Electronic Supplementary Material (ESI) for Inorganic Chemistry Frontiers.

Supplementary information

Structural phase transition drives outright photoluminescence quenching and dielectric duple bistable

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Experimental Section

Detailed methods of measurements

Single-crystal X-ray diffraction. Single crystal X-ray diffraction data for (TEMA)$PbBr_3$, (TECM) $PbBr_3$ and (TEBM)$PbBr_3$ were obtained using a Rigaku Saturn 724 diffractometer using Mo-Kα Radiation (λ= 0.71073 Å). The refinement of the structure factor was achieved by the method of least squares on SHELXT and OLEX2 software packages. The figures of three compounds were displayed by Diamond and VESTA software. Table S1-S6 summarize the data collection and bond length and bond angle of these crystals. These X-ray crystal structures have been stored at the Cambridge Crystallography Data Center (storage number CCDC 2329832-2329835) and are available free of charge from CCDC at www.ccdc.cam.ac.uk/getstructures.

Differential Scanning Calorimetry (DSC). DSC measurement was performed on powder sample of (TEMA) $PbBr_3$, (TECM) $PbBr_3$ and (TEBM) $PbBr_3$ by a NETZSCH-214 instrument. The sample was placed in aluminum crucible under nitrogen at atmospheric pressure. The experiment was conducted under nitrogen and atmospheric pressure, with heating and cooling rates of 20 $K \cdot min^{-1}$.

Dielectric Measurements. The temperature-dependent dielectric permittivity ε ($\varepsilon = \varepsilon' - \varepsilon''$, where ε' is the real part, and ε'' is the imaginary part) of these four compounds was performed through a Tonghui TH2828A Precision LCR meter with an AC voltage of 1 V. The powder is pressed into thin sheets, and the copper wire and sample are made into electrodes using silver glue. then, measure the dielectric constant of the sample at different temperatures and frequencies using the TH2828A instrument.

Powder X-ray diffraction. Powder X-ray diffraction (PXRD) measurements were performed at room temperature on a Rigaku D/MAX 2000 PC X-ray diffractometer. The diffraction pattern is recorded at 2θ between 5-50° within the range, the step size is 0.02°. Variable temperature powder X-ray diffraction pattern tested in the temperature range of 298-463K through programmed heating and cooling.

Infrared (IR) Spectroscopy. Firstly, mix the dry sample with KBr powder in a 1:100 ratio, grind and press it into a transparent and smooth thin sheet, and The IR spectra of these three compounds were charactered at room temperature using a Shimadzu IR-60 spectrometer in the range from 4000 to 400 cm^{-1}.

UV-visible (UV-vis) Spectrophotometry. UV-vis absorption spectra of these compounds were characterized using a Shimadzu UV-2600 spectrophotometry equipped with a xenon lamp as the excitation source at room temperature. The calculated optical bandgaps (E_g) are based on Tauc equation (1), where α is the absorption coefficient, h is Planck′s constant, v is the frequency of vibration and A is the proportional constant. The value of the exponent n denotes the nature of the sample transition when n = 2 represents the indirect bandgap of semiconductors and n =1/2 represents the direct bandgap of semiconductors.

$$(\alpha hv)^{1/n} = A(hv - Eg) \quad (1)$$

Raman Spectroscopy

Raman spectroscopy measurements were carried out using the Horiba LabRAM HR-800 spectrometer with gratings of 600 and 1800 mm^{-1}. A solid-state laser with the wavelength of 532 nm and the power of 10 mW was used as an excitation source. An Olympus BX41 microscope with the (10x)/0.75 numerical aperture objective lens was used to focus the laser beam on a sample surface.

Density Functional Theory (DFT) Calculations. The band structure and partial density state were performed based on density function theory (DFT) by using the Vienna Ab-initio Simulation Package (VASP).[1] Firstly, the crystallographic structures of compounds obtained from SC-XRD measurement were further optimized geometrically, employing the exchange-correlation interactions within the generalized gradient approximation (GGA) on the basis of the Perdew-Burke-Ernzerh (PBE) function.[2] Secondly, the band structure and partial density state of optimized structures were calculated by the PBE function with considering spin-orbit coupling (SOC) and without considering SOC, respectively. Meanwhile, the plane wave cut-off energy, the force and energy convergence criterions were set to be 520 eV, 0.02 eV/Å and 10^{-6} eV per atom, respectively, and the mesh samplings in the Brillouin zone were 1 × 1 × 2 for (TEMA)$PbBr_3$ and (TECA)$PbBr_3$ and 2 × 2 × 4 for (TEBA)$PbBr_3$. In addition, the other parameters and convergent criteria were the default values. Finally, the post-processing analysis was performed by using VASPKIT.[3]

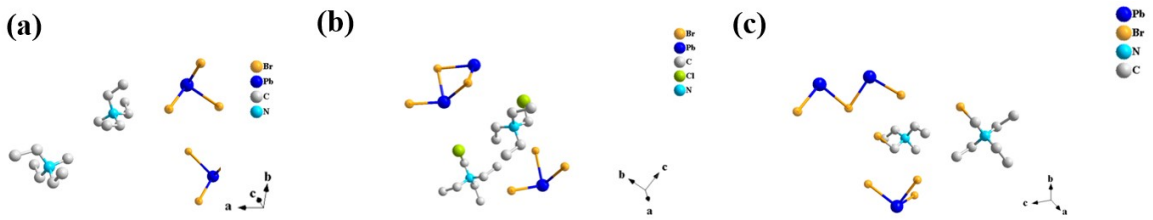

Fig. S1 The Molecular structure units of (TEMA)$PbBr_3$ (a), (TECA) $PbBr_3$ (b) and (TEBA)$PbBr_3$.

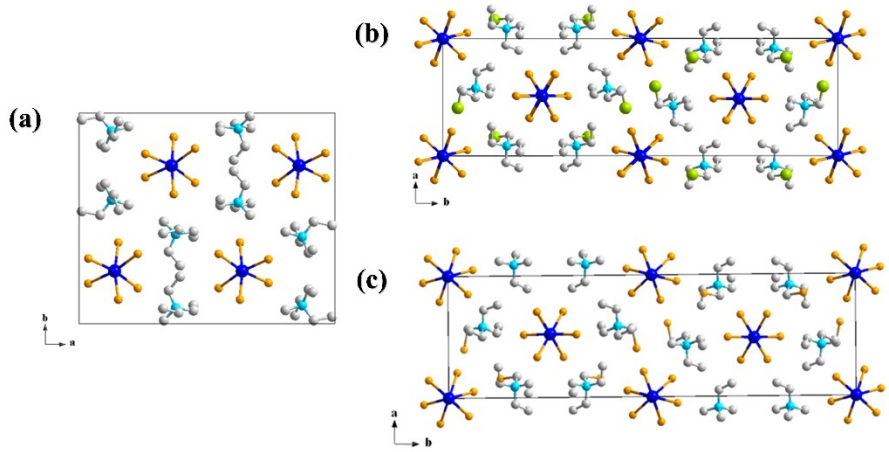

Fig. S2 The packing structures (without hydrogen atoms) of (TEMA)$PbBr_3$ (a), (TECA) $PbBr_3$ (b) and (TEBA)$PbBr_3$.

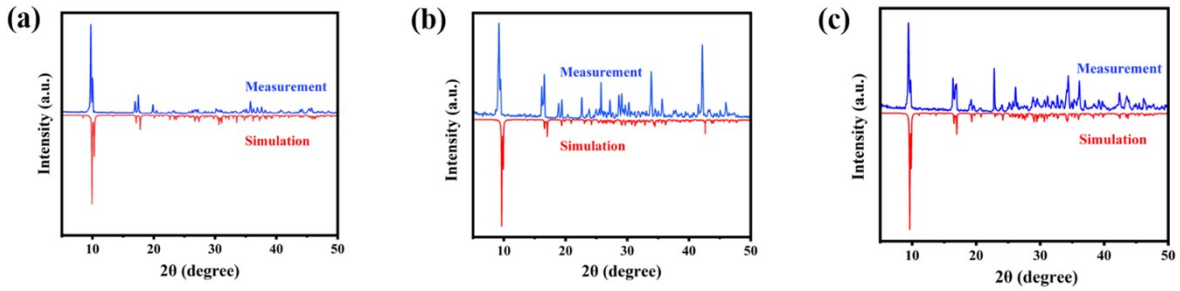

Fig. S3 The measured and simulated PXRD patterns of (TEMA)$PbBr_3$ (a), (TECA) $PbBr_3$ (b) and (TEBA)$PbBr_3$ (c).

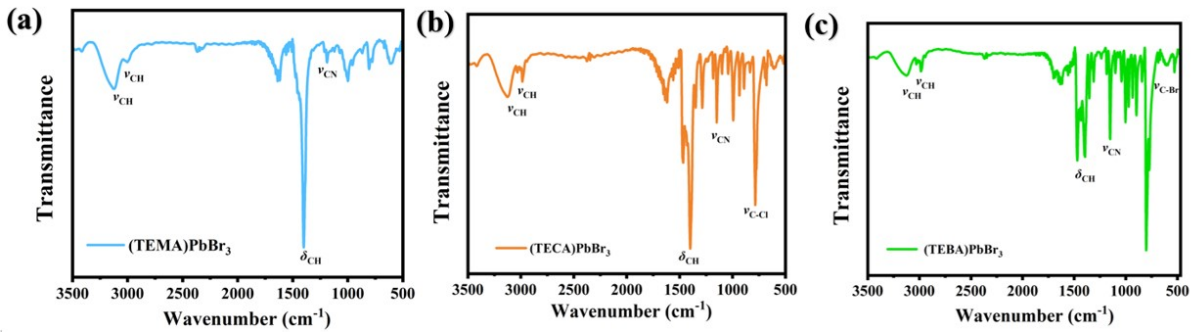

Fig. S4 The infrared spectrum of (TEMA)$PbBr_3$ (a), (TECA) $PbBr_3$ (b) and (TEBA)$PbBr_3$ (c).

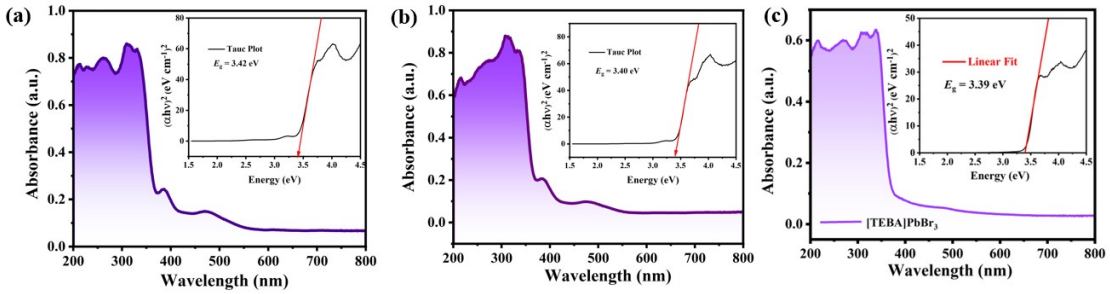

Fig. S5 UV-visible absorption spectra of (TEMA)$PbBr_3$ (a) and (TECA)$PbBr_3$ (b) and (TEBA)$PbBr_3$.

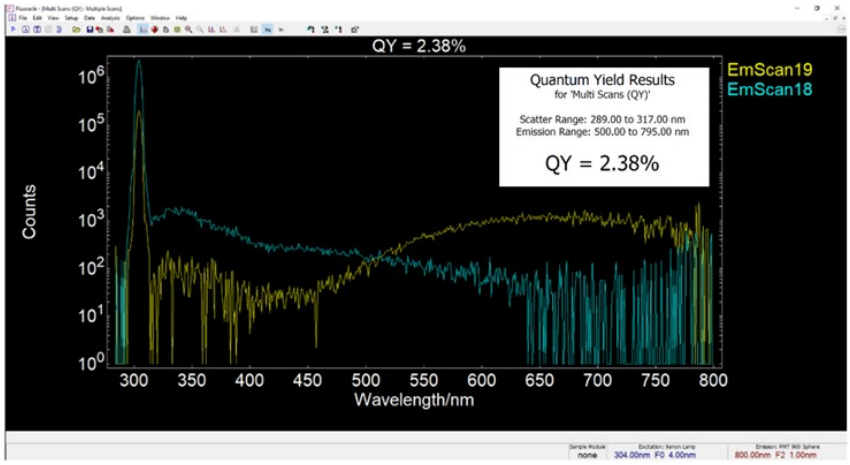

Fig. S6 The photoluminescence quantum efficiency of (TECA)$PbBr_3$ at room temperature.

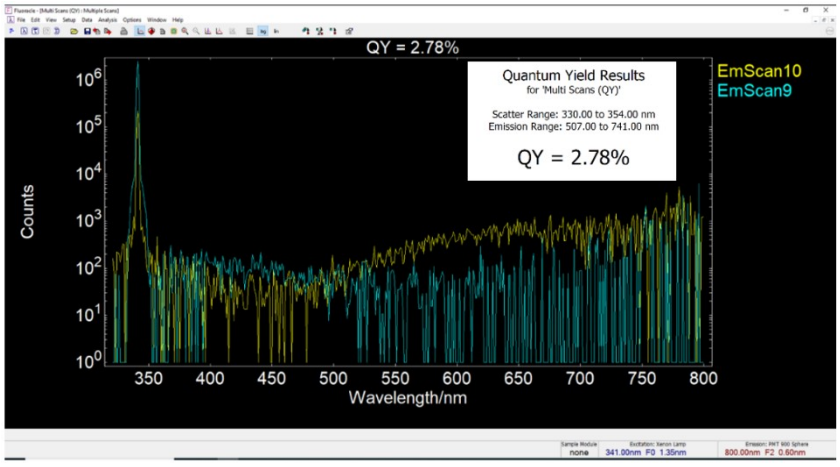

Fig. S7 The photoluminescence quantum efficiency of (TEBA)$PbBr_3$ at room temperature.

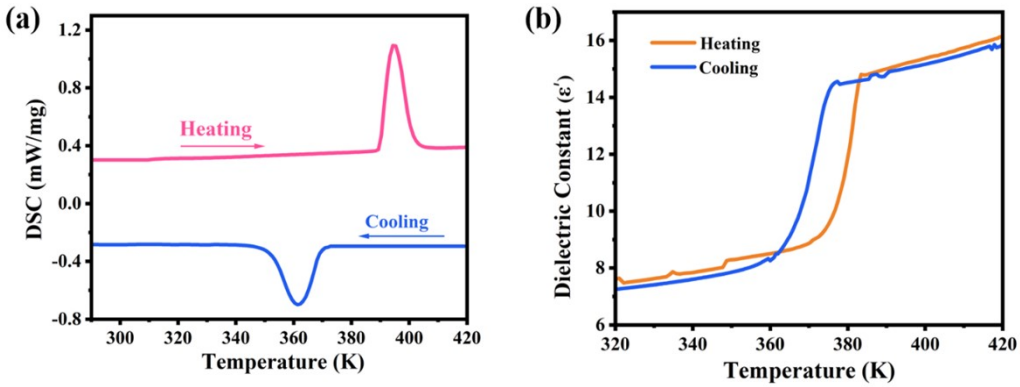

Fig. S8 (a) DSC curve of polycrystalline sample of (TECA)$PbBr_3$ during heating-cooling cycle. (b) The temperature dependent dielectric constant (ε′) of (TECA)$PbBr_3$ was measured during a heating-cooling cycle.

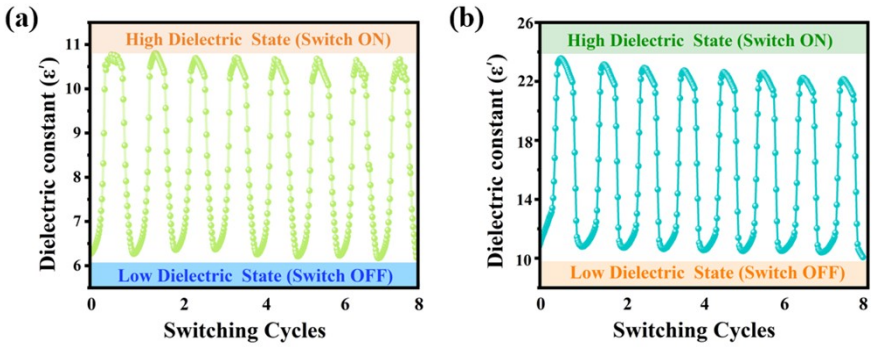

Fig. S9 (a) Temperature response of (TECA)$PbBr_3$ to a dielectric bistable cycle at 1 MHz. (b) Temperature response of (TEBA)$PbBr_3$ to a dielectric bistable cycle at 1 MHz.

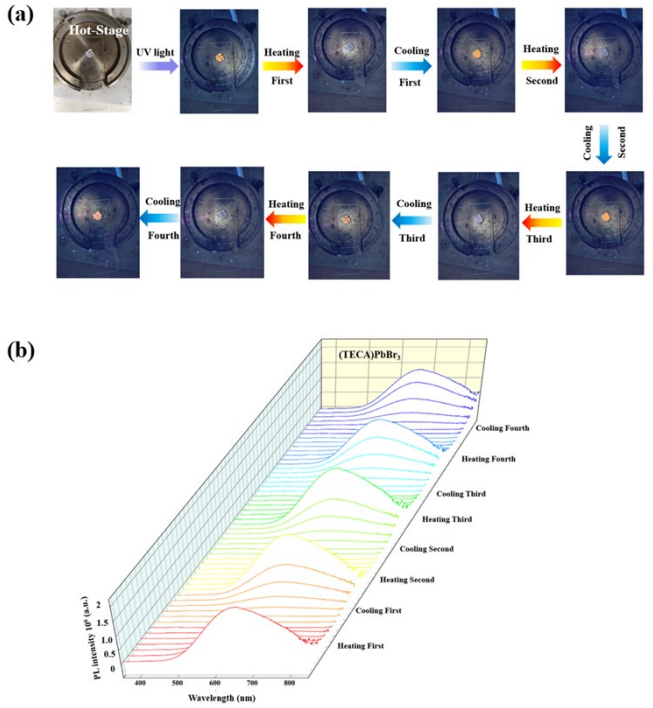

Fig. S10 (a) Thermal reversible photoluminescence quenching-activation cycles of (TECA)$PbBr_3$ (b) Thermal reversible PL spectra of (TECA)$PbBr_3$.

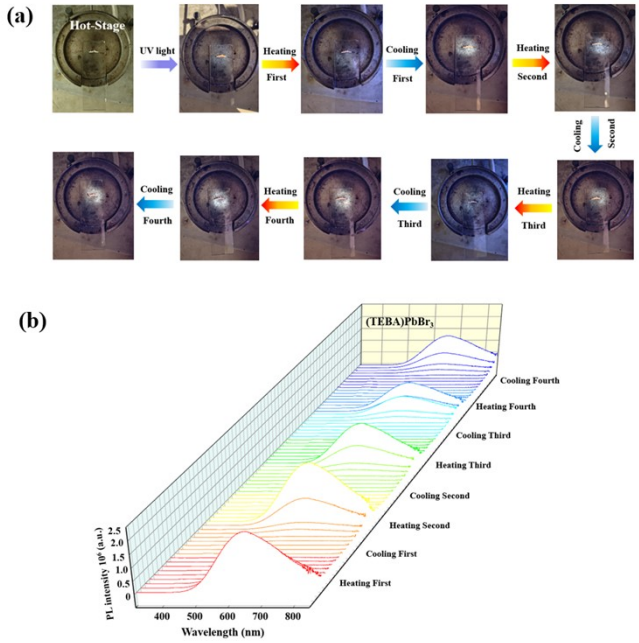

Fig. S11 (a) Thermal reversible photoluminescence quenching-activation cycles of (TEBA)$PbBr_3$ (b) Thermal reversible PL spectra of (TEBA)$PbBr_3$.

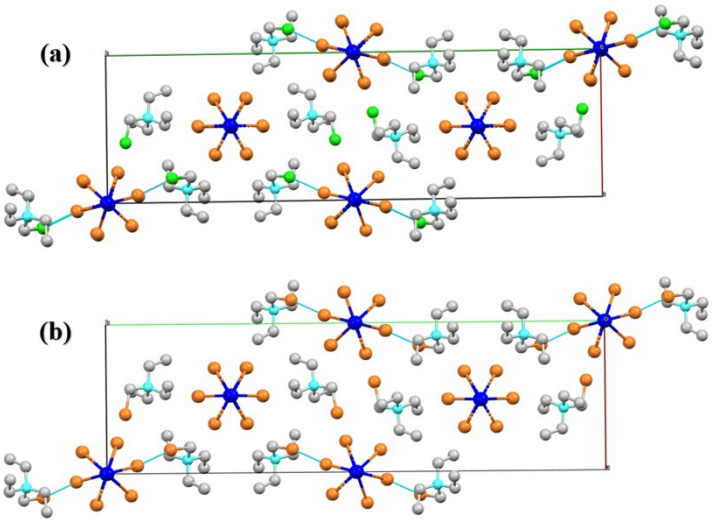

Fig. S12 The halogen-halogen interactions diagram of (TECA)$PbBr_3$ (a) and (TEBA)$PbBr_3$ (b). The blue line in the figure represents the halogen-halogen interactions.

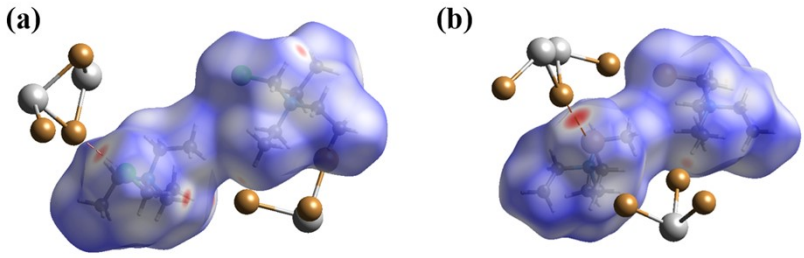

Fig. S13 The Hirshfeld d_{norm} surfaces of (TECA)$PbBr_3$ (a) and (TEBA)$PbBr_3$, which the brown line in the figure represents the halogen-halogen interactions.

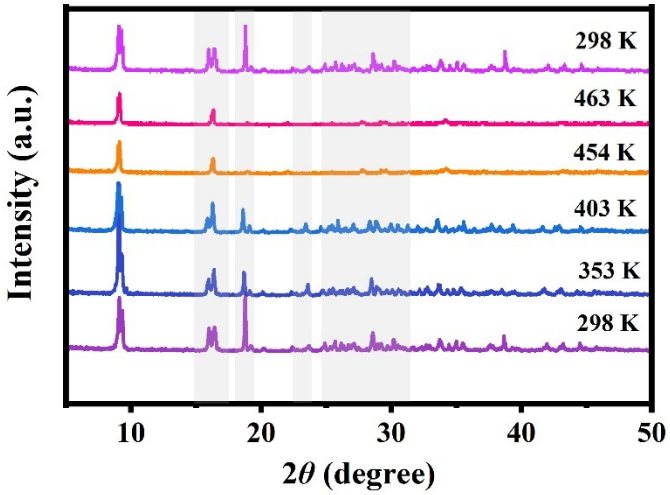

Fig. S14 The variable temperature PXRD patterns of (TEBA)$PbBr_3$ between 298-463 K.

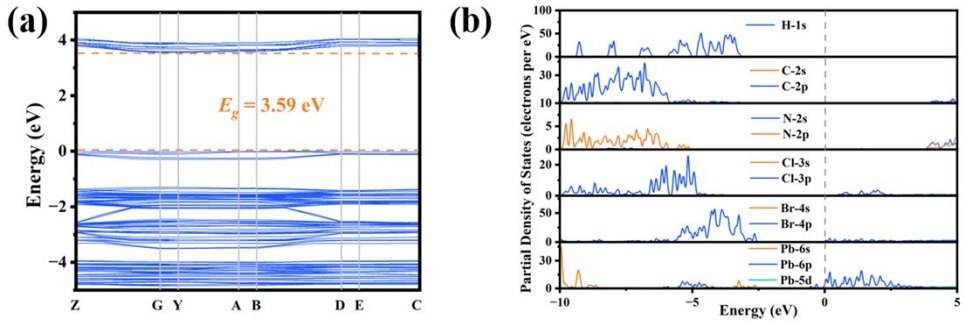

Fig. S15 The calculated band structure and PDOS of (TECA)$PbBr_3$.

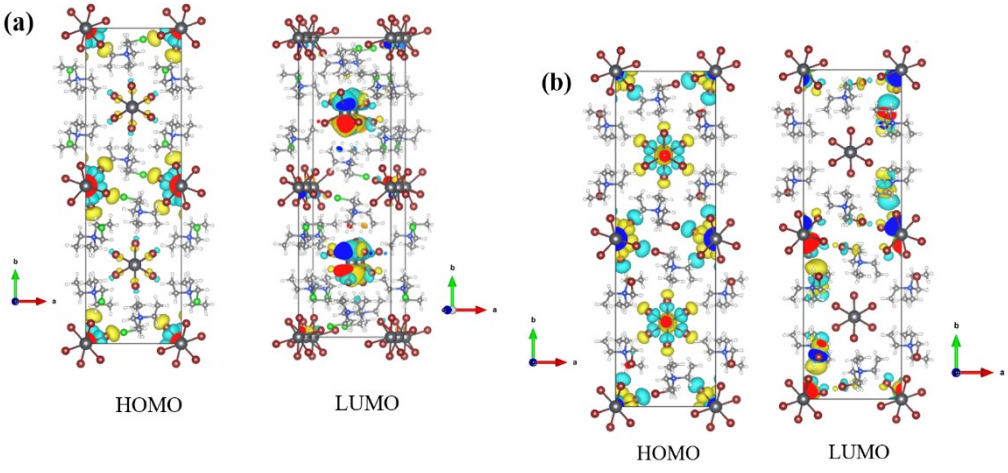

Fig. S16 The calculated frontier molecular orbital (FMO) diagram: HOMOs and LUMOs of (TECA)$PbBr_3$ (c) and (TEBA)$PbBr_3$ (f) along the *c* axis.

Table S1 Crystal data and structure refinement for (TEMA)$PbBr_3$ at 198 K and 295 K.

Compound	**(TEMA)$PbBr_3$**	
Temperature	198.00(10) K	295 K
Empirical formula	$C_{14}H_{36}Br_6N_2Pb_2$	$C_7H_{18}Br_3NPb$
Formula weight	1126.29	563.14
Crystal system	monoclinic	hexagonal
Space group	$P2_1/c$	$P6_3/mmc$
a/Å	20.4048(11)	10.2305(10)
b/Å	16.8153(9)	10.2305(10)
c/Å	7.9462(4)	7.8573(10)
α/°	90	90
β/°	92.425(5)	90
γ/°	90	120
V/Å^3	2724.0(2)	712.19(17)
Z	4	2
F(000)	2032	508
Radiation	Mo Kα (λ = 0.71073)	Mo Kα (λ = 0.71073)
GOF	1.187	0.987
R_1[I>=2σ (I)]	0.0956	0.0818
wR_2[I>=2σ (I)]	0.2324	0.1712

Table S2 Crystal data and structure refinement for (TECA)$PbBr_3$ at 300 K.

Compound	**(TECA)$PbBr_3$**
Temperature	300.0 K
Empirical formula	$C_{14}H_{34}Br_6Cl_2N_2Pb_2$
Formula weight	1195.17
Crystal system	monoclinic
Space group	$P2_1/c$
a/Å	10.8700(5)
b/Å	35.6974(15)
c/Å	7.7943(3)
α/°	90
β/°	100.977(2)
γ/°	90
V/Å^3	2969.1(2)

Z	4
F(000)	2160
Radiation	Mo Kα (λ = 0.71073)
GOF	1.266
R_1[I>=2σ (I)]	0.0383
wR_2[I>=2σ (I)]	0.1070

Table S3 Crystal data and structure refinement for (TEBA)$PbBr_3$ at 284 K.

Compound	**(TEBA)$PbBr_3$**
Temperature	284 (1) K
Empirical formula	$C_{14}H_{34}Br_8N_2Pb_2$
Formula weight	1284.09
Crystal system	monoclinic
Space group	$P2_1/c$
a/Å	10.9245(5)
b/Å	35.8983(18)
c/Å	7.8168(4)
α/°	90
β/°	101.353(5)
γ/°	90
V/Å^3	3005.5(3)
Z	4
F(000)	2304
Radiation	Mo Kα (λ = 0.71073)
GOF	1.129
R_1[I>=2σ (I)]	0.0719
wR_2[I>=2σ (I)]	0.1713

Table S4 The bond lengths (Å) and angles (º) of (TEMA)$PbBr_3$ in the RTP.

Atom–Atom	**Length [Å]**	**Atom–Atom–Atom**	**Angle [°]**
Br1–Pb1	2.986(3)	Pb1–Br1–Pb1	81.31(7)
Br1–Pb1$^{\#1}$	3.111(3)	Pb1–Br2–Pb1	81.74(8)
Br2–Pb1$^{\#1}$	3.088(3)	Pb1–Br3–Pb1	82.02(8)
Br2–Pb1	2.983(3)	Br1–Pb1–Br1	104.34(10)
Br3–Pb1	2.989(3)	Br1–Pb1–Br2	170.43(10)
Br3–Pb1$^{\#1}$	3.065(3)	Br1–Pb1–Br3	92.73(9)
Br4–Pb2	2.974(3)	Br1–Pb1–Br3	84.45(9)
Br4–Pb2$^{\#2}$	3.144(3)	Br2–Pb1–Br1	83.78(9)
Br5–Pb2$^{\#2}$	3.062(3)	Br2–Pb1–Br1	80.01(8)
Br5–Pb2	3.008(3)	Br2–Pb1–Br1	170.69(9)
Br6–Pb2	2.968(3)	Br2–Pb1–Br2	92.66(10)
Br6–Pb2$^{\#2}$	3.105(3)	Br2–Pb1–Br3	103.35(9)

C1–C2	1.540(10)	Br2–Pb1–Br3	82.35(9)
C2–N2	1.55(4)	Br3–Pb1–Br1	93.78(9)
C3–C4	1.521(7)	Br3–Pb1–Br1	81.09(9)
C3–N2	1.56(4)	Br3–Pb1–Br2	79.41(9)
C5–C6	1.539(10)	Br3–Pb1–Br2	103.93(9)
C6–N2	1.53(4)	Br3–Pb1–Br3	173.37(13)
C7–N2	1.48(4)	Pb2–Br4–Pb2	80.96(7)
C8–C9	1.537(10)	Pb2–Br5–Pb2	81.76(7)
C9–N1	1.56(4)	Pb2–Br6–Pb2	81.70(7)
C10–C11	1.541(10)	Br4–Pb2–Br4	93.17(9)
C10–N1	1.53(4)	Br4–Pb2–Br5	85.37(8)
C12–C13	1.522(7)	Br4–Pb2–Br5	104.02(9)
C13–N1	1.52(3)	Br4–Pb2–Br6	170.41(9)
C14–N1	1.49(4)	Br5–Pb2–Br4	81.60(8)
		Br5–Pb2–Br4	104.59(9)
		Br5–Pb2–Br5	168.62(12)
		Br5–Pb2–Br6	79.87(8)
		Br5–Pb2–Br6	91.87(9)
		Br6–Pb2–Br4	83.57(9)
		Br6–Pb2–Br4	171.54(10)
		Br6–Pb2–Br4	78.62(8)
		Br6–Pb2–Br5	82.98(9)
		Br6–Pb2–Br5	91.60(9)
		Br6–Pb2–Br6	105.24(11)
		C1–C2–N2	113(2)
		C4–C3–N2	111(2)
		N2–C6–C5	113(2)
		C2–N2–C3	106(2)
		C6–N2–C2	112(2)
		C6–N2–C3	113(2)
		C7–N2–C2	111(2)
		C7–N2–C3	109(2)
		C7–N2–C6	106(2)
		C8–C9–N1	111(2)
		N1–C10–C11	112(2)
		N1–C13–C12	114(2)
		C10–N1–C9	102.8(18)
		C13–N1–C9	114(2)
		C13–N1–C10	114(2)
		C14–N1–C9	109(2)
		C14–N1–C10	109(2)
		C14–N1–C13	109(2)

Symmetry codes: #1: +X, 1.5-Y, -0.5+Z; #2: +X, 1.5-Y, 0.5+Z; #3: +X, 0.5-Y, -0.5+Z; #4: +X, 0.5-Y, 0.5+Z.

Table S5 The bond lengths (Å) and angles (º) of (TECA)$PbBr_3$ in the RTP.

Atom–Atom	Length [Å]	Atom–Atom–Atom	Angle [°]
Br1–Pb1	2.9466(9)	Pb1–Br1–Pb1	79.84(2)
Br1–Pb1$^{\#1}$	3.1232(9)	Pb1–Br2–Pb1	81.02(3)
Br2–Pb1	2.9698(11)	Pb1–Br3–Pb1	79.70(3)
Br2–Pb1$^{\#2}$	3.0295(11)	Br1–Pb1–Br1	174.94(3)
Br3–Pb1	3.0123(11)	Br1–Pb1–Br2	94.46(3)
Br3–Pb1$^{\#2}$	3.0694(12)	Br1–Pb1–Br2	84.41(3)
Br4–Pb2	3.0640(10)	Br1–Pb1–Br3	83.50(3)
Br4–Pb3	3.0590(9)	Br1–Pb1–Br3	94.24(3)
Br5–Pb2	3.0005(9)	Br2–Pb1–Br1	99.93(3)
Br5–Pb3	2.9852(10)	Br2–Pb1–Br1	82.40(3)
Br6–Pb2$^{\#3}$	3.0447(10)	Br2–Pb1–Br2	98.22(4)
Br6–Pb3	3.0509(10)	Br2–Pb1–Br3	84.02(3)
C1–C2	1.636(12)	Br2–Pb1–Br3	82.06(3)
C2–N1	1.556(11)	Br2–Pb1–Br3	177.91(3)
C3–C4	1.544(12)	Br3–Pb1–Br1	81.53(3)
C4–N1	1.509(11)	Br3–Pb1–Br1	99.61(3)
C5–C6	1.580(13)	Br3–Pb1–Br2	177.46(3)
C6–N1	1.542(10)	Br3–Pb1–Br3	95.65(4)
C7–Cl1	1.757(10)	Pb3–Br4–Pb2	79.06(2)
C7–N1	1.515(11)	Pb3–Br5–Pb2	81.24(2)
C8–C9	1.571(14)	Pb2–Br6–Pb3	79.49(2)
C9–N2	1.546(11)	Br4–Pb2–Br4	180.0
C10–C11	1.599(18)	Br5–Pb2–Br4	84.42(3)
C11–N2	1.513(11)	Br5–Pb2–Br4	84.42(3)
C12–C13	1.533(15)	Br5–Pb2–Br4	95.58(3)
C13–N2	1.574(12)	Br5–Pb2–Br4	95.58(3)
C14–Cl2	1.790(11)	Br5–Pb2–Br5	180.0
C14–N2	1.517(12)	Br5–Pb2–Br6	95.86(3)
		Br5–Pb2–Br6	84.14(3)
		Br5–Pb2–Br6	84.14(3)
		Br5–Pb2–Br6	95.86(3)
		Br6–Pb2–Br4	99.46(3)
		Br6–Pb2–Br4	80.54(3)
		Br6–Pb2–Br4	80.54(3)
		Br6–Pb2–Br4	99.46(3)
		Br6–Pb2–Br6	180.0
		Br4–Pb3–Br4	180.00(3)
		Br5–Pb3–Br4	95.23(3)
		Br5–Pb3–Br4	84.77(3)
		Br5–Pb3–Br4	95.23(3)
		Br5–Pb3–Br4	84.77(3)

		Br5–Pb3–Br5	180.0
		Br5–Pb3–Br6	95.70(3)
		Br5–Pb3–Br6	95.70(3)
		Br5–Pb3–Br6	84.30(3)
		Br5–Pb3–Br6	84.30(3)
		Br6–Pb3–Br4	80.52(3)
		Br6–Pb3–Br4	80.52(3)
		Br6–Pb3–Br4	99.48(3)
		Br6–Pb3–Br4	99.48(3)
		Br6–Pb3–Br6	180.00(3)
		N1–C2–C1	112.9(7)
		N1–C4–C3	116.1(7)
		N1–C6–C5	114.7(7)
		N1–C7–Cl1	112.1(6)
		C4–N1–C2	113.7(7)
		C4–N1–C6	110.2(7)
		C4–N1–C7	103.2(6)
		C6–N1–C2	105.4(7)
		C7–N1–C2	111.7(7)
		C7–N1–C6	112.7(6)
		N2–C9–C8	112.6(8)
		N2–C11–C10	111.9(10)
		C12–C13–N2	115.6(8)
		N2–C14–Cl2	110.0(6)
		C9–N2–C13	106.9(7)
		C11–N2–C9	113.5(8)
		C11–N2–C13	112.0(8)
		C14–N2–C9	111.8(8)
		C14–N2–C11	101.0(8)
		C14–N2–C13	111.8(7)

Symmetry codes: #1: +X, 0.5-Y, -0.5+Z; #2: +X, 0.5-Y, 0.5+Z; #3: +X, +Y, 1+Z; #4: -X, 1-Y, 1-Z; #5: +X, +Y, -1+Z; #6: -X, 1-Y, 2-Z.

Table S6 The bond lengths (Å) and angles (º) of (TEBA)$PbBr_3$ in the RTP.

Atom–Atom	**Length [Å]**	**Atom–Atom–Atom**	**Angle [°]**
Pb1–Br3$^{\#1}$	3.0507(18)	Br3–Pb1–Br3	180.0
Pb1–Br3$^{\#2}$	3.0507(18)	Br3–Pb1–Br5	99.87(5)
Pb1–Br4$^{\#3}$	2.9749(18)	Br3–Pb1–Br5	99.87(5)
Pb1–Br4	2.9750(18)	Br3–Pb1–Br5	80.13(5)
Pb1–Br5	3.0651(19)	Br3–Pb1–Br5	80.13(5)
Pb1–Br5$^{\#3}$	3.0650(19)	Br4–Pb1–Br3	95.50(5)
Pb2–Br3	3.0512(19)	Br4–Pb1–Br3	84.50(5)
Pb2–Br3$^{\#1}$	3.0512(19)	Br4–Pb1–Br3	84.50(5)

Pb2–Br4[#1]	3.0079(17)	Br4–Pb1–Br3	95.50(5)
Pb2–Br4	3.0080(17)	Br4–Pb1–Br4	180.0
Pb2–Br5[#4]	3.0688(18)	Br4–Pb1–Br5	84.84(5)
Pb2–Br5[#3]	3.0688(18)	Br4–Pb1–Br5	95.16(5)
Pb3–Br6[#5]	3.1410(18)	Br4–Pb1–Br5	84.84(5)
Pb3–Br6	2.9382(17)	Br4–Pb1–Br5	95.16(5)
Pb3–Br7	2.965(2)	Br5–Pb1–Br5	180.0
Pb3–Br7[#6]	3.053(2)	Br3–Pb2–Br3	180.0
Pb3–Br8	2.999(2)	Br3–Pb2–Br5	99.94(5)
Pb3–Br8[#6]	3.090(2)	Br3–Pb2–Br5	99.94(5)
Br1–C7	1.93(2)	Br3–Pb2–Br5	80.06(5)
N1–C2	1.61(2)	Br3–Pb2–Br5	80.06(5)
N1–C4	1.56(2)	Br4–Pb2–Br3	83.94(5)
N1–C6	1.52(2)	Br4–Pb2–Br3	83.94(5)
N1–C7	1.49(2)	Br4–Pb2–Br3	96.06(5)
C1–C2	1.5403(10)	Br4–Pb2–Br3	96.06(5)
C3–C4	1.49(3)	Br4–Pb2–Br4	180.0
C5–C6	1.66(4)	Br4–Pb2–Br5	84.22(5)
Br2–C10	1.916(15)	Br4–Pb2–Br5	84.22(5)
N2–C9	1.56(2)	Br4–Pb2–Br5	95.78(5)
N2–C10	1.53(2)	Br4–Pb2–Br5	95.78(5)
N2–C12	1.54(2)	Br5–Pb2–Br5	180.00(6)
N2–C13	1.54(2)	Pb1–Br3–Pb2	79.66(4)
C8–C9	1.57(3)	Pb1–Br4–Pb2	81.57(4)
C11–C12	1.63(2)	Pb1–Br5–Pb2	79.16(4)
C13–C14	1.53(2)	Br6–Pb3–Br6	174.32(6)
		Br6–Pb3–Br7	94.57(6)
		Br6–Pb3–Br7	84.58(5)
		Br6–Pb3–Br8	93.21(6)
		Br6–Pb3–Br8	83.47(6)
		Br7–Pb3–Br6	82.60(5)
		Br7–Pb3–Br6	100.67(5)
		Br7–Pb3–Br7	98.01(7)
		Br7–Pb3–Br8	177.94(6)
		Br7–Pb3–Br8	81.18(6)
		Br7–Pb3–Br8	84.15(6)
		Br8–Pb3–Br6	81.63(6)
		Br8–Pb3–Br6	99.41(6)
		Br8–Pb3–Br7	177.01(6)
		Br8–Pb3–Br8	96.60(8)
		Pb3–Br6–Pb3	79.94(4)
		Pb3–Br7–Pb3	80.98(5)
		Pb3–Br8–Pb3	79.85(5)
		C4–N1–C2	113.4(12)

C6–N1–C2	108.4(15)
C6–N1–C4	110.8(15)
C7–N1–C2	109.0(14)
C7–N1–C4	111.6(14)
C7–N1–C6	103.0(15)
C1–C2–N1	123.2(15)
C3–C4–N1	117.0(14)
N1–C6–C5	111(2)
N1–C7–Br1	111.2(12)
C10–N2–C9	111.8(13)
C10–N2–C12	112.4(12)
C10–N2–C13	104.0(11)
C12–N2–C9	105.8(12)
C12–N2–C13	112.3(13)
C13–N2–C9	110.6(13)
N2–C9–C8	116.1(14)
N2–C10–Br2	112.7(10)
N2–C12–C11	114.7(12)
C14–C13–N2	115.1(14)

Symmetry codes: #1: -X, 1-Y, 1-Z; #2: +X, +Y, 1+Z; #3: -X, 1-Y, 2-Z; #4: +X, +Y, -1+Z; #5: +X, 0.5-Y, 0.5+Z; #6: +X, 0.5-Y, -0.5+Z.

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