Electronic Supplementary Information

Enhanced Luminescence in 1D Corrugated Lead Bromides via Reduced Flexibility of Trivalent Cations

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Experimental

Materials and general characterizations. All reagents were commercially available and used as received without further purification. Powder X-ray diffraction (PXRD) patterns were obtained on a Rigaku SmartLab X-ray diffraction instrument. Thermogravimetric analysis (TGA) was performed by a NETZSCH TG209 F3 system. Ultraviolet-vis (UV-vis) absorption spectra were measured with Shimadzu UV-2600 equipped with ISR-2600Plus integrating sphere. Photoluminescence (PL) spectra were obtained through analysis on an Edinburgh FLS1000 steady-state/transient-state fluorescence spectrometer. Elemental analysis (EA) of C, H, and N was performed on UNICUBE-Elementar elemental analyzer.

Single-crystal X-ray Diffraction. Crystallographic data were collected on a Rigaku Oxford Diffraction Supernova Dual Source, Cu at Zero equipped with an AtlasS2 CCD using Mo Kα radiation. CrystalClear1.3.5 package was used to collect data, refine cell, and reduce data. SHELXL-2014 package was used to solve the structures by direct methods. All non-hydrogen atoms were refined anisotropically. The details of crystal data are given in Tables S1 and S2. CCDC 2404396-2404397 contain the crystallographic data for $(PEA)_2Pb_2Br_{10}\cdot H_2O$ (b), and $(MPEA)PbBr_5\cdot H_2O$. The data can be obtained free of charge via http://www.ccdc.cam.ac.uk/conts/retrieving.html, or from the Cambridge Crystallographic Data Centre, 12 Union Road, Cambridge CB2 1EZ, UK; fax: +44 1223-336-033; or e-mail: deposit@ccdc.cam.ac.uk.

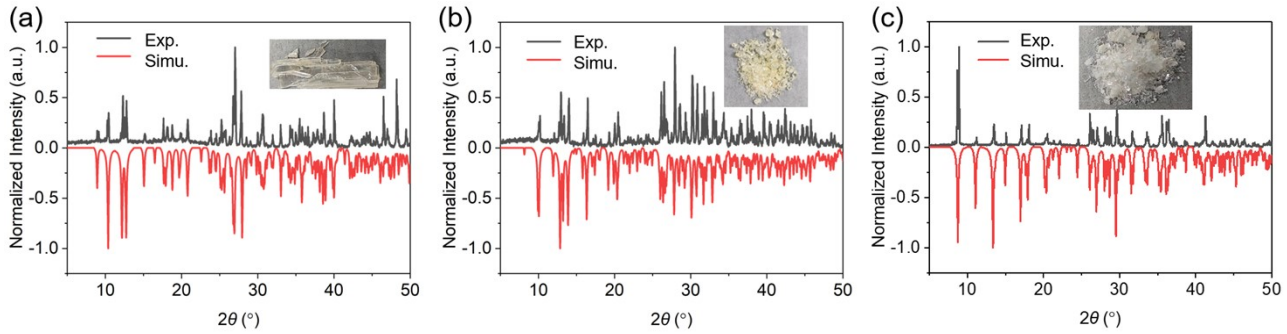

Fig. S1 PXRD patterns of $(DTA)_2Pb_2Br_{10}\cdot H_2O$ (a), $(PEA)_2Pb_2Br_{10}\cdot H_2O$ (b), and $(MPEA)_2Pb_2Br_{10}\cdot H_2O$ (c) at 298 K. Inset: Photos of the crystals that were synthesized.

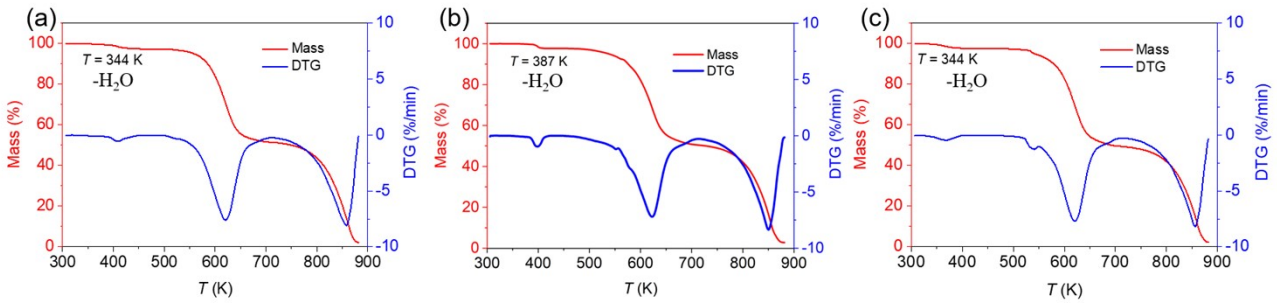

Fig. S2 TGA curves of $(DTA)_2Pb_2Br_{10}\cdot H_2O$ (a), $(PEA)_2Pb_2Br_{10}\cdot H_2O$ (b), and $(MPEA)_2Pb_2Br_{10}\cdot H_2O$ (c).

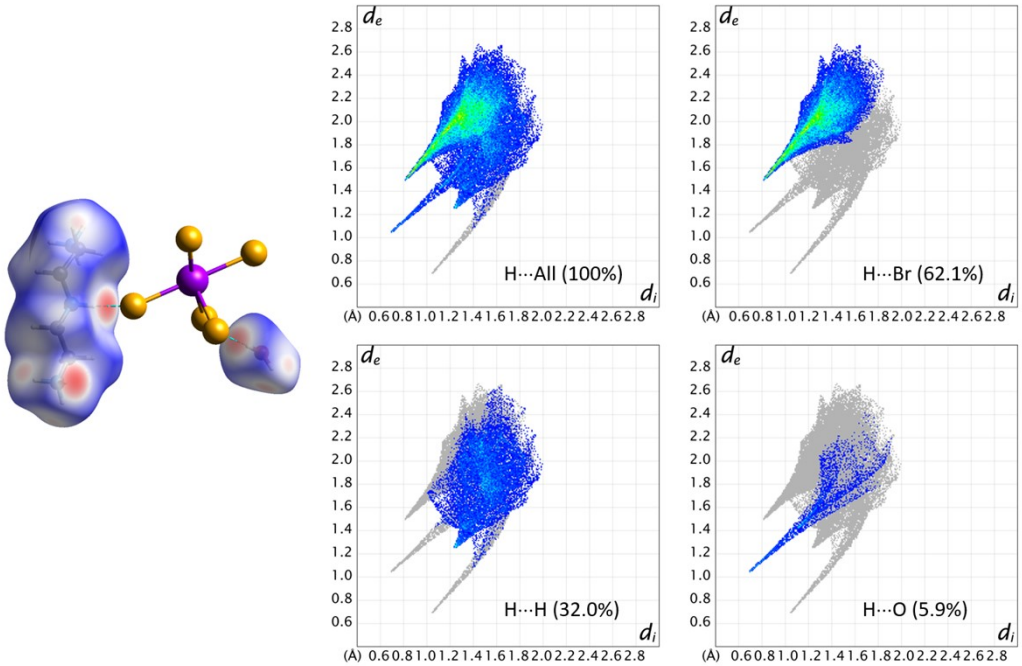

Figure. S3 (a) 3D d_{norm} surface of DTA and H_2O of $(DTA)PbBr_5\cdot H_2O$, (d-f), and (b-l) 2D fingerprint plots of DTA and H_2O at 293 K. Red, white and blue regions of the Hirshfeld surfaces indicate positive (close contact), neutral and negative isoenergies, respectively.

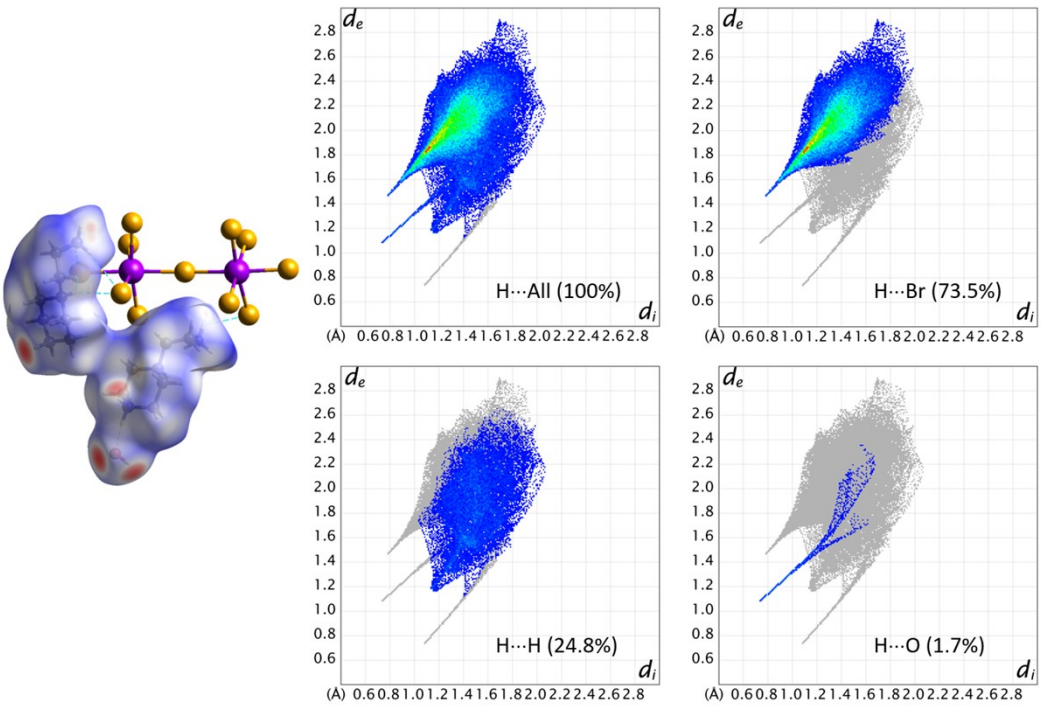

Fig. S4. (a) 3D d_{norm} surface of H_2O of $(PEA)_2Pb_2Br_{10}\cdot H_2O$. and (b-i) 2D fingerprint plots of H_2O at 293 K. Red, white and blue regions of the Hirshfeld surfaces indicate positive (close contact), neutral and negative isoenergies, respectively.

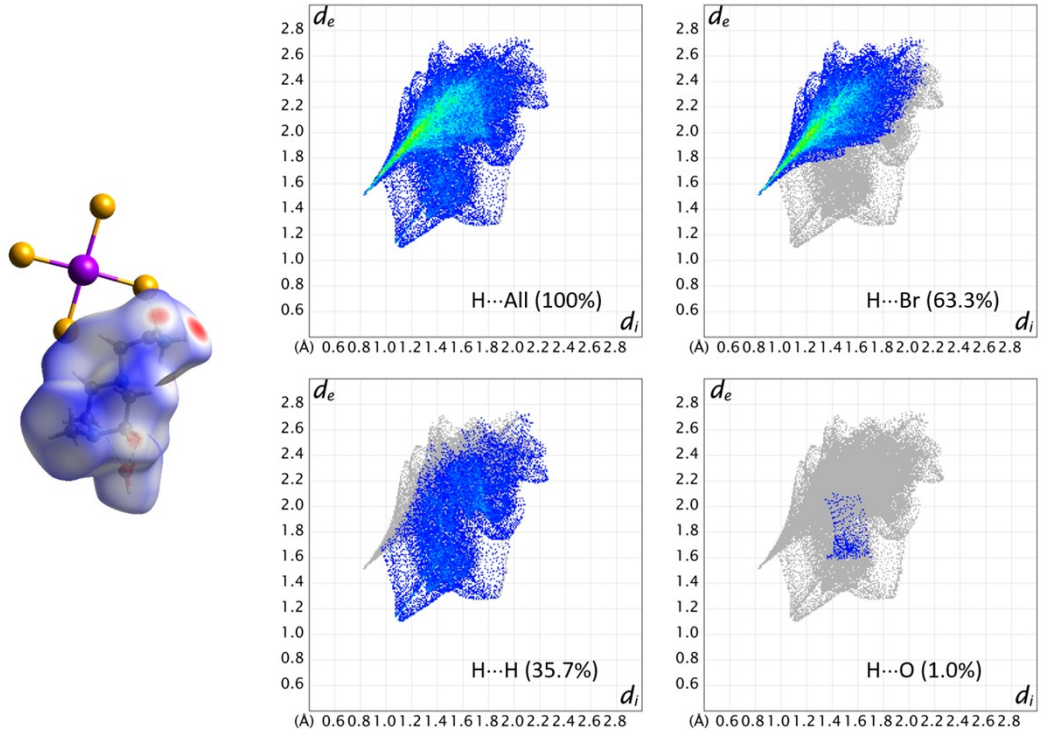

Fig. S5. (a) 3D d_{norm} surface of H_2O of $(MPEA)_2Pb_2Br_{10}\cdot H_2O$. and (b-i) 2D fingerprint plots of H_2O at 293 K. Red, white and blue regions of the Hirshfeld surfaces indicate positive (close contact), neutral and negative isoenergies, respectively.

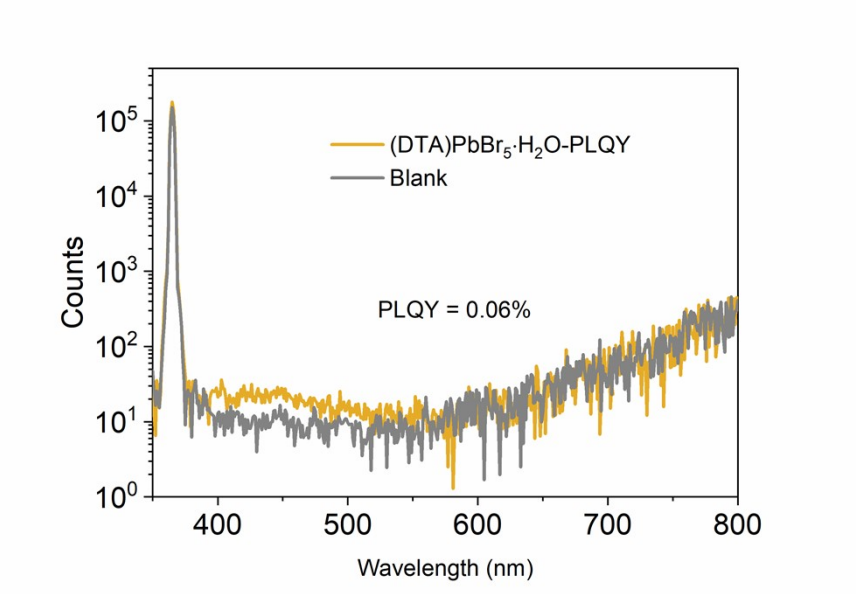

Fig. S6. Luminescence decays of (DTA)$PbBr_5 \cdot H_2O$ at 298 K.

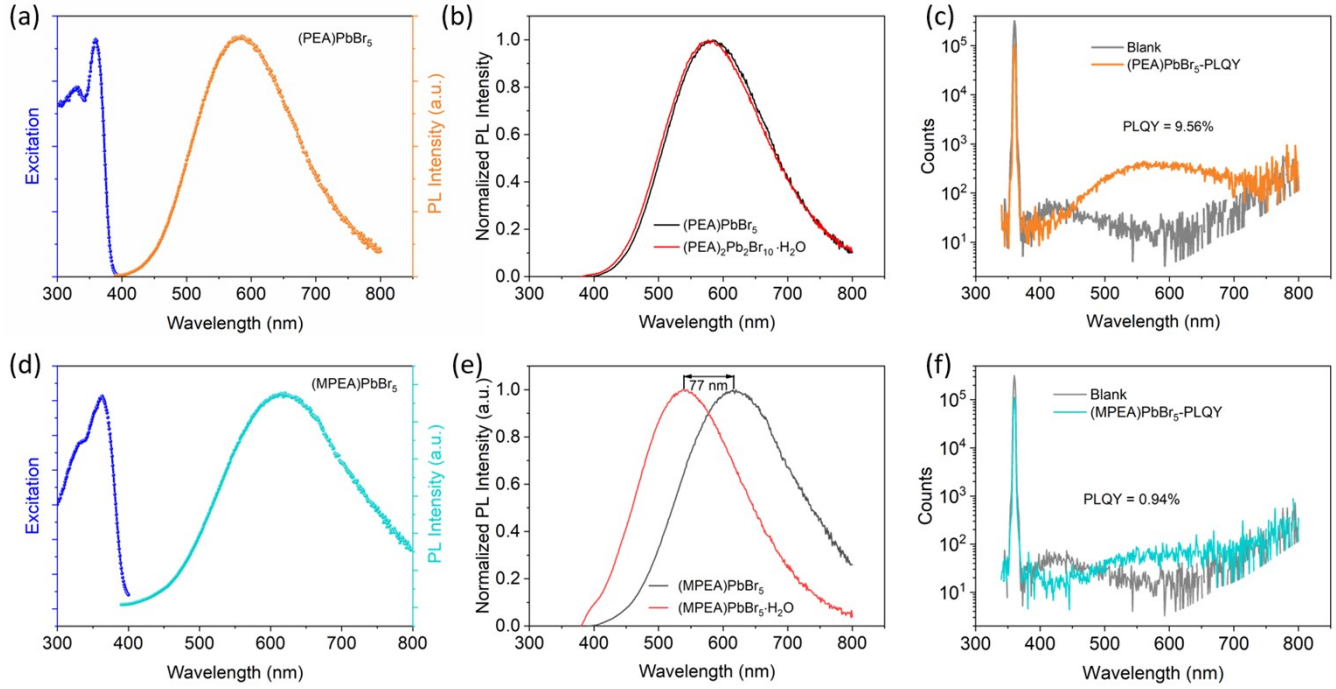

Fig. S7. PL properties after structural dehydration (a) Photoluminescence spectrum of (PEA)$PbBr_5$ at 298 K; (b) Comparison of fluorescence emission wavelengths; (c) PLQY of (MPEA)$PbBr_5$ at 298 K; (d) Photoluminescence spectrum of (MPEA)$PbBr_5$ at 298 K; (e) Comparison of fluorescence emission wavelengths. (f) PLQY and luminescence (MPEA)$PbBr_5$ at 298 K.

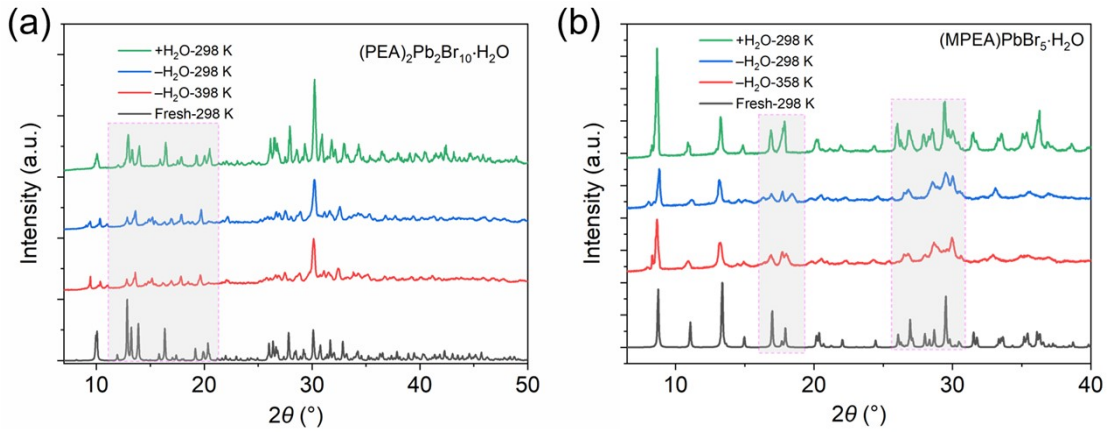

Fig. S8. PXRD measurement show the reversible dehydration/hydration transformation of $(PEA)_2Pb_2Br_{10}·H_2O$ and $(MPEA)PbBr_5·H_2O$.

Table S1. Crystallographic data and refinement parameters for $(PEA)_2Pb_2Br_{10}\cdot H_2O$ and $(MPEA)PbBr_5\cdot H_2O$.

	$(PEA)_2Pb_2Br_{10}\cdot H_2O$	$(MPEA)PbBr_5\cdot H_2O$
Formula	$C_{12}H_{38}Br_{10}N_6OPb_2$	$C_7H_{22}Br_5N_3OPb_2$
Formula weight	1495.96	771.01
Crystal system	Monoclinic	Monoclinic
space group	$P2_1/c$	$P2_1/m$
a / Å	13.8538(3)	10.2495(2)
b / Å	17.5673(4)	8.7968(2)
c / Å	13.8398(3)	10.3341(2)
α / º	90	90
β / º	96.191(2)	101.902(10)
γ / º	90	90
V / Å^3	3348.60(13)	911.72(3)
Z	4	2
D_{calc} / g·cm^{-3}	2.967	2.809
μ / mm^{-1}	21.993	30.770
Reflections collected	98359	7544
Independent	9279	1786
reflections	0.109	0.050
Rint	0.0516, 0.0813	0.0301, 0.0661
R_1[a] /wR_2[b] (I > 2σ(I))	0.0912, 0.0889	0.0322, 0.0670
R_1/wR_2 (all data)	1.067	1.067
GOF	1.96/−2.38	0.93/−1.07
$\Delta\rho$[c] / e·Å^{-3}		

[a] $R_1 = \Sigma| |F_o| - |F_c| | / |F_o|$. [b] $wR_2 = [\Sigma w(F_o^2 - F_c^2)^2] / \Sigma w(F_o^2)^2]^{1/2}$. [c] Maximum and minimum residual electron density.

Table S2. Selected hydrogen bonds for $(PEA)_2Pb_2Br_{10}\cdot H_2O$ and $(MPEA)PbBr_5\cdot H_2O$ (298 K).

D−H···A	D−H / Å	H···A / Å	D···A / Å	∠DHA / °
$(PEA)_2Pb_2Br_{10}\cdot H_2O$				
O(1)−H(1F)···Br(9)^{i}	0.84(2)	2.40(5)	3.197(8)	158(12)
O(1)−H(1G)···Br(1)^{ii}	0.84(2)	2.58(7)	3.197(7)	131(9)
C(3)−H(3B)···Br(9)^{iii}	0.97	2.83	3.364(8)	115.2
N(1)−H(1C)···Br(9)^{iii}	0.89	2.82	3.429(15)	126.4
N(1)−H(1E)···Br(10)	0.89	2.73	2.320(13)	125.3
N(2)−H(2B)···Br(9)^{iii}	0.91	2.69	3.390(7)	134.7
N(3)−H(3C)···Br(4)^{i}	0.89	2.62	3.465(9)	158.5
N(3)−H(3D)···O(1)	0.89	1.95	2.815(12)	165.4
N(4)−H(4C)···Br(1)	0.89	2.71	3.338(7)	128.8
N(4)−H(4E)···Br(2)^{iv}	0.89	2.84	3.311(8)	114.9
N(4)−H(4E)···Br(8)^{iv}	0.89	2.75	3.341(7)	125.4
N(5)−H(5)···Br(1)	0.91	2.75	3.488(6)	138.7
N(5)−H(5)···Br(2)	0.91	2.73	3.411(6)	132.3
N(6)−H(6C)···O(1)^{vi}	0.89	1.96	2.847(11)	175.5
N(6)−H(6D)···Br(5)^{ii}	0.89	2.61	3.377(8)	144.4
Symmetry codes: (i) x−y+3/2, z−1/2; (ii) −x+1, y−1/2, −z+3/2; (iii) −x, y−1/2, −z+3/2; (iv) −x+1, −y+2, −z+1; (v) x+1, y, z; (vi) −x+1, −y+1, −z+1.				
$(MPEA)PbBr_5\cdot H_2O$				
O(1)−H(1E)···Br(1)^{i}	0.85	2.61	3.353(7)	147.4
N(1)−H(1)···O(1)^{ii}	0.98	2.52	3.093(11)	117.4
C(2)−H(2A)···O(1)^{i}	0.97	2.55	3.225(10)	126.7
C(2)−H(2B)···O(1)	0.97	2.95	3.409(8)	110.1
N(3)−H(3C)···Br(2)^{iii}	0.89	2.32	3.142(12)	153.7
N(3)−H(3D)···Br(2)^{iv}	0.89	2.66	3.490(13)	154.7
N(3)−H(3E)···Br(2)	0.89	2.57	3.336(11)	145.3
Symmetry codes: (i) −x+1, y+1/2, −z+2; (ii) −x, y−1/2, −z+2; (iii) −x+1, −y+1, −z+1; (iv) −x+1, y+1/2, −z+1.				

Table S3. Bond Angles and Bond Length for $(PEA)_2Pb_2Br_{10}\cdot H_2O$, and $(MPEA)_2Pb_2Br_{10}\cdot H_2O$.

Bond Angles	Angle / °	Bond Lengths	Length / Å
$(PEA)_2Pb_2Br_{10}\cdot H_2O$			
Br(1)–Pb(1)–Br(2)	81.37(2)	Br(1)–Pb(1)	2.9422(8)
Br(1)–Pb(1)–Br(3)	84.584(19)	Br(2)–Pb(1)	2.9424(9)
Br(1)–Pb(1)–Br(4)	93.65(3)	Br(3)–Pb(1)	3.1976(3)
Br(1)–Pb(1)–Br(5)	93.95(3)	Br(4)–Pb(1)	2.9429(9)
Br(1)–Pb(1)–Br(6)	176.68(3)	Br(5)–Pb(1)	3.0048(9)
Br(2)–Pb(1)–Br(3)	165.62(2)	Br(6)–Pb(1)	3.0548(9)
Br(2)–Pb(1)–Br(4)	95.38(3)	Br(6)–Pb(2)	3.1150(9)
Br(2)–Pb(1)–Br(5)	92.24(3)	Br(7)–Pb(2)	3.0031(3)
Br(2)–Pb(1)–Br(6)	95.65(3)	Br(8)–Pb(2)	2.9458(8)
Br(4)–Pb(1)–Br(3)	88.55(2)	Br(9)–Pb(2)	2.9072(9)
Br(4)–Pb(1)–Br(5)	169.96(3)	Br(10)–Pb(2)	3.1059(10)
Br(4)–Pb(1)–Br(6)	85.15(3)	Br(11)–Pb(2)	2.9253(10)
Br(5)–Pb(1)–Br(3)	85.643(18)		
Br(5)–Pb(1)–Br(6)	87.60(3)		
Br(6)–Pb(1)–Br(3)	98.47(2)		
$(MPEA)_2Pb_2Br_{10}\cdot H_2O$			
Br(2)–Pb(1)–Br(1)	89.04(2)	Br(1)–Pb(1)	2.9422(8)
$Br(2)^{i}$–Pb(1)–Br(1)	89.04(2)	$Br(2)^{i}$–Pb(1)	3.0511(7)
Br(2)–Pb(1)–$Br(2)^{i}$	79.57(3)	Br(2)–Pb(1)	3.0511(7)
Br(3)–Pb(1)–Br(1)	178.88(3)	Br(3)–Pb(1)	2.9538(10)
Br(3)–Pb(1)–Br(2)	90.10(2)	Br(4)–Pb(1)	2.96601(19)
Br(3)–Pb(1)–$Br(2)^{i}$	90.10(2)	$Br(4)^{ii}$ –Pb(1)	2.96601(19)
Br(3)–Pb(1)–$Br(4)^{ii}$	87.838(15)		
Br(3)–Pb(1)–Br(4)	87.838(15)		
$Br(4)^{ii}$–Pb(1)–Br(1)	92.914(13)		
Br(4)–Pb(1)–Br(1)	92.914(13)		
$Br(4)^{ii}$–Pb(1)–Br(2)	92.318(15)		

$Br(4)^{ii}$–Pb(1)–$Br(2)^{i}$	171.625(16)
Br(4)–Pb(1)–Br(2)	171.625(16)
Br(4)–Pb(1)–$Br(2)^{i}$	92.318(15)
$Br(4)^{ii}$–Pb(1)–Br(4)	95.713(8)

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