

Electronic Supporting Information

**Large Optical Anisotropy Differentiation Induced by Anion-Directed  
Regulation of Structures**

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## Section S1. Experimental section

### Instrumentations.

Suitable single crystals were selected under an optical microscope. Crystal structures determination of  $(\text{Gu})_2\text{Sb}_3\text{F}_3(\text{HPO}_3)_4$  and  $(\text{Gu})\text{SbFPO}_4\cdot\text{H}_2\text{O}$  were performed on a Bruker SMART BREEZE diffractometer with graphite-monochromated  $\text{MoK}\alpha$  radiation ( $\lambda = 0.71073 \text{ \AA}$ ) at room temperature. All absorption corrections were performed by using the SADABS program. The structure was solved by direct methods and refined by full-matrix least squares on  $F^2$  using the SHELX-97 program package.<sup>[1,2]</sup> All of the structures were verified using the ADDSYM algorithm from the program PLATON and no higher symmetries were found.<sup>[3]</sup> Crystallographic data and structural refinements for the compound are summarized in Table S1. Atomic coordinates and isotropic displacement coefficients, and selected bond lengths for the compound are listed in Tables S2-S5.

Powder XRD patterns were obtained using a Rigaku Smartlab powder X-ray diffractometer with  $\text{CuK}\alpha$  radiation ( $\lambda = 1.54056 \text{ \AA}$ ), in the angular range of  $2\theta = 5\text{-}50^\circ$ , and with a scan step width of  $0.05^\circ$  and a fixed time of 0.2 s.

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  $800 \text{ }^\circ\text{C}$  at a rate of  $10 \text{ }^\circ\text{C}/\text{min}$  in a  $\text{N}_2$  atmosphere.

An infrared spectrum in the range of  $4000\text{-}400 \text{ cm}^{-1}$  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 tableting device was used to press the sample into a transparent sheet with a diameter of 13 mm and a thickness of about 1 mm for analysis.

The UV-vis diffuse reflectance spectrum of  $(\text{Gu})_2\text{Sb}_3\text{F}_3(\text{HPO}_3)_4$  and  $(\text{Gu})\text{SbFPO}_4\cdot\text{H}_2\text{O}$  were recorded using a Shimadzu UV-2600 spectrophotometer with  $\text{BaSO}_4$  plate as a standard (100% reflectance). The Kubelka-Munk function is used to calculate the absorption spectrum from the reflection spectrum:  $F(R) = \alpha/S = (1-R)^2/2R$ , where R is the reflectance,  $\alpha$  is the absorption coefficient, and S is the scattering coefficient.<sup>[4]</sup>

The birefringence of  $(\text{Gu})_2\text{Sb}_3\text{F}_3(\text{HPO}_3)_4$  and  $(\text{Gu})\text{SbFPO}_4\cdot\text{H}_2\text{O}$  were 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  $(\text{Gu})_2\text{Sb}_3\text{F}_3(\text{HPO}_3)_4$  and  $(\text{Gu})\text{SbFPO}_4\cdot\text{H}_2\text{O}$  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,  $\Delta n$  means the birefringence, and T denotes the thickness of the crystal.

### **Computational Descriptions.**

The first-principles calculations of  $(\text{Gu})_2\text{Sb}_3\text{F}_3(\text{HPO}_3)_4$  and  $(\text{Gu})\text{SbFPO}_4\cdot\text{H}_2\text{O}$  were carried out by using the CASTEP software package to understand the relationship between structure and properties.<sup>[5]</sup> The band structure, density of states (DOS)/partial DOS (PDOS), birefringence and electron-density difference map of  $(\text{Gu})_2\text{Sb}_3\text{F}_3(\text{HPO}_3)_4$  and  $(\text{Gu})\text{SbFPO}_4\cdot\text{H}_2\text{O}$  were computed. The generalized gradient approximation (GGA) with Perdew-Burke-Emzerh (PBE) functional was adopted for all calculations.<sup>[6]</sup> Norm-conserving were employed for all the atoms.<sup>[7]</sup> The criteria of convergences of energy are set as  $1.0\text{e-}6$  eV/atom. Moreover, different kinetic energy cutoffs and k-point samplings were selected for the compounds: 750 eV and  $2 \times 3 \times 2$  for  $(\text{Gu})_2\text{Sb}_3\text{F}_3(\text{HPO}_3)_4$ , 780 eV and  $4 \times 4 \times 2$  for  $(\text{Gu})\text{SbFPO}_4\cdot\text{H}_2\text{O}$ .<sup>[8]</sup> The rest parameters used in the calculations were set by the default values of the CASTEP. The valences of composed atoms were as follow: O  $2s^22p^4$ , C  $2s^22p^2$ , N  $2s^22p^3$ , F  $3s^23p^5$ , P  $3s^23p^3$ , F:  $2s^22p^5$ , H  $1s^1$  and Sb:  $5s^25p^3$ .

**Table S1.** Crystal data and structure refinement for (Gu)<sub>2</sub>Sb<sub>3</sub>F<sub>3</sub>(HPO<sub>3</sub>)<sub>4</sub> and (Gu)SbFPO<sub>4</sub>·H<sub>2</sub>O.

Compound	(Gu) <sub>2</sub> Sb <sub>3</sub> F <sub>3</sub> (HPO <sub>3</sub> ) <sub>4</sub>	(Gu)SbFPO <sub>4</sub> ·H <sub>2</sub> O
Formula Mass	862.34	313.82
Crystal System	Triclinic	monoclinic
Space Group	<i>C2/c</i>	<i>P2<sub>1</sub>/c</i>
<i>a</i> (Å)	15.9469(9)	6.6385(2)
<i>b</i> (Å)	9.2070(9)	6.6035(2)
<i>c</i> (Å)	15.4379(12)	18.0672(4)
$\alpha$ (°)	90	90
$\beta$ (°)	110.1400	97.113(2)
$\gamma$ (°)	90	90
<i>V</i> (Å <sup>3</sup> )	2128.0(3)	785.92(4)
<i>Z</i>	4	4
$\rho$ (calcd) (g/cm <sup>3</sup> )	2.692	2.652
Temperature (K)	293	293
$\lambda$ (Å)	0.71073	0.71073
<i>F</i> (000)	1624.0	600.0
$\mu$ (mm <sup>-1</sup> )	4.172	3.725
<i>R</i> <sub>1</sub> , <i>wR</i> <sub>2</sub> ( <i>I</i> > 2 $\sigma$ ( <i>I</i> )) <sup>a</sup>	0.0236/0.0525	0.0373/0.1223
GOF on <i>F</i> <sup>2</sup>	0.952	0.822

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

**Table S2.** Atomic coordinates and equivalent isotropic displacement parameters for  $(\text{Gu})_2\text{Sb}_3\text{F}_3(\text{HPO}_3)_4$ .  $U_{\text{eq}}$  is defined as one third of the trace of the orthogonalized  $U_{ij}$  tensor.

atom	$x$	$y$	$z$	$U_{\text{eq}}(\text{\AA}^2)$
Sb1	0.27350 (2)	0.35928 (2)	0.75190 (2)	0.02175 (7)
Sb2	0.500000	0.04235 (3)	0.750000	0.02175 (8)
P1	0.21451 (5)	0.58641 (8)	0.88886 (4)	0.01945 (14)
P2	0.38050 (5)	0.08662 (8)	0.88884 (5)	0.01953 (14)
F1	0.500000	-0.1647 (2)	0.750000	0.0259 (5)
F2	0.37722 (10)	0.46115 (17)	0.75046 (11)	0.0262 (4)
O1	0.44344 (14)	-0.0091 (2)	0.85824 (14)	0.0301 (5)
O2	0.13088 (13)	0.4906 (2)	0.85712 (14)	0.0299 (5)
O3	0.28871 (13)	0.5257 (2)	0.85801 (14)	0.0305 (5)
O4	0.28533 (13)	0.0261 (2)	0.85668 (14)	0.0303 (5)
O5	0.19202 (14)	0.7433 (2)	0.85766 (14)	0.0298 (5)
O6	0.38230 (13)	0.2434 (2)	0.85809 (14)	0.0302 (5)
N1	0.44610 (17)	0.4445 (3)	0.59668 (18)	0.0315 (6)
H1A	0.491358	0.397760	0.592798	0.038*
H1B	0.399915	0.397950	0.598291	0.038*
N2	0.51866 (17)	0.6602 (3)	0.59770 (18)	0.0314 (6)
H2A	0.563975	0.613656	0.593816	0.038*
H2B	0.519480	0.753588	0.599971	0.038*
N3	0.37519 (17)	0.6601 (3)	0.60077 (18)	0.0312 (6)
H3A	0.327979	0.613105	0.598894	0.037*
H3B	0.375728	0.753397	0.603032	0.037*
C1	0.44753 (19)	0.5882 (3)	0.60017 (18)	0.0249 (6)
H1	0.2393 (19)	0.589 (3)	0.9718 (19)	0.020 (7)*
H2	0.409 (2)	0.083 (3)	0.974 (2)	0.024 (8)*

**Table S3.** Selected Bond lengths (Å) and angles (deg) for (Gu)<sub>2</sub>Sb<sub>3</sub>F<sub>3</sub>(HPO<sub>3</sub>)<sub>4</sub>.

Sb1—O3	2.195 (2)	P1—O3	1.525 (2)
Sb1—O4 <sup>i</sup>	2.229 (2)	P1—O5	1.526 (2)
Sb1—O5 <sup>ii</sup>	2.223 (2)	P2—O1	1.527 (2)
Sb1—O6	2.208 (2)	P2—O4	1.530 (2)
Sb2—O1	2.206 (2)	Sb2—F1	1.906 (2)
P1—O2	1.532 (2)	Sb1—F2	1.9082 (15)
F2—Sb1—O3	77.99 (7)	O1—Sb2—O2 <sup>iv</sup>	85.10 (8)
F2—Sb1—O4 <sup>i</sup>	78.14 (7)	O2 <sup>ii</sup> —Sb2—O2 <sup>iv</sup>	155.24 (11)
O3—Sb1—O4 <sup>i</sup>	89.41 (8)	O1 <sup>iii</sup> —Sb2—O2 <sup>iv</sup>	89.62 (8)
O3—Sb1—O5 <sup>ii</sup>	155.55 (8)	O1 <sup>iii</sup> —Sb2—O2 <sup>ii</sup>	85.10 (8)
O3—Sb1—O6	85.79 (8)	O5—P1—O2	111.11 (12)
O5 <sup>ii</sup> —Sb1—O4 <sup>i</sup>	84.79 (8)	O1—P2—O4	111.94 (12)
O6—Sb1—O4 <sup>i</sup>	155.64 (8)	O6—P2—O1	111.44 (12)
O6—Sb1—O5 <sup>ii</sup>	89.77 (8)	O6—P2—O4	111.52 (12)
F1—Sb2—O1 <sup>iii</sup>	77.61 (6)	P2—O1—Sb2	126.43 (12)
F1—Sb2—O1	77.61 (6)	P1—O2—Sb2 <sup>v</sup>	127.26 (12)
F1—Sb2—O2 <sup>iv</sup>	77.62 (5)	P1—O3—Sb1	126.19 (12)
F1—Sb2—O2 <sup>ii</sup>	77.62 (6)	P2—O4—Sb1 <sup>ii</sup>	127.49 (12)
O1—Sb2—O1 <sup>iii</sup>	155.21 (11)	P1—O5—Sb1 <sup>i</sup>	127.00 (12)
O1—Sb2—O2 <sup>ii</sup>	89.62 (8)	P2—O6—Sb1	126.52 (12)

Symmetry codes: (i)  $-x+1/2, y+1/2, -z+3/2$ ; (ii)  $-x+1/2, y-1/2, -z+3/2$ ; (iii)  $-x+1, y, -z+3/2$ ; (iv)  $x+1/2, y-1/2, z$ ; (v)  $x-1/2, y+1/2, z$ .

**Table S4.** Atomic coordinates and equivalent isotropic displacement parameters, and calculated Bond Valence Sum for (Gu)SbFPO<sub>4</sub>·H<sub>2</sub>O.  $U_{\text{eq}}$  is defined as one third of the trace of the orthogonalized  $U_{ij}$  tensor.

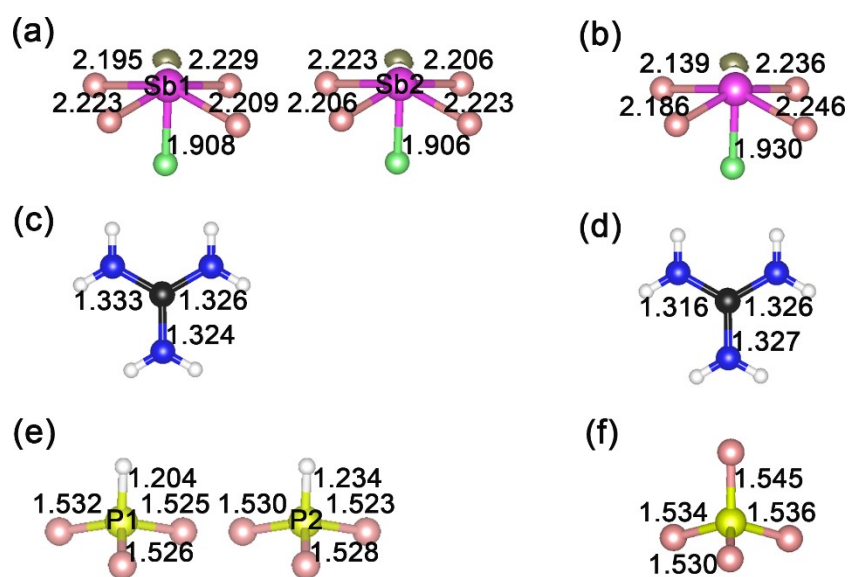
atom	$x$	$y$	$z$	$U_{\text{eq}}(\text{\AA}^2)$	BVS
Sb1	0.74604 (5)	0.73984 (4)	0.47499 (2)	0.01532 (17)	3.09
P1	0.7464 (2)	0.25211 (15)	0.50158 (9)	0.0145 (3)	4.81
F1	0.7088 (5)	0.7571 (3)	0.36751 (18)	0.0200 (7)	0.93
O1	0.5806 (5)	0.3125 (5)	0.54944 (18)	0.0194 (7)	1.78
O2	0.6791 (5)	0.0691 (5)	0.45270 (19)	0.0232 (7)	1.72
O3	0.9408 (6)	0.2055 (5)	0.5542 (2)	0.0218 (7)	1.70
O4	0.7869 (5)	0.4277 (5)	0.44890 (18)	0.0206 (7)	1.82
O5	0.8745 (7)	0.1567 (7)	0.3232 (2)	0.0445 (11)	2.50
H5A	0.861100	0.059760	0.353089	0.067*	/
H5B	0.846501	0.262190	0.346870	0.067*	/
N1	0.1585 (7)	0.5881 (8)	0.1747 (2)	0.0370 (11)	3.50
H1A	0.266304	0.574494	0.153272	0.044*	/
H1B	0.041199	0.589701	0.148522	0.044*	/
N2	0.0073 (6)	0.6249 (9)	0.2819 (3)	0.0422 (13)	3.50
H2A	0.017459	0.635071	0.329708	0.051*	/
H2B	-0.110272	0.626532	0.255936	0.051*	/
C1	0.1731 (8)	0.6067 (8)	0.2484 (3)	0.0276 (11)	4.13
N3	0.3517 (7)	0.6045 (8)	0.2892 (2)	0.0373 (12)	3.51
H3A	0.359646	0.614804	0.336888	0.045*	/
H3B	0.460396	0.592775	0.268102	0.045*	/



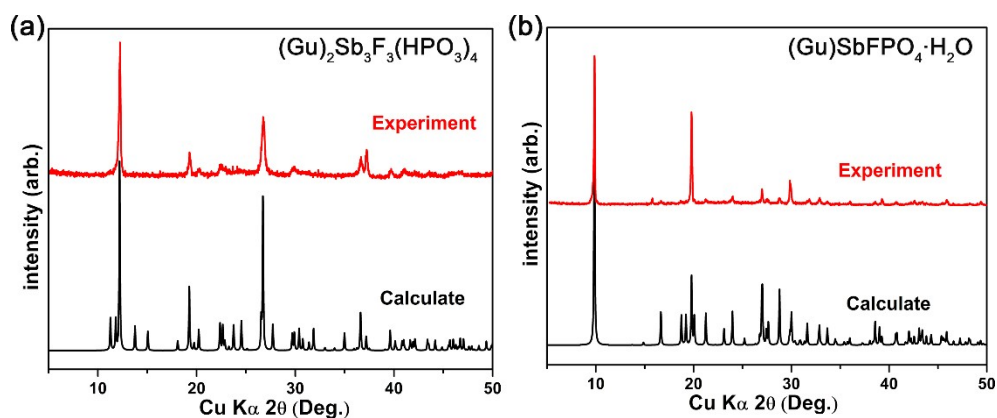
**Table S5.** Selected Bond lengths (Å) and angles (deg) for (Gu)SbFPO<sub>4</sub>·H<sub>2</sub>O.

Sb1—F1	1.930 (3)	P1—O2	1.530 (3)
Sb1—O1 <sup>i</sup>	2.186 (3)	P1—O3	1.536 (4)
Sb1—O2 <sup>ii</sup>	2.246 (3)	P1—O4	1.545 (3)
Sb1—O3 <sup>iii</sup>	2.236 (4)	N1—C1	1.327 (6)
Sb1—O4	2.139 (3)	N2—C1	1.326 (6)
P1—O1	1.534 (4)	C1—N3	1.316 (6)
F1—Sb1—O1 <sup>i</sup>	78.82 (14)	O2—P1—O1	110.62 (19)
F1—Sb1—O2 <sup>ii</sup>	76.39 (11)	O2—P1—O3	111.20 (19)
F1—Sb1—O3 <sup>iii</sup>	76.13 (14)	O2—P1—O4	107.3 (2)
F1—Sb1—O4	80.74 (11)	O3—P1—O4	109.55 (19)
O1 <sup>i</sup> —Sb1—O2 <sup>ii</sup>	87.00 (12)	P1—O1—Sb1 <sup>i</sup>	127.44 (19)
O1 <sup>i</sup> —Sb1—O3 <sup>iii</sup>	154.92 (13)	P1—O2—Sb1 <sup>iv</sup>	128.61 (19)
O3 <sup>iii</sup> —Sb1—O2 <sup>ii</sup>	88.31 (12)	P1—O3—Sb1 <sup>iii</sup>	123.8 (2)
O4—Sb1—O1 <sup>i</sup>	87.29 (13)	P1—O4—Sb1	123.44 (19)
O4—Sb1—O2 <sup>ii</sup>	157.09 (13)	N2—C1—N1	120.3 (5)
O4—Sb1—O3 <sup>iii</sup>	87.52 (12)	N3—C1—N1	120.6 (5)
O1—P1—O3	108.0 (2)	N3—C1—N2	119.1 (5)
O1—P1—O4	110.11 (19)		

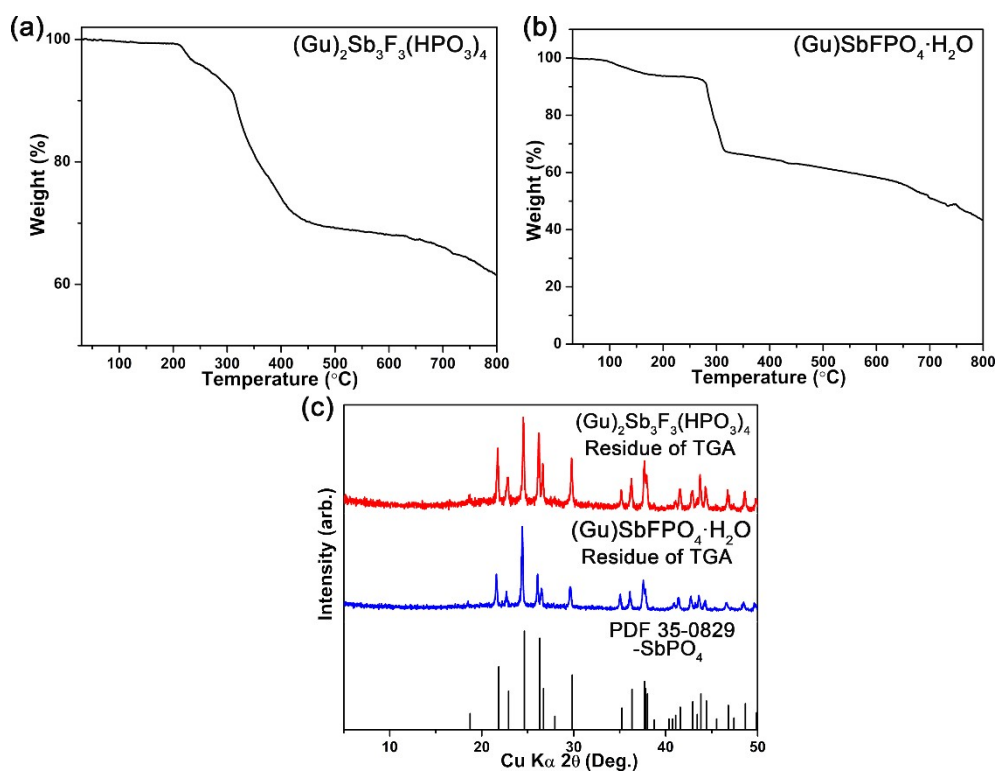
Symmetry codes: (i)  $-x+1, -y+1, -z+1$ ; (ii)  $x, y+1, z$ ; (iii)  $-x+2, -y+1, -z+1$ ; (iv)  $x, y-1, z$ .



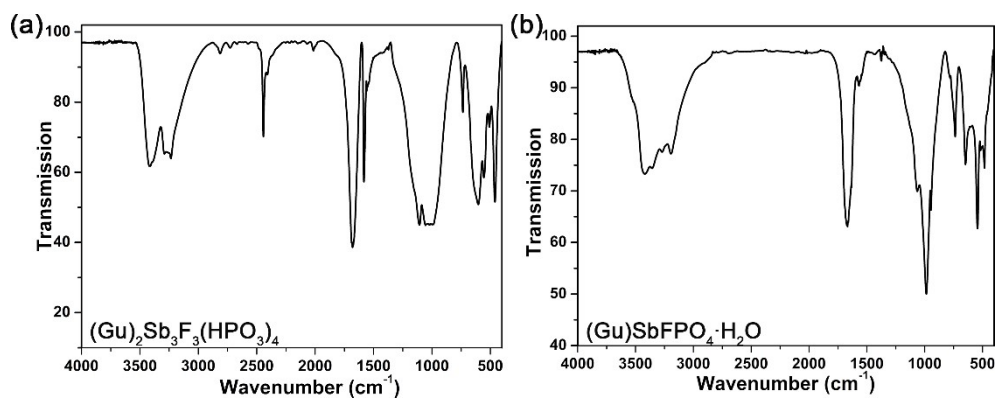
**Fig. S1** The bond lengths of (a)  $[\text{Sb1O}_4\text{F}]^{6-}$ ,  $[\text{Sb2O}_4\text{F}]^{6-}$  square pyramid; (c)  $[\text{C}(\text{NH}_2)_3]^+$  cation group, (e),  $[\text{HP1O}_3]^{2-}$ ,  $[\text{HP2O}_3]^{2-}$  tetrahedron in  $(\text{Gu})_2\text{Sb}_3\text{F}_3(\text{HPO}_3)_4$ ; The bond lengths of (b)  $[\text{SbO}_4\text{F}]^{6-}$  square pyramid, (d)  $[\text{C}(\text{NH}_2)_3]^+$  cation group, (f)  $[\text{PO}_4]^{3-}$  tetrahedron in  $(\text{Gu})\text{SbFPO}_4 \cdot \text{H}_2\text{O}$ .



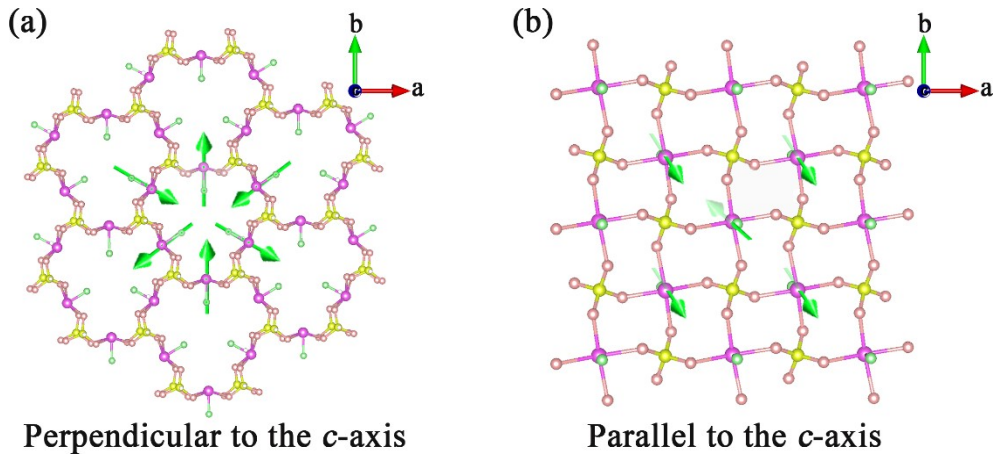
**Fig. S2** Calculated and experimental powder X-ray diffraction (PXRD) patterns for compounds  $(\text{Gu})_2\text{Sb}_3\text{F}_3(\text{HPO}_3)_4$  (a) and  $(\text{Gu})\text{SbFPO}_4 \cdot \text{H}_2\text{O}$  (b).



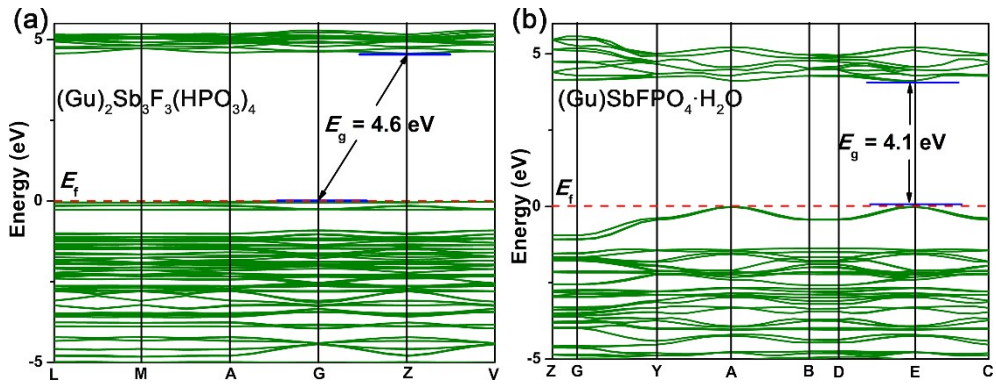
**Fig. S3** TGA curves of  $(\text{Gu})_2\text{Sb}_3\text{F}_3(\text{HPO}_3)_4$  (a) and  $(\text{Gu})\text{SbFPO}_4 \cdot \text{H}_2\text{O}$  (b) under  $\text{N}_2$  atmosphere; (c) Powder XRD patterns of the residue of TGA for  $(\text{Gu})_2\text{Sb}_3\text{F}_3(\text{HPO}_3)_4$  and  $(\text{Gu})\text{SbFPO}_4 \cdot \text{H}_2\text{O}$ .



**Fig. S4** IR spectra of compounds  $(\text{Gu})_2\text{Sb}_3\text{F}_3(\text{HPO}_3)_4$  (a) and  $(\text{Gu})\text{SbFPO}_4 \cdot \text{H}_2\text{O}$  (b).



**Fig. S5** Orientation of lone pairs on  $\text{SbO}_4\text{F}$  square pyramid in 2D layer in  $(\text{Gu})_2\text{Sb}_3\text{F}_3(\text{HPO}_3)_4$  (a) and  $(\text{Gu})\text{SbFPO}_4\cdot\text{H}_2\text{O}$  (b).



**Fig. S6** Calculated band structures of compounds  $(\text{Gu})_2\text{Sb}_3\text{F}_3(\text{HPO}_3)_4$  (a) and  $(\text{Gu})\text{SbFPO}_4\cdot\text{H}_2\text{O}$  (b).

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