

Supporting information for:

Colloidal Cesium Lead Halide Perovskite Nanoplatelets with Monolayer-Level Thickness Control by a Solution Synthesis Approach

Quinten A. Akkerman^{†φ}, Silvia Genaro Motti^{†¶}, Ajay Ram Srimath Kandada[‡], Edoardo Mosconi^Σ, Valerio D'Innocenzo^{†¶}, Giovanni Bertoni^{†§}, Sergio Marras[†], Brett A. Kamino[#], Laura Miranda[#], Filippo De Angelis^{ΩΣ}, Annamaria Petrozza[‡], Mirko Prato[†] and Liberato Manna[†]

[†] Nanochemistry Department, Istituto Italiano di Tecnologia, Via Morego 30, 16163 Genova, Italy

^φ Università degli Studi di Genova, Via Dodecaneso, 31, 16146, Genova, Italy

[‡] Center for Nano Science and Technology @Polimi, Istituto Italiano di Tecnologia, via Giovanni Pascoli 70/3, 20133 Milano, Italy

[¶] Dipartimento di Fisica, Politecnico di Milano, Piazza Leonardo da Vinci, 32, 20133, Milano, Italy

^Ω CompuNet, Istituto Italiano di Tecnologia (IIT), via Morego 30, I-16163 Genova, Italy

^Σ Computational Laboratory for Hybrid/Organic Photovoltaics, CNR-ISTM, Via Elce di Sotto, I-06123, Perugia, Italy

[§] IMEM-CNR, Parco Area delle Scienze 37/A, IT 43124 Parma, Italy

[#] OxfordPV Ltd. Centre for Innovation and Enterprise, Begbroke Science Park, Woodstock Road, Oxford OX5 1PF, United Kingdom

Corresponding Authors: mirko.prato@iit.it, liberato.manna@iit.it

Additional figures:

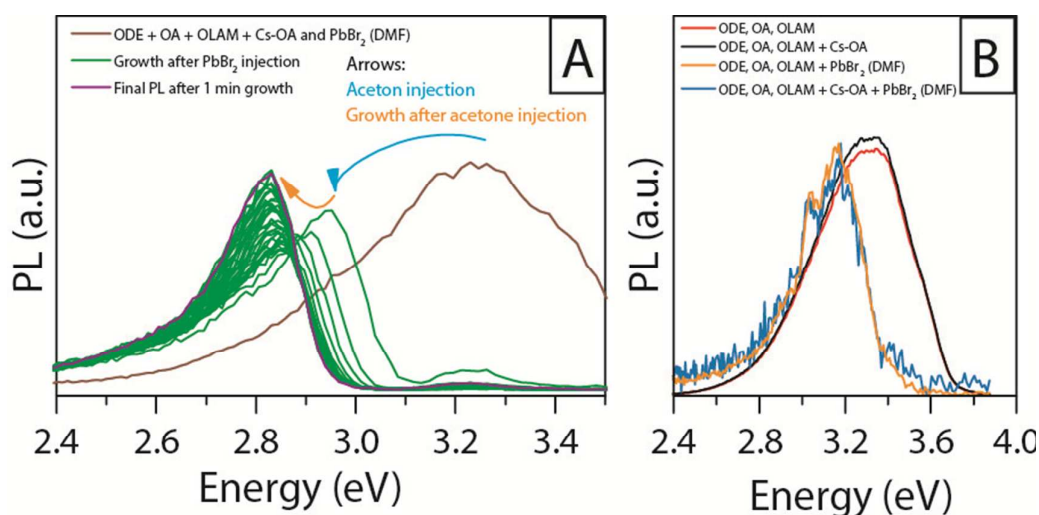


Figure SI1. (A) PL measurement over time during the growth of NPLs. Before acetone injection, the precursor solution was characterized by a broad emission peak centered at approx. 3.2 - 3.3 eV. Immediately after acetone injection, a narrower peak appeared at around 2.95 eV. Within seconds, this peak further red-shifted and narrowed (indicating the nucleation and growth of CsPbBr₃ NPLs), and finally settled to an energy value that depended on the amount of HBr added. (B) PL spectra collected on different precursor mixtures, all characterized by a broad emission around 3.2 eV, and with no PL at the energy value seen for CsPbBr₃ NPLs.

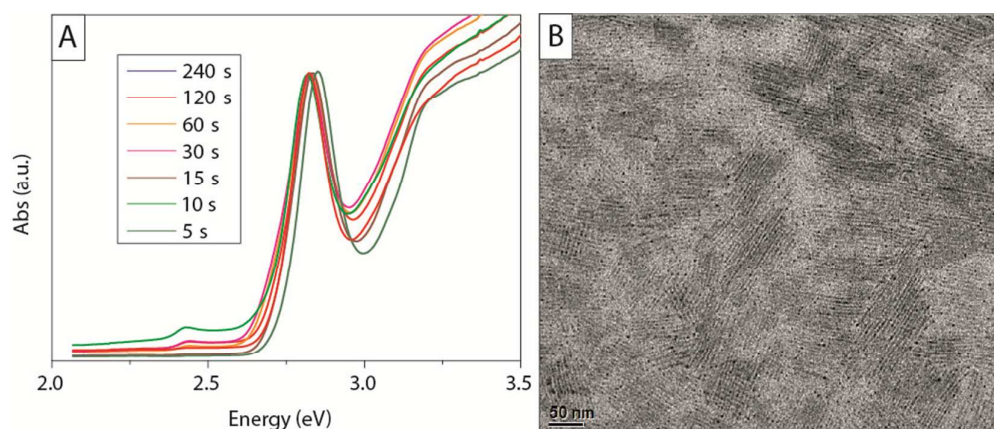


Figure SI2. (A) Absorption spectra of CsPbBr₃ NPLs obtained with different times between PbBr₂ and acetone injections, in the 5 seconds – 2minutes range. (B) TEM image of NPLs obtained after 240s between the injection of PbBr₂ and acetone.

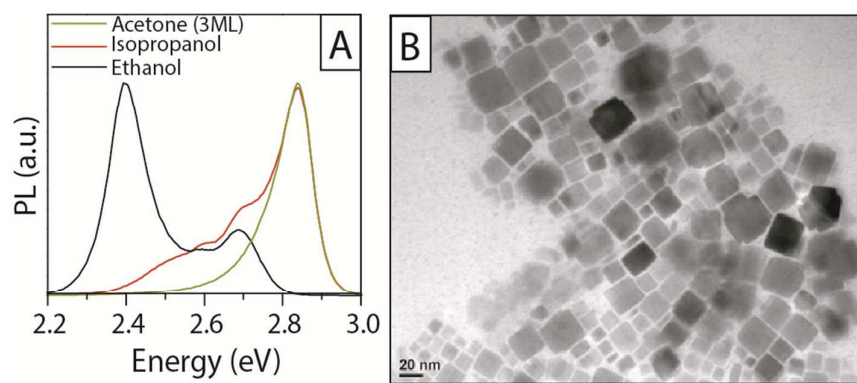


Figure SI3. (A) Comparison of PL spectra collected on CsPbBr₃ nanocrystals solutions obtained after using ethanol, isopropanol or acetone as triggers. (B) TEM image of CsPbBr₃ NCs obtained with EtOH instead of acetone.

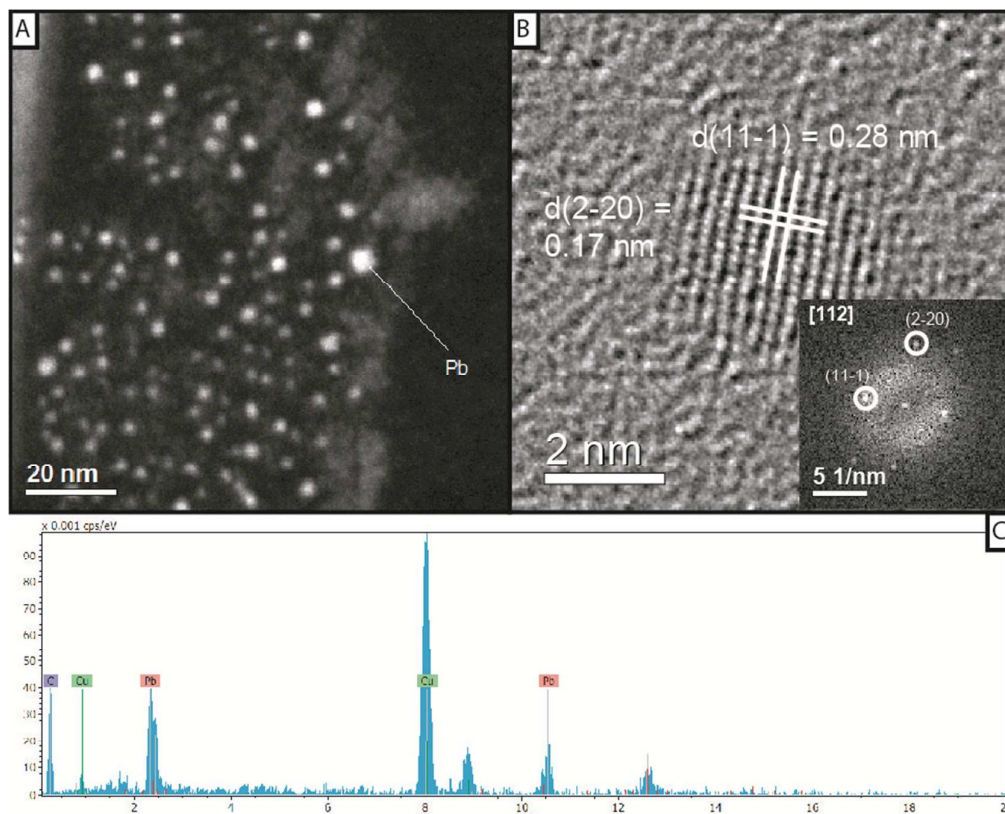


Figure S14. Analysis of lead NCs formed after e-beam irradiation. (A) Dark-STEM showing high density lead particles. (B) HRTEM of a lead particle, formed after electron irradiation in the TEM, with the lattice parameters compatible with metallic lead. (C) EDS analysis of the particle indicated only the presence of lead (the Cu peaks are from the copper support grid).

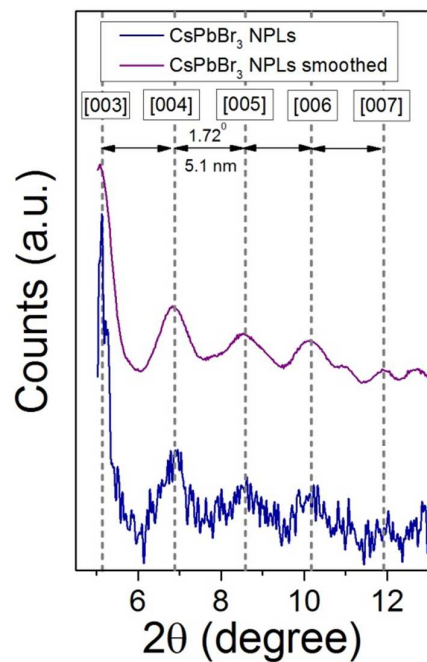


Figure S15. Low angle XRD showing reflections of stacked NPLs.

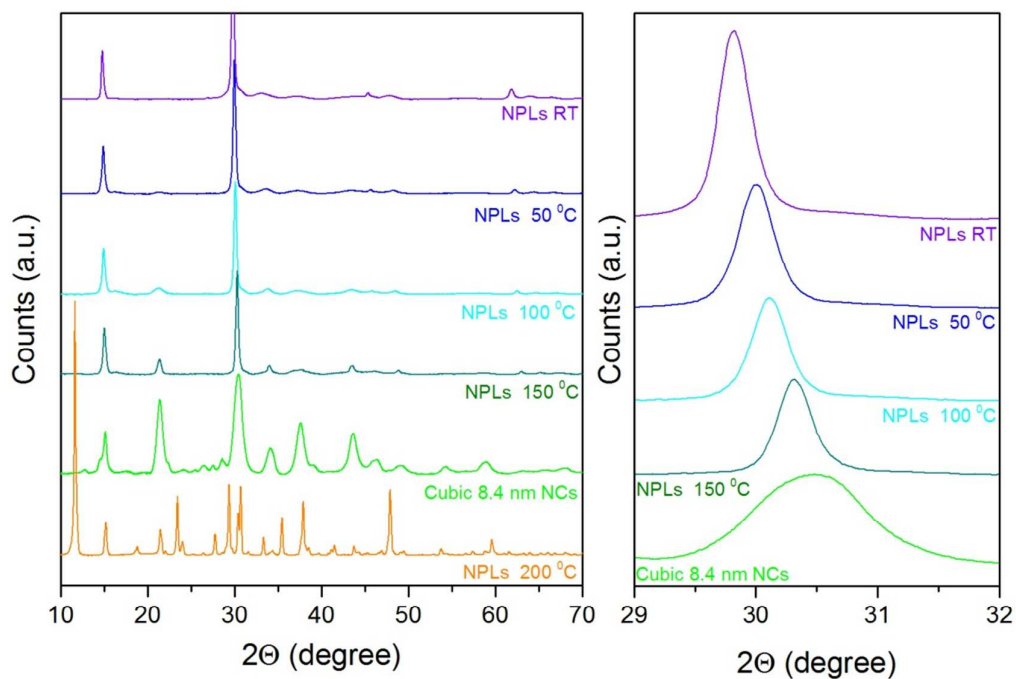


Figure S16. Evolution of XRD patterns of NPLs with annealing temperature. When going from room temperature (RT) up to 150 °C, the diffraction peaks shifted towards higher 2θ angles, indicating a progressive shrinking of the unit cell. Interestingly, the peak positions after the annealing at 150 °C closely matched with the positions observed for cube-shaped CsPbBr_3 NCs (green profile). Annealing to higher temperatures induced a phase change in the material, as shown in the example of the annealing performed at 200 °C (orange pattern).

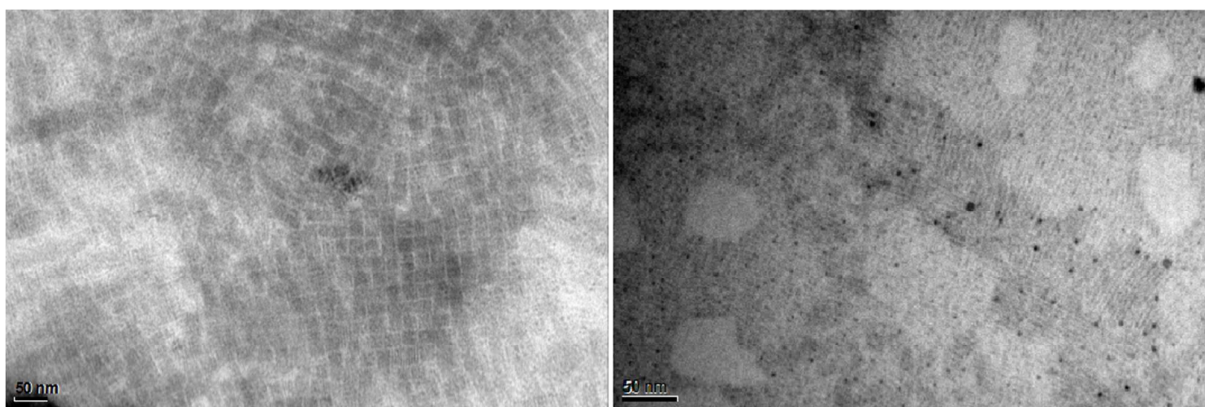


Figure S17. TEM images of the 4 ML CsPbBr_3 NPLs.

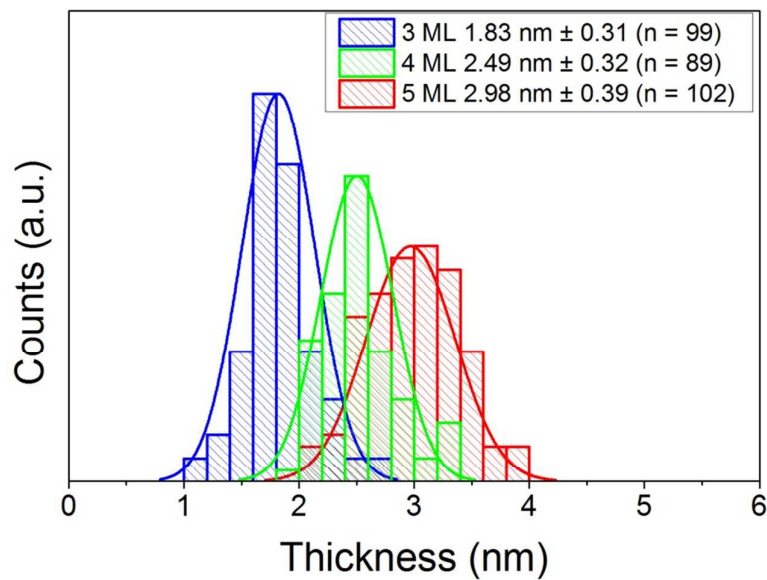


Figure S18. Thickness distribution of the 3 ML, 4 ML and 5 ML NPLs

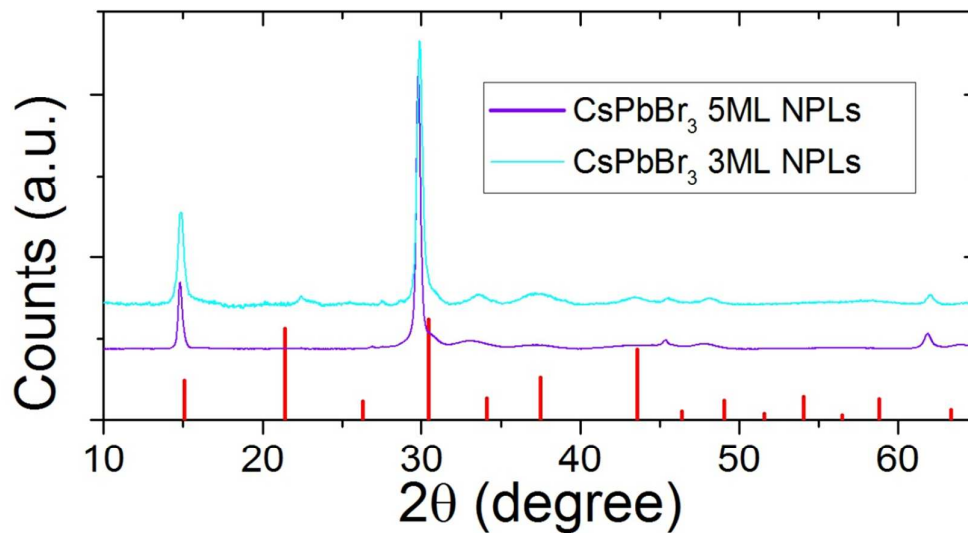


Figure S19. XRD patterns of 3 ML and 5 ML NPLs.

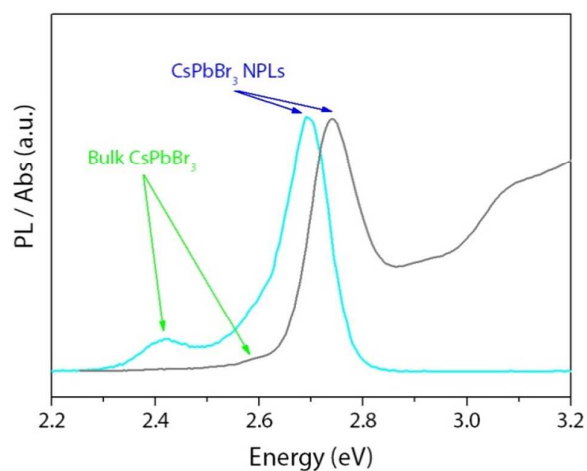


Figure S10. Partial degradation of the 5 ML NPLs, and formation of bulk CsPbBr₃ after 1 week in air.

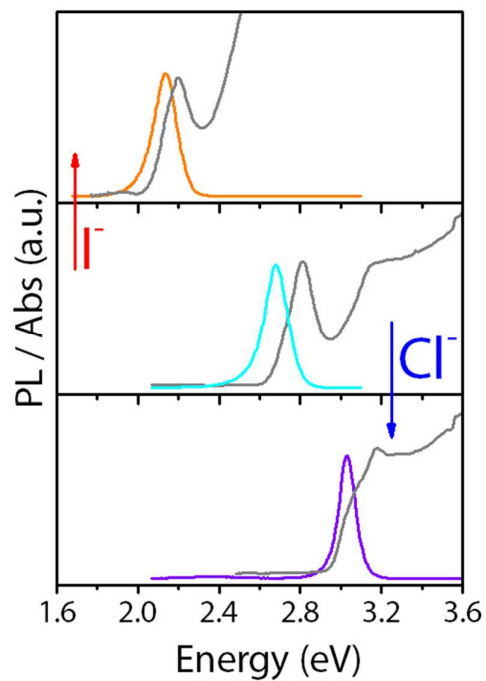


Figure S11. PL and absorption spectra of the exchanged 5 ML NPLs with Cl^- and I^- .

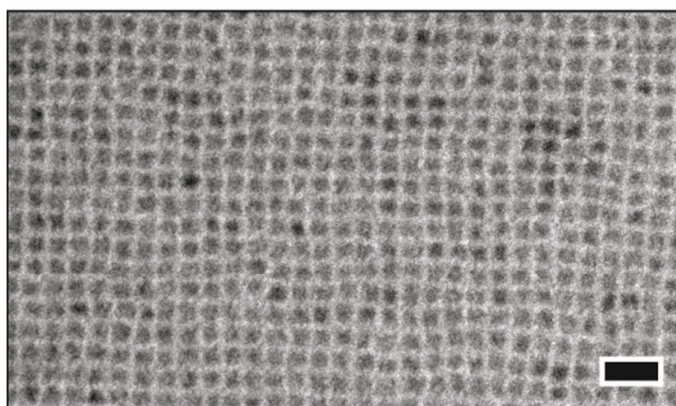


Figure S12. TEM image of cubic CsPbBr_3 NCs. The scale bar corresponds to 50 nm.

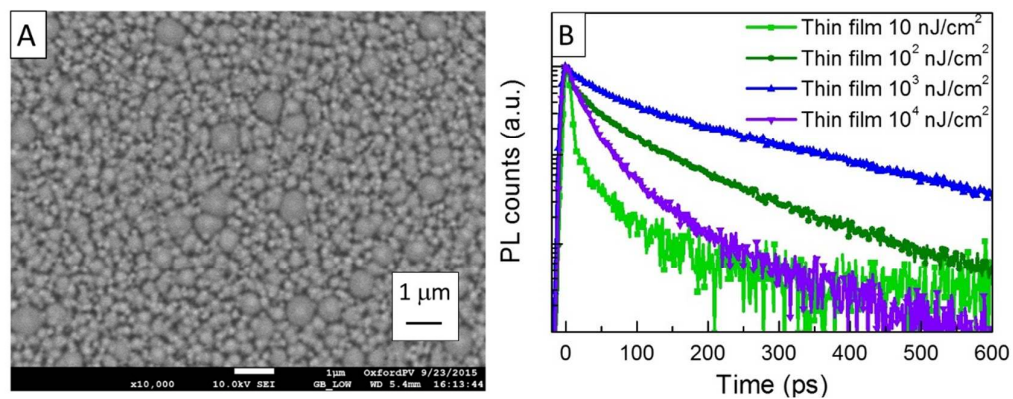


Figure S13. (A) SEM of CsPbBr_3 thin film and (B) intensity dependent PL dynamics.

Note S11: For thin films, the excitation density represents average number of photo-generated carriers in unit volume and can be calculated as:

$$n_p(P_{cw}) = \frac{P_{cw} \cdot \lambda_p}{RR \cdot hc \cdot A_p \cdot d(\lambda_p)}$$

Where P_{cw} is the pump power, λ_p is the pump wavelength, RR is the repetition rate, A_p is the spot size on sample and $d(\lambda_p)$ is the penetration depth, which can be evaluated as $d(\lambda_p) = d/\alpha(\lambda_p)$, where d is the sample thickness and $\alpha(\lambda_p)$ is the absorbance of the sample at the pump wavelength. In the trPL data presented for CsPbBr₃ thin films, the pump wavelength was 480nm, $RR=80$ MHz, the spot size was around 50 μ m, and the sample optical density was around 0.5. The pump powers varied from 50 μ W to 40mW, covering a range of excitation densities from 10^{15} to 10^{18} cm⁻³.

In the case of NC suspension, it is essential to estimate average number of excitations on each NC, rather than the excitations per unit volume. Since the NCs do not show any sign of strong confinement, one can assume that the value of absorptivity (α in cm⁻¹) at 400 nm (corresponding to bulk carrier absorption) is similar to that of the film, which can be evaluated around 10^4 cm⁻¹. One can then estimate the average number of carriers on each nanocrystal as $= \sigma \phi_{photon}$, where $\sigma = \alpha V^3$ (V is the volume of the NC) is the cross-section and ϕ_{photon} is the photon flux. For the range of pump fluences used, we evaluate that the average number of photo-excitations on each NC is much less than one (between 0.01 and 1), a regime that is comparable to the low-excitation regime of the thin films ($> 10^{16}$ cm⁻³), where there are no strong multi-particle interactions.

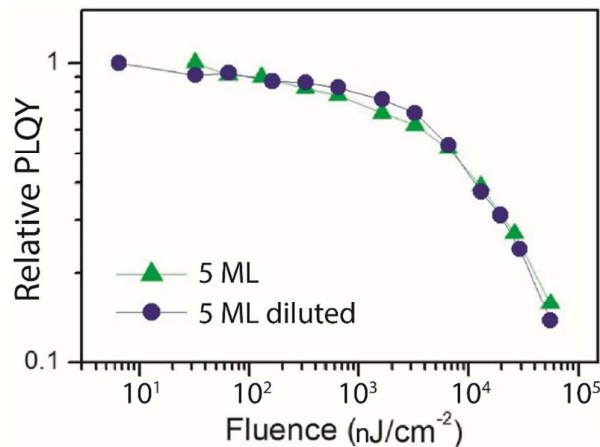


Figure S114. Relative PLQY of one sample of NPLs before and after a tenfold dilution.

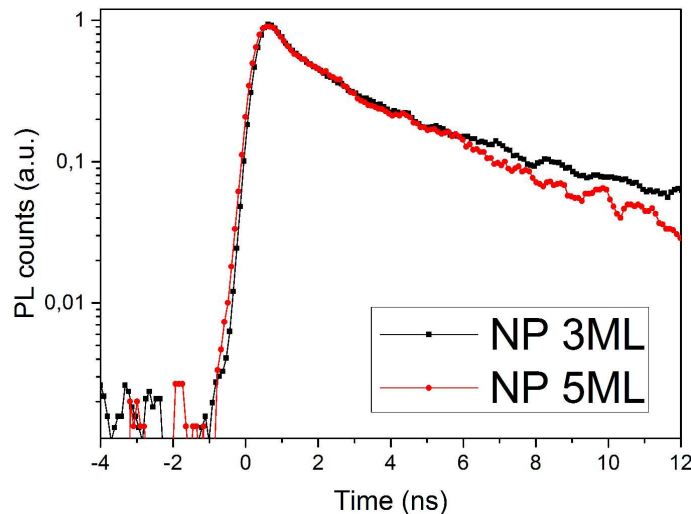


Figure S115. Comparison of PL dynamics for 3ML and 5ML samples. Pump wavelength for both the experiments was at 400 nm with a fluence of about 100 nJ/cm²