Electronic Supplementary Material (ESI) for ChemComm.

Supporting Information for

Enhanced mechanical properties of a metal-organic framework by polymer insertion

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Materials

All reagents and chemicals were obtained from commercial sources otherwise noted. Azobisisobutyronitrile (AIBN) was recrystallized from the methanol solution. Styrene (St) was purified by vacuum distillation prior to use. The MOF **1** was prepared by solvothermal synthesis previously reported[1]. Preparation of **1**⊃PSt was performed using the method in the reported work as below. [2]

Preparation of **1**⊃PSt

1 was evacuated (~ 0.1 kPa) overnight to remove solvent, and was then immersed in a solution of St (1 mL) and AIBN (6 mg) in flask under a nitrogen atmosphere. The mixture was left for 0.5 h to incorporate St and the initiator into the nanopores, and then excess St was removed under reduced pressure at room temperature over 0.5 h. Polymerization was performed at 70 °C for 48 h. Unreacted monomer was removed by washing with methanol and evacuating at 130 °C overnight to give a polymer composite (**1**⊃PSt).

Measurements

X-ray powder diffractometry (XRPD) diagrams were collected on a Rigaku SmartLab Diffractometer, using a Cu anode and a Kα monochromator (λ = 0.154 nm). Scanning electron microscopy (SEM) measurements were performed using Hitachi S-3000 N at an accelerating voltage of 5 kV. Samples were put on a conducting carbon tape attached by SEM grid, and then coated with platinum. N_2 adsorption measurements were performed on a BELSORP II mini (BEL-Japan, Inc.), and N_2 gas of high purity (99.9999%) was used. Samples were activated at 100 °C overnight before the measurement. IR spectra were measured using a JASCO FT/IR-4200. ^{1}H NMR spectra were obtained using a JEOL P-600 spectrometer operating at 600 MHz.

Nanoindentation

Nanoindentation measurement was performed using 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} (Fig. S1b,c). Before measurement, single crystal samples were vertically attached on a silicon wafer with adhesive (Fig. S1a). The values of hardness (*H*) were calculated from obtained load-displacement curves with Sawa and Tanaka method[3].

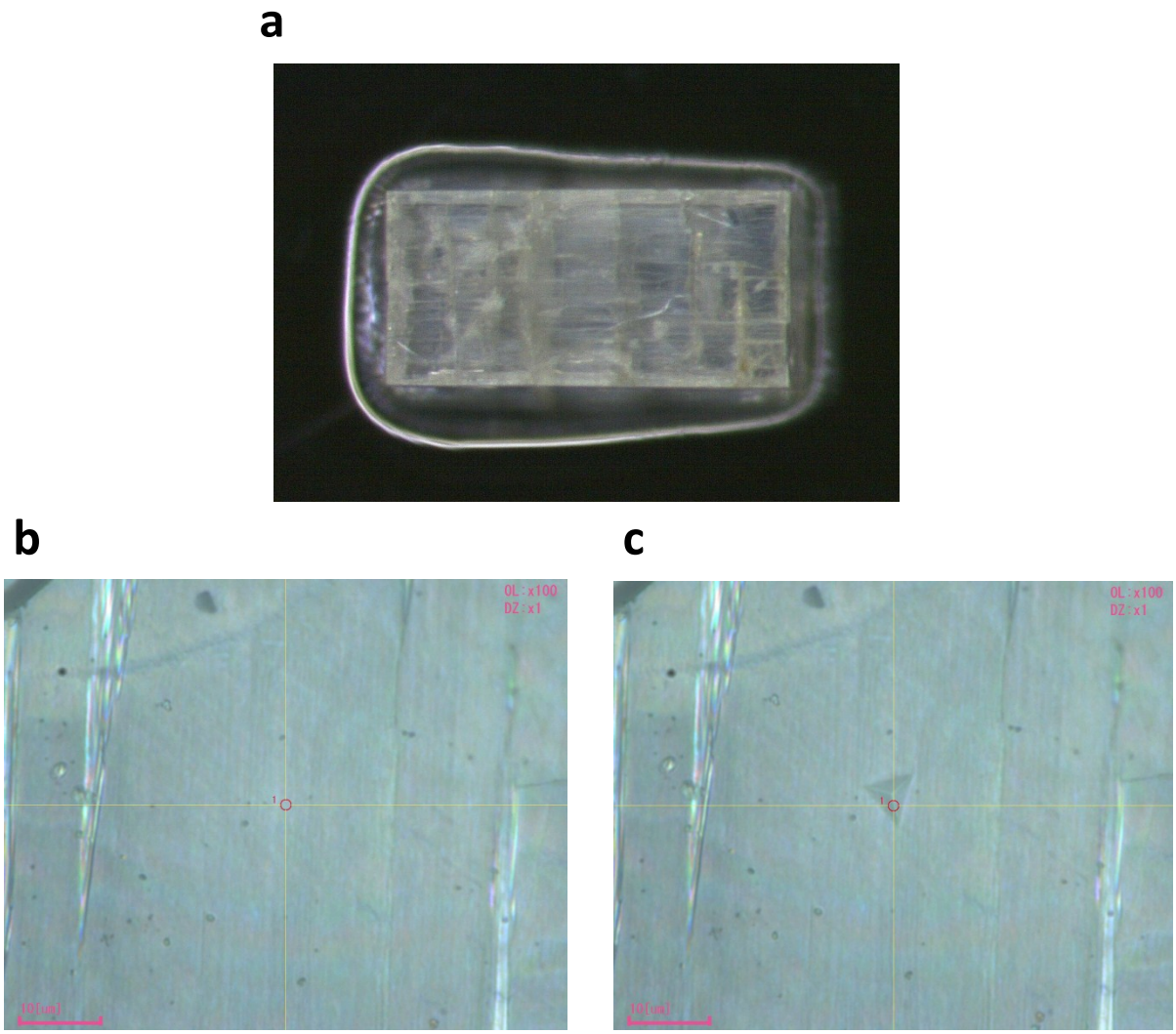

Fig. S1 (a) A single crystal of **1** attached on a Si wafer with adhesive. (b, c) The surface of a single crystal of **1** before and after indentation experiments.

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[5], S can be written as below

$$S = \frac{dP}{dh} = \frac{2}{\sqrt{\pi}} E_r \sqrt{A} \qquad (1)$$

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

$$\frac{1}{E_r} = \frac{1 - v_S^2}{E_S} + \frac{1 - v_I^2}{E_I} \qquad (2)$$

where E and v are elastic modulus and Poisson's ratio of the sample and the indenter with subscript S and I, 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 below;

$$C = \frac{\sqrt{\pi}}{2E_r\sqrt{23.96 h_A}} + C_f \qquad (3)$$

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.

$$H = \frac{P_{max}}{A} \qquad (4)$$

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

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

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;

$$\Delta h_c = \Delta h_{ET} + \Delta h_D \qquad (6)$$

Therefore, corrected projected contact area can be expressed as below;

$$A(h_A) = 23.96(h_A + \Delta h_c)^2 \qquad (7)$$

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. Then, H can be calculated from Eq. (4) by using obtained Δh_c.

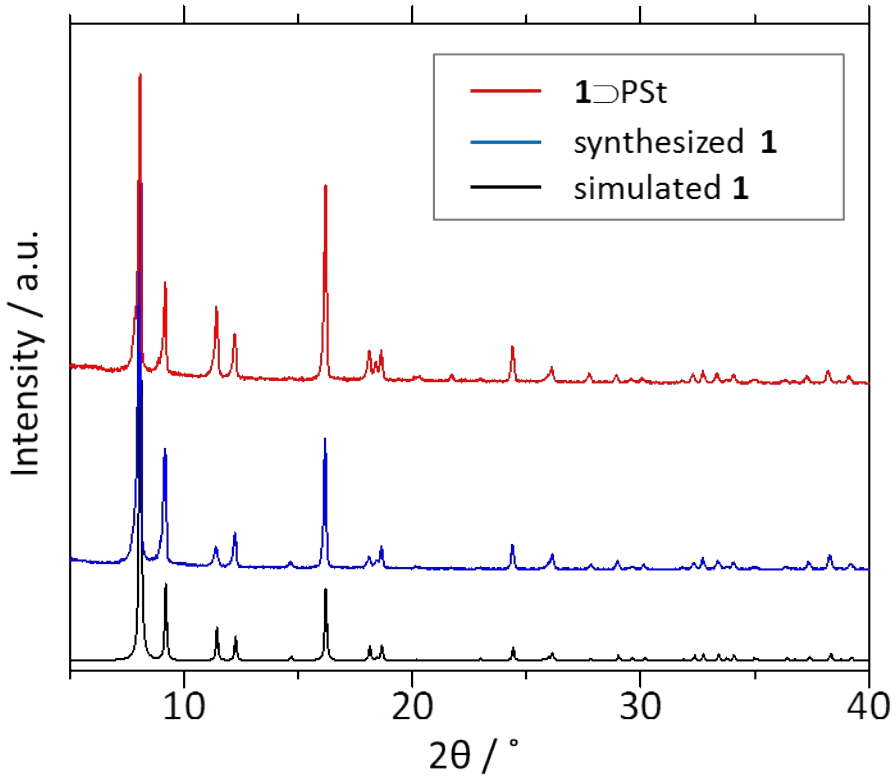

Fig. S2 XRPD patterns of simulated **1**, synthesized **1**, and **1**⊃PSt

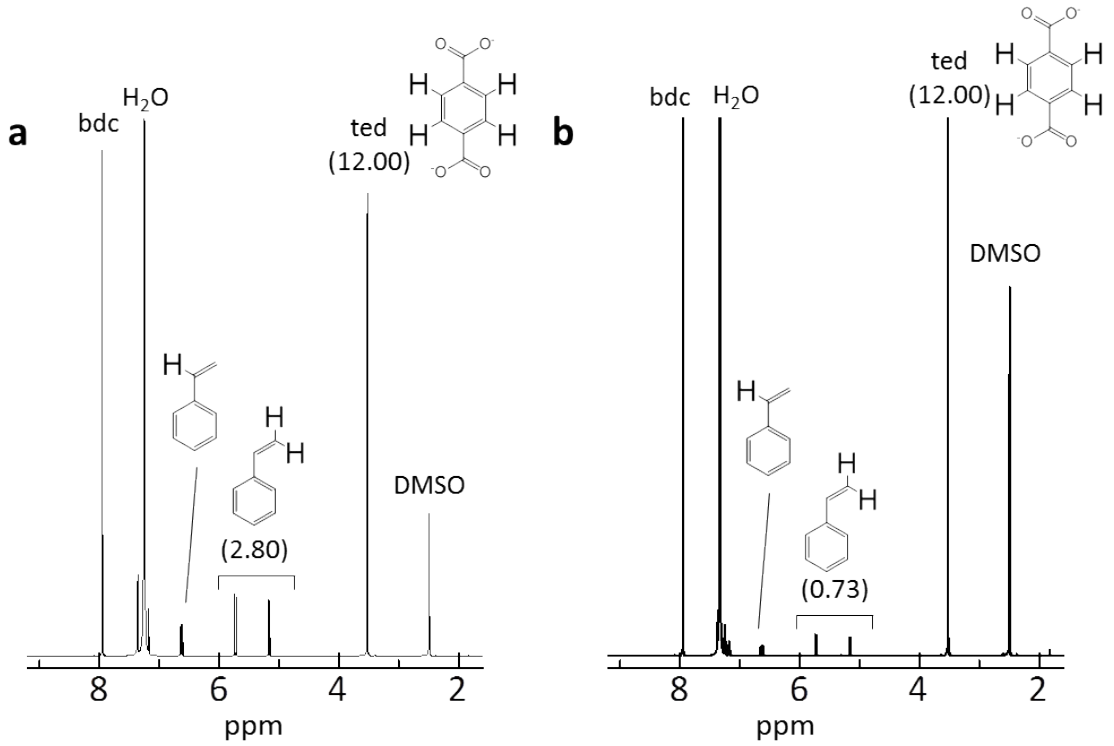

Fig. S3 ^{1}H NMR spectra of samples (a) after St incorporation into **1** and (b) after polymerization dissolved in the mixture of DMSO-d_6 and DCl (35wt% in D_2O) (9 : 1 (v/v)) (600 MHz). In the case of (b), insoluble PSt was removed by filtration before measurement. The values inside parentheses show integral values of corresponding peaks.

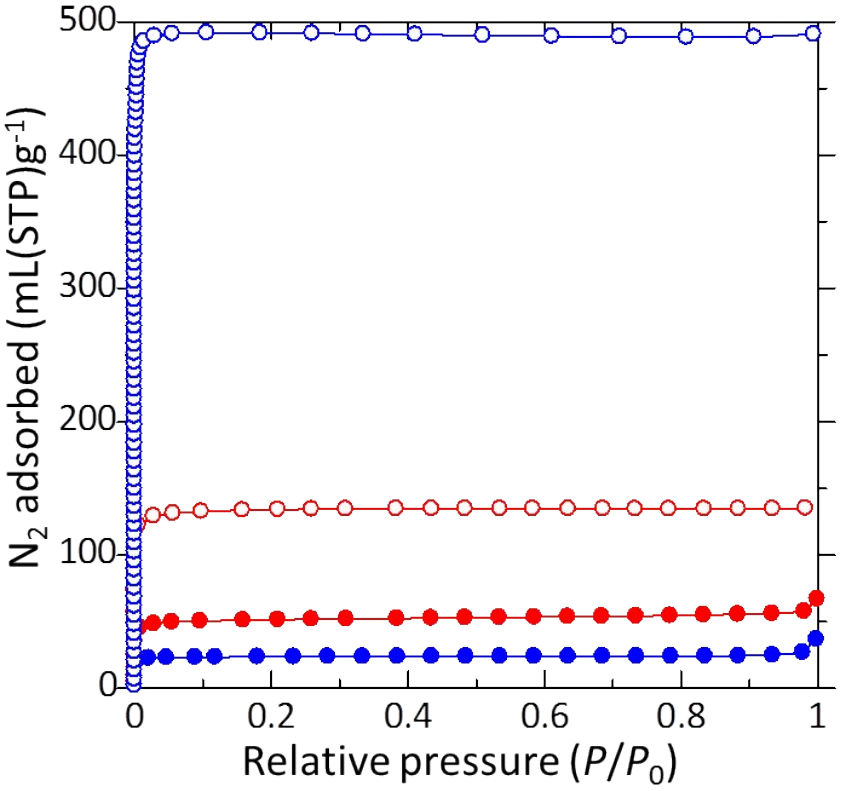

Fig. S4 N_2 gas adsorption isotherms of **1** alone (blue) and **1**⊃PSt (red). Open and closed circles correspond to uncompressed and compressed samples, respectively.

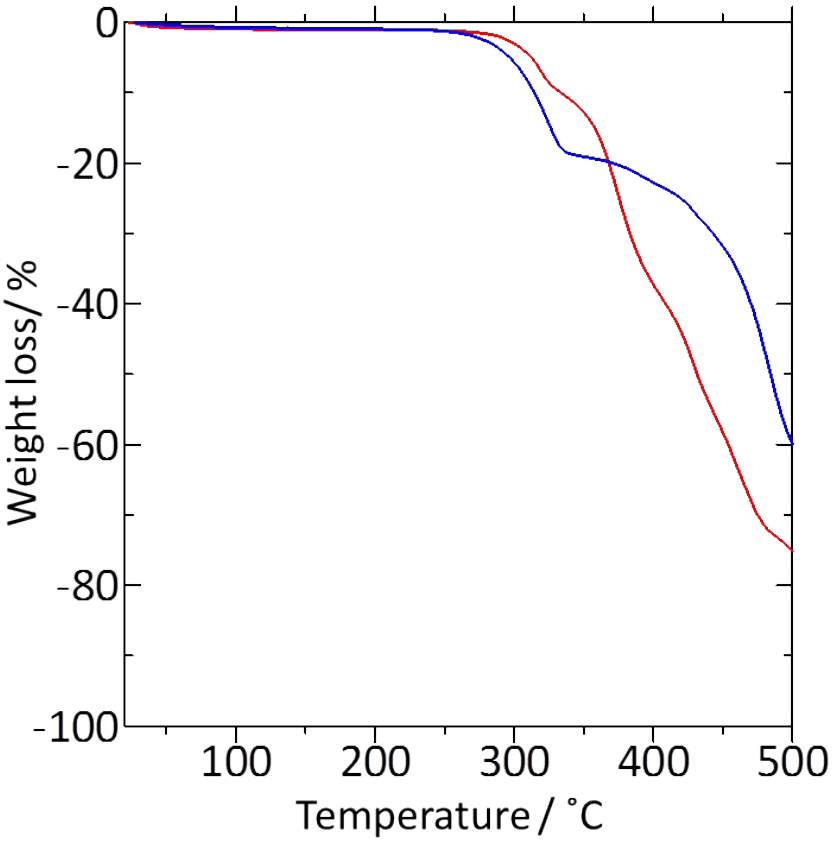

Fig. S5 Thermogravimetric curves of **1** (blue) and **1**⊃PSt (red) before pressure application.

a

b

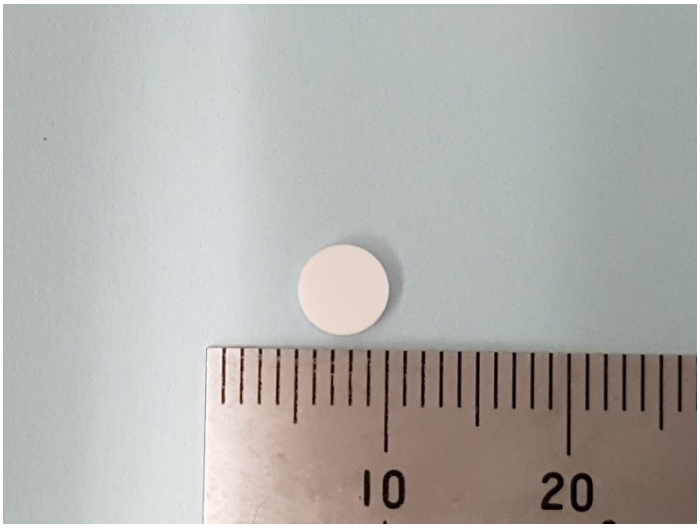

Fig. S6 (a) Hydraulic piston pelletizer used for the preparation of pellet samples. (b) The obtained pellet of **1** by compression.

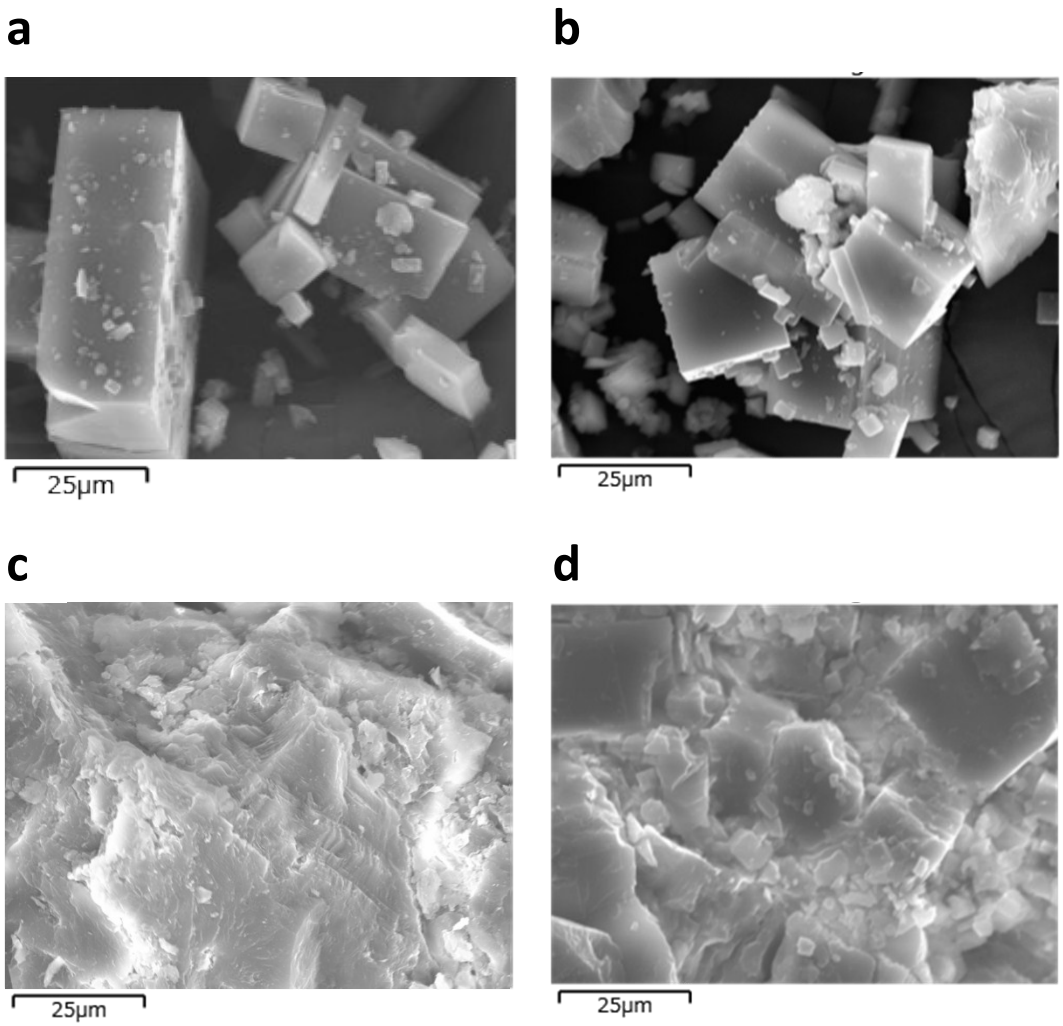

Fig. S7 SEM images of (a) pristine **1**, (b) **1**⊃PSt, (c) compressed **1**, and (d) compressed **1**⊃PSt.

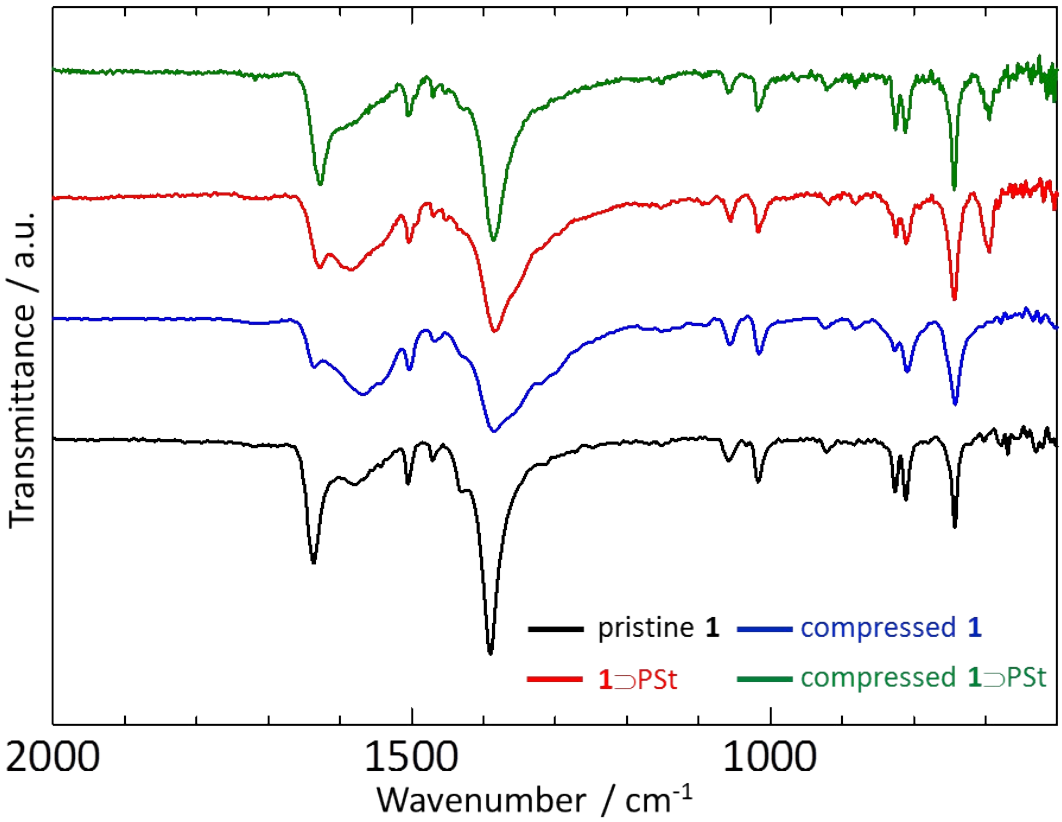

Fig. S8 IR spectra of **1** and **1**⊃PSt in the range of 600-2000 cm^{-1}.

	Hardness (GPa)	
	perpendicular to channels	**parallel to channels**
1	0.188 ± 0.044	0.133 ± 0.039
1⊃PSt	0.703 ± 0.034	0.341 ± 0.135
PSt	0.231 ±0.012	

Table S1 Hardness (*H*) of PSt, **1**, and **1**⊃PSt. Indentation measurements were performed along two different directions for **1** and **1**⊃PSt. The standard deviations were calculated from 16-32 indentation experiments.

References

(1) D. N. Dybtsev, H. Chun and K. Kim, *Angew. Chem. Int. Ed.*, 2004, **43**, 5033-5036.

(2) T. Uemura, K. Kitagawa, S. Horike, T. Kawamura, S. Kitagawa, M. Mizuno and K. Endo, *Chem. Commun*,. 2005, 5968-5970.

(3) T. Sawa and K. Tanaka, *J. Mater. Res.*, 2001, **16**, 3084-3096.
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(4) W. C. Oliver and G. M. Pharr, *J. Mater. Res.*, 1992, *7*, 1564-1583

(5) I. N. Sneddon, *Int. J. Engng Sci.*, 1965, **3**, 47-57.