Modeling the ligand tuning effect over the transition temperature in Spin-Crossover systems using Density Functional Methods

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Spin-crossover (SCO) systems are the focus of intense research due to their intrinsic behavior as molecular-level switches. The possibility of controlling a molecular property by means of an external stimulus makes those systems ideal candidates for molecular level based memory devices. 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 our results for the application of the meta-hybrid GGA functional TPSSh[1,2] for 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 displaying SCO. Our calculations reveal the origin of the SCO behavior in this family and the interplay between the phosphine size and the changes in the $T_{1/2}$. In fact, a linear relationship between the phosphine cone angle and the shift in the $T_{1/2}$ can be obtained and rationalized from the direct analysis of the underlying electronic structure in terms of the relevant molecular orbitals, results that match the experimental data.[5] Using the same methodology, 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, unrevealing the origin of the experimentally observed two-step transition 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.

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