

Electronic Supporting Information

**Designing excellent UV birefringent materials through the synergistic interaction of two highly distorted functional groups**

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## Section S1. Experimental section

### Instrumentations.

Suitable single crystals were selected under an optical microscope. Crystal structures determination of STC and STB were performed on a Bruker SMART BREEZE diffractometer with graphite-monochromated 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 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.

Energy dispersion analysis (EDS) was performed using the Hitachi S-3400N/Horiba Energy EX-250 instrument. The collected crystals were mounted on a plane and coated with 25 nm carbon, and the elements were analyzed qualitatively.

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 spectra of STC and STB were 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,  $\alpha$  is the absorption coefficient, and  $S$  is the scattering

coefficient.<sup>[4]</sup>

The birefringence of STC and STB 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 STC and STB 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 STC and STB 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 STC and STB were computed. The generalized gradient approximation (GGA) with Perdew-Burke-Ernzerh (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 1.0e-6 eV/atom. The kinetic energy cutoff of 850 eV and the k-point sampling of  $3 \times 6 \times 4$  were chosen for STC and STB.<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,  $2s^2p^6$ ; Cl,  $3s^23p^5$ ; Br,  $4s^24p^5$ ; Sb,  $5s^22p^3$ ; Te,  $5s^22p^4$ .

**Table S1.** Crystal data and structure refinement for STC and STB.

Compound	SbTeO <sub>3</sub> Cl	SbTeO <sub>3</sub> Br
Formula Mass	332.80	337.26
Crystal System	orthorhombic	orthorhombic
Space Group	<i>Pnma</i>	<i>Pnma</i>
<i>a</i> (Å)	11.1951(7)	11.4666(6)
<i>b</i> (Å)	5.4252(4)	5.4509(3)
<i>c</i> (Å)	7.2317(4)	7.3614(4)
$\alpha$ (°)	90	90
$\beta$ (°)	90	90
$\gamma$ (°)	90	90
<i>V</i> (Å <sup>3</sup> )	439.22(5)	460.11(4)
<i>Z</i>	4	4
$\rho$ (calcd) (g/cm <sup>3</sup> )	5.033	5.446
Temperature (K)	299	301
$\lambda$ (Å)	0.71073	0.71073
<i>F</i> (000)	576	648
$\mu$ (mm <sup>-1</sup> )	13.26	20.76
$R_1, wR_2$ ( $I > 2\sigma(I)$ ) <sup>a</sup>	0.043/0.103	0.018/0.038
GOF on $F^2$	1.47	1.01

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

**Table S2.** Atomic coordinates and equivalent isotropic displacement parameters, and calculated Bond Valence Sum for STC.  $U_{eq}$  is defined as one third of the trace of the orthogonalized  $U_{ij}$  tensor.

atom	x	y	z	$U_{eq}(\text{\AA}^2)$	BVS
Te1	0.42881 (12)	0.750000	0.67864 (19)	0.0135 (5)	3.73
Sb1	0.25168 (13)	0.250000	0.57745 (19)	0.0141 (5)	2.87
C1	0.4213 (7)	0.250000	0.9040 (9)	0.048 (2)	0.91
O2	0.3739 (9)	0.5022 (19)	0.5130 (14)	0.018 (2)	2.28
O1	0.2831 (13)	0.750000	0.809 (2)	0.017 (3)	2.17

**Table S3.** Selected Bond lengths (Å) and angles (deg) for STC.

Te1—O2	1.903 (11)	Sb1—O2 <sup>ii</sup>	1.991 (10)
Te1—O2 <sup>i</sup>	1.903 (11)	Sb1—O2	1.991 (10)
Te1—O1	1.883 (15)	Sb1—O1 <sup>iii</sup>	1.983 (15)
O2—Te1—O2 <sup>i</sup>	89.9 (7)	O1 <sup>iii</sup> —Sb1—O2	84.6 (4)
O1—Te1—O2	92.0 (4)	O1 <sup>iii</sup> —Sb1—O2 <sup>ii</sup>	84.6 (4)
O1—Te1—O2 <sup>i</sup>	92.0 (4)	Te1—O2—Sb1	124.1 (5)
O2 <sup>ii</sup> —Sb1—O2	86.8 (6)	Te1—O2—Sb1 <sup>iv</sup>	131.3 (8)
O2—Te2—O1—Sb1 <sup>iv</sup>	135.0 (3)	O2 <sup>i</sup> —Te1—O1—Sb1 <sup>iv</sup>	-135.0 (3)

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

**Table S4.** Atomic coordinates and equivalent isotropic displacement parameters, and calculated Bond Valence Sum for STB.  $U_{eq}$  is defined as one third of the trace of the orthogonalized  $U_{ij}$  tensor.

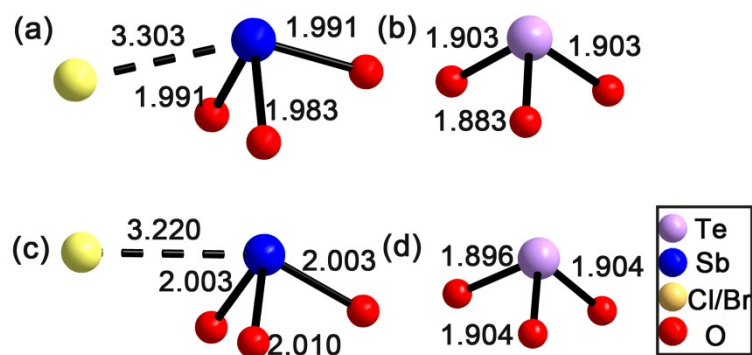
atom	x	y	z	$U_{eq}(\text{\AA}^2)$	BVS
Te1	0.42178 (2)	0.750000	0.66278 (4)	0.01172 (10)	3.68
Sb1	0.25162 (2)	1.250000	0.55310 (4)	0.01342 (10)	2.74
Br1	0.41839 (4)	1.250000	0.90469 (7)	0.02574 (13)	0.61
O1	0.2757 (3)	0.750000	0.7833 (4)	0.0156 (6)	2.15
O2	0.37373 (18)	0.9990 (4)	0.4976 (3)	0.0157 (4)	2.14



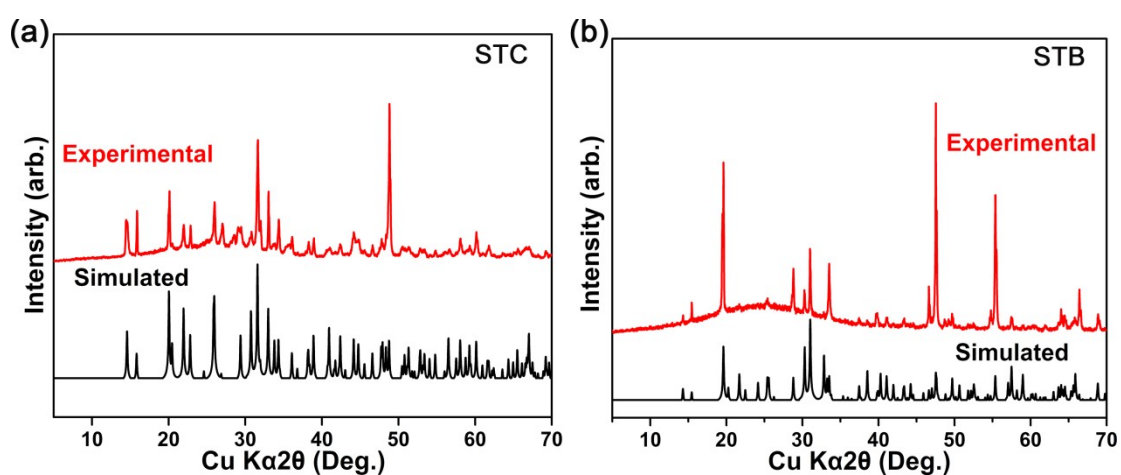
**Table S5.** Selected Bond lengths (Å) and angles (deg) for STB.

Te1—O1	1.896 (3)	Sb1—O1 <sup>ii</sup>	2.010 (3)
Te1—O2	1.904 (2)	Sb1—O2 <sup>iii</sup>	2.003 (2)
Te1—O2 <sup>i</sup>	1.904 (2)	Sb1—O2	2.003 (2)
O1—Te1—O2	92.47 (9)	O2—Sb1—O1 <sup>ii</sup>	84.63 (9)
O1—Te1—O2 <sup>i</sup>	92.47 (9)	O2—Sb1—O2 <sup>iii</sup>	86.19 (11)
O2—Te1—O2 <sup>i</sup>	90.95 (13)	Te1—O1—Sb1 <sup>iv</sup>	126.75 (17)
O2 <sup>iii</sup> —Sb1—O1 <sup>ii</sup>	84.63 (9)	Te1—O2—Sb1	124.05 (11)
O2—Te1—O1—Sb1 <sup>iv</sup>	-134.47 (6)	O2 <sup>i</sup> —Te1—O1—Sb1 <sup>iv</sup>	134.47 (6)

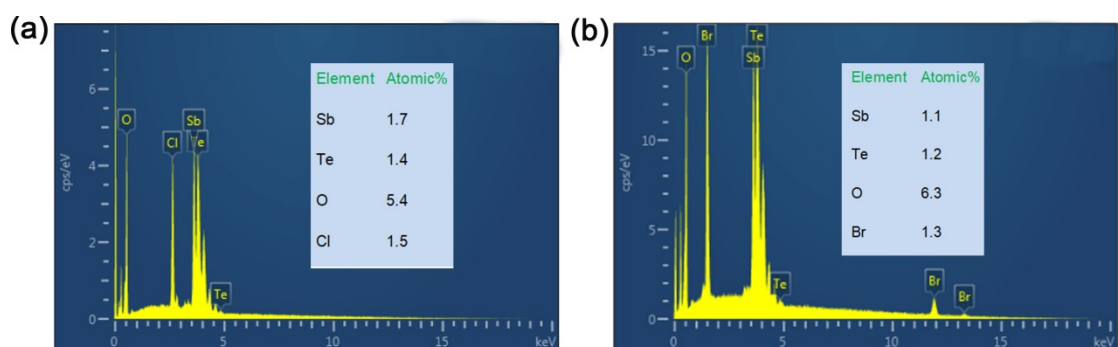
Symmetry codes: (i)  $x, -y+3/2, z$ ; (ii)  $-x+1/2, -y+2, z-1/2$ ; (iii)  $x, -y+5/2, z$ ; (iv)  $-x+1/2, -y+2, z+1/2$ .



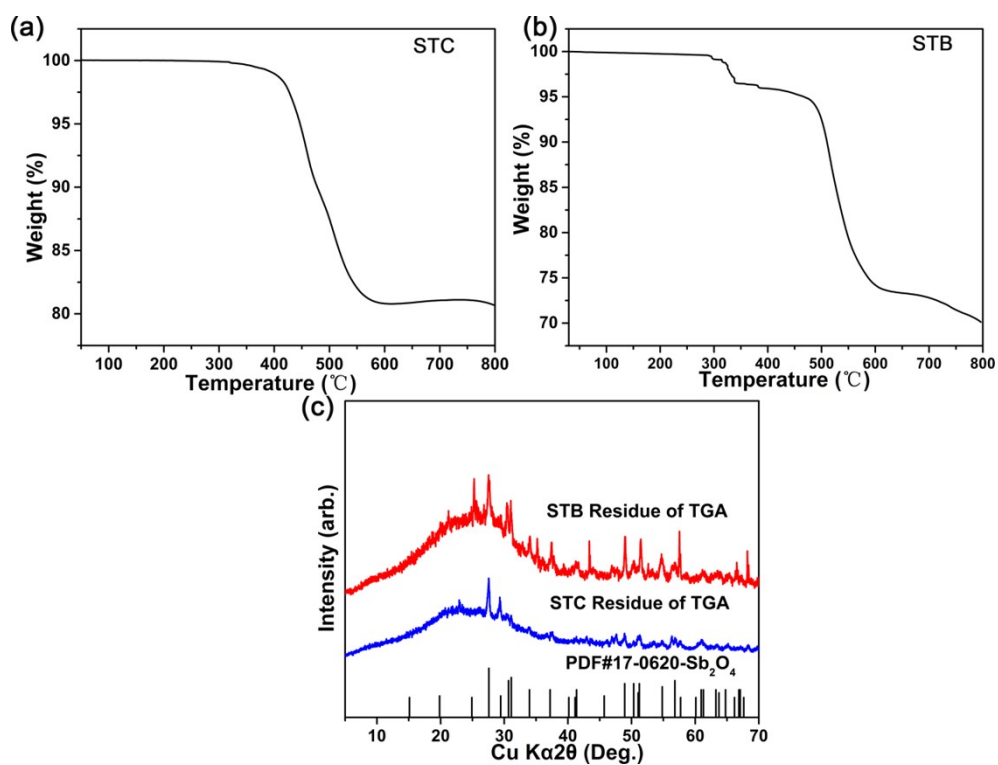
**Fig. S1** The bond lengths of (a)  $[\text{SbO}_3\text{Cl}]^{4+}$ , (b)  $[\text{TeO}_3]^{2-}$  trigonal pyramid in STC; The bond lengths of (c)  $[\text{SbO}_3\text{Br}]^{4+}$ , (d)  $[\text{TeO}_3]^{2-}$  trigonal pyramid in STB.



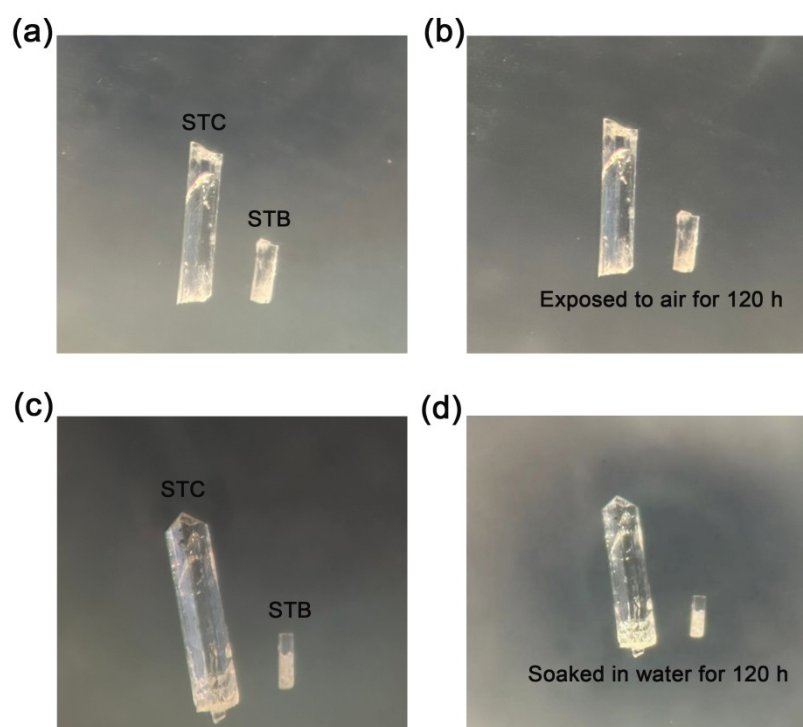
**Fig. S2** Calculated and experimental powder X-ray diffraction (PXRD) patterns for compounds STC (a) and STB (b).



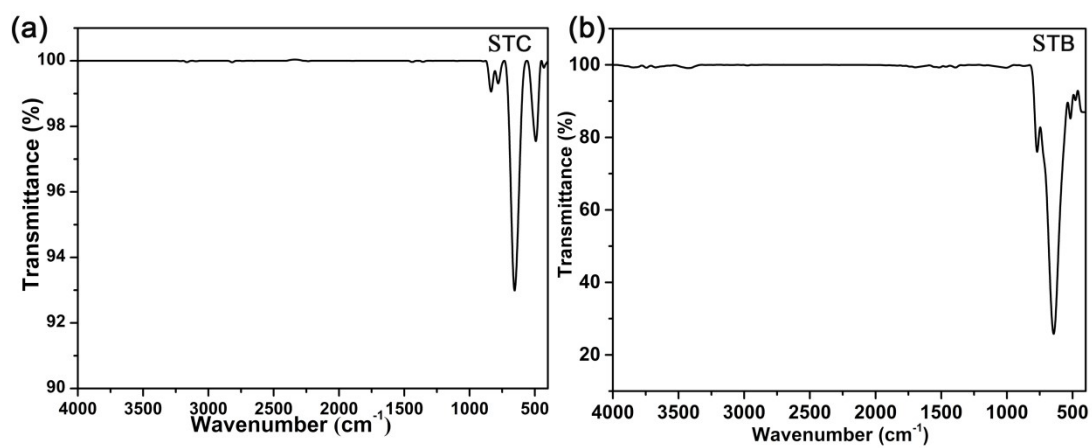
**Fig. S3** EDS spectra of compounds STC (a) and STB (b).



**Fig. S4** TGA curves of STC (a) and STB (b) under  $N_2$  atmosphere; (c) Powder XRD patterns of the residue of TGA for STC and STB.



**Fig. S5** Stability test of STC and STB in air (a and b); stability test of STC and STB in water (c and d).



**Fig. S6** IR spectra of compounds STC (a) and STB (b).

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