

1 **A Comparative Study of Light Emitting Diodes based on All-Inorganic Perovskite**  
2 **Nanoparticles (CsPbBr<sub>3</sub>) Synthesized at Room Temperature and by Hot Injection Method**

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9 **Abstract:** Perovskite nanoparticles (PeNPs) have been extensively studied for optoelectronic  
10 applications due to their extremely high photoluminescence quantum yield, tunable bandgap,  
11 and exceptionally narrow emission spectra. Therefore, PeNPsare considered excellent  
12 candidates for the development of high efficiency, low-cost, wide gamut and high purity color  
13 displays. However, their synthesis typically involves multi-step cumbersome processes that  
14 might hinder its commercial development. In this work, we reportgreen light-emitting diodes  
15 (LEDs) prepared using all inorganic PeNPs CsPbBr<sub>3</sub> synthesized at room temperature (RT) and  
16 compare their performance with those prepared by a traditional hot injection (HI) method.We  
17 provide insights into the morphology, optoelectronic properties of RT PeNPs via atomic force  
18 and transmission electron microscopy and employing them in LEDs.

19

20 **Keywords:** Perovskite, LED, CsPbBr<sub>3</sub>, Hot injection, Room Temperature

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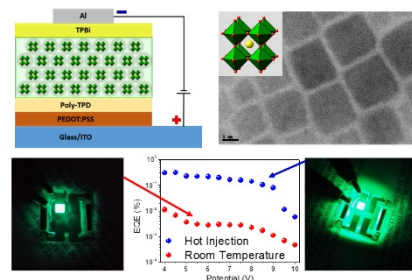
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26 **TOC:**

27 We have synthesized perovskite nanoparticles (PeNPs) through two different procedures, e.g.,  
28 hot injection (HI) and a room temperature synthesis (RT). The light-emitting diodes (LEDs)  
29 prepared using the two types of PeNPs show superior performance for HI PeNPs. The  
30 morphology and optoelectronic investigations revealed that the HI PeNPs are characterized by a  
31 lower thin film surface roughness, narrow size distribution, and a higher radiative yield that is  
32 responsible for the higher performance.

33

## 1 Introduction

2  
3 All inorganic perovskite nanoparticles with the general formula  $\text{CsPbX}_3$  ( $X = \text{Cl}^-$ ,  $\text{Br}^-$ ,  $\text{I}^-$ )  
4 have gained attention in the scientific community due to their outstanding optoelectronic  
5 properties, such as the extremely high photoluminescence quantum yield (as high as 90 %),  
6 narrow emission spectra (FWHM  $\approx 12 - 42$  nm), tunable bandgap depending on the particle size  
7 and composition, low preparation cost, and abundance of precursor materials.<sup>1-4</sup> Since  
8 their emergence in 2014, PeNPs have been considered an excellent candidate as primary  
9 semiconductor in photodetectors,<sup>5</sup> light-emitting electrochemical cells,<sup>6</sup> photochemical  
10 conversion,<sup>7</sup> solar cells,<sup>8,9</sup> lasers,<sup>10</sup> and light-emitting diodes.<sup>11-16</sup> The particularly interesting  
11 optoelectronic characteristics of PeNPs make this family of materials an exceptional alternative for  
12 the development of unprecedented high quality full color displays.

13 In just two years of research, LEDs based on PeNPs synthesized by the HI method have  
14 reached external quantum efficiencies (EQEs) beyond 8%,<sup>17</sup> which is an outstanding  
15 achievement compared to other technologies. Nowadays, the cadmium-based quantum dots (Cd-  
16 QDs) LEDs, that have been extensively investigated during the last two decades, show state of  
17 art EQE  $\sim 20.5\%$  for red LEDs.<sup>18,19</sup> Nonetheless, there are some limiting factors that hinder its  
18 industrial application for quotidian purposes. On one hand, Cd-QDs employ hazardous elements  
19 such as Cd in their synthesis, on the other hand, requires relatively high temperature, controlled  
20 atmosphere to avoid undesired oxidation reactions, use of expensive raw materials, and most  
21 importantly, sophisticated core/shell structures in order to reach high PLQY.

22 Soon after the first report of organic-inorganic hybrid PeNPs by Perez-Prieto and  
23 coworkers,<sup>20</sup> Kovalenko and coworkers synthesized,<sup>1</sup> for the first time, all-inorganic PeNPs via a  
24 hot injection method – a method that requires high temperature. However, a more recent low  
25 temperature compatible synthesis is reported in 2016.<sup>21</sup> The new methodology exploits a  
26 supersaturated recrystallization method, which transfers the  $\text{Cs}^+$ ,  $\text{Pb}^{2+}$  and the  $X^-$  ions dissolved  
27 in DMF to a non-polar solvent (toluene) at room temperature. Surprisingly, these PeNPs also  
28 presented PLQY values above 90%. This new method simplifies significantly the synthesis  
29 of the semiconductor nanocrystals without the need of high temperatures or controlled  
30 atmosphere. Despite the relative simplicity of the synthetic method and outstanding optical  
31 properties of the nanocrystals, their application in an optoelectronic device is not yet reported.

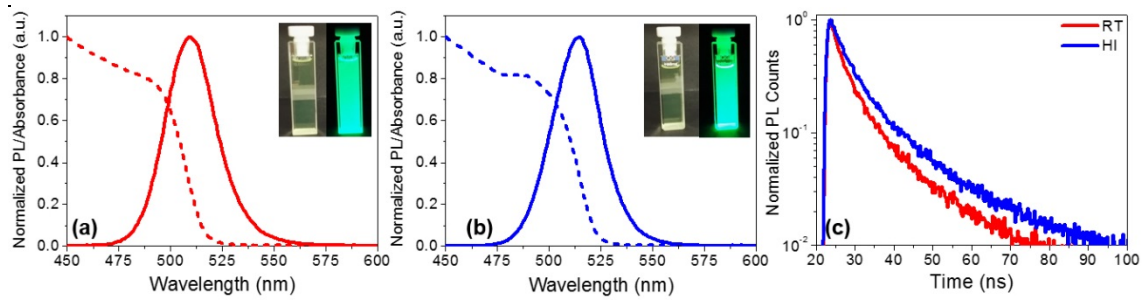
32 A crucial parameter to be taken into account towards the preparation of high  
33 efficiency LEDs based on PeNPs is the careful removal of excess organic solvents and surfactants  
34 present in the crude solution which are essential for a proper nucleation and controlled  
35 crystallization. Therefore, great attention must be paid on the purification process of the  
36 nanoparticles, which would otherwise decrease the PLQY or even lead to PeNP aggregation and  
37 subsequent precipitation. Swarnkar and coworkers recently developed a purification method using

1 methylacetate (MeOAc), an antisolvent that removes the excess non-volatile solvents and  
2 reagents without inducing agglomeration.<sup>8</sup> Li and coworkers demonstrated the preparation of  
3 LEDs with high efficiency from solution-processed CsPbBr<sub>3</sub> nanoparticles through balancing  
4 surface passivation and carrier injection via ligand density control using hexane/ethyl acetate  
5 mixed solvent.<sup>15</sup> Despite the growing research progress in PeNPs, the stability of colloidal  
6 solutions and stable device lifetime are yet to be demonstrated.

7 In this work, we report for the first time the preparation of green LEDs using CsPbBr<sub>3</sub>  
8 PeNPs synthesized at RT as a light-emitting material, which could be an important step forward  
9 from the industrial point of view, taking into account the simplicity of the synthetic method. We  
10 note that the RT PeNPs demonstrate an inferior performance due to relatively poorer size  
11 distribution, and perhaps due to the fact that no further purification was applied to it, compared  
12 to the HI PeNPs, where a solvent purification led to improved NP morphology.

## 14 **Results and Discussion**

15 Green light-emitting CsPbBr<sub>3</sub> PeNPs have been prepared through two different methods (see  
16 experimental section for further details). We use the HI method, previously reported in literature  
17 to yield suitable PeNPs for the preparation of LEDs to compare the optoelectronic properties  
18 of RT PeNPs. Both methodologies produced CsPbBr<sub>3</sub> NPs with cubic structure as determined by  
19 X-ray diffraction, see Figure S1 in the Supporting Information. Figure 1 shows the absorbance  
20 and photoluminescence (PL) spectra measured for the PeNPs prepared through the two different  
21 approaches. The RT nanoparticles exhibit a PLQY of 49 % (solution) and 15 % (film), whose  
22 emission maximum ( $\lambda_{em}^{max}$ ) is centered at 509 nm and the PL spectrum shows a FWHM of 29  
23 nm; whereas, the HI PeNPs showed a PLQY of 60% (solution) and 20 % (film) and the emission  
24 peak is centered at 514 nm (FWHM 28 nm). In both cases, the PL spectra are situated within the  
25 green spectral region with a slight bathochromic shift of 5 nm for the PeNPs synthesized  
26 through the HI method. This red-shift between the PL emission peaks of the two PeNPs is due to  
27 the purification performed on HI PeNPs as proposed by Li *et. al.*<sup>15</sup> In fact, we note a similar red-  
28 shift for HI PeNPs before and after purification (see Figure S2).

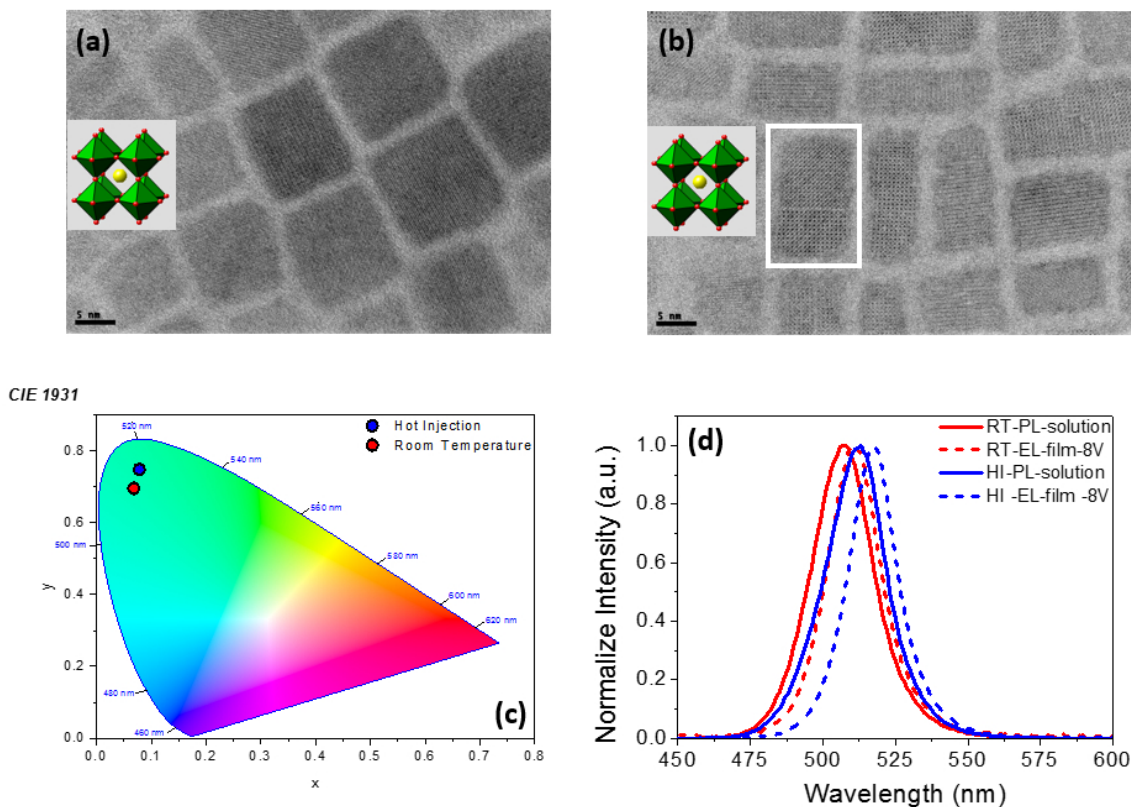


**Figure 1.** Absorbance (dashed line) and PL (solid line) spectra of the green light-emitting CsPbBr<sub>3</sub>PeNPs synthesized (a) at RT and (b) by the HI method. The PL spectra were measured using the  $\lambda_{\text{exc}} = 440$  nm for both nanoparticles. The insets show the solutions under white light and under UV light. (c) Transient PL decay curves for the RT (red) and HI (blue) PeNPs.

The Stokes shift observed in Figure 1(a) and Figure 1(b) for both types of PeNPs is also very similar, being  $\approx 105$  meV (21 nm) and  $\approx 118$  meV (24 nm) for the RT and HI, respectively. CdSe/CdS, CdSe/CdPbS and CdSe/CdZnS quantum dots typically show Stokes shift values of  $\approx 400$  meV, which are significantly larger than those observed for PeNPs.<sup>22</sup> The smaller Stokes shifts observed here imply that the PL of the PeNPs arises from the direct exciton recombination process, which is in good agreement with previous reports.<sup>23,24</sup> The absorbance onset of the PeNPs prepared at RT starts at 525 nm while that observed for the HI PeNPs starts at 531 nm. From the absorbance spectrum, it is possible to estimate the optical bandgap of the two types of PeNPs by using the Tauc plot, see Figure S3. The calculated bandgap matches closely, e.g., 2.40 eV and 2.37 eV for RT and HI method, respectively, as shown in Figure S3.<sup>25</sup> These results are in a good agreement with previous reports that have been used as a reference to this work.<sup>11,21</sup> Figure 1(c) shows the transient PL decay for both types of PeNPs (in solution). Although a distinction between slow and fast decay that is typically ascribed to non-radiative and radiative processes, respectively, is hard to make a quantitative analysis of the two shows a larger non-radiative lifetime for HI PeNPs. As recently reported by Tress, a longer non-radiative lifetime (or a higher radiative yield) leads to higher internal quantum efficiency (IQE).<sup>26</sup>

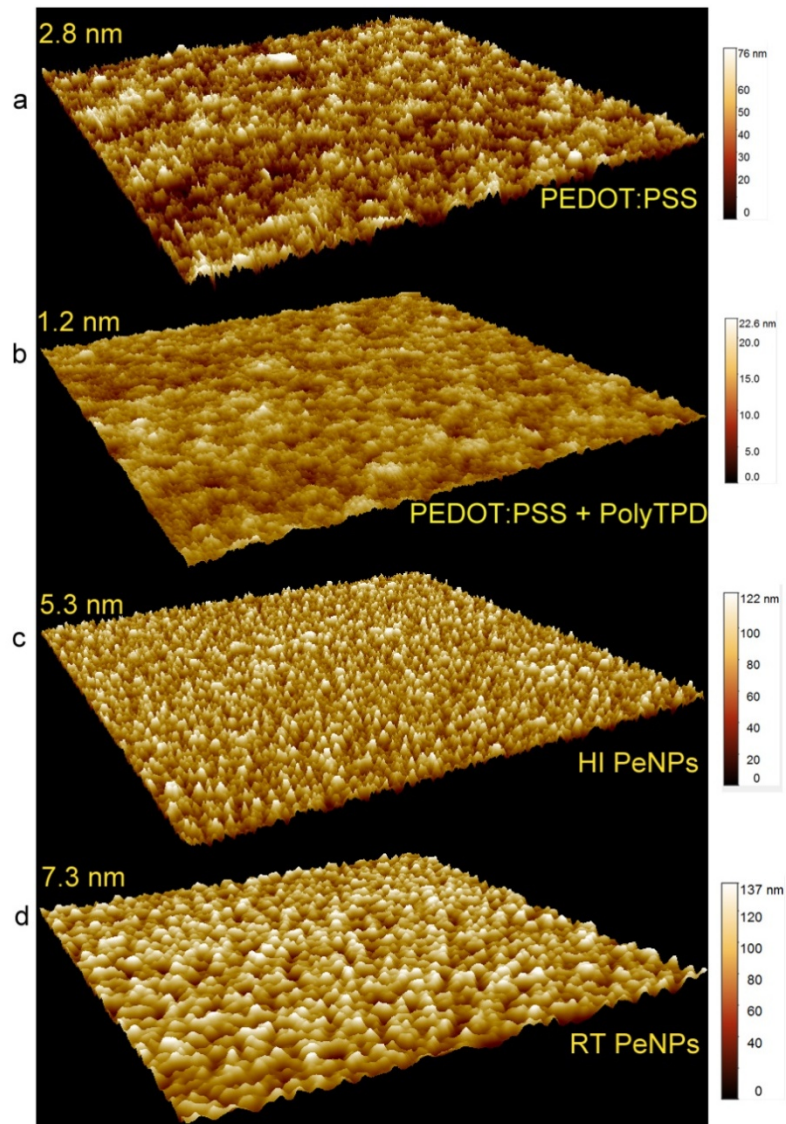
Figures 2(a) and 2(b) show the high-resolution transmission electron microscopy images (HR-TEM) of the RT and HI PeNPs, respectively. Both PeNPs show size distributions with values below 20 nm and well-defined crystalline planes for both types of nanoparticles. However, we clearly observe that the geometry for the two types of PeNPs studied is significantly different, being more rectangular for the RT nanocrystals and more square for the nanocrystals synthesized through the HI method. The PL spectra of the PeNPs were transformed into the corresponding chromaticity indexes and plotted in the CIE 1931 color space chromaticity diagram. As shown in Figure 2(c), the red dot (0.057, 0.642) and the blue dot (0.068, 0.696) represent those chromaticity indexes corresponding to the PL spectra of the RT

- 1 and HI PeNPs, respectively; the proximity of the CIE values to the curve edge indicates the pure
- 2 color nature of the emitted light.



3  
 4 **Figure 2.** HR-TEM images of the (a) RT and (b) HI PeNPs nanocrystals. White rectangle in (b) encircles defective  
 5 NPs. (c) Chromaticity indexes corresponding to the PL spectra for the RT (red) and HI (blue) PeNPs plotted in the  
 6 CIE 1931 diagram; and (d) PL in solution (solid lines) using hexane as solvent and the EL spectra (dashed lines) of the  
 7 PeNPs synthesized at RT and by HI method.

8  
 9 Figure 2(d) shows the PL spectra (in solution) and the electroluminescence (EL) spectra of a  
 10 complete device (8V) for the PeNPs synthesized at RT and by HI method. A small red-shift  
 11 between PL of NPs in solution and EL from PeNPs layers is evident for both kinds of NPs. The  
 12 red-shift in the spectra (for EL) could be explained by the so-called Stark effect, e.g., the red-  
 13 shift in presence of high electric field. Also the fact that recombination of hot electrons, which  
 14 are present due to the applied bias, is not the same as in the case of PL, radiative recombination  
 15 in a steady-state, and may lead to such a spectral shift.<sup>27</sup>

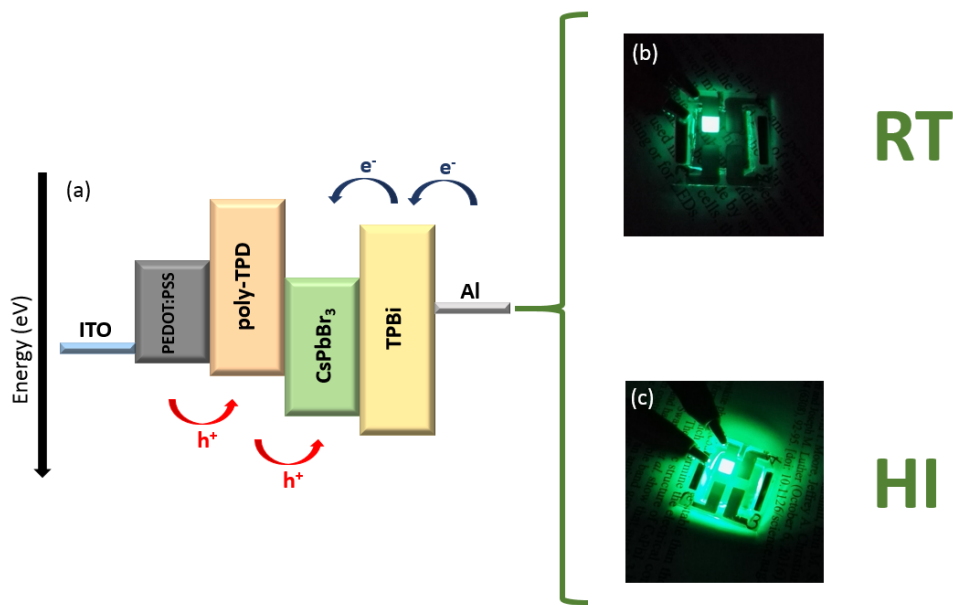


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2 **Figure 3.** AFM images of PEDOT:PSS (a), PEDOT:PSS with a thin layer of Poly-TPD on top (b), HI PeNPs (c) and  
 3 RT PeNPs (d) deposited on top of a PEDOT/Poly-TPD layer. The r.m.s. roughness is marked on top left of each  
 4 image. The scan area is  $10\ \mu\text{m} \times 10\ \mu\text{m}$ .

5 In order to determine the surface coverage and surface roughness of the films, we recorded  
 6 topography of as deposited films using atomic force microscopy (AFM) on relatively large area  
 7 ( $10\ \mu\text{m} \times 10\ \mu\text{m}$ ). The root mean square roughness calculated for PEDOT was 2.8 nm, which  
 8 reduced to 1.2 nm when a thin layer of Poly-TPD is deposited on top suggesting formation of a  
 9 smoother film (Figure 3(b)). The HI PeNPs showed a smaller r.m.s. roughness value (5.3 nm)  
 10 compared to RT PeNPs (7.3 nm) suggesting that the former leads to a smooth film formation  
 11 probably due to a narrow size distribution and smaller particle size. A lower surface roughness  
 12 and narrow size distribution are prerequisites to high performing devices. Furthermore, the RT  
 13 method leads to formation of small clusters with the film which might hinder the device  
 14 performance.

1 We employed both kinds of nanocrystals as an absorber material for LEDs, see experimental  
 2 section. Figure 4(a) depicts energy level diagram of the materials employed for the complete  
 3 devices, while Figure 4(b) and Figure 4(c) shows a photograph of the green LED at 8 V prepared  
 4 at RT and by HI, respectively. EL spectra at different applied voltage are depicted in Figure  
 5 S4. All the devices were prepared using ITO as the substrate, a thin layer of PEDOT:PSS as a  
 6 hole transport material on top of the ITO, then a poly-TPD layer as an electron blocking layer,  
 7 followed by the deposition of the PeNPs and a TPBi layer as an electron transport material.  
 8 To finally complete the devices, the thermal evaporation of aluminum electrodes was carried out.



9

10 **Figure 4.**(a) Energy diagram of the materials employed for the preparation of the PeNPs-LEDs. Bright green LEDs  
 11 driven at 8 Volts, using PeNPs prepared at (b) RT and (c) by HI method.

12 The performances of the LEDs prepared with both PeNPs was studied. Figure 5 shows the  
 13 electro-optical response of the LEDs prepared with the RT and HI PeNPs, respectively. Figure  
 14 5(a) shows the current density of both kinds of PeNPs. Devices prepared with PeNPs synthesized  
 15 through the HI method show lower current at low applied voltages. At voltages between 8 and 9  
 16 Volts both devices exhibit similar current densities. However, at voltages beyond 9 V, the HI  
 17 particles show higher current density values. These variations probably arise from the different  
 18 synthesis procedures (the HI involves high temperature synthesis and a subsequent purification  
 19 that yield a high quality PeNPs), see the experimental section. Figure 5(b) reveals significant  
 20 variations of the current efficiency values depending on the PeNP employed. The higher PLQY  
 21 and the lower currents contribute to the observed higher efficiency for HI LEDs. The maximum  
 22 current efficiency value was observed was  $0.7 \text{ Cd}\cdot\text{A}^{-1}$ , which correspond to those devices  
 23 prepared from the HI method particles. The data plotted in Figure 5(c) show that the maximum  
 24 luminance values range from  $303.2 \text{ Cd}\cdot\text{m}^{-2}$  for HI and  $2.66 \text{ Cd}\cdot\text{m}^{-2}$  for RT PeNPs, respectively.

1 Consequently, the maximum EQE values range from 0.31 % for the HI and 0.01% for the  
2 RTPeNPs. It is worth highlighting that all the devices show turn-on voltages at around 4 Volts  
3 regardless of the type of PeNPs employed and all the devices were measured from 4 to 10 V.

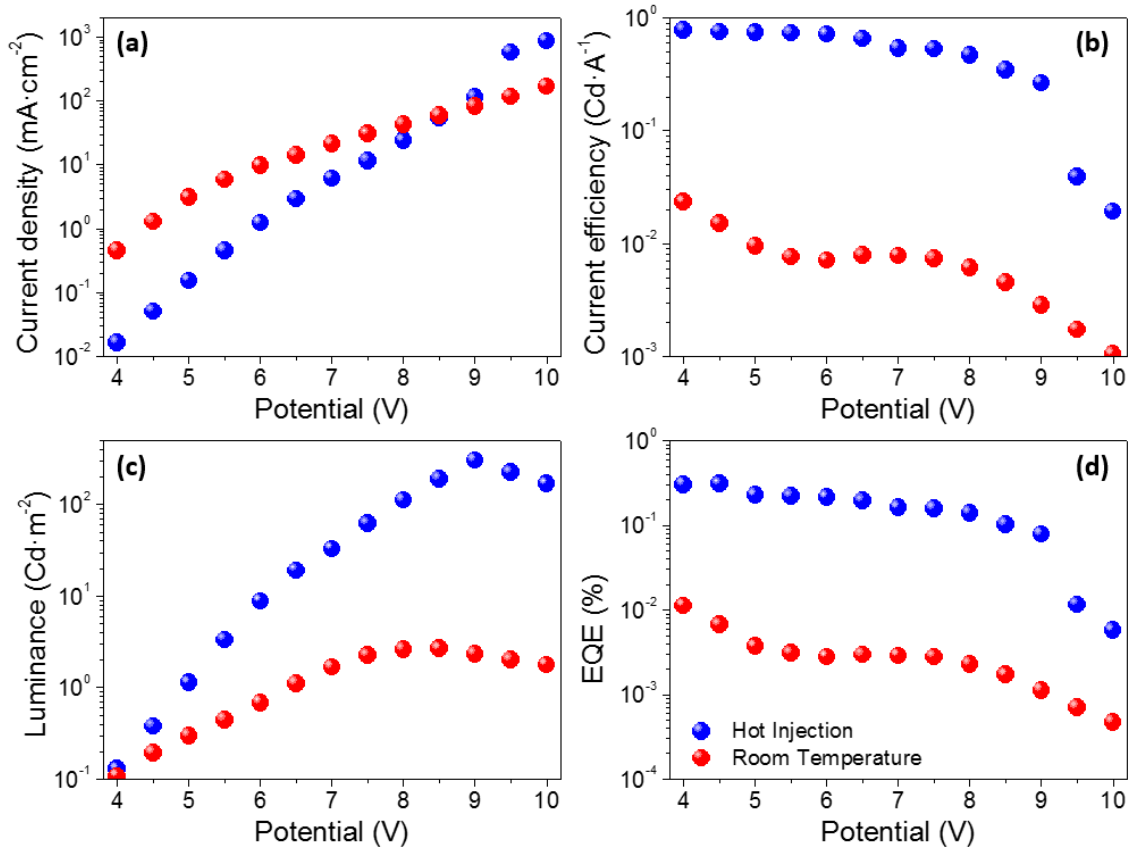
4 The clear difference in EQE of both kinds of nanoparticles, see Figure 5(d), where HI PeNPs  
5 exhibit a superior performance, can be attributed to several factors. The first concerns the  
6 synthesis process, the PeNPs synthesized by the HI method provide PeNPs with higher quality  
7 than those prepared at RT. Different factors could contribute to this result, on the one hand HI  
8 PeNPs presented a narrower size distribution, see Figure 2(a) and Figure 2(b), avoiding that  
9 small variations in the bandgap act as traps reducing the performance of the LEDs. On the other  
10 hand, the rectangular shape of PeNPs prepared at RT probably arises from the merging of  
11 different NPs and defects at the boundary between the original particles can be formed, see for  
12 example the NP encircled by a white rectangle in Figure 2(b). The higher radiative yield of  
13 the HI PeNPs (a ratio between non-radiative and radiative recombination) is another reason for  
14 their high performance (see the Figure 1(c)). The lower PLQY of the particles synthesized at RT  
15 compared to the ones prepared through the HI method also points to a higher degree of lattice  
16 defects for the RT PeNPs. Moreover, the purification method also introduces differences  
17 between both systems, being the second factor affecting the lower performance of devices  
18 prepared with RT nanoparticles. In a single synthesis exploiting the HI method, it is possible to  
19 prepare a larger amount of material and apply some purification processes to remove excess  
20 organic solvents, which is not possible with the synthesis at room temperature since the amount  
21 of material obtained after each synthesis is relatively small. Finally the lower roughness of HI  
22 PeNPs also favor the higher performance of this kind of nanoparticles.

23 It must be noted that the devices stability is still a question as both the LEDs starts to  
24 degrade at an applied bias 8 V see Figure S5, as also evident from a sudden drop in EQE  
25 (Figure 5(d)). However, the stability of these devices is in the scope of our future works and will  
26 be explained in details in our upcoming reports.

27

28





1

2 **Figure 5.** Analysis of the QD-LED performance: (a) current density curves ( $J/V$ ), (b) current efficiency, (c)  
 3 luminance and (d) EQE.

4

## 5 CONCLUSIONS

6 In summary, we have synthesized the perovskite nanoparticles (PeNPs) through two  
 7 different procedures, e.g., hot injection (HI) and a room temperature synthesis (RT). The light-  
 8 emitting diodes (LEDs) prepared using the two types of PeNPs shows superior performance for HI  
 9 PeNPs. The morphology and optoelectronic investigations revealed that the HI PeNPs are  
 10 characterized by a lower thin film surface roughness, narrow size distribution, and a higher  
 11 radiative yield that is responsible for the higher performance. Although the LED EQE efficiency  
 12 of the RT PeNPs is lower, their facile and large scale compatible offer potential for mass  
 13 production. A further improvement in the performance using RT PeNPs could be made via a  
 14 control over particle size distribution and their further purification.

15

## 16 Experimental Section

17 All the materials employed in this work were used as received from the commercial suppliers  
 18 and were used directly without further purification. Those precursors and solvents employed for

1 the PeNPs synthesis were purchased from Sigma Aldrich. Oleic acid (90 %), Oleylamine ( $\geq$  98  
2 %) 1-Octadecene (90 %), Hexane ( $\geq$  97 %), Toluene (99.8 %) Methyl acetate (99.5 %), N,N-  
3 Dimethylformamide (99.8%), Cesium bromide (99.999 %), Cesium carbonate (99.995 %).  
4 Lead(II) Bromide were purchased from TCI. The pre-patterned ITO substrates (20x20 mm)  
5 were purchased from Thin Film Devices (TFD), PEDOT:PSS (A14083) from HeraeusClevios  
6 and, Poly[N,N'-bis(4-butylphenyl)-N,N'-bisphenylbenzidine] (poly-TPD) ( $M_n$  100,000-  
7 150,000) from Ossila and 2,2',2''-(1,3,5-Benzinetriyl)-tris(1-phenyl-1-H-benzimidazole) (TPBi)  
8 were acquired from Sigma Aldrich.

## 9 **Hot Injection Method**

10 **Preparation of Cs-oleate:**  $\text{Cs}_2\text{CO}_3$  (0.814g) was loaded into 100 mL 3-neck flask along with  
11 octadecene (40mL, Sigma-Aldrich, 90%) and oleic acid (2.5 mL, OA, Sigma-Aldrich, 90%),  
12 dried for 1h at 120 °C, and then heated under  $\text{N}_2$  to 150 °C until all  $\text{Cs}_2\text{CO}_3$  reacted with OA.  
13 Since Cs-oleate precipitates out of ODE at roomtemperature, it has to be pre-heated to 100 °C  
14 before injection.

15 **Synthesis of  $\text{CsPbBr}_3$  NCs:** ODE (10 mL) and  $\text{PbBr}_2$  (0.138g) were loaded into 50 mL 3-neck  
16 flask and dried under vacuum for 1h at 120 °C. Dried oleylamine (1.0 mL, OLA) and dried OA  
17 (1.0 mL) were injected at 120 °C under  $\text{N}_2$ . After complete solubilization of a  $\text{PbBr}_2$  salt, the  
18 temperature was raised to 180 °C and Cs-oleate solution (0.8 mL, 0.125 M in ODE, prepared as  
19 described above) was quickly injected and, 5s later, the reaction mixture was cooled by the ice-  
20 water bath.<sup>1</sup>

21 **Purification of  $\text{CsPbBr}_3$  NCs:** The crude solution was cooled down with water bath and  
22 aggregated NCs were separated by centrifuging and removing as many solvents as possible  
23 involved in the synthesis process. Thereafter, after discarding the  
24 supernatant, the PeNPs were dispersed in hexane to only apply the purification process with  
25 MeOAc in the ratio of (1:3). The PeNPs were centrifuged for 10 min at 4,700 r.p.m. After that,  
26 they were dispersed again in hexane and stored at low temperature for 48h to precipitate Pb-  
27 oleate and Cs-oleate which solidify and precipitate at low temperatures. After this  
28 period the PeNPs were separated to the precipitated material. The solutions stored in the fridge are  
29 stables for months.

30 **Room Temperature Method:** To synthesized the  $\text{CsPbBr}_3$ , was necessary  $\text{PbBr}_2$  (0.4 mmol)  
31 and CsBr (0.4 mmol) dissolved in DMF (10 mL). When the precursors were totally solved, OA  
32 (1.0 mL) and OLA (0.5 mL) are added to stabilize the precursor solution. Then, 1.0 mL of the  
33 precursor solution was added drop by drop into toluene (10 mL) under vigorous stirring. Strong  
34 green emission was observed immediately after the injection.<sup>21</sup> The solutions stored in the fridge  
35 are stables for months.

1 **Purification of CsPbX<sub>3</sub> NCs:**After the synthesis of the PeNPs, each solution was centrifuged  
2 during 10 min at 4,700 r.p.m. The supernatant was discarded and the solid was dispersed in  
3 hexane. After that, all the material was placed in the same flask which was kept at low  
4 temperatures for 48 h. The precipitated material was removed and the final solution was  
5 concentrated to 10 mg·ml<sup>-1</sup>.

6 **Preparation of the NPs-based light-emitting diodes:** The ITO substrates were introduced in a  
7 soap solution and sonicated for 30 min. Then the substrates were firstly rinsed with Milli-Q  
8 water and secondly with ethanol. Next, the ITO substrates were introduced in a mixture of  
9 solvents consisting of isopropanol:acetone (1:1 v/v) and sonicated for 30 min. After that, the  
10 substrates were rinsed with ethanol and dried with compressed air. Then, the substrates were  
11 introduced in a UV-O<sub>3</sub> cleaner for 30 min and the PEDOT:PSS solution was spun-cast at 3,000  
12 r.p.m. during 60 s and treated at 150 °C for 30 min in air, to yield a thin layer (20 nm). Next, a  
13 poly-TPD layer (20 nm) was deposited by spin-casting (10 mg·ml<sup>-1</sup> in chlorobenzene) at 3,000  
14 r.p.m. for 60 s and subsequently annealed at 150 °C for 30 min in air. After that, the PeNPs  
15 solutions (10 mg·ml<sup>-1</sup>) in hexane were spun-cast at 2,000 r.p.m. during 20 s. Finally, a 20 nm of  
16 TPBi and a 100 nm aluminum top electrode was thermally evaporated at a rate of 0.5 Å·s<sup>-1</sup> and  
17 1.5-2 Å·s<sup>-1</sup> respectively; the active areas were encapsulated with adhesive tape and after that  
18 with a UV photo-curable epoxy resin from Lighting Enterprises (ELC4908-30) and a cover  
19 glass.

20 **Characterization equipment:**The absorbance spectra were registered with a UV/VIS Varian  
21 Cary 300 BIO spectrophotometer and for the PL spectra fluorometer from Horiba Fluorolog 3-  
22 11 were used. The performance of the LEDs (*J/V* curves, EL spectra, current efficiency,  
23 luminance and EQE) was quantified with an external quantum efficiency measurement system  
24 C9920-12 from Hamamatsu, based on an integrating sphere connected to a PMA-12 Photonic  
25 multi-channel detector through an optical fiber and using a Keithley 2400 as a current/voltage  
26 source meter. The photoluminescence quantum yield was measured with an absolute PL  
27 Quantum Yield measurement system with monochromatic light source C9920-02, -03 from  
28 Hamamatsu, connected to an integrating sphere. The high resolution transmission electronic  
29 microscopy (HR-TEM) images of the QDs were registered with a JEOL 2100 microscope. Time-  
30 resolved emission measurements were done with the technique of time correlated single photon  
31 counting (TCSPC) in an IBH-5000U apparatus. Samples were excited with a 464 nm NanoLED  
32 with a FWHM of 1.4 ns and a repetition rate of 100 kHz. Atomic force microscopy (Concept  
33 Scientific Instrument) was employed to probe surface roughness of the deposited films.

34

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