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Electronic Supplementary Information

Theoretical Prediction of the Mechanical Properties of Zeolitic Imidazolate Frameworks (ZIFs)

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1. Testing Computational parameters

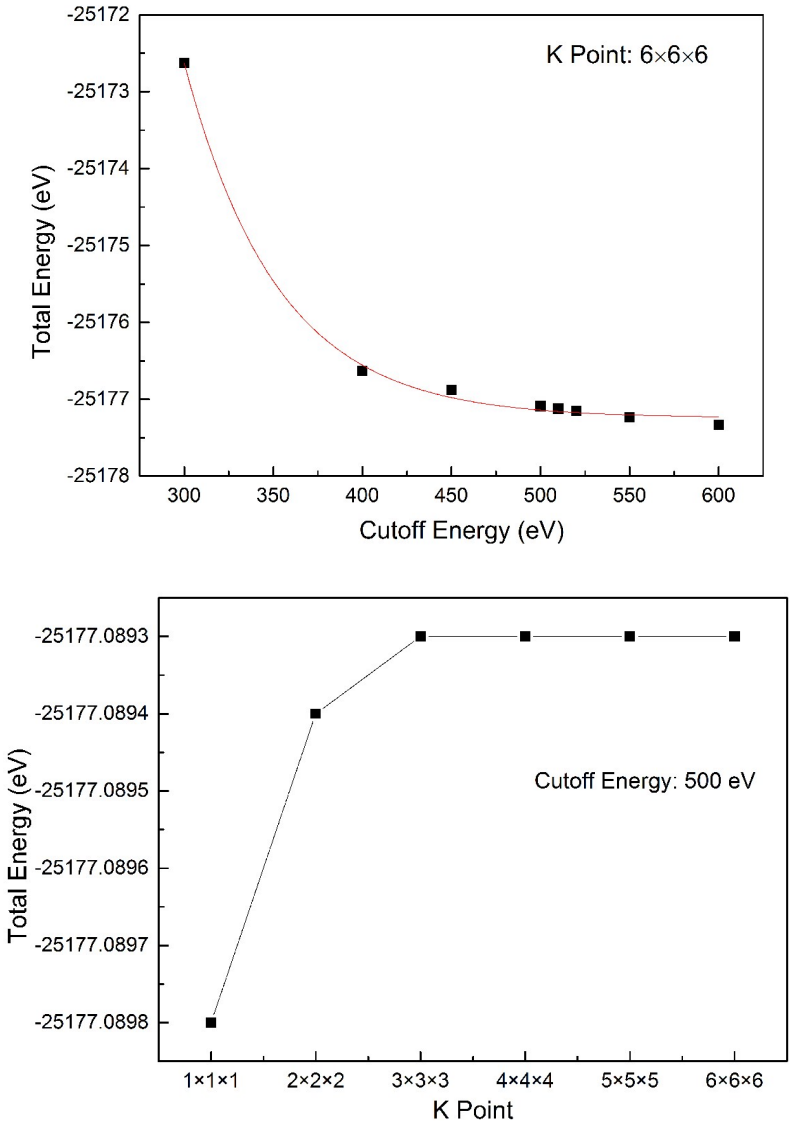

Figure S1. Testing the computational parameters.

Table S1 Unit cell parameters of ZIFs from experiment and calculations using different model. The values inside bracket are the difference between computational and experimental values.

	Unit Cell Parameter (Å)				
	Experiment	PBE-D	PBE	PW91-D	PW91
SALEM-2	16.830[S1]	17.017(0.187)	17.082(0.252)	16.804(0.026)	17.070(0.240)
ZIF-90	17.272[S2]	17.016(0.156)	17.256(0.016)	16.828(0.444)	17.244(0.028)
ZIF-Cl	16.982[S3]	17.082(0.100)	17.215(0.233)	17.042(0.060)	17.168(0.186)
ZIF-Br	17.065[S3]	17.121(0.056)	17.311(0.246)	17.094(0.029)	17.302(0.237)

Table S2 The values calculated for the Young's modulus *E* (GPa), the shear modulus *G* (GPa) and the bulk modulus *B* (GPa) of ZIFs using different models.

	G (GPa)				*E* (GPa)				*B* (GPa)			
	1	2	3	4	1	2	3	4	1	2	3	4
SALEM-2	1.44	2.33	1.99	2.43	1.99	3.18	2.14	3.30	8.04	10.14	4.91	10.70
ZIF-90	1.51	2.96	-2.70	2.78	2.05	5.39	9.50	3.43	8.58	9.54	11.57	8.36
ZIF-Cl	2.28	4.11	3.05	3.93	3.37	6.58	4.46	6.21	10.75	11.97	9.41	8.98
ZIF-Br	4.22	4.20	3.30	4.07	6.19	7.09	5.07	6.77	13.02	11.45	10.12	12.03
ZIF-I	5.92	6.17	4.98	6.48	10.95	11.60	11.46	12.28	12.26	10.72	10.59	12.39

1: PBE-D; 2: PBE; 3: PW91-D; 4: PW91

2. Predication of the mechanical properties of ZIF-8

The mechanical properties of ZIF-8 have been investigated both experimentally and by means of computational methods. It is necessary to verify the reliability of the current model through calculating the mechanical properties of ZIF-8. To date, according to our knowledge, only one experimental value for the shear modulus of ZIF-8 measured by Brillouin scattering is available in literature (Table S3). Although our model improved the reproduction of the experimental lattice parameters of ZIF-8 (Table S4), an accurate prediction of the absolute values of the elastic constants and the mechanical moduli remains challenging. There are two possible reasons.

First, for the DFT calculation, the temperature is assumed to be 0 K compared to room temperature (300 K) in the experiment. Because ZIFs are a type of polymer material, the effect of the temperature (softening) on the mechanical strength of ZIF-8 should be considered. Thus, it is reasonable to obtain larger elastic constants and mechanical moduli in the DFT calculation (0 K). The DFT overestimation of the elastic moduli of MOFs were also observed in MOF-5 (Table S5).

Second, the computed mechanical properties of the MOFs depend on the software configuration and the DFT parameters (Table S6). Therefore, we decided to focus on the relative variation of the elastic constants and mechanical moduli instead of the absolute values of the mechanical properties of the simulated MOFs. Here, all negative elastic constants and moduli indicate that the current MOF geometry is unreasonable. This outcome may be eliminated by breaking the current symmetry (I-

43m) during the geometry optimization process, which means that the initial structure will significantly deviate from the experimental geometry. In other words, these models are not a good starting point for calculating the elastic constants and moduli of MOFs.

Although the methyl group is usually considered to be an electron donating group (EDG), in ZIF-8 $–CH_3$ seems to be more electrophilic (Table S7). This may be attributed to the interaction of the geometries of the methyl group and the ZIF-8 SOD framework. Comparing the tetrahedron configuration of the methyl group in ZIF-8 with the simple shape of the –H, –Cl, –Br, –I, and –CHO groups investigated in this study, the effect of the geometry of the methyl group on the mechanical properties of ZIF-8 cannot be ignored. In order to isolate the effect of the electronegativity of the group, ZIF-8 was excluded in the main text.

Table S3 Single-crystal elastic constants (C_{ij}), Young's modulus (E), Shear modulus (G), and Bulk modulus (B) of ZIF-8 computed using different model.

	C11	C12	C44	E (GPa)	G (GPa)	B (GPa)
Experiment[S4]	9.523	6.865	0.967	2.78-3.77	0.97-1.33	7.75
B3LYP (0 K)[S4]	11.038	8.325	0.943	2.74-3.88	0.94-1.36	9.23
MD (300 K)[S5]	11.21	7.49	2.75	- - -	2.75	8.00
PBE (0 K)	14.615	9.233	7.124	7.47	4.82	11.03
PW91(0 K)	17.153	10.725	6.859	8.90	5.06	12.87
PBE-D (0 K)	15.166	9.206	7.155	8.21	5.04	11.19
PW91-D (0 K)	7.095	8.015	-1.529	-1.41	-0.95	7.71

Table S4 Lattice parameter of ZIF-8 from experiment and calculation using different models.

	Experiment	PBE-D	PBE	PW91-D	PW91	B3LYP[S4]
Lattice Parameter (Å)	16.986	17.029	17.220	16.725	17.216	17.348

Table S5 Young's moduli of MOF-5 obtained from experiment and DFT calculations.

	Method	Young's modulus (GPa)
Ref. S6	Experiment	7.9
Ref. S6-8	DFT calculation	21.1-21.9

Table S6 Single-crystal elastic constants (C_{ij}), Young's modulus (E), Shear modulus (G), and Bulk modulus (B) of ZIF-8 computed using different computational parameters.

	C11	C12	C44	E (GPa)	G (GPa)	B (GPa)
Model 1	14.615	9.233	7.124	7.47	4.82	11.03
Model 2	10.248	6.243	0.357	0.77	5.52	7.58

Model 1: GGA-PBE, 500 eV, 3×3×3 k-point.

Model 2: GGA-PBE, 340 eV, 2×2×2 k-point.

Table S7. Calculated atomic charges (*q*, *e*) of the ZIF-8, SALEM-2 and ZIF-Cl.

Type	Atomic charge					
	Zn	N	C1	C2	H2	X
ZIF-8(X=CH_3)	1.600	-0.510	0.240	-0.210	0.240	-0.090
SALEM-2(X=H)	1.520	-0.520	-0.030	-0.200	0.240	0.240
ZIF-Cl(X=Cl)	1.420	-0.510	0.190	-0.190	0.250	0.010

3. Synthesis and Characterization of ZIF-I

2-iodoimidazole (2-iim) (97%) was purchased from Sigma-Aldrich. Zinc nitrate hexahydrate (99%, 120 mg, 0.4 mmol) and 2-iim (160 mg, 1 mmol) were added to DMF (95%, 4 mL) in a glass vial. The mixture was homogenized through sonication for 2 min. Then, the solution was poured into the reaction kettle and heated in an oven for 2 days at a temperature of 120 °C. Thus the polyhedral ZIF-I crystals were obtained.

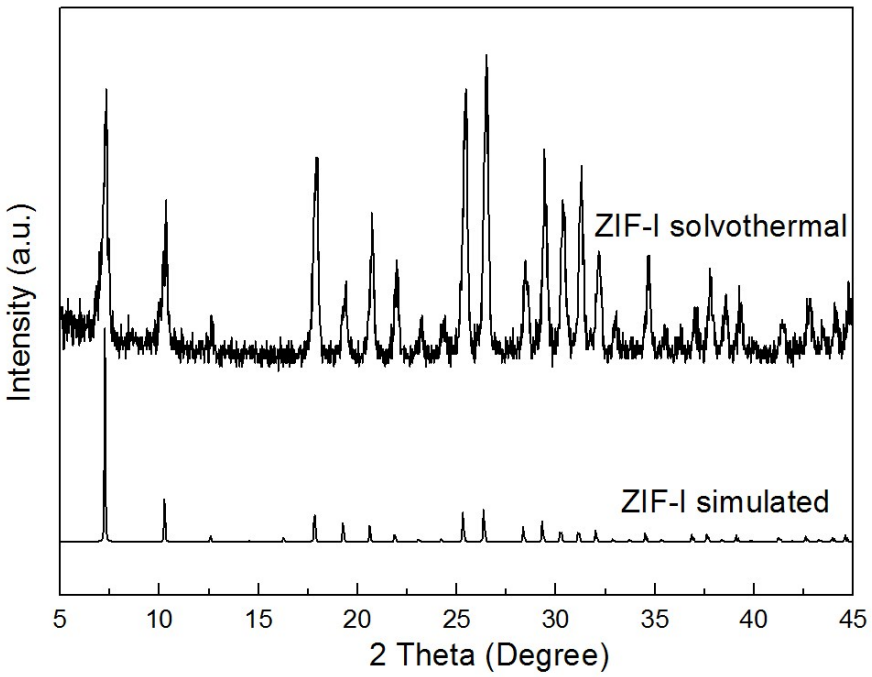

Figure S2. PXRD patterns of ZIF-I.

4. Cluster model

The finite cluster model of ZIFs consists of one Zn atom and four linkers forming a tetrahedron. Li ions, which were confirmed to best reproduce the charge density of the periodic ZIF,[S9] were used to saturate the dangling imidazolate nitrogen lone pairs.

The density functional theory calculations were performed using the Dmol3 code.[S10,11] The exchange correlation energy was described using the PW91 functional within the generalized gradient approximation (GGA-PW91).[S12] All electron for core treatment atoms were used. A double-numeric basis with polarization functions (DNP) was used for all atoms. We utilized a Methfessel–Paxton smearing of 0.005 hartrees. Furthermore, a global real space orbital cutoff of 5.1 Å of the atomic basis sets was assumed. The convergence criteria for the optimization of the structure and the energy calculation were 1.0×10^{-6} for SCF, 1.0×10^{-7} au for the energy, 2.0×10^{-3} au for the maximum force, and 5.0×10^{-4} nm for the maximum displacement.

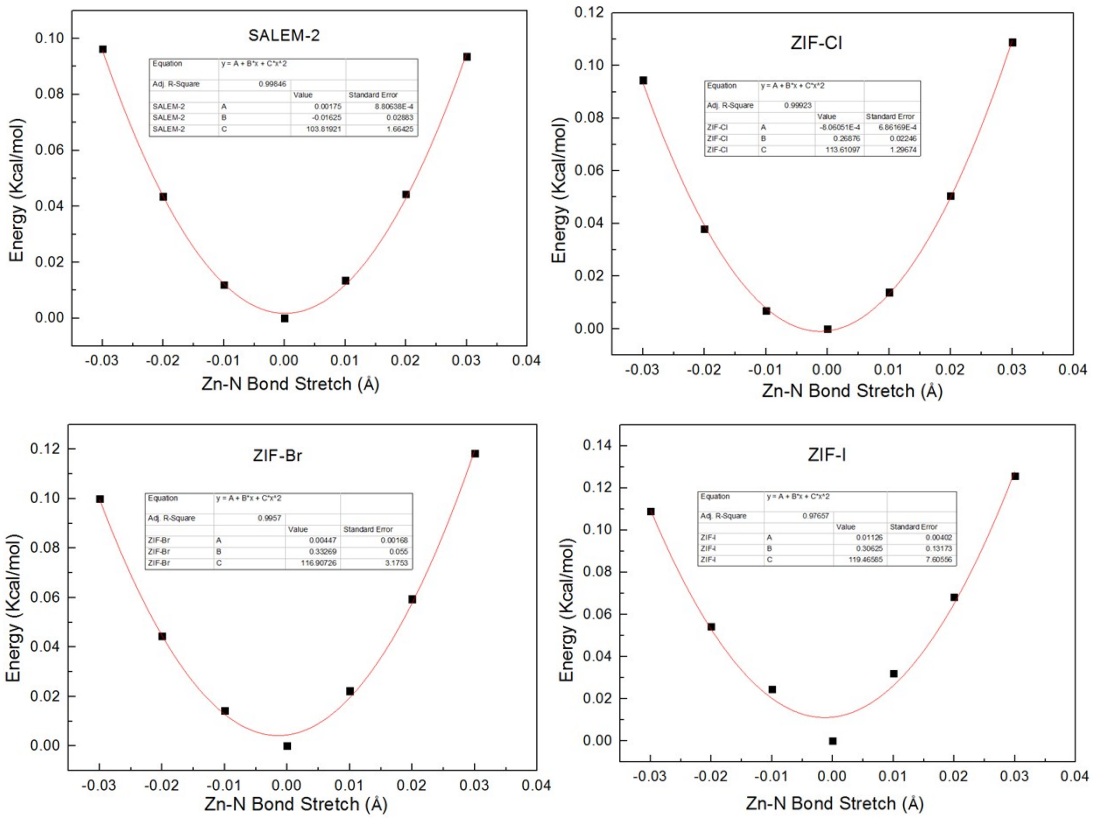

Figure S3. The fitting of the force parameters for Zn-N bond stretching in different ZIFs.

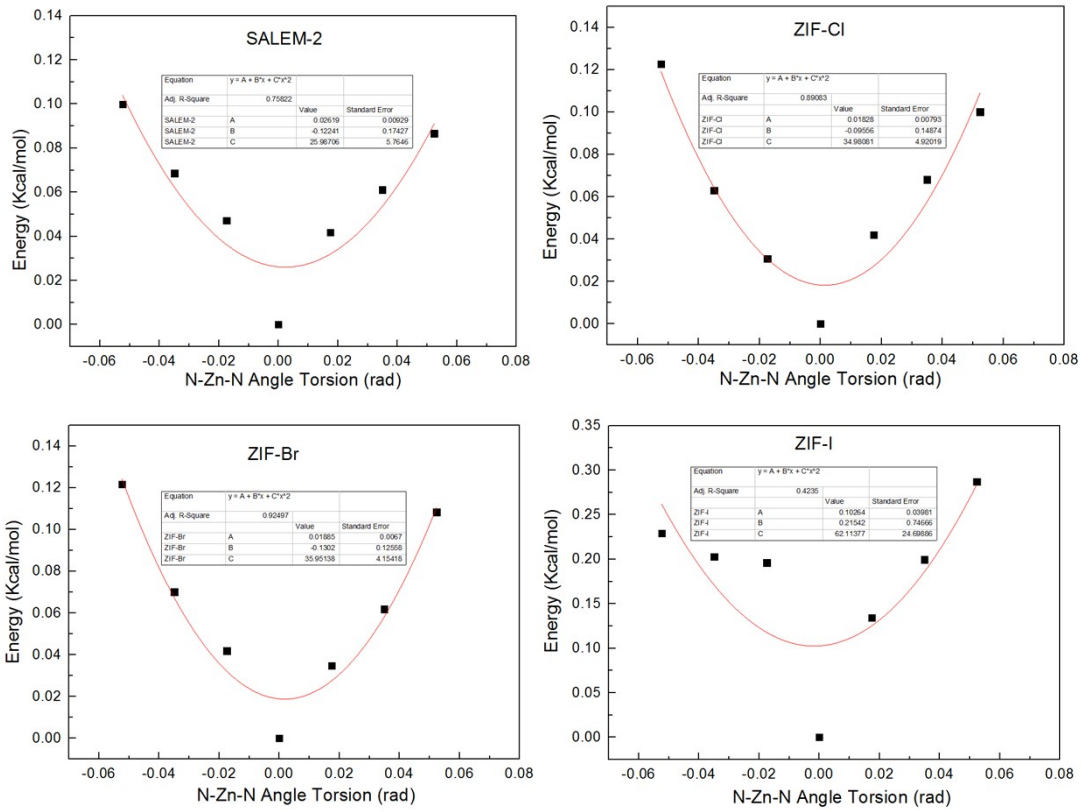

Figure S4. The fitting of the force parameters for N-Zn-N angle stretching in different ZIFs.

References:

S1. Karagiaridi, O.; Lalonde, M. B.; Bury, W.; Sarjeant, A. A.; Farha, O. K.; Hupp, J. T., Opening ZIF-8: A Catalytically Active Zeolitic Imidazolate Framework of Sodalite Topology with Unsubstituted Linkers. *J. Am. Chem. Soc.* **2012**, 134, 18790-18796.

S2. Morris, W.; Doonan, C. J.; Furukawa, H.; Banerjee, R.; Yaghi, O. M., Crystals as Molecules: Postsynthesis Covalent Functionalization of Zeolitic Imidazolate Frameworks. *J. Am. Chem. Soc.* **2008**, 130, 12626-12627.

S3. Li, K.; Olson, D. H.; Seidel, J.; Emge, T. J.; Gong, H.; Zeng, H.; Li, J., Zeolitic Imidazolate Frameworks for Kinetic Separation of Propane and Propene. *J. Am. Chem. Soc.* **2009**, *131*, 10368-10369.

S4. Tan, J.-C.; Civalleri, B.; Lin, C.-C.; Valenzano, L.; Galvelis, R.; Chen, P.-F.; Bennett, T. D.; Mellot-Draznieks, C.; Zicovich-Wilson, C. M.; Cheetham, A. K., Exceptionally Low Shear Modulus in a Prototypical Imidazole-Based Metal-Organic Framework. *Phys. Rev. Lett.* **2012**, *108*, 095502.

S5. Ortiz, A. U.; Boutin, A.; Fuchs, A. H.; Coudert, F.-X., Investigating the Pressure-Induced Amorphization of Zeolitic Imidazolate Framework Zif-8: Mechanical Instability Due to Shear Mode Softening. *J. Phys. Chem. Lett.* **2013**, *4*, 1861-1865.

S6. Bahr, D.; Reid, J.; Mook, W.; Bauer, C.; Stumpf, R.; Skulan, A.; Moody, N.; Simmons, B.; Shindel, M.; Allendorf, M. Mechanical Properties of Cubic Zinc Carboxylate IRMOF-1 Metal-Organic Framework Crystals. *Phys. Rev. B* **2007**, *76*, 184106-1-7.

S7. Zhou, W.; Yildirim, T. Lattice Dynamics of Metal-Organic Frameworks: Neutron Inelastic Scattering and First-Principles Calculations. *Phys. Rev. B* **2006**, *74*, 180301-1-4.

S8. Samanta, A.; Furuta, T.; Li, J. Theoretical Assessment of the Elastic Constants and Hydrogen Storage Capacity of Some Metal-Organic Framework Materials. *J. Chem. Phys.* **2006**, *125*, 084714-1-8.

S9. Zhang, C.; Han, C.; Sholl, D. S.; Schmidt, J. R., Computational Characterization of Defects in Metal–Organic Frameworks: Spontaneous and Water-Induced Point Defects in Zif-8. *The Journal of Physical Chemistry Letters* **2016**, *7*, 459-464.

S10. Delley, B., From Molecules to Solids with the $DMol^3$ Approach. *J. Chem. Phys.* **2000**, *113*, 7756-7764.

S11. Delley, B., An All-electron Numerical Method for Solving the Local Density Functional for Polyatomic Molecules. *J. Chem. Phys.* **1990**, *92*, 508-517.

S12. Perdew, J. P.; and Wang, Y., Accurate and Simple Analytic Representation of the Electron-gas Correlation Energy. *Phys. Rev. B* **1992**, *45*, 13244-13249.