Supporting information

Ligand & Band Gap Engineering: Tailoring the Protocol Synthesis for Achieving High-Quality $CsPbI_3$ Quantum Dots.

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1. Experimental

1.1. Materials and chemicals

All chemicals used for the synthesis were purchased from Sigma-Aldrich, unless otherwise specified. Cesium carbonate (Cs_2CO_3, 99.9 %), lead (II) iodide, (PbI_2, 99.99 %, TCI), 1-octadecene, (1-ODE, 90 %), oleic acid (OA, 90 %), oleylamine (OLA, ≥ 98 % primary amine), methyl acetate (MeOAc, anhydrous, 99.5 %), hexane (anhydrous, ≥99 %, mixture of isomers), hexane (≥ 97.0 %, CHROMASOLV for HPLC (GC) Honeywell), n-octane (anhydrous, ≥ 99 %), $CDCl_3$ (100%, 99.96 atom %D, contains 0.03% (v/v) TMS), PEDOT:PSS Clevios (P VP Al 4083), poly(N,N'-bis-4-butylphenyl-N,N'-bisphenyl)benzidine (Poly-TPD, Ossila), TPBi (2,2′,2"-(1,3,5-Benzinetriyl)-tris(1-phenyl-1-H-benzimidazole)) , lithium fluoride (99.99 %), aluminum pellets (Evaporation Materials Kurt J. Lesker) and ITO glasses (25 x 25 mm, Pilkington TEC10 ~10 Ωm^{-1}).

1.2. Synthesis and isolation of colloidal $CsPbI_3$ Perovskite Quantum Dots (QDs)

$CsPbI_3$ QDs were synthesized following the previous reports with some modifications.[1-3] First, Cs-oleate solution was prepared by mixing 0.814 g of Cs_2CO_3, 2.5mL of OA and 40 mL of 1-ODE into a 100 mL-three neck flask and heating at 120 °C under vacuum for 1 h until bubbling completely disapplied . Then the mixture was heated until 150 °C under N_2-purge in order to complete the formation of Cs-Oleate. Since the Cs-oleate become solid, before injection, the solution was heated to 100 °C under N_2 flow. In a 100 mL-three neck flask, PbI_2 (0.5 g) and dried 1-ODE (25 mL) were stirred and degassed under vacuum at 120 °C for 1 h. The flask was then purged with N_2 and kept under constant stirring. 1.5 mL to 4 mL of dried OA and OLA (depending to temperature of synthesis) were injected. The flask was put under vacuum again until the PbI_2 completely dissolved and the solution was no longer releasing gas (15 – 30 min). The synthesis temperature influences the QD size (170 °C for 9.14 nm, 180 °C for 10.60 nm, 185 °C for 12.84 nm, and 190 °C for 13.16 nm, QDs). 2 mL of pre-heated Cs-oleate solution was swiftly injected into the reaction mixture under N_2 atmosphere. After 5 s, the reaction was quenched by immediate immersion of the flask into an ice bath.

As-prepared $CsPbI_3$ QDs were precipitated by adding MeOAc (7.5 mL QDs crude solution: 17.5 mL MeOAc) and then centrifuged at 7500 RPM for 5 min. The QDs were dispersed in 7.5 mL of hexane and stored in the dark at 4 °C for at least 24 hours to precipitate excess Pb-oleate. The QDs solution was decanted and centrifuged again at 4000 RPM for 5 min before use. For device fabrication, hexane was dried, and the QDs were dissolved in n-octane at a concentration of ~20 mg/mL.

1.3. Characterization of $CsPbI_3$ QDs

The crystalline structure of the $CsPbI_3$ QDs was determined by using an X-ray diffractometer (Bruker AXS, D4 Endeavor advanced X-ray diffractometer, with Cu Kα radiation). Absortion spectra was performed on a Varian Cary 300 Bio spectrophotometer. Steady-state photoluminescence (PL) and photoluminescence quantum yield (PLQY) was measured using a Hamamatsu integrating sphere at excitation wavelength of 400 nm. PLQY is referred to QDs which were purified one time with methyl acetate and further dispersed in hexane. As reference, measurement was performed with cuvette containing only the HPLC-hexane in the same excitation wavelength. To avoid the influence of different concentrations of $CsPbI_3$ QD solutions on the PLQY measurements, we adjusted the concentrations to be an appropriate level, which is that the QDs solution was diluted in HPLC n-hexane until the measurement was 0.67 of absorbance at the wavelength of 400 nm. Time-resolved photoluminescence (TRPL) was measured through photoluminescence spectrophotometer (Fluorolog 3-11, Horiba). 405 nm pulsed laser (1 MHz frequency, NanoLED-405L, <100 ps of pulse width) was used to excite QDs. All measurements for the TRPL were performed under inert environment with N_2 purged solution to prevent extra excitation quenching. High-resolution transmission electron microscopy (HRTEM) images of perovskite nanoparticles were obtained with a field emission gun TECNAI G2 F20 microscope operated at 200 kV. The size distribution and particle size of QDs were obtained from the TEM images with ImageJ software. Nuclear magnetic resonance (NMR) characterization was carried out by using Bruker Avance III HD 400 MHz instrument, using $CDCl_3$ as solvent.

1.4. Fabrication of the $CsPbI_3$-based LED devices

In order to have the active area of 6 mm^2, 2.5 x 2.5 cm^2 ITO substrates (10 Ω/cm^2) were partially covered with scotch tape and then extra part of scotch tape was cut with laser printer (model LaserPro C180) at speed and power of 8 and 50% respectively) and left 12 mm width without tape. Then, the substrates were etched with Zinc powder and 6 M HCl (37% HCl was diluted with equal volume) one by one and wiped with tissue paper, rinsed with DI water. Later on scotch tape was removed and any remaining glue from tape were cleaned with paper and ethanol, and then substrates were introduced in a soap solution and sonicated for 15 min. The substrates were rinsed couple of times with DI water and sonicated again with ethanol for another 15 min. After that, ITO substrates were introduced into a mixture of isopropanol/acetone (1:1 v/v), sonicated for another 15 min and dried with compressed air or nitrogen. After that, the substrates were introduced into a UV–O_3 cleaner for 15 min and the solution of PEDOT: PSS was spin coated at 3000 rpm for 30 s and annealed at 140 °C for 10 min in air, to yield a thin layer (20 nm). Next, a Poly-TPD layer was spin coated (20 mg/mL in chlorobenzene) at different rpms (e.g. 4000 rpm) for 30 s, and subsequently annealed at 140 °C for 10 min in air. The solutions of QDs (20 mg/mL) in n-octane were spin-coated at 3000 rpm for 30 s. After that, 60 nm of TPBi, 1nm of LiF and 100 nm Al were thermally evaporated at rates of 0.2-0.3, 0.05 1.5–2 Å/s, respectively; the active areas were encapsulated with adhesive tape and then contacts covered with Cooper tape for the measurement.

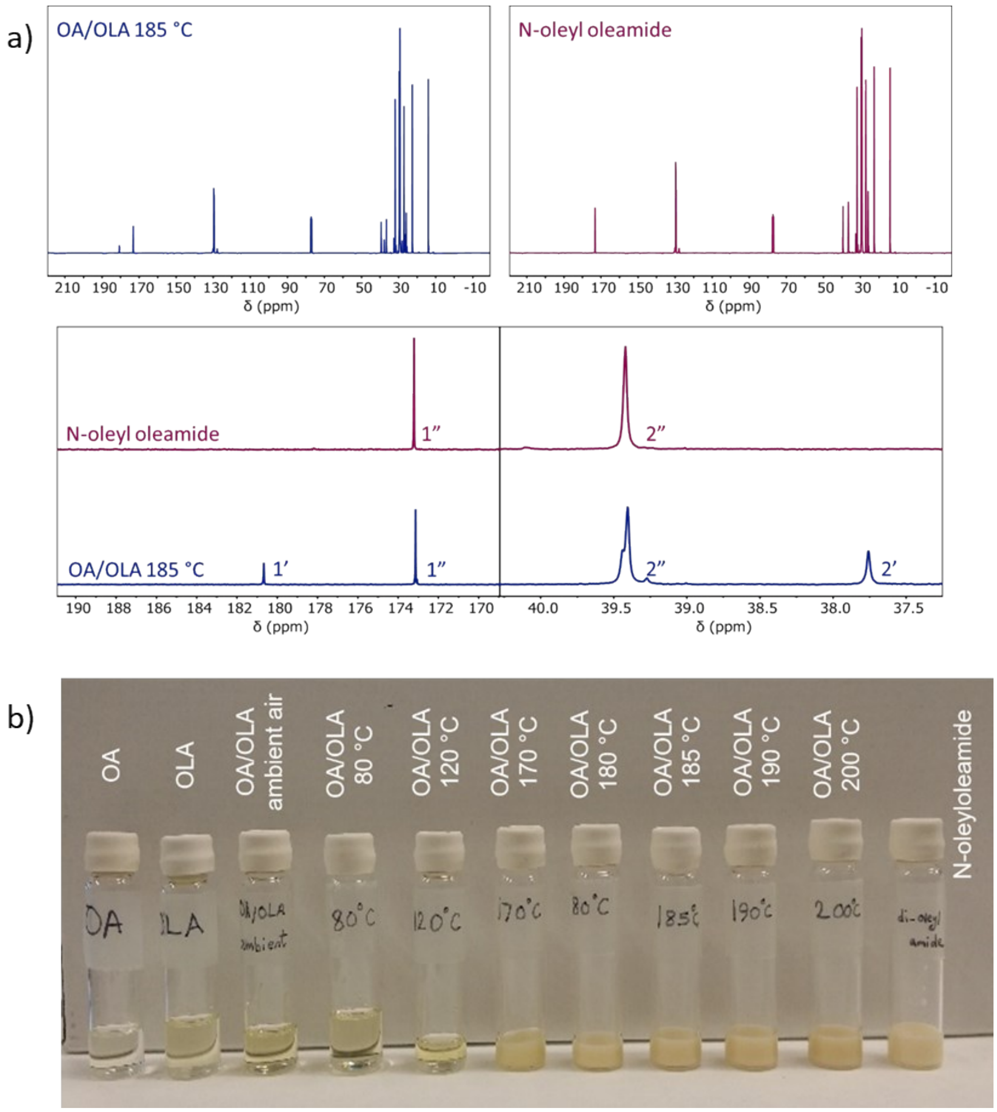

Figure S1. (a) ^{13}C-NMR of OA/OLA samples at 185 °C and pure N-oleyl-oleamide (NOA). In sample of OA/OLA at 185 °C, two signals corresponding to the carbonyl carbon atoms (1’ and 1”) are visible and also two signals of the carbon atoms next to carbonyl (2’, 2”). On the other hand, in the sample of pure N-oleyl-oleamide, only one signal of carbonyl group appeared. Besides ^{1}H-NMR of the samples, this is another proof that ammonium oleate salt is fully converted to carboxylic amide. **(b)** Image of OA/OLA mixtures (1:1 molar ratio) heated at diverse synthesis temperatures to carry out the formation of OLM and N-oleyl-oleamide compounds.

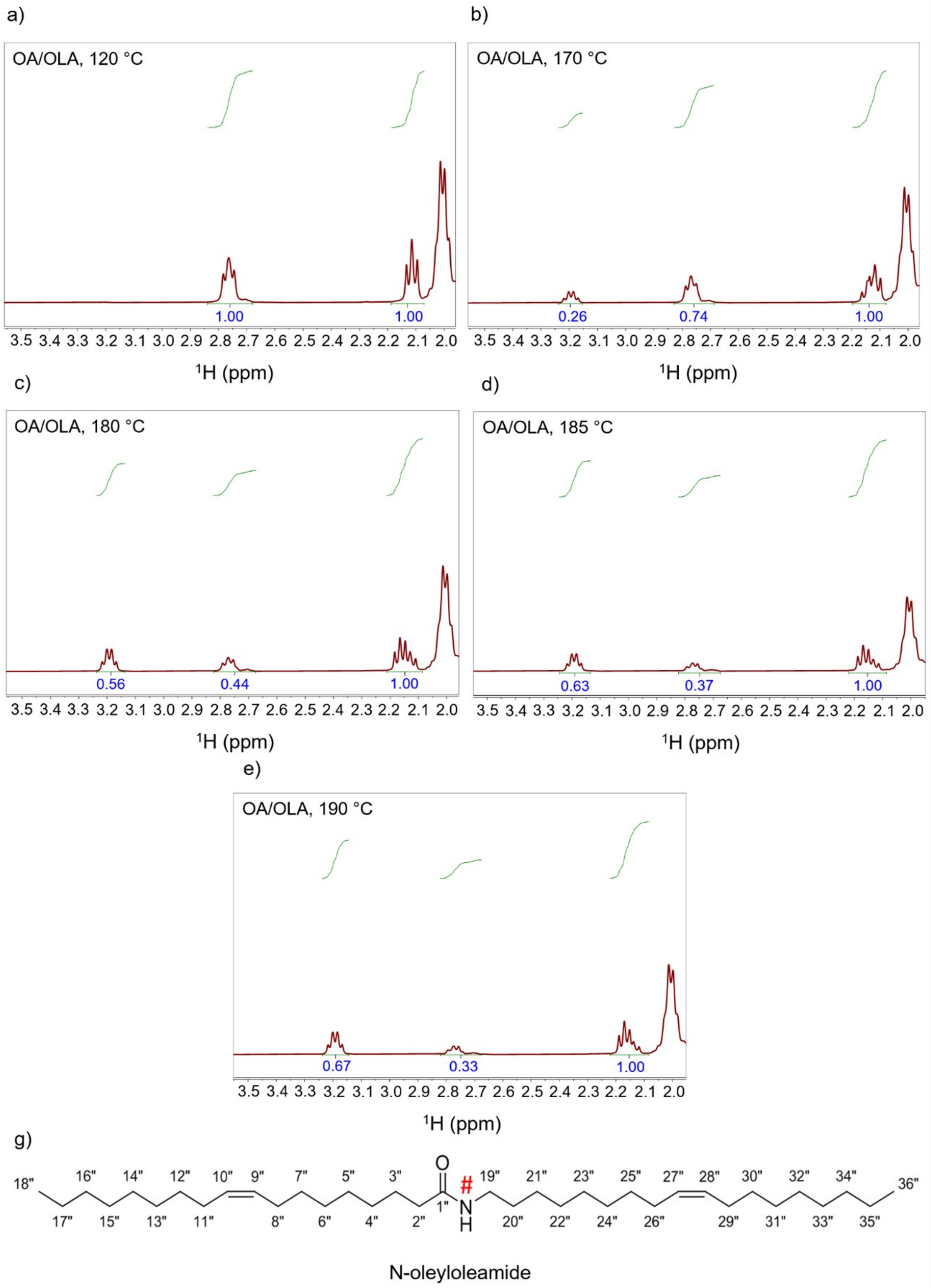

Figure S2. (a-f) ^{1}H -NMR spectra of OA/OLA mixtures (1:1 molar ratio) heated at different synthesis temperatures. (g) Structure of the oleyl-oleamide obtained from NMR measurements.

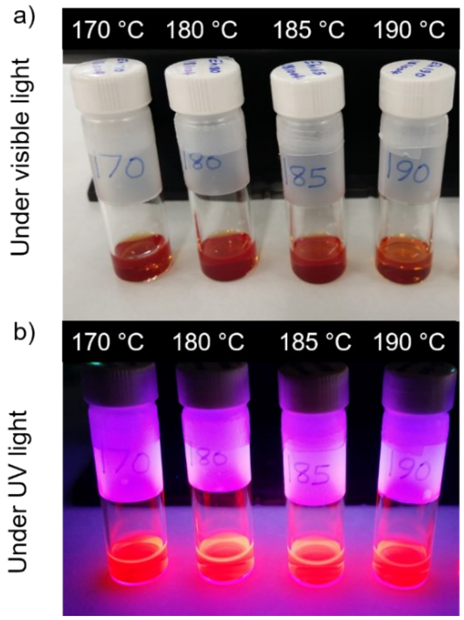

Figure S3. Pictures of the $CsPbI_3$ QDs solutions prepared at different synthesis temperature under (a) visible and (b) UV light.

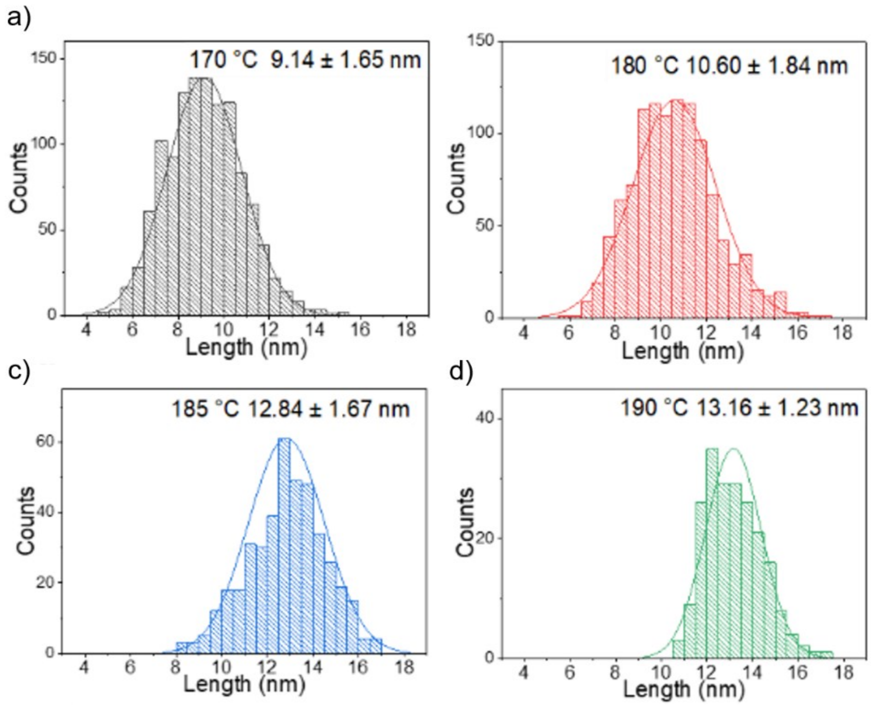

Figure S4. Histograms of the particle size distribution obtained from TEM images for the $CsPbI_3$ QDs synthesized at (a) 170 °C, (b) 180 °C, (c) 185 °C and (d) 190 °C. In order to avoid the selectivity in the QDs size during the measurements, all the QDs available in TEM images were measured for each sample.

Table S1. Summary of the calculation of surface/volume and OLM/surface ratios. Taking into account the size of the QDs grown, S, reported in Table 2 and Figure S4, and the cubic shape, see Figure 3, the surface volume ratio is calculated as $6S^2/S^3=6S^{-1}$. The total mass of QDs obtained after the synthesis is same independently of the T, and we consider it is limited by the amount of Cs-Oleate 0.25 mmol. Consequently, 0.25 mmols of $CsPbI_3$ are produced after the synthesis. Taking into account the Molecular Weight (MW)=720.82 gr/mol of $CsPbI_3$ and the density of the cubic phase, 4.54 gr/cm^{-3},[4] the total volume is obtained. Considering, the surface/volume ratio the total surface that has to be passivated is calculated. Finally, considering the number of final OLM moles calculated from NMR experiments and the total surface, we obtain the ratio of both magnitudes.

Temperature (° C)	Volume of OA | OLA (mL)	Number of moles of OLM after transformation (mmol)	Surface/ volume ratio ($10^6 \cdot cm^{-1}$)	Total volume (cm^3)	Total surface ($10^5 \cdot cm^2$)	OLM/Surface ratio ($10^{-5} \cdot mmol \cdot cm^{-2}$)
170	1.5 | 1.5	3.4	6.57	0.0397	2.60	1.30
180	2.9 | 3.0	4.0	5.66	0.0397	2.24	1.79
185	3.9 | 4.0	4.5	4.67	0.0397	1.85	2.43
190	3.9 | 4.0	4.0	4.56	0.0397	1.81	2.21

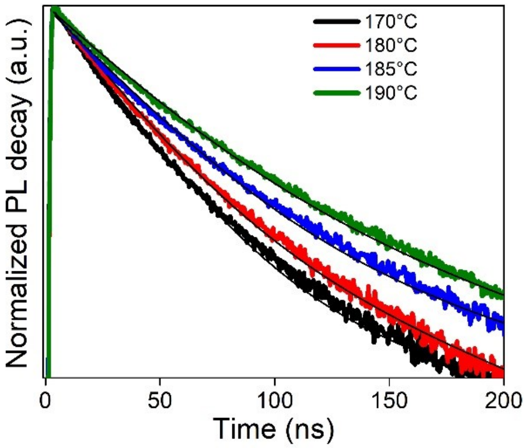

Figure S5. PL decay of $CsPbI_3$ QDs synthesized at different synthesis temperatures.

Table S2. Parameters extracted from the fitting to a double exponential of the of the PL decay data, plotted in Figure S5, and radiative and non-radiative recombination decay rate constants, K_r and K_{nr}, respectively. Expressions used in the calculations:[5] $\tau_{avg} = (\Sigma A_i \tau_i^2 / \Sigma A_i \tau_i)$, $\tau_{avg} = 1/(K_r + K_{nr})$ and $K_r = (PLQY/\tau_{avg})$, where absolute PLQY are used. Note that, calculation of Kr and Knr were estimated according to PLQY range (0.82-0.92) and τ_{avg} extracted from PL decays obtained for QDs samples after 6 months of storage under air conditions.

Temperature (°C)	**A_1 (%)**	**τ_1 (ns)**	**A_2 (%)**	**τ_2 (ns)**	**τ_{avg} (ns)**	**Absolute PLQY**	**K_r (10^7 s^{-1})**	**K_{nr} (10^7 s^{-1})**	**K_{nr}/ K_r**
170	80.8	25.3	19.2	123.4	77.9	0.82	1.05	0.23	0.220
180	72.8	26.6	27.2	88.7	61.0	0.88	1.44	0.20	0.138
185	**72.5**	**32.7**	**27.4**	**128.9**	**90.3**	**0.92**	**1.02**	**0.08**	**0.078**
190	64.6	35.7	35.4	114.4	85.8	0.90	1.06	0.10	0.094

Table S3. PLQY % (stability %) of QDs synthesized at different temperatures respect to initial values.

Temperature (°C)	**170**	**180**	**185**	**190**
PLQY% initial (stability %)	87 (100)	91 (100)	**93** **(100)**	92 (100)
PLQY% after 6 months (stability %)	82 (95)	88 (97)	**92** **(99)**	90 (98)
PLQY % After 15 months (stability %)	66 (76)	75 (82)	**86** **(92)**	84 (91)

Table S4. Chromaticity coordinates of synthesized QDs at different temperatures and red color in Rec. 2020 standard

Temperature (°C)	X	Y
170	0.7239	0.2761
180	0.7258	0.2742
185	0.7264	0.2736
190	0.7272	0.2728
Rec. 2020 standard for red color	0.708	0.292

References

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