

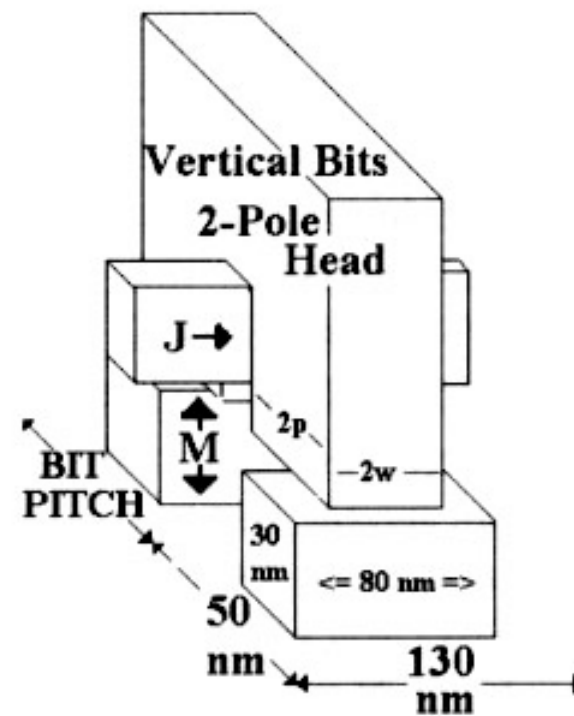
Molecular nanoMagnets for Information Technologies.

Marco Affronte
CNR-INFM-S3 & Univ. of Modena, Italy

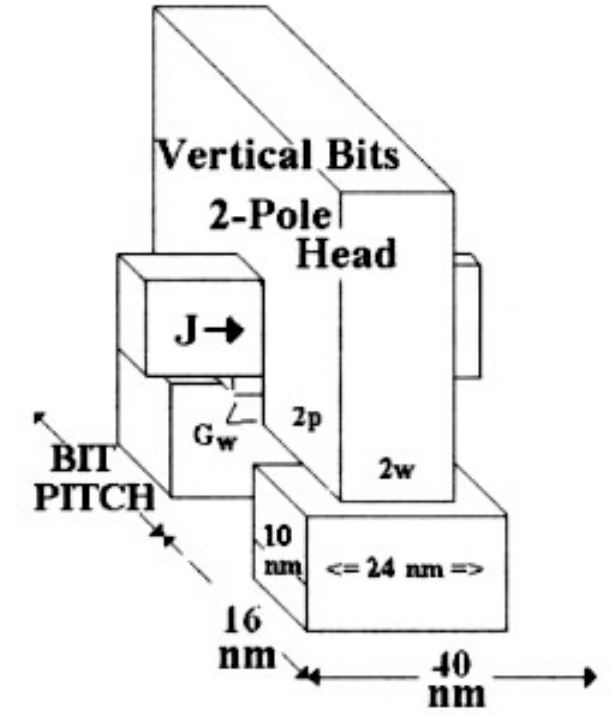
magnetic data storage



magnetic data storage

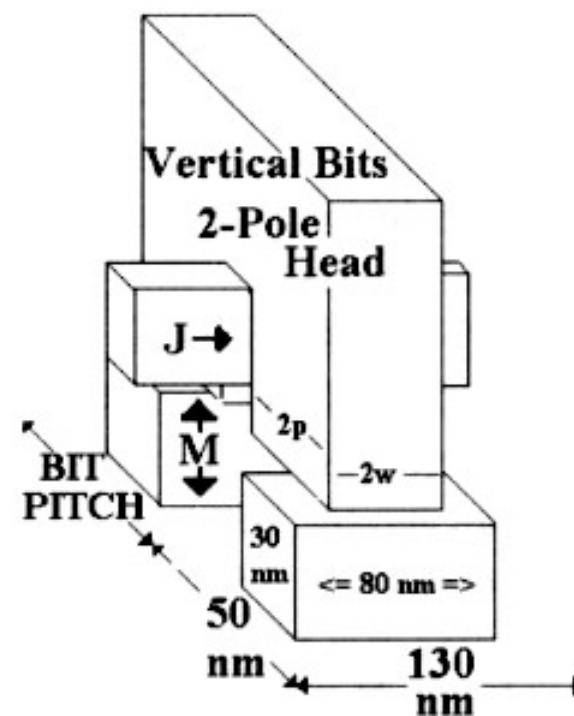


0.1 Tbit/in²
BAR: 2.6

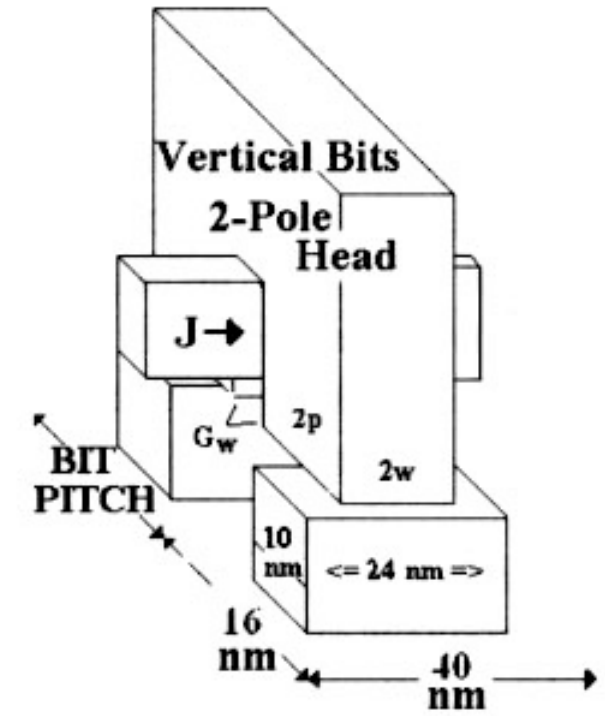


1 Tbit/in²
BAR: 2.5

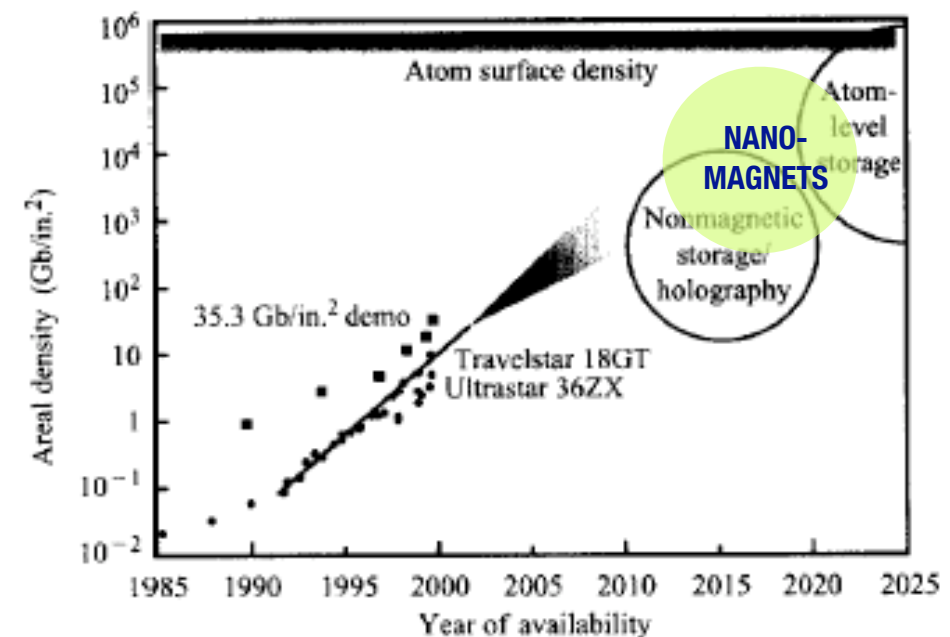
magnetic data storage



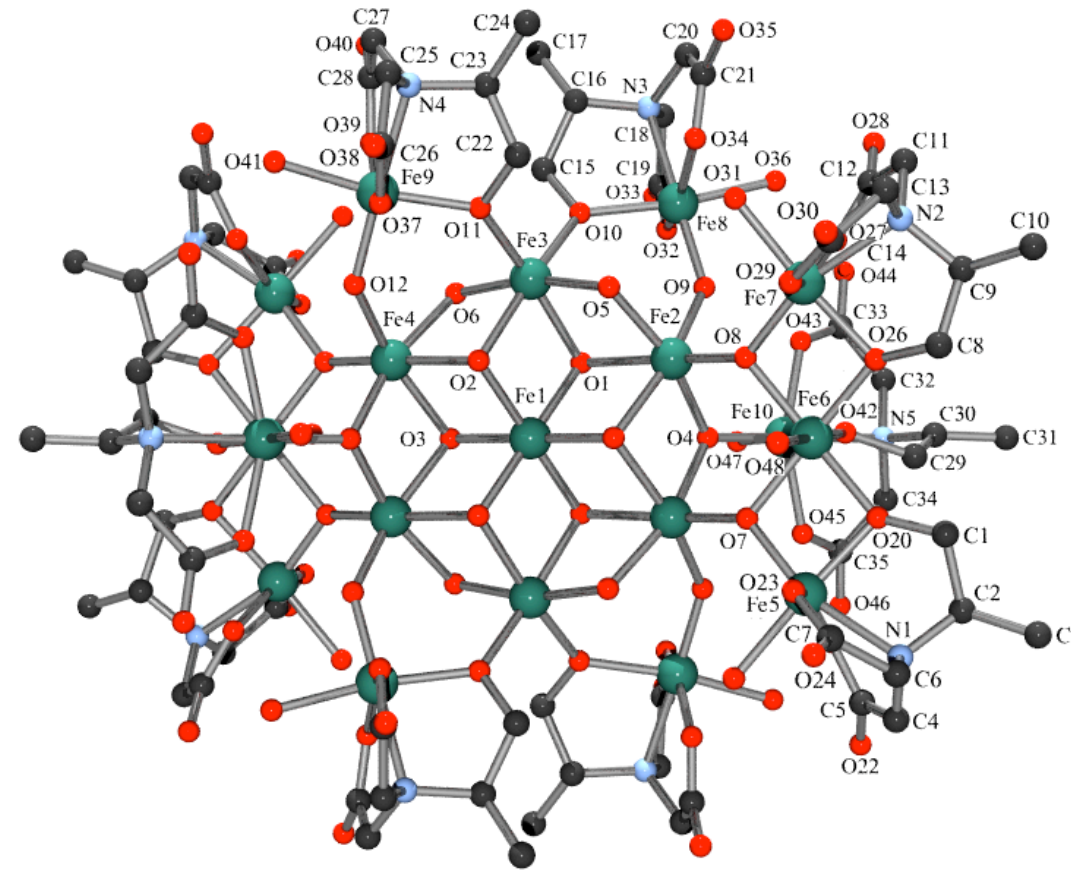
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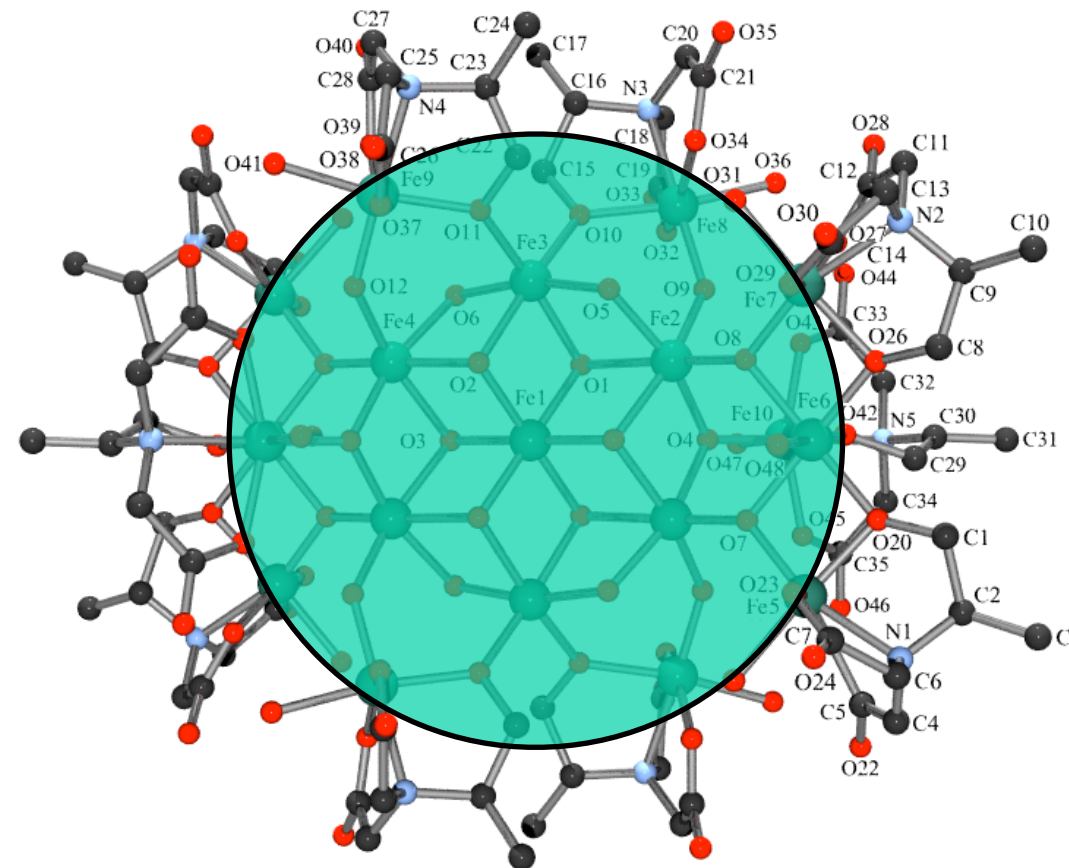


Single-Molecule Magnet



Single-Molecule Magnet

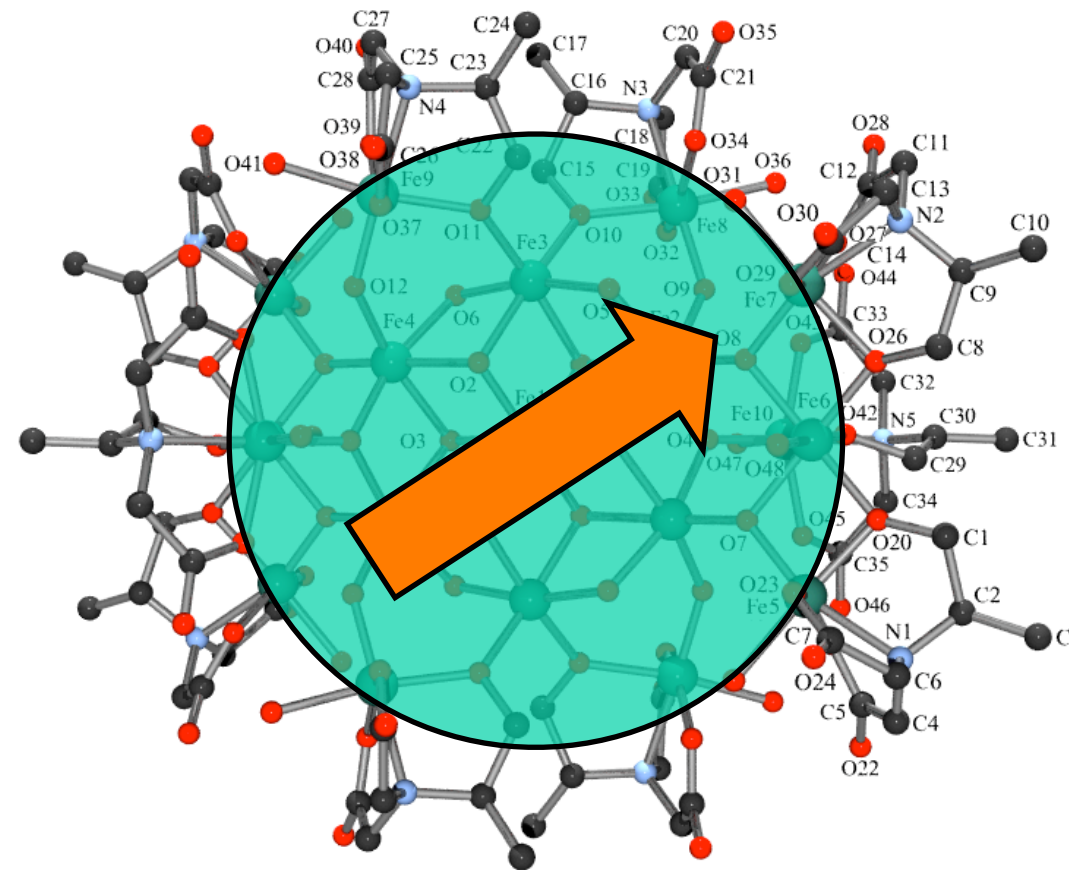
1 nm size



magnetic
core

Single-Molecule Magnet

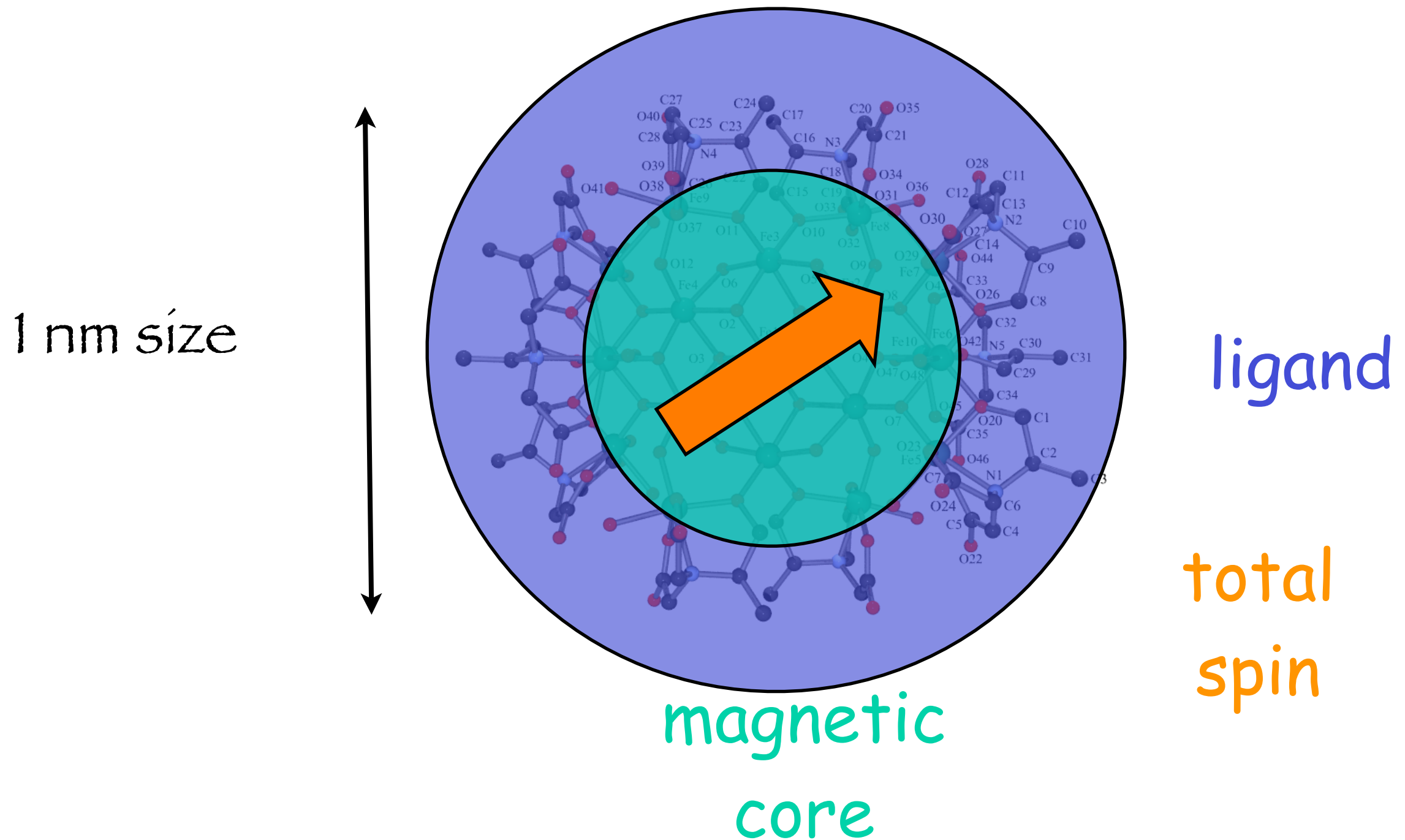
1 nm size



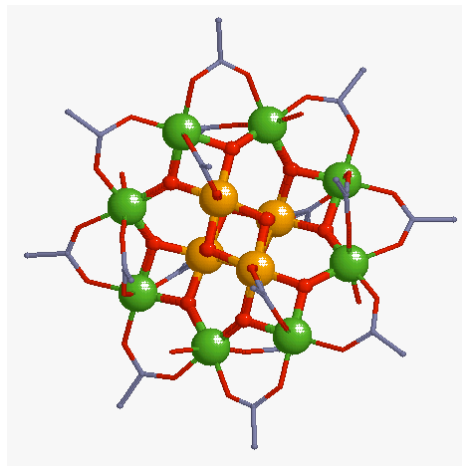
magnetic
core

total
spin

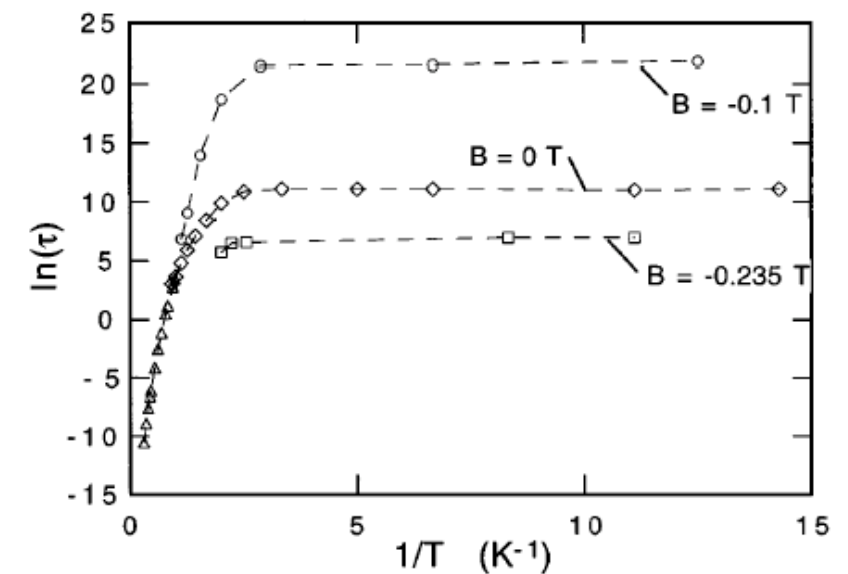
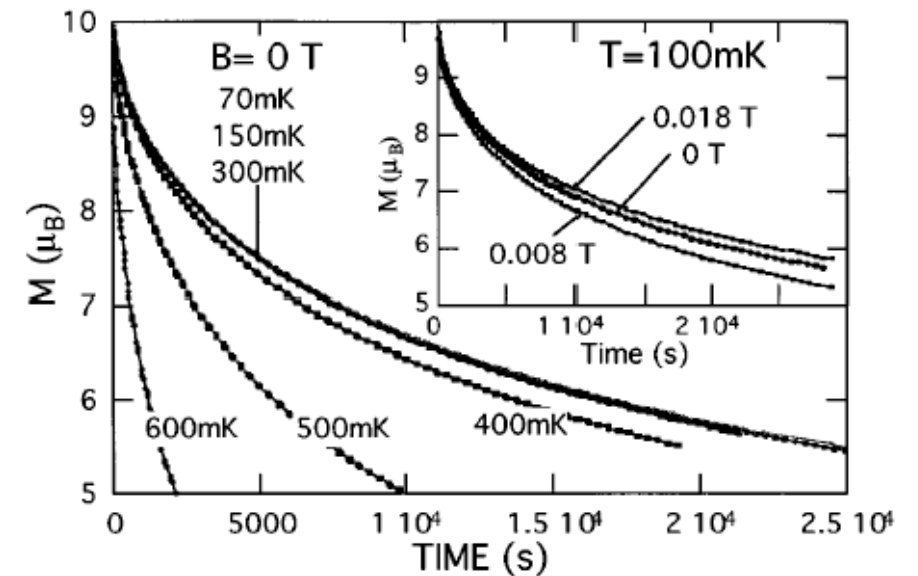
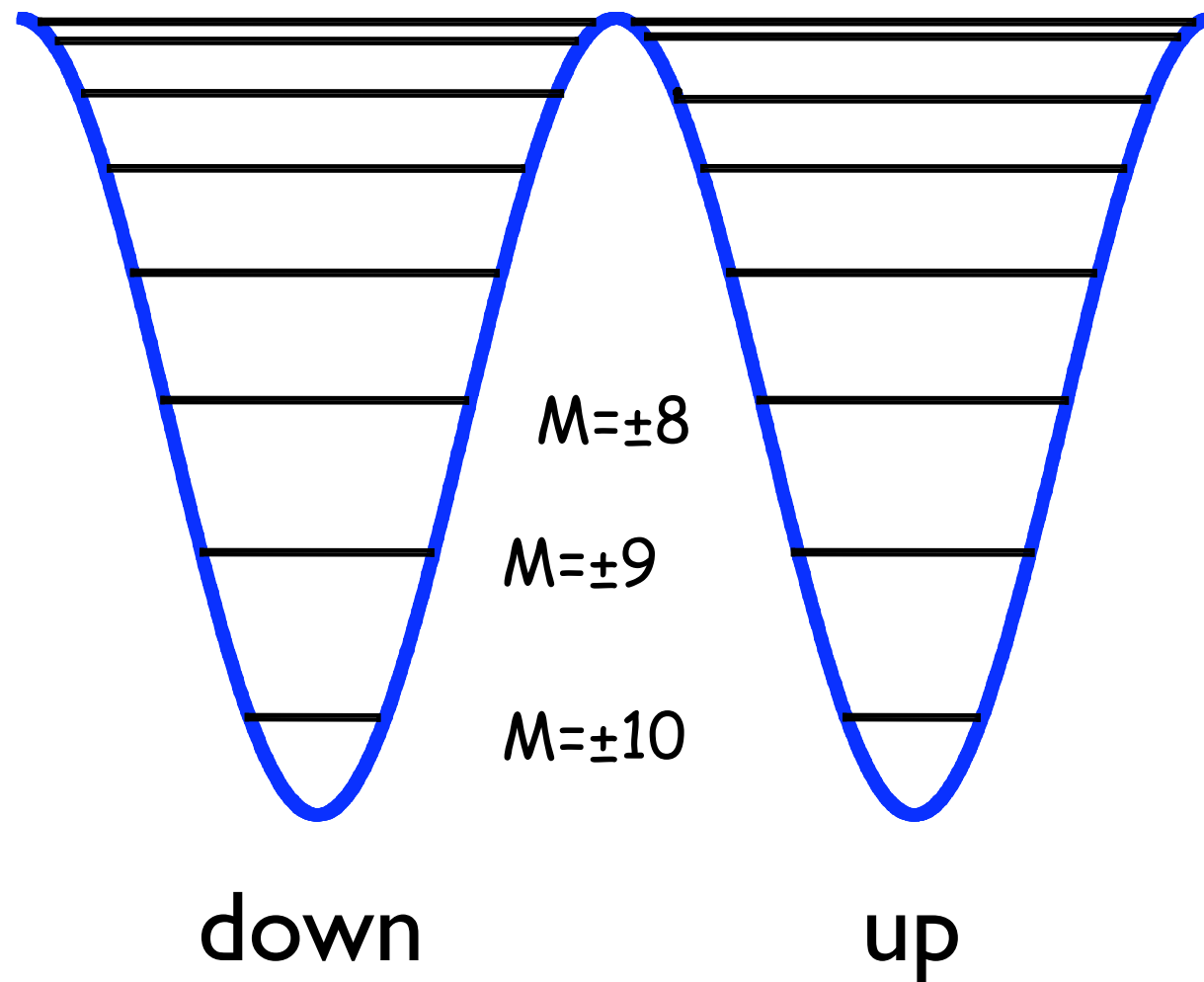
Single-Molecule Magnet



superparamagnetism and quantum tunneling

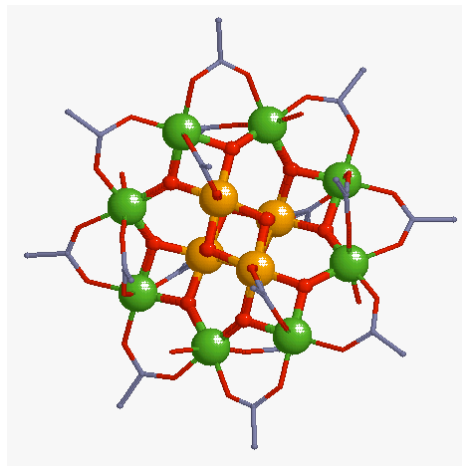


Mn₁₂

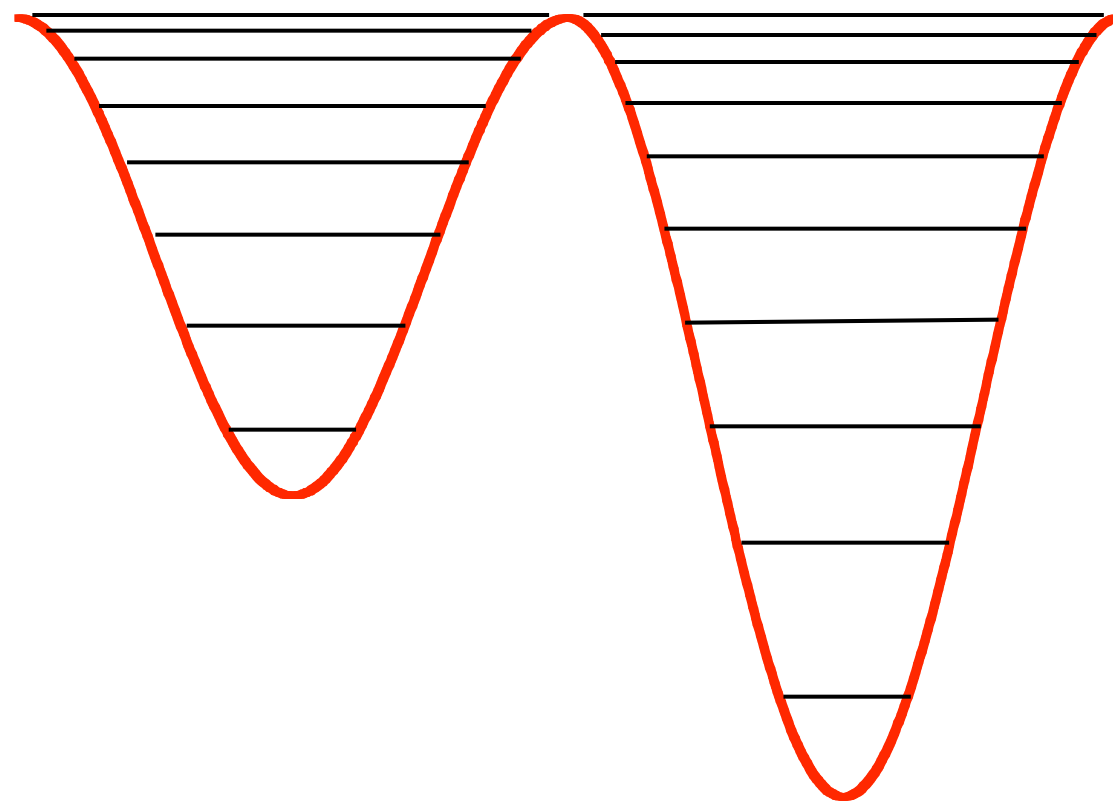


2002 Agilent Technology Award to Sessoli, Gatteschi, Barbara, Wernsdorfer, Friedman

superparamagnetism and quantum tunneling

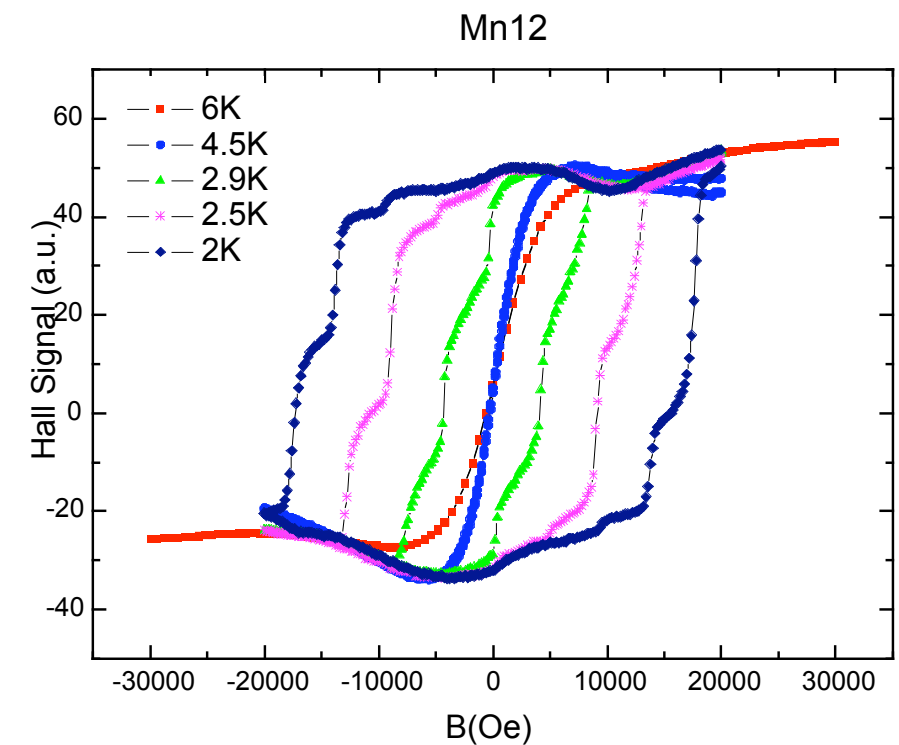


Mn12



down

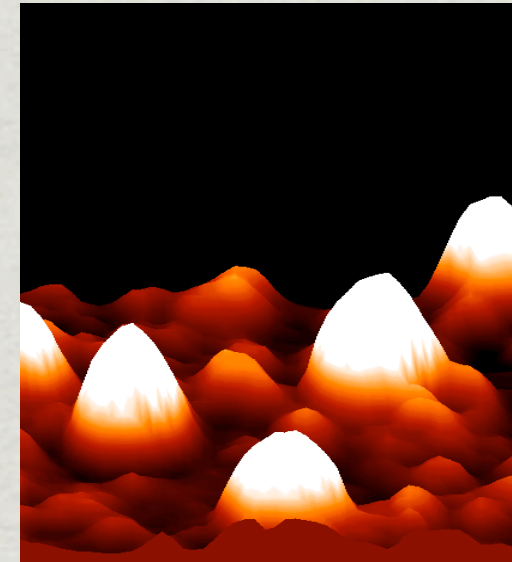
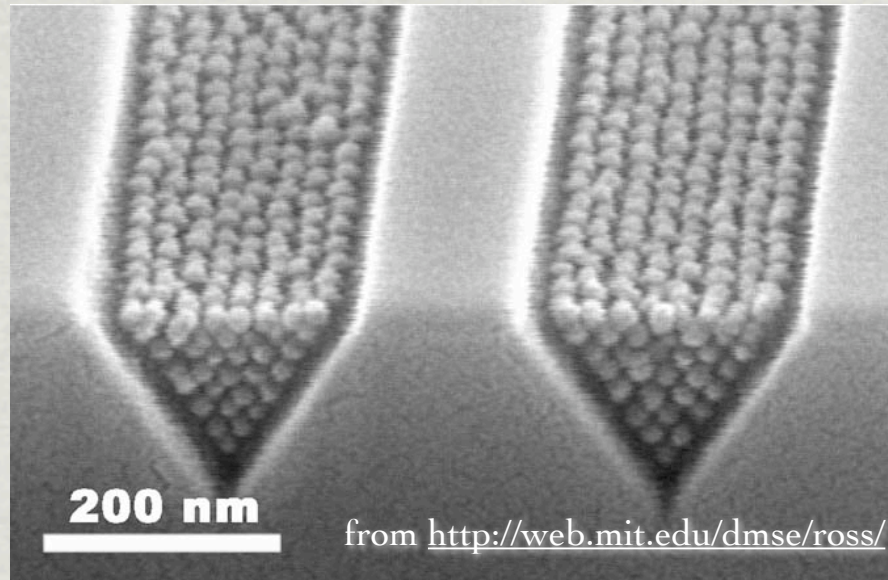
up



2002 Agilent Technology Award to Sessoli, Gatteschi, Barbara, Wernsdorfer, Friedman

nanomagnets with size of 1 or few nm

inorganic vs molecular

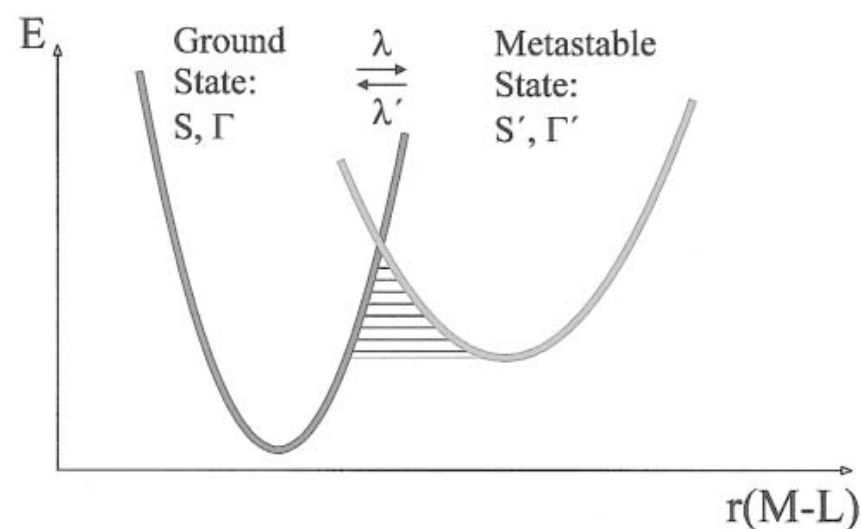


- high chemical stability;
- resistant up to high temperatures;
- high magnetocrystalline anisotropy (FePt: 10^8 erg/cm^3 , this implies that particles with size 3nm are thermally stable for 10yrs!).
- weak control on shape & shell

- excellent control on size shape and shell
- anisotropy barrier Mn12ac: 74K; Mn6: 80K
- chemically unstable at high temperature
- quantum tunneling; presence of excited states.

multi-functionality of molecules

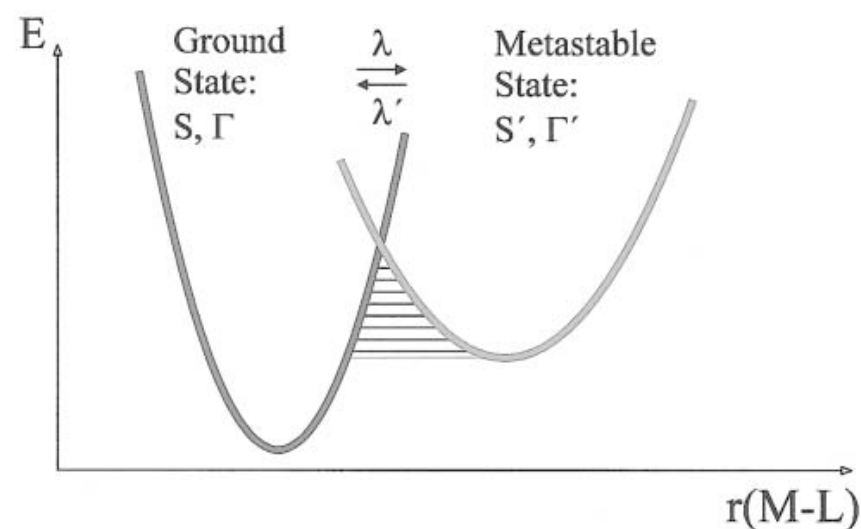
molecular bit: bistable states



*P. Gutlich et al. /
Coordination Chemistry Reviews 219–221 (2001) 839–879*

multi-functionality of molecules

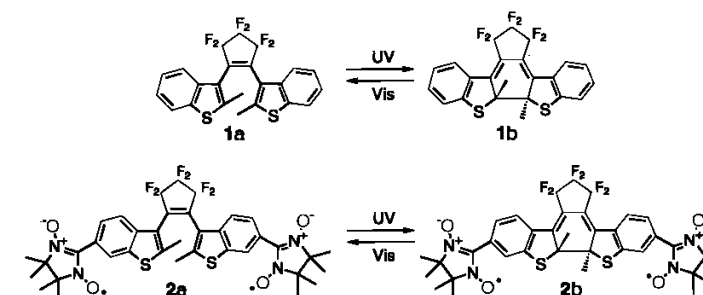
molecular bit: bistable states



P. Gutlich et al. /
Coordination Chemistry Reviews 219–221 (2001) 839–879

switchable with light

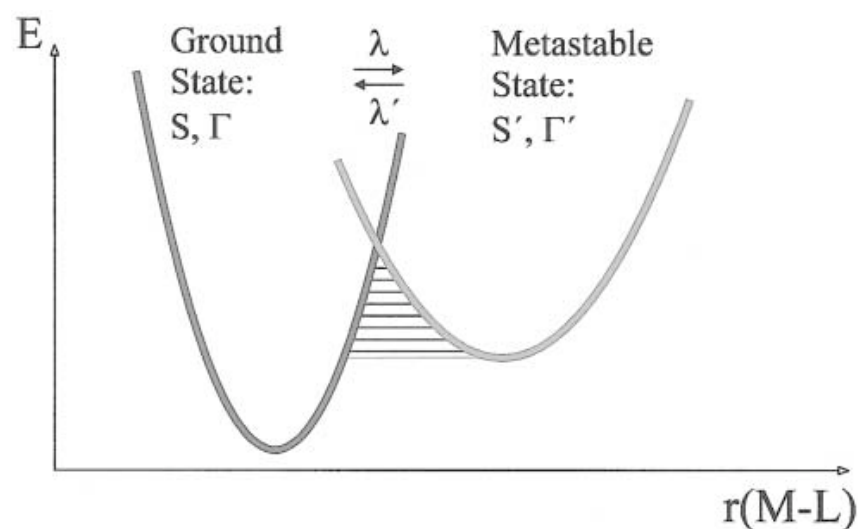
Scheme 1. Photochromic Diarylethenes



27196 *J. Am. Chem. Soc.*, Vol. 122, No. 30, 2000 Matsuda and Irie

multi-functionality of molecules

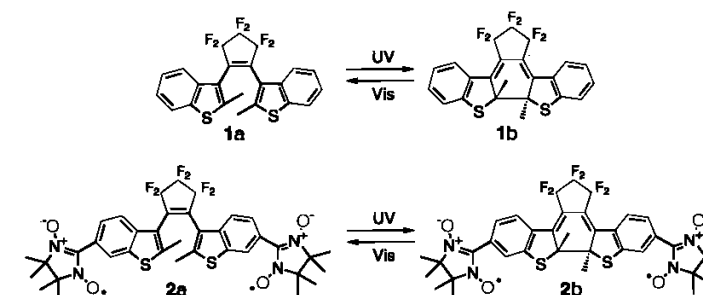
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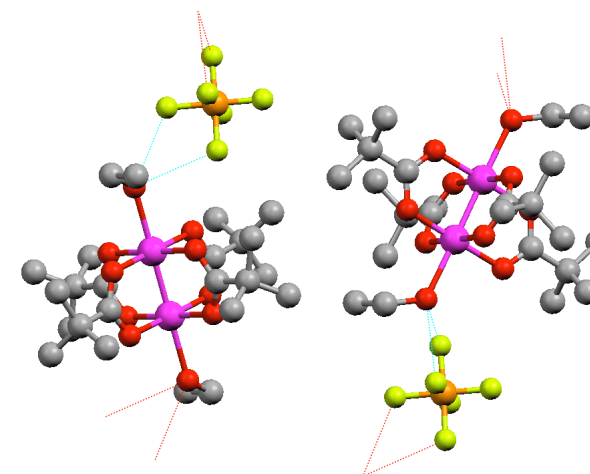
switchable with light

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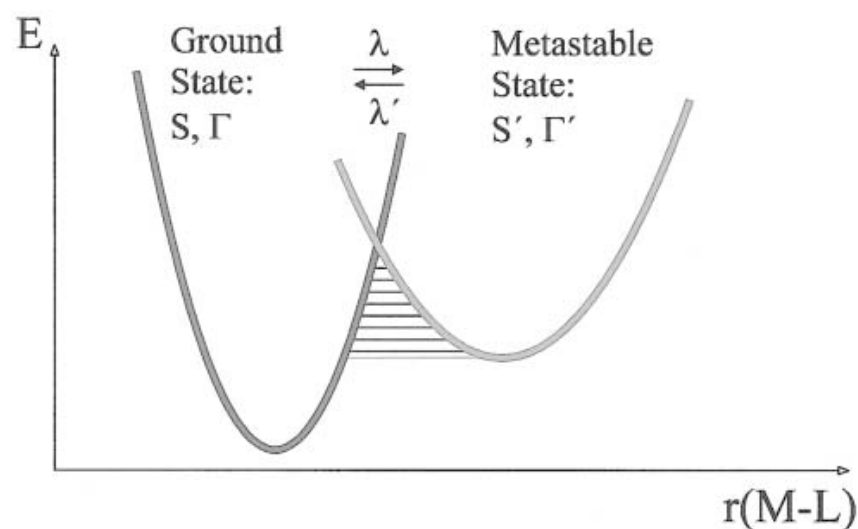
redox properties



$\text{Ru}_2\text{Piv}_4\text{PF}_6$ Sayama et al., *Bull. Chem. Soc. Jpn.* 76, 769–779

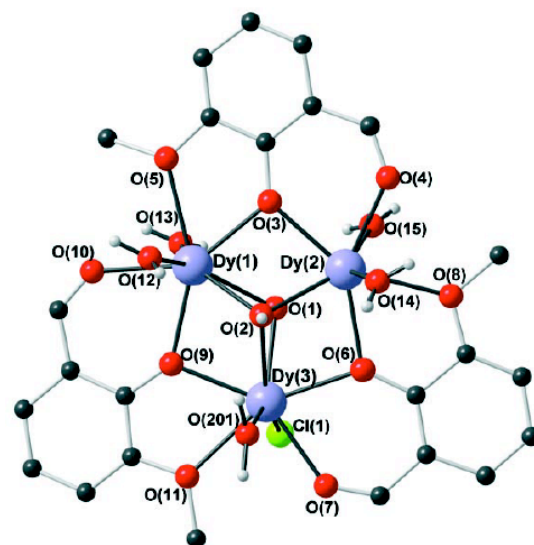
multi-functionality of molecules

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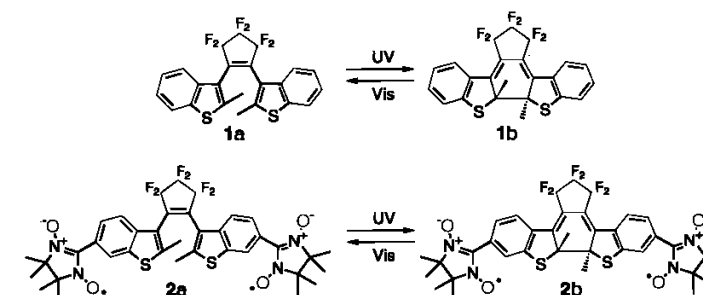
chirality



Tang et al. *Angew. Chem. Int. Ed.* 2006, 45, 1729–1733

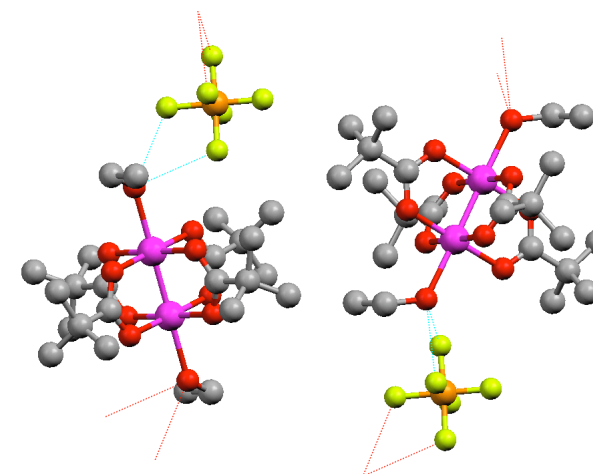
switchable with light

Scheme 1. Photochromic Diarylethenes



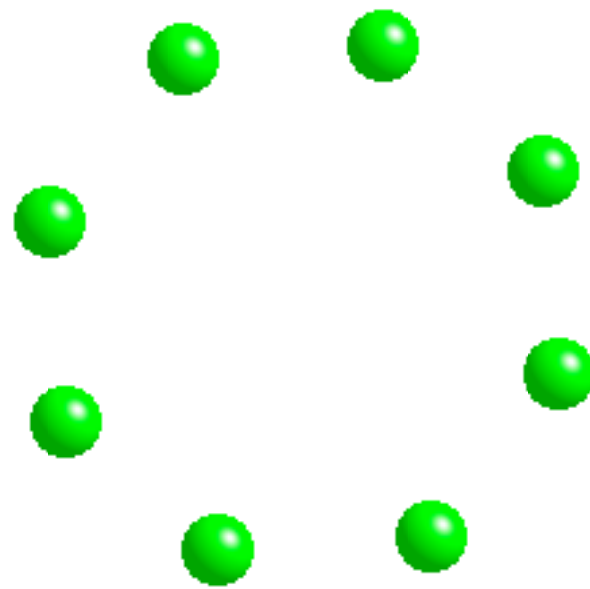
27196 *J. Am. Chem. Soc.*, Vol. 122, No. 30, 2000 Matsuda and Irie

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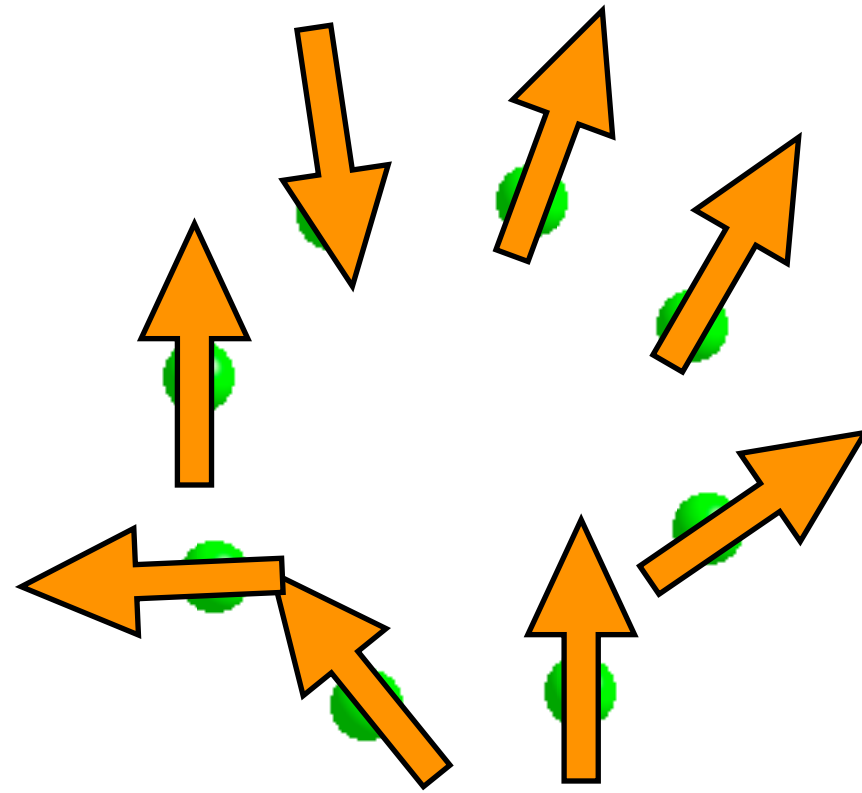


Ru₂Piv₄PF₆ Sayama et al., *Bull. Chem. Soc. Jpn.* 76, 769–779

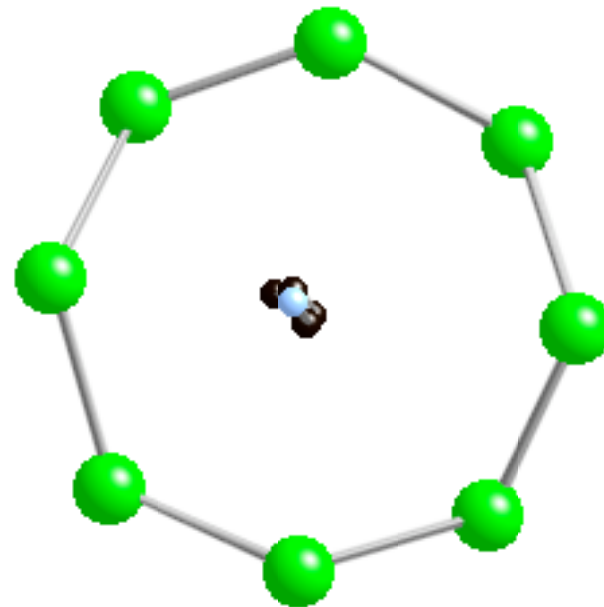
Molecules as building blocks for nanomagnetism



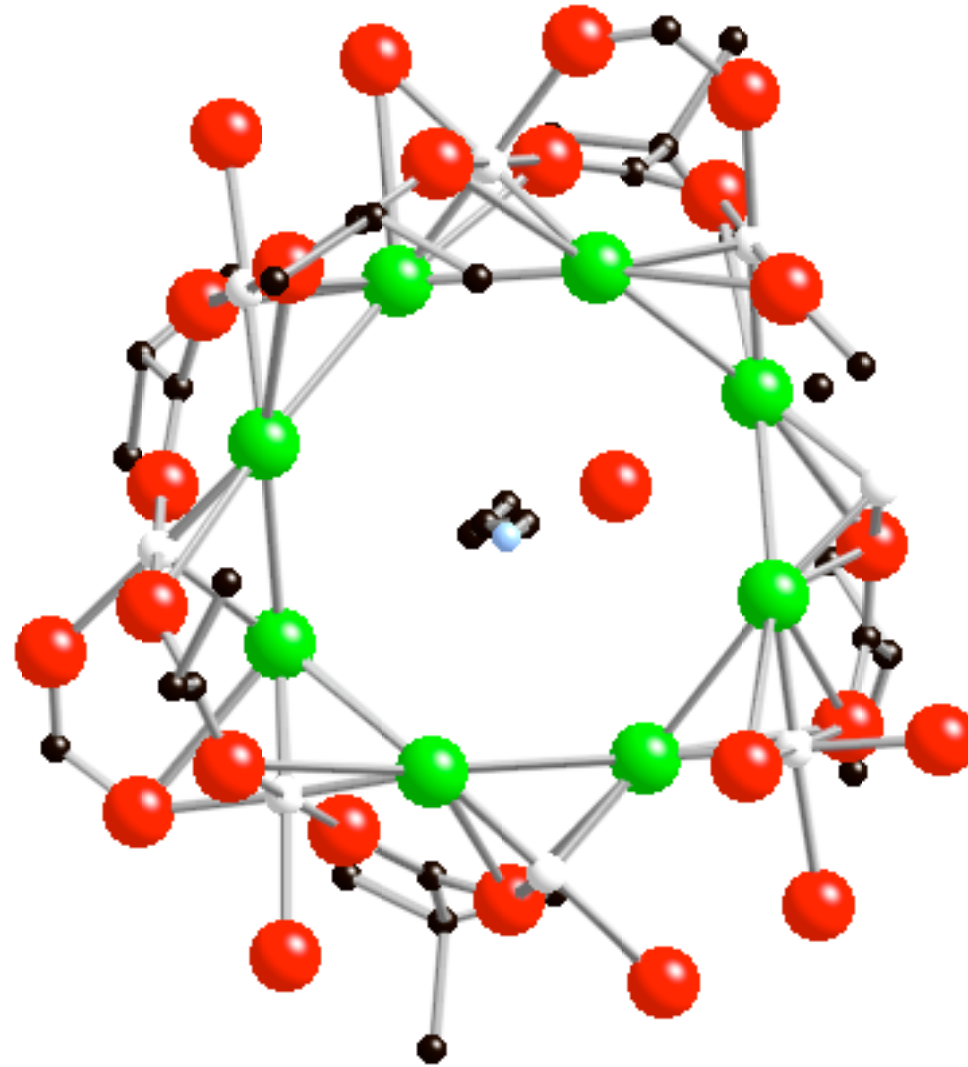
Molecules as building blocks for nanomagnetism



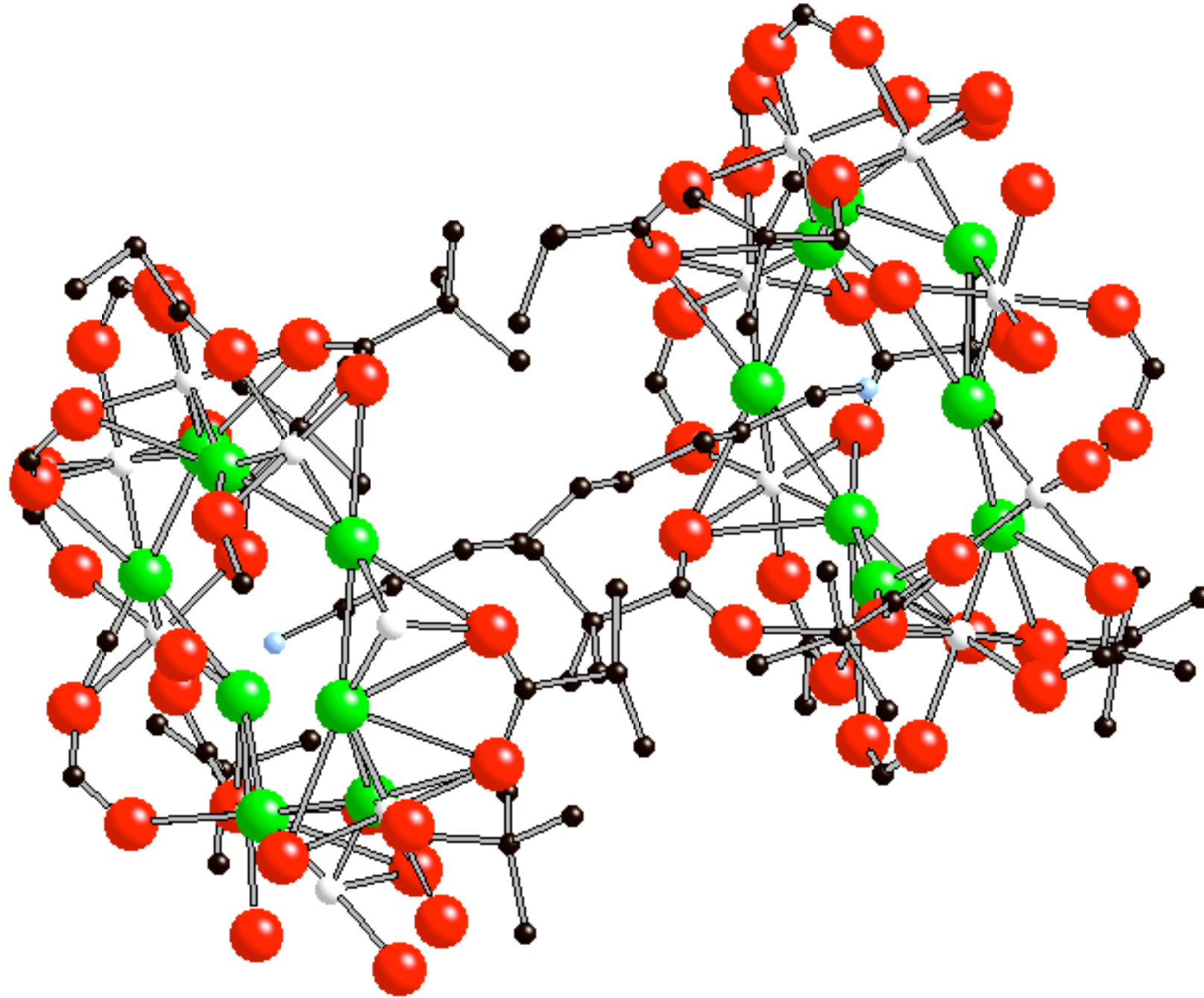
Molecules as building blocks for nanomagnetism



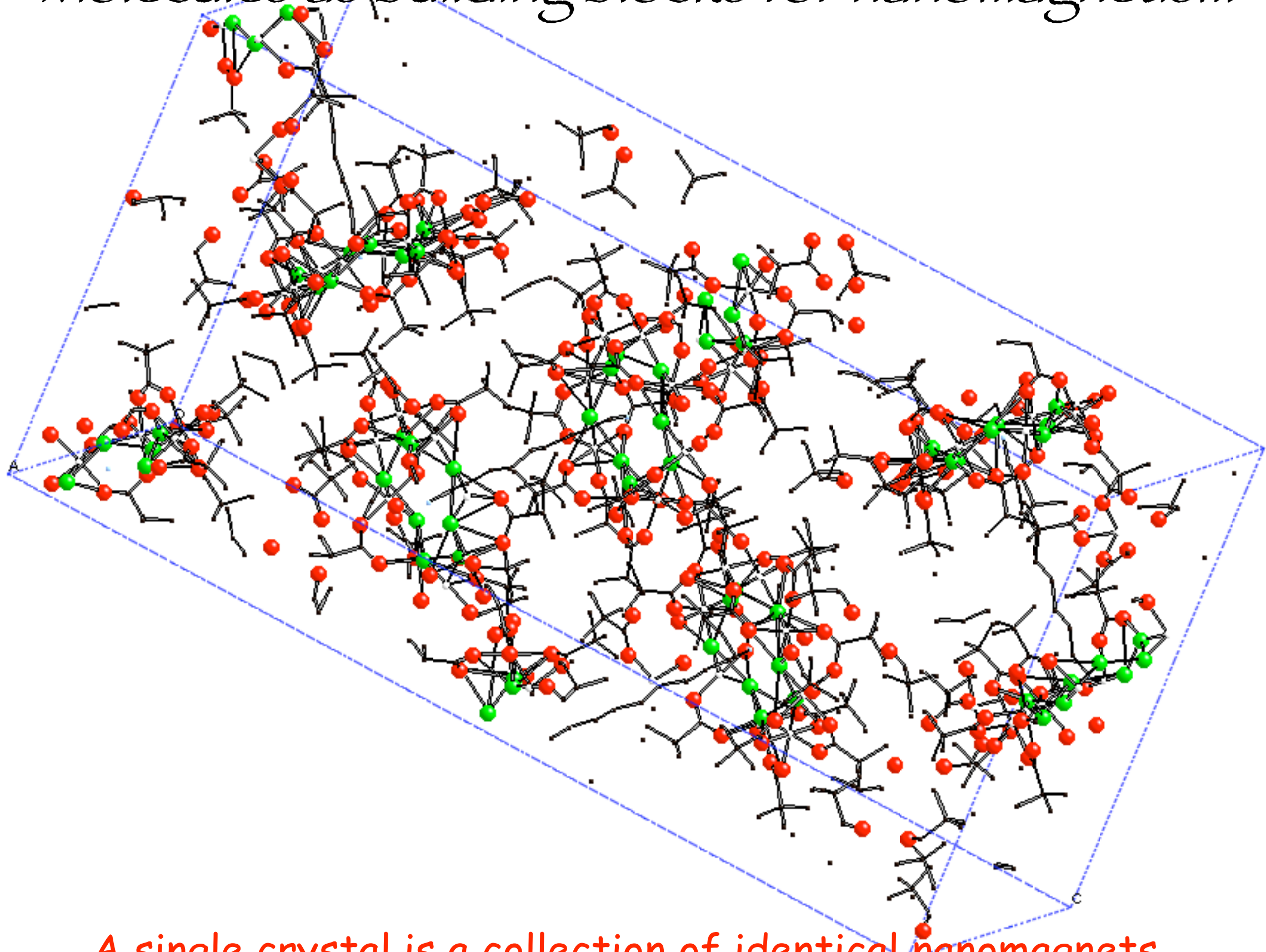
Molecules as building blocks for nanomagnetism



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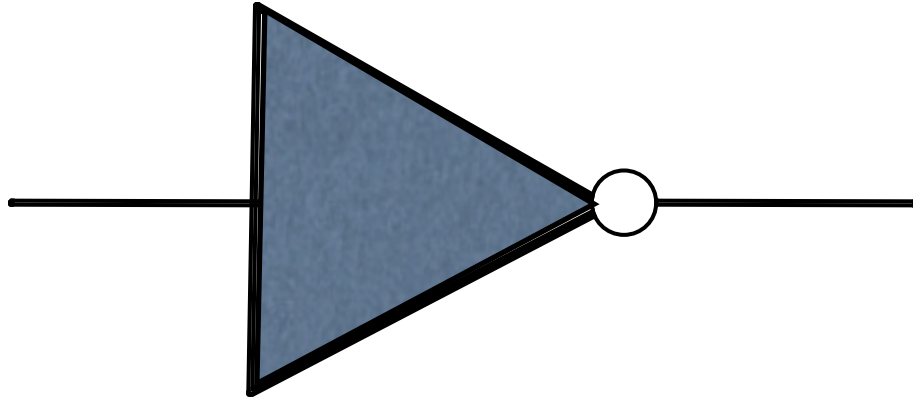


Molecules as building blocks for nanomagnetism

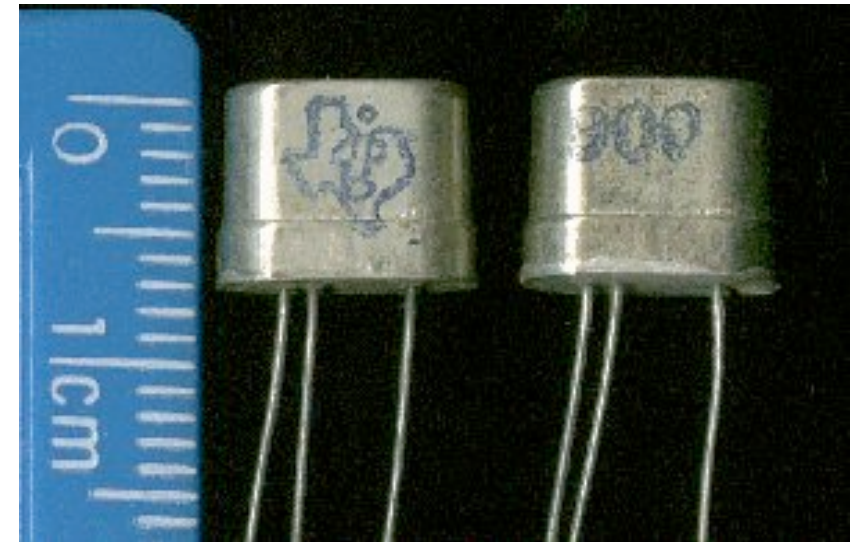


A single crystal is a collection of identical nanomagnets well separated one another and perfectly oriented

program



computing machine



processor

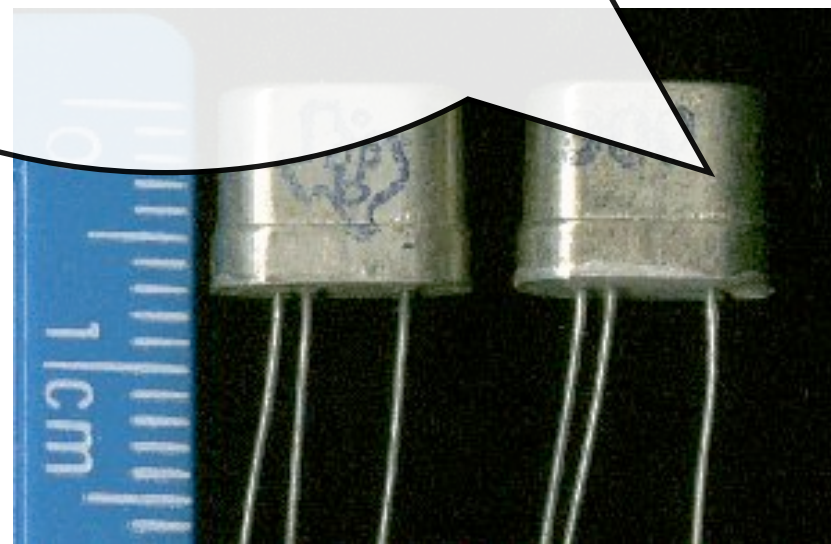
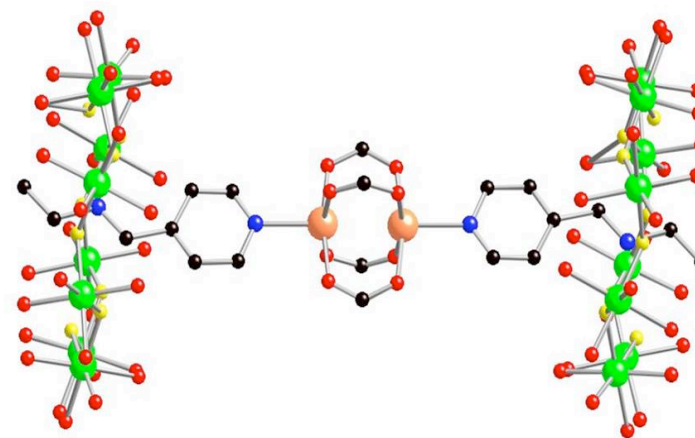


memory

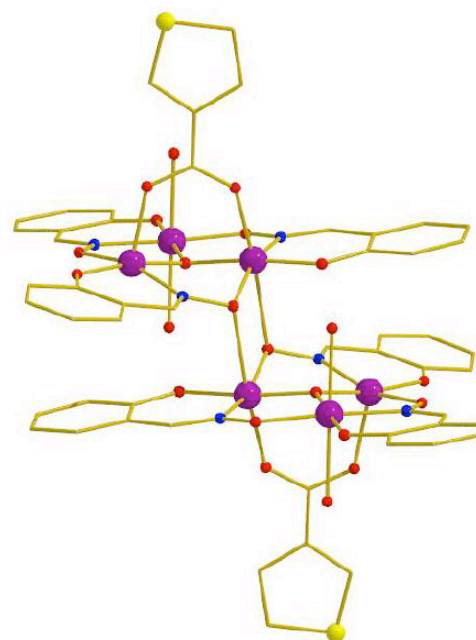
program

$$H|\Psi\rangle = i\hbar \frac{\partial}{\partial t} |\Psi\rangle$$

the “molecular”
computing machine



processor



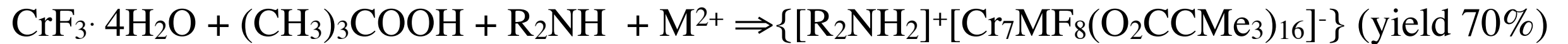
memory



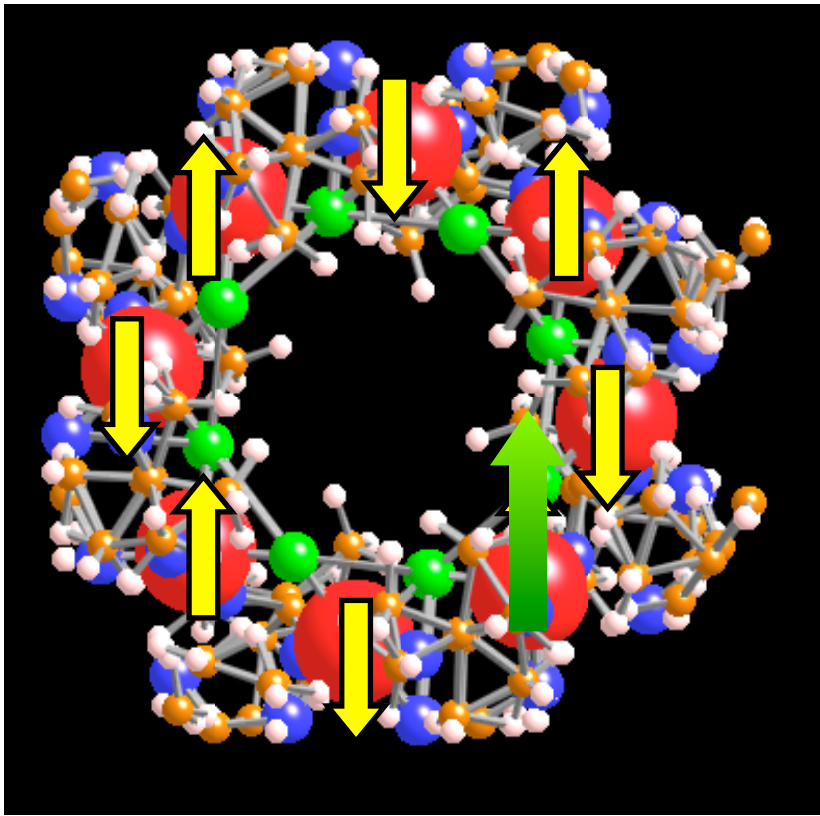
molecular spin clusters for quantum computation

- Identification of well-defined qubit
- Reliable state preparation
- Accurate quantum gate operations
- Low decoherence
- scalability
- Read-out

molecular engineering of Cr based rings

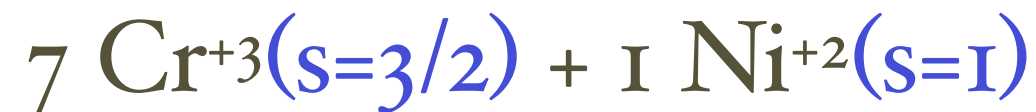


where R= *Et, Me and* M=Fe, Cd, Co, Mn, Ni

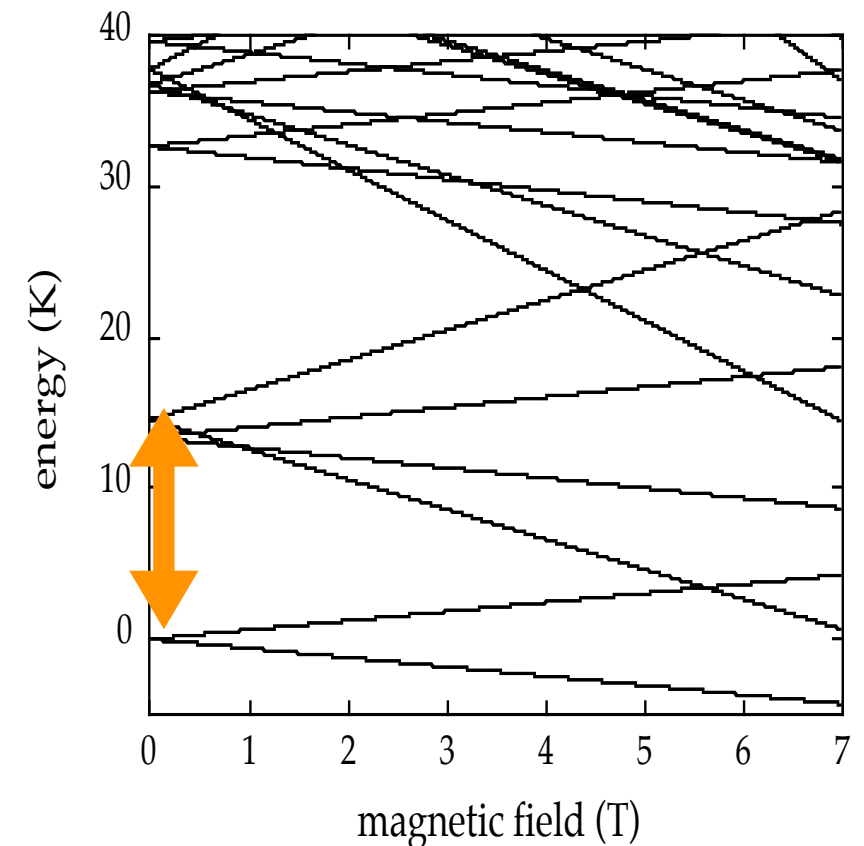


heterometallic Cr₇Ni wheels

Angew. Chem. Int. Ed. 42, 101 (2003).

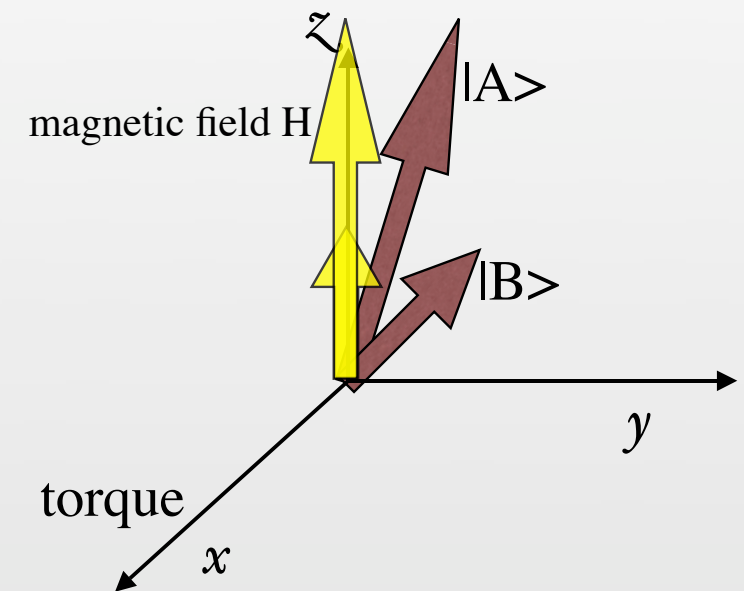
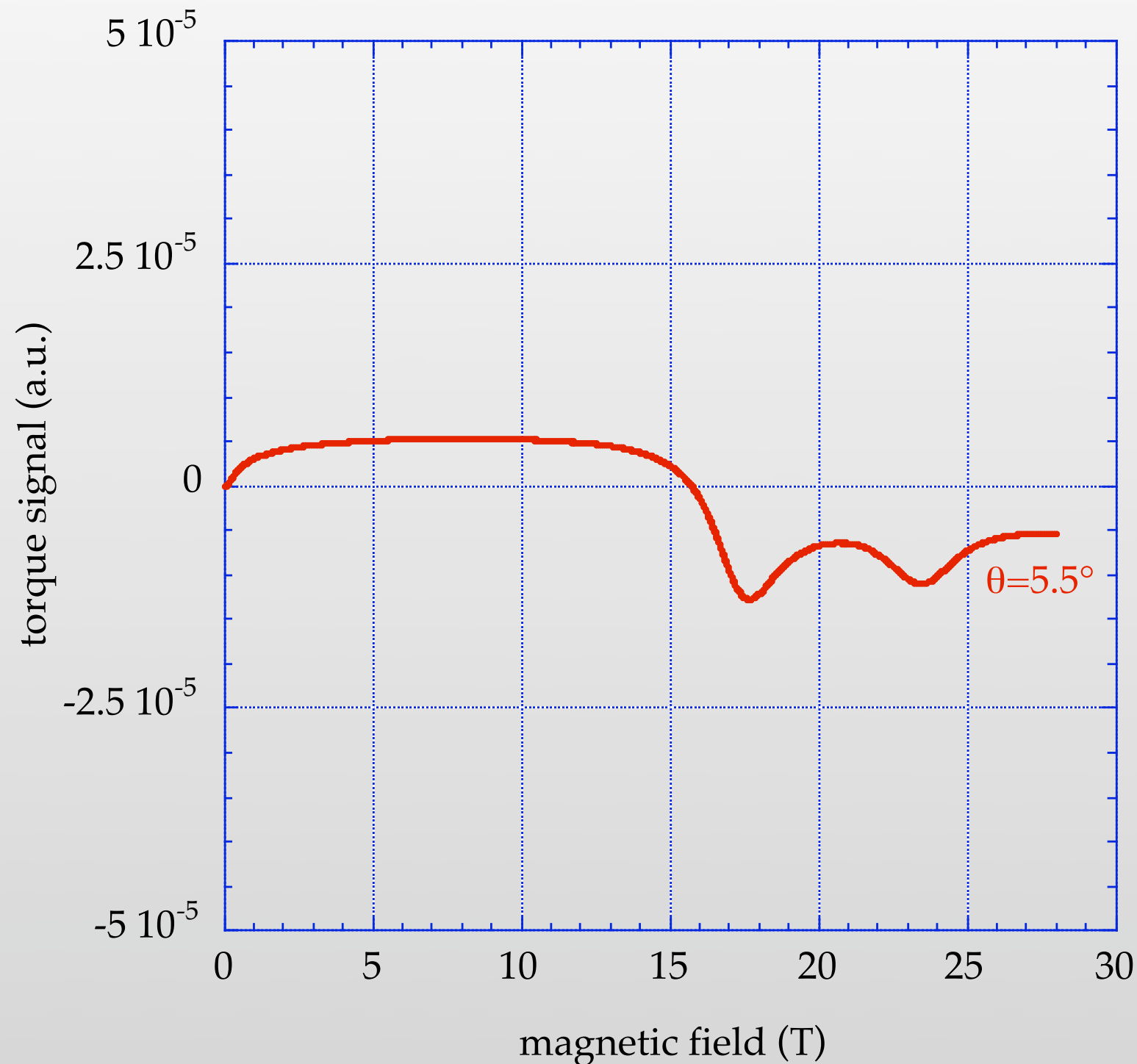
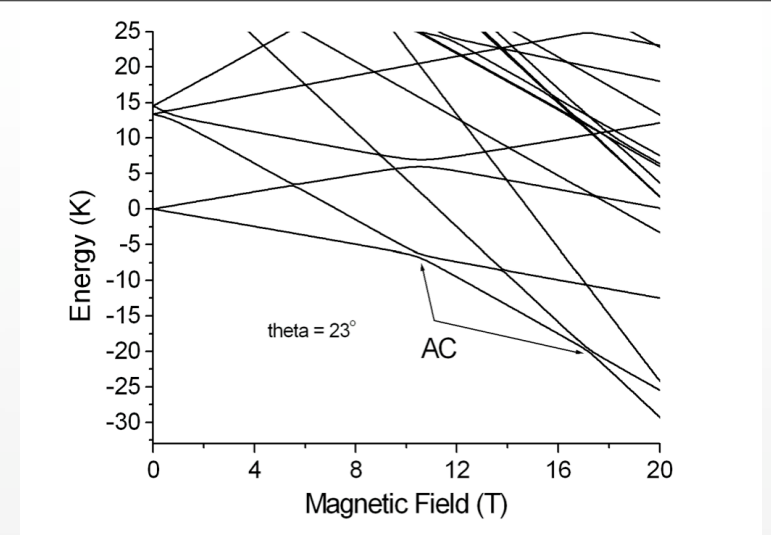


$$H = \sum_i J_i \mathbf{s}_i \cdot \mathbf{s}_{i+1} + \sum_i d_i \left[s_{z,i}^2 - s_i(s_i + 1)/3 \right] + \sum_{i>j} s_i \cdot \mathbf{D}_{ij} \cdot s_j + \mu_B \sum_i g_i \mathbf{s}_i \cdot \mathbf{B}$$



Molecular Engineering of antiferromagnetic rings for quantum computation.
F. Troiani, A. Ghirri, M. Affronte, S. Carretta, P. Santini, G. Amoretti, S. Piligkos, G. Timco, R.E.P. Winpenny **Phys. Rev. Lett.** 94, 207208 (2005).

AF rings behave like quantum objects:
quantum oscillations of the total spin

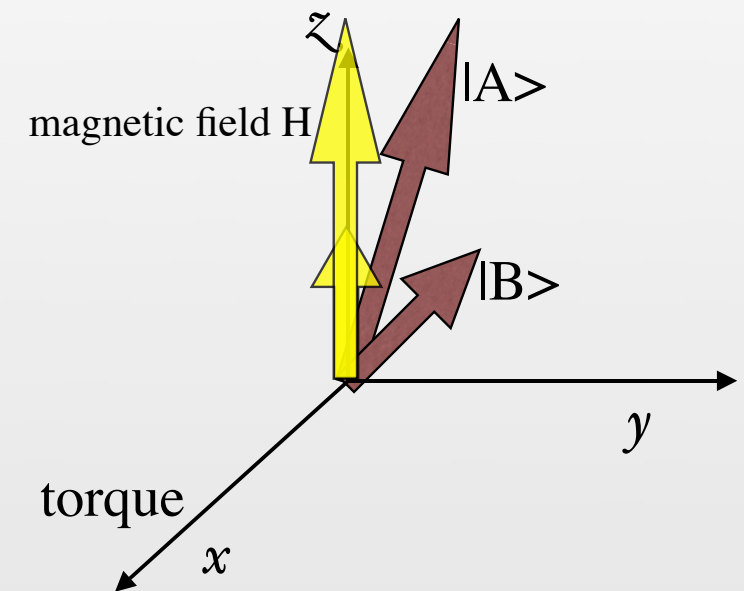
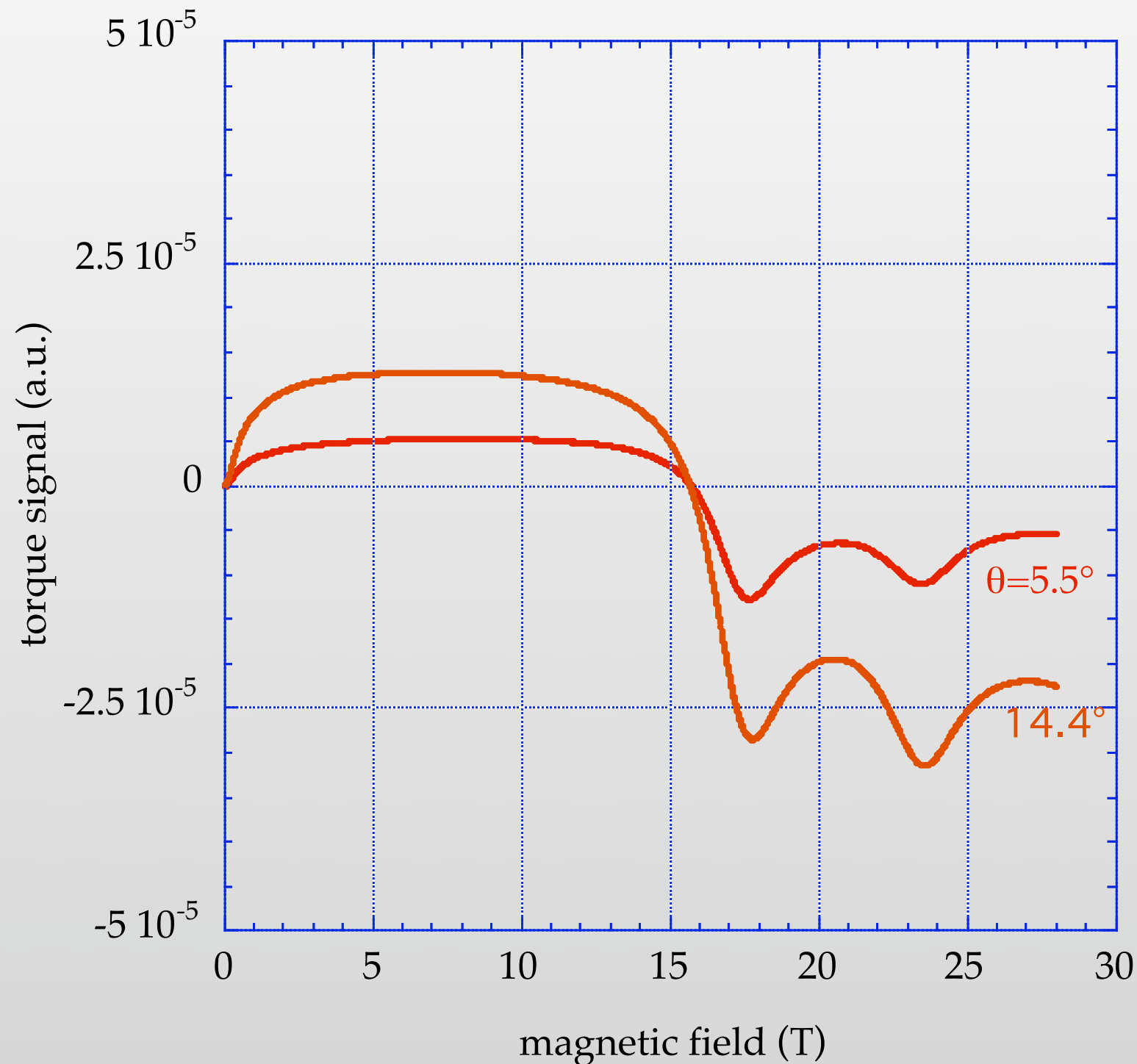
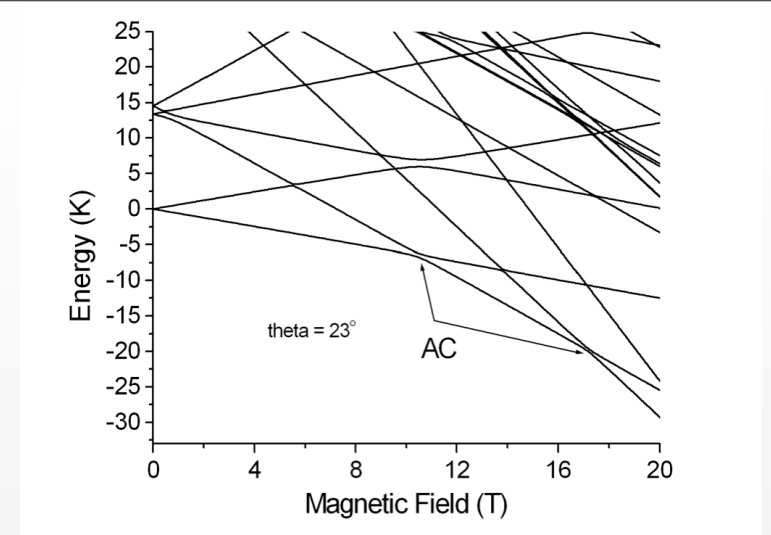


$$|G\rangle = \frac{1}{\sqrt{2}}(a|A\rangle + b|B\rangle)$$

$$(\Delta S_z)^2 = \langle S_z^2 \rangle - \langle S_z \rangle^2 = \frac{b^2}{2} - \frac{b^4}{4}$$

$$\tau = H \langle S_y \rangle \propto Hab \propto Hb\sqrt{2-b^2} \propto 2H\Delta S_z$$

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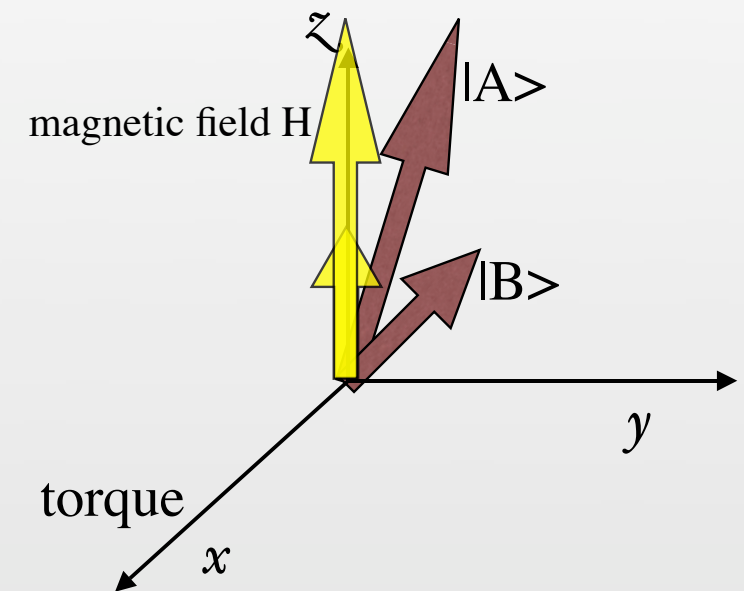
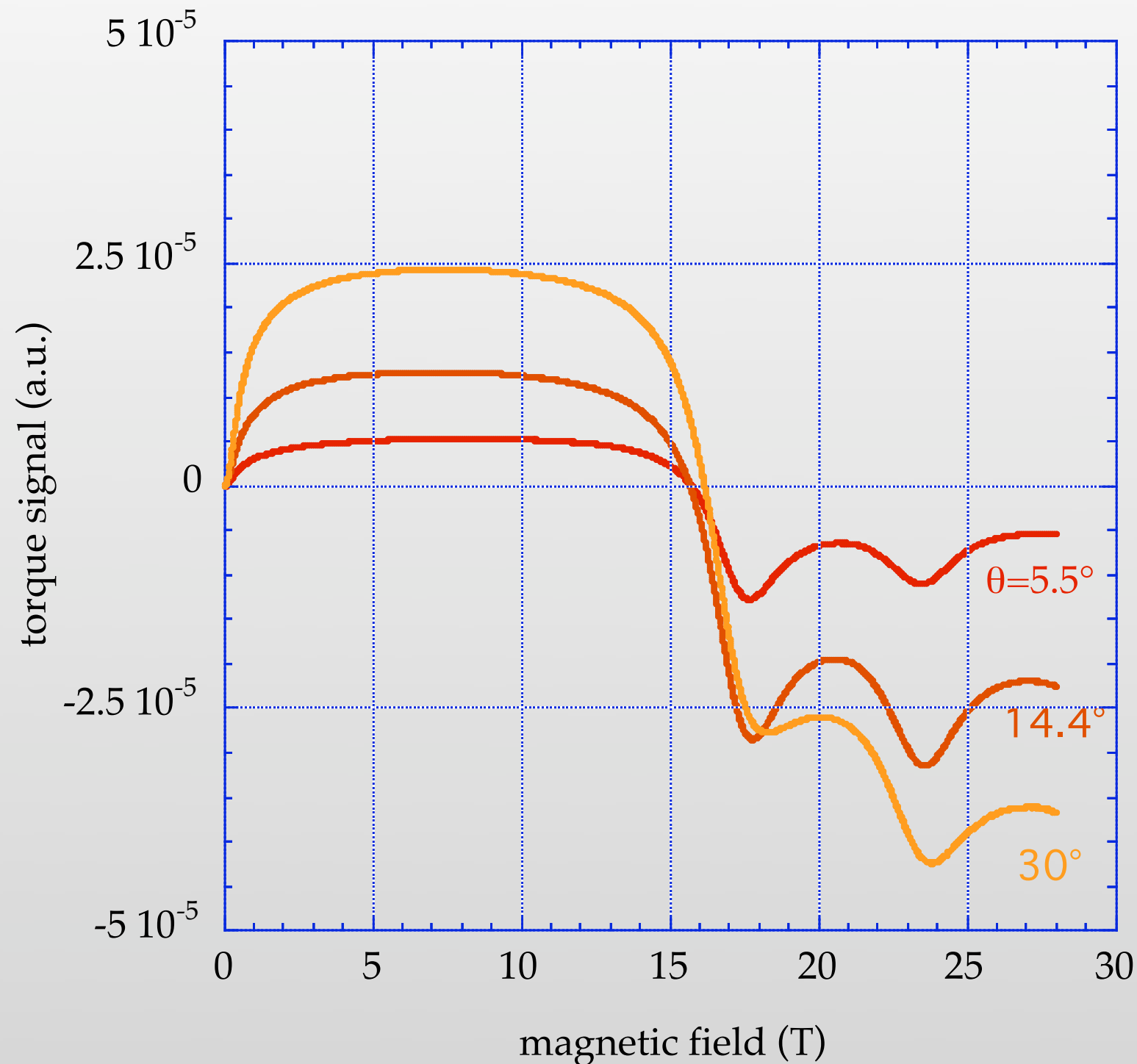
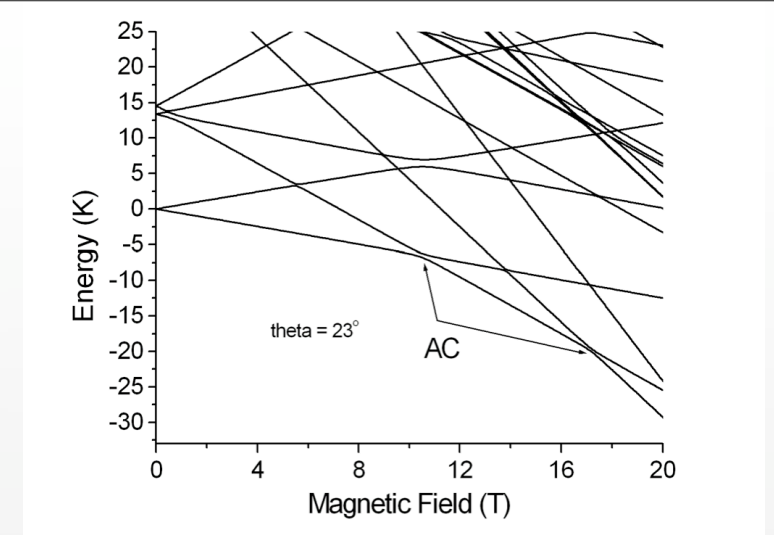


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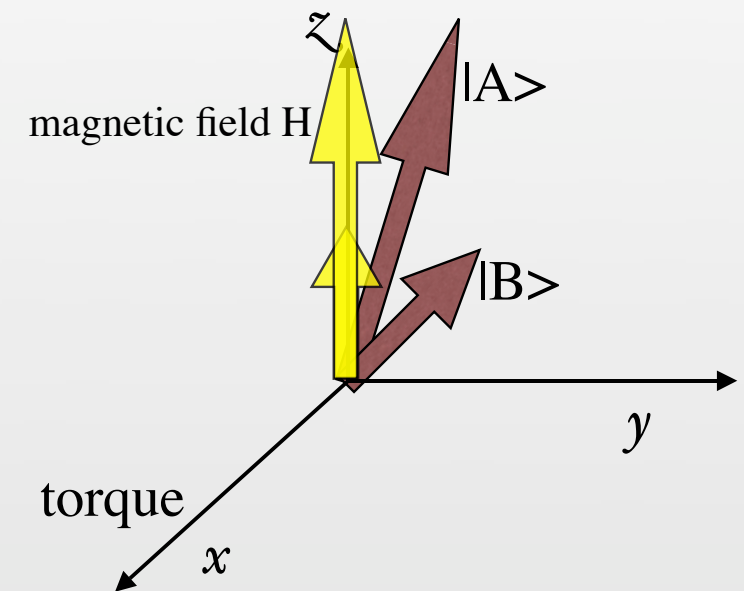
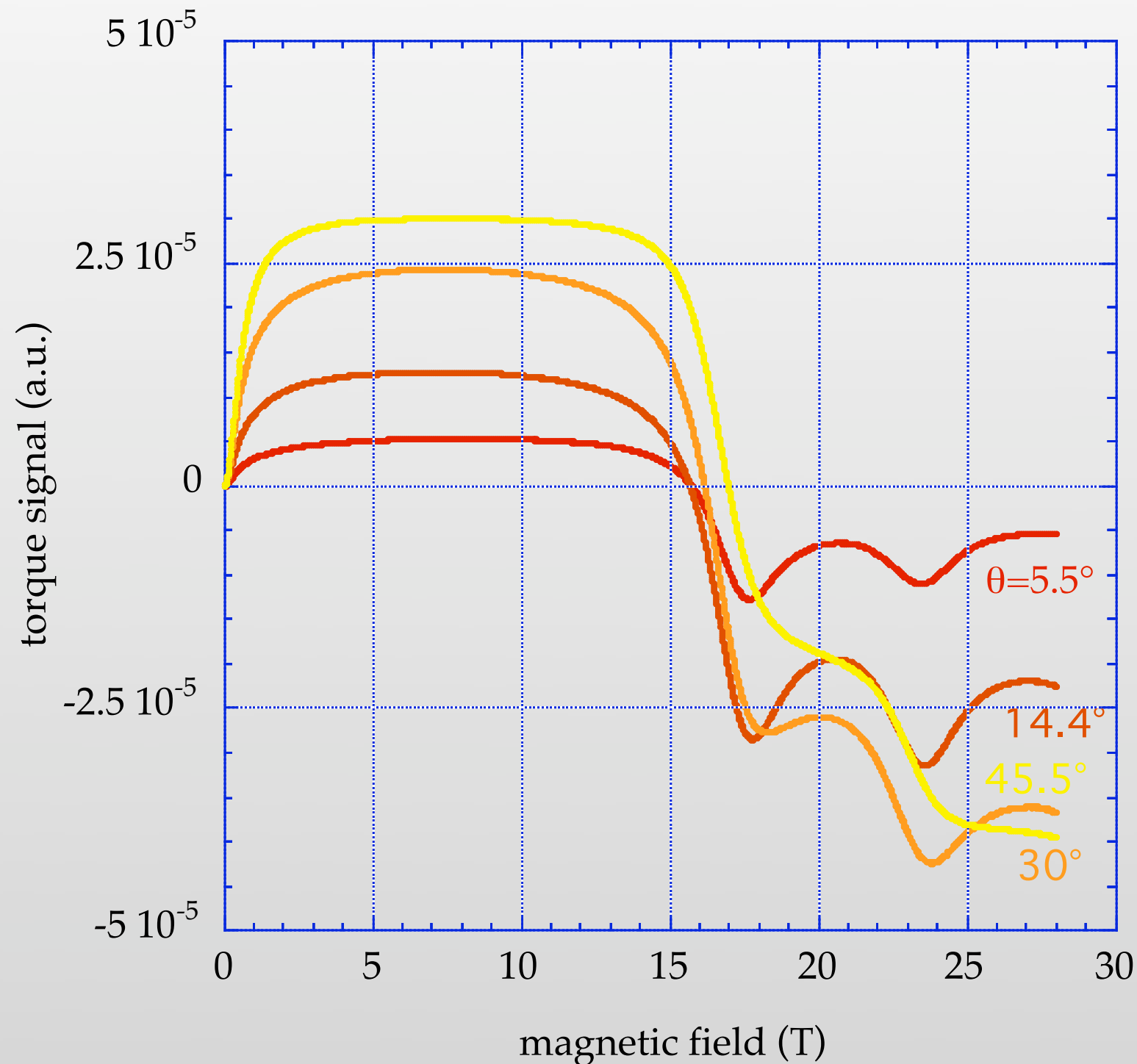
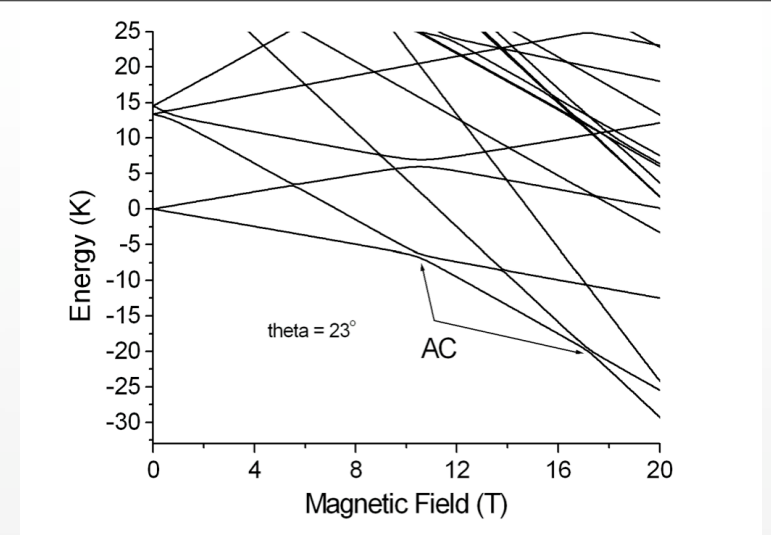


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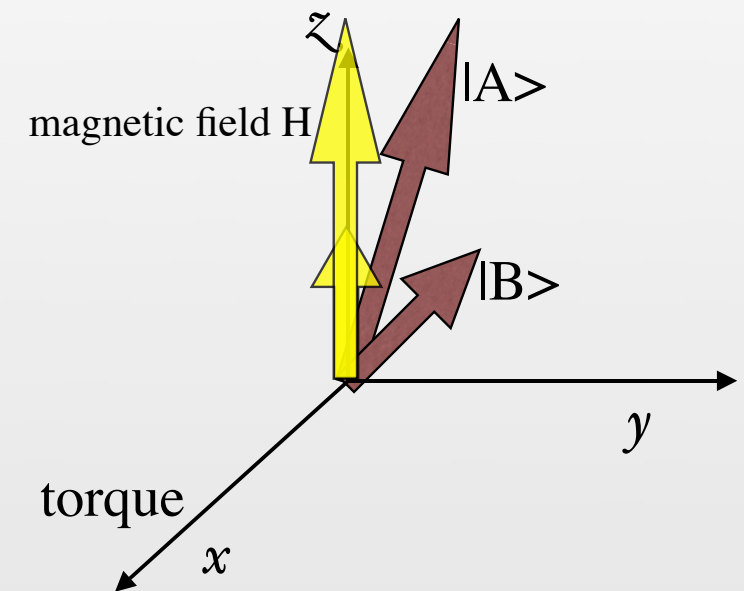
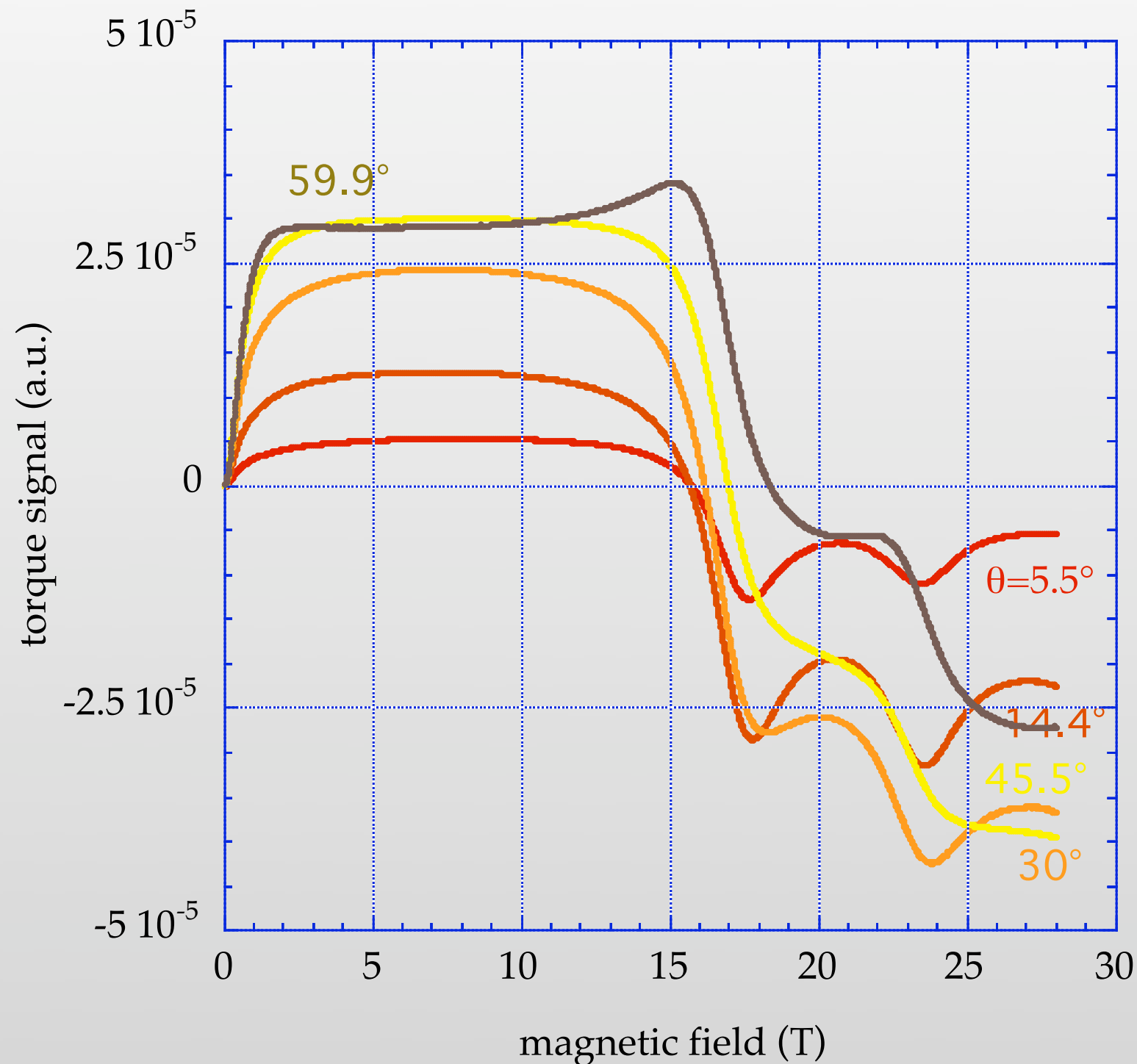
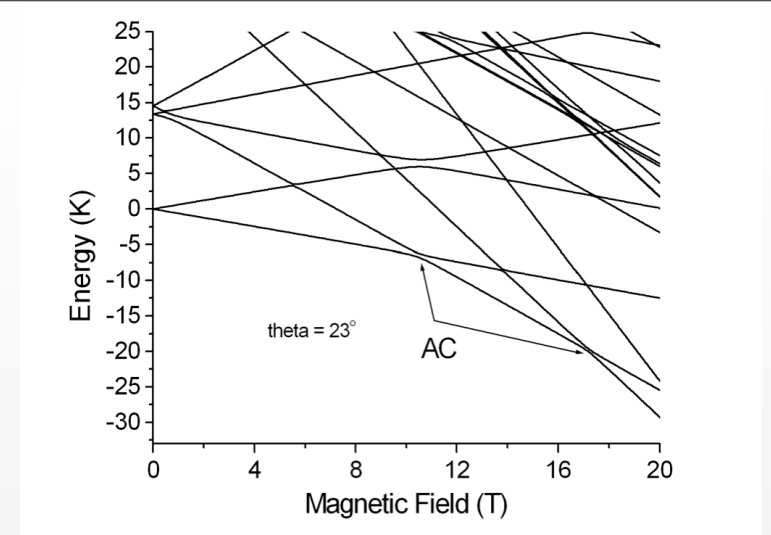


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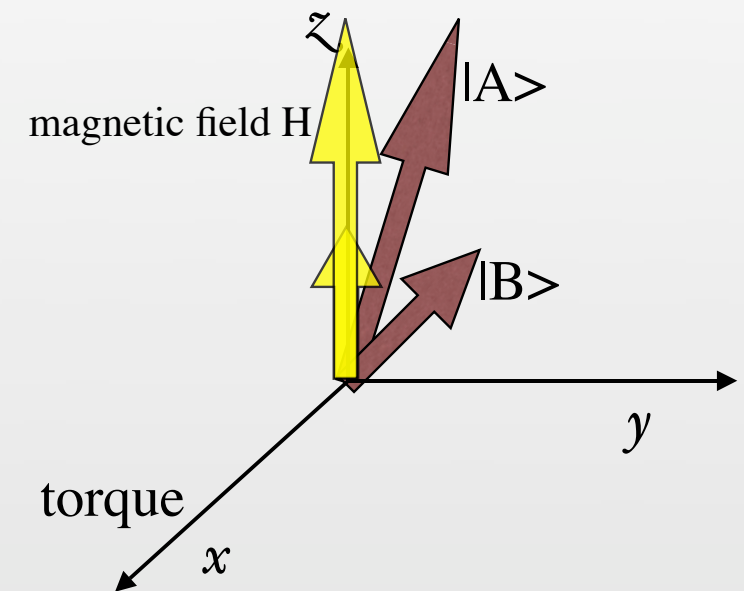
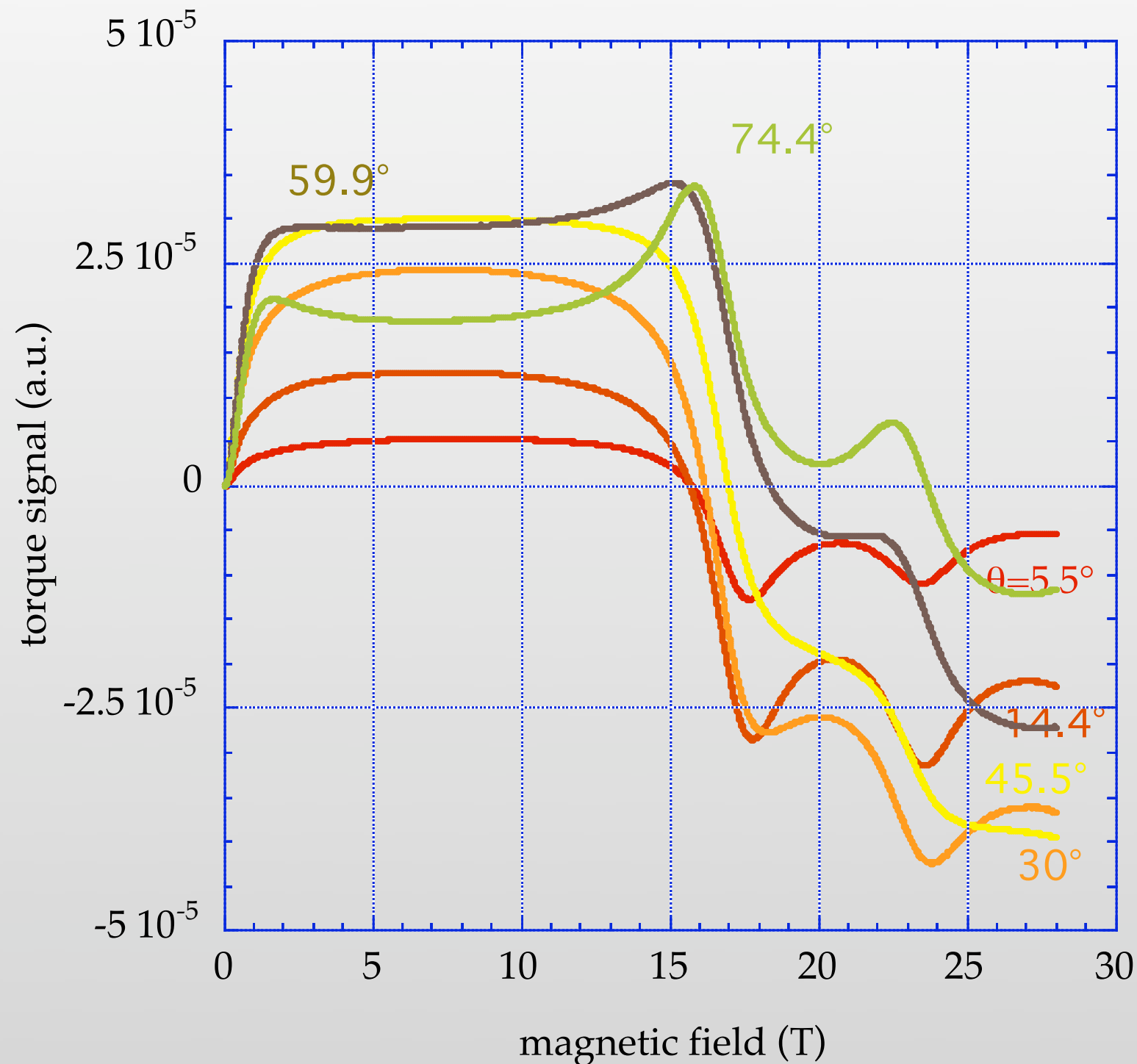
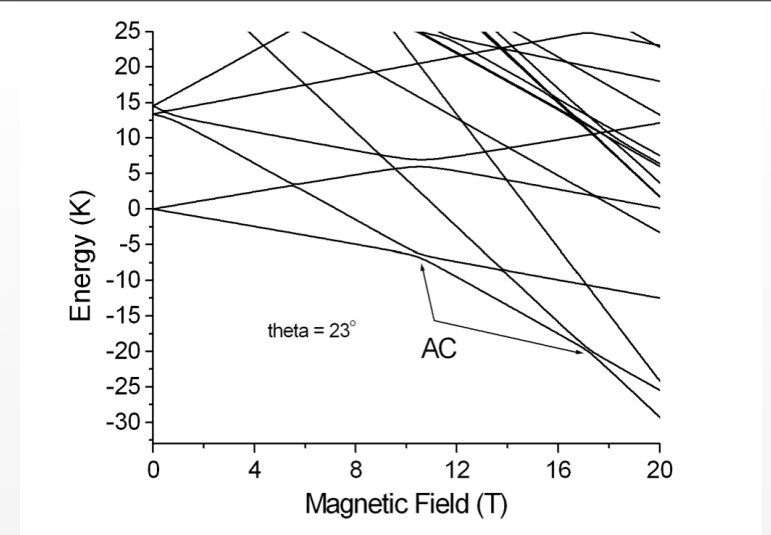


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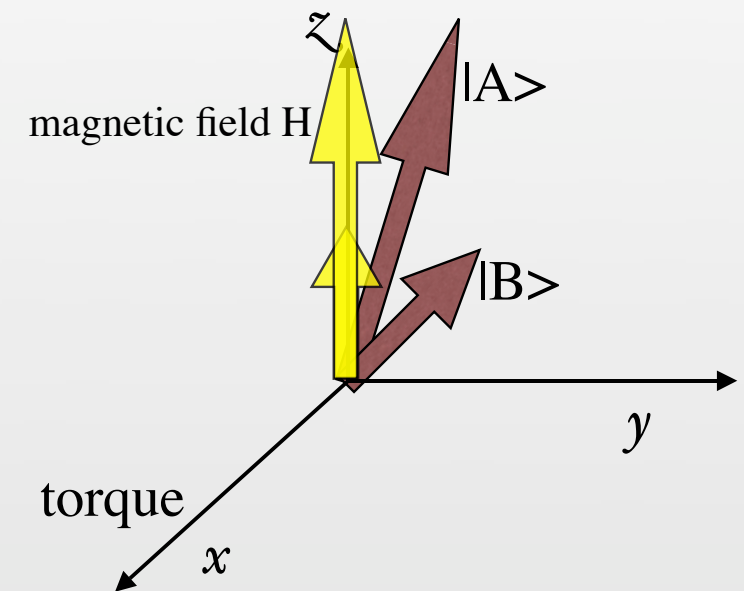
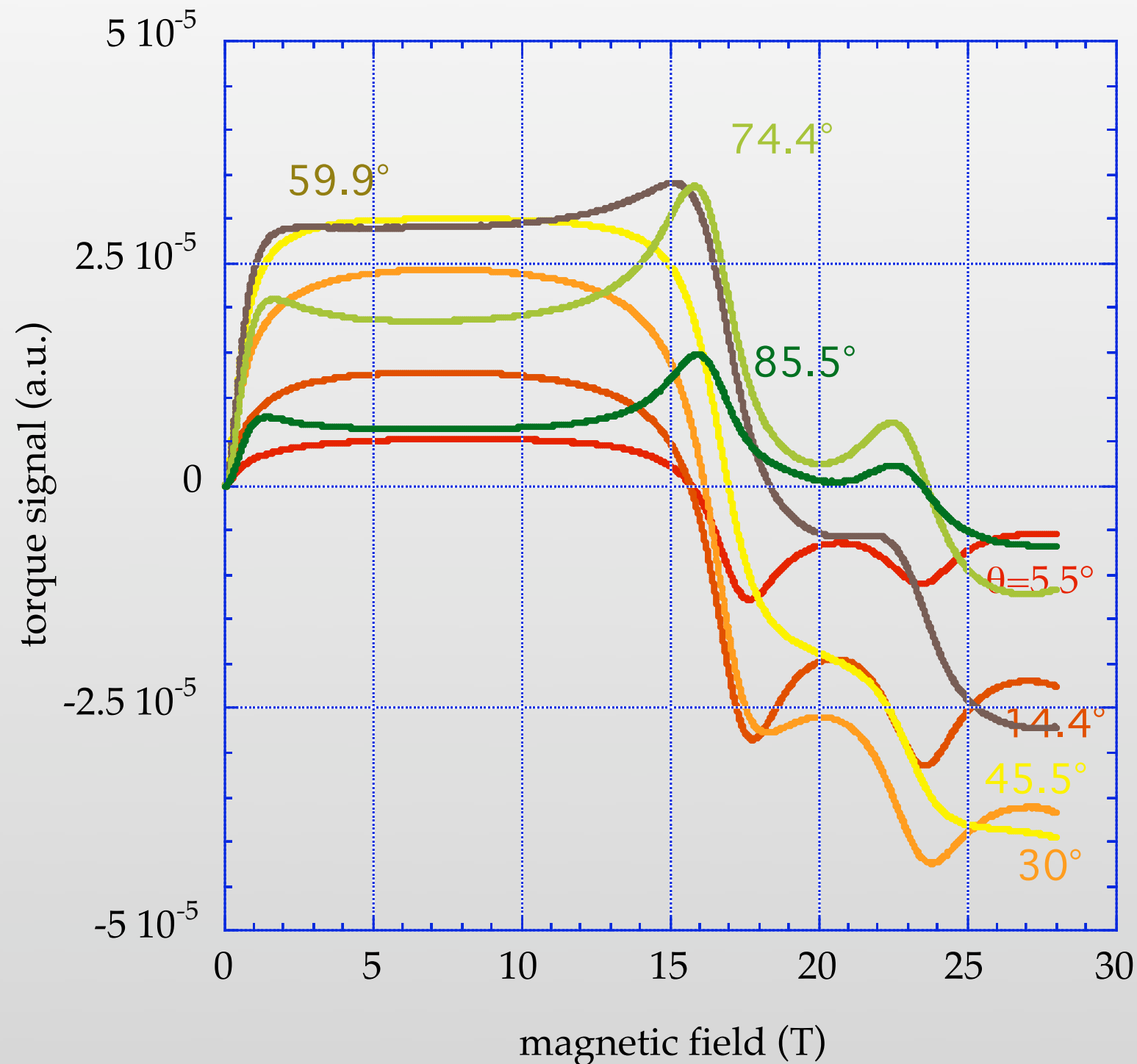
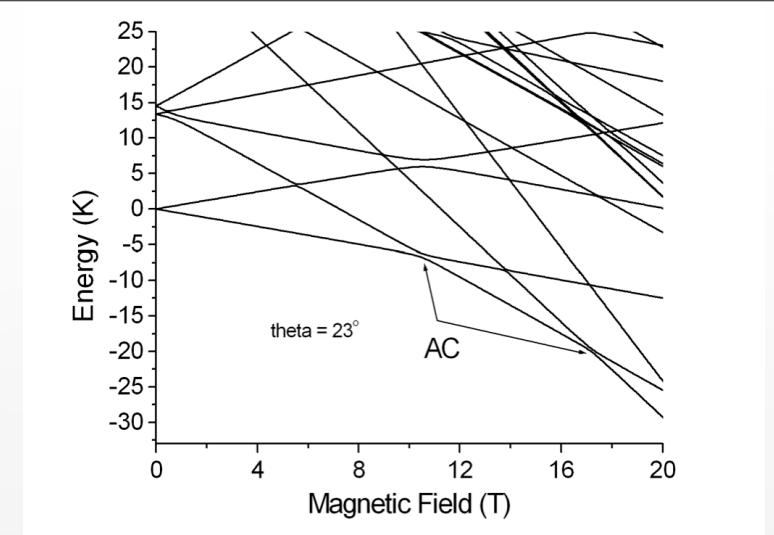


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Quantum bits

$$|\Psi\rangle = \alpha|\uparrow\rangle + \beta|\downarrow\rangle$$



Quantum bits

$$|\Psi\rangle = \alpha|\uparrow\rangle + \beta|\downarrow\rangle$$



Quantum bits

$$|\Psi\rangle = \alpha|\uparrow\rangle + \beta|\downarrow\rangle$$



Long decoherence

- Identification of well-defined qubit
- Reliable state preparation
- Accurate quantum gate operations
- **Low decoherence**
- scalability
- Read-out

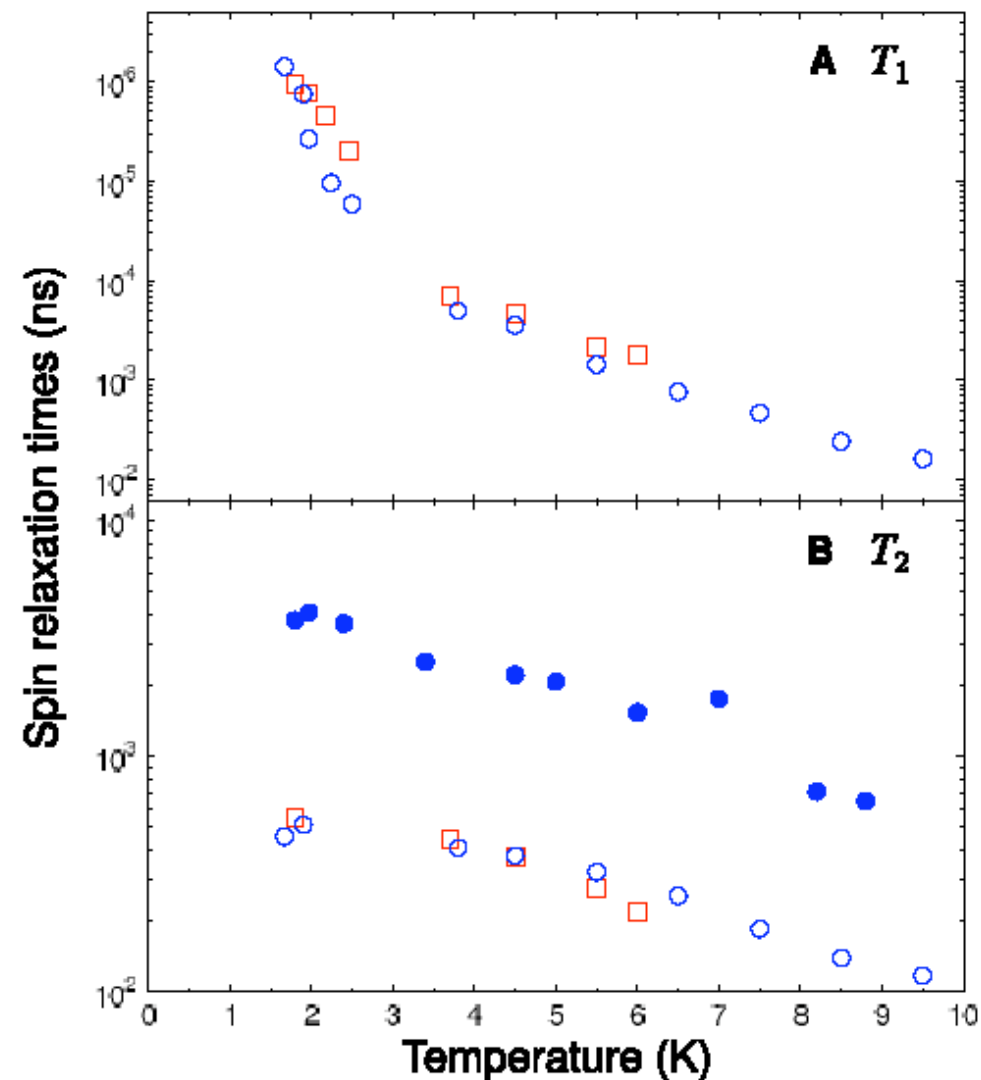
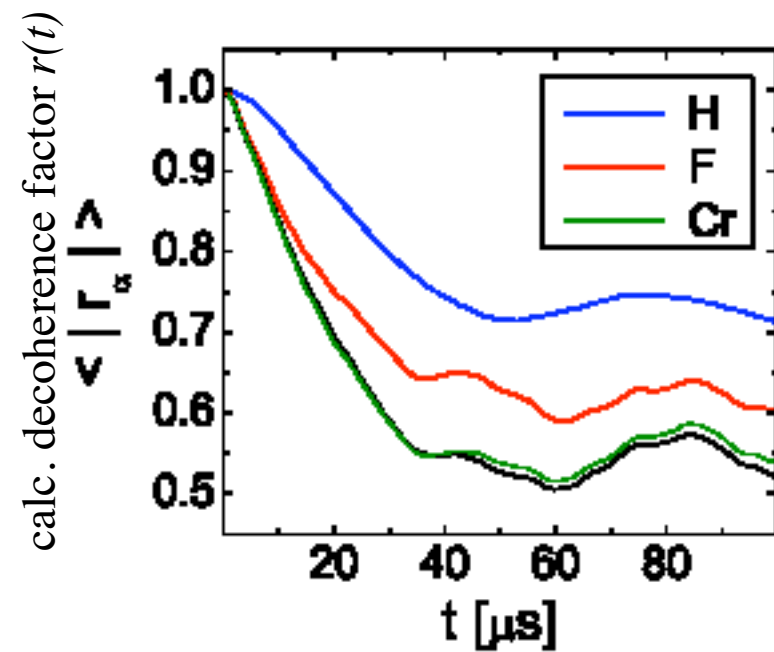


figure of merit
 $Q = t_g / T_2 > 100$

A. Ardavan, O. Rival, J.J.L. Morton, S. Blundell, A.M. Tyryshkin, G. Timco, R. Winpenny, *Phys. Rev. Lett.* **98**, 057201 (2007).

molecular engineering to reduce decoherence

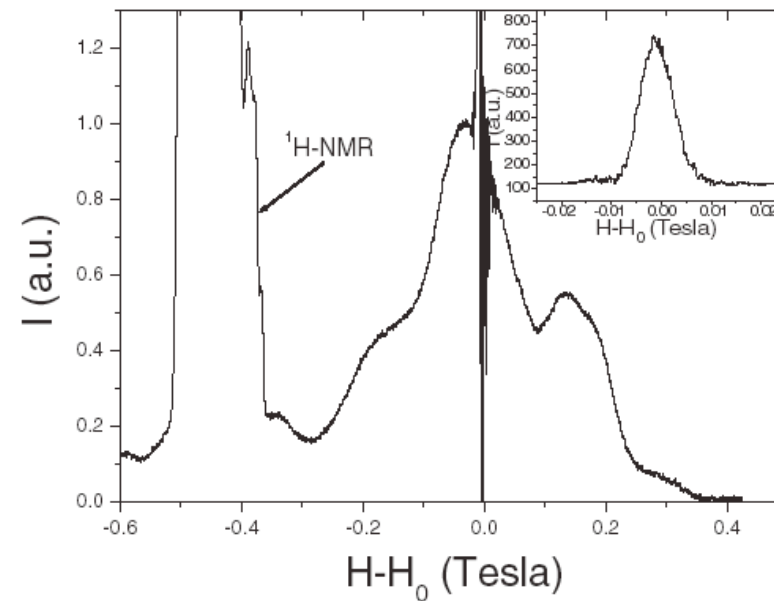
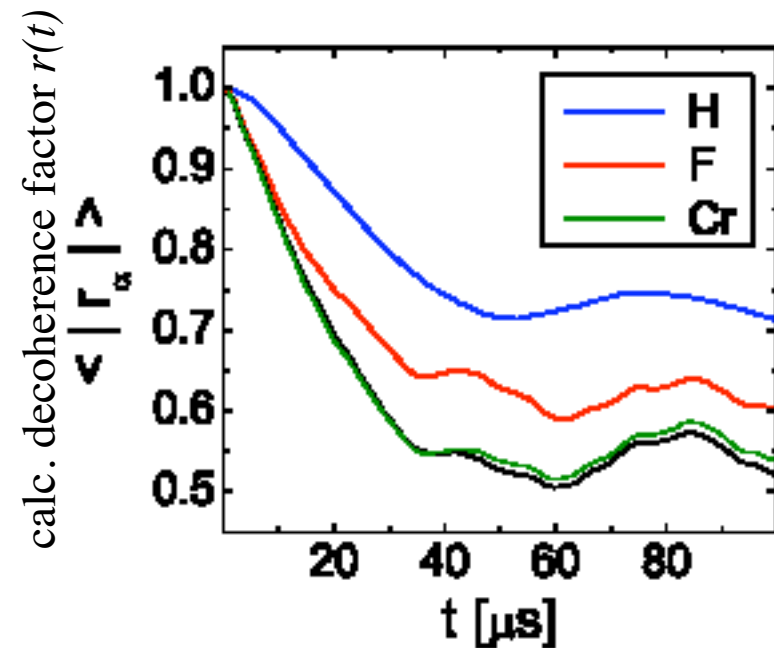


Decoherence induced by hyperfine interactions with nuclear spins in antiferromagnetic molecular rings

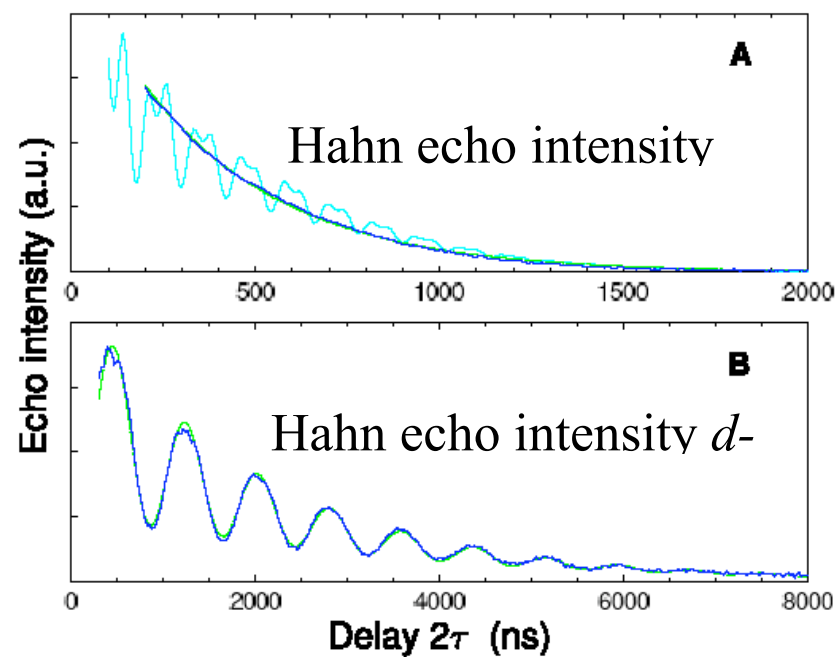
F. Troiani, V. Bellini, and M. Affronte

Physical Review B 77, 054428 (2008).

molecular engineering to reduce decoherence



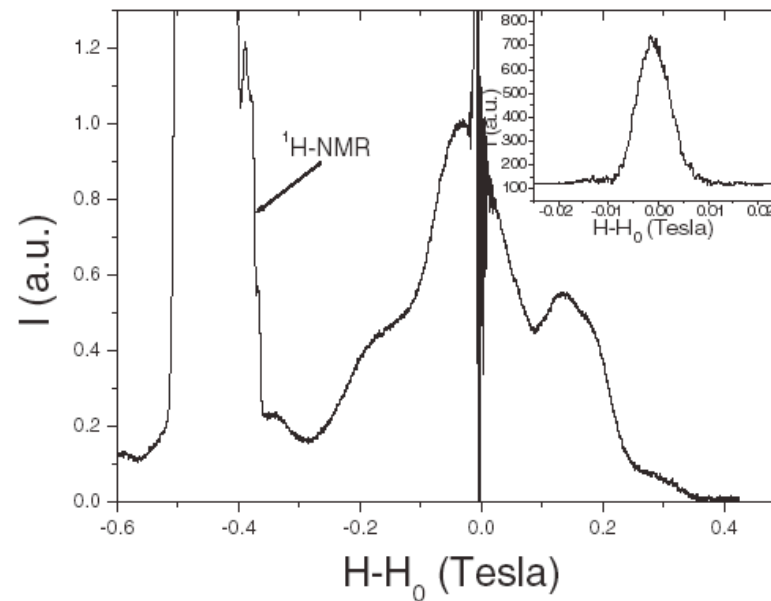
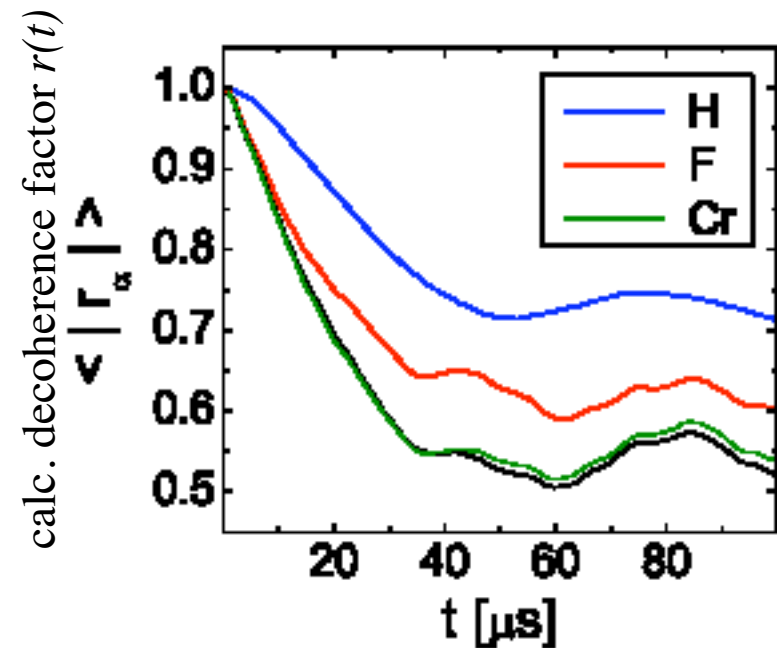
Micotti et al. PRL **97**, 267204 (2006)



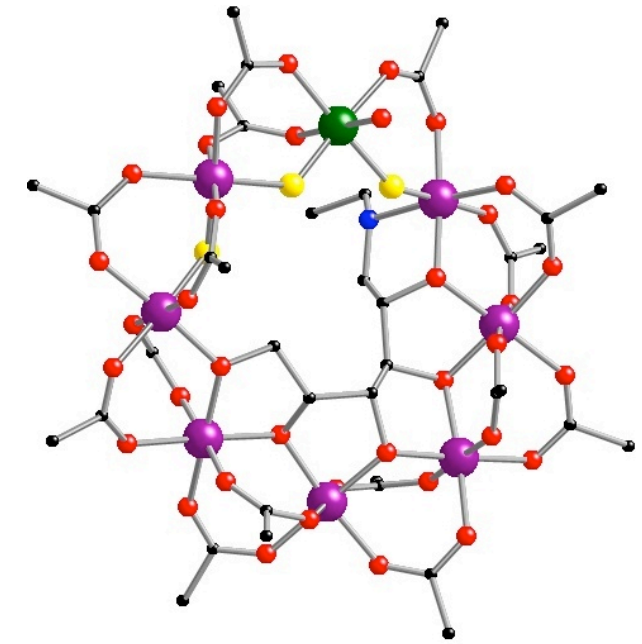
Ardavan et al. PRL **98**, 057201 (2007)

Decoherence induced by hyperfine interactions with nuclear spins in antiferromagnetic molecular rings
F. Troiani, V. Bellini, and M. Affronte
Physical Review B **77**, 054428 (2008).

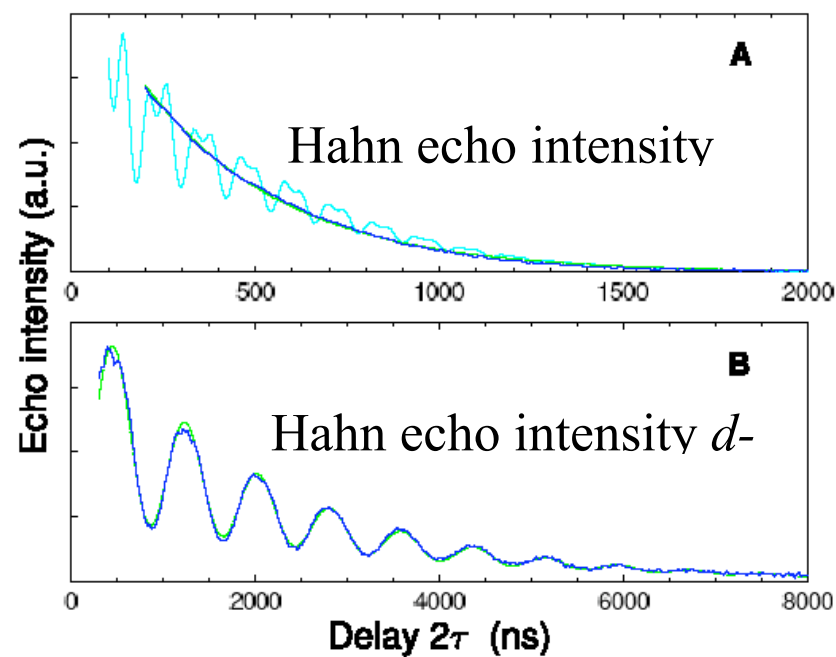
molecular engineering to reduce decoherence



Micotti et al. PRL **97**, 267204 (2006)



glued Cr₇Ni in which
fluoride groups are replaced by alkoxides
G.TIMCO ET AL. Angew. Chem. Int. Ed. 2008, 47, 9681

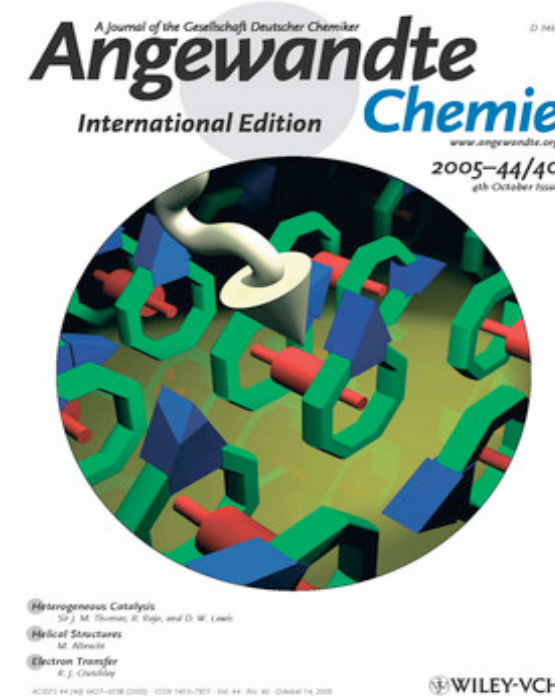
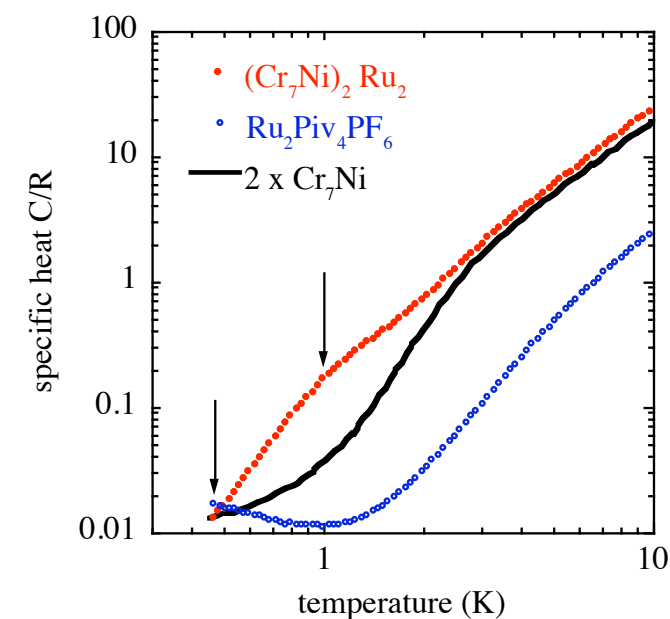
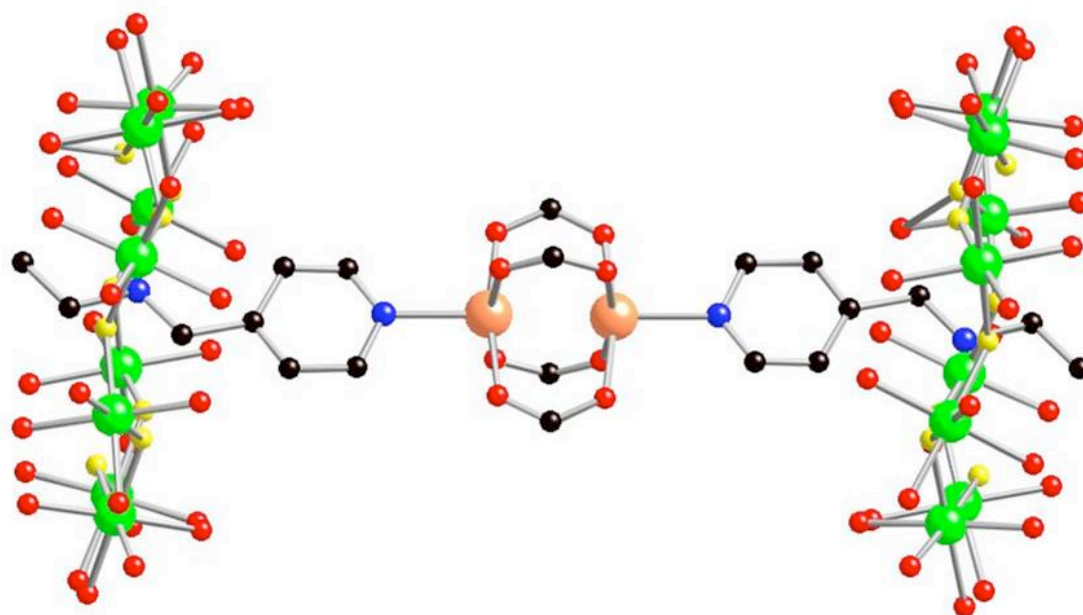


Ardavan et al. PRL **98**, 057201 (2007)

*Decoherence induced by hyperfine interactions with
nuclear spins in antiferromagnetic molecular rings*
F. Troiani, V. Bellini, and M. Affronte
Physical Review B **77**, 054428 (2008).

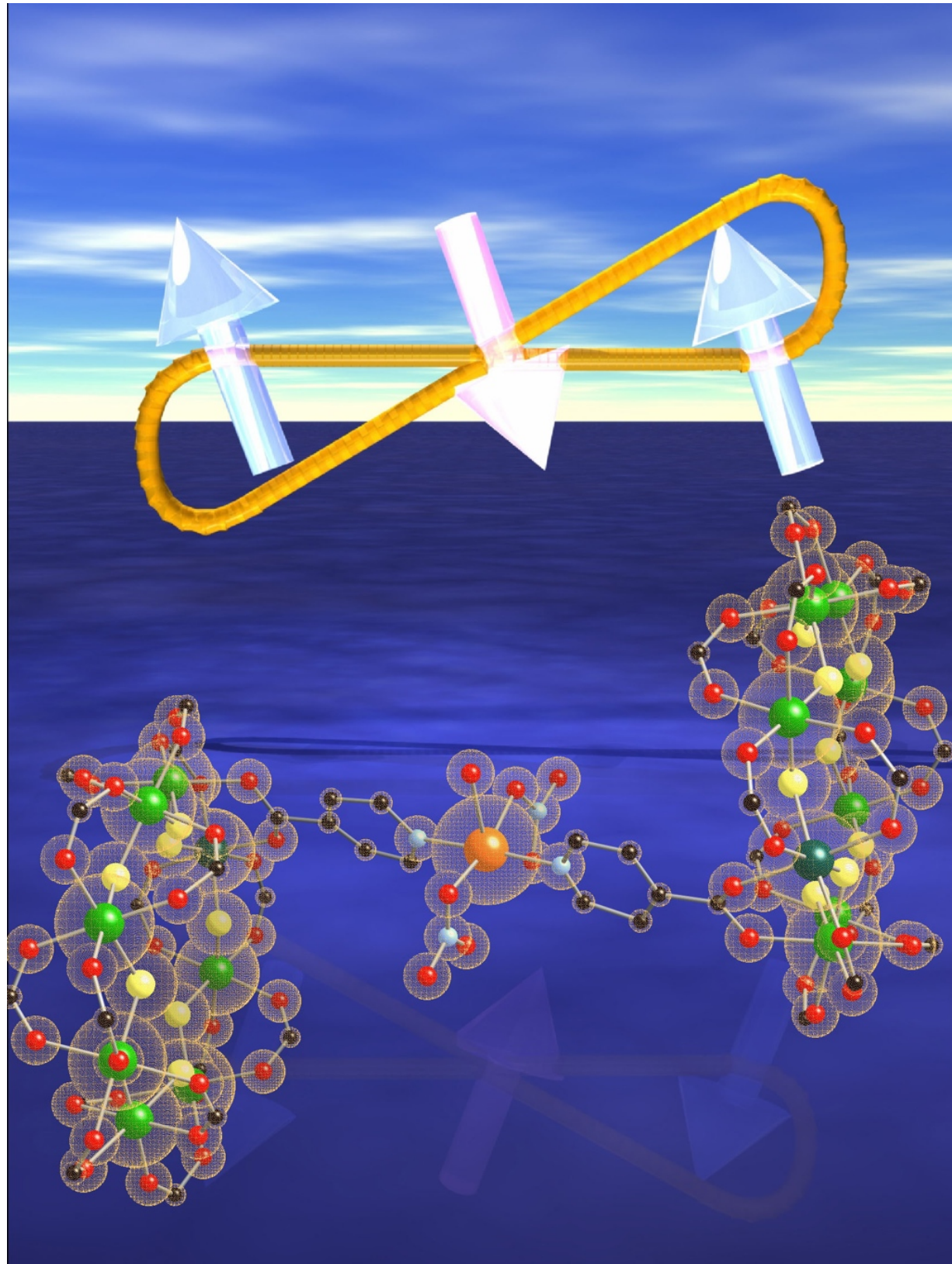
linking magnetic molecules.

M. Affronte et al. JMMM 310 (2007) e501



M. Affronte, I. Casson, M. Evangelisti, A. Candini, S. Carretta, C. A. Muryn, S.J. Teat, G. A. Timco, W. Wernsdorfer, and R. E. P. Winpenny
Angew. Chem. Int. Ed. 44, 6496 (2005).

supramolecular entanglement



- Identification of well-defined qubit
- Reliable state preparation
- **Accurate quantum gate operations**
- Low decoherence
- scalability
- Read-out

- separate objects with well defined states.
- weak coupling.
- the states of each subsystem can no longer be described independently from one to another

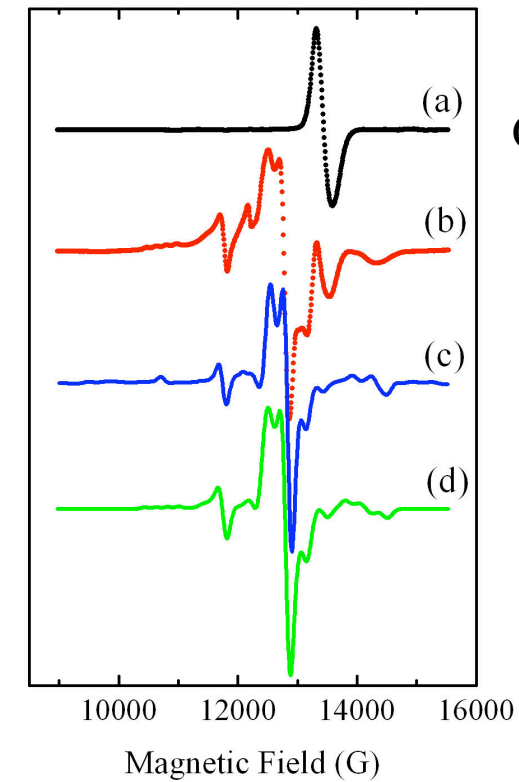
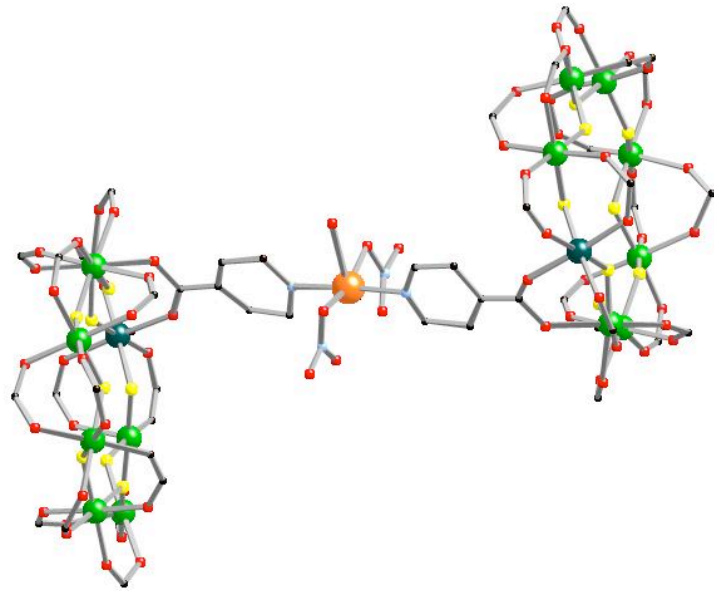
$$\frac{|00\rangle + |11\rangle}{\sqrt{2}}$$

*example: Bell state or EPR pair
(Einstein, Podolsky, Rosen)*

*A measurement of the second qubit always
gives the same result as the first*

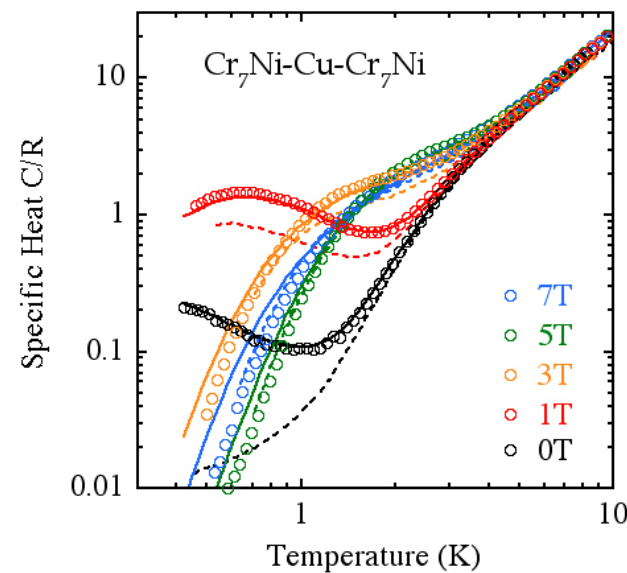
- different “degrees” of entanglement

generation of maximally entangled GHZ (Greenberger-Horne-Zeilinger) states in a tripartite molecular system



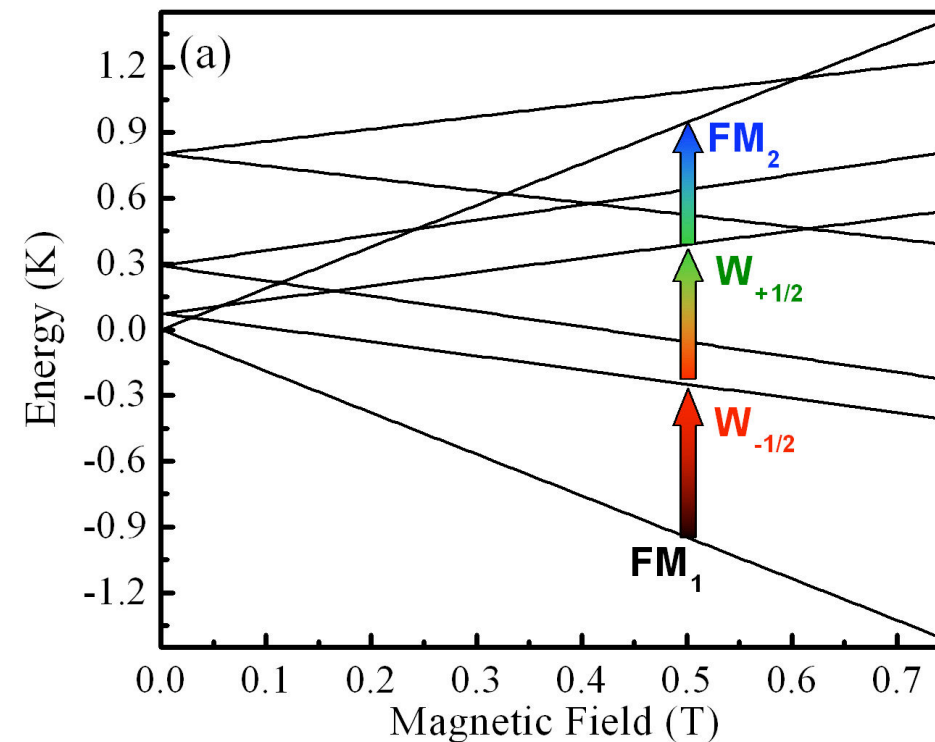
Cr₇Ni

Cr₇Ni-Cu-Cr₇Ni



$$|\text{GHZ}\rangle = (|\uparrow\uparrow\uparrow\rangle + |\downarrow\downarrow\downarrow\rangle) / \sqrt{2},$$

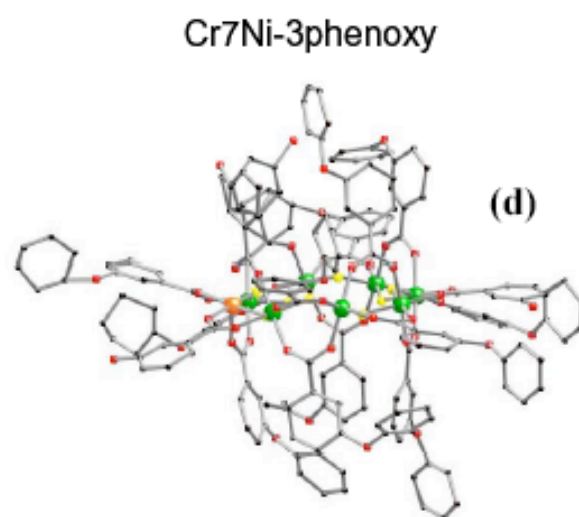
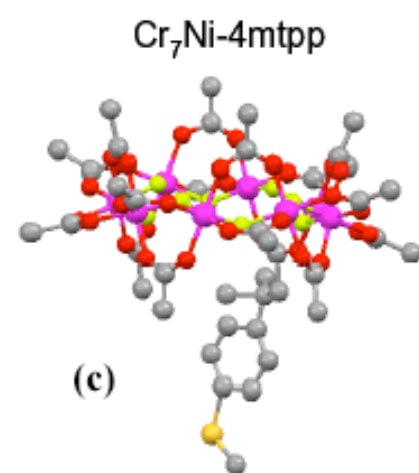
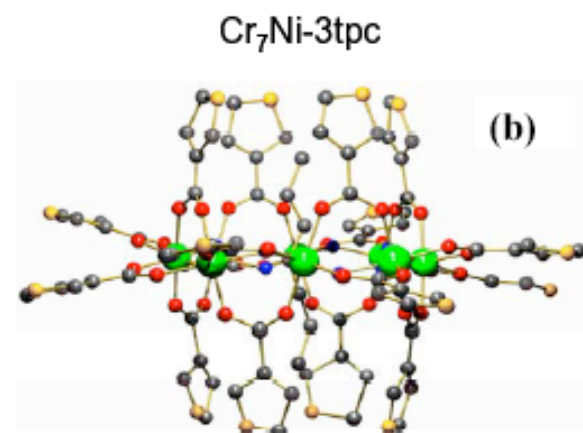
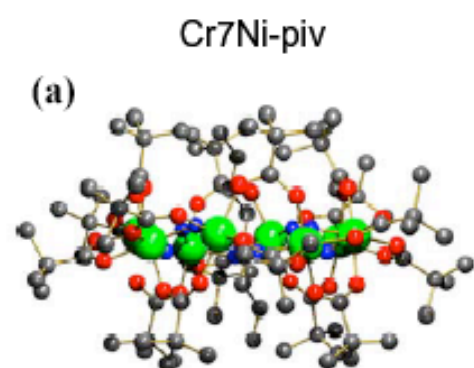
$$|W_{+1/2}\rangle = (|\uparrow\uparrow\downarrow\rangle + |\uparrow\downarrow\uparrow\rangle + |\downarrow\uparrow\uparrow\rangle) / \sqrt{3}; \quad |W_{-1/2}\rangle = (|\downarrow\downarrow\uparrow\rangle + |\downarrow\uparrow\downarrow\rangle + |\uparrow\downarrow\downarrow\rangle) / \sqrt{3}$$



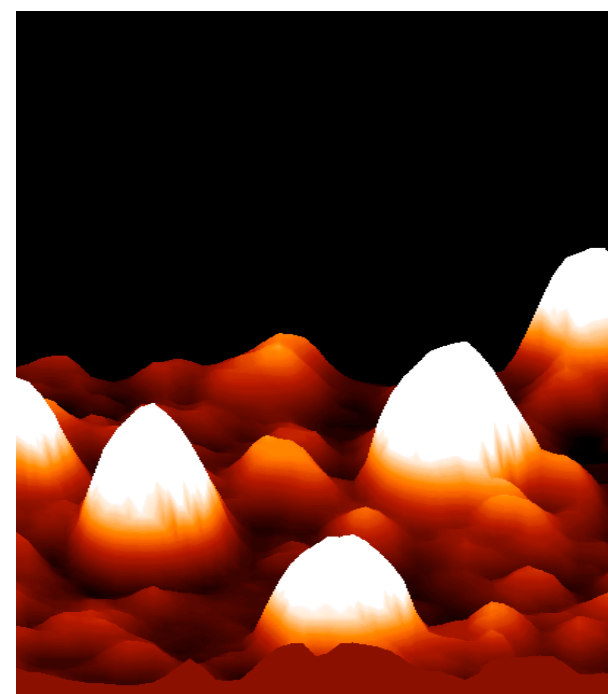
G.A. Timco, S. Carretta, F. Troiani, F. Tuna, R. J. Pritchard, C. Muryn, E. J. L. McInnes, A. Ghirri, A. Candini, P. Santini, G. Amoretti, M. Affronte, R. Winpenny.
Nature Nanotechnology (4, 173, March 2009).

molecules on surfaces

AF Cr₇Ni rings grafted on Au(111) surface

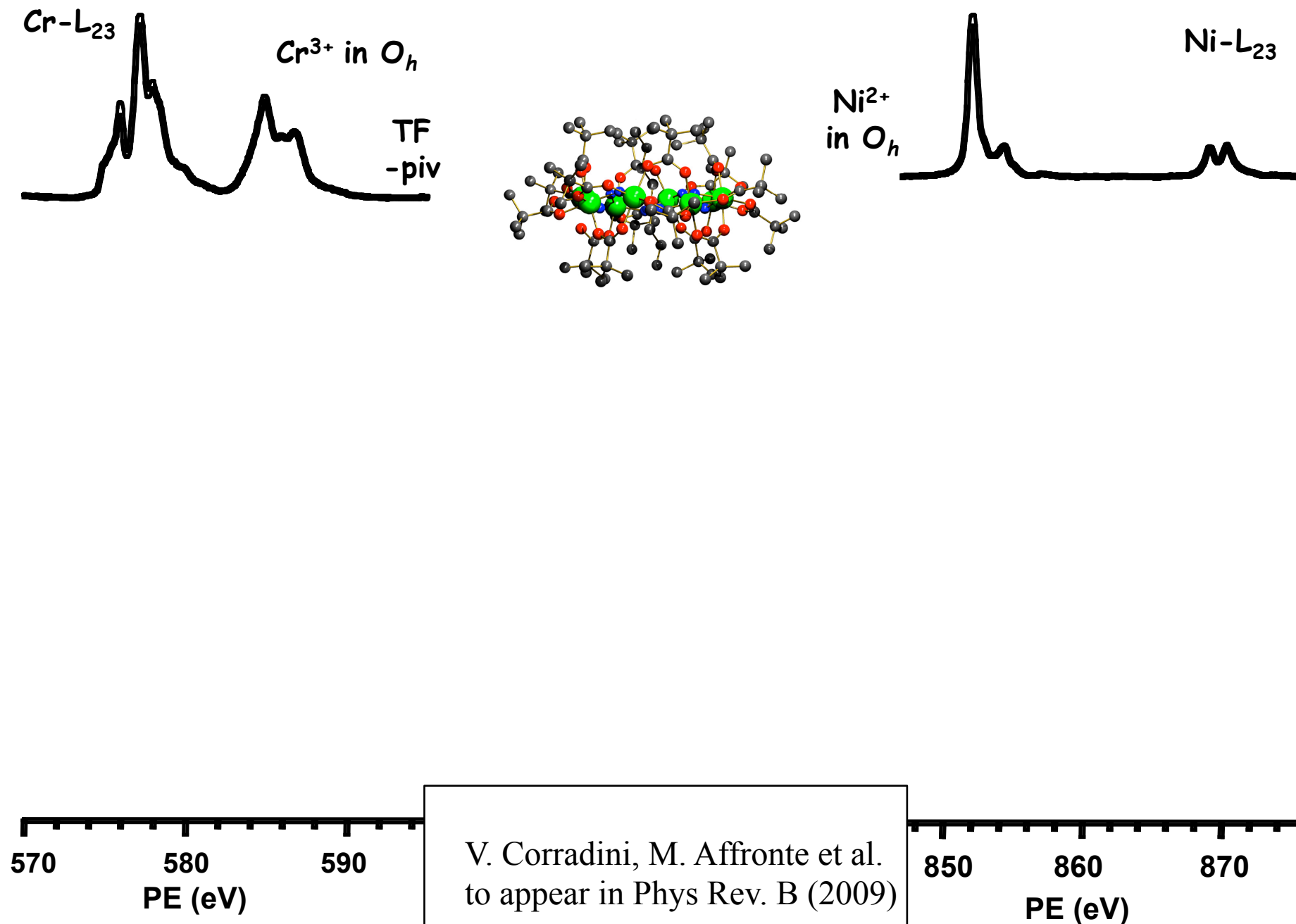


- Identification of well-defined qubit
- Reliable state preparation
- Accurate quantum gate operations
- Low decoherence
- **scalability**
- Read-out

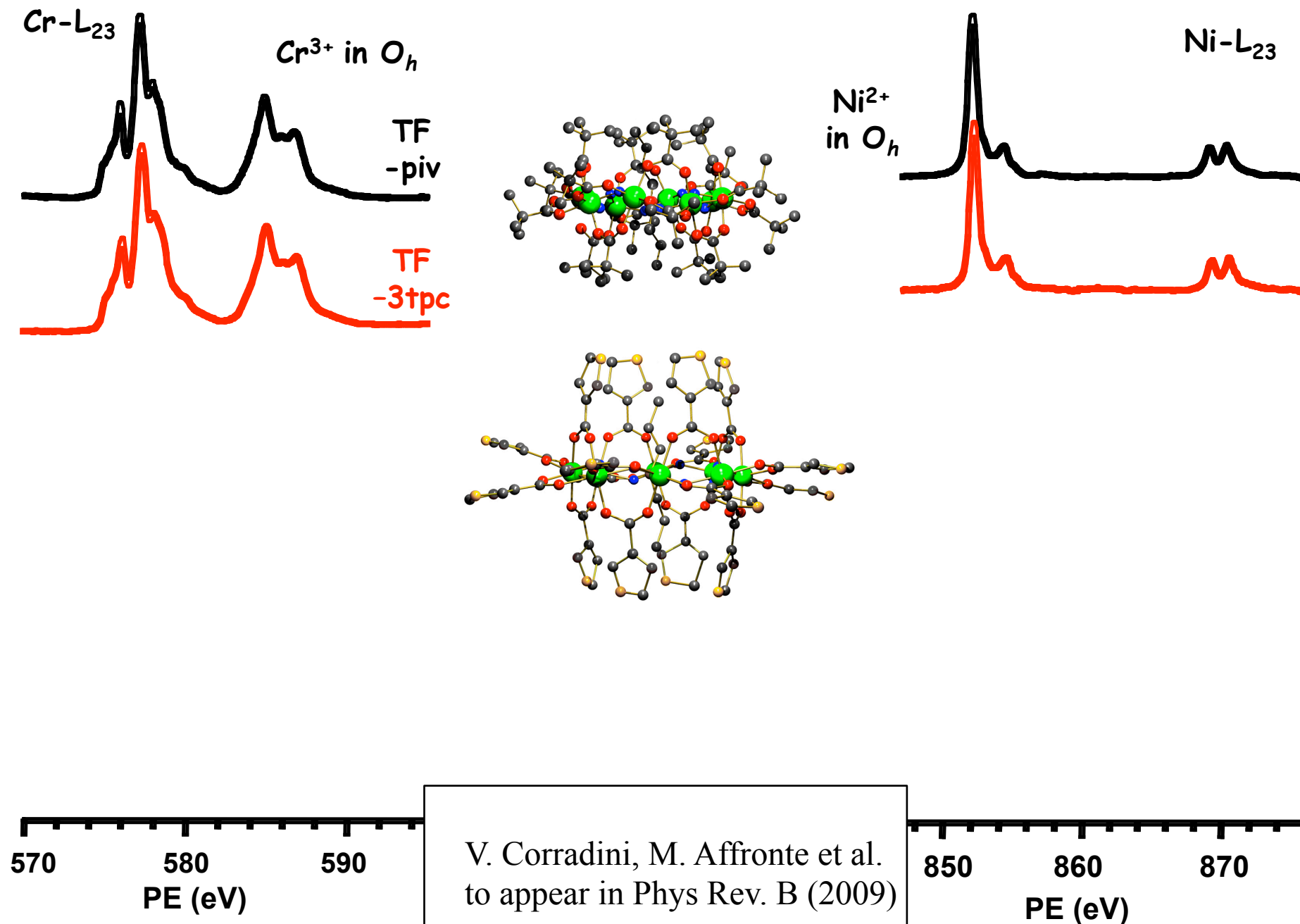


"Isolated Heterometallic Cr₇Ni Rings Grafted on Au(111) Surface" V. Corradini, R. Biagi, U. del Pennino, V. DeRenzi, A. Gambardella; M. Affronte, C. Muryn, G. Timco, REP Winpenny *Inor. Chem.* 46, 4968-4978 (2007)

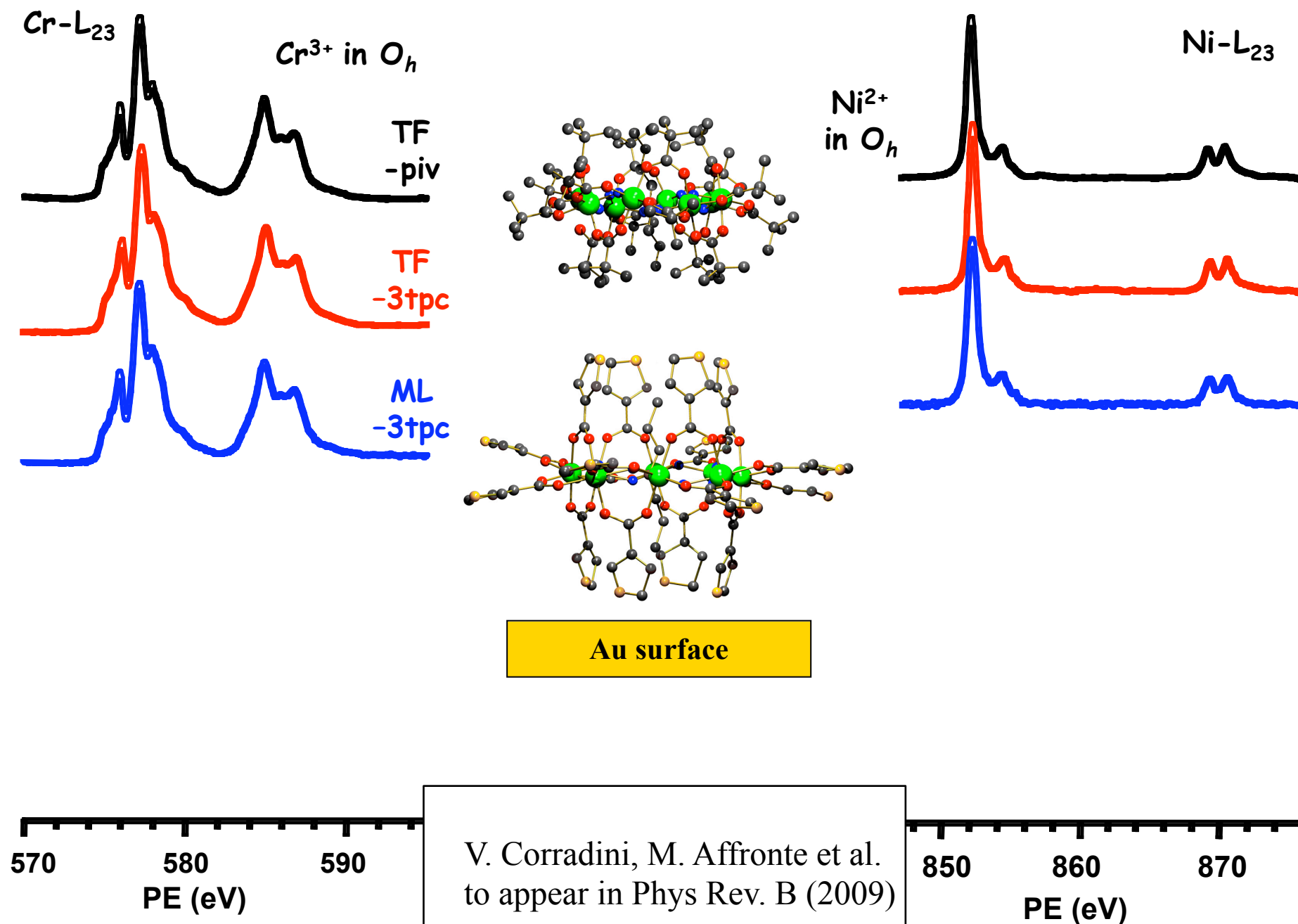
successful grafting of Cr₇Ni on Au surface



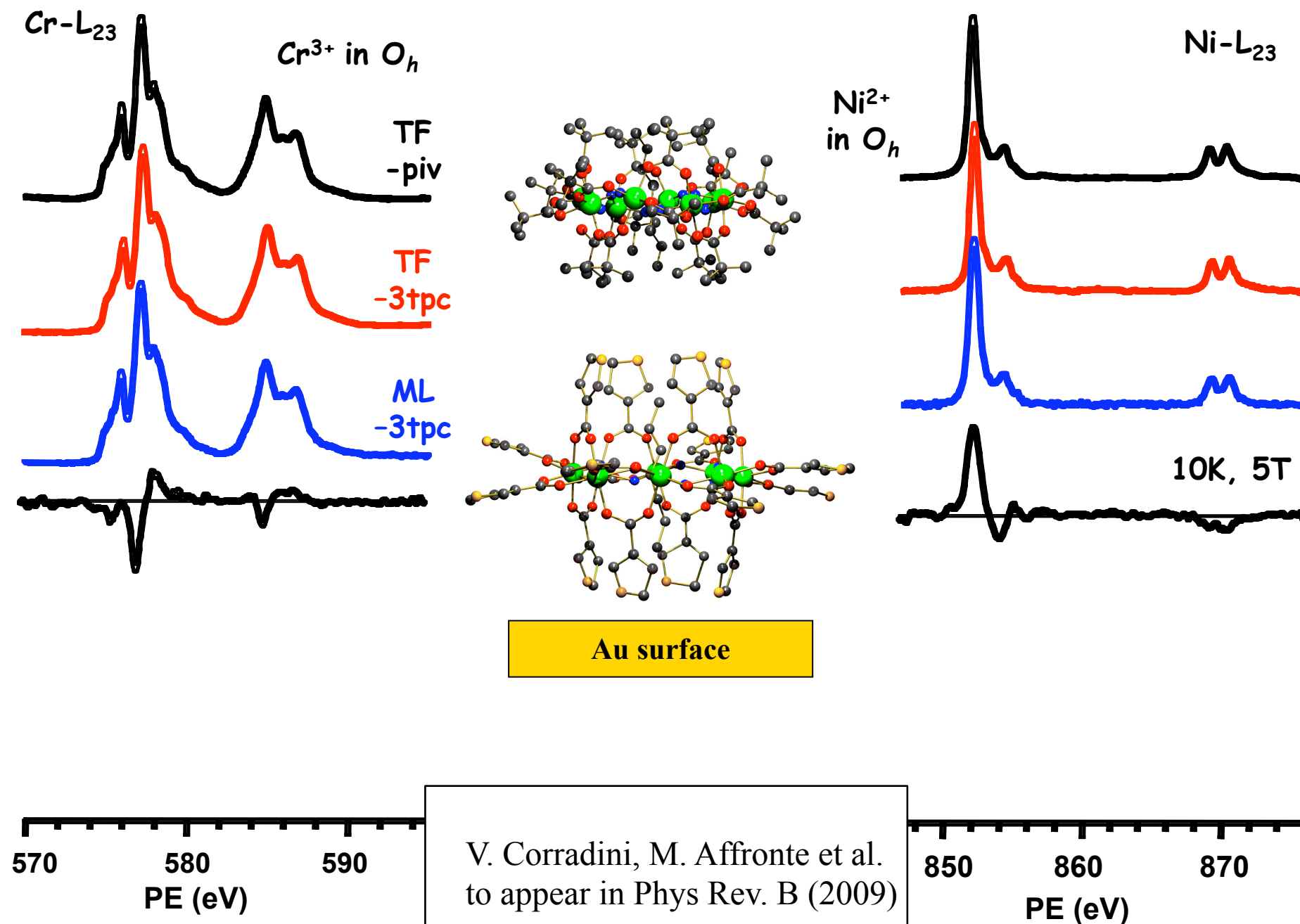
successful grafting of Cr₇Ni on Au surface



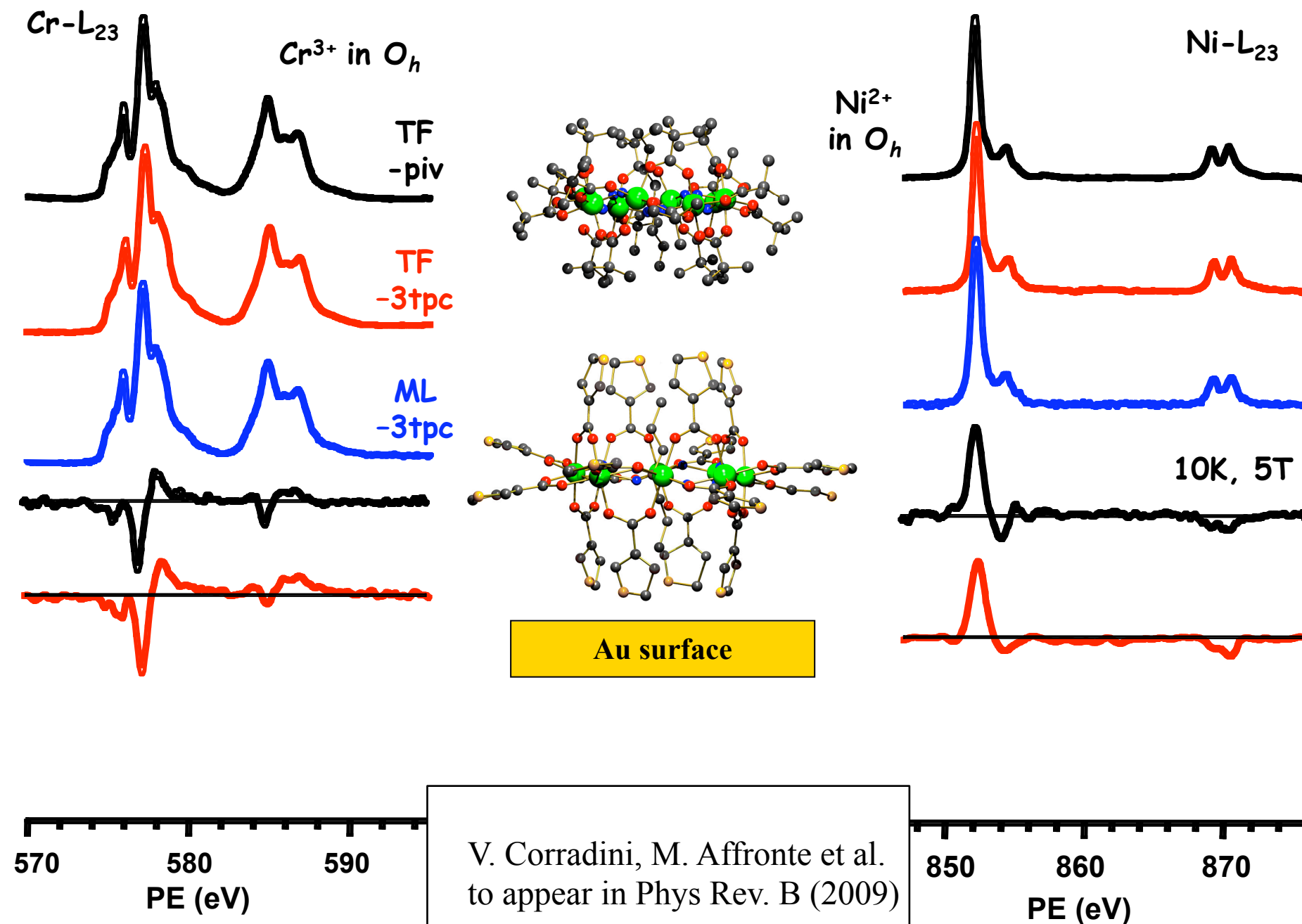
successful grafting of Cr₇Ni on Au surface



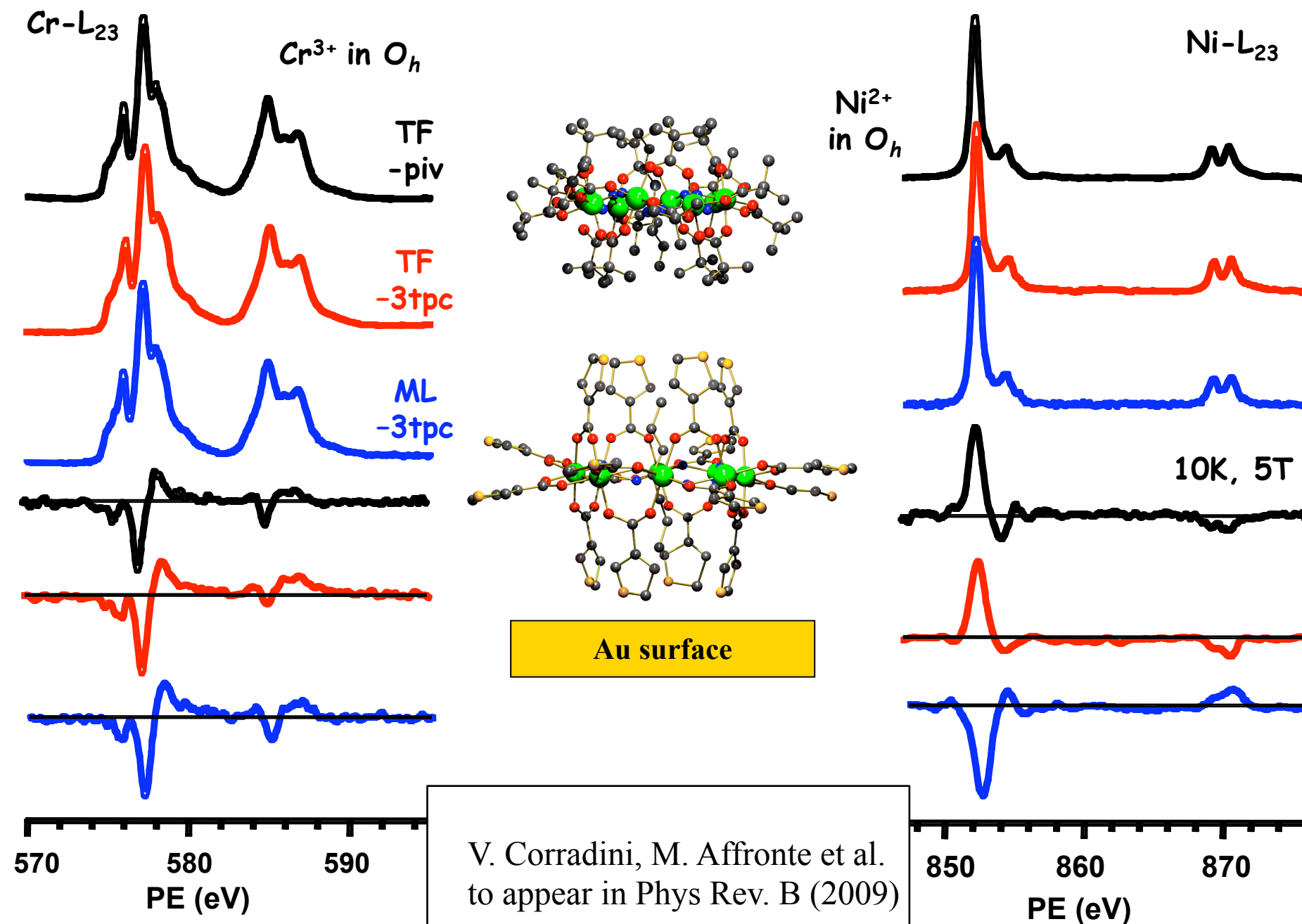
successful grafting of Cr₇Ni on Au surface



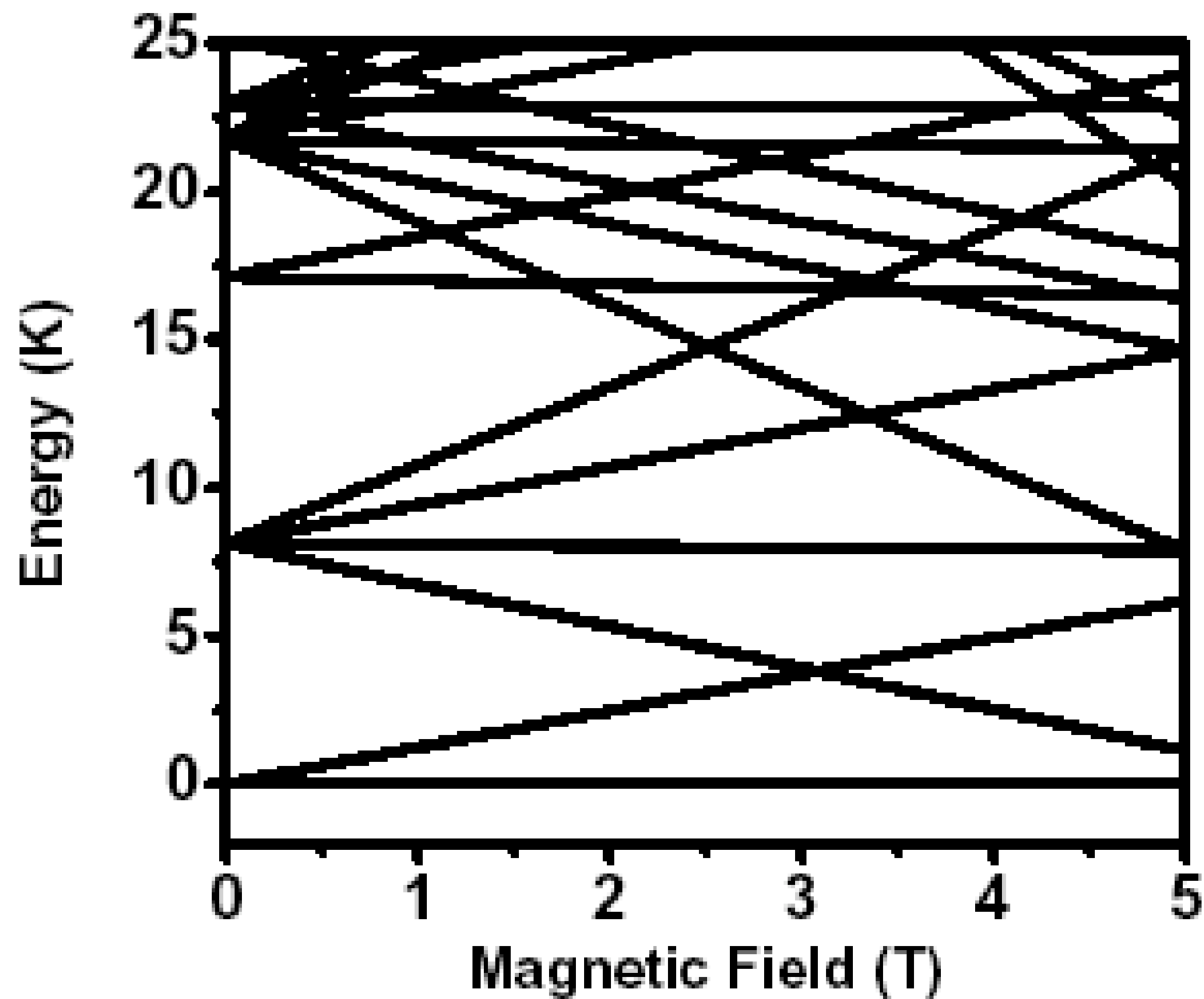
successful grafting of Cr₇Ni on Au surface



successful grafting of Cr7Ni on Au surface

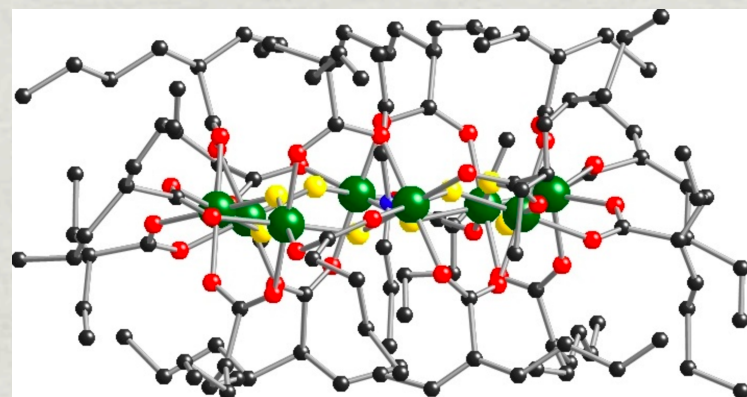


successful grafting of Cr₇Ni on Au surface

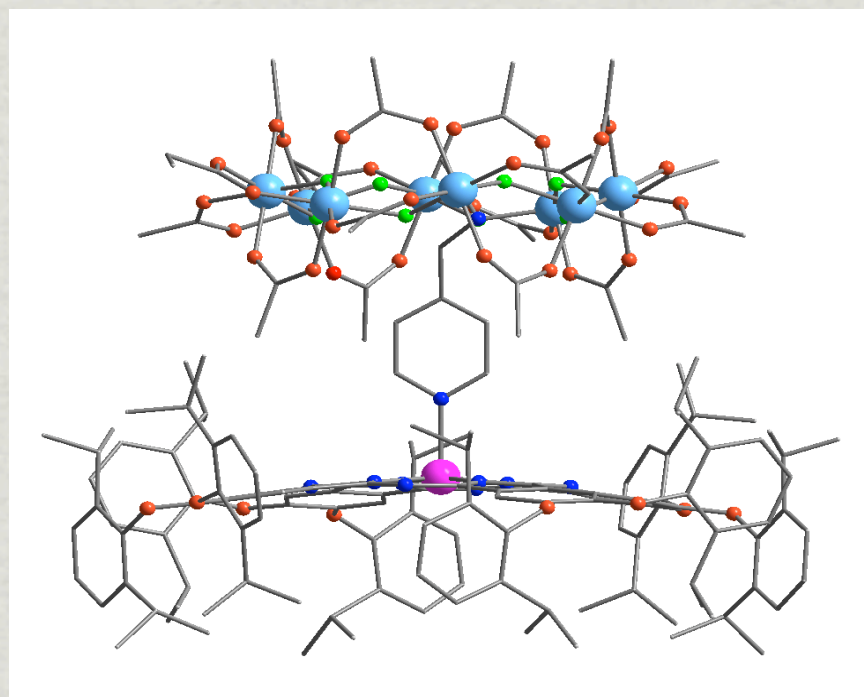


Cr7Ni on HOPG by liquid phase

ONE STEP

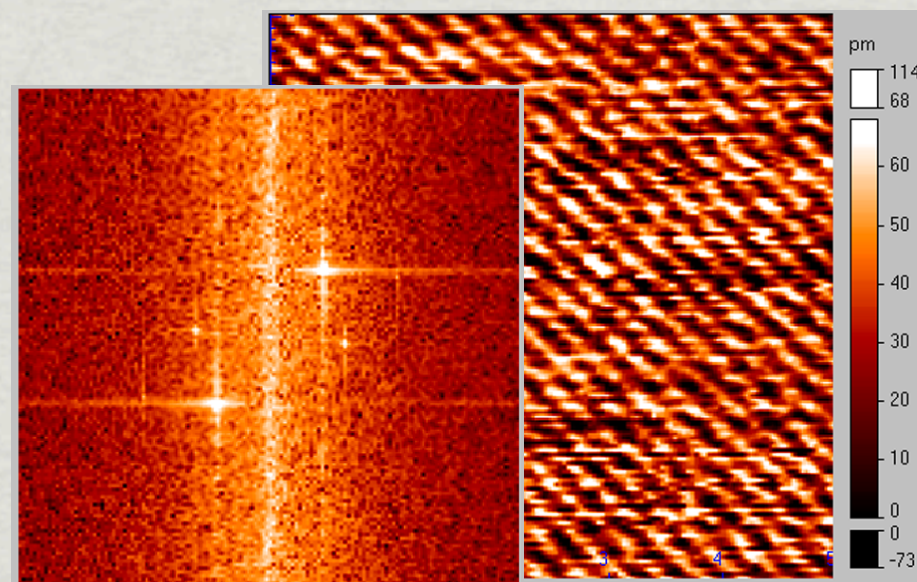
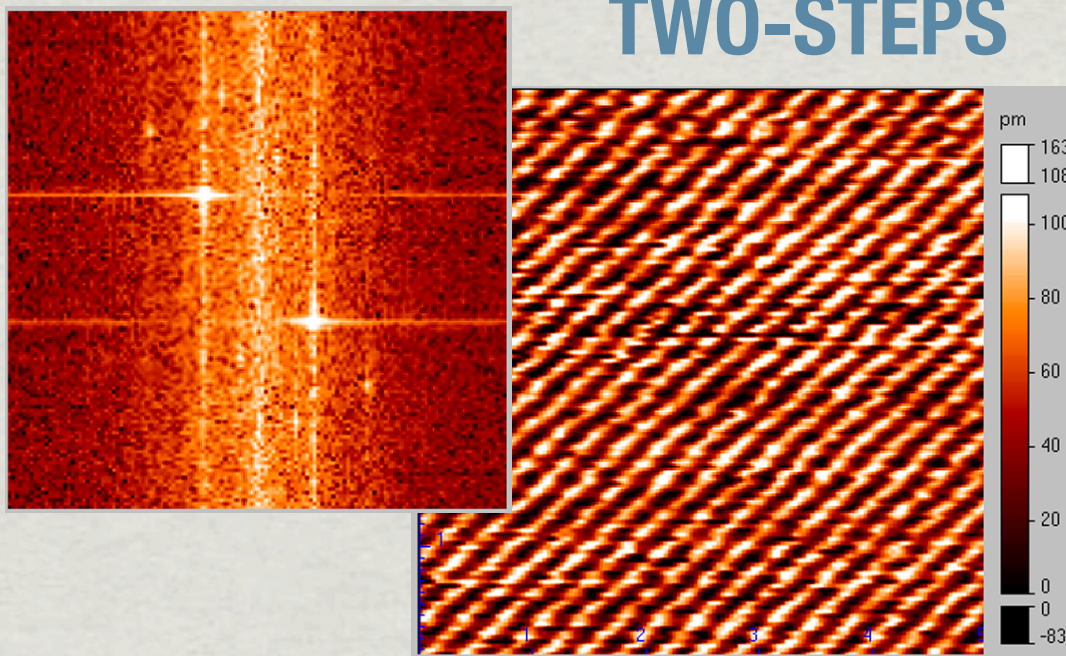


Cr7Ni 2-ethylhexanoate



CoPc+Cr7Ni

TWO-STEPS

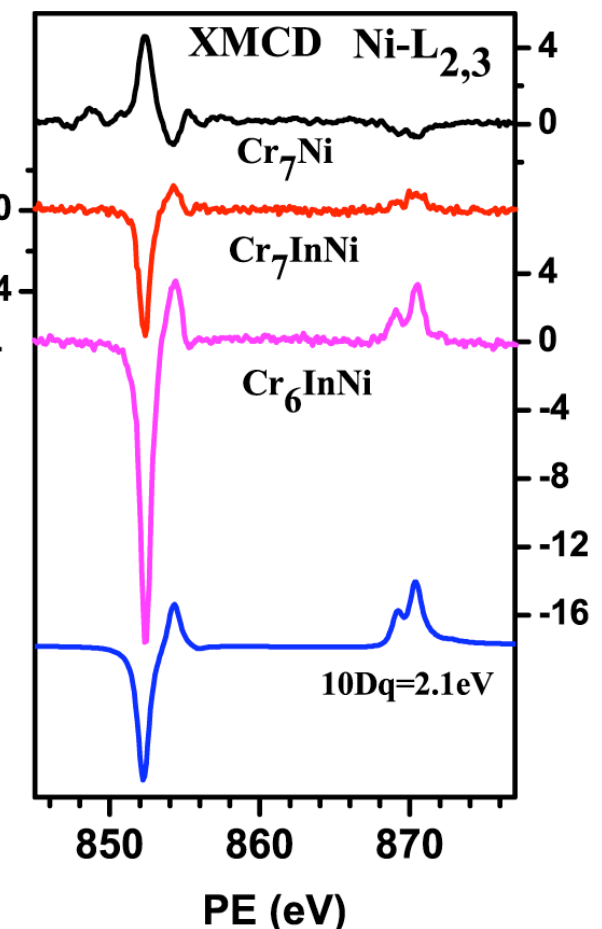
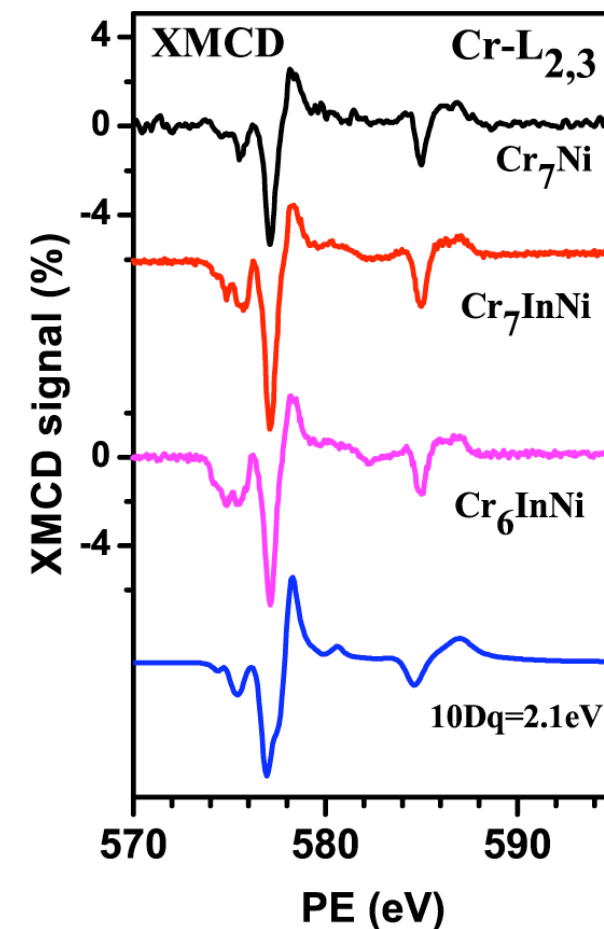
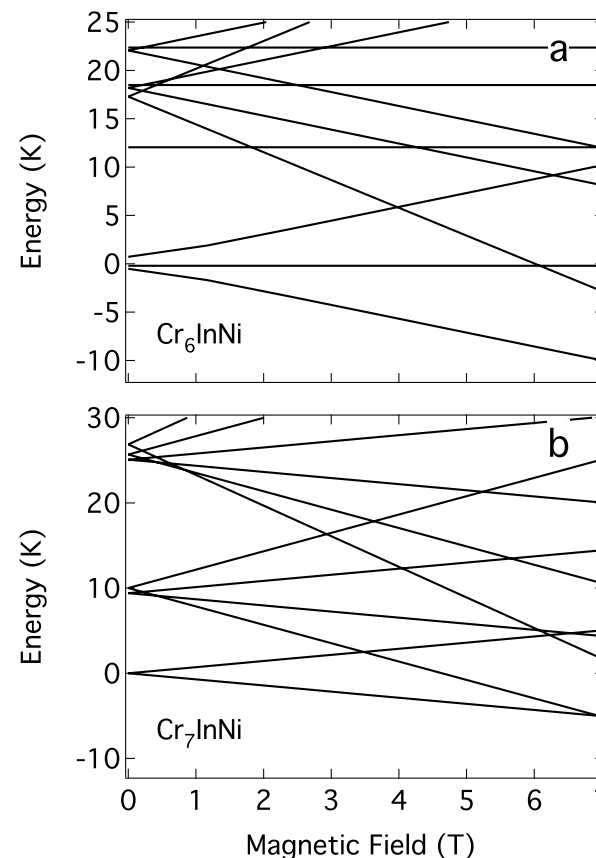
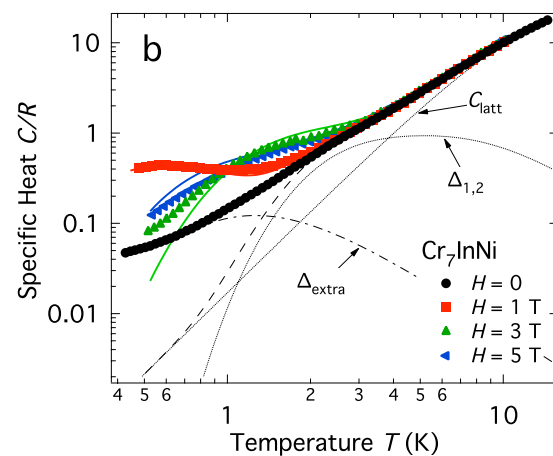
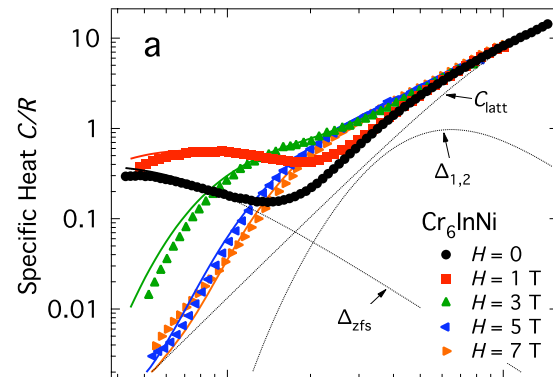
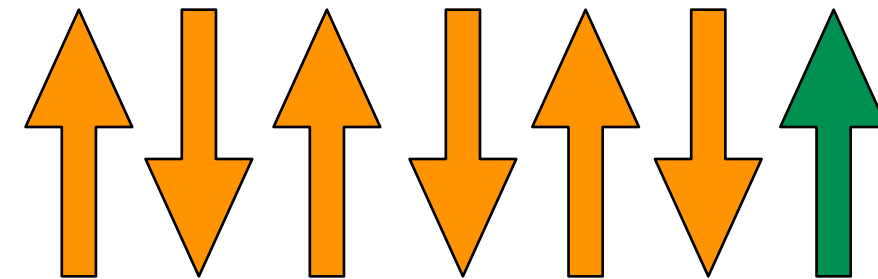
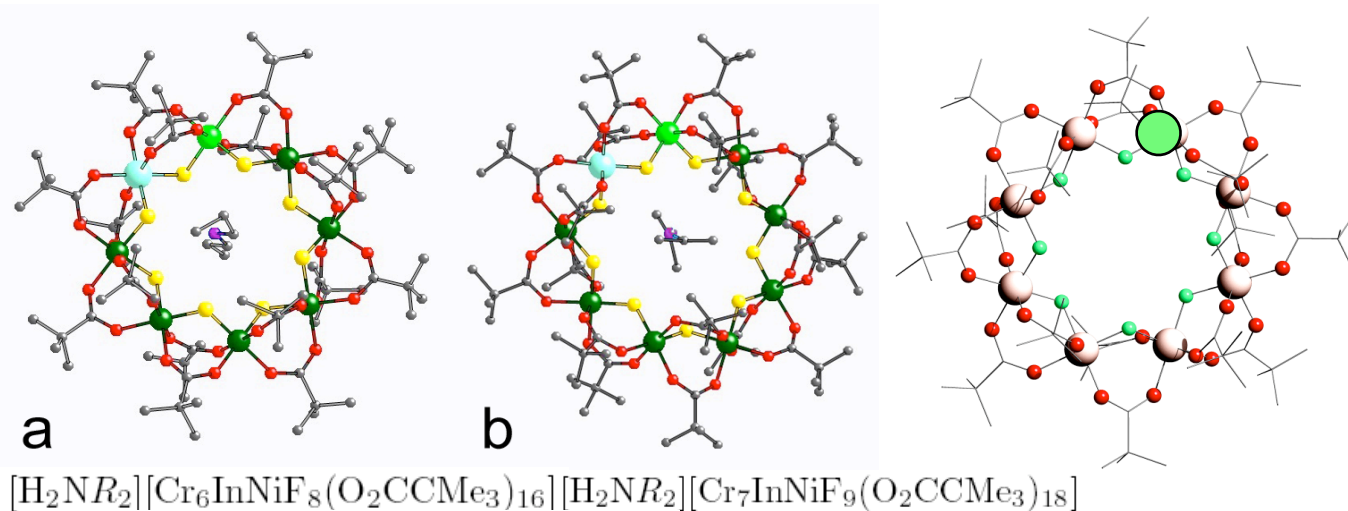


Tetratriacontane C₃₄H₇₀ / HOPG

read & write

XMCD as probe for local magnetization in AF rings

- Identification of well-defined qubit
- Reliable state preparation
- Accurate quantum gate operations
- Low decoherence
- scalability
- Read-out

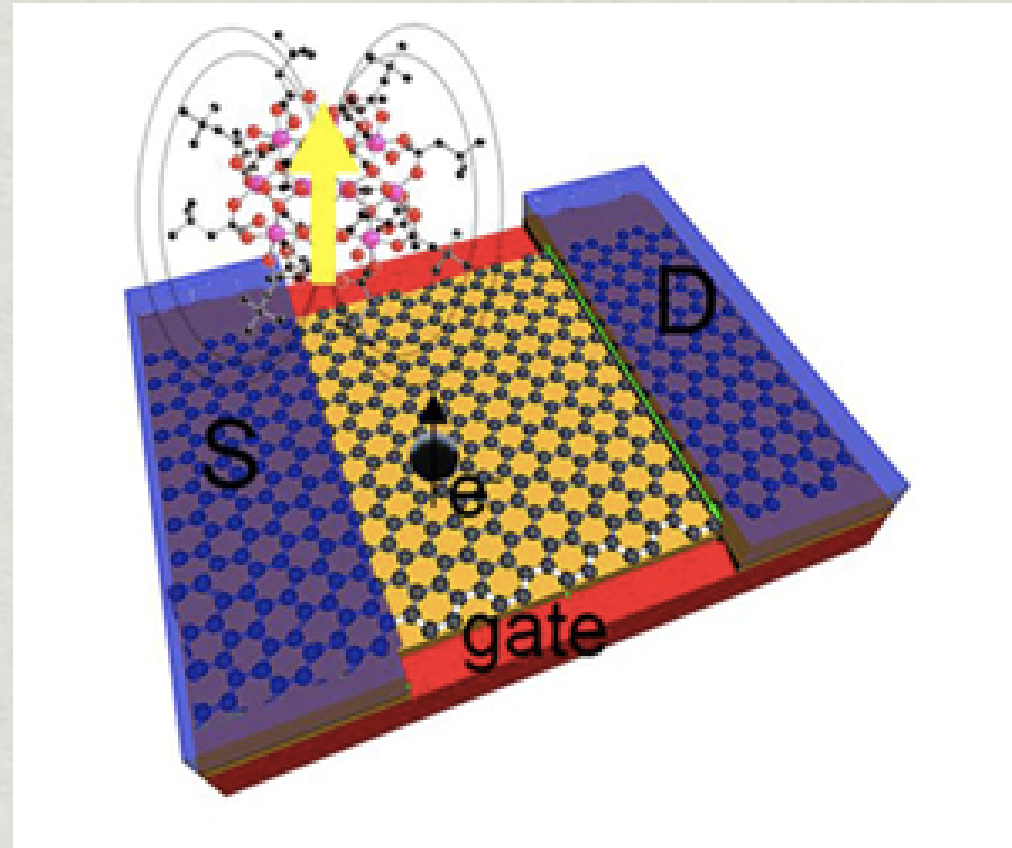


Probing edge magnetization in antiferromagnetic spin segments.

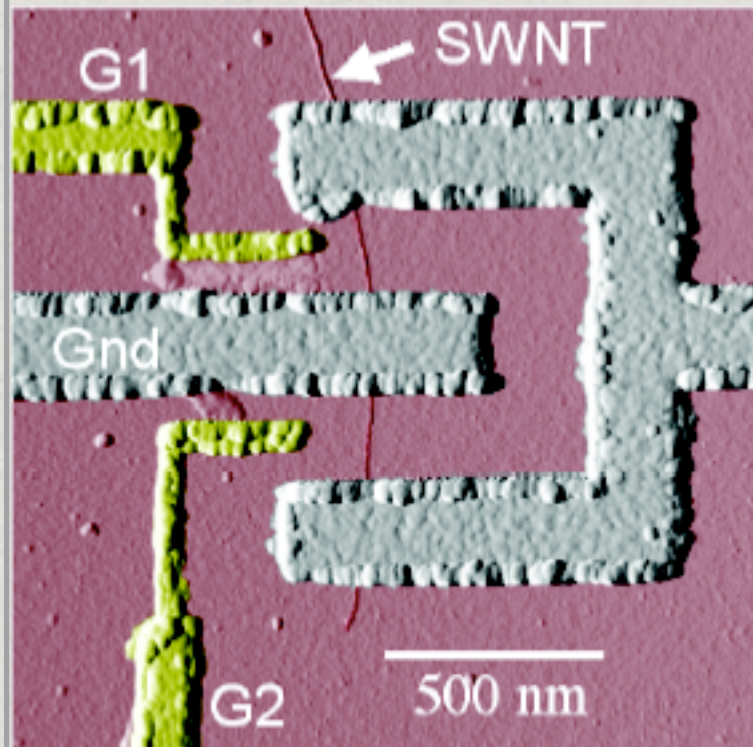
A. Ghirri, G. Lorusso, F. Moro, V. Corradini, M. Affronte, J. C. Cezar, C. Muryn, F. Tuna, G. Timco and R. E. P. Winpenny

submitted

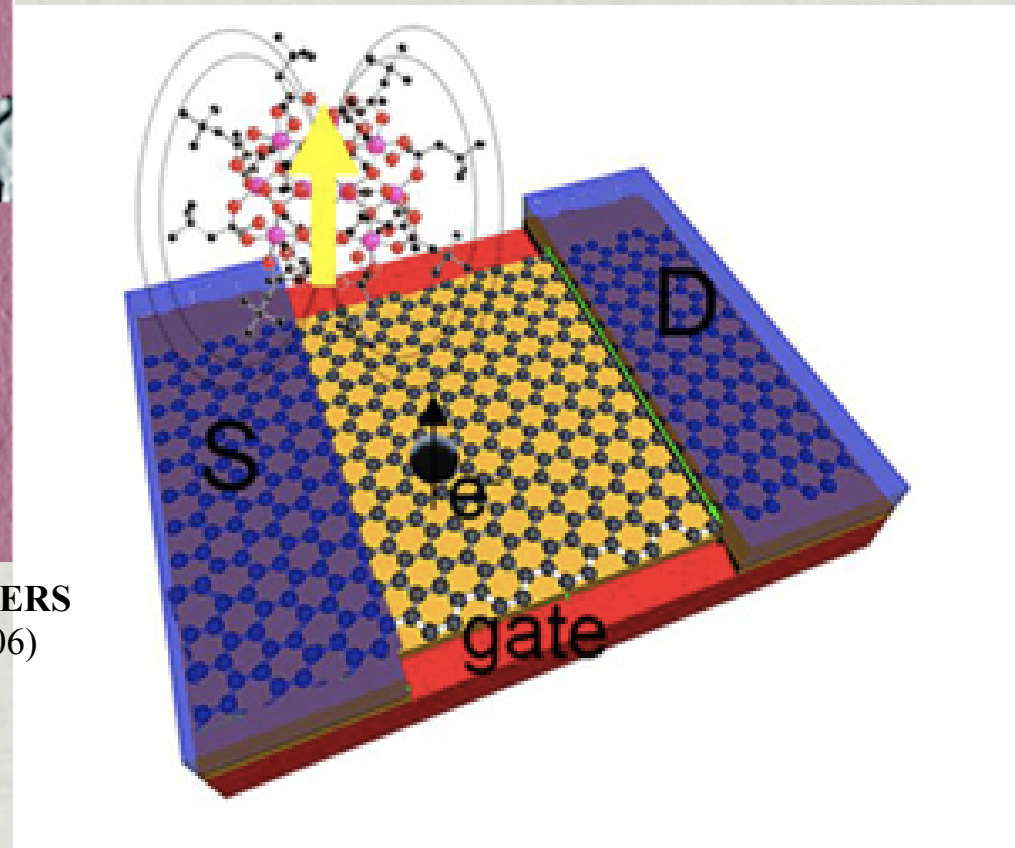
molecular spintronics



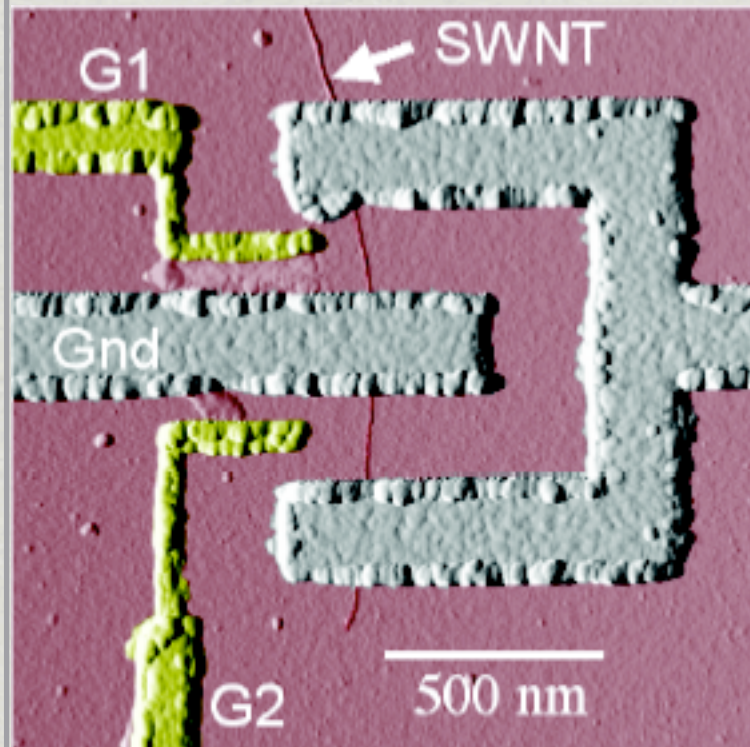
molecular spintronics



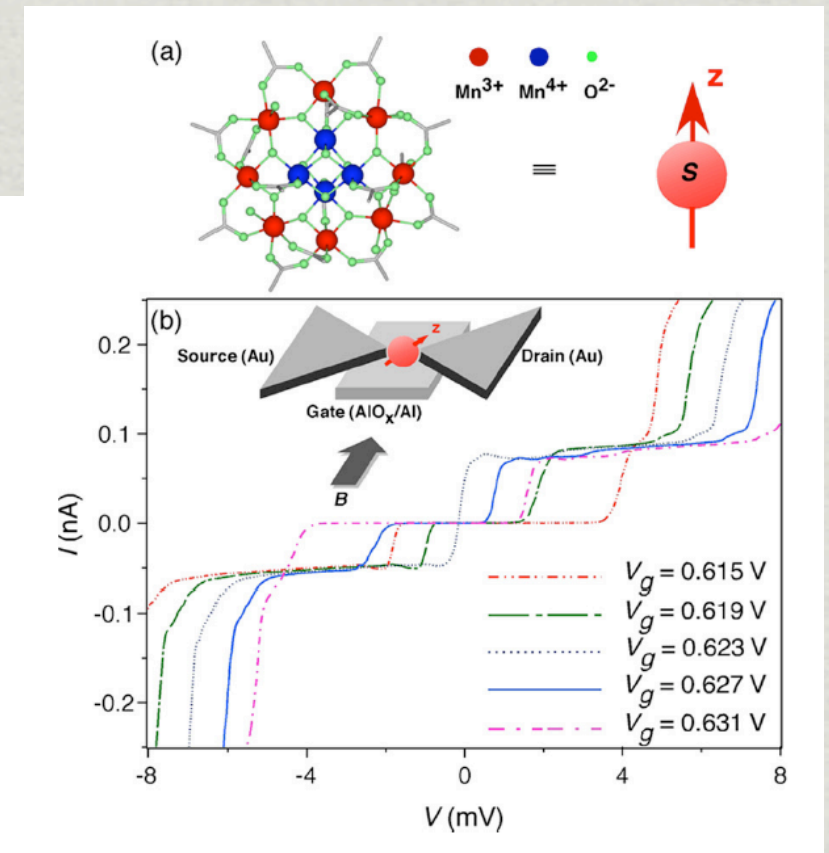
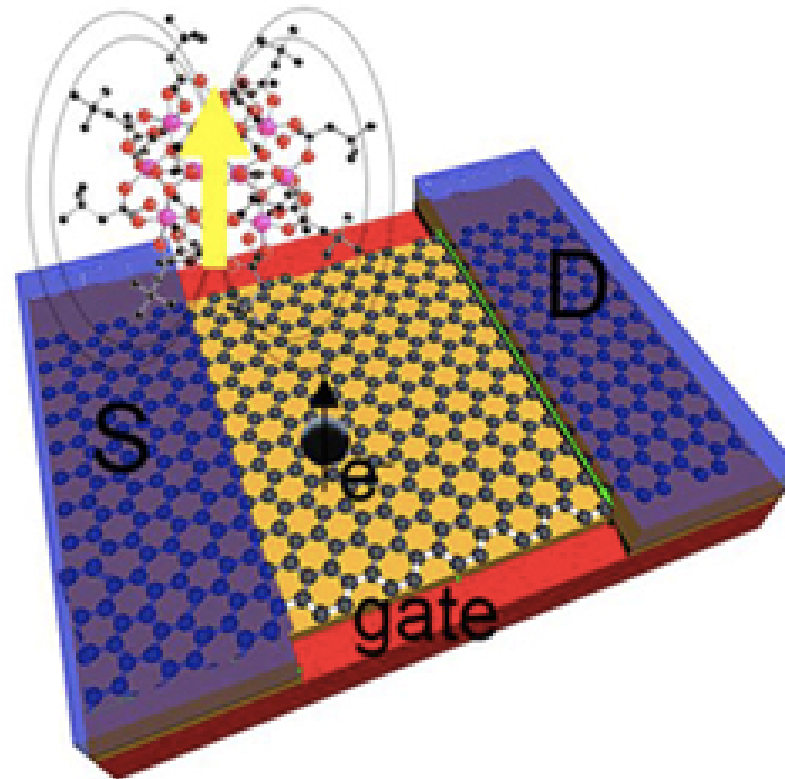
MAGNETIC FLUX NANO-MAGNETOMETERS
W. WERNSDORFER NATURE NANO 1 (2006)



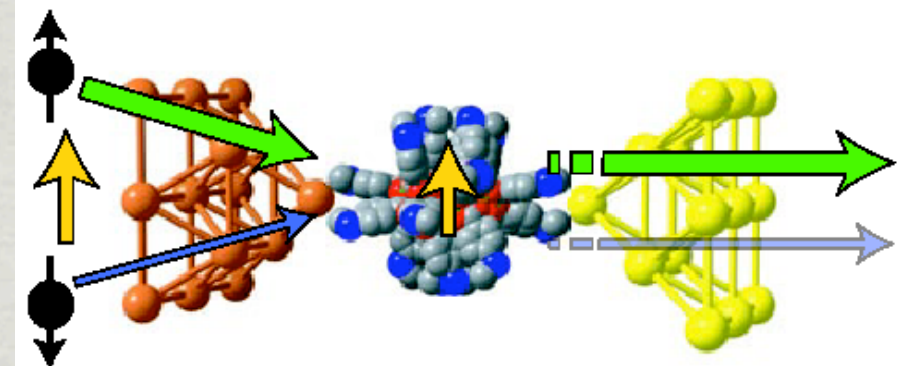
molecular spintronics



MAGNETIC FLUX NANO-MAGNETOMETERS
W. WERNSDORFER NATURE NANO 1 (2006)

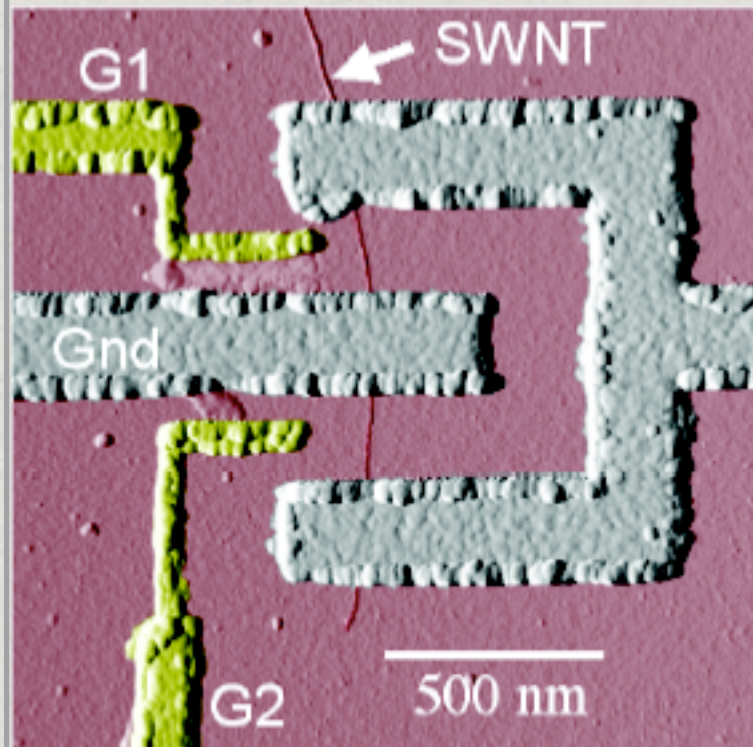


NANO-LETTERS. SEP 13 2006; 6 (9) : 2014.
PRL 96, 206801 (2006)

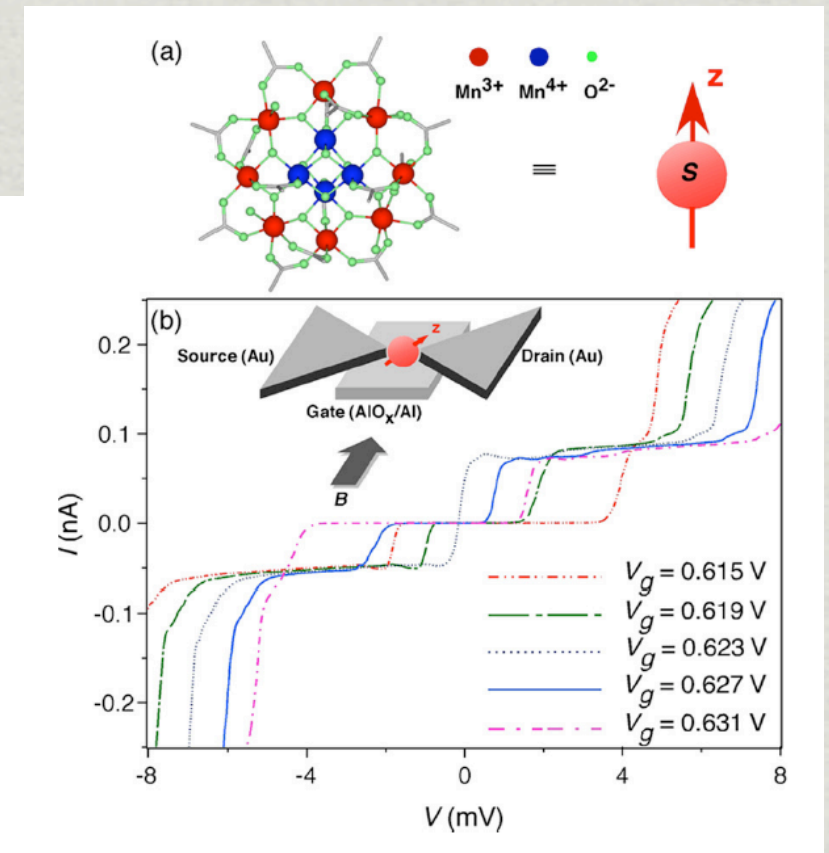
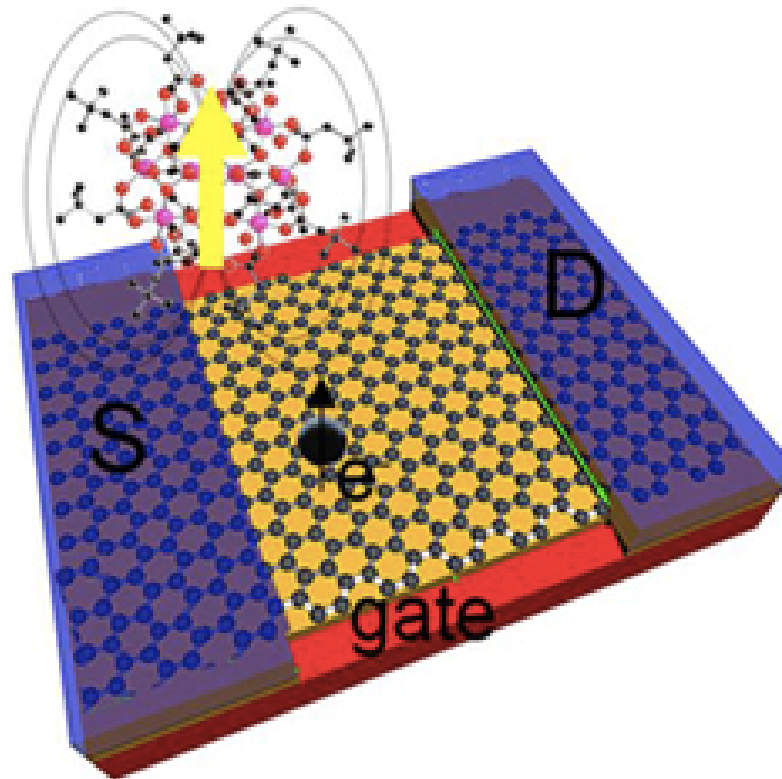


SPIN VALVE / SPIN TORQUE
NATURE MATERIALS | VOL 7 | MARCH 2008

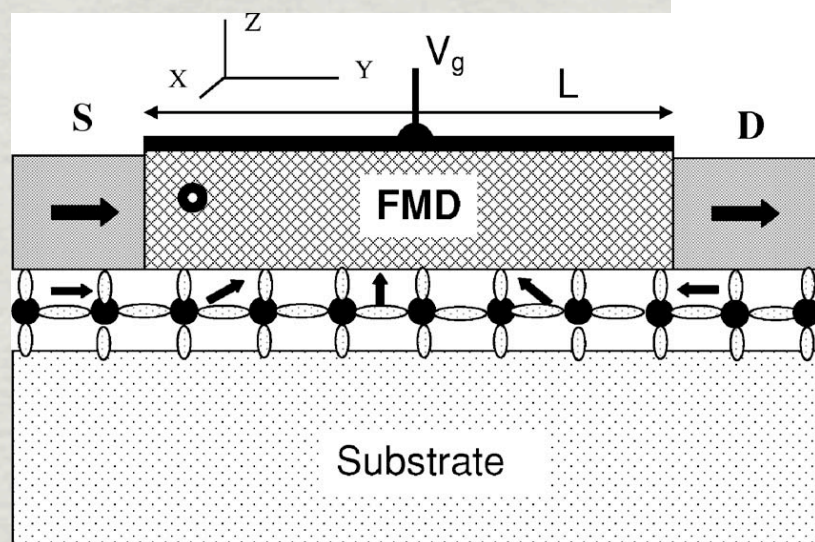
molecular spintronics



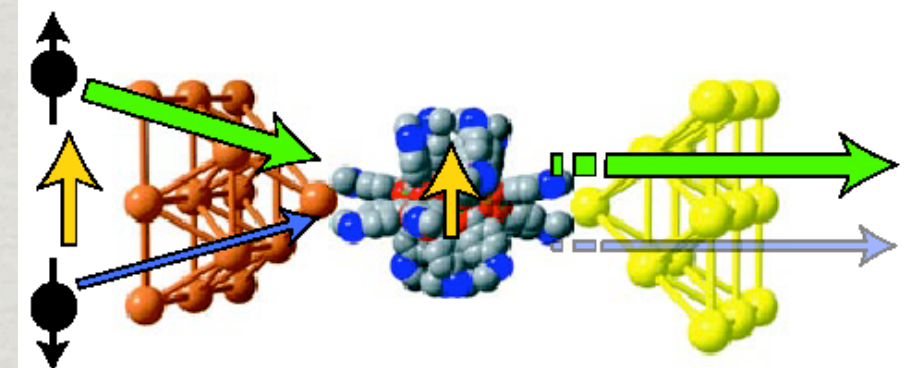
MAGNETIC FLUX NANO-MAGNETOMETERS
W. WERNSDORFER NATURE NANO 1 (2006)



NANO-LETTERS. SEP 13 2006; 6 (9) : 2014.
PRL 96, 206801 (2006)



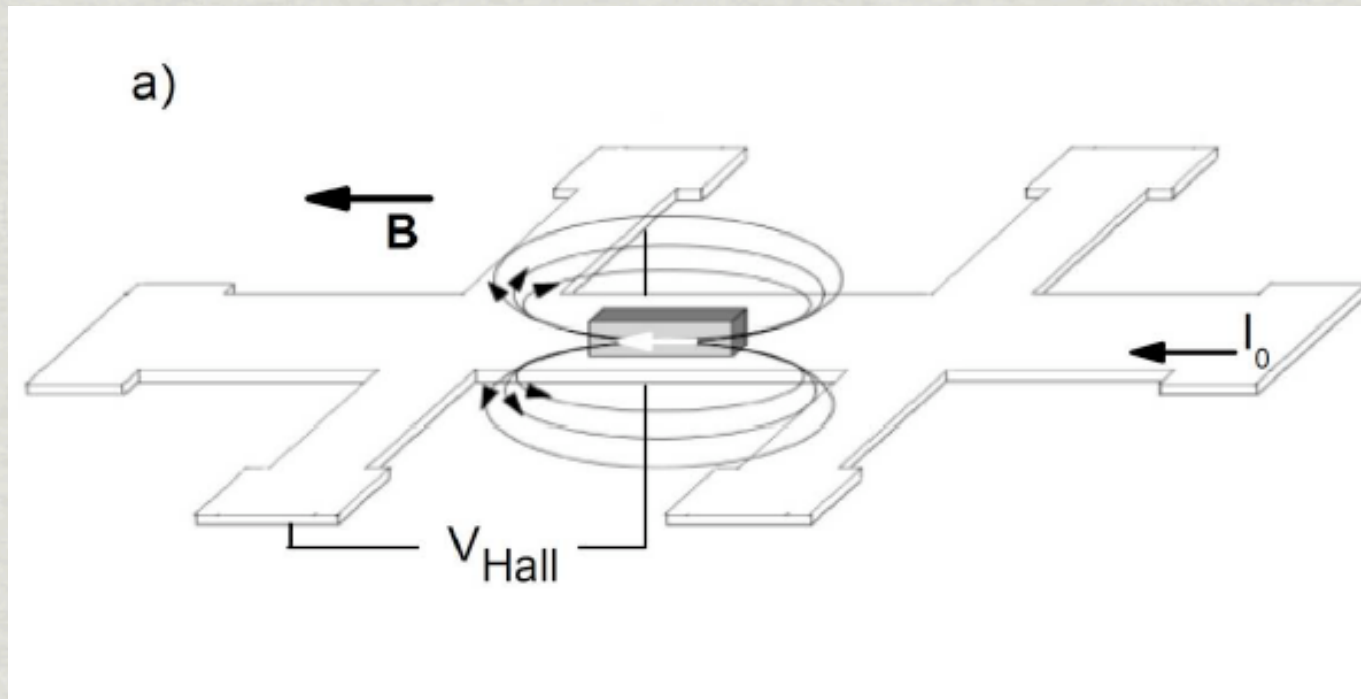
SPIN FET
APPLIED PHYSICS LETTERS 91, 153105 2007



SPIN VALVE / SPIN TORQUE
NATURE MATERIALS | VOL 7 | MARCH 2008

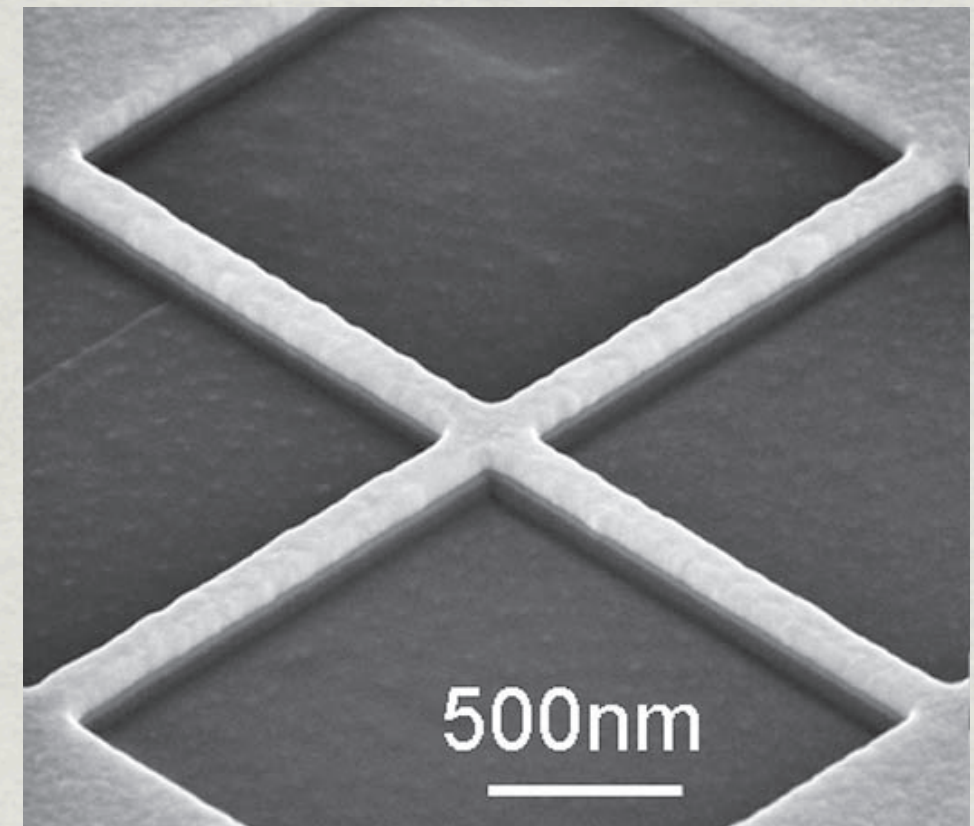
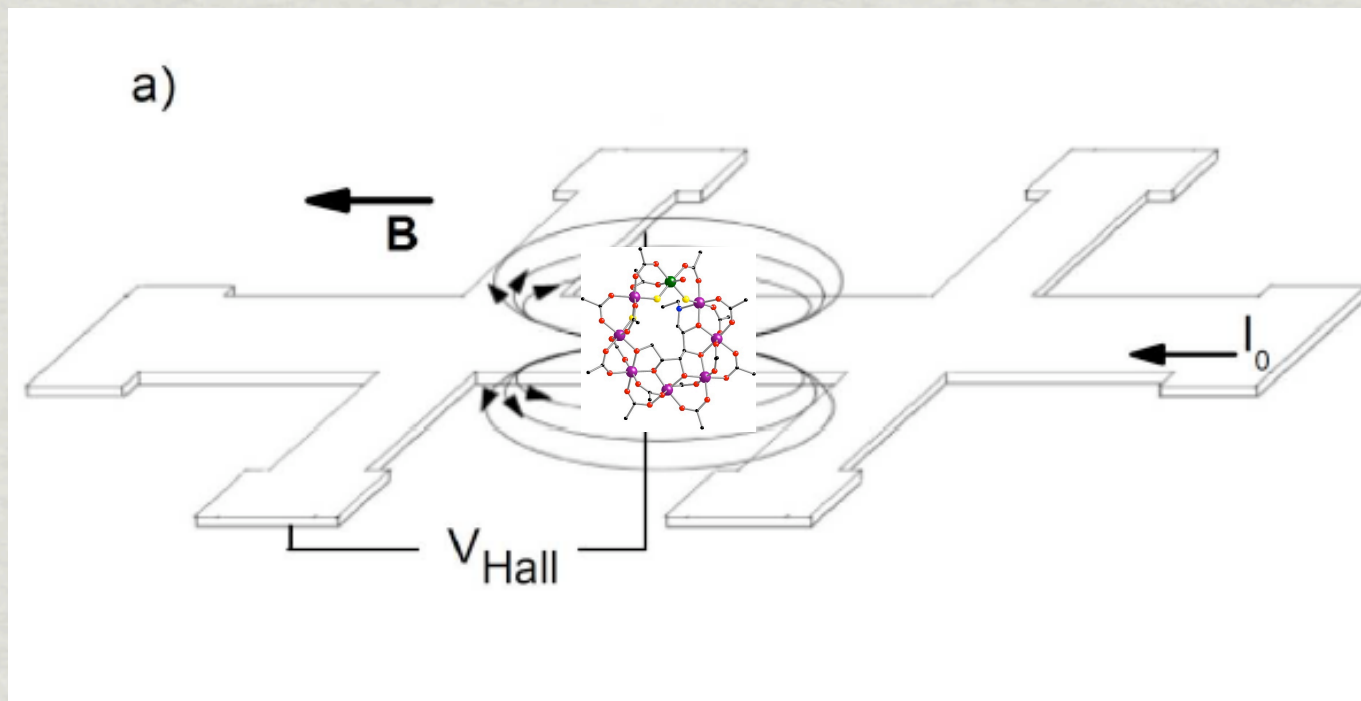
flux magnetometers

- Identification of well-defined qubit
- Reliable state preparation
- Accurate quantum gate operations
- Low decoherence
- scalability
- **Read-out**



flux magnetometers

- Identification of well-defined qubit
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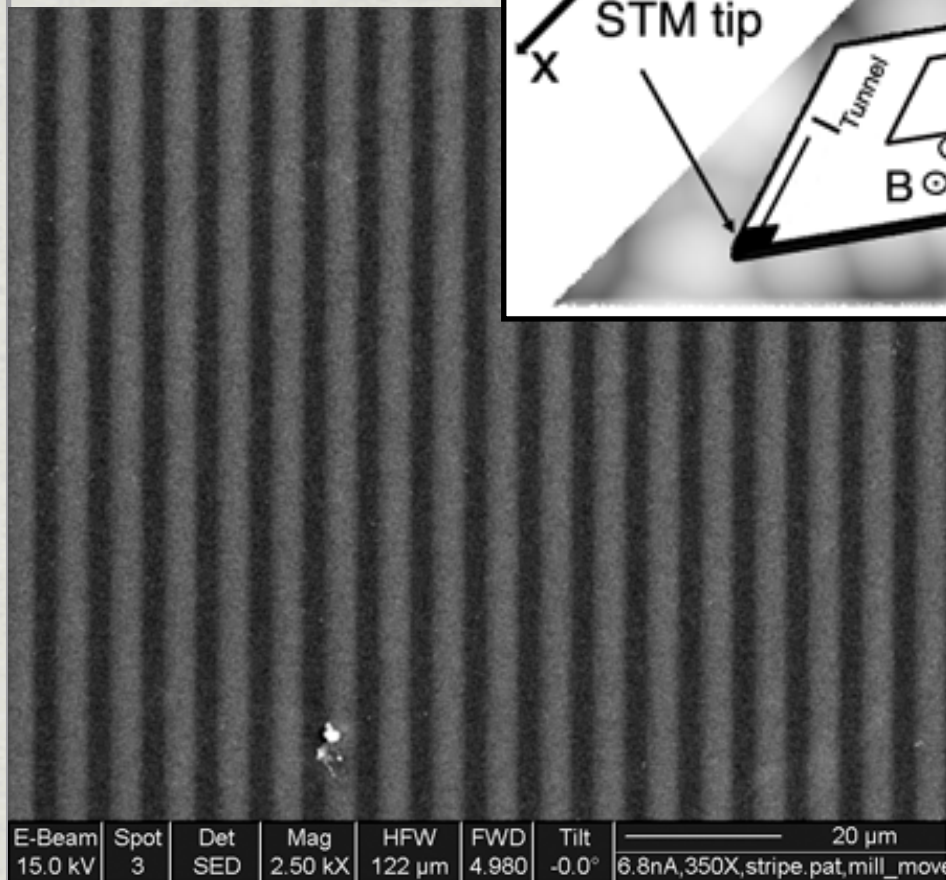
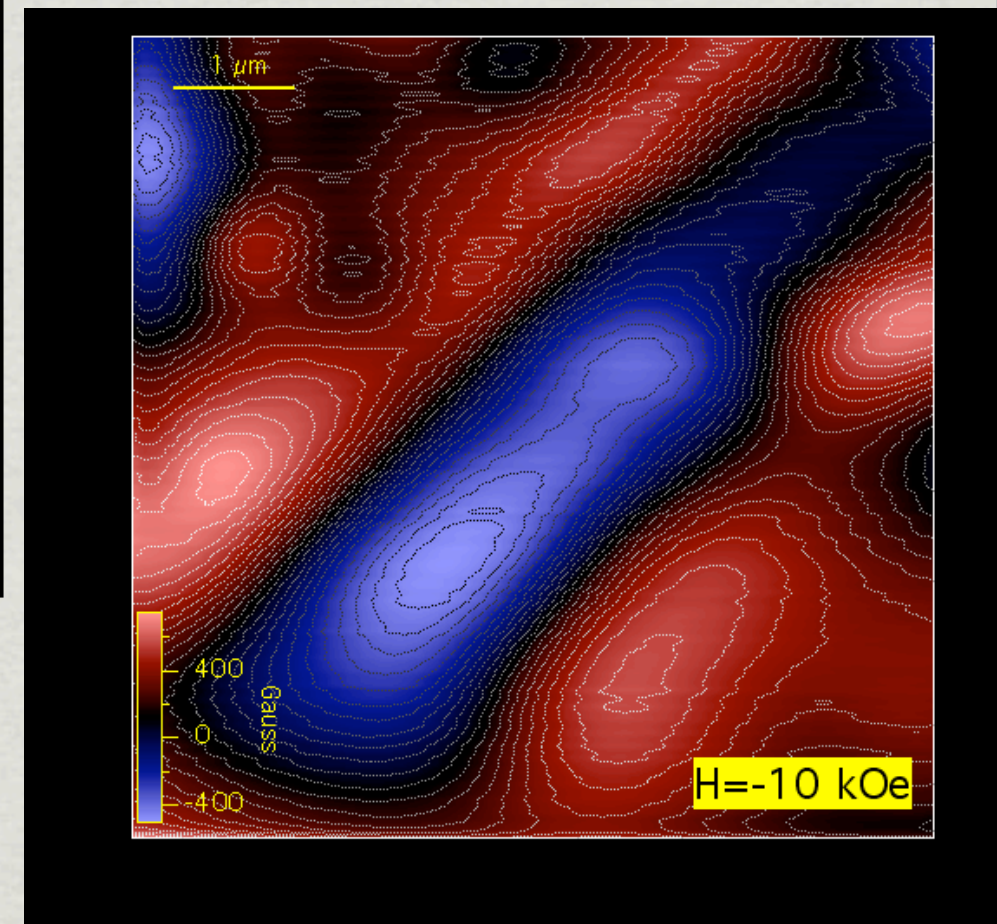
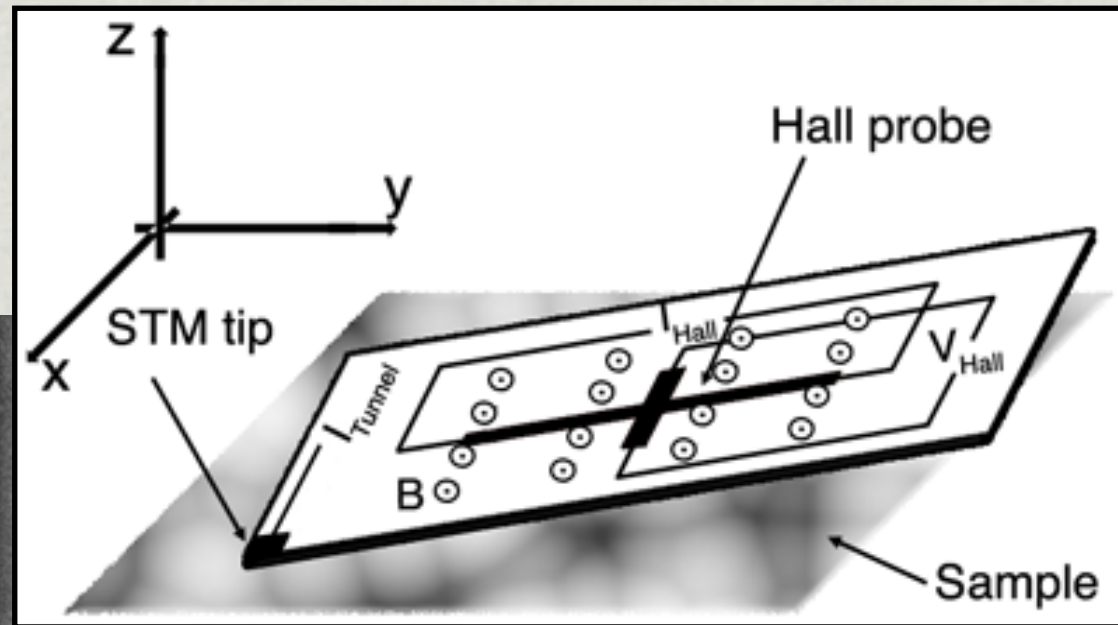
Hall nanoprobes fabricated by Focused Ion Beam.

A. Candini, M. Affronte, A. di Bona, G.C.Gazzadi, D. Ercolani, G. Biasiol, L.Sorba

Nanotechnology 17 (2006) 2105-2109.

also @ : <http://www.qdusa.com/resources/>

Scanning Hall Probe Microscope.

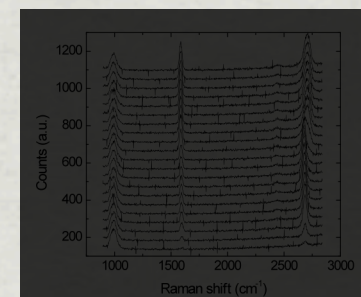
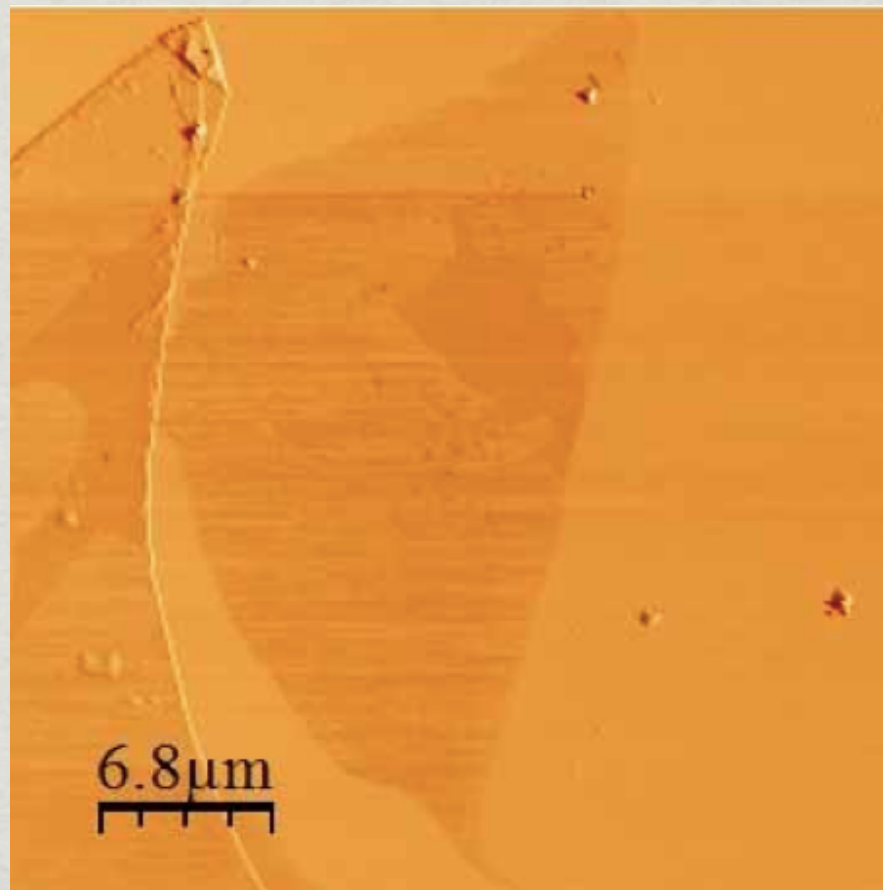
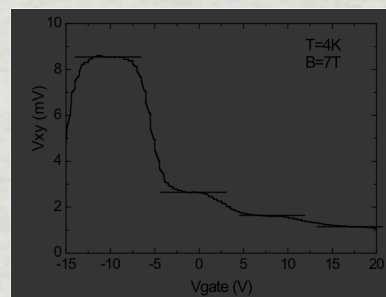
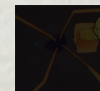
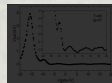
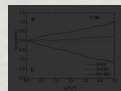


INSTRUMENT BY NANOMAGNETICS.

Magnetic imaging of prussian blue nanoparticles grafted on FIB-patterned substrates.

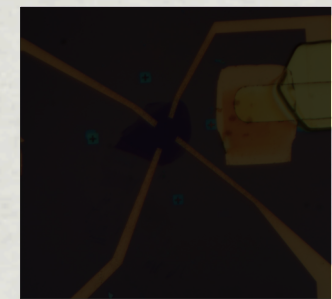
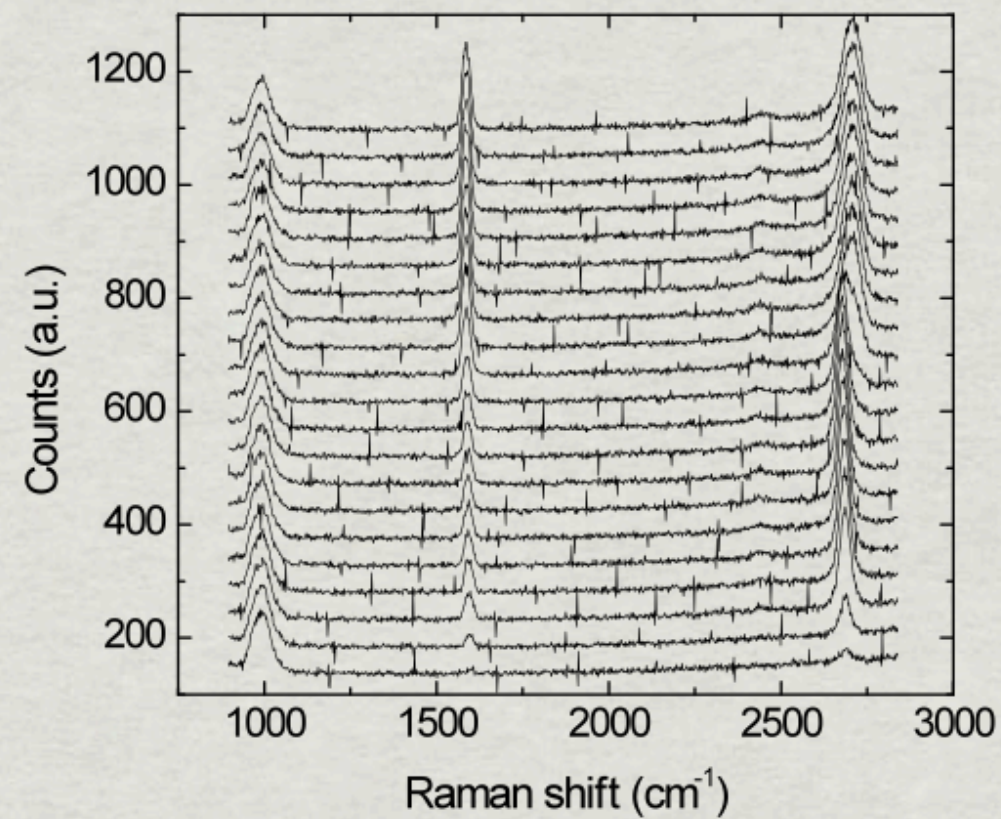
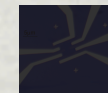
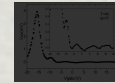
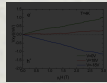
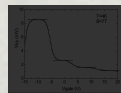
A. Ghirri, A. Candini, M. Evangelisti, G. C. Gazzadi, M. Affronte, F. Volatron, D. Brinzei, B. Fleury, L. Catala, C. David and T. Mallah, ***SMALL*** 4, No. 12, 2240–2246 (2008)

spintronics with graphene



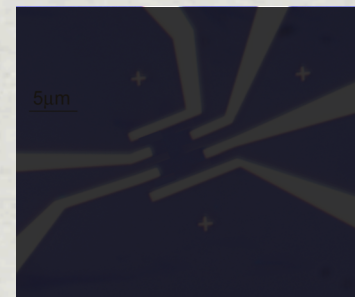
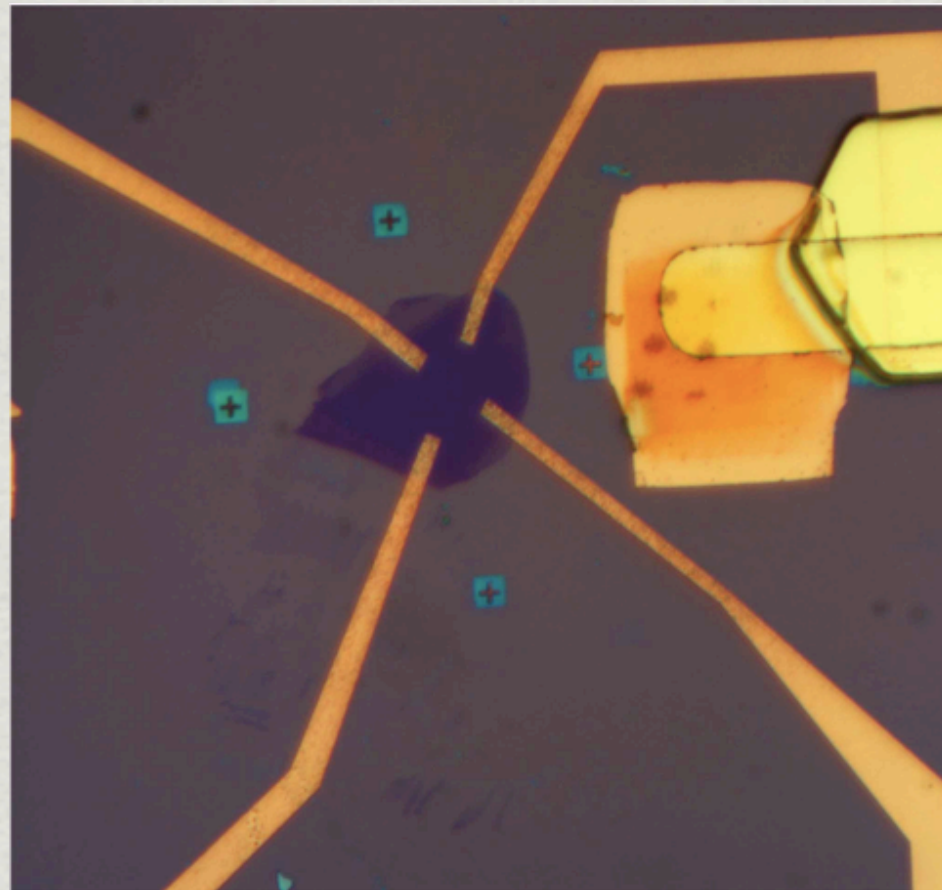
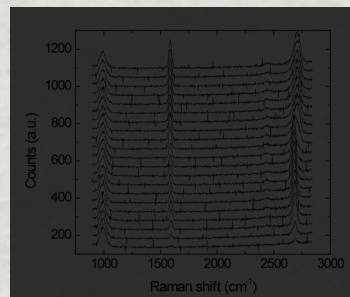
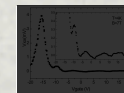
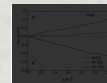
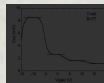
GRAPHENE @ S3:
A. CANDINI

spintronics with graphene



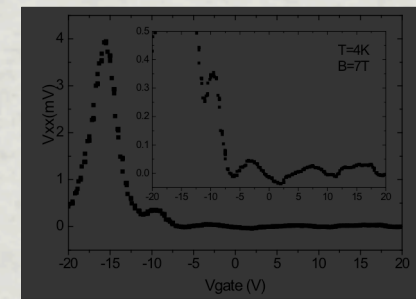
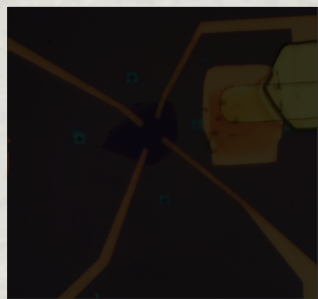
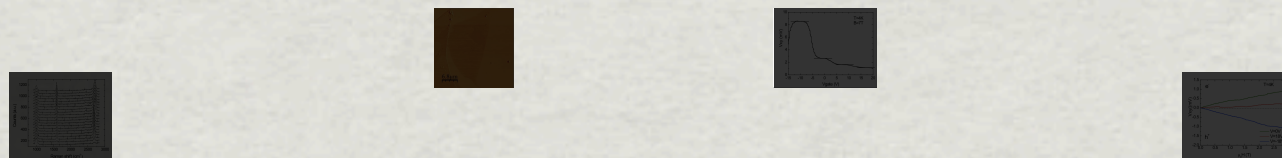
GRAPHENE @ S3:
A. CANDINI

spintronics with graphene



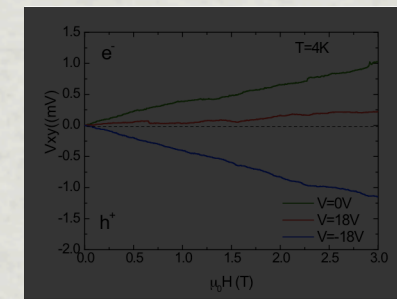
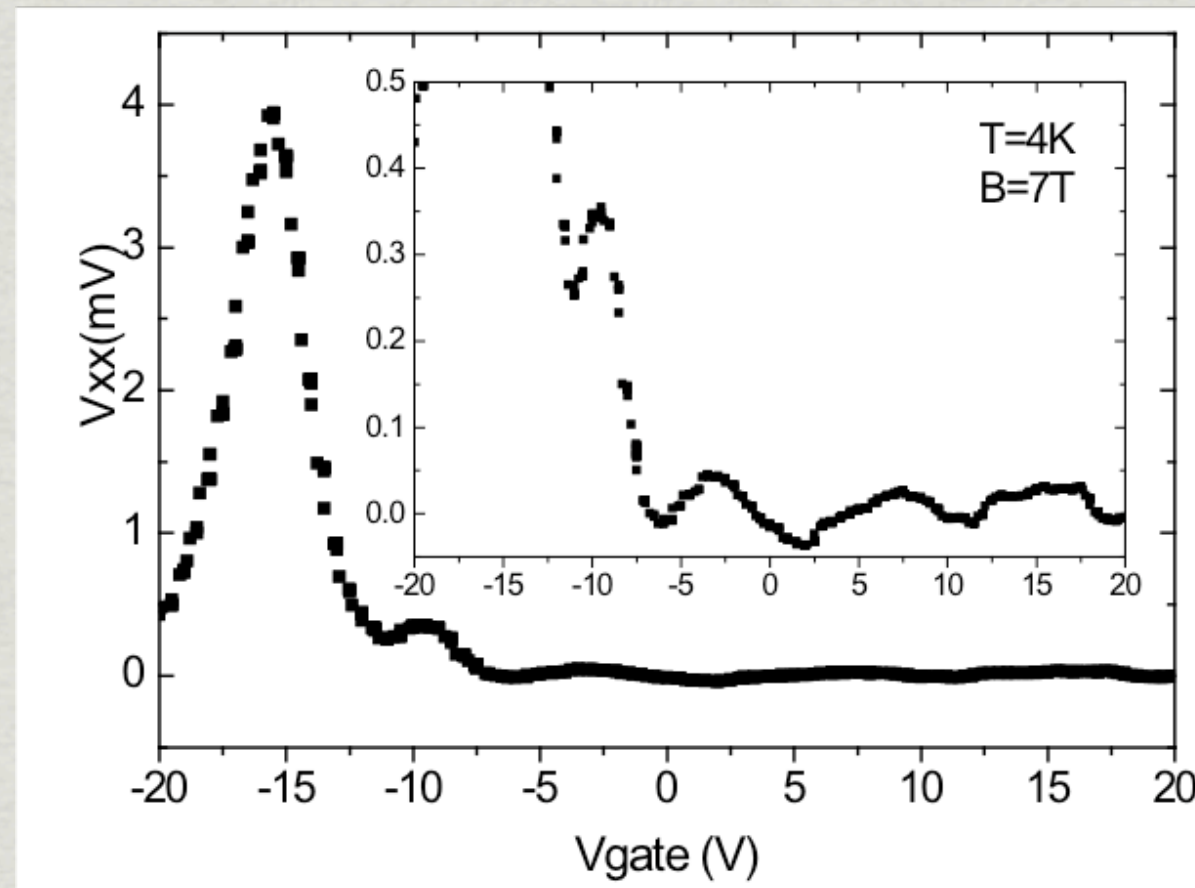
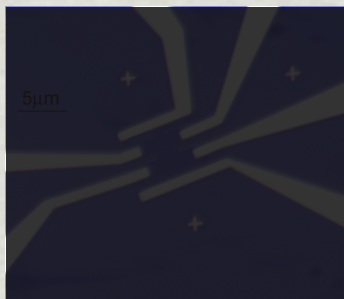
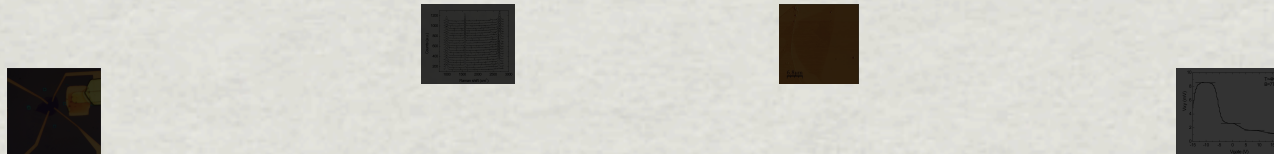
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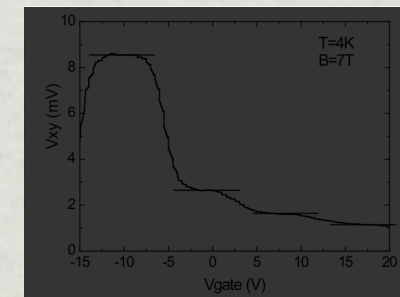
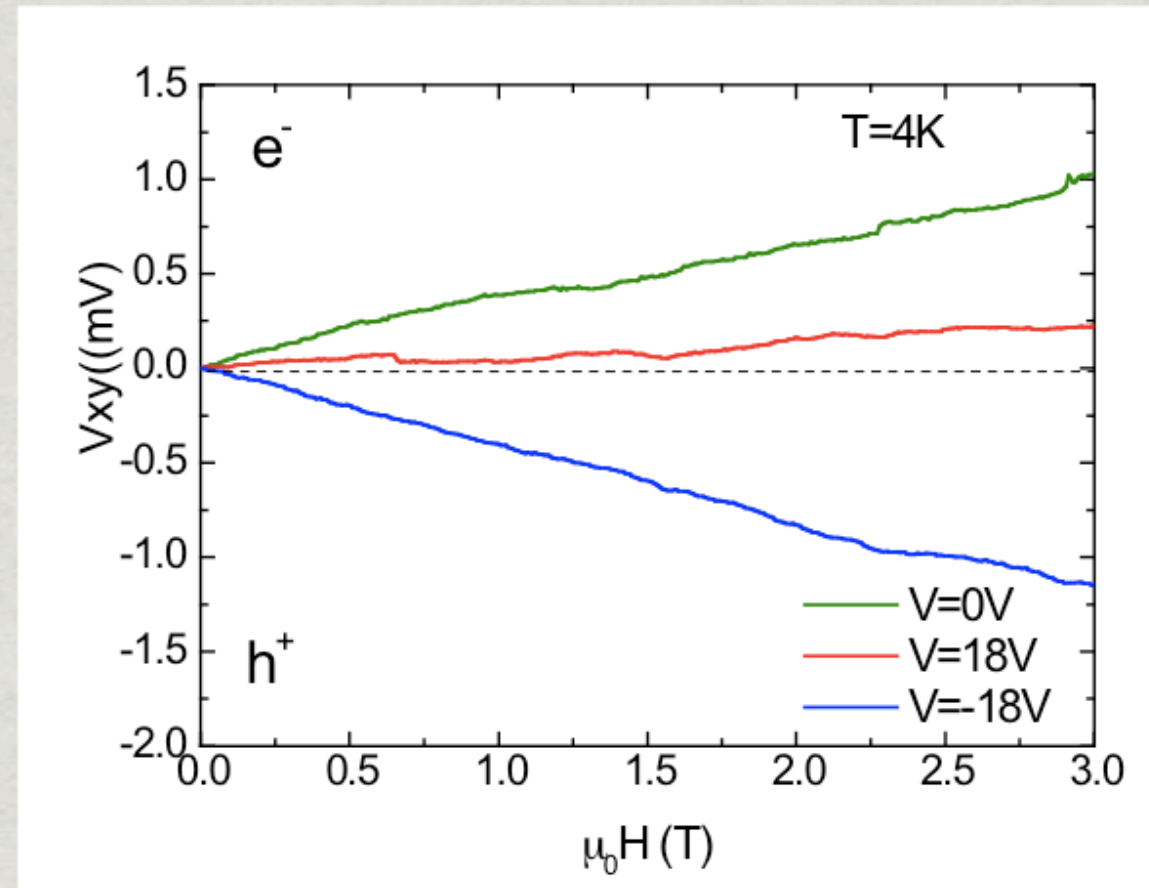
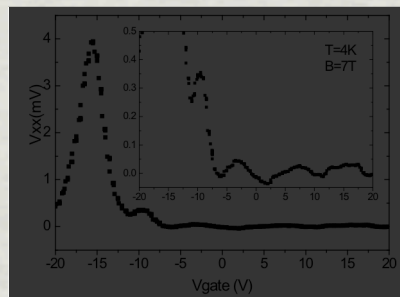
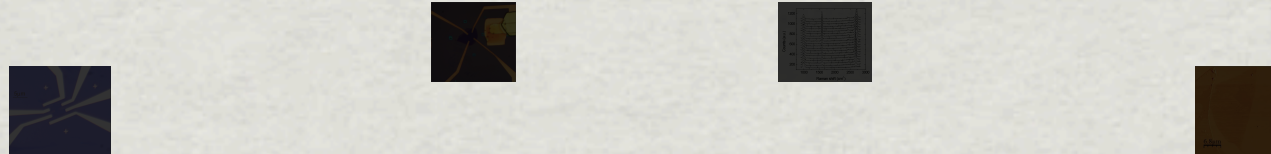
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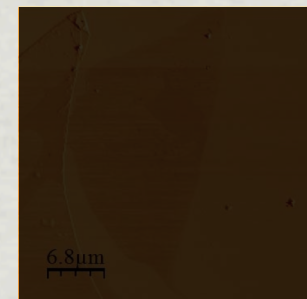
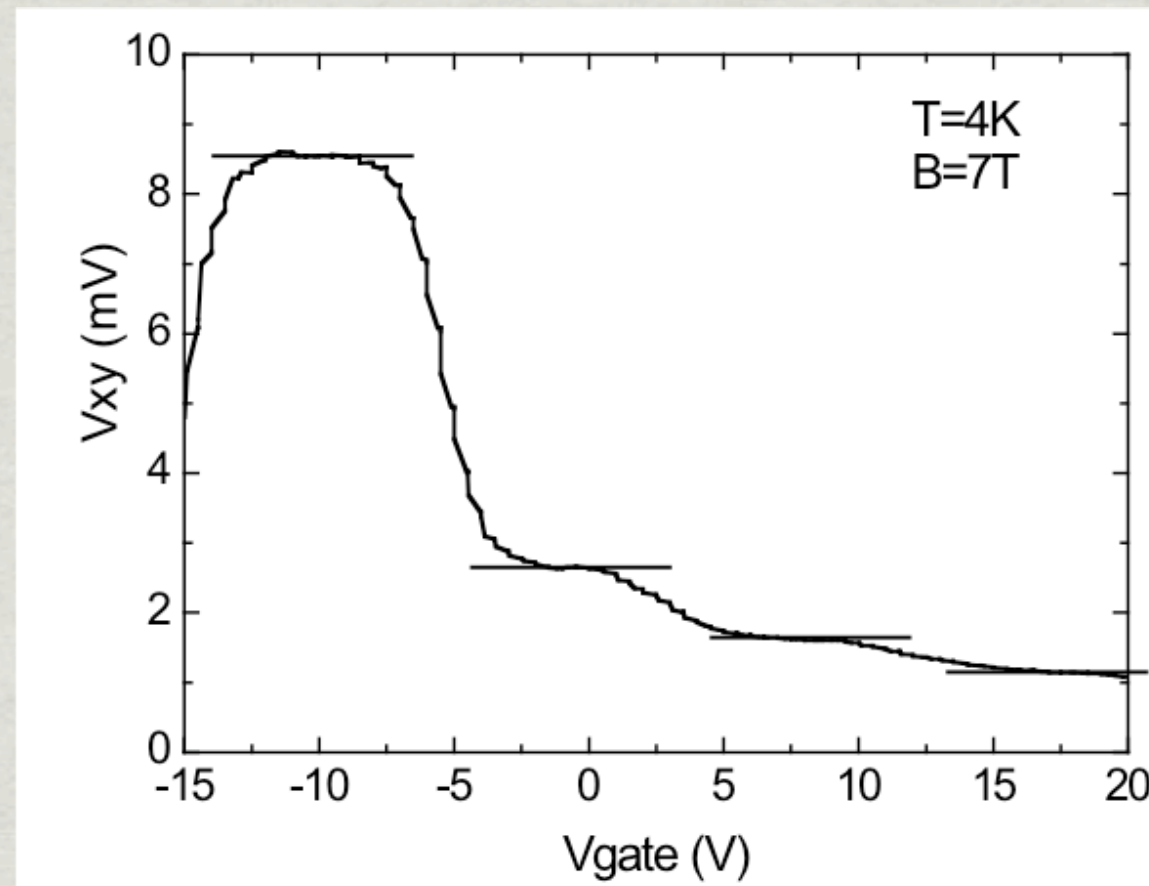
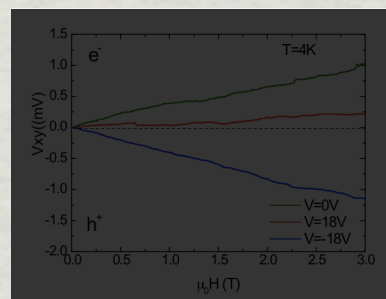
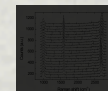
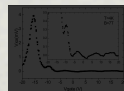
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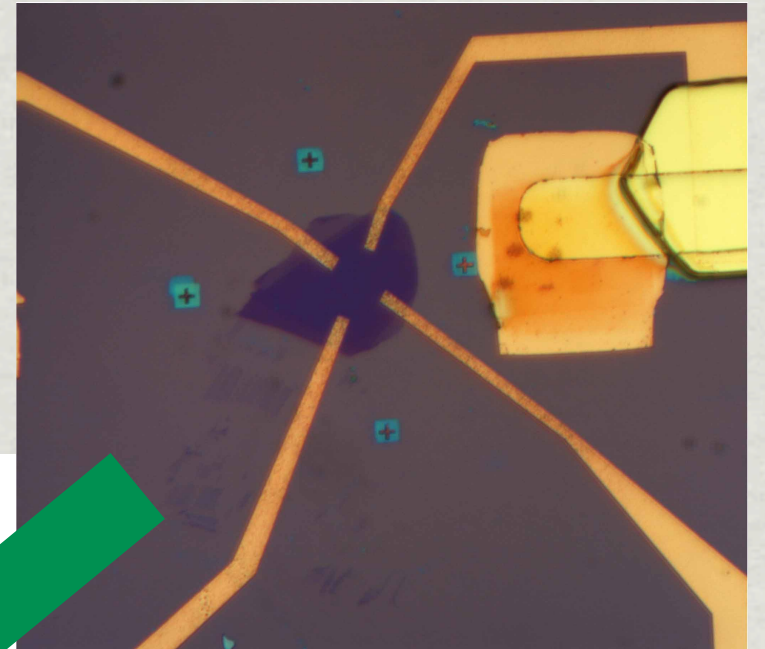
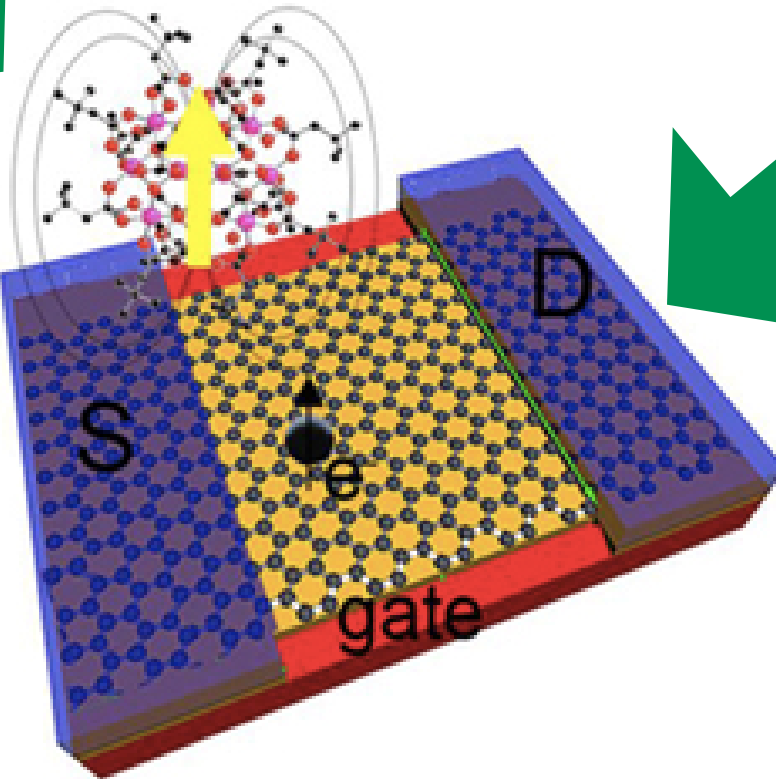
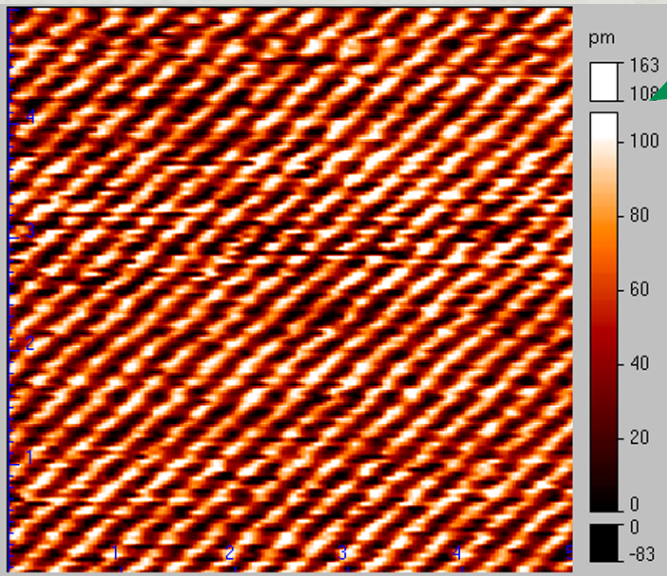
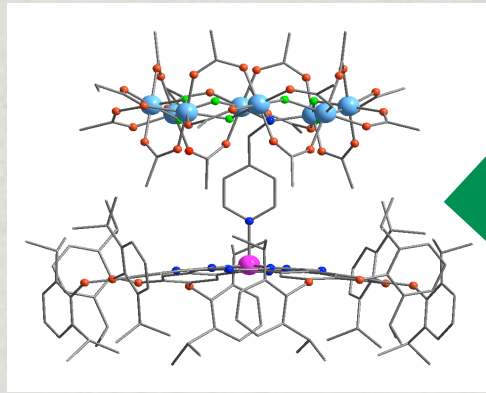
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soon: graphene-based molecular-devices



conclusions

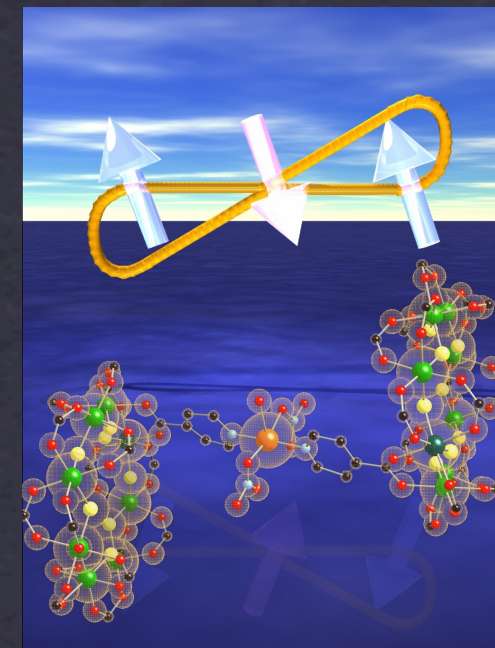
Molecular nanoMagnets for information technologies.

M. Affronte. J. Mater. Chem., 19, 1731 – 1737 (2009)

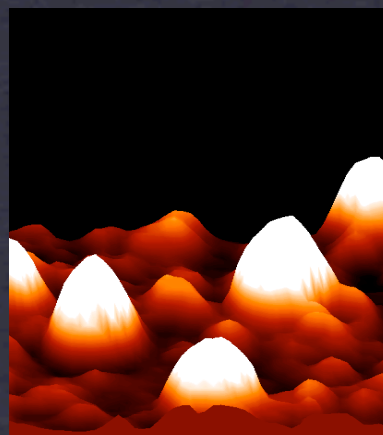
- information storage



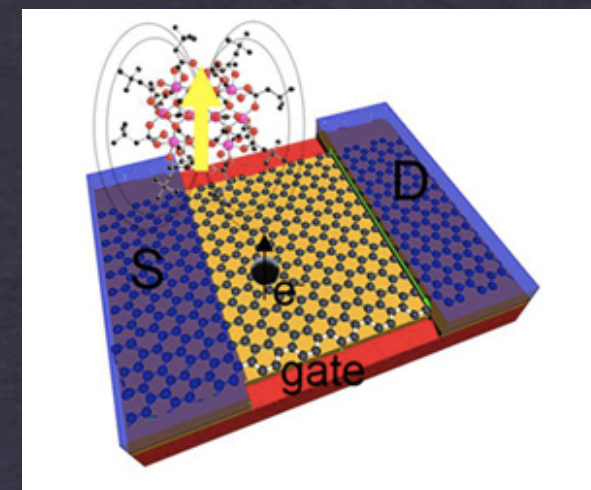
- molecular AF rings for quantum computation



- molecules at surfaces.



- molecular spintronics with graphene



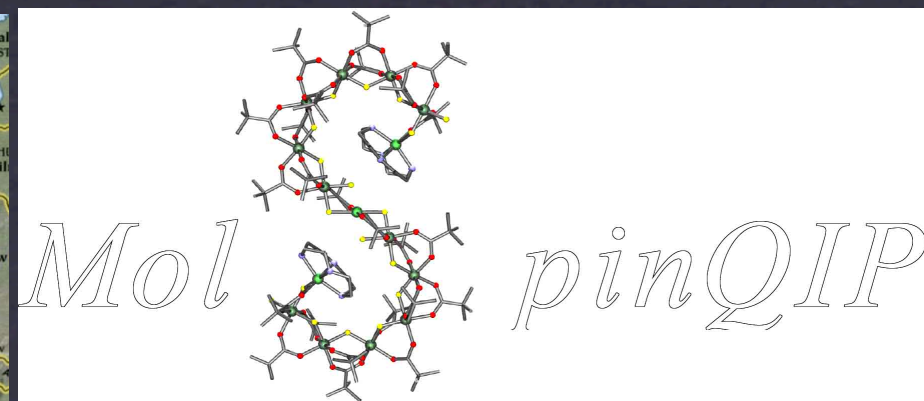
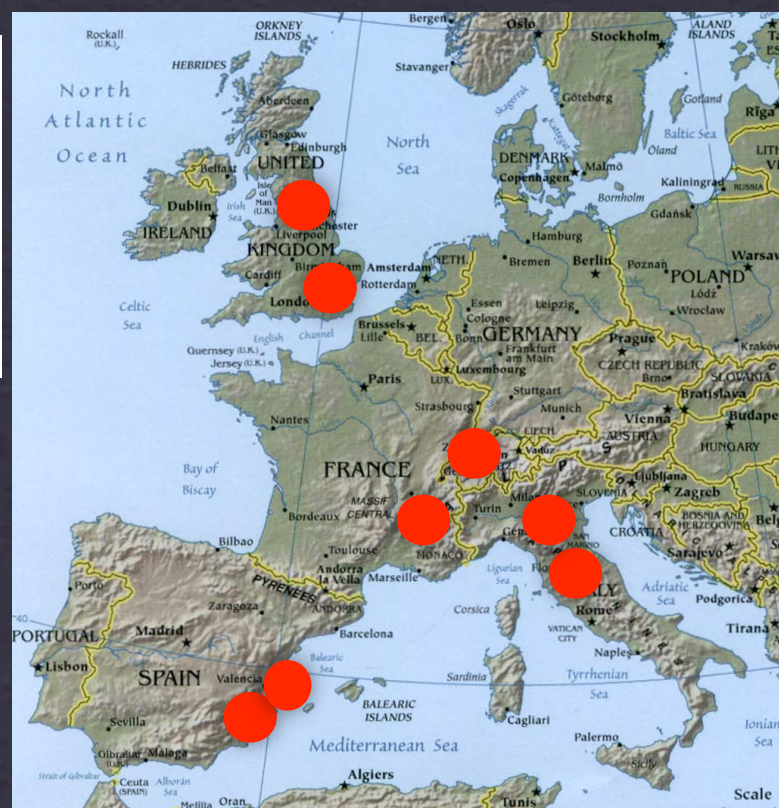
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