Supporting information: Purifying single photon emission from giant shell CdSe/CdS quantum dots at room temperature

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Supporting information includes:

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Synthesis of pure-phase wurtzite giant shell quantum dots. Materials: Cadmium oxide (CdO) (99.99%, Aldrich), n-octadecylphosphonic acid (ODPA) (97%, Plasma chem), Tetradecylphosphonic acid (TDPA) (97%, Plasma chem), trioctylphosphine oxide (TOPO) (Merck), trioctylphosphine (TOP) (97%, Strem chemicals), Selenium powder (Se) (99.5%, Aldrich) and solvents: hexane, toluene, methanol (ChemLab Analytical).

Synthesis of TOP-S: A solution of 0.5 M TOP-S is prepared by dissolving 512 mg of S in 16 mL TOP and 16 mL ODE under inert atmosphere at 120 °C for 20 min. Synthesis of Cd(ol)2: 2.568 g CdO (20.06 mmol), 20 mL oleic acid and 20 mL ODE were added to a 50 mL three-necked flask. The mixture is degassed at 120 °C for 30 minutes. Degassing is followed by heating the mixture to 280 °C under inert atmosphere for CdO to dissolve and then left for 10-15 minutes at 210 °C to obtain a colorless solution. Then, the reaction mixture is again degassed for 30 min at 120 °C.

The synthesis of CdSe/CdS core/shell quantum dots with a 3.4 nm CdSe core and 20 monolayers of CdS shell is based on the procedure in Ref. 1. For the shell growth, a 50 mL three neck flask is loaded with 60 nmol of previously synthesized CdSe cores in 10 mL ODE. The solution is degassed for 20 min at 150 °C and subsequently heated up to 300 °C. Meanwhile, in a separate vial, 2 mL 0.5 M TOP-S, 2 mL ODE, 1 mL TOP and 1 mL of oleic acid is mixed. This solution is then injected to the solution comprising CdSe cores in the flask under nitrogen flow at a rate of 0.8 mL per hour by means of a syringe pump. When the injection is completed, it is left to cool to room temperature. 25 mL of isopropanol is added in order the precipitate the quantum dots. The quantum dots are then centrifuged for 10 min at 5000 rpm. The supernatant is discarded and the precipitate redispersed in hexane.

Photoluminescence measurements. We spincoated quantum dot solutions on glass coverslips. We excite quantum dots with a blue pulsed laser (LHD-P-C-405; PicoQuant) in a custom-built scanning confocal microscope. An oil-immersion objective (CFI Apochromat 100×, NA=1.49; Nikon) is used to focus the laser on the sample and to collect generated photoluminescence. The emission can be detected with a spectrometer (Kymera 193i; Andor), an HBT interferometer consisting of two avalanche photo diodes (APD, SPCM-AQRH-14-TR, Excelitas Technologies),

and a time-correlated single photon counting unit (Time Tagger 20; Swabian Instruments). The spectral filtering is performed using a fixed-wavelength long-pass filter at 650 nm (FELH0650, Thorlabs) or a tunable long-pass filter (TLP01-704, Semrock).

The pump rate of 1 MHz limits the maximum output photoluminescence emission rate from a single quantum dot to 1 Mcounts/s. The count rates are corrected for the radiation pattern of a quantum dot and the collection efficiency $\eta \sim 30\%$ of our setup [2], hence representing the absolute quantum yield, or brightness, of the emission (detected counts are about a third of those reported here).

Fitting intensity correlation histograms. We fit intensity correlation histograms using a hybrid formula, which separates the photoluminescence of CdSe core from the classical emission of CdS shell:

$$g_2(\tau) = M \cdot S(\tau, k=0) + S(\tau, k \neq 0) \cdot F(\tau) + \alpha_{sh} \cdot S_{sh}(\tau, k), \tag{S1}$$

where M is the multiexciton contribution (the ratio of central to side peak areas), k is the peak number, $S(\tau, k)$ is a multiexponential function describing the shape of central and side peaks [3], $F(\tau)$ is a modulation function removing the wings of $k \neq 0$ peaks at the position of the central peak [4], α_{sh} and $S_{sh}(\tau, k)$ describe the relative quantum yield and lifetime of shell emission, respectively. We use the modulation function $F(\tau)$ to suppress wings of $k \neq 0$ peaks at the position of $k = 0$ peak (zero correlation time):

$$F(\tau) = 1 - \exp\left(-\frac{|\tau|}{\tau_e}\right),$$

where τ_e is an average decay time of slow emission states. This correction is necessary as we operate in the fast excitation regime ($T_{rep}/\tau_{X_0} = 0.7 - 4$, see statistics for τ_{X_0} in Fig. S3a).

The first part of Eq.S1 describes the core emission. We typically observe highly multiexponential decay dynamics at saturating pump fluency, which is due to contributions of neutral, bi-, and charged excitons. The multiexponential dynamics is reflected in the shape of the central and side peaks:

$$S(\tau, k) = \sum_j \sum_k A_j \exp\left(-\frac{|\tau \pm k \cdot T_{rep}|}{\tau_j}\right),$$

where A_j and τ_j are amplitudes and lifetimes of contributing states [5] (in case of QD16, $\tau_{X_0} = 354 \pm 24$ n for the neutral exciton, $\tau_{X_-} = 145 \pm 18$ ns for the charged exciton, and $\tau_{XX} = 56 \pm 15$ ns for the biexciton).

The final term in Eq.S1 describes the shell emission. The fast sub-nanosecond classical emission is contributing equally to all peaks in the intensity correlation histogram ($g_2(0) = 1$) and is modeled as an exponential decay function:

$$S_c(\tau, k) = \sum_k A_c \exp\left(-\frac{|\tau \pm k \cdot T_{rep}|}{\tau_c}\right),$$

where A_c and τ_c are amplitude and lifetime of CdSe shell emission ($\tau_c \sim 0.5 - 2.5$ ns).

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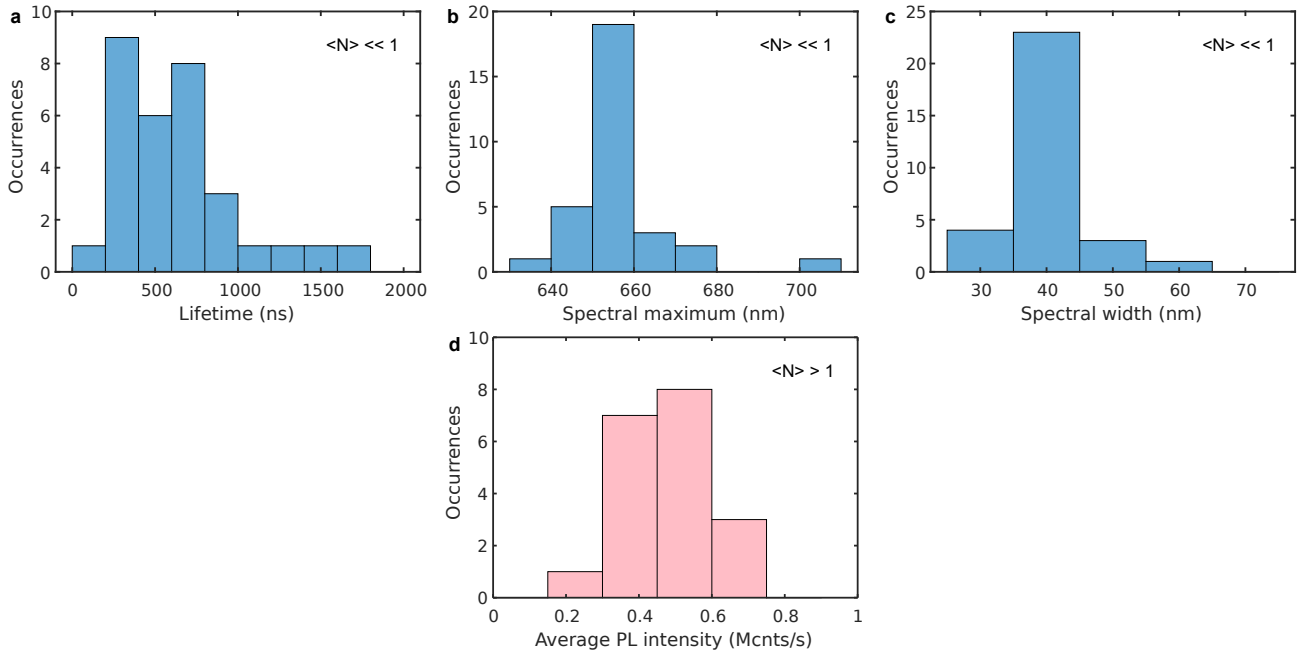

FIG. S1: Emission statistics of 32 individual quantum dots. **a** Neutral exciton X_0 lifetime. **b** Position of the maximum of photoluminescence spectrum at low pump fluency. **c** Full-width-at-half-maximum (FWHM) of spectrum at low pump fluency. **d** Photoluminescence intensity statistics of quantum dots at saturation. Quantum dots were excited at 1 MHz repetition rate. PL intensity was averaged over 2 minutes.

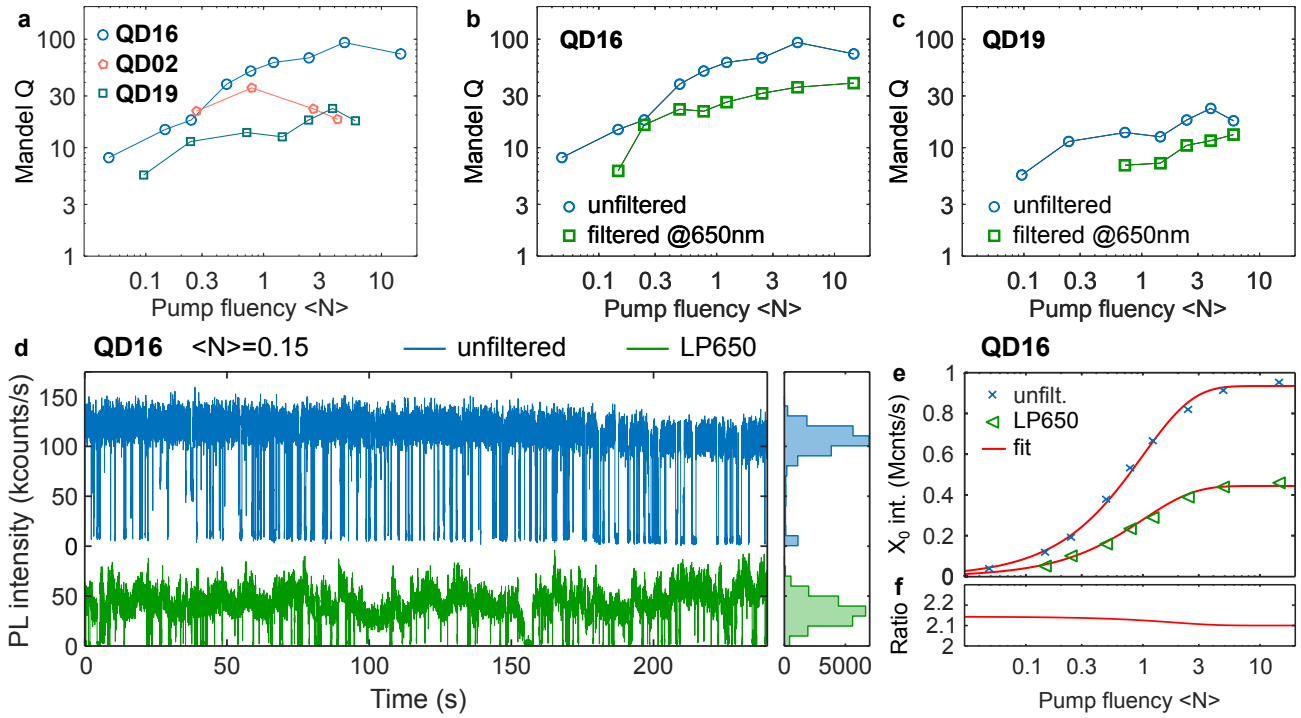

FIG. S2: Intensity stability of quantum dot emission. **a** Mandel Q factor of unfiltered quantum dot emission is calculated for a wide range of pump fluency $\langle N \rangle$. **b,c** Filtered emission with long-pass filter at 650 nm (green) is characterized by improved Mandel Q factor. **d** Unfiltered (blue) and filtered with long-pass filter at 650 nm (green) intensity time traces of QD16 and corresponding occurrences histograms. **e** Intensity saturation dynamics of unfiltered (blue crosses) and filtered with long-pass filter at 650 nm (green triangles) signals. The corresponding panel **f** shows that the ratio of unfiltered-to-filtered intensity is constant and is preserved across the used range of pump fluency.

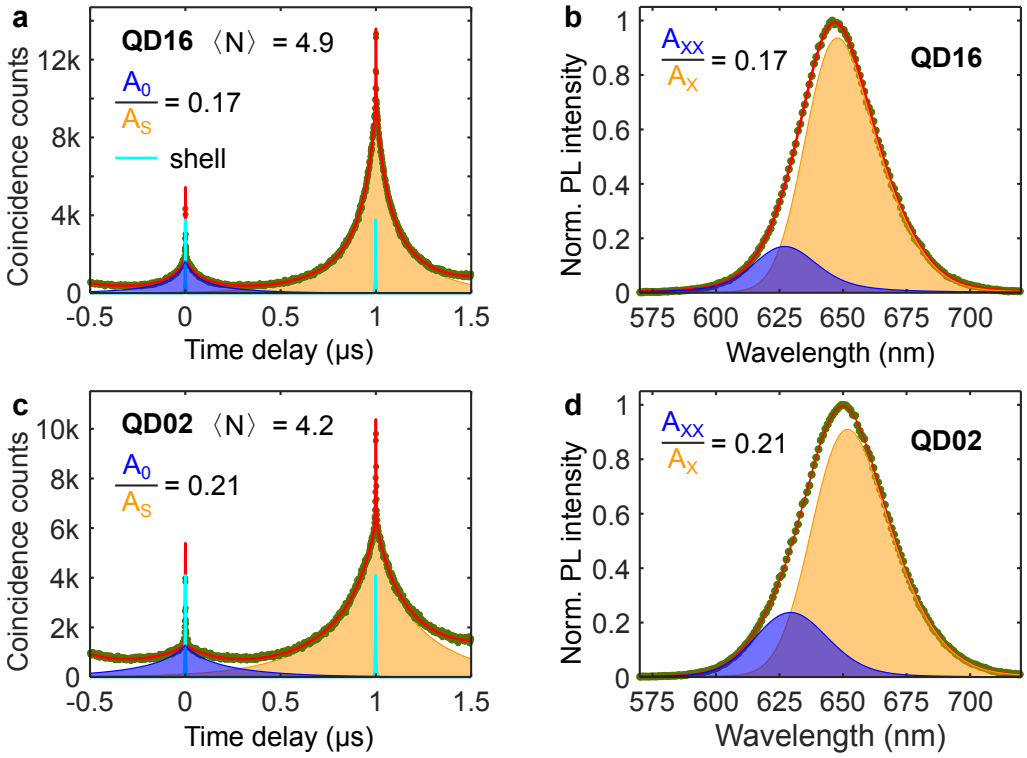

FIG. S3: Photoluminescence spectrum of QD16 and QD02 at high pump fluency $\langle N \rangle$. a,c The ratio of single to multiexciton emission A_0/A_S was extracted from the fit of a corresponding antibunching histogram, where A_0 and A_S are areas of the central (purple) and side (orange) peaks, respectively, excluding the shell state contribution (cyan). **b** The ratio of A_0 to A_S was used as a feeding parameter for the corresponding spectrum fit. The fit results in the position of exciton (orange) and biexciton (purple) emission maxima at 646 nm and 626 nm for QD16, and 652 nm and 629 nm for QD02, respectively.

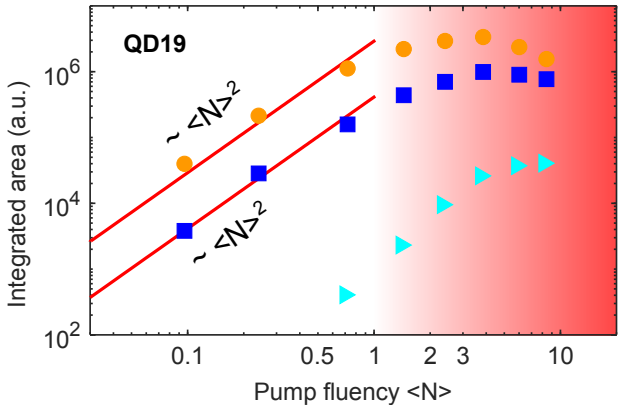

FIG. S4: The area of central and side peak grow quadratically with the pump fluency. Example of QD19, the analysis was done as in Fig. 2c. Orange circles and blue squares represent integrated areas of the central and side peaks in the intensity correlation histograms. The cyan triangles represent the contribution of the fast-emitting shell states. The red-shaded area highlights the saturation regime.

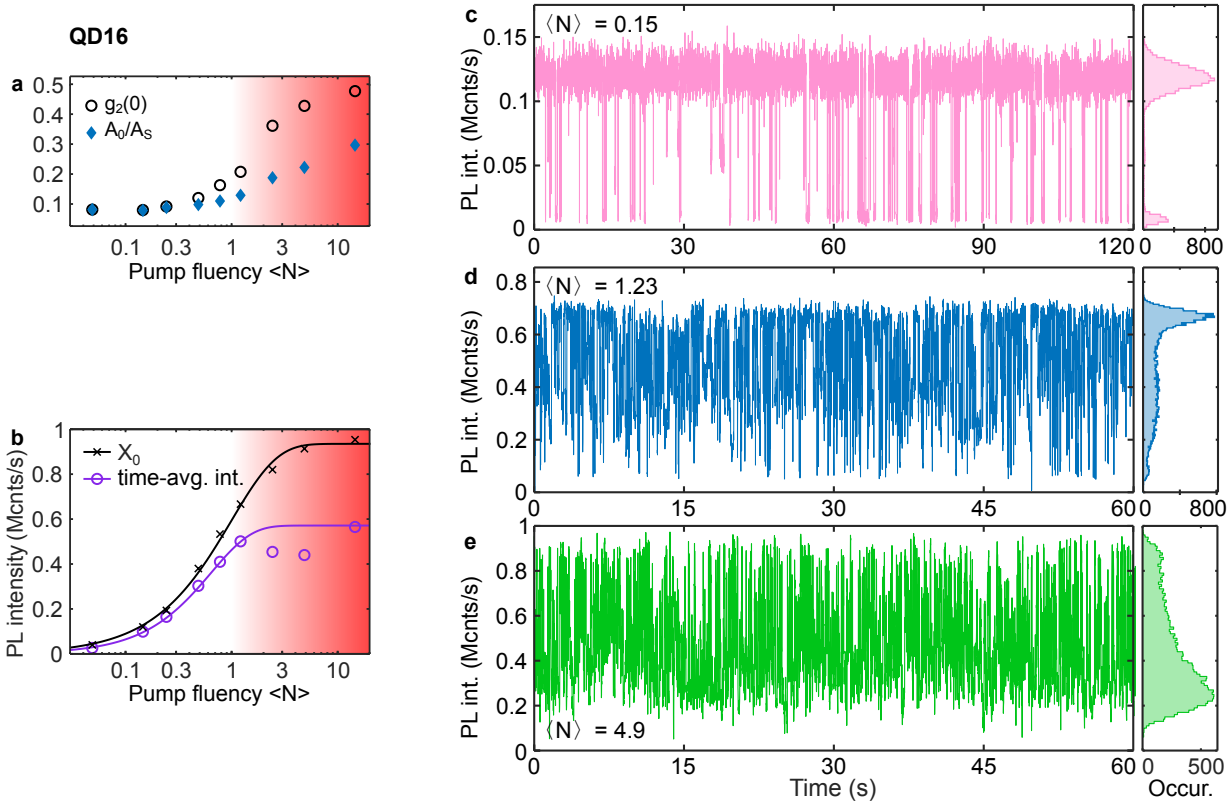

FIG. S5: Emission of QD16 at increasing pump fluency $\langle N \rangle$**.** **a** Degradation of single photon purity (circles) and increase of multiexciton contribution (diamonds) at increasing pump fluency. The difference between the two data sets is in the contribution of short-lived shell states. **b** Increase of time-averaged photoluminescence intensity (circles) and neutral exciton intensity (crosses) at increasing pump fluency. **c,d,e** Intensity time traces with corresponding occurrences histograms measured below, around, and above saturation (10 ms time bin). The intensity of the neutral exciton shown in panel **b** is taken as the average of the distribution with highest counts, see for instance the peaks in the insets of panel **c** and **d**.)

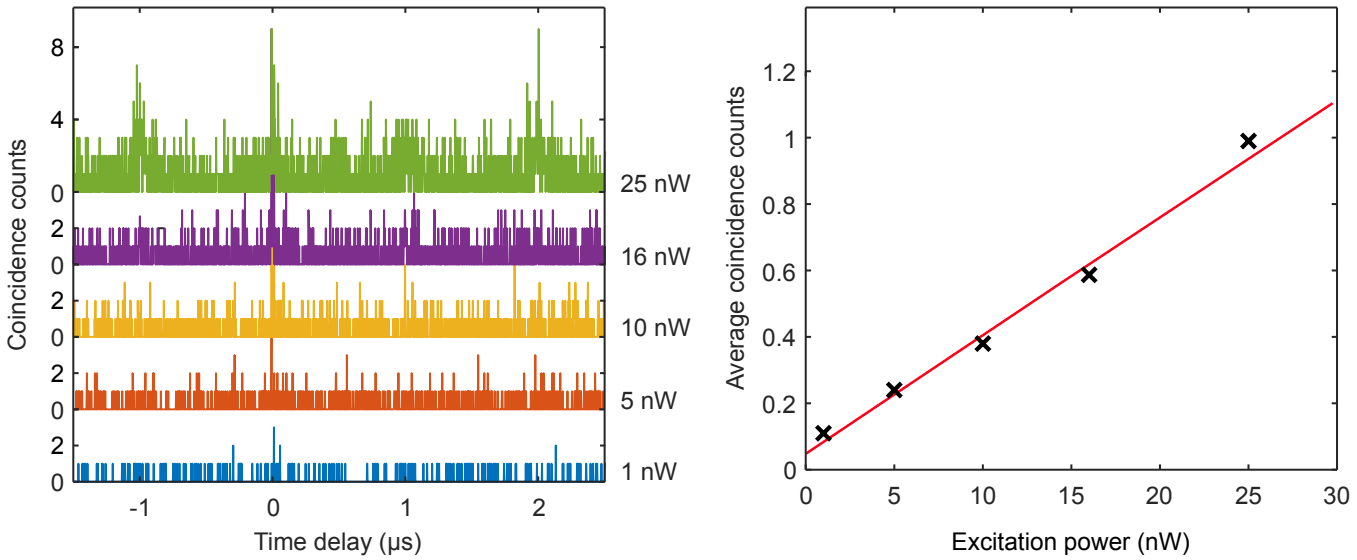

FIG. S6: Background emission at increasing excitation power. **a** Intensity correlation histograms were measured in a blank spot of a glass coverslip. The histograms are shifted by 4 counts along the vertical axis for clarity. The excitation powers below 16 nW correspond to the pump fluency of $\langle N \rangle < 1$ depending on a quantum dot. The background coincidence counts comes from dark counts and other stray light, glass substrate emission, accidental excitation and emission of quantum dots out of the focal spot. **b** Average coincidence counts grow linearly with the excitation power (red).

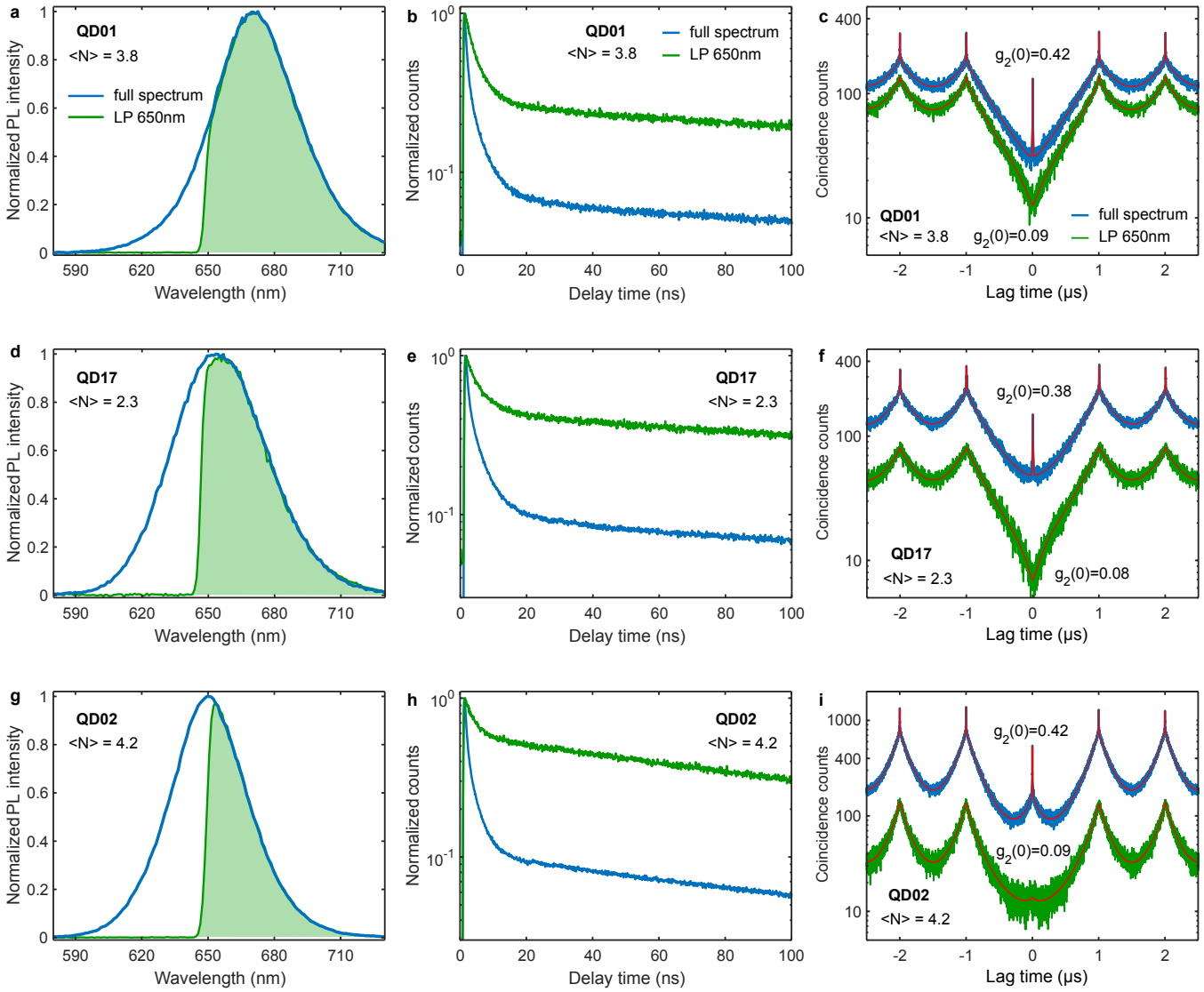

FIG. S7: More examples of filtering with a long-pass filter at 650 nm. a,d,g Full spectra (blue) and corresponding filtered part at 650 nm (green) of QD01, QD17, and QD02. **b,e,h** Lifetime histograms measured from the full spectra (blue) and corresponding filtered part (green). **c,f,i** Anti-bunching histograms measured from the full spectra (blue) and corresponding filtered part (green).

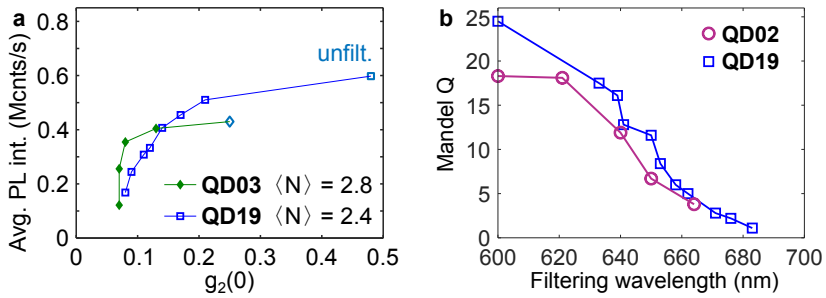

FIG. S8: Scanning through spectrum with a tunable long-pass filter. a Degree of antibunching $g_2(0)$ was acquired while cutting blue part of photoluminescence spectrum of QD03 and QD19. **b** A reduction of the intensity fluctuations (as characterized by the Mandel Q factor) when filtering more and more of the emission attributed to spurious states that are well spectrally isolated from the exciton emission.