Supporting Information

for

Vibrational Modes and Terahertz Phenomena of the Large-Cage Zeolitic Imidazolate Framework-71

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1.1 SYNTHESIS OF ZIF-71

ZIF-71 was synthesised by dissolving 2.155 g of 4,5-dichloroimidazolate (dcIm) in 144.96 ml of methanol and combining it with 0.72 g of zinc acetate, likewise, diluted in 144.96 ml of methanol. The obtained white colloidal solution was stirred for 24 hours at room temperature. Nanocrystals were isolated by centrifugation at 8000 rpm for 5 minutes and washed with fresh methanol, a procedure repeated three times to remove any excess reactants. Prior to the measurements, the material was exposed to heat (80 °C) and vacuum overnight to remove any solvent.

1.2 POWDER X-RAY DIFFRACTION

The purity and crystallinity of the powdered sample were confirmed using powder X-ray diffraction (PXRD). XRD patterns were recorded using a Rigaku MiniFlex diffractometer with a Cu Kα source (1.541 Å). Measurements were performed with a step size of 0.02° and step speed of 0.01° min⁻¹.
1.3 FTIR Measurements with Synchrotron Radiation

Fourier-transform infrared (FTIR) absorption spectroscopy experiments were performed at the Multimode InfraRed Imaging and Microspectroscopy (MIRIAM) Beamline (B22) at the Diamond Light Source. The absorbance spectra were measured using a Bruker Vertex 80V Fourier Transform IR (FTIR) interferometer (Bruker Optics, Germany). For comparison, the broadband IR spectrum was also measured with specular reflectance spectroscopy using the same interferometer equipped with the Pike Technologies VeeMAX II variable angle specular reflectance accessory. Absorbance spectra were measured on powder sample, and reflectance spectroscopy was probed on a pellet pressed with a (uniaxial) mechanical load of 1 ton. For both measurements, the broadband spectral range of the synchrotron source covered the visible to the low-energy THz region. A liquid helium-cooled bolometer in combination with a 6-µm Mylar multilayer beamsplitter in the interferometer allowed for measurements in the far-IR range.
spectral region between 0 and 650 cm\(^{-1}\). Mid-IR measurements (550 – 4000 cm\(^{-1}\)), on the other hand, were carried out using a KBr beamsplitter and an in-built detector. IR spectra were collected with a resolution of 2 cm\(^{-1}\) and 256 scans per spectral scan. All measurements were performed at vacuum (lower than 10\(^{-5}\) bar) maintained at room temperature. Background spectra were collected by measuring a mirror before the measurements.

FIG S2: Comparison of synchrotron-radiation SR-IR spectroscopy: a) Imaginary part of the complex refractive index, \(\kappa(\omega)\), determined from the specular reflectance spectrum via Kramer-Kronig Transform, b) ATR-FTIR absorbance spectrum.
1.4 **Inelastic Neutron Scattering Measurements**

Inelastic neutron scattering (INS) measurements were performed at the TOSCA spectrometer at the ISIS Neutron and Muon Source, Rutherford Appleton Laboratory (Chilton, UK). High-resolution ($\Delta E/E \approx 1.25\%$) spectra, covering the broadband range (20-4000 cm$^{-1}$), were collected from the bulk polycrystalline sample (~1 g) at 10 K. The pulsed, polychromatic beam of neutrons collided with the sample and the scattered neutrons were Bragg reflected by a pyrolytic graphite analyser. Higher-order reflections beyond (002) were suppressed by a cooled ($T < 30$ K) Beryllium filter, acting as a longpass filter to analyse neutrons of a consistent final energy. Accordingly, neutrons with a final energy of ~32 cm$^{-1}$ were passed towards the detector array composed by thirteen $^3$He tubes with effective length of 250 mm. Five banks were located in forward direction (scattering angle ~45°) and five in backwards direction (~135°). The use of a low final energy translated into a direct relationship between energy transfer (ET, cm$^{-1}$) and momentum transfer ($Q$, Å$^{-1}$) such that $ET \approx 16Q^2$. Energy transfer and spectral intensity, i.e. $S(Q, \omega)$, were then obtained using the Mantid software. The sample was wrapped in 4 cm × 4.6 cm aluminium sachet and placed into a 2.0 mm spaced flat aluminium cell, which was sealed with indium wire. To reduce the effect of the Debye-Waller factor on the experimental spectral intensity and allow comparison with the theoretical spectra, the sample cell was cooled to ~10 K by a closed cycle refrigerator. The INS spectrum was collected under vacuum over a duration of 5 hours.
FIG S3: Inelastic neutron scattering (INS) data with error bars for a powder sample of ZIF-71.

The neutron guide upgrade of the TOSCA spectrometer, completed in 2017, has increased the neutron flux at the sample position by as much as 82 times. This upgrade improves the performance through faster measurements and by reducing the required sample mass.⁴
1.5 **Density Functional Theory (DFT) Calculations**

*Ab initio* density functional theory (DFT) calculations, in principle, evaluate the force-fields acting on the electrons. As the second derivative of the energy, the force constant considers the interactions emerging from electrons and nuclei within the molecule. In the DFT approach, the terms involving the Coulomb interactions between the electrons (exchange-correlation energy) are modelled by functionals employing different levels of theory. Here the crystalline orbital is approximated by a linear combination of Bloch functions, built from localized functions (“atomic orbitals”). These atomic orbitals are represented as linear combinations of Gaussian-type functions whose constant coefficients are defined by the input. Commonly used, for instance, is the B3LYP functional, a hybrid model proposed by Becke (B3) to advance the gradient-corrected correlation of Lee et al. (LYP). Combined with the Grimme’s dispersion correction (B3LYP-D3), the DFT calculations yield theoretical IR spectra demonstrating the closest resemblance with experimental frequencies. All electron basis sets were used for Zn, C, N, Cl, and H atoms, containing 12,480 (BS1) and 16,032 (BS2) local functions for the 816 atoms per unit cell.

First, the geometry optimization was carried out using a quasi-Newtonian algorithm and was considered complete when the calculation converged to the thresholds for both the RMS and maximum value for the force and atomic displacement, simultaneously. The corresponding thresholds were $3 \times 10^{-5}$ (RMS on gradient), $1.2 \times 10^{-4}$ (RMS on displacement), $4.5 \times 10^{-5}$ (largest component of gradient), and $1.8 \times 10^{-4}$ (absolute value of largest displacement). Subsequently, the IR frequencies were calculated at the special point $\Gamma = (0,0,0)$. Here, the dynamical matrix (“mass-weighted Hessian matrix”) was obtained through numerically evaluating the first derivatives of the atomic gradients. The IR intensities
were then calculated with the Berry Phase approach; for a detailed description of the performed calculation, we refer to the work of Pascale et al.\(^9\) The continuous spectrum was obtained by fitting the calculated IR intensities with Lorentzian peak shapes with a FWHM of 10 cm\(^{-1}\). To improve the match with experimental data, the calculated IR spectra were scaled by using a scaling factor of 0.98.\(^10\) The INS spectrum was calculated from the output of the DFT frequency calculation using the Abins v1 execution in the Mantid software.\(^3\)

**FIG S4:** Comparison between infrared spectra of ZIF-71 obtained from synchrotron-radiation (SR) experiments and DFT simulations employing two different basis sets (BS1 and BS2).
FIG S5: Bulk shift of DFT simulated spectrum versus the experimental mid-IR spectrum of ZIF-71.
FIG S6: INS spectra derived from the phonon calculation compared with experimental measurement. No shift was applied, but the simulated spectrum for hydrogen (H) has been scaled down (normalization between 0 and 1) for better visualization.
1.6 **NanoFTIR Measurements**

The near-field optical measurements were performed with a neaSNOM instrument (neaspec GmbH) based on a tapping-mode atomic force microscopy (AFM) setup where the platinum-coated tip (NanoAndMore GmbH, cantilever resonance frequency 250 kHz, nominal tip radius ~20 nm) was illuminated by a broadband femtosecond laser. The coherent mid-infrared light was generated through the nonlinear difference-frequency combination of two beams from fiber lasers (TOPTICA Photonics Inc.) in a GaSe crystal. The spectra of two laser sources covering the range from 700 to 1400 cm\(^{-1}\) and 1000 to 1600 cm\(^{-1}\), respectively, were merged for the measurements. Demodulation of the optical signal at higher harmonics of the tip resonance frequency eliminated background contributions to yield the near-field signal, comprising amplitude and phase of the scattered wave from the tip. Employing a pseudo-heterodyne interferometric detection module, the complex optical response of the material is measured, where the real part refers to the nanoFTIR reflectance and the imaginary part depicts the nanoFTIR absorption spectrum. Each spectrum was acquired from an average of 10 Fourier-processed interferograms with 9 cm\(^{-1}\) spectral resolution, 1024 points per interferogram, and 10-ms integration time per pixel. The sample spectrum was normalized to a reference spectrum measured on the silicon substrate. All measurements were carried out under ambient conditions.
FIG S7: Local nanoFTIR spectra measured on individual ZIF-71 crystals reveal chemical homogeneity.

1.7 **AFM Nanoindentation**

AFM nanoindentation was performed with the Veeco Dimension 3100 instrument operating in indentation mode. A Bruker PDNISP probe with a cube-corner diamond indenter tip (cantilever spring constant 152 N/m, and contact sensitivity of 156.6 nm/V) was used. The nominal contact area was determined based on the indenter tip geometry established by Zeng and Tan.\(^{11}\) The mechanical properties – Young’s modulus (E) and hardness (H) – were derived from the set of indenter load-vs-displacement curves employing the Oliver and Pharr method, which is applicable to the cube-corner geometry.\(^{12}\) For a detailed description of the AFM nanoindentation methodology for metal-organic framework crystals, we refer to the work of Zeng and Tan.\(^{11}\)
1.8 Complete Assignment of Vibrational Modes of ZIF-71

Table S1: Complete assignment of all the vibrational modes of ZIF-71 between 0-170 cm\(^{-1}\) (<5.1 THz), 171-600 cm\(^{-1}\) (~5.1-18 THz), 601-1200 cm\(^{-1}\) (~18-36 THz), and 1201-4000 (~36-120 THz) based on the DFT simulations. Abbreviations: MR membered-ring, \(\nu\) stretching, \(\nu_s\) symmetric stretching, \(\nu_a\) asymmetric stretching, \(\delta\) bending, \(\delta_s\) scissoring, \(\rho\) rocking, \(\tau\) twisting, \(\omega\) wagging. Simulated vibrational modes that can be observed in experimental FTIR measurements are shown in grey.

Video clips of representative vibrational modes can be found as part of the electronic SI: (in cm\(^{-1}\)) 9.46, 10.45, 23.68, 37.42, 1076.38, and 1508.78.
| Frequency (cm⁻¹) | Intensity (a.u.) | Assignment |
|-----------------|-----------------|------------|
| FTIR BS1 BS2    | BS1 BS2         |            |
| 9.46 11.61      | 1 1             | 8MR gate-opening |
| 10.45 6.63      | 1 1             | Soft mode with shear deformation of 8MR and 6MR |
| 10.52 12.7      | 8 6             | ρ opposite linkers in 4MR, asym gate-opening |
| 17.25 1         | 1               | ρ opposite linkers in 6MR, asym gate-opening |
| 24 23.68 21.9   | 5 6             | 8MR gate-opening |
| 24.21 23.94     | 2 1             | 8MR, 4MR shearing, ρ Cl |
| 25.43 25.35     | 2 3             | 8MR breathing |
| 33 33.06 31.95  | 3 5             | υₚ Zn-N, N-C, ω Cl |
| 37.42 40.18     | 2 1             | 6MR gate-opening |
| 43 40.81        | 3               | υₛ Cl-C-N, small 6MR breathing |
| 46.11 47.47     | 2 1             | υₛ Zn-N, N-C, ω Cl, small 4MR and 8MR breathing |
| 53 51.21 53.74  | 5 4             | Flapping of neighbouring linkers, asym. gate-opening, υₛ Zn-N |
| 54.01 55.05     | 1 1             | υₛ Zn-N-C, 4MR breathing |
| 55.68 58.95     | 3 1             | υₛ Zn-N, 4MR and 8MR shearing, ring breathing |
| 61.39 62.87     | 2 2             | ω Cl, ring breathing, 4MR and 6MR shearing |
| 62 64.63 65.17  | 3 6             | Ring breathing, ω Cl, deformation of 8MR and 4MR |
| 66.35 68.83     | 1 3             | υₛ Zn-N, ring deformation, small pore deformation |
| 77.37 75.83     | 1 5             | τ Cl-C-N, ring breathing, very small pore deformation |
| 79.29 79.59     | 12 21           | τ Cl, 8MR aperture increase, υₛ Zn-N: 4MR pore stretching |
| 74 80.85 80.18  | 39 16           | υₛ Zn-N: 4MR pore deformation |
| 86.14 83.13     | 5 3             | τ Cl, υ C-H, 8MR and 4MR pore deformation, 6MR breathing |
| 91.56 85.82     | 2 1             | υₛ Cl-C-N, 6MR pore deformation, 8MR and 4MR deformation |
| 93.31 90.73     | 1 1             | 4MR breathing, 6MR and 8MR small deformation |
| 99.21 98.65     | 34 30           | υ ring, ω Cl, 4MR and 6MR aperture expansion |
| 103.96 102.09   | 4 2             | 6MR breathing (small) |
| 107.82 106.79   | 42 34           | 8MR breathing (small) |
| 111.95 110.15   | 4 7             | 4MR shearing, 6MR deformation |
| 112 113.09 112.11 | 168 99     | 4MR and 6MR deformation, 8MR expansion |
| 112 119.66 118.4 | 218 162  | 4MR and 8MR deformation, 6MR expansion |
| 121.91 121.28   | 19 19           | 8MR shearing, 6MR contraction |
| 125.35 123.79   | 163 171         | 8MR breathing, 4MR and 6MR deformation |
| 130.67 130.17   | 5 62            | δₛ Cl, υ N-C, 4MR and 8MR pore stretching |
| 129 133.15 132.41 | 600 651  | υ Zn-N, υ N-C-H, 4MR breathing |
| 156.81 158.22   | 1 1             | δ Cl, τ Zn-N, 6MR pore deformation |
| 161.39 163.13   | 10 10           | υₛ Zn-N, δₛ Cl, 6MR pore deformation |
| 170.61 171.61   | 21 9            | υₛ Cl, υₛ ring |
| 173.72 174.13   | 1 2             | υₛ ring, δₛ Cl |
| 177.17 177.78   | 15 29           | υ Zn-N δₛ Cl, 4MR and 6MR pore deformation |
Vibrational modes 171 - 600 cm⁻¹

| Frequency (cm⁻¹) | Intensity (a.u.) | Assignment |
|------------------|------------------|------------|
| FTIR BS1 BS2     | BS1 BS2          |            |
| 179.63           | 180.06           | 28 10      | δ Zn-N (tetrahedral deformation), ring deformation |
| 173 179.89       | 180.54           | 55 68.75   | δ Zn-N bending (tetrahedral deformation), ω Cl |
| 182.72           | 183.88           | 2 1        | ν Zn-N, ring deformation |
| 189.79           | 190.2            | 1 7        | δ Zn-N, ring stretching |
| 190 195.41       | 194.86           | 15 17      | δ Zn-N (tetrahedral deformation) |
| 223.49           | 223.06           | 25 20      | ν Zn-N, 4MR breathing |
| 229.01           | 227.38           | 169 272    | δ Zn-N, 8MR and 6MR deformation |
| 215 230.26       | 230.87           | 780 730    | δ Zn-N, pore deformation |
| 236.01           | 234.78           | 2 2        | δ Zn-N, δs Cl |
| 225 242.95       | 241.98           | 422 402    | ν Zn-N |
| 247 253.13       | 251.87           | 434 597    | δ Zn-N, 4MR and 8MR expansion |
| 254.65           | 253.26           | 77 71      | δ Zn-N, ω N-C-H |
| 256.51           | 253.87           | 45 9       | δ Zn-N, ω C-H |
| 256.79           | 254.08           | 5 5        | δ Zn-N, ω C-H |
| 257.44           | 255.53           | 185 156    | δ Zn-N |
| 262.35           | 260.99           | 138 188    | ω ring, 4MR asym. gate-opening |
| 263.05           | 261.87           | 296 155    | νa Zn-N, ω ring |
| 263.63           | 261.87           | 8 140      | δs Zn-N |
| 258 265.61       | 264.08           | 719 431    | ρ linker |
| 258 266.4        | 265.23           | 686 1082   | ω linker |
| 269.2            | 268.46           | 87 90      | ν Zn-N, ring deformation |
| 275.26           | 274.57           | 4 2        | νa Zn-N, ring stretch |
| 271 278.41       | 278.02           | 1165 1103  | νs Zn-N, ring and pore deformation |
| 281 284.04       | 283.7            | 1586 1504  | ρ Zn-N, ρ C-N-C, small 8MR breathing |
| 288.77           | 288.94           | 969 1020   | τ N-C, small 6MR breathing |
| 439.85           | 438.99           | 3 4        | ρ linker |
| 444.45           | 443.66           | 7 6        | ρ linker |
| 446.1            | 444.83           | 16 17      | νa N-C-Cl, only incomplete linkers |
| 449.12           | 447.88           | 14 7       | δs linker |
| 551.7            | 548.38           | 1 1        | δs N-C, 4MR deformation |
| 552.08           | 548.59           | 2 10       | τ N-Zn-N, 4MR expansion |
| 552.64           | 548.77           | 6 1        | τ N-Zn-N, |
| 553.65           | 550.39           | 4 8        | ω N-Zn-N |
| 554.53           | 1                | ω N-Zn-N, ring stretching |
| 558.19           | 554.87           | 153 167    | ω C-N, τ C-N-Zn |
| 560.49           | 557.14           | 14 15      | νa Zn-N (Zn fixed) |
| 563              | 559.47           | 120 80     | νa Zn-N (Zn fixed) |
| 563.75           | 559.85           | 41 95      | νa Zn-N (Zn fixed), ring shearing |
| 564.74           | 560.98           | 173 216    | νa Zn-N (Zn fixed), ring deformation |
| 552 565.57       | 561.99           | 1044 1000  | νa Zn-N (Zn fixed), in-plane ring deformation |
| Frequency (cm⁻¹) | Intensity (a.u.) | Assignment                      |
|-----------------|-----------------|---------------------------------|
| FTIR BS1 BS2    | BS1 BS2         |                                 |
| 660.64          | 6 5             | out-of-plane ring deformation    |
| 661.19          | 19 1            | out-of-plane ring deformation    |
| 662             | 3 10            | out-of-plane ring deformation    |
| 663.36          | 5 10            | out-of-plane ring deformation    |
| 674.43          | 1 1             | out-of-plane ring deformation    |
| 675.12          | 99 8            | out-of-plane ring deformation    |
| 676.38          | 250 375         | out-of-plane ring deformation    |
| 662             | 677.3 678.69    | 346 236 out-of-plane ring deformation |
| 677.77          | 678.96 681.17   | 157 354 out-of-plane ring deformation |
| 679.84          | 681.96          | 21 27 out-of-plane ring deformation |
| 680.36          | 681.96          | 65 56 out-of-plane ring deformation |
| 666             | 682.82 684.58   | 972 761 out-of-plane ring deformation |
| 823.1           | 830.44 831.07   | 3 14 out-of-plane ring deformation |
| 824.39          | 3 14            | out-of-plane ring deformation    |
| 821             | 825.09 832.29   | 70 116 out-of-plane ring deformation |
| 825.85          | 832.55          | 4 14 out-of-plane ring deformation |
| 830             | 826.46 833.13   | 99 62 out-of-plane ring deformation |
| 827.29          | 835.16 841.68   | 29 81 out-of-plane ring deformation |
| 1024.56         | 1027.14         | 12 8 in-plane ring deformation  |
| 1028.59         | 1030.85         | 6 7 in-plane ring deformation   |
| 1029.4          | 1031.71         | 4 2 in-plane ring deformation   |
| 1029.54         | 1032.1          | 8 10 in-plane ring deformation  |
| 1029.98         | 1032.58         | 4 5 in-plane ring deformation   |
| 1033.14         | 1035.74         | 15 18 in-plane ring deformation |
| 1033.49         | 1063.7          | 3 8 in-plane ring deformation   |
| 1056 1076.38    | 1074.7          | 24028 24045 in-plane ring deformation, ρ H-C-N |
| 1080.26         | 1078.22         | 2317 2381 in-plane ring deformation, ρ H-C-N |
| 1081.76         | 1079.72         | 2493 2912 in-plane ring deformation, ρ H-C-N |
| 1084.43         | 1082.53         | 596 513 in-plane ring deformation, ρ H-C-N |

Vibrational modes 601-1200 cm⁻¹ (Ring deformations)
### Vibrational modes 1201 - 4000 cm⁻¹

| Frequency (cm⁻¹) | Intensity (a.u.) | Assignment |
|-----------------|-----------------|------------|
| FTIR            | BS1             | BS2        | BS1 | BS2 |
| 1201            | 1216.57         | 1212.3     | 1839 | 1699 | δ CH, vₐ Cl-C-N, edges of unit cell |
|                 | 1220.54         | 1216.47    | 1    | 1008 | δ CH, v C-N |
| 1201            | 1224.07         | 1218.27    | 2414 | 1666 | δ CH, v C-N |
|                 | 1229.18         | 1225.51    | 63   | 340  | δ CH, v C-N |
| 1220.54         | 1224.07         | 1218.27    | 2414 | 1666 | δ CH, v C-N |
| 1233            | 1260.24         | 1245.5     | 3319 | 3431 | v C-N, ring breathing |
| 1260.38         | 1245.82         | 1224.07    | 1235 | 1174 | v C-N, ring breathing |
| 1233            | 1264.22         | 1249.53    | 46   | 184  | v C-N |
| 1229.18         | 1266.22         | 1251.13    | 2490 | 2191 | vₐ C-N |
| 1238            | 1270.56         | 1255.91    | 3175 | 4286 | vₐ C-N |
| 1220.54         | 1272.64         | 1237.63    | 548  | 411  | vₐ C-N |
| 1273.35         | 1257.97         | 368        | 13   | v C-N |
| 1276.42         | 1260.96         | 486        | 537  | v C-N |
| 1332.01         | 1317.33         | 190        | 1367 | v C-N |
|                 | 1333.06         | 1320.68    | 11   | 275  | vₐ C-N |
| 1333.06         | 1334.13         | 1322.32    | 238  | 19   | v C-N |
| 1334.13         | 1334.48         | 1323.73    | 5    | 164  | vₐ C-N |
| 1302            | 1335.65         | 1324.99    | 440  | 1741 | v C-N |
| 1336.15         | 1325.64         | 2          | 500  | vₐ C-N |
| 1337.46         | 1325.64         | 78         | 5    | v C-N |
| 1337.97         | 1326.37         | 300        | 83   | vₐ C-N |
| 1339.14         | 1326.95         | 532        | 371  | vₐ C-N |
| 1341.35         | 1328.42         | 1053       | 18   | vₐ C-N |
| 1341.77         | 1328.6          | 346        | 17   | v C-N |
| 1465            | 1508.78         | 1493.54    | 16845| 15950| δₛ N-CH |
| 1519.82         | 1505.77         | 22         | 193  | δₛ N-CH |
| 1488            | 1520.47         | 1506.45    | 1248 | 1509 | v C-N, δ CH |
| 1543.99         | 1532.58         | 74         | 60   | vₐ C-C-N |
| 1518            | 1545.61         | 1534.23    | 1168 | 1307 | vₐ C-C-N, v C-C, |
| 1551.32         | 1539.22         | 503        | 468  | vₐ N-C-N |
| 1552            | 1539.91         | 630        | 844  | vₐ N-C-N |
| 1554.49         | 1545.15         | 302        | 316  | v C-C, v C-N, |
| 1525            | 1556.6          | 1546.23    | 1331 | 1399 | v C-C, v C-N, δ N-C-N |
| 1562.84         | 1552379         | 488        | 519  | vₛ N-C-Cl (edge of unit cell) |
| 1563.73         | 1553.68         | 1273       | 1423 | vₛ N-C-Cl (edge of unit cell) |
| 3277            | 3251.24         | 158        | 134  | p CH |
| 3277.05         | 3251.28         | 15         | 10   | v CH |
| 3283.44         | 3260.16         | 31         | 38   | v CH |
| 3283.78         | 3260.53         | 12         | 14   | v CH |
| 3296.46         | 3270.69         | 19         | 31   | v CH |
| 3296.78         | 3270.95         | 2          | 3    | v CH |
| 3305.46         | 3281.78         | 74         | 86   | v CH |
| 3305.78         | 3281.96         | 4          | 3    | v CH |
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