Coupled Colloidal Quantum Dot Molecules

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Abstract

Coupling of atoms is the basis of chemistry, yielding the beauty and richness of molecules. We utilize semiconductor nanocrystals as artificial atoms to form nanocrystal molecules that are structurally and electronically coupled. CdSe/CdS core/shell nanocrystals are linked to form dimers which are then fused via constrained oriented attachment. The possible nanocrystal facets in which such fusion takes place are analyzed. Coherent coupling is manifested by a red shift of the band gap, in agreement with quantum mechanical simulations. Single nanoparticle spectroscopy unravels the attributes of coupled nanocrystal dimers. This sets the stage for nanocrystals chemistry to yield a diverse selection of coupled nanocrystal molecules constructed from controlled core/shell nanocrystal building blocks, which are of direct relevance for numerous applications in optics, displays, sensing and biological tagging.
Colloidal semiconductor Quantum Dots (CQDs) that contain hundreds to thousands of atoms have reached an exquisite level of control, side by side with gaining fundamental understanding of their size, composition and surface controlled properties leading to their technological applications (1). Inspired by molecular chemistry, in which functionality of molecules depends on how atoms couple, we apply similar concepts to enrich CQDs based materials. If CQDs were deemed as artificial atom building blocks (2, 3), how plentiful would be the selection of composition, properties and functionalities of the analogous artificial molecules? Herein we introduce the utilization of CQDs as basic elements in nanocrystal chemistry for construction of coupled colloidal nanocrystals molecules focusing on homodimer quantum dots (QDs), in analogy to homonuclear diatomic molecules.

Coupled quantum dots were prepared by means of molecular beam epitaxy (MBE) (4–6). However, MBE-grown double quantum dot structures exhibit some limitations. First, the size of MBE-grown QDs is larger than the colloidal ones, and the typically large distance between the QDs limits wave-function tunneling that yields coupling phenomenon. The resultant small energy scales of coupling confine their utility to low temperature operation in specialized cryogenic applications. Furthermore, MBE grown structures are inherently buried within a host semiconductor. In contrast, colloidal quantum dots are free in solution and accessible for wet-chemical manipulations through their surface functionalization. Using such knobs, CQD molecules were constructed by connection with DNA strands providing geometrical control (7), yet in such structures the linker DNA molecules form a barrier that minimizes quantum mechanical coupling. Addressing this limitation, core/multishell structures with concentric regions were first examples of coupling within CQDs architectures, where the wave-functions of two well regions within such NCs may interact leading to CQDs showing dual emission peaks (8). Other examples constitute synthesis of dot-in-rod structures and growing an additional quantum dot region on the rod apex thus yielding a coupled system (9), and dumbbell architectures (10). However, these progresses were either restricted by specific morphologies (11), specific materials and relatively large coupling barrier distance and height (12–14). Therefore, there is a lack of a general approach for producing coupled CQDs molecules in which there is flexibility to tailor the potential energy landscape and to tune the coupling strength.

To this end we introduce a facile and powerful strategy for coupled CQDs molecules with precise control over the composition and size of the barrier in between them to allow for tuning their electronic coupling characteristics and optical properties. This entails the use of core/shell CQDs as artificial atom building blocks. In terms of the band gap engineering, in first instance, tuning the core size is used to manipulate the wave-functions and energies of the electron and hole. On top of this, further control is afforded by the synthesis of shells on these cores. While the chemical bond is the basis for combining
atoms in molecules, connecting CQDs has to occur through adjoining of their crystal faces to form a continuous crystal. Thus, fusing two core/shell CQDs yields a homodimer with a tailored barrier dictated by the shell composition, thickness and fusion reaction conditions. We show below that such control yields coupled CQD dimers. This approach serves as a basis for a wide selection of CQD molecules utilizing the rich collection of the artificial atom core/shell CQD building blocks. Such CQD molecules bear significant promise for their utilization in numerous applications, including in light-emitting devices, displays, photovoltaics, quantum gates, biomedical sensors, electric field sensors, and more.

Exemplary coupled homodimer molecules were generated from CdSe/CdS core/shell (15, 16) CQDs via a procedure utilizing silica nanoparticles as a template for forming molecularly linked dimers (17), which are then fused via a high temperature reaction (Fig. 1a, full scheme in Fig. S1). Three different CdSe/CdS core/shell CQDs were studied (1.9/4.0 nm, 1.4/2.1 nm, and 1.2/2.1 nm core-radius/shell-thickness, see SI materials and methods for synthesis details and Fig. S2 for transmission electron microscopy (TEM) images and optical spectra). The TEM and high angle annular dark field (HAADF) scanning transmission electron microscopy (STEM) characterization manifests the wurtzite structure of the monomer CdSe/CdS QDs (Fig. S3). These CdSe/CdS CQDs were bonded via thiol linking to the surface of a SiO₂ nanoparticle template substrate (Fig. S4, S5). A second SiO₂ layer was grown for masking the remaining SiO₂ surface and to immobilize the bonded CQDs (Fig. S6), followed by treatment with a tetra-thiol linker (Fig. S7). Adding a second CQD leads to formation of a molecularly linked dimer structure (Fig. 1b, Fig. S8). Next, the SiO₂ template nanoparticles were selectively etched by HF treatment. Size-selective precipitation was used to separate a highly dimer enriched sample from monomers (Fig. 1c).
Fig. 1. **Coupled CQDs molecules.** (a) Scheme for fabrication of coupled CdSe/CdS CQD molecules. (b) The dimer@SiO$_2$ CQD structure. The dimer 1.9/4.0 nm CQD molecules (c) before, and (d) after the fusion procedure. (e) The 1.4/2.1 nm fused CdSe/CdS CQD molecules. Schematic structures are illustrated. Scale bars (b–e) are 50 nm and insets show higher magnification images. (f) The potential energy landscape and a cross-section of the calculated first electron wave-function without Coulombic interaction $\Psi_e$ (red), with Coulombic interaction $\Psi'_e$ (green) and hole wave-functions $\Psi_h$ (blue) of the coupled CQD molecules. (g) Calculated bonding and antibonding 2-dimensional electron wave-functions without (cross-section of the bonding state is the red curve in f) and (h) with Coulombic interaction (cross-section of the bonding state is the green curve in f). (i) Absorption and fluorescence spectra of monomers (blue), unfused (green), and fused 1.4/2.1 nm CdSe/CdS CQD molecules (red). (j) Calculated (red asterisk) and experimental (blue
circles) band gap red shift of monomer-to-respective-homodimer structures for CQD molecules with different core/shell dimensions.

The dimerization procedure yields a dimer structure with an organic insulating barrier. Hence, to achieve a coupled system a last step of fusion is required. The fusion procedure was performed while adding Cd-oleate and heating to 180 °C for 20 h. Fig. 1d-e presents the fused dimer structure after size selection procedure (Fig. S9-10). At this non-trivial important stage, the reaction parameters, including temperature, time and ligands type and concentration, have a significant influence on the coupled dimers formation. If the temperature was too high (above 240 °C), collapse of the dimer structures through linker bond cleavage may occur, as well as CQD ripening distorting the core/shell architectures. On the other hand, if the temperature was too low, the fusion rate would be too slow and inefficient. The dimer structure formation is also very sensitive to excess of ligands in the solution, which inhibits the fusion and leads to a decrease in the dimer yield. Therefore, careful tuning and choice of these reaction parameters is crucial for achieving high dimer yields and lower yields of dimer collapse and ripening, while achieving a continuous linking region of the shell materials forming the barrier between the two cores in the fused dimers. Further considerations of this important fusion step and the resultant interfacial structures are discussed later.

By dimer fusion, the potential energy landscape is changed and the monomer QD wave-functions may show hybridization (Fig. 1f), in analogy to homonuclear diatomic molecules. We utilized finite element software (COMSOL) to calculate the energy levels and wave-functions of the fused CdSe/CdS dimer and monomers within an effective-mass based approximation (Supplementary information and Table S1 for details). The conduction band in this system is demonstrating the fundamental textbook example of hybridization. According to this model, when the distance between two atoms is decreased, their wave-functions will hybridize to form a symmetric bonding state and anti-symmetric anti-bonding state with energy difference of twice the hopping energy. The bonding and anti-bonding electron wave-functions, which are in-phase and anti-phase superposition of the monomer wave-functions are presented in Fig.1g for the case of 1.4 nm core radius and a potential energy barrier between the dots of 4.2 nm (0.1eV band-offset), corresponding to the CQD molecules formed from 1.4/2.1 nm core/shell CQDs. Because of the quasi-type II nature of the CdSe/CdS interface, the monomers electron wave-functions are easily hybridized and leading to 23 meV energy spacing between the bonding and anti-bonding electron states. For the hole however, the valence band potential manifests a relatively high band offset of 0.64 eV, and this, combined with the heavier hole effective mass, yields minimal hole hybridization.

Considering the case of one exciton residing in the dimer and taking into account the Coulombic interaction between the electron-hole pair, since the hole wave-function is essentially not hybridized, the hole is in one of the dots and consequently the electron does not see a symmetric double QDs’ potential
anymore. The calculated two lowest energy levels wave-functions of the electron including the coulombic interaction are presented in Fig. 1h. One can see that the electron is localized in the dot which contains the hole as well. However, there is still significant tunneling-coupling observed for the electron wavefunction and a red shift is predicted. This is indeed confirmed experimentally in the emission and absorption spectrum, where only in the case of the fused dimer a red shift is observed compared to the monomer (603-607 nm in case of 1.4/2.1 nm core/shell QD), whereas, for the unfused organically linked dimer no red shift is seen (Fig. 1i, Fig. S11, and Table S2). Control of the monomer to dimer red shift is shown in Fig. 1j. While for the case of 1.2/2.1 nm core/shell CQDs the red shift is increased (13/14 meV calculated/experimental) due to the greater spill out of the electron wave-function to the shell because of the smaller core size. In the case of 1.9/4 nm core/shell CQD the red shift is negligible (0.5/0 meV calculated/experimental) because of the localization of the electron wave-function in the larger core.

We next consider further the nontrivial fusion stage and its consequences. Analysis by HAADF-STEM confirms that coupled dimer formation is indeed achieved based on fusion of the 1.9/4.0 nm core/shell QD monomers (Fig. 2). A continuous atomic lattice through the entire structure was formed upon fusing the two QDs shells (Fig. 2a). The core architecture in the coupled structure was maintained as demonstrated by the energy dispersive X-Ray spectroscopy (EDS) line scan measurement (Fig. 2b-c). A continuous distribution of Cadmium (both in core and shell) and Sulfur (only in shell) is identified along the line of the dimer axis. Along the same line, selective regions of the Selenium (only in core) are clearly identified signifying the cores locations.
**Fig. 2. Dimer Structure characterization and analysis.** HAADF-STEM image (a), EDS line scan data (b) and STEM-EDS (c) analysis of the coupled 1.9/4.0 nm CdSe/CdS molecules. Inset presents an atomic model. Scale bars 5 nm.

Underlying our fusion reaction strategy, is the process of oriented attachment - a crystal growth mechanism in which secondary mono-crystalline particles can be achieved through oriented and irreversible attachments of primary particles (18–24). In our case, dimers are first connected by molecular linkers, which constrain the initial relative crystal orientations between the two monomers. We studied this special case of “constrained oriented attachment”, and Fig. 3 shows exemplary orientation relationships observed for coupled molecules formed from the 1.9/4.0 nm CQDs and their detailed analysis. Both homo-plane and hetero-plane (misorientation) attachment relationships are observed. Homo-plane attachment orientation occurs via contact between homonymous faces (10\(\overline{1}0\)) and (10\(\overline{1}0\), (0002) and (0002), (10\(\overline{1}1\)) and (10\(\overline{1}1\)) (Fig. 3a-c, g, i, respectively), consistent with the CQD monomer crystal model built based on STEM analysis (Fig. S3). In such homo-plane attachment cases, both CQD monomers of a fused pair are projected under the same zone axis. This allowed accurate identification of fused faces at dimers orientated with its fusion axes normal to the projection zone axis (depicted in Fig. 3).
Hetero-plane attachment orientation is observed at fusion of heteronymous faces: $(0002) \parallel (10\bar{1}0)$ (Fig. 3e), $(0002) \parallel (10\bar{1}1)$, $(10\bar{1}1) \parallel (10\bar{1}0)$ (Fig. S12a,c).

**Fig. 3. Fusion orientation relationships in CQDs molecules.** Atomic structure model (a,d; Cadmium atoms - brown, Sulfur atoms - blue.), HAADF-STEM images (b,e), and FFT patterns (c,f) of the homo-plane (a-c) and hetero-plane (d-f) attachment of coupled CQD molecules with orientation relationship of attachment on $(10\bar{1}0) \parallel (10\bar{1}0)$ and $(0002) \parallel (10\bar{1}1)$, respectively. The HAADF-STEM (g, i) and atomic structure model (h, j) of homo-plane attachment on (0002), and $(10\bar{1}1)$ facets, respectively. Dashed orange arrows indicate the CQD fusion/molecular axis in plane of the image normal to projection $Z_A \parallel [\bar{1}2\bar{1}0]$. Note that for $(10\bar{1}0) \parallel (10\bar{1}0)$ homo-plane attachment, the homonymous $(10\bar{1}0)$ faces of A1 and A2 are
parallel (c), while for the hetero-plane attachment the heteronymous faces are parallel (0002)\textparallel(10\overline{1}0) (e).

(k) Distribution of observed homo- and hetero-plane attachment orientations on (10\overline{1}0), (0002), and (10\overline{1}1) faces. Inset shows the CQD model and faces.

The statistics of the orientation relationship within the CQD molecules is depicted in Fig. 3k (homonymous and heteronymous orientations are approximately equally abundant). The (10\overline{1}0)\textparallel(10\overline{1}0) and (0002)\textparallel(0002) face attachments are dominant, while the (10\overline{1}1)\textparallel(10\overline{1}1) attachment is much less common. This is consistent with an interplay between the relative reactivity, surface passivation and occurrence of the various faces on the monomer QDs. The (0002) facets, while in minority, manifest a Cd rich termination with 3 dangling bonds per atom, that can easily react with thiol linkers (25). Both (10\overline{1}0) and (10\overline{1}1) facets are plentiful but better passivated. However, linking to the (10\overline{1}1) facet is sterically hindered. The hetero-plane attachment statistics is also consistent with these considerations.

The generality of our formation strategy is well manifested also for the other CQD homodimers. Analytical and structural STEM analysis for the 1.4/2.1 nm core/shell CQDs are shown in Fig. 4 and Fig. S13, S14. Fusion conditions need to be tuned as smaller core/shell CQDs are more reactive. Therefore, shorter etching times were used, and also a shorter fusion process (~10h).
Fig. 4. Characterization of 1.4/2.1 nm CQDs molecule. Fourier filtered HAADF-STEM images of the coupled CdSe/CdS molecules with homo-plane attachment of (0002)||(0002) (a) and hetero-plane attachment of (10\overline{1}0)||(10\overline{1}1) faces (b). (c) EDS line scan data and (d) STEM-EDS analysis.

Further manifestations of coupling are observed in the fluorescence properties studied both in ensemble and as single particles, comparing monomers with unfused and fused dimers. For the 1.4/2.1 nm CQDs the fluorescence decays vary, with monomers showing a nearly single exponential lifetime of 25ns while fused dimers show nearly bi-exponential decay with a fast component of 5ns (Table S3). Unfused dimers show an intermediate behavior. Molecules of the larger 1.9/4.0 nm CQDs exhibit significantly smaller changes in lifetimes upon fusion, supporting the role of coupling in the variations observed for the 1.4/2.1nm CQDs (Fig. S15).

Fig. 5. Coupling effects through fluorescence measurements for 1.4/2.1 nm CQDs molecules. (a) Ensemble photoluminescence lifetime decay for monomer, unfused dimer and fused dimer. Time-tagged, time resolved data for single (b) CQD monomer and (c) fused dimer. Shown are, (i) photoluminescence intensity time trace, (ii) second order photon correlation and (iii) lifetime for the single particle (the green and dark grey lifetime curves were generated from data shaded in the same color in the corresponding time traces). The excitation fluence (<\text{N}>) for monomer and coupled dimer in the represented figures were
0.05 and 0.08, respectively. (d) Possible coupling mechanisms for shortening of lifetime in molecules. (e) Multicarrier configurations. (f) Pump fluence dependency of lifetime for an individual fused dimer. \( <N> \) values are 0.03 (brown trace), to 0.09 (green trace) and 0.18 (blue trace).

More detailed information is garnered from single nanoparticle fluorescence measurements on the 1.4/2.1 nm CQDs (Supplementary information for experimental details). The fluorescence from single monomers (Fig. 5b) exhibited a typical on-off bimodal distribution with a monoexponential fluorescence decay of the on-state (26), and strong photon antibunching (27). In comparison, individual fused dimers (Fig. 5c) under similar excitation conditions show more intense fluorescence consistent with their two-fold larger absorption cross section. However, flickering of the fluorescence with a distribution of intensities is observed rather than distinct on-off states, accompanied by a significantly lower antibunching contrast (\(-0.75\)). The lifetime measurements indicate systematic shortening of the average single particle lifetimes from the monomers through the unfused to the fused dimers, in line with the ensemble measurements (Figure S16 for representative traces and statistics of the lifetimes). Analyzing the lifetimes of the high intensity occurrences (green shaded regions in Fig. 5b,c), yields a significantly shortened average lifetime of 5ns for the single fused dimer compared with the monomer (29ns). It is noteworthy that within the fused dimers sample, we have detected \(~15\%\) of particles that have similar fluorescence characteristics as the CQD monomer sample, in line with their fraction from TEM analysis (Fig. S17-S18). This establishes that the fusion procedure in its entirety did not change the core/shell CQDs.

We consider two possible mechanisms related to coupling, both leading to shortening the lifetime in dimers. First, resonance energy transfer between the two dots (Fig. 5d(i)), a mechanism nearly equally active for unfused and fused dimers. Second, tunneling of the electron to the other dot (Fig. 5d(ii)) as already illustrated in Fig. 1. Tunneling in unfused dimers occurs by collisional electron transfer and is strongly dependent on the linker (28), while in the fused dimer the potential barrier for tunneling is modified and reduced substantially. Both mechanisms will be enhanced for the smaller CQD dimers, but tunneling is more strongly dependent on the size/distances. Indeed, the large CQD molecules, where tunneling probability is negligible according to our calculations (Fig. 1), show smaller changes in lifetimes with shortening in the case of dimers compared to monomers and little differences before and after fusion (Fig. 5c(ii), Fig. S15, S19) the notable lifetime shortening that is seen for the small CQD molecules upon fusion is indicative of the enhanced contribution of the tunneling mechanism in this case.

Next, we consider the photon statistics, which in CQDs are strongly influenced by multicarrier effects. In dimer CQD molecules, a new type of biexcitons can occur, with each exciton occupying a different core (Fig. 5e(i)). The large increase in the value of \( g^2 = \frac{\text{Area}_{(200 \text{ ns})}}{\text{Area}_{(200 \text{ ns})}} = \frac{QY(BX)}{QY(X)} \) at low excitation power observed for the dimers versus monomers can be explained by this new type of biexciton for which the
non-radiative Auger decay will be strongly suppressed increasing the biexciton quantum yield ($QY$) (Fig. S20). Moreover, the single particle exciton $QY$ will decrease for dimers on account of the tunneling of the electrons reducing the electron-hole overlap.

An additional difference in the dimers relates to the fluorescence flickering rather than distinct on-off fluorescence of the monomers (Fig. 5ci, Fig. S21). This indicates presence of multitude emitting configurations for dimers. Indeed, the lifetime traces for the high/low intensity regions in the dimer are not single exponential. The low intensity region is above background and not off and the lifetime has a $\sim$5ns component. All this indicates to trion formation (positive or negative). In small CQD monomers, the trion states are strongly quenched by the Auger decay yielding an off state behavior. In dimers, which have large volume and the excess carrier may occupy the second dot region forming a new type of trion (Fig. 5cii), the Auger rate is suppressed, and the trion can become emissive. Such an effect was reported for large CdSe/CdS core/shell manifesting gray state emission and is also observed by us for the large CQDs (29). The multitude possibilities for emissive trion formation can explain the larger distribution of observed fluorescence intensities and the lifetime behavior for the dimers. To further address this point, an excitation intensity dependence was performed varying the average exciton occupancy $<N>$ from 0.03 to 0.18 (Fig. 5f, Fig. S22). The lifetime decreases upon increasing the laser power, indicating the increasing contribution of trion formation consistent with this description (26, 30).

Formation of CQD homo-dimers reported herein manifests a multitude of coupling effects. Considering the rich selection of size and composition controlled CQDs emphasizes the analogy of these artificial atoms to atoms of the periodic table discovered by Mendeleev 150 years ago. This sets the stage for formation of a diverse variety of coupled CQD molecules with prodigious promise for their utilization in numerous opto-electronic applications.

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**Supplementary Materials:**

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Supplementary Materials for

Coupled Colloidal Quantum Dot Molecules

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Materials and Methods

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Materials and Methods:

Reagents: Oleylamine (OAm, 70%), oleic acid (OA, 99%), 1-octadecene (ODE, 90%), cadmium oxide (CdO, ≥99.99%), selenium (Se, 99.99%), trioctylphosphate oxide (TOPO, 99%), 1-octadecene (≥90%), pentaerythritol tetras(3-mercaptopropionate) (95%), ammonia aqueous (28.5%), tetrahydrofuran (THF, ≥99.9%), N-methylformamide (NMF, 99%), toluene (99.8%), hydrofluoric acid (HF, 48%), polyvinylpyrrolidone (PVP, 10k), ethanol (99%), tetraethyl orthosilicate (TEOS, 98%), hexane (95%) and (3-Mercaptopropyl) trimethoxysilane (MPTMS, 95%) were obtained from Sigma Aldrich. Trioctylphosphine (TOP, 97%) was purchased from Strem Chemicals. Octadecylphosphonic acid (ODPA, >99% was purchased from PCI synthesis. All the reagents were used as received without further purification.

CdSe core growth: Briefly, 60 mg CdO, 280 mg ODPA and 3 g TOPO were added to a 50 mL flask. The mixture was heated to 150 °C and degassed under vacuum for 1 hour. Under argon flow, the reaction mixture was heated to 320 °C to form a colourless clear solution. After adding 1.0 mL TOP to the solution, the temperature was brought up to 350 °C. At this point Se/TOP solution (60 mg Se in 0.5 mL TOP) was swiftly injected into the flask. The reaction was kept at 350 °C for suitable time and then stopped by removal of the heating mantle. The resulting CdSe particles were precipitated with acetone and redispersed in 3 mL hexane for use as a stock solution.

CdSe/CdS core-shell colloidal quantum dots synthesis: For the shell growth reaction, a hexane solution containing 200 nmol of CdSe colloidal quantum dots (CQDs) mixed with ODE (6 mL) and OAm (6 mL). The reaction solution was degassed under vacuum at room temperature for 30 min and at 90 °C for additional 30 min to completely remove the hexane, water and oxygen inside the reaction solution. Then the reaction solution was heated up to 310 °C under argon flow and magnetic stirring. During the heating, when the temperature reached 240 °C, a desired amount of cadmium (II) oleate (Cd-oleate, diluted in 6 mL ODE) and octanethiol (1.2 equivalent amounts to Cd-oleate, diluted in 6 mL ODE) was injected dropwise into the growth solution at a rate of 3 mL/h using a syringe pump. Upon precursor infusion, 2 mL oleic acid was quickly injected and the solution was further annealed at 310 °C for 30 min. The resulting CdSe/CdS core/shell CQDs were precipitated by adding ethanol, and then redispersed in hexane. The particles were further purified by additional two precipitation-redispersion cycles and finally suspended in ~2 ml hexane.

Silica nanoparticles (NPs) synthesis: 120 µL MPTMS precursor was mixed with 30 mL ammonia aqueous solution (1%) under strong stirring (31). After stirring for 1 min, the solution was stored overnight. The SiO2 NPs were collected by centrifugation and dispersed in 10 mL of ethanol. Then the SiO2 solution was mixed with PVP solvent (0.02 g/mL) for 30min. Finally, the nanoparticles were stored after the cleaning by centrifugation.
The synthesis of CdSe/CdS@SiO₂: 1mL of SiO₂ NPs (0.0079 mg/mL) was mixed with 0.5 nmol CdSe/CdS NPs using vortex for 5 min. Then 5 mL of ethanol was added into the vails to precipitate and remove the unattached NPs. After three washing cycles the final SiO₂@CdSe/CdS NPs were redispersed in 5 mL of ethanol.

The synthesis of SiO₂@CdSe/CdS@SiO₂: The CdSe/CdS@SiO₂ was dispersed in 5 mL of ethanol. Then 330 μL of ammonia solvent (28.5% wt %) was added into the solution with stirring for 5 min. Thereafter, 50 μL of TEOS was added dropwise into the solution. After stirring for 10 h, the resulting solvent was centrifuged (6000 rpm, 5 min) and redispersed in 5 mL of THF.

The synthesis of Dimer-CdSe/CdS@SiO₂: A tetraethyl linker ,pentaerythritol-tetraakis (3-mercapto-propionate), (200 μL) was added to the CdSe/CdS@SiO₂ solution. Then 0.6 nmol of CdSe/CdS NCs were added and the solution was stirred in an oil bath at 60 °C overnight. Samples were cleaned by centrifugation (6000 rpm,5 min) and redispersed with 10 mL of THF for storage.

The release of Dimer-CdSe/CdS: 1 mL of Dimer-CdSe/CdS@SiO₂ NCs was centrifuged (5000 rpm, 5 min), and later mixed with 2 mL of mixed HF/NMF solvent (10%) under stirring for 10 h. Upon etching, the color of the samples changed to light yellow, which indicates on the removal of the SiO₂. Thereafter, the samples were precipitated by centrifugation (6000 rpm, 10 min) and washed twice. Finally, the samples were redispersed in 2 mL of ethanol.

The synthesis of fused Dimer-CdSe/CdS CQDs: Dimer-CdSe/CdS NCs (in 2 mL of ethanol) were mixed with 2mL of ODE, 100 μL of Cd-oleate (0.2 M), and 50 μL of OAm. The reaction solution was degassed under vacuum at room temperature for 30 min and again at 90 °C for additional 30 min. Later, the reaction mixture was heated to 180 °C for 20 h under argon flow. The resulting fused particles were precipitated with ethanol and redispersed in 2 mL toluene for use as a stock solution.

Characterization: Absorption spectra were measured using a Jasco V-570 UV-Vis-NIR spectrophotometer. Fluorescence spectra and ensemble lifetimes were measured with fluorescence spectrophotometer (Edinburgh instruments, FL920). Transmission electron microscopy (TEM) was performed using a Tecnai G² Spirit Twin T12 microscope (Thermo Fisher Scientific) operated at 120 kV. High resolution TEM (HRTEM) measurements were done using Tecnai F20 G² microscope (Thermo Fisher Scientific) with an accelerating voltage of 200 kV. High resolution scanning-transmission electron microscopy (STEM) imaging and elemental mapping was done with Themis Z aberration corrected STEM (Thermo Fisher Scientific) operated at 300 kV and equipped with high angular annular dark field detector (HAADF) for STEM and Super-X energy dispersive X-Ray spectroscopy (EDS) detector for high collection efficiency elemental analysis. CQDs atomic structure
model were built by the VESTA software (32). Scanning electron microscopy imaging (SEM) was done with HR SEM Sirion (Thermo Fisher Scientific) operated at 5 kV.

**Single particle optical measurements:** Single particle measurements were performed with an inverted microscope (Nikon Eclipse-Ti) in epi-luminescence configuration. Dilute solution of quantum dots in 2wt% poly(methyl-methacrylate) were spin coated on glass coverslips (no.1, precleaned and thermally annealed) leading to minimum separation of 4-5μm between the dots as confirmed by wide field fluorescence microscopy. The excitation light from a pulsed diode laser (EPL375; Edinburgh Instruments) at a repetition rate of 5MHz was focused onto single particle through an oil immersion objective (100X; 1.4 NA) which was also used for collecting the emission. The emission light was passed through a dichroic mirror (T387lp) and additional longpass filter (580LP) before focusing onto two Avelanche Photodiodes (Perkin-Elmer; SPCM-AQRH-14) in a Hanbury-Brown-Twiss geometry. Photon statistics of the signal from the detector were performed using multichannel Time Tagger 20 (Swabian Instruments). Time traces, fluorescence lifetime and second order photon correlation were extracted from the time-tagged time-resolved data by using home written MATLAB code.
Supplementary Text

**Electronic structure calculation methods:** We have calculated the energy levels and the electron and hole wave-functions of the CdSe/CdS monomer and dimers using the multiphysics mode of COMSOL (33-34). Electron and hole states are calculated with a 3D single-band effective mass Hamiltonian. Interacting electron and hole states are obtained by iterative solution of the Schrödinger-Poisson equation, within a self-consistent Hartree procedure, taking into account the dielectric mismatch between the surroundings and the CQD. The dimensions we used in the calculation are based on experimental data. Material-dependent parameters such as effective masses \( m^*_{e,h}(r) \), dielectric constants \( \varepsilon(r) \), and conduction and valence band profiles \( V_{\text{confinement}}^{e,h}(r) \) used in this calculation are summarized in Table S1. The entire computational space extends further from the QD boundary allowing for electron and hole wavefunctions to extend outside of the QD boundaries and decay into free space.

We start the simulation by computing the non-interacting electron and hole states by solving the Schrödinger equation:

\[
\left( -\frac{\hbar^2}{2} \nabla \left( \frac{1}{m^*_{e,h}(r)} \nabla \right) + V_{\text{confinement}}^{e,h}(r) \right) \Psi^n_{e,h}(r) = E^n_{e,h} \Psi^n_{e,h}(r) \quad (i)
\]

We use von Neumann boundary-condition at the inner (between core-shell) and outer boundaries of the QD in order to impose the Ben-Daniel-Duke condition. At the edge of the computational domain (around 100 nm away from the QD) we set the Dirichlet boundary-condition by setting the wavefunction to zero. After normalization of the wavefunctions, the Poisson equation is solved to derive the hole or electron coulombic potential generated from the other particle \( \phi_{e,h}(r) \).

\[
\nabla (\varepsilon_0 \cdot \varepsilon(r) \nabla \phi_{e,h}(r)) = q_e < \Psi_{e,h}(r) | \Psi_{e,h}(r) > \quad (ii)
\]

With these potentials, Schrödinger equations are solved again for the electron and the hole with all of the contributions to the potentials:

\[
\left( -\frac{\hbar^2}{2} \nabla \left( \frac{1}{m^*_{e}(r)} \nabla \right) + V_{\text{confinement}}^{e}(r) + q_e \cdot \phi_{h}(r) \right) \Psi^n_{e}(r) = E^n_{e} \Psi^n_{e}(r) \quad (iii)
\]

\[
\left( -\frac{\hbar^2}{2} \nabla \left( \frac{1}{m^*_{h}(r)} \nabla \right) + V_{\text{confinement}}^{h}(r) + q_e \cdot \phi_{e}(r) \right) \Psi^n_{h}(r) = E^n_{h} \Psi^n_{h}(r) \quad (iv)
\]

This process is repeated iteratively until the electron and hole energies converge. In most cases, three iterations are sufficient to obtain a convergence. The emission energy was calculated by:

\[
E_{\text{emission}} = E_g + E^i_e + E^i_h - E_{\text{coulomb}} \quad (v)
\]
Where $E_g$ (1.76 eV) (35) is the energy gap of CdSe. $E_{\text{emission}}$ is calculated in a way which avoids the consideration of the coulomb potential twice (both for the electron and both for the hole).

### Table S1. Material parameters used in the simulations.

| Material | $V_{\text{conf}}^e$ | $V_{\text{conf}}^h$ | Environment | Units | Ref. |
|----------|----------------------|----------------------|-------------|-------|------|
| CdSe     | 0                    | 0                    | 5.1         | eV    | (35) |
| CdS      | 0.1                  | -0.64                | -5.64       | eV    | (35) |
|          | $m_e^*$              | 0.112                | 1           | $m_0$ | (36) |
|          | $m_{h\perp}^*$       | 0.48                 | 1           | $m_0$ | (36) |
|          | $m_{h\parallel}^*$   | 1.19                 | 1           | $m_0$ | (36) |
|          | $\varepsilon_{\perp}$| 9.29                 | 1           | -     | (36) |
|          | $\varepsilon_{\parallel}$ | 10.16           | 1           | -     | (36) |

**Consideration of Biexciton quantum yield (QY) to exciton QY ratio in fused dimers:** To consider the obtained $g^2$ value as the biexciton quantum yield, we kept the excitation fluence power significantly low so that the average number of excitons produced per pulse ($<N>$) always remained below 0.2 (27).

The average number of exciton produced per pulse is given by the formula $<N> = \sigma J E_{\text{photon}} A$, where $\sigma$ is the absorption cross section of the particle at the excitation wavelength (375 nm in our case), $J$ and $E_{\text{photon}}$ are the pulse energy and photon energy of the excitation light, respectively, and $A$ is the spot area. The absorption cross-section was calculated according to the procedure reported elsewhere (37). The value of absorption cross-section for the 1.4/2.1 nm CQDs and the corresponding fused dimer was found to be $2.3\times10^{-15}$ cm$^2$ and $5.7\times10^{-15}$ cm$^2$, respectively.

**Excitation power dependence study on single fused dimer:** The flickering nature of a fused dimer associated with a tri-exponential lifetime decay (comprising of ~2 ns, ~5 ns and ~25 ns components) was observed for the 1.4/2.1 Coupled CQDs. The flickering nature was intact upon changing the laser power and even at the lowest measurable excitation. The intensity traces followed a single distribution of intensities (much narrower than the high excitation) without reaching an off state (Fig. S22). Upon excitation of the particle by a short pulse laser, a charge state of the exciton can be created along with the neutral exciton which can contribute to the appearance of short decay components (26,30).

For the 1.4/2.1 nm monomer CQDs the contribution of the short fluorescence decay component was found to be negligible at similar excitation condition, whereas the decay for dimers comprised of these CQDs was dominated by the short components. With decrease in the excitation intensity, we observed an enhancement in the contribution of the ~25 ns component on account of the ~2 ns and ~5 ns...
components (Fig. 5f in the main manuscript). This clearly indicates on the enhanced photo-charging effect in case of fused dimers. Associated with the flickering of the intensity, we observed a lifetime distribution through the intensity traces (lower intensity traces have shorter lifetime as shown in figure 5c (iii)). Upon the decrease in photo-charging not only the average lifetime increases (from 4.5 ns at \(<N>\sim0.18\) to 7.2 ns at \(<N>\sim0.03\)), but also the lifetime distribution (commonly referred as lifetime flickering) decreases.
**Formation of coupled CQDs molecule dimers**

We utilized silica nanoparticles as a template (17) for the fabrication of coupled CQD molecules. The detailed route-line is depicted in Fig. S1. This was performed by the following steps:

1. Fabrication of SiO$_2$ nanoparticles, coated by MPTMS. This kind of SiO$_2$ particle presents thiol groups on their outer surface, which are later used for the binding of the QDs.
2. Core/shell NCs binding to the SiO$_2$ particle surface: mixing a solution of the chosen core/shell NCs with the SiO$_2$ nanoparticles allows their binding to the available thiol sites on the silica surface.
3. Growth of a secondary thin layer of SiO$_2$ on the QDs@SiO$_2$ for masking: In this manner the NCs are immobilized and cannot rotate or reorient while only a top hemisphere is remained exposed for further chemical functionlization of the NCs.
4. Selective surface decoration of the NCs by linker groups: Chemical grafting of a functional structure based on thiol group as linkers is then applied which selectively reacts only with the exposed NC hemisphere. Here, a tetrathiol ligand was added as a linker by a ligand exchange reaction on the exposed NCs surface (for example oleyamine).
5. Forming dimer geometry on the silica surface: Addition of a second NCs solution allows their conjugation, yielding a controlled formation of a dimer structure through the binding linker.
6. Dimer release: The dimers are released from the silica surface and seperated. Here, this can be achieved by selective SiO$_2$ etching using an HF/NMF solution.
7. Fusion to form the coupled NC molecule: The dimers are fused by addition of a suitable precursor and heated to form a continuous link between the two shell regions of the pre-made dimers.

Additional optional purification (size selective seperation) of the dimers from free monomer and higher linked oligemrs is possible in between steps 6 and 7, or after the fusion step.
Fig. S1. Scheme of the coupled CQDs molecule fabrication steps. Step 1: SiO₂ nanoparticles synthesis. Step 2: core/shell NCs binding to the SiO₂ particle surface. Step 3: masking by a secondary thin layer of SiO₂ growth on the QDs@SiO₂. Step 4: selective surface decoration of the NCs by linker groups. Step 5: dimer geometry formation on the silica surface. Step 6: dimer release. Step 7: fusion to form coupled CQD molecules.
CdSe@CdS Core/Shell NCs synthesis and characterization:

Fig. 2S shows electron microscopy and absorption and emission spectra characterizations for the different nanocrystal building blocks which were used in this work. For example, Fig. S2a-c, show CdSe cores (1.9 nm, radius) which were synthesized by hot-injection method. The absorption (581 nm) and photoluminescence (PL) spectra (597 nm) were measured after purification. The CdSe@CdS NCs (1.9/4.0 nm) were fabricated by CdS shell growth using the injection of Cd-oleate and octanethiol precursors. The PL spectrum (637 nm) after shell growth, shows a red-shift compared with the cores emission, this along with the enhancement of the fluorescence quantum yield indicates the successful fabrication of quasi-type II QDs.

Fig. S2. Quantum dots characterization. TEM micrographs, absorption and photoluminescence spectra of different sizes of CdSe/CdS core-shell CQDs: (a-c)1.9/4.0 nm, (d-f)1.4/2.1 nm, and (g-i)1.2/2.1 nm.
Structural characterizations

The core/shell structure of the monomer is directly identified by atomic resolution STEM HAADF imaging followed by fast Fourier transform (FFT) analysis (Fig. S3). Fig. S3a, b shows raw and Fourier filtered images of CQD monomers viewed under [1210] zone axes (ZA) of their wurtzite structure. At this orientation major low index atomic planes (0002), (10\bar{1}0), (10\bar{1}1) are clearly observed thus providing identification of boundary faces of a monomer crystal (labeled on inset in (a)). Atomic structure of CQDs at [0001] ZA with clearly visible perfect hexagonal motifs is depicted in Fig. S3g-h. The hexagonal close-packed (hcp) wurtzite structure of CQDs was further evidenced by the selected area electron diffraction (SAED) and X-ray powder diffraction (XRD) measurement (Fig. S3k-l).
**Fig. S3. Structural characterization of the coupled NCs.** Raw (a) and Fourier filtered (b) HAADF-STEM images of 1.9/4.0 nm CdSe/CdS CQD monomer viewed under $[\bar{1}2\bar{1}0]$ zone axis (ZA). Inset in (a) is a cartoon model built with VESTA software with bounding faces indexed based on STEM data. Magnified images of edge (shell) (c) and central (core) parts (d) of the CQD shown in (b). Sulfur, Selenium and Cadmium atoms are marked in blue, green and brown, respectively. Coherent growth of the shell lattice is identified. (e) and (f) are FFT and atomic structure model of (a), respectively. HAADF-STEM image of CdSe/CdS CQD under ZA [0001] (g) and atomic structure reconstruction imaging calculated for the same orientation (h). (i) High resolution HAADF-STEM image and atomic structure model (j) of CdSe/CdS CQD viewed under ZA $[\bar{1}2\bar{1}0]$. The core regions are marked with pink circles in (g) and (i). FFT patterns are inserted in (g), and (i). SAED (k) and XRD pattern acquired at large ensembles of CdSe/CdS CQDs (blue curve – experimental XRD data, red bars - theoretical positions for diffraction peaks of hcp) CdS (JCPDF 04-001-6853), black curve - integrated intensity of SAED (k)).
Step I - Silica nanoparticles characterization

The SiO$_2$ nanoparticles (step 1) were prepared as described in the methods section (31) and characterized by TEM (Fig. S4). These nanoparticles are inherently covered by thiol linkers from the MPTMS precursor allowing QDs binding at the next step. During the washing step, small amount of diluted base was utilized to avoid cascade and aggregation and to ensure a uniform binding on each SiO$_2$ sphere surface in the next step.

Fig. S4. TEM images of SiO$_2$ nanoparticles prepared by MPTMS precursor acquired at different magnifications.
Step II - Characterization of the Silica-QDs conjugates

Then SiO$_2$@QDs particles were prepared in step 2 by adding the CdSe/CdS QDs to the SiO$_2$ nanoparticles solution. The resulting particles were characterized by TEM and SEM as shown in Fig. S5. In order to avoid the NCs overlap and aggregation on the SiO$_2$ surface, the ratio of QDs added to the SiO$_2$ nanoparticles was controlled. In the sample below, a 1:500 SiO$_2$:QD ratio yielded well-separated and clearly resolved surface distribution of QDs. The CdSe/CdS@SiO$_2$ nanoparticles solution was cleaned twice from free and weakly bound QDs by centrifugation, discarding the supernatant and re-dispersion in toluene.

**Fig. S5.** CdSe/CdS@SiO$_2$ characterized with electron microscopy. TEM and SEM images acquired at different magnification of the CdSe/CdS@SiO$_2$ NPs produced with different loading ratios of (a-d) 1:2000, (e-h) 1:1000, and (i-l) 1:500. Scale bars are 100 nm.
Step III – formation of a silica masking layer

The secondary masking silica layer provides two functions: firstly, coverage of the inherent surface thiol groups of MPTMS in order to avoid the adsorption of additional CdSe-CdS NCs in the dimerization of step 5 (17). This enhances the efficiency of the dimer structure versus monomers. Secondly, to immobilizes the CdSe-CdS NCs such that they cannot rotate, exposing a hemisphere which emerges in the solvent and can be modified selectively by the chemical grafting of a functional structure/group.

In order to control the thickness of the secondary SiO$_2$ masking layer an optimized mixture of PVP and TEOS was necessary. If the PVP amount is too low, it usually results in inefficient masking. Conversely, if it is too high it could lead to a full QDs masking by the SiO$_2$ layer, which prevents the dimer formation in the next step. Additionally, the optimization of the TEOS amount was depicted as below. According to the calculation, 50 µL of TEOS leads to a hemisphere mask. Three different amounts of TEOS were tested in our system, 200 µL (Fig. S6a-d), 100 µL (Fig. S6e-h), and 50 µL (Fig. S6i-l), respectively. For the highest TEOS loading, the QDs were fully embedded inside the SiO$_2$ layer, as is clearly demonstrated in Fig. S6a-d, which is obviously useless for the next binding procedure. Instead, 50 µL of TEOS were utilized for the secondary essential minimal-limitation masking as well as valid immobilization to ensure the next dimer formation yield (Fig. S6i-l). Conclusively, after the growth of the secondary SiO$_2$ layer, the surface roughness of the CdSe-CdS@SiO$_2$ nanoparticles increases significantly, while the emergent QDs can still be discerned. The resulting nanoparticles by TEM and SEM with different magnification are all presented in Fig. S6.

![Fig. S6. TEM and SEM images acquired at different magnification of the SiO$_2$@CdSe/CdS@SiO$_2$ NPs produced with different amount of TEOS (a-d) 200, (e-h) 100, and (i-l) 50 µL. Scale bars are 100 nm.](image-url)
Step IV – linker binding

For the dimer formation step, the chosen linkers bound to the exposed region of the anchored QDs (step 4). A Tetra-thiol molecule was used as a bi-dentate linker molecule (Fig. S7). The thiol group strongly binds to the QD surface and can displace the existing surface ligands of the exposed QD hemisphere. In order to enhance the conjugation of the linkers, the surface modification procedure was performed under Argon flow, at 60 °C overnight. The excess linker molecules were removed by precipitation and centrifugation. Here, the cleaning step after the linker addition was significant for achieving high dimer formation yield.

Fig. S7. Chemical structure of the linker (pentaerythritol tetrakis(3-mercapto-propionate)).
**Step V – Dimer formation**

For the preparation of homodimers a QDs ratio of 1:1.2 to the original amount used in step 2 was used. The resulted structures are presented in Fig. S8.

![TEM images of SiO₂@dimer CdSe/CdS particles acquired at different magnifications. Scale bars are 20 nm. The dimer structure in the imaging was marked by the white frame.](image)

**Fig. S8.** TEM images of SiO₂@dimer CdSe/CdS particles acquired at different magnifications. Scale bars are 20 nm. The dimer structure in the imaging was marked by the white frame.

**Step VI – Dimers release**

Precisely controlled dimer CdSe-CdS molecules were successfully achieved as follows. The release and separation of the CdSe-CdS NCs dimers from the SiO₂ spheres was performed by selective etching process of the SiO₂ using an HF/NMF (10%) etching solution. The free dimers are shown in Fig. 1c. The freed dimers were separated by centrifugation decanting the supernatant and repeated ethanol/centrifugation cycles for three times.

**Step VII – Fusion to form the coupled NC molecule**

The fusion procedure plays a significant role in reduction of potential barrier in the coupled CQDs molecules. The choice of correct temperature, precursor amount and ligands lead to the fusion of two CQDs without ripening and collapse.
**Size selective separation process for 1.9/4.0 nm CQDs**

The fused dimer molecules as prepared by the procedure explained in the previous section contain some unreacted monomer CQDs which have been separated to achieve high yield of CQD molecule for further studies. Fig. S9 shows the released fused dimers, which were separated by centrifugation decanting the supernatant and repeated redispersion (ethanol)/precipitation (centrifugation) cycles for three times. Monomers were found mainly in the suspension, as shown in Fig. S9b. As seen in Fig. S9c, the monomers, along with possible higher order aggregates of CQDs can be well separated after this step, resulting in a purified solution of dimer structures.

**Fig. S9.** TEM images of fused 1.9/4.0 nm CdSe/CdS molecules before size selective separation process (a). The suspension (b) and the precipitate (c) of fused CdSe/CdS molecules after the size selective separation process. Inset, HRTEM image of fused CdSe/CdS molecules.
**Size selective separation process for 1.4/2.1 nm CQDs**

The size selection separation for other nanocrystal sizes is similar but may require slight modifications. For example, for 1.4/2.1 nm CdSe/CdS molecules low centrifugation rate was taken for efficient separation. The resulting dimers are presented in Fig. S10.

After the separation step, the sample was stored under argon atmosphere and kept in the glovebox for single nanoparticle measurement.

![Fig. S10. TEM images of fused 1.4/2.1 nm CdSe/CdS molecules](image)

**Fig. S10.** TEM images of fused 1.4/2.1 nm CdSe/CdS molecules (a) before size selective separation process. The suspension (b) and the precipitate (c) of fused CdSe/CdS molecules after the size selective separation progress. Inset, HRTEM image of fused CdSe/CdS molecules.
Spectral characterization of the various fused CQDs dimers

The red shift of the fluorescence was enhanced with a size decrease in the CdSe-CdS CQDs composing the fused dimers, that is, the smaller core-shell CQDs molecules present strong coupling properties. Additionally, upon fusion, the full width at half maximum (FWHM) measured from the fluorescence spectrum was obviously increased compared with that of the monomer sample.

Fig. S11. The PL intensity of monomer (black), and fused (red) CdSe-CdS CQDs molecules with core/shell size of 1.9/4.0 nm (a), and 1.2/2.1 nm (b), respectively.
Structural characterization of the fused 1.9/4.0 nm CQDs dimers

Fig. S12 shows HAADF-STEM images and atomic structure models of the fused 1.9/4.0 nm CdSe/CdS CQD molecules with hetero-plane orientation relationship at attachment. The analysis allowed to determine the (0002) faces (and thus C-axis orientation) for each CQD in a pair as indicated on the images and structure models in Fig. S12. It is clearly seen that the C-axes of the monomers in a heteronymous-plane fused dimer are randomly oriented unlike the distinct parallel alignment observed at homonymous-plane attachment (see main text).

**Fig. S12.** HAADF-STEM images and atomic structure models of the fused 1.9/4.0 nm CdSe/CdS molecules with hetero-plane attachment of (10\overline{1}0)\|\!(10\overline{1}1) (a-b), (0002)\|\!(10\overline{1}1) (c-d). For the atomic model, the Cadmium atoms are marked in brown and Sulfur atoms in blue.
Structural characterization of the fused 1.4/2.1 nm CQDs dimers

In our system, the attachment and fusion of the monomeric CdSe/CdS was based on the linker’s orientation. So the attachment orientation relationships for the smaller CdSe/CdS CQDs molecules were similar to those observed in the bigger CQDs. Yet, a small difference was still noticed. Namely, there are three main options for homonymous-plane attachment: (0002)|| (0002), (10\overline{1}0)|| (10\overline{1}0), and (10\overline{1}1)|| (10\overline{1}1). Fig. S13a shows the (10\overline{1}0)|| (10\overline{1}0) homonymous-plane attachment with (10\overline{1}0) faces of A1 parallel to those of A2 and a continuous lattice observed through the entire dimer.

Fig. S13. HAADF-STEM image and atomic structure model of the fused 1.4/2.1 nm CdSe/CdS molecules with homo-plane attachment on (10\overline{1}0)|| (10\overline{1}0) (a), and (10\overline{1}1)|| (10\overline{1}1) (b). For the atomic model, the Cadmium atoms are marked in brown and Sulfur atoms in blue.
Heteronomous-plane attachment of the fused 1.4/2.1 nm CQDs dimers

The hetero-plane attachment mainly based on (0002)∥(10\overline{1}0), (0002)∥(10\overline{1}1), and (10\overline{1}1)∥(10\overline{1}0) was also observed in the fused 1.4/2.1 nm CdSe/CdS molecules. In this case due to thin CdS shell (only 6 atomic layers thick), the core CdSe region (Cd: atom with high brightness, Se: atom with slight brightness) was directly identified at HAADF STEM image. Fig. S14 shows examples of heteronomous-plane attachments at (0002)∥(10\overline{1}0) (a) and (0002)∥(10\overline{1}1) (b).

**Fig. S14.** HAADF-STEM images and atomic structure model of the fused 1.4/2.1 nm CdSe/CdS molecules with heteronomous-plane attachment on (0002)∥(10\overline{1}0) (a), (0002)∥(10\overline{1}1) (b). For the atomic model, the Cadmium atoms are marked in brown and Sulfur atoms in blue.
Ensemble fluorescence lifetime measurements for 1.9/4.0 nm CQD and corresponding dimers

The molecule formed from bigger CQDs (1.9/4.0 nm) also exhibit a quenching in the ensemble lifetime upon dimer formation but at a much lower extent compared with molecules of the small CQDs (1.4/2.1 nm). This is due to reduced tunneling and hybridization both because of the longer barrier and also due to the larger cores with less wavefunction spilling into the shell.

Fig. S15. Ensemble fluorescence lifetime decay curves of the monomer (blue), unfused dimer (green) and fused dimer (red) for 1.9/4.0 nm CQD.
Single particle fluorescence lifetime for small CQD and corresponding dimers

The fluorescence decay of a single 1.4/2.1 nm CQD follows mostly a monoexponential decay of ~30 ns or a bi-exponential decay with a small contribution from a 5 ns component. The average lifetime for the single dimer particles is clearly quenched and follows mostly a tri-exponential decay. The distribution of the average lifetime for dimer particles is shifted to short values, which is more pronounced for the fused dimers than for the unfused ones.

Fig. S16. Single particle fluorescence lifetime decay data for monomer (blue), unfused dimer (green) and fused dimer (red) composed of 1.4/2.1 nm CQD. (a) Representative single particle fluorescence lifetime decays. (b) Histograms summarizing the distribution of the average lifetimes for all three types of particles. Further shortening of the lifetime is observed upon fusion.
Characterization of the monomer particles that were treated with the fusion procedure:

The CQDs are exposed to different conditions during the synthetic procedure such as binding, etching, fusion etc. An important control is to identify whether the inherent properties of the CQDs change during these processes, especially during etching and fusion. To this end, we studied the optical properties of single monomer particles that although did not form a dimer, still were treated with the complete synthetic procedures of the fusion protocol. The fraction of monomer particles found is in accordance with the size selective precipitation results and TEM analysis therein (~15%, Fig. S10). We found that the monomer CQDs undergoing the fusion protocol retain their optical properties exactly as the unprocessed monomers, such as single exponential lifetime of the on state, on-off blinking of fluorescence and strong photon antibunching.

Fig. S17. Single particle fluorescence lifetime of a monomer CQD (1.4/2.1 nm) found along with the fused dimers. Two examples of the fusion protocol treated monomers are shown in blue and red curves. The black curve represents the lifetime of a monomer particle that wasn’t treated with the fusion procedure.
Fig. S18. Time-tagged time-resolved analysis of the fusion protocol treated monomer CQD (1.4/2.1 nm). (i) A bimodal on-off distribution of the intensity was found (bin-50 ms). The black curve represents the background noise. (ii) Fluorescence lifetime of the on-state follows a single exponential decay of 31 ns. (iii) Strong photon antibunching with $g^2$ value of 0.09. All these observations for the fusion protocol treated monomer are highly correlated with the untreated monomer particle as explained in the previous section.
Single particle fluorescence lifetime for 1.9/4.0 nm CQDs and corresponding dimers

The shortening of the lifetime upon dimerization was also observed for the 1.9/4.0 nm CQD. When compared with the lifetime distribution of the smaller particle (Fig. S16) the degree of shortening was found to be lower in this case. A similar type of distribution in the averaged lifetime for unfused and fused dimer indicates absence of significant additional coupling upon fusion, consistent with decreased tunneling-coupling in these molecules constructed from the larger CQDs.

**Fig. S19.** Single particle fluorescence lifetime decay data for monomer (blue), unfused dimer (green) and fused dimer (red) composed of 1.9/4.0 nm CQD. (a) Representative single particle fluorescence lifetime decays (b) Histograms summarizing the distribution of average lifetimes for all three types of particles. For the sake of comparison, x-axis was kept the same as in Fig. S16.
Comparison of $g^2$ value for monomer and fused dimer

The antibunching at zero time delay accounts for the ratio of biexciton to exciton quantum yield (QY):

$$g^2 = \frac{\text{Area}_{(0\text{ns})}}{\text{Area}_{(200\text{ns})}} = \frac{QY(\beta X)}{QY(X)}$$

when the value of $<N>$ is kept well below 1. When the monomer (1.4/2.1 nm) and fused dimer were excited with similar $<N>$ (~0.06) value a much higher value of $g^2$ was obtained in the case of the fused dimer (0.68) than for the monomer (0.16) CQD. The possible pathways for the enhanced biexciton QY are explained in the main text.

![Graphs showing comparison of $g^2$ for monomer and fused dimer](image)

**Fig. S20.** Comparison of second order photon correlation at similar $<N>$ value for excitation. The $g^2$ value were found to be 0.16 and 0.68 for the monomer and the fused dimer, respectively.
Attributes of fluorescence from single unfused dimer

The fluorescence from single unfused dimers also exhibited flickering nature instead of distinct on-off characteristics and followed a multi-exponential decay. The lifetime is not uniform throughout the intensity range, but rather presents distributions when analyzed at different intensity levels (Fig. S21(ii)). The single unfused dimer also gives rise to lower antibunching contrast.

Fig. S21. Time-tagged time-resolved data for single unfused dimer comprised of 1.4/2.1 nm CQD(i) Photoluminescence time trace, (ii) fluorescence intensity dependent lifetime (the lifetime curves bear the same color code as the shaded area from (i)), and (iii) second order photon correlation ($g^2$).
Excitation intensity dependence of fluorescence flickering in dimer

The flickering nature of the fluorescence from a single fused dimer persists even in very low excitation conditions. The brown colored time trace in Fig. S22 was obtained in the lowest possible excitation (<\(N\)~0.03), where the flickering of fluorescence occurs without reaching an off state (black curve). With increase in the excitation intensity an increment of the extent of flickering was observed along with shortening of the lifetime as described in Fig. 5f in the main manuscript.

Fig. S22. Fluorescence time traces information with varying excitation intensity for a fused dimer comprised of 1.4/2.1 nm CQDs. The blue, green and brown curve represents the traces obtained from fused dimer with <\(N\)> value of 0.18, 0.09, 0.03, respectively. (a) Excitation fluence dependent PL time traces. The black curve represents the background noise in a similar configuration. (b) Intensity distribution of the traces in (a). Narrow distribution is observed with decreasing laser power.
**Table. S2.** The calculated and experimental monomer-to-dimer red shift for CdSe/CdS molecules with different core/shell diameters.

| Core/Shell (nm) | Monomer emission peak (nm) | Fused emission peak (nm) | Red-shift (meV)-Exp | Red-shift (meV)-Calc |
|----------------|-----------------------------|--------------------------|---------------------|----------------------|
| 1.9/4.0        | 637                         | 637                      | 0                   | 0.65                 |
| 1.4/2.1        | 603                         | 606.5                    | 11.8                | 11.3                 |
| 1.2/2.1        | 593                         | 597                      | 13.9                | 12.8                 |
Table S3. The ensemble fluorescence lifetime values for different types of CQDs and corresponding homodimers (in toluene).

| Core/Shell (nm) | Monomer |  |  |  |  |  |  |  |  |  |  |  |
|----------------|---------|---|---|---|---|---|---|---|---|---|---|---|
|                | $\tau_1(a_1)$ | $\tau_2(a_2)$ | $\tau_{avg}$ | $\tau_1(a_1)$ | $\tau_2(a_2)$ | $\tau_{avg}$ | $\tau_1(a_1)$ | $\tau_2(a_2)$ | $\tau_{avg}$ |  |  |  |
| 1.4/2.1        | 25      | 25 | 7.3 | 30 | 8.7 | 5.2 | 9.7 | 9.7 | (1.0) | (0.9) | (0.1) | (0.3) | (0.7) |
| 1.9/4.0        | 8.9     | 39 | 24.5 | 7.9 | 38 | 17.5 | 8.1 | 39 | 17.1 | (0.4) | (0.6) | (0.62) | (0.38) | (0.65) | (0.35) |

$\tau_i$ values are represented in ns scale, $a_i$ represents the weightage of a particular lifetime component.
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