Modeling Spin-crossover in condensed phase

From molecules to Metal-Organic Frameworks

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Outline

1. Background on Spin-Crossover

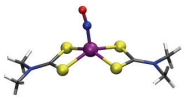
2. DFT applied to the calculation of thermochemical quantities in SCO systems
   - 2.1 Benchmarking
   - 2.2 Mononuclear systems
   - 2.3 Polynuclear systems

3. Ligand-Field Molecular Mechanics: Spin-Crossover MOFs
   - 3.1 LF-MM Methodology
   - 3.2 Application to the $\{Fe(pz)Pt(CN)_2\}$-SCOF

4. Conclusions and Outlook

Spin-Crossover phenomena

421. L .Cambi and L. Szegö: Über die magnetisch Susceptibilität der komplexen Verbindungen.
[Aus d. Instituto di Chimica Industriale d. Universität Mailand.]
[Eingegangen am 18. Juli 1931.]



$[Fe(^iPrNCS_2)_2(NO)]$

Temperature dependent magnetic measurements

Fe^{III} (d^5) → $5.92\mu_B$ / $1.73\mu_B$

L. Orgel (1956) "10th Solvay Conference", Brussels
Proposes and equilibrium between spin-states

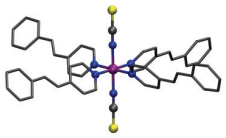
Molecular level manipulation of physical properties with an external stimuli

Molecular level switch

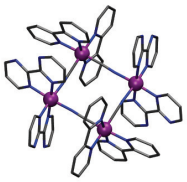
Ber. Dtsch. Chem. Ges. **1931**, *64*, 2591

Spin-Crossover phenomena

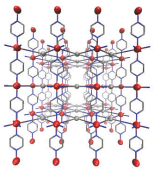
LD-LISC systems



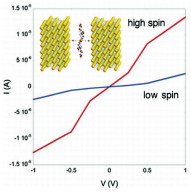
Polynuclear SCO



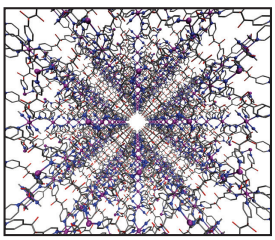
Spin-crossover frameworks (SCOFs)



Coherent quantum transport with SCO



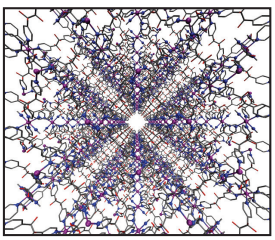
Spin-Crossover phenomena

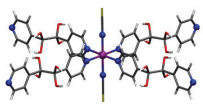


Metal-Organic Frameworks
- -Sensing applications
- -Molecular Level based memories
- -Optical devices

- -Complex systems
- -Thousands of atoms
- -Modeling can be tricky

Spin-Crossover phenomena





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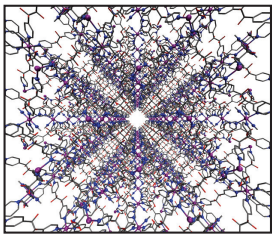

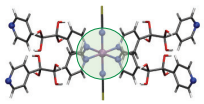

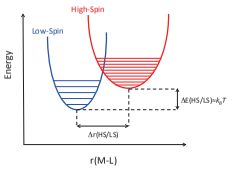

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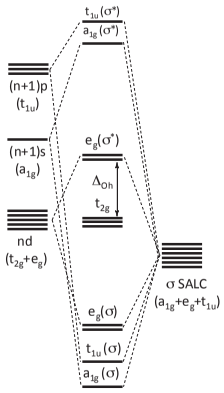
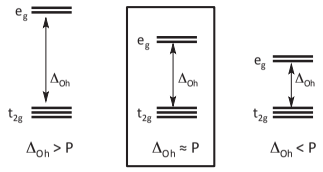
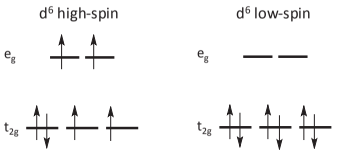
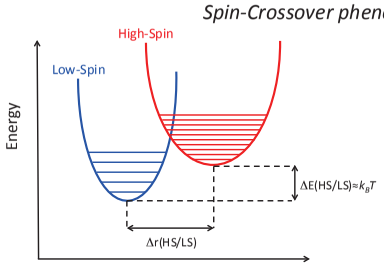
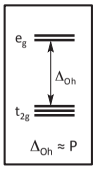






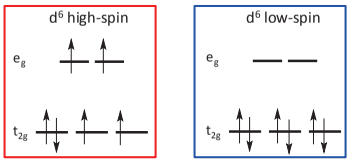
Spin-Crossover phenomena



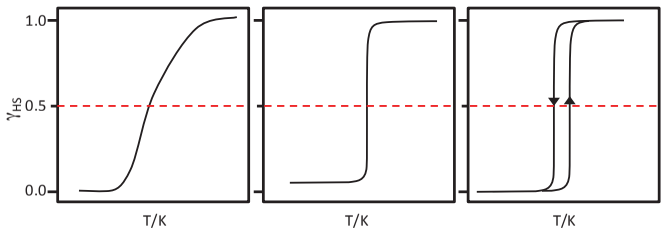


$\Delta G = \Delta H - T\Delta S$

LS ⇄ HS



Spin-Crossover phenomena

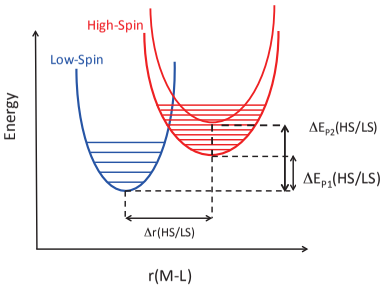


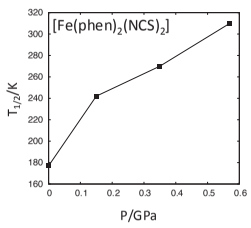
Magnetic susceptibility measurements
Optical spectroscopy and vibrational spectroscopy
Mössbauer spectroscopy
Crystallographic measurements using synchrotron-based techniques

Transition Temperature ($T_{1/2}$)

Spin-Crossover phenomena

Pressure perturbation



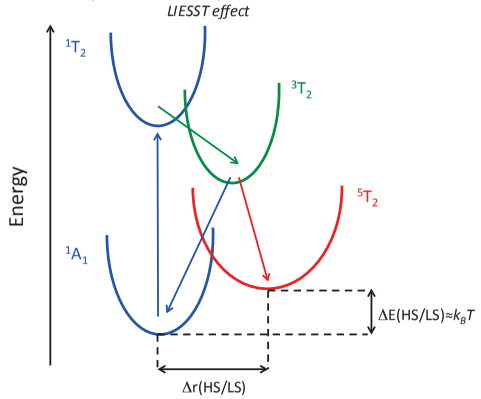


$T_{1/2}$ tuning using external pressure

Gütlich, P.; Goodwin, H. A. - Gütlich, P.; Goodwin, H. A.
Spin Crossover in Transition Metal Compounds I; Springer-Verlag, 2004.

Spin-Crossover phenomena

LIESST effect



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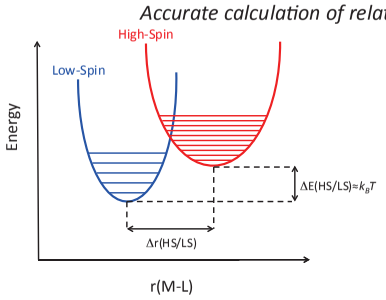
Spin Crossover in Transition Metal Compounds I; Springer-Verlag, 2004.

Accurate calculation of relative energies?



LS ⟶ HS

$$\Delta G = G^{HS} - G^{LS} = \Delta H - T\Delta S$$

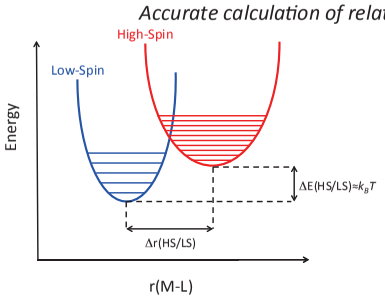
$$G^{S} = H^{S} - TS^{S} = E^{S}_{el} + E^{S}_{vib} - TS^{S}$$

$$\Delta G = \boxed{\Delta E_{el}} + \Delta E_{vib} - T\Delta S$$

$$\Delta E_{el} = E^{HS}_{el} - E^{LS}_{el}$$

Accurate calculation of ΔE_{el} is key in the calculation of thermodynamic quantities in SCO parameters

Accurate calculation of relative energies?



CASPT2/NEVPT2 methods

-system specific
-computationally expensive
-limitations in system size

DFT methods

-more general
-computationally cheap
-can afford large size systems

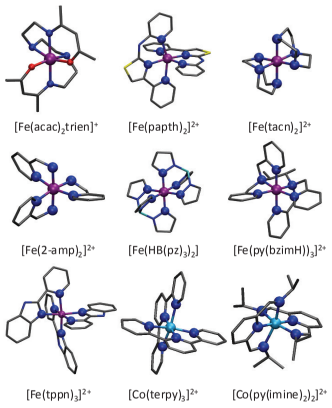
DFT functionals

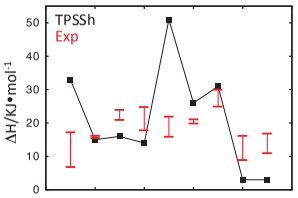
$$E_{XC}^{LSDA}[\rho] = \int \varepsilon_{XC}[\rho]\rho(\vec{r})d^3r \longrightarrow \text{LDA, LSDA, ...}$$

$$E_{XC}^{GGA}[\rho] = \int \varepsilon_{XC}[\rho,\vec{\nabla}\rho]\rho(\vec{r})d^3r \longrightarrow \text{PBE,PW91,BLYP,....}$$

$$E_{XC}^{meta-GGA}[\rho] = \int \varepsilon_{XC}[\rho,\vec{\nabla}\rho,\vec{\nabla}^2\rho]\rho(\vec{r})d^3r \longrightarrow \text{M06L,TPSS,...}$$

Development of an accurate DFT model for Spin-Crossover systems





Functional	MAE	LAE
BP86	50	86
B3LYP	40	52
TPSSh	11	32
TPSS	51	88
M06L	25	33
M06	101	137

Jensen, K. and Cirera, J., J. Phys. Chem. A **2009,** *113,* 10033

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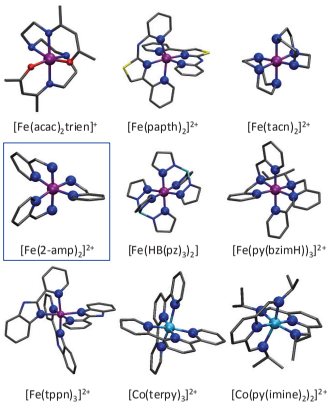

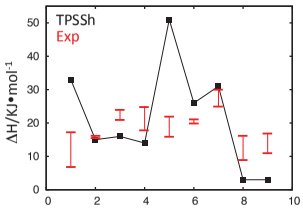

	Crystal	TPSSh	BP86	B3LYP
Fe-N_1	2.024	2.034	2.032	2.071
Fe-N_2	1.991	1.990	1.982	1.982
Fe-N_3	2.020	2.035	2.036	2.073
Fe-N_4	2.004	1.994	1.986	2.058
Fe-N_5	2.034	2.027	2.022	2.067
Fe-N_6	1.998	1.989	1.984	2.047
MAE		0.009	0.013	0.041

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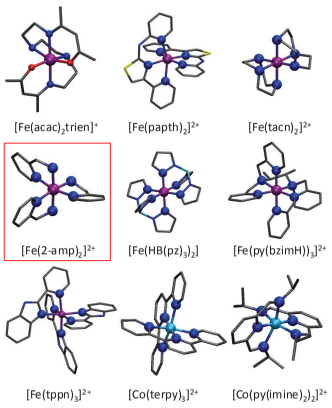
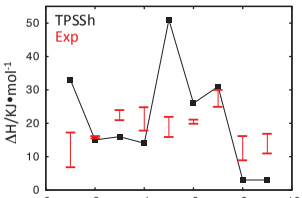
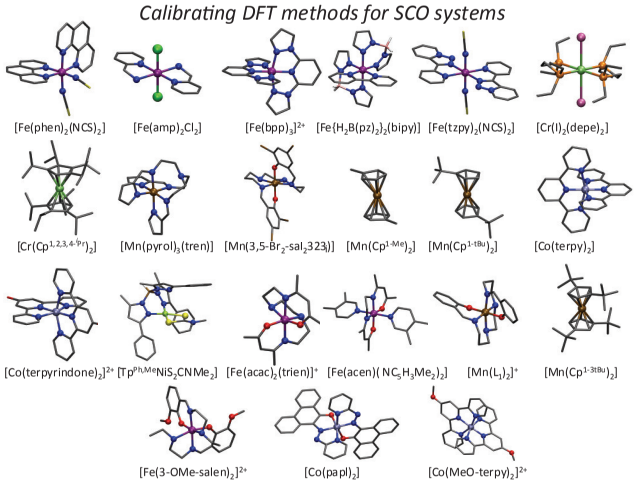




	Crystal	TPSSh	BP86	B3LYP
Fe-N_1	2.179	2.252	2.254	2.266
Fe-N_2	2.195	2.207	2.202	2.250
Fe-N_3	2.180	2.253	2.251	2.269
Fe-N_4	2.220	2.218	2.221	2.251
Fe-N_5	2.183	2.229	2.234	2.250
Fe-N_6	2.213	2.208	2.203	2.246
MAE		0.035	0.036	0.060

Jensen, K. and Cirera, J., J. Phys. Chem. A **2009,** *113,* 10033

Calibrating DFT methods for SCO systems



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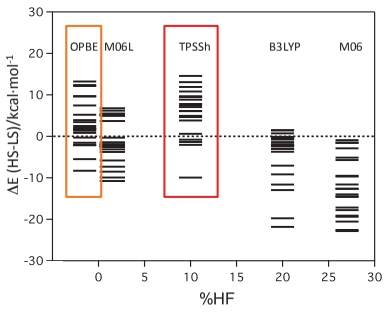


LS ⇄ HS

$$\Delta G = G^{HS} - G^{LS} = \Delta H - T\Delta S$$

$$G^S = H^S - TS^S = E^S_{el} + E^S_{vib} - TS^S$$

$$\Delta G = \Delta E_{el} + \Delta E_{vib} - T\Delta S$$

$$\Delta E_{el} = E^{HS}_{el} - E^{LS}_{el}$$

TPSSh/triple-ζ +polarization

Mean Average Error

	QZVP	TZVP
K	485	293
kcal/mol	0.96	0.58
cm^{-1}	337	204

Development of an accurate DFT model for Spin-Crossover systems

$$\Delta G = \Delta H - T\Delta S \quad \text{LS} \rightleftarrows \text{HS}$$

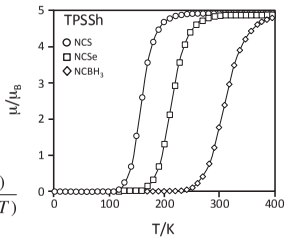
$$\Delta G(T) = G^{HS}(T) - G^{LS}(T)$$

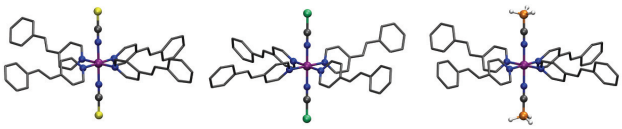
$$G^S = H^S - TS^S = E^S_{el} + E^S_{vib} - TS^S$$

$$G^S(T, v_i^S) = E^S + k_B T \sum_i \ln(1 - e^{-(h\nu_i/k_B T)})$$

$$\Delta G(T) = G^{HS}(T, v_i^{HS}) - G^{LS}(T, v_i^{LS})$$

$$\Delta G(T) = -RT \ln \frac{\gamma_{HS}(T)}{\gamma_{LS}(T)} = -RT \ln \frac{\gamma_{HS}(T)}{1 - \gamma_{HS}(T)}$$



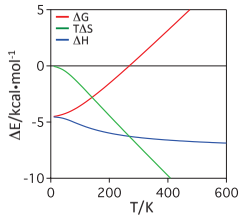


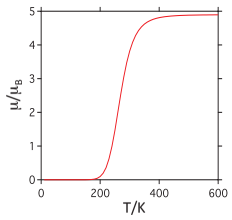
[Fe(stpy)$_4$(NCS)$_2$] [Fe(stpy)$_4$(NCSe)$_2$] [Fe(stpy)$_4$(NCBH$_3$)$_2$]

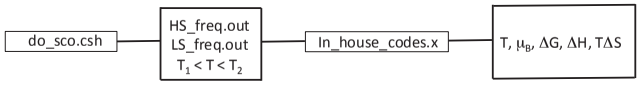
Cirera, J. and Paesani, F. , Inorg. Chem. **2012**, 51, 8194

Development of an accurate DFT model for Spin-Crossover systems

Modeling thermochemistry as a function of T







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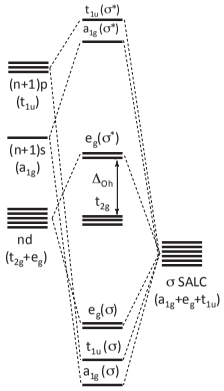

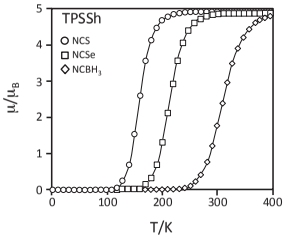

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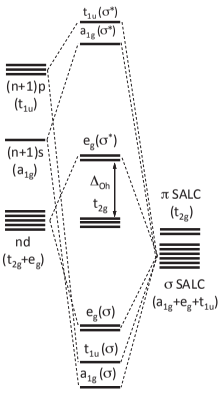

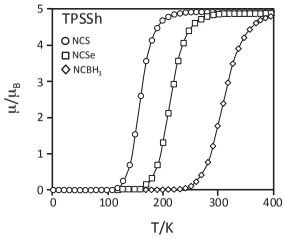

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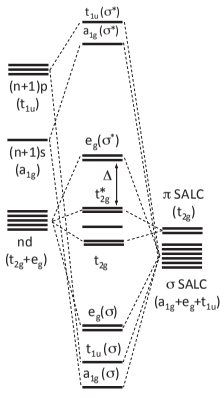
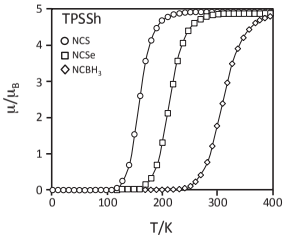
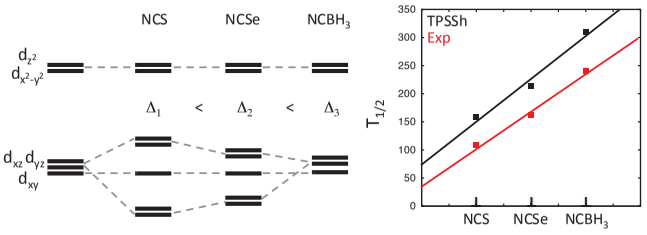
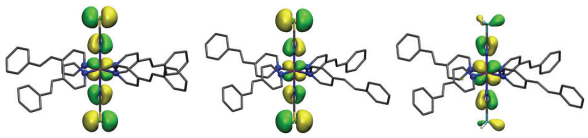




Cirera, J. and Paesani, F. , Inorg. Chem. **2012**, 51, 8194

Development of an accurate DFT model for Spin-Crossover systems

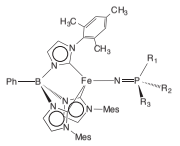




[Fe(stpy)$_4$(NCS)$_2$] [Fe(stpy)$_4$(NCSe)$_2$] [Fe(stpy)$_4$(NCBH$_3$)$_2$]

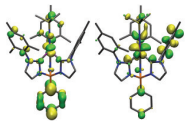
Cirera, J. and Paesani, F. , Inorg. Chem. **2012**, 51, 8194

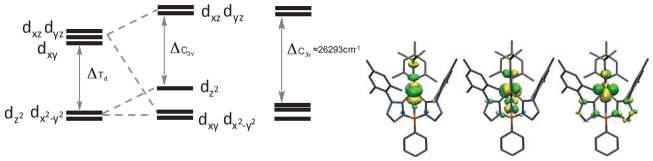
Steric control of $T_{1/2}$ in four coordinated Fe(II) SCO Systems



[PhB(MesIm)$_3$Fe-N=PR$_1$R$_2$R$_3$]

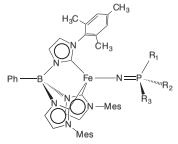
R_1	R_2	R_3	$T_{1/2}$/K
Me	Me	Me	340
Me	Me	Ph	271
^{n}Pr	^{n}Pr	^{n}Pr	214
Me	Ph	Ph	174
Ph	Ph	Ph	81





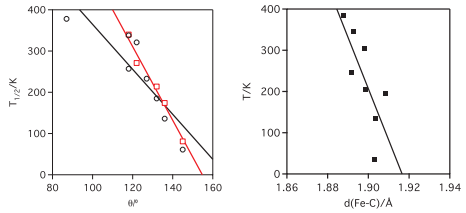
Cirera, J. and Ruiz, E. ,Inorg. Chem. **2016**, 55, 1657

Steric control of $T_{1/2}$ in four coordinated Fe(II) SCO Systems



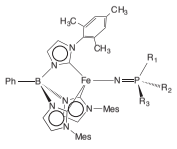
[PhB(MesIm)$_3$Fe-N=PR$_1$R$_2$R$_3$]

R_1	R_2	R_3	$T_{1/2}$/K	θ/°
Ph	Ph	Ph	81 / 61	145
^{n}Pr	^{n}Pr	^{n}Pr	214 / 185	132
Et	Et	Me	- / 233	127
Me	Ph	Ph	136 / 137	136
Me	Me	^{n}Pr	- / 257	118
Me	Me	Ph	271 / 321	122
Me	Me	Me	340 / 338	118
H	H	H	- / 378	87

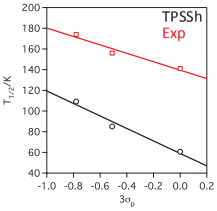


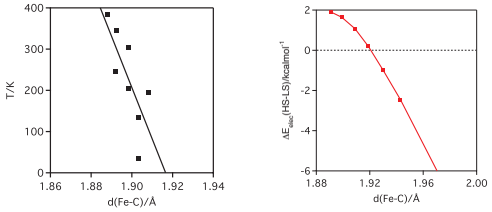
Cirera, J. and Ruiz, E. ,Inorg. Chem. **2016**, 55, 1657

Steric control of $T_{1/2}$ in four coordinated Fe(II) SCO Systems



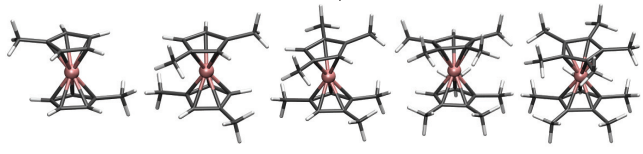
[PhB(MesIm)$_3$Fe-NP(p-X-C$_6$H$_4$)$_3$] (X= H, Me, OMe)



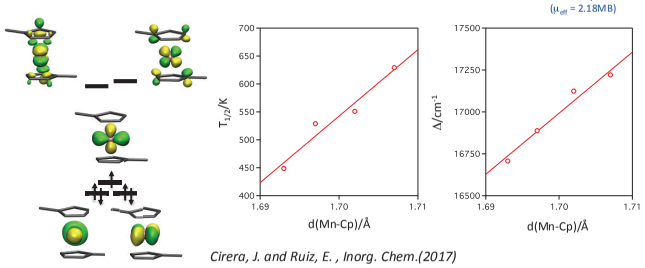


Cirera, J. and Ruiz, E. ,Inorg. Chem. **2016**, 55, 1657

Steric and electronic control of $T_{1/2}$ in [(Cp^R)$_2$Mn] SCO systems

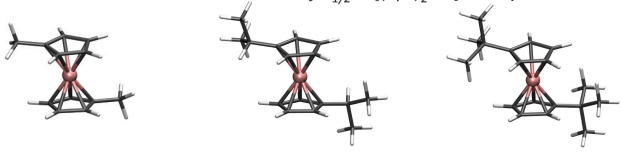


[(Cp$^{1,3\text{-Me}}$)$_2$Mn] SCO ($T_{1/2}$ = 303K) | [(Cp$^{1,3\text{-Me}}$)$_2$Mn] | [(Cp$^{1,3,4\text{-Me}}$)$_2$Mn] | [(Cp$^{1,2,3,4\text{-Me}}$)$_2$Mn] | [(Cp*)$_2$Mn] Low-spin (μ_{eff} = 2.18MB)

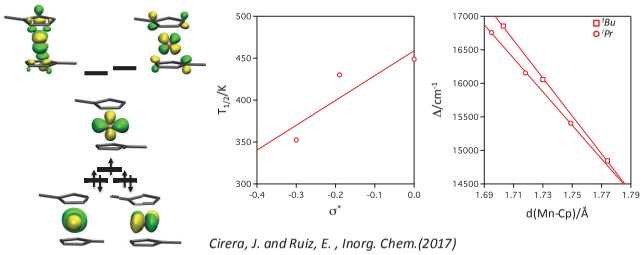


Cirera, J. and Ruiz, E. , Inorg. Chem.(2017)

Steric and electronic control of $T_{1/2}$ in [(Cp^R)$_2$Mn] SCO systems



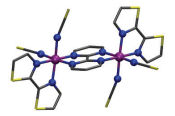
[(Cp$^{1\text{-Me}}$)$_2$Mn] SCO ($T_{1/2}$ = 303K) | [(Cp$^{1\text{-iPr}}$)$_2$Mn] SCO ($T_{1/2}$ = ??) | [(Cp$^{1\text{-tBu}}$)$_2$Mn] SCO ($T_{1/2}$ = 194K)



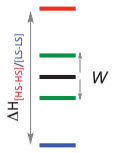
Cirera, J. and Ruiz, E. , Inorg. Chem.(2017)

Two-step spin-crossover transitions in Fe(II) dinuclear systems

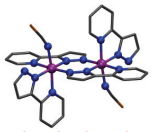
[Fe(bt)(NCS)$_2$]$_2$(μ-bpym)



[LS-LS]⇌[HS-LS]⇌[HS-HS]

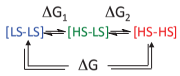


[Fe(pypzH)(NCSe)]$_2$(μ-pypz)



[LS-LS]⇌[HS-HS]

System	ΔH/kcal•mol^{-1}	W/kcal•mol^{-1}	ρ
[Fe(bt)(NCS)$_2$]$_2$(μ-bpym)	4.760	-1.141	-0.240
[Fe(pypzH)(NCSe)]$_2$(μ-pypz)	15.966	+0.488	+0.031



Cirera, J. and Ruiz, E. , J. Mater. Chem. C, 2015 (3), 7954

Two-step spin-crossover transitions in Fe(II) dinuclear systems

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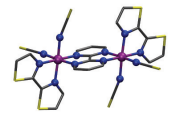
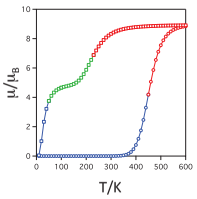
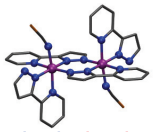


[LS-LS]⇌[HS-LS]⇌[HS-HS]

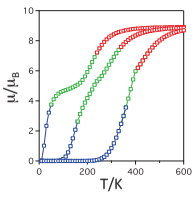


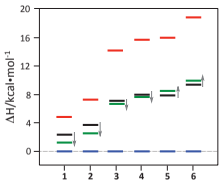
[Fe(pypzH)(NCSe)]$_2$(μ-pypz)



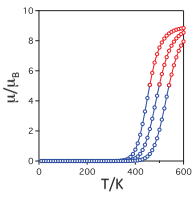
[LS-LS]⇌[HS-HS]

[Fe(bt)(NCX)$_2$]$_2$(μ-bpym)





[Fe(pypzH)(NCX)]$_2$(μ-pypz)



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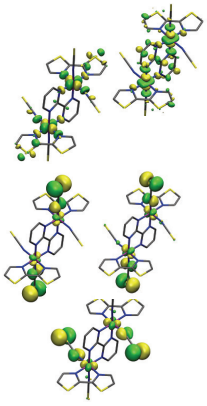
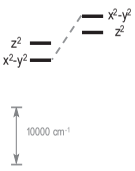
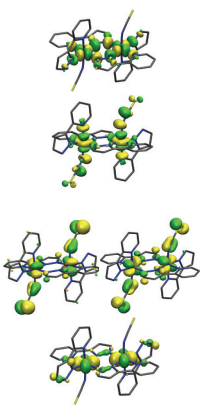




[Fe(pypzH)(NCS)]$_2$(μ-pypz)



Cirera, J. and Ruiz, E. , J. Mater. Chem. C, 2015 (3), 7954

Summary of SCO modelling in molecular systems

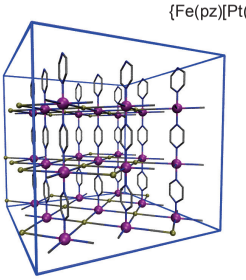
- The TPSSh functional allows for quantitaive calculation of $T_{1/2}$ in SCO molecular systems
- Correct modeling of the ligand field tuning effect over the $T_{1/2}$
- Structural effects on the transition temperature
- The reported methodology allows for the computer assisted design of new SCO systems with tailored properties

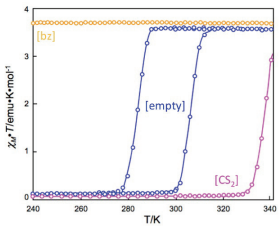
Electronic structure is a great starting point……
….but may not be enough

Spin crossover frameworks

MOF with open shell metal center can display thermally induced spin-crossover

{Fe(pz)[Pt(CN)$_4$]}



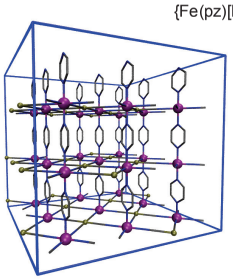


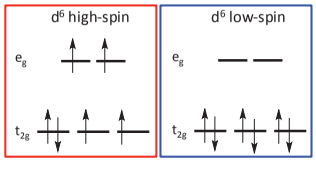
Memory Storage Devices
Chemical Sensing of Molecules
External control of physical properties

Angew. Chem. Int. Ed., 2009 (48), 4767

Modeling the transition temperature Spin-Crossover Frameworks
Ab initio based Ligand-Field Force Fields (LF-FF)

{Fe(pz)[Pt(CN)$_4$]}





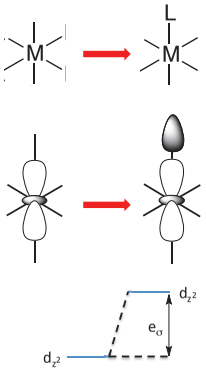
MM Energy Strain $E_{TOT} = \sum E_{str} + \sum E_{bend} + \sum E_{tor} + \sum E_{NB}$

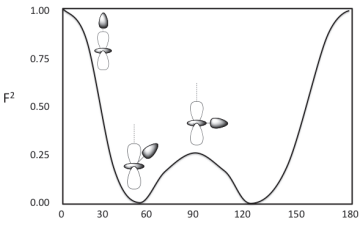
LFMM Energy Strain $E_{TOT} = \sum E_{str} + \sum E_{bend} + \sum E_{tor} + \sum E_{NB} + LFSE$

Coord. Chem. Rev., 2001 (212), 11
Coord. Chem. Rev., 2009 (253), 795

Spin crossover frameworks

Angular Overlap Model: Parameterization of the metal-ligand bond interactions





$$V_{ab}^{LF} = \sum_{\lambda} F_{\lambda,a} e_i^{\lambda}(r) F_{\lambda,b}^{*}$$

$$e_\lambda = a_0 + \sum_{k=1} a_k r^{-k}$$

Metal-Ligand interaction parameterized as function of the bond length and overlap

R. J. Deeth, Coord. Chem. Rev. 253, 2009, 795

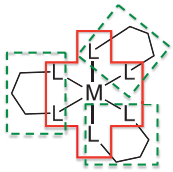
Ligand Field Molecular Mechanics (LFMM)

Inclusion of electronic effects into the MM simulation

$$E_{TOT} = \sum E_{str} + \sum E_{bend} + \sum E_{tor} + \sum E_{NB} + LFSE$$

Ligand Field Stabilization Energy (LFSE): Energy term dependent on the electronic configuration of the metal center

Coordination region is treated using the Angular Overlap Model (AOM) for the metal-ligand bond interaction (plus the usual stretching and L-L repulsion)



$e(\lambda) = e(r)$ Ligand bond interaction parameterized Experimental data/*ab initio* data

$$V^{LF} = \sum_{\lambda} F_\lambda E_\lambda F_\lambda^t$$

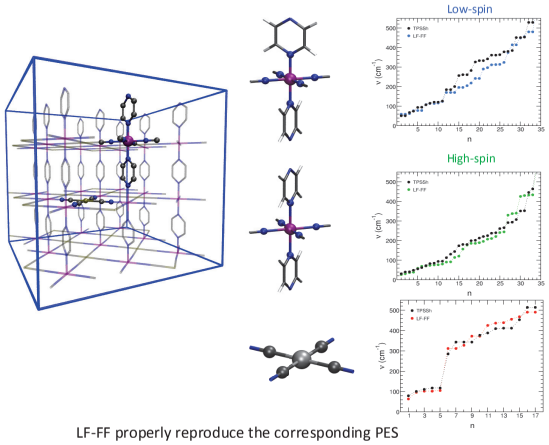
$$V^{LF} = V_\sigma^{LF} + V_{\pi x}^{LF} + V_{\pi y}^{LF} - V_{ds}^{LF}$$

$$W = QV^{LF}Q^T$$

➡ We can keep track of the d-orbital splitting along the MM simulation

Modeling the transition temperature Spin-Crossover Frameworks

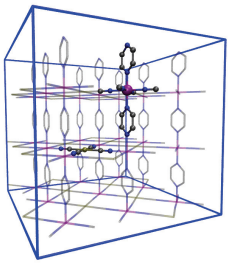
Ligand-Field Force Field validation: *ab initio* vs. LF-FF harmonic frequencies

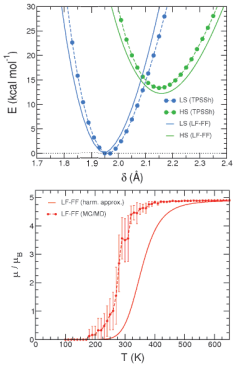


LF-FF properly reproduce the corresponding PES

Modeling the transition temperature Spin-Crossover Frameworks

Modeling SCO in the SBU: Harmonic frequencies and hybrid MC/MD simulations



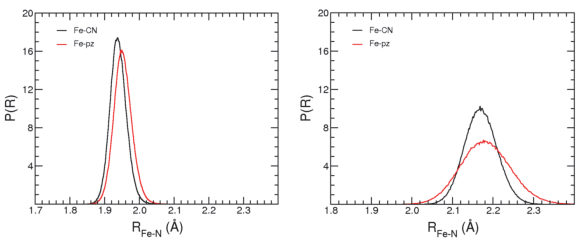


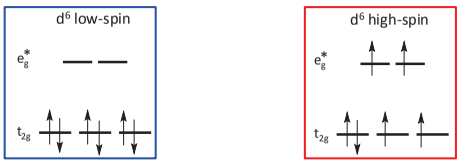
Hybrid Monte Carlo/ Molecular Dynamic simulations fully explore the potential landscape, thus including anharmonicity effects into the calculation of the $T_{1/2}$

Inorg. Chem., 2014 (53), 11020

Force Field validation for $[Fe(pz)_2Pt(CN)_4]$-MOF

a) b)





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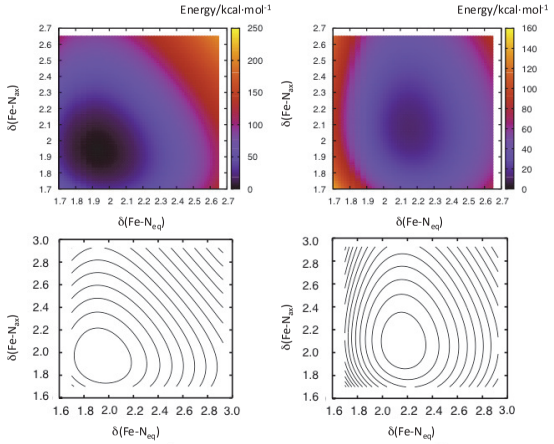
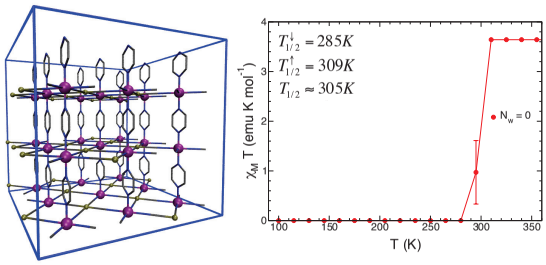


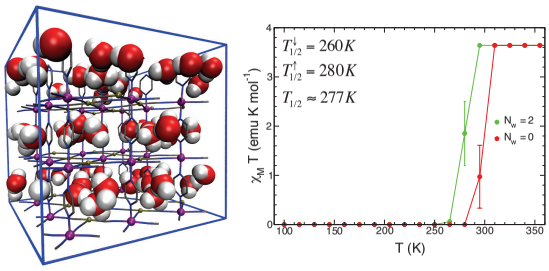
Modeling the transition temperature Spin-Crossover Frameworks
Ligand Field Molecular Mechanics: Hybrid MC / MD trajectories



Excellent agreement with available experimental data

Angew. Chem. Int. Ed., 2009 (48), 4767
Inorg. Chem., 2014 (53), 11020

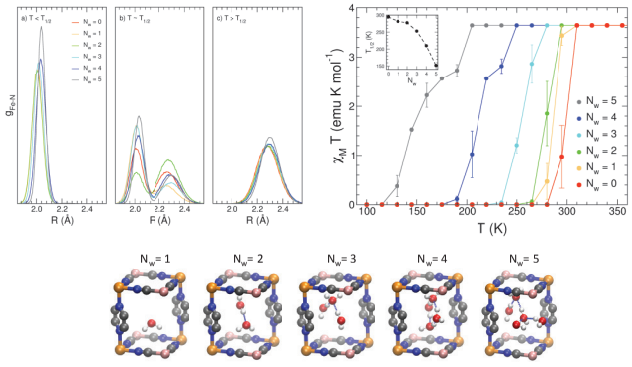
Modeling the transition temperature Spin-Crossover Frameworks
Ligand Field Molecular Mechanics: Hybrid MC / MD trajectories



Excellent agreement with available experimental data

Chem. - Eur. J., 2015 (21), 3664
J. Am. Chem. Soc., 2016 (138) , 6123

Modeling the transition temperature Spin-Crossover Frameworks
Water loading effect over the transition temperature



J. Am. Chem. Soc., 2016 (138) , 6123

Summary

- The newly implemented methodology allows for correct modeling of the Spin-Crossover behavior on the {Fe(pz)[Pt(CN)$_4$]} -MOF.
- Ligand Field Force Fields parameterized with the TPSSh functional correctly describe the relative energies between the alternative spin-states.
- Effect of water loading over the experimental shift on the $T_{1/2}$ can be rationalized on the basis of the pore expansion at higher loadings.
- Quantitative analysis of the water loading over the $T_{1/2}$ shift.
- *In silico* design of new SCOFs with tailored properties can be done within the LF-MM scheme

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Modeling Spin-crossover in condensed phase

From molecules to Metal-Organic Frameworks