Supporting Information

Controlling Crystallization of All-Inorganic Perovskite Films for Ultralow-Threshold Amplification Spontaneous Emission

Zi-Jun Yong,[†,○] Yang Zhou,[†,○] Ju-Ping Ma,[†,○] Ya-Meng Chen,[†,○] Jun-Yi Yang,[‡] Ying-Lin Song,[‡] Jing Wang,[§] and Hong-Tao Sun[†]*

[†] College of Chemistry, Chemical Engineering and Materials Science, State and Local Joint Engineering Laboratory for Novel Functional Polymeric Materials, Soochow University, Suzhou 215123, PR China

[‡] College of Physics, Optoelectronics and Energy, Soochow University, Suzhou 215123, PR China

[§] Ministry of Education Key Laboratory of Bioinorganic and Synthetic Chemistry, State Key Laboratory of Optoelectronic Materials and Technologies, School of Chemistry and Chemical Engineering, Sun Yat-sen University, Guangzhou 510275, PR China

* Email: timothyhsun@gmail.com

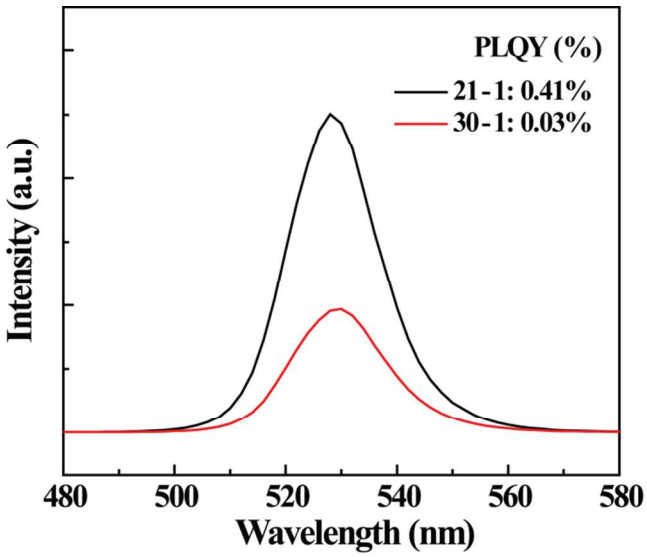

Figure S1. PL spectra and PLQYs of the $CsPbBr_3$ perovskite films prepared using a precursor with the CsBr and $PbBr_2$ molar ratio of 1 and at PA temperatures of 21 and 30 ºC. The films are denoted 21-1 and 30-1. Clearly, the PLQYs increase with the decrease of the PA temperature.

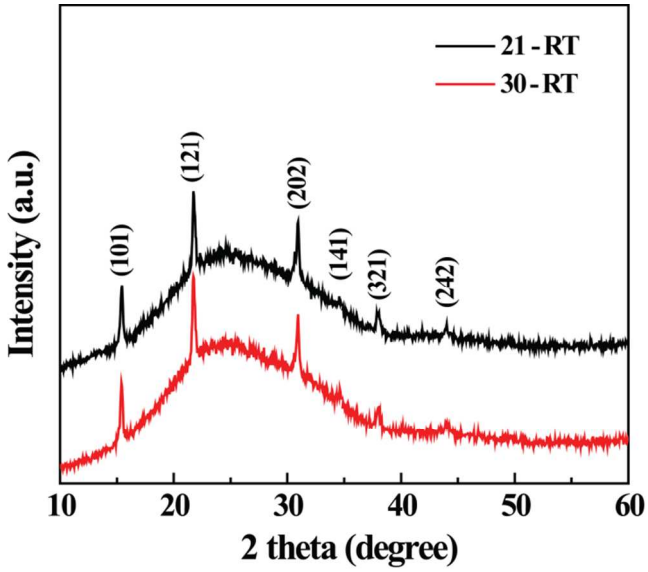

Figure S2. XRD patterns of $CsPbBr_3$ perovskite films prepared using PA temperatures of 21 and 30 ºC, followed by drying at room temperature. The films are denoted 21-RT and 30-RT. The films drying at room temperature also form orthorhombic $CsPbBr_3$ phase.

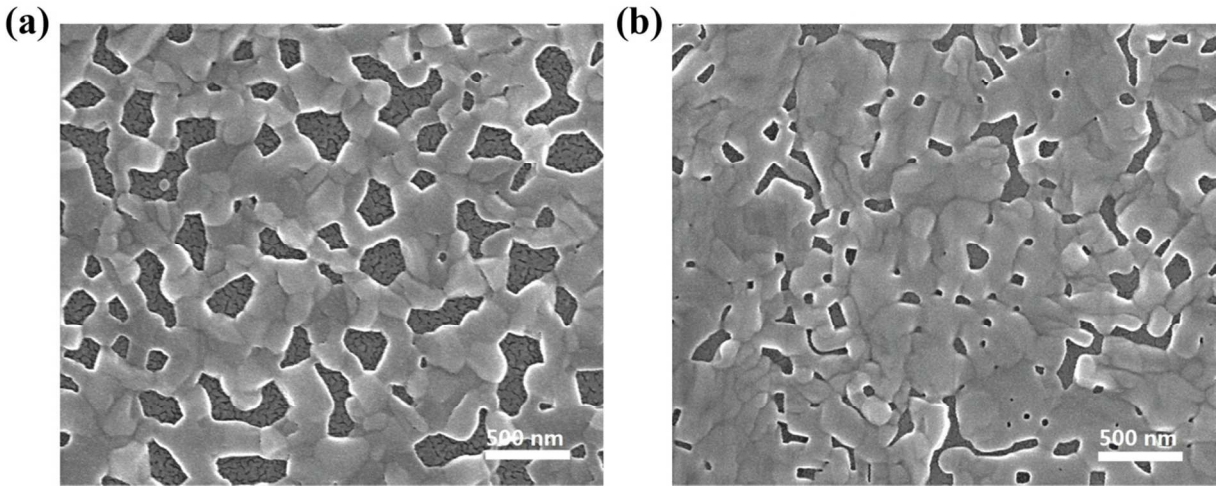

Figure S3. SEM images of the a) 23 and b) 25 films. When the PA temperature increases from 23 ºC to 25 ºC, the film morphology has changed dramatically.

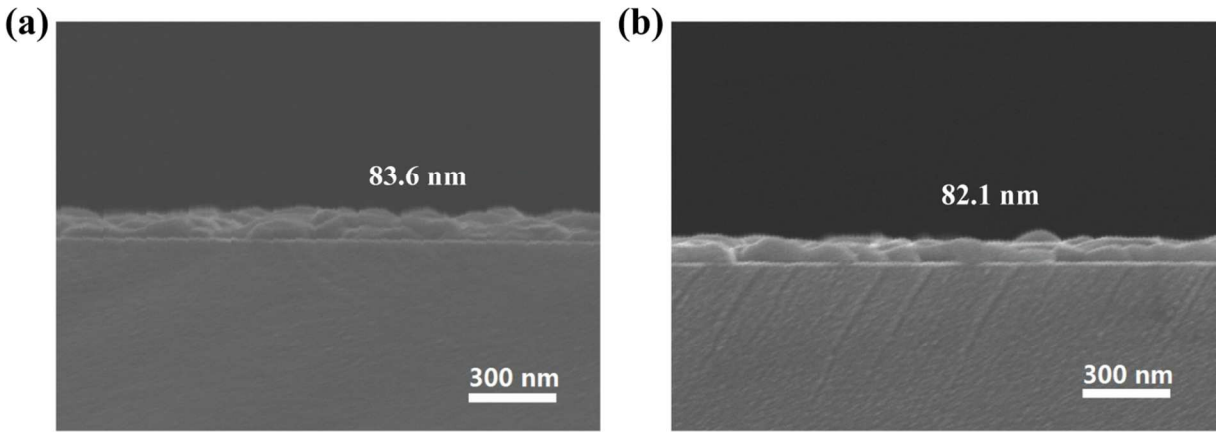

Figure S4. Cross-sectional SEM images of the **a)** 21 and **b)** 30 films. The thicknesses of the films are virtually identical.

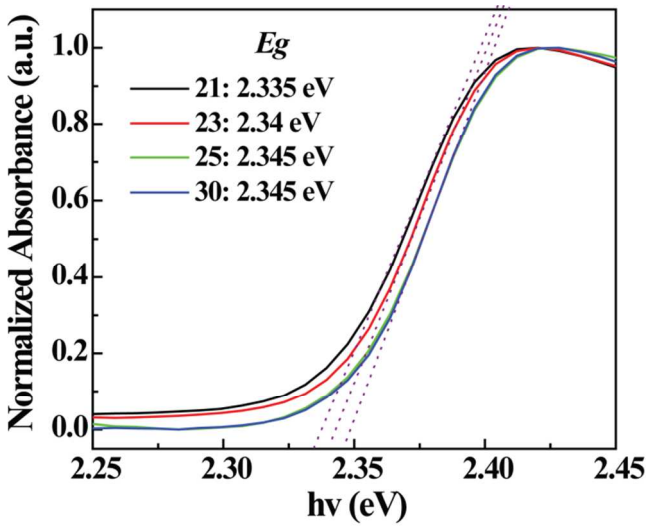

Figure S5. Absorption spectra of $CsPbBr_3$ perovskite films at different PA temperatures. The exciton absorption edge slightly shifts to high energy from 2.335 to 2.345 eV as the increase of the PA temperature from 21 to 30 ºC..

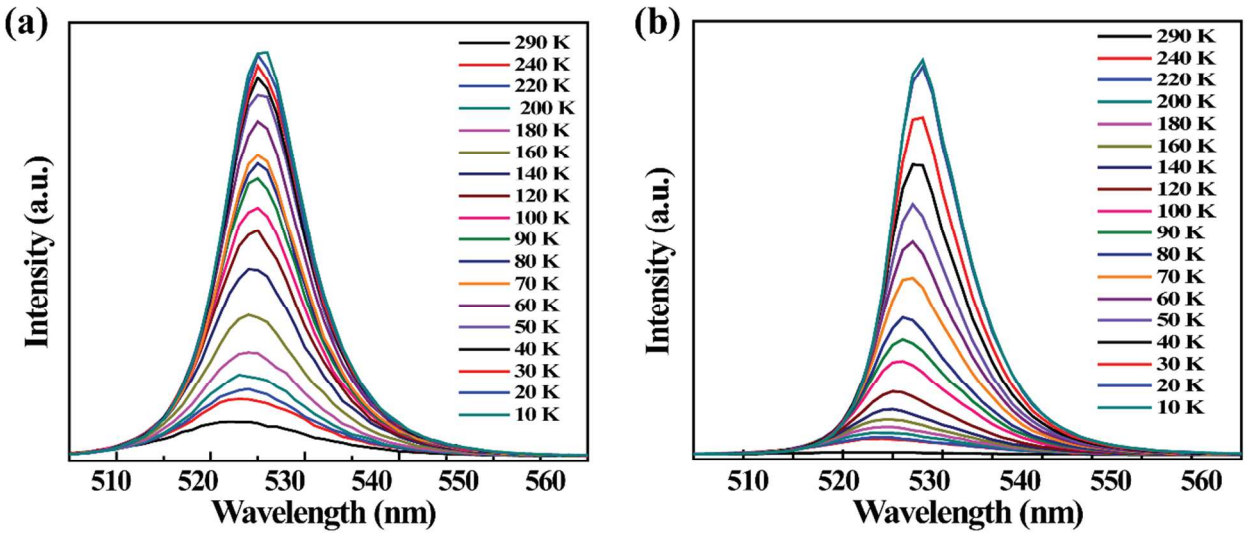

Figure S6. Temperature-dependent PL spectra of the **a)** 21 and **b)** 30 films from 10 K to 290 K.

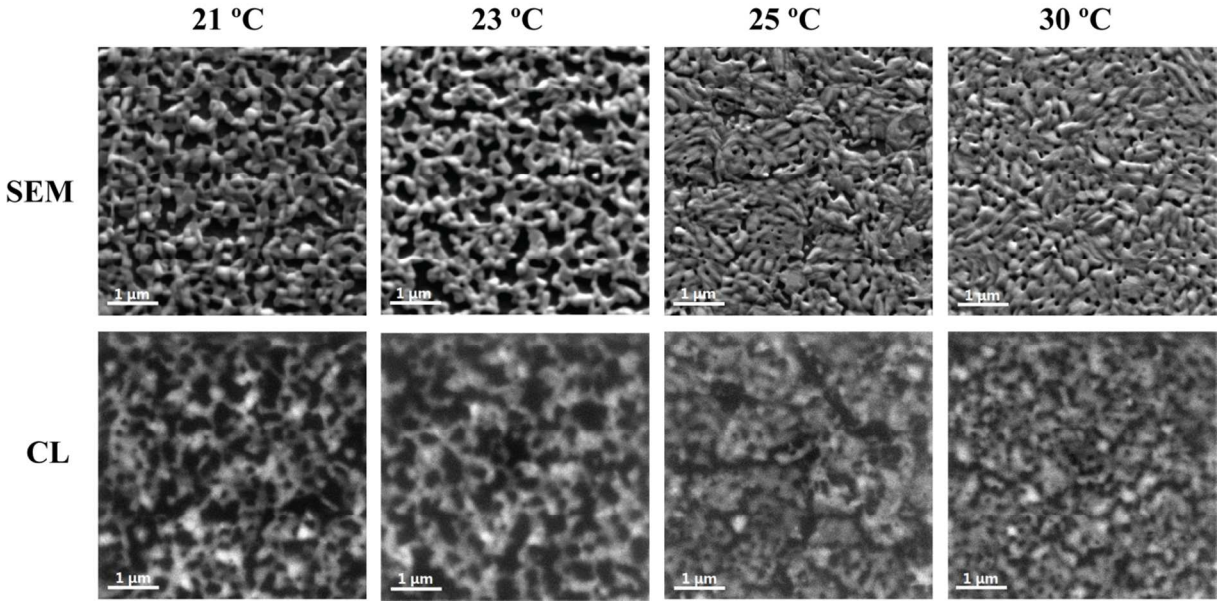

Figure S7. Secondary electron (SE) and CL images for the $CsPbBr_3$ films produced using different PA temperatures.

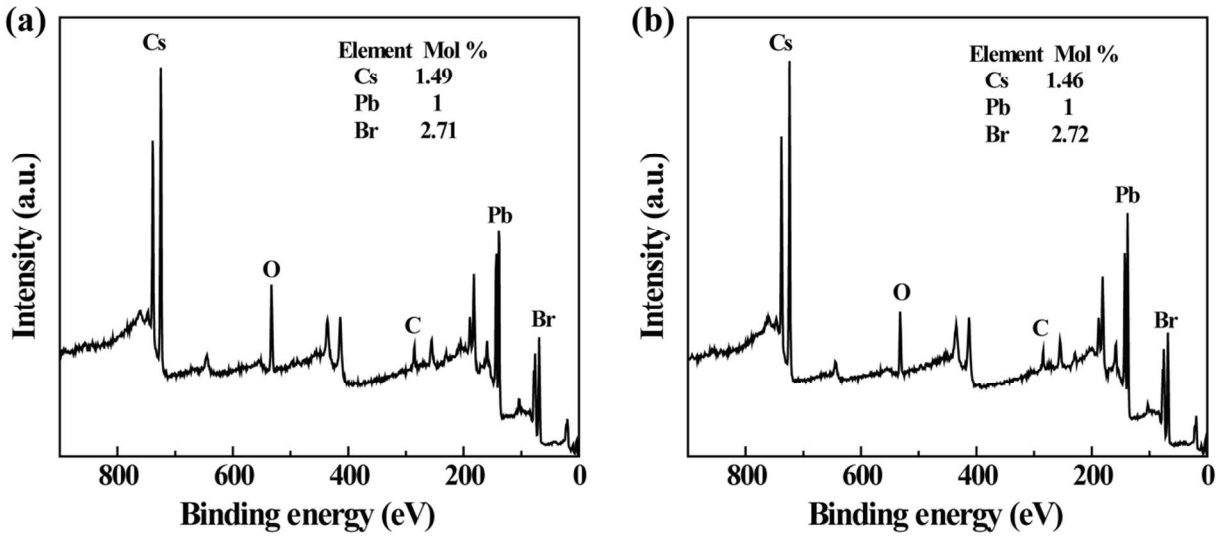

Figure S8. XPS survey spectra of the **a)** 23 and **b)** 25 films.

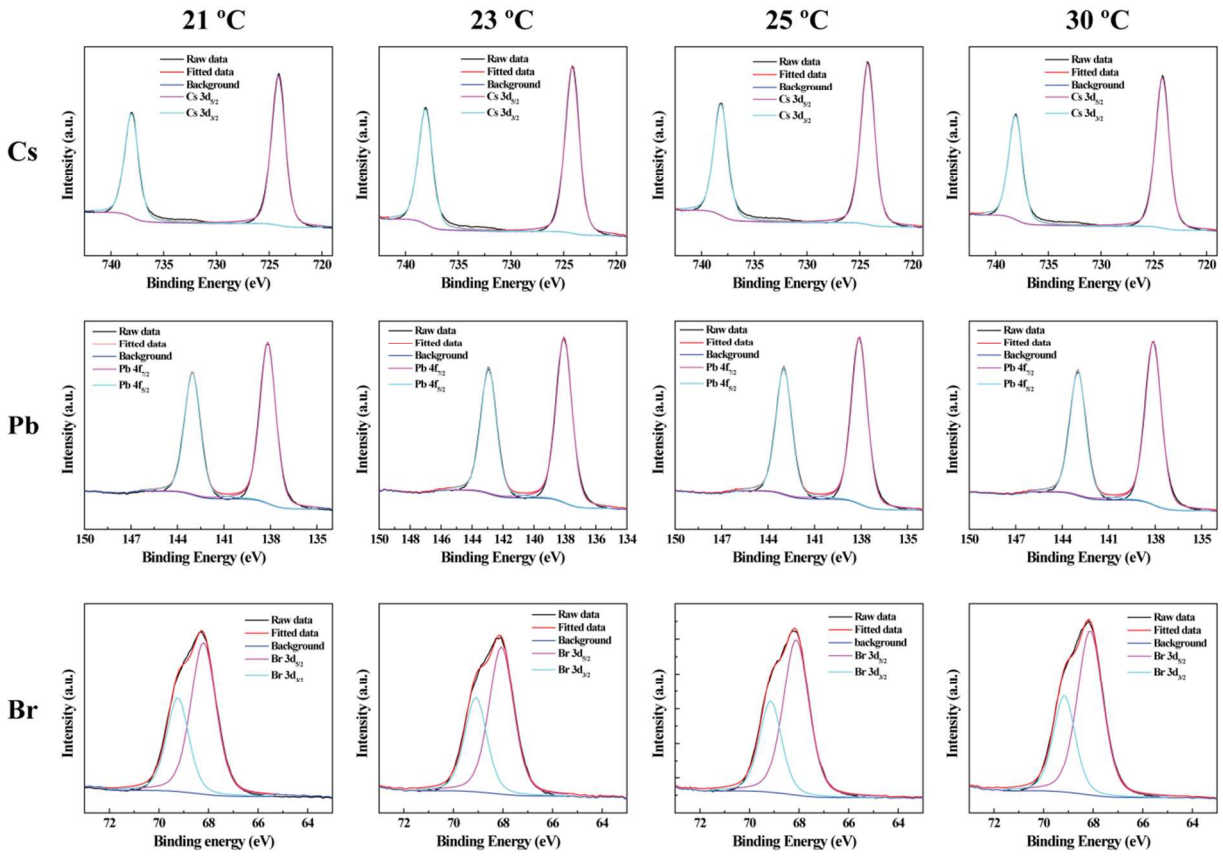

Figure S9. XPS spectra of Cs 3d, Pb 4f and Br 3d for the $CsPbBr_3$ perovskite films prepared using different PA temperatures.

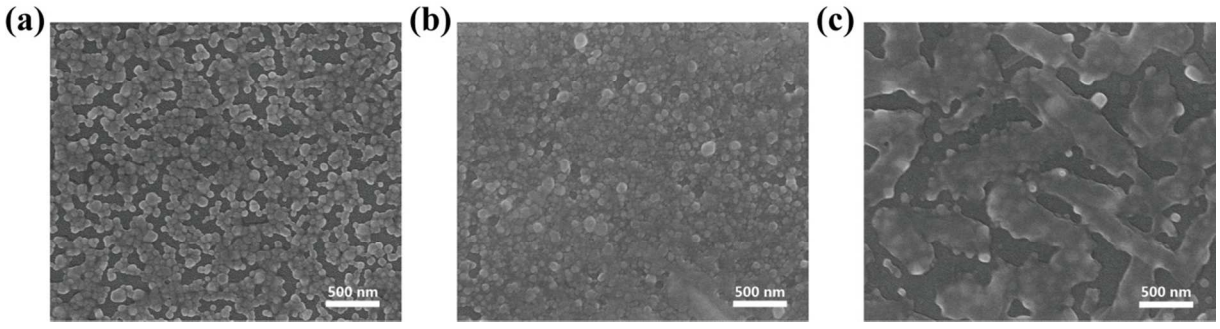

Figure S10. SEM images of the $CsPbBr_3$ perovskite films with varying PEG concentrations. **a)** the 6.25%-0.58% film. **b)** the 6.25%-1.71% film. **c)** the 6.25%-2.27% film.

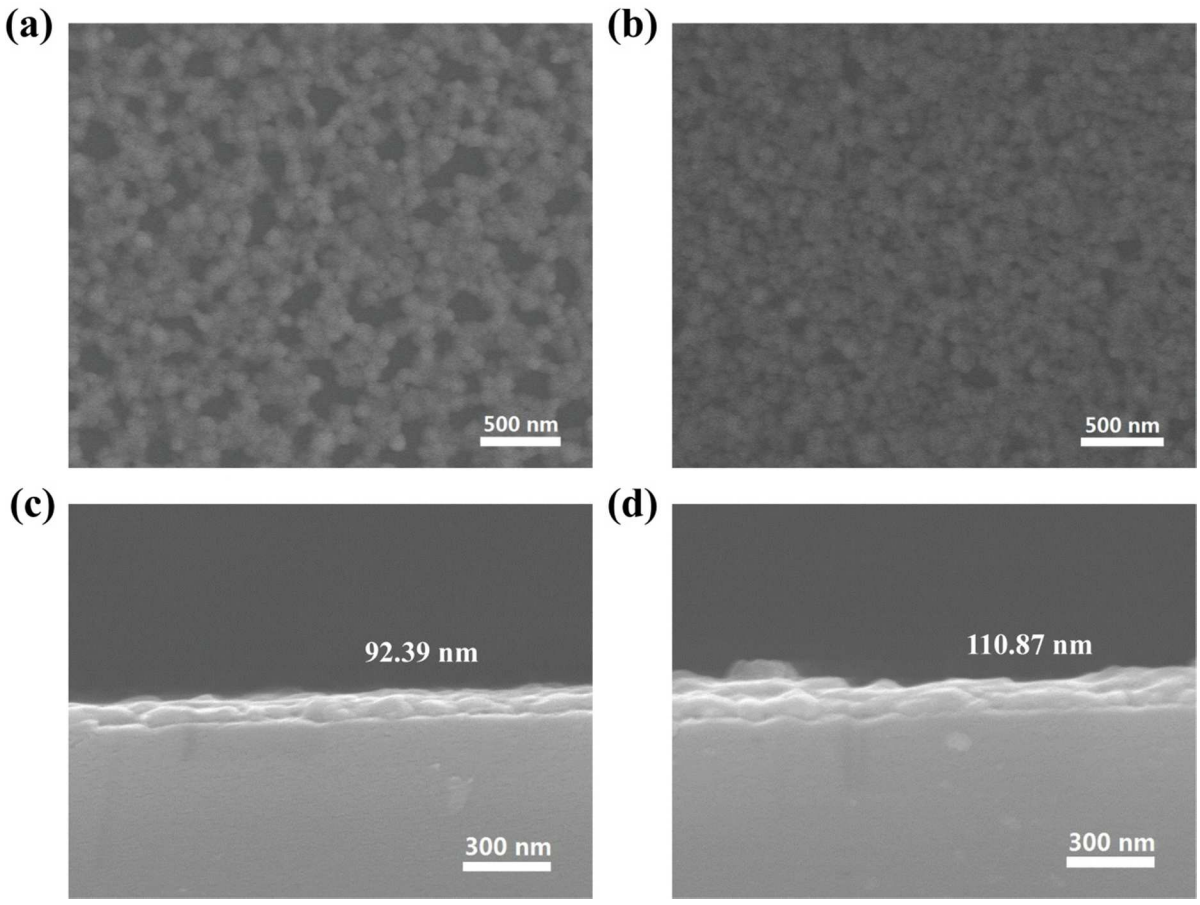

Figure S11. SEM images of the PEG-bearing $CsPbBr_3$ perovskite films. **a)** SEM image of the 15%-1.12% film. **b)** SEM image of the 15%-1.35% film. **c)** Cross-sectional SEM image of the 15%-1.35% film. **d)** Cross-sectional SEM image of the 15%-1.79% film. Note that the thickness of the 6.25%-1.15% film is only 32 nm.

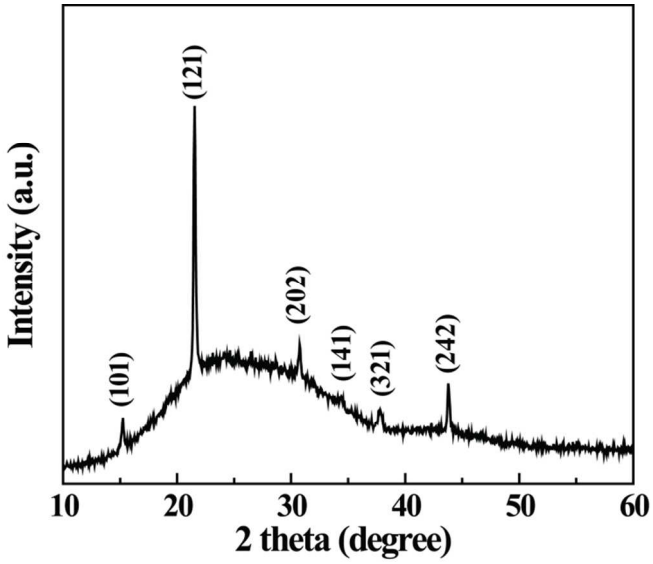

Figure S12. XRD pattern of the 15%-1.79% film. The film comprises orthorhombic $CsPbBr_3$ phase preferentially oriented with the (121) planes.

Table S1. The fitted lifetimes at 526 nm for the film fabricated at different PA temperature by a bi-exponential function.

Sample	A_1	τ_1 (ns)	A_2	τ_2 (ns)	τ_{ave} [a)] (ns)
21	0.4456	6.6061	0.5638	1.1015	3.53
23	0.4391	5.1669	0.5721	1.0686	2.85
25	0.3487	5.7109	0.7086	1.0611	2.59
30	0.3694	4.5089	0.6545	0.6048	2.01

[a)] Average lifetime calculated by the equation of $\tau_{ave}=(A_1\tau_1 +A_2\tau_2)/(A_1+A_2)$.

Table S2. ICP-MS analysis of the precipitate in DMSO solvent with different weight ratio of precursors.

Temperature	$CsBr:PbBr_2$ (molar ratio)	Concentration (wt.%)	Element molar ratio (Cs:Pb)
21 ºC	1.05:1	24.3	2.19:1
		26.1	6.58:1
30 ºC	1.05:1	24.3	3.74:1
		26.1	11.01:1

Table S3. Comparison of PLQYs for the PEG-bearing $CsPbBr_3$ perovskite films.

Sample	PLQY (%)
6.25%-0.58%	13.17%
6.25%-1.15%	30.63%
6.25%-1.71%	23.81%
6.25%-2.27%	19.43%
15%-1.12%	20.33%
15%-1.35%	22.01%
15%-1.79%	24.78%

Table S4. Representative experimental results of ASE using $CsPbBr_3$ perovskites as gain media.

Gain media	Pump source	ASE threshold ($\mu J\ cm^{-2}$)	Ref.
NCs [a)]	400nm, 35fs, 1kHz	192	1
NCs	400nm, 100fs, 1kHz	5.3	2
NCs	400nm, 100fs, 1 kHz	22	3
NWs [b)]	402nm 150fs, 250 kHz	6.2	4
NPs [c)]	400nm, 50fs, 1kHz	2.2	5
NCs	400nm, 100fs, 1kHz	2.14	6
NCs	405nm, 70fs, 1kHz	2.44	7
Films	400nm, 190fs, 1kHz	3.17	this work

[a)] NCs: nanocrystals casted films; [b)] NWs: individual nanowires as gain media; [c)] NPs: nanoplates casted films.

REFERENCES

(1) Pan, J.; Sarmah, S. P.; Murali, B.; Dursun, I.; Peng, W.; Parida, M. R.; Liu, J.; Sinatra, L.; Alyami, N.; Zhao, C.; Alarousu, E.; Ng, T. K.; Ooi, B. S.; Bakr, O. M.; Mohammed, O. F. Air-Stable Surface-Passivated Perovskite Quantum Dots for Ultra-Robust, Single-and Two-Photon-Induced Amplified Spontaneous Emission. *J. Phys. Chem. Lett.* **2015**, *6*, 5027-5033.

(2) Yakunin, S.; Protesescu, L.; Krieg, F.; Bodnarchuk, M. I.; Nedelcu, G.; Humer, M.; De Luca, G.; Fiebig, M.; Heiss, W.; Kovalenko, M. V. Low-Threshold Amplified Spontaneous Emission and Lasing from Colloidal Nanocrystals of Caesium Lead Halide Perovskites. *Nat. Commun.* **2015**, *6*, 8056-8063.

(3) Wang, Y.; Li, X.; Song, J.; Xiao, L.; Zeng, H.; Sun, H. All-Inorganic Colloidal Perovskite Quantum Dots: A New Class of Lasing Materials with Favorable Characteristics. *Adv. Mater.* **2015**, *27*, 7101-7108.

(4) Fu, Y.; Zhu, H.; Stoumpos, C. C.; Ding, Q.; Wang, J.; Kanatzidis, M. G.; Zhu, X.; Jin, S. Broad Wavelength Tunable Robust Lasing from Single-Crystal Nanowires of Cesium Lead Halide Perovskites ($CsPbX_3$, X= Cl, Br, I). *ACS Nano.* **2016**, *10*, 7963-7972.

(5) Zhang, Q.; Su, R.; Liu, X.; Xing, J.; Sum, T. C.; Xiong, Q. High-Quality Whispering-Gallery-Mode Lasing from Cesium Lead Halide Perovskite Nanoplatelets. *Adv. Funct. Mater.* **2016**, *26*, 6238-6245.

(6) Tong, Y.; Bladt, E.; Aygüler, M.; Manzi, A.; Milowska, K.; Hintermayr, V,; Docampo, P.; Bals, S.; Urban, A.; Polavarapu, L.; Feldmann, J. Highly Luminescent Cesium Lead Halide Perovskite Nanocrystals with Tunable Composition and Thickness by Ultrasonication. *Angew. Chem. Int. Ed.* **2016**, *55*, 13887-13892.

(7) Akkerman, Q. A.; Gandini, M.; Di Stasio, F.; Rastogi, P.; Palazon, F.; Bertoni, G.; Ball, J. M.; Prato, M.; Petrozza, A.; Manna, L. Strongly Emissive Perovskite Nanocrystal Inks for High-Voltage Solar Cells. *Nat. Energy.* **2016**, *2*, 16194-16200.