

# Supporting Information

## Unravelling the Water Adsorption Mechanism in the Mesoporous MIL-100(Fe) MOF

*Paulo G. M. Mileo,<sup>a</sup> Kyung Ho Cho,<sup>b</sup> Jaedeuk Park,<sup>b</sup> Sabine Devautour-Vinot,<sup>a</sup>*

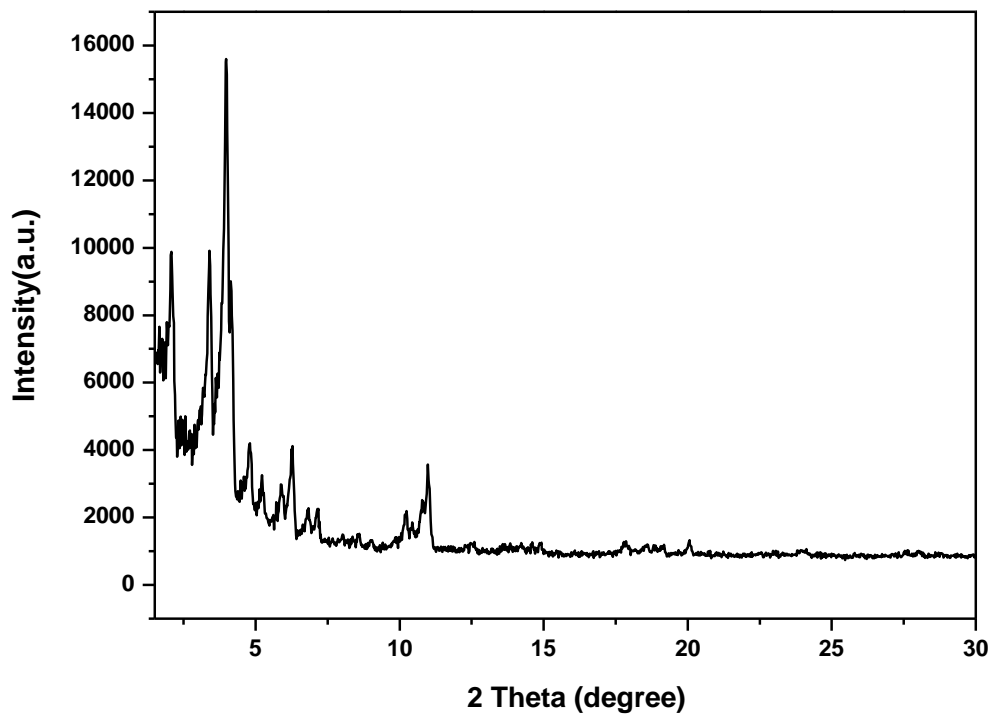
*Jong-San Chang<sup>b,c</sup> \* and G. Maurin<sup>a</sup> \**

<sup>a</sup> Institut Charles Gerhardt Montpellier, UMR-5253, Université de Montpellier, CNRS, ENSCM, Place E. Bataillon, 34095 Montpellier cedex 05, France.

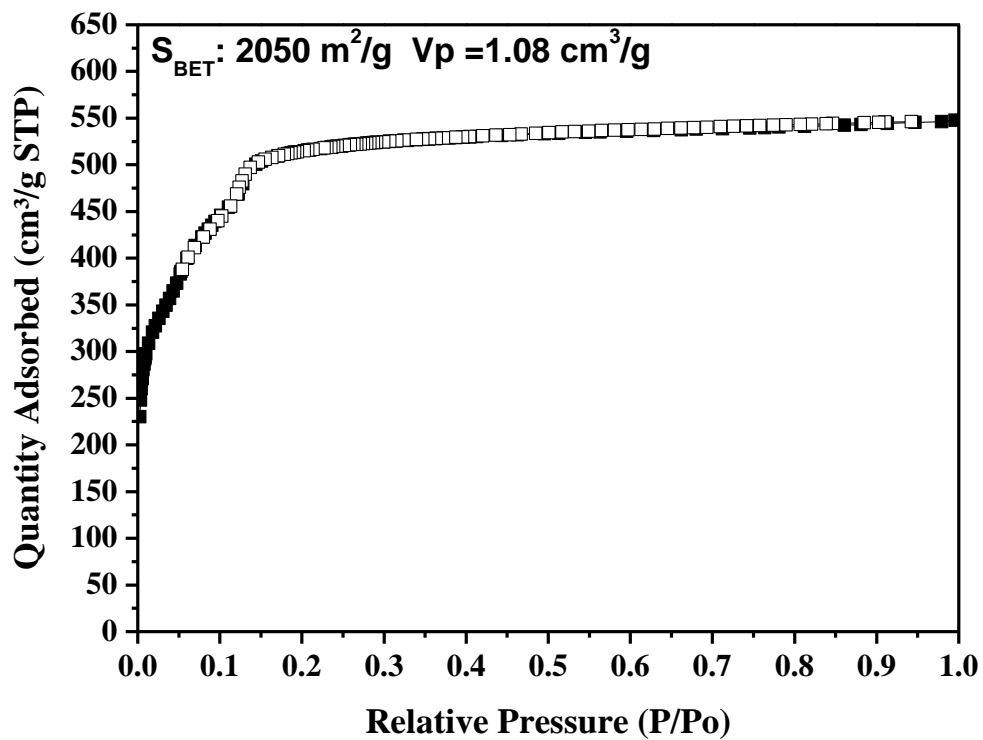
<sup>b</sup> Research Group for Nanocatalyst and Chemical Safety Research Center, Korea Research Institute of Chemical Technology (KRICT), Gajeong-ro 141, Yuseong, Daejeon 34114, South Korea.

<sup>c</sup> Department of Chemistry, Sungkyunkwan University, Suwon 440-476, South Korea

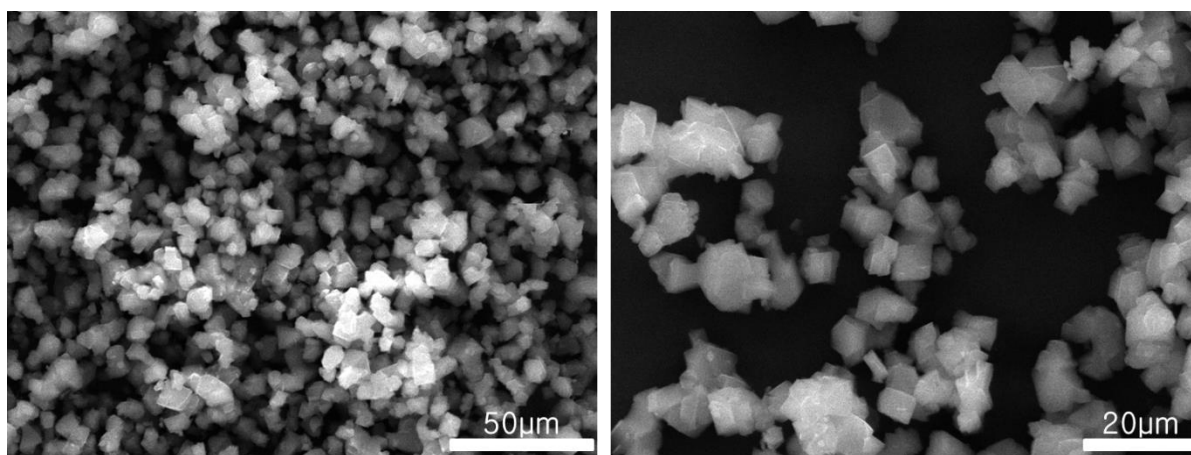
\*Corresponding authors: [guillaume.maurin1@umontpellier.fr](mailto:guillaume.maurin1@umontpellier.fr) and [jschang@kRICT.re.kr](mailto:jschang@kRICT.re.kr)



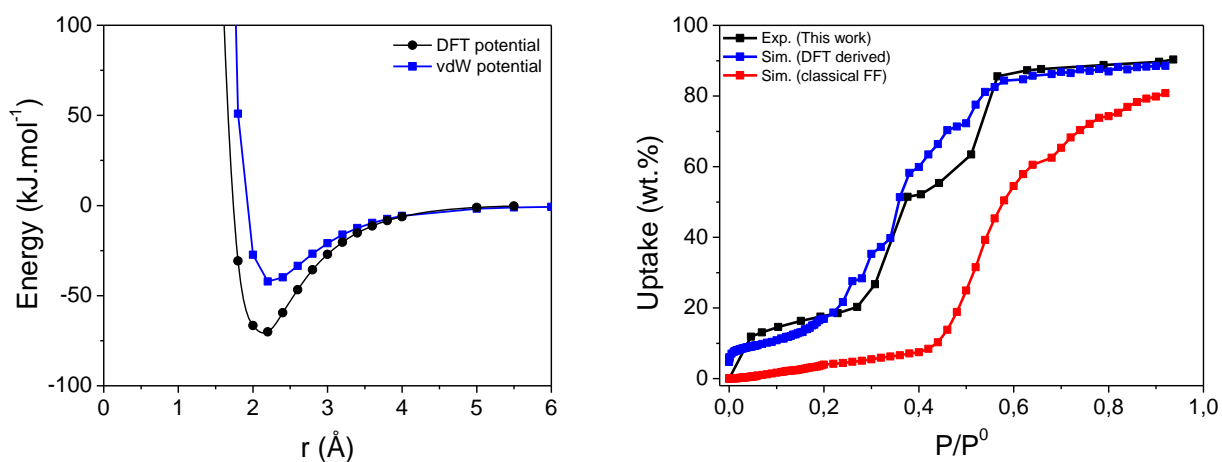
**Figure S1.** Powder X-ray diffraction pattern of as-synthesized MIL-100(Fe). The data were collected using Rigaku D/Max 2200 PC and Cu K $\alpha$  radiation



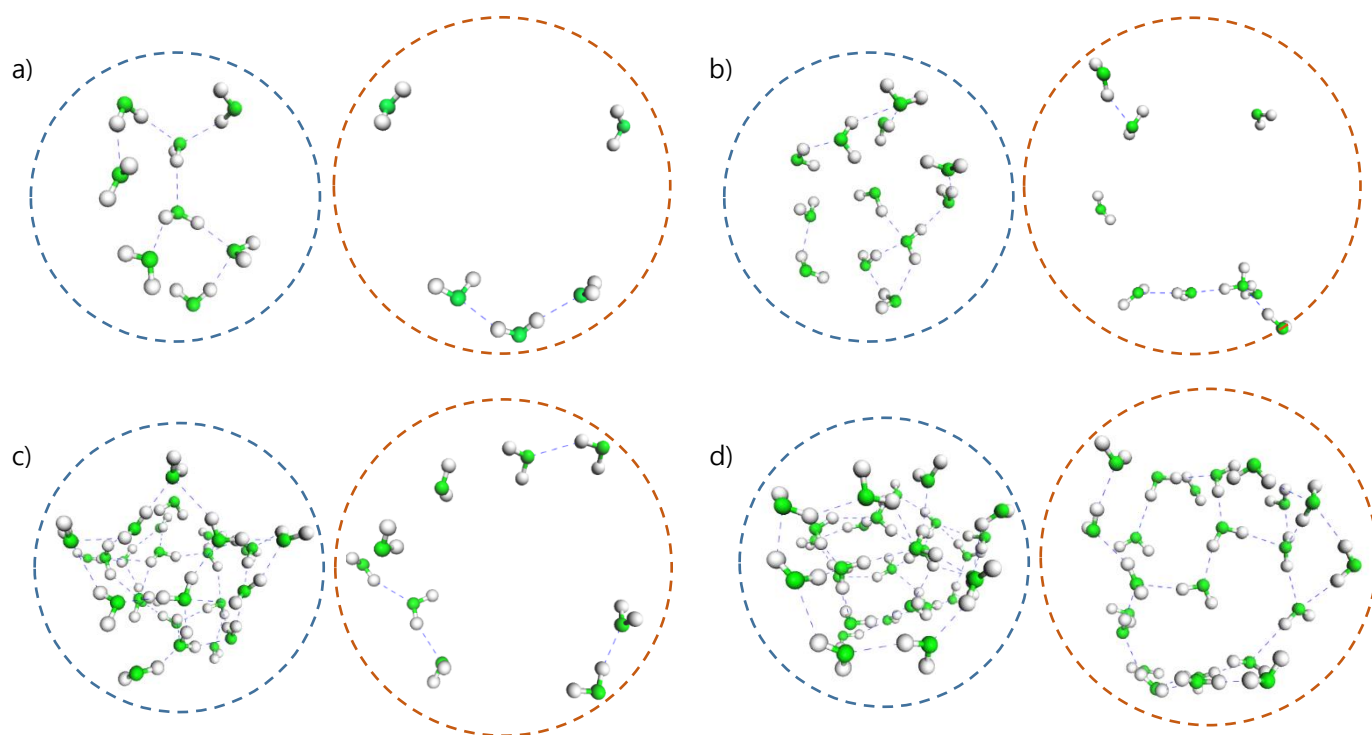
**Figure S2.** N<sub>2</sub> adsorption-desorption isotherms of dehydrated MIL-100(Fe) measured collected at 77 K.



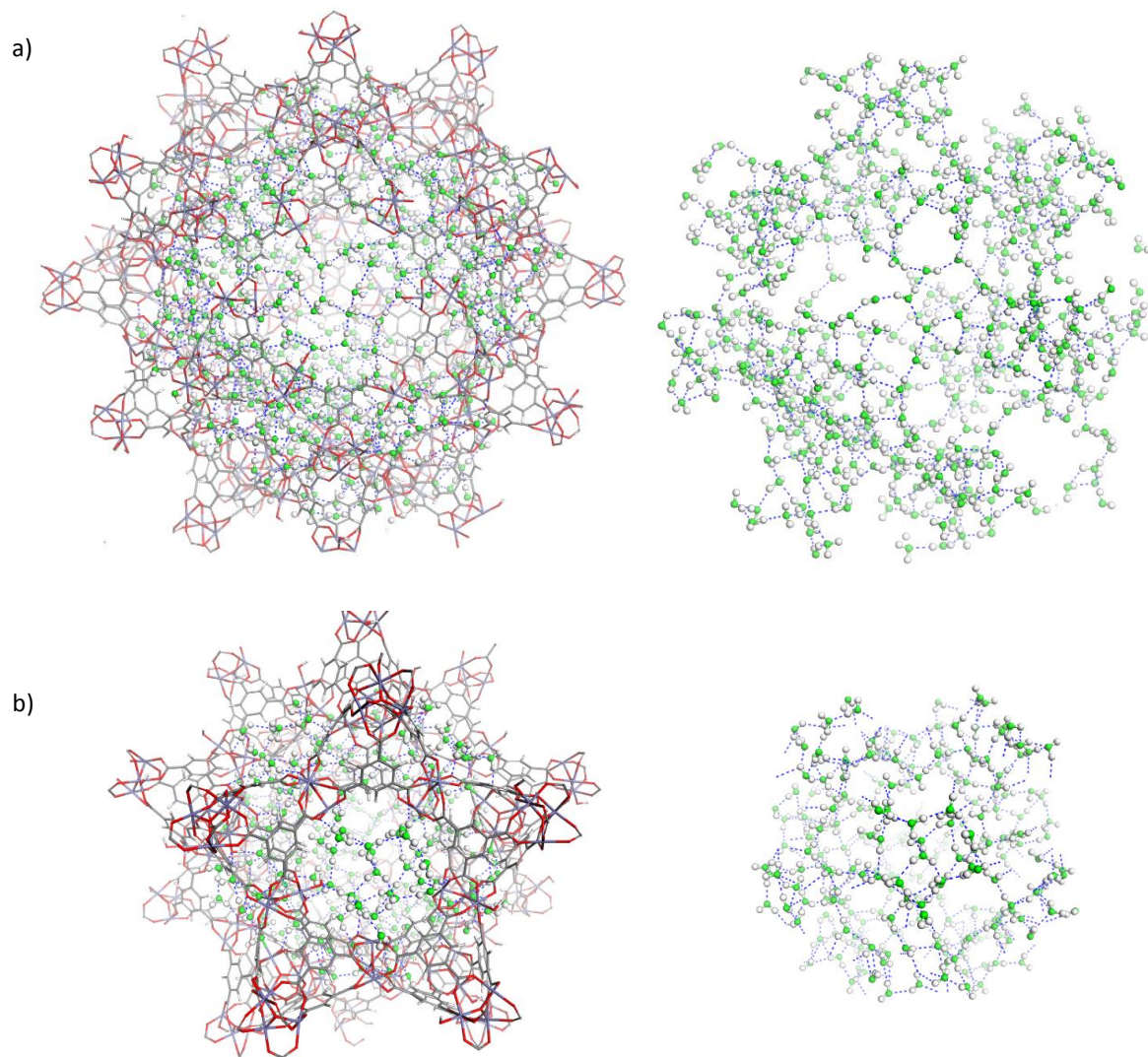
**Figure S3.** Scanning electron micrograph images of as-synthesized MIL-100(Fe) (SEM, Philips, XL30S FEG).



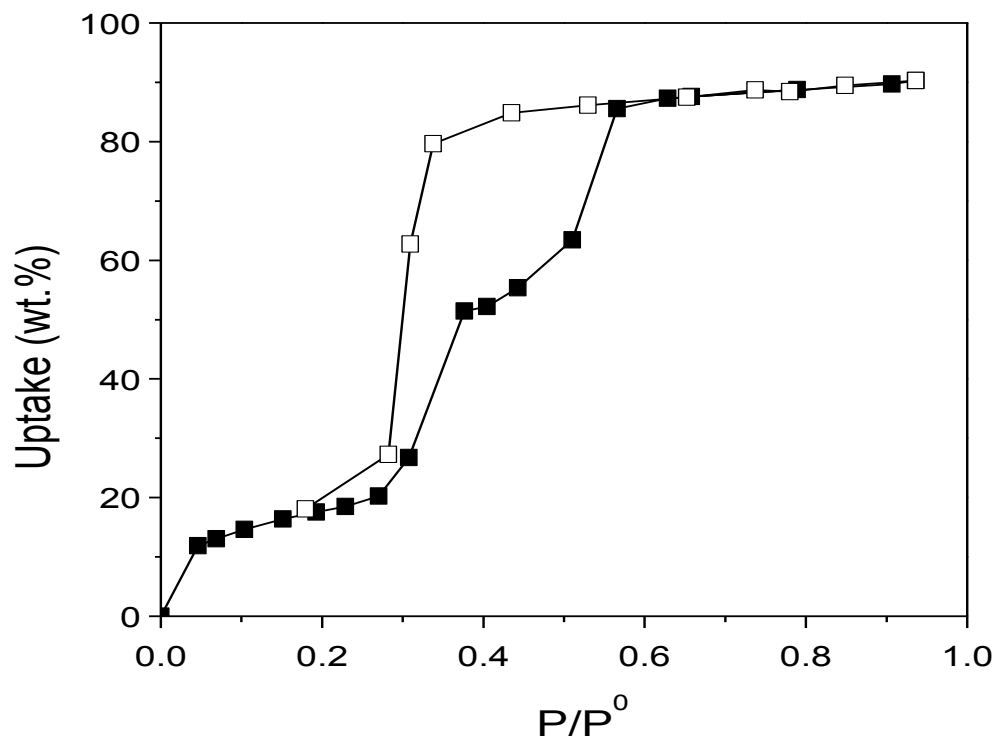
**Figure S4.** (a) Impact of the CUS-water interaction on the total cluster – water interaction potential. In black, the total DFT interacting potential and in blue, the interacting potential considering only coulombic and dispersive contributions from generic forcefields. (b) Impact of the consideration of the CUS-water forcefield for the water adsorption isotherm in the MIL-100(Fe) with the TIP-4P-Ew model.



**Figure S5.** Detailing of the progressive clustering of water molecules at the pentagonal and hexagonal windows (respectively represented by blue and red dashed circles) of the MIL-100(Fe) at  $P/P^0 = 0.1$  (a),  $0.2$  (b),  $0.3$  (c) and  $0.44$  (d).



**Figure S6.** Example of percolating clusters formed in the larger (a) and smaller (b) mesoporous cages of the MIL-100(Fe) at  $P/P^0 = 0.44$ .



**Figure S7.** Water desorption (empty squares) and adsorption (filled squares) curves at 303 K in the MIL-100(Fe).