**Supporting Information** for "Adsorption of N/S heterocycles in the flexible metal-organic framework MIL-53(Fe<sup>III</sup>) 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.