Electronic Supplementary Material (ESI) for Dalton Transactions.
This journal is © The Royal Society of Chemistry 2022

Electronic Supplementally Information for

Toughening and stabilizing MOF crystals via polymeric guest inclusion

Tomoya Iizuka,[1] Nobuhiko Hosono,[2] Takashi Uemura[2]*

[1]*Department of Advanced Materials Science, Graduated School of Frontier Sciences, The University of Tokyo, 5-1-5 Kashiwanoha, Kashiwa, Chiba 277-8561, Japan.*

[2]*Department of Applied Chemistry, Graduate School of Engineering, The University of Tokyo, 7-3-1 Hongo, Bunkyo-ku, Tokyo 113-8656, Japan.*

To whom corresponding should be addressed.
Email: uemurat@g.ecc.u-tokyo.ac.jp

1. Methods

Details of Nanoindentation Experiments

Nanoindentation experiments were performed using Elionix ENT-2100 nanoindenter. All indentation tests were performed to a maximum indentation depth of 1 μm with a Berkovich (i.e. three-sided pyramidal) diamond tip using the loading and unloading rates of 2×10^{-6} Ns^{-1}. Before measurement, single crystal samples were vertically attached on a silicon wafer with adhesive. The values of hardness (H) and elastic modulus (E) were calculated from obtained load–displacement curves using Sawa and Tanaka method.[1]

Sawa and Tanaka method

From the load–displacement curve, information of the maximum applied load P_{max}, the maximum penetration depth h_{max}, final penetration depth h_f, stiffness S (gradient of initial unloading curve, dP/dh) and the depth extrapolated stiffness to the h axis can be obtained. According to Sneddon,[2] S can be written as,

$$\boldsymbol{S = \frac{dP}{dh} = \frac{2}{\sqrt{\pi}} E_r \sqrt{A}}\,, \tag{1}$$

using composite elastic modulus E_r and real projected contact area A in the case of axisymmetric punch. Elastic modulus E_r is expressed by,

$$\frac{1}{E_r} = \frac{1 - v_S^2}{E_S} + \frac{1 - v_I^2}{E_I}\,, \tag{2}$$

where E and v are elastic modulus and Poisson's ratio of the sample and the indenter tip with subscript S and I, respectively. In this time, as the constant values of E_I, v_S and v_I, 1140 GPa, 0.17, and 0.07 were used, respectively.

Next step is determining the load frame compliance, C_f. The total measured compliance C, which is the inverse of the stiffness S, can be assumed to be the sum of the compliance of the sample and that of the load frame. Because former compliance is given by the inverse of the stiffness in Eq. (1), total compliance C can be written as,

$$C = \frac{\sqrt{\pi}}{2E_r\sqrt{23.96}} \frac{1}{h_A} + C_f\,. \tag{3}$$

When the first term on the right-hand side of the equation above is small, a plot C v.s. h_A^{-1} should be

linear, and the load frame compliance can be given as the intercept of the plot.

Hardness (H) is defined by dividing the maximum applied load P_{max} by A as follows,

$$H = \frac{P_{\max}}{A} . \tag{4}$$

In the case of an ideal Berkovich indenter tip, A can be written as a function of the contact depth h_A,

$$A = \sqrt{3}(\tan^2\alpha)h_A^2 = 23.96\, h_A^2 , \tag{5}$$

where α is an apical angle of the Berkovich tip (74.95˚). However, in the real indentation, the contact depth h_A should deviate from an ideal due to some conditions. Thus, correction of h_A should be done by adding Δh_c, which is the sum of the effective truncation length of the indenter tip, Δh_{ET}, and penetration depth by preload, Δh_D;

$$\Delta h_c = \Delta h_{ET} + \Delta h_D . \tag{6}$$

Therefore, corrected projected contact area can be expressed as follows,

$$A(h_A) = 23.96(h_A + \Delta h_c)^2 . \tag{7}$$

The procedure to determine the value of Δh_c is varying Δh_c until the $C - C_f$ versus $1/(h_A+\Delta h_c)$ plot regresses best to the linear relationship, and this step with trial and error is automatically calculated with the analytical software ENT ver. 7.48 in ENT-2100 nanoindenter. Then, H was calculated from Eq. (4) by using obtained Δh_c.

The elastic modulus, E_S, the composite elastic modulus, E_r, were determined based on the slope in the relationship between dP/dh and the corrected projected contact area A by Eq. (7) observed for the unloading process. For this study, the data range of 70–90% of the maximum load was used for calculation. Then, E_S was calculated using the equation,

$$E_S = \frac{1 - \nu_S^2}{\frac{1}{E_r} - \frac{1 - \nu_I^2}{E_I}} , \tag{8}$$

which is a transformation of Eq. (2).

2. Supplementary Figures

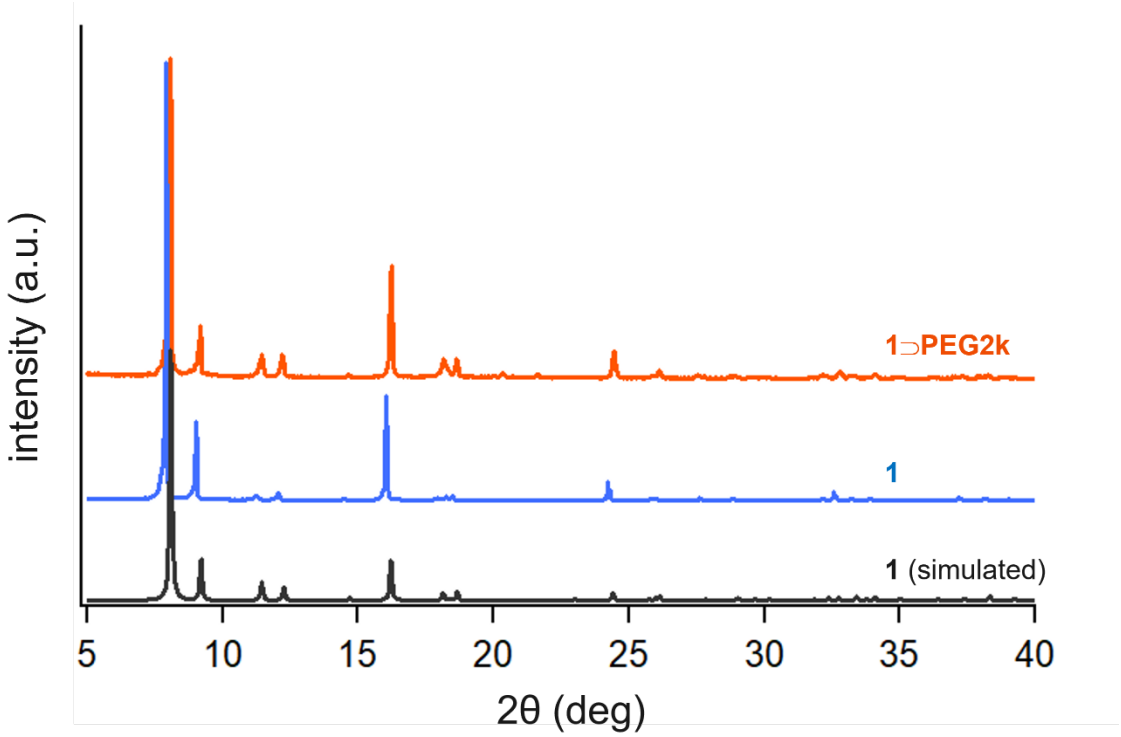

Fig. S1. XRPD patterns of the guest-free **1** and **1⊃PEG2k** with PEG loading of 41 wt% to **1** before compression test.

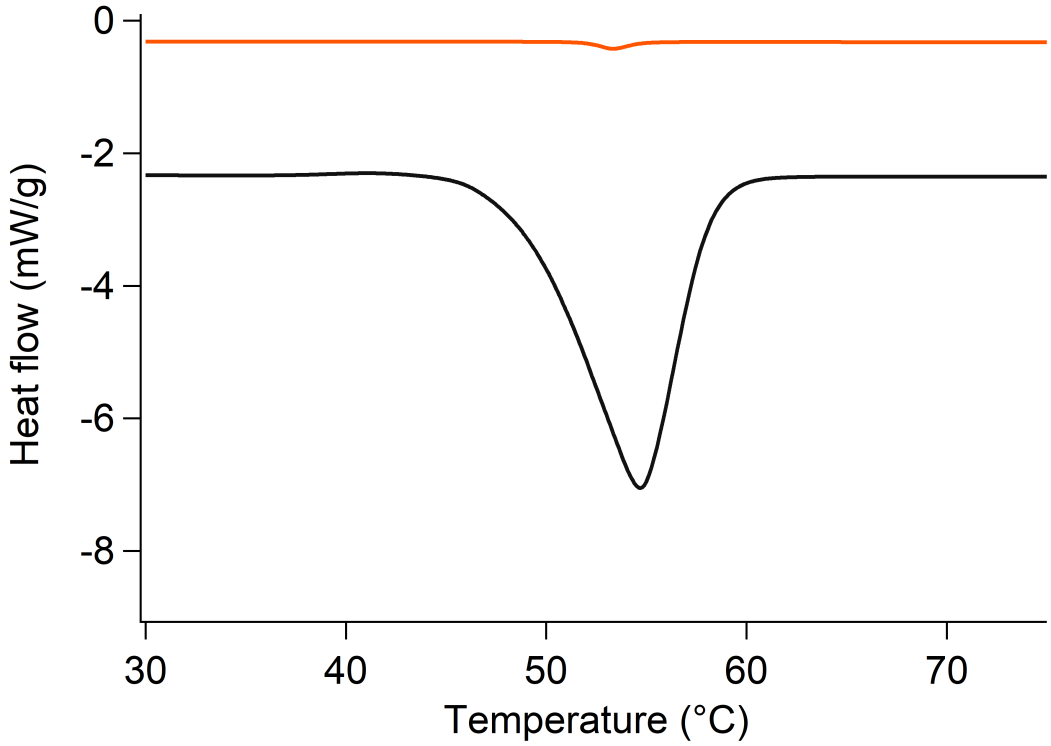

Fig. S2. DSC heating curves of pristine **PEG2k** (black) and **1**⊃**PEG2k** (orange) with the loading amount of 41 wt%. In order to ensure complete filling of **1** nanopores, the amount of PEG used for the **1**⊃**PEG2k** sample preparation was slightly excess of the maximum capacity. The amount of the excess PEG remained outside of **1** was observed to be negligibly small (<1 wt%) as found in the DSC curve.

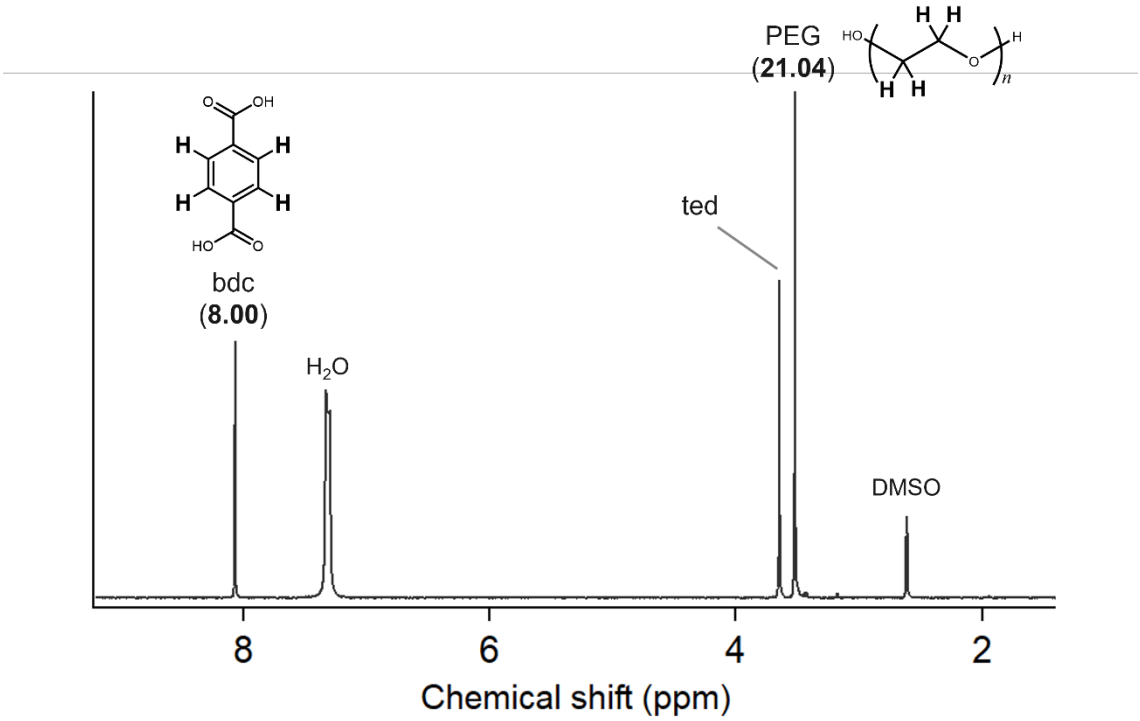

Fig. S3. A representative ^{1}H NMR spectrum of **1⊃PEG2k** digested in the mixture of DMSO-d_6 and DCl (35 wt% in D_2O) (9/1, v/v) (400 MHz) for the quantification of actual PEG loading amount. The integral values of proton signals for bdc and PEG were given in the parentheses. Based on the integral values, the actual incorporation ratio **PEG2k**/**1** was calculated to be 41 wt%.

(a)

(b)

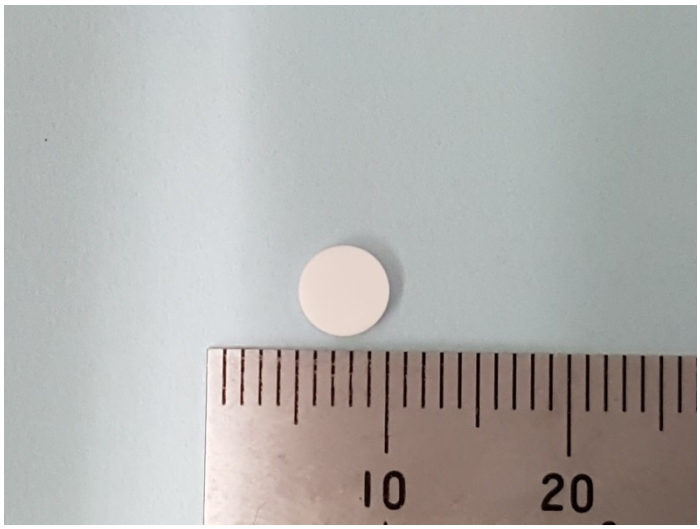

Fig. S4. Images of the compression experiment.[3] (a) **1**⊃PEG composite (10 mg) was compressed in a 5 mm-ϕ die of hydraulic piston pelletizer using 0.37 ton load (0.18 GPa) at room temperature. (b) The obtained pellet of **1** by compression.

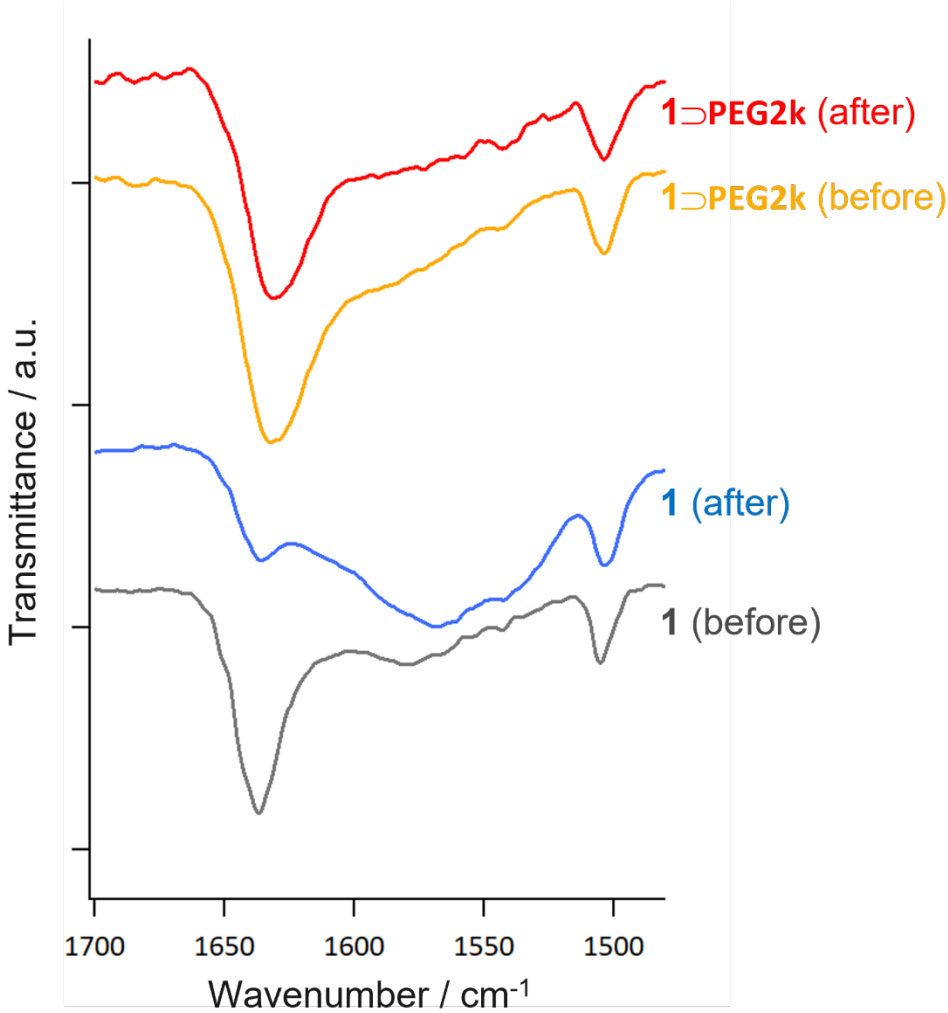

Fig. S5. FT-IR spectra of guest-free **1** and **1⊃PEG2k** before and after 0.18 GPa compression. The PEG loading amount of **1⊃PEG2k** was 41 wt% to **1**.

3. Supplementally Tables

Table S1. Molecular weights of PEG used in this study.[a]

M_n	M_w	M_w/M_n
200	220	1.07
380	410	1.07
540	580	1.06
1,960	2,030	1.04
4,290	4,530	1.05
10,560	11,370	1.07

[a)]Determined by SEC calibrated with PEG standards.

Table S2. Actual PEG loading amount of the composites used for compression and nanoindentation experiments, determined using ^{1}H NMR measurements.

	Actual loading amount of PEG (wt% to **1**)	
PEG M_n	compression	nanoindentation
90.12 (DME)	–	51
200 (**PEG200**)	43	–
380	40	–
540	41	47
1,960 (**PEG2k**)	41	–
4,290	–	52
10,560 (**PEG10k**)	48	40

4. Supplementary References

1. T. Sawa and K. Tanaka, *J. Mater. Res.*, 2001, **16**, 3084–3096.
2. I. N. Sneddon, *Int. J. Eng. Sci.*, 1965, **3**, 47–57.
3. T. Iizuka, K. Honjo and T. Uemura, *Chem. Commun.*, 2019, **55***,* 691–694.