Molecular functional materials at the nanoscale

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Coordination chemistry
a powerful tool for functional materials

2D coordination networks
Nanoparticles with peculiar behavior
SCO Molecules organized in 2D

CHEMISTRY OF MATERIALS
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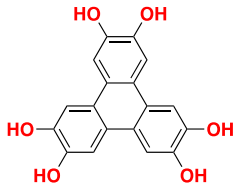
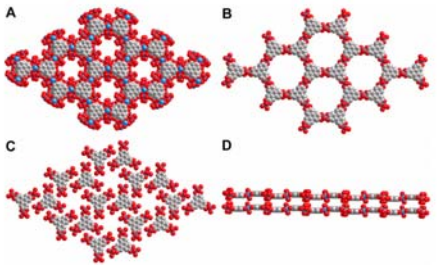
New Porous Crystals of Extended Metal-Catecholates

Mohamad Hmadeh,[†,‡] Zheng Lu,[†,‡] Zheng Liu,[§] Felipe Gándara,[†,‡] Hiroyasu Furukawa,[†,‡] Shun Wan,[†,‡] Veronica Augustyn,[⊥] Rui Chang,[⊥] Lei Liao,[§] Fei Zhou,[⊥] Emilie Perre,[⊥] Vidvuds Ozolins,[⊥] Kazu Suenaga,[§] Xiangfeng Duan,[‡] Bruce Dunn,[⊥] Yasuaki Yamamto,[∥] Osamu Terasaki,[#,□] and Omar M. Yaghi*[,†,‡,#,▽]

dx.doi.org/10.1021/cm301194a | Chem. Mater. 2012, 24, 3511−3513

Co(II)





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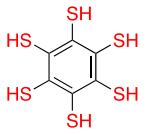
π-Conjugated Nickel Bis(dithiolene) Complex Nanosheet

Tetsuya Kambe,[†] Ryota Sakamoto,[†] Ken Hoshiko,[†] Kenji Takada,[†] Mariko Miyachi,[†] Ji-Heun Ryu,[‡] Sono Sasaki,[§,∥] Jungeun Kim,[∥] Kazuo Nakazato,[‡] Masaki Takata,[∥,⊥] and Hiroshi Nishihara*[,†]

dx.doi.org/10.1021/ja312380b | J. Am. Chem. Soc. 2013, 135, 2462−2465

Ni(II)



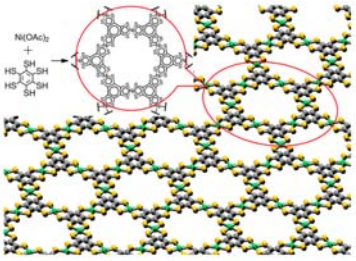
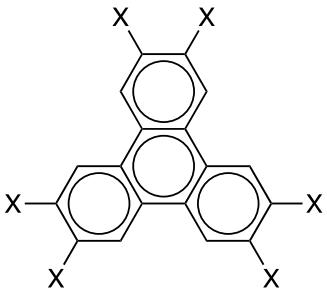


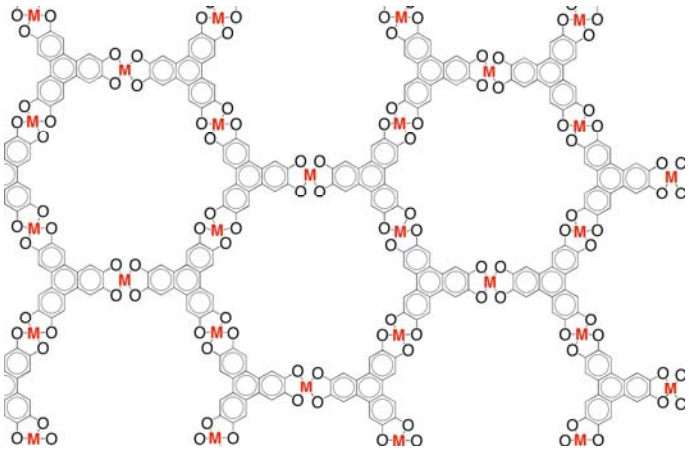
Figure 1. Schematic illustration and chemical structure of monolayer nickel bis(dithiolene) complex nanosheet 1. Countercations have been omitted for clarity. Gray, C; yellow, S; green, Ni.



X = **OH**

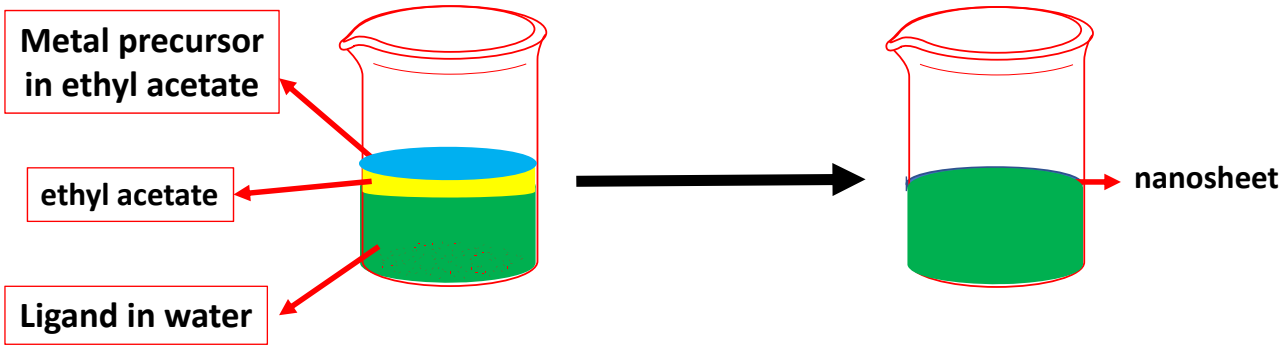
$NiCl_2$

base



M = **Ni**

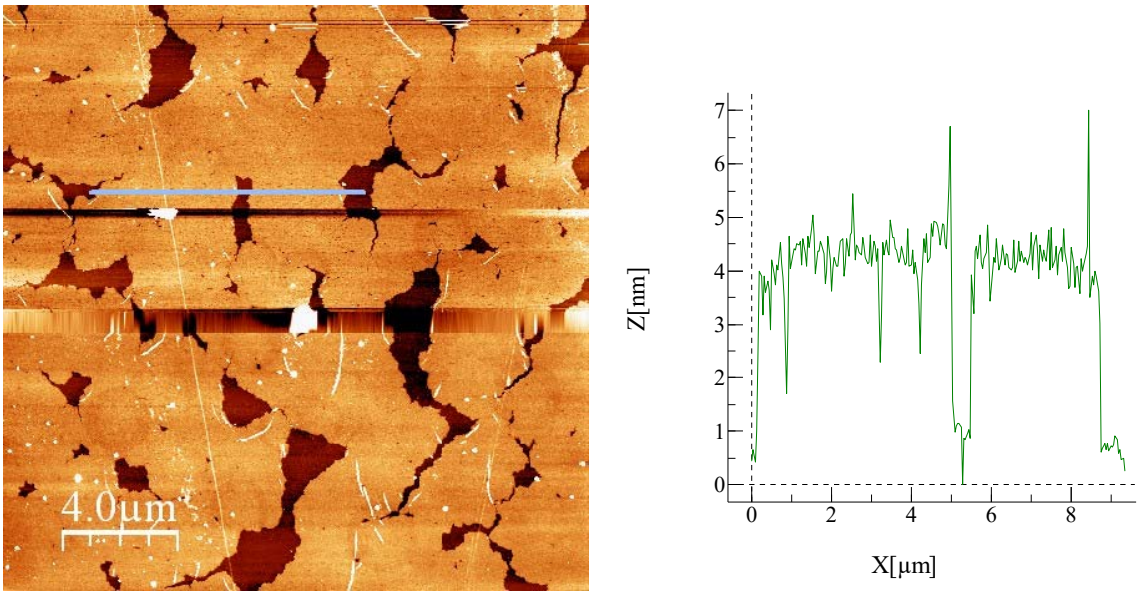
liquid/liquid or liquid/air interface

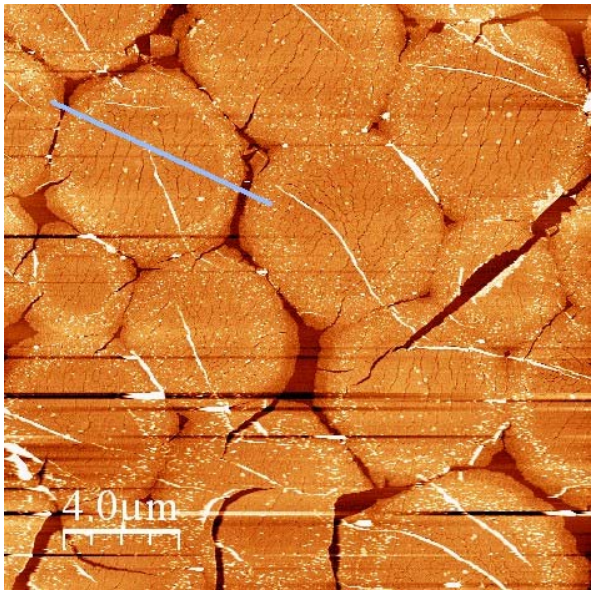


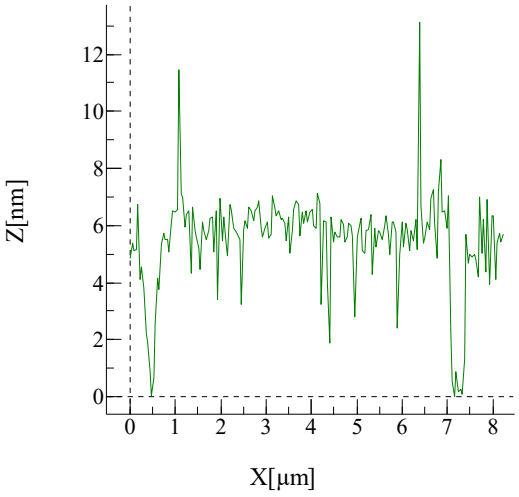
Transfer onto a substrate by Langmuir-Shaefer technique

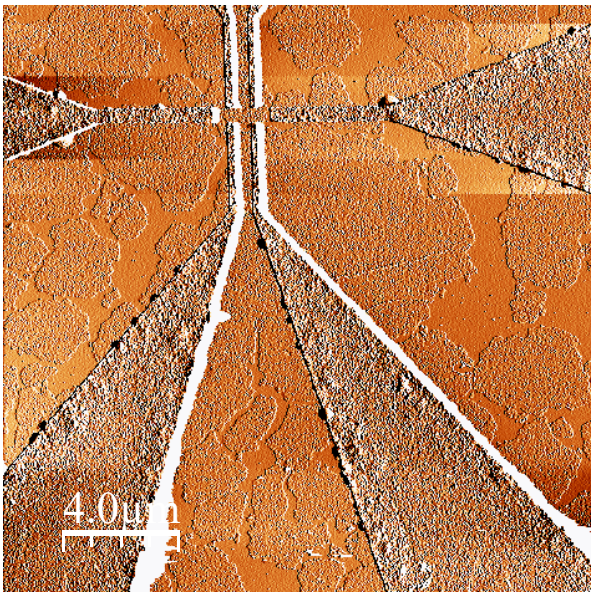
HOPG, Au, SiO_2

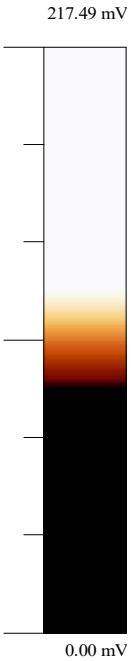
AFM imaging of the nanosheets





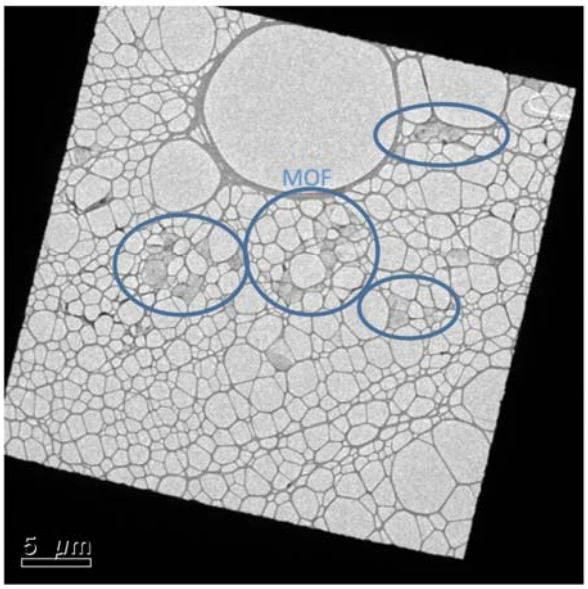






amplitude

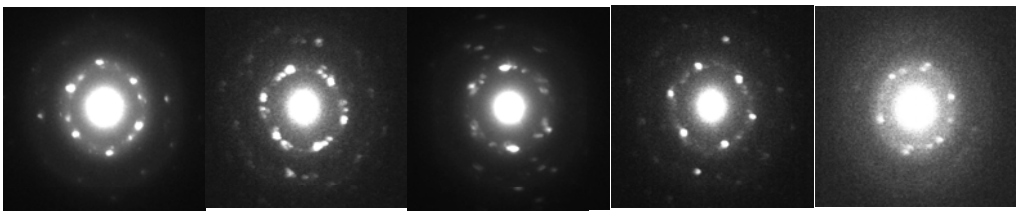
Observed at room temperature in CTEM mode.



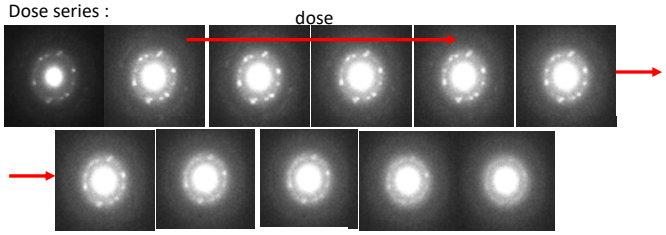
A. Gloter, LPS, Paris-Saclay

Chromatem STEM : Low temperature phase. MOF SMC525 (on lacey)

Some examples of diffraction. They are the first acquisition in a dose series.
Typical doses are 1 electrons / angstrom^2 @ LN2 temperature. This is more drastic condition than cryo-TEM…..



Dose series :

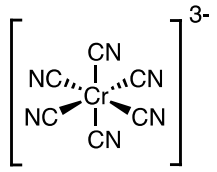


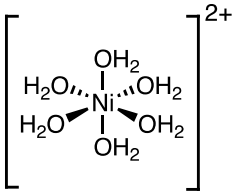
Dose rate of 1.2 electrons per angstrom^2 per acquisition.

The structure hardly survives 10 e-/A2

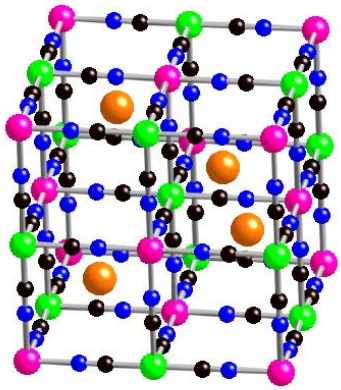
A. Gloter, LPS, Paris-Saclay

Design of Coordination Nanoparticles with Core-shell Architectures





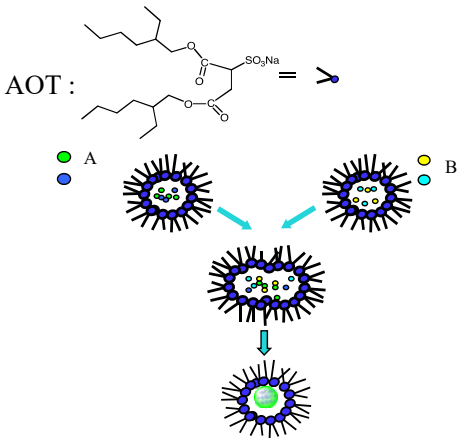
Face centered cubic structure



Cs^+ or Rb^+ in the tetrahedral sites

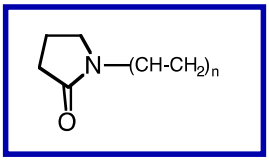
microemulsion

AOT :

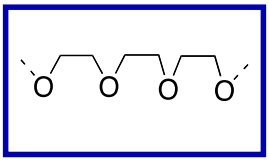


organic polymers

Polyvinylpyrrolidone



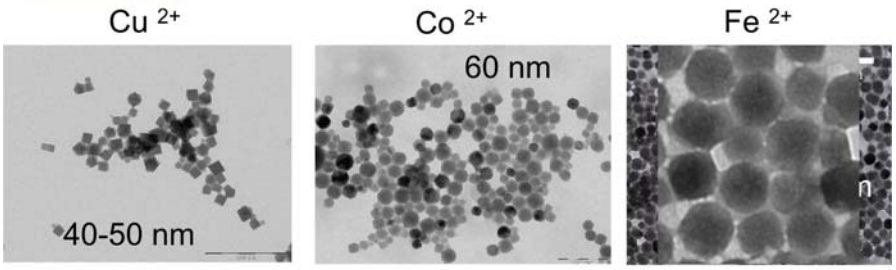
Polyethyleneglycol



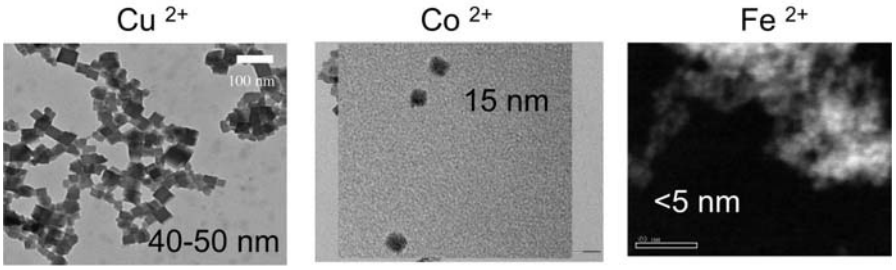
solvent = water
No stabilizing agents

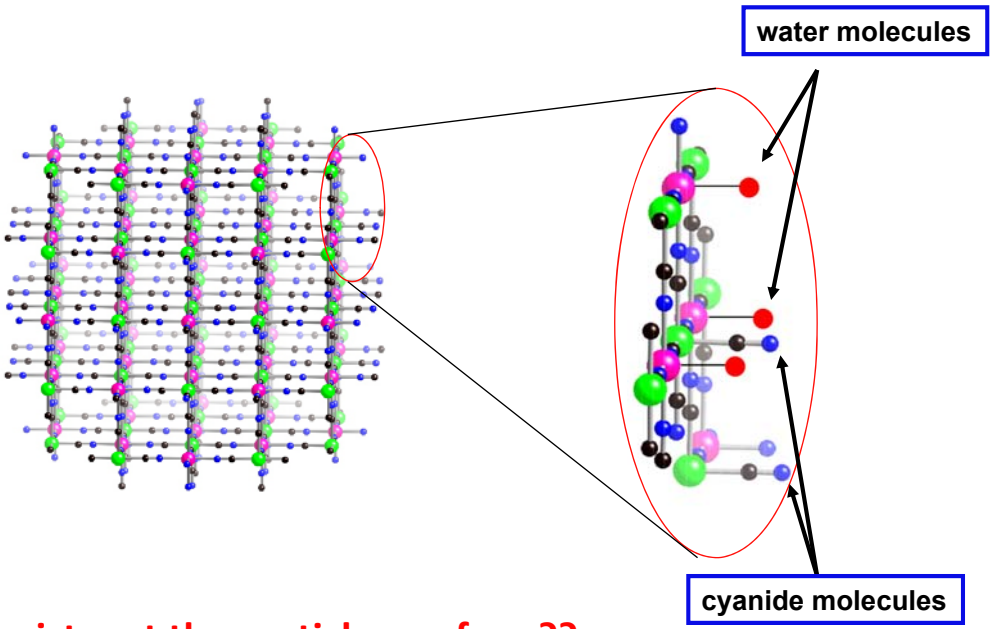
Cs^+	$Ni(H_2O)_6^{2+}$	$Cr(CN)_6^{3-}$	10 min	20 min	60 min
0	1	0,66	50 nm	300 nm	precipitate
0	1	1	10 nm	15 nm	15 nm
2	1	1	6 nm	6 nm	6 nm

$Cr(CN)_6^{3-}$

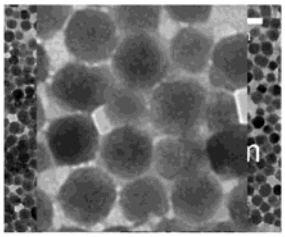


$Fe(CN)_6^{3-}$



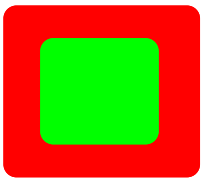


Chemistry at the particles surface ??

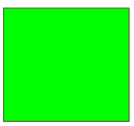


CsFeCr 40 nm particles

Growth of a CoCr PBA analog on a CsFeCr core ??



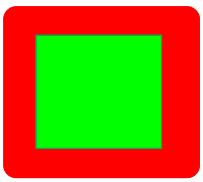
CsFeCr@CoCr



CsFeCr particules de 40 nm

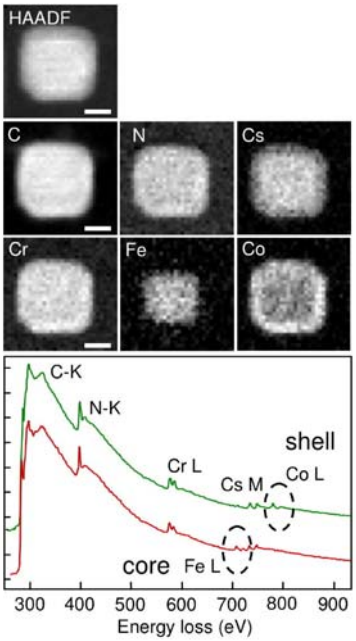
+ $Co(H_2O)_6$
+ $Cr(CN)_6$

eau →

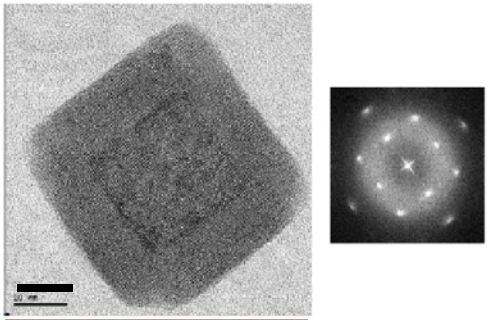


CsFeCr@CoCr

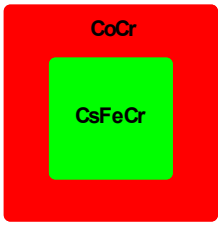
Elemental mapping

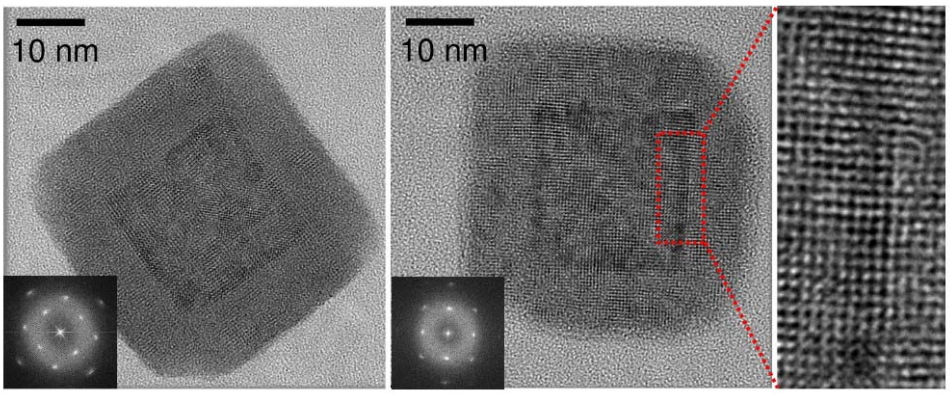


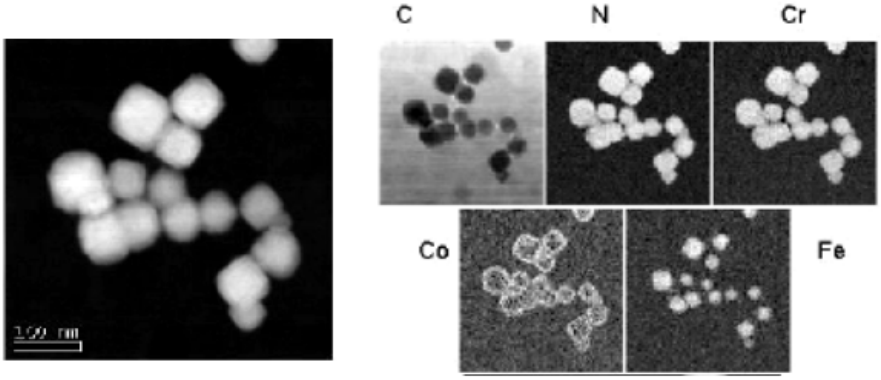
High resolution

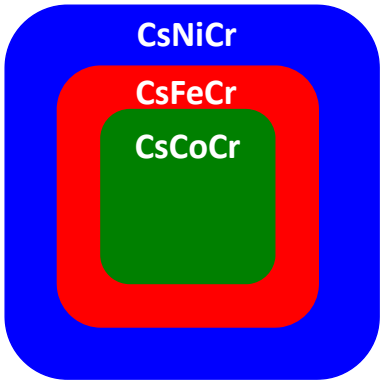


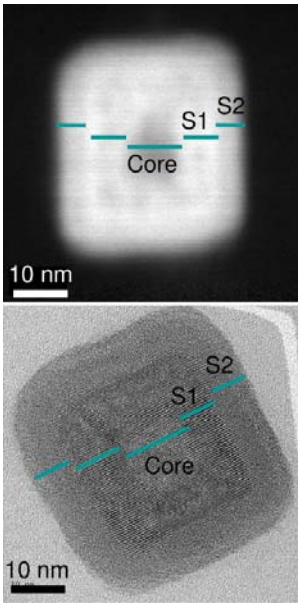
Scale bar 10 nm

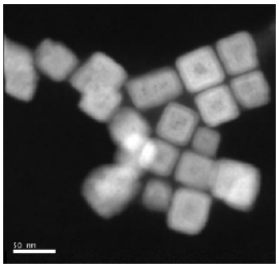


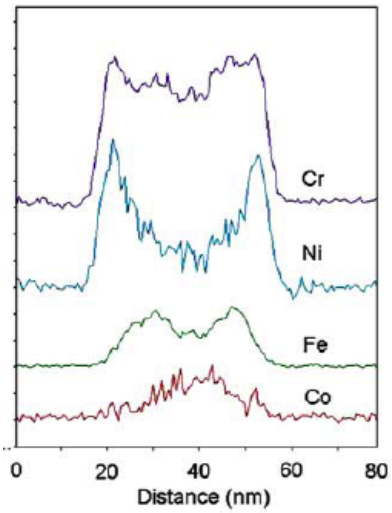



C
N
Cr
Co
Fe


CsNiCr
CsFeCr
CsCoCr

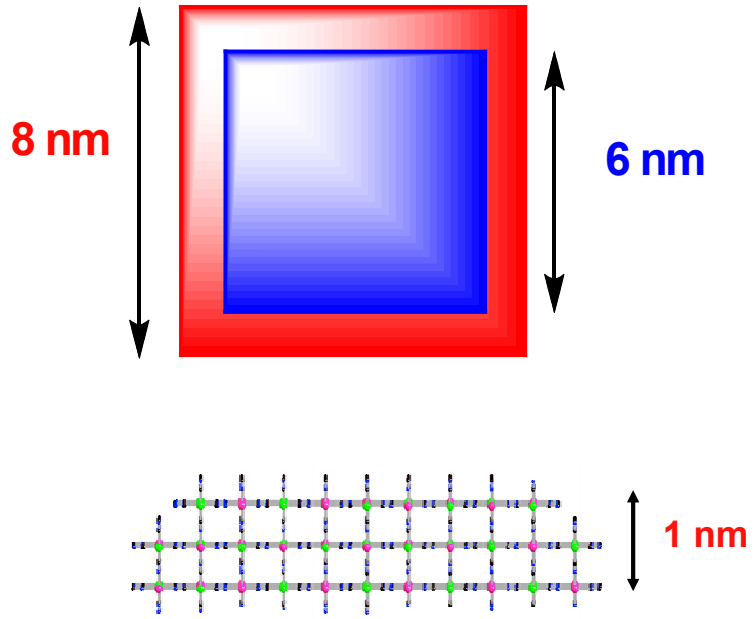




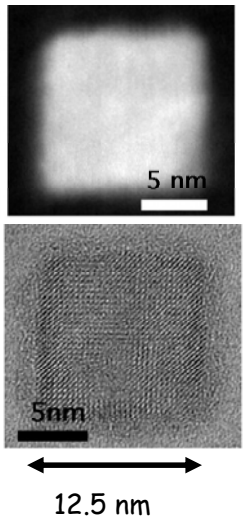


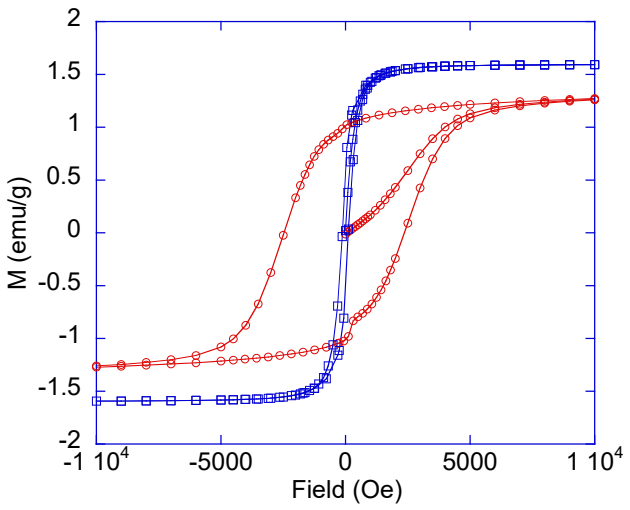
Design of Coordination Nanoparticles with Controlled Magnetic Behavior

Shell thickness control

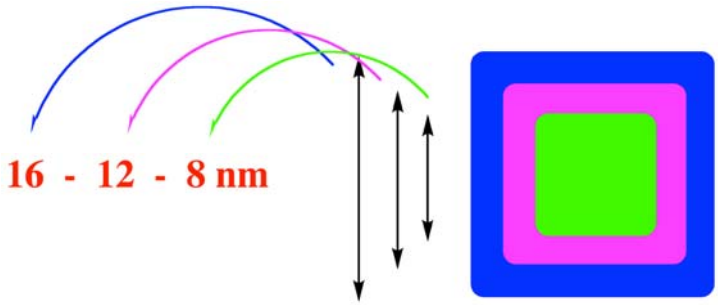


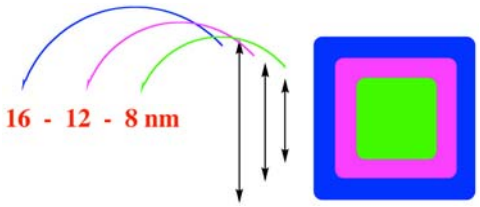
CsNiCr core 9.5 nm and CsCoCr shell of 1.5 nm

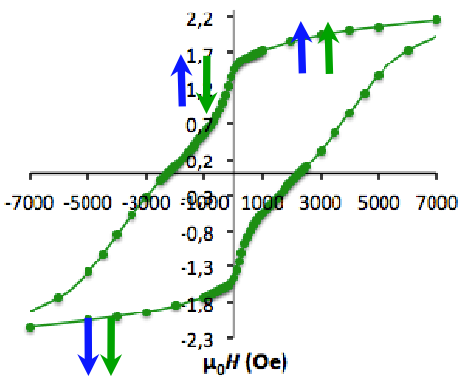


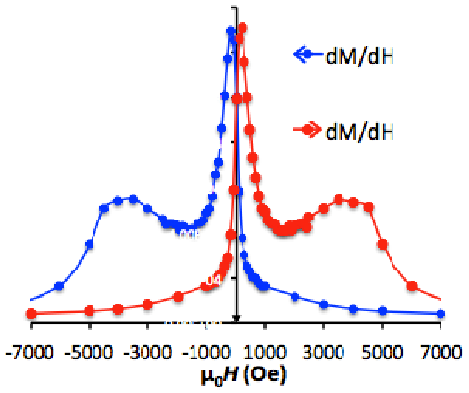


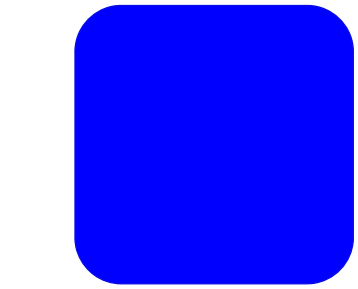
CsNiCr@CsNiCo^{III}@CsCo^{II}Cr

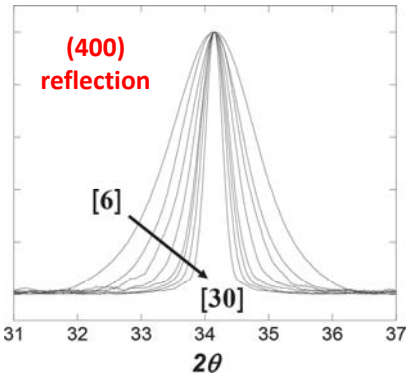


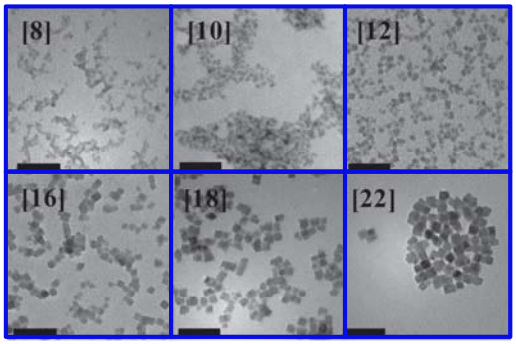


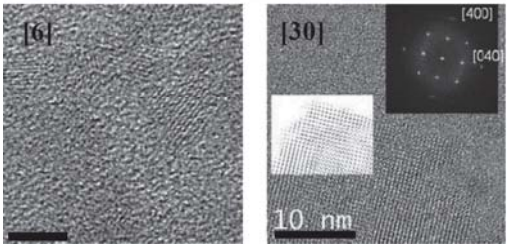


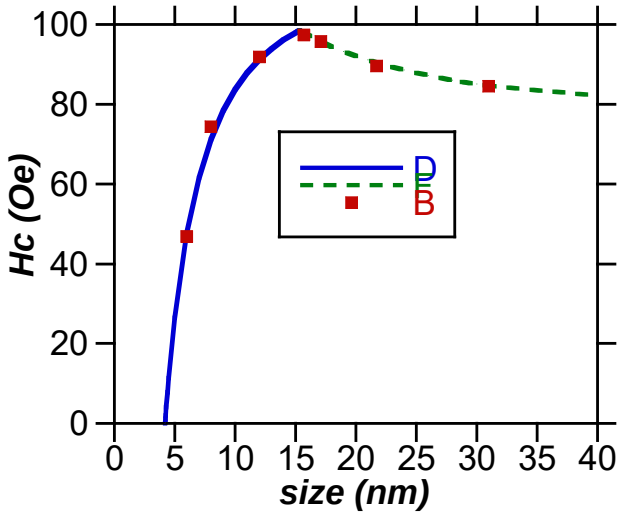












Single domain size = 14-15 nm

Blocking temperature around 23 K

Nanoparticles' preparation

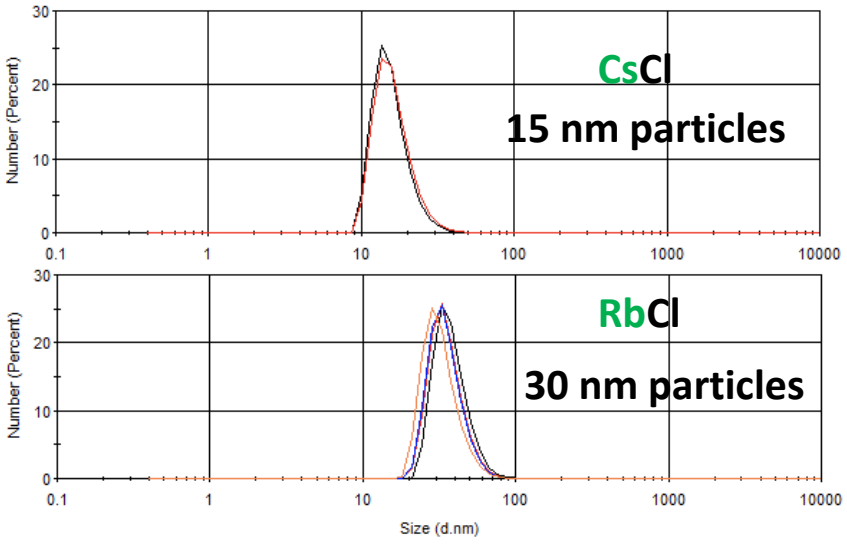
Fast addition

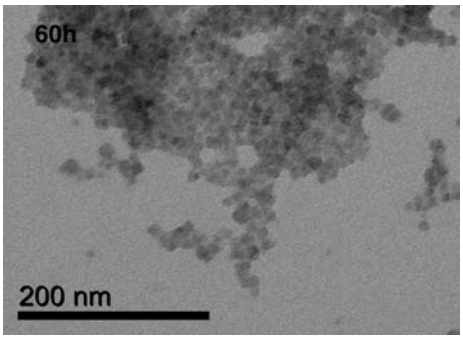
↓ Cs^{I} or Rb^{I}

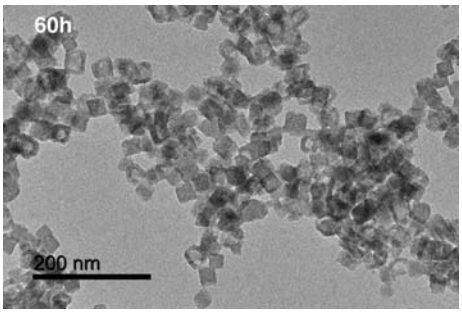
Small negatively charged particles
almost monodisperse

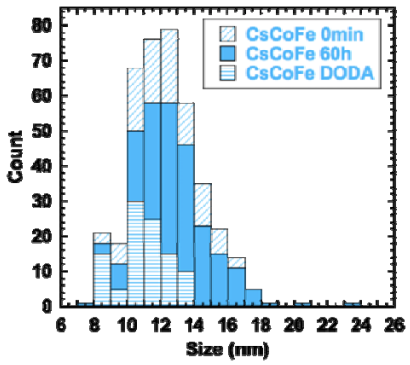
SIZE can be also tuned by the
precursors' concentration

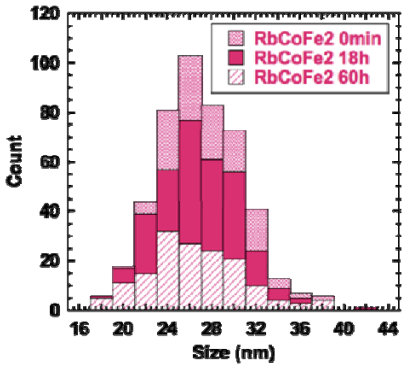
$$Co^{II}Cl_2 \bullet H_2O + K_3[Fe^{III}(CN)_6]^{3-} + ACl$$



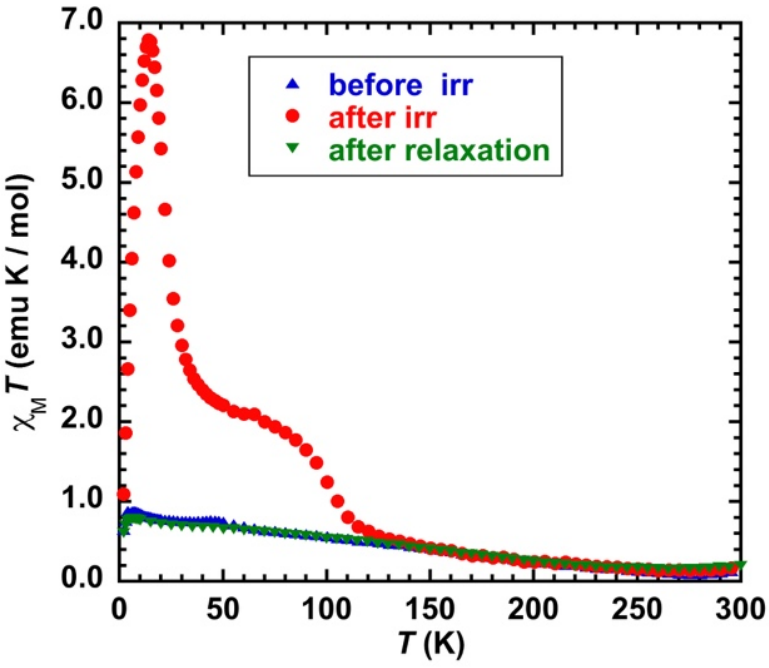






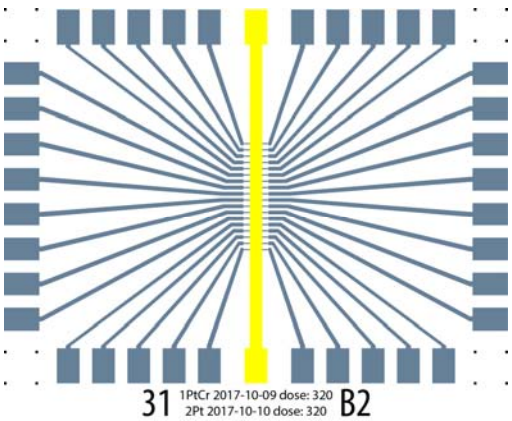


Photomganetic nanoparticles CsCoFe



Behaviour of a single particles
by
Transport studies

Single particle photo-induced transport properties



finger-like electrode lengths = 5 μ m

gaps width between fingers is around 13 nm

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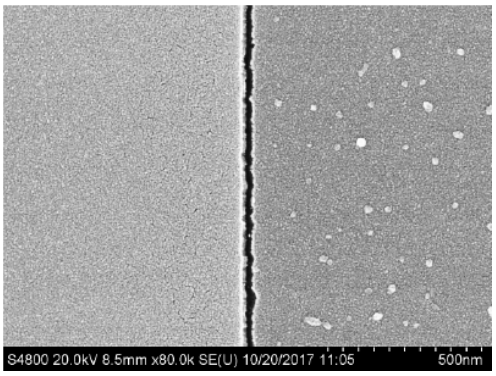
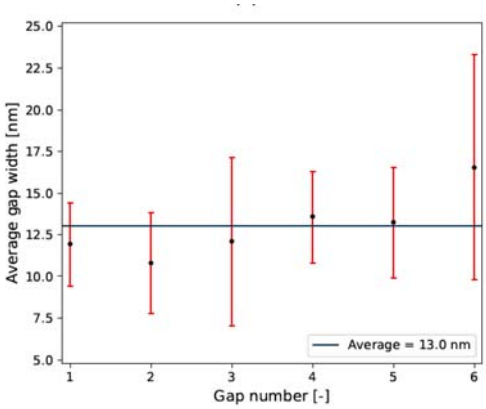
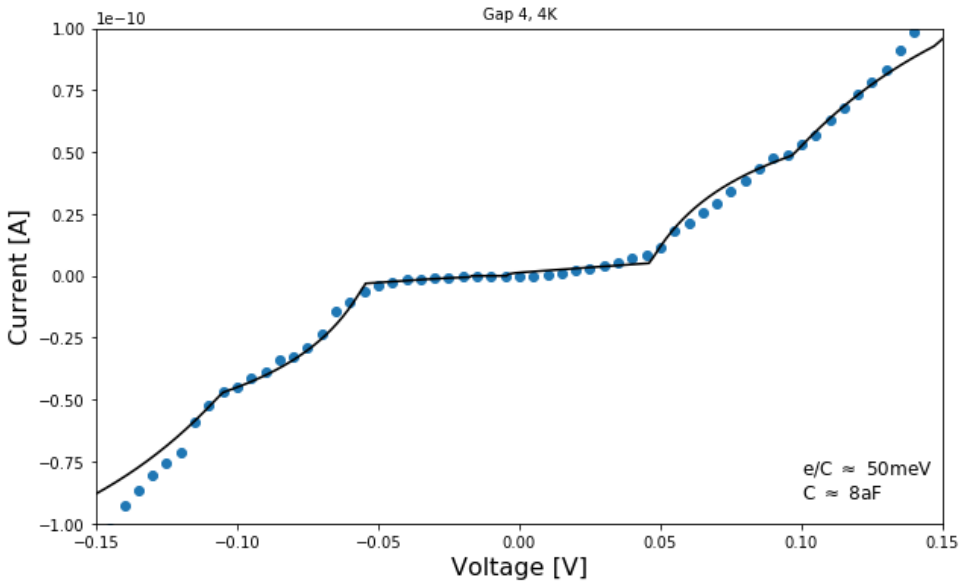
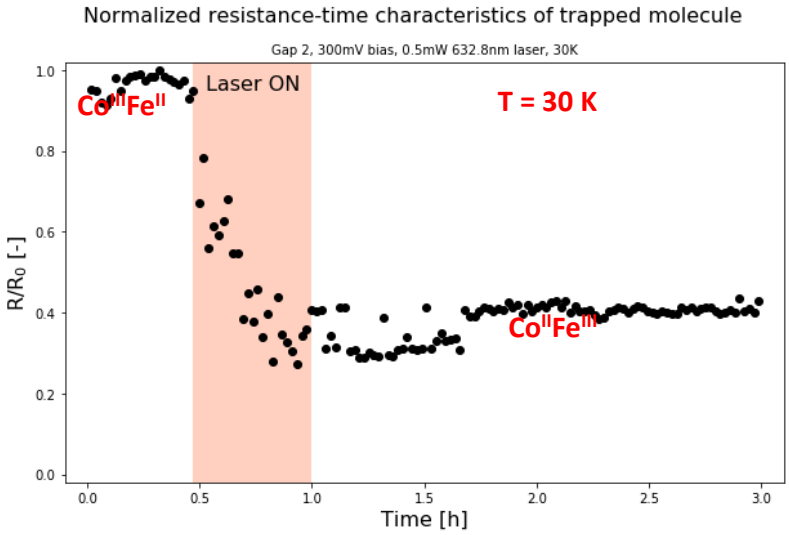

S4800 20.0kV 8.5mm x80.0k SE(U) 10/20/2017 11:05
500nm


Average gap width [nm]
Gap number [-]
Average = 13.0 nm


Gap 4, 4K
1e−10
Current [A]
Voltage [V]
e/C ≈ 50meV
C ≈ 8aF

CsCoFe 15 nm Single NanoParticle



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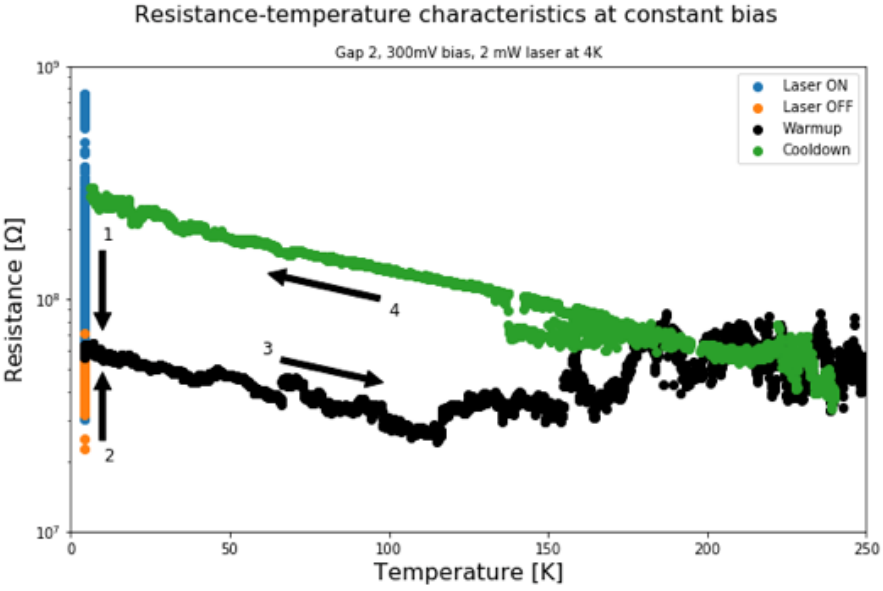

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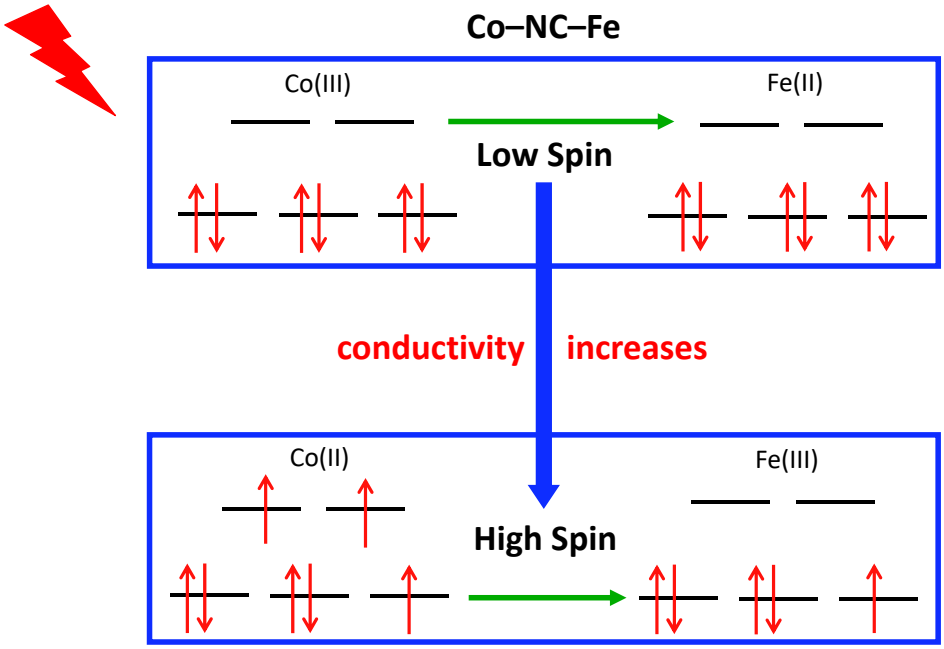
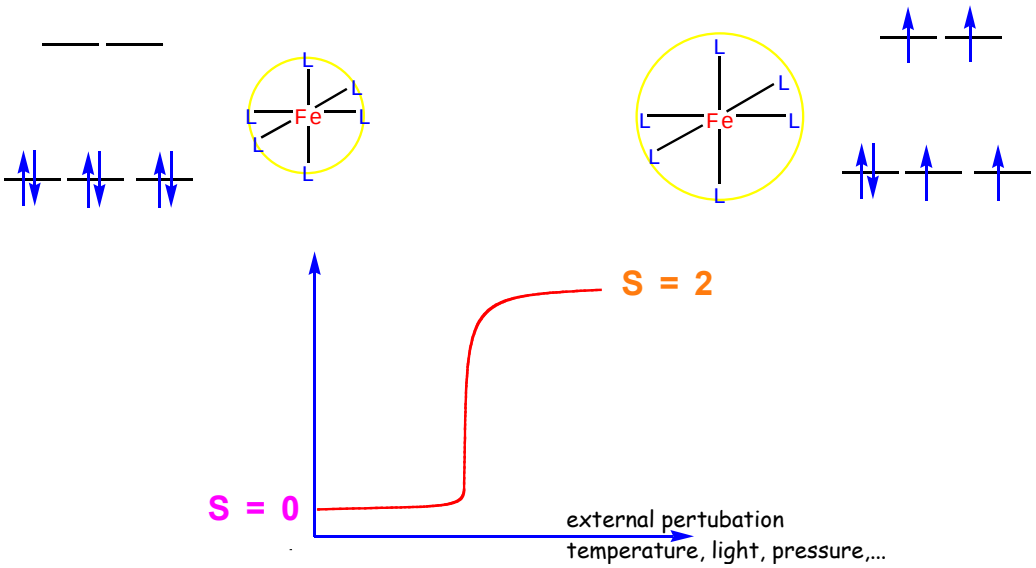
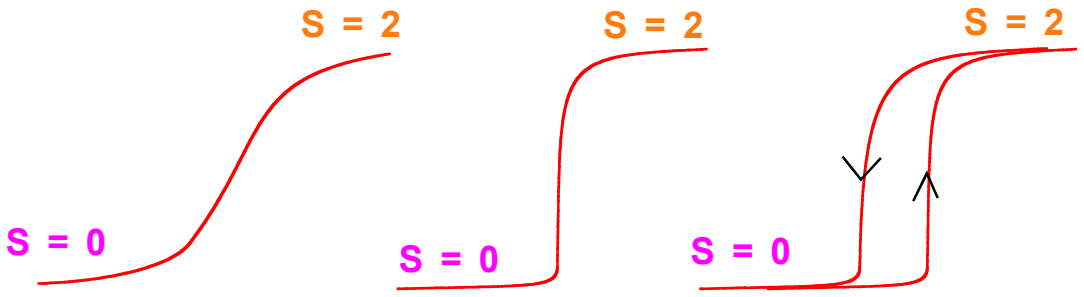


Spin Crossover (SCO) Nanoparticles





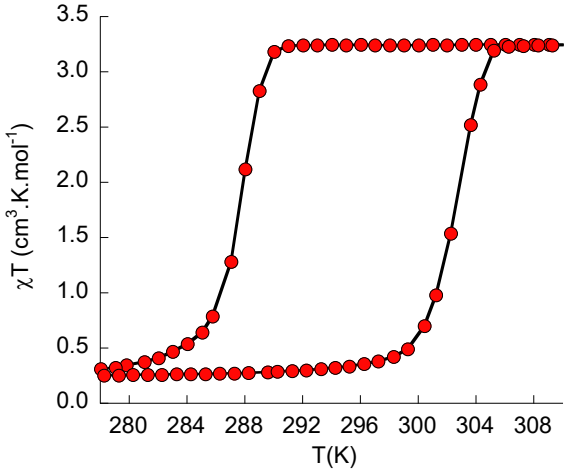
smooth conversion

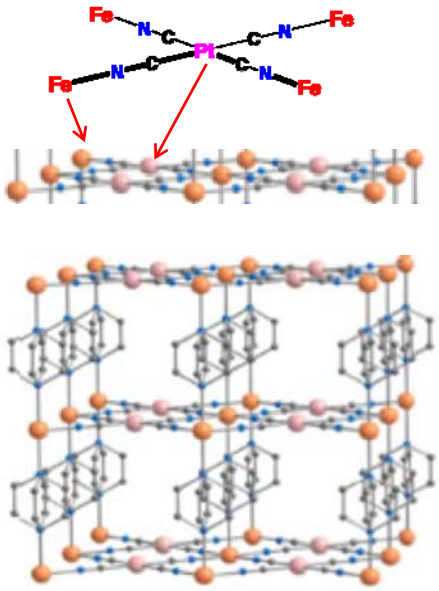
sharp transition

hysteresis loop and bistability

Only first order sharp transitions lead to hysteresis and bistability because of long range elastic interactions

$Fe(BF_4)_2$ + pyrazine + $K_2Pt(CN)_4$ ⟶ Fe(pyrazine)Pt(CN)$_4$



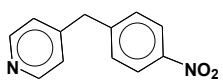


J. A. Real Inorg. Chem. 2001

Microemulsion of $Fe(BF_4)_2$ + pyrazine
+
Microemulsion of $K_2Pt(CN)_4$

↓

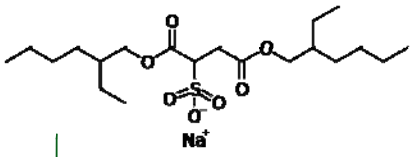
stable microemulsion
and
a change of color

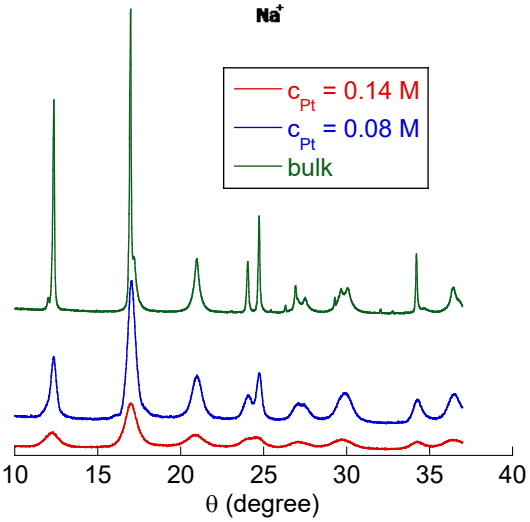


acetone ↓

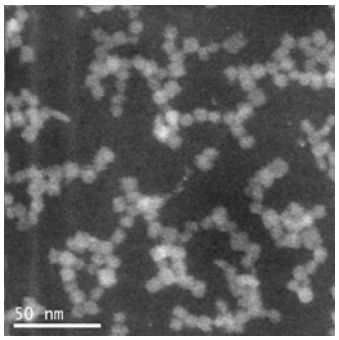
Orange powder

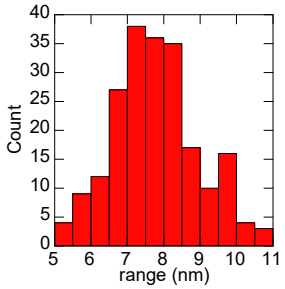
w = $[H_2O]/[AOT]$ = 10, c_{Pt} = 0.08, 0.14 M



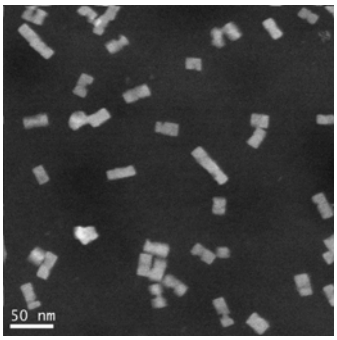


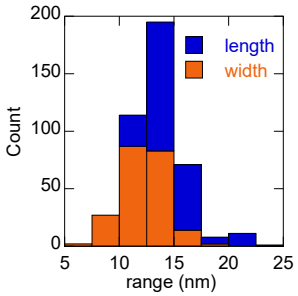
7.7x7.7 nm (σ = 1.1), c_{Pt} = 0.14M



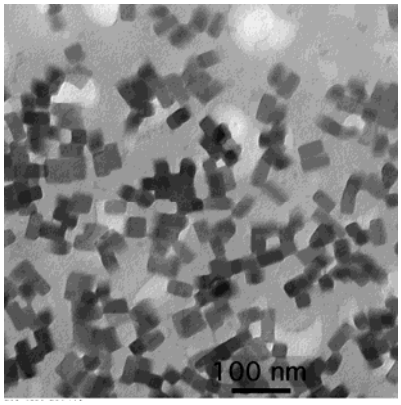


14.7x12.1 nm (σ = 2.1), c_{Pt} = 0.08M

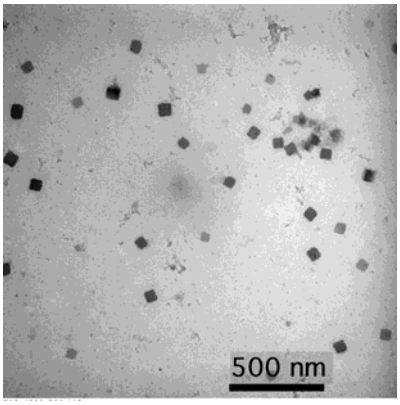


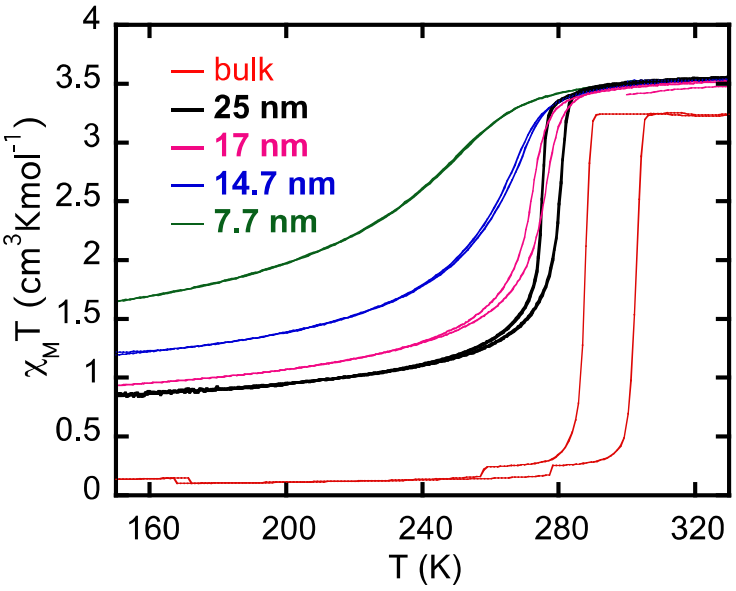


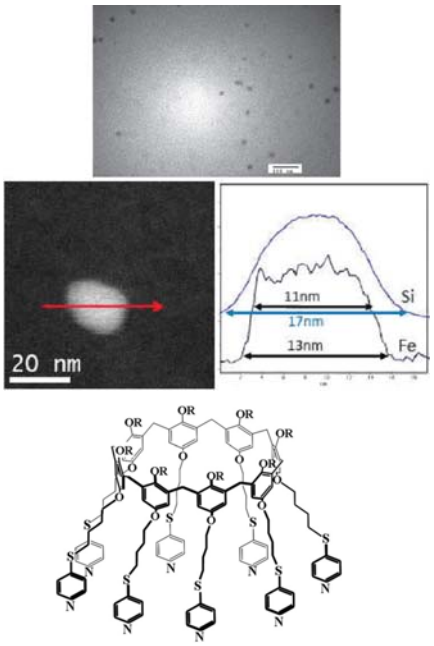
25x25 nm, c_{Pt} = 0.06 M

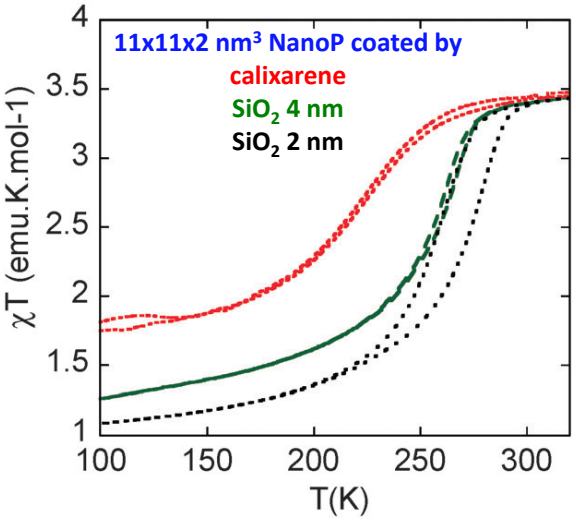


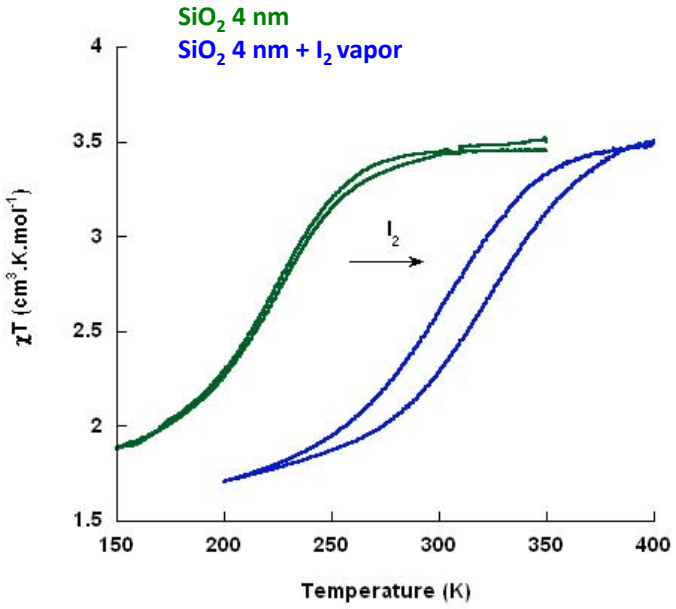
55x55 nm, c_{Pt} = 0.04 M



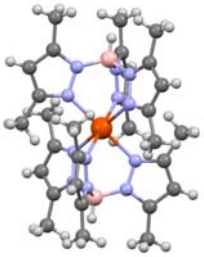

bulk
25 nm
17 nm
14.7 nm
7.7 nm
$\chi_M T$ (cm^3Kmol^{-1})
T (K)


20 nm
11nm
17nm
13nm
Si
Fe


11x11x2 nm³ NanoP coated by
calixarene
SiO_2 4 nm
SiO_2 2 nm
χT (emu.K.mol-1)
T(K)

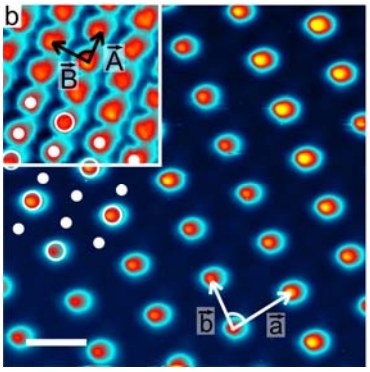


From SCO Nanoparticles to 2D organized SCO molecules

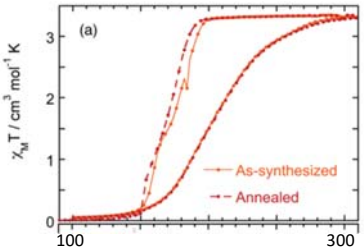


UHV sublimation

on Au(111)



STM at 4 K

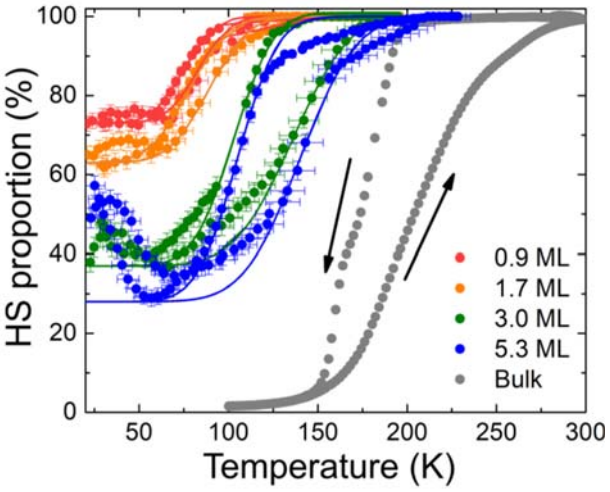


T_c = 180 K

Nat. Comm., **2016**, 12212

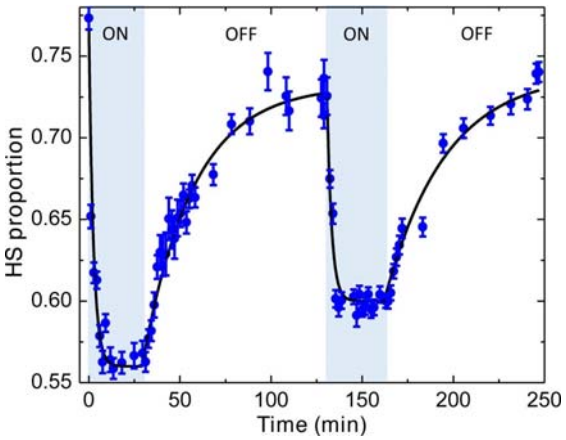
X-ray Absorption Spectroscopy

J. Phys. Chem. Lett. **2021**, 12, 6152−6158



J. Phys. Chem. Lett. **2023**, 14, 1949−1954

SCO on Cu(111)



Angew. Chem. **2020**, 132, 13443 – 13448

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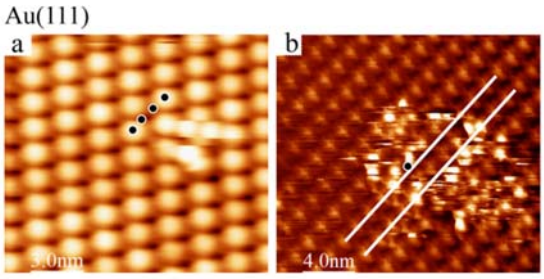
Sublimation on Cu(111)

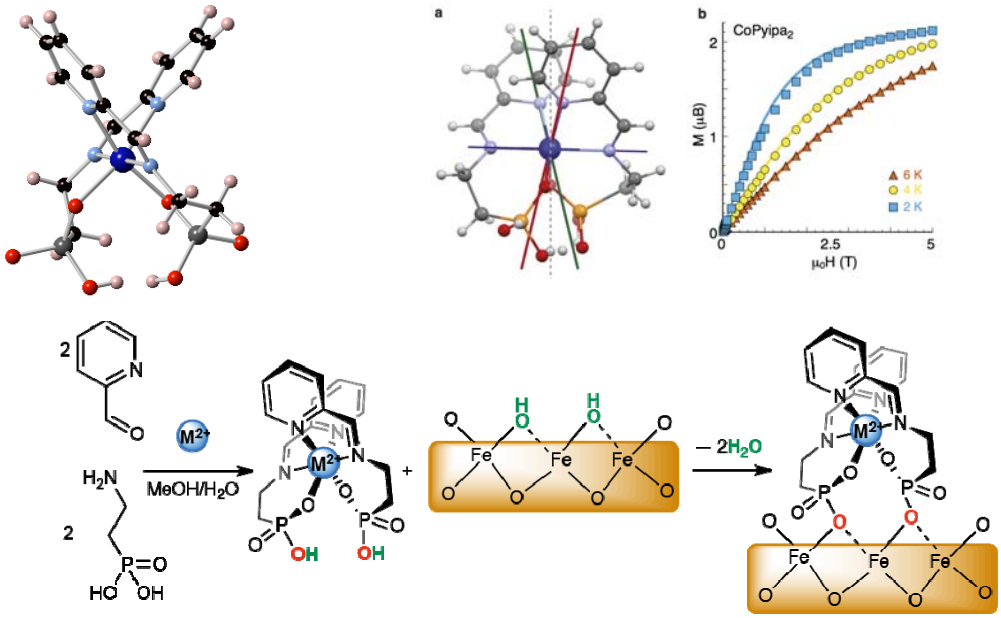
Voltage pulse induced SCO



J. Phys. Chem. Lett. **2021**, 12, 11029−11034

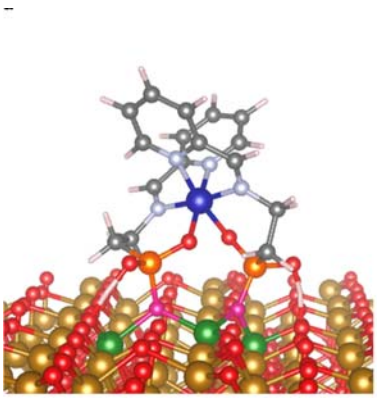
Coll. A. Bellec, V. Repain Univ Paris-Cité

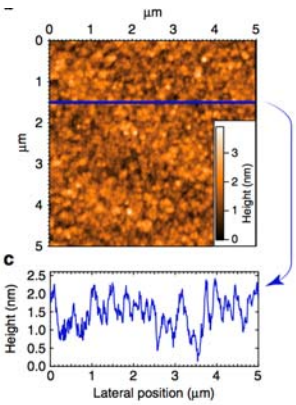
Single layer of magnetic molecules on ferrimagnetic Fe_3O_4

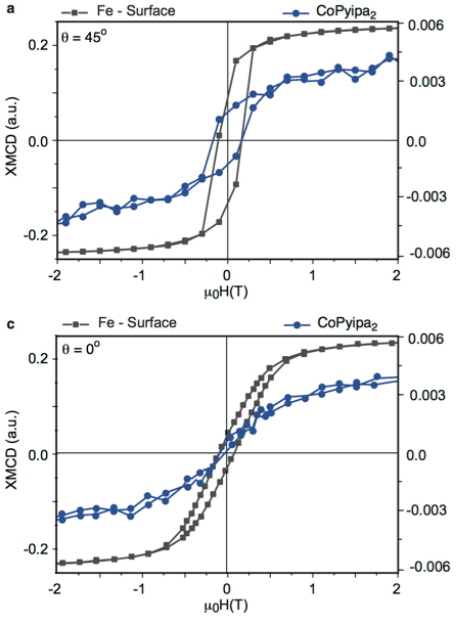


Nat. Comm. 2016, 13646 with V. Campbell

XMCD@DEIMOS, Soleil







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Thank You