Supporting Information

Surface Modification for Improving Photoredox Activity of $CsPbBr_3$ Nanocrystals

Syed Akhil, V. G. VasaviDutt, Nimai Mishra*

Department of Chemistry, SRM University-AP, Andhra Pradesh, Neerukonda, Guntur (Dt), Andhra Pradesh, India 522240.

*Email ID: nimai.m@srmap.edu.in

Experimental section:

Materials:

Cesium carbonate (Cs_2CO_3, 99.9%), lead acetate ($Pb(OAc)_2$, 98%), lead bromide ($PbBr_2$, 98%) oleic acid (OA, 90%), oleylamine (OAm, 90%) were purchased from Alfa Aesar. 1-octadecene (ODE, 90%), n-trioctylphosphine (TOP, 90%), p-benzoquinone (BQ, 98%) were purchased from Sigma Aldrich. Hydrobromic acid (HBr, 47%) was purchased from Merck Emparta. We used chemicals without any further purification.

All these samples were prepared in the open-air conditions and using magnetic stirrer with 800 rpm.

Synthesis of Cesium- oleate solution:

In 25 mL round bottomed flask were loaded with Cs_2CO_3 (0.2 g, 0.046 mmol), OA (0.88 mL, 5 mmol) and ODE (7.5 mL) and heated at 120 °C with continuous stirring, to form clear cesium oleate until Cs_2CO_3 dissolved.

Synthesis of amine-free $CsPbBr_3$ PNCs:

Amine free synthesis was adopted from our previously reported work.[1] In two neck round bottomed flask, $Pb(OAc)_2$ (0.061 g, 0.188 mmol), ODE (2mL) and OA (0.25 mL, 0.79 mmol) were loaded and heated at 100 °C with continuous stirring until to dissolve $Pb(OAc)_2$, then HBr (40.83 µL, 0.752 mmol) and TOP (1mL, 2.2 mmol) were added and temperature was raised to 150 – 160 °C to get the clear solution. Then preheated Cesium oleate (0.4 mL, 0.125 M) was quickly injected into the reaction and after 30 sec, the reaction was quenched into the ice water bath. Then crude green $CsPbBr_3$ PNCs were purified by centrifuging at 8,000 rpm for 8 minutes. The final precipitate was dispersed in hexane further use and supernatant was discarded.

Synthesis of amine-$CsPbBr_3$ PNCs:

Synthesis of Amine-$CsPbBr_3$ NCs was taken from modified literature procedure.[2] In which 5 mL ODE, 0.5 mL OAm, 0.5 OA and 69mg (0.188 mmol) $PbBr_2$ were taken in a vial and heated at 120 °C for 1 hour then temperature was raised to 140 °C where $PbBr_2$ was completely dissolved. Then preheated 0.4 mL cesium oleate was rapidly injected. Color of the solution was changed to yellowish green represents the formation of $CsPbBr_3$ NCs after the injection; then the reaction was quenched using ice water bath after 2 minutes. Then crude solution was purified using centrifugation and discarded the supernatant and precipitate was redispersed in hexane.

Synthesis of amine + TOP - $CsPbBr_3$ PNCs:

As mentioned above synthesis with the slight modification was done by adding TOP in the lead precursor.

Steady state experiment:

First, to prepare 10 mM solution, the electron scavengers Benzoquinone molecules were dissolved in toluene. Then significant amount of amine free-$CsPbBr_3$ NCs suspensions was added into PL cuvette and followed by various amounts of BQ solution into NCs (10, 20, 30, 40 μL for 33.3, 66.7, 99.9, 133.2 μM) and then make the total volume to 3 mL by adding sufficient toluene. In the same way the amine and amine + TOP capped $CsPbBr_3$ NCs were also done.

Characterizations of $CsPbBr_3$ NCs:

$CsPbBr_3$ NCs were dispersed in toluene with absorbance scanning mode UV-Visible absorption spectra were recorded in UV-Vis spectrophotometer UV-2600i Shimadzu. Photoluminescence (PL) spectra of the $CsPbBr_3$ NCs were measured in FlouroLog-3 (Horiba Jobin Yvon). Photoluminescence quantum yield PLQYs were measured using the cumarine 153 dye molecule as reference in ethanol (QY=0.546). By drop casting the $CsPbBr_3$ NCs on the well cleaned glass substrate powder X-ray diffraction (XRD) patterns were measured using Empyrean PANalytical X-Ray Diffractometer using Cu-Kα X-radiation (λ = 1.5406 Å) at 40 kV and 30 mA power. Transmission Electron Microscopy (TEM) for the samples by a drop of optimum solution of $CsPbBr_3$ NCs in hexane on copper (Cu) grid coated with carbon film using JEOL JEM-2100 High-Resolution Transmission Electron Microscope with 0.23 nm point resolution. $CsPbBr_3$ NCs samples were measured ATR-FTIR Attenuated total reflection - Fourier transform infrared spectroscopy spectra by using Bruker Alpha II spectrometer with broadband MCT detector. The time resolved photoluminescence measurements were measured by a time-correlated single photon counting by TCSPC Spectrometer (Horiba Jobin Yvon IBH) with laser diode, output at 372 nm used as excitation laser source. The lamp profile was recorded by using a dilute solution of Ludox in water which act as a scatter in the sample chamber. The fluorescence decay curves were analyzed using IBH DAS6 software.

Table-S1: Tri-exponential fits of the TCSPC data with the equation:

$$f(t) = A_1 e^{-\frac{t}{\tau_1}} - A_2 e^{-\frac{t}{\tau_2}}.$$

$\bar{\tau}$ is the intensity-averaged lifetime from a Bi-exponential fit using equation: $\bar{\tau} = \sum A_i * \tau_i^2 / \sum A_i * \tau_i$.

	[BQ] (μM)	A_1	τ_1 (ns)	A_2	τ_2 (ns)	$\bar{\tau}$ (ns)
$CsPbBr_3$ NCs-Amine free	0	0.82	3.98	0.18	26.1	17.03
	33.3	0.85	3.11	0.15	22.69	14.13
	66.7	0.86	2.82	0.14	20.02	12.04
	99.9	0.9	2.26	0.1	17.04	8.99
	133.2	0.92	1.65	0.08	12.53	5.977
$CsPbBr_3$ NCs-Amine + TOP	0	0.84	5.39	0.16	20.42	11.68
	33.3	0.86	4.03	0.14	16.21	8.84
	66.7	0.85	3.17	0.15	14.59	8.28
	99.9	0.87	3.44	0.13	14.42	7.66
	133.2	0.86	3.03	0.14	12.79	7.00
$CsPbBr_3$ NCs-Amine	0	0.87	4.68	0.13	19.39	10.30
	33.3	0.86	4.03	0.14	16.21	8.84
	66.7	0.87	3.44	0.13	14.42	7.66
	99.9	0.86	3.03	0.14	12.79	7.00
	133.2	0.86	2.55	0.14	11.12	6.11

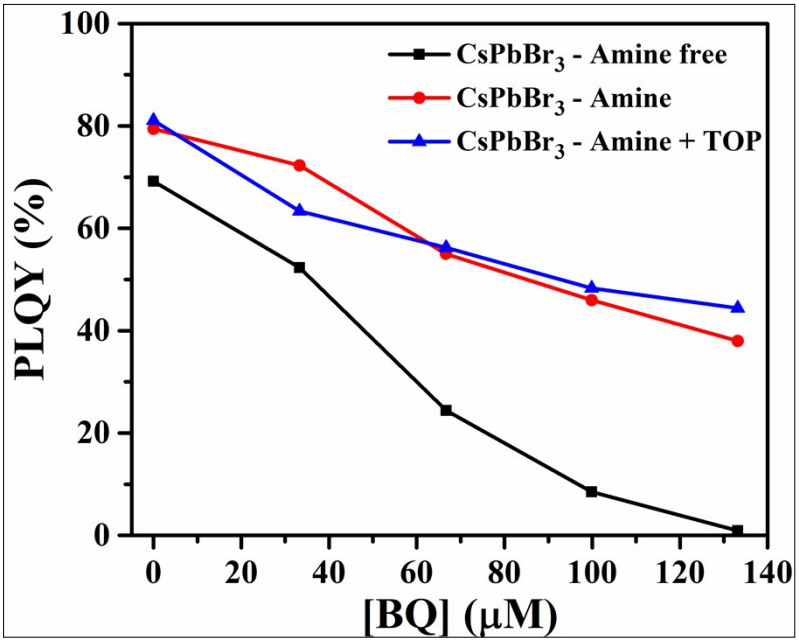

Figure-S1: Relative Photoluminescence quantum yield PLQY of three different surface capping groups with addition of different concentrations of Benzoquinone

References:

(1) Akhil, S.; Dutt, V. G. V.; Mishra, N. Completely Amine-Free Open Atmospheric Synthesis of High Quality Cesium Lead Bromide (CsPbBr3) Perovskite Nanocrystals. *Chemistry – A European Journal n/a* (n/a). https://doi.org/10.1002/chem.202003891.
(2) Dutt, V. G. V.; Akhil, S.; Mishra, N. Fast, Tunable and Reversible Anion-Exchange in CsPbBr3 Perovskite Nanocrystals with Hydrohalic Acids. *CrystEngComm* **2020**, *22* (30), 5022–5030. https://doi.org/10.1039/D0CE00722F.