Supporting Information

A novel supramolecular magnesoborate framework with snowflake-like channels built by unprecedented huge B_{69} cluster cages

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Experimental Section

All chemicals employed in this study were analytical reagent. Single crystal X-ray diffraction data of compound **1** was collected an Agilent Technologies SuperNova Dual Wavelength CCD diffractometer with graphite-monochromated Cu Kα radiation (λ = 1.54178 Å) at 293K. All crystal structures were determined using direct methods and refined with a full-matrix least squares fitting on F^2 by SHELX-97.[1] The PLATON/SQUEESE program[2] was used to remove scattering contributions from disordered guest molecules and to produce solvent-free diffraction intensities, which were used in the final structure refinement. IR spectra (KBr pellets) were recorded on an ABB Bomen MB 102 spectrometer. Thermogravimetric analysis (TGA) was performed on a Mettler Toledo TGA 1100 analyzer in an air atmosphere with a heating rate of 10 ºC/min. Powder XRD patterns were obtained using a Bruker D8 Advance X-ray diffractometer with CuKα radiation (λ = 1.54056 Å). The UV-vis-NIR diffuse reflection data were recorded at room temperature using a powder sample with $BaSO_4$ as a standard (100% reflectance) on a Shimadzu UV-3600 spectrophotometer equipped with an integrating sphere in the wavelength range of 200-800 nm. Photoluminesence spectrum was performed on a Perkin Elmer LS55 fluorescence spectrometer. Elemental analyses (C, H and N) were performed using a German Elementary Vario EL III instrument.

[1] (a) G. M. Sheldrick, *SHELXS97 Program for Refinement of Crystal Structures, University of Göttingen* **1997**.
(b) G. M. Sheldrick, *SHELXL97 Program for Solution of Crystal Structures, Germany, University of Gottingen* **1997**.
[2] A. L. Spek, *J. Appl. Crystallogr.* **2003**, *36*, 7-13.

Synthesis: A mixture of H_3BO_3 (618.0 mg, 10.0 mmol) and $Mg(NO_3)_2{\cdot}6H_2O$ (106 mg, 0.4 mmol) was added to 3.0 mL N,N-dimethylformamide (DMF) and stirred for about one hour, the final solution was sealed in a 30 mL teflon-lined stainless steel autoclave and heated at 220 °C for 7 days under autogenous pressure, and then cooled to room temperature. The pure, long colorless prism crystals of **1** were obtained (yield 38.0% based on $Mg(NO_3)_2{\cdot}6H_2O$). Anal. calcd for **1**: C, 6.44; N, 5.14; H, 3.36; found: C, 6.88; N, 5.31; H, 3.17. CCDC 1545011 contains the supplementary crystallographic data for this paper.

Table S1. Crystal Data and Structure Refinement for compound **1**.

Empirical formula	$C_{19}H_{118}N_{13}O_{131}B_{69}Mg_7$
Formula weight	3551.83
Temperature	293(2) K
Wavelength	1.54178 Å
Crystal system	hexagonal
Space group	*P*-31*c*
a	26.1715(2) Å
b	26.1715(2) Å
c	15.3862(0) Å
Volume	9126.81 $Å^3$
Z, Calculated density	2, 1.704 Mg/m^3
Absorption coefficient	1.149 mm^{-1}
F(000)	2910
Limiting indices	-29≤h≤30, -31≤k≤30, -13≤l≤18
Reflections collected / unique	43517 / 5399 [R_{int} = 0.0360]
Refinement method	Full-matrix least-squares on F^2
Data / restraints / parameters	5399 / 0 / 306
Goodness-of-fit on F^2	1.072
Final *R* indices [*I*>2sigmai]	R_1 = 0.0488, wR_2 = 0.1412
R indices (all data)	R_1 = 0.0524, wR_2 = 0.1438
Largest diff. peak and hole	0.659 and -0.586 e. $Å^{-3}$

Table S2. Calculated bond valence sum (BVS) for compound **1**.

Atom	Mg(1)	Mg(2)	B1(Δ)	B2(Δ)	B3(Δ)	B4(Δ)	B5(Δ)
BVS	2.160	2.060	3.125	3.143	3.075	3.066	3.085
Atom	B6(Δ)	B7(T)	B8(T)	B9(T)	B10(Δ)	B11(T)	B12(T)
BVS	3.051	3.059	3.053	2.996	3.039	3.042	3.115

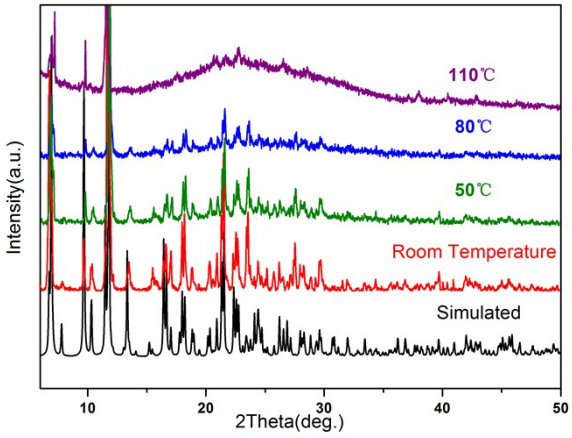

Figure S1. Simulated and experimental powder XRD patterns of **1** upon treatment at different temperatures.

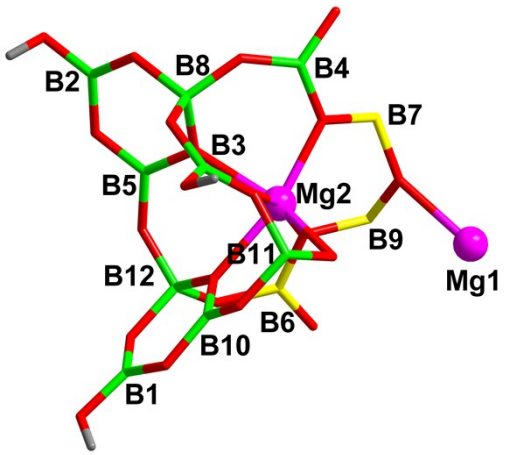

Figure S2. a) The asymmetric units of compound **1**.

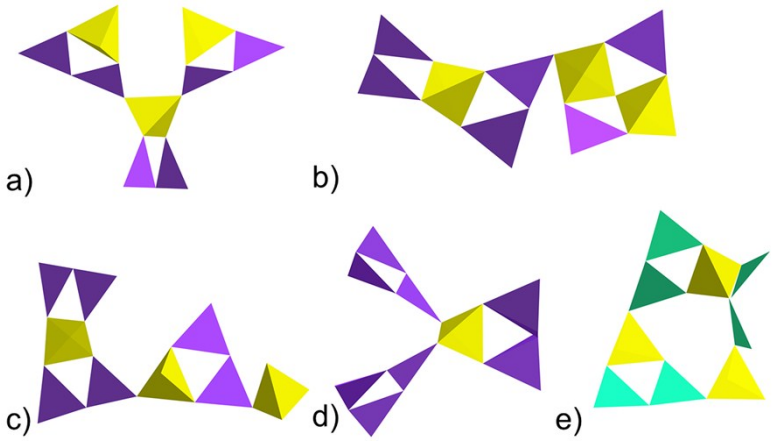

Figure S3. The reported B_9 cluster: a) B_9O_{19} 9:3[(3:2Δ+T)] in $BaLiB_9O_{15}$, $BaNaB_9O_{15}$ and $SrLiB_9O_{15}$, b) B_9O_{18} 9:[(5:4Δ+T)+(4:2Δ+2T)] in α-NaB_3O_5, c) B_9O_{19} 9:[(5:4Δ+T)+(3:2Δ+T)+(1:T)] in β-NaB_3O_5, d) B_9O_{17} 9:[(3:2Δ+T) +2(3:3Δ)] in CsB_9O_{14}, and e) The new B_9O_{19} cluster 9:[2(3:2Δ+T)+2(1:Δ)+(1:T)] in **1.**

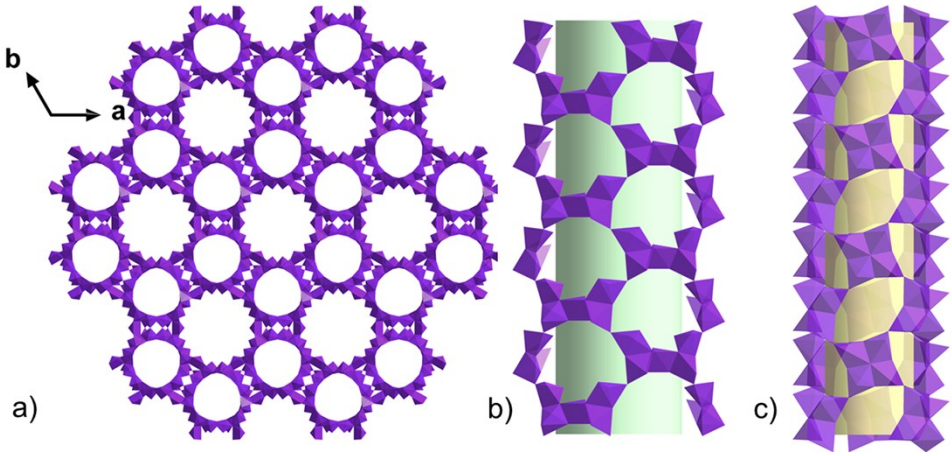

Figure S4. a) Projection of the 3D framework along the *c*-axis in FDU-4. b,c) 24MR and 12MR channels view normal to the [010] direction, respectively. The DMF and water guests are omitted for clarity.

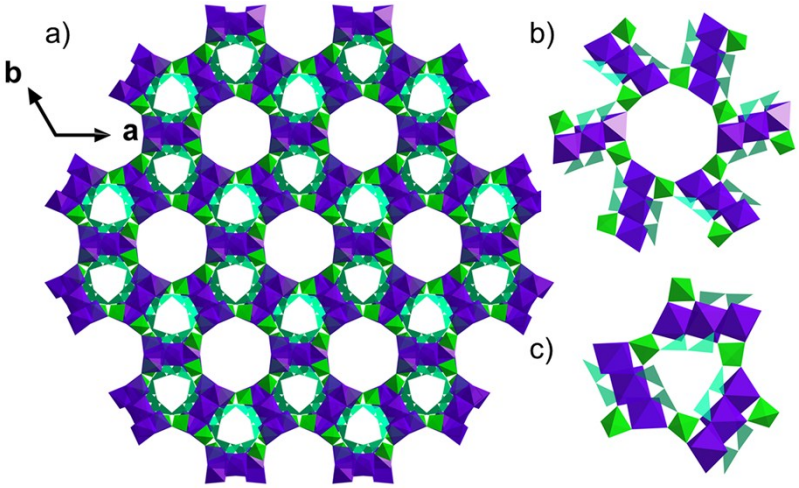

Figure S5. a) View of framework of PKU-3 along the *c*-axis. b,c) Side view of one 12R and 9R channel. AlO_6, purple; BO_4/BO_3, green.

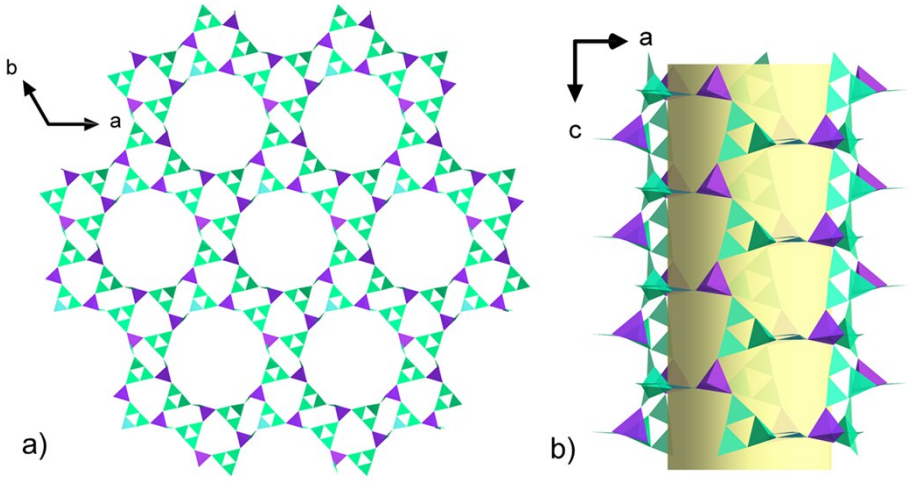

Figure S6. a) View of framework of BIT-1 along the c-axis. b) Side view of one 24R channel along the b-axis. AlO_4, purple; BO_4/BO_3, green.

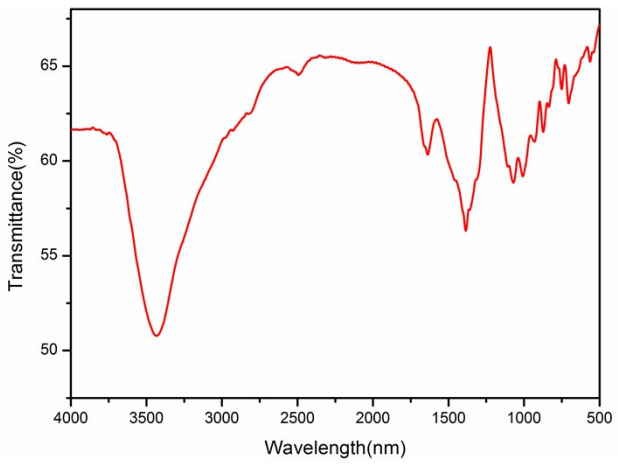

Figure S7. IR spectrums of compound **1**.

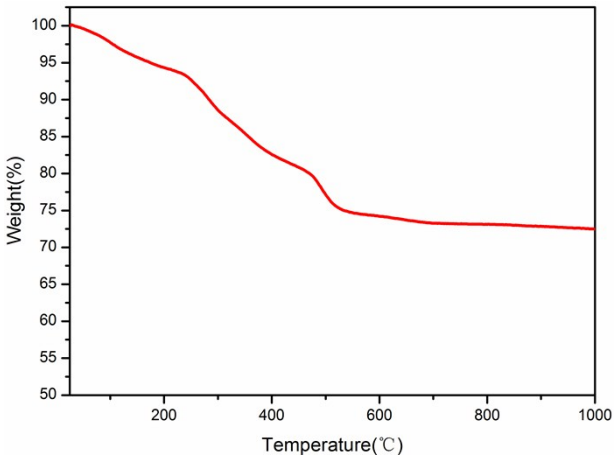

Figure S8. TG curves of compound **1**.

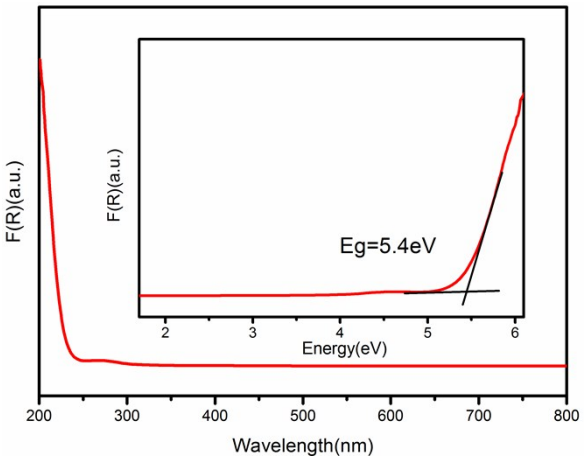

Figure S9. UV-vis optical diffuse reflectance spectra of compound **1**.