

Incorporation and Luminescence of Yb³⁺ in CdSe Nanocrystals

Rosa Martín-Rodríguez,^{*,‡} Robin Geitenbeek,[‡] and Andries Meijerink^{*}

Debye Institute for Nanomaterials Science, Department of Chemistry, Utrecht University, Princetonplein 5, 3584 CC Utrecht, The Netherlands

Supporting Information

ABSTRACT: Doping quantum dots (QDs) with lanthanide ions is promising to combine the efficient sharp line emission of lanthanides with the strong and size-tunable absorption of QDs. Incorporating lanthanide ions in II–VI QDs remains challenging, however, here we report successful coupling of CdSe QDs with the lanthanide ion Yb³⁺. Our spectroscopic results demonstrate that Yb³⁺ ions are first adsorbed on the CdSe surface and subsequently incorporated in the nanocrystalline semiconductor particles by growing a Se shell. Evidence for incorporation is provided by the fine structure of the CdSe QDs absorption in the excitation spectrum of the Yb³⁺ emission at 1000 nm and the long lifetime of the Yb³⁺ emission after shell overgrowth. Sensitized Yb³⁺ infrared emission may find application in optical amplifiers, solar concentrators, and bioimaging. The method described is a promising strategy for incorporating lanthanide ions in other II–VI QDs.

Doping quantum dots (QDs) with transition-metal and trivalent lanthanide (Ln³⁺) ions is a promising strategy to incorporate new optical and magnetic properties in nanomaterials. There is a growing interest in different classes of doped nanocrystals.^{1,2} Semiconductor nanocrystals or QDs are typically doped with 3d transition-metal ions, like Mn²⁺- and Co²⁺-doped CdS, CdSe, ZnO, or ZnS.^{3–5} An exciting feature of these nanocrystals is that the optical properties can be tuned through quantum confinement effects of the semiconductor host as well as through the type and concentration of transition-metal dopants.⁵ Lanthanide ions are usually incorporated into insulator nanocrystals, especially fluorides and phosphates, where Ln³⁺ ions substitute for chemically related rare earth ions.^{6,7} In these insulator nanocrystals the functionalities are solely determined by the lanthanide dopants. For optical applications the efficient line emission of lanthanide ions can be utilized, but a drawback is the weak and narrow band absorption lines, due to the parity forbidden character of the 4f–4f transitions. This limits applications where strong absorption is required. Incorporation of lanthanide ions in QDs offers the possibility to combine the strong and size-tunable absorption of QDs with the efficient narrow line emission of lanthanide ions in the visible (VIS) or infrared (IR). It has however been a challenge to incorporate lanthanide ions in II–VI QDs.^{8,9} A considerable number of publications have reported the incorporation and luminescence of Ln³⁺ ions inside or on the surfaces of II–VI QDs, especially for CdS and CdSe QDs.^{9–15} The ionic radii of Cd²⁺ and Ln³⁺ are similar (~1 Å), but the ions are chemically different. Ln³⁺ ions have a

preference for sites with high coordination numbers (six or higher) and are not easily substituted on a tetrahedral site in CdS or CdSe. There is also the necessity of charge compensation for a Ln³⁺ ion on a Cd²⁺ site. An important aspect is to demonstrate whether lanthanide ions are actually incorporated in the nanocrystals or adsorbed on the surfaces.

Common approaches to synthesize doped nanocrystals involve simultaneous growth of the semiconductor nanoparticles and incorporation of Ln³⁺ from a precursor added to the reaction mixture.^{10–13} Typical methods use acetates, nitrates, or organic complexes as the Ln³⁺ precursor. In a pioneering paper based on a single precursor method, Strouse found Eu³⁺ incorporation in CdSe, but no luminescence was reported.¹¹ Planelles et al. reported the presence of two different sites for Eu³⁺ in CdS nanocrystals, attributed to surface and interior sites.¹³ Mukherjee et al. recently demonstrated doping ZnS and CdS nanoparticles with Tb³⁺ and Eu³⁺ in which lanthanide ions show preference for surface sites.⁹

Strong evidence for the successful coupling of Ln³⁺ ions to QDs is the presence of the typical excitonic features of the QD host in the excitation spectrum of the Ln³⁺ emission, giving direct evidence for energy transfer from the QDs to Ln³⁺ ions. So far, none of the publications have shown excitation spectra of the Ln³⁺ emission with the characteristic excitonic structure arising from quantum confinement in the QD host. Here we report a three-step procedure for the synthesis of CdSe:Yb³⁺ nanocrystals. The Yb³⁺ ion has a strong near IR emission around 1000 nm and is particularly suitable for demonstrating incorporation in CdSe QDs due to the large shift of the emission wavelength from the CdSe QD emission in the VIS region. For the typically used Eu³⁺ and Tb³⁺ ions there is an overlap between the QD emission and the Eu³⁺ or Tb³⁺ emission. To synthesize CdSe:Yb³⁺ QDs, first CdSe QDs were prepared following the synthesis method based on Cd-oleate and Se in trioctylphosphine (TOP) precursors, as described by de Mello Donegá et al.¹⁶ Second, Yb incorporation was achieved by adapting the procedure described by Yang et al. for the doping of CdS/ZnS nanocrystals with Mn²⁺.¹⁷ Third, Se was added to complete the incorporation of the Yb³⁺ ions.¹⁷ Different parameters, such as the Yb precursor to CdSe ratio, the reaction temperature, and the growth time, were varied to optimize Yb incorporation. The detailed procedures are available in the Supporting Information (SI). Briefly, in a typical experiment, ~0.5 mL of a hexane solution of CdSe QDs (~140 nmol) was mixed with 12 mL 1-octadecene (ODE) and 3 mL oleylamine (OLA) and

Received: July 27, 2013

Published: September 3, 2013

heated to 265 °C under nitrogen. Yb and Se precursors solutions were prepared by dissolving ytterbium acetate in OLA, and Se in ODE. The Yb precursor solution was added dropwise, and dopant incorporation was allowed for 30 min at 265 °C. A small aliquot was taken for comparison. Finally, the third reaction step involved dropwise addition of the Se precursor solution to grow a Se shell and incorporate the Yb³⁺ ions inside the QDs. The samples were purified by precipitating with acetone and redispersing in toluene. Different Yb:CdSe molar ratios were tested in order to maximize Yb³⁺ luminescence intensity. The best ratio was found to be ~175:1, a larger dopant excess than found for doping of CdS/ZnS nanocrystals with Mn²⁺, ~50:1.¹⁷

Figure 1a shows the TEM image of the as-synthesized CdSe:Yb³⁺ QDs. A highly monodisperse sample consisting of

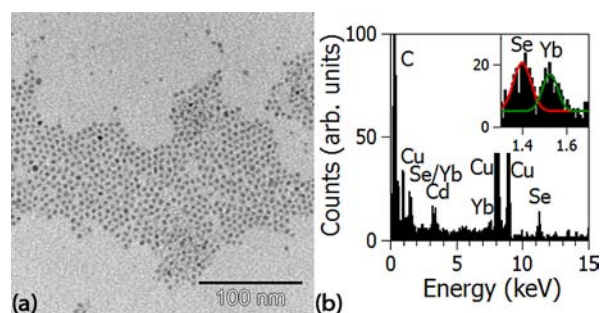


Figure 1. (a) TEM image of the CdSe:Yb³⁺ nanocrystals. (b) EDX analysis of the nanocrystals. Cu peaks are due to the copper grid used as support for imaging. Inset shows a zoom-in of the area with overlapping Se and Yb peaks, which were fitted to two Gaussians.

nearly spherical particles was obtained with an average size of 4.2 ± 0.4 nm. This value is slightly larger than the diameter of the CdSe particles before Yb incorporation (3.9 ± 0.5 nm, see SI). This increase in size confirms the successful growing of a Se shell and thus is consistent with a model in which Yb³⁺ ions are attached to the surface and subsequently incorporated by adding ca. one monolayer of Se. During the growth of the Se shell, diffusion of Yb³⁺ ions further into the CdSe QDs may occur. Elemental analysis by energy dispersive X-ray spectroscopy (EDX) (Figure 1b) confirms that Cd, Se, and the dopant Yb are present in the sample. The Se and Yb peaks overlap, but the inset in Figure 1b clearly shows the presence of two distinct peaks. From the integration of the EDX representative peaks, the concentration of Yb³⁺ in the sample was estimated to be $\sim 8 \pm 4\%$, in good agreement with the incorporation of Yb³⁺ on the surface of CdSe QDs.

Luminescence spectroscopy gives insight in the location of the dopant ions in the QDs. Successful coupling of luminescent Yb³⁺ ions to CdSe QDs can be investigated through emission, excitation, and luminescence lifetime measurements. Figure 2a presents the emission and excitation spectra of the QDs after incorporation of Yb³⁺. They resemble the CdSe QDs spectra before Yb incorporation and show the typical narrow band excitonic emission around 585 nm. The excitonic emission intensity is about five times lower than before Yb incorporation (see SI). The fact that the excitonic emission is still observed in the CdSe:Yb³⁺ QDs is noteworthy and indicates that the QD emission is not completely quenched by the energy transfer to the Yb³⁺ dopant ions. This suggests that diffusion of Yb³⁺ ions inside the QDs is limited or absent. In addition, the 5-fold decrease of the CdSe excitonic emission

after Yb³⁺ incorporation provides an estimate of the upper limit for the energy transfer probability, $\sim 80\%$. The excitation spectrum shows the typical QD fine structure due to quantum confinement effects.¹⁸ Figure 2b shows the emission spectrum in the IR region for CdSe after Yb incorporation but before Se overgrowth. An emission line around 975 nm is observed with a shoulder extending beyond 1000 nm. The intensity decreases strongly after washing the sample (red line in Figure 2b). The emission line is assigned to the ${}^2F_{5/2} \rightarrow {}^2F_{7/2}$ emission of Yb³⁺.

Figure 2c depicts the IR emission after Se overgrowth and shows that the line shifts to 985 nm and is narrower (from a full width at half-maximum of 115 cm^{-1} before, to 50 cm^{-1} after Se overgrowth). A second peak around 1030 nm is observed. The emission intensity does not decrease after washing the sample. These results strongly suggest that Yb³⁺ is incorporated in the CdSe QDs after Se overgrowth. Before Se overgrowth, the Yb³⁺ ions are situated on the surface, and the variation in environment (anion coordination) causes inhomogeneous broadening of the ${}^2F_{5/2} \rightarrow {}^2F_{7/2}$ emission line. After Se overgrowth narrow line emission is observed with two peaks, one at 985 nm and one at 1030 nm, due to transitions to different crystal field components of the ${}^2F_{7/2}$ ground state. This is typical for Yb³⁺ in a well-defined crystallographic site. The red shift after Se overgrowth from 975 to 985 nm is explained by an increase in covalency for Yb³⁺ in a full Se-coordination compared to Yb³⁺ on the surface with Se-coordination on one side and (less covalent) O and/or N coordination from the ligands on the other side. The influence of the surrounding ligands on the emission wavelength of *f-f* transitions of lanthanides is small, but increasing covalency gives rise to a significant red shift, especially for lanthanides at the beginning (Ce, Pr, Nd) and the end (Tm, Yb) of the lanthanide series.¹⁹ Further insight can be obtained from comparison with Yb³⁺ emission spectra in bulk CdSe. Unfortunately, no information is available in the literature on Yb³⁺ emission spectra in CdSe. Emission spectra of Yb³⁺ have been reported by Bryant for Yb³⁺ incorporated by ion implantation and annealing in other II–VI semiconductors (CdS, CdTe, ZnTe).^{20,21} Narrow emission lines are observed around 990 (strong), 1030, and 1075 nm (weak), in line with the present observations. The emission lines are assigned to Yb³⁺ on tetrahedral Cd²⁺ or Zn²⁺ lattice sites and defect related sites. Based on the analysis of the emission spectra it is plausible that the present synthesis procedure leads to incorporation of Yb³⁺ on Cd-lattice sites in CdSe QDs.

Excitation spectra provide crucial evidence for incorporation of dopant ions in QDs. Efficient energy transfer occurs from the QD host to dopants. As a result, in the excitation spectrum of the dopant emission the characteristic features of the QD absorption are present, as has been observed for 3d transition-metal ions in QDs.^{17,22} If the QD absorption features do not appear in the excitation spectrum, this is a strong indication that the dopant is not inside the QD but rather at the surface or even in the solution where ions like Eu³⁺ and Tb³⁺ can also show emission. None of the studies on incorporation of Ln³⁺ ions in II–VI QDs have reported excitation spectra in which the typical QD fine structure with 1S–1S, 1P–1P transitions is observed.^{9–13} This may be related to the choice of ion, typically Tb³⁺ or Eu³⁺, with the emitting states at energies similar to or higher than the QD exciton, which may prevent energy transfer. It may also be due to poor incorporation of the Ln³⁺ ions. Figure 2d shows the excitation spectrum of the Yb³⁺ emission at 985 nm (black line) together with the QD absorption spectra of

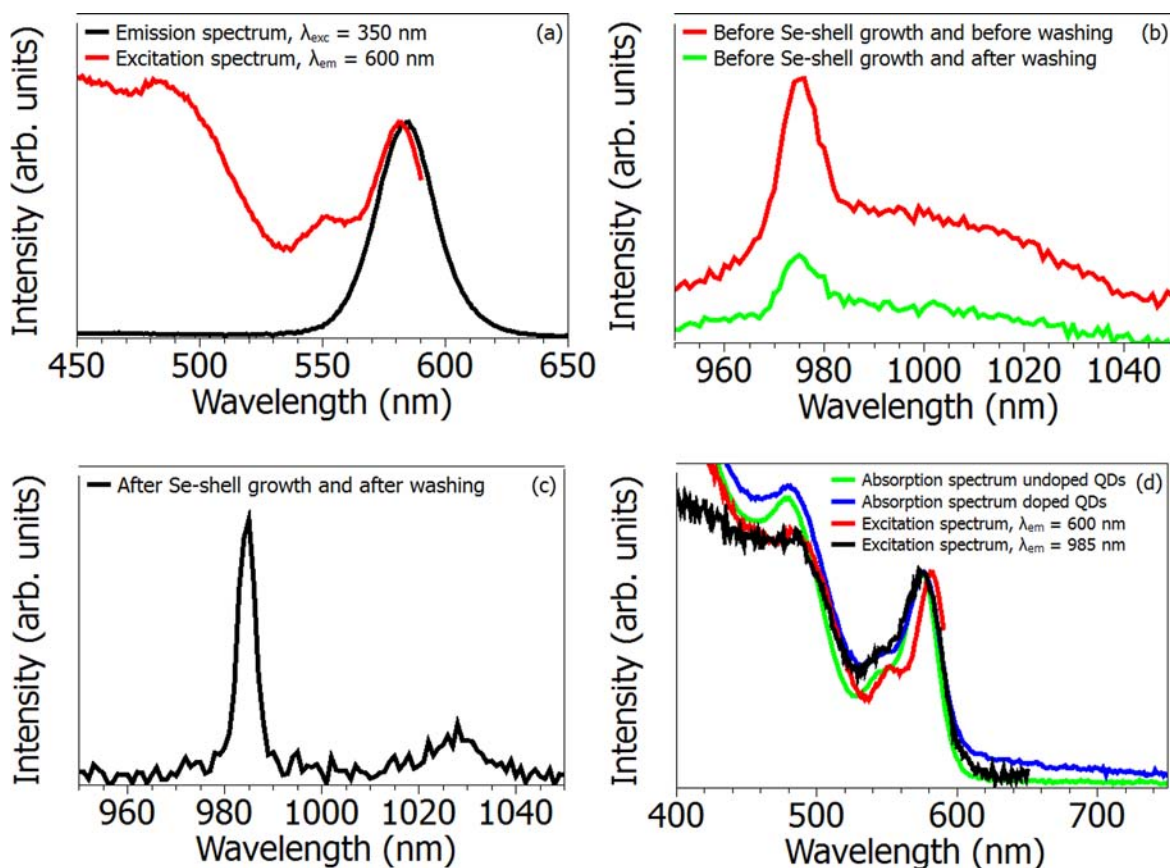


Figure 2. (a) Excitonic emission ($\lambda_{\text{exc}} = 350$ nm, black) and excitation ($\lambda_{\text{em}} = 600$ nm, red) spectra of CdSe:Yb³⁺ QDs. The spectra are normalized to the first excitonic peak. (b) Yb³⁺ emission spectra of doped CdSe QDs upon excitation at 580 nm previous to Se shell overgrowth, before (red) and after (green) washing. (c) Yb³⁺ emission spectra upon CdSe excitation at 580 nm in CdSe:Yb³⁺ QDs prepared by the three-step procedure (after Se growth). (d) Absorption spectra of undoped (green) and Yb³⁺-doped (blue) CdSe QDs. Excitation spectra of CdSe (red) and Yb³⁺ (black) emission, at 600 and 985 nm respectively, in CdSe:Yb³⁺ QDs. Spectra are normalized to the first excitonic peak. All spectra were recorded at room temperature.

the doped and undoped QDs (before and after Yb³⁺ incorporation, blue and green lines) and the excitation spectrum of the QD emission at 600 nm (red line). All spectra show distinct features at 580, 550, and 480 nm which are typical for CdSe QDs of ~ 4 nm.²³ The similarity between Yb³⁺ and CdSe excitation spectra demonstrates that Yb³⁺ emission is sensitized by CdSe excitation. This is a strong indication of the successful coupling of Yb³⁺ ions to the CdSe QDs. The observations cannot identify if the Yb³⁺ ions are primarily in the surface layer or have diffused further into the CdSe QDs. However, it is clear that the large surface-to-volume ratio of CdSe QDs facilitates the charge compensation needed for the incorporation of trivalent Yb³⁺ in the divalent Cd²⁺ site.

A final evidence of the Yb³⁺ incorporation can be obtained from luminescence lifetime measurements. The IR emission of Yb³⁺ is only efficient in hosts with low vibrational energies. In proximity to high-energy vibrations like C–H (~ 3000 cm⁻¹) or O–H (~ 3300 cm⁻¹) the emission is quenched by multiphonon relaxation, as it takes only 3 or 4 vibrational quanta to bridge the energy gap of $\sim 10\,000$ cm⁻¹ to the ground state. As a result, nonradiative decay dominates for Yb³⁺ in the excited ²F_{5/2} state in organic media or water, giving low quantum yields and short luminescence lifetimes, in the range of μ s.^{24,25} The radiative lifetime of the ²F_{5/2} → ²F_{7/2} emission is typically 0.5–1 ms. A luminescence lifetime in the ms range is strong evidence that there are no solvent or organic capping molecules in the

immediate coordination sphere of Yb³⁺. Figure 3 shows the luminescence decay curves of the Yb³⁺ emission before and after Se overgrowth. Before overgrowth, a 27 μ s decay time is observed, slightly longer than the ~ 10 μ s lifetime typically observed for Yb³⁺ emission in organic complexes.^{24–26} The short decay time is explained by multiphonon relaxation

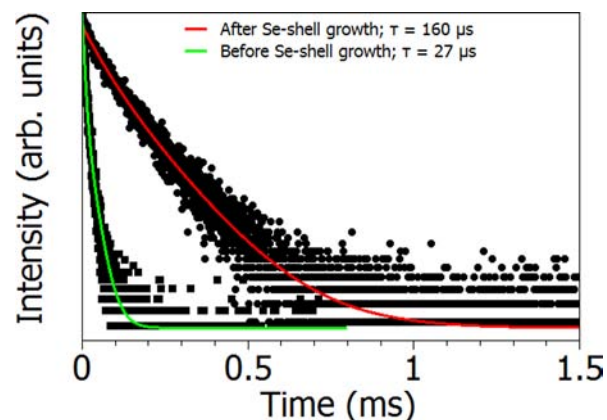


Figure 3. Yb³⁺ luminescence (~ 980 nm) decay in CdSe:Yb³⁺ QDs upon pulsed excitation at 580 nm before (green) and after (red) Se-shell overgrowth (the luminescence intensity is given on a logarithmic scale).

involving C–H vibrations. After Se overgrowth, a considerably longer 0.16 ms decay time is observed, suggesting that Yb^{3+} is incorporated inside the CdSe host and not coordinated by solvent or capping molecules. The lengthening of the lifetime not only provides evidence for successful incorporation in the CdSe matrix, it also shows that efficient IR emission from CdSe: Yb^{3+} nanocrystals is possible. This is promising for application as nanoprobe in biomedical imaging, since both emission and excitation wavelength can be tuned to the IR transparency window in biological systems. In the field of IR optical amplifiers, the search for efficient narrow line IR emitters with strong absorption has initiated research focused on optimizing the efficiency of Yb^{3+} in completely fluorinated organic complexes.^{25,26} Lanthanide-doped QDs are promising as alternative with options to extend to even longer wavelengths in the IR through incorporation of Tm^{3+} or Er^{3+} in II–VI or IV–VI QDs.

We have reported a new three-step synthesis procedure for the incorporation of trivalent lanthanide ions in QDs. Yb^{3+} was chosen as probe for its simple electronic structure and IR emission, well separated from the QD emission. The synthesis method presented involves three steps: synthesis of QDs, integration of the dopant ions on the QDs surfaces, and shell overgrowth. Luminescence spectra demonstrate successful incorporation of Yb^{3+} ions in CdSe QDs. The observation of the characteristic QD absorption features in the excitation spectrum of the Yb^{3+} emission and the long luminescence lifetime show that Yb^{3+} is coupled to the CdSe QDs and decoupled from surface ligands. The synthesis method is promising for obtaining other Ln^{3+} -doped QDs, combining strong and size-tunable optical absorption of the QD host with narrow line lanthanide emission in the VIS and IR spectral regions.

■ ASSOCIATED CONTENT

📄 Supporting Information

Experimental procedures, synthesis methods, and supporting figures. This material is available free of charge via the Internet at <http://pubs.acs.org>.

■ AUTHOR INFORMATION

Corresponding Authors

R.MartinRodriguez@uu.nl

A.Meijerink@uu.nl

Author Contributions

‡These authors contributed equally.

Notes

The authors declare no competing financial interest.

■ ACKNOWLEDGMENTS

Financial support from the EU-FP7 NanoSpec project (grant agreement 246200) and the SIA RAAK project Spectrale Conversie Folies (project no. 2011-19-17M) is gratefully acknowledged. The authors are grateful to Professor Daniel R. Gamelin for the critical reading of the manuscript and useful suggestions.

■ REFERENCES

- (1) Jana, S.; Manna, G.; Srivastava, B. B.; Pradhan, N. *Small* **2013**, *9*, 1002. <http://dx.doi.org/10.1002/sml.201300635>.
- (2) Norris, D. J.; Efros, A. L.; Erwin, S. C. *Science* **2008**, *319*, 1776.

- (3) Erwin, S. C.; Zu, L.; Haftel, M. I.; Efros, L.; Kennedy, T. A.; Norris, D. J. *Nature* **2005**, *436*, 91.
- (4) Ochsenbein, S. T.; Gamelin, D. R. *Nat. Nanotechnol.* **2011**, *6*, 112.
- (5) Beaulac, R.; Archer, P. I.; van Rijssel, J.; Meijerink, A.; Gamelin, D. R. *Nano Lett.* **2008**, *8*, 2949.
- (6) Boyer, J. C.; Vetrone, F.; Cuccia, L. A.; Capobianco, J. A. *J. Am. Chem. Soc.* **2006**, *128*, 7444.
- (7) Lehmann, O.; Meyssamy, H.; Kömpe, K.; Schnablegger, H.; Haase, M. *J. Phys. Chem. B* **2003**, *107*, 7449.
- (8) Bol, A. A.; van Beek, R.; Meijerink, A. *Chem. Mater.* **2002**, *14*, 1121.
- (9) Mukherjee, P.; Sloan, R. F.; Shade, C. M.; Waldeck, D. H.; Petoud, S. *J. Phys. Chem. C* **2013**, *117*, 14451.
- (10) Chengelis, D. A.; Yingling, A. M.; Badger, P. D.; Shade, C. M.; Petoud, S. *J. Am. Chem. Soc.* **2005**, *127*, 16752.
- (11) Raola, O. E.; Strouse, G. F. *Nano Lett.* **2002**, *2*, 1443.
- (12) Dethlefsen, J. R.; Mikhailovsky, A. A.; Burks, P. T.; Døssing, A.; Ford, P. C. *J. Phys. Chem. C* **2012**, *116*, 23713.
- (13) Planeles-Aragó, J.; Cordoncillo, E.; Ferreira, R. A. S.; Carlos, L. D.; Escribano, P. *J. Mater. Chem.* **2011**, *21*, 1162.
- (14) Chowdhury, P. S.; Patra, A. *Phys. Chem. Chem. Phys.* **2006**, *8*, 1329.
- (15) Sadhu, S. *J. Lumin.* **2007**, *126*, 387.
- (16) de Mello Donegá, C.; Hickey, S. G.; Wuister, S. F.; Vanmaekelbergh, D.; Meijerink, A. *J. Phys. Chem. B* **2003**, *107*, 489.
- (17) Yang, Y.; Chen, O.; Angerhofer, A.; Cao, Y. C. *J. Am. Chem. Soc.* **2008**, *130*, 15649.
- (18) Norris, D. J.; Bawendi, G. *Phys. Rev. B* **1996**, *53*, 16338.
- (19) Ellens, A.; Andres, H.; Ter Heerd, M. L. H.; Wegh, R. T.; Meijerink, A.; Blasse, G. *Phys. Rev. B* **1997**, *55*, 180.
- (20) Bryant, F. J. *Prog. Cryst. Growth Charact.* **1983**, *6*, 191.
- (21) Bryant, F. J.; Fewster, R. H. *Radiation Effects* **1973**, *20*, 239.
- (22) Pradhan, N.; Peng, X. G. *J. Am. Chem. Soc.* **2007**, *129*, 3339.
- (23) Dabbousi, B. O.; Rodriguez-Viejo, J.; Mikulec, F. V.; Heine, J. R.; Mattoussi, H.; Ober, R.; Jensen, K. F.; Bawendi, M. G. *J. Phys. Chem. B* **1997**, *101*, 9463.
- (24) Dang, S.; Yu, J. B.; Wang, X. F.; Guo, Z. Y.; Sun, L. N.; Deng, R. P.; Feng, J.; Fan, W. Q.; Zhang, H. J. *J. Photochem. Photobiol., A* **2010**, *214*, 152.
- (25) Hou, Y.; Shi, J.; Chu, W.; Sun, Z. *Eur. J. Inorg. Chem.* **2013**, *3063*.
- (26) Hebbink, G. A.; Stouwdam, J. W.; Reinhoudt, D. N.; Van Veggel, F. C. *Adv. Mater.* **2002**, *14*, 1147.