Electronic Supplementary Information (ESI)

Tunable hybrid perovskites with Narrow bandgap and Multistage phase transition properties: 2,2-difluoroethylamine·Antimony Hexabromide

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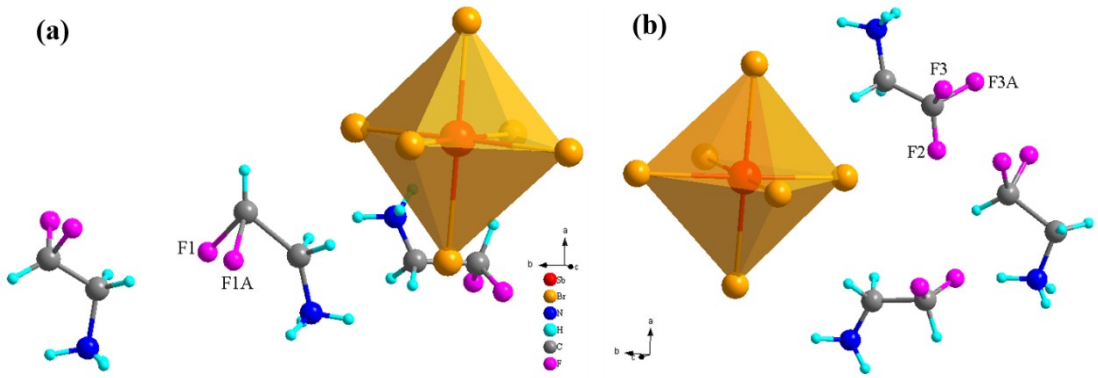

Fig. S1. The coordination environment of 1 at (a) T_{tr}-3 and (b) T_{tr}-4

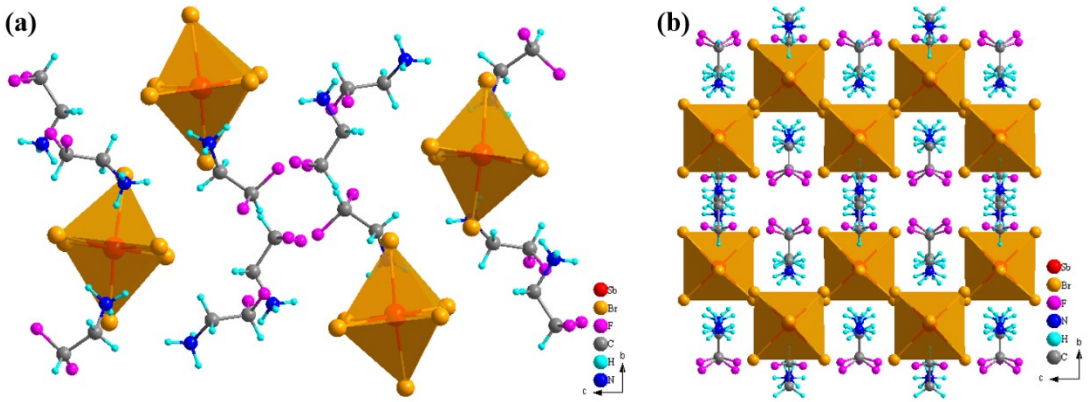

Fig. S2. Packing diagram of 1 along the a-axis for (a) T_{tr}-1 and (b) T_{tr}-4.

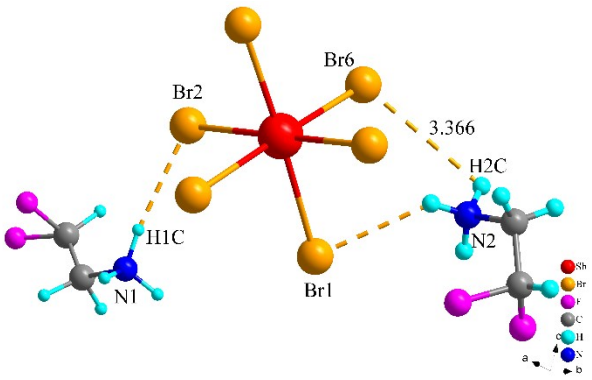

Fig. S3. hydrogen bond diagram of 1 along the a-axis for T_{tr}-1.

Powder X-ray diffraction (PXRD) and Infrared absorption (IR) spectroscopy

X-ray powder diffraction testing was performed on 1 to further verify the structural accuracy. By comparing the results of the X-ray powder diffraction test with the PXRD analysis results of the single-crystal structure simulation (Fig. S4a), the data of 1 can be well fitted, which confirms that the experimentally obtained 1 is pure phase. As shown in figure S4b, 3500-3400cm^{-1} is the characteristic peak of N-H. 3300-2800 cm^{-1} is the characteristic peak of C-H stretching vibration. The characteristic peak in the range of 1465-1340 cm^{-1} is caused by the bending vibration of C-H, and 1400-730 cm^{-1} is the stretching peak of C-F.

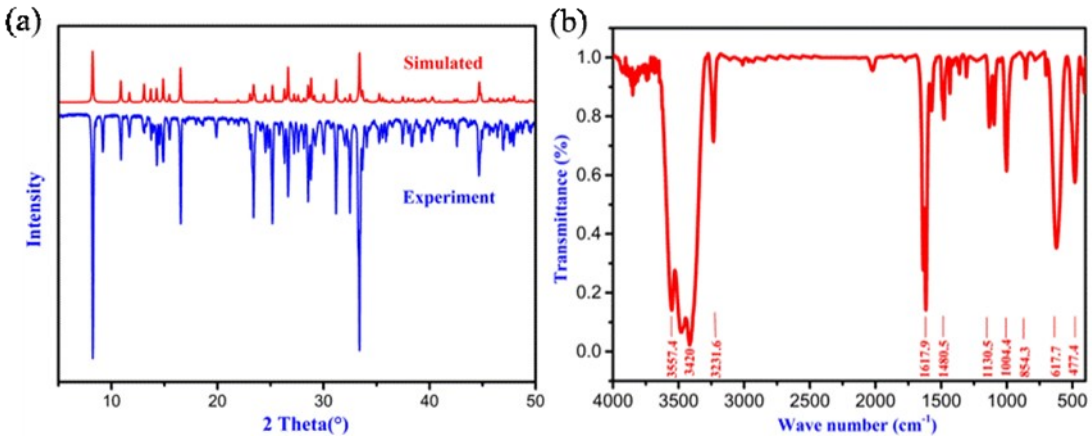

Fig. S4. (a) A comparison via measured PXRD (powder x-ray diffraction) and simulated XRD pattern from the "cif" file at room temperature; (b) The IR spectra of 1 at room temperature.

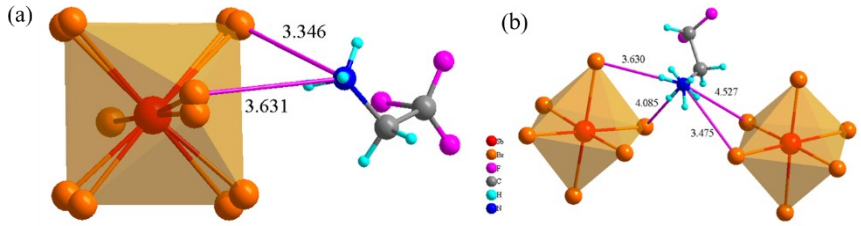

Fig. S5. The distance between N atom and Br atom (a) at T_{tr-2} (b) at T_{tr-3}.

Table S1 The crystallographic data of compound 1

Number	T_{tr}-1	T_{tr}-2	T_{tr}-3	T_{tr}-4
Empirical formula	$C_6H_{18}Br_6F_6N_3Sb$	$C_6H_{18}Br_6F_6N_3Sb$	$C_6H_{18}Br_6F_6N_3Sb$	$C_6H_{14}Br_6F_7N_3Sb$
Formula weight	847.44	847.44	847.44	862.41
Temperature（K）	133	232.97	273	292.99
Crystal system	monoclinic	monoclinic	orthorhombic	orthorhombic
Space group	$P2_1/c$	$P2_1/c$	*Pnnm*	*Pnnm*
a (Å)	8.0145(3)	8.0374(9)	12.3891(5)	12.3766(5)
b (Å)	12.1192(4)	12.3053(11)	21.5246(9)	21.5176(8)
c (Å)	21.2967(7)	21.3990(15)	8.0726(3)	8.0757(3)
V (Å^3)	2067.64(12)	2116.4(3)	2152.72(15)	2150.68(14)
Z	4	4	4	4
Density (g/cm^3)	2.722	2.660	2.615	2.663
m (mm^{-1})	12.975	12.676	12.462	12.483
F (000)	1560.0	1560.0	1560.0	1580.0
Data/restraints/ parameters	3660/54/202	4862/2/202	2808/1/121	2046/2/127
GOF	1.151	1.072	1.046	1.111
R_1, $wR_2[I > 2\sigma(I)]$	R_1=0.2014, wR_2 =0.5057	R_1=0.1348, wR_2 =0.3599	R_1=0.0484, wR_2 =0. 1401	R_1=0.0487, wR_2 =0.1486
R_1, wR_2 (all data)	R_1=0.2043, wR_2 = 0.5062	R_1=0.1652, wR_2 =0.3752	R_1=0. 0707, wR_2 = 0. 1517	R_1=0.0554, wR_2 = 0.1529
$\triangle\rho_{max}$ / $\triangle\rho_{min}$ (eÅ^{-3})	11.64/-3.75	3.00/-2.48	1.70/-1.16	1.10/-1.07

Table S2 Hydrogen bonds parameters of T_{tr}-2 and T_{tr}-3.

D-H···A	D-H	H···A	D···A	∠D-H···A
T_{tr}-1				
N2--H2C···Br6	0.88	2.46	3.32(4)	165
N2--H2D···Br1	0.89	2.55	3.40(5)	159
N1—H1C···Br2	0.89	2.55	3.38(4)	156
T_{tr}-2				
N2--H2C···Br6	0.89	2.68	3.35(3)	133
N2--H2D···Br3	0.89	2.64	3.46(3)	151
N2--H2E···Br1	0.89	2.86	3.59(3)	140
T_{tr}-3				
N1--H1B···Br3	0.89	2.67	3.517(10)	159
N1--H1C···Br3	0.89	2.89	3.538(11)	131

[1]2-x, -y, 1-z

Table S3 Bond angles[°] for 1.

Number	T_{tr}-1		T_{tr}-2	
Bond angles[°]	Br1-Sb1-Br6	175.2(2)	Br2-Sb1-Br6	87.51(10)
	Br1-Sb1-Br5	88.35(18)	Br1-Sb1-Br2	89.20(10)
	Br1-Sb1-Br2	88.48(18)	Br1-Sb1-Br6	177.39(12)
	Br6-Sb1-Br5	93.06(19)	Br1-Sb1-Br4	90.63(11)
	Br6-Sb1-Br2	96.12(19)	Br1-Sb1-Br3	88.72(10)
	Br4-Sb1-Br1	86.20(18)	Br5-Sb1-Br2	88.49(10)
	Br4-Sb1-Br6	89.24(19)	Br5-Sb1-Br6	94.21(11)
	Br4-Sb1-Br5	90.54(19)	Br5-Sb1-Br1	90.58(11)
	Br4-Sb1-Br2	174.6(2)	Br5-Sb1-Br4	91.01(12)
	Br4-Sb1-Br3	95.34(19)	Br5-Sb1-Br3	177.67(12)
	Br5-Sb1-Br2	88.61(18)	Br4-Sb1-Br2	179.47(10)
	Br3-Sb1-Br1	88.35(18)	Br4-Sb1-Br6	90.83(11)
	Br3-Sb1-Br6	90.73(18)	Br4-Sb1-Br3	89.79(11)
	Br3-Sb1-Br5	173.1 (2)	Br3-Sb1-Br2	90.71(9)
	Br3-Sb1-Br2	85.20(18)	Br3-Sb1-Br6	90.00(9)
Number	T_{tr}-3		T_{tr}-4	
Bond angles[°]	Br3-Sb1-Br2	89.73(3)	Br4-Sb1-Br1	89.74(3)
	Br3-Sb1-Br2^{1}	89.73(3)	Br4-Sb1-Br1^{1}	89.74(3)
	Br2^{1}-Sb1-Br2	89.70(3)	Br2-Sb1-Br4	88.92(3)
	Br4^{1}-Sb1-Br3	88.90(3)	Br2^{1}-Sb1-Br4	88.92(3)
	Br4-Sb1-Br3	88.90(3)	Br2-Sb1-Br2^{1}	94.25(4)
	Br4^{1}-Sb1-Br2	88.01(3)	Br2^{1}-Sb1-Br1	177.40(3)
	Br4-Sb1-Br2	177.33(3)	Br2-Sb1-Br1	87.95(3)
	Br4^{1}-Sb1-Br2^{1}	177.33(3)	Br2^{1}-Sb1-Br1^{1}	87.95(3)
	Br4-Sb1-Br2^{1}	88.01(3)	Br2-Sb1-Br1^{1}	177.40(3)
	Br4-Sb1-Br4^{1}	94.26(4)	Br2-Sb1-Br3	90.94(3)
	Br4^{1}-Sb1-Br1	90.99(3)	Br2^{1}-Sb1-Br3	90.94(3)
	Br4-Sb1-Br1	90.99(3)	Br1^{1}-Sb1-Br1	89.81(4)
	Br1-Sb1-Br3	179.84(4)	Br3-Sb1-Br4	179.80(4)
	Br1-Sb1-Br2^{1}	90.39(3)	Br3-Sb1-Br1	88.92(3)
			Br3-Sb1-Br1^{1}	90.41(3)

Table S4 Bond lengths [Å] for 1.

Number	T_{tr}-1		T_{tr}-2	
Bond lengths [Å]	Sb1-Br1	2.778(6)	Sb1-Br2	2.875(3)
	Sb1-Br6	2.820(6)	Sb1-Br6	2.899(3)
	Sb1-Br4	2.690(6)	Sb1-Br1	2.718(3)
	Sb1-Br5	2.845(6)	Sb1-Br5	2.716(3)
	Sb1-Br2	2.961(6)	Sb1-Br4	2.738(3)
	Sb1-Br3	2.750(6)	Sb1-Br3	2.874(3)
Number	T_{tr}-3		T_{tr}-4	
Bond lengths [Å]	Sb1-Br2	2.8826(10)	Sb1-Br4	2.8756(11)
	Sb1-Br3[1]	2.8949(8)	Sb1-Br2[1]	2.7221(9)
	Sb1-Br3	2.8949(8)	Sb1-Br2	2.7221(9)
	Sb1-Br4[1]	2.7238(8)	Sb1-Br1	2.8876(9)
	Sb1-Br4	2.7237(8)	Sb1-Br1[1]	2.8876(9)
	Sb1-Br5	2.7445(11)	Sb1-Br3	2.7426(13)

Entropy change calculated by DSC:

(1) Heating process

$\Delta S_1 = R\ln N_1$

$$\Delta S_1 = \int_{T_2}^{T_1} \frac{Q}{T} dT \approx \frac{\Delta H}{T_c} = \frac{0.3976\ J\cdot g^{-1} \times 847.44\ g\cdot mol^{-1}}{155.4\ K} = 2.168\ J\cdot mol^{-1}\cdot K^{-1}$$

$$N_1 = \exp\left(\frac{\Delta S1}{R}\right) = \exp\left(\frac{2.168\ J\cdot mol^{-1}\cdot K^{-1}}{8.314 J\cdot mol^{-1}\cdot K^{-1}}\right) = 0.261$$

$\Delta S_2 = R\ln N_2$

$$\Delta S_2 = \int_{T_2}^{T_1} \frac{Q}{T} dT \approx \frac{\Delta H}{T_c} = \frac{0.7800\ J\cdot g^{-1} \times 847.44\ g\cdot mol^{-1}}{201.9\ K} = 3.274\ J\cdot mol^{-1}\cdot K^{-1}$$

$$N_2 = \exp\left(\frac{\Delta S2}{R}\right) = \exp\left(\frac{3.274\ J\cdot mol^{-1}\cdot K^{-1}}{8.314 J\cdot mol^{-1}\cdot K^{-1}}\right) = 0.394$$

$\Delta S_3 = R\ln N_3$

$$\Delta S_3 = \int_{T_2}^{T_1} \frac{Q}{T} dT \approx \frac{\Delta H}{T_c} = \frac{0.0099\ J\cdot g^{-1} \times 862.41\ g\cdot mol^{-1}}{251.7\ K} = 0.0340\ J\cdot mol^{-1}\cdot K^{-1}$$

$$N_3 = \exp\left(\frac{\Delta S3}{R}\right) = \exp\left(\frac{0.0340\ J\cdot mol^{-1}\cdot K^{-1}}{8.314 J\cdot mol^{-1}\cdot K^{-1}}\right) = 0.0041$$

(2) Cooling process

$\Delta S_1 = R\ln N_1$

$$\Delta S_1 = \int_{T_2}^{T_1} \frac{Q}{T} dT \approx \frac{\Delta H}{T_c} = \frac{0.3604\ J \cdot g^{-1} \times 847.44\ g \cdot mol^{-1}}{151.7\ K} = 2.013\ J \cdot mol^{-1} \cdot K^{-1}$$

$$N_1 = \exp\left(\frac{\Delta S1}{R}\right) = \exp\left(\frac{2.013\ J \cdot mol^{-1} \cdot K^{-1}}{8.314 J \cdot mol^{-1} \cdot K^{-1}}\right) = 0.242$$

$\Delta S_2 = R\ln N_2$

$$\Delta S_2 = \int_{T_2}^{T_1} \frac{Q}{T} dT \approx \frac{\Delta H}{T_c} = \frac{0.7562\ J \cdot g^{-1} \times 847.44\ g \cdot mol^{-1}}{199.9\ K} = 3.206\ J \cdot mol^{-1} \cdot K^{-1}$$

$$N_2 = \exp\left(\frac{\Delta S2}{R}\right) = \exp\left(\frac{3.206\ J \cdot mol^{-1} \cdot K^{-1}}{8.314 J \cdot mol^{-1} \cdot K^{-1}}\right) = 0.386$$

$\Delta S_3 = R\ln N_3$

$$\Delta S_3 = \int_{T_2}^{T_1} \frac{Q}{T} dT \approx \frac{\Delta H}{T_c} = \frac{0.0570\ J \cdot g^{-1} \times 862.41\ g \cdot mol^{-1}}{264.8\ K} = 0.186\ J \cdot mol^{-1} \cdot K^{-1}$$

$$N_3 = \exp\left(\frac{\Delta S3}{R}\right) = \exp\left(\frac{0.186\ J \cdot mol^{-1} \cdot K^{-1}}{8.314 J \cdot mol^{-1} \cdot K^{-1}}\right) = 0.0224$$