Cations localisation within the pores of the crystal structure of a terbium-based luminescent MOF as a chemical sensor

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Metal organic frameworks (MOFs) are porous coordination polymers widely studied for their porosity and their applications, primarily in the storage and separation of molecules. Due to their high degree of coordination, lanthanide ions (Ln) can form stable MOFs. Furthermore, Ln ions exhibit an interesting luminescence signature with numerous very narrow emission bands, often in the visible spectrum, such as in the green region for the Tb^{3+} ion. It is possible to trap analytes within the host structure of Ln based MOFs and obtain a rapid response by measuring the luminescence intensity, thereby making these materials chemical sensors [1-3].
A MOF built from 2-hydroxy-1,4 benzene-dicarboxylate ligand ($OH\text{-}C_8H_3O_4$) and having the chemical formula $Ln(OH\text{-}C_8H_4O_4)(OH\text{-}C_8H_3O_4)\cdot 8H_2O$ has previously been reported for some lanthanides [4]. It possesses a cubic (Ia-3) structure with large square section channels (11×11 Å, Fig. 1) in which analytes can be trapped. The heteronuclear isotype MOF based on Tb^{3+} and La^{3+}, which emits green light, was synthesised by simple precipitation. The addition of La^{3+} ions (33% by Ln atom) is essential to stabilise this crystal structure type. The MOF in powder form was suspended in solutions of analytes (including Cr^{3+} and Fe^{3+} ions), with the resulting materials being termed analyte@MOF. A significant attenuation of the luminescence of the analyte@MOF is observed, making the MOF a detector for Cr^{3+} and Fe^{3+}. The chemical interactions between the MOF host structure and the analytes were investigated using powder X ray diffraction data recorded at the CRISTAL beamline at SOLEIL (at 140 K) with a Mythen detector. Tentative Rietveld refinements appear to demonstrate that the analytes are trapped within the pores of the host framework. The distances Cr Tb are short enough to cause luminescence quenching. The results are also discussed in the light of XPS spectroscopy experiments.

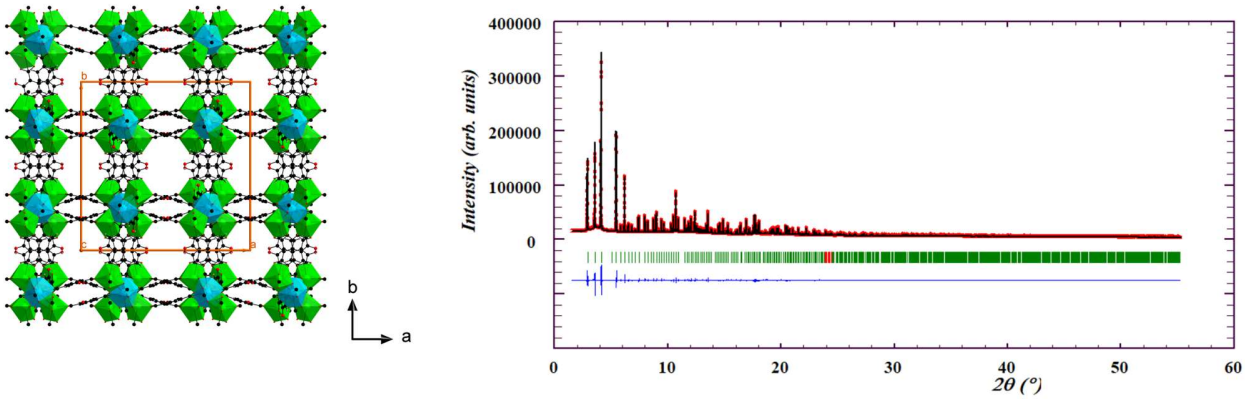


Figure 1. *On the left, a projection of the MOF crystal structure (empty pores). On the right, a Rietveld refinement of the powder pattern of Cr@MOF (CRISTAL beamline, SOLEIL).*

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[3] J.-X. Wang. et al., ACS Appl. Mater. Interfaces (2022). 14, 9970.
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