

## In Situ Diffraction Studies on Gas-Loaded Porous Framework Materials

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### Introduction.

One of our principal areas of research focuses on the capture and removal of harmful gases, such as carbon dioxide (CO<sub>2</sub>) and sulphur dioxide (SO<sub>2</sub>), by recently developed porous metal-organic frameworks (MOFs) and covalent organic frameworks (COFs).<sup>1</sup> MOF materials are porous frameworks constructed from metal ions or clusters bridged by functional organic ligands. MOFs usually adopt 3D extended crystalline structures, offering great promise for analysing the structural phase behaviour using diffraction methods. Capture and storage of CO<sub>2</sub> in MOFs is potentially of great significance in the development of the “Low-Carbon Economy” and thereby in the mitigation of global warming. However, the CO<sub>2</sub> adsorption capacities in MOFs under dynamic conditions have remained insufficient for practical applications, and strategies to enhance CO<sub>2</sub>/host interaction and hence adsorption capacity are required.

In this study, we have (i) determined the crystal structures of two COF samples (JJ104, JJ108) (Figure 1); (ii) investigated the factors controlling the capture capacity of CO<sub>2</sub> and SO<sub>2</sub> from gas mixtures under dynamic conditions; (iii) studied framework phase changes under different sample environments. We had previously established the solvated crystal structures of two framework materials (MIL-53 and NOTT-112) from single-crystal diffraction methods, and these materials show highly unusual gas uptakes with stepwise adsorption and hysteretic desorption isotherms. However, it was only by carrying out *in situ* powder X-ray diffraction measurements at ESRF Beamline ID31 that we were able to probe the interactions between adsorbed gas molecules and framework material and to study changes in the local framework structure upon guest inclusion.

### Experiment.

Monochromatic beam ( $\lambda = 0.495891 \text{ \AA}$ ), high resolution detector, Cryostream heater, *in situ* sample cell, gas loading/controlling system, data collection in capillary mode.

### Results and discussion.

#### Part I. Structure determination of covalent organic frameworks (COFs).

We have synthesised two organic molecular networks (denoted as JJ104, JJ108, see Figure) based on a dative boron-nitrogen bond. The Scheme below shows the experimental details used in this study. One equivalent of tetranitrophenylmethane was reacted with two equivalents of i) diboronate or ii) diboric acid in toluene/THF 2:1 v/v). These reactions gave pale, pink powders. Powder diffraction patterns confirmed the crystallinity of these materials. PXRD pattern for unprotected sample (JJ108) also showed 4 unindexed lines. PXRD pattern for JJ104 was indexed on a tetragonal cell with  $a = 16.85007$ ,  $c = 7.17798 \text{ \AA}$ ,  $V = 2038.0 \text{ \AA}^3$ . The structure of JJ104 was solved by *ab initio* methods in the tetragonal space group  $I4_1/a$  from this PXRD data. The un-indexed lines correspond to a small amount of boronic acid present as an impurity. Structure determination confirms the binding details of tetranitrophenylmethane network and hydrogen bonding interactions between these functional organic molecules. This structural analysis gives important insights into the inclusion of boronic acid into this network *via* a dative bond.

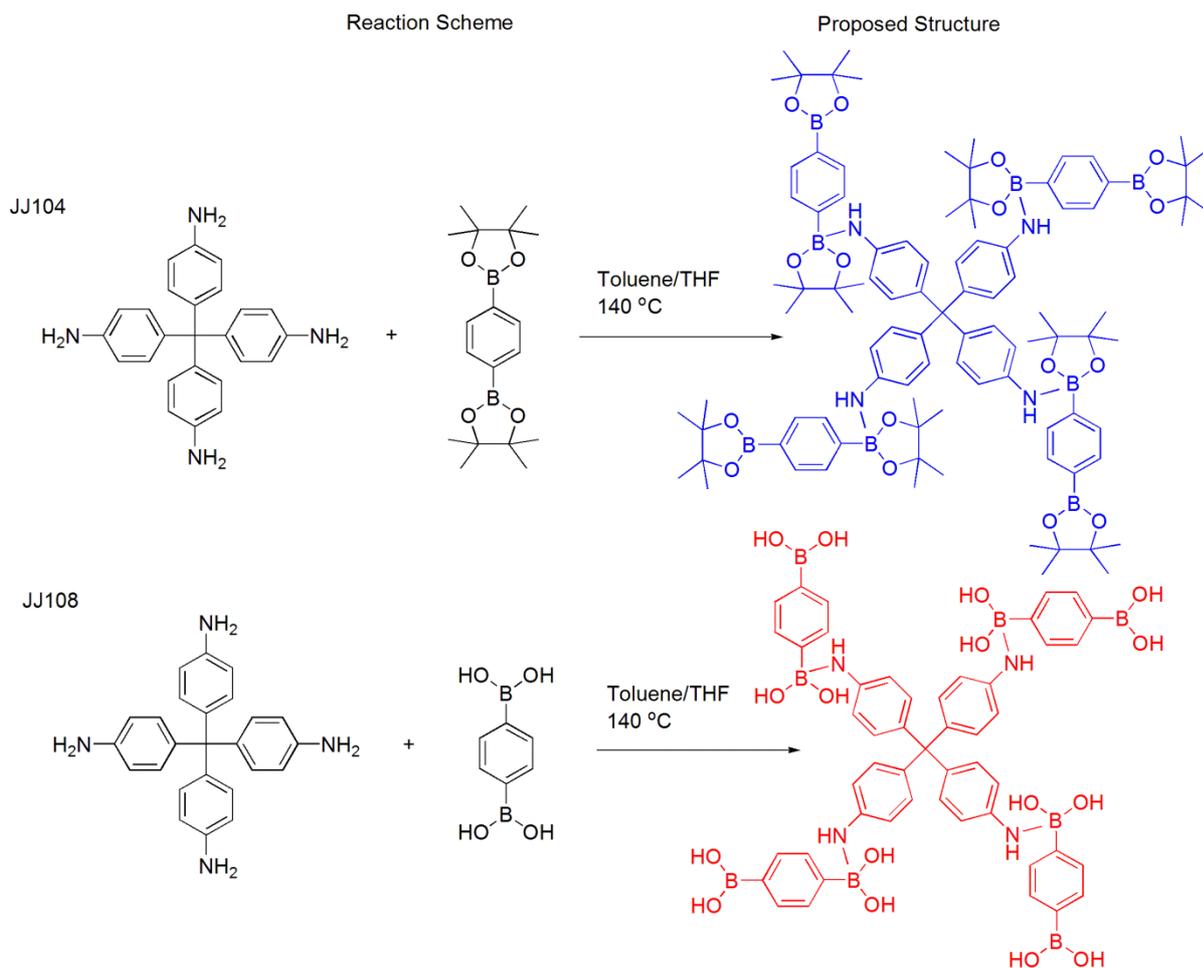


Figure 1. Synthetic schemes for two COFs samples (JJ104, JJ108).

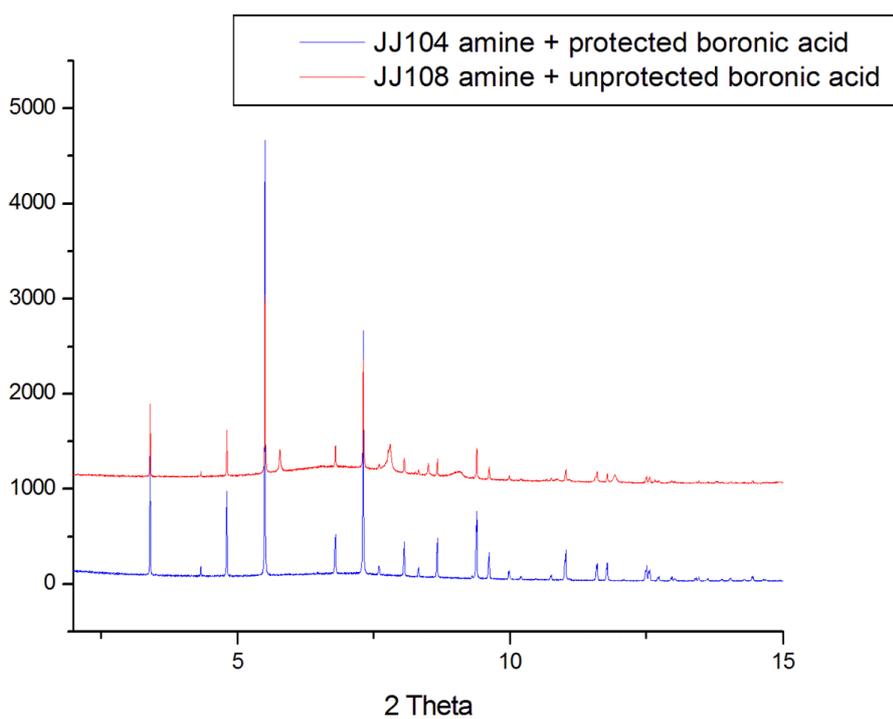


Figure 2. Comparison of the PXRD patterns for COFs sample synthesised from different routes.

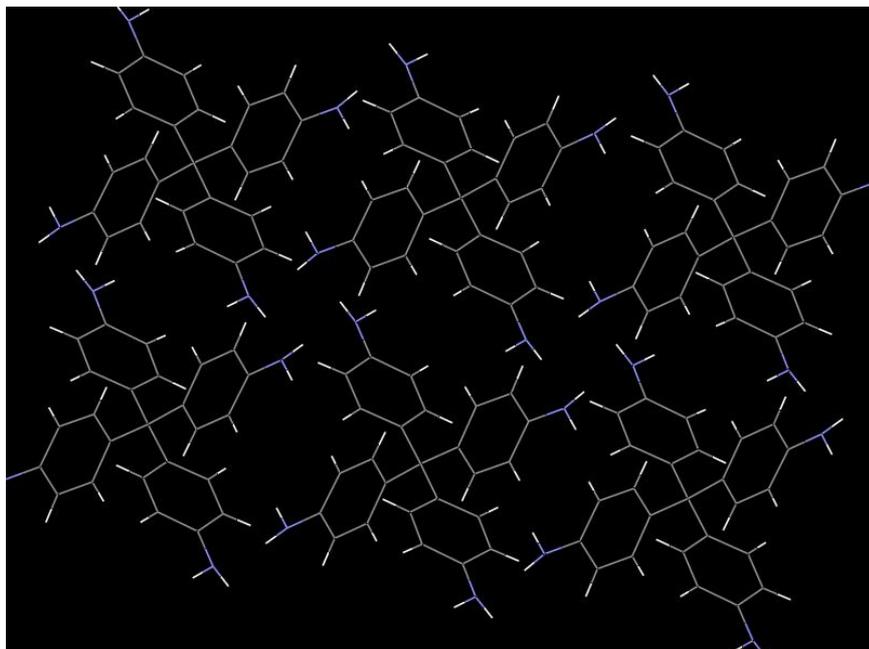


Figure 3. View of X-ray crystal structure for COF sample JJ104.

## Part II. Investigation of structural change of MIL-53(Al) with adsorption of SO<sub>2</sub> or CO<sub>2</sub>

We have recently developed a high pressure system for large scale synthesis of MOF materials. An important MOF material MIL-53(Al) was successfully produced using this system and required a much shorter synthesis time. It is interesting to study the structural dynamics of this MOF by *in situ* powder diffraction methods, because MIL-53(Al) exhibits dramatic framework transition linked to changes in pore volume, the so-called “breathing effect”. The framework pores can either expand or contract depending on the gas loadings, leading to the formation of distinct narrow pore (*np*) and large pore phase (*lp*) phases.

Two different experiments were carried out on MIL-53(Al) samples using the gas rig with SO<sub>2</sub> or CO<sub>2</sub>. The sample was firstly degassed under vacuum at 473 K, and then 10 psi of SO<sub>2</sub> was loaded at ambient temperature. Comparison of the PXRD patterns shows that the peaks shift to lower angles upon SO<sub>2</sub> loading (Figure 4); this corresponds to an expansion of the unit cell, suggesting the SO<sub>2</sub> was adsorbed into the framework pores. A second experiment was carried out with a fresh sample of MIL-53(Al), and again the sample was firstly degassed under vacuum at 473 K: ~15 psi of CO<sub>2</sub> gas was loaded into the desolvated material at ambient temperature. The PXRD pattern shows no noticeable shift in peak position, indicating no change in structure caused by the gas uptake. These results suggest the nature of MIL-53(Al) obtained from high pressure synthesis system is different from that obtained from traditional solvothermal reactions. Further investigations into the structural details of these samples are currently underway.

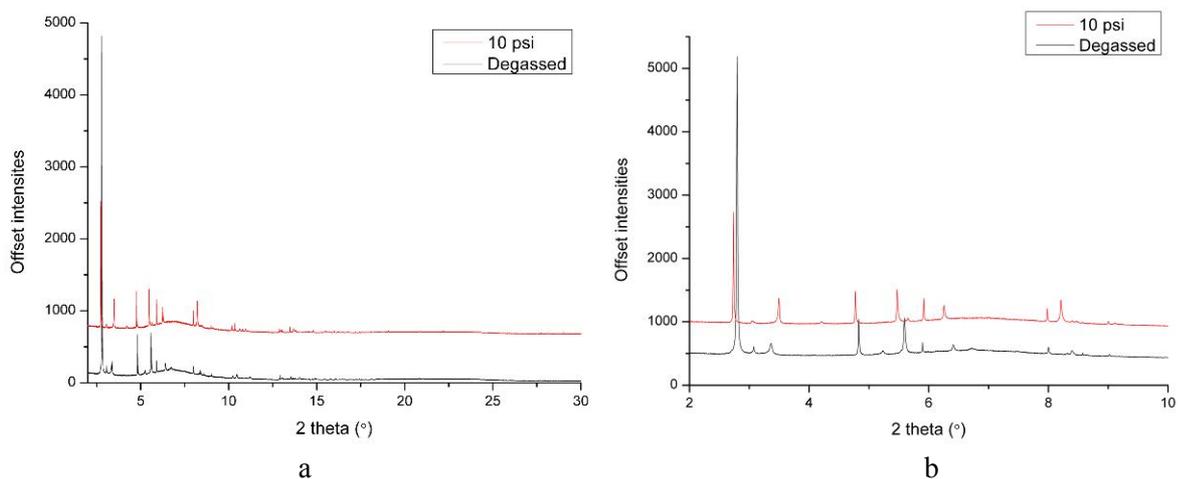


Figure 4. (a) Comparison of powder diffraction patterns of the desolvated MIL-53(Al) and the SO<sub>2</sub>-loaded (10 psi) MIL-53(Al) samples at ambient temperature. (b) A detailed view is shown in figure b.

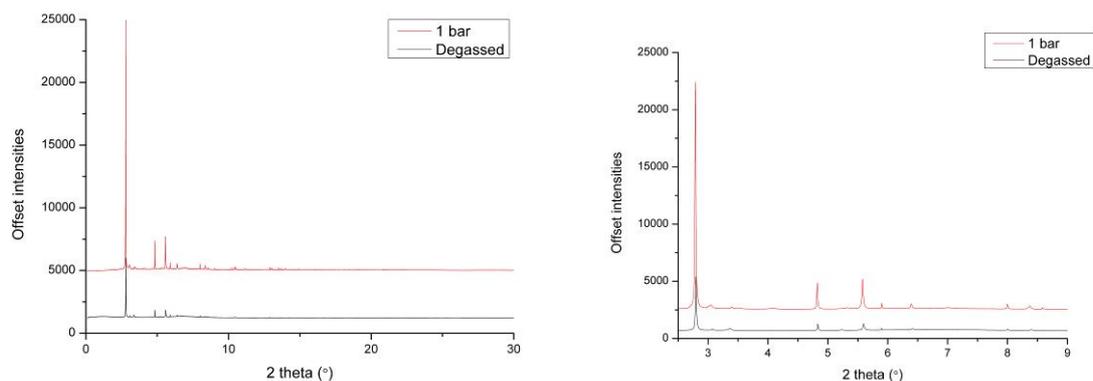


Figure 5. Comparison of powder diffraction patterns of desolvated MIL-53(Al) sample and CO<sub>2</sub>-loaded (15 psi) MIL-53(Al) sample at ambient temperature. A detailed view is shown in figure b.

### Part III. Investigation of structural change of a metal-ligand polyhedral framework NOTT-112

NOTT-112 is a polyhedral framework material comprising functional organic linkers and exposed Cu(II) sites (Figure 6). The X-ray powder diffraction data for the *in situ* desolvated and SO<sub>2</sub>-loaded (1.0 bar) sample were successfully recorded. The high crystallinity of the desolvated sample was confirmed with bulk purity. The PXRD pattern for the SO<sub>2</sub>-loaded NOTT-112 at 298 K and 1.0 bar shows shifts of peak positions and decrease of peak intensities, suggesting that the adsorption of SO<sub>2</sub> into the framework pores, and the framework structure was partially destroyed after SO<sub>2</sub> loading.

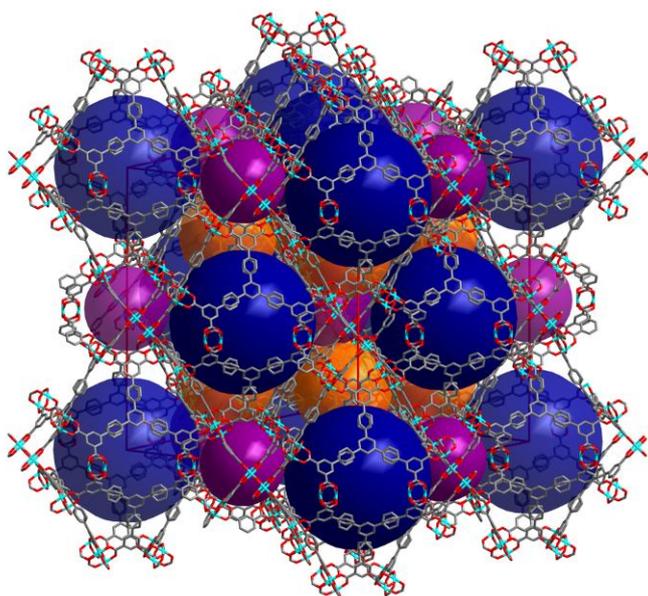


Figure 6. View of single crystal structure of NOTT-112.

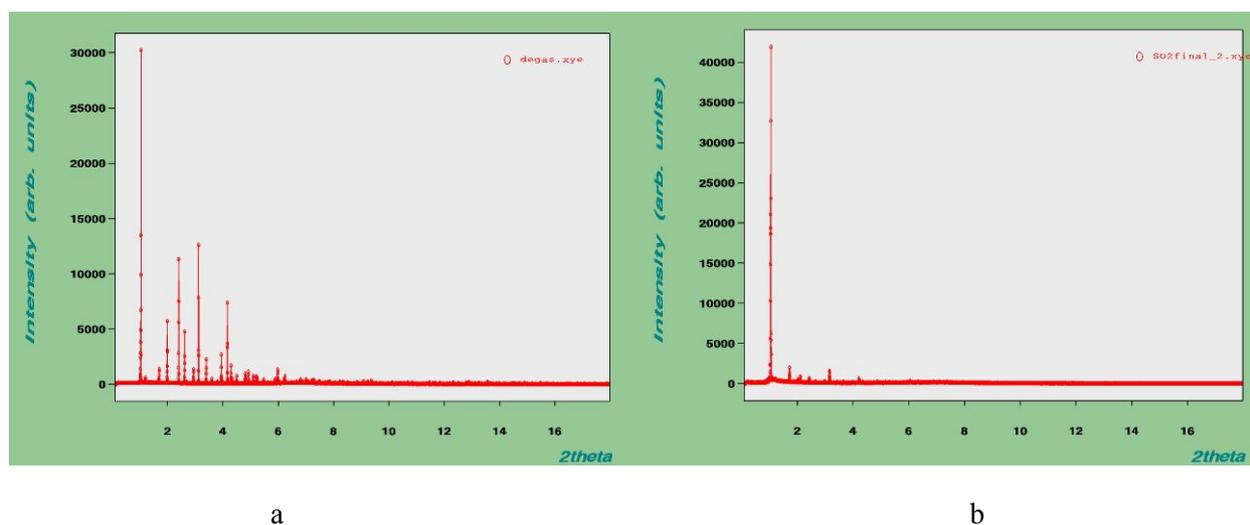


Figure 7. Synchrotron X-ray powder diffraction pattern for desolvated NOTT-112 (a) and SO<sub>2</sub>-loaded (15 psi) NOTT-112 at 298 K.

## Conclusion.

We were able to determine the supramolecular structure for COF materials (JJ104, JJ108) and gain the insight of the hydrogen bonding interactions between these functional molecules. *In situ* PXRD study were carried out with MIL-53(Al) and NOTT-112 samples as a function of CO<sub>2</sub> and SO<sub>2</sub> pressure, and we will explain the details for the framework phase behaviour upon gas loadings. This helped us to understand their unusual gas adsorption capacity and selectivity at a molecular basis.

## Reference:

1. J. R. Long and O. M. Yaghi, *Chem. Soc. Rev.*, 2009, **38**, 1201-1507.