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Photoluminescence Quenching of Single CdSe Nanocrystals by Ligand Adsorption

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ABSTRACT

We study the effects of octadecanethiol on the photoluminescence intensity and blinking dynamics of single CdSe nanocrystal quantum dots. The number of luminescent nanocrystals per unit area, the intensity histograms of the luminescent nanocrystals, and the single nanocrystal blinking behavior are analyzed in samples with and without added octadecanethiol. We find that the individual nanocrystals within an ensemble do not quench uniformly with thiol addition. The data suggest that the binding of a single octadecanethiol molecule to a CdSe nanocrystal can decrease the photoluminescence quantum yield of that single nanocrystal by at least 50%. These results are important for interpreting photoluminescence-based studies of nanocrystal−ligand binding constants and surface chemistry.

Colloidal semiconductor nanocrystals are promising chromophores for use in applications ranging from light-emitting diodes (LEDs)[1–6] to photodiodes[7–9] and biosensors.[10] Nanocrystals are attractive for these applications because of their size-tunable band gaps, spectrally narrow photoluminescence, high photoluminescence quantum yields, photostability (compared with organic chromophores),[11] and solution processability. The control of nanocrystal surface chemistry is critical to the optimization of many of these desirable properties, including processability, photostability, and photoluminescence quantum yield. Although nanocrystals used in biological labeling are typically encased in an inorganic shell, their photoluminescence behavior can still be sensitive to the presence of small surface-active molecules in solution.[12–14] For nanocrystal-based optoelectronic devices such as LEDs and photodiodes, it would be advantageous to use surface ligands that can facilitate charge injection or extraction[15] (for LEDs or photodiodes, respectively) and that bind strongly to the nanocrystal surface to retain processability while minimizing the excess free ligand in nanocrystal solutions.[6,16–18]

Because of the increasing importance of nanocrystal−ligand interactions, a number of groups have studied the effects of ligand binding in common preparations of CdSe nanocrystals.[12–14,19–28] Most of these studies have focused primarily on the changes in the photoluminescence intensity of large ensembles of particles in solution.[13,19–23,27,28] These studies have confirmed that alkanethiols generally quench the photoluminescence of CdSe nanocrystals,[20,22,23,27] while primary alkylamines can both enhance and quench nanocrystal photoluminescence depending on the amine concentration in solution.[19,20,22,23,28] In addition, it has also become standard practice to use the absorption or photoluminescence intensity as a proxy for fractional surface coverage in order to generate Langmuir adsorption isotherms (or modified versions thereof) to extract ligand binding affinities.[22,23,28,29] However, in most cases, the validity of the underlying assumptions behind this method have not been checked at the microscopic level.[23]

In contrast to the number of solution measurements on large ensembles of nanocrystals, there have been far fewer studies of the effects of surface ligands on CdSe nanocrystal photoluminescence at the single-nanocrystal level.[12,14,24–26] The existing single-nanocrystal studies have tended to focus on the effects of different ligands on the photoluminescence intermittency (or blinking) of single nanocrystals.[12,14,24–26] However, a better understanding of the effects of ligand binding on single nanocrystal photoluminescence is critical to interpreting existing ligand binding data derived from solution photoluminescence measurements. For instance, a given concentration of alkanethiol could quench the photoluminescence of a nanocrystal solution by 50% in two different ways: (1) by uniformly reducing the quantum yield of every nanocrystal by half or (2) by completely quenching the photoluminescence of half of the nanocrystals via a single binding event. Distinguishing between these cases is required to accurately extract ligand binding constants from ensemble solution quenching data.[23] Even if the actual behavior lies

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somewhere between the extremes, single-molecule measurements present a straightforward means to identify the effects of ligand binding on individual nanocrystals. We have previously shown that the effects of thiols on nanocrystal photoluminescence intensity vary with nanocrystal surface composition (e.g., the photoluminescence intensity of CdSe nanocrystal solutions decreases with increasing octadecanethiol concentration, while the photoluminescence intensity of CdSe/ZnS core/shell nanocrystal solutions does not).[23] In this paper, we study the photoluminescence of single CdSe nanocrystals in the presence and absence of 1-octadecanethiol in order to directly test the assumptions underlying the use of photoluminescence as a proxy for fractional surface coverage in solution-based photoluminescence quenching experiments with nanocrystals. We note that the nanocrystals studied here are CdSe core nanocrystals and are thus more sensitive reporters of their local environment than core/shell nanocrystals with an inorganic shell.

The CdSe nanocrystals used in this study were synthesized following the CdO-precursor route of Peng et al.,[30] as previously described.[23] After synthesis, the nanocrystals were extracted twice from hexanes and methanol. The nanocrystals were then re-suspended in toluene and stored in the dark. Before use, the nanocrystal solutions were filtered through a 0.2 μm PTFE filter. For the single-nanocrystal studies, 3−5 nM CdSe nanocrystal solutions in toluene were mixed on a vortexer, sonicated for 10 s, and immediately spin-coated onto a coverglass (VistaVision™ No. 1.5, VWR catalogue #16004−326) at a spin speed of 2000 rpm for 30 s. The nanocrystal concentration was determined by diluting a CdSe solution with an optical density (O.D.) ~1.5 at the first CdSe absorbance peak (565 nm) by a factor of 2000. The initial solution concentration was determined using the empirical formula for the extinction coefficient of CdSe nanocrystals reported by Yu et al.[31] The coverglasses were cleaned in boiling RCA1 solution (*hazard:* 1 part NH_4OH, 1 part H_2O_2, and 4 parts nanopure H_2O) for ~50 min prior to deposition of the nanocrystals. The cleaned coverglasses were stored in purified Milli-Q water prior to spin-coating with nanocrystals. For samples with thiol, 1-octadecanethiol was mixed with a nanocrystal solution; the final solution had a nanocrystal concentration of 3−5 nM and a final octadecanethiol concentration of 1×10^{-5} M. The solution octadecanethiol concentration of 1×10^{-5} M was chosen to give a roughly 50% reduction in the photoluminescence of the spin-coated nanocrystal samples when processed as described above. We note that comparing the ensemble intensity values of these spin-coated samples to equilibrated solution experiments is complicated, since the samples were likely not at equilibrium (given the short mixing times and uncertainty in concentrations introduced during spin-coating). Furthermore the free "native" ligand concentrations were not as carefully controlled as in our previous studies.[23] Nevertheless, the samples need not be fully equilibrated to test whether thiol binding leads to uniform or nonuniform quenching of the photoluminescence at the single-nanocrystal level.

The dispersed nanocrystal samples were imaged using a 40× oil immersion objective (Nikon S Fluor) in an epi-illumination geometry on a Nikon TE2000-U inverted microscope. The nanocrystals were excited with a 532 nm cw laser (CrystaLaser GCL-025-L) converted to circular polarization using a $\lambda/4$ waveplate. The laser beam was defocused with a convex lens (focal length = 125 mm) prior to entering the microscope objective. The power density at the sample surface was ~100 W × cm^{-2}. Nanocrystal photoluminescence was collected by the objective and passed through a 532 nm beam splitter, a StopLine notch filter (Semrock NF01−532U-25), and a 40 nm emission bandpass filter centered at 575 nm. Finally, the light was collected by a Roper Scientific liquid nitrogen cooled CCD (Spec-10: 400B/LN). Images of a 40 μm × 40 μm area at the center of the defocused laser spot were collected with a 100 ms integration time, a 50 ms dead time, an analog-to-digital converter speed of 2 MHz, a gain setting of 3 (corresponding to 16 detected electrons per A/D units generated), and hardware binning the pixels by 2 in both the x and y direction for a sample image area corresponding to 1 μm^2 per pixel. Images were collected continuously for ~50 min under $N_2(g)$ after purging the sample chamber for 20 min with $N_2(g)$. Because of changes in the background signal from the coverglass, we excluded the first 5 min of each run from data analysis (the total observation time was typically 45 min). Aside from the difference in background, the samples behaved qualitatively similarly over the entire observation period. The power variation from the center pixel to the corners of the imaged area was less than 10%. All images were analyzed using IgorPro software version 5.04 with macros written by the author. Power-law fits to the photoluminescence intermittency data were performed using both log-least-squares[32] and the maximum likelihood estimation method.[33]

All of the particles that we observe exhibit blinking; however, the qualitative nature of the blinking behavior varies from particle to particle. Figure 1 shows intensity time traces and corresponding intensity histograms of two different CdSe nanocrystals. The time trace in Figure 1A is an example of digital blinking, similar to that reported in the literature for CdSe/ZnS core/shell nanocrystals.[32,34,35] Discrete intensity levels of this nanocrystal are seen in Figure 1B. Figure 1C plots the intensity time trace of a nanocrystal that appears to blink in nondigital fashion. The intensity histogram for this particle (Figure 1D) displays a continuum of intensity levels, in contrast with the discrete levels apparent in Figure 1B. The majority (>75%) of the nanocrystals we observe exhibit emission similar to that shown in Figure 1C,D, with a comparatively small fraction exhibiting the digital blinking, shown in Figure 1A,B.

Many of the pioneering single-nanocrystal blinking studies of CdSe/ZnS core/shell nanocrystals describe digital two-level blinking.[32,34,35] However, studies of single-nanocrystal blinking with CdSe nanocrystal cores (no inorganic shell) have often reported broader distributions of emission intensities.[24,34,36] More recently, single-molecule studies of core/shell nanocrystals have also reported nanocrystal photoluminescence intermittency with multiple emissive intensities.[25,26,36−39] The source of a continuous distribution

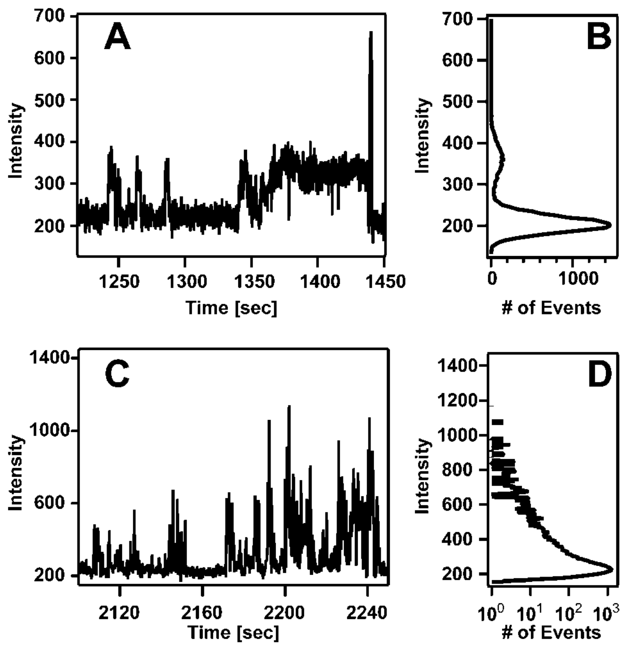

Figure 1. (A) Photoluminescence intensity versus time trace for a nanocrystal exhibiting apparent two-level blinking behavior; (B) the intensity histogram for the digital two-level nanocrystal shown in A. (C) Photoluminescence intensity versus time trace for a typical continuous intensity nanocrystal; (D) the intensity histogram for the nanocrystal shown in C.

of intensities (as opposed to the two-level) blinking is a matter of current study and could range from multiple “on” intensity levels for single nanocrystals[38,39] to clustering effects[40] or multiple individual nanocrystals being imaged by a single pixel.[40]

From AFM measurements (Figure S1, Supporting Information), we rule out the presence of multiple individual nanocrystals in the focal area of a single pixel in our samples. Although we cannot rule out the possibility that some of the blinking particles are aggregated clusters of nanocrystals, we note that the existence of clusters will not significantly impair our ability to constrain the effects of ligand adsorption on quenching dynamics. If the nanocrystals are coupled electronically or by energy transfer,[40] quenching the luminescence of one nanocrystal in a cluster should quench the luminescence of all of the nanocrystals in close proximity.[41] Thus, any possible clustering will only place a more stringent limit on the quenching effects of an alkanethiol ligand binding to a CdSe nanocrystal, and so we include nanocrystals with both “two-level digital” and “continuous” intensity distributions in the analysis that follows.

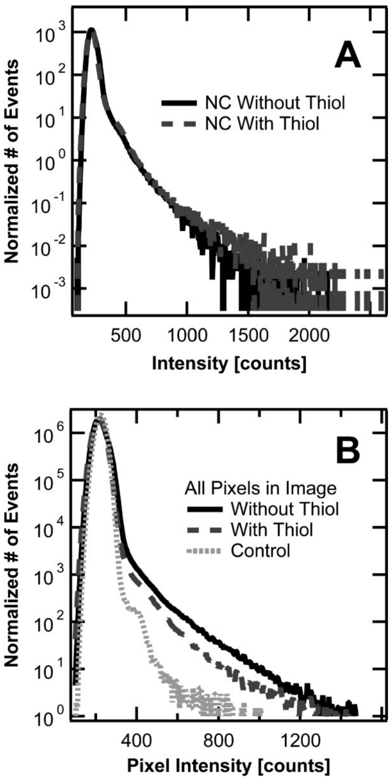

Figure 2. (A) Normalized nanocrystal (NC) intensity histograms (normalized by the number of observed nanocrystals) in samples with thiol (dashed gray line) and without thiol (solid black line), using a detection threshold of 375 counts. (B) Normalized intensity histogram including all pixels in the field of view for samples with thiol (dashed gray line), without thiol (solid black line), and the normalized intensity histogram of a control coverglass without nanocrystals (dotted light gray line).

Table 1. Number of Photoluminescent Nanocrystals Found at Different Detection Thresholds in a 40 μm × 40 μm Sample Area with Thiol and without Thiol

threshold	avg # of nanocrystals per sample area without thiol	avg # of nanocrystals per sample area with thiol	ratio
500	37	16	2.3
450	50	23	2.2
400	69	32	2.2
375	89	44	2.0

In order to determine how the ligand affects the photoluminescence of individual nanocrystals, we now compare the photoluminescence of dilute nanocrystal samples spin-coated from solutions with and without 1-octadecanethiol. Table 1 compares the number of luminescent nanocrystals observed in samples spin-coated from solutions with thiol (thiol concentration = 10^{-5} M) and without thiol. Although there is no change in the density of nanocrystals as determined by AFM (Figure S1, Supporting Information), we observe approximately half as many photoluminescent nanocrystals in samples with added thiol.

Figure 2A shows the intensity histogram for all of the observed nanocrystals in samples with and without thiol, normalized both by the number of nanocrystals observed and by the length of observation time. Even though there are fewer observable nanocrystals in the samples with added thiol, we see that the intensity histograms are nearly identical, even at high intensity values. Thus, although we observe fewer luminescent nanocrystals in samples with thiol, the distribution of emission intensities of the observed nanocrystals does not change. Our image analysis protocol for identifying single nanocrystals relies on a thresholding procedure. To rule out the effect of the threshold on the data analysis, we processed the images with different threshold levels and reached similar conclusions regardless of the threshold level. In the extreme case, we can analyze the

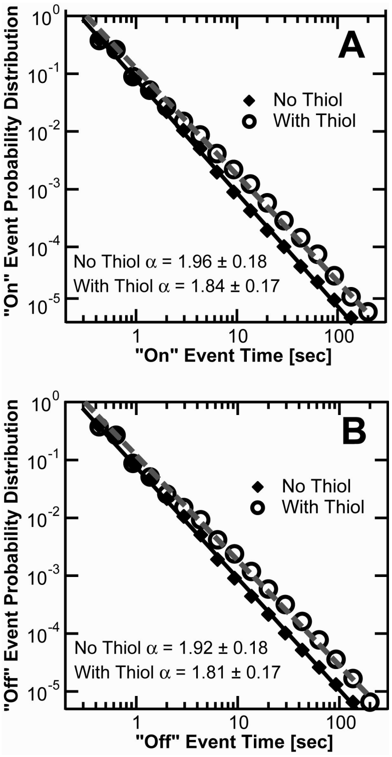

Figure 3. Plots of the probability distributions for the observed nanocrystals to be in the "on" (A) and the "off" (B) states for a given amount of time in samples with thiol (open circles) and without thiol (solid diamonds). The probability distributions are fit as power-law distributions using a log-least-squares method and a blinking threshold of 280 counts.

intensity histogram from every pixel in every image as shown in Figure 2B. We note that, while the shapes of the intensity histograms are very similar for samples with and without thiol, the samples with added thiol have fewer total events that are distinguishable from the background luminescence.

The simplest explanation of these results is that there are fewer "on" nanocrystals in the samples with added thiol and that those nanocrystals that are "on" are emitting with nearly the same intensity distribution as the nanocrystals in the absence of thiol. However, since single nanocrystals exhibit photoluminescence intermittency, we must consider whether thiols are permanently turning the nanocrystals "off," or whether ligand adsorption is changing the kinetics of nanocrystal photoluminescence intermittency so that particles spend different amounts of time in "on" and "off" states (without changing the intensity distribution of the "on" level). At the single-nanocrystal level, the "on" and "off" probability distributions of nanocrystals have been shown to exhibit power-law statistics over many orders of magnitude.[32,34,35,42,43] The power-law equation can be written as

$$P(t) = At^{-\alpha} \tag{1}$$

where $P(t)$ is the probability that an "on" or "off" event lasting time t occurs, A is the normalization constant, and α is the power-law exponent that describes the distribution.

Figure 3 shows the "on" and "off" time histograms for nanocrystal samples with and without added thiol. In both cases, we observe the classic power-law behavior that has been reported for a wide range of nanocrystal samples.[24,32,34–38] The solid lines in Figure 3A,B are power-law fits using the log-least-squares method[32] with the uncertainty in the fit taken to reflect the range of experimentally observed sample-to-sample variation. Significantly, the effect of adding the thiol on either the "on" or the "off" power-law is negligible, and the difference is within the sample-to-sample variation observed for samples without added thiol (a summary of power-law exponents calculated using different thresholds and with different fitting methods is included in Supporting Information).

Several previous studies have reported that ligand absorption can alter CdSe nanocrystal blinking statistics.[12,14,24,25] Thiolates formed in aqueous solution have been reported to reduce blinking by significantly increasing "on" times of streptavidin-functionalized CdSe/ZnS nanocrystals, while alkylamines have been reported to lower the "on" power-law exponent and raise the "off" power-law exponent compared with the as-synthesized CdSe nanocrystals (i.e., the probability of long "on" events and short "off" events were increased, resulting in more luminescent particles). Barnes et al. reported that CdSe nanocrystals with oligo(phenylene vinylene) surface ligands exhibit less blinking but lower overall photoluminescence intensity, compared with CdSe/ZnS nanocrystals.[25,26] In addition, Fomenko and Nesbitt observed that propyl gallate inhibited blinking and reversibly altered the radiative and nonradiative decay rates of CdSe/ZnS nanocrystals in basic aqueous solution.[14] In contrast, we observe little, if any, change in the observed blinking or the "on" and "off" power-law exponents upon addition of octadecanethiol to our nanocrystal samples, despite the observed decrease in the average number of "on" particles in each image upon thiol addition. This suggests that, rather than changing the "on" or "off" time distributions, the octadecanethiol is quenching the photoluminescence of some of the CdSe nanocrystals to a point below our observation threshold so that we observe only those nanocrystals with no adsorbed thiol (or thiol adsorbed to sites that somehow do not affect the nanocrystal photoluminescence), and thus exhibit no change in their blinking kinetics. It is notable that the nanocrystal/ligand systems discussed above vary considerably. Some studies were performed with CdSe core nanocrystals spin-coated from organic solution, while others were performed in aqueous solution with tethered CdSe/ZnS water-solubilized and streptavidin-functionalized core/shell nanocrystals. The differences in the reported effects of each ligand on nanocrystal photoluminescence are likely due to different interactions between the nanocrystals and the ligands in each study. For example, the increase in the radiative and nonradiative decay rates of CdSe/ZnS nanocrystals in the presence of propyl gallate is suspected to suppress blinking,[14] while our data are consistent with octadecanethiol binding introducing a large nonradiative decay rate on CdSe core nanocrystals,[27] thus quenching their photoluminescence.

The data above suggest that thiol addition turns some nanocrystals "off" and removes them from observation in our experiment. Thus, when the total photoluminescence of

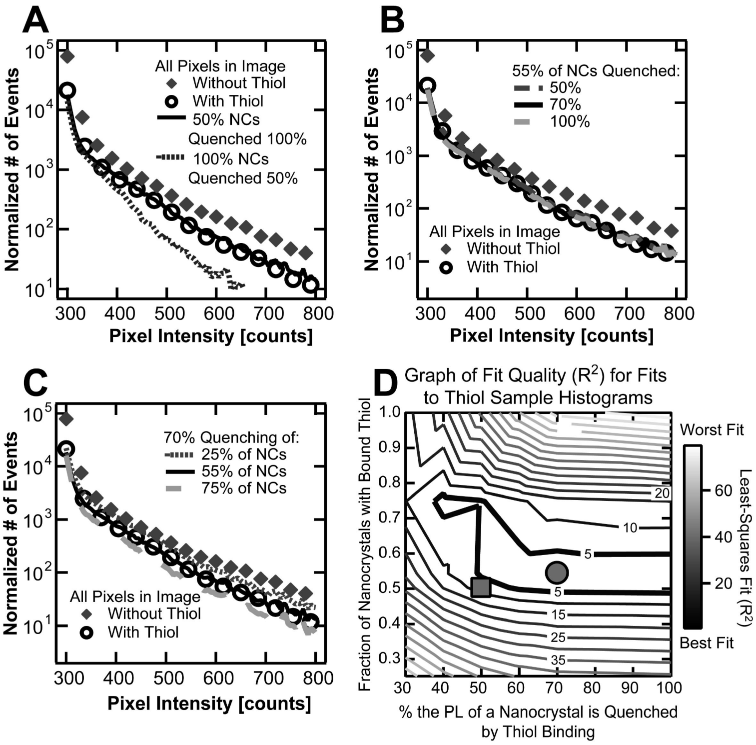

Figure 4. Intensity histograms of all pixels in samples with thiol (open circles) and without thiol (solid diamonds) compared with fits assuming different percentages of nanocrystals are quenched with different efficiencies; (A) data and fits assuming 50% of the nanocrystals have their photoluminescence quenched by 100% (solid black line) or 100% of the nanocrystals have their photoluminescence quenched by 50% (dotted gray line); (B) data and fits assuming 55% of the nanocrystals are quenched by 50% (dashed and dotted dark gray line), 70% (solid black line), or 100% (dashed light gray line); and (C) data and fits assuming 25% (dotted dark gray line), 55% (solid black line), and 75% (dashed light gray line) of the nanocrystals are quenched by 70%. (D) Contour plot of the fit quality (R^2 from least-squares analysis) for fits to nanocrystal intensity histograms with thiol. The fit quality when 55% of the nanocrystals are quenched by 70% is indicated with a circle. The fit quality for half of the nanocrystals being quenched by 50% is marked by a square.

a CdSe nanocrystal ensemble is quenched by 50% due to the addition of octadecanethiol, it is more likely that 50% of the nanocrystals are completely “off” rather than that the quantum yield of every nanocrystal is decreased by 50%. One explanation for this behavior is that a single thiol binding event significantly quenches the photoluminescence of a single nanocrystal. However, because of the fact that nanocrystal ensembles are heterogeneous, it is likely that the nanocrystals each have different numbers of surface sites. There could even be CdSe nanocrystals in the ensemble with no thiol binding sites;[44] such nanocrystals will not be affected by thiol. If we increase the thiol concentration in our single-nanocrystal samples, the number of observed nanocrystals continues to decrease, indicating that we have not reached this limit and that most of our nanocrystals can be quenched by thiol binding.

In order to better quantify the degree of the photoluminescence quenching induced by adsorption of thiols to single nanocrystals, we fit the experimental intensity histograms from Figure 2 to a simple model that includes both the fraction of the nanocrystals that are quenched, χ, and the fractional decrease in the photoluminescence of the quenched nanocrystal, η, as inputs (additional details in Supporting Information). Figure 4A−C shows the expected intensity distributions for several combinations of χ and η. In agreement with the previous discussion, the dotted gray line in Figure 4A shows that uniform quenching of all nanocrystals by 50% is incompatible with the experimental data. On the other hand, complete quenching of 50% of the nanocrystals is reasonably consistent with the data (black line in Figure 4A). If we freely vary χ and η, we obtain a best fit to the data where ~55% of the nanocrystals are quenched by at least 50%, as shown in Figure 4D. There is a broad local minimum in the goodness of fit in the range of 50−100% quenching of 50−60% of the nanocrystals (see Supporting Information for further details). For simplicity, we have assumed that the thiols bind to equivalent surface sites and have similar effects on nanocrystal photoluminescence. It is possible that there are different surface sites which bind thiols with different affinities and which might produce different changes in nanocrystal photoluminescence. However, given that we do not observe changes in the nanocrystal intensity distribution upon thiol addition, our data are consistent with at most two classes of binding sites: those that do not affect the photoluminescence quantum yield and those that strongly quench it by at least 50%.

In summary, the simplest explanation for our data is that binding a single 1-octadecanethiol molecule to an as-synthesized CdSe nanocrystal can quench the photoluminescence of that nanocrystal by at least 50%. Although we cannot determine whether all thiol binding events have the same effect on CdSe nanocrystal photoluminescence without a separate analytical technique to measure thiol binding on single nanocrystals, we have shown that the number of luminescent nanocrystals decreases with increasing thiol concentration, while the intensity distribution of the remaining observable nanocrystals does not change. Furthermore, the photoluminescence intermittency statistics of the observed nanocrystals does not change between samples with and without thiol. These results underscore the importance of single-nanocrystal measurements in understanding the heterogeneous effects of ligand binding on photoluminescence and indicate that CdSe nanocrystal photoluminescence is not always linearly proportional to the fraction of thiol-bound surface sites. When a solution of nanocrystals is 50% quenched by the addition of alkanethiol, it is more likely that 50% of the nanocrystals will have a single thiol bound than that all of the nanocrystals will be 50% saturated with thiol ligands. Thus, we conclude that ensemble photoluminescence should not be used as a general proxy for measuring surface coverage of a ligand without confirmation by a separate analytical technique. Furthermore, the binding constants so far reported for thiol adsorption to CdSe nanocrystals should probably be viewed as upper limits in the context of the other assumptions made when analyzing solution data. These results indicate that more detailed models describing changes in nanocrystal solution photoluminescence due to ligand binding are needed: the model formulated by Tachiya for micellar systems could be an attractive starting point.[45] Measuring and controlling ligand binding to colloidal nanocrystals remains an important scientific and technological challenge for applications ranging from LEDs to solar cells, and single-nanocrystal spectroscopy should serve as a valuable complement to ensemble studies.

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Supporting Information Available: AFM Micrographs of samples, discussion of log-least-squares and maximum likelihood estimator fits to Figure 3 data and calculated intensity histograms in Figure 4. This material is available free of charge via the Internet at http://pubs.acs.org

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