# Surface Passivation of Luminescent Colloidal Quantum Dots with Poly(Dimethylaminoethyl methacrylate) through a Ligand Exchange Process

Xiao-Song Wang, Tieneke E. Dykstra, Mayrose R. Salvador, Ian Manners, Gregory D. Scholes,* and Mitchell A. Winnik*

*Department of Chemistry, University of Toronto, 80 St. George Street, Toronto, M5S 3H6 Ontario Canada*

Received February 25, 2004; E-mail: gscholes@chem.utoronto.ca; mwinnik@chem.utoronto.ca

Nanocrystals (NCs) of semiconductor materials, so-called quantum dots (QD), have been attracting a broad range of attention from a variety of disciplines owing to their novel optical, electrical, and catalytic properties.[1] The processibility of colloidal nanocrystals is exploited in a diversity of applications by tuning their organic surface characteristics. For example, a water-soluble surface is required for biological labels,[2] an electron conductive layer is important for solar cells,[3] and a polymerizable surface is needed to make photoluminescent (PL) polymer composites.[4]

NCs are commonly prepared by an organometallic route in the presence of excess trioctylphosphine oxide (TOPO). The TOPO ligand passivates the NC surface and leads to particles with a high luminescence quantum yield (QY). However, this hydrophobic TOPO layer is often neither suitable nor robust enough for many applications. Moreover, these monodentate ligands are labile and in dynamic equilibrium with the surrounding medium. When the excess TOPO is removed from the colloidal NC solution, the particles become unstable and begin to aggregate.[5] Within the aggregate, the QY is diminished. Therefore, there is a pressing need to learn how to modify the surface of NCs, not only to confer a diversity of characteristics, but also to provide colloidal stability to NC solutions. In the present communication, we demonstrate the passivation of CdSe/ZnS quantum dots using an amine-containing polymer, polydimethylaminoethyl methacrylate (PDMAEMA), that acts as a multidentate ligand.

Polymers can be envisaged as versatile surface modifiers because of their processibility and tunable functionality. In practice, two methods have been used to modify NCs with polymers: (i) Encapsulation of NCs including their original ligands with polymers through ionic or hydrophobic interaction[6] and (ii) surface grafting through living polymerization.[7] Surface grafting, unfortunately, usually results in a diminished photoluminescence QY relative to the original NCs. Polymer encapsulation can preserve the QY, but generally leads to composite structures containing many NC particles, rather than single encapsulated particles.[8] This type of encapsulation can generate a thick organic outer layer that is often undesirable.

Another alternative for manipulating the NC surface involves ligand exchange. In the past, most of the examples involved replacing TOPO with another monodentate ligand. Polydentate ligands provide enhanced coordination interactions due to a cooperative, amplifying effect of multiple binding sites. Bawendi and co-workers recently developed a multidentate oligomeric alkyl phosphine ligand to passivate NCs,[9] leading to a thin and stable organic shell. That work established a proof of concept, but required an elaborate synthesis of the phosphine oligomers.

Conventional homopolymers can be thought of as multidentate ligands if a suitable functionality can be introduced as a pendant group in the repeat unit. For example, PDMAEMA contains a tertiary amine in the repeat unit, as shown below. The synthesis of
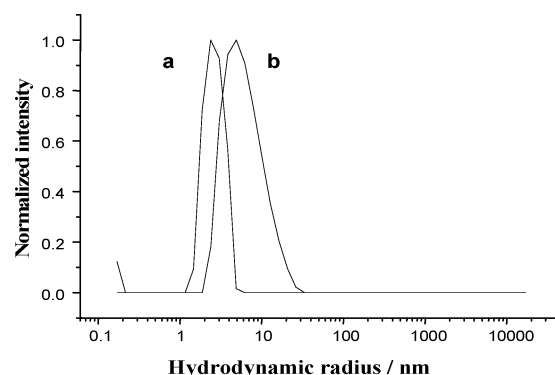


**Figure 1.** CONTIN plots of the $R_h$ of NCs in toluene in the (a) absence and (b) presence of PDMAEMA homopolymer.

well-defined samples of PDMAEMA has been greatly simplified as a result of recent advances in living polymerization.[10] Here we report a facile modification of the surface of TOPO-coated NCs using PDMAEMA homopolymer as a multidentate ligand. We show that the polymer replaces TOPO groups on the nanoparticles. The modified NCs form colloidally stable solutions in TOPO-free hydrophobic solvents such as toluene. They also form stable solutions in protic solvents such as methanol.
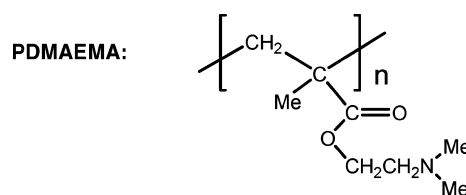


We have synthesized PDMAEMA through living free-radical polymerization;[5] hence, the degree of polymerization (DP) and polydispersity index (PDI) are well-controlled. High-quality CdSe/ZnS core−shell colloidal quantum dots were prepared using established procedures.[5,11] In this study, PDMAEMA with a degree of polymerization of 30 and PDI of 1.3 is shown to displace TOPO ligands on CdSe/ZnS (core−shell) NCs after mixing the polymer with a dilute colloidal solution of NCs in toluene at room temperature. The colloidal NC solutions before and after addition of the polymer were characterized by dynamic light scattering, which provided the hydrodynamic radius, $R_h$, of the particles. As shown in the CONTIN plot in Figure 1, there is a clear shift of $R_h$ from ca. 3.0 to 5.9 nm, suggesting a layer of polymer has been deposited on the particle surface. While the peak at higher radius is broader than that of the original particles, this is not an indication of particle aggregation. As shown by TEM experiments,[5] the diameters of the NC particles before and after surface modification are virtually identical, indicating that the particles remain discrete.
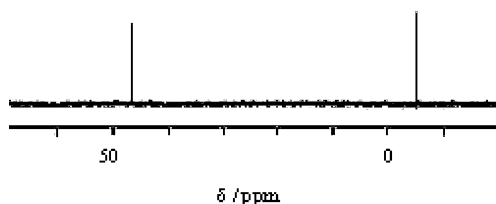
**Figure 2.** ³¹P NMR of NCs in the presence of PDMAEMA with triphenylphosphine as an internal reference.
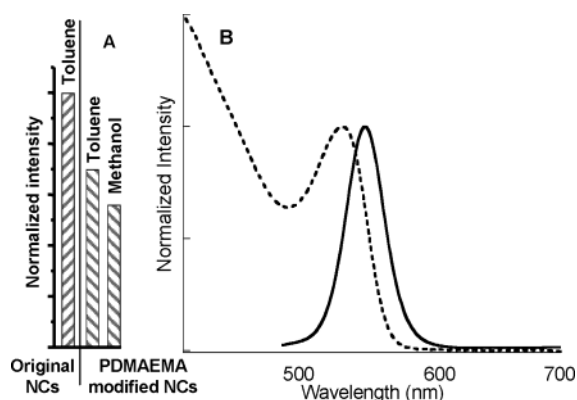


**Figure 3.** (A) Photoluminescence intensity of NCs before and after surface modification with PDMAEMA. (B) UV−vis and fluorescence (FL, excited at 475 nm) spectra for PDMAEMA modified NCs.

Therefore, the observed increase in particle size by DLS measurement can be attributed to the adsorption of a polymer layer on the NCs.

The experiments described above do not provide information about the fate of the TOPO ligand on the particle surface when the particles are exposed to the polymer. To address this question, we carried out ³¹P NMR measurements of the NCs in CDCl₃. According to Bawendi,[12] high-resolution ³¹P NMR measurements of TOPO-capped CdSe quantum dots in solution usually exhibit several broad signals associated with the bound TOPO ligand. The complexity of the NMR signal suggests that a variety of phosphorus chemical environments are available to TOPO ligands bound to the NC surface, which may include bound dimers of TOPO.[13]

In our experiments on NCs in a CDCl₃ solution (ca. 30 mg/5 mL) in the absence of PDMAEMA, we did not observe any ³¹P signals, presumably because of the low concentration of the nanoparticles. However, when PDMAEMA (50 mg) was added, a sharp ³¹P signal appeared at 47 ppm (Figure 2), which corresponds to free TOPO ligand in CDCl₃.[12] This result emphasizes the fact that ligand replacement occurred. We were able to quantify the amount of TOPO released by carrying out the ³¹P NMR experiment in the presence of a known amount of triphenylphosphine as an internal standard (peak at −5 ppm). In this way, we determined that approximately 10 mg of TOPO (26 $\mu$mol) was released from the 30 mg of NCs present in the solution.

Surface modification of the NCs with PDMAEMA had only a modest effect on the photoluminescent QY[14] of the particles. In Figure 3, we compare the luminescence intensity of NCs in toluene, before and after addition of the polymer. The small (ca. 30%) drop in luminescence intensity was rapid upon polymer addition, and the QY of the toluene solution appeared to remain stable thereafter.

As a result of this polymer modification, the NCs become miscible with protic solvents, such as methanol. To transfer the polymer-capped NCs to methanol, methanol was simply added to the solid remaining after evaporation of toluene. The resulting solution appeared to be homogeneous and, when excited at 475 nm, displayed a strong photoluminescence peaked at 545 nm, close to the emission peak of the original sample (544 nm), suggesting that there is no significant agglomeration of NCs upon solvent change. There was no evidence for any subsequent instability of colloidal suspension in methanol.

In conclusion, we have developed a ligand exchange method to modify NCs with an amine-containing polymer, PDMAEMA, which led to NCs securely bound by a layer of a "conventional" homopolymer. The modified NCs retain 70% of their original photoluminescence quantum yield. As a result of this surface modification, the NCs become soluble in polar media, such as methanol. This method establishes the utility of using simple homopolymers, which can be synthesized in a controlled manner, as robust multidentate ligands for NC surface modification. These polymers provide colloidal stability as well as surface passivation. The extension of this work to copolymers should be straightforward, opening the door to new strategies for introducing functional groups on the particle surface without sacrificing any of the attractive features provided by homopolymer adsorption.

**Supporting Information Available:** CdSe/Zns and PDMAEMA syntheses and TEM images of NCs before and after surface modification. This material is available free of charge via the Internet at http://pubs.acs.org.

## References

(1) Alivisatos, A. P. *Science* **1996**, *271*, 933−937.
(2) Jovin, T. M. *Nat. Biotechnol.* **2003**, *21*, 32−33.
(3) Huynh, W. U.; Dittmer, J. J.; Alivisatos, A. P. *Science* **2002**, *295*, 2425−2427.
(4) (a) Zhang, H.; Cui, Z. C.; Wang, Y.; Zhang, K.; Ji, X. L.; Lu, C. L.; Yang, B.; Gao, M. Y. *Adv. Mater.* **2003**, *15*, 777−780. (b) O'Brien, P.; Cummins, S. S.; Darcy, D.; Dearden, A.; Masala, O.; Pickett, N. L.; Ryley, S.; Sutherland, A. J. *Chem. Commun.* **2003**, 2532−2533.
(5) See Supporting Information.
(6) (a) Potapova, I.; Mruk, R.; Prehl, S.; Zentel, R.; Basche, T.; Mews, A. *J. Am. Chem. Soc.* **2003**, *125*, 320−321. (b) Cyr, P. W.; Tzolov, M.; Hines, M. A.; Manners, I.; Sargent, E. H.; Scholes, G. D. *J. Mater. Chem.* **2003**, *13*, 2213−2219.
(7) Farmer, S. C.; Patten, T. E. *Chem. Mater.* **2001**, *13*, 3920−3926. (b) Skaff, H.; Ilker, M. F.; Coughlin, E. B.; Emrick, T. *J. Am. Chem. Soc.* **2002**, *124*, 5729−5733.
(8) Dubertret, B.; Skourides P.; Norris, D. J.; Noireaux, V.; Brivanlou, A. H.; Libchaber, A. *Science* **2002**, *298*, 1759−1762.
(9) Kim S.; Bawendi, M. G. *J. Am. Chem. Soc.* **2003**, *125*, 14652−14653.
(10) Wang, X. S.; Armes, S. P. *Macromolecules* **2000**, *33*, 6640−6647.
(11) (a) Murray, C. B.; Noms, D. J.; Bawendi, M. G. *J. Am. Chem. Soc.* **1993**, *115*, 8706−8715. (b) Hines, M. A.; Guyot-Sionnest, P. *J. Phys. Chem.* **1996**, *100*, 468−471.
(12) Kuno, M.; Lee, J. K.; Dabbousi, B. O.; Mikulec, F. V.; Bawendi, M. G. *J. Chem. Phys.* **1997**, *106*, 9869−9882.
(13) Lorenz, J. K.; Ellis, A. B. *J. Am. Chem. Soc.* **1998**, *120*, 10970−10975.
(14) The quantum yields were measured using rhodamine 6G as a standard for optical densities ranging from 0.02 to 0.5. The spectra were corrected for lamp fluctuations and detector response. The QY was found by dividing the integrated fluorescence intensity by the optical density at the excitation wavelength (475 nm).

JA0489339