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Mechanical Properties of a Metal-Organic Framework Containing Hydrogen-Bonded Bifluoride Linkers

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Synthesis. $[Cu_2F(HF)(HF_2)(pyz)_4][(SbF_6)_2]_n$ (**1**) was synthesized according to procedure given in literature.[1]

Single Crystal X–ray Diffraction Study. Single-crystal cell measurements of framework **1** were collected with an Oxford CCD diffractometer with graphite–monochromated Mo–$K\alpha$ radiation (λ= 0.71073 Å). Data reduction, absorption corrections and face indexation were applied and determined using the CrysAlis^{Pro} program.[2]

Table S1. Lattice parameters of framework **1.**

Framework	**1**
empirical formula	$C_{16}H_{18}N_8F_{16}Sb_2Cu_2$
formula weight/g mol^{-1}	996.96
crystal system	orthorhombic
space group	*Cmca*
a/Å	13.629(6)
b/Å	20.009(10)
c/Å	19.957(10)
α/deg	89.66(4)
β/deg	89.89(4)
γ/deg	89.95(4)
V/Å^3	5442(5)

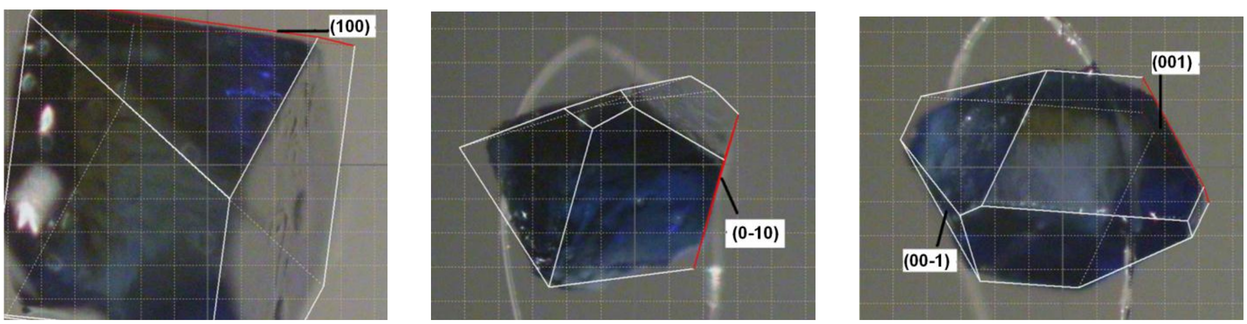

Figure S1. Face indexing of single-crystals of framework **1**.

Nanoindentation Methodology.

The nanoindentation experiments were performed on the {200}, {020} and {002} facets using a nanoindenter (Triboindenter of Hysitron, Minneapolis, USA) with an in-situ imaging capability. The machine continuously monitors and records the load (P) and displacement (h) of the indenter with resolutions of 1 nN and 0.2 nm, respectively. A Berkovich tip (tip radius of ~100 nm) is used to indent the crystals and tests were conducted under load control. In order to identify flat regions for the experiment, the crystal surfaces were imaged prior to indentation using the same indenter tip. A loading and unloading rate of 0.6 mN/s and a hold time of 30 s at peak load were employed. A minimum of 9 indentations were performed on each crystallographic facet. The indentation impressions were captured immediately after unloading. Contact stiffness, S is determined from the initial slope of the unloading segment of the P–h curves (i.e. $S = dP/dh$), therefore E and H can be found only at the maximum indentation depth. It is utilized to calculate the reduced modulus, E_r, through[3]:

$$E_r = \frac{\sqrt{\pi}}{2\beta}\frac{S}{\sqrt{A_c}}$$

where A_c is the contact area under load (based on the calibrated tip area function) and β is a constant that depends on the geometry of the indenter (β = 1.034 for a Berkovich tip). Note that this method, proposed by Oliver and Pharr ($O\&P$)[4] to extract the sample elastic modulus from the reduced modulus, assumes isotropic elastic properties, which is normally not the case for single crystals. The ‘‘indentation modulus”, E_r, is given by:

$$\frac{1}{E_r} = \frac{1-\nu_i^{\,2}}{E_i} + \frac{1-\nu_s^{\,2}}{E_s}$$

where v and E are Poisson’s ratio and elastic modulus, respectively; and the subscripts i and s refer to the indenter and test material, respectively. The indenter properties used in this study are E_i = 1141 GPa and $\nu_i = 0.07$.

The indentation hardness, H, can be determined from the maximum indentation load, P_{max}, divided by the contact area, A:

$$H = \frac{P_{\max}}{A}$$

A is a function of the contact depth, h_c, and can be determined by the following equation:

$$A(h_c) = C_0 h_c^{\,2} + C_1 h_c + C_2 h_c^{\,1/2} + C_3 h_c^{\,1/4} + \ldots\ldots + C_8 h_c^{\,1/128}.$$

It may be noted that only the constant C_0 is used, if it is assumed that a Berkovich indenter has a perfect tip. However, for imperfect tips, higher-order terms have to be taken into account and these are obtained from the tip-area function calibration for a given tip.

The contact depth can be estimated from the load-displacement data using

$$h_c = h_{\max} - \varepsilon \frac{P_{\max}}{S}$$

where h_{max} is the maximum indentation depth and $0.75(P/S)$ denotes the extent of elastic recovery (h_e).

References:

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