Electronic Supporting Information for

Evidence of Carrier Diffusion between Emission States in CdSe/ZnS Core-Shell Quantum Dots: A Comprehensive Investigation Combining Fluorescence Lifetime Correlation Spectroscopy (FLCS) and Single Dot Photoluminescence Studies

Debopam Acharjee,[a] Mrinal Kanti Panda,[a] Asit Baran Mahato,[a] Ayendrila Das,[a] and Subhadip Ghosh[a,b]*

[a]*School of Chemical Sciences, National Institute of Science Education and Research (NISER), An OCC of Homi Bhabha National Institute (HBNI), Khurda, Odisha 752050, India.*

[b]*Center for Interdisciplinary Sciences (CIS), National Institute of Science Education and Research (NISER), An OCC of Homi Bhabha National Institute (HBNI), Khurda, Odisha 752050, India.*

*Email: sghosh@niser.ac.in

Contents list:

1. Chemicals Used

CdSe/ZnS core-shell quantum dots (QDs) (product number 748056), octadecene (ODE, technical grade, ~90%), toluene (~99.9%), poly(methyl methacrylate) (PMMA) were purchased from Merck.

2. Instruments Used

2.1. Absorption and Emission Spectra Measurements

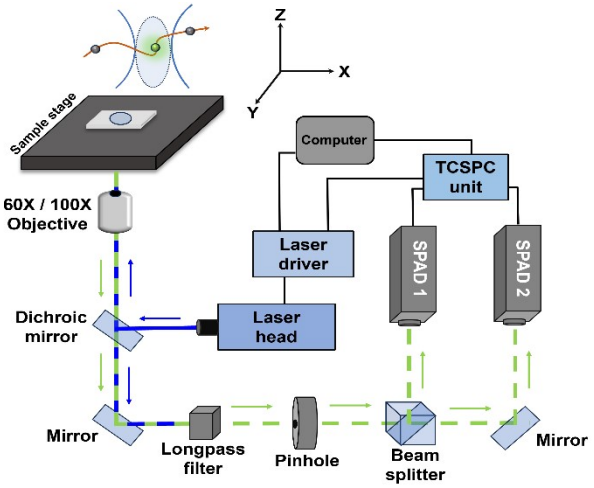
Steady state absorption and PL spectra were recorded using a double beam spectrophotometer (model number V-730) from Jasco and a spectrofluorometer (model number FS5) from Edinburgh Instrument.

The absorption and photoluminescence (PL) spectra were recorded after diluting the QD sample to micromolar (μM) concentration in octadecene (ODE) and transferring it to a one cm path length Hellma quartz cuvette for measurements. The spectrophotometer scanned a broad wavelength range from 425 to 650 nm, utilizing a spectral bandwidth of 1 nm to ensure high spectral resolution of the absorption spectrum.

PL spectra were recorded by collecting emission at a 90-degree angle relative to the excitation beam. The samples were excited at 450 nm using a 150 W xenon arc lamp (CW Ozone-free) and an excitation grating. Emission intensity was measured over a broad wavelength range from 450 to 650 nm, with a wavelength accuracy of ±0.5 nm.

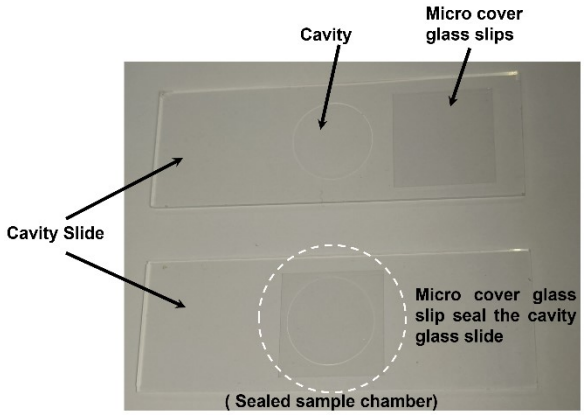
2.2. FCS, FLCS, Single Particle Blinking and Anti-bunching Studies

FCS, FLCS, anti-bunching, single particle PL intensity and lifetime trajectories were recorded in a confocal microscope (model MT 200) purchased from PicoQuant.



Scheme 1. Schematic of confocal microscope utilized for FCS, FLCS, anti-bunching and single dot blinking studies.

In our FCS/FLCS study, we used a home-made sample chamber (shown below) to avoid spreading of liquid sample (QDs dispersed in ODE) over the surface of glass slide during the measurement.



First we took a cavity slide, where a few drops of QD solution were placed. Consequently, a coverslip was placed over cavity filled sample. No glue or sealing additive was used to stick coverslip with cavity slide, and also we ensured no air bubble formation inside the chamber. Next, this loaded chamber was flipped and placed over a 60x water objective of the microscope for FCS/FLCS studies. We used a pulse diode laser, emitting at ~375 nm (irf ~140 ps, repetition rate ~10 MHz) for FLCS excitation at different powers (~0.02 kW/cm² to ~0.2 kW/cm²). A ~430 nm long pass filter was placed in the emission path to block the excitation laser from reaching to the detector. The fluorescence signal from QDs was split and then directed to two SPADs using a 50/50 beam splitter. FCS and FLCS analyses were performed by SymPhoTime 64 software provided by PicoQuant. All FCS and FLCS studies were repeated 3 times with freshly prepared sample. FCS and FLCS parameters reported throughout the manuscript and Table 1 are the statistical means of all three measurements. Since our FLCS and FLID analyses utilized the lifetime information of the emitted photons, we enabled time-tagged timer resolved fluorescence (TTTR) mode during data collection. SymPho Time 64 software, purchased from PicoQuant enabled construction and fitting of FCS and FLCS curves. Our MT-200 confocal microscope was integrated with TCSPC that allowed us to access the lifetime information of the detected photons from individual QDs and that can be utilized in constructing PL lifetime trajectory, FLID plot and FLCS curves.

Separate ACFs can be obtained for individual emitting centres in FLCS utilizing their excited state lifetimes. Success of FLCS relies on the assumption of different emission canters having different excited state lifetime, which is, however, be the case in most of the studies. The core of FLCS lies in statistical separation of PL contributions of similar excited state

lifetimes at a single photon level. More details on fundamental approach, instrumental set-up, data collection and construction of correlation curves of FLCS can be found elsewhere.[1-2]

For the single particle blinking and anti-bunching studies, a ~pM QD solution (dispersed in 1% PMMA in toluene) was spin-coated on a coverslip to prepare surface-immobilized QDs, embedded in a PMMA matrix and mutually separated by a distance longer than the spatial resolution of the microscope. As mentioned earlier, we enabled time-tagged time-resolved mode while recording PL trajectories to register the lifetime data simultaneously. Experimental set-up and the configurations in single particle blinking study was kept exactly same as FLCS, except, here 100x oil immersion objective and 422 nm pulse diode laser with much lower excitation powers (2 W/cm^2- 20 W/cm^2) were used.

The Hanbury Brown and Twiss (HBT) scheme was considered in our anti-bunching study involving two detectors and right combination of filter sets as discussed elsewhere.[3-6] All experiments were performed at room temperature under ambient environment.

2.3. Powder-XRD Study

The Bruker Davinci D8 advanced diffractometer was utilized for XRD measurements, with CuKα radiation at a wavelength of $\lambda = 1.5418$ Å.

2.4. DLS Study

DLS measurement was performed using Malvern Zetasizer Nano ZS instrument. The QDs were dispersed in ODE and loaded in quartz cuvette for the measurement. Three consecutive measurements were taken for better precision.

2.5. FT-IR Study

FT-IR measurement was performed using Perkin-Elmer RXI FT-IR spectrophotometer.

2.6. Transmission Electron Microscopy (TEM)

TEM measurements were performed in JEM-2100 (200 kV) from JEOL.

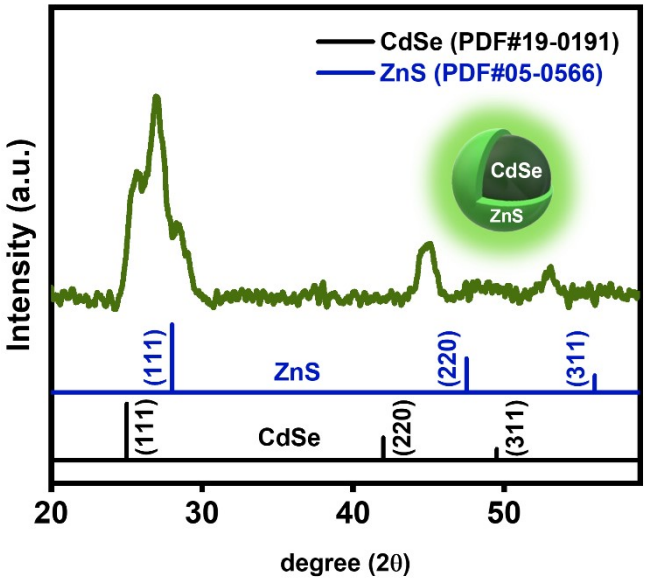


Fig. S1 The XRD pattern of CdSe/ZnS QDs closely aligns with the reported patterns.[7-9] Peaks near 2θ ~25 degrees correspond to the (111) plane. Comparing reference peaks and reported literature suggests a cubic zinc blende crystal structure.[9] The absence of peaks from a separate ZnS phase indicates that ZnS has formed a coating around the CdSe core.

+

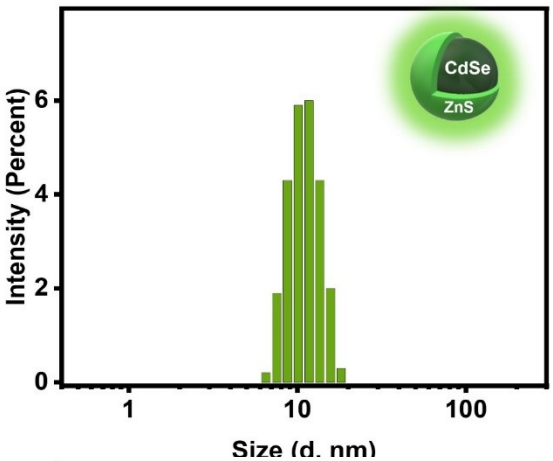


Fig. S2 Dynamic light scattering (DLS) data showing the distribution of QD size.

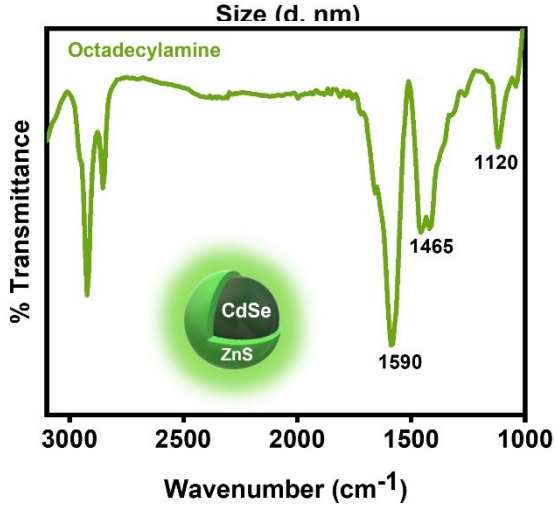


Fig. S3 Fourier transform infrared (FTIR) spectroscopy data show characteristic peaks of different functional groups of the capping agent (octadecylamine).

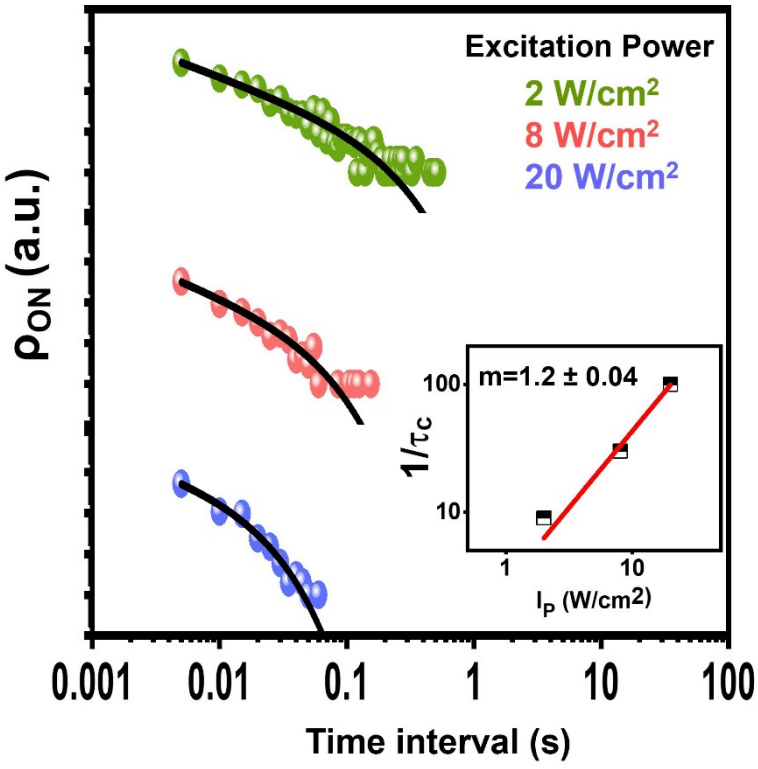


Fig. S4 Probability distributions of ON-time durations (ρ_{on}) at different pump intensities. The inset shows a plot of $1/\tau_C$ at various pump intensities (symbols) alongside a fit to I_p^m (solid line).

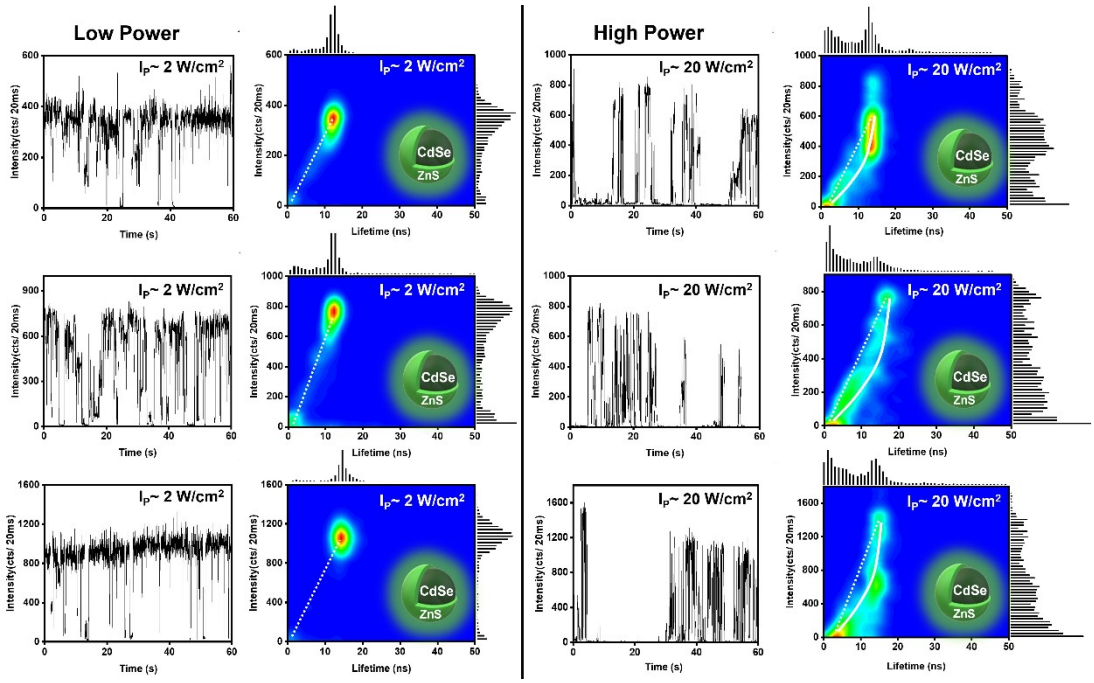


Fig. S5 PL intensity trajectories along with FLID maps for three randomly chosen QDs at low excitation power (left columns). The right two columns depict the same plots from the same three particles at high power.

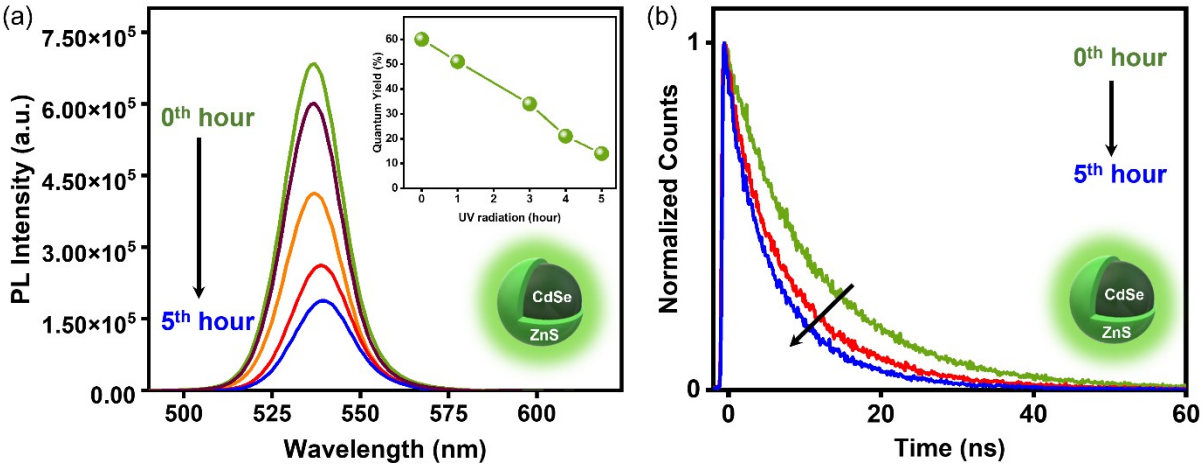


Fig. S6 (a) PL spectra of QDs dispersed in hexane as a function of UV irradiation time. The QDs in colloidal solution were exposed to UV light for an extended period (~5 hours), resulting in a reduction of the photoluminescence quantum yield (PLQY) to approximately 14%. The inset presents PLQY as a function of UV irradiation time. (b) Time-resolved PL decay curves of QDs dispersed in hexane, recorded after various durations of UV exposure.

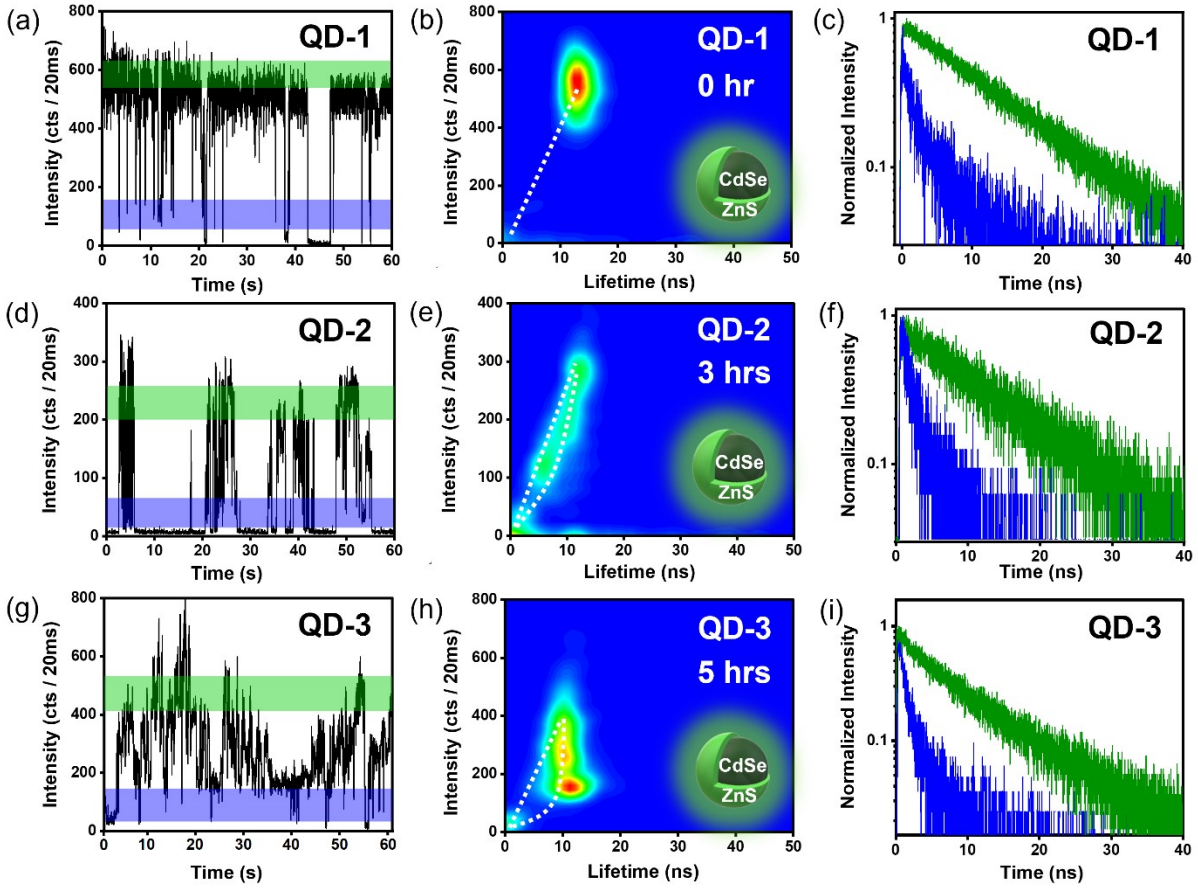


Fig. S7 PL intensity trajectories (a, d, g), corresponding FLIDs (b, e, h), and time-resolved PLs of ON (green) and OFF states (blue) (c, f, i) of three different QDs (QD1-QD3), exposed to UV-light for different times; 0 hr (a-c, QD1), 3 hrs (d-f, QD2) and 5 hrs (g-i, QD3). In all the cases, QDs were excited with low power (~2 W/cm^2). FLID pattern changes drastically with UV-irradiation time (b, e, h). FLID of UV unexposed QD demonstrates NBC blinking feature only (linear diagonal trajectory) (b), whereas FLID of 5 hrs UV exposed QD additionally exhibits trion blinking (curved trajectory) and sometimes HC blinking too (vertical broadening) (h). FLID of 3 hrs UV exposed QD demonstrates NBC and trion blinking (e). Fig. S8-S9 demonstrates the same data repeated on other QDs.

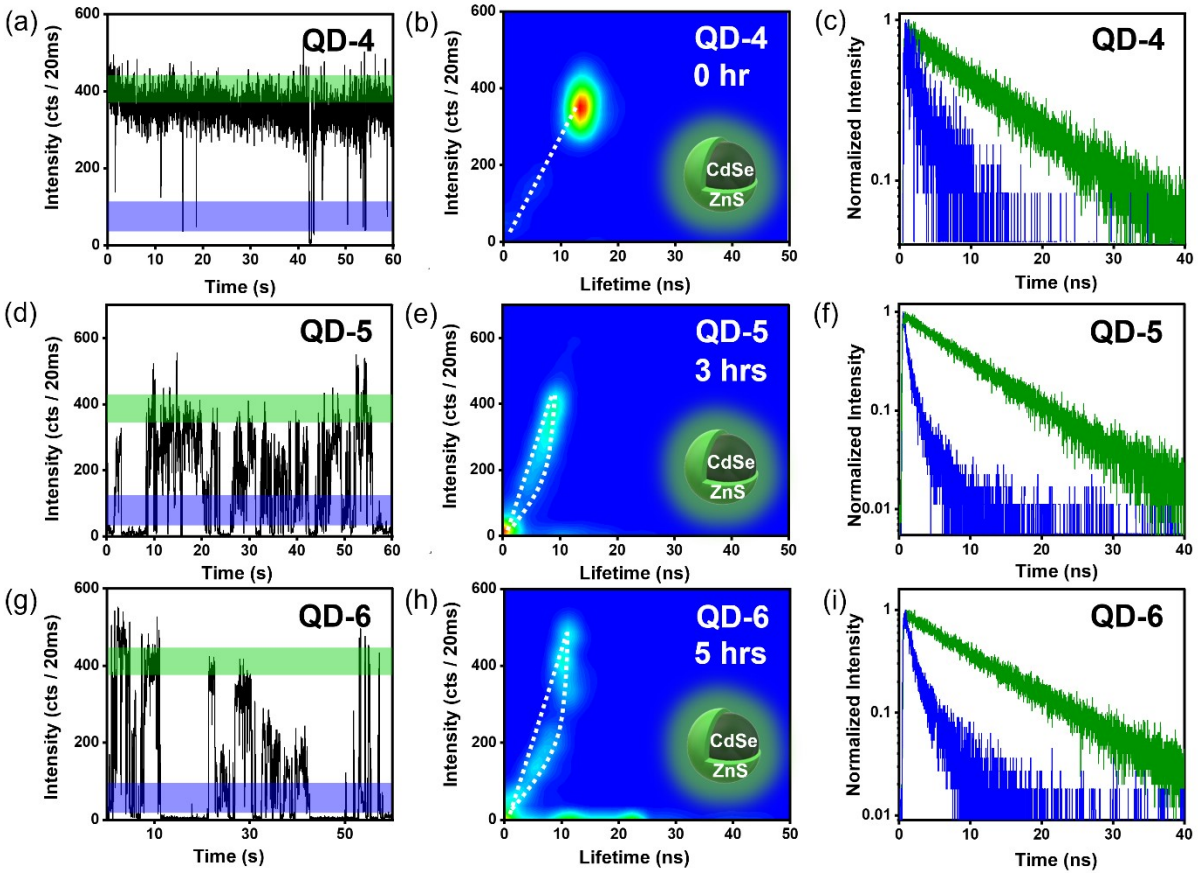


Fig. S8 The same data as Fig. S7, but here repeated on other QDs. PL intensity trajectories (a, d, g), corresponding FLIDs (b, e, h), and time-resolved PLs of ON (green) and OFF states (blue) (c, f, i) of three different QDs (QD4-QD6), exposed to UV-light for different times; 0 hr (a-c, QD4), 3 hrs (d-f, QD5) and 5 hrs (g-i, QD6). In all the cases, QDs were excited with low power (~2 W/cm^2). FLID pattern changes drastically with UV-irradiation time (b, e, h). FLID of UV unexposed QD demonstrates NBC blinking feature only (linear diagonal trajectory) (b), whereas FLID of 5 hrs UV exposed QD additionally exhibits trion blinking (curved trajectory) and sometimes HC blinking too (vertical broadening) (h). FLID of 3 hrs UV exposed QD demonstrates NBC and trion blinking (e). Fig. S9 demonstrates the same data repeated on other QDs.

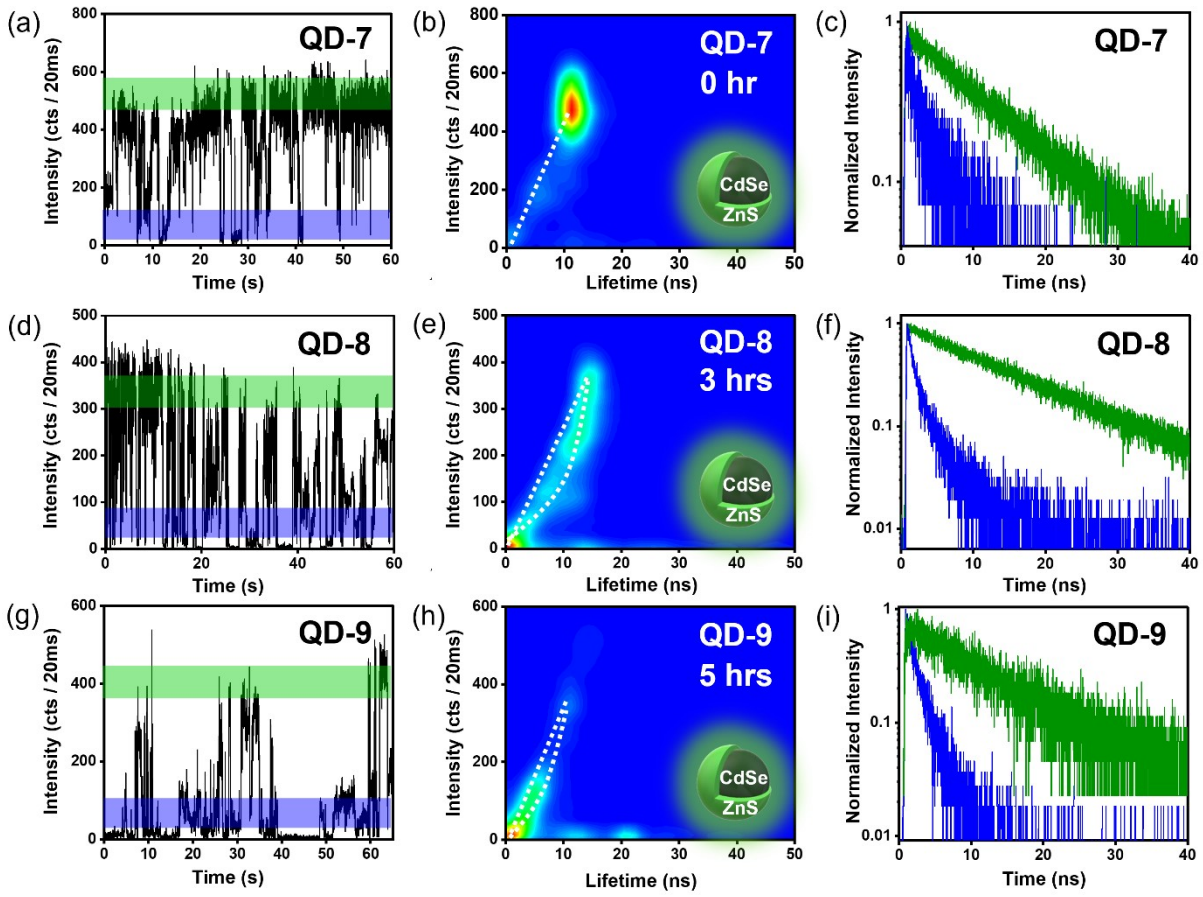


Fig. S9 The same data as Fig. S7-S8, but here repeated on other QDs. PL intensity trajectories (a, d, g), corresponding FLIDs (b, e, h), and time-resolved PLs of ON (green) and OFF states (blue) (c, f, i) of three different QDs (QD7-QD9), exposed to UV-light for different times; 0 hr (a-c, QD7), 3 hrs (d-f, QD8) and 5 hrs (g-i, QD9). In all the cases, QDs were excited with low power (~2 W/cm^2). FLID pattern changes drastically with UV-irradiation time (b, e, h). FLID of UV unexposed QD demonstrates NBC blinking feature only (linear diagonal trajectory) (b), whereas FLID of 5 hrs UV exposed QD additionally exhibits trion blinking (curved trajectory) and sometimes HC blinking too (vertical broadening) (h). FLID of 3 hrs UV exposed QD demonstrates NBC and trion blinking (e).

References

1. PicoQuant GmbH. Fluorescence Lifetime Correlation Spectroscopy (FLCS). Picoquant.com. https://www.picoquant.com/applications/category/life-science/fluorescence-lifetime-correlation-spectroscopy-flcs, (accessed 2024-07-26).
2. P. Kapusta and M. Wahl, PicoQuant, FLCS – fluorescence lifetime correlation spectroscopy.Picoquant.com. https://www.picoquant.com/images/uploads/page/files/7272/appnote_flcs.pdf, (accessed 2024-07-26).
3. R. Brown and R. Q. Twiss, *Nature*, 1956, **177**, 27–29.
4. H. Paul, *Rev. Mod. Phys.*,1982, **54**, 1061.
5. T. Basch´e, W. E. Moerner, M. Orrit and H. Talon, *Phys. Rev. Lett.*, 1992, **69**, 1516–1519.
6. M. K. Panda, D. Acharjee, N. Nandi, S. Koley and S. Ghosh, *Chem. Eur. J.* 2024. https://doi.org/10.1002/chem.202401938.
7. B.-O. Dabbousi, J. Rodriguez-Viejo, F.-V. Mikulec, J.R. Heine, H. Mattoussi, R. Ober, K.-F. Jensen and M.G. Bawendi, *J. Phys. Chem. B*, 1997, **101**, 9463–9475.
8. N. T. Vo, H. D. Ngo, N. P. D. Thi, K. P. N. Thi, A. P. Duong and V. Lam, *J. Nanomater.*, 2016, **8564648**, 1–8.
9. H. Li, J. Jiao, Q. Ye, Z. Wu, D. Luo and D. Xiong, *J. Mater. Sci.: Mater. Electron.*, 2021, **32**, 22024–22034.