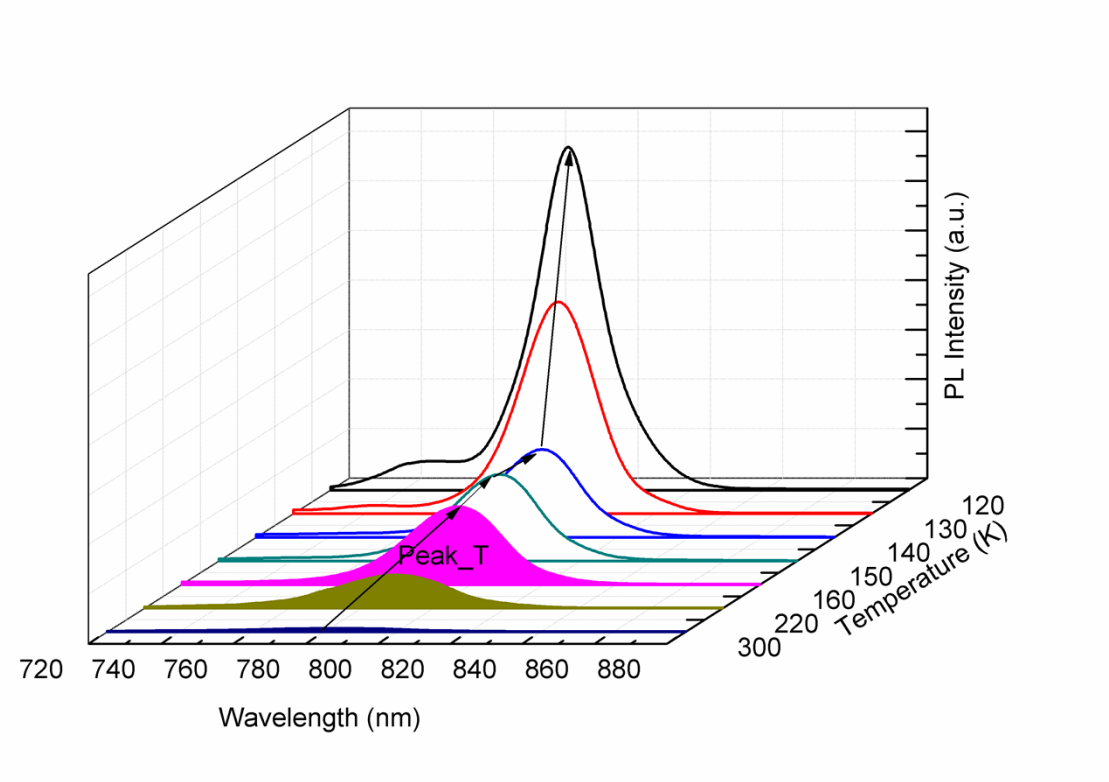
Electronic Supplementary Material (ESI) for Physical Chemistry Chemical Physics.

Supplement Information

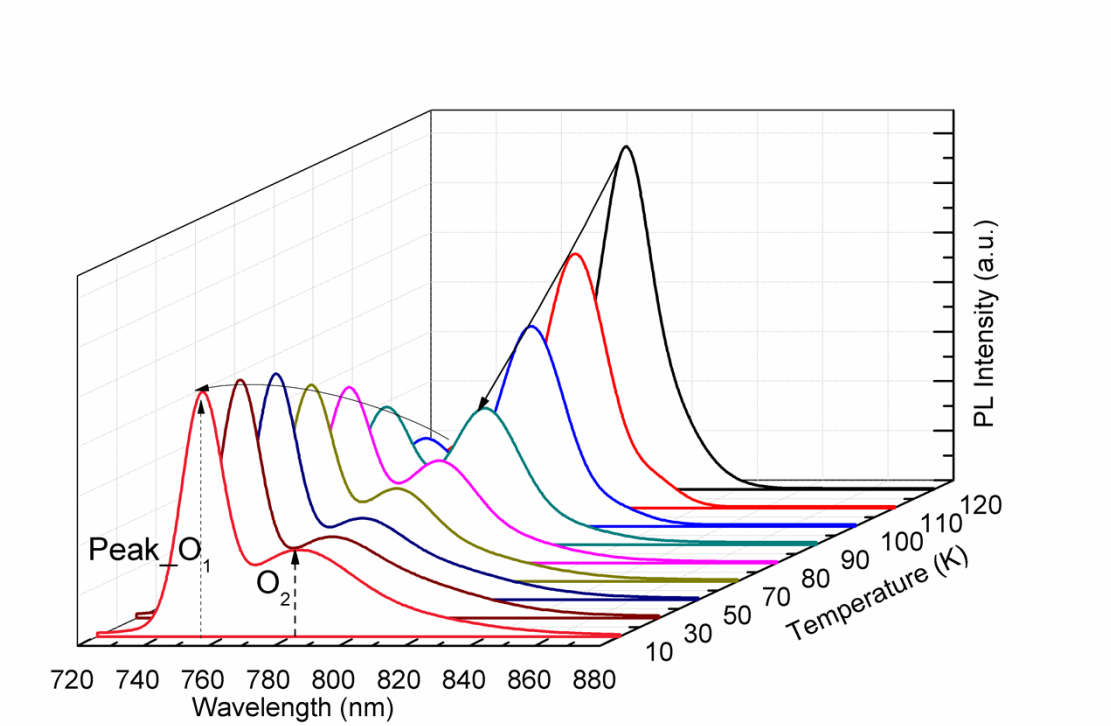
Characterization of an abnormal photoluminescence behavior upon crystal-phase transition of perovskite $CH_3NH_3PbI_3$

1. Temperature dependence of PL properties for the $MAPbI_3$ in tetragonal and orthorhombic phase.

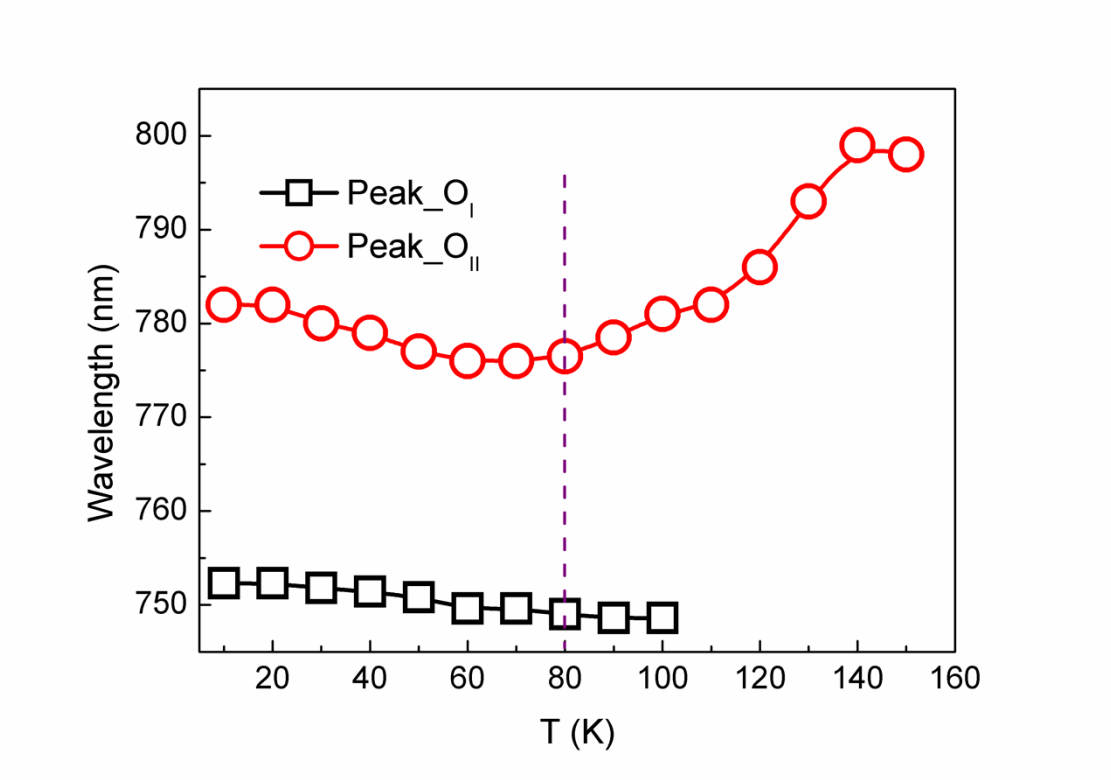
The stack of the PL spectra are plotted here to identify the changes in the maximum and the shapes of the PL curves, since the variation in intensity of the PL spectra has been shown in the main text.



(a)



(b)



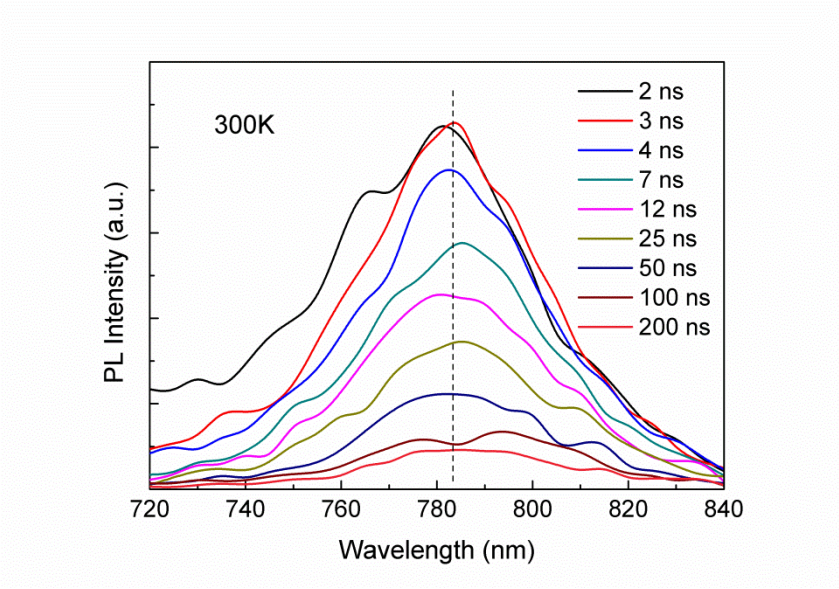
(c)

Fig.S1. (a-b) PL spectra of $MAPbI_3$ perovskite-crystal film at variable temperatures,

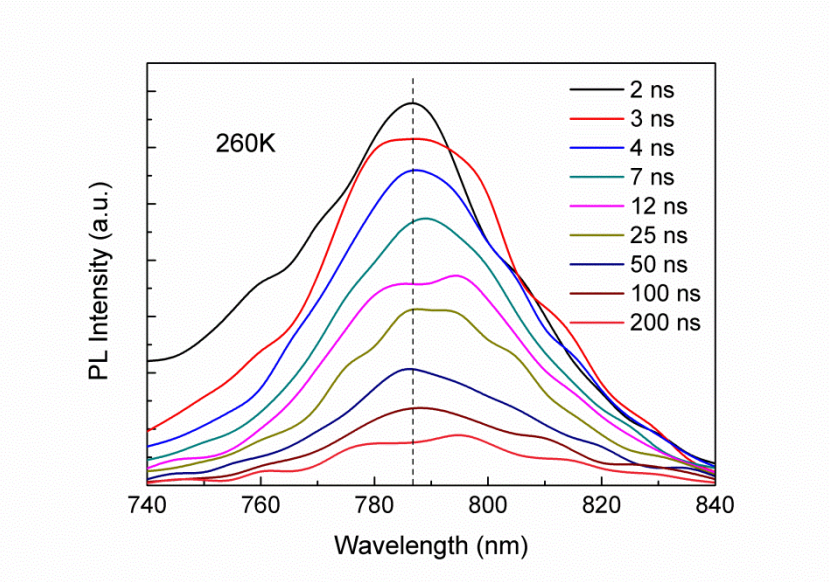
the arrows indicate the evolution tendency of the PL intensity. (c) Evolution of the position of Peak_O_{I-II} with a decrease in *T*.

2. TRPL spectra of $MAPbI_3$.

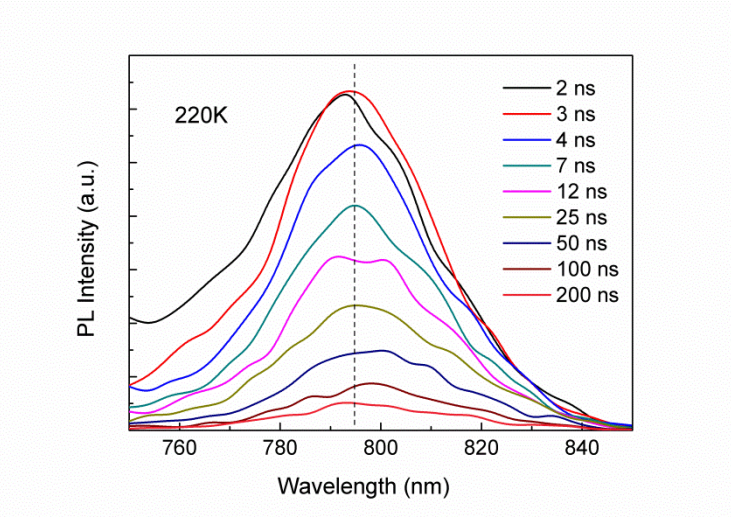
The little shift in the emission maximum suggests that the Peak_T could not be due to DAP recombination. It is noted that when *T* falls to 180K, there is a less than 3 nm shift in Peak_T, and no emergence of higher energy PL feature suggests that the phase transition has not happened yet.



(a)


260K
2 ns
3 ns
4 ns
7 ns
12 ns
25 ns
50 ns
100 ns
200 ns
PL Intensity (a.u.)
740
760
780
800
820
840
Wavelength (nm)

(b)


220K
2 ns
3 ns
4 ns
7 ns
12 ns
25 ns
50 ns
100 ns
200 ns
PL Intensity (a.u.)
760
780
800
820
840
Wavelength (nm)

(c)

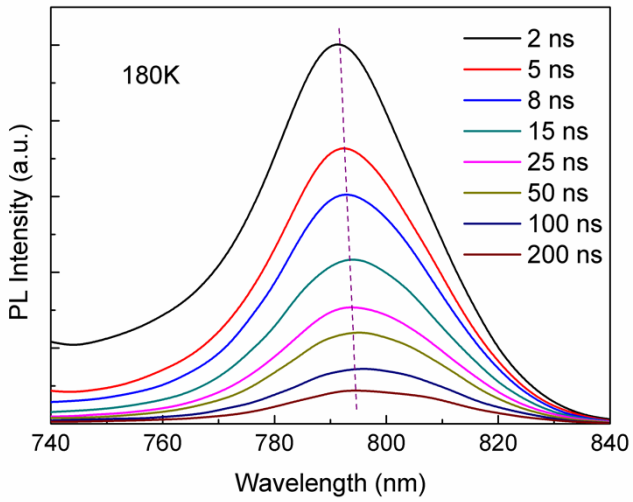


Fig. S2 TRPL spectra of the $MAPbI_3$ measured at (a) 300K, (b) 260K, (c) 220K and (d) 180K.

3. XRD patterns and crystal structure of the $MAPbI_3$ in tetragonal and orthorhombic phase

In the high-temperature region, $MAPbI_3$ perovskite has a tetragonal structure, the space group of which is determined to be I4/mcm (NO. 140). The orthorhombic phase with space group of Pnma (NO.62) is determined in the low-temperature range. Refined atomic position parameters for tetragonal and orthorhombic $MAPbI_3$ in Fig.S3(c-d) are obtained from the Ref. 6.[1] The black arrow in Fig. S1(c) highlights the transverse displacement of the I atom. The refined lattice parameters of the $MAPbI_3$ under different temperatures ranging from 13 to 300K are tabulated in TABLE SI.

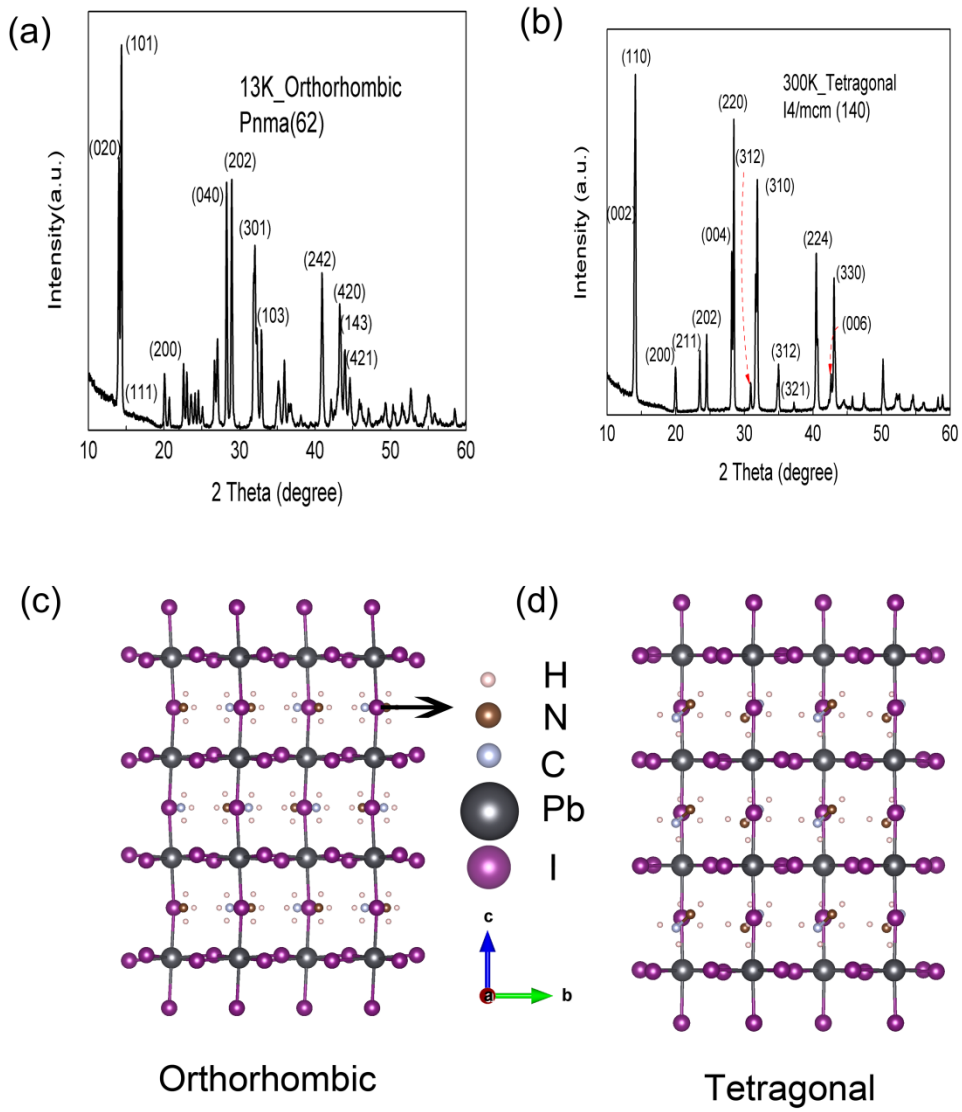


Fig.S3 (a) and (b): XRD patterns of $MAPbI_3$ perovskite at 13 and 300 K, respectively; (c) and (d): crystal structures of the tetragonal and orthorhombic $MAPbI_3$ perovskite.

TABLE SI: Refined lattice parameters determined from the low temperature single crystal X-ray diffraction experiments

	Lattice

Phase	Space Group	*T*(K)	parameters (Å)		
			a	b	c
Tetragonal	I4/mcm (140)	300	8.866(1)	12.668(1)	8.866(1)
		250	8.830(1)	12.683(1)	8.830(1)
		200	8.790(2)	12.662 (3)	8.790(2)
		180	8.791(1)	12.678(1)	8.791(1)
Orthorhombic	Pnma (62)	150	8.825(4)	12.682(5)	8.594(3)
		140	8.869(1)	12.628(1)	8.587(1)
		130	8.868(1)	12.625(2)	8.594(1)
		120	8.868(2)	12.621(1)	8.594(2)
		110	8.868(2)	12.623(1)	8.592(2)
		100	8.864(1)	12.620(1)	8.587(1)
		90	8.866(1)	12.619(1)	8.583(2)
		75	8.864(1)	12.618(0)	8.581(3)
		50	8.863(1)	12.614(1)	8.577(1)
		25	8.856(2)	12.613(0)	8.574(3)
		13	8.855(2)	12.614(0)	8.571(2)

References:

1. Feng, J. and B. Xiao, *Crystal Structures, Optical Properties, and Effective Mass Tensors of CH3NH3PbX3(X = I and Br) Phases Predicted from HSE06.* The Journal of Physical Chemistry Letters, 2014. **5**(7): p. 1278-1282.