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Supporting Information

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Mechanical Properties of Dense Zeolitic Imidazolate Frameworks (ZIFs): A High-Pressure X-ray Diffraction, Nanoindentation and Computational Study of the Zinc Framework Zn(Im)₂, and its Lithium–Boron Analogue, LiB(Im)₄

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SI-1: Squeeze Output from PLATON

Pressure (GPa)	Residual Electron Density (No. of electrons per unit cell)
0	8
0.52	8
0.76 ^[a]	16
1.01	8
1.44	5
1.69 ^[a]	17

[a] Denotes pressure study done at DIAMOND light source.

SI-2: Experimental Bond Length Evolution with Pressure

LiB(Im)₄

Pressure (GPa)	Li-N1	Li-N4	Li-N6	Li-N8
0	2.038(51)	2.0717(53)	2.1033(52)	2.0839(53)
0.515	1.9887(121)	2.0673(125)	2.0866(100)	2.0340(128)
0.76	1.9983(55)	2.0289(59)	2.0597(60)	2.0702(73)
1.01	1.9782(171)	2.0335(183)	2.0532(157)	2.0302(176)
1.44	1.9679(72)	2.0079(74)	2.0393(68)	2.0427(75)
1.69	1.9482(166)	2.0087(179)	2.0364(148)	2.0014(174)

Pressure (GPa)	B-N2	B-N3	B-N5	B-N7
0	1.5418(39)	1.5428(39)	1.5418(41)	1.5319(39)
0.515	1.5284(96)	1.5641(11)	1.5227(84)	1.5215(95)
0.76	1.5344(44)	1.5439(46)	1.5343(43)	1.5319(45)
1.01	1.5275(12)	1.5384(128)	1.5373(121)	1.5251(135)
1.44	1.5322(45)	1.5389(48)	1.5282(43)	1.5319(47)
1.69	1.5172(128)	1.5434(126)	1.5306(117)	1.5199(140)

Zn(Im)₂

Pressure (GPa)	Zn1-N1	Zn1-N3	Zn1-N5	Zn1-N7	Zn2-N2	Zn2-N4	Zn2-N6	Zn2-N8
0	1.975(4)	1.993(4)	1.977(4)	1.979(4)	1.991(4)	1.987(4)	2.005(4)	1.975(3)
0.0001	1.94(2)	1.96(2)	1.94(2)	1.97(2)	2.00(2)	2.04(2)	2.06(2)	2.00(2)
0.092	1.95(2)	1.95(2)	1.93(2)	2.02(2)	1.95(2)	2.01(2)	2.04(2)	1.95(2)
0.295	1.90(2)	1.93(2)	1.90(2)	1.99(2)	1.94(2)	2.03(2)	2.05(2)	1.93(2)
0.543	1.91(2)	1.87(2)	1.96(2)	1.95(2)	2.01(2)	2.05(3)	1.93(3)	1.94(2)

NB: The data for Zn(Im)₂ are those previously published in Ref 11.

SI-3: Experimental N-M-N Angular Evolution with Pressure

LiB(Im)₄

Pressure (GPa)	N1-Li-N4	N1-Li-N6	N1-Li-N8	N4-Li-N6	N4-Li-N8	N6-Li-N8
0	114.98	106.53	117.39	107.01	106.95	102.85
0.515	113.95	104.96	119.62	108.57	106.07	102.67

Pressure (GPa)	N2-B-N3	N2-B-N5	N2-B-N7	N3-B-N5	N3-B-N7	N5-B-N7
0	110.80	111.36	107.99	107.85	109.81	109.02
0.515	110.32	112.27	108.54	107.07	109.03	109.56

Zn(Im)₂

Pressure (GPa)	N1-Zn-N3	N1-Zn-N5	N1-Zn-N7	N3-Zn-N5	N3-Zn-N7	N5-Zn-N7	N2-Zn-N4	N2-Zn-N6	N2-Zn-N8	N4-Zn-N6	N4-Zn-N8	N6-Zn-N8
0	111.1	107.8	113.9	106.4	105.9	111.6	107.9	110.1	111.9	104.3	116.3	105
0.54	111.4	108	114.3	111	102.2	109.9	109	108.6	111.6	102.8	117.6	106.6

NB: The data for Zn(Im)₂ are those previously published in Ref 11.

SI-4: Comparison of Simulated and Experimental Unit cell Parameters

Note: Simulated parameters are given in normal font, experimental in *italic*, and percentage discrepancies in parenthesis (%).

Structure	Zn(lm) ₂	Zn(lm) ₂	LiB(lm) ₄	LiB(lm) ₄
Pressure, GPa	0.0 <i>ambient</i>	0.5 <i>0.543</i>	0.0 <i>ambient</i>	0.5 <i>0.515</i>
a, Å	23.5960 <i>23.5028</i> (0.3965)	22.9835 <i>23.0474</i> (-0.2773)	22.4746 <i>22.4721</i> (0.0111)	22.2184 <i>22.2099</i> (0.0381)
b, Å	23.5960 <i>23.5028</i> (0.3965)	23.2679 <i>23.0474</i> (0.9566)	22.4746 <i>22.4721</i> (0.0111)	22.2757 <i>22.2099</i> (0.2963)
c, Å	12.4695 <i>12.4607</i> (0.0703)	12.5021 <i>12.4020</i> (0.8067)	11.3445 <i>11.5072</i> (-1.4142)	11.2330 <i>11.4191</i> (-1.6298)
α, °	90.0000 <i>90.0000</i> (0.0000)	90.0000 <i>90.0000</i> (0.0000)	90.0000 <i>90.0000</i> (0.0000)	90.0000 <i>90.0000</i> (0.0000)
β, °	90.0000 <i>90.0000</i> (0.0000)	90.0000 <i>90.0000</i> (0.0000)	90.0000 <i>90.0000</i> (0.0000)	90.0000 <i>90.0000</i> (0.0000)
γ, °	90.0000 <i>90.0000</i> (0.0000)	90.0000 <i>90.0000</i> (0.0000)	90.0000 <i>90.0000</i> (0.0000)	90.0000 <i>90.0000</i> (0.0000)
Unit cell volume, Å ³	6942.6 <i>6883.1</i> (0.8649)	6685.8 <i>6587.7</i> (1.4893)	5730.2 <i>5811.1</i> (-1.3925)	5559.5 <i>5632.8</i> (-1.3006)

SI-5: Comparison of Simulated and Experimental Fractional Atomic Positions

Note: Simulated positions shown are those converted from P1 symmetry.

Element	Experimental position			Simulated position			Error (sim. - exp.)		
	x	y	z	x	y	z	x	y	z
Zn(lm) ₂ structure (experimental: ambient, simulated: 0.0 GPa)									
H	0.5964	0.5183	0.0703	0.5917	0.5166	0.0568	-0.0047	-0.0017	-0.0135
C	0.6801	0.5149	0.8881	0.6829	0.5143	0.8643	0.0028	-0.0006	-0.0238
H	0.7057	0.4990	0.8397	0.7128	0.4927	0.8127	0.0071	-0.0063	-0.0270
C	0.9297	0.3341	0.1426	0.9292	0.3320	0.1183	-0.0005	-0.0021	-0.0243
H	0.9014	0.3205	0.0971	0.8940	0.3177	0.0694	-0.0074	-0.0028	-0.0277
C	0.8501	0.5070	0.4188	0.8474	0.5068	0.3981	-0.0027	-0.0002	-0.0207
H	0.8358	0.4891	0.4797	0.8305	0.4822	0.4642	-0.0053	-0.0069	-0.0155
C	0.6411	0.3806	0.7626	0.6424	0.3817	0.7389	0.0013	0.0012	-0.0237
H	0.6366	0.4190	0.7475	0.6372	0.4266	0.7227	0.0006	0.0076	-0.0248
C	0.6547	0.3048	0.8462	0.6583	0.3026	0.8235	0.0036	-0.0022	-0.0227
H	0.6625	0.2783	0.8995	0.6681	0.2745	0.8898	0.0056	-0.0038	-0.0097
C	0.7927	0.3566	0.4926	0.7903	0.3540	0.4681	-0.0024	-0.0026	-0.0245
H	0.7563	0.3590	0.4637	0.7499	0.3570	0.4277	-0.0064	-0.0020	-0.0360
C	0.7517	0.4064	0.1387	0.7517	0.4039	0.1148	0.0000	-0.0025	-0.0239
H	0.7608	0.4433	0.1181	0.7631	0.4456	0.0857	0.0023	0.0023	-0.0324
C	0.7092	0.3262	0.1502	0.7058	0.3246	0.1371	-0.0034	-0.0015	-0.0131
H	0.6835	0.2965	0.1412	0.6731	0.2929	0.1263	-0.0104	-0.0036	-0.0149
C	0.7552	0.3257	0.2149	0.7527	0.3242	0.2029	-0.0025	-0.0015	-0.0120
H	0.7667	0.2951	0.2569	0.7671	0.2922	0.2588	0.0004	-0.0029	0.0019
N	0.6515	0.4860	0.9645	0.6528	0.4859	0.9431	0.0013	-0.0001	-0.0214
N	0.9217	0.3715	0.2244	0.9222	0.3713	0.1997	0.0005	-0.0002	-0.0247
N	0.8592	0.4817	0.3220	0.8577	0.4819	0.2994	-0.0015	0.0002	-0.0226
N	0.6530	0.3620	0.8599	0.6561	0.3609	0.8363	0.0030	-0.0011	-0.0236
N	0.8408	0.3639	0.4378	0.8407	0.3640	0.4146	-0.0001	0.0001	-0.0232
N	0.7069	0.3781	0.1002	0.7054	0.3754	0.0814	-0.0015	-0.0027	-0.0188
N	0.7822	0.3767	0.2093	0.7817	0.3747	0.1883	-0.0005	-0.0021	-0.0210
Zn	0.6482	0.4038	0.9972	0.6491	0.4029	0.9747	0.0010	-0.0009	-0.0225
Zn	0.8502	0.3991	0.2924	0.8506	0.3991	0.2687	0.0004	0.0000	-0.0237

Element	Experimental Position			Simulated Position			Error (sim. – exp.)		
	x	y	z	x	y	z	x	y	z

Zn(lm)₂ structure (experimental: 0.543 GPa, simulated: 0.5 GPa)

Zn	0.6463	0.4011	0.9986	0.6499	0.4008	0.9739	0.0036	-0.0003	-0.0247
Zn	0.8476	0.3937	0.2931	0.8522	0.3939	0.2669	0.0046	0.0002	-0.0262
H	0.6011	0.5215	0.0743	0.5956	0.5169	0.0525	-0.0055	-0.0046	-0.0218
C	0.6827	0.5123	0.8870	0.6869	0.5120	0.8581	0.0042	-0.0003	-0.0289
H	0.7074	0.4951	0.8369	0.7167	0.4892	0.8065	0.0093	-0.0059	-0.0304
C	0.9306	0.3292	0.1410	0.9327	0.3298	0.1115	0.0021	0.0006	-0.0295
H	0.9028	0.3156	0.0927	0.8972	0.3151	0.0617	-0.0056	-0.0005	-0.0310
C	0.8502	0.5065	0.4240	0.8490	0.5031	0.3975	-0.0012	-0.0034	-0.0265
H	0.8359	0.4886	0.4862	0.8323	0.4775	0.4632	-0.0036	-0.0111	-0.0230
C	0.6462	0.3791	0.7640	0.6476	0.3817	0.7394	0.0014	0.0026	-0.0246
H	0.6452	0.4188	0.7508	0.6430	0.4277	0.7255	-0.0022	0.0089	-0.0253
C	0.6531	0.2996	0.8453	0.6598	0.2994	0.8208	0.0067	-0.0002	-0.0245
H	0.6573	0.2712	0.8981	0.6673	0.2695	0.8861	0.0100	-0.0017	-0.0120
C	0.7892	0.3546	0.4890	0.7891	0.3514	0.4636	-0.0001	-0.0032	-0.0254
H	0.7525	0.3562	0.4583	0.7486	0.3528	0.4204	-0.0039	-0.0034	-0.0379
C	0.7515	0.3987	0.1390	0.7544	0.3978	0.1121	0.0029	-0.0009	-0.0269
H	0.7632	0.4346	0.1125	0.7687	0.4390	0.0802	0.0055	0.0044	-0.0323
C	0.7039	0.3219	0.1610	0.7027	0.3205	0.1395	-0.0012	-0.0014	-0.0215
H	0.6765	0.2926	0.1549	0.6676	0.2899	0.1301	-0.0089	-0.0027	-0.0248
C	0.7500	0.3211	0.2277	0.7500	0.3187	0.2062	0.0000	-0.0024	-0.0215
H	0.7593	0.2916	0.2759	0.7624	0.2864	0.2645	0.0031	-0.0052	-0.0114
N	0.6532	0.4829	0.9670	0.6562	0.4840	0.9379	0.0030	0.0011	-0.0291
N	0.9199	0.3643	0.2270	0.9245	0.3690	0.1937	0.0046	0.0047	-0.0333
N	0.8571	0.4795	0.3260	0.8589	0.4784	0.2982	0.0018	-0.0011	-0.0278
N	0.6538	0.3584	0.8640	0.6575	0.3586	0.8366	0.0037	0.0002	-0.0274
N	0.8398	0.3599	0.4350	0.8415	0.3589	0.4122	0.0017	-0.0010	-0.0228
N	0.7038	0.3719	0.1050	0.7058	0.3709	0.0802	0.0020	-0.0010	-0.0248
N	0.7806	0.3705	0.2130	0.7827	0.3678	0.1880	0.0021	-0.0027	-0.0250

Element	Experimental Position			Simulated Position			Error (sim. – exp.)		
	x	y	z	x	y	z	x	y	z

LiB(lm)₄ structure (experimental: ambient, simulated: 0.0 GPa)

Li	0.4014	0.3556	0.5811	0.3988	0.3545	0.5789	-0.0026	-0.0011	-0.0022
B	0.4021	0.1489	0.2989	0.4012	0.1473	0.2989	-0.0008	-0.0016	0.0000
N	0.3795	0.2813	0.4889	0.3751	0.2813	0.4866	-0.0043	0.0000	-0.0023
N	0.3826	0.1978	0.3848	0.3814	0.1952	0.3884	-0.0012	-0.0027	0.0036
N	0.4691	0.1539	0.2717	0.4683	0.1530	0.2701	-0.0008	-0.0009	-0.0016
N	0.5653	0.1309	0.2634	0.5658	0.1324	0.2625	0.0005	0.0015	-0.0009
N	0.3679	0.1535	0.1831	0.3653	0.1530	0.1830	-0.0026	-0.0005	-0.0001
N	0.3889	0.0884	0.3547	0.3886	0.0858	0.3547	-0.0003	-0.0026	0.0000
C	0.4098	0.2490	0.4133	0.4065	0.2495	0.4094	-0.0033	0.0005	-0.0039
C	0.3295	0.2483	0.5111	0.3273	0.2459	0.5170	-0.0023	-0.0025	0.0059
C	0.3308	0.1981	0.4487	0.3304	0.1928	0.4572	-0.0004	-0.0052	0.0085
C	0.5128	0.1161	0.3036	0.5131	0.1158	0.3050	0.0003	-0.0003	0.0014
C	0.5554	0.1813	0.2017	0.5547	0.1828	0.1961	-0.0007	0.0015	-0.0056
C	0.4974	0.1963	0.2050	0.4950	0.1962	0.2002	-0.0024	-0.0001	-0.0048
C	0.3870	0.1388	0.0758	0.3847	0.1398	0.0716	-0.0024	0.0009	-0.0042
C	0.2950	0.1507	0.0568	0.2898	0.1521	0.0572	-0.0051	0.0014	0.0004
C	0.3075	0.1609	0.1694	0.3042	0.1609	0.1738	-0.0033	0.0000	0.0044
C	0.3697	0.0381	0.3010	0.3673	0.0364	0.2986	-0.0023	-0.0017	-0.0024
C	0.3896	0.0121	0.4730	0.3910	0.0079	0.4739	0.0014	-0.0042	0.0009
C	0.4014	0.0708	0.4659	0.4037	0.0677	0.4678	0.0023	-0.0031	0.0019
H	0.4463	0.2606	0.3828	0.4474	0.2637	0.3676	0.0011	0.0031	-0.0152
H	0.2993	0.2592	0.5620	0.2943	0.2599	0.5809	-0.0050	0.0007	0.0189
H	0.3018	0.1685	0.4485	0.3024	0.1537	0.4597	0.0006	-0.0148	0.0112
H	0.5063	0.0828	0.3497	0.5054	0.0772	0.3602	-0.0009	-0.0056	0.0105
H	0.5846	0.2027	0.1625	0.5896	0.2058	0.1487	0.0050	0.0031	-0.0138
H	0.4799	0.2290	0.1692	0.4697	0.2316	0.1592	-0.0102	0.0026	-0.0100
H	0.4267	0.1308	0.0593	0.4311	0.1317	0.0517	0.0044	0.0009	-0.0076
H	0.2571	0.1530	0.0244	0.2465	0.1543	0.0162	-0.0106	0.0013	-0.0082
H	0.2804	0.1710	0.2272	0.2768	0.1720	0.2493	-0.0036	0.0010	0.0221
H	0.3581	0.0371	0.2235	0.3511	0.0378	0.2088	-0.0070	0.0007	-0.0147
H	0.4156	0.0949	0.5256	0.4209	0.0986	0.5328	0.0053	0.0037	0.0072

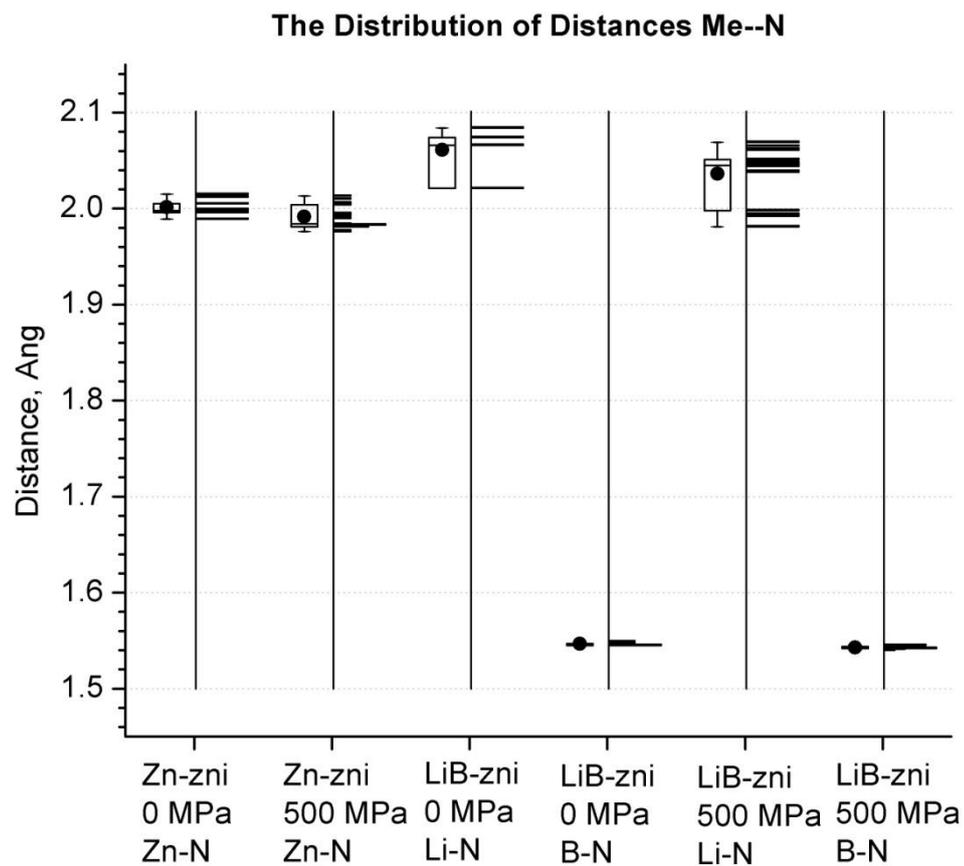
Element	Experimental Position			Simulated Position			Error (sim. – exp.)		
	x	y	z	x	y	z	x	y	z

LiB(lm)₄ structure (experimental: 0.515 GPa, simulated: 0.5 GPa)

Li	0.3996	0.3546	0.5806	0.3955	0.3547	0.5766	-0.0041	0.0001	-0.0040
B	0.3998	0.1478	0.3001	0.4000	0.1459	0.2985	0.0002	-0.0019	-0.0016
N	0.3761	0.2816	0.4907	0.3724	0.2813	0.4860	-0.0037	-0.0003	-0.0047
N	0.3805	0.1965	0.3869	0.3800	0.1937	0.3896	-0.0005	-0.0028	0.0027
N	0.4684	0.1539	0.2715	0.4671	0.1531	0.2675	-0.0013	-0.0008	-0.0040
N	0.5658	0.1320	0.2597	0.5660	0.1347	0.2575	0.0002	0.0027	-0.0022
N	0.3660	0.1522	0.1844	0.3631	0.1521	0.1826	-0.0029	-0.0001	-0.0018
N	0.3884	0.0865	0.3553	0.3884	0.0836	0.3541	0.0000	-0.0029	-0.0012
C	0.4063	0.2494	0.4143	0.4044	0.2492	0.4087	-0.0019	-0.0002	-0.0056
C	0.3273	0.2467	0.5144	0.3248	0.2448	0.5185	-0.0025	-0.0019	0.0041
C	0.3287	0.1943	0.4524	0.3289	0.1909	0.4596	0.0002	-0.0034	0.0072
C	0.5134	0.1173	0.3015	0.5135	0.1164	0.3011	0.0001	-0.0009	-0.0004
C	0.5542	0.1837	0.1976	0.5532	0.1857	0.1918	-0.0010	0.0020	-0.0058
C	0.4948	0.1973	0.2041	0.4927	0.1977	0.1975	-0.0021	0.0004	-0.0066
C	0.3856	0.1413	0.0743	0.3829	0.1420	0.0691	-0.0027	0.0007	-0.0052
C	0.2928	0.1500	0.0576	0.2869	0.1523	0.0560	-0.0059	0.0023	-0.0016
C	0.3044	0.1585	0.1721	0.3012	0.1587	0.1744	-0.0032	0.0002	0.0023
C	0.3688	0.0359	0.3022	0.3667	0.0336	0.2979	-0.0021	-0.0023	-0.0043
C	0.3909	0.0087	0.4731	0.3925	0.0047	0.4738	0.0016	-0.0040	0.0007
C	0.4020	0.0686	0.4672	0.4049	0.0652	0.4676	0.0029	-0.0034	0.0004
H	0.4426	0.2621	0.3819	0.4454	0.2639	0.3658	0.0028	0.0018	-0.0161
H	0.2968	0.2573	0.5663	0.2916	0.2587	0.5831	-0.0052	0.0014	0.0168
H	0.3004	0.1634	0.4542	0.3013	0.1509	0.4637	0.0009	-0.0125	0.0095
H	0.5077	0.0836	0.3487	0.5069	0.0770	0.3562	-0.0008	-0.0066	0.0075
H	0.5829	0.2061	0.1571	0.5877	0.2100	0.1438	0.0048	0.0039	-0.0133
H	0.4756	0.2300	0.1693	0.4661	0.2330	0.1572	-0.0095	0.0030	-0.0121
H	0.4260	0.1358	0.0561	0.4299	0.1354	0.0478	0.0039	-0.0004	-0.0083
H	0.2544	0.1514	0.0252	0.2430	0.1545	0.0151	-0.0114	0.0031	-0.0101
H	0.2766	0.1669	0.2309	0.2735	0.1676	0.2515	-0.0031	0.0007	0.0206
H	0.3563	0.0351	0.2246	0.3494	0.0351	0.2079	-0.0069	0.0000	-0.0167
H	0.4160	0.0930	0.5276	0.4226	0.0964	0.5329	0.0066	0.0034	0.0053

SI-6: DFT Bond Length Evolution with Pressure

The chart shows the statistical analysis of the distribution of bond distances in both the DFT optimized structures of **1** and **2**.



SI-7: DFT N-M-N Angular Evolution with Pressure

The chart shows the statistical analysis of the distribution of bond angles in both the DFT optimized structures of 1 and 2.

