EXPLORING THE LIGAND CHEMICAL SPACE IN SPIN-CROSSOVER MOLECULES WITH ELECTRONIC STRUCTURE METHODS

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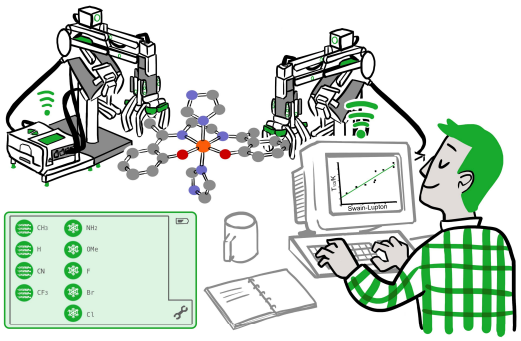
Spin-Crossover (SCO) systems are molecular compounds in which two alternative electronic states with similar energies are accessible by means of an external stimulus, commonly the temperature. The particular temperature with equal populations of both spin states is defined as the transition temperature ($T_{1/2}$), a key value in the physical characterization of such systems. This natural switching behavior turns these systems in perfect candidates for molecular-level based applications, due to their potential use in actual nanodevices. However, the design of new SCO systems that can operate at specific $T_{1/2}$ is quite challenging from the synthetic point of view.

In this communication, we will show how the use of electronic structure methods at the Density Functional Theory (DFT) level can be used to do *in silico* screening of new SCO molecules.[1,2] In particular, we will show how this tools help us in the ligand design of the air stable Fe(III) complexes with N_4O_2 coordination environment, and the unusual anionic $[Fe(OEt\text{-}L_1\text{-}pH)(NCS)_3]^-$ (OEt-L_1-pH = tris(pyridin-2-yl)ethoxymethane) molecule, exploring the ligand chemical space of their respective ligands, and how different chemical modifications can lead to a fine tuning degree of their respective $T_{1/2}$.[3,4] Our results not only reproduce the available experimental data in a quantitative way, but allow for a broad screening of ligand functionalization, thus generating guidelines for synthetic chemists to design new members of such families with specific $T_{1/2}$values.

The presented results validate the use of DFT methods to accurately compute $T_{1/2}$ in SCO systems, explaining the observed trends in terms of the electronic structure of the systems. But more importantly, these calculations open the door to the computer assisted design of new SCO materials that can operate at specific temperatures, thus accelerating the discovery of new SCO devices with a customized $T_{1/2}$.



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[2] J. Cirera and E. Ruiz, *J. Phys. Chem. A*, **2020**, 124, 5053−5058

[3] D. Vidal, J. Cirera and J. Ribas-Ariño, *PCCP*, **2023**, in press

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