### **Supporting Information**

## **Fe<sup>III</sup>/Fe<sup>II</sup> Regular Charge Order in Metal-Organic Framework**

#### Manuela Eloísa Medina, Yves Dumont, Jean-Marc Grenèche and Franck Millange<sup>\*</sup>

#### Synthesis and Characterization of Fe<sub>0.5</sub><sup>III</sup>Fe<sub>0.5</sub><sup>III</sup>(OH,F)(O<sub>2</sub>C-C<sub>6</sub>H<sub>4</sub>-CO<sub>2</sub>).DMA<sub>0.5</sub>

 $Fe_{0.5}^{III}Fe_{0.5}^{II}(OH,F)(O_2C-C_6H_4-CO_2).DMA_{0.5}$  was synthesized under solvothermal conditions from an equimolar amount of iron(III) chloride hexahydrate FeCl<sub>3</sub>.6H<sub>2</sub>O (Aldrich, 97%, 1mmol), terephthalic acid HO<sub>2</sub>C-C<sub>6</sub>H<sub>4</sub>-CO<sub>2</sub>H (Alfa, 97%, 1mmol), hydrofluoric acid (5*M*, 1 mmol) in N,N'dimethylformamide (Aldrich, 99%, 1mL) heated at 423 K (1h/12h/1h). Reactants were stirred a few minutes before introducing the resulting suspension in a Teflon-lined steel autoclave. The main difference with the solvothermally synthesis of the pure ferric Fe<sup>III</sup>Fe(OH,F)(O<sub>2</sub>C-C<sub>6</sub>H<sub>4</sub>-CO<sub>2</sub>).DMF concerns the initial volume of DMF used (Aldrich, 99%, 5mL) and the reaction time (3 days at 423 K).

Quantitative elemental analyses (performed using ICP-MES for Fe, Schöniger flask combustion followed by titration for fluorine and by combustion analysis for CHN, by Medac Ltd., U.K.) gave the following results: Fe: 22.0%; C: 41.6%; H: 3.38%; N: 2.68% and F: 1.31% which compare well with those calculated from the formula  $Fe_{0.5}^{III}Fe_{0.5}^{II}(OH)_{0.8}F_{0.2}(O_2C-C_6H_4-CO_2).DMA_{0.5}$ : Fe: 21.5%; C: 41.5%; H: 3.41%; N: 2.69% and F:1.46%.

Orange parallelepiped-shaped crystals were selected under polarizing optical microscope and glued on a glass fiber for single-crystal X-ray diffraction experiment. X-ray intensity data were collected in a Bruker SMART CCD diffractometer equipped with a normal focus, 2,4 kW sealed tube X-ray source (MoK<sub>a</sub> radiation,  $\lambda = 0,71073$  Å). Data were collected at room temperature and also at 100K, over a hemisphere of the reciprocal space by a combination of three sets of exposures. Each exposure of 20 s covered 0.3° in  $\varpi$ . Unit cell dimensions were determined by a least-squares fit of 50 reflections with  $I > 20\sigma$  (I). The structure was solved by direct methods. The final cycles of refinement were carried out by full-matrix least-squares analyses with anisotropic thermal parameters for all non-hydrogen atoms. Calculations were carried out with SMART software, for data collection and reduction, and SHELXTL.<sup>1</sup>

The <sup>57</sup>Fe Mössbauer spectra were recorded in transmission geometry using a conventional constant acceleration spectrometer with a  ${}^{57}$ Co(Rh) source. The powdered sample was located either in a bath cryostat at liquid nitrogen temperature under helium gas or at room atmosphere at 300K. The isomer shift values are quoted to that of  $\alpha$ -Fe standard at 300K.

# <u>S1: Comparison between the collected powder pattern of $Fe_{0.5}^{III}Fe_{0.5}^{III}(OH,F)(O_2C-C_6H_4-CO_2).DMA_{0.5}$ and the calculated powder pattern from the structural model.</u>



<u>Figure S1.</u> Simulated powder pattern (top) of  $Fe_{0.5}^{III}Fe_{0.5}^{III}(OH,F)(O_2C-C_6H_4-CO_2)$ .DMA<sub>0.5</sub> from single crystal data and powder pattern of the bulk (bottom) using Cu K<sub>a</sub> radiation.

# S2: Characterisation for Fe<sup>III</sup>(OH,F)(O<sub>2</sub>C-C<sub>6</sub>H<sub>4</sub>-CO<sub>2</sub>).H<sub>2</sub>O after rehydration

The structure of the Fe<sup>III</sup>(OH,F)-(O<sub>2</sub>C-C<sub>6</sub>H<sub>4</sub>-CO<sub>2</sub>).H<sub>2</sub>O material has been described previously.<sup>2</sup> In this fluorinated version, Fe<sup>III</sup>(OH,F)-(O<sub>2</sub>C-C<sub>6</sub>H<sub>4</sub>-CO<sub>2</sub>).H<sub>2</sub>O, the MIL-53 framework is in its "closed" form and only one type of channel is observed showing the influence of the presence of some fluoride ions. There are hydrogen bonding interactions (i) between water molecules and the framework hydroxide ions that bridge the Fe(III) centers that form the backbone of the infinite inorganic chains running parallel to *c* and (ii) between guest water molecules located in lozenge shaped channels running parallel to the inorganic chains. The closest O--O contacts provide clear evidence for the presence of two types of hydrogen bonds: O1-Ow1 = 2.746(5) Å between guest water and the framework and Ow1-Ow1 = 2.865(9) Å leading to water dimerization.





<u>Figure S2</u>. Two views of the structure of  $Fe^{III}(OH,F)-(O_2C-C_6H_4-CO_2)$ . H<sub>2</sub>O (top) in the (*ab*) plane showing oxygens of water molecules within the lozenge-shaped channels and (bottom) in the (*bc*) plane showing hydrogen bonding interactions (dotted lines) between water and framework oxygens.

## S3: Magnetic susceptibility vs temperature $\gamma(T)$ and magnetization vs field M(H) of <u>Fe<sub>0.5</sub><sup>III</sup>Fe<sub>0.5</sub><sup>II</sup>(OH,F)(O<sub>2</sub>C-C<sub>6</sub>H<sub>4</sub>-CO<sub>2</sub>).DMA<sub>0.5</sub></u>

In order to precise the characteristics of the magnetic transition peaked at 17K and 41K, we have performed both magnetic susceptibility  $\chi$ =M/H vs temperature  $\chi$ (T) at fixed magnetic field (fig. S3), and magnetization curves vs field M(H) at fixed temperatures (fig. S4). The figure S3 shows that the antiferromagnetic 3D long range order, associated to the 17 K sharp peak, is destroyed by a magnetic field of 5.5 T with a magnetization increasing to a saturation value at low temperature. The broad peak at 41K is not affected by field as high than 5.5 T. The ferrimagnetic intra-chain order has a spin flop critical field H<sub>c</sub> between 1 T and 5.5 T. This critical field H<sub>c</sub> corresponds to the ordering 3D energy. A more precise value of H<sub>c</sub> can be deduced from the magnetic field dependent magnetization M(H) of the polycrystalline powder. Figure S4 shows that H<sub>c</sub> seems to saturate at around 2 T below 10K. No hysteresis has been found at lower field than H<sub>c</sub> for T=5K, 10K, 20K, 30K, 40K, 50K, showing the very low ferrimagnetic response. This is coherent with the positive upturn of the 1/ $\chi$  versus T data below 150K and 41K (figure 4).



Figure S3. Temperature dependence of the magnetic susceptibility  $\chi$  at 1 Tesla (diamonds) and at 5.5 Tesla (stars).



<u>Figure S4</u>. Magnetic field dependence of the magnetic moment per molecule (cycles  $-5.5T \rightarrow +5.5T \rightarrow -5.5T$ ) for different temperatures.

- <sup>1</sup> Software for the SMART System V5.04 and SHELXTL V5.1; Bruker-Siemens Analytical X-Ray Instrument Inc., Madison, WI, 1998.
- F. Millange, N. Guillou, M. E. Medina, G. Ferey, A. Carlin-Sinclair, K. M. Golden, and R. I. Walton, *Chem. Mat.*, 2010, 22, 4237.