

# Supplementary Information for: Nucleation of Zeolitic Imidazolate Frameworks: from molecules to nanoparticles

Salvador R.G. Balestra,<sup>1,2</sup> \* Bruno Martínez-Haya,<sup>1</sup> Norge Cruz-Hernández,<sup>3</sup> Dewi W. Lewis,<sup>4</sup> Scott M. Woodley,<sup>4</sup> Rocio Semino,<sup>2,5</sup> Guillaume Maurin,<sup>2</sup> A. Rabdel Ruiz-Salvador,<sup>1</sup> \* and Said Hamad<sup>1</sup> \*

1) Departamento de Sistemas Físicos, Químicos y Naturales, Universidad Pablo de Olavide, Ctra. Utrera km 1, 41013 Seville, Spain

E-mail: [salrodgom@upo.es](mailto:salrodgom@upo.es), [rruisal@upo.es](mailto:rruisal@upo.es), [said@upo.es](mailto:said@upo.es)

2) ICGM, Univ. Montpellier, CNRS, ENSCM, Montpellier, France

3) Departamento de Física Aplicada I, Escuela Politécnica Superior, Universidad de Sevilla, Sevilla, Spain

4) Department of Chemistry, University College London, 20 Gordon St., London, WC1H 0AJ, UK

5) Sorbonne Université, CNRS, Physico-chimie des Electrolytes et Nanosystèmes Interfaciaux, PHENIX, F-75005 Paris, France

## 1. Section S1. Formation free energies of clusters with implicit and explicit solvation

**Table S1.** Formation free energies of small  $Zn_zIm_lA_a$  clusters with various additional species, namely  $H_2O$ , and  $HIm$  molecules, and  $NO_3^-$  counterions.

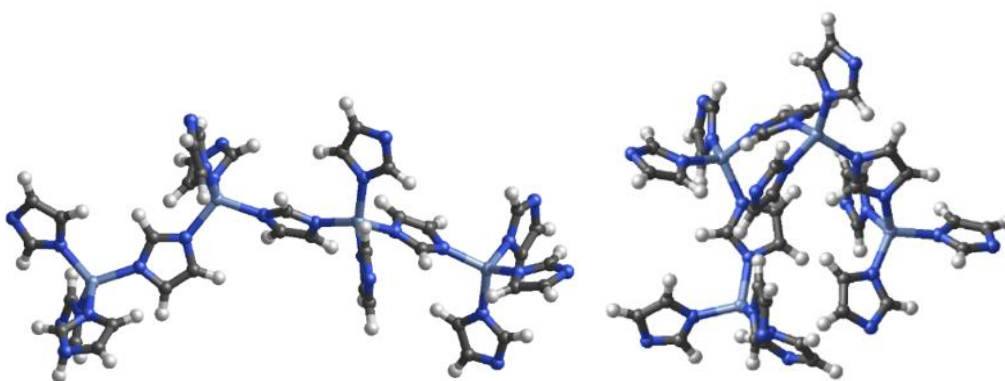
$z$ $Zn^{2+}$	$l$ $Im^-$	$l$ H-mIm	$a$ $H_2O$	$a$ $NO_3^-$	$q$ [e-]	$\Delta g_c^s$ [eV] RwB97X/6-311++G(d,p)
1	1			1	0	-2.724
1	1			2	-1	-3.008
1	1			3	-2	-2.990
1	2			1	-1	-3.793
1	2			2	-2	-3.665
1	3			1	-2	-4.250
1	2	2			0	-11.606
1	4				0	-13.925
2	1			6	-3	-2.788
2	2			5	-3	-3.160
2	3			4	-3	-3.522
2	3			4	-3	-3.504
0	1		4		-1	0.299 *
1	0		4		+2	-0.649
1	1		4		+1	-2.055
1	2		4		0	-3.186
1	3		4		-1	-4.120
1	4		4		-2	-4.749
1	-	4	-	-	-2	-10.573
1	-	-	-	4	-2	-2.256
1	-	1	-	3	-1	-2.630
1	1	1	-	2	-1	-3.267
1	2	1	-	1	-1	-3.966
1	-	2	-	2	0	-6.324
1	1	2	-	1	-1	-8.202

\* No division by zero.

## 2. Section S2. Internal and free energies of formation of clusters in vacuo and with implicit solvation.

**Table S2.** Internal ( $U$ ) and free energies of formation per Zn atom, ( $g$ ), of small clusters (from 1 to 4 Zn atoms), both in gas phase ( $g$ ) and using ethanol as implicit solvent ( $s$ ), calculated with wB97X/6-311++G(d,p) calculations. We also report the solvation energy, and the Root-Mean-Square Zn\_01\_imi\_05.xyzDeviation (RMSD) between the superimposed optimized clusters in vacuo and solvated (no hydrogen atoms).

System, $\Omega$			$q$ [ $e^-$ ]	$\Delta U_{ZPC}^g$ [eV] wB97X/6-311++G(d,p)	$\Delta g_c^s$ [eV] wB97X/6-311++G(d,p)	$\Delta g_c^s$ [eV] Cycle	$\sqrt{ \vec{r}^s - \vec{r}^g ^2}$ [Å/atom]
$z$ $Zn^{2+}$	$l$ $Im^-$	$l$ $mlm^-$					
1	1	-	1	-16.230	-1.943	-2.125	0.0025
1	2	-	0	-25.270	-3.634	-3.739	0.0564
1	3	-	-1	-28.075	-4.528	-4.408	0.0437
1	4	-	-2	-27.228	-4.759	-4.852	0.0980
1	5	-	-3	-22.561	-4.125	-4.106	0.7601
1	6	-	-4	-15.968	-3.248	-3.395	0.0821
2	1	-	3	-8.8375	-1.552	-1.582	0.0727
2	2	-	2	-16.426	-2.476	-2.576	0.0715
2	3	-	1	-22.669	-3.382	-3.502	0.2829
2	4	-	0	-25.730	-3.864	-3.953	0.5060
2	5	-	-1	-27.561	-4.289	-4.320	0.5143
2	6	-	-2	-27.511	-4.610	-4.580	0.0111
2	7	-	-3	-26.522	-4.716	-4.770	0.3849
4	4	-	4	-23.670	-2.873	-2.971	0.0026
1	-	1	1	-16.763 *	-1.966	-2.184	0.1989
1	-	2	0	-25.325	-3.528	-3.766	0.2443
1	-	3	-1	-27.929	-4.508	-4.383	0.0376
1	-	4	-2	-26.875	-4.855	-4.555	0.0654
2	-	5	-1	-27.413	-4.336	-4.238	0.7074
2	-	7	-3	-26.435	-4.803	-4.680	0.2754
4	-	4	4	-16.802	-2.849	-3.024	0.272



**Figure S1.** Open versus folded configurations for the  $Zn_4Im_{13}$  cluster, obtained from optimization in vacuo (left) and in implicit ethanol (right).

### 3. Section S3. Stability of bulk-like, ring clusters.

**Table S3.** Formation free energies per Zn atom,  $\Delta g_c^s$ , of Im-bearing clusters, calculated using ethanol as implicit solvent at levels wB97X/6-311++G(d,p) and GFN2-xTB.

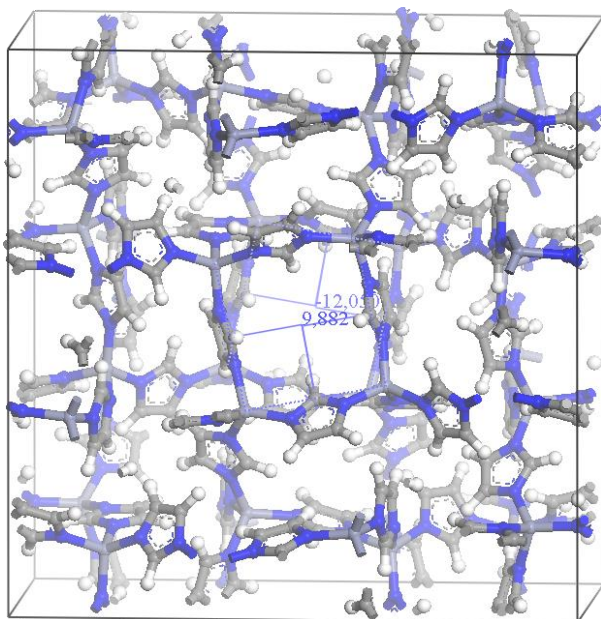
<i>Label</i> (when necessary)	$z$ $Zn^{2+}$	$l$ $Im^-$	$q$ [ $e^-$ ]	$\Delta g_c^s$ [eV] wB97X/6- 311++G(d,p)	Thermo. Cycle	$\Delta g_c^s$ [eV] GFN2-xTB
Zn – Im bond	1	1	1	-1.943	-2.125	-32.651
	1	2	0	-3.635	-3.739	-36.116
Trigonal Zn	1	3	-1	-4.528	-4.408	-38.359
<b>1FCZ</b>	1	4	-2	<b>-4.759</b>	<b>-4.852</b>	<b>-39.653</b>
PentaCoordinated Zn	1	5	-3	-4.125	-4.106	-39.602
Octahedral Zn	1	6	-4	-3.248	-3.395	-39.280
	2	1	3	-1.552	-1.582	-29.758
	2	2	2	-2.477	-2.576	-33.381
	2	3	1	-3.382	-3.502	-35.420
	2	4	0	-3.864	-3.953	-36.737
$\pi$ - $\pi$	2	5	-1	-4.107	-4.121	-38.329
Planar configuration	2	5	-1	-4.290	-4.320	-38.019
1 Trigonal & 1 Tetrahedral Zn's	2	6	-2	-4.612	-4.580	-38.737
Eclipsed 2FCZs	2	7	-3	-4.679	-4.708	-39.451
Staggered 2FCZs	2	7	-3	<b>-4.716</b>	<b>-4.770</b>	<b>-39.450</b>
3MR (anti-parallel)	3	3	3	-2.750	<b>-2.831</b>	<b>-34.290</b>
Linear	3	3	3	-2.616	-2.722	-33.735
3MR (parallel)	3	3	3	<b>-2.752</b>	-2.865	-34.319
	3	4	2	-3.260	-3.381	-35.104
	3	5	1	-3.523	-3.631	-36.542
	3	6	0	-4.159	-4.213	-37.676
	3	7	-1	-4.223	-4.247	-37.862
<b>sFCZs</b>	3	10	-4	<b>-4.799</b>	<b>-9.834</b>	<b>-39.338</b>
4MR (undercoordinated)	4	4	4	-2.873	-2.971	-34.437
4MR (3 Bi 1 Tri)	4	5	3	-3.224	-3.346	-35.329
4MR (3 Bi 1 Tetra)	4	6	2	-3.460	-3.726	-36.159
4MR (2 Bi 2 Tri)	4	6	2	-3.617	-3.710	-35.886
4MR (1 Bi 3 Tri)	4	7	1	<b>-3.895</b>	<b>-4.002</b>	<b>-36.926</b>
4MR-SOD	4	12	-4	-4.693	<b>-4.732</b>	<b>-39.355</b>
<b>4MR-zni</b>	4	12	-4	<b>-4.740</b>	-4.736	-39.336
<b>4FCZs</b>	4	13	-5	-4.535	-4.265	-39.397
Hyper tetrahedron	5	4	6	-2.040	-2.166	-32.629
Flat configuration	5	10	0	-4.168	-4.001	-37.658
6MR (undercoordinated)	6	6	6	-2.938	-2.994	-34.428
4MR-4MR	6	12	0	-4.258	<b>-4.300</b>	<b>-37.651</b>
6MR (undercoordinated)	6	12	0	<b>-4.290</b>	-4.331	-37.884
<b>6MR (fully coordinated)</b>	6	18	-6	<b>-4.6187</b>	-4.541	-39.371

**Table S4.** Formation free energies per Zn atoms,  $\Delta g_c^s$ , of mIm-bearing clusters, calculated using ethanol as implicit solvent at levels wB97X/6-311++G(d,p) (thermodynamic cycle) and GFN2-xTB.

Label (when necessary)	$z$ $Zn^{2+}$	$l$ $mIm^-$	$q [e^-]$	$\Delta g_c^s$ [eV] wB97X/6- 311++G(d,p)	$\Delta g_c^s$ [eV] GFN2-xTB
	1	1	1	-2.184	-33.108
	1	2	0	-3.766	-33.700
	1	3	-1	-4.383	-35.596
1FCZ* (Tetrahedron)	1	4	-2	<b>-4.555</b>	<b>-36.390</b>
	2	1	3	-1.583	-28.166
	2	2	2	-2.476	-34.001
	2	3	1	-3.510	-36.046
$\pi$ - $\pi$	2	5	-1	-4.238	-38.415
	2	5	-1	-4.336	-38.436
	2	6	-2	-4.534	-38.666
2FCZs* (Eclipsed)	2	7	-3	<b>-4.804</b>	<b>-39.902</b>
Linear	3	3	3	-2.758	-34.394
S3R	3	3	3	-2.897	-34.851
	3	4	2	-3.415	-35.857
	3	5	1	-3.573	-37.072
S4R (cycle)	4	4	4	-3.024	-35.204
S4R (full ring, SOD)	4	12	-4	-4.802	-39.853
S4R (full ring, <i>zni</i> )	4	12	-4	-4.763	-39.799
6MR	6	18	-6	-4.368	-39.511

\* FCZs = Fully Coordinated Zn cations

**4. Section S4. Dihedral angles between the four Zn atoms in the 4MR in the zni crystal structure.**



**Figure S2.** Two examples of dihedral angles between four Zn atoms in the 4MR in the zni crystal structure.

**5. Section S5. Formation energies of large clusters, calculated using the linear relation between GFN2-xTB and wB97X/6-311++G(d,p) energies.**

**Table S5.** Formation energies of large clusters, calculated using the linear relation between GFN2-xTB and wB97X/6-311++G(d,p) energies. For clusters whose structures are obtained from crystal building units of ZIFs the label consists in the code of the topology of the ZIF, in italics.

<i>Label</i>	$z$ $Zn^{2+}$	$l$ $Im^{-}$	$l$ $mIm^{-}$	$q$ [ $e^{-}$ ]	$\Delta g_c^s$ [eV] GFN2-xTB/ wB97X
<i>lov</i>	5	6	-	+4	-3.333
<i>nat</i>	6	8	-	+4	-3.649
D3R	6	9	-	+3	-3.981
S6R	6	18	-	-6	-4.722
S6R	6	-	18	-6	-4.699
D4R	8	20	-	-4	-4.728
D4R	8	-	20	-4	-4.656
S8R	8	24	-	-8	-4.660
S8R	8	-	24	-8	-4.655
D6R	12	30	-	-6	-4.712
<i>rth</i>	12	29	-	-5	-3.525
D8R	16	40	-	-8	-4.707
<i>mep</i>	20	50	-	-10	-4.716
<i>sod</i>	24	60	-	-12	-3.838
<i>sod</i>	24	-	60	-12	-3.136
<i>Continuous random network</i>	41	88	-	3	-5.544
<i>zni</i>	60	120	-	0	-5.371
<i>SALEM-2</i>	144	288	-	0	-5.490

**Table S6.** Formation energies of periodic structures, calculated using the linear relation between GFN2-xTB and wB97X/6-311++G(d,p) energies.

<i>Label</i>	$z$ $Zn^{2+}$	$\Delta g_c^s$ [eV] GFN2-xTB/ wB97X
<i>zni</i>	32	-6.187
<i>coi</i>	16	-6.031
<i>dia</i>	16	-6.035
<i>cri</i>	8	-5.972
BCT	8	-5.936
SOD	12	-5.861
GIS	16	-5.972
MER	32	-5.905