
Colloidal quantum dots enable tunable liquid-state lasers

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Supplementary Note 1. Calculations of electronic states

We utilized quantum-mechanical effective-mass calculations performed with custom Python code to obtain the transition energies and wavefunctions of single excitons and biexcitons in type-(I+II) quantum dots (QDs). These calculations employed a finite-difference mesh approach implemented using cylindrical coordinates. At each discretized mesh point, the Schrödinger and Poisson equations were solved within the self-consistent field and effective mass approximation¹. The calculations were performed for type-(I+II) QDs with the following structure: CdSe ($r = 2.6$ nm)/ ZnSe ($l = 1.7$ nm)/ CdS ($h = 2.2$ nm)/ ZnS ($d = 0.3$ nm) QDs. These dimensions correspond to the QDs used in most of the experiments described in the main article.

A. Single excitons

The single-exciton wavefunction ($\Psi_X(r_e, r_h)$) was obtained from:

$$\Psi_X(r_e, r_h) = \psi_e(r_e)\psi_h(r_h) \quad (\text{S1})$$

$$\left[-\frac{\hbar^2}{2m_e^*(r)} \nabla^2 + V_{CB}(r) \right] \psi_e(r) = E_e \psi_e(r) \quad (\text{S2})$$

$$\left[-\frac{\hbar^2}{2m_h^*(r)} \nabla^2 + V_{VB}(r) \right] \psi_h(r) = E_h \psi_h(r) \quad (\text{S3})$$

In the above equations, $\psi_e(r_e)$ and $\psi_h(r_h)$ are the electron and hole wavefunctions, respectively, $V_{CB}(r)$ and $V_{VB}(r)$ are the conduction- and valence-band confinement potentials, respectively, m_e^* and m_h^* are the electron and hole effective masses, respectively, and E_e and E_h are the electron and hole energy eigenvalues, respectively. We allowed the ψ_e to adapt in response to the Coulomb attraction exerted by the hole, and vice versa. We employed the calculated electron and hole wavefunctions to obtain the Coulomb potentials ($\phi_{e,h}$) using the Poisson equation:

$$\nabla \cdot (\epsilon \epsilon_0 \nabla \phi_{e,h}(r)) = -q |\psi_{e,h}(r)|^2 \quad (\text{S4})$$

where ϵ represents the permittivity of the material, ϵ_0 is the vacuum permittivity, and q is the elementary charge. Having obtained these potentials, we use them in the Schrödinger-Poisson equations for both the electron and the hole:

$$\left[-\frac{\hbar^2}{2m_e^*(r)} \nabla^2 + V_{CB}(r) + q\phi_h(r) \right] \psi_e(r) = E_e \psi_e(r) \quad (\text{S5})$$

$$\left[-\frac{\hbar^2}{2m_h^*(r)} \nabla^2 + V_{VB}(r) - q\phi_e(r) \right] \psi_h(r) = E_h \psi_h(r) \quad (\text{S6})$$

The solutions of eqs S5 and S6 were used in eq S4 to compute the ‘corrected’ Coulomb potentials, which then were again utilized in eqs S5 and S6 to obtain the next iteration for the wavefunctions. This iterative process continued until the energies of the electron and hole states converged. Typically, about four iterations were required to achieve a convergence error of $\Delta E_{e,h}/E_{e,h} \leq 0.1\%$. The exciton energy (E_X) was computed from:

$$E_X = E_e + E_h \quad (\text{S7})$$

The calculations performed led to the identification of two different exciton states near the band edge, classified as direct (X_d) and indirect (X_i) excitons. Their energies are $E_d = 2.037$ eV and $E_i = 1.988$ eV. The corresponding wavefunctions are displayed in Supplementary Fig. 2.

B. Biexcitons

The energies of the three biexciton states ($X_i X_d$, $X_i X_i$, $X_d X_d$) were obtained using the results of calculations for single excitons. To account for the multi-carrier Coulomb interactions in a particular $X_m X_n$ biexciton state ($m, n = i$ or d , for indirect and direct exciton, respectively), we included an additional interaction term expressed as

$$E_{e \text{ or } h, m-e \text{ or } h, n} = \int \psi_{e \text{ or } h, m}(r) q \phi_{e \text{ or } h, n}(r) \psi_{e \text{ or } h, m}(r) dV. \quad (\text{S8})$$

The biexciton energies were calculated using the following expressions:

$$E_{id} = E_i + E_d + E_{e,d-h,i} + E_{e,d-e,i} + E_{h,d-h,i} + E_{h,d-e,i} \quad (S9)$$

or

$$E_{id} = E_i + E_d + E_{e,i-h,d} + E_{e,i-e,d} + E_{h,i-h,d} + E_{h,i-e,d} \quad (S10)$$

$$E_{ii} = 2E_i + E_{e,i-h,i} + E_{e,i-e,i} + E_{h,i-h,i} + E_{h,i-e,i} \quad (S11)$$

$$E_{dd} = 2E_d + E_{e,d-h,d} + E_{e,d-e,d} + E_{h,d-h,d} + E_{h,d-e,d} \quad (S12)$$

Calculations yield $E_{id} = 4.024$ eV, $E_{ii} = 4.020$ eV, and $E_{dd} = 4.074$ eV. Based on this, the X_iX_i and X_iX_d biexcitons are energetically more favorable than the X_dX_d biexciton. Therefore, when analyzing the experimental data, we take into account only the X_iX_i and X_iX_d states. The emission energies of these states can be found from:

$$hv_{id} = E_{id} - E_i \quad (S13)$$

$$hv_{ii} = E_{ii} - E_i \quad (S14)$$

These expressions yield $hv_{id} = 2.036$ eV and $hv_{ii} = 2.032$ eV. Both of these spectral energies lie near the energy of the X_d state (2.037 eV).

Supplementary Note 2. Modeling of photoluminescence dynamics

Using the three-level scheme shown in the inset of Fig. 2d (main article), we formulated the following rate equations governing the temporal evolution of the populations of direct (n_d) and indirect (n_i) exciton states ($n_d + n_i = 1$):

$$\frac{dn_d}{dt} = -\frac{n_d}{\tau_d^*} + \frac{n_i}{\tau_{i-d}} \quad (S15)$$

$$\frac{dn_i}{dt} = -\frac{n_i}{\tau_i^*} + \frac{n_d}{\tau_{d-i}} \quad (S16)$$

where

$$\frac{1}{\tau_d^*} = \frac{1}{\tau_d} + \frac{1}{\tau_{d-i}} \quad (\text{S17})$$

$$\frac{1}{\tau_i^*} = \frac{1}{\tau_i} + \frac{1}{\tau_{i-d}} \quad (\text{S18})$$

The solutions of these coupled differential equations can be presented as follows:

$$n_d = C_1 e^{-\frac{t}{\tau_{f,X}}} + C_2 e^{-\frac{t}{\tau_{s,X}}} \quad (\text{S19})$$

$$n_i = C_3 e^{-\frac{t}{\tau_{f,X}}} + C_4 e^{-\frac{t}{\tau_{s,X}}} \quad (\text{S20})$$

$$\frac{1}{\tau_{s(f),X}} = \frac{1}{2} \frac{1}{\tau_d^*} [(1 + \beta) \pm \sqrt{(1 + \beta)^2 - 4\beta(1 - \alpha_1\alpha_2)}] \quad (\text{S21})$$

where

$$\beta = \frac{\tau_d^*}{\tau_i^*} \quad (\text{S22})$$

$$\alpha_1 = \frac{\tau_d^*}{\tau_{d-i}} \quad (\text{S23})$$

$$\alpha_2 = \frac{\tau_i^*}{\tau_{i-d}} \quad (\text{S24})$$

The dynamics of the total photoluminescence (PL) intensity (I) emitted by the X_i and X_d states was obtained from:

$$I(t) = \frac{n_d}{\tau_d} + \frac{n_i}{\tau_i} = \left(\frac{C_1}{\tau_d} + \frac{C_3}{\tau_i}\right) e^{-\frac{t}{\tau_{f,X}}} + \left(\frac{C_2}{\tau_d} + \frac{C_4}{\tau_i}\right) e^{-\frac{t}{\tau_{s,X}}} \quad (\text{S25})$$

Based on eqs S19 and S20

$$\frac{C_3}{C_1} = \tau_{i-d} \left(\frac{1}{\tau_d^*} - \frac{1}{\tau_{f,X}} \right) \quad (\text{S26})$$

$$\frac{C_4}{C_2} = \tau_{i-d} \left(\frac{1}{\tau_d^*} - \frac{1}{\tau_{s,X}} \right) \quad (\text{S27})$$

Next, we expressed the ratio of the amplitudes of the fast (a_f) and slow (a_s) PL components as

$$\frac{a_f}{a_s} = \frac{\frac{C_1}{\tau_d} + \frac{C_3}{\tau_i}}{\frac{C_2}{\tau_d} + \frac{C_4}{\tau_i}}, \quad (\text{S28})$$

and the ratio of the time-integrated PL intensities originating from the X_d (A_d) and X_i (A_i) states as

$$\frac{A_d}{A_i} = \frac{\frac{C_1\tau_{f,X}}{\tau_d} + \frac{C_2\tau_{s,X}}{\tau_d}}{\frac{C_2\tau_{f,X}}{\tau_i} + \frac{C_4\tau_{s,X}}{\tau_i}} \quad (\text{S29})$$

We then used eqs S21 and S25-S29 to simulate the measured PL dynamics. In our simulations, we used the experimentally determined time constants of the fast ($\tau_{f,X} = 29$ ns) and slow ($\tau_{s,X} = 697$ ns) PL components, the measured ratio of their amplitudes ($a_f/a_s = 1.25$), and the ratio of A_d and A_i ($= 0.114$) determined from the deconvolution of the experimental PL spectra (Supplementary Fig. 1). Based on the best agreement between the measured and calculated dynamics, we obtained the following set of relaxation parameters of the excitonic system described by the scheme in the inset of Fig. 2d (main article): $\tau_d = 44$ ns, $\tau_i = 735$ ns, $\tau_{d-i} = 85$ ns, and $\tau_{i-d} = 8800$ ns.

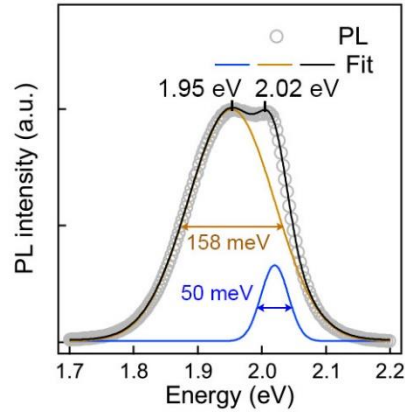
Supplementary Note 3. Evaluation of biexciton emission quantum yields

Long biexciton lifetimes in type-(I+II) QDs are expected to result in high biexciton emission efficiencies. The PL quantum yield of the X_iX_d -state can be estimated from $q_{id} = \tau_{f,XX}/\tau_{id,rad}$, where $\tau_{id,rad}$ is its radiative time constant. Neglecting the weak contribution of the indirect transition, the number of radiative pathways for the X_iX_d state is twice as large as that for the X_d state², that is, $\tau_{id,rad} \approx \tau_d/2$. This yields $\tau_{id,rad} = 22$ ns and $q_{id} = 61\%$. The latter is 1.6 larger than that of the continuously graded cg-QDs (Supplementary Table 1), confirming the strong suppression of Auger recombination in type-(I+II) QDs. This is further supported by observations of high biexciton PL

efficiencies obtained using single-dot two-photon correlation studies (Methods) according to which q_{id} is ~76% (average over 26 QDs; see Fig. 3c and Supplementary Fig. 5).

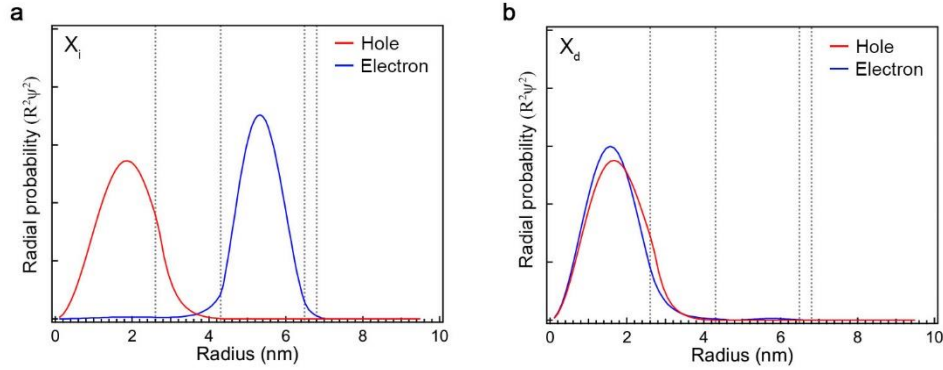
Supplementary Note 4. Evaluation of critical QD concentrations

The critical QD concentration needed for lasing ($n_{QD,cr}$) was calculated from $n_{QD,cr} = (\gamma\tau_g)^{-1}$, where $\gamma = c\sigma_g/(\beta n_r)$, τ_g is the optical gain lifetime, σ_g is the optical gain cross-section, c is the speed of light, n_r is the refractive index of the active medium, and β is a dimensionless constant which depends on the specifics of the QD-optical cavity system³⁻⁵. The parameter β is a multiplier that determines the relationship between the nominal rise time of stimulated emission ($\tau_{SE} = n_r/(cG_o)$; here G_o is the saturated gain coefficient) and the actual rise time of the cavity mode for a given laser configuration (τ_0): $\tau_0 = \beta\tau_{SE}$. Previous microcavity simulations in ref. 4 used $\beta = 20$. For the fairly long cavity (several centimeters) used in the present study, we expect a slower lasing mode rise time, which should result in a larger β value. In our estimations, we assume that β is 10 times larger than in ref. 4, that is, $\beta = 200$. Using this value together with $n_r = 1.496$ (for toluene), and $\sigma_g = 5.2 \times 10^{-16} \text{ cm}^2$ and $\tau_g = 3 \text{ ns}$ (obtained from the performed TA measurements), we obtain $n_{QD,cr}$ of $\sim 6 \times 10^{15} \text{ cm}^{-3}$ or $\sim 11 \text{ } \mu\text{mol L}^{-1}$. This is comparable with the lowest QD concentration used in our lasing experiments ($7.9 \text{ } \mu\text{mol L}^{-1}$).

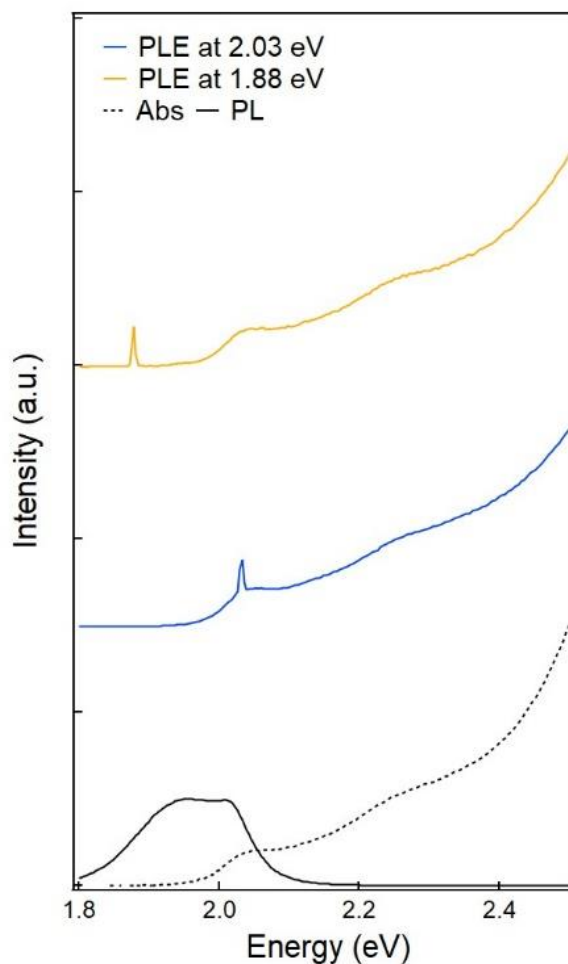


Supplementary Fig. 1 | Double-band deconvolution of the PL spectrum of type-(I+II) QDs.

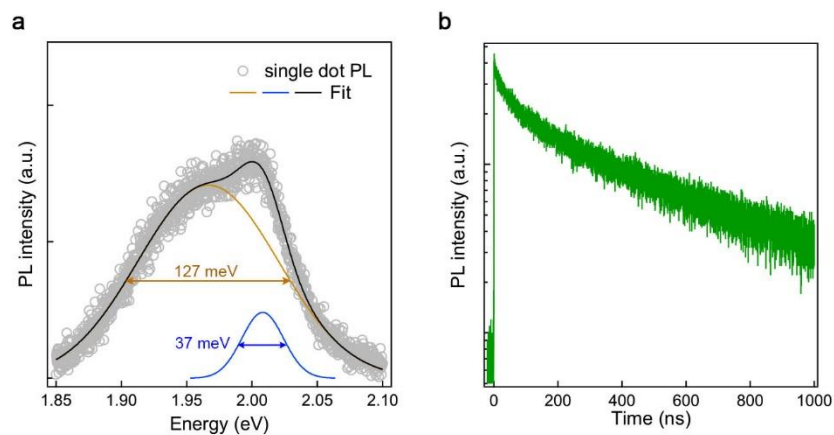
The PL spectrum of type-(I+II) CdSe ($r = 2.6$ nm)/ZnSe ($l = 1.7$ nm)/CdS ($h = 2.2$ nm)/ZnS ($d = 0.3$ nm) QDs recorded using low-intensity (sub-single exciton) excitation (open grey circles) and a fit (black line) obtained by summing two Gaussian bands (gold and blue lines), whose peak positions and full width at half-maximum are indicated in the figure. The PL spectrum was recorded using continuous wave (cw) 2.76 eV excitation.



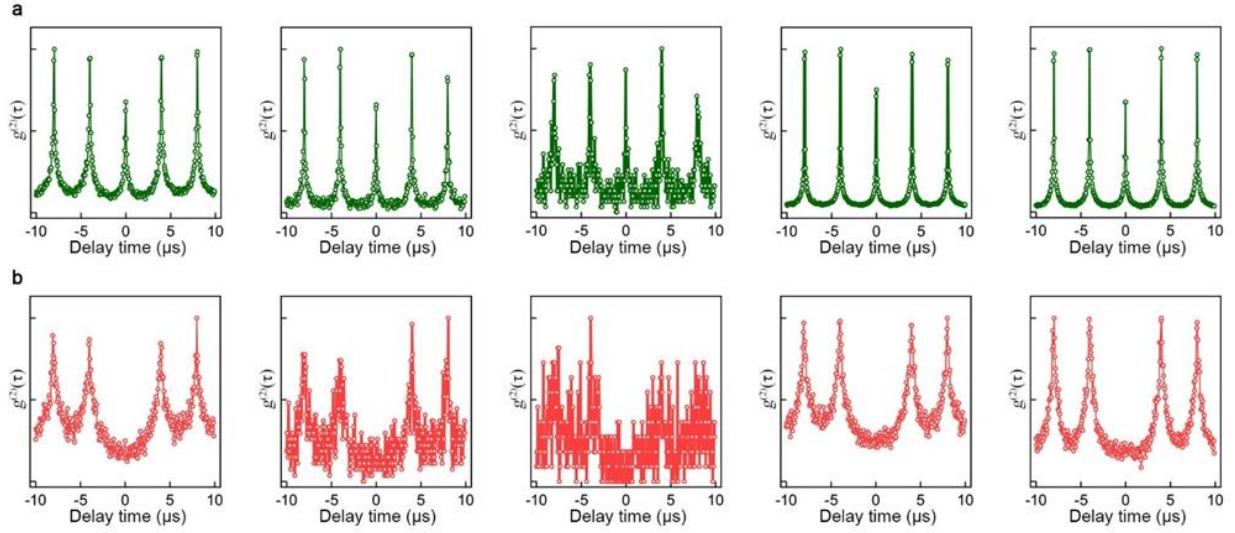
Supplementary Fig. 2 | Radial distributions of the electron and hole probabilities for the band-edge and the first excited quantized states. a,b, Calculated electron (blue lines) and hole (red lines) radial probabilities for the lowest energy (a) and the first excited (b) states of the type-(I+II) CdSe ($r = 2.6$ nm)/ZnSe ($l = 1.7$ nm)/CdS ($h = 2.2$ nm)/ZnS ($d = 0.3$ nm) QD. These two states correspond to indirect (X_i) and direct (X_d) excitons, respectively.



Supplementary Fig. 3 | Photoluminescence excitation (PLE) spectra of type-(I+II) QDs. PLE spectra of type-(I+II) QDs with $r = 2.6$ nm, $l = 1.7$ nm, $h = 2.2$ nm, and $d = 0.3$ nm measured using detection at 1.88 eV (yellow) and 2.03 eV (blue). These two energies correspond to indirect and direct excitons, respectively. The optical absorption and PL spectra of the same sample are shown as dotted and solid black lines, respectively. The shapes of both PLE spectra generally reproduce the shape of the absorption spectrum. This indicates a highly efficient formation of direct and indirect excitons, independent of the energy of the initially excited electronic states.



Supplementary Fig. 4 | PL measurements of an individual type-(I+II) QD. **a**, Measured PL spectrum (open grey circles) of a single type-(I+II) CdSe ($r = 2.6$ nm)/ZnSe ($l = 1.7$ nm)/CdS ($h = 2.2$ nm)/ZnS ($d = 0.3$ nm) QD fitted to the sum (black line) of two Gaussian bands (cyan and orange lines). **b**, Corresponding PL dynamics recorded without spectral filtering. All data were collected using low-intensity sub-single-exciton excitation with a pump photon energy of 2.54 eV.



Supplementary Fig. 5 | Second-order intensity correlation ($g^{(2)}$) measurements of individual type-(I+II) QDs. **a**, $g^{(2)}$ measurements conducted for 5 individual type-(I+II) QDs without photon discrimination using pulsed 2.54 eV excitation. **(b)** Gated $g^{(2)}$ measurements performed for the same QDs but selecting photons arriving with a time delay of 200 ns or more relative to the excitation pulse. Based on the ungated $g^{(2)}$ measurements, the average biexciton PL quantum yield (q_{xx}) is 77% (averaged over 5 QDs). In total, $g^{(2)}$ studies were performed for 26 QDs. The corresponding average q_{xx} is 76%.

Supplementary Table 1 | Comparison of gain-relevant characteristics of type-(I+II) QDs and continuously graded QDs (cg-QDs).

	cg-QDs^{6,7}	Type-(I+II) QDs
Optical gain lifetime (τ_g)	0.72 ns for $\langle N \rangle = 32$	3.0 ns for $\langle N \rangle = 34$
Biexciton PL quantum yield (q_{xx})	0.38	0.76
Material gain (G)	780 cm ⁻¹	1,110 cm ⁻¹

Supplementary Table 2 | Comparison of lasing characteristics of type-(I+II) QDs and the laser dye rhodamine 6G.

	Type-(I+II) QDs	Rhodamine 6G
Concentration ($\mu\text{mol L}^{-1}$)	14	~1,600
Lasing threshold*	44 mJ cm ⁻² ($h\nu_{\text{las}} = 1.988$ eV)	12 mJ cm ⁻² ($h\nu_{\text{las}} = 2.12$ eV)
Lasing range*	1.96 eV – 2.10 eV (140 meV)	2.06 eV – 2.14 eV (80 meV)
Gain bandwidth**	260 meV (1.99 eV – 2.25 eV)	190 meV (2.06 eV – 2.25 eV)
Characteristic decay time of the output intensity (stability assessment)	No noticeable degradation for 5 hours	~30 min

$h\nu_{\text{las}}$ is the spectral energy of lasing.

*When measuring the lasing threshold and lasing range, the QD and dye concentrations were adjusted such that to match their optical gain coefficients.

**The gain bandwidth of the QD and dye samples was measured using 190 fs, 2.4 eV pump pulses with a per-pulse fluence of 7 mJ cm⁻².

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