Electronic Supplementary Material (ESI) for Journal of Materials Chemistry C.


**Supporting Information**

# Engineering anomalous elastic properties of coordination polymers and their amorphization by employing flexible linkers

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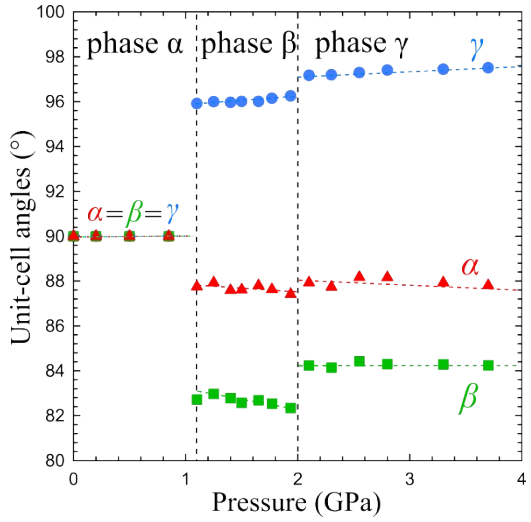


Figure S1. The unit-cell angles of $Cd(HDA)_2(NO_3)_2$ as a function of pressure. Lines are for guiding the eye only. ESDs are smaller than plotted symbols.

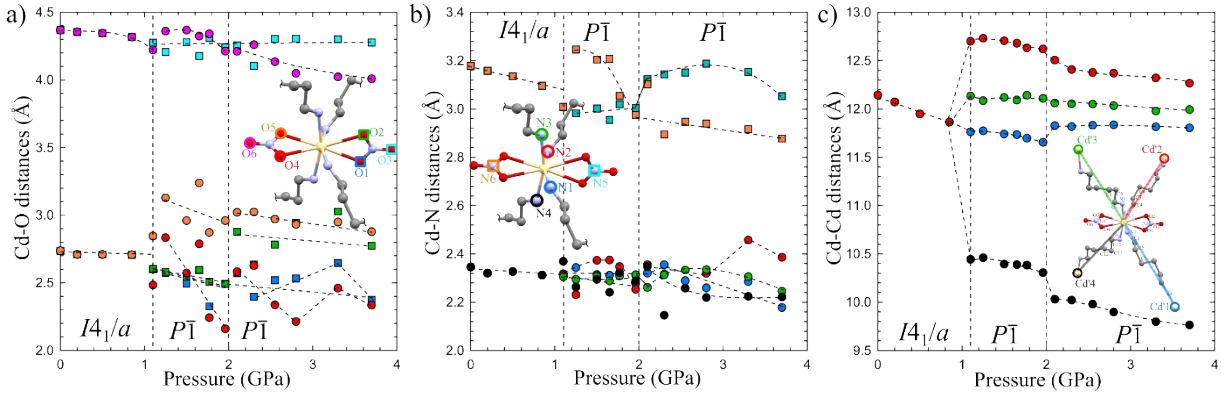


Figure S2. $Cd(HDA)_2(NO_3)_2$ coordination sphere presented as Cd-O (a), Cd-N (b) and (c) pressure-induced reduction of the Cd-Cd' distances in the function of pressure. Lines are for guiding the eye only. ESDs are smaller than plotted symbols.

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Figure S3. The molecular volume (a) unit-cell parameters (b) and unit-cell angles (c) of $Cd(HDA)_2(NO_3)_2$ presented as a function of temperature. Lines are for guiding the eye only. ESDs are smaller than plotted symbols.

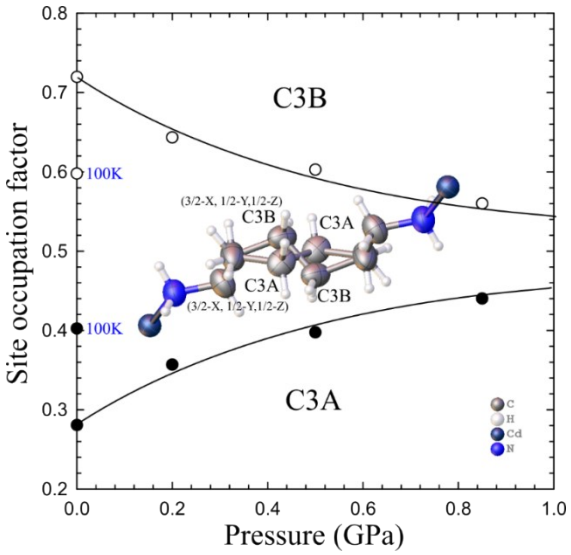
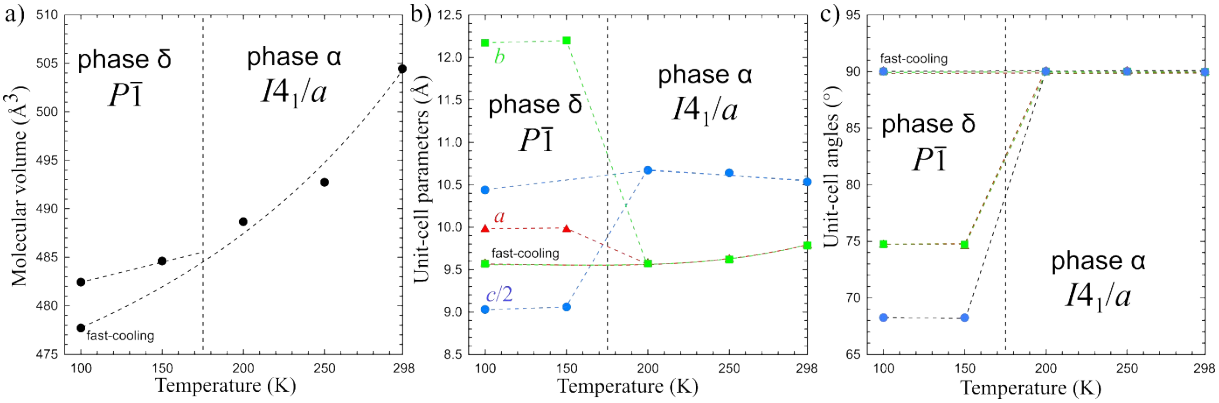



Figure S4. Site occupation factor of the disordered carbon atoms in HDA linker in α-phase. Full symbols represent the C3A atom, and open symbols C3B.



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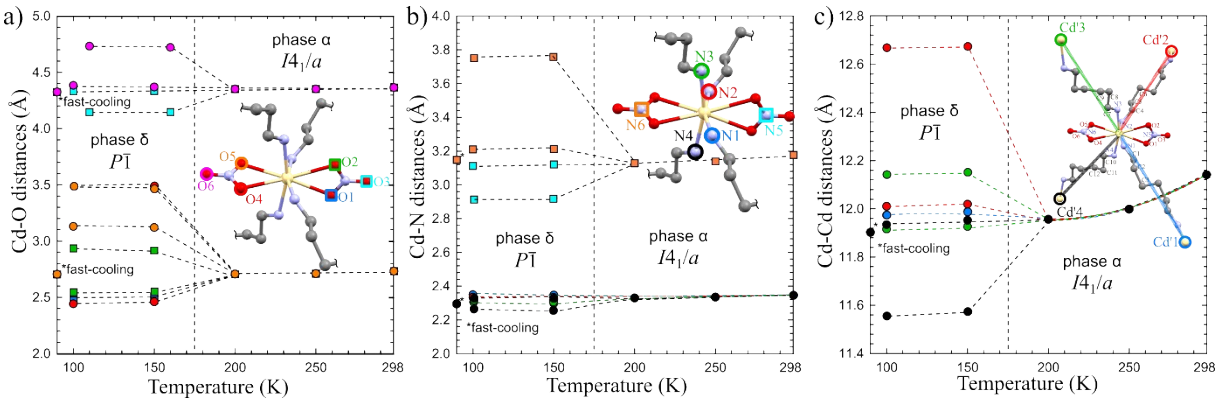


Figure S5. $Cd(HDA)_2(NO_3)_2$ coordination sphere presented as Cd-O (a), Cd-N (b) and (c) pressure-induced reduction of the Cd-Cd' distances in the function of temperature. Lines are for guiding the eye only. ESDs are smaller than plotted symbols.

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Figure S6. $Cd_2(HDA)_3(NO_3)_4$ coordination sphere presented as Cd-O (a), Cd-N (b) distances and (c) pressure-induced reduction of the Cd-Cd' in the function of pressure. Lines are for guiding the eye only. ESDs are smaller than plotted symbols, despite the model for the measurement collected at 4.30 GPa which due to a partial amorphization and additional constrains require for refining the structure is of lower quality.

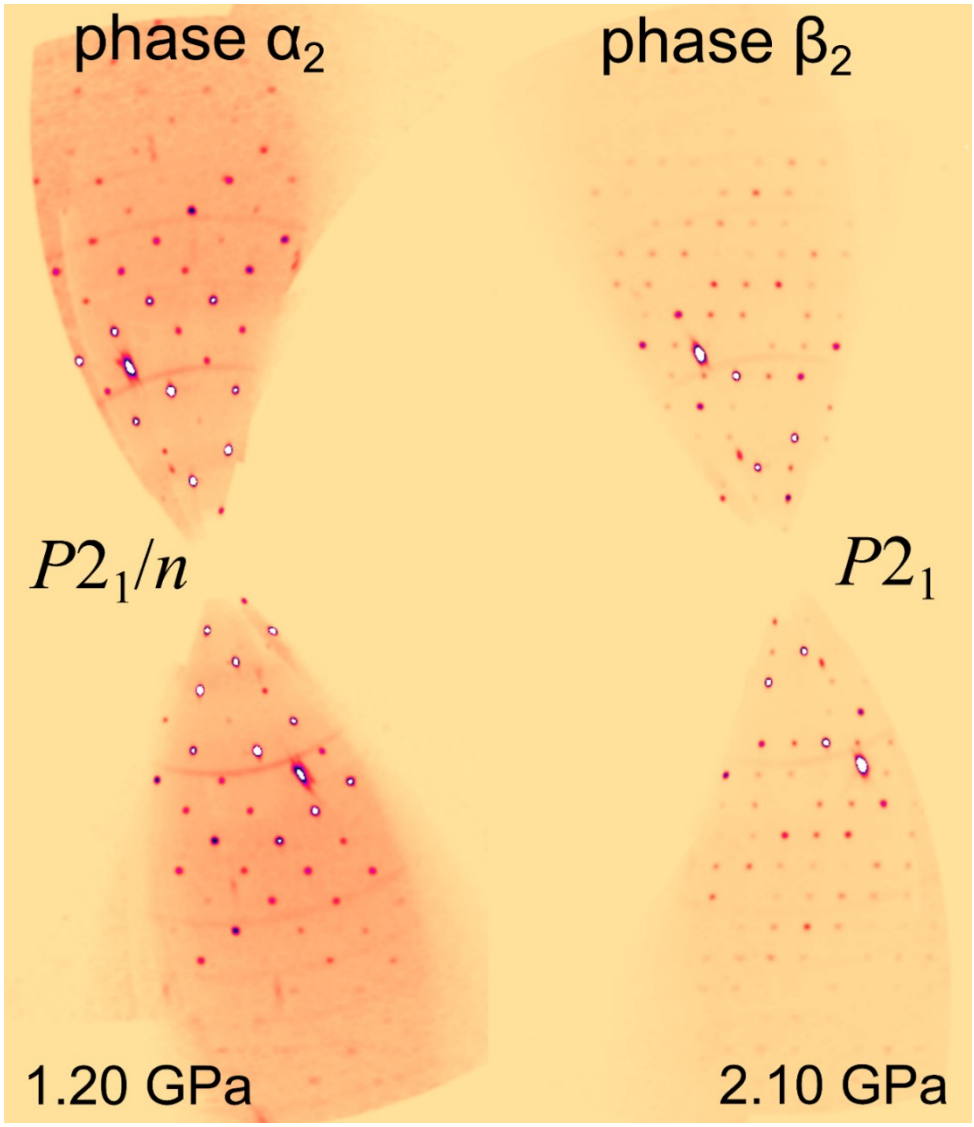
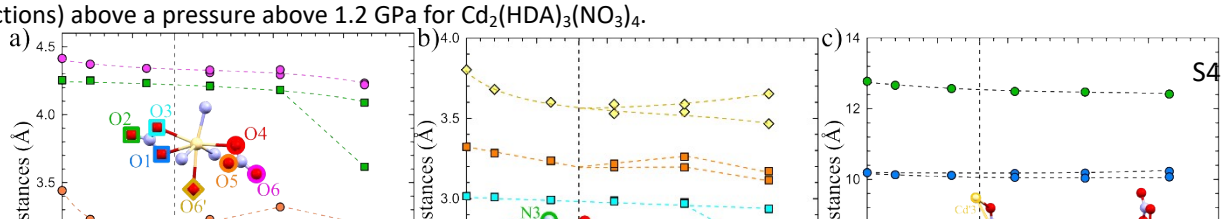



Figure S7. The h0l layers presenting the disappearance of the n glide plane (connected with appearance h + l = n reflections) above a pressure above 1.2 GPa for $Cd_2(HDA)_3(NO_3)_4$.



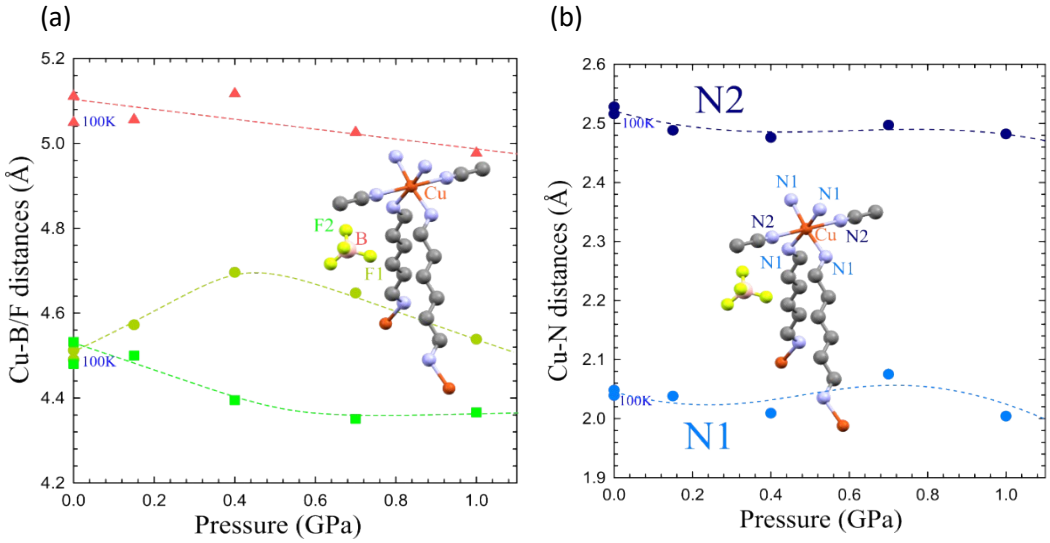



Figure S8. Changes in the $Cu(HDA)_2(MeCN)_2 \cdot 2BF_4$ coordination sphere presented as a distances (a) Cu-B and Cu-F and (b) Cu-N distances pressure-induced reduction of the Cu-Cu' distance. Lines are for guiding the eye. ESDs are smaller than plotted symbols.

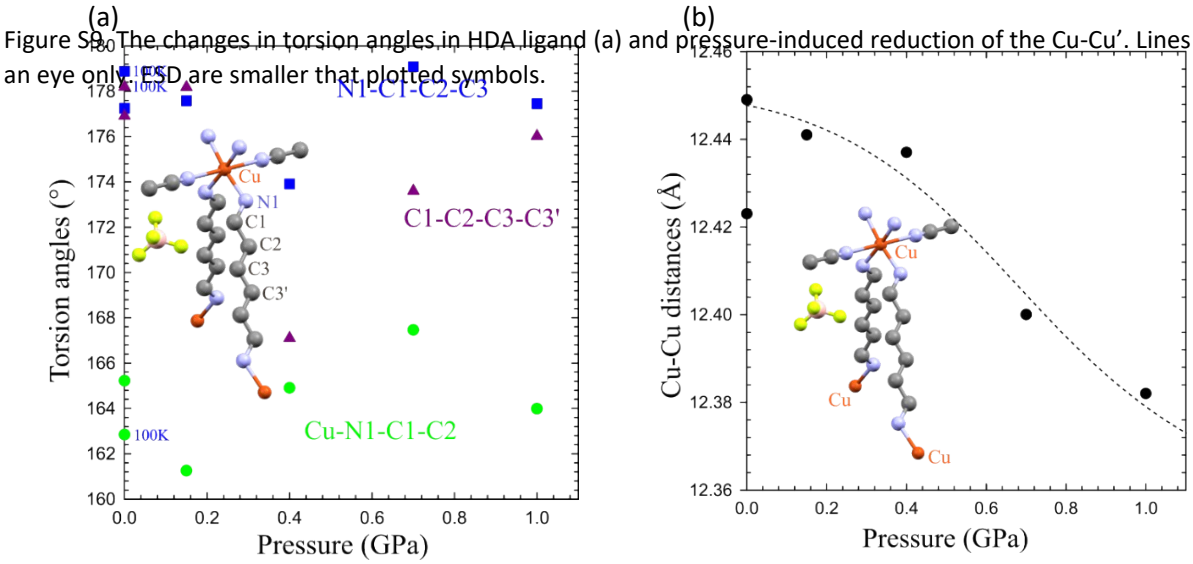



Figure S9. The changes in torsion angles in HDA ligand (a) and pressure-induced reduction of the Cu-Cu'. Lines are for guiding an eye only. ESD are smaller that plotted symbols.

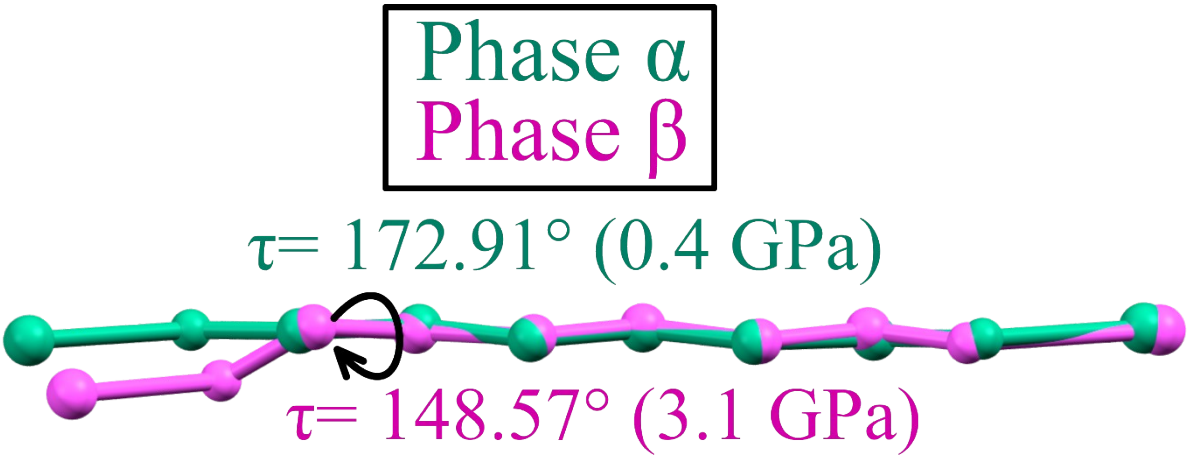
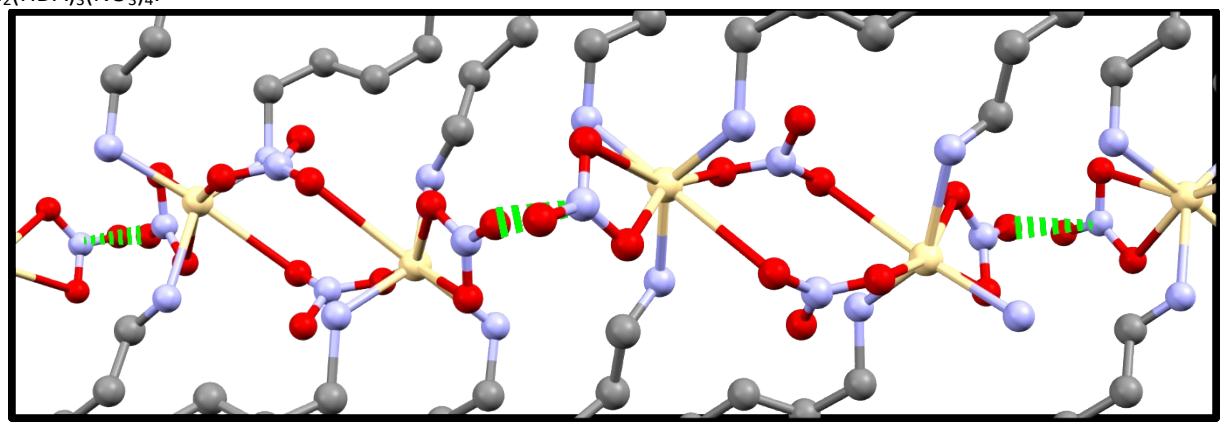



Figure S10. Conformational changes in the HDA linker in $Cd_2(HDA)_3(NO_3)_4$, $C_i$-symmetric HDA from phase α (green) superimposed on HDA of phase β (pink). The torsion angles N3-C7-C8-C9 (τ) indicates the conformational change between phase α at 0.4 GPa (green) and phase β at 3.1 GPa (pink).

Figure S11. The adjacent binuclear centers bonded by a π-hole interaction $NO_3\cdots NO_3$ between bidentate nitrate groups in $Cd_2(HDA)_3(NO_3)_4$.



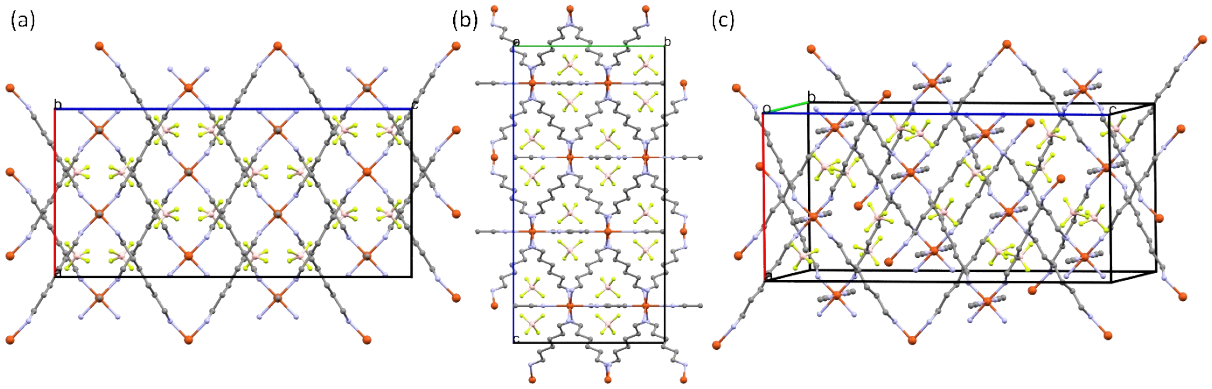



Figure S12. $Cu(HDA)_2(MeCN)_2 \cdot 2BF_4$ structures projected along direction (a) [010], (b) [100], (c) view on the diamond-like framework.

(a)

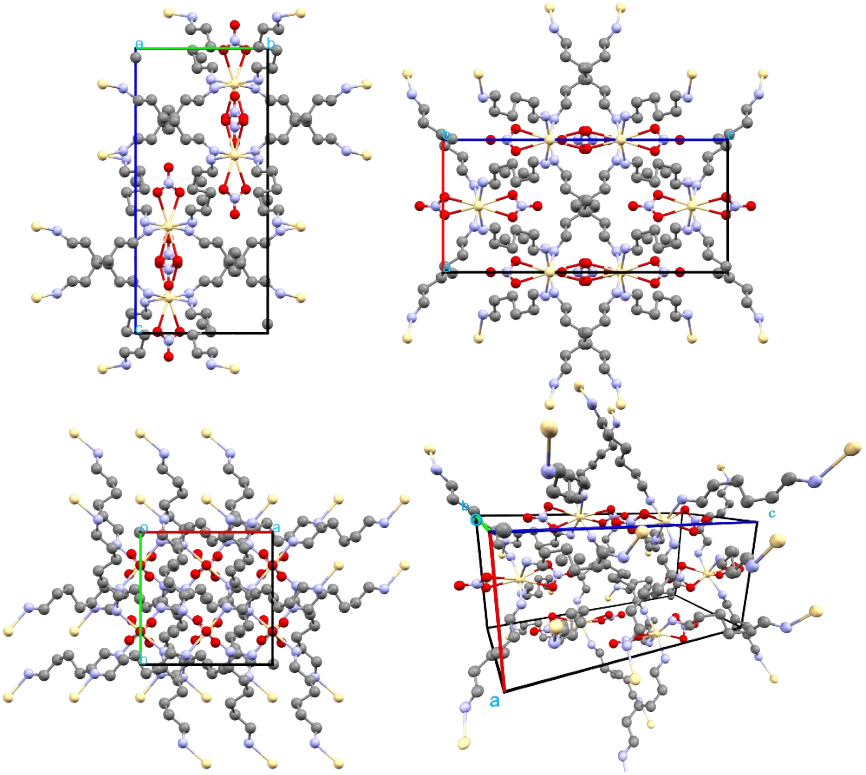
(c)

(d)

(a) (b)

(c) (d)

Figure S13. $Cd(HDA)_2(NO_3)_2$ structures projected along direction (a) [100], (b) [010], (c) [001], [d] stereographic projection of the framework.



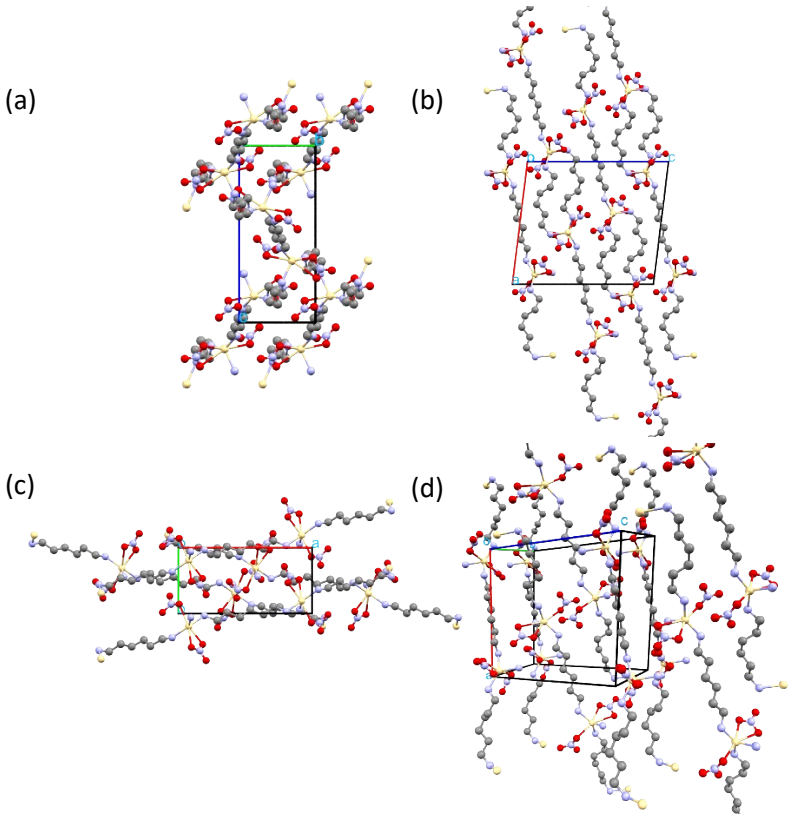



Figure S14. $Cd_2(HDA)_3(NO_3)_4$ structures projected along direction (a) [100], (b) [010], (c) [001], [d] stereographic projection of the framework.

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Figure S15. The crystal structure of (a) $Cd(HDA)_2(NO_3)_2$ ,(b) $Cd_2(HDA)_3(NO_3)_4$ , and (c) $Cu(HDA)_2(MeCN)_2{\cdot}2BF_4$ with the void spaces calculated by program Mercury[1] as contact surface with probe radius 0.8 Å and grid step 0.1 Å. There are no voids larger than 0.8 Å in radius, capable of absorbing guest molecules.

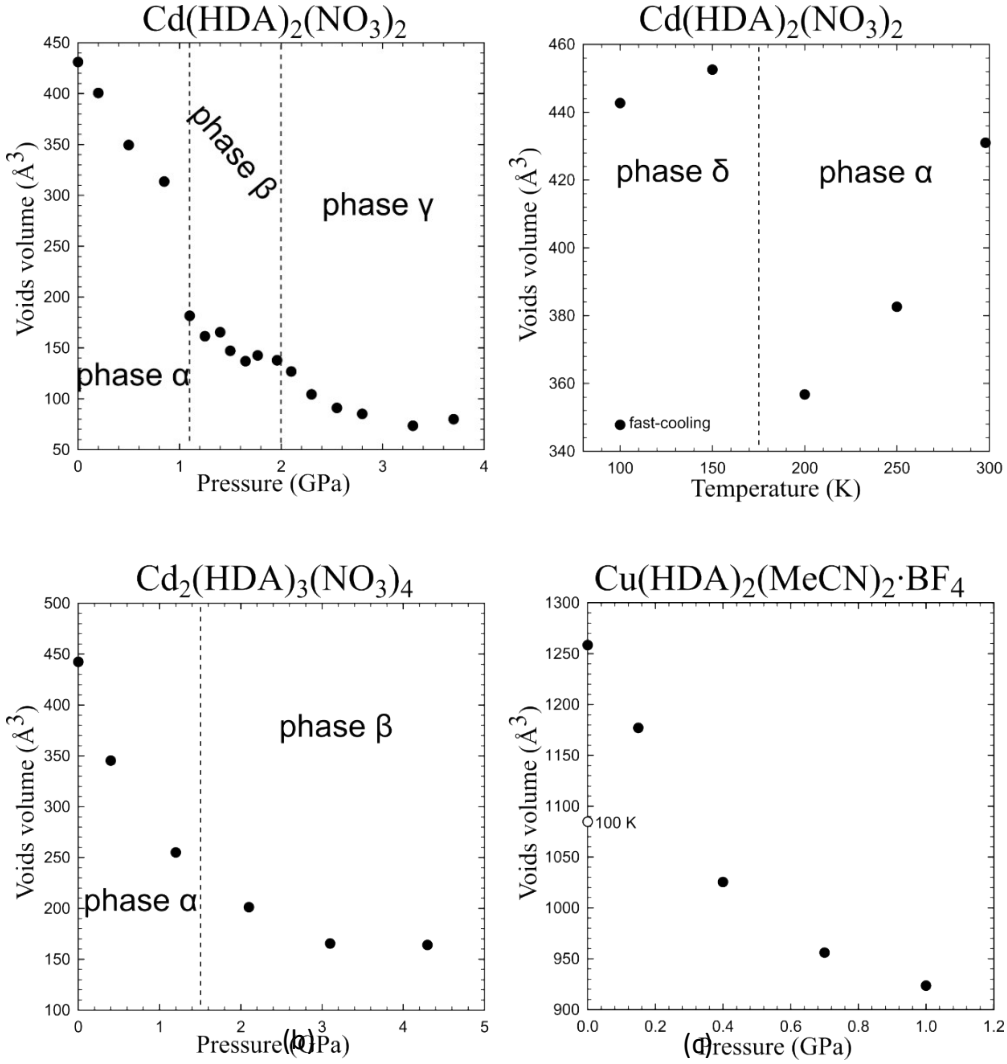
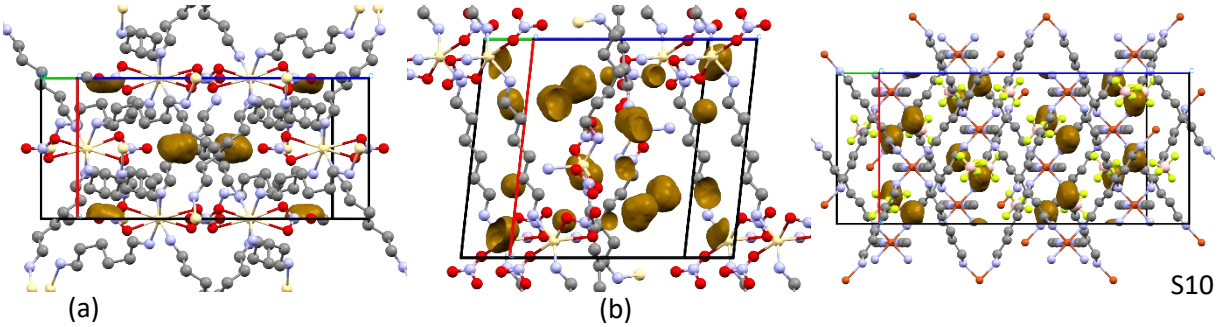
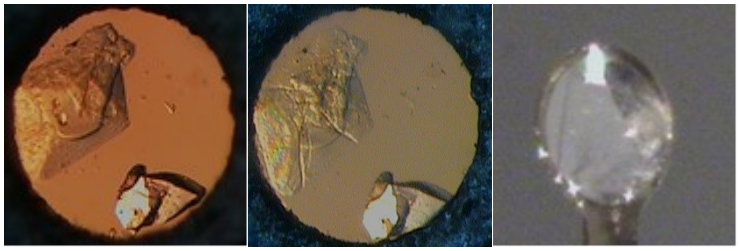



Figure S16. Change in the volume of the free voids calculated by Mercury[1] as contact surface with probe radius 0.3 Å and grid step 0.1 Å for (a) $Cd(HDA)_2(NO_3)_2$ (top left) phases α, β, γ and (b) phase δ; (c) $Cd_2(HDA)_3(NO_3)_4$ phases α and β; (d) $Cu(HDA)_2(MeCN)_2$ (bottom right).



(a) (b) (c)

Figure S17. $Cd(HDA)_2(NO_3)_2$ crystal at (a) 0.7 GPa, (b) 3.6 GPa in DAC as well as (c) the recovered single-crystal mounted on a nylon loop for the X-ray diffraction experiment at room-conditions. The unit-cell dimensions of the crystal before and after the compression are compared below:



| $Cd(HDA)_2(NO_3)_2$ | *a* (Å) | *b* (Å) | *c* (Å) | *V* (Å$^3$) |
|---|---|---|---|---|
| as-synthesized | 9.7855(7) | 9.7855(7) | 21.071(3) | 2017.7(4) |
| post-compressed | 9.7589(4) | 9.7589(4) | 21.026(5) | 2002.4 (8) |

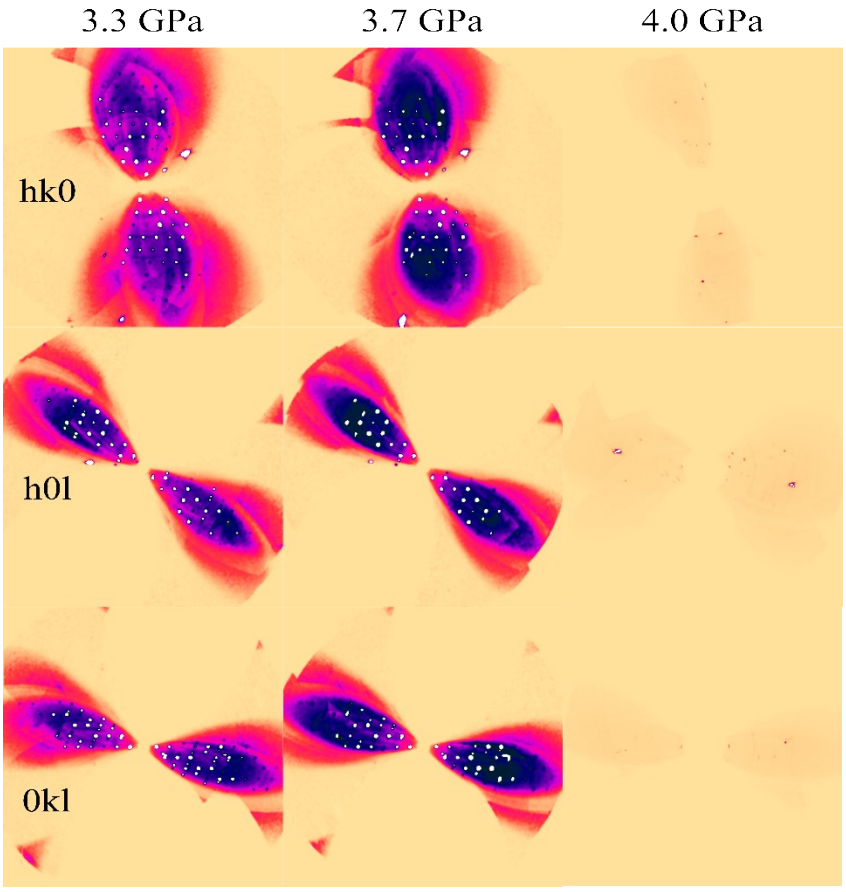



Figure S18. Reconstruction of reciprocal layers for the $Cd(HDA)_2(NO_3)_2$ crystal, showing decrease in the reflection intensities.

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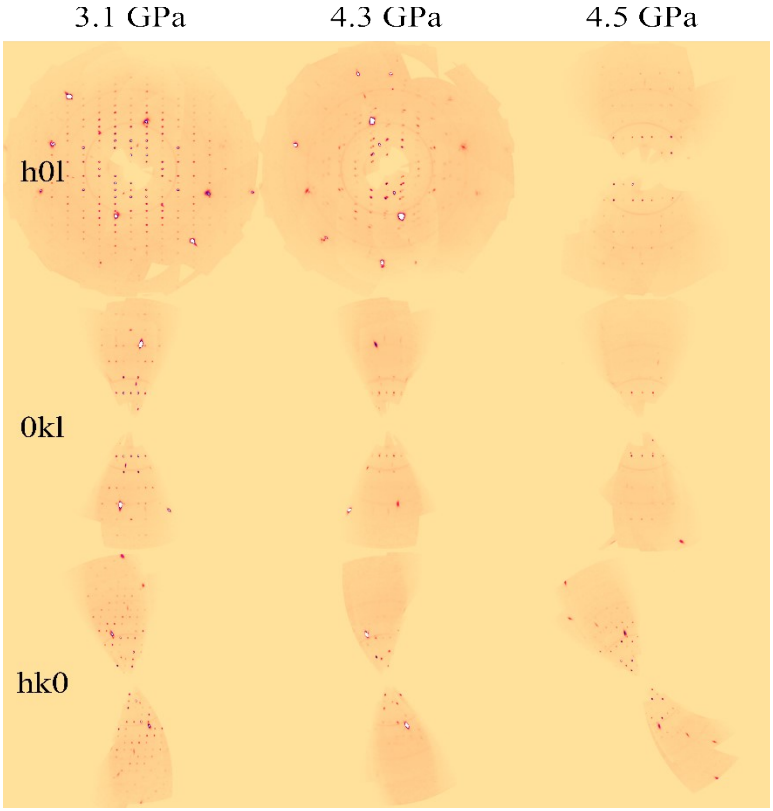
Figure S19. Reconstruction of reciprocal layers for the $Cd_2(HDA)_3(NO_3)_4$ crystal, showing decrease in the reflection intensities.



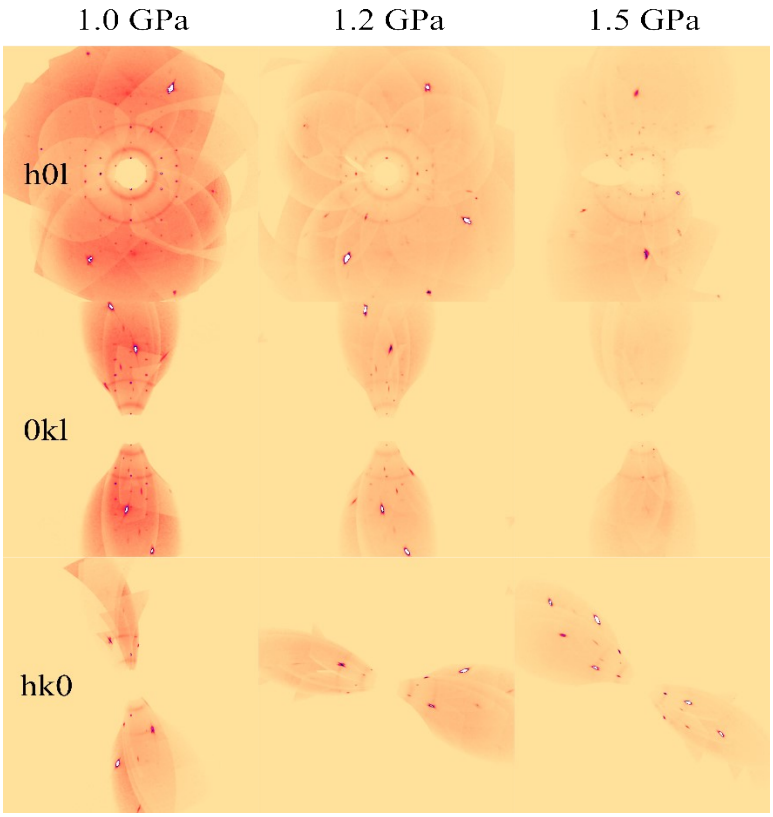



Figure S20. Reconstruction of reciprocal layers for the $Cu(HDA)_2(MeCN)_2$· crystal, showing decrease in the reflection intensities.

Reference:

(1) Macrae, C. F.; Bruno, I. J.; Chisholm, J. A.; Edgington, P. R.; Mccabe, P.; Pidcock, E.; Rodriguez-monge, L.; Taylor, R.; Streek, J. Van De; Wood, P. A. Mercury CSD 2 . 0 – New Features for the Visualization and Investigation of Crystal Structures. *J. Appl. Cryst.* **2008**, *41*, 466–470. https://doi.org/10.1107/S0021889807067908.

**Table S1.** Selected large volume changes at phase transitions and compressibilities of our coordination polymers and other compounds reported in the literature.

| Material | Application | ΔV/V (%) at $p_c$ | Volume compressibility ($GPa^{-1}$) at 0.1 MPa | Reference |
|---|---|---|---|---|
| $Cd(HDA)_2(NO_3)_2$ | Shock-absorber | (α→β) 5% at 1.1 GPa<br>(β→γ) 1% at 2.0 GPa | α 0.092(2)<br>β 0.027(3)<br>γ 0.062(2) | This work |
| $Cd_2(HDA)_3(NO_3)_4$ | Shock-absorber | 4% at 1.5 GPa | α 0.141(4)<br>β 0.043(2) | This work |
| $Cu(HDA)_2(MeCN)_2{\cdot}2BF_4$ | Shock-absorber | N/A | 0.219(2) | This work |
| MIL53(Al) | Nano-shock | 41% at 19 | Theory prediction | *Chem. Commun.*, |

| | | | | | |
|---|---|---|---|---|---|
| | absorber | MPa | | | **2014**, 50, 9462 |
| MIL53(Cr) | Nano-damper | 6% at 53.5 MPa | N/A | | *J. Phys. Chem. C* **2012**, 116, 13289-13295 |
| CUK-1 | Nano-springs | 21% at 0.4 GPa | I<br>II | 0.292(3)<br>0.068(3) | *Chem. Sci.,* **2021**, 12, 5682 |
| $MHy_2PbBr_4$ | Photodetector | 1% at 4.1 GPa | III<br>IV | 0.043(1)<br>0.026(1) | *Chem. Mater.* **2022**, 34, 7867−7877 |
| $[FA]Mn(H_2POO)_3$ | Solar-cell | 2% at 3.9 GPa | α<br>γ | 0.030(1)<br>0.003(2) | *J. Phys. Chem. C* **2021,**125,26958-26966 |
| AMU3·DMF | Sensor | 2% at 0.4 GPa | α<br>β | 0.128(3)<br>0.024(2) | *Mater. Adv*. **2021**,2, 4677-4684 |
| AMU3·MeCN | Sensor | 1% at 0.7 GPa | α<br>β | 0.051(2)<br>0.005(2) | *Mater. Adv*. **2021**,2, 4677-4684 |
| $Ag_3[Co(CN)_6]$ | Optical material | 16% at 0.19 GPa | I<br>II | 0.152(2)<br>0.026(3) | *Proc. Natl. Acad. Sci.* **2008,** 105, 18708-18713 |
| $T[PrA][Mn(dca)_3]$ | Barocaloric | 1% at 6.89 MPa | N/A | | *Nat. Commun*., **2017** 8, 15715 |
| NPG | barocaloric | 4.9% | N/A | | *Nat. Commun*., **2019** 10, 1803 |

**Table S2.** Crystallographic data of $Cd(HDA)_2(NO_3)_2$ phases α, β and γ.

| Phase | Phase | | β | αβ | α γ | α γ | β γ | β γ | β γ | γβ | β γ |
|---|---|---|---|---|---|---|---|---|---|---|---|
| CCDC number | CCDC number | | 2262346 | 2262338 2262347 | 2262339 2262348 | 2262340 2262349 | 2262341 2262350 | 2262342 2262351 | 2262343 2262352 | 2262344 2262353 | 2262345 2262354 |
| Pressure | | | 0.0001 | 0.2 | 0.5 | 0.85 | 1.1 | 1.25 | 1.4 | 1.5 | 1.65 |
| Temperature (K) | | | 293 | 293 | 293 | 293 | 293 | 293 | 293 | 293 | 293 |
| Formula weight | | | 234.42 | 234.42 | 234.26 | 233.32 | 234.42 | 234.42 | 234.42 | 234.42 | 234.42 |
| Wavelength (Å) | | | 0.71073 | 0.71073 | 0.71073 | 0.71073 | 0.71073 | 0.71073 | 0.71073 | 0.71073 | 0.71073 |
| Crystal system | | | tetragonal | tetragonal | tetragonal | tetragonal | triclinic | triclinic | triclinic | triclinic | triclinic |
| Space group | | | $I4_1/a$ | $I4_1/a$ | $I4_1/a$ | $I4_1/a$ | $P\bar{1}$ | $P\bar{1}$ | $P\bar{1}$ | $P\bar{1}$ | $P\bar{1}$ |
| Unit cell dimensions | *a* (Å) | | 9.7855(7) | 9.7210(7) | 9.6225(8) | 9.5693(6) | 9.350(2) | 9.369(2) | 9.3296(18) | 9.3399(16) | 9.340(3) |
| | *b* (Å) | | 9.7855(7) | 9.7210(7) | 9.6225(8) | 9.5693(6) | 9.7253(18) | 9.730(2) | 9.719(3) | 9.7227(16) | 9.701(4) |
| | *c* (Å) | | 21.071(3) | 21.012(2) | 20.790(3) | 20.504(3) | 11.181(5) | 11.176(3) | 11.132(6) | 11.104(3) | 11.109(4) |
| | *α (°)* | | 90 | 90 | 90 | 90 | 110.90(3) | 111.06(2) | 110.81(4) | 110.89(2) | 111.06(4) |
| | *β(°)* | | 90 | 90 | 90 | 90 | 105.07(3) | 105.360(20) | 105.15(3) | 105.022(19) | 105.20(3) |
| | *γ(°)* | | 90 | 90 | 90 | 90 | 95.909(17) | 95.987(19) | 95.96(2) | 96.004(14) | 95.86(3) |
| Volume (Å$^3$) | | | 2017.7(4) | 1985.6(4) | 1925.0(4) | 1877.5(4) | 895.3(5) | 893.9(4) | 888.7(6) | 887.9(4) | 884.6(6) |
| Z/Z′ | | | 8/0.5 | 8/0.5 | 8/0.5 | 8/0.5 | 4/2 | 4/2 | 4/2 | 4/2 | 4/2 |
| Molecular volume (*V/Z*) | | | 252.21 | 248.2 | 240.625 | 234.69 | 223.82 | 223.47 | 222.17 | 221.98 | 221.15 |
| Calculated density (g/cm$^3$) | | | 1.543 | 1.568 | 1.617 | 1.651 | 1.709 | 1.742 | 1.752 | 1.754 | 1.760 |
| Absorption (mm$^{-1}$) | | | 1.120 | 1.138 | 1.174 | 1.203 | 1.261 | 1.264 | 1.272 | 1.273 | 1.278 |
| *F*(000) | | | 968.0 | 968.0 | 967.0 | 963.0 | 468.0 | 484.0 | 484.0 | 484.0 | 484.0 |
| Crystal size (mm) | | | 0.099 × 0.067 × 0.056 | 0.25 × 0.16 × 0.05 | 0.25 × 0.16 × 0.05 | 0.25 × 0.16 × 0.05 | 0.24 × 0.15 × 0.05 | 0.24 × 0.15 × 0.05 | 0.24 × 0.15 × 0.05 | 0.24 × 0.15 × 0.05 | 0.24 × 0.15 × 0.05 |
| 2$\vartheta$-range for data collection (°) | | | 7.046 to 57.566 | 8.386 to 52.606 | 7.158 to 52.85 | 7.216 to 59.988 | 4.592 to 54.042 | 4.13 to 56.774 | 6.898 to 51.33 | 4.596 to 56.574 | 4.15 to 56.496 |
| Min/max indices: *h, k, l* | | | -13/13,-6/7,-13/27 | -12/12,-5/6,-24/23 | -9/9,-10/10, -24/24 | -10/9,-11/11,-25/26 | -11/11,-12/12,-9/9 | -8/8,-11/11, -14/14 | -11/11,-11/11,-11/11 | -12/12,-12/12, -8/8 | -7/7,-11/10,-13/13 |
| Reflect. Collected/unique | | | 1809/949 | 4280/671 | 2434/586 | 3228/687 | 5566/852 | 15465/1139 | 5909/858 | 7141/891 | 6284/87 |
| $R_{int}$ | | | 0.0270 | 0.1310 | 0.0383 | 0.0642 | 0.1353 | 0.1148 | 0.2850 | 0.1418 | 0.1620 |
| Refinement method | | | Full-matrix least-squares on F$^2$ | | | | | | | | |
| Completeness (%) | | | 84.3 | 69.5 | 62.8 | 64.0 | 35.6 | 40.05 | 25.8 | 34.7 | 35.8 |
| Data/restrains/parameters | | | 949/1/68 | 671/6/68 | 586/0/68 | 687/0/62 | 852/400/226 | 1139/403/227 | 858/406/226 | 891/403/226 | 877/300/226 |
| Goodness-of-fit on F$^2$ | | | 1.078 | 1.167 | 1.040 | 1.162 | 1.675 | 1.080 | 1.808 | 1.101 | 1.084 |
| Final R1/wR$^2$ (I>2σ1) | | | 0.0457/0.0816 | 0.0771/0.1761 | 0.0322/0.0636 | 0.0669/0.1172 | 0.1154/0.3078 | 0.0806/0.1835 | 0.1980/0.4378 | 0.0851/0.2049 | 0.0866/0.2119 |
| R1/wR$^2$ (all data) | | | 0.0726/0.0944 | 0.1322/0.2479 | 0.0501/0.0693 | 0.1133/0.1731 | 0.1691/0.3855 | 0.1078/0.2064 | 0.2897/0.5365 | 0.1307/0.2517 | 0.1071/0.2348 |
| Largest diff. peak/hole (e.Å$^{-3}$) | | | 0.27/-0.29 | 0.51/-0.52 | 0.27/-0.24 | 0.69/-0.74 | 0.84/-0.90 | 0.57/-0.60 | 0.94/-0.89 | 0.71/-0.86 | 0.65/-0.80 |

$w=1/(\sigma^2 F_o^2+w_1^2*P^2+w_2*P)$, where $P=(\mathrm{Max}(F_o^2,0)+2*F_c^2)$

| Pressure | | 1.77 | 1.96 | 2.1 | 2.3 | 2.55 | 2.8 | 3.3 | 3.7 |
|---|---|---|---|---|---|---|---|---|---|
| Temperature (K) | | 293 | 293 | 293 | 293 | 293 | 293 | 293 | 293 |
| Formula weight | | 234.42 | 234.42 | 234.42 | 234.42 | 234.42 | 234.42 | 234.42 | 234.42 |
| Wavelength (Å) | | 0.71073 | 0.71073 | 0.71073 | 0.71073 | 0.71073 | 0.71073 | 0.71073 | 0.71073 |
| Phase | | α | α | α | δ | δ | α | | |
| Crystal system | | triclinic | triclinic | triclinic | triclinic | triclinic | triclinic | triclinic | triclinic |
| Space group | | $P\bar{1}$ | $P\bar{1}$ | $P\bar{1}$ | $P\bar{1}$ | $P\bar{1}$ | $P\bar{1}$ | $P\bar{1}$ | $P\bar{1}$ |
| Unit cell dimensions | *a* (Å) | 9.319(3) | 9.2950(18) | 9.264(3) | 9.234(2) | 9.202(3) | 9.188(2) | 9.147(2) | 9.127(2) |
| | *b* (Å) | 9.7075(18) | 9.6793(19) | 9.585(3) | 9.5879(16) | 9.608(2) | 9.5899(16) | 9.5510(17) | 9.5346(18) |
| | *c* (Å) | 11.051(5) | 10.957(3) | 11.069(4) | 10.970(5) | 10.973(6) | 10.926(4) | 10.842(5) | 10.805(5) |
| | *α (°)* | 110.92(3) | 110.80(2) | 110.41(3) | 110.44(3) | 110.88(4) | 110.87(2) | 110.73(3) | 110.62(3) |
| | *β(°)* | 104.97(3) | 104.87(2) | 105.98(3) | 106.00(3) | 106.16(4) | 106.04(3) | 106.08(3) | 106.02(3) |
| | *γ(°)* | 96.149(18) | 96.250(16) | 97.17(3) | 97.186(17) | 97.29(2) | 97.405(17) | 97.435(17) | 97.498(18) |
| Volume (Å$^3$) | | 879.9(5) | 868.6(4) | 858.6(5) | 848.0(5) | 842.5(6) | 836.4(4) | 823.5(5) | 818.3(5) |
| Z/Z' | | 4/2 | 4/2 | 4/2 | 4/2 | 4/2 | 4/2 | 4/2 | 4/2 |
| Molecular volume (*V/Z*) | | 219.98 | 217.15 | 214.65 | 212.0 | 210.62 | 209.10 | 205.87 | 204.57 |
| Calculated density (g/cm$^3$) | | 1.770 | 1.793 | 1.813 | 1.836 | 1.848 | 1.862 | 1.883 | 1.899 |
| Absorption (mm$^{-1}$) | | 1.284 | 1.301 | 1.316 | 1.333 | 1.341 | 1.351 | 1.372 | 1.381 |
| *F*(000) | | 484.0 | 484.0 | 484.0 | 484.0 | 484.0 | 484.0 | 484.0 | 484.0 |
| Crystal size (mm) | | 0.24 × 0.15 × 0.05 | 0.24 × 0.15 × 0.05 | 0.24 × 0.15 × 0.05 | 0.24 × 0.15 × 0.05 | 0.24 × 0.15 × 0.05 | 0.24 × 0.15 × 0.05 | 0.24 × 0.15 × 0.05 | 0.24 × 0.15 × 0.05 |
| 2$\vartheta$-range for data collection (°) | | 4.606 to 56.526 | 4.616 to 56.56 | 5.772 to 59.798 | 7.308 to 49.648 | 4.69 to 56.71 | 4.698 to 55.666 | 4.714 to 56.584 | 4.718 to 56.344 |
| Min/max indices: *h, k, l* | | -12/12,-12/12,-8/8 | -12/12,-12/12,-8/8 | -11/11,-9/10, -10/10 | -10/10,-11/11,-9/9 | -12/11,-12/12,-8/9 | -11/11,-12/12,-8/8 | -11/11,-12/12,-9/9 | -11/11,-12/12,-9/9 |
| Reflect. Collected/unique | | 6027/885 | 5986/858 | 5871/985 | 5773/665 | 5255/826 | 5631/788 | 6161/825 | 7462/806 |
| $R_{int}$ | | 0.0895 | 0.0810 | 0.1217 | 0.1092 | 0.1037 | 0.0932 | 0.0762 | 0.1696 |
| Refinement method | | Full-matrix least-squares on $F^2$ | | | | | | | |
| Completeness (%) | | 34.1 | 34.6 | 25.7 | 22.8 | 34.7 | 34.2 | 35.3 | 35.8 |
| Data/restrains/parameters | | 885/421/227 | 858/386/226 | 985/208/208 | 665/386/208 | 826/464/197 | 788/363/209 | 825/409/208 | 806/443/208 |
| Goodness-of-fit on $F^2$ | | 1.111 | 1.164 | 1.056 | 1.589 | 1.073 | 1.057 | 1.068 | 1.731 |
| Final R1/w$R^2$ (I>2σ1) | | 0.0949/0.2060 | 0.0888/0.2164 | 0.0732/0.1909 | 0.1111/0.3163 | 0.0957/0.2051 | 0.1094/0.2692 | 0.0879/0.1954 | 0.1337/0.3530 |
| R1/w$R^2$ (all data) | | 0.1599/0.2567 | 0.1438/0.2706 | 0.1497/0.2402 | 0.1506/0.3571 | 0.1652/0.2626 | 0.1402/0.3037 | 0.1206/0.2253 | 0.1802/0.4103 |
| Largest diff. peak/hole (e.Å$^{-3}$) | | 0.75/-0.68 | 0.78/-0.87 | 0.34/-0.31 | 0.61/-0.83 | 0.83/-0.62 | 0.88/-0.67 | 0.83/-0.83 | 0.89/-1.36 |

$w=1/(\sigma^2 F_o^2+w_1^2 * P^2+w_2 * P)$, where $P=(\mathrm{Max}(F_o^2,0)+2 * F_c^2)$

**Table S2.** Crystallographic data of $Cd(HDA)_2(NO_3)_2$ phases α and δ.

| CCDC number | | 2262371 | 2262354 | 2262355 | 2262356 | 2262357 | 2262358 |
|---|---|---|---|---|---|---|---|
| Pressure | | 0.0001 | 0.0001 | 0.0001 | 0.0001 | 0.0001 | 0.0001 |
| Phase | | α | α | α | β | β | β |
| Temperature (K) | | 293 | 250 | 200 | 150 | 100 | 100* |
| CCDC number | | 2262359 | 2262360 | 2262361 | 2262362 | 2262363 | 2262364 |
| Formula weight | | 234.42 | 234.42 | 234.42 | 468.83 | 468.83 | 234.42 |
| Pressure | | 0.0001 | 0.4 | 1.2 | 2.1 | 3.1 | 4.3 |
| Wavelength (Å) | | 0.71073 | 0.71073 | 0.71073 | 0.71073 | 0.71073 | 0.71073 |
| Crystal system | | tetragonal | tetragonal | tetragonal | triclinic | triclinic | tetragonal |
| Space group | | $I4_1/a$ | $I4_1/a$ | $I4_1/a$ | $P\bar{1}$ | $P\bar{1}$ | $I4_1/a$ |
| Unit cell dimensions | *a* (Å) | 9.7855(7) | 9.6193(2) | 9.5708(2) | 9.9696(8) | 9.9729(8) | 9.5843(7) |
| | *b* (Å) | 9.7855(7) | 9.6193(2) | 9.5708(2) | 12.2010(9) | 12.1703(10) | 9.5843(7) |
| | *c* (Å) | 21.071(3) | 21.2771(8) | 21.3382(7) | 18.1134(16) | 18.0586(17) | 20.900(2) |
| | *α (°)* | 90 | 90 | 90 | 74.552(7) | 74.687(7) | 90 |
| | *β(°)* | 90 | 90 | 90 | 74.701(7) | 74.744(7) | 90 |
| | *γ(°)* | 90 | 90 | 90 | 68.229(7) | 68.239(7) | 90 |
| Volume (Å$^3$) | | 2017.7(4) | 1968.79(11) | 1954.58(10) | 1938.4(3) | 1929.7(3) | 1919.9(3) |
| Z/Z' | | 8/0.5 | 8/0.5 | 8/0.5 | 8/4 | 8/4 | 8/0.5 |
| Molecular volume (*V/Z*) | | 252.21 | 246.10 | 244.32 | 242.30 | 241.21 | 240.00 |
| Calculated density (g/cm$^3$) | | 1.543 | 1.582 | 1.593 | 1.607 | 1.614 | 1.622 |
| Absorption (mm$^{-1}$) | | 1.120 | 1.148 | 1.156 | 1.166 | 1.171 | 1.177 |
| *F*(000) | | 968.0 | 968.0 | 968.0 | 968.0 | 968.0 | 968.0 |
| Crystal size (mm) | | 0.099 × 0.067 × 0.056 | 0.307 × 0.213 × 0.127 | 0.307 × 0.213 × 0.127 | 0.307 × 0.213 × 0.127 | 0.307 × 0.213 × 0.127 | 0.325 × 0.256 × 0.198 |
| 2$\vartheta$-range for data collection (°) | | 7.046 to 57.566 | 4.648 to 61.302 | 4.664 to 61.208 | 5.422 to 52.746 | 4.664 to 61.304 | 7.166 to 56.718 |
| Min/max indices: *h, k, l* | | -13/13,-6/7,-13/27 | -12/13,-13/13,-28/29 | -12/13,-13/13, -28/29 | -12/12,-15/15,-22/22 | -14/13,-17/17,-24/25 | -12/12,-10/12, -25/27 |
| Reflect. Collected/unique | | 1809/949 | 12931/1449 | 12842/1444 | 19863/7845 | 23553/10332 | 5245/1155 |
| $R_{int}$ | | 0.0270 | 0.0330 | 0.0316 | 0.0687 | 0.0774 | 0.0358 |
| Refinement method | | Full-matrix least-squares on $F^2$ | | | | | |
| Completeness (%) | | 84.3 | 100 | 100 | 99.2 | 99.2 | 99.1 |
| Data/restrains/parameters | | 949/1/68 | 1449/0/68 | 1444/0/68 | 7845/12/451 | 10332/0/451 | 1155/31/68 |
| Goodness-of-fit on $F^2$ | | 1.078 | 1.071 | 1.059 | 1.088 | 1.088 | 1.180 |
| Final R1/w$R^2$ (I>2σ1) | | 0.0457/0.0816 | 0.0261/0.0572 | 0.0212/0.0463 | 0.0862/0.2192 | 0.0939/0.2258 | 0.0713/0.1590 |
| R1/w$R^2$ (all data) | | 0.0726/0.0944 | 0.0337/0.0598 | 0.0269/0.0486 | 0.1280/0.2468 | 0.1538/0.2613 | 0.0775/0.1613 |
| Largest diff. peak/hole (e.Å$^{-3}$) | | 0.27/-0.29 | 0.39/-0.21 | 0.31/-0.18 | 3.81/-1.14 | 4.95/-1.44 | 1.51/-0.83 |

$w=1/(\sigma^2 F_o^2+w_1^2 * P^2+w_2 * P)$, where $P=(\mathrm{Max}(F_o^2,0)+2*F_c^2)$

*fast-cooled crystal

**Table S3.** Crystallographic data of $Cd_2(HDA)_3(NO_3)_4$ phases α and β.

| Temperature (K) | | 293 | 293 | 293 | 293 | 293 | 293 |
|---|---|---|---|---|---|---|---|
| Formula weight | | 410.73 | 410.73 | 410.73 | 410.73 | 410.73 | 410.73 |
| Phase | | α | α | α | α | α | α* |
| Wavelength (Å) | | 0.71073 | 0.71073 | 0.71073 | 0.71073 | 0.71073 | 0.71073 |
| CCDC number | | 2262365 | 2262366 | 2262367 | 2262368 | 2262369 | 2262370 |
| Crystal system | | monoclinic | monoclinic | monoclinic | monoclinic | monoclinic | monoclinic |
| Space group | | $P2_1/n$ | $P2_1/n$ | $P2_1/n$ | $P2_1$ | $P2_1$ | $P2_1$ |
| Unit cell dimensions | *a* (Å) | 14.3304(4) | 14.316(10) | 14.276(14) | 14.206(12) | 14.188(11) | 14.10(4) |
| | *b* (Å) | 7.0034(2) | 6.8838(4) | 6.7318(5) | 6.6183(4) | 6.5088(3) | 6.4726(15) |
| | *c* (Å) | 16.3600(7) | 15.7250(18) | 15.218(2) | 14.9354(14) | 14.7051(11) | 14.568(5) |
| | *α (°)* | 90 | 90 | 90 | 90 | 90 | 90 |
| | *β(°)* | 97.033(3) | 97.17(3) | 96.72(4) | 96.11(3) | 95.70(3) | 94.60(11) |
| | *γ(°)* | 90 | 90 | 90 | 90 | 90 | 90 |
| Volume (Å$^3$) | | 1629.56(10) | 1537.5(11) | 1452.5(14) | 1396.2(12) | 1351.2(10) | 1325(4) |
| Z/Z' | | 4/1 | 4/1 | 4/1 | 4/1 | 4/1 | 4/1 |
| Molecular volume (*V/Z*) | | 407.39 | 384.37 | 363.12 | 349.05 | 337.80 | 331.25 |
| Calculated density (g/cm$^3$) | | 1.674 | 1.774 | 1.878 | 1.954 | 2.019 | 2.059 |
| Absorption (mm$^{-1}$) | | 1.373 | 1.455 | 1.540 | 1.602 | 1.655 | 1.688 |
| *F*(000) | | 836.0 | 836.0 | 836.0 | 836.0 | 836.0 | 836.0 |
| Crystal size (mm) | | 0.324 × 0.222 × 0.193 | 0.385 × 0.293 × 0.08 | 0.385 × 0.293 × 0.08 | 0.385 × 0.293 × 0.08 | 0.385 × 0.293 × 0.08 | 0.385 × 0.293 × 0.08 |
| 2$\vartheta$-range for data collection (°) | | 5.728 to 56.624 | 5.222 to 52.998 | 3.702 to 53.334 | 5.486 to 53.508 | 5.568 to 53.32 | 3.868 to 49.408 |
| Min/max indices: *h, k, l* | | -17/15,-8/9,-19/17 | -8/8,-8/8,-19/19 | -8/8,-8/8, -18/18 | -7/7,-8/8,-18/18 | -7/7,-8/8,-17/18 | -7/7,-7/7, -17/17 |
| Reflect. Collected/unique | | 11904/3524 | 12275/1061 | 11532/1001 | 11452/1834 | 10939/1726 | 8713/1508 |
| $R_{int}$ | | 0.0244 | 0.0727 | 0.0943 | 0.0821 | 0.0580 | 0.3401 |
| Refinement method | | Full-matrix least-squares on $F^2$ | | | | | |
| Completeness (%) | | 99.9 | 35.3 | 35.0 | 33.3 | 32.9 | 33.1 |
| Data/restrains/parameters | | 3524/6/190 | 1061/172/184 | 1001/151/190 | 1834/518/380 | 1726/716/379 | 1508/800/313 |
| Goodness-of-fit on $F^2$ | | 1.033 | 1.065 | 1.063 | 1.103 | 1.122 | 1.253 |
| Final R1/w$R^2$ (I>2σ1) | | 0.0369/0.0794 | 0.0479/0.1092 | 0.0524/0.1272 | 0.0523/0.1262 | 0.0658/0.1799 | 0.1558/0.3622 |
| R1/w$R^2$ (all data) | | 0.0529/0.0885 | 0.0842/0.1301 | 0.0848/0.1518 | 0.0807/0.1579 | 0.0915/0.2495 | 0.2921/0.4524 |
| Largest diff. peak/hole (e.Å$^{-3}$) | | 1.36/-0.73 | 0.51/-0.71 | 0.50/-0.41 | 0.40/-0.56 | 0.90/-1.36 | 0.82/-0.61 |

$w=1/(\sigma^2 F_o^2+w_1^2 P^2+w_2 P)$, where $P=(\mathrm{Max}(F_o^2,0)+2F_c^2)$

**Table S4.** Crystallographic data of $Cu(HDA)_2(MeCN)_2 \cdot 2BF_4$.

| Pressure | | 0.0001 | 0.15 | 0.4 | 0.7 | 1.0 | 0.0001 | 1.2* |
|---|---|---|---|---|---|---|---|---|
| Temperature (K) | | 293 | 293 | 293 | 293 | 293 | 100 | 293 |
| Formula weight | | 551.68 | 551.68 | 551.68 | 551.68 | 551.68 | 551.68 | 551.68 |
| Wavelength (Å) | | 0.71073 | 0.71073 | 0.71073 | 0.71073 | 0.71073 | 0.71073 | 0.71073 |
| Crystal system | | orthorhombic | orthorhombic | orthorhombic | orthorhombic | orthorhombic | orthorhombic | orthorhombic |
| Space group | | *Fddd* | *Fddd* | *Fddd* | *Fddd* | *Fddd* | *Fddd* | *Fddd* |
| Unit cell dimensions | *a* (Å) | 12.9608(7) | 12.99(4) | 13.19(3) | 13.23(3) | 13.220(10) | 13.084(2) | 13.26(4) |
| | *b* (Å) | 14.1880(8) | 13.946(12) | 13.731(6) | 13.517(6) | 13.480(3) | 13.9110(14) | 13.340(9) |
| | *c* (Å) | 27.6850(17) | 27.191(7) | 26.844(8) | 26.501(5) | 26.429(3) | 27.113(3) | 26.110(6) |
| Volume ($Å^3$) | | 5091.0(5) | 4924(17) | 4862(12) | 4737(12) | 4710(4) | 4934.9(10) | 4620(15) |
| Z/Z' | | 8/0.25 | 8/0.25 | 8/0.25 | 8/0.25 | 8/0.25 | 8/0.25 | 8/0.25 |
| Molecular volume (*V/Z*) | | 636.37 | 615.5 | 607.75 | 592.12 | 588.75 | 616.86 | 577.5 |
| Calculated density ($g/cm^3$) | | 1.443 | 1.488 | 1.507 | 1.547 | 1.556 | 1.488 | |
| Absorption ($mm^{-1}$) | | 0.933 | 0.963 | 0.976 | 1.001 | 1.007 | 0.962 | |
| *F*(000) | | 2301.0 | 2296.0 | 2296.0 | 2296.0 | 2296.0 | 2300.0 | |
| Crystal size (mm) | | 0.438 × 0.322 × 0.111 | 0.325 × 0.173 × 0.07 | 0.325 × 0.173 × 0.07 | 0.325 × 0.173 × 0.07 | 0.325 × 0.173 × 0.07 | 0.438 × 0.322 × 0.111 | |
| 2$\vartheta$-range for data collection (°) | | 6.134 to 56.422 | 10.346 to 53.442 | 6.252 to 63.146 | 6.15 to 57.094 | 8.838 to 56.92 | 6.01 to 57.842 | |
| Min/max indices: *h, k, l* | | -16/16,-11/18,-36/20 | -6/7,-15/16,-31/34 | -6/6,-19/13, -28/28 | -6/6,-13/13,-35/35 | -6/6,-16/15,-35/35 | -11/15,-18/18, -20/36 | |
| Reflect. Collected/unique | | 3238/1347 | 2590/462 | 1551/516 | 2412/390 | 4151/497 | 3465/1277 | |
| $R_{int}$ | | 0.0278 | 0.3349 | 0.3341 | 0.3050 | 0.2052 | 0.0296 | |
| Refinement method | | Full-matrix least-squares on $F^2$ | | | | | | |
| Completeness (%) | | 99.7 | 39.5 | 38.1 | 34.2 | 38.6 | 90.1 | |
| Data/restrains/parameters | | 1347/0/79 | 462/92/79 | 516/57/79 | 390/94/79 | 497/69/79 | 1277/0/79 | |
| Goodness-of-fit on $F^2$ | | 1.059 | 0.901 | 0.868 | 0.939 | 0.983 | 1.067 | |
| Final R1/$wR^2$ (I>2σ1) | | 0.0533/0.1454 | 0.0921/0.1926 | 0.0887/0.1585 | 0.0869/0.2116 | 0.0770/0.1866 | 0.0477/0.1174 | |
| R1/$wR^2$ (all data) | | 0.0603/0.1547 | 0.2220/0.2579 | 0.3838/0.2732 | 0.2445/0.2934 | 0.2296/0.2656 | 0.0555/0.1229 | |
| Largest diff. peak/hole ($e.Å^{-3}$) | | 0.80/-0.46 | 0.21/-0.26 | 0.23/-0.20 | 0.19/-0.28 | 0.22/-0.21 | 0.89/-0.42 | |

$w=1/(\sigma^2F_o^2+w_1^2*P^2+w_2*P)$, where $P=(\mathrm{Max}(F_o^2,0)+2*F_c^2)$

* The measurement at 1.2 GPa, due to the reduced reflections intensities caused by the partial amorphization of the sample, provides the unit-cell parameters only.

**Table S5.** Torsion angles of HDA linkers in $Cd(HDA)_2(NO_3)_2$ structures under pressure.

| Pressure (GPa) | HDA | τ0 (°) | τ1 (°) | τ2 (°) | τ3 (°) | Conformation code |
|---|---|---|---|---|---|---|
| 0.0001 | Site A | 172.34 | 151.88 | 61.54 | 180 | $TTG^+T$ |

| | | | | | | |
|---|---|---|---|---|---|---|
| | Site B | 172.34 | -168.77 | -71.49 | 180 | TTG$^-$T |
| 0.2 | Site A | 172.96 | 142.15 | 76.46 | 180 | TTG$^+$T |
| | Site B | 172.96 | -169.07 | -71.14 | 180 | TTG$^-$T |
| 0.5 | Site A | 171.23 | 155.44 | 58.14 | 180 | TTG$^+$T |
| | Site B | 171.23 | -167.26 | -67.03 | 180 | TTG$^-$T |
| 0.85 | Site A | 170.24 | 160.77 | 41.38 | 180 | TTG$^+$T |
| | Site B | 170.24 | -165.47 | -82.52 | 180 | TTG$^-$T |
| 1.1 | HDA-1 | 170.32 | 176.97 | 63.85 | 180 | TTG$^+$T |
| | HDA-2 | -169.37 | 176.57 | 158.89 | 180 | TTTT |
| | HDA-3 | 163.46 | -177.93 | -66.37 | 180 | TTG$^-$T |
| | HDA-4 | -178.27 | 59.67 | 48.72 | 180 | TG$^+$G$^+$T |
| 1.25 | HDA-1 | -179.5 | 175.64 | 58.79 | 180 | TTG$^+$T |
| | HDA-2 | -169.78 | 177.65 | 157.63 | 180 | TTTT |
| | HDA-3 | 163.12 | -178.01 | -62.4 | 180 | TTG$^-$T |
| | HDA-4 | -178.59 | 64.95 | 49.61 | 180 | TG$^+$G$^+$T |
| 1.4 | HDA-1 | 174.62 | 173.42 | 73.72 | 180 | TTG$^+$T |
| | HDA-2 | -164.26 | 152.54 | 148.73 | 180 | TTTT |
| | HDA-3 | 167.89 | 166.78 | -49.64 | 180 | TTG$^-$T |
| | HDA-4 | -158.64 | 46.26 | 66.84 | 180 | TG$^+$G$^+$T |
| 1.5 | HDA-1 | 178.47 | 165.88 | 58.76 | 180 | TTG$^+$T |
| | HDA-2 | -168.02 | -179.88 | 160.84 | 180 | TTTT |
| | HDA-3 | 156.14 | 178.28 | -58.48 | 180 | TTG$^-$T |
| | HDA-4 | -175.59 | 47.27 | 64.09 | 180 | TG$^+$G$^+$T |
| 1.65 | HDA-1 | -177.38 | 177.74 | 56.32 | 180 | TTG$^+$T |
| | HDA-2 | -170.47 | 174.4 | 153.76 | 180 | TTTT |
| | HDA-3 | 158.67 | -173.98 | -57.98 | 180 | TTG$^-$T |
| | HDA-4 | -169.85 | 47.8 | 60.2 | 180 | TG$^+$G$^+$T |
| 1.77 | HDA-1 | 177.3 | 179.13 | 49.58 | 180 | TTG$^+$T |
| | HDA-2 | -161.44 | -179.61 | 157.08 | 180 | TTTT |
| | HDA-3 | 158.02 | -179.48 | -65.05 | 180 | TTG$^-$T |
| | HDA-4 | -177.6 | 55.41 | 58.86 | 180 | TG$^+$G$^+$T |
| 1.96 | HDA-1 | -179.15 | 176.03 | 59.42 | 180 | TTG$^+$T |
| | HDA-2 | -171.27 | 179.89 | 159.36 | 180 | TTTT |
| | HDA-3 | 157.75 | 177.22 | -61.5 | 180 | TTG$^-$T |
| | HDA-4 | -176.68 | 56.91 | 58.35 | 180 | TG$^+$G$^+$T |
| 2.1 | HDA-1 | 169.64 | 169.32 | 65.36 | 180 | TTG$^+$T |
| | HDA-2 | -172.35 | -178.84 | 177.37 | 180 | TTTT |
| | HDA-3 | 167.63 | -178.12 | -70.72 | 180 | TTG$^-$T |
| | HDA-4 | 171.9 | -58.72 | -58.05 | 180 | TG$^-$G$^-$T |
| 2.3 | HDA-1 | 173.05 | 161.79 | 61.74 | 180 | TTG$^+$T |
| | HDA-2 | -172.36 | 172.96 | 168.96 | 180 | TTTT |
| | HDA-3 | 161.79 | -173.32 | -57.09 | 180 | TTG$^-$T |
| | HDA-4 | 160.74 | -68.64 | -41.74 | 180 | TG$^-$G$^-$T |
| 2.55 | HDA-1 | 172.15 | 170.78 | 62.94 | 180 | TTG$^+$T |
| | HDA-2 | -165.74 | -177.79 | 157.96 | 180 | TTTT |
| | HDA-3 | 165.07 | -175.89 | -57.18 | 180 | TTG$^-$T |
| | HDA-4 | 173.04 | -55.74 | -46.68 | 180 | TG$^-$G$^-$T |
| 2.8 | HDA-1 | 176.41 | 178.95 | 63.61 | 180 | TTG$^+$T |
| | HDA-2 | -156.99 | -171.79 | 151.05 | 180 | TTTT |
| | HDA-3 | 165.29 | -178.13 | -57.43 | 180 | TTG$^-$T |
| | HDA-4 | 178.73 | -64.68 | -29.74 | 180 | TG$^-$G$^-$T |
| 3.3 | HDA-1 | 174.8 | 171.13 | 63.14 | 180 | TTG$^+$T |

| | | | | | | |
|---|---|---|---|---|---|---|
| | HDA-2 | -147.02 | -179.73 | -166.69 | 180 | TTTT |
| | HDA-3 | 167.9 | -177.37 | -65.45 | 180 | TTG$^-$T |
| | HDA-4 | 168.32 | -39.68 | -54.54 | 180 | TG$^-$G$^-$T |
| 3.7 | HDA-1 | 179.84 | -178.01 | 60.61 | 180 | TTG$^+$T |
| | HDA-2 | -150.83 | -171.8 | -172.57 | 180 | TTTT |
| | HDA-3 | 174.44 | -172.09 | -74.73 | 180 | TTG$^-$T |
| | HDA-4 | 167.29 | -50.6 | -40.9 | 180 | TG$^-$G$^-$T |

**Table S6.** Torsion angles of HDA linkers in $Cd(HDA)_2(NO_3)_2$ structures under temperature. Inv indicate $C_i$ symmetric HDA linkers.

| Temperature (K) | HDA | τ0 (°) | τ1 (°) | τ2 (°) | τ3 (°) | τ4 (°) | τ5 (°) | τ6 (°) | Conformation code |
|---|---|---|---|---|---|---|---|---|---|
| 298 | Site A | 171.43 | 152.67 | 62.63 | 180 | inv | inv | inv | TTG$^+$T |
| | Site B | 171.43 | -169.05 | -68.01 | 180 | inv | inv | inv | TTG$^-$T |
| 250 | Site A | 170.42 | 151.56 | 62.69 | 180 | inv | inv | inv | TTG$^+$T |
| | Site B | 170.42 | -169.84 | -66.99 | 180 | inv | inv | inv | TTG$^-$T |
| 200 | Site A | 171.43 | 152.67 | 62.63 | 180 | inv | inv | inv | TTG$^+$T |
| | Site B | 171.43 | -169.05 | -68.01 | 180 | inv | inv | inv | TTG$^-$T |
| 150 | HDA-1 | -173.07 | 172.07 | 60.03 | -178.07 | -63.08 | -173.46 | 173.73 | TTG$^+$TG$^-$TT |
| | HDA-2 | -176.74 | -177.38 | -64.87 | 180 | inv | inv | inv | TTG$^-$T |
| | HDA-3 | 166.08 | -178.07 | -65.46 | 180 | inv | inv | inv | TTG$^-$T |
| | HDA-4 | 171.65 | 175.42 | 53.79 | 180 | inv | inv | inv | TTG$^+$T |
| | HDA-5 | -176.54 | 177.2 | -169.21 | 180 | inv | inv | inv | TTTT |
| | HDA-6 | -178.43 | -71.04 | -176.36 | 180 | inv | inv | inv | TG$^-$TT |
| | HDA-7 | 162.17 | -66.75 | 178.75 | 180 | inv | inv | inv | TG$^-$TT |
| 100 | HDA-1 | -173.82 | 171.69 | 61.42 | -177.8 | -64.03 | -173.25 | 173.5 | TTG$^+$TG$^-$TT |
| | HDA-2 | -176.88 | -178.77 | -63.19 | 180 | inv | inv | inv | TTG$^-$T |
| | HDA-3 | 165.62 | -177.88 | -65.69 | 180 | inv | inv | inv | TTG$^-$T |
| | HDA-4 | 170.81 | 175.26 | 55.88 | 180 | inv | inv | inv | TTG$^+$T |
| | HDA-5 | -177.61 | 177.03 | -168.96 | 180 | inv | inv | inv | TTTT |
| | HDA-6 | -177.87 | -71.00 | -176.73 | 180 | inv | inv | inv | TG$^-$TT |
| | HDA-7 | 161.91 | -67.74 | 178.95 | 180 | inv | inv | inv | TG$^-$TT |
| 100 -fast cooling | Site A | 172.4 | 151.63 | 62.4 | 180 | inv | inv | inv | TTG$^+$T |
| | Site B | 172.4 | -168.94 | -71.22 | 180 | inv | inv | inv | TTG$^-$T |

**Table S7.** Torsion angles of HDA linkers in $Cd_2(HDA)_3(NO_3)_4$ structures under pressure. Inv indicate $C_i$ symmetric HDA linkers.

| Pressure (GPa) | HDA | τ0 (°) | τ1 (°) | τ2 (°) | τ3 (°) | τ4 (°) | τ5 (°) | τ6 (°) | Conformation code |
|---|---|---|---|---|---|---|---|---|---|
| 0.0001 | HDA-1 | -174.43 | 58.12 | 175.63 | -74.64 | 176.29 | -172.84 | 68.71 | TG$^+$TG$^-$TTG$^+$ |
| | HDA-2 | 178.98 | -176.24 | -177.35 | 180 | inv | inv | inv | TTTT |
| 0.4 | HDA-1 | -172.33 | 56.4 | 176.67 | -76.67 | 175.32 | -170.61 | 70.42 | TG$^+$TG$^-$TTG$^+$ |
| | HDA-2 | 178.53 | -174.96 | -177.41 | 180 | inv | inv | inv | TTTT |
| 1.2 | HDA-1 | -169.6 | 55.12 | 175.78 | -76.5 | 176.48 | -169.82 | 70.33 | TG$^+$TG$^-$TTG$^+$ |

| | | | | | | | | | |
|---|---|---|---|---|---|---|---|---|---|
| | HDA-2 | 177.55 | -172.05 | -177.63 | 180 | inv | inv | inv | TTTT |
| 2.1 | HDA-1 | -168.57 | 54.3 | 174.86 | -75.86 | 176.14 | -171.51 | 74.69 | $TG^+TG^-TTG^+$ |
| | HDA-2 | 172.97 | -162.28 | -175.6 | -176.88 | 179.4 | 177.71 | -178.13 | TTTTTTT |
| | HDA-3 | 164.79 | -51.39 | -176.5 | 75.39 | -176.65 | 169.96 | -69.88 | $TG^-TG^+TTG^-$ |
| 3.1 | HDA-1 | -164.75 | 42.21 | 179.64 | -65.83 | 175.77 | -176.64 | 75.29 | $TG^+TG^-TTG^+$ |
| | HDA-2 | 174.31 | -150.95 | -173.45 | -175.71 | -178.91 | -179.57 | 178.85 | TTTTTTT |
| | HDA-3 | 159.1 | -56.09 | -179.09 | 79.66 | -176.15 | 173.53 | -74.13 | $TG^-TG^+TTG^-$ |
| 4.3 | HDA-1 | -171.21 | 49.14 | 174.69 | -75.15 | 171.21 | -177.09 | 76.55 | $TG^+TG^-TTG^+$ |
| | HDA-2 | 177.25 | -124.48 | -169.88 | 169.36 | -175.72 | 171.13 | 172.2 | TTTTTTT |
| | HDA-3 | 176.05 | -44.28 | -160.91 | 80.71 | 169.59 | 148.25 | -52.85 | $TG^-TG^+TTG^-$ |

**Table S8.** Torsion angles of HDA linkers in $Cu(HDA)_2(MeCN)_2 \cdot 2BF_4$ structures under pressure.

| Pressure (GPa)/Temperature (K) | HDA | τ0 (°) | τ1 (°) | τ2 (°) | τ3 (°) | Conformation code |
|---|---|---|---|---|---|---|
| 0.0001 / 298 | HDA-1 | 165.22 | 177.25 | 176.91 | 180 | TTTT |
| 0.15 / 298 | HDA-1 | 162.84 | 178.88 | 178.19 | 180 | TTTT |
| 0.4 / 298 | HDA-1 | 161.25 | 177.58 | -178.18 | 180 | TTTT |
| 0.7 / 298 | HDA-1 | 165.14 | 174.17 | 166.76 | 180 | TTTT |
| 1.0 / 298 | HDA-1 | 167.46 | -179.08 | 173.6 | 180 | TTTT |
| 0.0001 / 100 | HDA-1 | 163.98 | -177.45 | -176.02 | 180 | TTTT |