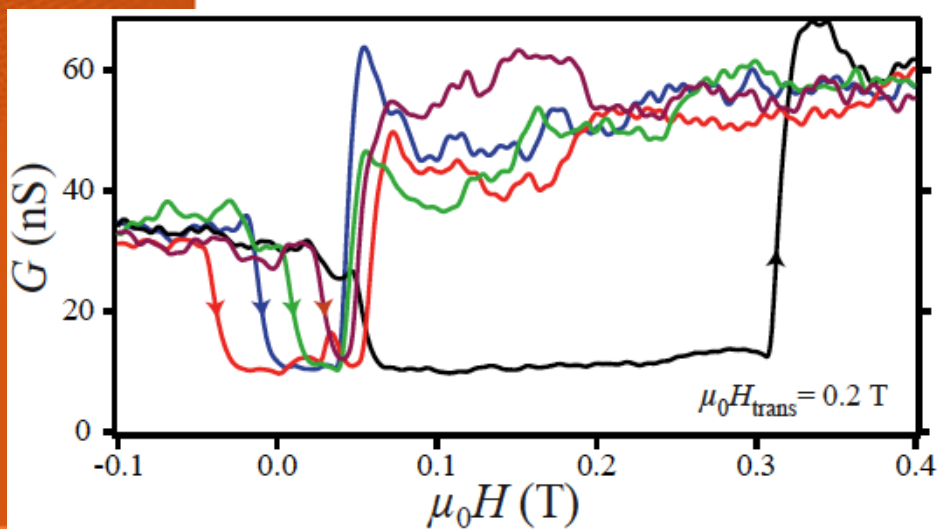
SMM spin reversal detection



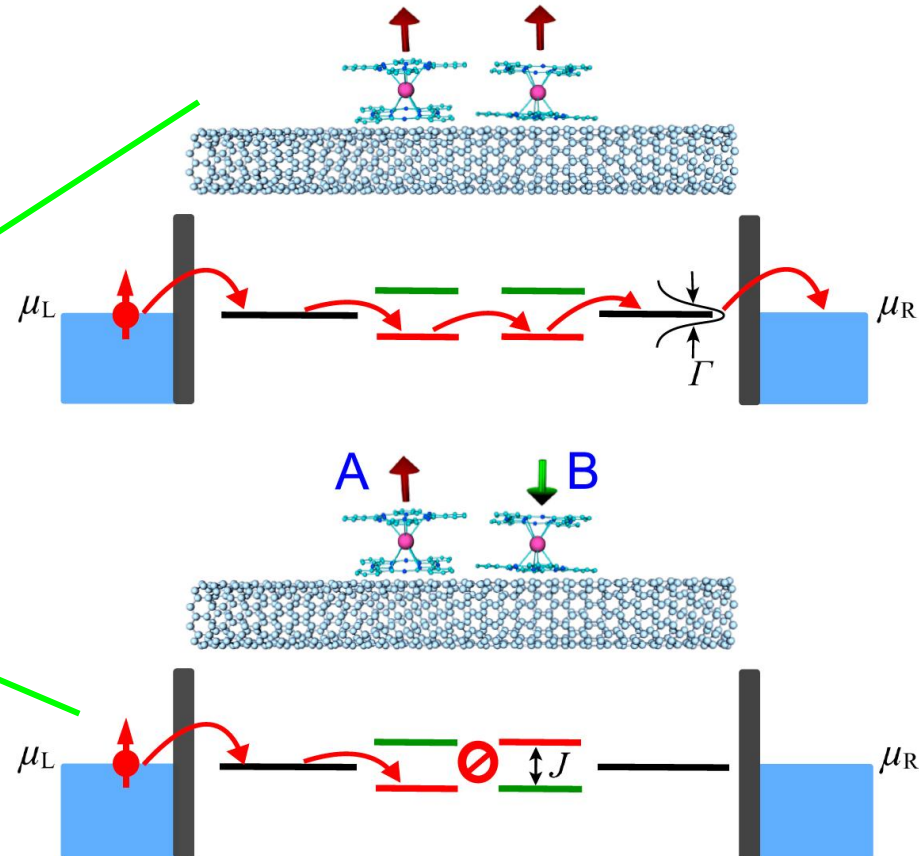
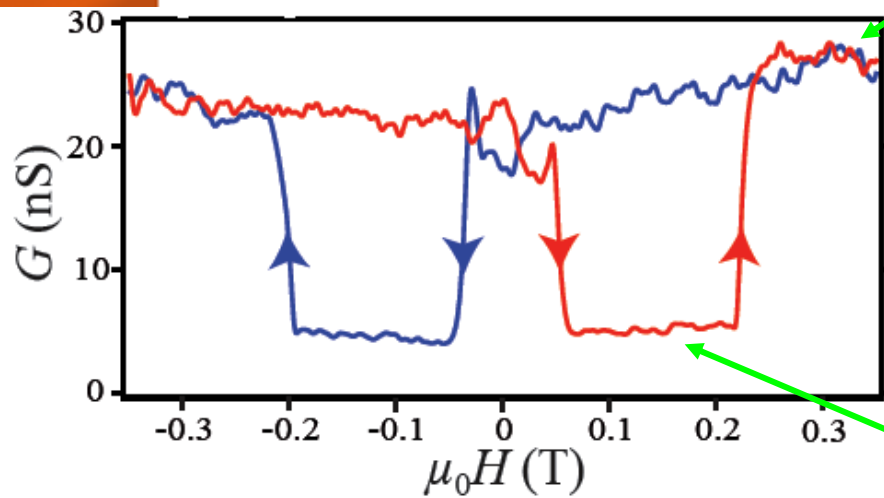
conductance
close to a degeneracy point



Quantum Tunneling of Magnetization at avoided level crossings corresponding to the four nuclear spin states



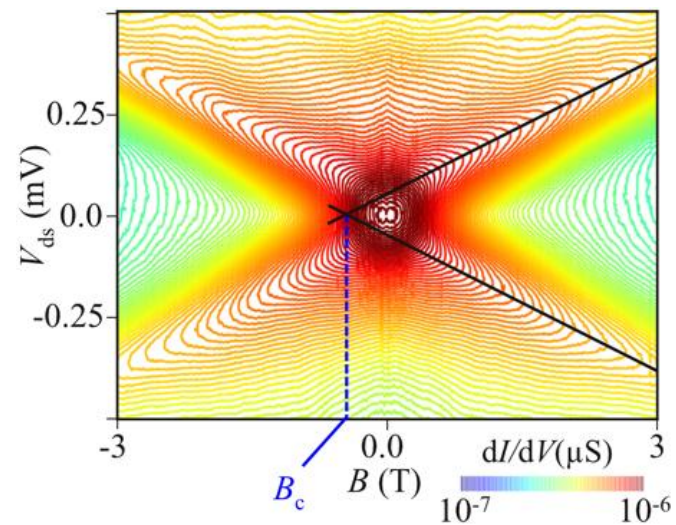
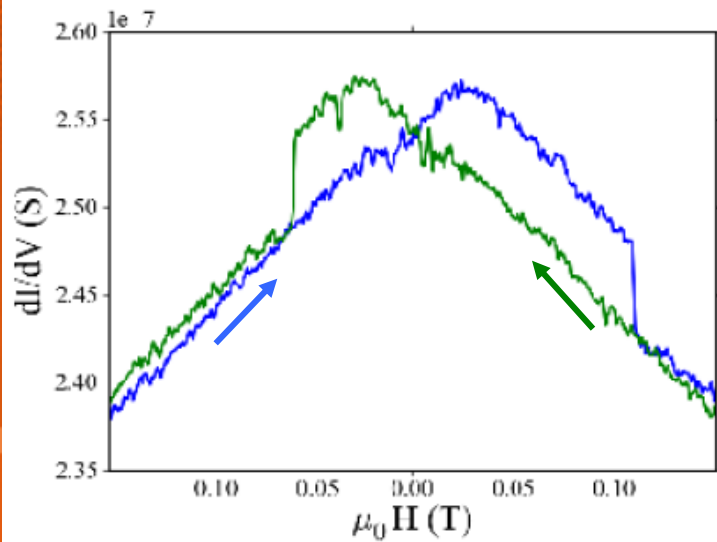
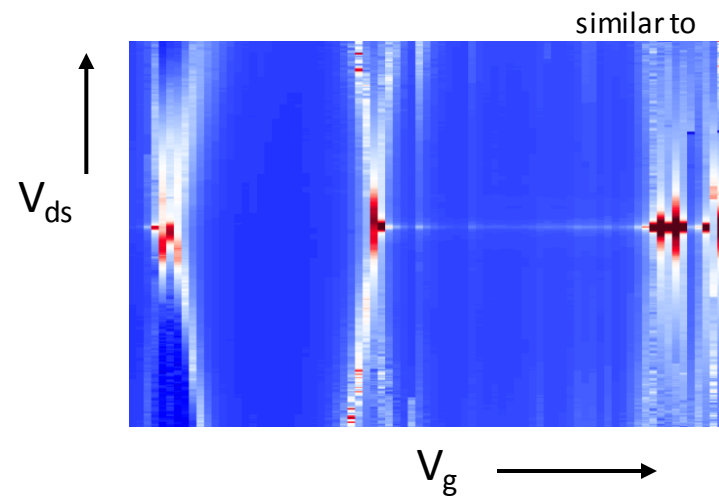
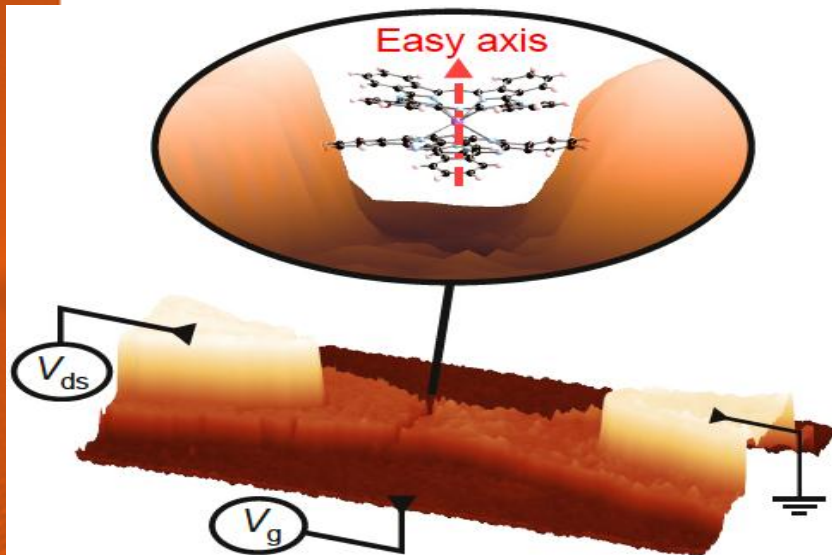
Spin valve behavior



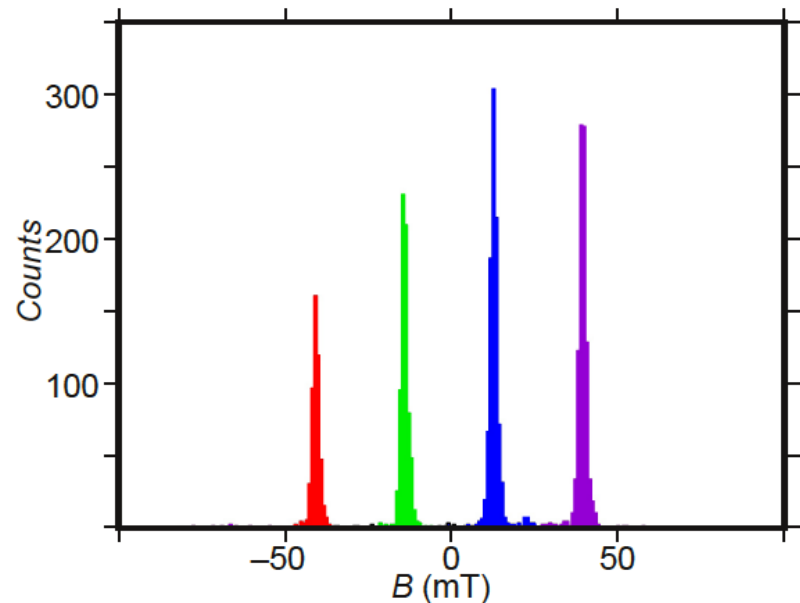
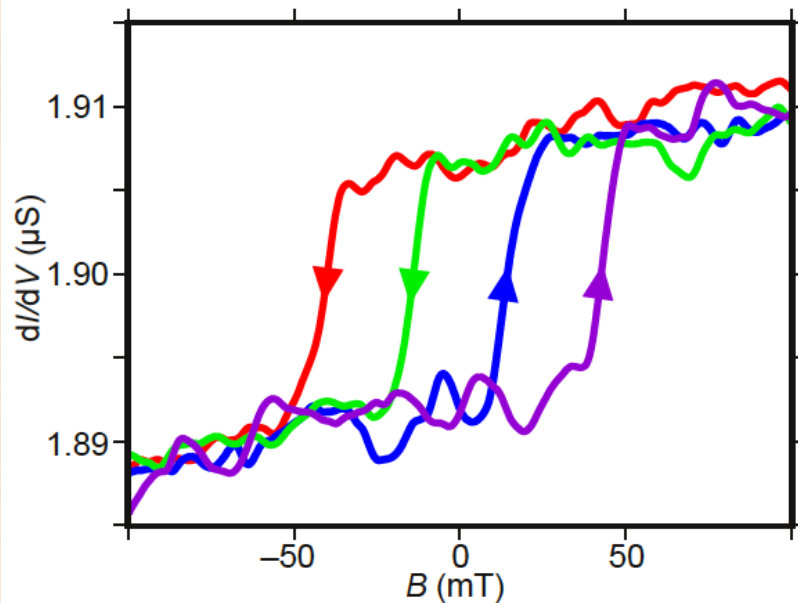
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Device characteristics



Statistics of conductance jumps



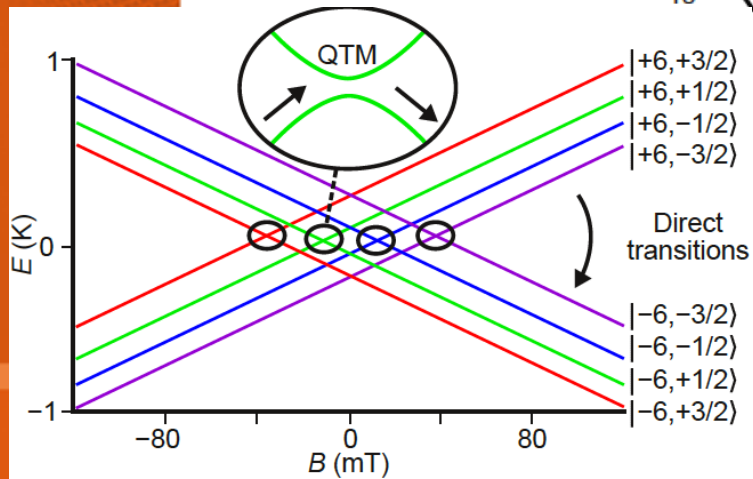
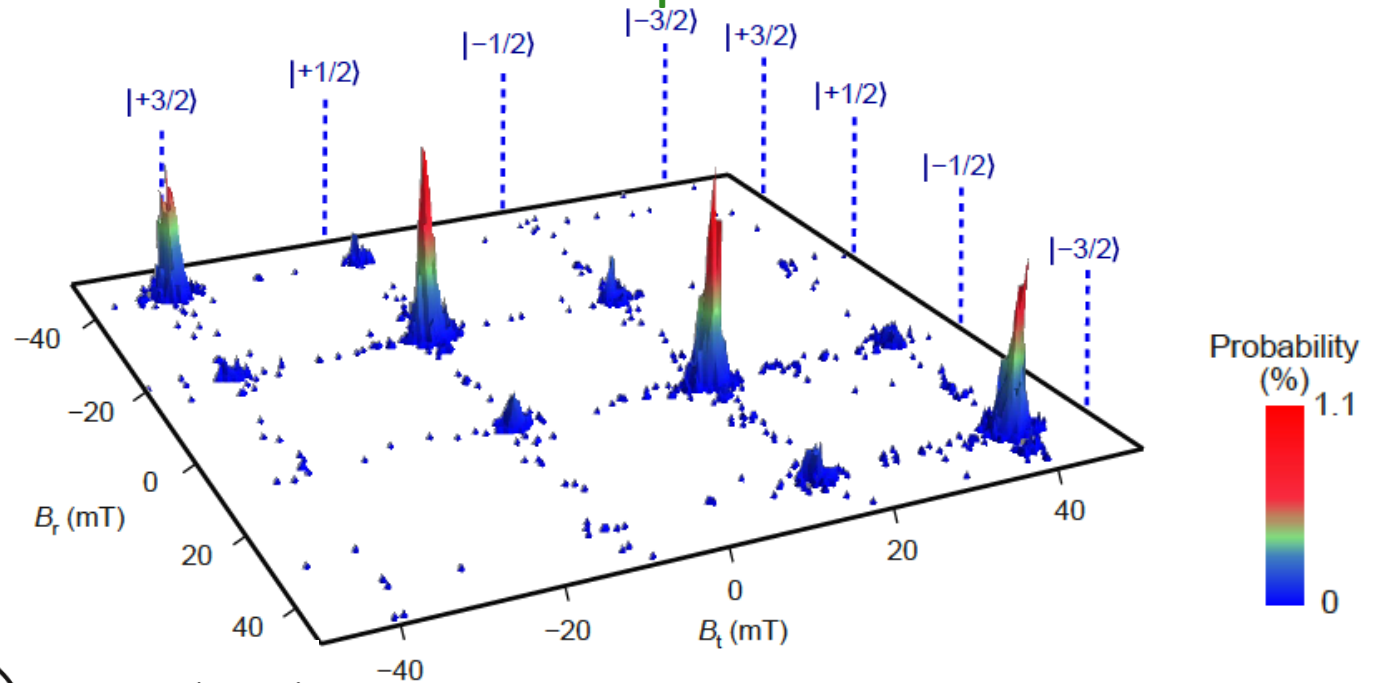
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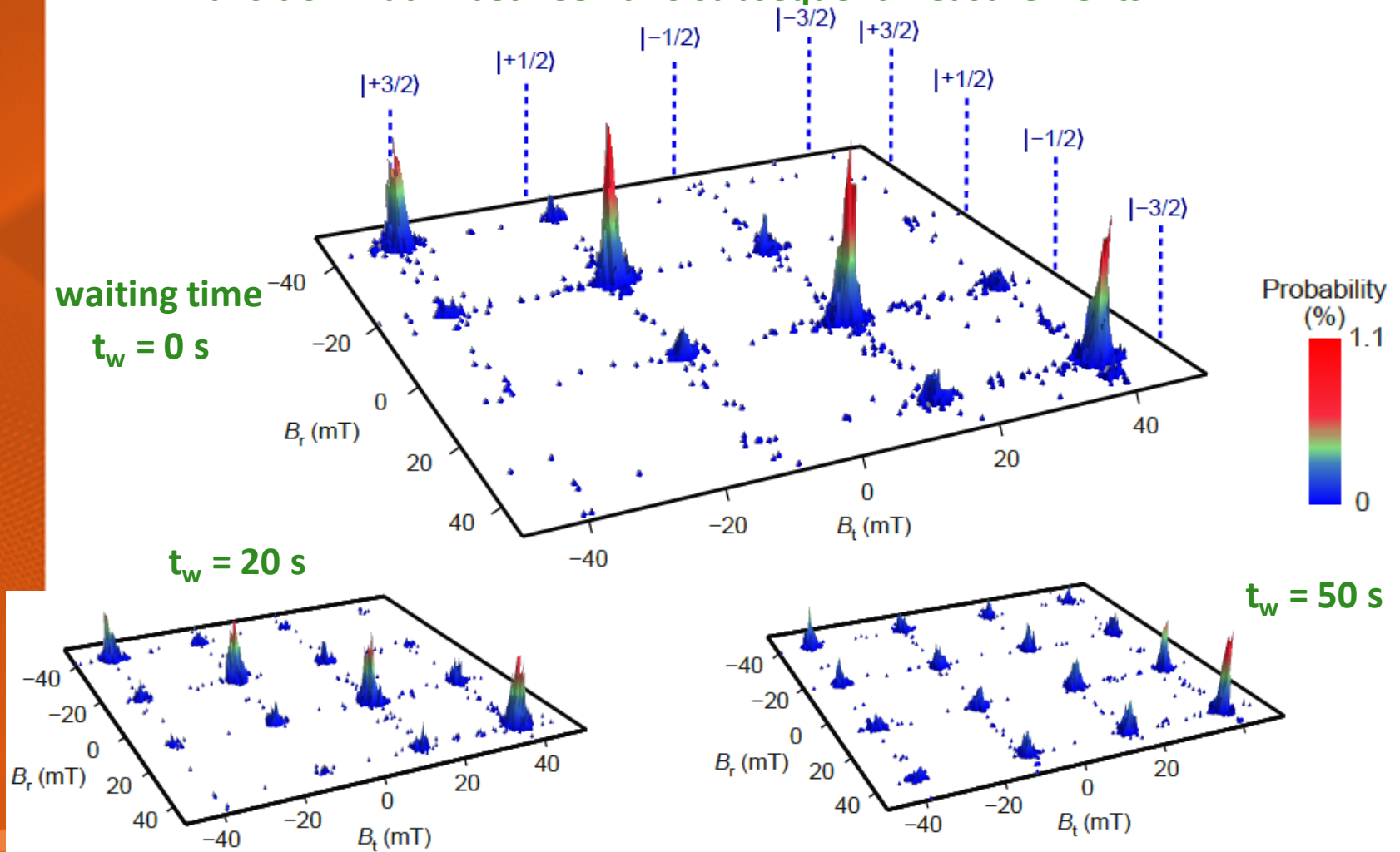
Single Nuclear Spin Detection

Transition matrix between two subsequent measurements



Single Nuclear Spin Detection

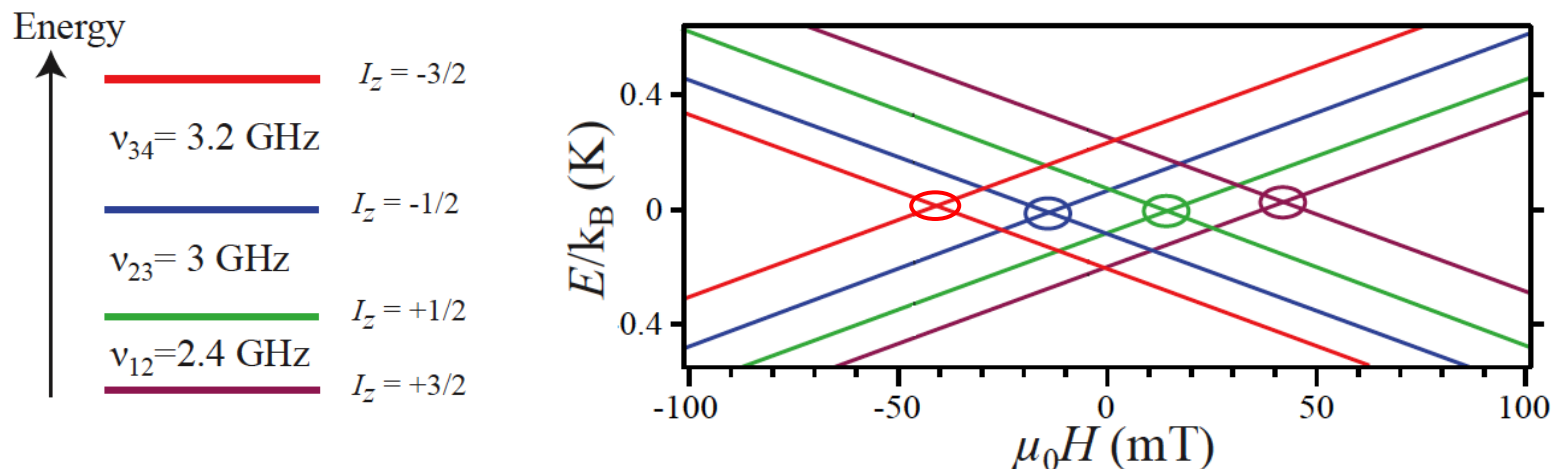
Transition matrix between two subsequent measurements



Lifetime of the order of 10 seconds !

Project:

TbPc₂ might be an excellent candidate to perform the Grover algorithm



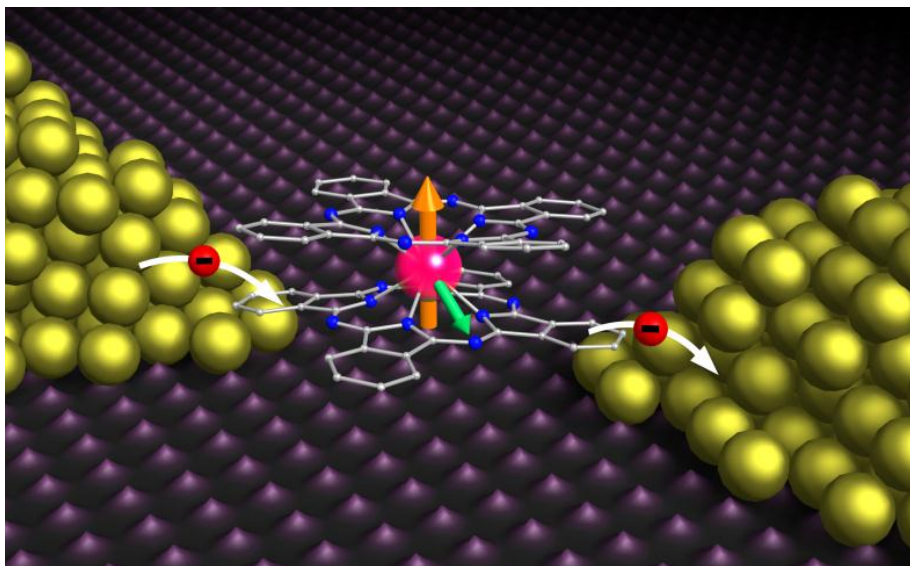
- synthesis of perfectly identical SMMs
- different energy-level spacing
- observation of long energy-level lifetimes (≈ 10 s)

The Grover algorithm with large nuclear spins in semiconductors

Leuenberger, M. N. & Loss, D., Phys. Rev. B 68, 165317 (2003)

Résultats marquants et récents

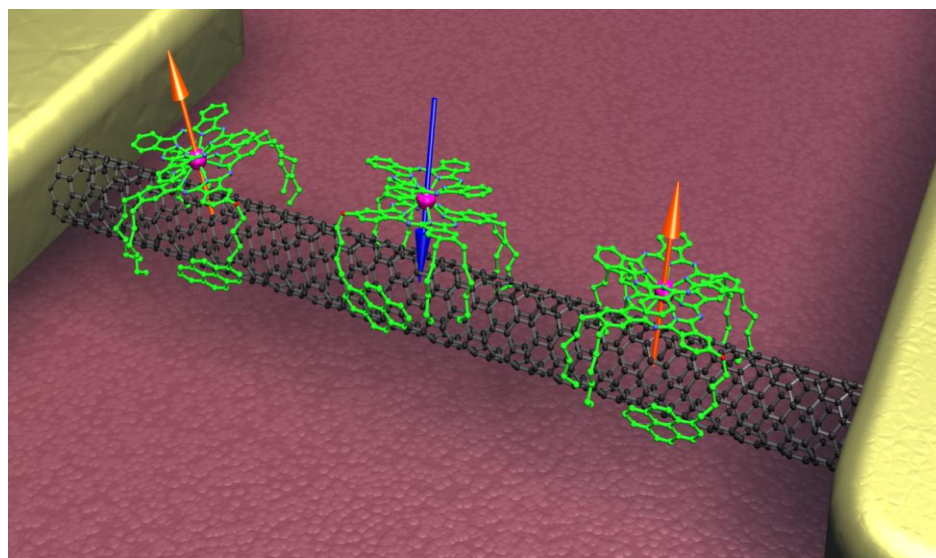
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Molecular spin-valve



Supramolecular Spin Valves

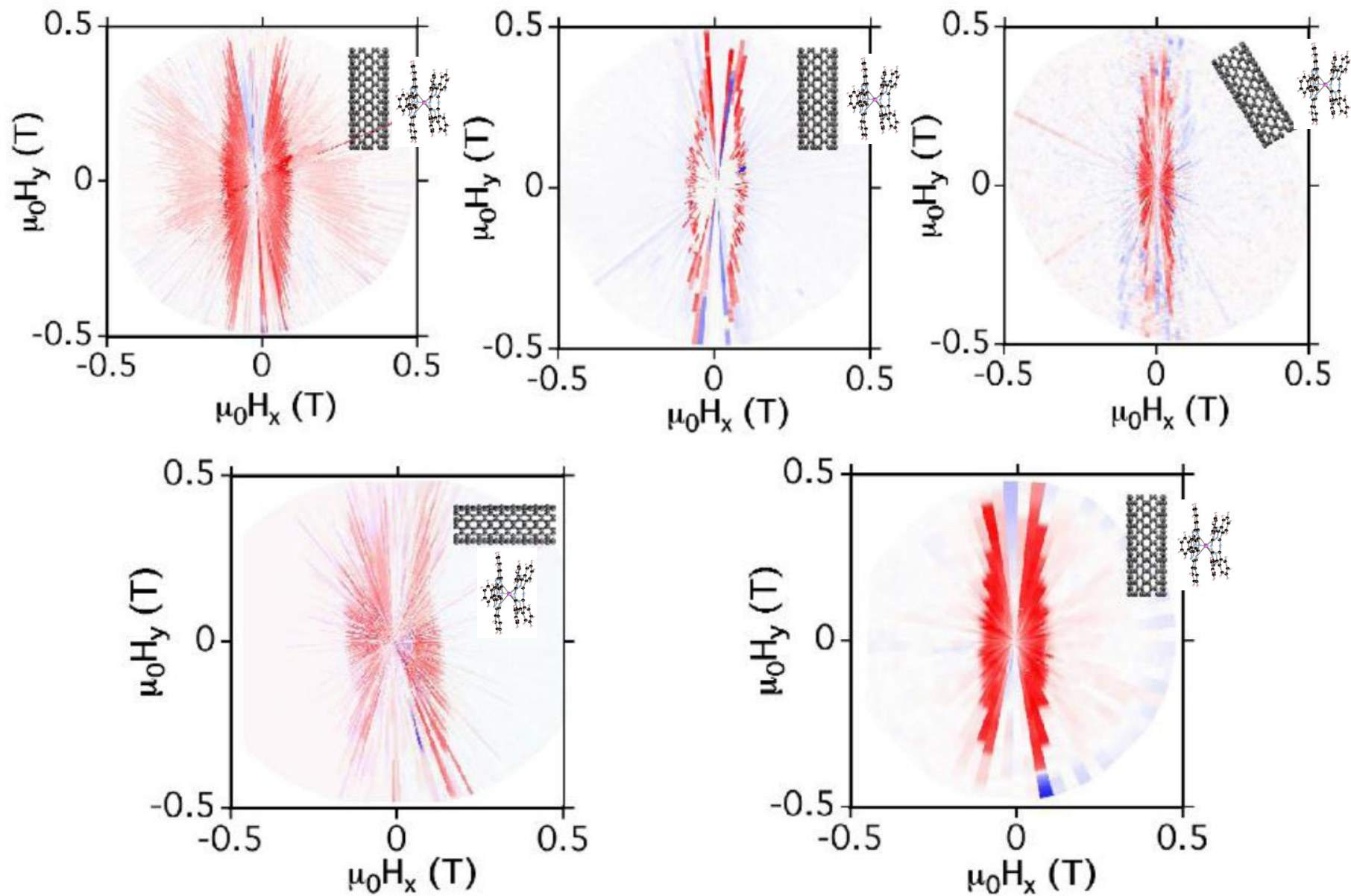
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Quelques indicateurs d'impact (production scientifique, brevets, recrutements...)

- > 100 publications
- > 8 joint publications
- > 60 joint presentations
- 1 thésard
- 5 post-docs

Merci !!

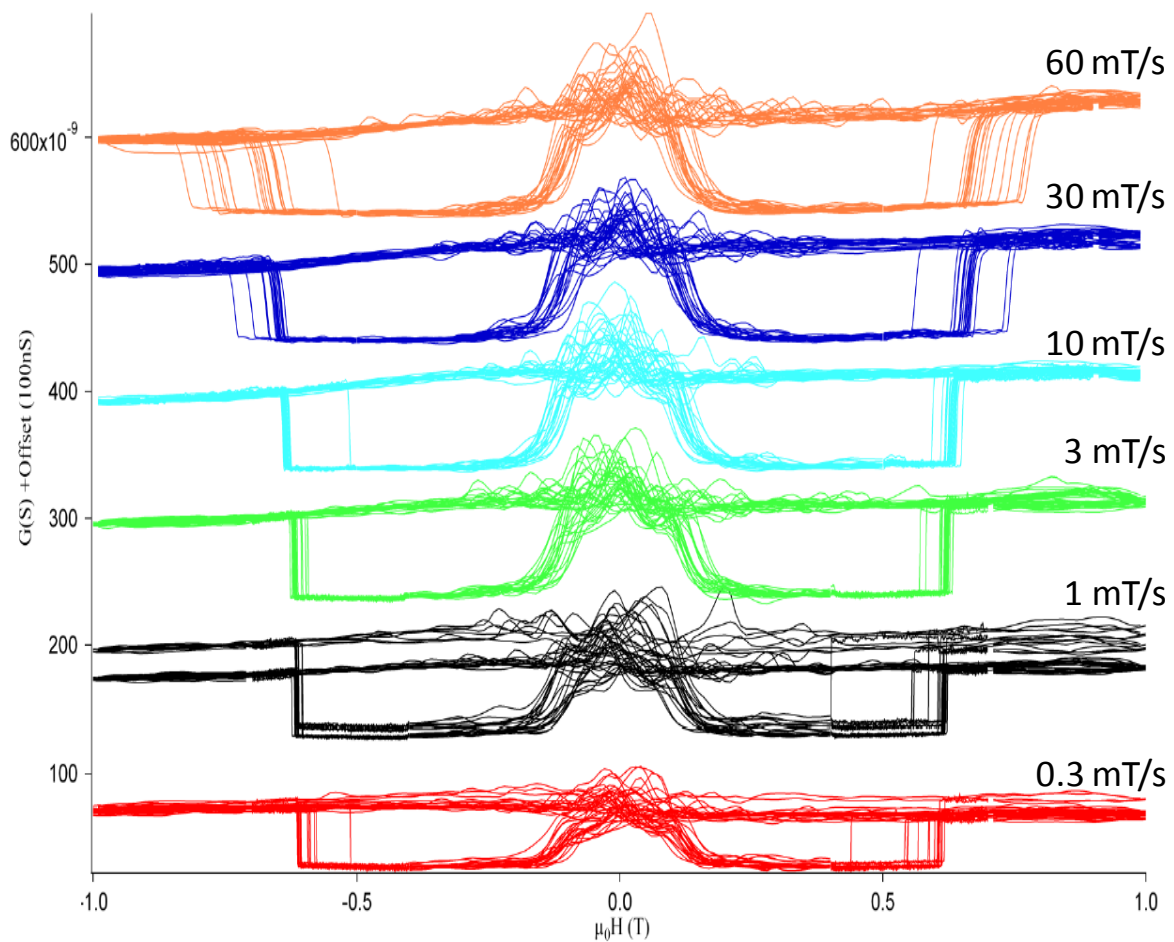
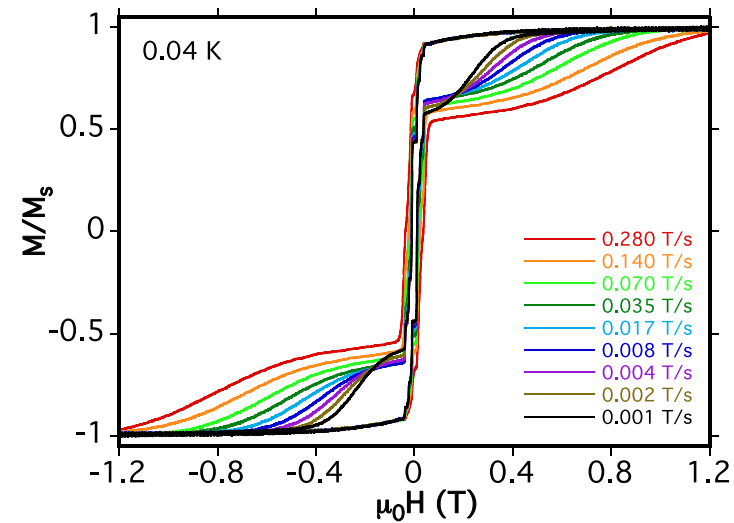
Anisotropy - molecule orientation



Field sweep rate dependence

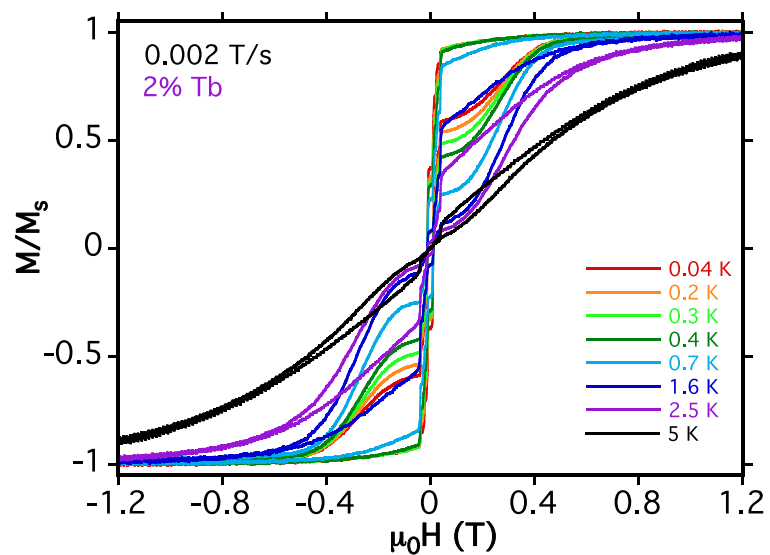
Crystal of 2% of TbPc_2

Supramolecular Spin Valves

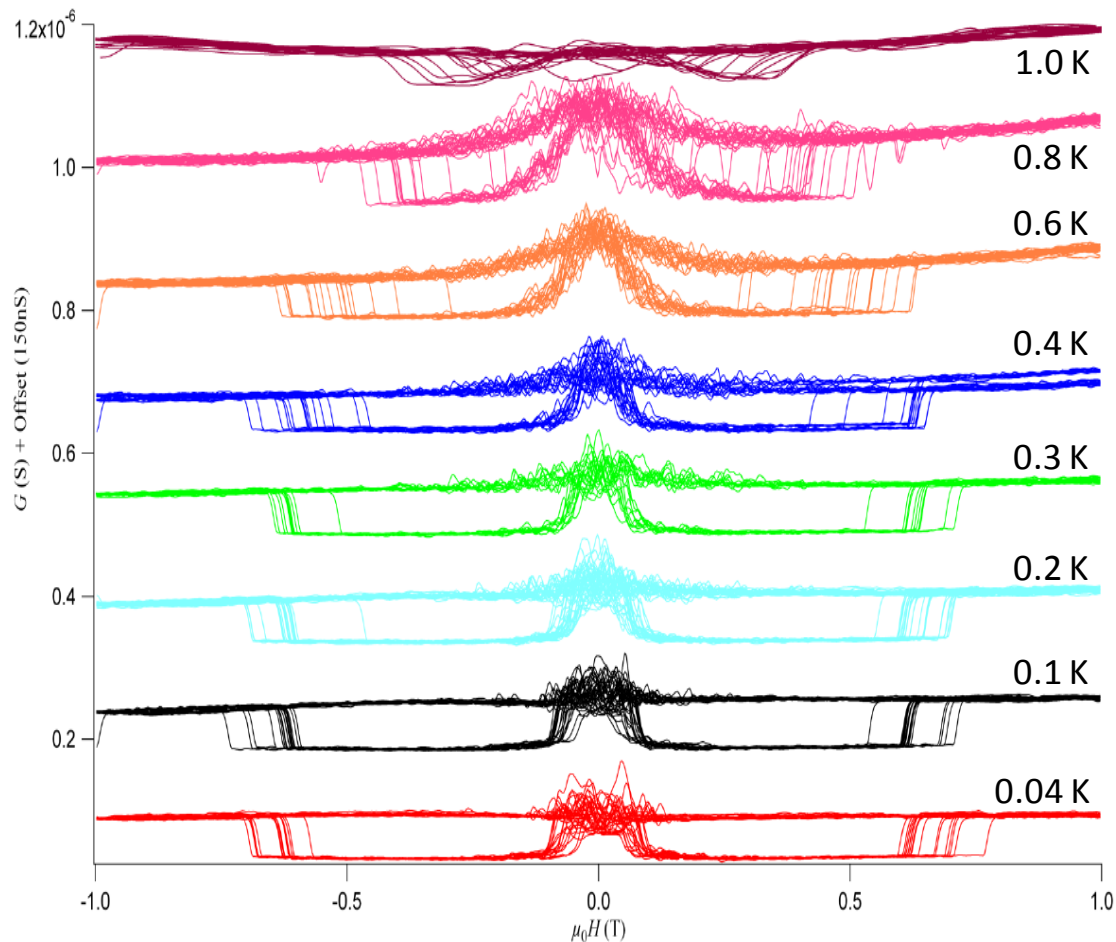


Temperature dependence

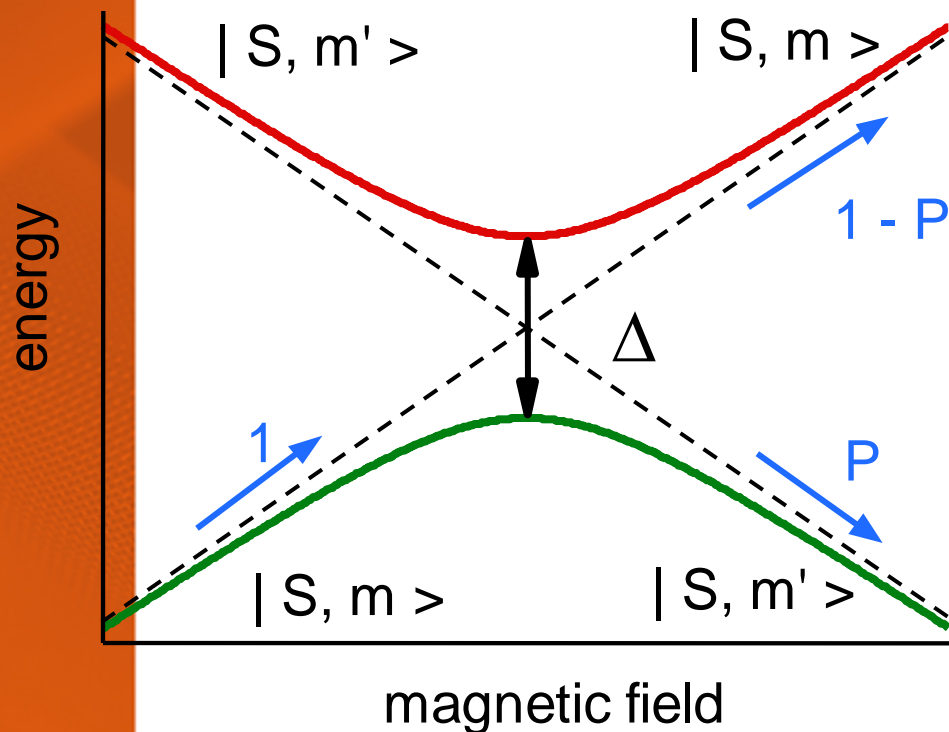
Crystal of 2% of TbPc₂



Supramolecular Spin Valves



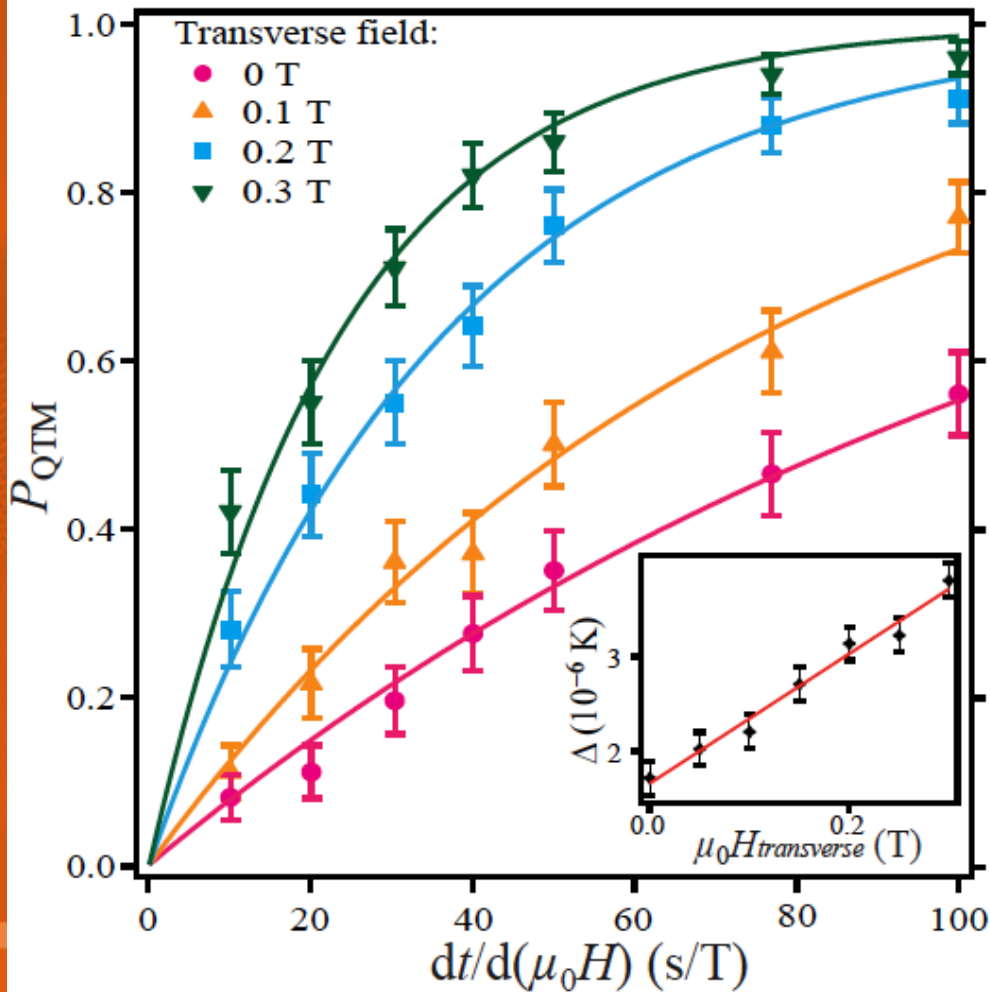
Tunneling probability at an avoided level crossing Landau-Zener model (1932)



$$P = 1 - \exp\left[-c \frac{\Delta^2}{dH/dt}\right]$$

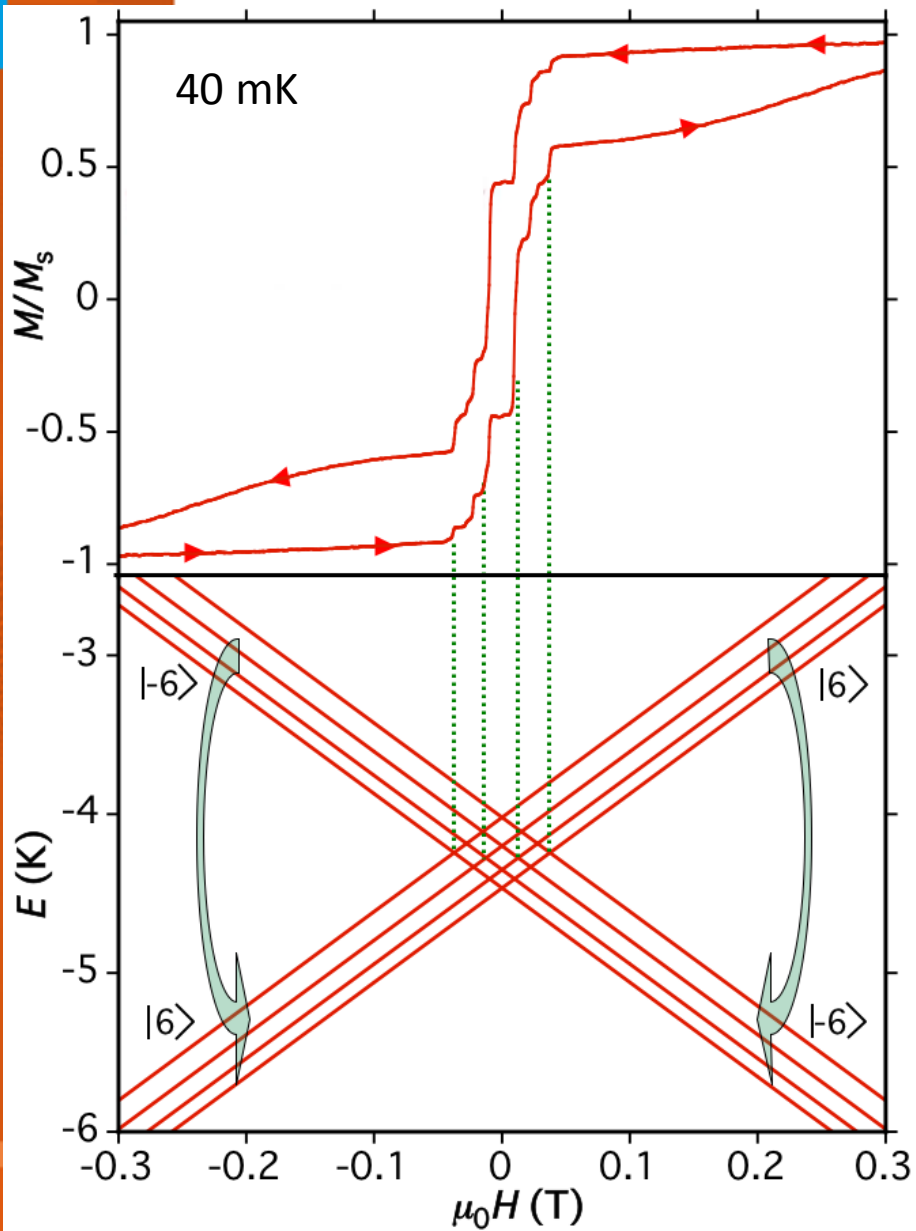
$$c = \frac{\pi}{2\hbar g\mu_B |m - m'| \mu_0}$$

Landau-Zener tunneling probability

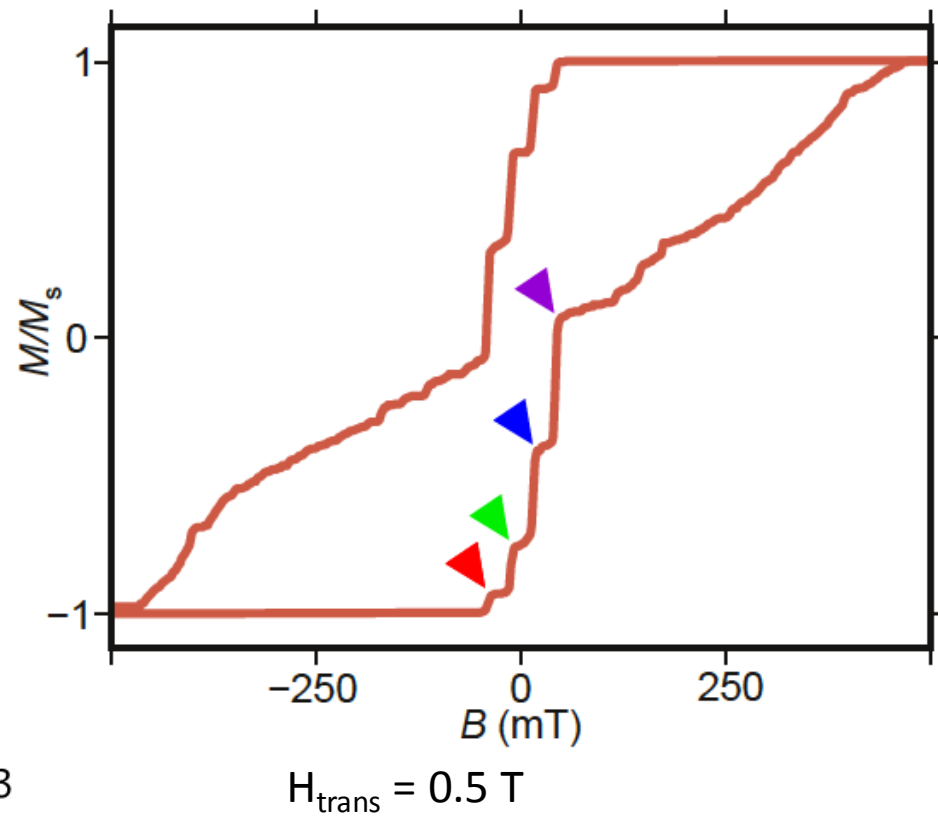


$$P = 1 - \exp\left[-c \frac{\Delta^2}{dH/dt}\right]$$

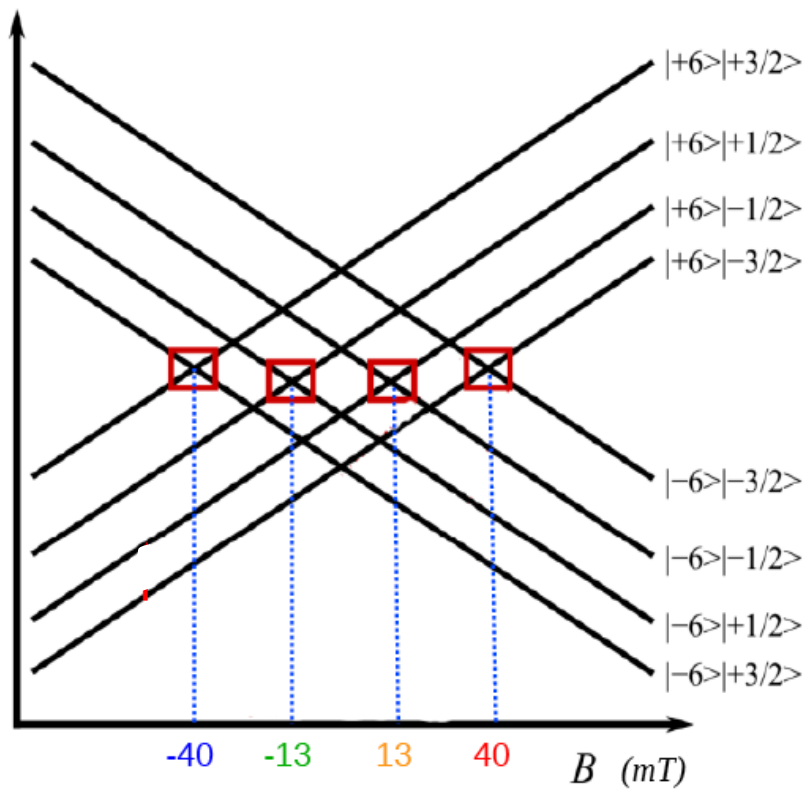
$$c = \frac{\pi}{2\hbar g\mu_B |m - m'| \mu_0}$$



QTM
Hysteresis loops



Single Nuclear Spin Detection



$|+3/2\rangle$ $|+1/2\rangle$ $|-1/2\rangle$ $|-3/2\rangle$

