

## Electronic Supplementary Information (ESI)

### ***Quantum mechanical predictions to elucidate the anisotropic elastic properties of zeolitic imidazolate frameworks: ZIF-4 vs. ZIF-zni***

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# 1 *Ab Initio* Density Functional Theory (DFT) Calculations

## 1.1 CRYSTAL09 [1,2]: Additional Computational Details

The Pack–Monkhorst/Gilat shrinking factors for the  $k$ -point sampling of reciprocal space were set to  $2 \times 2$ , corresponding to  $8 \times 8$  points at which the Hamiltonian matrix was diagonalized. The accuracy of the integral calculations was increased by setting the tolerances to 7, 7, 7, 7 and 16. For the numerical integration of the exchange–correlation term, 75 radial points and 974 angular points were adopted in a Lebedev scheme in the region of chemical interest. The self-consistent field iterative procedure was converged to a tolerance in total energy of  $\Delta E = 1 \times 10^{-8}$  a.u.

## 2 Final Optimised Geometry (DFT) vs. Experimental Lattice Parameters

### 2.1 ZIF-4

➤ Orthorhombic space group: *Pbca*

Lattice parameters	<i>a</i> (Å)	<i>b</i> (Å)	<i>c</i> (Å)	Angles $\alpha/\beta/\gamma$ (°)	Volume (Å <sup>3</sup> )
DFT PBE/BS1	15.576	15.837	18.543	90/90/90	4574.045
Expt. (233 K) Ref.[3]	15.3950(17)	15.3073(17)	18.426(2)	90/90/90	4342.2
% Deviation	+1.18%	+3.46%	+0.63%	0%	+5.34%

### 2.2 ZIF-zni

➤ Tetragonal space group: *I4<sub>1</sub>cd*

Lattice parameters	<i>a</i> (Å)	<i>b</i> (Å)	<i>c</i> (Å)	Angles $\alpha/\beta/\gamma$ (°)	Volume (Å <sup>3</sup> )
DFT PBE/BS1	23.763	23.763	12.496	90/90/90	7056.035
Expt. (298 K) Ref.[4]	23.5028(4)	23.5028(4)	12.4607(3)	90/90/90	6883.06
% Deviation	+1.11%	+1.11%	+0.28%	0%	+2.51%

### 3 Computed Elastic Stiffness Tensors $C_{ij}$ 's and Compliance Tensors $S_{ij}$ 's

Notations adopted:

$$\text{Stiffness tensor } C_{ijkl} = \begin{bmatrix} C_{11} & C_{12} & C_{13} & C_{14} & C_{15} & C_{16} \\ & C_{22} & C_{23} & C_{24} & C_{25} & C_{26} \\ & & C_{33} & C_{34} & C_{35} & C_{36} \\ & & & C_{44} & C_{45} & C_{46} \\ & & & & C_{55} & C_{56} \\ & & & & & C_{66} \end{bmatrix}$$

*symm.*  
 $C_{ij} = C_{ji}$

$$\text{Compliance tensor } S_{ijkl} = [C_{ijkl}]^{-1}$$

#### 3.1 ZIF-4 (Orthorhombic *Pbca*) with nine independent elastic constants

- **Stiffness Tensor**

$$C_{ijkl} = \begin{bmatrix} 4.266 & 1.221 & 1.916 & 0 & 0 & 0 \\ & 3.492 & 1.526 & 0 & 0 & 0 \\ & & 5.015 & 0 & 0 & 0 \\ & & & 1.029 & 0 & 0 \\ & & & & 1.927 & 0 \\ & & & & & 2.453 \end{bmatrix} \text{ GPa}$$

*symm.*

- **Compliance Tensor**

$$S_{ijkl} = \begin{bmatrix} 294.157 & -61.9845 & -93.5226 & 0 & 0 & 0 \\ & 343.35 & -80.7955 & 0 & 0 & 0 \\ & & 259.717 & 0 & 0 & 0 \\ & & & 971.817 & 0 & 0 \\ & & & & 518.941 & 0 \\ & & & & & 407.664 \end{bmatrix} \text{ TPa}^{-1}$$

*symm.*

### 3.2 ZIF-zni (Tetragonal $I4_1cd$ ) with six independent elastic constants

- **Stiffness Tensor**

$$C_{ijkl} = \begin{bmatrix} 19.010 & 13.257 & 13.377 & 0 & 0 & 0 \\ & 19.010 & 13.377 & 0 & 0 & 0 \\ & & 23.384 & 0 & 0 & 0 \\ & & & 1.557 & 0 & 0 \\ & & & & 1.557 & 0 \\ \text{symm.} & & & & & 1.759 \end{bmatrix} \text{ GPa}$$

- **Compliance Tensor**

$$S_{ijkl} = \begin{bmatrix} 116.393 & -574.39 & -33.726 & 0 & 0 & 0 \\ & 116.393 & -33.726 & 0 & 0 & 0 \\ & & 81.351 & 0 & 0 & 0 \\ & & & 642.185 & 0 & 0 \\ & & & & 642.185 & 0 \\ \text{symm.} & & & & & 568.579 \end{bmatrix} \text{ TPa}^{-1}$$

## 4 References

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