Supporting Information

3D Negative Thermal Expansion in Orthorhombic MIL-68(In)

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Synthesis:

MIL-68(In) was synthesized by solvothermal reaction as reference.[1] A mixture of $In(NO_3)_3 \cdot 6H_2O$ (408.2 mg), terephthalic acid (200 mg) and DMF (5 ml) was stirred at room temperature for 1 hour, then transferred to a Teflon-lined autoclave and heated for 48h at 100 °C. The resulting products were filtered off and washed several times with ethanol. To fully remove the guest DMF molecules encapsulated within the channels, the products were immersed in ethanol for three days and then calcined at 220 °C overnight.

TGA:

Thermal gravimetric analysis (TGA) was performed under air atmosphere with a heating rate of 5°C/min using a Labsys Evo system (by SETARAM) from room temperature to 620°C. The weight loss of as-synthesized sample at 200°C corresponds to the loss of DMF solvent. For the activated sample, no weight loss and phase transition occurred before deposition (nearly 450 °C).

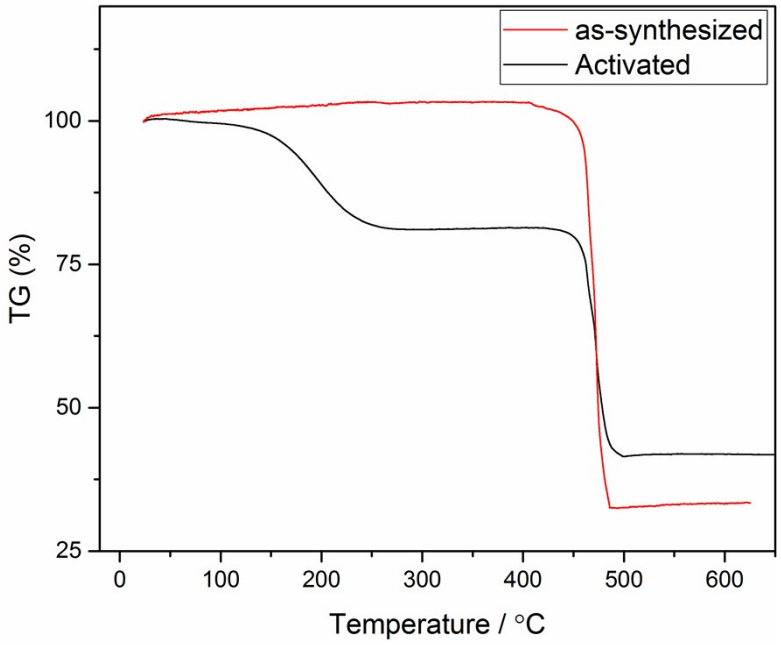

Figure S1. TGA curves of the as-synthesised and activated MIL-68(In), the weight loss at 450 °C infers the deposition of the sample.

HRSXRD and Lebail fitting:

Variable temperature high resolution synchrotron X-ray diffraction data was collected at the BL44B2 beamline of Spring-8 synchrotron radiation facility using a constant wavelength of λ=0.5 Å. For low temperature diffraction, the sample was loaded in 0.3mm thick glass capillary and rotated to obtain a homogeneous diffraction pattern at 125 K, 150 K, 200 K, 250 K, and 300 K. For high temperature diffraction, the sample was loaded in 0.3mm thick quartz capillary and rotated to obtain a homogeneous diffraction pattern from 300 to 600 K with an interval of 50 K. Lebail fitting was used in the GSAS suite programs.[2-3]

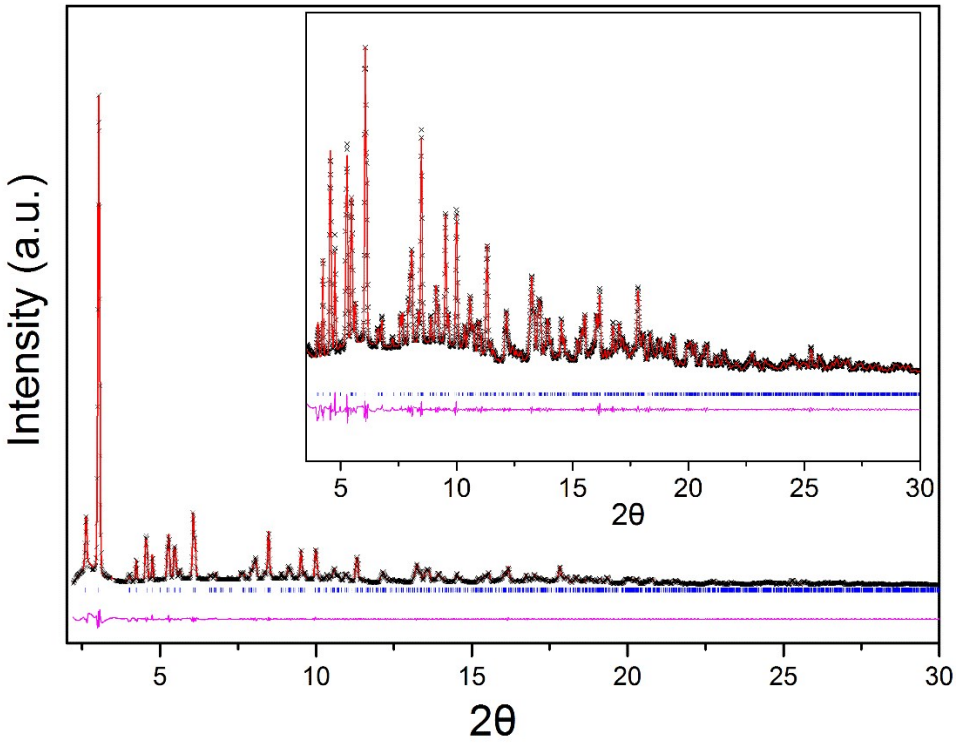

Figure S2. Lebail fitting patterns for SXRD data collected at 300K, the insert shows the fitted data at high angles with five times zoom in. Experimental data are given as black symbols, the fitted profiles as a solid red line and the difference (data-fit) as pink line, peak position as blue symbols. (R_p= 0.0208, R_{wp}=0.0337, Chi^2=6.398)

Table S1. Lattice parameters extracted from SXRD using Lebail fitting.

Temperature/ K	a (Å)	b (Å)	c (Å)	V(Å^3)
125	21.8796(5)	37.3959(8)	7.2352(1)	5919.9(3)
150	21.8754(6)	37.3943(10)	7.2343(1)	5917.8(3)
200	21.8617(6)	37.3878(10)	7.2320(1)	5911.2(3)
250	21.8563(5)	37.3803(9)	7.2304(1)	5907.2(3)
300	21.8476(6)	37.3703(10)	7.2274(1)	5900.8(3)
300(HT furnace)	21.8462(4)	37.3693(10)	7.2278(1)	5900.6(2)
350	21.8453(7)	37.3700(13)	7.2263(2)	5899.2(4)
400	21.8436(8)	37.3644(13)	7.2260(2)	5897.7(5)

450	21.8337(5)	37.3588(11)	7.2244(1)	5892.8(3)
500	21.8269(9)	37.3568(18)	7.2236(2)	5890.0(6)
550	21.8252(9)	37.3549(18)	7.2225(2)	5888.4(6)
600	21.8207(12)	37.3479(20)	7.2214(3)	5885.1(8)

SCXRD:

Variable temperature single crystal X-ray diffraction was carried out at 3W1A Beijing Synchrotron Radiation Facility (BSRF) with a wavelength of 0.72 Å. The data was collected from 125 to 250 K with an interval of 25 K using a Mar CCD 165 mm detector by the ω-scan technique. Before testing, the sample was activated under 200°C for 2 hours, and sealed into a capillary under vacuum. The data was solved and refined using SHELX-97.[4] All non-hydrogen atoms were refined anisotropically. PLATON/SQUEEZE program was used to remove the contribution from the few residual guest solvents to the intensity data.[5]

Table S2. Crystallographic data of compound MIL-68(In) at different temperatures.

	125 K	150 K	175 K
Empirical formula	C24H12In3O15	C24H12In3O15	C24H12In3O15
Formula weight	884.70	884.70	884.70
Temperature/K	125	150	175
Crystal system	Orthogonal	Orthogonal	Orthogonal
Space group	Cmcm	Cmcm	Cmcm
a/Å	21.892(10)	21.884(4)	21.872(10)
b/Å	37.916(8)	37.906(13)	37.897(8)
c/Å	7.2570(15)	7.2530(15)	7.2500(15)
α/°	90.00	90.00	90.00
β/°	90.00	90.00	90.00
γ/°	90.00	90.00	90.00
Volume/Å^3	6024(3)	6017(3)	6009(3)
Z	4	4	4
ρcalcg/cm^3	0.962	0.962	0.962
μ/mm^{-1}	1.172	1.172	1.172
F(000)	1644.0	1644.0	1644.0
Goodness-of-fit on F^2	1.076	1.082	1.073
Final R indexes [I>=2σ (I)]	R1 = 0.0689, wR2 = 0.1721,	R1 = 0.0754, wR2 = 0.1950	R1 = 0.0751, wR2 = 0.1942
Final R indexes [all data]	R1 = 0.0761, wR2 = 0.1750,	R1 = 0.0828, wR2 = 0.1985	R1 = 0.0826, wR2 = 0.1976
CCDC number	1811824	1811825	1811829

	200 K	225 K	250 K
Empirical formula	C24H12In3O15	C24H12In3O15	C24H12In3O15
Formula weight	884.70	884.70	884.70
Temperature/K	200	225	250

Crystal system	Orthogonal	Orthogonal	Orthogonal
Space group	Cmcm	Cmcm	Cmcm
a/Å	21.860(4)	21.851(4)	21.841(10)
b/Å	37.890(13)	37.882(13)	37.870(8)
c/Å	7.2480(15)	7.2460(15)	7.2460(15)
α/°	90.00	90.00	90.00
β/°	90.00	90.00	90.00
γ/°	90.00	90.00	90.00
Volume/Å^3	6003(3)	5998(3)	5993(3)
Z	4	4	4
ρcalcg/cm^3	0.962	0.962	0.962
μ/mm^{-1}	1.172	1.172	1.172
F(000)	1644.0	1644.0	1644.0
Goodness-of-fit on F^2	1.076	1.125	1.073
Final R indexes [I>=2σ (I)]	R1 = 0.0741, wR2 = 0.1972,	R1 = 0.0729, wR2 = 0.1972	R1 = 0.0731, wR2 = 0.2029
Final R indexes [all data]	R1 = 0.0816, wR2 = 0.2007,	R1 = 0.0800, wR2 = 0.2007	R1 = 0.0807, wR2 = 0.2068
CCDC number	1811828	1811827	1811826

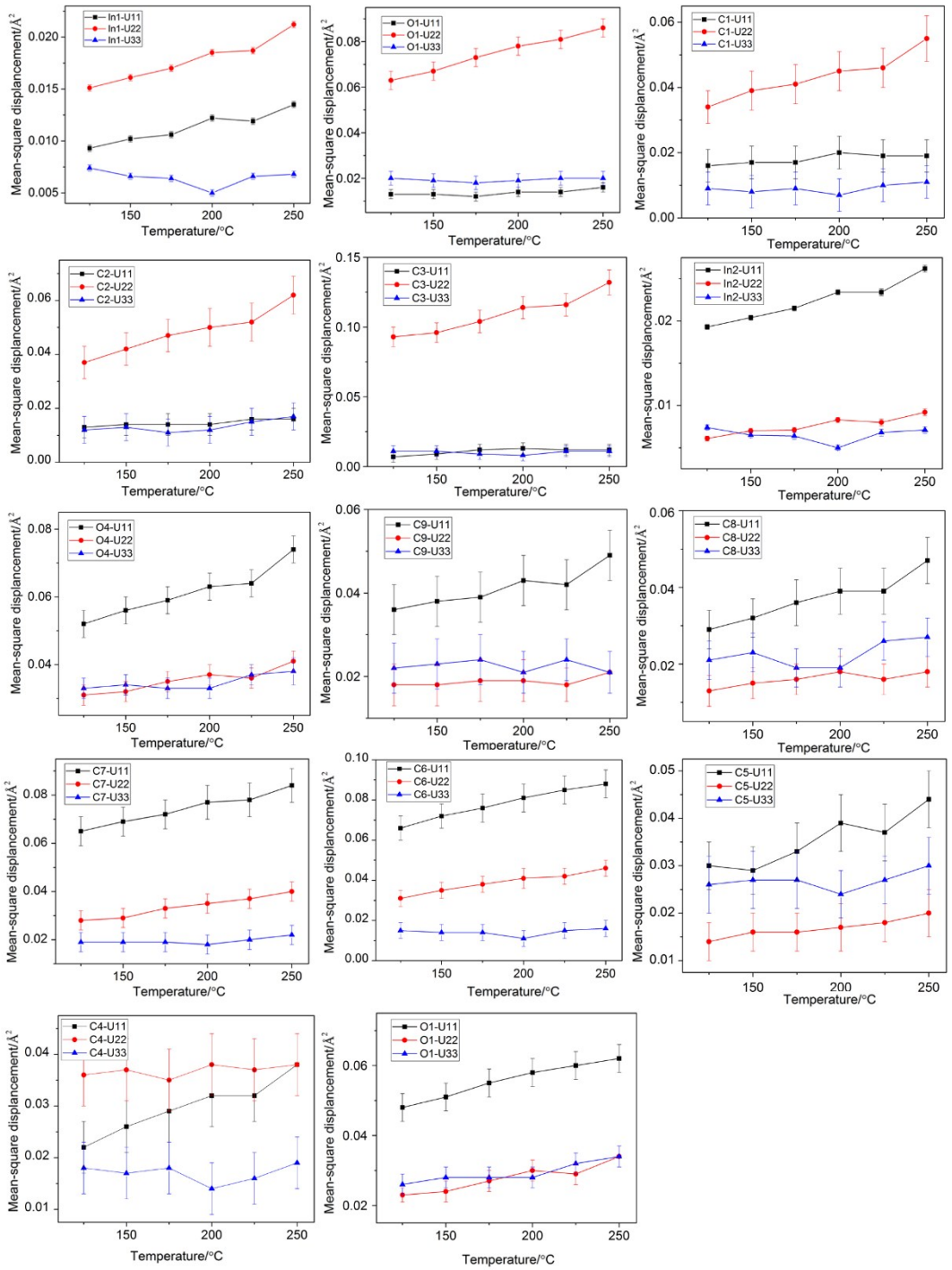

Figure S3. Temperature dependent changes of U11, U22, U33 of the linkage In1-BDC1-In1' (In1, O1, C1, C2, C3), and In1-BDC2-In2 (In2, O4, C9, C8, C7, C6, C5, C4, O2). The black square, red circle

and blue triangle represents U11, U22, and U33 respectively.

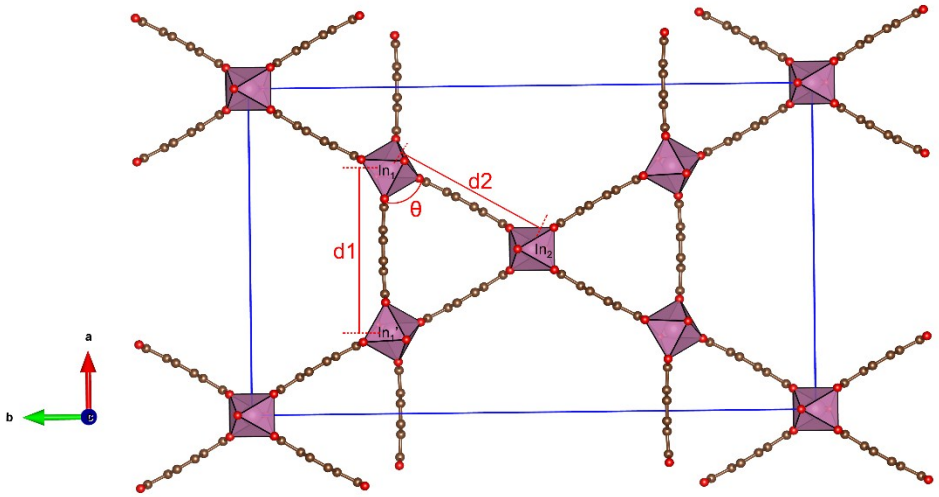

Figure S4. Crystal structure viewing along the c-axis. d1 means the distance between two bridged In1 atoms, d2 means the distance between bridged In1 and In2, and θ means the angle ∠In1'…In1…In2.

Table S3. Temperature dependent changes of d1, d2, and θ

Temperature (K)	d1 (In_1…In_1) (Å)	d2 (In_1…In_2) (Å)	θ (In_1'…In_1…In_2) (°)	Vector component along b (Å)	C1…C1' (Å)	C4…C9' (Å)
125	10.946	10.946	60.00	9.480	5.823	5.829
150	10.942	10.942	60.00	9.476	5.821	5.822
175	10.936	10.939	60.01	9.474	5.814	5.817
200	10.930	10.936	60.02	9.471	5.806	5.814
225	10.926	10.933	60.02	9.470	5.808	5.815
250	10.921	10.929	60.03	9.468	5.805	5.815

PDF:

The variable temperature synchrotron X-ray total scattering of pair distribution function (PDF) was collected at the beamline 11-ID-C with the wavelength λ=0.1173 Å. G(r) function was computed using PDFgetX2.[6] The temperature range from 175 to 450 K with an interval of 75 K.

Reference:

[1] C. Volkringer, M. Meddouri, T. Loiseau, N. Guillou, J. Marrot, G. Ferey, M. Haouas, F. Taulelle, N. Audebrand, M. Latroche, *Inorganic chemistry* **2008**, *47*, 11892-11901.

[2] A. Le Bail, H. Duroy, J. Fourquet, *Materials Research Bulletin* **1988**, *23*, 447-452.

[3] B. H. Toby, *Journal of applied crystallography* **2001**, *34*, 210-213.

[4] G. Sheldrick, *Göttingen, Germany* **1997**.

[5] A. L. Spek, *Acta Crystallographica Section C: Structural Chemistry* **2015**, *71*, 9-18.

[6] X. Qiu, J. W. Thompson, S. J. Billinge, *Journal of Applied Crystallography* **2004**, *37*, 678-678.