

Assembly and Separation of Semiconductor Quantum Dot Dimers and Trimers

Xiangxing Xu,[†] Sven Stöttinger,[†] Glauco Battagliarin,[‡] Gerald Hinze,[†] Enrico Mugnaioli,[†] Chen Li,[‡] Klaus Müllen,[‡] and Thomas Basché^{*,†}

[†]Institut für Physikalische Chemie, Johannes Gutenberg-Universität Mainz, Welderweg 11, 55099 Mainz, Germany

[‡]Max-Planck-Institut für Polymerforschung, Mainz, Germany

 Supporting Information

ABSTRACT: Repeated precipitation of colloidal semiconductor quantum dots (QD) from a good solvent by adding a poor solvent leads to an increasing number of QD oligomers after redispersion in the good solvent. By using density gradient ultracentrifugation we have been able to separate QD monomer, dimer, and trimer fractions from higher oligomers in such solutions. In the corresponding fractions QD dimers and trimers have been enriched up to 90% and 64%, respectively. Besides directly coupled oligomers, QD dimers and trimers were also assembled by linkage with a rigid terrylene diimide dye (TDI) and separated again by ultracentrifugation. High-resolution transmission electron micrographs show that the interparticle distances are clearly larger than those for directly coupled dots proving that the QDs indeed are cross-linked by the dye. Moreover, energy transfer from the QDs to the TDI “bridge” has been observed. Individual oligomers (directly coupled or dye-linked) can be readily deposited on a substrate and studied simultaneously by scanning force and optical microscopy. Our simple and effective scheme is applicable to a wide range of ligand stabilized colloidal nanoparticles and opens the way to a detailed study of electronic coupling in, e.g., QD molecules.

Colloidal nanoparticles (NPs) have been employed as building blocks to assemble NP molecules and superlattices with particular stoichiometry and symmetry.¹ It has been shown that electronic interactions between adjacent NPs in such structures lead to properties altered from those of the isolated components.^{1a,2} To assemble small NP oligomers from solution, the main challenges are to find effective coupling mechanisms and to separate particular NP oligomers from a possibly wide distribution of products. So far, most of such oligomers were built from noble metal (Au, Ag) NPs. Because of the strong Au–S bond, thiol-modified conjugated bridges or DNA have been prominent motifs in the formation of Au NP dimers, trimers, pyramids, or even three-dimensional superlattices.³ To purify metal NP oligomers after synthesis, gel electrophoresis and anion exchange high-performance liquid chromatography (AE-HPLC) have been employed.³ DNA approaches have also been successful for assembling semiconductor quantum dots (QDs) into dimers and higher oligomers.⁴ Early efforts to generate discrete QD oligomers rested on small bifunctional molecules like bis-(acyl hydrazide).⁵ Size selective precipitation yielded CdSe QD

dimers purified up to a level of ~70%. More recently, Koole et al. investigated mixtures of CdTe QD oligomers cross-linked by 1,6-hexanedithiol.⁶ While in the case of metal NPs the plasmon properties of the assemblies can be modulated by interparticle separation,⁷ distance dependent excitation and charge transfer are strong motivations to study QD oligomers. Recent experiments have even provided first indications for wave function overlap in oligomers of small CdTe QDs.⁶ Moreover, signatures of electronic coupling have been reported for colloidal QD molecules with inorganic interconnections^{8a} and for a pair of self-assembled QDs.^{8b} To look for a similar effect in colloidal QD dimers, protocols are needed for the production of purified dimers in which the distance can be accurately controlled.

The approaches described before typically result in a distribution of QD oligomers, and a method is sought which allows for efficient separation. Here, it will be shown that postpreparation density gradient ultracentrifugation is a powerful tool for purifying QD oligomers assembled with or without a specific linking agent. Density gradient ultracentrifugation has been recently applied to separate single-walled carbon nanotubes, graphene, and NPs.⁹

Colloidal QDs dispersed in organic solvents are capped by hydrophobic ligands such as long-chain aliphatic amines or oleic acid. By addition of a bad solvent (methanol) to a solution of QDs in a good solvent (toluene), the QDs will precipitate and can be separated from the solvent mixture by conventional centrifugation. This is a standard purification process by which QDs are removed from the raw reaction solution. An often overlooked fact is that by this procedure ligands may detach from the QD surface, leading to the onset of aggregation. Consequently, by repeating the precipitation/dissolution cycles many times and depending on the binding strength of the ligands, a larger and larger fraction of the material may aggregate and finally become insoluble in the good solvent. We show that the degree of aggregation induced by the precipitation/dissolution cycles can be controlled, yielding a distribution of directly coupled QD oligomers in the good solvent. Subsequently, dimers and trimers can be separated and enriched by density gradient ultracentrifugation. The QDs used in this study are CdSe/CdS/ZnS core/shell particles (see Supporting Information) because of their favorable photo-physical properties like high luminescence yields.¹⁰

The density gradient in the ultracentrifugation tube was built with cyclohexane–CCl₄ mixtures, with the gradient from bottom to top adjusted from 90 to 40% with respect to the CCl₄

Received: August 16, 2011

Published: October 17, 2011

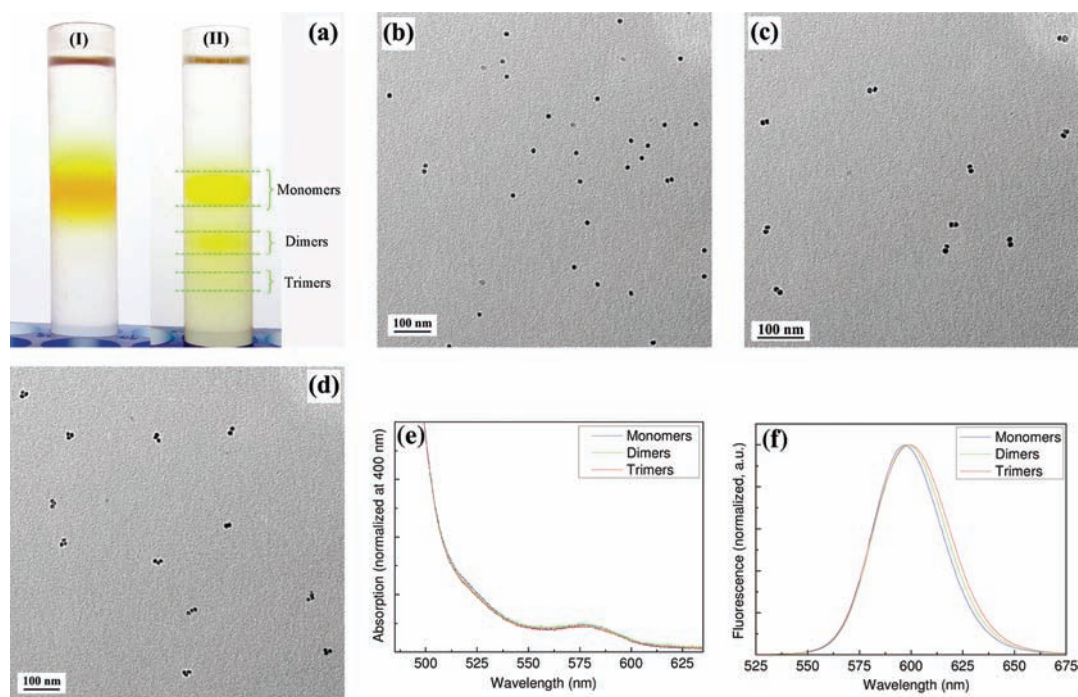


Figure 1. (a) Distribution of QDs in the tube after density gradient ultracentrifugation: (I) QDs precipitated directly from the growth solution and redispersed in cyclohexane; (II) QDs precipitated again and redispersed in cyclohexane. TEM images of QD monomers (b), dimers (c), and trimers (d) taken from the corresponding bands in a-II. UV-vis absorption (e) and fluorescence emission (f) spectra ($\lambda_{\text{exc}} = 450 \text{ nm}$) measured in cyclohexane- CCl_4 .

volume ratio. On top of the gradient solution 0.1–0.2 mL of the QD solutions were applied. A typical ultracentrifugation took ~ 10 min at 56 000 rpm. In Figure 1a(I), the distribution of QDs precipitated from the growth solution and dispersed in toluene is shown along the tube after ultracentrifugation. Obviously, in this case no clearly separated bands appear and transmission electron microscopy (TEM) images recorded with material carefully removed from the center of the band indicate the presence of mainly monomers. After precipitating/dispersing the same particles again, subsequent ultracentrifugation leads to several bands along the gradient in the tube (Figure 1a(II)). To determine their composition, material was again removed by a pipet and after further dilution studied by TEM.

In Figure 1b–d the TEM images of particles from the three bands marked in Figure 1a(II) are shown. It is clearly seen that the first band is due to monomers, while the second and third bands are mainly composed of dimers and trimers. Larger aggregates are found closer to the bottom of the tube. The appearance of well separated oligomer bands after ultracentrifugation depends on the concentration of QDs, the amount of bad solvent added to the good solvent, and the number of precipitation/dispersion cycles. Hence, for a given concentration of QDs several attempts might be necessary to find the right conditions for oligomer formation and subsequent purification by the ultracentrifuge.

Using the dimer or trimer solutions from the first round ultracentrifugation, a second or even a third round can be applied for further purification. A second round ultracentrifugation has been found to yield purities of $\sim 90\%$ and $\sim 64\%$ for QD dimers and trimers, respectively. The difference in purity of the dimer and trimer bands can be explained by the fact that the more QDs an oligomer contains, the more topological connections can exist. Consequently, the broadening of the frictional coefficient and the effective radius broaden the corresponding band.¹¹

The UV-vis absorption and emission spectra of QD monomers, dimers, and trimers are shown in Figure 1e, f. While no difference was found in the absorption spectra, a slight red shift was noticed in the emission spectra when going from monomers to trimers. Similar red shifts have recently been reported for mixtures of CdTe oligomers and attributed to electronic excitation energy transfer from smaller to larger QDs.⁶ Since our QD monomers are covered by thick shells of higher band gap materials, excitation delocalization is unlikely in our structures, which is supported by the absence of shifts in the absorption spectra. Hence, in accordance with the before mentioned study we suppose that the excitation energy within an oligomer is preferentially transferred to the larger particle from which emission then occurs. This effect which leads to an effective enhancement of emission from slightly larger particles with a slightly smaller band gap gives rise to the minor red shift found in the emission spectra.

In a recent study we had shown that terylene diimide dyes furnished with a dicarboxylic anchor effectively bind to QD surfaces.¹² Energy transfer from QD to dye has been observed in these complexes and assigned to a FRET (fluorescence resonance energy transfer) type process. To assemble QD oligomers by a rigid dye bridge, we synthesized a bifunctional terylene diimide (TDI) which carries two dicarboxylic anchors at its imide nitrogens (Figure 2c). TDI linked QD oligomers were prepared by mixing QDs dissolved in toluene and TDI dissolved in methanol to yield a QD to TDI ratio of typically 1:3. The TDI molecules exchange the oleic acid/oleylamine ligands on the QD surface and cross-link the QDs. After precipitation the particles were dissolved in cyclohexane and the solution was transferred to the ultracentrifuge. Several bands appeared along the tube, and TEM images (see Supporting Information) of the various fractions showed that again monomers, dimers, and trimers

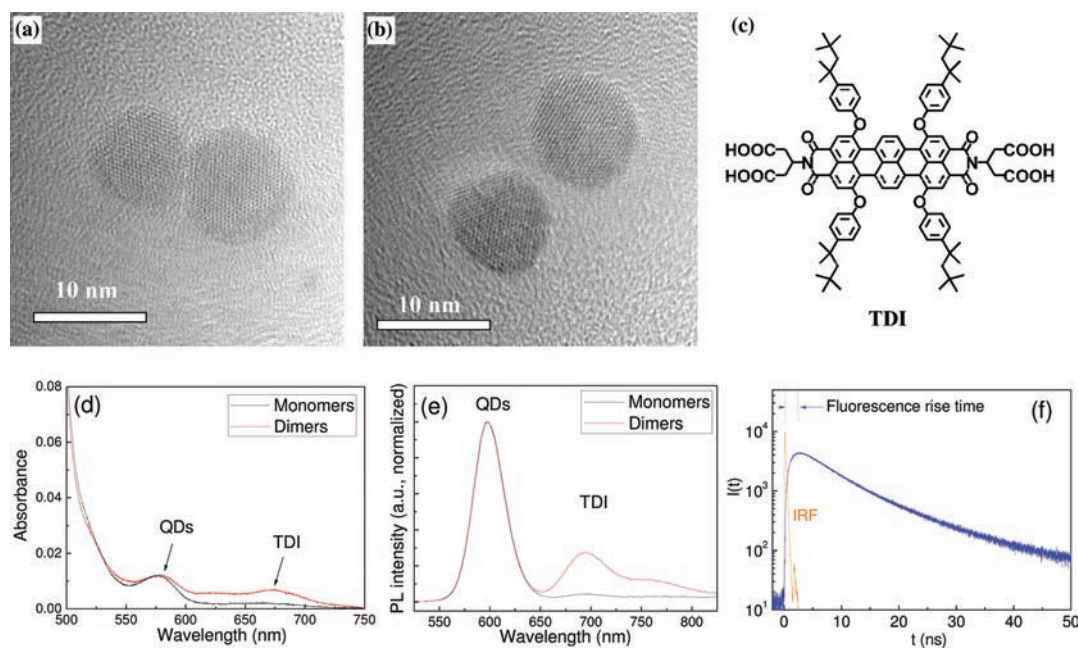


Figure 2. Typical HRTEM images of a directly coupled QD dimer (a) and a TDI linked QD dimer (b). The chemical structure of the TDI molecule is shown in (c). UV-vis absorption (d) and fluorescence ($\lambda_{\text{exc}} = 450 \text{ nm}$) (e) spectra in cyclohexane of QD monomers and TDI linked QD dimers, taken from the corresponding bands in the ultracentrifugation tube. Fluorescence rise/decay curve (blue) of TDI in TDI linked QD dimers ($\lambda_{\text{exc}} = 450 \text{ nm}$, $\lambda_{\text{det}} = 693 \text{ nm}$) and instrumental response function (orange) (f).

could be separated. Although the synthesis conditions were different for the TDI linked QD oligomers, directly coupled QD oligomers may have formed too.

This possibility can be largely ruled out by high-resolution TEM (HR-TEM) measurements. In Figure 2a,b HR-TEM images of a directly coupled QD dimer and a QD dimer cross-linked by TDI are shown. While the two QDs are in close contact in the first case, there is a clear interparticle distance in the second case caused by the TDI bridge. By analyzing ~ 20 dimers for each case, we found that in $\sim 95\%$ of the directly coupled dimers the QDs touched each other. In contrast, for the TDI cross-linked dimers, in $\sim 70\%$ of the images a clear separation between the QDs was found. The actual percentage for TDI cross-linking is expected to be higher, because gaps between particles may be obscured by the orientation of dimers relative to the electron beam. The observation of close contact in directly coupled dimers also supports the assumption that in this case the loss of ligands is responsible for the formation of oligomers.

The fact that we have been using a bridge which can be easily accessed by optical absorption and emission further supports cross-linking by TDI. In Figure 2d absorption spectra of the monomer and dimer fractions are shown. In addition to the QD band gap transition at 575 nm the TDI long wavelength band can be found at 670 nm. In a control experiment we had verified that unbound TDI remains in the top layer of the gradient solution after ultracentrifugation and does not interfere in these measurements. Notably, for the QD monomers only a weak TDI absorption band is found. This indicates that under our experimental conditions (QD/TDI ratio of 1:3) TDI indeed effectively cross-links the QDs in solution and complexes in which only one TDI is bound to QD are rarely found. This conclusion is corroborated by the emission spectra. At an excitation wavelength of 450 nm where TDI absorption is negligible the emission spectrum of the dimer fraction shows QD as well as TDI emission due to energy transfer from QD to TDI.¹² In the monomer fraction the TDI emission signal

again is very weak. While this can partly be attributed to the presence of only a single energy donor (QD) and concomitantly smaller transfer efficiency, the main reason for the lack of TDI signal, however, is the low probability for the existence of 1:1 complexes.

By performing a second round ultracentrifugation the purity of the TDI linked QD dimers can be increased up to $\sim 70\%$. The yield of these dimers (1–5%) was found to largely depend on the QD/TDI ratio, the best results being obtained at a ratio of $\sim 1:3$. Lower ratios gave less dimers, while higher ratios led to aggregation by excessive cross-linking.

To get more quantitative information on the energy transfer dynamics, fluorescence rise/decay curves have been measured for TDI linked QD dimers. In these experiments the QD donors were selectively excited by short light pulses ($\lambda_{\text{exc}} = 450 \text{ nm}$) while detecting the emission signal from the TDI acceptor. In Figure 2f a rise/decay curve is shown together with the instrumental response function (IRF). The rising part of the curve is significantly shifted toward longer times compared to the IRF, because it takes some finite time for the excitation energy to be transferred from QD to TDI. From the exponential rise of the emission signal we extract a time constant of 1.3 ns, which is a reasonable number within a simple FRET picture.¹²

Although we have shown that QD oligomers can be substantially enriched by ultracentrifugation, their purity still is not 100%. While this seems to be within reach by further improvement of the experimental protocols, another way to achieve 100% purity, at least in spectroscopic investigations, is to study single oligomers. Such an approach calls for a combination of techniques which provide structural and spectroscopic information at the single particle level.¹³ In Figure 3a, an image of isolated TDI linked QD dimers is shown, which was taken with an atomic force microscope. For these experiments the dimers were deposited on glass substrates from a solution with a very low concentration. The AFM image unambiguously proves that individual QDs

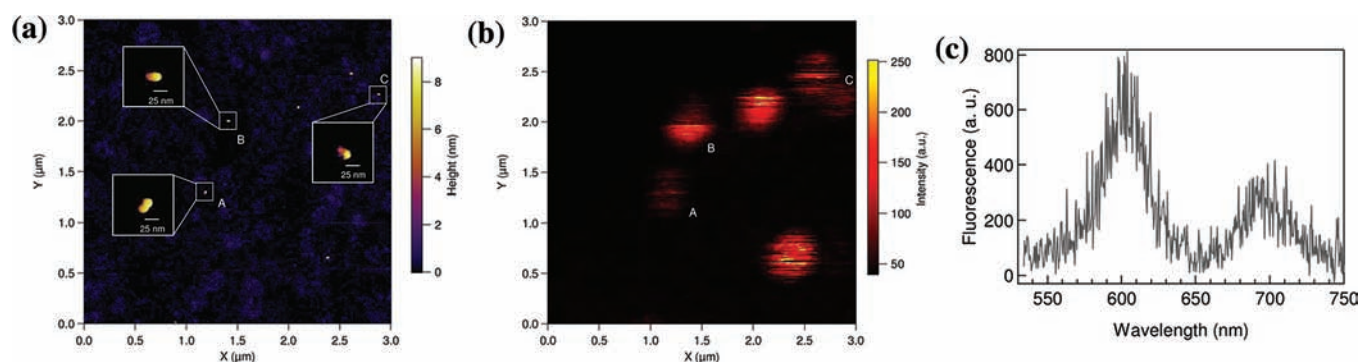


Figure 3. (a) A typical AFM image (height image) of TDI linked QD dimers. Three selected dimers are marked as A, B, and C. (b) Fluorescence image of the same sample area. (c) Emission spectrum of dimer A ($\lambda_{\text{exc}} = 470 \text{ nm}$). The lateral resolution of the AFM was estimated to be $\sim 8 \text{ nm}$.¹⁴

within a dimer can be resolved with this technique. Employing confocal fluorescence microscopy, the emission of the same set of dimers could be simultaneously imaged (Figure 3b). The stripes in the fluorescence spots are due to QD blinking. The emission spectra taken from single dimers were found to be composed by QD and TDI emission (Figure 3c).

In summary, QD dimers and trimers have been assembled by either direct coupling of particles through loss of ligands or by cross-linking the particles with a rigid bifunctional dye bridge. Subsequent separation and enrichment of small oligomers was achieved by density gradient ultracentrifugation. The two-step procedure (assembly/separation) was also successfully applied to other types of QDs (CdSe, CdSe/ZnS). An interesting future option is to prepare heterodimers in which either particles of the same composition but different sizes are connected or the composition of the particles differ. With regard to electronic coupling in such oligomers, by which we mean the full range of interactions from energy and charge transfer up to delocalized wave functions, accurate distance control is of utmost importance. Our approach provides twofold access to this crucial parameter: The shell thicknesses as well as the use of linkers with varying lengths are ways to tune the distance between particles. The strongest coupling is expected in small core-only particles where large size quantization may lead to clear signatures of QD molecules.⁸ On the other hand a conjugated dye linker may serve as a conductive bridge for charge flow in a QD heterodimer.

■ ASSOCIATED CONTENT

Supporting Information. Experimental details, TEM images, and spectra. This material is available free of charge via the Internet at <http://pubs.acs.org>.

■ AUTHOR INFORMATION

Corresponding Author

Thomas.Basche@uni-mainz.de

■ ACKNOWLEDGMENT

This work was supported by the German Science Foundation (SFB 625).

■ REFERENCES

(1) (a) Murray, C. B.; Kagan, C. R.; Bawendi, M. G. *Science* **1995**, *270*, 5240. (b) Gu, H. W.; Zheng, R. K.; Zhang, X. X.; Xu, B. *J. Am. Chem. Soc.* **2004**, *126*, 5664. (c) Salant, A.; Amitay-Sadovsky, E.; Banin, U.

J. Am. Chem. Soc. **2006**, *128*, 10006. (d) Shevchenko, E. V.; Talapin, D. V.; Kotov, N. A.; O'Brien, S.; Murray, C. B. *Nature* **2006**, *439*, 55.

(2) (a) Talapin, D. V.; Murray, C. B. *Science* **2005**, *310*, 86. (b) Williams, K. J.; Tisdale, W. A.; Leschkes, K. S.; Haugstad, G.; Norris, D. J.; Aydil, E. S.; Zhu, X.-Y. *ACS Nano* **2009**, *3*, 1532. (c) Sheikholeslami, S.; Jun, Y. W.; Jain, P. K.; Alivisatos, A. P. *Nano Lett.* **2010**, *10*, 2655. (d) Shao, L.; Woo, K. C.; Chen, H. J.; Jin, Z.; Wang, J. F.; Lin, H. Q. *ACS Nano* **2010**, *4*, 3053.

(3) (a) Alivisatos, A. P.; Johnson, K. P.; Peng, X. G.; Wilson, T. E.; Loweth, C. J.; Bruchez, M. P.; Schultz, P. G. *Nature* **1996**, *382*, 609. (b) Brousseau, L. C.; Novak, J. P.; Marinakos, S. M.; Feldheim, D. L. *Adv. Mater.* **1999**, *11*, 447. (c) Aldaye, F. A.; Sleiman, H. F. *J. Am. Chem. Soc.* **2007**, *129*, 4130. (d) Yim, T. J.; Wang, Y.; Zhang, X. *Nanotechnology* **2008**, *19*, 435605. (e) Claridge, S.; Liang, H. W.; Basu, S. R.; Fréchet, J. M. J.; Alivisatos, A. P. *Nano Lett.* **2008**, *8*, 1202. (f) Mastroianni, A. J.; Claridge, S. A.; Alivisatos, A. P. *J. Am. Chem. Soc.* **2009**, *131*, 8455. (g) Maye, M. M.; Kumara, M. T.; Nykypanchuk, D.; Sherman, W. B.; Gang, O. *Nat. Nanotechnol.* **2010**, *5*, 116.

(4) (a) Fu, A. H.; Micheel, C. M.; Cha, J.; Chang, H.; Yang, H.; Alivisatos, A. P. *J. Am. Chem. Soc.* **2004**, *126*, 10832. (b) Antelman, J.; Wilking-Chang, C.; Weiss, S.; Michalet, X. *Nano Lett.* **2009**, *9*, 2199. (c) Wang, Q. B.; Wang, H. N.; Lin, C. X.; Sharma, J.; Zou, S. L.; Liu, Y. *Chem. Commun.* **2010**, *46*, 240. (d) Maye, M. M.; Gang, O.; Cotlet, M. *Chem. Commun.* **2010**, *46*, 6111.

(5) Peng, X. G.; Wilson, T. E.; Alivisatos, A. P.; Schultz, P. G. *Angew. Chem., Int. Ed. Engl.* **1997**, *36*, 145.

(6) Koole, R.; Liljeroth, P.; Donega, C. D. M.; Vanmaekelbergh, D.; Meijerink, A. *J. Am. Chem. Soc.* **2006**, *128*, 10436.

(7) (a) Sonnichsen, C.; Reinhard, B. M.; Liphardt, J.; Alivisatos, A. P. *Nat. Biotechnol.* **2005**, *6*, 741. (b) Sebban, D. S.; Mock, J. J.; Smith, D. R.; LaBean, T. H.; Lazarides, A. A. *Nano Lett.* **2008**, *8*, 1803.

(8) (a) Choi, C. L.; Alivisatos, A. P. *Annu. Rev. Phys. Chem.* **2010**, *61*, 369. (b) Bayer, M.; Hawrylak, P.; Hinzer, K.; Fafard, S.; Korkusinski, M.; Wasilewski, Z. R.; Stern, O.; Forchel, A. *Science* **2001**, *291*, 451.

(9) (a) Dadosh, T.; Gordin, Y.; Krahne, R.; Khivrich, I.; Mahalu, D.; Frydman, V.; Sperling, J.; Yacoby, A.; Bar-Joseph, I. *Nature* **2005**, *436*, 677. (b) Chen, G.; Wang, Y.; Tan, L. H.; Yang, M. X.; Tan, L. S.; Chen, Y.; Chen, H. Y. *J. Am. Chem. Soc.* **2009**, *131*, 4218. (c) Sun, X. M.; Luo, D. C.; Liu, J. F.; Evans, D. G. *ACS Nano* **2010**, *4*, 3381. (d) Ghosh, S.; Bachilo, S. M.; Weisman, R. B. *Nat. Nanotechnol.* **2010**, *5*, 443.

(10) Xie, R. G.; Kolb, U.; Li, J.; Basché, T.; Mews, A. *J. Am. Chem. Soc.* **2005**, *127*, 7480.

(11) Sharma, V.; Park, K.; Srinivasarao, M. *Proc. Natl. Acad. Sci. U.S.A.* **2009**, *106*, 4981.

(12) Ren, T.; Mandal, P. K.; Erker, W.; Liu, Z. H.; Avlasevich, Y.; Puhl, L.; Müllen, K.; Basché, T. *J. Am. Chem. Soc.* **2008**, *130*, 17242.

(13) Koberling, F.; Mews, A.; Philipp, G.; Kolb, U.; Potapova, I.; Burghard, M.; Basché, T. *Appl. Phys. Lett.* **2002**, *81*, 1116.

(14) Bustamante, C.; Keller, D. *Phys. Today* **1995**, *12*, 32.