Hybrid light emitting diodes based on stable, high brightness all-inorganic CsPbI$_3$ perovskite nanocrystals and InGaN

Chengxi Zhang,$^{1,2,4}$ Lyudmila Turyanska$^{1,3,4}$ Haicheng Cao,$^4$ Lixia Zhao,$^4$

Michael W. Fay,$^5$ Robert Temperton,$^1$ James O’Shea,$^1$ Neil R. Thomas,$^6$

Kaiyou Wang,$^7$ Weiling Luan,$^2$ Amalia Patanè$^1$

$^1$School of Physics and Astronomy, University of Nottingham, NG7 2RD, UK

$^2$East China University of Science and Technology, Shanghai 200237, China

$^3$School of Chemistry, University of Lincoln, Lincoln LN6 7TS, UK

$^4$Semiconductor Lighting Research and Development Center, Institute of Semiconductors, Chinese Academy of Sciences, Beijing 100083, China

$^5$Nanoscale and Microscale Research Centre, University of Nottingham, NG7 2RD, UK

$^6$Centre for Biomolecular Sciences, School of Chemistry, University of Nottingham, University Park, NG7 2RD, UK

$^7$State Key Laboratory of Superlattices and Microstructures, Institute of Semiconductors, Chinese Academy of Sciences, Beijing 100083, China

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*Corresponding authors*
amalia.patane@nottingham.ac.uk
lyudmila.turyanska@nottingham.ac.uk
xi1273424183@163.com
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.

![Chemical structure of the capping ligands](image)

**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 3d, Pb 4f and I 3d. The high-resolution XPS spectra at the energy of the Pb 4f and N 1s 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 $T_{\text{IDA}} = 40 \, ^\circ\text{C}$ and $80 \, ^\circ\text{C}$, respectively (Table S1). Thus the concentration of N increases in all the IDA-treated NCs. The nitrogen arises from the protonated amine groups ($\text{NH}_3^+$) 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 ($T_{IDA} = 40 \degree C$ and $80 \degree C$). (b) High resolution spectra in the N- and Pb-regions for $T_{IDA} = 80 \degree C$.

Table SI: Pb:N molar ratio estimated from XPS.

<table>
<thead>
<tr>
<th>Samples</th>
<th>Pb : N atomic ratio</th>
</tr>
</thead>
<tbody>
<tr>
<td>Control</td>
<td>1:1.8</td>
</tr>
<tr>
<td>$T_{IDA} = 40 \degree C$</td>
<td>1:3.3</td>
</tr>
<tr>
<td>$T_{IDA} = 80 \degree C$</td>
<td>1:3.8</td>
</tr>
</tbody>
</table>

Figure S3. NMR spectrum of IDA-treated CsPbI$_3$ nanocrystals ($T_{IDA} = 40 \degree C$).
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 °C).](image)

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

<table>
<thead>
<tr>
<th></th>
<th>Pb (AT%)</th>
<th>Cs (AT%)</th>
<th>I (AT%)</th>
<th>Pb/Cs</th>
<th>Pb/I</th>
</tr>
</thead>
<tbody>
<tr>
<td>Control</td>
<td>0.79±0.01</td>
<td>1.02±0.02</td>
<td>2.35±0.01</td>
<td>1:1.3</td>
<td>1:3</td>
</tr>
<tr>
<td>T_{IDA} = 40 °C</td>
<td>0.31±0.01</td>
<td>0.38±0.02</td>
<td>0.96±0.02</td>
<td>1:1.2</td>
<td>1:3</td>
</tr>
<tr>
<td>T_{IDA} = 60 °C</td>
<td>0.18±0.01</td>
<td>0.21±0.01</td>
<td>0.56±0.02</td>
<td>1:1.2</td>
<td>1:3.1</td>
</tr>
<tr>
<td>T_{IDA} = 80 °C</td>
<td>0.07±0.01</td>
<td>0.07±0.01</td>
<td>0.18±0.01</td>
<td>1:1</td>
<td>1:2.6</td>
</tr>
</tbody>
</table>

**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 Pb\(^{2+}\):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.](image)

**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 (λ = 375 nm, P = 2.17 µW). 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
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 ($T > 100 \, ^\circ\text{C}$) 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 $T = 130 \, ^\circ\text{C}$.

**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 structure and 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 CsPbI$_3$ 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**