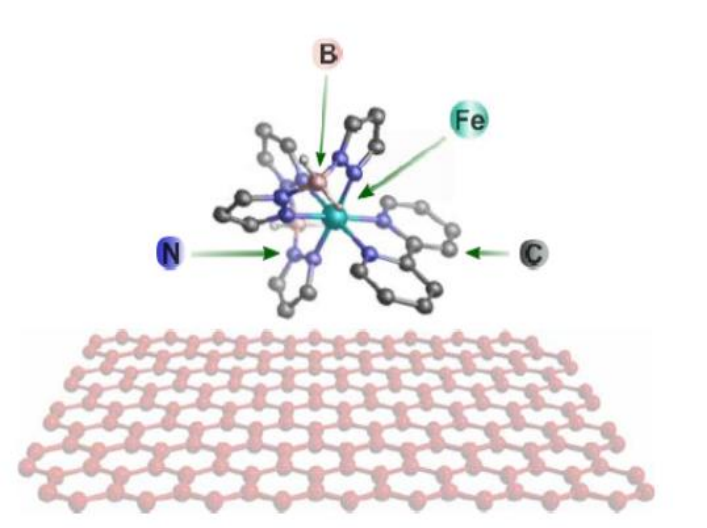
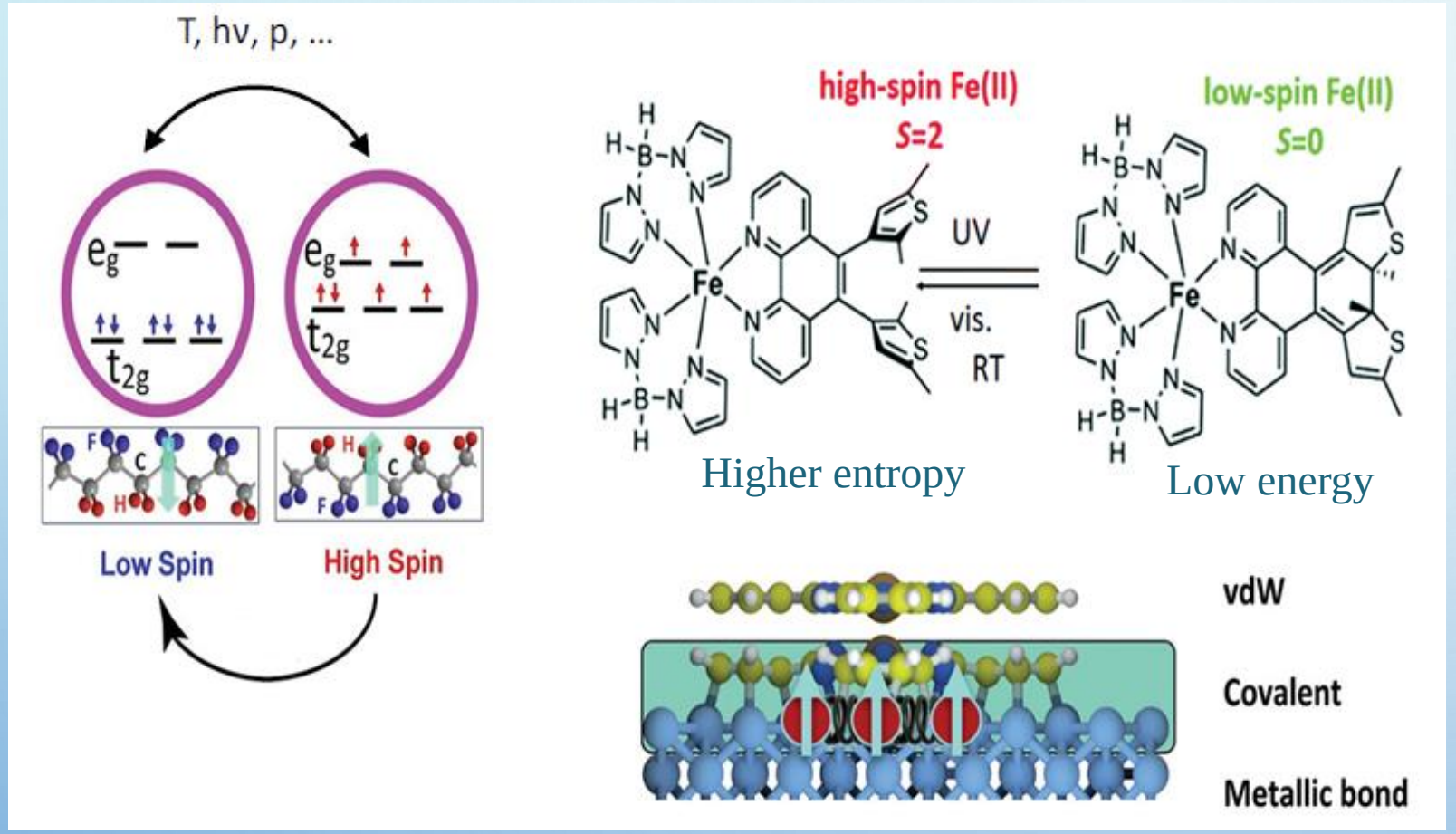
Thermal- and light-induced switching of spin-crossover complexes by XAS

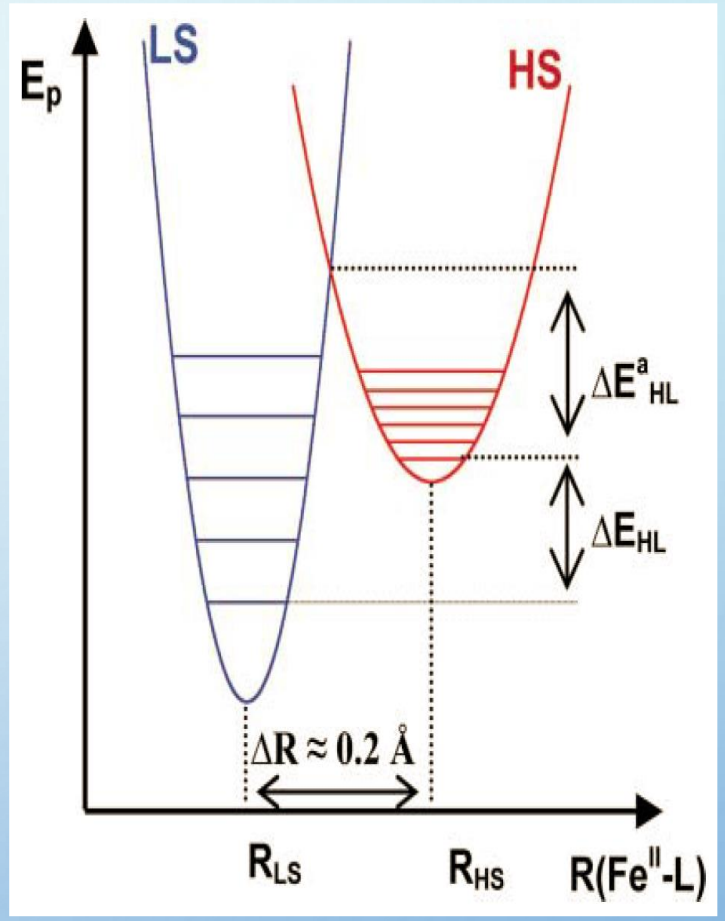
Dr. Sangeeta Thakur, Freie Universität Berlin, Germany



Spin-crossover molecules :



L. Kipgen et.al. Advanced materials 2021, 2008141



J. Real *et al.*, *Dalton Trans.*, 2062 (2005)

Gibbs free energy: G = H – TS

H = U + PV

Temperature-induced spin-crossover switching :

Individual molecules :

$$G_{tot} = \gamma_{HS} G_{HS}(T) + (1-\gamma_{HS}) G_{LS}(T) - TS_{mix} \qquad \frac{\partial G_{tot}}{\partial \gamma_{Hs}} = 0$$

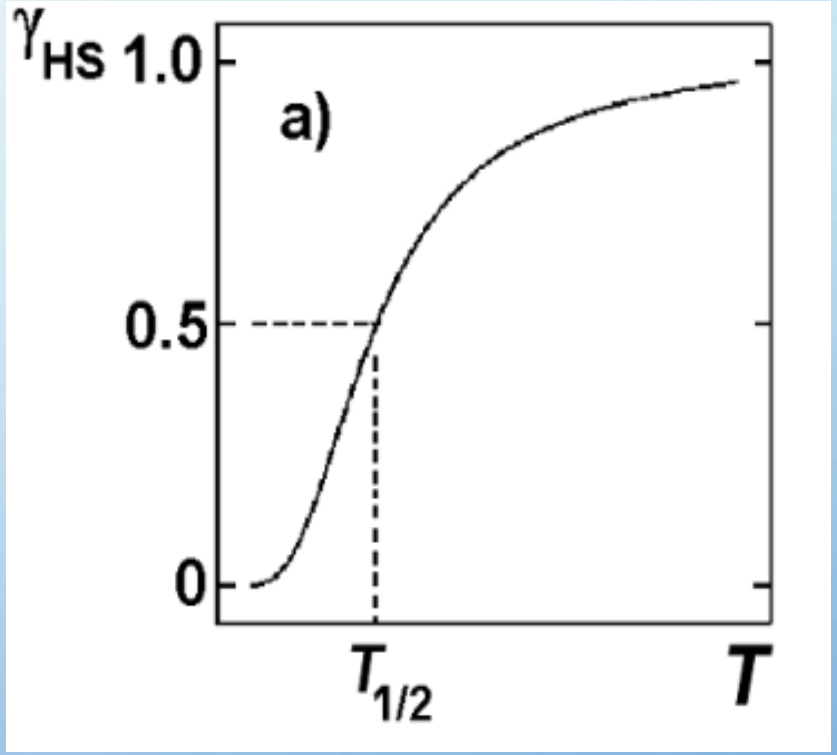
$$S_{mix} = -k_B [\gamma_{HS} \ln \gamma_{HS} + \gamma_{LS} \ln \gamma_{LS}] = -k_B [\gamma_{HS} \ln \gamma_{HS} + (1-\gamma_{HS}) \ln (1-\gamma_{HS})]$$

$$\ln \left(\frac{1-\gamma_{HS}}{\gamma_{HS}}\right) = \frac{\Delta H - T\Delta S}{RT}$$

"van't Hoff formula"

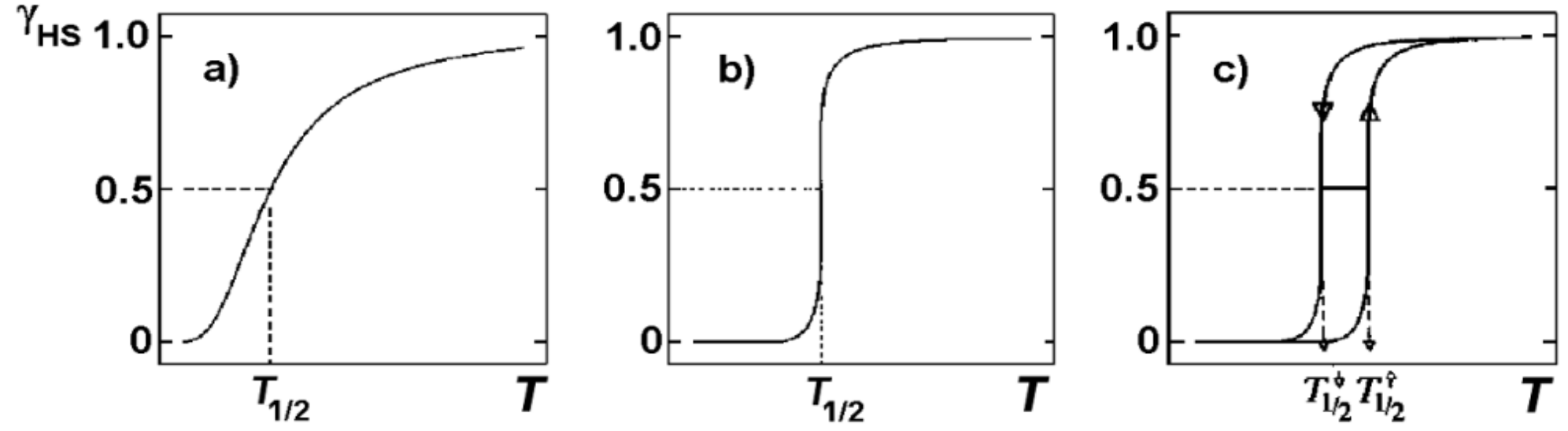
With

$$\Delta H = H_{HS} - H_{LS} \quad , \Delta S = S_{HS} - S_{LS}$$



P. Gutlich et al., in: *Magnetism: Molecules to Materials IV*, ed. by J. S. Miller and M. Drillon, Wiley-VCH (2003).

Temperature-induced cooperative switching :



(from P. Gutlich et al., in: *Magnetism: Molecules to Materials IV*, ed. by J. S. Miller and M. Drillon, Wiley-VCH (2003)

In SCO crystals: preference for the spin state of the majority of molecules

- elastic interactions
(pressure from surrounding molecules)

- electrostatic interactions
(fluctuations in the Madelung field)

M. Kepenekian *et al*., J. Am. Chem. Soc. **131**, 11498 (2009);
Phys. Rev. B **79**, 094428 (2009).

Cooperative switching

$$\ln\left(\frac{1-\gamma_{HS}}{\gamma_{HS}}\right) = \frac{\Delta H - T\Delta S + \Gamma(1-2\gamma_{HS})}{RT}$$

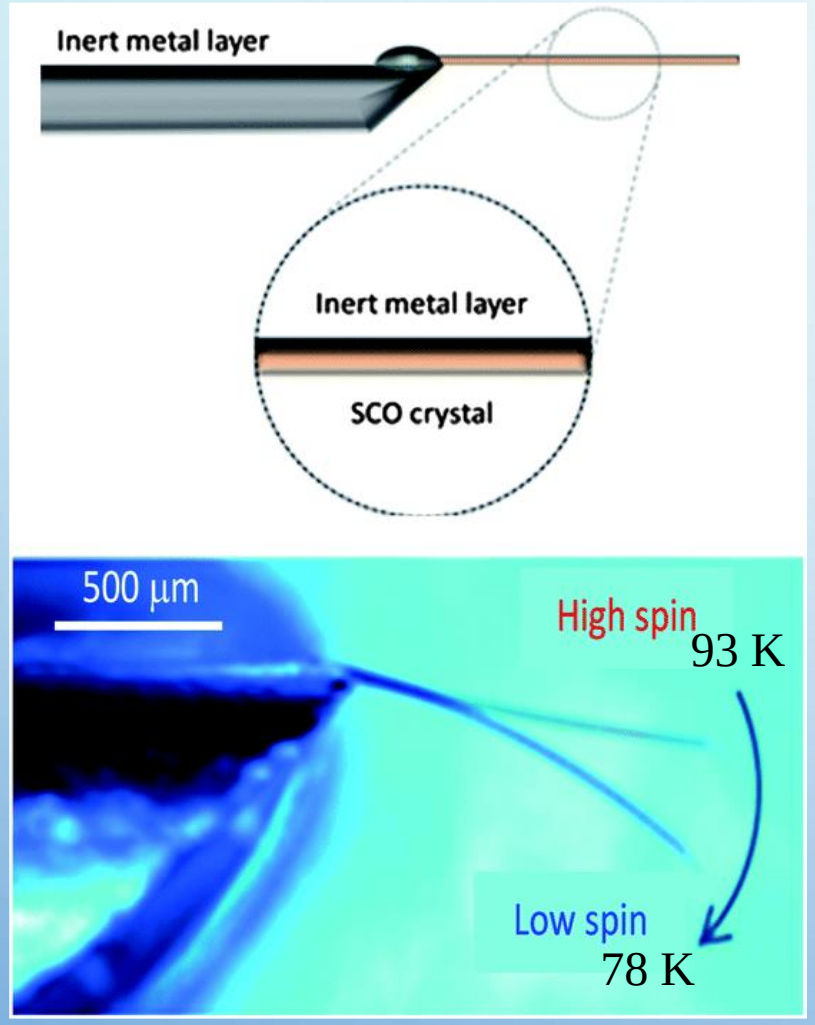
Γ is the strength of interaction

"Slichter–Drickamer model"

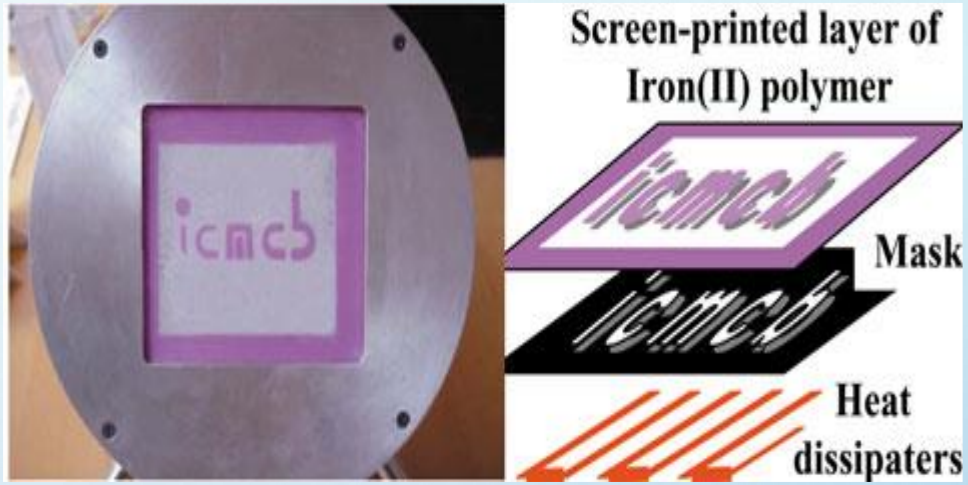
C. P. Slichter *et al*., J. Chem. Phys. **56**, 2142 (1972)

Applications of spin-crossover molecules :

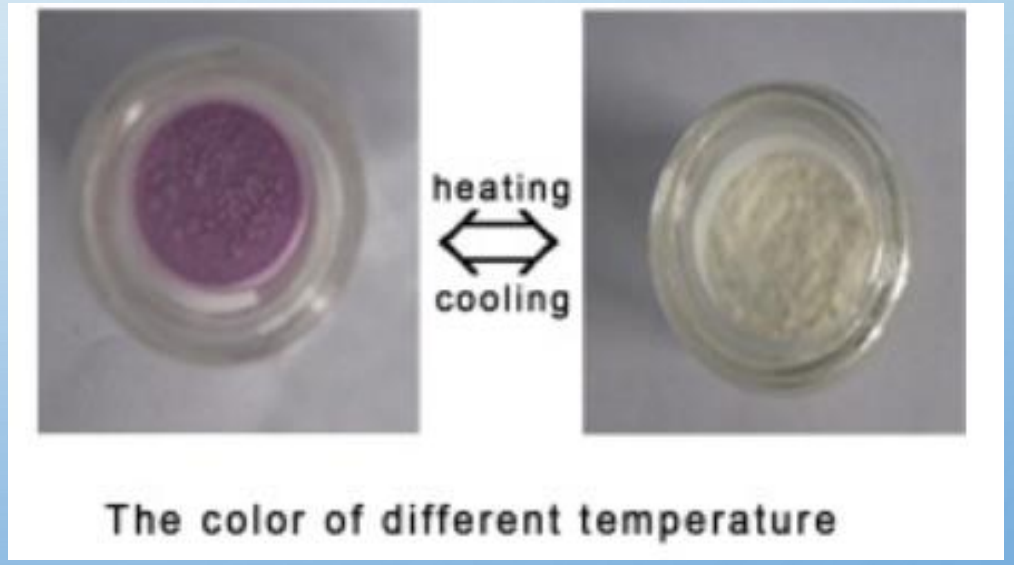
SCO-induced actuation



G. Molnar et al., J. Mater. Chem. C **2**, 1360 (2014)



J.-F. Letard et al., Top. Curr. Chem. **235**, 221 (2004).



Wen-ping Wang et al., Inorg. Chem. Commun. **56**, 125 (2015).

Motivation :

Try to achieve spin-crossover transition on a surface (submonolayer regime).

To use this as a switch in a future molecular spin electronics.
-immobilization and contact

Acknowledgements :

FU Berlin:

- Prof. Wolfgnag Kuch
- Marcel
- Jorge
- Ivar
- Sebastien
- Jendrik
- Pinchi-lu
- Lalmin
- Lucas

– Christian Lotze

U Kiel:

– Sascha Ossinger
– Clara Trommer
– Felix Tuczek

HZB:

– Florin Radu
– Chen Luo

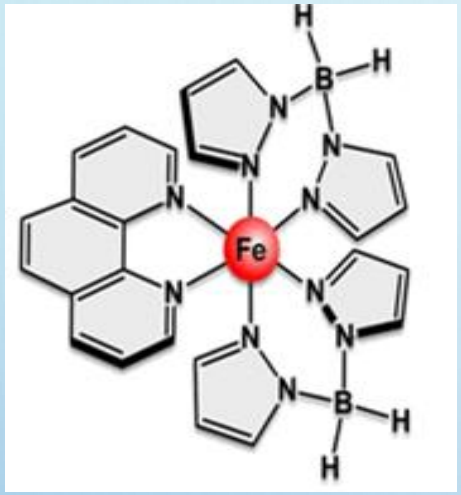
Karlsruhe Institute of Technology

- Senthil Kuppusamy Kumar
- Mario Ruben

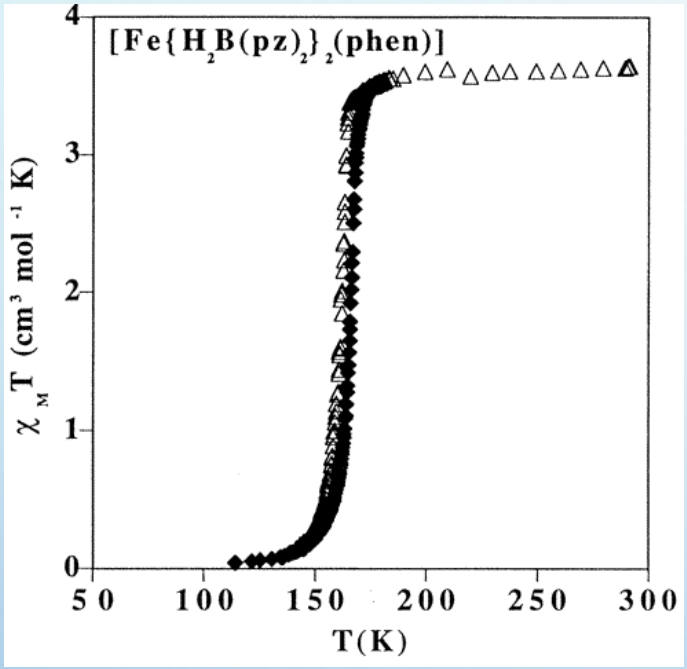
Financial support

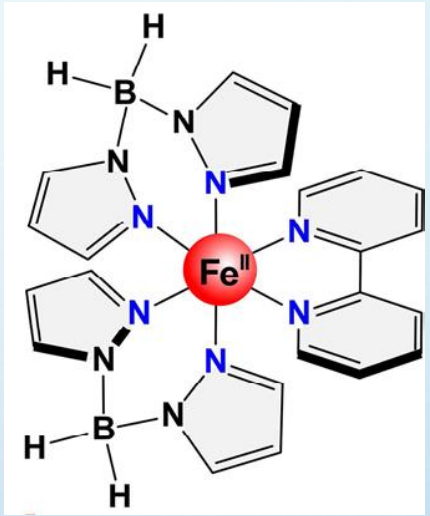
BMBF through project VEKMAG (BMBF 05K13KEA and 05K16KE3)

The spin-crossover molecules :

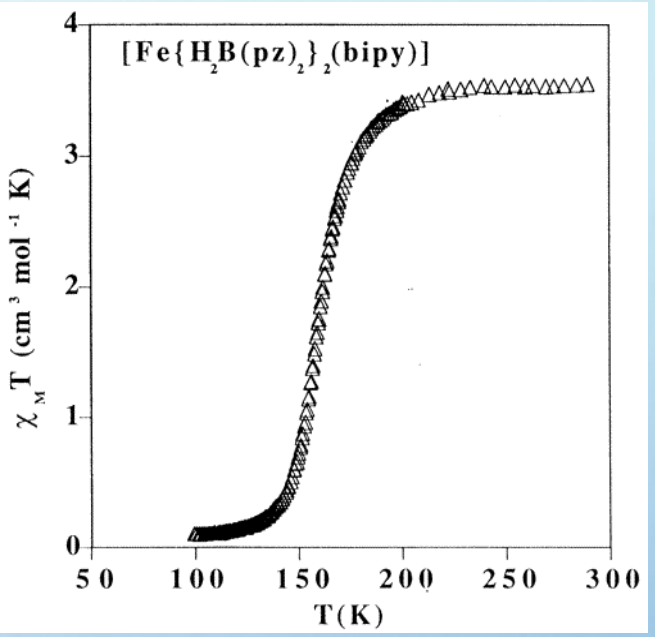


[FeII(bpz)2(phen)]





[FeII(bpz)2(bipy)]

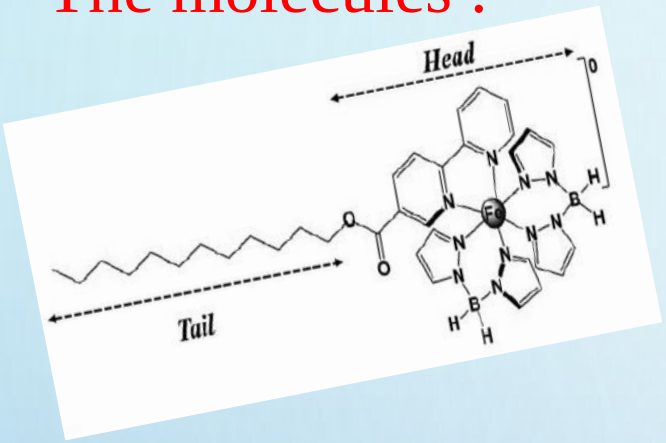


José Antonio Real , *Inorganic Chemistry* **1997** *36* (14), 3008-3013

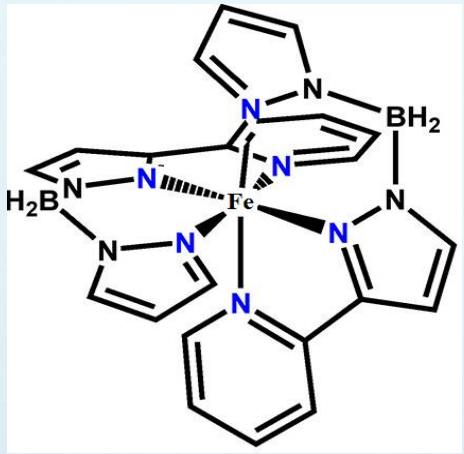
- Neutral Fe(II) complexes
- Easy to sublimate at T=160°C
- Ideally suited for vacuum deposition

bpz = dihydrobis(pyrazolyl)borate
phen = 1,10-phenanthroline
bipy = 2,2-bipyridine

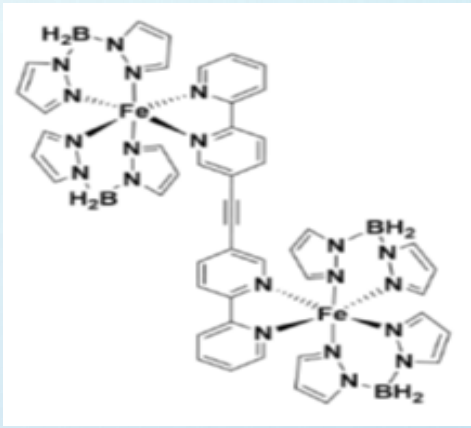
The molecules :



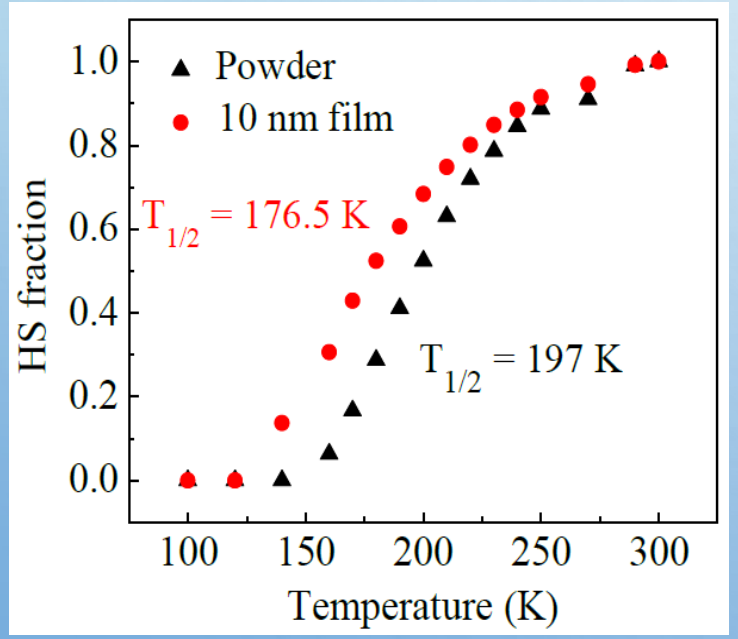
$[Fe(bpz)_2(COOC_{12}H_{25}\text{-}bpy)]$



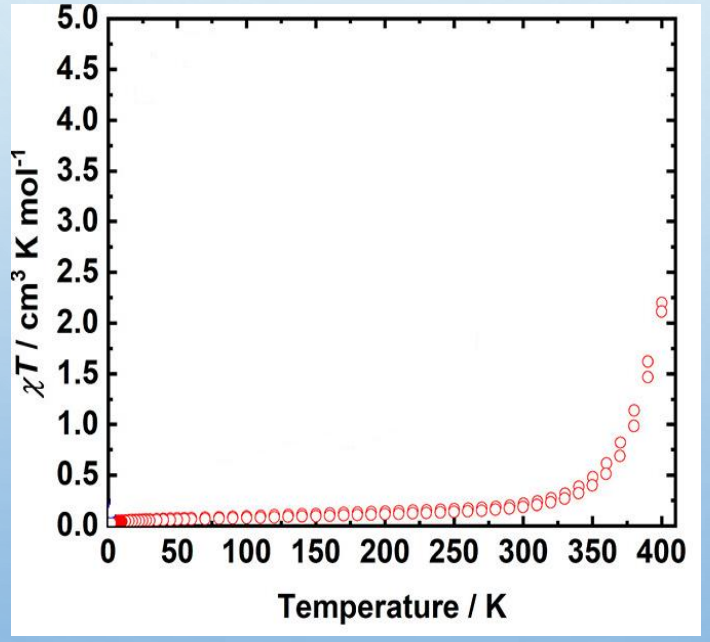
$Fe[H_2B(pz)(pypz)]_2$



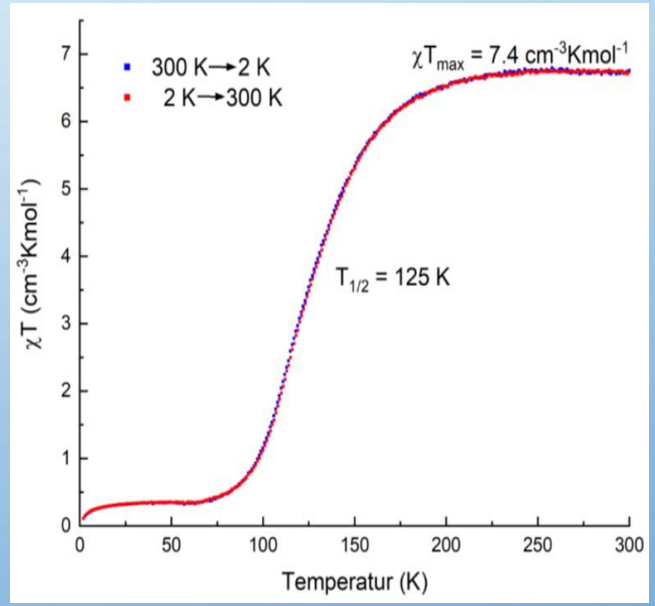
$[\{Fe(H_2B(pz)_2)_2\}_2\ \mu\text{-}(bipy\text{-}ac\text{-}bipy)]$



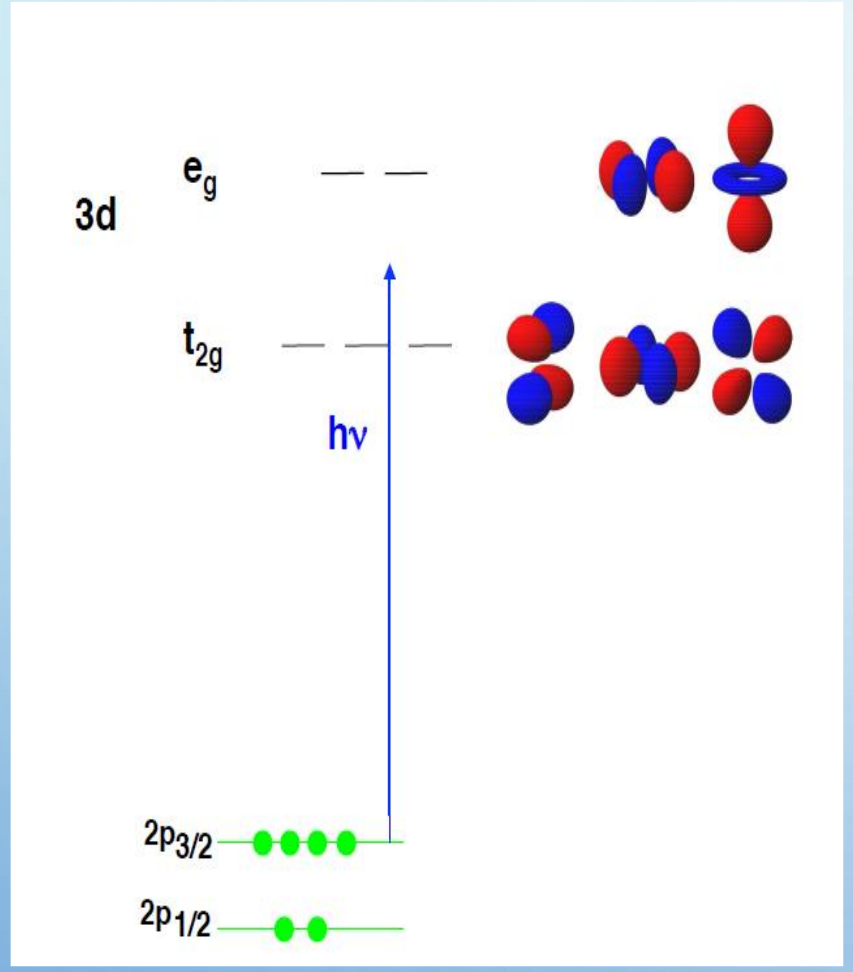
S. Kumar, Advanced Materials 2018, 30, 1705416.



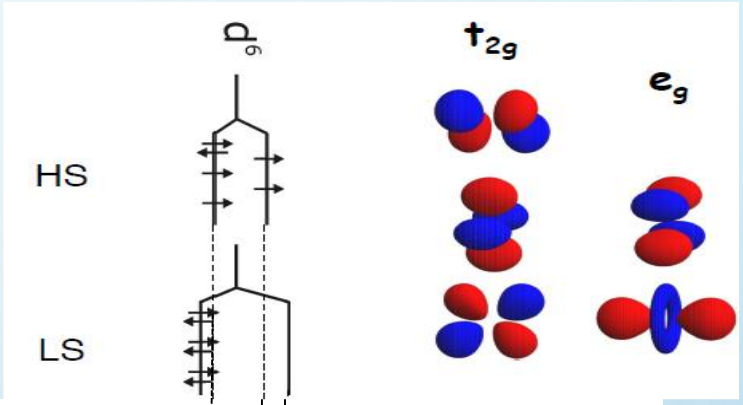
S. Ossinger, Inorg. Chem. 2020, 59, 7966-7979.

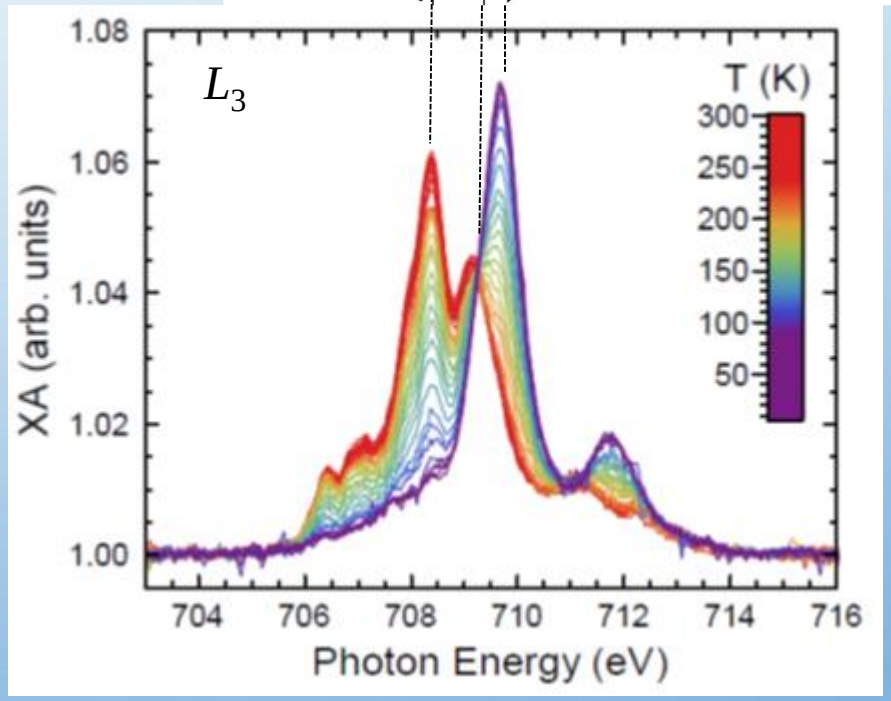


X-ray absorption spectroscopy (XAS):



XAS of Fe(II) spin-crossover molecule





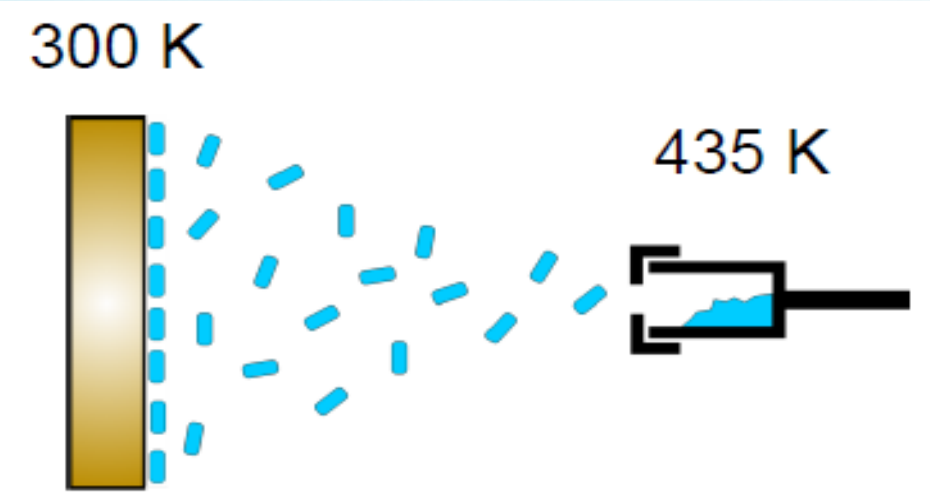
M. Bernien ACS Nano 9, 8960-8966, 2015.

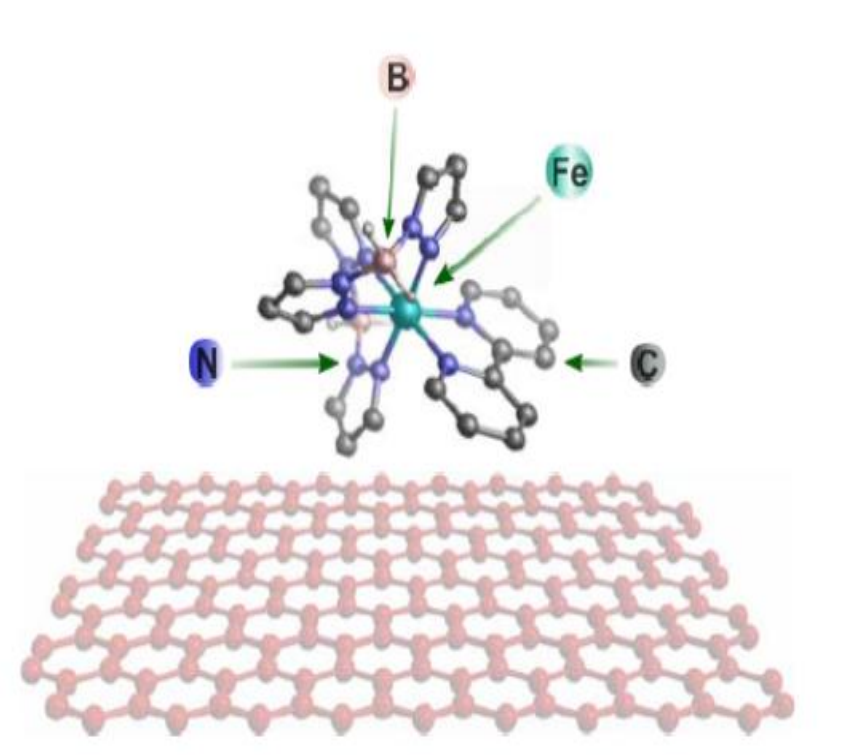
X-ray absorption Experiments :

– UE 46 PGM-1

– PM-2 VEKMAG

Sample preparation:

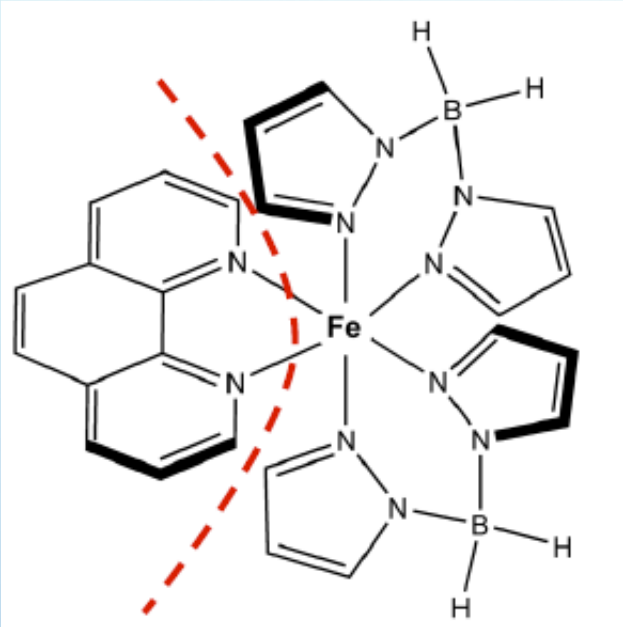




L. Kipgen Thesis

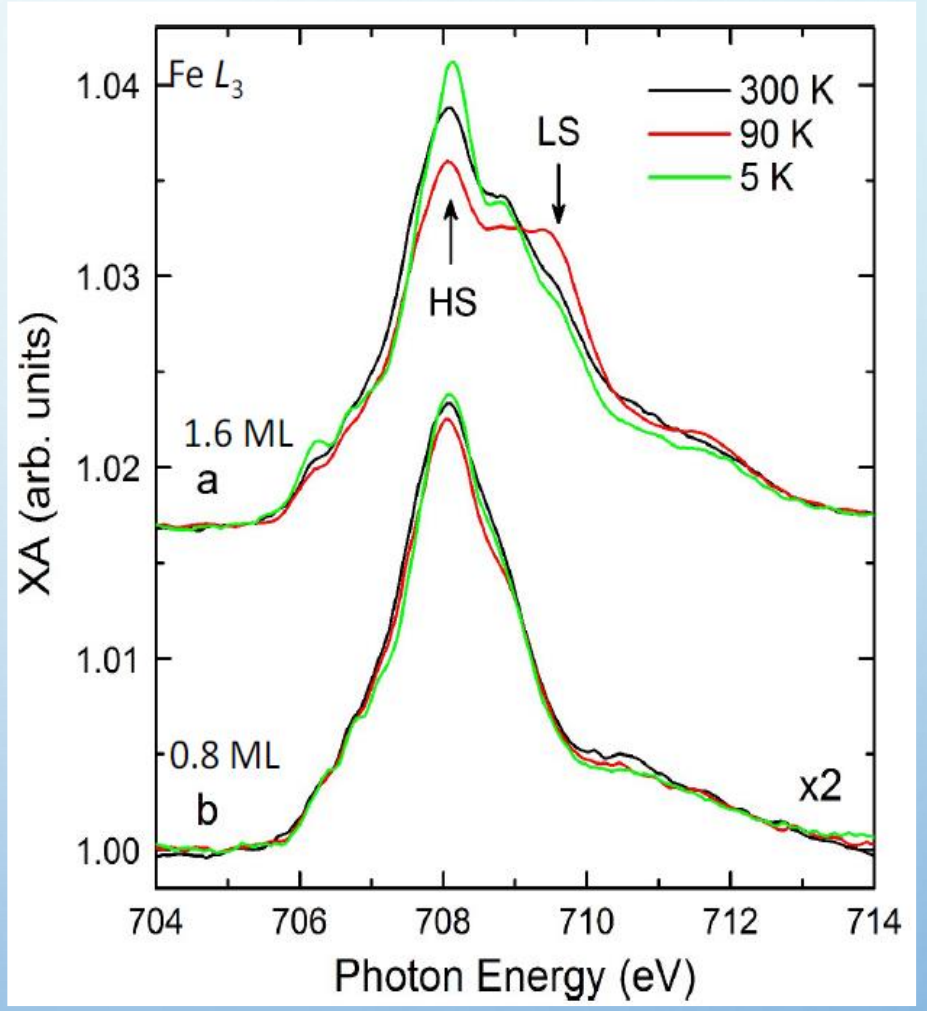
- Substrate : highly oriented pyrolytic graphite (HOPG)
- Clean surface by cleaving at 10^{-6} mbar with a carbon tape
- Thermal deposition in UHV

Deposition of $[Fe^{II}(bpz)_2phen]$ on Au(111):



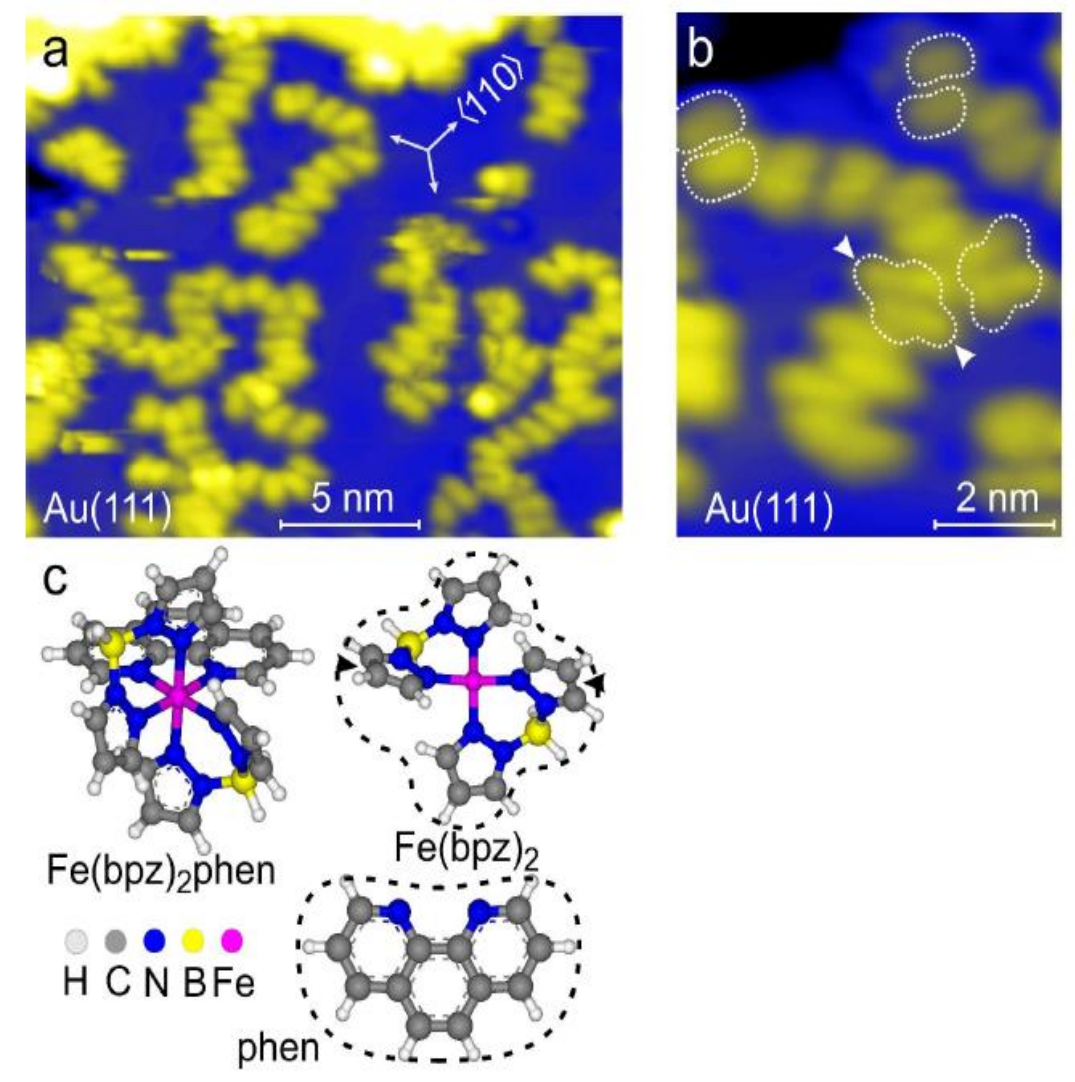
$[Fe^{II}(bpz)_2phen]$

- Spin transition only at higher coverages : only molecules in 2nd layer switch



T. G. Gopakumar et.al., Chem. Eur. J. 19, 15702 (2013).

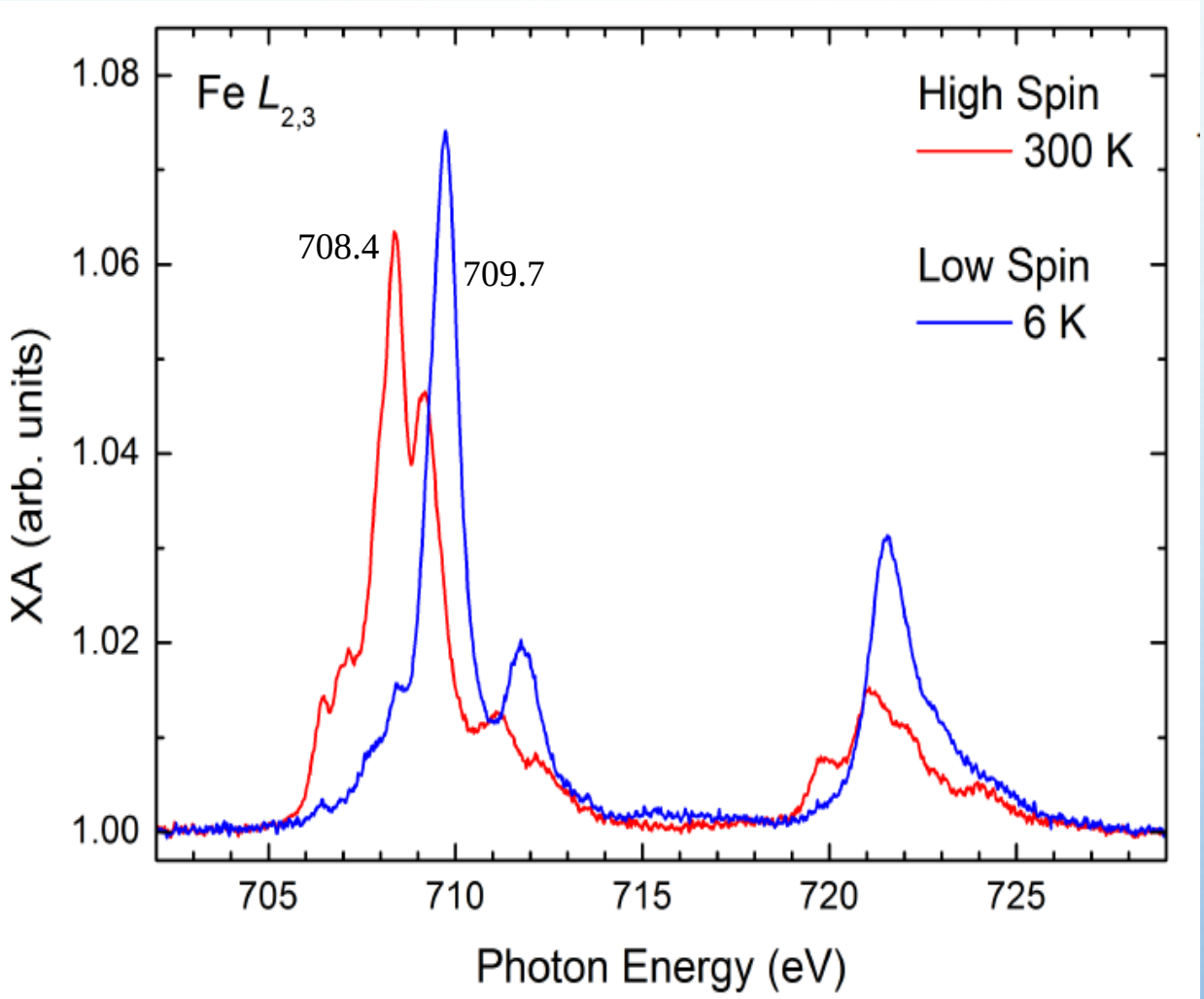
Deposition of $[Fe^{II}(bpz)_2phen]$ on Au(111):



- Molecules in 1st layer decompose into $Fe(bpz)_2$ and phen

T. G. Gopakumar et.al., Chem. Eur. J. 19, 15702 (2013).

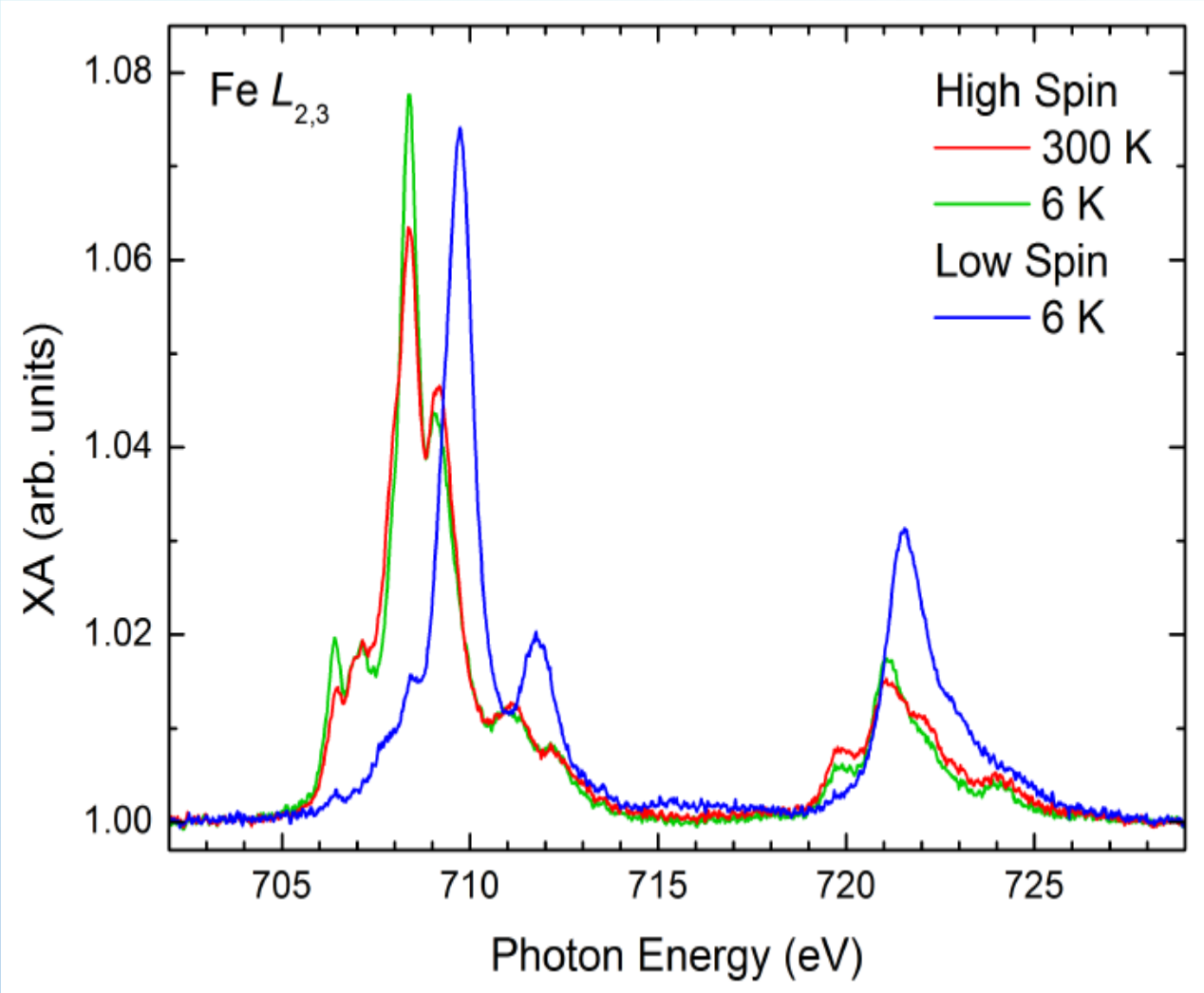
Deposition of $[Fe^{II}(bpz)_2phen]$ on HOPG :



M. Bernien et. al. ACS Nano 9, 8960 (2015)

- 0.7 ML of $[Fe(bpz)_2phen]$ on HOPG
- Strong temperature-dependent changes of lineshape representing the high spin and low spin state
- Nearly complete interconversion

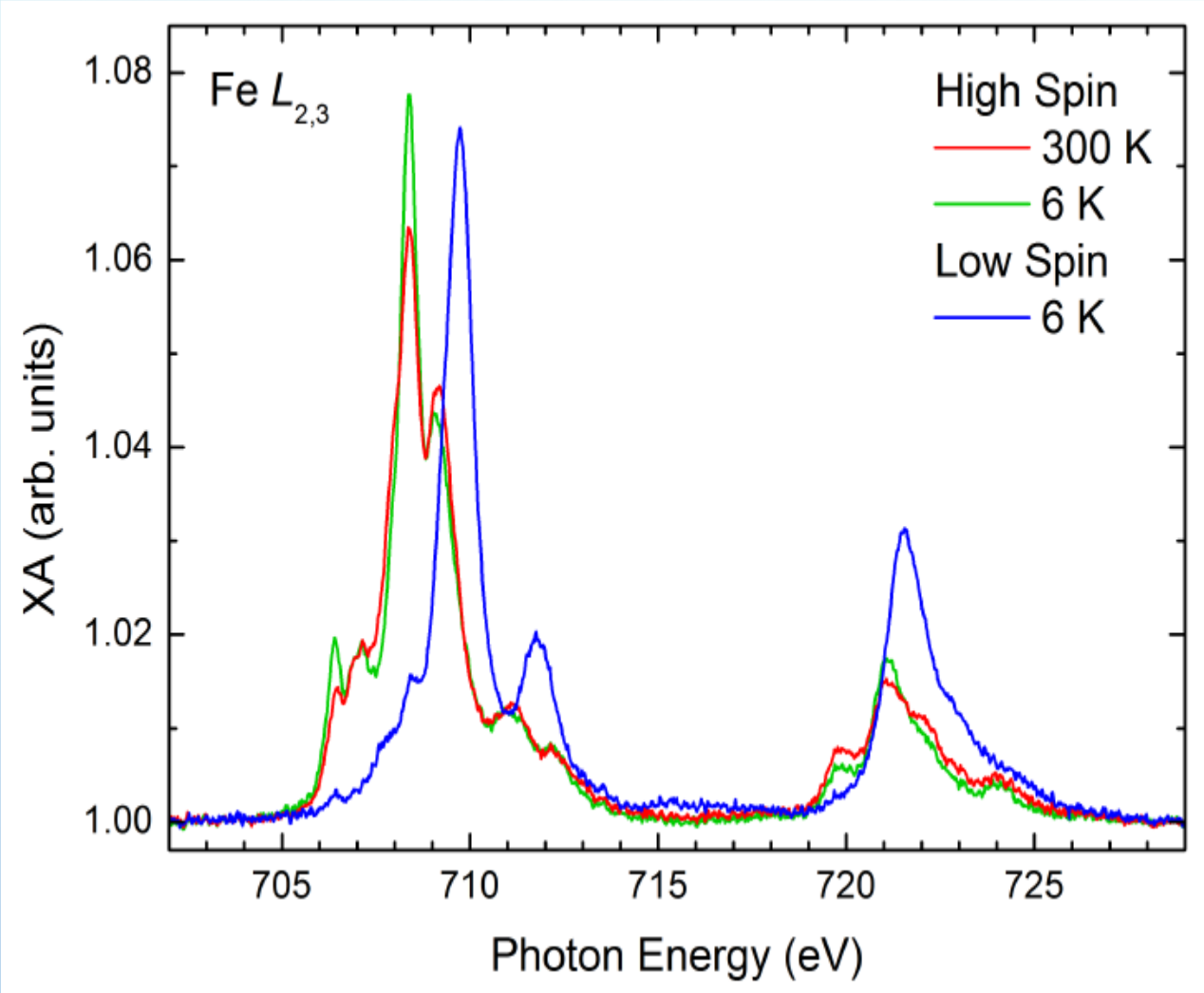
Deposition of $[Fe^{II}(bpz)_2phen]$ on HOPG :



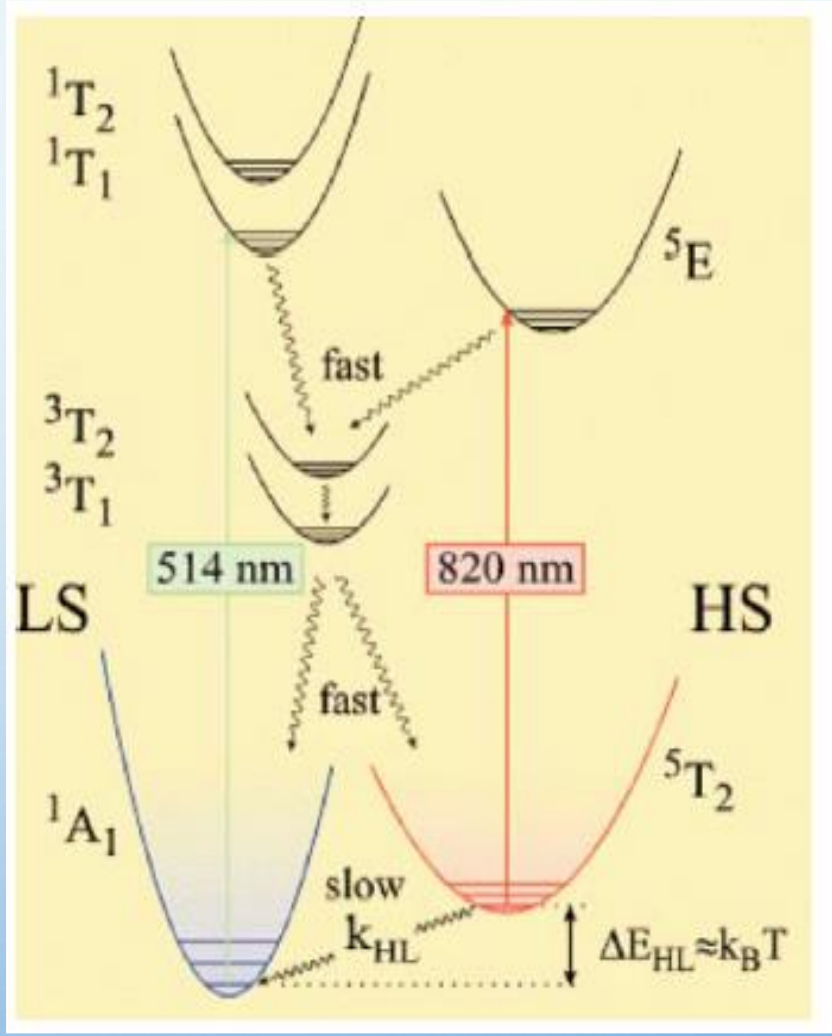
- After illumination with green light (520 nm) for 34 min at 5 K complete low spin to high spin transition (Light-induced Excited Spin state Trapping)

M. Bernien et. al. ACS Nano 9, 8960 (2015).

Deposition of $[Fe^{II}(bpz)_2phen]$ on HOPG :



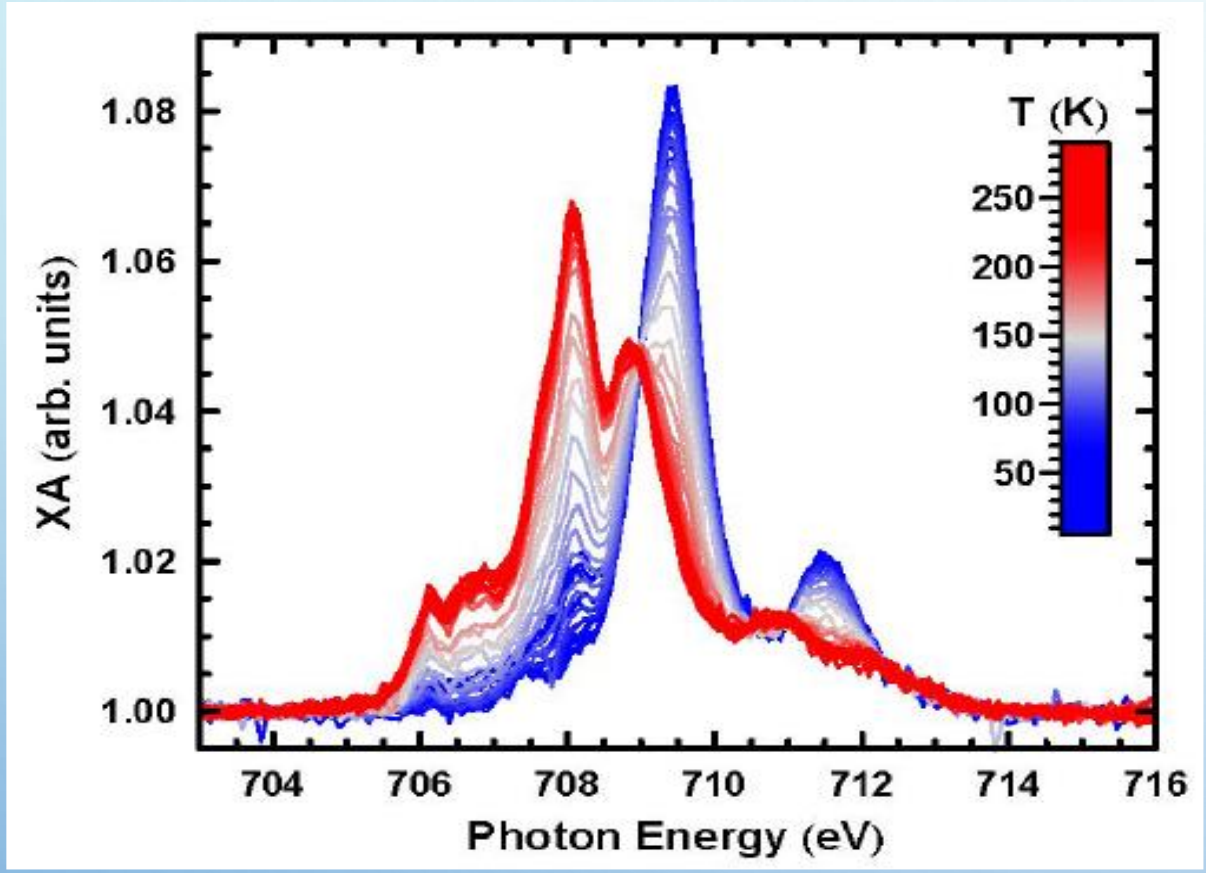
M. Bernien et. al. ACS Nano 9, 8960 (2015).

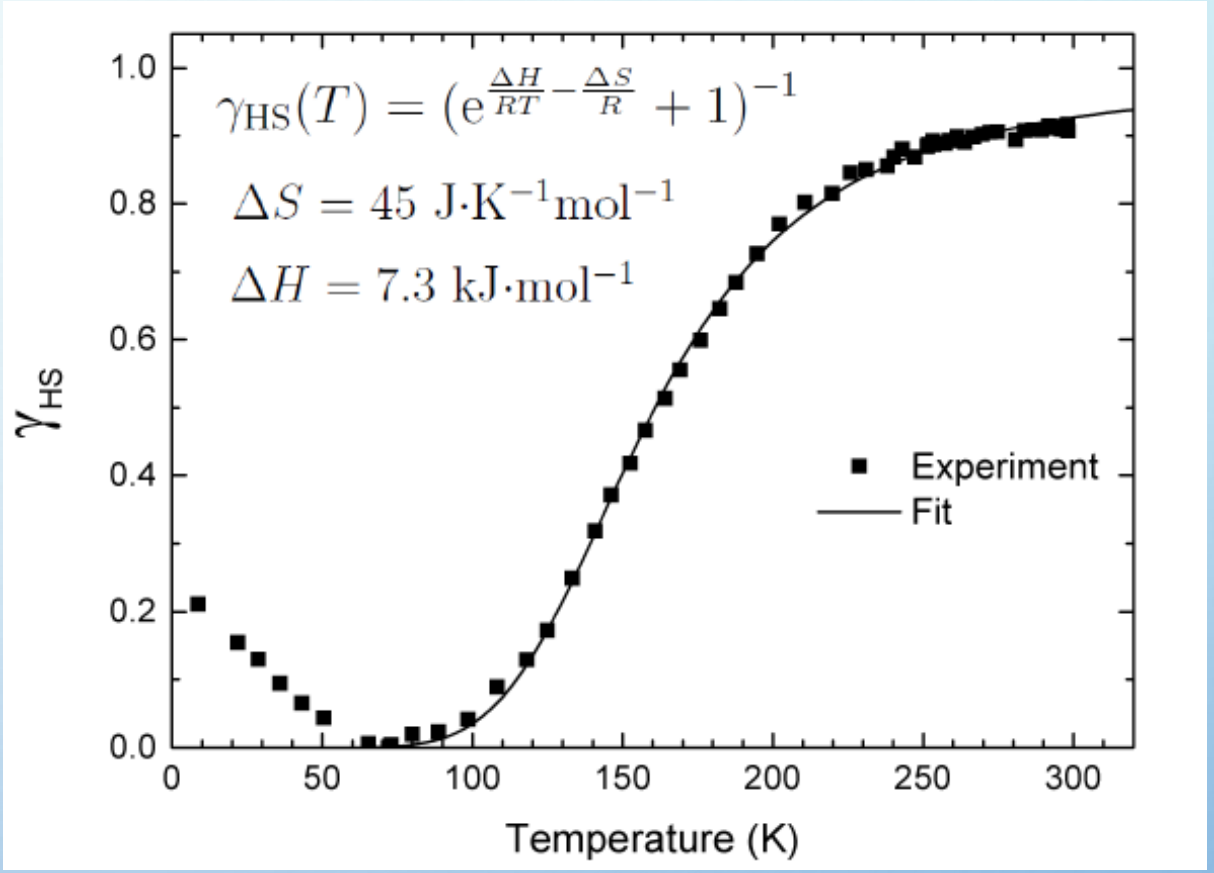


J. Real et al., Dalton Trans., 2062 (2005).

Light induced excited spin state trapping (LIESST).

Thermal spin crossover:

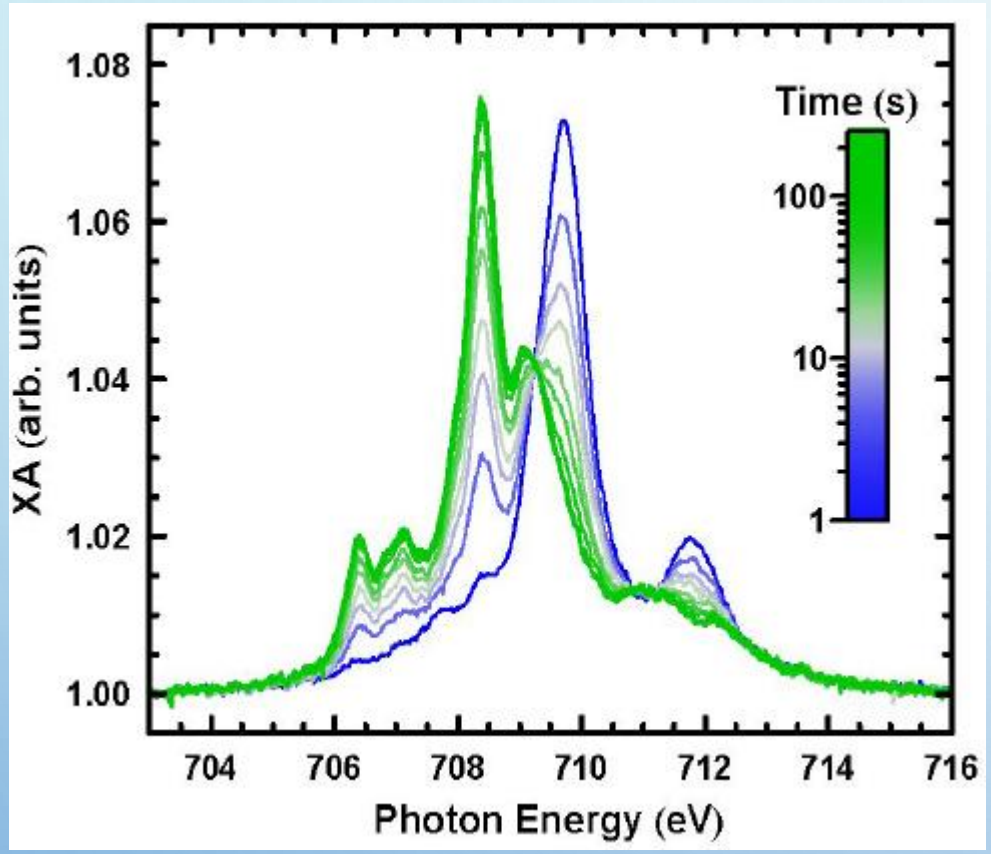


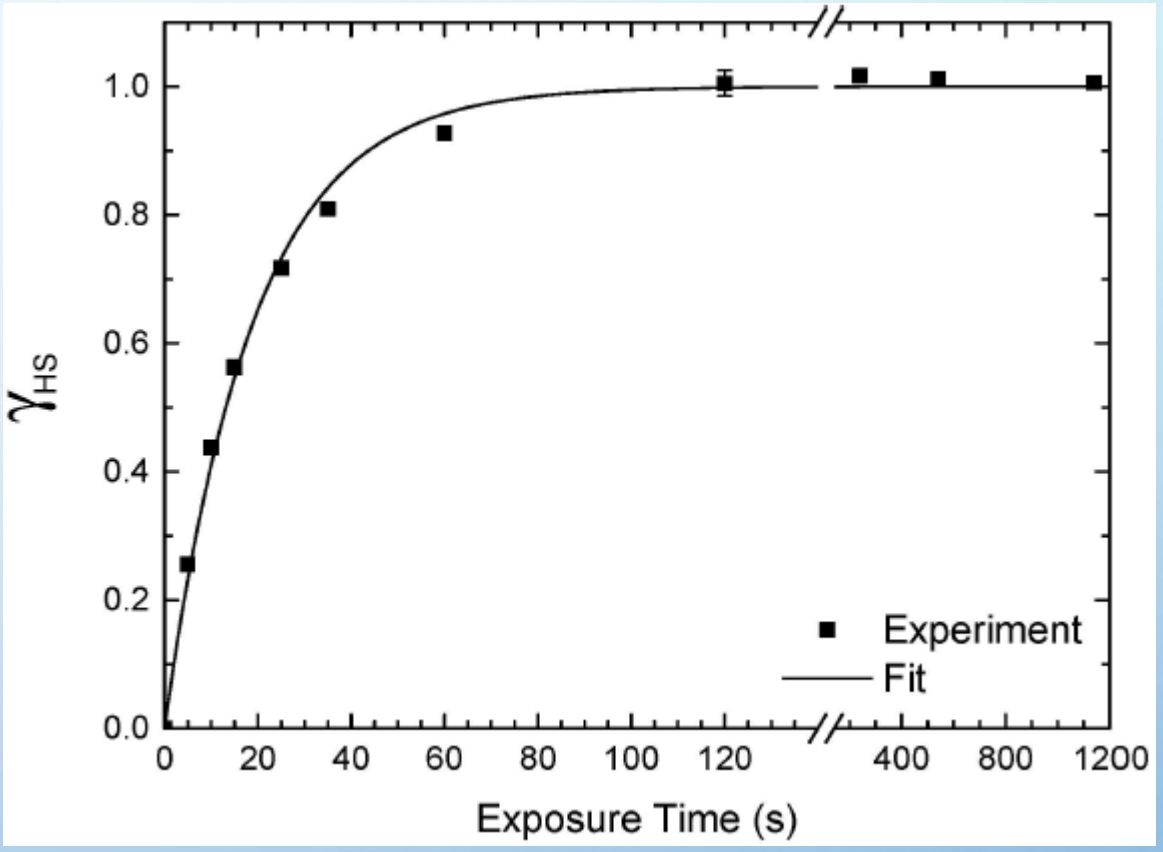


M. Bernien et. al. ACS Nano 9, 8960 (2015)

- Determination of high-spin fraction by two-component fitting
- Transition temperature $T_{1/2}$ = 161 K the same as in bulk
- Below 70 K: x-ray induced switching

Efficiency of light – induced switching :

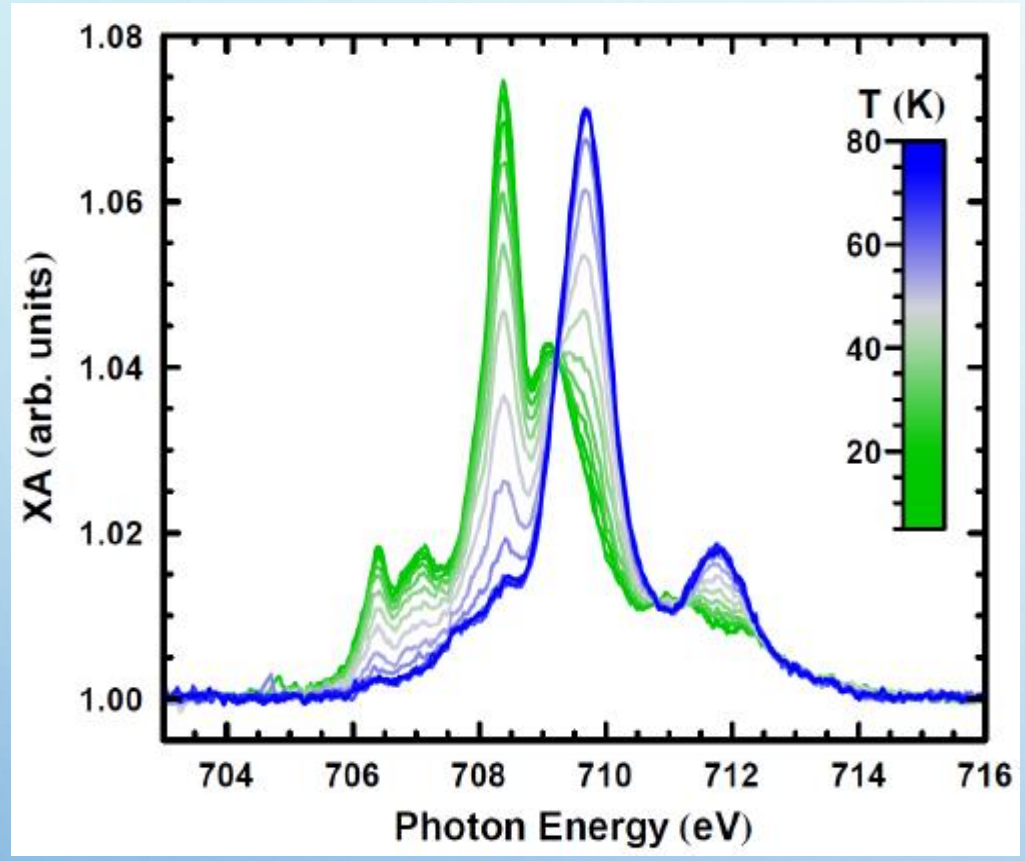


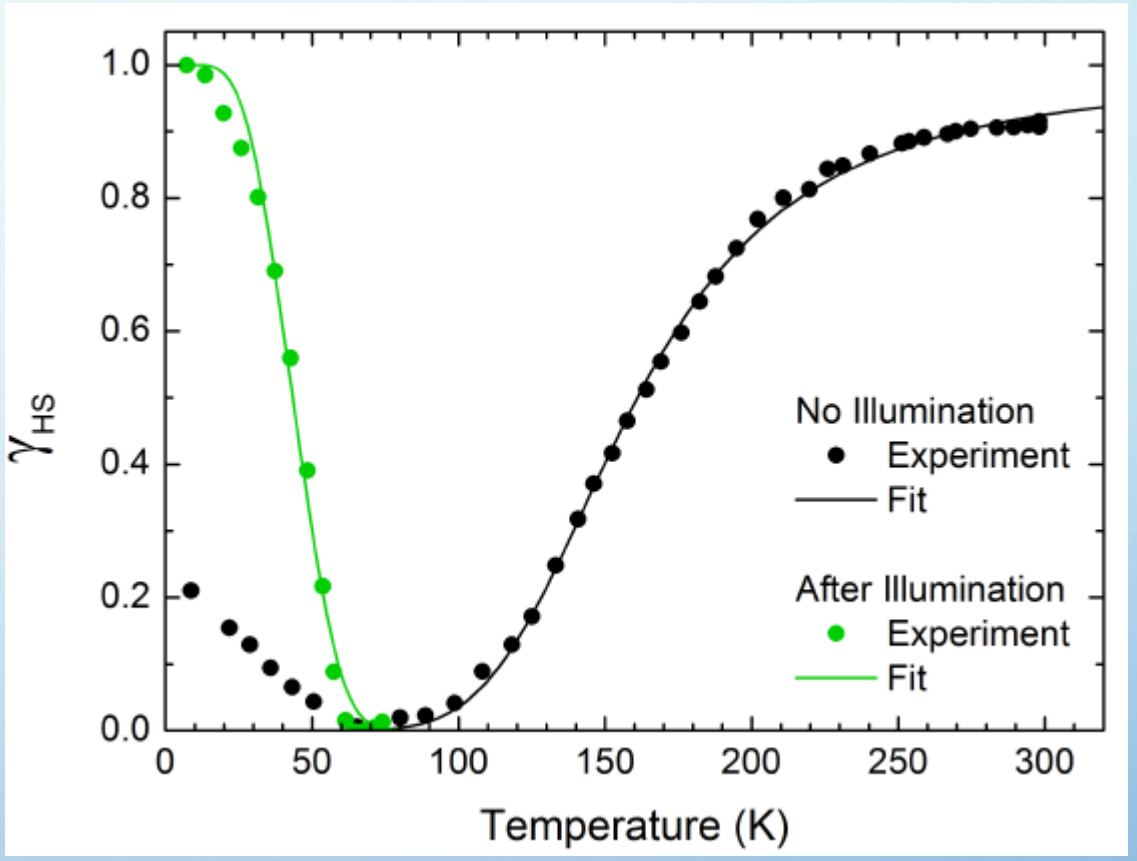


M. Bernien et. al. ACS Nano 9, 8960 (2015)

- Evolution of the Fe-L_3 lineshape as a function of exposure time at T = 5 K
- Flux density (green LED, 520 nm) , ϕ = 4.6 x 10^{14} photons.s^{-1} mm^{-2}
- Highly efficient spin conversion with a time constant of τ = 20.4 s

Thermal relaxation of high – spin state :

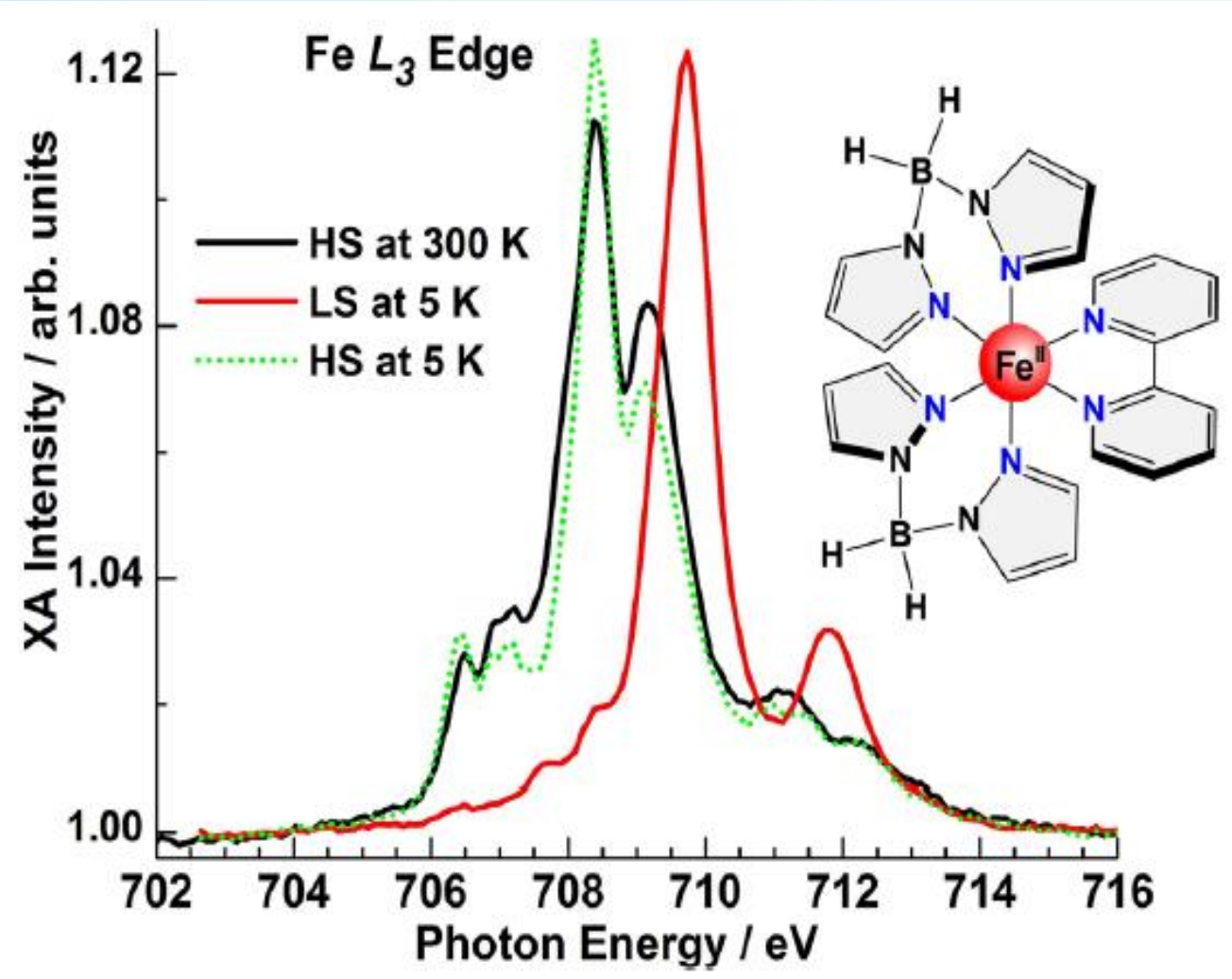




M. Bernien et. al. ACS Nano 9, 8960 (2015).

- Temperature-dependent evolution of the Fe-L_3 lineshape after illumination with green light
- Effective barrier height E_A = 789 J. mol^{-1}
- Barrier height lower by factor 2.5 compared to bulk , indicating that the HS state is destabilized on the HOPG surface.

Modification of molecule :

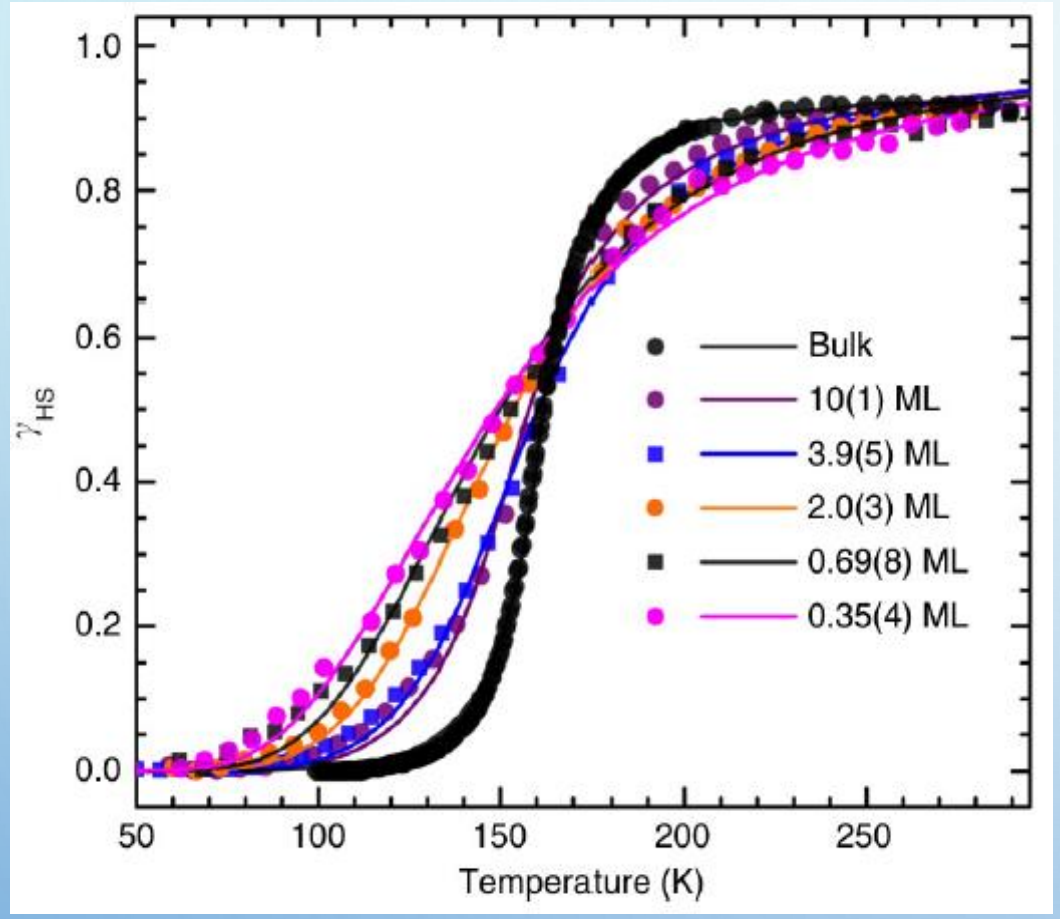


0.8 ML of Fe(bpz)-bipy on HOPG

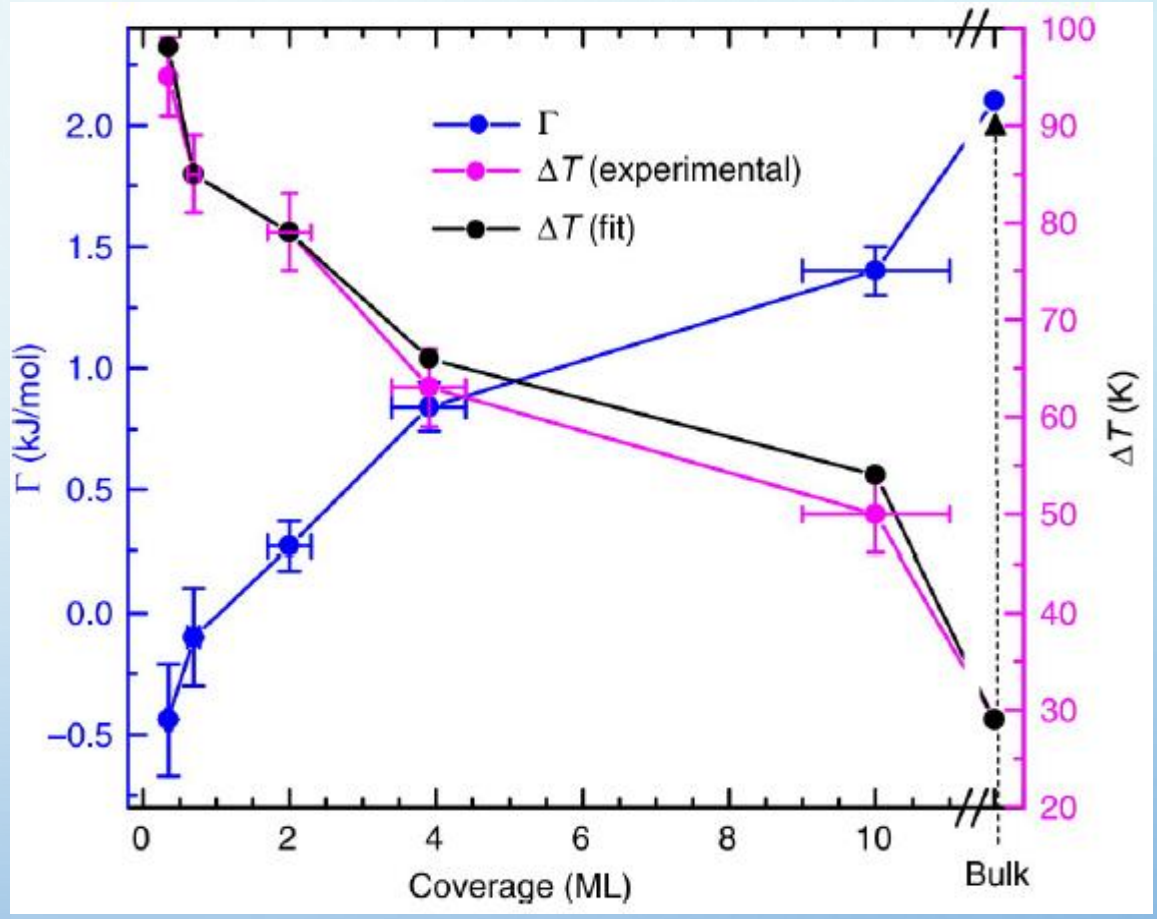
L. Kipgen et. al. , J. Phys.: Condens. Matter 29 (2017) 394003

What about cooperativity?

[Fe(bpz)$_2$bipy] on HOPG



Bulk data from N. Moliner et al. J. Phys. Chem. B 106, 4276 (2002)



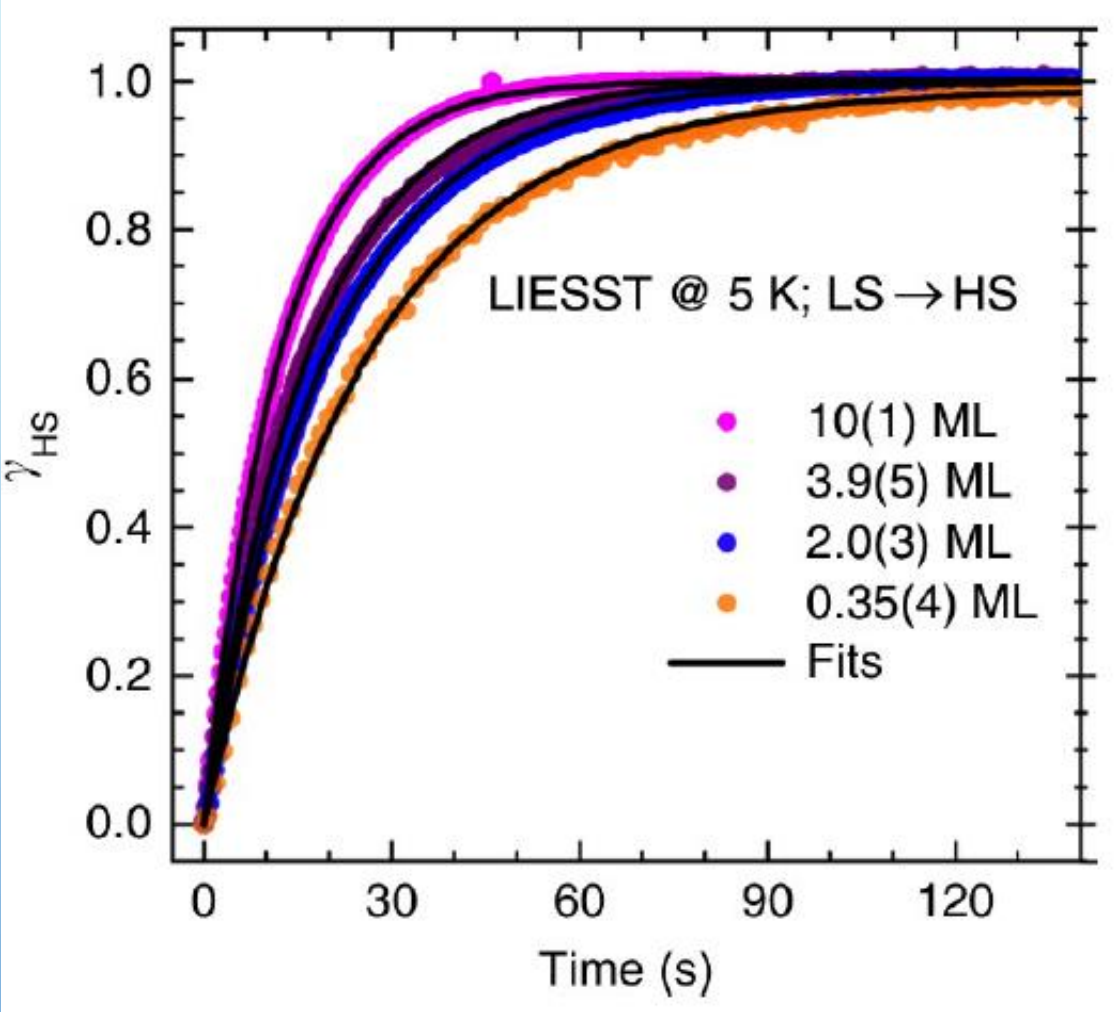
L. Kipgen et. al. , Nat. Commun. 9, 2984 (2018)

ΔT (transition width) is the temperature difference at which 80 % of the molecules are in the HS and LS states, respectively.

$$\ln\left(\frac{1-\gamma_{HS}}{\gamma_{HS}}\right) = \frac{\Delta H - T\Delta S + \Gamma(1-2\gamma_{HS})}{RT}$$

C. P. Slichter and H. G. Drickamer, J. Chem. Phys. 56, 2142 (1972)

No cooperativity in light-induced switching:



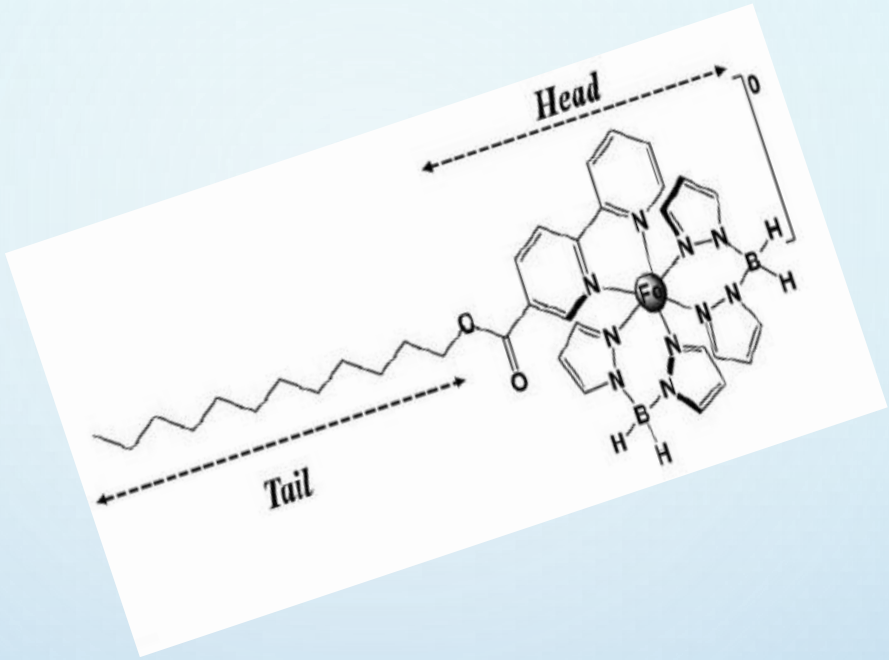
L. Kipgen et al., Nat. Commun. 9, 2984 (2018)

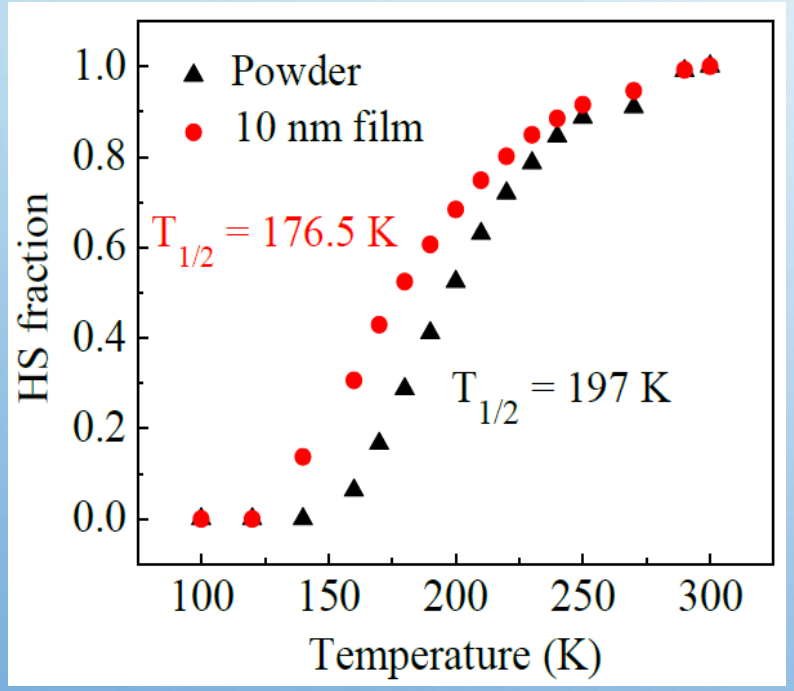
Each curve is fitted by a mono-exponential function, with different rate constants :

r = 0.0369, 0.0505, 0.0589 and 0.0827 s^{-1} for 0.35, 2.0 , 3.9 and 10 Ml, respectively.

No indication for cooperativity in the light-induced excited spin-state trapping single-molecule event

Modification of ligand :





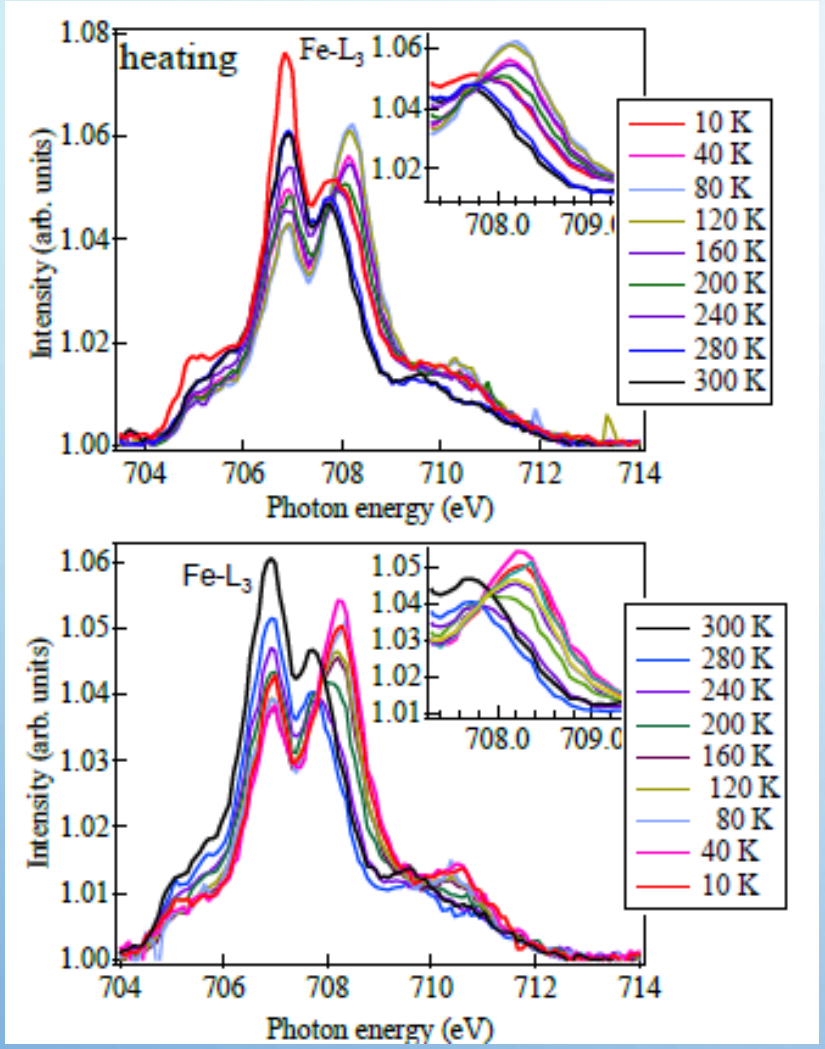
- The C_{12}-complex is studied on SiO_2/Si
  S. Kumar Adv. Mater., 30, 1705416 (2018).

- How will the molecule organize on HOPG?

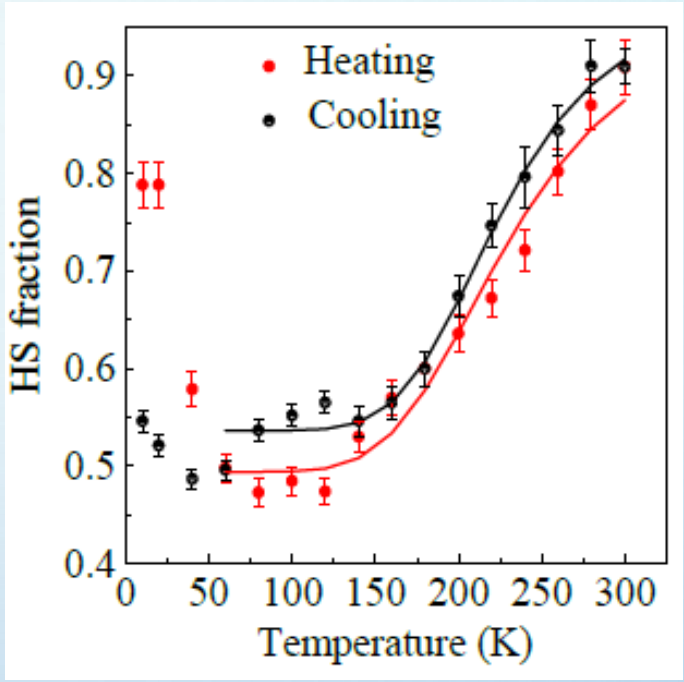
- Role of molecule-surface interaction and self-assembly pattern in determining SCO?

XAS Temperature dependence:

0.4 ML /HOPG



S. Thakur et. al., Journal of Physical Chemistry C (2021), 125, 25.



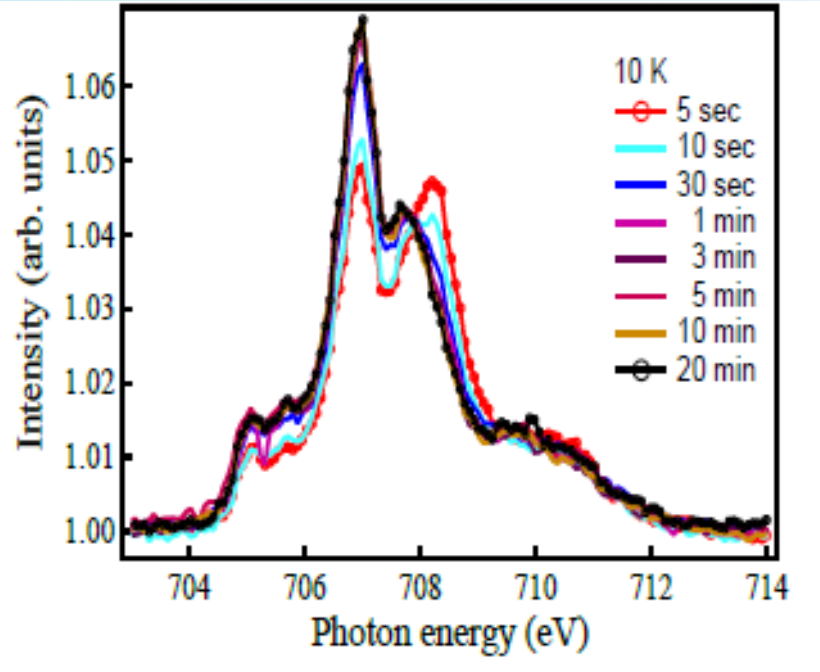
γ_{HS} (T) = x + (1-x) [exp(ΔH/RT-ΔS/R) + 1]$^{-1}$, where ΔH and ΔS are the enthalpy and entropy difference.

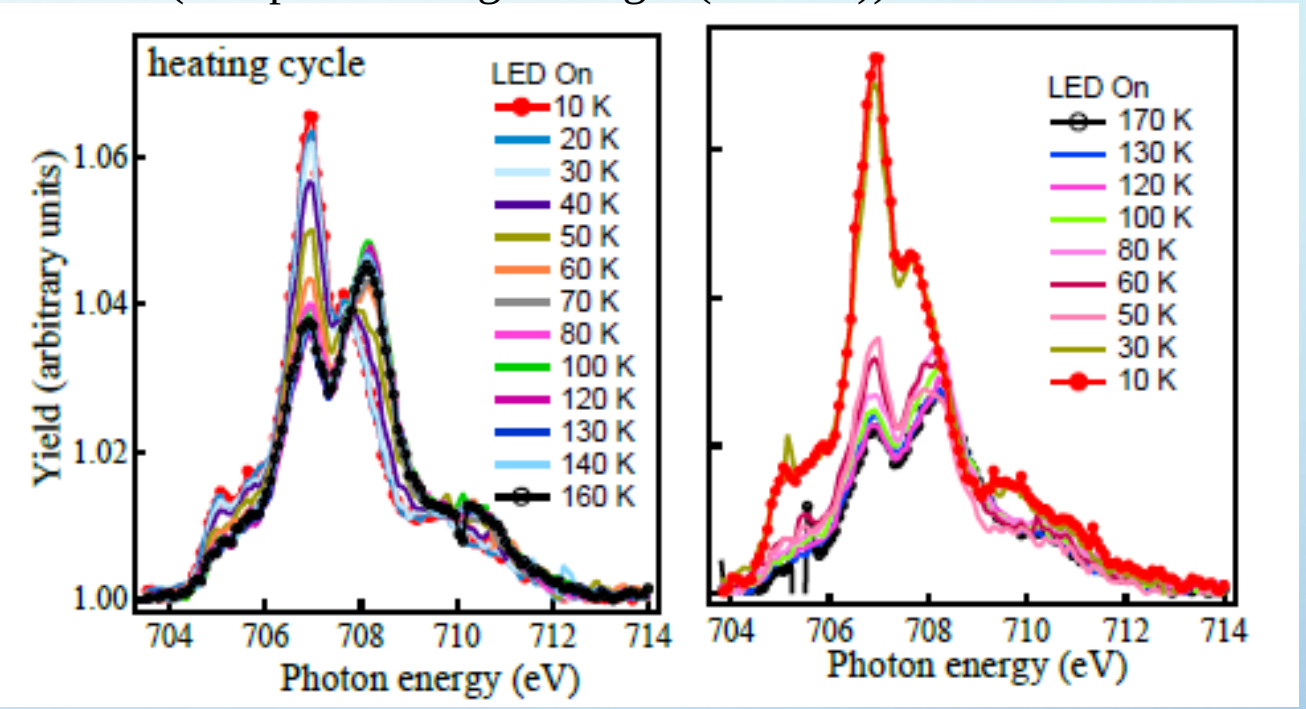
- Maximum LS fraction of 42% were observed at 80 K and 40 K, respectively.
- ΔS = 43 (5) JK^{-1} mol^{-1}, ΔH = 10(1) kJ mol^{-1} , and x = 0.49(1) were obtained for the heating branch. On the other hand ,

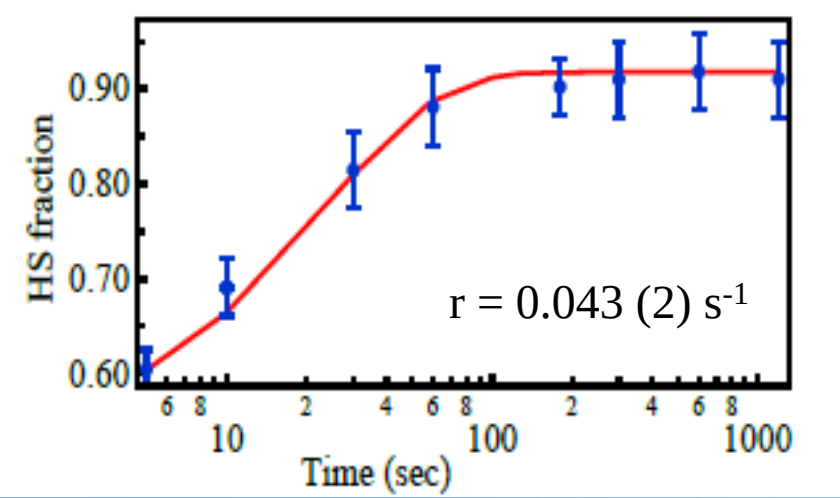
ΔS = 53 (4) JK^{-1} mol^{-1}, ΔH = 12(1) kJ mol^{-1}, and x = 0.53(1) were obtained for the cooling branch.

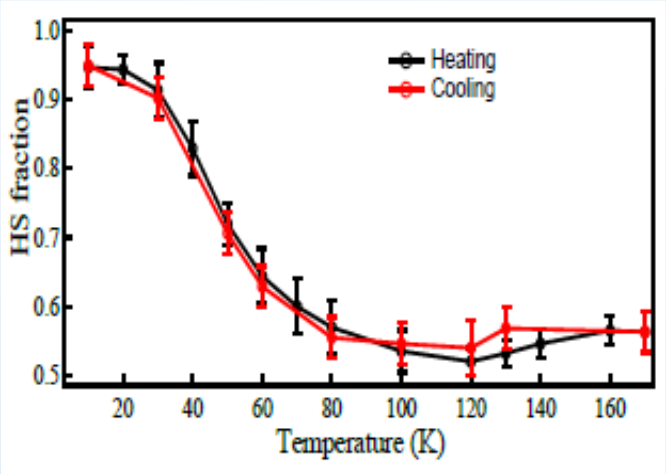
Fe L_3 edge spectra after green light exposure :

XAS (Temperature + green light (520 nm))





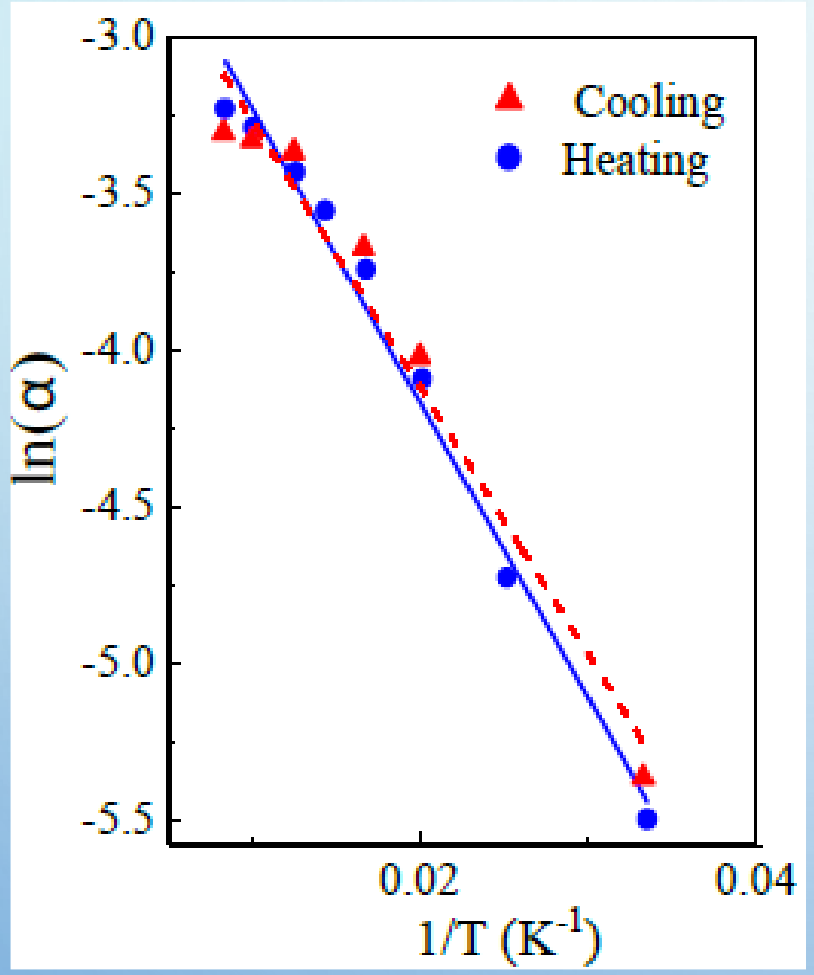




- Below 30K, the spin state is dominated by the light-induced metastable HS state.
- Between 30 and 80 K, there is a rapid interconversion between HS and LS states.

S. Thakur et. al., Journal of Physical Chemistry C (2021), 125, 25.

Rate Constant:



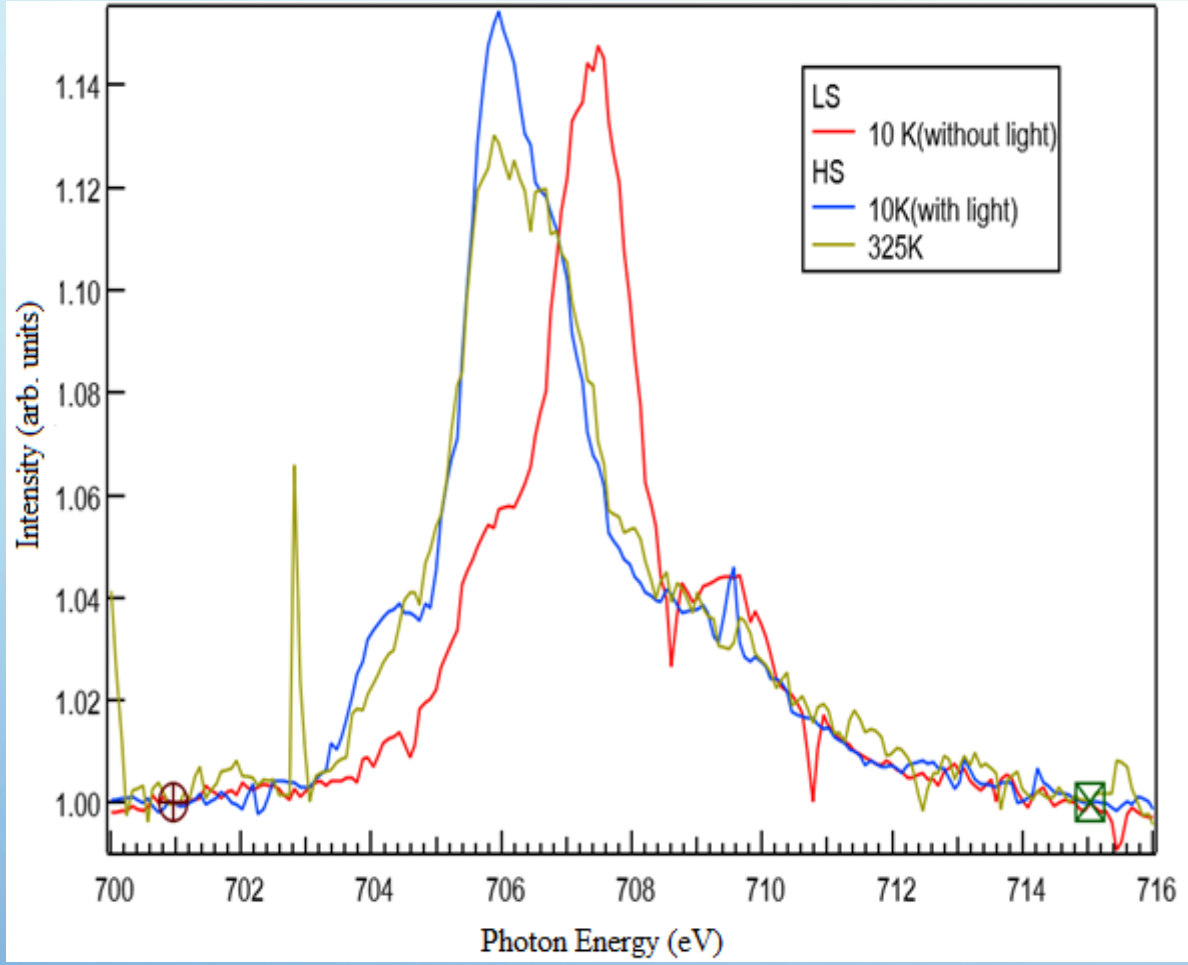
$\alpha(T) = r(1/\gamma HS - 1)$

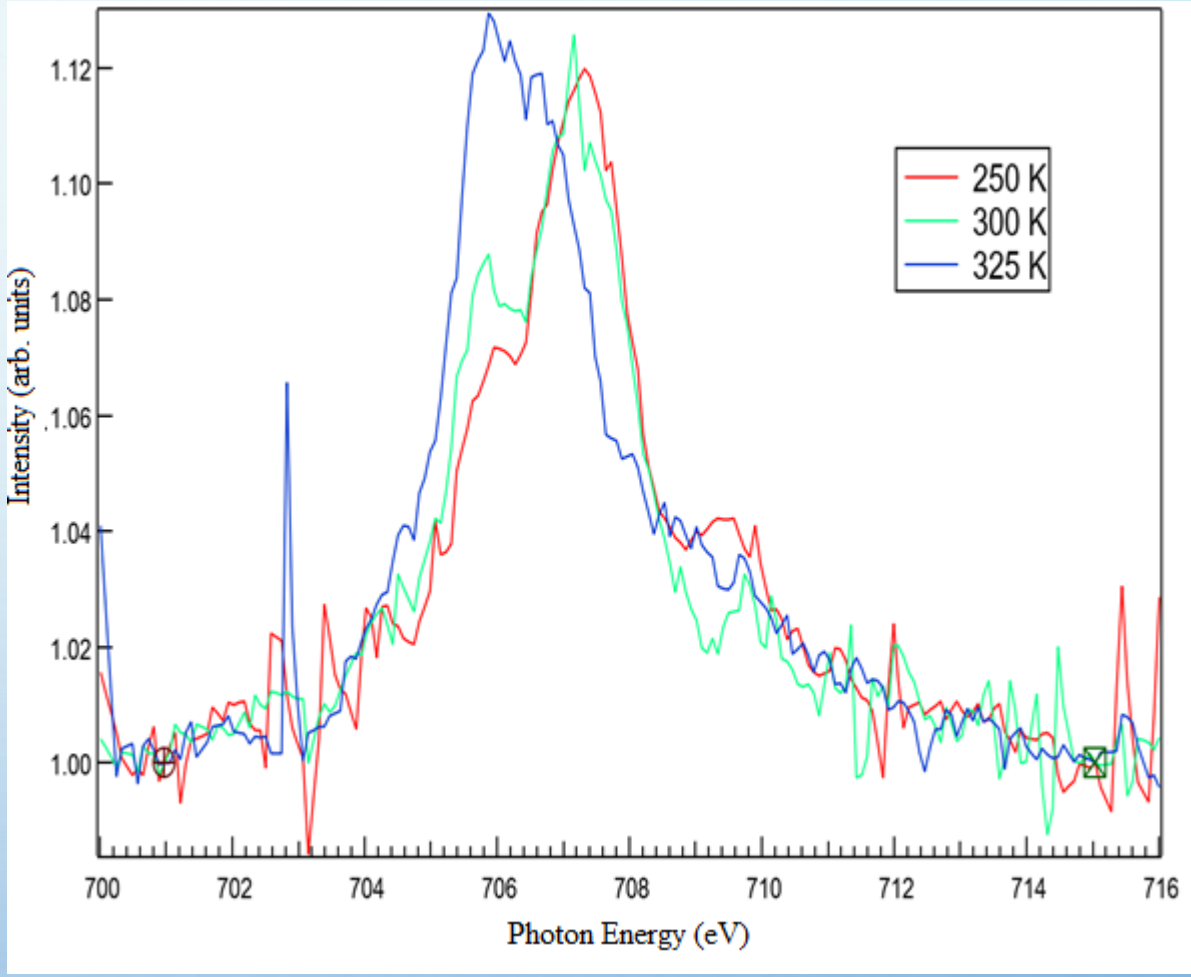
- E_a = 787(32) and 709(56) J/mol were obtained for heating and cooling cycles, respectively.
- The value of E_a is around 4 times smaller than in the parent bulk material indicating less stable light- and temperature-induced HS state on the HOPG substrate by faster thermal backconversion.

Main results :

- Purely thermal SCO behavior was observed only from 50 % of the molecules, while the remaining 50% are in a temperature-Independent HS state.
- The light-induced LS-to-HS switching of the molecules was observed at low temperature upon irradiation of the sample with green light.

XAS on Fe$\{H_2B(pz)(pypz)\}_2$ (0.8ML) on HOPG :

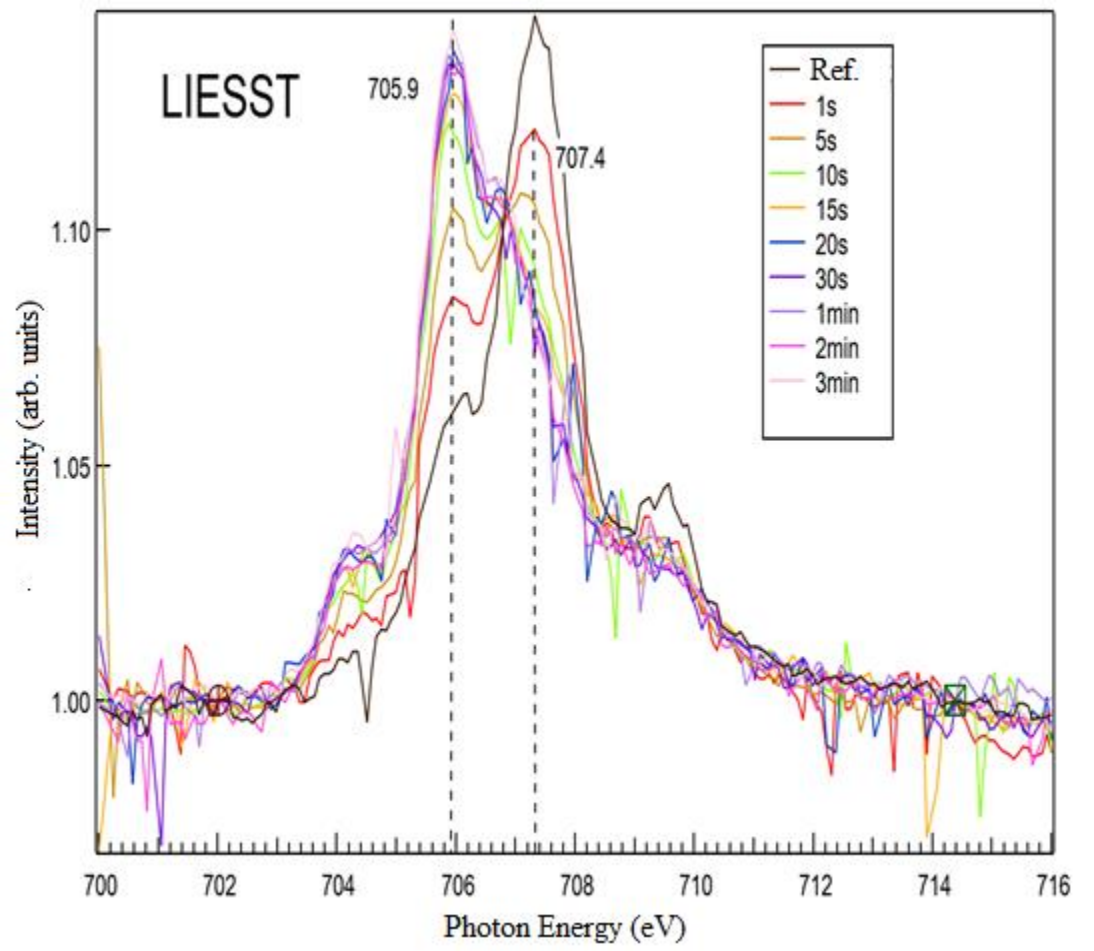


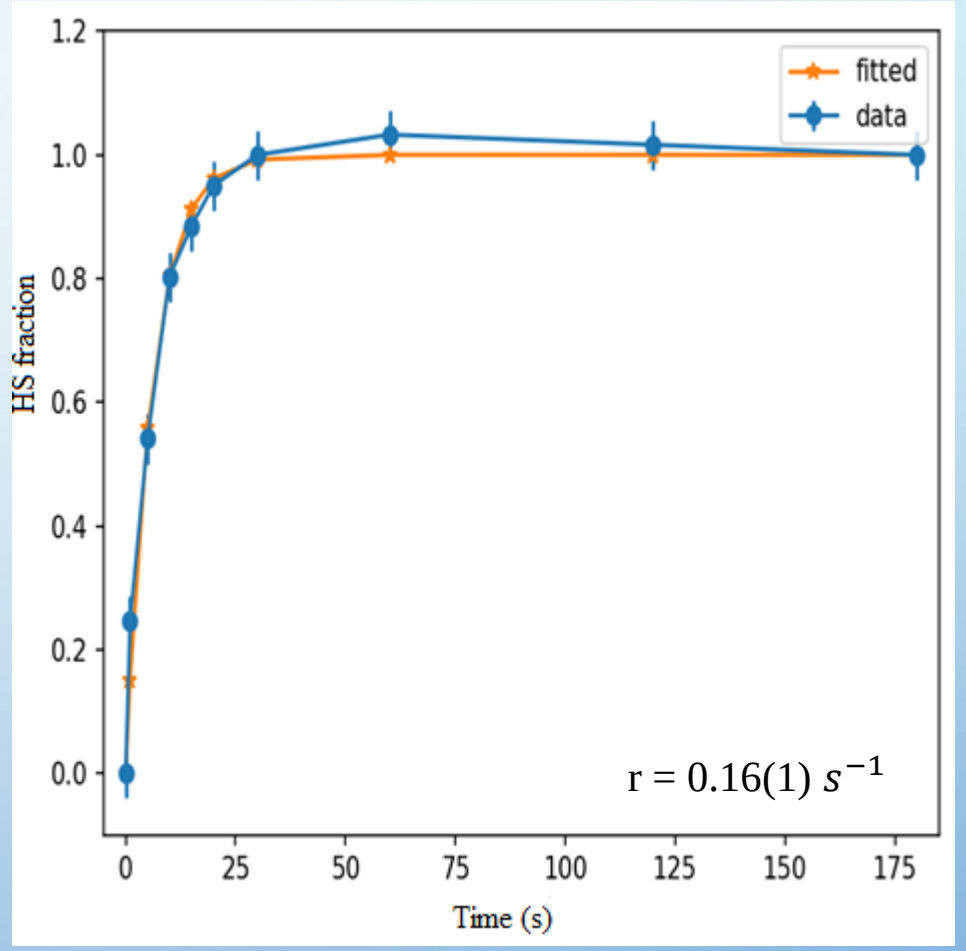


$T_{1/2}$ in between of 300 K and 325 K : above room temperature

Beamtime Oct. 2021

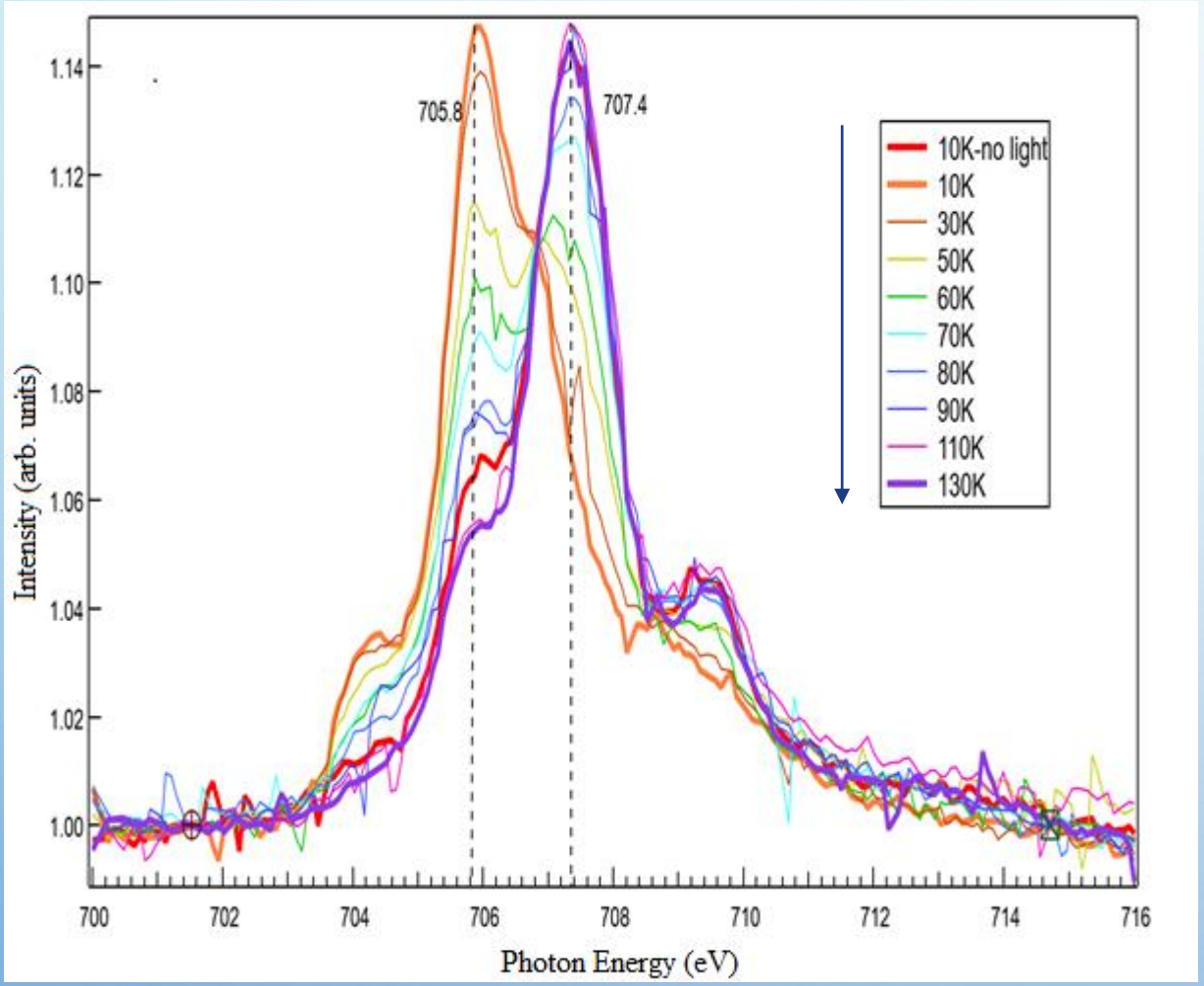
$Fe\{H_2B(pz)(pypz)\}_2$ (0.8ML) on HOPG :

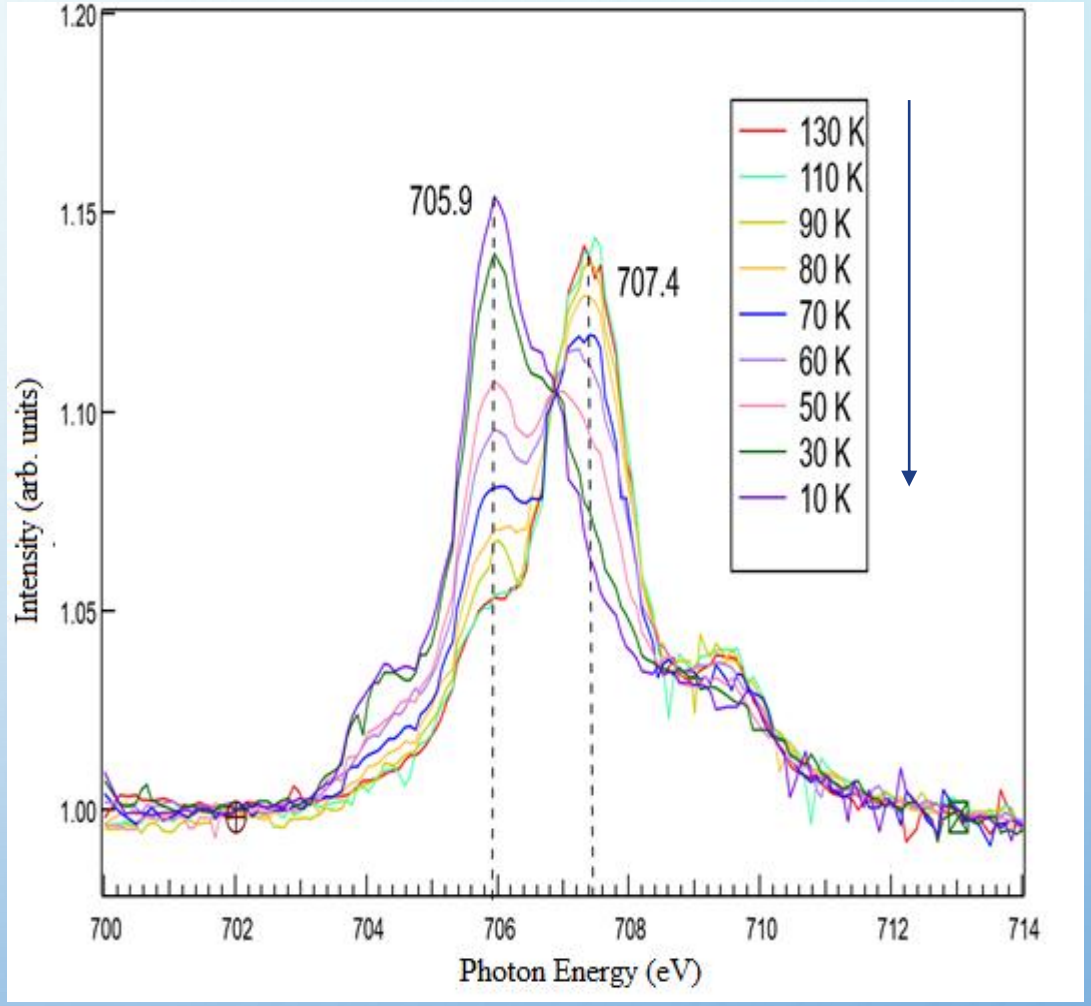




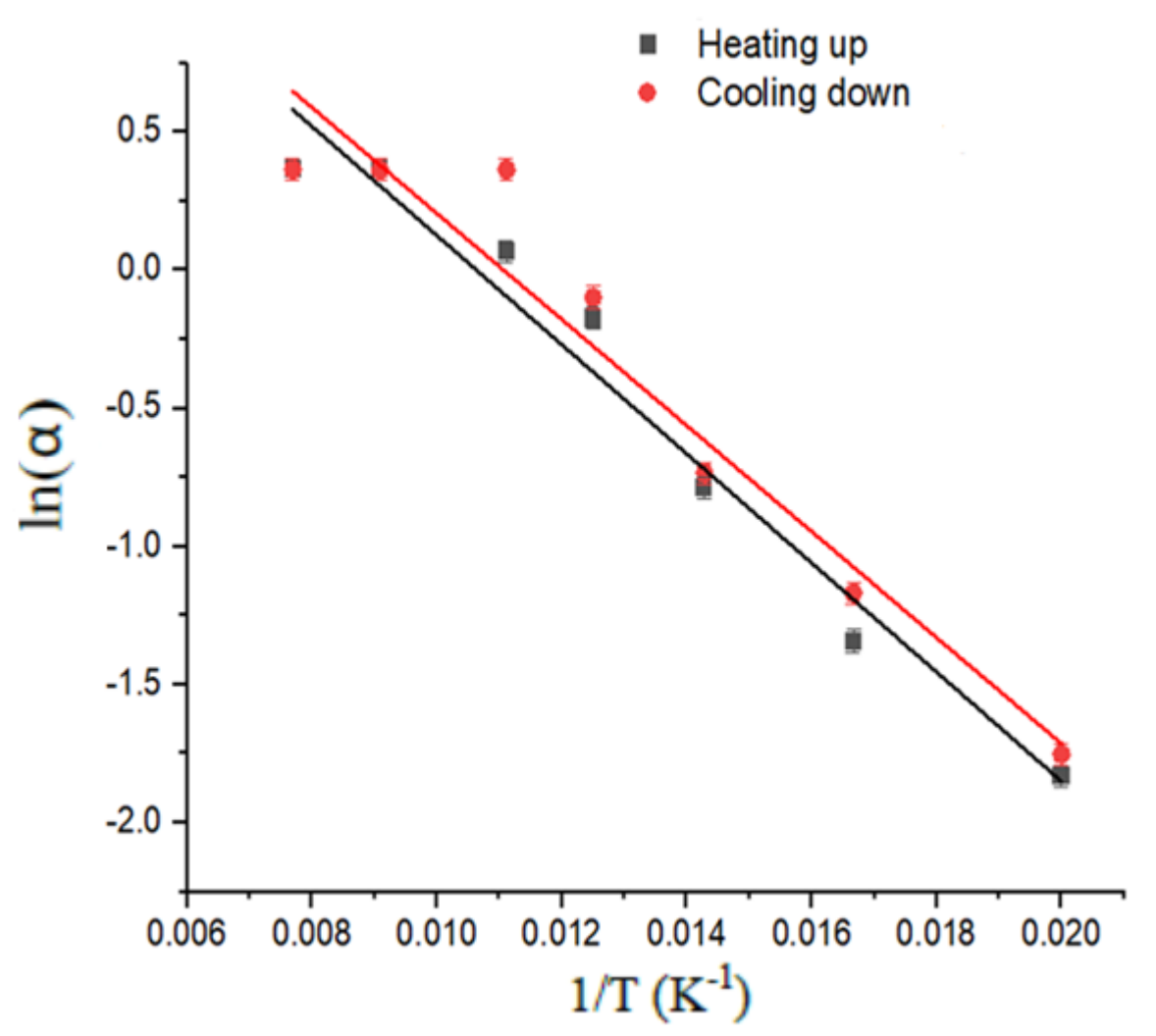
$Fe\{H_2B(pz)(pypz)\}_2$ (0.8ML) on HOPG :

Light + Temperature





$Fe\{H_2B(pz)(pypz)\}_2$ (0.8ML) on HOPG :



Heating up process :

- Activation energy (J/mol): 1603.32(5)
  pre-exponential factor (s^{-1}): 8.16 (6)

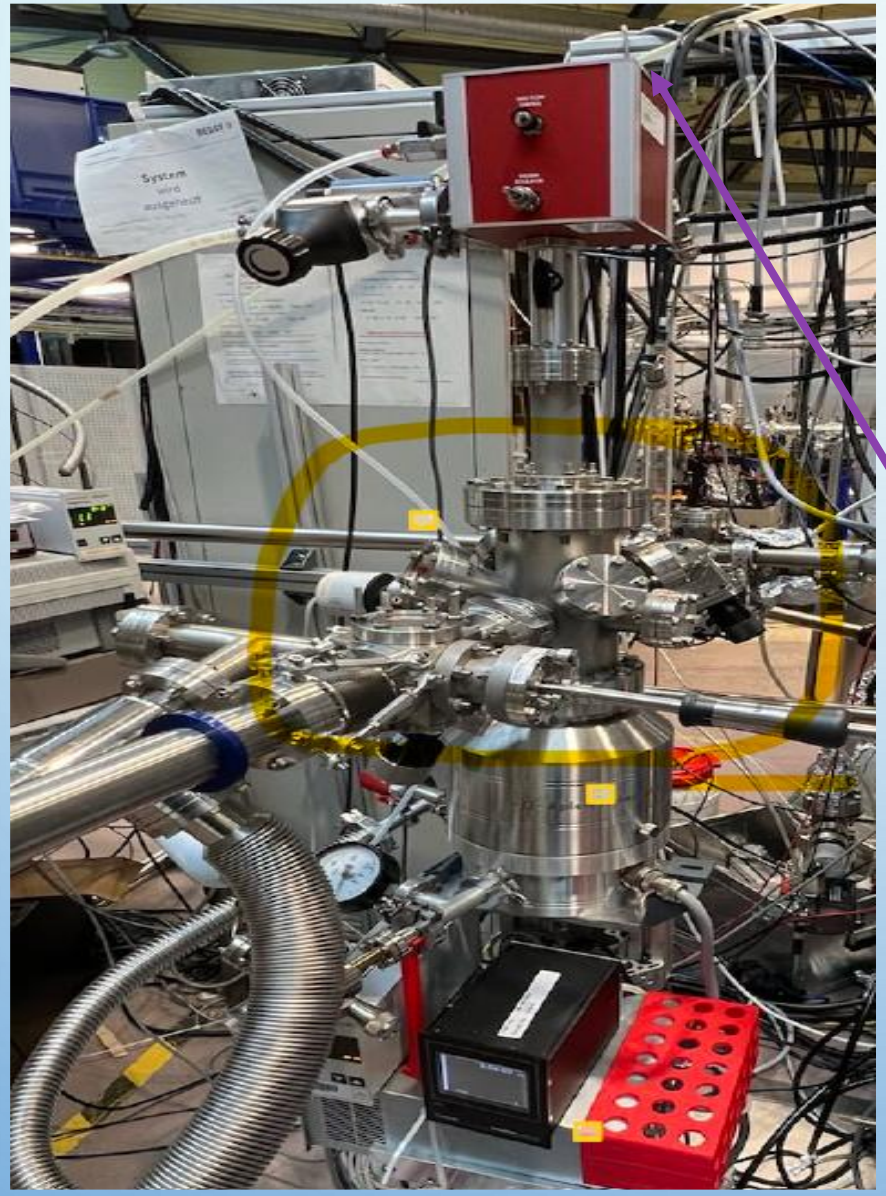
Cooling down Process :

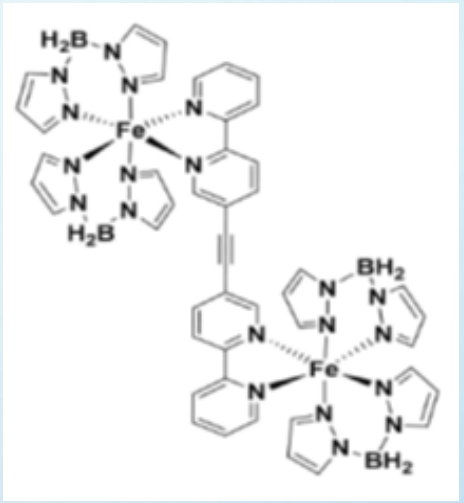
- Activation energy (J/mol): 1560.06(6)
  pre-exponential factor (s^{-1}): 8.33 (1)

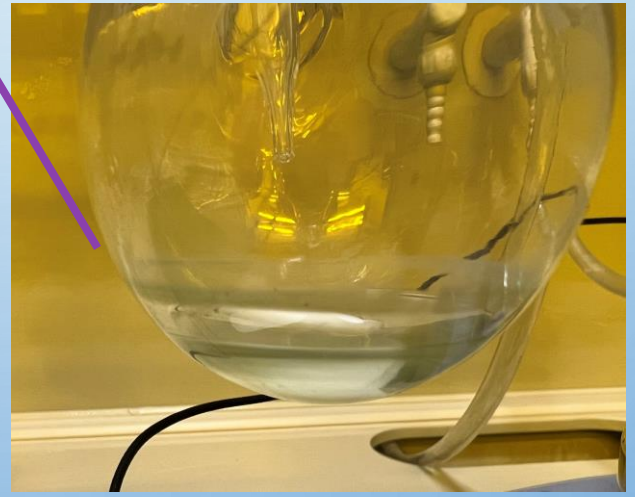
Main results:

- The highvalue of E_a indicating more stable light- and temperature-induced HS state on the HOPG substrate.
- Very fast LS-to-HS conversion with light make this SCO molecules very attractive for the realization of light-addressable SCO-based switching.

Deposition of molecules by pulsed liquid injection system:



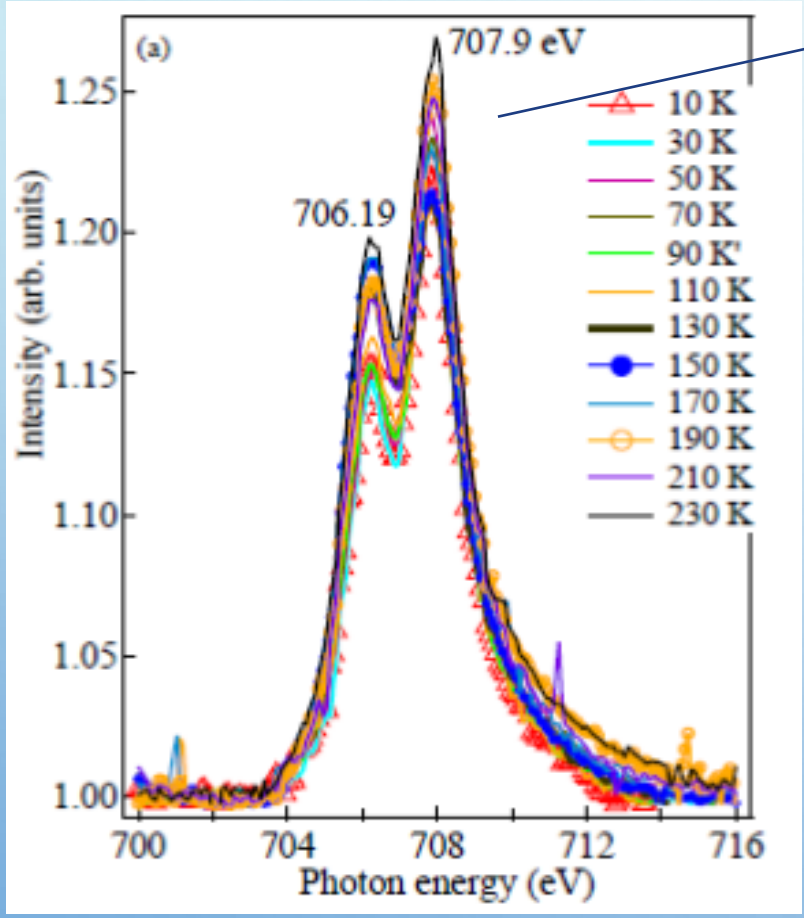




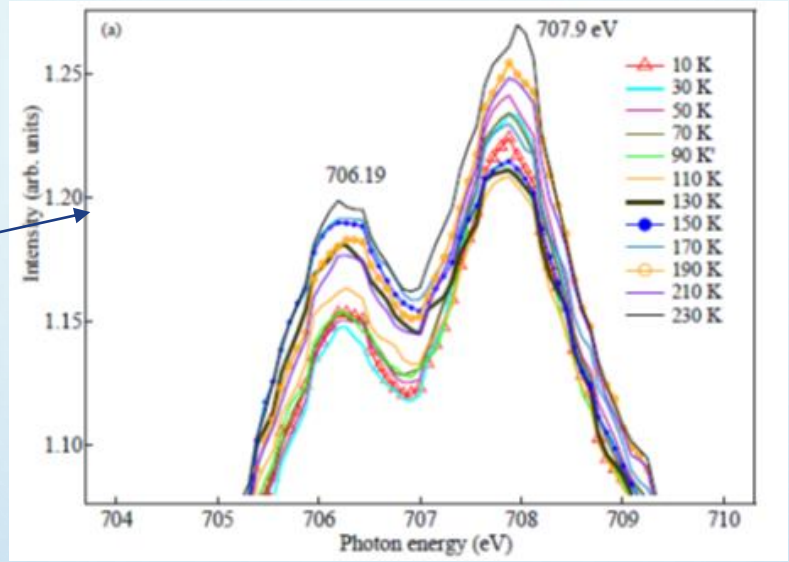
Solution is made with the concentration as 1.5 mg of molecules in 10 mL of THF

XAS measurements with temperature and light :

Temperature dependence



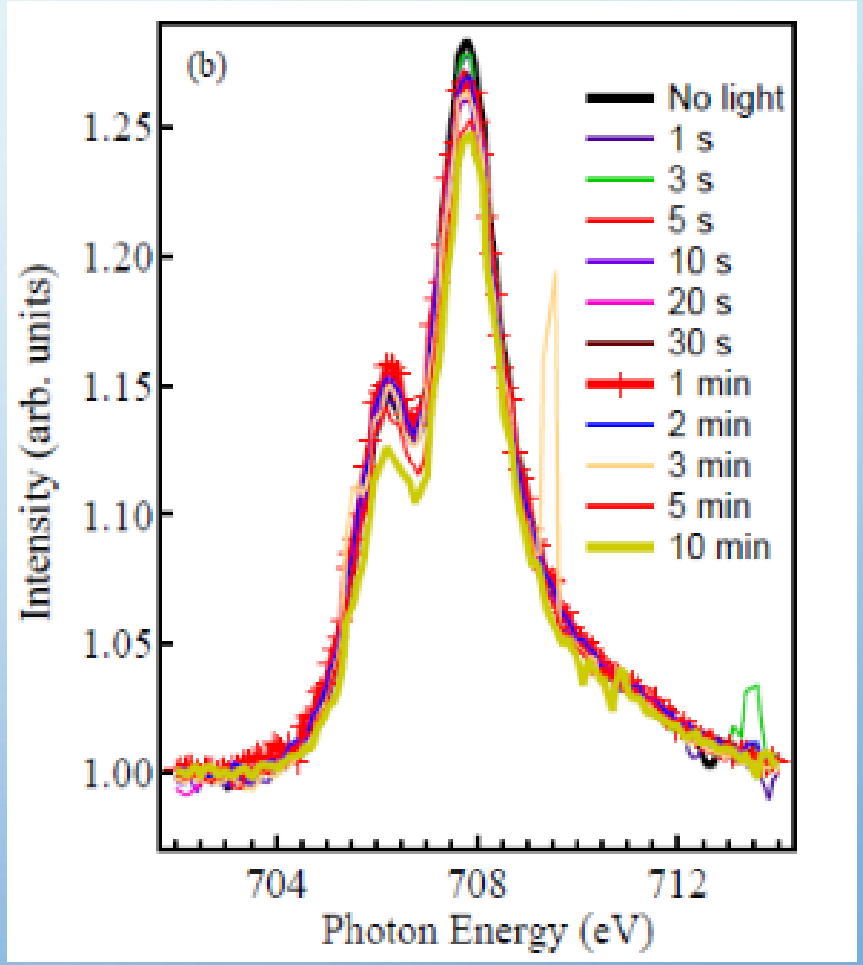
90 ms deposition of molecules



$T_{1/2}$ ~ 150 K

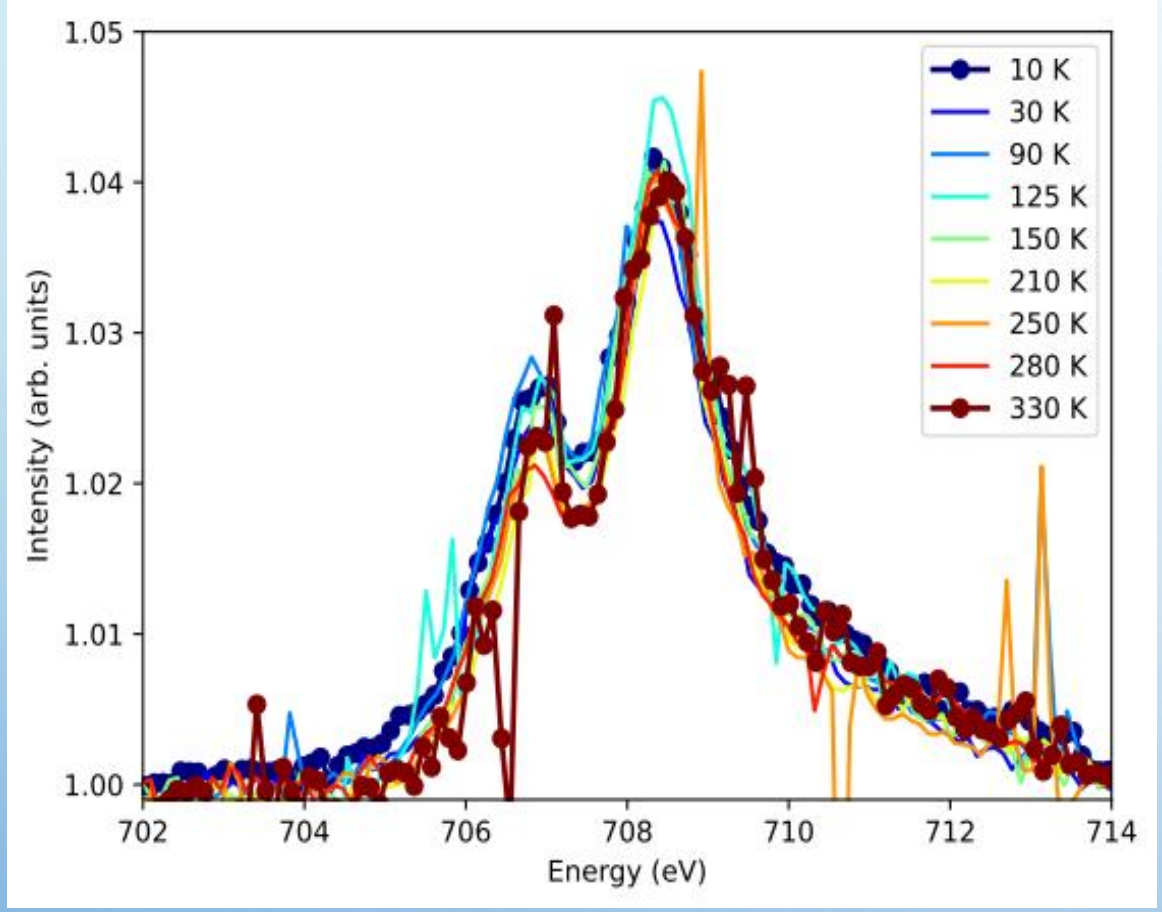
0.75 Ml on HOPG

LIESST

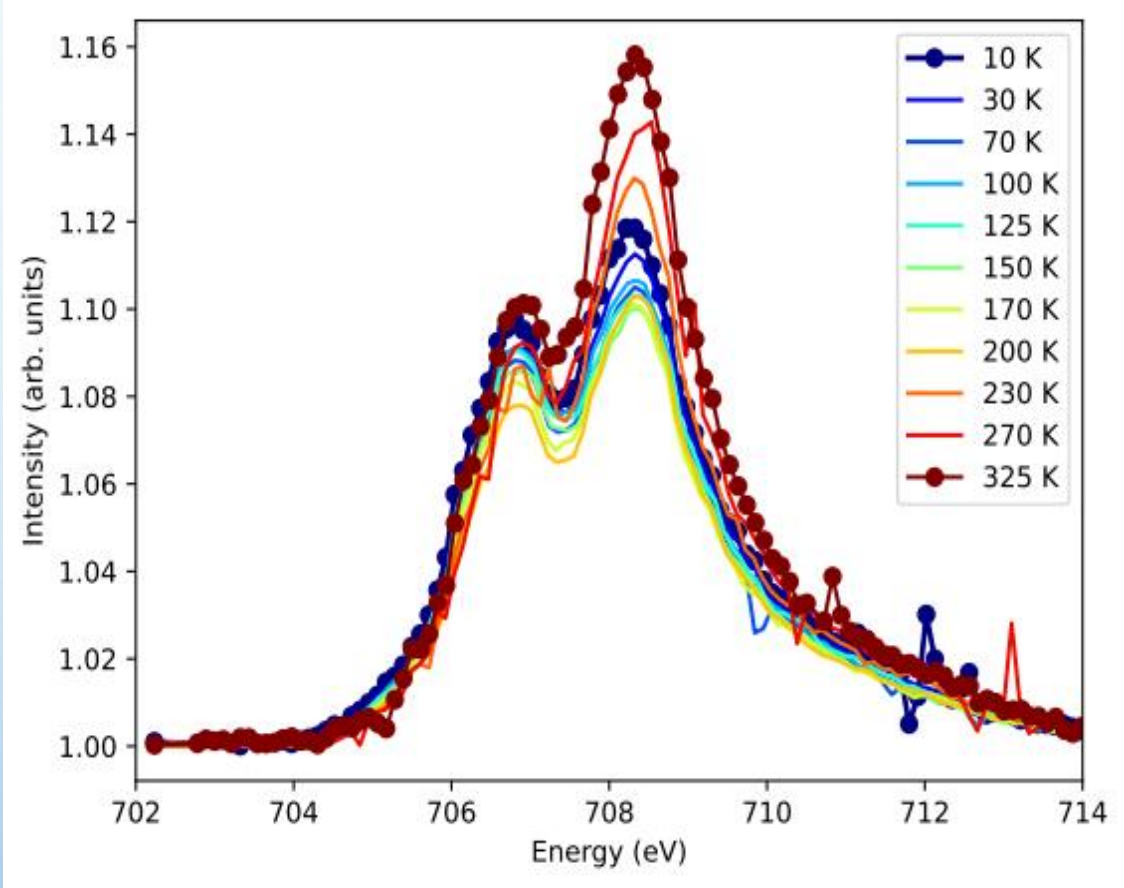


Beamtime Oct. 2021

XAS measurements:



Deposition for 100 ms

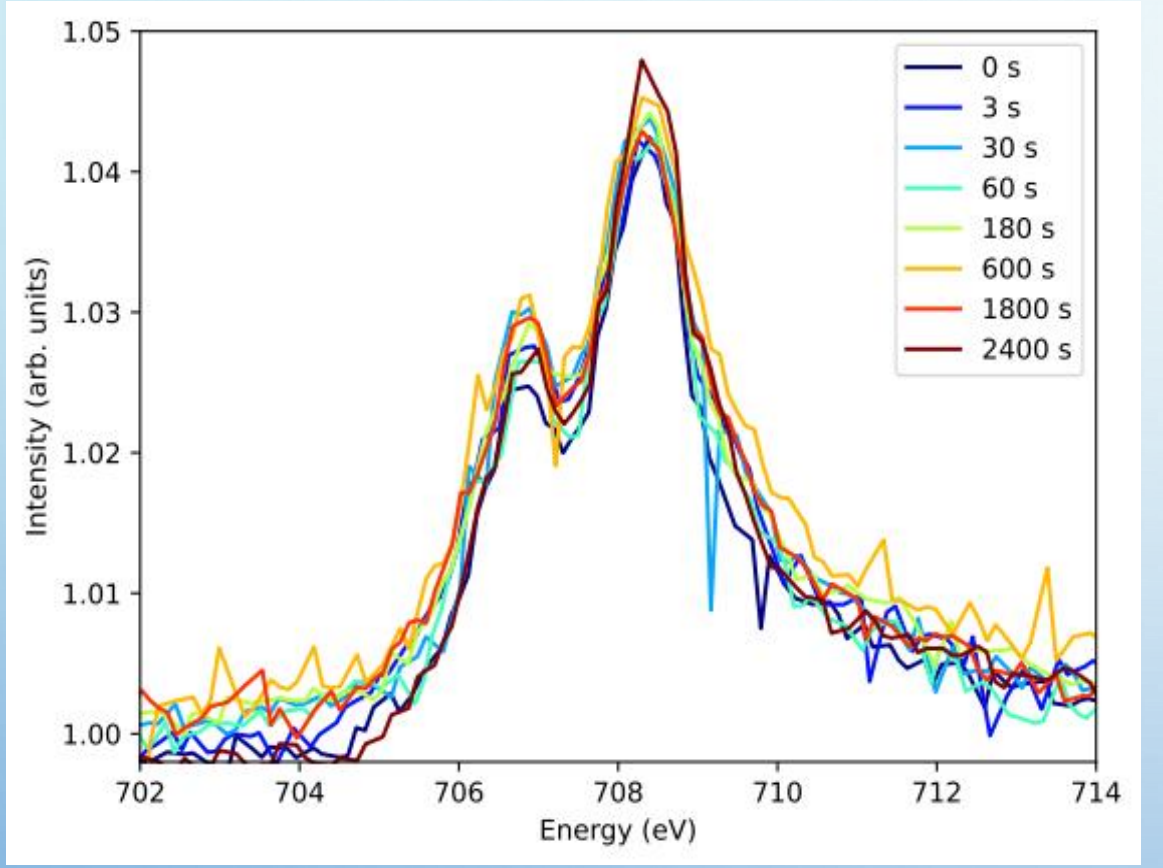


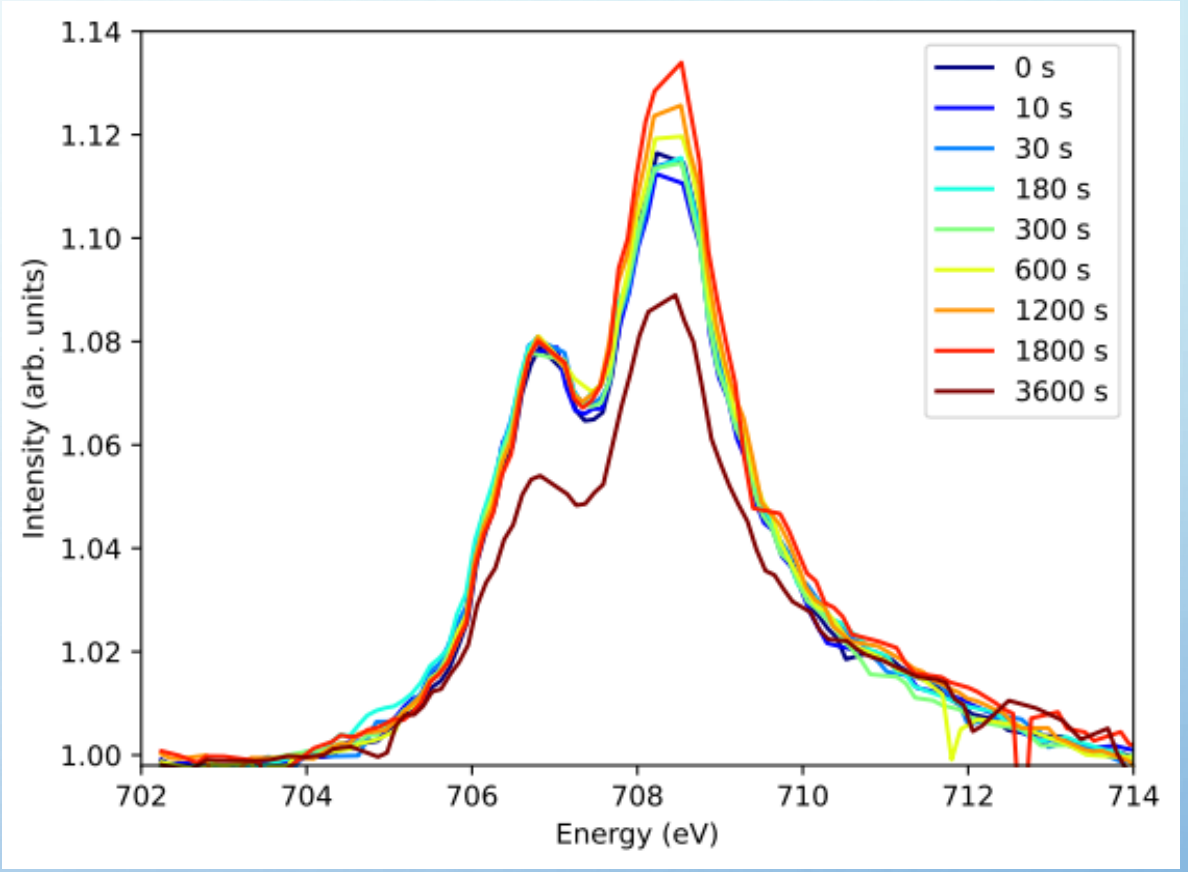
Deposition for 500 ms

March beamtime 2022

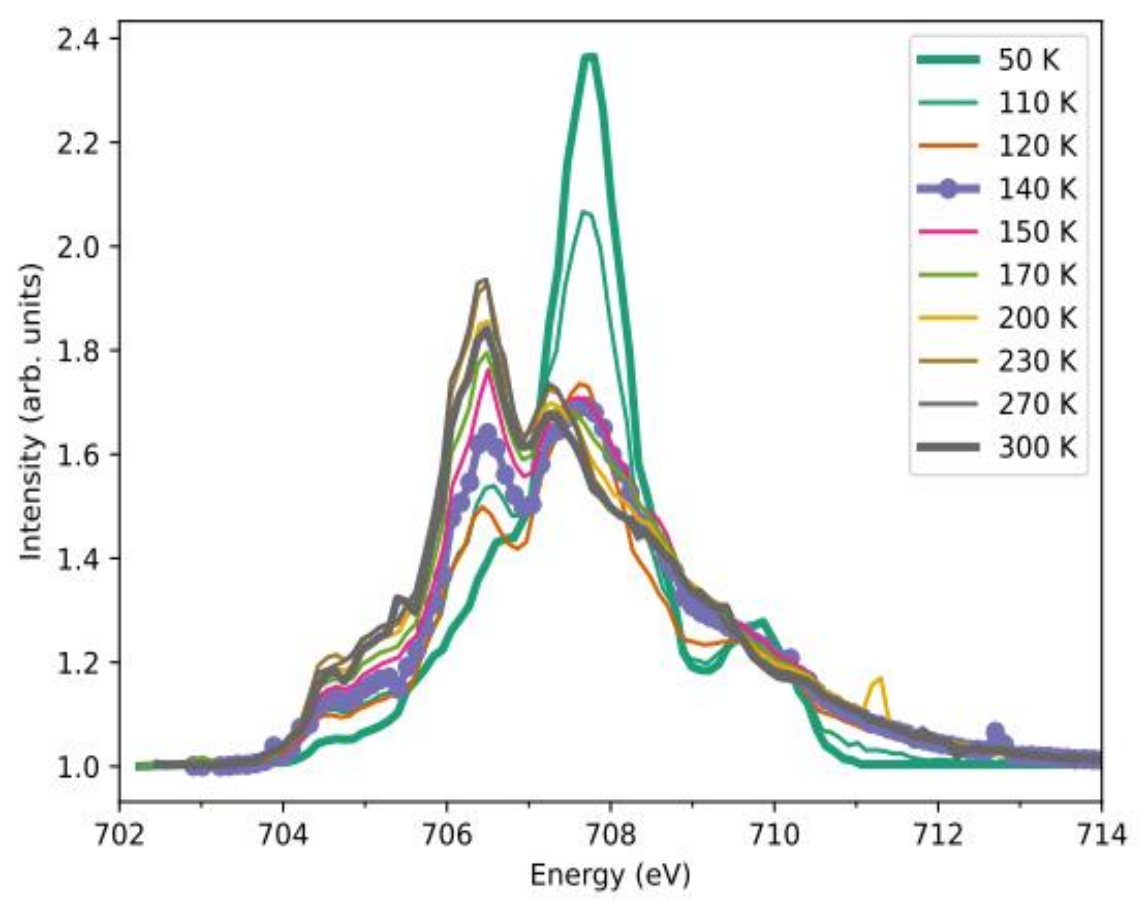
XAS measurements:

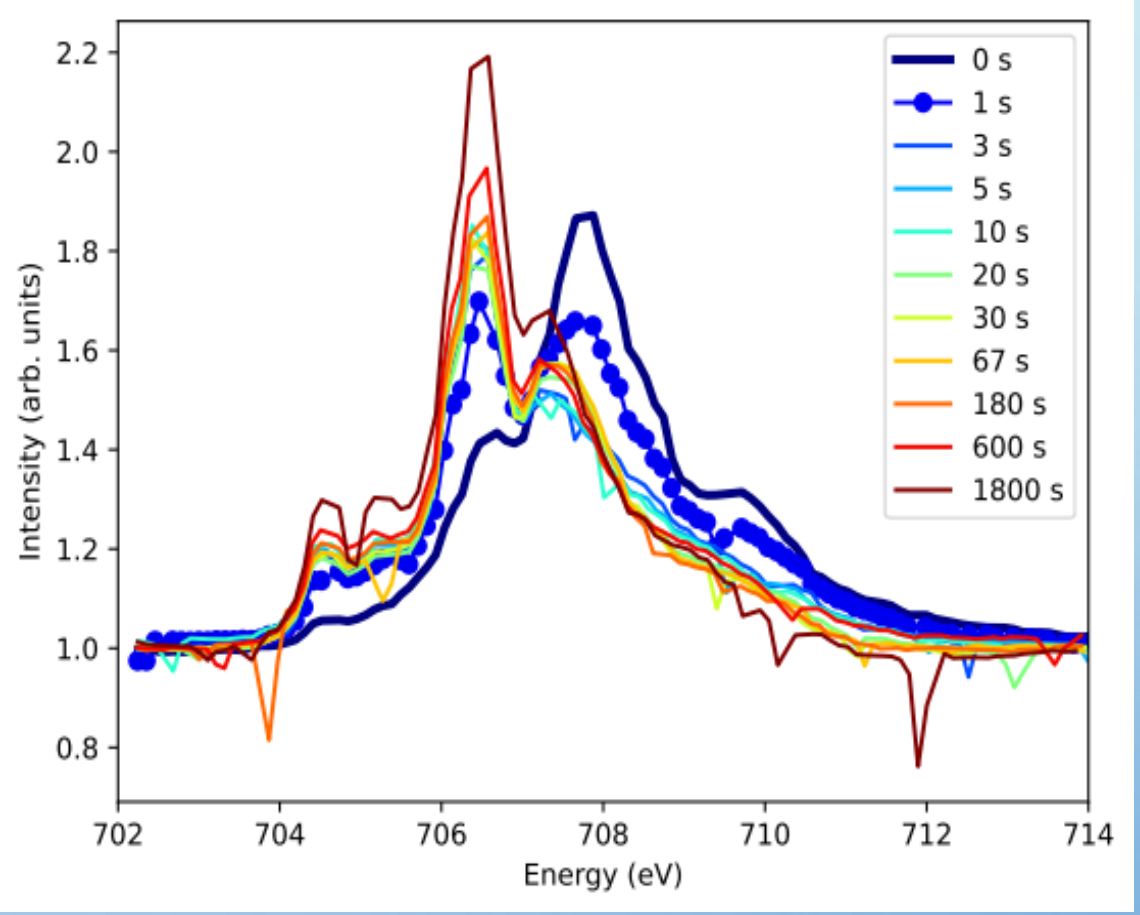
LIESST Measurements





XAS measurements on bulk sample of bi-nuclear Fe complex:

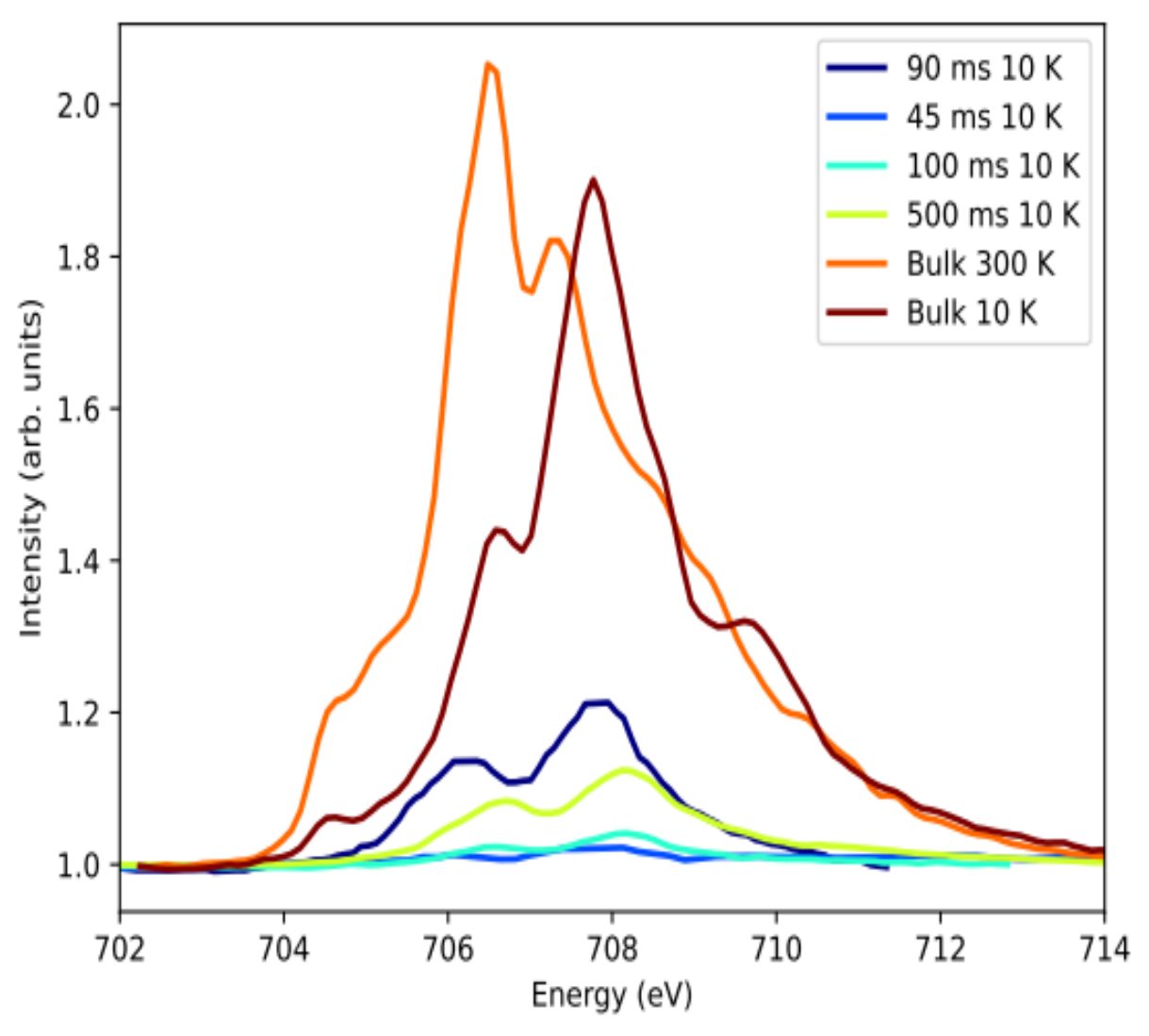




Complete switching from HS-to-LS with temperature and with light.

$T_{1/2}$ ~ 145 K

Comparison of the XAS of bulk and thin films of bi-nuclear complex:



- Comparison with bulk XAS measurements confirm that Fe is in FeII valence state and no oxidation of Fe happens during ALI deposition.

- Molecules seems to be locked in mix HS and LS state on HOPG

- May be the presence of solvent is affecting the spin cross over properties.

Summary:

The modifications of the molecule and of the ligands in the SCO complexes shows interesting behavior in bulk although Its challenging to realize the SCO properties on surfaces mainly in the sub-monolayer regime.

Future plans:

- To check the cooperativity affects in the SCO molecules by depositing thicker layers by thermal deposition.
- To explore the properties of the bi-nuclear SCO complexes after deposition by the pulsed liquid injection system on different substrates (e.g Au).
- Try other big/small SCO complexes by pulsed liquid injection system.

Summary:

The modifications of the molecule and of the ligands in the SCO complexes shows interesting behavior in bulk although Its challenging to realize the SCO properties on surfaces mainly in the sub-monolayer regime.

Future plans:

- To check the cooperativity affects in the SCO molecules by depositing thicker layers by thermal deposition.
- To explore the properties of the bi-nuclear SCO complexes after deposition by the pulsed liquid injection system on different substrates (Au).
- Try other big/small SCO complexes by pulsed liquid injection system.

Thank you