Supporting information for

Simultaneous Photonic and Excitonic Coupling in Spherical Quantum Dot Supercrystals

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Experimental details

Nanocrystal synthesis

Materials: All reagents are purchased from Sigma-Aldrich and are used as received. 1-Octadecene (ODE, technical grade), oleic acid (OA, technical grade), CdO (≥ 99.99% trace metals basis), selenium (powder ~ 100 mesh, 99.99% trace metals basis), trioctylphosphine (TOP), hexane (reagent grade), and ethanol (200 proof, reagent grade).

Summary: CdSe nanocrystals were synthesized according to the recipe from Chernomordik et al.1 with minor modifications. A brief description of the synthetic approach follows below.

Precursor preparation: A 1M TOP:Se complex is made by stirring 0.790g (10mmol) of Se powder in 10mL of TOP in a nitrogen-filled glovebox for overnight. All of the Se powder should be dissolved to form a transparent, yellow-tinted solution before use in the synthesis. Prior to synthesis, 3mL of the 1M TOP:Se is mixed with 7mL of ODE and loaded into a glass syringe placed in a syringe pump set for a rate of 10mL/hour. The cadmium oleate precursor solution is prepared by mixing 0.512g of CdO, 6.28g of OA, and 25g of ODE (32mL) in a 100mL round-bottom flask. While stirring, the reagents are degassed at 100°C for one hour. Afterwards, the flask atmosphere is switched to nitrogen and the temperature is raised to 260°C. The temperature is held constant until the color of the mixture changes from dark-red to colorless, indicating the formation of cadmium oleate. Subsequently, the temperature was dropped to 100°C and the flask was placed under vacuum for 30 minutes. This is done to remove the water produced during the reaction. After switching the atmosphere again to nitrogen, the temperature was raised to 260°C. Meanwhile, 0.063g (0.8mmol) of Se powder is added to 5mL of ODE and sonicated for 20 minutes.

Nanocrystal synthesis: The Se/ODE mixture is injected at 260°C by using a 22mL plastic syringe equipped with a 16G needle. Immediately thereafter, the temperature controller is set to 240°C. After 60 seconds from injection, the TOP:Se/ODE solution is added dropwise at a rate of 10mL/hour. After 60 minutes, the reaction is quenched by removing the heating
mantle and dropping the flask in a container full of water at room-temperature. Note: the 1 hour time yields the nanocrystals with the lowest polydispersity. The reaction mixture is split into enough 50mL centrifuge tubes such that there are 5mL of mixture in each tube. Approximately 20mL of hexane is added to each tube and each tube is then capped and vortexed. 25mL of ethanol is added to each tube, and the tubes are centrifuged at 8000g for 5min. Often, this first precipitation results in a slightly colored supernatant and it is discarded while keeping the precipitated QDs. The QD product is washed twice more by dispersing each QD precipitate in 10mL of hexane, and then precipitating with an equal volume of ethanol. After the final wash, the QD product is dispersed into hexanes at 50mg/mL and filtered by using a 200nm PTFE or PVDF syringe filter. Note: in absence of 200 proof ethanol, we suggest using a mixture of 3 : 1 isopropanol:ethanol.

**Small-angle X-ray scattering**

Small angle X-ray scattering patterns were collected using a Pilatus 1M detector at BM26B beamline, DUBBEL at ESRF. The duration of each measurement was set to 100 seconds collection time. The sample to detector distance was set to 2.9m, achieving a q-range of 0.001 − 4nm⁻¹. The beam energy was set to 12keV.

The wavevector is defined as \( q = \frac{4\pi}{\lambda} \sin (\theta/2) \), where \( \lambda \) is the wavelength of incident X-rays and \( \theta \) is the scattering angle. The form factor was extracted by fitting the experimental scattering pattern of diluted CdSe quantum dots in hexane to a spherical form factor \( F \):

\[
F(q, r) = 3V(r)\frac{(\sin (qr) - qr \cos (qr))}{(qr)^3}
\]

where \( r \) is the particle radius and \( V(r) \) is the volume of a sphere of radius \( r \). To account for size dispersion, we averaged over form factors of radius \( r \) varying around an average value \( r_0 \) where the contribution of each form factor was weighed with a Gaussian distribution \( G(r, r_0, W) \) centered around \( r = r_0 \) and of width \( W \). The result is:
\[ F_{G}(q, r_0, W) = \int_{0}^{+\infty} F(q, r)^2 G(r, r_0, W) dr \]

The fitting procedure was performed either using self-developed code in Matlab, or using Sasfit software. The polydispersity was calculated as \( PD(\%) = 100W/(2r_0) \). The mean crystalline domain size \( \xi \) was determined through the Scherrer equation as \( \xi = 2\pi K/\Delta q \), where \( K = 1 \) is the Scherrer constant for a spherical shaped crystals and \( \Delta q \) is the full-width at half-maximum of the 111 peak of the face-centered cubic diffraction pattern.

### Electron microscopy

For low resolution electron microscopy, we used a Verios XHR SEM microscope (FEI). The microscope was operated at 30\(kV\) and 100\(pA\). Bright field images, collected in transmission mode using a STEM detector, and secondary electron images, were collected simultaneously to investigate the internal and surface structure of the supercrystals, Figure S6 c-d. For high resolution electron microscopy, we used a Technai F20 TEM with field emission gun operating at 200\(kV\). The microscope has a 1.2mm Cs and is equipped with a Gatan UltranScan 1000P CCD camera. Magnification and focus were varied in order to yield information about the crystal structure and super structure of the particle sytems. In all cases, fast-Fourier transforms of the images were extracted by using ImageJ.

### Mie theory

#### Software

Mie theory calculations on dielectric spheres were done using MatScat, an open source software available at https://nl.mathworks.com/matlabcentral/fileexchange/36831-matscat. The Mie calculations of energy density and field were independently verified using finite element modelling (COMSOL Multiphysics 5.2). We also tested the behavior of Mie resonances for spheroids of different aspect ratios by using SMARTIES, another open source
Refractive index input

The complex refractive index for CdSe QDs was derived from ellipsometry data available in the literature by Diroll et al. for 5.1 nm CdSe QDs capped with oleic acid,\textsuperscript{10} blue shifting the spectra by 8 nm to match the position of the first exciton peak in our samples. Specifically, the complex refractive index, \( \tilde{n} = n + ik \), is reported in the supplementary spreadsheet of the publication of Diroll et al., page 1, columns A (wavelength, \( \lambda \)), T (real part of the refractive index, \( n \)), and U (imaginary part of the refractive index, \( k \)).\textsuperscript{10} The value of the refractive index used for the near-field simulations was: \( \tilde{n}(\lambda = 400\text{nm}) = n + ik = 1.8173 + i0.0916. \) The complex refractive index for silicon was also determined from the literature.\textsuperscript{11}

Whispering gallery modes (WGM)

According to Mie theory, the largest superstructures in the ensemble studied in this work should display a number of whispering gallery modes (WGM). In a typical high index, micron-size Mie particle, the WGM are expected to be narrow (high quality factor), and sparse (large free spectral range). However, in between these sharp resonances, the response is dominated by broader features due to the non-resonant part of all the multipoles, and not by any particular WGM. At the slightest loss, deformation, or polydispersity the WGM signature would disappear. The QDs employed in this work are lossy, as the imaginary part of the refractive index is greater than zero, contributing in part to this effect. The study of individual superstructures allows us to exclude polydispersity as a cause for the disappearance of WGM resonances. In Figure S8, we investigate the role of the silicon substrate (a) and of the superstructures’ aspect ratio (b). We show that even if the superstructures underwent a deformation to result in an aspect ratio lower than unity, the WGM resonances would shift but not disappear. However, the presence of the silicon substrate employed in
this study quickly results in the disappearance of these sharpest resonances as the guided modes leak into the high-index substrate. Using a lower refractive index material as support and QDs with a higher photoluminescence quantum yield should mitigate the absorption losses.

**Photo-lithography**

The mask was custom-made by Delta Mask b.v., Enschede (The Netherlands). The mask is made of quartz, with a chromium coating. 12 x 12 mm single-side polished silicon substrates were cleaned in acetone, sonicated in water, followed by cleaning with base piranha (15 minutes at 75 °C), and a final 60s O2 plasma descum step (Oxford Instruments Plasma Technologies Plasmalab 80 Plus). Next the sample was spincoated with HMDS as adhesive layer, followed by spinning Ma-N1410 as optical resist. The target thickness was 1.5µm. Next we exposed using a Suss Mask aligner MA BA 6(365 nm i-line) at a nominal dose of 325 mJ/cm². After development, the sample was evaporated with 15 nm of Cr after development using PVD (Polyteknik Flextura M508E) and lift-off was done in 1-methyl-2-pyrrolidone at 60°C.

**Ensemble optical absorption measurements**

Optical absorption spectra were measured using a Perkin Elmer Lambda 950 UV/Vis/NIR spectrophotometer with integrating sphere. A 5g/L dispersion of supercrystal in 6g/L sodium dodecyl sulfate in water was drop-casted on a quartz substrate. The measurement was performed by placing the substrate at the front of the integrating sphere, so to allow for the collection of transmitted and forward-scattered light.
Single supercrystal dark-field microscopy

We perform reflective dark field microscopy using a home-built setup that is based on a Nikon universal illuminator unit (Nikon LV-UEPI 2 system) and a 100W halogen lamp, equipped with objectives from the CFI LU Plan Fluor BD series (20x NA 0.45, 50x NA 0.8, and 100x NA 0.9). Samples are imaged with a $f = 200\text{mm}$ achromatic tube lens. Directly after the tube lens, a 70/30 beam splitter (Thorlabs BS022) directs 70% of the light onto the entrance facet of a collection fiber, while the remaining 30% is used to form an image on a CMOS color camera (Imaging Source DFK 21AU04). The collection fiber (Thorlabs M16L01, 50µm core, NA 0.22) is multi-mode, and leads to an Avaspec 2048TEC-2-USB2 spectrometer (thermo-electrically cooled 2048 pixel Si CCD, 600/mm grating, 75mm focal length). This spectrometer has a resolving power of around $0.3\text{nm/pixel}$ and a detection range from 500 to 1000 nm. No polarization optics are used. Spectra in this work are taken with the 100x objective, with illumination through the objective reflective mantle at angles just beyond the collection NA.

Sample preparation consisted in 2 minutes of plasma cleaning of the lithographically-patterned substrates, followed by spin-coating (1500rpm, 30s and 3000rpm, 10s) of a dispersion of CdSe QD supercrystals ($5 \times 10^{-3} \text{g/L}$) in water (sodium dodecyl sulfate 6g/L).

The measurement protocol consisted of:

- finding a supercrystal previously imaged by SEM using the lithographically patterned substrate;
- focusing and collecting the dark field signal from the supercrystal by integrating for a time $\Delta t$: $I_{\text{sample}}(\lambda, \Delta t)$;
- collecting the reference dark field signal from the silicon substrate in proximity of the location of the supercrystal: $I_{\text{substrate}}(\lambda, \Delta t')$;
- calculating the background subtracted signal from the supercrystal as: $I_{\text{sample,bs}} = \frac{I_{\text{sample}}(\lambda, \Delta t)}{\Delta t} - \frac{I_{\text{substrate}}(\lambda, \Delta t')}{\Delta t'}$.
• correcting for the wavelength-dependence of the source, optics, and CCD by measur-
ing the dark field signal from a broad-band light-scattering target, namely a glass
coverslip coated with a thick layer of white paint for integrating spheres: \( I_{ref,bs} = I_{ref}(\lambda, \Delta t'')/\Delta t'' - I_{substrate}(\lambda, \Delta t')/\Delta t' \). The corrected dark-field signal from the su-
percrystal then reads: \( I_{sample,corrected} = I_{sample,bs}/I_{ref,bs} \).

**Transient absorption**

Femtosecond transient absorption (TA) measurements were based on a 5 kHz Ti:sapphire
femtosecond amplifier (Spectra Physics Solstice-Ace) which produces 75 fs pulses peaking
at \( \lambda = 800\,nm \) (FWHM=30 nm) at 350\( \mu \)J/pulse. This beam is split in two parts by a
beam splitter (80%/20%) to generate the pump and the probe, respectively. The pump
(\( \lambda = 400\,nm \)) is produced by frequency-doubling the fundamental \( \lambda = 800\,nm \) (type I phase-
matching) in a 250\( \mu \)m \( \beta \)-BBO crystal. The pump beam is chopped at 500 Hz and focused on
a 200\( \mu \)m light path quartz flow cell by a parabolic mirror with \( f=150 \) mm. Its polarization
is controlled by a waveplate. A probe beam consists of a supercontinuum pulse (\( \lambda = 400 –
700\,nm \)) generated by focusing the \( \lambda = 800\,nm \) beam on a \( D_2O \)-filled 1\( \text{mm} \) light path quartz
cuvette. The probe is focused on the sample by the same parabolic mirror used to focus
the pump. The pump-probe delay is controlled by a motorized delay stage which yields a
temporal resolution of 70 fs. The probe and the pump overlap within the same portion of
the sample. After the sample, the probe beam is dispersed through a Brewster-angle silica
prism and focused on the detector by a lens. The spectral resolution is 3 nm. Pump and
probe are synchronized with a camera detector system with 1024 pixels (Glaz Linescan-I)
with single-shot capability. A typical signal is obtained by averaging 5000 pumped and 5000
unpumped spectra for each delay, and scanning over the pump-probe delay 40 times. A
schematic of the setup is shown in Figure S9.
Supplementary figures

Figure S1: QD supercrystals. (a) Histogram of the diameters of QD supercrystals as determined by the dark-field STEM micrograph shown in (b). Dark-field STEM (c) and secondary electron (d) micrographs of a single supercrystal showing supercrystal fringes and surface details, respectively.
$u_E$, $\lambda = 400$ nm, $\sigma = 550$ nm

Figure S2: Map of the electric field energy density, $u_E \sim n(\lambda)^2|E|^2$, within and in proximity of a QD supercrystal of diameter $\sigma = 550$nm for $\lambda = 400$nm. The geometric cross section of supercrystal is outlined by a dotted white line. The directions of the incident plane wave, $k_{inc}$, and of the electric field, $E$, are specified for three different planes. Scale bars indicate $\lambda/2$. 

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Figure S3: **Size-fractionation of QD supercrystals.** (Top left) A dispersion of polydisperse QD supercrystals in 6g/L sodium dodecyl sulfate, SDS, in water is gently layered on a 1:1v/v mixture of water and glycerol, 6g/L SDS. Under the effect of gravity, the polydisperse supercrystals separate according to size. The fractions were collected after 1 hour of fractionation by gently removing 1mL of dispersion per fraction from the top of the mixture. The excess glycerol was removed by 3 cycles of centrifugation and redispersion in 6g/L SDS in water. (Right) SEM micrographs of fractions of increasing average size of QD supercrystals. (Bottom left) Average hydrodynamic diameter, $\sigma_H$, measured with dynamic light scattering (DLS) on the collected fractions. The average size of supercrystals increases with fraction number until saturation. The saturation is likely due to the dominance of sedimentation over diffusion of the largest supercrystals whose size cannot therefore be estimated by using DLS.
Figure S4: Absorption spectra of size-fractionated QD supercrystals. Details of the fractionation process are reported in Figure S3. The absorption spectrum of dispersed QDs is also reported for reference (solid black line).
Figure S5: **Simplified dark-field setup schematic.** (Left and top-right) Schematics of setup’s geometry. An incident beam of white light impinges at an angle $\theta_i$ on the QD supercrystals deposited on a silicon substrate. The collection angle $\theta_c < \theta_i$ purposely misses the reflected beam to allow for a dark-field measurement. (Bottom-right) Representative SEM micrographs of a QD supercrystal at intermediate (left) and high (right) magnifications.
Figure S6: Photo-lithographically patterned silicon substrate used to correlate optical properties of individual supercrystals (measured using dark-field microscopy, DF) with their diameters (measured using scanning electron microscopy, SEM). (a) Overview of the checkerboard pattern labeled ‘A’. The light areas describe a 3nm layer of chromium sputtered on silicon. Each square has a side of 100µm and each side is 10µm wide. (b) The same checkerboard pattern after spin-coating a 0.005g/L dispersion of CdSe supercrystals in 6g/L sodium dodecyl sulfate in water. Excess surfactant is visible on the substrate. (c) Detail of the square labeled ‘A1’. A single supercrystal is visible at the top of the image. (d) Detail of the supercrystal. Supercrystal diameter: σ = 1480nm. The insets show images of the same supercrystal collected under bright field (BF) and dark field conditions.
Figure S7: Map of the scattering efficiency of CdSe QD supercrystals as a function of excitation wavelength, $\lambda$, and supercrystal diameter, $\sigma$, as modeled from Mie theory. The dotted white line describes the imaginary part of the refractive index of QDs used in the modeling, $k$. 
Figure S8: **Effects of surrounding medium and aspect ratio on the scattering cross section of individual QD supercrystals.** (a) We modeled the influence of the silicon substrate by calculating the absorption cross section of a supercrystal embedded respectively in air and silicon, and performing a weighted average to simulate the experimental condition of a supercrystal in air deposited on a silicon substrate. The presence of a silicon medium in proximity of the supercrystal dampens the sharper resonances of the spectrum. This likely explains why we do not observe these sharper resonances experimentally. (b) Altering the aspect ratio of the supercrystals alters the theoretical scattering cross section. A 5% deviation from 1 already causes a significant shift in the peak position of the resonances, while also broadening the local minimum corresponding to the first exciton peak of the nanocrystals. Since we do not observe neither of these conditions, we conclude that the aspect ratio is not altered by deposition of the supercrystal on a substrate. Supercrystal diameter, calculated as the average of the long and short axes of the ellipsoid: $\sigma = 2187\, nm$. 
Figure S9: **Schematic of the experimental setup of transient absorption ultrafast spectroscopy.** The ultrafast 800nm pulses generated by a Ti:sapphire laser are split by a 80% – 20% beamsplitter. The high power beam is doubled in frequency by using a BBO crystal and used to pump the sample. The low power beam is used to generate the white light probe beam. The dispersion of supercrystals is continously flowed through a microfluidic cell to avoid irradiation-induced sample damage.

Figure S10: 2D maps of the normalized negative transient-absorption signal relative to the samples treated in the main text.
Figure S11: **Size-separated SCs with the smallest diameters available.** (a) Low-magnification scanning electron micrograph of size-separated QD supercrystals of the smallest average size available. These supercrystals were size-separated by centrifuging the dispersion of polydisperse supercrystals at 10000g for 10 min. (b) Histogram of supercrystal diameters. Average diameter: 130 nm. (Inset) Close-up of an individual QD supercrystal of \( \sim 100 \text{nm} \) diameter.

Figure S12: **Cooling kinetics for the samples discussed in the main text.** Pump-probe kinetics traces recorded at \( \lambda = 620 \text{nm} \) with the least-squares fitting curves for all samples discussed in the main text. The kinetics are fit to a superposition of four exponential components \( \sum_{i=1}^{4} A_i \exp \left( -t/\tau_i \right) \) of which the fastest one describes state filling (exponential rise) and the slower ones describe charge carrier recombination (exponential decays). The time constant describing state filling amounts to \( \tau = 0.7 \text{ps} \) for samples 1, 2, 3, 5, and 0.6 ps for sample 4.
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