Supporting Information

High Stable $CsPbBr_3$ Quantum Dots Coated with Alkyl Phosphate for White Light-Emitting Diodes

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Methods

Materials: Lead (II) bromide ($PbBr_2$, > 98%, Aldrich), Cesium bromide (CsBr, 99.9%, Aldrich), 1-Tetradecylphosphonic acid (98%, Alfa Aesar), Oleylamine (OAm, 70%, Aldrich), Oleic acid (OA, 90%, Aldrich), N, N-Dimethylformamide (DMF, 99.8%, Aladdin), Cyclohexane (>99.5%, Aladdin), Toluene (99.5%, Sinopharm Chemical Reagent Co., Ltd, China). All reagents were used as received without further purification.

Characterizations: The UV/vis absorption spectra were recorded with a Cary 5000 UV/vis/NIR spectrophotometer (Varian Instruments) equipped with double out of plane Littrow monochromator. The photoluminescence (PL) spectra within the range 293K-400K and the decay curves were measured using an Edinburgh Instruments FSP920 Time Resolved and State Fluorescence Spectrometers equipped with a 450 W Xe lamp, a 60W μF900 μs flash lamp, TM300 excitation monochromator and double TM300 emission monochromators, and themo-electic cooled red-sensitive PMT. The spectral resolution of the steady measurements was about 0.05 nm in UV/vis. The sample was mounted in an Oxford OptistatDN2 nitrogen cryostat for PL measurements above room temperature (RT). The absolute photoluminescence quantum yield (PLQY) of the sample was measured using a barium sulfate coated integrating sphere (150 mm in diameter) attached to the FSP920. Electroluminescence (EL) spectra were recorded at a forward current and measured using an Ocean Optics Instruments QE65000. The XRD measurements were measured on a Rigaku D/MAX 2200 VPC using a Cu Kr radiation ($\lambda = 1.5405$Å). The sample were scanned from $10° < 2\theta < 60°$ at increment of 10°/min. Transmission electron microscope (TEM) and energy dispersive spectrometer (EDS) were performed on

JEOL-JEM 2100F and FEI Tecnai G2 Spirit instrument. X-ray photoelectron spectroscopy (XPS) measurements were carried out on a multifunctional imaging electron spectrometer (Thermo ESCALAB 250XI). Fourier transformation infra-red (FTIR) spectra were taken by using a Fourier transformation infra-red spectrometer (Bruker, EQUINOX 55).

Synthesis of $CsPbBr_3$/TDPA QDs: Firstly, $PbBr_2$ (0.4 mmol), CsBr (0.4mmol), 1-Tetradecylphosphonic acid (100 mg), and OAm (0.5 mL) were added to DMF (10 mL) with vigorous stirring to form the precursor solution. Secondly, 1 mL of the precursor solution was quickly injected into toluene (10 mL) solution under vigorous stirring. Thirdly, the QDs were centrifuged at 6000 rpm for 5 min, and washed twice by cyclohexane, and then the precipitate was dried in the open air for 48 h. Finally, the $CsPbBr_3$/TDPA QDs were dispersed in toluene for further using.

Synthesis of pure $CsPbBr_3$ QDs: Typically, $PbBr_2$ (0.4 mmol), CsBr (0.4 mmol), OA (1.0 mL), and OAm (0.5 mL) were added to DMF (10 mL) with vigorous stirring to form the precursor solution. Then, 1 mL of the precursor solution was quickly injected into toluene (10 mL) solution under vigorous stirring. Finally, the QDs was centrifuged at 6000 rpm for 5 min, and washed twice by cyclohexane. Then $CsPbBr_3$ QDs were dispersed in toluene for further using.

Large-scale synthesis of $CsPbBr_3$/TDPA QDs: A mixture of $PbBr_2$ (2.0 mmol), CsBr (2 mmol), 1-Tetradecylphosphonic acid (500 mg), and OAm (2.0 mL) were added to DMF (50 mL) with vigorous stirring. Then, 50 mL of precursor solution was injected into toluene (500 mL) solution under stirring. Finally, the QDs were centrifuged at 6000 rpm for 5 min, and washed twice by cyclohexane, and then the precipitate was dried in the open air for 48 h. About 1.4 g $CsPbBr_3$/TDPA QDs were obtained by grinding the dried solid in an agate mortar (Figure S1).

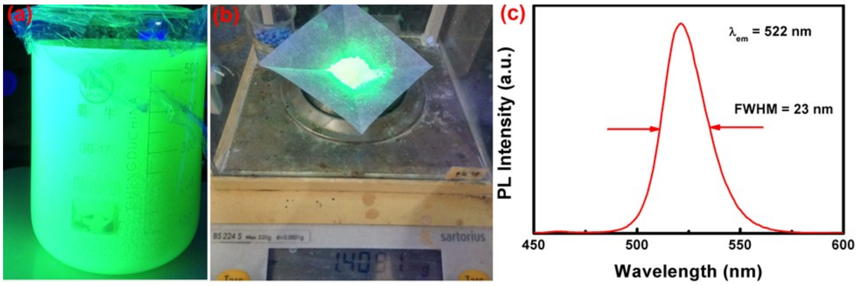

Fig. S1. The images of $CsPbBr_3$/TDPA QDs solution (a) and powders (b) under 365 nm UV light. (c)The PL spectrum of the $CsPbBr_3$/TDPA powders by large-scale synthesis route.

Synthesis of KSiF:Mn^{4+} phosphors: Typically, 4 mmol of SiO_2 , 0.045mmol $Mn(HPO_4)_2$, and 120 mmol KHF_2 were added to 15 mL water in a Teflon vessel. After ultrasonic vibration for 30 min, the Teflon vessel was heated to 180°C for 6 hours. Then, the autoclave was cooled to room temperature. The products were collected by centrifugation and washed by water and dried under vacuum at 40°C for 24 hours.

Stability Tests:

For water stability test, 0.5 mg/mL QDs powder added to water solution with vigorous stirring for different time. Then, the QDs was collected by centrifugation and dispersed in toluene with the same absorption density. The PL properties of the sample were measured by FSP920.

For thermal stability test, the powders were bedded in a sample cavity and heated to the desired temperature by Oxford OptistatDN2 nitrogen cryostat. The sample was kept for 10 min to reach thermal equilibrium, which would guarantee a uniform temperature both on the surface and in the interior of sample, and then the PL spectrum was measured by using a fluorescence spectrophotometer.

Fabrication of WLEDs and performance measurement: The $CsPbBr_3$/TDPA QDs and KSF phosphors were blended with silicone resin A (SN3050 A, Jiangmen Kanhoo Industry Co., LTD) and silicone resin B (SN3050 B, Jiangmen Kanhoo Industry Co., LTD, A: B = 1:1, wt%) followed by curing the blended gel at 120℃ for about 20 min. The obtained mixture slurry was directly coated onto a blue LED chip (λ_{peaks} = 453 nm) and formed a down-conversion layer. Finally, the optical properties of the fabricated devices were measured by using an integrating sphere with an analyser system (Labsphere LED-1100).

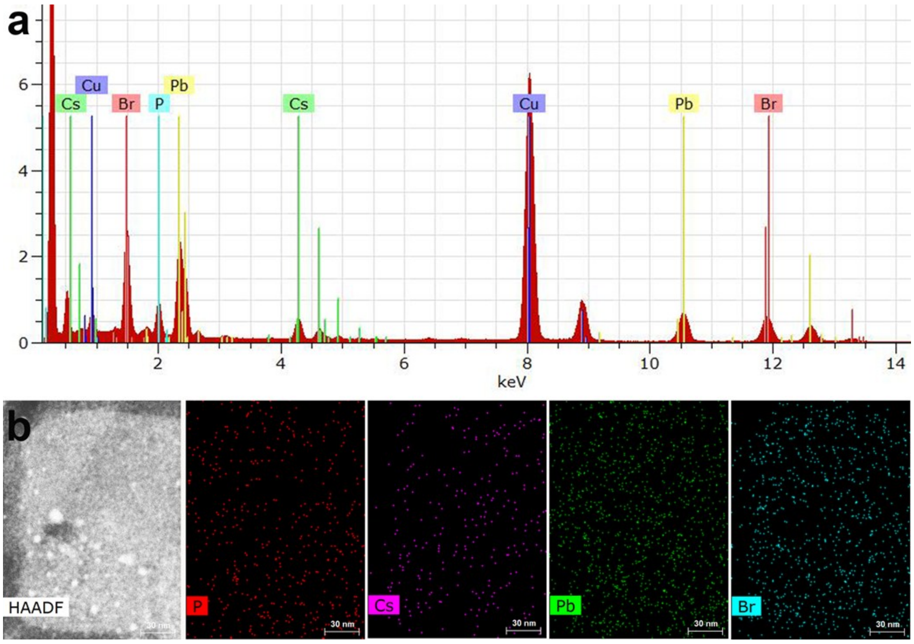

Fig. S2. (a) EDS spectrum of $CsPbBr_3$/TDPA QDs shows the presence of Cs, Pb, Br, and P elements. (b) The HAADF image and EDS mapping (in STEM mode) of P, Cs, Pb, and Br of $CsPbBr_3$/TDPA QDs.

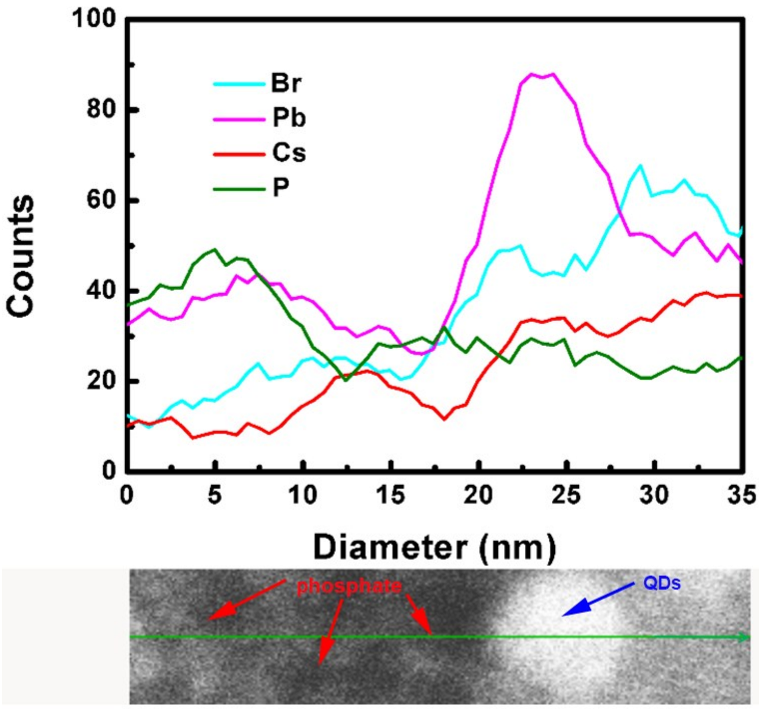

Fig. S3. EDS line scan across the diameter of the $CsPbBr_3$/TDPA QDs.

We try to investigate the elements distribution of one QDs particle by EDS line profiles across the QDs (Fig. S3), which confirms the existence of P ,Cs, Pb, and Br elements in one particle. However, the signal intensity of P is low on $CsPbBr_3$ QDs region and high out of the QDs due to few phosphate on the surface of the QDs and the QDs embedded in the phosphate layers, which is similar as which is similar as $CsPbBr_3$ embedded in SiO_2 (Adv. Mater. 2016, 28 (45), 10088).

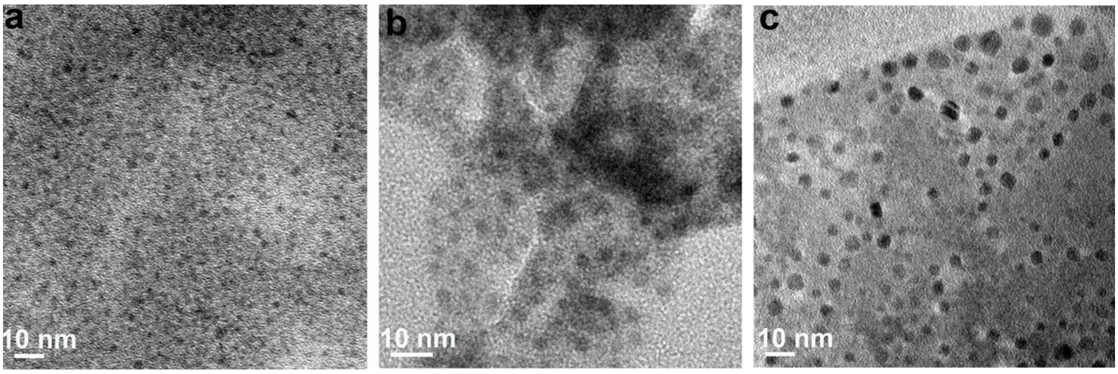

Fig. S4. The TEM images of the $CsPbBr_3$/TDPA QDs prepared with different concentration of TDPA (a: 11mg/mL, b: 7.5mg/mL and c: 5 mg/mL).

To investigate the influence of TDPA concentration, the QDs were synthesized with different concentration of TDPA. As shown in Fig. S4, the TEM images of the QDs prepared with 11mg/mL, 7.5mg/mL and 5 mg/mL of TDPA concentration. The average crystalline size of as-prepared QDs is measured as 3.5, 4.4, and 5.0 nm, respectively, indicating that high TDPA concentration leads to smaller QDs, which corresponds well with the absorption and PL spectra in Fig. 3.

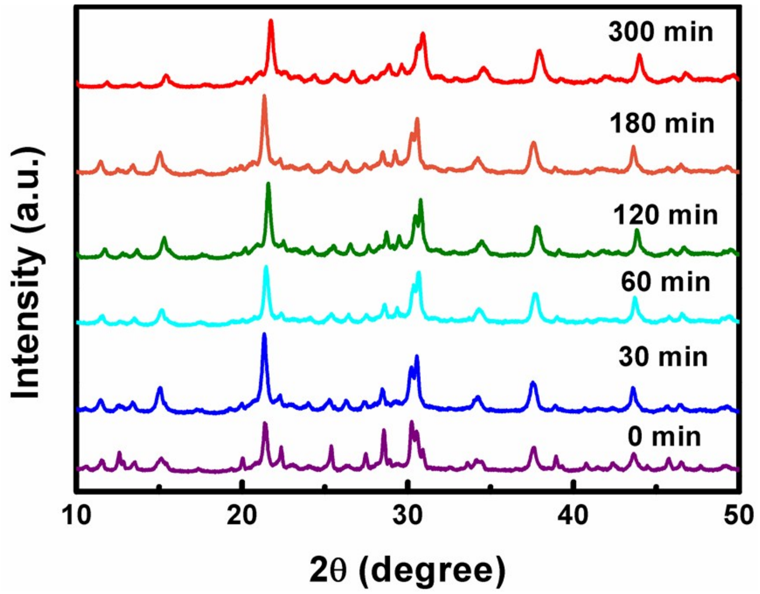

Fig. S5. The XRD patterns of $CsPbBr_3$/TDPA QDs dispersed in water for different time (0, 30, 60, 120, 180, 300 min).

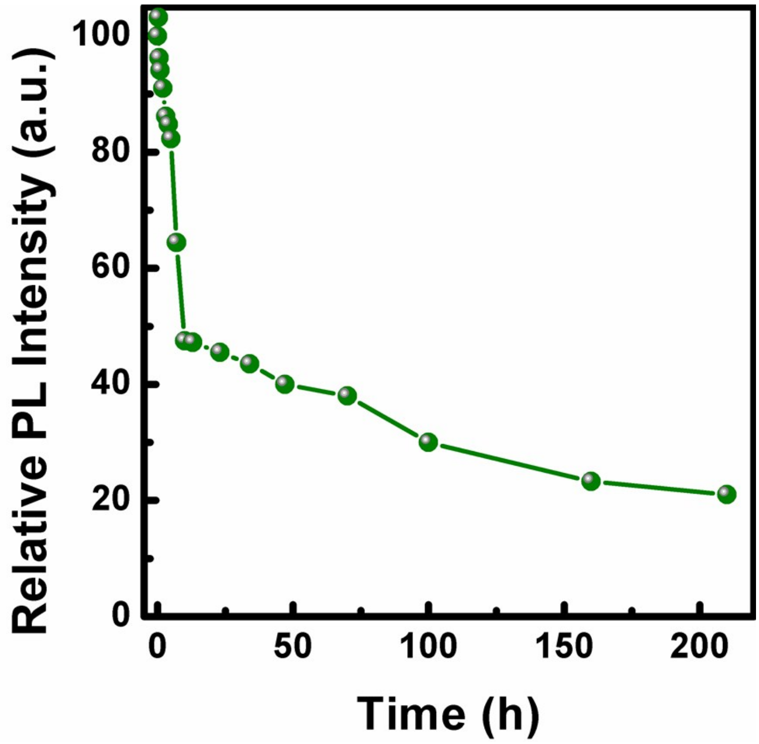

Fig. S6. The relative PLQY of $CsPbBr_3$/TDPA QDs as a function of time in water (0-210h).

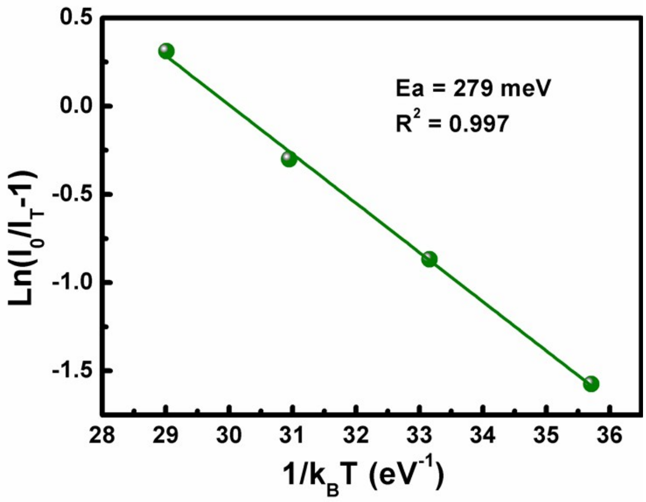

Fig. S7. Arrhenius fitting thermal quenching and the calculated activation energy (E_a) of $CsPbBr_3$/TDPA QDs.

The thermal quenching data of the $CsPbBr_3$/TDPA QDs were fitted using the following Arrhenius equation to calculated the activation energy

$$I_T = \frac{I_0}{1 + A\exp(-\frac{E_a}{k_B^T})} \qquad \text{(S1)}$$

Where I_0 is the initial emission intensity, I_T is the intensity at different temperature, E_a is activation energy of thermal quenching, A is a constant, and k_B is the Boltzmann constant.

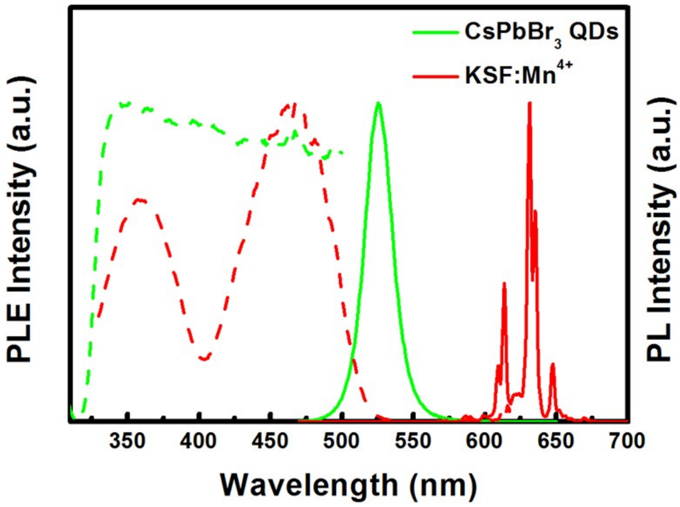

Fig. S8. The PLE and PL spectra of $CsPbBr_3$/TDPA QDs and $K_2SiF_6:Mn^{4+}$ phosphors.

Tab. S1. Comparison of the device performance between our work and the reported WLEDs.

Green-Emitting Materials	Red-Emitting Materials	Efficiency (lm/W)	NTSC (%)	Stability of Materials	Stability of Device	Ref.
Mesoporous SiO_2-$CsPbBr_3$	Mesoporous SiO_2-$CsPb(Br/I)_3$	-	113	Prevent the anion-exchange and high thermal stability	-	[1]
Mesoporous SiO_2-$CsPbBr_3$/SDDA@PMMA	$K_2SiF_6:Mn^{4+}$	-	102	High thermal stability	-	[2]
$CsPbBr_3/SiO_2$	$CsPb(Br/I)_3/SiO_2$	61.2	120	Keep high PL after in the air for 5 days	After working 10h latter, the fluoresce	[3]

					nce of WLED degraded a little.	
$CH_3NH_3PbBr_3$ - Polymer	CdSe QDs-Polymer	-	-	High water and thermal stability	-	[4]
$CH_3NH_3PbBr_3$ - Polymer	$K_2SiF_6:Mn^{4+}$	109	121	-	-	[5]
$CsPbBr_3$-Polymer	-	-	-	High water and thermal stability	-	[6]
$CsPbBr_3/ZnS$	-	-	-	Enhances the photostability	-	[7]
$CsPbBr_3/SiO_2/Al_2O_3$	-	-	-	High photostability	-	[8]
$CsPbBr_3$/TDPA QDs	$K_2SiF_6:Mn^{4+}$	63	122	High water and thermal stability	High stability	Our work

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