

Control of the Bistability in Molecular Switches: a Combined Theoretical and Experimental Approach

Context and Goal. Bistable molecular materials are the focus of intensive research efforts due to their potential applications in sensors, electronic devices, and solid refrigerants. These molecular systems can change their spin state under external stimuli (temperature, pressure, light), triggering sudden modification of their physical and mechanical properties. If Spin Transition (ST) complexes are the most studied Magnetic Switches, the cyanide-bridged FeCo coordination clusters emerged recently as a new promising family of molecular switches, in which the spin transition is accompanied by a metal-to-metal electron transfer (ET). Both systems share many similarities, and one of the main challenges remains the control of their transition temperature and their thermal bi-stability domain: the temperature range in which a material can exist in both spin-state. **This requires a better understanding of the physics behind spin-state transformation**, the ultimate goal being the design of new molecular switches with predictable and optimized properties.

Scientific approach. Magnetic bi-stability is attributed to cooperativity of ST systems, that is to say the ability for a molecule having its spin state changed to trigger the spin state change of the adjacent molecules. As the ST process of a molecule is always accompanied by a local volume change, the 1st order transition in crystal lattices is facilitated by mechano-elastic interactions, which propagate the local volume change on long scale. Two main approaches are proposed in the literature for rationalizing the bi-stability domain of the Magnetic Switches.

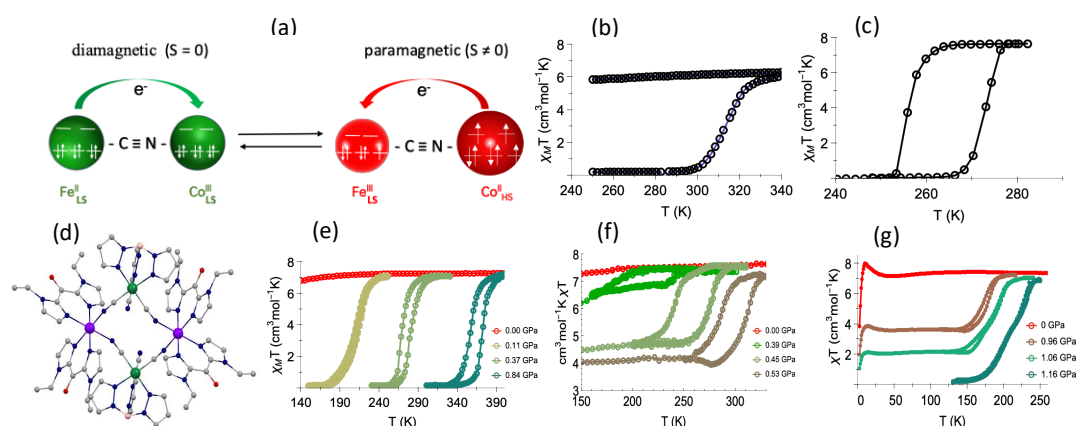
1. **The chemists' approach**, consists in describing supramolecular interactions that are believed to ensure the communication between adjacent molecules. Cooperative behavior could thus be promoted by strong supramolecular interactions (π - π stackings, H-bonds). However, the efficiency of intermolecular interactions is never quantitatively evaluated in term of elastic interactions.
2. **The physicists' approach**, consist in developing microscopic models which can reproduce all kind of transitions observed in solid-state. The approach is gaining increasing success but the models remain very simple in comparison to the complex structure of actual molecular systems. More importantly, it cannot provide the direct structure-property relationships that are particularly useful for the design of the compounds of desired and predictable properties.

Our project aims at building a bridge between the two approaches by extracting from high-pressure measurements on molecular switches the actual mechano-elastic properties of real system and correlate them to specific intermolecular interactions. This will help providing to the physicist the estimate of elastic interaction in true system and the actual elastic interaction topology.

Scientific Approach. Our group is expert in the design of FeCo complexes that exhibit controllable electron transfer - coupled spin transition (ETCST). In recent years, we have begun exploring the relatively unstudied pressure stimulus to trigger reversible ETCST. We demonstrated that remarkable magnetic behavior (unprecedented in charge-transfer switches) can be achieved in a family of square complexes with the general formula: $\{[\text{Fe}(\text{R}^1\text{Tp})(\text{CN})_3]_2[\text{Co}(\text{R}^2\text{bik})_2]_2\} \cdot (\text{A})_2$ (where A stands for the counter-anion, R^1Tp represents tris(pyrazol-1-yl)borate derivatives and R^2bik , bis(vinylimidazole-2-yl)ketone derivatives).¹ The change in ligand's substituents or counter-anion can modify the crystal packing, thus influencing the supramolecular interactions and the core structure of the complexes. This leads to a diversity in ETCST process (see figure).^{2,3} Importantly, we recently proposed a way to bridge the gap between the physicists' and chemists' views. High-pressure X-ray diffraction analysis on one of these complexes allowed us to obtain both the crystal structure data and the elastic properties. We succeeded to simulate the pressure-enhanced cooperativity of the complex's ETCST by using a mechano-elastic model, while tracking the structural origin of the phenomenon.² Importantly, we were able to correlate elastic properties in given directions to specific intermolecular interaction. This gives a new method to rank the efficiency of intermolecular interactions in promoting elastic interaction and cooperative effects. This will be confronted to the theoretival models designed by ADSU partner and ultimately help the design of new molecular switches.

Our partner at Sorbonne University Abu Dhabi SUAD has strong expertise in numerical simulation of spin transition systems, particularly in understanding the interplay between elasticity, nucleation dynamics, and cooperative effects in spin transition materials. The partner's research integrates microscopic modeling, Monte Carlo simulations, and heat diffusion approaches to explore how external stimuli such as temperature, pressure, and light excitation influence the structural and magnetic bistability of molecular systems.^[4-7] A key aspect of their work is the spatiotemporal evolution of spin domains during ST transitions, where they have demonstrated that intermolecular elastic interactions play a crucial role in the nucleation, growth, and

stabilization of spin domains. Our partner will establish specific microscopic model for each ETCST- active square complex and will provide a strong theoretical counterpart to the ETCST behaviors of polymetallic FeCo complexes. While the experimental approach focuses on tuning supramolecular interactions through the change of chemical composition, the numerical simulations offer predictive insights into how these structural modifications influence the macroscopic bistability and cooperative behavior of these materials. Notably, the respective experimental data of these systems can be directly incorporated into numerical models to simulate pressure-induced cooperativity and domain evolution. This insight is particularly relevant for a deeper understanding of the structural origins of cooperative effects of ETCST-active materials, where supramolecular interactions and intermolecular elastic forces play a critical role in controlling the switching mechanism.



Various thermally activated ETCST behaviors of $\{[\text{Fe}^{\text{R1}}\text{Tp}(\text{CN})_3]_2[\text{Co}^{\text{R2}}\text{bik}]_2\} \cdot (\text{A})_2 \cdot \text{S}$ square complexes with and without pressure application. (a) Schema of ETCST. (b) Thermal ETCST of **1** ($\text{R}_1 = \text{H}$, $\text{R}_2 = \text{vinyl}$, $\text{A} = \text{PF}_6^-$ and $\text{S} = \text{nH}_2\text{O} \cdot \text{mMeOH}$) under ambient pressure. (c) Cooperative thermal ETCST of **3** ($\text{R}_1 = \text{H}$, $\text{R}_2 = \text{vinyl}$, $\text{A} = \text{ClO}_4^-$ and $\text{S} = 2\text{CNCH}_3$) under ambient pressure. (d) Molecular structure of **2** ($\text{R}_1 = \text{H}$, $\text{R}_2 = \text{vinyl}$, $\text{A} = \text{BF}_4^-$ and $\text{S} = 2 \text{MeOH}$). (e) Thermal ETCST of **2** under various pressures. (f) Thermal ETCST of **3** ($\text{R}_1 = \text{H}$, $\text{R}_2 = \text{vinyl}$, $\text{A} = \text{PF}_6^-$ and $\text{S} = 2\text{MeOH}$) under different pressures. (g) Thermal ETCST of **4** ($\text{R}_1 = 2 \text{methyl}$, $\text{R}_2 = 2 \text{methyl}$, $\text{A} = \text{BF}_4^-$ and $\text{S} = 2\text{MeOH}$) under different pressures.

By bridging theoretical modeling with experimental studies on bistable FeCo molecular switches, this collaboration aims to develop a unified framework that links supramolecular chemistry, elastic interactions, and cooperative phase transitions. The combined expertise of both teams will allow us to refine the design of new switchable materials, optimize their cooperative response under external stimuli, and develop predictive strategies for tailoring bistability in molecular-based electronic and magnetic devices. The recruited PhD candidate will at first design and synthesize new polymetallic FeCo complexes in Paris, tuning their molecular structures to control bistability under external stimuli such as pressure, temperature, and light. He or She will then characterize these materials using techniques like X-ray diffraction, Raman spectroscopy, SQUID magnetometry to analyze their spin-state switching behavior. Additionally, He or She will use computational modeling on a HPC station in SU Abu Dhabi, United Arab Emirates to investigate and predict bistability under different conditions.

Profile and skills required: We are looking for a highly motivated student with a master's degree in chemistry, physics, or materials science who is eager to work at the intersection of experiments and simulations. While basic programming experience (Python, Matlab, Fortran, or similar) is a plus.

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