Bistability in Molecular Materials: From Spin-State Switching to Functional 2D Heterostructures

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REU Photochemistry Café
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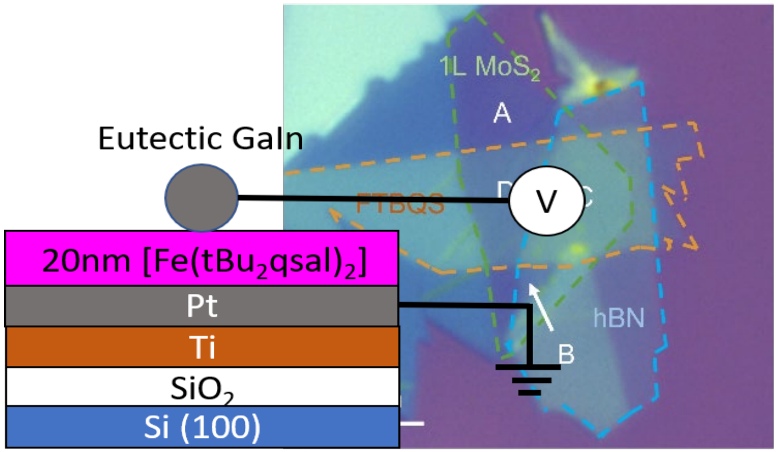
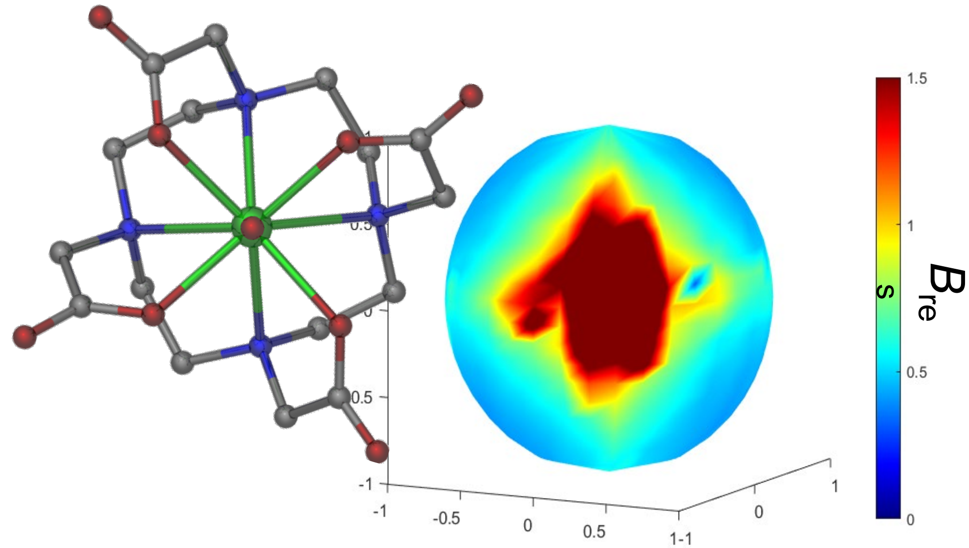
Inorganic Materials in the Shatruk Group

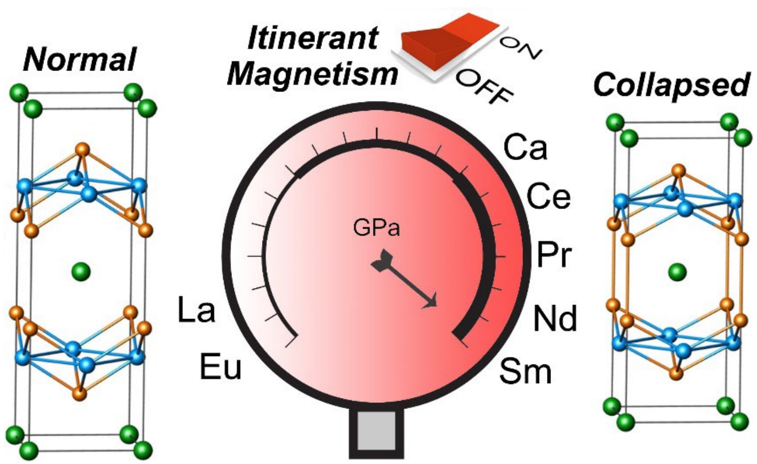
Spin-State Switching & Hybrid 2D Materials



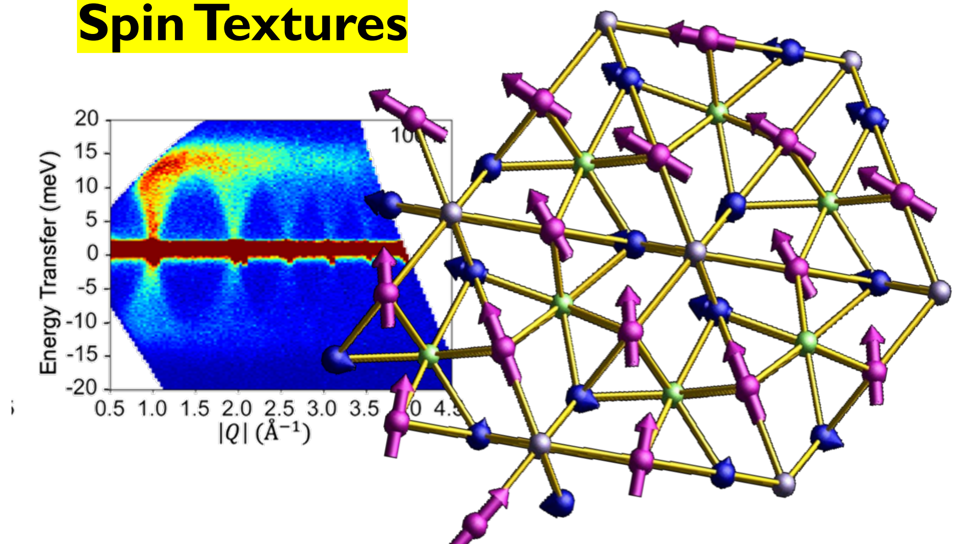
Molecular Spin Qubits



Itinerant Magnetism & Magnetic Refrigeration



Unconventional Spin Textures



Motivation for Research

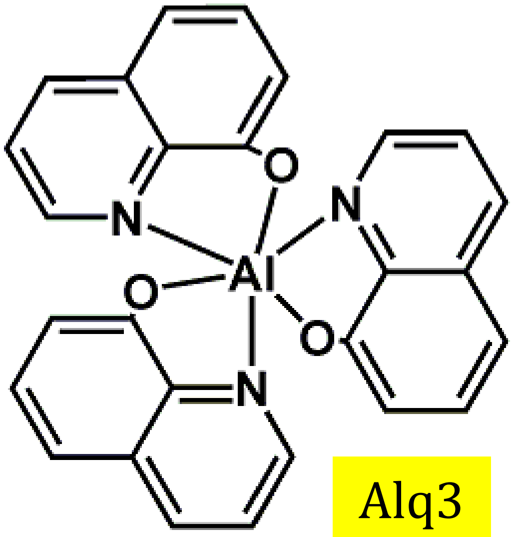
- Electricity is a great thing, but…
  - electrical connections unavoidably add weight and mechanical constraints to the device architecture
  - wires corrode, requiring regular maintenance and/or replacement

- 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

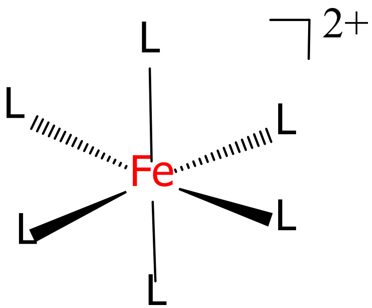
State of the Art

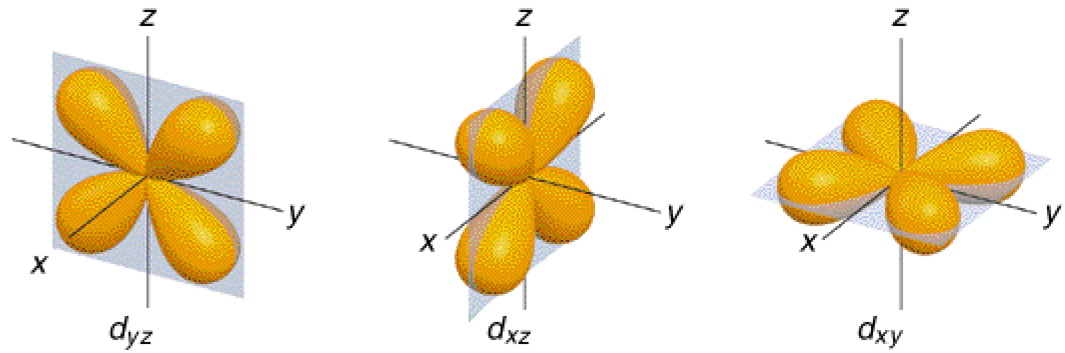
- Extended-structure materials
  - doped semiconductors (Si, GaP, GaAs, etc.)
  - polymers (CD drives)

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

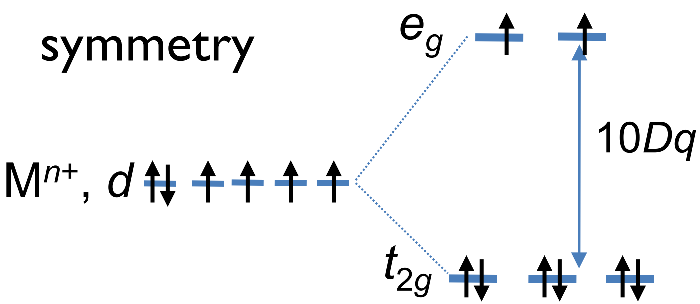


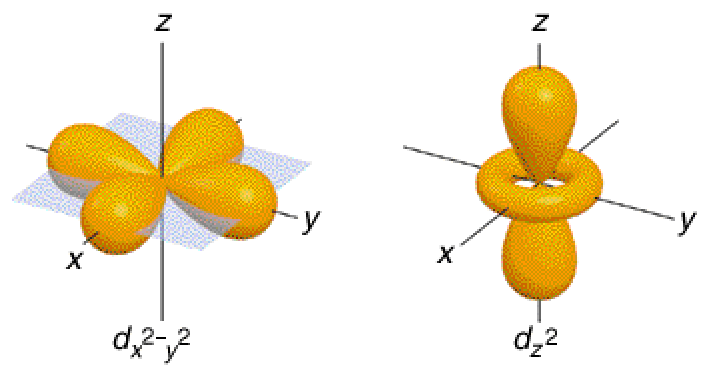
Splitting of d-Orbitals by Ligand Field





Octahedral symmetry

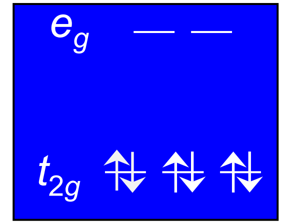




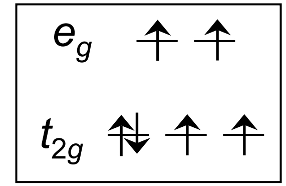
Spectrochemical series of ligand-field strength:

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

I. Spin Crossover (SCO)



LS, $S = 0$



HS, $S = 2$

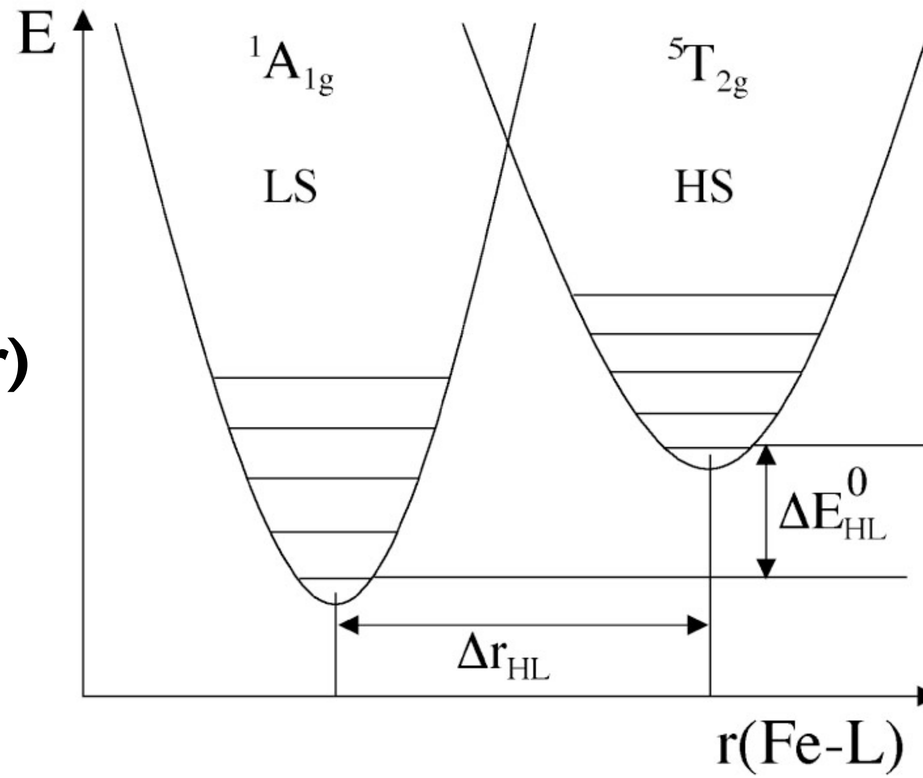
Entropy driven transition

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

Triggered by changes in temperature, pressure, or photoexcitation

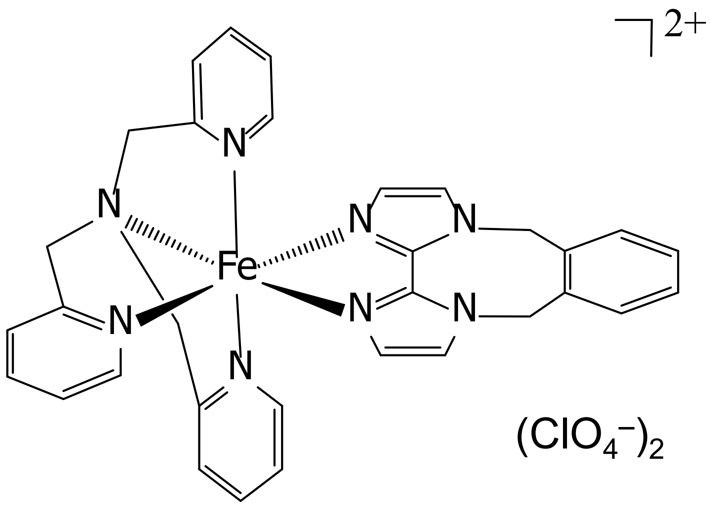
Dramatic changes in:

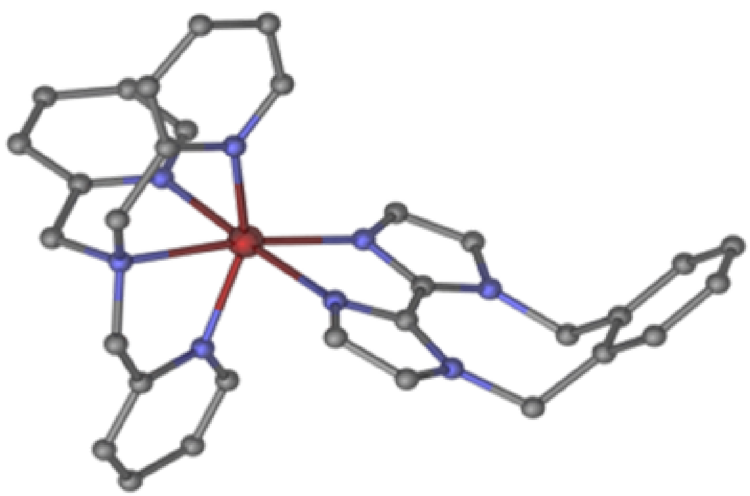
- magnetic moment
- **M-L bond lengths**
- **absorption spectrum (color)**



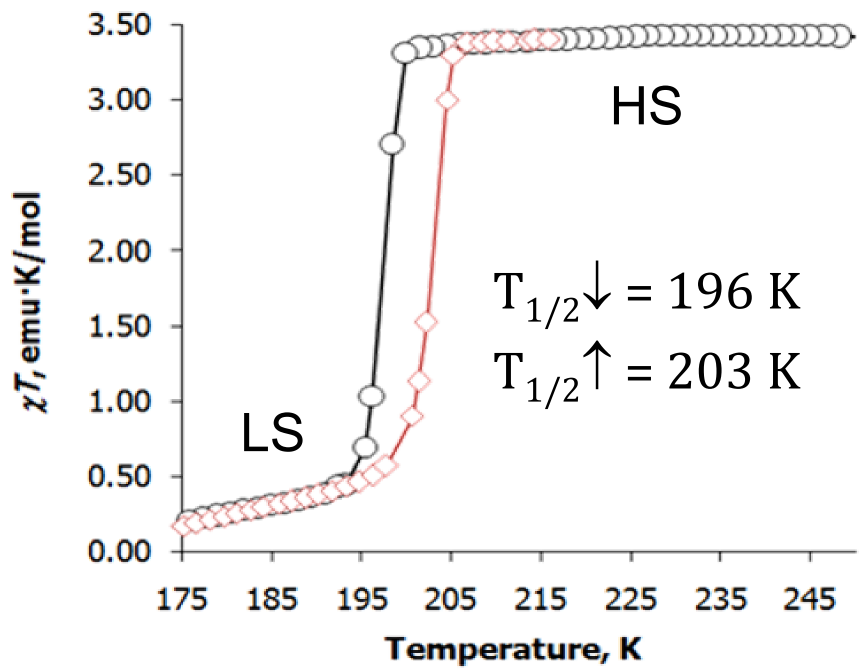
Hauser, A. *Top. Curr. Chem.* **2004**, 233, 49-58
Shatruk, M.; Phan, H.; et al. *Coord. Chem. Rev.* **2015**, *289-290*, 62-73

Example of Fe(II) SCO Complex





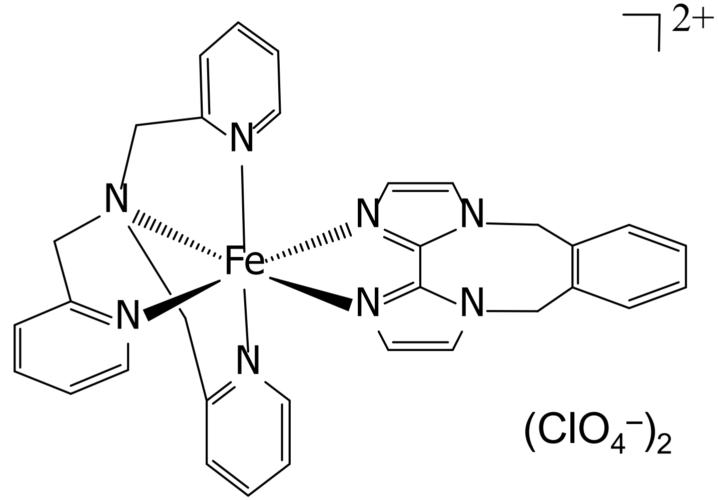
SCO with hysteresis ($\Delta T \sim 7$ K)



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

LS State Bleaching

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



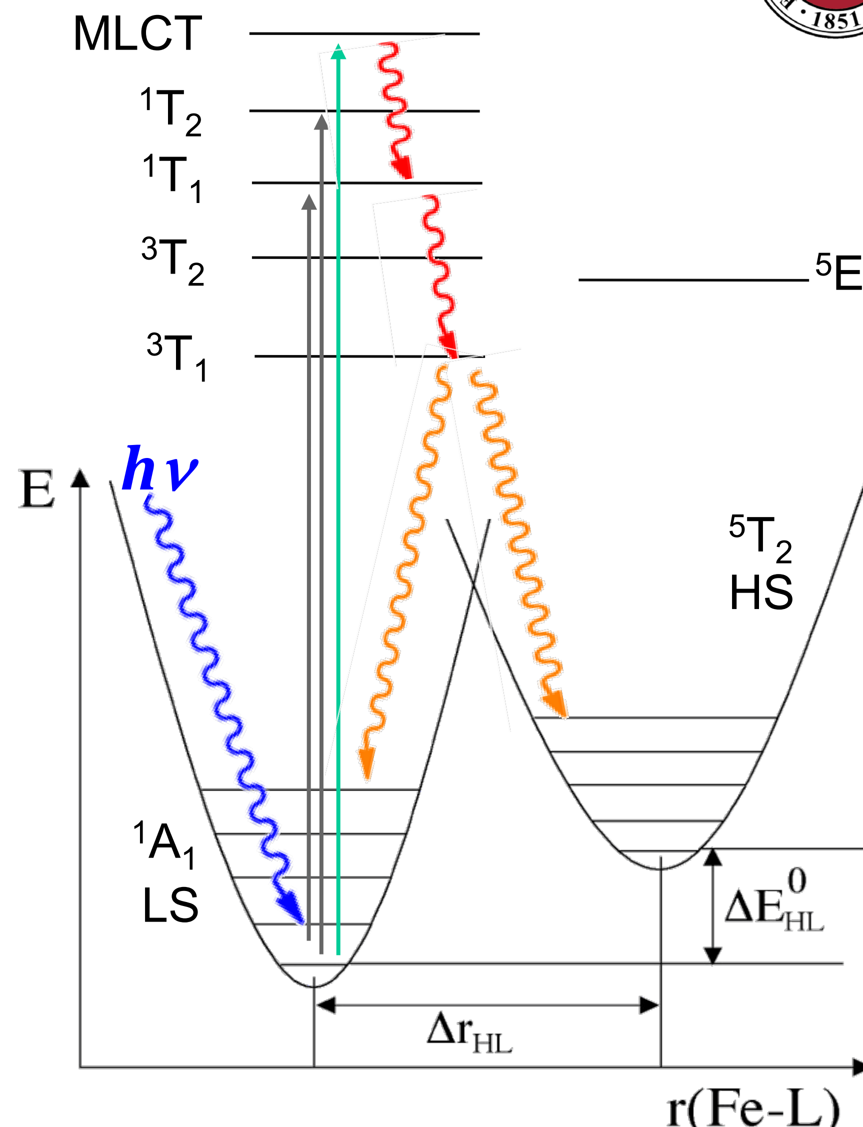
The abrupt change in color due to drastically different optical properties of the HS and LS states

Photomagnetism (LIESST)

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

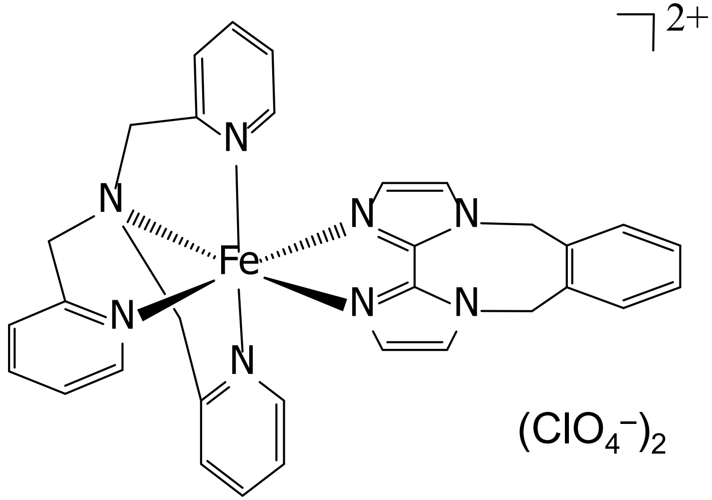
Light-Induced Excited Spin-State Trapping (LIESST)

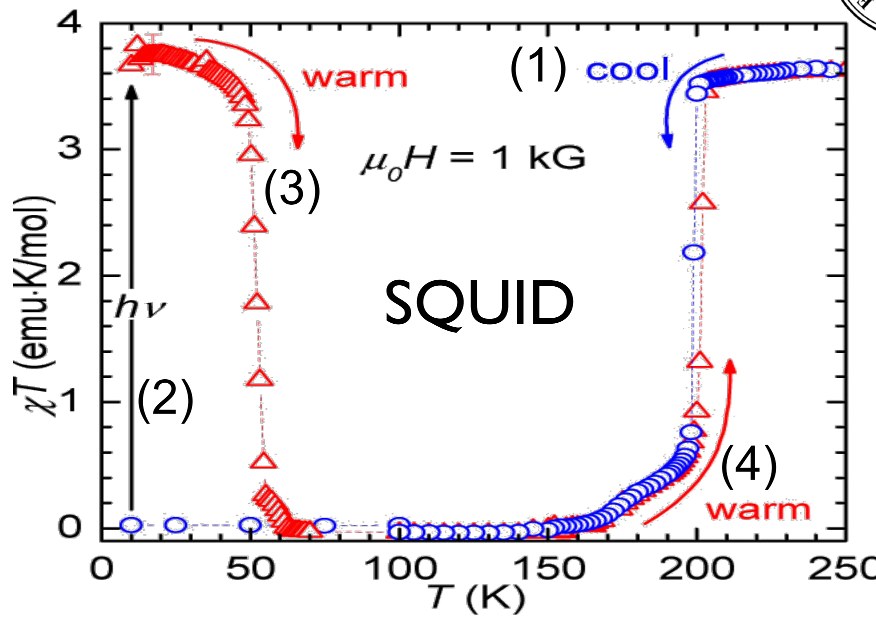
At sufficiently low temperature, the HS state will be trapped until it can acquire enough energy to undergo thermally activated relaxation to the LS state

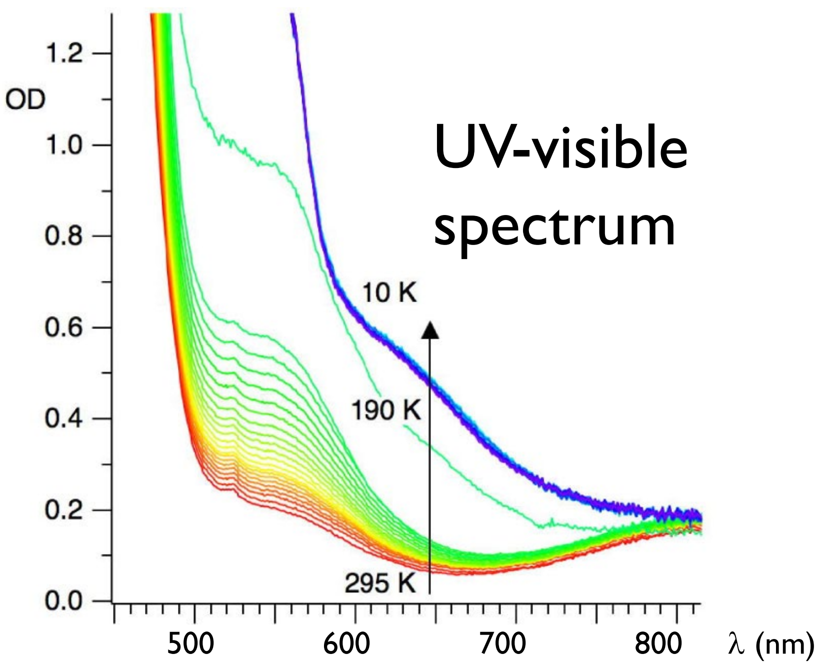


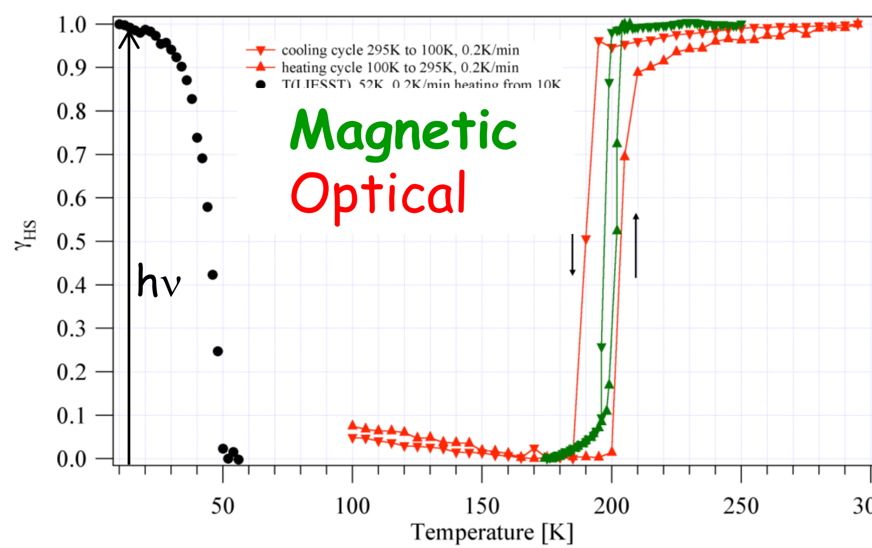
Electronic transitions of Fe(II) SCO complexes

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



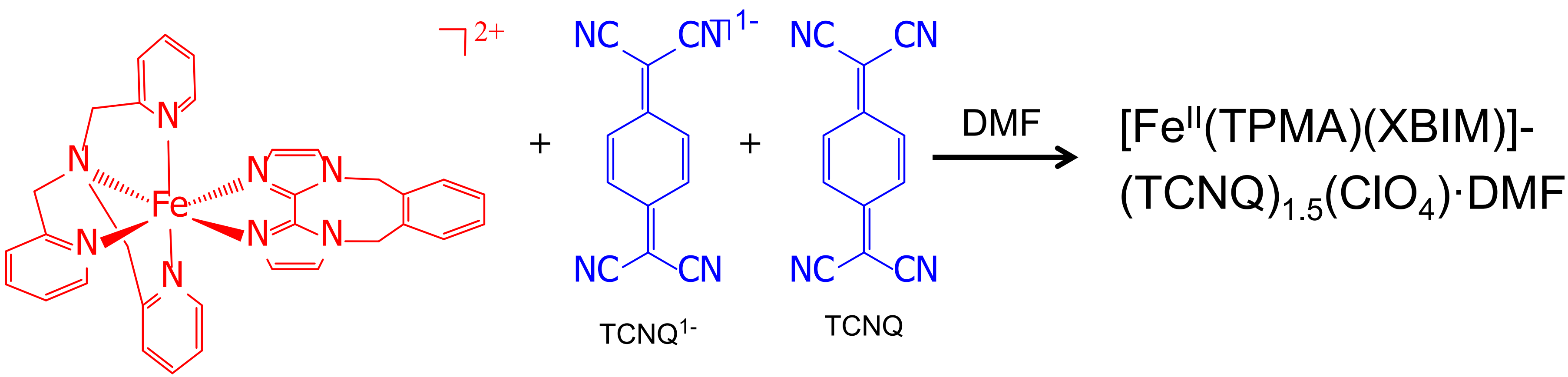


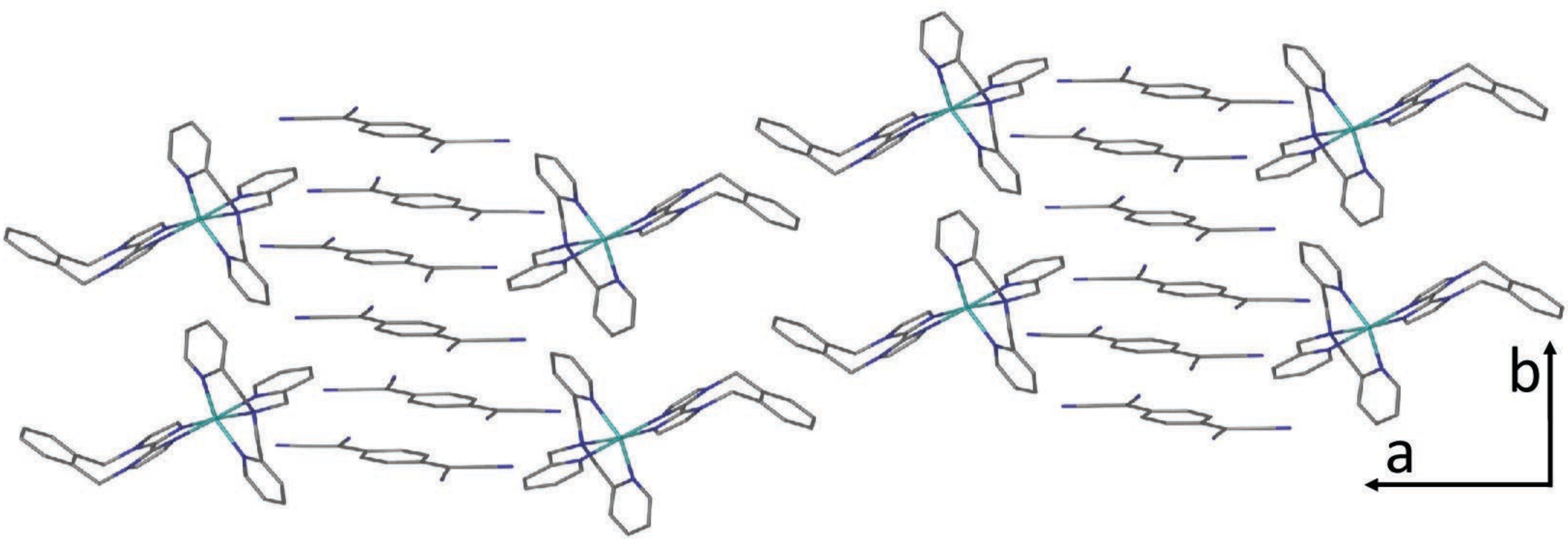




Phan, H.; Chakraborty, P.; Calm, Y.; Chen, M.; Kovnir, K.; Keniley, L. K.; Hoyt, J. M.; Knowles, E. S.; Besnard, C.; Meisel, M.; Hauser, A.; Achim, C.; Shatruk, M. *Chem. Eur. J.* **2012**, *18*, 15805

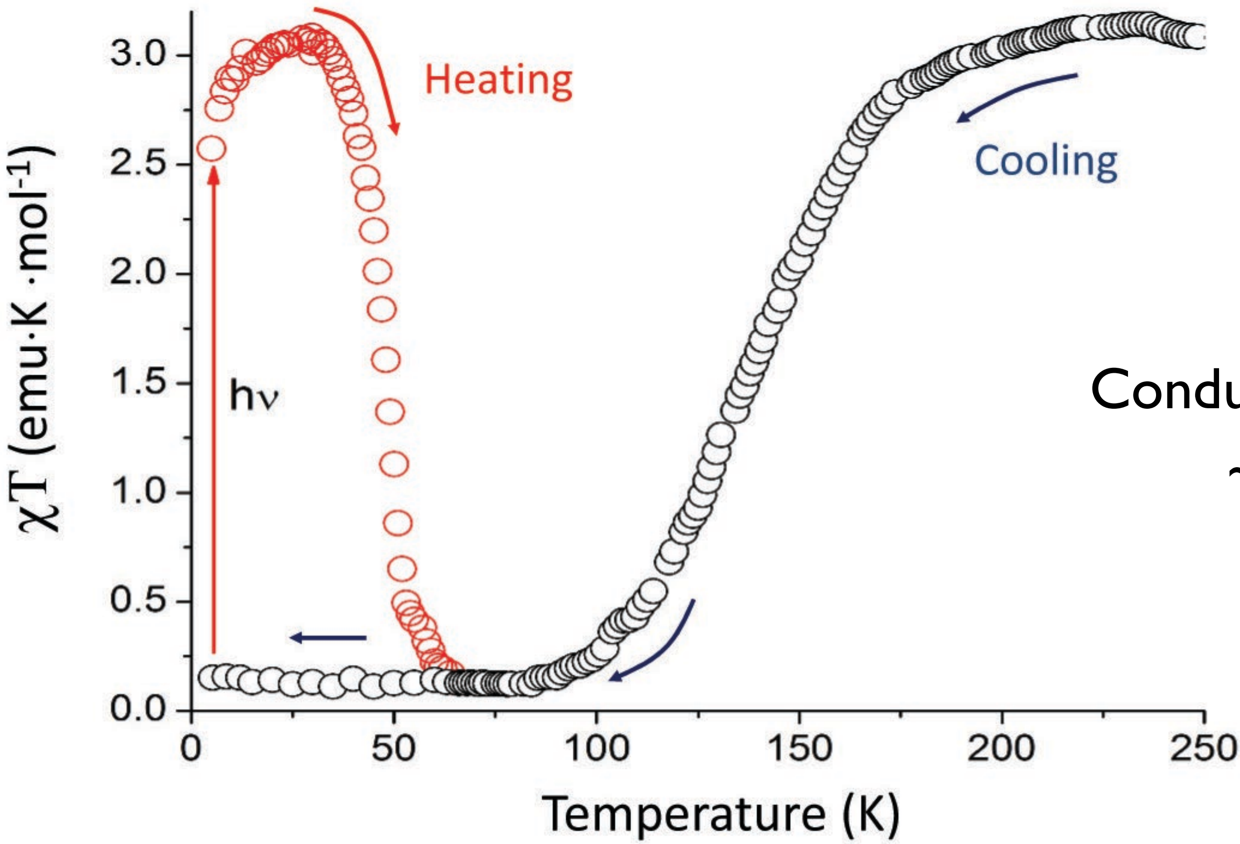
Combining SCO and Conductivity





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:

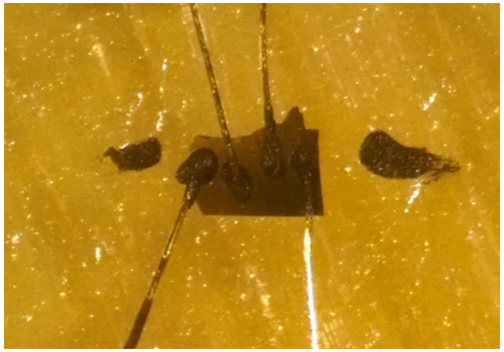
Semiconductors: 10^{-6} – 10^{1} S/cm

"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

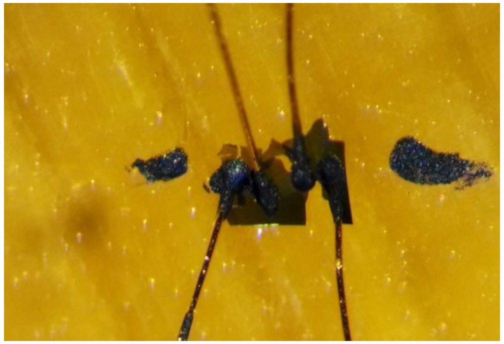
Conductivity Measurements

12 μm gold wire



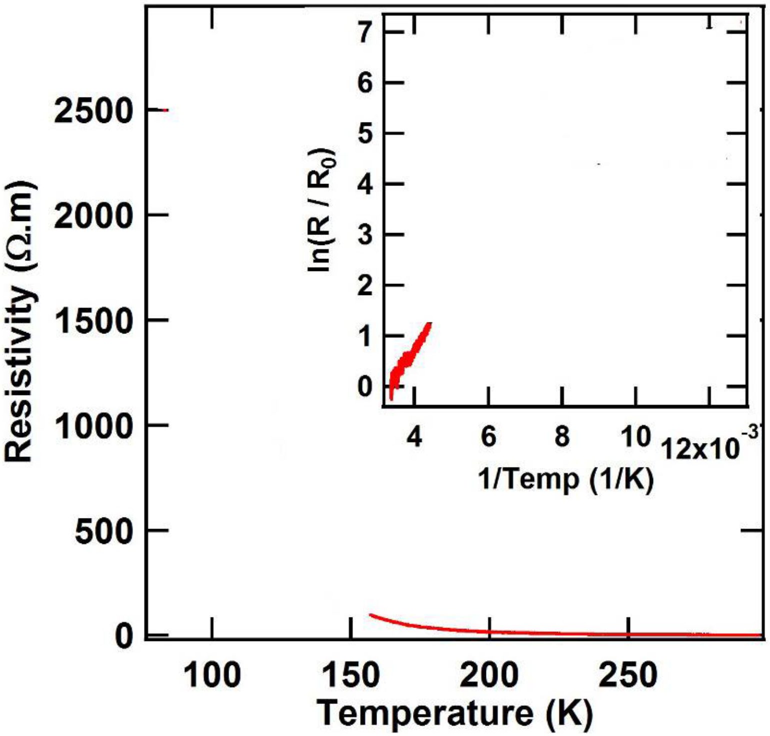
Before Cooldown

After Cooldown



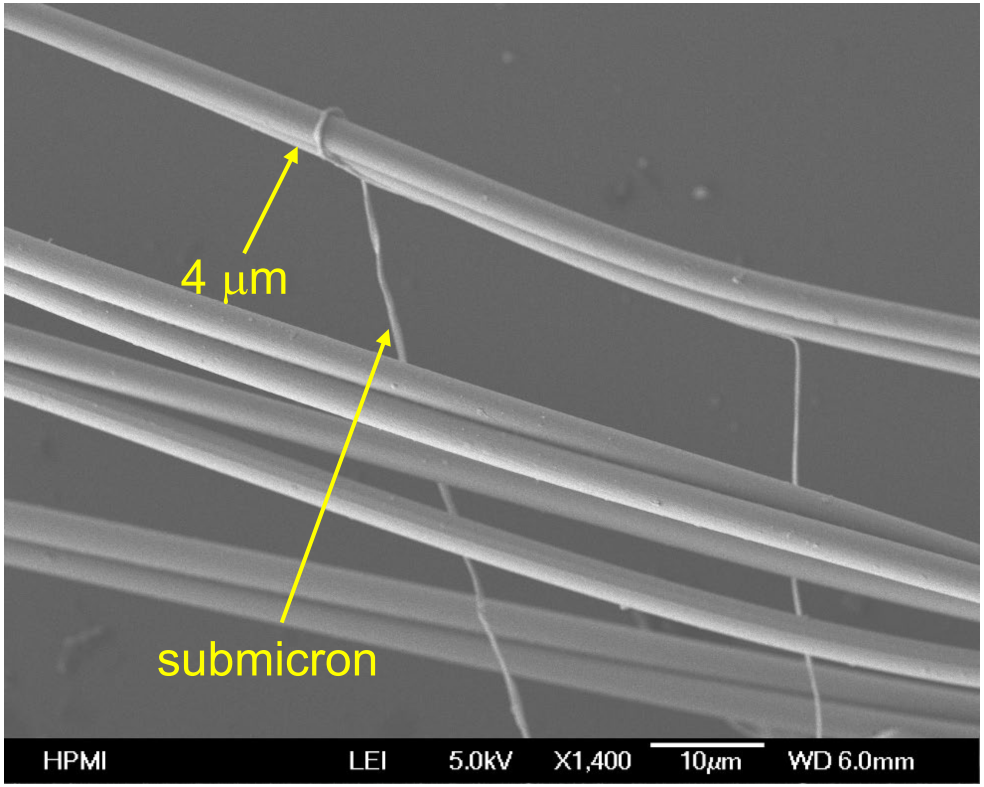
Tiny, brittle, and semi-transparent crystals

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

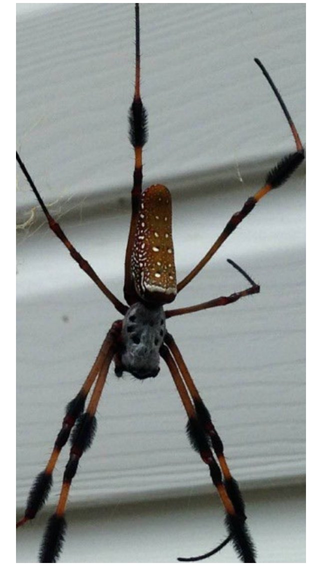


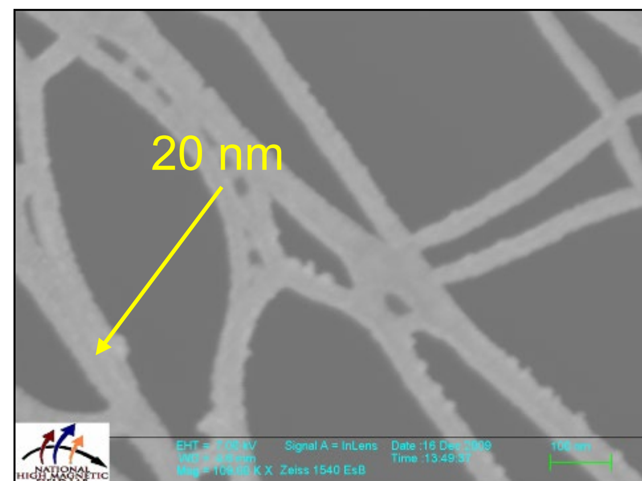
Carbon paste, 4-probe measurement

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

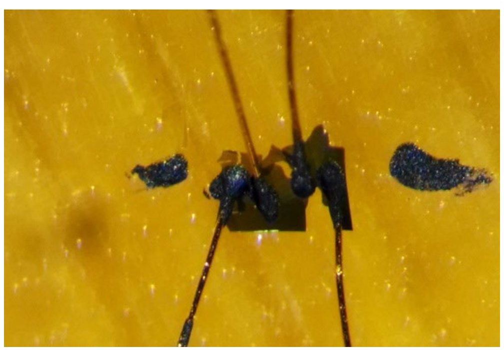
Conductivity Measurements

Tiny, brittle, and semi-transparent crystals

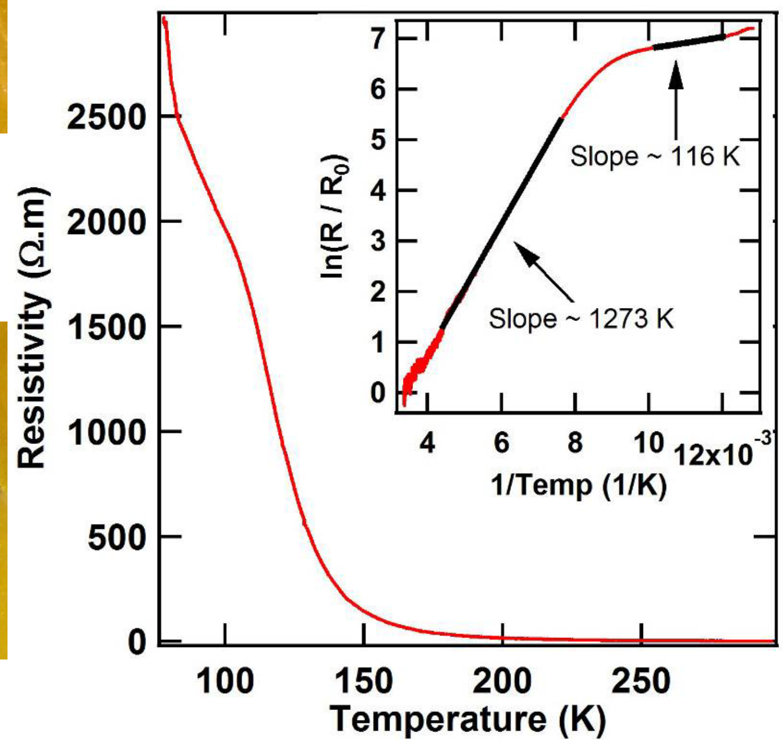
12 μm gold wire

Before Cooldown

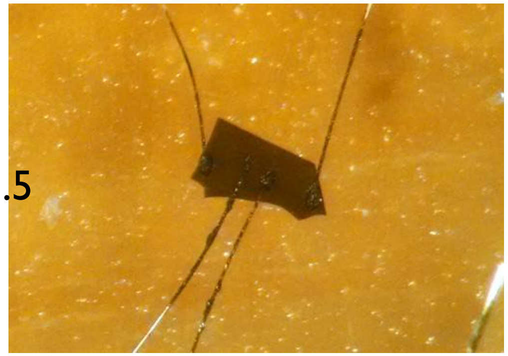
After Cooldown



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



4 μm spider silk wire



Before Cooldown

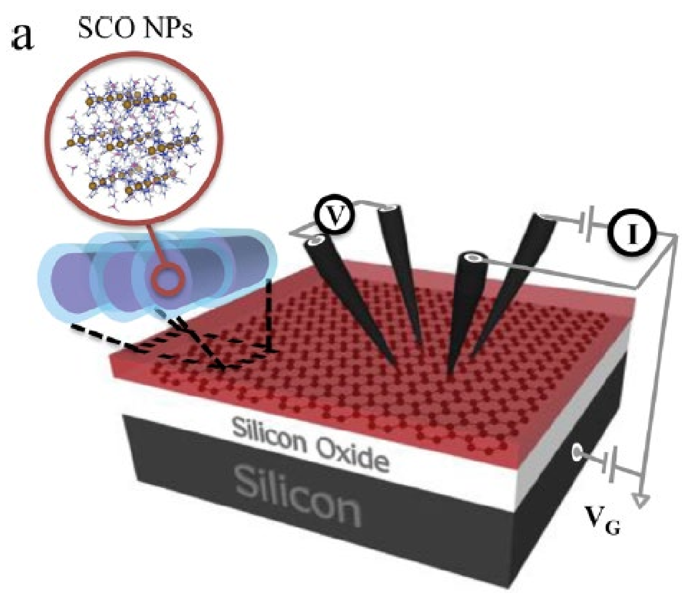
After Cooldown

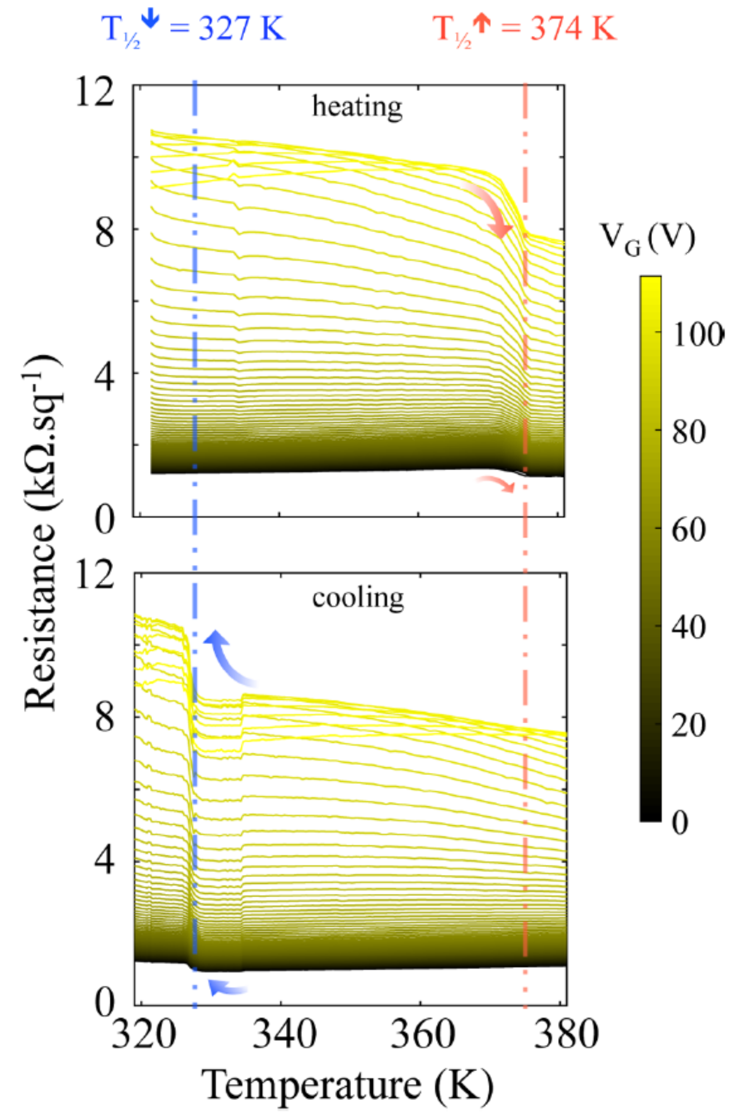
Carbon paste, 4-probe measurement

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





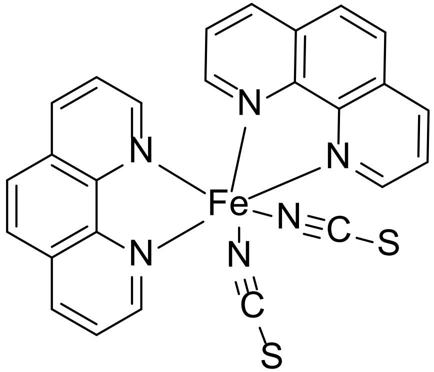
Adapted from: Dugay, J.; Aarts, M.; Gimenez-Marques, M.; Kozlova, T.; Zandbergen, H. W.; Coronado, E.; van der Zant, H. S. J. *Nano Lett.* **2017**, *17*, 186-193

Depositing Molecules on Substrates

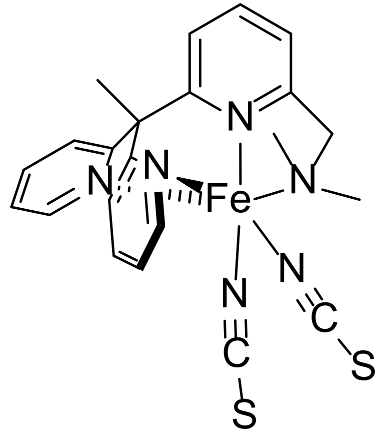
Source ⟶	Solution	Gas Phase	Solid
Generality	High	Moderate	Low(?)
Scalability	High	Moderate	Moderate
Purity	Low	High	Moderate
Requirements			
e-neutrality	n/a	✓	o
solubility	✓	n/a	n/a
volatility	n/a	✓	n/a
thermal stability	o	✓	o
surface stability	✓	✓	o

✓ = required o = desired

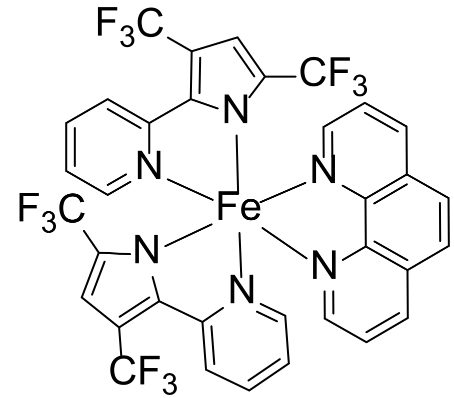
Gas-Phase Deposition of SCO Films



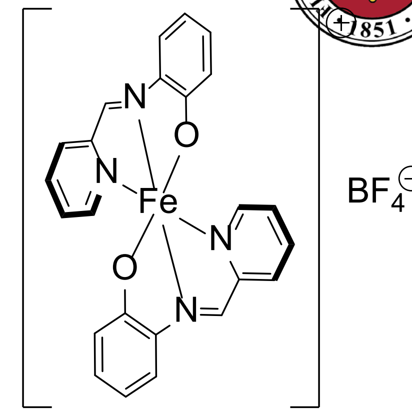
180 °C
10^{-8} mbar



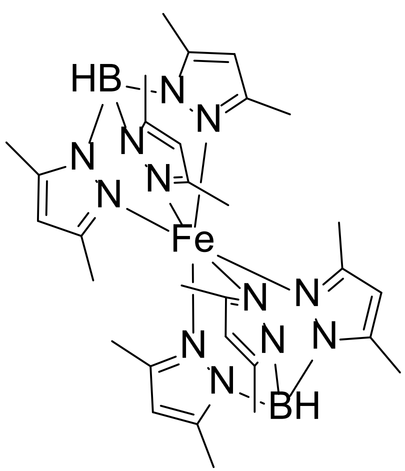
237 °C
10^{-9} mbar



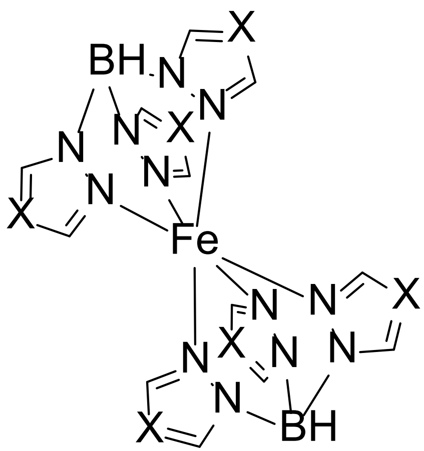
160 °C
10^{-9} mbar



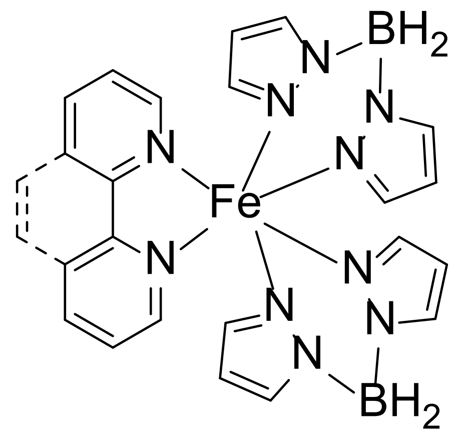
100 °C
10^{-9} mbar



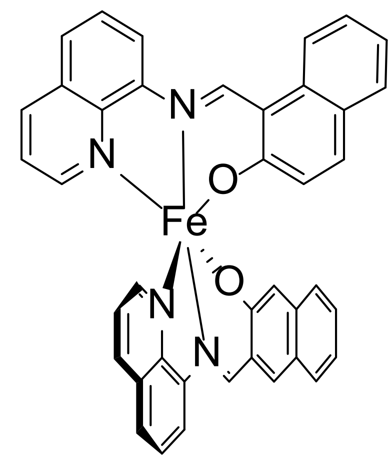
140 °C
10^{-8} mbar



190 °C
10^{-5} mbar



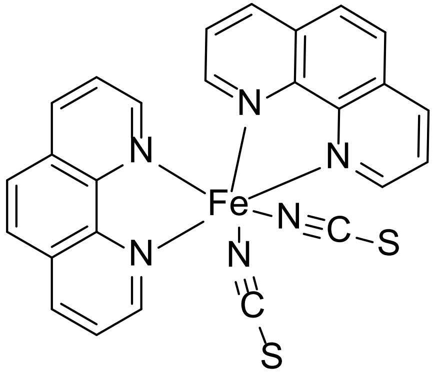
162 °C
10^{-2} mbar



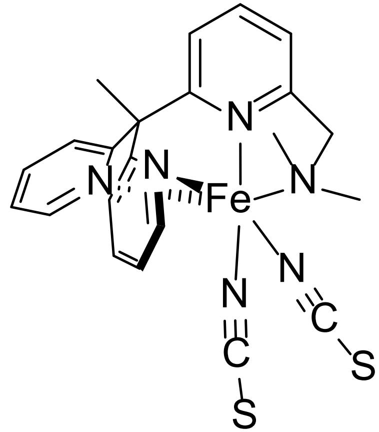
217 °C
10^{-9} mbar

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

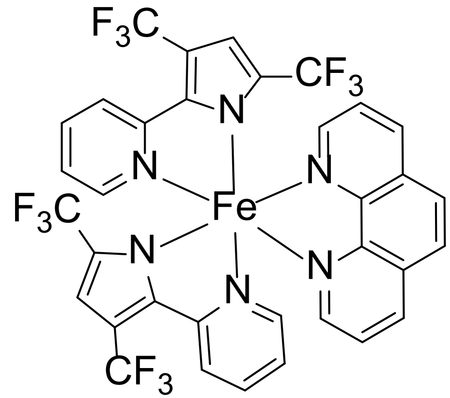
Gas-Phase Deposition of SCO Films



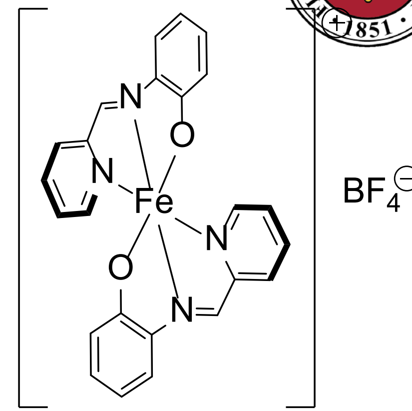
180 °C
10^{-8} mbar



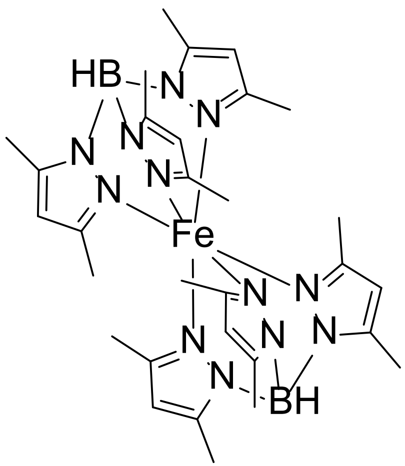
237 °C
10^{-9} mbar



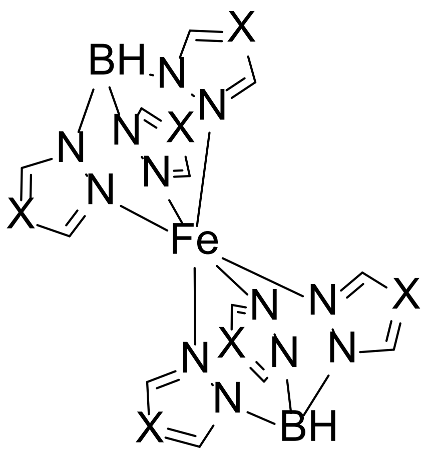
160 °C
10^{-9} mbar



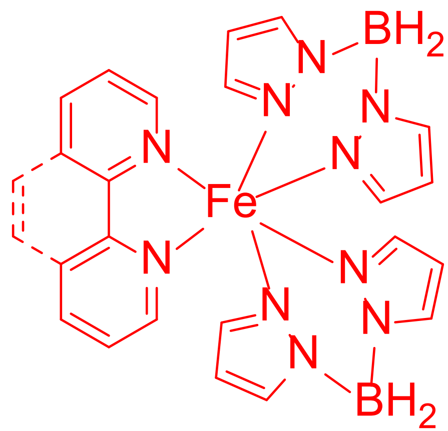
100 °C
10^{-9} mbar



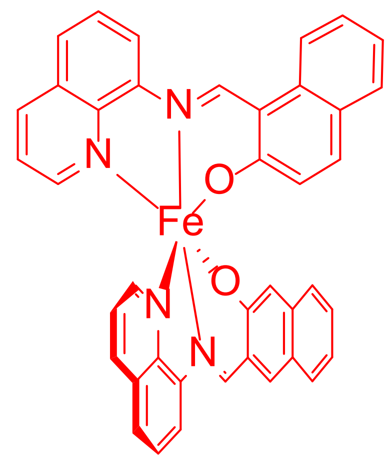
140 °C
10^{-8} mbar



190 °C
10^{-5} mbar



162 °C
10^{-2} mbar



217 °C
10^{-9} mbar

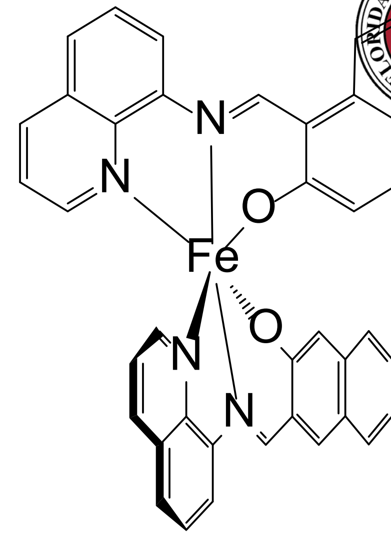
Kumar, K. S.; Ruben, M. *Angew. Chem. Int. Ed.* **2021**, *60*, 7502-7521

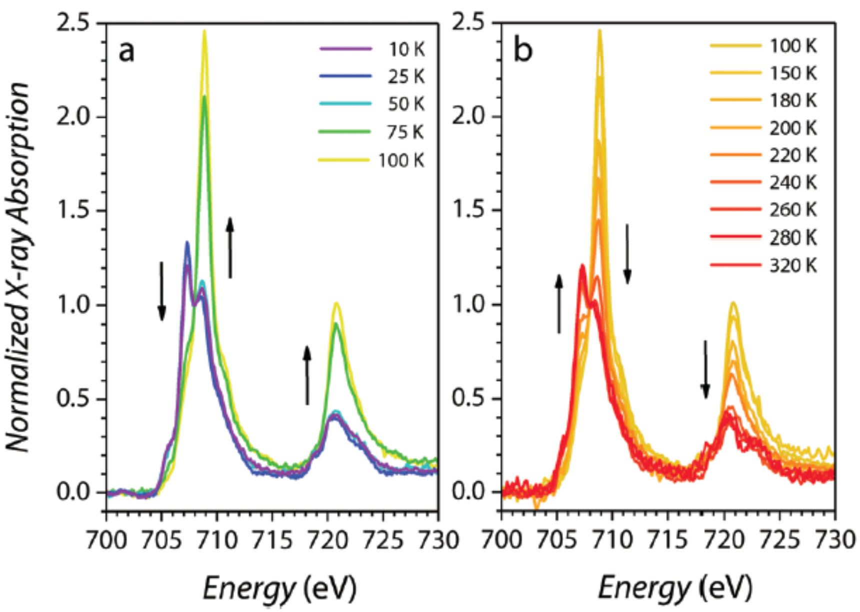
[Fe(qnal)$_2$] on Au(111)

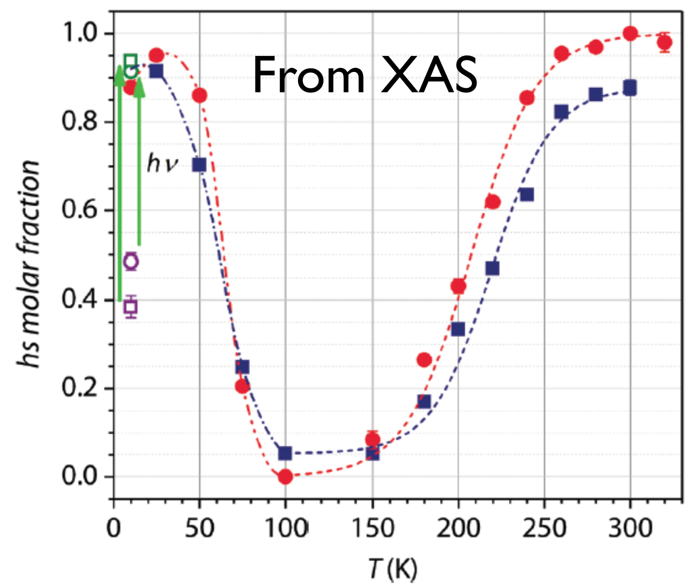
- Thickness: 300 nm
- $T_{1/2}$ similar to bulk
- SCO more gradual
- LIESST effect

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

Methods:
- UV-Vis, XAS







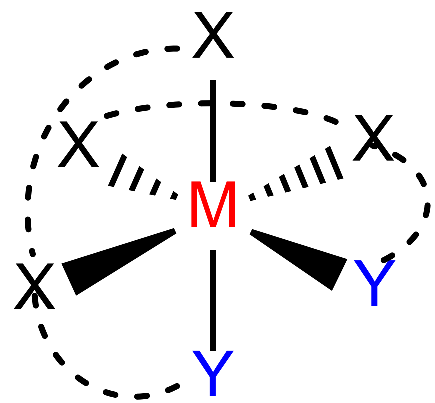
Adapted from: Atrozi, M.; Sessoli, R.; Mannini, M.; et al. *J. Mater. Chem. C* **2018**, *6*, 8885

Molecular Design Challenge

Cooperativity: ***strong*** intermolecular interactions

Volatility: ***weak*** intermolecular interactions

Challenge: increase the volatility while preserving the abrupt spin transition

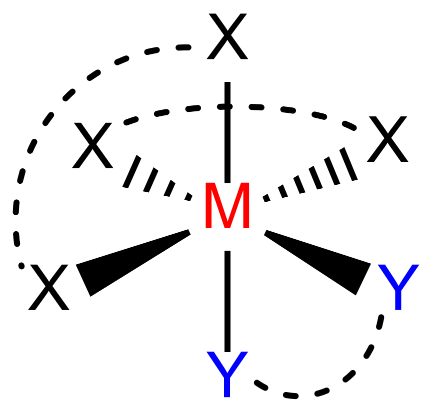


Solution: use asymmetric design by separating the cooperative and "volatilizing" functions

Miguel Gakiya

Criteria:

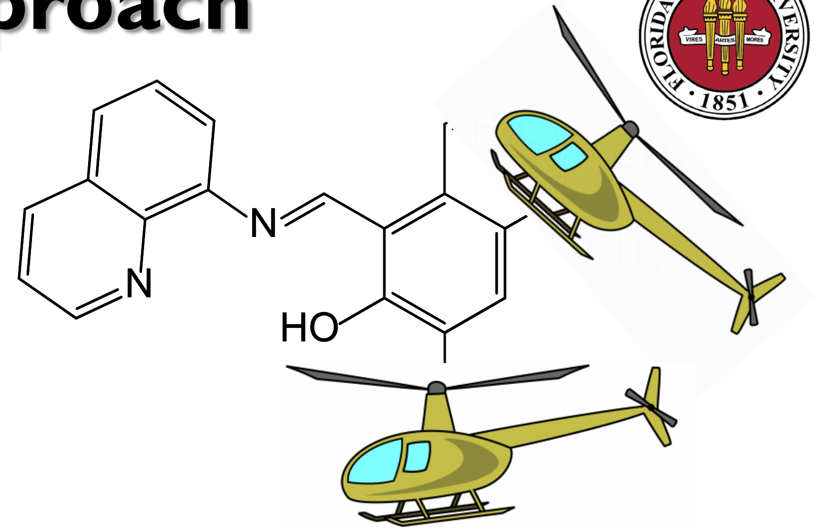
- neutral complexes
- easy synthetic modification
- asymmetric ligand structure
- only chelating (clamping) ligands

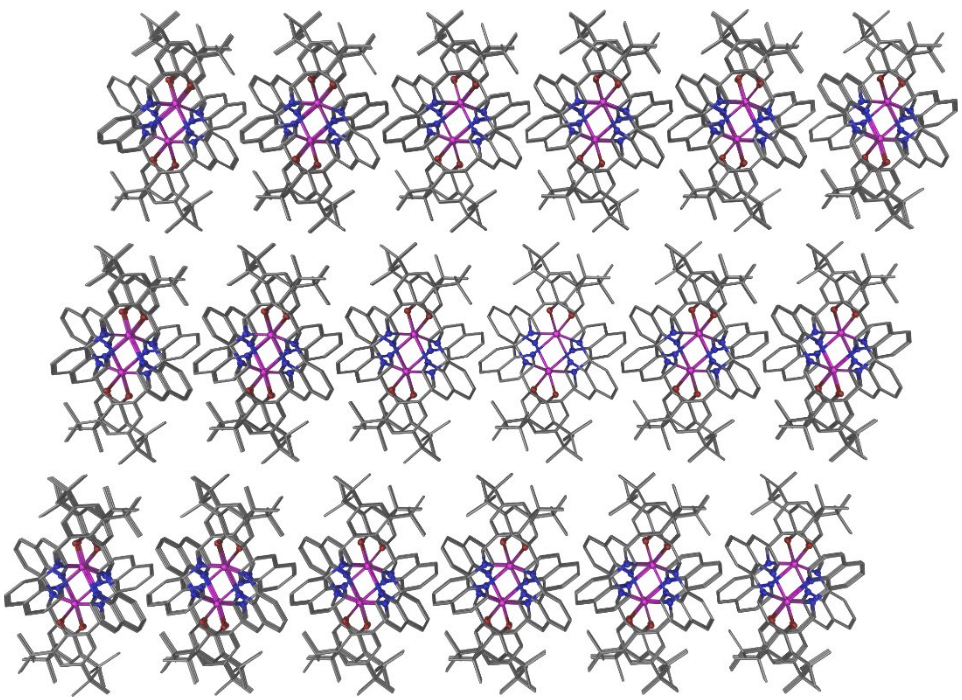


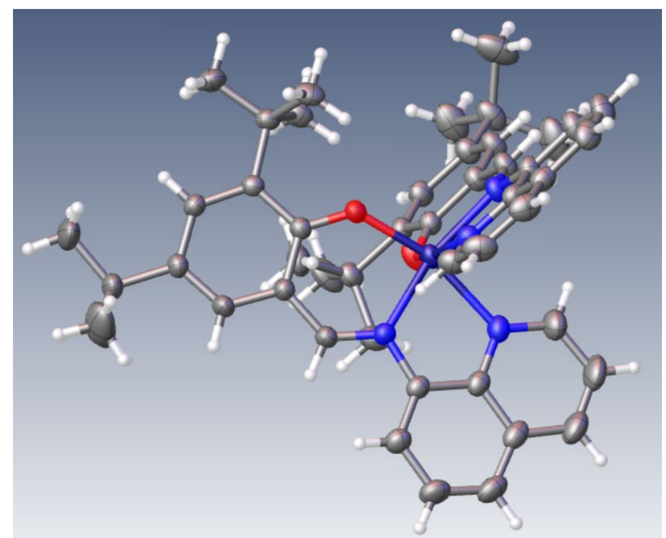
Synthetic Approach

Introduce the asymmetry of interactions to boost volatility

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



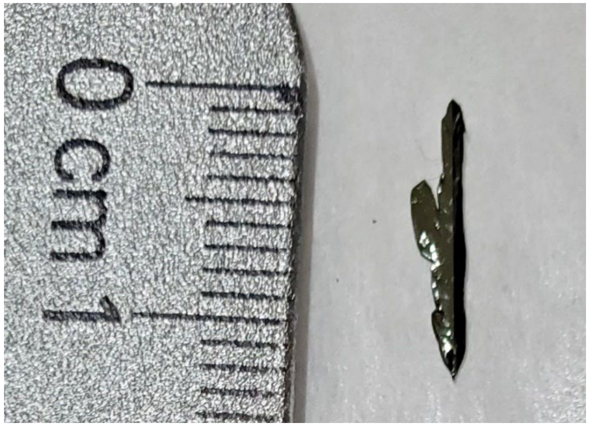




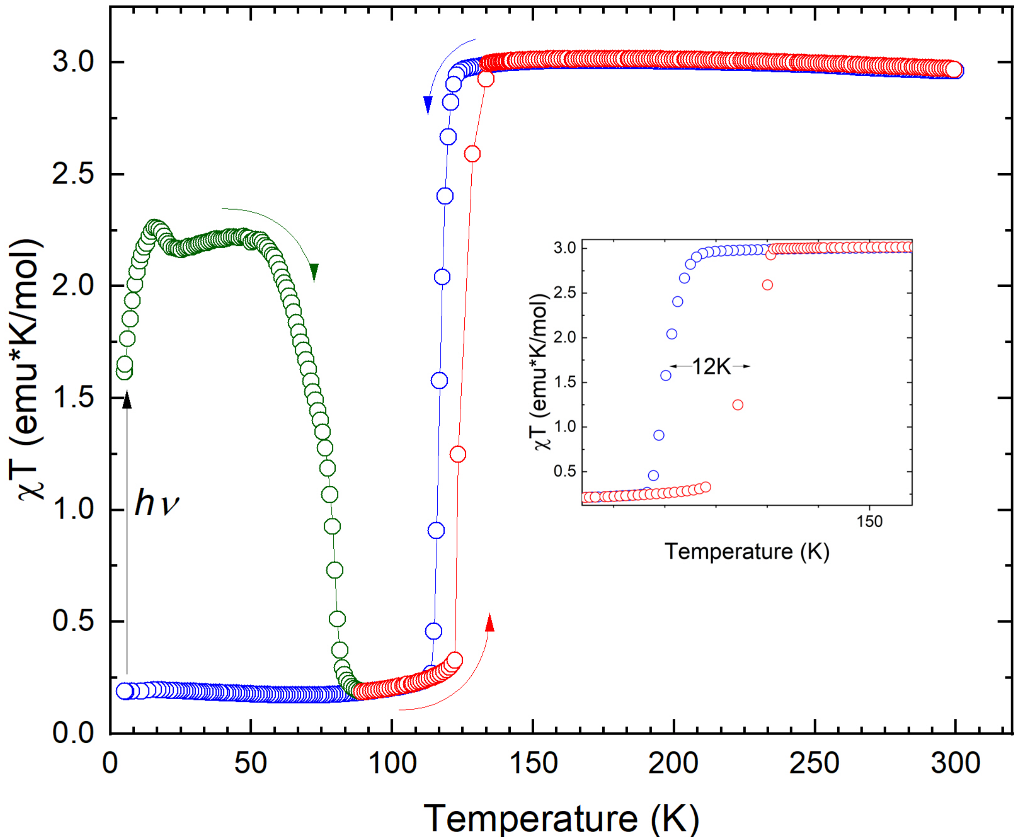
[Fe(tBu$_2$qsal)$_2$]

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$_2$qsal)$_2$]



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



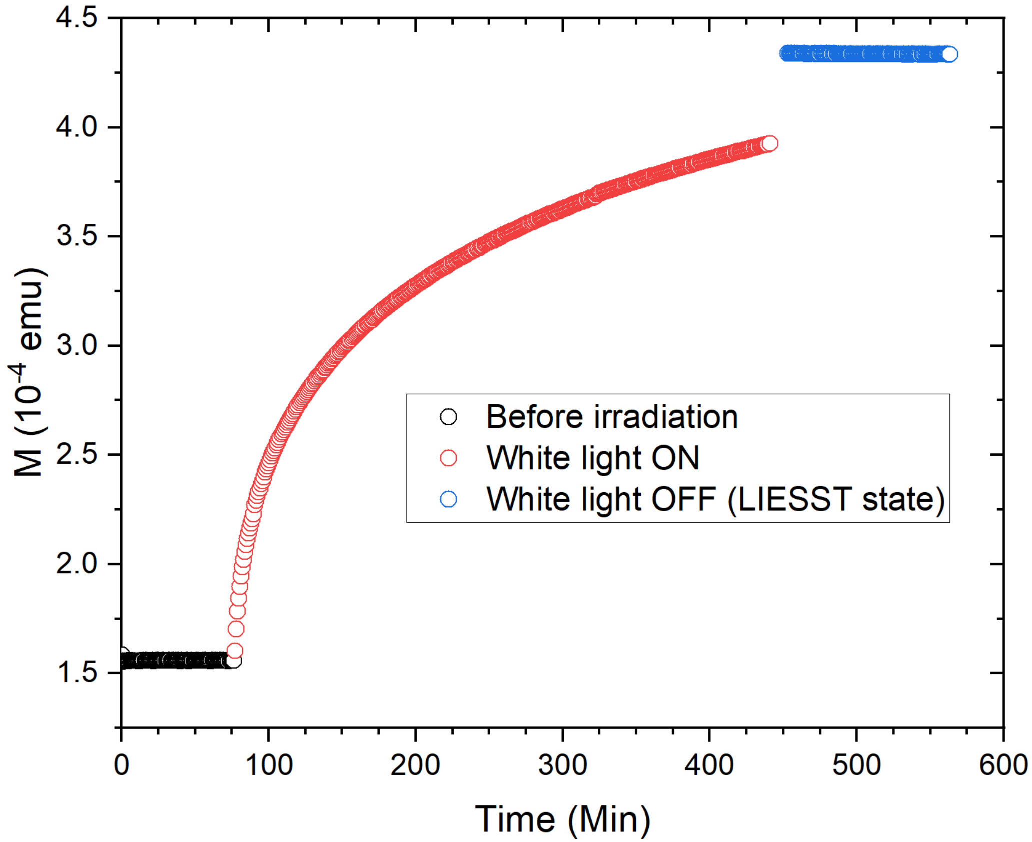
$T_{1/2}$ = 117 K / 129 K
T_{LIESST} = 84 K

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

Photomagnetism of [Fe(tBu$_2$qsal)$_2$]

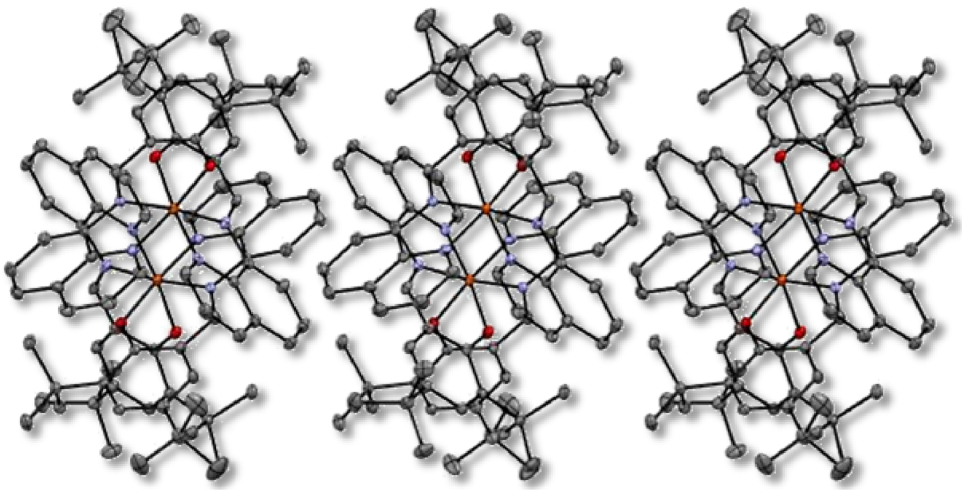
Irradiation with a white Xe lamp at 5 K

Note the increase in magnetization after the lamp is turned off: an indication of slight sample cooling

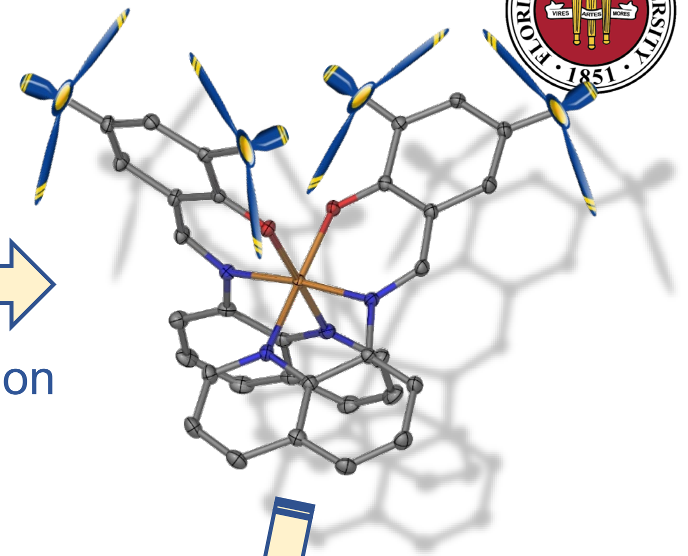


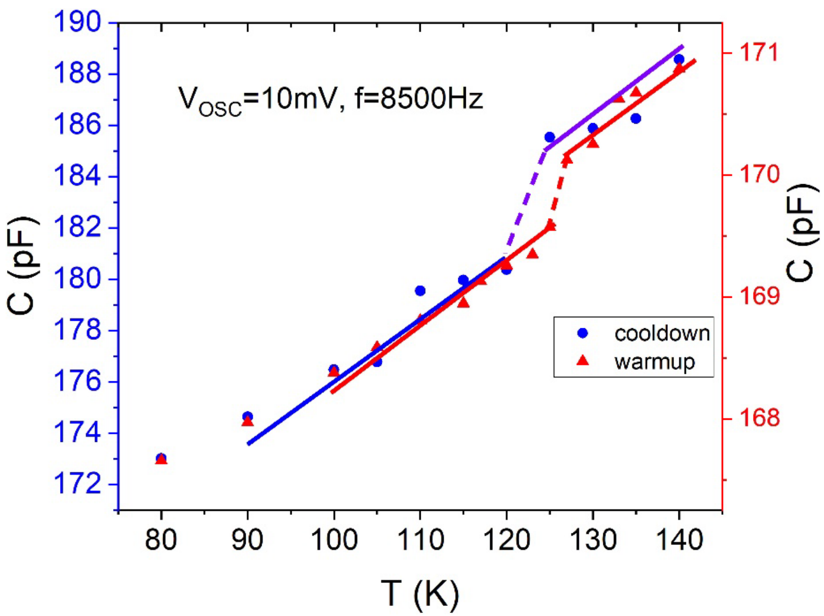
Gakiya-Teruya, M.; Jiang, X.; Le. D.; Rahman, T. S.; Hebard, A. F.; Shatruk, M.; et al. *J. Am. Chem. Soc.* **2021**, *143*, 14563-14572

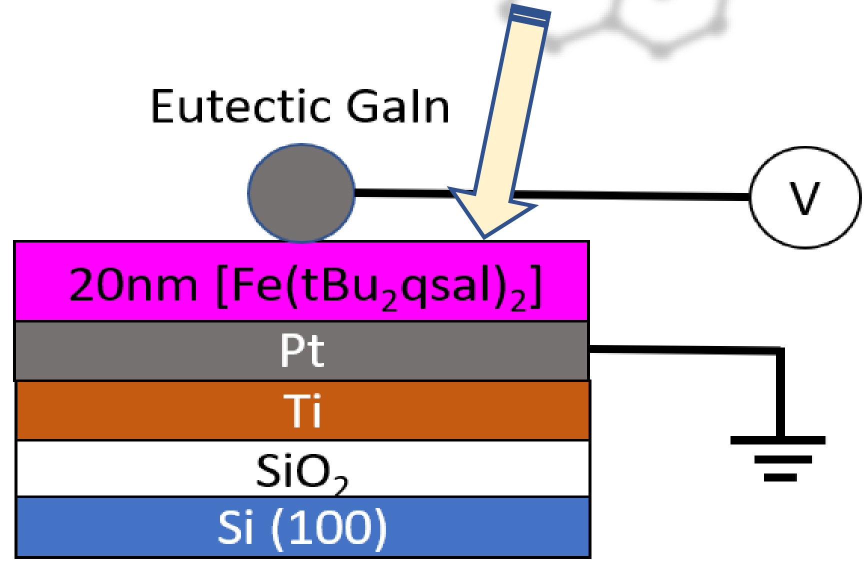
Thin-Film Capacitor



Sublimation



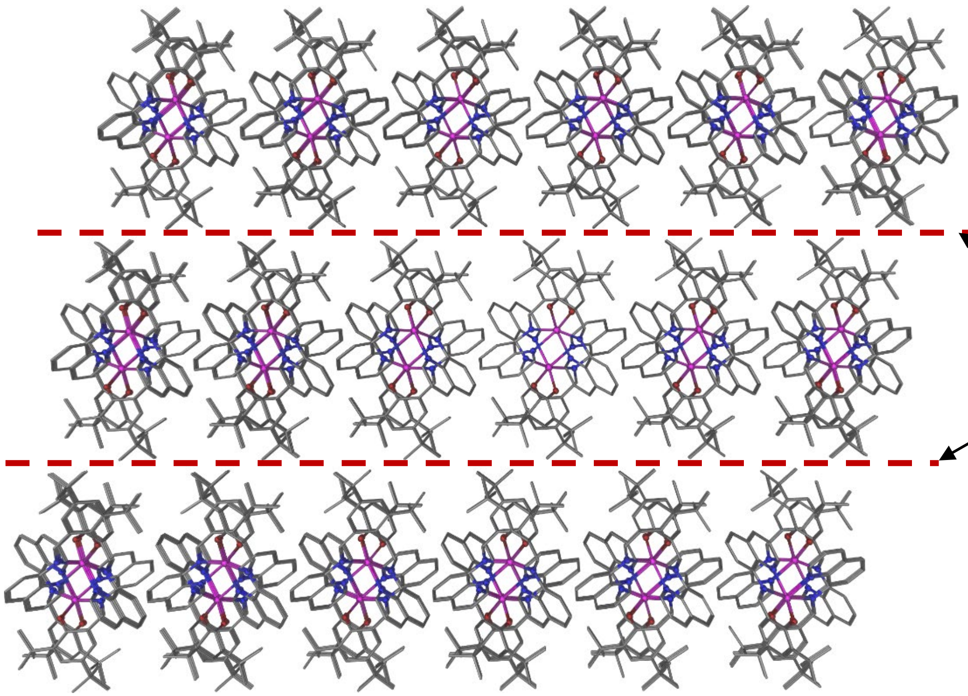


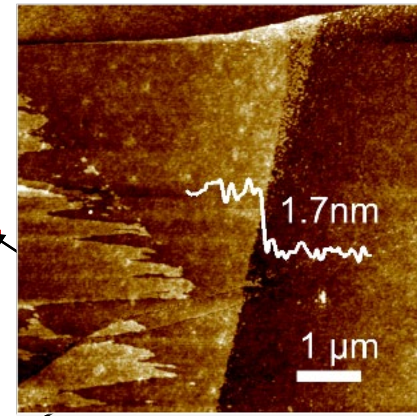


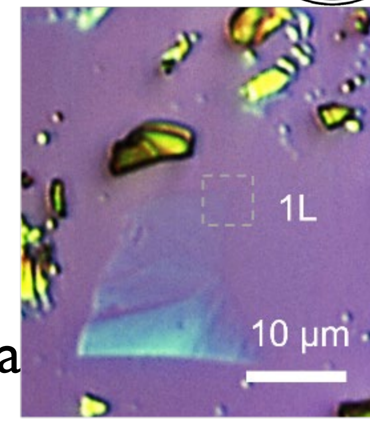
$T_{1/2} \approx 122\ K / 127\ K$

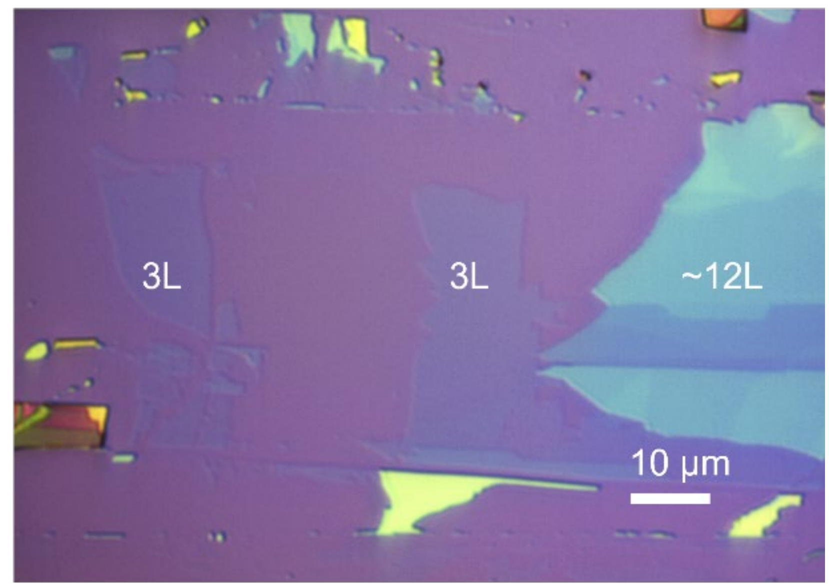
Gakiya-Teruya, M.; Jiang, X.; Le. D.; Rahman, T. S.; Hebard, A. F.; Shatruk, M.; et al. *J. Am. Chem. Soc.* **2021**, *143*, 14563-14572

Mechanical Exfoliation







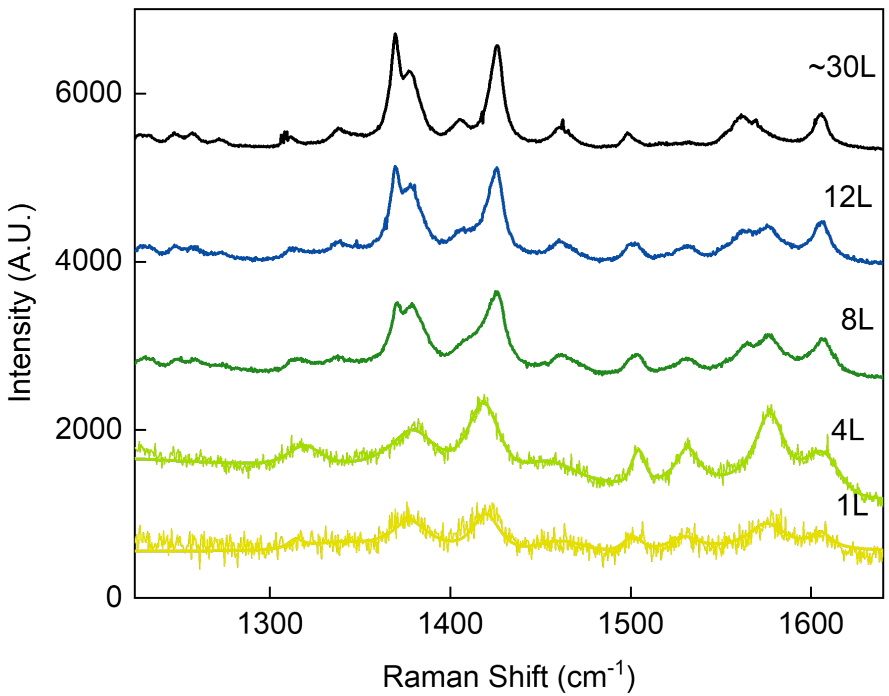


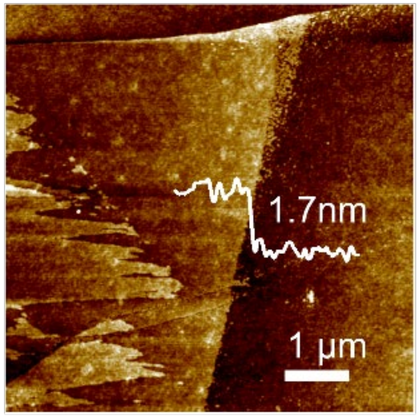
<u>Mechanical exfoliation</u>:

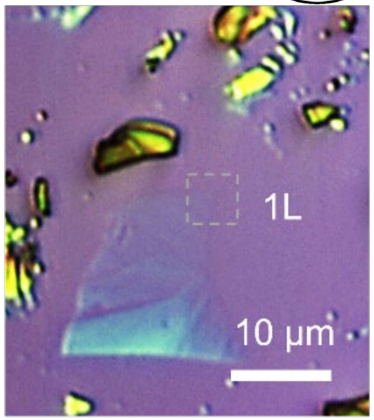
Successful exfoliation down to a single molecular layer (1.7 nm thickness)

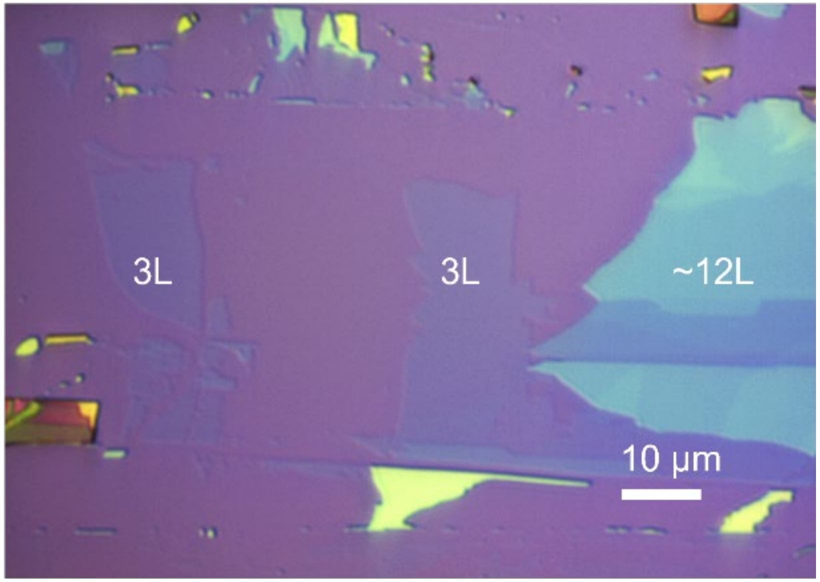
Koptur-Palenchar, J. J.; Gakiya-Teruya, M.; Shatruk, M.; Zhang, X. X; et al. *npj 2D Mater. Appl.* **2022**, *6*, 59

Mechanical Exfoliation









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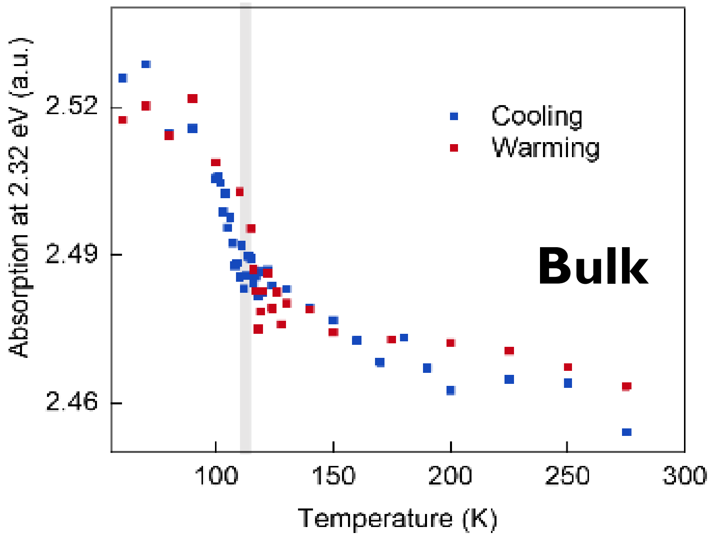
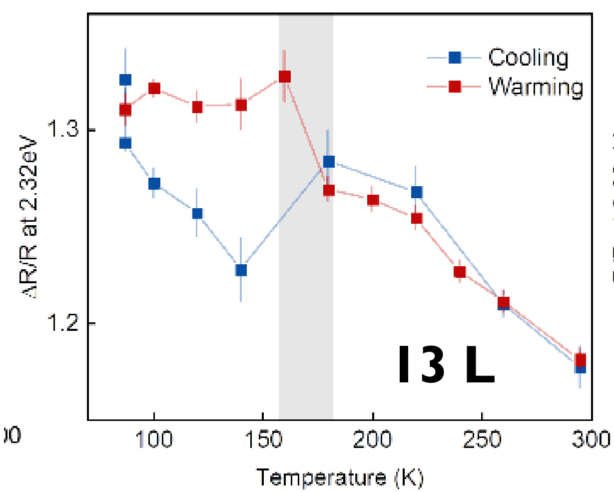
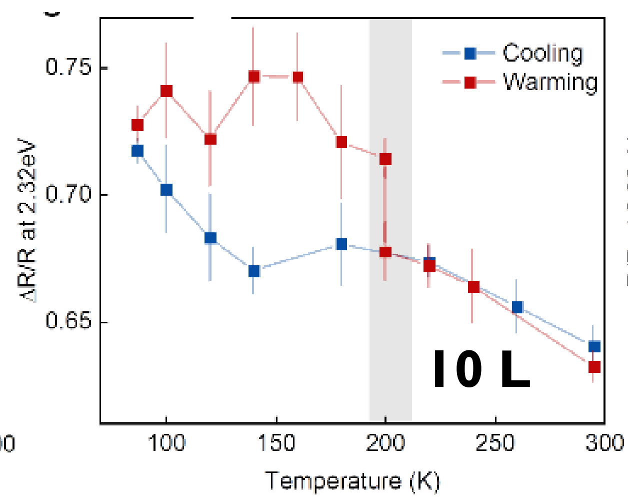
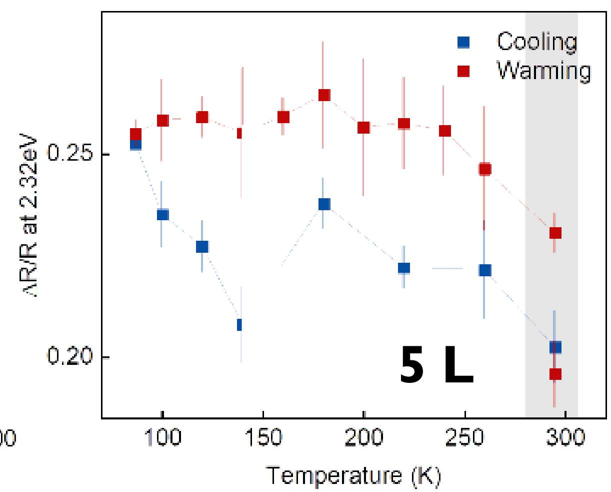
Thickness Dependence of SCO



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

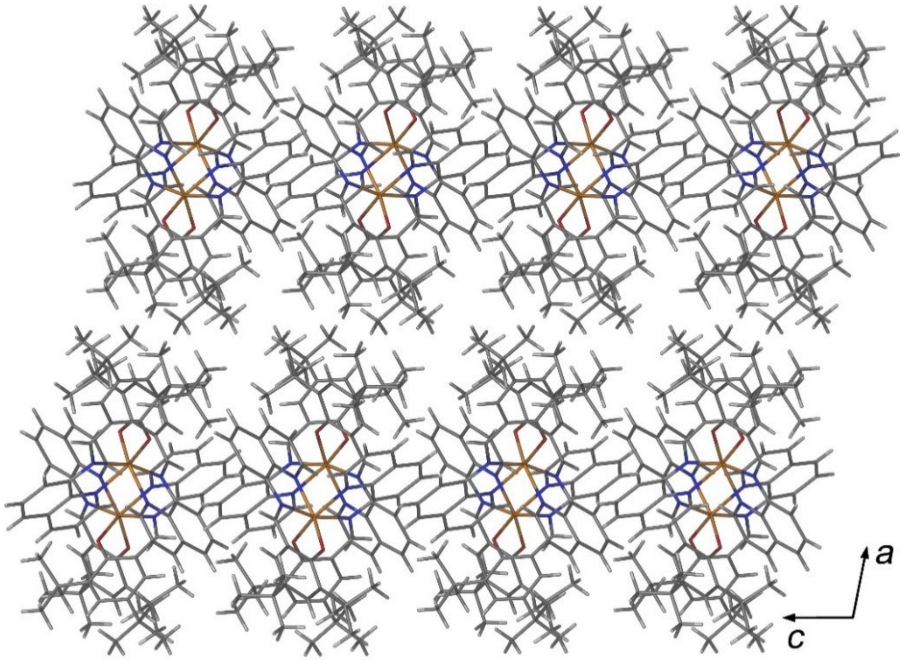


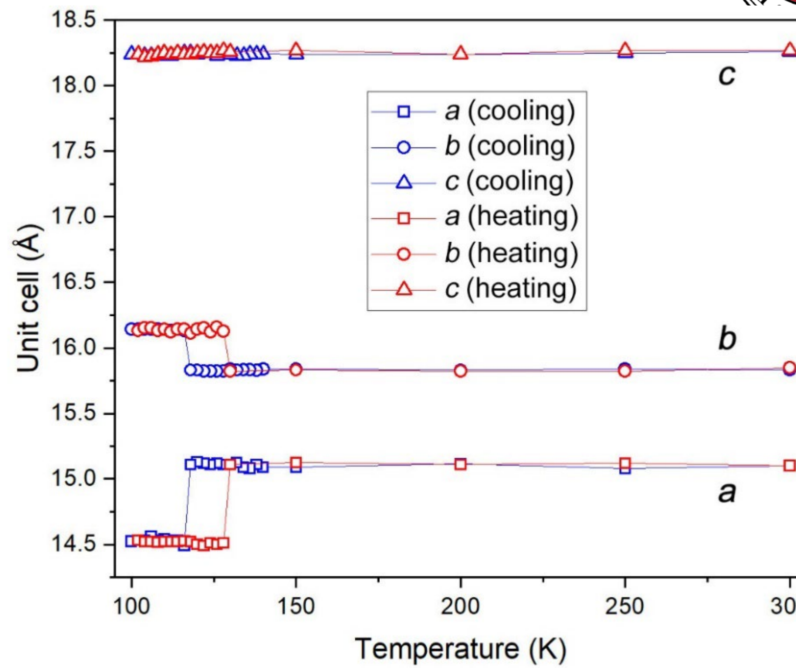




Koptur-Palenchar, J. J.; Gakiya-Teruya, M.; Shatruk, M.; Zhang, X. X; et al. *npj 2D Mater. Appl.* **2022**, *6*, 59

Thickness Dependence of SCO





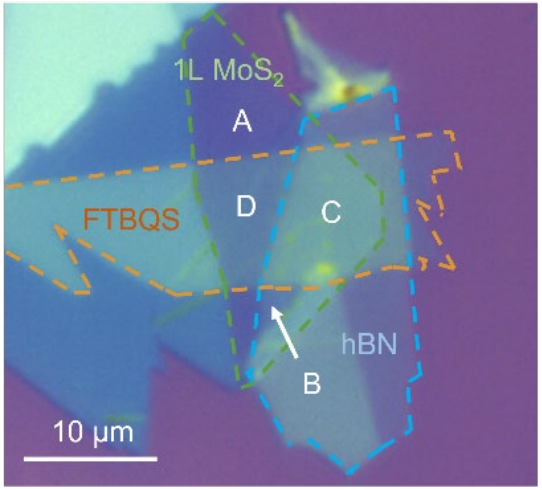
# of layers	$\Delta T_{1/2}$
Bulk	12 K
13	~45 K
10	~90 K
5	~200 K

Hypothesized reason:

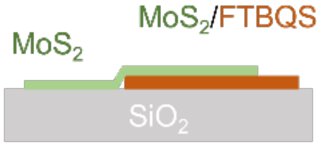
- Interfacial strain combined with the restriction of domain wall motion

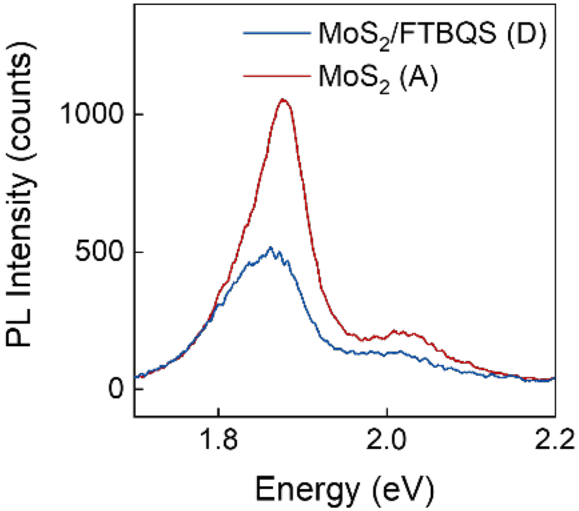
Koptur-Palenchar, J. J.; Gakiya-Teruya, M.; Shatruk, M.; Zhang, X. X; et al. *npj 2D Mater. Appl.* **2022**, *6*, 59

2D Heterostructures

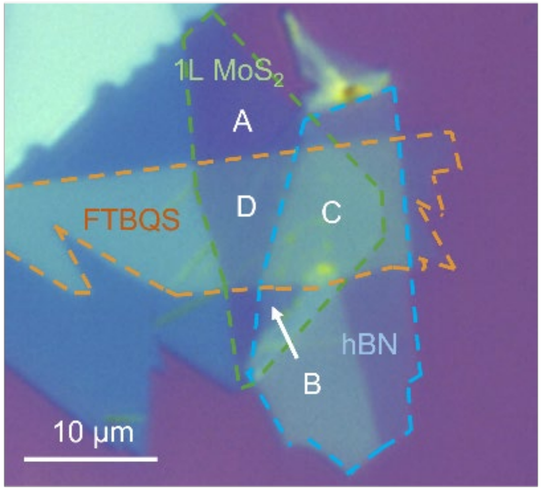


Assembled by the PDMS stamp method





2D Heterostructures



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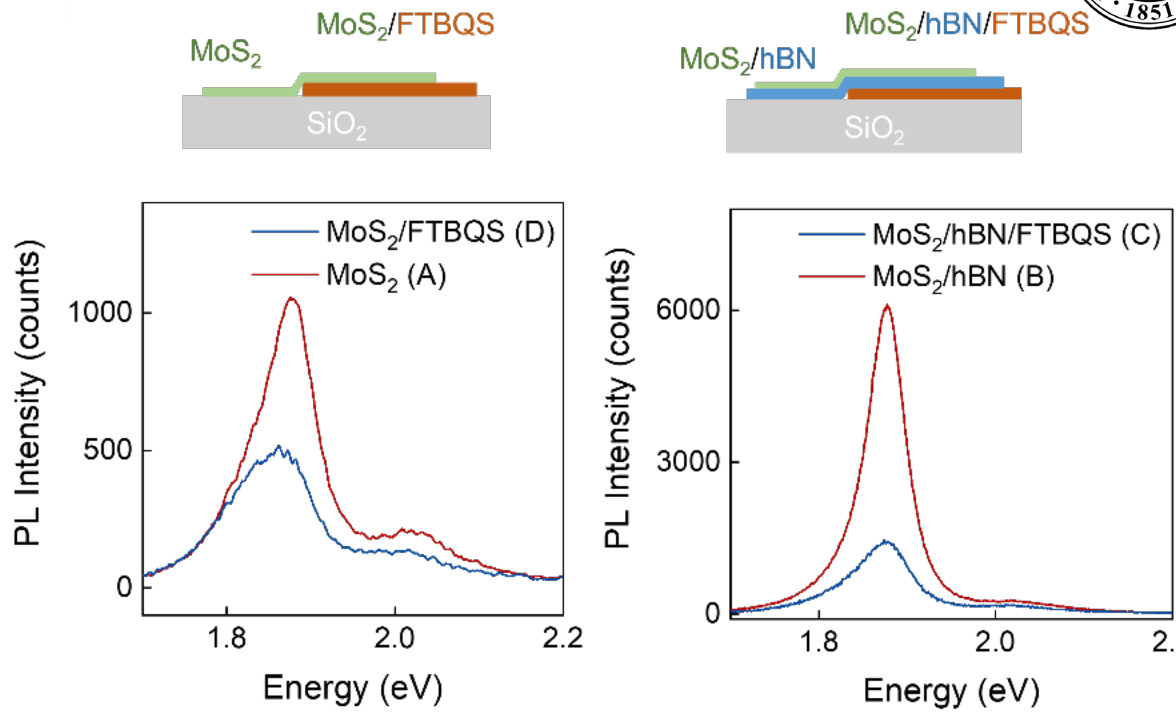
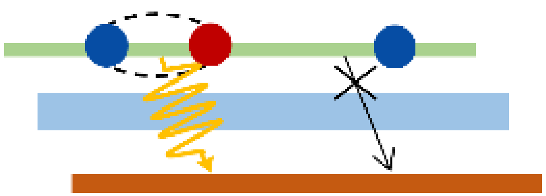
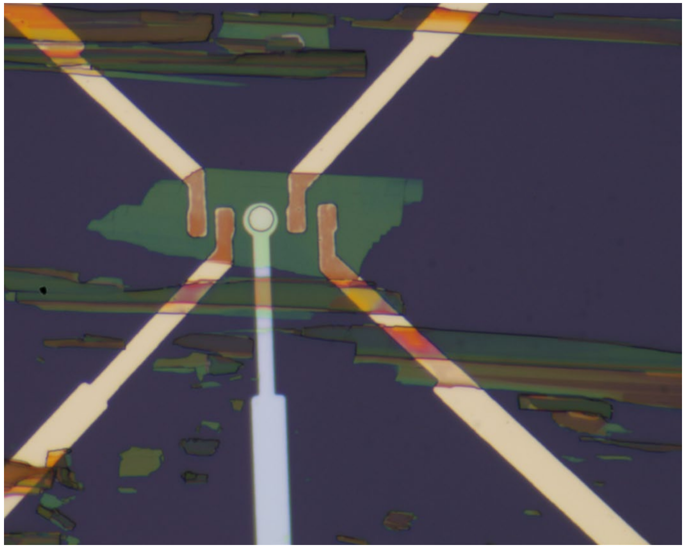




1L MoS_2
hBN
FTBQS

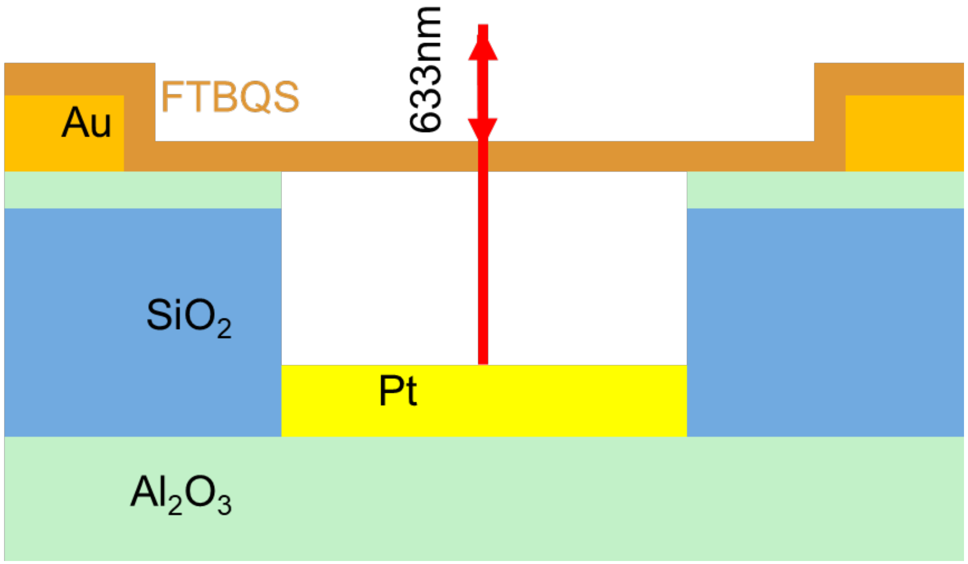
- Charge transfer blocked by hBN
- The Förster energy transfer still allowed

Nanomechanical Resonator

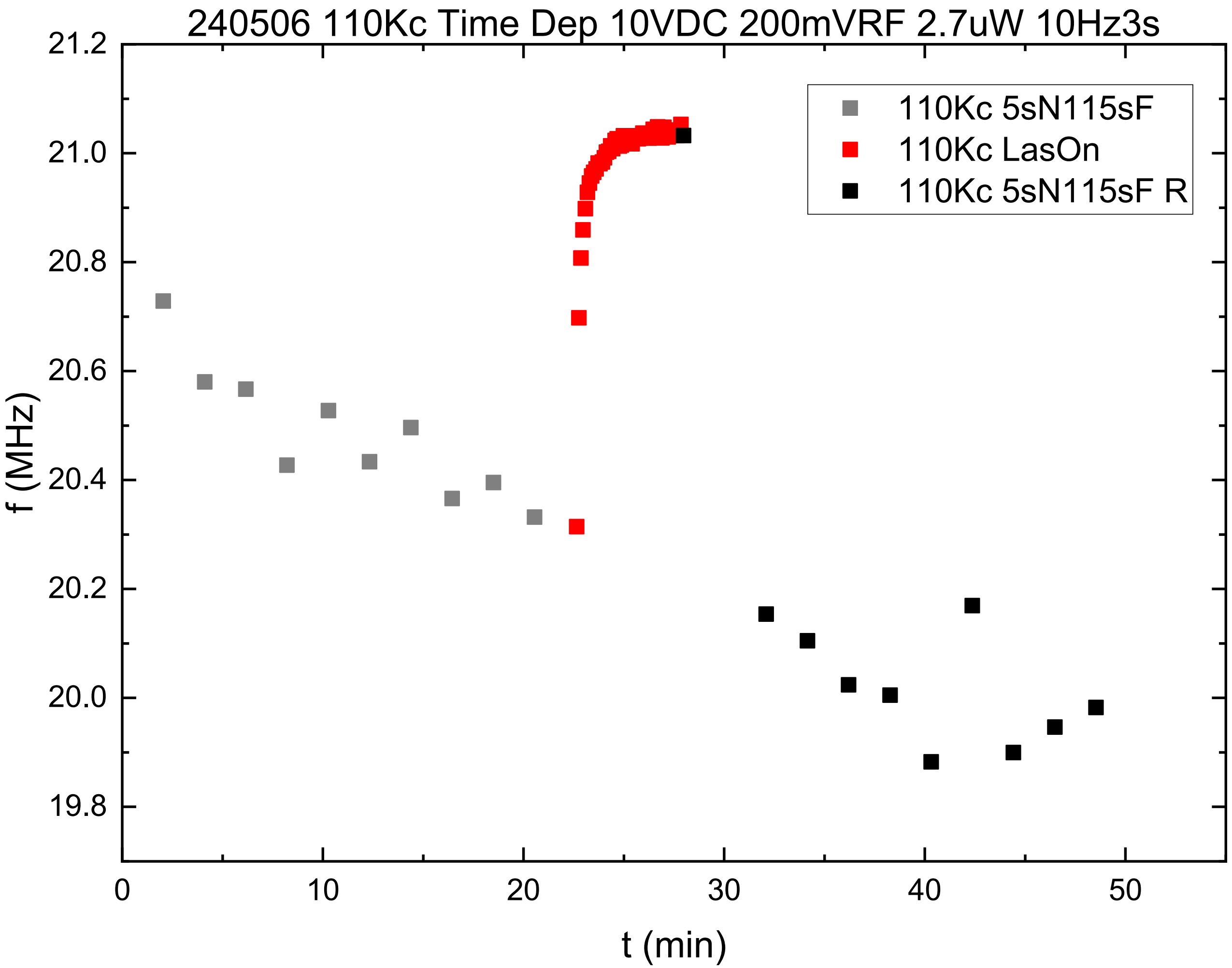


Changes in distance from membrane to backgate change device reflectivity

Resonant motion = max. Δ reflectance



Nanomechanical Resonator



Rapid LS → HS transition
upon irradiation at 110 K

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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Prof. Xiao-Xiao Zhang
and John Koptur-Palenchar
(University of Florida)