Second Harmonic Generation from Symmetry Breaking Stimulated by Organic Cations Mixing in Zero-Dimensional Hybrid Metal Halides

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Table *S*1. Structure information of reported single and mixed cation HOIMH.

Compound	Space group	Ref.
$(CH_6N)SbBr_4$	*Pnma* (62)	[1]
$(C_3H_{10}N)SbBr_4$	*Pnma* (62)	[1]
$(C_3H_{10}N)(CH_6N)SbBr_5$	*Pna2₁* (33)	[1]
$(C_2H_8N)_3Sb_2Br_9$	$P2_1/c$ (14)	[2]
$(C_7H_{10}N)_3SbBr_6$	$P2_1/c$ (14)	[3]
$(C_2H_8N)(C_7H_{10}N)_2SbBr_6$	*Pc* (7)	[1]
$(C_2H_8N)_2BiBr_5$	*Acam* (64)	[4]
$(C_7H_{10}N)_3BiBr_6$	$P2_1/c$ (14)	[3]
$(C_2H_8N)(C_7H_{10}N)_2Bi_2Br_9$	$Pna2_1$ (33)	[1]
$Cs_2AgBiBr_6$	*Fm*3*m* (225)	[5]
$(C_4H_9N)_4AgBiBr_8$	$P2_1/c$ (14)	[6]
$(C_4H_9N)_2CsAgBiBr_7$	$P2_1$ (4)	[7]
$Cs_2AgBiBr_6$	*Fm*3*m* (225)	[5]
$(C_3H_{10}N)_4AgBiBr_8$	*C*2/*m* (12)	[8]
$(C_3H_{10}N)_2CsAgBiBr_7$	$P2_1$ (4)	[9]
$Cs_2AgBiBr_6$	*Fm*3*m* (225)	[5]
$(C_4H_{12}N)_4AgBiBr_8$	$P2_1/c$ (14) / *Pbca* (61)	[9, 10]
$(C_4H_{12}N)_2CsAgBiBr_7$	$P2_1$ (4)	[9]

Table *S*2. Crystal data and structure refinement for $(C_9N_3H_{15})(C_9H_{14}SO)BiBr_6$ and $(C_9N_3H_{15})(C_9H_{14}SO)SbBr_6$ at 150.0 K.

Compound	$(C_9N_3H_{15})(C_9H_{13}SO)BiBr_6$	$(C_9N_3H_{15})(C_9H_{13}SO)SbBr_6$
Empirical formula	$C_{18}H_{28}BiBr_6N_3OS$	$C_{18}H_{28}Br_6N_3OSSb$
Formula weight	1022.93	936.00
Temperature	150.0 K	150.0 K
Wavelength	0.71073 Å	0.71073 Å
Crystal system	orthorhombic	orthorhombic
Space group	$P2_12_12_1$	$P2_12_12_1$
Unit cell dimensions	a = 9.8987(6) Å b = 16.3369(12) Å c = 17.8274(14) Å	a = 9.9212(3) Å b = 16.2506(5) Å, c = 17.7298(5) Å,
Volume	2882.9(4) Å^3	2858.50(15) Å^3
Z	4	4

Density (calculated)	2.357 g/cm^3	2.175 g/cm^3
Absorption coefficient	14.520 mm^{-1}	9.441 mm^{-1}
F (000)	1896	1769
θ range for data collection	2.285 to 24.990°	2.405 to 24.999°
Index ranges	$-11 \le h \le 11$, $-19 \le k \le 19$, $-21 \le l \le 21$	$-11 \le h \le 11$, $-19 \le k \le 19$, $-21 \le l \le 21$
Reflections collected	40191	26578
Independent reflections	5067 [R_{int} = 0.0763]	4994 [R_{int} = 0.0503]
Completeness to θ = 24.990°	99.7%	99.1%
Refinement method	Full-matrix least-squares on F^2	Full-matrix least-squares on F^2
Data / restraints / parameters	5067 / 134 / 222	4994 / 68 / 227
Goodness-of-fit	1.034	1.052
Final R indices [$I > 2\sigma(I)$]	R_{obs} = 0.0373, wR_{obs} = 0.0832	R_{obs} = 0.0419, wR_{obs} = 0.1091
R indices [all data]	R_{all} = 0.0508, wR_{all} = 0.0885	R_{all} = 0.0469, wR_{all} = 0.1120
Largest diff. peak and hole	1.460 and -1.475 e·Å^{-3}	1.860 and -1.639 e·Å^{-3}

$(C_9N_3H_{15})(C_9H_{14}SO)BiBr_6$: $R = \Sigma||F_o|-|F_c|| / \Sigma|F_o|$, $wR = \{\Sigma [w (|F_o|^2 - |F_c|^2)^2] / \Sigma[w(|F_o|^4)]\}^{1/2}$ and $w = 1/[\sigma^2(F_o^2) + (0.0432P)^2 + 3.8996P]$ where $P = (F_o^2 + 2F_c^2)/3$
$(C_9N_3H_{15})(C_9H_{14}SO)SbBr_6$: $R = \Sigma||F_o|-|F_c|| / \Sigma|F_o|$, $wR = \{\Sigma [w (|F_o|^2 - |F_c|^2)^2] / \Sigma[w(|F_o|^4)]\}^{1/2}$ and $w = 1/[\sigma^2(F_o^2) + (0.0677P)^2 + 4.8082P]$ where $P = (F_o^2 + 2F_c^2)/3$

Table *S*3. Atomic coordinates (×10^4) and equivalent isotropic displacement parameters (Å^2×10^3) for $(C_9N_3H_{15})(C_9H_{14}SO)BiBr_6$ at 150.0 K with estimated standard deviations in parentheses.

Label	x	y	z	Occupancy	U_{eq}^*
Bi(1)	-8793(1)	-3916(1)	-1528(1)	1	36(1)
Br(4)	-8725(2)	-2258(1)	-874(1)	1	36(1)
Br(6)	-10897(2)	-4211(1)	-394(1)	1	41(1)
Br(2)	-10886(2)	-3386(2)	-2475(1)	1	46(1)
Br(5)	-6552(2)	-4260(1)	-534(1)	1	46(1)
Br(3)	-6954(2)	-3440(2)	-2624(1)	1	46(1)
Br(1)	-8852(2)	-5506(1)	-2073(1)	1	52(1)
S(1)	-9108(5)	-8957(3)	-673(3)	1	70(2)
N(1)	-7420(12)	-2591(7)	848(7)	1	39(3)

N(3)	-11667(11)	-3610(8)	2100(8)	1	45(3)
N(2)	-9514(11)	-3479(7)	1615(7)	1	38(3)
C(1)	-8662(15)	-2164(8)	1150(9)	1	42(3)
C(3)	-8321(13)	-3897(9)	1296(9)	1	42(4)
C(4)	-7102(13)	-3336(9)	1298(8)	1	37(3)
C(8)	-12319(16)	-4594(10)	2982(10)	1	49(4)
C(7)	-11043(18)	-4918(10)	2932(9)	1	56(4)
C(2)	-9846(13)	-2738(9)	1171(9)	1	36(3)
C(5)	-10390(13)	-3882(10)	2035(8)	1	36(3)
C(9)	-12619(14)	-3931(10)	2548(9)	1	47(4)
C(6)	-10058(15)	-4568(10)	2492(10)	1	50(4)
C(11)	-9180(20)	-9974(12)	-1011(12)	1	76(2)
C(10)	-8680(20)	-9146(12)	284(11)	1	76(2)
O(1)	-10814(13)	-8675(8)	-607(8)	1	72(2)
C(15)	-10750(20)	-5859(12)	1181(12)	1	76(2)
C(18B)	-10830(40)	-7810(30)	-105(17)	0.500(8)	76(2)
C(18A)	-10950(18)	-7980(8)	-211(8)	0.500(8)	76(2)
C(12)	-10398(16)	-7253(9)	-477(6)	1	76(2)
C(13)	-10310(13)	-6575(7)	-9(8)	1	76(2)
C(14)	-10772(14)	-6624(7)	726(7)	1	76(2)
C(16)	-11324(14)	-7350(8)	992(6)	1	76(2)
C(17)	-11413(15)	-8028(7)	524(8)	1	76(2)

*U_{eq} is defined as one third of the trace of the orthogonalized U_{ij} tensor.

Table *S*4. Anisotropic displacement parameters ($Å^2×10^3$) for $(C_9N_3H_{15})(C_9H_{14}SO)BiBr_6$ at 150.0 K with estimated standard deviations in parentheses.

Label	U_{11}	U_{22}	U_{33}	U_{12}	U_{13}	U_{23}
Bi(1)	32(1)	38(1)	38(1)	0(1)	0(1)	-6(1)
Br(4)	36(1)	37(1)	36(1)	0(1)	0(1)	0(1)
Br(6)	41(1)	42(1)	41(1)	-5(1)	2(1)	-2(1)
Br(2)	42(1)	56(1)	40(1)	8(1)	-3(1)	-7(1)
Br(5)	42(1)	50(1)	46(1)	5(1)	-4(1)	2(1)
Br(3)	43(1)	53(1)	43(1)	-3(1)	7(1)	-6(1)
Br(1)	45(1)	44(1)	66(2)	0(1)	1(1)	-19(1)
S(1)	76(3)	67(2)	67(3)	-3(2)	-8(2)	7(2)
N(1)	46(7)	38(7)	34(7)	-9(5)	6(6)	2(6)
N(3)	44(7)	45(7)	45(8)	2(6)	2(6)	6(6)
N(2)	36(6)	28(6)	51(8)	6(5)	2(6)	8(6)
C(1)	43(8)	37(8)	46(9)	-2(8)	2(8)	13(7)

C(3)	33(7)	36(8)	59(11)	1(6)	-3(6)	-9(8)
C(4)	35(7)	42(8)	35(9)	-1(6)	3(6)	4(7)
C(8)	47(9)	58(11)	41(10)	-16(8)	-2(8)	12(9)
C(7)	68(11)	46(9)	55(11)	3(9)	2(10)	31(8)
C(2)	33(7)	36(8)	37(9)	-1(6)	-8(6)	9(7)
C(5)	31(7)	50(9)	27(8)	-2(7)	1(6)	-4(7)
C(9)	39(8)	53(10)	47(10)	-7(7)	2(7)	6(9)
C(6)	35(7)	51(10)	63(12)	5(7)	2(8)	18(9)
C(11)	81(3)	73(3)	75(3)	0(2)	-10(2)	4(2)
C(10)	81(3)	73(3)	75(3)	0(2)	-10(2)	4(2)
O(1)	78(3)	69(3)	69(3)	-4(2)	-8(2)	8(2)
C(15)	81(3)	73(3)	75(3)	0(2)	-10(2)	4(2)
C(0AA)	81(3)	73(3)	75(3)	0(2)	-10(2)	4(2)
C(18A)	81(3)	73(3)	75(3)	0(2)	-10(2)	4(2)
C(12)	81(3)	73(3)	75(3)	0(2)	-10(2)	4(2)
C(13)	81(3)	73(3)	75(3)	0(2)	-10(2)	4(2)
C(14)	81(3)	73(3)	75(3)	0(2)	-10(2)	4(2)
C(16)	81(3)	73(3)	75(3)	0(2)	-10(2)	4(2)
C(17)	81(3)	73(3)	75(3)	0(2)	-10(2)	4(2)

The anisotropic displacement factor exponent takes the form: $-2\pi^2[h^2a^{*2}U_{11} + ... + 2hka^*b^*U_{12}]$.

Table *S*5. Bond lengths [Å] for $(C_9N_3H_{15})(C_9H_{14}SO)BiBr_6$ at 150.0 K with estimated standard deviations in parentheses.

Label	Distances	Label	Distances
Bi(1)-Br(4)	2.9493(14)	C(8)-C(9)	1.36(2)
Bi(1)-Br(6)	2.9429(16)	C(7)-C(6)	1.38(2)
Bi(1)-Br(2)	2.8091(16)	C(5)-C(6)	1.42(2)
Bi(1)-Br(5)	2.8943(16)	O(1)-C(0AA)	1.68(4)
Bi(1)-Br(3)	2.7811(17)	O(1)-C(18A)	1.344(17)
Bi(1)-Br(1)	2.7741(15)	C(15)-C(14)	1.49(2)
S(1)-C(11)	1.77(2)	C(0AA)-C(12)	1.20(3)
S(1)-C(10)	1.787(19)	C(0AA)-C(17)	1.31(2)
S(1)-O(1)	1.754(14)	C(18A)-C(12)	1.3900
N(1)-C(1)	1.513(19)	C(18A)-C(17)	1.3900
N(1)-C(4)	1.491(18)	C(12)-C(13)	1.3900
N(3)-C(5)	1.345(17)	C(13)-C(14)	1.3900
N(3)-C(9)	1.343(18)	C(14)-C(16)	1.3900
N(2)-C(3)	1.478(17)	C(16)-C(17)	1.3900

N(2)-C(2)	1.482(18)	C(1)-C(2)	1.501(19)
N(2)-C(5)	1.322(17)	C(3)-C(4)	1.515(19)
C(1)-C(2)	1.501(19)	C(8)-C(7)	1.37(2)
C(3)-C(4)	1.515(19)	C(8)-C(9)	1.36(2)
C(8)-C(7)	1.37(2)	C(7)-C(6)	1.38(2)

Table *S*6. Bond angles [°] for $(C_9N_3H_{15})(C_9H_{14}SO)BiBr_6$ at 150.0 K with estimated standard deviations in parentheses.

Label	Angles	Label	Angles
Br(6)-Bi(1)-Br(4)	83.96(4)	N(2)-C(3)-C(4)	110.8(11)
Br(2)-Bi(1)-Br(4)	88.36(5)	N(1)-C(4)-C(3)	108.9(11)
Br(2)-Bi(1)-Br(6)	86.64(5)	C(9)-C(8)-C(7)	118.0(15)
Br(2)-Bi(1)-Br(5)	173.25(5)	C(8)-C(7)-C(6)	121.9(15)
Br(5)-Bi(1)-Br(4)	85.36(5)	N(2)-C(2)-C(1)	110.5(11)
Br(5)-Bi(1)-Br(6)	95.14(4)	N(3)-C(5)-C(6)	115.3(13)
Br(3)-Bi(1)-Br(4)	90.35(5)	N(2)-C(5)-N(3)	120.1(14)
Br(3)-Bi(1)-Br(6)	172.64(5)	N(2)-C(5)-C(6)	124.4(12)
Br(3)-Bi(1)-Br(2)	88.53(5)	N(3)-C(9)-C(8)	119.7(14)
Br(3)-Bi(1)-Br(5)	89.04(5)	C(7)-C(6)-C(5)	119.4(14)
Br(1)-Bi(1)-Br(4)	177.23(5)	C(0AA)-O(1)-S(1)	105.5(16)
Br(1)-Bi(1)-Br(6)	94.15(5)	C(18A)-O(1)-S(1)	110.7(11)
Br(1)-Bi(1)-Br(2)	93.56(5)	C(12)-C(0AA)-O(1)	110(2)
Br(1)-Bi(1)-Br(5)	92.81(5)	C(12)-C(0AA)-C(17)	147(4)
Br(1)-Bi(1)-Br(3)	91.69(5)	C(17)-C(0AA)-O(1)	103(3)
C(11)-S(1)-C(10)	99.9(9)	O(1)-C(18A)-C(12)	120.1(12)
O(1)-S(1)-C(11)	103.3(8)	O(1)-C(18A)-C(17)	118.7(12)
O(1)-S(1)-C(10)	102.2(9)	C(12)-C(18A)-C(17)	120.0
C(4)-N(1)-C(1)	110.9(11)	C(0AA)-C(12)-C(13)	106.9(19)
C(9)-N(3)-C(5)	125.5(14)	C(12)-C(13)-C(14)	120.0
C(3)-N(2)-C(2)	110.5(12)	C(13)-C(14)-C(15)	117.4(12)
C(5)-N(2)-C(3)	120.8(12)	C(13)-C(14)-C(16)	120.0
C(5)-N(2)-C(2)	124.3(12)	C(16)-C(14)-C(15)	122.4(12)
C(2)-C(1)-N(1)	110.8(11)	C(17)-C(16)-C(14)	120.0
N(2)-C(3)-C(4)	110.8(11)	C(0AA)-C(17)-C(16)	105(2)
N(1)-C(4)-C(3)	108.9(11)		

Table *S*7. Atomic coordinates (×10^4) and equivalent isotropic displacement parameters (Å^2×10^3) for $(C_9N_3H_{16})(C_9H_{14}SO)SbBr_6$ at 150.0 K with estimated standard deviations in parentheses.

Label	x	y	z	Occupancy	U_{eq}*
Sb(1)	-1211(1)	-6100(1)	-8448(1)	1	33(1)
Br(1)	-1278(2)	-7752(1)	-9115(1)	1	35(1)
Br(2)	822(2)	-6623(1)	-7525(1)	1	42(1)
Br(3)	886(2)	-5780(1)	-9596(1)	1	40(1)
Br(4)	-1132(2)	-4563(1)	-7884(1)	1	47(1)
Br(5)	-3458(2)	-5727(1)	-9417(1)	1	44(1)
Br(6)	-2977(2)	-6569(1)	-7376(1)	1	42(1)
S(1)	-908(5)	-11070(3)	-9369(3)	1	66(1)
O(1)	856(12)	-11385(7)	-9475(7)	1	68(2)
C(10)	-815(19)	-10043(10)	-9019(10)	1	72(1)
C(11)	-1350(20)	-10884(11)	-10311(10)	1	72(1)
C(16)	141(18)	-13507(12)	-9859(11)	1	72(1)
C(17A)	604(17)	-12869(8)	-9947(6)	0.45(3)	72(1)
C(18A)	592(16)	-13424(6)	-10543(8)	0.772(4)	72(1)
C(15)	999(13)	-13173(6)	-11257(6)	1	72(1)
C(14)	1418(13)	-12367(7)	-11375(5)	1	72(1)
C(13)	1430(13)	-11812(5)	-10778(7)	1	72(1)
C(12)	1023(14)	-12063(7)	-10064(6)	1	72(1)
C(17B)	300(30)	-12930(20)	-9410(20)	0.55(3)	72(1)
C(18B)	-120(80)	-13830(50)	-10650(50)	0.228(4)	72(1)
N(1)	-7604(10)	-7592(7)	-9172(6)	1	40(2)
N(2)	-5521(10)	-8490(6)	-8430(6)	1	36(2)
N(3)	-3346(10)	-8635(7)	-7924(6)	1	43(3)
C(1)	-7911(12)	-8354(8)	-8726(7)	1	39(3)
C(2)	-6712(12)	-8916(8)	-8731(8)	1	39(3)
C(3)	-5178(12)	-7759(7)	-8843(7)	1	36(3)
C(4)	-6349(13)	-7169(7)	-8855(7)	1	37(3)
C(5)	-4626(12)	-8894(8)	-7993(7)	1	36(3)
C(6)	-4963(14)	-9603(9)	-7532(9)	1	50(3)
C(7)	-4014(14)	-9944(9)	-7110(8)	1	50(3)
H(K)	-4238.65	-10415.99	-6820.2	1	60
C(8)	-2683(15)	-9639(9)	-7072(7)	1	47(3)
C(9)	-2397(13)	-8977(9)	-7490(8)	1	48(3)

*U_{eq} is defined as one third of the trace of the orthogonalized U_{ij} tensor.

Table *S*8. Anisotropic displacement parameters ($Å^2×10^3$) for$(C_9N_3H_{16})(C_9H_{14}SO)SbBr_6$ at 150.0 K with estimated standard deviations in parentheses.

Label	U_{11}	U_{22}	U_{33}	U_{12}	U_{13}	U_{23}
Sb(1)	30(1)	34(1)	36(1)	1(1)	0(1)	-5(1)
Br(1)	33(1)	36(1)	37(1)	0(1)	1(1)	0(1)
Br(2)	39(1)	50(1)	38(1)	7(1)	-3(1)	-6(1)
Br(3)	39(1)	41(1)	41(1)	-5(1)	0(1)	-1(1)
Br(4)	40(1)	41(1)	59(1)	0(1)	0(1)	-15(1)
Br(5)	41(1)	47(1)	44(1)	6(1)	-4(1)	2(1)
Br(6)	38(1)	48(1)	41(1)	-1(1)	6(1)	-4(1)
S(1)	67(2)	62(2)	68(2)	-2(2)	-5(2)	11(2)
O(1)	68(2)	66(2)	71(2)	-1(2)	-5(2)	11(2)
C(10)	75(2)	68(2)	74(2)	3(2)	-11(2)	5(2)
C(11)	75(2)	68(2)	74(2)	3(2)	-11(2)	5(2)
C(16)	75(2)	68(2)	74(2)	3(2)	-11(2)	5(2)
C(17A)	75(2)	68(2)	74(2)	3(2)	-11(2)	5(2)
C(18A)	75(2)	68(2)	74(2)	3(2)	-11(2)	5(2)
C(15)	75(2)	68(2)	74(2)	3(2)	-11(2)	5(2)
C(14)	75(2)	68(2)	74(2)	3(2)	-11(2)	5(2)
C(13)	75(2)	68(2)	74(2)	3(2)	-11(2)	5(2)
C(12)	75(2)	68(2)	74(2)	3(2)	-11(2)	5(2)
C(17B)	75(2)	68(2)	74(2)	3(2)	-11(2)	5(2)
C(18B)	75(2)	68(2)	74(2)	3(2)	-11(2)	5(2)
N(1)	33(5)	51(6)	37(6)	10(5)	0(5)	-4(5)
N(2)	29(5)	39(5)	41(5)	-3(4)	-3(4)	10(5)
N(3)	35(6)	46(6)	50(6)	-4(5)	-1(5)	12(5)
C(1)	30(6)	47(7)	40(6)	3(6)	1(5)	-5(6)
C(2)	37(6)	38(6)	43(7)	-2(5)	-8(5)	6(6)
C(3)	34(6)	29(6)	44(7)	-5(5)	0(5)	0(5)
C(4)	39(7)	36(6)	35(6)	2(6)	4(5)	6(5)
C(5)	32(6)	36(6)	38(7)	5(5)	5(5)	3(5)
C(6)	39(7)	45(7)	66(9)	2(6)	13(7)	20(7)
C(7)	44(8)	52(8)	54(8)	1(7)	6(7)	20(7)
C(8)	54(8)	54(8)	33(7)	7(7)	-8(6)	2(6)
C(9)	37(6)	66(9)	41(7)	6(6)	0(6)	7(7)

The anisotropic displacement factor exponent takes the form: $-2\pi^2[h^2a^{*2}U_{11} + ... + 2hka^*b^*U_{12}]$.

Table *S*9. Bond lengths [Å] for $(C_9N_3H_{16})(C_9H_{14}SO)SbBr_6$ at 150.0 K with estimated standard deviations in parentheses.

Label	Distances	Label	Distances
Sb(1)-Br(1)	2.9335(13)	C(15)-C(14)	1.3900
Sb(1)-Br(2)	2.7322(15)	C(15)-C(18B)	1.88(9)
Sb(1)-Br(3)	2.9563(15)	C(14)-C(13)	1.3900
Sb(1)-Br(4)	2.6910(14)	C(13)-C(12)	1.3900
Sb(1)-Br(5)	2.8795(15)	C(12)-C(17B)	1.97(4)
Sb(1)-Br(6)	2.6945(15)	N(1)-C(1)	1.501(17)
S(1)-O(1)	1.833(13)	N(1)-C(4)	1.529(16)
S(1)-C(10)	1.782(18)	N(2)-C(2)	1.471(15)
S(1)-C(11)	1.751(17)	N(2)-C(3)	1.436(15)
O(1)-C(12)	1.527(15)	N(2)-C(5)	1.349(15)
C(16)-C(17A)	1.14(2)	N(3)-C(5)	1.343(16)
C(16)-C(18A)	1.30(2)	N(3)-C(9)	1.336(17)
C(16)-C(17B)	1.24(4)	C(1)-C(2)	1.500(17)
C(16)-C(18B)	1.52(8)	C(3)-C(4)	1.507(16)
C(17A)-C(18A)	1.3900	C(5)-C(6)	1.451(18)
C(17A)-C(12)	1.3900	C(6)-C(7)	1.32(2)
C(17A)-C(17B)	1.01(4)	C(7)-C(8)	1.412(19)
C(18A)-C(15)	1.3900	C(8)-C(9)	1.34(2)
C(18A)-C(18B)	0.99(9)	C(15)-C(14)	1.3900
C(15)-C(18B)	1.88(9)		

Table *S*10. Bond angles [°] for $(C_9N_3H_{16})(C_9H_{14}SO)SbBr_6$ at 150.0 K with estimated standard deviations in parentheses.

Label	Angles	Label	Angles
Br(1)-Sb(1)-Br(3)	84.23(4)	C(18B)-C(18A)-C(17A)	126(5)
Br(2)-Sb(1)-Br(1)	88.50(4)	C(18B)-C(18A)-C(15)	103(5)
Br(2)-Sb(1)-Br(3)	87.01(4)	C(18A)-C(15)-C(14)	120.0
Br(2)-Sb(1)-Br(5)	173.91(5)	C(18A)-C(15)-C(18B)	31(3)
Br(4)-Sb(1)-Br(1)	177.98(5)	C(14)-C(15)-C(18B)	143(3)
Br(4)-Sb(1)-Br(2)	92.57(5)	C(13)-C(14)-C(15)	120.0
Br(4)-Sb(1)-Br(3)	94.12(4)	C(12)-C(13)-C(14)	120.0
Br(4)-Sb(1)-Br(5)	92.76(5)	O(1)-C(12)-C(17B)	94.3(12)
Br(4)-Sb(1)-Br(6)	91.13(5)	C(17A)-C(12)-O(1)	123.0(9)
Br(5)-Sb(1)-Br(1)	86.26(4)	C(17A)-C(12)-C(17B)	28.9(12)
Br(5)-Sb(1)-Br(3)	95.54(4)	C(13)-C(12)-O(1)	116.3(9)
Br(6)-Sb(1)-Br(1)	90.61(4)	C(13)-C(12)-C(17A)	120.0

Br(6)-Sb(1)-Br(2)	88.27(4)	C(13)-C(12)-C(17B)	148.8(12)
Br(6)-Sb(1)-Br(3)	173.09(5)	C(16)-C(17B)-C(12)	102(2)
Br(6)-Sb(1)-Br(5)	88.68(5)	C(17A)-C(17B)-C(16)	60(2)
C(10)-S(1)-O(1)	104.4(8)	C(17A)-C(17B)-C(12)	41.9(16)
C(11)-S(1)-O(1)	100.9(8)	C(16)-C(18B)-C(15)	103(5)
C(11)-S(1)-C(10)	100.6(8)	C(18A)-C(18B)-C(16)	58(4)
C(12)-O(1)-S(1)	112.1(9)	C(18A)-C(18B)-C(15)	46(4)
S(1)-C(10)-H(R)	109.5	C(1)-N(1)-C(4)	110.1(9)
C(17A)-C(16)-H(3AA)	142.0	C(4)-N(1)-H(A)	109.6
C(17A)-C(16)-C(18A)	69.0(11)	C(4)-N(1)-H(B)	109.6
C(17A)-C(16)-C(17B)	49.7(19)	C(3)-N(2)-C(2)	113.2(10)
C(17A)-C(16)-C(18B)	105(3)	C(5)-N(2)-C(2)	120.6(10)
C(18A)-C(16)-H(3AA)	125.6	C(5)-N(2)-C(3)	122.7(10)
C(18A)-C(16)-C(18B)	40(3)	C(9)-N(3)-C(5)	126.0(12)
C(17B)-C(16)-H(3AA)	104.2	C(2)-C(1)-N(1)	109.7(10)
C(17B)-C(16)-C(18A)	119(2)	N(2)-C(2)-C(1)	110.4(10)
C(17B)-C(16)-C(18B)	152(4)	N(2)-C(3)-C(4)	110.6(10)
C(16)-C(17A)-C(18A)	60.8(12)	C(3)-C(4)-N(1)	110.3(9)
C(16)-C(17A)-C(12)	173.7(16)	N(2)-C(5)-C(6)	123.9(11)
C(18A)-C(17A)-C(12)	120.0	N(3)-C(5)-N(2)	121.5(11)
C(17B)-C(17A)-C(16)	70(2)	N(3)-C(5)-C(6)	114.5(11)
C(17B)-C(17A)-C(18A)	131(2)	C(7)-C(6)-C(5)	119.1(13)
C(17B)-C(17A)-C(12)	109(2)	C(6)-C(7)-C(8)	123.0(13)
C(16)-C(18A)-C(17A)	50.2(11)	C(9)-C(8)-C(7)	117.0(13)
C(16)-C(18A)-C(15)	168.6(12)	N(3)-C(9)-C(8)	120.3(13)
C(17A)-C(18A)-C(15)	120.0	C(18B)-C(18A)-C(17A)	126(5)
C(18B)-C(18A)-C(16)	82(5)	C(18B)-C(18A)-C(15)	103(5)
O(1)-C(12)-C(17B)	94.3(12)	C(18A)-C(15)-C(14)	120.0
C(17A)-C(12)-O(1)	123.0(9)	C(18A)-C(15)-C(18B)	31(3)
C(17A)-C(12)-C(17B)	28.9(12)	C(14)-C(15)-C(18B)	143(3)
C(13)-C(12)-O(1)	116.3(9)	C(13)-C(14)-C(15)	120.0
C(13)-C(12)-C(17A)	120.0	C(12)-C(13)-C(14)	120.0
C(13)-C(12)-C(17B)	148.8(12)	C(16)-C(17B)-C(12)	102(2)

2. Figures

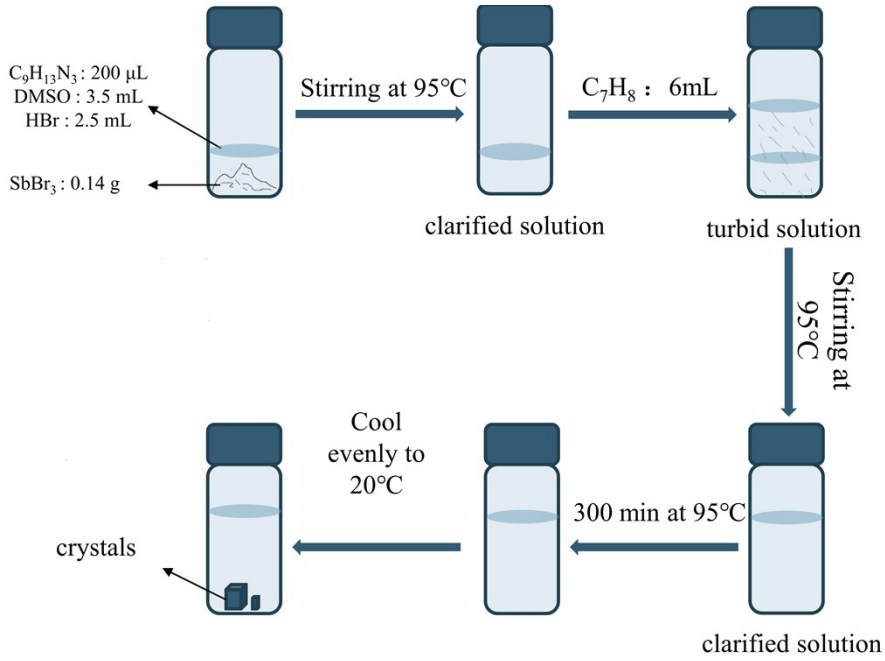

Figure *S*1. The schematic diagram of the synthesis process of $(C_9N_3H_{15})(C_9H_{13}SO)SbBr_6$.

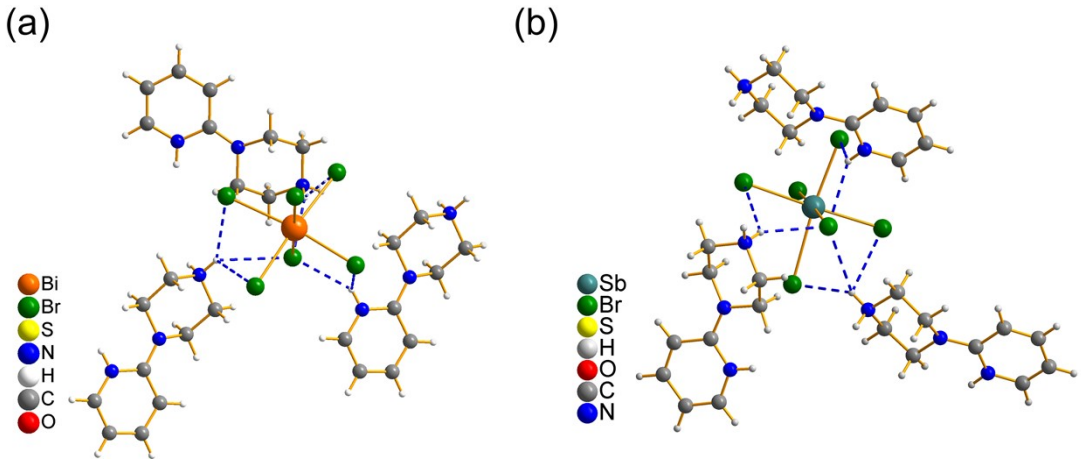

Figure *S*2. (a) Hydrogen bond network in $(C_9N_3H_{15})(C_9H_{13}SO)BiBr_6$, (b) hydrogen bond network in $(C_9N_3H_{15})(C_9H_{13}SO)SbBr_6$.

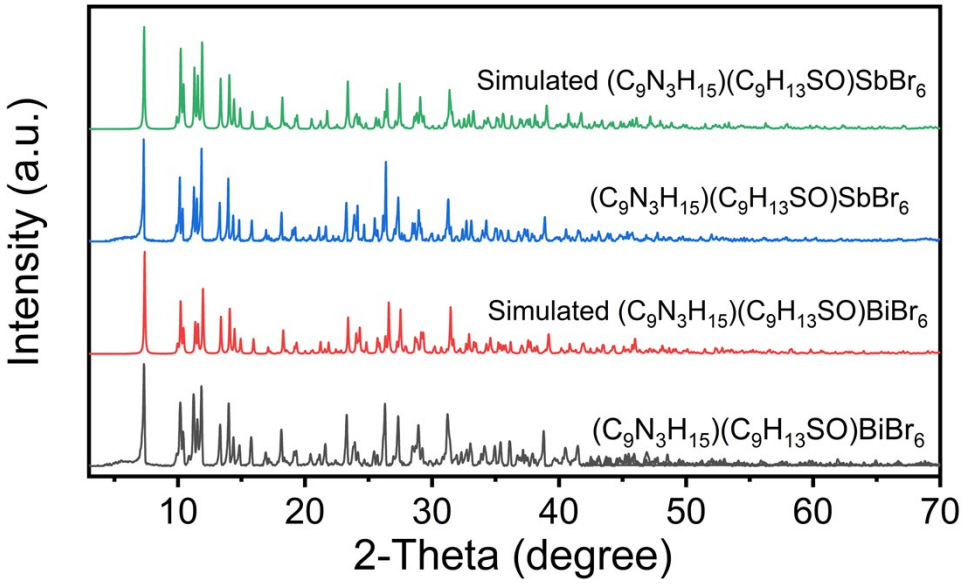

Figure *S*3. Experimental and simulated PXRD patterns of $(C_9N_3H_{15})(C_9H_{13}SO)SbBr_6$ and $(C_9N_3H_{15})(C_9H_{13}SO)BiBr_6$.

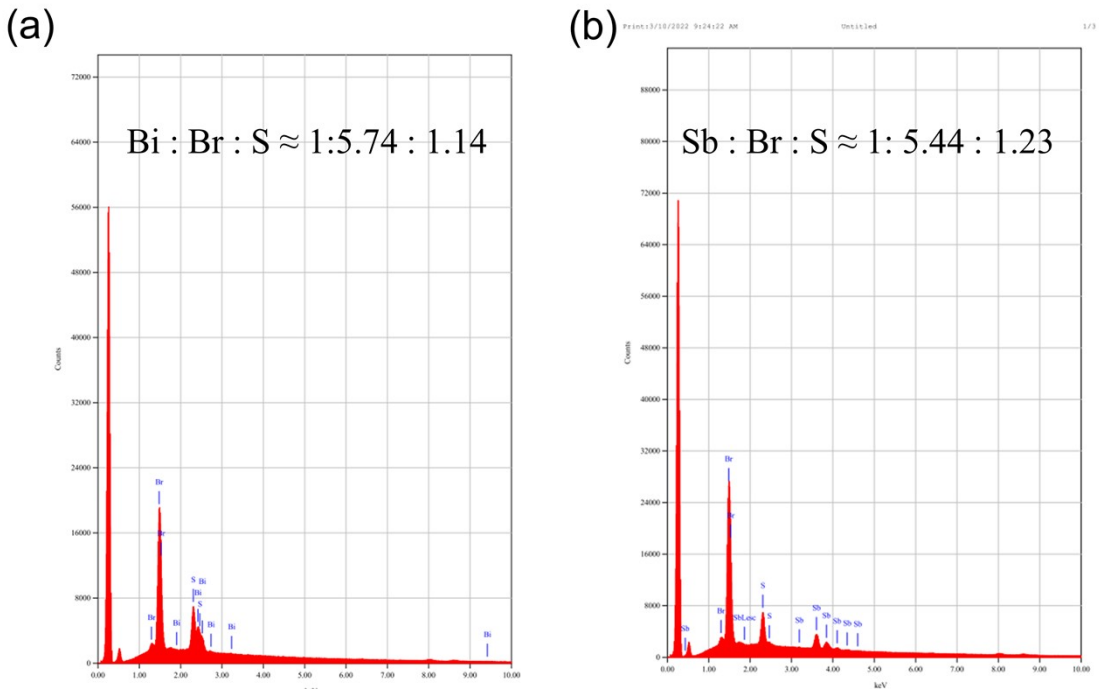

Figure *S*4. The EDS analysis of *M* (Bi/Sb), Br and S in $(C_9N_3H_{15})(C_9H_{13}SO)BiBr_6$ (a) and $(C_9N_3H_{15})(C_9H_{13}SO)SbBr_6$ (b).

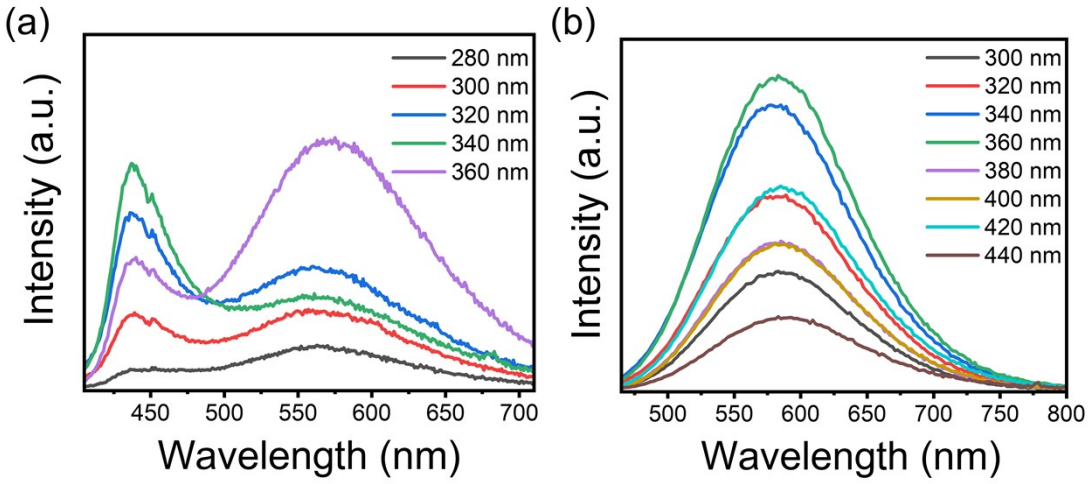

Figure *S*5. PL spectra of $(C_9N_3H_{15})(C_9H_{13}SO)BiBr_6$ (a) and $(C_9N_3H_{15})(C_9H_{13}SO)SbBr_6$ (b) upon excitation at different wavelengths at RT.

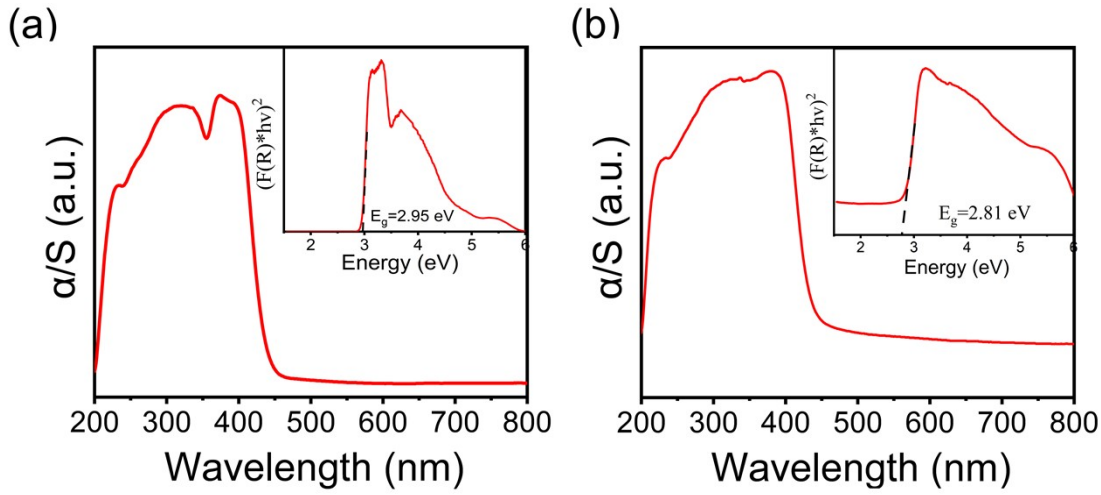

Figure *S*6. UV–vis absorption spectra of $(C_9N_3H_{15})(C_9H_{13}SO)BiBr_6$ (a) and $(C_9N_3H_{15})(C_9H_{13}SO)SbBr_6$ (b), the illustrations are the band gap determined from a Tauc plot.

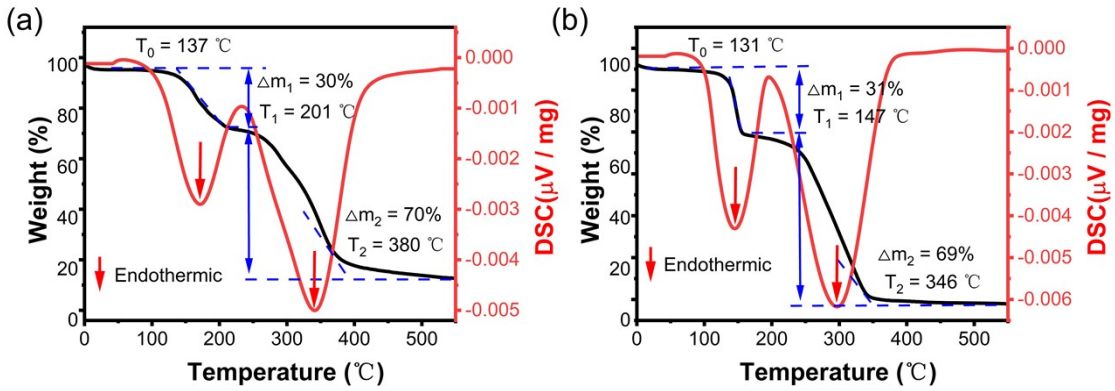

Figure *S*7. TGA and DSC curves of $(C_9N_3H_{15})(C_9H_{13}SO)BiBr_6$ (a) and $(C_9N_3H_{15})(C_9H_{13}SO)BiBr_6$ (b).

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