Electronic Supplementary Material (ESI) for Physical Chemistry Chemical Physics. This journal is © the Owner Societies 2015

## **Supplementary Information**

## A Combined Experimental and Computational NMR Study of Crystalline and Amorphous Zeolitic Imidazolate Frameworks

Emma F. Baxter,<sup>a</sup> Thomas D. Bennett,<sup>a</sup> Caroline Mellot-Draznieks,<sup>b</sup> Christel Gervais,<sup>c</sup> Frédéric Blanc<sup>d</sup> and Anthony K. Cheetham<sup>a\*</sup>

<sup>a</sup> Department of Materials Science and Metallurgy, University of Cambridge, 27 Charles Babbage Road, Cambridge, CB3 OFS, United Kingdom.

<sup>b</sup> Laboratoire de Chimie des Processus Biologiques UMR 8229, Collège de France-CNRS Université Pierre et Marie Curie, Collège de France 11 Place Marcelin Berthelot, 75231, Paris Cedex 05, France

<sup>c</sup> Sorbonne Universités, UPMC Univ Paris 06, CNRS, Collège de France, UMR 7574, Chimie de la Matière Condensée de Paris, Paris, France.

<sup>d</sup> Department of Chemistry and Stephenson Institute for Renewable Energy, University of Liverpool, Crown Street, Liverpool, L69 7ZD, United Kingdom.

\* Corresponding Author

E-mail: akc30@cam.ac.uk (A.K.C)

### Synthesis

All reactants were purchased from Sigma Aldrich or Fischer unless otherwise stated.

ZIF-4 was synthesis according to a modified version of a known literature procedure.<sup>1</sup> A mixture of zinc nitrate hexahydrate, Zn(NO<sub>3</sub>)<sub>2</sub>.6H<sub>2</sub>O (1.2 g, 4.04 mmol) and solid imidazole, H-Im (0.9 g, 13.24 mmol) were dissolved in 90 ml of DMF. The flask was capped and heated to 100 °C (at a rate of 5 °C / minute) and held at this temperature for 72 hours. The mother liquid was removed through filtration and the white crystals were washed with DMF (3 x 10 ml) followed by solvent exchange with DCM (20 ml) overnight. The resulting solution was filtered yielding ZIF-4 with DCM held within the pores. The ZIF-4 was activated at 180 °C under vacuum for 5 hours to eliminate any DCM in the pores. ZIF-zni was prepared according to a literature procedure<sup>2</sup> and activated at 120 °C under vaccum for 5 hours to evacuate the pores of the ethanol solvent. ZIF-8 was obtained from BASF and activated at 100 °C under vacuum for 5 hours.

### **Powder X-Ray Diffraction Data**

#### Diffraction patterns of crystalline and amorphous ZIFs

The following data PXRD was collected on a Bruker-AXS D8 diffractometer (2 $\theta$  range 5-60°) with a LynxEye position sensitive detector in Bragg-Brentano parafocusing geometry and radiation of (Cu K $\alpha$ )1 ( $\lambda$  =1.540598 Å). The data was analysed using the program X'pert HighScore Plus.

# Computational Method and Importance of Dispersive Corrections for Geometry Optimizations

All electronic and structural calculations were performed with the Kohn-Sham DFT framework using periodic boundary conditions. The *Vienna ab initio package* (VASP) <sup>3</sup> a planewave code, was employed for the geometry optimizations of all the structures. A 500 eV plane-wave cutoff was found suitable for the convergence of the systems to within 0.01 eV/atom. Starting from the experimentally determined unit-cell of each hybrid structure, both lattice parameters and atomic positions were fully relaxed in space group *P*1 with the semi-local Perdew-Burke-Ernzerhof exchange-correlation functional using D2 dispersion corrections.<sup>4</sup>

It is reasonable to question the need of dispersion-corrected DFT calculations. In the present study, the simulation of the dense zni structure (in fact the densest of the family) and that of the relatively dense ZIF-4 structure require the use of dispersion-corrected DFT calculations, as explained in the following section.

We were the among the first ones to investigate the role of dispersion in hybrid frameworks and their contribution, by comparing calculations from structures optimized with and without dispersion corrections (erf). The latter work, performed on the highly flexible MIL-53 systems, specifically demonstrated that, unlike dispersion-free DFT methods, DFT-dispersion ones are mandatory to predict the stabilization of the densest form of MIL-53 (its so-called "closed" pore form) with respect to its "open" pore version, in line with the experimental observations (See Table 1 in <sup>5</sup>). Subsequently, we have also demonstrated through several computational studies that dispersion-corrected DFT calculations are also required to explore ZIFs' energy landscape.<sup>6, 7</sup> We specifically compared in <sup>6</sup> DFT calculations (without dispersion correction) and DFT-D2 ones on a series of ZIFs. These calculations again established that dispersion interactions have a key role in the simple inverse relationship between density and thermodynamic stability, confirmed by a thermochemical analysis study of MOFs by Navrotsky et al.<sup>8</sup> More recently, we have shown how DFT-D calculations may predict the structure-directing influence of functionalized linkers in ZIFs.<sup>7</sup> Finally, DFT-D calculations were used to capture the mechanical properties of hybrid frameworks.<sup>8</sup>

In the present work, having in mind that the ZIF-zni crystal structure is the densest one of this family, dispersion forces are expected to play a crucial role and DFT-D calculations were thus adopted from the start.



Figure S1. PXRD of crystalline (top) and amorphous ZIF-4 (bottom).



Figure S2. PXRD of crystalline (top) and amorphous ZIF-zni (bottom).



Figure S3. PXRD of crystalline (top) and amorphous ZIF-8 (bottom).

## **Computational Results**

 Table S1. ZIF-8 experimental and calculated <sup>13</sup>C and <sup>15</sup>N isotropic chemical shifts, proposed assignment by comparison with experimental values and asymmetric unit cells.

ZIF-8	$\delta_{\text{iso}}$ (ppm)		Diff				Diff
	Calc	Ехр	(ppm)		Calc	Ехр	(ppm)
C3	10.7	13.7	3.0	N1	215.4	214.4	1.0
C2	125.3	124.2	1.1				
C1	151.1	151.2	0.1				
A DECAR		A A A	X LUNI	X		Zn1 C2 N1 C2 N1	C1

 Table S2: ZIF-zni calculated <sup>13</sup>C and <sup>15</sup>N chemical shift and proposed assignment by comparison with experimental values.

ZIF- zni	δ <sub>iso</sub> (ppm)		Diff		$\delta_{\text{iso}}$ (ppm)		Diff	7
	Calc	Ехр	(ppm)		Calc	Ехр	(ppm)	and the
C1	141.7	142.7	1.0	N1	212.0	212.2	0.2	$\left[ \right]$
C3	127.4	126.2	1.2	N2	215.8	215.2	0.6	
C2	126.9	125.3	1.6					
C10	141.4	142.0	0.6	N7	214.3	214.1	0.2	Ħ
C12	129.4	127.8	1.6	N8	211.1	210.3	0.8	
C11	126.7	125.3	1.4					
С7	141.5	142.4	0.9	N6	216.1	215.5	0.6	
C9	131.1	128.2	2.9	N5	217.6	216.6	1.0	
C8	125.5	124.8	0.7					Zn:
C4	140.9	142.0	1.1	N4	216.2	215.5	0.7	Ĭ
C5	127.1	125.9	1.2	N3	218.7	217.2	1.5	
C6	124.6	124.5	0.1					



Table S3: ZIF-4 calculated <sup>13</sup>C and <sup>15</sup>N chemical shift and proposed assignment by comparison with experimental values.

ZIF-4	4 δ <sub>iso</sub> (ppm)		Diff		$\delta_{iso}$ (ppm	ו)	Diff	
	Calc	Ехр	(ppm)		Calc	Ехр	(ppm)	
C4	124.9	123.9	1.0	N3	212.1	212.0	0.1	Zn1
C8	141.5	142.7	0.2	N6	217.2	215.2	2.0	
C9	128.4	125.6	2.8					RERE
C1	144.1	143.9	0.2	N1	209.6	211.3	1.7	
C2	126.4	124.5	1.9	N2	216.2	214.1	2.1	
С3	126.8	124.8	2.0					
C6	125.4	124.0	1.4	N7	211.5	212.0	0.5	N7 C6
C7	143.5	143.5	0.0	N5	218.1	216.1	2.0	Zn2 <sub>C7</sub> N5 <sup>C1</sup> <sub>N2</sub>
C10	129.0	125.8	3.2					C8 N3
C5	127.2	125.6	1.6	N8	214.1	213.6	0.5	C9C4 N4 C2
C11	141.0	142.5	1.5	N4	218.0	215.6	2.4	CII C5
C12	127.5	125.6	1.9					N8 C12

Table S4:  $^{67}$ Zn calculated and experimental  $^9$  chemical shifts and Cq values for crystalline ZIFs.\*

		δ <sub>iso</sub> (	ppm)	C <sub>Q</sub> (MHz)		
		Calc	Exp	Calc	Exp	
ZIF-8	Zn1	297	293	3.3	1.6	
ZIF-4	Zn1	291	315	9.5	5	
	Zn2	295	300	5.9	3.8	
ZIF-zni	Zn1	300		6.9		
	Zn2	299		7.8		

\* Note that the state of solvation of the samples in reference 9 was not the same as in our calculations, which were performed on desolvated systems.

715	<sup>13</sup> C		<sup>15</sup> N		
ZIF	$\delta_{iso}$ (ppm)	Assignements	$\delta_{iso}$ (ppm)	Assignements	
a 715 ani	126	N <b>C</b> C	214 7	с <b>л</b> с	
<i>u<sub>m</sub></i> ∠iF-2111	143	N <b>C</b> N	214.7		
~ 7IE /	126	N <b>C</b> C	214.0	CNC	
<i>u<sub>m</sub></i> 217-4	143	N <b>C</b> N	214.0		
	15	<b>C</b> H <sub>3</sub>			
	118	N <b>C</b> C <sup>10</sup>			
a <sub>m</sub> ZIF-8	126	N <b>C</b> C	215.2	C <b>N</b> C	
	148	NCCH3N 10			
	152	N <b>C</b> CH₃N			

Table S5. <sup>13</sup>C and <sup>15</sup>N chemical shifts and spectral assignements for amorphous ZIFs

Table S6. Number of scans for <sup>13</sup>C and <sup>15</sup>N CP MAS experiments at 20 T unless otherwise specified.

ZIF	Number of scans				
	<sup>13</sup> C CP	<sup>15</sup> N CP			
ZIF-zni	2048	11096			
ZIF-4	2048	16384			
ZIF-8	2048	20480			
ZIF-4 at 9.4 T	256	n/a			
a <sub>m</sub> ZIF-zni	2048	16384			
a <sub>m</sub> ZIF-4	5120	16384			
a <sub>m</sub> ZIF-8	4096	25282			



**Figure S4.** <sup>13</sup>C CP MAS of crystalline ZIF-4 recorded at (a) 9.4 T under MAS at  $v_{rot}$  = 12.5 kHz and at (b) 20 T under MAS at  $v_r$ = 21 kHz. <sup>1</sup>H decoupling during acquisition was achieved with SPINAL-64<sup>11</sup> with  $v_1$ (<sup>1</sup>H) = 83 kHz. Spinning sidebands are marked with asterisks. The left and right inserts show magnified views of the 146-140 ppm and 128-120 ppm regions, respectively.

- 1 K. S. Park, Z. Ni, A. P. Côté, J. Y. Choi, R. Huang, F. J. Uribe-Romo, H. K. Chae, M. O'Keeffe and O. M. Yaghi, *Proc. Natl. Acad. Sci.*, 2006, **103**, 10186-10191.
- 2 P. J. Beldon, L. Fábián, R. S. Stein, A. Thirumurugan, A. K. Cheetham and T. Friščić, *Angew. Chem. Int. Ed.*, 2010, **49**, 9640-9643.
- 3 G. Kresse and J. Furthmüller, *Phys. Rev. B*, 1996, **54**, 11169--11186.
- 4 S. Grimme, J. Comput. Chem., 2006, **27**, 1787-1799.
- 5 A. M. Walker, B. Civalleri, B. Slater, C. Mellot-Draznieks, F. Corà, C. M. Zicovich-Wilson, G. Román-Pérez, J. M. Soler and J. D. Gale, *Angew. Chem. Int. Ed.*, 2010, **49**, 7501-7503.
- 6 R. Galvelis, B. Slater, A. K. Cheetham and C. Mellot-Draznieks, *CrystEngComm*, 2012, **14**, 374-378.
- 7 R. Galvelis, B. Slater, R. Chaudret, B. Creton, C. Nieto-Draghi and C. Mellot-Draznieks, *CrystEngComm*, 2013, **15**, 9603-9612.
- 8 J. T. Hughes, T. D. Bennett, A. K. Cheetham and A. Navrotsky, *J. Am. Chem. Soc.*, 2013, **135**, 598-601.
- 9 A. Sutrisno, V. V. Terskikh, Q. Shi, Z. Song, J. Dong, S. Y. Ding, W. Wang, B. R. Provost, T. D. Daff, T. K. Woo and Y. Huang, *Chem. Eur. J.*, 2012, **18**, 12251-12259.
- 10 C. López, R. Claramunt, M. Á. García and J. Elguero, *cent.eur.j.chem.*, 2004, **2**, 660-671.
- 11 B. M. Fung, A. K. Khitrin and K. Ermolaev, J. Magn. Reson., 2000, **142**, 97-101.