Electronic Supporting Information

$[C(NH_2)_3]BiCl_2SO_4$: An Excellent Birefringent Material by a Multifunctional Group Synergy

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Section S1. Experimental section

Instrumentations.

Suitable single crystals were selected under an optical microscope. Crystal structure determination of $GuBiCl_2SO_4$ was performed on a Bruker SMART BREEZE diffractometer with graphite-monochromated MoKα radiation (λ = 0.71073 Å) 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. [1,2] All of the structures were verified using the ADDSYM algorithm from the program PLATON and no higher symmetries were found.[3] 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-S3.

Elemental analysis was performed on a scanning electron microscope FESEM, SU-8010. The collected crystals of $GuBiCl_2SO_4$ were mounted on one flat face and coated with 25 nm carbon, respectively. And the element was qualitatively analyzed.

Powder XRD patterns were obtained using a Rigaku Smartlab powder X-ray diffractometer with CuKα radiation (λ = 1.54056 Å), in the angular range of 2θ = 5-50°, and with a scan step width of 0.05° 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 ℃ at a rate of 10 ℃/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 1 mm for analysis.

The UV-vis diffuse reflectance spectrum of $GuBiCl_2SO_4$ was recorded using a Shimadzu UV-2600 spectrophotometer with $BaSO_4$ 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, α is the absorption coefficient, and S is the scattering

coefficient.[4]

The photoluminscence (PL) properties of $GuBiCl_2SO_4$ was characterized by an Edinburgh FS-5 fluorescence spectrometer with a calibrated integrating sphere system. The time-resolved PL decay was measured on a Fluoromax-3 fluorescence spectrometer.

The birefringence of $GuBiCl_2SO_4$ 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 $GuBiCl_2SO_4$ 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.

Computational Descriptions.

The first-principles calculations of $GuBiCl_2SO_4$ were carried out by using the CASTEP software package to understand the relationship between structure and properties.[5] The band structure, density of states (DOS)/partial DOS (PDOS), birefringence and electron-density difference map of $GuBiCl_2SO_4$ were computed. The generalized gradient approximation (GGA) with Perdew-Burke-Emzerh (PBE) functional was adopted for all calculations.[6] Norm-conserving were employed for all the atoms.[7] The criteria of convergences of energy are set as 1.0e-6 eV/atom. Moreover, the kinetic energy cutoff of 800 eV for $GuBiCl_2SO_4$ was chosen and the k-point sampling in the Brilliouin zone was used to be 5×5×5 for $GuBiCl_2SO_4$.[8] 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 $2s^22p^3$, Cl $3s^23p^5$ S $3s^23p^4$, H $1s^1$ and Bi $6s^26p^35d^{10}$.

The Vienna ab initio Simulation Package (VASP), a planewave code (with PAW scalar-relativistic pseudopotentials),[9], was employed for calculating the electronic structures of bulk $GuBiCl_2SO_4$. During all the calculations, the generalized gradient approximation (GGA) with the Perdew-Burke-Ernzerhof (PBE) functional,[6] and the density functional dispersion correction (DFT-D3) employing the BJ-damping (-D3(BJ)) were applied.[10] The VASPKIT and VESTA softwares were used to obtain the orbital wavefunctions.[11]

Table S1. Crystal data and structure refinement for $GuBiCl_2SO_4$.

Compound	$GuBiCl_2SO_4$
Formula Mass	872.06
Crystal System	Triclinic
Space Group	$P\bar{1}$
a (Å)	6.4179 (2)
b (Å)	12.8984 (4)
c (Å)	12.9703 (4)
α (°)	61.965 (3)
β (°)	88.400 (2)
γ (°)	76.935 (2)
V(Å^3)	919.33 (5)
Z	2
ρ(calcd) (g/cm^3)	3.150
Temperature (K)	293
λ (Å)	0.71073
F(000)	792
μ (mm^{-1})	19.968
R_1, wR_2 ($I>2\sigma(I)$)[a]	0.0335/ 0.1041
GOF on F^2	1.144

[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 and equivalent isotropic displacement parameters, and calculated Bond Valence Sum for $GuBiCl_2SO_4$. $U_{(eq)}$ is defined as one third of the trace of the orthogonalized U_{ij} tensor.

atom	*x*	*y*	*z*	U_{eq}(Å^2)	BVS
Bi1	0.19954 (4)	0.26400 (3)	0.66499 (3)	0.01618 (10)	2.94
Bi2	−0.34574 (4)	0.40729 (3)	0.33280 (3)	0.01636 (10)	2.94
S1	0.6841 (3)	0.28964 (19)	0.65623 (18)	0.0156 (4)	5.90
S2	0.1408 (3)	0.42725 (18)	0.34328 (18)	0.0158 (4)	6.06
Cl1	0.3219 (4)	0.1448 (2)	0.8865 (2)	0.0336 (6)	0.77
Cl2	0.1986 (4)	0.0803 (2)	0.6435 (2)	0.0344 (6)	0.92
Cl3	−0.3327 (4)	0.1936 (2)	0.3835 (2)	0.0301 (5)	0.96
Cl4	−0.2874 (4)	0.4796 (2)	0.1141 (2)	0.0338 (6)	0.76
O1	0.8559 (9)	0.2304 (6)	0.7538 (5)	0.0228 (14)	1.82
O2	0.7875 (9)	0.3455 (6)	0.5465 (5)	0.0238 (14)	1.74
O3	0.5143 (10)	0.3773 (6)	0.6718 (6)	0.0267 (15)	1.72
O4	0.5759 (8)	0.1983 (5)	0.6561 (5)	0.0185 (12)	1.86
O5	0.2748 (10)	0.3864 (6)	0.4524 (6)	0.0270 (14)	1.78
O6	0.2864 (9)	0.4502 (6)	0.2483 (5)	0.0224 (14)	1.84
O7	−0.0285 (9)	0.5341 (6)	0.3151 (6)	0.0278 (15)	1.81
O8	0.0376 (10)	0.3315 (6)	0.3544 (6)	0.0241 (14)	1.91
C1	0.2193 (15)	0.7893 (9)	−0.0293 (9)	0.029 (2)	4.27
C2	0.7660 (14)	−0.1333 (9)	0.7661 (10)	0.031 (2)	4.08
N1	0.8048 (14)	−0.2514 (8)	0.8256 (9)	0.047 (3)	3.49
H1A	0.797433	−0.286442	0.900275	0.057*	/
H1B	0.837610	−0.294026	0.790067	0.057*	/
N2	0.7746 (14)	−0.0804 (10)	0.6487 (10)	0.053 (3)	3.41
H2A	0.805077	−0.124327	0.614334	0.063*	/
H2B	0.749562	−0.002930	0.608286	0.063*	/
N3	0.7151 (13)	−0.0651 (7)	0.8183 (8)	0.041 (2)	3.50
H3A	0.706855	−0.098321	0.892905	0.049*	/
H3B	0.690204	0.012402	0.777649	0.049*	/
N4	0.1878 (17)	0.6874 (9)	0.0519 (9)	0.052 (3)	2.48
H4A	0.212683	0.625150	0.040899	0.063*	/
H4B	0.142024	0.682205	0.116718	0.063*	/
N5	0.2893 (15)	0.7992 (9)	−0.1290 (8)	0.043 (2)	3.54
H5A	0.314800	0.737608	−0.141184	0.052*	/
H5B	0.309498	0.867219	−0.182119	0.052*	/
N6	0.1742 (12)	0.8848 (8)	−0.0119 (8)	0.035 (2)	3.52
H6A	0.124652	0.878857	0.052406	0.042*	/
H6B	0.194272	0.952876	−0.065020	0.042*	/

Table S3. Selected Bond lengths (Å) and angles (deg) for $GuBiCl_2SO_4$.

Bi1—Cl2	2.513 (2)	S2—O8	1.477 (6)
Bi1—Cl1	2.581 (2)	S2—O7	1.444 (6)
Bi1—O4	2.391 (5)	S2—O6	1.482 (6)
Bi1—O5	2.551 (7)	S1—O4	1.497 (6)
Bi1—O7^{i}	2.717 (6)	S1—O3	1.467 (6)
Bi1—O1^{ii}	2.490 (6)	S1—O2	1.478 (6)
Bi2—Cl3	2.497 (2)	S1—O1	1.480 (6)
Bi2—Cl4	2.582 (2)	N2—C2	1.351 (14)
Bi2—O3^{i}	2.717 (6)	C2—N1	1.309 (13)
Bi2—O8	2.405 (6)	C2—N3	1.325 (13)
Bi2—O2^{ii}	2.607 (6)	N5—C1	1.315 (13)
Cl2—Bi1—Cl1	95.19 (9)	O6^{ii}—Bi2—O3^{i}	80.3 (2)
Cl2—Bi1—O5	93.37 (17)	O6^{ii}—Bi2—O2^{ii}	129.0 (2)
Cl2—Bi1—O7^{i}	156.73 (14)	O5—S2—O6	107.0 (4)
Cl1—Bi1—O7^{i}	90.26 (16)	O8—S2—O5	110.3 (4)
O4—Bi1—Cl2	80.88 (16)	O8—S2—O6	108.8 (4)
O4—Bi1—Cl1	80.59 (15)	O7—S2—O5	112.8 (4)
O4—Bi1—O5	73.4 (2)	O7—S2—O8	107.2 (4)
O4—Bi1—O7^{i}	122.37 (19)	O7—S2—O6	110.8 (4)
O4—Bi1—O1^{ii}	152.0 (2)	O3—S1—O4	105.3 (3)
O5—Bi1—Cl1	150.91 (15)	O3—S1—O2	112.9 (4)
O1^{ii}—Bi1—O5	130.9 (2)	O1—S1—O4	110.2 (4)
O1^{ii}—Bi1—O7^{i}	75.4 (2)	S1—O4—Bi1	108.3 (3)
Cl3—Bi2—Cl4	95.86 (9)	S1—O3—Bi2^{i}	153.8 (4)
Cl3—Bi2—O3^{i}	154.97 (14)	S2—O5—Bi1	129.2 (3)
Cl3—Bi2—O2^{ii}	92.40 (15)	S2—O8—Bi2	108.8 (3)
Cl4—Bi2—O3^{i}	100.52 (16)	S2—O7—Bi1^{i}	150.9 (4)
Cl4—Bi2—O2^{ii}	151.81 (14)	S1—O2—Bi2^{iii}	129.4 (3)
O8—Bi2—Cl3	81.23 (16)	S1—O1—Bi1^{iii}	107.1 (3)
O8—Bi2—Cl4	81.79 (17)	S2—O6—Bi2^{iii}	108.4 (3)
O8—Bi2—O3^{i}	119.6 (2)	N1—C2—N2	118.8 (10)
O8—Bi2—O2^{ii}	72.9 (2)	N1—C2—N3	121.5 (10)
O8—Bi2—O6^{ii}	154.5 (2)	N3—C2—N2	119.7 (10)
O2^{ii}—Bi2—O3^{i}	82.0 (2)	N5—C1—N6	120.0 (10)
O6^{ii}—Bi2—Cl3	84.55 (16)	N4—C1—N5	121.0 (11)
O6^{ii}—Bi2—Cl4	78.69 (15)	N4—C1—N6	119.0 (11)

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

Table S4. Summarization of bismuth-based luminescence compounds.

Compounds	Emission peak (nm)	Emission range (nm)	Mechanism	Refer
$[NEt_4]_3BiCl_6$	475	NA	S → P transition	[12]
$Rb_7Bi_3Cl_{16}$	610	500-800	$[Bi_2Cl_{10}]^{4-}$ dimer	[13]
$(C_6H_{14}N)_3Bi_2I_9$	601	NA	$[Bi_2I_9]^{3-}$ dimer	[14]
$(PMA)_3BiBr_6$	405; 510	400-700	S → P transition	[15]
$(EnrofloH_2)BiCl_5 \cdot Cl \cdot 2(H_2O) \cdot H_3O$	459	420-550	organic cation	[16]
$[(C_6H_{11}NH_3)_4BiBr_6]Br \cdot CH_3CN$	441	400-500	$[BiBr_6]^{3-}$ octahedron	[17]
$(C_8NH_{12})_4BiBr_7 \cdot H_2O$	450	400-600	free excitons	[18]

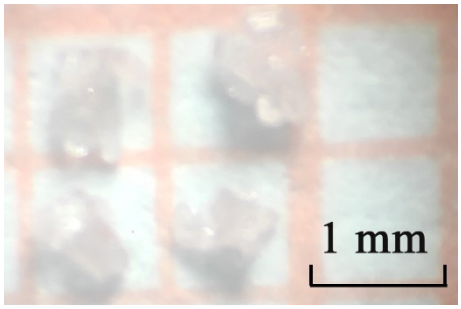

Fig. S1 Photograph of $GuBiCl_2SO_4$ crystals.

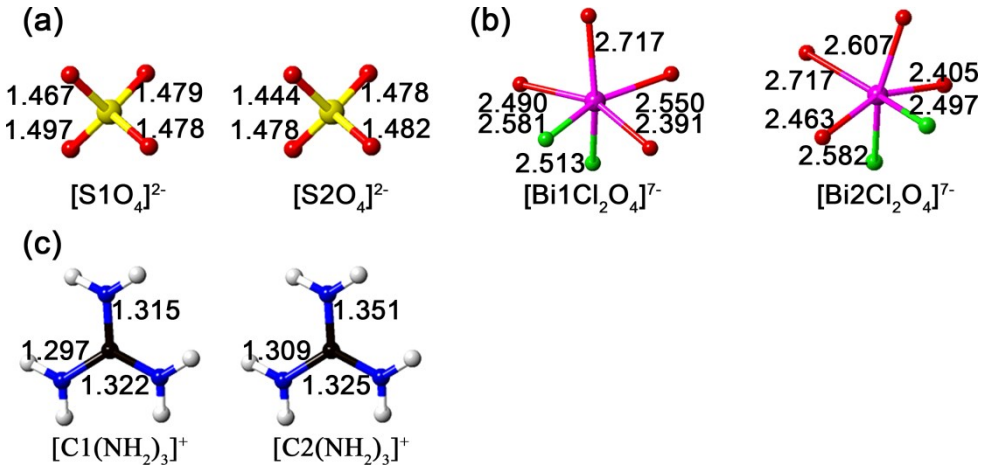

Fig. S2 Bond lengths of (a) $[S1O_4]^{2-}$, $[S2O_4]^{2-}$ tetrahedra, (b) $[Bi1Cl_2O_4]^{7-}$, $[Bi2Cl_2O_4]^{7-}$ polyhedra and $[C1(NH_2)_3]^{+}$, $[C2(NH_2)_3]^{+}$ groups in $GuBiCl_2SO_4$.

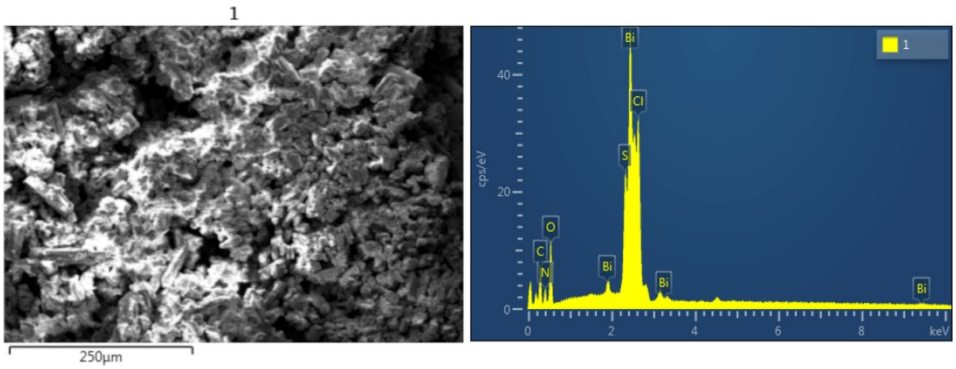

Fig. S3 Energy-dispersive analysis by X-ray (EDX) data for $GuBiCl_2SO_4$.

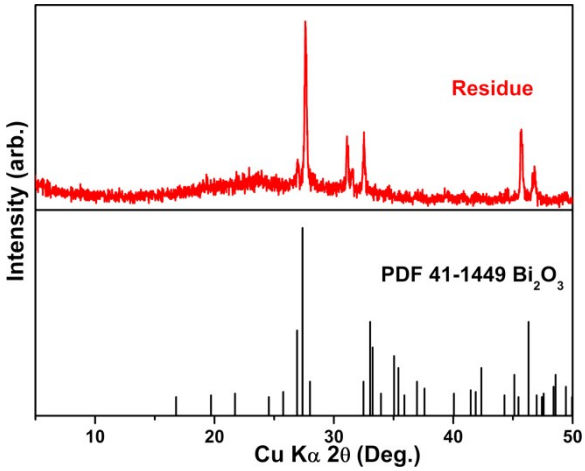

Fig. S4 Powder X-ray diffraction pattern for the residue of $GuBiCl_2SO_4$ for TGA.

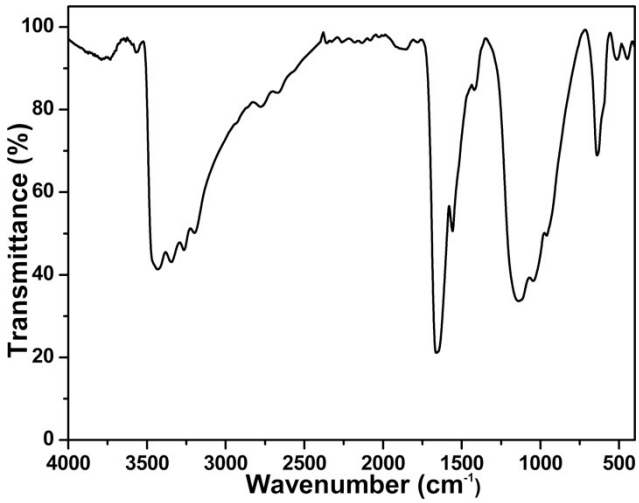

Fig. S5 IR spectrum of compound $GuBiCl_2SO_4$. (In a dry environment, 100 mg KBr and 1 mg solid sample were fully ground in an agate mortar, and a special tabletting device was used to press the sample into a transparent sheet with a diameter of 13 mm and a thickness of about 1 mm for analysis.)

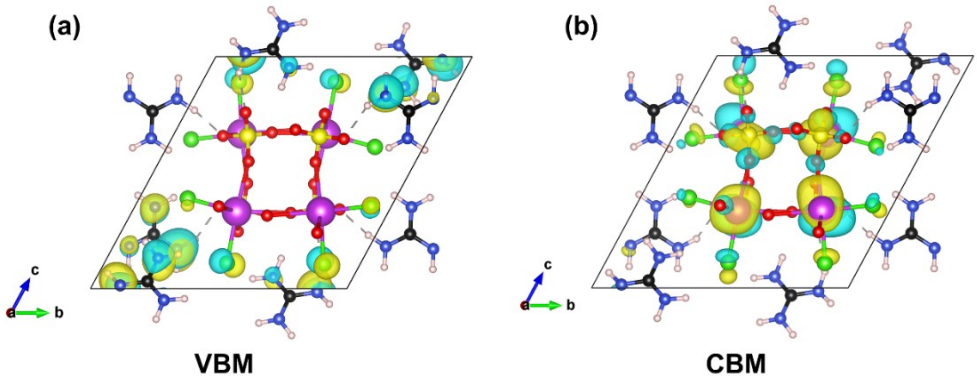

Fig. S6 Valence-band maximum (VBM) (a) and conduction-band minimum (CBM) (b) orbital wave function of $GuBiCl_2SO_4$.

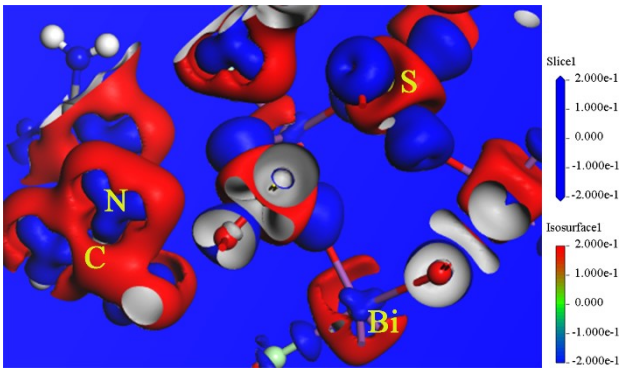

Fig. S7 3D EDD map of $GuBiCl_2SO_4$.

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