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Structural dimension engineering and high-temperature dielectric-optical switchings in fluorine-substituted lead-bromide hybrid perovskites

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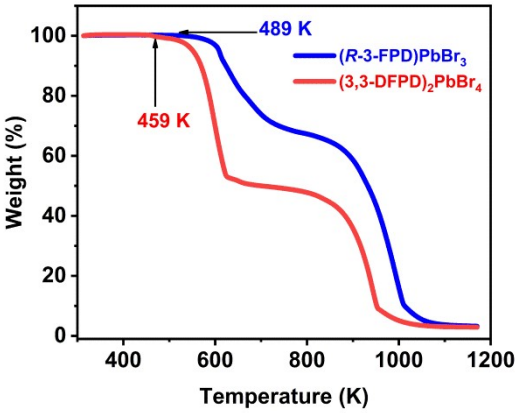

Fig. S1 TGA curves of (*R*-3-FPD)$PbBr_3$ and (3,3-DFPD)$_2PbBr_4$.

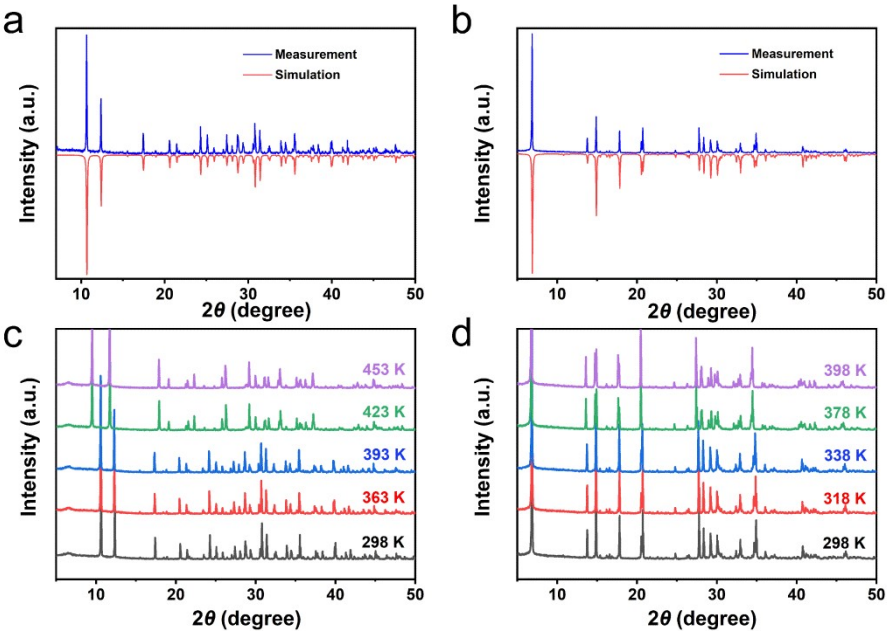

Fig. S2 The measured and simulated PXRD patterns for (*R*-3-FPD)$PbBr_3$ (a) and (3,3-DFPD)$_2PbBr_4$ (b) at room temperature. Variable-temperature PXRD patterns for (*R*-3-FPD)$PbBr_3$ (c) and (3,3-DFPD)$_2PbBr_4$ (d).

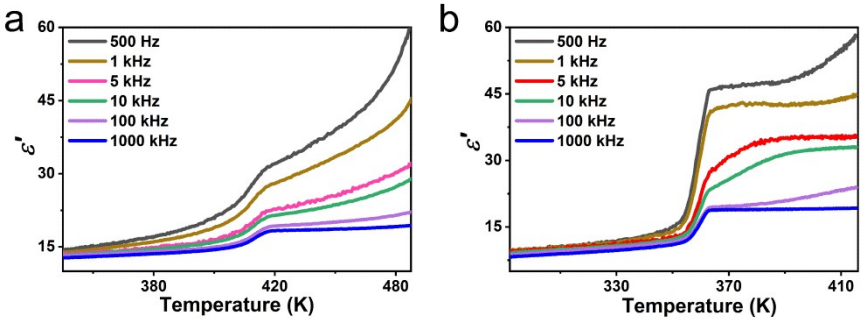

Fig. S3 Temperature dependence of the real part (ε') of the dielectric constant of (*R*-3-FPD)$PbBr_3$ (a) and (3,3-DFPD)$_2PbBr_4$ (b) at different frequencies in a heating run.

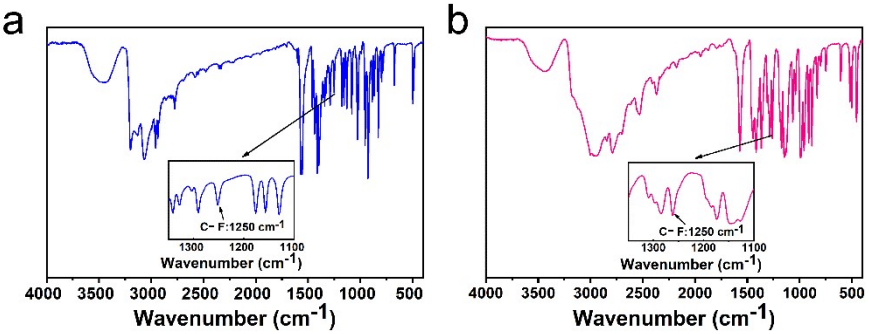

Fig. S4 IR spectra for (*R*-3-FPD)$PbBr_3$ (a) and (3,3-DFPD)$_2PbBr_4$ (b). The insets denote the C–F vibration at around 1250 cm^{-1}.

Table S1 Crystal data and structure refinement for (*R*-3-FPD)$PbBr_3$ and (3,3-DFPD)$_2PbBr_4$.

Compound	[*R*-3-FPD]$PbBr_3$	[3,3-DFPD]$_2PbBr_4$
Temperature/K	293	293
Empirical formula	$C_5H_{11}Br_3FNPb$	$C_{20}H_{40}Br_8F_8N_4Pb_2$
Formula weight/g mol^{-1}	551.07	1542.22
Crystal system	orthorhombic	tetragonal
Space group	$P2_12_12_1$	$P4_12_12$
a/Å	7.8341(5)	12.2050(3)
b/Å	10.1533(6)	12.2050(3)
c/Å	14.2642(9)	51.295(3)
α/°	90	90
β/°	90	90
γ/°	90	90
Volume/Å^3	1134.60(12)	7641.0(6)
Z	4	8
D_cg/cm^3	3.226	2.681
F(000)	976	5632
GOF	1.011	1.040
R_1	0.0658	0.071
wR_2	0.1687	0.1575

Table S2 Selected Pb−Br bond lengths [Å] and Br−Pb−Br bond angles [°] for (*R*-3-FPD)$PbBr_3$.

Atoms	Length/Å	Atoms	Length/Å
Pb1-Br2^1	2.9258(16)	Pb1-Br3	3.1419(16)
Pb1-Br2	3.1999(16)	Pb1-Br4^1	3.2323(15)
Pb1-Br3^1	2.9351(16)	Pb1-Br4	2.8657(15)
Atoms	Angle/°	Atoms	Angle/°
Br2^1-Pb1-Br2	172.00(5)	Br3^1-Pb1-Br4^1	81.66(4)
Br2^1-Pb1-Br3	95.34(4)	Br4-Pb1-Br2	83.29(4)
Br2^1-Pb1-Br3^1	88.45(5)	Br4-Pb1-Br2^1	89.65(5)
Br2^1-Pb1-Br4^1	81.79(4)	Br4-Pb1-Br3^1	88.94(4)
Br2-Pb1-Br4^1	105.78(4)	Br4-Pb1-Br3	84.34(4)
Br3-Pb1-Br2	80.27(4)	Br4-Pb1-Br4^1	167.41(4)
Br3^1-Pb1-Br2	95.15(4)	Pb1^2-Br2-Pb1	79.43(4)
Br3^1-Pb1-Br3	172.25(5)	Pb1^2-Br3-Pb1	80.26(3)
Br3-Pb1-Br4^1	105.54(4)	Pb1-Br4-Pb1^2	79.76(4)

Symmetry codes: ^{1}-1/2+X, 3/2-Y, 1-Z; ^{2}1/2+X, 3/2-Y, 1-Z

Table S3 Hydrogen bonds for (*R*-3-FPD)$PbBr_3$.

D-Hd···A	d(D-H)/Å	d(H···A)/Å	d(D···A)/Å	<DHA/°
N(1)-H(1A)···Br(4)[2]	0.89	2.90	3.463(11)	122.9
N(1)-H(1B)···Br(3)	0.89	2.64	3.484(12)	158.1
C(4)-H(4B)···F(3)[1]	0.97	2.57	3.177(19)	120.6
N(1)-H(1B)···F(3)[1]	0.89	2.57	2.896(16)	102.7
N(1)-H(1A)···F(3)[1]	0.89	2.64	2.896(16)	97.7

Symmetry codes: [1]-1/2+X, 5/2-Y, 1-Z; [2]1/2+X, 3/2-Y, 1-Z

Table S4 Selected Pb−Br bond lengths [Å] and Br−Pb−Br bond angles [°] for (3,3-DFPD)$_2PbBr_4$.

Atoms	Length/Å	Atoms	Length/Å
Pb1-Br3	2.9906(15)	Pb2-Br5[2]	3.1978(14)
Pb1-Br6	2.9514(14)	Pb2-Br5	2.9533(14)
Pb1-Br6[1]	3.1817(15)	Pb2-Br8	3.0749(15)
Pb1-Br7	2.9931(15)	Pb2-Br9	2.8736(14)
Pb1-Br10	2.8735(14)	Pb2-Br10	3.2699(14)
Pb2-Br4	2.9207(14)		
Atoms	**Angle/°**	**Atoms**	**Angle/°**
Br3-Pb1-Br6[1]	89.50(4)	Br5-Pb2-Br5[2]	175.689(17)
Br3-Pb1-Br7	171.75(4)	Br5-Pb2-Br8	83.09(4)
Br6-Pb1-Br3	89.29(4)	Br5[2]-Pb2-Br10	74.80(4)
Br6-Pb1-Br6[1]	177.934(18)	Br5-Pb2-Br10	103.39(5)
Br6-Pb1-Br7	82.47(4)	Br8-Pb2-Br5[2]	100.92(4)
Br7-Pb1-Br6[1]	98.75(4)	Br8-Pb2-Br10	95.38(4)
Br10-Pb1-Br3	91.07(5)	Br9-Pb2-Br4	88.57(5)
Br10-Pb1-Br6	89.47(5)	Br9-Pb2-Br5	89.25(5)
Br10-Pb1-Br6[1]	92.23(5)	Br9-Pb2-Br5[2]	92.40(4)
Br10-Pb1-Br7	88.42(5)	Br9-Pb2-Br8	88.84(4)
Br4-Pb2-Br5[2]	88.63(4)	Br9-Pb2-Br10	167.05(5)
Br4-Pb2-Br5	87.43(4)	Pb2-Br5-Pb2[3]	166.33(6)
Br4-Pb2-Br8	170.21(4)	Pb1-Br6-Pb1[4]	168.79(7)
Br4-Pb2-Br10	89.20(4)	Pb1-Br10-Pb2	176.63(7)

Symmetry codes: [1]1/2+X,-1/2-Y,-1/4-Z; [2]-1/2+X, -3/2-Y, -1/4-Z; [3]1/2+X,-3/2-Y,-1/4-Z; [4]-1/2+X, -1/2-Y, -1/4-Z

Table S5 Hydrogen bonds for $(3,3\text{-DFPD})_2PbBr_4$.

D-Hd···A	d(D-H)/Å	d(H···A)/Å	d(D···A)/Å	<DHA/°
N(3)-H(3A)···Br(7)[1]	0.89	2.6	3.476(15)	168.4
N(1)-H(1A)···Br(8)	0.89	2.44	3.312(12)	166.9
N(4)-H(4A)···Br(7)[3]	0.89	2.48	3.371(12)	176.4
N(4)-H(4B)···Br(3)[1]	0.89	2.49	3.349(11)	161.8
N(15)-H(15A)···Br(8)[5]	0.89	2.6	3.492(19)	178.1
N(15)-H(15B)···Br(4)	0.89	2.47	3.319(18)	159.4
C(1)-H(1C)···F(74)[2]	0.97	2.42	3.36(2)	163.0
C(6)-H(6B)···F(21)	0.97	2.43	3.39(2)	173.3
C(18)-H(18A)···F(8)	0.97	2.38	3.35(2)	177.6
C(45)-H(45B)···F(74)[6]	0.97	2.44	3.36(2)	158.3

Symmetry codes: [1]1/2-X,1/2+Y,1/4-Z; [2]1/2-Y,-1/2+X,1/4+Z; [3]1+X,1+Y,+Z; [4]3/2-X,1/2+Y,1/4-Z;[5]1/2-X,-1/2+Y,1/4-Z; [6]1+Y,-1+X,-Z