Hybrid light emitting diodes based on stable, high brightness all-inorganic CsPbI₃ perovskite nanocrystals and InGaN

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SI1. XPS and NMR studies

Our inorganic CsPbI₃ nanocrystals (NCs) were synthesized by modifying and developing a method from Chen et al. [S1]. The NCs are capped with oleic acid (OA) and oleylamine (OLA) and bidentate 2, 2'iminodibenzoic acid (IDA) is used for ligand replacement. The chemical structure of the capping ligands is shown in Figure S1.



Figure S1 Chemical structure of the molecules used as capping ligands in the synthesis of CsPbI₃ perovskite nanocrystals.

We have examined the chemical composition of the nanocrystals using different techniques. Figure S2 shows the X-ray photoelectron spectroscopy (XPS) spectra for the control and IDA-based samples. The survey spectra in Figure S2a show all the elements expected in the CsPbI₃ NCs with no significant change in the binding energy of Cs 3*d*, Pb 4*f* and I 3*d*. The high-resolution XPS spectra at the energy of the Pb 4*f* and N 1*s* peaks (Figure S2b) enable us to estimate the atomic ratio of N:Pb in different samples: this ratio increases from 1.8 in the control sample to 3.3 and 3.8 in the IDA-treated NCs at $T_{IDA} = 40$ °C and 80 °C, respectively (Table S1). Thus the concentration of N increases in all the IDA-treated NCs. The nitrogen arises from the protonated amine groups (NH₃⁺) in the OLA and the NH⁻ group in the IDA (Figure S1).

The IDA-ligand replacement is supported by nuclear magnetic resonance (NMR) spectra showing characteristic peaks in the aromatic region (~10 ppm) (Figure S3).



Figure S2 (a) XPS spectra for control and IDA-treated samples ($T_{IDA} = 40$ °C and 80 °C). (b) High resolution spectra in the N- and Pb-regions for $T_{IDA} = 80$ °C.

Table SI : Pb:N molar ratio estimated from XPS.				
Samples	Pb : N atomic ratio			
Control	1:1.8			
$T_{\rm IDA} = 40 {}^{\rm o}{\rm C}$	1:3.3			
$T_{\rm IDA} = 80 \ ^{\rm o}{\rm C}$	1:3.8			



Figure S3. NMR spectrum of IDA-treated CsPbI₃ nanocrystals ($T_{\text{IDA}} = 40 \text{ }^{\circ}\text{C}$).

Studies of the NCs by energy-dispersive X-ray (EDX) spectroscopy (Figure S4) indicate that the ratio between the atomic percentages of Pb:Cs:I in different samples is close to the expected stoichiometry 1:1:3 (Table S2).



Figure S4. EDX spectrum and TEM image (inset) for IDA-based NCs ($T_{IDA} = 80 \text{ °C}$).

Table S2: Atomic (AT) % of Pb, Cs and I, and corresponding AT ratio from EDX studies.

	Pb (AT%)	Cs (AT%)	I (AT%)	Pb/Cs	Pb/I
Control	0.79 ± 0.01	1.02 ± 0.02	2.35 ± 0.01	1:1.3	1:3
$T_{\rm IDA} = 40 {}^{\rm o}{\rm C}$	0.31 ± 0.01	0.38 ± 0.02	0.96 ± 0.02	1:1.2	1:3
$T_{\rm IDA} = 60 {}^{\rm o}{\rm C}$	0.18 ± 0.01	0.21 ± 0.01	0.56 ± 0.02	1:1.2	1:3.1
$T_{\rm IDA} = 80 \ ^{\rm o}{\rm C}$	0.07 ± 0.01	0.07 ± 0.01	0.18 ± 0.01	1:1	1:2.6

SI2. Optical properties: photoluminescence and absorption

The PL, QY and absorption spectra of nanocrystals with different amounts of IDA were studied at room temperature (Figure S5a-b-c-d). The following concentrations of IDA were used: 16 mM, 32 mM and 64 mM, corresponding to molar ratios Pb²⁺:IDA of 5:1, 5:2 and 5:4, respectively. All IDA-based solutions were stored in a fridge (T = 5 °C) and retained colloidal

and optical stability over a period of at least 1 month. Representative PL and absorption spectra are in Figure S5a and S5b. As shown in Figure S5c for freshly prepared solutions, the greatest increase of QY is observed for Pb^{2+} :IDA = 5:1. This increase is accompanied by a red-shift of the PL peak by 25 meV. These data suggest that for Pb^{2+} :IDA = 5:1, the replacement of OA by IDA provides the most effective surface defect passivation. Further increase in IDA may result into an excess of IDA in solution; furthermore, IDA that strongly binds to the Pb-ions on the NC surface may prevent the NC growth.



Figure S5. a) PL spectra, **b)** absorption, and **c)** PL QY of NC solutions with different amount of IDA. (**d)** Photo of NC solutions under white (left) and UV (right) light, 2 weeks after synthesis.

SI3. Optical properties: UV illumination

We have examined the stability of the PL signal over a period of 30 min under unfocused UV light ($\lambda = 375$ nm, $P = 2.17 \mu$ W). The PL of the IDA treated nanocrystals is only weakly affected by exposure to UV light: a 6% decrease of the PL intensity is observed after 30 minutes

(Figure S6a). For the untreated control sample, a continuous decrease of PL intensity by 25 % is observed after 30 minutes (Figure 6Sb). Exposure of the NCs to visible light does not affect the PL intensity. Also, exposure of the NCs to high temperatures (T > 100 °C) degrades the PL signal. This is accompanied by a shortening of the PL lifetime from tens to a few nanoseconds (Figure 6Sc).



Figure S6. PL intensity under UV light for the control (**a**) and IDA treated samples (**b**). (**c**) Time-resolved PL before and after heating the NCs in air. The lifetime of the PL peak emission decreases from 14.0 ns to 2.4 ns after heating in air at T = 130 °C.

SI4. Morphological properties

Figure S7a-d show representative transmission electron microscopy (TEM), high resolution TEM and selective area electron diffraction (SAED) images for nanocrystals with and without IDA ligands. They reveal their crystalline structureand a systematic decrease of the size of the nanocrystals with increasing temperature of the IDA replacement.



Figure S7. a) TEM and HRTEM images of control and IDA-capped CsPbI₃ nanocrystals treated at **b**) T_{IDA} =40 °C, **c**) T_{IDA} =60 °C, and **d**) T_{IDA} =80 °C. Insets in parts a-b-c show the selected area electron diffraction (SAED) images.

References

[S1] Chen, X.; Peng, L. C.; Huang, K. K.; Shi, Z.; Xie, R. G.; Yang, W. S. Non-injection gramscale synthesis of cesium lead halide perovskite quantum dots with controllable size and composition. Nano Res. 2016, 9, 1994-2006.