# Experimental report

08/02/2016

**Proposal:** **7-05-426** **Council:** 4/2014

**Title:** Investigation of the binding and rotating door mechanism for CO2 sorption in the 1D spin-crossover coordination polymer Fe(btzx)3(ClO4)2

**Research area:** Physics

**This proposal is a new proposal**

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**Samples:** Fe(C10N8H10)3(ClO4)2

| Instrument | Requested days | Allocated days | From | To |
|---|---|---|---|---|
| IN5 | 3 | 3 | 06/10/2014 | 09/10/2014 |
| IN1 LAG | 3 | 3 | 30/09/2014 | 03/10/2014 |

## Abstract:

Fe(btzx)3(ClO4)2 (btzx = 1,4-bis(tetrazol-1-yl-methyl)benzene) is a FeII coordination polymer with no permanent channels that displays internal voids of ca. 9 Å in diameter, each being capable to accept one molecule of CO2 at 1 bar and 273 K. X-ray diffraction has provided direct structural evidence of the location of the gas molecules inside the cavities. The mechanism for the gas molecules to enter is unclear, although the most plausible mechanism for CO2 sorption consists in the rotation of the phenyl rings of the btzx, as this would permit the connection between voids of different chains. In this proposal we intend to investigate, by means of quasielastic and inelastic neutron scattering, the mechanism of CO2 sorption. In order to elucidate the pathway of entrance of the gas molecules in the internal voids, quasielastic neutron scattering will be used to verify the rotating door mechanism. In addition, a high energy dynamics study at IN1-Lagrange would provide with information of the interaction between the CO2 molecules and the framework. For this purpose, we apply for beam time at IN5 and IN1-Lagrange to investigate the dynamic properties of this 1D coordination polymer.

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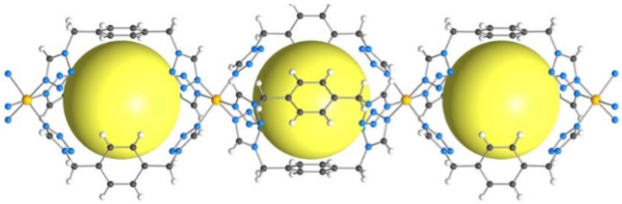

Figure 1. (a) Crystal structure of compound **1**. The yellow spheres are a visual indication of the empty space of the internal voids, where the CO2 molecules are physisorbed

The Inelastic Neutron Scattering (INS) spectra shown in Figure 2a was measured at 5 K in the range of energy transfers from 16 to 4000 $cm^{-1}$ with and energy resolution of $\Delta E/E \approx 2$ using LAGRANGEIn the present experiment the energy transfer was calculated by substracting 4.5 meV, the energy of the PG crystals in the ellipsoid, from the energy of the incoming neutrons selected with a focusing Cu(220) single crystal and bent Si(111) and Si(311) reflections. The background spectrum from the cryostat and an empty sample holder was measured separately and then substracted from the raw INS spectrum of the sample. Data sets were then normalized for monitor counts and corrected for empty cell. The sample was placed in an Al cell connected to the gas injection stick. For the measurement of the $CO_2$-loaded compound, the samples were saturated with $CO_2$ by injecting gas at 900 mbar at room temperature and then cooled while keeping the gas pressure constant.

We have succeeded to observe the scattering of the adsorbed CO2 molecules despite their small scattering cross-section. As far as we know, this is the first time that the neutron vibrational spectrum of adsorbed CO2 in a MOF has been measured. Specifically, we unambiguously observe an increase in band intensity at 650 $cm^{-1}$ (81 meV) upon CO2 sorption, which is the only change observed in the 500–800 $cm^{-1}$ region (Figure 2b) that corresponds to the bending of the CO2 molecule.

Furthermore, combination of INS and Density Functional Theory (DFT) calculations allow a full description of the experimental spectra. Figure 3a shows the calculated spectra of bare CCP-1 and loaded with CO2, showing an excellent agreement with the experimental spectra. The vibrational spectra of CCP-1 remains practically unchanged upon CO2 sorption, which is consistent with a minor distortion of the framework.

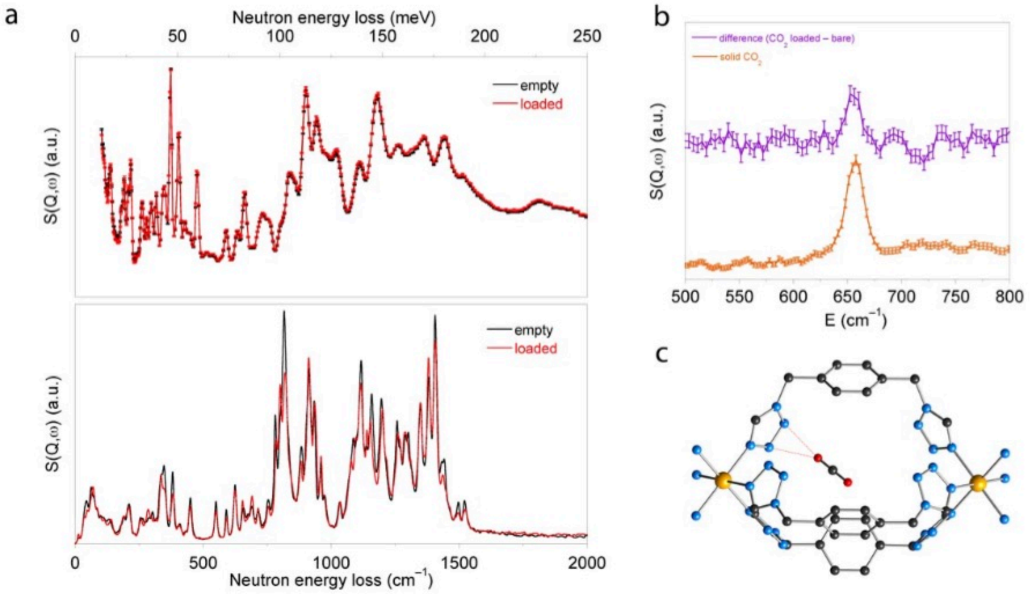

Figure 2 (a) Comparison of the experimental (top) and DFT-calculated (bottom) INS spectra for bare CCP-1 (in black) and CCP-1 loaded with $CO_2$ (in red). (b) Difference plot for experimental INS spectra CCP-1 loaded with $CO_2$ and bare CCP-1, and that of solid $CO_2$. (c) Crystal structure of the CCP-1 loaded with $CO_2$, showing the end-on interaction between the gas molecules and the framework. Hydrogen atoms and anions omitted for clarity. Key: Fe, orange; C, gray; N, blue; O, red.

Diffusion mechanism. Given the lack of permanent channels in compounds CCP-1 and CCP-2, the most plausible mechanism for gas sorption consists in the rotation of the phenyl rings of the btzx ligands, which block the access to the cavity. In order to gain insight on the mechanistic aspects of the gas sorption, we have combined Quasielastic Neutron Scattering (QENS) experiments with Molecular Dynamics simulations. QENS experiments were performed in the direct time-of-flight spectrometer IN5 using two different incident neutron wavelengths: $\lambda$=5 Å, giving an energy resolution of 0.1 meV (FWHM) and a Q-range of 0.2–2.2 Å$^{-1}$, and $\lambda$=8 Å, resulting in a resolution of 0.25 meV and a Q-range of 0.2-1.4 Å$^{-1}$. The sample was placed inside a cylindrical aluminium sample holder allowing the gas injection. Bare and $CO_2$-loaded **CCP-1** was measured at 10 selected temperatures between 10 K and 320 K, with acquisition times of 1 hour. For the measurement of the $CO_2$-loaded compound, the samples were saturated with $CO_2$ by injecting gas at 900 mbar at room temperature and then cooled while keeping the gas pressure constant.

[1] M. Giménez-Marqués, N. Calvo Galve, M. Palomino, S. Valencia, F. Rey, G. Sastre, I. J. Vitórica-Yrezábal, M. Jiménez-Ruiz, J. A. Rodríguez-Velamazán, M. A. González, E. Coronado, G. Mínguez Espallargas, *Nature Chem., submitted*