Electronic Supplementary Material (ESI) for Journal of Materials Chemistry C.


# Electronic Supplementary Information

## Large-Scale Room-Temperature Synthesis and Optical Properties of Perovskite-Related $Cs_4PbBr_6$ Fluorophors

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**Table S1** Summary of products via IIR reaction by changing polarity of 'oil phase'

| Oil Phase | Aqueous Phase | Crystalline Phase |
|---|---|---|
| **n-hexane** | DMF | Pure $Cs_4PbBr_6$ |
| **n-heptane** | | Pure $Cs_4PbBr_6$ |
| **p-xylene** | | $Cs_4PbBr_6$ (major) + $CsPbBr_3$ |
| **toluene** | | $Cs_4PbBr_6$ + $CsPbBr_3$ |
| **ethyl acetate** | | $Cs_4PbBr_6$ + $CsPbBr_3$ (major) |
| **tert-butyl alcohol** | | Pure $CsPbBr_3$ |

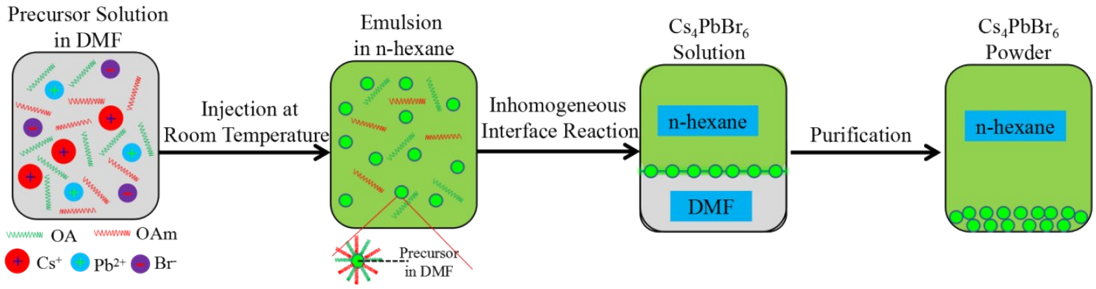



**Figure S1** Schematic diagram of $Cs_4PbBr_6$ synthesizing process via inhomogeneous interface reaction.

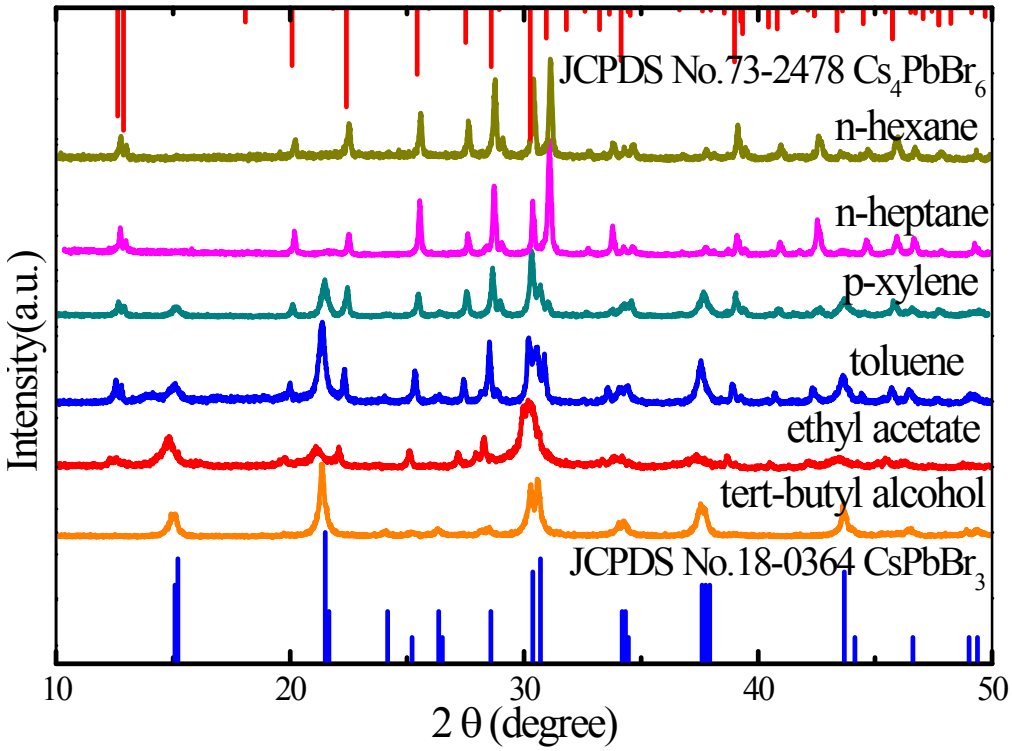



**Figure S2** XRD patterns of the products using different solvents as 'oil phase'.

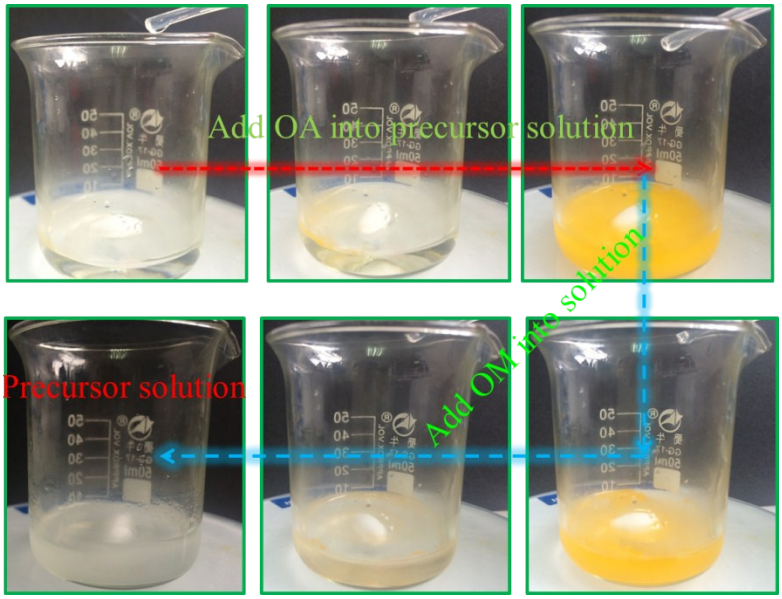



**Figure S3** Photographs of the precursor solution with the addition of only OM (top) and both OM and OA (bottom), showing that OM is indispensible to protect $Cs^{+}$, $Pb^{2+}$, and $Br^{-}$ in precursor solution.

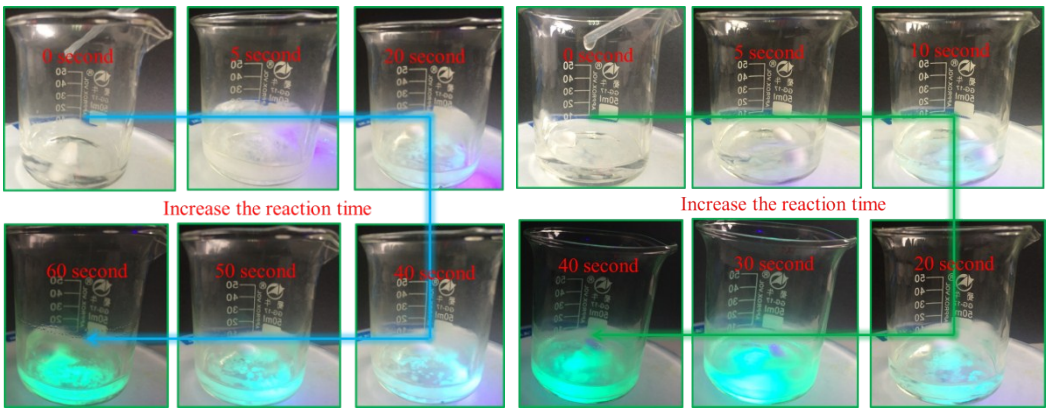



**Figure S4** Luminescent photographs of the reaction system with the addition of OM (left) and both OM and OA (right) under UV illumination, showing that OA can accelerate the reaction to achieve the final products.

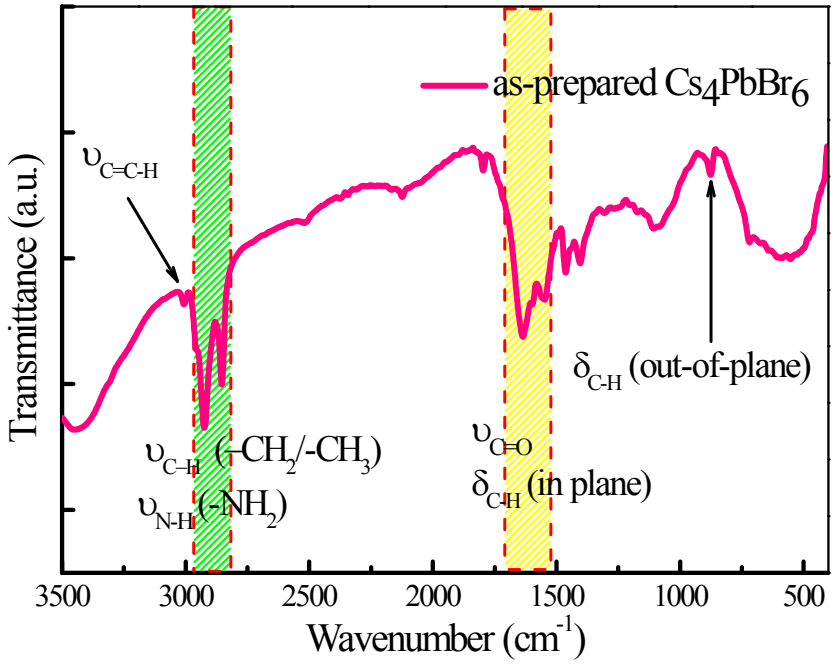



**Figure S5** FITR spectrum of the as-prepared $Cs_4PbBr_6$ sample.

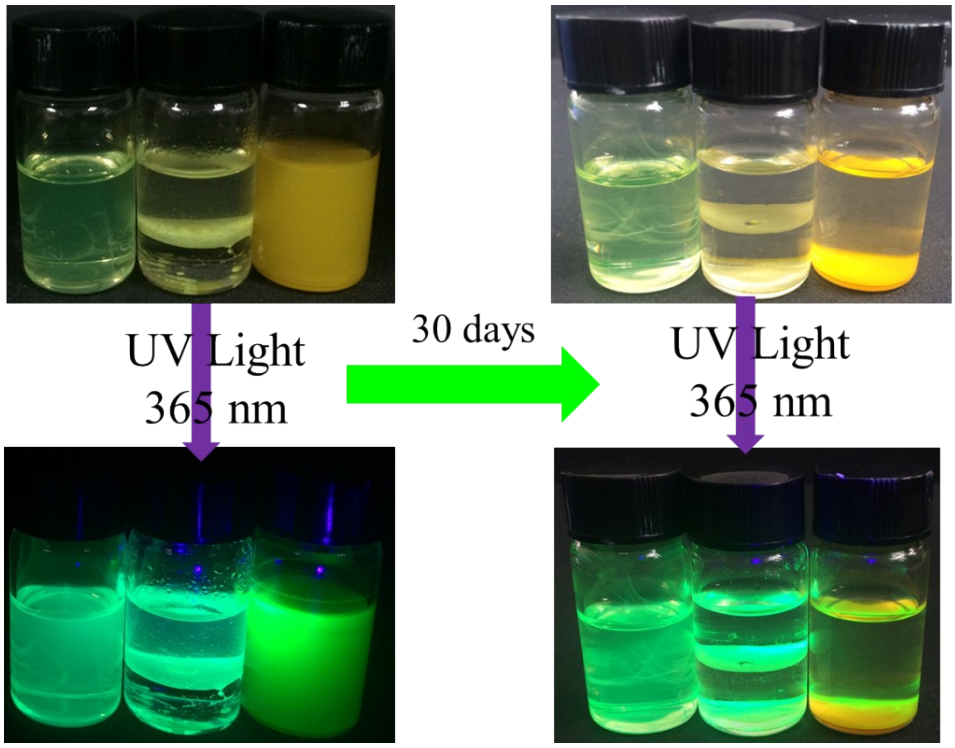
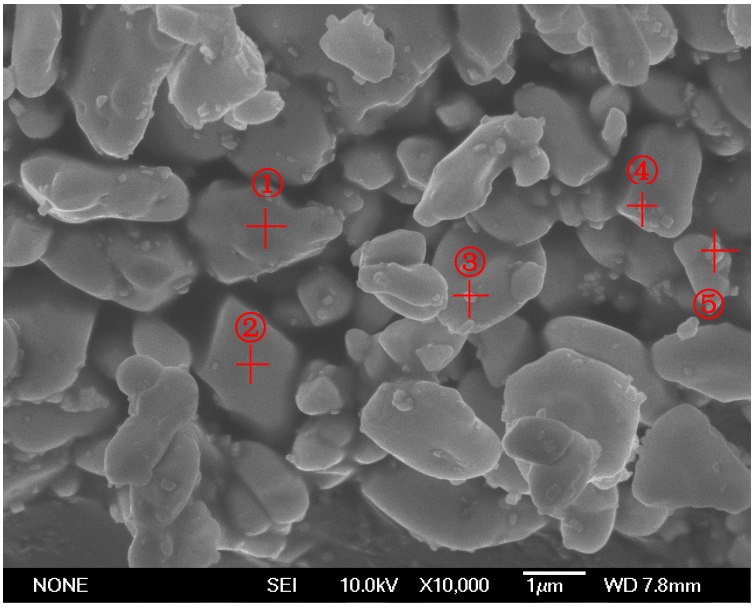
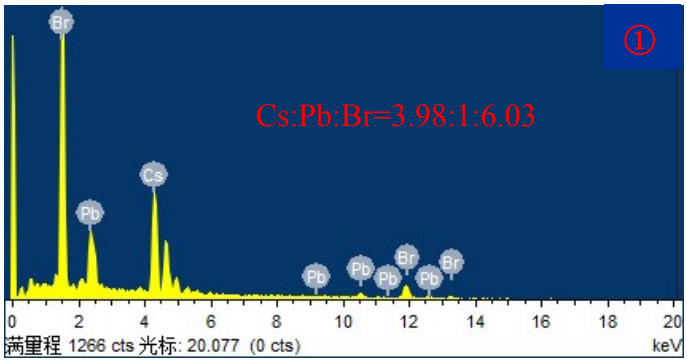
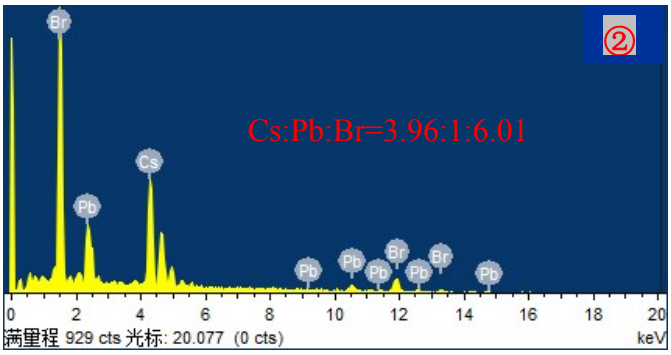
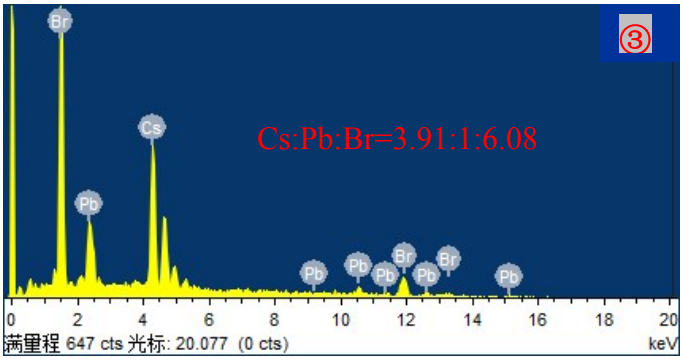



**Figure S6** Photographs of the fresh products (left) and the corresponding samples stored for 30 days (right) under daylight and UV light irradiation. These three samples are prepared by using different solvents as 'oil phase' (from left to right: middle-polar toluene, weak-polar n-hexane and strong-polar tert-butyl alcohol).


①
②
③
④
⑤
NONE
SEI
10.0kV X10,000
1μm
WD 7.8mm


①
Cs:Pb:Br=3.98:1:6.03
Br
Cs
Pb
0 2 4 6 8 10 12 14 16 18 20
满里程 1266 cts 光标: 20.077 (0 cts)
keV


②
Cs:Pb:Br=3.96:1:6.01
Br
Cs
Pb
0 2 4 6 8 10 12 14 16 18 20
满里程 929 cts 光标: 20.077 (0 cts)
keV


③
Cs:Pb:Br=3.91:1:6.08
Br
Cs
Pb
0 2 4 6 8 10 12 14 16 18 20
满里程 647 cts 光标: 20.077 (0 cts)
keV

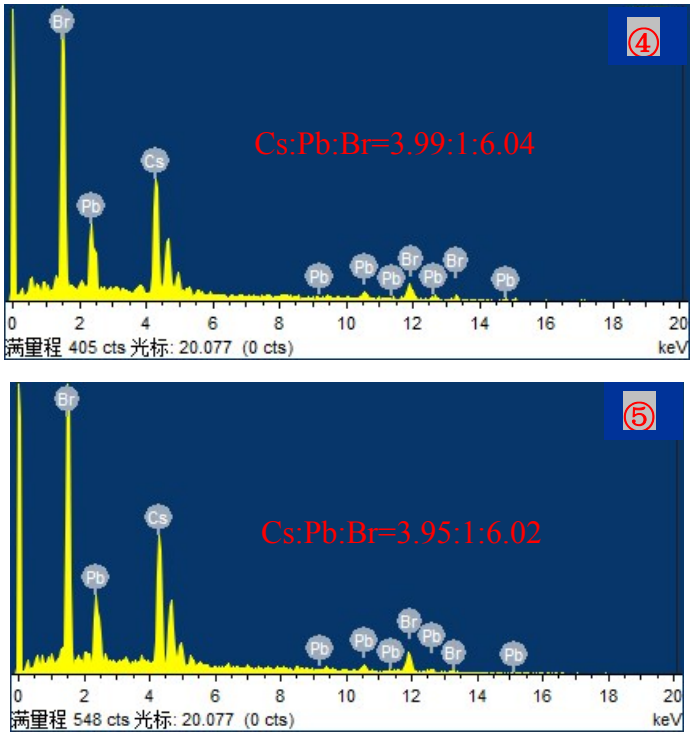



**Figure S7** SEM image and EDS spectra of $Cs_4PbBr_6$ sample by detecting different regions, showing the approximate atomic ratio of 4:1:6 for the $Cs_4PbBr_6$ sample.

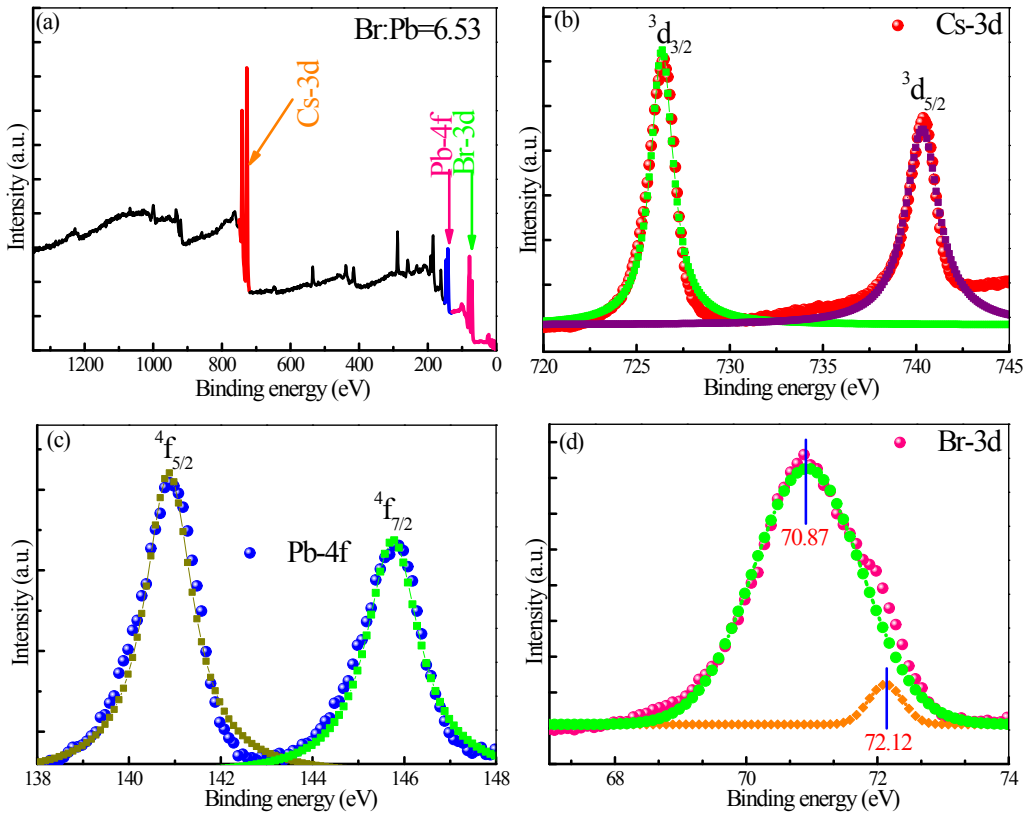



**Figure S8** (a) XPS full spectrum of $Cs_4PbBr_6$ sample. High-resolution XPS spectra of (b) Cs-3d, (c) Pb-4f and (d) Br-3d states.

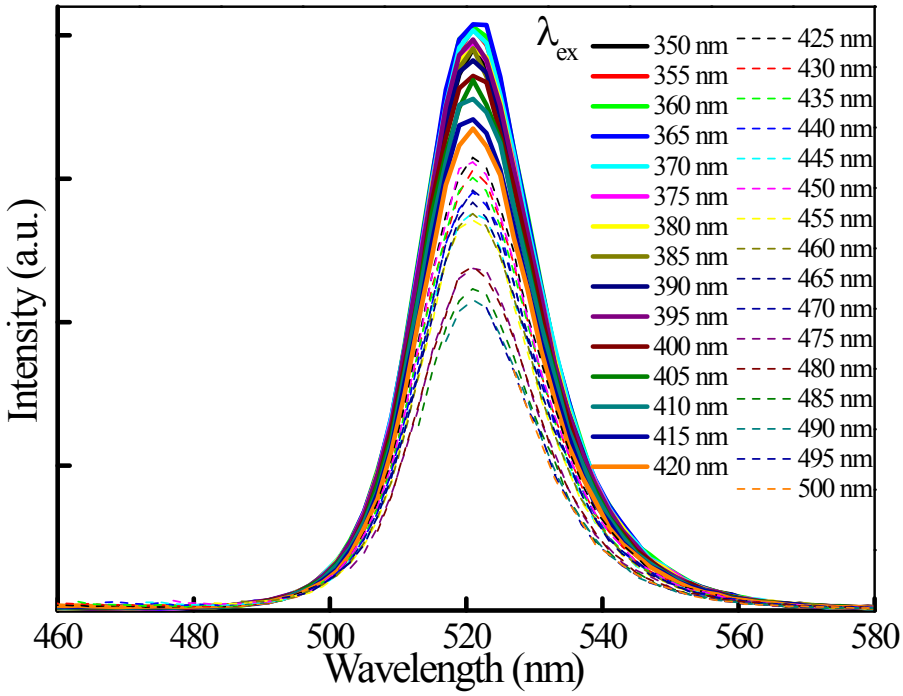



**Figure S9** PL spectra recorded under the excitation of diverse wavelength lights ranging from 350 to 500 nm.

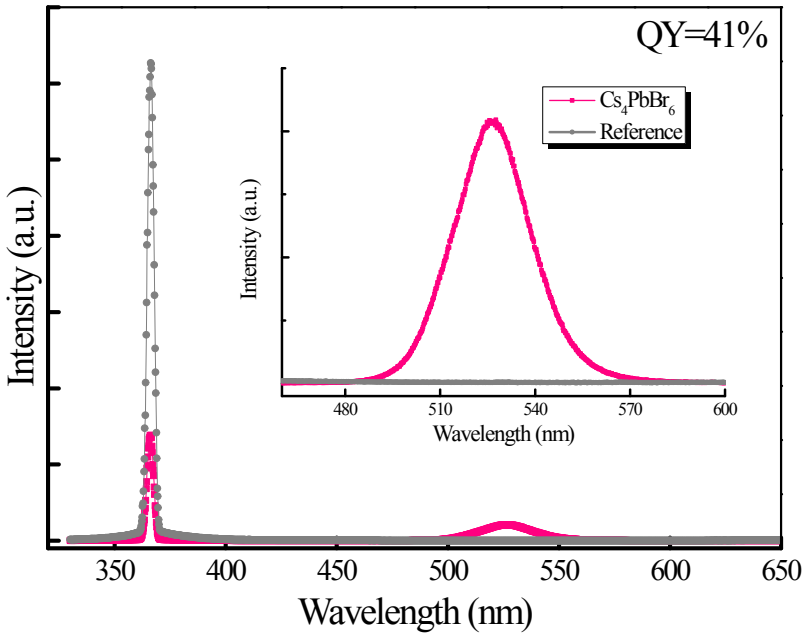



**Figure S10** Quantitative excitation and emission spectra of $Cs_4PbBr_6$ and reference samples recorded by a spectrofluoremeter equipped with an integrating sphere for QY measurement. Inset shows the magnified emission spectra in the wavelength range of 450-600 nm.

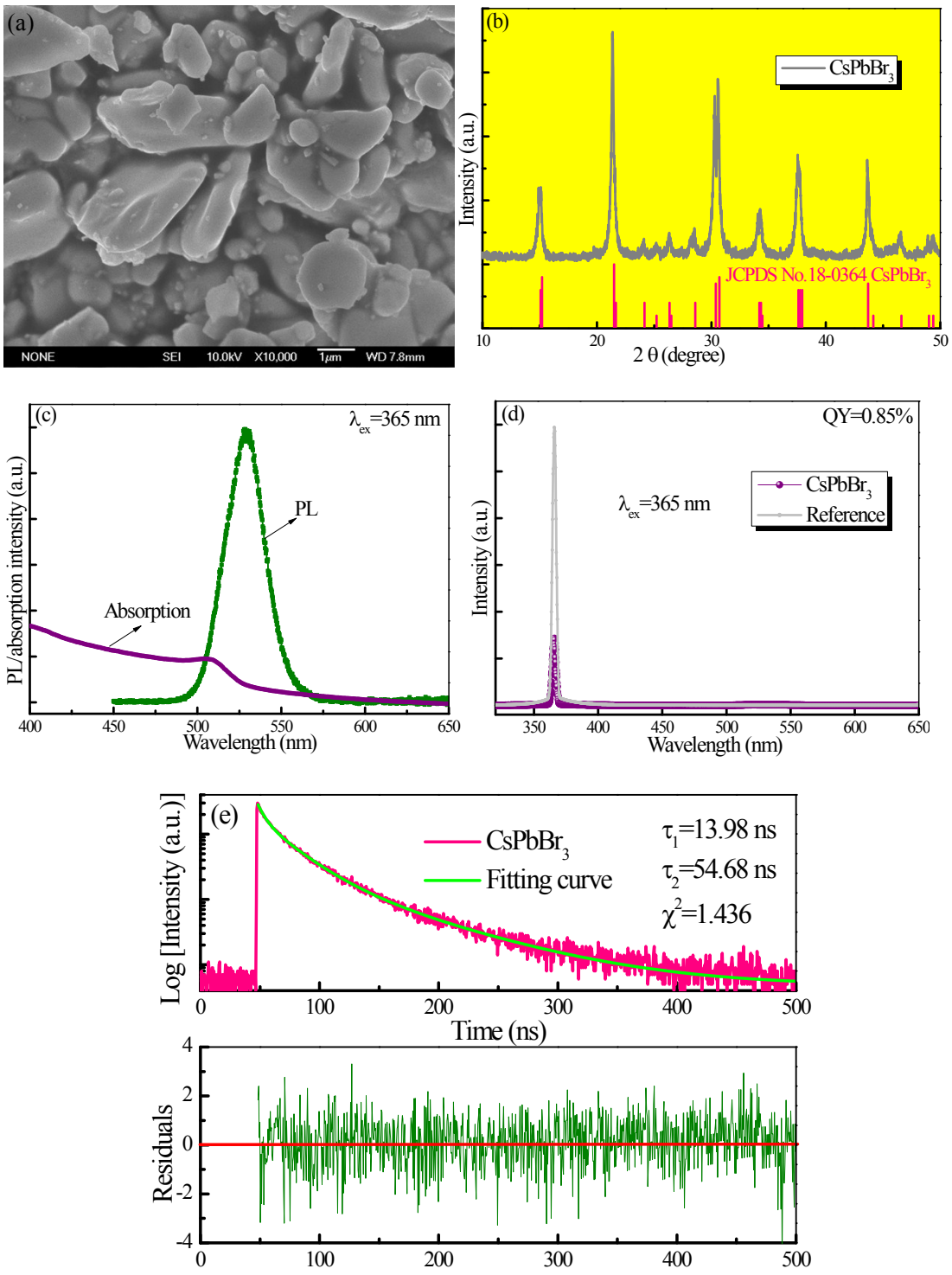



**Figure S11** Structural and spectral characterizations of the fabricated $CsPbBr_3$ sample: (a) SEM image, (b) XRD pattern, (c) PL/absorption, (d) QY measurement and (e) decay curve.

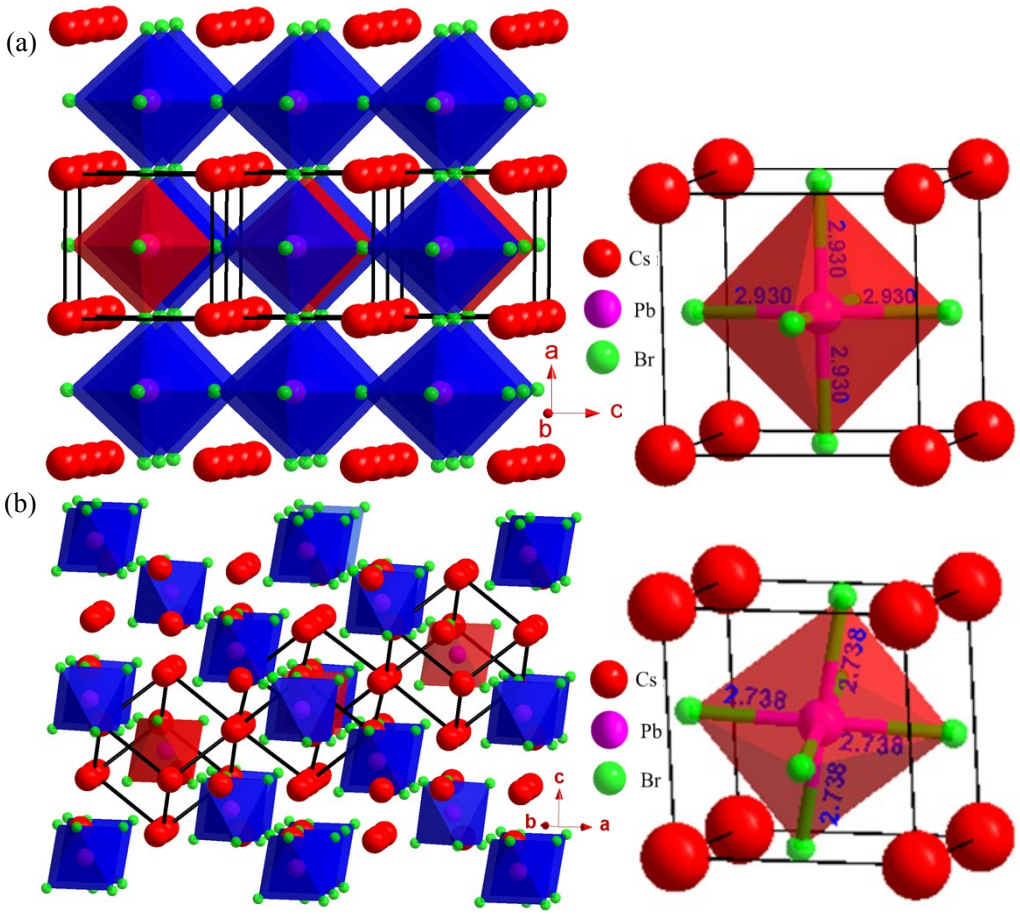



**Figure S12** Schematic illustration of (a) monoclinic $CsPbBr_3$ and (b) rhombohedral $Cs_4PbBr_6$ crystal structures. $PbBr_6^{4-}$ octahedral geometries in $Cs^+$ simple cubic lattices are also provided.

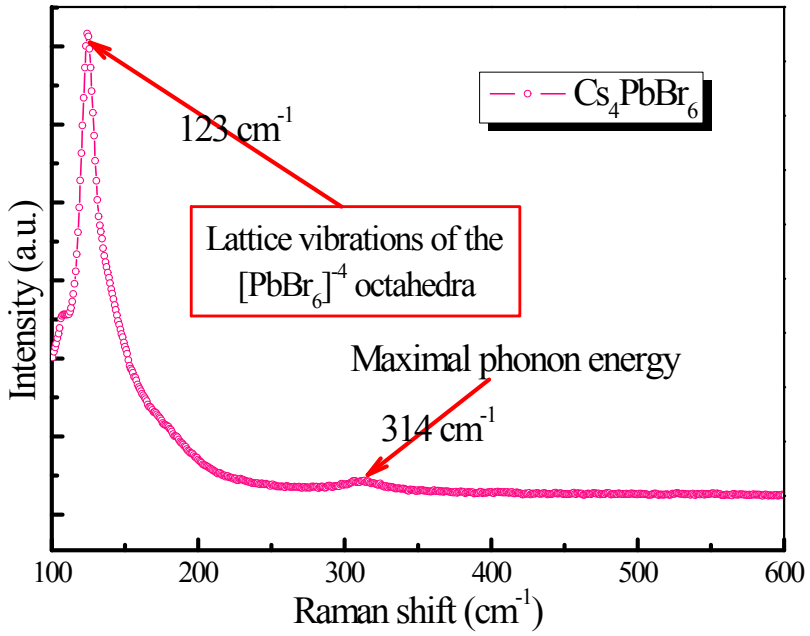



**Figure S13** Raman spectrum of $Cs_4PbBr_6$ sample

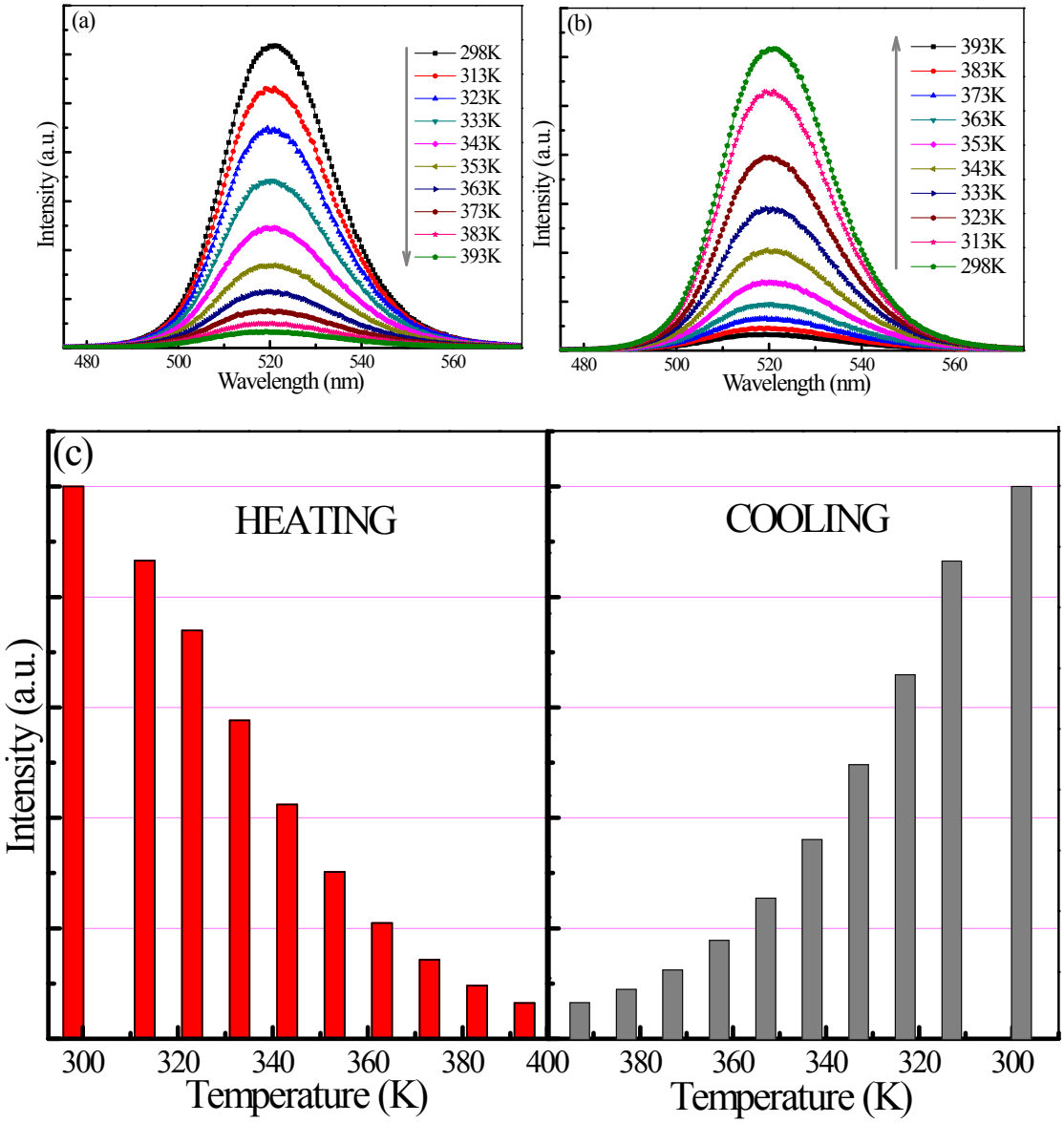



**Figure S14** Temperature-dependent PL spectra on cycling processes of heating (a) and cooling (b) in the temperature range from 298 K to 393 K. (c) The corresponding PL integrated intensity as a function of temperature.

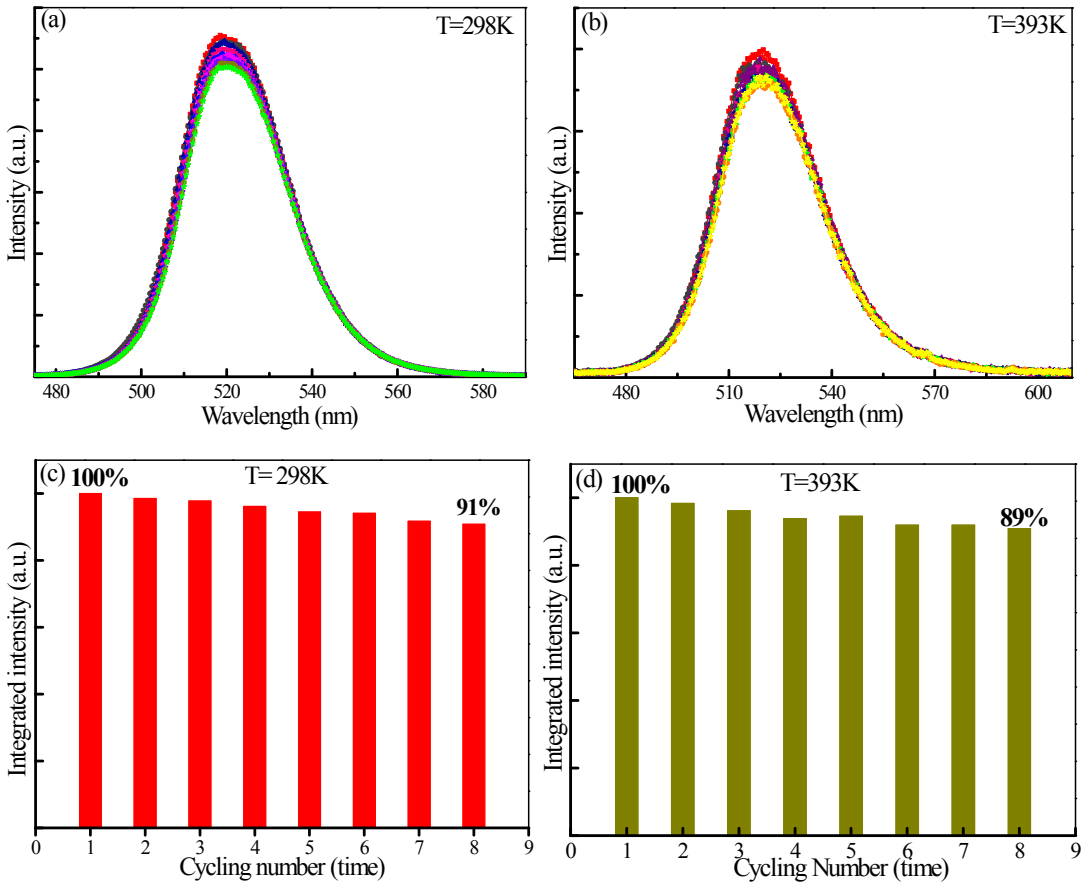



**Figure S15** PL spectra and the corresponding integrated intensity of the $Cs_4PbBr_6$ sample recorded at the (a, c) 298 K and (b, d) 393 K respectively after eight-time cycling experiments.

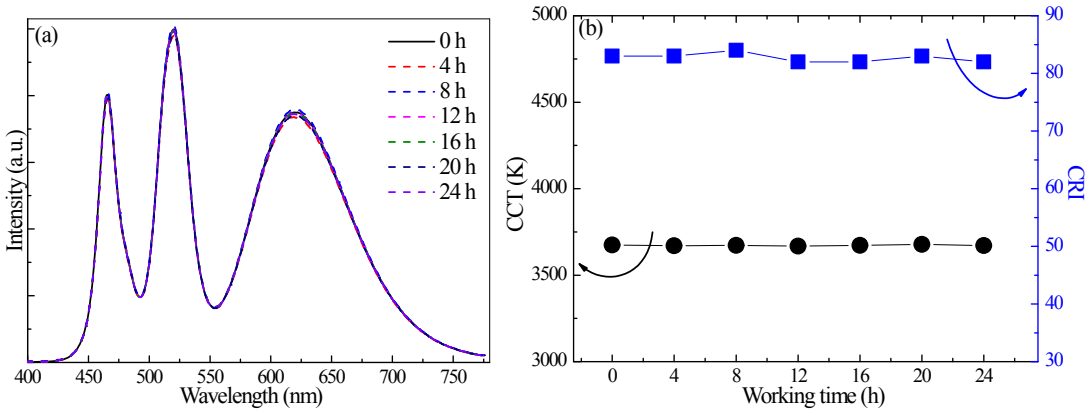



**Figure S16** (a) Electroluminescence spectra of WLED at different working time intervals. (b) The related CCT and CRI versus working time intervals.