Electronic Supplementary Material (ESI) for Inorganic Chemistry Frontiers.

Supporting Information

Structural Phase Transition and Dielectric Anisotropy Properties of a Lead-free Organic-inorganic Hybrid

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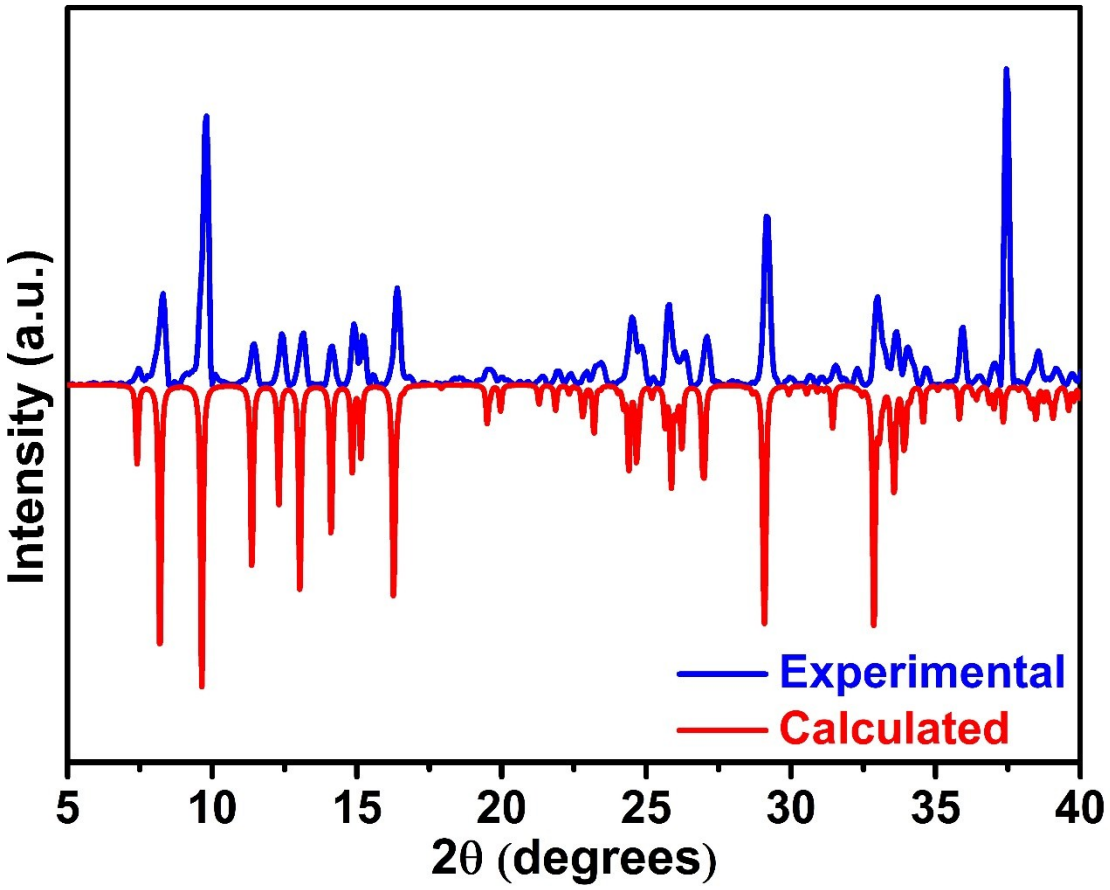

Figure S1. Experimental and simulated PXRD Patterns of **1**.

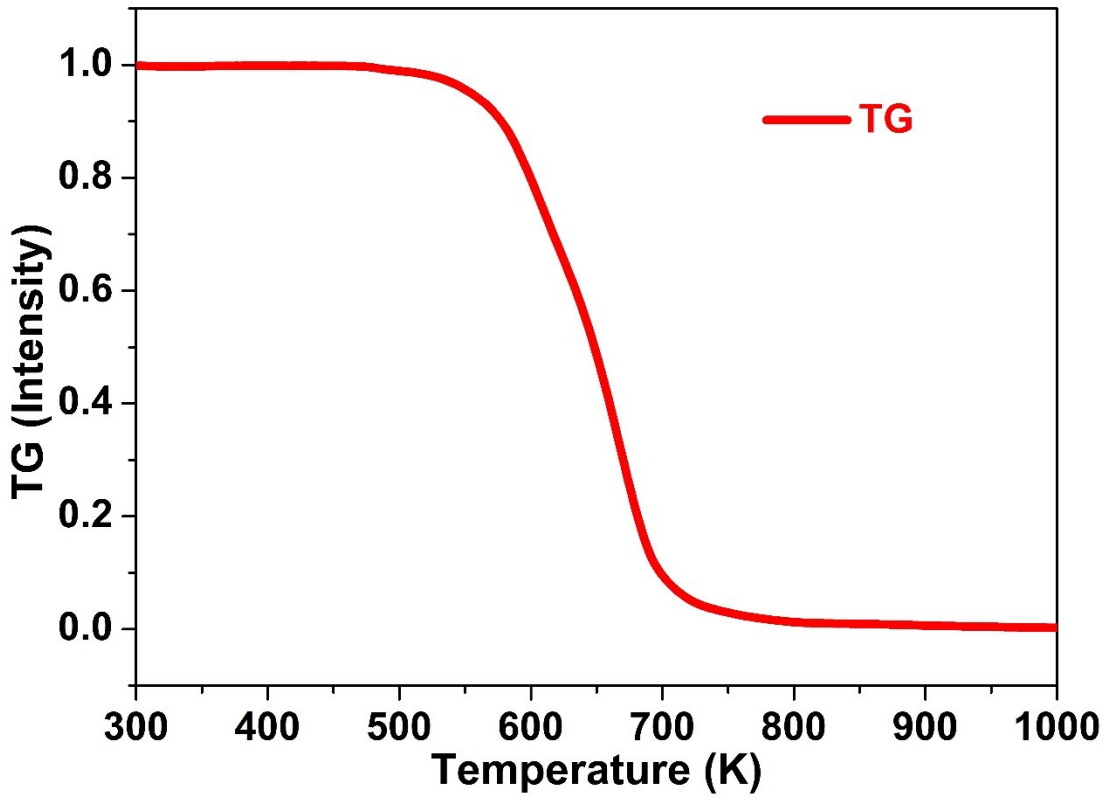

Figure S2 Thermo-Gravimetric (TG) curves of **1.**

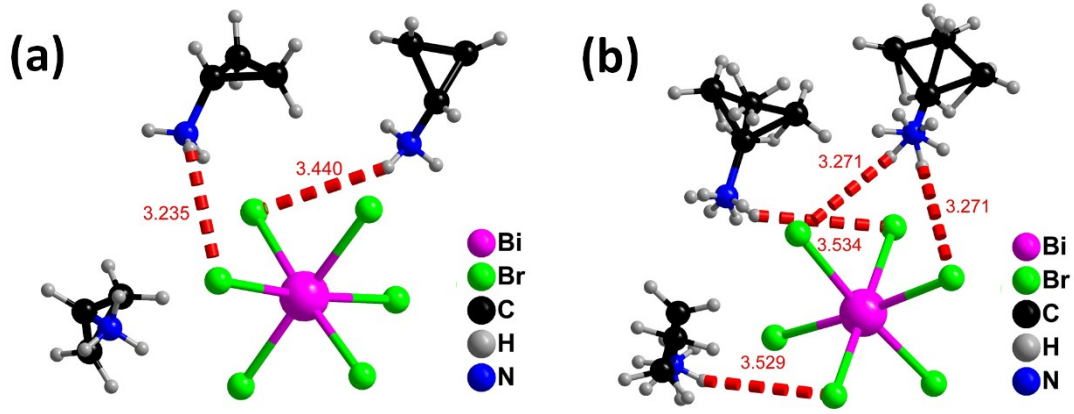

Figure S3. Asymmetric unit of **1** at (a) LTP and (b) HTP. Red imaginary lines represent the N-H-Br hydrogen bonds.

Tables

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

Empirical formula	$C_9H_{24}BiBr_6N_3$	$C_9H_{24}BiBr_6N_3$
Formula weight	862.75	862.75
Temperature/K	100	300
Crystal system	monoclinic	monoclinic
Space group	C2/c	C2/m
a/Å	29.2975(13)	22.2211(5)
b/Å	8.1370(3)	8.3379(2)
c/Å	22.1923(9)	12.2913(3)
α/°	90	90.00
β/°	126.2400(10)	103.8660(10)
γ/°	90	90.00
Volume/Å^3	4267.0(3)	2210.94(9)
Z	8	4
F(000)	3136.0	1568.0
2Θ range for data collection/°	4.552 to 55.216	4.44 to 55.02
Index ranges	-38 ≤ h ≤ 38, -10 ≤ k ≤ 10, -28 ≤ l ≤ 28	-28 ≤ h ≤ 28, -10 ≤ k ≤ 10, -15 ≤ l ≤ 15
Reflections collected	42653	22778
Data/restraints/parameters	4921/0/175	2717/30/118
Goodness-of-fit on F^2	1.160	1.091
Final R indexes [I>=2σ (I)]	R_1 = 0.0228, wR_2 = 0.0575	R_1 = 0.0471, wR2 = 0.1297

Table S2. Bond Lengths for **1** at LTP.

Atom	Atom	Length/Å	Atom	Atom	Length/Å
Bi1	Br6	2.8662(5)	C8	C9	1.499(7)
Bi1	Br2	2.9299(5)	N1	C1	1.473(6)
Bi1	Br4	2.8182(5)	C1	C2	1.489(7)
Bi1	Br1	2.8976(5)	C1	C3	1.486(7)
Bi1	Br5	2.7955(5)	C4	C6	1.484(7)
Bi1	Br3	2.8267(5)	C4	N2	1.465(6)
N3	C7	1.468(6)	C4	C5	1.467(8)
C7	C8	1.488(7)	C6	C5	1.495(9)

C7	C9	1.494(7)	C2	C3	1.500(8)

Table S3. Bond Lengths for **1** at HTP.

Atom	Atom	Length/Å	Atom	Atom	Length/Å
Bi1	Br1	2.8080(10)	N1	C1	1.467(10)
Bi1	Br1[1]	2.8080(10)	C3	C2	1.495(10)
Bi1	Br3	2.9093(10)	C3	C1	1.481(10)
Bi1	Br3[1]	2.9093(10)	C2	C1	1.472(10)
Bi1	Br4	2.7835(15)	C8	C7	1.489(10)
Bi1	Br2	2.9052(15)	C8	C9	1.502(10)
C4	C5	1.493(10)	C8	C9[1]	1.502(10)
C4	C5[2]	1.493(10)	C7	C9	1.486(10)
C4	C6	1.489(10)	C7	C9[1]	1.486(10)
C4	N2	1.497(10)	C7	N3	1.492(10)
C5	C6	1.489(10)			

[1]+X, 1-Y, +Z; [2]+X, -Y, +Z

Table S4. Bond Angles for **1** at LTP.

Atom	Atom	Atom	Angle/˚	Atom	Atom	Atom	Angle/˚
Br6	Bi1	Br2	85.760(13)	N3	C7	C8	118.0(4)
Br6	Bi1	Br1	89.997(14)	N3	C7	C9	119.3(4)
Br4	Bi1	Br6	88.101(14)	C8	C7	C9	60.4(3)
Br4	Bi1	Br2	89.633(14)	C7	C8	C9	60.0(3)
Br4	Bi1	Br1	174.936(14)	C7	C9	C8	59.6(3)
Br4	Bi1	Br3	88.356(14)	N1	C1	C2	117.4(4)
Br1	Bi1	Br2	85.545(14)	N1	C1	C3	117.8(4)
Br5	Bi1	Br6	89.732(13)	C3	C1	C2	60.6(4)
Br5	Bi1	Br2	174.165(14)	N2	C4	C6	117.6(5)
Br5	Bi1	Br4	93.924(15)	N2	C4	C5	119.3(5)
Br5	Bi1	Br1	90.759(14)	C5	C4	C6	60.9(4)
Br5	Bi1	Br3	88.204(14)	C4	C6	C5	59.0(4)
Br3	Bi1	Br6	175.770(14)	C1	C2	C3	59.6(3)
Br3	Bi1	Br2	96.530(14)	C1	C3	C2	59.8(3)
Br3	Bi1	Br1	93.721(14)	C4	C5	C6	60.2(4)

Table S5. Bond Angles for **1** at HTP.

Atom	Atom	Atom	Angle/˚	Atom	Atom	Atom	Angle/˚
Br1	Bi1	Br1[1]	95.08(5)	C6	C4	N2	122(2)
Br1	Bi1	Br3	175.18(4)	C6	C5	C4	59.9(5)
Br1[1]	Bi1	Br3	89.09(4)	C1	C3	C2	59.3(5)
Br1	Bi1	Br3[1]	89.09(4)	C5	C6	C4	60.2(5)
Br1[1]	Bi1	Br3[1]	175.18(4)	C5[2]	C6	C4	60.2(5)
Br1[1]	Bi1	Br2	90.15(3)	C5	C6	C5[2]	108(2)
Br1	Bi1	Br2	90.15(3)	C1	C2	C3	59.9(5)
Br3[1]	Bi1	Br3	86.65(5)	N1	C1	C3	126(3)
Br4	Bi1	Br1	89.24(4)	N1	C1	C2	173(3)
Br4	Bi1	Br1[1]	89.24(4)	C2	C1	C3	60.8(5)
Br4	Bi1	Br3[1]	93.25(4)	C7	C8	C9[1]	59.6(5)
Br4	Bi1	Br3	93.25(4)	C7	C8	C9	59.6(5)
Br4	Bi1	Br2	179.09(5)	C9	C8	C9[1]	97(2)
Br2	Bi1	Br3[1]	87.41(3)	C8	C7	N3	116.4(15)
Br2	Bi1	Br3	87.41(3)	C9[1]	C7	C8	60.6(5)
C5	C4	C5[2]	107(2)	C9	C7	C8	60.6(5)
C5[2]	C4	N2	122.3(16)	C9[1]	C7	C9	99(2)
C5	C4	N2	122.3(16)	C9	C7	N3	127.1(15)
C6	C4	C5	59.9(5)	C9[1]	C7	N3	127.1(15)
C6	C4	C5[2]	59.9(5)	C7	C9	C8	59.8(5)

[1]+X, 1-Y, +Z; [2]+X, -Y, +Z

Table S6. N-H···Br Hydrogen bonds of **1** at LTP.

D-H	d (D-H)	d (H-A)	<DHA	d (D-A)	A
N3-H3A	0.910	2.449	175.01	3.356	Br1 [-x+1/2, y-1/2, -z+1/2]
N3-H3B	0.910	2.892	130.91	3.555	Br6 [-x+1/2, y+1/2, -z+1/2]
N3-H3B	0.910	2.741	131.08	3.409	Br2 [-x+1/2, y+1/2, -z+1/2]
N3-H3C	0.910	2.557	144.96	3.343	Br6
N1-H1A	0.910	2.444	168.97	3.341	Br2 [-x+1/2, -y+1/2, -z]
N1-H1B	0.910	2.454	148.62	3.266	Br6
N1-H1C	0.910	2.593	140.07	3.342	Br1 [-x+1/2, -y+1/2, -z]
N2-H2A	0.910	2.745	131.06	3.412	Br4 [-x, -y, -z]
N2-H2A	0.910	2.881	128.82	3.524	Br5 [-x, -y+1, -z]
N2-H2B	0.910	2.737	146.92	3.535	Br4
N2-H2B	0.910	2.951	124.98	3.552	Br3
N2-H2C	0.910	2.619	163.05	3.499	Br3 [-x, -y+1, -z]

Table S7. N-H···Br Hydrogen bonds of **1** at HTP.

D-H	d (D-H)	d (H-A)	<DHA	d (D-A)	A
N1-H1A	0.900	3.066	136.19	3.768	Br1
N1-H1A	0.900	3.066	136.19	3.768	Br1 [x, -y+1, z]
N1-H1A	0.900	2.992	114.34	3.462	Br4
N1-H1B	0.900	2.607	156.39	3.450	Br1 [-x+1/2, -y+1/2, -z]
N1-H1C	0.900	2.607	156.39	3.450	Br1 [-x+1/2, y+1/2, -z]
N2-H2C	0.900	2.423	154.31	3.257	Br2 [-x+1/2, -y+1/2, -z+1]
N2-H2D	0.900	2.506	155.17	3.345	Br3 [x-1/2, y-1/2, z]
N2-H2E	0.900	2.506	155.17	3.345	Br3 [x-1/2, -y+1/2, z]
N3-H3C	0.900	3.006	138.80	3.731	Br1 [-x+1/2, y+1/2, -z+1]
N3-H3D	0.900	2.928	114.66	3.403	Br3 [-x+1/2, -y+3/2, -z+1]
N3-H3D	0.900	2.643	142.72	3.403	Br3 [-x+1/2, y-1/2, -z+1]
N3-H3E	0.900	3.015	137.74	3.731	Br1 [-x+1/2, -y+1/2, -z+1]
N3-H3E	0.900	2.888	111.18	3.321	Br2