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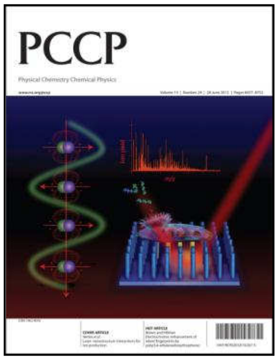

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Adsorption of N/S heterocycles in the flexible metal-organic framework MIL-53(Fe^{III}) studied by *in situ* energy dispersive X-ray diffraction

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Abstract

The adsorption of N/S-containing heterocyclic organic molecules in the flexible iron(III) terephthalate MIL-53, $Fe^{III}(OH)_{0.6}F_{0.4}(O_2C\text{-}C_6H_4\text{-}CO_2).(H_2O)$, from the liquid phase was studied with *in situ* energy dispersive X-ray diffraction (EDXRD), in order to follow the adsorption-induced expansion of the structure. For comparison with the diffraction data, liquid phase adsorption isotherms were recorded for uptake of benzothiophene, benzothiazole and indole in isopropanol and in heptane. The solvent not only influences pore opening but is also a competing guest. The *in situ* EDXRD experiments allow the kinetics of guest uptake and the competition with solvent to be monitored directly. Indole uptake is limited; this adsorbate is barely capable of opening the closed, either hydrated or dehydrated, MIL-53(Fe) structure, or of penetrating the isopropanol-containing material in the concentration range under study. When isopropanol is used as a solvent, the guest molecules benzothiophene and benzothiazole must be present at a certain threshold concentration before substantial adsorption into the metal-organic framework takes place, eventually resulting in full opening of the structure. The fully expanded structures of benzothiophene or benzothiazole loaded MIL-53(Fe) materials have *Imma* symmetry and a unit cell volume of *ca* 1600 Å^3, upon uptake of the guest molecules by the closed form (unit cell volume ~ 1000 Å^3) no intermediate crystalline phases are seen. Successful uptake by MIL-53(Fe) requires that the adsorbate is primarily a good hydrogen bond acceptor; additionally, based on UV-visible spectroscopy, a charge-transfer interaction between the S atoms of benzothiophene and the aromatic rings in the MOF pore wall is proposed.

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The 'breathing' metal organic framework MIL-53 effectively adsorbs sulfur-containing heterocycles with an expansion of its structure; the selectivity of uptake of guests has been monitored using time-resolved energy-dispersive X-ray diffraction.

1. Introduction

The removal of sulfur and nitrogen organic compounds from petrochemical streams is not only vital for reducing the environmental impact of exhaust engines,[1] but also improves the processability of the streams by limiting the formation of the corresponding N- or S-oxyacids.[2] The most important industrial route for the removal of sulfur compounds is the hydrodesulfurisation technology (HDS), in which the S-compounds are hydrogenated over a solid Co-Mo or Ni-Mo catalyst.[3] However, the presence of N-compounds deactivates the HDS catalyst and prevents a deep hydrodesulfurisation.[4,5] In order to reach the imposed sulfur content in fuels (<10 ppm S),[6] it is therefore important to first remove the nitrogen compounds.[7] Alternatively, adsorptive removal of the S-compounds using microporous materials is a potentially effective, low energy desulfurisation strategy.

Suitable adsorbents for N- or S-compounds are zeolites,[8] activated carbon[9] and metal-organic frameworks (MOFs).[6,7] MOFs are hybrid crystalline materials consisting of nodes of metal ions bridged by organic linkers.[10] The combined organic and inorganic nature of the materials gives rise to interesting properties such as a well-defined pore structure, high internal surface areas, remarkable structural flexibility and unusual sorption kinetics.[11] These properties make MOFs an excellent class of materials for adsorption and purification applications.

Maes *et al.* have shown that MOFs like the Fe-trimesate MIL-100(Fe) or the Cu-trimesate Cu-BTC are capable of removing the nitrogen or sulfur compounds from a N/S-contaminated fuel. The MOFs studied so far in denitrogenation or desulfurisation contain coordinatively unsaturated metal sites (CUS) and have a rigid structure.[7,12-17] Using coordinatively unsaturated metal sites increases the heat of adsorption,[18] and therefore the energy input required for desorption of adsorbed molecules.[19] This can be a critical problem in future applications, where recyclable adsorbents are desired and raises the question whether it would be possible to use coordinatively saturated MOFs as hosts for N/S removal from fuel feeds.[20-21]

To our knowledge there has not yet been a study on the removal of N/S-compounds from solvents on fully coordinatively saturated, flexible MOFs, where the influence of structural flexibility on the adsorption behaviour of such compounds plays a role. Therefore this paper reports an investigation of the effect of framework flexibility in the coordinatively saturated MIL-53(Fe)[22] on the adsorption of N/S-compounds, whereby the solvent properties appear to have a key influence on the uptake and breathing behaviour. The MIL-53 structure, Figure 1, is found for various metals (Al, Cr, Fe…) and the material shows a remarkable reversible flexibility where the connectivity of the structure is maintained but pore volume changes in response to external stimuli such as temperature, pressure or guest molecules.[22-24] By studying the uptake of N/S-compounds out of a polar solvent, isopropanol, and an apolar solvent, heptane, the competition between the adsorbates and the solvent can be investigated. In order to follow the reversible expansion of the structure, energy-dispersive X-ray diffraction (EDXRD) is used. This technique allows the use of intense, white-beam X-rays over a wide energy range which permits the study of the temporal evolution of crystalline phases within large volume reaction vessels with rapid data collection by virtue of the fixed solid-state detector.[25-27] Some of us have previously applied the method to study the effect of liquid phase guest molecules on the structure of flexible MOFs.[28,29] In this paper we turn our attention to the industrially relevant adsorption of N/S heterocycles to understand the mechanism of their uptake.

2. Experimental

2.1 Preparation of MIL-53(Fe)

Hydrated MIL-53, MIL-53(Fe)[H_2O], was synthesised using a solvothermal method from $FeCl_3{\cdot}6H_2O$ (Aldrich, 97 %, 6 g), 1,4-benzenedicarboxylic acid (Aldrich, 98%, 3.7 g), hydrofluoric acid (Aldrich, 40%, 1.2 mL) in *N*,*N'*-dimethylformamide (Aldrich 99%, 100 mL) and H_2O (3.2 mL). All reagents were obtained from chemical suppliers and used without further purification. Reactants were stirred continuously under reflux for 3 h. The light orange MIL-53(Fe)[DMF] powder was washed with methanol, resulting in complete exchange of DMF molecules by the solvent to give MIL-53(Fe)[MeOH]. Finally, MIL-53(Fe)[H_2O] was obtained after drying in air at 70°C for 1 hour. Quantitative elemental analyses gave the following results: Fe: 18.5%; C: 37.1%; H: 2.4% and F: 2.9%. This compares well with values calculated from the formula $Fe^{III}(OH)_{0.6}F_{0.4}(O_2C\text{-}C_6H_4\text{-}CO_2).(H_2O)$: Fe: 21.83%; C: 37.56%; H: 2.58% and F: 2.97%. Laboratory powder X-ray diffraction, infrared spectroscopy and thermodiffractometry were also used to confirm the identity and purity of the solid products in comparison to literature data (see ESI).[30]

2.2 Physicochemical characterisation

Laboratory PXRD data were collected using a Bruker D8 Advance diffractometer with a Cu anode giving an average ($K_{\alpha1}/K_{\alpha2}$) wavelength of 1.5418 Å. FTIR-spectra of MIL-53(Fe)[H_2O], MIL-53(Fe)[guest] and MIL-53(Fe)[solvent] were measured using a PerkinElmer Spectrum™ 100 FTIR. Spectra were acquired at 4 cm^{-1} resolution in the 4000-550 cm^{-1} range. Hydrated MIL-53(Fe) was stirred overnight in either pure solvent or a solution containing guest and solvent. The sample was then filtered, allowed to dry in air, and a small amount was loaded on the diamond plate for analysis. Thermogravimetric (TG) data were recorded using a Mettler Toledo TGA/DSC1 instrument. Approximately 10 mg of powder were loaded into an alumina crucible; the sample was heated in air to 1000°C at a rate of 10°C/min.

2.3 High-resolution powder XRD

The high-resolution powder diffraction beamlines ID31 of the European Synchrotron Radiation Facility (Grenoble, France) or I11 of the Diamond Light Source (Harwell, Oxford) were used to measure powder XRD data. On ID31 the incident X-ray wavelength was 0.79989 Å and on I11 the incident X-ray wavelength was 0.8260 Å. MIL-53(Fe) was studied in the presence of an excess of guest. Finely powdered sample was loaded into 1 mm diameter quartz capillaries and saturated solutions of the guest dissolved in isopropanol were then injected. The capillaries were centrifuged to concentrate the solid at the end of the tube before being sealed; this minimised background noise due to the liquid during data collection. Samples were rapidly spun during data collection to ensure good powder averaging. Extraction of the peak positions, pattern indexing profile fitting analysis attempts to localise the guests and Rietveld refinement were carried out with the TOPAS software.[31] Unit cells and space groups were found by the LSI-Indexing method with satisfactory figures of merit and confirmed by pattern matching using the Le Bail method. The already published atomic coordinates of the fully expanded skeleton[32] were used as starting model in the Rietveld refinement. The independent terephthalate ion was treated as a rigid body, and the anisotropic line broadening effect was corrected by using spherical harmonics series.[33] Neither difference Fourier calculations nor simulated annealing allowed us to localise the adsorbed guest molecules. We assume that the guest molecules are disordered within the pores of this material.

2.4 Time-resolved EDXRD

Beamline F3 of the HASYLAB facility at DESY (Hamburg, Germany) was used to measure *in situ* EDXRD data of the interaction between suspensions of MIL-53(Fe) and solutions of guest molecules. Beamline F3 received white-beam radiation with energy 13.5 – 65 keV; the incident X-ray beam was collimated to dimensions $20 \times 20\ \mu m^2$. Scattered X-rays were detected using a single-element germanium solid-state detector. The precise angle of the detector was calibrated using a set of Bragg peaks measured from a solid polycrystalline sample of hydrated MIL-53(Fe) and the energy calibration of the detector was performed using a glass containing a series of heavy elements with well-separated fluorescence lines. Note that since the data were recorded during several visits to the beamline the detector angles were slightly different between each run. The detectors were recalibrated for each measurement.

In the EDXRD experiment the *d*-spacing (d/Å) of each characteristic Bragg peak is defined by an energy (*E*/ keV), related to the fixed angle of the detector (2θ) by Equation 1.[34]

$$d = \frac{6.1992}{E \sin\theta} \qquad (1)$$

A 15 mm (diameter) Pyrex® test tube containing a suspension of 400 mg of MIL-53(Fe)[H_2O] in 3 mL of solvent (isopropanol, anhydrous, 99.5% or heptane, 99%) along with a Teflon-coated magnetic stirrer bar formed the basic experimental setup. Experiments using both hydrated and dehydrated MIL-53(Fe) were performed; however the combination of heptane and hydrated MIL-53(Fe) was not possible since mixing of the hydrated powder with the hydrocarbon was ineffective. To obtain dehydrated MIL-53(Fe), the tube containing the sample and the stirrer bar was predried at 110 °C. The tube was fitted with an airtight septum, while hot, and the anhydrous solvent was added to the dry powder directly *via* a needle attached to a syringe. The guest molecules were dissolved in either dry isopropanol or heptane to give a 0.39 M solution, which was added dropwise to the test tube (containing the solid adsorbent and 3 mL additional solvent) using an automated syringe pump set to a calibrated rate of 10 mL hour^{-1}. The concentration of guest after 10 mL of the solution had been added was therefore 0.30 M (corresponding to 2.5 molar equivalents of guest per Fe atom). EDXRD data were accumulated in 60 s intervals. Most transformations continued to proceed after addition of the 10 mL solution was complete. The suspension was stirred rapidly to ensure that a uniform amount of sample was always in the beam. Raw EDXRD data were converted using the programs DLConverter[35] and PowDLL[36] into a format suitable for reading into the program XFIT[37] where peak fitting using Pseudo-Voigt functions was undertaken to determine Bragg peak areas with time/concentration to produce extent of structural transformation curves.

2.5 Diffuse reflectance UV-vis spectroscopy (DRS)

The MIL-53(Fe) samples were pretreated at 110°C. Samples of MIL-53(Fe)[^{i}PrOH] and MIL-53(Fe)[benzothiophene] were prepared by stirring dehydrated MIL-53(Fe) for a period of 2 hours in pure isopropanol or in a solution of benzothiophene in isopropanol (0.3 M). The solvent was evaporated and the sample was placed in the sample holder. Spectra were recorded with a Cary Series UV-Vis-NIR spectrophotometer from Agilent Technologies in the range of 4000-50000 cm^{-1}. The UV-Vis scan rate was 2000 cm^{-1}/min and the NIR scan rate was 1200 cm^{-1}/min.

2.6 Adsorption isotherm measurements

Liquid phase batch adsorption experiments were carried out at 298 K in 1.8 ml glass vials filled with 0.025 g of adsorbent and a solution of heptane or isopropanol containing either indole, benzothiophene or benzothiazole (of chosen concentration) following a literature procedure.[38,39] Uptakes were directly calculated from GC output data. The material MIL-53(Fe) was either used directly in the hydrated form or was dehydrated at 110 °C.

3. Results and Discussion

3.1 Equilibrium adsorption isotherms

The adsorption isotherms for the individual compounds in solvents, Figure 2, show remarkable differences in shape and in the corresponding highest uptake in the studied concentration range. Uptake of indole can only be observed when it is dissolved in heptane, while no uptake is measured at all out of isopropanol for the hydrated nor for the dehydrated MIL-53(Fe). The highest uptake of indole out of heptane, *viz.* 22 wt%, is measured for the hydrated material, whereas only 6 wt% uptake is observed for the dehydrated, closed material. The latter number is so low that it could well be due to adsorption of the polar indole on the outer surface of a polar solid in the highly apolar heptane medium. For benzothiophene, the adsorption isotherms differ in shape depending on the solvent used: in heptane, the isotherm has a slightly decreasing slope, with a negative second derivative. By contrast, in isopropanol, the curve has an almost sigmoidal shape, with an initially positive second derivative. In heptane, benzothiophene starts to adsorb at the lowest concentrations; in isopropanol, there is initially no uptake but at a concentration of 0.05 M the uptake increases dramatically, resulting in a clear step in the isotherm. Such a behaviour is characteristic of a 'gate opening' effect.[40,41] For the dehydrated material, the uptake out of isopropanol (47 wt%) is three times higher than the uptake out of heptane (15 wt%). For the hydrated material, the difference in uptake between heptane and isopropanol is smaller, with 22 wt% and 31 wt% respectively.

The uptake of benzothiazole out of heptane is the highest of all compounds in this study and is the same for the hydrated and the dehydrated solid MIL-53 phase (59 wt%). The isotherm for benzothiazole uptake in heptane is similar in shape as the benzothiophene isotherm. Again, for the isotherm in isopropanol, a clear step can be observed starting at a threshold concentration of 0.04 M. This concentration seems the minimum below which no substantial adsorption can occur. The uptake by the dehydrated phase (28 wt%) is almost two times lower than the uptake by the hydrated material (48 wt%).

Taking into account the molar mass of the unit cell of MIL-53(Fe) and the number of Fe atoms in each unit cell, the total number of heterocycles per Fe can be calculated. The results thus shown in Table 1 are calculated for the highest uptake reached in the tested concentration range in Figure 2. The plateau in the isotherm for benzothiazole adsorption in heptane is reached at 59 wt %, corresponding to approximately one molecule per Fe atom in the structure (Table 1). This is in good agreement with previously reported data where the structural refinement of MIL-53(Fe) fully loaded with 2,6-lutidine in water also revealed one molecule for each Fe atom in the structure.[32] MIL-53(Fe) is capable in heptane of adsorbing 99% of the benzothiazole present at the low initial concentration, leaving only 2.75 ppm in solution (this is close to the detection limit of the apparatus used). The presence of water, which may be the case in the real situation of impure fuels, does not compromise the adsorption behaviour of MIL-53(Fe): the hydrated MIL-53(Fe) shows the same high affinity for benzothiazole, Figure 2c *cf.* Figure 2f.

3.2 High-resolution powder XRD

The unit cell parameters for each phase fully-exchanged with the heterocyclic guests indicate a completely expanded structure as can be seen in Table 2 (see ESI for final profile fits). The whole profile analysis of their patterns show that systematic extinctions are compatible with the *Imcm* space group and lead to unit cell volume of approximately 1590 Å^3. This unit cell volume and symmetry are similar to the situation when 2,6-lutidine and water are co-adsorbed into MIL-53(Fe).[32] Unlike in the case of 2,6-lutidine and other bulky guest molecules, however, we were unable to locate and refine the positions of the guest molecules within the MIL-53(Fe) host. This may suggest some positional disorder in the guest orientations relative to the framework structure of MIL-53.

3.3 *In situ* EDXRD

Time-resolved EDXRD was measured during the dropwise addition of each heterocycle to a test tube containing a suspension of MIL-53(Fe) in the chosen solvent. This allowed direct observation of the guest-induced structural changes with increasing time and concentration. EDXRD data collected before the addition of the heterocycles show that the degree of expansion of the framework is dependent upon the solvent used. When dehydrated MIL-53(Fe) is suspended in heptane it remains in a closed form for several hours (see below). Thus before the introduction of guests the presence of (110) and (200) Bragg peaks corresponding to a monoclinic phase with V ~ 900 Å^3 are seen (Figures 3a, 4a and 5a). However, there was some evidence for pore opening in heptane after standing for approximately 15 hours, with the appearance of high *d*-spacing features in the EDXRD (see ESI). When MIL-53(Fe), hydrated or dehydrated, is suspended in isopropanol the material is predominantly in a half-open state, as expected from previous studies.[29] This is confirmed by the presence of (110) and (200) Bragg peaks corresponding to a *C*2/*c* monoclinic phase of volume ~1200 Å^3 visible at the beginning of the experiment before addition of any guest (Panels (b) and (c) of Figures 3, 4 and 5). In the experiments performed using the dehydrated material, the absence of Bragg peaks due to the hydrated phase at the start of the experiments confirmed that the material had been dried effectively. The contour graphs for benzothiophene and indole adsorption by hydrated MIL-53(Fe) in isopropanol (Figures 3c and 5**Figure** c) show that the hydrated phase is still present to a minor extent at the beginning of these experiments.

The EDXRD contour graphs do not show evidence for any intermediate phases during the addition of the guest molecules, nor any evolution of structure. The fully-open product phase was confirmed by comparison with simulated peak positions from the unit cells, determined from high-resolution powder XRD as described above. During the experiments only starting phase or fully expanded product phase were seen and the peak positions of these remained at the same *d*-spacing during their decay and growth, respectively. These results are in good agreement with previous work published on the uptake of alcohols,[29] and other molecules by the same host, where a ‘forceps’ mechanism was proposed to describe the abrupt opening of the MIL-53 structure.[22]

The EDXRD contour graphs for addition of benzothiophene (Figure 3) and benzothiazole (Figure 4) to MIL-53 show that the time required for the fully expanded product to appear differs for each adsorbate. In contrast, the results of the indole experiments show that the framework does not expand in response to the guest under the dilute conditions that were used for these experiments (Figure 5). Noting the timescale on the contour graphs it can be seen that the response to benzothiazole was fastest, followed by benzothiophene and that the distinction was more pronounced when the experiments were performed in isopropanol. This suggests that the driving force to reach the equilibrium is considerably larger for benzothiazole. The interaction with indole is clearly weaker since no expansion of MIL-53(Fe) was observed in the same period of time. Indeed, expansion in indole/isopropanol was still not seen after the suspension was left for 20 hours.

By integrating the strongest Bragg reflection shown by the initial phase, and plotting the inverse of the normalised data, extent-of-conversion graphs can be created, Figure 6. These can be used to compare the conversion of MIL-53(Fe) from its closed or half-open state to its fully open state as the guests indole, benzothiophene or benzothiazole are added. In doing this we have assumed that the decreasing peak area of the starting phase is inversely related to the growth of the fully open phase, *i.e.*, we assume that the initial phase is replaced directly by the open phase, as indicated by the contour graphs.[22,29] This approach was adopted as the concentration of guest solutions used meant that most of the experiments did not go to completion in the timescale of the experiments.

The concentration of the guest solution can be calculated for any given time since the rate of addition of the guest solutions was controlled and measured by the electronic syringe pump during each experiment; this allows the extent of conversion graphs to be plotted as a function of guest concentration in the surrounding solution, Figure 6. It can be seen that after complete addition of benzothiophene at 60 minutes (when a concentration of 0.3 M is reached), the reaction has reached between 60-80% of full conversion, whereas the experiments involving benzothiazole approached between 85 and 95% of full conversion. The difference between the behaviour towards the two guests is more notable in isopropanol as solvent compared to heptane as solvent. These graphs also show that when the experiments were performed in isopropanol there was a threshold concentration that is needed to be reached (typically between 0.05 and 0.1

M) before adsorption of the guests was observed, whereas the experiments in heptane show that sorption was seen almost immediately at the lower concentrations, well below 0.05 M. This observation may initially appear counterintuitive, since in the isopropanol solvent the host MIL-53(Fe) is already partially expanded, but the results are consistent with the presence of a reasonably strong hydrogen bond interaction between isopropanol and the framework, which means that displacement of the solvent by the new guest is more difficult. The difference in the extent of conversion that has been reached at the final concentration of 0.3 M is likely due to the difference in strength of the interaction between guest and host. The stronger the guest-host interaction, the more easily the guest will displace the isopropanol. Benzothiazole is a better hydrogen acceptor than benzothiophene, in line with its known behaviour as a weak base (pK_b = 11.56), and with the fact that it possesses two atoms that are potential H-bond acceptors.[43] Therefore it should interact more strongly with the framework μ-(OH) groups along the backbone of MIL-53(Fe), explaining why it displaces isopropanol more easily.

3.4 Interaction of the guest molecules with the MIL-53 framework

Figure 7 shows the evolution of the colour of MIL-53(Fe) with increasing concentration of benzothiophene in isopropanol. This is quantified in Figure 8 which shows diffuse reflectance spectroscopy results. Both visual inspection and diffuse reflectance results show that a new absorption arises when benzothiophene acquires access to the pores above the 0.05 M threshold concentration. As the Fe^{III}-atoms are six-fold coordinated and present no coordinatively unsaturated sites,[22] no ligand-to-metal or metal-to-ligand charge transfers are possible.[44] To determine whether the colour change is induced by a specific interaction of benzothiophene with the linkers of the MOF, UV-Vis spectra were recorded for solutions of benzothiophene, terephthalic acid and a mixture of both. While the separate compounds are transparent between 500 and 600 nm, the mixed solution displays a clear transition around 538 nm, in the same spectral region as the increased absorption by benzothiophene-containing MIL-53(Fe). This suggests that the observed colour change arises from terephthalate-benzothiophene interactions inside the pores, somewhat similar to a location of thiophene in the vanadium (IV) terephthalate MIL-47 previously seen by crystallography, where the sulfur atom of thiophene is oriented towards the benzene ring of the terephthalate linker.[21] A plausible explanation is that a sulfur-aromatic interaction occurs;[21] such an interaction is weak but has been observed by crystallography on systems of biological origin.[45,46]

To determine whether the solvent molecules are present inside the pores together with the heterocycles once the fully open MIL-53 is produced, IR spectra were measured for fully loaded structures, Figure 9. The IR spectra of the hydrated MIL-53(Fe) and of MIL-53(Fe) soaked in the respective solvents are compared with the spectra of the materials saturated with a solution of the heterocyles dissolved in the respective solvent (note that excess liquid was removed from the surface of the solids before taking the measurements). For monitoring the presence of heptane inside the pores the region due to aliphatic C-H vibrations around 2900 cm^{-1} was examined. The only material that shows a band at 2921 cm^{-1} is the material that is loaded with pure heptane and allowed to equilibrate for at least 15 hours (as noted above, at this extended time there is some evidence for heptane uptake by the material). The solids containing the solution of benzothiophene or benzothiazole in heptane do not show any bands in the 2900 cm^{-1} region, suggesting that once the guest is added this displaces any heptane, or rather that the heterocylic guest is taken in preference to the heptane and none of the solvent is taken up simultaneously. Regarding the presence of isopropanol, MIL-53(Fe) fully exchanged with isopropanol has a characteristic OH band located at 3334 cm^{-1}, the aliphatic CH stretch at 2934 cm^{-1} and a C-OH stretch at 950 cm^{-1}. As none of these bands can be found in the structures fully exchanged with the solutions of benzothiophene or benzothiazole in IPA, it can be concluded that only the heterocycles are present at high concentration inside the pores, and the solvent is fully displaced.

3.5 Comparison of adsorption isotherms and *in situ* diffraction

In order to understand the mechanism of adsorption in isopropanol, it is instructive to compare the adsorption isotherms for the hydrated and the dehydrated material with the corresponding graphs showing the extent of conversion of the initial to the final phase derived from EDXRD (Figure 2 *vs* Figure 6). Note that the adsorption isotherms are recorded after equilibrium is reached, while for the EDXRD extent of conversion data equilibrium is not necessarily reached. Despite the dynamic nature of the EDXRD recordings, a clear agreement can be seen with the isotherms measured independently. This convincingly proves that the threshold concentration as observed in the isotherm is directly related to opening of the structure, *e.g.*, by benzothiazole or benzothiophene. As the isopropanol is present inside the structure, it has to be displaced before the heterocycles can force the structure open further and are able to adsorb inside the pores. Indole is not capable of opening the structure, as no extent of conversion is detected nor any adsorption out of isopropanol. Close inspection of the low concentration domain of the adsorption isotherm shows following preference order: benzothiazole > benzothiophene > indole. In order to rationalise this order, the hydrogen bond donor and acceptor abilities of the compounds are taken into account. Benzothiazole and benzothiophene are both H-bond acceptor molecules through the lone pair electrons of the sulfur atom for both compounds and the nitrogen atom for benzothiazole, while indole is a clear H-bond donor through the N-H entity. When considering the H-bond acceptor strength, benzothiazole is the strongest through the N atom, followed by benzothiophene and finally indole.[43] When considering the uptake preference of the heterocycles, it appears that the strongest H-bond acceptor is taken up the fastest and at lowest concentration, while the strongest H-bond donor is taken up the slowest and only at high concentrations. To confirm this hypothesis, the adsorption of pyridine and pyrrole (ESI) out of the same solvents was checked, confirming that the hydrogen bond donor (pyrrole) is not adsorbed from isopropanol, while the hydrogen bond acceptor (pyridine) is.

It is important to consider the case of indole in isopropanol (Figures 4b and 4c). Here we observed a decrease in Bragg peak intensity of the starting material, despite no appearance of a fully expanded product. One explanation for this behaviour is that this represents the onset of a weak interaction with indole and that some loss of crystallinity, or amorphisation of the half-open starting material is taking place. This effect is not seen for other guest molecules we have studied here, or previously,[28,29,32] since strong host-guest interactions and/or high concentrations of guests mean that the fully open product phase is seen immediately and any initial loss of crystallinity is hidden. It may be observed that the indole can be forced into the MIL-53(Fe) structure from isopropanol if a saturated solution is used; hence under the dilute conditions we have studied in this work, we may just be observing the beginning of a weak interaction with indole.

Finally we consider competitive uptake of pairs of guest molecules by the measurement of adsorption isotherms (note this is not possible using EDXRD since all guests give essentially the same fully-expanded structure). Figure 10 shows the results of these experiments. Using isopropanol the results are in line with those of the single guest uptake studies described above: benzothiazole is taken in preference to both benzothiophene and indole, and benzothiophene is preferred to indole. Indole is barely adsorbed from isopropanol solution. In contrast, when heptane is used as solvent, uptake of indole along with the other guest becomes more significant, and indole is even somewhat preferred over benzothiophene. We suggest that benzothiophene initiates pore opening, so that co-adsorption of indole can occur.

4. Conclusions

The results we have presented show the complementarity of using time-resolved *in situ* diffraction (made possible using the wide energy range of synchrotron radiation) to measure a structural change, with adsorption isotherms measured chromatographically and spectroscopic studies of the uptake of guest molecules in porous, flexible metal-organic framework materials. Fully loaded MIL-53(Fe) with the fused-ring N/S heterocycles benzothiophene and benzothiazole from solution, leads to completely expanded structures having an *Imma* space group and a cell volume of approximately 1600 Å^3. The uptake of N/S-molecules by the flexible MIL-53(Fe) shows a remarkable sequence of preference, where strong H-bond acceptors such as benzothiazole and benzothiophene are superior in respect to both adsorption capacity and kinetics. The effect is also enhanced by evidence for a sulfur-aromatic interaction between guest and host terephthalate linkers. Thus MIL-53(Fe) preferentially binds S/N heterocycles that can act as H-bond acceptors and these replace completely the solvent that may be initially present in the structure. The expansion of the structure is dependent on the properties of the solvent: the aliphatic solvent heptane results in a direct uptake, as opposed to the polar isopropanol which results in a stepwise uptake of guest molecules after a threshold concentration is reached. MIL-53(Fe) contains no coordinatively unsaturated metal sites for the strong binding of N/S-containing guest molecules; it therefore offers an attractive approach for the development of a recyclable host for the selective adsorption of such pollutant molecules in the solution phase under ambient conditions.

Acknowledgments

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Materials project "Creating and Characterising Next Generation Advanced Materials" with support from Advantage West Midlands (AWM) and part funded by the European Regional Development Fund (ERDF). We are grateful to Vickie Cheung (Warwick) for measurement of some of the infrared spectra. DEDV thanks FWO, IAP 7/05 and KULeuven (Metusalem funding) for support.

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Table 1: Number of heterocycles per Fe atom in MIL-53(Fe), as calculated from the maximum uptakes in Figure 2.

MIL-53(Fe) host	Solvent	Indole	Benzothiophene	Benzothiazole
Hydrated	isopropanol	0.00	0.55	0.83
	heptane	0.44	0.40	1.10
Dehydrated	isopropanol	0.00	0.83	0.49
	heptane	0.12	0.27	1.01

Table 2. Unit cell data for the MIL-53(Fe)[heterocycle] materials resulting from refinements against high-resolution powder diffraction data.

	MIL-53(Fe)[benzothiazole]	**MIL-53(Fe)[benzothiophene]**
	ESRF (ID31), λ = 0.79984 Å	DIAMOND (Ill), λ = 0.82599 Å
a / Å	15.7551(3)	15.7988(6)
b / Å	14.6273(3)	14.5796(6)
c / Å	6.89905(6)	6.9072(1)
V / $Å^3$	1589.92(5)	1591.01(8)
S. G.	*Imcm*	*Imcm*

Figure Captions

Figure 1: The crystal structures of MIL-53(Fe) in various forms: (a) fully open as found for 2,6-lutidine, water (guest molecules not shown);[32] (b) half-open as found for isopropanol (guest molecules not shown)[29] and (c) closed as found for water (oxygen of water molecule shown as green sphere).[22]

Figure 2. Adsorption isotherms for indole (squares), benzothiophene (diamonds) and benzothiazole (triangles) in competition with the solvents heptane or isopropanol (IPA) at 298 K, for: (a)-(c) hydrated MIL-53(Fe) and (d)-(f) dehydrated MIL-53(Fe).

Figure 3. Contour EDXRD maps showing the behaviour of MIL-53(Fe) upon the addition of benzothiophene in heptane with dehydrated MIL-53 (a), in isopropanol with dehydrated MIL-53 (b), and in isopropanol with hydrated MIL-53 (c). Also shown are the first (black) and the last (red) patterns of the respective contour maps.

Figure 4. Contour EDXRD maps showing the behaviour of MIL-53(Fe) upon the addition of benzothiazole in heptane with dehydrated MIL-53 (a), in isopropanol with dehydrated MIL-53 (b), and in isopropanol with hydrated MIL-53 (c). Also shown are the first (black) and the last (red) patterns of the respective contour maps.

Figure 5. Contour maps showing the behaviour of MIL-53(Fe) upon the addition of indole in heptane with dehydrated MIL-53 (a), in isopropanol with dehydrated MIL-53 (b), and in isopropanol with hydrated MIL-53 (c). Also shown are the first (black) and the last (red) patterns of the respective contour maps.

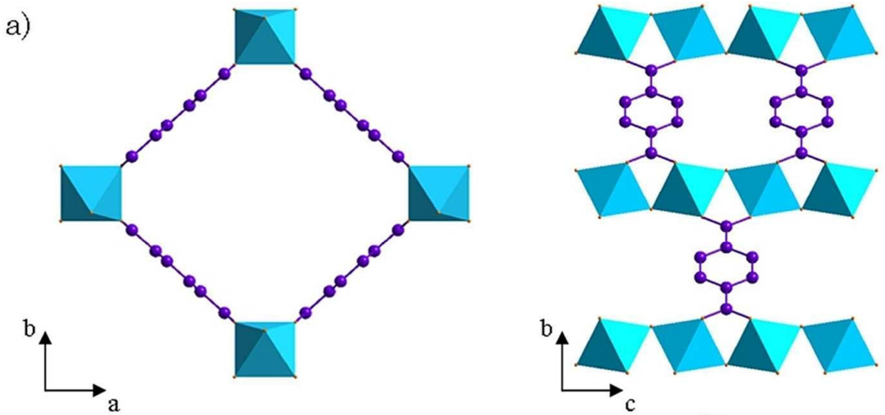
Figure 6. Extent of conversion graphs plotted as a function of concentration for benzothiophene (BTP) and benzothiazole (BTZ) a) in isopropanol with dehydrated MIL-53(Fe), b) in heptane with dehydrated MIL-53(Fe) and c) in isopropanol with hydrated MIL-53(Fe).

Figure 7. Colour changes for MIL-53(Fe) exposed to increasing benzothiophene concentrations in isopropanol (right). The respective samples are marked on the corresponding adsorption isotherm (left).

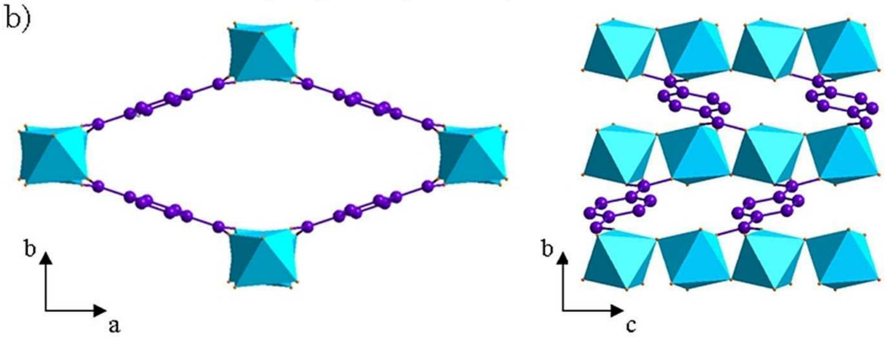
Figure 8. (a) Diffuse reflectance spectra for MIL-53(Fe)[^{i}PrOH] (red) and for MIL-53(Fe)[^{i}PrOH] exposed to 0.18 M benzothiophene (blue); (b) UV-Vis spectra of benzothiophene (orange) and terephthalic acid (purple), and their equimolar mixture in dimethylformamide (green).

Figure 9. IR-spectra of MIL-53(Fe) with different adsorbed solvents or solutions (BTZ = benzothiazole, BTP = benzothiophene, IND = indole, IPA = isopropanol). Vibrational features due to the solvent are indicated by the shaded boxes.

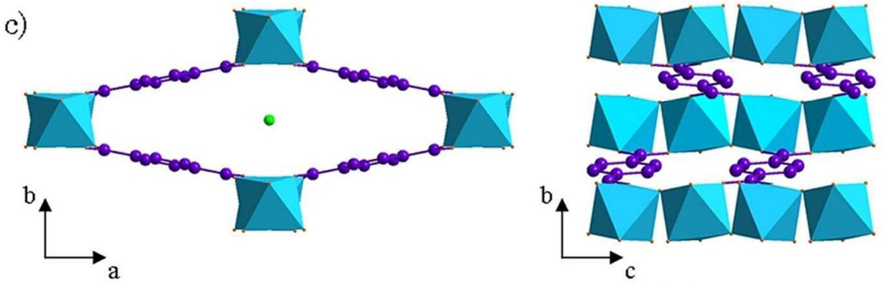
Figure 10 Competitive adsorption experiments for pairs of heterocyclic guest molecules in (top) heptane, (bottom) isopropanol; α quantifies the separation factor. The starting concentration of each guest molecule was 0.1 M.



Fully-open (*Imcm*) $V \approx 1600$ Å^3



Half-open (*C2/c*) V ≈ 1200 Å3



Hydrated (*C2/c*) $V \approx 1000$ Å^3

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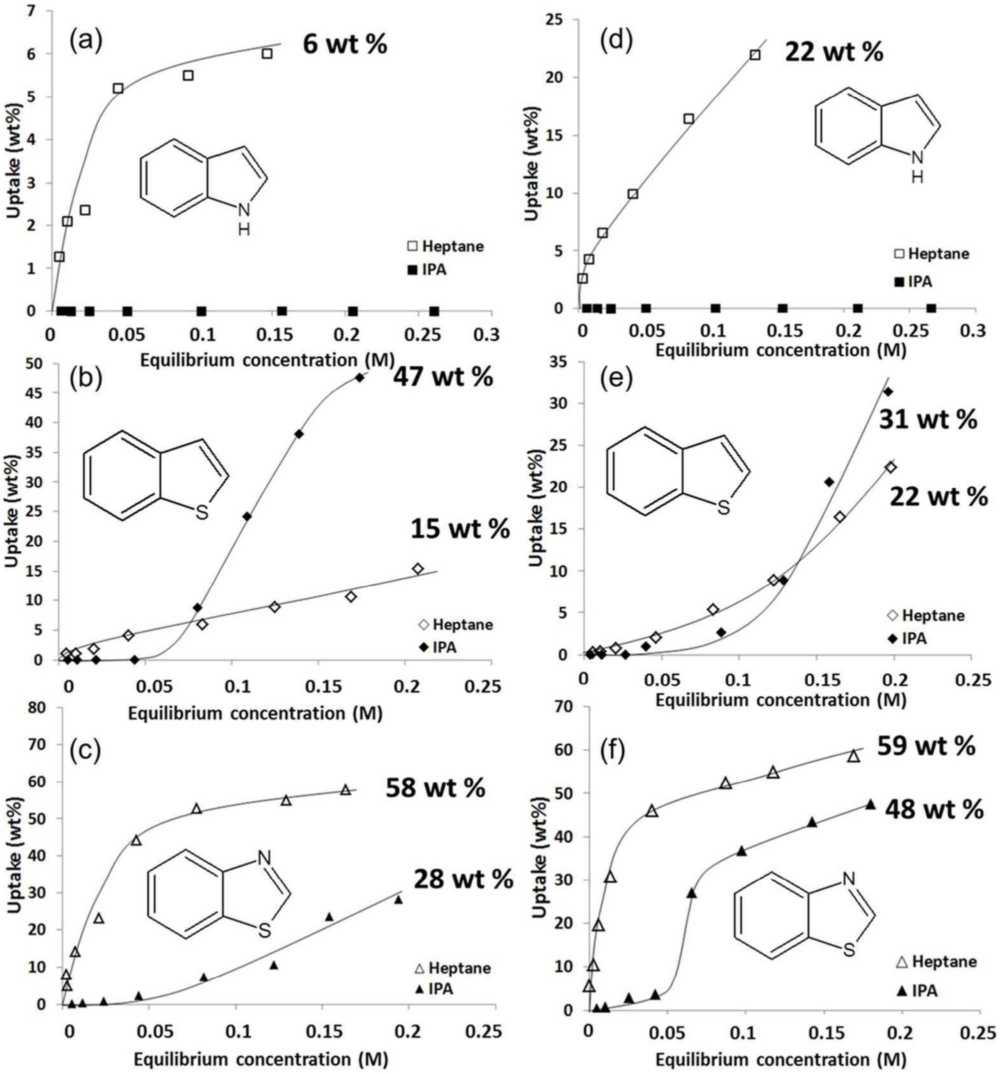

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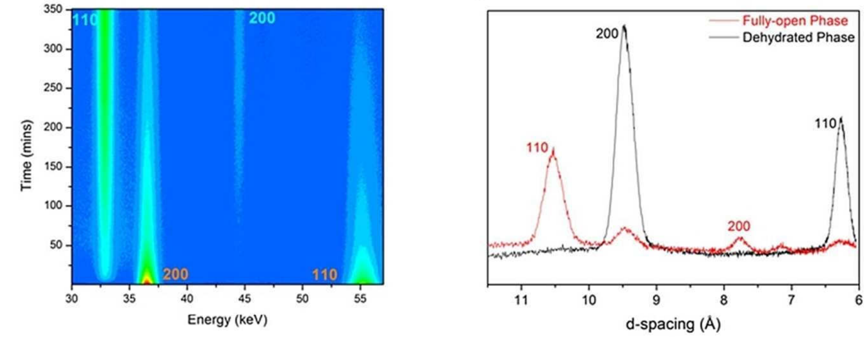
a) Heptane – dehydrated MIL-53



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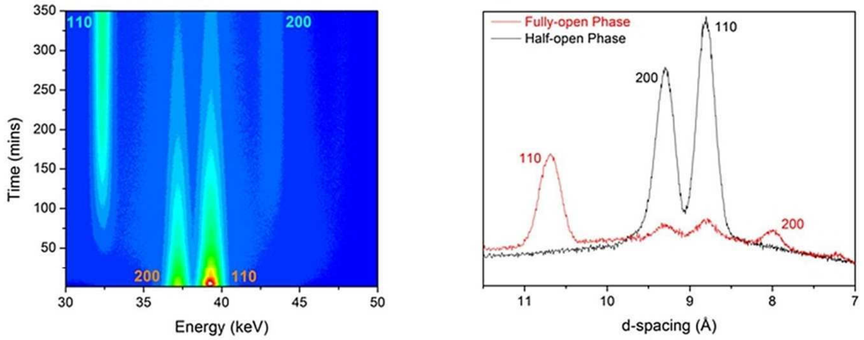
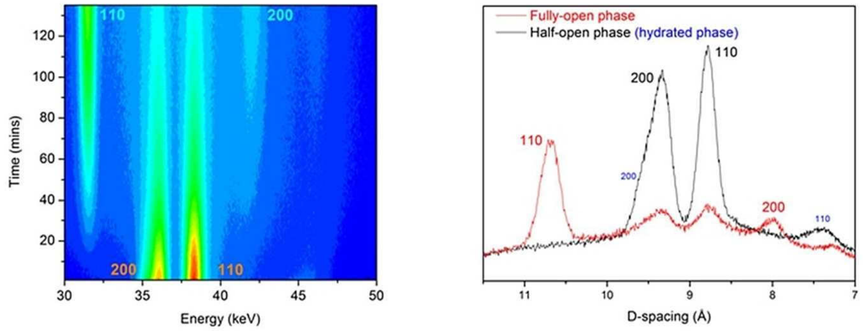


c) Isopropanol – hydrated MIL-53



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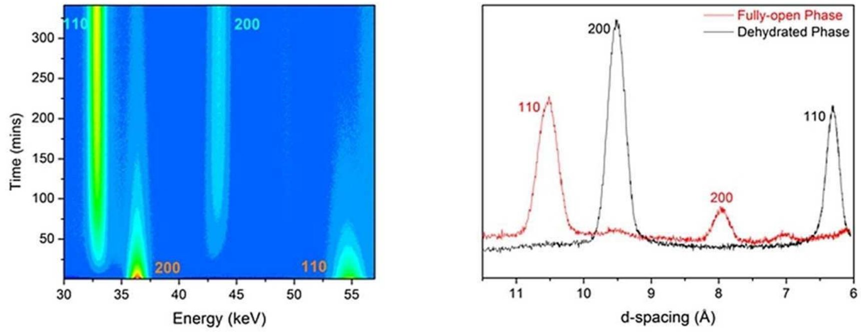

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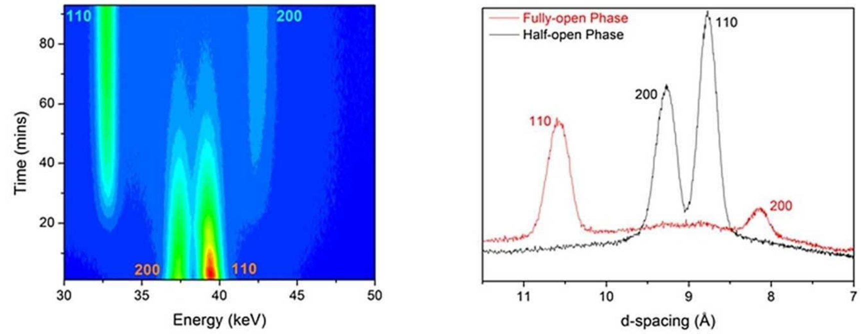
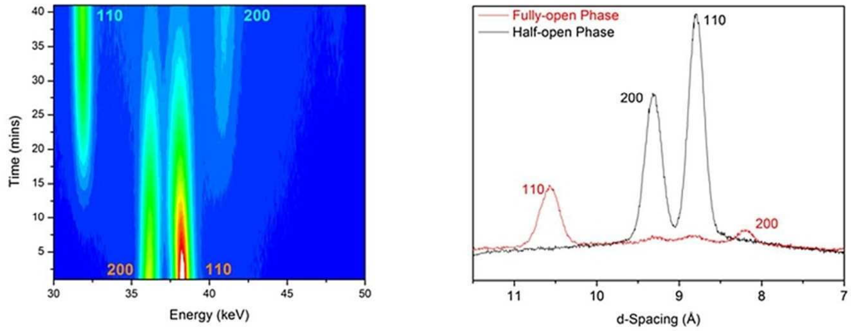


c) Isopropanol – hydrated MIL-53



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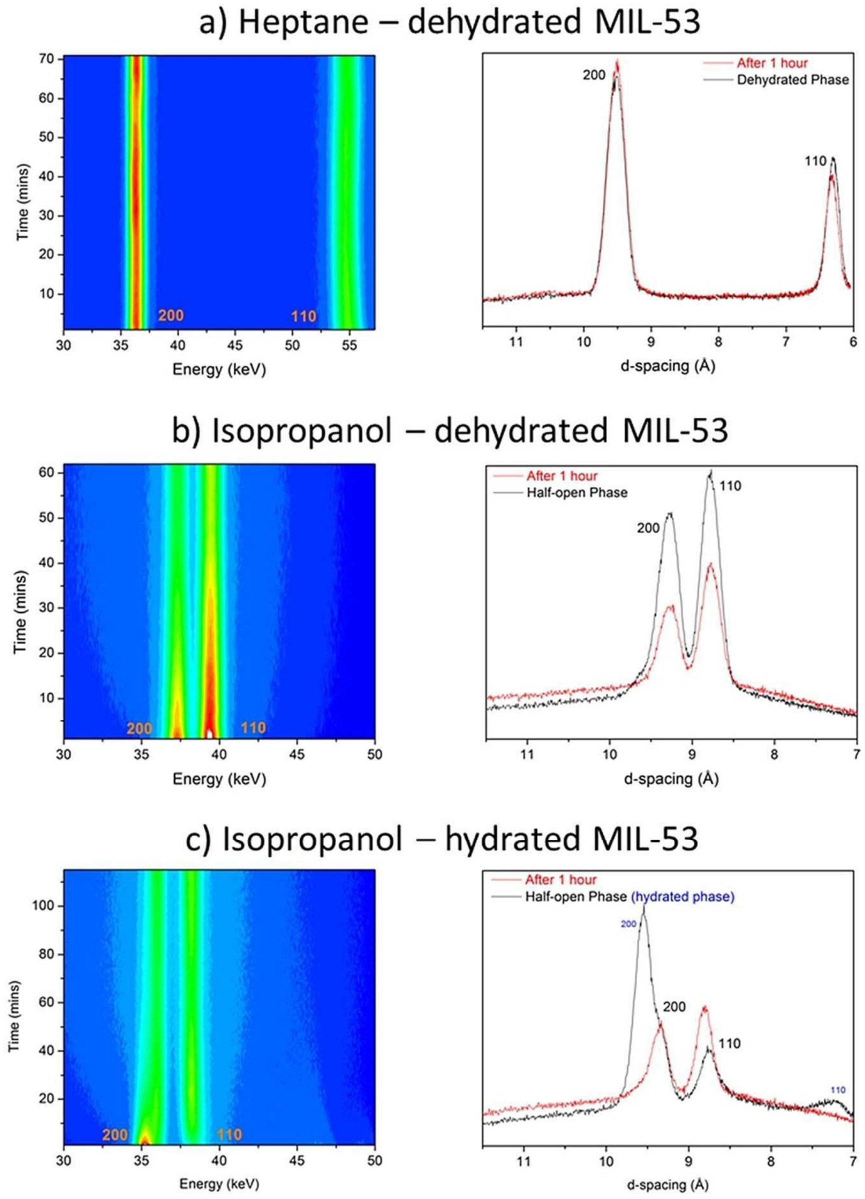

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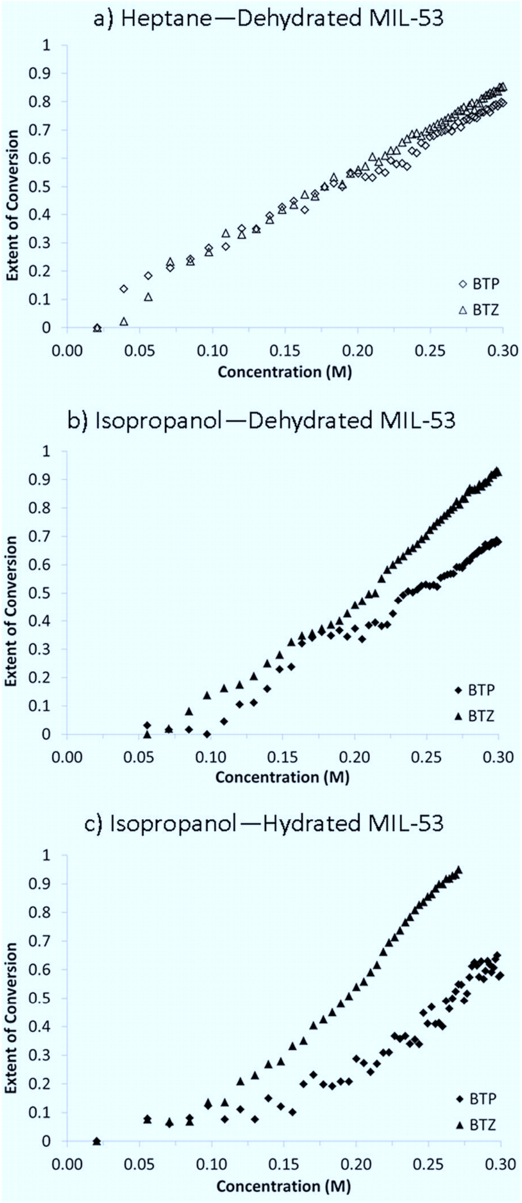

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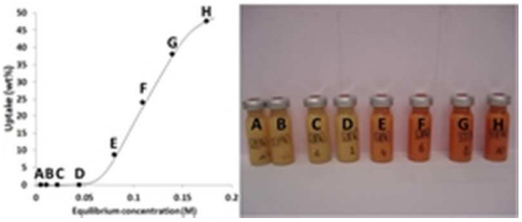

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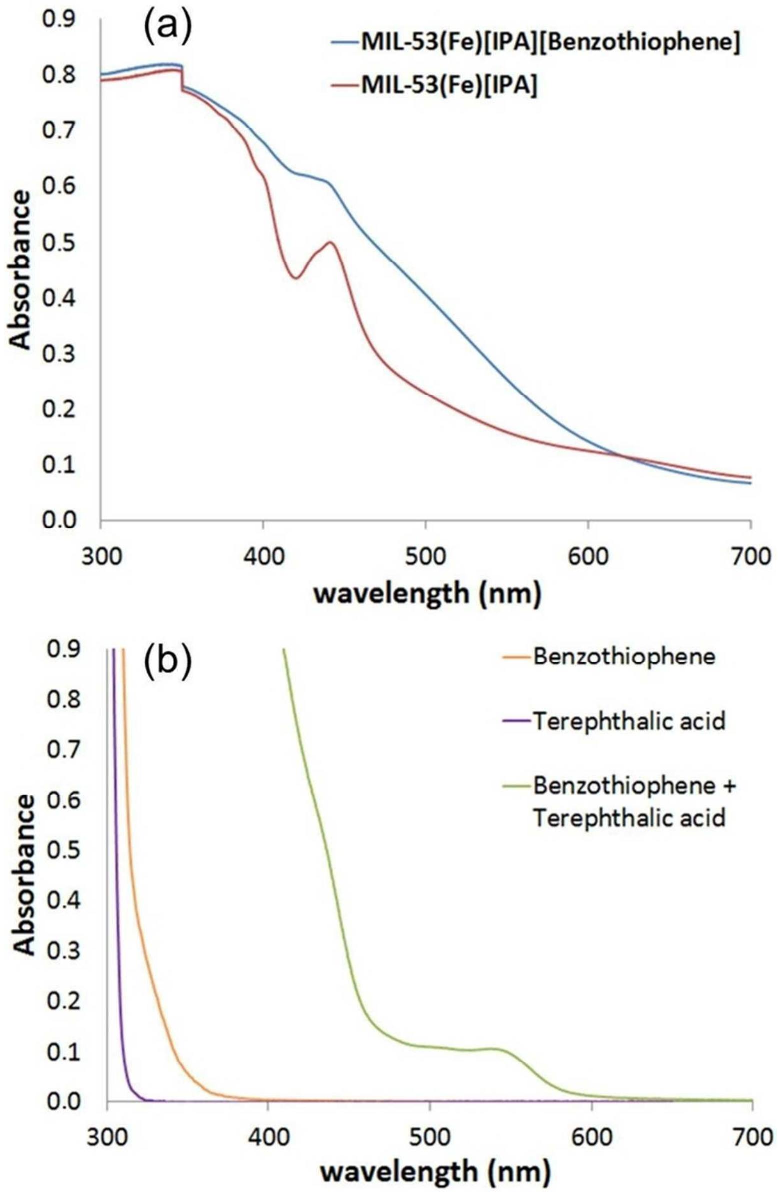

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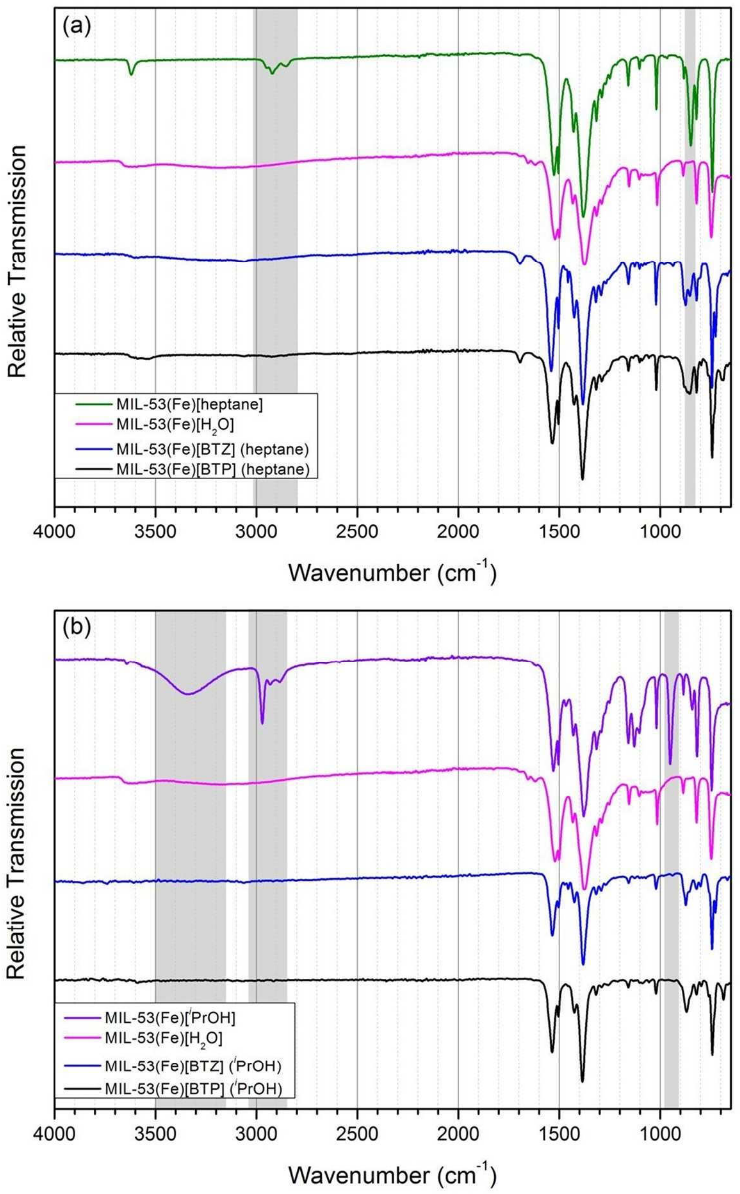

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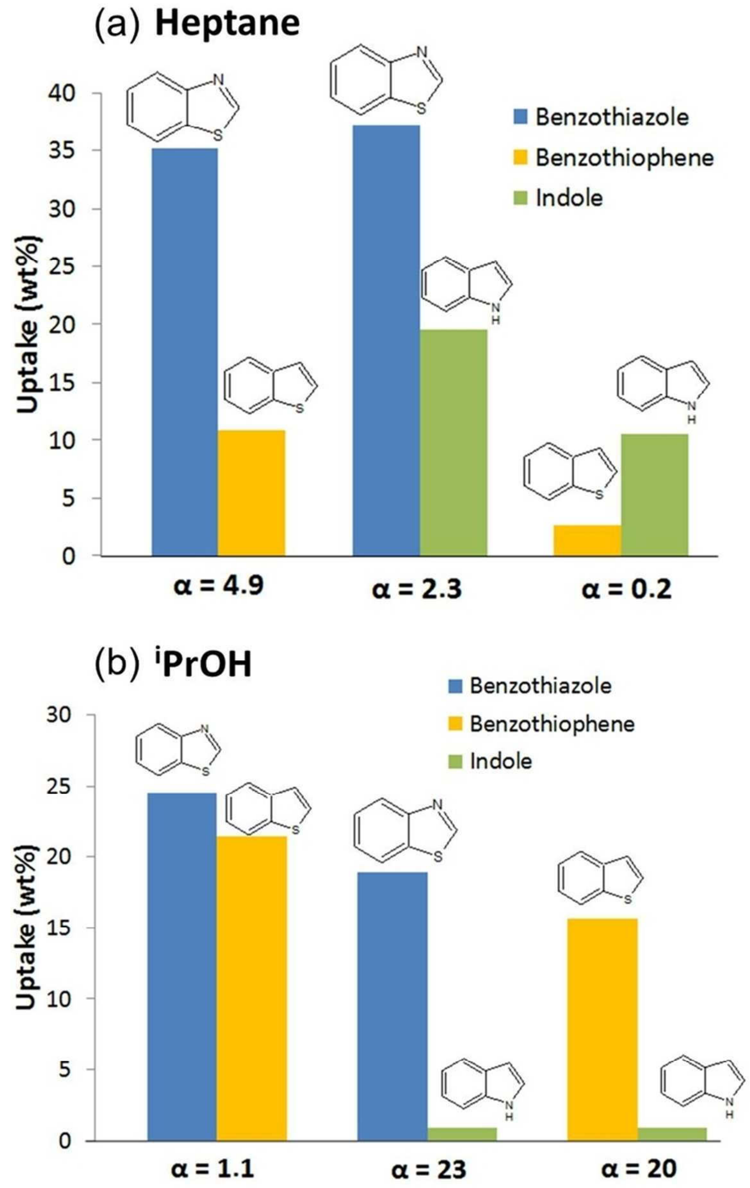

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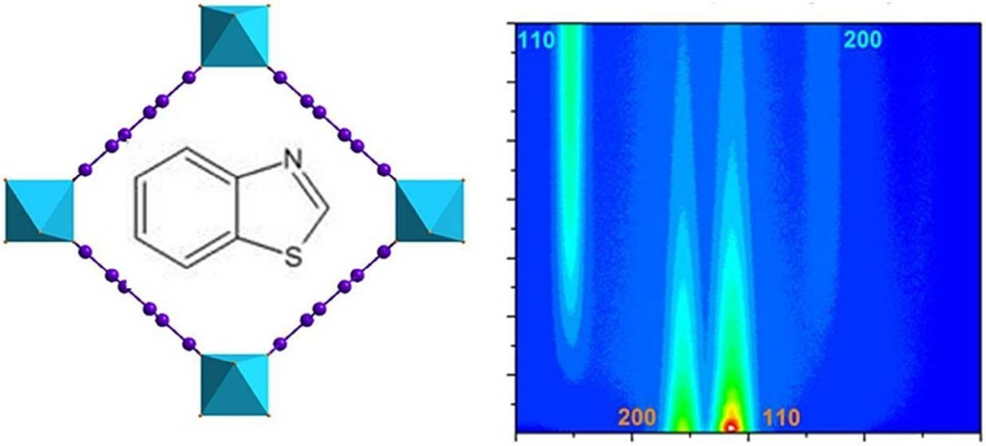

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Supporting Information for "Adsorption of N/S heterocycles in the flexible metal-organic framework MIL-53(Fe^{III}) studied by *in situ* energy dispersive X-ray diffraction"

Ben Van de Voorde, Alexis S.Munn, Nathalie Guillou, Franck Millange, Dirk E. De Vos and Richard I. Walton

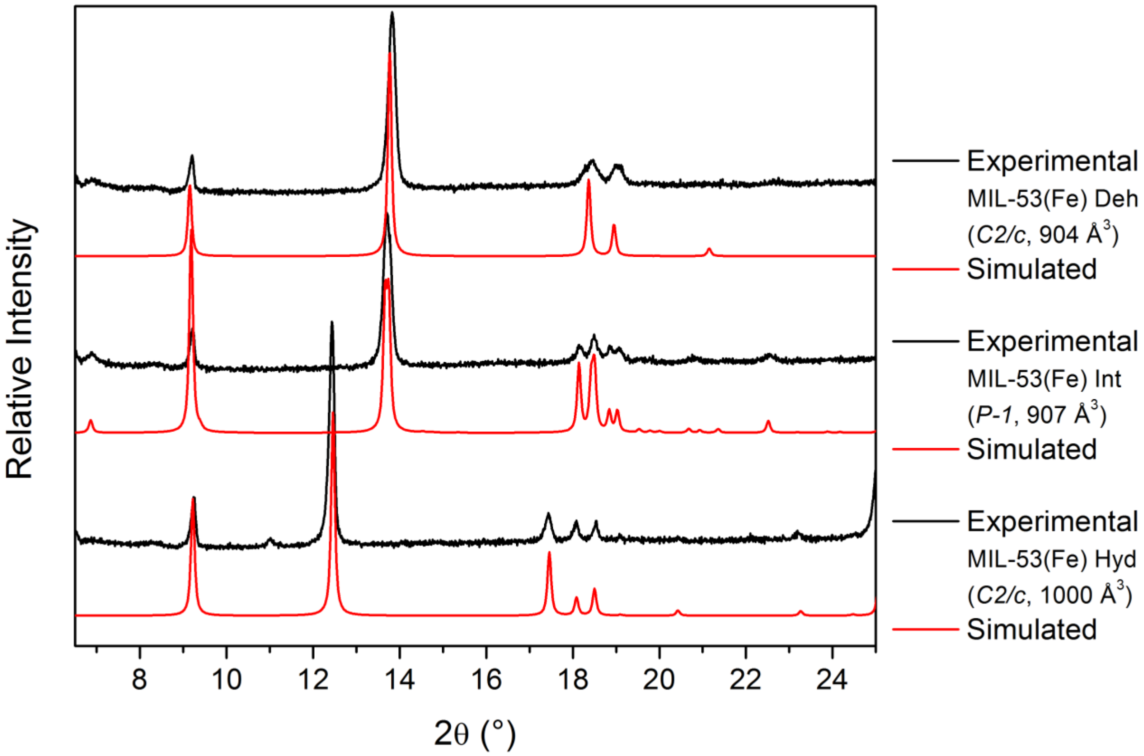

FIGURE S1: Powder XRD confirming the identity of the MIL-53(Fe) sample (observed, black, and simulated from published crystal structures, red). The bottom patterns are the hydrated phase and the middle and top patterns are measured under increasing nitrogen flow, showing dehydration of the material via the expected triclinic phase.

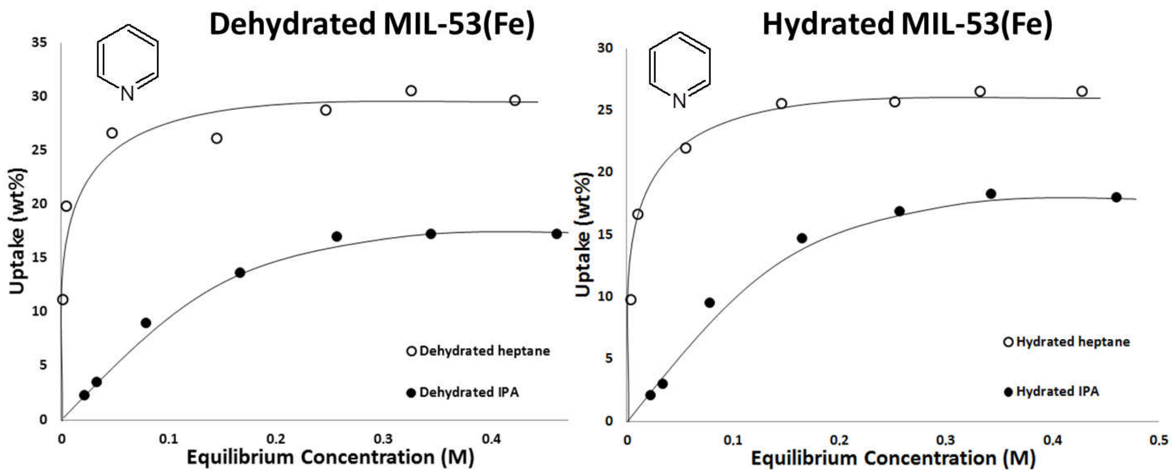

FIGURE S2: Single-compound adsorption isotherms of pyridine from heptane (open symbols) and isopropanol (IPA) (closed symbols) at 298 K, (left) dehydrated MIL-53(Fe), (right) hydrated MIL-53(Fe).

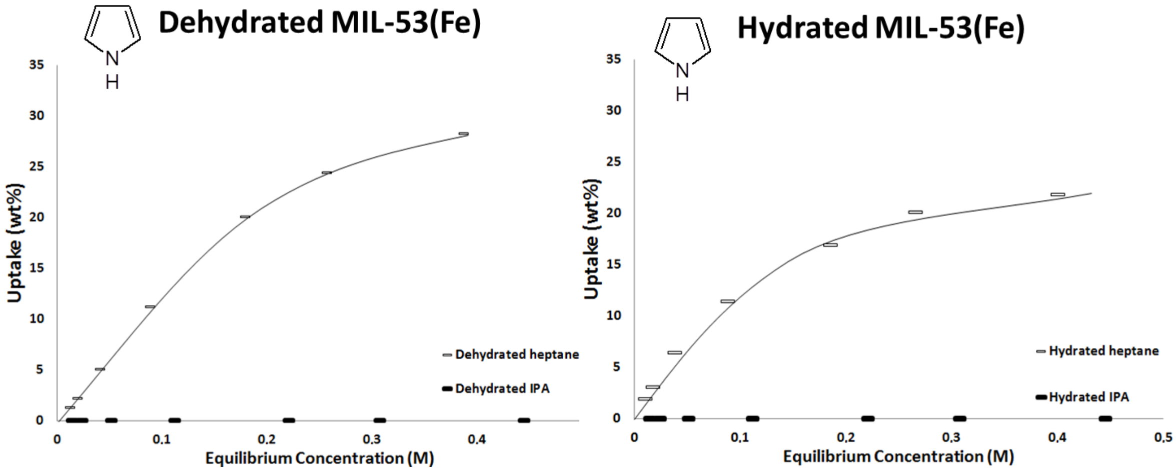

FIGURE S3: Single-compound adsorption isotherms of pyrrole from heptane (open symbols) and isopropanol (IPA) (closed symbols) at 298 K, (left) dehydrated MIL-53(Fe), (right) hydrated MIL-53(Fe).

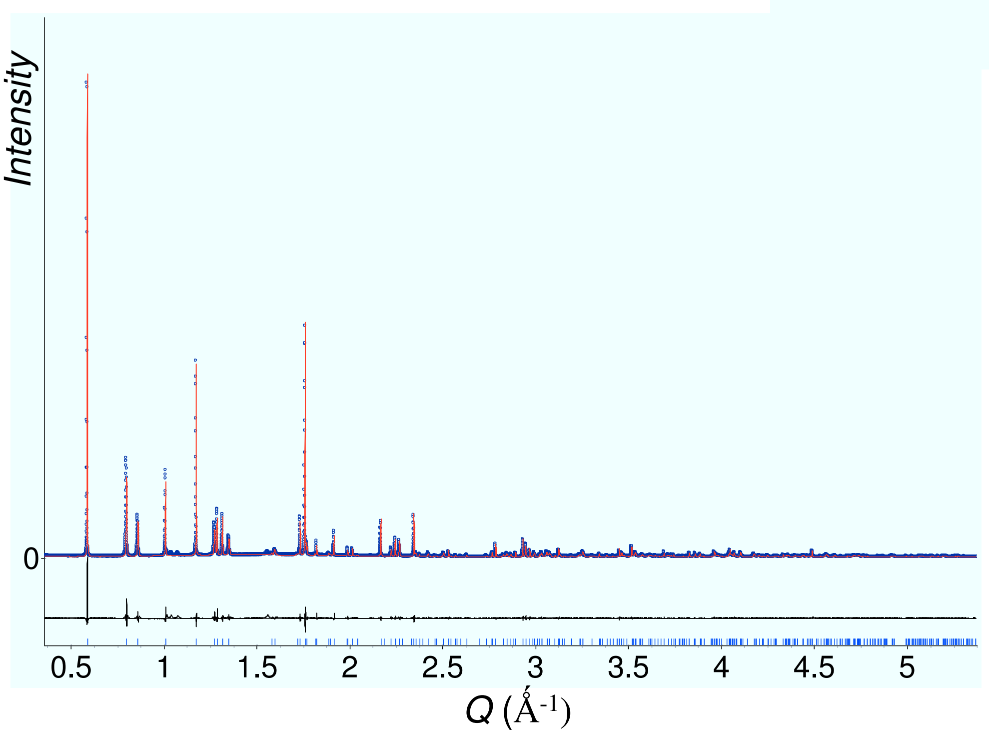

FIGURE S3: Final profile fit for MIL-53(Fe)[benzothiazole] (Data measured on ID31, ESRF).

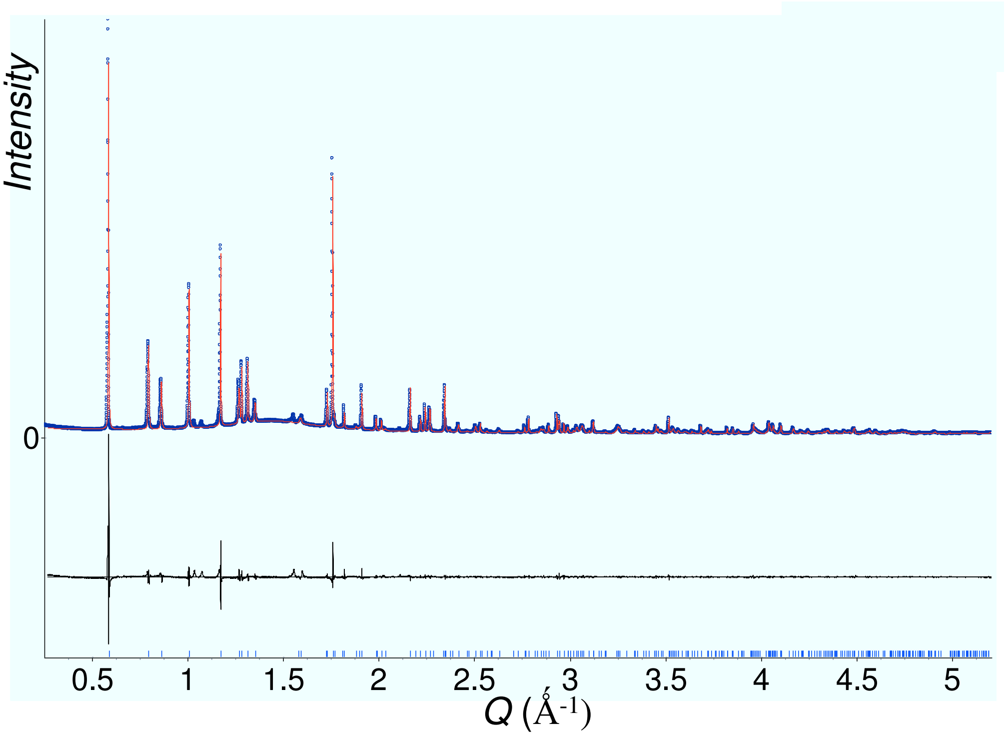

FIGURE S4: Final profile fit for MIL-53(Fe)[benzothiophene] (Data measured on I11, Diamond Light Source).

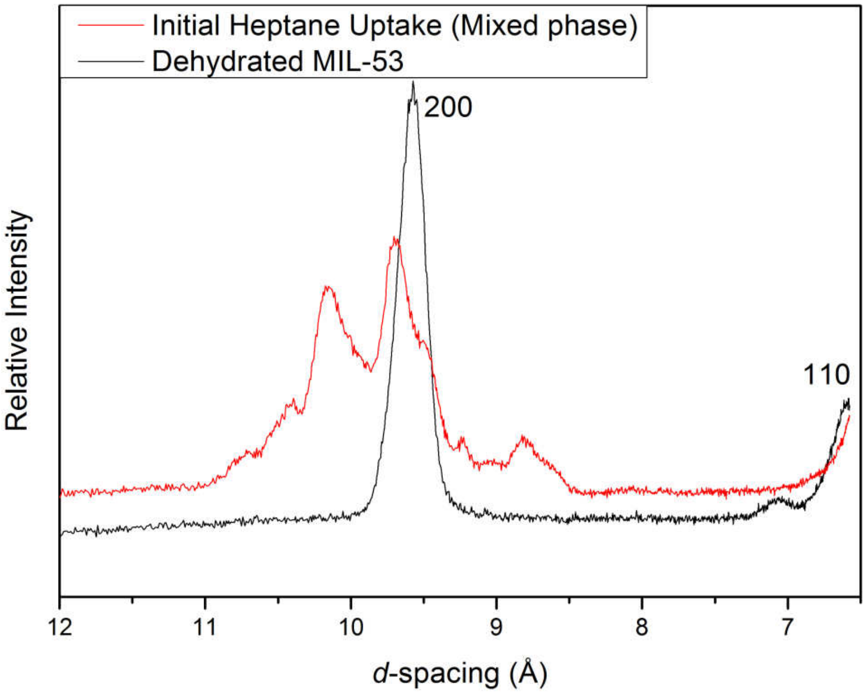

FIGURE S5: EDXRD patterns of dehydrated MIL-53(Fe) and after standing in heptane for 15 hours showing some extra Bragg peaks indicative of pore opening.