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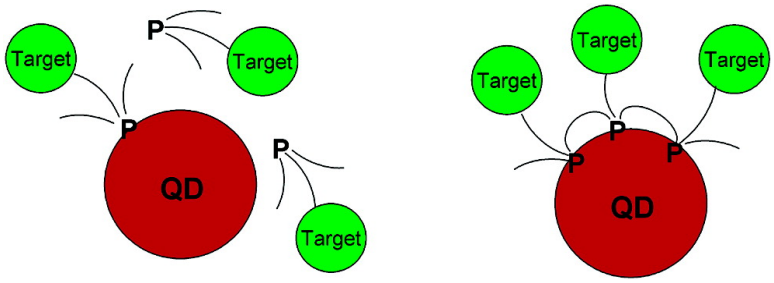

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Oligomeric Ligands for Luminescent and Stable Nanocrystal Quantum Dots

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Colloidal nanocrystal quantum dots (QDs) consist of an inorganic nanoparticle that is surrounded by a layer of organic ligands. This organic ligand shell dictates the surface chemistry of the QDs and is therefore critical to processing, functionalization, and incorporation into various substrates. Ligand-exchange with various thiol ligands, including dithiols and thiol dendrimers, has been extensively studied,[1] and more sophisticated architectures have been built on these thiol ligands covalently, electrostatically, or via sol−gel chemistry.[2] However, ligand-exchange with thiols usually diminishes the quantum yield (QY) of the as-grown QD photoluminescence (PL). Encapsulating QDs and their initial ligands with macromolecules such as polymers or lipids can preserve QY, but generally adds a large volume to the QDs, resulting in a final size that may be bulkier than desired.[3] For example, the increased size can diminish imaging sensitivity by decreasing the number of QDs that can be attached to a target. For in vivo imaging, bulky QDs may have limited accessibility to target systems. For many applications, thin functionalizable organic shells are ideal. For example, thin shells are desired for potential sensors that function by energy transfer to and from QDs.[4] We report a new family of oligomeric phosphine ligands. These electronically passivate QDs as well as the initial growth ligands, yet form thin and secure organic shells that allow tunable compatibility in diverse environments and flexibility for further chemistry.

Alkyl phosphines passivate CdSe and CdSe/ZnS (core/shell) QDs effectively as a major component of the growth ligands. However, monomeric alkyl phosphines are labile as are many other mondentate ligands. A considerable concentration of free monodentate ligands is required in solution to keep the QDs well passivated. When QD growth solutions are diluted or embedded in an environment in which no excess ligands are present, QYs tend to decrease and the QDs aggregate. We have developed oligomeric phosphines (OPs) to overcome this behavior. As polydentate ligands, OPs bind more effectively to QD surfaces. For example, they can securely anchor targets as illustrated in Figure 1. To avoid aggregation of the QDs, the outermost part of the organic shell must be compatible with the bulk environment. Chart 1 shows the chemical structures of representative OPs that are functionalized with different moieties. By changing the R group, OPs can be easily modified with many functional groups, allowing homogeneous incorporations into various matrices. The organic shell is designed to form three thin, concentric sublayers around the QD: (i) an inner phosphine layer, (ii) a linking layer, and (iii) an outer functionalized layer. The inner phosphine layer passivates the QD surface; the linking layer protects it; while the outer functionalized layer delivers desirable chemical properties, including miscibility, the ability to copolymerize with other polymer matrices, cross-linking on the surface of the dots, and further chemical modifications such as conjugations to biomolecules. Scheme 1 shows the synthetic routes for OPs (see Supporting Information for details). They consist of two major steps: (i) oligomerization of monomeric alkyl phosphines and (ii) introduction of functionality. Trishydroxypropylphosphine (THPP) is used as a monomeric alkyl phosphine, along with

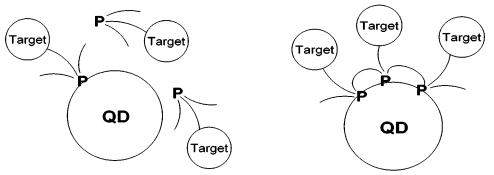
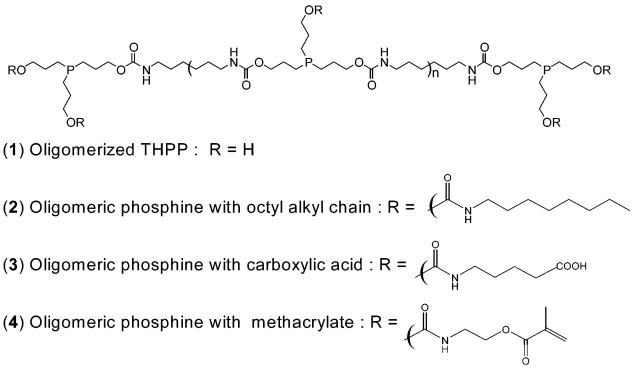
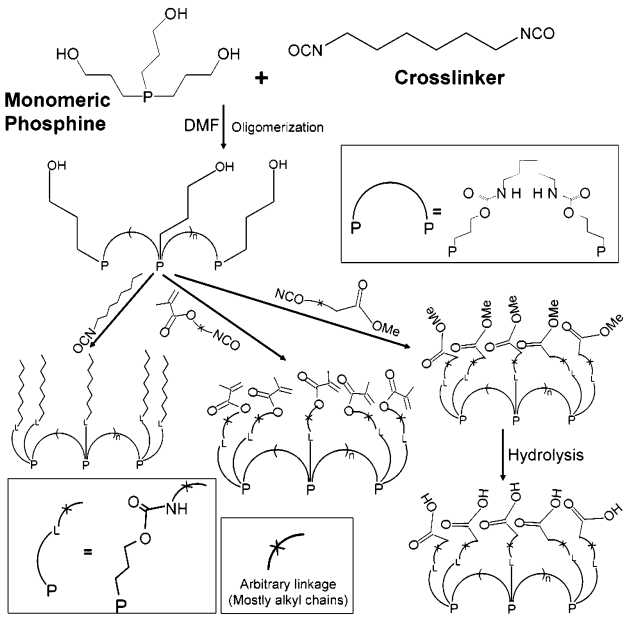


Figure 1. Illustration of the enhanced affinity of oligomeric phosphines to QD surfaces in comparison to monomeric phosphines.

Chart 1. Chemical Structures of Representative Oligomeric Phosphines



Scheme 1. Synthesis and Functionalization of Oligomeric Phosphines



diisocyanatohexane (DIH) as a cross-linker. The degree of oligomerization (i.e., the length of the oligomers) is controlled by the stoichiometry of the phosphine unit and the cross-linker. Figure 2 shows the mass spectrum of oligomerized THPP (**1**). A distribution of different oligomers such as trimer, tetramers, pentamers, and

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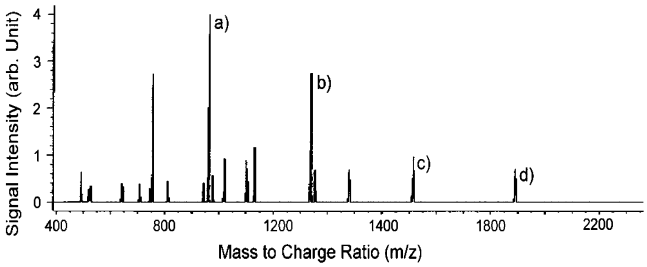

Figure 2. Mass spectrum of oligomerized THPP (**1**). Peaks from multiple charges are merged to equivalent peaks from single charges. (a), (b), (c), and (d) represent trimer, tetramers, pentamers, and hexamers, respectively.

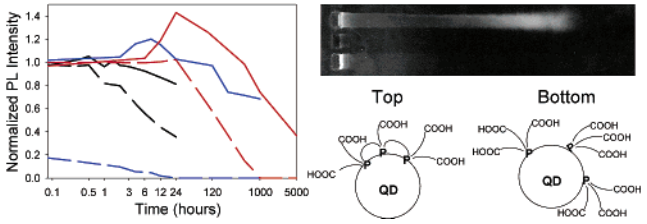

Figure 3. (Left) Photoluminescence intensity of CdSe/ZnS (core/shell) quantum dots ligand-exchanged by different ligands; (red) in extremely dilute THF soluntions (oligomeric phosphine with octyl alkyl chain (solid) and trioctylphosphine (dashed)); (blue) in dilute pH 10 potassium hydroxide aqueous solutions (oligomeric phosphine with carboxylic acid (solid) and mercaptoundecanoic acid (dashed)); (black) in 100% fetal bovine serum at 37 °C (oligomeric phosphine with carboxylic acid after cross-linking around quantum dots (solid) and the non-cross-linked control (dashed)). (Right) Electrophoreses (1.0% agarose gel in pH 8.2 trisborate buffer) of CdSe/ZnS (core/shell) quantum dots ligand-exchanged by oligomeric phophine with carboxylic acid (bottom). Simplified structures of the oligomeric phosphine and the monomeric phosphine are illustrated.

hexamers is shown. The oligomers larger than the trimer include branched isomers. The hydroxy group in THPP reacts readily with the isocyanato group in DIH at room temperature, yielding carbamate linkages.[5] This is observed in the IR as a decrease in the OH vibration at 3400 cm^{-1}, concurrent with an increase in the carbamate carbonyl peak at 1700 cm^{-1}. Chemical functionality can be introduced to **1** by further reaction of the remaining hydroxyl groups with any molecules containing an isocyanate group and an additional functional group.

Figure 3 (left) shows PL stability tests of identical QDs with various ligands. Oligomeric phosphines with octyl alkyl chain (**2**) are compared to trioctylphosphine (TOP) (red lines). **2** passivates QDs more efficiently than TOP, maintaining the PL over months. Oligomeric phosphines with carboxylic acid (**3**) and mercaptoundecanoic acid (MUA) are compared in dilute NaOH (pH 10) aqueous solutions (blue lines). The QD sample loses ~80% of its initial QY after ligand-exchange by the thiol ligand MUA, while **3** maintains the initial QY (consistently in the 20−40% range) through the ligand-exchange process and for weeks following. **3** efficiently passivates QDs in various buffer solutions of pH ranging from 5.5 to 12 and in high salt concentration solutions. To passivate QDs even more efficiently, the chemical flexibility of **3** is exploited for further cross-linking around QDs after ligand-exchange. **3** is cross-linked by 2,6-diaminopimelic acid via amide couplings and compared to the initial sample before cross-linking, both in 100% fetal bovine serum at 37 °C (black lines). The cross-linked ligand passivates the QDs efficiently, with a loss of less than 20% of the initial QY after 24 h in serum at 37 °C. Electrophoresis is used to confirm the efficient binding affinity of OPs (Figure 3 right). The top elution represents a QD sample with **3**. The control run on the bottom uses a monomeric phosphine with a carboxylic acid functional group. Both ligands are functionalized identically, starting from THPP, with the oligomerization omitted for the control ligand. Faster elution with the oligomerized ligand corresponds to better preservation of the carboxylate charges around the QDs. The control monomeric phosphine is more easily removed from the QDs by the electric field, leaving the QDs behind and causing them to stop traveling in the gel. The QDs with OPs can travel back and forth in the gel as the electric field is alternated.

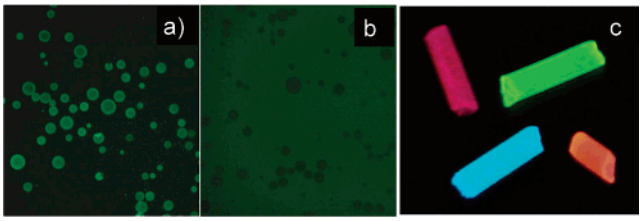

Figure 4. Fluorescence microscopy images of biotinylated agarose beads incubated with streptavidin conjugated CdSe/ZnS(core/shell) quantum dots (a), and beads incubated with unconjugated control sample (b). Fluorescence image of different color QD-polymer composite sticks.

To demonstrate the versatility of OPs, streptavidin is conjugated to **3**. Figure 4a and b shows fluorescence microscope images of QD solutions with biotinylated beads. Figure 4a shows that streptavidin conjugated QDs bind specifically to biotinlyated agarose beads. The beads adsorb most of the QDs, leaving the background dark. Repeating the experiment with unconjugated QDs results in a complementary image with dark beads and a bright background. Both images are taken after incubation without additional processing. When washed, streptavidin conjugated QDs remain on the beads, while no detectable QDs are observed on the control sample.

Oligomeric phosphines with methacrylate (**4**) can enable homogeneous incorporation (i.e., copolymerization) of QDs into many polymer matrices without the need for additional free ligands such as TOP in the matrix (Figure 4c). The polymerizable ligands **4** can become incorporated into host polymers and offer synthetic routes to micrometer- and submicrometer-sized polymer-QD composites.

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Supporting Information Available: Detailed procedures for the synthesis of oligomeric phosphines, ligand-exchanges thereof, cross-linking and streptavidin conjugation of oligomeric phosphine with carboxylic acid, and the protocol for polymer-quantum dot sticks (PDF). This material is available free of charge via the Internet at http://pubs.acs.org.

References

(1) (a) Bruchez, J. M.; Moronne, M.; Gin, P.; Weiss, S.; Alivisatos, A. P. *Science* **1998**, *281*, 2013. (b) Chan, W. C. W.; Nie, S. *Science* **1998**, *281*, 2016. (c) Mattoussi, H; Mauro, J. M.; Goldman, E. R.; Anderson, G. P.; Sundar, V. C.; Mikulec, F. V.; Bawendi, M. G. *J. Am. Chem. Soc.* **2000**, *122*, 12142. (d) Wang, Y. A.; Li, J. J.; Chen, H. Y.; Peng, X. G. *J. Am. Chem. Soc.* **2002**, *124*, 2293.

(2) (a) Guo, W. H.; Li, J. J.; Wang, Y. A.; Peng, X. G. *J. Am. Chem. Soc.* **2003**, *125*, 3901. (b) Goldman, E. R.; Balighian, E. D.; Mattoussi, H.; Kuno, M. K.; Mauro, J. M.; Tran, P. T.; Anderson, G. P. *J. Am. Chem. Soc.* **2002**, *124*, 6378. (c) Gerion, D.; Pinaud, F.; Williams, S. C.; Parak, W. J.; Zanchet, D.; Weiss, S.; Alivisatos, A. P. *J. Phys. Chem. B* **2001**, *105*, 8861.

(3) (a) Wu, X. Y.; Liu, H. J.; Liu, J. Q.; Haley, K. N.; Treadway, J. A.; Larson, J. P.; Ge, N. F.; Peale, F.; Bruchez, M. P. *Nat. Biotechnol.* **2003**, *21*, 452. (b) Dubertret, B.; Skourides, P.; Norris, D. J.; Noireaux, V.; Brivanlou, A. H.; Libchaber, A. *Science* **2002**, *298*, 1759.

(4) Tran, P. T.; Goldman, E. R.; Anderson, G. P.; Mauro, J. M.; Mattoussi, H. *Phys. Status Solid B* **2002**, *229*, 427.

(5) Ulrich, H. *Chemistry and technology of isocyanates*; J. Wiley & Sons: Chichester, New York, 1996.

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