Supporting Information:
Anomalous compressibility of a chiral metal-organic framework

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High-pressure X-ray studies

High-pressure experiments were carried out in a Merrill-Bassett diamond-anvil cell (DAC), modified by mounting the diamond anvils directly on the steel support with conical windows.[1] The gasket was made of a pre-indented 0.3 mm thick steel foil, with a 0.4 mm spark-eroded hole. Glycerol, Daphne 7474 and a mixture of methanol, ethanol and water (in the ratio: 16:3:1),[2] were used as the pressure-transmitting media for compressing single crystals of DMOF. The pressure in the DAC was calibrated by the R1 ruby-line shift, measured by a Photon Control Spectrometer of enhanced resolution, affording an accuracy of 0.02 GPa.[2,3] The DAC was centred by the gasket-shadow method.[4] X-Ray diffraction data were measured with an Xcalibur Eos diffractometer and MoKα radiation. The high-pressure structures of DMOF were refined starting from its ambient-pressure model and using the full-matrix least squares method of SHELXL[6] within the Olex2 interface.[7] The final crystal data are summarised in Table 1 and in the SI. Owing to strongly disordered solvent molecules trapped in the pores of DMOF for all high-pressure measurements, the Platon subroutine SQUEEZE was applied.[5]

The structures have been deposited with the Cambridge Crystallographic Data Centre in the CIF format, no. 1956801-1956804, 1956866-1956870 for DMOF compressed in glycerol and 1956872-1956875 Daphne 7474 and 1956823-1956826, 1956193 for the structures compressed

in MEW. Copies of this information can be obtained free of charge from www: http://www.ccdc.cam.ac.uk.

Table S1. Compressibility related to crystallographic axes between 0.1 MPa - 1.70 GPa calculated for (*m*-btcp)$_2$(bpdc)$_2$Zn(II) with Birch-Murnaghan Coefficients in non-penetrating media: Daphne 7474 and glycerol.

			Directions			Empirical parameters			
Axes	**K(TPa^{-1})**	**σK(TPa^{-1})**	**a**	**b**	**c**	**ε_0**	**λ**	**P_c**	**ν**
X_1	57.3464	6.3797	1	0	0	1.4071e-02	-4.7713e-02	-0.4021	1.1658
X_2	23.6407	4.7860	0	0	1	1.1970e-03	-2.6089e-02	0.0010	0.8826
X_3	-15.5525	3.1476	0	1	0	5.4438e-03	1.0770e-02	0.0010	1.6833
V	66.6108	2.4646							

Birch-Murnaghan Coefficients

	B_0 (GPa)	**σB_0 (GPa)**	**V_0 (Å^3)**	**σV_0 (Å^3)**	**B'**	**σB'**	**P_c (GPa)**
2nd	11.0507	0.7131	5191.7321	21.4783	4	n/a	0
3rd	13.1024	2.4939	5172.8458	26.4805	1.6482	2.4952	0

Table S2. Compressibility related to crystallographic axes calculated for (*m*-btcp)$_2$(bpdc)$_2$Zn(II) with Birch-Murnaghan Coefficients in the mixture of methanol:ethanol:water, in pressure between two measurements 0.1 MPa and 1.18 GPa, with program PASCal.[6]

			Direction				Empirical parameters		
Axes	**K(TPa^{-1})**	**σK(TPa^{-1})**	**a**	**b**	**c**	**ε_0**	**λ**	**P_c**	**ν**
X_1	27.2332	6.5588	0	1	0	-3.9955e-02	7.6928e+01	-3.2142	-6.4130
X_2	10.1260	5.4559	1	0	0	-6.2470e-04	-1.4772e-03	-0.4944	3.9832
X_3	-44.5916	2.6869	0	0	1	9.3921e-01	-8.8988e-01	-0.0262	-0.0163
V	-5.6106	589.1069							

Birch-Murnaghan Coefficients

	B_0 (GPa)	**σB_0 (GPa)**	**V_0 (Å^3)**	**σV_0 (Å^3)**	**B'**	**σB'**	**P_c (GPa)**
2nd	-181.2014	40.1061	5146.4333	1206.9104	4	n/a	0

References

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Table S3. Detailed crystallographic data of DMOF compressed in glycerol with their deposited CCDC numbers.

Pressure		0.10 GPa	0.40 GPa	Pressure	0.50 GPa	0.19 GPa	0.70 GPa	0.45 GPa	0.80 GPa	0.7 GPa	1.20 GPa	0.9 GPa	1.35 GPa		1.50 GPa	1.70 GPa
Hydrostatic medium		glycerol	glycerol	Hydrostatic medium	glycerol	Daphne 7474 oil	glycerol	Daphne 7474 oil	glycerol	Daphne 7474 oil	glycerol	Daphne 7474 oil	glycerol		glycerol	glycerol
CCDC numbers		1956803	1956801		1956804		1956802		1956870		1956867		1956869		1956866	1956868
Formula weight		828.09	828.09		828.09		828.09		828.09		828.09		828.09		828.09	828.09
Empirical formula		$C_{39}H_{24}F_6N_2O_4S_2Zn$	$C_{39}H_{24}F_6N_2O_4S_2Zn$		$C_{39}H_{24}F_6N_2O_4S_2Zn$		$C_{39}H_{24}F_6N_2O_4S_2Zn$		$C_{39}H_{24}F_6N_2O_4S_2Zn$		$C_{39}H_{24}F_6N_2O_4S_2Zn$		$C_{39}H_{24}F_6N_2O_4S_2Zn$		$C_{39}H_{24}F_6N_2O_4S_2Zn$	$C_{39}H_{24}F_6N_2O_4S_2Zn$
Wavelength (Å)		0.71073	0.71073		0.71073		0.71073		0.71073		0.71073		0.71073		0.71073	0.71073
Crystal system		orthorhombic	orthorhombic		orthorhombic		orthorhombic		orthorhombic		orthorhombic		orthorhombic		orthorhombic	orthorhombic
Space group		$P2_12_12_1$	$P2_12_12_1$		$P2_12_12_1$		$P2_12_12_1$		$P2_12_12_1$		$P2_12_12_1$		$P2_12_12_1$		$P2_12_12_1$	$P2_12_12_1$
Unit cell dimensions	a (Å)	7.033(3)	6.9346(16)		6.890(3)		6.8072(17)		6.730(2)		6.638(6)		6.555(8)		6.513(9)	6.399(7)
	b (Å)	25.167(15)	25.153(13)		25.19(2)		25.266(16)		25.256(15)		25.42(3)		25.56(3)		25.67(3)	25.71(3)
	c (Å)	29.00(4)	28.98(2)		28.95(3)		28.63(3)		28.79(4)		28.23(8)		28.14(7)		27.96(7)	27.86(7)
Volume (Å^3)		5134(9)	5055(5)		5026(7)		4924(6)		4893(7)		4762(16)		4716(15)		4675(14)	4615(14)
Z/Z'		4/1	4/1		4/1		4/1		4/1		4/1		4/1		4/1	4/1
Molecular volume (V/Z)		1283.5	1263.75		1256.5		1231.0		1223.25		1190.5		1179.0		1168.75	1153.75
Calculated density (g/cm^3)		1.071	1.088		1.094		1.117		1.124		1.155		1.166		1.176	-
Absorption (mm^{-1})		0.613	0.622		0.626		0.639		0.643		0.661		0.667		0.673	-
F(000)		1680.0	1680.0		1680.0		1680.0		1680.0		1680.0		1680.0		1680.0	-
Crystal size (mm)		0.307 × 0.214 × 0.126	0.308 × 0.215 × 0.125		0.308 × 0.215 × 0.124		0.308 × 0.216 × 0.124		0.308 × 0.216 × 0.122		0.308 × 0.216 × 0.122		0.308 × 0.216 × 0.122		0.308 × 0.216 × 0.122	0.309 × 0.216 × 0.122
2θ-range for data collection (°)		8.068 to 29.168	8.13 to 27.166		7.956 to 51.194		8.208 to 29.406		8.254 to 34.44		8.17 to 22.886		8.228 to 20.448		8.268 to 20.314	-
Min/max indices: h, k, l		-4/4, -17/17, -16/16	-4/4, -15/15, -17/17		-6/8, -22/19, -23/23		-4/4, -16/16, -18/18		-5/5, -20/20, -17/17		-3/3, -13/13, -13 /13		-3/3, -12/12, -11 /11		-3/3, -12/12, -11/11	-
Reflect. collected/unique		9017/1405	8705/1171		4301/2130		10158 /1418		14627/1987		4271/622		3011/438		2763/417	-
R_{int}		0.3847	0.2726		0.2156		0.4441		0.4867		0.3085		0.2840		0.4812	-
Refinement method		Full-matrix least-squares on F^2														
Completeness (%)		75	75		23		76		55		73		72		71	-
Data/restrains/parameters		1405/781/414	1171/485/414		2130/745/414		1418/760/414		1987/611/414		622/204/106		438/75/102		417/128/107	-
Goodness-of-fit on F^2		1.180	1.397		0.915		1.227		1.028		1.176		1.096		1.067	-
Final R_1/wR_2 [(I>2σ(I)]		0.1196/0.3102	0.1125/0.2978		0.0974/ 0.1962		0.1273/0.3142		0.1161/0.2770		0.1168/0.2985		0.1498/0.3469		0.1431/0.3430	-
R_1/wR_2 (all data)		0.1849/0.3718	0.0734/0.3413		0.2676/0.2827		0.2030/0.3895		0.2405/0.3690		0.1569/0.3456		0.1988/0.3943		0.2106/0.4045	-
Largest diff. peak/hole (e Å^{-3})		0.25/-0.19	0.24/-0.26		0.14/-0.17		0.29/-0.19		0.23/-0.20		0.15/-0.17		0.25/-0.17		0.09/-0.11	-

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

Table S4. Detailed crystallographic data of Daphne 7474 with their DMOF compressed in deposited CCDC numbers.

CCDC numbers		1956873	1956874	1956875	1956872
Formula weight		828.09	828.09	828.09	828.09
Empirical formula		$C_{39}H_{24}F_6N_2O_4S_2Zn$	$C_{39}H_{24}F_6N_2O_4S_2Zn$	$C_{39}H_{24}F_6N_2O_4S_2Zn$	$C_{39}H_{24}F_6N_2O_4S_2Zn$
Wavelength (Å)		0.71073	0.71073	0.71073	0.71073
Crystal system		orthorhombic	orthorhombic	orthorhombic	orthorhombic
Space group		$P2_12_12_1$	$P2_12_12_1$	$P2_12_12_1$	$P2_12_12_1$
Unit cell dimensions	a (Å)	7.011(17)	7.007(6)	6.881(9)	6.801(17)
	b (Å)	25.05(2)	25.170(15)	25.14(3)	25.11(6)
	c (Å)	28.81(5)	28.46(19)	28.2(3)	27.98(8)
Volume (Å^3)		5059(16)	5019(34)	4871(51)	4813(20)
Z/Z'		4/1	4/1	4/1	4/1
Molecular volume (V/Z)		1264.75	1254.75	1217.75	1203.25
Calculated density (g/cm^3)		-	1.096	1.129	-
Absorption (mm^{-1})		-	0.627	0.646	-
F(000)		-	1680.0	1680.0	-
Crystal size (mm)		0.232 × 0.183 × 0.11	0.232 × 0.183 × 0.11	0.232 × 0.183 × 0.11	0.232 × 0.183 × 0.11
2θ-range for data collection (°)		-	8.102 to 24.034	8.028 to 22.828	-
Min/max indices: h, k, l		-	-4/4, -14/14, -6/6	-3/3, -14/14, -7/7	-
Reflect. collected/unique		-	5280/434	4756/399	-
R_{int}		-	0.5890	0.8895	-
Refinement method		Full-matrix least-squares on F^2			
Completeness (%)		-	41	46	-
Data/restrains/parameters		-	434/88/90	399/102/90	-
Goodness-of-fit on F^2		-	1.074	1.029	-
Final R_1/wR_2 [(I>2σ(I)]		-	0.1234/0.2840	0.1387/0.3305	-
R_1/wR_2 (all data)		-	0.1766/0.3380	0.2365/0.4268	-
Largest diff. peak/hole (e Å^{-3})		-	0.18/-0.17	0.18/-0.18	-

w=1/(σ$^2F_o^2$+w_1^2*P^2+w_2*P), where P=(Max(F_o^2,0)+2*F_c^2)

Table S5. Detailed crystallographic data of DMOF compressed in MEW with their deposited CCDC numbers.

Pressure		0.1 MPa	0.25 GPa	0.56 GPa	0.85 GPa	1.18 GPa
Hydrostatic medium		-	Methanol:ethanol:water	Methanol:ethanol:water	Methanol:ethanol:water	Methanol:ethanol:water
CCDC numbers		1956193	1956826	1956824	1956823	1956825
Formula weight		900.18	828.09	828.09	828.09	828.09
Empirical formula		$C_{42}H_{30}F_6N_3O_5S_2Zn$	$C_{39}H_{24}F_6N_2O_4S_2Zn$	$C_{39}H_{24}F_6N_2O_4S_2Zn$	$C_{39}H_{24}F_6N_2O_4S_2Zn$	$C_{39}H_{24}F_6N_2O_4S_2Zn$
Wavelength (Å)		1.54184	0.71073	0.71073	0.71073	0.71073
Crystal system		orthorhombic	orthorhombic	orthorhombic	orthorhombic	orthorhombic
Space group		$P2_12_12_1$	$P2_12_12_1$	$P2_12_12_1$	$P2_12_12_1$	$P2_12_12_1$
Unit cell dimensions	a (Å)	7.11393(12)	7.1001(8)	7.1015(18)	7.072(4)	7.029(3)
	b (Å)	24.9253(4	24.68(2)	24.22(3)	24.225(15)	24.125(10)
	c (Å)	29.0241(8)	29.899(7)	30.248(17)	30.38(5)	30.55(4)
Volume (Å^3)		5146.45(19)	5240(5)	5202(8)	5205(10)	5181(8)
Z/Z'		4/1	4/1	4/1	4/1	4/1
Molecular volume (V/Z)		1286.61	1310.0	1300.5	1301.25	1295.25
Calculated density (g/cm^3)		1.162	1.050	1.057	1.057	1.062
Absorption (mm^{-1})		1.947	0.600	0.605	0.604	0.607
F(000)		1836.0	1680.0	1680.0	1680.0	1680.0
Crystal size (mm)		0.307 × 0.213 × 0.127	0.303 × 0.135 × 0.063	0.234 × 0.084 × 0.052	0.302 × 0.137 × 0.063	0.234 × 0.084 × 0.052
2θ-range for data collection (°)		7.048 to 155.29	4.408 to 46.498	4.376 to 41.632	8.394 to 20.458	8.15 to 29.386
Min/max indices: h, k, l		-8/8, -31/18, -35/36	-7/7, -16/17, -32/32	-7/7, -17/18, -28/29	-3/3, -11/12, -12/11	-5/5, -16/17, -15/15
Reflect. collected/unique		44199/10708	26565/4239	20936/3431	3350/446	9614 /1221
R_{int}		0.0374	0.3620	0.3619	0.1889	0.3500
Refinement method		Full-matrix least-squares on F^2				
Completeness (%)		100	54	64	67	65
Data/restrains/parameters		10708/123/565	4239/719/414	3431/768/414	446/57/91	1221/144/91
Goodness-of-fit on F^2		1.660	1.057	1.098	1.168	1.593
Final R_1/wR_2 [(I>2σ(I)]		0.1227/ 0.3691	0.1470/0.3636	0.1391/ 0.3428	0.1023/ 0.2449	0.1710/0.4073
R_1/wR_2 (all data)		0.1330/0.3851	0.3584/0.4778	0.3125/ 0.4536	0.1386/0.2875	0.2384/0.4798
Largest diff. peak/hole (e Å^{-3})		1.34/-1.13	0.29/-0.47	0.43/-0.48	0.27/-0.29	0.52/-0.50

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