Computational Study Of Spin-Crossover Systems Embedded In Carbon Nanohoops

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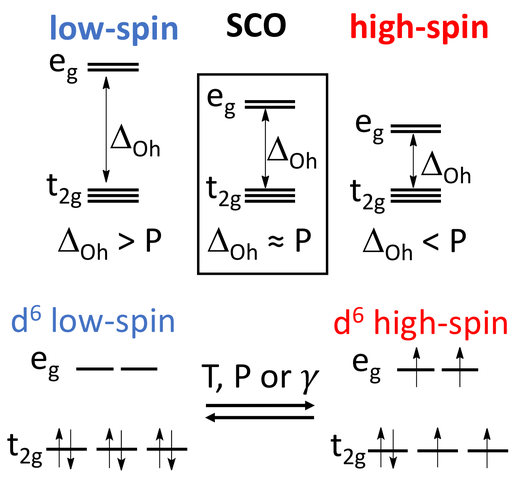
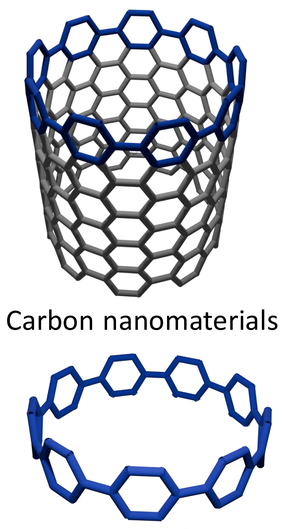
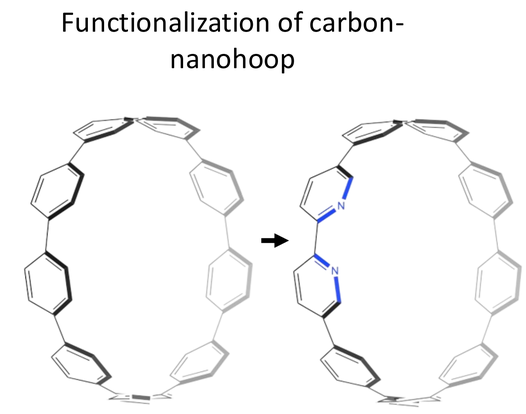
INTRODUCTION

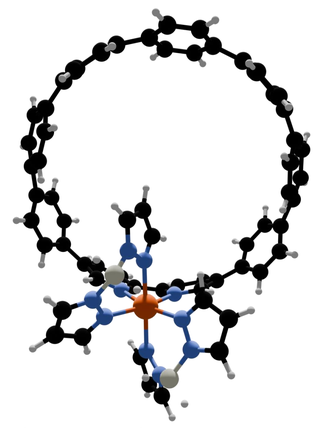
Spin-Crossover (SCO) systems are transition metal complexes which have two electronic states close in energy and can be alternated with an external stumuli such as temperature, pressure or light.
Since each state has different properties, SCO systems are a promising candidate as molecular switch.[1]



Recent studies have shown that SCO systems can have electronic transport that depends on the spin of the metal.[2] Carbon nanostructures have attracted attention due to its conductive properties. This structures can be functionalized thus allowing to act as ligands in a SCO system. This systems can be used as nanoelectronic devices which allow or not the pass of electrons depending on the spin of the metal.

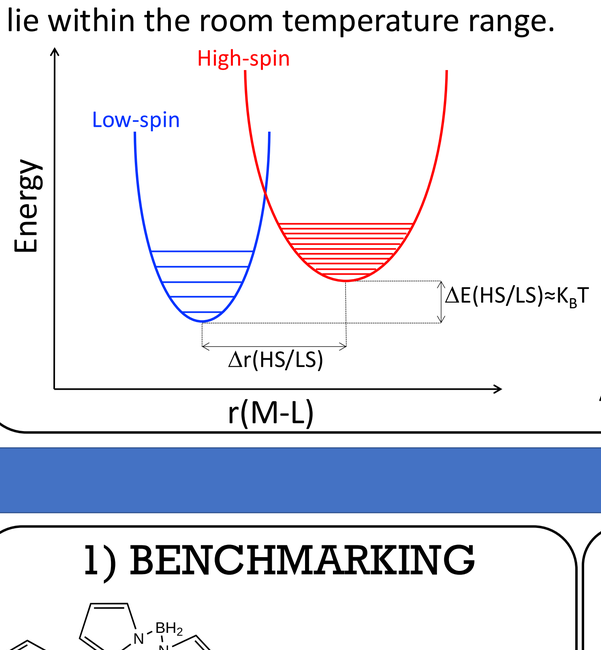






COMPUTATIONAL DETAILS - MODELLING THE TRANSITION

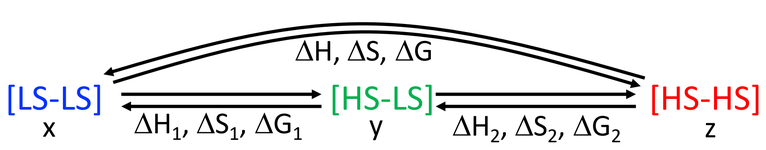
A key parameter to characterize this systems is the transition temperature ($T_{1/2}$), defined as the temperature where both spin states have equal population. For actual technological applications it should lie within the room temperature range.



LS ⇄ HS

$$\Delta G = \Delta H - T\Delta S$$
$$\Delta H = \Delta E_{el} + \Delta E_{vibr} \ (> 0)$$
$$\Delta S \ (> 0)$$
$$\Delta H = \boldsymbol{T}\Delta S \Rightarrow \Delta G = 0$$
$$\boldsymbol{T_{1/2}} = \frac{\Delta H}{\Delta S}$$
$$\Delta G = -RTln(K_{eq})$$
$$\Delta G = 0 \Rightarrow K_{eq} = 1 \Rightarrow \gamma_{HS} = \gamma_{LS}$$

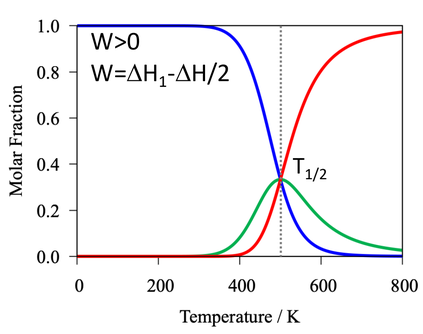
For dinuclear systems, a variation of Slichter and Drickamer's model is needed.[3,4]

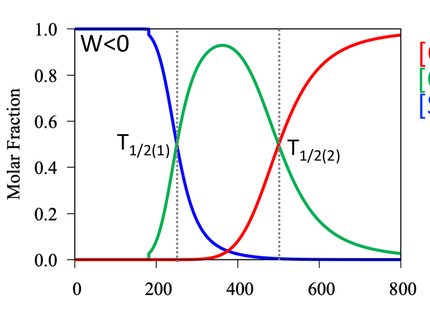


$$\Delta G = y(\Delta H_1 + T\Delta S_1) + z(\Delta H - T\Delta S) + \gamma(xy + yz + 2zx) + RT(x\ln(x) + y\ln(y) + z\ln(z))$$

Equilibrium conditions:

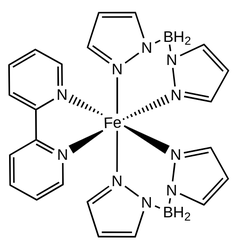
$$\begin{cases} x + y + z = 1 \\ \left(\frac{\partial \Delta G(x,y)}{\partial x}\right)_T = 0 \\ \left(\frac{\partial \Delta G(x,y)}{\partial y}\right)_T = 0 \end{cases}$$



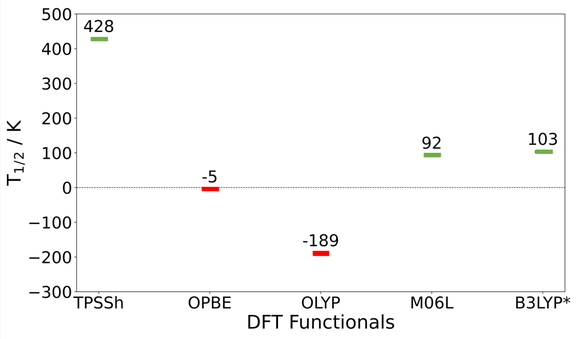


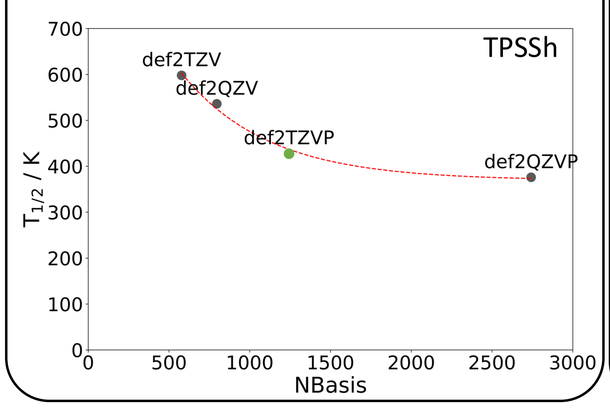
RESULTS

1) BENCHMARKING

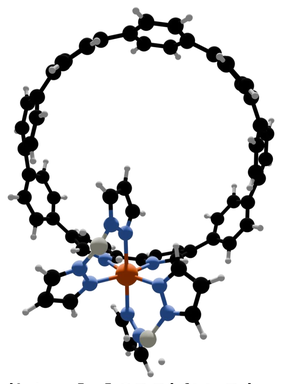


$[Fe(bipy)\{H_2B(pz)_2\}_2]$
$T_{1/2}$ (exp)= 160K



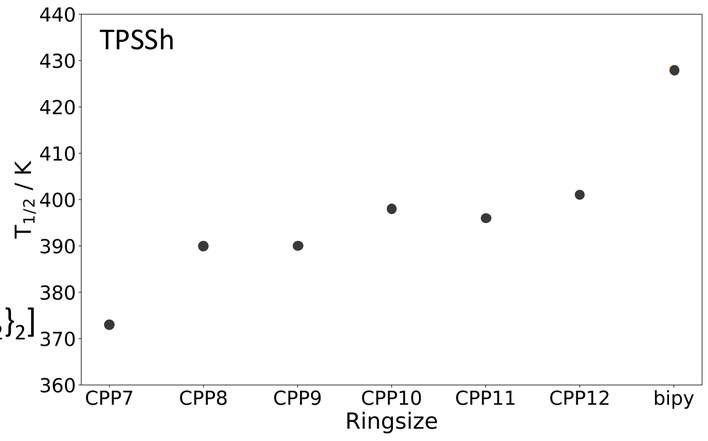


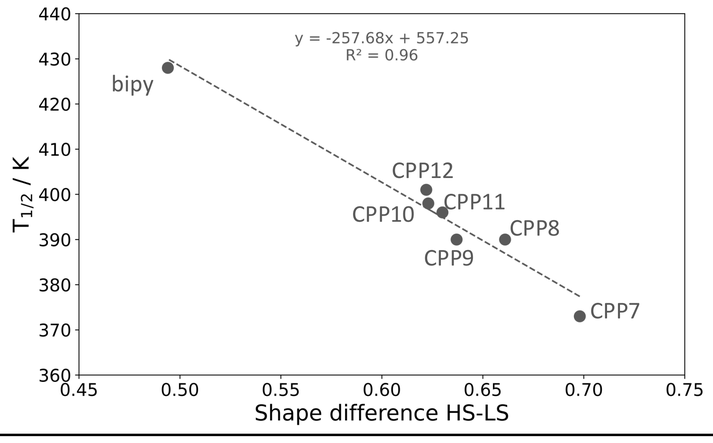
2) MONONUCLEAR bipy[n]CPP-SCO



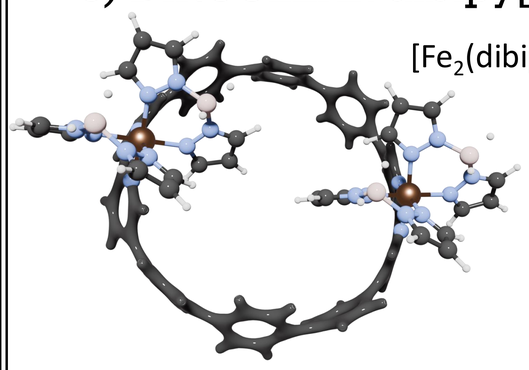
$[Fe(bipy[n]CPP)\{H_2B(pz)_2\}_2]$
for n=7-12

$T_{1/2}$ [K]	TPSSh	M06L	B3LYP*
CPP7	373	-72	33



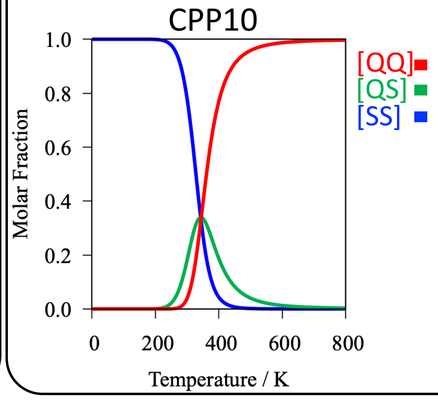


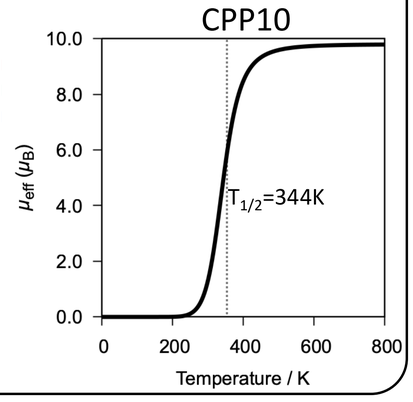
3) DINUCLEAR dibipy[n]CPP-SCO



$[Fe_2(dibipy[n]CPP)\{H_2B(pz)_2\}_4]$
for n=10-12

	ΔH (QQ-SS) [kJ mol⁻¹]	ΔS (QQ-SS) [kJ K⁻¹ mol⁻¹]	W [kJ mol⁻¹]	$T_{1/2}$ [K]
CPP10	58.3	0.170	-0.072	344
CPP11	58.5	0.165	0.122	354
CPP12	55.7	0.162	0.922	343





CONCLUSIONS

1) **TPSSh/def2TZVP** is the optimal method to characterize this systems.
2) In the mononuclear system, **having a nanoring instead of a bipyridine it diminishes the $T_{1/2}$** because the constrains of the nanoring makes it more difficult to the iron to have a perfect octahedral environment. Also, a **bigger nanoring means a less torsional environment, more octahedrality and higher $T_{1/2}$**.
3) In the **dinuclear system, the size of the nanoring has had no impact on neither the $T_{1/2}$ nor the type of transition** (being always a one-step transition).

BIBLIOGRAPHY

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[4] Navarro, L.; Garcia-Duran, A.; Cirera, J. *Dalton Trans.* **2024**, 53, 14592

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