# Geometric Switching of Linear to Area Negative Thermal Expansion in Uniaxial Metal–Organic Frameworks

# SUPPLEMENTARY INFORMATION

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## 1 Rietveld fits

The neutron powder diffraction Rietveld fits of  $Zn(ISN)_2$  and  $InD(BDC)_2$  for all temperatures are shown in Figure S1. The difference Fourier maps from these fits indicated that the pores of  $Zn(ISN)_2$  and  $InD(BDC)_2$  were not fully desolvated, and previous work with an intelligent



Figure S1:  $Zn(ISN)_2$  and  $InD(BDC)_2$  Rietveld fits. Experimental data are shown as points, the fitted profile as a solid red line, and the difference (data-fit) as a blue line.

gravimetric analysis (IGA) on  $Zn(ISN)_2$  showed that the pores are mostly occupied by water molecules, <sup>S1</sup> as is also known in the crystal structures. <sup>S2, S3</sup> For InD(BDC)<sub>2</sub>, the diffraction quality was worse compared to that of  $Zn(ISN)_2$ , most probably owing to the large neutron absorption cross-section of indium. Despite the slight mismatch in intensity, the positions of the peaks are well defined for all temperatures in both frameworks, and therefore we can reliably use the lattice parameters extracted from these fits in our analysis shown in the main text.

The intensity fit can be improved by modelling solvent within the pores [Fig. S2]. The extra pore density in  $\text{Zn}(\text{ISN})_2$  was modelled using water molecules, referred to as  $\text{Zn}(\text{ISN})_2$ ·guest. In the case of  $\text{InD}(\text{BDC})_2$ , the pore density was modelled using oxygen atoms ( $\text{InD}(\text{BDC})_2$ ·guest) because the nature and quantity of the disordered solvent was ill-determined.



Figure S2: Rietveld fits of  $Zn(ISN)_2$  and  $InD(BDC)_2$  at 12 K, modelled with guests in the pores. Experimental data are shown as points, the fitted profile as a solid red line, and the difference (data-fit) as a blue line.

#### 2 Atomic coordinates

The atomic coordinates and equivalent isotropic thermal parameters for  $\text{Zn}(\text{ISN})_2$  and  $\text{InD}(\text{BDC})_2$ at 12 K are given in Tables S1 and S2. In  $\text{Zn}(\text{ISN})_2$ , the C2 atom was used as the position for the rigid body of the isonicotinate, whereas a dummy atom x1—which was refined at zero occupancy—was used for the centre of the rigid body for the terephthalate ligand in InD(BDC)<sub>2</sub>. For the InD(BDC)<sub>2</sub>, the data were of insufficient quality to adequately model the deuterium atom, and was subsequently kept fixed in the centre of the pore.

Space Group	$P6_2$			
$a~(\text{\AA})$	15.5190(6)			
c (Å)	6.1280(5)			
V (Å <sup>3</sup> )	1278.12(14)			
Ζ	3			
$\mathrm{wR}_p$	3.21%			
Atom	x	y	z	$U_{\rm eq}~({\rm \AA}^2)$
C2	0.22895(12)	0.76386(14)	0.3978(7)	0.0184(12)
C3	0.28796	0.85692	0.48066	0.0184(12)
C4	0.36339	0.92783	0.35785	0.0184(12)
N1	0.37982	0.90569	0.15214	0.0184(12)
C5	0.32081	0.81264	0.06925	0.0184(12)
C6	0.24538	0.74172	0.19206	0.0184(12)
C1	0.14553	0.68544	0.53358	0.0184(12)
01	0.09382	0.60121	0.44819	0.0184(12)
O2	0.13416	0.71037	0.72167	0.0184(12)
D1	0.27615	0.87283	0.62849	0.0184(12)
D2	0.40579	0.99471	0.41742	0.0184(12)
D3	0.33262	0.79673	-0.07858	0.0184(12)
D4	0.20298	0.67485	0.13249	0.0184(12)
Zn1	0.5	1	0	$0.029(5)^*$

**Table S1:** Crystallographic details determined by powder neutron diffraction for  $Zn(ISN)_2$  at 12 K. \*Refined isotropically.

Space Group	$P6_{4}22$			
a (Å)	14.5310(15)			
c (Å)	12.273(2)			
V (Å <sup>3</sup> )	2244.2(6)			
Ζ	3			
$\mathrm{wR}_p$	2.31%			
Atom	x	y	z	$U_{\rm iso}$ (Å <sup>2</sup> )
x1	0.508820(10)	0.254410(10)	$\frac{1}{3}$	_
In1	0.5	0	0	0.0378(16)
C1	0.50881	0.13161	0.14542	0.061(2)
C2	0.50882	0.19604	0.24401	0.061(2)
C3	0.60420	0.27329	0.28833	0.061(2)
C4	0.41344	0.17716	0.28902	0.061(2)
D1	0.34806	0.12422	0.25864	0.061(2)
D3	0.66958	0.28623	0.25748	0.061(2)
01	0.59479	0.14034	0.11189	0.061(2)
O2	0.42402	0.07511	0.09344	0.061(2)
D5	0	0	0	0.61(7)

 ${\bf Table \ S2:} \ {\rm Crystallographic \ details \ determined \ by \ powder \ neutron \ diffraction \ for \ {\rm InD}({\rm BDC})_2 \ {\rm at} \ 12 \, {\rm K}.$ 

### 3 Variable-temperature lattice parameter data

Variable-temperature lattice parameter data are given in Tables S3 and S4, as determined using Rietveld fits to neutron powder diffraction data. Tables S5 and S6 show the lattice parameter data when a Rietveld model is used that includes solvent within the pores for the frameworks. As expected, the lattice parameters obtained from both the empty and solvent-containing Rietveld models are the same within error. The errors for each temperature were calculated using the difference between the temperature at the start and end of the corresponding measurement.

T (K)	a (Å)	c (Å)	V (Å <sup>3</sup> )
11.970(14)	15.5190(6)	6.1280(5)	1278.12(14)
43(7)	15.5164(6)	6.1325(6)	1278.65(15)
96(2)	15.5078(5)	6.1500(5)	1280.88(14)
134(3)	15.4994(6)	6.1664(6)	1282.89(15)
169(15)	15.4906(6)	6.1862(6)	1285.55(16)
238.1(14)	15.4821(6)	6.2051(6)	1288.05(16)
285(4)	15.4753(6)	6.2251(6)	1291.08(16)

Table S3: Variable-temperature lattice parameter data for  $Zn(ISN)_2$  as determined using powder neutron diffraction upon warming from 10 K to 300 K.

T (K)	a (Å)	c (Å)	V (Å <sup>3</sup> )
11.96(7)	14.5310(15)	12.273(2)	2244.2(6)
42(3)	14.5474(15)	12.265(2)	2247.8(6)
95.8(8)	14.5831(15)	12.249(2)	2256.0(6)
138(4)	14.6266(15)	12.231(2)	2266.2(7)
188(2)	14.6788(16)	12.206(2)	2277.7(7)
238(3)	14.7304(16)	12.183(2)	2289.5(7)
285.2(5)	14.7859(17)	12.154(3)	2301.3(7)

**Table S4:** Variable-temperature lattice parameter data for  $InD(BDC)_2$  as determined using powder neutron diffraction upon warming from 10 K to 300 K.

T (K)	a (Å)	c (Å)	V (Å <sup>3</sup> )
11.970(14)	15.5190(5)	6.1282(5)	1278.16(13)
43(7)	15.5163(5)	6.1327(5)	1278.67(13)
96(2)	15.5076(5)	6.1501(5)	1280.85(13)
134(3)	15.4984(5)	6.1667(5)	1282.79(14)
169(15)	15.4892(5)	6.1868(5)	1285.44(14)
238.1(14)	15.4811(5)	6.2059(6)	1288.05(14)
285(4)	15.4748(5)	6.2257(5)	1291.13(13)

**Table S5:** Variable-temperature lattice parameter data for  $Zn(ISN)_2$ ·guest as determined using powder neutron diffraction upon warming from 10 K to 300 K.

T (K)	$a~({ m \AA})$	c (Å)	V (Å <sup>3</sup> )
11.96(7)	14.5291(11)	12.2738(17)	2243.8(5)
42(3)	14.5475(12)	12.2628(19)	2247.5(5)
95.8(8)	14.5838(11)	12.2472(17)	2255.8(5)
138(4)	14.6285(12)	12.2296(19)	2266.4(5)
188(2)	14.6818(12)	12.2035(19)	2278.1(5)
238(3)	14.7335(12)	12.1809(19)	2289.9(5)
285.2(5)	14.7900(13)	12.152(2)	2302.0(5)

**Table S6:** Variable-temperature lattice parameter data for  $InD(BDC)_2$ ·guest as determined using powder neutron diffraction upon warming from 10 K to 300 K.

### 4 Framework angle derivation

The three unique framework angles  $(\theta_1, \theta_2, \theta_3)$  can be expressed in terms of the lattice parameter a and the hinge link distance r. We begin the derivation by using the relationship between the dot product of two vectors

$$\mathbf{r}_1 \cdot \mathbf{r}_2 = r^2 \cos \theta,\tag{1}$$

hence the framework angle is given by

$$\theta = \cos^{-1} \left( \frac{\mathbf{r}_1 \cdot \mathbf{r}_2}{r^2} \right). \tag{2}$$

The hinge link  $\mathbf{r}$  vectors for calculating the three framework angles are given here in cartesian vectors  $\mathbf{i}$ ,  $\mathbf{j}$ ,  $\mathbf{k}$  and are shown in Figure S3.

$$\mathbf{r}_{1} = \frac{1}{2}a\mathbf{i} + \frac{2}{3}c\mathbf{k}$$

$$\mathbf{r}_{2} = -\frac{1}{4}a\mathbf{i} + \frac{\sqrt{3}}{4}a\mathbf{j} - \frac{2}{3}c\mathbf{k}$$

$$\mathbf{r}_{3} = -\frac{1}{2}a\mathbf{i} + \frac{2}{3}c\mathbf{k}$$

$$\mathbf{r}_{4} = -\frac{1}{4}a\mathbf{i} + \frac{\sqrt{3}}{4}a\mathbf{j} - \frac{2}{3}c\mathbf{k}$$

The magnitude of these  $\mathbf{r}$  vectors is given by

$$r = \sqrt{\frac{a^2}{4} + \frac{4c^2}{9}}.$$
 (3)

Using the equations above, we can define the framework angles with respect to the lattice parameter a and the hinge link distance r [Table S7].

We can differentiate the framework angles with respect to temperature to obtain a relationship which relates  $\alpha_{\theta}$  to  $\alpha_{a}$  by approximating that  $\alpha_{r} = 0$ . Below we show the differentiation of  $\theta_{1}$ ,  $\theta_{2}$ , and  $\theta_{3}$  whereby we imply  $\alpha_{r} = 0$ .



Figure S3: Framework structure of  $InD(BDC)_2$  with the ligands replaced by rods, whereby the **r** vectors and the three unique framework angles are shown. The fractional coordinates of the metal sites which are used for **r** vector calculations are shown in brackets.

**Table S7:** Derivation of  $\theta_i$  in terms of its lattice parameter a and hinge link distance r.

$$\begin{aligned}
\theta_{1} &= \cos^{-1} \left( -1 + \frac{3a^{2}}{8r^{2}} \right) \\
\frac{d\theta_{1}}{dT} &= -\frac{1}{\sqrt{1 - \left( -1 + \frac{3a^{2}}{8r^{2}} \right)^{2}}} \frac{d}{dT} \left( \frac{3a^{2}}{8r^{2}} \right) \\
&= -\frac{8r^{2}}{\sqrt{48r^{2} - 9a^{2}}} \frac{6a}{8r^{2}} \frac{da}{dT} \\
&= -\frac{6a\alpha_{a}}{\sqrt{48r^{2} - 9a^{2}}} \\
\alpha_{\theta_{1}} &= -\frac{6a\alpha_{a}}{\theta_{1}\sqrt{48r^{2} - 9a^{2}}}
\end{aligned} \tag{4}$$

$$\theta_{2} = \cos^{-1}\left(-1 + \frac{a^{2}}{8r^{2}}\right)$$

$$\frac{d\theta_{2}}{dT} = -\frac{1}{\sqrt{1 - \left(-1 + \frac{a^{2}}{8r^{2}}\right)^{2}}} \frac{d}{dT} \left(\frac{a^{2}}{8r^{2}}\right)$$

$$= -\frac{8r^{2}}{a\sqrt{16r^{2} - a^{2}}} \frac{2a}{8r^{2}} \frac{da}{dT}$$

$$= -\frac{2a\alpha_{a}}{\sqrt{16r^{2} - a^{2}}}$$

$$\alpha_{\theta_{2}} = -\frac{2a\alpha_{a}}{\theta_{2}\sqrt{16r^{2} - a^{2}}}$$
(5)

$$\theta_{3} = \cos^{-1}\left(1 - \frac{a^{2}}{2r^{2}}\right)$$

$$\frac{d\theta_{3}}{dT} = -\frac{1}{\sqrt{1 - \left(1 - \frac{a^{2}}{2r^{2}}\right)^{2}}} \frac{d}{dT} \left(-\frac{a^{2}}{2r^{2}}\right)$$

$$= -\frac{2r^{2}}{a\sqrt{4r^{2} - a^{2}}} - \frac{2a}{2r^{2}} \frac{da}{dT}$$

$$= \frac{2a\alpha_{a}}{\sqrt{4r^{2} - a^{2}}}$$

$$\alpha_{\theta_{3}} = \frac{2a\alpha_{a}}{\theta_{3}\sqrt{4r^{2} - a^{2}}}$$
(6)

Equations (4), (5), and (6) show that the expansivities in  $\theta_i$  are dependent only on  $\alpha_a$ . We can calculate the expansivities for the three framework angles by using the Equations (4), (5), (6) and the known values of  $a, r, and \alpha_a$ . By implying  $\alpha_r = 0$ , we can observe the angle expansivity without effects from bond deformation (*i.e.* purely geometric hinging). For Zn(ISN)<sub>2</sub> at 285 K: a = 15.4752 Å, r = 8.78 Å, and  $\alpha_a = -10.9$  MK<sup>-1</sup>. For InD(BCD)<sub>2</sub> at 285 K: a = 14.786 Å, r = 10.969 Å, and  $\alpha_a = 64$  MK<sup>-1</sup>. Table S8 compares the angle expansivities when  $\alpha_r = 0$  is implied and the experimental values measured from the structures. What we can see is that the values between the two are very similar, indicating that bond deformation along the **r** vector does not change the geometric hinging of the framework substantially.

i	calculated $\alpha_i$ (MK <sup>-1</sup> )		experimental $\alpha_i$ (MK <sup>-1</sup> )	
<i>i</i>	$\operatorname{Zn}(\operatorname{ISN})_2$	$\mathrm{InD}(\mathrm{BDC})_2$	$\operatorname{Zn}(\operatorname{ISN})_2$	$InD(BDC)_2$
r	0	0	4.7(4)	9.2(3)
$ heta_1$	18	-49	26.3(11)	-41(2)
$\theta_2$	5	-19	6.9(3)	-15.9(8)
$\theta_3$	-19	80	-27.0(12)	68(3)

Table S8: Framework angle expansivities calculated from the derivation above and compared to the experimentally obtained values in  $Zn(ISN)_2$  and  $InD(BDC)_2$ .

#### 5 Lattice parameter evolution on desolvated phases

In order to clarify the effect of solvent on the thermal expansivities for both systems, the powdered samples of  $\text{Zn}(\text{ISN})_2$  and  $\text{InD}(\text{BDC})_2$  were each heated up to 520 K within a Siemens D5000 diffractometer. X-ray diffraction patterns were collected using heating and cooling cycles while maintaining a Helium flow in the sample chamber. Figure S4 shows the relative changes in lattice parameters for  $\text{Zn}(\text{ISN})_2$  and  $\text{InD}(\text{BDC})_2$  during sequential heating and cooling cycles. The dehydration of  $\text{InD}(\text{BDC})_2$  can be clearly seen in the first heating cycle, while the change in peak intensities indicate dehydration in  $\text{Zn}(\text{ISN})_2$ . Further heating of  $\text{InD}(\text{BDC})_2$  above 520 K gave rise to a phase transition.

The expansivities calculated from the dehydrated  $\text{Zn}(\text{ISN})_2$  and  $\text{InD}(\text{BDC})_2$  samples (*i.e.* using lattice parameters after the first heating cycle) are shown in Table S9. It can be seen that the anisotropy of thermal expansion is the same as solvated phases of  $\text{Zn}(\text{ISN})_2$  and  $\text{InD}(\text{BDC})_2$ , while the magnitudes are slightly modified. By calculating the geometric parameters as detailed in section 4, we can see that the  $\alpha_{\theta}$  show the same anisotropy as the solvated phases and also that they are larger in magnitude [Table S9]. This means that the desolvated phases of  $\text{Zn}(\text{ISN})_2$ and  $\text{InD}(\text{BDC})_2$  show greater geometric hinging, and in the case of  $\text{Zn}(\text{ISN})_2$ , favour greater transverse vibrational modes of the linker (giving rise to negative  $\alpha_r$  values). Consequently, the analysis presented in the manuscript—which relies on the direction of anisotropy in  $\text{Zn}(\text{ISN})_2$ and  $\text{InD}(\text{BDC})_2$ —is clearly unaffected by frameworks guest occupancy.

Parameter $i$	$\alpha_i \; (\mathrm{MK}^{-1})$		
	$\operatorname{Zn}(\operatorname{ISN})_2$	$InD(BDC)_2$	
a, b	-16.1(4)	75.2(17)	
с	52.3(10)	-47(5)	
V	20.1(3)	103(4)	
r	-0.55(12)	10(2)	
$ heta_1^*$	27	-56	
$\theta_2^*$	7	-22	
$\theta_3^*$	-28	92	

**Table S9:** Thermal expansivities of the unit cell and geometric parameters of desolvated  $\text{Zn}(\text{ISN})_2$ and  $\text{InD}(\text{BDC})_2$ , calculated using linear fits to X-ray data. \*Denotes that the  $\alpha_{\theta}$  values are calculated assuming  $\alpha_r = 0$  as detailed in section 4.



Figure S4: Relative changes in lattice parameters for  $Zn(ISN)_2$  and  $InD(BDC)_2$  for heating (red) and cooling (blue) cycles in the temperature range of 350–520 K. The *a*, *b* lattice parameters are represented by filled circles, while open circles symbolise the *c* lattice parameter. The changes in lattice parameter reported are calculated relative to the smallest or largest value (PTE and NTE axes, respectively) across the ensemble of heating/cooling cycles. The dotted lines in the second cooling cycle of  $Zn(ISN)_2$  are guides to the eye.

## References

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