MODELING THE LIGAND TUNING EFFECT OVER THE TRANSITION TEMPERATURE IN SPIN-CROSSOVER SYSTEMS USING DENSITY FUNCTIONAL METHODS

Jordi Cirera*, Eliseo Ruiz and Santiago Alvarez

Departament de Química Inorgànica and Institut de Química Teòrica i Computacional, Av. Diagonal 645, 08028 Barcelona, Spain. jordi.cirera@qi.ub.es

Spin-crossover (SCO) systems are the focus of intense research due to their intrinsic behavior as molecular-level switches. A key parameter in the physical characterization of SCO systems is the transition temperature ($T_{1/2}$), defined as the temperature with equal populations of both spin-states. In this communication we present the results of our application of the meta-hybrid GGA functional TPSSh[1,2] to the accurate calculation of transition temperatures in SCO systems.[3,4] In particular, we will show the results on a family of tetracoordinated [$PhB(MesIm)_3Fe–N=PR_3$] systems, an unusual coordination number among SCO systems. Our calculations reveal a linear relationship between the phosphine cone angle and the $T_{1/2}$, which can be rationalized from the direct analysis of the underlying electronic structure in terms of the relevant molecular orbitals and is in excellent agreement with the experimental data.[5] We will also present the results for a series of binuclear iron(II) compounds of general formula $[FeL_1(NCX)_2]_2L_2$ (X = S, Se or BH_3), for which the stability of the different spin-states can be calculated as a function of the NCX ligand. Those results can be correlated with the experimentally two-step transition observed for some of them. Using the reported methodology, quantitative information about the ligand effect on the d-based molecular orbitals and its implications on the $T_{1/2}$ can be obtained, which can be of great help in the rational design on SCO systems with tailored properties.

(1) Perdew, J. P.; Tao, J. M.; Staroverov, V. N.; Scuseria, G. E. *J. Chem. Phys.* **2004**, *120*, 6898.
(2) Tao, J. M.; Perdew, J. P.; Staroverov, V. N.; Scuseria, G. E. *Phys. Rev. Lett.* **2003**, 91.
(3) Cirera, J.; Paesani, F. *Inorg. Chem.* **2012**, *51*, 8194.
(4) Cirera, J.; Alvarez, S. *Dalton Trans.* **2013**, *42*, 7002.
(5) Lin, H-.J.; Siretanu, D.; Dickie, D.A.; Subedi, D.; Scepaniak, J.J.; Mitcov, D.; Clérac, R.; Smith, J.M., *J. Am. Chem. Soc.* **2014**, *136*, 13326.