Electronic Supplementary Information for

Layered Hybrid Lead Perovskite Single Crystals: Phase Transformations and Tunable Optical Properties

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Experimental Section

Experimental Section

Single-crystal X-ray diffraction and Powder X-ray diffraction studies. Single-crystal X-ray diffraction and powder X-ray diffraction measurements were depicted elsewhere. [1]

UV-vis-NIR diffuse reflectance spectra measurements. UV–vis-NIR diffuse reflectance spectroscopy was carried out using a Varian Cary 5000 spectrophotometer equipped with an integrating sphere over the spectral range 200-1200 nm. The $PEA_2MA_{n-1}Pb_nI_{3n+1}$ (n =1~3) single crystals were dried and grinded into powders. A $BaSO_4$ plate was used as the standard (100% reflectance). The absorption spectrum was calculated from the reflectance spectrum using the Kubelka-Munk function: $\alpha/S = (1-R)^2/(2R)$,[2] where α is the absorption coe□cient, *S* is the scattering coe□cient, and R is the reflectance.

Thermogravimetric analysis Measurements. Differential scanning calorimetry (DSC) and thermogravimetric analysis (TGA) were carried out using a TGA/DSC1/1600HT analyzer (METTLER TOLEDO Instruments). The $PEA_2MA_{n-1}Pb_nI_{3n+1}$ (n=1~3) sample were placed in a platinum crucible, and heated at a rate of 10 °C min-1 from room temperature to 800 °C under flowing nitrogen gas.

PL spectra and PL decay time measurements. The microarea PL images were collected using a Nikon fluorescence microscope and the PL spectra of P $PEA_2MA_{n-1}Pb_nI_{3n+1}$ (n =1~3) were gathered with a Carl Zeiss Jena LSM 780 confocal laser fluorescence microscope. The decay times of as-prepared microcrystals of $PEA_2MA_{n-1}Pb_nI_{3n+1}$ (n =1~3) were measured at room temperature under 445 nm wavelength irradiations.

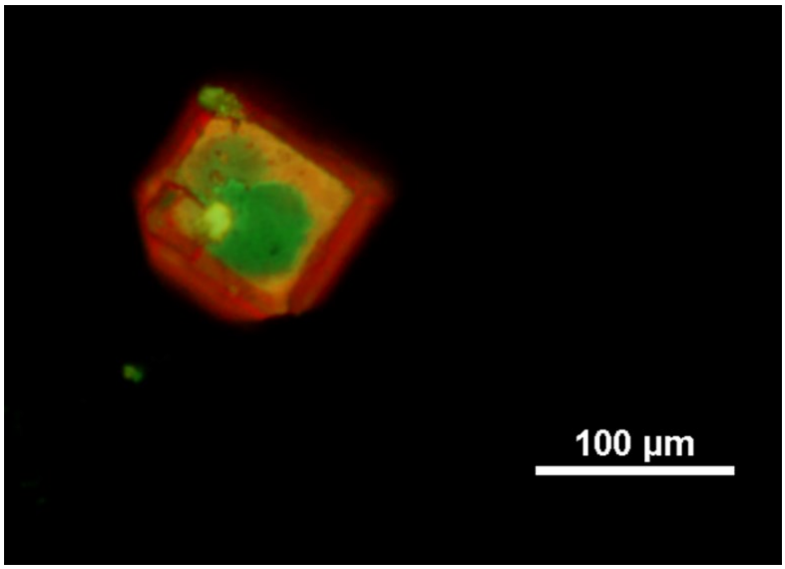

Fig. S1 Fluorescence photo of the monoclinic PEA_2PbI_4 single crystal covered on the surface of triclinic PEA_2PbI_4 single crystal under UV-445 nm irradiation.

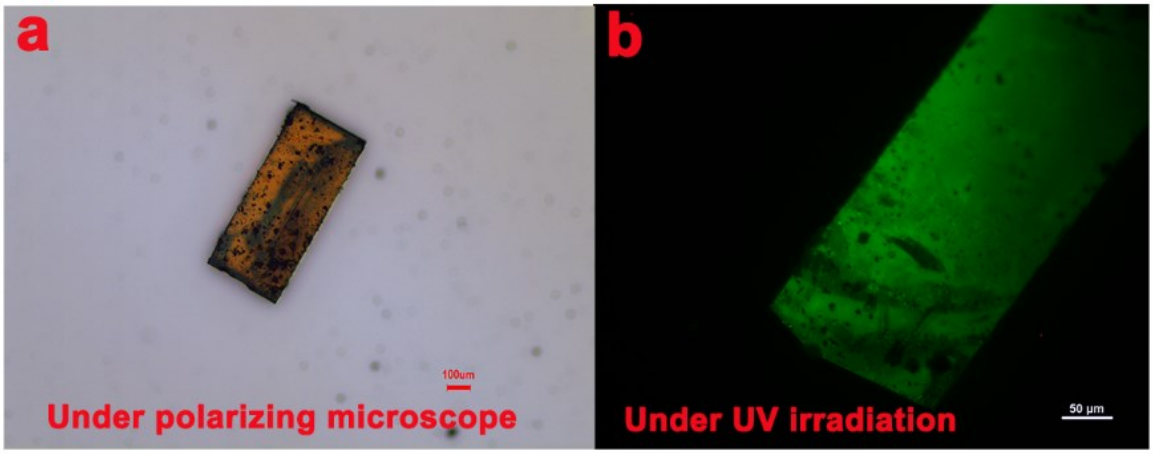

Fig. S2 Green emissive PEA_2PbI_4 single crystal obtained by the phase transformation processes induced by CH_3OH solvent. (a) PEA_2PbI_4 single crystal under polarizing microscope; (b) Green fluorescence of PEA_2PbI_4 single crystal under UV-445 nm irradiation.

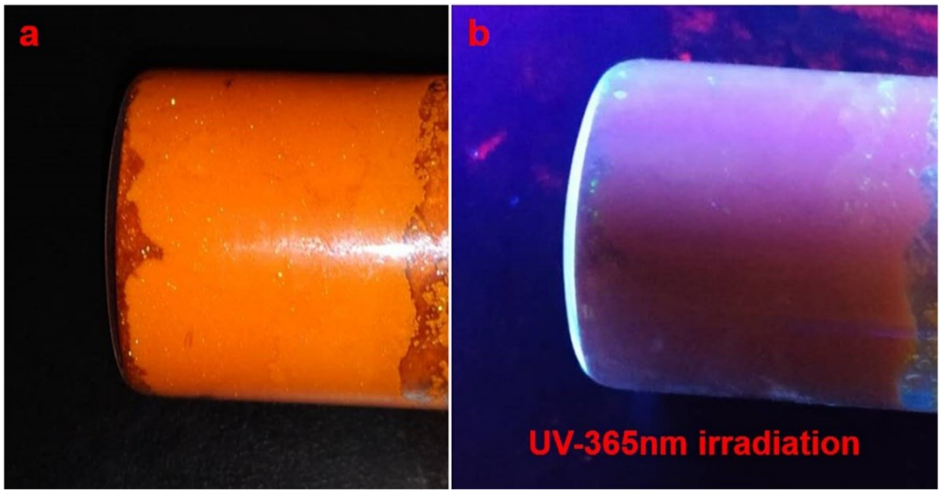

Fig. S3 Red emissive PEA_2PbI_4 single crystal obtained by the phase transformation processes. (a) PEA_2PbI_4 single crystal under ordinary light; (b) Red fluorescence of PEA_2PbI_4 single crystal under UV-365 nm irradiation.

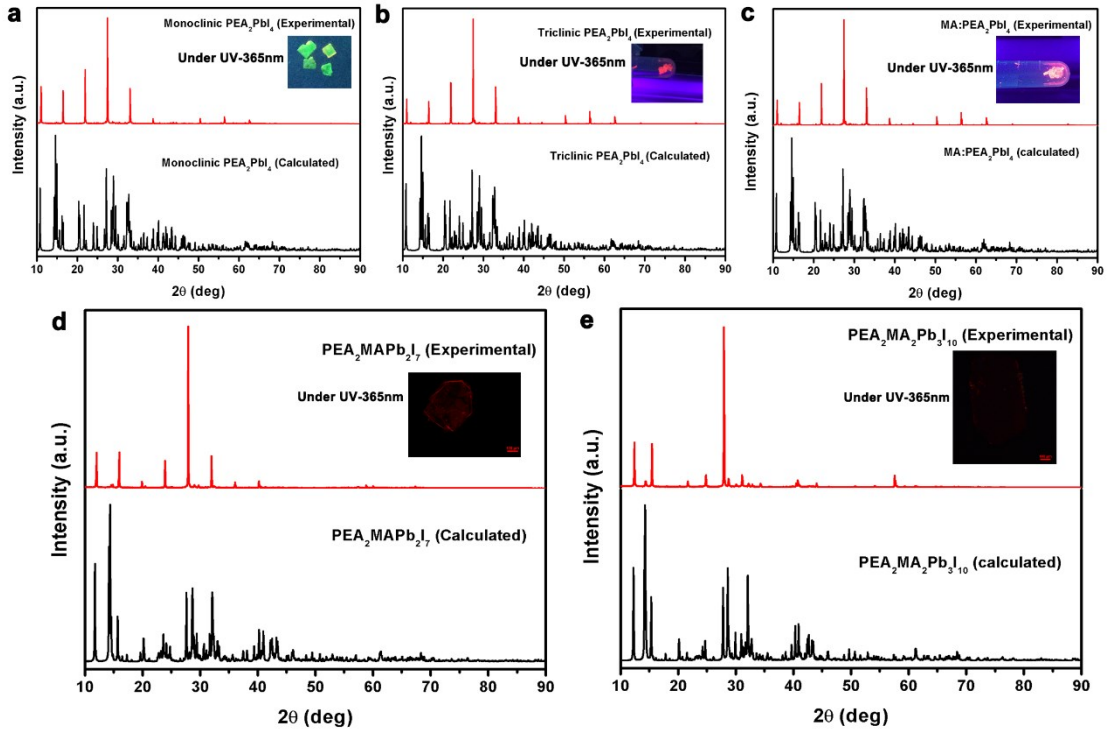

Fig. S4 Calculated and powder XRD patterns of $PEA_2MA_{n-1}Pb_nI_{3n+1}$ (n =1~3)

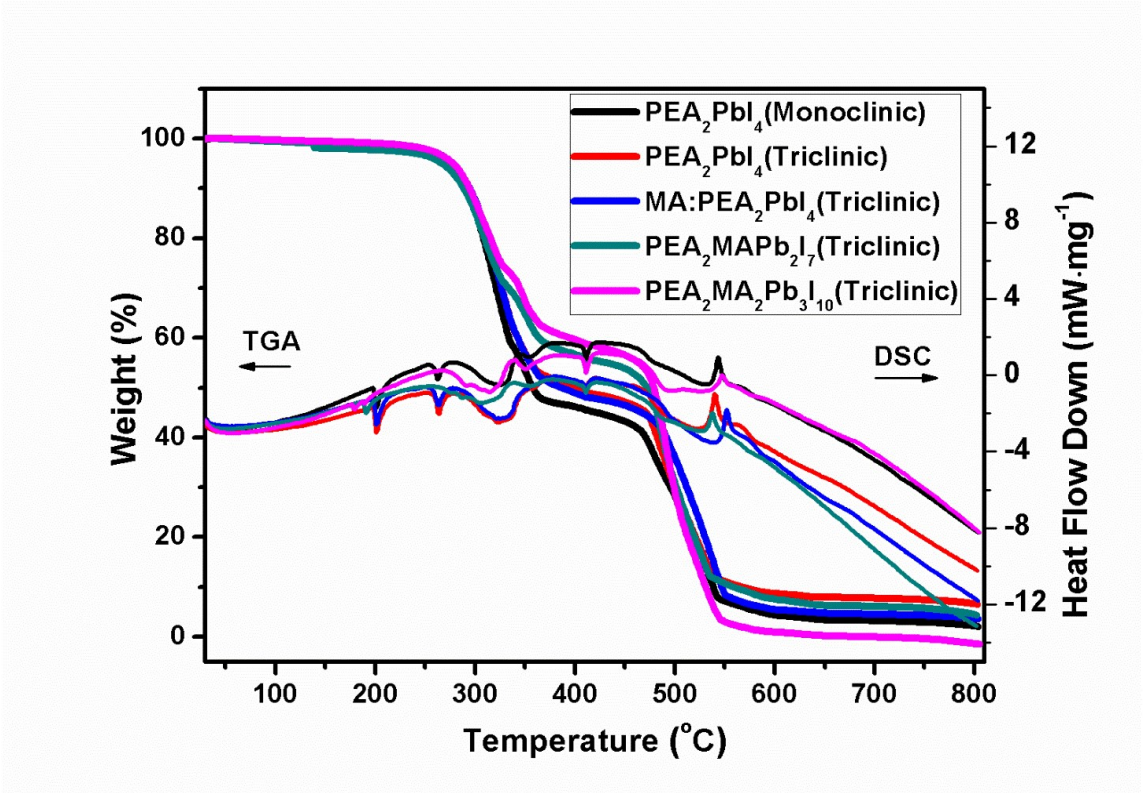

Fig. S5 Thermal properties (TGA/DSC) of $PEA_2MA_{n-1}Pb_nI_{3n+1}$ (n =1~3)

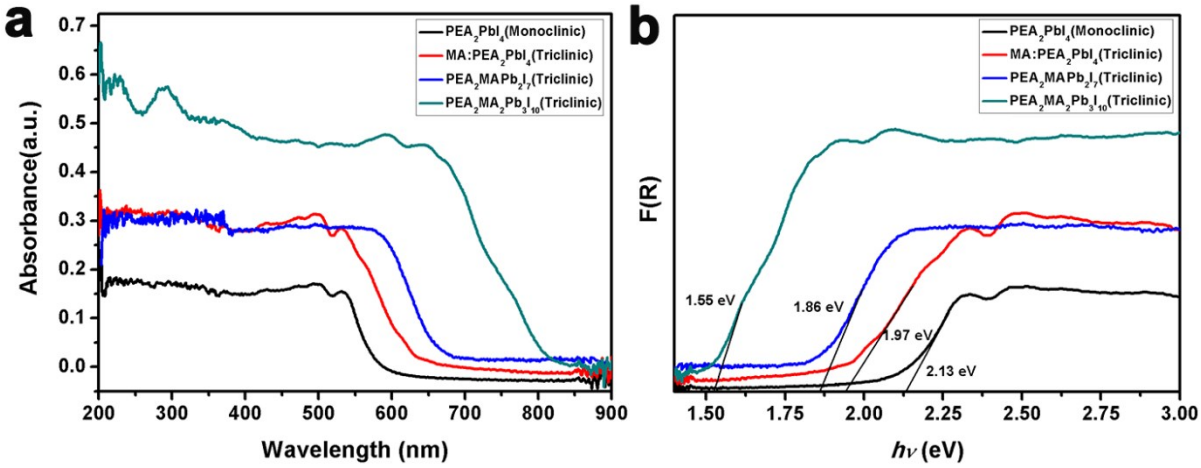

Fig. S6 UV-vis spectra and band gap of $PEA_2MA_{n-1}Pb_nI_{3n+1}$ (n =1~3). (a) Tunable UV-vis spectra of $PEA_2MA_{n-1}Pb_nI_{3n+1}$ (n =1~3); (b) Tunable band gap of $PEA_2MA_{n-1}Pb_nI_{3n+1}$ (n =1~3) from 2.13 to 1.55 eV.

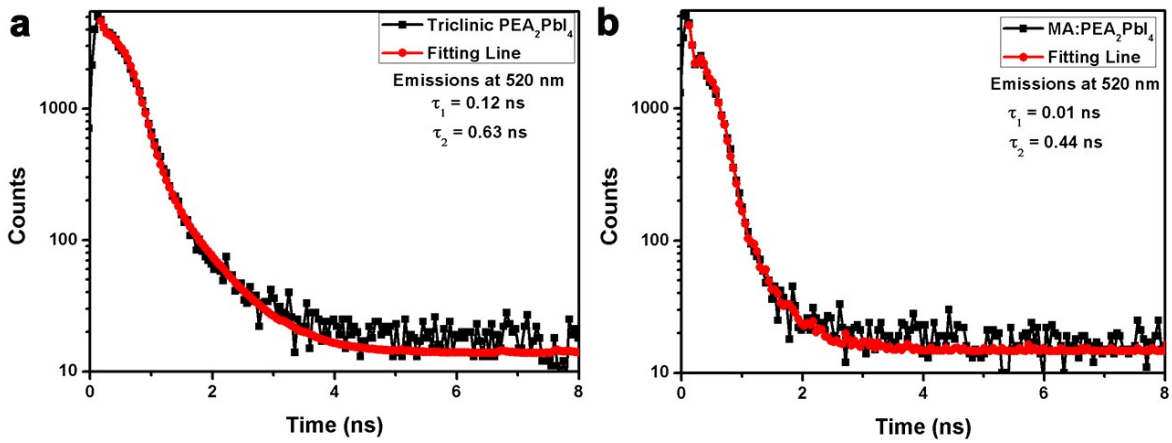

Fig. S7 PL decay lifetime of Triclinic PEA_2PbI_4 and MA: PEA_2PbI_4 under 445 nm irradiations and emission at 520 nm.

Table. S1 Crystal data and structure refinements for $PEA_2MA_{n-1}Pb_nI_{3n+1}$ (n =1~3)

Empirical formula	$C_{16}H_{24}N_2PbI_4$		$C_{16}H_{24}N_2PbI_4$	$C_{17}H_{30}N_3Pb_2I_7$	$C_{18}H_{36}N_4Pb_3I_{10}$
Formula weight/ g·mol^{-1}	959.16		959.16	1579.12	2199.08
Temperature/K			296(2)		
Wavelength/ Å			0.71073		
Crystal color	Orangish	Orangish	Reddish	Brownish	Blackish
Crystal system	Monoclinic	Triclinic	Triclinic	Triclinic	Triclinic
Space group	*C*2/m (no.12)	*P*-1 (no. 2)	*P*-1 (no. 2)	*P*-1 (no. 2)	*P*-1 (no. 2)
a/Å	32.824(6)	8.7350(16)	8.7497(8)	8.8092(5)	8.8201(14)
b/Å	6.1669(11)	8.7359(16)	8.7510(8)	8.8168(4)	8.8198(14)
c/Å	6.2114(11)	16.673(3)	16.6830(15)	22.8196(12)	29.038(5)
α/°	90	99.694(5)	99.7643(10)	97.072(4)	93.198(2)
β/°	93.205(2)	95.220(6)	95.2258(10)	93.983(4)	95.495(2)
γ/°	90	90.393(5)	90.3394(10)	90.199(4)	90.123(2)
Volume/Å^{-3}	1255.4(4)	1248.6(4)	1253.4(2)	1754.52(15)	2245.0(6)
Crystal size (mm^3)	0.22 x 0.15 x 0.1	0.2 x 0.1 x 0.05	0.3 x 0.2 x 0.15	0.2 x 015 x 0.15	0.2 x 015 x 0.15
Z	2	2	2	2	2
Density/g·cm^{-3}	2.537	2.551	2.422	2.989	3.253
μ(mm^{-1})	11.639	11.703	11.651	15.752	18.112
F (000)	856	856	808	1376	1896
Completeness to theta	99.1%	99.9%	99.8%	99.76%	99.8%
GOF on F^2	1.204	1.175	1.090	1.052	1.107
Absorption correction	Semi-empirical from equivalents				
Extinction coefficient	0.0142(8)	0.00005(19)	0.0033(3)	0.00075(9)	0.00106(7)
Refinement method	Full-matrix least-squares on F^2				
Data / restraints / parameters	1565/0/95	4403/0/239	4421/0/230	8472/0/164	7904/0/420
R_1, wR_2 [I > 2σ (I)]	0.0328, 0.0899	0.0525, 0.1418	0.0467, 0.1302	0.0546, 0.1443	0.0607, 0.1573
R_1, wR_2 (all data)	0.0371, 0.1051	0.0682, 0.1482	0.0514, 0.1382	0.0747, 0.1592	0.0830, 0.1734
Min/Max Δρ /eÅ^{-3}	-1.174/ 2.020	-1.600/3.513	-1.393/6.894	-1.896/2.705	-1.438/2.354
CCDC	1815922	1815926	1815923	1815925	1815924

References

[1] Y. Dang, Y. Liu, Y. Sun, D. Yuan, X. Liu, W. Lu, G. Liu, H. Xia and X. Tao, *CrystEngComm* 2015, **17**, 665.

[2] W. M. Wendlandt and H. G. Hecht, *Reflectance Spectroscopy, Interscience, New York,* 1966, **62.**