

Study of Fluorescence Enhancement of Colloidal CdSe/ZnS Quantum Dots Bound to Hexadecylamine by Single-Molecule Measurements

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Fluorescence enhancement of colloidal CdSe/ZnS quantum dots (QDs) by the binding of hexadecylamine (HDA) ligands was investigated at the single-QD level. The blinking behavior of individual CdSe/ZnS QDs can be dramatically modified by additional HDA ligands. Both the ratio of the mean on/off time lengths and the total number of emitted photons within the on-time duration can be enhanced, by factors of up to 2.8 and 13, respectively. Consequently, the blinking rate can be suppressed down to 18%. The fluorescence decay curve is closer to a single-exponential decay profile and has a longer measured lifetime. These results suggest that HDA ligands can further improve surface passivation.

I. Introduction

Colloidal CdSe quantum dots (QDs; also referred to as semiconductor nanocrystals) have attracted much attention because of potential applications in biological markers based on their excellent fluorescence properties, including brightness, high photostability, and emission-color tunability.^{1,2} Recently, single colloidal QDs have been identified as promising nanobiosensors for use as single-molecule probes.³ However, most investigations are based on ensemble measurements, which merely reflect the average properties of inhomogeneous samples. With the advent of single-molecule detection, some particular phenomena that are masked in ensemble-averaged experiments have been discovered. Fluorescence intermittency (blinking)⁴ and the existence of completely dark QDs mixed with bright ones (blinking QDs)⁵ are the most interesting and important phenomena. The blinking behavior (random alternation of fluorescence between bright and dark states) is a universal phenomenon and can suppress the emission efficiency and degrade the performance of practical applications in bioprobes. Accordingly, the blinking behavior of a single QD bound to different ligands must be studied further to improve fluorescence efficiency.

Fluorescence efficiency depends strongly on the surface conditions of colloidal QDs because of their large surface-to-volume ratio. The electronic wavefunction could extend to the exterior of the QD core and interact with surface ligands or the surrounding environment, even when coated with a thin ZnS shell.⁶ Therefore, surfactant molecular ligands attached to the surface of the colloidal QDs strongly affect the photophysical properties.^{7,8} Previous reports have demonstrated that the blinking behavior can be altered by varying the local nano-environment, such as the surrounding matrix⁹ and the ambient

atmosphere.¹⁰ HDA ligands with high boiling points are superior agents as growth solvents for high-temperature chemical synthesis methods. Recently, highly fluorescent colloidal QDs with a narrow size distribution were synthesized by introducing HDA agents.^{11,12} However, the mechanism of fluorescence enhancement is not clear, especially from the aspect of single QDs. At the single-QD level, the enhancement of the emission efficiency for HDA-capped CdSe/ZnS QDs is attributed to the contribution of both the increase in the number of bright QDs and the enhanced intrinsic brightness of individual QDs. The former was demonstrated by the combination of atomic force microscopy with fluorescence measurements.⁵ However, the latter has not been studied in detail. An important question concerns how much of the enhancement is due to the prolongation of on-time duration and how much is related to the enhancement of quantum yields (QYs) within the on-time duration.

We investigated the blinking statistical behavior of individual colloidal CdSe/ZnS QDs modified by HDA ligands to clarify the above issue. The blinking statistical behavior can be dramatically altered by additional HDA ligands. The on/off time ratio, the total number of emitted photons within the on-time duration, and the blinking rate were measured to study the dependence of fluorescence efficiency on these factors. The fluorescence decay curve is closer to a single-exponential decay profile and has a longer measured lifetime.

II. Experimental Details

The approaches proposed by Talapin et al.¹¹ were followed to synthesize CdSe QDs with original trioctylphosphine oxide (TOPO) molecules, TOPO/HDA molecules, ZnS–TOPO, and a mixture of ZnS–TOPO/HDA surfaces. For measurements single isolated QDs, an extremely dilute colloidal solution was dispersed onto a clean glass coverslip by spin coating.¹³ In this case, the mean separation between each QD exceeded 1 μm and was monitored by far-field optical microscopy. (The spot size of the excitation laser was about 0.3 μm .) Fluorescence measurements were performed using a laser scanning confocal

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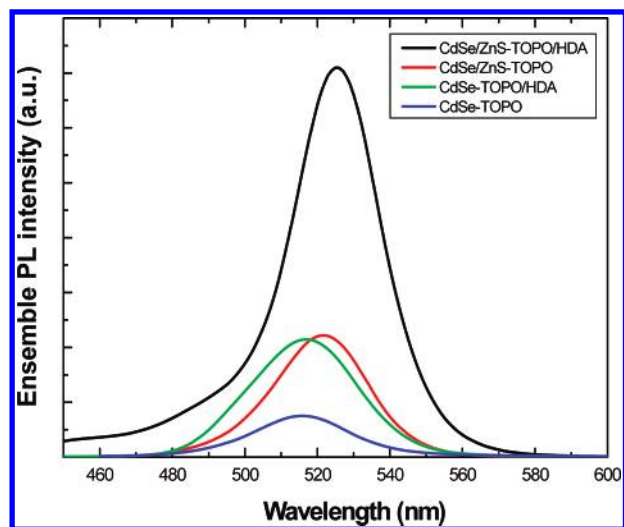


Figure 1. Fluorescence spectra of ensembles of colloidal CdSe QDs with TOPO, TOPO/HDA, ZnS shells, and ZnS/HDA surfaces.

microscope equipped with a piezo-scanner with nanometer spatial resolution (MT200, PicoQuant). Excitation pulses at the wavelength of 405 nm and a repetition rate of 10 MHz were focused to a nearly diffraction-limited spot by an oil-immersion objective (NA = 1.4). Fluorescence was collected by the same objective and guided to a single-photon avalanche photon diode after passing through a 50- μm confocal pinhole. Then, the fluorescence signals and a synchronized laser reference were fed into a very fast electronics system (TimeHarp 200, PicoQuant) to perform a time-correlated analysis.

Time-tagged, time-resolved (TTTR) measurements using the TimeHarp 200 electronics (PicoQuant GmBH) were also obtained for each single QD during single-QD fluorescence measurements. TTTR measurements differ from conventional time-correlated single-photon-counting techniques. For TTTR acquisition modes, both the relative start–stop time (time duration between laser pulses and single-photon emission) and the absolute arrival time (from the experimental start to single-photon emission) can be recorded simultaneously.¹⁴ The fluorescence decay profiles can be constructed by constructing a histogram of the relative start–stop times for many cycles in time-resolved modes. The transient fluorescence time traces can be formed by integrating all photons in a given bin time (1 ms) in time-tagged modes. From these time traces, one can construct histograms of on (off) time and burst sizes (total number of emitted photons during the on-time duration) for blinking statistical analysis.

For ensemble fluorescence measurements, the concentrated suspension sample was directly excited using a xenon lamp whose light was passed through a monochromator. Fluorescence was dispersed by a spectrometer and guided to a photomultiplied tube.

III. Results and Discussion

Figure 1 shows the fluorescence spectra of ensemble colloidal CdSe QDs capped with TOPO ligands (hereafter denoted as sample a), a mixture of TOPO/HDA (sample b), CdSe core QDs capped with ZnS shells (sample c), and CdSe QDs capped with ZnS shells and then further modified with HDA ligands (sample d). The emission peaks of ZnS-capped QDs (samples c and d) are red-shifted as a result of the extension of electronic wave function to the exterior of the QD core.⁶ Additionally, the enhancement of emission intensity can be observed because of

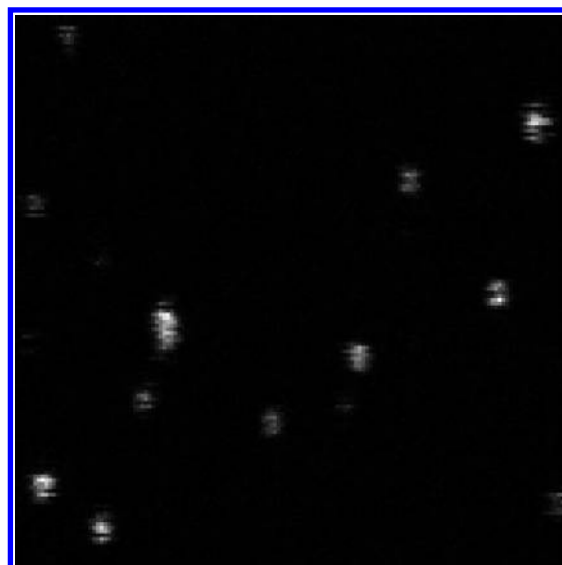


Figure 2. Fluorescence intensity images of a $6 \times 6 \mu\text{m}^2$ area from single colloidal CdSe/ZnS QDs.

the extra capping and the attachment of the HDA ligands. We also found that the contributions to fluorescence enhancement are almost the same for the organic HDA molecule and the inorganic ZnS shell. The most pronounced enhancement in fluorescence intensity occurred for CdSe/ZnS–TOPO/HDA QDs. From the ensemble-measurement perspective, this enhancement of emission is generally assigned to the passivation of surface trap states around QDs.¹¹

To study the origin of emission enhancement at the single-QD level, the fluorescence from single-isolated QDs of samples a–d was investigated. Figure 2 shows a typical fluorescence image of a $6 \times 6 \mu\text{m}^2$ area for CdSe/ZnS–TOPO QDs. Streaky patterns with a diffraction-limited spot of ~ 300 nm can be observed and are attributed to the fluorescence intermittency of single QDs. This characteristic is a hallmark of fluorescence emission from a single isolated QD.⁴ In order to examine the emission behavior of a single QD, the laser spot was moved to a specific QD position to record the transient fluorescence time traces. The sections of fluorescence time traces for samples a–d are shown in Figure 3a–d, respectively. For the single-QD measurements, to avoid dot-to-dot heterogeneity, more than tens of individual QDs from the same sample were measured and averaged for comparison. The bin time (integration time) was 1 ms for recording the fluorescence time traces. These traces clearly reveal blinking phenomena, especially for samples b–d. The dark periods are generally attributed to the formation of charged QDs by ionization processes.¹⁵ When a charged QD absorbs a photon from the excitation laser beam, it generates a three-particle charged exciton state (neutral exciton plus one charge) within the QDs. In this case, the fast Auger process (on the time scale of picoseconds) quenches the radiative emission (on the time scale of nanoseconds) through its faster energy transfer from the recombination of a neutral exciton and the charge particle.¹⁶ As a result, the QD enters a dark (off) state, and no fluorescence can be detected. Once the charged QD is neutralized, it can emit a fluorescence photon and recover the bright (on) state. To obtain more information from the fluorescence intermittency, the general approach is to define an intensity threshold to distinguish between the on and off states.¹⁷ Therefore, the lengths of the on and off time durations can be determined according to this predefined threshold. A histogram of the length of on/off time durations based on all experimental data can then be constructed.

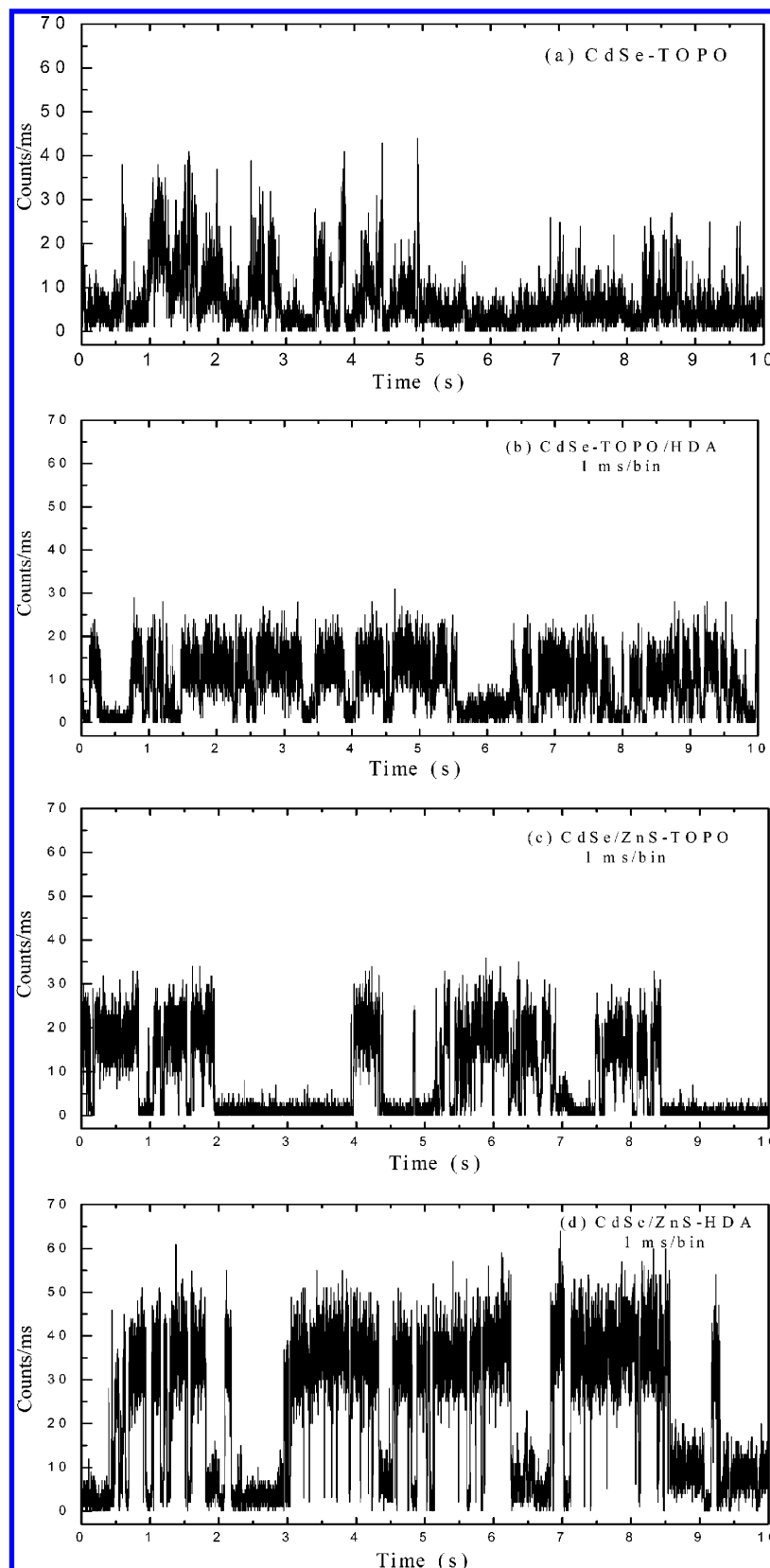


Figure 3. Fluorescence intensity time traces for single CdSe QDs with (a) original TOPO, (b) TOPO/HDA, (c) ZnS shells, and (d) ZnS/HDA.

Histograms of the on-time length plotted on a log–log scale are shown in Figure 4. The distribution follows a universal power-law behavior.¹⁸ For comparison, the mean on time can be obtained by a simple arithmetic average. We discovered that the mean on-time length can be increased by factors of 2.3 and 5 for samples c and d compared to sample a, but the

corresponding off time is also increased (not shown). These results can be elucidated by the ionization model.¹⁵ The high-band-gap ZnS-capped layer blocks the ejection of electrons from (or return of electrons to) the interior QD core to (from) the outside trap states, which is located either in the surrounding matrix⁴ or on the particle surface.¹⁹ Accordingly, the increasing

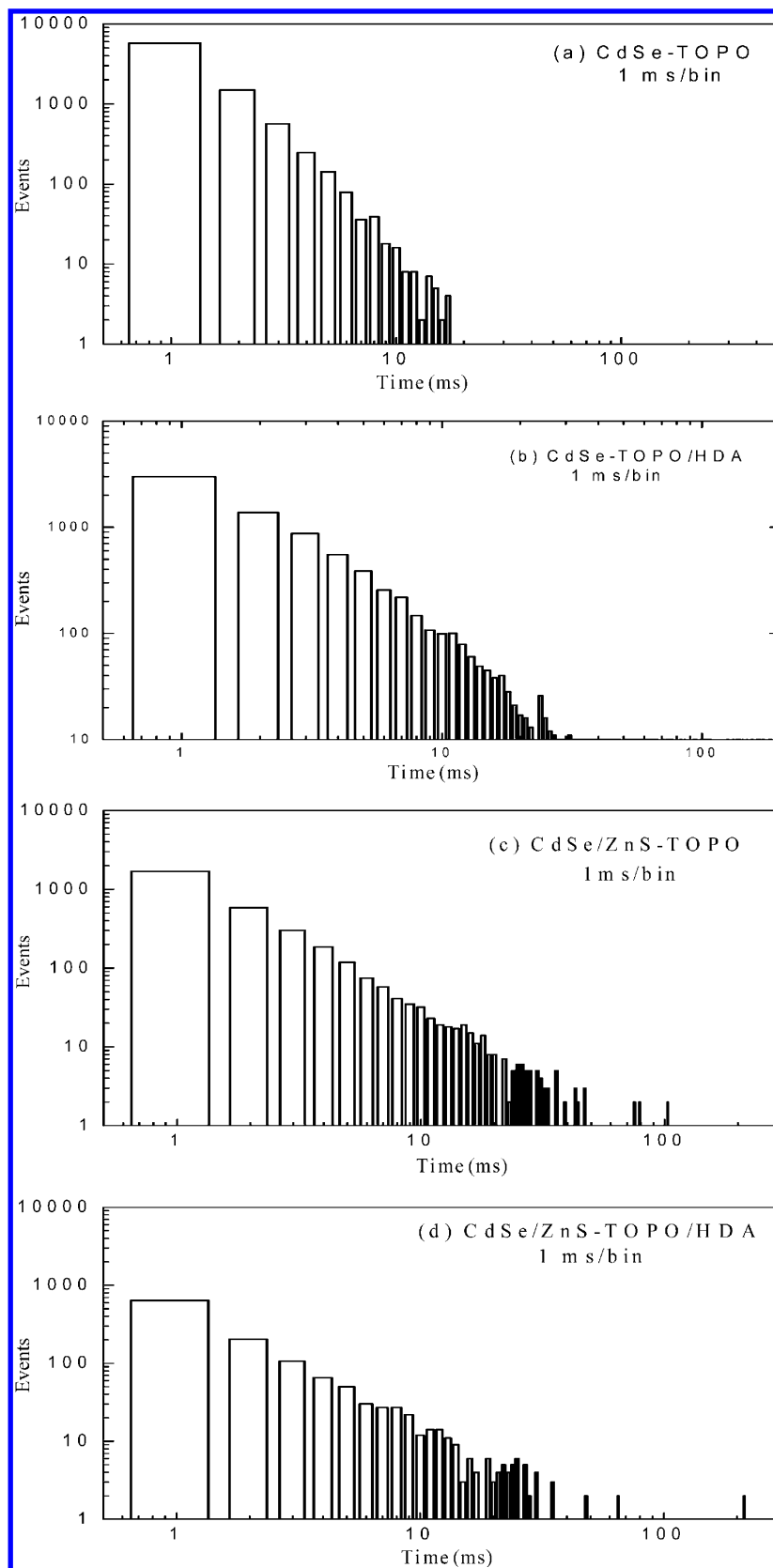


Figure 4. Histograms of on-time duration for single CdSe QDs with (a) original TOPO, (b) TOPO/HDA, (c) ZnS shells, and (d) ZnS/HDA.

on-time duration is accompanied by an increasing off time. Therefore, the ratio of mean on time to the mean off time needs to be considered to account for the emission properties. The ratios of on/off times are almost equal for bare TOPO and ZnS-capped QDs. Therefore, the fluorescence enhancement of individual QDs with ZnS shells does not originate from the

increasing on/off time ratio. Compared to samples b and c (with similar ensemble fluorescence intensities), the overall fluorescence intensity from single QDs is almost the same, but with different blinking rates. Interestingly, the mean on time increased, and the off time decreased for the CdSe/ZnS QDs modified by HDA ligands (sample d). Hence, we mainly focused

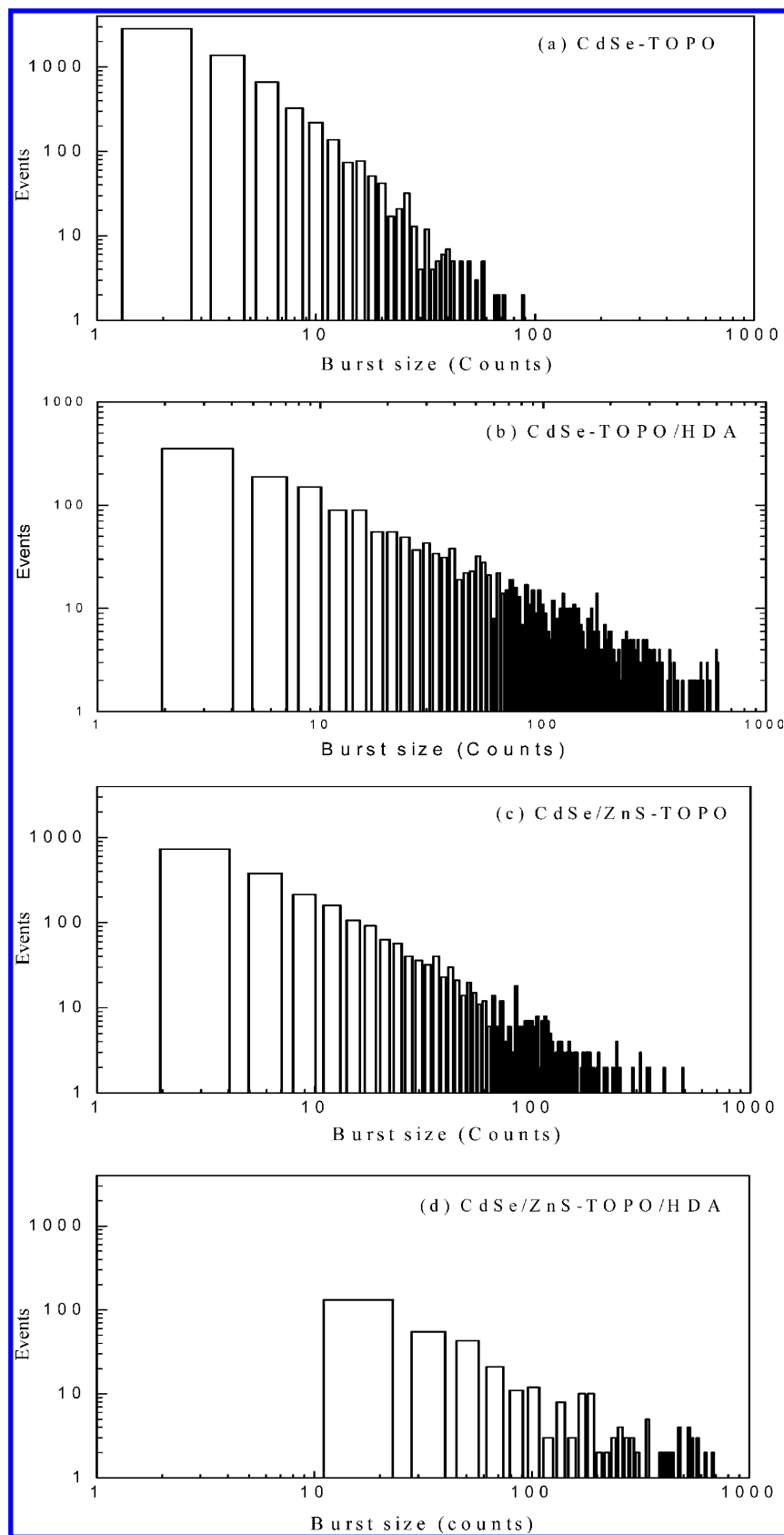


Figure 5. Histograms of burst sizes for single CdSe QDs with (a) original TOPO, (b) TOPO/HDA, (c) ZnS shells, and (d) ZnS/HDA.

on the influence of additional HDA molecules on the blinking behavior for CdSe/ZnS QDs.

In addition to the ratio of the on- and off-time lengths, the number of emitted photons within the on-time duration should be taken into account to fully understand blinking behavior. In

Figure 3, the fluorescence intensity within the on-time duration clearly varies with different surfaces. Histograms of the burst sizes of Figure 3 are shown in Figure 5. The burst size is defined as the total number of emitted photons above the threshold for a given on-time duration. This burst size can be calculated by

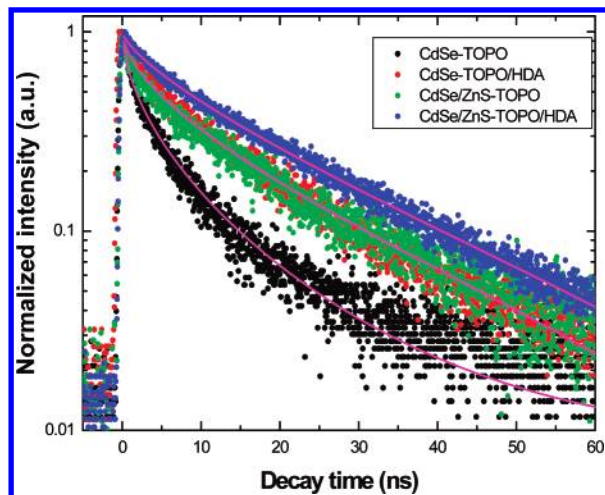


Figure 6. Fluorescence decay profiles for single CdSe QDs with original TOPO, TOPO/HDA, ZnS shells, and ZnS/HDA.

computer from TTTR measurements. From the burst-size histogram, the number of bursts and the mean burst size can be obtained. The burst number is related to blinking rate, and the burst sizes are dependent on the length of the on-time duration and the QYs within the on-time duration. The mean burst size can be enhanced up to 13-fold, accompanied by a suppression of the blinking rate down to 18% by the attachment of HDA ligands to CdSe/ZnS QDs.

Next, we discuss the possible role of HDA ligands in fluorescence enhancement for CdSe/ZnS QDs. HDA materials are superior agents as coordinating solvents for high-temperature organometallic synthesis methods because of their high boiling points. In addition, the lower steric occupation than for TOPO causes a high degree of surface passivation.^{11,12} After capping with additional HDA ligands around CdSe/ZnS QDs, three considerable modifications of blinking behavior can be found: extension of the on-time length, enhancement of fluorescence intensity within the on-time duration, and shortening of the off-time length. According to an ionization model, the on time can be ceased upon ejection of photogenerated electrons from the QD core to outside trap states located either in the surrounding matrix or on the particle surface and recovers once the ejected electrons return to the QDs. Therefore, both extension of on-time length and enhancement of fluorescence intensity can be explained by a higher degree of surface passivation. This leads to a reduction in surface states around the particle surface, which act as traps for photogenerated electrons. This can also be demonstrated by time-resolved fluorescence measurements of single QDs (next paragraph). For shortening of the off-time length, we suggest that the HDA ligands could act as electron donors to donate electrons to neutralize the charged QDs.²⁰ This overall contribution causes the burst size to increase by up to 13-fold for HDA-capped CdSe/ZnS QDs.

To verify the above suggestions, we performed time-resolved fluorescence measurements to monitor the photoexcited carrier dynamics of single QDs. Figure 6a–d shows the fluorescence decay profiles for samples a–d, respectively. All decay profiles exhibit universally nonexponential behavior, but they have different average lifetimes. We also found that the decay profile of ZnS/HDA-capped QDs is closest to a single-exponential curve with the longest lifetime. Possible reasons are as follows: A previous report demonstrated that the measured lifetimes vary with time because of a fluctuation in nonradiative decay rates, but they strongly correlate with the fluorescence intensity (i.e., strong fluorescence intensity is associated with

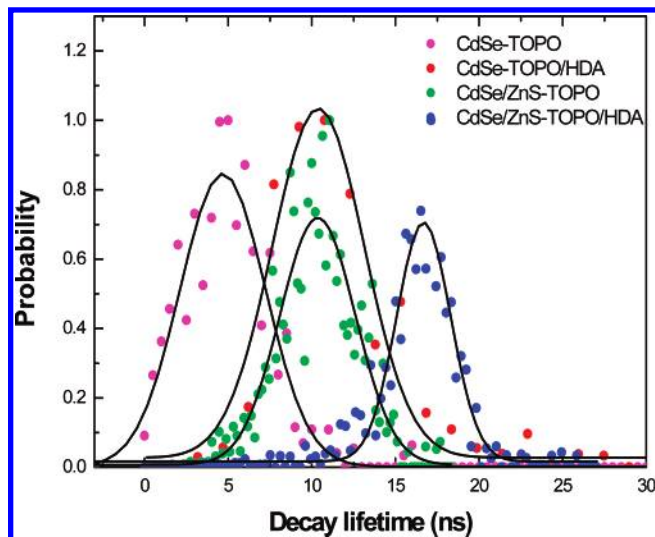


Figure 7. Distribution of fluorescence lifetimes for CdSe QDs with original TOPO, TOPO/HDA, ZnS shells, and ZnS/HDA.

longer lifetime).²¹ The measured decay rates are the sums of radiative and nonradiative decay rates. In general, the radiative process is not affected by the surface capping, and only the nonradiative decay channels can be modified. For ZnS/HDA-capped QDs, the nonradiative decay channel can be suppressed by a high degree of passivation of surface trap states. Thus, the fluorescence intensity and measured lifetimes increase. Furthermore, a stretched exponential function of the form $I(t) = I_0 \exp[-(t/\tau)^\beta]$ was fitted to the experimental data. This equation is usually used to describe a decay process with nonseparable superposition decay rates, where τ is a mean lifetime constant and β ($0 < \beta \leq 1$) is a stretched dispersion parameter that represents the degree of spread of lifetime distribution.^{21,22} For $\beta = 1$, the fluorescence decay curve exhibits a pure single-exponential profile with the narrowest lifetime distribution, which means that radiative processes dominate. ZnS/HDA-capped QDs have the longest lifetime and the largest β value. These results can also be reflected in the distribution of lifetimes. Figure 7 shows the probability of occurrence of a lifetime, which can be obtained by using so-called maximum likelihood estimator fitting methods for every 200 ms throughout the fluorescence measurements.^{23,24} We also found that ZnS/HDA-capped QDs have the narrowest lifetime distribution, which is consistent with their having the largest β value. This implies that nonradiative decay channels can be suppressed by a high degree of passivation of surface trap states.

IV. Conclusion

The fluorescence of CdSe/ZnS QDs has been investigated at the single-QD level, and it was found that the fluorescence can be enhanced by the attachment of HDA ligands. The blinking behavior of individual CdSe/ZnS QDs can be dramatically modified by additional HDA ligands. The on-/off-time ratio and the total number of emitted photons within the on-time duration can be enhanced by factors of up to 2.8 and 13, respectively. Consequently, the blinking rate can be suppressed down to 18%. The fluorescence decay curve is closer to a single-exponential decay profile and has a longer measured lifetime. These results suggest that HDA ligands can provide a high degree of surface passivation.

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Supporting Information Available: Additional experimental results and figures. This material is available free of charge via the Internet at <http://pubs.acs.org>.

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- (24) Based on the TTTR measurements, we can obtain the distribution of fluorescence lifetimes with a 200-ms integration time. In this case, maximum likelihood estimator fitting methods can be performed by using the simple single-exponential decay function $I(t) = I_0 \exp(-t/\tau)$.