Electronic Supplementary Material (ESI) for Materials Chemistry Frontiers.

Supporting Information

$[C_5H_{12}N]_2SnBr_6$: A Lead-Free Phase Transition Compound with Switchable Quadratic Nonlinear Optical Properties

Xinxin Hu,[ab] Haojie Xu,[ab] Wuqian Guo,[ab] Shiguo Han,[a] Yi Liu,[a] Yu Ma,[ab] Qingshun Fan,[ab] Junhua Luo[a] and Zhihua Sun*[ac]

[a] State Key Laboratory of Structural Chemistry, Fujian Institute of Research on the Structure of Matter, Chinese Academy of Sciences, Fuzhou, Fujian 350002, China

[b] University of Chinese Academy of Sciences, Beijing 100049, China

[c] Fujian Science & Technology Innovation Laboratory for Optoelectronic Information of China, Fuzhou, Fujian 350108, P. R. China.

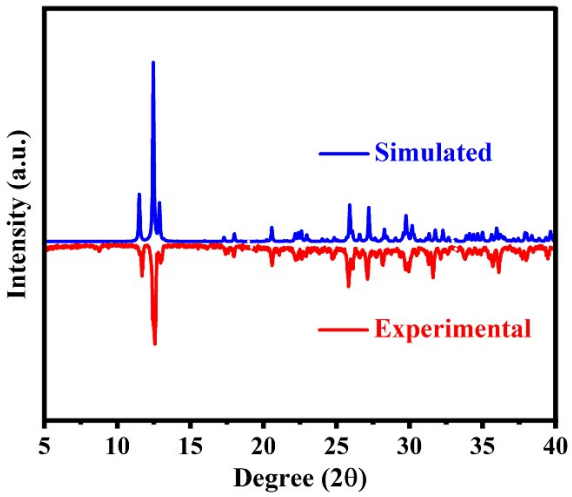

Figure S1. Experimental and simulated PXRD patterns for **1** at room temperature.

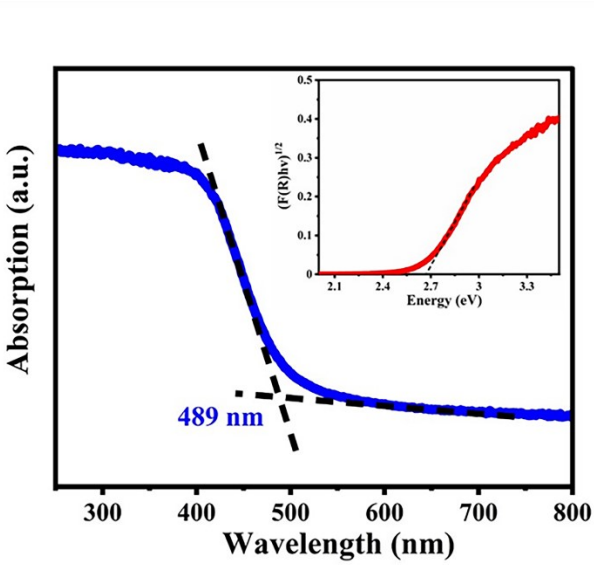

Figure S2. UV-vis absorption spectra of **1**. Inset: the optical properties estimated by *Tauc* Plot.

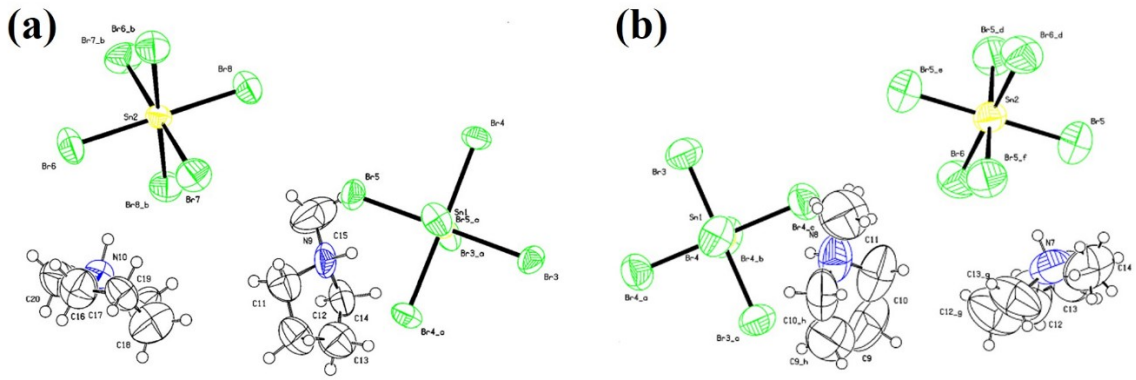

Figure S3. (a) The thermal ellipsoid variation of **1** at 300 K and (b) 360 K, respectively.

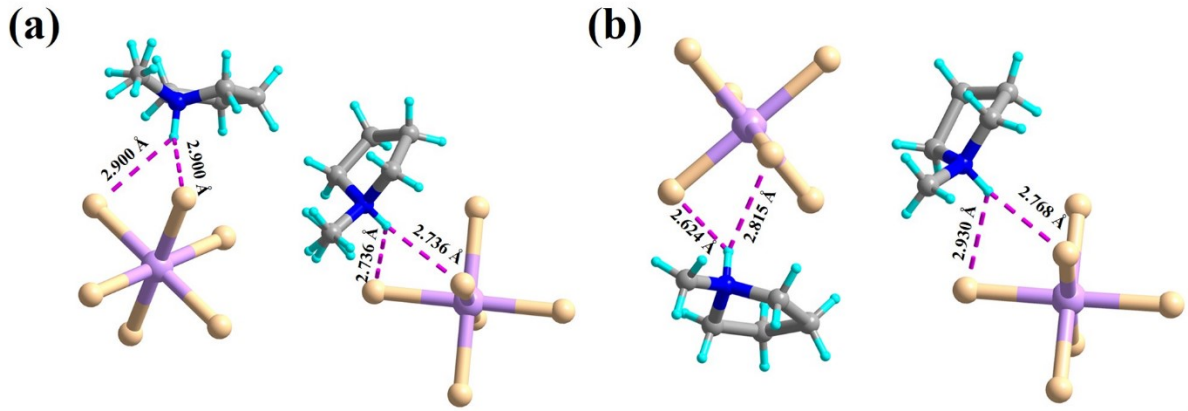

Figure S4. (a) The N-H···Br hydrogen bonds between N and Br atoms at 360 K and (b) 300 K.

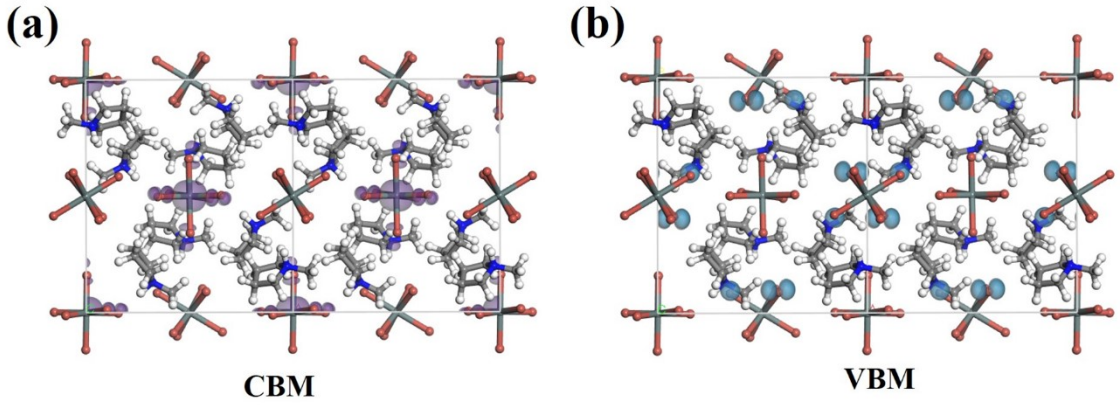

Figure S5. (a) Calculated charge-density distribution of the CBM and (b) VBM of **1.**

Table S1. Crystal data and structure refinement of **1**

Empirical formula	$C_{10}H_{24}Br_6N_2Sn$	$C_{10}H_{24}Br_6N_2Sn$
Temperature（K）	360	300
Formula weight	770.46	770.46
Crystal system	Orthorhombic	Orthorhombic
Space group	*Pbam*	*Pba*2
Unit cell dimensions (Å)	a = 13.9302 (10)	a = 15.5317 (4)
	b = 15.5956 (9)	b = 13.8474 (3)
	c = 10.1118 (8)	c = 10.0184 (3)
Volume ($Å^3$)	2196.8 (3)	2157.39 (10)
Z, Calculated density (g/cm^3)	4, 2.330	4, 2.372
F (000)	1432.0	1432.0
Radiation	Mo Kα (λ = 0.71073)	Ga Kα (λ = 1.3405)
2 θ range for data collection/°	6.406 to 54.978	7.43 to 120.258
Limiting indices	$-18 \le h \le 18$	$-20 \le h \le 20$
	$-18 \le k \le 20$	$-7 \le k \le 17$
	$-13 \le l \le 13$	$-12 \le l \le 12$
Reflections collected	40197	15344
Completeness	99.7 %	99.9 %
Data/ restraints/ parameters	2661/1/99	4550/3/176
Goodness-of-fit on F^2	1.014	1.060
Final R indexes [I>2sigma(I)]	R_1 = 0.0449, wR_2 = 0.1031	R_1 = 0.0515, wR_2 = 0.1474
Final R indexes [all data]	R_1 = 0.0648, wR_2 = 0.1455	R_1 = 0.0618, wR_2 = 0.1557

Table S2. Bond Lengths [Å] for **1** at 360 K

Atom-Atom	Length/ Å	Atom-Atom	Length/ Å
Sn1-Br3	2.5936 (11)	Sn2-Br6	2.5886 (14)
Sn1-Br3[1]	2.5936 (11)	N7-C14	1.537 (18)
Sn1-Br4[2]	2.5977 (9)	N7-C13[5]	1.398 (13)
Sn1-Br4[1]	2.5977 (9)	N7-C13	1.398 (13)
Sn1-Br4[3]	2.5976 (9)	N8-C10	1.412 (112)
Sn1-Br4	2.5976 (9)	N8-C10[2]	1.412 (12)
Sn2-Br5	2.6019 (10)	C8-C11	1.47 (2)
Sn2-Br5[4]	2.6020 (10)	C10-C9	1.493 (17)
Sn2-Br5[5]	2.6020 (10)	C9-C9[2]	1.55 (3)
Sn2-Br5[6]	2.6020 (10)	C12-C12[5]	1.435 (17)
Sn2-Br6[4]	2.599 (14)	C12-C13	1.568 (14)

Symmetry transformation used to generate equivalent atoms:
[1]-X,1-Y,2-Z; [2]+X,+Y,2-Z; [3]-X,1-Y,+Z; [4]1-X,1-Y,1-Z; [5]+X,+Y,1-Z; [6]1-X,1-Y,+Z

Table S3. Bond Lengths [Å] for **1** at 300 K

Atom-Atom	Length/ Å	Atom-Atom	Length/ Å
Sn1-Br3	2.593 (3)	N9-C14	1.45 (3)
Sn1-Br3[1]	2.593 (3)	N9-C15	1.46 (2)
Sn1-Br4	2.5929 (9)	N9-C11	1.45 (3)
Sn1-Br4[1]	2.5928 (9)	N10-C16	1.42 (3)
Sn1-Br5[1]	2.594 (3)	N10-C20	1.506 (16)
Sn1-Br5	2.594 (3)	N10-C19	1.46 (3)
Sn2-Br8[2]	2.607 (4)	C14-C13	1.46 (2)
Sn2-Br8	2.607 (4)	C16-C17	1.46 (3)
Sn2-Br7	2.5827 (9)	C18-C19	1.64 (5)
Sn2-Br7[2]	2.5827 (9)	C18-C17	1.43 (3)
Sn2-Br6[2]	2.599 (4)	C11-C12	1.52 (2)
Sn2-Br6	2.599 (4)	C12-C13	1.56 (4)

Symmetry transformation used to generate equivalent atoms: [1]1-X,1-Y,+Z; [2]1-X,-Y,+Z

Table S4. Bond angles for **1** at 360 K

Atom-Atom-Atom	**Angle/ °**	**Atom-Atom-Atom**	**Angle/ °**
Br3-Sn1-Br3[1]	180.0	Br5[5]-Sn2-Br5[6]	180.00 (4)
Br3[1]-Sn1-Br4[2]	88.83 (3)	Br5[4]-Sn2-Br5	89.73 (4)
Br3-Sn1-Br4[1]	88.83 (3)	Br6-Sn2-Br5[5]	89.73 (4)
Br3[1]-Sn1-Br4[1]	91.17 (3)	Br6[4]-Sn2-Br5[6]	89.73 (4)
Br3[1]-Sn1-Br4	88.83 (3)	Br6-Sn2-Br5	90.27 (4)
Br3-Sn1-Br4[3]	88.83 (3)	Br6-Sn2-Br5[6]	90.27 (4)
Br3-Sn1-Br4[2]	91.17 (3)	Br6[4]-Sn2-Br5[5]	90.27 (4)
Br3-Sn1-Br4	91.17 (3)	Br6[4]-Sn2-Br5[4]	90.27 (4)
Br3[1]-Sn1-Br43	91.17 (3)	Br6-Sn2-Br5[4]	89.73 (4)
Br4-Sn1-Br4[2]	89.06 (5)	Br6-Sn2-Br6[4]	180.0
Br4[1]-Sn1-Br4[3]	89.06 (5)	C13-N7-C14	110.6 (10)
Br4-Sn1-Br4[1]	180.00 (4)	C13[6]-N7-C14	110.6 (10)
Br4-Sn1-Br4[3]	90.94 (5)	C13-N7-C13[6]	111.6 (16)
Br4[2]-Sn1-Br4[3]	180.0	C10[2]-N8-C10	105.8 (14)
Br4[1]-Sn1-Br4[2]	90.94 (5)	C10[2]-N8-C11	110.1 (10)
Br5-Sn2-Br5[4]	180.0	C10-N8-C11	110.1 (10)
Br5-Sn2-Br5[5]	90.32 (5)	N8-C10-C9	104.3 (13)
Br5[4]-Sn2-Br5[5]	89.68 (5)	C10-C9-C9[2]	103.7 (8)
Br5[4]-Sn2-Br5[6]	90.32 (5)	C12[6]-C12-C13	106.2 (6)
Br5-Sn2-Br5[6]	89.68 (5)	N7-C13-C12	103.5 (11)

Symmetry transformation used to generate equivalent atoms:
[1]-X,1-Y,2-Z; [2]+X,+Y,2-Z; [3]-X,1-Y,+Z; [4]1-X,1-Y,1-Z; [5]+X,+Y,1-Z; [6]1-X,1-Y,+Z

Table S5. Bond angles for **1** at 300 K

Atom-Atom-Atom	**Angle/ °**	**Atom-Atom-Atom**	**Angle/ °**
Br3[1]-Sn1-Br3	91.40 (16)	Br7-Sn2-Br62	89.47 (14)
Br3[1]-Sn1-Br5[1]	179.36 (15)	Br7-Sn2-Br6	90.51 (14)
Br3-Sn1-Br5[1]	89.21 (4)	Br7[2]-Sn2-Br6	89.47 (14)
Br3[1]-Sn1-Br5	89.21 (4)	Br6-Sn2-Br82	89.69 (4)
Br3-Sn1-Br5	179.36 (15)	Br6[2]-Sn2-Br8	89.69 (4)
Br4[1]-Sn1-Br3	91.13 (9)	Br6[2]-Sn2-Br8[2]	179.17 (14)
Br4-Sn1-Br3[1]	91.13 (9)	Br6-Sn2-Br8	179.17 (14)
Br4-Sn1-Br3	88.85 (9)	Br6-Sn2-Br6[2]	89.98 (19)
Br4[1]-Sn1-Br3[1]	88.85 (9)	C14 N9 C15	114 (2)
Br4[1]-Sn1-Br4	180.0 (2)	C11 N9 C14	104.9 (11)
Br4-Sn1-Br5	91.33 (9)	C11 N9 C15	114 (3)
Br4[1]-Sn1-Br5[1]	91.33 (9)	C16 N10 C20	111 (2)
Br4[1]-Sn1-Br5	88.69 (9)	C9 N10 C20	107.0 (13)
Br5-Sn1-Br5[1]	88.69 (9)	C16 N10 C20	115 (3)
Br4[1]-Sn1-Br4[2]	90.19 (16)	N9 C14 C13	102.1 (19)
Br8-Sn2-Br8[2]	90.64 (18)	N10 C16 C17	104 (2)
Br7[2]-Sn2-Br82	90.26 (13)	C17 C18 C19	101 (2)
Br7-Sn2-Br8	90.26 (13)	N9 C11 C12	109 (2)
Br7[2]-Sn2-Br8	89.77 (14)	N10 C19 C18	104 (2)
Br7-Sn2-Br8[2]	89.77 (14)	C18 C17 C16	106 (3)
Br7-Sn2-Br7[2]	180.0 (3)	C11 C12 C13	100 (2)
Br7[2]-Sn2-Br6[2]	90.50 (14)	C14 C13 C12	108 (3)

Symmetry transformation used to generate equivalent atoms: [1]1-X,1-Y,+Z; [2]1-X,-Y,+Z

Calculation of 'ΔH', 'ΔS' and 'N' For 1:

According to Boltzmann equation:

$\Delta S = nR\ln N$,

Where

ΔS is entropy change extracted from the C_p data,

R is the gas constant,

n denotes the number of guest particles per mole, and

N = the number of possible orientations for the disordered system.

The ΔS, ΔH and N values on the heating process of 1 are calculated as follows:

$\Delta H = 1.156\ J.g^{-1} \times 770.46\ g.mol^{-1} = 890.7\ J.\ mol^{-1}$

$\Delta S = \int_{T1}^{T2} \frac{Q}{T} dT \approx \frac{\Delta H}{T_c} = 2.53\ J\ mol^{-1}\ K^{-1}$

The N value is calculated to be 1.36.