

Optical control of spin-crossover molecules adsorbed on metallic substrates

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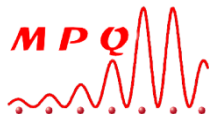
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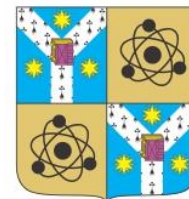
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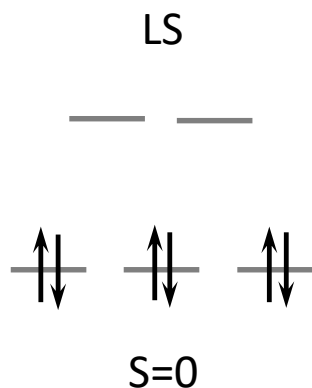
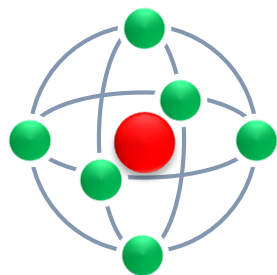
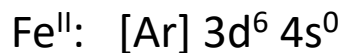


FET-Open project

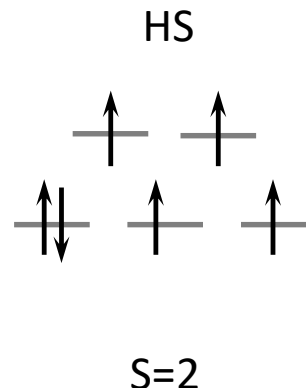
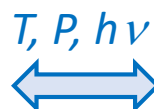


Spin-crossover molecules

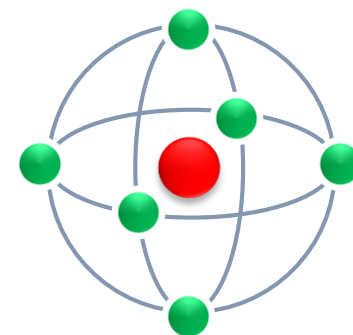
Transition metal ion (Cr, Mn, Fe, Co) surrounded by organic ligands



$$\Delta_{O\text{LS}} > \Pi$$



$$\Delta_{O\text{HS}} < \Pi$$



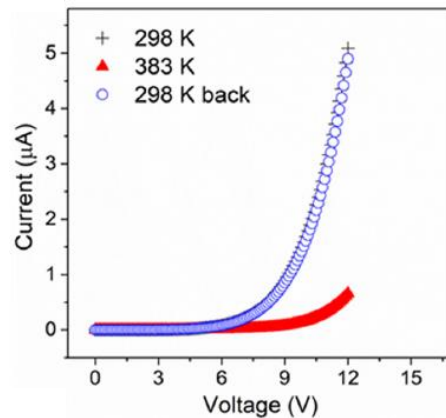
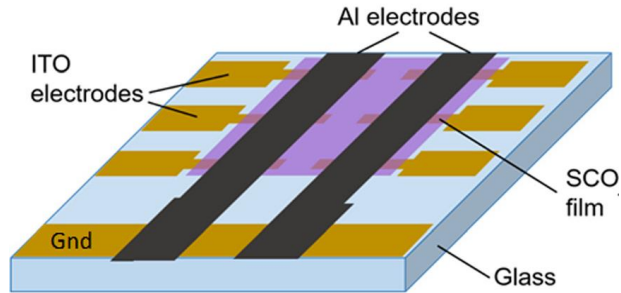
Δ_{O} : ligand field
 Π : pairing energy

● Central ion
● Ligands

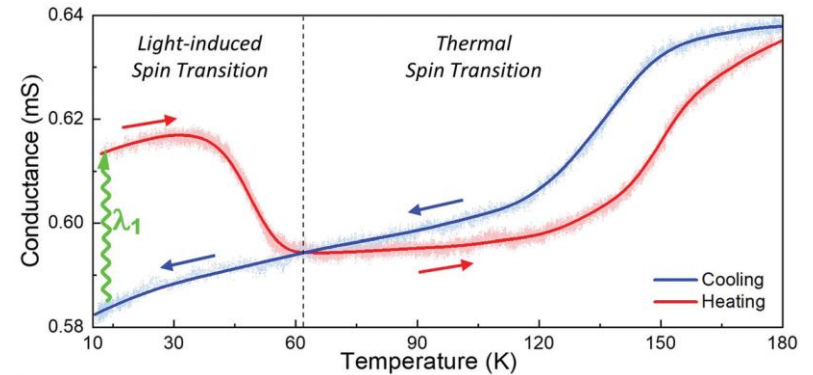
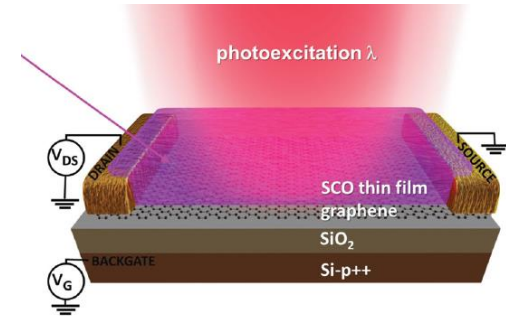
Volume change: 2-6%

Incorporation in devices

Metallic contacts



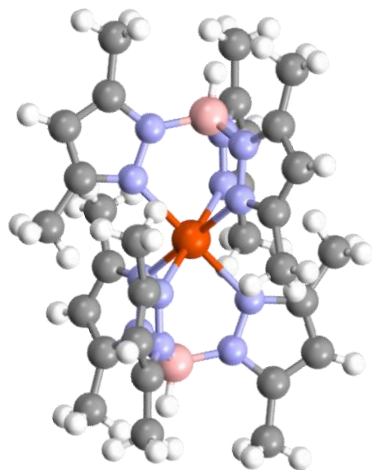
Graphene based



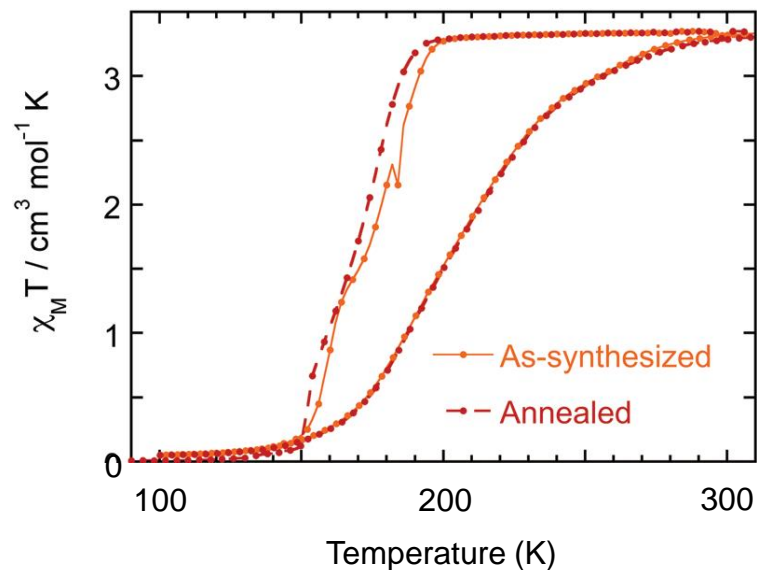
Lefter *et al.*, *Adv. Mater.*, 28, 7508 (2016)
Shalabaeva *et al.*, *Appl. Phys. Lett.*, 112, 013301 (2018)
Zhang *et al.*, *J. Phys. Cond. Matter.*, 32, 214010 (2021)

Dugay *et al.*, *Nano Lett.*, 17, 186 (2017)
N. Konstantinov *et al.*, *J. Chem. Mater. C*, 9, 2712 (2021)
M. Gavara-Edo *et al.*, *Adv Mater*, 34, 2202551 (2022)

Optical switching properties at the interface with metal?



Polycrystalline powder



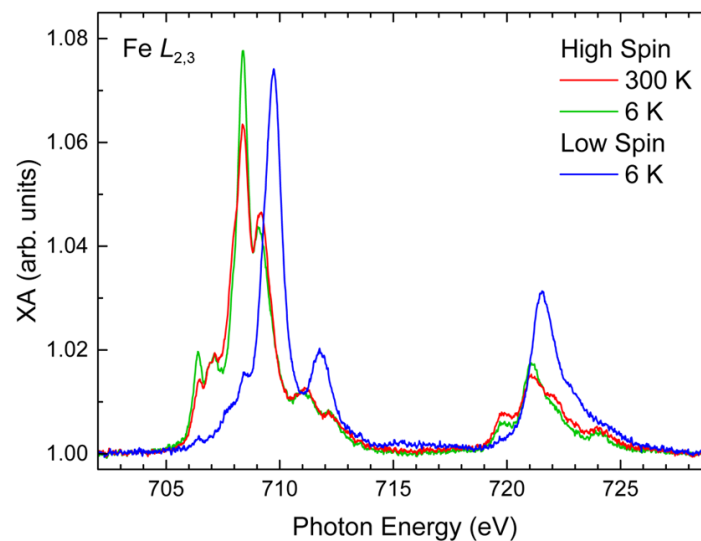
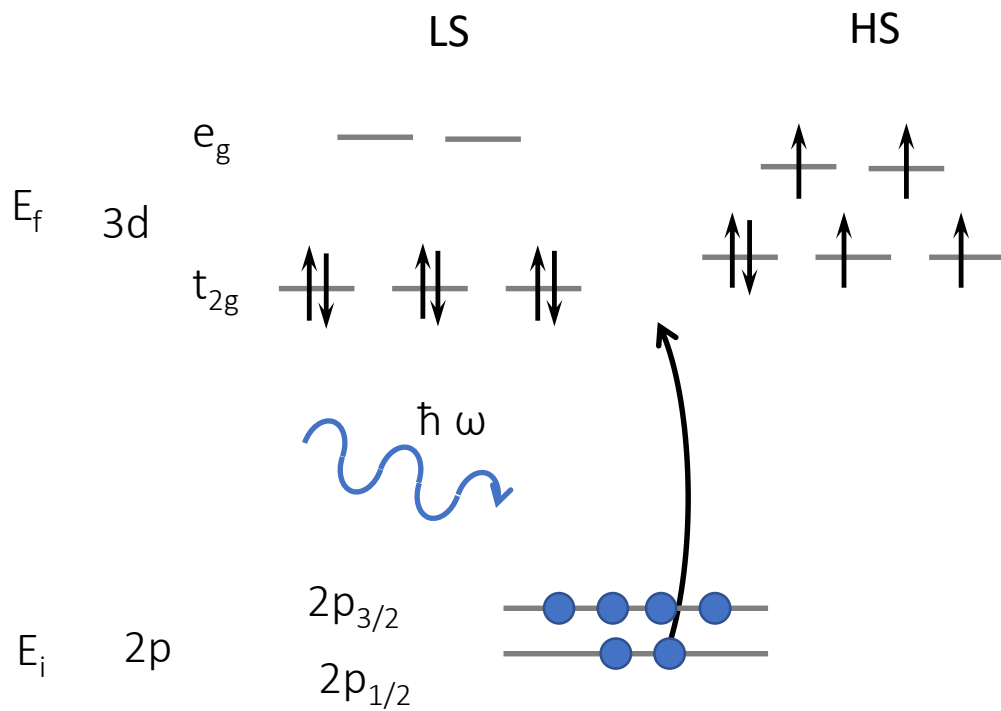
$$\begin{aligned} T_{\downarrow} &= 174 \text{ K} \\ T_{\uparrow} &= 205 \text{ K} \\ T_{1/2} &= 189.5 \text{ K} \end{aligned}$$

- Sublimable under ultra-high vacuum
- Self-assembled in dense network on metallic substrates (Au(111), Cu(111) or Ag(111))
- Epitaxial relationship between the molecular network and the substrate

Collaboration M.-L. Boillot and T. Mallah (Université Paris Saclay, France)
lasco *et al.*, *J. Mater. Chem. C*, **5**, 11067 (2017)
Fourmental *et al.*, *J. Phys. Chem. Lett.*, **10**, 4103-4109 (2019)

X-Ray absorption spectroscopy (XAS)

At the Fe $L_{2,3}$ edge



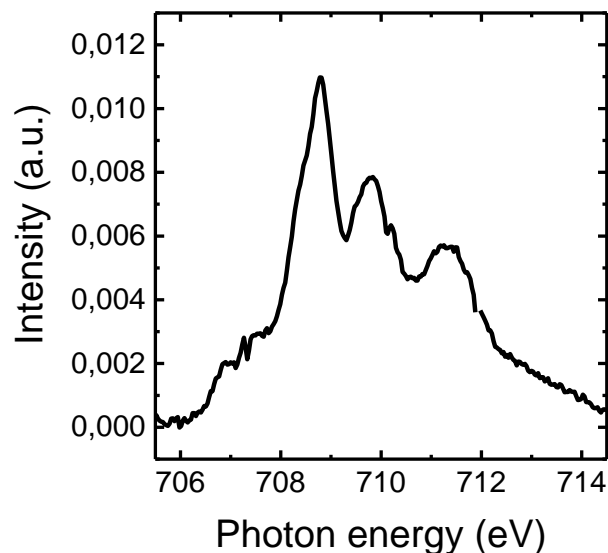
Bernien *et al.*, ACS Nano, 9, 8960 (2015)

Element specific
Sensitive to the spin state of the molecules

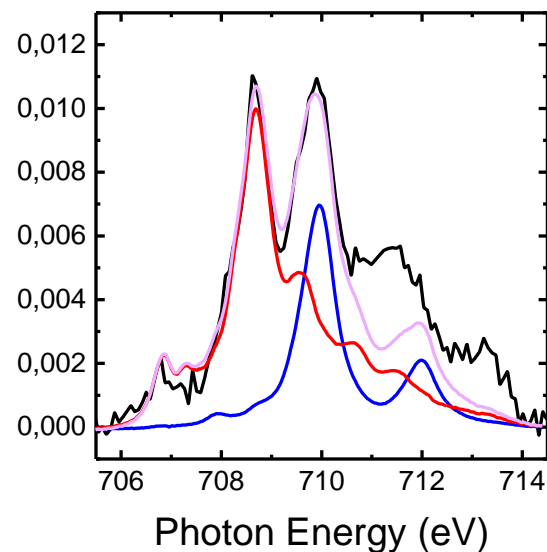
FeSCO sub-monolayer on Au(111)

FeMPz (0.5ML) / Au(111)

300 K



4 K



HS proportion:

100 %

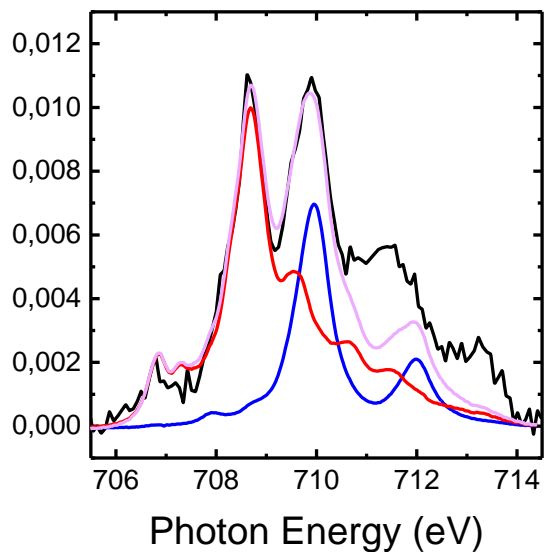
65.6 ± 1.3 %

Thermal transition: HS to a mixed spin state phase
Mixed spin state phase originates from epitaxial relationship

FeSCO sub-monolayer on Au(111)

FeMPz (0.5ML) / Au(111)

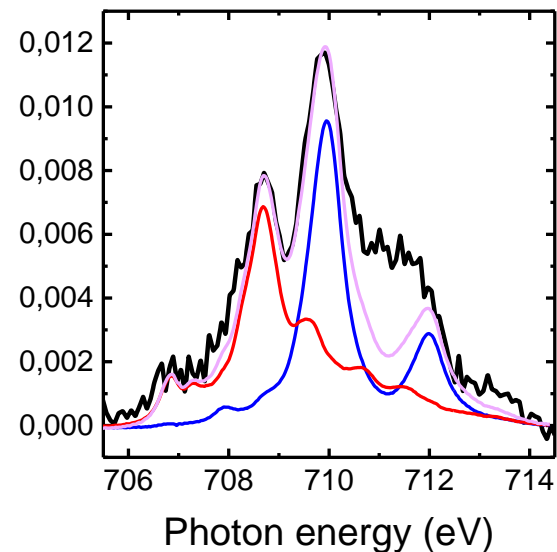
4 K



HS proportion: $65.6 \pm 1.3 \%$

4 K

Blue light illumination
(405 nm – 0.5 mW.cm⁻²)

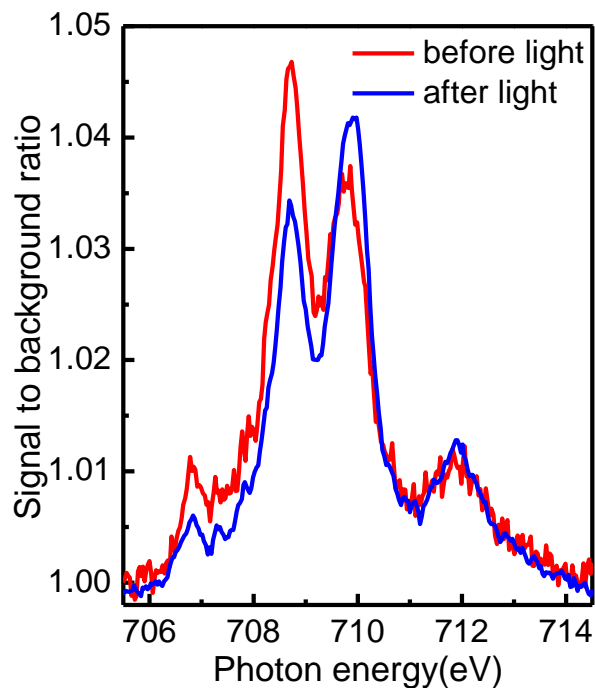


HS proportion: $49.7 \pm 1.2 \%$

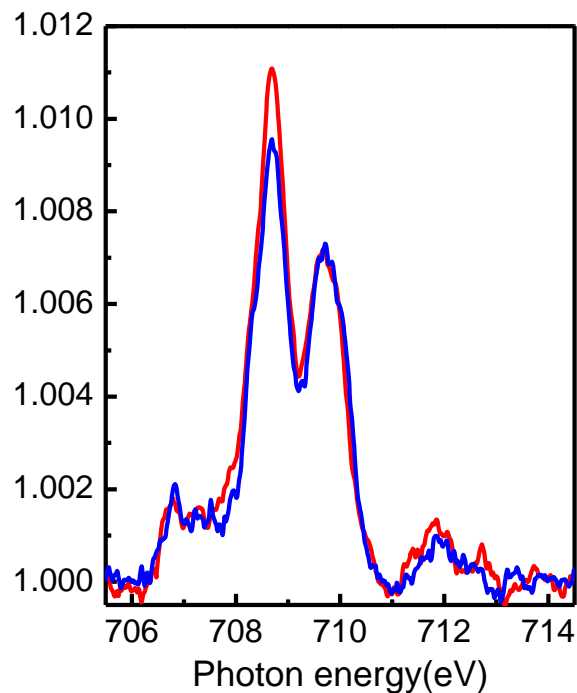
Under blue light: HS to LS conversion

Influence of the metal

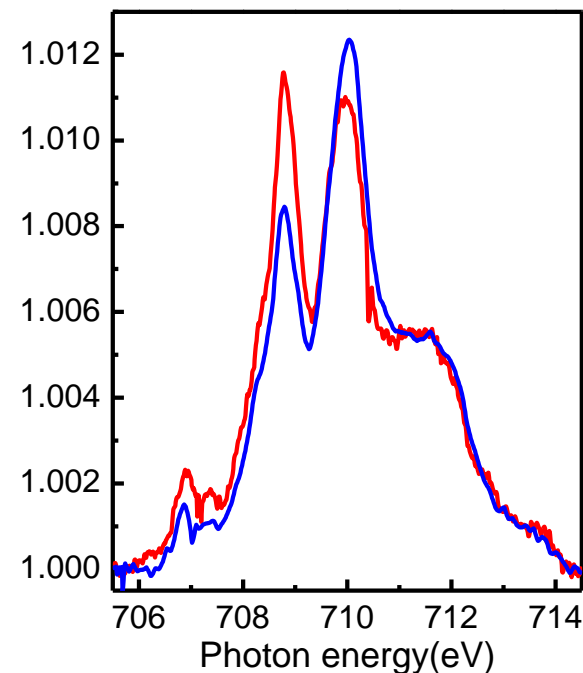
FeMPz (0.4ML) / Cu(111)



FeMPz (0.5ML) / Ag(111)



FeMPz (0.5ML) / Au(111)



Before light: $75.0 \pm 0.7 \%$

After light: $54.9 \pm 0.6 \%$

$78.6 \pm 1.3 \%$

$73.8 \pm 1.6 \%$

$65.6 \pm 1.3 \%$

$49.7 \pm 1.2 \%$

Anomalous light induced effect from HS to LS on Au(111) and Cu(111)

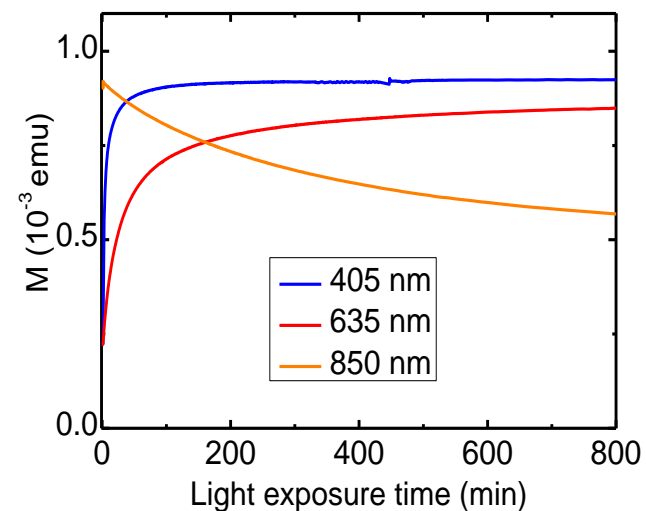
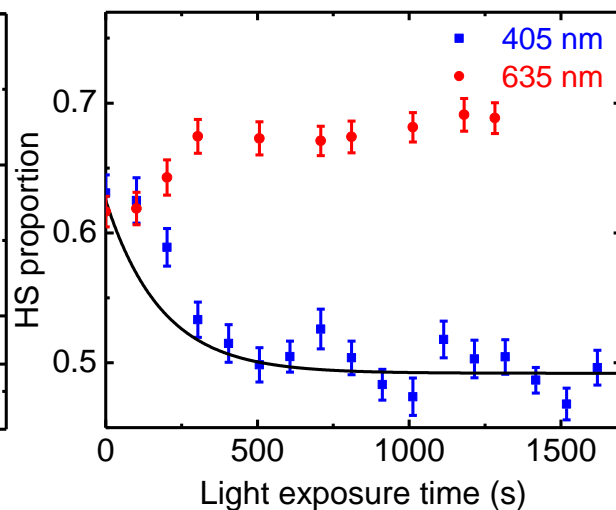
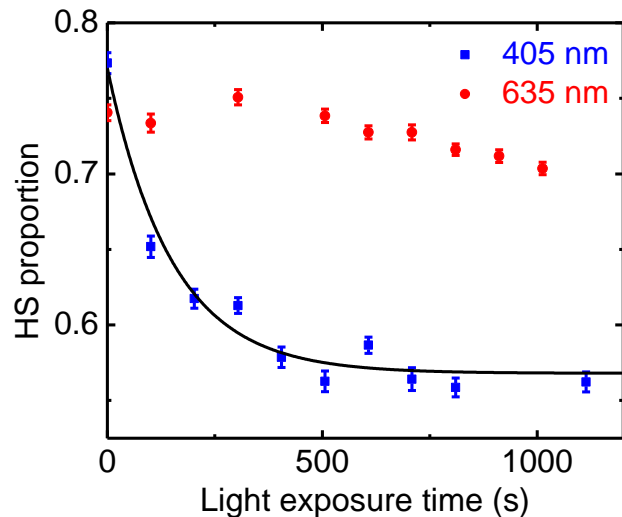
Zhang *et al.*, *Angew. Chem.*, 59, 13341-13346 (2020)

Selectivity with the wavelength

Cu(111)

Au(111)

bulk

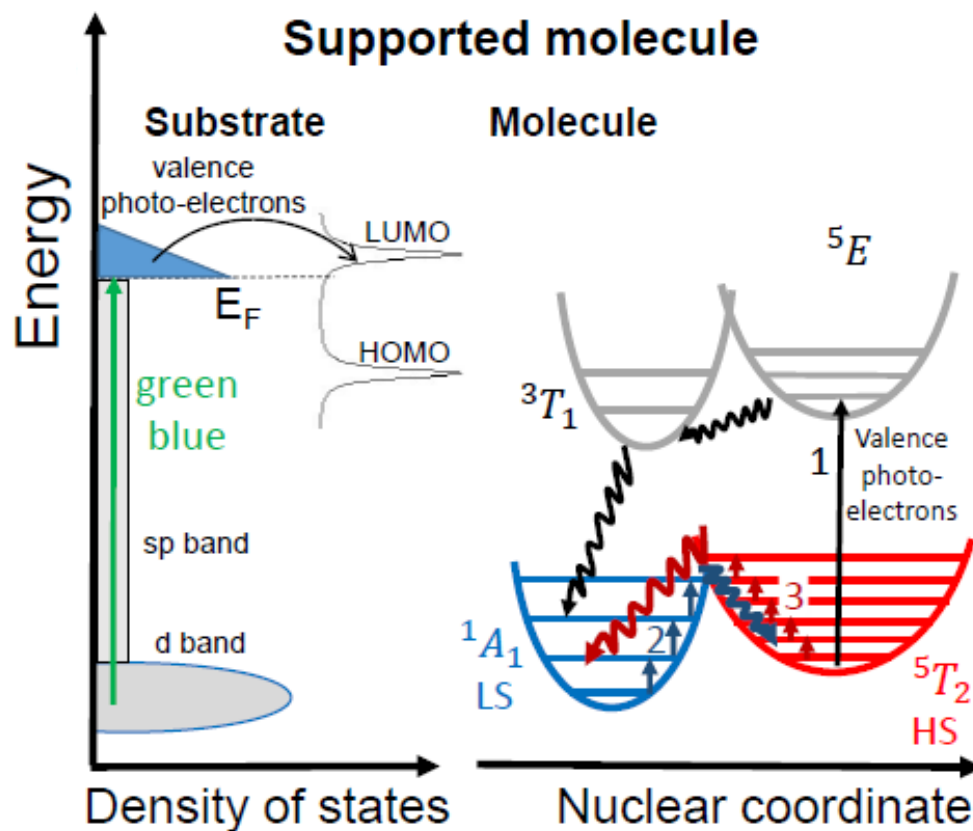


Efficient conversion with blue light
No effect of the red light

Zhang *et al.*, *Angew. Chem.*, 59, 13341-13346 (2020)

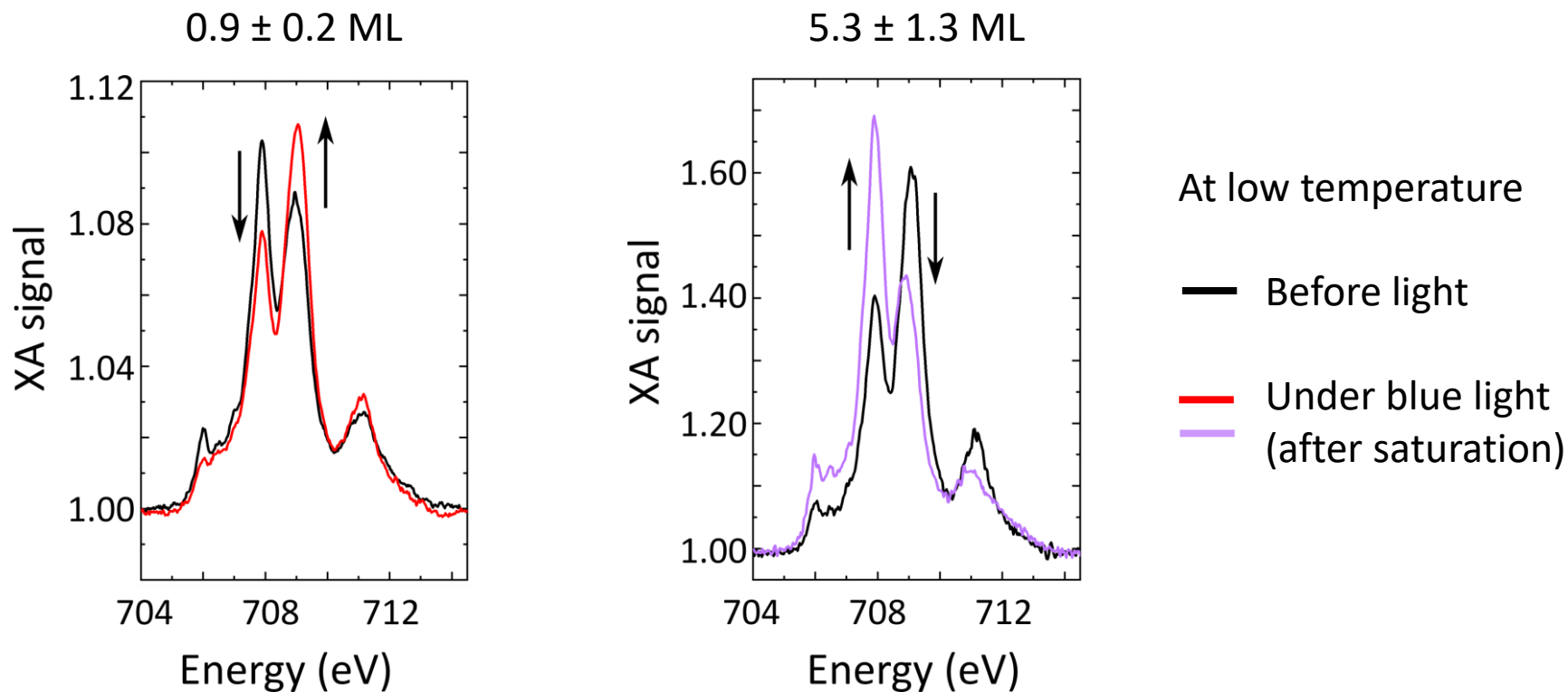
Substrate induced spin switching

Substrate photo-electrons excite molecular vibrations



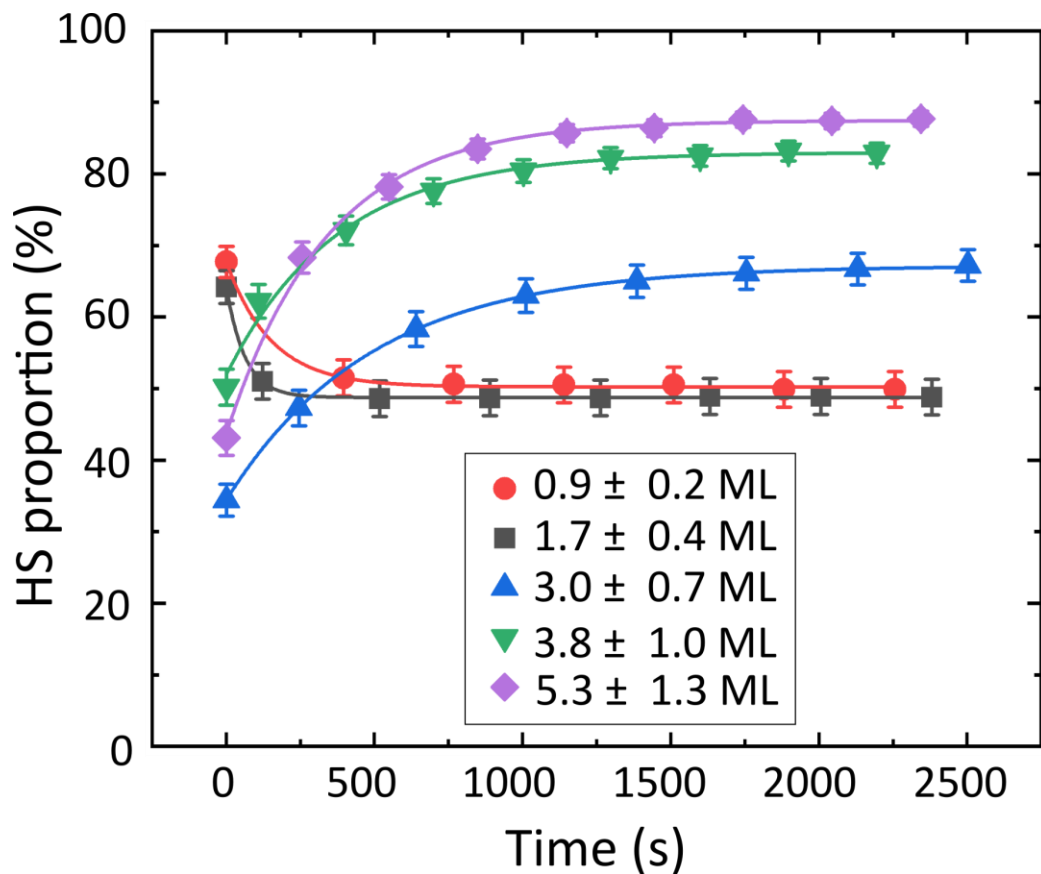
Nature of the substrate influences the light switching

Zhang *et al.*, *Angew. Chem.*, 59, 13341-13346 (2020)



LS-to-HS conversion recovered for larger film thickness

Kelai *et al.*, *J. Phys. Chem. Lett.*, **14**, 1949-1954 (2023)



Anomalous light induced switching limited to the first molecular layers
LIESST effect recovered for films larger than 3 ML

Kelai *et al.*, *J. Phys. Chem. Lett.*, **14**, 1949-1954 (2023)

Light induced thermal hysteresis

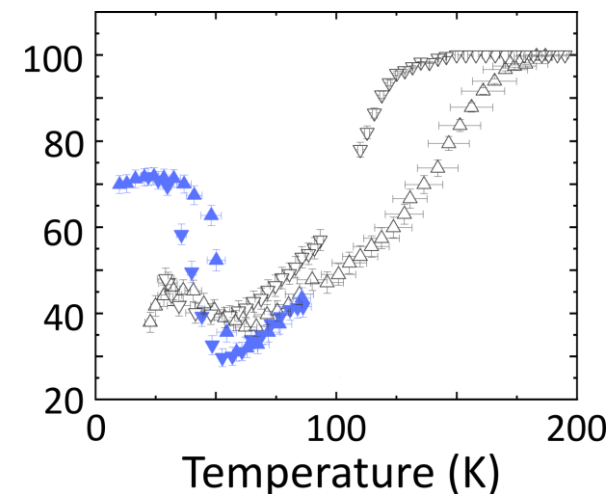
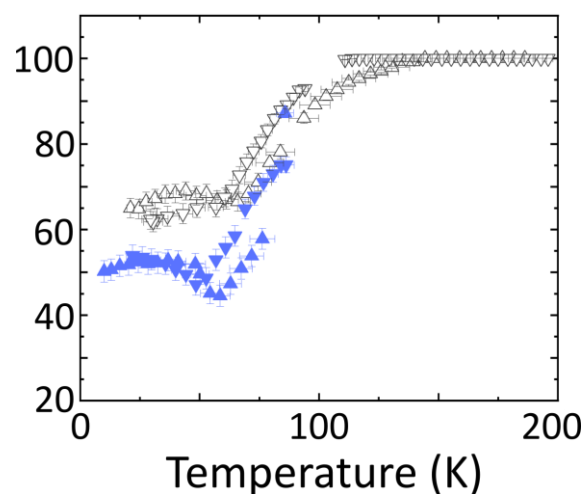
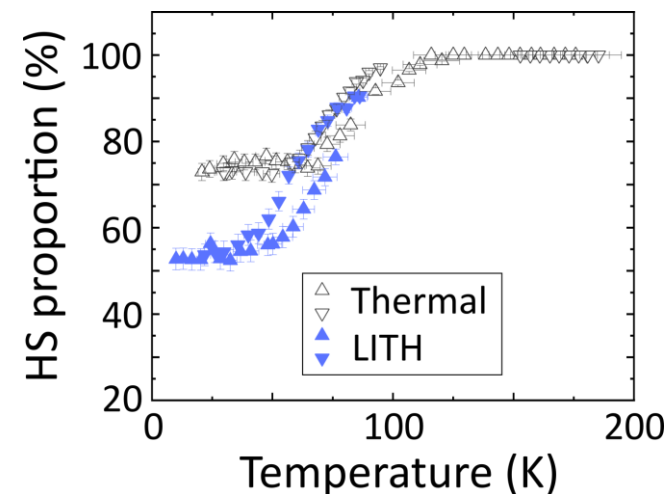
Cu(111)

1 K.min⁻¹

0.9 ± 0.2 ML

1.7 ± 0.4 ML

3.0 ± 0.7 ML



Sub-monolayer: extension of the thermal conversion
Light overcomes epitaxial constrain

1.7 ML: Intermediate behavior

3.0 ML: LITH

Kelai *et al.*, *J. Phys. Chem. Lett.*, **14**, 1949-1954 (2023)

Behavior of FeMPz on metallic substrates (Au(111) and Cu(111)):

Light induced conversion:

Anomalous light-induced spin-state switching in the interfacial layer

Conversion mediated by the metallic substrate

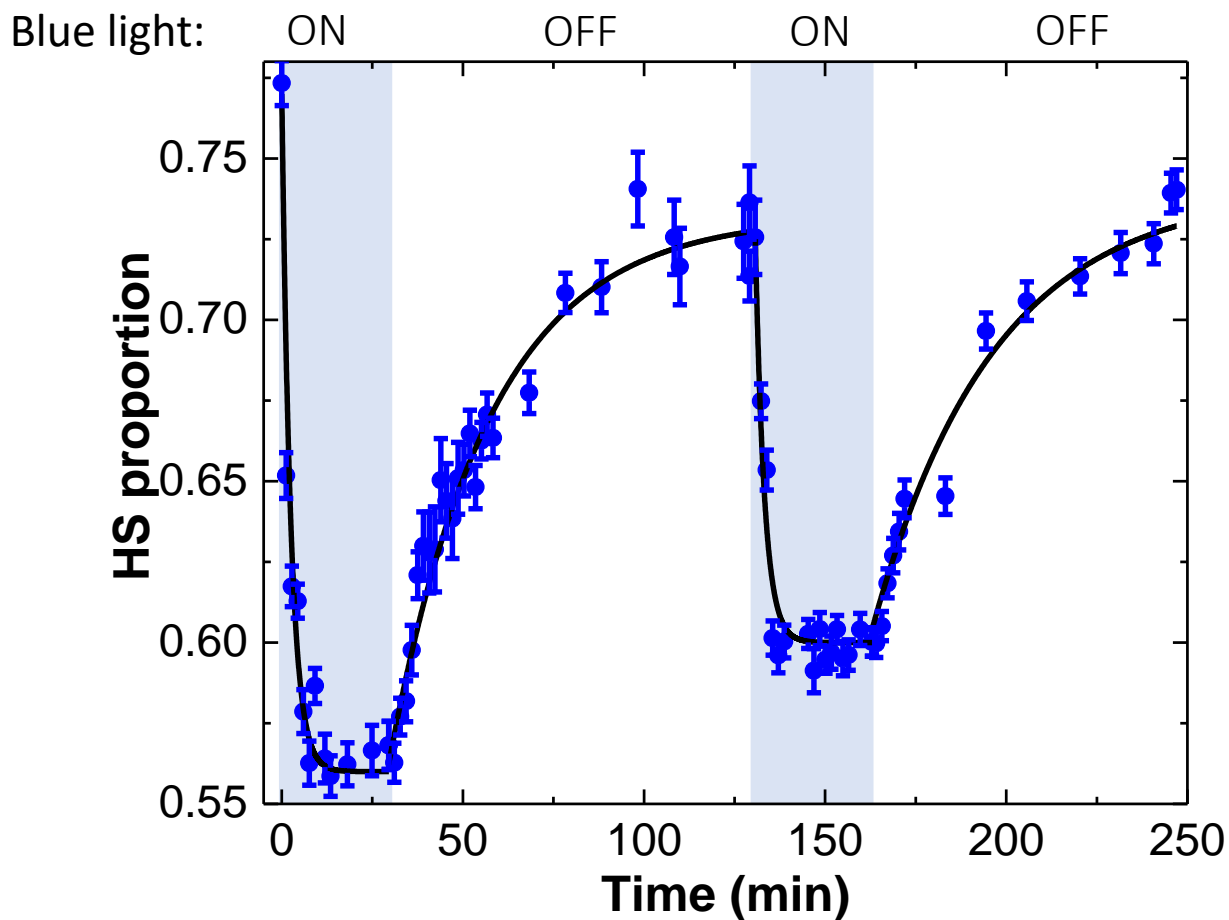
LIESST effect recovered at coverage larger than 3 ML

Light-induced thermal hysteresis

Kelai *et al.*, *J. Phys. Chem. Lett.*, **14**, 1949-1954 (2023)
Zhang *et al.*, *Angew. Chem. Ed. It.*, **59**, 13341-13346 (2020)

Reversible switching

FeMPz (0.6ML) / Cu(111)



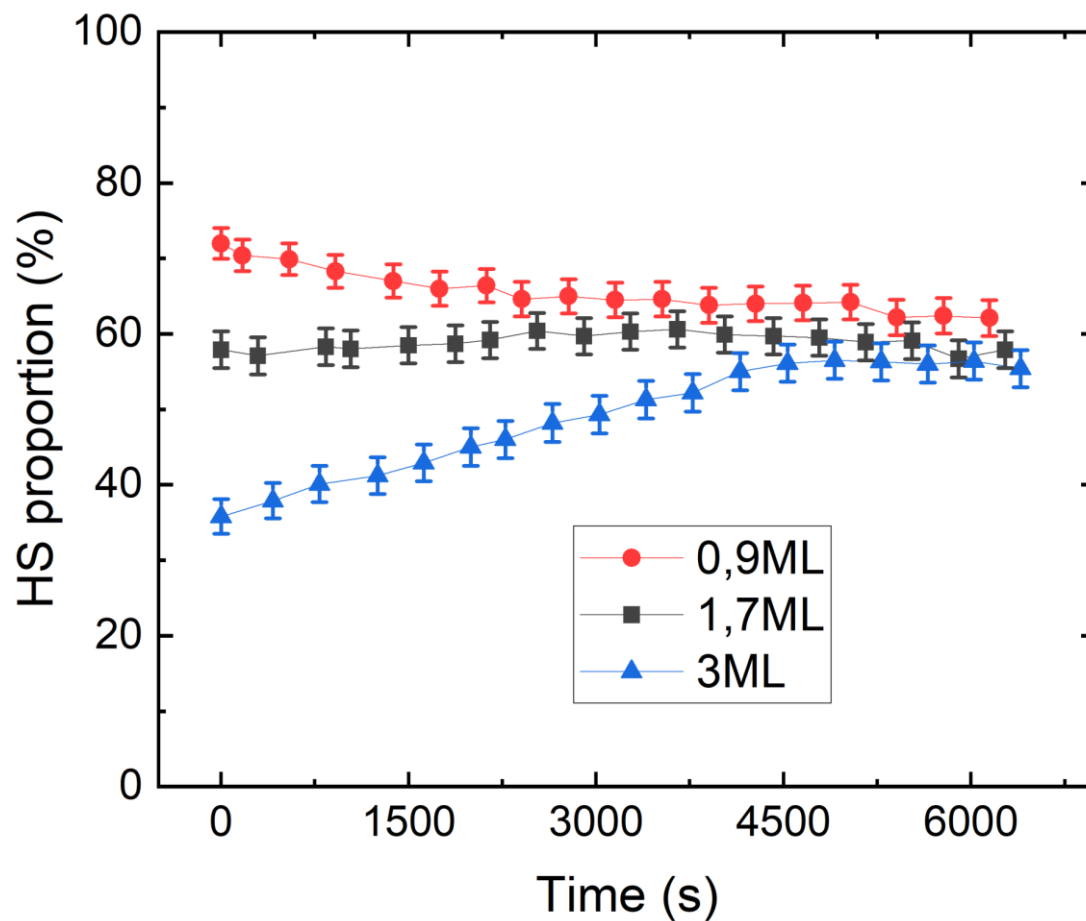
Typical times:

Light: 2min30

X-ray: 30min

Zhang *et al.*, *Angew. Chem.*, 59, 13341-13346 (2020)

Light switching under red light

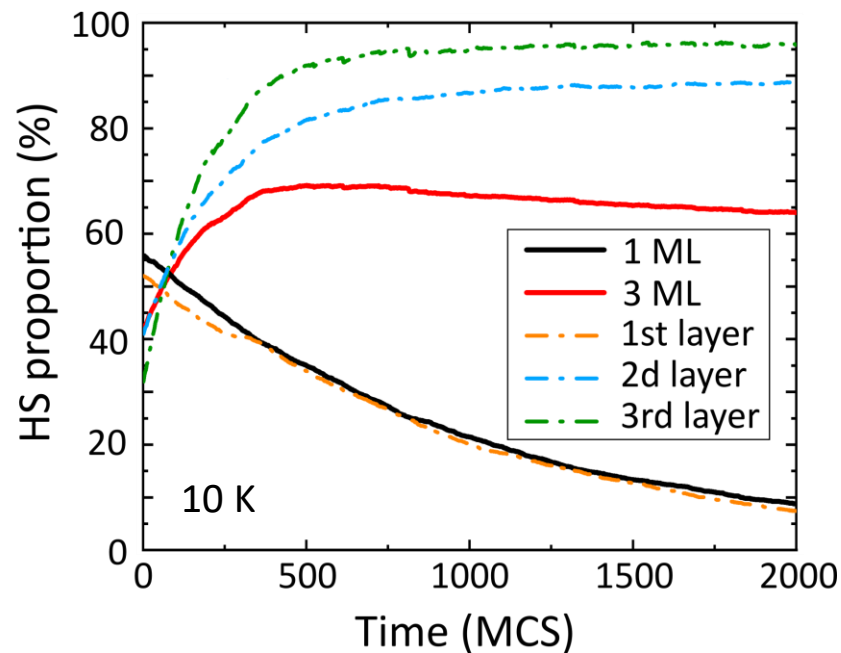
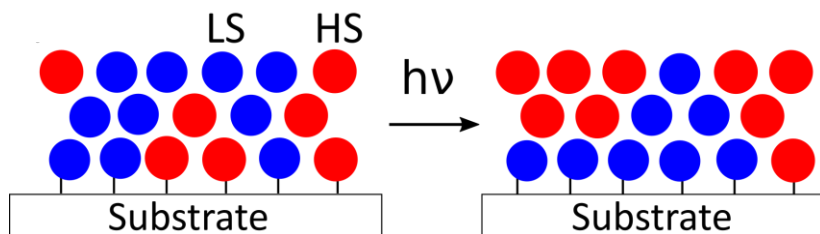


Simulation of the photoexcitation

$I\sigma_1$: HS-to-LS probability (first layer)

$I\sigma_2$: LS-to-HS probability (other layers)

$$I\sigma_1 (10^{-5}) < I\sigma_2 (10^{-4})$$



Qualitative reproduction of experimental results

→ Anomalous light-induced spin-state switching confined to the interfacial layer

Collaboration C. Enachescu (University Iasi, Romania)

Kelai *et al.*, *J. Phys. Chem. Lett.*, **14**, 1949-1954 (2023)

