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


Supporting Information

# Lattice constriction and trapped excitons: a structure-property relationship unveiled in $CsPbBr_3$ QDs

Vishaka V Halali, Jesna K George, Altaf Pasha, Sarina K, R Geetha Balakrishna*

*Centre for Nano and Material Sciences, Jain University, Ramanagaram, Bangalore 562112, India*

***Corresponding Author**: br.geetha@jainuniversity.ac.in***

## 1. Materials and Methods

Lead (II) Bromide ($PbBr_2$, 99%), cesium carbonate ($Cs_2CO_3$, 99.9%), oleic acid (OA, 99%), oleyl amine (OAM, 70%), 1-octadecene (ODE, 90%) and lanthanum (III) bromide ($LaBr_3$) were purchased from Sigma Aldrich. DI $H_2O$ and all other chemicals were of analytical standards used without purification. For transmission electron microscopy (TEM), the $CsPbBr_3$ PQD's dropped cast onto copper grids with carbon support by slowly evaporating at room temperature. Transmission Electron Microscope (TEM) image and energy dispersive spectrometer (EDS) spectra were recorded using (Titan Themis 300kV from FEI, now Thermo). Attenuated total reflectance infrared (ATR-IR) spectra were recorded with a Bruker Alpha Eco-ATR spectrometer in the scan range of 4000-500cm$^{-1}$ for the entire sample. UV-Vis absorption and PL spectra were recorded by Shimadzu UV-1800 spectrophotometer using a 10 mm quartz cuvette and Shimadzu RF 5301PC Spectro fluorophotometer respectively. X-ray diffraction patterns were recorded on an Ultima-IV X-ray diffraction (Rigaku Corporation, Japan) using Ni-filtered Cu Kα radiation with a 2θ scan speed of 2.0$^{\circ}$ min$^{-1}$ and a 2θ scan range of 5-80$^{\circ}$ at 40KV and 30Ma. X-ray photoelectron spectra were recorded using multi-technique X-ray photoelectron spectroscopy with XPS-mapping capability AXIS ULTRA 165. Time Resolved Fluorescence Spectrometer (TRPL), Horiba Jobin Yuvon Fluorocube-01-NL Fluorescence Life time System determined the fluorescence life Time.

## 2. Synthesis of $CsPbBr_3$ perovskite QDs

All- Inorganics $CsPbBr_3$ perovskite QD's were synthesized through the hot-injection method by the following steps as reported in our previous literature [1].

## 3. Preparation of $La^{3+}$ metal ion solution

The stock solution (3 μM) was prepared by dissolving 0.1 mM of Lanthanum bromide in 0.5 ml ethyl acetate followed by ultrasonic treatment for 10 min to obtain a transparent solution. It was then made upto 10mL.

## 4. Doping of $La^{3+}$ into CsPbBr3

The synthesized $CsPbBr_3$ perovskite QDs (0.3 mg) dispersed in 2 ml toluene were mixed with 2μL of 0.4 μM lanthanum ions (in toluene) and made up to 5 mL. The mixture was then loaded into the cuvette and characterized after shaking for 60 seconds to ensure complete reaction between the perovskite QDs and the enhancer ($La^{3+}$ ions).

## 5. Structural and optical properties for the $CsPbBr_3$ perovskite QDs

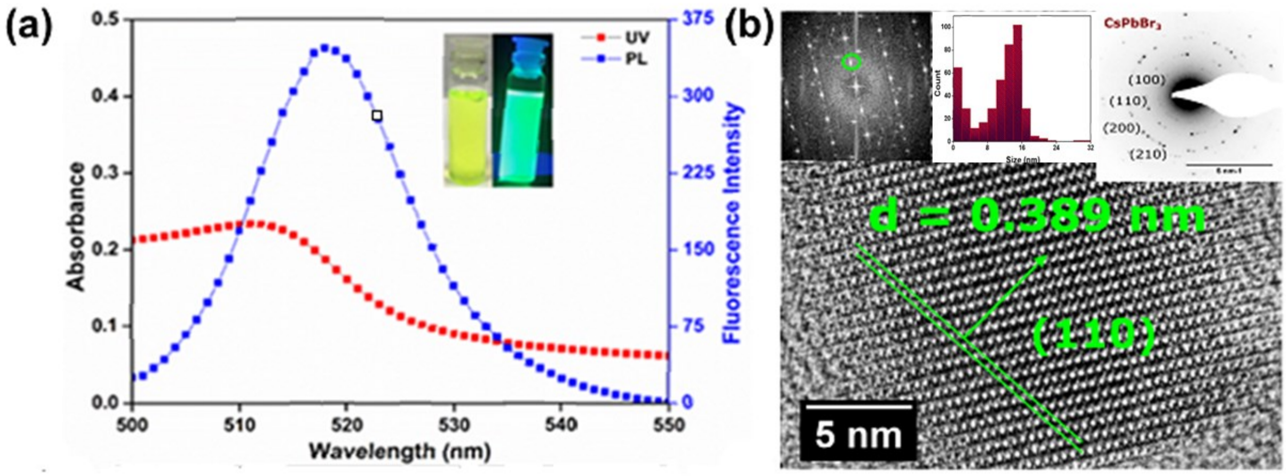



**Fig. S1(a) Absorption and emission spectra of $CsPbBr_3$ perovskite QDs dispersed in toluene; (b) HRTEM image inset: particle size distribution, SAED pattern**

The $CsPbBr_3$ perovskite QDs were synthesized in the presence of OAM and OA as co-solvent via previously reported procedure. From Fig. S1(a) it could be seen that $CsPbBr_3$ PQDs have an obvious absorption peak at 508 nm and an intense emission peak at 518 nm. By varying the excitation wavelength from 370 to 460 nm, there is no change in the emission wavelength and PL intensity of $CsPbBr_3$ perovskite QDs, an indication of their independence property of emission wavelength on the excitation energy (Fig. S1(a)). Transmission electron microscopy (TEM) image of the as-prepared $CsPbBr_3$ perovskite QDs was measured in Fig. S1(b) from which it could be seen that the $CsPbBr_3$ perovskite QDs arranged orderly without any aggregation presented a cubic phase with a uniform average edge. The high-resolution TEM (HRTEM) image in inset of Fig. S1(b) reveals the well-resolved lattice fringes with the interplanar distance about 3.89 Å, which coincides with the (110) plane and demonstrates the high crystalline nature of the QDs. Inset of Fig. S1(b) also show cube shaped particles with an average particle size of 16 -19 nm. In our study, the XRD pattern of the $CsPbBr_3$ QDs in Fig. S2 indicates the perovskite phase of $CsPbBr_3$ (*JCPDS* No. 96-153-3063). The Cs: Pb: Br atom ratio of the $CsPbBr_3$ PQDs measured by the energy-dispersive spectrometer (EDS) is consistent with the stoichiometry of 1:1:3 Fig. S4.

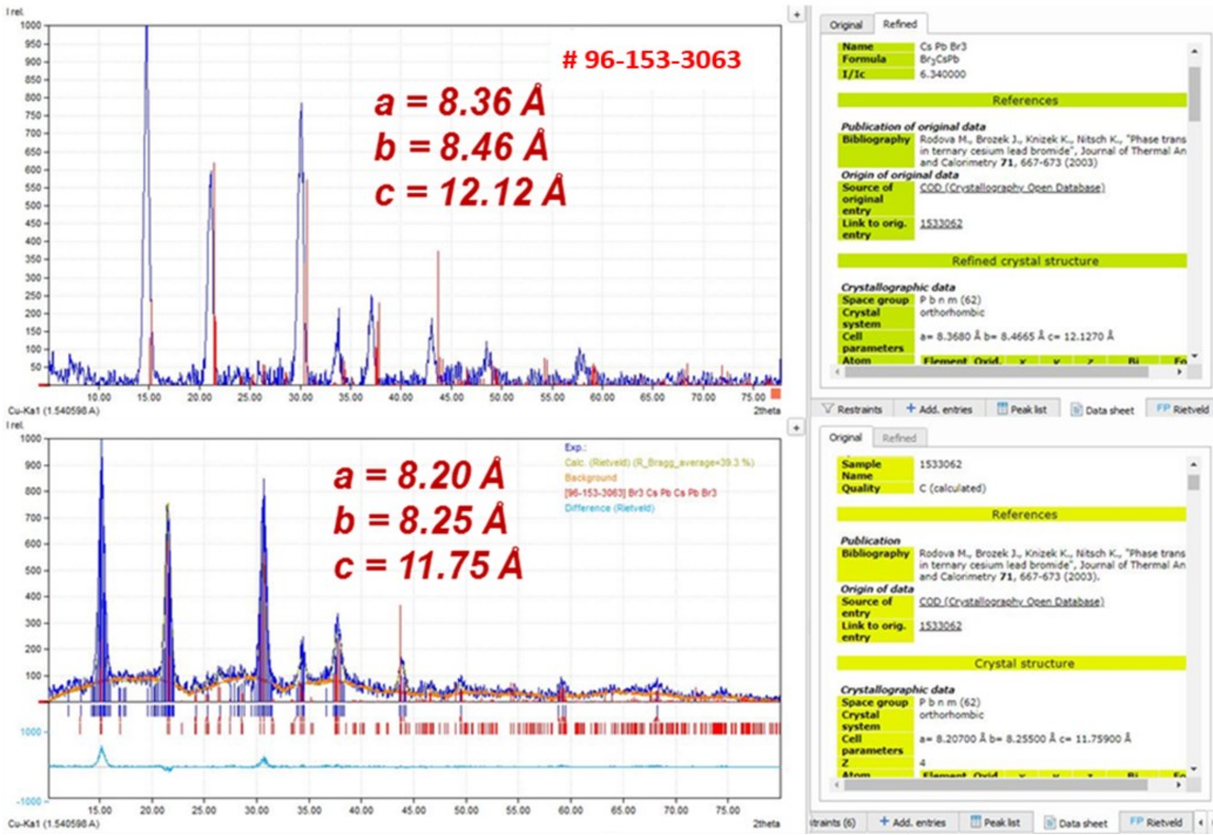



**Fig. S2 XRD reitveld refinement graphs of $CsPbBr_3$ perovskite QDs and $CsPbBr_3$-$La^{3+}$ perovskite QDs**

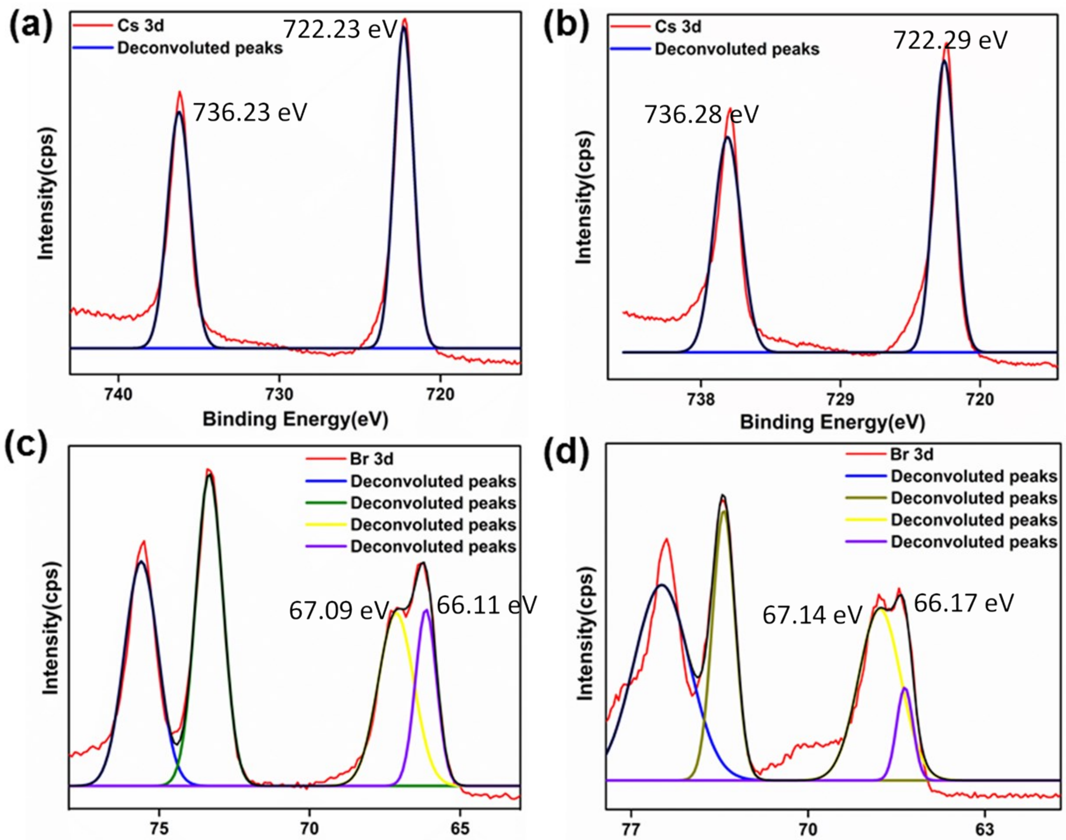
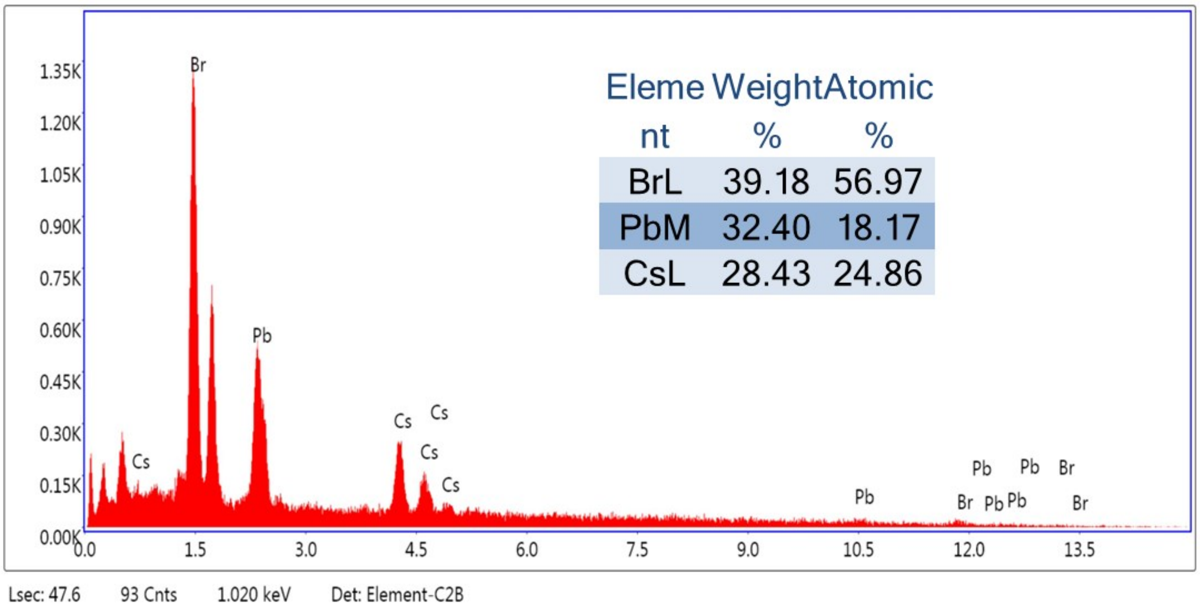



**Fig S3 High-resolution XPS spectra corresponding to Cs 3d and Br 3d of $CsPbBr_3$ and $CsPbBr_3$-$La^{3+}$ perovskite QDs**

**$CsPbBr_3$ perovskite QDs**




**$CsPbBr_3$-$La^{3+}$ perovskite QDs**

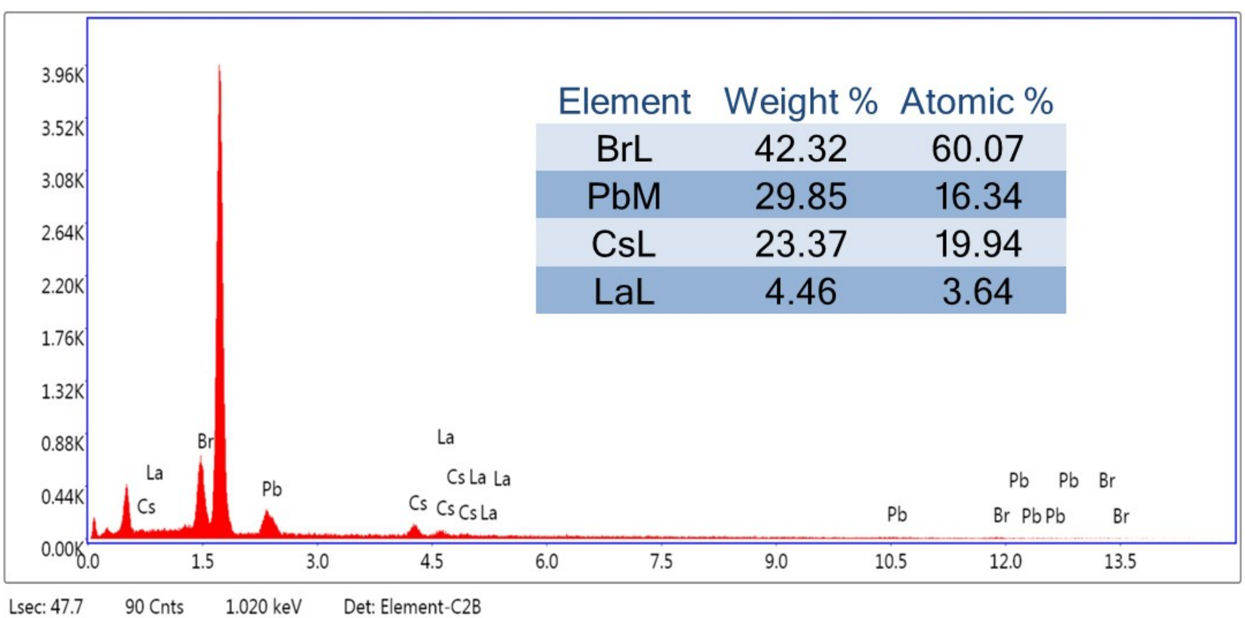


**Fig. S4 EDS spectrum and Quantification of elemental composition in $CsPbBr_3$ and $CsPbBr_3$-$La^{3+}$ perovskite QDs.**

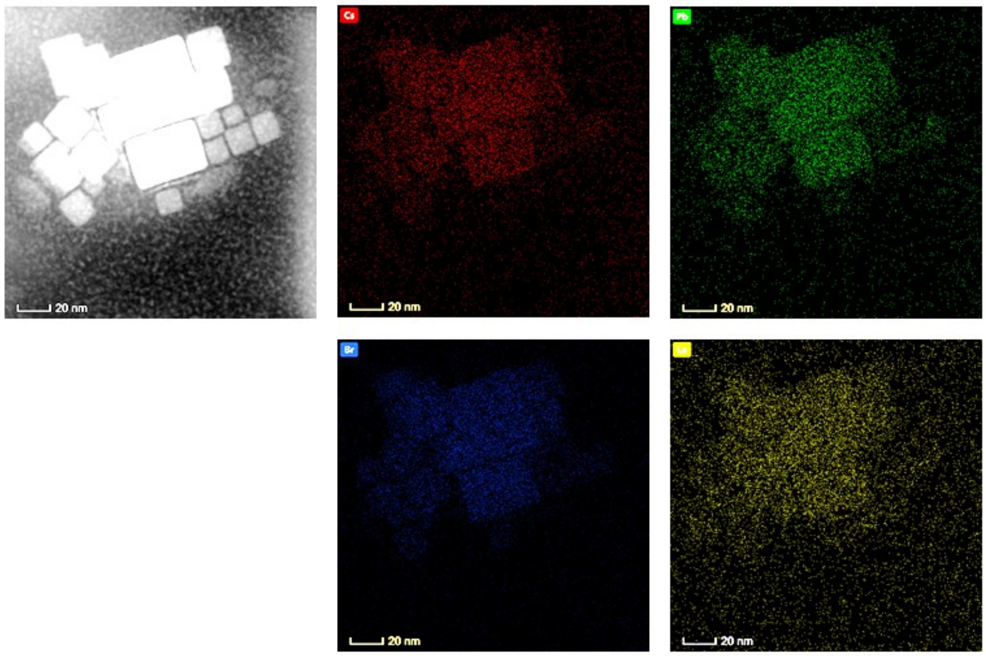
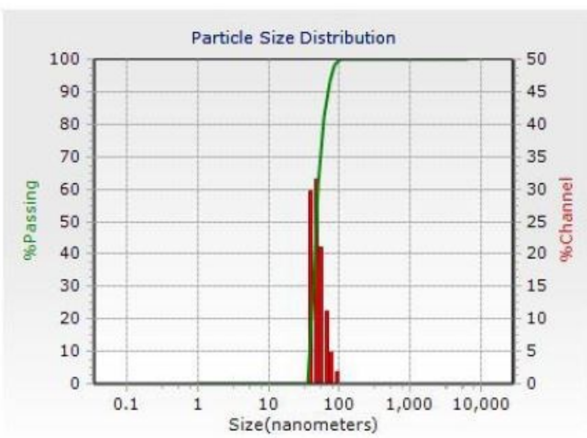



**Fig. S5 Elemental mapping of Cs, Pb, Br and La ions**

**(a) $CsPbBr_3$ perovskite QDs**

| Microtrac Total Solutions in Particle Characterization | Particle Size Analysis |
|---|---|
| FLEX 11.0.0.2 | 1<br>1 |
| Particle Size / Zeta Potential | - |
| Acquired 05-07-2019 10:11 | Zetatrac S/N: **W3231** |

C:\Microtrac\FLEX 11.0.0.2\Databases\MAR 2019.MDB




| Zeta Potential | |
|---|---|
| Mobility | -0.01u/s/V/cm |
| Zeta Potential | -2.3 mv |
| Charge | -0.00242 fC |
| Polarity | Negative |
| Conductivity | 271 uS/cm |
| Field Strength | 5.0 kV/m |
| Sample Information | |
| Fluid | |
| Viscosity | 0.532 |
| Temperature | 28.97 C |
| Dielectric Const | 2.2 |
| Dispersant | |
| pH | |
| Concentration | |
| Particle | |
| Concentration | 0 |

**- Particle Size Summary -**

| Summary | |
|---|---|
| Data | Value |
| MV(nm): | 4,990 |
| MN(nm): | 52.10 |
| MA(nm): | 2,265 |
| CS: | 2.649 |
| SD: | 11.02 |
| PDI: | 623.7 |
| Mz: | 4,922 |
| si: | 1,509 |
| Ski: | -678.61727 |
| Kg: | 979.4 |

| Percentiles | |
|---|---|
| %Tile | Size(nm) |
| 10.00 | 38.90 |
| 20.00 | 40.90 |
| 30.00 | 43.10 |
| 40.00 | 45.40 |
| 50.00 | 47.90 |
| 60.00 | 50.70 |
| 70.00 | 54.40 |
| 80.00 | 59.50 |
| 90.00 | 67.70 |
| 95.00 | 75.70 |

| Peaks Summary | | |
|---|---|---|
| Dia(nm) | Vol% | Width |
| 47.9 | 100 | 22.04 |

**- Measurement Information -**

| Title | |
|---|---|
| Particle Size Analysis | |
| Identifiers | |
| 1 | |
| 1 | |
| Database Record | 52 |
| Run Number | 1 of 1 |
| Date | 05-07-2019 |
| Time | 10:11 |
| Acquired Date | 05-07-2019 |
| Acquired Time | 10:11 |
| Serial Number | W3231 |
| Calculated Data | |
| Above Residual | 0 |
| Below Residual | 0 |
| Loading Index | 0.846 |
| Conc. Index | 0.2701 |
| RMS Residual | 0.033% |
| Cell Temp (C) | 28.97 |
| Viscosity(cp) | 0.5320 |
| Reflected Pwr (uW) | 1.02 |
| Recalculation Status | |
| Live-Meas : : Original : | |

## (b) $CsPbBr_3$-$La^{3+}$ perovskite QDs

Microtrac
Total Solutions in Particle Characterization

**Particle Size Analysis**

| | |
|---|---|
| FLEX | 2 |
| 11.0.0.2 | 2 |

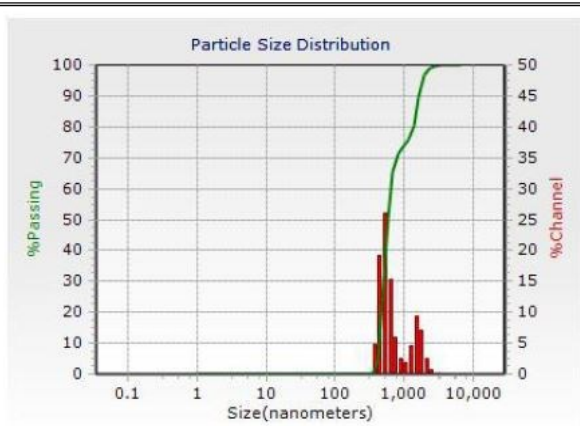
-

**Particle Size / Zeta Potential**

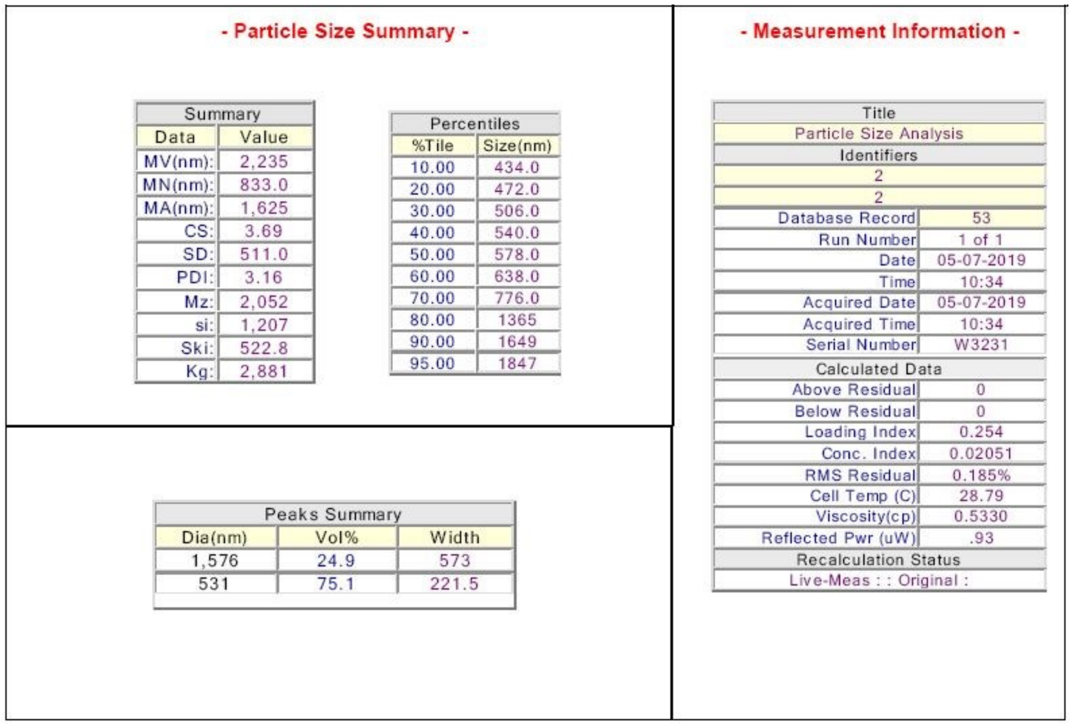
Acquired 05-07-2019 10:34

Zetatrac S/N: W3231

C:\Microtrac\FLEX 11.0.0.2\Databases\MAR 2019.MDB




| Zeta Potential | |
|---|---|
| Mobility | 0.01u/s/V/cm |
| Zeta Potential | 2.3 mv |
| Charge | 0.00076 fC |
| Polarity | Positive |
| Conductivity | 3 uS/cm |
| Field Strength | 5.0 kV/m |
| Sample Information | |
| Fluid | |
| Viscosity | 0.533 |
| Temperature | 28.79 C |
| Dielectric Const | 2.2 |
| Dispersant | |
| pH | |
| Concentration | |
| Particle | |
| Concentration | 0 |



- Particle Size Summary -

| Summary | |
|---|---|
| Data | Value |
| MV(nm): | 2,235 |
| MN(nm): | 833.0 |
| MA(nm): | 1,625 |
| CS: | 3.69 |
| SD: | 511.0 |
| PDI: | 3.16 |
| Mz: | 2,052 |
| si: | 1,207 |
| Ski: | 522.8 |
| Kg: | 2,881 |

| Percentiles | |
|---|---|
| %Tile | Size(nm) |
| 10.00 | 434.0 |
| 20.00 | 472.0 |
| 30.00 | 506.0 |
| 40.00 | 540.0 |
| 50.00 | 578.0 |
| 60.00 | 638.0 |
| 70.00 | 776.0 |
| 80.00 | 1365 |
| 90.00 | 1649 |
| 95.00 | 1847 |

| Peaks Summary | | |
|---|---|---|
| Dia(nm) | Vol% | Width |
| 1,576 | 24.9 | 573 |
| 531 | 75.1 | 221.5 |

- Measurement Information -

| Title | |
|---|---|
| Particle Size Analysis | |
| Identifiers | |
| 2 | |
| 2 | |
| Database Record | 53 |
| Run Number | 1 of 1 |
| Date | 05-07-2019 |
| Time | 10:34 |
| Acquired Date | 05-07-2019 |
| Acquired Time | 10:34 |
| Serial Number | W3231 |
| Calculated Data | |
| Above Residual | 0 |
| Below Residual | 0 |
| Loading Index | 0.254 |
| Conc. Index | 0.02051 |
| RMS Residual | 0.185% |
| Cell Temp (C) | 28.79 |
| Viscosity(cp) | 0.5330 |
| Reflected Pwr (uW) | .93 |
| Recalculation Status | |
| Live-Meas : : Original : | |

**Fig. S6 DLS and Zeta potential values of $CsPbBr_3$ perovskite QDs and $CsPbBr_3$-$La^{3+}$ perovskite QDs**

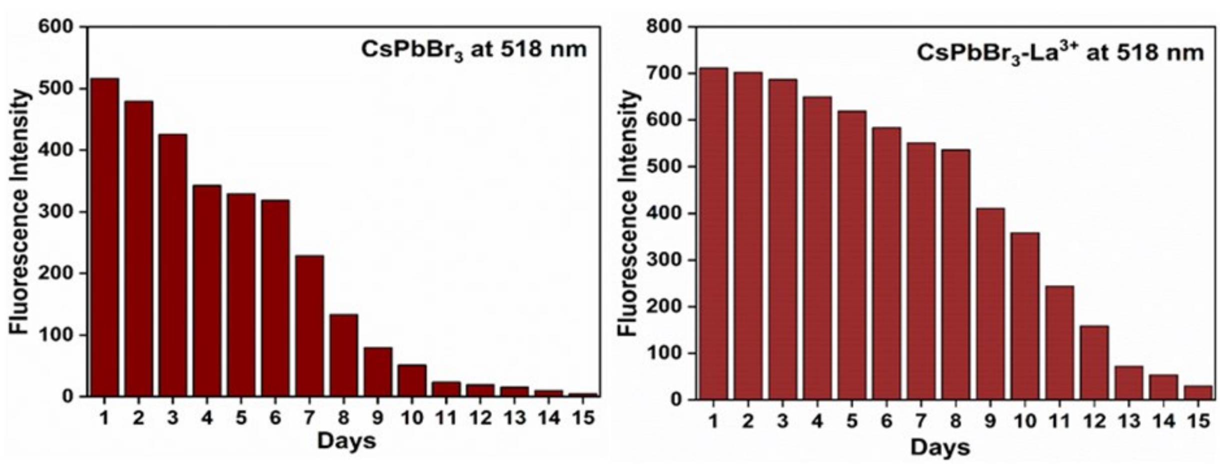



**Fig. S7 Stability measurement by tracking changes in PL intensity**

## References

1. Liu, Y., Tang, X., Zhu, T., Deng, M., Ikechukwu, I. P., Huang, W., … Qiu, F. (2018). All-inorganic CsPbBr3 perovskite quantum dots as a photoluminescent probe for ultrasensitive Cu2+ detection. Journal of Materials Chemistry C, 6(17), 4793–4799. doi:10.1039/c8tc00249e.