A spin crossover porous hybrid architecture for potential sensing applications

Antoine TISSOT\textsuperscript{a,b}*, Xavier KESSE\textsuperscript{b}, Styliani GIANNPOULOU\textsuperscript{a}, Ingrid STENGER\textsuperscript{c}, Laurent BINET\textsuperscript{d}, Eric RIVIERE\textsuperscript{e}, Christian SERRE\textsuperscript{a,b}*

1/ Synthesis
All reactants were purchased from commercial suppliers and used without further purification.

* MIL-100(Al) has been prepared as previously described with microwave-assisted hydrothermal synthesis (A. Garcia Marquez et al., Eur. J. Inorg. Chem. 2012, 5165–5174). Aluminum nitrate nonahydrate (1.43 g, 5.68 mmol) and trimethyl trimesate (1.21 g, 4.82 mmol) were dissolved in distilled water (20 mL) with vigorous stirring. Nitric acid (4 mL, 4 M) was added, and the reaction mixture was stirred for 5 min at room temperature and then introduced into the microwave oven. After hydrothermal treatment at 210 °C (1600 W) for 20 minutes, the resulting mixture was cooled down and a yellow solid was recovered by centrifugation. MIL 100(Al) was further activated by dispersing the recovered solid into methanol overnight (50 mL).

* The Fe(sal\textsubscript{2}trien)\textsuperscript{+} complex has been synthesized in the pores of MIL-100(Al) through a 2 step process: first, 100 mg of MIL-100(Al) and 200 mg of Fe(NO\textsubscript{3})\textsubscript{3}.9H\textsubscript{2}O (0.50 mmol) has been dispersed in 10 mL of CHCl\textsubscript{3}. The dispersion has been left for stirring 24h and the resulting solid has been collected by centrifugation. In a second step, it has then been redispersed in 10 mL of CHCl\textsubscript{3} containing an excess of the in-situ synthesized sal\textsubscript{2}trien ligand (obtained by adding 213 \textmu L of 3,6-Diazaoctane-1,8-diamine (1.43 mmol) and 293 \textmu L of salicylaldehyde (1.37 mmol) to the solution) and left 24h for stirring. The resulting purple solid has been collected by centrifugation and washed several times with ethanol and water until a clear supernatant is obtained, indicating that all the complexes synthesized outside the MOF porosity have been removed. The purple solid has then been dried under vacuum before characterization.

2/ Methods

- powder XRD:
The powder diffraction data were measured at room temperature on 0.7 mm glass capillaries with a Bruker D8 Advance diffractometer in Debye-Scherrer geometry, in the 2\texttheta range 2-40°. The diffractometer is equipped with a Ge(111) monochromator producing Cu K\alpha radiation (\lambda = 1.540598 Å) and a LynxEye detector.

- Thermogravimetric analysis (TGA):
TGA were performed on Mettler Toledo TGA/DSC 1, STAR®System apparatus under N\textsubscript{2} atmosphere, at a heating rate of 5 °C.min\textsuperscript{-1} up to 600 °C.

- Raman spectroscopy:
The Raman scattering spectra were recorded in backscattering geometry using a high-resolution Raman spectrometer setup (Labram HR800 from HORIBA Jobin-Yvon). An Argon ion laser operating at 514.5 nm is focused onto the sample through a 50x objective with a numerical aperture of 0.50 to form an illumination spot of about 2 \textmu m in diameter. A 1800 lines/mm grating enables us to have each pixel of the charge-coupled detector covering 0.57 cm\textsuperscript{-1}. The laser power was kept below 1.2 mW to avoid sample heating.

- N\textsubscript{2} porosimetry:
N2 sorption measurements were performed at 77 K on Micromeretics Triflex apparatus. Prior to measurement, the solids were soaked in methanol for 1 day in order to fully exchange guest molecules. Then, the samples (ca. 40 mg) were activated by heating the powder at 150 °C under secondary vacuum for 12h.

- EPR spectroscopy:
Electron Paramagnetic Resonance (EPR) spectra were recorded at 10 K on a Bruker Elexsys E500 spectrometer operating at X band (9.3993 GHz) equipped with a SHQ cavity and an Oxford Instruments ESR900 cryostat. A modulation of the magnetic field at 100 kHz with amplitude of 5 G was applied to detect the absorption first derivative. The microwave power was kept at suitable low values (10 mW) to avoid saturation effects.
- **magnetic measurements:**
Magnetic measurements were carried out with a Quantum Design SQUID Magnetometer with an applied field of 5 kOe for the dried MIL100(Al)@Fe(sal$_2$trien) and 20 KOe for the hydrated compound. The samples were sealed in a quartz glass tube. To avoid artefacts, the sample holder was symmetrized with another quartz glass tube (Nieves Casañ-Pastor et al., *J. Appl. Phys.*, **1991**, 69, 5088-5091).

- **optical measurements:**
The optical spectra have been measured with a Varian Cary 300 Bio UV-Vis spectrometer equipped with an integration sphere in diffuse reflectance mode.

3/ **Evaluation of the loading by SEM-EDS and ICP-MS analysis**

![Figure S1: SEM image of the MIL-100(Al)@Fe(sal$_2$trien) sample.](image)

The SEM image evidences that the sample is composed by 100 nm large nanocrystals. This size corresponds to the one of the MIL-100(Al) particles used for the loading of the complex. The homogeneity of the sample is a first indication of the successful loading of the complex in the pore of the MOF, as we don’t see particles which may be correspond to the pure complex. To further evidence the homogenous loading of the Iron complex in the MOF, EDS analysis has been performed on different points of the sample. The results are given in the following table:

<table>
<thead>
<tr>
<th>Spectrum</th>
<th>1</th>
<th>2</th>
<th>3</th>
<th>4</th>
<th>5</th>
<th>6</th>
<th>7</th>
<th>8</th>
<th>9</th>
</tr>
</thead>
<tbody>
<tr>
<td>Al / atm %</td>
<td>93.07</td>
<td>92.92</td>
<td>92.65</td>
<td>92.80</td>
<td>93.49</td>
<td>92.28</td>
<td>90.80</td>
<td>91.20</td>
<td>93.44</td>
</tr>
<tr>
<td>Fe / atm %</td>
<td>6.93</td>
<td>7.08</td>
<td>7.35</td>
<td>7.20</td>
<td>6.51</td>
<td>7.72</td>
<td>9.20</td>
<td>8.80</td>
<td>6.56</td>
</tr>
</tbody>
</table>

<table>
<thead>
<tr>
<th></th>
<th>Al / atm %</th>
<th>Fe / atm %</th>
</tr>
</thead>
<tbody>
<tr>
<td>Max.</td>
<td>93.49</td>
<td>9.20</td>
</tr>
<tr>
<td>Min.</td>
<td>90.80</td>
<td>6.51</td>
</tr>
<tr>
<td>Average</td>
<td>92.52</td>
<td>7.48</td>
</tr>
<tr>
<td>Standard deviation</td>
<td>0.94</td>
<td>0.94</td>
</tr>
</tbody>
</table>

Iron is homogeneously distributed in the whole sample, the average value of Iron and Aluminum content are (in atomic %):

For MIL-100(Al), one unit-cell contain 864 Aluminum atoms (96×9). EDS gives an Al/Fe ratio of 12.4. Therefore, we can calculate the number of Iron atom per unit-cell: 864/12.4 = 69.8. The N$_2$ sorption isotherm at 77 K indicates that the Iron complexes are only located in the large pores of the structure. In the MTN topology, each unit-cell contains 8 large cages. Therefore, we can calculate the average number of complexes per large cage: 69.8/8 = 8.7.

At this stage, we can evaluate the average occupancy of the large cage. This cage can be modeled by a sphere with a diameter of 25 Å, which corresponds to a volume of $V_{MOF}=4/3.\pi.(25/2)^3=8180$ Å$^3$. On the other hand, we can estimate the volume of the Fe(sal$_2$trien)(NO$_3$) complex at $V_{complex} = 540$ Å$^3$ from its single crystal structure. The experimental value of 8.7 complexes
per cage thus corresponds to an occupancy of $8.7 \times 540/8180 = 0.57$, which is in qualitative agreement with the pore size distribution extracted from the N$_2$ sorption experiment, which indicates that around 50% of the large cages are occupied.

Dosing of Fe by ICP-MS:

9.61mg of purple hybrid solid has been dissolved in 10mL of concentrated nitric acid. A concentration of Fe in solution of 15.5ppm has been obtained by ICP-MS analysis of this solution, which corresponds to loading of Fe in the composite of 1.66 wt%.

The MOF formula is Al$_9$L$_6$O$_{12}$ with $L = C_9O_6H_3$ and $x=30$ according to TGA, which corresponds to a molar weight of MM=2217.0 g.mol$^{-1}$. The complex formula is FeC$_{20}$H$_{24}$N$_5$O$_5$, which corresponds to a molar weight of MM=469.9 g.mol$^{-1}$. Therefore, the composite formula is Al$_9$L$_6$O$_{12}$·30H$_2$O·(FeC$_{20}$H$_{24}$N$_5$O$_5$)$_x$, MM=(2217+469.9x) g.mol$^{-1}$, $x$ representing the amount of complex loaded in the MOF. Considering the iron dosing by ICP-MS, a value of $x=0.77$ can be obtained, which corresponds to an Al/Fe ratio of 11.7. This is in perfect line with the Al/Fe ratio of 12.3 obtained by EDX analysis.

4/ Thermogravimetric Analysis

![Figure S2: Thermogravimetric analysis of MIL-100(Al) after thermal treatment under vacuum at 150°C (black) and loaded with water (blue) and DMF (red).](image)

TGA analysis has been performed on MIL-100(Al) after thermal treatment under vacuum at 150°C for 6h (ie. in the conditions used for activation before N$_2$ sorption analysis). No significant mass loss is detected between 20 and 80°C, indicating that the water molecules initially located in the pores have been removed. After this thermal treatment, the powder has been exposed at room temperature to an atmosphere previously saturated with water or DMF vapours. TGA have been performed again after 1 night in contact with the vapours to evaluate the maximum water and DMF loading in MIL-100(Al). In both cases, around 30 wt% of vapour can be loaded in the MOF.

5/ Magnetic properties

The magnetic measurements have been processed as follows:

In a first state, the magnetization has been corrected from the diamagnetic contribution of both the sample holder (quartz tube) and the host diamagnetic MOF. This correction was performed empirically in order to get a MT product which remains constant at low temperature (below 200 K).

Then, the magnetization has been normalised by the magnetic field and the mass of compound loaded in the sealed tube (MOF + complex + solvent). This normalization leads to a magnetic susceptibility expressed by unit of mass, as shown in Figure S3.

Further normalization in order to get the magnetic susceptibility by mole of Fe(III) complex has not been performed due to the number of hypotheses needed for such purpose (diamagnetic correction, loading of complex in the MOF, amount of solvent in the pores…). Nevertheless, the magnetic susceptibility measurements unambiguously evidence that the HS fraction is much larger at any temperature in the unsolvated solid, compared to the hydrated one.
Figure S3: Evolution of the product of the massic magnetic susceptibility by the temperature as function of the temperature for MIL-100(Al)@Fe(sal₃trien) in both dry and hydrated states.

6/ Optical Spectroscopy

Figure S4: Optical absorption spectrum of MIL-100(Al) and MIL-100(Al)@Fe(sal₃trien), evidencing the color change of the solid upon complex loading.

In order to probe the influence of water loading on the optical spectrum, the sample was first dehydrated with a thermal treatment at 150°C under vacuum. The sample was then let in the sample holder in contact with air in order to absorb the water vapour from the atmosphere. Several cycles have been performed on the same sample in order to check the reproducibility of the process.
Figure S5: (left) Differential absorption spectrum monitored upon water sorption and (right) evolution of the absorbance at 510 and 660 nm upon water sorption.

7/ Infrared Spectroscopy

Figure S6: InfraRed spectra of MIL-100(Al), MIL-100(Al)@Fe(sal₃trien) and Fe(sal₃trien)NO₃.