Supporting Information

Self-healing ferroelastic metal-organic framework sensing guests, pressure and chemical environment

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Synthesis of AMU3

Single crystals of $Cd(BDC)_2(AZPY)$ (BDC=terephthalic acid; AZPY=4,4'-azobispyridine), abbreviated as AMU3, were obtained using a diffusion method, similar to those described previously.[1–4] In our present study, the two layers containing the substrates, 0.092 g (0.3 mmol) of cadmium nitrate (Sigma-Aldrich) and 0.049 g (0.3 mmol) of terephthalic acid (Sigma-Aldrich) dissolved in 5 mL of DMF and 0.056 g (0.3 mmol) of 4,4'-azobispyridine (Sigma-Aldrich) dissolved in 5 mL of MeOH, were separated by the mixture of 1 mL of DMF with 1 mL of MeOH providing the diffusion environment. After 1 week, orange block crystals appeared.

Raman spectra collection

Raman scattering from AMU3 were collected. High-pressure measurements were performed for polycrystalline sample in DAC (diamond anvil cell) with methanol:ethanol:water mixture (16:3:1 volume ratio) as hydrostatic liquid. High-pressure Raman measurements were performed with customized in-house Raman spectrometer, equipped in M266 laser from Solar Laser Systems, and multichannel detector from Hamamatsu Photonics. For data collection and processing program SpectroLab were used.

The main Raman lines for AMU3 are observed at about 1600, 1550, 1500, 1465, 1412, 1250, 1170, 1115, 1020 and 660 cm^{-1}. Data were collected to 5 GPa and the changes in the position and shape of the peaks are shown in Figure S1. The Raman spectra of AMU3 display the expected increase in the frequency of vibrations with pressure, with the exception of small drops in the Raman shifts at the phase-transition point at 0.4 GPa.

Supporting Information

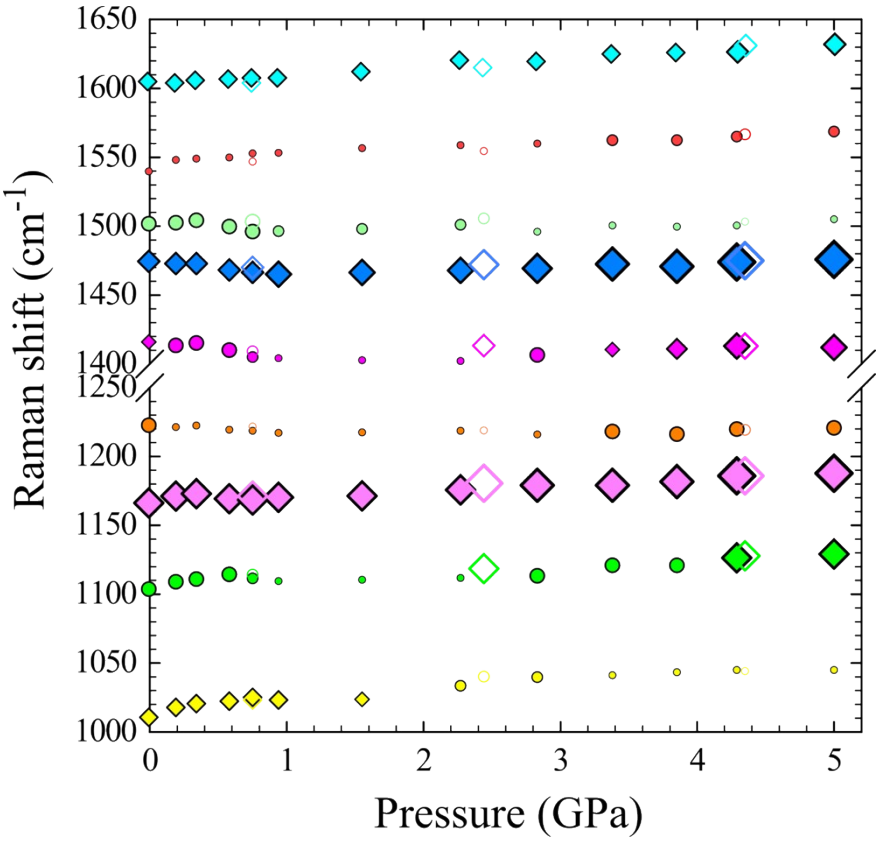
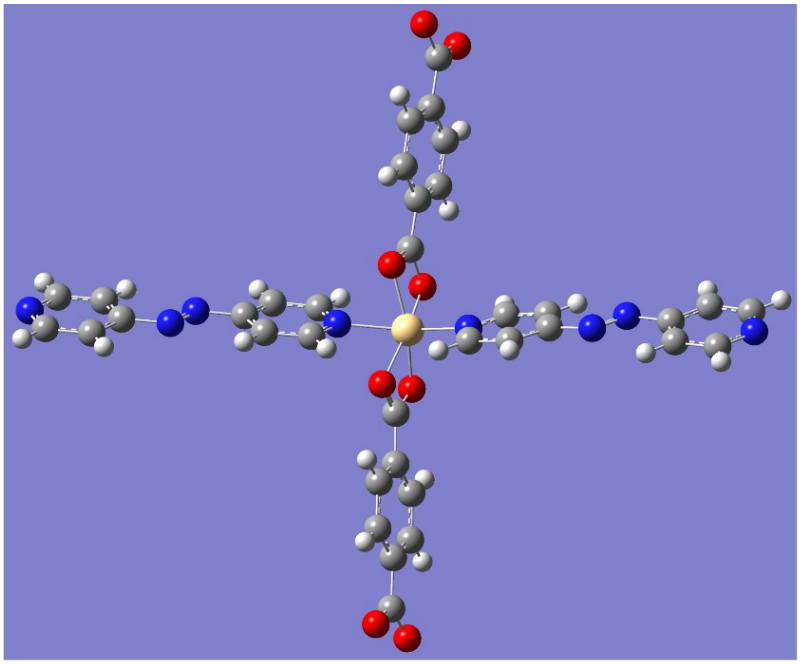


Figure S1. Pressure evolution of the Raman spectra of AMU3. Diamonds indicate sharp peaks and circles indicate broad peaks. Open symbols define the decompression measurements. The size of plotted symbols represents the bond intensities.

Theoretical studies

Lowest energy molecular geometries and harmonic vibrational energies were calculated using the Gaussian16 software package.[5] The electron density was modeled by Gaussian-type orbitals. The B3LYP functional and the STO-3G basis set were used along with default settings in Gaussian16. The computational work consisted of two steps: (1) structure optimization based on input coordinates generated from a crystallographic information file (CIF) and (2) calculation of vibrational frequencies.

a)



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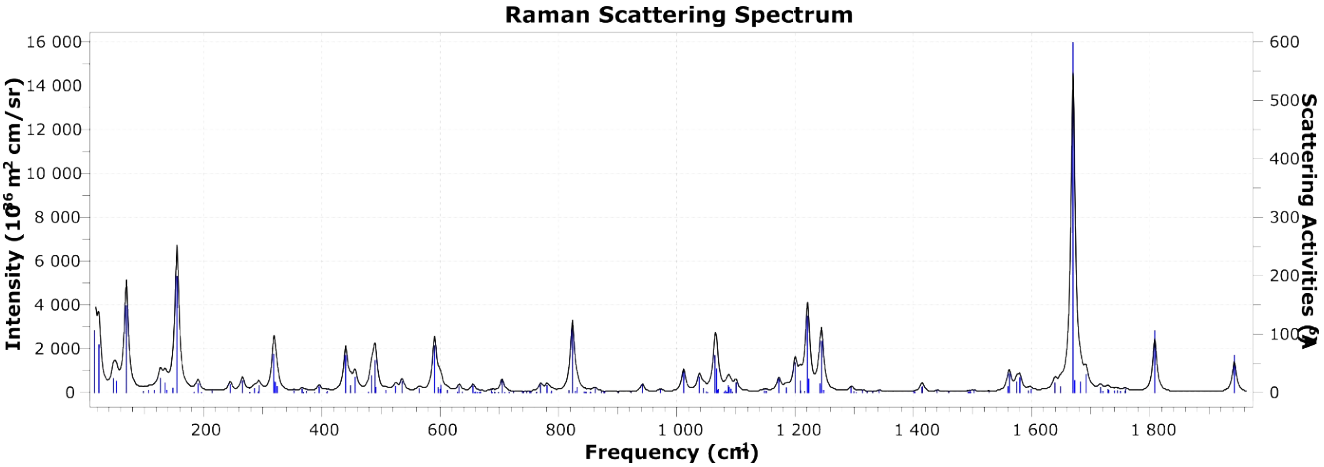

Figure S2. a) Part of polymer used for calculations and b) calculated Raman spectra.

Supporting Information

Crystal structure

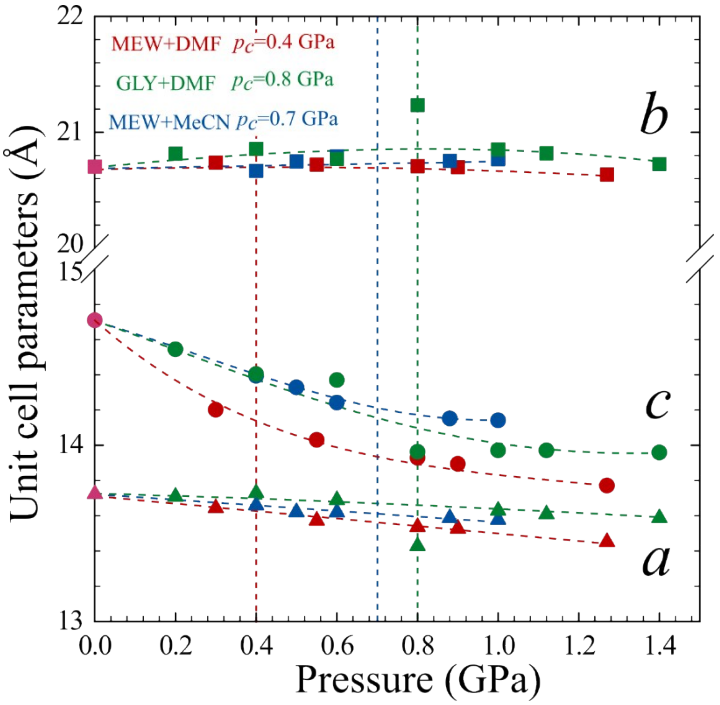

Figure S3. Unit cell parameters of three series of AMU3 in the function of pressure. Red color indicate AMU3·DMF with methanol:ethanol:water mixture (MEW,16:3:1 vol. ratio) used as pressure transmitting medium (PTM); green mark AMU3·DMF with glycerine (GLY) used as PTM, and blue for AMU3·MeCN with MEW as a PTM. The monoclinic phase β were calculated to corresponding phase α. The ESD's are smaller than plotted symbols.

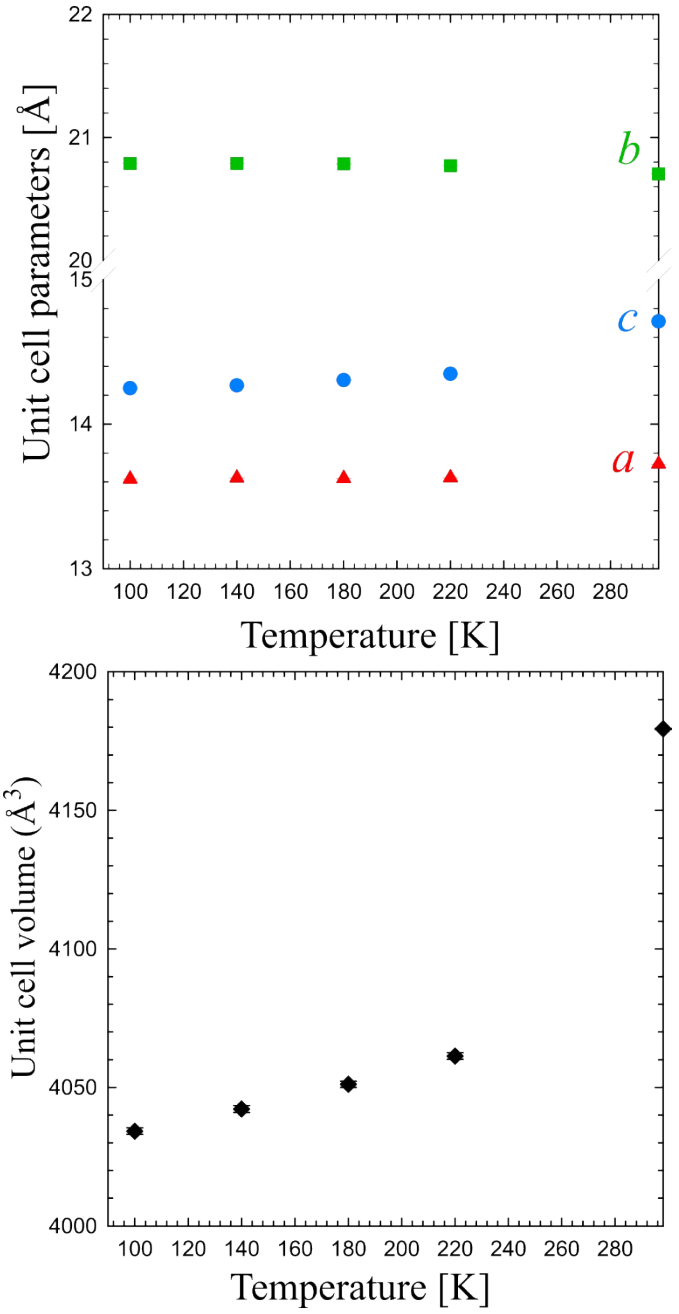

Figure S4. Unit cell parameters of AMU3·DMF in the function of temperature. The ESD's are smaller than plotted symbols.

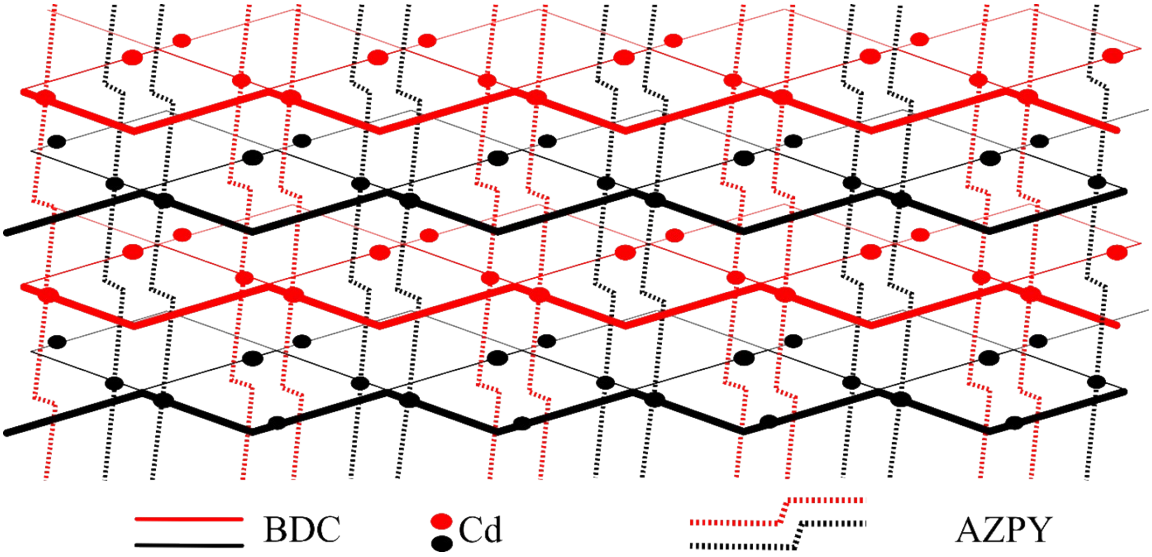

Figure S5. Coordination scheme of AMU3. Red and black colour indicate interwoven frameworks.

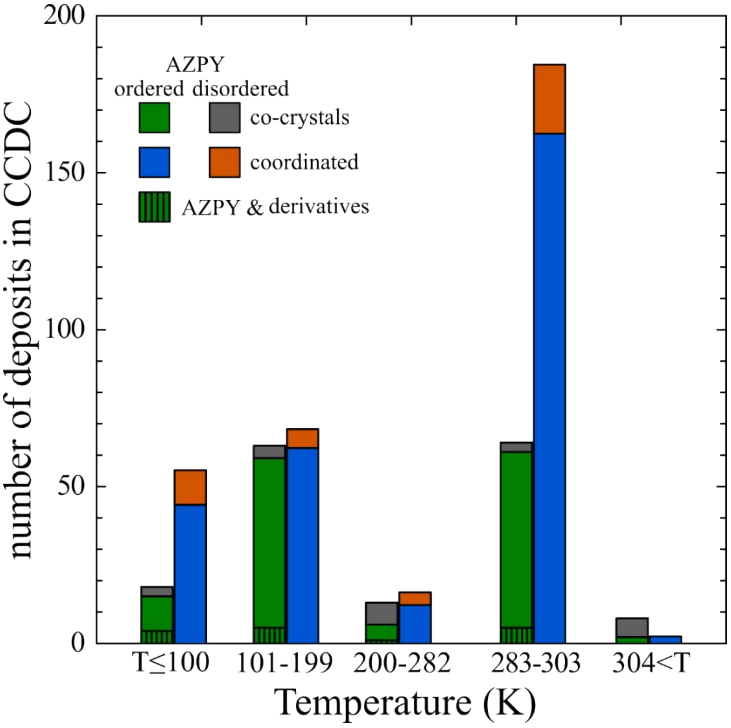

Figure S6. Number of crystal structures with ordered and disordered AZPY molecules, found in the CCDC.

Supporting Information

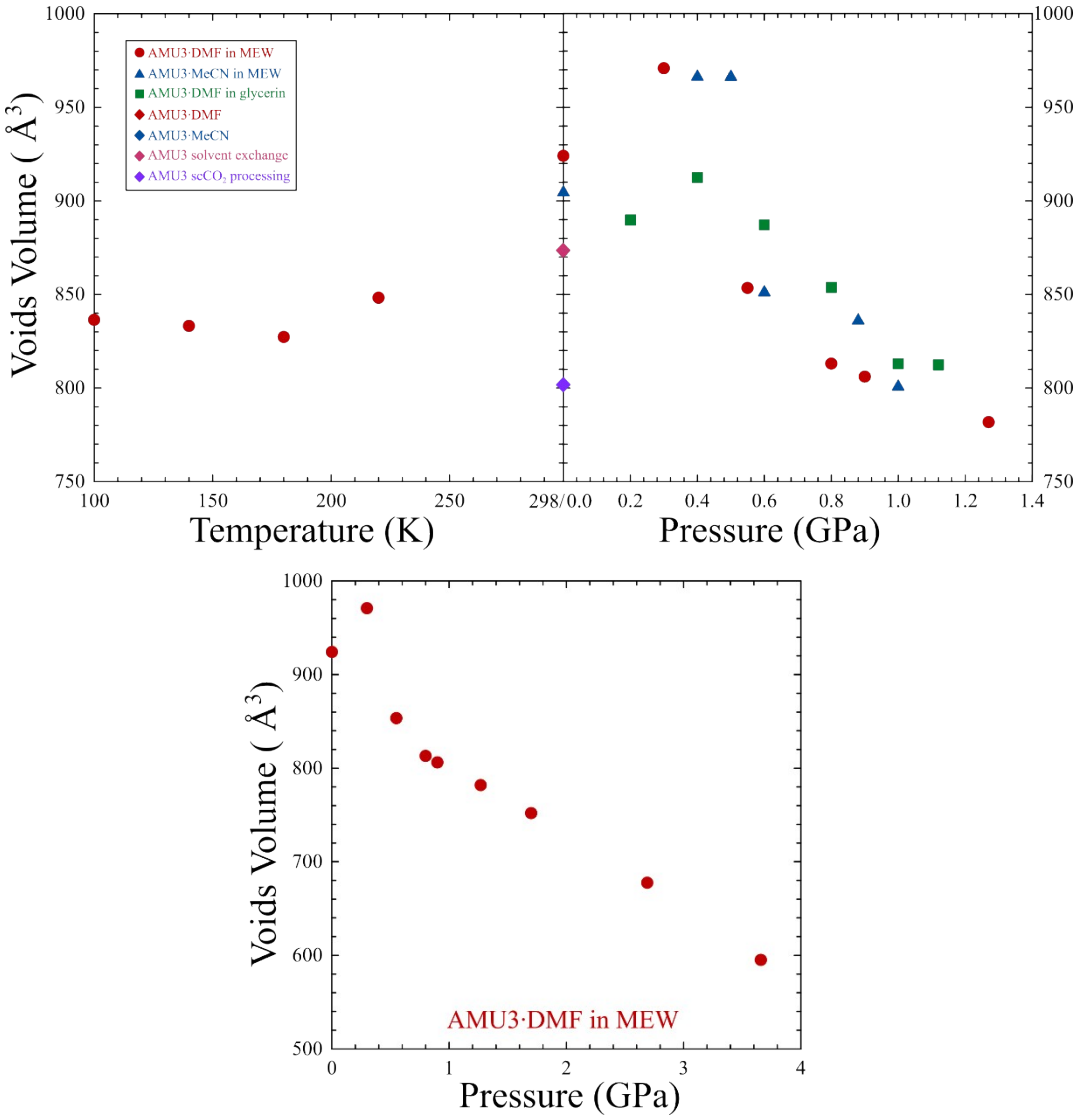

Figure S7. (Top) Voids volume as a function of temperature (left) and pressure range to 1.4 GPa (right) and to 4 GPa for AMU3·DMF compressed in MEW (down). The voids volume was calculated by Mercury based on Contact Surface (probe radius 1.4 Å, grid 0.2 Å), after removing the guest molecules by solvent mask tool in *OLEX2* (Solvent r =1.2Å). Maximum probe radius for crystal at 3.66 GPa is 1.6 Å, for lower pressures is 1.7 Å.

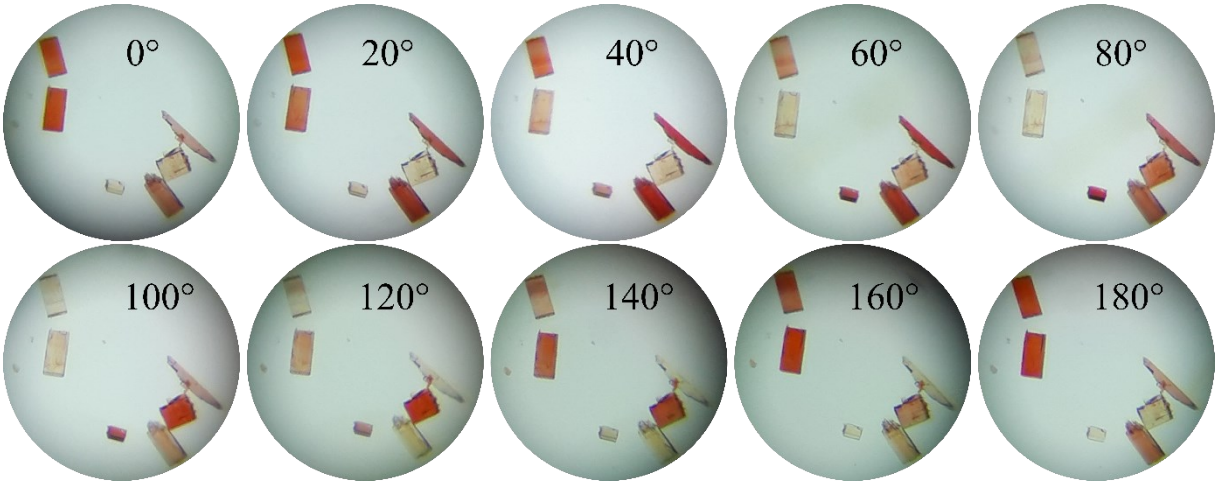

Figure S8. Pleochroic effect of α-AMU3·DMF illustrated for several crystals viewed in the polarized transmitting light with its polarization vector rotated in 20° steps.

Table S1. Compressibility related to crystallographic axes calculated for the α-AMU3·DMF compressed in MEW with Birch-Murnaghan coefficients, calculated in the range between 0.1 MPa and 0.3 GPa, by using program PASCal.[6]

Axes	K(TPa^{-1})	σK(TPa^{-1})	Direction			Empirical parameters			
			a	*b*	*c*	ε_0	λ	P_c	ν
X_1	117.4039	0.0000	-0.0000	-0.0000	1.0000	0.0000e+00	0.0000e+00	0.0000	0.0000
X_2	19.6896	0.0000	-1.0000	-0.0000	0.0000	0.0000e+00	0.0000e+00	0.0000	0.0000
X_3	-5.6482	0.0000	-0.0000	1.0000	-0.0000	0.0000e+00	0.0000e+00	0.0000	0.0000
V	128.9364	0.0000							

Birch-Murnaghan Coefficients

	B_0 (GPa)	σB_0 (GPa)	V_0 (Å^3)	σV_0 (Å^3)	B'	σB'	P_c (GPa)
2nd	7.0275	-	4179.4470	-	4	n/a	0

Table S2. Compressibility related to crystallographic axes calculated for the β-AMU3·DMF compressed in MEW with Birch-Murnaghan coefficients, calculated in the range between 0.55 GPa and 3.66 GPa, by using program PASCal.[6]

Axes	K(TPa^{-1})	σK(TPa^{-1})	Direction			Empirical parameters			
			a	*b*	*c*	ε_0	λ	P_c	ν
X_1	29.1191	0.8824	-0.9618	0.0000	-0.2737	7.1074e-01	-4.3570e-01	-5.3478	0.2752
X_2	16.7470	0.6913	0.0000	1.0000	0.0000	1.6169e-02	-3.4807e-02	0.3112	0.5566
X_3	-20.2868	2.0559	-0.1243	0.0000	-0.9922	-1.8152e-03	1.8071e-02	0.5500	1.1061
V	24.7714	1.6435							

Birch-Murnaghan Coefficients

	B_0 (GPa)	σB_0 (GPa)	V_0 (Å^3)	σV_0 (Å^3)	B'	σB'	P_c (GPa)
2nd	31.8236	2.6027	1995.1809	8.2906	4	n/a	0
3rd	8.8670	24.3892	2043.9090	94.3160	34.0779	93.9301	0

Table S3. Compressibility related to crystallographic axes calculated for the α-AMU3·MeCN compressed in MEW with Birch-Murnaghan coefficients, calculated in the range between 0.1 MPa and 0.6 GPa, by using program PASCal.[6]

Axes	K(TPa^{-1})	σK(TPa^{-1})	Direction			Empirical parameters			
			a	*b*	*c*	ε_0	λ	P_c	ν
X_1	55.5424	0.0000	-0.0000	-0.0000	1.0000	3.4881e-02	-1.4554e-03	-2.8429	3.0451
X_2	15.3337	0.0000	-1.0000	0.0000	0.0000	9.4307e-05	-1.3341e-02	0.0001	1.4366
X_3	-61.8400	0.0000	-0.0000	1.0000	-0.0000	-1.3866e-03	2.0257e-01	-0.0009	7.2082
V	51.8958	1.5945							

Birch-Murnaghan Coefficients

	B_0 (GPa)	σB_0 (GPa)	V_0 (Å^3)	σV_0 (Å^3)	B'	σB'	P_c (GPa)
2nd	17.9943	1.2091	4157.0463	6.2797	4	n/a	0
3rd	11.0043	3.7452	4158.6782	6.4407	47.8662	35.0213	0

Table S4. Compressibility related to crystallographic axes calculated for the β-AMU3·MeCN compressed in MEW with Birch-Murnaghan coefficients, calculated in the range between 0.88 GPa and 1.0 GPa, by using program PASCal.[6]

Axes	K(TPa^{-1})	σK(TPa^{-1})	Direction			Empirical parameters			
			a	*b*	*c*	ε_0	λ	P_c	ν
X_1	7.6993	0.0000	0.8676	0.0000	0.4973	0.0000e+00	0.0000e+00	0.0000	0.0000
X_2	5.8914	0.0000	0.0000	-1.0000	0.0000	0.0000e+00	0.0000e+00	0.0000	0.0000
X_3	-7.9250	0.0000	-0.2239	0.0000	0.9746	0.0000e+00	0.0000e+00	0.0000	0.0000
V	5.6657	0.0000							

Birch-Murnaghan Coefficients

	B_0 (GPa)	σB_0 (GPa)	V_0 (Å^3)	σV_0 (Å^3)	B'	σB'	P_c (GPa)
2nd	172.6900	-	2004.9188	-	4	n/a	0

Table S5. Compressibility related to crystallographic axes calculated for the α-AMU3·DMF compressed in glycerin with Birch-Murnaghan coefficients, calculated in the range between 0.1 MPa and 0.6 GPa, by using program PASCal.[6]

Axes	K(TPa^{-1})	σK(TPa^{-1})	Direction			Empirical parameters			
			a	*b*	*c*	ε_0	λ	P_c	ν
X_1	21.2944	0.0000	0.0000	0.0000	1.0000	1.1515e+01	-1.1544e+01	-0.1613	0.0014
X_2	134.8696	0.0000	-1.0000	0.0000	0.0000	-4.0568e-04	-5.8865e-03	-0.3838	60.1440
X_3	-0.0000	0.0000	0.0000	-1.0000	0.0000	5.2535e-03	-3.5312e-03	-0.9942	-69.6077
V	37.2038	1.3219							

Birch-Murnaghan Coefficients

	B_0 (GPa)	σB_0 (GPa)	V_0 (Å^3)	σV_0 (Å^3)	*B'*	σ*B'*	P_c (GPa)
2nd	25.2643	1.9169	4182.0983	4.4772	4	n/a	0
3rd	32.8453	4.0463	4178.7449	2.6344	-15.7684	8.4553	0

Table S6. Compressibility related to crystallographic axes calculated for the β-AMU3·DMF compressed in glycerin with Birch-Murnaghan coefficients, calculated in the range between 0.8 MPa and 1.4 GPa, by using program PASCal.[6]

Axes	K(TPa^{-1})	σK(TPa^{-1})	Direction			Empirical parameters			
			a	*b*	*c*	ε_0	λ	P_c	ν
X_1	13.6329	0.0000	0.9845	-0.0000	-0.1753	2.5300e-04	-3.6075e-02	0.8000	0.2588
X_2	39.3449	0.0000	-0.0000	1.0000	-0.0000	3.0240e-04	-1.4978e-03	0.4138	58.7250
X_3	-0.0000	0.0000	0.4900	-0.0000	0.8717	1.4766e-02	-6.1514e-07	-0.0161	-49.6266
V	31.1247	2.2667							

Birch-Murnaghan Coefficients

	B_0 (GPa)	σB_0 (GPa)	V_0 (Å^3)	σV_0 (Å^3)	*B'*	σ*B'*	P_c (GPa)
2nd	100.0000	51.6822	2000.9179	12.1531	4	n/a	0
3rd	0.4406	1587.4222	2125.7005	9160.1240	809.6616	2894074.1633	0

References:

(1) Andrzejewski, M.; Katrusiak, A. Piezochromic Topology Switch in a Coordination Polymer. *J. Phys. Chem. Lett.* **2017**, *8* (5), 929–935. https://doi.org/10.1021/acs.jpclett.7b00019.

(2) Sobczak, S.; Katrusiak, A. Zone-Collapse Amorphization Mimicking the Negative Compressibility of a Porous Compound. *Cryst. Growth Des.* **2018**, *18* (2), 1082–1089. https://doi.org/10.1021/acs.cgd.7b01535.

(3) Andrzejewski, M.; Katrusiak, A. Piezochromic Porous Metal-Organic Framework. *J. Phys. Chem. Lett.* **2017**, *8* (1), 279–284. https://doi.org/10.1021/acs.jpclett.6b02458.

(4) Cai, W.; Katrusiak, A. Giant Negative Linear Compression Positively Coupled to Massive Thermal Expansion in a Metal-Organic Framework. *Nat. Commun.* **2014**, *5*, 1–8. https://doi.org/10.1038/ncomms5337.

(5) Frisch, M. J.; Trucks, G. W.; Schlegel, H. B.; Scuseria, G. E.; Robb, M. A.; Cheeseman, J. R.; Scalmani, G.; Barone, V.; Petersson, G. A.; Nakatsuji, H.; et al. Gaussian 16, Rev. C.01. *Gaussian, Inc.:Wallingford CT*. 2016.

(6) Cliffe, M. J.; Goodwin, A. L. PASCal: A Principal Axis Strain Calculator for Thermal Expansion and Compressibility Determination. *J. Appl. Crystallogr.* **2012**, *45* (6), 1321–1329. https://doi.org/10.1107/S0021889812043026.

Table S7. Crystallographic data of Cd(BDC)(AZPY) (abbreviated as AMU3) activated and in low temperature measurements.

Compound		$scCO_2$ processed	in acetonitrile	in chloroform	as- synthesized	AMU3·DMF	AMU3·DMF	AMU3·DMF	AMU3·DMF
CCDC number		2046185	2046186	2046187	2046188	2046189	2046192	2046190	2046191
Temperature (K)		298	298	298	298	220	180	140	100
Formula weight		460.72	501.77	460.72	533.81	532.80	532.80	532.80	532.80
Wavelength (Å)		1.54184	1.54184	1.54184	1.54184	0.71073	0.71073	0.71073	0.71073
Crystal system		orthorhombic	Orthorhombic	orthorhombic	orthorhombic	orthorhombic	orthorhombic	orthorhombic	orthorhombic
Space group		*Cmce*	*Cmce*	*Cmce*	*Cmce*	*Cmce*	*Cmce*	*Cmce*	*Cmce*
Unit cell	*a* (Å)	13.6516(14)	13.6976(4)	13.6548(10)	13.7238(4)	13.649(2)	13.625(3)	13.627(2)	13.620(2)
	b (Å)	20.855(2)	20.7250(7)	20.8439(15)	20.7039(6)	20.820(3)	20.771(4)	20.790(3)	20.790(3)
	c (Å)	14.2061(15)	14.6495(5)	14.1944(12)	14.7091(4)	14.371(3)	14.303(4)	14.267(3)	14.247(3)
Volume ($Å^3$)		4044.5(7)	4158.7(2)	4040.0(5)	4179.4(2)	4084.0(12)	4047.8(15)	4042.2(13)	4034.2(12)
Z/Z'		8/0.5	8/0.5	8/0.5	8/0.5	8/0.5	8/0.5	8/0.5	8/0.5
Molecular volume (*V/Z*)		505.56	519.84	505.00	522.42	510.50	505.97	505.27	504,27
Calculated density (g/cm^3)		1.513	1.603	1.475	1.697	1.733	1.739	1.751	1.758
Absorption (mm^{-1})		8.908	8.731	8.916	8.764	1.115	1.125	1.127	1.129
F(000)		1824.0	2000.0	1728.0	2144.0	2136.0	2112.0	2136.0	2144.0
Crystal size (mm)		0.078 × 0.043 × 0.026	0.154 × 0.081 × 0.05	0.205 × 0.068 × 0.028	0.186 × 0.067 × 0.04	0.186 × 0.083 × 0.042	0.186 × 0.083 × 0.042	0.186 × 0.083 × 0.042	0.186 × 0.083 × 0.042
2ϑ-range for data collection		8.48 to 152.698	8.532 to 153.614	9.94 to 152.868	8.542 to 152.866	5.67 to 46.502	5.696 to 46.5	6.738 to 52.742	6.746 to 52.742
Min/max indices: *h, k, l*		-16/14,-25/26,-17/17	-12/17,-26/25,-18/18	-16/15, -23/26, -17/17	-17/16, -24/26, -18/14	-15/7, -23/21, -9/15	-15/7, -23/20, -9/15	-17/7, -25/23, -9/17	-17/7, -25/23, -9/17
Reflect. Collected/unique		8944/2010	18009/2270	7949/2178	8571/2261	4129/1531	4001/1515	5058/2136	5277/2149
R_{int}		0.2472	0.0458	0.0388	0.0237	0.1318	0.1315	0.1730	0.1796
Refinement method		Full-matrix least-squares on F^2							
Completeness (%)		92	100	100	100	100	100	99	99
Data/restrains/parameters		2010/200/139	2270/0/155	2178/0/139	2261/0/182	1531/195/160	1515/166/160	2136/165/160	2149/221/182
Goodness-of-fit on F^2		1.008	1.096	1.084	1.073	0.998	1.048	0.980	0.987
Final R1/wR^2 (I>2σ1)		0.1234/0.2648	0.0569/0.1763	0.0746/0.2099	0.0446/0.1275	0.0719/0.1192	0.0741/0.1293	0.0913/0.1202	0.0897/0.1296
R1/wR^2 (all data)		0.2427/0.3443	0.0601/0.1817	0.0846/0.2218	0.0464/0.1300	0.1512/0.1560	0.1505/0.1687	0.2178/0.1721	0.2117/0.1843
Largest diff. peak/hole (e.Å$^-$		1.63/-1.12	1.48/-1.04	2.38/-1.81	1.73/-1.30	1.00/-0.63	1.05/-0.64	1.54/-0.65	1.39/-0.98

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

Pressure/phase		0.3 GPa/α	0.55 GPa /β	0.8 GPa /β	0.9 GPa /β	1.27 GPa /β	1.7 GPa /β	2.69 GPa /β	3.66 GPa /β
CCDC number		2046198	2046204	2046199	2046200	2046201	2046205	2046203	2046202
Formula weight		460.72	460.72	460.72	460.72	460.72	460.72	460.72	460.72
Wavelength (Å)		0.71073	0.71073	0.71073	0.71073	0.71073	0.71073	0.71073	0.71073
Crystal system		orthorhombic	Monoclinic	monoclinic	monoclinic	monoclinic	monoclinic	monoclinic	monoclinic
Space group		*Cmce*	$P2_1/n$	$P2_1/n$	$P2_1/n$	$P2_1/n$	$P2_1/n$	$P2_1/n$	$P2_1/n$
Unit cell dimensions	*a* (Å)	13.643(3)	12.230(3)	12.162(3)	12.132(3)	11.996(4)	11.854(3)	11.600(4)	11.362(6)
	b (Å)	20.739(3)	14.03(2)	13.928(18)	13.893(18)	13.77(3)	13.68(2)	13.487(18)	13.31(3)
	c (Å)	14.20(2)	12.539(2)	12.574(3)	12.591(2)	12.629(4)	12.773(3)	13.080(5)	13.269(8)
	β (°)	90	113.56(2)	113.67(3)	113.69(2)	113.84(4)	114.04(3)	114.57(4)	115.07(7)
Volume ($Å^3$)		4019(6)	1973(3)	1951(3)	1943(3)	1908(5)	1891(3)	1861(3)	1818(5)
Z/Z'		8/0.5	4/1	4/1	4/1	4/1	4/1	4/1	4/1
Molecular volume (*V/Z*)		502.37	493.25	487.75	485.75	477.00	472.75	465.25	454.50
Calculated density (g/cm^3)		1.523	1.551	1.569	1.575	1.603	1.618	1.644	1.683
Absorption (mm^{-1})		1.115	1.136	1.149	1.153	1.174	1.185	1.204	1.233
F(000)		1824.0	912.0	912.0	912.0	912.0	912.0	912.0	2144.0
Crystal size (mm)		0.285 × 0.106 × 0.076	0.285 × 0.106 × 0.076	0.284 × 0.106 × 0.076	0.284 × 0.105 × 0.076	0.282 × 0.104 × 0.076	0.281 × 0.104 × 0.076	0.278 × 0.103 × 0.076	0.275× 0.100 × 0.076
2*ϑ*-range for data collection (°)		7.15 to 43.924	6.672 to 43.868	11.02 to 43.93	6.028 to 43.93	6.068 to 43.914	6.088 to 43.898	8.472 to 34.446	8.492 to 27.4
Min/max indices: *h, k, l*		-14/14, -21/21, -5/5	-12/12, -5/5, -13/13	-12/12, -5/5, -13/13	-12/12, -6/6, -13/13	-12/12, -5/5, -13/13	-12/12, -5/5, -13/13	-9/9, -7/7, -10/10	-7/7, -5/5, -8/8
Reflect. Collected/unique		9246/586	8399/1065	7377/1054	8888/1077	4710/1006	8417/1034	5230/652	2771/314
R_{int}		0.1485	0.1594	0.2204	0.1738	0.1749	0.1680	0.2298	0.1420
Refinement method;		Full-matrix least-squares on F^2							
Completeness (%)		46	44	44	45	43	45	58	56
Data/restrains/parameters		586/221/139	1065/370/208	1054/248/166	1077/310/208	1006/373/208	1034/377/136	652/391/208	314/385/52
Goodness-of-fit on F^2		1.040	1.318	1.112	1.089	1.135	1.271	1.330	1.118
Final R1/wR^2 (I>2σ1)		0.0598/0.0,1634	0.1385/0.3414	0.1204/0.2983	0.1111/0.2794	0.1215/0.3063	0.1182/0.3253	0.1298/0.3112	0.1784/0.4696
R1/wR^2 (all data)		0.0971/0.1907	0.1924/0.3887	0.1962/0.3597	0.1674/0.3280	0.2013/0.3686	0.1716/0.3782	0.1842/0.3737	0.2192/0.5564
Largest diff. peak/hole ($e.Å^{-3}$)		0.37/-0.47	1.61/-1.57	0.95/-1.12	1.03/-1.15	1.00/-1.11	0.78/-1.09	0.74/-0.64	0.65/-0.80

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

Table S8. Crystallographic data of compressed AMU3·DMF with MEW as PTM.

Pressure/phase		0.2 GPa /α	0.4 GPa /α	0.6 GPa /α	0.8 GPa /β	1.0 GPa /β	1.12 GPa /β	1.4 GPa /β
CCDC number		2046210	2046207	2046211	2046209	2046208	2046205	2046409
Formula weight		533.81	533.81	460.72	460.72	460.72	460.72	460.72
Wavelength (Å)		0.71073	0.71073	0.71073	0.71073	0.71073	0.71073	0.71073
Crystal system		orthorhombic	Orthorhombic	orthorhombic	monoclinic	monoclinic	monoclinic	monoclinic
Space group		*Cmce*	*Cmce*	*Cmce*	$P2_1/n$	$P2_1/n$	$P2_1/n$	$P2_1/n$
Unit cell dimensions	*a* (Å)	13.707(2)	13.729(2)	13.688(3)	12.56(3)	12.275(11)	12.241(12)	12.177(7)
	b (Å)	20.816(4)	20.856(4)	20.77(5)	13.962(5)	13.969(8)	13.970(11)	13.957(9)
	c (Å)	14.544(3)	14.403(2)	14.369(3)	12.60(3)	12.634(9)	12.627(11)	12.601(7)
	β (°)	90	90	90	115.1(3)	113.67(8)	113.67(9)	113.52(6)
Volume ($Å^3$)		4150.1(12)	4124.0(12)	4085(9)	2001(8)	1984(3)	1978(3)	1964(3)
Z/Z’		8/0.5	8/0.5	8/0.5	4/1	4/1	4/1	4/1
Molecular volume (*V/Z*)		518.76	515.5	510.62	500.25	496.00	494.50	491.00
Calculated density (g/cm^3)		1.709	1.720	1.498	1.529	1.542	1.547	N/A
Absorption (mm^{-1})		1.098	1.105	1.097	1.120	1.130	1.133	N/A
F(000)		2144.0	2144.0	1824.0	912.0	912.0	912.0	N/A
Crystal size (mm)		0.303 × 0.128 × 0.063	0.303 × 0.128 × 0.063	0.302 × 0.128 × 0.063	0.301 × 0.127 × 0.063	0.301 × 0.127 × 0.063	0.300 × 0.127 × 0.063	0.300 × 0.127 × 0.063
2θ-range for data collection (°)		11.328 to 50.914	11.34 to 49.426	9.228 to 49.422	8.4 to 49.424	8.358 to 54.686	11.388 to 50.976	N/A
Min/max indices: h, k, l		-15/15, -21/21, -13/13	-15/15, -21/21, -14/14	-16/16, -8/8, -16/16	-9/9, -16/16, -10/9	-10/11, -14/14, -	-10/11, -13/13, -14/10	N/A
Reflect. Collected/unique		7456/1168	7579/1387	7027/763	3273/998	6911/1597	4071/1328	N/A
Rint		0.2133	0.1686	0.1988	0.1845	0.2393	0.2060	N/A
Refinement method;		Full-matrix least-squares on F2						
Completeness (%)		59	75	42	29	42	37	N/A
Data/restrains/parameters		1168/302/182	1387/274/168	763/375/131	998/667/124	1597/406/208	1328/291/208	N/A
Goodness-of-fit on F2		1.380	2.007	1.266	1.275	1.064	1.041	N/A
Final R1/wR2 (I>2σ1)		0.1448/0.3534	0.2497/0.5497	0.1183/0.3180	0.1519/0.3813	0.1424/0.3587	0.1435/0.3394	N/A
R1/wR2 (all data)		0.2456/0.4519	0.3614/0.6414	0.2354/0.4450	0.2790/0.5058	0.2808/0.4493	0.2950/0.4466	N/A
Largest diff. peak/hole ($e.Å^{-3}$)		1.22/-1.11	1.78/-2.25	0.91/-1.03	0.52/-0.53	0.74/-0.98	0.73/-0.89	N/A

Table S9. Crystallographic data of compressed AMU3·DMF with glycerine as PTM

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

Pressure		0.4 GPa /α	0.5 GPa /α	0.6 GPa /α	0.88 GPa /β	1.0 GPa /β
CCDC number		2046219	2046217	2046216	2046220	2046218
Formula weight		501.77	501.77	460.72	460.72	460.72
Wavelength (Å)		0.71073	0.71073	0.71073	0.71073	0.71073
Crystal system		orthorhombic	Orthorhombic	orthorhombic	monoclinic	monoclinic
Space group		*Cmce*	*Cmce*	*Cmce*	$P2_1/n$	$P2_1/n$
Unit cell dimensions	*a* (Å)	13.659(4)	13.6209(16)	13.6195(11)	12.372(3)	12.368(2)
	b (Å)	20.669(7)	20.750(2)	20.7923(17)	14.15(3)	14.14(2)
	c (Å)	14.39(6)	14.33(2)	14.241(15)	12.433(4)	12.444(2)
	β (°)	90	90	90	113.58(3)	113.65(2)
Volume (Å^3)		4063(17)	4049(6)	4033(4)	1995(4)	1994(4)
Z/Z'		8/0.5	8/0.5	8/0.5	4/1	4/1
Molecular volume (*V/Z*)		507.87	506.12	504.12	498.75	498.50
Calculated density (g/cm^3)		1.611	1.646	1.518	1.534	1.535
Absorption (mm^{-1})		1.111	1.116	1.111	1.123	1.124
F(000)		1928.0	2000.0	1824.0	912.0	912.0
Crystal size (mm)		0.387 × 0.068 × 0.051	0.387 × 0.068 × 0.051	0.387 × 0.068 × 0.051	0.387 × 0.068 × 0.051	0.386 × 0.068 × 0.051
2*ϑ*-range for data collection (°)		7.204 to 46.698	7.158 to 42.454	9.628 to 46.502	8.368 to 37.686	9.648 to 41.624
Min/max indices: *h, k, l*		-15/15, -20/22, -4/5	-13/13, -21/21, -4/4	-15/15, -23/23, -5/5	-11/11, -5/5, -11/11	-12/12, -5/5, -12/12
Reflect. Collected/unique		7441/566	7254/457	9945/630	5526/689	8181/858
R_{int}		0.2847	0.2013	0.0964	0.1862	0.0991
Refinement method;		Full-matrix least-squares on F^2				
Completeness (%)		36	38	42	44	41
Data/restrains/parameters		566/288/119	457/303/139	630/350/139	689/551/208	858/347/196
Goodness-of-fit on F^2		1.071	1.108	1.537	1.299	1.654
Final R1/wR^2 (I>2σ1)		0.1000/0.2365	0.0718/0.2102	0.1170/0.3271	0.1125/0.2923	0.1267/0.3430
R1/wR^2 (all data)		0.2139/0.3175	0.1222/0.2531	0.1573/0.3717	0.1775/0.3577	0.1803/0.4056

Table S10. Crystallographic data of compressed AMU3·MeCN with MEW as PTM.

Largest diff. peak/hole (e.Å^{-3})	0.82/-0.43	0.59/-0.39	1.36/-2.24	0.88/-0.60	1.09/-1.19

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