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Supporting information

Biphenyl Tetracarboxylic Acid based Metal-Organic Frameworks: A Case of Topology-Dependent Thermal Expansion

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Materials and Synthesis

All reagents and solvents were used as received from commercial supplier without further purification.

Synthesis of InOF-1

156 mg of $In(NO_3)_3•5H_2O$ and 33 mg of H4BPTC ligand were dissolved in a 5 mL solution of N,N-dimethylformamide and acetonitrile (1:1). To this solution, 0.2 mL of nitric acid was added. After stirring at room temperature for 30 minutes, the solution was transferred to a Teflon-lined autoclave and heated for 3 days at 85°C. The resulting product was filtered, washed multiple times with ethanol, and then dried under ambient air.

Synthesis of InOF-2

22 mg of $InCl_3•4H_2O$ and 33 mg of H_4BPTC ligand were dissolved in a 5 mL solution of N,N-diethylformamide and acetonitrile (1:1). To this solution, 0.2 mL of nitric acid was added. After stirring at room temperature for 30 minutes, the solution was transferred to a Teflon-lined autoclave and heated for 10 days at 85°C. The resulting product was filtered, washed multiple times with ethanol, and then dried under ambient air.

Synthesis of InOF-12

33 mg of $InCl_3$ and 33 mg of H_4BPTC ligand were dissolved in a 6 mL solution of N,N-dimethylacetamide and ethanol (1:1). To this solution, 0.1 mL of nitric acid was added. After stirring at room temperature for 30 minutes, the solution was transferred to a Teflon-lined autoclave and heated for 5 days at 85°C. The resulting product was filtered, washed multiple times with ethanol, and then dried under ambient air.

Synthesis of InOF-13

A mixture of 33 mg of $InCl_3$, 33 mg of H_4BPTC ligand and 11 mg of dabco (1,4-Diazabicyclo[2.2.2]octane) was dissolved in a 5 mL solution of N,N-diethylformamide. To this solution, 0.1 mL of nitric acid was added. After stirring at room temperature for 30 minutes, the solution was transferred to a Teflon-lined autoclave and heated for 5 days at 85°C. The resulting product was filtered, washed multiple times with ethanol, and then dried under ambient air.

Characterization

Before measurements, all samples were dried under vacuum at 60˚C for 3h to eliminate the influence of adsorbed water molecules. The in situ variable temperature powder X-ray diffraction data were collected on a laboratory diffratometer (PANalytical X'PertPro) with Cu-Kα radiation. The scan was carried out using the TTK-450 non-ambient stage from 123K to 473K with an interval of 25 or 50K.

Variable temperature high-resolution synchrotron based X-ray diffraction data were collected using the 11-BM-B beamline (Advanced Photon Soures, Argonne National Laboratory). The wavelength was calibrated to λ =0.4589340 Å using a CeO_2 standard. The sample was loaded into a 0.8mm diameter Kapton capillary, which was then spun at several radians per second to improve particle statistics. The temperature was controlled from 100 to 400K (in intervals of 25K) using an Oxford Cryostream 700+ N_2 gas blower.

Lebail fitting and Rietveld refinements of the diffraction data were performed using the GSAS and EXPGui software.[1]

Single crystal X-ray diffraction (SCXRD) data were collected using an Oxford SuperNova diffractometer with microsource Cu-Kα radiation (λ = 1.54184 Å) and equipped with a 800 Cryostream low-temperature unit (Oxford, Cryosystems, Oxford, U.K.). All diffraction data of InOF-1 was collected continuously at 110K, 150K, 200K, 250K, 300K and 350K with a heating rate of 5K/min. The single crystal specimen was mounted on a glass fibre. The measurement temperatures were controlled by an open-flow dry N_2 cryostat. Before data collection, the specimen was hold at target temperature for 10 min. The structure was solved by the direct method and refined with a full-matrix least-squares technique using Olex2.[2] The hydrogen atoms were generated geometrically and refined using a riding model. The twin law [−1, 0, 0, 0, -1, 0, 0, 0, −1, 2] was identified by the "TwinRotMat" program. The percentage of twin is given by a batch scale factor (BASF) of 0.42.

Raman measurements were performed with a multichannel modular triple Raman systems (JY-HR800) with confocal microscopy. The solid-state diode laser (532 nm) from Coherent Company-Verdi-2 was used as an excited source.

DFT calculations were performed using the CASTEP program.[3] Prior to the vibrational calculations, the crystal structure was fully optimized. Vibrational properties were calculated using the linear response formalism, where the phonon frequencies were obtained by the second derivative of the total energy with respect to the given perturbation.

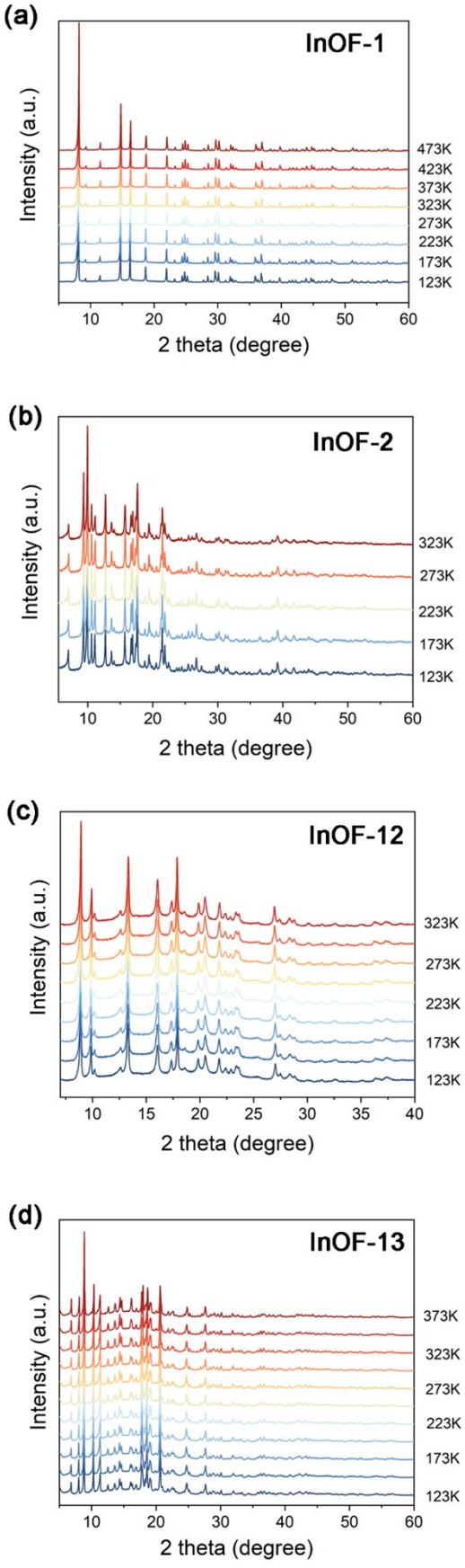

Figure S1 Laboratory VT-PXRD patterns of InOF-1(a), InOF-2 (b), InOF-12 (c) and InOF-13 (d).

Table S1 Unit cell volumes of InOF-1, InOF-2, InOF-12 and InOF-13 extracted by the Lebail fitting based on the VT-PXRD results.

	V_{InOF-1} (Å^3)	V_{InOF-2} (Å^3)	$V_{InOF-12}$ (Å^3)	$V_{InOF-13}$ (Å^3)
123K	2964.979	3552.121	1746.210	3336.808
148	-	-	1747.724	3338.094
173	2964.114	3552.655	1749.847	3347.006
198	-	-	1751.389	3354.92
223	2962.470	3555.701	1752.285	3355.495
248	-	-	1753.789	3358.51
273	2961.735	3562.027	1757.267	3360.801
298	-	-	1760.056	3364.087
323	2960.075	3566.216	1760.500	3369.436
348	-	-	-	3374.624
373	2958.585	-	-	3379.576
398	-	-	-	-
423	2958.065	-	-	-
448	-	-	-	-
473	2957.811	-	-	-

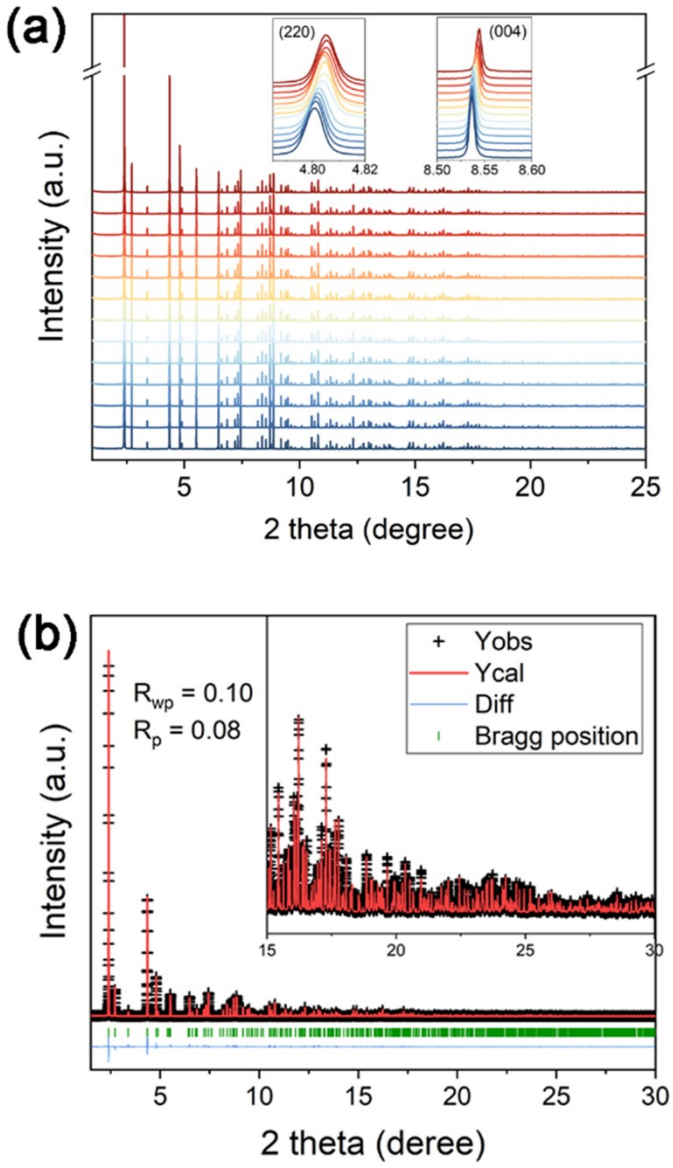

Figure S2 (a) Synchrotron based VT-XRD patterns of InOF-1, (b) Rietveld refinement pattern of InOF-1 that measured at 100K (R_{wp} = 0.10, R_p = 0.08).

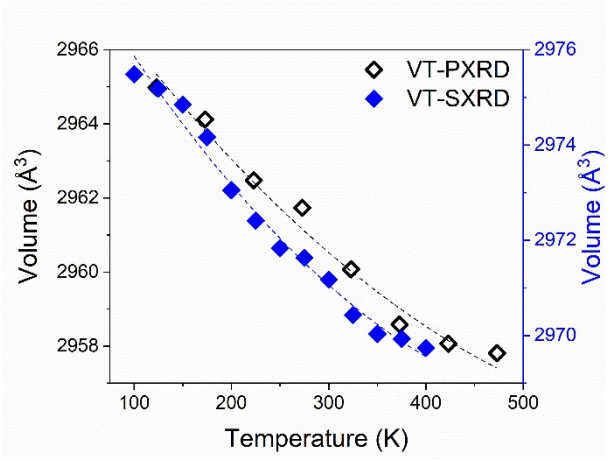

Figure S3 Temperature dependent unit cell volume changes of InOF-1 that obtained based on the VT-PXRD data (black empty diamonds) and VT-SXRD data (blue filled diamonds)

Table S2 Lattice parameters of InOF-1 that obtained based on the VT-SXRD data.

Temperature (K)	*a(b)* (Å)	*c* (Å)	*V* (Å^3)
100	15.52088	12.35165	2975.48365
125	15.51997	12.35184	2975.18225
150	15.51911	12.35182	2974.84771
175	15.51768	12.35128	2974.16780
200	15.51558	12.34997	2973.04909
225	15.51500	12.34825	2972.41226
250	15.51490	12.34600	2971.83186
275	15.51487	12.34523	2971.63502
300	15.51435	12.34415	2971.17583
325	15.51306	12.34313	2970.43465
350	15.51257	12.34224	2970.03379
375	15.51272	12.34156	2969.93105
400	15.51315	12.34008	2969.73774

Table S3 Crystallographic data of compound InOF-1 at different temperatures.

	InOF-1-110 K	InOF-1-150 K	InOF-1-200 K
Empirical formula	$C_8H_3O_5In$	$C_8H_3O_5In$	$C_8H_3O_5In$
Formula weight	293.92	293.92	293.92

Temperature/K	110	150	200
Crystal system	Tetragonal	Tetragonal	Tetragonal
Space group	$I4_122$	$I4_122$	$I4_122$
a/Å	15.4846	15.4819	15.4791
b/Å	15.4846	15.4819	15.4791
c/Å	12.3372	12.3361	12.3348
α/°	90.00	90.00	90.00
β/°	90.00	90.00	90.00
γ/°	90.00	90.00	90.00
Volume/Å^3	2958.13	2956.83	2955.45
Z	8	8	8
ρcalcg/cm^3	1.32	1.32	1.32
μ/mm^{-1}	12.776	12.782	12.778
F(000)	1120	1120	1120
Goodness-of-fit on F^2	1.156	1.201	1.173
Final R indexes [I>=2σ (I)]	R1 = 0.0243, wR2 = 0.0661	R1 = 0.0216, wR2 = 0.0642	R1 = 0.0220, wR2 = 0.0666
Final R indexes [all data]	R1 = 0.0249, wR2 = 0.0668,	R1 = 0.0223, wR2 = 0.0645	R1 = 0.0228, wR2 = 0.0670
CCDC number	2336419	2336420	2336421

	InOF-1-250 K	InOF-1-300 K	InOF-1-350 K
Empirical formula	$C_8H_3O_5In$	$C_8H_3O_5In$	$C_8H_3O_5In$
Formula weight	293.92	293.92	293.92
Temperature/K	250	300	350
Crystal system	Tetragonal	Tetragonal	Tetragonal
Space group	$I4_122$	$I4_122$	$I4_122$
a/Å	15.4763	15.4732	15.4711
b/Å	15.4763	15.4732	15.4711
c/Å	12.3336	12.3324	12.3310
α/°	90.00	90.00	90.00
β/°	90.00	90.00	90.00
γ/°	90.00	90.00	90.00
Volume/Å^3	2954.09	2952.65	2951.49
Z	8	8	8
ρcalcg/cm^3	1.322	1.322	1.322
μ/mm^{-1}	12.793	12.800	12.805
F(000)	1120	1120	1120
Goodness-of-fit on F^2	1.162	0.905	1.073
Final R indexes [I>=2σ (I)]	R1 = 0.0269, wR2 = 0.0777,	R1 = 0.0204, wR2 = 0.0588	R1 = 0.0222, wR2 = 0.0624
Final R indexes [all data]	R1 = 0.0275, wR2 = 0.0780,	R1 = 0.0219, wR2 = 0.0598	R1 = 0.0253, wR2 = 0.0638
CCDC number	2336422	2336423	2336424

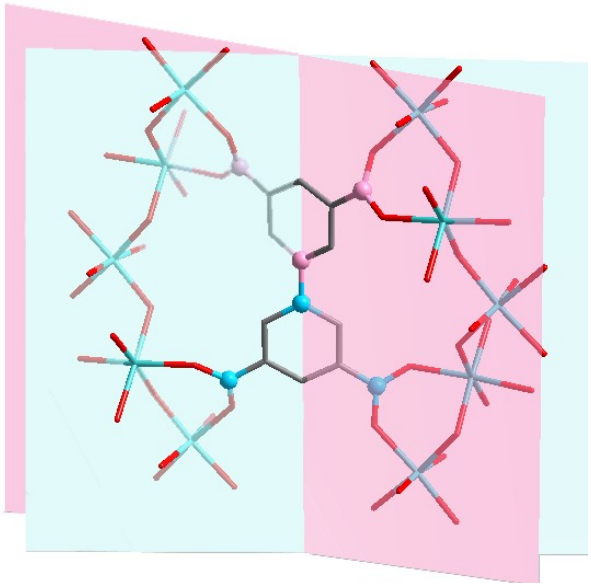

Figure S4 Definition of the dihedral angle *β*. Each plane is built based on three carbon atoms (including one carbon atom in the phenyl and two carboxylate C atoms, shown as large balls).

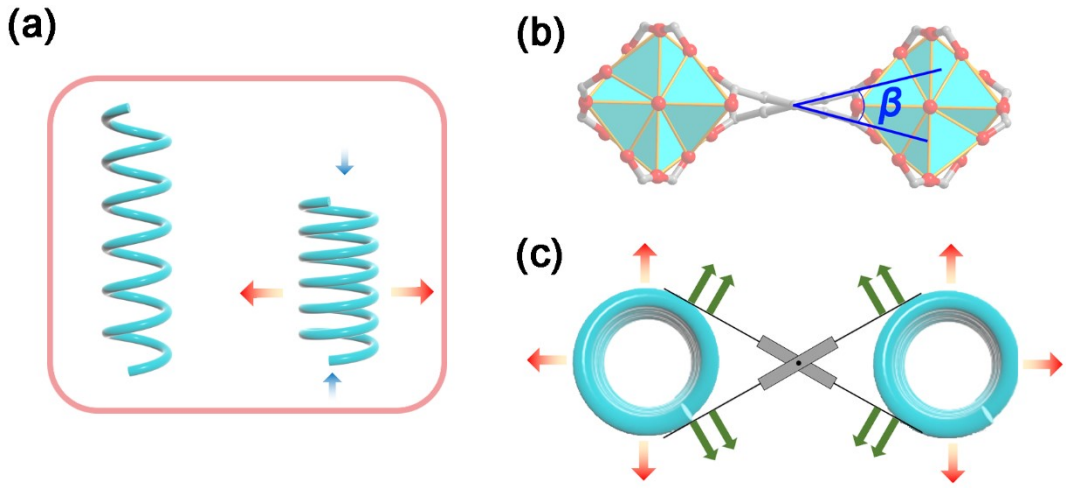

Figure S5 (a) Spring-like distortion of the 1D helical $[InO_6]_\infty$ chain. (b) Crystal structure of InOF-1 viewing along *c*-axis. (c) Illustration of the 1D helical $[InO_6]_\infty$ chain expansion drove twisting of BPTC ligand.

Reference:

1 a) A. C. Larson, R. B. Von Dreele, *Report lAUR* 1994, 86; b) B. H. Toby, *J. Appl. Cryst.* 2001, **34**, 210.

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3 S. J. Clark, M. D. Segall, C. J. Pickard, P. J. Hasnip, M. I. Probert, K. Refson, M. C. Payne, *Z. Krist-Cryst Mater.* 2005, **220**, 567.