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Origin of high piezoelectricity of a Bismuth-based organic-inorganic hybrid crystal

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S1. DFT calculations

The initial configurations of *R*-BB and *S*-BB were constructed from the single crystal structure without structural optimization. The single point energy and excited state calculation of *R*-BB and *S*-BB were performed by Gaussian. Both single point energy and excited state were calculated using B3LYP functional and def2-SVP basis set. The obtained data were analyzed in Multiwfn, and the VMD was used to draw the image.

S2. The calculation method of 36 vibration mode [1,2]

The frequency constant of the face shear vibration for a square plate sample can be calculated by

$$f_r \cdot l = \frac{F}{2}\sqrt{\frac{1}{\rho s_{66}^E}}$$

from the measured resonance frequency, the elastic compliance of the face shear vibration $s_{66}^E \left(10^{-12} m^2/N\right)$ can be determined by

$$s_{66}^E = \frac{F^2}{4\rho(f_r l)^2}$$

where $l\,(m)$ is the electrode length, $\rho\,(kg/m^3)$ is the crystal density, and $f_r\,(MHz)$ is the resonance frequency, F is a correction constant with value equal to $F = \frac{2\kappa_0 \alpha}{\pi}$, κ_0=2.0288 and $\alpha \cong 1$.

The electromechanical coupling factor k_{36} is given by

$$k_{36}^2 = 1 - \left(\frac{f_r}{f_a}\right)^2$$

where $f_a\,(MHz)$ is the antiresonance frequency.

The shear piezoelectric constant d_{36} of the single crystal for a square plate sample can be calculated by

$$d_{36} = k_{36}\sqrt{\varepsilon_{33}^T s_{66}^E}$$

$$\varepsilon_{33}^T = \frac{C^T t}{lw}$$

$\varepsilon_{33}^{T}\ (pF/m)$ is the 33 component of the free dielectric constant, w (m) is the electrode width, and t (m) is the electrode thickness.

Thus the final calculated result of k_{36} is 42.2% and d_{36} is 46.54 pC/N.

S3. Supplementary Data

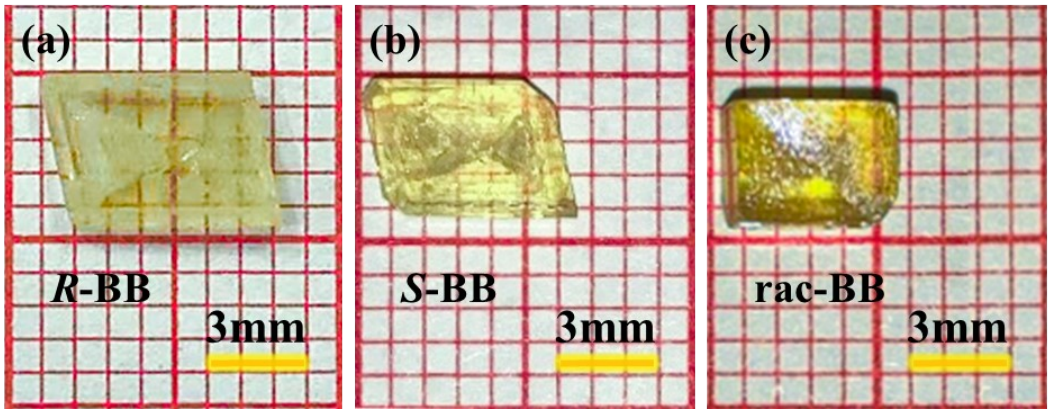

Figure S1. (a) R-BB, (b) S-BB and (c) rac-BB crystal macro topography

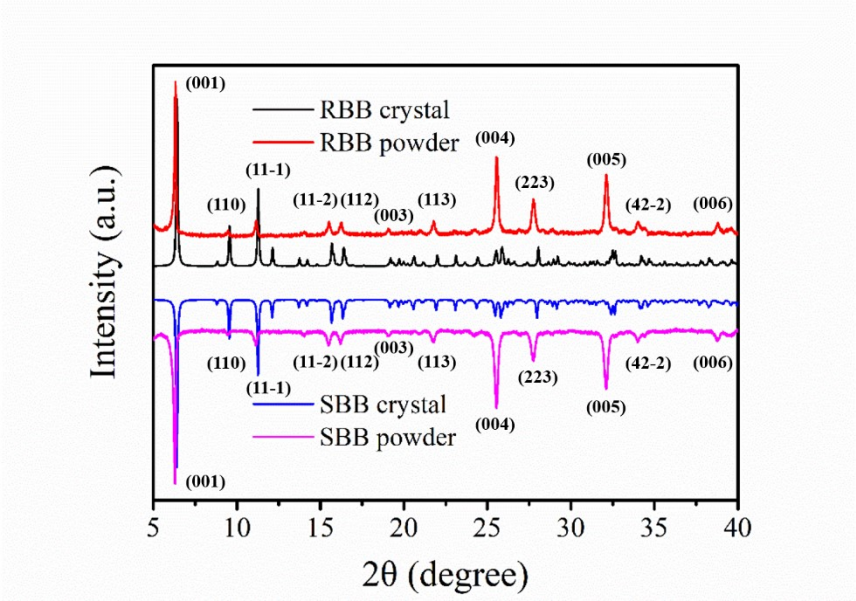

Figure S2. Comparison of single crystal XRD and PXRD of *R*-BB and *S*-BB

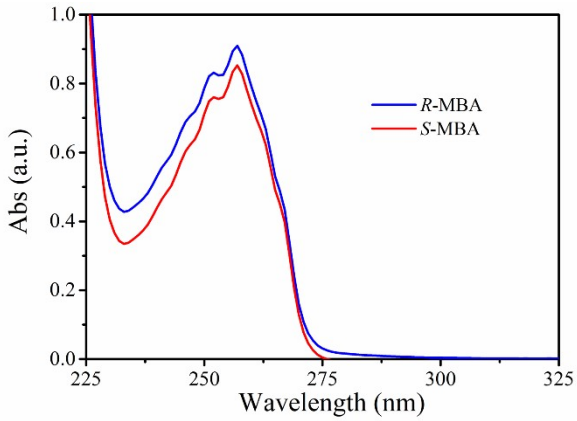

Figure S3. UV-Vis absorption spectrum of the *R*-MBA and *S*-MBA ligands

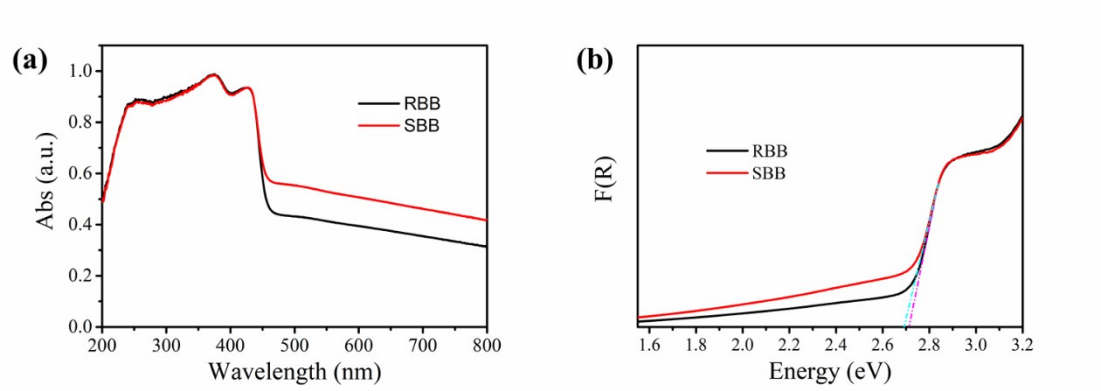

Figure S4. (a) UV-Vis DRS and (b) UV-Vis DRS spectrum corresponding Kubelka-Munk-transformed reflectance spectrum of *R*-BB and *S*-BB crystals

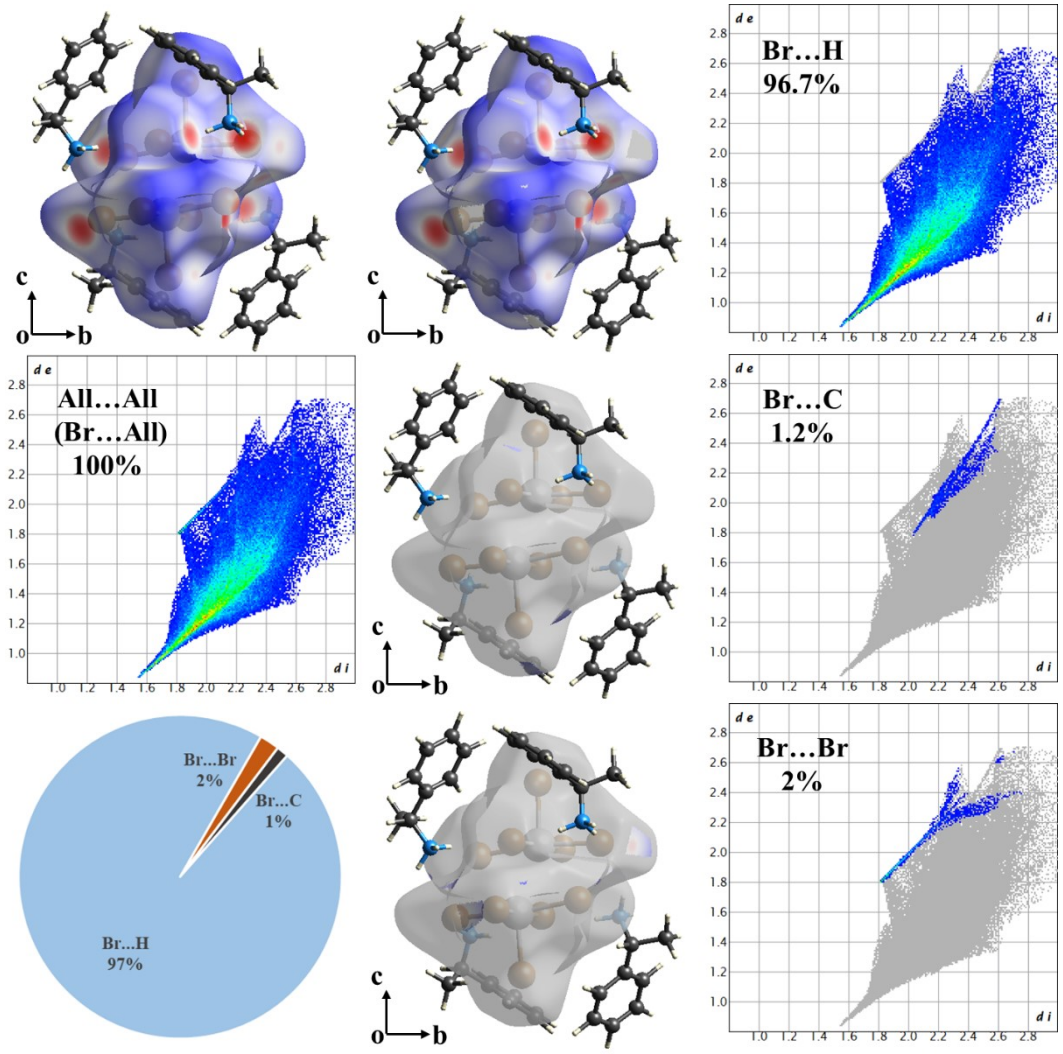

Figure S5. Hirshfeld Surface analysis of the close contact interactions within the *R*-BB crystal. The two-dimensional fingerprint plots provided show several types of interactions. The intermolecular contact [H···Br] has the highest contribution to 96.7%, which confirms the greatest number of H-bonds observed in the crystal structure and indicates the dominate contribution to the dipoles formation.

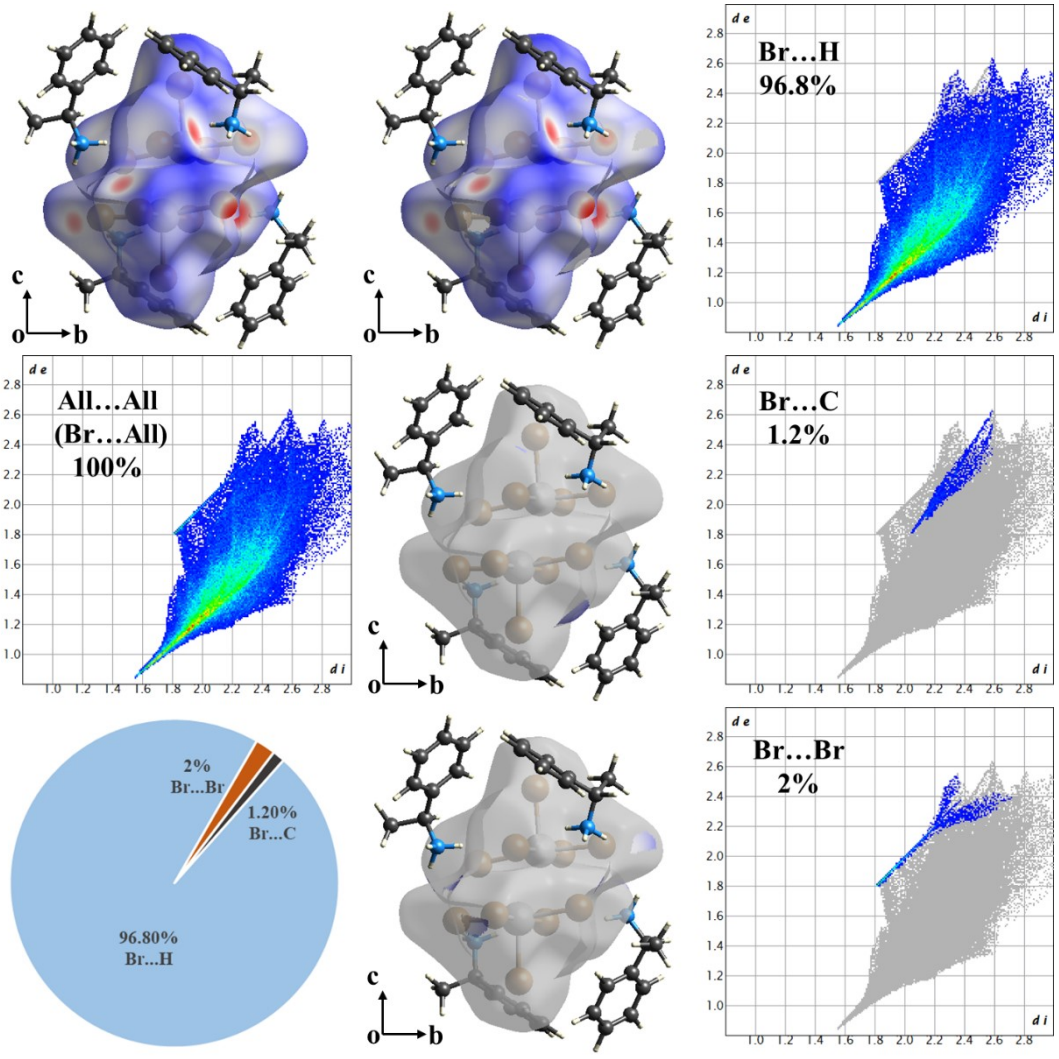

Figure S6. Hirshfeld Surface analysis of the close contact interactions within the *S*-BB crystal. The intermolecular contact [H···Br] has the highest contribution to 96.8%

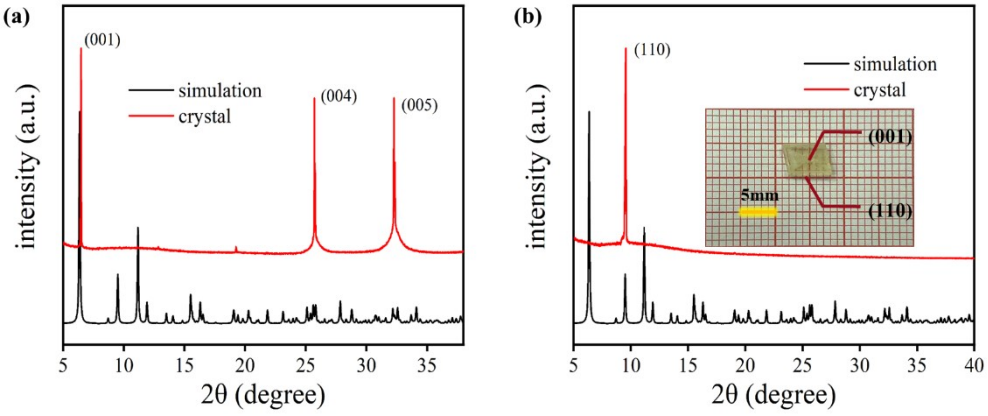

Figure S7. XRD was performed in different directions of the crystal to determine the crystal orientation and identify the (001) and (110) crystal faces

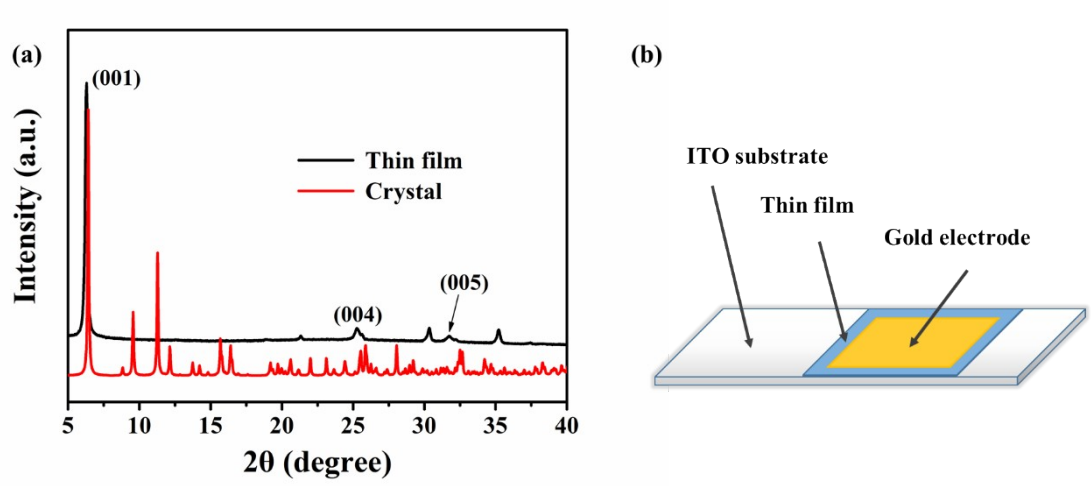

Figure S8. (a) Crystal orientation identification of thin film and (b) Schematic diagram of thin film sample preparation

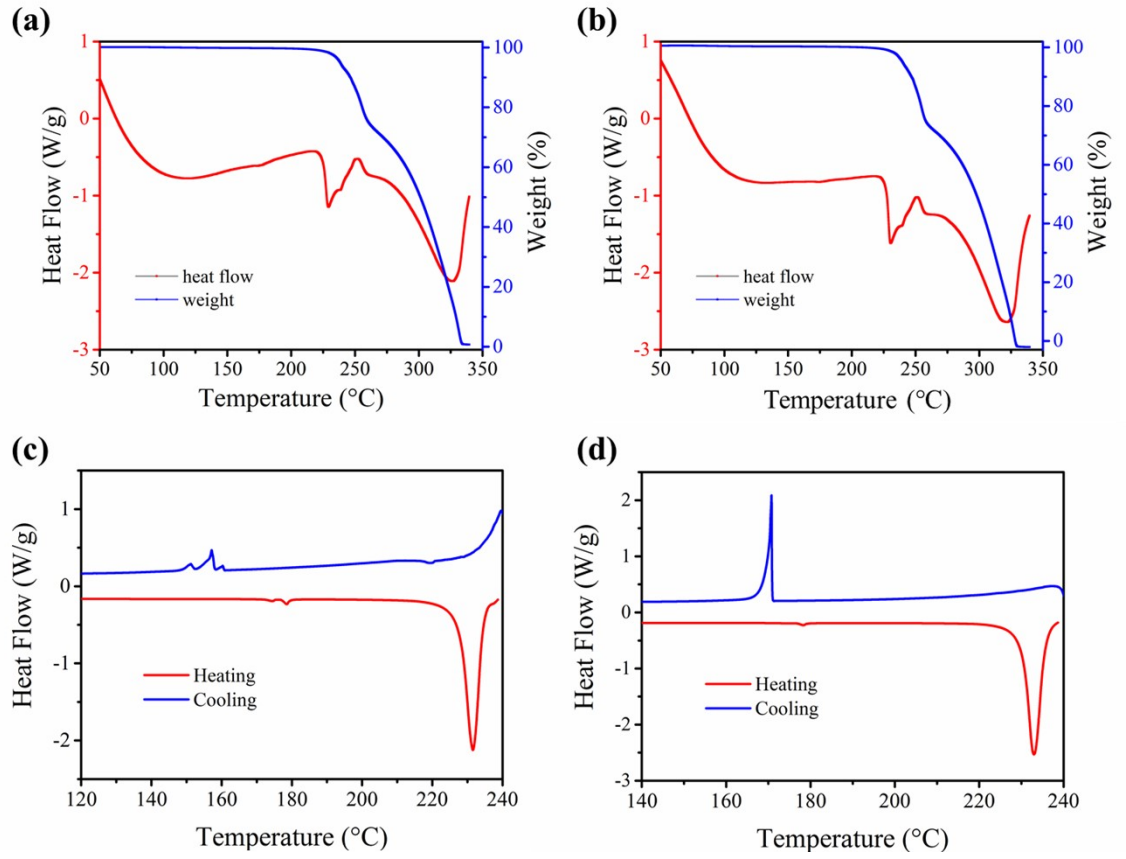

Figure S9. Simultaneous thermal analysis images of (a) *R*-BB and (b) *S*-BB and DSC images of (c) *R*-BB and (d) *S*-BB. If the temperature rises near the melting temperature, a pair of endothermic and exothermic peaks can be clearly seen on the DSC image, while exothermic peaks cannot be seen if the end point is far away from the melting temperature.

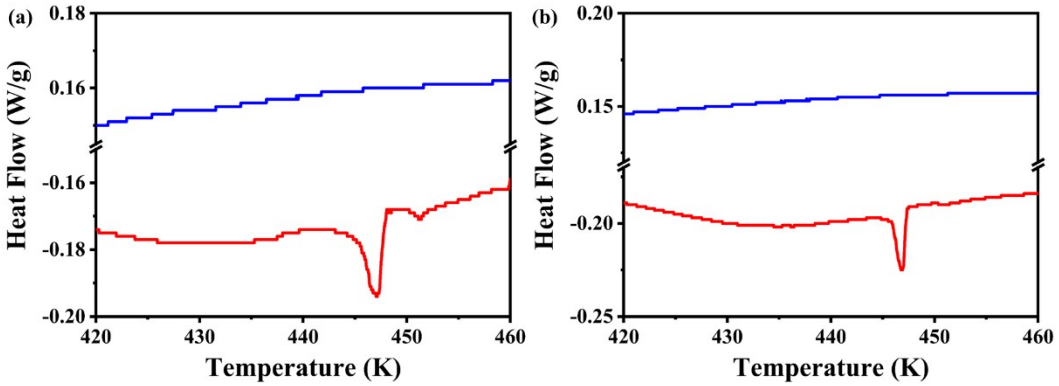

Figure S10. DSC images of (a) R-BB and (b) S-BB. No exothermic peaks appear when the end point is far away from the melting temperature.

Table S1. Crystallographic data sheet of *R*-BB、*S*-BB and rac-BB

Compound	*R*-BB	*S*-BB	rac-BB
Empirical formula	$C_{32}H_{48}Bi_2Br_{10}N_4$	$C_{32}H_{48}Bi_2Br_{10}N_4$	$C_{32}H_{48}Bi_2Br_{10}N_4$
Formula weight	1705.80	1705.80	1705.80
Temperature/K	173.0	173.0	173.0
Crystal system	monoclinic	monoclinic	monoclinic
Space group	$P2_1$	$P2_1$	$P2_1/c$
a/Å	11.9715(10)	11.9892(15)	13.7062(7)
b/Å	14.5680(11)	14.601(2)	14.5646(7)
c/Å	13.7897(13)	13.821(2)	11.9207(6)
α/°	90	90	90
β/°	93.389(3)	93.225(4)	93.110(2)
γ/°	90	90	90
Volume/Å^3	2400.7(4)	2415.5(6)	2376.2(2)
Z	2	2	2
ρ_{calc}g/cm^3	2.360	2.345	2.384
μ/mm^{-1}	15.668	15.572	15.830
F(000)	1568.0	1568.0	1568.0
Crystal size/mm^3	0.1 × 0.08 × 0.08	0.1 × 0.1 × 0.08	0.1 × 0.08 × 0.08
Radiation	MoKα (λ = 0.71073)	MoKα (λ = 0.71073)	MoKα (λ = 0.71073)
2Θ range for data collection/°	3.408 to 56.666	3.402 to 55.842	4.084 to 55.04
Index ranges	-15 ≤ h ≤ 15,	-15 ≤ h ≤ 15,	-17 ≤ h ≤ 17,

	-19 ≤ k ≤ 19, -18 ≤ l ≤ 18	-19 ≤ k ≤ 19, -18 ≤ l ≤ 18	-18 ≤ k ≤ 18, -15 ≤ l ≤ 15
Reflections collected	37239	70209	32491
Independent reflections	11740 [R_{int} = 0.0685, R_{sigma} = 0.0746]	11393 [R_{int} = 0.0855, R_{sigma} = 0.0563]	5364 [R_{int} = 0.0658, R_{sigma} = 0.0422]
Data/restraints/parameters	11740/163/442	11393/217/442	5364/108/222
Goodness-of-fit on F^2	0.963	1.007	1.016
Final R indexes [I>=2σ (I)]	R_1 = 0.0364, wR_2 = 0.0660	R_1 = 0.0321, wR_2 = 0.0697	R_1 = 0.0253, wR_2 = 0.0535
Final R indexes [all data]	R_1 = 0.0522, wR_2 = 0.0714	R_1 = 0.0410, wR_2 = 0.0734	R_1 = 0.0350, wR_2 = 0.0565
Largest diff. peak/hole / e $Å^{-3}$	1.03/-0.64	1.10/-1.17	0.83/-0.87
Flack parameter	-0.026(9)	-0.011(7)	/

Table S2. The bond length of the Bi-Br bond of crystal $(RMBA)_4Bi_2Br_{10}$

Atom	Atom	Length/Å	Atom	Atom	Length/Å
Bi1	Br1	3.1369(17)	Bi2	Br1	3.0040(14)
Bi1	Br3	2.6859(18)	Bi2	Br2	2.6882(18)
Bi1	Br4	2.8482(16)	Bi2	Br5	2.7599(14)
Bi1	Br6	2.8498(16)	Bi2	Br7	3.1141(17)
Bi1	Br7	3.0288(13)	Bi2	Br8	2.8304(16)
Bi1	Br9	2.7165(14)	Bi2	Br10	2.8583(16)

Table S3. The Br-Bi-Br bond angles of crystal $(RMBA)_4Bi_2Br_{10}$

Atom	Atom	Atom	Angle/°	Atom	Atom	Atom	Angle/°
Br3	Bi1	Br1	168.90(4)	Br2	Bi2	Br1	89.77(4)
Br3	Bi1	Br4	89.71(5)	Br2	Bi2	Br5	91.03(5)
Br3	Bi1	Br6	96.98(5)	Br2	Bi2	Br7	172.22(4)
Br3	Bi1	Br7	86.67(4)	Br2	Bi2	Br8	89.89(5)
Br3	Bi1	Br9	93.69(5)	Br2	Bi2	Br10	97.88(5)
Br4	Bi1	Br1	86.31(5)	Br5	Bi2	Br1	178.18(5)
Br4	Bi1	Br6	173.24(6)	Br5	Bi2	Br7	95.57(5)

Br4	Bi1	Br7	89.82(5)	Br5	Bi2	Br8	89.27(5)
Br6	Bi1	Br1	86.93(5)	Br5	Bi2	Br10	89.15(5)
Br6	Bi1	Br7	89.58(4)	Br8	Bi2	Br1	92.37(4)
Br7	Bi1	Br1	82.96(4)	Br8	Bi2	Br7	86.08(5)
Br9	Bi1	Br1	96.69(5)	Br8	Bi2	Br10	172.09(5)
Br9	Bi1	Br4	90.50(5)	Br10	Bi2	Br1	89.12(4)
Br9	Bi1	Br6	90.07(5)	Br10	Bi2	Br7	86.36(5)
Br9	Bi1	Br7	179.52(6)	Bi2	Br1	Bi1	96.60(4)
Br1	Bi2	Br7	83.75(4)	Bi1	Br7	Bi2	96.57(4)

Table S4. The bond length of the Bi-Br bond of crystal $(SMBA)_4Bi_2Br_{10}$

Atom	Atom	Length/Å	Atom	Atom	Length/Å
Bi1	Br1	2.8554(14)	Bi2	Br3	3.0061(11)
Bi1	Br2	2.6898(15)	Bi2	Br4	3.1206(14)
Bi1	Br3	3.1486(14)	Bi2	Br5	2.6964(14)
Bi1	Br4	3.0325(11)	Bi2	Br6	2.8647(14)
Bi1	Br8	2.8606(14)	Bi2	Br7	2.8351(14)
Bi1	Br10	2.7187(11)	Bi2	Br9	2.7646(12)

Table S5. The Br-Bi-Br bond angles of crystal $(SMBA)_4Bi_2Br_{10}$

Atom	Atom	Atom	Angle/°	Atom	Atom	Atom	Angle/°
Br1	Bi1	Br3	86.32(4)	Br5	Bi2	Br3	89.82(4)
Br1	Bi1	Br4	89.83(4)	Br5	Bi2	Br4	172.23(3)
Br1	Bi1	Br8	173.26(4)	Br5	Bi2	Br6	97.86(5)
Br2	Bi1	Br1	89.68(4)	Br5	Bi2	Br7	90.02(4)
Br2	Bi1	Br3	168.90(3)	Br5	Bi2	Br9	90.82(4)
Br2	Bi1	Br4	86.83(4)	Br6	Bi2	Br3	89.09(4)
Br2	Bi1	Br8	97.00(4)	Br6	Bi2	Br4	86.38(4)
Br2	Bi1	Br10	93.59(4)	Br7	Bi2	Br3	92.42(3)
Br4	Bi1	Br3	82.81(3)	Br7	Bi2	Br4	85.97(4)
Br8	Bi1	Br3	86.95(4)	Br7	Bi2	Br6	171.99(4)
Br8	Bi1	Br4	89.60(4)	Br9	Bi2	Br3	178.25(4)

Br10	Bi1	Br1	90.38(4)	Br9	Bi2	Br4	95.77(4)
Br10	Bi1	Br3	96.78(4)	Br9	Bi2	Br6	89.21(4)
Br10	Bi1	Br4	179.52(5)	Br9	Bi2	Br7	89.20(4)
Br10	Bi1	Br8	90.14(4)	Bi2	Br3	Bi1	96.65(3)
Br3	Bi2	Br4	83.71(3)	Bi1	Br4	Bi2	96.70(3)

Table S6. The bond length of the Bi-Br bond of crystal $(rac\text{-}MBA)_2BiBr_5$

Atom	**Atom**	**Length/Å**	**Atom**	**Atom**	**Length/Å**
Bi1	Br1	2.8395(4)	Bi1	Br4	3.0152(5)
Bi1	Br2	2.7460(5)	Bi1	$Br4^1$	3.1146(4)
Bi1	Br3	2.6874(5)	Bi1	Br5	2.8663(4)

Table S7. The Br-Bi-Br bond angles of crystal $(rac\text{-}MBA)_2BiBr_5$

Atom	**Atom**	**Atom**	**Angle/°**	**Atom**	**Atom**	**Atom**	**Angle/°**
Br1	Bi1	$Br4^1$	86.820(12)	Br3	Bi1	Br2	93.177(15)
Br1	Bi1	Br4	87.421(13)	Br3	Bi1	Br4	87.096(14)
Br1	Bi1	Br5	173.413(13)	Br3	Bi1	$Br4^1$	168.769(15)
Br2	Bi1	Br1	89.574(14)	Br3	Bi1	Br5	89.342(13)
Br2	Bi1	$Br4^1$	97.332(14)	Br4	Bi1	$Br4^1$	82.618(13)
Br2	Bi1	Br4	176.993(14)	Br5	Bi1	$Br4^1$	86.712(12)
Br2	Bi1	Br5	90.018(14)	Br5	Bi1	Br4	92.979(13)
Br3	Bi1	Br1	97.245(14)	Bi1	Br4	$Bi1^1$	97.383(13)

Table S8. Crystallographic data sheet for *R*-BB and *S*-BB after heat treatment

Compound	*R*-BB	*S*-BB
Empirical formula	$C_{32}H_{48}Bi_2Br_{10}N_4$	$C_{32}H_{48}Bi_2Br_{10}N_4$
Formula weight	1705.80	1705.80
Temperature/K	173(2)	173(2)
Crystal system	monoclinic	monoclinic
Space group	$P2_1$	$P2_1$
a/Å	12.0027(7)	13.7909(5)
b/Å	14.4943(8)	14.4589(6)

c/Å	13.8026(7)	12.0013(4)
α/°	90	90
β/°	93.175(5)	93.108(3)
γ/°	90	90
Volume/Å^3	2397.6(2)	2389.55(15)
Z	2	2
ρ_{calc}g/cm^3	2.363	2.371
μ/mm^{-1}	15.689	15.742
F(000)	1568.0	1568.0
Crystal size/mm^3	0.060 × 0.050 × 0.040	0.060 × 0.050 × 0.040
Radiation	MoKα (λ = 0.71073)	MoKα (λ = 0.71073)
2Θ range for data collection/°	5.622 to 53.466	4.626 to 53.464
Index ranges	-15 ≤ h ≤ 15, -18 ≤ k ≤ 18, -15 ≤ l ≤ 16	-15 ≤ h ≤ 16, -18 ≤ k ≤ 18, -15 ≤ l ≤ 15
Reflections collected	26684	24122
Independent reflections	9609 [R_{int} = 0.0827, R_{sigma} = 0.0976]	9545 [R_{int} = 0.0591, R_{sigma} = 0.0884]
Data/restraints/parameters	9609/241/441	9545/230/441
Goodness-of-fit on F^2	1.012	0.980
Final R indexes [I>=2σ (I)]	R_1 = 0.0534, wR_2 = 0.1009	R_1 = 0.0457, wR_2 = 0.0831
Final R indexes [all data]	R_1 = 0.0732, wR_2 = 0.1062	R_1 = 0.0649, wR_2 = 0.0885
Largest diff. peak/hole / e Å^{-3}	1.69/-2.04	1.45/-1.59
Flack parameter	0.025(15)	0.017(11)

Table S9. The bond length of the Bi-Br bond of crystal $(RMBA)_4Bi_2Br_{10}$ after heat treatment

Atom	Atom	Length/Å	Atom	Atom	Length/Å
Bi1	Br6	2.343(3)	Bi2	Br9	2.345(2)
Bi1	Br2	2.794(3)	Bi2	Br7	2.756(2)
Bi1	Br1	2.884(3)	Bi2	Br4	2.891(3)

Bi1	Br5	2.899(3)	Bi2	Br10	2.906(3)
Bi1	Br3	3.075(3)	Bi2	Br8	3.122(3)

Table S10. The Br-Bi-Br bond angles of crystal $(RMBA)_4Bi_2Br_{10}$ after heat treatment

Atom	Atom	Atom	Angle/°	Atom	Atom	Atom	Angle/°
Br6	Bi1	Br2	164.47(11)	Br9	Bi2	Br7	169.32(11)
Br6	Bi1	Br1	94.69(9)	Br9	Bi2	Br4	90.92(10)
Br2	Bi1	Br1	91.32(8)	Br7	Bi2	Br4	83.28(8)
Br6	Bi1	Br5	90.93(9)	Br9	Bi2	Br10	96.06(10)
Br2	Bi1	Br5	82.87(8)	Br7	Bi2	Br10	90.14(8)
Br1	Bi1	Br5	174.18(8)	Br4	Bi2	Br10	172.73(7)
Br6	Bi1	Br3	92.12(10)	Br9	Bi2	Br8	88.18(10)
Br2	Bi1	Br3	102.63(8)	Br7	Bi2	Br8	101.17(8)
Br1	Bi1	Br3	85.55(8)	Br4	Bi2	Br8	94.54(9)
Br5	Bi1	Br3	95.77(8)	Br10	Bi2	Br8	83.67(8)

Table S11. The bond length of the Bi-Br bond of crystal $(SMBA)_4Bi_2Br_{10}$ after heat treatment

Atom	Atom	Length/Å	Atom	Atom	Length/Å
Bi1	Br7	2.346(2)	Bi2	Br8	2.339(2)
Bi1	Br5	2.7545(19)	Bi2	Br3	2.7956(19)
Bi1	Br2	2.882(2)	Bi2	Br1	2.875(2)
Bi1	Br10	2.902(2)	Bi2	Br6	2.901(2)
Bi1	Br4	3.115(2)	Bi2	Br9	3.075(2)

Table S12. The Br-Bi-Br bond angles of crystal $(SMBA)_4Bi_2Br_{10}$ after heat treatment

Atom	Atom	Atom	Angle/°	Atom	Atom	Atom	Angle/°
Br7	Bi1	Br5	169.15(8)	Br8	Bi2	Br3	164.65(7)
Br7	Bi1	Br2	90.92(8)	Br8	Bi2	Br1	94.77(7)
Br5	Bi1	Br2	83.15(7)	Br3	Bi2	Br1	91.20(6)
Br7	Bi1	Br10	96.07(8)	Br8	Bi2	Br6	90.94(8)
Br5	Bi1	Br10	90.22(7)	Br3	Bi2	Br6	82.95(6)

Br2	Bi1	Br10	172.81(6)	Br1	Bi2	Br6	174.15(6)
Br7	Bi1	Br4	88.10(7)	Br8	Bi2	Br9	92.09(7)
Br5	Bi1	Br4	101.41(6)	Br3	Bi2	Br9	102.50(6)
Br2	Bi1	Br4	94.81(6)	Br1	Bi2	Br9	85.34(6)
Br10	Bi1	Br4	83.75(6)	Br6	Bi2	Br9	95.73(6)

Table S13. Distortion calculation of bond length and bond Angle

	R-BB	*S*-BB	*R*-BB after heat treatment	*S*-BB after heat treatment
Δd	0.002806	0.002839	0.00807	0.008011
σ^2	15.5824	15.6942	38.7871	41.4208

Reference

[1] S. Zhang, W. Jiang, R. Meyer Jr, F. Li, J. Luo, and W. Cao, *J. Appl. Phys.*, 2011, **110**, 064106.

[2] C. Shen, H. Zhang, Y. Zhang, H. Xu, H. Yu, J. Wang and S. Zhang, *Crystals,* 2014, **4**, 141-151.