Supporting Information

Optofluidic Lasers with Aqueous Quantum Dots

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Representative TEM Image of the QDs Used in this Study

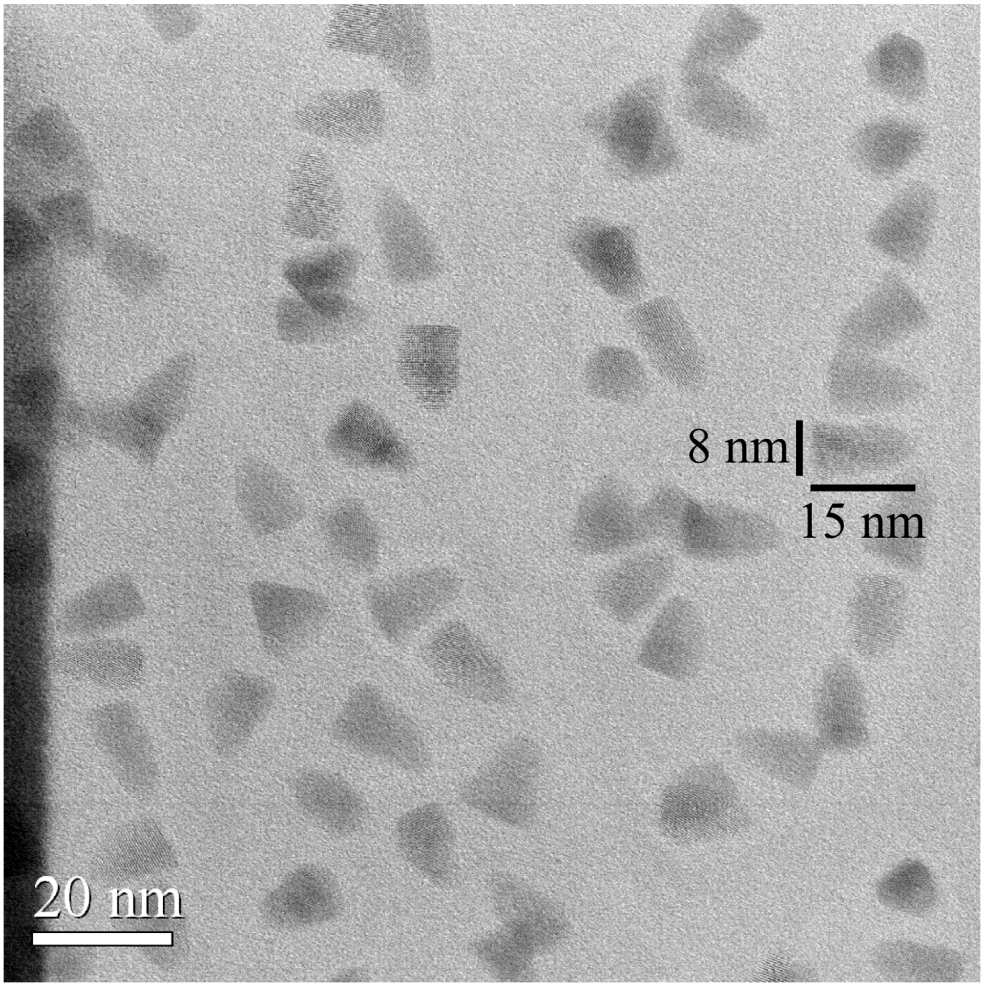

Figure S1: Representative TEM image of Qdot® 655 QDs used in this study. Average dimensions are estimated to be 8x15 nm.

Laser Spot Size Analysis

Pump laser spot size was determined by measuring transmission behind a blade that is placed at the focus and translated perpendicularly with respect to the incoming beam direction. The results of these measurements together with the fit assuming a Gaussian spot size are shown in Fig. S2. The fit function used was : $y(x) = A\int_x^\infty e^{-\frac{(x-x_0)^2}{2\sigma^2}}dx$. Fit revealed the following parameter values: $A = 0.033$ μJ/μm, $x_0 = 733.66$ μm, $\sigma = 272.01$ μm. Based on the value of σ we determine the FWHM of the Gaussian as $FWHM = 2\sqrt{2\ln 2}\,\sigma = 640.53$ μm. We report this value as 650 μm considering the measurement error.

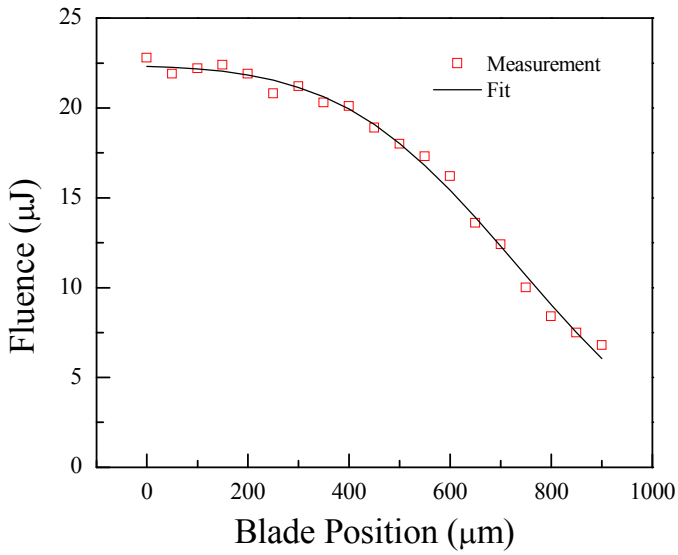

Figure S2: Pump laser transmission as a function of lateral position of the blade placed at the focus.

Absorption Cross-Section Measurement

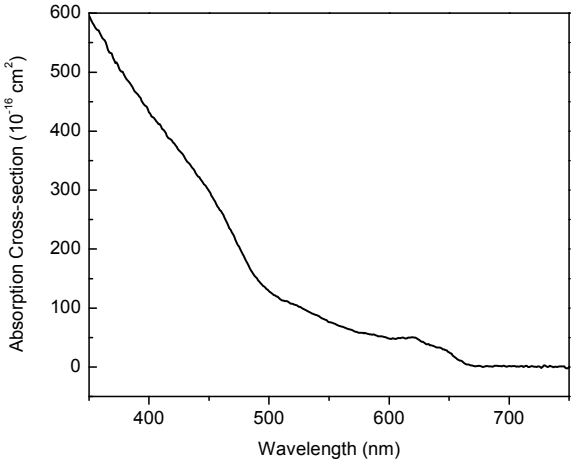

Figure S3: Absorption cross section of Qdot® 655 QDs based on absorbance test with 800 nM solution.

Quantum Yield Measurement

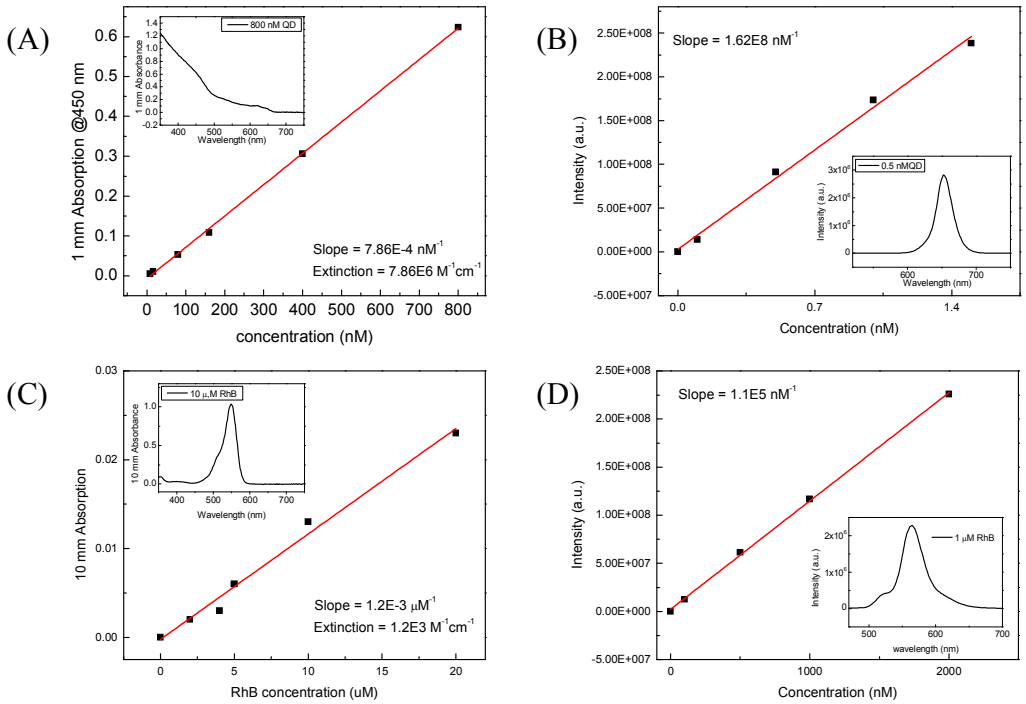

Figure S4: (A,C) Absorbance of Qdot® 655 (A) and RhB (C) at 450 nm, with inset showing the absorption spectrum. (B,D) Integrated fluorescence intensity vs. concentration for Qdot® 655 (B) and RhB (D) with inset showing the emission spectra. Integration is taken over a 230-nm span between 470-700 nm for RhB and 520-750 nm for QD 655.

To determine the quantum yield of our quantum dots (QDs), we ran absorption and fluorescence tests of our quantum dots (in borate buffer) in parallel with Rhodamin B (RhB) (in ethanol). Experimental results are shown in Figure S1. Fluorescence test was performed with FluoroMax-4 spectrofluorometer (Horiba Scientific). Absorption test was performed with NanoDrop 2000c spectrophotometer (Thermal Scientific). Excitation (absorption) wavelength was at 450 nm. Fluorescence efficiency (FL-slope)/extinction coefficient (ε) is derived from the slope in the concentration-dependency diagram for fluorescence/absorption. Using the equation:

$$\Phi_s = \Phi_{ref} \times \frac{FL\text{-}slope_s}{FL\text{-}slope_{ref}} \times \frac{RI_s^2}{RI_{ref}^2} \times \frac{\varepsilon_{ref}}{\varepsilon_s}, \qquad \text{(S1)}$$

where ϕ is the quantum yield and RI is the refractive index of the solvent (for water, RI=1.33; for ethanol, RI=1.36), we calculate that $\phi_{QD} = 0.15$. ($\phi_{ref} = 0.7$ for RhB in ethanol [1]). This number is in good agreement with quantum yields reported for other QDs of the same family (Qdot® probes) [2].

Fluorescence Lifetime Measurement

Results of the time correlated photon counting experiments performed using a fluorescence lifetime spectrometer (TemPro, Horiba) are shown in Fig. S3. A mono-exponential fit reveals 33 ns fluorescence lifetime for Qdot® 655 QDs.

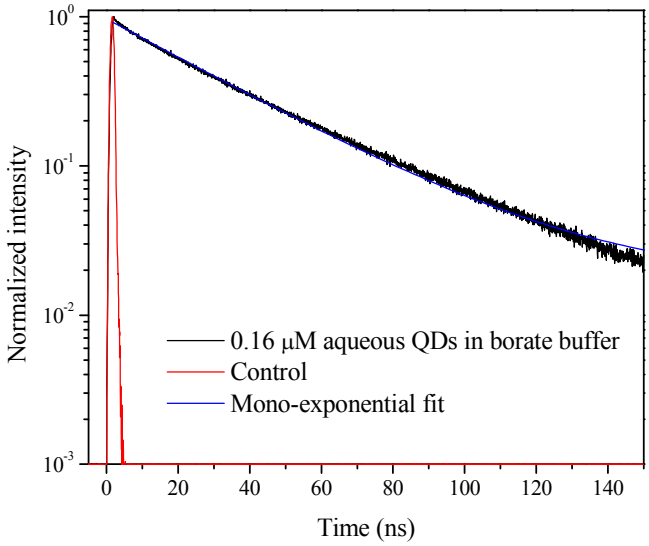

Figure S5: Fluorescence decay curve obtained with 0.16 μM aqueous Qdot® 655 solution in borate buffer. Control shows the instrumentation response obtained with the borate buffer solution without QDs. Mono-exponential fit reveals 33 ns fluorescence lifetime.

Fluorescence Quantum Distribution Calculation

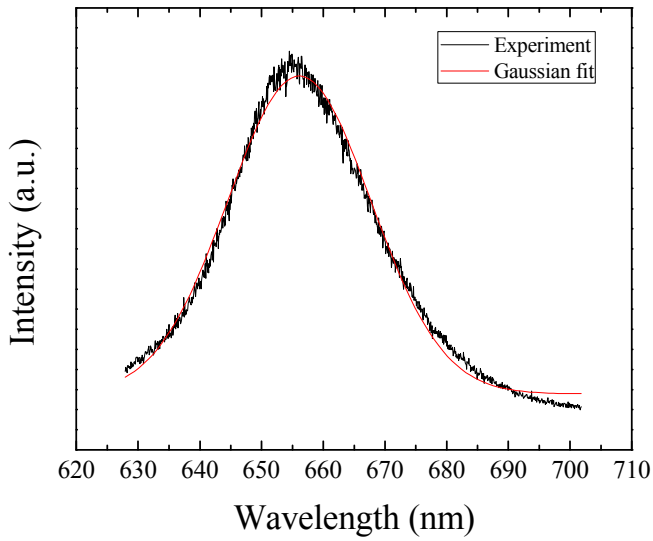

Figure S6: Qdot® 655 fluorescence spectrum. Gaussian fit reveals 656 nm center wavelength, 11.6 nm standard deviation, and 27.3 nm FWHM

Based on the emission spectrum and Gaussian fit shown in Fig. S4, and the fluorescence quantum yield (q=0.15), QD fluorescence quantum distributions at 656 nm and 665 nm are calculated as follows:

$$E(\lambda) = \frac{q}{w\sqrt{2\pi}} \exp[-\frac{(\lambda-\lambda_0)^2}{2w^2}] \text{ where } \int E(\lambda)\cdot d\lambda = q$$

Therefore,

$$E(656nm) = \frac{q}{w\sqrt{2\pi}} \exp[-\frac{(656-656)^2}{2w^2}] = \frac{q}{w\sqrt{2\pi}} = \frac{0.15}{11.6nm \times 2.5} = 5.16\cdot 10^{-3}\, nm^{-1}$$

$$E(665nm) = \frac{q}{w\sqrt{2\pi}} \exp[-\frac{(9nm)^2}{2w^2}] = \frac{q}{w\sqrt{2\pi}} \cdot 0.74 = 3.8\cdot 10^{-3}\, nm^{-1}$$

Procedure Used for Surface Immobilization of QDs

To functionalize the inner surface of the OFRR, the OFRR was first cleaned by flowing HCl/ethanol (v:v=1:1) through the capillary for 30 minutes. After rinsed by DI water and dried with air flow, the OFRR was silanized with (3-aminopropyl)-trimethoxysilane (3-APTMS, 5% in methanol) for 30 minutes and rinsed with methanol. For subsequent attachment of a single layer of QDs on the OFRR inner surface, the silanized OFRR was activated with freshly prepared homofunctional amine-to-amine cross-linker bis(sulfosuccinimidyl) suberate (BS^3) (0.1 mg/mL in phosphate-buffered saline (PBS)) for 30 minutes and rinsed with PBS before incubation with the QDs. Then 1 μM QD solution was flown through the OFRRs for 30 minutes (flow rate 2 μL/min). Finally, the OFRR was rinsed and filled with PBS buffer to be ready for optical experiments. The flow rate for the incubation steps was 5 μL/min if not noted specifically.

REFERENCES

1. Arbeloa, F. L.; Ojeda, P. R.; Arbeloa, I. L. Flourescence self-quenching of the molecular forms of Rhodamine B in aqueous and ethanolic solutions. *J. Lumin.* 1989, 44, 105-112.
2. Wu, Y.; Lopez, G. P.; Sklar, L. A.; Buranda, T. Spectroscopic characterization of streptavidin functionalized quantum dots. *Anal. Biochem.* 2007, 364, 193-203.