Supporting Information for

Controlling Superstructure-Property Relationships via Critical Casimir Assembly of Quantum Dots

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Chemicals: 1-Octadecene (90%, Aldrich), Acetonitrile (MeCN, anhydrous 99.8%, Sigma-Aldrich), Cadmium oxide (≥99.99%, Aldrich), Ethanol absolute (99.6%), Hexane (anhydrous 95%, Aldrich), MilliQ water, N-methylformamide (NMF, >99.0%, TCI Europe), Oleic acid
(90%, Sigma Aldrich), Selenium (≥99.99%, Strem Chemicals), Triocetylphosphine (TOP, 97% Aldrich), 2,6-dimethylpyridine (redistilled, 99+%, Sigma Aldrich).

**QD synthesis:** CdSe QDs were synthesized and washed by following the literature, with minor modifications. Relevant modifications to the published recipe were: (1) we added the TOP:Se in ODE solution at a rate of 10 mL/hour by means of a syringe pump; (2) the reaction flask was quenched by means of a cold water bath as soon as the injection was completed. The monodispersity of the product was qualitatively and quantitatively addressed by measuring respectively the full-width half-maximum of the first exciton peak in the absorption spectrum, electron microscopy and SAXS form factor extracted from dilute dispersions. The concentration of CdSe quantum dots was estimated from sizing curves available in the literature.

**Ligand synthesis:** \((\text{NH}_4)_4\text{Sn}_2\text{S}_6\) ligands were synthesized by following the literature, with minor modifications. Specifically, (1) we found important washing the SnS\(_2\) thoroughly to remove excess NaCl; (2) to speed up the reaction (average time to completion was 1 hour), we sonicated the dispersion of SnS\(_2\) powder in \((\text{NH}_4)_2\text{S}\) in water rather than stirring it. The final solution (100 mM ligand in H\(_2\)O) is clear and light brown-yellow and was filtered with an 800 nm MCE filter to remove unreacted SnS\(_2\).

**Ligand exchange:** Native oleate ligands were replaced with thiostannate complexes adapting the procedure reported in the literature with minor modifications. Briefly, we mixed the ligand solution in H\(_2\)O with NMF to obtain a 40 mM concentration of ligands in NMF/H\(_2\)O mixture. We layered an equal volume of CdSe QDs in hexane at a concentration of 40 μM on top of the
polar mixture. We stirred the two-phase system for about 20 minutes until all the QDs had migrated to the polar phase following ligand exchange. The apolar phase was colourless at the end of the exchange. To wash the QDs, we transferred the polar phase containing the QDs to a centrifuge tube and mixed it with an equal volume of MeCN, followed by centrifuging at 3000g for 15 minutes. This resulted in the QDs to precipitate. We redispersed the QDs in binary mixture by adding a solution of 32% v/v Lutidine in H₂O to the dry pellet and vortexing the centrifuge tube vigorously for 1 minute; after redispersion, we filtered the dispersion with a 200 nm PTFE syringe filter. Ligand exchange was always carried out immediately prior to assembly experiments. This is due to the fact that QDs passivated with molecular ligands are colloidally metastable and begin aggregating spontaneously after several hours from the exchange. We have recently observed that this effect can be significantly reduced by adjusting the pH of the binary mixture adding 10 mM NaOH.

**Critical Casimir assembly:** We first study the phase separation of the solvent. We experimentally determine the phase separation temperature Tₛ of the binary solvent containing the QDs. We used a thermostated water bath with temperature control of 0.05 K and heated the prepared mixture, stored in a flame sealed NMR tube, until opalescence was detected and the sample turned turbid. Such an effect is due to the onset of phase separation, namely the formation of light-scattering droplets, allowing to pinpoint phase separation temperature Tₛ precisely. After the determination of Tₛ, the assembly was carried out on a distinct, but identically prepared sample, by holding the binary mixture containing the QDs for a certain time t at a temperature T, and therefore resulting in ΔT=Tₛ-T. Prior to the assembly, a substrate was placed horizontally at the bottom of the vessel to collect the sedimented superstructures. The
choice of substrate depended on the type of characterization technique: (1) carbon-coated copper grids for electron microscopy, (2) 1 mm-thick quartz substrates for spectrophotometry and time-resolved microwave conductivity, (3) patterned substrates for field-effect transistors.

**Electron microscopy:** For STEM studies we used a Verios XHR SEM (FEI). The microscope was operated at 20 kV and 100 pA in transmission mode using a STEM detector. Bright field and high angle annular dark field (HAADF) images were simultaneously recorded. We analyzed the STEM images by using ImageJ software to adjust the contrast and measure the diameter of QDs.

**Box-counting method:** The box-counting method was used by following a reported MatLab script with minor modifications. Namely, the script was modified to be able to independently measure the fractal dimension of several superstructures of size exceeding a certain threshold within the field of view. The magnification of micrographs used for box-counting was set to 50000x-100000x.

**Diffusion limited aggregation:** Diffusion limited aggregation structures with variable sticking coefficient were generated via a code freely available online. Their fractal dimension $d_f$ was then measured via the box-counting method.

**Physical meaning of the fractal dimension:** Fractals are self-similar objects across different length scales, characterized by a fractal dimension $d_f \leq d$, where $d$ is the dimension of the surrounding space. If $d_f < d$, the object requires less particles to percolate space. By contrast, as $d_f \to d$ the density of the object increases, minimizing empty volume.

The superstructure fractal morphology does not appear to change significantly during growth (Figure S1); This is consistent with expectations from DLVO theory. The probability, $p$, of two particles irreversibly binding upon collision determines the number of morphological
The superstructure will explore during growth. If $p \ll 1$, the superstructure can undergo restructuring during the assembly, assuming progressively more compact morphologies, increasing in fractal dimension and decreasing in free energy. Consequently, the interparticle potential determining $p$, in turn also determines the final morphology and fractal dimension of the superstructure: $d_f = d(f(p))$. Since both the electrostatic repulsion from the charged ligands and the solvent-mediated Casimir attraction are unchanged during the course of the assembly, we do not expect the superstructures’ morphology to evolve in time.

The value of the fractal dimension of a superstructure provides insight in the interparticle potential experienced by the QDs during assembly. High fractal dimension superstructures $d_f \approx d$ are desirable in a device to maximize the number of conductive paths. One of the most used methods to measure the fractal dimension of an object is box-counting. This method consists in counting how many $N \geq 1$ non-overlapping squares of side length $\ell$ are needed to completely cover an object of size $L \geq \ell$. The dependence of $N$ on $\ell$ is determined by varying the size of the box; for a fractal, $N \sim \ell^{-d_f}$. By using the box-counting method on a QD superstructure assembled at $\Delta T = 7.8$ K for 84 hours, we directly reveal the fractal nature of the object, obtaining $d_f = 1.73$ (Figure 3a). To understand the physical meaning of this value, we run two-dimensional diffusion-limited aggregation simulations, where diffusing particles irreversibly stick upon collision with a probability $0.001 \leq p \leq 1$ (Figure S5). Structures that grow with $d_f \approx 1.73$ correspond to a sticking probability of $p \approx 0.01$-$0.02$, meaning that two particles will only irreversibly bind 1-2 times per 100 collision events.

**Spectrophotometry:** Optical absorption spectra in the visible/near infrared range were measured using a Perkin Elmer Lambda 950 UV/Vis/NIR spectrophotometer.
**Time-resolved microwave conductivity:** The samples’ photoconductivity was measured using the time-resolved microwave conductivity (TRMC) technique. A detailed description of the technique and methods can be found elsewhere.\(^{10}\) The 1 mm thick quartz substrate was placed in a microwave cavity driven at 8.5 GHz, and illuminated at a wavelength of 630 nm, 3 ns pulsed Nd:YAG laser at a 10 Hz repetition rate. The change in microwave power is measured and averaged over 1-10 minutes depending on the photon flux. The photon flux is reduced with a series of neutral density filters (increasing the averaging time with decreasing photon fluence) from \(10^{15}\) to \(10^{13}\) cm\(^{-2}\) to determine where higher order recombination processes no longer limit the signal. The mobility values reported here are given at a photon fluence where the mobility is independent of fluence (~ \(10^{14}\) cm\(^{-2}\)).

**Field-effect transistors:** Bottom gate/bottom contact field-effect transistors were fabricated on Si/SiO\(_2\) wafers carrying ITO/Au electrodes (Fraunhofer) with a channel width of 10 mm and length of 2.5 \(\mu\)m. The wafers were cleaned by sonication in acetone (10 minutes) and isopropanol (10 minutes) before sample deposition. The electrical measurements were performed using a Keithley 4200SCS Semiconductor Characterization System in a nitrogen-filled glovebox. The samples were briefly heated to 120ºC to remove any adsorbed water. The mobilities were extracted using the gradual channel approximation in the saturation regime.\(^{11}\)

**Atomic force microscopy:** The samples prepared on the FET-substrates were used for obtaining morphology data; areas near the measured devices were chosen for reliability. The topology of
the different films was characterized using a WITec Alpha SNOM-AFM equipped with a 40 N/m tip, operated in tapping mode in air.

**Small-angle X-ray scattering:** Small angle X-ray scattering patterns were collected using a Pilatus 1M detector at BM26B beamline, DUBBLE at ESRF. The duration of each measurement was set to 100 seconds collection time. The sample-to-detector distance was set to 2.9 meters, achieving a q-range of 0.001–4 nm$^{-1}$. The beam energy was set to 12 keV. The wavevector is defined as $q=4\pi\lambda\sin(\theta/2)$, where $\lambda$ is the wavelength of incident X-rays and $\theta$ is the scattering angle.

**QD characterization:** After background subtraction and azimuthal averaging, the form factor was extracted by fitting the experimental scattering pattern of diluted CdSe quantum dots in hexane $I_{QD}(q)$ to a spherical form factor $F$:

$$F(q,r)=3V(r)\left(\frac{\sin(qr)-qr\times\cos(qr)}{qr^3}\right)$$

where $r$ is the particle radius, $q$ is the wavevector 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:

$$F_G(q,r_0,W)=\int_{0}^{+\infty}F(q,r)^2 \times G(r,r_0,W)dr$$
Fitting procedure was performed either using self-developed code in Matlab, or using Sasfit software.\textsuperscript{14} The polydispersity is calculated as $PD=100 \times W/(2r_0)$ \%. The structure factor $S(q)$ was obtained by dividing the scattering pattern $I(q)$ after background subtraction by the particle form factor:

$$S(q) = \frac{I(q) - I_{bg}(q)}{F_G(q,r_0,W)}$$

**Binary mixture characterization:** The size of solvent density fluctuations $\xi$ was determined as a function of temperature by measuring the scattering pattern $I(q)$ of the binary mixture at temperature $T$. The predicted behaviour is described by the Ornstein-Zernike relation:\textsuperscript{15}

$$I(q,\Delta T) = \frac{I(0)}{1 + [q \times \xi(\Delta T)]^2}$$

The value of $\xi$ can be extracted by plotting $I(q)^{-1}$ as a function of $q^2$ and performing a linear fit.

**Pair-potential modeling:** The pair-potential was calculated as a sum of three components:

**Van der Waals attraction:** This component was modeled following the literature:\textsuperscript{16,17}

$$\frac{U_{vdW}}{k_B T} = -\frac{A}{3k_B T} \times \left\{ \frac{(\sigma_{QD}/2)^2}{4(\sigma_{QD}/2)d + d^2} + \frac{(\sigma_{QD}/2)^2}{(2(\sigma_{QD}/2) + d)^2} + \frac{1}{2} \ln \frac{4(\sigma_{QD}/2)d + d^2}{(2(\sigma_{QD}/2) + d)^2} \right\}$$

where $\sigma_{QD}=6.5$ nm is the diameter of the quantum dots, $d$ is the interparticle distance, $k_B$ is Boltzmann’s constant, $T$ is the temperature, and $A$ is the Hamaker constant. The latter was calculated following the
literature for semiconductor particles interacting through a dielectric medium:\textsuperscript{16,17}

\[
A = \frac{3}{4} k_B T + \frac{3h\nu_m}{16\sqrt{2}} \frac{\left(\sqrt{2} + c\right)^3 - \left(\sqrt{2} + 2c\right)\left(n^2 - 1\right) + \frac{\left(n^2 - 1\right)^2}{c}}{\left(\left(\sqrt{2} + c\right)^2 + n^2 - 1\right)^{3/2}}, \quad c \equiv \nu_m/\nu_d
\]

where $h$ is Planck’s constant, $n$ is the refractive index of the dielectric medium and $\nu_m$ and $\nu_d$ are the main electronic absorption frequencies in the UV for the constituent material of the particles and of the dielectric medium, respectively.\textsuperscript{17}

Being unable to find a value for CdSe, we take the value for CdS as an approximation, $\nu_m = 1.1 \times 10^{15} \text{s}^{-1}$.\textsuperscript{18} For the dielectric medium, we take the value for water: $\nu_d = 3.0 \times 10^{15} \text{s}^{-1}$.\textsuperscript{17}

**Electrostatic repulsion:** This component was modelled following the literature:\textsuperscript{3,19}

\[
U_{ES} = \frac{\pi \varepsilon_0 \sigma_Q \zeta^2}{k_b T} \exp\left(-\frac{d}{\lambda_D}\right)
\]

where $\varepsilon_0$ is the vacuum permittivity, $\varepsilon \approx 75$ is the dielectric constant of the binary mixture calculated as molar average, $\zeta = -40 \text{ mV}$ is the zeta potential, $\lambda_D = 4.8 \text{ nm}$ is the Debye screening length (calculated assuming that 1\% of the initial concentration of free ligands is still present in solution after washing). A study in the literature reported the zeta potential to lie in the range of -50 to -80 mV.\textsuperscript{3} We experimentally measured -30 mV in NMF (data not shown).
Critical Casimir attraction: For the critical Casimir potential we have used the expression calculated assuming the Derjaguin approximation is valid (\(\xi/\sigma_{\text{OD}} < 1\)): \(^{20}\)

\[
\frac{U_{\text{CC}}}{k_B T} = -\frac{\pi \sigma_{\text{OD}}}{\xi} \exp \left( - \frac{d}{\xi} \right)
\]

This approximation does not strictly hold under these experimental conditions, since \(\xi/\sigma_{\text{OD}}\) ranges between 0.3 and 3. We assume that the general behaviour of the potential still holds, especially for what concerns the length scale of attraction, allowing us to make some qualitative considerations on the total pair potential. The correlation length was extracted by interpolating the experimental data of Figure S2d.
Figure S1. Top: Bright-field STEM micrographs portraying a snapshot, in time, of the growing superstructures at $\Delta T=7.8$ K after deposition on the TEM grid. Bottom: zoomed-in and zoomed-out micrographs. Individual QDs are clearly visible, 6.5 nm in diameter, and appear to assemble in a disordered fashion. As the assembly proceeds, QD superstructures grow further to reach the micrometer scale, and eventually sediment onto the substrate (Figure 1). After 24 hours, the TEM grid appears completely covered with QD superstructures.
Figure S2. **In situ small-angle X-ray scattering (SAXS).** (a) Form factor $P(q)$ for a dispersion of CdSe QDs ($r_{\text{QD}}=1.44$ nm) in hexane (black curve). Evolution in time of the structure factor $S(q)$ for a dispersion of the same dots in a critical Casimir solution, colored curves ($c_{\text{Lut}}=30\%$, $\Delta T=0.2$ K). The structure factor decreases in intensity over time and changes in shape. The development of a power law-like behaviour around $0.1 \text{ nm}^{-1}$ can be ascribed to an increase in fractal dimension since for a fractal: $S(q)\sim q^{-d_f}$. We observe this behaviour only in a very limited range of $q$. We attribute this to the strongly scattering solvent density fluctuations (d),
complicating the decoupling of scattered signal from the nanoparticles and solvent. (b) Evolution in time of the Kratky plot. The area under the curve is proportional to the concentration of QDs in solution. The decrease in time indicates sedimentation. (c) Time evolution of the fractal dimension as extracted from the slope around 0.1 nm\(^{-1}\) in (a), circles. Time evolution of the concentration of QDs in solution as determined from (b), relatively to the first time point (squares). Between 60 and 90 minutes QDs begin to sediment (drop in concentration); simultaneously, the observed fractal dimension starts to increase, settling at a value of \(d_f \approx 1.7\) at the end of the experiment. (d) Measured solvent correlation length \(\xi\) as a function of the distance in temperature \(T_s - T\) from the phase separation temperature \(T_s\). \(\xi\) is experimentally extracted from the azimuthally averaged scattering patterns \(I\) of a binary mixture recorded as a function of temperature, and plotted against the square of the scattering vector \(q\). The Ornstein-Zernike relation predicts a behaviour of the type \(I(0)/I(q) = 1 + (\xi q)^2\).\(^{15,22}\) Inset: Raw data used to extract \(\xi\) as a function of temperature.
Figure S3. TRMC results. A) Yield times the sum of electron and hole mobility versus the absorbed fluence for the TRMC measurements in the open cell configuration. B)-F) Decay transients for the different ΔT values used in the assembly process. The traces are color-coded in order of the rainbow going from highest fluence in red to lowest fluence in purple with the peak value of each trace is plotted in panel A.
Figure S4. Selected FET curves. (a) Output curves of a device prepared with $\Delta T=7.8$ K showing n-type characteristics; (b) transfer curves of representative devices prepared at different temperatures, measured at 25 V channel bias.
Figure S5. Simulations of diffusion limited aggregation. (a) Simulated structures using two-dimensional diffusion limited aggregation, with variable sticking probability. As the sticking probability decreases, the structures appear more and more compact (higher fractal dimension). (b) Measured two-dimensional fractal dimension values of structures shown in (a), red dots. These values can be converted to three-dimensional fractal dimension values, blue dots. The mass density $d_m$ of structures is also shown, black dots: $d_m = \log(n)/\log(r)$, where $n$ is the total number of particles composing the structure and $r$ is the largest radius enclosing the structure.
Supporting references:


(7) Diffusion Limited Aggregation in 2 Dimensions with a Radial Creation Radius and Variable Stick Probability.


