Supporting Information

Thermomechanical properties of metal-organic framework HKUST-1 crystals

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Debye temperature of HKUST-1

According to the Debye theory,[S1] the Debye temperature θ_D corresponds to the temperature of the highest normal mode of vibration of the HKUST-1 crystal, i.e., the highest temperature that can be obtained due to a single normal vibration. Mathematically, the Debye temperature is given by

$$\theta_D = \frac{h\nu_m}{k_B}, \tag{S1}$$

where h is the Planck's constant, ν_m is the Debye frequency, and k_B is the Boltzmann's constant.

Linear temperature dependence of the Young's modulus

Wachtman et al. proposed the following equation for the Young's modulus E at different temperatures:[S2]

$$E = E_0 - BT\exp(-T_0/T), \tag{S2}$$

where E_0 is the Young's modulus at absolute zero, T is the temperature, B is an arbitrary constant that depends on the Grüneisen constant, and T_0 is another constant related to the Debye temperature.

Based on the Taylor series expansion, Equation S2 can be rewritten as:

$$E = E_0 - BT\left[1 - \frac{T_0}{T} + \frac{1}{2}\left(\frac{T_0}{T}\right)^2 - \frac{1}{6}\left(\frac{T_0}{T}\right)^3 + \cdots\right], \tag{S3}$$

Considering the fact that the temperature considered in the compression tests is much larger than T_0, the higher-order terms in Equation S3 can be approximately ignored. Thus, we obtained the following linear temperature dependence of the Young's modulus and hardness:

$$E = E_0 + BT_1 - BT\,. \tag{S4}$$

Definition of the strain in the strain-fluctuation method

The strain ε_{ij} has the following definition, which is a widely used method introduced previously.[S3,S4]

$$\varepsilon_{ij} = \frac{1}{2}\left[\langle h\rangle_{ik}^{-T} h_{kl}^{T} h_{lm} \langle h\rangle_{mj}^{-1} - \delta_{ij}\right]. \tag{S5}$$

Here, $h_{ij} = \{\mathbf{a}, \mathbf{b}, \mathbf{c}\}_{ij}$ is a matrix with components of the principal axes (**a**, **b** and **c**) of the simulation box, which can be extracted from MD simulations and has the ability to describe the size and shape of the simulation box. The matrix $\langle h\rangle_{ij}$ describes the average shape of the system as the reference state. $\langle h\rangle_{ij}^{-T}$ is the inverse of the transpose of $\langle h\rangle_{ij}$. δ_{ij} is the Kronecker tensor.

References

(S1) Hill, T. L. *An Introduction to Statistical Thermodynamics*. New York: Dover, 1986.

(S2) Wachtman, J. B.; Tefft, W. E.; Lam, D. G.; Apstein, C. S. Exponential temperature dependence of Young's modulus for several oxides. *Phys. Rev.* 1961, 122, 1754-1759.

(S3) Parrinello, M.; Rahman, A. Strain fluctuations and elastic constants. *J. Chem. Phys.* 1982, 76, 2662-2666.

(S4) Rogge, S. M. J.; Waroquier, M.; Van Speybroeck, V. Reliably modeling the mechanical stability of rigid and flexible metal-organic frameworks. *Acc. Chem. Res.* 2018, 51, 138-148.

Supplementary figures

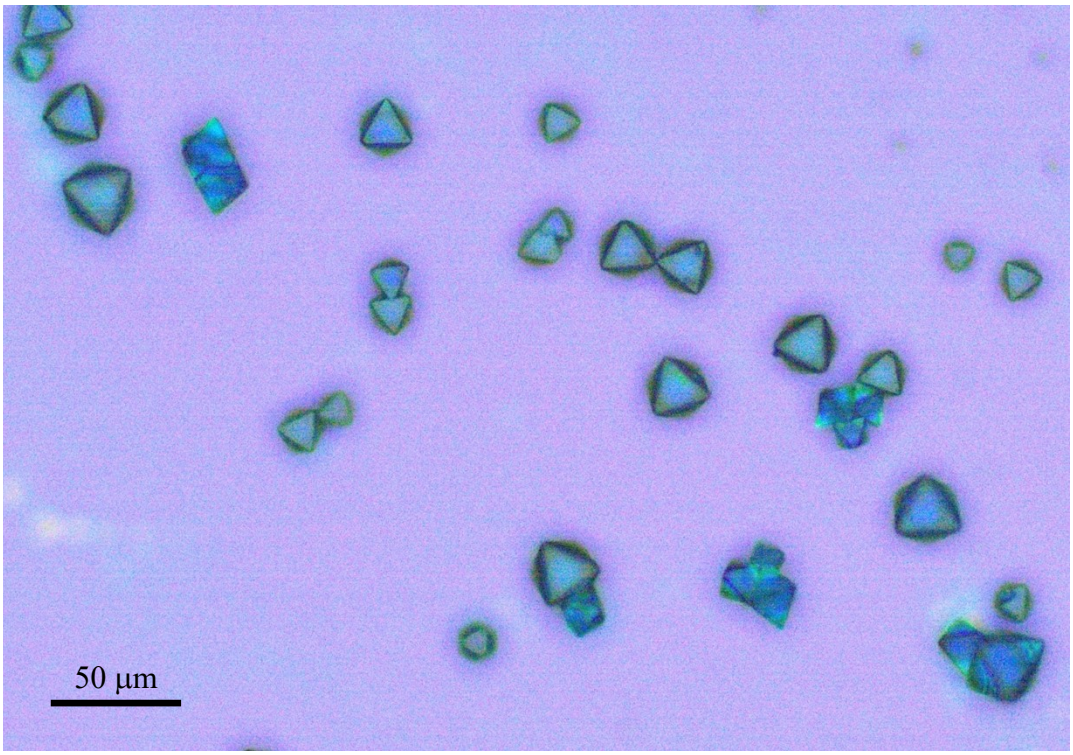

Figure S1. Optical microscope images of the synthesised HKUST-1 crystals.

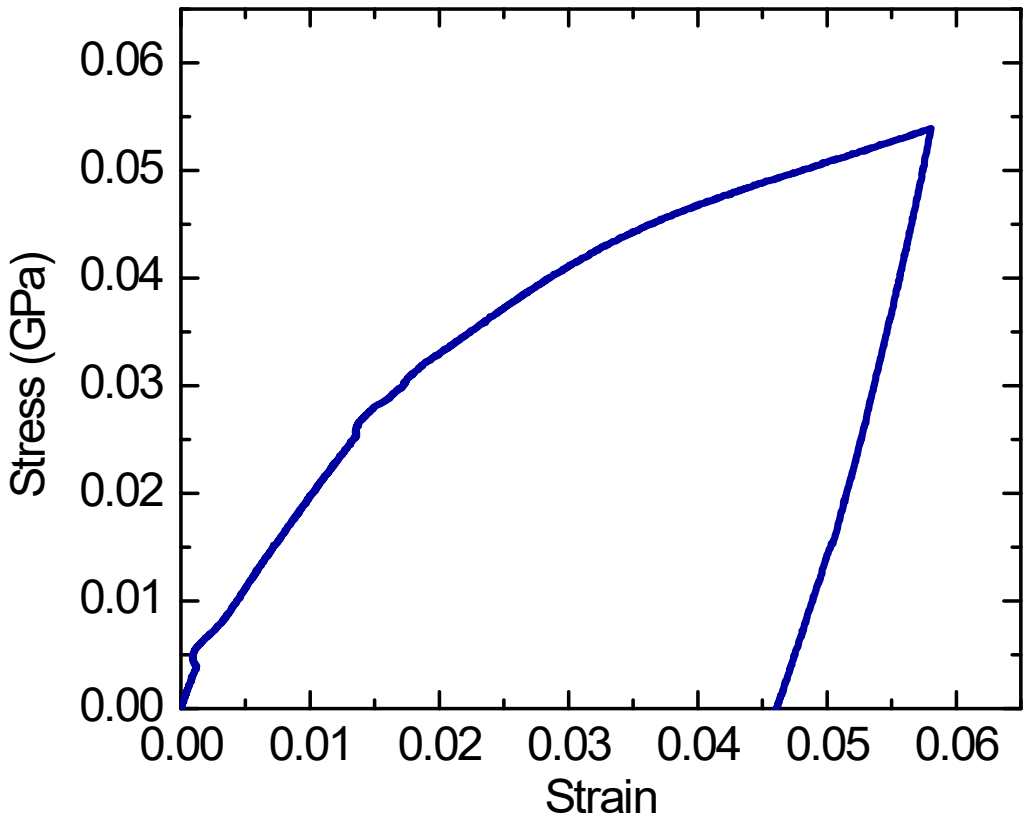

Figure S2. Stress versus strain plot for the compression of crystals at the temperature of 175 °C. Here a relatively small stress was applied.

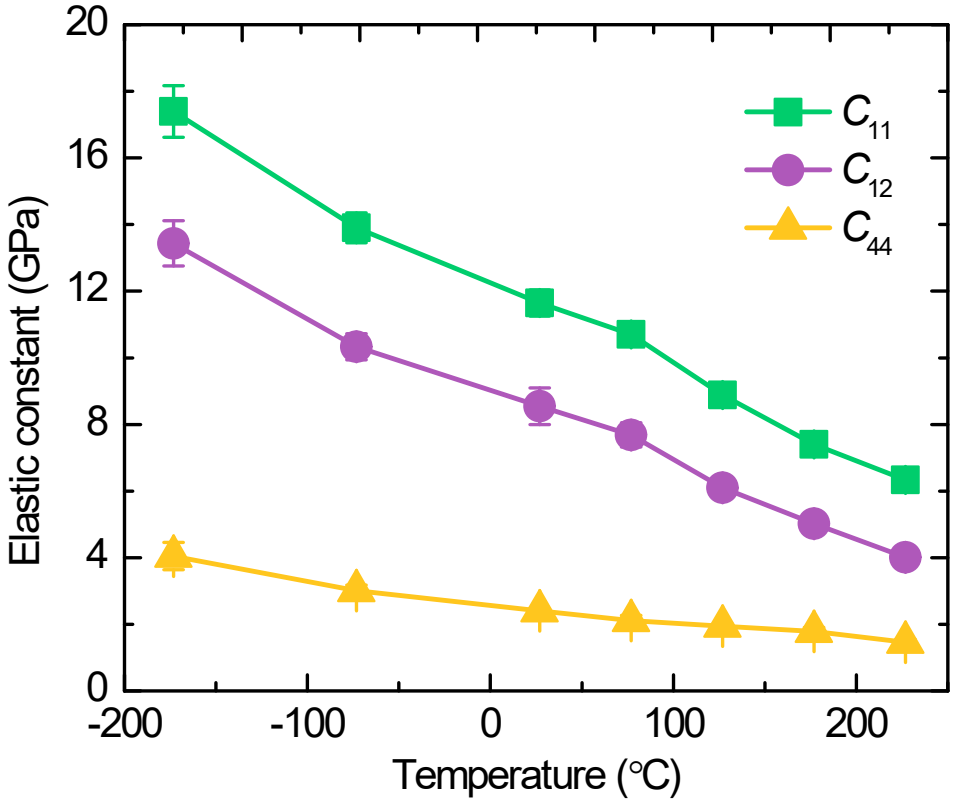

Figure S3. Elastic constants of crystalline HKUST-1 at various temperatures.

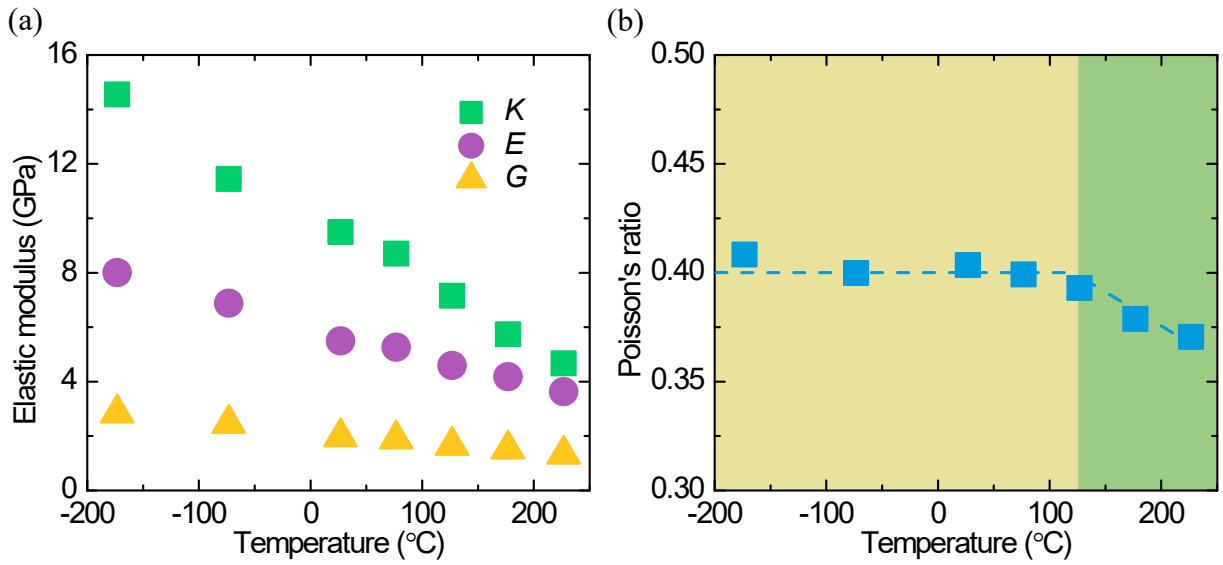

Figure S4. Elastic properties of the crystalline HKUST-1 at various temperatures ranging from –173 °C to 227 °C, predicted from the strain-fluctuation method. (a) The bulk modulus *K*, Young's modulus *E*, shear modulus *G* and (b) the Poisson's ratio. Here, the dashed line is drawn to guide the eye.

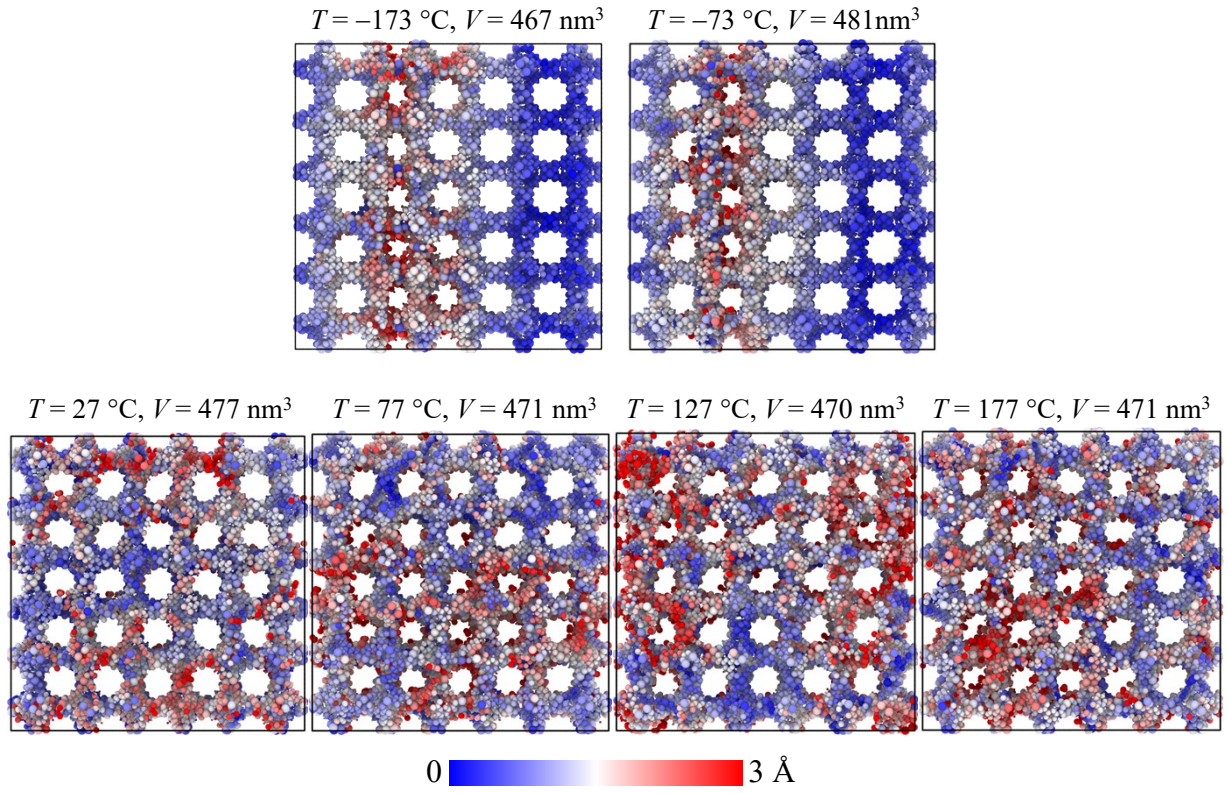

Figure S5. Structures and atomic displacements of metastable structures of HKUST-1 simulated at different temperatures (T). Here, the metastable structures were extracted from the structures with the volumes (V) at the negative slopes in Figure 5a.

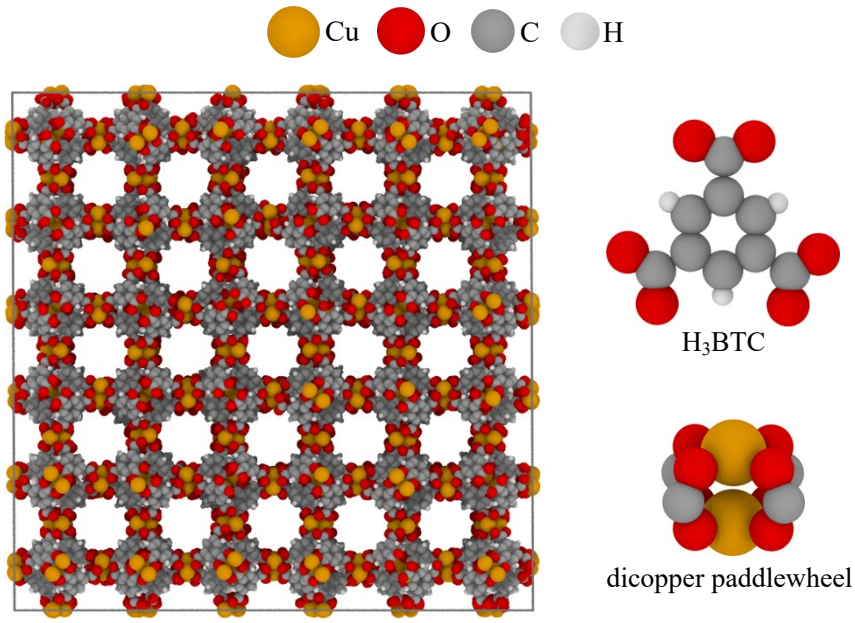

Figure S6. Atomistic model of HKUST-1 together with its building units.

Supplementary table

Table S1. The fitting parameter *B* in the Wachtman's formula for the present HKUST-1 and other traditional materials.

Material	*B* (GPa °C $^{-1}$)	Reference
HKUST-1	0.030	This work
Aluminium	0.041	a
Copper	0.038	b
Gold	0.020	c
Silver	0.013	c
Silicon	0.011	d
AlN	0.024	e

[a]Kamn, C. N.; Alers, G. A. *J. Appl. Phys.* 1964, 35, 327

[b]Overton Jr., W. C.; Gaffney, J. *Phys. Rev.* 1955, 98, 969

[c]Neighbours, J. R.; Alers, G. A. *Phys. Rev.* 1958, 111, 707

[d]McSkimin, H. J. *J. Appl. Phys.* 1953, 24, 988

[e]Bruls, R. J.; Hintzen, H. T.; de With, G.; Metselaar, R. *J. Eur. Ceram. Soc.* 2001, 21, 263