Supplemental Material

Tracking Thermal-Induced Amorphization of a Zeolitic Imidazolate Framework via Synchrotron In Situ Far-Infrared Spectroscopy

Matthew R. Ryder, a,b Thomas D. Bennett, c Chris S. Kelley, b Mark D. Frogley, b Gianfelice Cinque, b Jin-Chong Tan a

aDepartment of Engineering Science, University of Oxford, Parks Road, Oxford OX1 3PJ, United Kingdom
bDiamond Light Source, Harwell Campus, Didcot, Oxford OX11 0DE, United Kingdom
cDepartment of Materials, University of Cambridge, Cambridge CB3 0FS, United Kingdom

*Correspondence to: jin-chong.tan@eng.ox.ac.uk
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1 Materials Synthesis and Characterization

The ZIF-4 sample was synthesized and evacuated according to the synthetic procedure in our previous work.[1, 2]

Fig. S1. Powder X-Ray Diffraction of ZIF-4 comparing the experimental spectrum for the sample used in the measurements and the simulated spectrum from the CIF file in the literature.[3]

The ZIF-8 sample was purchased from Sigma-Aldrich, Basolite® Z1200.
2 Synchrotron Radiation Far-Infrared (SR FIR) Absorption

The Far-infrared (FIR) absorption spectroscopy experiments were performed at the Multimode InfraRed Imaging and Microspectroscopy (MIRIAM) Beamline (B22) at the Diamond Light Source synchrotron facility.[4] One of the primary motivations to use synchrotron radiation (SR) was the increased brightness of the beam (photon flux density significantly higher than conventional sources). Therefore allowing for us to obtain high signal-to-noise data of the FIR spectral region.

The specific experimental setup was similar to that used by Greenaway et al. for the in situ mid-infrared microspectroscopy of CO$_2$ adsorption on single crystals of functionalized Sc-MOFs.[5] The work contained in this paper concentrated on the far-infrared spectral region via the utilization of a multilayer coated 6-micron mylar beamsplitter, and an IR Labs liquid helium cooled Si bolometer.

A small quantity of ZIF-4 powder was loaded on the heat stage of the Linkam cell, and the cell was sealed with an IR grade double polished Si window and mounted onto the microscope. There was a constant flow of nitrogen, and the sample was allowed to equilibrate for approximately 5 minutes at each temperature point. The following settings were used to obtain the spectral data:

<table>
<thead>
<tr>
<th>Data Acquisition Parameters</th>
<th></th>
</tr>
</thead>
<tbody>
<tr>
<td>Optical Aperture</td>
<td>6 mm</td>
</tr>
<tr>
<td>Scanner Velocity</td>
<td>40 Hz</td>
</tr>
<tr>
<td>Spectral Resolution</td>
<td>2 cm$^{-1}$</td>
</tr>
<tr>
<td>Phase Resolution</td>
<td>16 Hz</td>
</tr>
<tr>
<td>Number of Scans*</td>
<td></td>
</tr>
<tr>
<td>ZIF-4</td>
<td>256</td>
</tr>
<tr>
<td>ZIF-8</td>
<td>64</td>
</tr>
</tbody>
</table>

*The number of scans obtained for the ZIF-8 spectral measurements was less due to time constraints at the end of the beamtime.
3 Ab Initio Quantum Mechanical Calculations

All density functional theory (DFT) calculations were performed using the periodic ab initio code CRYSTAL14.[6] The vibrational frequencies and elastic constants of ZIF-zni were calculated using the exact methodology and computational parameters from our previous work of the THz vibrations of ZIFs[2] and the elasticity of unsubstituted imidazole containing ZIFs[7] respectively.

The theoretical IR spectra were calculated at the PBE level of theory[8] and corrected with an empirical Grimme dispersion term (PBE-D).[9] The mass-weighted Hessian matrix for the calculation of the vibrational frequencies was obtained by numerical differentiation of the analytical first derivatives, calculated at geometries obtained by displacing each of the 3N atomic coordinates of the equilibrium geometry. All electron TZVP basis sets were used for all atoms, the same as our previous work on the THz vibrations of ZIFs.[2]

The elastic constants were calculated at the B3LYP level of theory.[10] This allowed for the mechanical properties of ZIF-zni to be obtained via tensorial analysis as described in detail in our previous work on the mechanical properties of MOFs.[7, 11, 12]
4 ZIF-4 Peak Fitting and Spectral Curve Fitting

The peaks located in the 250-350 cm\(^{-1}\) spectral region were fitted using a Gaussian in the OriginPro 9.1 software. The result can be seen below for the room temperature spectrum. The error values were within a range comparable to the size of the symbols used in Figure 3 of the main text and hence error bars were unnecessary.

![Graph showing peak fitting method for the 298 K peak of ZIF-4](image)

Fig. S2. Spectrum showing the fitting method for the 298 K peak of ZIF-4.
The curve fitting was also performed using the OriginPro 9.1 software from the equation stated in the main text:

\[
\nu(T) = \nu_0 - \frac{X_R T_C}{e^{\frac{T}{T_C}} - 1}
\]

\[
T_C = \frac{h\nu_0}{k_B}
\]

This yielded the \(X_R\) values that are stated in the text. The resultant values with associated errors for each tetrahedral environment are shown below.

<table>
<thead>
<tr>
<th>Tetrahedra</th>
<th>(X_R)</th>
<th>Standard Error</th>
<th>Adj. R-Squared</th>
<th>Reduced Chi-Square</th>
</tr>
</thead>
<tbody>
<tr>
<td>Zn(Im)(_4)</td>
<td>0.04541</td>
<td>8.19764E-4</td>
<td>0.97001</td>
<td>1.19234</td>
</tr>
<tr>
<td>Zn(mlm)(_4)</td>
<td>0.03152</td>
<td>3.91277E-4</td>
<td>0.99515</td>
<td>0.13183</td>
</tr>
</tbody>
</table>
5 Young’s Modulus 3-D Plot for ZIF-zni

Figure. S3. 3-D Young’s modulus representation surface $E(\theta, \varphi)$ of ZIF-zni in GPa.
6 Shear Modulus 3-D Plot for ZIF-zni

Figure. S4. 3-D shear modulus representation surface $G(\theta, \varphi, \chi)$ of ZIF-zni. Colour coding used: blue and green represent the maximum and minimum moduli in GPa.
7 Linear Compressibility 3-D Plot for ZIF-zni

Figure. S5. 3-D linear compressibility representation surface $\beta(\theta, \varphi)$ of ZIF-zni in TPa$^{-1}$. 
8 Poisson’s Ratio 3-D Plot for ZIF-zni

Figure. S6. 3-D Poisson’s ratio representation surface $\nu(\theta, \varphi, \chi)$ of ZIF-zni. Colour coding used: blue and green represent the maximum and minimum values.
9 References


