Principles of Materials Design for Efficient Spin-State Switching in Ultrathin Layers

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Outline

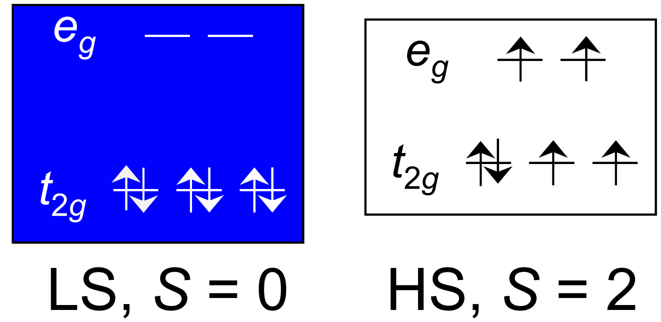
- ❖ Spin Crossover: Quick Introduction
- ❖ Spin Crossover at Nanoscale
  - Thin films
  - Ultrathin films
  - Single molecules
- ❖ Spin Crossover Films via Gas Phase
- ❖ Spin Crossover Films via Exfoliation

Intro: Spin Crossover

Entropy driven transition

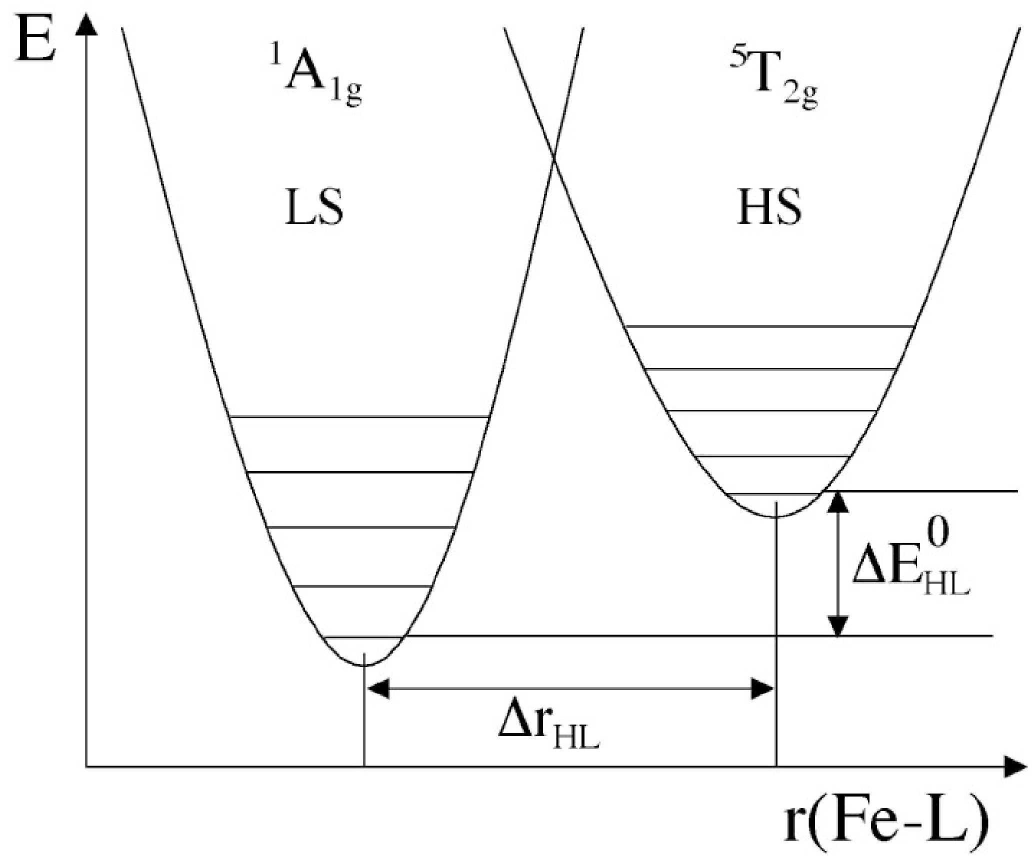
Observed for d^4, d^5, d^6, d^7 ions

Triggered by changes in temperature, pressure, or photoexcitation



Dramatic changes in:

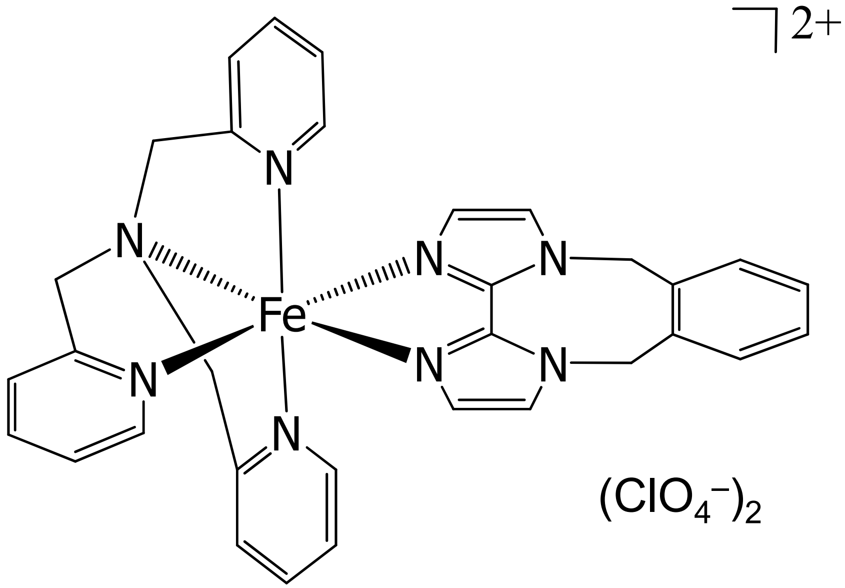
- magnetic moment
- **M-L bond lengths**
- **absorption spectrum (color)**



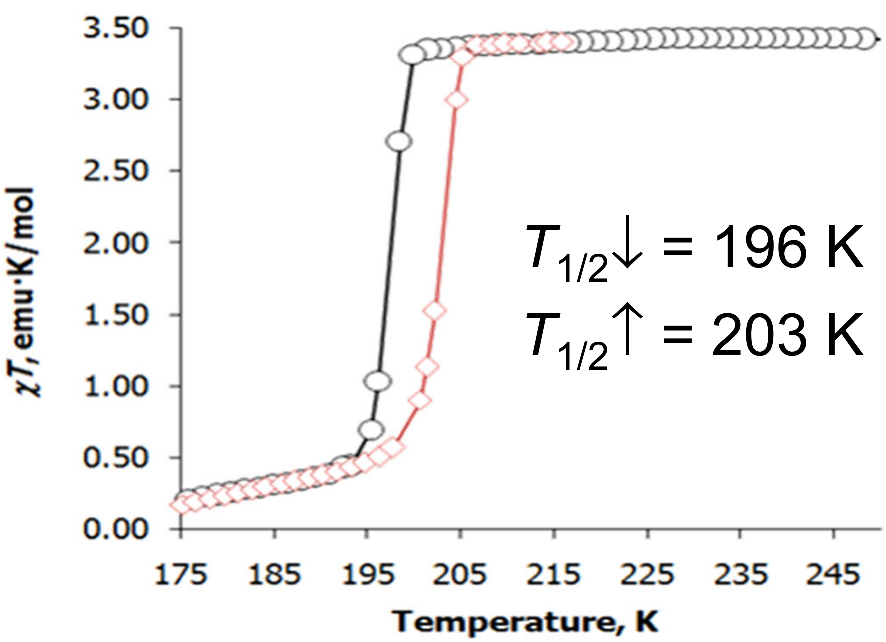
The pronounced structural and optical changes make SCO materials appealing for practical applications

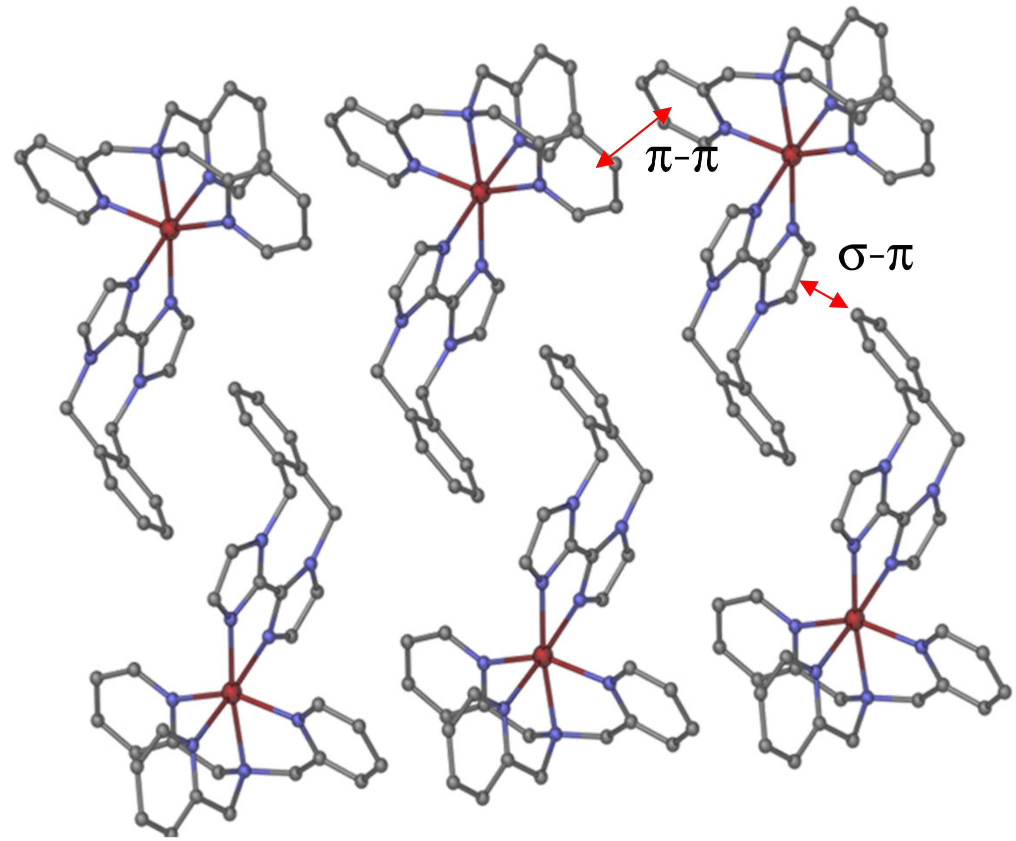
Shatruk, M.; Phan, H.; et al. *Coord. Chem. Rev.* **2015**, *289-290*, 62
Kumar, K. S.; Ruben, M. *Coord. Chem. Rev.* **2017**, *346*, 176

Spin Crossover: Example



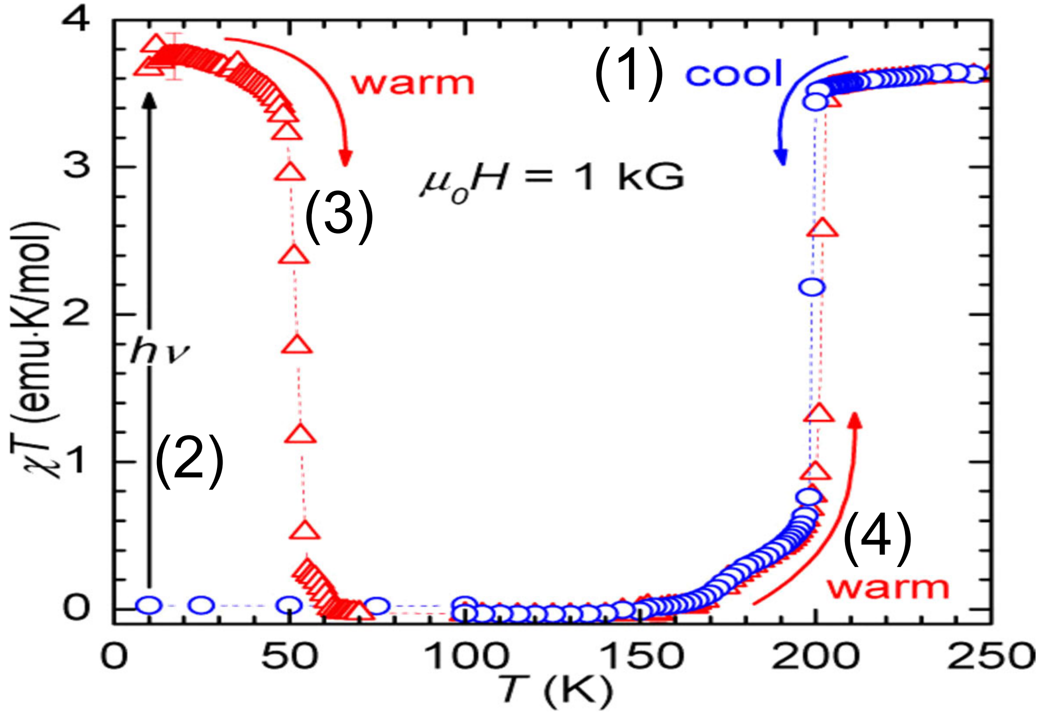
$d(Fe\text{-}N)_{av}$, Å	
123 K (LS)	210 K (HS)
2.002(4)	2.184(4)

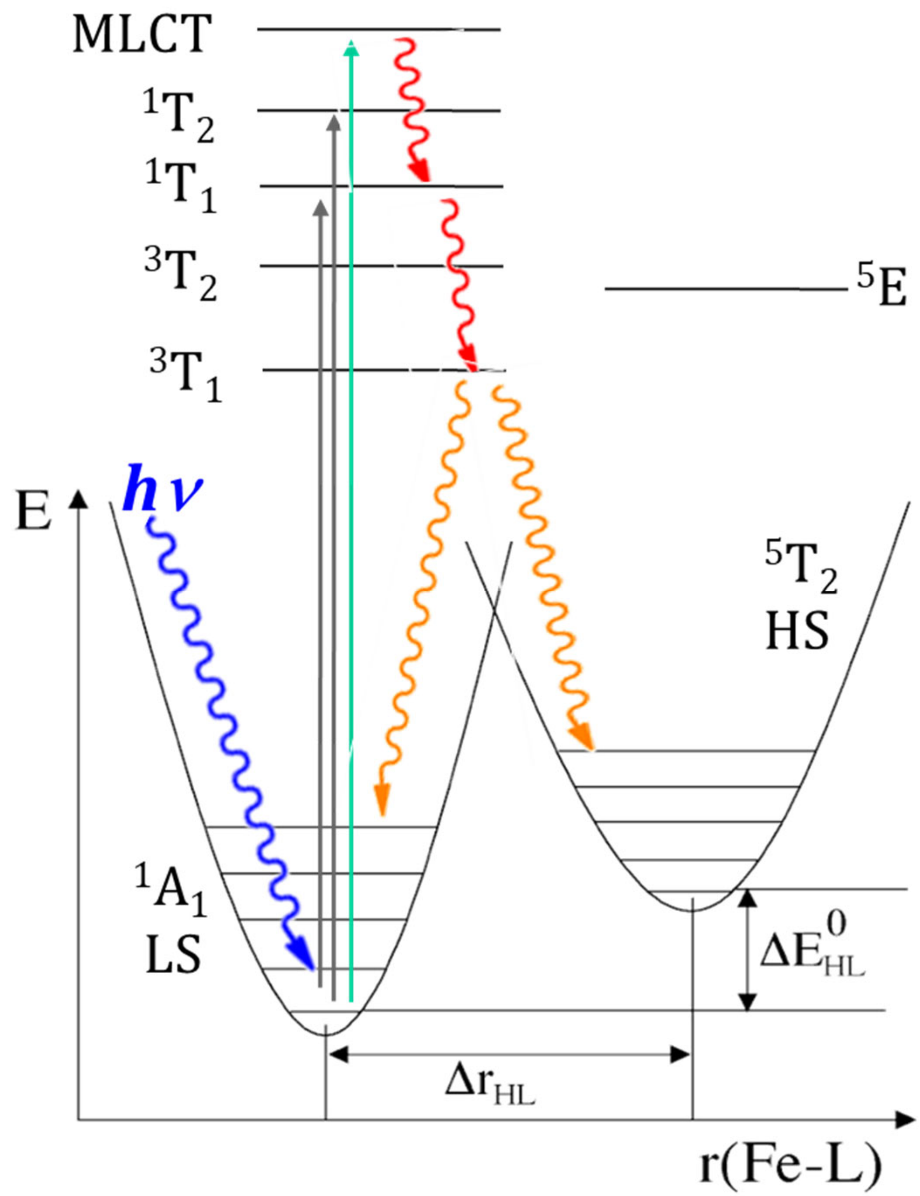




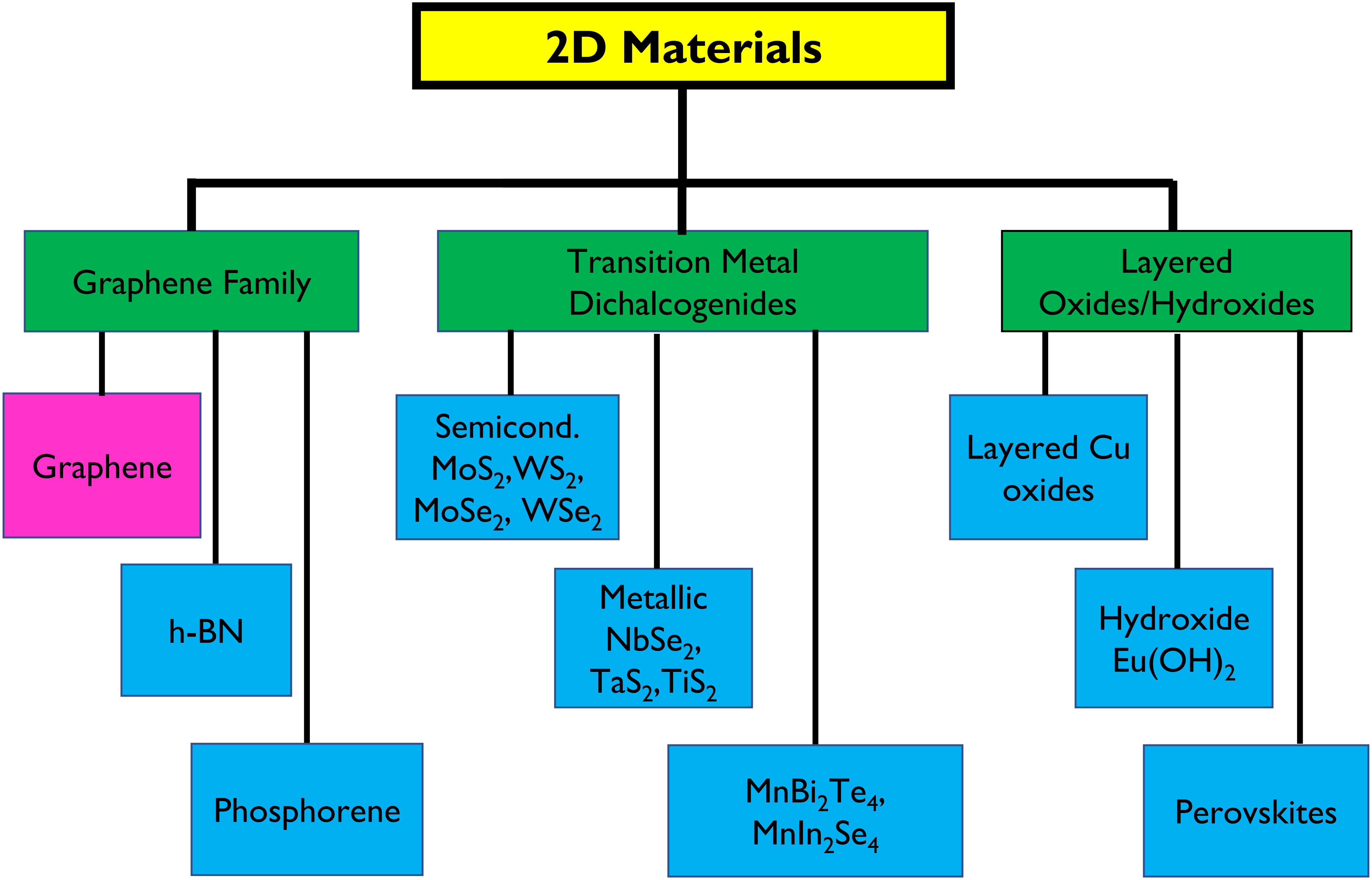
Phan, H.; Chakraborty, P.; Hauser, A.; Shatruk, M.; et al. *Chem. Eur. J.* **2012**, *18*, 15805

Multi-Channel Switching





Phan, H.; Chakraborty, P.; Hauser, A.; Shatruk, M.; et al. *Chem. Eur. J.* **2012**, *18*, 15805



2D Materials
Graphene Family
Transition Metal Dichalcogenides
Layered Oxides/Hydroxides
Graphene
h-BN
Phosphorene
Semicond. MoS_2, WS_2, $MoSe_2$, WSe_2
Metallic $NbSe_2$, TaS_2, TiS_2
$MnBi_2Te_4$, $MnIn_2Se_4$
Layered Cu oxides
Hydroxide $Eu(OH)_2$
Perovskites

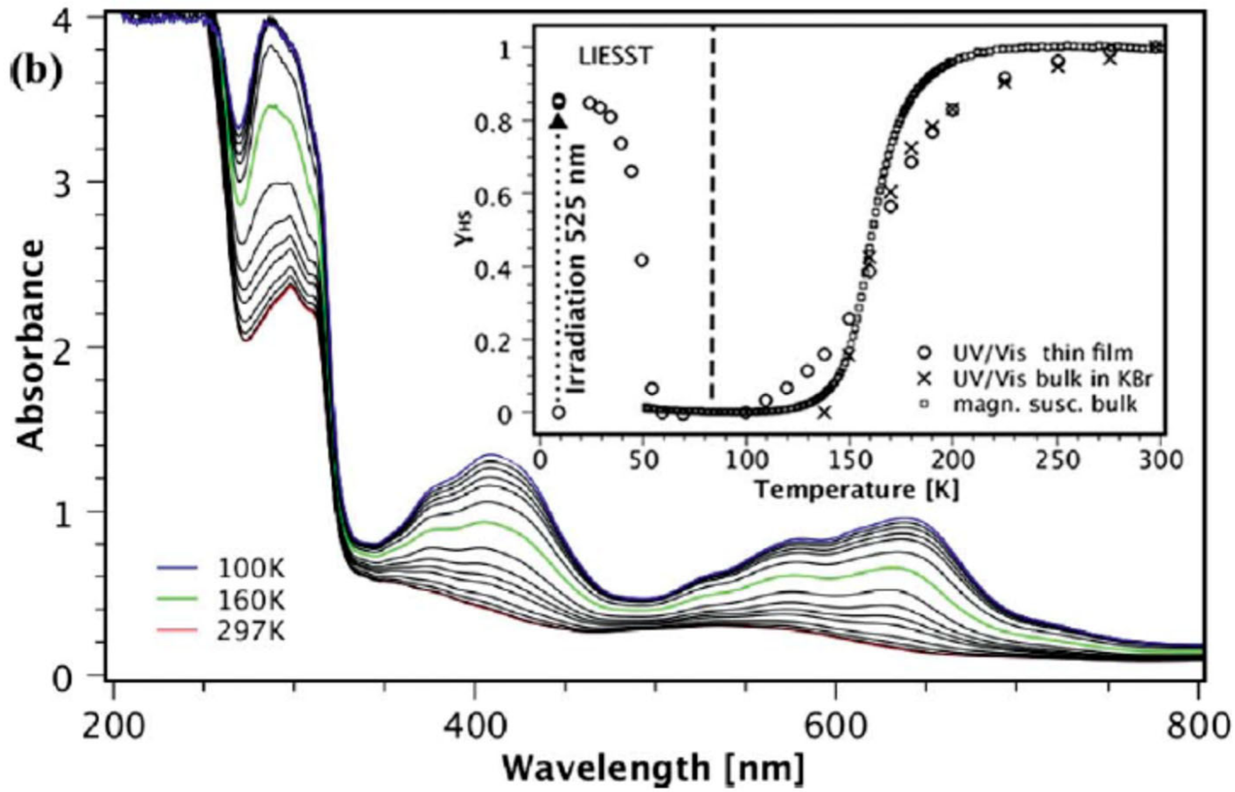
I. Thin Films of SCO Materials

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

- Substrates: Si, glass, ITO-coated glass, polymer tape
- Thickness: 400-500 nm
- $T_{1/2}$ similar to bulk
- Visible color change
- SCO more gradual
- LIESST effect (saturated in ~5 min)

Vacuum deposition

(10^{-2} mbar, 160-190 °C)



Methods:

- UV-Vis spectroscopy
- DFT calculations

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

FSU

I. Thin Films of SCO Materials

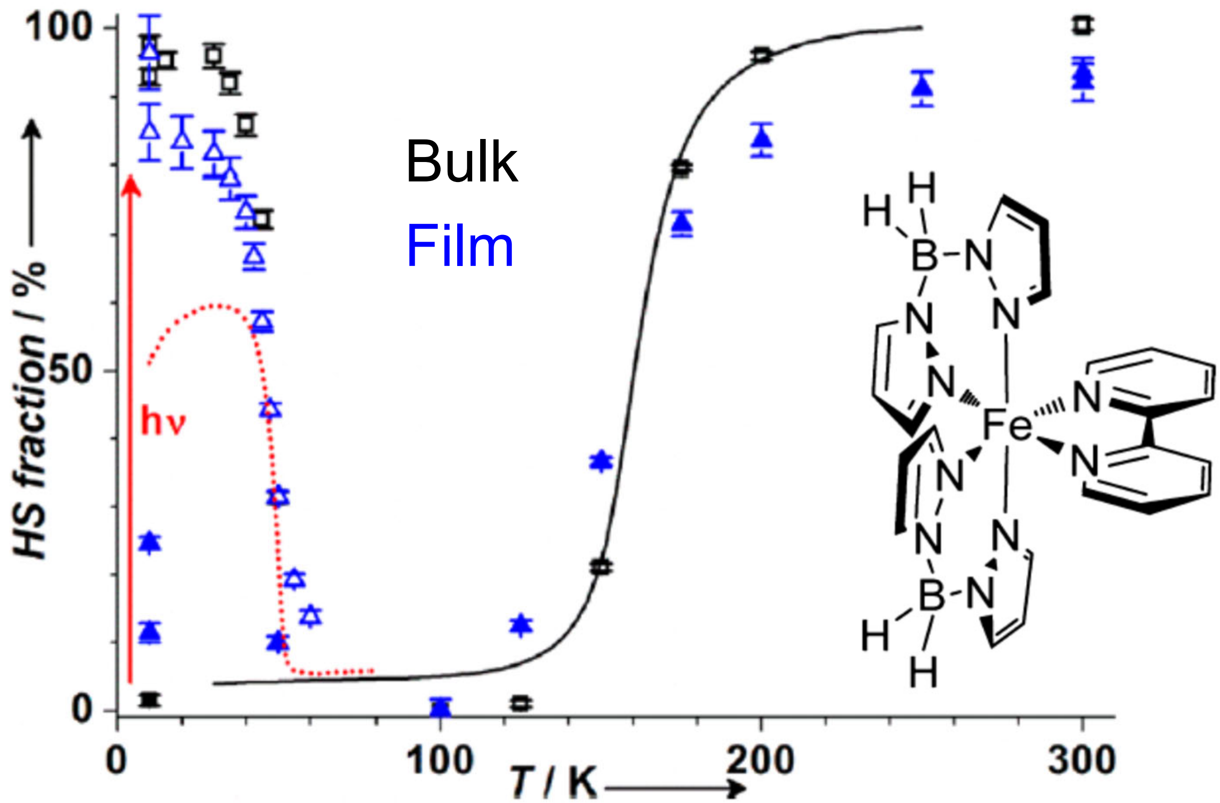
$[Fe(H_2Bpz_2)_2(bpy)]$ on Au(111)

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

Vacuum deposition

(10^{-6} mbar, 130 °C)

XAS quantification



Methods:

- UV-Vis, X-ray spectroscopies

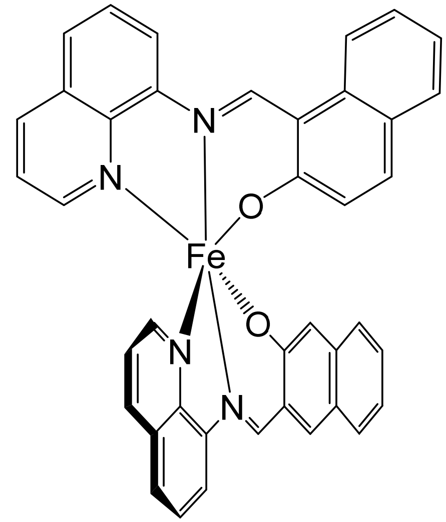
Adapted from: Warner, B.; Sessoli, R.; Rosa, P.; et al. *J. Phys. Chem. Lett.* **2013**, *4*, 1546

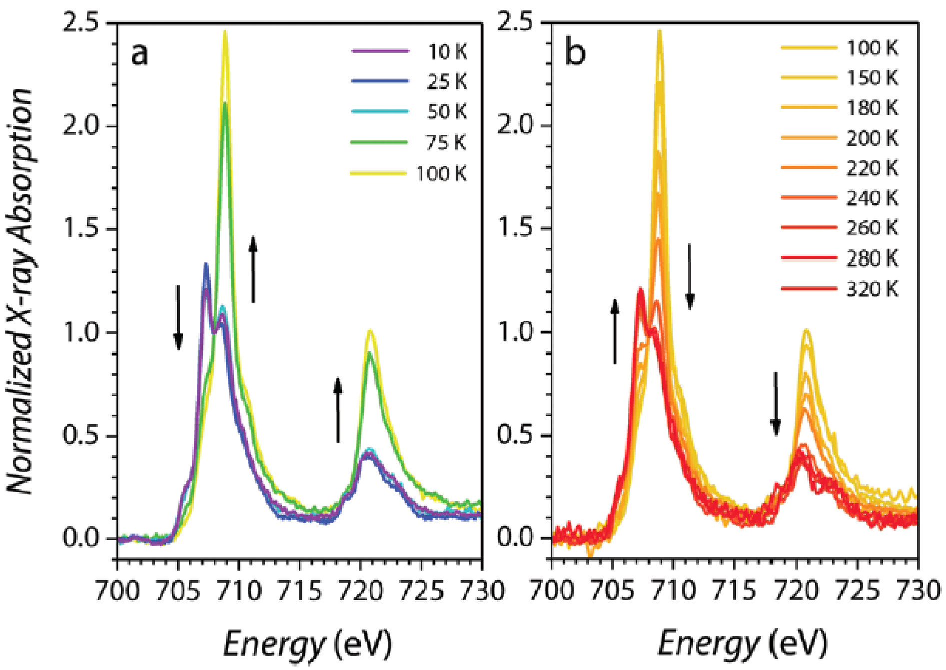
I. Thin Films of SCO Materials

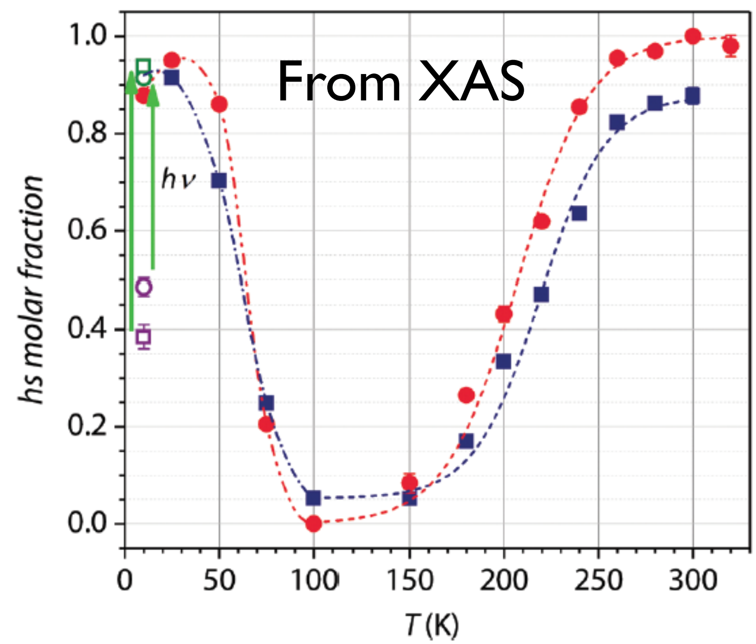
[Fe(qnal)$_2$ on Au(111)
- Thickness: 50 nm
- $T_{1/2}$ similar to bulk
- SCO more gradual
- LIESST, SOXIESST

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

II. Ultrahin Films of SCO Materials

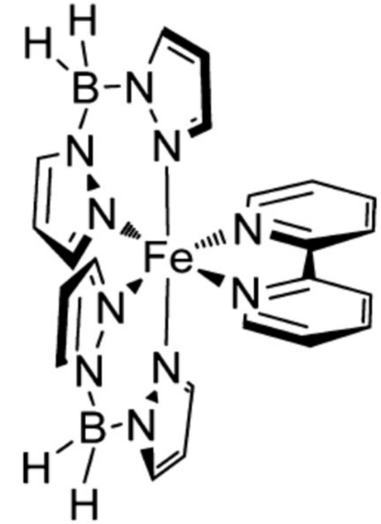
$[Fe(H_2Bpz_2)_2(bpy)]$ on Au(111)

- Submonolayers (0.03-0.14 ML)
- ≈20% showed SCO, 53% HS-, 27% LS-pinned
- SCO more gradual
- LIESST, SOXIESST

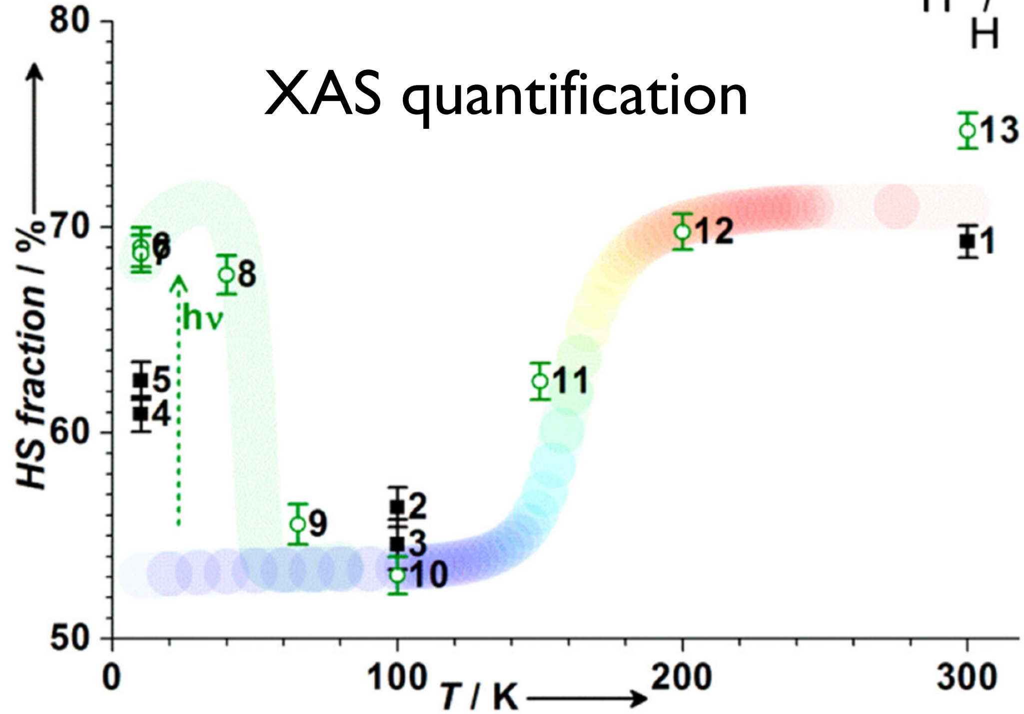
Vacuum deposition (10^{-6} mbar, 130 °C)

Methods:

- UV-Vis, XAS



XAS quantification

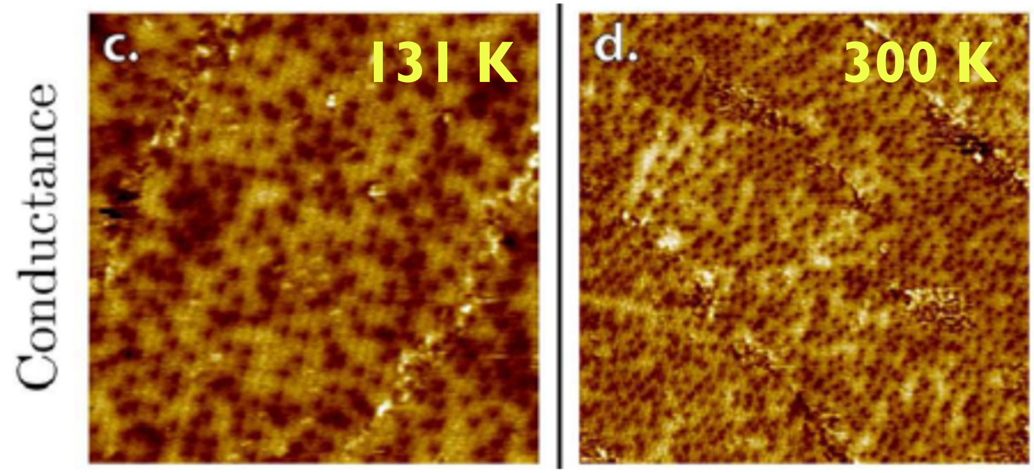


Adapted from: Warner, B.; Sessoli, R.; Rosa, P.; et al. *J. Phys. Chem. Lett.* **2013**, *4*, 1546

II. Ultrathin SCO Films

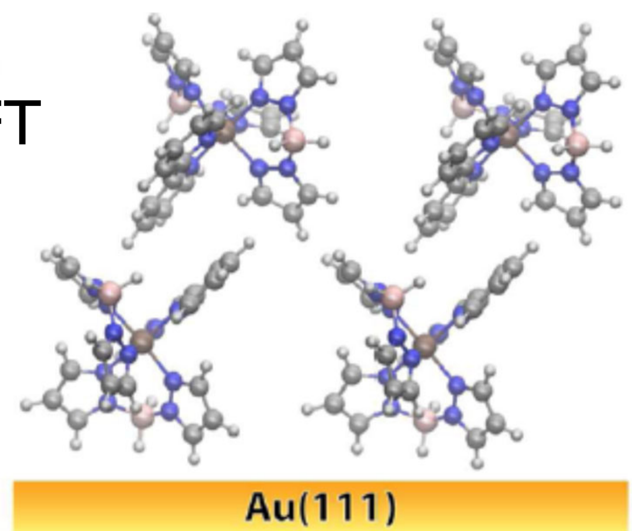
$[Fe(H_2Bpz_2)_2(bpy)]$ on Au(111)

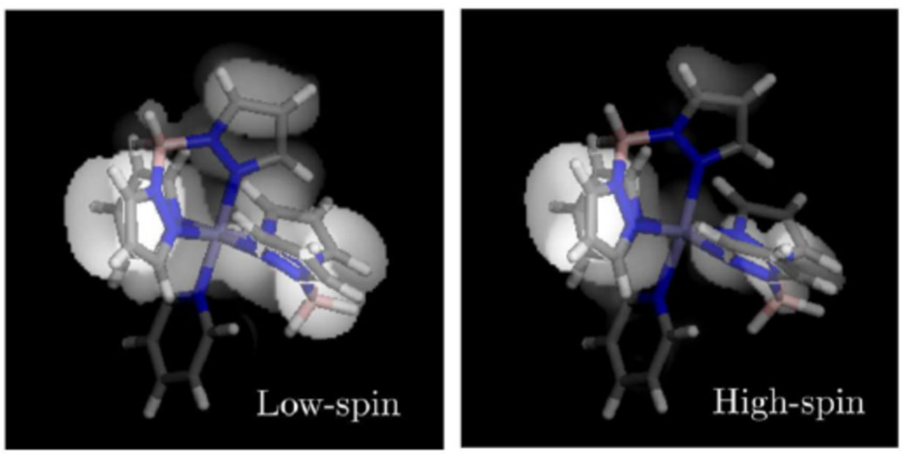
- A bilayer film
- HS and LS states co-exist (1:1) in the 131–300 K range
- Temperature-independent
- HS: smaller transport gap



Methods:

- STM, DFT



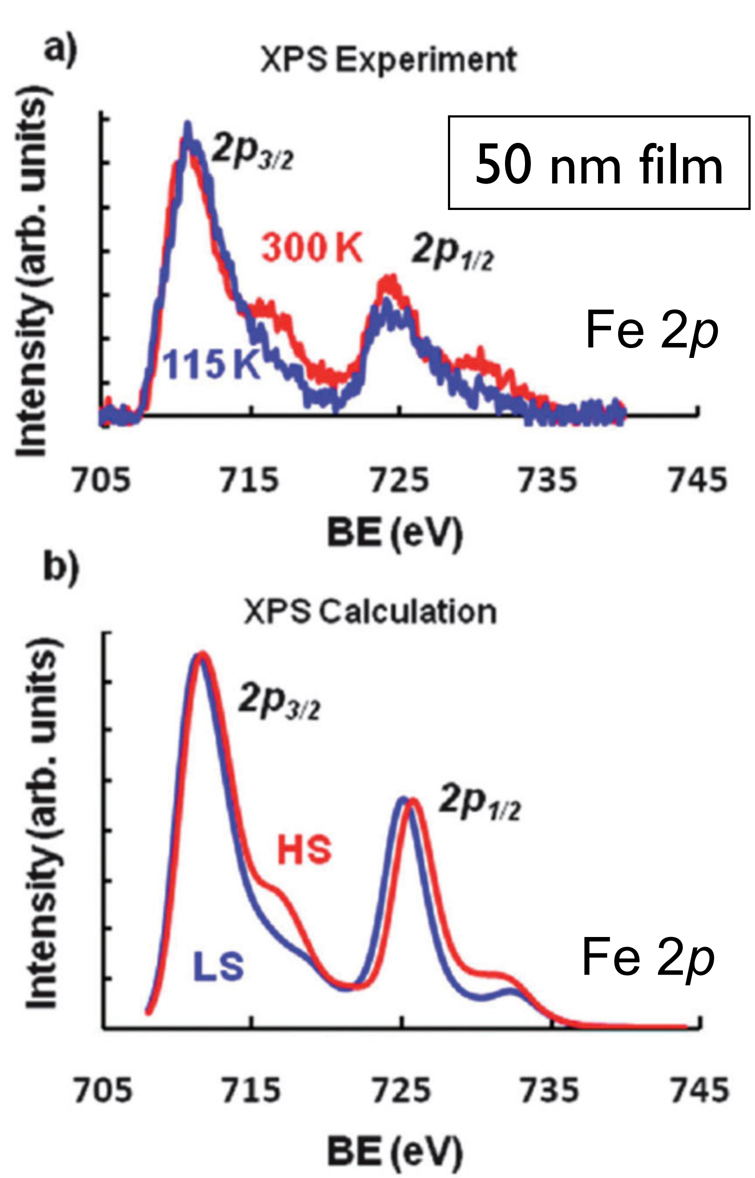


Adapted from: Pronschinske, A.; Dougherty, D. B.; et al. *Nano Lett.* **2013**, *13*, 1429

II. Ultrathin SCO Films

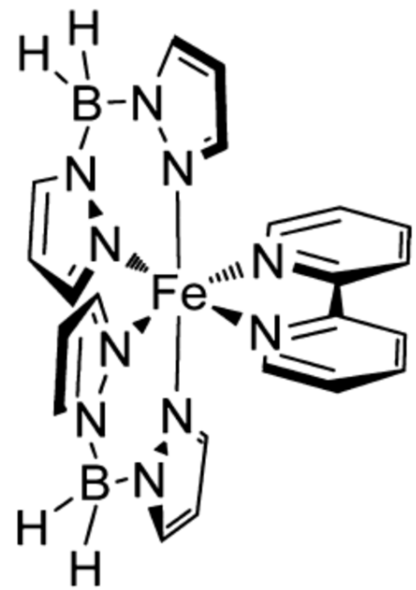
$[Fe(H_2Bpz_2)_2(bpy)]$ on Au(111)

- Well-ordered bilayer
- Loss of order in the 3rd layer
- 50 nm film: grainy structure but SCO observed by XPS



Methods:

- STM, XPS, UPS, DFT



Adapted from: Pronschinske, A.; Dougherty, D. B.; et al. *Chem. Commun.* **2013**, *49*, 10446

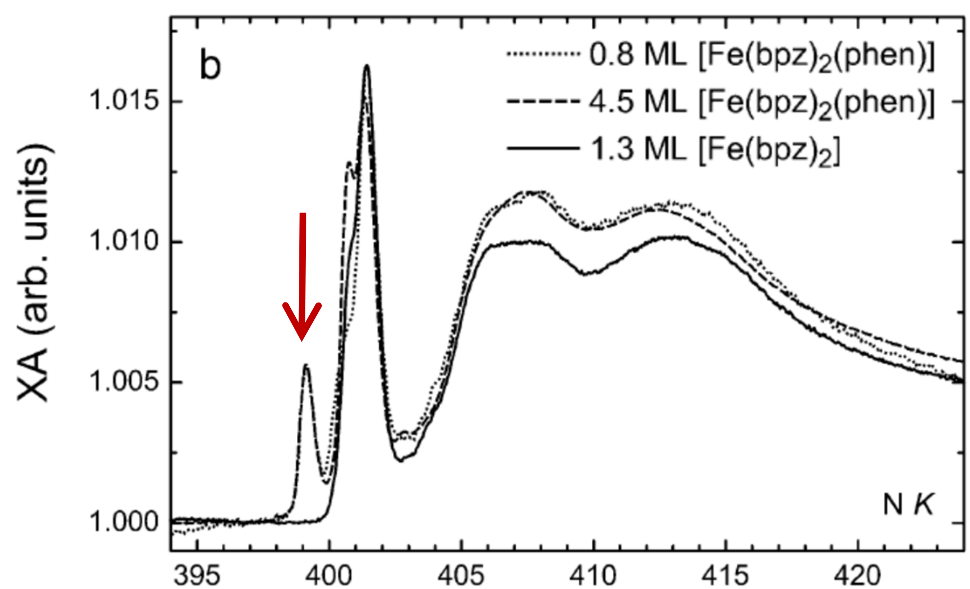
II. Ultrathin SCO Films

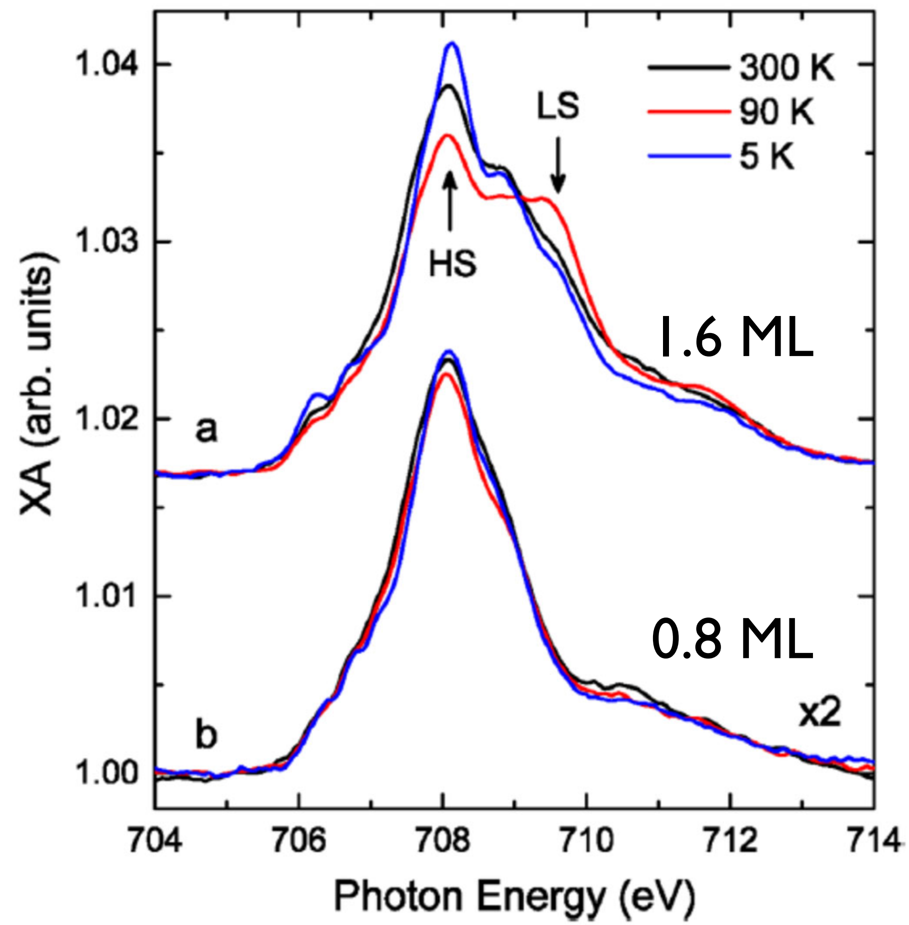
$[Fe(H_2Bpz_2)_2(phen)]$ on Au(111)

- Sub-monolayer: decomposition to $[Fe(H_2Bpz_2)_2]$ (loss of ligand!)
- Only the 2nd layer shows SCO

Methods:

- STM, NEXAFS





Adapted from: Gopakumar, T. G.; Berndt, R.; Kuch, W.; Tuczek, F.; et al. *Chem. Eur. J.* **2013**, *19*, 15702

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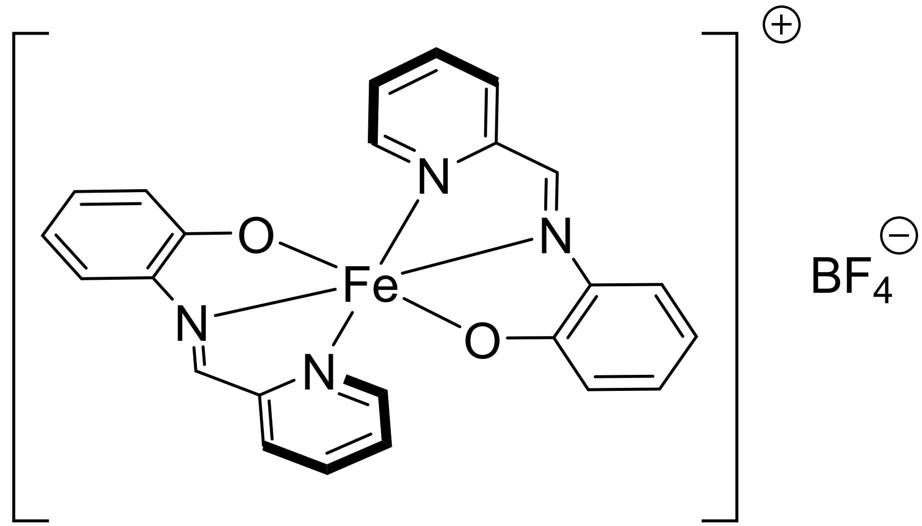
II. Ultrathin SCO Films

$[Fe(pap)_2](BF_4)_2$ on $Cu_2N/Cu(100)$

- First example of deposition for a charged SCO complex

Vacuum deposition

(10^{-9} mbar, 350 °C)



We would like to stress that since the charge state of the adsorbed molecules cannot be unambiguously determined from our data (see below), they are henceforth referred to as $Fe(pap)_2$, that is, without specifying their charge.

We speculate that the counterions are still present at the surface but are attached to the more reactive Cu trenches. They do not affect the measurements of single $Fe(pap)_2$ molecules on Cu_2N islands.

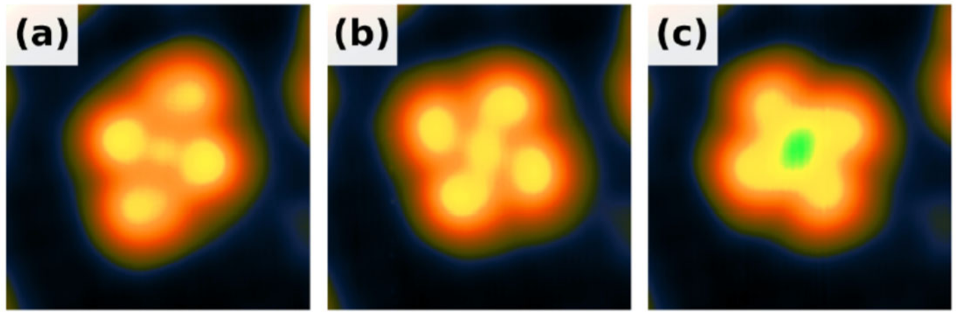
Adapted from: Jasper-Toennies, T.; Gruber, M.; Karan, S.; Jacob, H.; Tuczek, F.; Berndt, R. *Nano Lett.* **2017**, *17*, 6613

FSU

II. Ultrathin SCO Films

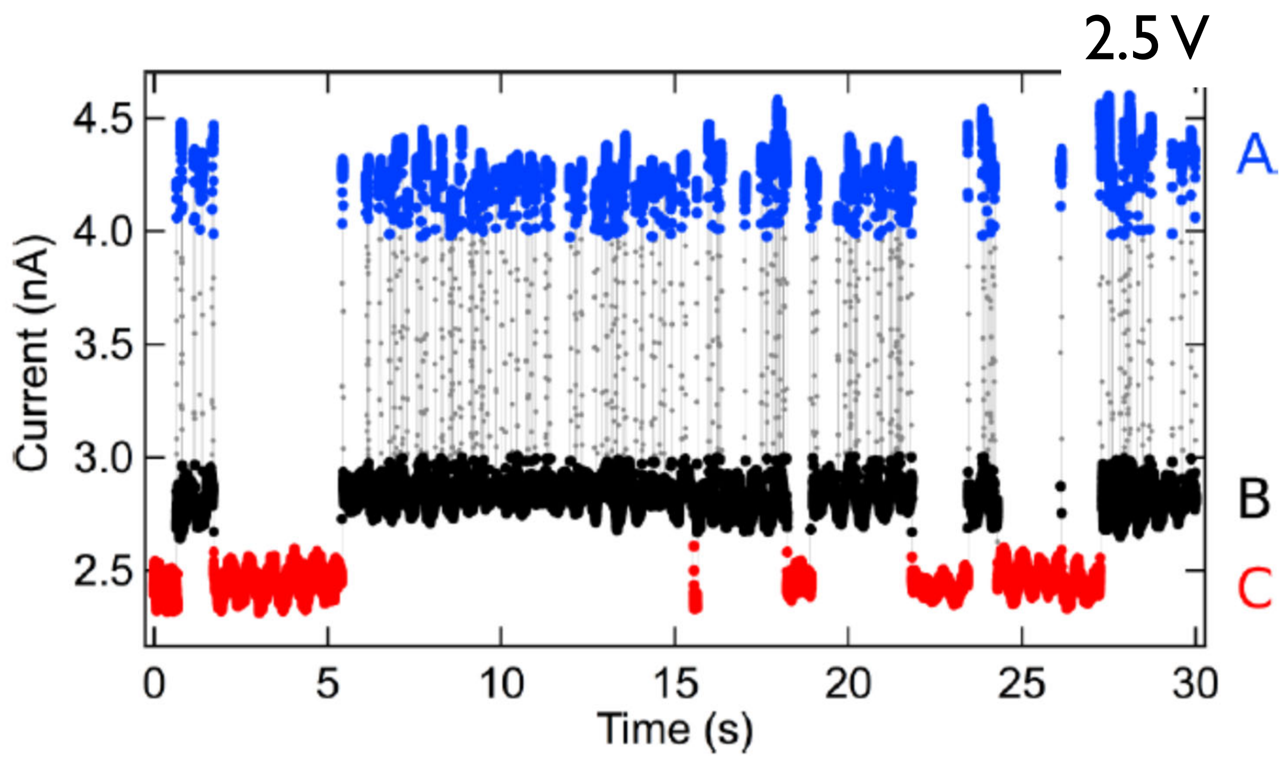
$[Fe(pap)_2](BF_4)_2$ on $Cu_2N/Cu(100)$

- First example of deposition for a charged SCO complex
- Switching between 3 states
- Switching achieved >1.8 V



Methods:

- STM, DFT



A lot of Qs:

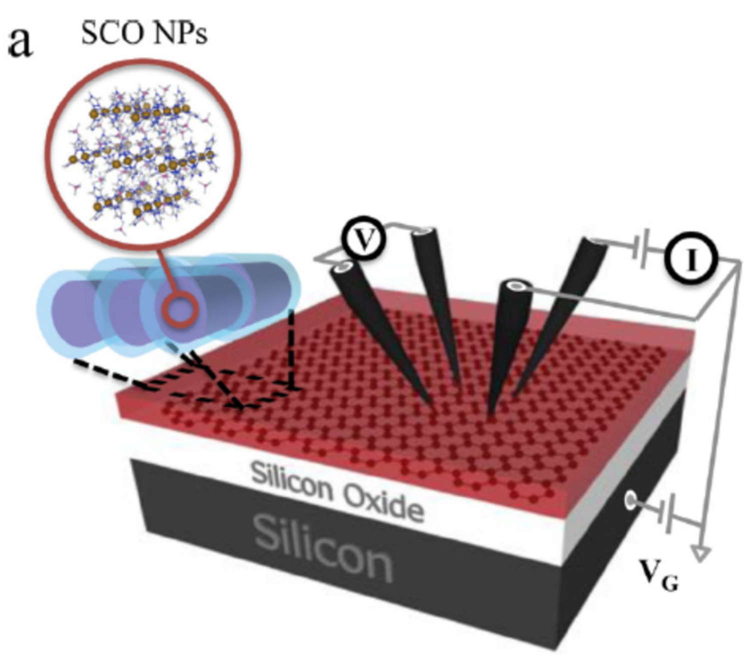
- what are 3 states?
- what is resting state?
- what would be observed w/ $[Fe(pap)_2]$

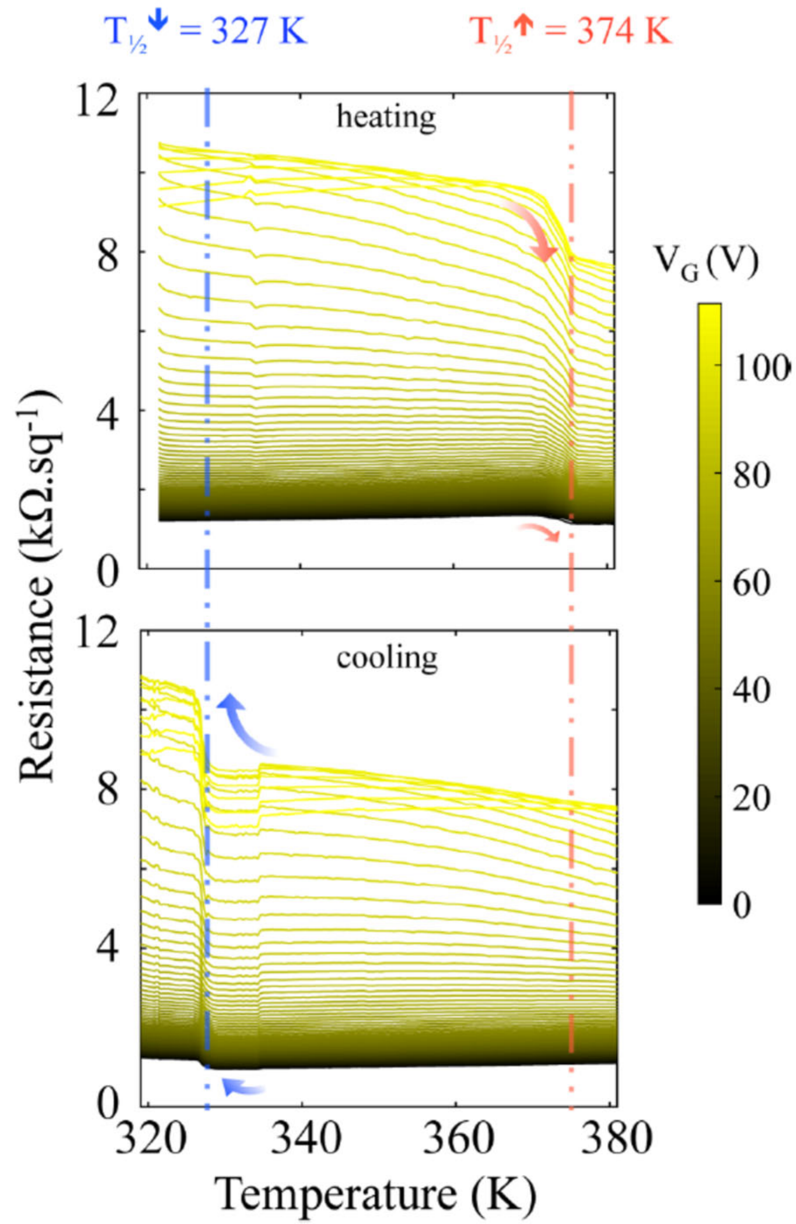
Adapted from: Jasper-Toennies, T.; Gruber, M.; Karan, S.; Jacob, H.; Tuczek, F.; Berndt, R. *Nano Lett.* **2017**, *17*, 6613

II. Ultrathin SCO Films

SCO nanoparticles on graphene

- Deposited by contact printing from the surface of an ethyleneglycol droplet
- Nanorods: *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

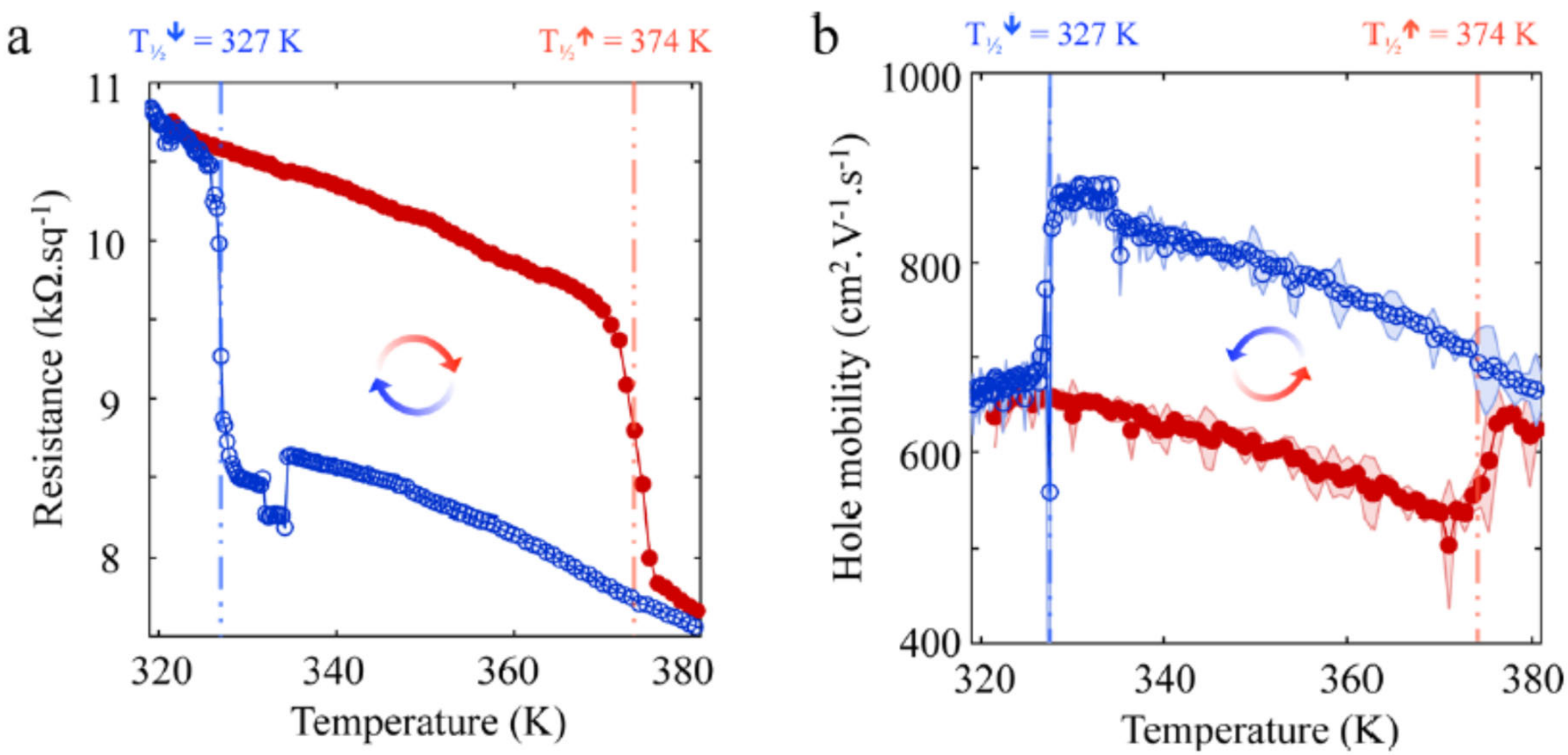
II. Ultrathin SCO Films

SCO nanoparticles on graphene

- The SCO switching behavior reproduces what is observed for the bulk material and is coupled to graphene's transport

What's the mechanism?

- The Dirac voltage doesn't change
- The coupling is likely structural and not of charge-transfer type
- Hypothesis: dielectric switching



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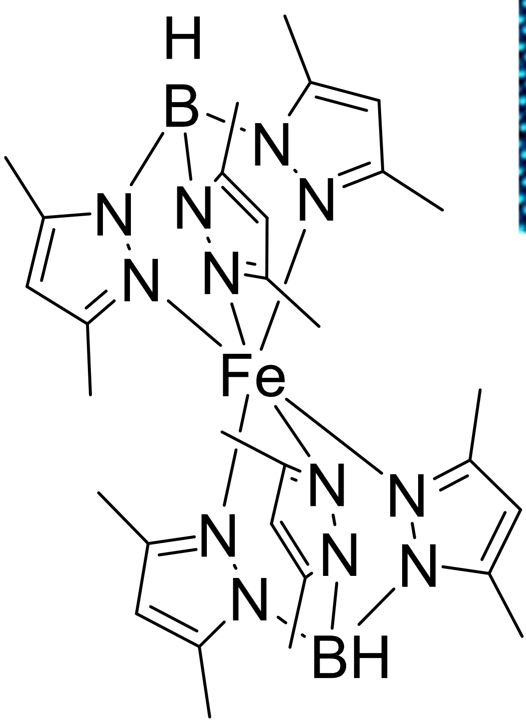
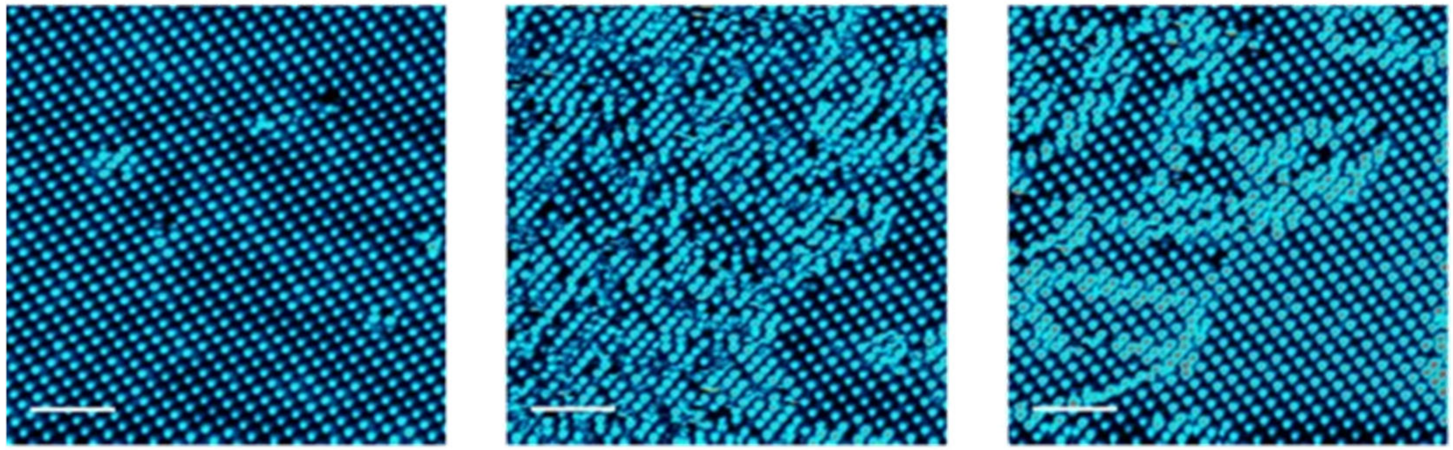
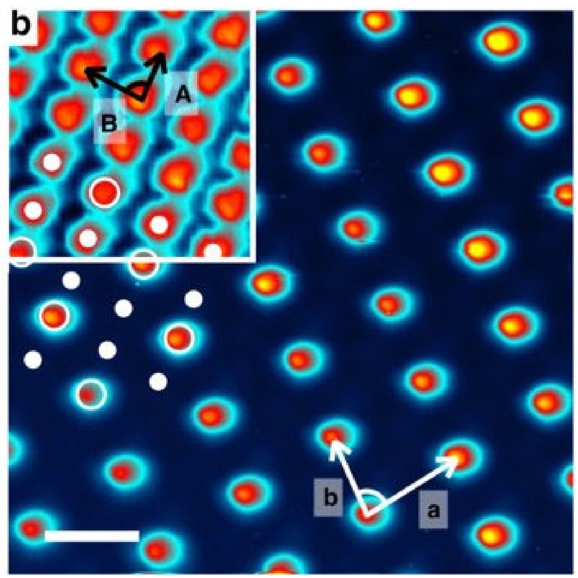
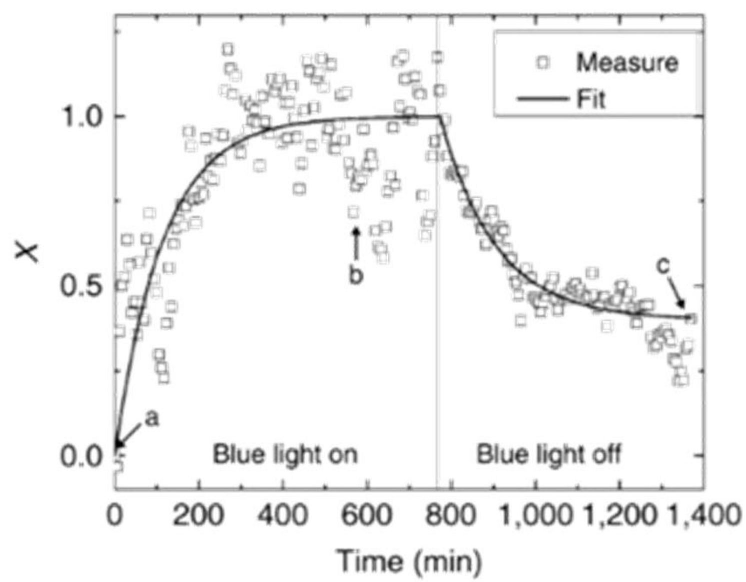
II. Ultrathin SCO Films

Vacuum deposition; (10^{-10} mbar, 320 °C)









Adapted from: Bairagi, K.; Iasco, O.; Bellec, A.; Repain, V.; et al. *Nat. Commun.* **2016**, 7, 12212

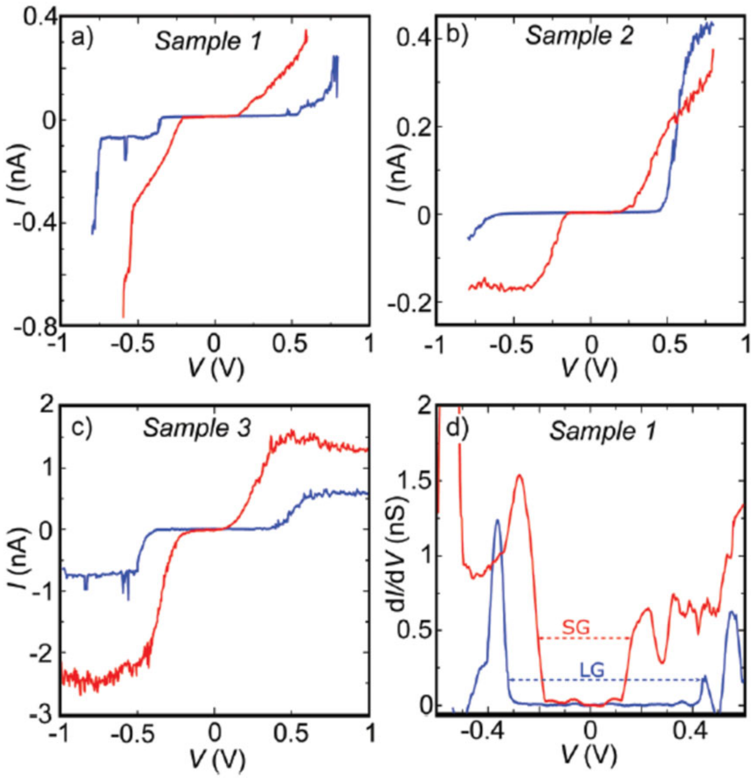
III. Single Molecules

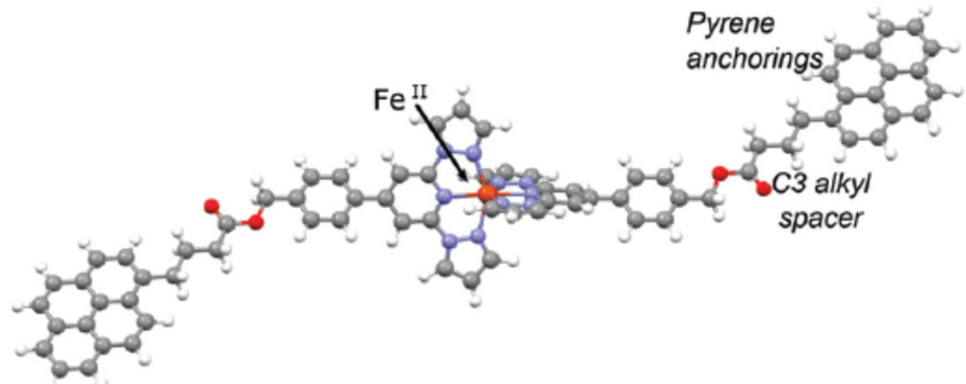
$[Fe(L)_2]^{2+}$ in a graphene break junction

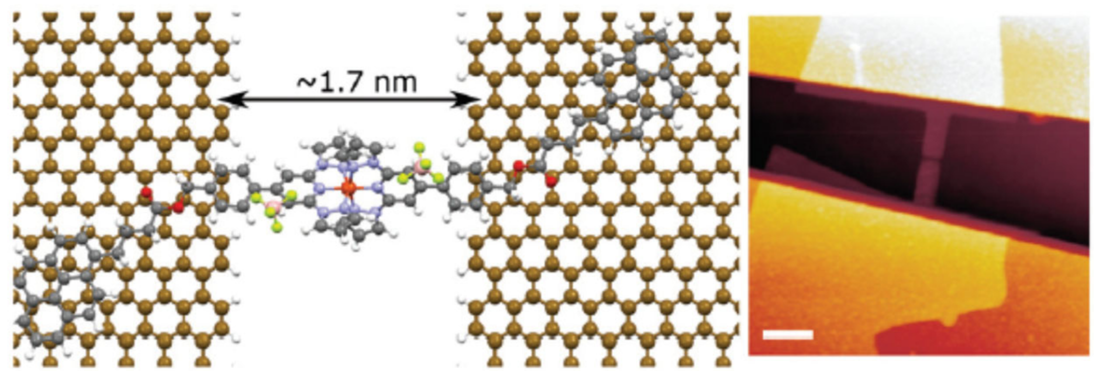
- Typical electro-burned gap ~ 1-2 nm
- Molecular length ~ 4 nm
- Consistent bistability at 4 K (purely stochastic behavior)

Solution deposition:

- drop-casting a 10^{-4} M solution in acetonitrile





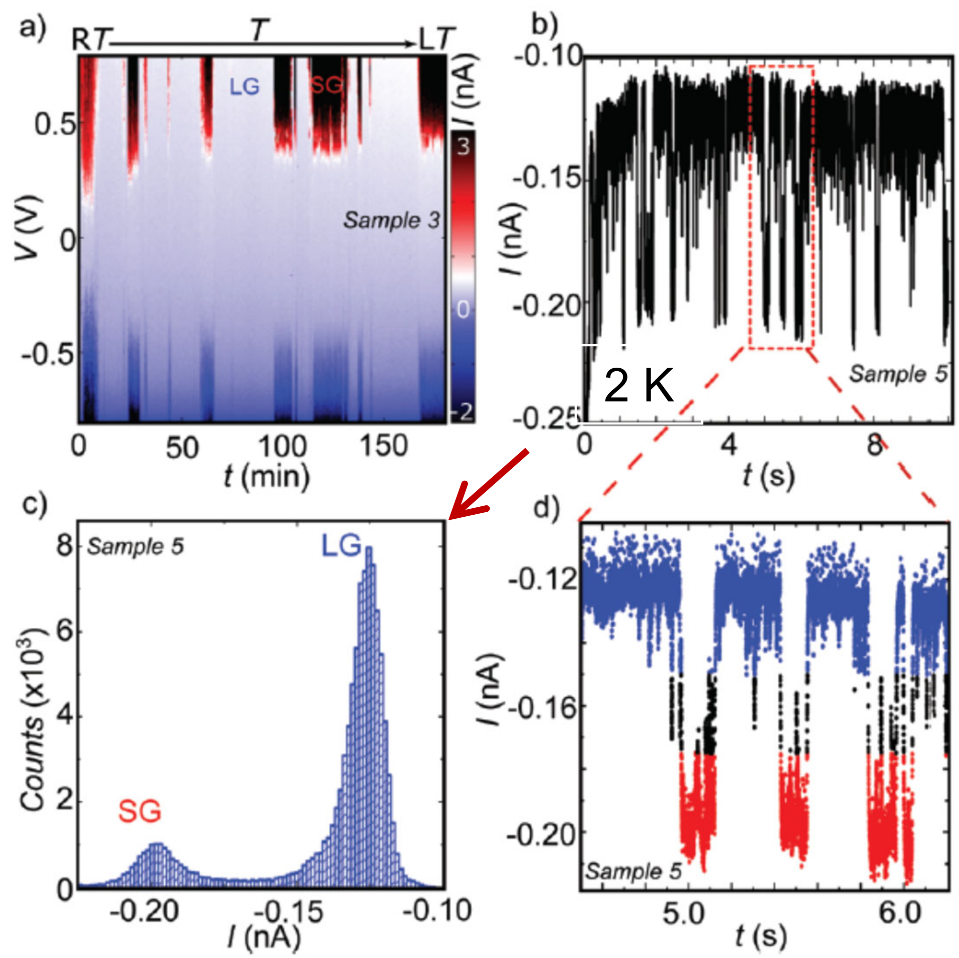


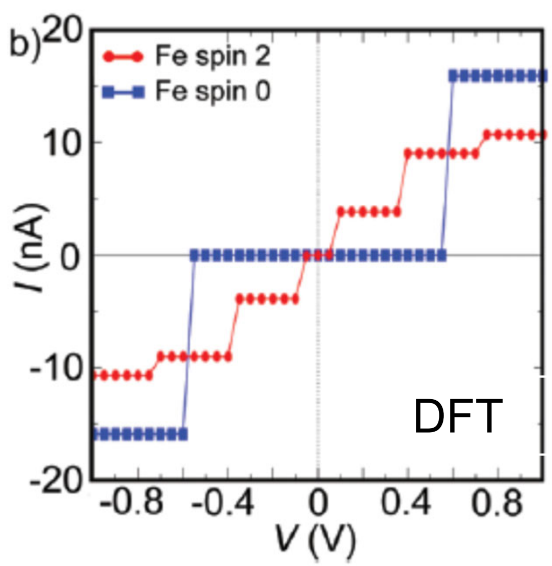
Adapted from: Burzurí, E.; Ruben, M.; Ferrer, J.; van der Zant, H. S. J. *Nanoscale* **2018**, *10*, 7905-7911

III. Single Molecules

$[Fe(L)_2]^{2+}$ in graphene break junction

- The large-gap / small-gap states have been assigned to HS / LS states, respectively
- The switching persists well beyond the SCO temperature observed in the bulk





Adapted from: Burzurí, E.; Ruben, M.; Ferrer, J.; van der Zant, H. S. J. *Nanoscale* **2018**, *10*, 7905-7911

Outline

- ❖ Spin Crossover: Quick Introduction
- ❖ Spin Crossover at Nanoscale
  - Thin films
  - Ultrathin films
  - Single molecules
- ❖ Spin Crossover Films via Gas Phase
- ❖ Spin Crossover Films via Exfoliation

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

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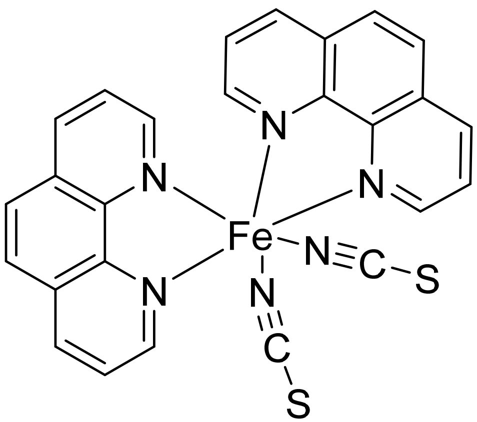
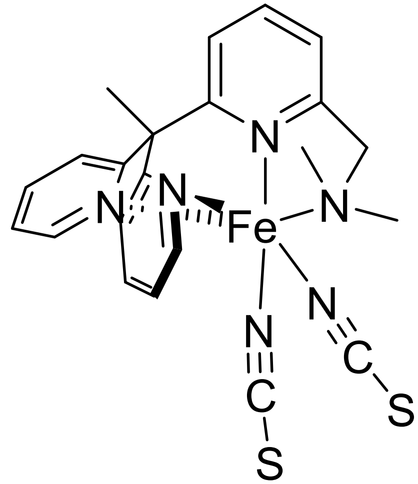
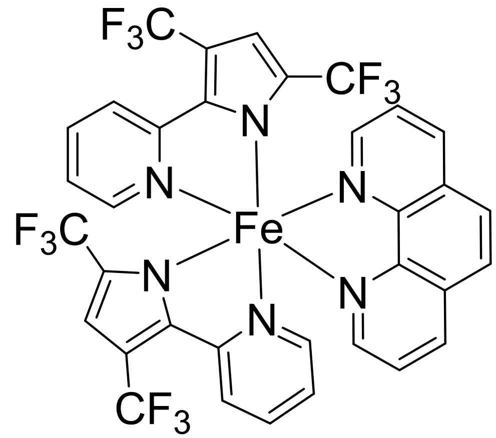
Gas-Phase Deposition of SCO Films



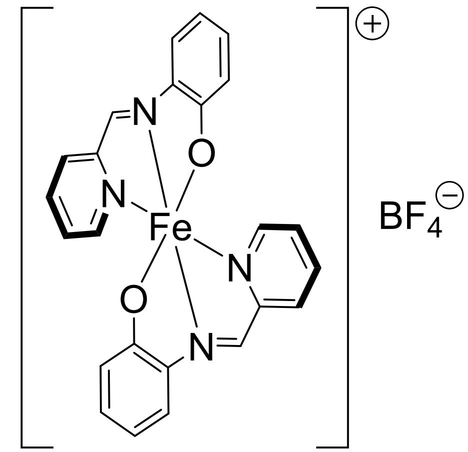
180 °C
10^{-8} mbar



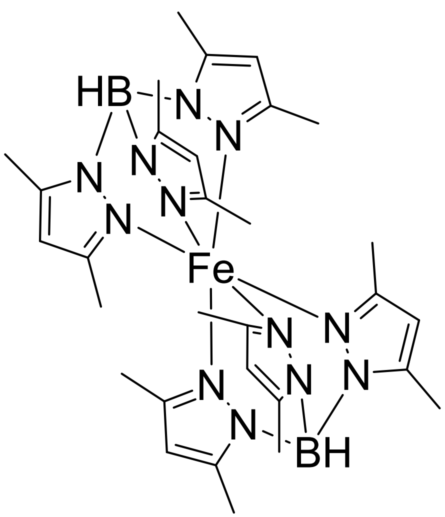
237 °C
10^{-9} mbar



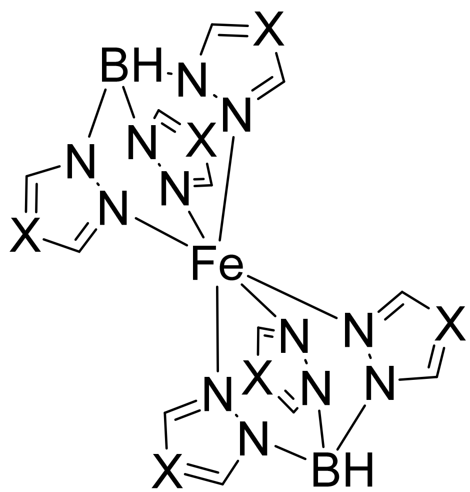
160 °C
10^{-9} mbar



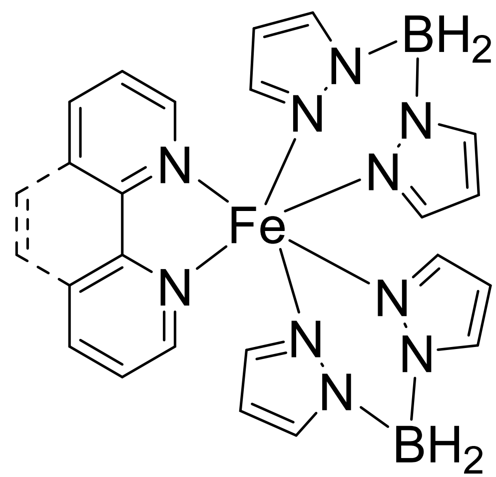
100 °C
10^{-9} mbar



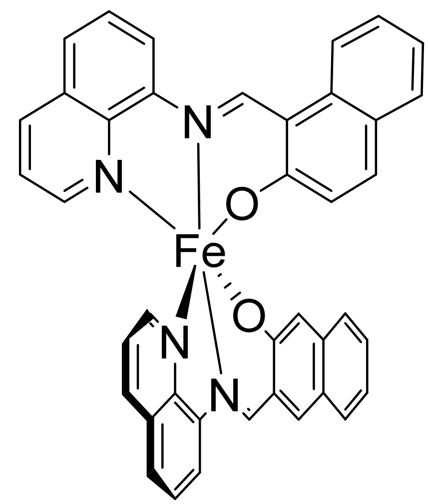
140 °C
10^{-8} mbar



190 °C
10^{-5} mbar



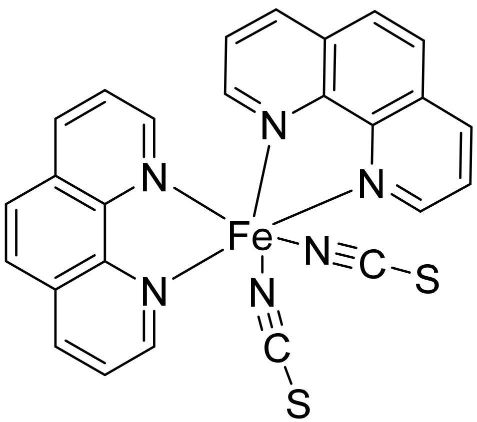
162 °C
10^{-2} mbar



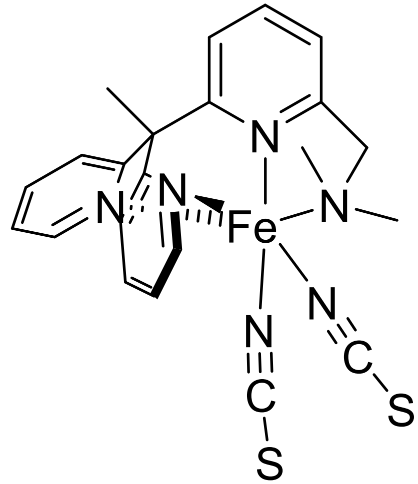
217 °C
10^{-9} mbar

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

Gas-Phase Deposition of SCO Films



180 °C
10^{-8} mbar



237 °C
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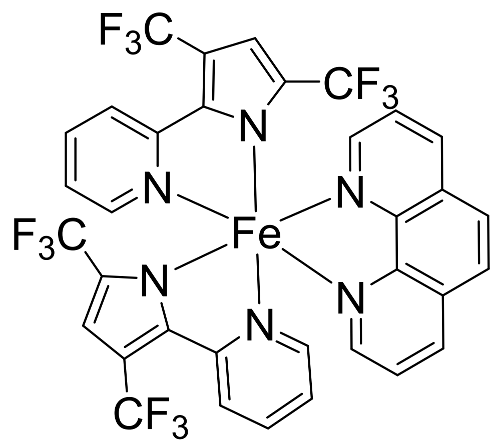
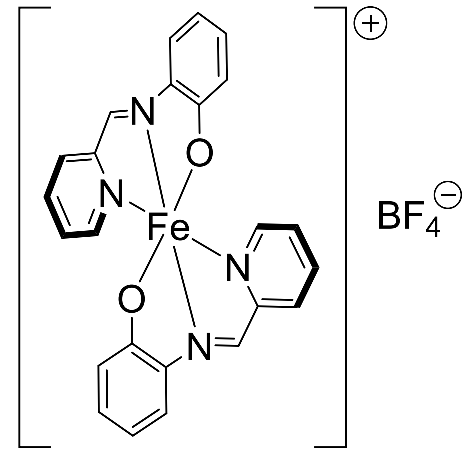
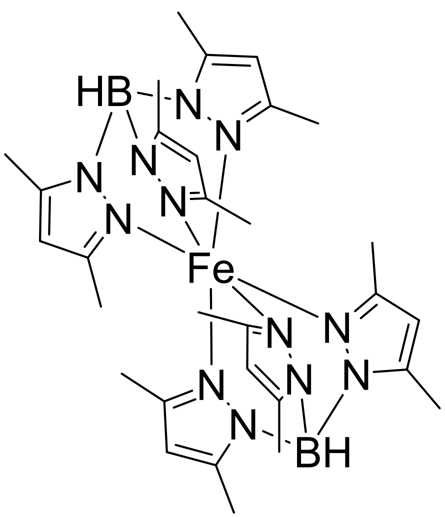


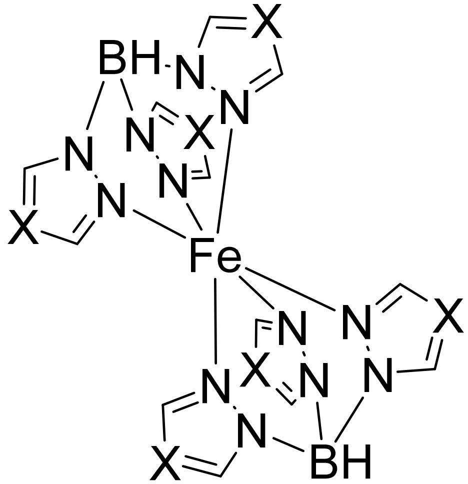
160 °C
10^{-9} mbar



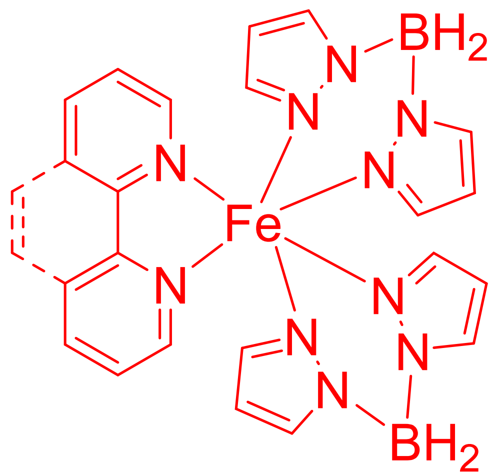
100 °C
10^{-9} mbar



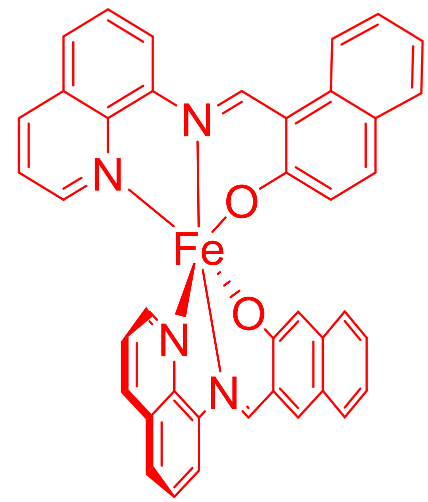
140 °C
10^{-8} mbar



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

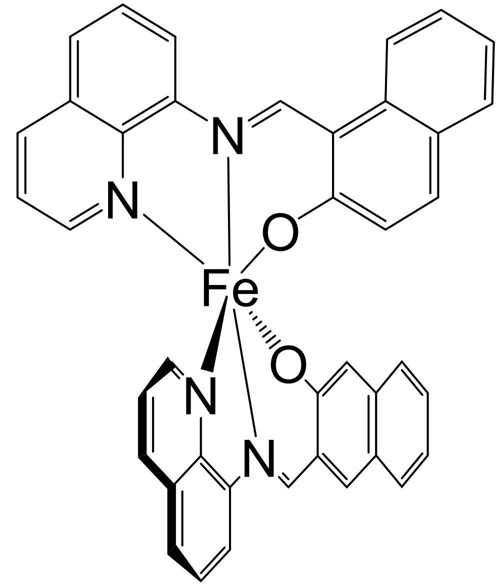
[Fe(qnal)$_2$] on Au(111)

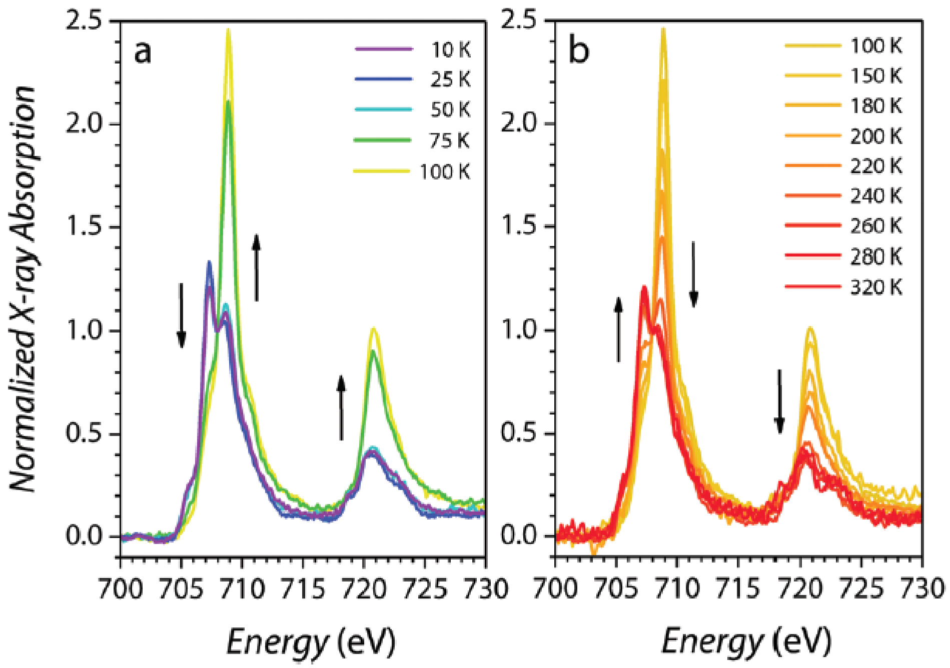
- Thickness: 300 nm
- $T_{1/2}$ similar to bulk
- SCO more gradual
- LIESST effect

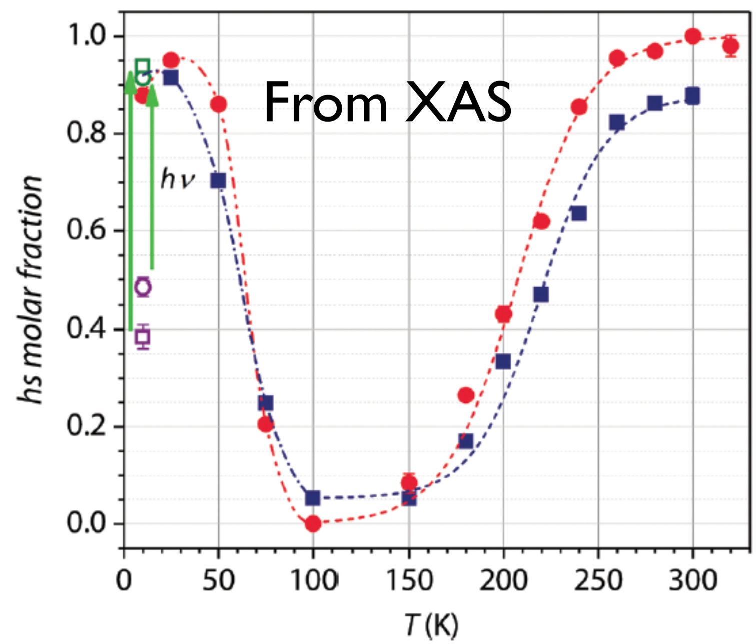
Vacuum deposition
(10^{-8} mbar, 350 °C)

Methods:

- UV-Vis, XAS







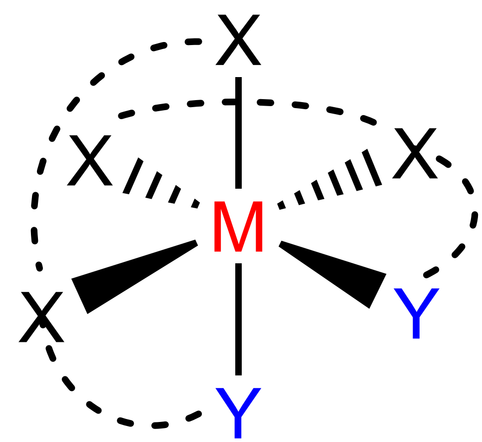
Adapted from: Atrozi, M.; Sessoli, R.; Mannini, M.; et al. *J. Mater. Chem. C* **2018**, *6*, 8885

Molecular Design Challenge

Cooperativity: ***strong*** intermolecular interactions

Volatility: ***weak*** intermolecular interactions

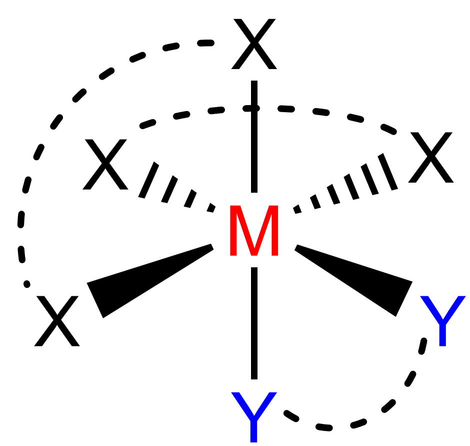
Challenge: increase the volatility while preserving the abrupt spin transition



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

Criteria:

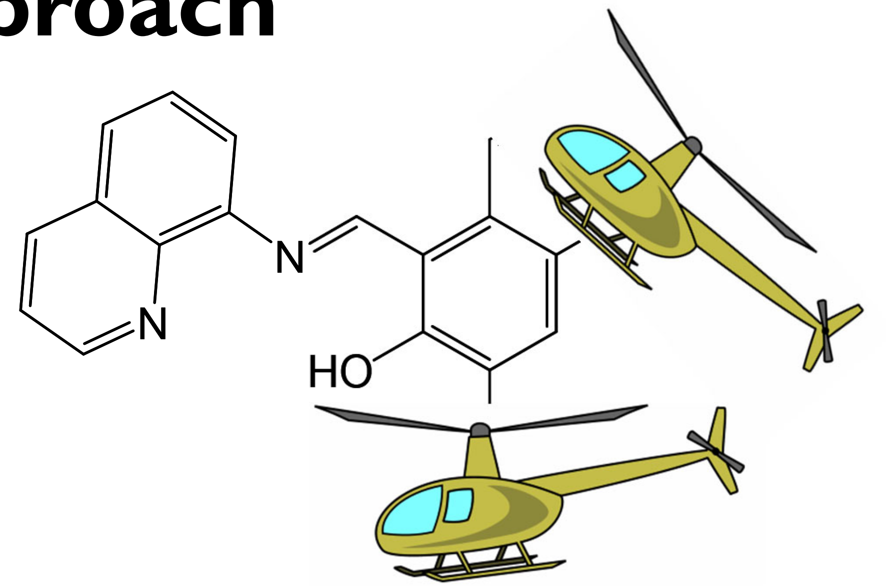
- neutral complexes
- easy synthetic modification
- asymmetric ligand structure
- only chelating (clamping) ligands

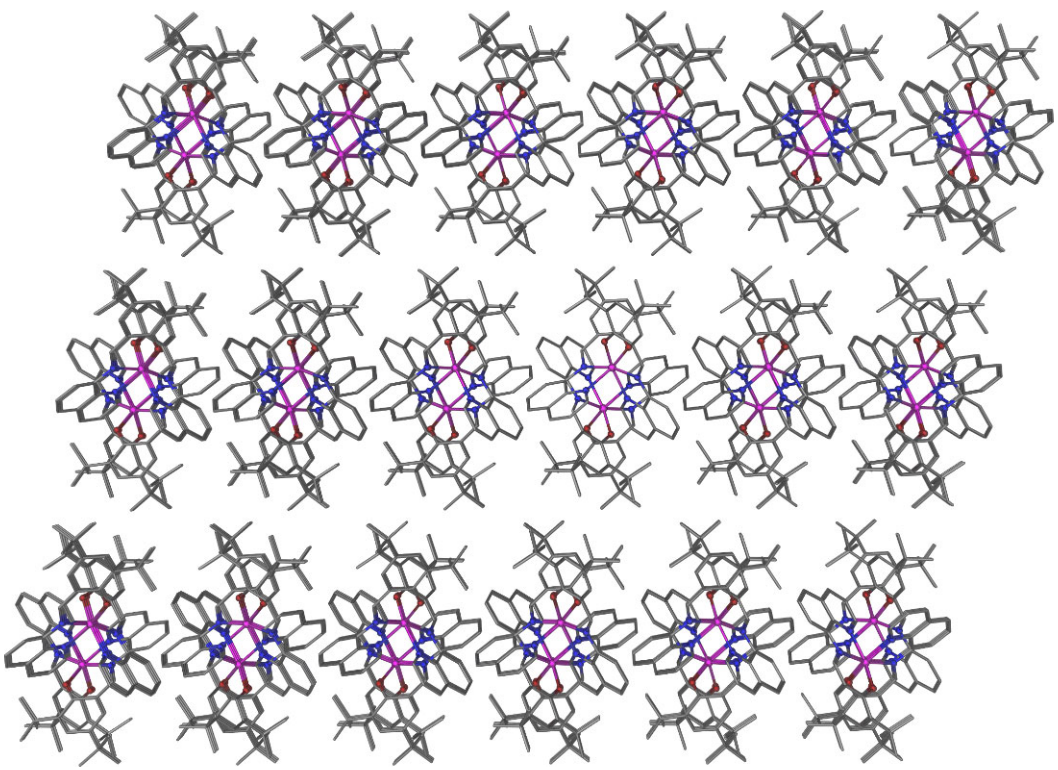


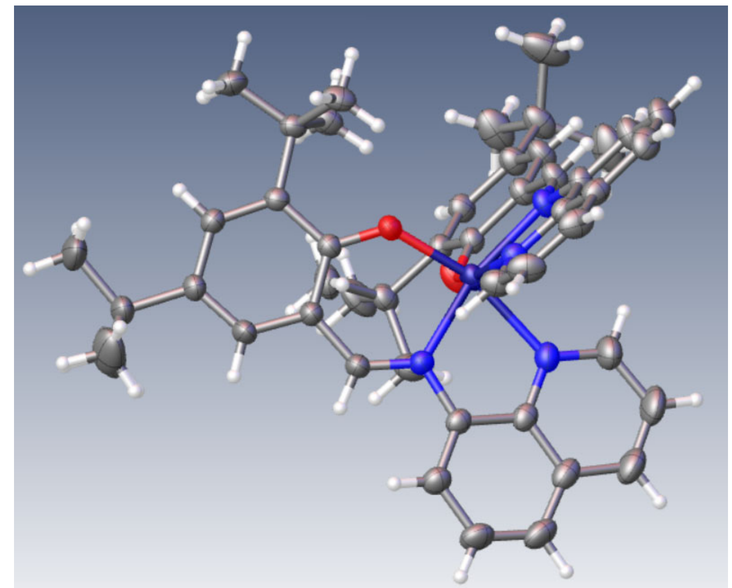
Synthetic Approach

Introduce the asymmetry of interactions to boost volatility

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



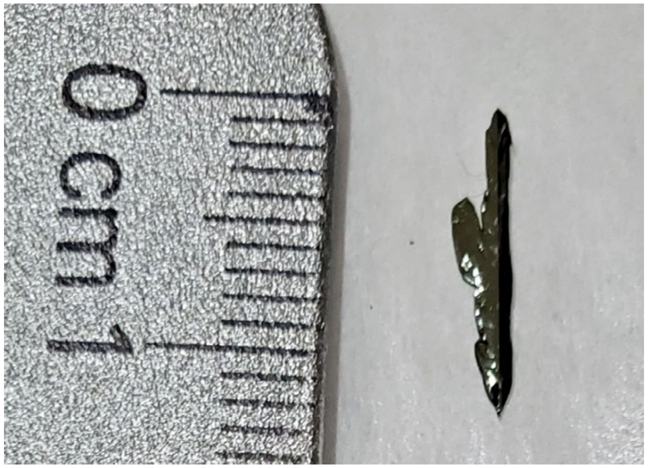




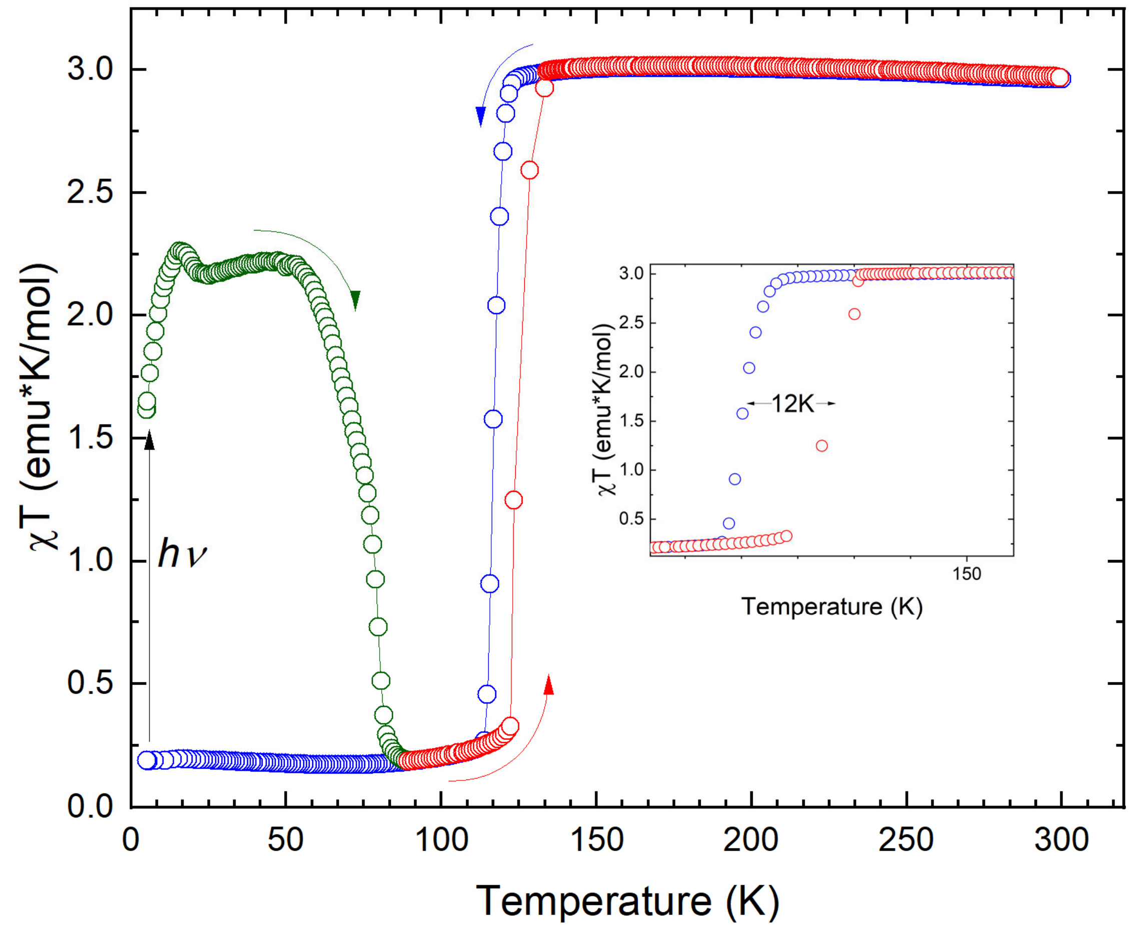
$[Fe(\mathit{t}Bu_2qsal)_2]$

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 $[Fe(tBu_2qsal)_2]$



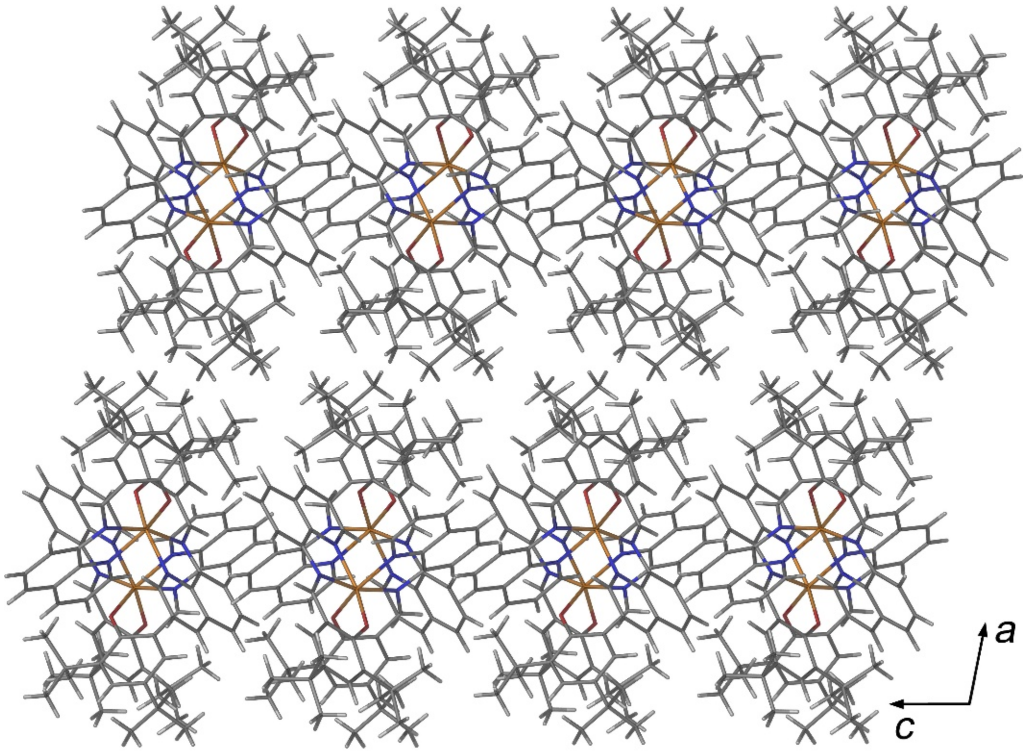
Crystals grown
by vapor transport at
$>10^{-5}$ mbar & 300 °C

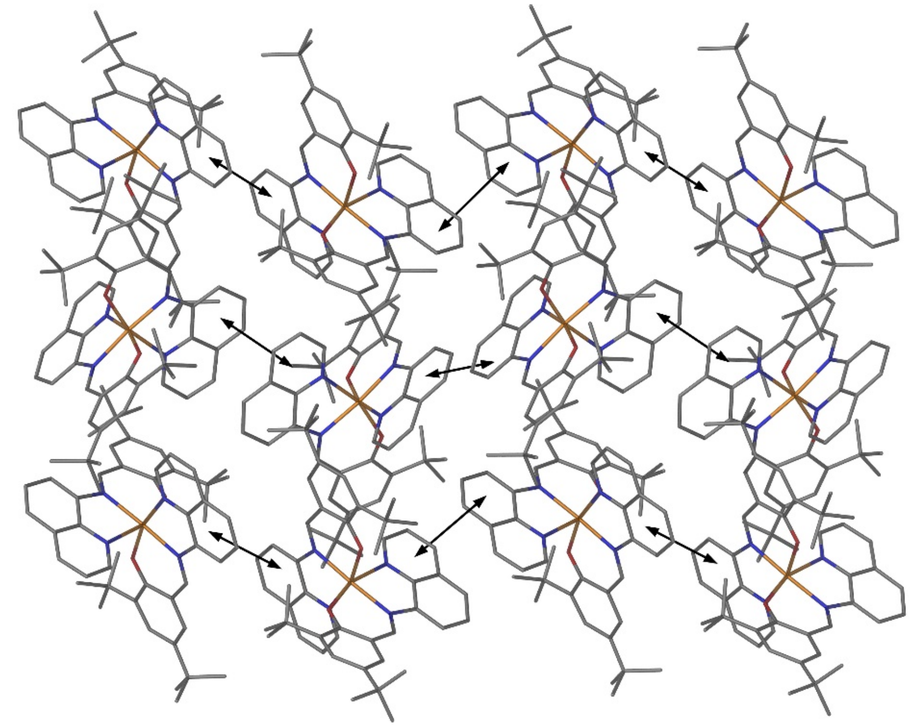


$T_{1/2}$ = 117 K / 129 K
T_{LIESST} = 84 K

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

Structural Anisotropy





A single molecular layer

Calculated cohesion energies:

- 0.888 mJ/m^2 along [100]
- 0.927 mJ/m^2 along [001]
- 1.236 mJ/m^2 along [010]

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

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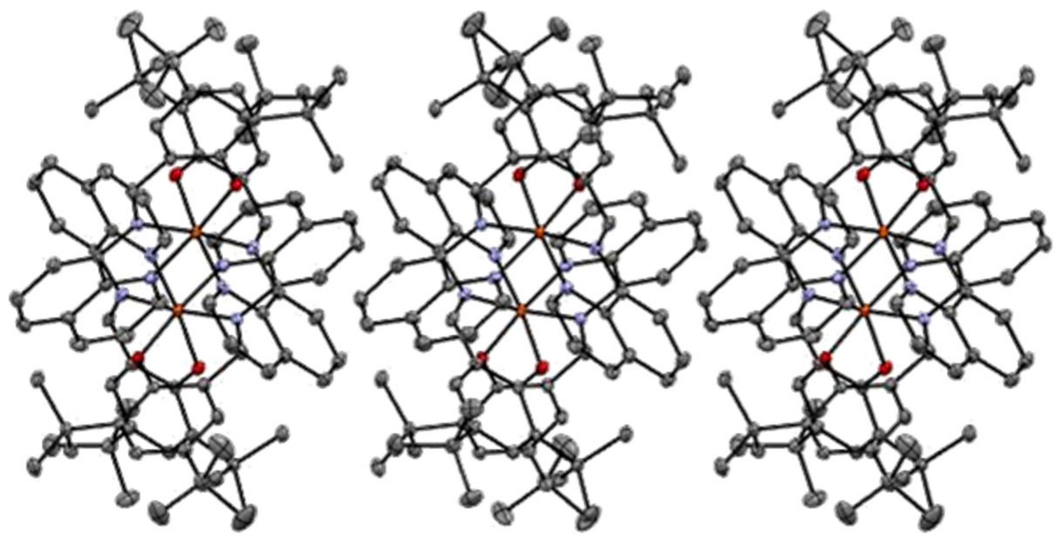
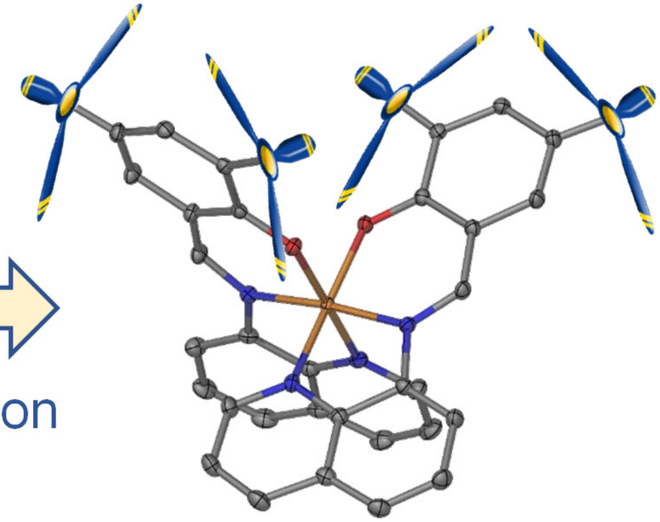
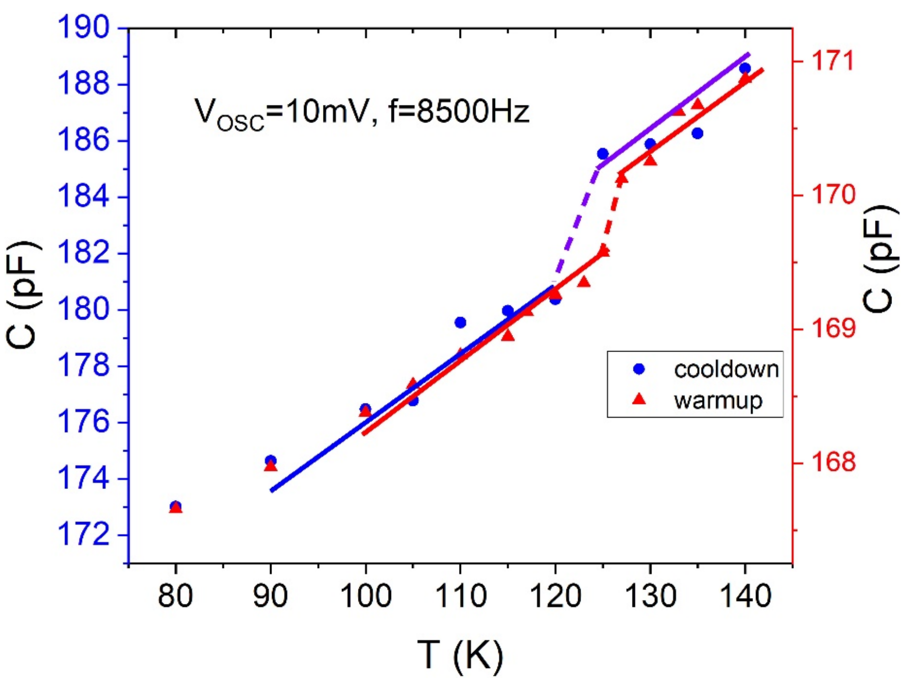
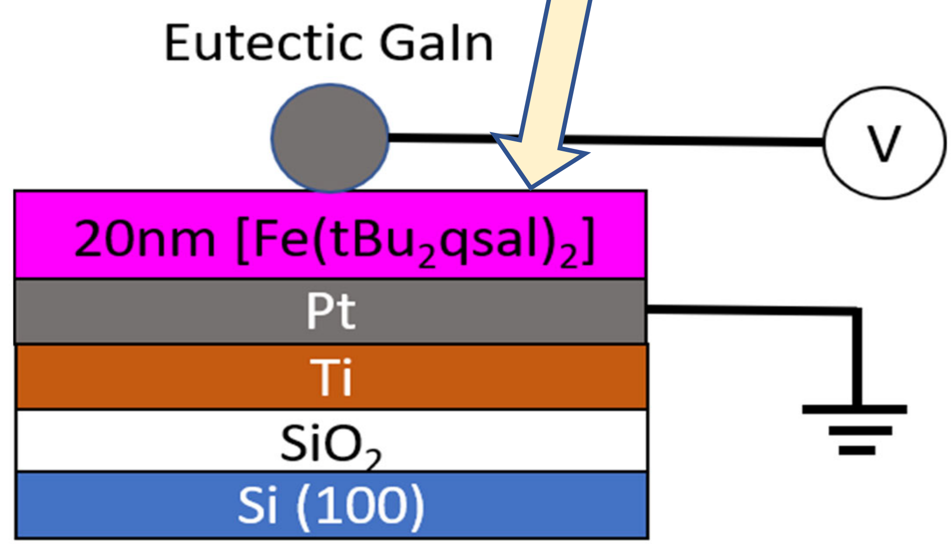
Thin-Film Capacitor



Sublimation



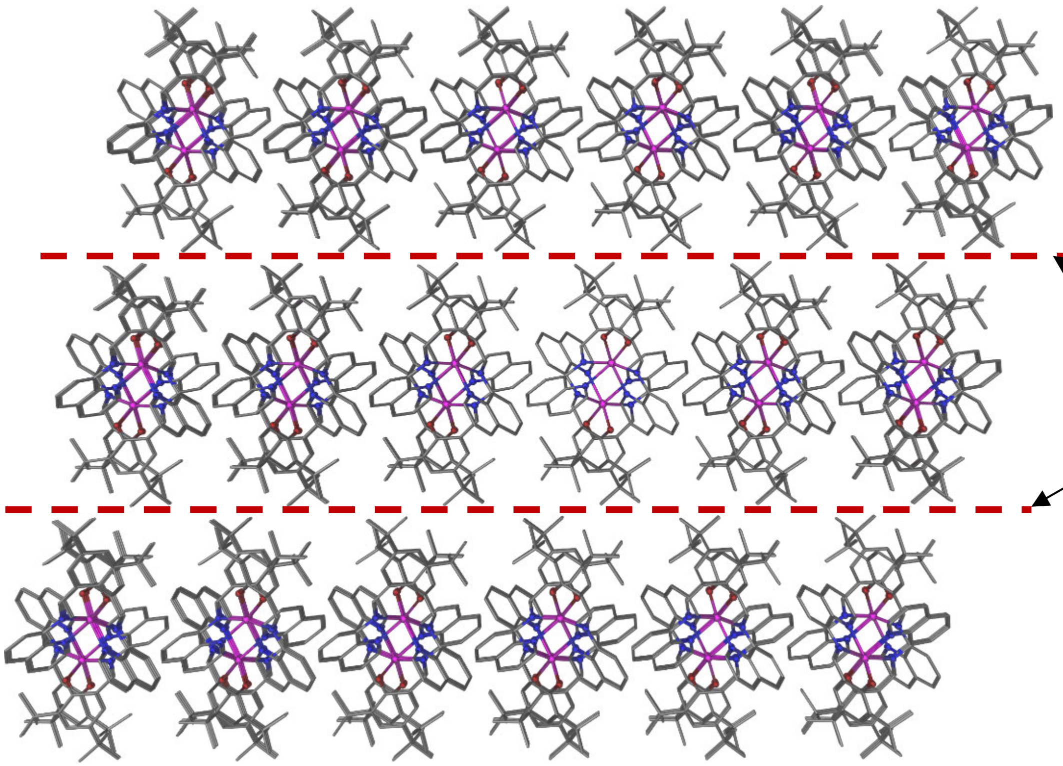


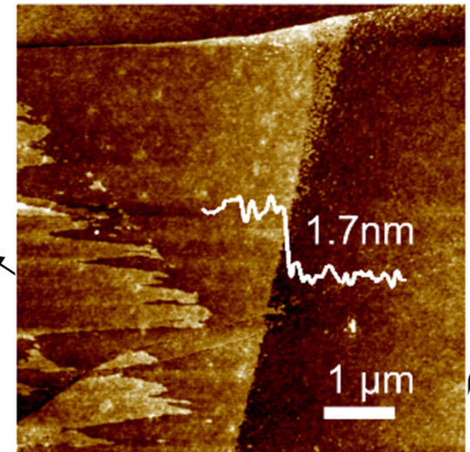


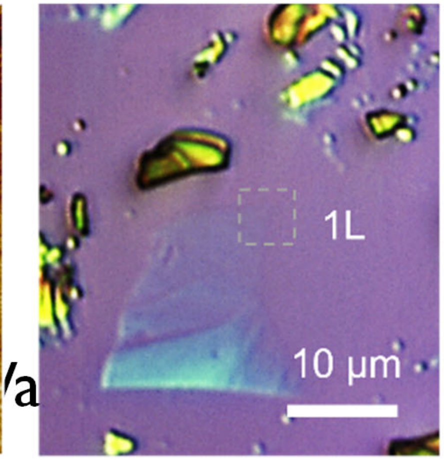
$T_{1/2}$ ≈ 122 K / 127 K

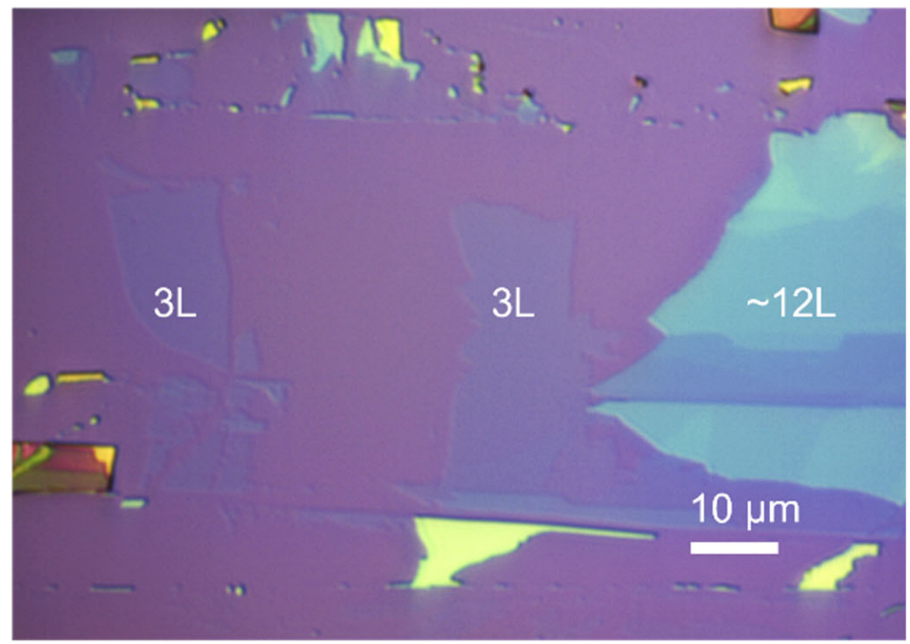
Gakiya-Teruya, M.; Jiang, X.; Le. D.; Rahman, T. S.; Hebard, A. F.; Shatruk, M.; et al. *J. Am. Chem. Soc.* **2021**, *143*, 14563-14572

Mechanical Exfoliation





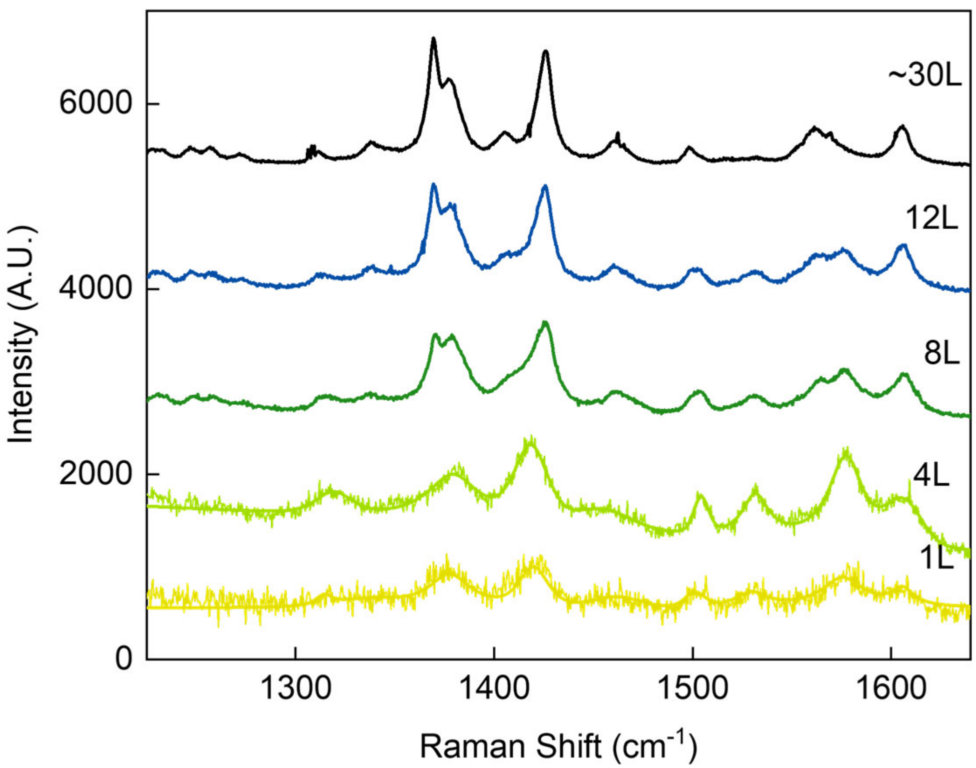


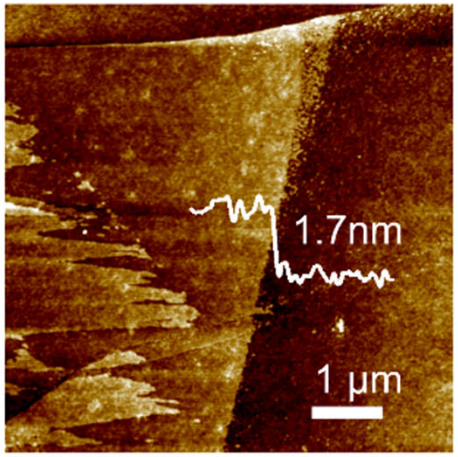


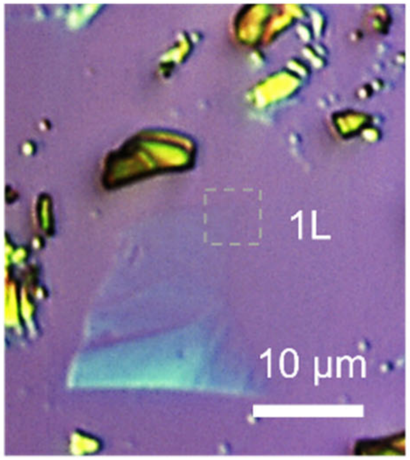
Successful exfoliation to a single molecular layer (1.7 nm thickness)

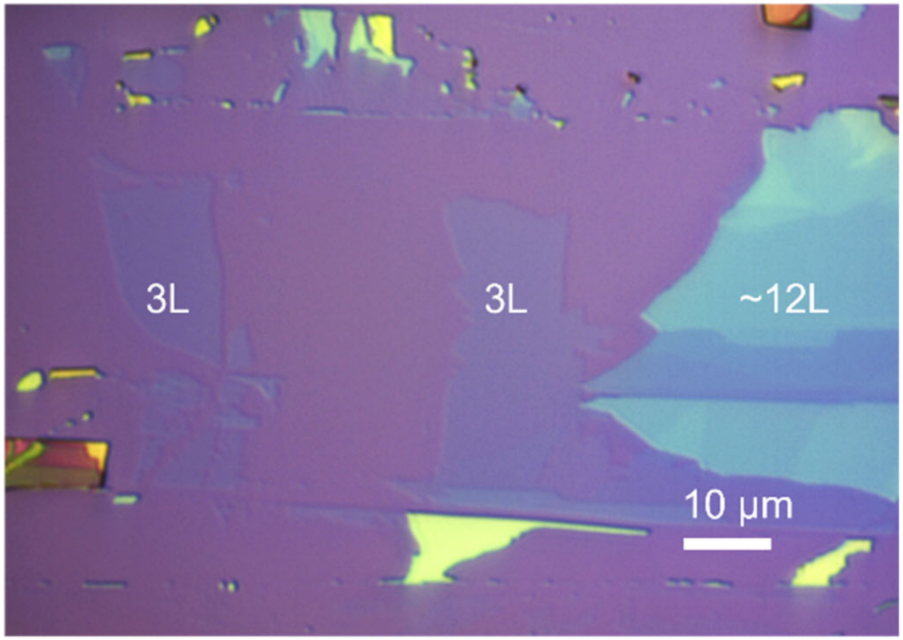
Koptur-Palenchar, J. J.; Gakiya-Teruya, M.; Shatruk, M.; Zhang, X. X; et al.
npj 2D Materials **2022**, *6*, 59

Mechanical Exfoliation









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

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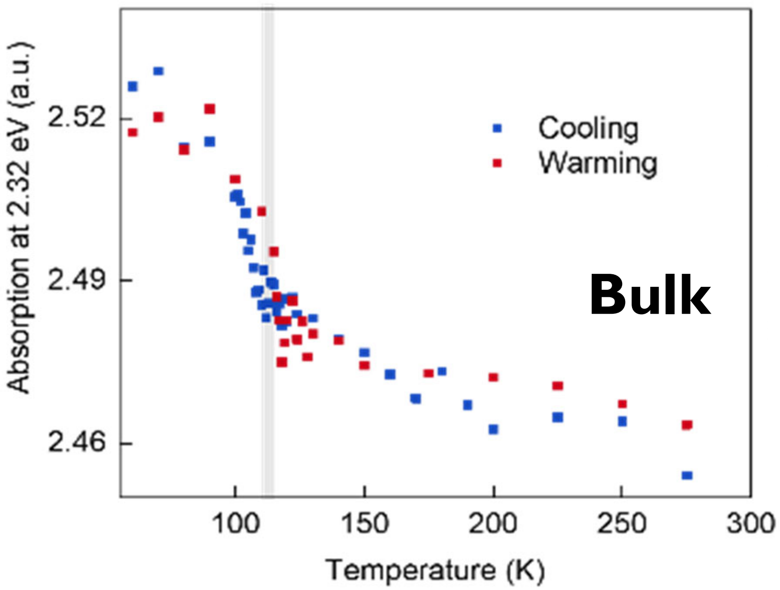
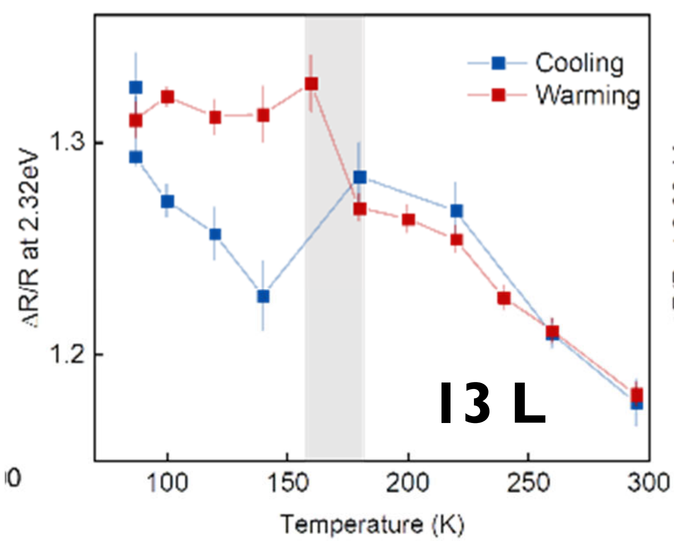
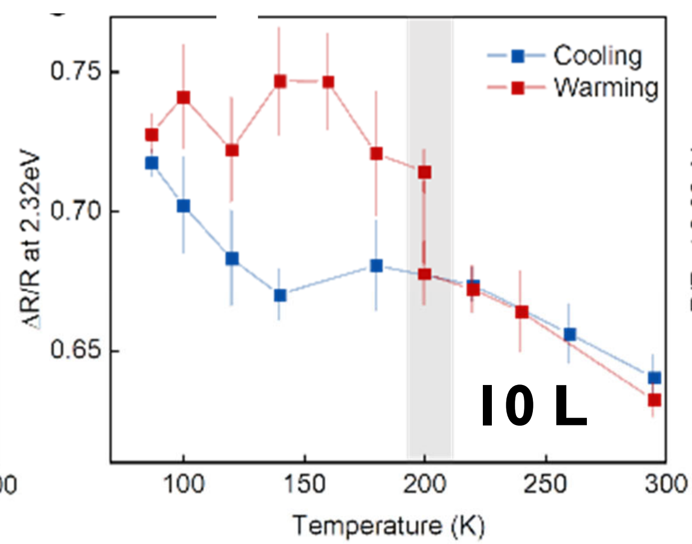
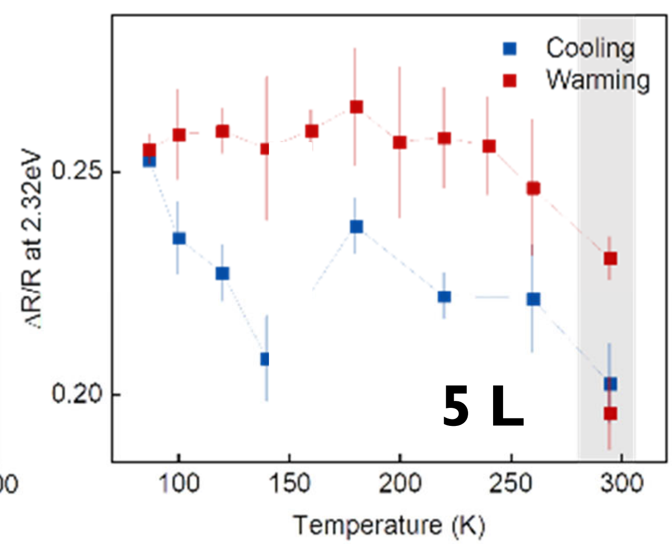
Thickness Dependence of SCO



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 Materials **2022**, *6*, 59

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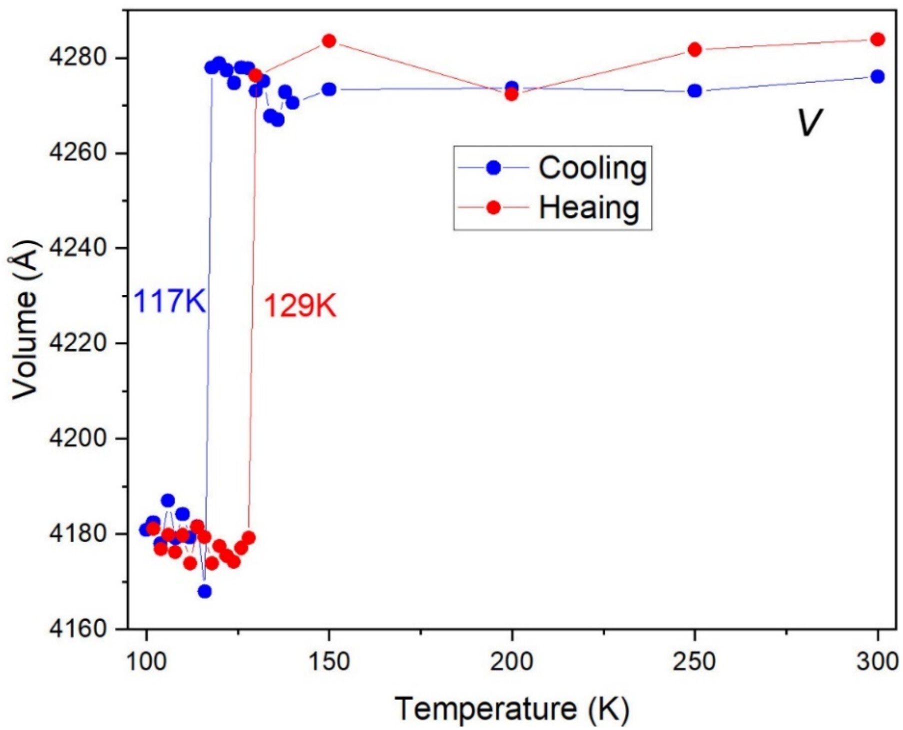
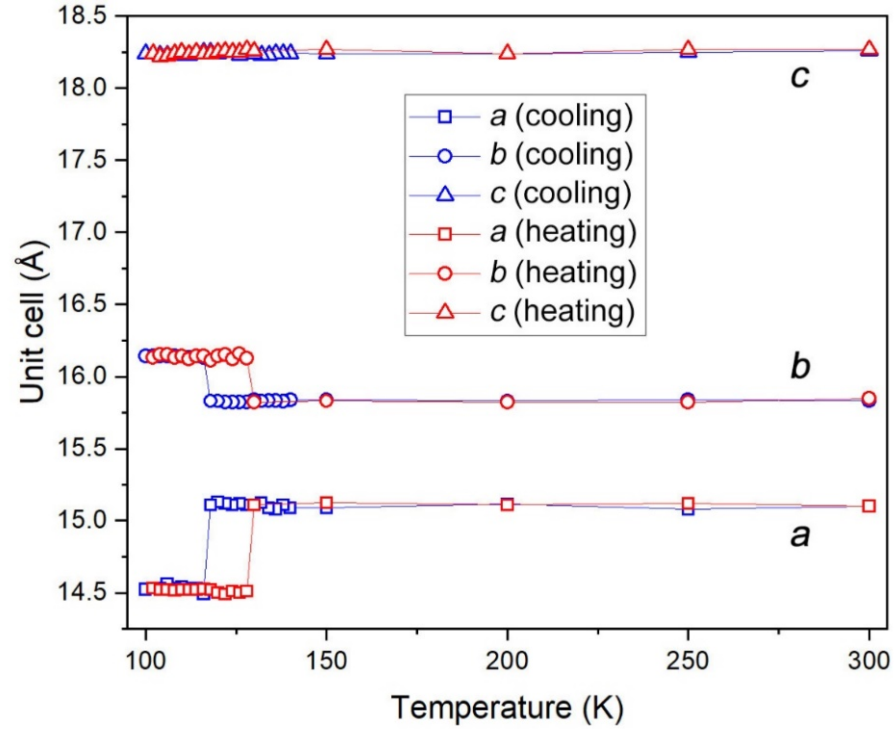
Thickness Dependence of SCO





# 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 Materials* **2022**, *6*, 59

Summary & Outlook

- 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

FSU

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PDSTM-2027 in Tallahassee:
The Capital of Florida & Magnets

Oct 24-28
2027