Functional Si and CdSe Quantum Dots: Synthesis, Conjugate Formation, and Photoluminescence Quenching by Surface Interactions

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Surface-bound organic ligands profoundly influence the properties of nanoparticles. Ligands largely dictate the solution miscibility and solid-state packing of nanoparticles, while making them hydrophobic, hydrophilic, amphiphilic, and compatible (or incompatible) with a given host matrix. Congruent with the optoelectronic properties of some types of nanoparticles, such as semiconductor quantum dots of various compositions,[1,2] surface-bound organic ligands can also interact electronically with nanoparticles.[3] For example, energy and charge transfer events between conjugated polymers and nanoparticles open routes to novel light emitting devices,[4] sensors,[5] and photovoltaic materials[6,7] that represent emerging applications of nanotechnology. Quantum dots are advantageous in this context, providing broad UV−visible spectral coverage, yet exhibiting narrow photoluminescence emission profiles that can be tuned (based on size) to tailor their electronic interactions with surface-bound ligands and/or a surrounding host matrix. While fluorescent cadmium selenide quantum dots (CdSe QDs) are effective energy transfer donors and electron acceptors when used in conjunction with various dye molecules and polymers, examples of CdSe QDs interacting with other luminescent semiconductor nanoparticles are sparse, due largely to the absence of interparticle interactions required to hold the particles in close proximity. A few studies have been devoted to quantum dots as light sensitizers in electronically coupled assemblies, such as the elegant report by Klimov and co-workers on hole transfer in Ru-polypyridine/CdSe complexes following visible light excitation.[8]

ABSTRACT Silicon quantum dots (QDs) were prepared with a corona of di-*n*-octyl phosphine oxides, by performing hydrosilylation chemistry on the surface of hydrogen-terminated Si QDs. These novel Si QDs proved well-suited to serve as "ligands" for other semiconductor QDs, such as CdSe, by interaction of the phosphine oxide corona with the CdSe surface. A pronounced photoluminescence quenching of CdSe quantum dots was observed upon introduction of the phosphine oxide functionalized Si QDs to a CdSe QD solution. Surface functionalization of the Si QDs proved critically important to observing these effects, as conventional (alkane-covered) Si QD samples gave no evidence of electronic interactions with TOPO-covered CdSe. In a comparative system, phosphine oxide terminated oligo(phenylene vinylene) molecules acting as CdSe QD ligands provide a similar fluorescence quenching, with exciton decay kinetics supporting the formation of an electronically interacting hybrid materials system.

**KEYWORDS:** quantum dots · luminescence · hole transfer · nanostructures

Silicon quantum dots (Si QDs) are quantum-confined photoluminescent structures which absorb UV light and exhibit blue emission. The quantum confinement increases the probability of radiative recombination through direct band gap transitions and reduces phonon-assisted indirect band gap transitions.[9] Recent studies indicate a higher photovoltaic efficiency of nanoparticulate Si relative to crystalline silicon[10] and the ability of Si QDs to store electrons,[11] making them promising components of photovoltaic devices. Their lack of absorption in the visible region could be overcome by surface functionalization with visible light absorbing dyes or quantum dots. State-of-the-art syntheses of Si QDs that exhibit strong quantum confinement involve the solution-phase reduction of silicon salts.[12] For example, reduction of $SiCl_4$, as described by Tilley and co-workers, generates hydrogen-terminated Si QDs which are amenable to surface functionalization by hydrosilylation reactions of alkene-terminated organic molecules.

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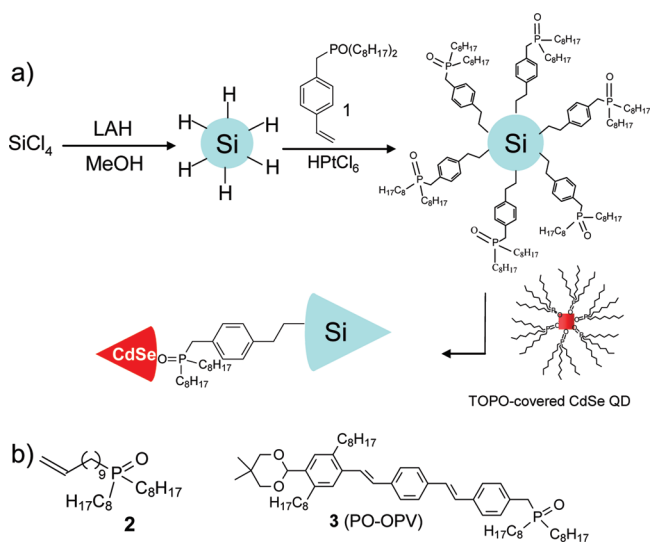
Figure 1. (a) Hydrosilylation of Si QDs provides a corona of phosphine oxides that serve as ligands for CdSe QDs; (b) chemical structures of ligands 2 and 3, designed for surface modification of Si and CdSe QD surfaces, respectively.

Here we describe a novel surface functionalization of one semiconductor nanoparticle composition that renders it suitable as a "ligand" for a different semiconductor nanoparticle composition. Specifically, we combine surface-tailored Si QDs with CdSe QDs, using their photoluminescent properties to reveal inter-nanoparticle interactions in solution. The disparate nature of the surface binding modes for these systems (*i.e.*, covalent binding to Si and noncovalent coordination to CdSe) enables the generation of nanoparticle conjugates, in which close contact between the different particles mirrors the way in which organic ligands passivate nanoparticle surfaces.

The covalent nature of ligand binding to the Si QD surface is atypical among semiconductor nanoparticles but useful for providing robust routes to internanoparticle conjugation. Figure 1 shows the preparation of Si QDs by reduction of silicon salts in solution, as described by Tilley and co-workers.[13] Subsequent surface hydrosilylation by Karstedt's coupling,[14] using di-*n*-octylphosphine oxide functionalized vinyl benzene (compound 1[15]), gave Si QDs with the desired surface phosphine oxide functionality. While this synthesis generally gave particles in the 2−3 nm diameter range, with blue solution photoluminescence ($\lambda_{max} \sim$ 360 nm), the presence of a minor distribution of larger particles ($\sim$8 nm diameter) proved convenient for transmission electron microscopy (TEM) imaging of the nanoparticle conjugate assemblies (shown later). The hydrosilylation chemistry fixes ligand 1 to the Si NP surface, providing a corona of phosphine oxides, a functional group well-known for surface passivation of CdSe QDs. FTIR spectroscopy of these 1-covered Si NPs (Figure S1 in Supporting Information) revealed signals characteristic of the ligands (aromatic C−H stretching at 2926 cm^{-1} and P═O stretching at 1134 cm^{-1}), while chloroform solu-

tions of these particles absorbed broadly (onset at 350 nm) and showed the expected photoluminescence emission at $\sim$360 nm (Figure S2). Longer wavelength emission, indicative of Si QD surface oxide passivation, was not seen.[9] This synthesis provides, for the first time, functional Si QDs that are predisposed as ligands for other nanoparticles, such as CdSe QDs as described below.

When Si QDs functionalized with *n*-hexyl chains, prepared by known methods,[16] were mixed in solution ($\sim$10 mM) with tri-*n*-octylphosphine oxide (TOPO)-covered CdSe QDs (0.1 μM based on their extinction coefficient[17]), the solution photoluminescence was dominated by CdSe. This measurement was done by exciting a chloroform solution of the mixture at 550 nm, outside the absorption range of the Si QDs. When the sample was excited at 300 nm (*i.e.*, exciting both CdSe and Si), the PL emission spectrum was still dominated by the CdSe QDs due to their much greater UV absorbance. However, addition of Si QDs ($\sim$1 mM), functionalized with a corona of phosphine oxide 1, to a solution of TOPO-covered CdSe QDs (0.1 μM) led to a striking and complete quenching of the QD fluorescence (Figure 2). Moreover, systematically increasing the Si QD concentration (calculated based on the SiCl$_4$ precursor in the QD preparation) gave a gradual, then complete, quenching of the CdSe QD emission. Figure 2 also shows that a plot of fluorescence quenching *versus* concentration is nonlinear, deviating from the linear behavior observed for classically interacting donor−acceptor small molecules. We expect that this behavior arises from the mixed assembly conjugates of CdSe and Si QDs produced through the multivalent interactions that can arise in these assemblies.

In general, the type of fluorescence quenching observed when combining these functional luminescent nanoparticles in solution would be attributed to either Förster resonance energy transfer (FRET) or a charge transfer process. As FRET occurring from the lower band gap CdSe QDs to the wider band gap Si QDs is not feasible, a charge transfer mechanism from CdSe to Si is anticipated. The higher band energy of Si NPs (E_{HOMO} −5.5 eV and E_{LUMO} −2.7 eV for a 4 nm diameter particle)[18] supports a hole transfer mechanism from the CdSe QDs to the Si NPs. The kinetics of the opposite process, involving electron transfer from CdSe QDs to TiO$_2$ NPs, was reported recently, with the charge transfer kinetics found to depend on the diameter (band gap) of the CdSe QDs.[19]

The Si−CdSe nanoparticle conjugates produced in solution were imaged by transmission electron microscopy (TEM) following evaporation of the nanoparticle solution onto a carbon-coated grid. The TEM characterization shown in Figure 3 was performed on a sample which contained a population of larger ($\sim$8 nm diameter) Si QDs, in order to differentiate them from the smaller ($\sim$4 nm diameter) CdSe QDs. TEM shows nu-

merous structures in which the smaller CdSe QDs are in close proximity to the larger Si QDs, held as such by the phosphine oxide functionalization of the Si QD surface. Such nanoconjugate structures are related, though not as finely organized, to the elegant structures reported by Mirkin and Lestinger[20] in which multiple smaller gold nanoparticles assemble around a larger gold nanoparticle, driven by DNA hybridization to bridge the ligands between the smaller and larger particles. The nanoparticle conjugates described here are distinct in that they consist of two different nanoparticle compositions, both fluorescent semiconductor QDs, and use simple organic ligands to connect the assemblies, exploiting the covalent connection of the ligands to the Si QDs, and the noncovalent ligand−metal interactions of the phosphine oxides with CdSe QDs. The phosphine oxides hold the Si QDs in close proximity to CdSe, enabling charge transfer in solution that leads to the observed fluorescence quenching.

The experiments described above used CdSe quantum dots with a TOPO ligand periphery, providing facile access to the semiconductor nanoparticle surface by ligand exchange. However, CdSe and other QDs are often covered with a wider band gap semiconductor, such as ZnS, which markedly increases their photoluminescence intensity.[21] We found that the presence of a ZnS shell around the CdSe QDs changes the behavior of the components in solution. For example, ZnS-covered CdSe core−shell QDs were prepared by reported procedures,[21] and the solution PL emission was measured with and without the presence of 1-covered Si QDs. As shown in Figure 4, the PL emission from the core−shell nanoparticles was not quenched by addition of 1-covered Si QDs, indicating that the presence of the ZnS shell acts as a barrier to charge transfer, thus preserving the CdSe fluorescence emission.

It is important to note that the fluorescence of TOPO-covered CdSe QDs is not quenched upon addition of pure phosphine oxide 1 (i.e., ligand only), ruling out any appreciable role of ligand 1 in the fluorescence quenching seen when using 1-covered Si QDs. In an attempt to probe what, if any, role is inherent to the composition of the bridging ligand on the quenching associated with nanoparticle conjugation, an alkene-functionalized aliphatic phosphine oxide (shown as compound 2 in Figure 1) was prepared and used to functionalize Si QDs. Addition of a 0.1 mM solution of 2-covered Si QDs to the CdSe QDs also led to complete quenching of the CdSe PL emission. Interestingly, an approximately 10-fold lower concentration of 2-covered Si QDs (0.1 mM) completely quenched the CdSe QD fluorescence (0.1 μM), compared to the 1-covered Si QDs (1.0 mM) measured under same conditions. We speculate that a higher quenching efficiency from the 2-covered silicon QDs might arise from a denser ligand coverage in the alkyl case relative to
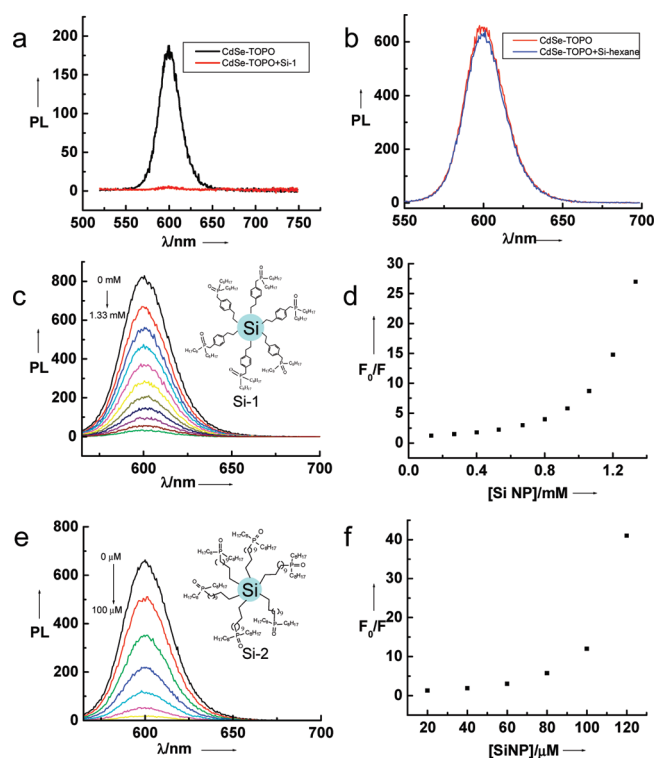
Figure 2. (a) Quenching of CdSe fluorescence emission by addition of 1-functionalized Si QDs. The concentration of Si QDs is 1 mM; (b) photoluminescence emission spectrum of CdSe QDs in the presence of 10 mM hexyl-covered Si QDs; (c) fluorescence changes of CdSe QDs in the presence of varying concentration of 1-functionalized Si QDs; (d) plot of the ratio of fluorescence (before and after addition of Si QDs functionalized with ligand 1) vs Si QD concentration; (e) fluorescence changes of CdSe QDs in the presence of varying concentrations of Si QDs functionalized with 2; (f) plot of the ratio of the fluorescence (before and after the addition of 2-functionalized Si QDs) vs the concentration of Si NPs.

the aryl case (for steric reasons) that would allow more efficient conjugation of these particles to the CdSe QDs.

It is interesting to note that fluorescence quenching seen for CdSe QD solutions by surface functionalization with Si QDs was also seen when using conjugated polymers as ligands, which have higher HOMO levels and more narrow band gaps than the insulating ligands 1 and 2. Specifically, the fluorescence emission of TOPO-covered CdSe QDs in solution was quenched gradually by the successive addition of phosphine oxide functionalized oligo(phenylene vinylene) 3 (PO-OPV).[22] The spectral properties of PO-OPV 3 are dis-
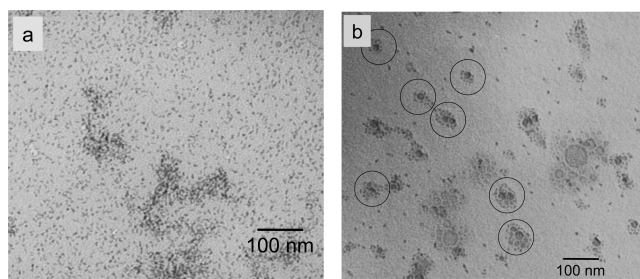
Figure 3. TEM images of CdSe QDs: (a) TOPO-covered CdSe; (b) CdSe QDs + 1-functionalized Si NPs. Some assemblies are circled for clairty.
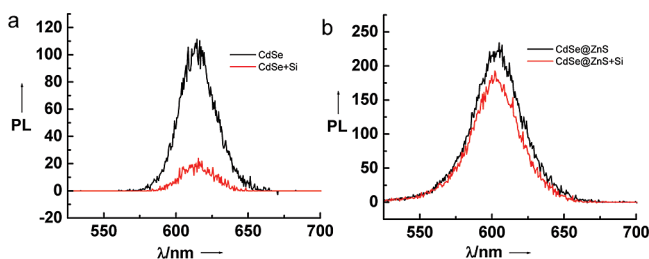
Figure 4. (a) Comparison of fluorescence changes of (a) CdSe and (b) CdSe@ZnS core–shell nanoparticles after the addition of phosphine oxide functionalized Si NPs (1 mM in chloroform).

tinct and well-separated from CdSe QDs, allowing a selective excitation of either the QDs or the surface-bound OPV ligand. Excitation at 550 nm selects for 6 nm diameter CdSe QDs and the QD solution fluorescence diminishes upon continued addition of PO-OPV. Figure 5 compares the fluorescence of CdSe QDs at different solution concentrations of PO-OPV. This gradual and substantial fluorescence quenching indicates that the PO-OPV molecules added to the CdSe solution displace surface-bound TOPO ligands, enabling dissociation of excitons, generated on the QDs, into the ligand periphery, resulting in diminished fluorescence. The exciton decay kinetics of these CdSe QDs were probed by time-correlated single photon counting (TCSPC) measurements in the presence of PO-OPV, by exciting a chloroform solution of CdSe (0.1 μM) at 532 nm and collecting the emission at 600 nm (also shown in Figure
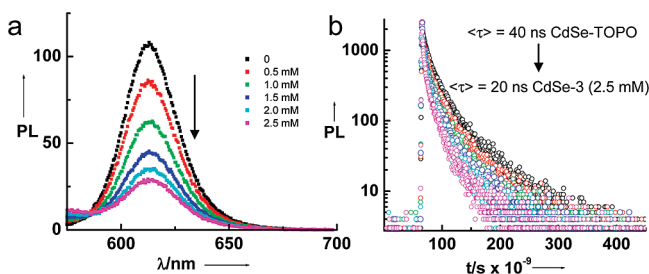

Figure 5. (a) Fluorescence spectra of CdSe QDs in the presence of different concentrations (0 to 2.5 mM) of PO-OPV; (b) fluorescence−time profile of CdSe QDs in the presence of PO-OPV.

5). The multiexponential decay seen for the CdSe emission showed an average lifetime of ~40 ns in the absence of PO-OPV,[23,24] while the presence of **3** (2.5 mM PO-OPV solution in chloroform) decreased the fluorescence lifetime of the CdSe QDs to ~20 ns. QD fluorescence quenching by PO-OPV can be explained by hole transfer from the QDs to the surface-bound OPV ligands, set up by the relative electronegativities of the two components and the higher HOMO energy of OPV (−5 eV) compared to the valence band of CdSe QDs (−6.2 eV).[25] Lower homologue ligands such as compound **1** do not influence the QD fluorescence, as the low lying HOMO precludes hole transfer. The importance of quantum dot surface accessibility in these systems cannot be overstated—for both the Si−CdSe and OPV−CdSe conjugates, the relatively labile (noncovalent) interactions of the initially present TOPO ligands enables a ligand exchange that, in turn, affects the fluorescence intensity. Note that when we performed similar experiments starting from PEG-thiol-covered CdSe QD solutions (the thiols being more strongly adsorbed to the CdSe surface relative to phosphine oxides) fluorescence quenching was not observed nor were nanoparticle conjugates by TEM. These contrasting results arise from thiol ligands providing more effective shielding of the QD surface from incoming ligands.

In summary, we have shown a pronounced photoluminescence quenching of CdSe quantum dots when combined in solution with phosphine oxide terminated Si QDs, as well as similarly functionalized OPV ligands. Surface functionalization of the Si QDs proved key to this process, as conventional (alkane-covered) Si QD samples give no evidence of such optoelectronic interactions with CdSe QDs. Going forward, the ability to prepare and organize functionalized semiconductor nanoparticles into electronically interacting nanoscale systems presents new opportunities in self-directed self-assembly that might be exploited in sensors, photovoltaics, displays, and other applications.

METHODS

Preparation of Ligand-Functionalized Si QDs. Inside an inert atmosphere glovebox, tetra-*n*-octylammonium bromide (1.5 g) was added to toluene (100 mL) and stirred for 15 min. SiCl$_4$ (100 μL) was added, and the solution was stirred for 1 h. A solution of lithium aluminum hydride in THF (1M, 2 mL) was added slowly, and the mixture was stirred for 3 h. Si−H-terminated Si QDs were isolated following addition of methanol (20 mL). Chloroplatinic acid hexahydrate (40 mL, 0.05 M in isopropanol) and phosphine oxide functionalized ligand (0.8 mmol) were added, and the mixture was stirred for 3 h. After the hydrosilylation reaction, the phosphine oxide functionalized Si NPs were isolated by extraction into hexane.

Optical and Spectroscopic Measurements. UV/visible spectra were recorded on a Perkin-Elmer Lambda 25 spectrophotometer and photoluminescence measurements on a Perkin-Elmer LS55B. Low-resolution transmission electron microscopy (TEM) was performed on a JEOL 200CX microscope. TEM grids were purchased from Ted

Pella, Inc. and consisted of 3−4 nm amorphous carbon film supported on a 400-mesh copper grid. Emission lifetimes were measured using Horiba Jobin Yvon single photon counting system, and the fluorescence decay data were analyzed further using the IBH software library.

Supporting Information Available: Experimental procedures for the synthesis of **1**-covered Si QDs, CdSe−ZnS core−shell

QDs, and alkene **2**, as well as FT-IR, photoluminescence, and TEM micrograph of the functional quantum dots. This material is available free of charge *via* the Internet at http://pubs.acs.org.

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