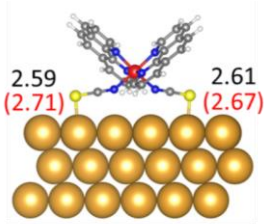
MODELLING OF SPIN-CROSSOVER MOLECULES INTERACTING WITH SUBSTRATES

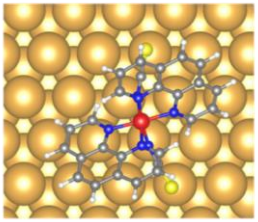
Carmen J. Calzado

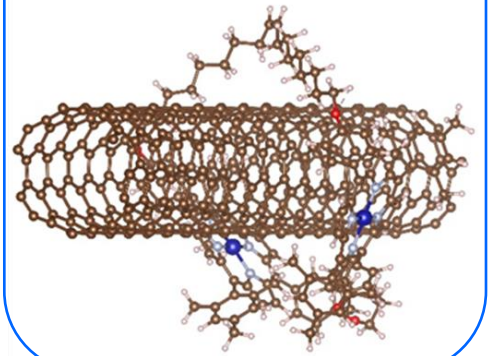
UNIVERSIDAD DE SEVILLA

GOBIERNO DE ESPAÑA
MINISTERIO DE CIENCIA E INNOVACIÓN
UNIÓN EUROPEA
Fondo Europeo de Desarrollo Regional (FEDER)
Una manera de hacer Europa
JUNTA DE ANDALUCIA
CONSEJERÍA DE ECONOMÍA, CONOCIMIENTO, EMPRESAS Y UNIVERSIDAD

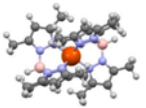
deposited

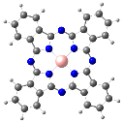




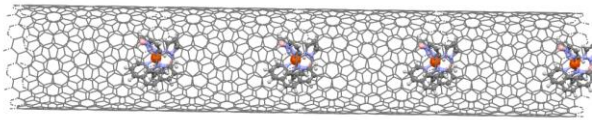


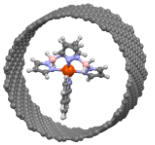
Fe(II) SCO
M-phthalocyanine
M-porphyrin



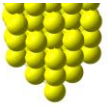


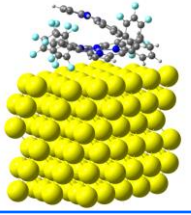
encapsulated



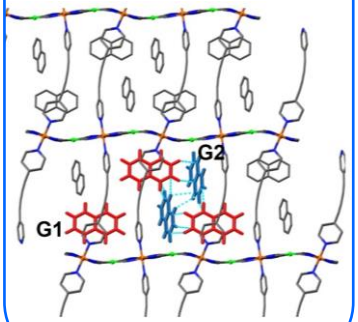


junctions





SCO-MOFs



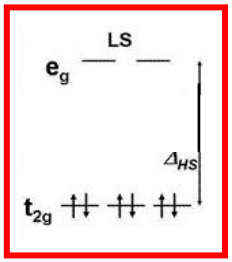
Outline

- Spin-crossover complexes
- SCO on substrates
- Methodology
- [Fe(scorpionate)$_2$] on Au(111)

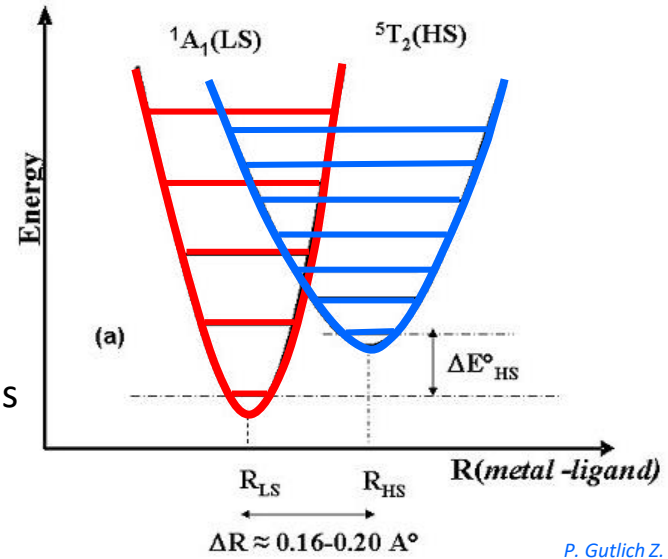
SPIN-CROSSOVER COMPLEXES

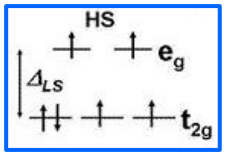
- Reversible transition bewteen two spin states
- Switching promoted by external stimuli as T, P, hν, E, B, presence of an analyte...
- Fe(II) d^6 complexes, with (quasi)-octahedral core FeN_6

S=0 LS → S=2 HS



short Fe-N distances
strong ligand field
LS favoured





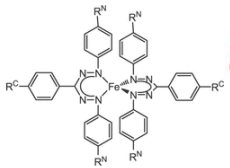
long Fe-N distances
weak ligand field
HS favoured

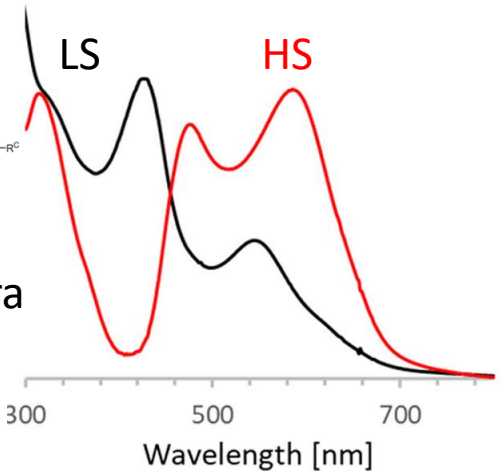
P. Gutlich Z. Anorg. Allg. Chem. 2012, 638, 15-43

LS → HS spin transition accompanied by **changes** in:

- Fe-N distances (increase of 10%)
  - octahedron volume (increase of 25%)
  - unit cell volume (~ 15%)

- Colour

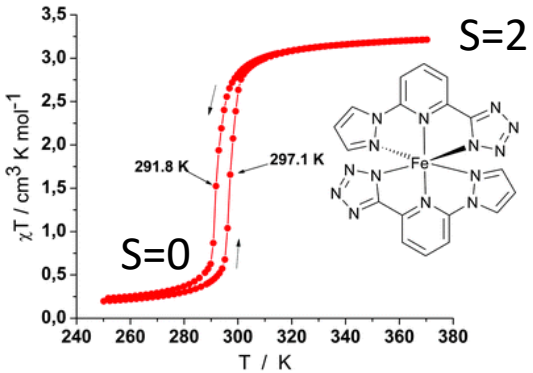




UV-vis spectra

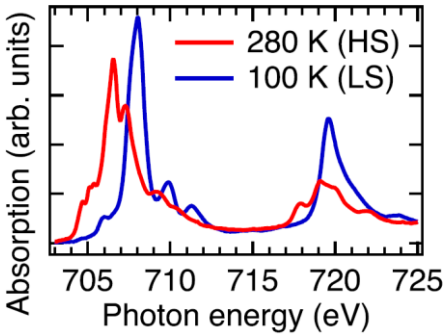
F. Milocco et al. J. Am. Chem. Soc. 2020, 142, 47, 20170

- Magnetic susceptibility



D.Gentili et al. ***J. Mater. Chem. C***, 2015,**3**, 7836-7844

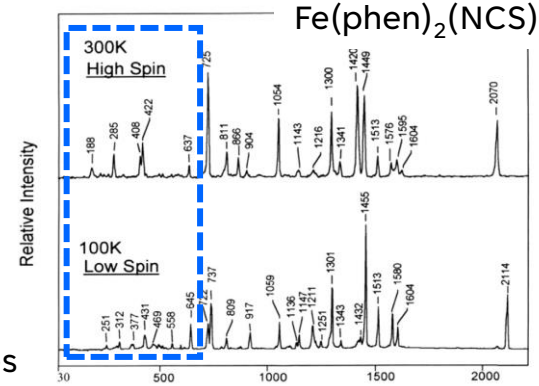
- XAS spectra Fe $L_{2,3}$ edge



Gruber *et al.* J. Chem. Phys. **146**, 092312 (2017)

- IR & Raman spectra

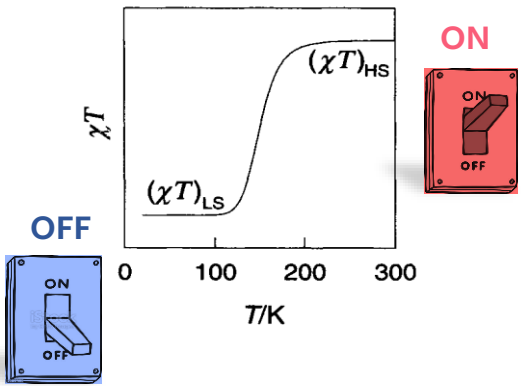
$Fe(phen)_2(NCS)_2$



Fe-N modes

$\nu_{Fe-N}(LS) > \nu_{Fe-N}(HS)$

William Nicolazzi*, Azzedine Bousseksou
C. R. Chimie 21 (2018) 1060–1074



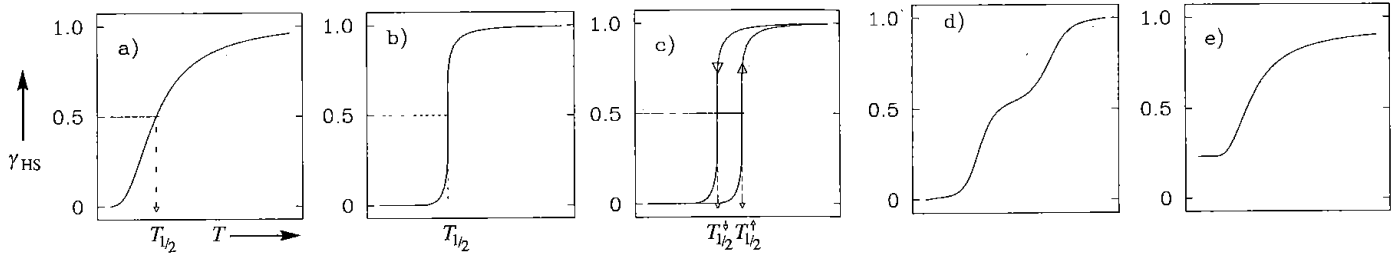
change in property = output signal

molecular switch ON/OFF

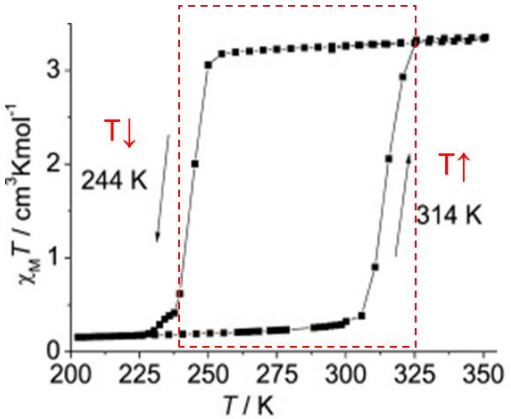
Fraction of HS molecules at each temperature γ_{HS}

- Established from experimental data
- Different behaviours:

gradual abrupt hysteresis two-steps incomplete



- when T= $T_{1/2}$ → γ_{HS}= γ_{LS}=1/2



hysteresis → "memory effect"

Applications as data storage devices

SPIN-CROSSOVER ON SUBSTRATES

Key points

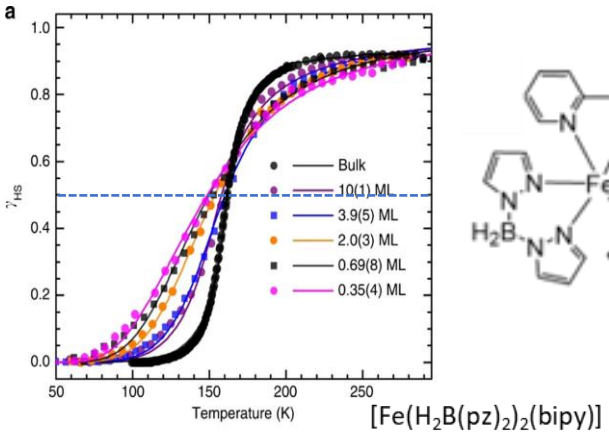
- Maintain integrity of the molecule
- Control position and orientation of molecule on the surface
- Deposition implies size reduction: bulk → film → single-molecule

Modification of intermolecular interactions

Once deposited:

- Change in the transition temperature
- Hysteresis loop reduces /disappears
- Coexistence of HS and LS molecules at low temp
- Suppression of the spin transition
- Electronic coupling between molecule-surface states

non-innocent supports



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

very few SCO molecules candidates for molecular devices

FOR MOST OF THE SYSTEMS THERE IS NO INFORMATION ABOUT

- Interaction molecule/substrate
- Adsorption sites, geometry and energy
- Electronic structure of the molecule
- Hybridization molecule/substrate

OUR AIM

Multiscale theoretical study oriented to

- Provide keys to **interpret** the properties
- Determine molecule/substrate interaction **mechanism**
- Find out **synergies** between molecule and substrate, that can modulate their properties

METHODOLOGY

Wavefunction-based methods

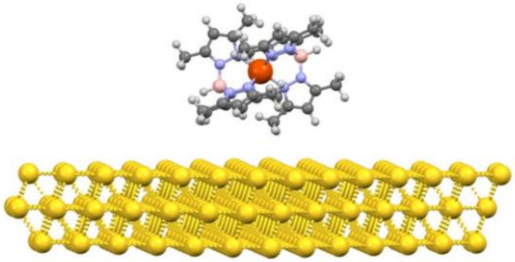
CASSCF/CASPT2/NEVPT2

Isolated molecules

Benchmark calculations
Ligand-field parameters
LIESST mechanism

DFT-based methods

Molecular and periodic calculations
Adsorption sites & energies
Density of states, electronic structure
STM images – Tersoff /Hamann approx
Transport properties - NEGF approx
UV-Vis and IR spectra



KEY POINTS:

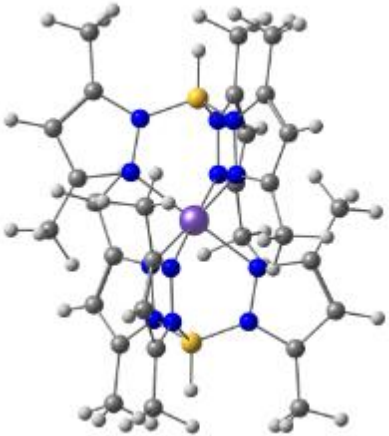
- Accurate determination of structural changes
- Correct balance of electronic correlation energy:

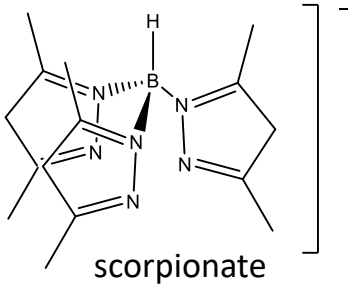
  LS (closed-shell) versus **HS** (open-shell)
- Zero-point and thermal corrections → ΔH, ΔS

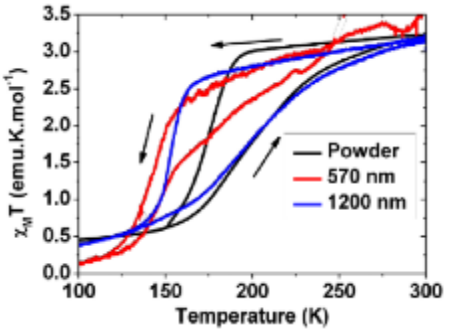
- DFT (functional dependent) and CASSCF/PT2 (expensive) approaches
- Model for the substrate → fragment vs periodic approach

Fe(II) -pyrazolylborate SCO deposited on Au(111) surface

Fe-pyrazolylborate $Fe^{II}[(Me_2Pz)_3BH]_2$







Davesne et al. JCP 2015, 142, 194702
Iasco et al. J.Mater.Chem. C 2017, 5, 11067

- Neutral complex, first reported in the 60's
- 2015: SCO properties conserved upon sublimation

Thin films of Fe-pz on Si/SiO_2 and quartz by thermal evaporation

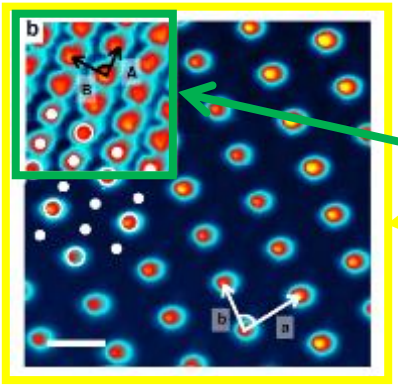
- Transition temperatures shifted to lower temp
- Spin transition is not complete at low temperature (~20% HS)
- Light induced spin transition LIESST is preserved

Monolayer Fe-pz/ Au(111)

K. Bairagi et al. *Nat. Commun.* **2016**, *7*, 12212
JPCC **2018**, 122, 727

STM and XPS

- Fe-pz on Au(111) is not degraded
- Incomplete SCO transition: mixed spin state at low temperature



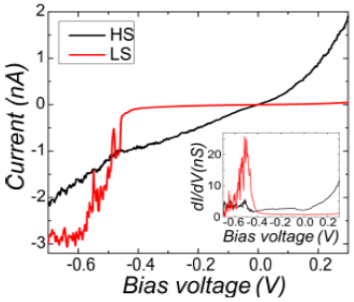
Spin-dependent **superstructure** can be observed for specific scanning voltages:

- V= −1.5 V all molecules bright
- V= +0.3 V only one molecule over three brights

Superstructure 3 molecules/unit cell: 2 LS : 1 HS

I-V curves recorded at constant height

- Different conductance for HS and LS molecules



Grazing incidence x-ray diffraction (GIXD)

- Epitaxial relationship between Fe-pz monolayer and substrate

Fourmental et al. JPC Lett. **2019**, 10, 4103

Anomalous LIESST effect Fe-pz/Ag(111), Au(111), Cu(111)

XAS Fe-pz/ Au(111) 1LS:2HS

Angew. Chem. Int. Ed. 2020, 59, 13341–13346

Our aim:
why mixed spin states at low temperature

Benchmark calculations on isolated molecule

ΔH_{HL}exp: 10.2 kJ/mol

Code	Method employed		HS-LS (kJ/mol)	
MOLCAS	CASPT2	IPEA= 0.25 au	12.1	CAS(10e, 12MO)
		IPEA= 0.4 au	22.1	
		IPEA= 0.5 au	28.3	
	NEVPT2	Strongly contracted	20.3	
		Partially contracted	9.7	
ORCA	rPBE	Single molecule	**10.0**	
	rPBE + ZPC		**1.3**	
	rPBE + D3		52.7	
	rPBE + D3 + ZPC		44.0	
VASP	PBE	Single molecule **Periodic conditions**	76.3	
	SCAN		74.8	
	revPBE		29.7	
	rPBE		**18.2**	
	rPBE+D3		65.5	

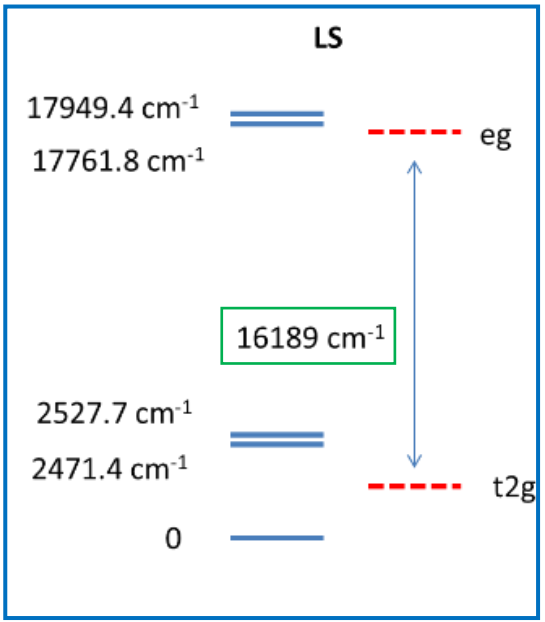
Dispersion corrections → large overestimation of HS-LS

Zero-point corrections → reduce the HS-LS gap, but expensive for periodic approaches

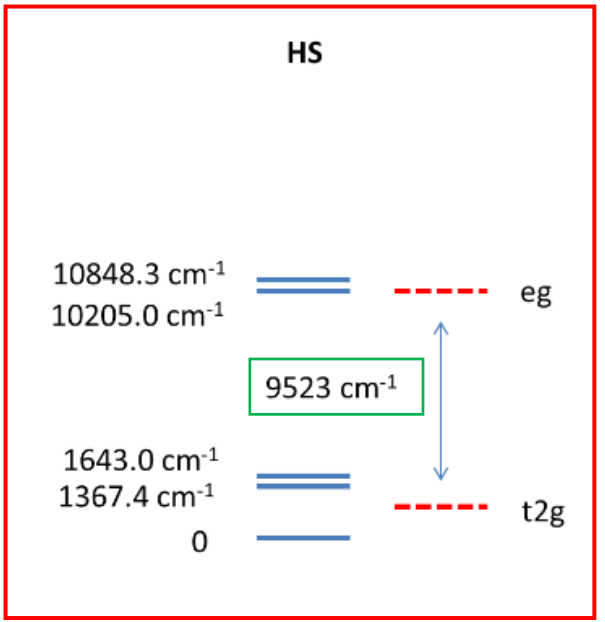
Use rPBE as alternative to DFT+U

Fe ligand field parameters

Low temp x-ray geometry



High temp x-ray geometry

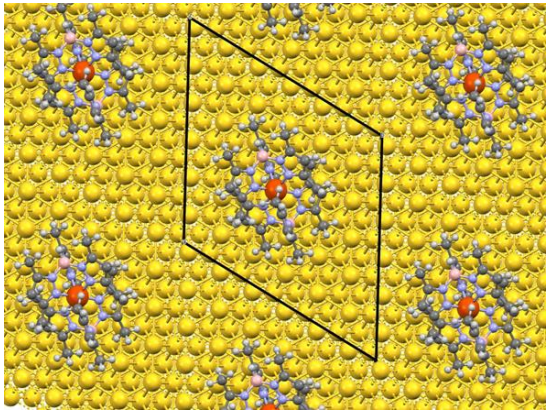


Ligand field strength $\Delta_{LS} \sim 2\Delta_{HS}$

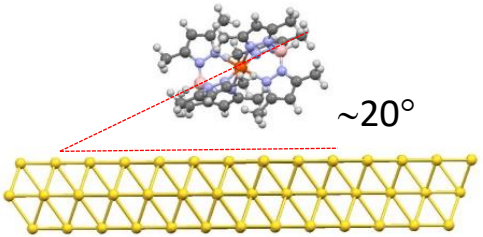
ΔR (Fe-N) ~0.2Å

Ab initio ligand field theory (AILFT)
SA-CASSCF(6,5) (5Q, 45T, 50S)

Fe-pz molecule/Au(111)



- rPBE calculations, 1molecule/cell
- periodic conditions, unit cell large enough to avoid intermolecular interactions



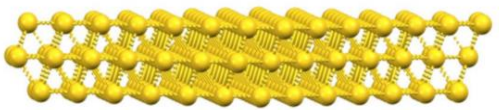
Molecule tilted toward surface,
B-Fe-B axis forms angle ~20°

- Adsorption energy is spin-dependent:
- **LS: –32.2 kJ/mol** **HS: –25.3 kJ/mol**

- HS-LS **gap enhanced** once deposited

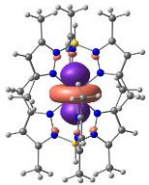
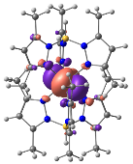
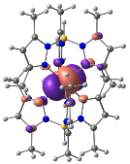
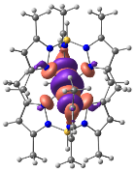
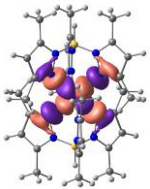
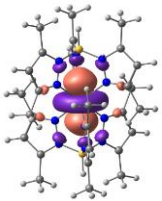
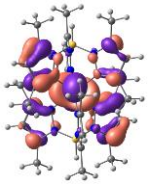
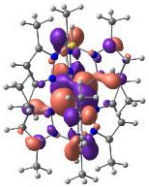
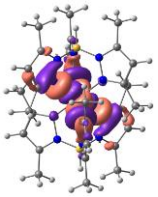
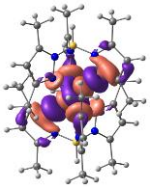
HS- LS 18.2 kJ/mol

HS- LS 25.1 kJ/mol



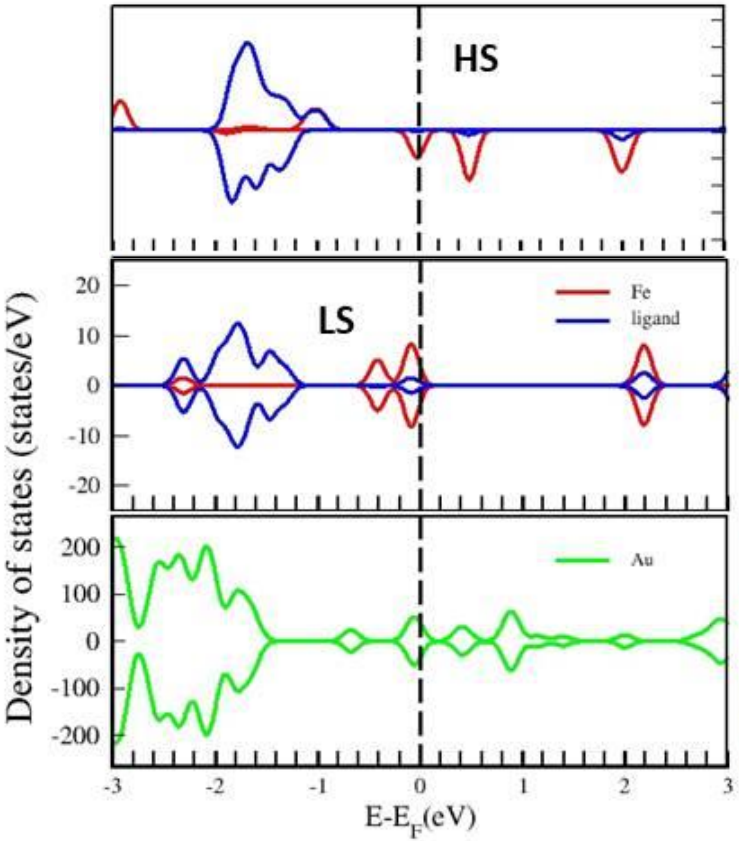
Ligand-metal hybridization LS > HS

CASSCF(10,12)

	t_{2g}-like			e_g-like	
HS					
occ	2	1	1	1	1
LS					
occ	2	2	2	0	0

Fe ligand field → **energy** and **composition** of Fe 3d-like orbitals

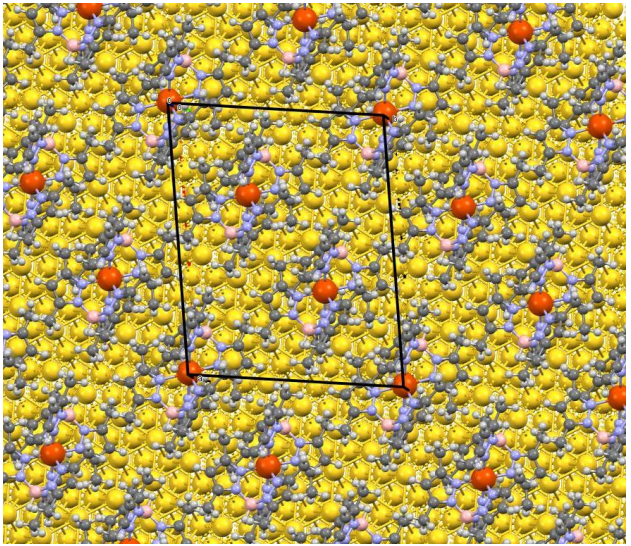
Projected density of states



Close to the Fermi:

- Fe 3d, with **larger hybridization** with ligands for LS than HS
- In line with the strength of the ligand field, stronger for LS than HS
- More spatially extended orbitals for LS → promote **stronger interations** with Au(111)
- General feature of SCO molecule-subtrate interaction

Fe-pz monolayer/Au(111)



rPBE calculations + ZPE
- 4 layers of gold
- 3 molecules per unit cell

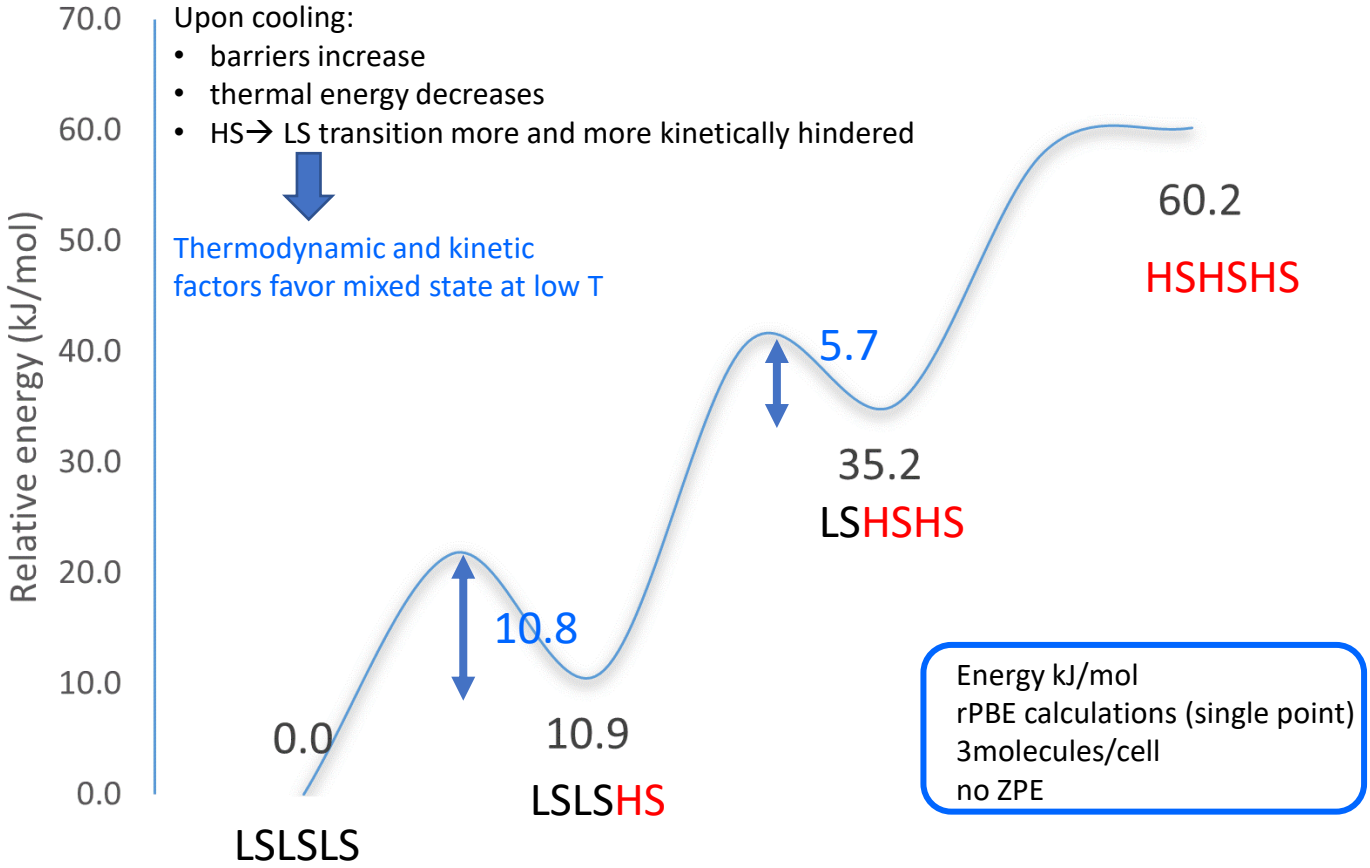
molecules and upper gold layer relaxed

- LS→ HS transition energy lower in presence of intermolecular interactions
- Molecules stabilized by interaction with surface
- Pure LS and mixed LSLSHS almost degenerate → in line with experiments

	LSLSLS	LSLSHS	LSHSHS	HSHSHS
Relative energy (kJ/mol)	**Pure LS**	**33 % HS**	**66 %HS**	**Pure HS**
3 molecules/Au(111)	0.0	10.9– 11.6	35.2 – 33.1	60.2
ZPE corrected	*0.0*	*1.0 – 1.7*	*15.5 – 13.4*	*30.5*
3 molecules w/o substrate	0.0	19.1	44.6	73.4

1 molecule/Au(111) HS-LS = 25.1 kJ mol^{-1} (15.2 kJ mol^{-1} with ZPE)

Activation barriers for succesive spin transitions on cooling

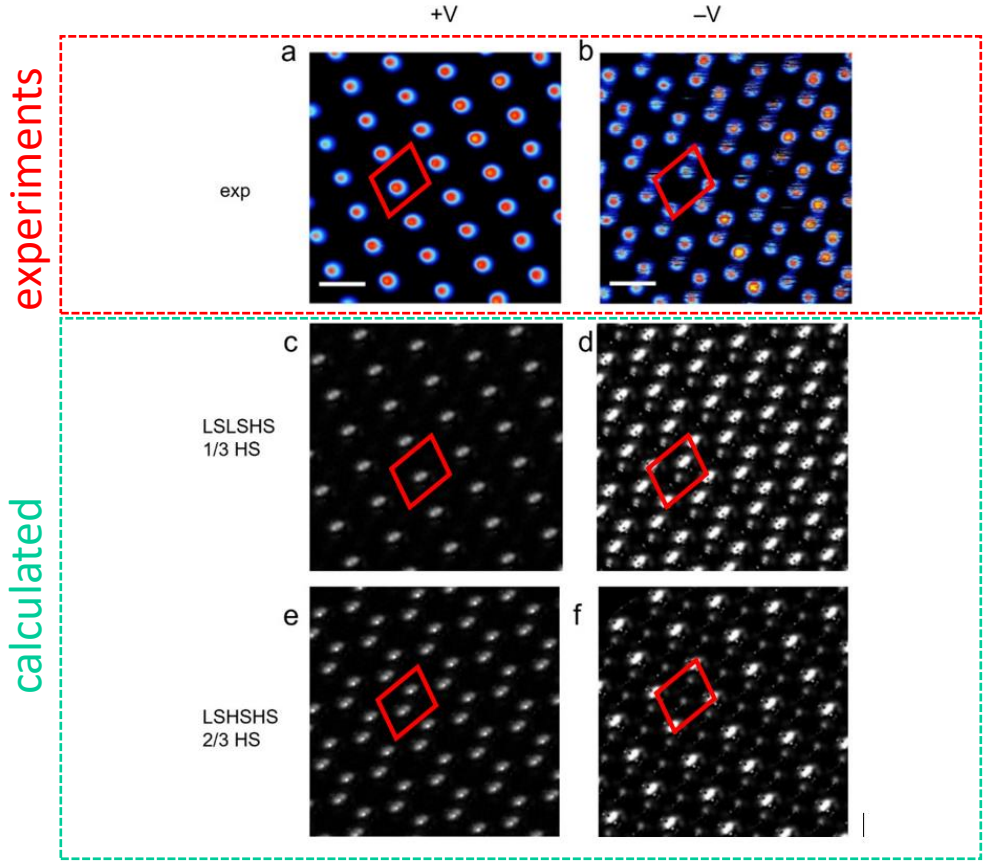


STM images

constant height

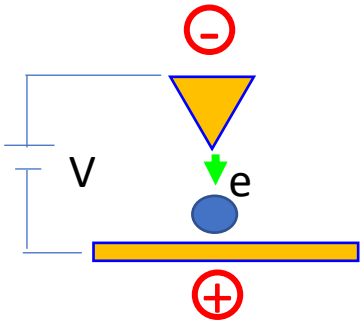
K. Bairagi et al. *Nat. Commun.* **2016**, *7*, 12212

Sánchez-de-Armas, Calzado
Inorg. Chem. Front. 2022, 9,753

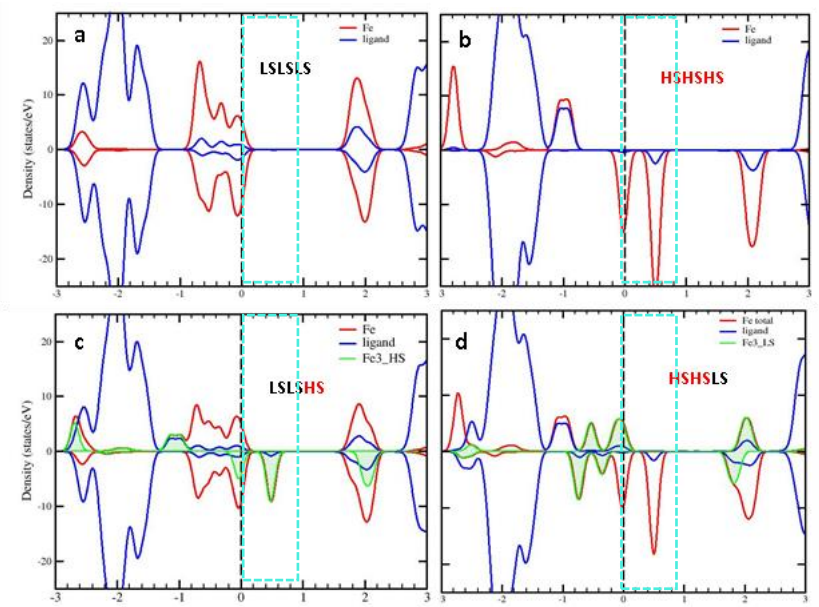


Positive sample voltage

electrons TIP → sample

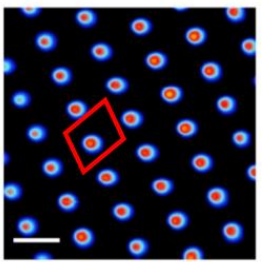


virtual states of sample

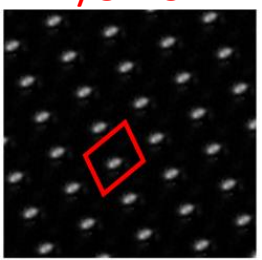


V > 0

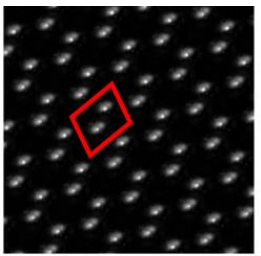
exp



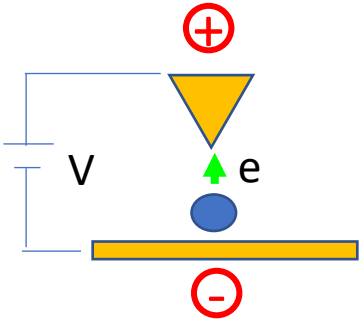
1/3 HS



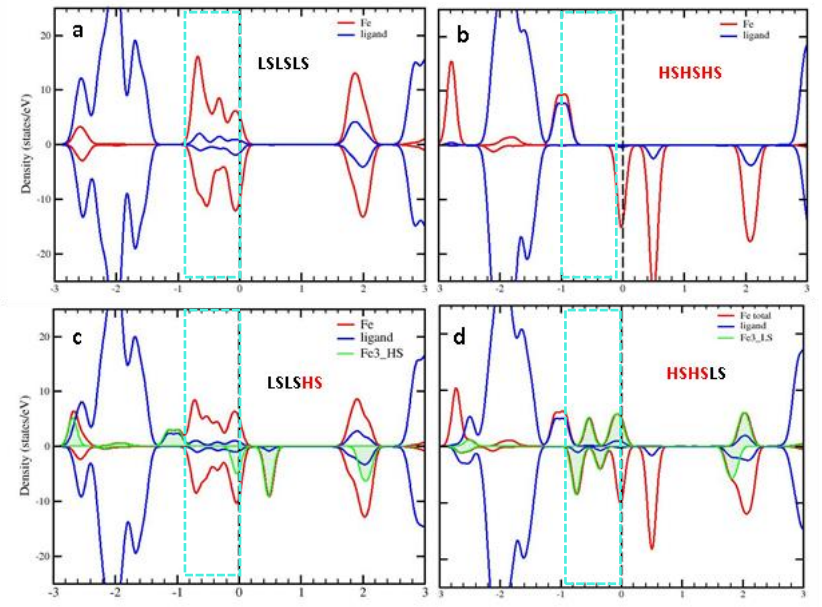
2/3 HS



Negative sample voltage
electrons sample →TIP

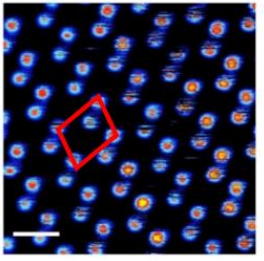


occupied states of sample

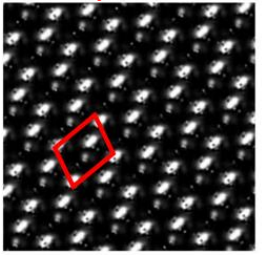


V < 0

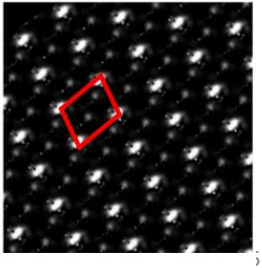
exp



1/3 HS



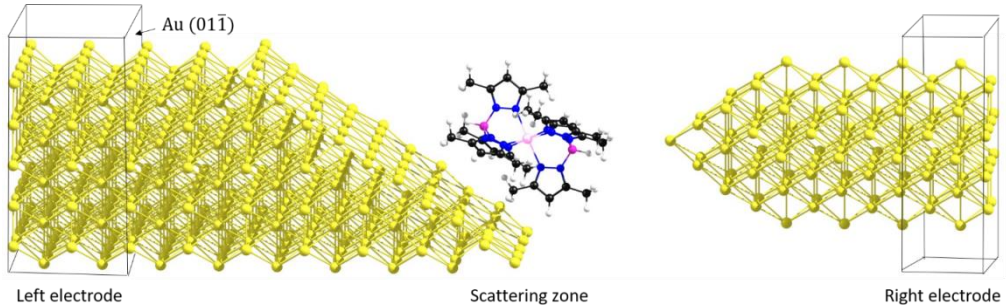
2/3 HS



Sánchez-de-Armas, Calzado
Inorg. Chem. Front. 2022, 9,753

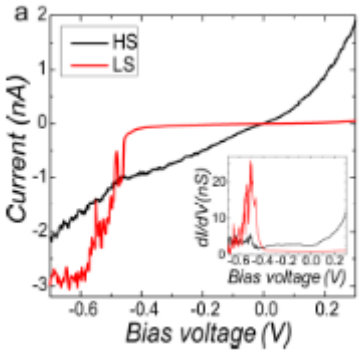
Transport properties

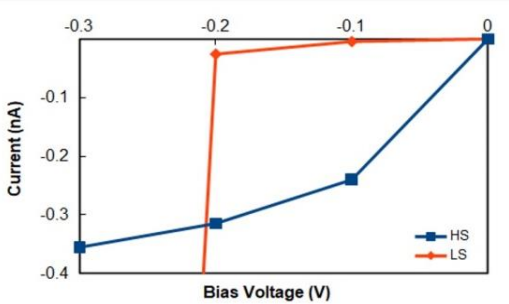
DFT-NEGFT
TRANSIESTA



Molecular junction scheme

I-V curves at constant height over LS (red) molecule and HS (black) molecule





Simulated I-V curves at constant height

Montenegro et al. Chem. Eur. J. 2021

Conclusions

- Mixed spin states thermodinamically and kinetically favoured
- Deposition increases HS-LS gap
- Interaction with substrate is spin-dependent: LS > HS
  - Related to the stronger Fe ligand field of LS state
  - Larger ligand-metal hybridization
  - General feature of SCO on Surface

- PDOS explain STM images
- I-V curves correctly reproduced
- Pathway for LIEEST phenomenon

Acknowledgments

- Rocío Sánchez de Armas
- David Arias
- Iman Jaber El Lala
- Nicolás Montenegro
- Jhon Zapata

UNIVERSIDAD D SEVILLA

UNIVERSIDAD DE SANTIAGO DE CHILE

Universidad de los Andes Colombia

- Talal Mallah
- Cyrille Barreteau

ICMMO cea

- Enrique Burzurí
- Emilio M. Pérez
- José Sánchez Costa

instituto IMDEA nanociencia EXCELENCIA SEVERO OCHOA 2017-2021

MolDev-Q Mag4Dev

UNIVERSIDAD D SEVILLA

GOBIERNO DE ESPAÑA MINISTERIO DE CIENCIA E INNOVACIÓN

AGENCIA ESTATAL DE INVESTIGACIÓN

UNIÓN EUROPEA
Fondo Europeo de Desarrollo Regional (FEDER)
Una manera de hacer Europa

JUNTA DE ANDALUCIA
CONSEJERÍA DE ECONOMÍA, CONOCIMIENTO, EMPRESAS Y UNIVERSIDAD