# **Supporting Information**

# Type I vs Quasi-Type II Modulation in CdSe@CdS Tetrapods: Ramifications for Noble Metal Tipping

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## 1) Experimental

## a. Materials and Characterization

All chemicals were commercially available and used as received, unless otherwise noted. 1octadecene (ODE, 90%) was purchased from Acros. Gold (III) chloride (AuCl<sub>3</sub>, 99.99%), cadmium oxide (CdO, 99.998%), hexadecylamine (HDA, 98%), myristic acid (99.99%), and elemental sulfur (99.5%) were purchased from Alfa Aesar. Cadmium (II) acetylacetonate (Cd(acac)<sub>2</sub>) (99.9%), didodecyldimethylammonium bromide (DDAB, 98%), oleic acid (OLAC, 90%), and oleylamine (OLAM, 70%) were purchased from Sigma Aldrich. octadecylphosphine acid (ODPA) (97%), elemental selenium (99.99%), trioctylphosphine (TOP) (97%), and trioctylphosphine oxide (TOPO) (90%) were purchased from Strem. Absolute ethanol was commercially available from Decon labs and used as received. Acetone, methanol, isopropanol, and toluene were commercially available from Fisher Scientific. All reactions reported herein are performed in flame dried glassware under Ar atmosphere using standard Schlenk techniques, with a vacuum pressure of approximately 1 mmHg using an Edwards High Vacuum International vacuum pump (Model RV12, Sussex England). An Omega temperature controller CSC32K with a K-type thermocouple and Glas-Col fabric heating mantle were used for high temperature syntheses reported herein (> 150 °C), unless otherwise noted. All centrifugation steps were performed on an Eppendorf 5804 benchtop centrifuge with rotor radius of 11 cm. UV-Vis measurements were obtained using an Agilent 8453 spectrophotometer. Fluorescence measurements were obtained using a FL3-11 Fluorolog-3 Spectrofluorometer (Jobin Yvon-Spex Instruments SA). Low resolution bright field TEM images (all not specifically labeled "high resolution") were obtained using a Technai Spirit transmission electron microscope (FEI) at 120 kV or a CM200 LaB6 (Philips) at 200 kV using in-house prepared carbon coated copper grids (Cu, hexagon, 300 mesh). Image analysis was perfomed using ImageJ software (Rasband, W.S., National Institutes of Health, http://rsb.info.nih.gov/ij/) from bright field TEM images at a minimum of 110000x magnification by sizing a minimum of 100 nanoparticles. High-resolution TEM (HRTEM), bright field scanning TEM (STEM), high angle annular dark field STEM (HAADF-STEM) images and EDX maps were obtained using a JEM-ARM200F (Jeol) double-corrected Cold Field Emission TEM operated at 200 kV. Thermogravimetric analysis was carried out under nitrogen atmosphere using a TGA Q50 instrument and software from TA Instruments. SEM images were taken on a Hitachi 4800 FE-SEM (30kV accelerating voltage) on the as-prepared samples (no metallic overcoating).

The transient absorption set-up used for this study has been described in details in our previous work.<sup>1-</sup> <sup>2</sup> Briefly, transient absorption measurements were conducted in a Helio spectrometer (Ultrafast Systems LLC) with pump and probe beams derived from a regeneratively amplified Ti: Sapphire laser system (Coherent Legend, 800nm, 150fs, 2.4mJ/pulse, and 1kHz repetition rate). The 800nm output was split equally into two parts by beamsplitter. One part was used to pump a Coherent Optical Parametric Amplifier (OPA) to generate two tunable near-IR pulses from 1100nm to 2500 nm, signal and idler beam respectively. The signal beam was used to generate the 580nm and 590nm excitation through frequency-doubling by a BBO crystal. 400nm pump was also made by frequency-doubling of 800nm fundamental beam in a BBO crystal. A series of neutral-density filter wheels were used to adjust the power of pump to eliminate the non-linear response of the CdS tetrapods and maintain the system under the single exciton condition. The pump beam was focused at the sample with a beam waist around 400um. A white light continuum (WLC) from 420 to 800nm was generated by attenuating and focusing ~10uJ/s of the 800nm pulse into a sapphire window. The WLC was split into

a probe and reference beam. The probe beam was focused with an Al parabolic mirror onto the sample with a beam waist of about 150um. The decay between pump and probe was controlled by a delay stage. Pump beam was chopped by a synchronized chopper to 500Hz. The instrument response of the system was determined to be  $\sim$ 230fs by measuring the solvent response.

# b. Synthesis of Zincblende (ZB) CdSe Nanocrystals (NCs)

# i. ZB CdSe NCs – Diameter: 1.8 – 2.4 nm

## 1. General Considerations

The synthesis of ultrasmall zincblende CdSe NCs reported herein was inspired by the methods of Hens and coworkers.<sup>3</sup> In general, the synthesis of ultrasmall CdSe nanocrystals (of zincblende or wurtzite crystal structure) can be challenging owing to the necessity of rapid quenching steps to arrest particle growth and the low yields of nanocrystals that results from these procedures. Through incorporation of strong binding ligands (HDA/ODA) in the nanocrystal synthesis, as well as a constant growth temperature, nanocrystals within the 1.8-2.4 nm size range could be reproducibly synthesized in higher molar yield than any other procedure reported herein ( $5.5 \times 10^{-7}$  moles). In general, quenching of the reaction within 100 seconds of selenium precursor injection results in nanoparticles below 2.1 nm in size, whereas long reaction times (1000 seconds) result in a maximum particle size of 2.4 nm. Kinetic studies allowed for plotting of CdSe NC size as a function of reaction time (Figure S1), which was helpful in determining reaction time for the desired particle size.

Additionally, we found that standard purification procedures designed to minimize organic content resulted in irreversible aggregation of the synthesized particles in this size regime. Consequently, purification methods were developed to remove excess solvent/precursor, while maintaining stability of the nanocrystals in ODE/OLAC dispersion. This not only served to stabilize the nanocrystals over time, but in our hands also made the preparation of quantum dot stock solutions for tetrapod synthesis easier and more reproducible than when using dried nanocrystal powders.

# 2. Preparation of 1.0 M TOP=Se Stock Solution

A trioctylphosphinie selenide (TOP=Se) stock solution of concentration 1.0 M selenium in TOP was prepared by addition of selenium powder (789.6 mg, 0.01 mol) to a 20 mL scintillation vial equipped with a  $\frac{1}{2}$ " PTFE coated stir bar and fitted with a septum. The vial was evacuated of air and backfilled with Ar three times. Then, 10.0 mL of TOP (97%) was added to the vial via syringe, and the resulting mixture was sonicated, stirred, and vortex mixed until homogeneous.

## 3. Preparation of Cd(OLAC)<sub>2</sub>

To a 250 mL three neck round bottom flask equipped with a 1" PTFE coated stirbar and a reflux condenser was added Cd(acac)<sub>2</sub> (248.5 mg, 0.800 mmol) followed by OLAC (1.02 g, 1.13 mL; 3.60 mmol) and 1-ODE (10.0 mL). The contents of the flask were evacuated and backfilled with Ar at 50°C three times, followed by heating to 150°C under Ar for 15 minutes. Over the course of the 15 minutes, a homogeneous colorless and transparent solution formed, indicating complexation of the cadmium precursor. Subsequently, 1-ODE was injected (30.0 mL), and the flask was cooled to room temperature under Ar for the synthesis of the ZB CdSe NCs.

#### 4. Synthesis of ZB CdSe NCs on a 300 mg scale

To the same flask used to prepare the Cd(acac)<sub>2</sub> precursor was HDA (1.12 g, 4.80 mmol), followed by ODA (0.040 g, 0.15 mmol). The flask was evacuated and backfilled with Ar at 50°C three times to evacuate any air introduced during the addition of HDA/ODA. Next, the flask was heated to 170°C under Ar at 300 RPM, wrapped with cotton, and incubated at 170°C for 30 minutes. To initiate growth of the nanocrystals, the previously prepared TOP=Se stock solution was injected (8.0 mL) to the reaction solution at 170°C (with the cotton wrap still on), and the reaction was quenched by rapid injection of hexanes (30.0 mL) at the desired timepoint (10-600 seconds, see Figure S1). The reaction flask was then allowed to cool to room temperature for workup.

Workup of 1.8 - 2.4 nm CdSe NCs was performed by separating the crude reaction mixture into three 45 mL centrifuge tubes (~15 mL each), followed by centrifugation at 10,000 RPM for 10 minutes to crash out the excess HDA. A pristine white pellet of HDA was obtained, with a transparent orange/yellow supernatant which contained the NCs. The supernatant from each tube was decanted into a new centrifuge tube, followed by equal volumes of IPA and MeOH. Thus, 15 mL of IPA and 15 mL of MeOH were added to the 15 mL of supernatant in each tube (for a typical synthesis), resulting in a cloudy white emulsion. Centrifugation at 10,000 RPM for 20 minutes yielded a viscous yellow oil (~3 mL) and a clear/colorless supernatant. The multiple yellow oil droplets suspended in the supernatant were allowed to settle for 5 minutes prior to careful removal of the supernatant via syringe. Subsequently, a solution of OLAC in ODE (0.3 mL, 10 vol%) was added to each centrifuge tube to prevent aggregation of the ultrasmall ZB CdSe NCs. Subsequenty, the same process was repeated, wherein 3.0 mL of IPA and 3.0 mL of MeOH were added to the ~3.0 mL of viscous oil containing the CdSe NCs. The cloudy yellow emulsions were then centrifuged at 10,000 RPM for 10 minutes to yield a highly viscous orange "pellet" of < 0.3 mL volume each. The oil was viscous enough that the clear/colorless supernatant was easily decanted. Subsequently, a solution of OLAC in ODE (0.03 mL, 10 vol%) was added to each pellet to prevent aggregation of the ultrasmall ZB CdSe NCs. This yielded 276.55 mg (97.90 wt% organics by TGA, 5.49x10<sup>-7</sup> mol ZB CdSe QD) of a viscous yellow oil. Storage of the purified samples prepared from this procedure under an inert N<sub>2</sub> atmosphere ensured stability of the particles over multiple months.



**Figure S1. Effect of Reaction Time on NC Diameter.** (a) UV-Visible spectra of crude kinetic timepoints between 10-70 seconds for the synthesis of 1.8 - 2.4 nm ZB CdSe NCs. (b) UV-Visible spectra of kinetic timepoints between 80-600 seconds for the synthesis of 1.8 - 2.4 nm ZB CdSe NCs. (c) Plot of ZB CdSe NC diameter as a function of reaction time, as determined from the sizing curve shown in Figure 2 of the main text. Minimum sizes approaching 1.8-2.1 nm could be reproducibly obtained by quenching the reaction in under 100 seconds, whereas long reaction times (~ 15 minutes) resulted in a maximum particle size of ~ 2.4 nm.

#### ii. ZB CdSe NCs – Diameter: 2.8 – 4.4 nm

#### 1. General Considerations

The synthesis of zincblende CdSe NCs in the 2.8 - 4.4 nm size regime developed herein was inspired by the methods of Cao and Talapin.<sup>4-5</sup> Similar to the procedure for the synthesis of ultrasmall CdSe NCs, the synthesis of nanocrystals in the 3.0 - 4.4 nm size range relied on reaction time as the sole handle for final particle size. In this case, nanocrystals between 2.8-2.9 nm could be obtained if the reaction was quenched within 100 seconds of injection of stabilizing ligand, whereas particles between 3.0 - 4.4 nm in size were accessible by annealing the reaction mixture at 240°C for extended periods of time (past 10 hours). Over the course of this annealing step, CdSe NC morphology was observed to shift from spherical to cubic in nature. Kinetic studies of this reaction allowed for plotting of CdSe NC size as a function of reaction time (Figure S2), which was helpful in determining reaction time for the desired particle size.

#### 2. Preparation of Capping Ligand Stock Solution

To a 20 mL scintillation vial was added 1-ODE (8.0 mL) along with OLAM (1.63 g, 2.00 mL, 6.08 mmol), and OLAC (179 mg, 0.200 mL, 0.634 mmol). The solution was sparged for 20 minutes with Ar and subsequently homogenized via vortex mixing.

#### 3. Preparation of Cadmium Myristate

To a 250 mL three neck round bottom flask equipped with a  $\frac{1}{2}$ " PTFE coated stir bar and reflux condensor was added CdO (115.5 mg, 0.900 mmol), myristic acid (435 mg, 1.91 mmol), and 1-ODE (7.5 mL). The reaction flask was evacuated of air and backfilled with Ar three times. Subsequently, the contents of the flask were heated to 250°C at a stir rate of 300 RPM. Over the course of 10 minutes, the solution changed from deep red and opaque (characteristic of CdO) to colorless and transparent, indicating complexation of cadmium and formation of active Cd-

myristate species. Upon the observed color change, 1-ODE (48.0 mL) was injected and the solution was cooled to room temperature.

## 4. Synthesis of ZB CdSe NCs on a 200 mg scale

To the same 250 mL three neck round bottom flask in which the cadmium myristate was synthesized was added elemental selenium powder (36.0 mg, 456.0 µmol). After Se addition, the flask was evacuated of air and backfilled with Ar three times, followed by heating to 240°C at a stir rate of 300 RPM. Once at 240°C, 7.65 mL of the previously-prepared capping ligand stock solution was injected dropwise via syringe into the reaction flask over the course of 1 minute. This resulted in a temperature drop to 225-230 °C. After the ODE/OLAM/OLAC injection, the reaction was the reaction was quenched by rapid injection of 1-ODE (40.0 mL) at the desired timepoint (30 seconds-3600 seconds, see Figure S2). The reaction flask was then allowed to cool to room temperature for workup.

Workup of the 2.9 - 4.4 nm CdSe NCs was performed by separating the crude reaction mixture into six 45 mL centrifuge tubes (~ 20 mL each), followed by addition of acetone to result in a total volume of 45 mL. Centrifugation at 10,000 RPM for 10 minutes yielded a viscous orange or red oil (depending on particle size) and a yellow tinted and transparent supernatant. The supernatant was decanted, and the viscous oil was redispersed in 20 mL of acetone and 5 mL of methanol. Centrifugation at 10,000 RPM for 10 minutes yielded a solid orange or red pellet and a colorless and transparent supernatant. The pellets were dried *en vacuo* at room temperature overnight to yield 157.21 mg (97.18 wt% organics by TGA,  $5.02x10^{-8}$  mol) of an orange solid.



**Figure S2. Effect of Reaction Time on NC Diameter.** (a) UV-Visable spectra of crude kinetic timepoints between 0-60 seconds for the synthesis of 2.9 - 4.4 nm ZB CdSe NCs. (b) UV-Visable spectra of kinetic timepoints between 70-3600 seconds for the synthesis of 2.9 - 4.4 nm ZB CdSe NCs. (c) Plot of ZB CdSe NC diameter as a function of reaction time, as determined from the sizing curve shown in Figure 2 of the main text. Minimum sizes approaching 2.8/2.9 nm could be reproducibly obtained by quenching the reaction in under 100 seconds, whereas long reaction times (1-10 hrs) resulted in a maximum particle size of ~ 4.4 nm.

## iii. ZB CdSe NCs – Diameter: 4.4–5.8 nm

## 1. General Considerations

Access to zincblende CdSe nanocrystals of the 4.4 - 5.8 nm size range was afforded by a slight modification to the procedure previously described for 2.9 - 4.4 nm nanocrystals. Instead of varying reaction time, it was found that variation of selenium concentration allowed for tuning of nanocrystal size after a 20 hour reaction at 240°C. Interestingly, with decreasing selenium concentration, increasing particle size was observed (Table S1). Increasing particle size also corresponded to a decrease in NC yield, indicative of fewer nucleation events at the early stages of the reaction, which would be expected in a precursor-starved reaction.

### 2. Preparation of Capping Ligand Stock Solution

To a 20 mL scintillation vial was added 1-ODE (8.0 mL) along with OLAM (1.63 g, 2.00 mL, 6.08 mmol), and OLAC (179 mg, 0.200 mL, 0.634 mmol). The solution was sparged for 20 minutes with Ar and subsequently homogenized via vortex mixing.

#### 3. Preparation of Cadmium Myristate

To a 250 mL three neck round bottom flask equipped with a  $\frac{1}{2}$ " PTFE coated stir bar and reflux condensor was added CdO (115.5 mg, 0.900 mmol), myristic acid (435 mg, 1.91 mmol), and 1-ODE (7.5 mL). The reaction flask was evacuated of air and backfilled with Ar three times. Subsequently, the contents of the flask were heated to 250°C at a stir rate of 300 RPM. Over the course of 10 minutes, the solution changed from deep red and opaque (characteristic of CdO) to colorless and transparent, indicating complexation of cadmium and formation of active Cd-myristate species. Upon the observed color change, 1-ODE (48.0 mL) was injected and the solution was cooled to room temperature.

#### 4. Synthesis of ZB CdSe NCs on a 300 mg scale

To the same 250 mL three neck round bottom flask in which the cadmium myristate was synthesized was added 167.1-456.0  $\mu$ mol (13.2 – 36.0 mg) of selenium powder, depending on the desired particle size (see Table S1 for correlation of Se addition and particle size). After Se addition, the flask was evacuated of air and backfilled with Ar three times, followed by heating to 240°C at a stir rate of 300 RPM. Once at 240°C, 7.65 mL of the previously-prepared capping ligand stock solution was injected dropwise via syringe into the reaction flask over the course of 3 minutes. The mixture was allowed to react for 20 hours at 240 °C (± 5 °C), allowing for the the formation of high quality ZB CdSe NCs. After 20 hours, the reaction was quenched by removing from heat and allowing the crude solution to cool naturally to room temperature. The reaction mixture was then worked up as described below.

Workup of the 4.4 - 5.8 nm CdSe NCs was performed by separating the crude reaction mixture into six 45 mL centrifuge tubes (~ 12.5 mL each), followed by addition of acetone to result in a total volume of 45 mL. Centrifugation at 10,000 RPM for 10 minutes yielded a viscous orange oil and a clear/colorless supernatant. The supernatant was decanted, and the viscous oil was redispersed in 20 mL of acetone and 5 mL of methanol. Centrifugation at 10,000 RPM for 10 minutes yielded a solid orange pellet and a colorless and transparent supernatant. The pellets were dried *en vacuo* at room temperature overnight to yield 316.72 mg (90.49 wt% organics by TGA,  $1.01 \times 10^{-7}$  mol) of an orange solid.

Amount of	[Se]	Reaction	Particle Diameter
Selenium		Time	
116 µmol	18.4 mM	20 hrs	5.77± 1.14 nm
(9.20 mg)			
168 µmol	26.6 mM	20 hrs	5.39± 0.76 nm
(13.3 mg)			
374 µmol	59.1 mM	20 hrs	$5.11 \pm 0.69 \text{ nm}$
(29.5 mg)			
456 µmol	72.2 mM	20 hrs	$4.36 \pm 0.504$ nm
(36.0 mg)			

Table S1: Effect of Amount of Selenium C	<b>Concentration Particle Diameter</b>
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### iv. ZB CdSe NCs – Diameter: 5.9 – 8.0 nm

### 1. General Considerations

The procedure for accessing zincblende CdSe nanocrystals of the 5.9 - 8.0 nm size range was adopted from our previously reported procedures for 6.2 nm CdSe nanocrystals.<sup>6-7</sup> We found that while this reaction was not sensitive to air or moisture, a minimum of 20 minutes of reaction time was required to produce nanocrystals from which tetrapods could be synthesized reproducibly. For the purposes of this study, the reaction was stopped at 45 minutes to obtain 6.2 nm CdSe NCs, with further reaction times of 1 hour resulting in a maximum particle size of 8.0 nm.

### 2. Preparation of a Cd(acac)<sub>2</sub> Stock Solution

In a 50 mL three-neck round bottom flask equipped with a reflux condenser and  $\frac{1}{2}$ " PTFE coated stirbar was added Cd(acac)<sub>2</sub> (398 mg; 1.28 mmol), followed by OLAC (6.68 g, 7.50 mL, 23.6 mmol). The contents of the flask were subsequently heated to 150°C while stirring at 300 RPM until a clear and colorless solution formed (approximately 15 minutes).

#### 3. Synthesis of ZB CdSe NCs on a 500 mg Scale

The synthesis of zincblende CdSe NCs was adapted from the literature.<sup>6</sup> To a 50 mL three-neck round bottom flask fitted with a reflux condenser and a  $\frac{1}{2}$ " PTFE-coated stir bar was added elemental selenium (78.9 mg, 1.00 mmol) followed by 1-ODE (15 mL). The flask was then heated under ambient air to 300 °C while stirring at 300 RPM until a yellow-tinted and transparent solution was formed (approximately 30 minutes). Upon reaching 300°C, 5.0 mL of the OLAC/Cd(acac)<sub>2</sub> solution was switly added to the ODE/Se solution via a glass syringe, resulting in a rapid color change from clear/yellow-tinted to a deep red (indicative of the formation of CdSe species) and a temperature decrease to ~ 270°C. The temperature was then maintained between 270-275°C for the desired reaction time (0-60 minutes), yielding ZB CdSe nanocrystal of cubic crystal habit. After the desired reaction time, 1-ODE (10 mL) was injected to rapidly cool the reaction mixture, the heating mantle was removed, and the crude mixture was allowed to cool to room temperature. The reaction mixture was then worked up as described below.

Workup of the 5.9 - 8.0 nm CdSe NCs was performed by separating the crude reaction mixture into two 45 mL centrifuge tubes (~15 mL each), followed by dilution to 25 mL with toluene. The clear, dark red dispersions were then precipitated with 10 mL of EtOH, resulting in cloudy red dispersions. Centrifugation at 9,000 RPM for 7 minutes to yield dark red pellets and red/transparent supernatants. The supernatants were decanted, and the pellets were dispersed in 25 mL of toluene followed by vortex mixing until homogenous. Once again, 10 mL of ethanol was added to each

tube, and the mixtures were centrifuged at 9000 RPM for 7 minutes, yielding dark red pellets and light red/transparent supernatants. The supernatants were decanted, and the pellets were dried in vacuo at 50 °C overnight to yield 463.29 mg (32.93 wt% organics by TGA, 3.74x10<sup>-7</sup> mol) of a red solid.

#### v. Optical Properties of Synthesized ZB CdSe Seeds



Figure S3. Optical Properties of Synthesized ZB CdSe Nanocrystals. (a) Absorption (solid line) and emission (dashed line) spectra of zincblende CdSe NCs with effective diameters of 2.0 nm, 2.8 nm, 3.7 nm, and 6.2 nm. (b) Sizing curve of zincblende CdSe NCs synthesized herein, with band-gap energies determined from the low-energy absorption maxima, and sizes determined manually from TEM analysis. (n = 100 per sample)

# c. Synthesis of CdSe seeded CdS Tetrapods (CdSe@CdS TPs) via Incremental Injection i. General Consideration

The tetrapod synthesis reported herein was inspired by our previously reported methods, as well as procedures for the seeded growth of CdSe@CdS nanorods that has been extensively published on to date.<sup>6-10</sup> In general, we found the synthesis of tetrapods through standard hot injction methods to be highly sensitive to air and moisture as well as zincblende CdSe seed concentration. While issues of air/moisture could be mitigated through standard Schlenk line techniques and heating solid reagents at 50 °C in vacuo prior to use, the challenge of zincblende CdSe seed concentration persisted, especially at small seed sizes where concentration determination in traditionally challenging. We posited that nonoptimized seed concentrations led to homonucleation of CdS species, resulting in product mixtures of nanorods and tetrapods from the hot injection method. To mitigate this, the sulfur precursor was incrementally injected to a reaction mixture containing zincblende CdSe quantum dots, allowing for slow-growth of tetrapod species without CdS homonucleation (Figure 3 of the main text). While initially developed for small seed sizes (~ 2.0 nm), where concentration of seeds was approximated through geometric considerations, this incremental injection approach proved universal to all seed sizes studied herein. From this method, highly uniform tetrapods could be obtained in high purity and yield, regardless of the zincblende CdSe seed size (Figure S4-S7).

#### ii. Preparation of ZB CdSe NC/TOP Stock Solution

A quantum dot stock solution of concentration 1.7  $\mu$ M in TOP was prepared by addition of CdSe quantum dots of the desired size (13.57 mg – 24.14 mg, for 2.0 – 6.2 nm ZB CdSe NCs, respectively; MW<sub>2.0nm</sub>= 6.95x10<sup>5</sup> g/mol with 97.9% organics; MW<sub>6.2nm</sub>= 1.24x10<sup>6</sup> g/mol with 32.8% organics; 1.95x10<sup>-8</sup> mol in all cases) to a 20 mL scintillation vial fitted with a rubber septum. The vial was

## iii. Preparation of TOP=S Stock Solution

A trioctylphosphine sulfide (TOP=S) stock solution of concentration 0.59 M sulfur in TOP was prepared by addition of sulfur powder (262.5 mg; 8.19 mmol) to a 20 mL scintilliation vial and fitted with a septum. The vial was evacuated of air and backfilled with Ar three times. Then, 15.0 mL of TOP (97%) was added to the vial via syringe, and the resulting mixture was sonicated and vortexed mixed until homogeneous.

# iv. Synthesis of CdSe@CdS Tetrapods from 2.0-6.2 nm ZB CdSe NCs

The synthesis of CdSe@CdS tetrapods was modified from our previously-reported literature procedures.<sup>6-7</sup> To a 50 mL three neck round-bottom flask equipped with a 1" PTFE coated stirbar and reflux condenser was added TOPO (5.40 g, 140 mmol), ODPA (0.285 g, 0.852 mmol), OLAC (0.912 g, 1.02 mL, 32.3 mmol), and CdO (0.110 g, 0.857 mmol). The contents of the flask were subsequently degassed at 150°C in vacuo for 30 minutes while stirring at 300 RPM. The reaction mixture was then heated to 300°C under Ar to dissolve the CdO and form a clear and colorless solution. To this solution, TOP (1.01 g, 1.22 mL, 27.3 mmol) was then injected into the flask and the temperature was allowed to recover to 350°C. After equilibrating at 350°C for 30 minutes, a freshly prepared 1.7 µM stock solution of ZB CdSe QDs of the desired core-size in TOP (97%) was swiftly injected into the reaction mixture. After approximately 4 seconds, the first injection of a freshly prepared 0.55 M stock solution of TOP=S (0.20 mL) was injected into the flask, and the tetrapod shell was allowed to grow for 3 minutes postinjection at 350°C. This process was repeated three additional times (0.80 mL of TOP=S injected total, 12 minute reaction time). After each injection, alioquots were taken for TEM imaging to monitor the growth of the tetrapod NCs (Figure S4). After the final growth perior, the heating mantle was removed and the flask was allowed to cool naturally to 110 °C whereupon toluene (10 mL) was injected to prevent solidification of the low melting point solid (TOPO). Purification was carried out through three precipitation/redispersion cycles using a 1:1 mixutre of MeOH:IPA as the nonsolvent mixture, and toluene for redispersion.

To purify the crude product from excess TOPO/ODPA, as well as unreacted S species, two centrifugation steps were performed using 50 mL centrifuge tubes. The room temperature product was distributed evenly between two centrifuge tubes, each a volume of ~10 mL of crude reaction mixture. In order to precipitate the nanocrystals, 5 mL of methanol was then added to each tube, resulting in cloudy yellow dispersions. The mixtures were then centrifuged at 9000 rpm for 9 minutes to yield yellow/orange pellets and clear and colorless supernatants. The supernatants were then decanted and each pellet was dispersed in 10 mL of toluene and vortex mixed until homogenous. As before, 5 mL of methanol was then added to each tube to precipitate the nanocrystals, resulting in cloudy yellow dispersions. The mixture were then centrifuged at 9000 rpm for 9 minutes to yield supersions. The mixture were then centrifuged at 9000 rpm for 9 minutes to yield was then added to each tube to precipitate the nanocrystals, resulting in cloudy yellow dispersions. The mixture were then centrifuged at 9000 rpm for 9 minutes to yield yellow, was then added to each tube to precipitate the nanocrystals, resulting in cloudy yellow dispersions. The mixture were then centrifuged at 9000 rpm for 9 minutes to yield yellow, was then added to each tube to precipitate the nanocrystals, resulting in cloudy yellow dispersions. The mixture were then centrifuged at 9000 rpm for 9 minutes to yield yellow, was then added to each tube to precipitate the nanocrystals, resulting in cloudy yellow dispersions. The mixture were then centrifuged at 9000 rpm for 9 minutes to yield yellow, was then added to each tube to precipitate the nanocrystals, resulting in cloudy yellow dispersions. The mixture were then centrifuged at 9000 rpm for 9 minutes to yield yellow, was solid. Transmission electron-microscope imaging confirmed the formation of uniform CdSe@CdS tetrapods with nearly no nanorod/quantum dot impurities, and the materials were sized using ImageJ software (L<sub>arm</sub>

To confirm the purify of tetrapod nanomaterials produced via this synthesis, investigation into the % impurities of a standard *incremental injection* tetrapod synthesis were done via TEM imaging, with n=1226 particles investigated in a 3µm region of a carbon-coated TEM grid (Figure S5).



**Figure S4. Kinetic study of tetrapod growth from 2.0 nm ZB CdSe NCs by incremental injection.** (a) Initial product distribution 3 minutes after the first injection of TOP=S. (b) Product distribution 3 minutes after the second injection of TOP=S. (c) Product distribution 3 minutes after the third injection of TOP=S. (d) Product distribution 3 minutes after the fourth injection of TOP=S. Scale bars are 100 nm.



**Figure S5. SEM imaging of CdSe@CdS Tetrapods.** SEM image of submonolayer assembly of 2.8 nm seeded CdSe@CdS TPs on an indium-tin oxide (ITO) substrate. Scale bar is 500 nm.



**Figure S6. Elemental Mapping of CdSe@CdS Tetrapods.** (a) HAADF-STEM image of two 6.2 nm seeded CdSe@CdS tetrapod heterostructures. (b-g) Corresponding EDX elemental maps for Cd, S, Se, and the superimposed Cd/S and Cd/Se maps. Note that Se is located at the center of each tetrapod. Scale bar is 20 nm.

## d. Synthesis of Singly Au-Tipped CdSe@CdS Tetrapods (Au-CdSe@CdS TPs) on 8 mg Scale i. Preparation of DDAB Stock Solution

To a tarred 20 mL glass scintillation vial was added DDAB in an Ar-filled glovebox, followed by sealing the vial with a tarred rubber septum and removing from the glovebox. After removing from the glovebox, the vial fitted with the septum and loaded with the surfactant was remassed, and the mass of DDAB added was determined by difference. An appropriate quantity of anhydrous, Ar-sparged toluene was then added to the vial under standard Schlenk line techniques to result in a concentration of 9.01 mM DDAB in toluene. The contents of the vial were then sonicated for 5 minutes until homogeneous, resulting in a clear and colorless solution. As an example, a typical preparation would result in 81.1  $\mu$ mol (0.03750 g) of DDAB added to the vial as determined by difference, and 9.0 mL of anhydrous, Ar-sparged toluene would then be added to the vial. It should be noted that this preparation could be performed entirely in the glovebox, if equipped with an analytical balance. However, in our experience, massing by difference resulted in consistent results if care was taken to keep the surface of the vial free of debris or oils while transferring between the glovebox and analytical balance.

## ii. Preparation of AuCl<sub>3</sub> Stock Solution

To a tarred 20 mL glass scintillation vial was added AuCl<sub>3</sub> in an Ar-filled glovebox, followed by sealing the vial with a tarred rubber septum and removing from the glovebox. After removing from the glovebox, the vial fitted with the septum and loaded with AuCl<sub>3</sub> was remassed, and the mass of AuCl<sub>3</sub> added was determined by difference. An appropriate quantity of the previously prepared DDAB stock solution was then added to the vial under standard Schlenk line techniques to result in a concentration of 8.80 mM of AuCl<sub>3</sub> in the DDAB stock. The contents of the vial were then sonicated for 5 minutes until homogeneous, resulting in a clear and light yellow/orange solution. As an example, a typical preparation would result in 35.8  $\mu$ mol (0.01087 g) of AuCl<sub>3</sub> added to the vial as determined by difference, and 4.07 mL of the previously prepared DDAB stock would then be added to the vial. The stock solution was then cooled and stored at -4°C.

## iii. Preparation of CdSe@CdS Tetrapod Stock Solution

To a tarred 1 dram vial was added CdSe@CdS tetrapods ( $2.21x10^{-9}$  mol; generally ~ 27 mg at ~70 % organics) and the vial was fitted with a rubber setpum. The vial was evacuated of air and backfilled with Ar three times. Anhydrous, Ar-sparged toluene (6.80 mL) was then added to the vial to result in a concentration of 0.325 µM tetrapods in toluene. The vial was then vortex mixed for 5 minutes until a homogeneous, clear and light yellow/orange solution was obtained. It should be noted that the vial should not be sonicated, as this was observed to result in fragmentation of the tetrapods, presumably due to mechanical strain imparted by the cavitation process.

## iv. Synthesis of Au-CdSe@CdS Tetrapods using 365 nm irradiation

The synthesis of Au-CdSe@CdS tetrapods was adapted from our previous literature.<sup>6-7</sup> A 1 dram vial was equipped with a 10 mm stirbar, sealed with a rubber septum, and evacuated of air and backfilled with Ar three times. The previously prepared CdSe@CdS tetrapod stock solution (0.68 mL, 2.21x10<sup>-10</sup> mol CdSe@CdS TPs) was then added to the reaction vial, and the vial was cooled at -4 °C for 15 minutes. The AuCl<sub>3</sub>:DDAB stock solution was also cooled at -4 °C for 15 minutes prior to use. Once cooled, the AuCl<sub>3</sub> stock solution (0.25 mL, 2.2  $\mu$ mol AuCl<sub>3</sub>) was added to the reaction vial containing the CdSe@CdS tetrapod stock, and the resulting solution was irradiated at 365 nm in a custom-built photochemical reactor with continuous stirring (600 RPM) between 2.5 – 60 minutes depending upon

the size of the CdSe seed used to prepare the tetrapod sample (see Figure 7 of the main text). Throughout the course of the reaction, the color of the solution was observed to change from light yellow/orange to deep amber, while remaining entirely homogeneous. Formation of a precipitate or a purple-colored solution was consistent with non-selective tipping of the tetrapods (multiple tipping), which was found to result from trace moisture in the system and/or inadequate cooling of the precursors prior to the reaction. The custom-built photochemical reactor was constructed from a TLC UV-lamp affixed atop a magnetic stir plate, and covered with a black box to prevent external irradiation from ambient lighting.

To purify the crude product from excess gold precursor and DDAB surfactant, one centrifugation step was performed. The crude product was added to a single 15 mL centrifuge tube, followed by diluting to 2 mL with acetone in order to precipitate the nanocrystals, resulting in a cloudly, amber dispersion. The mixture was then centrifuged at 9000 RPM for 7 minutes to yield an amber pellet and a clear and colorless supernatant. Transmission electron microscopy confirmed the formation of selectively Autipped CdSe@CdS tetrapods with no free Au NPs.

# e. Synthesis of Singly Au-tipped CdSe@CdS Tetrapods (Au-CdSe@CdS TPs) on 2500 mg Scale

# i. Preparation of DDAB Stock Solution

To a tarred 120 mL glass bottle was added DDAB in an Ar-filled glovebox, followed by sealing the bottle with a tarred rubber septum and removing from the glovebox. After removing from the glovebox, the bottle fitted with the septum and loaded with the surfactant was remassed, and the mass of DDAB added was determined by difference. An appropriate quantity of anhydrous, Ar-sparged toluene was then added to the bottle under standard Schlenk line techniques to result in a concentration of 9.01 mM of DDAB in toluene. The contents of the bottle were then sonicated for 5 minutes until homogeneous, resulting in a clear and colorless solution. For this reaction, this resulted in 884.5  $\mu$ mol (409.2 mg) of DDAB being added to the bottle as determined by difference, and 92.37 mL of anhydrous, Ar-sparged toluene was then added using Ar via standard Schlenk line techniques.

## ii. Preparation of AuCl<sub>3</sub> Stock Solution

To a tarred 120 mL glass bottle was added AuCl<sub>3</sub> in an Ar-filled glovebox, followed by sealing the bottle with a tarred rubber septum and removing from the glovebox. After removing from the glovebox, the bottle fitted with the septum and loaded with AuCl<sub>3</sub> was remassed, and the mass of AuCl<sub>3</sub> added was determined by difference. An appropriate quantity of the previously prepared DDAB stock solution was then added to the bottle under standard Schlenk line techniques to result in a concentration of 8.80 mM of AuCl<sub>3</sub> in the DDAB stock. The contents of the bottle were then sonicated for 5 minutes until homogeneous, resulting in a clear and light yellow/orange solution. For this reaction, this resulted in 424.0  $\mu$ mol (128.6 mg) of AuCl<sub>3</sub> being added to the bottle as determined by difference, and 96.33 mL of the previously prepared DDAB stock was then added to the bottle under Ar using standard Schlenk line techniques . The stock solution was then cooled and stored at -4°C.

# iii. Preparation of CdSe@CdS Tetrapod Stock Solution

To a tarred glass bottle was added  $CdSe_{2.8}$ @CdS Tetrapods (1.004 g, 70 wt% organics by TGA,  $L_{arm} = 37.2$  nm, 81.3 nmol) and the bottle was fitted with a rubber septum. The bottle was evacuated of air and backfilled with Ar three times. Anhydrous, Ar-sparged toluene (250.0 mL) was then added to the bottle using stanrdard Schlenk line techniques to result in a concentration of 0.325  $\mu$ M tetrapods in toluene. The bottle was then vortex mixed for 5 minutes until a homogeneous, clear and light yellow/orange

solution was obtained. It should be noted that the solution was not sonicated, as this can result in fragmentation of the tetrapods, presumably due to mechanical strain imparted by the cavitation process.

## iv. Synthesis of Au-CdSe@CdS Tetrapods using Ambient Sunlight

A 500 mL three-neck round bottom flask equipped with a 1" PTFE-coated stir bar was evacuated of air for 30 minutes, and backfilled with Ar. This process was repeated two additional times for a total of three evacuation/backfilling cycles. Subsequently, 250 mL of the previously prepared 0.325  $\mu$ M stock solution of tetrapods (CdSe quantum dot core diameter = 2.8 nm) in anhydrous, sparged toluene was injected into the flask, along with 36.2 mL of IPA (10% by volume sacrificial hole scavenger). The flask was carefully wrapped in aluminum foil in order to minimize exposure to ambient light light. Subsequently, 90.4 mL of the previously prepared AuCl<sub>3</sub> stock solution (at -4°C) was injected *via* syringe. The reaction flask was taken outdoors (still wrapped in aluminum foil to prevent premature initiation of the reaction), stirred at 300 RPM, and the aluminum foil was removed from the flask in order to expose the reaction mixture to Tucson, AZ sunlight at midday. During the course of 90 seconds, the solution turned from a bright orange, translucent color (characteristic of CdSe@CdS tetrapods) to a deep purple and slightly translucent color (Figure S10). The flask was then wrapped with aluminum foil, and the product was subsequently worked up through one precipitation/redispersion cycle using acetone as the nonsolvent and toluene for redispersion, yielding 2500 mg of Au-CdSe@CdS tetrapods.



Figure S7. Images of Large Scale Tipping Reactions. (A-I) Images of large scale tipping reaction taken at 10 second intervals over the course of 90 seconds of total reaction time. The  $T_0$  sample can be seen in Figure 9A of the main text.

#### 2) Electron Diffraction Analysis of Zinc Blende CdSe Nanocrystal



**Figure S8. Selected Area Electron Diffraction Pattern for CdSe NCs.** (A) SAED pattern of 2.8 nm CdSe NCs, (B) SAED pattern of 3.7 nm CdSe NCs, (C) SAED pattern of 6.2 nm CdSe NCs.

Selected area electron diffraction pattern analysis was performed on the 2.8 nm, 3.7 nm, and 6.2 nm CdSe seeds from which the tetrapod samples described in the main text were prepared. For the 2.8 nm and 3.7 nm samples (Figure S9A-B), reflections from the zincblende (111), (220), and (311) planes could be clearly seen, confirming the crystal structure of these nanocrysrals as zincblende. For the 6.2 nm sample, additional (400) and (331) reflections were observed (Figure S9C), corresponding to lower intensity zincblende CdSe reflections.

3) Transient Kinetics of CdS and CdSe exciton bleach features at 580 nm excitation for 2.8 nm Seeded CdSe@CdS tetrapods



**Figure S9. Transient Kinetics of Exciton Bleach in Quasi-Type II Tetrapods.** Transient kinetics of exciton bleach recovery in quasi-type II CdSe<sub>2.8</sub>CdS<sub>35</sub> tetrapod probed at CdS rod (500 nm) and CdSe seed (620 nm) exciton bands after selective excitation of CdSe seed at 580 nm. Thin solid line is a biexponential fit to the exciton bleach kinetics. The formation of exciton bleach can be fit by a rise time of 5.7 fs after convolution with instrument response function.



4) Comparison of Transient Spectra of CdSe@CdS Tetrapods and CdSe@CdS Quantum Dots

**Figure S10. Transient Absorption Spectra of CdSe@CdS Tetrapods and Quantum Dot Seeds.** Comparison of the transient absorption spectra of CdSe@CdS tetrapods and CdSe quantum dot seeds for (a) 2.8 nm seeded CdSeCdS TPs, (b) 3.7 nm seeded CdSeCdS TPs, and (c) 6.2 nm seeded CdSeCdS TPs. The transient spectra are averaged spectra at 1- 2 ps after excitation. The quantum dots were excited at 400 nm and the tetrapods were excited at 580 nm for 2.8 nm and 3.7 nm seeds and 590 nm for 6.2 nm seed

Transient absorption spectra of tetrapods recorded at 400 nm excitations (of CdS rod) show pronounced bleach of CdS rod at 480nm and smaller bleach of CdSe seed (Figure S12 a, b, c). The transient spectra of selective excitation of CdSe seed within the CdSe@CdS tetrapods (at 580 nm for 2.8 and 3.7 nm seeds, and 590 nm for 6.2 nm seeds) show more pronounced bleach of the lowest energy CdSe exciton bands (Figure S12 a, b, c). Comparison with CdSe seed only quantum dots of the same sizes (Figure S12b and c) show that the transient spectra of CdSe@CdS tetrapods with 3.7 nm and 6.2 nm seeds agree well with those of the CdSe quantum dots (slight blue shift), and contain negligible contribution of the bleach CdS rod. For CdSe@CdS tetrapods with 2.8 nm seed, the transient spectrum shows clear contribution of CdS rod bleach in addition to the CdSe exciton bands.

#### 5) Relevant Thermogravimetric Analysis (TGA) Data



Figure S11. TGA data for the series of ZB CdSe NCs used to seed the growth of CdSe@CdS tetrapod samples. (A) 2.0 nm ZB CdSe NCs, (B) 2.8 nm ZB CdSe NCs, (C), 4.4 nm ZB CdSe NCs, (D) 6.2 nm ZB CdSe NCs.

For the zincblende CdSe quantum dots synthesized herein, we observed two consistent onsets of decomposition in all samples at approximately 250 °C and 400 °C, corresponding to the loss of ligands used in the passivation and complexing of Cd/Se species, as well as residual ODE solvent. For 2.0 nm, 2.8 nm, and 3.7 nm samples, an additional low temperature decomposition onset was observed at 100 °C, corresponding to toluene remaining from the purification of the nanocrystals.

## 6) Molar Mass Calculations for CdSe NCs and Tetrapods

Molar mass calculations for CdSe NCs as well as CdSe@CdS tetrapods followed our previously reported methods, utilizing geometric appoximations and percent organic (as determined by TGA) to calculate nanomaterial molecular weight. <sup>6-7</sup> For example, CdSe NCs are geometrically approximated to be spheres at sizes below 3 nm, cubes as sizes above 3 nm, and tetrapod arms are model as cylinders of uniform diameter.

7) Statistical Analysis of Tetrapod Arm Lengths and Diameters



**Figure S12. Statistical analysis on tetrapod arm dimensions.** (A) Representative TEM image of sized tetrapod arms, where the length of the arm is taken from the tip of the tetrapod arm to the point at which the CdS arm connects to the central tetrapod region. (B) Statistics of tetrapod arm lengths measured for tetrapods synthesized from each core size discussed in the main text, demonstrating ~ 35 nm long tetrapod arm lengths for each sample (n=100). (C) A statistically accurate representative schematic of an average tetrapod arm, demonstrating the criteria for width analysis. Each tetrapod arm is bisected along it's length into five portions of equal length (each segment is 20% of the total measured length), and the width at each segment is taken individually. (D) The tapered nature of the tetrapod arms requires this detailed analysis method, which demonstrates highly uniform tapering for all tetrapod samples studied here (n=100 for each width measurement).

#### 8) References

- [1] Wu, K., Rodriguez-Cordoba, W. E., Liu, Z., Zhu, H., Lian, T., ACS Nano 2013, 7, 7173-7185.
- [2] Wu, K., Hill, L. J., Chen, J., McBride, J. R., Pavlopolous, N. G., Richey, N. E., Pyun, J., Lian, T., ACS Nano 2015, 9, 4591-4599.
- [3] Karel Čapek, R., Moreels, I., Lambert, K., De Muynck, D., Zhao, Q., Van Tomme, A., Vanhaecke, F., Hens, Z., *The Journal of Physical Chemistry C* 2010, 114, 6371-6376.
- [4] Talapin, D. V., Nelson, J. H., Shevchenko, E. V., Aloni, S., Sadtler, B., Alivisatos, A. P., Nano Lett. 2007, 7, 2951-2959.
- [5] Yang, Y. A., Wu, H., Williams, K. R., Cao, Y. C., Angew. Chem. Int. Ed. Engl. 2005, 44, 6712-6715.
- [6] Pavlopoulos, N. G., Dubose, J. T., Pinna, N., Willinger, M.-G., Char, K., Pyun, J., Angew. Chem. Int. Ed. 2016, 55, 1787-1791.
- [7] Pavlopoulos, N. G., Dubose, J. T., Hartnett, E. D., Char, K., Pyun, J., *ACS Macro Lett.* 2016, Ahead of Print.
- [8] Hill, L. J., Bull, M. M., Sung, Y., Simmonds, A. G., Dirlam, P. T., Richey, N. E., DeRosa, S. E., Shim, I.-B., Guin, D., Costanzo, P. J., Pinna, N., Willinger, M.-G., Vogel, W., Char, K., Pyun, J., ACS Nano 2012, 6, 8632-8645.
- [9] Hill, L. J., Richey, N. E., Sung, Y., Dirlam, P. T., Griebel, J. J., Lavoie-Higgins, E., Shim, I.-B., Pinna, N., Willinger, M.-G., Vogel, W., Benkoski, J. J., Char, K., Pyun, J., ACS Nano 2014, 8, 3272-3284.
- [10] Carbone, L., Nobile, C., De Giorgi, M., Sala, F. D., Morello, G., Pompa, P., Hytch, M., Snoeck, E., Fiore, A., Franchini, I. R., Nadasan, M., Silvestre, A. F., Chiodo, L., Kudera, S., Cingolani, R., Krahne, R., Manna, L., *Nano Lett.* 2007, 7, 2942-2950.