Computational study of Spin-Crossover Systems Embedded in Carbon Nanorings

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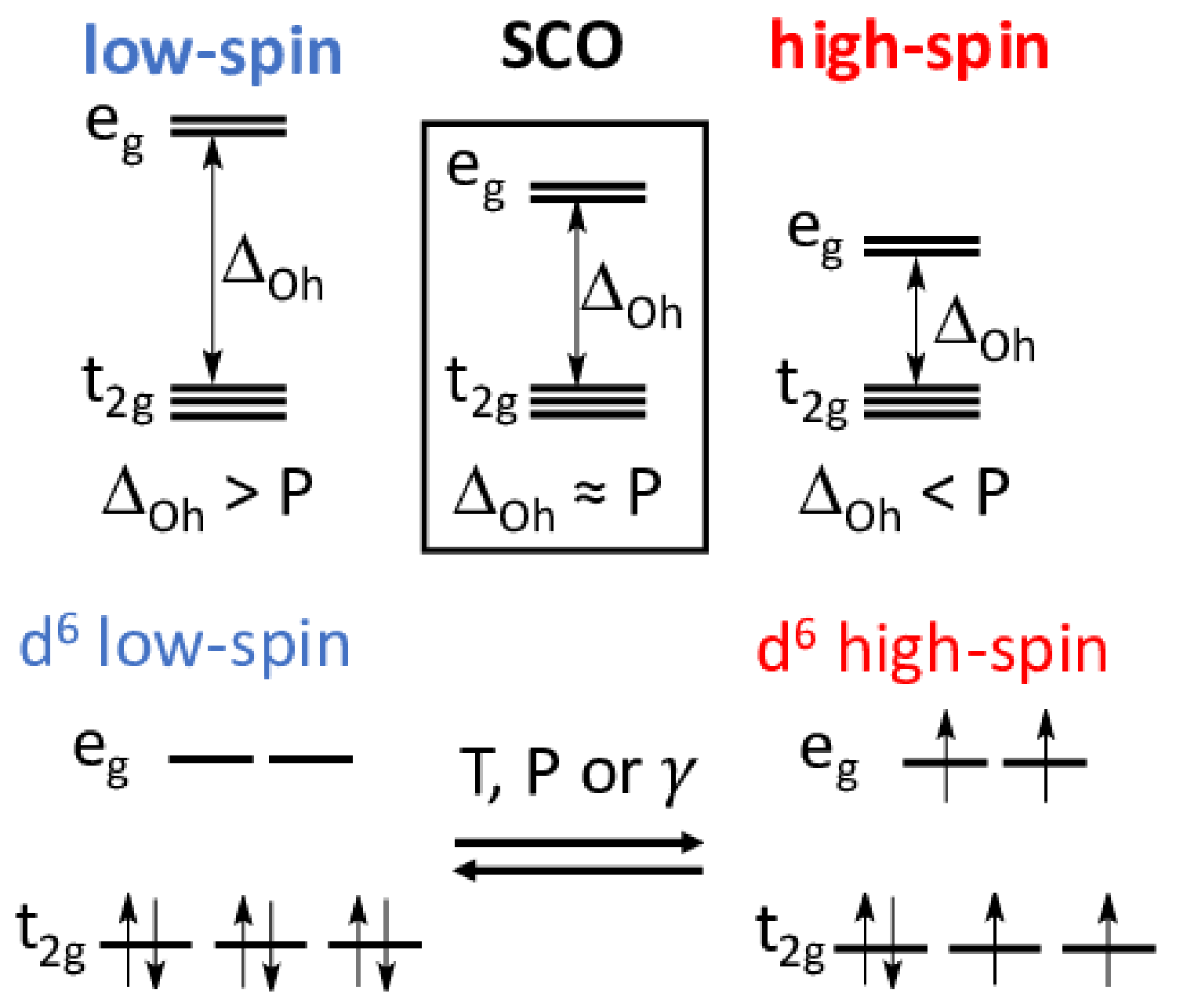
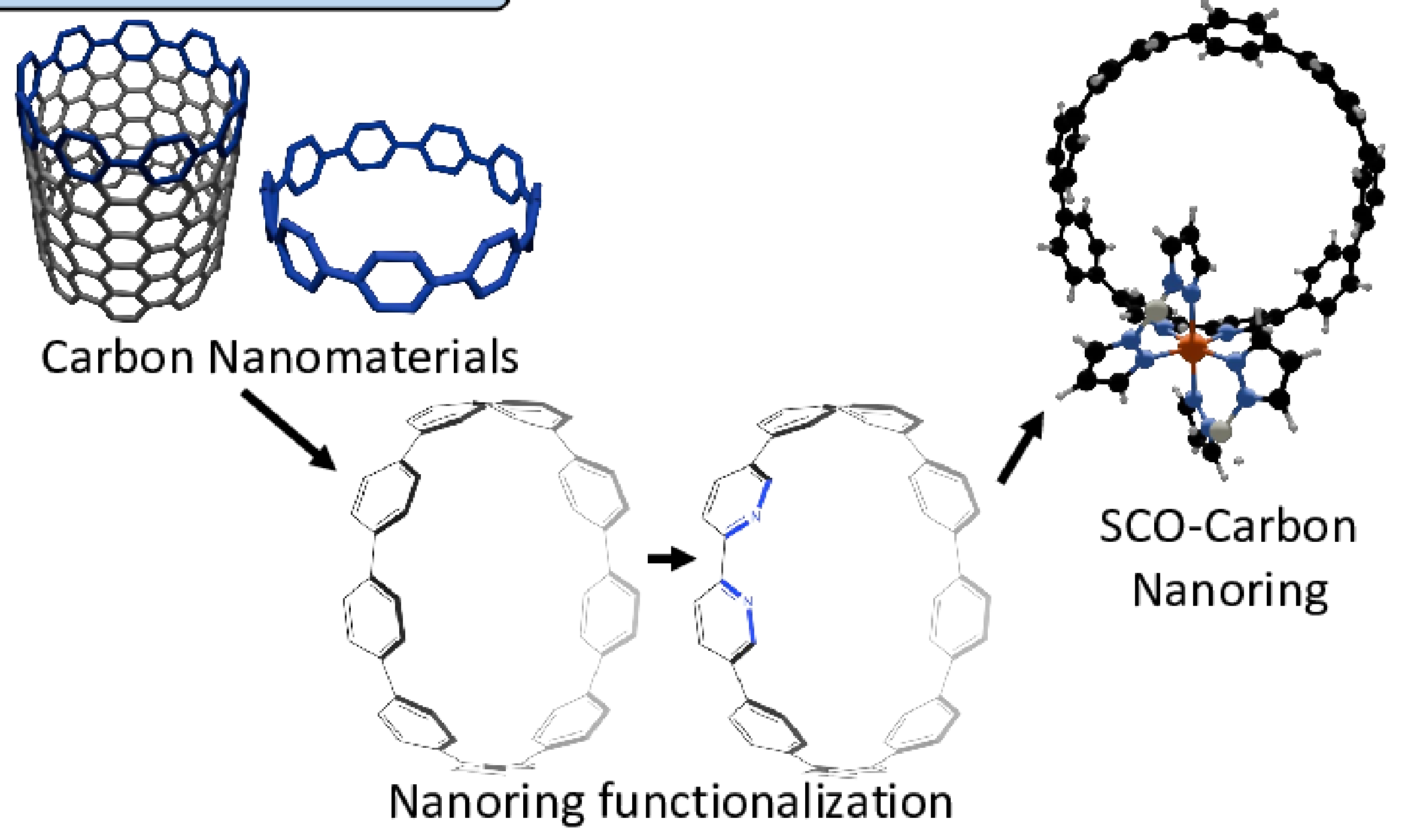
INTRODUCTION

Spin-Crossover (SCO) systems are transition metal complexes with two electronic states close in energy but differing in spin configuration. This allows the molecule to switch between states in response to external stimuli such as temperature or pressure, making them excellent candidates for molecular switches, with potential applications in memory storage devices among others.[1]

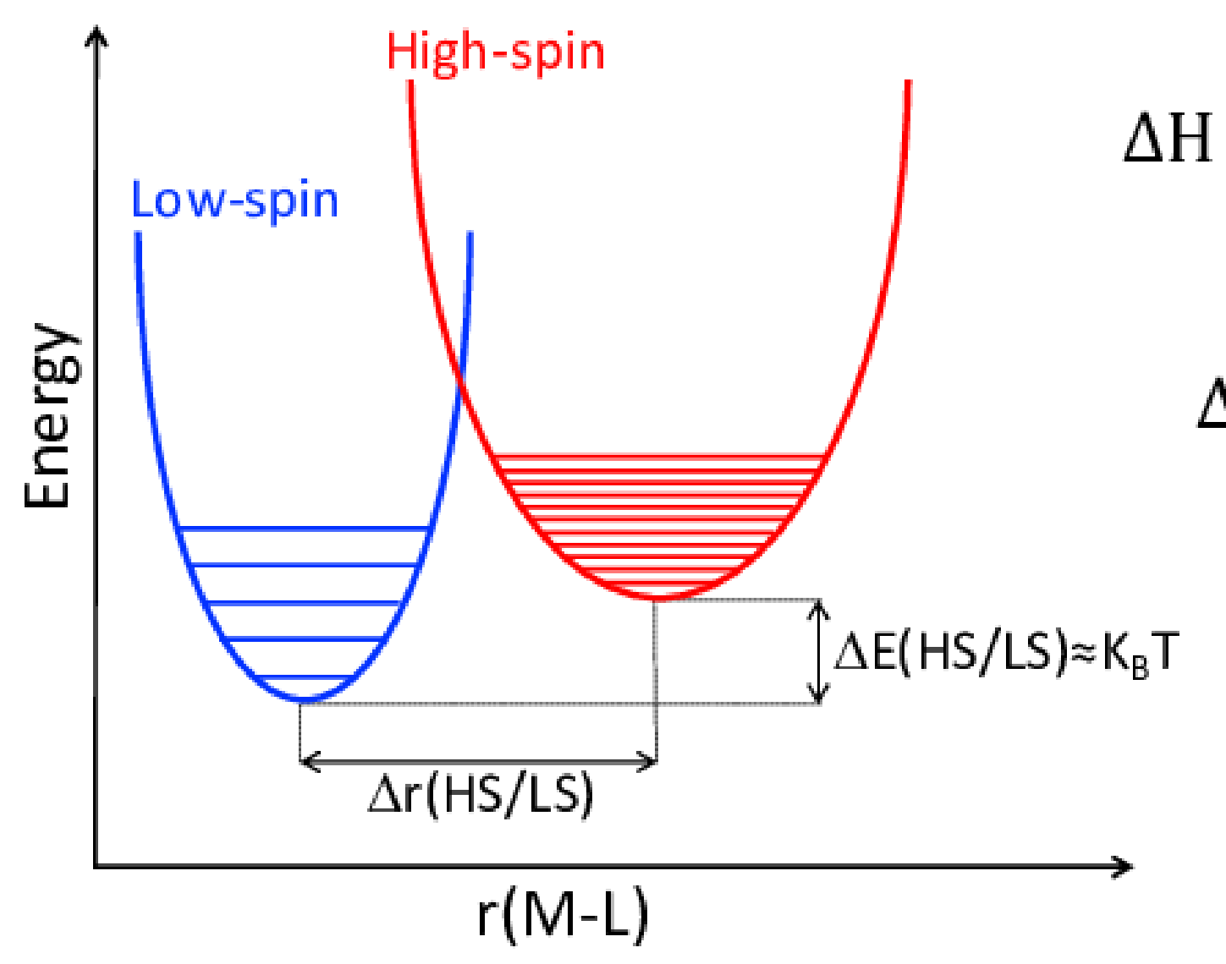




However, SCO systems are often structurally fragile. To enhance their robustness, carbon nanostructures, specifically carbon nanorings, have been proposed as ligands prior a functionalization.[2] These carbon nanostructures also exhibit interesting conductive properties.

MONONUCLEAR MODEL

A key parameter in characterizing these systems is the transition temperature ($T_{1/2}$), defined as the temperature at which both spin states are in equilibrium. For technological applications, $T_{1/2}$ must fall within the room temperature range, making its accurate prediction crucial.



$$LS \rightleftarrows HS$$

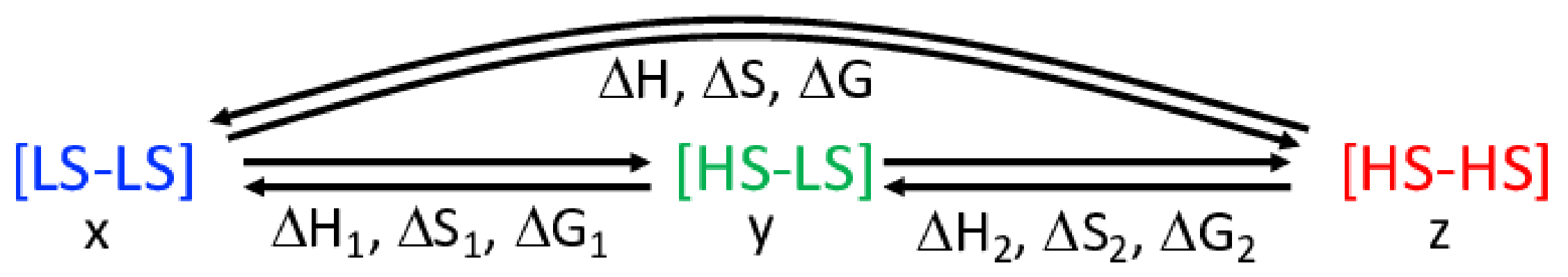
$$\Delta G = \Delta H - T\Delta S$$
$$\Delta H = \Delta E_{el} + \Delta E_{vibr} \; (>0)$$
$$\Delta S \; (>0)$$

$$\Delta H = \boldsymbol{T}\Delta S \Rightarrow \Delta G = 0$$
$$\boldsymbol{T_{1/2}} = \frac{\Delta H}{\Delta S}$$

$$\Delta G = -RTln(K_{eq})$$
$$\Delta G = 0 \Rightarrow K_{eq} = 1$$
$$\Rightarrow \gamma_{HS} = \gamma_{LS}$$

POLYNUCLEAR MODEL

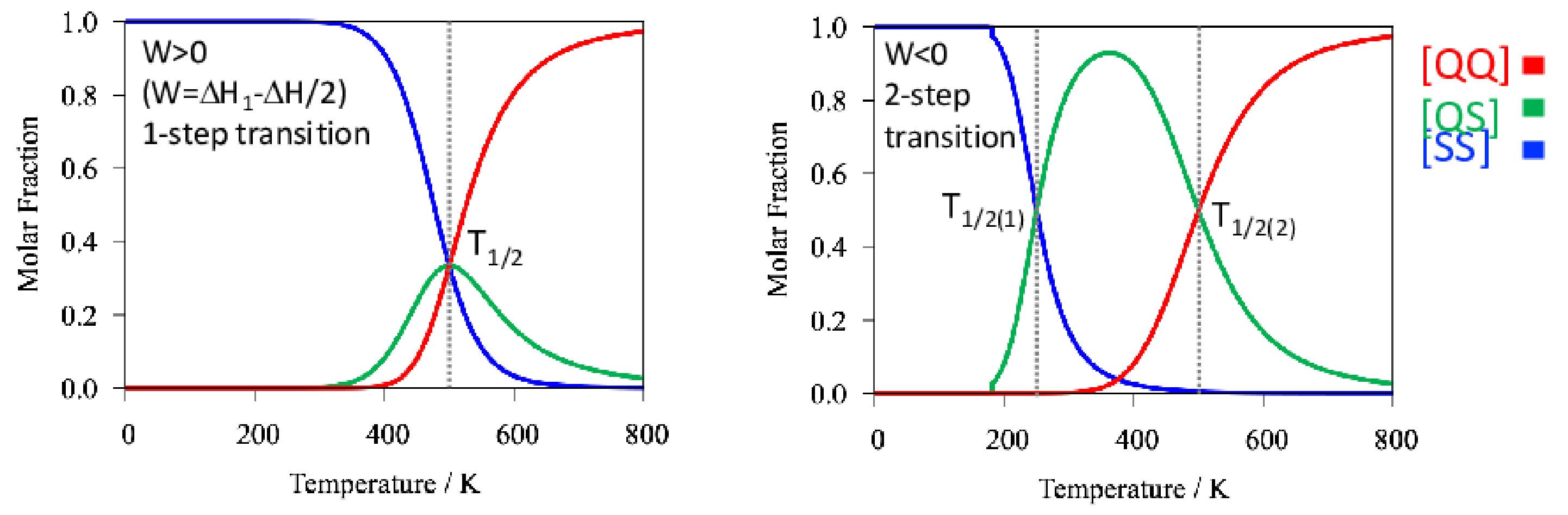
In polynuclear systems, a variation of Slichter & Drickamer's model is needed to model the transition.[3,4]



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

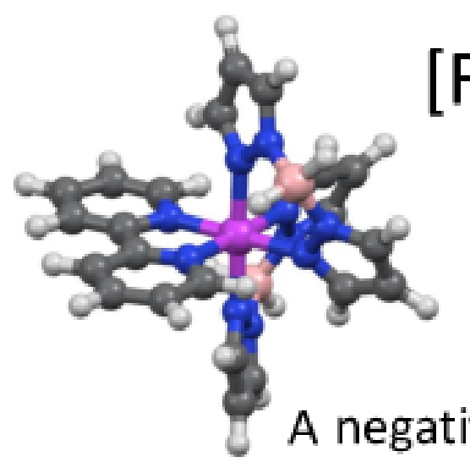
Equilibrium conditions:

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



BENCHMARKING

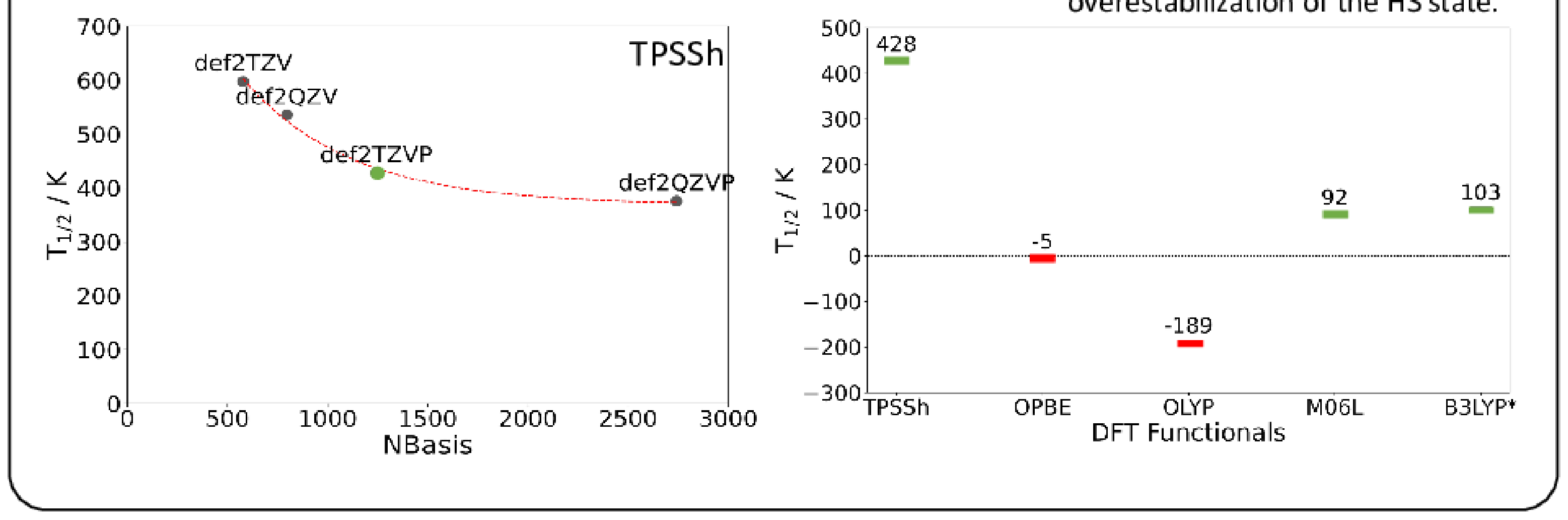
Accurate calculations of electronic energy differences (ΔE_{el}), and consequently of $T_{1/2}$ are not trivial.[5] Therefore, an initial benchmark was necessary to identify the most suitable functional for studying this system.



$[Fe(bipy)\{H_2B(pz)_2\}_2]$

$T_{1/2}$ (exp)= 160K

A negative $T_{1/2}$ value results from an overestabilization of the HS state.

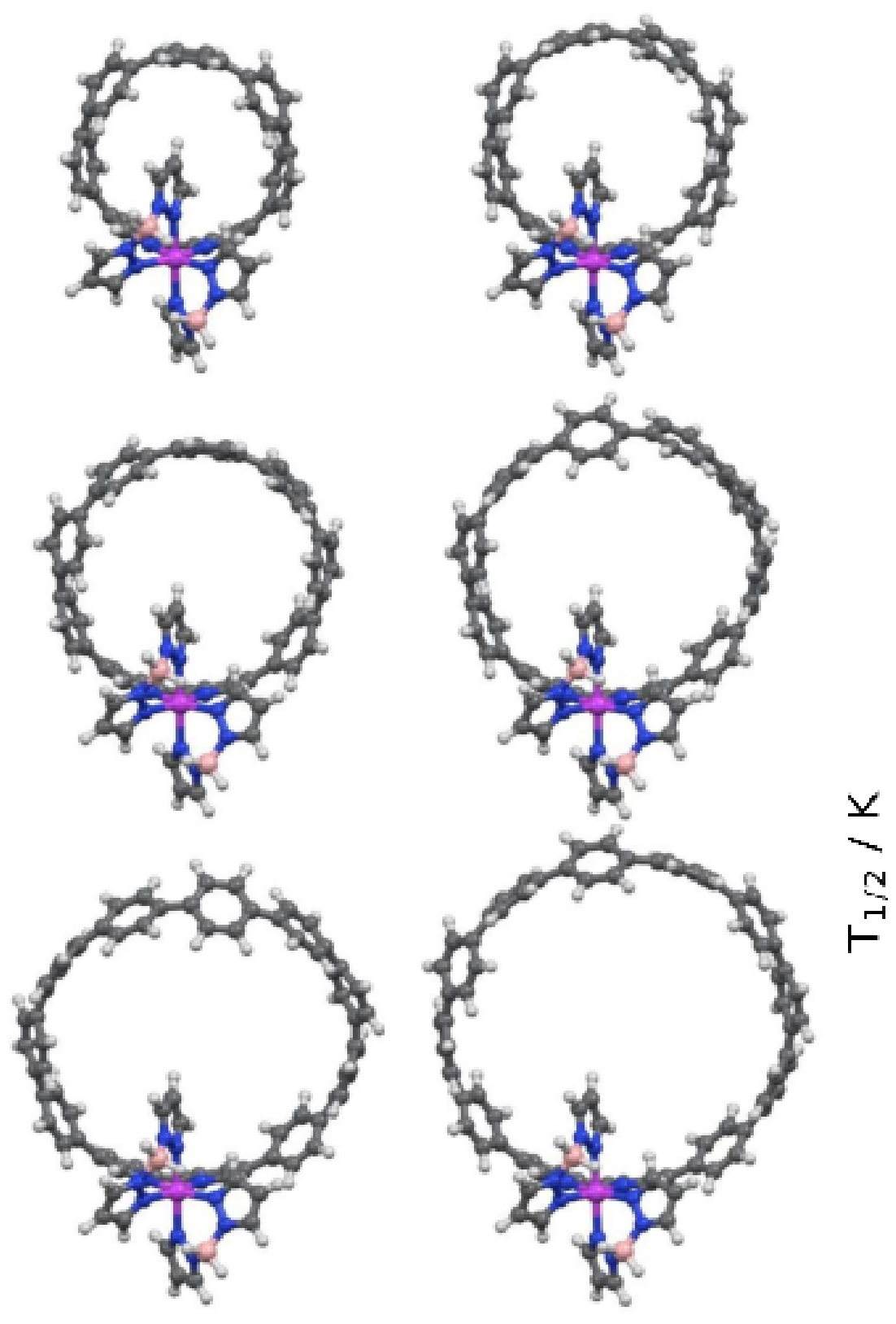


RESULTS

1) How can nanoring size affect $T_{1/2}$?

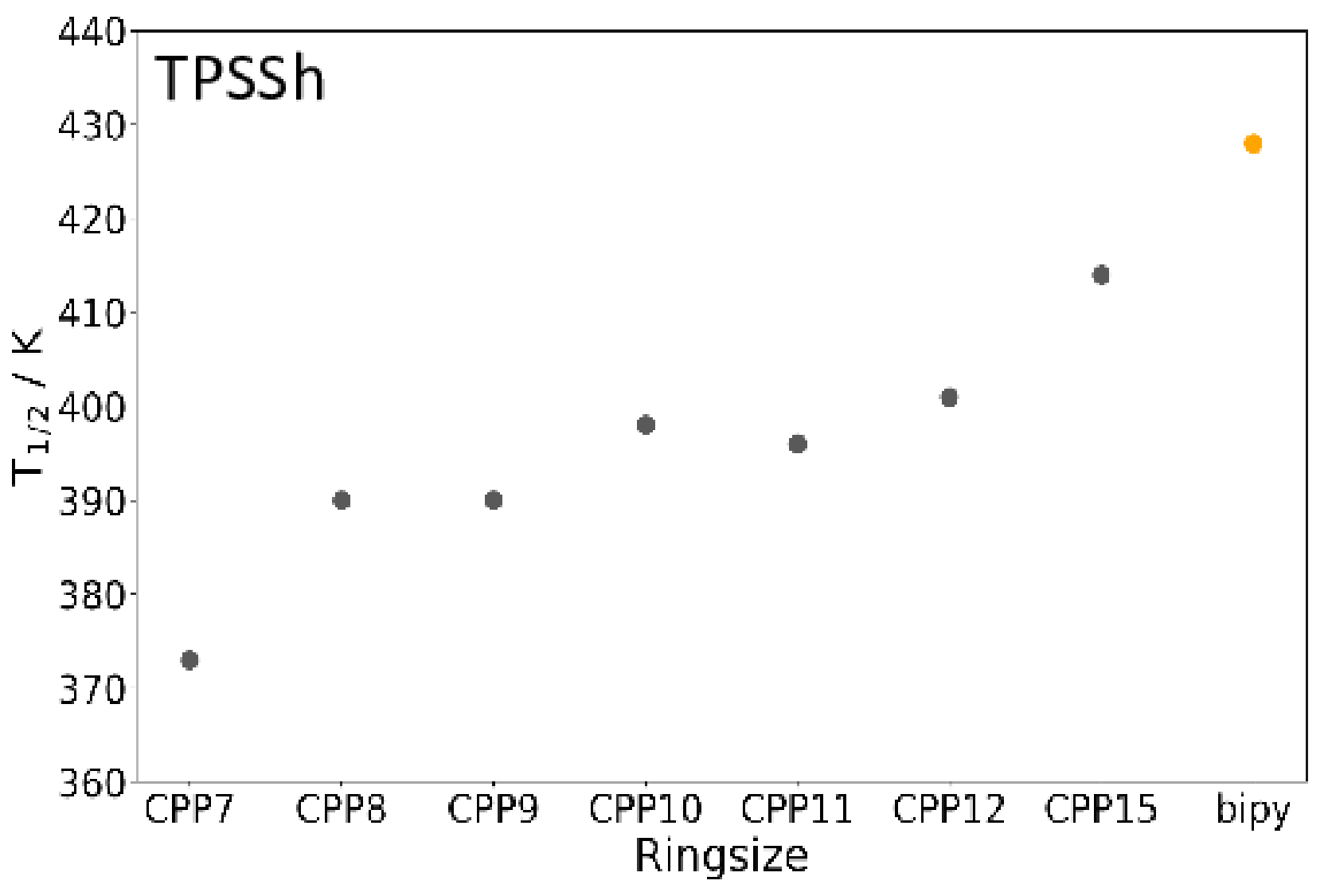
Once the most suitable method for this system has been selected based on the Benchmark results (TPSSh, M06L or B3LYP* with def2TZVP), the effect of different modifications on the system on the $T_{1/2}$ can be studied. The first modification considered is the nanoring size.

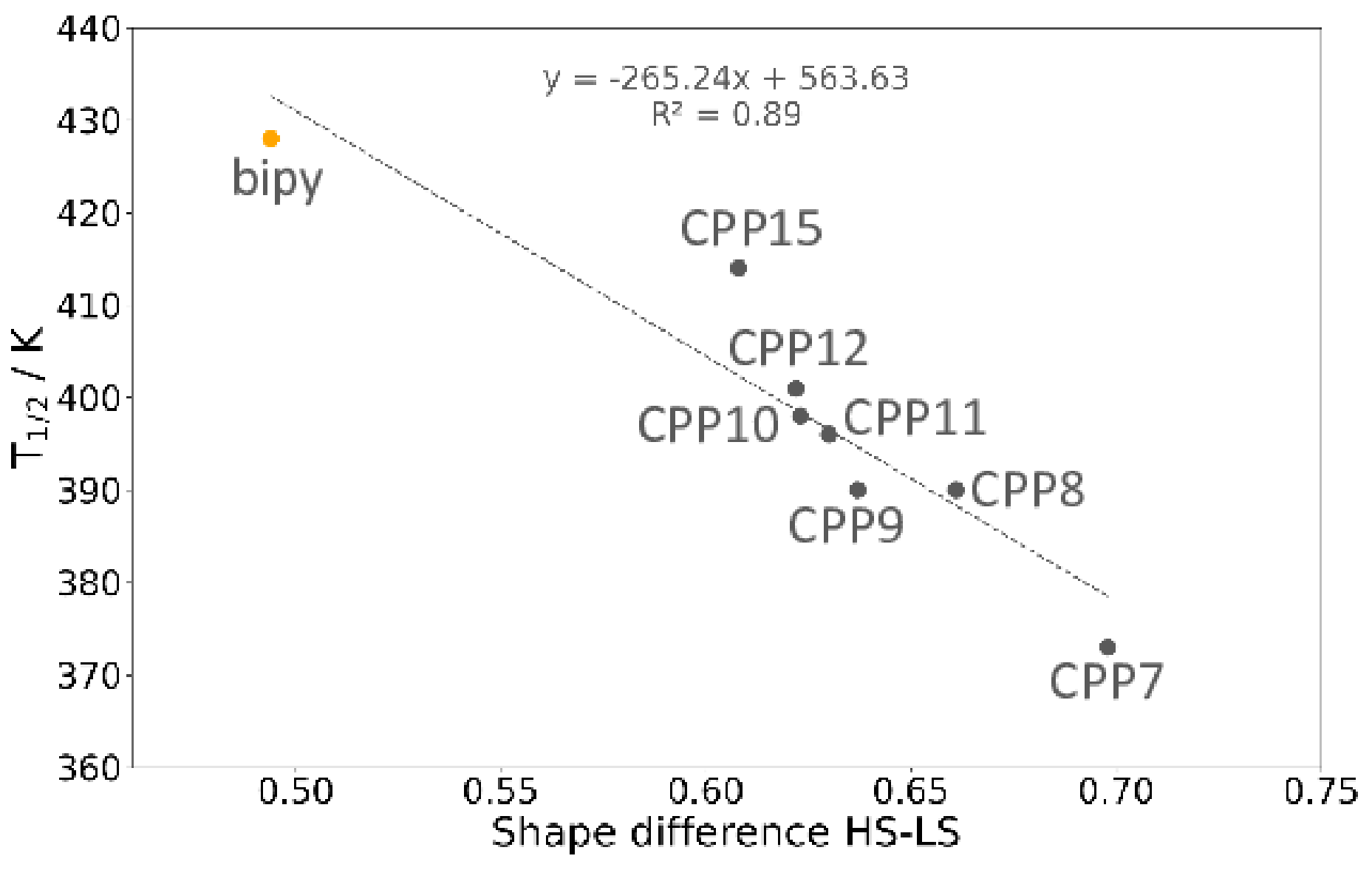
$[Fe(bipy[n]CPP)\{H_2B(pz)_2\}_2]$
for n=7-12



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

The calculations with the carbon nanoring shows that M06L and B3LYP* overstabilize the HS state, and therefore only TPSSh/def2TZVP can be used.



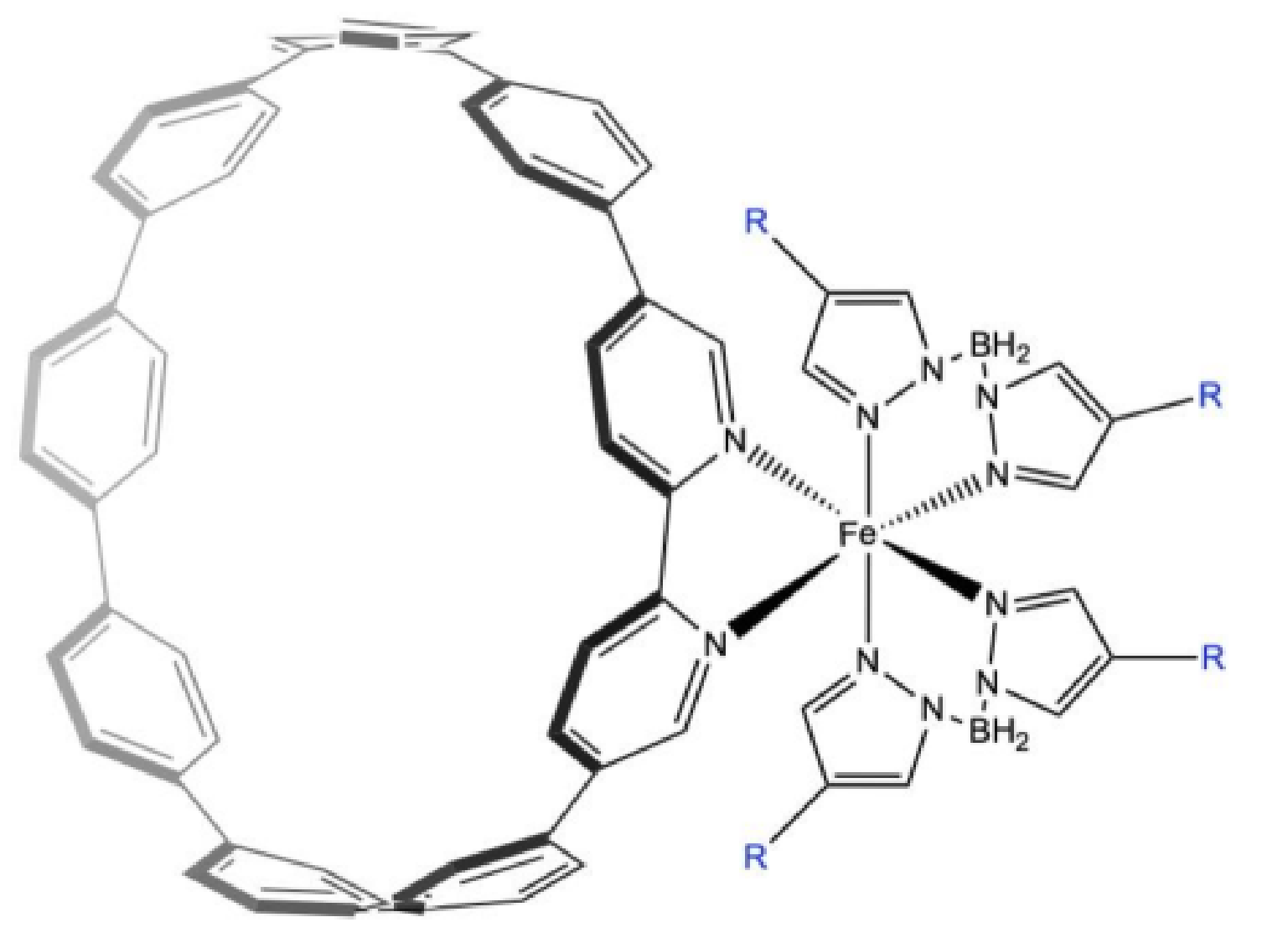


With the Shape program, the octahedrality of the metal was calculated to explain the observed trend between nanoring size and $T_{1/2}$. The LS state wants to have a perfect octahedral environment. Ring strain destabilize the LS state, thereby lowering $T_{1/2}$.

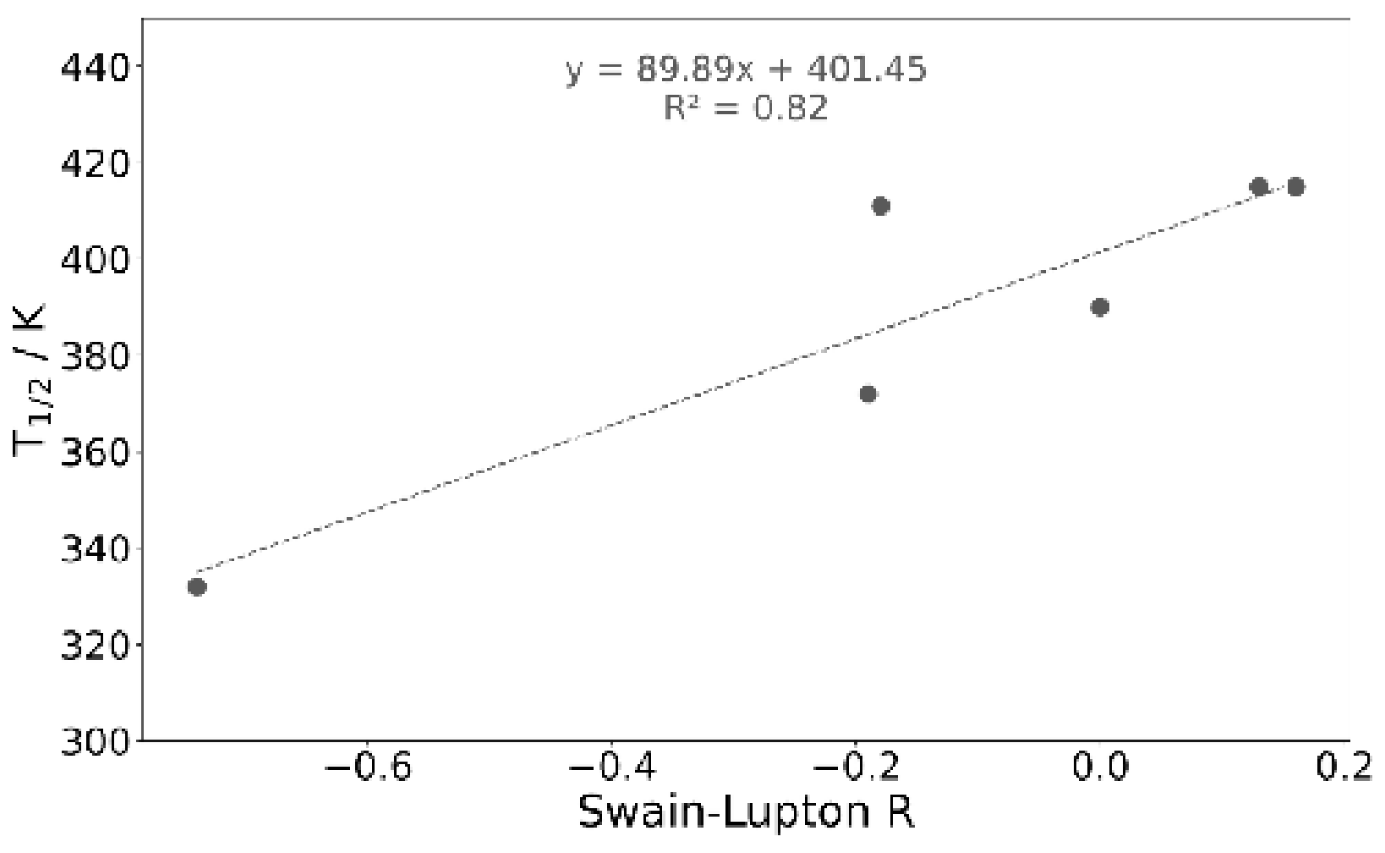
Smaller nanorings→ More tension → Less octahedricity→ **Smaller $T_{1/2}$**
Bigger nanorings→ Less tension → More octaedricity→ **Higher $T_{1/2}$**

2) How can ligand modifications tune $T_{1/2}$?

The second modification considered is ligand substitution. While keeping the carbon nanoring size constant, several modifications to the pyrazole ring have been introduced to assess their effect on the $T_{1/2}$.



$[Fe\{H_2B(pz\text{-}R)_2\}_2(CPP(9))]$
R = H, NO_2, CH_3, Cl, NH_2, CF_3

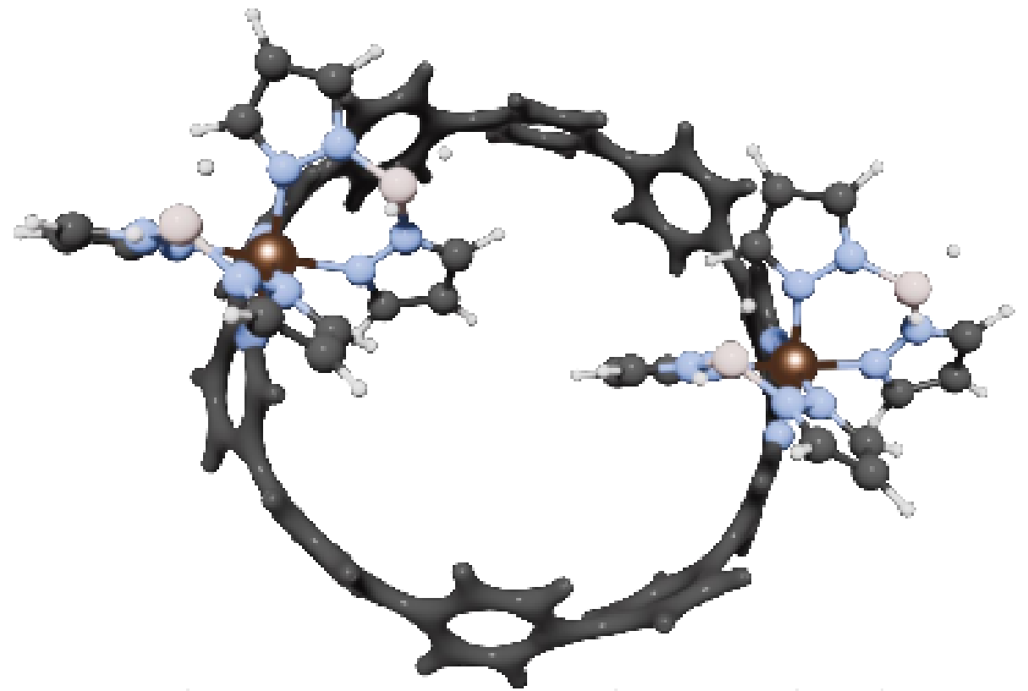


More negative S-L → Electron donating group (NH_2) → Lower Δ_O → **Lower $T_{1/2}$**

More positive S-L → Electron withdrawing group (CF_3) → Higher Δ_O → **Higher $T_{1/2}$**

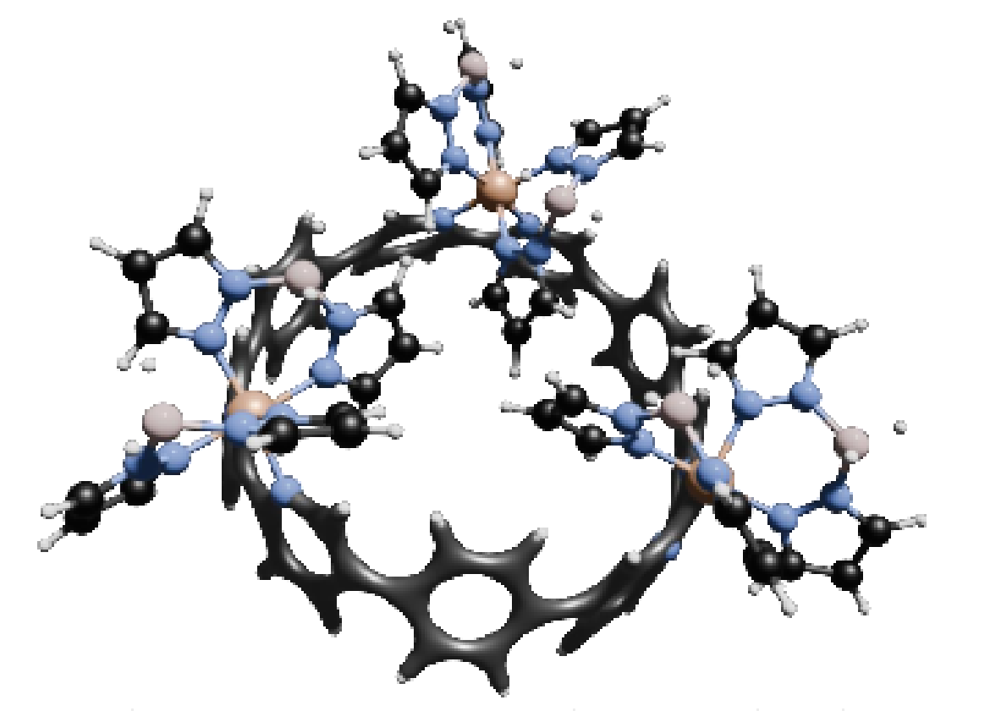
3) Does the addition of extra metal centers influence the spin transition?

Since carbon nanorings can be functionalized multiple times, different dinuclear and trinuclear systems have been studied to evaluate the effect of introducing additional metal centers.



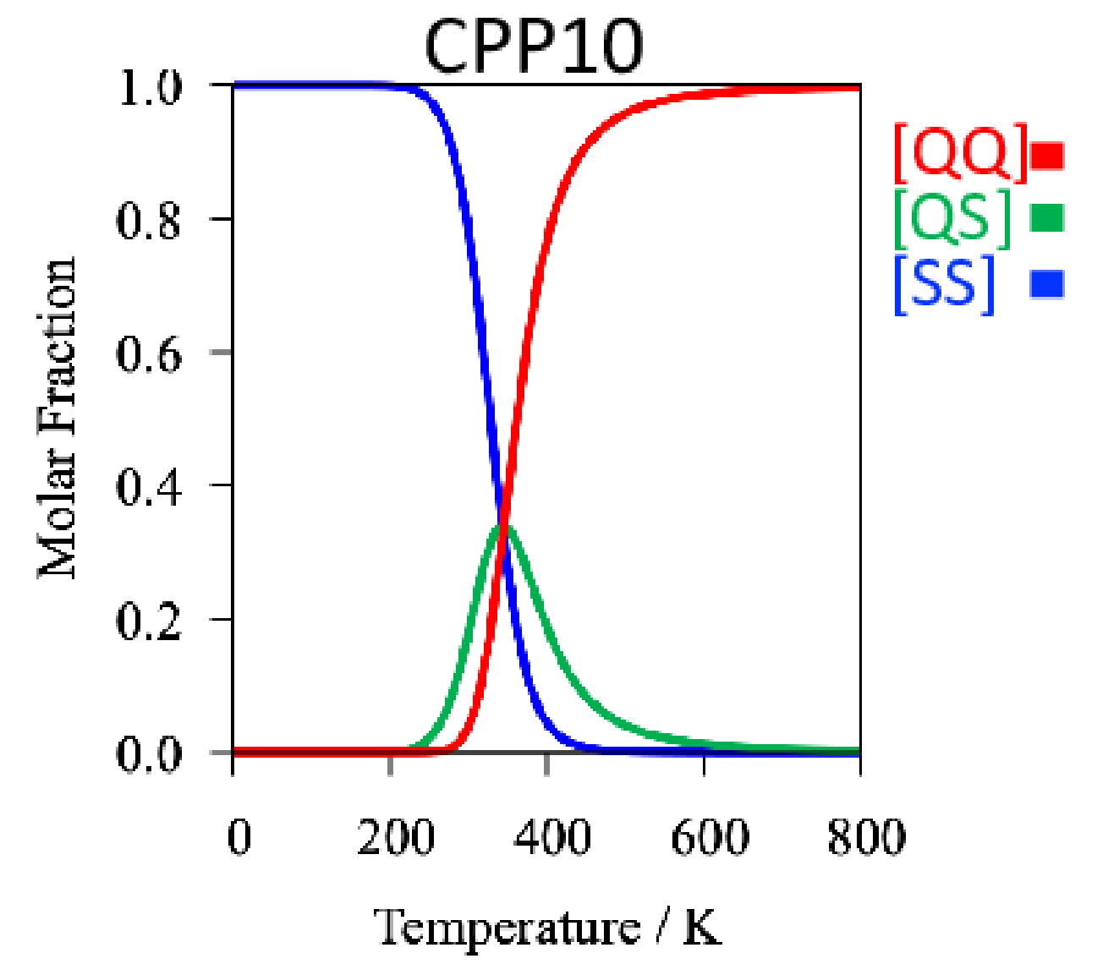
$[Fe_2(dibipy[n]CPP)\{H_2B(pz)_2\}_4]$

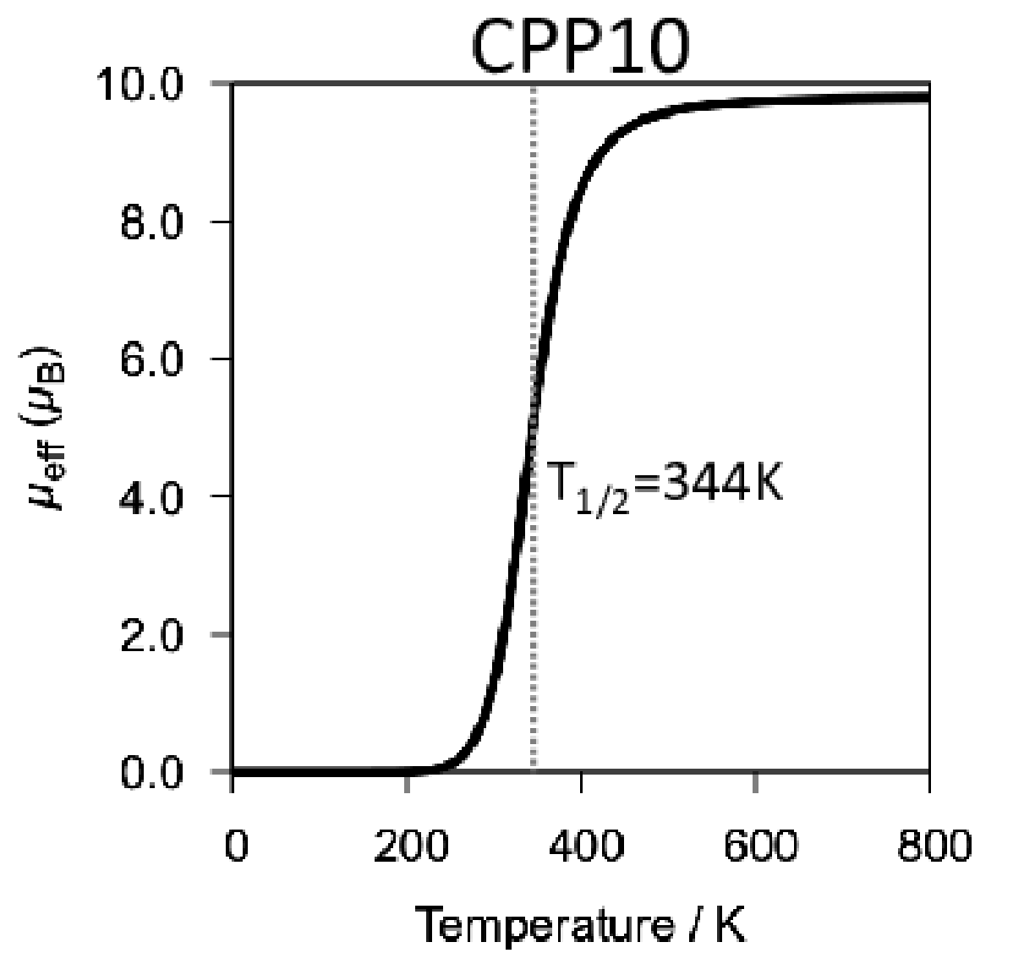
Fe_2	W [kJ mol^{-1}]	$T_{1/2}$ [K]
CPP8	2.363	321
CPP10	-0.072	344
CPP11	0.122	354
CPP12	0.922	343
CPP14	-0.227	376



$[Fe_3(tribipy[n]CPP)\{H_2B(pz)_2\}_6]$

Fe_3	W_1 [kJ mol^{-1}]	W_2 [kJ mol^{-1}]	$T_{1/2}$ [K]
CPP9	0.055	-2.289	342
CPP12	0.316	-1.048	365
CPP15	0.043	0.046	372





In most cases, W values are positives. In those cases where W is negative, its value is too small to allow the presence of a two-step transition. Therefore, **a one-step transition is observed in all cases.**

CONCLUSIONS

1) **TPSSh/def2TZVP** is the most suitable method to characterize this system.
2) In the mononuclear system, **replacing bipyridine with a nanoring decreases the $T_{1/2}$** because the strain of the nanoring makes it more difficult to adopt an ideal octahedral geometry. Moreover, **increasing the nanoring size reduces the steric strain, making it easier to achieve an octahedral environment thereby increasing the $T_{1/2}$.**
3) When modifying the pyrazole ring, **more electron-donating substituents decrease the ligand field splitting (Δ_O), which leads to lower $T_{1/2}$ vales.**. Conversely, **more electron-withdrawing groups increases Δ_O and thus raise $T_{1/2}$.**
4) In **polynuclear systems, increasing the nanoring size follows the same trend observed in mononuclear systems, with the transition consistently occurring as a one-step process.**

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Fundings: Grant PRE2022-101850; María de Maeztu Unit of Excellence (CEX2021-001202-M)
Project: PID2023-146774NB-I00 (MICINN) financed by MICIU/AEI/10.13039/501100011033 and by FEDER, UE