Supporting Information

Tuning the High-Pressure Phase Behaviour of Highly Compressible Zeolitic Imidazolate Frameworks: From Discontinuous to Continuous Pore Closure by Linker Substitution

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Supporting Information

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1. Experiments and methods

Synthesis: The syntheses of ZIF-4(Zn) and ZIF-62(M) with (M represents Zn or Co cations) were performed according to published protocols\cite{5,6}. M(NO$_3$)$_2$·6H$_2$O (4.0 mmol) and varying ratios of imidazole and benzimidazole (total molar amount 13.2 mmol, detailed ratios are given in Table 1) were dissolved in 90 mL N$_2$N-dimethylformamide (DMF). The obtained solution was then transferred into nine 12 mL borosilicate vials as divided in ~10 mL portions. The tightly sealed reaction vials were transferred to a preheated oven (100°C for the Zn-based compounds, 130°C for the Co-based compounds) for crystallization in 7 d. After cooling to room temperature, the reaction mixtures were recombined, the crystals filtered off and washed three times with 20 mL DMF. The ZIFs were obtained as truncated octahedrally shaped single crystals.

Activation: The crystals were washed with dichloromethane (DCM; 3 × approx. 30 mL) and then placed in fresh DCM (approx. 100 mL) for exchanging the DMF template overnight. The exchange process was repeated two times using fresh DCM. Afterwards, the solid material was filtered off, washed again with fresh DCM (3 × approx. 30 mL) and dried under dynamic vacuum (p approx. 10$^{-4}$ kPa) at 120°C for about 20 h to obtain the desolvated materials in the form of single crystals.

| Compound      | $n_{\text{HIm}}$/mmol | $m_{\text{HIm}}$/mg | $n_{\text{Hbim}}$/mmol | $m_{\text{Hbim}}$/mg | im:bim | $x^a$ (applied) | $x^a$ (found) |
|---------------|------------------------|---------------------|-------------------------|-----------------------|--------|----------------|---------------|
| ZIF-62(Zn)-bim$_{0.35}$ | 11.55                  | 786                 | 1.66                    | 196                   | 7:1    | 0.25          | 0.35          |
| ZIF-62(Zn)-bim$_{0.30}$ | 11.88                  | 808                 | 1.32                    | 156                   | 9:1    | 0.20          | 0.30          |
| ZIF-62(Zn)-bim$_{0.25}$ | 12.14                  | 826                 | 1.06                    | 125                   | 11.5:1 | 0.16          | 0.25          |
| ZIF-62(Zn)-bim$_{0.17}$ | 12.70                  | 865                 | 0.500                   | 60                    | 28:1   | 0.069         | 0.17          |
| ZIF-62(Zn)-bim$_{0.05}$ | 13.09                  | 891                 | 0.104                   | 12                    | 126:1  | 0.016         | 0.05          |
| ZIF-62(Zn)-bim$_{0.02}$ | 13.14                  | 894                 | 0.063                   | 7                     | 210:1  | 0.009         | 0.02          |
| ZIF-62(Co)-bim$_{0.37}$ | 11.55                  | 786                 | 1.66                    | 196                   | 7:1    | 0.25          | 0.37          |
| ZIF-62(Co)-bim$_{0.27}$ | 12.14                  | 827                 | 1.056                   | 125                   | 11.5:1 | 0.16          | 0.27          |

$^a x = 2·c(\text{bim})/(c(\text{im}) + c(\text{bim}))$; c = molar concentration in the synthesis solution or the solid.

Single crystal X-ray diffraction (SCXRD) data of activated (guest-free) ZIF crystals were collected on a Bruker D8 Venture diffractometer using either MoK$_{\alpha}$ or CuK$_{\alpha}$ radiation. The Oxford cryostream of N$_2$ was used for cooling down the measurement temperature to 100 K. Data collection, integration and reduction was performed with the APEX3 software package. Structure solution and refinement were conducted with the Olex2\cite{3} interface using SHELXS and SHELXL\cite{4}. Crystallographic information files for the SCXRD structures can be obtained under CCDC deposition numbers 2130178-2130185.

High pressure PXRD (HP-PXRD) was performed at beamline I15 of Diamond Light Source (Oxon., UK, experiment number CY21603-2) using a monochromatic X-ray beam ($\lambda = 0.4246$ Å) and a 2D Perkin Elmer area detector. Finely ground powders were filled into soft plastic capillaries (1.8 mm of inner diameter) evenly mixed with silicone oil AP-100 as non-penetrating pressure transmitting medium (PTM). We used a hydraulic high pressure cell\cite{5,6}, the capillaries were sealed with the adhesive epoxy paste (Araldite-2014-
1) and loaded into a sample carrier with an arch-shaped open head and insert into a metal block chamber which was subsequently filled with water to transmit the hydrostatic pressure. HP-PXRD was then performed through two diamond windows of the metal block unit along the beam direction, with adjusting the water pressure in situ (see reference [6] for more details). The overall pressure range for the HP-PXRD is from ambient to 4000 bar (= 0.4 GPa), while the pressure step size varied with smaller step sizes around the phase transitions (100 bar in the pressure range from ambient to 2000 bar and 250 bar in the pressure range from 2000 to 4000 bar). The detailed pressure steps applied in this study can be seen in the stacked diffraction patterns (Section 9).

Variable temperature PXRD (VT-PXRD) was performed at beamline P02.1 of PETRA III in DESY (Deutsches Elektronen-Synchrotron, Hamburg, Germany, project number I-20170615) with a monochromatic X-ray incident beam (\(\lambda = 0.2073\) Å) and using a Perkin Elmer XRD1621 (2048 x 2048 pixels active area) detector. The finely ground powder was filled into quartz capillaries (0.6 mm inner diameter) and cooled from 300 K to 100 K using an Oxford Cryostream. The measuring temperatures were indicated by the internal thermocouple of the cryosystem.

**PXRD data treatment and analysis:** Diffraction patterns were obtained via radial integration of the 2D detector images by the software DAWN[7]. Subsequent profile refinements (Le Bail method[8]) were performed with Jana2006[9] software, and structural refinement (Rietveld method[10,11]) were performed with the TOPAS academic V6 software[12]. The profile refinements were conducted from ambient to higher pressures in the op range, while the refinements of cp ranges were conducted with the opposite direction from high to low pressures. For the dual-phase range (coexistence of op and cp phase), the refinements were conducted from low to high pressures again. The specific pressure ranges for refinements are given in the tables in Section 10 of the Supplementary Information. Further details on the Rietveld refinements can be found in Section 13.

**Infrared (IR) spectroscopy** was performed using a diamond ATR (attenuated total reflectance) unit in reflection mode on a Spectrum Two FT-IR spectrometer (\(\tilde{\nu} = 400\) cm\(^{-1}\) - 4000 cm\(^{-1}\)) from Perkin Elmer.

**\(^1\)H NMR spectroscopy** was performed on digested ZIF samples with Bruker DPX-300, DPX-500 or Agilent DD2 500 spectrometers using a solvent mixture of DMSO-\(d_6\) (0.5 mL) and DCl/D\(_2\)O (35 wt\%, < 0.1 mL). The data were processed with the ACD/Labs software. Data were referenced to the residual proton signal of DMSO and chemical shifts of \(^1\)H are given relative to tetramethylsilane.
2. Infrared spectroscopy

**Figure S1.** FT-IR spectra of desolvated ZIF samples.
3. $^1$H NMR spectroscopy

![NMR spectrum](image)

**Figure S2.** The background spectrum of $^1$H NMR of the DMSO solvent with a drop of DCl/D$_2$O, which shows a weak signal at approx. 1.25 ppm (marked with ?, cannot be identified) coming from impurities. The signals for DMSO (2.5 ppm) and D$_2$O (ca. 6 ppm) are marked with * and # respectively.
Figure S3. $^1$H NMR spectrum of a dissolved sample of ZIF-62(Zn)-bim$_{0.02}$ in DMSO-$d_6$ and DCl/D$_2$O. The top panel shows the signals in the aromatic region (from 7.5 to 10 ppm), and the bottom panel shows the full spectrum.
Figure S4. $^1$H NMR spectrum of a dissolved sample of ZIF-62(Zn)-bim$_{0.05}$ in DMSO-$d_6$ and DCl/D$_2$O. The top panel shows the signals in the aromatic region (from 7.5 to 10 ppm), and the bottom panel shows the full spectrum.
Figure S5. $^1$H NMR spectrum of a dissolved sample of ZIF-62(Zn)-bim$_{0.17}$ in DMSO-$d_6$ and DCl/D$_2$O. The top panel shows the signals in the aromatic region (from 7.5 to 10 ppm), and the bottom panel shows the full spectrum.
Figure S6. $^1$H NMR spectrum of a dissolved sample of ZIF-62(Zn)-bim$_{0.25}$ in DMSO-$d_6$ and DCI/D$_2$O. The top panel shows the signals in the aromatic region (from 7.5 to 10 ppm), and the bottom panel shows the full spectrum.
Figure S7. $^1$H NMR spectrum of a dissolved sample of ZIF-62(Zn)-bim$_{0.30}$ in DMSO-$d_6$ and DCl/D$_2$O. The top panel shows the signals in the aromatic region (from 7.5 to 10 ppm), and the bottom panel shows the full spectrum.
Figure S8. $^1$H NMR spectrum of a dissolved sample of ZIF-62(Zn)-bim$_{0.35}$ in DMSO-$d_6$ and DCI/D$_2$O. The top panel shows the signals in the aromatic region (from 7.5 to 10 ppm), and the bottom panel shows the full spectrum.
Figure S9. $^1$H NMR spectrum of a dissolved sample of ZIF-62(Co)-bim$_{0.27}$ in DMSO-$d_6$ and DCI/D$_2$O. The top panel shows the signals in the aromatic region (from 7.5 to 10 ppm), and the bottom panel shows the full spectrum.
Figure S10. $^1$H NMR spectrum of a dissolved sample of ZIF-62(Co)-bim$_{0.37}$ in DMSO-$d_6$ and DCl/D$_2$O. The top panel shows the signals in the aromatic region (from 7.5 to 10 ppm), and the bottom panel shows the full spectrum.
**H NMR analysis of sample homogeneity**

Based on the HP-PXRD data, we assume that ZIF-62(Zn)-bim0.05 is the sample displaying the most inhomogeneous linker distribution. With the aim to provide some additional information on the homogeneity of this sample, we recorded H NMR spectra of five individual ZIF-62(Zn)-bim0.05 single crystals after digestion in DCl/D2O/DMSO-d6. The sizes of the single crystals were all around 100 µm. Within the margin of error of a H NMR experiment of such highly diluted samples (i.e. only one ZIF crystal with a mass of about 10 µg diluted in 0.5 mL solvent mixture) the fraction of bim was effectively equal to x = 0.05 for each of the five single crystals (the determined values are x = 0.04, 0.06, 0.05, 0.06 and 0.06). These NMR data establish that the linker distribution is homogeneous on the length scale of the single crystals.

![Aromatic region of the H NMR spectrum of the first single crystal (SC) of ZIF-62(Zn)-bim0.05 dissolved in DMSO-d6 and DCl/D2O.](image)

**Figure S11.** Aromatic region of the H NMR spectrum of the first single crystal (SC) of ZIF-62(Zn)-bim0.05 dissolved in DMSO-d6 and DCl/D2O.
Figure S12. Aromatic region of the $^1$H NMR spectrum of the second single crystal (SC) of ZIF-62(Zn)-bim$_{0.05}$ dissolved in DMSO-$d_6$ and DCI/D$_2$O.

Figure S13. Aromatic region of the $^1$H NMR spectrum of the third single crystal (SC) of ZIF-62(Zn)-bim$_{0.05}$ dissolved in DMSO-$d_6$ and DCI/D$_2$O.
Figure S14. Aromatic region of the $^1$H NMR spectrum of the forth single crystal (SC) of ZIF-62(Zn)-bim$_{0.05}$ dissolved in DMSO-$d_6$ and DCI/D$_2$O.

Figure S15. Aromatic region of the $^1$H NMR spectrum of the fifth single crystal (SC) of ZIF-62(Zn)-bim$_{0.05}$ dissolved in DMSO-$d_6$ and DCI/D$_2$O.
4. Single crystal X-ray diffraction

| Compound          | ZIF-62(Zn)-bim0.02 | ZIF-62(Zn)-bim0.05 | ZIF-62(Zn)-bim0.17 | ZIF-62(Zn)-bim0.25 | ZIF-62(Zn)-bim0.30 | ZIF-62(Zn)-bim0.35 | ZIF-62(Co)-bim0.27 | ZIF-62(Co)-bim0.37 |
|-------------------|--------------------|--------------------|--------------------|--------------------|--------------------|--------------------|--------------------|--------------------|
| CCDC number       | 2130178            | 2130182            | 2130181            | 2130183            | 2130179            | 2130180            | 2130185            | 2130184            |
| Empirical formula | C$_{6}$H$_{6}$Co$_{4}$N$_{2}$Zn | C$_{6}$H$_{6}$Co$_{4}$N$_{2}$Zn | C$_{6}$H$_{6}$Co$_{4}$N$_{2}$Zn | C$_{6}$H$_{6}$Co$_{4}$N$_{2}$Zn | C$_{6}$H$_{6}$Co$_{4}$N$_{2}$Zn | C$_{6}$H$_{6}$Co$_{4}$N$_{2}$Zn | C$_{6}$H$_{6}$Co$_{4}$N$_{2}$Zn | C$_{6}$H$_{6}$Co$_{4}$N$_{2}$Zn |
| Formulas weight   | 200.38             | 201.88             | 207.88             | 211.88             | 214.38             | 216.88             | 211.05             | 216.05             |
| Temperature / K   | 100.00             | 100.00             | 100.00             | 100.00             | 100.00             | 101.29             | 100.00             | 100.00             |
| Crystal system    | orthorhombic       | orthorhombic       | orthorhombic       | orthorhombic       | orthorhombic       | orthorhombic       | orthorhombic       | orthorhombic       |
| Space group       | Pbca               | Pbca               | Pbca               | Pbca               | Pbca               | Pbca               | Pbca               | Pbca               |
| $a$ / Å           | 15.2978(7)         | 15.3192(7)         | 15.3148(7)         | 15.3406(6)         | 15.3469(8)         | 15.4165(10)        | 15.2865(12)        | 15.3237(18)        |
| $b$ / Å           | 15.2347(6)         | 15.2274(6)         | 15.2179(7)         | 15.2685(6)         | 15.5456(8)         | 15.4511(10)        | 15.1940(13)        | 15.5154(19)        |
| $c$ / Å           | 18.2360(8)         | 18.2218(7)         | 17.9437(8)         | 17.9129(6)         | 18.1763(10)        | 17.9896(11)        | 17.6340(15)        | 17.955(2)          |
| $\alpha$ / $^\circ$ | 90                 | 90                 | 90                 | 90                 | 90                 | 90                 | 90                 | 90                 |
| $\beta$ / $^\circ$ | 90                 | 90                 | 90                 | 90                 | 90                 | 90                 | 90                 | 90                 |
| $\gamma$ / $^\circ$ | 90                 | 90                 | 90                 | 90                 | 90                 | 90                 | 90                 | 90                 |
| Volume / Å$^3$    | 4250.0(3)          | 4250.6(3)          | 4189.9(3)          | 4195.7(3)          | 4336.4(4)          | 4285.2(5)          | 4095.7(6)          | 4268.9(9)          |
| $Z$               | 16                 | 16                 | 16                 | 16                 | 16                 | 16                 | 16                 | 16                 |
| $\rho_{calc}$ g/cm$^3$ | 1.260             | 1.278             | 1.377             | 1.343             | 1.406             | 1.454             | 1.434             | 1.432             |
| $\mu$ / mm$^{-1}$ | 2.264             | 2.264             | 2.930             | 2.904             | 2.228             | 2.904             | 1.636             | 1.573             |
| $F(000)$          | 1617.0             | 1642.0             | 1671.0             | 1704.0             | 1850.0             | 1891.0             | 1784.0             | 1860.0             |
| Crystal size / mm$^3$ | 0.215 × 0.156 × 0.115 | 0.215 × 0.156 × 0.105 × 0.083 × 0.094 + 0.094 × 0.365 + 0.211 × 0.315 + 0.211 × 0.232 + 0.121 × 0.213 + 0.198 × 0.175 |
| Crystal radiation | MoKα (λ = 0.71073) | MoKα (λ = 0.71073) | CuKα (λ = 0.71073) | CuKα (λ = 0.71073) | MoKα (λ = 0.71073) | MoKα (λ = 0.71073) | MoKα (λ = 0.71073) | MoKα (λ = 0.71073) |
| 2θ range for data collection / $^\circ$ | 5.326 to 51.104 | 5.318 to 61.484 | 9.562 to 148.264 | 9.548 to 133.266 | 5.24 to 50.46 | 9.478 to 118.052 | 5.33 to 50.52 | 5.252 to 48.058 |
| Index ranges     | s ≤ k ≤ 20, s ≤ 18 | s ≤ k ≤ 22, s ≤ 22 | -18 ≤ s ≤ 18, -18 | -18 ≤ s ≤ 18, -18 | -18 ≤ s ≤ 18, -18 | -17 ≤ s ≤ 16, -17 | -17 ≤ s ≤ 16, -17 | -17 ≤ s ≤ 16, -17 |
| Reflections collected | 116163            | 185873             | 60009             | 55211             | 84365             | 48078             | 86936             | 49506             |
| Independent reflections | 0.0712, R$_{int}^*$ | 0.0468, R$_{int}^*$ | 0.0599, R$_{int}^*$ | 0.0788, R$_{int}^*$ | 0.0433, R$_{int}^*$ | 0.0525, R$_{int}^*$ | 0.0504, R$_{int}^*$ | 0.0652, R$_{int}^*$ |
| Data/restraints/parameters | 3974/180/287 | 6587/192/295 | 4192/104/293 | 3696/144/292 | 3909/299/298 | 3068/121/318 | 3695/249/298 | 3342/298/298 |
| Goodness-of-fit on $F^2$ | 1.047              | 1.086              | 1.046              | 1.055              | 1.122              | 1.116              | 1.121              | 1.163              |
| Final R indexes (I ≥ 2σ(I)) | 0.0285, wR$_{2}^*$ | 0.0272, wR$_{2}^*$ | 0.0503, wR$_{2}^*$ | 0.0545, wR$_{2}^*$ | 0.0468, wR$_{2}^*$ | 0.0597, wR$_{2}^*$ | 0.0550, wR$_{2}^*$ | 0.0721, wR$_{2}^*$ |
| Final R indexes [all data] | 0.0378, wR$_{2}^*$ | 0.0376, wR$_{2}^*$ | 0.0672, wR$_{2}^*$ | 0.0710, wR$_{2}^*$ | 0.0529, wR$_{2}^*$ | 0.0453, wR$_{2}^*$ | 0.0701, wR$_{2}^*$ | 0.1130, wR$_{2}^*$ |
| Largest diff. peak/hole / e Å$^3$ | 0.54/-0.23 | 0.52/-0.29 | 0.53/-0.25 | 0.40/-0.29 | 1.14/-0.38 | 0.38/-0.26 | 0.52/-0.47 | 0.61/-0.43 |
Table S2. Occupancies of bim\textsuperscript{−} on the two crystallographically independent positions im1 and im2 determined by single crystal diffraction

| Position | ZIF-62(Zn)-bim\textsubscript{x} | ZIF-62(Co)-bim\textsubscript{x} |
|----------|---------------------------------|---------------------------------|
|          | 0.02 0.05 0.17 0.25 0.30 0.35 0.27 0.37 | 0.02 0.05 0.17 0.25 0.30 0.35 0.27 0.37 |
| 1        | 0.04 (fixed) 0.05 (fixed) 0.104(2) 0.173(2) 0.396(3) 0.355(2) 0.120(2) 0.361(3) | 0.04 (fixed) 0.05 (fixed) 0.104(2) 0.173(2) 0.396(3) 0.355(2) 0.120(2) 0.361(3) |
| 2        | - 0.05 (fixed) 0.236(2) 0.327(2) 0.204(3) 0.345(2) 0.420(2) 0.379(3) | - 0.05 (fixed) 0.236(2) 0.327(2) 0.204(3) 0.345(2) 0.420(2) 0.379(3) |
5. Variable temperature PXRD

**Figure S16.** Stacked VT-PXRD patterns for ZIF-4(Zn) collected during cooling down from 300 K to 100 K with 10 K per step and a subsequent return to 300 K.

**Figure S17.** Stacked VT-PXRD patterns for ZIF-62(Zn)-bim$_{0.02}$ collected during cooling down from 300 K to 100 K with 10 K per step and a subsequent return to 300 K.
Figure S18. Stacked VT-PXRD patterns for ZIF-62(Zn)-bim$_{0.17}$ collected during cooling down from 300 K to 100 K with 10 K per step and a subsequent return to 300 K.

Figure S19. Stacked VT-PXRD patterns for ZIF-62(Zn)-bim$_{0.35}$ collected during cooling down from 300 K to 100 K with 10 K per step and a subsequent return to 300 K.
Figure S20. Stacked VT-PXRD patterns for ZIF-62(Co)-bim$_{0.27}$ collected during cooling down from 300 K to 100 K with 10 K per step and a subsequent return to 300 K.
6. Le Bail refinements of VT-PXRD patterns

The entire sets of diffraction patterns for each ZIF-62(M)-bim$_x$ compound discussed here have been fitted according to the Le Bail method\textsuperscript{[8]}. The full crystallographic data are compiled in following Tables.

**Table S3.** Crystallographic data for \textit{ap} phase of ZIF-4(Zn) determined via profile refinement of the VT-PXRD data collected in the range from 140 to 300 K. All the phases maintain the orthorhombic crystal system with \textit{Pbca} symmetry.

| Temperature / K | $a$ / Å | $b$ / Å | $c$ / Å | $V$ / Å$^3$ | $R_{wp}$/ % | $R_p$/ % | $\chi$ |
|-----------------|--------|--------|--------|----------|----------|----------|-----|
| 140             | 15.3416(6) | 15.2700(6) | 18.2041(6) | 4264.59(19) | 0.75 | 0.49 | 0.23 |
| 150             | 15.3698(6) | 15.2933(5) | 18.2048(6) | 4279.11(19) | 0.72 | 0.48 | 0.22 |
| 160             | 15.3957(6) | 15.3086(6) | 18.2041(6) | 4290.47(19) | 0.71 | 0.47 | 0.22 |
| 170             | 15.4167(6) | 15.3369(5) | 18.2009(6) | 4303.50(19) | 0.72 | 0.48 | 0.22 |
| 180             | 15.4278(4) | 15.3709(5) | 18.1980(4) | 4315.46(15) | 0.64 | 0.45 | 0.20 |
| 190             | 15.4444(3) | 15.3986(3) | 18.1873(2) | 4325.35(7)  | 0.53 | 0.37 | 0.16 |
| 200             | 15.4539(2) | 15.4147(2) | 18.17574(19)| 4329.79(6)  | 0.62 | 0.43 | 0.19 |
| 210             | 15.4650(3) | 15.4284(2) | 18.16391(19)| 4333.92(6)  | 0.63 | 0.43 | 0.19 |
| 220             | 15.4753(3) | 15.4413(3) | 18.15262(19)| 4337.74(6)  | 0.62 | 0.43 | 0.19 |
| 230             | 15.4831(3) | 15.4532(3) | 18.14161(19)| 4340.63(6)  | 0.61 | 0.43 | 0.19 |
| 240             | 15.4884(3) | 15.4677(3) | 18.1283(2)  | 4342.98(6)  | 0.64 | 0.44 | 0.20 |
| 250             | 15.4937(3) | 15.4778(4) | 18.1188(2)  | 4345.06(7)  | 0.65 | 0.45 | 0.20 |
| 260             | 15.4964(4) | 15.4892(4) | 18.1093(2)  | 4346.73(6)  | 0.64 | 0.44 | 0.20 |
| 270             | 15.4986(4) | 15.5031(4) | 18.0995(2)  | 4348.88(6)  | 0.64 | 0.44 | 0.20 |
| 280             | 15.5002(4) | 15.5144(4) | 18.0917(2)  | 4350.61(6)  | 0.61 | 0.43 | 0.19 |
| 290             | 15.5005(4) | 15.5262(3) | 18.0839(2)  | 4352.16(7)  | 0.67 | 0.45 | 0.21 |
| 300             | 15.5042(3) | 15.5324(3) | 18.0758(2)  | 4352.96(6)  | 0.62 | 0.43 | 0.19 |
Table S4. Crystallographic data for op phase of ZIF-62(Zn)-bim_{0.02} determined via profile refinement of the VT-PXRD data collected in the range from 110 to 300 K. All the phases maintain the orthorhombic crystal system with Pbcn symmetry.

| Temperature / K | a / Å     | b / Å     | c / Å     | V / Å³   | Rwp / % | Rp / % | χ          |
|-----------------|-----------|-----------|-----------|----------|---------|--------|-------------|
| 110             | 15.1622(8)| 15.2415(7)| 18.2112(8)| 4208.5(3)| 0.85    | 0.51   | 0.26        |
| 120             | 15.2467(8)| 15.2842(9)| 18.2486(7)| 4252.5(2)| 0.88    | 0.54   | 0.27        |
| 130             | 15.2777(7)| 15.3157(8)| 18.2506(7)| 4270.4(2)| 0.86    | 0.53   | 0.26        |
| 140             | 15.2995(6)| 15.3335(6)| 18.2488(6)| 4281.07(19)| 0.79 | 0.51 | 0.24        |
| 150             | 15.3174(4)| 15.3506(5)| 18.2390(5)| 4288.56(14)| 0.65 | 0.43 | 0.20        |
| 160             | 15.3343(4)| 15.3723(4)| 18.2274(5)| 4296.62(13)| 0.60 | 0.39 | 0.18        |
| 170             | 15.3516(4)| 15.3864(5)| 18.2146(5)| 4302.38(13)| 0.59 | 0.38 | 0.18        |
| 180             | 15.3684(4)| 15.3994(5)| 18.2011(4)| 4307.54(13)| 0.57 | 0.38 | 0.17        |
| 190             | 15.3846(5)| 15.4105(5)| 18.1862(4)| 4311.68(12)| 0.54 | 0.37 | 0.16        |
| 200             | 15.3993(5)| 15.4209(5)| 18.1735(4)| 4315.68(11)| 0.50 | 0.35 | 0.15        |
| 210             | 15.4108(5)| 15.4339(5)| 18.1637(4)| 4320.21(12)| 0.50 | 0.35 | 0.15        |
| 220             | 15.4209(5)| 15.4458(5)| 18.1525(3)| 4323.70(11)| 0.48 | 0.33 | 0.15        |
| 230             | 15.4341(5)| 15.4527(5)| 18.1406(3)| 4326.51(10)| 0.42 | 0.31 | 0.13        |
| 240             | 15.4426(4)| 15.4644(4)| 18.1305(3)| 4329.77(9)| 0.41 | 0.30 | 0.13        |
| 250             | 15.4536(5)| 15.4712(4)| 18.1213(3)| 4332.57(9)| 0.38 | 0.29 | 0.12        |
| 260             | 15.4608(4)| 15.4816(4)| 18.1129(3)| 4335.46(9)| 0.38 | 0.28 | 0.12        |
| 270             | 15.4724(4)| 15.5001(4)| 18.0980(3)| 4340.32(9)| 0.38 | 0.28 | 0.12        |
| 280             | 15.4759(4)| 15.5098(4)| 18.0909(3)| 4342.33(9)| 0.38 | 0.27 | 0.12        |
| 290             | 15.4789(4)| 15.5185(4)| 18.0847(3)| 4344.11(9)| 0.39 | 0.28 | 0.12        |
| 300             | 15.4816(4)| 15.5272(4)| 18.0786(3)| 4345.84(8)| 0.37 | 0.27 | 0.11        |
Table S5. Crystallographic data for op phase of ZIF-62(Zn)-bim0.17 determined via profile refinement of the VT-PXRD data collected in the range from 100 to 300 K. All the phases maintain the orthorhombic crystal system with \( \text{Pbca} \) symmetry.

| Temperature / K | \( a / \AA \)       | \( b / \AA \)       | \( c / \AA \)       | \( V / \AA^3 \)       | \( R_{wp} / \% \)  | \( R_p / \% \)  | \( \chi \) |
|----------------|---------------------|---------------------|---------------------|-----------------------|---------------------|---------------------|-------|
| 100            | 15.2385(4)          | 15.3011(4)          | 18.1313(5)          | 4227.60(17)           | 0.88                | 0.56                | 0.26              |
| 110            | 15.2611(4)          | 15.3217(4)          | 18.1185(4)          | 4236.58(14)           | 0.77                | 0.53                | 0.23              |
| 120            | 15.2955(4)          | 15.3470(4)          | 18.1249(4)          | 4254.65(14)           | 0.77                | 0.52                | 0.23              |
| 130            | 15.3297(4)          | 15.3740(4)          | 18.1363(4)          | 4274.35(14)           | 0.79                | 0.53                | 0.23              |
| 140            | 15.3581(4)          | 15.3940(4)          | 18.1436(4)          | 4289.57(14)           | 0.80                | 0.54                | 0.24              |
| 150            | 15.3751(4)          | 15.4120(4)          | 18.1425(4)          | 4299.09(14)           | 0.76                | 0.51                | 0.23              |
| 160            | 15.3905(5)          | 15.4232(5)          | 18.1372(4)          | 4305.27(14)           | 0.73                | 0.50                | 0.22              |
| 170            | 15.4040(5)          | 15.4321(5)          | 18.1326(4)          | 4310.40(13)           | 0.70                | 0.49                | 0.21              |
| 180            | 15.4113(4)          | 15.4456(4)          | 18.1237(3)          | 4314.11(12)           | 0.65                | 0.46                | 0.19              |
| 190            | 15.4198(4)          | 15.4577(4)          | 18.1174(4)          | 4318.36(12)           | 0.64                | 0.46                | 0.19              |
| 200            | 15.4285(4)          | 15.4658(4)          | 18.1104(3)          | 4321.39(11)           | 0.59                | 0.43                | 0.18              |
| 210            | 15.4386(4)          | 15.4726(4)          | 18.1036(3)          | 4324.49(11)           | 0.59                | 0.43                | 0.18              |
| 220            | 15.4455(5)          | 15.4812(4)          | 18.0997(4)          | 4327.91(11)           | 0.59                | 0.43                | 0.18              |
| 230            | 15.4517(4)          | 15.4890(4)          | 18.0908(3)          | 4329.70(10)           | 0.55                | 0.42                | 0.16              |
| 240            | 15.4578(4)          | 15.4992(4)          | 18.0843(3)          | 4332.70(10)           | 0.54                | 0.40                | 0.16              |
| 250            | 15.4667(4)          | 15.5062(4)          | 18.0796(3)          | 4336.01(9)            | 0.52                | 0.39                | 0.15              |
| 260            | 15.4675(4)          | 15.5155(4)          | 18.0776(4)          | 4338.35(10)           | 0.58                | 0.40                | 0.17              |
| 270            | 15.4711(4)          | 15.5227(4)          | 18.0728(3)          | 4340.24(9)            | 0.51                | 0.38                | 0.15              |
| 280            | 15.4738(4)          | 15.5303(4)          | 18.0661(3)          | 4341.50(10)           | 0.51                | 0.38                | 0.15              |
| 290            | 15.4774(3)          | 15.5366(3)          | 18.0621(3)          | 4343.31(9)            | 0.48                | 0.36                | 0.14              |
| 300            | 15.4792(3)          | 15.5436(3)          | 18.0585(3)          | 4344.91(9)            | 0.50                | 0.37                | 0.15              |
Table S6. Crystallographic data for op phase of ZIF-62(Zn)-bim_0.35 determined via profile refinement of the VT-PXRD data collected in the range from 100 to 300 K. All the phases maintain the orthorhombic crystal system with Pbca symmetry.

| Temperature / K | a / Å     | b / Å     | c / Å     | V / Å³   | $R_{wp}$ / % | $R_p$ / % | χ  |
|-----------------|-----------|-----------|-----------|----------|--------------|-----------|-----|
| 100             | 15.4514(5)| 15.6497(4)| 18.1790(4)| 4395.87(13)| 0.99         | 0.63      | 0.31|
| 110             | 15.4503(5)| 15.6645(4)| 18.1729(4)| 4398.20(14)| 1.06         | 0.65      | 0.33|
| 120             | 15.4579(5)| 15.6724(4)| 18.1690(4)| 4401.65(14)| 1.05         | 0.64      | 0.33|
| 130             | 15.4645(5)| 15.6769(4)| 18.1698(4)| 4405.00(13)| 1.02         | 0.63      | 0.32|
| 140             | 15.4732(3)| 15.6908(3)| 18.1705(3)| 4411.56(10)| 0.74         | 0.49      | 0.23|
| 150             | 15.4771(3)| 15.7006(3)| 18.1696(3)| 4415.19(9)| 0.74         | 0.48      | 0.23|
| 160             | 15.4801(3)| 15.7097(3)| 18.1698(2)| 4418.68(9)| 0.70         | 0.46      | 0.22|
| 170             | 15.4822(3)| 15.7179(3)| 18.1699(2)| 4421.60(9)| 0.69         | 0.46      | 0.22|
| 180             | 15.4839(3)| 15.7273(2)| 18.1701(2)| 4424.76(8)| 0.65         | 0.44      | 0.20|
| 190             | 15.4855(3)| 15.7350(2)| 18.1694(2)| 4427.22(8)| 0.65         | 0.44      | 0.20|
| 200             | 15.4881(3)| 15.7452(2)| 18.1700(2)| 4431.00(8)| 0.64         | 0.43      | 0.20|
| 210             | 15.4887(3)| 15.7518(2)| 18.1691(2)| 4432.83(8)| 0.62         | 0.43      | 0.19|
| 220             | 15.4904(3)| 15.7598(2)| 18.1677(2)| 4435.20(7)| 0.60         | 0.42      | 0.18|
| 230             | 15.4921(3)| 15.7674(2)| 18.1662(2)| 4437.49(7)| 0.59         | 0.42      | 0.18|
| 240             | 15.4932(3)| 15.7738(2)| 18.1654(2)| 4439.38(7)| 0.57         | 0.41      | 0.18|
| 250             | 15.4951(3)| 15.7814(2)| 18.1647(2)| 4441.89(7)| 0.58         | 0.41      | 0.18|
| 260             | 15.4958(3)| 15.7880(2)| 18.1632(2)| 4443.60(7)| 0.60         | 0.42      | 0.19|
| 270             | 15.4964(3)| 15.7954(2)| 18.1626(2)| 4445.72(7)| 0.57         | 0.40      | 0.18|
| 280             | 15.4980(3)| 15.8033(2)| 18.1624(2)| 4448.33(7)| 0.56         | 0.40      | 0.17|
| 290             | 15.4983(3)| 15.8105(2)| 18.1622(2)| 4450.40(7)| 0.56         | 0.40      | 0.17|
| 300             | 15.4991(3)| 15.8173(2)| 18.1620(2)| 4452.50(7)| 0.57         | 0.39      | 0.18|
**Table S7.** Crystallographic data for *op* phase of ZIF-62(Co)-bim0.27 determined via profile refinement of the VT-PXRD data collected in the range from 100 to 300 K. All the phases maintain the orthorhombic crystal system with *Pbca* symmetry.

| Temperature / K | a / Å  | b / Å  | c / Å  | V / Å³  | \(R_{wp}\) / % | \(R_p\) / % | \(\chi\) |
|----------------|-------|--------|--------|---------|---------------|-------------|--------|
| 100            | 15.4514(5) | 15.6497(4) | 18.1790(4) | 4395.87(13) | 0.99          | 0.63        | 0.31    |
| 110            | 15.4503(5) | 15.6645(4) | 18.1729(4) | 4398.20(14) | 1.06          | 0.65        | 0.33    |
| 120            | 15.4579(5) | 15.6724(4) | 18.1690(4) | 4401.65(14) | 1.05          | 0.64        | 0.33    |
| 130            | 15.4645(5) | 15.6769(4) | 18.1698(4) | 4405.00(13) | 1.02          | 0.63        | 0.32    |
| 140            | 15.4732(3) | 15.6908(3) | 18.1705(3) | 4411.56(10) | 0.74          | 0.49        | 0.23    |
| 150            | 15.4771(3) | 15.7006(3) | 18.1696(3) | 4415.19(9)  | 0.74          | 0.48        | 0.23    |
| 160            | 15.4801(3) | 15.7097(3) | 18.1698(2) | 4418.68(9)  | 0.70          | 0.46        | 0.22    |
| 170            | 15.4822(3) | 15.7179(3) | 18.1699(2) | 4421.60(9)  | 0.69          | 0.46        | 0.22    |
| 180            | 15.4839(3) | 15.7273(2) | 18.1701(2) | 4424.76(8)  | 0.65          | 0.44        | 0.20    |
| 190            | 15.4855(3) | 15.7350(2) | 18.1694(2) | 4427.22(8)  | 0.65          | 0.44        | 0.20    |
| 200            | 15.4881(3) | 15.7452(2) | 18.1700(2) | 4431.00(8)  | 0.64          | 0.43        | 0.20    |
| 210            | 15.4887(3) | 15.7518(2) | 18.1691(2) | 4432.83(8)  | 0.62          | 0.43        | 0.19    |
| 220            | 15.4904(3) | 15.7598(2) | 18.1677(2) | 4435.20(7)  | 0.60          | 0.42        | 0.18    |
| 230            | 15.4921(3) | 15.7674(2) | 18.1662(2) | 4437.49(7)  | 0.59          | 0.42        | 0.18    |
| 240            | 15.4932(3) | 15.7738(2) | 18.1654(2) | 4439.38(7)  | 0.57          | 0.41        | 0.18    |
| 250            | 15.4951(3) | 15.7814(2) | 18.1647(2) | 4441.89(7)  | 0.58          | 0.41        | 0.18    |
| 260            | 15.4958(3) | 15.7880(2) | 18.1632(2) | 4443.60(7)  | 0.60          | 0.42        | 0.19    |
| 270            | 15.4964(3) | 15.7954(2) | 18.1626(2) | 4445.72(7)  | 0.57          | 0.40        | 0.18    |
| 280            | 15.4980(3) | 15.8033(2) | 18.1624(2) | 4448.33(7)  | 0.56          | 0.40        | 0.17    |
| 290            | 15.4983(3) | 15.8105(2) | 18.1622(2) | 4450.40(7)  | 0.56          | 0.40        | 0.17    |
| 300            | 15.4991(3) | 15.8173(2) | 18.1620(2) | 4452.50(7)  | 0.57          | 0.39        | 0.18    |
7. Thermal expansivity

The thermal expansivity ($\alpha$) as a function of temperature has been determined along each crystallographic axis in the range from 100 to 300 K (140 to 300 K for ZIF-4 and 110 to 300 K for ZIF-62(Zn)-bim$_{0.02}$). The refined lattice parameters and the unit cell volume were fitted using an $n^{th}$ order polynomial function [$y(T) = a_0 + a_1 \cdot T + \cdots + a_n \cdot T^n$] or an exponential function [$y(T) = y_0 + A \cdot e^{b \cdot T}$] as suitable (where $y(T)$ is the lattice parameter or the unit cell volume at the temperature $T$; all other variables are fitting parameters)\textsuperscript{13}. The expansivity $\alpha_y(T)$ is derived from the numerically calculated derivative of the respective fitting function $y(T)$ according to the following function:

$$\alpha_y(T) = \frac{dy}{y \cdot dT}$$
Figure S21. Empirical fits to lattice parameter of ZIF-4(Zn) as a function of temperature.

Figure S22. Expansibility of ZIF-4(Zn) as a function of temperature determined by empirical fits to the lattice parameters.
Figure S23. Empirical fits to lattice parameter of ZIF-62(Zn)-bim0.02 as a function of temperature.

Figure S24. Expansibility of ZIF-62(Zn)-bim0.02 as a function of temperature determined by empirical fits to the lattice parameters.
Figure S25. Empirical fits to lattice parameter of ZIF-62(Zn)-bim$_{0.17}$ as a function of temperature.

Figure S26. Expansibility of ZIF-62(Zn)-bim$_{0.17}$ as a function of temperature determined by empirical fits to the lattice parameters.
Figure S27. Empirical fits to lattice parameter of ZIF-62(Zn)-bim0.35 as a function of temperature.

Figure S28. Expansibility of ZIF-62(Zn)-bim0.35 as a function of temperature determined by empirical fits to the lattice parameters.
Figure S29. Empirical fits to lattice parameter of ZIF-62(Co)-bim$_{0.27}$ as a function of temperature.

Figure S30. Expansibility of ZIF-62(Co)-bim$_{0.27}$ as a function of temperature determined by empirical fits to the lattice parameters.
8. Contour maps of the HP-PXRD data of the ZIF-62(Co)-bim$_x$ samples

**Figure S31.** Contour map of the HP-PXRD data of ZIF-62(Co)-bim$_{0.27}$ and ZIF-62(Co)-bim$_{0.37}$. The lower signal-to-noise ratio of ZIF-62(Co)-bim$_{0.37}$ compared to ZIF-62(Co)-bim$_{0.27}$ is due to a lower packing density of the ZIF crystallites in the case of ZIF-62(Co)-bim$_{0.37}$. However, this fact does not compromise the validity of the data analysis. Each map is generated from 29 PXRD patterns recorded at pressure points between 1 bar and 4000 bar (see main text for the pressure step sizes).
9. Stack plots of the HP-PXRD data

Figure S32. Stacked HP-PXRD patterns for ZIF-62(Zn)-bim$_0$0.02 collected during pressure increase from 1 bar to 4000 bar followed by pressure release to 1 bar. The reflections of op and cp phases are present in parallel from 700 to 1400 bar. In the pressure range from 700 to 900 bar the patterns were refined using a dual phase model containing both phases, op and cp. From 1000 to 1400 bar, the intensity of the reflections of the op phase is already too weak, so that the op phase was not included in the profile fits. The dashed lines mark the positions of selected reflections of the op phase at 1 bar.

Figure S33. Stacked HP-PXRD patterns for ZIF-62(Zn)-bim$_0$0.05 collected during pressure increase from 1 bar to 4000 bar followed by pressure release to 1 bar and subsequent pressure jump experiments with two times cycling between 1 bar and 4000 bar. The reflections of op and cp phases are present in parallel from 700 to 1800 bar. In the pressure range from 700 to 1000 bar the patterns were refined using a dual phase model containing both phases, op and cp. From 1100 to 1800 bar, the intensity of the reflections of the op phase is already too weak, so that the op phase was not included in the profile fits. The dashed lines mark the positions of selected reflections of the op phase at 1 bar.
Figure S34. Stacked HP-PXRD patterns for ZIF-62(Zn)-bim$_{0.17}$ collected during pressure increase from 1 bar to 4000 bar followed by pressure release to 1 bar and subsequent pressure jump experiments with two times cycling between 1 bar and 4000 bar. The reflections of $op$ and $cp$ phases are present in parallel from 1100 to 1800 bar. In the pressure range from 1200 to 1400 bar the patterns were refined using a dual phase model containing both phases, $op$ and $cp$. At 1100 bar the intensity of the reflections of the $cp$ phase is too weak, so that the pattern was only refined using the $op$ phase. From 1500 to 1800 bar, the intensity of the reflections of the $op$ phase is already too weak, so that the $op$ phase was not included in the profile fits. The dashed lines mark the positions of selected reflections of the $op$ phase at 1 bar.

Figure S35. Stacked HP-PXRD patterns for ZIF-62(Zn)-bim$_{0.25}$ collected during pressure increase from 1 bar to 4000 bar followed by pressure release to 1 bar. The reflections of $op$ and $cp$ phases are present in parallel from 1200 to 1800 bar. In the pressure range from 1300 to 1700 bar the patterns were fit using a dual phase model containing both phases, $op$ and $cp$. At 1200 bar the intensity of the reflections of the $cp$ phase is too weak, so that the pattern was only refined using the $op$ phase. At 1800 bar the intensity of the reflections of the $op$ phase is too weak, so that the pattern was only refined using the $cp$ phase. The dashed lines mark the positions of selected reflections of the $op$ phase at 1 bar.
Figure S36. Stacked HP-PXRD patterns for ZIF-62(Zn)-bim$_{0.30}$ collected during pressure increase from 1 bar to 4000 bar followed by pressure release to 1 bar and subsequent pressure jump experiments with two times cycling between 1 bar and 4000 bar. The reflections of op and cp phases are present in parallel from 1300 to 1600 bar. In the pressure range from 1400 to 1500 bar the patterns were refined using a dual phase model containing both phases, op and cp. At 1300 bar the intensity of the reflections of the cp phase is too weak, so that the pattern was only refined using the op phase. At 1600 bar the intensity of the reflections of the op phase is too weak, so that the pattern was only refined using the cp phase. The dashed lines mark the positions of selected reflections of the op phase at 1 bar.

Figure S37. Stacked HP-PXRD patterns for ZIF-62(Zn)-bim$_{0.35}$ collected during pressure increase from 1 bar to 4000 bar followed by pressure release to 1 bar and subsequent pressure jump experiments with two times cycling between 1 bar and 4000 bar. The transition from op to cp is continuous here so that only a single phase could be fitted to each of the PXRD patterns. The dashed lines mark the positions of selected reflections of the op phase at 1 bar.
Figure S38. Stacked HP-PXRD patterns for ZIF-62(Co)-bim$_{0.27}$ collected during pressure increase from 1 bar to 4000 bar followed by pressure release to 1 bar and subsequent pressure jump experiments with two times cycling between 1 bar and 4000 bar. The reflections of op and cp phases are present in parallel from 1600 to 2000 bar. At 1600 bar the intensity of the reflections of the cp phase is too weak, so that the pattern was only refined using the op phase. From 1700 to 2000 bar the intensity of the reflections of the op phase is too weak, so that the pattern was only refined using the cp phase. The dashed lines mark the positions of selected reflections of the op phase at 1 bar.

Figure S39. Stacked HP-PXRD patterns for ZIF-62(Co)-bim$_{0.37}$ collected during pressure increase from 1 bar to 4000 bar followed by pressure release to 1 bar and a subsequent pressure jump experiment cycling between 1 bar and 4000 bar. The transition from op to cp is continuous here so that only a single phase could be fitted to each of the PXRD patterns. The dashed lines mark the positions of selected reflections of the op phase at 1 bar.
Figure S40. Overlays of normalized PXRD patterns of ZIF-62(Zn)-bim0.35 recorded at 1 bar (left) and at 4000 bar (right) while cycling between these two pressures. The peak widths do not change during cycling, which indicates that the pressure-induced reversible macro-strain (materials compression and phase transformation) is not accompanied by irreversible formation of micro-strain upon pressure cycling.
10. Le Bail refinements of HP-PXRD patterns

The entire sets of diffraction patterns for each ZIF-62(M)-bim$_{x}$ compound discussed here have been fitted according to the Le Bail method$^8$. Profile fits for selected patterns of each material are shown below for reference. The full crystallographic data are compiled in Tables S8 to S15.

10.1. ZIF-62(Zn)-bim$_{0.02}$

![Profile refinement (Le Bail method) of the PXRD pattern of ZIF-62(Zn)-bim$_{0.02}$ at ambient pressure.](image1)

**Figure S41.** Profile refinement (Le Bail method) of the PXRD pattern of ZIF-62(Zn)-bim$_{0.02}$ at ambient pressure.

![Dual-phase profile refinement (Le Bail method) of the PXRD pattern of ZIF-62(Zn)-bim$_{0.02}$ at 700 bar.](image2)

**Figure S42.** Dual-phase profile refinement (Le Bail method) of the PXRD pattern of ZIF-62(Zn)-bim$_{0.02}$ at 700 bar.
Figure S43. Profile refinement (Le Bail method) of the PXRD pattern of ZIF-62(Zn)-bim$_{0.02}$ at 4000 bar.

Figure S44. Relative changes of lattice parameters of ZIF-62(Zn)-bim$_{0.02}$ determined via profile refinement of the HP-PXRD data collected in the range from 1 to 4000 bar. The dual phase fits have been performed from 700 to 900 bar.
Table S8. Crystallographic data for ZIF-62(Zn)-bim$_{0.02}$ determined via profile refinement of the HP-PXRD data collected in the range from 1 to 4000 bar. All the phases maintain the orthorhombic crystal system with Pbca symmetry.

| Pressure / bar | Phase | $a / \text{Å}$ | $b / \text{Å}$ | $c / \text{Å}$ | $V / \text{Å}^3$ | $R_{wp} / \%$ | $R_p / \%$ | $\chi$ |
|---------------|-------|----------------|----------------|----------------|----------------|----------------|----------------|-------|
| 1             | $op$  | 15.4585(6)     | 15.5083(7)     | 18.0653(6)     | 4329.6(3)      | 0.70           | 0.45           | 0.19  |
| 100           | $op$  | 15.4380(7)     | 15.4756(7)     | 18.0467(6)     | 4311.6(3)      | 0.72           | 0.45           | 0.20  |
| 200           | $op$  | 15.4036(10)    | 15.4469(8)     | 18.0317(8)     | 4290.4(4)      | 0.94           | 0.56           | 0.26  |
| 300           | $op$  | 15.3708(7)     | 15.4253(6)     | 18.0072(7)     | 4269.5(3)      | 0.84           | 0.52           | 0.23  |
| 400           | $op$  | 15.3466(8)     | 15.3980(7)     | 17.9957(7)     | 4252.5(4)      | 0.90           | 0.56           | 0.24  |
| 500           | $op$  | 15.3141(7)     | 15.3650(7)     | 17.9693(7)     | 4228.2(3)      | 0.97           | 0.60           | 0.26  |
| 600           | $op$  | 15.2769(8)     | 15.3364(8)     | 17.9450(7)     | 4204.4(4)      | 0.99           | 0.60           | 0.27  |
| 700           | $op$  | 15.2500(15)    | 15.2854(15)    | 17.9327(13)    | 4180.26(4)     | 1.42           | 0.79           | 0.39  |
| 700           | $cp$  | 14.3141(12)    | 14.4287(9)     | 16.6557(10)    | 3440.0(5)      | 1.42           | 0.79           | 0.39  |
| 800           | $op$  | 15.1790(8)     | 15.2789(9)     | 17.9011(11)    | 4151.6(4)      | 0.92           | 0.50           | 0.25  |
| 800           | $cp$  | 14.3111(8)     | 14.4300(6)     | 16.6160(7)     | 3431.3(4)      | 0.92           | 0.50           | 0.25  |
| 900           | $op$  | 15.1667(7)     | 15.2770(13)    | 17.8959(15)    | 4146.5(5)      | 1.18           | 0.60           | 0.32  |
| 900           | $cp$  | 14.3019(9)     | 14.4314(8)     | 16.5883(9)     | 3423.8(4)      | 1.18           | 0.60           | 0.32  |
| 1000          | $cp$  | 14.3290(8)     | 14.4348(8)     | 16.5681(10)    | 3426.9(8)      | 1.28           | 0.62           | 0.35  |
| 1100          | $cp$  | 14.3345(7)     | 14.4442(9)     | 16.5569(10)    | 3428.1(3)      | 1.32           | 0.66           | 0.36  |
| 1200          | $cp$  | 15.16678(8)    | 15.2769(7)     | 17.8959(4)     | 4146.5(7)      | 1.17           | 0.63           | 0.32  |
| 1300          | $cp$  | 14.3166(6)     | 14.4334(7)     | 16.5480(9)     | 3419.4(4)      | 2.56           | 1.52           | 0.70  |
| 1400          | $cp$  | 14.2887(15)    | 14.4143(13)    | 16.4882(2)     | 3395.8(8)      | 2.44           | 1.45           | 0.66  |
| 1500          | $cp$  | 14.2837(13)    | 14.4150(12)    | 16.4698(18)    | 3391.1(7)      | 2.45           | 1.52           | 0.66  |
| 1600          | $cp$  | 14.2716(12)    | 14.4108(12)    | 16.4402(17)    | 3381.2(7)      | 2.26           | 1.42           | 0.61  |
| 1700          | $cp$  | 14.2644(12)    | 14.4155(11)    | 16.4320(16)    | 3378.9(7)      | 2.17           | 1.37           | 0.58  |
| 1800          | $cp$  | 14.2556(11)    | 14.4126(11)    | 16.4208(17)    | 3373.8(6)      | 2.08           | 1.34           | 0.56  |
| 1900          | $cp$  | 14.2510(10)    | 14.4072(10)    | 16.4027(16)    | 3367.8(6)      | 2.25           | 1.43           | 0.61  |
| 2000          | $cp$  | 14.2466(12)    | 14.4062(11)    | 16.3772(18)    | 3361.3(7)      | 2.23           | 1.42           | 0.60  |
| 2250          | $cp$  | 14.2375(12)    | 14.4023(11)    | 16.3626(18)    | 3355.2(7)      | 2.15           | 1.35           | 0.58  |
| 2500          | $cp$  | 14.2081(12)    | 14.3970(11)    | 16.2963(17)    | 3333.5(7)      | 2.13           | 1.32           | 0.58  |
| 2750          | $cp$  | 14.2033(12)    | 14.4038(11)    | 16.2495(18)    | 3324.4(7)      | 2.04           | 1.31           | 0.55  |
| 3000          | $cp$  | 14.1960(12)    | 14.3988(11)    | 16.1969(17)    | 3310.7(7)      | 1.86           | 1.15           | 0.50  |
| 3250          | $cp$  | 14.1826(12)    | 14.3897(11)    | 16.1560(16)    | 3297.2(7)      | 1.85           | 1.16           | 0.50  |
| 3500          | $cp$  | 14.1641(11)    | 14.3877(10)    | 16.1006(15)    | 3281.2(7)      | 2.02           | 1.21           | 0.54  |
| 3750          | $cp$  | 14.1601(12)    | 14.3964(11)    | 16.0685(17)    | 3275.6(7)      | 2.20           | 1.25           | 0.59  |
| 4000          | $cp$  | 14.1496(13)    | 14.4029(12)    | 15.9990(19)    | 3260.5(8)      | 2.30           | 1.33           | 0.61  |
10.2. ZIF-62(Zn)-bim$_{0.05}$

Figure S45. Profile refinement (Le Bail method) of the PXRD pattern of ZIF-62(Zn)-bim$_{0.05}$ at ambient pressure.

Figure S46. Dual-phase profile refinement (Le Bail method) of the PXRD pattern of ZIF-62(Zn)-bim$_{0.05}$ at 800 bar.
Figure S47. Profile refinement (Le Bail method) of the PXRD pattern of ZIF-62(Zn)-bim$_{0.05}$ at 4000 bar.

Figure S48. Relative changes of lattice parameters of ZIF-62(Zn)-bim$_{0.05}$ determined via profile refinement of the HP-PXRD data collected in the range from 1 to 4000 bar. The dual phase fits have been performed from 700 to 1000 bar.
Table S9. Crystallographic data for ZIF-62(Zn)-bim0.05 determined via profile refinement of the HP-PXRD data collected in the range from 1 to 4000 bar. All the phases maintain the orthorhombic crystal system with Pbca symmetry.

| Pressure / bar | Phase | \( a / \text{Å} \) | \( b / \text{Å} \) | \( c / \text{Å} \) | \( V / \text{Å}^3 \) | \( R_{wp} / \% \) | \( R_p / \% \) | \( \chi \) |
|---------------|-------|-----------------|-----------------|-----------------|----------------|----------------|----------------|--------|
| 1             | op    | 15.4174(6)      | 15.4821(6)      | 17.9990(7)      | 4296.3(3)      | 0.88           | 0.58           | 0.23   |
| 100           | op    | 15.3822(11)     | 15.4590(12)     | 17.9912(12)     | 4278.2(6)      | 1.54           | 0.92           | 0.41   |
| 200           | op    | 15.3298(10)     | 15.4286(10)     | 17.9442(12)     | 4244.1(6)      | 1.37           | 0.85           | 0.37   |
| 300           | op    | 15.3731(14)     | 15.4003(13)     | 17.9684(10)     | 4254.0(5)      | 1.55           | 1.03           | 0.41   |
| 400           | op    | 15.3324(14)     | 15.3645(11)     | 17.9398(9)      | 4226.2(5)      | 1.41           | 0.92           | 0.38   |
| 500           | op    | 15.2852(12)     | 15.3357(12)     | 17.9054(10)     | 4197.2(5)      | 1.44           | 0.89           | 0.39   |
| 600           | op    | 15.2850(15)     | 15.3117(15)     | 17.9060(10)     | 4190.7(5)      | 1.65           | 1.09           | 0.44   |
| 700           | op    | 15.2112(9)      | 15.2734(6)      | 17.8746(7)      | 4152.8(3)      | 0.97           | 0.64           | 0.26   |
| 800           | cp    | 14.3326(8)      | 14.4722(8)      | 16.6037(7)      | 3444.0(3)      | 0.97           | 0.64           | 0.26   |
| 900           | op    | 15.1818(11)     | 15.2566(9)      | 17.8794(10)     | 4141.3(5)      | 1.23           | 0.68           | 0.33   |
| 1000          | op    | 15.1344(9)      | 15.2537(10)     | 17.8397(11)     | 4118.4(4)      | 1.18           | 0.65           | 0.32   |
| 1100          | cp    | 14.3244(6)      | 14.4399(9)      | 16.6094(10)     | 3435.5(4)      | 1.18           | 0.65           | 0.32   |
| 1200          | cp    | 14.3178(9)      | 14.4384(12)     | 16.5546(11)     | 3422.3(6)      | 1.50           | 0.71           | 0.40   |
| 1300          | cp    | 14.3014(9)      | 14.4259(11)     | 16.5267(13)     | 3409.6(6)      | 1.54           | 0.72           | 0.41   |
| 1400          | cp    | 14.2930(10)     | 14.4200(11)     | 16.5194(14)     | 3404.8(6)      | 1.51           | 0.73           | 0.40   |
| 1500          | cp    | 14.2630(12)     | 14.4084(11)     | 16.5077(16)     | 3392.4(6)      | 1.73           | 0.76           | 0.46   |
| 1600          | cp    | 14.2512(7)      | 14.4048(5)      | 16.4962(9)      | 3386.4(4)      | 0.93           | 0.54           | 0.24   |
| 1700          | cp    | 14.2706(14)     | 14.3936(14)     | 16.459(2)       | 3380.7(8)      | 2.26           | 1.27           | 0.60   |
| 1800          | cp    | 14.2457(14)     | 14.3872(12)     | 16.444(2)       | 3370.4(8)      | 2.19           | 1.21           | 0.57   |
| 1900          | cp    | 14.2380(13)     | 14.3890(12)     | 16.4375(18)     | 3367.6(8)      | 2.09           | 1.16           | 0.54   |
| 2000          | cp    | 14.2104(11)     | 14.3806(11)     | 16.4122(16)     | 3353.9(7)      | 1.96           | 1.10           | 0.51   |
| 2250          | cp    | 14.1894(11)     | 14.3691(11)     | 16.3703(16)     | 3337.7(7)      | 1.98           | 1.18           | 0.51   |
| 2500          | cp    | 14.1691(12)     | 14.3650(11)     | 16.3317(17)     | 3324.1(7)      | 1.95           | 1.21           | 0.50   |
| 2750          | cp    | 14.1448(12)     | 14.3472(11)     | 16.2727(18)     | 3302.4(7)      | 1.95           | 1.23           | 0.51   |
| 3000          | cp    | 14.1322(12)     | 14.3468(11)     | 16.2326(18)     | 3291.2(7)      | 1.92           | 1.22           | 0.50   |
| 3250          | cp    | 14.1311(13)     | 14.3528(11)     | 16.1694(18)     | 3279.5(7)      | 1.84           | 1.08           | 0.47   |
| 3500          | cp    | 14.1189(13)     | 14.3529(12)     | 16.1262(17)     | 3267.9(7)      | 1.81           | 1.08           | 0.47   |
| 3750          | cp    | 14.1043(11)     | 14.3512(10)     | 16.0954(15)     | 3257.9(6)      | 1.64           | 0.99           | 0.43   |
| 4000          | cp    | 14.1043(11)     | 14.3512(10)     | 16.0954(15)     | 3257.9(6)      | 1.64           | 0.99           | 0.43   |
10.3. ZIF-62(Zn)-bim$_{0.17}$

**Figure S49.** Profile refinement (Le Bail method) of the PXRD pattern of ZIF-62(Zn)-bim$_{0.17}$ at ambient pressure.

**Figure S50.** Dual-phase profile refinement (Le Bail method) of the PXRD pattern of ZIF-62(Zn)-bim$_{0.17}$ at 1200 bar.
Figure S51. Profile refinement (Le Bail method) of the PXRD pattern of ZIF-62(Zn)-bim$_{0.17}$ at 4000 bar.

Figure S52. Relative changes of lattice parameters of ZIF-62(Zn)-bim$_{0.17}$ determined via profile refinement of the HP-PXRD data collected in the range from 1 to 4000 bar. The dual phase fits have been performed from 1200 to 1400 bar.
| Pressure / bar | Phase | a / Å     | b / Å     | c / Å     | V / Å³   | Rwp / %  | Rp / %  | χ       |
|---------------|-------|-----------|-----------|-----------|----------|-----------|---------|---------|
| 1             | op    | 15.4304(7)| 15.5072(6)| 17.9182(7)| 4299.5(3)| 1.39      | 0.93    | 0.36    |
| 100           | op    | 15.4486(6)| 15.4868(8)| 17.9159(6)| 4286.4(3)| 1.55      | 1.00    | 0.41    |
| 200           | op    | 15.4251(6)| 15.4671(8)| 17.8964(7)| 4269.8(3)| 1.47      | 0.97    | 0.38    |
| 300           | op    | 15.4048(8)| 15.4384(11)| 17.8739(8)| 4250.7(3)| 1.64      | 1.07    | 0.42    |
| 400           | op    | 15.3776(6)| 15.4190(8)| 17.8585(6)| 4234.4(3)| 1.51      | 0.97    | 0.39    |
| 500           | op    | 15.3571(6)| 15.3911(9)| 17.8352(7)| 4215.6(3)| 1.52      | 0.96    | 0.40    |
| 600           | op    | 15.3225(7)| 15.3616(10)| 17.8153(7)| 4193.4(4)| 1.77      | 1.10    | 0.47    |
| 700           | op    | 15.2924(6)| 15.3470(10)| 17.8016(8)| 4177.9(4)| 1.82      | 1.17    | 0.48    |
| 800           | op    | 15.2478(6)| 15.3134(9)| 17.7796(9)| 4151.5(4)| 1.79      | 1.15    | 0.47    |
| 900           | op    | 15.1974(8)| 15.2741(10)| 17.7521(10)| 4120.7(5)| 2.03      | 1.26    | 0.53    |
| 1000          | op    | 15.1417(8)| 15.2403(10)| 17.7284(10)| 4091.1(5)| 1.97      | 1.21    | 0.52    |
| 1100          | op    | 15.0568(7)| 15.1956(7)| 17.6946(9)| 4048.5(4)| 1.35      | 0.78    | 0.36    |
| 1200          | op    | 14.9589(11)| 15.1571(12)| 17.6296(14)| 3997.2(7)| 1.76      | 0.90    | 0.48    |
| 1200          | cp    | 14.4615(11)| 14.7356(10)| 17.1805(15)| 3661.1(7)| 1.76      | 0.90    | 0.48    |
| 1300          | op    | 14.881(2)| 15.065(2)| 17.549(3)| 3934.0(12)| 2.27      | 1.26    | 0.61    |
| 1300          | cp    | 14.4238(16)| 14.7236(16)| 17.156(2)| 3643.5(12)| 2.27      | 1.26    | 0.61    |
| 1400          | op    | 14.819(2)| 15.013(2)| 17.502(2)| 3893.9(9)| 1.80      | 0.98    | 0.48    |
| 1400          | cp    | 14.4162(14)| 14.6928(13)| 17.1500(17)| 3632.6(9)| 1.80      | 0.98    | 0.48    |
| 1500          | cp    | 14.4517(11)| 14.7003(10)| 17.1701(13)| 3647.7(6)| 1.32      | 0.84    | 0.35    |
| 1600          | cp    | 14.4420(10)| 14.7086(9)| 17.1438(11)| 3641.7(2)| 1.62      | 0.93    | 0.43    |
| 1700          | cp    | 14.4569(9)| 14.6933(9)| 17.1504(10)| 3643.0(9)| 1.47      | 0.83    | 0.39    |
| 1800          | cp    | 14.405(2)| 14.653(3)| 17.156(3)| 3621.2(15)| 3.93      | 2.17    | 1.03    |
| 1900          | cp    | 14.3795(18)| 14.623(2)| 17.138(3)| 3603.6(13)| 3.56      | 1.96    | 0.93    |
| 2000          | cp    | 14.3920(17)| 14.568(2)| 17.135(2)| 3592.5(12)| 3.16      | 1.78    | 0.82    |
| 2250          | cp    | 14.3836(13)| 14.5316(17)| 17.117(2)| 3577.9(9)| 2.77      | 1.61    | 0.73    |
| 2500          | cp    | 14.3732(11)| 14.5048(14)| 17.0844(17)| 3561.8(8)| 2.30      | 1.42    | 0.60    |
| 2750          | cp    | 14.3577(10)| 14.4714(14)| 17.0344(15)| 3539.4(7)| 2.20      | 1.36    | 0.57    |
| 3000          | cp    | 14.3384(11)| 14.4403(13)| 17.0070(14)| 3521.3(6)| 2.21      | 1.39    | 0.58    |
| 3250          | cp    | 14.3223(12)| 14.4210(13)| 16.9894(14)| 3509.0(6)| 2.09      | 1.33    | 0.54    |
| 3500          | cp    | 14.3123(12)| 14.3741(13)| 16.9489(13)| 3486.8(6)| 2.10      | 1.33    | 0.55    |
| 3750          | cp    | 14.2800(12)| 14.3605(11)| 16.9329(13)| 3472.4(6)| 2.08      | 1.28    | 0.55    |
| 4000          | cp    | 14.2408(10)| 14.3436(8)| 16.8935(11)| 3450.7(5)| 1.66      | 1.11    | 0.43    |
10.4. ZIF-62(Zn)-bim$_{0.25}$

Figure S53. Profile refinement (Le Bail method) of the PXRD pattern of ZIF-62(Zn)-bim$_{0.25}$ at ambient pressure.

Figure S54. Dual-phase profile refinement (Le Bail method) of the PXRD pattern of ZIF-62(Zn)-bim$_{0.25}$ at 1300 bar.
**Figure S55.** Profile refinement (Le Bail method) of the PXRD pattern of ZIF-62(Zn)-bim0.25 at 4000 bar.

**Figure S56.** Relative changes of lattice parameters of ZIF-62(Zn)-bim0.25 determined via profile refinement of the HP-PXRD data collected in the range from 1 to 4000 bar. The dual phase fits have been performed from 1300 to 1700 bar.
Table S11. Crystallographic data for ZIF-62(Zn)-bim$_{0.25}$ determined via profile refinement of the HP-PXRD data collected in the range from 1 to 4000 bar. All the phases maintain the orthorhombic crystal system with Pbca symmetry.

| Pressure / bar | Phase  | $a$ / Å   | $b$ / Å   | $c$ / Å   | $V$ / Å$^3$ | $R_{wp}$ / % | $R_p$ / % | $\chi$ |
|---------------|--------|-----------|-----------|-----------|-------------|-------------|-----------|-------|
| 1             | $op$   | 15.4258(4)| 15.4925(6)| 18.0003(6)| 4301.8(3)   | 0.67        | 0.45      | 0.18   |
| 100           | $op$   | 15.4021(11)| 15.4651(12)| 17.9871(12)| 4284.4(6)   | 1.58        | 0.82      | 0.44   |
| 200           | $op$   | 15.3810(11)| 15.4386(12)| 17.9692(12)| 4267.0(6)   | 1.57        | 0.86      | 0.44   |
| 300           | $op$   | 15.3585(11)| 15.4207(14)| 17.9556(12)| 4252.6(6)   | 1.67        | 0.92      | 0.46   |
| 400           | $op$   | 15.3360(12)| 15.3895(14)| 17.9359(13)| 4233.1(6)   | 1.70        | 0.91      | 0.47   |
| 500           | $op$   | 15.2995(12)| 15.3617(12)| 17.9117(12)| 4209.7(6)   | 1.71        | 0.91      | 0.48   |
| 600           | $op$   | 15.2820(11)| 15.3407(14)| 17.9028(12)| 4197.1(6)   | 1.64        | 0.90      | 0.45   |
| 700           | $op$   | 15.2509(12)| 15.3184(14)| 17.8887(12)| 4179.2(6)   | 1.74        | 0.92      | 0.48   |
| 800           | $op$   | 15.2126(11)| 15.2845(13)| 17.8662(12)| 4154.2(6)   | 1.78        | 0.95      | 0.49   |
| 900           | $op$   | 15.1725(11)| 15.2643(14)| 17.8460(12)| 4133.1(7)   | 1.72        | 0.93      | 0.47   |
| 1000          | $op$   | 15.1315(5)| 15.2259(6)| 17.8246(6)| 4106.6(3)   | 0.77        | 0.48      | 0.21   |
| 1100          | $op$   | 15.0746(6)| 15.1888(6)| 17.7999(6)| 4075.6(4)   | 0.84        | 0.57      | 0.23   |
| 1200          | $op$   | 15.0062(11)| 15.1573(12)| 17.7812(13)| 4044.4(7)   | 1.47        | 0.87      | 0.41   |
| 1300          | $op$   | 14.9433(5)| 15.1247(4)| 17.7815(5)| 4018.85(13)| 0.73        | 0.42      | 0.20   |
| 1300          | $cp$   | 14.4522(19)| 14.677(2)| 17.320(2)| 3673.90(12)| 0.73        | 0.42      | 0.20   |
| 1400          | $op$   | 14.8960(11)| 15.1083(8)| 17.7771(10)| 4000.8(2)   | 0.99        | 0.55      | 0.28   |
| 1400          | $cp$   | 14.447(2)| 14.6846(18)| 17.298(3)| 3669.7(2)   | 0.99        | 0.55      | 0.28   |
| 1500          | $op$   | 14.8522(18)| 15.0861(12)| 17.7667(14)| 3980.8(4)   | 0.93        | 0.48      | 0.26   |
| 1500          | $cp$   | 14.4360(15)| 14.6843(14)| 17.340(2)| 3675.8(4)   | 0.93        | 0.48      | 0.26   |
| 1600          | $op$   | 14.8456(19)| 15.0424(19)| 17.742(2)| 3962.0(7)   | 1.48        | 0.80      | 0.41   |
| 1600          | $cp$   | 14.4149(18)| 14.664(2)| 17.260(3)| 3648.4(7)   | 1.48        | 0.80      | 0.41   |
| 1700          | $op$   | 14.846(3)| 15.025(2)| 17.704(2)| 3949.0(10)| 1.66        | 0.86      | 0.46   |
| 1700          | $cp$   | 14.400(2)| 14.648(2)| 17.289(4)| 3646.7(10)| 1.66        | 0.86      | 0.46   |
| 1800          | $op$   | 14.857(2)| 15.027(3)| 17.697(3)| 3950.9(11)| 1.78        | 0.96      | 0.49   |
| 1900          | $cp$   | 14.344(2)| 14.680(2)| 17.200(4)| 3621.9(12)| 2.23        | 1.10      | 0.62   |
| 2000          | $cp$   | 14.384(2)| 14.644(2)| 17.200(4)| 3623.0(13)| 2.15        | 1.06      | 0.60   |
| 2250          | $cp$   | 14.3678(19)| 14.636(2)| 17.145(4)| 3605.3(12)| 2.11        | 1.12      | 0.59   |
| 2500          | $cp$   | 14.3489(19)| 14.577(2)| 17.151(4)| 3587.5(10)| 1.82        | 0.92      | 0.51   |
| 2750          | $cp$   | 14.3491(19)| 14.574(2)| 17.130(4)| 3582.3(11)| 2.09        | 1.11      | 0.59   |
| 3000          | $cp$   | 14.3301(15)| 14.584(2)| 17.152(3)| 3584.5(8)| 1.59        | 0.87      | 0.45   |
| 3250          | $cp$   | 14.179(4)| 14.655(7)| 16.326(6)| 3393(4)| 2.37        | 1.14      | 0.67   |
| 3250          | $cp$   | 14.2779(17)| 14.625(3)| 17.185(4)| 3588.6(9)| 1.55        | 0.82      | 0.44   |
| 3500          | $cp$   | 14.2639(13)| 14.5331(19)| 17.119(2)| 3548.7(8)| 1.15        | 0.63      | 0.32   |
| 3750          | $cp$   | 14.2556(15)| 14.496(2)| 17.107(2)| 3535.2(9)| 1.35        | 0.63      | 0.38   |
| 4000          | $cp$   | 14.076(4)| 14.549(5)| 17.244(8)| 3532(4)| 1.74        | 0.90      | 0.49   |
10.5. ZIF-62(Zn)-bim$_{0.30}$

**Figure S57.** Profile refinement (Le Bail method) of the PXRD pattern of ZIF-62(Zn)-bim$_{0.30}$ at ambient pressure.

**Figure S58.** Dual-phase profile refinement (Le Bail method) of the PXRD pattern of ZIF-62(Zn)-bim$_{0.30}$ at 1400 bar.
Figure S59. Profile refinement (Le Bail method) of the PXRD pattern of ZIF-62(Zn)-bim\textsubscript{0.30} at 4000 bar.

Figure S60. Relative changes of lattice parameters of ZIF-62(Zn)-bim\textsubscript{0.30} determined via profile refinement of the HP-PXRD data collected in the range from 1 to 4000 bar. The dual phase fits have been performed at 1400 and 1500 bar.
| Pressure / bar | Phase | \(a\) / Å | \(b\) / Å | \(c\) / Å | \(V\) / Å\(^3\) | \(R_{wp}\)/% | \(R_p\)/% | \(\chi\) |
|---------------|------|------------|------------|------------|----------------|----------------|----------------|--------|
| 1             | \(op\) | 15.4618(7) | 15.5194(7) | 17.8660(9) | 4287.1(3)     | 0.98           | 0.67           | 0.24    |
| 100           | \(op\) | 15.4395(9) | 15.4948(8) | 17.8541(9) | 4271.3(3)     | 1.17           | 0.76           | 0.28    |
| 200           | \(op\) | 15.4138(9) | 15.4738(8) | 17.8311(11) | 4252.9(4)     | 1.23           | 0.77           | 0.30    |
| 300           | \(op\) | 15.3779(9) | 15.4478(8) | 17.8175(10) | 4232.4(4)     | 1.17           | 0.71           | 0.28    |
| 400           | \(op\) | 15.3297(11)| 15.4256(8) | 17.7986(10) | 4208.8(4)     | 1.21           | 0.74           | 0.29    |
| 500           | \(op\) | 15.3040(10)| 15.3999(6) | 17.7719(8) | 4188.3(4)     | 1.11           | 0.71           | 0.27    |
| 600           | \(op\) | 15.3230(8) | 15.3789(9) | 17.7524(10) | 4183.4(4)     | 1.19           | 0.75           | 0.29    |
| 700           | \(op\) | 15.2901(7) | 15.3507(8) | 17.7207(8) | 4159.3(3)     | 1.04           | 0.67           | 0.25    |
| 800           | \(op\) | 15.2513(7) | 15.3232(8) | 17.7045(8) | 4137.5(4)     | 1.10           | 0.69           | 0.27    |
| 900           | \(op\) | 15.2167(6) | 15.2938(7) | 17.6920(8) | 4117.3(4)     | 1.06           | 0.70           | 0.25    |
| 1000          | \(op\) | 15.1697(7) | 15.2611(9) | 17.6716(10) | 4091.1(5)     | 1.21           | 0.77           | 0.29    |
| 1100          | \(op\) | 15.1141(7) | 15.2194(8) | 17.6459(9) | 4059.0(4)     | 1.14           | 0.74           | 0.28    |
| 1200          | \(op\) | 15.0201(8) | 15.1781(10)| 17.6228(10)| 4017.6(6)     | 1.31           | 0.81           | 0.32    |
| 1300          | \(op\) | 14.9345(8) | 15.1380(9) | 17.6204(9) | 3983.6(5)     | 1.00           | 0.58           | 0.25    |
| 1400          | \(op\) | 14.9417(14)| 15.1554(14)| 17.6407(16)| 3994.7(9)     | 1.17           | 0.62           | 0.29    |
| 1400          | \(cp\) | 14.5917(13)| 14.8702(13)| 17.4522(17) | 3786.8(8)     | 1.17           | 0.62           | 0.29    |
| 1500          | \(op\) | 14.8832(15)| 15.1011(14)| 17.624(2)  | 3960.9(9)     | 1.21           | 0.65           | 0.30    |
| 1500          | \(cp\) | 14.5784(13)| 14.8273(14)| 17.3729(17)| 3755.3(9)     | 1.21           | 0.65           | 0.30    |
| 1600          | \(cp\) | 14.471(2)  | 14.820(3)  | 17.366(4)  | 3724.3(17)    | 2.48           | 1.31           | 0.61    |
| 1700          | \(cp\) | 14.4675(19)| 14.794(2)  | 17.340(3)  | 3711.4(14)    | 2.09           | 1.18           | 0.52    |
| 1800          | \(cp\) | 14.4507(16)| 14.712(2)  | 17.283(2)  | 3674.3(11)    | 2.03           | 1.12           | 0.50    |
| 1900          | \(cp\) | 14.4238(13)| 14.6447(14)| 17.2412(16)| 3641.9(8)     | 2.22           | 1.36           | 0.55    |
| 2000          | \(cp\) | 14.4218(13)| 14.6344(16)| 17.2418(17)| 3639.0(9)     | 2.05           | 1.29           | 0.50    |
| 2250          | \(cp\) | 14.4253(12)| 14.5994(15)| 17.2118(17)| 3624.8(8)     | 1.87           | 1.18           | 0.46    |
| 2500          | \(cp\) | 14.4132(10)| 14.5592(13)| 17.1661(14)| 3602.7(2)     | 1.60           | 1.06           | 0.38    |
| 2750          | \(cp\) | 14.4015(10)| 14.5325(12)| 17.1386(13)| 3586.9(6)     | 1.42           | 0.95           | 0.34    |
| 3000          | \(cp\) | 14.3966(8) | 14.5313(12)| 17.1299(11)| 3583.6(6)     | 1.34           | 0.91           | 0.32    |
| 3250          | \(cp\) | 14.3779(9) | 14.4942(13)| 17.0867(12)| 3560.8(6)     | 1.38           | 0.93           | 0.33    |
| 3500          | \(cp\) | 14.3701(8) | 14.4734(14)| 17.0688(12)| 3550.0(6)     | 1.37           | 0.93           | 0.32    |
| 3750          | \(cp\) | 14.3522(8) | 14.4321(12)| 17.0322(10)| 3527.9(5)     | 1.28           | 0.88           | 0.31    |
| 4000          | \(cp\) | 14.3354(9) | 14.4160(13)| 17.0147(11)| 3516.2(5)     | 1.27           | 0.85           | 0.31    |
10.6. ZIF-62(Zn)-bim$_{0.35}$

Figure S61. Profile refinement (Le Bail method) of the PXRD pattern of ZIF-62(Zn)-bim$_{0.35}$ at ambient pressure.

Figure S62. Profile refinement (Le Bail method) of the PXRD pattern of ZIF-62(Zn)-bim$_{0.35}$ at 4000 bar.
Figure S63. Relative changes of lattice parameters of ZIF-62(Zn)-bim0.35 determined via profile refinement of the HP-PXRD data collected in the range from 1 to 4000 bar. The intermediate region with higher compressibility is between 1100 and 2200 bar (shaded in pink).
| Pressure / bar | \(a \, \text{Å} \) | \(b \, \text{Å} \) | \(c \, \text{Å} \) | \(V \, \text{Å}^3 \) | \(R_{wp} \, \% \) | \(R_p \, \% \) | \(\chi \) |
|---------------|-----------------|-----------------|-----------------|-------------|-------------|-------------|-----|
| 1             | 15.4850(6)      | 15.6086(8)      | 17.9633(9)      | 4341.7(4)   | 1.33        | 0.88        | 0.36 |
| 100           | 15.4709(5)      | 15.5960(8)      | 17.9580(10)     | 4333.0(4)   | 1.30        | 0.85        | 0.35 |
| 200           | 15.4395(7)      | 15.5863(10)     | 17.9356(10)     | 4316.1(5)   | 1.56        | 1.04        | 0.43 |
| 300           | 15.4313(6)      | 15.5687(10)     | 17.9204(11)     | 4305.3(5)   | 1.39        | 0.94        | 0.37 |
| 400           | 15.4093(6)      | 15.5423(9)      | 17.9194(11)     | 4291.6(5)   | 1.38        | 0.96        | 0.38 |
| 500           | 15.3870(6)      | 15.5164(10)     | 17.9188(12)     | 4278.1(5)   | 1.42        | 0.99        | 0.38 |
| 600           | 15.3577(7)      | 15.5087(11)     | 17.8862(14)     | 4260.1(6)   | 1.55        | 1.03        | 0.42 |
| 700           | 15.3354(8)      | 15.4827(12)     | 17.8913(15)     | 4248.0(7)   | 1.68        | 1.13        | 0.45 |
| 800           | 15.3133(8)      | 15.4846(13)     | 17.8613(16)     | 4235.3(8)   | 1.72        | 1.15        | 0.46 |
| 900           | 15.2763(8)      | 15.4726(13)     | 17.8028(15)     | 4208.0(7)   | 1.73        | 1.12        | 0.47 |
| 1000          | 15.2350(10)     | 15.4461(14)     | 17.7704(17)     | 4181.8(8)   | 1.95        | 1.28        | 0.53 |
| 1100          | 15.2223(14)     | 15.4515(17)     | 17.764(2)       | 4178.2(11)  | 2.37        | 1.52        | 0.65 |
| 1200          | 15.1454(13)     | 15.3577(17)     | 17.813(2)       | 4143.2(11)  | 2.26        | 1.54        | 0.62 |
| 1300          | 15.0926(16)     | 15.308(2)       | 17.806(2)       | 4113.9(13)  | 2.69        | 1.80        | 0.74 |
| 1400          | 15.010(2)       | 15.274(2)       | 17.759(3)       | 4071.6(16)  | 3.17        | 2.02        | 0.87 |
| 1500          | 14.921(2)       | 15.225(2)       | 17.720(3)       | 4025.4(17)  | 3.33        | 2.12        | 0.93 |
| 1600          | 14.845(2)       | 15.176(3)       | 17.727(3)       | 3993.5(18)  | 3.76        | 2.31        | 1.04 |
| 1700          | 14.770(3)       | 15.123(3)       | 17.667(4)       | 3946(2)     | 4.80        | 2.94        | 1.33 |
| 1800          | 14.694(3)       | 15.053(3)       | 17.583(4)       | 3889(2)     | 5.49        | 3.35        | 1.52 |
| 1900          | 14.628(3)       | 14.984(3)       | 17.503(4)       | 3836(2)     | 5.74        | 3.51        | 1.61 |
| 2000          | 14.593(3)       | 14.944(3)       | 17.456(3)       | 3807(2)     | 5.61        | 3.50        | 1.57 |
| 2250          | 14.537(2)       | 14.878(2)       | 17.385(3)       | 3760.1(18)  | 4.98        | 3.08        | 1.39 |
| 2500          | 14.5074(18)     | 14.8446(19)     | 17.346(2)       | 3735.6(14)  | 4.30        | 2.65        | 1.19 |
| 2750          | 14.4957(17)     | 14.8296(18)     | 17.331(2)       | 3725.6(13)  | 4.13        | 2.50        | 1.15 |
| 3000          | 14.4698(16)     | 14.7979(17)     | 17.2980(19)     | 3703.9(12)  | 3.99        | 2.35        | 1.11 |
| 3250          | 14.4472(15)     | 14.7660(16)     | 17.2695(18)     | 3684.0(11)  | 3.73        | 2.17        | 1.04 |
| 3500          | 14.4277(14)     | 14.7274(14)     | 17.2466(17)     | 3664.6(10)  | 3.22        | 1.95        | 0.90 |
| 3750          | 14.4125(13)     | 14.6913(14)     | 17.2341(16)     | 3649.1(10)  | 3.15        | 1.99        | 0.88 |
| 4000          | 14.3961(13)     | 14.6699(14)     | 17.2145(16)     | 3635.5(10)  | 3.08        | 2.00        | 0.87 |
10.7. ZIF-62(Co)-bim$_{0.27}$

**Figure S64.** Profile refinement (Le Bail method) of the PXRD pattern of ZIF-62(Co)-bim$_{0.27}$ at ambient pressure.

**Figure S65.** Profile refinement (Le Bail method) of the PXRD pattern of ZIF-62(Co)-bim$_{0.27}$ at 4000 bar.
Figure S66. Relative changes of lattice parameters of ZIF-62(Zn)-bim$^{0.27}$ determined via profile refinement of the HP-PXRD data collected in the range from 1 to 4000 bar.
Table S14. Crystallographic data for ZIF-62(Co)-bim\textsubscript{0.27} determined via profile refinement of the HP-PXRD data collected in the range from 1 to 4000 bar. All the phases maintain the orthorhombic crystal system with \textit{Pbca} symmetry.

| Pressure / bar | Phase | \(a / \text{Å}\) | \(b / \text{Å}\) | \(c / \text{Å}\) | \(V / \text{Å}^3\) | \(R_{wp} / \%\) | \(R_p / \%\) | \(\chi\) |
|---------------|-------|-----------------|-----------------|----------------|----------------|----------------|----------------|---------|
| 1             | \textit{op} | 15.4448(14) | 15.4944(12) | 17.7816(12) | 4255.3(5) | 1.90 | 1.25 | 0.44 |
| 100           | \textit{op} | 15.4378(12) | 15.4844(12) | 17.7776(11) | 4249.6(5) | 1.77 | 1.17 | 0.41 |
| 200           | \textit{op} | 15.4138(11) | 15.4576(11) | 17.7477(11) | 4228.6(5) | 1.73 | 1.15 | 0.40 |
| 300           | \textit{op} | 15.3971(12) | 15.4379(13) | 17.7221(11) | 4212.5(5) | 1.77 | 1.15 | 0.40 |
| 400           | \textit{op} | 15.3713(12) | 15.4120(13) | 17.6983(11) | 4192.8(5) | 1.68 | 1.11 | 0.38 |
| 500           | \textit{op} | 15.3441(12) | 15.3881(13) | 17.6694(11) | 4172.0(5) | 1.62 | 1.06 | 0.37 |
| 600           | \textit{op} | 15.3198(12) | 15.3588(13) | 17.6394(11) | 4150.4(5) | 1.56 | 1.00 | 0.36 |
| 700           | \textit{op} | 15.2853(11) | 15.3327(11) | 17.6124(10) | 4127.4(5) | 1.44 | 0.94 | 0.33 |
| 800           | \textit{op} | 15.2604(9)  | 15.3101(10) | 17.5872(9)  | 4109.0(4) | 1.28 | 0.85 | 0.29 |
| 900           | \textit{op} | 15.2223(9)  | 15.2863(10) | 17.5590(10) | 4085.9(4) | 1.34 | 0.90 | 0.30 |
| 1000          | \textit{op} | 15.1943(8)  | 15.2648(9)  | 17.5457(10) | 4069.5(4) | 1.24 | 0.83 | 0.28 |
| 1100          | \textit{op} | 15.1565(6)  | 15.2331(8)  | 17.5231(9)  | 4045.7(4) | 1.11 | 0.73 | 0.25 |
| 1200          | \textit{op} | 15.1117(6)  | 15.2014(9)  | 17.4854(9)  | 4016.7(4) | 1.26 | 0.78 | 0.29 |
| 1300          | \textit{op} | 15.0496(7)  | 15.1582(10) | 17.4570(10) | 3982.4(5) | 1.44 | 0.88 | 0.33 |
| 1400          | \textit{op} | 14.9718(9)  | 15.1061(10) | 17.4382(14) | 3943.9(6) | 1.73 | 1.07 | 0.39 |
| 1500          | \textit{op} | 14.8693(12) | 15.0584(13) | 17.4470(16) | 3906.5(8) | 1.95 | 1.29 | 0.44 |
| 1600          | \textit{op} | 14.713(2)   | 15.004(2)   | 17.456(2)   | 3853.6(6) | 4.56 | 2.92 | 1.03 |
| 1700          | \textit{op} | 14.888(5)   | 14.895(4)   | 17.307(3)   | 3837.8(16)| 1.44 | 0.87 | 0.33 |
| 1800          | \textit{cp} | 14.379(2)   | 14.749(2)   | 17.348(3)   | 3679.1(8) | 3.92 | 2.32 | 0.87 |
| 1900          | \textit{cp} | 14.376(2)   | 14.617(2)   | 17.293(2)   | 3634.0(7) | 4.29 | 2.46 | 0.95 |
| 2000          | \textit{cp} | 14.374(3)   | 14.588(4)   | 17.270(4)   | 3621(2)   | 3.85 | 2.18 | 0.85 |
| 2250          | \textit{cp} | 14.362(2)   | 14.534(2)   | 17.216(3)   | 3593.7(15)| 3.12 | 1.79 | 0.69 |
| 2500          | \textit{cp} | 14.3592(19) | 14.496(2)   | 17.183(2)   | 3576.7(12)| 2.65 | 1.57 | 0.59 |
| 2750          | \textit{cp} | 14.3462(17) | 14.461(18)  | 17.154(2)   | 3558.9(11)| 2.45 | 1.45 | 0.54 |
| 3000          | \textit{cp} | 14.3362(15) | 14.4273(17) | 17.128(2)   | 3542.6(10)| 2.27 | 1.34 | 0.50 |
| 3250          | \textit{cp} | 14.3261(15) | 14.3991(19) | 17.1008(19) | 3527.6(10)| 2.28 | 1.33 | 0.50 |
| 3500          | \textit{cp} | 14.3116(16) | 14.372(2)   | 17.0769(18) | 3512.6(9) | 2.22 | 1.31 | 0.48 |
| 3750          | \textit{cp} | 14.2935(16) | 14.350(2)   | 17.0498(16) | 3497.0(8) | 2.02 | 1.22 | 0.44 |
| 4000          | \textit{cp} | 14.2718(16) | 14.325(2)   | 17.0236(16) | 3480.3(8) | 2.01 | 1.23 | 0.44 |
10.8. ZIF-62(Co)-bim$_{0.37}$

**Figure S67.** Profile refinement (Le Bail method) of the PXRD pattern of ZIF-62(Co)-bim$_{0.37}$ at ambient pressure.

**Figure S68.** Profile refinement (Le Bail method) of the PXRD pattern of ZIF-62(Co)-bim$_{0.37}$ at 4000 bar.
Figure S69. Relative changes of lattice parameters of ZIF-62(Co)-bim\textsubscript{0.37} determined via profile refinement of the HP-PXRD data collected in the range from 1 to 4000 bar. The intermediate region with stronger compressibility along the $a$ and $b$ axes and weaker compressibility along the $c$ axis is between 1400 and 2000 bar, shaded by the pinkish background.
Table S15. Crystallographic data for ZIF-62(Co)-bim$_{0.37}$ determined via profile refinement of the HP-PXRD data collected in the range from 1 to 4000 bar. All the phases maintain the orthorhombic crystal system with Pbca symmetry.

| Pressure / bar | $a$ / Å | $b$ / Å | $c$ / Å | $V$ / Å$^3$ | $R_{wp}$ / % | $R_p$ / % | $\chi$ |
|---------------|---------|---------|---------|-------------|--------------|----------|-------|
| 1             | 15.4641(8) | 15.5124(10) | 17.7305(8) | 4253.3(4) | 0.44 | 0.30 | 0.18 |
| 100           | 15.4462(8) | 15.4907(9) | 17.7072(7) | 4236.9(3) | 0.34 | 0.23 | 0.35 |
| 200           | 15.4080(10) | 15.4603(10) | 17.6767(9) | 4210.8(4) | 0.39 | 0.28 | 0.16 |
| 300           | 15.4048(12) | 15.4489(14) | 17.6680(11) | 4204.8(5) | 0.44 | 0.29 | 0.18 |
| 400           | 15.373(3) | 15.456(3) | 17.640(4) | 4191(2) | 2.25 | 1.38 | 0.93 |
| 500           | 15.3613(11) | 15.4123(14) | 17.6224(11) | 4172.2(6) | 0.46 | 0.30 | 0.19 |
| 600           | 15.3340(10) | 15.3859(14) | 17.6005(12) | 4152.4(6) | 0.46 | 0.30 | 0.19 |
| 700           | 15.3028(11) | 15.3576(15) | 17.5641(14) | 4127.8(7) | 0.53 | 0.34 | 0.22 |
| 800           | 15.2768(12) | 15.3292(17) | 17.5503(15) | 4110.0(8) | 0.61 | 0.39 | 0.25 |
| 900           | 15.2459(14) | 15.313(2) | 17.5282(19) | 4092.2(9) | 0.70 | 0.43 | 0.29 |
| 1000          | 15.2194(16) | 15.288(2) | 17.499(2) | 4071.5(10) | 0.75 | 0.47 | 0.31 |
| 1100          | 15.1816(17) | 15.260(2) | 17.470(2) | 4047.5(11) | 0.80 | 0.50 | 0.32 |
| 1200          | 15.1515(18) | 15.243(2) | 17.448(3) | 4029.7(13) | 0.89 | 0.53 | 0.36 |
| 1300          | 15.099(2) | 15.202(2) | 17.437(3) | 4002.3(13) | 0.96 | 0.60 | 0.38 |
| 1400          | 15.050(2) | 15.195(3) | 17.432(3) | 3986.4(14) | 1.01 | 0.65 | 0.40 |
| 1500          | 14.980(2) | 15.139(2) | 17.412(3) | 3948.5(16) | 1.07 | 0.69 | 0.42 |
| 1600          | 14.902(3) | 15.107(3) | 17.389(3) | 3914.6(18) | 1.14 | 0.73 | 0.45 |
| 1700          | 14.842(3) | 15.085(3) | 17.424(4) | 3901(2) | 1.25 | 0.81 | 0.49 |
| 1800          | 14.776(4) | 15.046(4) | 17.418(4) | 3872(2) | 1.29 | 0.83 | 0.51 |
| 1900          | 14.717(4) | 14.999(4) | 17.404(4) | 3842(2) | 1.32 | 0.85 | 0.52 |
| 2000          | 14.638(4) | 14.943(4) | 17.397(4) | 3806(2) | 1.41 | 0.93 | 0.55 |
| 2250          | 14.595(4) | 14.920(4) | 17.407(4) | 3790(3) | 1.95 | 1.25 | 0.75 |
| 2500          | 14.517(3) | 14.808(3) | 17.348(4) | 3730(2) | 1.61 | 1.05 | 0.63 |
| 2750          | 14.459(3) | 14.732(3) | 17.296(4) | 3684(2) | 1.67 | 1.08 | 0.65 |
| 3000          | 14.430(3) | 14.692(3) | 17.265(3) | 3660(2) | 1.68 | 1.08 | 0.66 |
| 3250          | 14.391(3) | 14.647(3) | 17.217(3) | 3629(2) | 1.64 | 1.05 | 0.64 |
| 3500          | 14.389(3) | 14.642(3) | 17.208(3) | 3625(2) | 1.65 | 1.05 | 0.64 |
| 3750          | 14.357(3) | 14.604(3) | 17.167(3) | 3600(2) | 1.67 | 1.06 | 0.66 |
| 4000          | 14.3106(17) | 14.501(2) | 17.129(2) | 3554.7(11) | 0.54 | 0.35 | 0.21 |
Figure S70. Overall volume contraction (i.e. relative volume change from 1 to 4000 bar) of the op-to-cp phase transition of the ZIF-62(Co)-bim materials.
11. Compressibility and bulk moduli

The compressibility ($\kappa$) has been determined along each primary crystallographic direction and for the volume as a function of pressure. The refined lattice parameters ($y$) and the unit cell volume were fitted using a 1st or 2nd order polynomial function $[y(p) = a_0 + a_1p + a_2p^2$, with $a_2 = 0$ for 1st order]. The compressibilities $\kappa_y(p)$ were derived from the numerically calculated derivative of the respective fitting function $y(p)$ according to the following function:

$$\kappa_y(p) = -\frac{1}{y} \frac{dy}{dp}$$

The inverse of the fitted compressibility at ambient pressure is recognised as the bulk modulus $K_0$ of the material.

Only data of the single-phase regions have been included in the fits. If both phases, $op$ and $cp$, are present at a certain pressure, the corresponding crystallographic data are deemed to be less accurate due to a potential correlation between the fitting parameters for the $op$ and $cp$ phases. Thus, these data have not been included in the determination of the materials’ linear and volume compressibilities.

For ZIF-62(Zn)-bim0.35 the data have been split into three regions: one for $op$, one for $cp$ and one intermediate region, where the framework shows a very strong continuous contraction from the $op$ to the $cp$ phase.

![Figure S71. Polynomial fit to the lattice parameters of the op phase of ZIF-62(Zn)-bim0.02 as a function of pressure.](image)
Figure S72. Polynomial fit to the lattice parameters of the **cp** phase of ZIF-62(Zn)-bim$_{0.02}$ as a function of pressure.

Figure S73. Linear compressibilities $\kappa_I$ and volume compressibility $\kappa_V$ of the **op** and **cp** phases of ZIF-62(Zn)-bim$_{0.02}$. 
Figure S74. Polynomial fit to the lattice parameters of the op phase of ZIF-62(Zn)-bim$_{0.05}$ as a function of pressure.
**Figure S75.** Polynomial fit to the lattice parameters of the cp phase of ZIF-62(Zn)-bim$_{0.05}$ as a function of pressure.

**Figure S76.** Linear compressibilities $\kappa_i$ and volume compressibility $\kappa_V$ of the op and cp phases of ZIF-62(Zn)-bim$_{0.05}$. 

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Figure S77. Polynomial fit to the lattice parameters of the op phase of ZIF-62(Zn)-bim$_{0.17}$ as a function of pressure.
Figure S78. Polynomial fit to the lattice parameter of the cp phase of ZIF-62(Zn)-bim$_{0.17}$ as a function of pressure.

Figure S79. Linear compressibilities $\kappa_l$ and volume compressibility $\kappa_V$ of the op and cp phases of ZIF-62(Zn)-bim$_{0.17}$. 
Figure S80. Polynomial fit to the lattice parameters of the op phase of ZIF-62(Zn)-bim$_{0.25}$ as a function of pressure.
Figure S81. Polynomial fit to the lattice parameters of the \textit{cp} phase of ZIF-62(Zn)-bim$_{0.25}$ as a function of pressure.

Figure S82. Linear compressibilities $\kappa_{i}$ and volume compressibility $\kappa_{V}$ of the \textit{op} and \textit{cp} phases of ZIF-62(Zn)-bim$_{0.25}$. 
Figure S83. Polynomial fit to the lattice parameters of the op phase of ZIF-62(Zn)-bim$_{0.30}$ as a function of pressure.
Figure S84. Polynomial fit to the lattice parameters of the cp phase of ZIF-62(Zn)-bim$_{0.30}$ as a function of pressure.

Figure S85. Linear compressibilities $\kappa_2$ and volume compressibility $\kappa_V$ of the op and cp phases of ZIF-62(Zn)-bim$_{0.30}$. 
Figure S86. Polynomial fit to the lattice parameters of the op phase of ZIF-62(Zn)-bim$_{0.35}$ as a function of pressure.
Figure S87. Polynomial fit to the lattice parameters of the intermediate phase (transition region between the \textit{op} and \textit{cp} phases) of ZIF-62(Zn)-bim$_{0.35}$ as a function of pressure.
**Figure S88.** Polynomial fit to the lattice parameters of the cp phase of ZIF-62(Zn)-bim$_{0.35}$ as a function of pressure.

**Figure S89.** Linear compressibilities $\kappa_l$ and volume compressibility $\kappa_V$ of the op, intermediate and cp phases of ZIF-62(Zn)-bim$_{0.35}$. 

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Figure S90. Polynomial fit to the lattice parameters of the op phase of ZIF-62(\text{Co})-bim\textsubscript{0.27} as a function of pressure.
**Figure S91.** Polynomial fit to the lattice parameters of the cp phase of ZIF-62(Co)-bim$_{0.27}$ as a function of pressure.

**Figure S92.** Linear compressibilities $\kappa_T$ and volume compressibility $\kappa_V$ of the op and cp phases of ZIF-62(Co)-bim$_{0.27}$. 

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**Figure S93.** Polynomial fit to the lattice parameters of the op phase of ZIF-62(Co)-bim0.37 as a function of pressure.
Figure S94. Polynomial fit to the lattice parameters of the intermediate phase (transition region between the \textit{op} and \textit{cp} phases) of ZIF-62(Co)-bim\textsubscript{0.37} as a function of pressure.
Figure S95. Polynomial fit to the lattice parameters of the \textit{cp} phase of ZIF-62(Co)-bim$_{0.37}$ as a function of pressure.

Figure S96. Linear compressibilities $\kappa_1$ and volume compressibility $\kappa_V$ of the \textit{op}, intermediate and \textit{cp} phases of ZIF-62(Co)-bim$_{0.37}$. 
**Table S16.** General ambient pressure bulk moduli ($K_0$) of the ZIF-62(M)-bim$_x$ samples.

| Sample               | ZIF-62(Zn)-bim$_{0.02}$ | ZIF-62(Zn)-bim$_{0.05}$ | ZIF-62(Zn)-bim$_{0.17}$ | ZIF-62(Zn)-bim$_{0.25}$ | ZIF-62(Zn)-bim$_{0.30}$ | ZIF-62(Zn)-bim$_{0.35}$ | ZIF-62(Co)-bim$_{0.27}$ | ZIF-62(Co)-bim$_{0.37}$ |
|----------------------|--------------------------|--------------------------|--------------------------|--------------------------|--------------------------|--------------------------|--------------------------|--------------------------|
| General bulk modulus | 2.3 ± 0.1                | 2.6 ± 0.2                | 3.2 ± 0.5                | 2.9 ± 0.3                | 3.0 ± 0.4                | 4.1 ± 0.5                | 3.3 ± 0.6                | 2.8 ± 0.2                |
| ($K_0$) / GPa         |                          |                          |                          |                          |                          |                          |                          |                          |

**Figure S97.** Pressure dependent bulk modulus ($K$) of op (left) and cp (right) phases of ZIF-62(M)-bim$_x$. 
12. Compression work

The pressure-volume work done on the system upon compression of the various ZIF-62(M)-bim$_x$ samples was calculated by numerically integrating the pressure ($p$) vs. volume change ($\Delta V$) curve for the entire pressure range ($\Delta V(p) = V_0 - V(p)$, with $V_0 =$ volume at 1 bar, $V(p) =$ volume at $p$; both determined from profile refinements of the HP-PXRD data). The critical phase transition pressures (plateaus in the $p$ vs $\Delta V$ curves) is the mean pressure of the phase transition range.

![Graphical representation for the determination of the pressure-volume work done upon compression of the ZIF-62(M)-bim$_x$ samples via integration of the pressure vs. volume change curves.](image)

Figure S98. Graphical representation for the determination of the pressure-volume work done upon compression of the ZIF-62(M)-bim$_x$ samples via integration of the pressure vs. volume change curves.
13. Rietveld refinements of PXRD patterns

Based on the profile fits (see Section 10), we further performed sequential Rietveld refinements of the HP-PXRD data of ZIF-62(Zn)-bim\textsubscript{0.02} and ZIF-62(Zn)-bim\textsubscript{0.35} for all diffraction patterns collected in the range from 1 bar to 4000 bar.

In order to perform the refinements, we simplified the structural model derived from the single crystal diffraction data (see Section 4) for ZIF-62(Zn)-bim\textsubscript{0.35}. For the sake of simplicity, only one of the two partially occupied crystallographic positions of bim\textsuperscript{−} was included in the model (position 1 in Fig. 1 of the article). Position 1 is occupied by 0.355(2) in the SCXRD structure of ZIF-62(Zn)-bim\textsubscript{0.35}, while position 2 is only occupied by 0.345(2). In the simplified model for Rietveld refinement only position 1 is half occupied by bim\textsuperscript{−} (with an occupancy of 0.5) and half occupied by the smaller im\textsuperscript{−} linker. The other partially occupied bim\textsuperscript{−} is described only by an im\textsuperscript{−} linker. Thus, the chemical composition of the refined model is Zn(im\textsubscript{1.75}(bim\textsubscript{0.25}). This reduction of structural complexity was necessary to avoid overrefinement of the PXRD data. The bim\textsuperscript{−} and im\textsuperscript{−} linkers were constrained as rigid bodies during the refinements. The organic linker as a rigid group has six degrees of freedom (rotations about and translations along the three crystallographic axes). In order to maintain a reasonable shape of the Zn\textsubscript{N} tetrahedra, the Zn–N bond distances were restrained to be 2 Å (with 0.005 Å tolerance) and the N–Zn–N bond angles were softly restrained to be 109.4° (with 5° tolerance). The atomic displacement parameters were refined and were set to 6.0 Å\textsuperscript{2} for C, 5.0 Å\textsuperscript{2} for N and 4.5 Å\textsuperscript{2} for Zn atoms. The patterns were sequentially refined starting with the diffraction pattern recorded at 1 bar moving across the series to the pattern recorded at 4000 bar. The converged structure at a certain pressure was used as the starting model for the fit of the pattern belonging to the next pressure. Plots of the refined patterns at 1 bar and 4000 bar are displayed in Figure S95 as an example.

ZIF-62(Zn)-bim\textsubscript{0.02} contains only a very small concentration of bim\textsuperscript{−} linkers (total occupancy of the bim\textsuperscript{−} linker in the asymmetric unit is only 4%). Hence, the bim\textsuperscript{−} linkers are not included in the structural model for ZIF-62(Zn)-bim\textsubscript{0.02} so that the model is largely identical to the model of the op phase ZIF-4 (Zn(im\textsubscript{2})\textsubscript{2}). This reduced model was obtained by omitting the four carbon atoms unique to the bim\textsuperscript{−} linker from the Rietveld-refined model derived from the PXRD pattern recorded at 1 bar for ZIF-62(Zn)-bim\textsubscript{0.35}. The cp phase of ZIF-62(Zn)-bim\textsubscript{0.02}, was refined using the published model of the cp phase of ZIF-4\textsuperscript{14}. The constraints and restraints applied are the same as for ZIF-62(Zn)-bim\textsubscript{0.35}. The refinements are performed based on the op phase in the pressure range from ambient to 600 bar and on the cp phase from 4000 to 700 bar backwards. The resultant Rietveld fits at pressures of (a) ambient, (b) 4000 bar, (c) 600 bar, (d) 700 bar and (e) 800 bar can be seen in Figure S96.

In the last step of each refinement, spherical harmonics with 8\textsuperscript{th} order have been applied to correct for preferred orientation.\textsuperscript{15} The plastic capillaries could not be spun while in the HP cell, thus powder averaging is limited and preferred orientation needed to be corrected.

The crystallographic data for both series of Rietveld refinements can be obtained in cif-format from the CCDC database (https://www.ccdc.cam.ac.uk/structures) quoting the deposition numbers 2130193-2130221 (for ZIF-62(Zn)-bim\textsubscript{0.02}) and 2130225-2130253 (for ZIF-62(Zn)-bim\textsubscript{0.35}).
Figure S99. Comparison of crystal structures of (a) ZIF-62(Zn)-bim$_{0.02}$ and (b) ZIF-62(Zn)-bim$_{0.35}$ at ambient pressure and of (c) ZIF-62(Zn)-bim$_{0.02}$ and (d) ZIF-62(Zn)-bim$_{0.35}$ under 4000 bar. The void volume was calculated using a probe radius of 1.5 Å (i.e. the common radius of water-sized probe$^{[16]}$).

Figure S100. Plots of the Rietveld-refined PXRD patterns of (a) the op phase (at ambient pressure) and (b) the cp phase (at 4000 bar) of ZIF-62(Zn)-bim$_{0.35}$.
Figure S101. Plots of the Rietveld-refined PXRD patterns of (a) the op phase (at ambient pressure), (b) the cp phase (at 4000 bar), and in the transition region at (c) 600 bar (op phase), (d) 700 bar (cp phase) and (e) 800 bar (cp phase) of ZIF-62(Zn)-bim$_{0.02}$. The poorer fits at 700 and 800 bar are associated to the presence of residual reflections stemming from the op phase (not fitted).

Table S17. Lattice parameters and agreement factors from the Rietveld refinements of the op and cp phases of ZIF-62(Zn)-bim$_{0.02}$ and ZIF-62(Zn)-bim$_{0.35}$.

| Phase | op | 600 | 700 | 800 | 4000 bar | op | 1 bar | 4000 bar |
|-------|----|-----|-----|-----|-----------|----|-------|---------|
| Space group | Pbca | Pbca | Pbca | Pbca | Pbca | Pbca | Pbca | Pbca |
| $a$ / Å | 15.4786(15) | 15.3249(12) | 14.441(2) | 14.438(3) | 14.4068(18) | 15.482(4) | 14.416(4) |
| $b$ / Å | 15.4833(11) | 15.2976(10) | 14.369(3) | 14.361(2) | 14.1610(15) | 15.572(3) | 14.575(3) |
| $c$ / Å | 18.0544(13) | 17.9434(11) | 16.602(3) | 16.602(3) | 15.954(2) | 17.967(4) | 17.164(5) |
| $V$ / Å$^3$ | 4326.9(6) | 4206.5(5) | 3445.1(11) | 3442.2(10) | 3254.9(7) | 4331.8(5) | 3606.4(4) |
| $R_{wp}/R_{Bragg}/\chi^2$ | 2.02/1.36/ | 2.39/2.05/ | 9.72/3.66/ | 7.09/3.71/ | 4.52/2.48/ | 7.17/5.08/ | 7.73/5.92/ |
| | 0.52 | 0.62 | 2.54 | 1.83 | 1.14 | 1.76 | 1.95 |
Table S18. Representative torsion angles of from the structures of ZIF-62(Zn)-bim$_{0.02}$ and ZIF-62(Zn)-bim$_{0.35}$ at 1 bar and 4000 bar.

| Linker   | Torsion angle / ° | ZIF-62(Zn)-bim$_{0.02}$ 1 bar | ZIF-62(Zn)-bim$_{0.02}$ 4000 bar | ZIF-62(Zn)-bim$_{0.35}$ 1 bar | ZIF-62(Zn)-bim$_{0.35}$ 4000 bar |
|----------|-------------------|-------------------------------|----------------------------------|-------------------------------|----------------------------------|
| im1      | C1a-N1a-Zn1-N1a   | -133(9)                       | -112(10)                        | -110(15)                      | -98(16)                          |
| im2      | C2a-N2a-Zn1-N3a   | -147(8)                       | -97(11)                         | -157(18)                      | -171(21)                         |
| im3      | C3a-N3a-Zn1-N4a   | 129(9)                        | 162(10)                         | 139(33)                       | 128(20)                          |
| im4      | C4a-N4a-Zn1-N1a   | 83(11)                        | 77(11)                          | 77(23)                        | 70(27)                           |
14. Porosity and pore size analysis

The pressure-dependent evolution of the porous features of the structures of ZIF-62(Zn)-bim$_{0.02}$ and ZIF-62(Zn)-bim$_{0.35}$ derived via Rietveld refinement were further analysed with the software package Zeo++. In order to resolve the symmetry-imposed disorder of the bim$^-$ groups at position 2, the symmetry of the ZIF-62(Zn)-bim$_{0.35}$ structures was reduced from Pbca to the subgroup Pbc$_{21}$ (Figure S97). This allowed us to generate idealized structural models for ZIF-62(Zn)-bim$_{0.35}$ without any disorder and a chemical composition of Zn(im)$_{1.75}$(bim)$_{0.25}$ (as close as it gets to the correct composition Zn(im)$_{1.65}$(bim)$_{0.35}$ without reducing the symmetry further).

![Image](image.jpg)

Figure S102. Cut-out of the idealized structure of ZIF-62(Zn)-bim$_{0.35}$ with Pbc$_{21}$ symmetry at 1 bar. The disorder of the bim$^-$ linker is resolved and only one linker is pointing into the pore of the 8-ring.

Using Zeo++ the accessible pore volume of the structures was calculated as a function of mechanical pressure using a probe of 1.5 Å radius. Moreover, we also calculated the corresponding pore size distribution (PSD) as function of mechanical pressure. Note that the PSD is calculated by multiplying the volume-normalized PSD histograms (as obtained from Zeo++) with the accessible pore volume at the corresponding pressures.
Figure S103. 3D plot of the pore size distributions of ZIF-62(Zn)-bim$_{0.02}$ and ZIF-62(Zn)-bim$_{0.35}$ as a function of mechanical pressure.
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Author contributions

J.S. synthesized the ZIFs and collected and analysed PXRD, SCXRD, IR spectroscopy and NMR spectroscopy data. J.S. performed the crystallographic analysis. R.P. and S.H. helped with the Rietveld refinements. L.F.-B. helped with the initial syntheses. J.S., R.P., L.F.-B. and P.K. performed HP-PXRD with G.K., P.V. and C.L.H. performing preliminary experiments. R.P., L.F.-B. and S.H. performed the VT-PXRD experiments. J.S. and S.H. wrote the paper. All authors participated in discussing the data and contributed to revising the manuscript.