Chloride-Induced Thickness Control in CdSe Nanoplatelets - Supporting Information

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1. Experimental section

Materials. Cadmium nitrate tetrahydrate (99.997%), sodium myristate (≥99%), cadmium(II) acetate (Cd(OAc)2; 99.995%), cadmium acetate dihydrate (Cd(OAc)2.2H2O), cadmium chloride (CdCl2, 99.99%), cadmium oxide (CdO, ≥99.99%), selenium powder (Se, ≥99.5%), octadecene (ODE; 90%), oleic acid (OlAc, 90%), hexane (≥95%), and ethanol (≥99.8%) were purchased from Sigma Aldrich. All chemicals were used without further purification.

Cadmium myristate (Cd(myr)2) preparation: 3 g of cadmium nitrate tetrahydrate was dissolved in 200 mL of methanol. In another round bottom flask 5 g of sodium myristate was dissolved in 500 mL of methanol using sonication. The cadmium solution was then added dropwise to the myristate solution and stirred for 2 h at room temperature. The resulting precipitate of cadmium myristate was filtered and washed several times with methanol, and was dried overnight in a freeze dryer.

Preparation of cadmium chloride/cadmium oleate solution (CdCl2/CdOlAc). 20 mg of CdCl2 and 80 mg of CdO dispersed in 10 mL of oleic acid were heated for 15 min at 200°C under argon flow and then sonicated for 30 min at room temperature to obtain a white suspension.

Synthesis of 4.5 ML CdSe NPLs, emitting at 510 nm: 170 mg of Cd(myr)2 (0.3 mmol), 24 mg of Se powder and 15 mL of ODE were mixed in a 50 mL three neck flask and degassed under vacuum at 120 °C for one hour. Then the mixture was heated under argon flow, with the temperature set at 240 °C. When the solution turned deep orange (around 220 °C), 90 mg of Cd(Ac)2 powder was added. The reaction was then maintained at 240 °C for 10 minutes.
Synthesis of CdSe NPLs emitting at 554 nm: CdSe NPLs emitting at 510 nm, synthesized as described above, were subsequently heated to 280 °C, then 1.5 mL of CdCl$_2$/CdOIAc solution was injected and the reaction was kept at the growth temperature for 5 hours.

Synthesis of CdSe NPLs emitting at 584 nm: CdSe NPLs emitting at 510 nm, synthesized as described above, were subsequently heated to 300 °C, then 1 mL of CdCl$_2$/CdOIAc solution was injected and the reaction was kept at the growth temperature for 5 hours.

Synthesis of CdSe NPLs emitting at 607 nm: The synthesis procedure was the same as that for 584 nm emitting NPLs, except that the growth temperature and time were 315 °C and 2 hours, respectively.

Synthesis of CdSe NPLs emitting at 625 nm: The synthesis procedure was the same as that for 584 nm emitting NPLs, except that the growth temperature and time were 320 °C and 5 hours, respectively.

Post-synthesis sample purification: The reaction was quenched by removing the heating mantle. When the temperature reached around 160 °C, 2 mL of oleic acid was added to the flask. When solution reached room temperature, 15 mL of hexane was added. The mixture was then centrifuged at 3000 rpm for 10 min. The precipitate containing the NPLs was resuspended in 20 mL of hexane. The resultant dispersion was centrifuged at 6000 rpm for 10 minutes to remove fractions of larger-sized NPLs as the precipitant. The decant contains the final NPLs. For TEM and XPS characterization, the NPLs were further purified twice with ethanol to remove organic impurities.

Synthesis of NPLs emitting at 584 nm with aspect ratio 2.9:1 and 1.2:1. The synthesis procedures are same as described above for the synthesis method of 584 nm emitting NPLs, only at the time of 4.5 ML synthesis the added 90 mg of Cd(Ac)$_2$ powder was replaced by 180 mg Cd(Ac)$_2$.2H$_2$O and 200 mg Cd(Ac)$_2$.2H$_2$O respectively.

Synthesis of thicker NPLs using purified 4.5 ML NPLs, using the CdO/CdCl$_2$ route and CdCl$_2$ route. The 4.5 ML NPLs were first synthesized and purified as described above. The purified NPLs were dispersed in 15 mL ODE and then heated to 300 °C, at which point a precursor mixture of 2 mg CdCl$_2$ – 8 mg CdO – 1 mL OA, or 2 mg CdCl$_2$– 1 mL OA was injected respectively. In both syntheses, after 2 hours of reaction time we observed a loss of absorption features for the NPLs, suggesting sample degradation. Hence, the synthesis was stopped at 2 hours. Quenching of the reaction and sample purification was performed as described above.

Characterization
Optical characterization. Absorbance spectra of NPLs in hexane were recorded using a Varian Cary 5000 UV-VIS-NIR spectrophotometer. Steady-state and time-resolved photoluminescence (PL) emission and excitation spectra were measured using an Edinburgh Instruments FLS920 spectrofluorometer. The steady-state PL was collected by exciting the samples at 400 nm with a Xenon lamp. A nanointegrating sphere was used for PL quantum efficiency measurements. The PL decay traces were recorded by exciting the samples at 405 nm using a 50 ps laser diode at a repetition rate of 0.05-1 MHz. The data were collected at the PL peak position with an emission bandwidth of 2 nm.

X-ray diffraction. XRD patterns were measured on a PANanalytical Empyrean X-ray diffractometer equipped with a 1.8 kW CuKα ceramic X-ray tube, PIXcel$^{3D}$ 2x2 area detector and operating at 45 kV and 40 mA, using Parallel-Beam (PB) geometry and symmetric
reflection mode, from 20° to 70° 2θ. Samples were prepared by drop casting a concentrated NPL dispersion onto a miscut silicon substrate. We calculated the zinc blende lattice constant α for each NPL sample by averaging the experimental lattice constants obtained from the first three XRD peaks, associated with the (001), (110) and (111) crystallographic planes, using the following equations: \( d = \frac{\lambda}{2 \cdot \sin \theta} \) and \( \alpha = d \cdot (h^2 + k^2 + l^2)^{1/2} \).

**Transmission electron microscopy (TEM).** Overview BF-TEM analyses of the samples were carried out using a JEOL JEM-1011 TEM (W filament, operated at 100 kV). For high-resolution TEM and STEM-EDS, an image-Cs-corrected JEOL JEM-2200FS TEM was used, with an in-column filter (Ω-type) and a Bruker XFlash-5060 SDD detector. Samples were prepared by drop casting about 100 µL of a dilute NPL dispersion onto carbon-coated Cu grids for BF-TEM analyses and onto ultrathin carbon-on-holey carbon-coated Cu grids for HRTEM analyses.

**X-ray photoelectron spectroscopy (XPS).** The samples were prepared by drop-casting a few µL of NPL dispersion onto a graphite substrate (HOPG, ZYB quality, NT-MDT) and were subsequently transferred to the XPS setup. Measurements were conducted with a Kratos Axis Ultra DLD spectrometer, using a monochromatic Al Kα source operated at 20 mA and 15 kV. The pressure in the analysis chamber was maintained below \( 5 \times 10^{-9} \) Torr for data acquisition. The Kratos charge neutralizer system was used on all specimens. Survey scan analyses were carried out with an analysis area of 300 x 700 microns and a pass energy of 160 eV. High resolution analyses were carried out with the same analysis area and a pass energy of 20 eV. Spectra have been charge corrected to the main line of the C 1s spectrum set to 284.8 eV. Spectra were analysed using CasaXPS software (version 2.3.17). Quantitative analysis results were obtained by evaluating the areas under the main Cd 3d, Cl 2p and Se 3d peaks, after normalization to the corresponding relative sensitivity factors (RSF, as provided by instrument manufacturer).
2. Standard synthesis of CdSe NPLs

![TEM images and absorption and photoluminescence spectra](image1.png)

**Figure S1.** TEM images and corresponding absorption and photoluminescence spectra of 3.5 ML, 4.5 ML and 5.5 ML CdSe NPLs prepared by literature methods.\(^1\),\(^2\)

3. Rectangular and Square shaped NPLs

![Control experiment](image2.png)

**Figure S2.** Control experiment with rectangular NPLs (22.3 nm by 7.7 nm, aspect ratio of 2.9:1). We have injected the CdCl\(_2\) solution at 300°C. (a) Absorption and PL spectra and TEM of (b) initial NPLs and (c) final NPLs.
Figure S3. Control experiment with square NPLs (14.5 nm by 12.4 nm, aspect ratio of 1.2:1) at 300°C. (a) Absorption and PL spectra and TEM of (b) initial NPLs and (c) final NPLs.

4. Temporal evolution at 280°C, 300°C and 320°C

Figure S4. Absorption (a, c and e) and PL (b, d and f) spectra of the temporal evolution of different reactions at 280°C, 300°C and 320°C, respectively. The colour codes are labelled on the top of the figure.
5. Control experiments with purified 4.5 ML NPLs

Figure S5. Control experiment with purified 4.5 ML NPLs at 300°C in the presence of (a) 2 mg CdCl₂ and 8 mg CdO in 1 mL OA and (b) 2 mg CdCl₂ in 1 mL OA.

6. TEM images and lateral size determination of the CdSe NPLs

Figure S6. (a-e) TEM images of full NPL series and image of the corresponding dispersion under UV illumination. (f) Table with the length and the width of both the starting NPLs and the corresponding final sample. The data have been obtained by sampling 100 NPLs.
7. Control experiments

**Figure S7.** Time dependent absorption and PL spectra of the control experiments, performed at 300°C. Top panel: annealing without adding precursors results in the growth of the quantum dots. Middle panel: reaction with a cadmium oleate solution, containing 9.4 mg CdO (0.073 mmol) in 1 mL of oleic acid. It results in broad absorption and PL spectra. Bottom panel: reaction with 13.6 mg CdCl₂ (0.073 mmol) suspended in 1 mL of oleic acid. It results in sharp optical features of thicker NPLs.
8. XPS results

Figure S8. (a) X-ray photoelectron spectra of the different CdSe NPLs. (b) Detail of the spectra around the chlorine 2p peak. Spectra should be compared to the background spectrum of 4.5 ML NPLs, where no CdCl$_2$ was used.

9. PL decay results

Table S1. The fitting results of the PL decay curves of different CdSe NPLs. The amplitude-weighted average decay times is calculated according to $\tau_{av} = \frac{\sum A_i \tau_i}{\sum A_i}$.

| Sample name & emission @ | $A_1$  | $\tau_1$ | $A_2$  | $\tau_2$ | $A_3$  | $\tau_3$ | $A_4$  | $\tau_4$ | $\tau_{av}$ (ns) |
|------------------------|--------|----------|--------|----------|--------|----------|--------|----------|-----------------|
| 4.5 ML_{em}@510nm      | 6145.3 | 2.48     | 3283.8 | 5.53     | 811.66 | 13.93    | 164.96 | 65.37    | 5.33            |
| 5.5 ML_{em}@554nm      | 1321.6 | 0.47     | 5755.5 | 4.6      | 2576.5 | 13.59    | 353.49 | 67.81    | 8.6             |
| 6.5 ML_{em}@584nm      | 1603.2 | 0.78     | 4508.6 | 4.69     | 3604.8 | 12.22    | 306.56 | 56.26    | 8.35            |
| 7.5 ML_{em}@607nm      | 1827.9 | 0.65     | 3545.4 | 4.93     | 4132.2 | 14.57    | 516.51 | 57.81    | 10.85           |
| 8.5 ML_{em}@625nm      | 1805.8 | 0.6      | 3903   | 4.09     | 3758.1 | 15.17    | 523.34 | 64.22    | 10.78           |
10. Comparison of PLE and absorbance spectra.

![Figure S9](image)

**Figure S9.** Absorption and photoluminescence excitation spectra of the CdSe NPLs.

11. Theoretical considerations

**NUMERICAL MODEL**

In order to obtain a spectral assignment of the different absorption/PLE peaks, we calculated neutral exciton states using \(k\cdot p\) theory. As a first approximation, we considered quantum confinement in the thin direction of the platelet (\(z\)) as the main physical factor determining energy and wave function, and disregard comparatively minor effects, such as electron-hole interaction. The exciton Hamiltonian is then simply \(H_x = H_e + H_h\) where \(H_e\) and \(H_h\) are obtained from the 8-band Pidgeon-Brown (PB) Hamiltonian for zinc-blende.\(^3\)

\[
H_{PB} = \begin{pmatrix}
E_g + \frac{\gamma_3}{2} p_z^2 & 0 & \sqrt{\frac{3}{2}} V p_z & \frac{i}{\sqrt{3}} V p_z & 0 & 0 & 0 & 0 \\
0 & -\frac{\gamma_1+2\gamma_2}{2} p_z^2 & 0 & 0 & 0 & 0 & 0 & 0 \\
\sqrt{\frac{3}{2}} V p_z & 0 & -\frac{\gamma_1+2\gamma_2}{2} p_z^2 & -i\sqrt{3} \gamma_2 p_z^2 & 0 & 0 & 0 & 0 \\
\sqrt{\frac{3}{2}} V p_z & 0 & i\sqrt{3} \gamma_2 p_z^2 & -\frac{\gamma_3}{2} p_z^2 - \Delta & 0 & 0 & 0 & 0 \\
0 & 0 & 0 & 0 & E_g + \frac{\gamma_3}{2} p_z^2 & 0 & \sqrt{3} V p_z & \frac{i}{\sqrt{3}} V p_z \\
0 & 0 & 0 & 0 & \sqrt{3} V p_z & 0 & -\frac{\gamma_1+2\gamma_2}{2} p_z^2 & 0 \\
0 & 0 & 0 & 0 & i\sqrt{3} \gamma_2 p_z^2 & 0 & -\frac{\gamma_1+2\gamma_2}{2} p_z^2 & -i\sqrt{3} \gamma_2 p_z^2 \\
0 & 0 & 0 & 0 & -\frac{i}{\sqrt{3}} V p_z & 0 & i\sqrt{3} \gamma_2 p_z^2 & -\frac{\gamma_3}{2} p_z^2 - \Delta
\end{pmatrix}
\]
$E_g$ is the bulk band gap, $\alpha, \gamma_1, \gamma_2$ are mass parameters, $\Delta$ is the split-off band energy splitting, $V$ relates to the Kane energy $E_p = 2m_0V^2$ and $p_z$ is the momentum operator along the quantum confined direction. Notice that the Hamiltonian is blocked into two identical submatrices, referring to states with angular momentum $J_z > 0$ or $J_z < 0$. In what follows we focus on a single block, knowing that eigenstates will be Kramers-degenerate. Notice also that considering the operator $p_z$ is more strict than replacing it by the square root of the free-electron energy expectation value, as quantum confinement is critical in this problem. For CdSe mass parameters available in the literature, $H_{zz}^{PB}$ becomes a non-elliptical (or nearly so) Hamiltonian, so that spurious solutions arise. To circumvent this problem, we consider that CdSe has a wide gap and neglect the coupling of conduction band with valence subbands. We are then left with a single-band effective mass Hamiltonian for conduction electrons:

$$H_z^e = \frac{p_z^2}{2m^*} + V^e(z)$$

where the effective mass $m^*$ relates to $\alpha$ as:

$$\frac{1}{m^*} = \frac{1}{m_0} \left( \alpha + \frac{E_p}{3} \left[ \frac{2}{E_g} + \frac{1}{E_g + \Delta} \right] \right)$$

with $m_0$ the free electron mass and $V^e(z)$ the electron confining potential along $z$. The heavy hole Hamiltonian is also single-band:

$$H_z^{hh} = -\frac{\gamma_1^L - 2\gamma_2^L}{2} p_z^2 + V^h(z)$$

but the light hole and split-off hole are coupled through a two-band Hamiltonian:

$$H_z^{h-so} = \begin{pmatrix} -\frac{\gamma_1^L - 2\gamma_2^L}{2} p_z^2 + V^h(z) & -i\sqrt{2}\gamma_2^L p_z^2 \\ i\sqrt{2}\gamma_2^L p_z^2 & -\frac{\gamma_2^L}{2} p_z^2 - \Delta + V^h(z) \end{pmatrix}$$

The Luttinger parameters are related to the gamma parameters as:

$$\gamma_1^L = \gamma_1 + \frac{E_p}{3E_g}; \quad \gamma_2^L = \gamma_2 + \frac{E_p}{6E_g}$$

and $V^h(z)$ is the hole confining potential along $z$, defined by the band offset between CdSe and the surrounding ligands (oleic acid).

In order to calculate the absorption intensity we consider that, in the absence of magnetic fields or other terms lifting time-reversal symmetry, the transition rate from a valence band state

$$\Psi_{h,J_z} = \sum_i f_i |u_{J_z}^i\rangle$$

to a pair of degenerate conduction band states $\Psi_{e,\pm J_z} = f_e |u_{\pm J_z}^e\rangle$ is proportional to:

$$\Gamma_{h\to e} \propto |\langle \Psi_{h,J_z} |\vec{p}\cdot\vec{e}| \Psi_{e,1/2}\rangle + \langle \Psi_{h,J_z} |\vec{p}\cdot\vec{e}| \Psi_{e,-1/2}\rangle|^2$$
Here $\vec{p}$ is the transition momentum operator and $\vec{e} = \{R_x \hat{x}, R_y \hat{y}, R_z \hat{z}\}$ equals the light polarization vector including local field factor corrections $R_i$ due to dielectric screening.

In CdSe NPLs, the quasi-2D geometry and the strong dielectric mismatch with ligands leads to $R_z \ll R_x, R_y$. We then neglect transitions arising from $z$-polarized light. The Bloch functions that we use are:

\[
\begin{align*}
    u_{1/2}^e &= |S\rangle \uparrow, \\
    u_{3/2}^{hh} &= \frac{1}{\sqrt{2}} |X + iY\rangle \uparrow, \\
    u_{1/2}^{ih} &= \frac{1}{\sqrt{6}} |X + iY\rangle \downarrow - \frac{2}{3} |Z\rangle \uparrow, \\
    u_{1/2}^{so} &= \frac{1}{\sqrt{3}} |X + iY\rangle \downarrow + \frac{1}{3} |Z\rangle \uparrow, \\
    u_{1/2}^{ee} &= \frac{1}{\sqrt{3}} |X - iY\rangle \downarrow + \frac{1}{3} |Z\rangle \uparrow,
    \end{align*}
\]

For interband transitions arising from heavy hole states, the rate becomes simply proportional to the overlap squared of the electron and hole envelope functions:

\[
\Gamma_{hh \rightarrow e} \propto \left| \frac{\langle f_{hh} | f_e \rangle}{\sqrt{2}} \right|^2 P_K^2
\]

with $P_K$ the Kane matrix element. For transitions arising from coupled light hole-split off hole states, the rate equals:

\[
\Gamma_{lh-so \rightarrow e} \propto \left| \frac{\langle f_{lh} | f_e \rangle}{\sqrt{6}} + \frac{\langle f_{so} | f_e \rangle}{\sqrt{3}} \right|^2 P_K^2
\]

Notice that split-off hole and especially light hole states have a weaker contribution to the absorption spectrum than heavy hole states. This is because the Bloch function has a finite $z$-component, which is optically dim in platelets due to dielectric screening.

**Table S2.** Parameters used for calculations of the CdSe NPL transitions (unless otherwise specified).

| Parameter          | Value (units) | Ref. |
|--------------------|---------------|------|
| $m^*$              | 0.12 ($m_0$)  | 5,6  |
| $\gamma^L_1$      | 2.04          | 8    |
| $\gamma^L_2$      | 0.58          | 8    |
| $E_g$              | 1.66 (eV)     | 6    |
| $\Delta$           | 0.39 (eV)     | 6    |
| $V^e(z)$ CdSe/ligand | 0 / 2.5 (eV) | 10   |
| $V^h(z)$ CdSe/ligand | 0 / -2.5 (eV)| 10   |
| $a_0$              | 6.08 (Å)      | 6    |
For the CdSe/ligand band offset, we considered an oleic acid homo-lumo gap of 6.6 eV (similar to linoleic acid\textsuperscript{10}) and assumed that it is distributed symmetrically between conduction and valence bands. To determine the platelet thickness, we consider that each monolayer equals half the bulk CdSe lattice constant $a_0$. Hamiltonians are integrated numerically using a finite differences scheme.

**ROBUSTNESS AGAINST PARAMETERS**

*Figure S10* shows the NPL optical transitions for an increasing number of CdSe monolayers, calculated using different sets of parameters, within the range found in the literature. Solid lines correspond to parameters of *Table S2* (same as used in the main text), dashed lines are the same parameters but using a higher CdSe/ligand band offset of 5 eV, and dotted lines are the same parameters but using slightly different Luttinger parameters\textsuperscript{4} (i.e. lighter hole masses), which also have been reported by another recent study.\textsuperscript{11} Both lighter hole masses and (especially) the higher band offset lead to blue shifted transitions, in particular for the thinnest NPLs. Nevertheless, while quantitative agreement with experimental data varies, in all instances we obtained a robust sequence of transitions, and peaks can be assigned according the sequence discussed in the main text, independent of hole masses and band offsets used.

*Figure S10*. Calculated NPL optical transitions for different NPL thicknesses, using parameters of Table S1 (solid line), a higher conduction and valence band offset (dashed line), and lighter hole masses along the confinement direction (dotted line).
IMPACT OF LIGHT HOLE- SPLIT OFF HOLE COUPLING

To illustrate the impact of light hole-split off hole interaction, Figure S11 compares the absorption spectra with (purple lines) and without (orange lines) considering off-diagonal terms in $H_{lh-so}^{th}$. The interaction transforms otherwise independent light hole and split-off hole exciton states into coupled states, whose absorption energy is shifted with respect to the non-interacting case (horizontal arrows in the figure). Light hole states are stabilized and split-off states destabilized. Figure S11 reveals that the coupling (and hence the associated energetic shift) is more pronounced for thinner NPLs. Also, the coupling is much more pronounced for excited states ($lh_{2}$, $so_{2}$) than for nodeless states ($lh_{1}$, $so_{1}$). The former experience sizable energy shifts due to a strong light hole-split off hole coupling even for the thicker NPLs (see arrow for 8.5 ML NPLs). All of these trends can be explained using an analytical model, as we shall see in the following section.

Figure S11. Optical transitions of NPLs with different thickness, calculated with the numerical model, including (purple lines) and excluding (orange lines) the light-hole – split-off sub-band interaction.

The strength of the coupling between light hole and split-off hole is shown in Figure S12, which plots the weight of the light hole component for the lowest-energy light hole-split-off state for two different NPL thicknesses (4.5 ML and 8.5 ML), as a function of the CdSe/ligand valence band offset. One can see that the admixture is enhanced when quantum confinement is strong, i.e. for high band offsets and thin NPLs. For a 4.5 ML NPL with band offset exceeding 3.5 eV, the lowest hole state has ~80% light hole component and ~20% split-off component. This is far from the nearly pure light hole character often assumed in the literature. For excited states the admixture is even larger (not shown). This is a characteristic result of colloidal NPLs. Typical epitaxial quantum wells are thicker ($L_z=3-20$ nm) and are formed in semiconductor-semiconductor heterostructures with valence band offsets that are substantially smaller than 1 eV. In turn, colloidal NPLs with thicknesses $L_z$ below 2 nm are now regularly synthesized and few-eV valence band offsets can be considered, as organic surface ligands have large homo-lumo gaps compared to the semiconductor NPLs.
Figure S12. Weight of light hole component in the lowest-energy coupled light hole-split off hole state of colloidal NPLs with different thickness (4.5 or 8.5 ML) and CdSe/ligand band offset.

SEMI-ANALYTICAL MODEL

For better insight into the physics of NPL electronic excitations, in what follows we assume an infinite potential barrier between the CdSe NPL and the surrounding medium. While this simplification tends to overestimate confinement energies compared to experiment, it allows us to use a basis set formed by analytical functions and to make an assessment of excitonic and dielectric confinement effects based on our previous model.\textsuperscript{13} We can write the full Hamiltonian now as:

$$H_X = H_e + H_h + \frac{a_B^2}{2\mu_p} + V_{e-h} + V_e^{self} + V_h^{self}$$

The third term is the kinetic energy due to the electron-hole relative motion, $a_B^2$ is the 2D Bohr radius, $\mu_p$ the in-plane reduced exciton mass, $V_{e-h}$ the direct Coulomb interaction between electron and hole including dielectric mismatch, and $V_j^{self}$ the self-energy term due to the Coulomb interaction of a carrier with its own image charges on the nanoparticle/ligand interface.

We consider the first two terms of the Hamiltonian above. Setting Dirichlet boundary conditions, the eigenfunctions $\psi_x = \psi_e \psi_h$ can be expanded on the basis formed by

$$\psi_e = \sqrt{\frac{2}{L_z}} \sin \left( \frac{n_e \pi x}{L_z} \right) |u^{c}_{1/2}\rangle$$

for electrons,

$$\psi_h = \psi_{hh} = \sqrt{\frac{2}{L_z}} \sin \left( \frac{n_{hh} \pi x}{L_z} \right) |u^{hh}_{3/2}\rangle$$

for heavy holes and

$$\psi_h = \psi_{lh-so} = \left\{ \sqrt{\frac{2}{L_z}} \sin \left( \frac{n_{lh} \pi x}{L_z} \right) |u^{lh}_{1/2}\rangle, \sqrt{\frac{2}{L_z}} \sin \left( \frac{n_{so} \pi x}{L_z} \right) |u^{so}_{1/2}\rangle \right\}$$

for coupled light hole-split-off states.
Single-band (electron and heavy hole) Hamiltonians give particle-in-a-box energies, while the two-band (light hole – split off hole) Hamiltonian becomes a Hubbard Hamiltonian:

\[
H_{lh-so}^z = \begin{pmatrix}
E_{lh} & -t \\
-t & E_{so}
\end{pmatrix}
\]

Here \(E_{so}\) and \(E_{lh}\) are (particle-in-a-box) energies for split-off hole and light hole, and \(t\) is the coupling energy:

\[
t = \sqrt{2} \gamma_2^L \pi^2 \frac{n_{lh} n_{so}}{L_z^2} \delta(n_{lh}, n_{so})
\]

One can see that the coupling term scales proportional to the number of nodes in the \(z\) direction \((n_{lh}, n_{so})\) and is inversely proportional to the square of the NPLs thickness \(L_z\), which explains the numerical results of Figure S11. After diagonalizing, \(H_{lh-so}^z\) light hole and split-off hole energies are modified as:

\[
E_{lh-so} = \frac{E_{lh} + E_{so}}{2} \pm \sqrt{\left(\frac{E_{lh} - E_{so}}{2}\right)^2 + t^2}
\]

In analogy with diatomic molecules, we call the lowest (highest)-energy solution the bonding (antibonding) coupled light hole-split off hole state, and label it as LH-SO (LH-SO*). The corresponding wave functions are given by:

\[
\Psi_{lh-so} = N(\pm c_1 |lh\rangle + |so\rangle)
\]

where \(N\) is the normalization coefficient and \(c_1\) equals:

\[
c_1 = \frac{E_{lh} - E_{so} + \sqrt{(E_{lh} - E_{so})^2 + 4t^2}}{2t}
\]

The previous equation shows that the degree of admixture is intimately related to the coupling energy \(t\). Because \(t\) is larger for excited states than for low-energy ones, their admixture -and the related energy splitting- is larger, in agreement with what we observe in the numerical simulations.

**COULOMB AND DIELECTRIC MISMATCH EFFECTS**

Exciton binding energies are large in colloidal NPLs (100-300 meV)\(^{13,14,15,16}\), due to the quasi-2D geometry and the dielectric mismatch between the semiconductor and the surrounding medium (typically organic ligands). In terms of energy, these effects are still secondary to quantum confinement, and have therefore little influence on the spectral assignment. However, they have implications in determining various opto-electronic properties such as the oscillator strength.\(^{13}\) To obtain some insight into their influence for the excited state transitions, we include terms \(V_{e-h}, V_{e}^{self}, V_{h}^{self}\), calculated with freely available computational codes,\(^{13}\) using dielectric constants \(\varepsilon_{in}=10\) (CdSe) and \(\varepsilon_{out}=2\) (oleic acid), assuming for simplicity \(a_B = a_B^D\) (2D limit of Bohr radius). Because a hard wall confinement potential overestimates the quantum confinement, for each NPL thickness we fit the electron effective mass along \(z\) so as
to match the emission energy of the fundamental exciton (heavy hole, $n=1$) transition. From 4.5 ML to 8.5 ML, the corresponding masses are $0.367m_0$, $0.310m_0$, $0.264m_0$, $0.226m_0$, $0.203m_0$. The in-plane electron effective mass is kept at $0.12m_0$.

**Figure S13.** Optical transitions of NPLs with different thickness, calculated with the semi-analytical model. Solid lines are independent-particle calculations. Dashed lines add the Coulomb interaction, assuming a dielectrically homogeneous system. Dotted lines include the Coulomb interaction considering dielectric mismatch.

**Figure S13** shows the resulting optical transitions considering an independent-particle approximation ($H_e + H_h$, solid line), considering Coulomb interactions in a dielectrically homogeneous system with $\varepsilon_{\text{in}} = \varepsilon_{\text{out}} = 10$ (dashed line), and Coulomb interactions in a realistic, dielectrically mismatched, system (dotted line). Compared to the independent-particle results, the Coulomb interaction redshifts the peaks by $\sim 0.1$ eV (dashed lines). This shift arises from the large exciton Coulomb binding energy, $V_{e-h}$, which overcomes the additional kinetic energy from the electron-hole relative motion, $a_B^2/2\mu_p$. A more realistic situation, however, requires adding dielectric mismatch between the NPLs and the environment. While this enhances the binding energy, $V_{e-h}$, it has an even stronger effect in the repulsive self-energy, $V_{e\text{self}} + V_{h\text{self}}$. A net blue shift is obtained compared to the case of the bare Coulomb interaction (dashed lines). **Figure S13** reveals that this behavior, which was recently observed for the exciton ground state, is even more pronounced for excited states, where the blue shift results in a shift back to similar energies as the independent-particle calculations. This is because the excited states have a larger density charge near the semiconductor/ligand interface, and hence are more sensitive to image charges.
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