Experimental report

24/04/2026

Proposal: 6-07-146 **Council:** 10/2024

Title: Modulation of Spin-Crossover in Metal¿Organic Frameworks by Ionic-Liqid Guests

Research area: Materials

This proposal is a resubmission of 6-07-130

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Samples: [Fe(pz)Ni(CN)4]@[Bmim]2[NiCl4]
[Fe(pz)Ni(CN)4]@[Emim][TFSI]2
[Fe(pz)Ni(CN)4]@[Emim]2[CoSCN]
Fe(pz)Ni(CN)4

Instrument	Requested days	Allocated days	From	To
IN5	2	1	14/05/2025	16/05/2025
IN16B Si 111 BATS	3	3	16/05/2025	19/05/2025

Abstract:

The control over the spin crossover (SCO) transition in microporous metal-organic frameworks (MOFs) is of current interest due to their potential application. Although tuning the SCO transition by including volatile guests into [Fe(pz)Ni(CN)4] has interesting potential implications for gas-adsorption, the thermal stability of the guest loaded materials is limited. Here is where the incorporation of ionic liquids (ILs) as guest of SCO MOFs (SCO-MOF@IL) makes the difference. Their chemical versatility enables the combination of myriad of organic/inorganic components. Despite previous studies focusing on the structure of SCO-MOF@IL, the aspect of IL dynamics within [Fe(pz)Ni(CN)4] remains unexplored. Studying the dynamics of [Fe(pz)Ni(CN)4]@IL is crucial as it can unveil the interactive behaviours between IL-MOF, potentially leading to enhanced material properties, and SCO transition control. The mobility of the IL when confined in MOF is related with the internal pressure that it applies to the framework, that in turn is linked to the complete/partial locking of the SCO transition. These findings will contribute to the development of new materials with tunable properties.

Experiment n°: 6-07-146

Instrument: IN16B, IN5

Dates of experiment: 14/05/2025-19/05/2025

Title: Modulation of Spin-Crossover in Metal-Organic Frameworks by Ionic-Liquid Guests

The ionic liquid 1-ethyl-3-methylimidazolium bis(trifluoromethanesulfonyl)imide (EMIM–TFSI) is a room-temperature salt with a melting point around –17 °C (≈256 K). The cation $EMIM^+$ is a small aromatic imidazolium ring with short ethyl and methyl substituents, while the $TFSI^-$ anion is a bulky, flexible imide; both ions have comparable longest dimensions of roughly 0.7–0.8 nm. The charge is strongly delocalized over the imidazolium ring and over the N–S–O framework of $TFSI^-$, which weakens Coulomb coupling and favours liquid behaviour at low temperature. In the liquid, $EMIM^+$ and $TFSI^-$ interact via long-range electrostatics, supplemented by directional hydrogen bonding between ring/side-chain C–H groups and the sulfonyl oxygens, as well as dispersion interactions; each cation is coordinated by several anions and frequently exchanges "partners" on a picosecond–tens-of-picoseconds timescale. $[Fe(pz)Ni(CN)_4]$ is a Hofmann-type metal–organic framework composed of Fe^{2+} centers octahedrally coordinated by cyanide-bridged $[Ni(CN)_4]^{2-}$ units in the equatorial plane and pyrazine (pz) ligands in the axial positions. This connectivity generates a three-dimensional network with one-dimensional ultramicroporous channels of roughly 4 × 4 Å cross-section and an interlayer separation of about 7 Å. The Fe^{2+} sites undergo a spin-crossover transition between low-spin and high-spin states, so that $[Fe(pz)Ni(CN)_4]$ provides a well-defined, switchable host lattice in which the structure and dynamics of confined guest species such as ionic liquids can be systematically investigated.

Comparing QENS spectra of vanadium, MOF, and TFSI ionic liquids at q of 0.29 $Å^{-1,}$ which are normalized to unity at the maximum position, one can assume that the dynamics of hydrogen atoms in MOFs are relatively minor compared to the dynamics of ionic liquids within the experimental time window to probe. Most of the QENS scattering will come from ionic liquids.

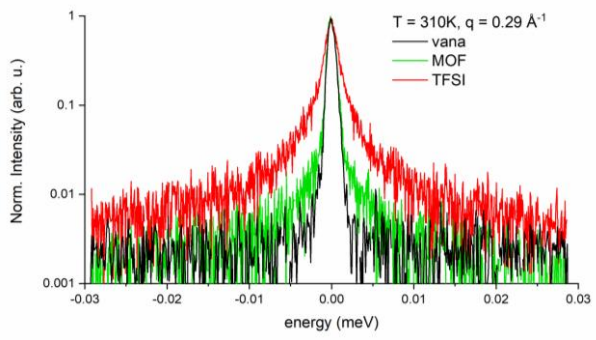

Figure 1. Comparison of QENS spectrum measured from Vanadium (black line), MOF (green line), and TFSI IL (red line) at q of 0.29 $Å^{-1}$ and at the temperature of 310K.

Another aspect to consider is the coherent scattering from the MOF, which is visible in the diffraction image (where all intensities are summed over the measurement's energy range).

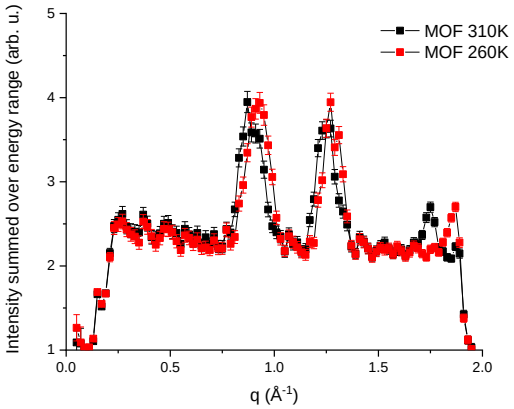

Figure 2. Comparison of MOF diffractograms measured at 310 K (black curve) and 260 K (red curve).

However, it seems that diffraction peaks do not affect the QENS broadening, as shown in the figures below, where QENS spectra of MOF 310K at q of 0.43 Å^{-1} and 0.59 Å^{-1} (q region before the first coherent peak) are compared with the QENS spectrum of MOF 310K at q of 0.95 Å^{-1}, where the scattering contribution of coherent scattering is present as a spike of elastic intensity.

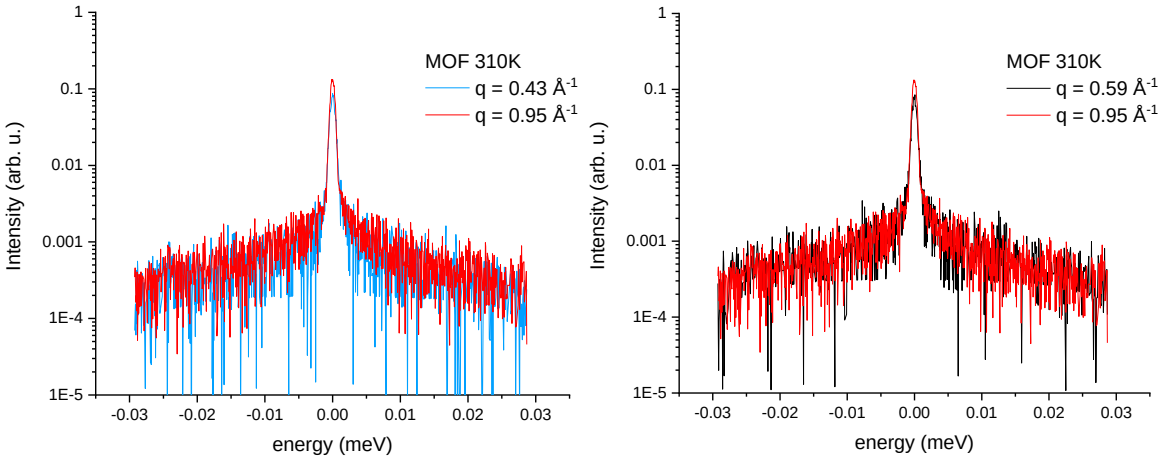

Figure 3. QENS spectra of MOF at 310K (left panel) and 260K (right panel). The figure shows that quasielastic broadening is independent of the coherent scattering and does not change whether it is measured in the q region of the coherent peaks or not.

It is a solid approximation that the coherent scattering from MOF will not affect the analysis of the QENS broadening in the mixed samples. The following analysis will focus on the dynamics of ionic liquids at two temperatures and how the MOF is restricting these dynamical motions.

Each QENS spectrum was fitted by a sum of an elastic contribution identical to the resolution function and two Voigt functions representing the convolution of a Lorentzian with the Gaussian resolution function. The HWHM of the Lorentzian curves as a function of Q^2 provides information on the type of motions. While Lorentzians exhibiting constant HWHM overall Q groups are indicative of relatively localized motions, like e.g., a rotational diffusion, the Lorentzian HWHM of a jump-diffusion follows

$$HWHM(\mathrm{Q}) = \frac{\mathrm{DQ}^2}{1+\mathrm{DQ}^2\tau},$$

Where τ represents the residence time before the jump, and D is the jump-diffusion constant.

The final model contained one quasielastic broadening with fixed HWMM of 0.025 meV and another quasielastic contribution with HWHM(q) corresponding to the jump-diffusion type of motion. It was possible to observe the change in the jump-diffusion motion of the EMIM cation as a function of the IL load and temperature.

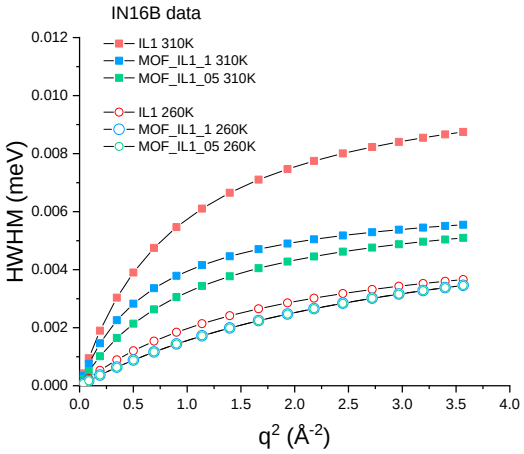

Figure 4. HWHM dependences. The plots show the HWHM Γ as a function of q for the IN16B data. Solid squares correspond to measurements at 310 K, while open circles correspond to 260 K. The red symbols represent the HWHM of the IL without MOF, the blue symbols correspond to the sample $[Fe(pz)Ni(CN)_4]@(ET)_{1.0}$ (1:1 filling), and the green symbols indicate the HWHM for the sample $[Fe(pz)Ni(CN)_4]@(ET)_{0.5}$, where only half of the MOF cells are filled with IL.

From the HWHM(q) dependences one can see that the MOF significantly restricts the dynamics of the IL at 310 K. Still, the comparison between the cases of high and low load, suggests that not all IL molecules experience the same degree of confinement: a fraction of the IL may remain outside the ultramicropores or in larger voids and can therefore move more freely. It is also possible that IL molecules move in and out of the MOF cells and, at high loading, cannot find an empty neighbouring cell as easily as in the sample with lower IL content, which further slows down the effective jump diffusion.

At 260 K, the HWHM(q) curves for all samples are very similar, indicating that the dynamics are strongly reduced on the 20–800 ps timescale. In this regime, once an IL molecule enters a MOF cell, its motion is so slow that it effectively remains trapped inside the pore and can no longer escape within the experimental time window.

These are the results obtained for the moment. The rest of the data is still under treatment.