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Antiquenching Luminescence

Temperature Antiquenching of the Luminescence
from Capped CdSe Quantum Dots**

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Celso de Mello Donegá, Daniël Vanmaekelbergh, and
Andries Meijerink*

Their efficient and tunable luminescence make semiconductor quantum dots (QDs) very promising for application in optoelectronic devices and as luminescent labels.^[1–3] Surface passivation with aliphatic capping molecules, such as trioctylphosphane (TOP), trioctylphosphaneoxide (TOPO) and hexadecylamine (HDA), plays a crucial role in obtaining luminescence quantum yields close to unity.^[4,5] Herein we demonstrate that the quantum yield of efficient TOP/TOPO/HDA-capped CdSe QDs gradually decreases above 20 K but

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increases sharply when the QDs are heated above a transition temperature of around 250 K. This observation is unique as it is the opposite of the commonly observed temperature quenching of luminescence. To understand the mechanism behind the temperature anti-quenching, the TOP/TOPO/HDA cap was exchanged with various alkylamines. We observe that the transition temperature shifts systematically to higher temperatures as the length of the alkyl chains increases. This indicates that a phase transition in the capping layer is involved and directly affects reconstruction of the CdSe surface. Surface reconstruction is required to remove surface (quenching) states.^[6] In addition, our results show how chemical exchange of the capping provides control over the temperature-dependent optical properties of QDs.

The influence of quantum confinement on the electronic and optical properties of semiconductor nanocrystals is of great fundamental and practical interest. Especially for direct bandgap II–VI semiconductors such as CdSe and CdTe, the increasing control over the size, shape, and surface chemistry has enabled the production of QDs with tunable (from blue to red) narrow-band luminescence and quantum yields close to unity.^[4,7,8] Research on these QDs continues to contribute to a better understanding of the influence of quantum size effects on the semiconductor core. The role of the semiconductor surface and its interaction with the passivation layer has not reached the same level of understanding. The capping layer is considered to be there merely to confine the charge carriers by providing a potential barrier and to passivate the dangling lone pairs of surface atoms. The large surface area makes nanocrystals ideal systems to investigate surface properties that cannot be studied in bulk systems. Even though the study of surface properties is recognized to be one of the important new areas of research in solid-state chemistry,^[9] only a few studies address this aspect of semiconductor nanocrystals. The present work provides insight into the role of the surface and the effect of its interaction with the aliphatic capping layer on the energy-level structure of CdSe QDs.

The most widely applied synthetic methods for strongly luminescent QDs are based on the growth of nanometer-sized crystallites of the semiconductor material inside a shell of coordinating molecules.^[4,7,8] The role of the ligands is twofold. First, inside a shell of coordinating ligands the semiconductor crystallites grow to a size that is determined by the kinetics of the binding and unbinding of the ligands. The second role of the ligands is to passivate dangling lone pairs to prevent nonradiative recombination at surface sites. The luminescence quantum yield is known to be very sensitive to subtle changes in the synthetic procedure, thus indicating that the surface structure is a key factor for the occurrence of band-gap states that quench the exciton luminescence.^[5,10]

For this study, high-quality CdSe QDs were synthesized by hot injection of the precursors $(\text{Cd}(\text{Me})_2$ and Top–Se in TOP) into a coordinating solvent mixture (TOPO/HDA).^[5,10] The suspension of QDs shows a bright orange exciton luminescence with a quantum efficiency of 60 % at room temperature. Luminescence decay curves are shown in Figure 1a at various temperatures between 4 and 300 K. At 4 K a biexponential decay is observed with a fast component due to emission from the singlet exciton state (spin-allowed) and a slow component

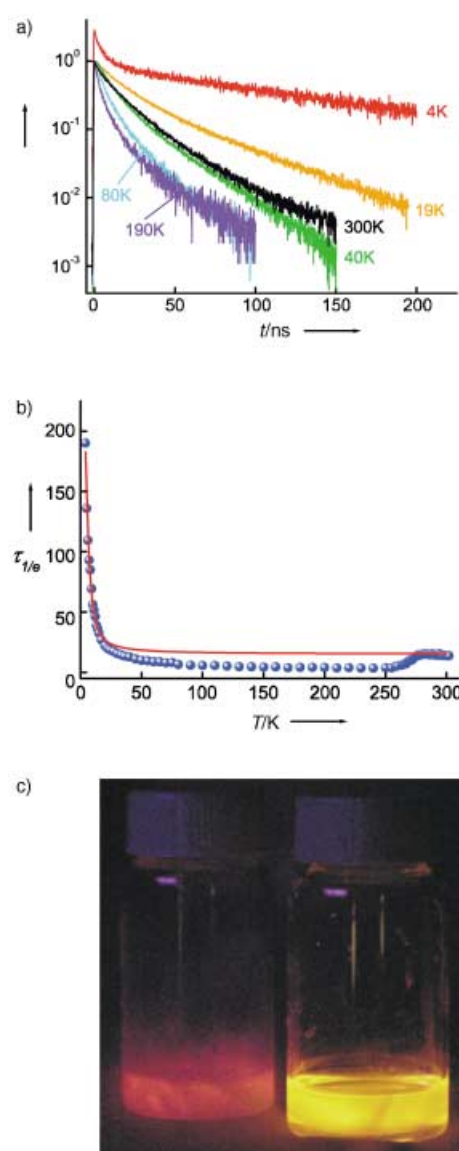


Figure 1. Temperature dependence of the exciton luminescence for TOP/TOPO/HDA-capped CdSe QDs. a) Luminescence decay curves are shown for TOP/TOPO/HDA-capped CdSe QDs at various temperatures between 4 and 300 K. Excitation is with a picosecond diode laser at 406 nm. b) The luminescence lifetime ($\tau_{1/e}$) of the exciton emission as determined from the curves in (a) is shown as a function of temperature. The drawn line is a fit to a three-level model with a lower-energy emitting triplet state and a higher-energy singlet state separated by 1.8 meV. c) The quenching of luminescence at low temperatures: Both vials contain a solution of TOP/TOPO/HDA-capped CdSe QDs and are illuminated with a UV lamp (360 nm). The vial on the left is cooled to 160 K while the brightly luminescing solution in the vial on the right is at 300 K. I = intensity, arbitrary units.

due to emission from the triplet state (spin-forbidden). As the temperature is raised, the radiative lifetime decreases due to thermalization between the triplet and singlet states similar to that previously reported.^[11–13] The temperature dependence of the lifetime is well described by a three-level model with decay rates for the triplet and singlet states of $5 \times 10^6 \text{ s}^{-1}$ and $1.25 \times 10^8 \text{ s}^{-1}$, respectively, and an energy difference of 1.8 meV between the two states. Above 20 K, the decay

curves become increasingly non-exponential (i.e., deviating from single-exponential decay) until a relatively fast ($\tau_{1/e} \approx 4$ ns) and strongly non-exponential decay curve is observed at 220 K. Luminescence life times ($\tau_{1/e}$) for the non-exponential decay curves are defined as the time in which the intensity drops to $1/e$ of the initial intensity. As the temperature is raised from 250 to 300 K the decay time becomes longer and the decay curves return to a single exponential with $\tau_{1/e} \approx 20$ ns. In Figure 1 b the $\tau_{1/e}$ times determined from the decay curves are plotted as a function of temperature. The drawn line represents the temperature dependence of the radiative lifetime, calculated by using the three-level model. The luminescence lifetimes are in good agreement with the measured $\tau_{1/e}$ values between 4 and 20 K and above 280 K. Between 20 and 280 K the luminescence decay is faster than that calculated, thus suggesting that nonradiative relaxation provides an additional recombination channel in this temperature regime. The non-exponential character of the decay curves shows that the nonradiative decay rates vary for different QDs. The observation that the luminescence intensity decreases between 20 and 250 K confirms the presence of nonradiative relaxation. Temperature quenching of luminescence is commonly observed and ascribed to thermally activated (phonon-induced) processes. Temperature quenching above 20 K has previously been reported for TOP/TOPO-capped CdSe QDs but without recovery of luminescence at higher temperatures.^[12]

Measurements of the intensity of luminescence between 250 and 300 K show that the lengthening of $\tau_{1/e}$ in this temperature range is accompanied by a recovery of the intensity. This is a striking observation; as nonradiative relaxation processes are usually thermally induced, it is unexpected to observe a rise in quantum efficiency with increasing temperature. The long (radiative) lifetime (≈ 20 ns), almost single exponential decay, and high quantum efficiency ($\approx 60\%$) for the CdSe QDs at room temperature show, however, that the temperature quenching of the luminescence between 20 and 250 K is reversed to temperature anti-quenching above 250 K. We conjecture that the striking recovery of purely radiative decay above the threshold temperature is due to subtle displacements of the semiconductor surface atoms induced by a phase transition in the capping layer. To verify if a phase transition is involved, the capping layer of the CdSe QDs was exchanged by using exactly the same procedure for alkylamines with linear chains varying in length between 6 and 18 carbon atoms. Capping exchange was carried out by mixing TOP/TOPO/HDA-capped QDs with a 20-fold excess of hexylamine (C_6), decylamine (C_{10}), dodecylamine (C_{12}), hexadecylamine (C_{16}), or octadecylamine (C_{18}), and stirring the mixture for 12 h at 70 °C. In Figure 2 luminescence decay curves and emission spectra are shown for CdSe QDs after capping exchange with hexylamine. Just as for the TOP/TOPO/HDA-capped QDs, the intensity of the exciton luminescence increases (Figure 2a) in the same temperature regime at which the decay curves evolve towards a single exponential while $\tau_{1/e}$ increases (Figure 2b). The temperature at which this transition takes place (≈ 235 K) is, however, considerably lower than that for the TOP/TOPO/HDA-capped QDs. In

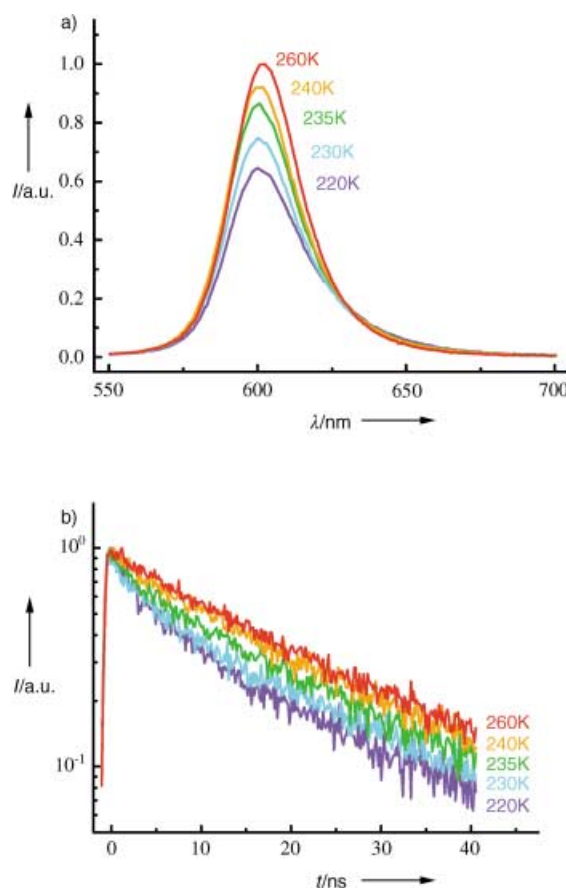


Figure 2. Luminescence of CdSe QDs after exchange of the capping molecules with hexylamine (C_6). a) The emission spectra show an increase in intensity of luminescence with increasing temperature around the anti-quenching temperature. b) Luminescence decay curves of the exciton emission at 604 nm for various temperatures around the anti-quenching temperature for the same hexylamine capped QDs. Excitation is with a picosecond diode laser at 406 nm.

Figure 3 the temperature dependence of the luminescence intensity and $\tau_{1/e}$ are plotted as a function of temperature for CdSe QDs after capping exchange with hexylamine, decylamine, dodecylamine, hexadecylamine, and octadecylamine. Figures 3 a–e show that for all types of capping layers, there is an excellent correlation between the temperature dependence of the lifetime and the luminescence intensity, which proves that the lengthening of the lifetime with increasing temperature corresponds to a decrease in the nonradiative relaxation rates. The decrease in intensity from 220 K to 240 K in Figure 3 c is due to the commonly observed quenching of the QD exciton emission.^[12] The anti-quenching temperature shifts to higher temperatures as the length of the alkyl chain increases. In Figure 3 f the anti-quenching temperature, defined as the temperature at which the intensity and luminescence lifetime have increased to 50% of the total recovery, is plotted as a function of the number of carbon atoms in the capping alkylamine; the temperature effect is clearly shown.

With experimental evidence for the effect of a phase transition in the ligand shell on the luminescence of CdSe

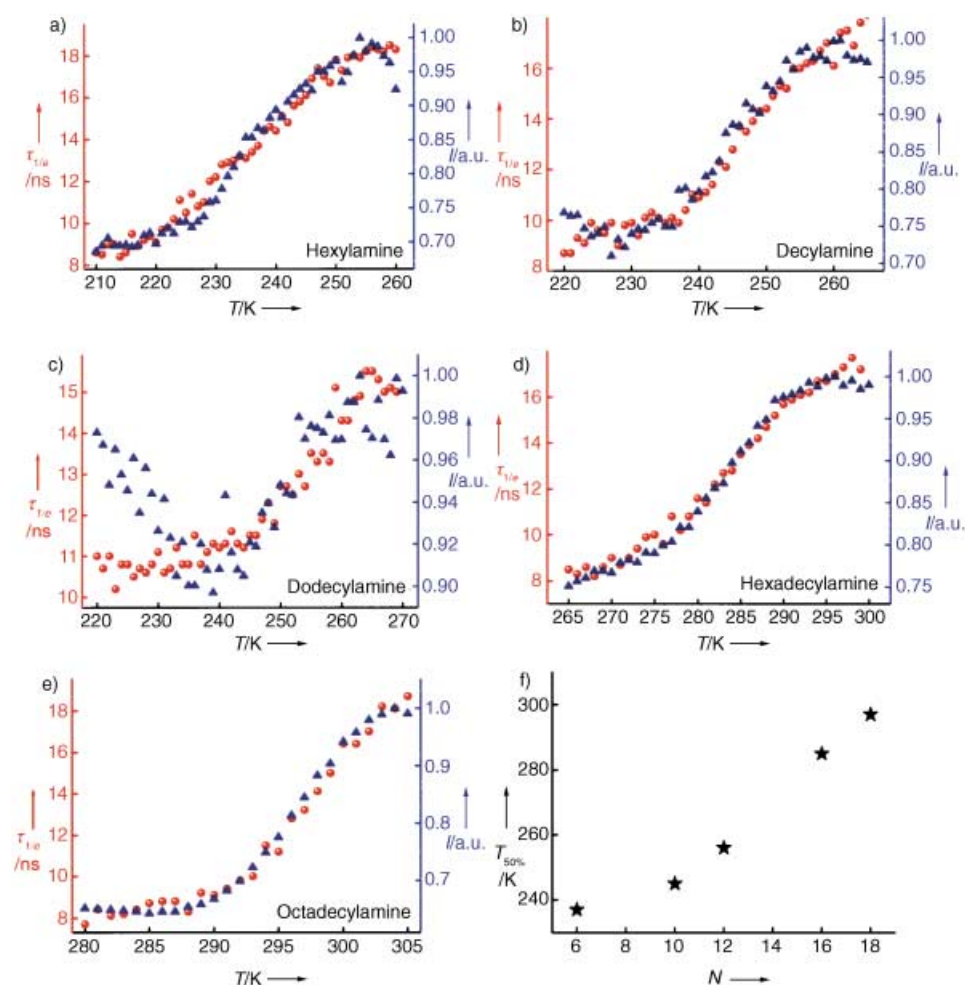


Figure 3. Influence of the capping molecules on the anti-quenching temperature for CdSe QDs. The temperature dependence of the luminescence lifetime ($\lambda_{em} = 604$ nm) and the integrated luminescence intensity (at 406 nm excitation) of CdSe QDs after capping exchange with a) hexylamine, b) decylamine, c) dodecylamine, d) hexadecylamine, and e) octadecylamine are shown. f) The anti-quenching temperatures ($T_{50\%}$) obtained from figures (a–e) are plotted as a function of the number of carbon atoms (N) in the alkyl chains of the passivating alkylamine capping molecules.

QDs, the next step was to understand the nature of the phase transition and how it affects the luminescence efficiency. Theoretical modeling of TOPO-capped CdSe QDs indicates that small displacements of the surface Cd and Se atoms are required to prevent surface (quenching) states with energies in the forbidden gap.^[6] If the capping layer of alkyl chains is in a frozen state then this surface relaxation may be hampered, which means that the luminescence-quenching centers remain active. The phase behavior of the alkylamine passivation layers on QDs has been studied and can be described by the same interactions as those in self-assembled monolayers (SAM).^[14] Experimental and theoretical work on the phase behavior of *n*-alkanes, *n*-alkylamines, and *n*-alkylthiols (SAM and bulk) shows a complex behavior with various phase transitions.^[15,16] A solid–liquid phase transition for long-chained alkylamines occurs above room temperature and cannot explain the observed changes below room temperature. At lower temperatures, phase transitions occur in the ordered phase. In the lowest temperature phase, the alkyl

chains are ordered by orientation. At higher temperatures (typically between 200 and 300 K for C_6 to C_{20} alkanes) a transition occurs to a phase in which rotational motion is possible (the locked rotator phase). At even higher temperatures a second phase transition takes place to the unlocked-rotator phase in which the tilt direction of the alkyl chains can fluctuate between nearest-neighbor molecules. Phase-transition molecular-dynamics simulations show that for SAMs of hexadecylamine, the transition temperature is around 275 K.^[15] This temperature is very close to the temperature at which the recovery of the luminescence intensity and lengthening of the decay time is observed for QDs capped with hexadecylamine. A transition to a phase in which neighboring ligand molecules can have different tilt angles is consistent with an onset of relaxation of those atoms bound to the ligands. As the tilt angle for neighboring alkyl chains can change, a vertical displacement of surface atoms bound to the polar head groups becomes possible. This surface reconstruction is not possible when the alkyl chains are ordered and have fixed tilt angles. Further evidence that supports the role of a phase transition is provided by an increase in temperature of between 10 to 15 K each time the alkyl chain length increases by two carbon atoms (Figure 3 f), which is very similar to increases previously reported.^[15,16] Room temperature X-ray scattering experiments have shown the outward displacement of surface Se

atoms and the inward displacement of Cd atoms in CdSe QDs at 300 K.^[17] Temperature-dependent X-ray-scattering experiments are expected to show that this surface reconstruction is hampered as the sample is cooled below the transition temperature of the capping layer.

The surprising observation of temperature anti-quenching of the luminescence from capped CdSe QDs gives insight into the importance of the interaction between the capping layer and the semiconductor core on the energy-level structure of QDs. It shows that the organic passivation layer not only passivates dangling lone pairs but also plays an active role in surface reconstruction. Chemical exchange of the capping molecules can be adapted to gain control over the temperature-dependent optical properties of QDs.

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