Supporting Information

Novel low-dimensional lead-free bismuth-based perovskite-like $(BrC_5H_{13}N)_3Bi_2Br_9$: synthesis, structural investigations and optoelectronic properties

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Table of Contents:

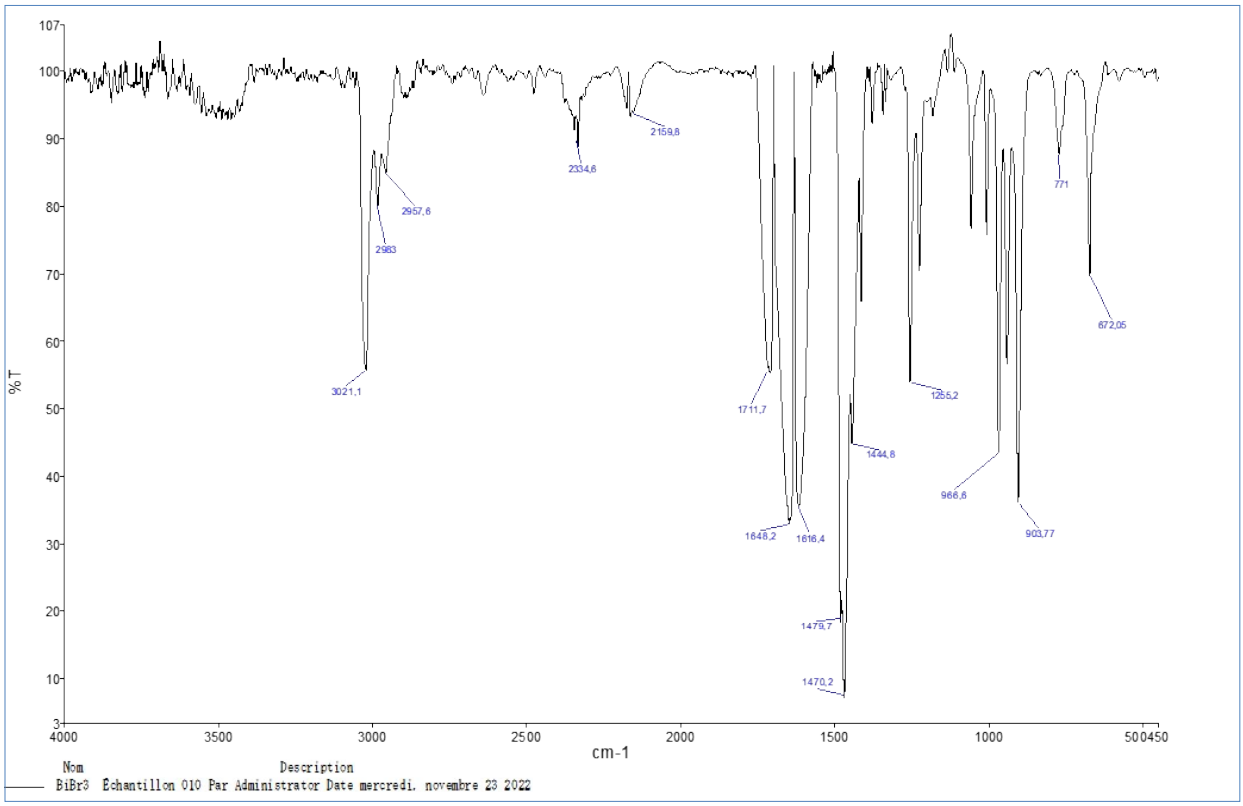

Figure S1. IR Spectrum of $(BrC_5H_{13}N)_3Bi_2Br_9$, verifying the phase purity.

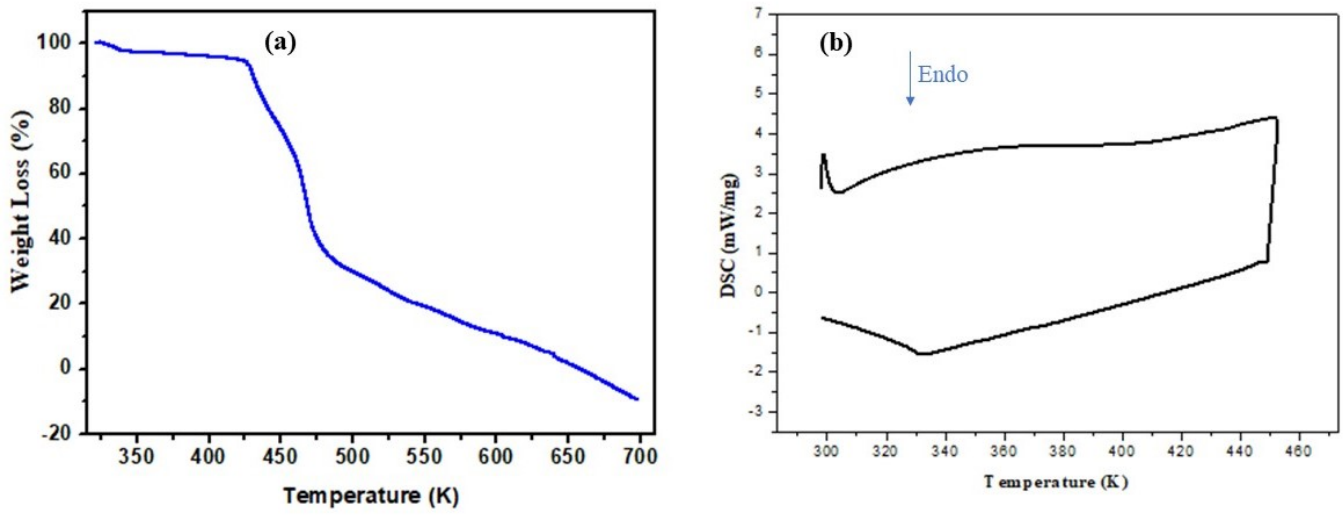

Figure S2. (a) The thermogravimetric analysis profile and **(b)** DSC runs obtained upon heating and cooling for $(BrC_5H_{13}N)_3Bi_2Br_9$.

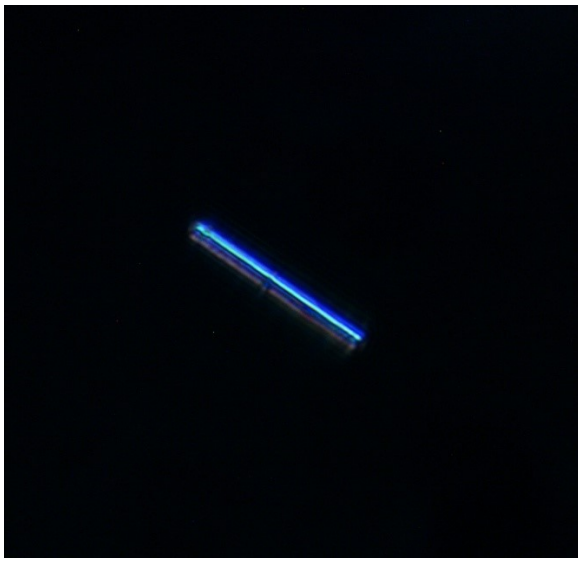

Figure S3. Cross Polarized Optical Microscopy image of a $(BrC_5H_{13}N)_3Bi_2Br_9$ crystal. The image dimension is 77x77μm.

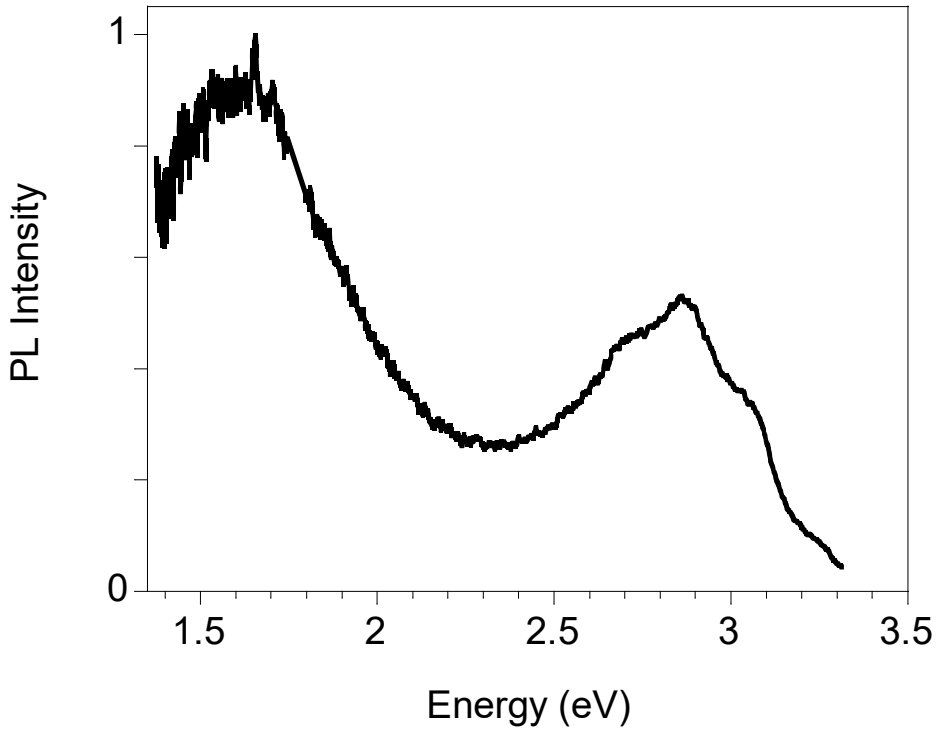

Figure S4. Normalized photoluminescence spectrum of a cast film of $(BrC_5H_{13}N)_3Bi_2Br_9$ excited at 3.54 eV.

Table S1. Some IR-frequencies in $(BrC_5H_{13}N)_3Bi_2Br_9$.

Wavenumber (cm^{-1})	**Attribution**
3021–2963	C–H stretching (ethylenic)
1470–1444	CH_3–N bending (out of plane)
1255.2–1223	Deformation of CH_2–Br group
672.05	Stretching vibration of Br–CH_2 group

Table S2. Crystallographic data and structure refinement parameters for $(BrC_5H_{13}N)_3Bi_2Br_9$ at 295 K.

Empirical formula	$Bi_2Br_9 \cdot 3(C_5H_{13}BrN)$
Formula weight ($g.mol^{-1}$)	1638,37
Temperature (K)	295
Crystal system	Orthorhombic
Space group	$P2_12_12_1$
a (Å)	9,1942 (6)
b (Å)	11,9957 (13)
c (Å)	35,471 (2)
α (°)	90
β (°)	90
γ (°)	90
V ($Å^3$)	3912,1 (6)
Z	4
λ (Cu-Kα) (Å)	1.54184
*ρ*cal ($g.cm^{-1}$)	2.782
Absorption correction	Multi-scan
Crystal size (mm^3)	0.19 × 0.14 × 0.04
Crystal color	Yellowish
hkl range	$-10 \leq h \leq 11$; $-14 \leq k \leq 15$; $-44 \leq l \leq 34$
θ range for data collection (deg)	2.5 – 76.7
Refinement method	Full-matrix least-squares on F^2
No. of collected reflections	17189
No. of independent reflections	7995
Observed reflections / restrains / parameters / refined parameters	7071/ 26 / 316
R_{int}	0.082
F(000)	2944
Goodness of fit	1.04
R indices	$R_1 = 0.060$, $wR_2 = 0.145$
Flack parameter	0.178(15)

Table S3. Selected bond distances (Å) and angles (°) for $(BrC_5H_{13}N)_3Bi_2Br_9$.

Distances (Å)		**Angles (°)**	
Br1—Bi1	2.734 (2)	Bi1—Br4—Bi2	81.21 (6)
Br2—Bi1	2.733 (2)	Bi2—Br5—Bi1	83.41 (5)
Br3—Bi1	2.736 (2)	Bi1—Br6—Bi2	82.24 (6)
Br4—Bi1	3.007 (2)	Br2—Bi1—Br1	92.00 (8)
Br4—Bi2	3.063 (2)	Br2—Bi1—Br3	93.47 (7)
Br5—Bi2	2.928 (2)	Br1—Bi1—Br3	94.55 (8)
Br5—Bi1	3.009 (2)	Br2—Bi1—Br6	91.97 (8)
Br6—Bi1	2.987 (2)	Br1—Bi1—Br6	92.74 (8)
Br6—Bi2	3.020 (2)	Br3—Bi1—Br6	170.74 (8)
Br7—Bi2	2.811 (2)	Br2—Bi1—Br4	171.85 (8)
Br8—Bi2	2.696 (3)	Br1—Bi1—Br4	94.96 (8)
Br9—Bi2	2.744 (3)	Br3—Bi1—Br4	90.20 (7)
		Br6—Bi1—Br4	83.48 (6)
		Br2—Bi1—Br5	92.45 (7)
		Br1—Bi1—Br5	172.22 (8)
		Br3—Bi1—Br5	91.54 (7)
		Br6—Bi1—Br5	80.74 (7)
		Br4—Bi1—Br5	80.18 (7)
		Br8—Bi2—Br9	95.05 (12)
		Br8—Bi2—Br7	91.81 (9)
		Br9—Bi2—Br7	94.54 (10)
		Br8—Bi2—Br5	93.44 (8)
		Br9—Bi2—Br5	91.72 (8)
		Br7—Bi2—Br5	171.45 (7)
		Br8—Bi2—Br6	90.74 (10)
		Br9—Bi2—Br6	171.35 (9)
		Br7—Bi2—Br6	91.69 (8)
		Br5—Bi2—Br6	81.51 (7)
		Br8—Bi2—Br4	171.15 (10)
		Br9—Bi2—Br4	91.64 (9)
		Br7—Bi2—Br4	93.43 (8)
		Br5—Bi2—Br4	80.56 (6)
		Br6—Bi2—Br4	81.99 (7)

Table S4. Selected bond distances (Å) and angles (°) for $(BrC_5H_{13}N)_3Bi_2Br_9$.

Distances (Å)		**Angles (°)**	
C1—Br10	1,97 (3)	C2—C1—Br10	106 (2)
C6—Br11	2,05 (4)	C7—C6—Br11	100 (3)
C11A—Br12	1,92 (6)	C12A—C11A—Br12	108 (5)
C11B—Br12	2,05 (9)	C12B—C11B—Br12	96 (6)
C2—N1	1.97 (3)	N1—C2—C1	114 (2)
C3—N1	1.50 (3)	C6—C7—N2	113 (3)
C4—N1	1.50 (3)	N3—C12A—C11A	109 (4)
C5—N1	1.47 (3)	C11B—C12B—N3	102 (5)
C7—N2	1.56 (3)	C4—N1—C5	113 (2)
C8—N2	1.48 (3)	C4—N1—C3	108 (2)
C9—N2	1.52 (3)	C5—N1—C3	111 (2)
C10—N2	1.48 (4)	C4—N1—C2	111.7 (19)
C12A—N3	1.50 (6)	C5—N1—C2	113 (2)
C12B—N3	1.64 (7)	C3—N1—C2	101 (2)
C13—N3	1.51 (4)	C10—N2—C8	108 (2)
C14—N3	1.44 (4)	C10—N2—C9	111 (3)
C15—N3	1.54 (5)	C8—N2—C9	110 (2)
C1—C2	1.50 (2)	C10—N2—C7	106 (2)
C6—C7	1.44 (5)	C8—N2—C7	110 (2)
C11A—C12A	1.53 (3)	C9—N2—C7	110.5 (18)
C11B—C12B	1.52 (9)	C14—N3—C12A	117 (3)
		C14—N3—C13	109 (3)
		C12A—N3—C13	116 (4)
		C14—N3—C15	111 (3)
		C12A—N3—C15	96 (3)
		C13—N3—C15	106 (3)
		C14—N3—C12B	92 (3)
		C13—N3—C12B	107 (5)
		C15—N3—C12B	131 (4)

Table S5. Hydrogen-bonding geometry (Å, °) for $(BrC_5H_{13}N)_3Bi_2Br_9$.

D—H···*A*	*D*—H	H···*A*	*D*···*A*	*D*—H···*A*
C1—H1A···Br8$^{(i)}$	0.97	3.04	4.00 (4)	172
C1—H1B···Br2$^{(ii)}$	0.97	2.89	3.78 (4)	153
C2—H2A···Br3$^{(iii)}$	0.97	3.01	3.93 (3)	159
C3—H3B···Br9	0.96	3.11	3.97 (4)	150
C3—H3C···Br1$^{(iii)}$	0.96	2.98	3.48 (3)	114
C3—H3C···Br3$^{(iii)}$	0.96	3.08	3.90 (3)	144
C4—H4A···Br2$^{(ii)}$	0.96	3.10	3.92 (2)	144
C5—H5A···Br1$^{(ii)}$	0.96	3.02	3.93 (3)	159
C5—H5B···Br8$^{(i)}$	0.96	3.05	3.68 (3)	125
C5—H5C···Br7$^{(iv)}$	0.96	2.97	3.82 (3)	148
C6—H6A···Br3$^{(v)}$	0.97	2.87	3.72 (4)	146
C6—H6B···Br3	0.97	2.88	3.80 (3)	157
C7—H7B···Br2$^{(i)}$	0.97	3.13	4.04 (3)	158
C9—H9B···Br10	0.96	3.00	3.79 (3)	140
C10—H10C···Br5$^{(i)}$	0.96	3.09	3.57 (3)	113
C11A—H11A···Br6$^{(i)}$	0.97	3.06	3.94 (8)	153
C11A—H11B···Br4	0.97	2.87	3.53 (9)	126
C11B—H11D···Br1$^{(vi)}$	0.97	2.75	3.69 (9)	163
C12A—H12A···Br1$^{(vi)}$	0.97	3.02	3.95 (4)	163
C12B—H12C···Br4	0.97	2.97	3.86 (10)	153
C13—H13C···Br7	0.96	2.85	3.49 (4)	125
C15—H15B···Br1$^{(vi)}$	0.96	3.12	3.98 (4)	151
C15—H15C···Br7$^{(iv)}$	0.96	3.00	3.89 (5)	155

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