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Supporting information for

The energy landscapes of zeolitic imidazolate frameworks (ZIFs): towards quantifying the presence of substituents on the imidazole ring

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Table S1. Total energies, densities, selected distances and angles in $Zn(F\text{-}imid)_2$

Structure type	Energy, eV/Zn(F-imid)$_2$	Difference, eV/Zn(F-imid)$_2$	ρ, g/cm^3	Zn-N, Å	N-Zn-N, degr.	Closest H…H contact, Å	C-H…F, Å (*)
coi	-5037.8004	0.0000	2.040	1.947-2.000	99.10-126.87	2.170	2.068-2.378
zni	-5037.7658	0.0346	1.948	1.953-1.997	98.68-117.74	2.097	2.065-2.195
irl	-5037.6472	0.1532	1.888	1.967-2.011	92.01-117.74	2.703	2.090-2.319
unj	-5037.4308	0.3696	1.360	1.949-1.987	99.78-119.52	2.610	2.192-2.366
neb	-5037.3408	0.4596	1.586	1.963-1.998	105.29-116.16	2.522	-
uni	-5037.3080	0.4924	1.415	1.950-2.014	97.08-116.89	2.685	2.114-2.223
unc	-5037.2690	0.5314	1.528	1.968-1.999	98.17-126.74	2.584	2.100-2.339
dia	-5037.2274	0.5730	1.258	1.954-1.993	100.39-117.72	2.820	2.210
cfc	-5037.2220	0.5784	1.216	1.961-1.993	94.87-118.10	2.609	2.041-2.444
crb	-5037.2156	0.5848	1.183	1.958-1.990	104.64-114.64	2.696	2.108-2.348
gsi	-5037.2154	0.5850	1.674	1.943-2.018	92.69-133.22	2.389	2.227-2.489
dft	-5037.1968	0.6036	1.089	1.954-1.985	103.30-114.91	2.823	2.435-2.454
cag	-5037.1541	0.6463	1.504	1.954-1.985	105.53-114.62	2.218	-
mer	-5037.1253	0.6751	0.906	1.958-1.976	104.47-113.36	2.804	2.312-2.396
lon	-5037.1058	0.6946	1.221	1.967-2.003	96.49-121.75	2.785	2.137-2.181
sra	-5037.0961	0.7043	1.113	1.946-1.997	99.26-123.99	2.796	2.380-2.438
sod	-5037.0887	0.7117	0.986	1.955-1.970	104.97-114.42	2.828	2.280-2.297
lta	-5037.0711	0.7293	0.812	1.953-2.007	100.23-118.17	2.242	2.283-2.423
unh	-5037.0249	0.7755	1.371	1.980-2.010	98.69-126.76	2.761	-
pcb	-5037.0183	0.7821	0.976	1.954-1.977	99.77-127.16	2.674	2.355
lcs	-5037.0119	0.7885	1.283	1.956-1.958	104.83-112.27	2.817	-
mmt	-5036.9988	0.8016	1.337	1.962-2.026	96.24-135.20	2.156	2.123-2.397
gis	-5036.9437	0.8567	0.884	1.955-1.980	97.18-119.84	2.585	-
pcl	-5036.9302	0.8702	0.996	1.941-1.996	95.74-123.74	2.509	2.297
qtz	-5036.8242	0.9762	1.489	1.974-1.977	99.97-127.85	2.315	-

(*) The angle ∠C-H…F was assumed to be greater than 120°.

Table S2. Total energies, densities, selected distances and angles in $Zn(mim)_2$

Structure type	Energy, eV/$Zn(mim)_2$	Difference, eV/$Zn(mim)_2$	ρ, g/cm^3	Zn-N, Å	N-Zn-N, degr.	Closest H…H contact, Å (*)
zni	-4138.2084	0.0000	1.722	1.987-2.035	101.2-118.9	1.943
crb	-4138.1410	0.0674	1.343	1.971-2.009	98.98-121.65	2.335
coi	-4138.1065	0.1019	1.764	1.997-2.056	99.14-119.84	2.022
dia	-4138.0617	0.1467	1.555	1.975-1.990	98.62-115.24	2.445
uni	-4138.0526	0.1558	1.369	1.967-2.012	98.25-125.17	2.338
sod	-4138.0494	0.1590	0.946	1.969-1.973	107.29-110.61	2.292
qtz	-4138.0349	0.1735	1.451	1.974-1.982	101.26-123.75	2.141
unc	-4138.0030	0.2054	1.303	1.971-2.023	98.51-125.52	2.166
cfc	-4137.9951	0.2133	1.132	1.963-1.991	97.28-119.524	2.452
lon	-4137.9798	0.2286	1.115	1.967-1.998	96.43-119.10	2.540
irl	-4137.9740	0.2344	1.311	1.966-2.015	93.46-127.91	2.249
mmt	-4137.9660	0.2424	1.498	1.964-2.050	94.64-135.91	2.089
gis	-4137.9199	0.2885	0.828	1.981-2.003	100.40-119.80	2.101
unj	-4137.9028	0.3056	1.152	1.974-2.007	102.34-120.47	2.274
cag	-4137.8966	0.3118	1.091	1.979-2.002	100.44-117.60	2.431
pcl	-4137.8884	0.3200	0.943	1.973-2.006	95.66-128.46	2.068
gsi	-4137.8834	0.3250	1.362	1.975-2.030	92.48-131.47	2.044
sra	-4137.8784	0.3300	0.968	1.970-2.000	101.25-123.13	2.117
dft	-4137.8714	0.3370	0.951	1.975-2.008	100.89-116.50	2.352
mer	-4137.8669	0.3415	0.842	1.979-2.023	101.99-119.05	2.151
neb	-4137.8620	0.3464	1.406	1.978-2.003	101.86-122.71	2.153
pcb	-4137.8356	0.3728	0.874	1.964-2.022	97.90-123.81	1.994
lcs	-4137.7763	0.4321	1.166	1.998-2.003	100.52-115.9	2.288
lta	-4137.6618	0.5466	0.795	1.976-2.025	98.59-117.79	2.040
unh	-4137.3129	0.8955	1.096	1.995-2.052	97.71-128.51	2.139

(*) Short H…H contacts (~1.8 Å) within CH_3-groups are not considered.

Table S3. Total energies of experimentally characterized $Zn(imid)_2$ polymorphs*

Framework topology	Space group	Total energy, eV per formula unit $Zn(imid)_2$
coi	$I4_1$	-3761.1530
zni	$I4_1cd$	-3761.0871
cag	*Pbca*	-3760.7415
mer	$I4/mmm$	-3760.6374
gis	$I4_1/amd$	-3760.6314
dft	$P4_2/mnm$	-3760.6047
crb	*Pbca*	-3760.5177

* Referred to the basis set used in the present paper (the same as in I. A. Baburin, S. Leoni and G. Seifert, *J. Phys. Chem. B*, 2008, **112**, 9437)

Basis set parameters

I. $Zn(mim)_2$:

```
%block PAO.Basis                 # Define Basis set
HGGAtm2     1                    # Species label, number of l-shells
 n=1   0   2 P   1                   # n, l, Nzeta, Polarization, NzetaPol
   4.709      3.760
   1.000      1.000
CGGAtm2     2                    # Species label, number of l-shells
 n=2   0   2                         # n, l, Nzeta
   4.088      3.347
   1.000      1.000
 n=2   1   2 P   1                   # n, l, Nzeta, Polarization, NzetaPol
   4.870      3.475
   1.000      1.000
NGGAtm2     2                    # Species label, number of l-shells
 n=2   0   2                         # n, l, Nzeta
   3.684      2.869
   1.000      1.000
 n=2   1   2 P   1                   # n, l, Nzeta, Polarization, NzetaPol
   4.280      2.905
   1.000      1.000
ZnGGAtm2    2                    # Species label, number of l-shells
 n=4   0   2 P   1                   # n, l, Nzeta, Polarization, NzetaPol
   5.893      5.399
   1.000      1.000
 n=3   2   2                         # n, l, Nzeta
   3.154      1.775
   1.000      1.000
%endblock PAO.Basis
```

II. $Zn(F\text{-}im)_2$:

```
%block PAO.Basis                 # Define Basis set
HGGAtm2     1                    # Species label, number of l-shells
 n=1   0   2 P   1                   # n, l, Nzeta, Polarization, NzetaPol
   4.709      3.760
   1.000      1.000
CGGAtm2     2                    # Species label, number of l-shells
 n=2   0   2                         # n, l, Nzeta
   4.088      3.347
   1.000      1.000
 n=2   1   2 P   1                   # n, l, Nzeta, Polarization, NzetaPol
   4.870      3.475
   1.000      1.000
NGGAtm2     2                    # Species label, number of l-shells
 n=2   0   2                         # n, l, Nzeta
   3.684      2.869
   1.000      1.000
 n=2   1   2 P   1                   # n, l, Nzeta, Polarization, NzetaPol
   4.280      2.905
   1.000      1.000
FGGAtm2     2                    # Species label, number of l-shells
 n=2   0   2                         # n, l, Nzeta
   3.012      2.204
   1.000      1.000
 n=2   1   2 P   1                   # n, l, Nzeta, Polarization, NzetaPol
   3.588      2.260
   1.000      1.000
ZnGGAtm2    2                    # Species label, number of l-shells
 n=4   0   2 P   1                   # n, l, Nzeta, Polarization, NzetaPol
   5.893      5.399
   1.000      1.000
 n=3   2   2                         # n, l, Nzeta
   3.154      1.775
   1.000      1.000
%endblock PAO.Basis
```