Experimental report

19/09/2024

Proposal:	**5-31-3011**	**Council:**	10/2023

Title: Modulation of Spin-Crossover in Metal¿Organic Frameworks by magnetic and non-magnetic ionic-liquid guests

Research area: Materials

This proposal is a new proposal

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Samples: [Fe(pz)Ni(CN)4]
[Fe(pz)Ni(CN)4]@EMIM-TFSI

Instrument	Requested days	Allocated days	From	To
D20	3	2	02/04/2024	04/04/2024

Abstract:

The study focuses on the modulation of the spin-crossover (SCO) behaviour of [Fe(pz)Ni(CN)4] metal-organic framework. This SCO of [Fe(pz)Ni(CN)4] can be influenced by the inclusion of solvents in its pores, but this strategy often compromises the chemical stability of the system due to solvent volatility. To advance this research, the impact of hosting non-volatile ionic liquids (ILs), which can contain diamagnetic/paramagnetic components within the MOF's pores is explored. ILs can modify the SCO behaviour shifting or expanding the temperature range where it occurs, or even partially or fully blocking it. However, determining the precise location of ILs in the MOF's crystal structure is challenging due to it disorderly distribution and the similarity between the X-ray scattering factors of the IL and the host-framework. The objective pursued by this experiment is to uncover the crystal and magnetic structural changes induced by ILs when integrated into MOF, especially above and below the temperatures of the SCO transition. Additionally, the study seeks to identify the ILs' location within the MOF's pores and investigate any magnetic ordering generated at low temperatures.

Experiment nº: 5-31-3011

Instrument: D20

Dates of experiment: 02/04/2024-04/04/2024

Title: Modulation of Spin-Crossover in Metal-Organic Frameworks by magnetic and non-magnetic ionic-liquid guests

The control over the spin crossover (SCO) transition in microporous metal-organic frameworks (MOFs) is of current interest not only for their intrinsic fundamental properties, but also due to their potential application. SCO- MOFs are usually build up from iron ions that can be reversibly switched between low-spin (LS) and high-spin (HS) electronic configurations by an external stimulus (i.e. T, P, light, pulsed magnetic fields, and even by chemical species). HS and LS states of microporous SCO reveal differences in magnetism, optical properties and dielectric constant, which opens the perspective to engineer switchable materials highly appealing for their application as optical devices, sensors, actuators or memory-storage systems[1].

Among the multiple microporous SCO materials, [Fe(pz)Ni(CN)4]·Guest, (where pz is pyrazine) exhibits hysteretic spin-crossover at ambient conditions and is robust to the adsorption and desorption of a wide range of small molecular guests. The wide-research developed on these Hoffman-type materials demonstrated that the temperature of the SCO transition is modulated (I) by the order-disorder transition of the crystal structure and, specifically, of the pyrazine pillars[2]; and (II) by the internal pressure and chemical interactions of the guest molecules with the host framework, particularly by their effects on the coordination environment of the iron ions of the structure[3]. Although tuning the SCO transition by including volatile guests into $[Fe(pz)Ni(CN)_4]$ has interesting potential implications for sensing or gas-adsorption/separation, the thermal stability of the guest loaded materials is limited to the desorption temperature of the solvent. Here is where the incorporation of ionic liquids (ILs) as guest of SCO-microporous MOFs makes the difference. ILs are salts in the liquid state that exhibit a negligible vapour pressure. Their chemical versatility enables the combination of a myriad of organic and inorganic cation and anion components, which endow the IL with specific properties. Furthermore, the inclusion of metal-based anions into the IL gives rise to magnetic liquids. Overall, by selecting the proper constituents of the IL, we can install permanent guest molecules within SCO-MOFs, hence inducing a modulation of: (I) the internal pressure of the IL-guest to the framework (molecular size of the IL and host-guest chemical affinity), and (II) the paramagnetic response of the host altered by the paramagnetic ordering of the ILs encapsulated within the pore space.

Our study is focused on the integration of different amounts of EMIM-TFSI, EMIM-$NiCl_4$, EMIM-CoSCN and EMIM-$FeCl_4$ ILs into the pore space of $[Fe(pz)Ni(CN)_4]$ until reaching full-saturation of the pore space. With IL incorporation, we have verified that both the loading of the IL and the characteristics of the IL can be used to modulate or even suppress the SCO transition temperature. The objective of this experiment was to investigate, by temperature dependent neutron diffraction, samples comprising MOF and MOF with IL incorporated, below (150K) and above (250K) the MOF SCO temperature transition. The obtained neutron diffraction data (Figure 1) reveals that the MOF itself does not change its crystalline structure when analysed below the SCO (150K) or above SCO (250K). In addition, the incorporation of IL into the MOF framework in some cases do not change the crystalline structure of the MOF, as it happens for EMIM-CoSCN and EMIM-$NiCl_4$ samples. However, in other cases, for high-spin configuration, meaning above SCO (250K), the crystalline structure of the MOF changes (Figure 2) as with the case of EMIM-TFSI and EMIM-$FeCl_4$ samples. In this latter case, additional reflections when loading IL to MOF appear. These are clearly related to a superstructure, but we are still trying to determine if the super-oder comes from the magnetic contribution of the framework, or from the ordering of the IL molecules within the pore space MOF.

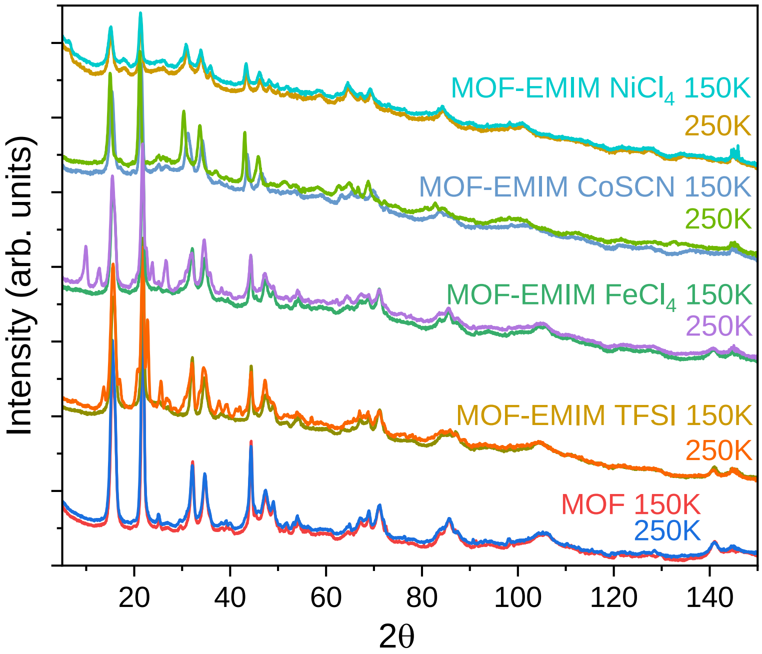

Figure 1. Powder neutron diffraction data obtained from D20 at different temperatures for MOF and MOF with loaded IL samples.

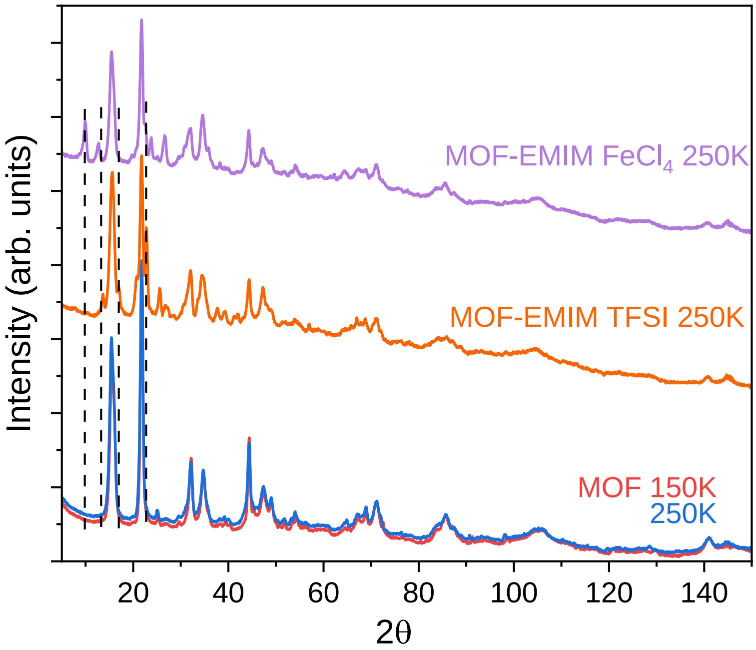

Figure 2. Powder neutron diffraction data obtained from D20 at different temperatures for MOF and MOF with loaded IL samples where different crystalline pattern was detected (marked by dashed lines).