

Supporting Information, Spatially Indirect Emission in a Luminescent Nanocrystal Molecule

Methods

Tetrapod synthesis. CdSe/CdS tetrapods were synthesized and purified following Talapin et al.¹. Transmission electron microscopy to image the tetrapod samples was performed using a Phillips Tecnai G² 20, and core and arm sizes were measured using ImageJ. For the studies in this work, three different tetrapod samples with average \pm standard deviation arm dimensions [length, width] of [15.7 ± 2.3 , 5.2 ± 0.8], [32.4 ± 2.5 , 5.1 ± 0.7], and [42.7 ± 3.8 , 4.0 ± 0.5] nm are reported in the paper as samples with 15 nm, 30 nm, and 45 nm arms respectively for clarity.

Immobilization onto glass substrates. Transparent coverglass (no. 1.0) substrates were cleaned in ‘piranha’ solution (25% H₂O₂:75% H₂SO₄) at 60° C, then sonicated in deionized water. The glass surfaces were etched using a 1M KOH solution and then thoroughly rinsed with deionized water. The substrates were soaked in a (3-Aminopropyl)triethoxysilane/acetone solution (3% v/v) to produce a slightly hydrophobic surface. A drop of CdSe/CdS tetrapods (~70 pM) were then spin coated (2000 rpm for 1 min.) onto the substrate surface. Tetrapods on the surface were located on average >1 μ m distance apart from each other, ensuring a near-unity probability of having a single tetrapod localized within a diffraction-limited laser spot size.

Microscope design. A home-built sample scanning confocal microscope was used for fluorescence spectroscopy of single tetrapods. Laser light (2.33 eV or 2.54 eV) was spatially filtered using a single mode optical fiber and focused on the sample by a 60x oil objective (NA = 1.43). The diameter of the diffraction-limited laser spot is 460 nm (2.33 eV) or 420 nm (2.54

eV). The sample was mounted on a piezoelectric stage with 100 μm x 100 μm travel. The sample was raster scanned in 100 nm steps to obtain a fluorescence image of the immobilized tetrapods. Individual tetrapods were then positioned at the waist of the excitation laser. Photoluminescence emission from the sample was collected by the same objective and split using a broadband beam-splitter to simultaneously measure intensity time traces and photoluminescence spectra. A single photon counting Avalanche Photodiode (MPD, Italy) measured intensity time traces (0.01 s integration time) from 10% of the emitted beam that was bandpass filtered (600-700 nm). The remaining 90% of emission was sent through a spectrometer (300 BLZ grating, centered at 640 nm) and imaged on a charge coupled device (CCD) camera (Andor iXon X3 897) to measure luminescence spectra (0.1 s integration time). Each particle was illuminated for 40 s.

Single particle measurements. To study the effects of arm length, CdSe/CdS tetrapods with arm lengths of 15 nm (78 particles), 30 nm (171 particles), or 45 nm (108 particles) were excited with a 2.54 eV laser at 1.0 μW laser power. To study effects of incident photon flux, tetrapods with 30 nm arms were excited at 2.54 eV with laser powers of 0.3 μW (55 particles), 1.0 μW (171 particles), 3.0 μW (62 particles), or 18.0 μW (47 particles). The effect of excitation energy was investigated by exciting 45 nm-arm tetrapods with 2.33 eV (130 particles) or 2.54 eV (108 particles) at 1.0 μW laser power. For the twice-compared conditions of (30 nm CdS arms, 2.54 eV excitation, 1.0 μW laser power) and (45 nm CdS arms, 2.54 eV excitation, 1.0 μW laser power), the same respective tetrapod cohorts were used. Emitters which did not exhibit blinking behavior² were not included in the single particle analysis. Only particles that exhibited multiple peaks at energy differences greater than 40.0 meV were considered as multiple emitters,

eliminating any contributions from exciton coupling to longitudinal optical phonons in CdSe or CdS. In total, 260,400 spectral frames from 651 single tetrapods were analyzed.

Total histogram analysis. We collected 400 spectral frames (0.1 s integration time) per particle. Data was confirmed to be from single particles by ensuring that the corresponding intensity profile exhibited complete on/off blinking (Fig. S1, Supporting Information). To quantify the energy difference between peaks (Fig. 2d), the following analysis was performed: for each particle exhibiting multiple-peak emission, each spectral frame was fit to 0, 1, or 2 Lorentzian curves (depending on the number of emissions observed in that frame) (Fig. S3a, Supporting Information). The intensity-weighted peak energies from each frame were then plotted on a histogram (Fig. S3b, Supporting Information), representing the frequency of emission at a given energy over time for a single particle. These peaks were fit to Gaussian curves, and the maximum of the lower-energy Gaussian peak was considered as the zero-energy difference reference point for that particle. The area-weighted peak positions for a given particle were then plotted versus the change in energy from the lowest excited state (pink histogram in Fig. S3c, Supporting Information), and this data was compared across multiple tetrapods. All peak position histograms for tetrapods under a given condition were summed to give an overall histogram of emission energies relative to the reference point (Fig. 2d, black outlined plot in Fig. S3c, Supporting Information). Tetrapods which showed a blue-shift of the emission peak over time, commonly observed in quantum dots due to photooxidation³, were not included in this plot for clarity.

Area and shape of peaks in the relative transition energy histogram. The ratio of the lower and higher energy P2 peak areas for tetrapods with 45 nm arms is found to be 7.5:1 from our

experimental data in Fig. 2d. Considering three strained arms and a Boltzmann-weighted distribution based on the energy difference between the levels, a ratio of peak areas is estimated to be 22:1. The lower value of the ratio observed in practice is possibly due to a reduced indirect transition rate caused by interfacial strain. The shape of the peaks in the total histogram is expected to be Gaussian for an ergodic system. However, size and surface polydispersity in our sample results in heterogeneous, non-ergodic optoelectronic behavior: energy levels and fluorescence quantum yields differ among individual tetrapods. Some tetrapods emitted significantly more photons than others over their spectral collection time, biasing the total histogram towards the spectral features of the brighter tetrapods. Furthermore, differing amounts of strain in the tetrapod arms and core due to heterogeneity in immobilization positions or tetrapod dimensions may also cause dispersion in the energy of the CdS conduction band relative to the ground state.

Energy of indirect transition. The analysis in the paper assumes that the lowest energy transition is the direct transition, which is likely given that the bulk CdS conduction band is at a higher energy than that of the bulk CdSe, and also because the conduction band offset of CdS in a CdSe/CdS nanorod was measured to be +0.3 eV in STM studies⁴. Electronic structure calculations demonstrate that an electronic wavefunction primarily located in the CdS arms is at higher energy than one largely existing in the CdSe core⁵. However, recent experiments by Borys et al. suggest that some colloiddally-synthesized tetrapods may have a type-II band alignment, an observation also made more likely due to the thicker, less quantum-confined arms used in that study⁶. It is possible that some of the tetrapods studied here had a lower-energy indirect emission relative to the direct transition, whether due to the intrinsic structure of the tetrapod or the

imposed strain; this would change the peak positions observed in our total histogram analysis as well as the relative areas under each peak. A total histogram plotting only data from tetrapods in which the lowest emission energy observed was also the most frequent emission shows similar behavior to that seen in Fig. 2d, supporting the general conclusions from our analysis. Further experiments combining single particle fluorescence spectroscopy with lifetime measurements will allow definitive assignment of emission peak energies to a direct or indirect transition.

Indirect lifetime measurement. Following the expression in the main body of the paper, we used

$$\gamma = \alpha * [(1 - e^{-k_{\text{direct}}(\alpha+1)/(\alpha*I)}) * \phi_{\text{direct}}] / [(1 - e^{-k_{\text{indirect}}(\alpha+1)/(\alpha*I)}) * \phi_{\text{indirect}}] \quad (1),$$

where $\gamma = N_{\text{em,direct}} / N_{\text{em,indirect}}$, $\alpha = e^{-E_0/kT} / (e^{-E_1/kT} + e^{-E_2/kT})$ with E_0 , E_1 , and E_2 representing the energies of the lowest, middle, and highest energy transitions observed, I = the incident photons per second, ϕ_{direct} and ϕ_{indirect} the intrinsic (low intensity) quantum yields of the respective materials, and $k_{\text{direct}} = 1/10$ ns for CdSe quantum dots similarly sized to our tetrapod core using previously reported values⁷.

$\gamma = (1 - \gamma_{P2} * \gamma_{I2}) / (\gamma_{P2} * \gamma_{I2})$, where γ_{P2} is the fraction of emission under peak P2 in total histograms for each cohort such as the one shown in Fig. 2d and γ_{I2} is the fraction of tetrapods emitting multiple peaks (data shown in Fig. 2b). Using the data from each intensity cohort, we calculate the following values:

Power (μW)	γ_{P2}	γ_{I2}	γ
0.3	0.5322	0.1455	11.9199

1.0	0.5051	0.1111	16.8253
3.0	0.3462	0.0968	28.8507
18.0	0.2841	0.0426	81.6446

To calculate α , we used the total histogram from the 0.3 μW data (low intensity regime) to calculate E_0 , E_1 , and E_2 by taking probability-weighted values of the energy peaks over the change in energy values $[-40.5 \text{ meV}, 40.5 \text{ meV}]$, $[41.5 \text{ meV}, 89.5 \text{ meV}]$, and $[90.5 \text{ meV}, 150.5 \text{ meV}]$ respectively. We calculated $E_0 = 0.0067 \text{ eV}$, $E_1 = 0.0634 \text{ eV}$, and $E_2 = 0.1146 \text{ eV}$. Then, $\alpha = 7.9817$.

To calculate ϕ_{direct} and ϕ_{indirect} , we plotted γ as a function of the incident power to obtain a γ value at 0 μW incident power (representing the intrinsic quantum yield limit). This data fit to a quadratic plot of $\gamma = -0.154x^2 + 6.75x + 10.04$ with $R^2 = 0.9999$ with x = the incident power. Setting $\gamma(x=0) = 10.04$ into equation (1), we calculated an expression for ϕ_{indirect} as a function of ϕ_{direct} . Using a value of $\phi_{\text{direct}} \sim 0.3$ (30% intrinsic quantum yield for a typical sample), $\phi_{\text{indirect}} = 0.22$. Taking an average of k_{indirect} from the 0.3 μW , 1.0 μW , and 3.0 μW data sets weighted by the number of particles observed in each cohort, we calculated a lifetime for the indirect transition of $\tau_{\text{indirect}} = 204 \pm 30 \text{ ns}$. The 18.0 μW data was not included in the τ_{indirect} calculation due to fast photobleaching and therefore many fewer fluorescence spectra observed compared to the other data sets.

Supporting Figure Captions.

Figure S1. Fluorescence intensity blinking verifies collection of emission from a single particle.

A sample intensity trajectory of a single CdSe/CdS tetrapod with 45 nm arm length, excited with 2.33 eV photons at 0.60 kW/cm².

Figure S2. Multiple radiative transitions near the expected CdSe band gap are observed in tetrapods under all the conditions studied. Shown are spectra from tetrapods with [CdS arm size, excitation energy, excitation intensity] of (a) [15 nm, 2.54 eV, 1.0 μ W], (b) [30 nm, 2.54 eV, 1.0 μ W], (c) [45 nm, 2.54 eV, 1.0 μ W], (d) [30 nm, 2.54 eV, 0.3 μ W], (e) [30 nm, 2.54 eV, 3.0 μ W], (f) [30 nm, 2.54 eV, 18.0 μ W], (g) [45 nm, 2.33 eV, 1.0 μ W].

Figure S3. Obtaining energy change histograms from raw emission spectra. (a) Each raw spectrum (black) from a single tetrapod (0.1 s integration time, 40s total observation time) is fit to a Lorentzian function (blue). The center of the Lorentzian peak(s) (pink lines) and the fitted peak areas are recorded. The peak width represents the intrinsic linewidth under experimental conditions. (b) The Lorentzian peak centers from each frame are weighted by their corresponding peak areas, and plotted as a weighted histogram (pink) representing the probability of emission for the single tetrapod under study. The peak widths represent the distribution of spectral diffusion for the particle. The peaks in this histogram are fit to Gaussian peaks (black), and the center of the lowest energy peak is set as the zero-point reference energy for this tetrapod. (c) The area-weighted peak centers from all frames relative to the zero-point energy for a given tetrapod are plotted to form an energy change histogram for that tetrapod (pink); data from all

tetrapods within a sample cohort are summed together to plot an energy change histogram representing cohort statistical behavior (black).

References.

1. Talapin, D. V.; Nelson, J. H.; Shevchenko, E. V.; Aloni, S.; Sadtler, B.; Alivisatos, A. P. *Nano Lett.* **2007**, 7, (10), 2951-2959.
2. Kuno, M.; Fromm, D. P.; Hamann, H. F.; Gallagher, A.; Nesbitt, D. J. *J. Chem. Phys.* **2000**, 112, (7), 3117-3120.
3. Sark, W. G. J. H. M. v.; Frederix, P. L. T. M.; Heuvel, D. J. V. d.; Gerritsen, H. C.; Bol, A. A.; Lingen, J. N. J. v.; Donegá, C. d. M.; Meijerink, A. *J. Phys. Chem. B.* **2001**, 105, 8281-8284.
4. Steiner, D.; Dorfs, D.; Banin, U.; Sala, F. D.; Manna, L.; Millo, O. *Nano Lett.* **2008**, 8, 2954-2958.
5. Lutich, A. A.; Mauser, C.; Como, E. D.; Huang, J.; Vaneski, A.; Talapin, D. V.; Rogach, A. L.; Feldmann, J. *Nano Lett.* **2010**, 10, (11), 4646-4650.
6. Borys, N. J.; Walter, M. J.; Huang, J.; Talapin, D. V.; Lupton, J. M. *Science* **2010**, 330, 1371-1374.
7. Califano, M.; Franceschetti, A.; Zunger, A. *Nano Lett.* **2005**, 5, (12), 2360-2364.