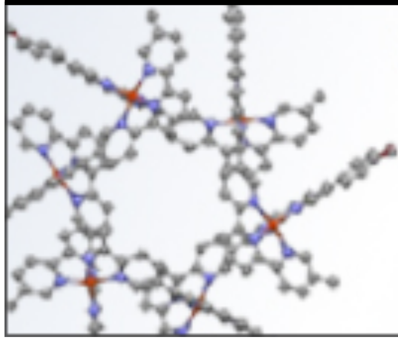
Molecular Approach to 2D materials

E. Coronado



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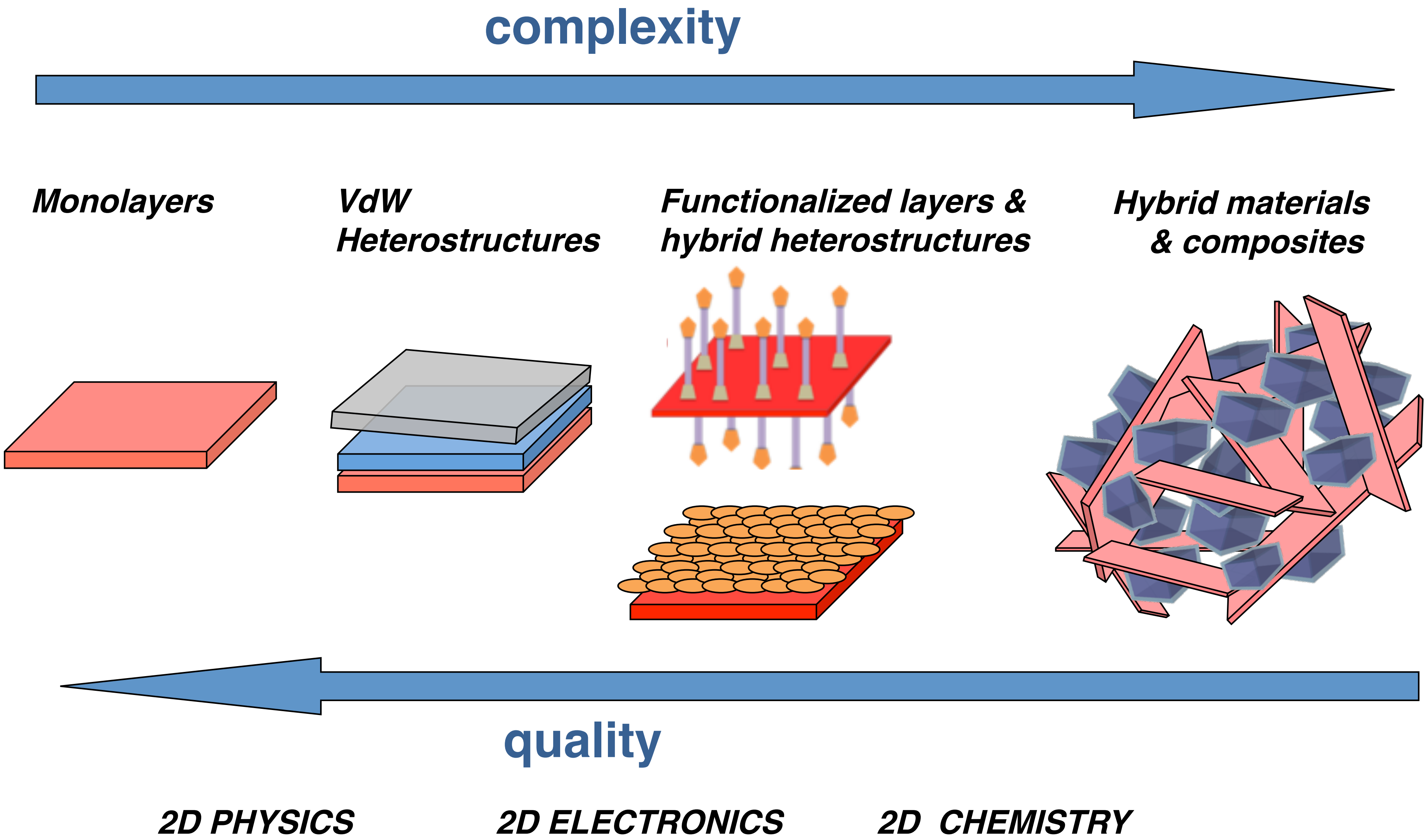
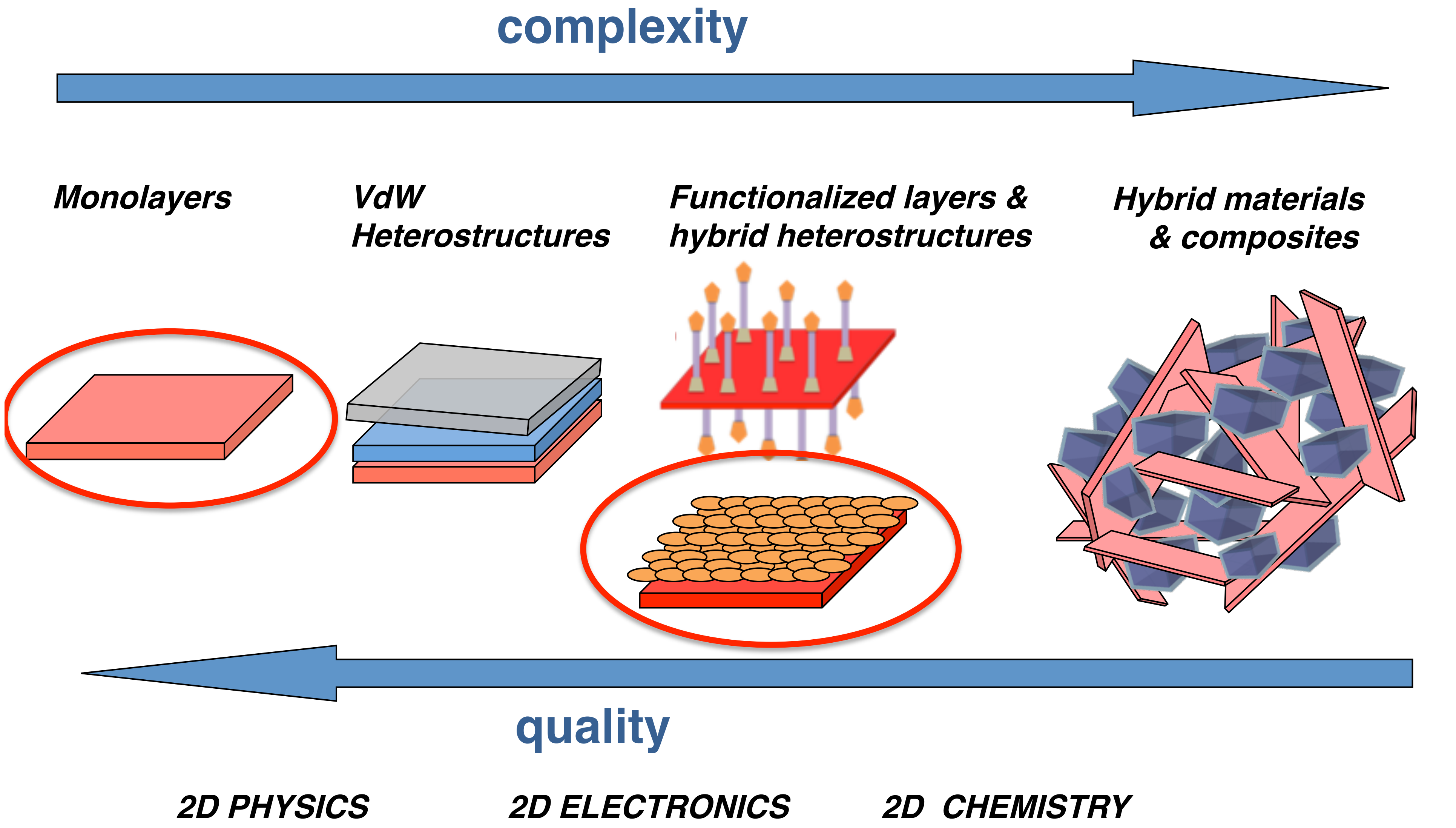
Vniversitat de València

Instituto de Ciencia Molecular

2D Materials



2D Materials



MOLECULAR APPROACH TO 2D MATERIALS

Molecular monolayers

2D magnets

Molecular/2D heterostructures

Smart materials

E. Coronado, *Nature Rev. Mater.* 5, 87-104 (2020)

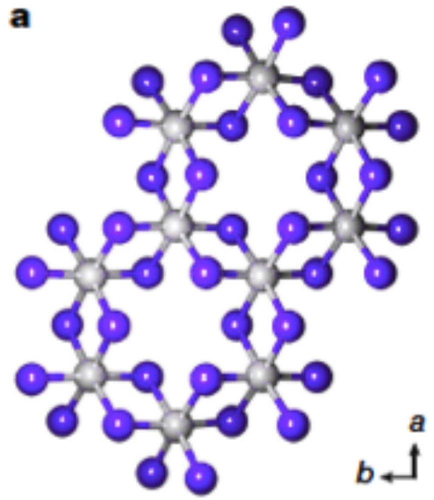
CHALLENGES (in Physics)

- ***Ferromagnetism in the 2D limit***

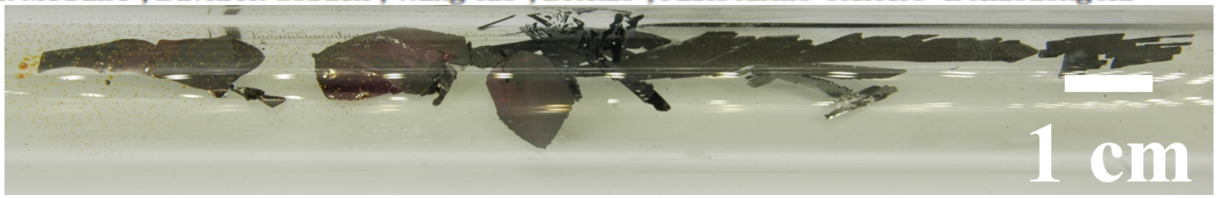
270 | NATURE | VOL 546 | 8 JUNE 2017

Layer-dependent ferromagnetism in a van der Waals crystal down to the monolayer limit

Bevin Huang[1*], Genevieve Clark[2*], Efrén Navarro-Moratalla[3*], Dahlia R. Klein[3], Ran Cheng[4], Kyle L. Seyler[1], Ding Zhong[1], Emma Schmidgall[1], Michael A. McGuire[5], David H. Cobden[1], Wang Yao[6], Di Xiao[4], Pablo Jarillo-Herrero[3] & Xiaodong Xu[1,2]



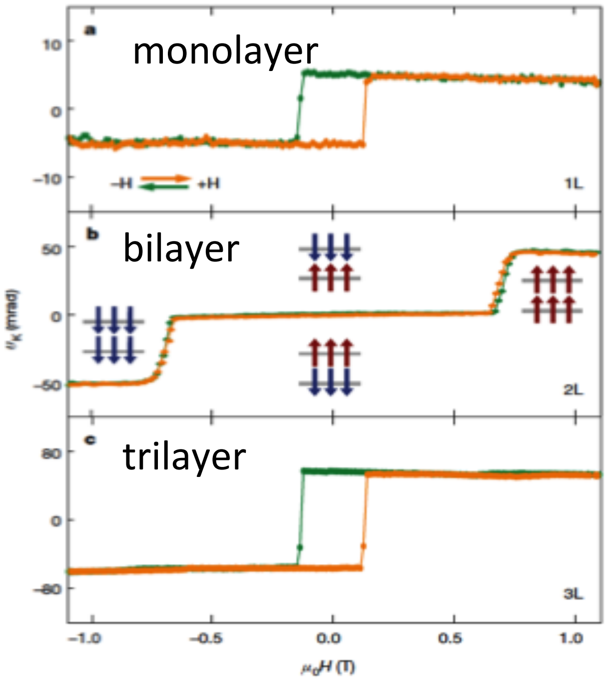
CrI_3

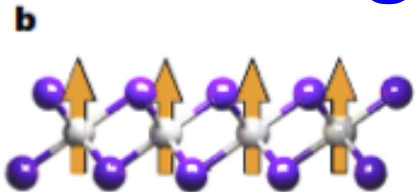


Big crystals

(≈ cm)

Highly unstable !!!





CrI_3: Ising ferromagnet

QUESTIONS:

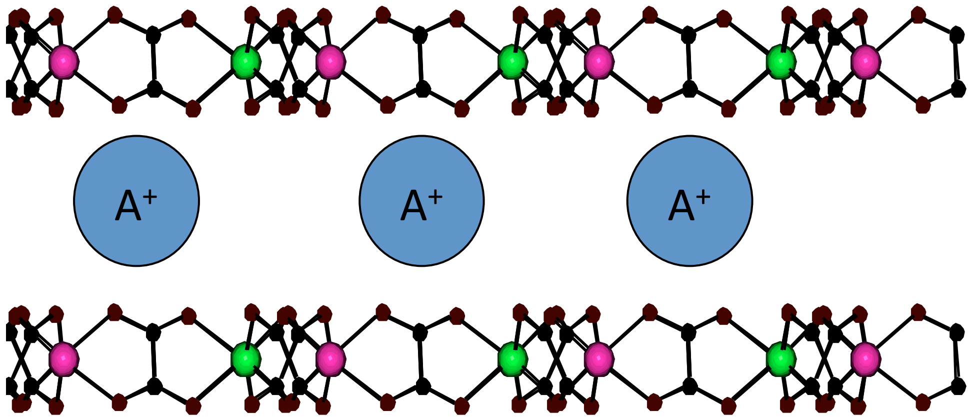
Can we isolate monolayers of molecular-based magnets?

Can we measure the magnetism in the 2D limit?

Magnetic layered coordination polymers

Bimetallic oxalato complexes

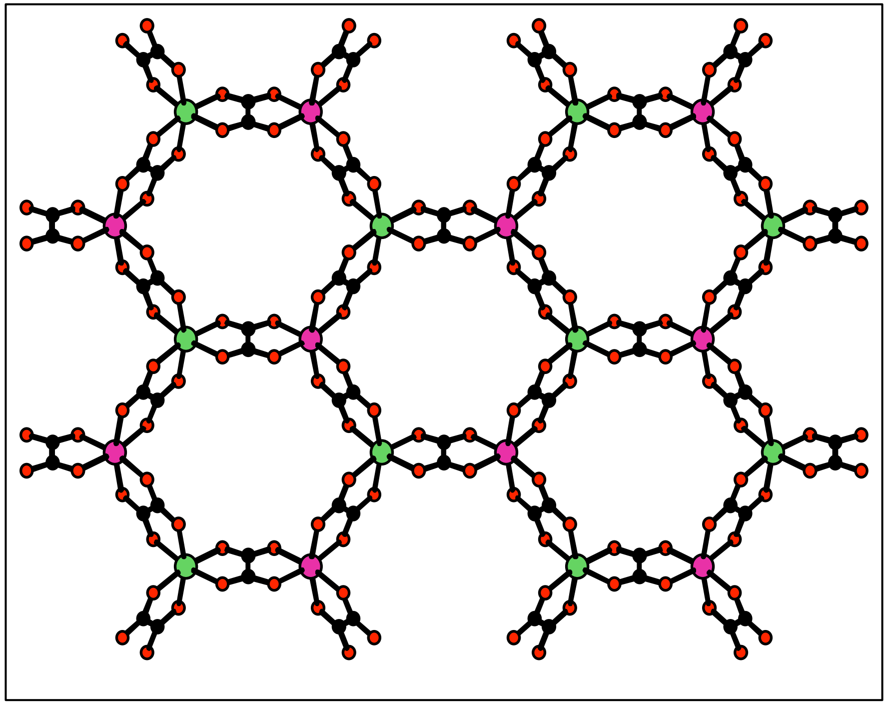
SOLUTION SYNTHESIS



Stable

Charged layers

Very small crystals (≈ 0.1 mm)



$[M^{II}M^{III}(ox)_3]^{-}(A)^{+}$

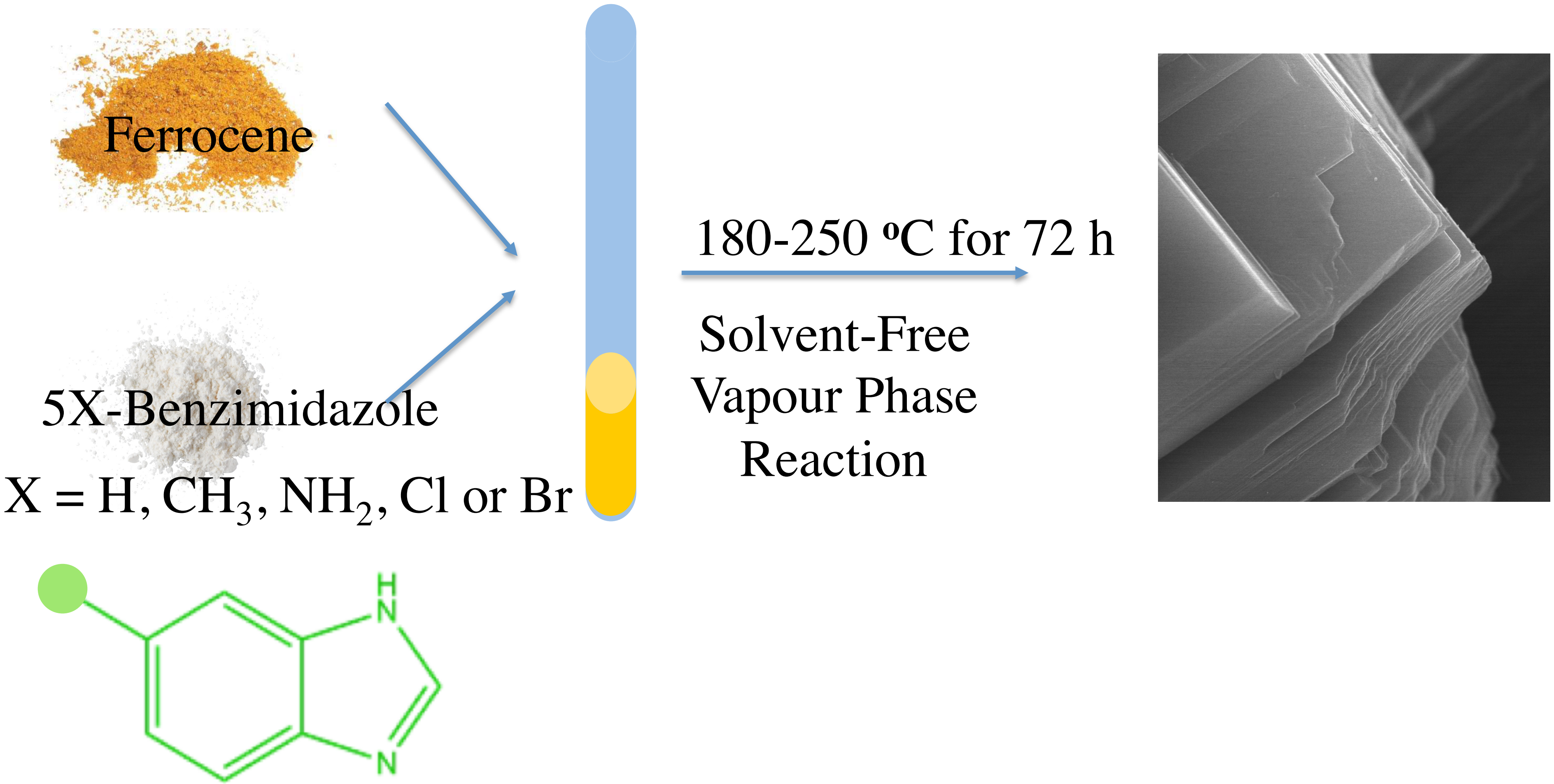
M^{II} = Mn, Co, Ni, Cu, Zn

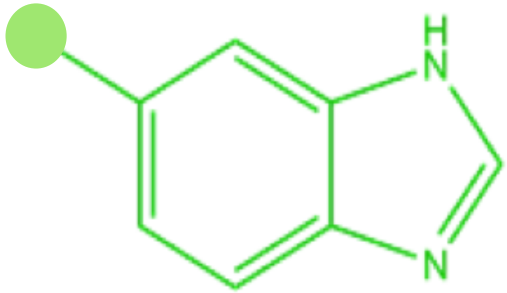
M^{III} = Cr, Fe, Ru

Insulating Magnets; Multifunctional Materials

Magnetic layered coordination polymers

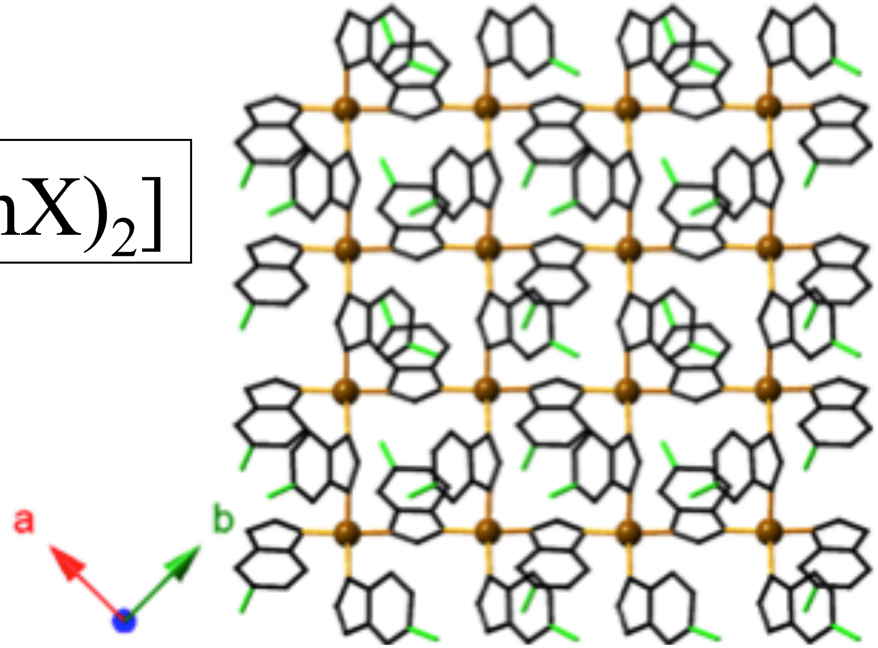
$[Fe(bimX)_2]$ **DRY SYNTHESIS**



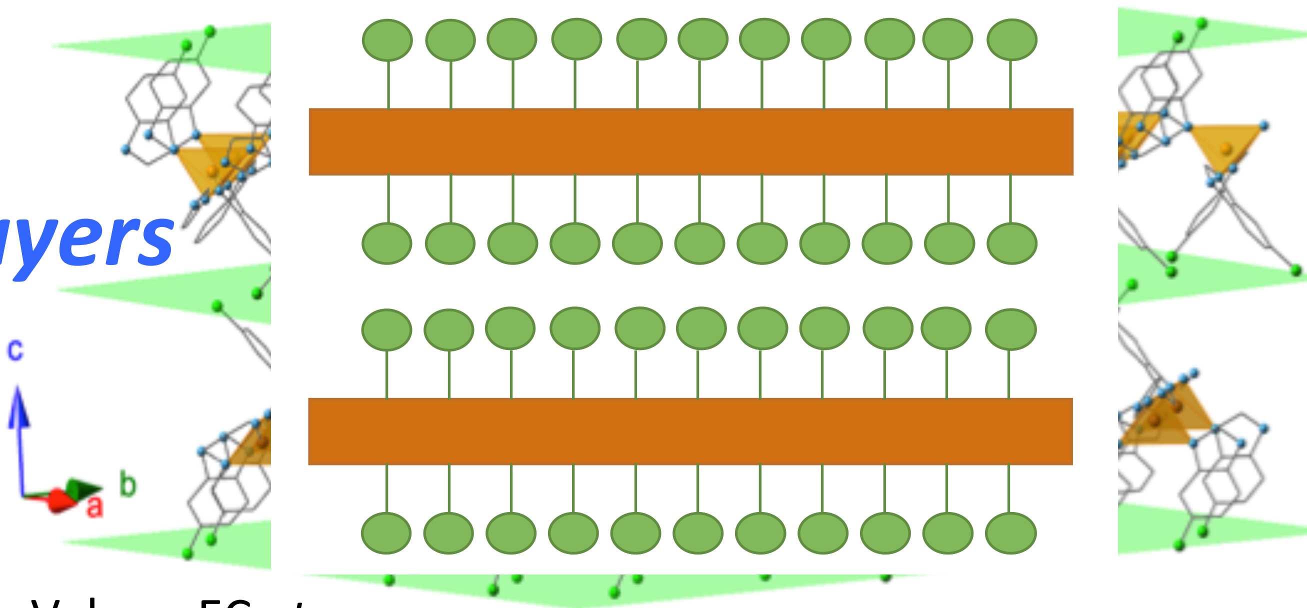


5X-Benzimidazole
X = H, CH_3, NH_2, Cl or Br

$[Fe(bimX)_2]$



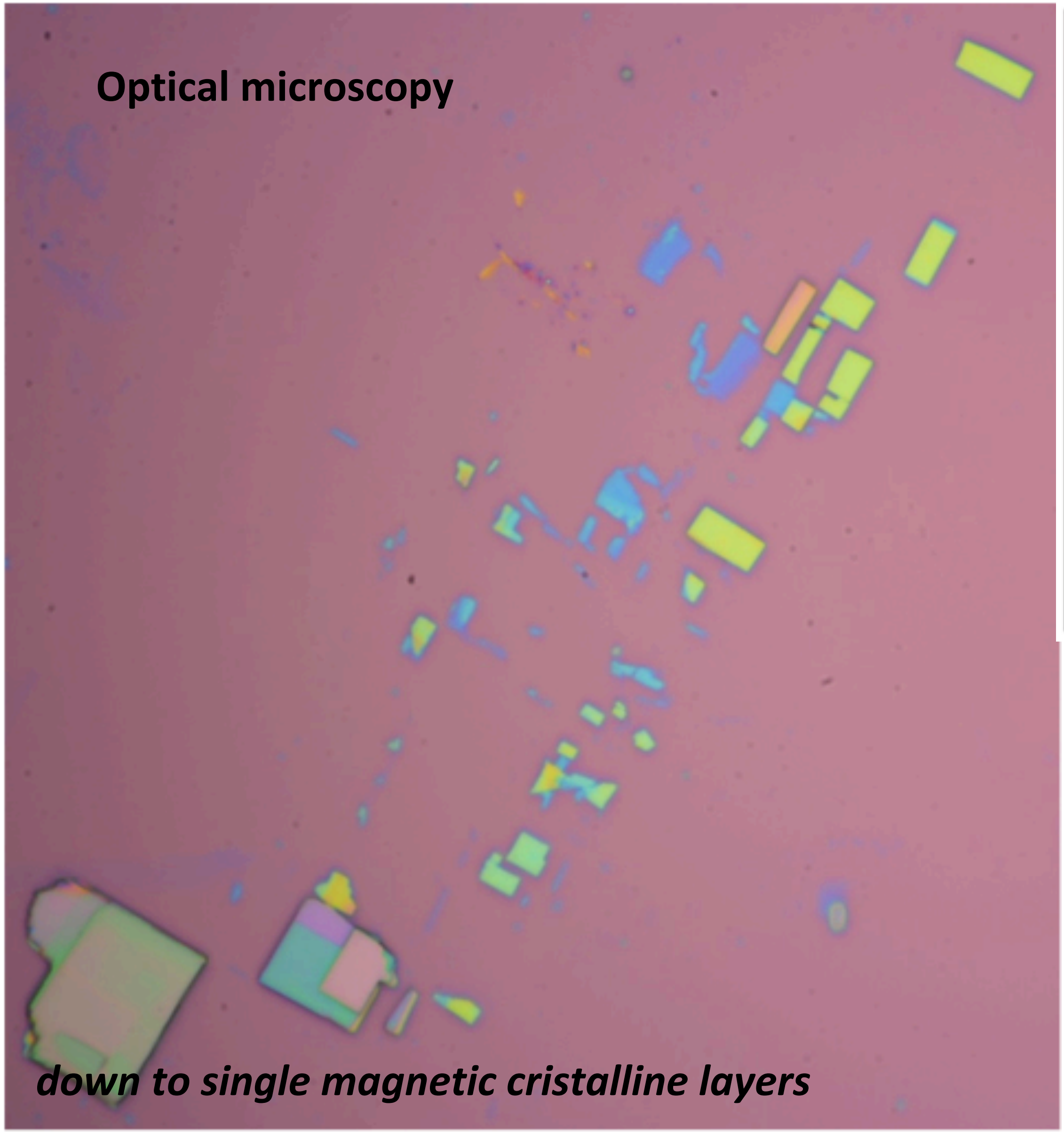
Neutral vdW layers

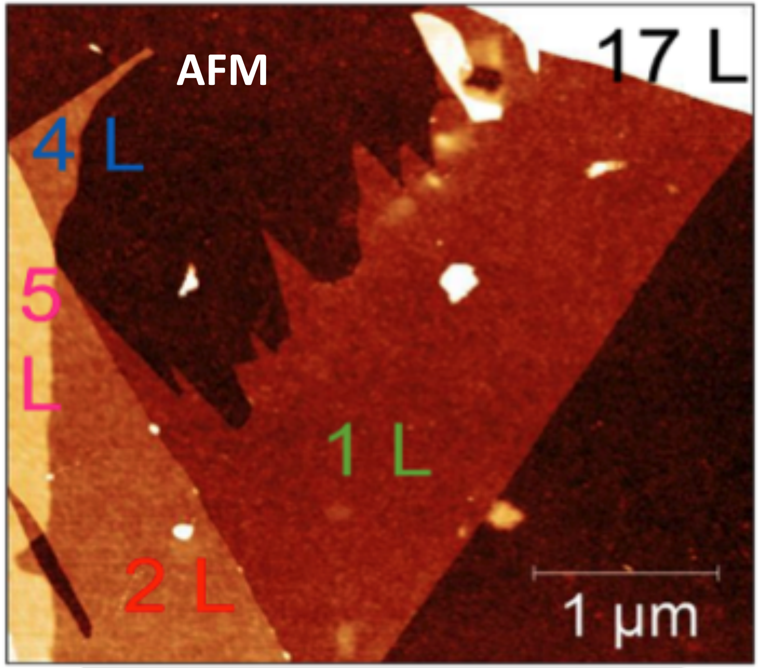


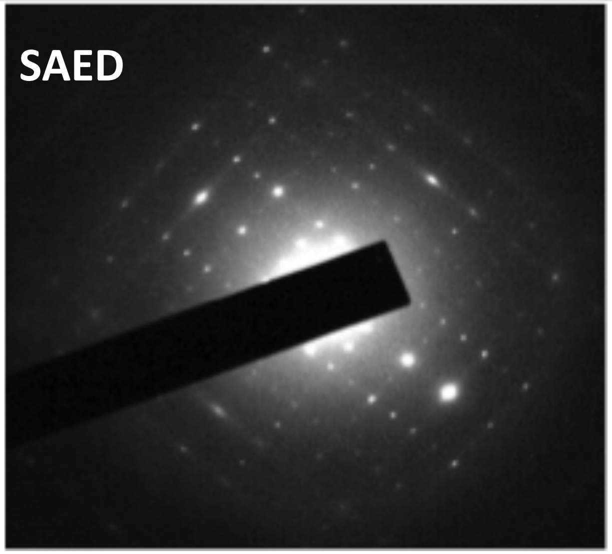
J. López-Cabrelles, S. Mañas-Valero, EC *et al. Nature Chem.* **10***,* 1001 (2018)

$[Fe(bimX)_2]$

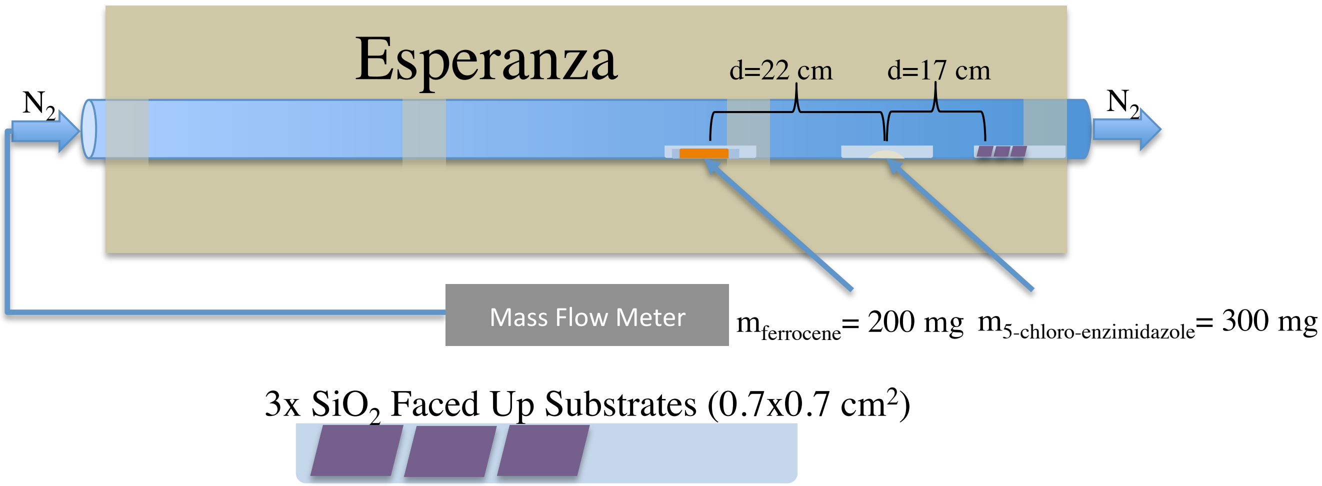
MICROMECHANICAL EXFOLIATON

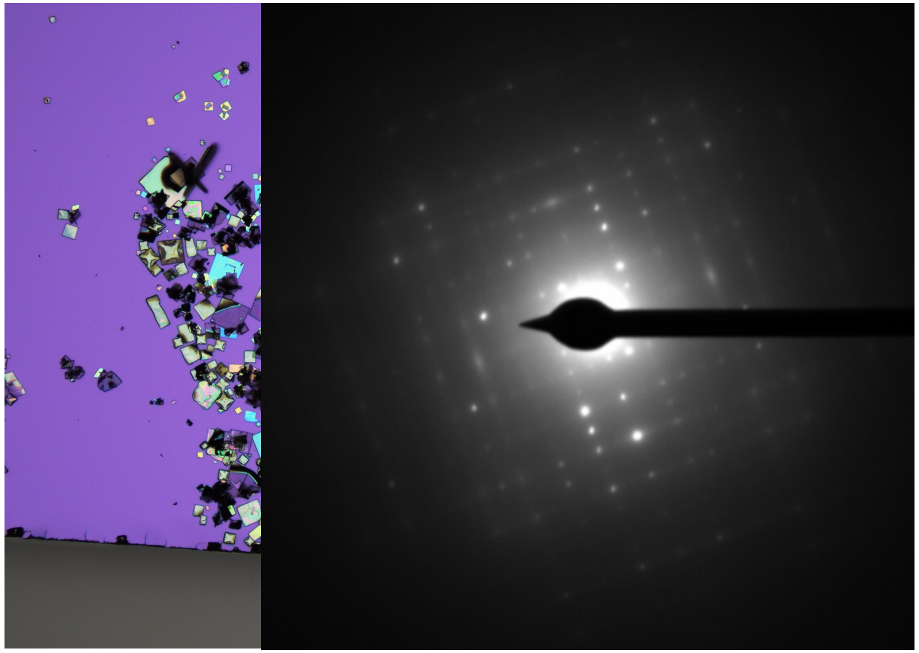


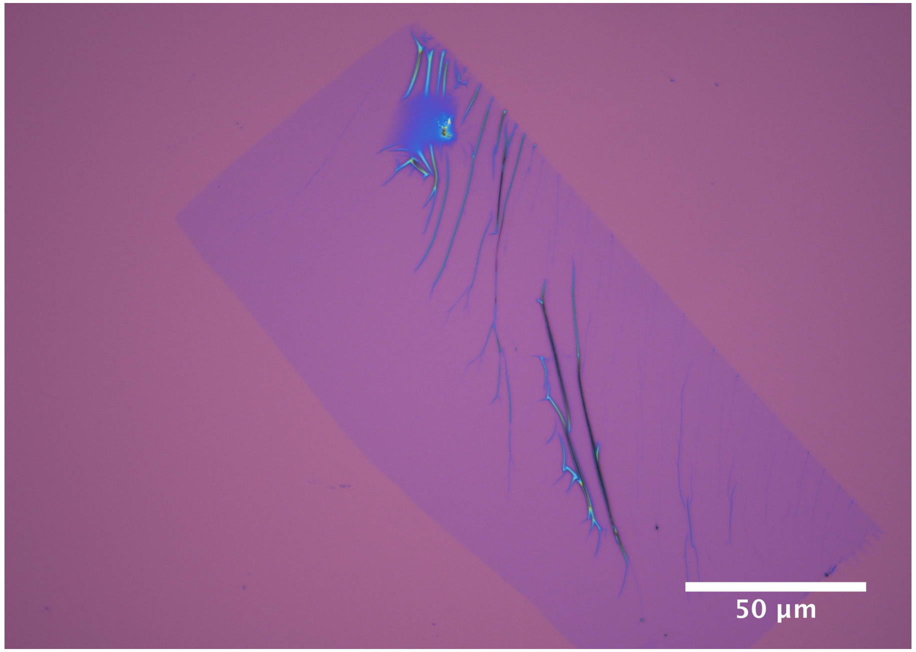




$[Fe(bimX)_2]$ CVD GROWTH of 2D CRYSTALS





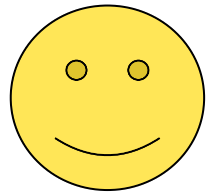


Miguel Gavara

large crystals! 4nm thick

QUESTIONS:

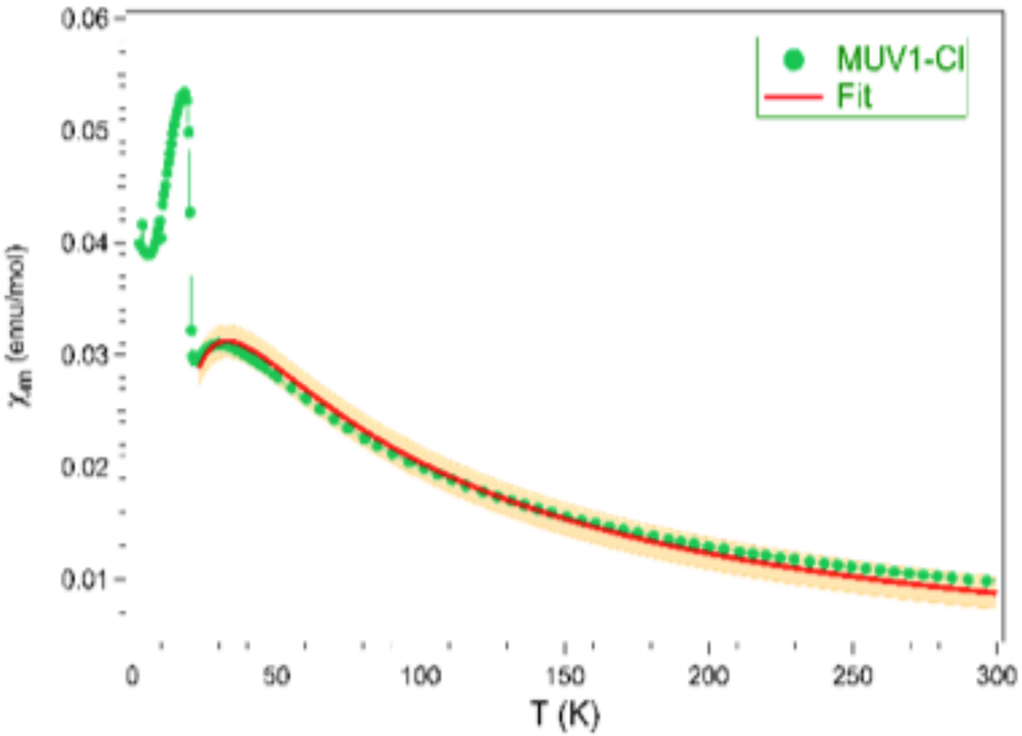
Can we isolate monolayers of molecular-based magnets?



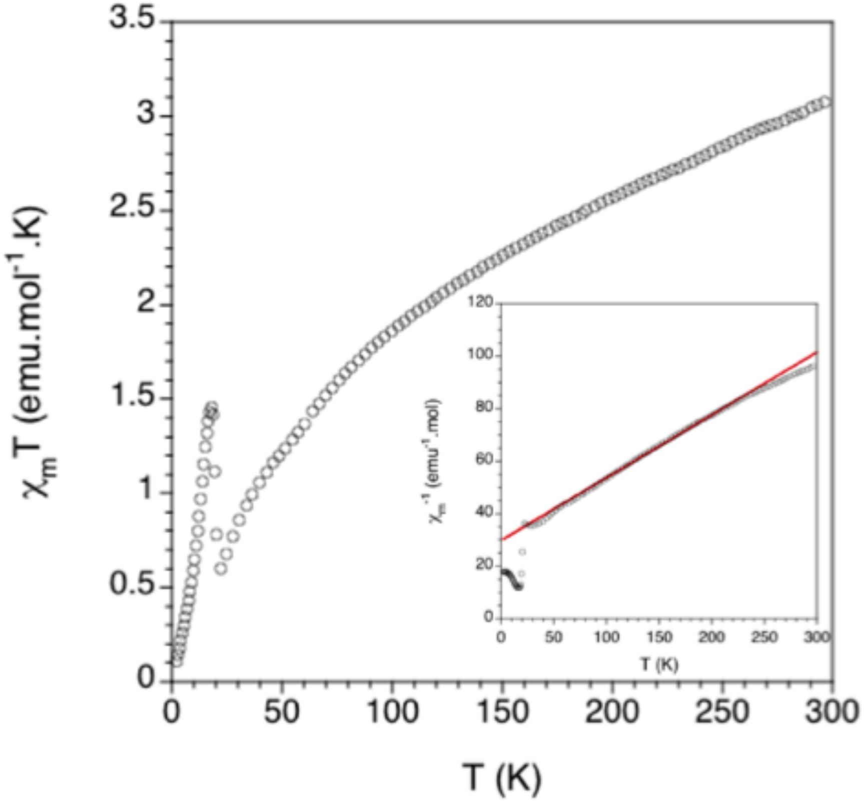
Can we measure the magnetism in the 2D limit?

[Fe(BImX)$_2$]

Magnetic properties (bulk)



Fit to a S= 2 Square-lattice
(J = - 22.9 cm^{-1})



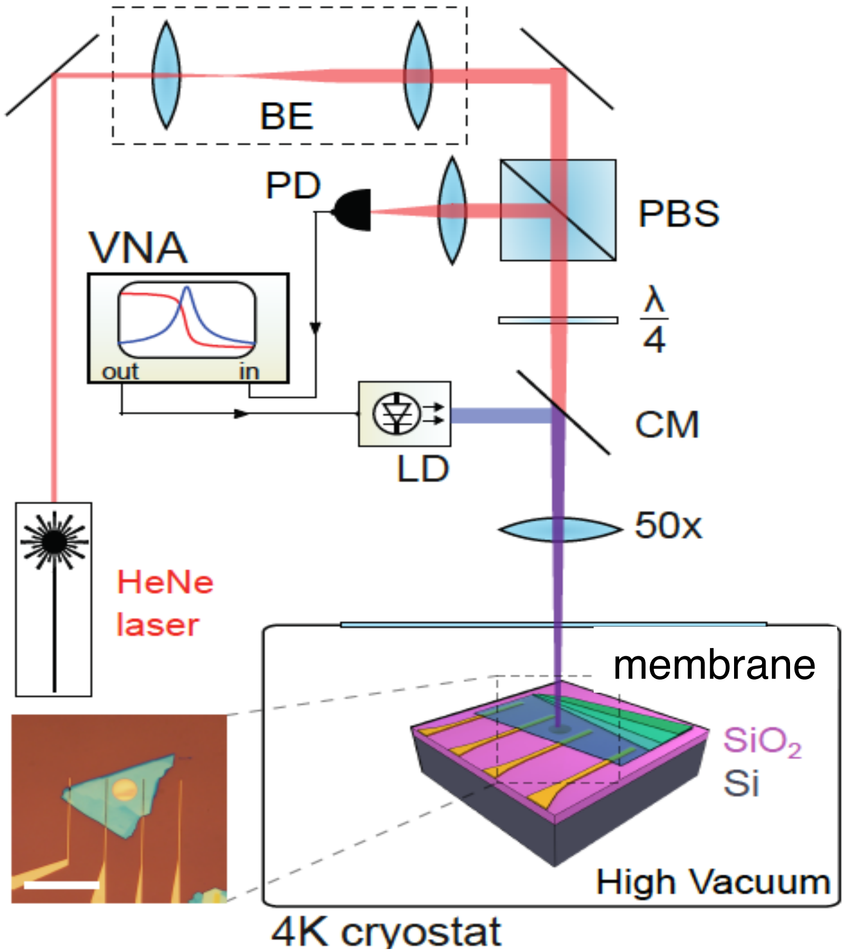
Canted antiferromagnet with T_c = 20 K

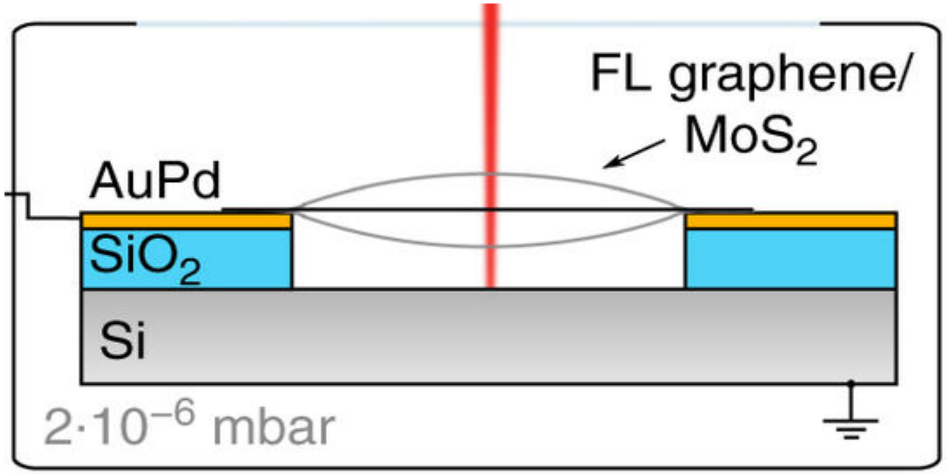
MECHANICAL PROPERTIES

(D. Davidovikj, H. Van der Zant)

Mechanical motion of suspended membranes

Laser interferometry

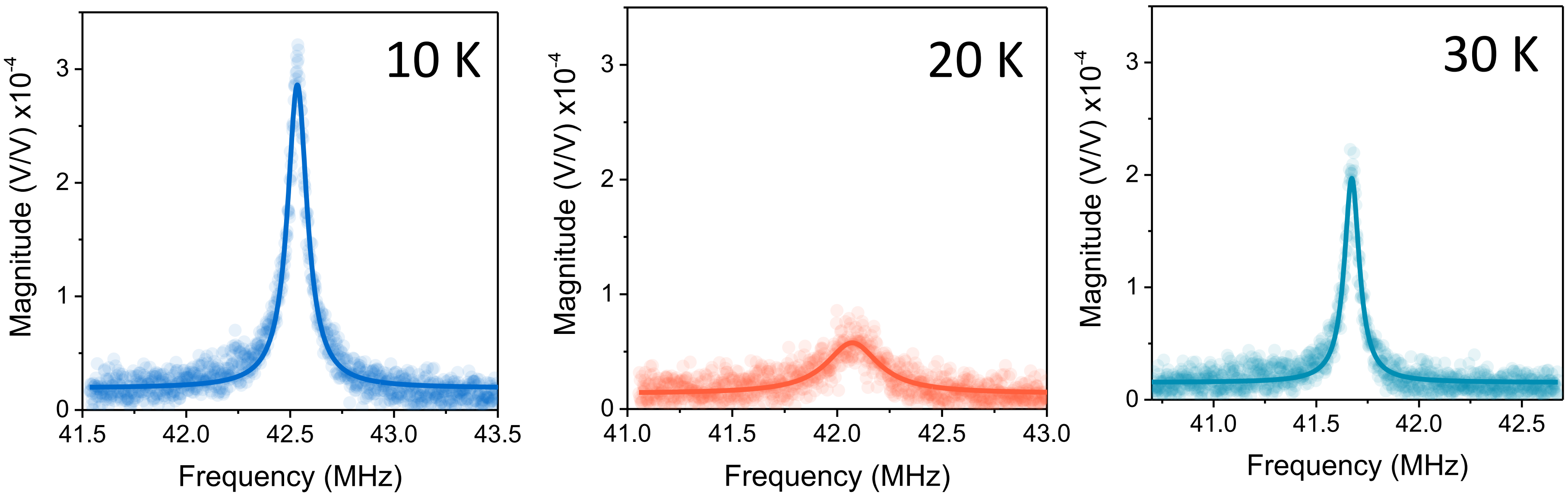




Micro drum

MAGNETIC TRANSITION?
(from mechanical properties)

HYPOTHESIS *Mechanical change at T_c*



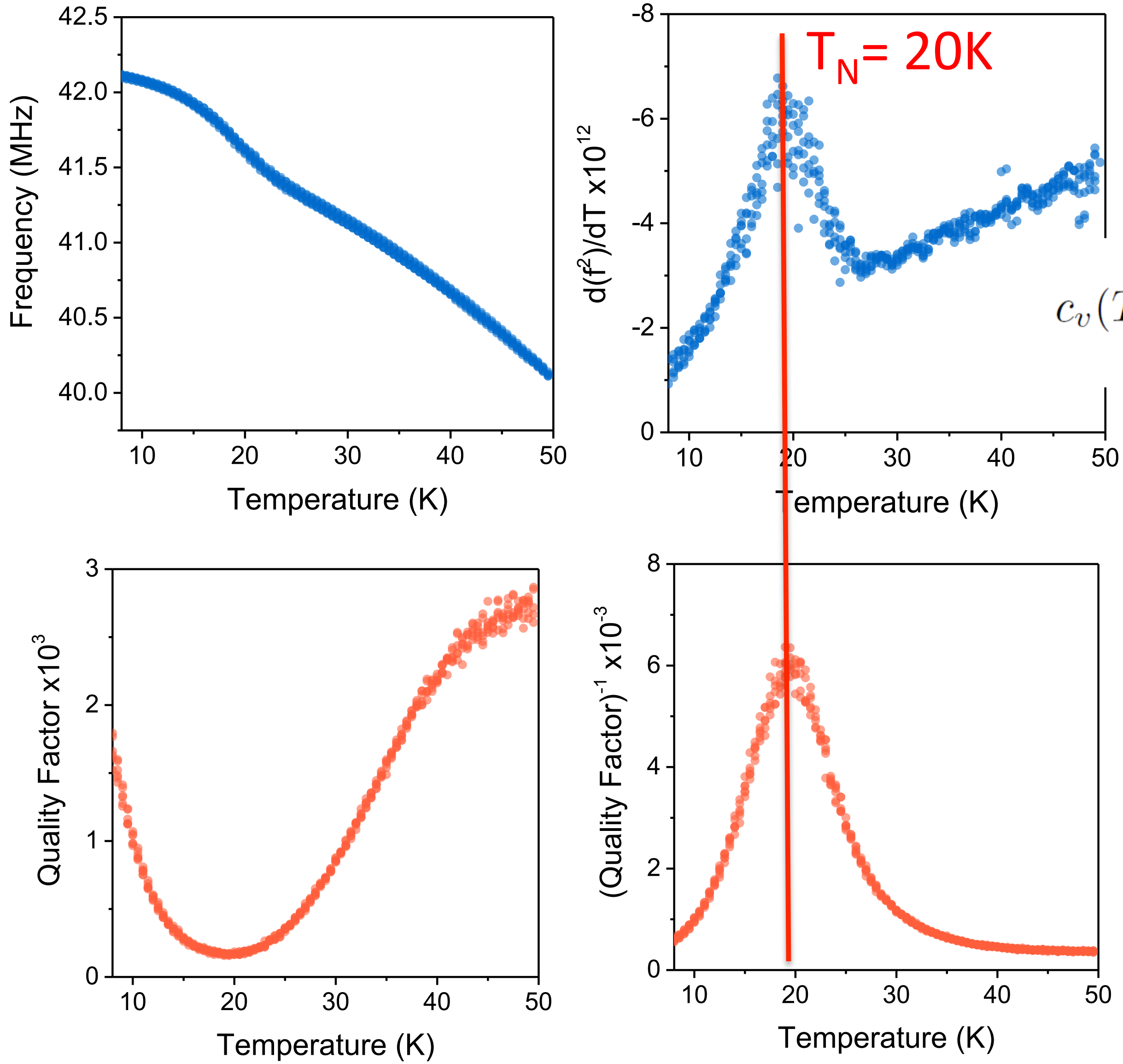
f_o = *fundamental mechanical resonance frequency*
Q = *quality factor*

Change in f_o with T

Change in Q with T

MAGNETIC TRANSITION? (from mechanical properties)

(D. Davidovikj, H. Van der Zant)



f_0 is related to specific heat

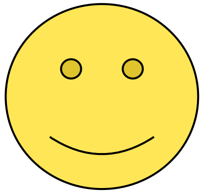
$$c_v(T) = \frac{KV_M}{\gamma}\left(\alpha_{\text{Si}} - \frac{1}{\mu^2}\frac{\text{d}[f_0^2(T)]}{\text{d}T}\right)$$

Q is related to specific heat

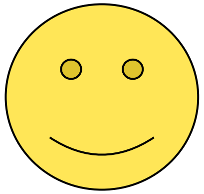
$$Q^{-1}(T) \propto c_v(T)T$$

QUESTIONS:

Can we isolate monolayers of molecular-based magnets?



Can we measure the magnetism in the 2D limit?



Take home message

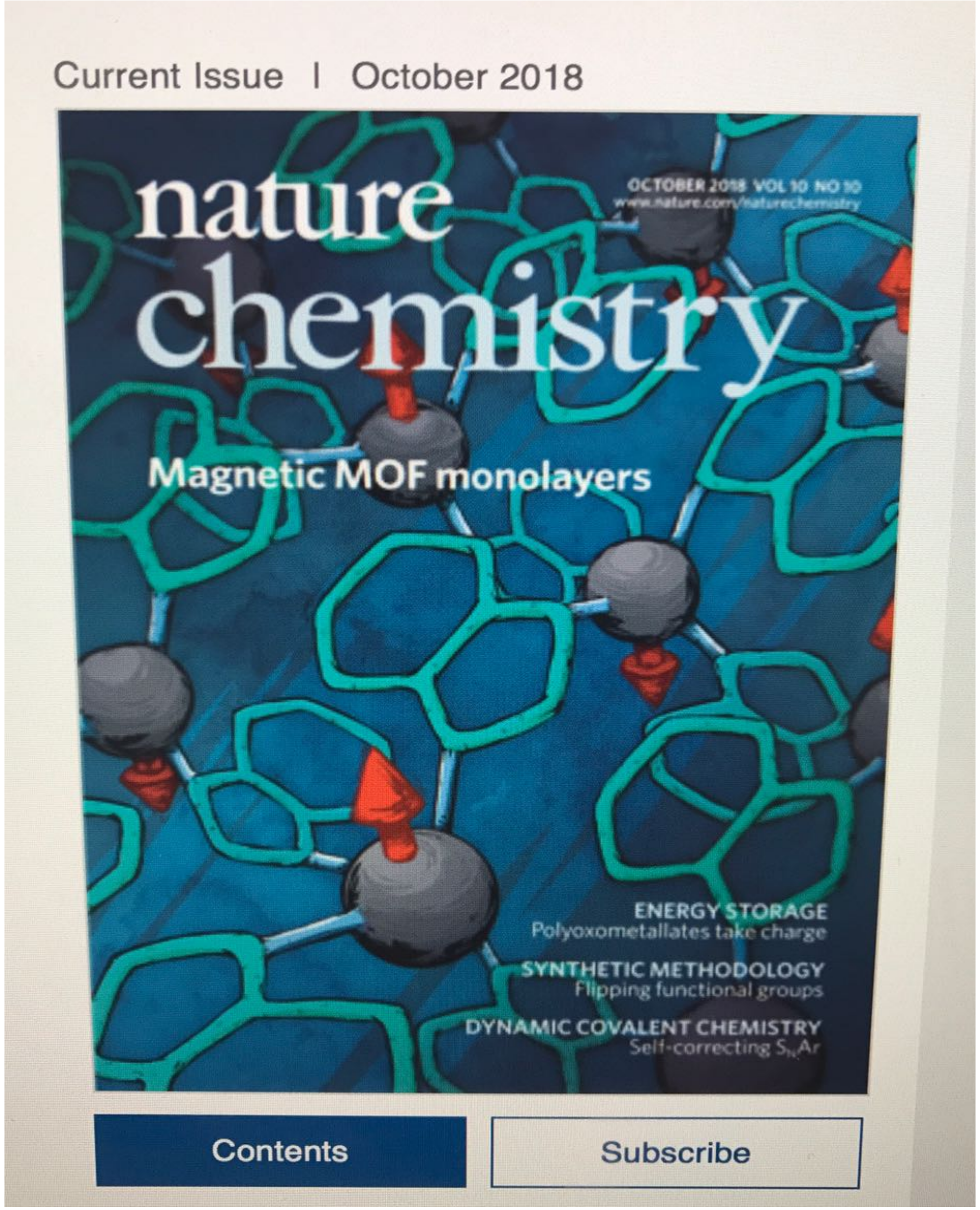
Layered coordination polymers can provide a source of chemically stable 2D magnetic monolayers

Magnetic characterization of the AF layers is possible

CHALLENGES:

- ***Fabrication of heterostructures***
- ***Integration in spintronic devices***

J. López-Cabrelles, S. Mañas-Valero *et al.* *Nature Chem.* **10**, 1001 (2018)



MOLECULAR APPROACH TO 2D MATERIALS

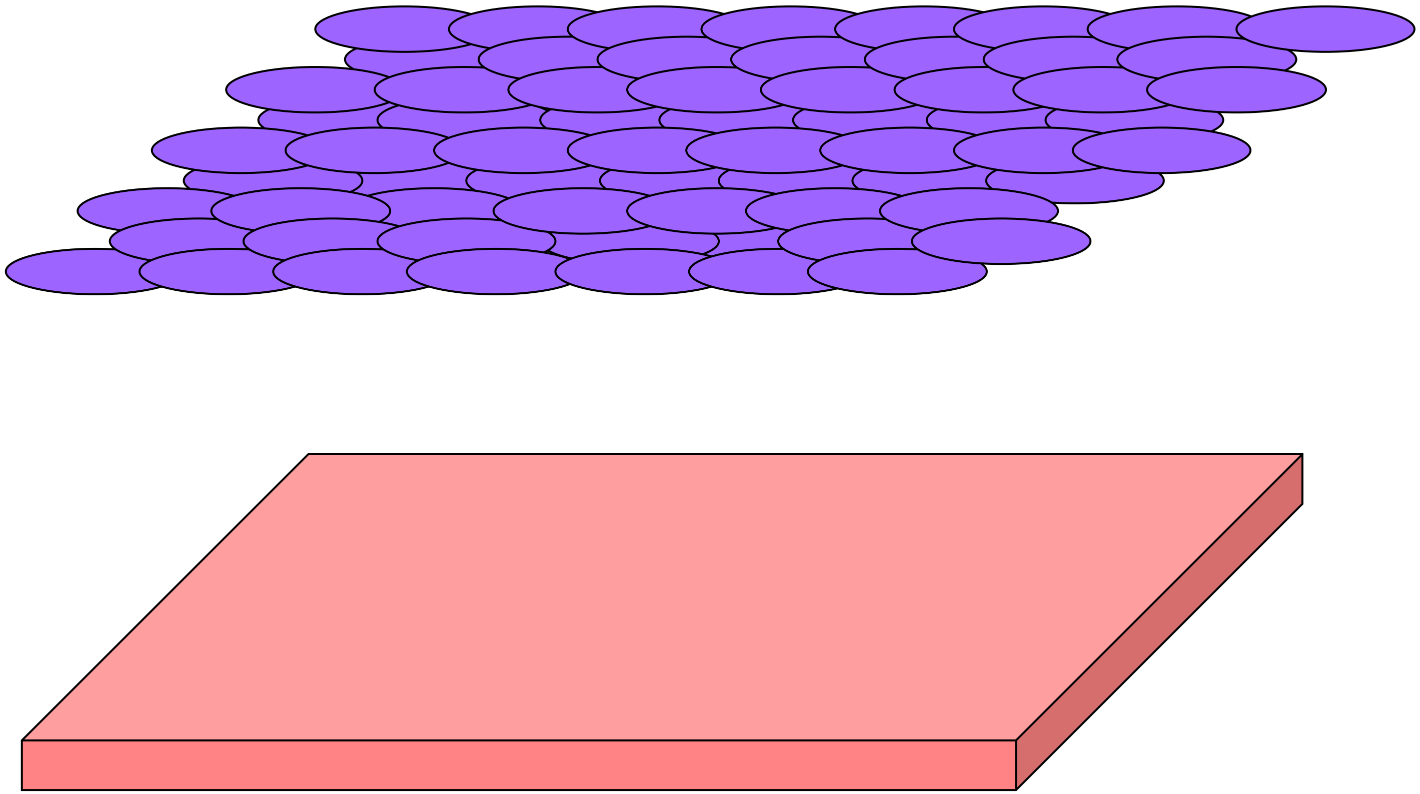
Molecular monolayers

2D magnets

Molecular/2D heterostructures

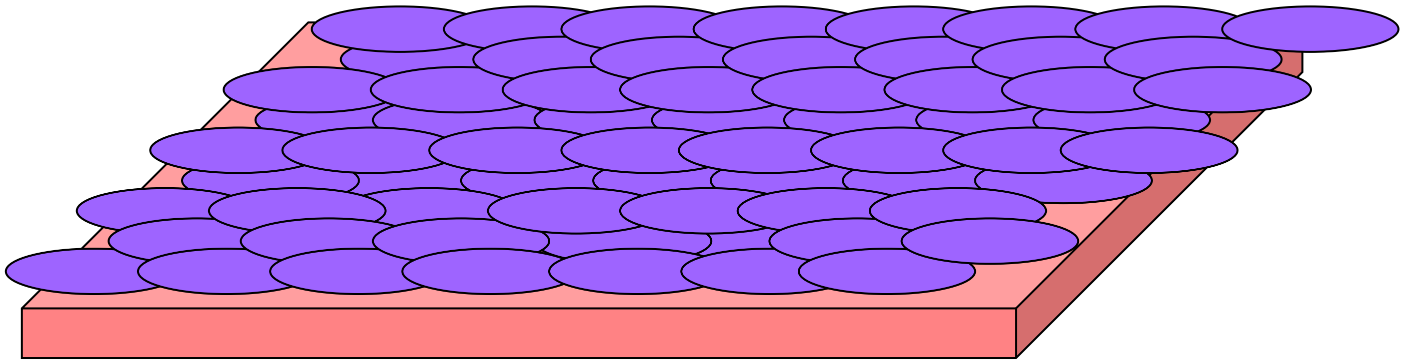
Smart materials

MOLECULAR/2D HETEROSTRUCTURES

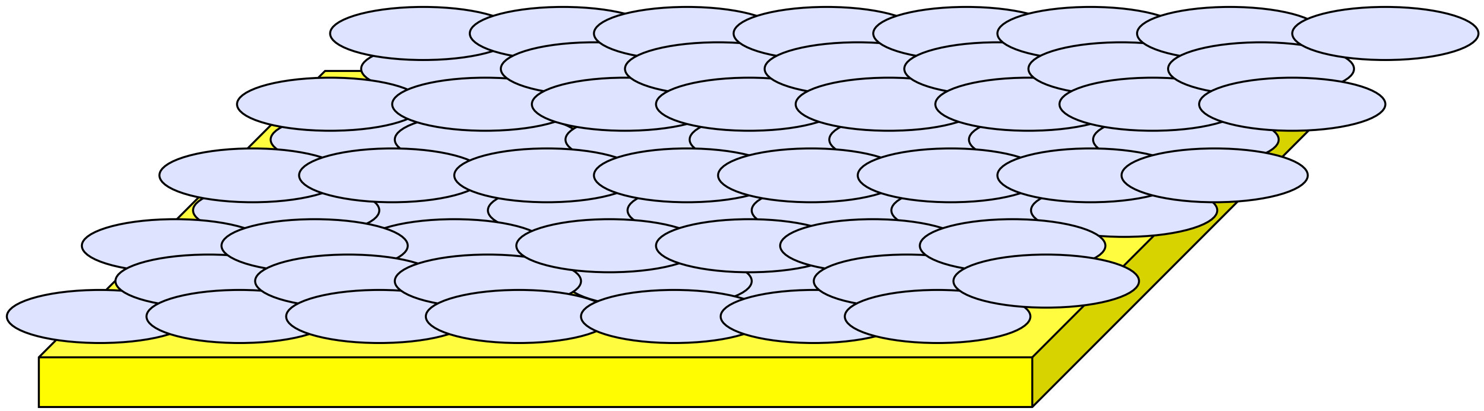


Universitat de València

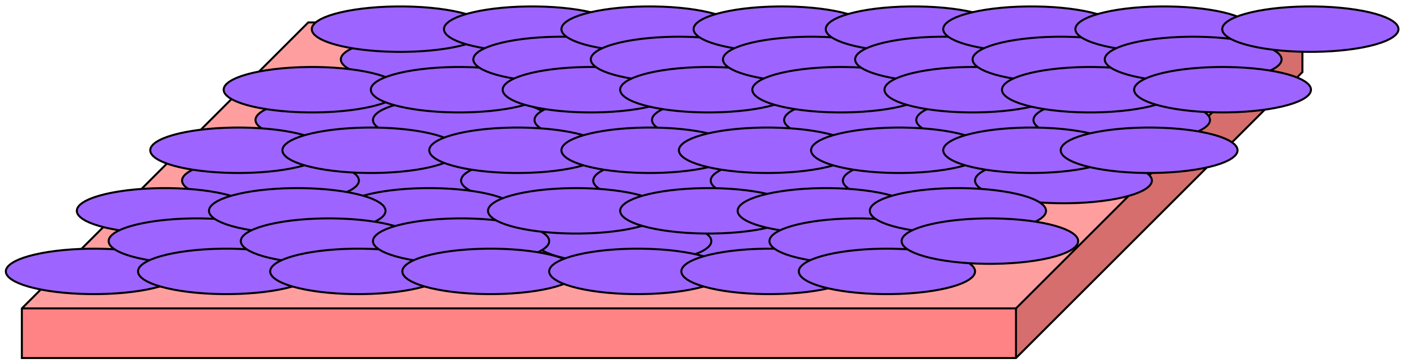
MOLECULAR/2D HETEROSTRUCTURES



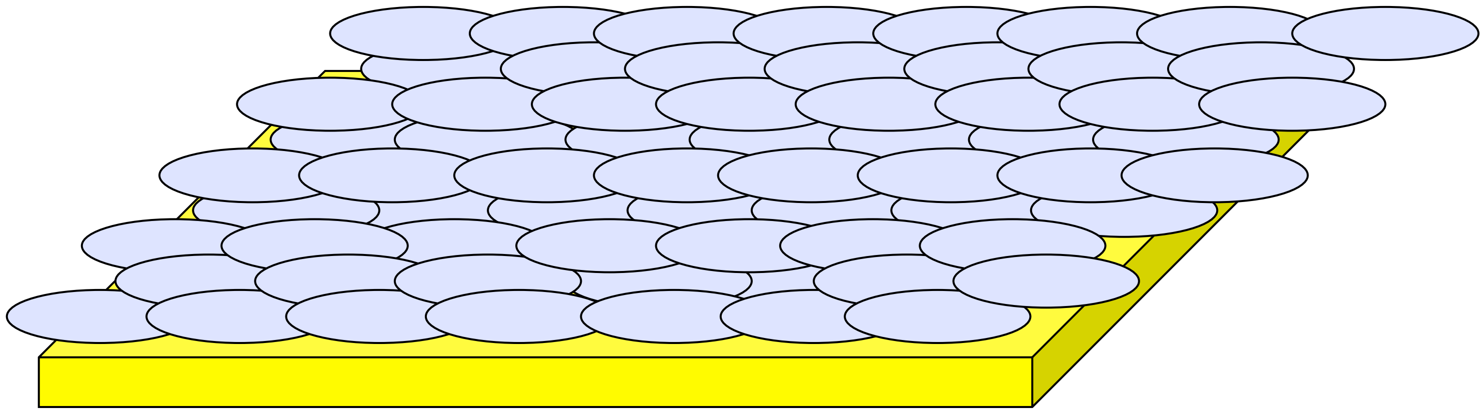
MOLECULAR/2D HETEROSTRUCTURES



MOLECULAR/2D HETEROSTRUCTURES

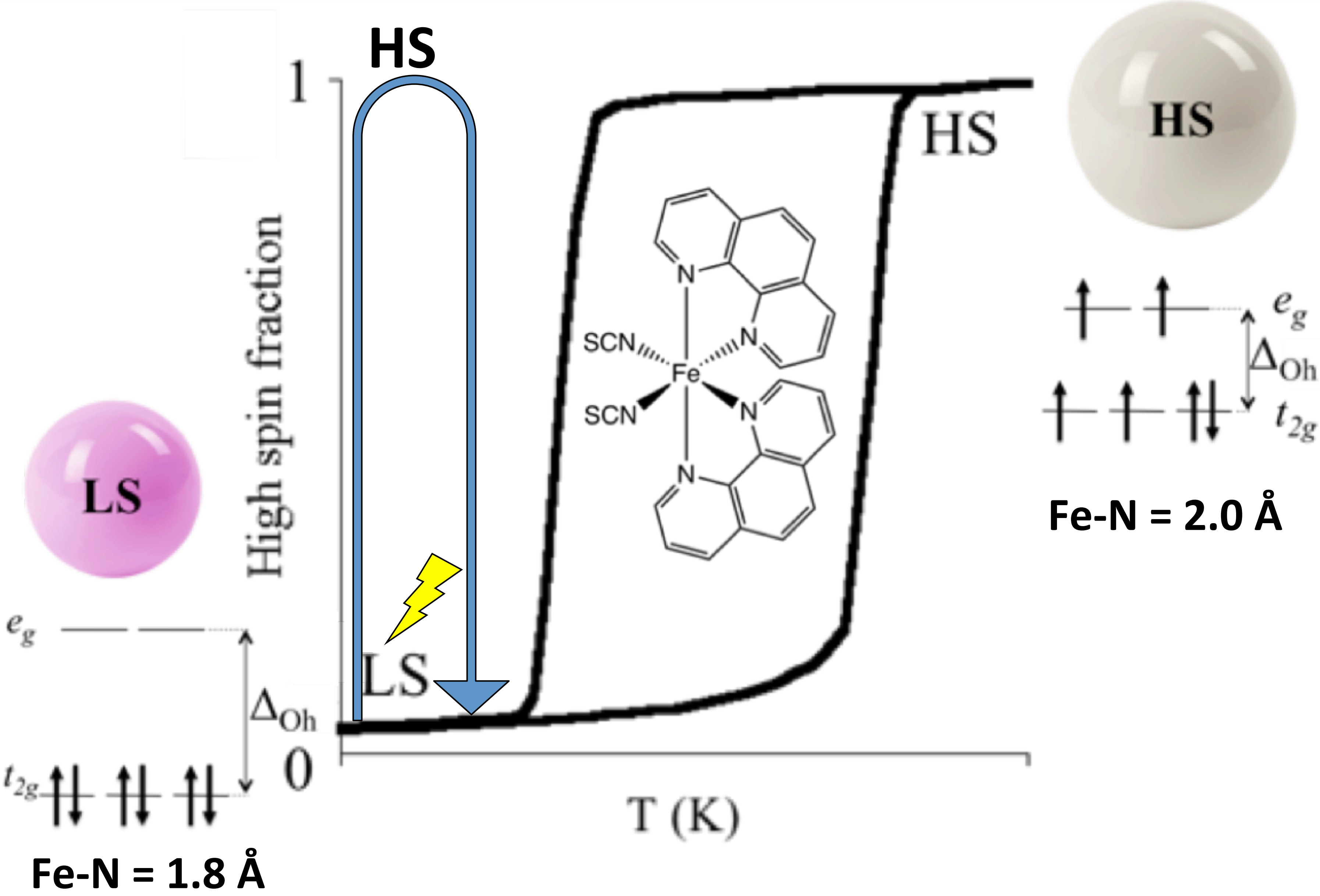


MOLECULAR/2D HETEROSTRUCTURES



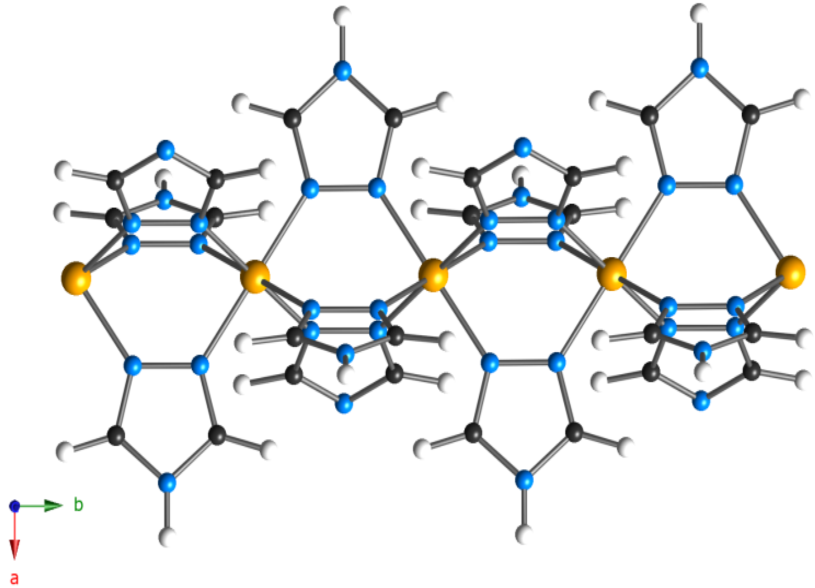
Stimuli-responsive molecules + 2D material* = *Smart 2D heterostructure

Molecular switches: Spin-crossover (SCO)

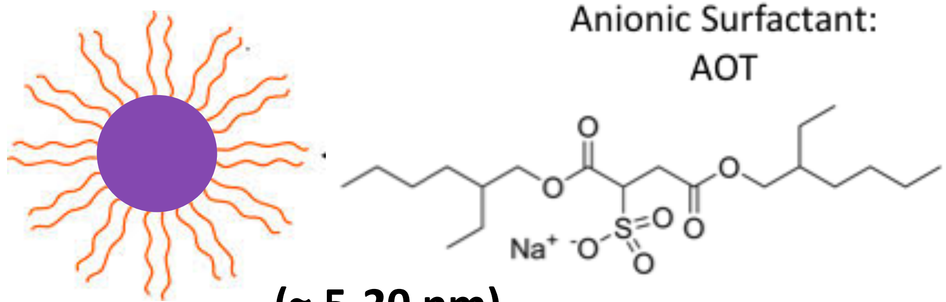


SCO nanoparticles

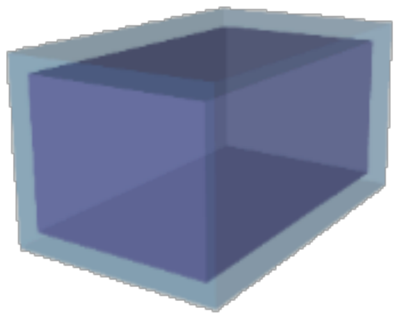
$[Fe(HTrz)_2(Trz)](BF_4)$



Anionic Surfactant:
AOT



(≈ 5-20 nm)



$SCO@SiO_2$

(40-80 nm) **(≈2 nm)**

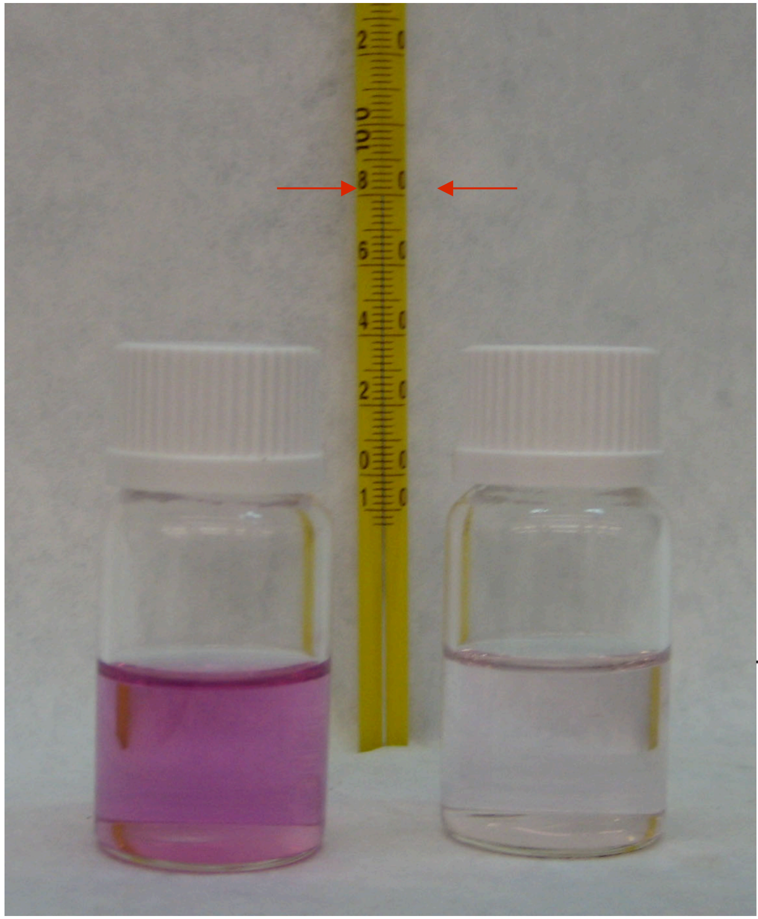
J. R. Galán, EC et al. Adv. Mater. **2007**, *19*, 1359 and *Inorg. Chem.* **2010**, *49*, 5706

M. Giménez-Marqués, EC et al. J. Mater. Chem. C **2015**, *3*, 7946

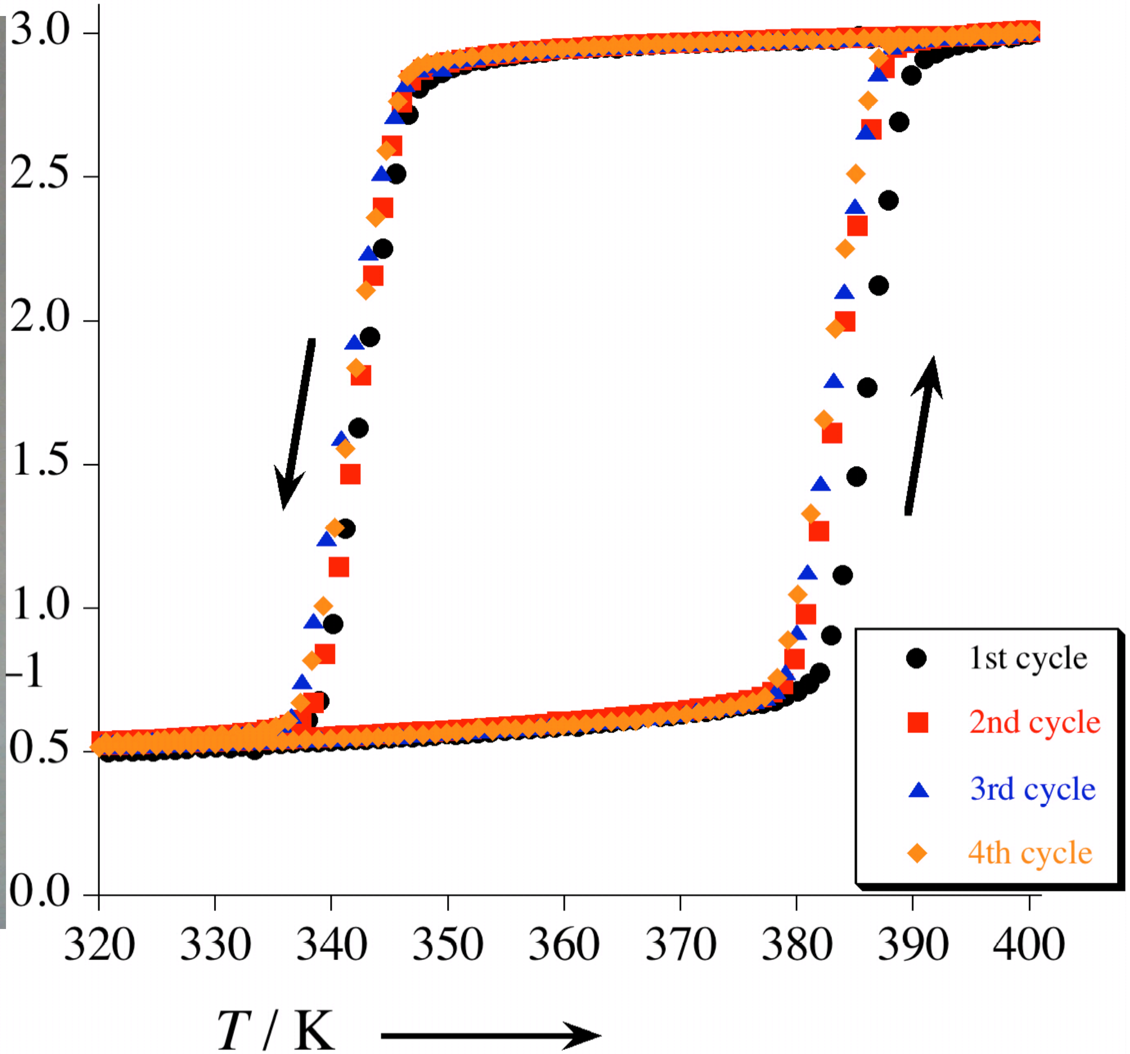
R. Torres et al. Dalton Trans. **2019**, DOI: 10.1039/c9dt02086a

Optical and Magnetic measurements

MAGNETIC BISTABILITY

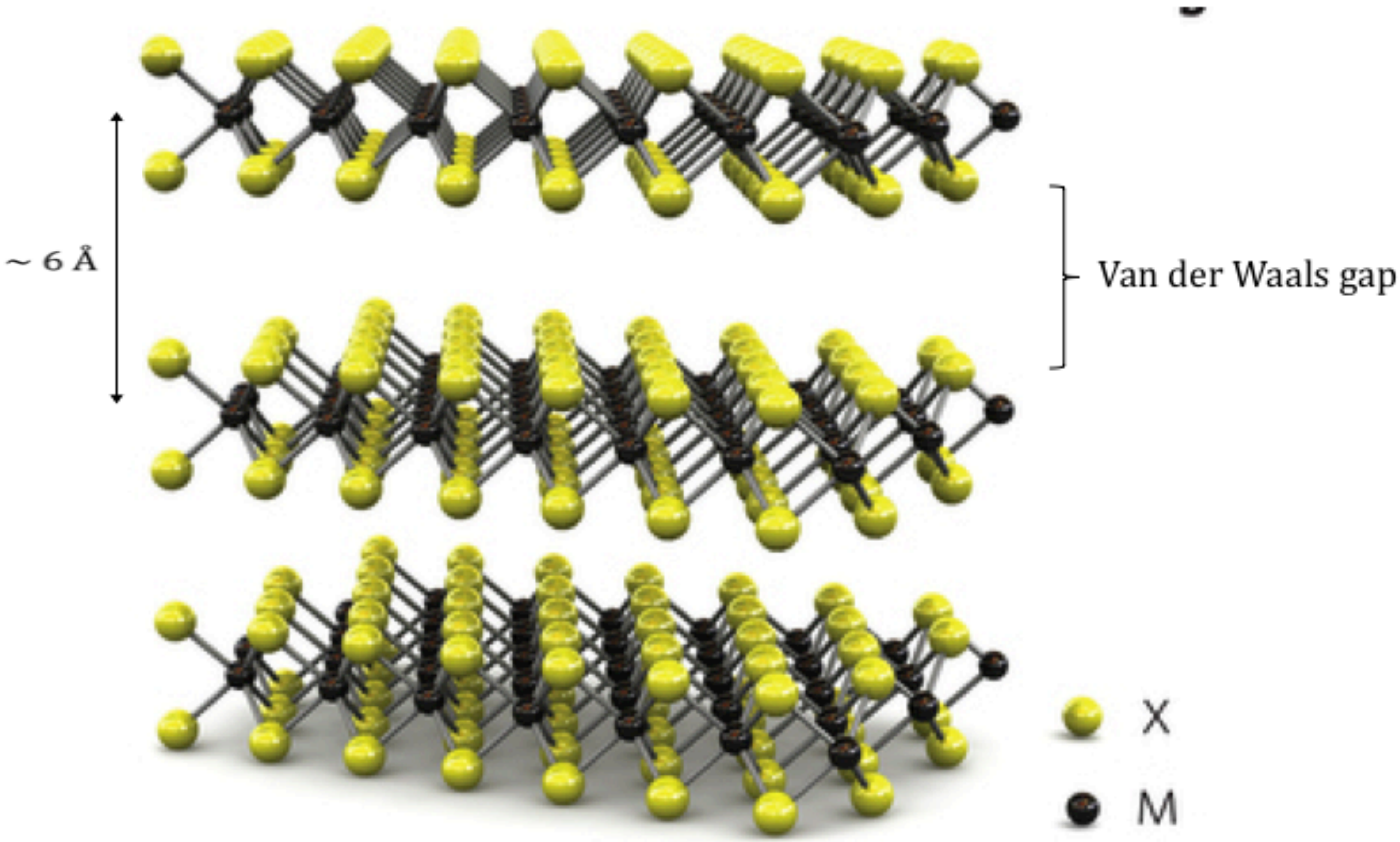


Suspension in octane



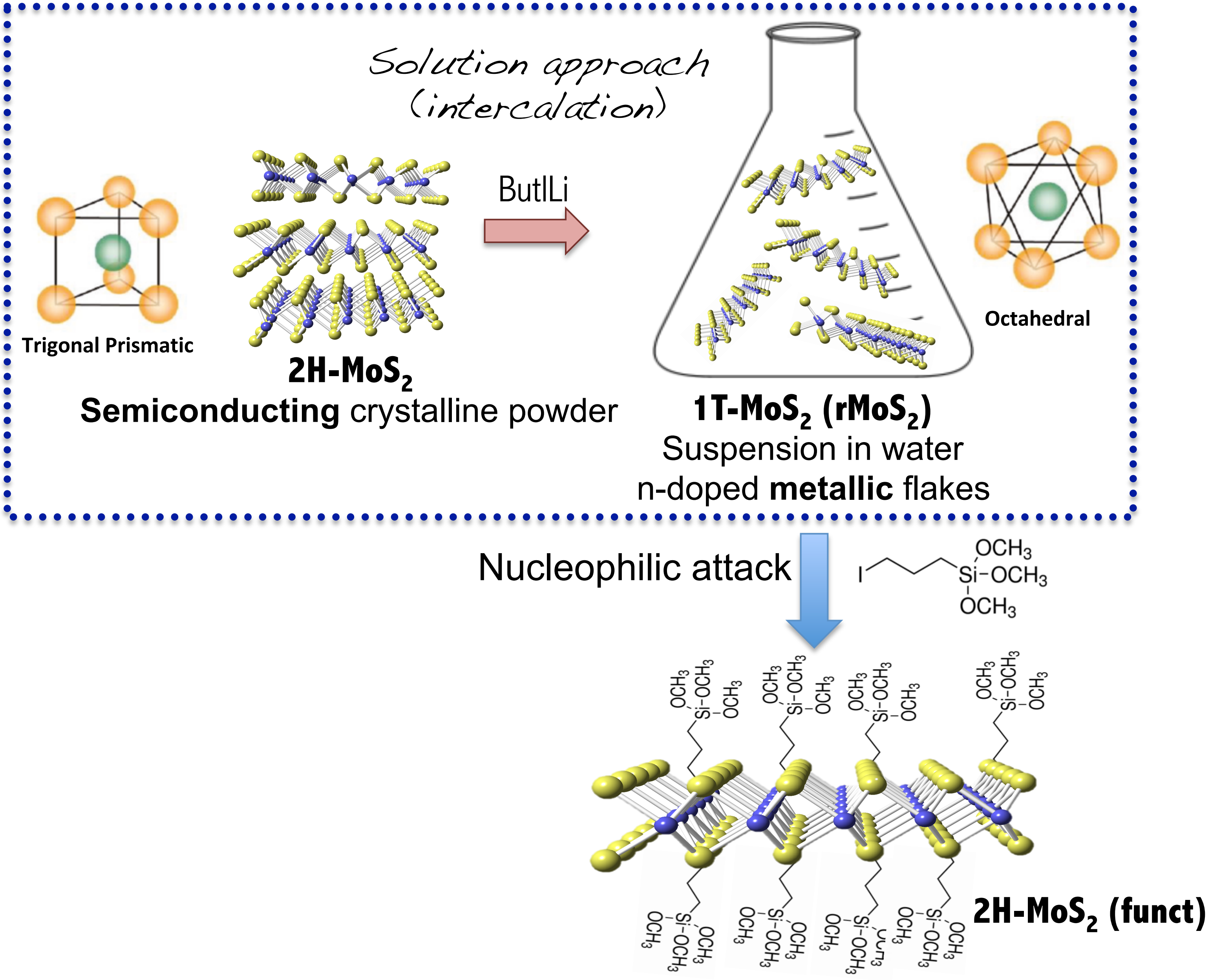
MX_2 (Transition metal dichalcogenides)

M = Ti, Zr, Hf, Nb, Ta, Mo, W…; X = S, Se, Te

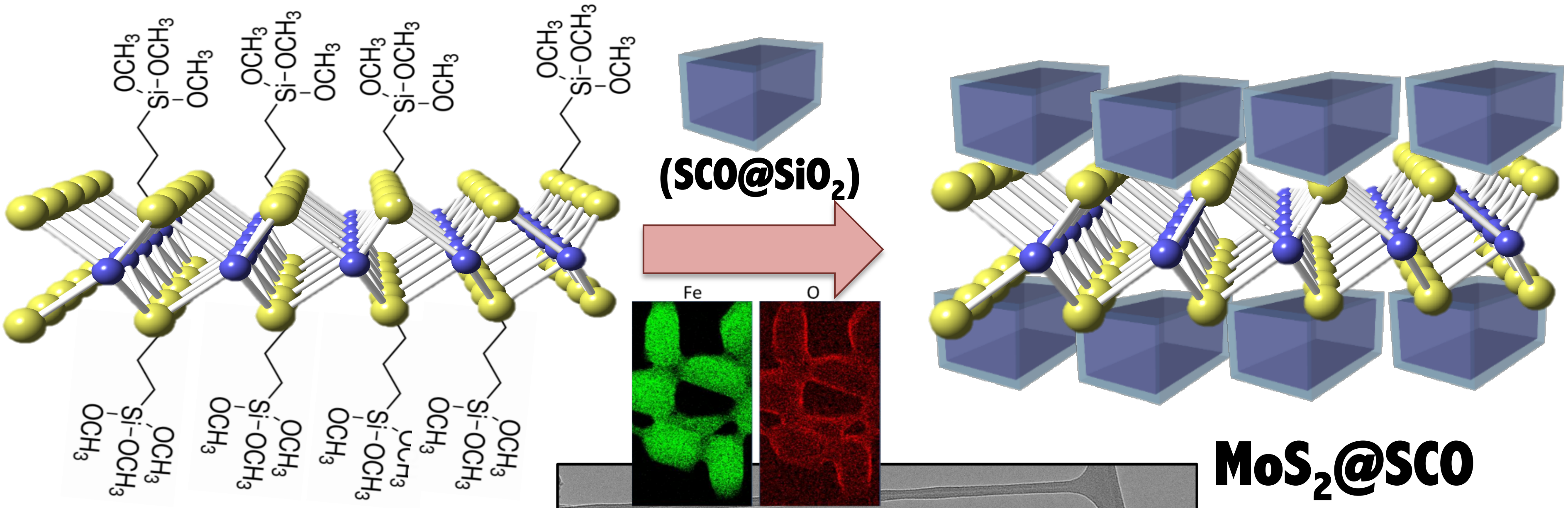


Insulators, Semiconductors, Conductors, Superconductors

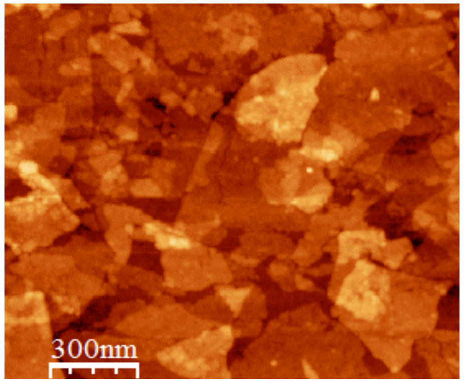
TRANSITION METAL DICHALCOGENIDES (TMDCs)

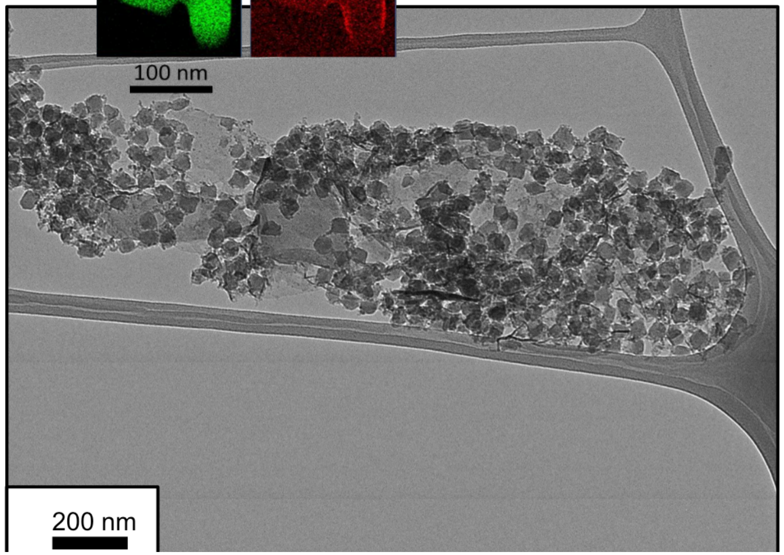


SCO@SiO_2 nanoparticles on MoS_2



2H-MoS_2 (funct)

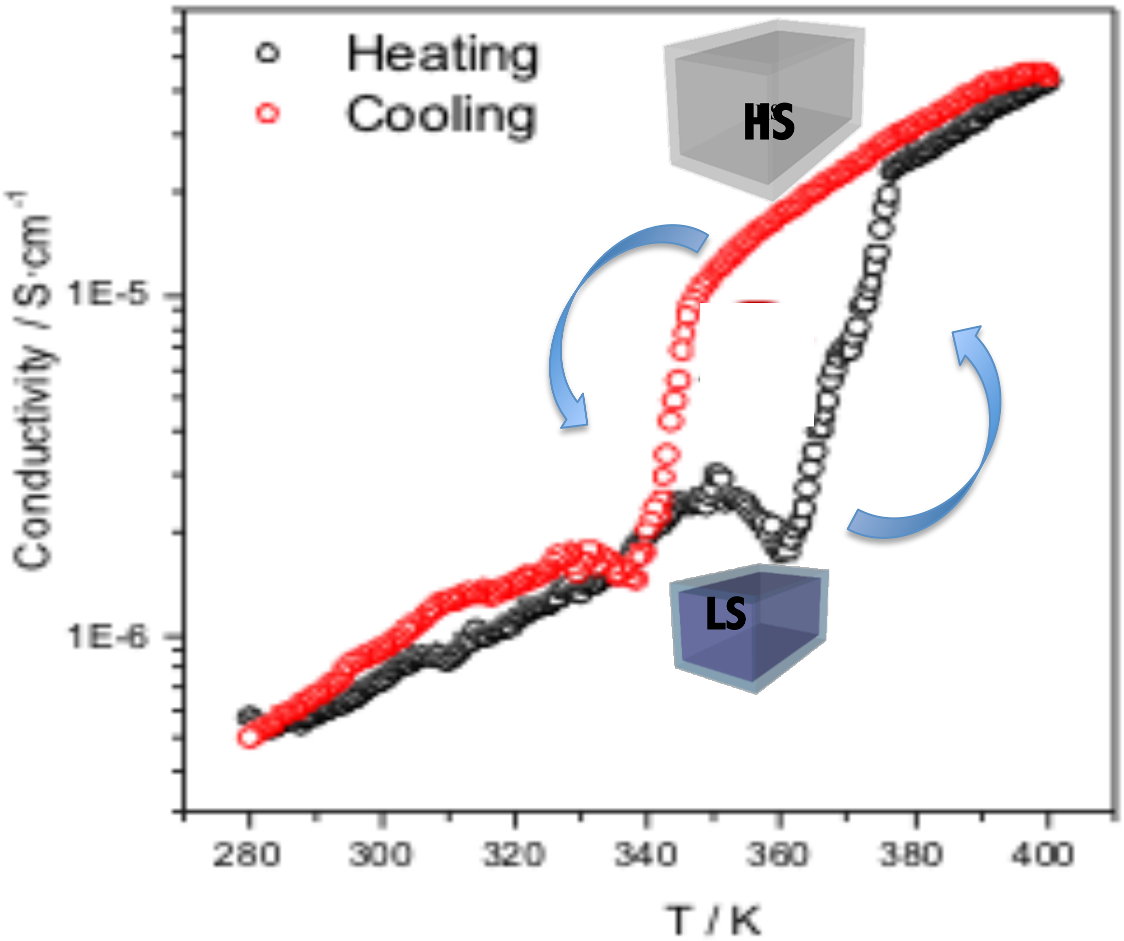




Ramon Torres
Marc Morant
Alicia Forment

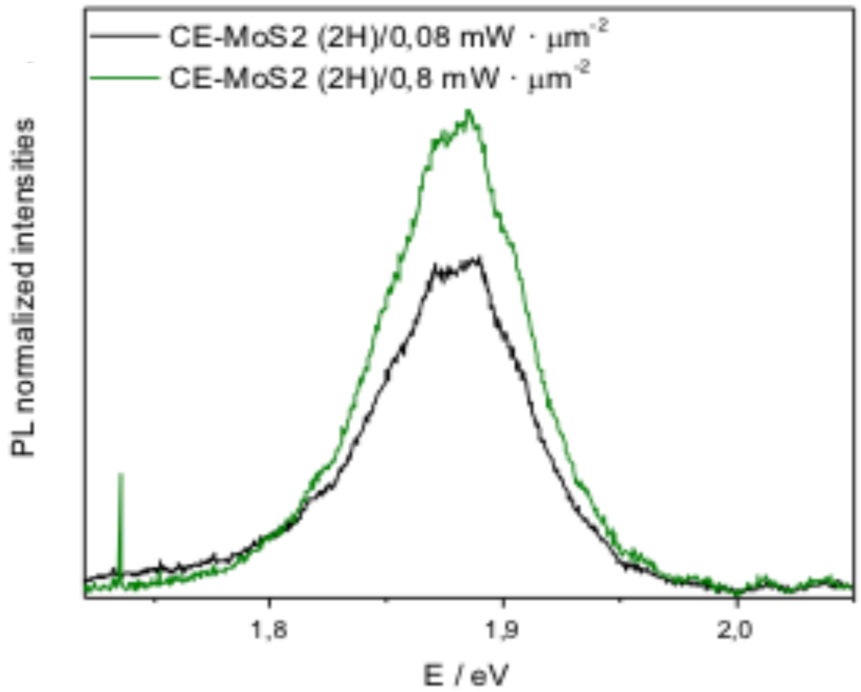
$SCO@SiO_2$ nanoparticles on MoS_2

TRANSPORT *Electrical sensing of the spin*

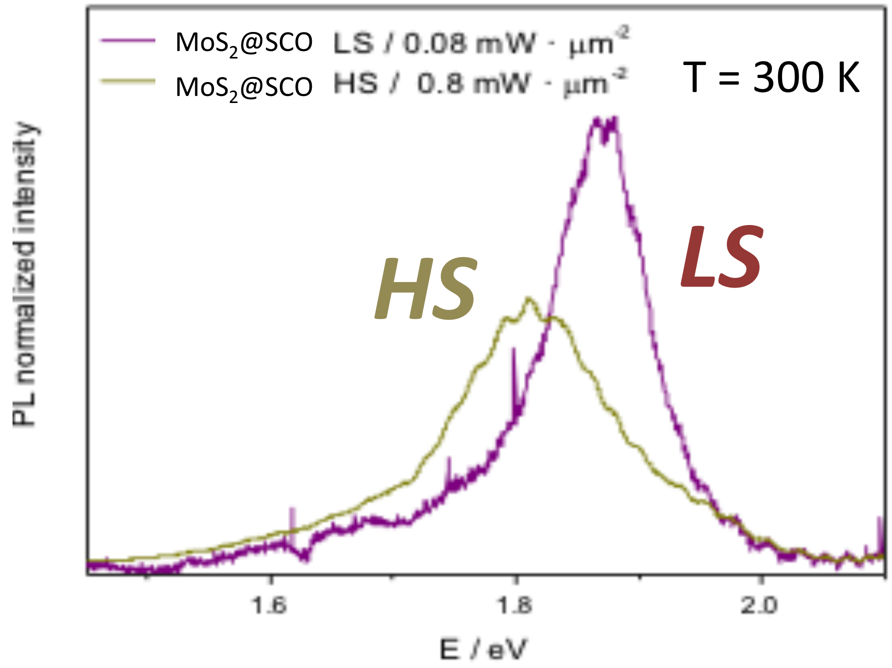


SCO@SiO_2 nanoparticles on MoS_2

Smart molecular/2D heterostructure



PHOTOLUMINESCENCE



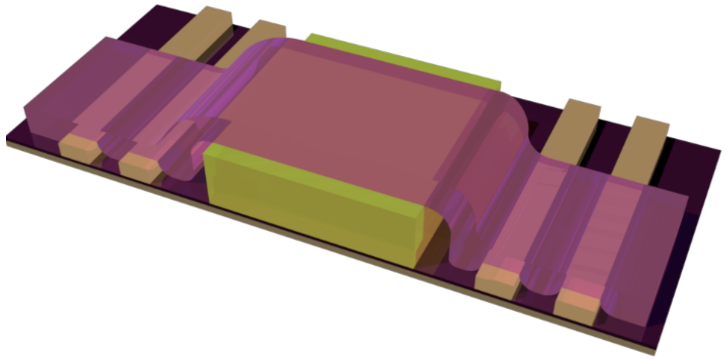
Light-induced strain on the MoS_2

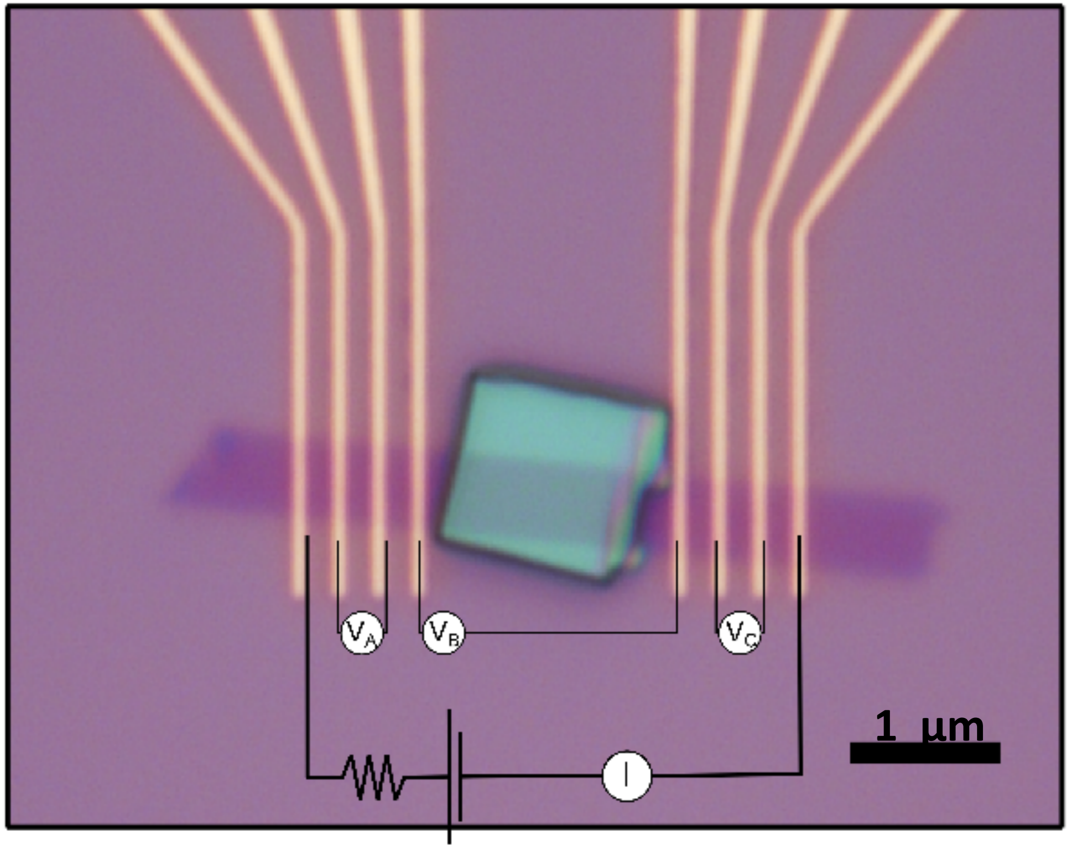
Optical sensing of the spin

Red shift (60 meV)

ca. 1 % of tensile strain

Hybrid electronic devices



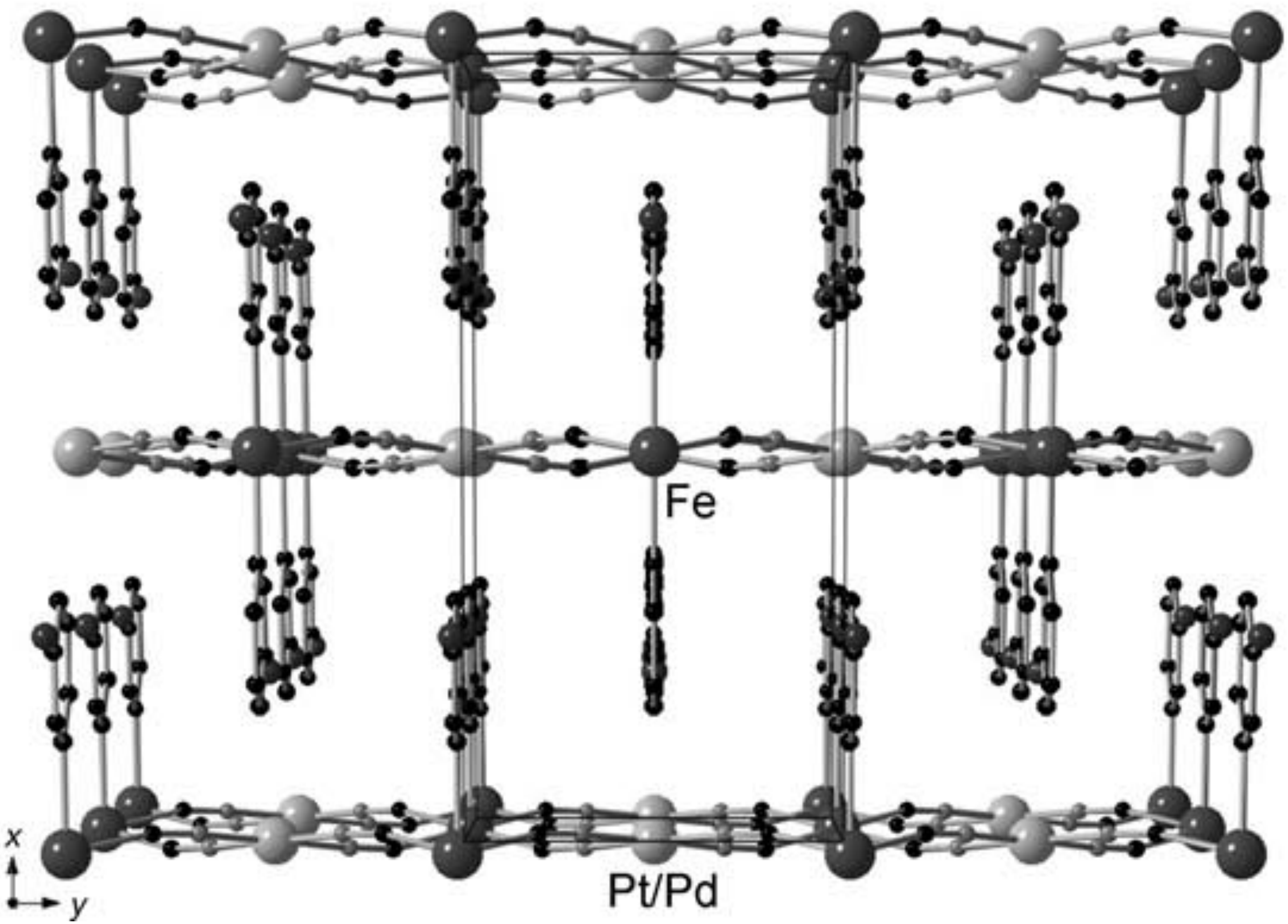


SCO crystal/graphene heterostructure

Carla Boix, Samuel Mañas

SCO crystal :

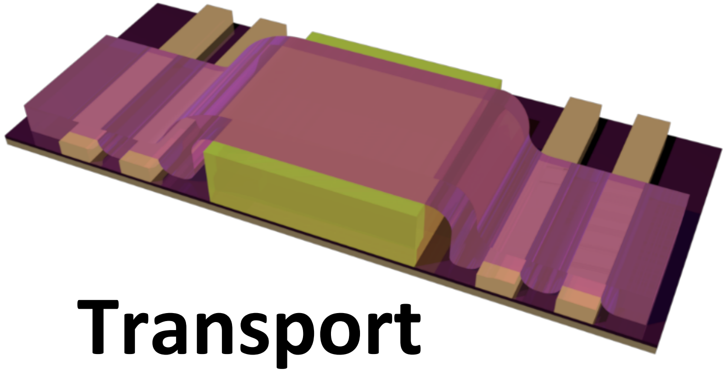
{$Fe^{II}(3\text{-}Xpy)_2[Pt^{II}(CN)_4]$} interdigitated 2D MOF



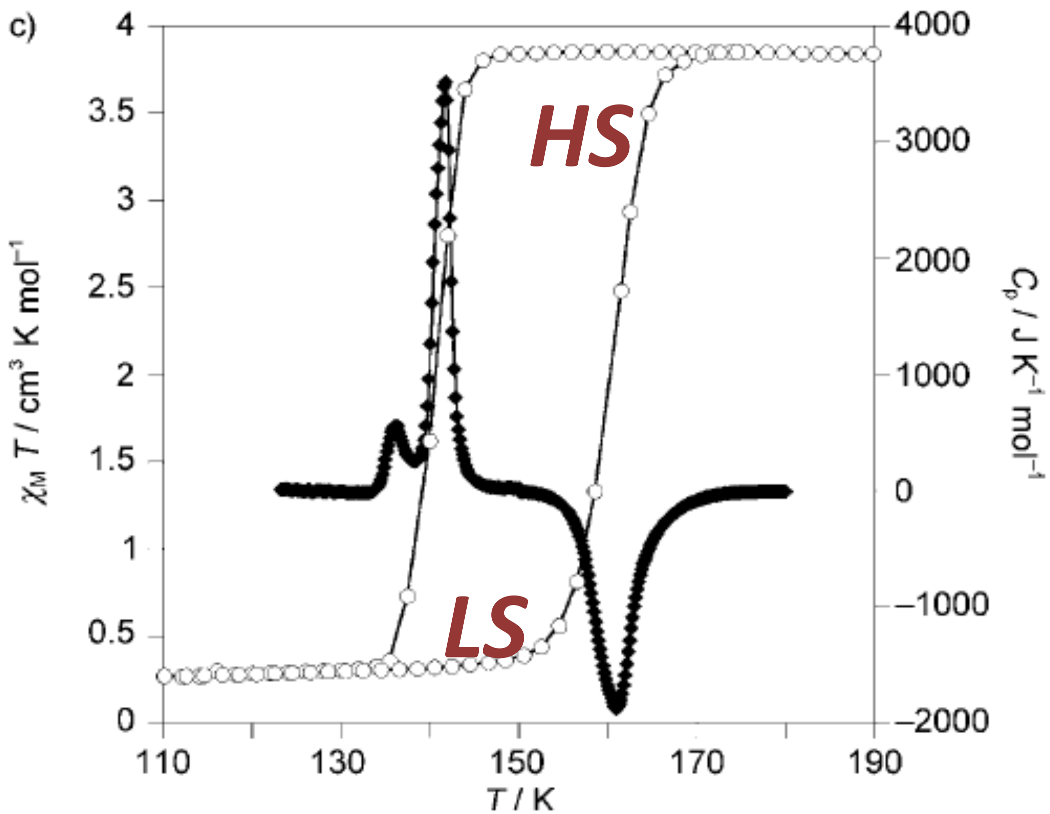
V. Martínez *et al. Chem. Eur. J.* **2009**, 15, 10960

Hybrid electronic devices

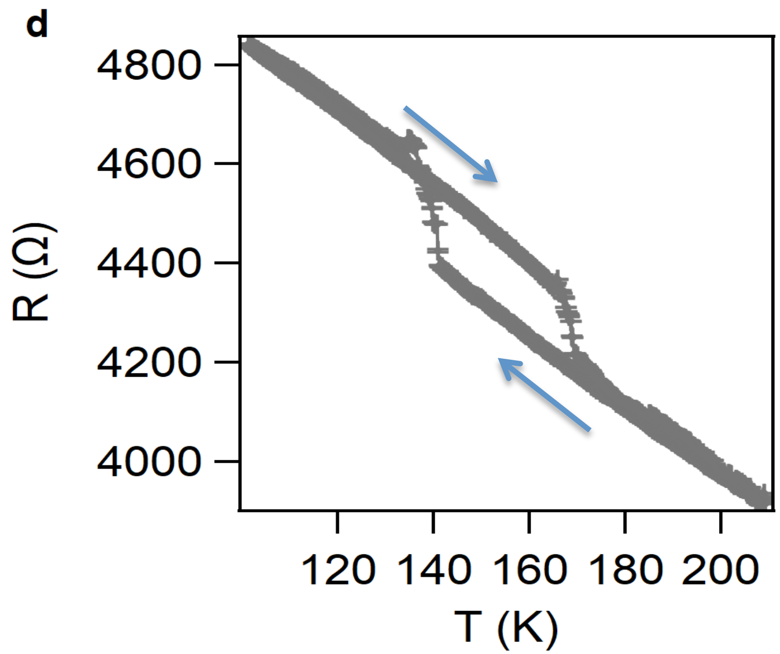
Electrical sensing of the spin



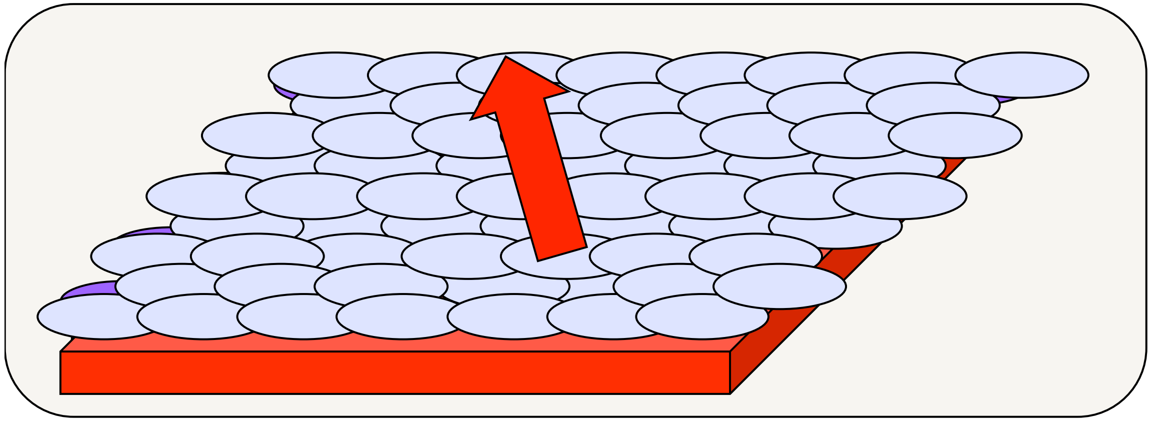
Magnetism



Transport



Take home message

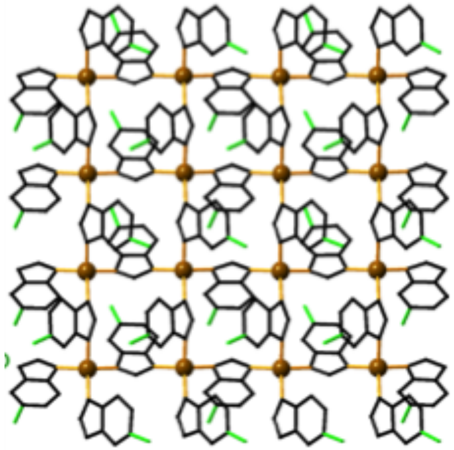


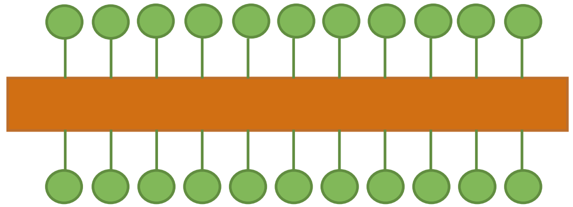
Smart molecular/2D heterostructures:

A new class of 2D heterostructures showing a molecular control over the properties of the 2D material

MOLECULAR APPROACH TO 2D MATERIALS

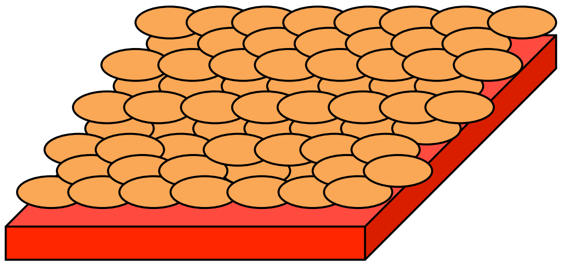
MOLECULAR MONOLAYERS





2D magnets

MOLECULAR / 2D HETEROSTRUCTURES



Smart 2D materials

Acknowledgment

Univ. Valencia (ICMol)

- **Javier López Cabrelles**
- **Samuel Mañas Valero**
- **Carla Boix**
- **Miguel Gavara**
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- **Ramón Torres-Cavanillas**
- **Victor García**
- Guillermo Minguez Espallargas
- Alicia Forment
- Mónica Giménez-Marqués
- Miguel Clemente-León

TU Delft

- H. Van der Zant
- D. Davidovikj
- M. Siskins

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EIMM

Instituto de Ciencia Molecular

- European Union:

COSMICS

FATMOLS

SINFONIA

erc European Research Council

SPINMol

Mol-2D

- Spanish MINECO

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PROGRAMA ingenio 2010

Consolider

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