Interface and Matrix Effects on Spin Transition Solids

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Ligand Field Splitting

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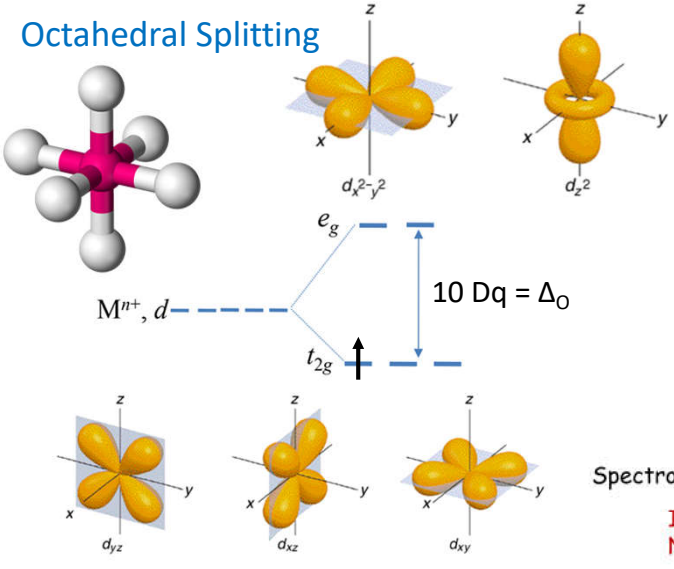
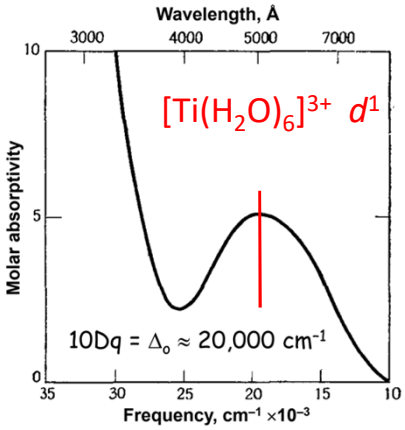
Octahedral Splitting





Spectrochemical series of ligand-field strength:

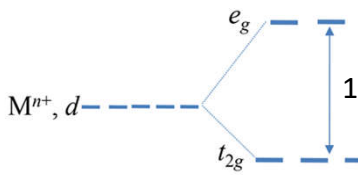
$I^- < Br^- < Cl^- < SCN^- < NO_3^- < F^- < OH^- < H_2O <$
$NCS^- < py < NH_3 < en < NO_2^- < PPh_3 < CN^- < CO$

High Spin vs Low Spin

For d^4, d^5, d^6, d^7 complexes can be high spin or low spin

Δ_O (10Dq) – ligand field splitting

Π – electron pairing energy



Π ≈ 15,000 cm^{-1}

LS, S = 1/2	HS, S = 5/2	LS, S = 0	HS, S = 2
$\Delta_O > \Pi$	$\Delta_O < \Pi$	$\Delta_O > \Pi$	$\Delta_O < \Pi$

Spectrochemical series of ligand-field strength:

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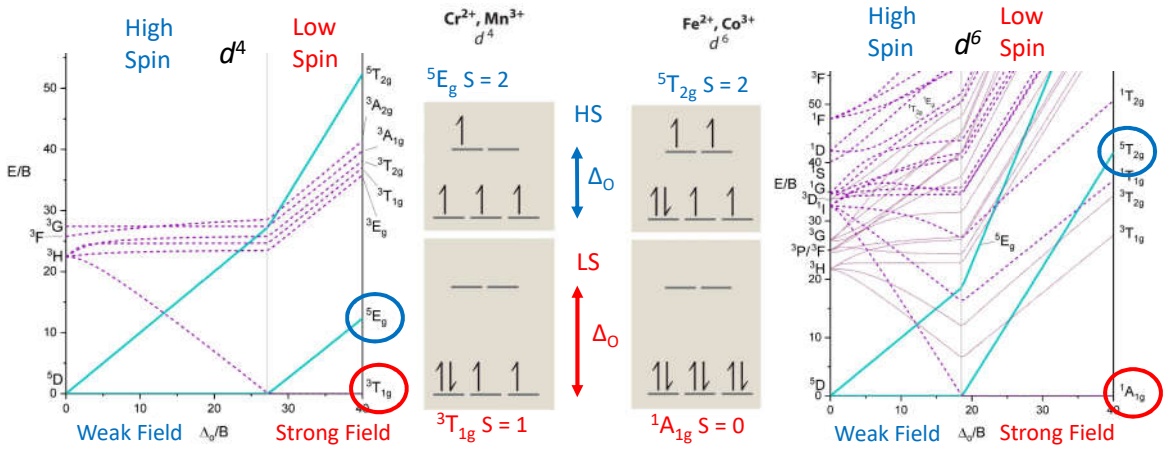
High Spin vs Low Spin

Tanabe-Sugano



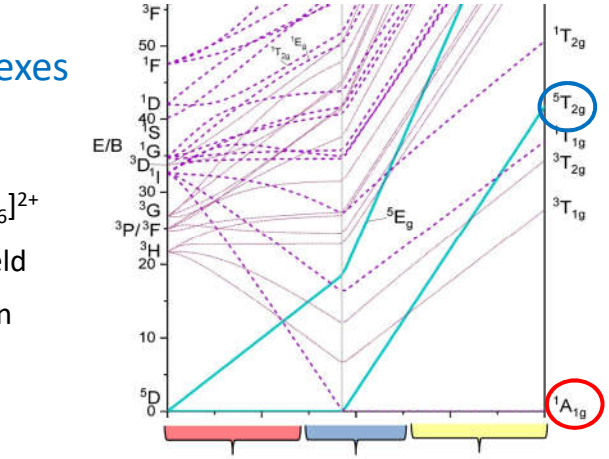
Spin Crossover (SCO)

d^6 complexes

$[Fe(H_2O)_6]^{2+}$

Weak Field

High Spin



$[Fe(CN)_6]^{4-}$

Strong Field

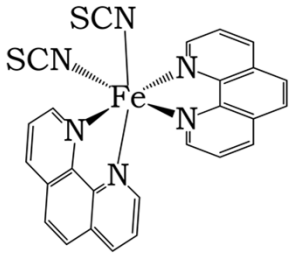
Low Spin

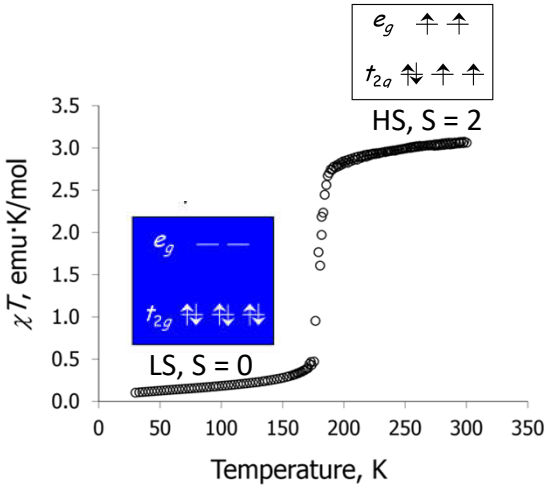
Spectrochemical series of ligand-field strength:

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

Spin Crossover (SCO)

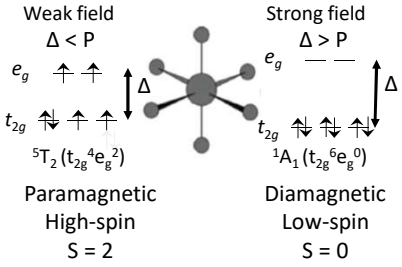
The first reported SCO complex of Fe(II)



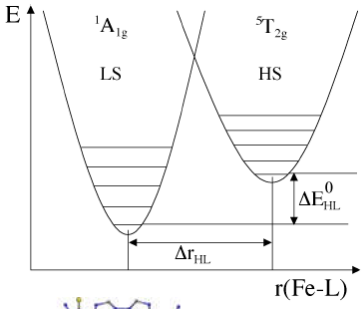


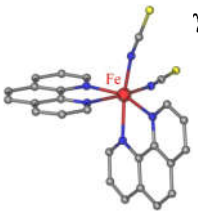
König, Madeja *Chem. Commun.* **1966**, 61-62.

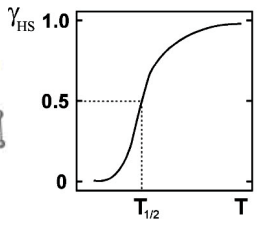
Spin Crossover

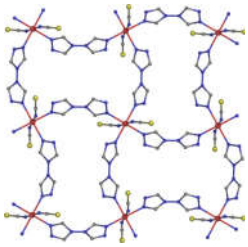


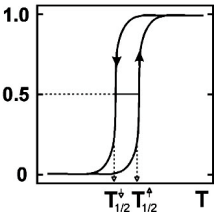
r(Fe–L): 1.95-2.00 Å 2.15-2.20 Å







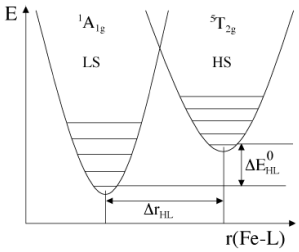


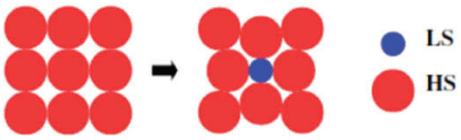


Gütlich, Hauser, Spiering *Angew. Chemie* **1994**, *33*, 2024

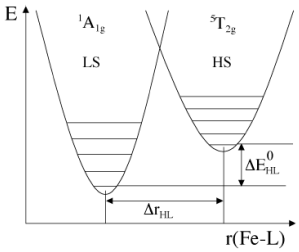
Spin Crossover

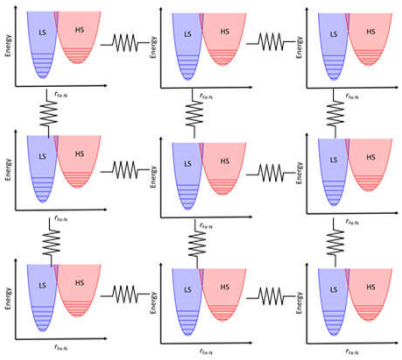
r(Fe–L): 1.95-2.00 Å 2.15-2.20 Å



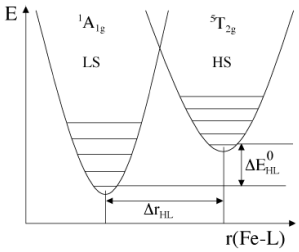


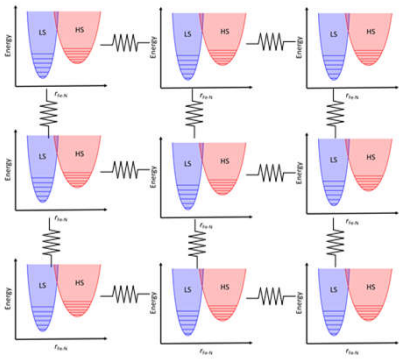
Spin Crossover

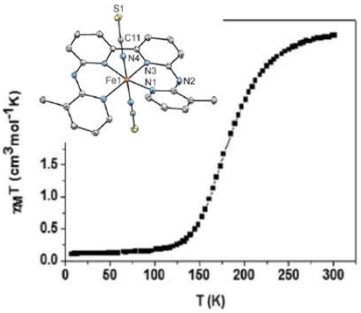


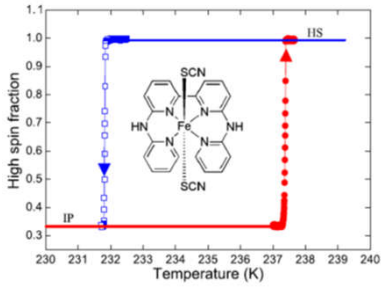


Spin Crossover





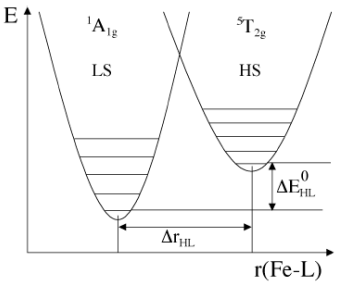




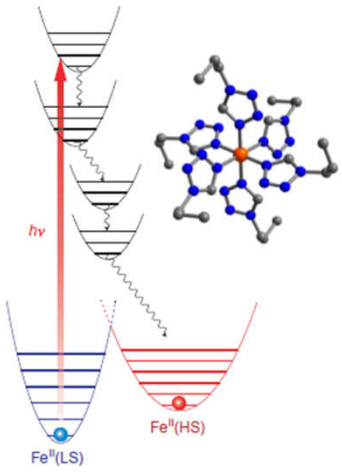
Arcis-Castíllo *et al*. *Chem. Eur. J.* **2011**, *17*, 14826

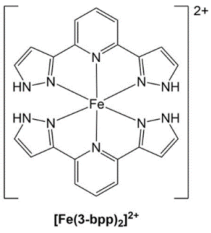
LIESST

Light induced excited state spin trapping

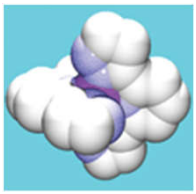


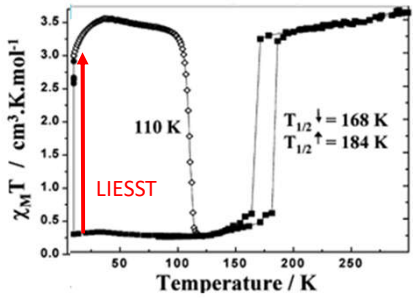
$[Fe(ptz)_6](BF_4)_2$





$[Fe(3\text{-}bpp)_2]^{2+}$



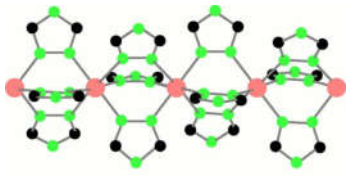


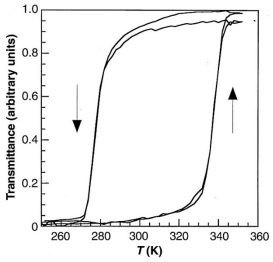
Feng *et al. J. Am. Chem. Soc.*, **2013**, *135*, 15880
Decurtins *et al. Chem. Phys. Lett.* **1984**, *105*, 1
Ohkoshi *et al. Nature Chem.* **2011**, *3*, 564

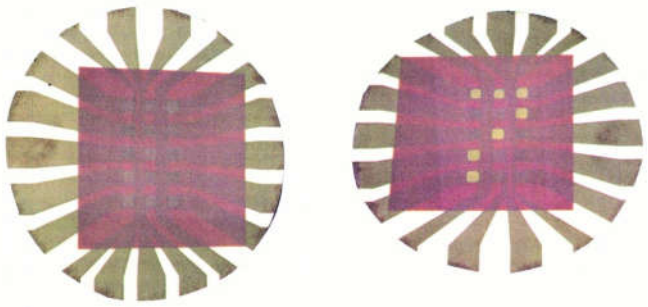
J.-F. Letard *J. Mat. Chem.* 2006, **16**, 2550-2559

Spin Crossover as Materials

$[Fe(NH_2trz)_3](NO_3)_{1.7}(BF_4)_{0.3}$







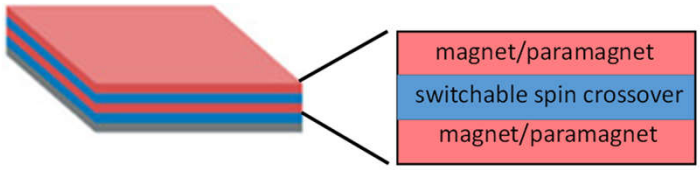
Areas of Interest:

- Displays
- Information Storage
- Molecular Switches
- Catalysts
- MRI Contrast
- Sensors
- Mechanical Actuators

Kahn and Martinez *Science* **1998**, *279*, 44

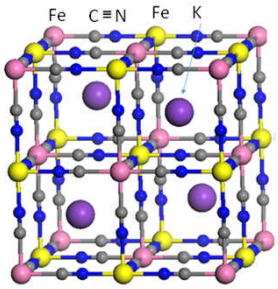
Original Idea:

Use spin crossover to switch magnetic coupling in thin film heterostuctures



Prussian Blue

$K_3[Fe^{III}(CN)_6] + Fe^{II}Cl_2 \longrightarrow KFe^{III}[Fe^{II}(CN)_6]$

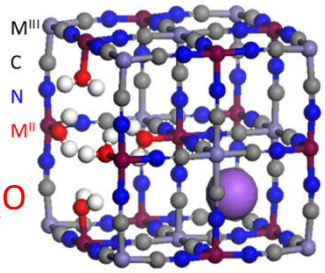


…and Prussian Blue Analogues

MM'-PBA

FeFe-PBA	NiFe-PBA
NiCr-PBA	CrCr-PBA
CoFe-PBA	CuCo-PBA
CoCr-PBA	MnFe-PBA

$A_jM_k^{II}[M'^{III}(CN)_6]_l \cdot nH_2O$

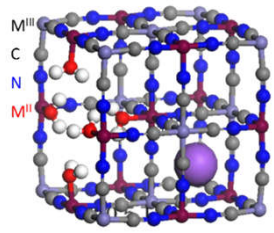


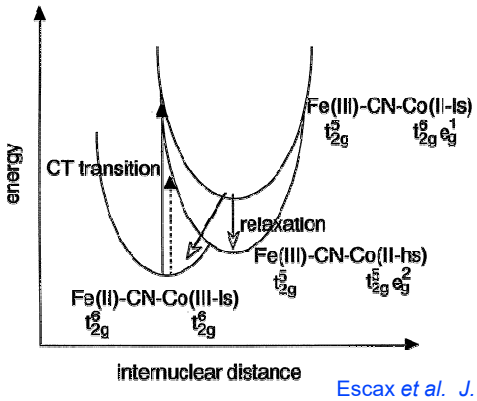
Prussian Blue Analogues

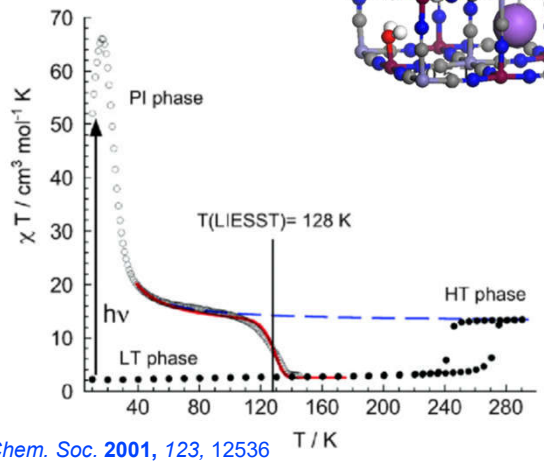
magnet/paramagnet
switchable spin crossover
magnet/paramagnet

$Na_2Co_4[Fe(CN)_6]_{3.3}{\cdot}14H_2O$

"CoFe PBA"



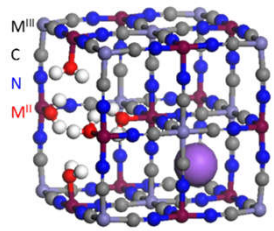




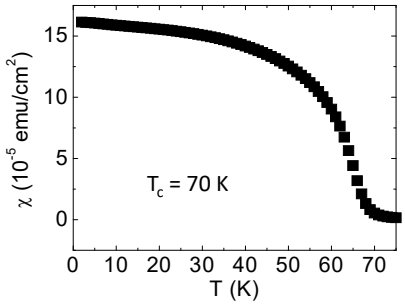
Escax *et al.* *J. Am. Chem. Soc.* **2001,** *123,* 12536
Le Bris *et al. New. J. Chem.* **2009**, *33*, 1255

Prussian Blue Analogues

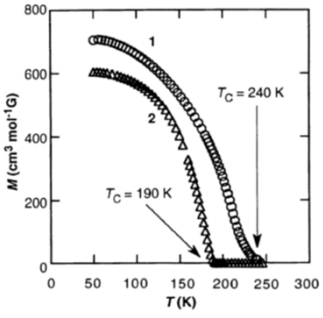
magnet/paramagnet
switchable spin crossover
magnet/paramagnet



$K_{0.2}Ni_{1.4}[Cr(CN)_6]{\cdot}nH_2O$ NiCr-PBA



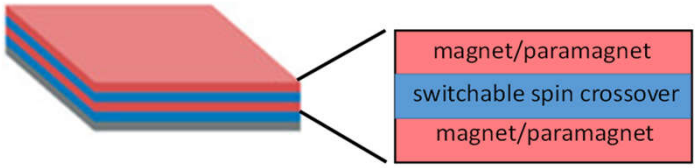
$Cr^{II}_3[Cr^{III}(CN)_6]_2.10H_2O$ CrCr-PBA



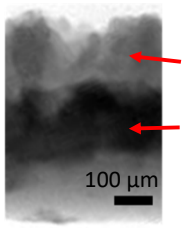
Mallah et al. *Science*, **1993**, *262*, 1554

Original Idea:

Use spin crossover to switch magnetic coupling in thin film heterostuctures

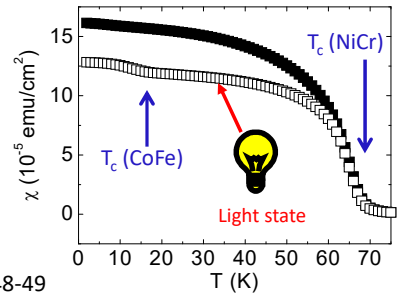


NiCr-PBA ferromagnet
CoFe-PBA SCO
NiCr-PBA ferromagnet



$Rb_{0.8}Ni_4[Cr(CN)_6]_3 \cdot nH_2O$

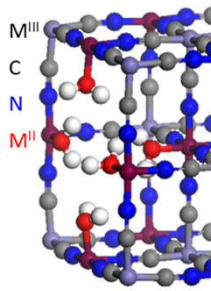
$Rb_{0.7}Co_4[Fe(CN)_6]_3 \cdot nH_2O$



D. M. Pajerowski *et al. J. Am. Chem. Soc.* **2010**, *132*, 4048-49

Prussian Blue Analogues

Nanoparticles and Heterostructures



$A_jM_k^{II}[M'^{III}(CN)_6]_l \cdot nH_2O$

MM'-PBA

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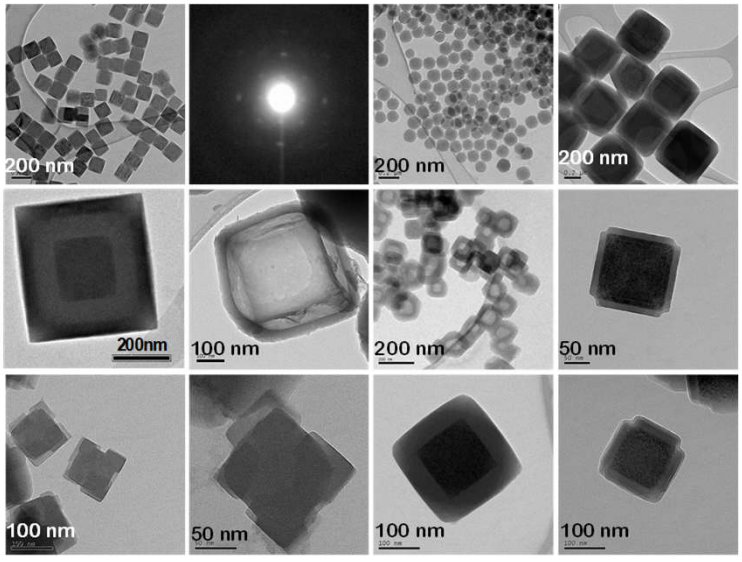
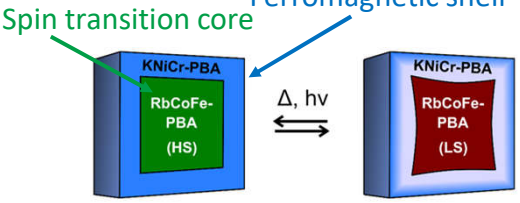
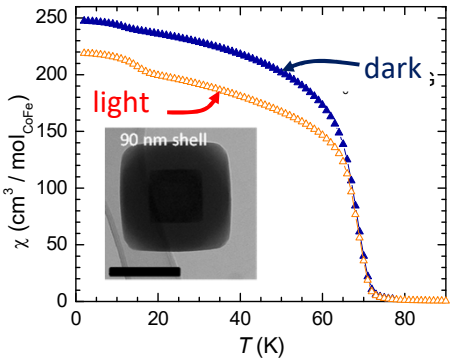


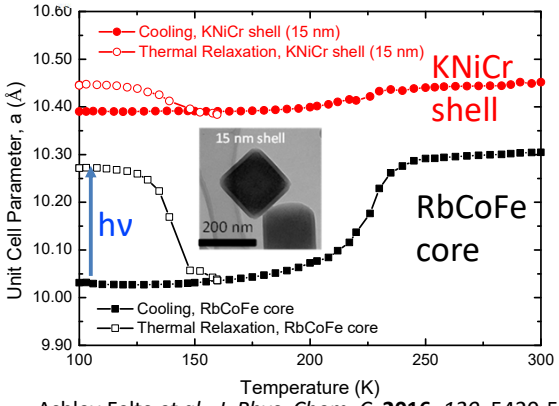
Olivia Risset

Spin Transition Heterostructures

$Rb_{0.7}Co_4[Fe(CN)_6]_{2.9}@Rb_{0.8}Ni_4[Cr(CN)_6]_{2.9}$





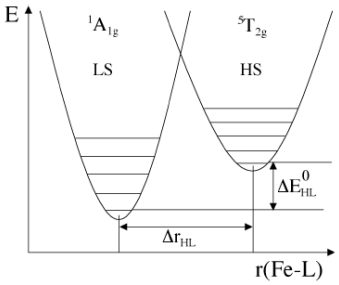


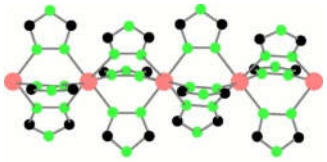
M. Dumont *et al. Inorganic Chemistry* **2011**, *50*, 4295-4300

Ashley Felts *et al. J. Phys. Chem. C* **2016**, *120*, 5420-5429

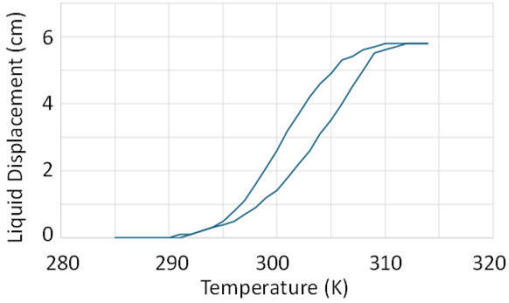
Spin Crossover Materials as Actuators

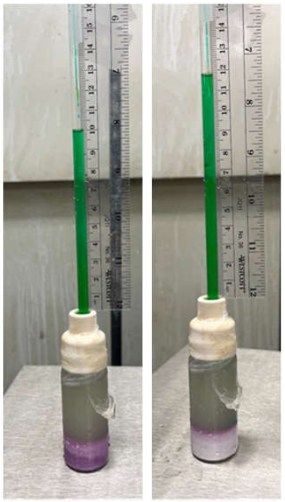
r(Fe–L): 1.95-2.00 Å 2.15-2.20 Å



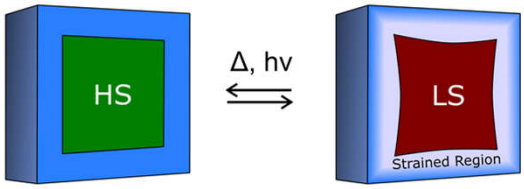


$[Fe(NH_2trz)_3]Br_2$

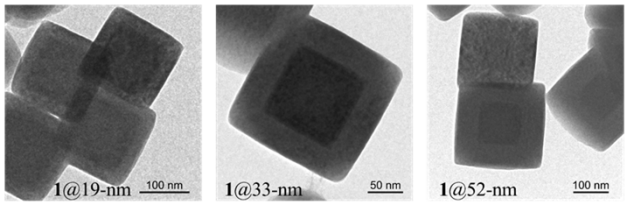


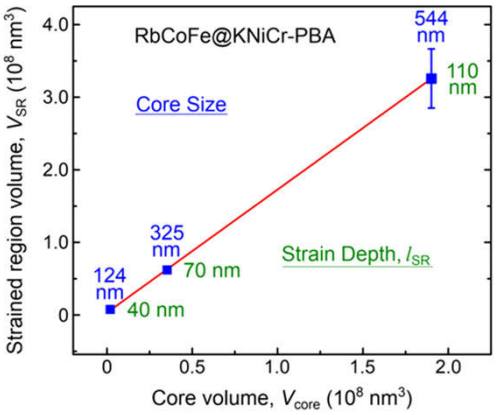


Strain Depth in Shell



What is the strained depth, or strained volume?



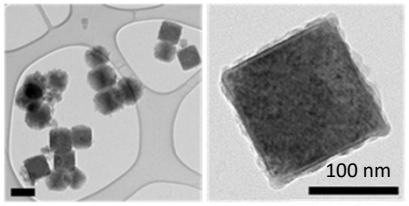


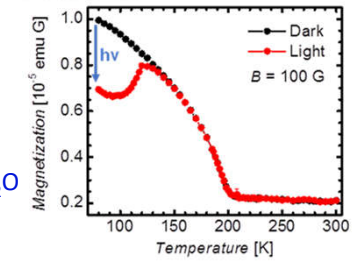
Strain region can exceed 100 nm.

John Cain *et al. Chem. Mater.* **2021**, *33*, 246–255

Spin Transition Heterostructures

$Rb_{0.19}Co[Fe(CN)_6$ light-switchable core
$K_{0.13}Cr[Cr(CN)_6]_{0.71}$ magnetic shell

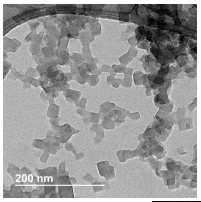




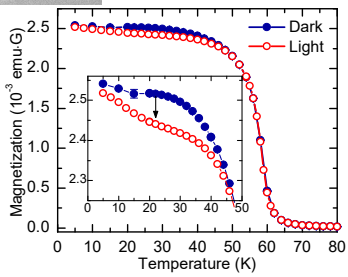
$\{Rb_{0.19}Co[Fe(CN)_6]_{0.73}\}_{0.80}$@
$\{K_{0.13}Cr[Cr(CN)_6]_{0.71}\}_{0.20}\cdot nH_2O$

Olivia Risset et al. *Chem. Mater.* **2015**, 27, 6185-6188

Hofmann-type SCO core with NiCr-PBA

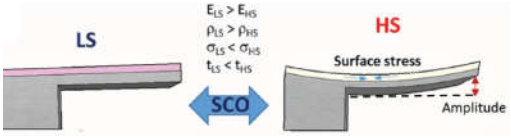


$Fe(phpy)_2[Pt(CN)_4]$@
KNiCr-PBA

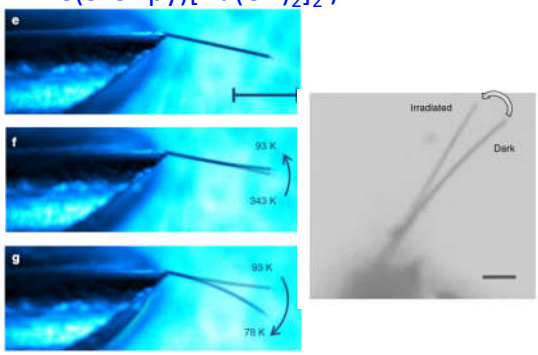


Corey Gros, et al. *J. Am. Chem. Soc.* **2014**, *136*, 9846

SCO as Mechanical Actuators



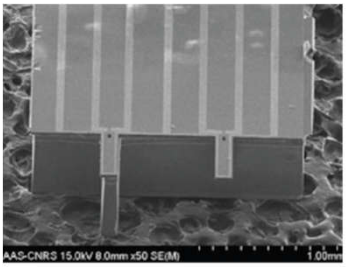
Fe(3-CNpy)[Au(CN)$_2$]$_2$ /Al

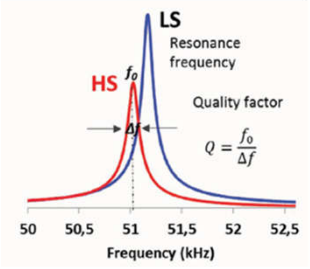


LCC Toulouse

Shepherd *et al. Nat. Comm.* **2013**, 3607

[Fe(HB(tz)$_3$)$_2$]



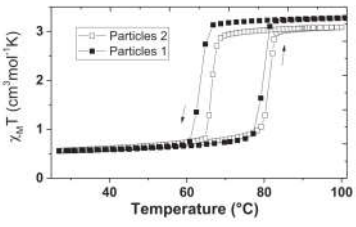


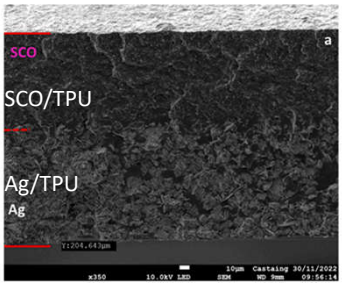
Molnàr *et al. Adv. Mater.* **2018**, *30*, 17003862

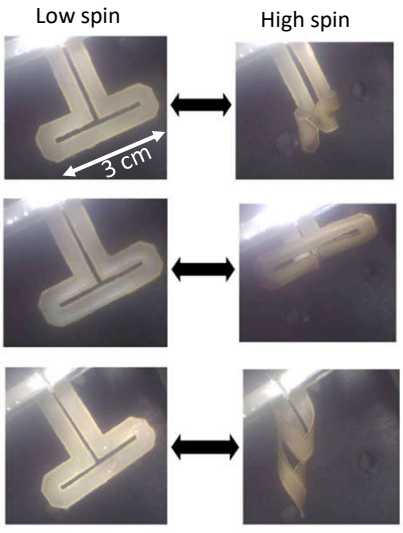
SCO as Mechanical Actuators

Bilayer of thermoplastic polyurethane (TPU) composites

[Fe(Htrz)$_{1.8}$(trz)$_1$(NH$_2$trz)$_{0.2}$](BF$_4$)•0.7H$_2$O







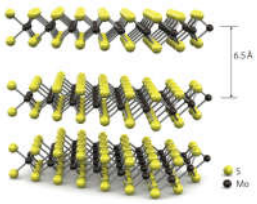
LCC Toulouse

Piedrahita-Bello *et al. Sensors & Actuators: B. Chemical* 393 (**2023**) 134147

Spin Crossover as Phase Change Material
to Actuate Strain in 2D Material

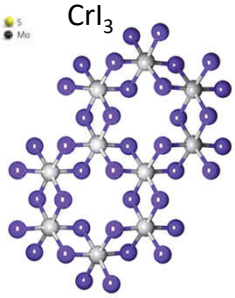
2D Materials

- Semiconductors
- Superconductors
- Magnets
- Topological phases
- Catalysts
- Sliced bread

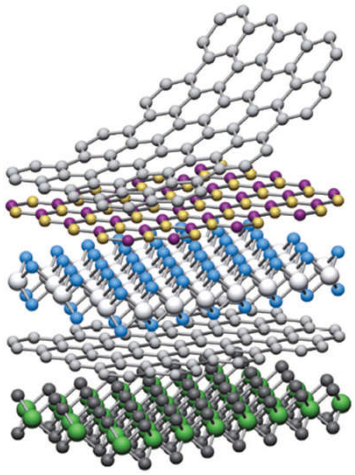


MoS_2

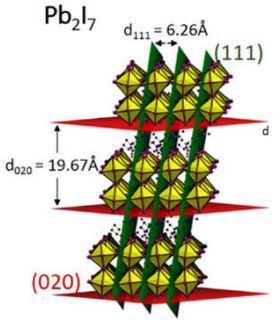
CrI_3



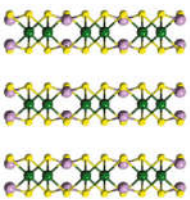
van der Waals heterostructures



Pb_2I_7



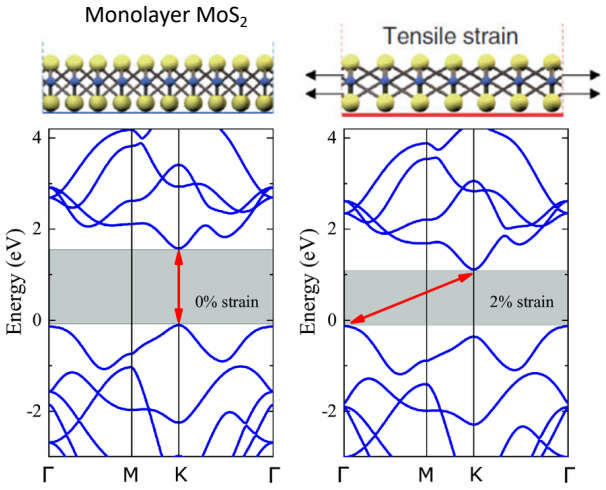
$FePS_3$



Geim and Grigorieva Nature 2013, 499, 419

2D and strain

2D materials can endure very high strain

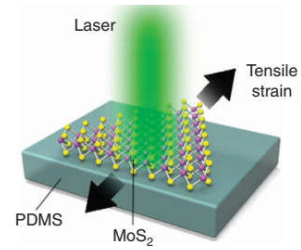


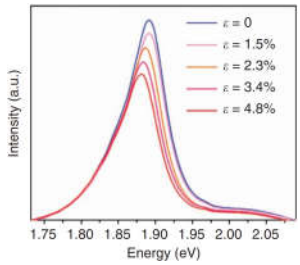
Strain-tunable properties:

- Bandgap
- Band structure
- Magnetic coupling
- Magnetic anisotropy
- Topological phases
- Spin-orbit coupling
- Dielectric properties
- Carrier mobility

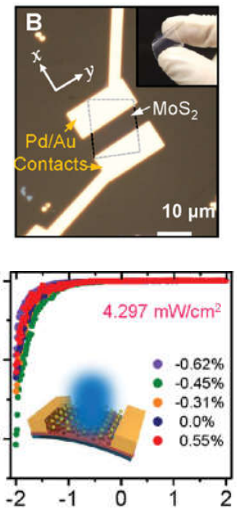
Pető, J. et al. *npj 2D Mater Appl* **2019**, *3* (1).

MoS_2 Nanosheets and Strain

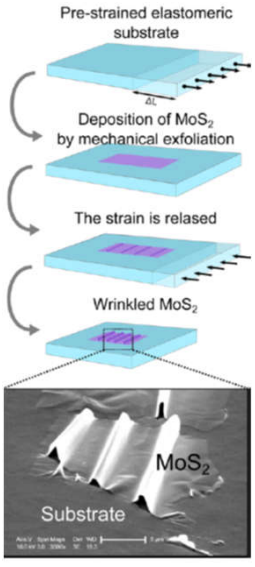




Lee, J.-U. *et. al. Nature Communications*, **2017**, 8:1370
Liu, Z. *et. al. Nature Communications*, **2014**, 5:5246

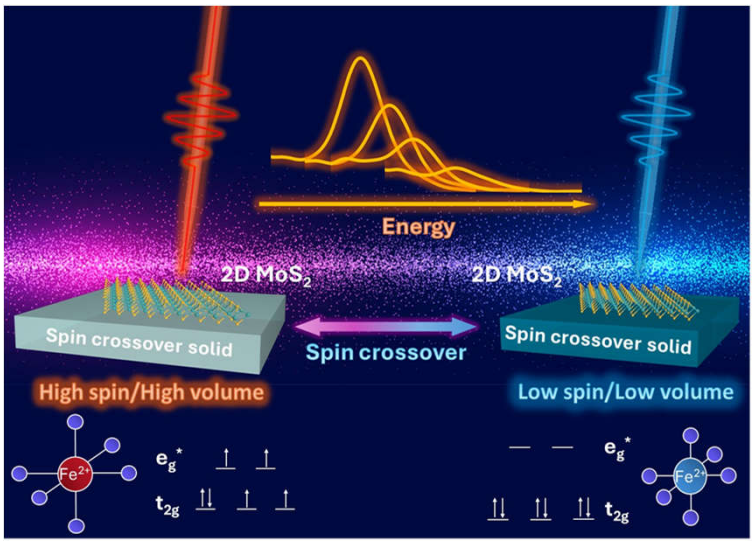


Wu et al. Adv. Mater. **2016**,
DOI: 10.1002/adma.201602854



Castellanos-Gomez, A. et al
Nano. Lett. **2013**, 13, 5361–5366.

Spin Crossover as Phase Change Material to Actuate Strain in 2D Material

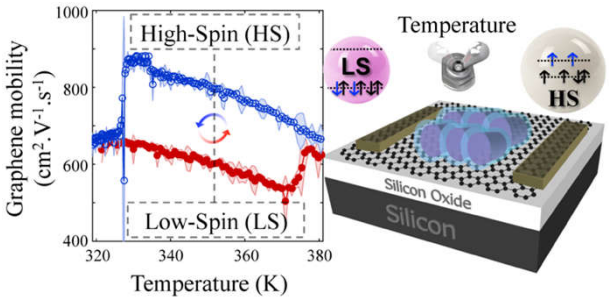


Tao Yuwen

SCO Solids Coupled to 2D Materials

Nanoparticles

$[Fe(Htrz)_2(trz)](BF_4)$/ graphene
Surfactant stabilized nanoparticles

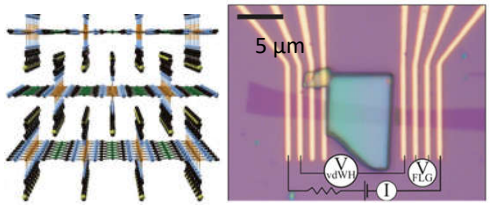


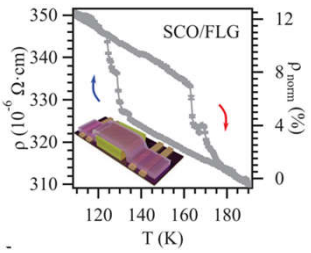
Dugay *et al. Nano Lett.* **2017**, *17*, 186

Konstantinov *et al. J. Mat. Chem. C* **2021**, *9*, 2712

Single Crystals

$\{Fe\text{-}(3\text{-Clpyridine})_2\text{-}[PtII(CN)_4]\}$/graphene





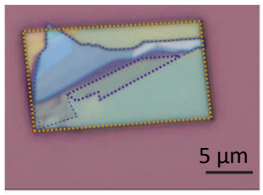
Boix-Constant et al. *Adv. Mater.* **2022**, *34*, 2110027

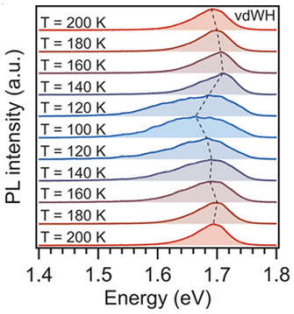
van Geest *et al. Adv. Mater.* **2020**, *32*, 1903573

SCO Solids Coupled to 2D Materials

Metal Dichalcogenides

{Fe-(3-Clpyridine)$_2$-[PtII(CN)$_4$]}/WSe_2

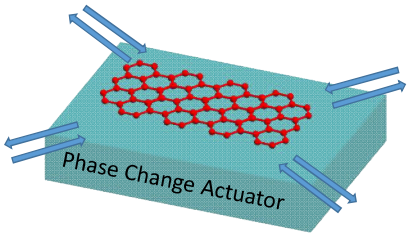


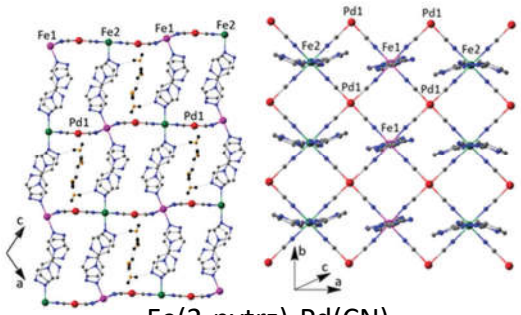


Boix-Constant et al. *Adv. Mater.* **2022**, *34*, 2110027

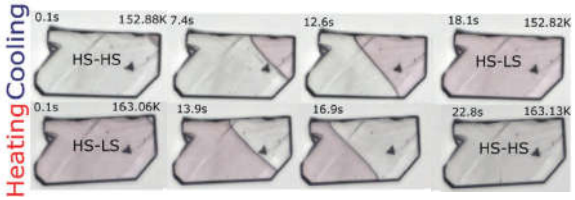
Torres-Cavanillas *et al. Nat. Chem.* **2021**, *13*, 1101

Spin Transition as Phase Change Actuator



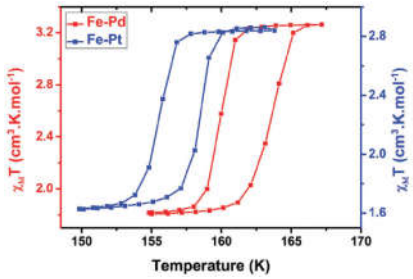


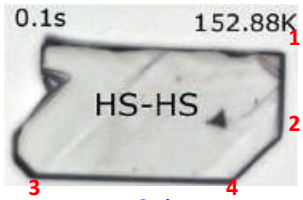
Fe(2-pytrz)$_2$Pd(CN)$_4$



Houcem Fourati *et al. Phys.Chem.Chem.Phys.*, **2018**, *20*, 10142

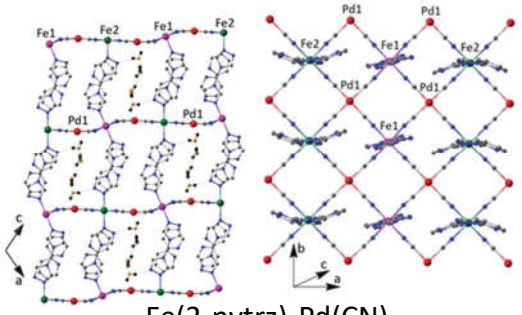
Spin Transition as Phase Change Actuator



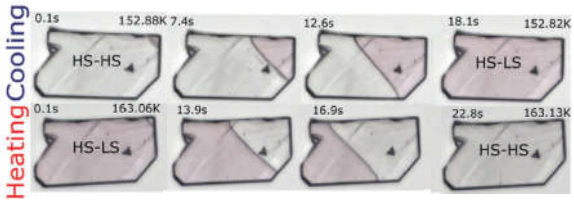


~ 2.2%

~ 1.6%

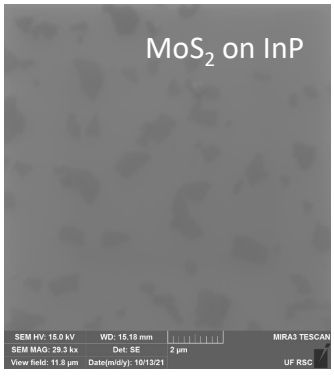


$Fe(2\text{-pytrz})_2Pd(CN)_4$

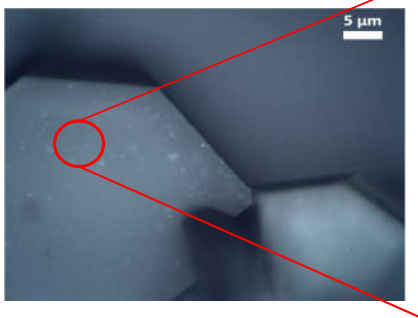


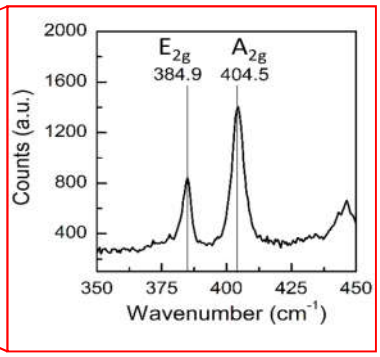
Houcem Fourati *et al. Phys.Chem.Chem.Phys.*, **2018**, *20*, 10142

MoS_2 Electrochemical Exfoliation and Spin Cast



MoS_2 on $Fe(II)(pytrz)Pd(CN)_4$





Raman peak energies indicate monolayer and bilayer nanosheets.

$Fe(2\text{-}pytrz)_2Pd(CN)_4/\ MoS_2$

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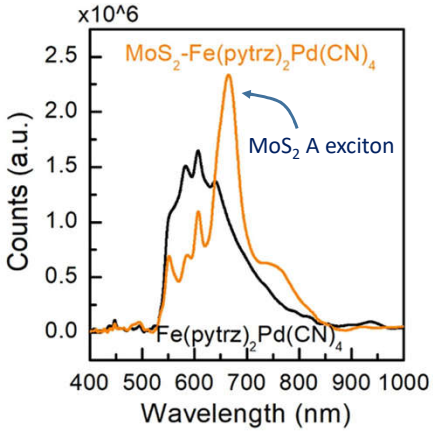
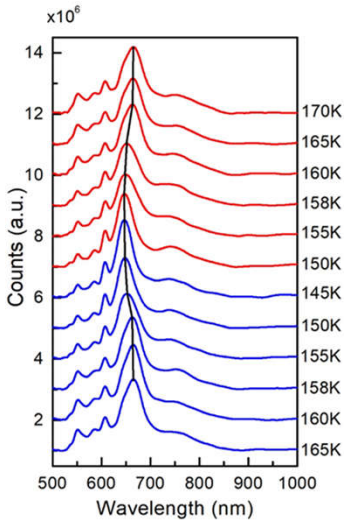
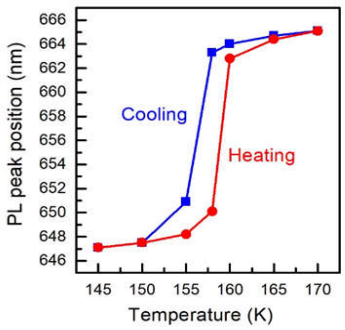
Heterostructure Photoluminescence





MoS_2 A exciton position



T. Yuwen *et al. Chem. Mater.* **2024**, 36, 18, 8714–8724

$Fe(2\text{-}pytrz)_2Pd(CN)_4/\ MoS_2$

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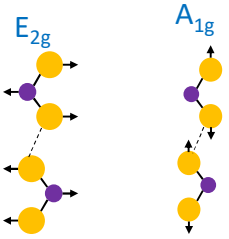
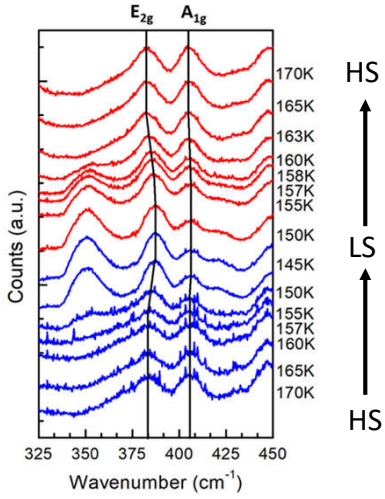
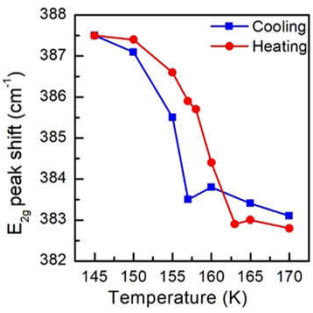
Raman Spectroscopy of Heterostructure





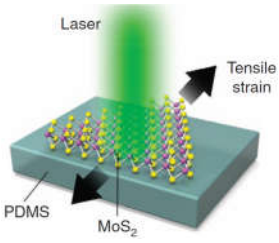
HS
LS
HS

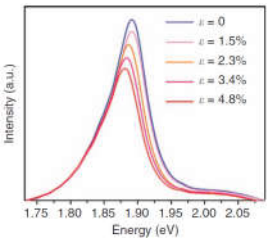
E_{2g} position vs temp.

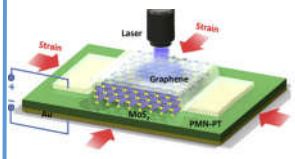


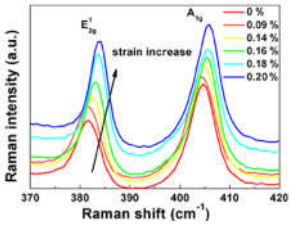
T. Yuwen *et al. Chem. Mater.* **2024**, 36, 18, 8714–8724

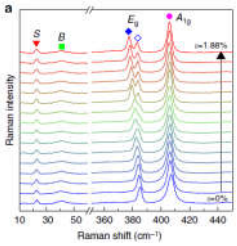
Strain in MoS_2









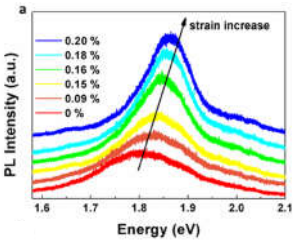


Tensile Strain

Raman E_{2g} and PL shift to lower energy.

Compressive Strain

Raman E_{2g} and PL shift to higher energy.



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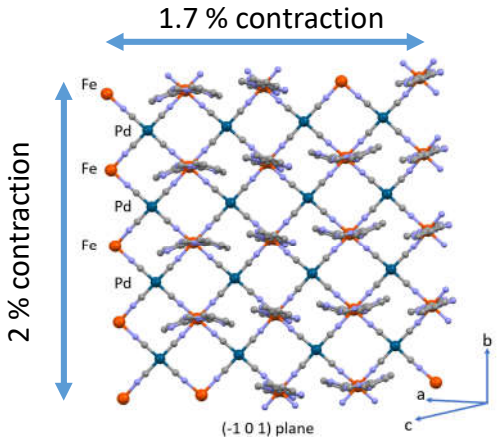
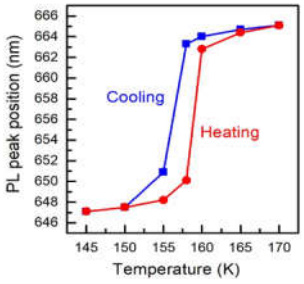
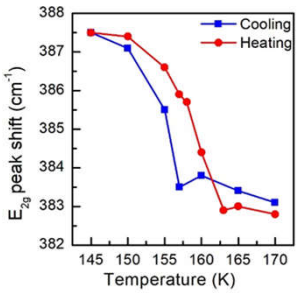
$Fe(2\text{-pytrz})_2Pd(CN)_4$/ MoS_2





MoS_2 Photoluminescence

0.2 % Compressive Strain

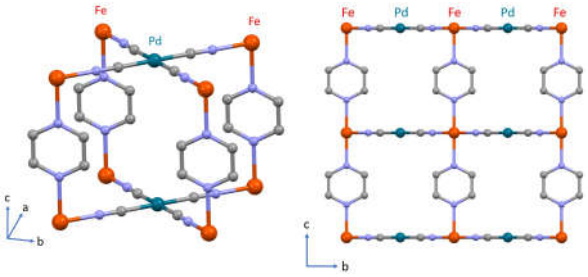


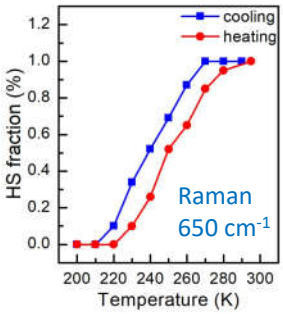
MoS_2 Raman E_{2g}

0.5 % Compressive Strain

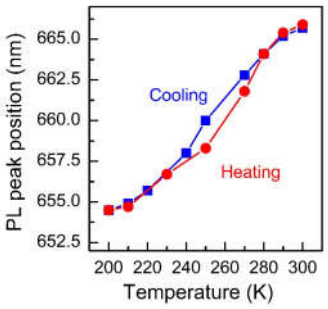
Tao Yuwen *Chem. Mater.* **2024**, 36, 18, 8714–8724

$Fe(pz)_2Pd(CN)_4$/ MoS_2

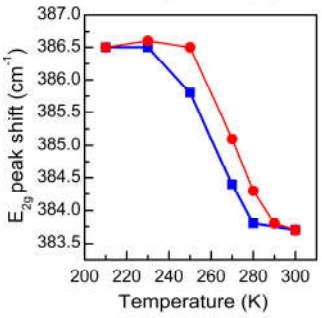




$Fe(pz)_2Pd(CN)_4$



MoS_2 Photoluminescence

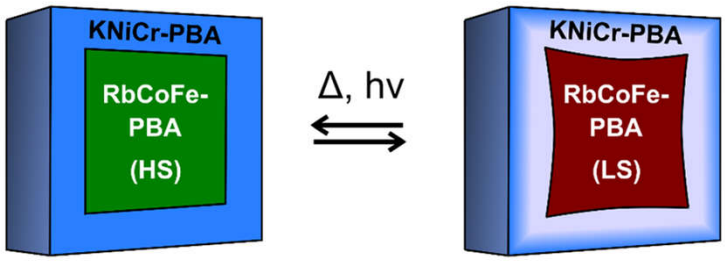


MoS_2 Raman E_{2g}

0.4 % Compressive Strain

T. Yuwen *et al. Chem. Mater.* 2024, 36, 18, 8714–8724

Matrix Effects

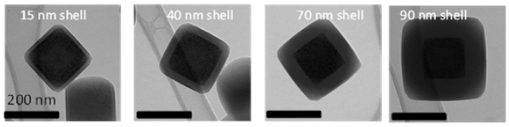


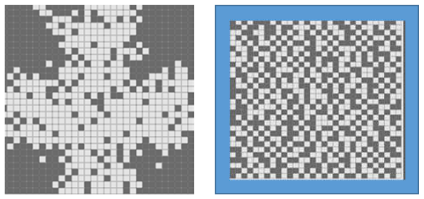
How does the shell alter the spin transition in the core?

Effect of shell on core

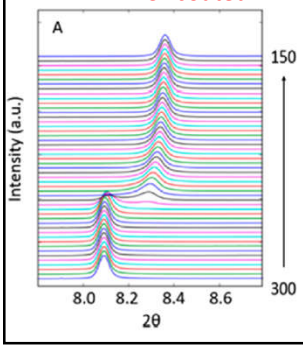
Ashley Felts *J. Am. Chem. Soc.* **2018**, *140*, 5814-5824

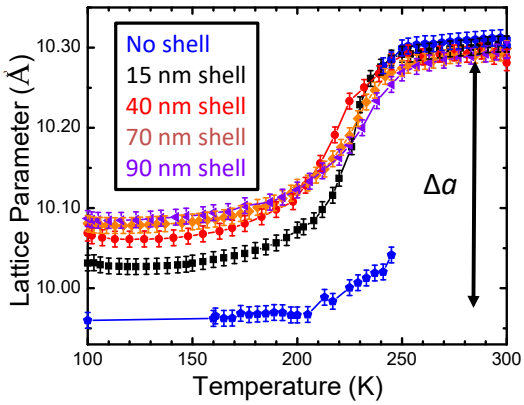
RbCoFe@KNiCr Core: $Rb_{0.2}Co_4[Fe(CN)_6]_{2.9}\bullet nH_2O$





122 nm Uncoated



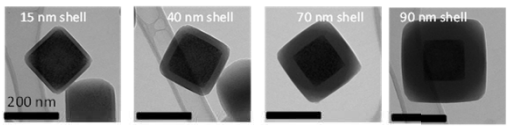


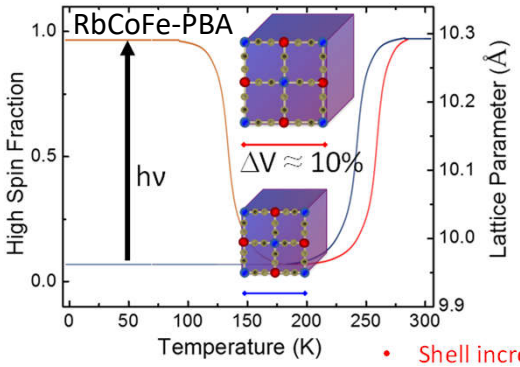
- The shell changes the cooperativity of the core phase transition
- The shell changes Δ*a* of the spin transition core

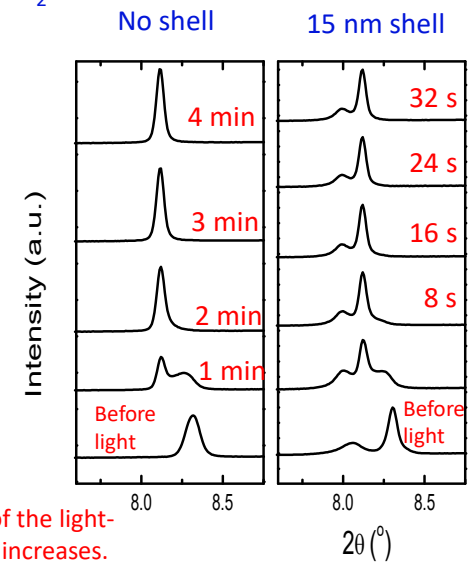
Effect of shell on core

Ashley Felts *J. Am. Chem. Soc.* **2018**, *140*, 5814-5824

RbCoFe@KNiCr Core: $Rb_{0.2}Co_4[Fe(CN)_6]_{2.9}\bullet nH_2O$

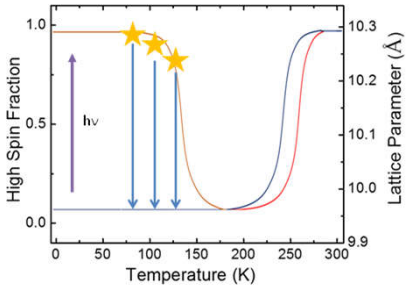


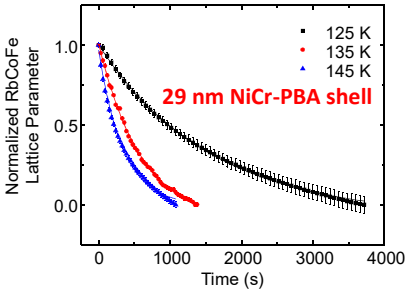




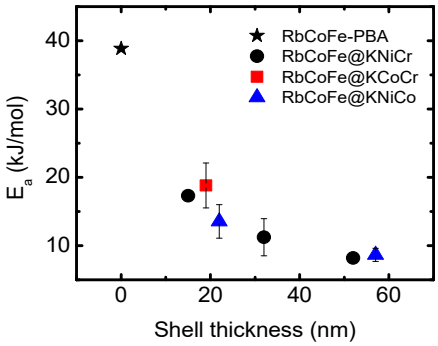
- Shell increases the rate of the light-induced LS-HS transition increases.

Effect of shell on core





Relaxation of light-induced high spin state



- E_a of core HS-LS transition decrease with thicker shells.

Wanhong He *et al. J. Mat. Chem.* **2021**, *9*, 10830
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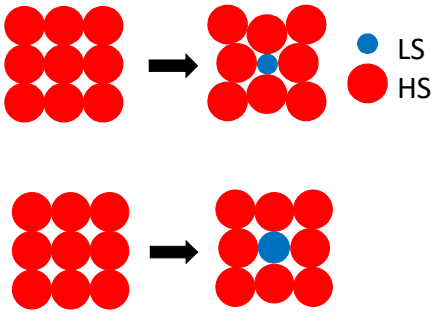
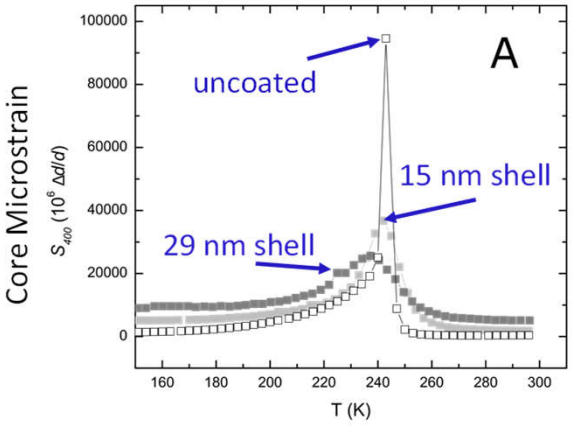
Core Microstrain





- Stiffness of the core increases as shell becomes thicker.
- Reorganization energy is lowered.

Wanhong He *et al. J. Mat. Chem.* **2021**, *9*, 10830
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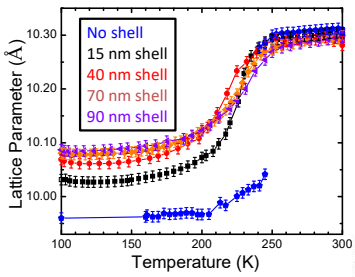
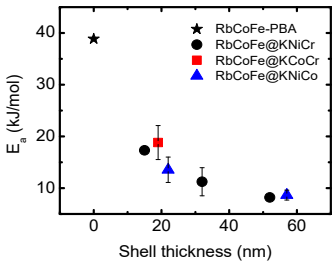
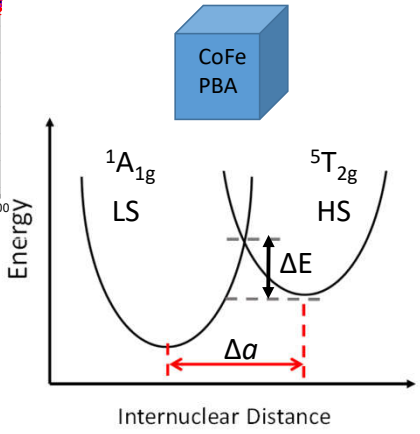
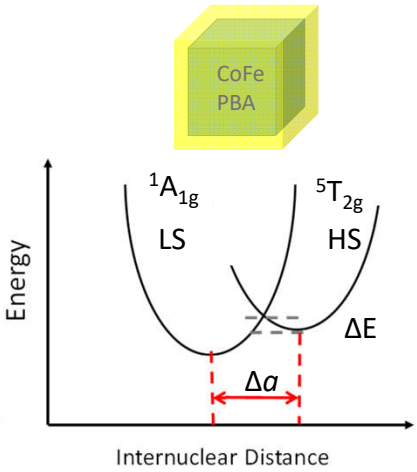
Effect of shell on core









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