Bistability in Molecular Materials: From Spin-State Switching to Controlling Molecular Spin Qubits

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REU Photochemistry Café
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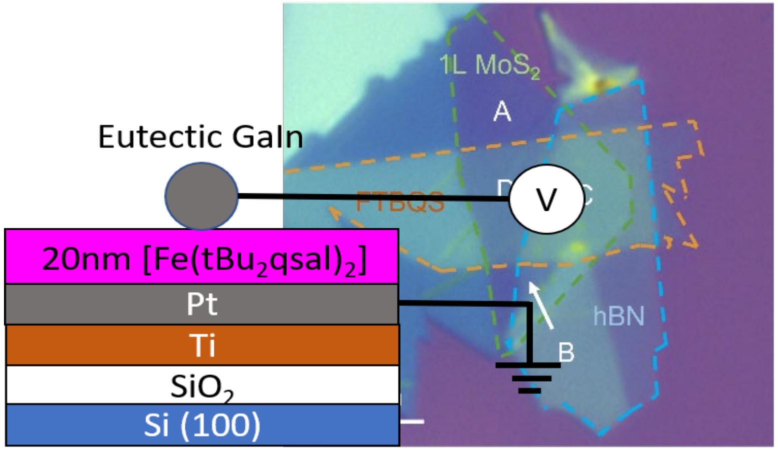
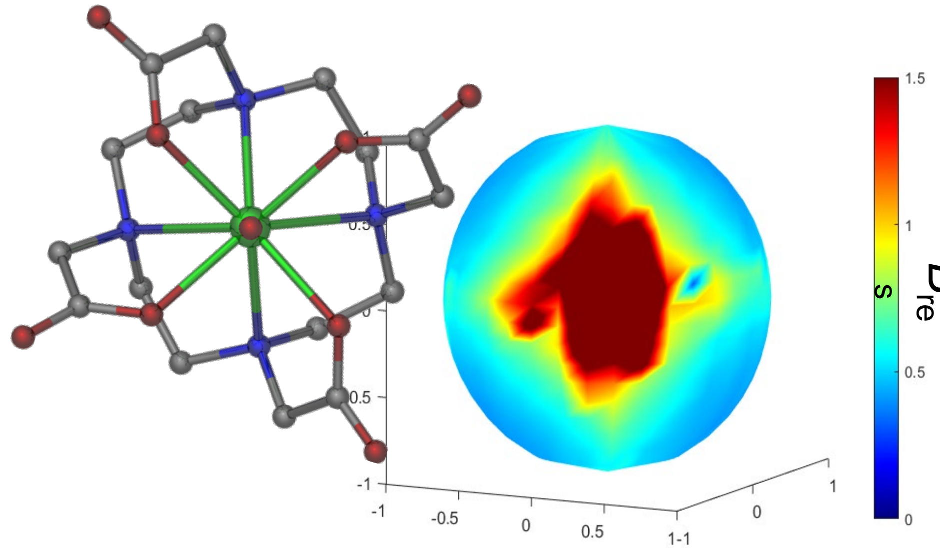
Inorganic Materials in the Shatruk Group

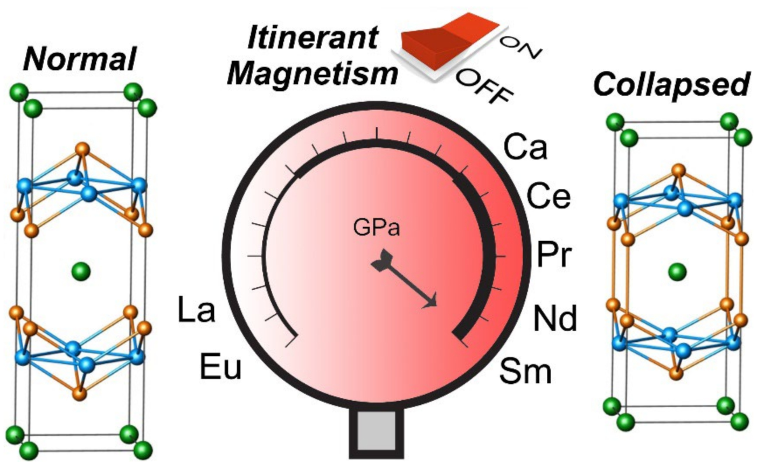
- **Spin-State Switching & Hybrid 2D Materials**



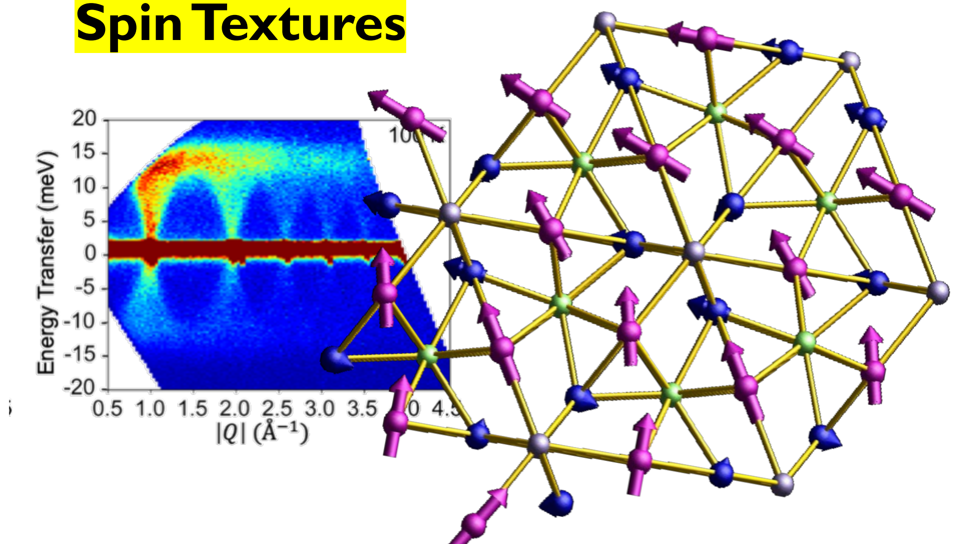
- **Molecular Spin Qubits**



- **Itinerant Magnetism & Magnetic Refrigeration**



- **Unconventional Spin Textures**



Motivation for Research

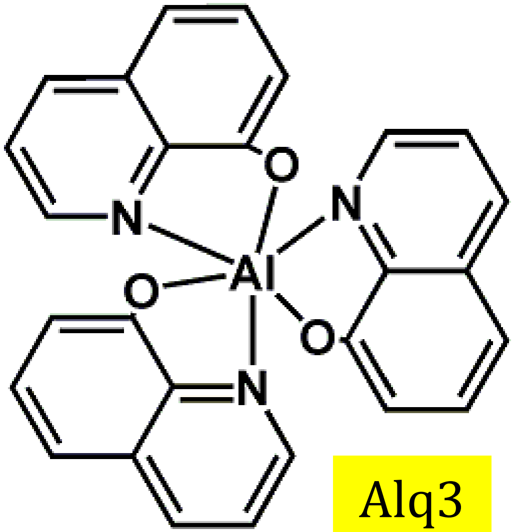
- Electricity is a great thing, but…
  - electrical connections unavoidably add weight and mechanical constraints to the device architecture
  - wires corrode, requiring regular maintenance and/or replacement

- Light as an alternative:
  - fibers don't rust
  - the signal is transmitted with the speed of light
  - lower maintenance costs
  - opto-mechanical actuation
  - optical write/read-out

State of the Art

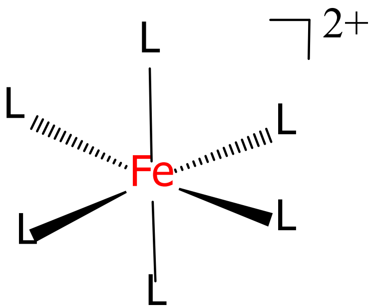
- Extended-structure materials
  - doped semiconductors (Si, GaP, GaAs, etc.)
  - polymers (CD drives)

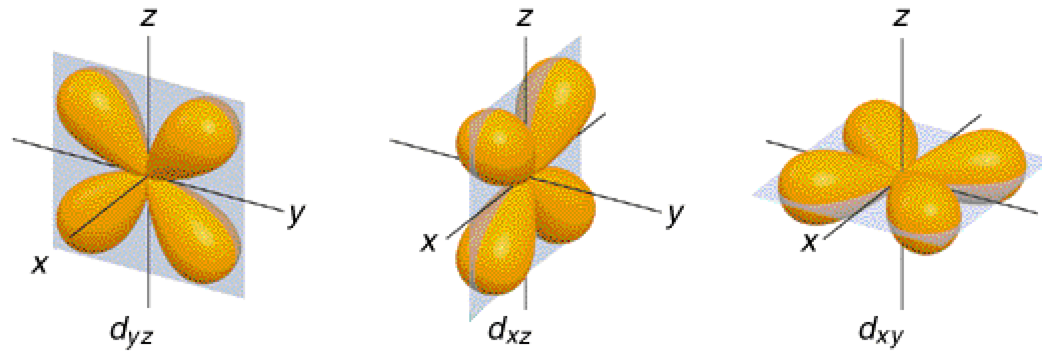
- Molecular materials:
  - much higher storage density
  - light weight
  - high synthetic tunability
  - precise control over the photophysical properties



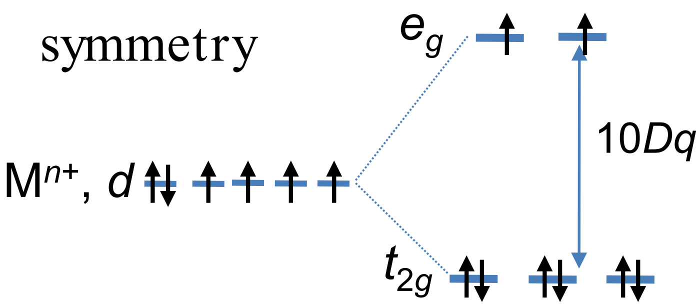
Alq3

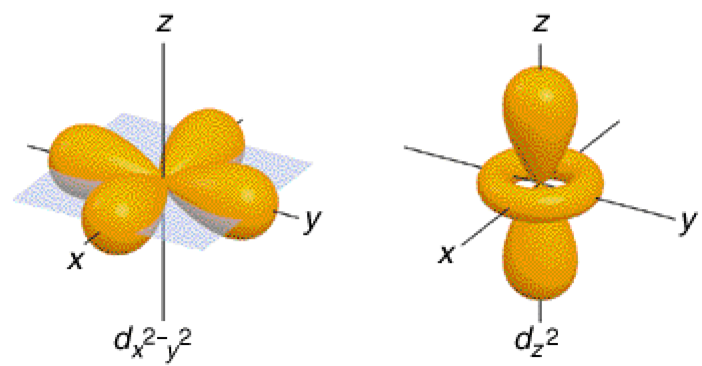
Splitting of d-Orbitals by Ligand Field





Octahedral symmetry

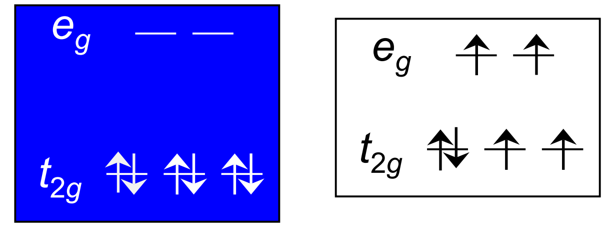




Spectrochemical series of ligand-field strength:

$I^- < Br^- < Cl^- < SCN^- < NO_3^- < F^- < OH^- < H_2O <$
$NCS^- < py < NH_3 < en < NO_2^- < PPh_3 < CN^- < CO$

I. Spin Crossover (SCO)



LS, $S = 0$ HS, $S = 2$

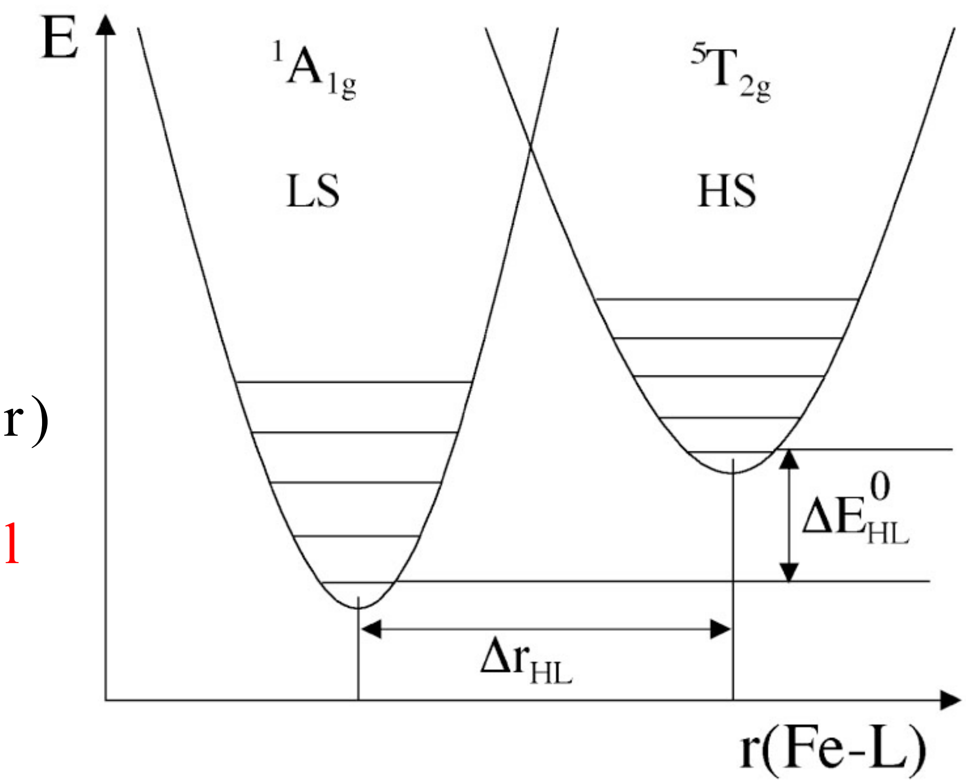
Entropy driven transition

Observed for d^4, d^5, d^6, d^7 ions

Triggered by changes in temperature, pressure, or photoexcitation

Dramatic changes in:

- magnetic moment
- M-L bond lengths
- absorption spectrum (color)

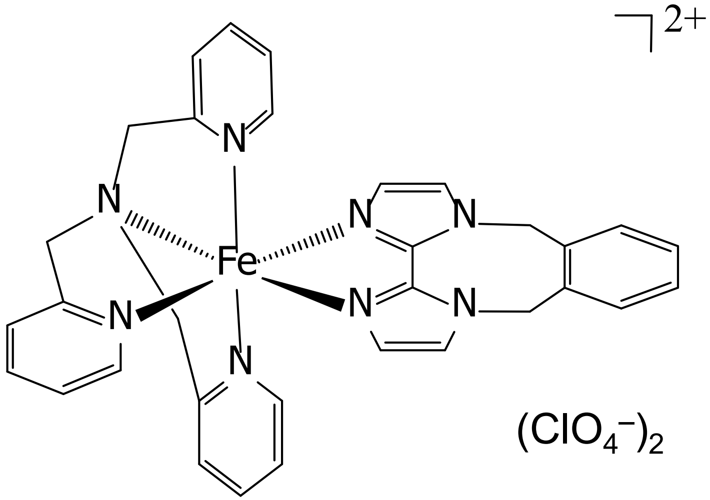


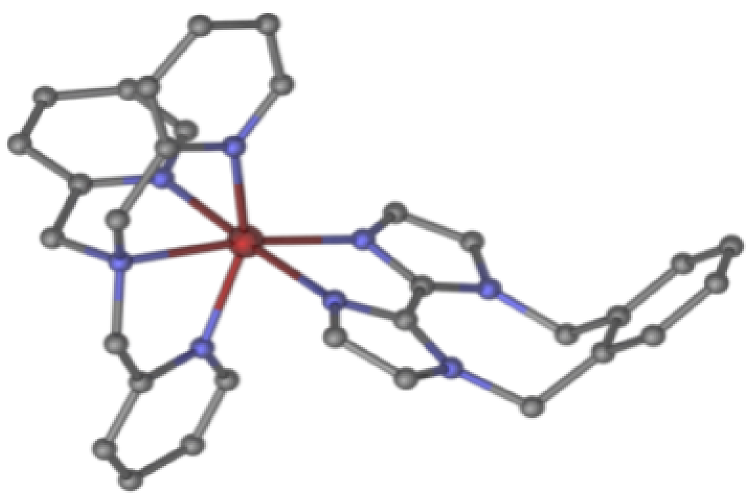
Can we leverage the structural and optical changes that accompany SCO to create multifunctional materials?

Hauser, A. *Top. Curr. Chem.* 2004, 233, 49-58

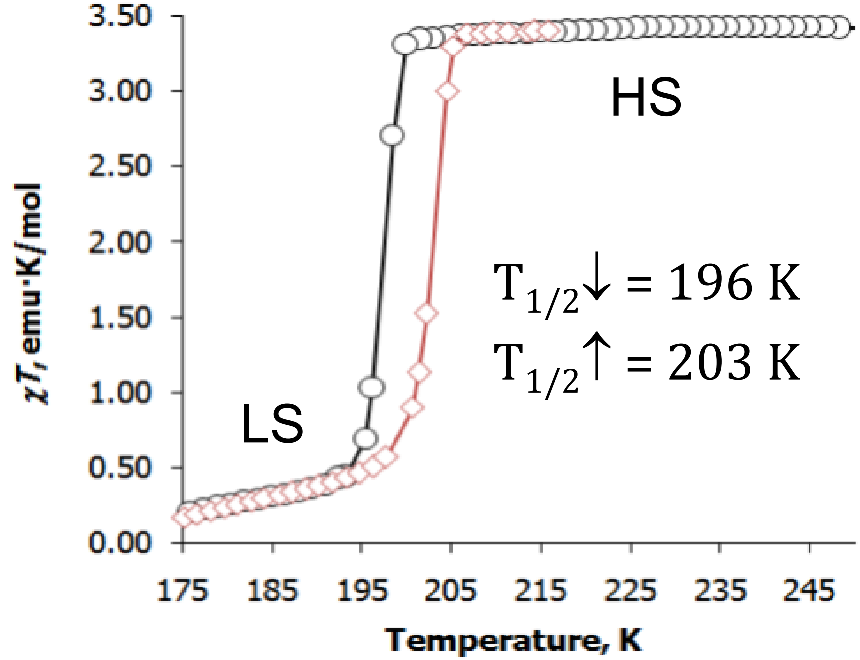
Shatruk, M.; Phan, H.; et al. *Coord. Chem. Rev.* 2015, *289-290*, 62-73

Example of Fe(II) SCO Complex





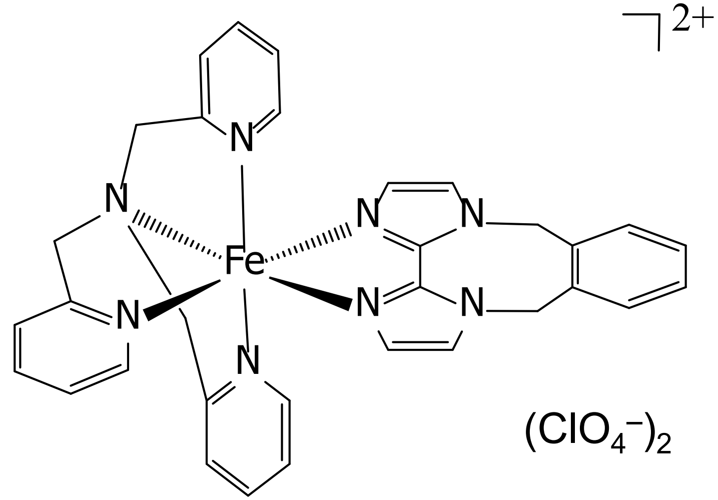
SCO with hysteresis (ΔT ~ 7 K)



d(Fe-N)$_{av}$, Å	
123 K (LS)	210 K (HS)
2.002(4)	2.184(4)

LS State Bleaching

[Fe(tpma)(xbim)]$(ClO_4)_2$



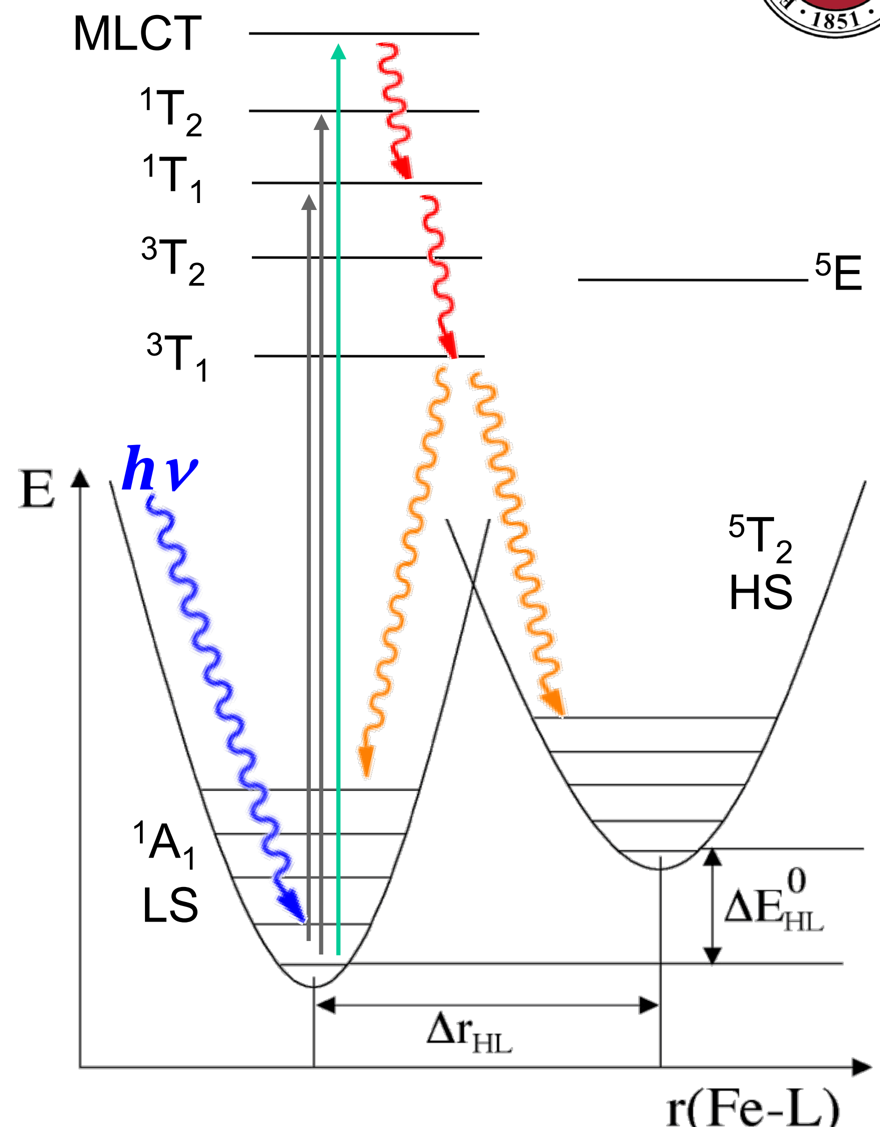
The abrupt change in color due to drastically different optical properties of the HS and LS states

Photomagnetism (LIESST)

Irradiation into characteristic absorption bands of the LS species results in a light-induced population of the HS state

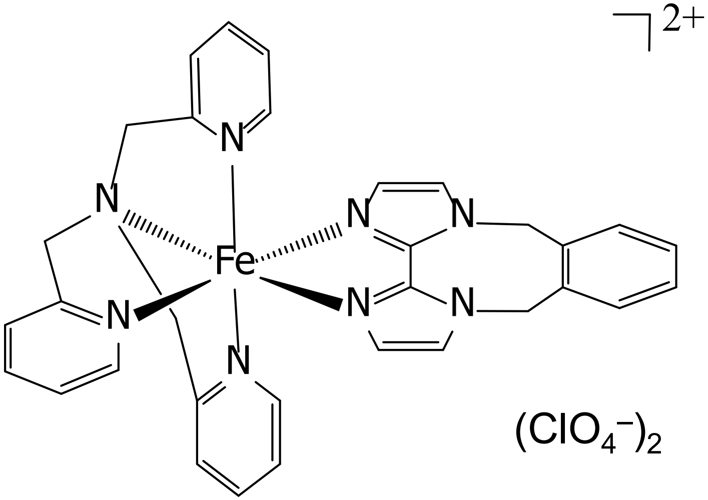
Light-Induced Excited Spin-State Trapping (LIESST)

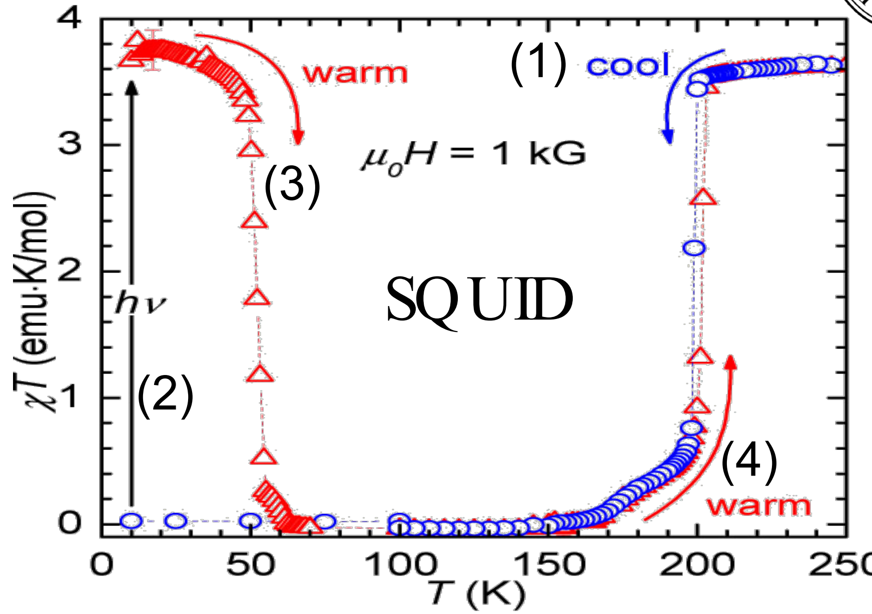
At sufficiently low temperature, the HS state will be trapped until it can acquire enough energy to undergo thermally activated relaxation to the LS state

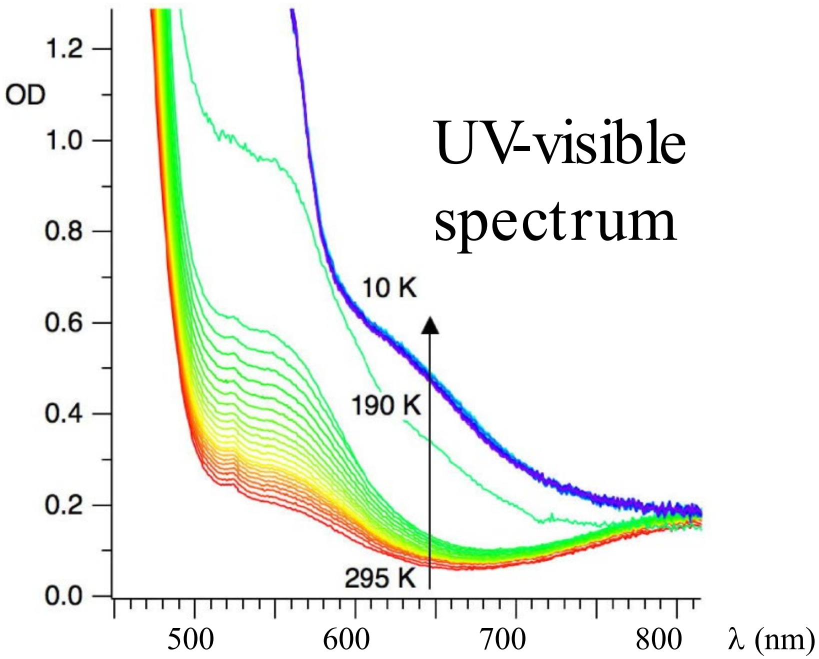


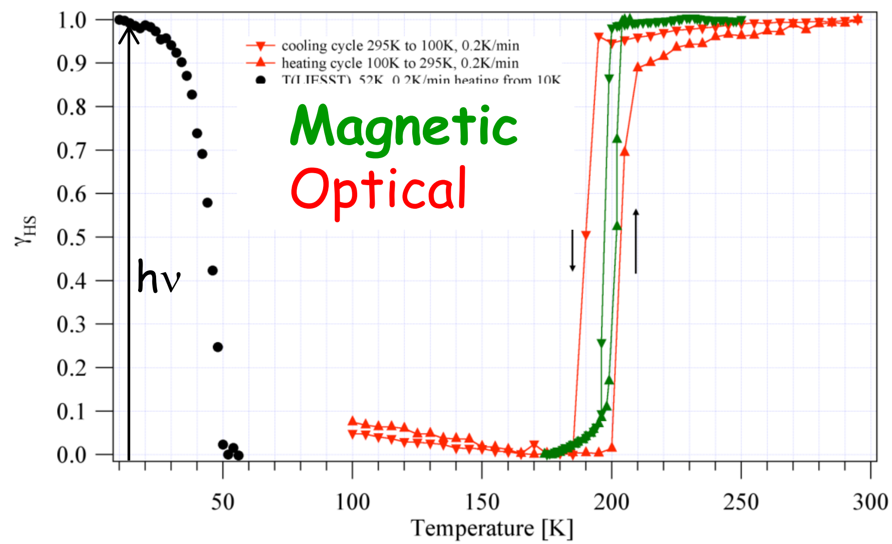
Electronic transitions of Fe(II) SCO complexes

LIESST in [Fe(tpma)(xbim)]$(ClO_4)_2$



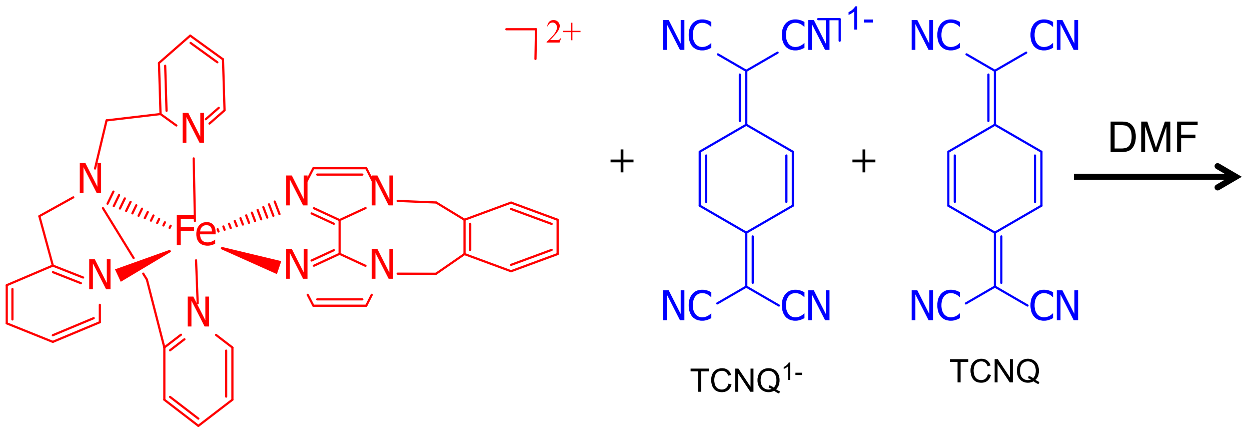




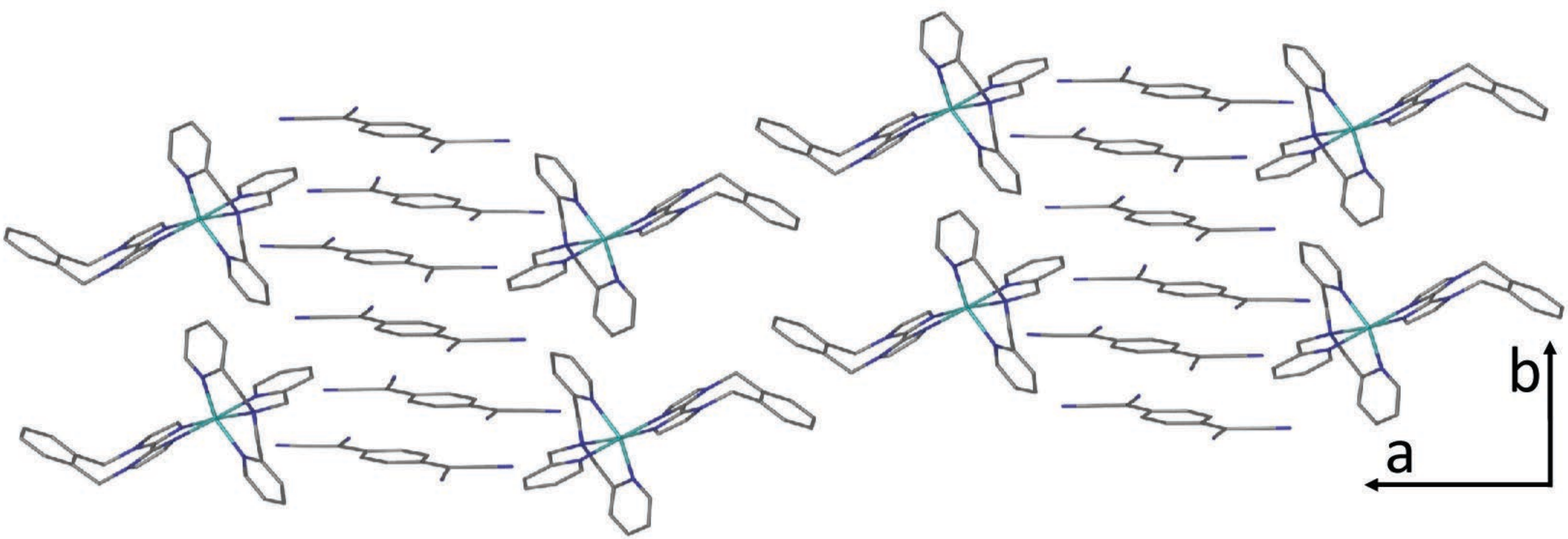


Phan, H.; Chakraborty, P.; Calm, Y.; Chen, M.; Kovnir, K.; Keniley, L. K.; Hoyt, J. M.; Knowles, E. S.; Besnard, C.; Meisel, M.; Hauser, A.; Achim, C.; Shatruk, M. *Chem. Eur. J.* 2012, *18*, 15805

Combining SCO and Conductivity

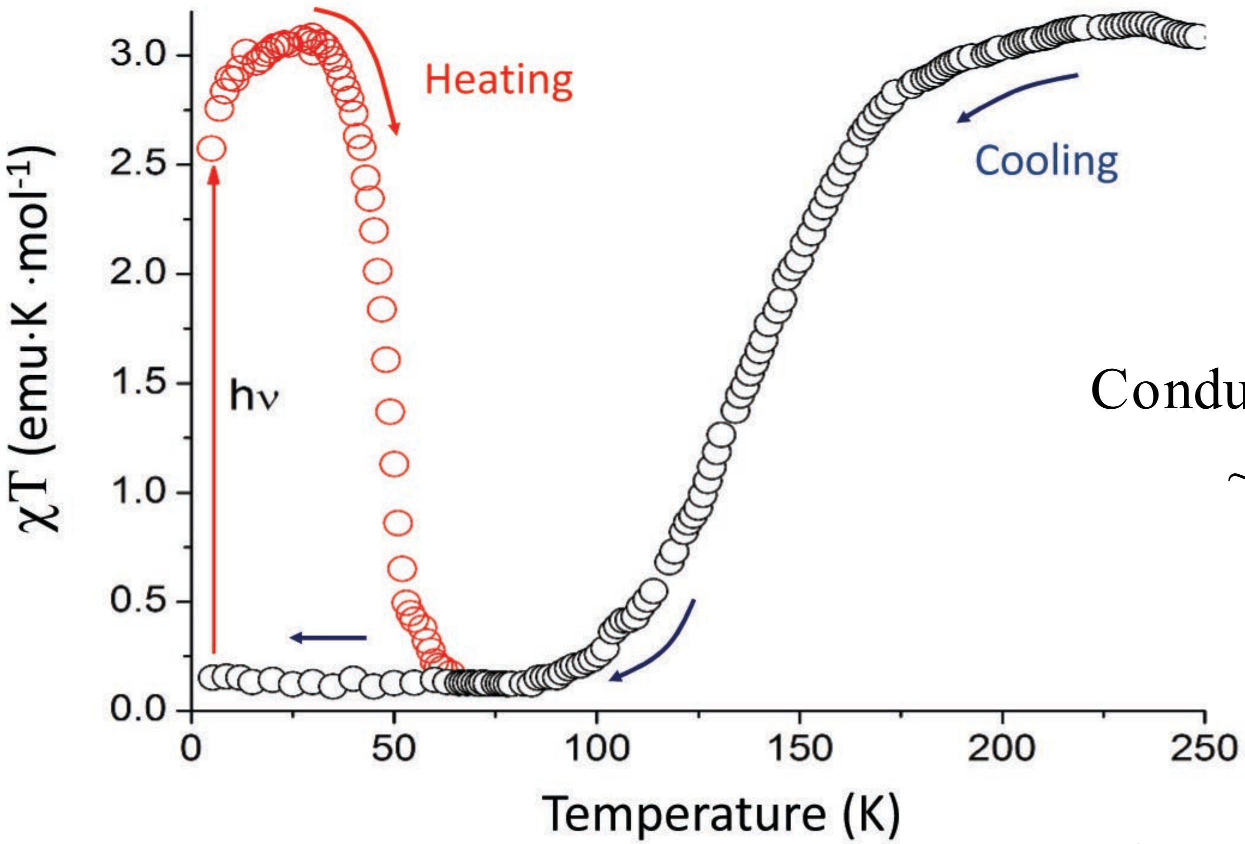


$[Fe^{II}(TPMA)(XBIM)]$-$(TCNQ)_{1.5}(ClO_4)\cdot DMF$



Phan, H.; Benjamin, S. M.; Steven, E.; Brooks, J. S.; Shatruk, M. *Angew. Chem.* 2015, *54*, 823-827

SCO, LIESST, and Conductivity



Conductivity at 300 K
~ 0.2 S/cm

For reference:

Semiconductors: 10^{-6} – 10^{1} S/cm

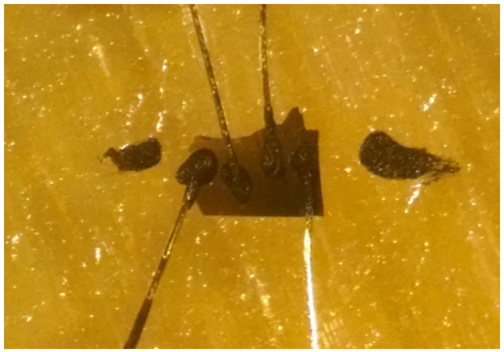
"Bad" metals: 10^{1} – 10^{3} S/cm

Phan, H.; Benjamin, S. M.; Steven, E.; Brooks, J. S.; Shatruk, M. *Angew. Chem. Int. Ed.* 2015, *54*, 823-827

Conductivity Measurements

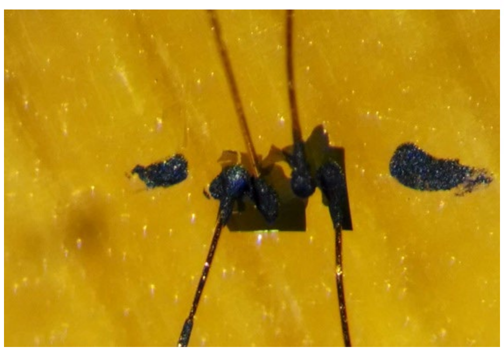
Tiny, brittle, and semi-transparent crystals

12 µm gold wire

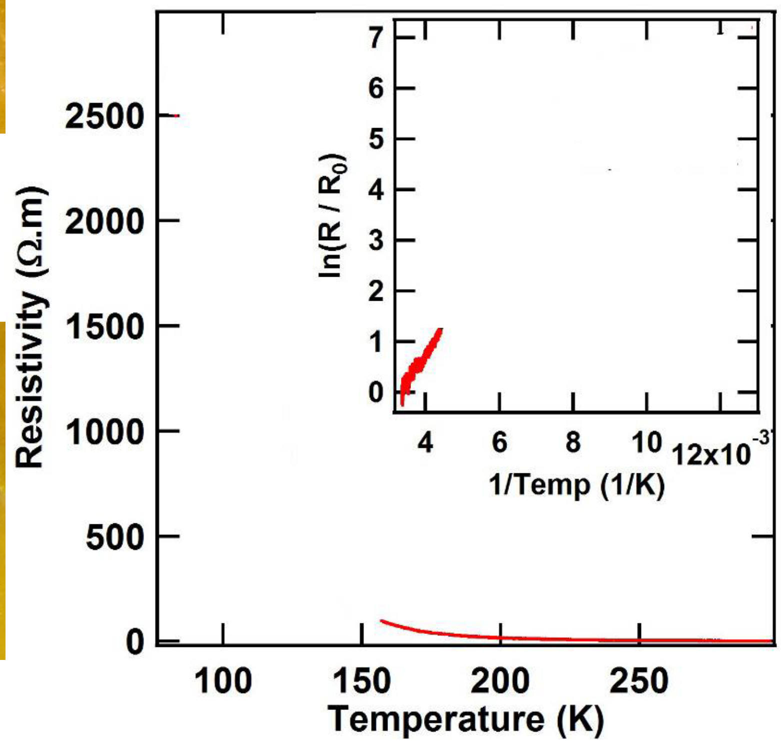


Before Cooldown

After Cooldown

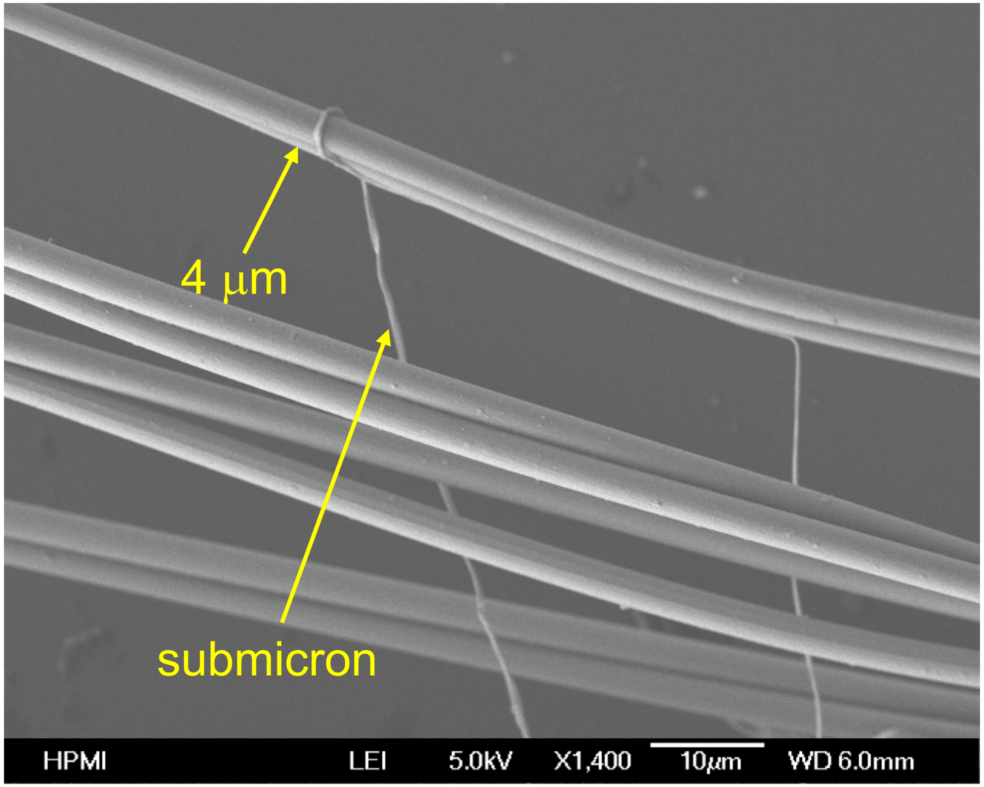


$\mathrm{Fe(tpma)(xbim)]ClO_4(TCNQ)_{1.5}}$

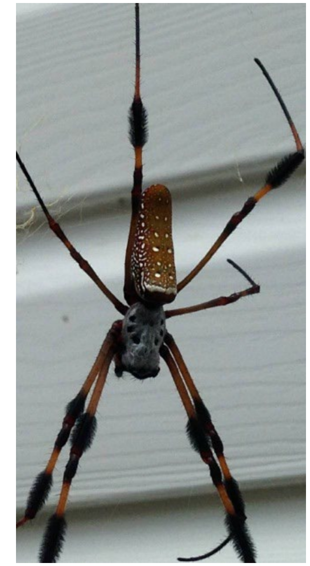


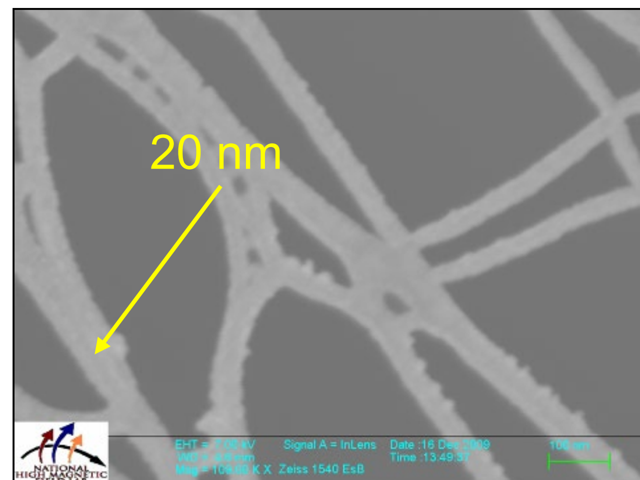
Carbon paste, 4-probe measurement

Nature to the Rescue!



Nephila Clavipes





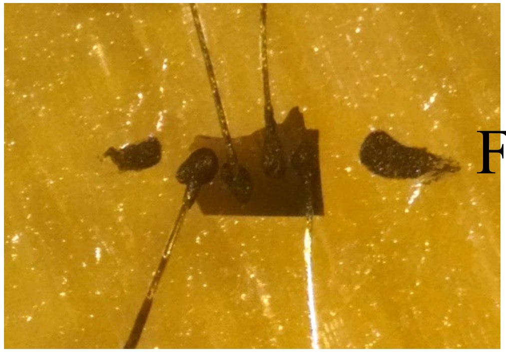
- 21 nm Au is sputtered onto spider silk fibers, rendering them electrically conducting
- The silk wires can be flexed but care should be taken not to over-stretch them

Steven E. et al., *Sci. Technol. Adv. Mater.* 2011, *12*, 055002

Conductivity Measurements

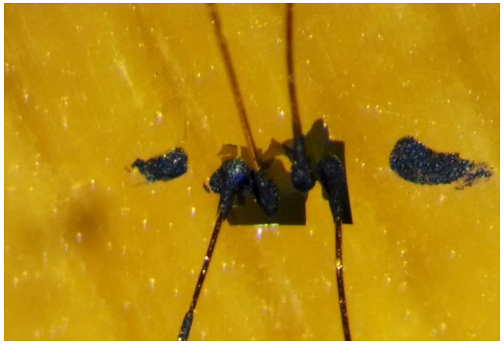
Tiny, brittle, and semi-transparent crystals

12 μm gold wire

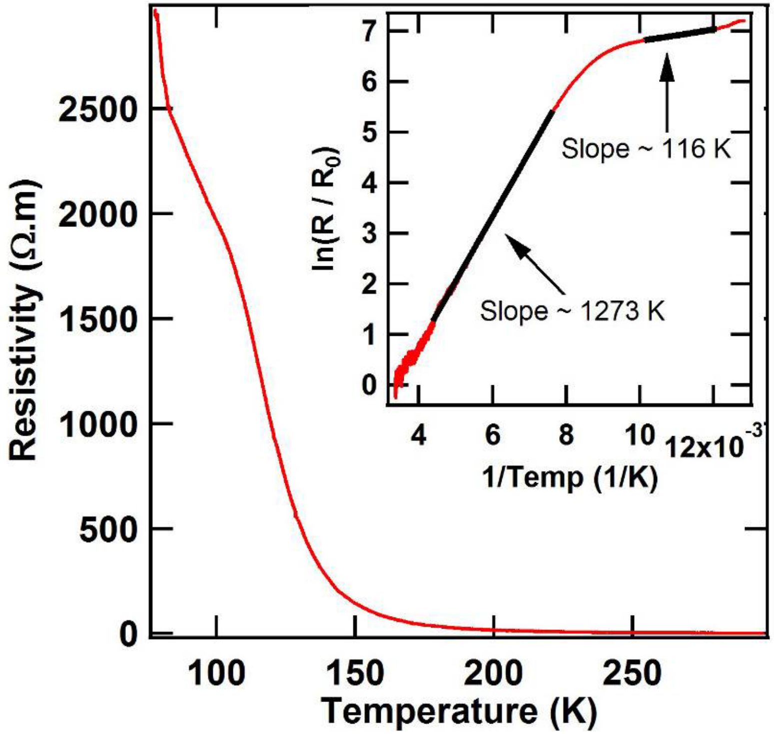


Before Cooldown

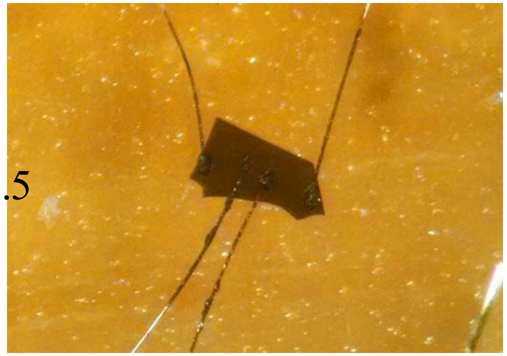
After Cooldown



$Fe(tpma)(xbim)]ClO_4(TCNQ)_{1.5}$



4 μm spider silk wire



Before Cooldown

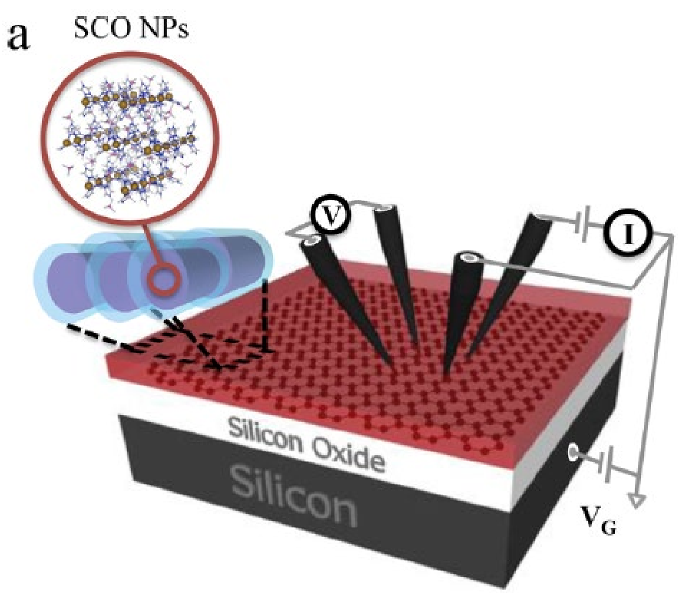
After Cooldown

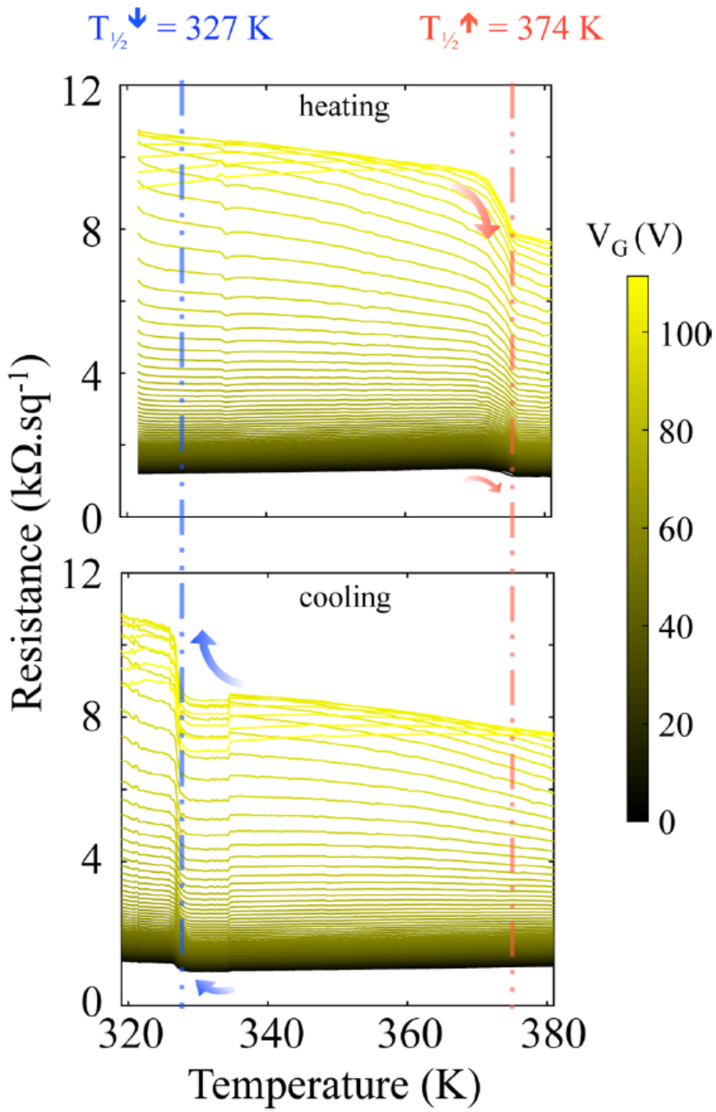
Carbon paste, 4-probe measurement

II. Ultrathin SCO Films

SCO nanoparticles on graphene

- Deposited by contact printing from the surface of an ethyleneglycol droplet)
- NP rods: *l* ~ 25 nm, *d* ~ 9 nm





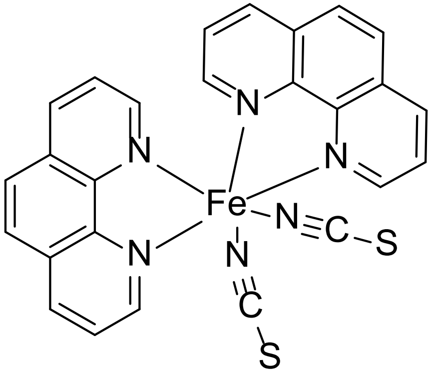
Adapted from: Dugay, J.; Aarts, M.; Gimenez-Marques, M.; Kozlova, T.; Zandbergen, H. W.; Coronado, E.; van der Zant, H. S. J. *Nano Lett.* 2017, *17*, 186-193

Depositing Molecules on Substrates

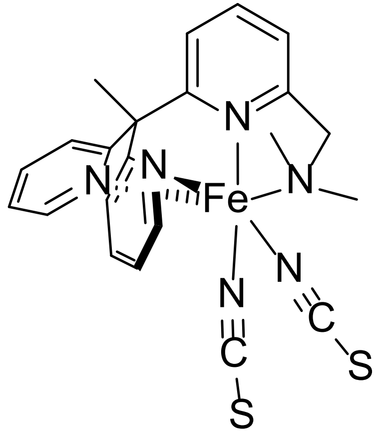
Source ⟶	Solution	Gas Phase	Solid
Generality	High	Moderate	Low(?)
Scalability	High	Moderate	Moderate
Purity	Low	High	Moderate
Requirements			
e-neutrality	n/a	✓	o
solubility	✓	n/a	n/a
volatility	n/a	✓	n/a
thermal stability	o	✓	o
surface stability	✓	✓	o

✓ = required   o = desired

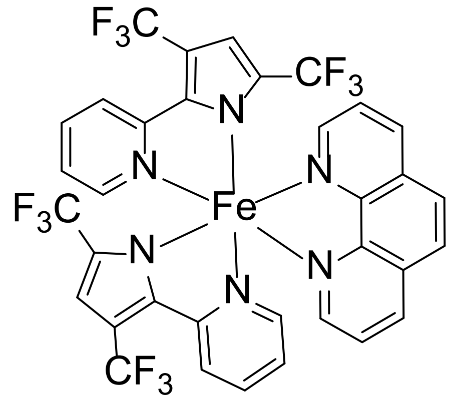
Gas-Phase Deposition of SCO Films



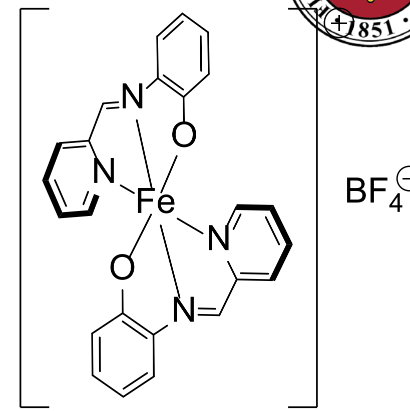
180 °C
10^{-8} mbar



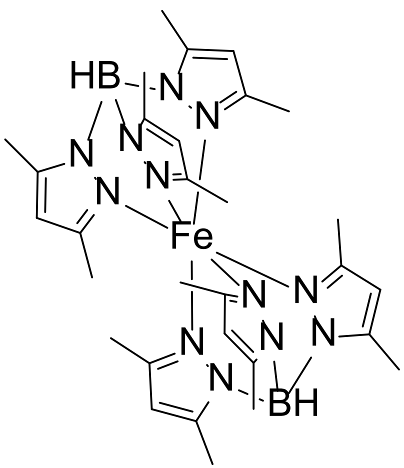
237 °C
10^{-9} mbar



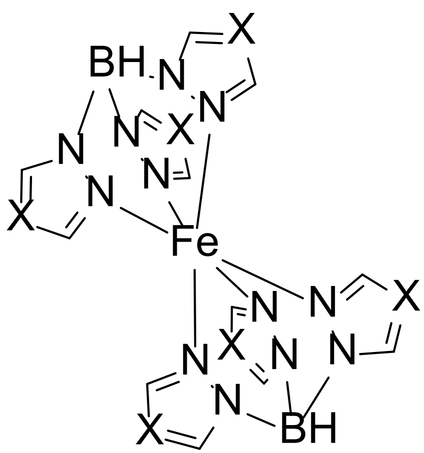
160 °C
10^{-9} mbar



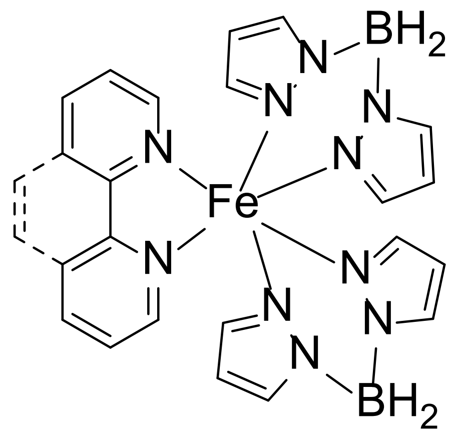
100 °C
10^{-9} mbar



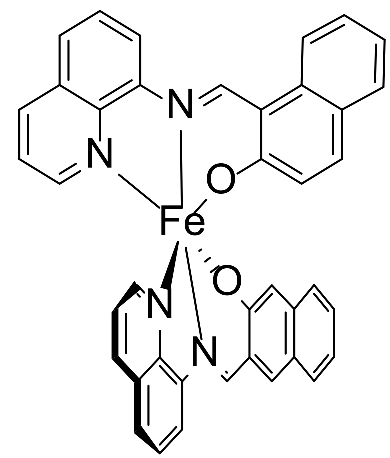
140 °C
10^{-8} mbar



190 °C
10^{-5} mbar



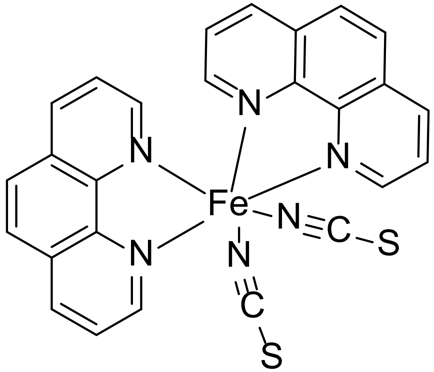
162 °C
10^{-2} mbar



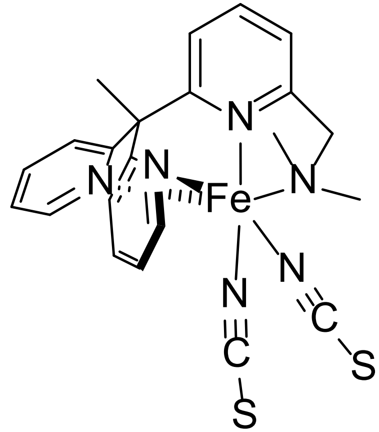
217 °C
10^{-9} mbar

Kumar, K. S.; Ruben, M. *Angew. Chem. Int. Ed.* **2021**, *60*, 7502-7521

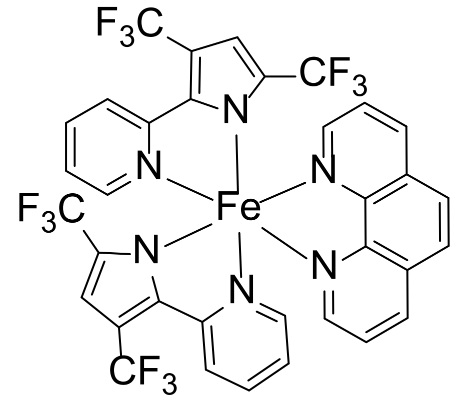
Gas-Phase Deposition of SCO Films



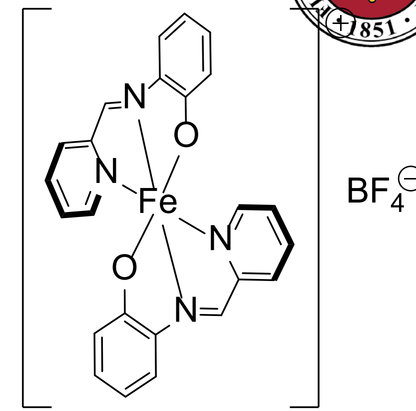
180 °C
10^{-8} mbar



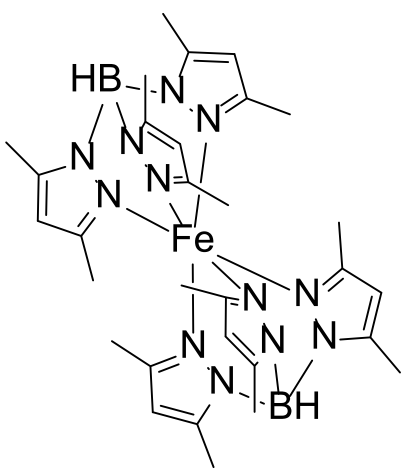
237 °C
10^{-9} mbar



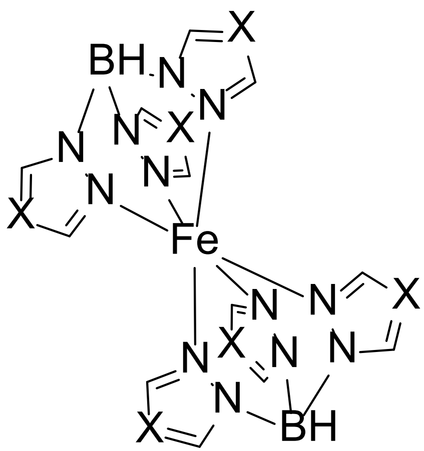
160 °C
10^{-9} mbar



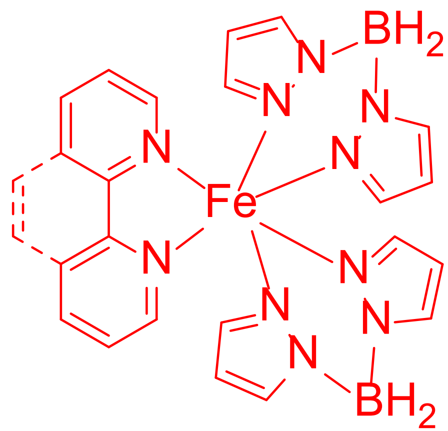
100 °C
10^{-9} mbar



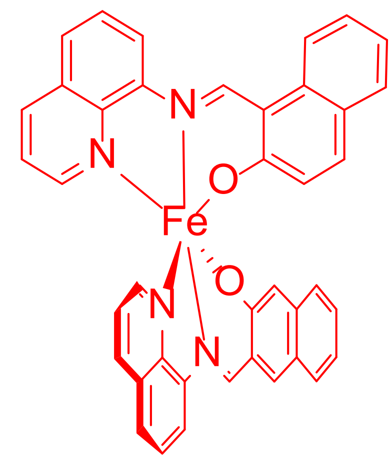
140 °C
10^{-8} mbar



190 °C
10^{-5} mbar



162 °C
10^{-2} mbar



217 °C
10^{-9} mbar

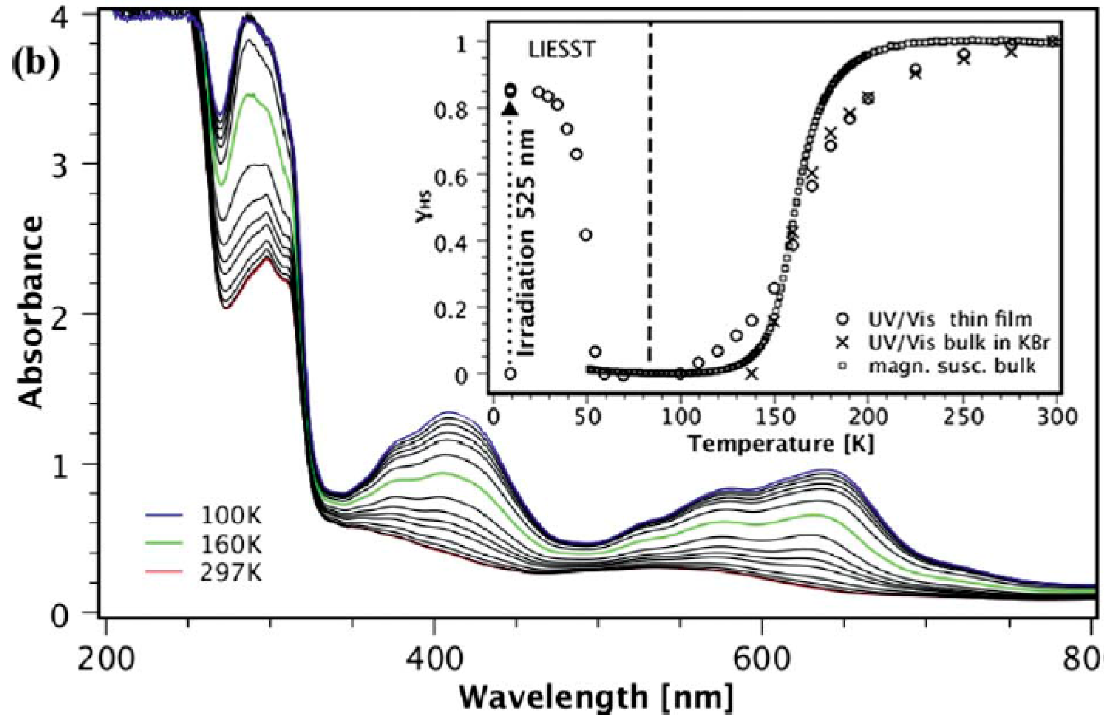
Kumar, K. S.; Ruben, M. *Angew. Chem. Int. Ed.* **2021**, *60*, 7502-7521

Gas-Phase Deposition of SCO Films

$[Fe(H_2Bpz_2)_2(L_2)]$ (L_2 = bpy, phen)

- Substrates: Si, glass, ITO-coated glass, polymer tape
- Thickness: 400-500 nm
- $T_{1/2}$ similar to bulk
- SCO more gradual
- LIESST effect

Vacuum deposition (10^{-2} mbar, 160-190 °C)



Methods:

- UV-Vis spectroscopy
- DFT

Adapted from: Naggert, H.; Quandt, E.; Tuczek, F.; et al. *Dalton Trans.* **2011**, *40*, 6364-6366

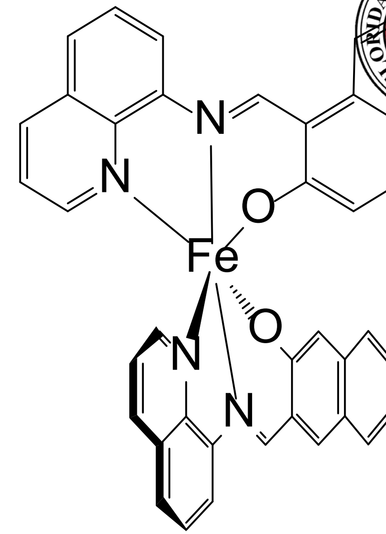
$[Fe(qnal)_2]$ on Au(111)

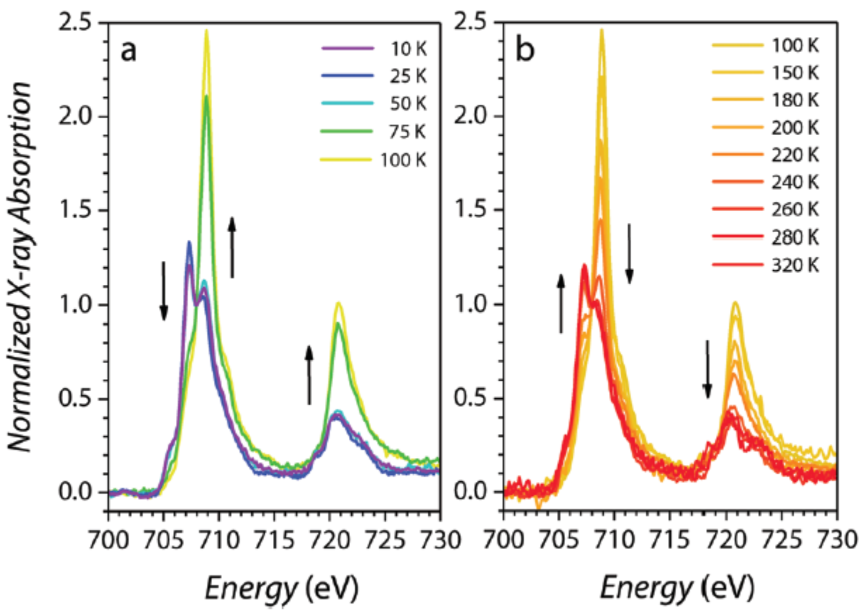
- Thickness: 300 nm
- $T_{1/2}$ similar to bulk
- SCO more gradual
- LIESST effect

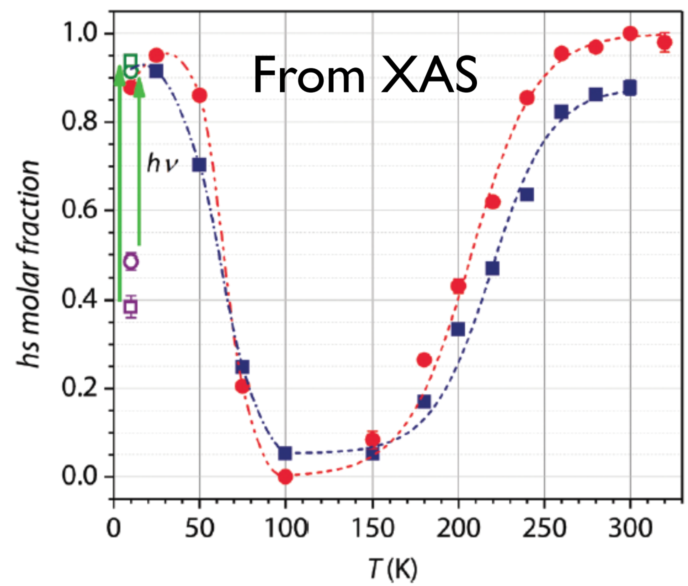
Vacuum deposition (10^{-8} mbar, 350 °C)

Methods:

- UV-Vis, XAS







Adapted from: Atrozi, M.; Sessoli, R.; Mannini, M.; et al. *J. Mater. Chem. C* **2018**, *6*, 8885

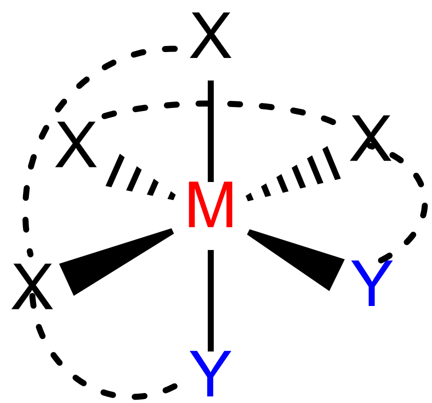
Molecular Design Challenge

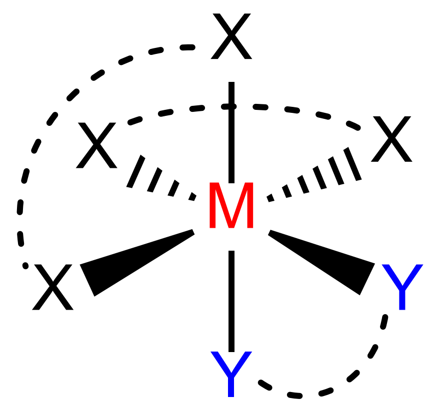
Cooperativity: ***strong*** intermolecular interactions

Volatility: ***weak*** intermolecular interactions

Challenge: increase the volatility while preserving the abrupt spin transition

Solution: use asymmetric design by separating the cooperative and "volatilizing" functions





Miguel Gakiya

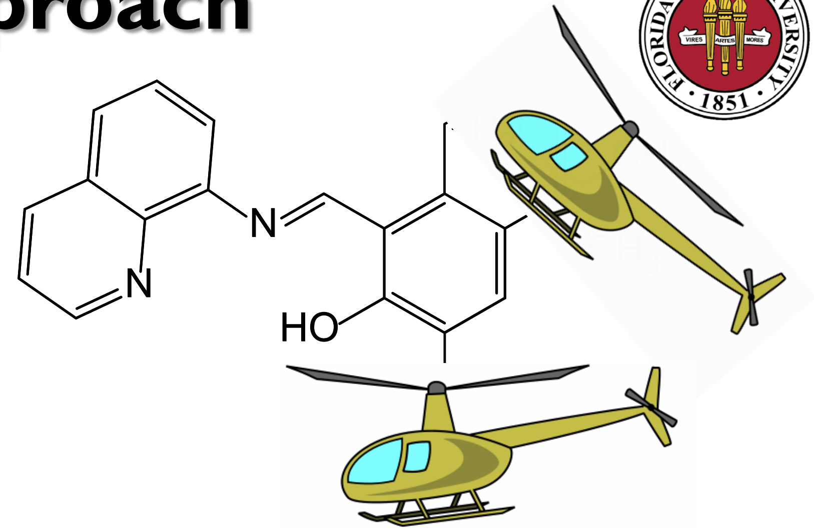
Criteria:

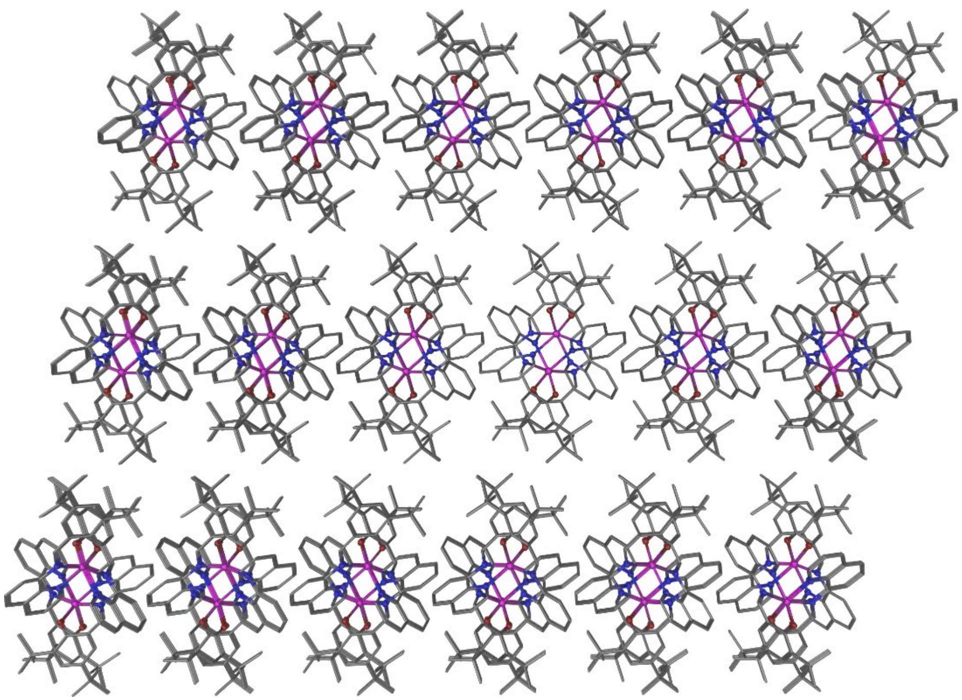
- neutral complexes
- easy synthetic modification
- asymmetric ligand structure
- only chelating (clamping) ligands

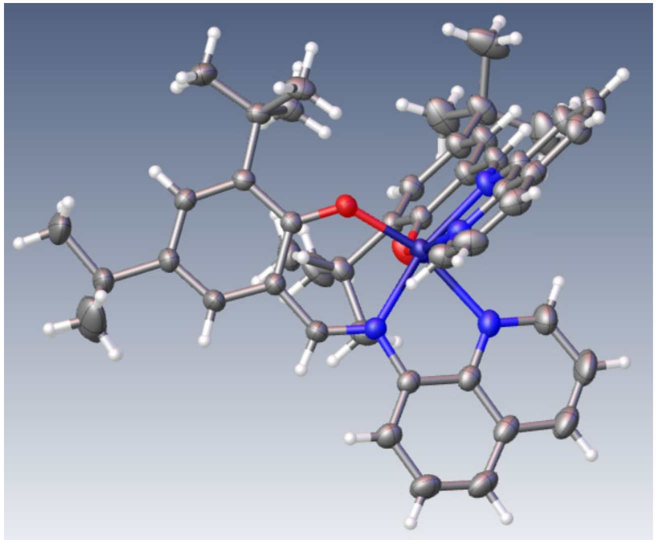
Synthetic Approach

Introduce the asymmetry of interactions to boost volatility

- the cooperativity will be preserved
- the volatility should be much higher



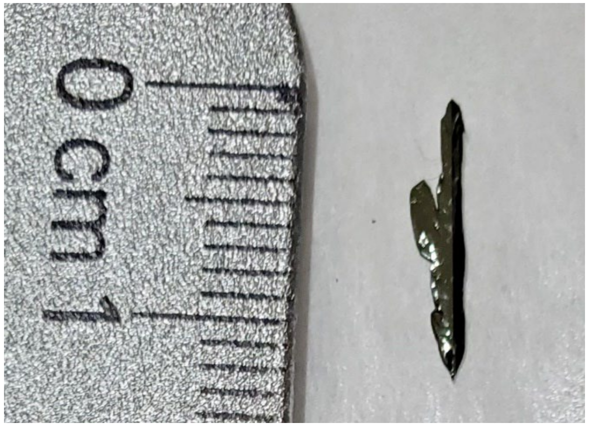




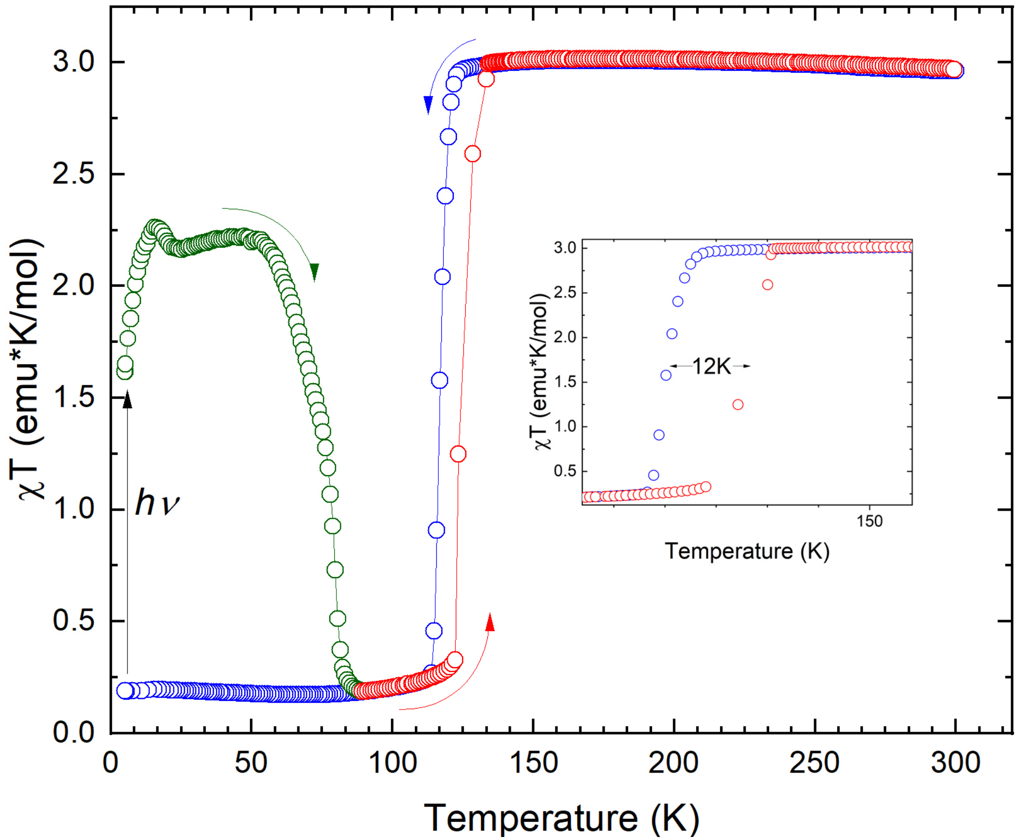
$[Fe(tBu_2qsal)_2]$

Gakiya-Teruya, M.; Jiang, X.; Le. D.; Rahman, T. S.; Hebard, A. F.; Shatruk, M.; et al. *J. Am. Chem. Soc.* **2021**, *143*, 14563-14572

Properties of $[Fe(tBu_2qsal)_2]$



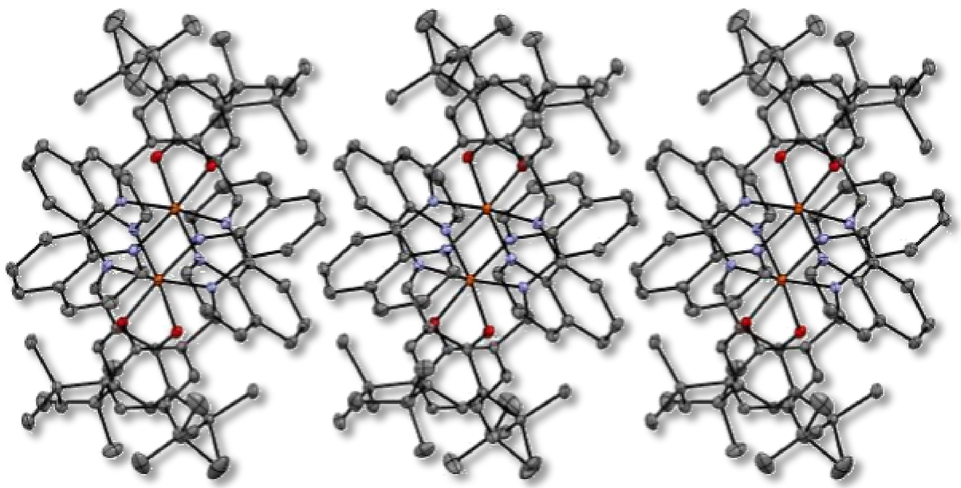
Crystals grown
by vapor transport at
$>10^{-5}$ mbar & 300 °C



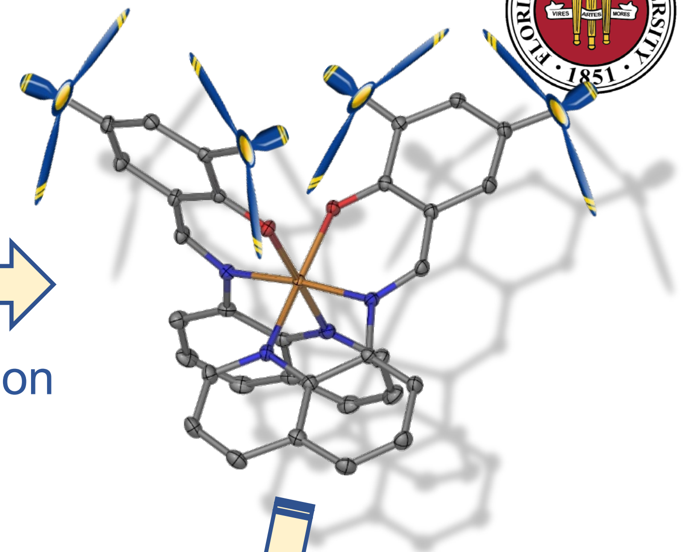
$T_{1/2}$ = 117 K / 129 K
T_{LIESST} = 84 K

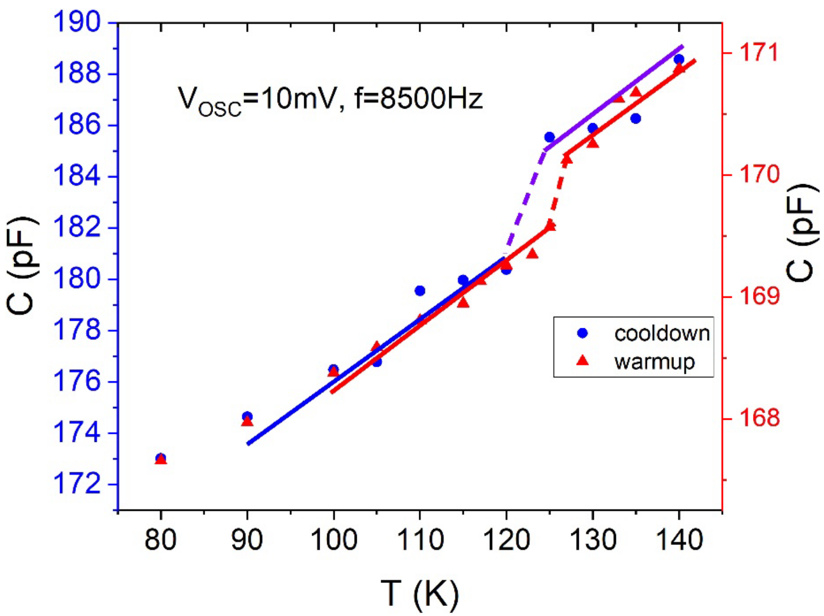
Gakiya-Teruya, M.; Jiang, X.; Le. D.; Rahman, T. S.; Hebard, A. F.;
Shatruk, M.; et al. *J. Am. Chem. Soc.* **2021**, *143*, 14563-14572

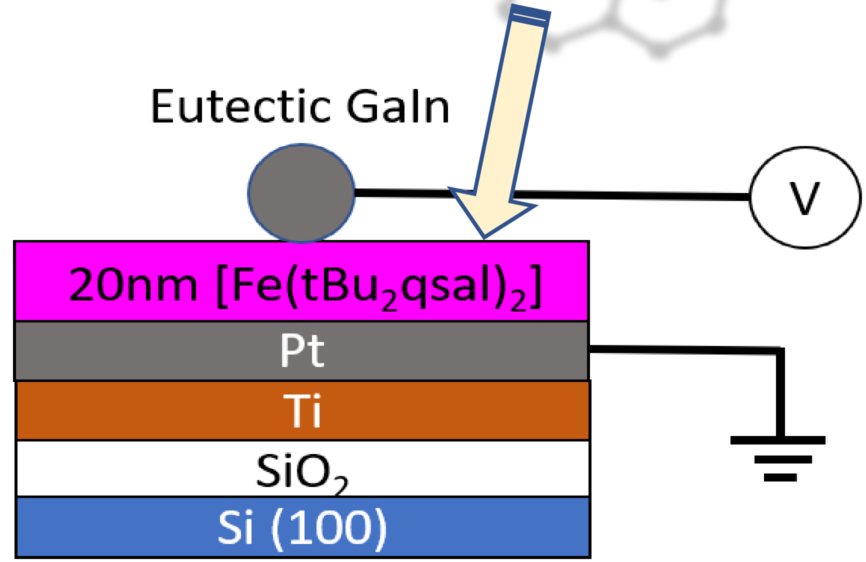
Thin-Film Capacitor



Sublimation



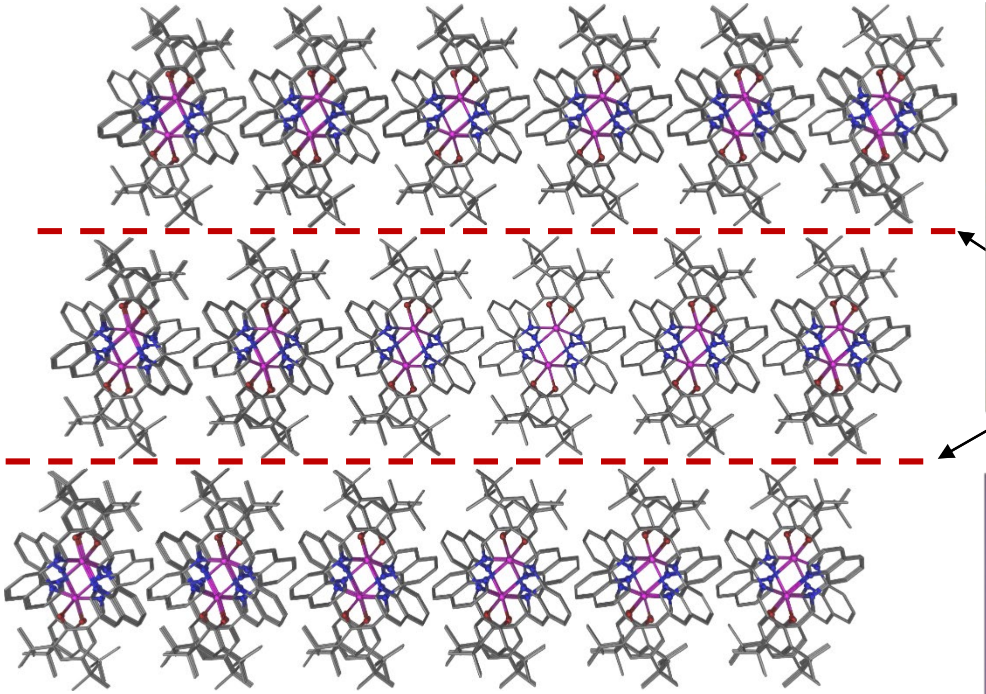


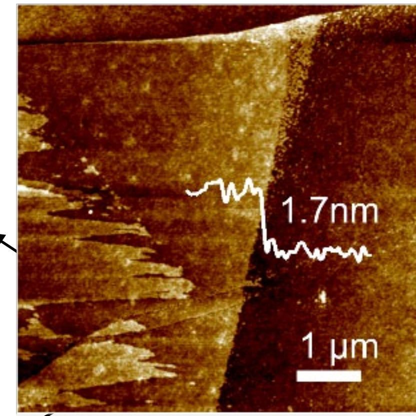


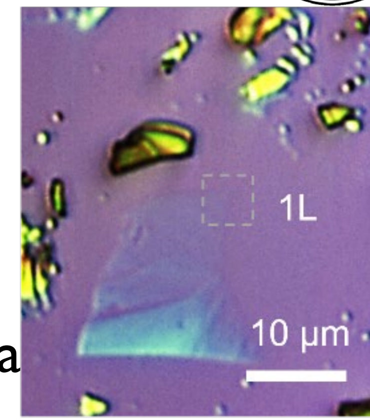
$T_{1/2}$ ≈ 122 K / 127 K

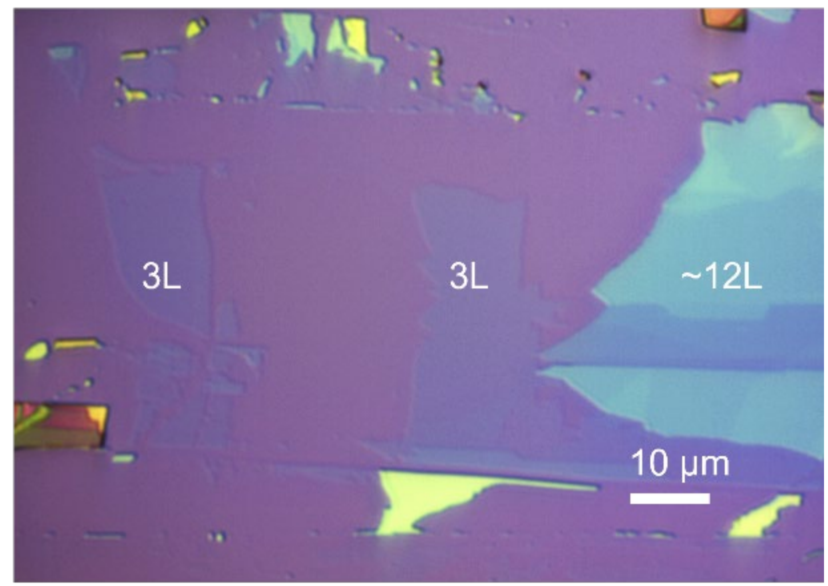
Gakiya-Teruya, M.; Jiang, X.; Le. D.; Rahman, T. S.; Hebard, A. F.; Shatruk, M.; et al. *J. Am. Chem. Soc.* **2021**, *143*, 14563-14572

Mechanical Exfoliation







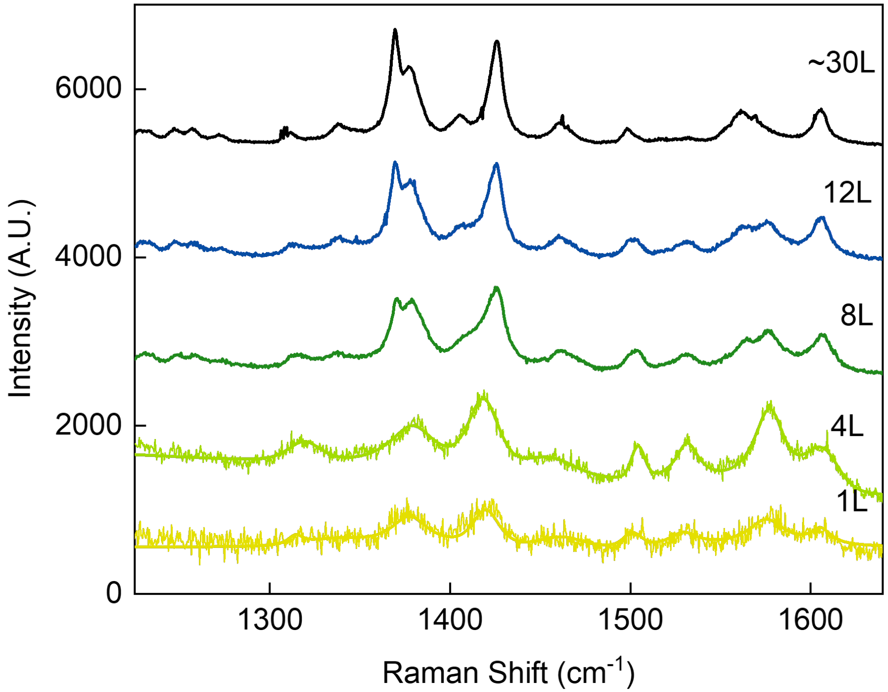


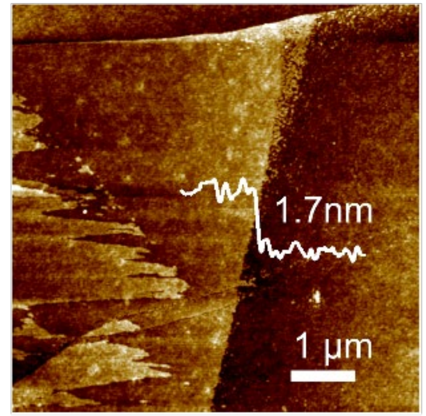
<u>Mechanical exfoliation</u>:

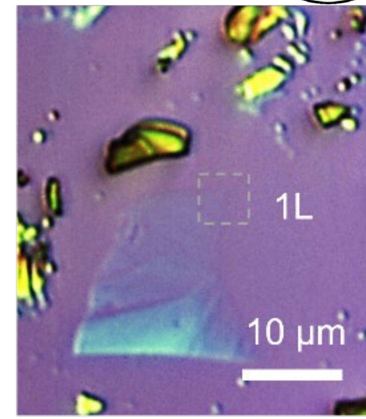
Successful exfoliation down to a single molecular layer (1.7 nm thickness)

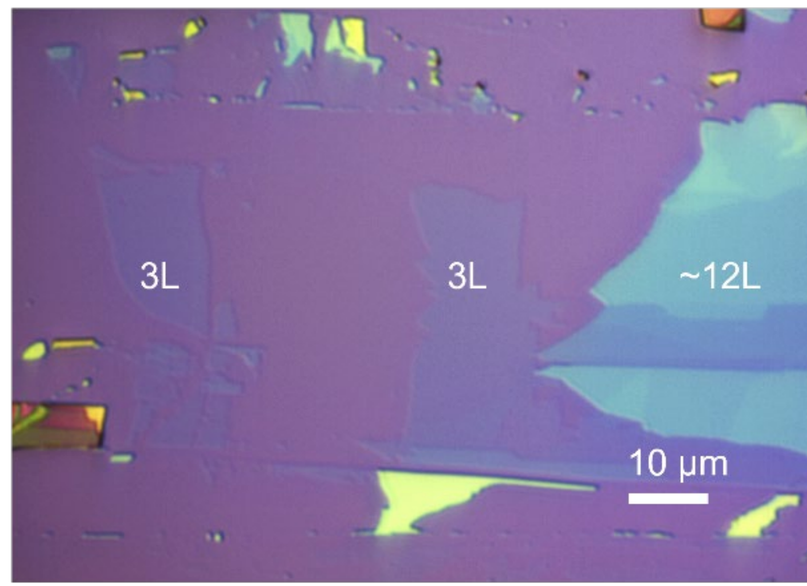
Koptur-Palenchar, J. J.; Gakiya-Teruya, M.; Shatruk, M.; Zhang, X. X; et al. *Under Review*

Mechanical Exfoliation









<u>Mechanical exfoliation</u>:

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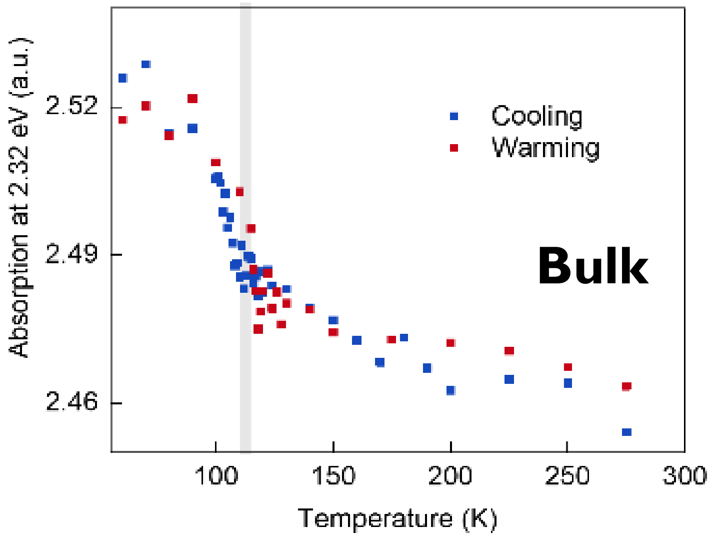
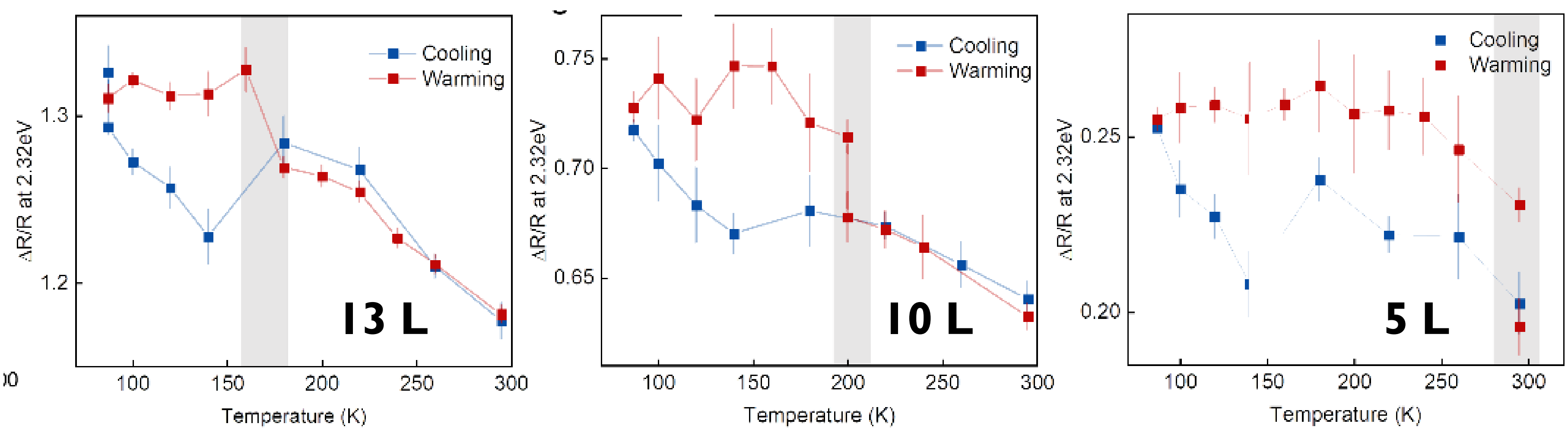
Koptur-Palenchar, J. J.; Gakiya-Teruya, M.; Shatruk, M.; Zhang, X. X; et al. *Under Review*

Thickness Dependence of SCO

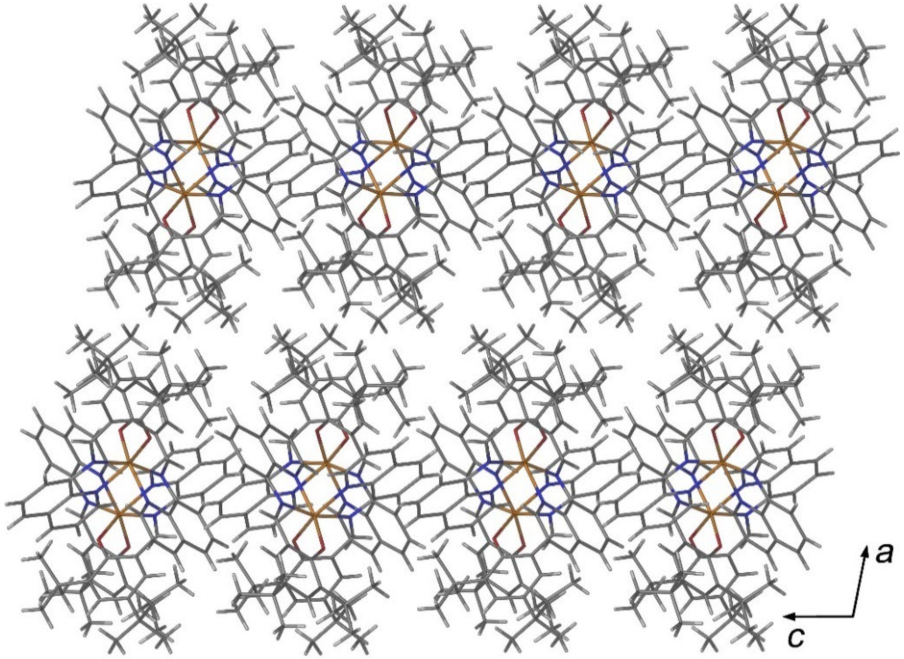


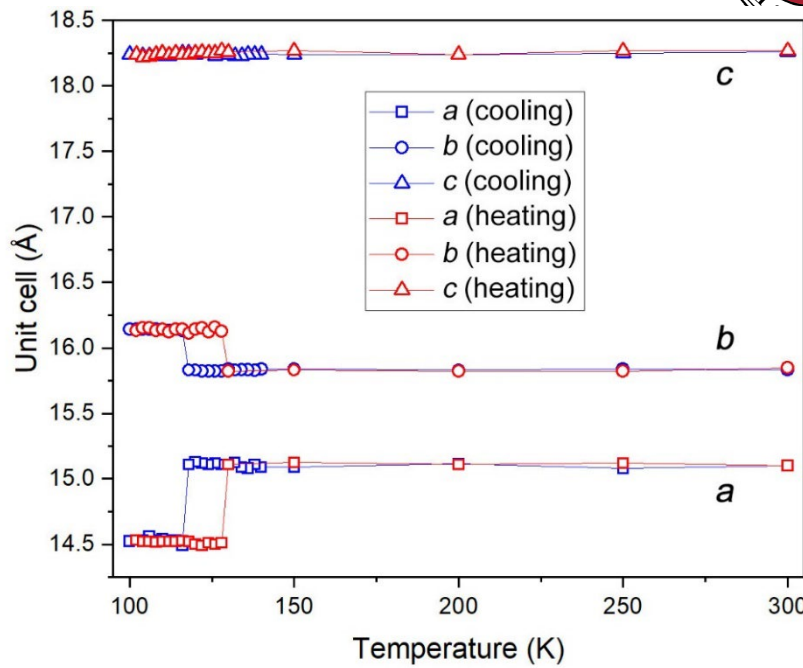
The normalized reflection contrast measurements suggest increased hysteresis in the 2D SCO material



Koptur-Palenchar, J. J.; Gakiya-Teruya, M.; Shatruk, M.; Zhang, X. X; et al. *Under Review*

Thickness Dependence of SCO





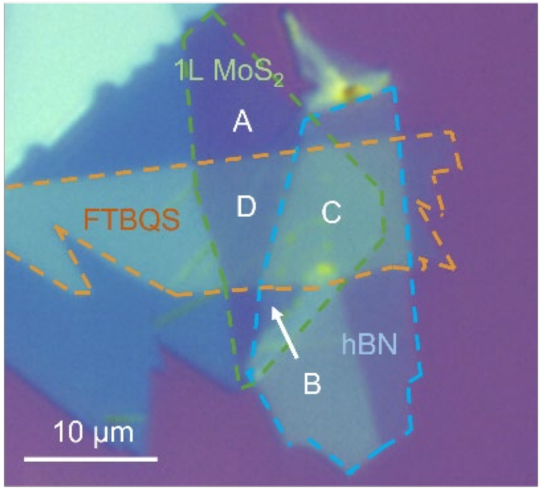
# of layers	$\Delta T_{1/2}$
Bulk	12 K
13	~45 K
10	~90 K
5	~200 K

Hypothesized reason:

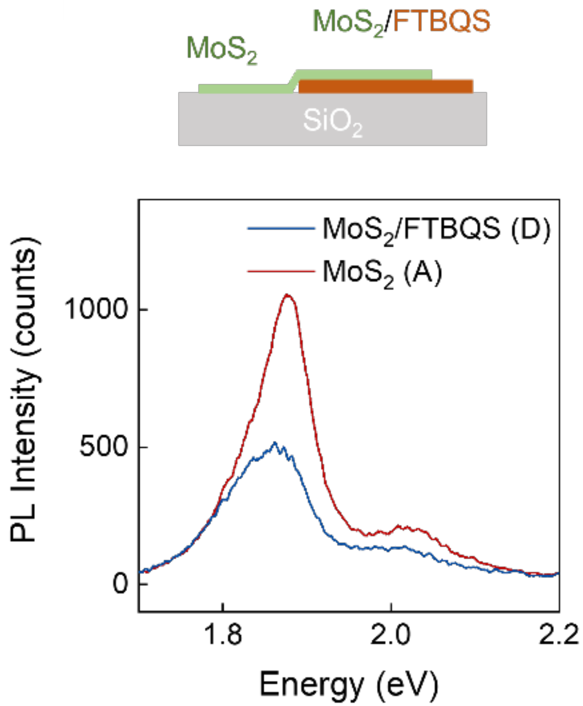
- Interfacial strain combined with the restriction of domain wall motion

Koptur-Palenchar, J. J.; Gakiya-Teruya, M.; Shatruk, M.; Zhang, X. X; et al. *Under Review*

2D Heterostructures

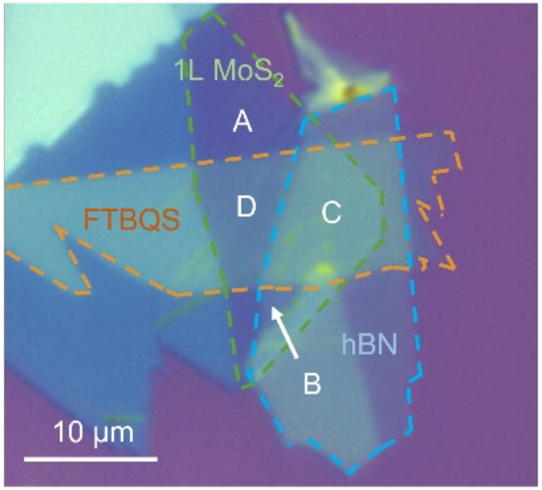


Assembled by the PDMS stamp method



Koptur-Palenchar, J. J.; Gakiya-Teruya, M.; Shatruk, M.; Zhang, X. X; et al. *Under Review*

2D Heterostructures



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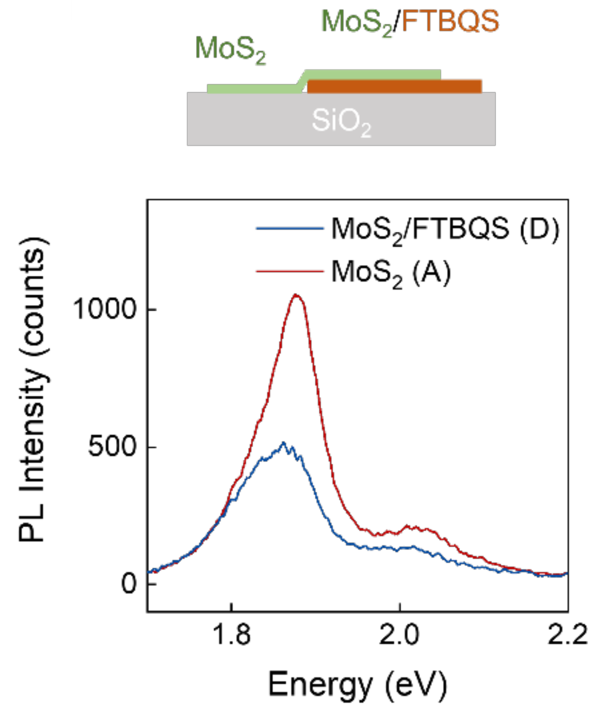
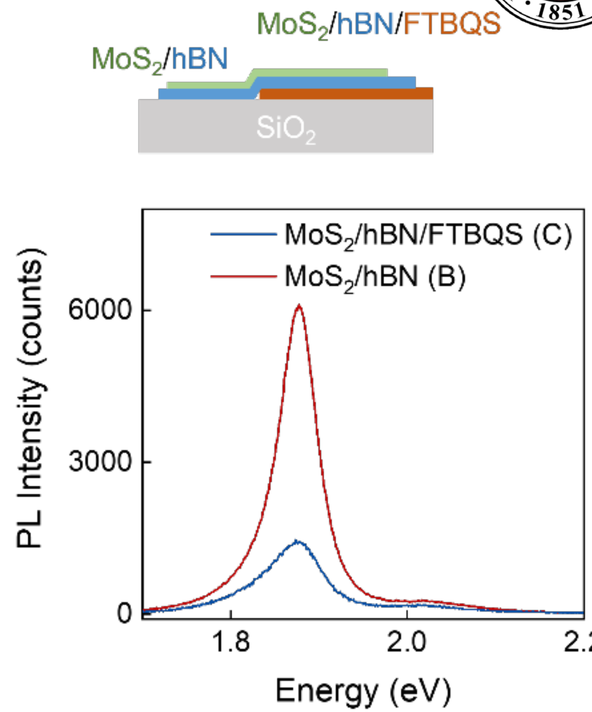
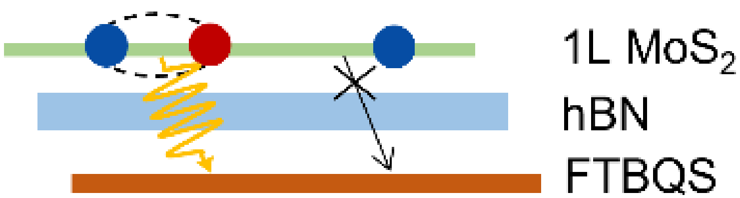




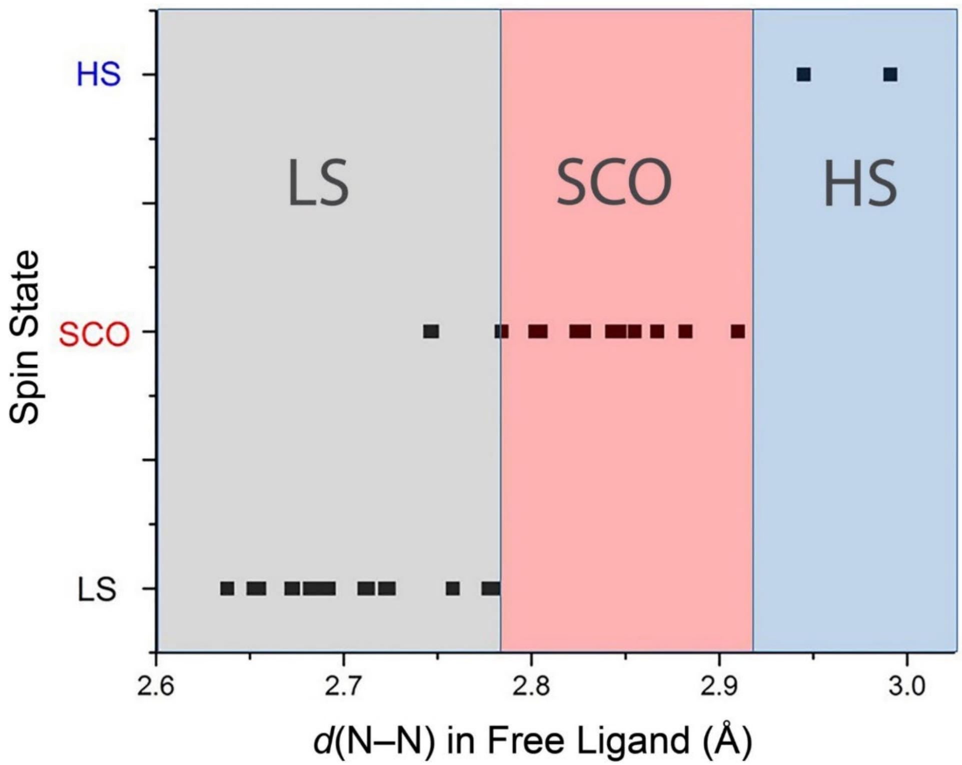


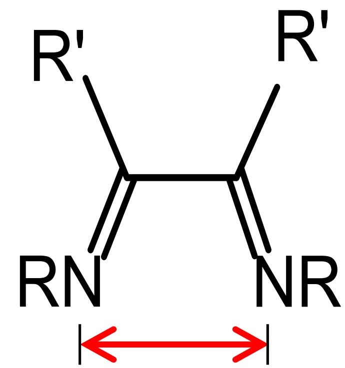
- Charge transfer blocked by hBN
- The Förster energy transfer still allowed

Koptur-Palenchar, J. J.; Gakiya-Teruya, M.; Shatruk, M.; Zhang, X. X; et al. *Under Review*

What's Next?

- Investigating heterostructures
- Tuning the SCO temperature





d(N–N)
in the free, non-coordinated ligand
(experimental or calculated values)

Phan, H.; Hrudka, J. J.; Igimbayeva, D.; Lawson Daku, L. M.; Shatruk, M. *JACS* **2017**, *139*, 6437-6447

Summary

- Using the principle of asymmetric design, we can engineer increased volatility of materials while preserving the abrupt SCO
- The structural hierarchy allows mechanical exfoliation of ultrathin SCO flakes

Future Efforts

- Elucidating the role of substrates
- Extending the approach to other types of magnetic molecules (SMMs, radicals)
- Investigation of heterostructures and devices with inorganic 2D materials

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Gerald Ciani

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and John Koptur-Palenchar
(University of Florida)