MODULATION OF THE SPIN-CROSSOVER BEHAVIOUR IN [Fe₂] METAL-ORGANIC CAGES

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Spin-crossover (SCO) compounds are molecular systems containing first-row transition metal ions that can alternate between two different electronic states which are close in energy. In SCO compounds, an external stimulus (commonly temperature, but also pressure or electromagnetic radiation) is used to change the spin state of the metal centre. The temperature with equal populations of both spin states is defined as the transition temperature (T₁/₂) and is a key parameter in the physical characterization of such systems. This switching behaviour turns such systems in perfect candidates for molecular-level based applications and has raised a lot of attention from the chemistry and physics community over the last years.[1]

In this work, a computational method to study the SCO behaviour on dinuclear metal-organic cages of general formula [Fe₂L₃R₃]⁺⁺ (L=1,3-bis(3-(pyridin-2-yl)-1H-pyrazol-5-yl)benzene, R = -H, -F or CH₃) was carried out, in order to analyse the effect of different guest molecules (X = H-, F-, Cl-, Br-, I-, BF₄-) on the tuning of the T₁/₂.[2-4] Using the TPSSh/TZVP method, we computed the thermochemistry and transition temperatures for the cages with several guests molecules and different ligand functionalization.[5] Our results illustrate a dual effect. On one side, there is a correlation between the guest size and the decrease of the T₁/₂, and, on the other hand, the ligand functionalization allows us to increase or decrease the ligand field around the metal centre, thus modulating the SCO properties of the system. Our results illustrate how the interplay between host-guest chemistry and ligand field fine-tuning around the metal centre can be used in order to design, with computational tools, metal-organic cages that can be used as molecular level sensors in specific conditions.

Left, illustration of the [Fe₂L₃R₃]@Cl⁻ system, and right, calculated magnetic moment vs. temperature curve for the systems [Fe₂L₃R₃]@F⁻ and [Fe₂L₃R₃]@Cl⁻.

References