

Guest Induced Spin-State Switching in Hoffmann-type Coordination Polymers

The reversible interconversion between the high-spin (HS) and low-spin (LS) states in transition metal complexes is being studied in the presence of different stimuli. The advantage of the porous Hoffmann-type framework is that the adsorption and desorption of gas molecules can play an important role in switching the spin state. The study of the guest-induced spin-crossover behavior of these materials is initiated in this short project.

Molecular magnetism, particularly spin-state switching in transition metal complexes[1], is a thriving field of research for its potential applications in memory devices, magnetic sensing etc[2-3]. For studying spin-state switching, the stimuli like light, pressure, and temperature are used for the 3d transition-based complexes and materials[4-5]. Interestingly gas-responsive spin-state switching is a unique field of research as a very-selected group of scientists can do it and need a high level of technical knowledge and scientific understanding. The Miyasaka group has the expertise in studying gas-responsive magnetic property changes in the framework materials and is credited globally with developing this area of research[6-8]. They also study the single-crystal to the single-crystal transformation of these materials using X-ray crystallography in the presence of different guest molecules, mainly gases and solvents as well. The group is globally known for the design of materials using redox-active ligands and [Ru₂] paddlewheel units as building blocks[6]. These special classes of complexes go through “gate opening” phenomena and are followed by structural changes that initiate the electron transfer between the metal and redox active ligand as well as a change in magnetic properties in the materials. On a different aspect, it is needless to mention that the extreme sensitivity of the spin-crossover(SCO) phenomenon to minute structural changes imposes a formidable challenge in designing SCO materials with targeted properties. In that context, Hoffmann-type coordination polymers (HCPs) having the general formula $\{M(L)_n[M'(CN)_4]\}$ or $[M(L)_n\{M''(CN)_2\}_2]$ where (M=Mn, Fe, Co, Cu, Zn or Cd, M'=Ni, Pd or Pt, M''=Ag or Au, L=pillar ligand) are of great interest[9], as the polymeric network exhibits stronger cooperativity between the SCO sites linked through covalent bonds to create a rigid lattice. Additionally, the organic linkers determine the shape and size of the framework and supramolecular interactions present in the solid state. Guest molecules inside the pores influence the cooperativity via weak interactions and create a pressure effect.

We have designed and synthesized a few crystalline Hoffmann frameworks by changing the organic linkers and the tetracyanometallates(Palladium and Platinum).

The complex we studied is a 2D framework with methyl isonicotinate acts as a pillar(pendant) ligand to form a 2D interdigitated structure[Fig. 1]. The complexes show different spin-state switching behavior in the presence and absence of solvent guest molecules in the pores[Fig. 2]. The complex retain its crystallinity after removal of the guest solvent molecules and the structure of the desolvated samples was also determined using X-ray crystallography[Fig 1]. The BET surface area measurement found that the framework of interest shows pressure-induced structural phase change and may have the potential to show gas-induced spin state switching behavior. The sample went through the initial screening, and the rest of the measurements will be done once a large amount of the sample would be prepared. During my visit, I also experienced the complex setup of gas-induced magnetic data collection that coupled a BET instrument with the MPMS5 magnetometer. The tubing, valves, and pressure gauges are assembled fascinatingly to obtain the results of the highest authenticity.

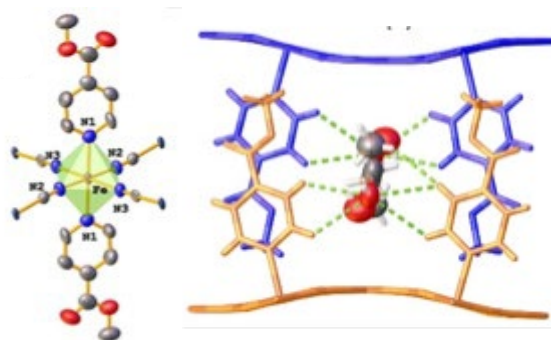


Fig 1. Asymmetric unit of $[Fe^II(L)_2Pd(CN)_4] \cdot 1.3MeOH$ (L = methyl isonicotinate), and position solvent molecules in between the layers.

The complex experimental setup to collect the single crystal X-ray data of the porous frameworks under a positive pressure of a gas is very challenging and an excellent experience for learning. Also, in this case, the gas pressure of the capillary containing the crystal is controlled by a BET instrument. Some of the magnetic materials we design are porous, highly stable, and suitable for studying their gas-responsive

magnetic properties as well as structural changes in the presence and absence of guest gas molecules.

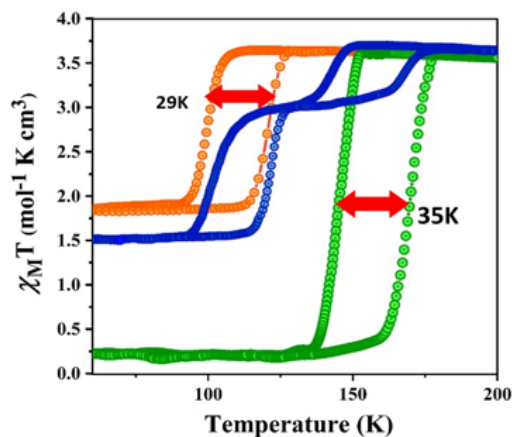


Fig. 2. Variable temperature magnetic susceptibility plot of $\text{Fe}(\text{4-acetyl pyridine})_2[\text{Pd}(\text{CN})_4] \cdot 1.5 \text{ MeOH}$ (1·1.5MeOH), (solvated: orange), 1·0.4MeOH (partial desolvated: blue) and 1 (Complete desolvated: green).

Overall, the work initiated during my stay at ICC-IMR is very much collaborative in nature and will need further experiments to conclude. We look forward to completing all the experiments and characterization to write a paper together, where ICC-IMR will be acknowledged with due credits.

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