Electronic Supplementary Material (ESI) for ChemComm.

Electronic Supplementary Information for:

Investigation of the terahertz vibrational modes of ZIF-8 and ZIF-90 with terahertz time-domain spectroscopy

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S1. PXRD patterns for ZIF-8 and ZIF-90 (298 K, CuK□ radiation)

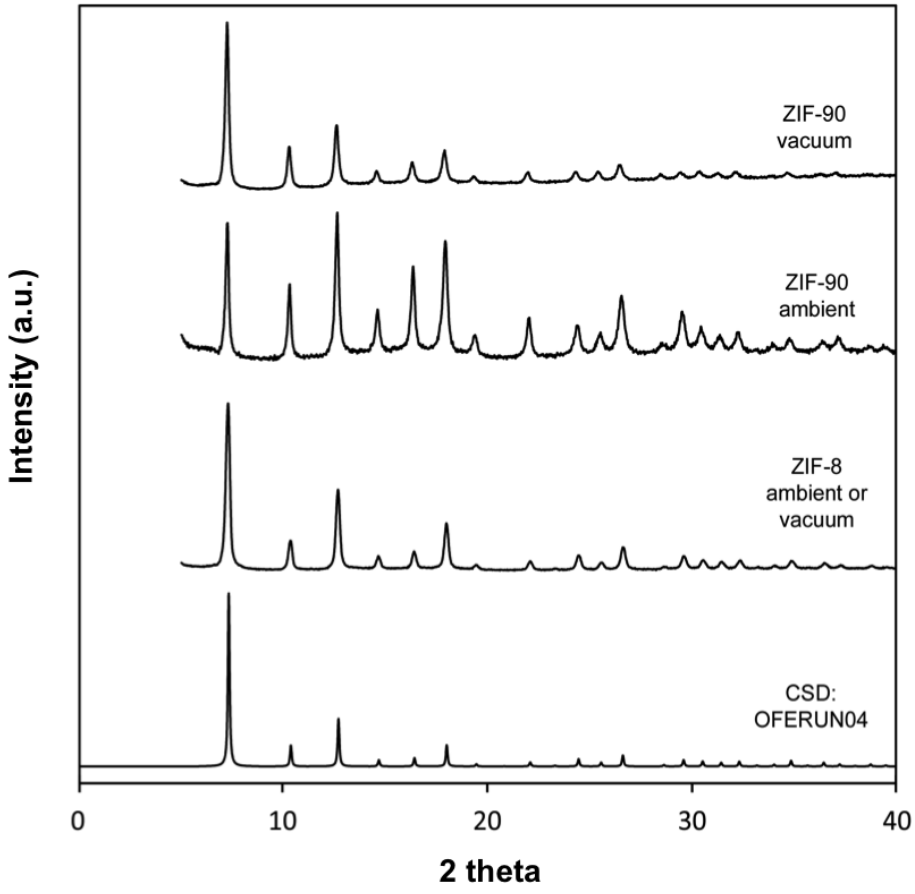

Figure S1. Powder X-ray diffraction (PXRD) patterns for simulated ZIF-90[S1] and experimental ZIF-8 and ZIF-90 at vacuum and ambient conditions.

S2. PXRD: variation in relative intensities for ZIF-90

The changes in the observed relative intensities for the Bragg peaks in the PXRD pattern of ZIF-90 under ambient conditions and under vacuum are attributed to water adsorption/desorption. A coarse model illustrating the consistency of this interpretation was prepared as follows:

(1) The crystal structure of the empty framework was extracted from the Cambridge Structural Database (refcode: OFERUN04[S1]).

(2) The structure in space group I–43m was expanded to I1 (*i.e.* all non-translational symmetry elements were removed).

(3) O atoms were placed at positions corresponding to a dodecahedron around the unit-cell origin, with O…O edges ≈ 2.5 Å (radius of enclosing sphere = 3.5 Å). The I-centring places a dodecahedron also in the void at (½,½,½).

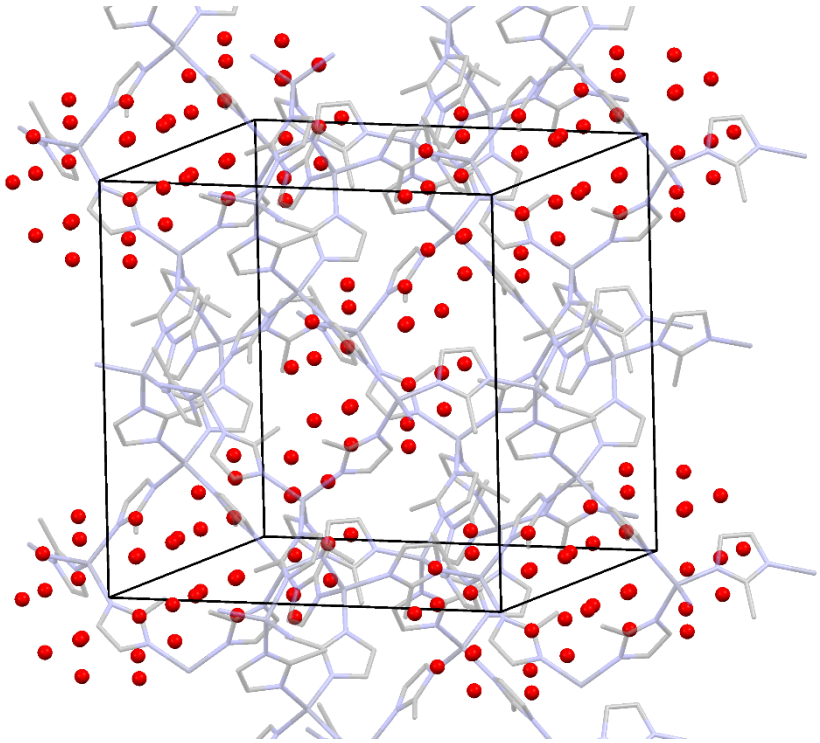

Figure S2. Crystalline model for ZIF-90, grey and blue, with adsorbed water molecules, red spheres.

Note that this model is not chemically or energetically rigorous – it is only intended to create a reasonable electron density distribution in the voids of ZIF-90. The simulated PXRD pattern shows changes in the relative intensities of the Bragg peaks compared to the empty ZIF-90 structure, which correspond to those seen by experiment:

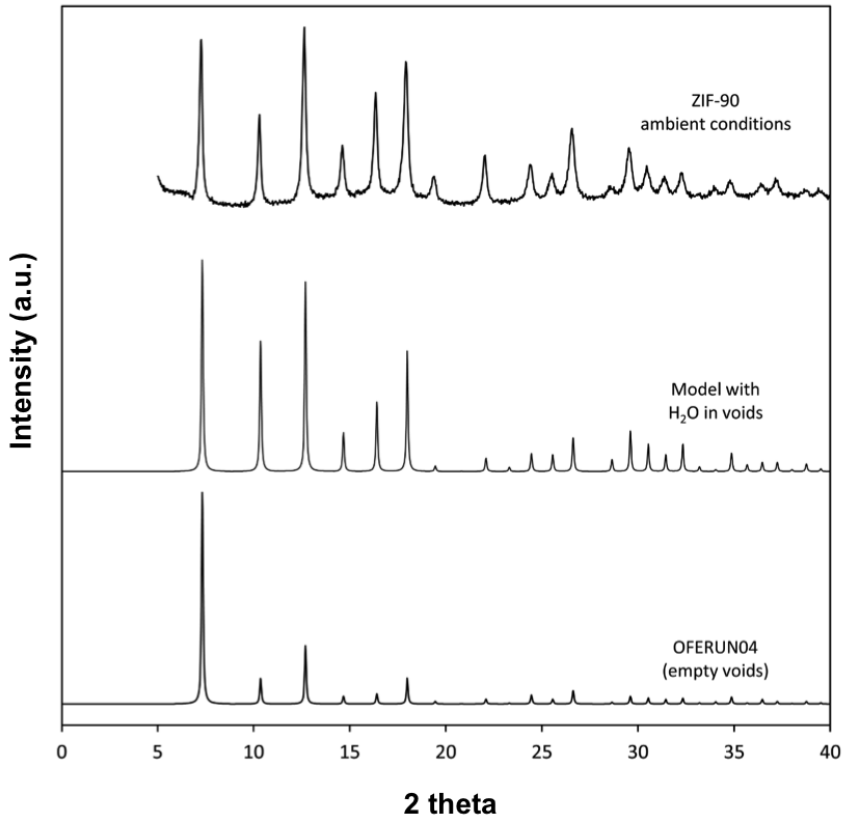

Figure S3. Powder X-ray diffraction (PXRD) patterns for simulated empty ZIF-90 and water adsorbed ZIF-90, and experimental ZIF-90 at ambient conditions. Note the changes in the relative intensities.

S3. References

S1. A.-X. Zhu, R.-B. Lin, X.-L. Qi, Y. Liu, Y.-Y. Lin, J.-P. Zhang, X.-M. Chen, *Micro. Meso. Mat.* 2012, **157**, 42.