Electronic Supplementary Material (ESI) for Materials Chemistry Frontiers.

Supporting Information

Monofluorine Substitution Achieved High-T_c Dielectric Transition in a One-Dimensional Lead Bromide Hybrid Photoluminescent Perovskite Semiconductor

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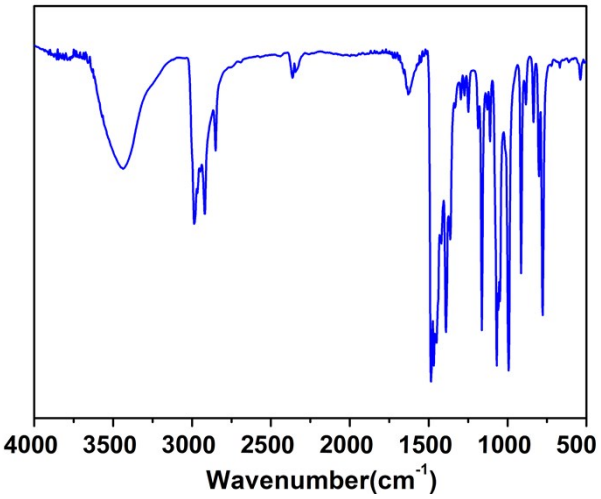

Fig. S1 IR spectrum for **1**.

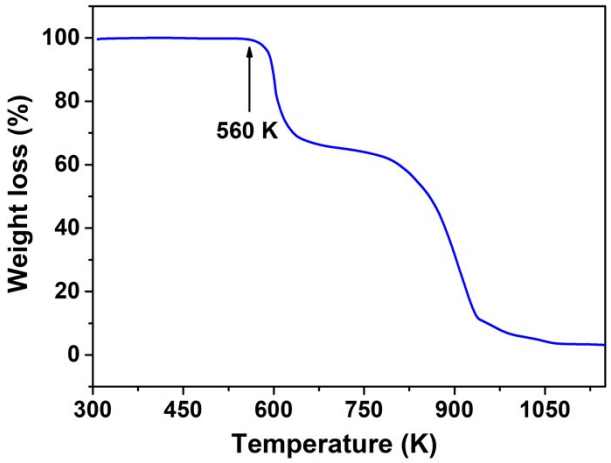

Fig. S2 TGA spectrum for **1**.

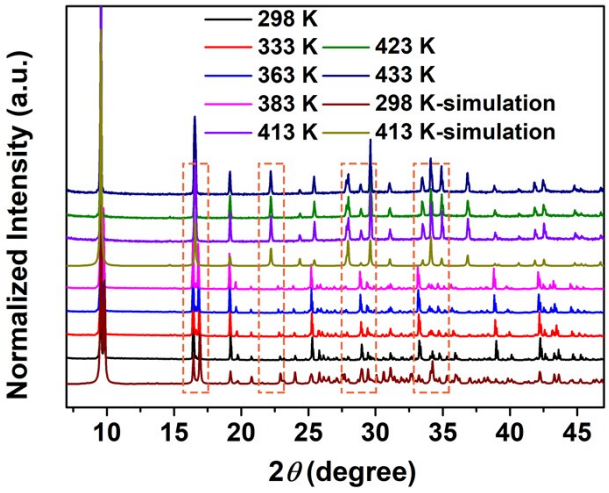

Fig. S3 Measured and simulated patterns of the powder X-ray diffraction (PXRD) for **1** at variable temperatures.

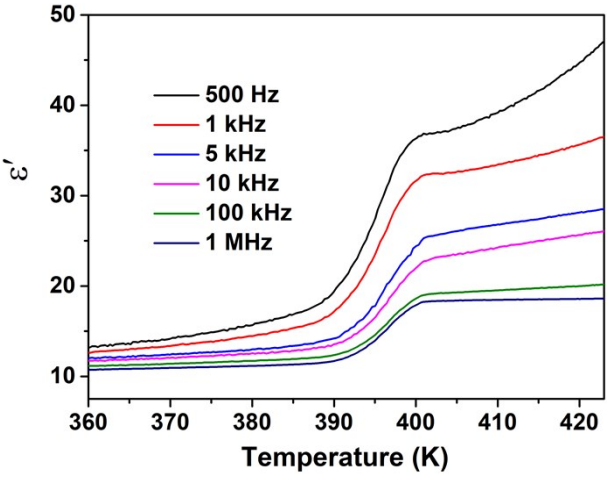

Fig. S4 Temperature-dependence of the real part (ε') of dielectric constant performed on the polycrystalline sample of **1** at muti-frequencies.

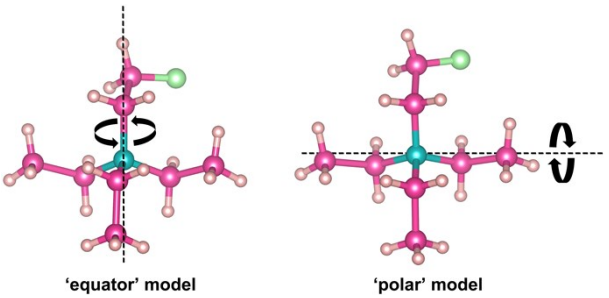

Fig. S5 The rotation models used during the DFT calculation for **1**, the neighbouring cations and anions are omitted for clarity. The balls with light pink, pink, light green,and the dark cyan colors represent H, C, F, N atoms, respectively.

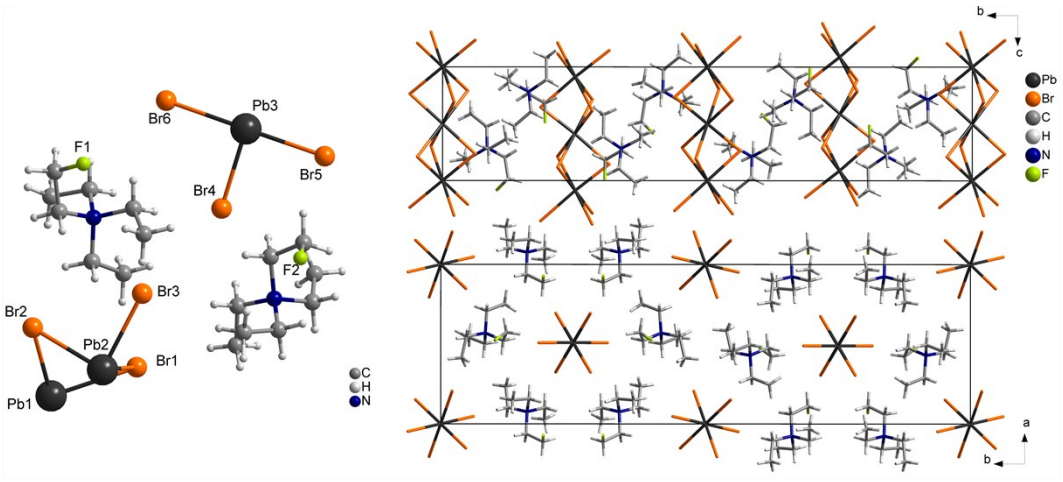

Fig. S6 Asymmetric unit and unit packing structures for **1** at 298 K.

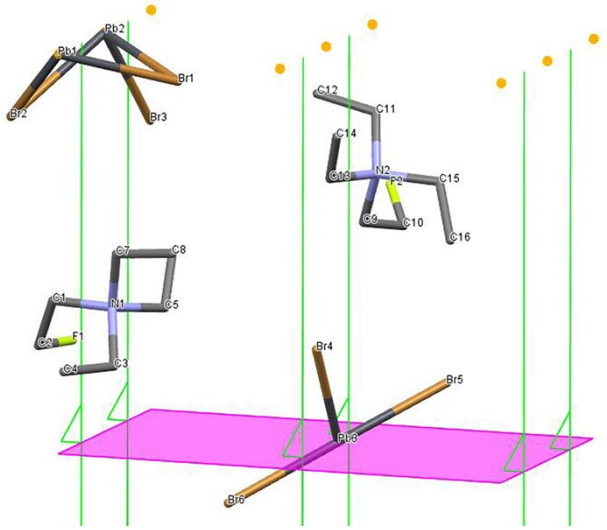

Fig. S7 Symmetric elements on the asymmetric unit of **1** at 298 K.

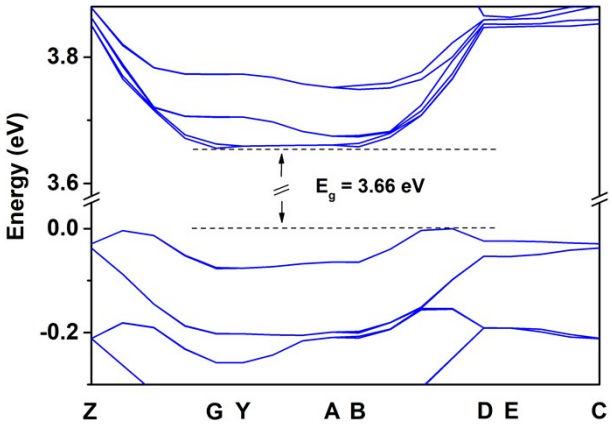

Fig. S8 Zoom-in band structure of **1** at 298 K.

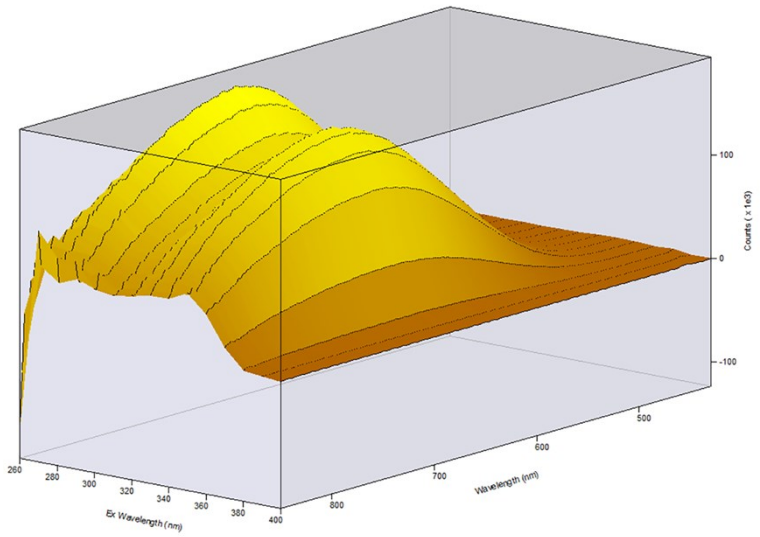

Fig. S9 Excitation emission map.

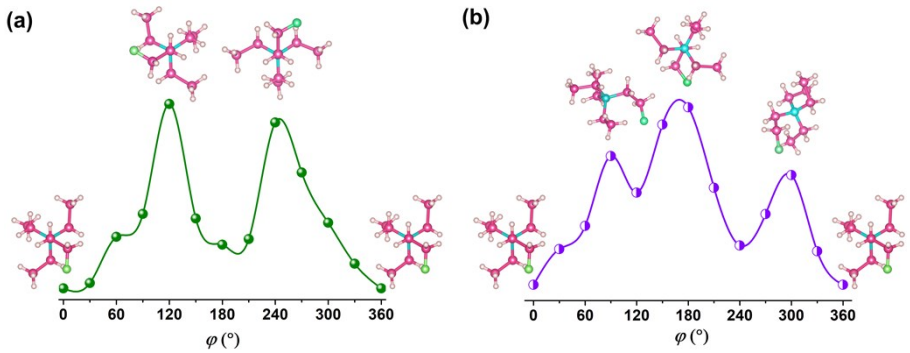

Fig. S10 Positions of maximums and minimums on the potential energy curves of **1** in the 'equator' (a) and 'polar' (b) rotation models. Segments besides the central FTEA cation are omitted for clarity. The balls with light pink, pink, light green, and the dark cyan colors represent H, C, F, N atoms, respectively.

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

Temperature (K)	298 K	413 K
Crystal system	Monoclinic	Hexagonal
Space group	$P2_1/c$	$P6_3/mmc$
a / Å	10.9652(5)	10.6877 (14)
b / Å	35.9203(14)	10.6877 (14)
c / Å	7.8176(3)	7.9460(11)
β / °	100.805(4)	90
γ / °	90	120
Volume /(Å^3)	3024.6(2)	786.1(2)
Z	4	2
Mr	595.14	577.10
Mu/mm^{-1}	19.064	18.324
Radiation type	Mo-Kα; λ = 0.71073 Å	Mo-Kα; λ = 0.71073 Å
Dcalc / g cm^{-3}	2.614	2.438
F(000)	2160	523.9
GOF	1.103	1.062
R_1[I > 2σ (I)]	0.0668	0.0631
wR_2 [I > 2σ (I)]	0.1219	0.168
R_{int}	0.0442	0.0547

Table S2. Bond lengths [Å] and bond angles [°] for **1** at 298 K.

Pb1−Br1	3.0677(11)	C1−C2	1.469(19)
Pb1−Br2	3.0622(11)	C2−F1	1.343(19)
Pb1−Br3	2.9945(11)	C3−C4	1.57(2)
Pb2−Br1	3.0450(11)	C5−C6	1.487(18)
Pb2−Br2	3.0731(11)	C7−C8	1.511(17)
Pb2−Br3	3.0056(10)	C9−C10	1.481(19)
Pb3−Br4	2.9450(10)	C11−C12	1.506(15)
Pb3−Br5	3.0003(12)	C13−C14	1.501(15)
Pb3−Br6	3.0508(13)	C15−C16	1.515(15)

		N1−C1	1.530(14)
		N1−C3	1.522(14)
		N1−C5	1.507(13)
		N1−C7	1.522(14)
		C10−F2	1.34(2)
Br3−Pb2−Br1	95.83(3)	F1−C2−C1	112.4(15)
Br3−Pb2−Br2	95.60(3)	C3−N1−C1	111.1(9)
Br1−Pb2−Br2	80.67(3)	C6−C5−N1	115.4(11)
Br2−Pb1−Br1	80.48(3)	C1−N1−C7	107.1(8)
Pb2−Br1−Pb1	79.50(3)	C1−N1−C5	110.8(9)
Pb1−Br2−Pb2	79.15(3)	C7−N1−C1	107.1(8)
Br4−Pb3−Br6	84.56(3)	C5−N1−C3	106.6(9)
Br5−Pb3−Br6	179.51(4)	C5−N1−C7	110.5(9)
		C7−N1−C3	110.9(10)
		C2−C1−N1	118.1(12)
		C4−C3−N1	113.4(13)

Table S3. Bond lengths [Å] and bond angles [°] for **1** at 413 K.

Pb1−Br1	3.024(4)	C3−C4	1.550(11)
C1−N1	1.485(19)	C5−C6	1.550(11)
C3−N1	1.495(19)	C7−C8	1.549(11)

C5−N1	1.497(19)		
C7−N1	1.502(19)		
C1−C2	1.551(11)		
$Pb1^{i}$–Br1−Pb1	82.13(12)	C1−N1−C3	110.1(17)
$Br1^{ii}$ −Pb1−Br1	98.47(9)	C1−N1−C5	109.6(17)
$Br1^{iii}$–Pb1−Br1	81.53(9)	C1−N1−C7	110.0(17)
$Br1^{iv}$ −Pb1−Br1	180.0	C3−N1−C7	109.0(17)
$Br1^{ii}$–Pb1−$Br1^{iii}$	98.47(9)	C5−N1−C7	108.9(17)
Br1−Pb1−$Br1^{v}$	81.53(9)	N1−C3−C4	100.9(16)
		N1−C5−C6	100.6(16)
		N1−C7−C8	101.2(16)

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