Supporting Information

$(NH_4)_3[B(OH)_3]_2(COOH)_3$: a Graphite-like UV Nonlinear Optical Material with Large Birefringence via Structural Optimization

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Section S1. Materials and Methods

Synthesis

All starting analytical grade reagents H_3BO_3 (≥ 99.5%) and NH_4COOH (≥ 99.5%), were commercially available and used without further processing. The starting material H_3BO_3 was purchased from KESHI, and NH_4COOH was purchased from MACKLIN.

$(NH_4)_3[B(OH)_3]_2(COOH)_3$ was synthesized by solvent evaporation through reacting of H_3BO_3 (0.126 g, 2mmol) with NH_4COOH (0.062g, 1mmol) and 10 mL of deionized water. The mixture was stirred at room temperature for 20 minutes, after the solution was dissolved to colorless and transparent solution, then transferred to a refrigerator and evaporated at 5 °C. Finally, colorless transparent rod-shaped crystals grew out in 30 days, and the crystals were washed with alcohol and dried in air. $(NH_4)_3[B(OH)_3]_2(COOH)_3$ was obtained in yields of about 47% (on the basis of B).

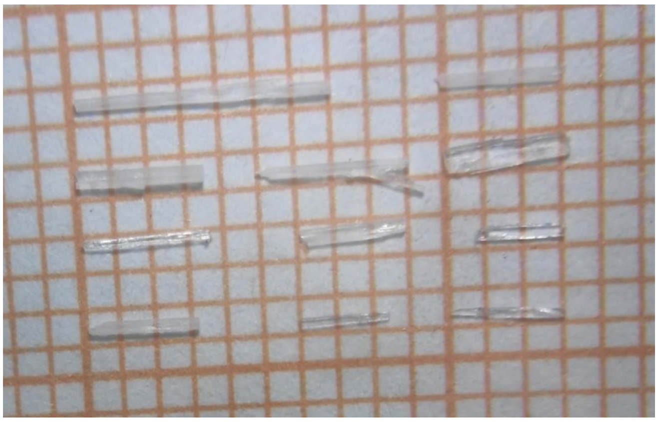

Figure S1 The crystal photograph of $(NH_4)_3[B(OH)_3]_2(COOH)_3$.

Instruments

Single-crystal X-ray diffraction data of $(NH_4)_3[B(OH)_3]_2(COOH)_3$ is obtained in a monochromatic MoKα radiation equipped with graphite on a Bruker D8 Venture diffractometer at 150 (2) K. The structure was solved by direct method, and refined by full matrix least squares fitting on F^2 with SHELX-2014.[1] The anisotropic displacement parameters of all atomic sites except hydrogen atoms in $(NH_4)_3[B(OH)_3]_2(COOH)_3$ have been optimized. Table S1 summarizes the relevant crystallographic data and experimental details. Tables S2-S3 list the atomic coordinates and isotropic displacement coefficients, and the selected bond lengths for $(NH_4)_3[B(OH)_3]_2(COOH)_3$.

X-ray diffraction pattern of crystalline material of the title compound was obtained from Smart Lab powder. CuKα radiation (λ = 1.540598Å) was used on a Smart Lab powder X-ray diffractometer in a 2θ angle range of 5 to 70 ° with a scan step size of 0.08 degrees and a fixed time of 0.2 s at room temperature.

Thermogravimetric analysis (TGA) was performed on a Netzsch STA 409 PC. A 10 mg crystal sample was sealed in a platinum crucible and heated from room temperature to 800 ° C at a rate of 10 ˚C/min in a N_2 atmosphere.

An infrared spectrum in the range of 4000-400 cm^{-1} was recorded on a Vertex 70 Fourier transform infrared (FT-IR) spectrometer with KBr as the diluent. KBr (100 mg) and solid sample (1 mg) were fully ground in an agate mortar, and a special tabletting device was used to press the sample into a transparent sheet with a diameter of 13 mm and a thickness of about 1mm for analysis.

The Shimadzu UV-2600 spectrophotometer was used to record the UV-vis diffuse reflectance spectrum of the compound at room temperature and scanned at 200-800 nm. $BaSO_4$ was used as a 100% reflectance standard and Kubelka-Munk function is used to calculate the absorption spectrum.[2,3]

The birefringence of $(NH_4)_3[B(OH)_3]_2(COOH)_3$ was characterized by using the polarizing microscope equipped (ZEISS Axio Scope. A1) with Berek compensator. The wavelength of the light source was 546 nm. Owing to the clear boundary lines of the first-, second- and third-order interference color, the relative error was small enough. Before the scanning, the small and transparent $(NH_4)_3[B(OH)_3]_2(COOH)_3$ crystals were chosen to measure, in order to improve the accuracy of the birefringence. The formula for calculating the birefringence is listed below,

$$R = | N_e - N_o | \times T = \Delta n \times T$$

Here, R represents the optical path difference, Δn means the birefringence, and T denotes the thickness of the crystal.

The Kurtz and Perry method was used to measure powder second harmonic generation (SHG) signals at room temperature.[4] As far as we know, the SHG efficiency mainly depends on the particle size, and samples of crystalline compounds are ground and divided into the following particle sizes: 25-45, 45-58, 58-75, 75-106, 106-150, and 150-212 μm. SHG measurements were performed using Q-switched Nd: YAG lasers with visible light at 1064 nm. Microcrystalline KDP with the same particle size was used as a reference for visible SHG.

In order to better understand the electronic structure of $(NH_4)_3[B(OH)_3]_2(COOH)_3$, the theoretical calculations was processed using density functional theory (DFT) in the CASTEP program suite.[5] All the calculations were treated by the formulation of the Perdew-Burke-Ernzerhof (PBE) functional in Generalized Gradient Approximation (GGA) on geometrically optimized structure.[6] And the adopted convergence criteria is 1.0e-6 eV/atom, the plane-wave cut-off energy of 830 eV was used, and the k-point meshes were set with a density of 3×10×2 in the Brillouin zone and the coordinates of k-points were Z(0.000, 0.000, 0.500), G(0.000,0.000,0.000), Y(0.000,0.500,0.000), A(-0.500,0.500,0.000), B(-0.500,0.000,0.000), D(-0.500,0.000,0.500), E(-0.500,0.500,0.500), C(0.000,0.500,0.500), respectively. Norm-conserving pseudopotential is used. [7]

Table S1 Crystal data and structure refinement for $(NH_4)_3[B(OH)_3]_2(COOH)_3$.

Formula	**$(NH_4)_3[B(OH)_3]_2(COOH)_3$**
Formula Mass(amu)	312.83
Crystal system	monoclinic
Space group	*Pn*
a (Å)	10.6478 (12)
b (Å)	3.6669 (5)
c (Å)	18.5931 (18)
V (Å^3)	725.90 (15)
α (°)	90
β (°)	90.737(4)
γ (°)	90
Z	2
D_{calcd}(g·cm^{-3})	1.431
Temperature (K)	150 (2)
λ (Å)	0.71073
F(000)	332
μ (mm^{-1})	0.14
GOF on F^2	1.094
R_1,wR_2 (I>2σ(I))[a]	0.0342/ 0.0750
R_1,wR_2 (all data)	0.0424/ 0.0793

[a] $R_1(F) = \sum||F_o| - |F_c|| / \sum|F_o|$. $wR_2(F_o^2) = [\sum w(F_o^2 - F_c^2)^2 / \sum w(F_o^2)^2]^{1/2}$

Table S2 Atomic coordinates (×10^4) and equivalent isotropic displacement parameters (Å^2×10^3) for $(NH_4)_3[B(OH)_3]_2(COOH)_3$. U(eq) is defined as one third of the trace of the orthogonalized U_{ij} tensor.

atom	*x*	*y*	*z*	U(eq)
O(1)	-2108(2)	-5662(5)	-6600(1)	38(1)
O(2)	-3577(2)	-4953(5)	-5122(1)	36(1)
O(3)	-4511(2)	-4641(5)	-6279(1)	35(1)
O(4)	-2052(2)	-5065(5)	-7795(1)	38(1)
O(5)	-5791(2)	-5165(5)	-5252(1)	35(1)
O(6)	1437(2)	-6077(5)	-4295(1)	36(1)
O(7)	-7500(2)	-3950(5)	-6286(1)	38(1)
O(8)	-761(2)	-5654(5)	-4181(1)	35(1)
O(9)	-2480(2)	-4894(5)	-3172(1)	40(1)
O(10)	-9253(2)	-4358(5)	-5639(1)	40(1)
O(11)	-4233(2)	-6376(5)	-3781(1)	39(1)
O(12)	532(2)	-6193(5)	-3142(1)	36(1)
N(1)	-1052(2)	-617(6)	-2201(1)	31(1)
N(2)	-6391(2)	-10662(6)	-4004(1)	30(1)
N(3)	-11439(2)	-202(6)	-5408(1)	31(1)
C(1)	-1640(2)	-6180(7)	-7201(2)	34(1)
C(2)	-8626(2)	-3255(7)	-6163(1)	35(1)
C(3)	-3604(3)	-5839(8)	-3224(2)	41(1)
B(1)	-4627(3)	-4931(7)	-5554(2)	30(1)
B(2)	398(3)	-5980(8)	-3871(2)	31(1)

Table S3 Selected Bond Distances (Å) and angles (deg) for $(NH_4)_3[B(OH)_3]_2(COOH)_3$.

O(1)-C(1)	1.244(3)	O(12)-B(2)	1.363(3)
O(2)-B(1)	1.368(3)	O(1)-C(1)-O(4)	127.1(2)
O(3)-B(1)	1.359(3)	O(7)-C(2)-O(10)	126.7(2)
O(4)-C(1)	1.251(3)	O(11)-C(3)-O(9)	128.0(3)
O(5)-B(1)	1.371(3)	O(3)-B(1)-O(2)	120.0(2)
O(6)-B(2)	1.368(3)	O(3)-B(1)-O(5)	120.4(2)
O(7)-C(2)	1.249(3)	O(2)-B(1)-O(5)	119.6(2)
O(8)-B(2)	1.362(3)	O(8)-B(2)-O(12)	120.6(2)
O(9)-C(3)	1.248(3)	O(8)-B(2)-O(6)	119.5(2)
O(10)-C(2)	1.255(3)	O(12)-B(2)-O(6)	119.9(2)
O(11)-C(3)	1.241(3)		

Table S4. The birefringence of $(NH_4)_3[B(OH)_3]_2(COOH)_3$ and several well-known UV optical materials with planar π-conjugated structure groups.

Crystals	Birefringence
$(NH_4)_3[B(OH)_3]_2(COOH)_3$[a]	0.156@546 nm^{Exp}
α-BaB_2O_4 (α-BBO)[19a]	0.122@546 nm^{Exp}
$Na_3Ba_2(B_3O_6)_2F$[19b]	0.114@546 nm^{Exp}
$KSrCO_3F$[18a]	0.112@532 nm^{Exp}
$Li_2Na_2B_2O_5$[19c]	0.097@532 nm^{Exp}
$Ba_2NO_3(OH)_3$[9d]	0.080@532 nm^{Cal}
$KBe_2BO_3F_2$[19d]	0.076@546 nm^{Exp}
$Li_4Sr(BO_3)_2$[19e]	0.056@532 nm^{Cal}

[a] This work; Exp = experimental value , Cal = calculated value.

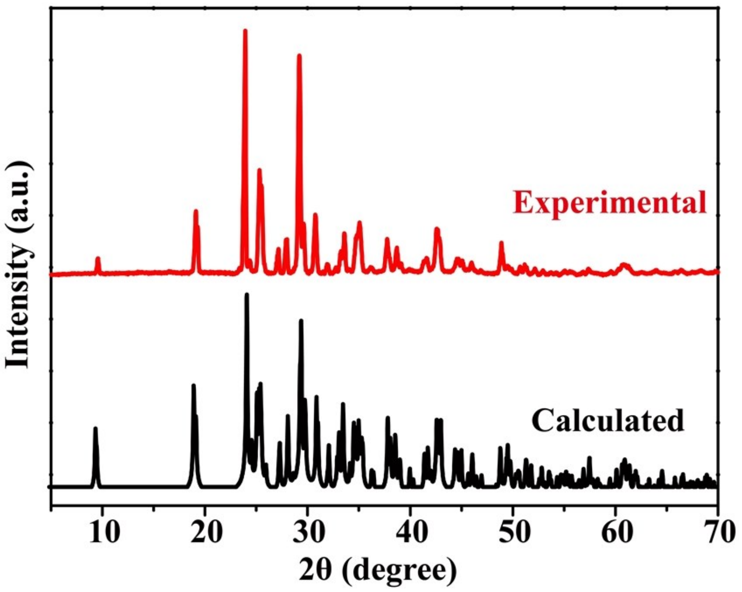

Figure S2 Experimental and calculated XRD patterns for $(NH_4)_3[B(OH)_3]_2(COOH)_3$.

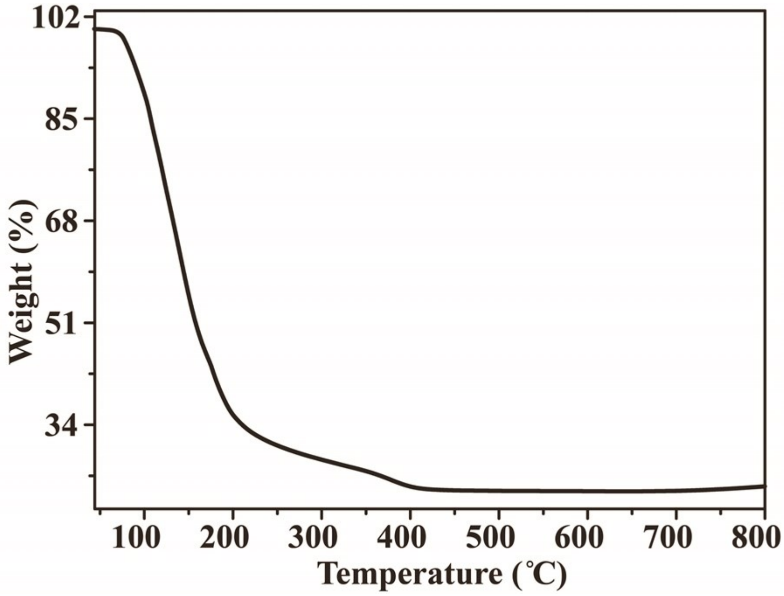

Figure S3 TG curve for $(NH_4)_3[B(OH)_3]_2(COOH)_3$.

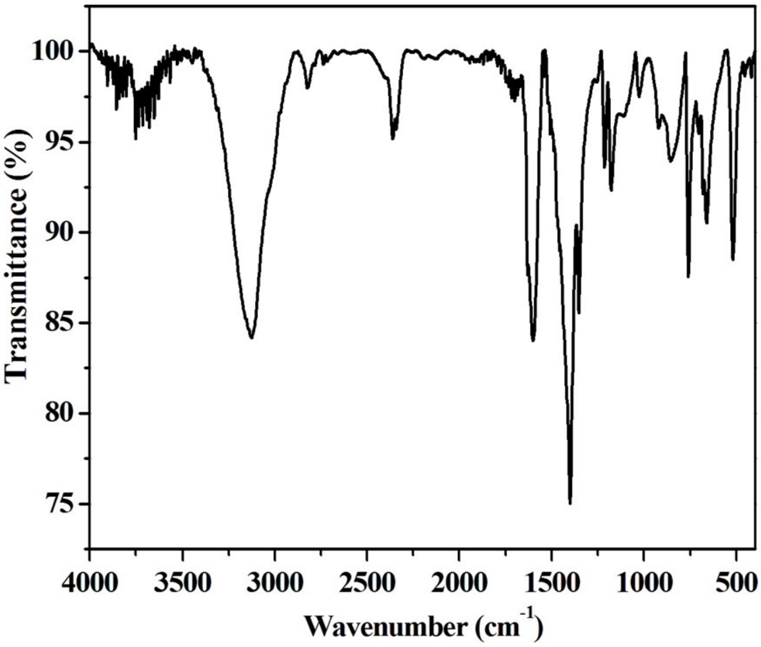

Figure S4 The IR spectrum of compound $(NH_4)_3[B(OH)_3]_2(COOH)_3$.

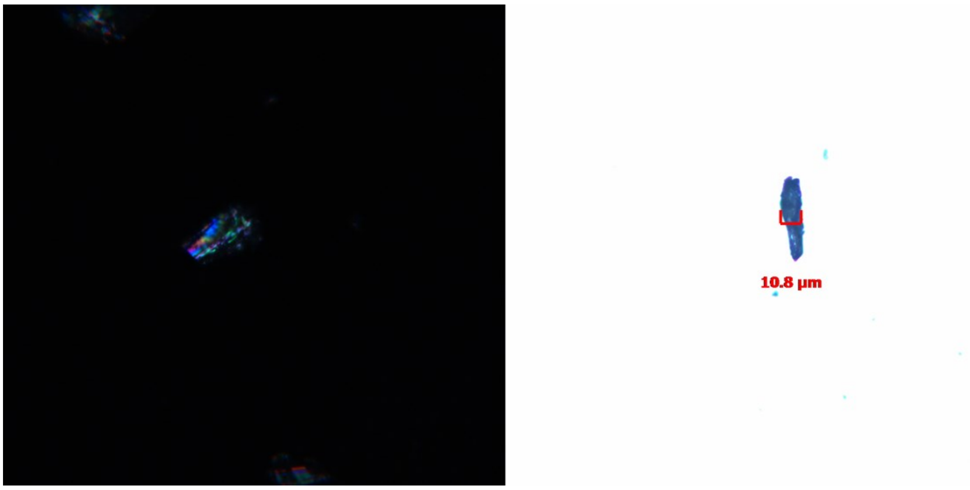

Figure S5 Birefringence measurements on the $(NH_4)_3[B(OH)_3]_2(COOH)_3$ crystal. (a) A $(NH_4)_3[B(OH)_3]_2(COOH)_3$ single crystal under the polarizing microscope and (b) the thickness of $(NH_4)_3[B(OH)_3]_2(COOH)_3$ crystal.

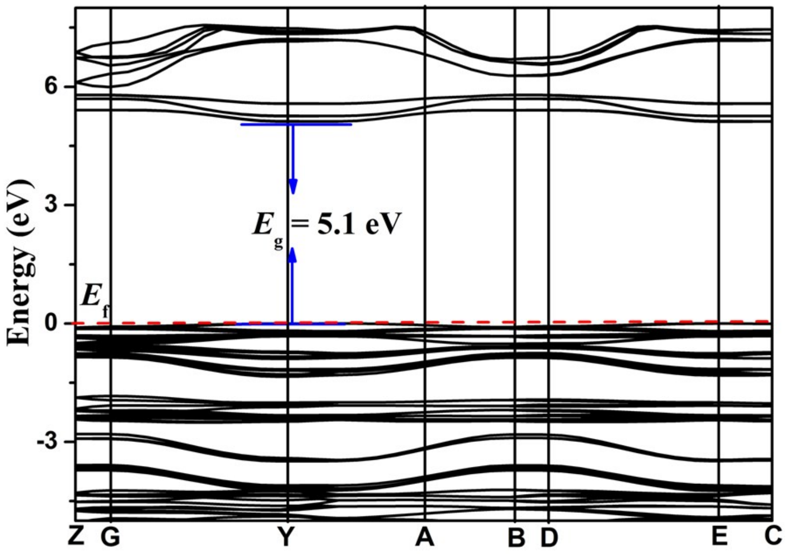

Figure S6 Calculated band structure for $(NH_4)_3[B(OH)_3]_2(COOH)_3$ (the Fermi level is set at 0 eV).

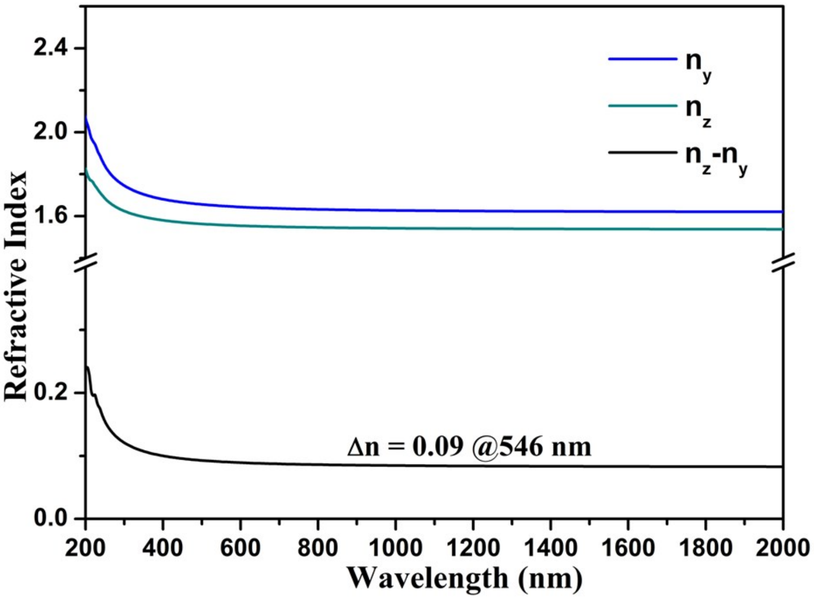

Figure S7 The calculated refractive indices and birefringence of α-BaB_2O_4 (α-BBO).

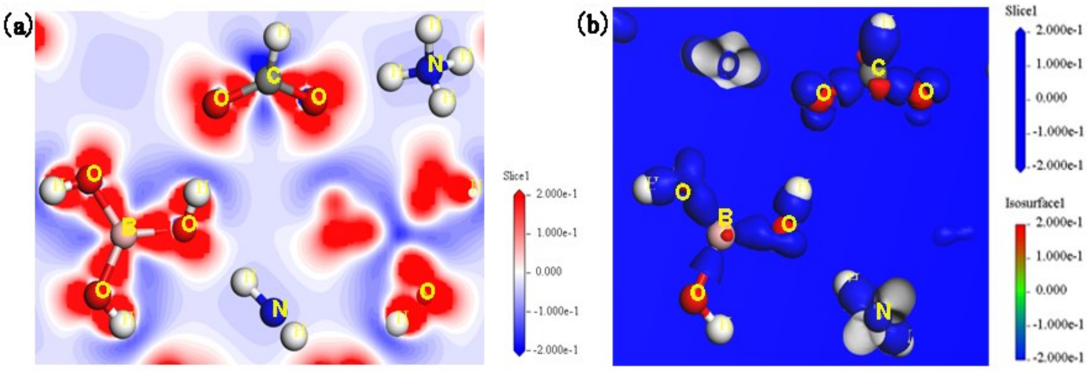

Figure S8 Electron-density difference maps for $(NH_4)_3[B(OH)_3]_2(COOH)_3$.

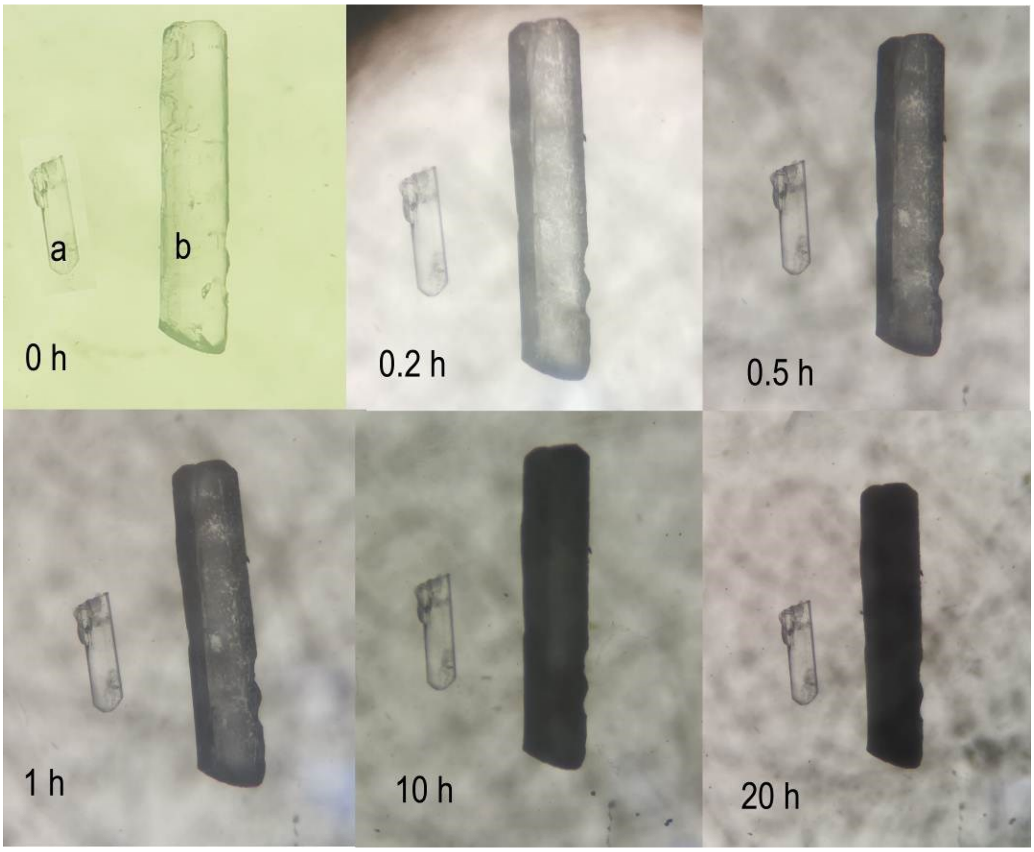

Figure S9 Physicochemical stability comparison tests for $(NH_4)_3[B(OH)_3]_2(COOH)_3$ (a) and $(HCOOH)_3[B(OH)_3]_2{\cdot}3H_2O$ (b) after exposure to the air.

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