Supplementary Information

H/F substitution activating tunable dimensions and dielectric-optical properties in organic lead-bromide hybrids

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Synthesis. All the chemical reagents were purchased from a commercial approach and used without further purification. All compounds referred to in the paper were synthesized in a general procedure by mixing the piperidine derivatives and $PbBr_2$ in a concentrated hydrobromic acid solution. Specifically, 4,4-difluoropiperidine (10 mmol) and $PbBr_2$ (5 mmol) were dissolved in a concentrated hydrobromic acid solution (20 mL) with continuous stirring for 30 minutes. Then the clear solution was slowly evaporated at 60 ºC and a larger number of transparent crystals of $[4,4\text{-DFPD}]_2PbBr_4$ were collected after two days. For $[4\text{-FPD}]_6Pb_5Br_{16}$, transparent crystals were obtained by the slow evaporation of hydrobromic acid solution containing 4-fluoropiperidine (5 mmol) and $PbBr_2$ (5 mmol) for two days. Concerning $[PD]PbBr_3$, piperidine hydrobromide (6 mmol) and $PbBr_2$ (4 mmol) were mixed in hydrobromic acid (10 mL), and then the mixture was slowly evaporated at 60 ºC to receive strip crystals. Their purity confirmed by powder X-ray diffraction is shown in Figure S1.

Single-crystal X-ray crystallography. Variable-temperature single-crystal X-ray diffraction measurements of $[PD]PbBr_3$, $[4\text{-FPD}]_6Pb_5Br_{16}$ and $[4,4\text{-DFPD}]_2PbBr_4$ were carried out by Rigaku Oxford Diffraction 2018 diffractometer with Mo-Kα radiation (λ = 0.71073 Å). Crystal data was collected with the Crystalclear software package (Rigaku, 2018). Olex2 software was utilized to solve the crystal structures in a direct method and the refinement of crystal structures on F^2 was performed on the SHELXLTL software package (SHELXLTL-2014) in the full-matrix least-squares manner. Due to the disordered structures of $[PD]PbBr_3$, $[4\text{-FPD}]_6Pb_5Br_{16}$, and $[4,4\text{-DFPD}]_2PbBr_4$ in the high-temperature phase (HTP), some restriction instructions should be adopted to handle the disordered cations. All non-hydrogen atoms were refined with anisotropy, and all H atoms were generated geometrically at the calculated positions. Drawing of asymmetric units and packing diagrams of crystals was conducted on the Diamond software. CSD deposition numbers **2195159-2195167** can be obtained free of charge from the CCDC via www.ccdc.cam.ac.uk/getstructures.

Thermal measurements. Differential scanning calorimetry (DSC) measurements of $[PD]PbBr_3$, $[4\text{-FPD}]_6Pb_5Br_{16}$ and $[4,4\text{-DFPD}]_2PbBr_4$ were performed on the

NETZCSCH DSC 214 instrument. The polycrystalline samples were placed into an aluminum crucible and were measured with a heating/cooling rate of 20 K min^{-1} under nitrogen. Thermal stability was measured on polycrystalline powder samples by PerkinElmer TGA 8000 at a rate of 30 K min^{-1} in a nitrogen atmosphere.

Dielectric measurements. Complex dielectric permittivity ε ($\varepsilon = \varepsilon' - i\varepsilon''$) measurements were performed on a Tonghui TH2828A using the polycrystalline sample, which was pressed into cylindrical tablets. Then silver glue equably on both sides of those tablets was applied and connected with a socket by copper wire to form a capacitor.

Second harmonic generation measurement. The second harmonic generation (SHG) measurements were performed on an Ins 1210058 optical testing stage (INSTEC Instruments) with a Vibrant 355 II laser generator (OPOTEK). The laser beam was excited by pulsed Nd:YAG at a wavelength of 1064 nm, 5 ns pulse duration, 1.6 MW peak power and 10 Hz repetition rate.

Ultraviolet−visible absorption. UV−vis diffuse reflectance spectroscopy measurements were carried out on a Shimadzu (Tokyo, Japan) UV-3600 Plus spectrophotometer operating at room temperature from 200 to 900 nm with $BaSO_4$ used as a 100% reflectance reference.

Fluorescence spectra. Fluorescence was detected by a commercial Raman spectrometer equipped with a syncerity OE detector (Horiba, LabRAM HR Evolution) under a 325 nm He-Cd laser excitation with the reflection method. The photoluminescence spectra were dispersed by a 600-groove per millimeter diffraction grating and accumulated 3 times with exposing 3 seconds at each measurement.

Powder X-ray diffraction. Powder X-ray diffraction (PXRD) patterns were performed on a Rigaku D/MAX 2000 with Cu-Kα radiation. The measurement in the angle ranges from 5 to 50° with a step size of 0.02˚.

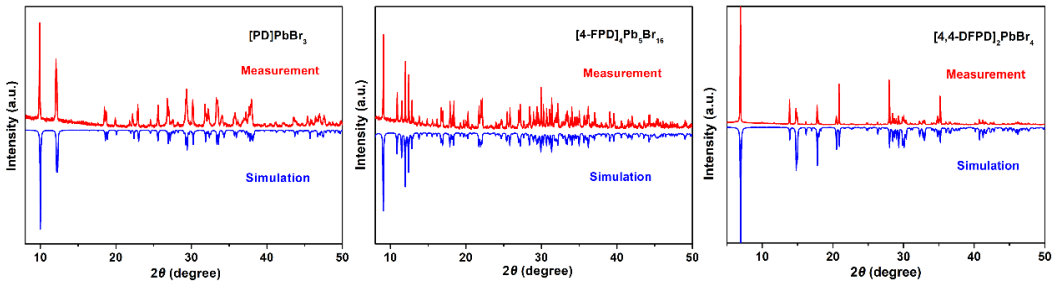

Figure S1. The phase purity of [PD]$PbBr_3$, [4-FPD]$_6Pb_5Br_{16}$, and [4,4-DFPD]$_2PbBr_4$.

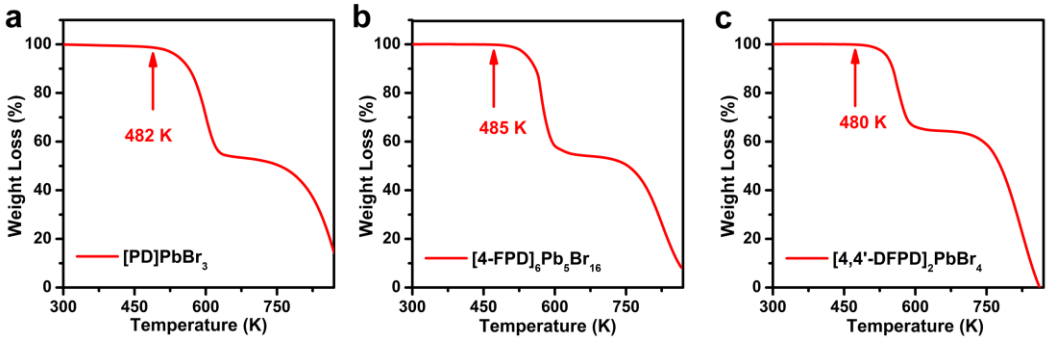

Figure S2. TG curves for [PD]$PbBr_3$ (a), [4-FPD]$_6Pb_5Br_{16}$ (b), and [4,4-DFPD]$_2PbBr_4$ (c).

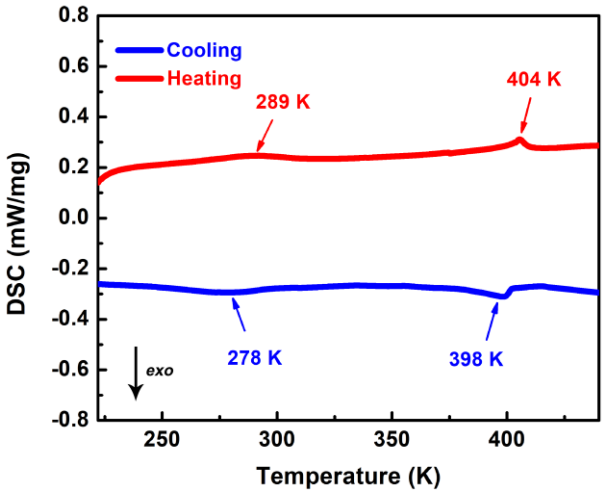

Figure S3. DSC curve in a heating and cooling run for [PD]$PbBr_3$. The arrow of exo indicates the exothermic direction.

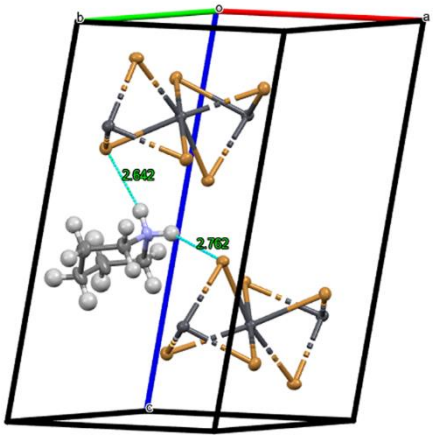

Figure S4. Weak N−H···Br hydrogen bonding interactions between PD cations and inorganic framework in [PD]$PbBr_3$ at 197 K.

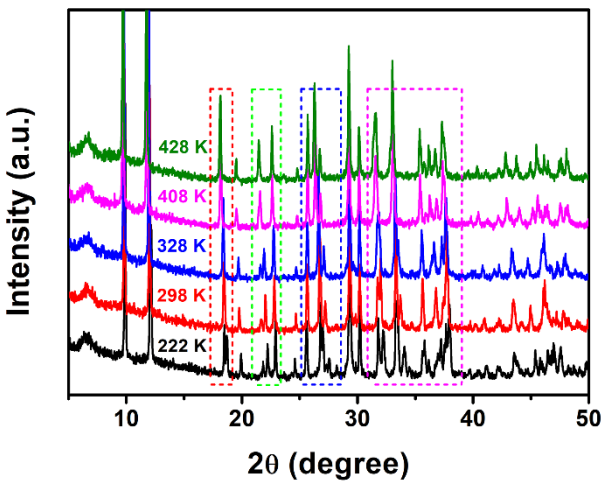

Figure S5. Variable-temperature PXRD patterns of [PD]$PbBr_3$.

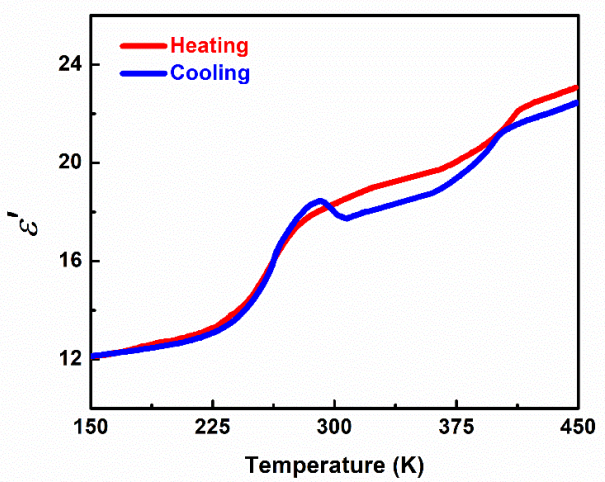

Figure S6. The temperature-dependent real part of the dielectric constant (ε') performed on the powder sample of [PD]$PbBr_3$ at 1 MHz.

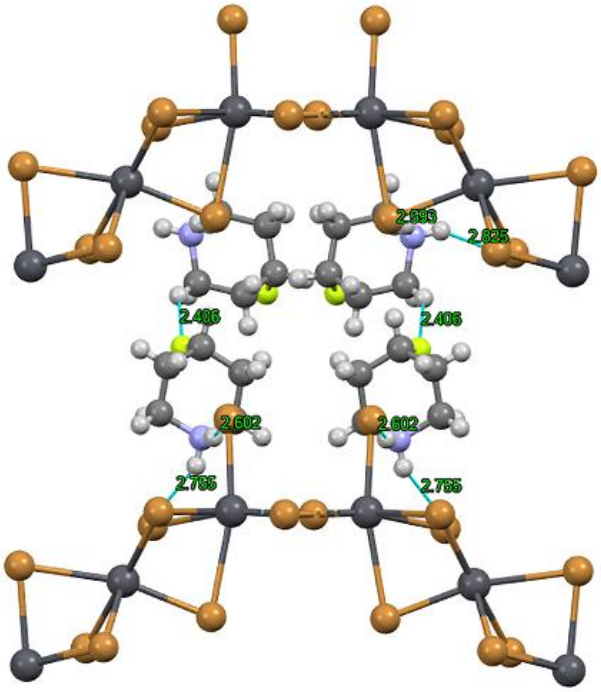

Figure S7. Hydrogen bonds of C–H···F and N–H···Br existed between 4-FPD cations and between 4-FPD cations and inorganic framework in $[4\text{-FPD}]_6Pb_5Br_{16}$.

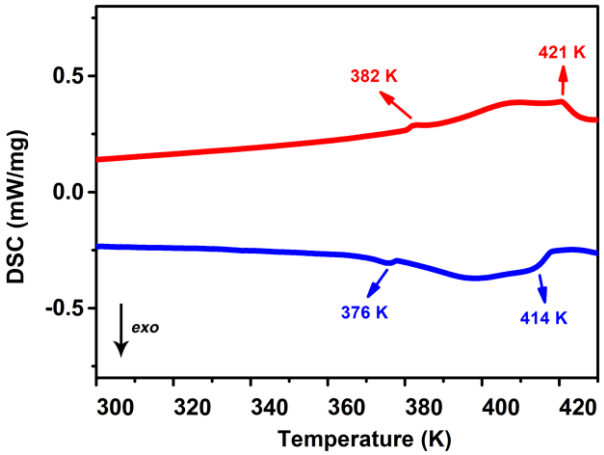

Figure S8. DSC curve in heating and cooling run for $[4\text{-FPD}]_6Pb_5Br_{16}$. The arrow of exo indicates the exothermic direction.

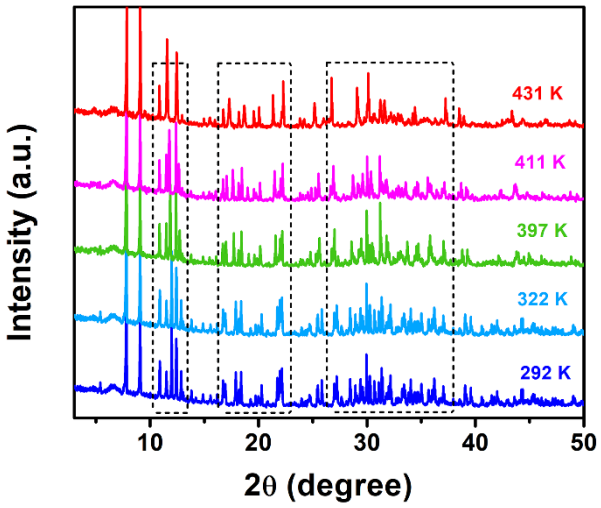

Figure S9. Variable-temperature PXRD patterns of $[4\text{-FPD}]_6Pb_5Br_{16}$.

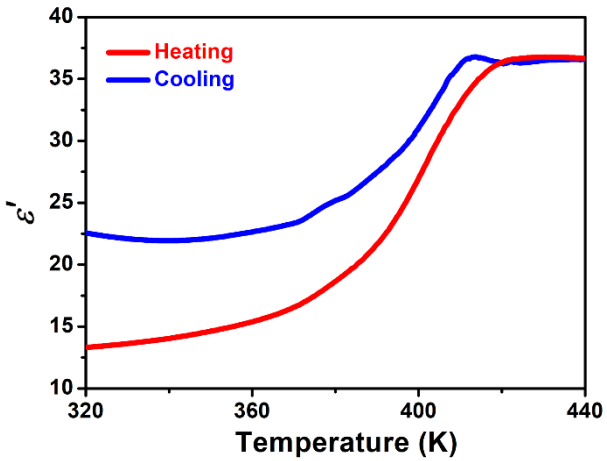

Figure S10. The temperature-dependent real part of the dielectric constant (ε') performed on the powder sample of $[4\text{-FPD}]_6Pb_5Br_{16}$ at 1 MHz.

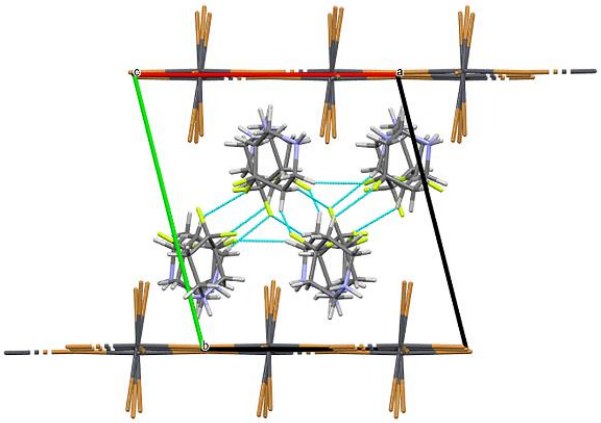

Figure S11. Complex hydrogen bonds existed between 4,4-DFPD cations in [4,4-DFPD]$_2$PbBr$_4$.

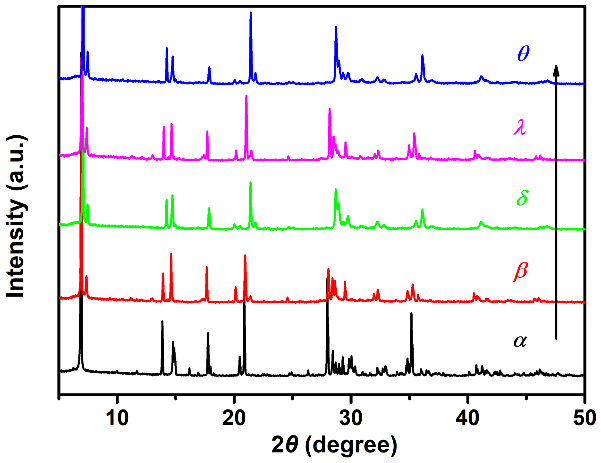

Figure S12. Variable-temperature PXRD patterns of [4,4-DFPD]$_2$PbBr$_4$. The black arrow denotes subsequential test order.

Table S1. Crystal structure and refinement details of $[PD]PbBr_3$ and $[4\text{-}FPD]_6Pb_5Br_{16}$.

Compounds	$[PD]PbBr_3$	$[PD]PbBr_3$	$[PD]PbBr_3$	$[4\text{-}FPD]_6Pb_5Br_{16}$	$[4\text{-}FPD]_6Pb_5Br_{16}$
Temperature	197 K	323 K	423 K	299 K	440 K
Crystal	Monoclinic	Monoclinic	Orthorhombic	Monoclinic	Orthorhombic
Formula	533.06	533.06	533.06	2931.17	2931.17
Space	$P2_1/n$	$P2_1/n$	$Cmcm$	$P2_1/c$	$Cmca$
a / Å	9.6329(3)	9.8560(5)	8.2943(6)	12.5612(5)	8.3832(7)
b / Å	7.9359(2)	7.8629(4)	18.2287(15)	32.8585(16)	24.1380(15)
c / Å	14.9282(5)	15.1092(7)	7.8044(5)	8.1977(3)	33.398(2)
α / deg	90	90	90	90	90
β / deg	102.867(3)	102.382(5)	90	104.943(4)	90
γ / deg	90	90	90	90	90
V / Å^3	1112.54(6)	1143.68(10)	1179.98(15)	3269.1(2)	6758.2(8)
Z	4	4	2	2	4
Radiation	Mo-Kα	Mo-Kα	Mo-Kα	Mo-Kα	Mo-Kα
Dcalc / g	3.182	3.096	1.466	2.978	2.889
GOF	1.059	1.047	1.070	1.028	1.019
R_1	0.0446	0.0593	0.0658	0.0354	0.0465
wR_2	0.1374	0.1853	0.2058	0.0692	0.1369

Table S2. Hydrogen bonds for $[PD]PbBr_3$ at 197 K

D-H···A	d(D-H)/Å	d(H···A)/Å	d(D···A)/Å	∠DHA/°
N(8)-H(8A)···Br(3)	0.91	2.64	3.534(8)	166.7
N(8)-H(8B)···Br(2)[1]	0.91	2.76	3.538(8)	143.9

Symmetry codes: [1] 1-X,1-Y,1-Z

Table S3. Hydrogen bonds for $[4\text{-FPD}]_6Pb_5Br_{16}$ at 299 K

D-H···A	d(D-H)/Å	d(H···A)/Å	d(D···A)/Å	∠DHA/°
C(3)-H(3)···F(1)[1]	0.98	2.86	3.511(13)	124.2
N(1)-H(1A)···Br(1)[2]	0.89	2.6	3.464(7)	163.2
N(1)-H(1B)···Br(3)[3]	0.89	2.76	3.464(7)	137.5
N(1)-H(1B)···Br(4)[2]	0.89	3	3.540(7)	120.7
C(9)-H(9A)···F(1)[4]	0.97	2.74	3.353(11)	121.7
C(1)-H(1C)···F(12A)[1]	0.97	2.48	3.422(13)	162.8
C(10)-H(10)···F(1)[4]	0.98	2.78	3.459(11)	126.8
C(4)-H(4A)···F(1)[1]	0.97	2.82	3.495(13)	127.1
C(8)-H(8A)···F(23)	0.97	2.41	3.216(10)	140.7
N(2)-H(2C)···Br(7)[5]	0.89	2.82	3.477(7)	131.3
N(2)-H(2C)···Br(8)	0.89	2.92	3.511(7)	125.8
N(2)-H(2D)···Br(5)	0.89	2.59	3.447(7)	161.2
N(3)-H(3A)···Br(6)[6]	0.89	2.83	3.609(13)	146.8
N(3)-H(3B)···Br(8)[7]	0.89	2.71	3.583(12)	167.2
C(14)-H(14A)···F(12A)[8]	0.97	2.62	3.518(17)	154.3
C(15)-H(15A)···Br(4)[7]	0.97	2.88	3.609(17)	132.3

Symmetry codes: [1]+X,+Y,1+Z; [2]1+X,+Y,1+Z; [3]1+X,+Y,+Z; [4]+X,1/2-Y,1/2+Z; [5]+X,+Y,-1+Z; [6]1-X,-Y,1-Z; [7]1-X,-Y,-Z; [8]2-X,-Y,-Z

Table S4. Selected Bond lengths [Å] and bond angles [°] for $[4\text{-FPD}]_6Pb_5Br_{16}$ at 299 K.

Pb(1)-Br(1)	2.8194(9)	Pb(2)-Br(3)	2.9659(9)
Pb(1)-Br(3)	3.1643(10)	Pb(2)-Br(4)	3.0067(9)
Pb(1)-Br(4)	3.0577(10)	Pb(2)-Br(8)	3.0764(10)
Pb(1)-Br(2)#1	3.0044(11)	Pb(2)-Br(6)	3.2074(11)
Pb(1)-Br(2)	2.9111(10)	Pb(3)-Br(7)	3.0266(9)
Pb(2)-Br(5)	2.9012(9)	Pb(3)-Br(8)	3.0154(9)
Pb(2)-Br(7)	3.0547(9)	Pb(3)-Br(6)	3.0298(9)
Br(1)-Pb(1)-Br(3)	94.19(3)	Br(3)-Pb(2)-Br(6)	99.47(3)
Br(1)-Pb(1)-Br(4)	92.90(3)	Br(4)-Pb(2)-Br(8)	88.61(3)
Br(1)-Pb(1)-Br(2) #1	97.50(3)	Br(4)-Pb(2)-Br(6)	108.87(3)
Br(1)-Pb(1)-Br(2)	87.46(3)	Br(8)-Pb(2)-Br(6)	80.38(3)
Br(4)-Pb(1)-Br(3)	83.50(3)	Br(7)#2-Pb(3)-Br(6)	98.25(3)
Br(2)#1-Pb(1)-Br(3)	100.35(3)	Br(7)-Pb(3)-Br(6)	81.75(3)
Br(2)-Pb(1)-Br(4)	85.54(3)	Br(7)-Pb(3)-Br(6)#2	98.25(3)
Br(2)-Pb(1)-Br(2) #1	90.211(12)	Br(7)#2-Pb(3)-Br(6)#2	81.75(3)
Br(5)-Pb(2)-Br(7)	90.64(3)	Br(8)-Pb(3)-Br(7)#2	90.20(3)
Br(5)-Pb(2)-Br(3)	89.80(3)	Br(8)#2-Pb(3)-Br(7)	90.19(3)
Br(5)-Pb(2)-Br(4)	81.39(3)	Br(8)#2-Pb(3)-Br(7)#2	89.80(3)
Br(5)-Pb(2)-Br(8)	91.04(3)	Br(8)-Pb(3)-Br(7)	89.81(3)
Br(7)-Pb(2)-Br(8)	88.16(3)	Br(8)-Pb(3)-Br(6)#2	95.72(3)
Br(7)-Pb(2)-Br(6)	78.49(3)	Br(8)#2-Pb(3)-Br(6)	95.72(3)
Br(3)-Pb(2)-Br(7)	95.52(3)	Br(8)#2-Pb(3)-Br(6)#2	84.28(3)
Br(3)-Pb(2)-Br(4)	87.86(3)	Br(8)-Pb(3)-Br(6)	84.28(3)
Symmetry codes:#1 +X,1/2-Y,1/2+Z; # 2 1-X,-Y,1-Z			

Table S5. Selected Bond lengths [Å] and bond angles [°] for $[4\text{-FPD}]_6Pb_5Br_{16}$ at 440 K.

Br(1)-Pb(1)	2.7908(14)	Pb(2)-Br(3)	3.0154(9)
Pb(1)-Br(3)	3.0846(9)	Pb(2)-Br(6)	3.1691(14)
Pb(1)-Br(2)	2.9983(3)	Pb(2)-Br(4)	2.8833(13)
Pb(3)-Br(6)	3.0251(13)	Pb(2)-Br(5)	3.0597(10)
Pb(3)-Br(5)	3.0105(10)	Br(2)-Pb(1)#5	2.9983(3)
Br(1)-Pb(1)-Br(3)#1	94.66(3)	Br(5)#1-Pb(3)-Br(5)	88.48(4)
Br(1)-Pb(1)-Br(3)	94.65(3)	Br(5)#4-Pb(3)-Br(5)#3	88.48(4)
Br(1)-Pb(1)-Br(2)#2	91.37(4)	Br(5)#4-Pb(3)-Br(5)	91.52(4)
Br(1)-Pb(1)-Br(2)	91.38(4)	Br(5)#1-Pb(3)-Br(5)#3	91.52(4)
Br(3)-Pb(1)-Br(3)#1	84.47(4)	Br(3)#1-Pb(2)-Br(3)	86.88(4)
Br(2)#2-Pb(1)-Br(3)#1	93.108(19)	Br(3)-Pb(2)-Br(6)	104.19(3)
Br(2)-Pb(1)-Br(3)	93.107(19)	Br(3)#1-Pb(2)-Br(6)	104.19(3)
Br(2)#2-Pb(1)-Br(2)	88.692(11)	Br(3)#1-Pb(2)-Br(5)#1	93.07(3)
Br(5)#3-Pb(3)-Br(6)	97.11(3)	Br(3)-Pb(2)-Br(5)	93.07(3)
Br(5)#1-Pb(3)-Br(6)#3	97.11(3)	Br(4)-Pb(2)-Br(3)	83.70(3)
Br(5)#4-Pb(3)-Br(6)	97.11(3)	Br(4)-Pb(2)-Br(3)#1	83.70(3)
Br(5)#4-Pb(3)-Br(6)#3	82.89(3)	Br(4)-Pb(2)-Br(5)#1	92.25(3)
Br(5)-Pb(3)-Br(6)	82.90(3)	Br(4)-Pb(2)-Br(5)	92.24(3)
Br(5)#3-Pb(3)-Br(6)#3	82.89(3)	Br(5)#1-Pb(2)-Br(6)	79.77(3)
Br(5)#1-Pb(3)-Br(6)	82.89(3)	Br(5)-Pb(2)-Br(6)	79.77(3)
Br(5)-Pb(3)-Br(6)#3	97.10(3)	Br(5)-Pb(2)-Br(5)#1	86.70(4)
Symmetry codes:#1 1-X,+Y,+Z; #2 1/2+X,+Y,1/2-Z; #3 1-X,1-Y,-Z; #4 +X,1-Y,-Z			

Table S6. Crystal structure and refinement details of $[4,4\text{-DFPD}]_2PbBr_4$.

Phase	*α*	*δ*	*λ*	*θ*
Temperature (K)	293 K	293 K	420 K	293 K
Crystal System	Triclinic	Orthorhombic	Tetragonal	Orthorhombic
Formula Weight	2312.32	771.11	333.13	1486.02
Space Group	$P\bar{1}$	*Aea*2	*I*4/*mmm*	*Fmmm*
a / Å	12.1732(3)	8.8209(11)	6.2229(5)	8.6355(9)
b / Å	13.4785(4)	24.830(3)	6.2229(5)	24.748(2)
c / Å	18.4607(5)	8.6568(10)	25.276(5)	8.8106(8)
α / deg	76.808(2)	90	90	90
β / deg	89.923(2)	90	90	90
γ / deg	76.288(2)	90	90	90
V / Å^3	2860.53(14)	1896.1(4)	978.8(2)	1882.9(3)
Z	2	4	2	2
Radiation Type	Mo-Kα	Mo-Kα	Mo-Kα	Mo-Kα
Dcalc / g cm^{-3}	2.685	2.701	6.217	2.621
GOF	1.023	1.044	1.014	1.022
R_1	0.0880	0.0903	0.0541	0.0633
wR_2	0.2395	0.2709	0.1378	0.1715

Table S7. Hydrogen bonds for $[4,4\text{-DFPD}]_2PbBr_4$ at 290 K (in α phase)

D-H···A	d(D-H)/Å	d(H···A)/Å	d(D···A)/Å	∠DHA/°
C(00U)-H(00C)···F(00Q)[1]	0.97	2.57	3.47(2)	153.8
C(00U)-H(00D)···F(00P)[2]	0.97	2.74	3.38(2)	123.7
C(00V)-H(00G)···F(1)[3]	0.97	2.63	3.24(2)	121.2
C(00V)-H(00G)···F(00T)[2]	0.97	2.69	3.48(2)	139.3
C(00Z)-H(00A)···F(00J)[4]	0.97	2.52	3.37(2)	146.1
C(011)-H(01B)···F(00Y)[5]	0.97	2.67	3.42(2)	135
C(012)-H···F(00J)[5]	0.97	2.82	3.61(2)	139.8
C(012)-H···F(00P)[6]	0.97	2.94	3.63(3)	128.5
C(015)-H(01U)···F(00I)[8]	0.97	2.85	3.63(3)	138.7
C(015)-H(01U)···F(00N)	0.97	2.94	3.62(2)	128.5
C(017)-H(01R)···F(00I)	0.97	2.53	3.34(2)	141.7
C(01A)-H(01M)···F(00N)[1]	0.97	2.84	3.43(3)	120.7
C(01A)-H(01N)···F(00O)[1]	0.97	2.56	3.45(2)	152.4
C(01B)-H(5)···F(00O)[3]	0.97	2.72	3.46(2)	132.7
C(01D)-H(01F)···F(00Q)[10]	0.97	2.71	3.53(2)	142.5
C(01F)-H(2)···F(00O)[11]	0.97	2.91	3.56(2)	125
C(01F)-H(2)···F(00T)[6]	0.97	2.84	3.61(2)	137.2
C(01I)-H(F)···F(00Q)[12]	0.97	2.89	3.57(3)	128.1
C(01I)-H(F)···F(00Y)[9]	0.97	2.86	3.65(2)	138.9
N(00X)-H(00E)···Br(06)	0.89	2.55	3.424(14)	167.2
N(00X)-H(00F)···Br(09)	0.89	2.49	3.288(14)	150.2
N(013)-H(01K)···Br(0A)[7]	0.89	2.52	3.308(15)	148.7
N(013)-H(01L)···Br(05)[7]	0.89	2.5	3.371(15)	166.8
N(016)-H(01C)···Br(06)[7]	0.89	2.81	3.466(14)	131.8
N(016)-H(01D)···Br(0A)	0.89	2.62	3.465(18)	159.4
N(018)-H(1)···Br(08)	0.89	2.51	3.371(14)	162.7
N(018)-H(A)···Br(0E)[6]	0.89	2.87	3.620(13)	143.6
N(01C)-H(6)···Br(05)[9]	0.89	2.75	3.425(14)	133.2
N(01C)-H(C)···Br(09)	0.89	2.62	3.460(16)	157
N(01G)-H(01W)···Br(07)[9]	0.89	2.5	3.366(16)	165.6
N(01G)-H(01X)···Br(0D)	0.89	2.95	3.675(15)	139.3

Symmetry codes: [1]+X,-1+Y,+Z; [2]1-X,1-Y,2-Z; [3]1+X,-1+Y,+Z; [4]-1+X,+Y,+Z; [5]-1+X,1+Y,+Z; [6]-X,2-Y,2-Z; [7]-X,2-Y,1-Z; [8]+X,1+Y,+Z; [9]1-X,2-Y,1-Z; [10]-X,3-Y,1-Z; [11]-X,3-Y,2-Z; [12]1-X,3-Y,1-Z

Table S8. Selected Bond lengths [Å] and bond angles [°] for $[4,4\text{-DFPD}]_2PbBr_4$ at 290 K (in *a* phase).

Pb(1)-Br(6)	2.9185(12)	Pb(2)-Br(C)#1	3.2208(11)
Pb(1)-Br(A)	3.0218(13)	Pb(2)-Br(E)#2	3.2264(12)
Pb(1)-Br(B)	3.0632(4)	Pb(2)-Br(F)	2.9797(13)
Pb(1)-Br(D)	3.0197(13)	Pb(3)-Br(4)#3	3.2374(11)
Pb(1)-Br(F)	3.1119(13)	Pb(3)-Br(8)	2.9956(13)
Pb(1)-Br(G)	3.0579(4)	Pb(3)-Br(9)	2.9946(13)
Pb(2)-Br(4)	2.9093(11)	Pb(3)-Br(C)	2.9009(12)
Pb(2)-Br(5)	2.9491(13)	Pb(3)-Br(D)	3.1945(13)
Pb(2)-Br(7)	3.0027(12)	Pb(3)-Br(E)	2.9968(12)
Br(6)-Pb(1)-Br(B)	86.68(3)	Br(5)-Pb(2)-Br(F)	85.54(4)
Br(6)-Pb(1)-Br(D)	88.07(4)	Br(7)-Pb(2)-Br(C)#1	97.06(3)
Br(6)-Pb(1)-Br(F)	92.21(4)	Br(7)-Pb(2)-Br(E)#2	103.54(4)
Br(6)-Pb(1)-Br(G)	91.84(3)	Br(C)#1-Pb(2)-Br(E)#2	77.79(4)
Br(A)-Pb(1)-Br(B)	82.14(3)	Br(F)-Pb(2)-Br(7)	82.02(4)
Br (A) -Pb(1)-Br (F)	90.97(4)	Br(F)-Pb(2)-Br(C)#1	98.03(4)
Br(A)-Pb(1)-Br(G)	99.99(3)	Br(8)-Pb(3)-Br(4)#3	95.91(3)
Br(B)-Pb(1)-Br(F)	84.43(3)	Br(8)-Pb(3)-Br(D)	103.50(4)
Br(D)-Pb(1)-Br(A)	89.80(4)	Br(8)-Pb(3)-Br (E)	82.09(4)
Br(D)-Pb(1)-Br(B)	100.70(3)	Br(9)-Pb(3)-Br(4)#3	80.60(3)
Br(D)-Pb(1)-Br(G)	91.32(3)	Br(9)-Pb(3)-Br(D)	87.72(3)
Br(G)-Pb(1)-Br(F)	83.55(3)	Br(9)-Pb(3)-Br(E)	86.94(4)
Br(4)-Pb(2)-Br(5)	86.89(3)	Br(C)-Pb(3)-Br(8)	89.16(3)
Br(4)-Pb(2)-Br(7)	88.54(3)	Br(C)-Pb(3)-Br(9)	96.95(4)
Br(4)-Pb(2)-Br (E)#2	87.37(4)	Br(C)-Pb(3)-Br(D)	87.03(4)
Br(4)-Pb(2)-Br(F)	96.53(4)	Br(C)-Pb(3)-Br(E)	90.81(4)
Br(5)-Pb(2)-Br(C)#1	90.62(3)	Br(D)-Pb(3)-Br(4)#3	79.56(3)
Br(5)-Pb(2)-Br(E)#2	89.29(4)	Br(E)-Pb(3)-Br(4)#3	102.32(4)
Symmetry codes:#1 -X,2-Y, 1-Z; #2 +X,+Y,-1+Z; #3 1-X,2-Y,1-Z			

Table S9. Selected Bond lengths [Å] and bond angles [°] for $[4,4\text{-DFPD}]_2PbBr_4$ at 293 K (in δ phase).

Pb(1)-Br(2)#1	3.060(3)	Pb(1)-Br(3)	2.9516(17)
Pb(1)-Br(2)	3.167(3)		
Br(2)#1-Pb(1)-Br(2)#2	86.68(11)	Br(3)#3-Pb(1)-Br(2)#3	88.32(6)
Br(2)#2-Pb(1)-Br(2)#3	89.493(9)	Br(3)#3-Pb(1)-Br(2)	94.02(6)
Br(2) #3-Pb(1)-Br(2)	94.34(10)	Br(3)-Pb(1)-Br(2)#1	86.26(6)
Br(2)#1-Pb(1)-Br(2)	89.492(8)	Br(3)#3-Pb(1)-Br(2)#2	86.26(6)
Br(3)-Pb(1)-Br(2)	88.32(6)	Br(3)-Pb(1)-Br(2)#3	94.03(6)
Br(3)-Pb(1)-Br(2)#2	91.23(6)	Br(3)#3-Pb(1)-Br(2)#1	91.23(6)
Symmetry codes:#1 -1/2-X,+Y,1/2+Z; #2 -1/2+X,-Y,1/2+Z; #3 -1-X,-Y,+Z			

Table S10. Selected Bond lengths [Å] and bond angles [°] for $[4,4\text{-DFPD}]_2PbBr_4$ at 420 K (in λ phase).

Pb(1)-Br(2)	3.1114(3)	Pb(1)-Br(0)	2.918(3)
Br(2)#1-Pb(1)-Br(2)#2	90.0	Br(0)-Pb(1)-Br(2)#2	90.0
Br(2)-Pb(1)-Br(2)#2	90.0	Br(0)#4-Pb(1)-Br(2)#3	90.0
Br(2)#1-Pb(1)-Br(2)#3	90.0	Br(0)#4-Pb(1)-Br(2)	90.0
Br(2)-Pb(1)-Br(2)#3	90.0	Br(0)-Pb(1)-Br(2)#1	90.0
Br(0)-Pb(1)-Br(2)	90.0	Br(0)-Pb(1)-Br(2)#3	90.0
Br(0)#4-Pb(1)-Br(2)#1	90.0	Br(0)#4-Pb(1)-Br(2)#2	90.0
Symmetry codes:#1 +X,1+Y,+Z; #2 -Y,+X,+Z; #3 1-Y,+X,+Z; #4 1-X,1-Y,1-Z			

Table S11. Selected Bond lengths [Å] and bond angles [°] for $[4,4\text{-DFPD}]_2PbBr_4$ at 293 K (in θ phase).

Pb(1)-Br(2)	3.0842(2)	Pb(1)-Br(3)	2.9345(13)
Br(2)#1-Pb(1)-Br(2)#2	91.150(8)	Br(3)-Pb(1)-Br(2)	90.0
Br(2)#1-Pb(1)-Br(2)#3	88.850(8)	Br(3)#4-Pb(1)-Br(2)#1	90.0
Br(2)-Pb(1)-Br(2)#3	91.150(8)	Br(3)#4-Pb(1)-Br(2)#3	90.0
Br(2)-Pb(1)-Br(2)#2	88.850(8)	Br(3)-Pb(1)-Br(2)#1	90.0
Br(3)#4-Pb(1)-Br(2)#2	90.0	Br(3)#4-Pb(1)-Br(2)	90.0
Br(3)-Pb(1)-Br(2)#3	90.0	Br(3)-Pb(1)-Br(2)#2	90.0
Symmetry codes:#1 -1/2+X,+Y,-1/2+Z; #2 2-X,1-Y,+Z; #3 5/2-X,1-Y,-1/2+Z; #4 2-X,1-Y,2-Z			