Supplementary Information for: Atomistic insights into the pre-nucleation phase of Zeolitic Imidazolate Frameworks growth

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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.

$z\ \boldsymbol{Zn^{2+}}$	$l\ \boldsymbol{Im^-}$	l H-mIm	$a\ \boldsymbol{H_2O}$	a $\boldsymbol{NO_3^-}$	q [e-]	$\Delta \boldsymbol{g_c^s}$ [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, $\boldsymbol{\Omega}$			q $[e^-]$	ΔU^g_{ZPc} [eV] wB97X/6-311++G(d,p)	Δg^s_c [eV] wB97X/6-311++G(d,p)	Δg^s_c [eV] *Cycle*	$\sqrt{\frac{\left\vert\vec{r^s}-\vec{r^g}\right\vert^2}{}}$ [Å/atom]
z Zn^{2+}	l Im^-	l mIm^-					
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

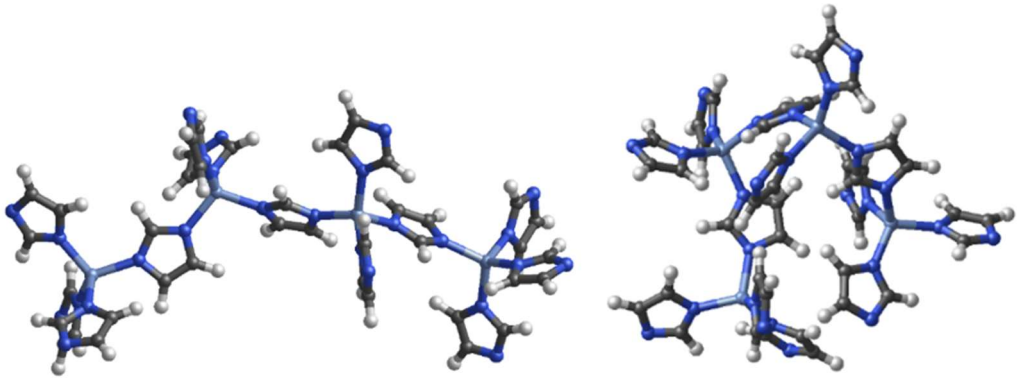

Figure S1. Open versus folded configurations for the Zn_4Im_{13} cluster, obtained from optimization in vacuo (left) and in implicit ethanol (right).

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

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

Label (when necessary)	z Zn^{2+}	l Im^-	q $[e^-]$	Δg_c^s [eV] wB97X/6-311++G(d,p)	Thermo. Cycle	Δg_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
1FCZ	1	4	-2	**-4.759**	**-4.852**	**-39.653**
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
π-π	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	**-4.716**	**-4.770**	**-39.450**
3MR (anti-parallel)	3	3	3	-2.750	**-2.831**	**-34.290**
Linear	3	3	3	-2.616	-2.722	-33.735
3MR (parallel)	3	3	3	**-2.752**	-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
sFCZs	3	10	-4	**-4.799**	**-9.834**	**-39.338**
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	**-3.895**	**-4.002**	**-36.926**
4MR-*SOD*	4	12	-4	-4.693	**-4.732**	**-39.355**
4MR-*zni*	4	12	-4	**-4.740**	-4.736	-39.336
4FCZs	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	**-4.300**	**-37.651**
6MR (undercoordinated)	6	12	0	**-4.290**	-4.331	-37.884
6MR (fully coordinated)	6	18	-6	**-4.6187**	-4.541	-39.371

Table S4. Formation free energies per Zn atoms, Δg_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 $\boldsymbol{Zn^{2+}}$	l $\boldsymbol{mIm^-}$	q [$\boldsymbol{e^-}$]	$\boldsymbol{\Delta g_c^s}$ [eV] wB97X/6-311++G(d,p)	$\boldsymbol{\Delta g_c^s}$ [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	**-4.555**	**-36.390**
	2	1	3	-1.583	-28.166
	2	2	2	-2.476	-34.001
	2	3	1	-3.510	-36.046
π-π	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	**-4.804**	**-39.902**
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, *zni*)	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.

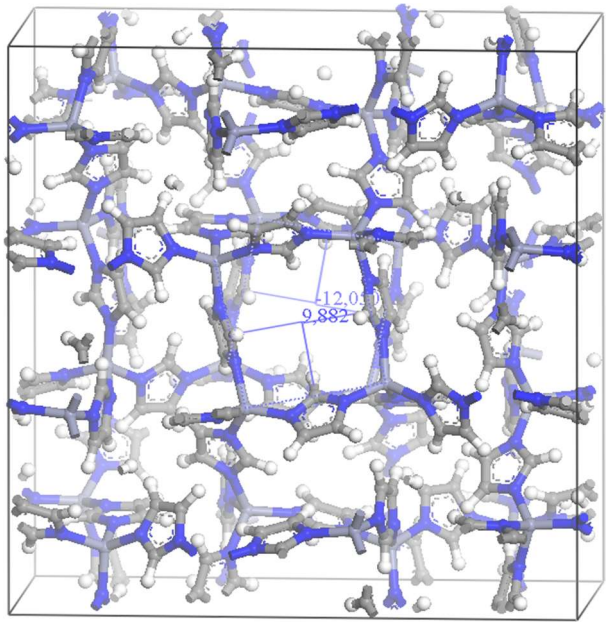

Figure S2. Two examples of dihedral angles between four Zn atoms in the 4MR in the zni crystal structure.

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.

Label	z $\boldsymbol{Zn^{2+}}$	l $\boldsymbol{Im^{-}}$	l $\boldsymbol{mIm^{-}}$	q $[\boldsymbol{e^{-}}]$	$\Delta \boldsymbol{g_c^s}$ [eV] GFN2-xTB/ wB97X
lov	5	6	-	+4	-3.333
nat	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
rth	12	29	-	-5	-3.525
D8R	16	40	-	-8	-4.707
mep	20	50	-	-10	-4.716
sod	24	60	-	-12	-3.838
sod	24	-	60	-12	-3.136
Continuos random network	41	88	-	3	-5.544
zni	60	120	-	0	-5.371
SALEM-2	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.

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