Gradient CdSe/CdS Quantum Dots with room temperature biexciton unity quantum yield

Supplementary Information

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EXPERIMENTAL SECTION :

Chemicals: 1-Octadecene (ODE, 90 %, Aldrich), oleylamine (70 %, Fluka), oleic acid (90 %, Aldrich), sodium myristate (99 %, Fluka), cadmium nitrate (99.999 %, Aldrich), cadmium oxide (99.99 %, Aldrich), selenium powder 100 mesh (99.99 %, Aldrich), sulfur (99.998 %, Aldrich), trioctylphosphine (TOP, 90 %, Cytec), trioctylphosphine oxide (TOPO, 90 %, Cytec) and tetradecylphosphonic acid (TDPA, 97 %, PCI synthesis) were used as received.

Precursors preparation

♦ S-ODE: Sulfur stock solution in ODE (octadecene) (S-ODE 0.1 M) was prepared by heating 320 mg of sulfur in 100 mL of degassed ODE at 120 °C until complete dissolution.

♦ Cadmium oleate: 0.5 M $Cd(oleate)_2$ in oleic acid was synthesized by heating 3.2 g of CdO in 50 mL of oleic acid at 160 °C under Ar for 1 h until all the CdO was dissolved. Then this solution was degassed under vacuum at 70 °C for 30 min.

♦ Cadmium myristate was prepared by a procedure published previously[1].

♦ Se-ODE: Selenium stock solution in ODE (Se-ODE 0.1 M) was prepared by first suspending 790 mg of selenium in 10 mL of ODE. This mixture was injected by small portions in 90 mL of degassed ODE at 170 °C, so that it becomes limpid again after each injection, while the temperature was raised progressively to 205°C. The solution was then kept at 205 °C for 30 min.

♦ TOP-Se : Selenium stock solution in TOP (trioctylphosphine) (TOP-Se 1 M) was prepared by dissolving under stirring overnight 7.9g of Se in 100 mL of TOP.

Synthesis of CdSe cores : CdSe nanocrystals were prepared by a procedure adapted by Cassette[28] from Li et al[10]. A mixture of 0.75 mL of $Cd(oleate)_2$ 0.5 M, 1.3 mL of heated TOPO and 5 mL of ODE was degassed under vacuum at 70°C during 30 min and heated under argon flow up to 300°C. A mixture of 4 mL of TOP-Se 1 M and 3 mL of oleylamine was injected and the solution was annealed for 2 min at 280°C. The mixture was cooled down to room temperature and the nanocrystals were washed with ethanol and dispersed in 10 mL of hexane. The nanocrystals obtained with this protocol were around 3 nm diameter.

Formation of a CdS shell on CdSe cores

In a three-neck flask, a mixture of freshly-made CdSe cores (120 nmol), ODE (5 mL) and cadmium myristate (10 mg) was degassed for 30 min at 70 °C under vaccum. The flask was then filled with argon and heated up to 260 °C. At this temperature, oleylamine (2 mL) was injected and the reaction was further stirred for 20 min. 4.5 mL of a mixture of S-ODE (0.1 M, 16.5 mL) and cadmium oleate (0.5 M, 3.5 mL) were added dropwise (2.25 mL/h). After injection, the temperature was raised to 310 °C. Then, the remaining 15.5 mL of the precursors' mixture were added dropwise (5 mL/h). The reaction solution was then annealed for 4h30 at 310°C. The core/shell CdSe/CdS QDs were finally washed with ethanol and redispersed in hexane. The CdSe/CdS QDs were characterized optically and by electronic microscopy. Their final diameter was around 50 nm.

Characterizations: The absorption measurements were realized on a Cary 5E UV-visible spectrometer. The fluorescence and photoluminescence excitation (PLE) spectra were acquired with an Edinburgh Instruments FCS900 spectrometer equipped with a R928-P Hamamatsu photomultiplier. Scanning Transmission electron microscopy pictures were taken using a JEOL 2200 FS in HAADF-STEM configuration. EDX analyses (on Titan Themis) were performed with a probe current of 150 pA and a probe size of 0.12 nm (FWHM), and the half-angle of convergence of the probe was 30 mrad.

For ensemble measurements, optical absorption and photoluminescence spectroscopy are performed using respectively an UV visible spectrometer (Varian Cary 5E) and photoluminescence spectrometer (Edinburgh Instruments F900) with a Xenon lamp excitation at 350nm. The ensemble lifetime measurements are performed using a pulsed laser diode at 377 nm with a repetition rate of 100 kHz. For individual QD emission statistics, the nanocrystals were diluted in a mixture of hexane/octane (9:1), drop-casted on a cover-slit (or sapphire substrate for low temperature measurements) and observed under an epi-fluorescence microscope (Olympus IX71). Single nanocrystals were excited with a pulsed laser diode emitting at 405 nm (LDH-D-C- 405, Picoquant; pulse duration, 70 ps; tunable frequency from 31.25 kHz to 80 MHz). The nanocrystal fluorescence was collected with a ×60, 0.7 NA objective for air and vacuum comparative measurements, or an oil objective x 100, 1.4 NA and sent into a confocal microscope (Microtime 200, Picoquant) with a Hanbury Brown and Twiss setup (SPAD PDM; time resolution, 50 ps). The signal was recorded using a HydraHarp 400 module (Picoquant) in a time-tagged, time-resolved mode.

The number of excitons per QD per pulse was estimated by the following equation:

$$< N >= \frac{P/f}{hc/\lambda} \cdot \frac{\sigma}{A}$$

where P is the average power, f the repetition rate, h Planck's constant, c the speed of light, λ the excitation wavelength, σ the absorption cross-section and A the cross-section of the excitation beam.[1] The absorption cross-section of the QDs were calculated thanks to

$$\sigma \approx 3.43 \times 10^{-16}\ (R + H)^3\ cm^2/nm^3$$

where R and H are the approximate radius of the core and the thickness of the shell in nm[2] (the formula was adapted using a corrective factor to take into account the difference in the excitation wavelength).

In order to allow a better comparison between traces, we decided to show <N> not per pulse, but per µs, *i.e.* <N> corrected by the repetition rate of the laser with the reference taken at 1 MHz.

The "noise" data were acquired using the same setup and the same acquisition parameters than the PL signal of the individual QDs, with the difference that the excited spot was not a QD but a spot in its surrounding (another spot on the glass slide where there was no QD).

SUPPLEMENTARY FIGURES:

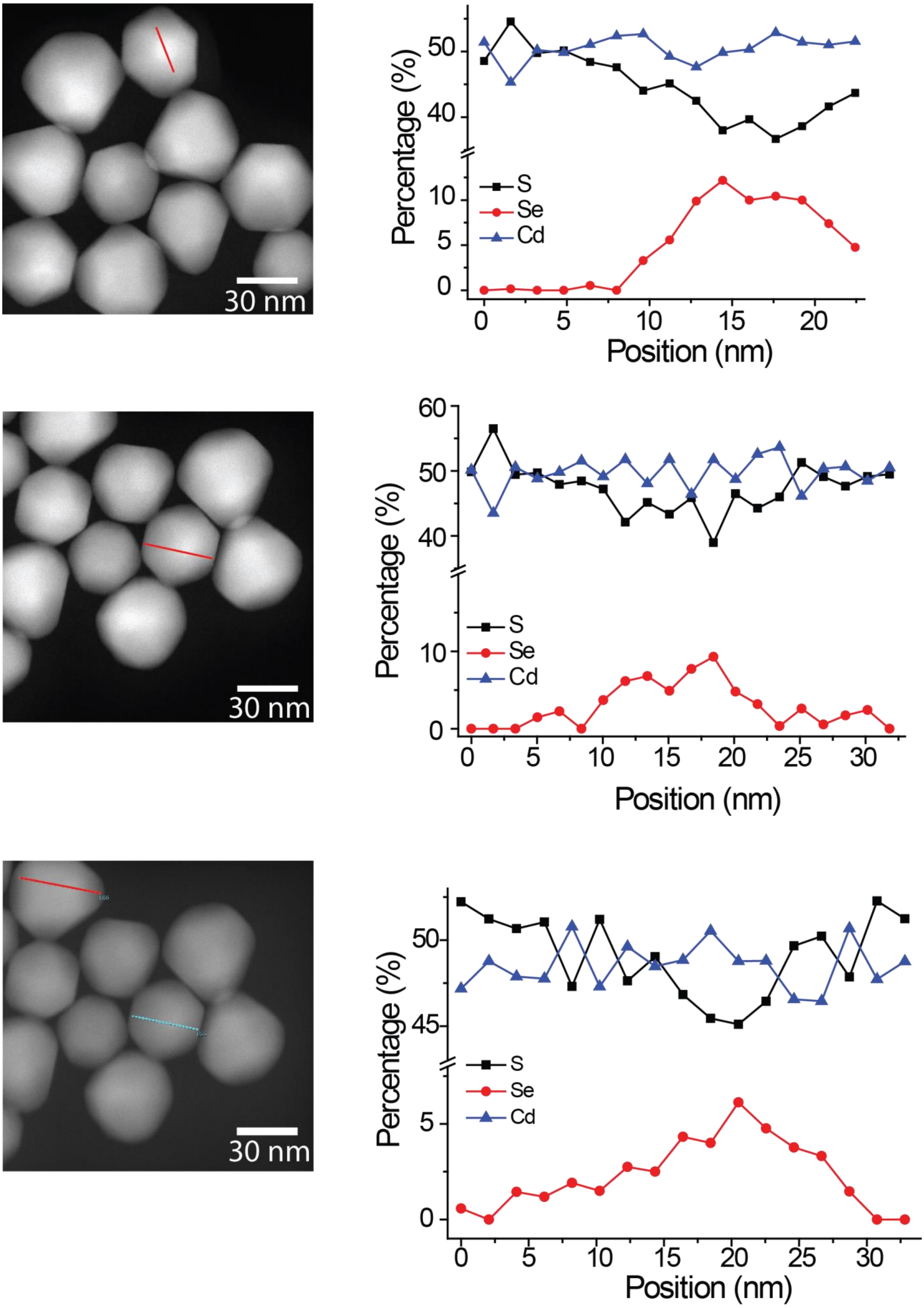

Figure S1: STEM images and EDX profile of different b-QDs

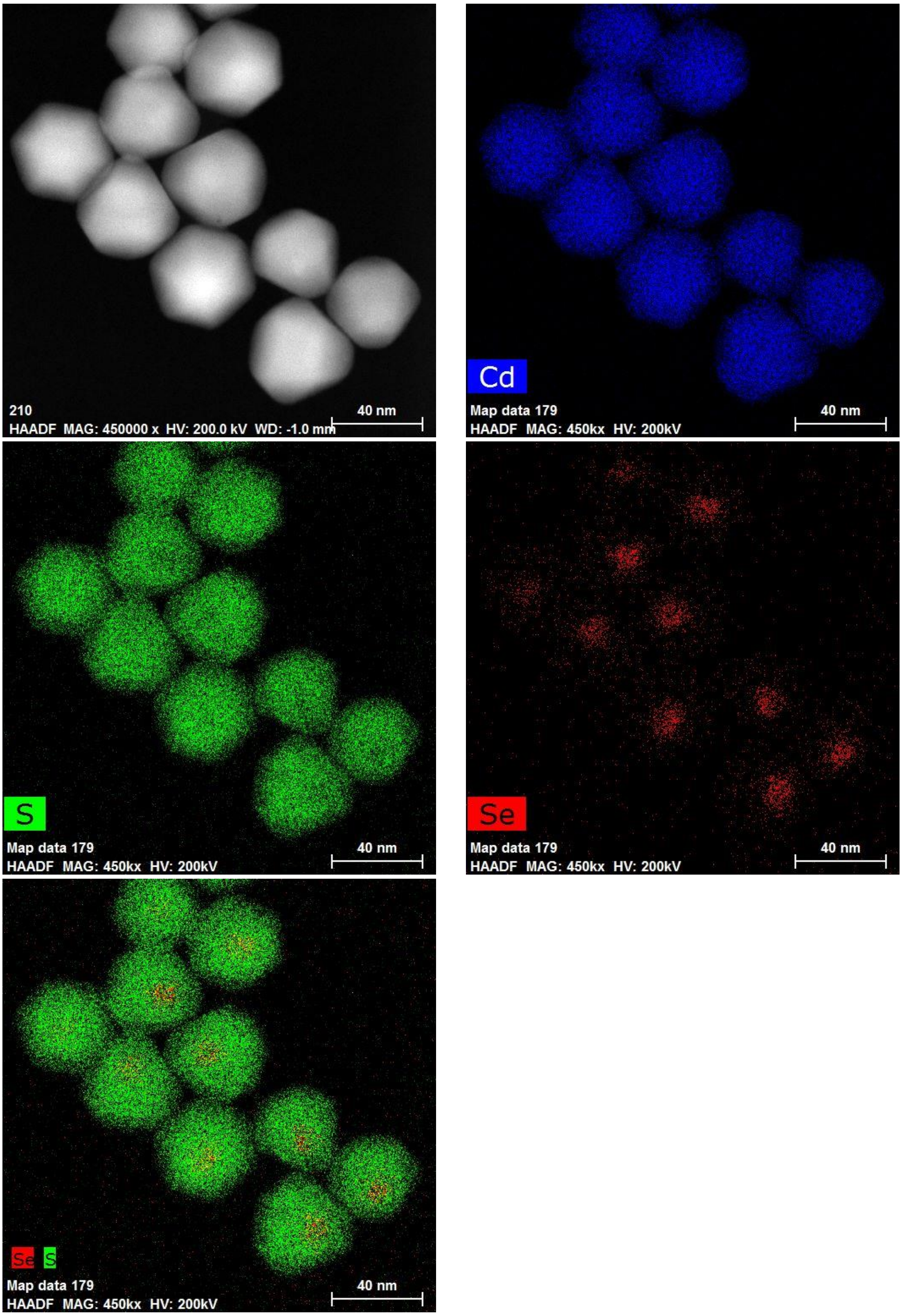

Figure S2: STEM images and EDX maps of Cd, S and Se contents in b-QDs

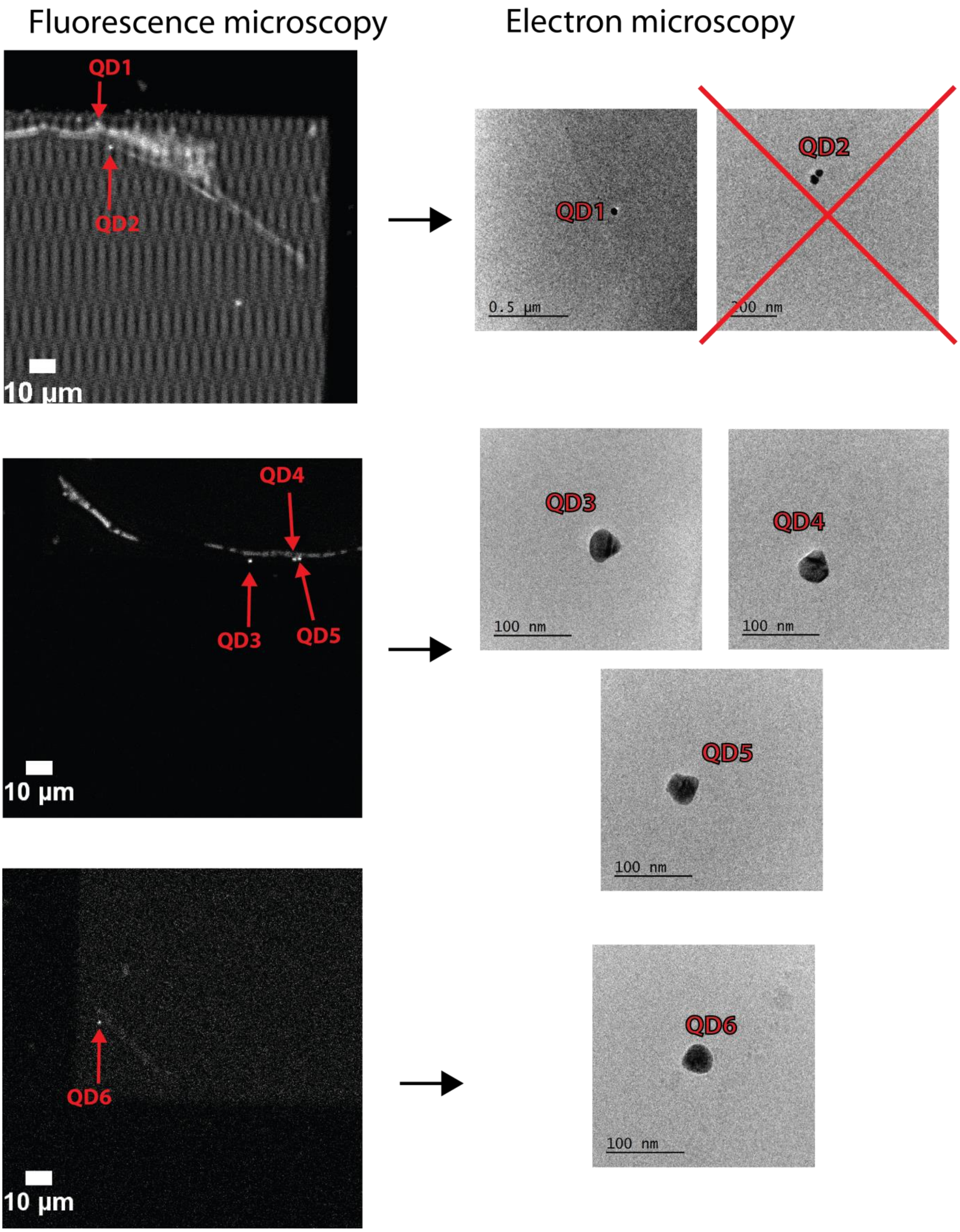

Figure S3: Optical fluorescence microscopy images of b-QDs and TEM images of the same QDs observed on Silicon Nitride grids with 9 Silicon Nitride windows (100x100µm). Only the single dots were kept for analysis, the aggregates were not studied.

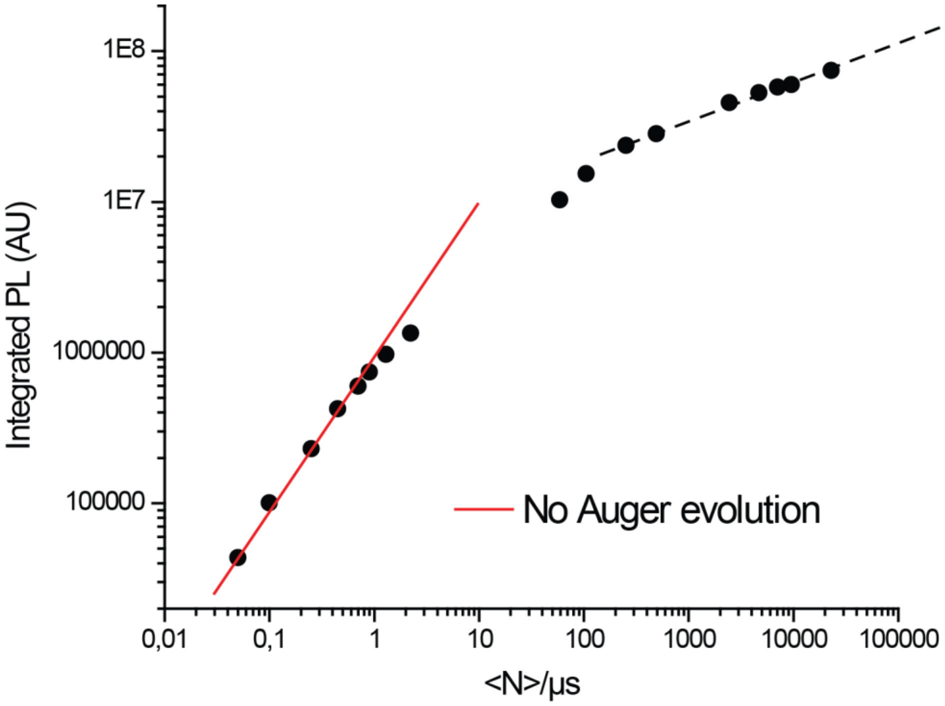

Figure S4: Integrated PL signal as a function of excitation power. The x axis represents here the number of excitons per QD per µs. The emission intensity increases linearly with the excitation intensity up to 1 exciton/µs with a slope consistent with no Auger recombination. When more excitons/µs are created, we still have a linear variation of the emission intensity vs the excitation power, but with a lower slope. This lower slope shows that even at higher fluence, no saturation occurs: although Auger processes happen for >10 excitons/µs, they do not increase in efficiency when the fluence increases (see reference 21 of main text).

References

(1) Fisher, B.; Caruge, J.-M.; Chan, Y.-T.; Halpert, J.; Bawendi, M. G. *Chem. Phys.* **2005**, *318* (1-2), 71–81.

(2) Park, Y.-S.; Malko, a. V.; Vela, J.; Chen, Y.; Ghosh, Y.; García-Santamaría, F.; Hollingsworth, J. a.; Klimov, V. I.; Htoon, H. *Phys. Rev. Lett.* **2011**, *106* (18), 187401.