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Controlled Assembly of Quantum Dot Heterostructures

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14. ABSTRACT
The primary goals of this project were to learn how to control nanocrystal surface chemistry and to selectively functionalize semiconductor nanocrystals. This research was motivated by opportunities to incorporate semiconductor nanocrystals into various devices such as solar cells, solid-state lighting, photodetectors, field-effect transistors, and data storage systems. Unfortunately, current approaches to construct macroscale assemblies from nanocrystal building blocks produce materials with poor transport properties and ill-defined structure. In response, our research group has sought a long-term goal of developing new strategies for coupling colloidal nanocrystal building blocks through molecular linkers that can facilitate the efficient transport of charge carriers across the particle-particle interface and provide long-range order to the resulting assembly.

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Abstract
The primary goals of this project were to learn how *to control nanocrystal surface chemistry* and *to selectively functionalize semiconductor nanocrystals*. This research was motivated by opportunities to incorporate semiconductor nanocrystals into various devices such as solar cells, solid-state lighting, photodetectors, field-effect transistors, and data storage systems. Unfortunately, current approaches to construct macroscale assemblies from nanocrystal building blocks produce materials with poor transport properties and ill-defined structure. In response, our research group has sought a long-term goal of developing new strategies for coupling colloidal nanocrystal building blocks through molecular linkers that can facilitate the efficient transport of charge carriers across the particle-particle interface and provide long-range order to the resulting assembly. A critical first step in achieving this goal is to gain control over nanocrystal surface chemistry in order to selectively functionalize nanocrystals with molecular linker components, and this represents the focus of this AFOSR Young Investigator Award.

Towards this goal, this research project: 1) Deployed tools traditionally employed by molecular chemists to learn how to control and selectively functionalize semiconductor nanocrystal surfaces, 2) Investigated how the surfaces of semiconductor nanocrystals change upon the addition of charge carriers, and 3) Exploited controlled ligand exchange reactions to map out the native surface composition of semiconductor nanocrystals. Collectively, these studies have provided an enhanced molecular-level picture of the nanocrystal surface and identified opportunities to control the surface structure through post-synthetic modifications.

Project Summary
Nanocrystals are attractive for applications including solar cells, solid-state lighting, photodetectors, field-effect transistors and data storage systems because they are inexpensive, solution processable and have tunable electronic and optical properties. However, current approaches to construct macroscale assemblies from nanocrystal building blocks produce materials with poor transport properties and ill-defined structure. In response, our research group has sought a long-term goal of developing new strategies for coupling colloidal nanocrystal building blocks through molecular linkers that can facilitate the efficient transport of charge carriers across the particle-particle interface and provide long-range order to the resulting assembly. To achieve this goal, it is critical to gain control over nanocrystal surface chemistry in order to selectively functionalize nanocrystals with molecular linker components

Efforts during *Year 1* this project focused on quantifying ligand exchange reactions at CdSe and PbS nanocrystal surfaces using custom designed ligands that allowed free and surface-bound populations to be monitored via ^{1}H NMR. In *Year 2* of this project, we continued and completed work examining ligand exchange reactions on PbS nanocrystals and began to investigate how the surfaces of semiconductor nanocrystals change upon the addition of charge carriers. In *Years 3-4 (no-cost extension)*, we exploited the insight gained into controlled ligand exchange reactions to systematically map out native surface composition of PbS nanocrystals and to further our investigations of nanocrystal surface changes upon addition of charge carriers. These studies have addressed challenges associated with the selective surface modification necessary to access discrete heterostructures.

Controlling Ligand Exchange Reactions

To determine how to modify the surfaces of nanocrystals in a controlled, selective manner, we carried out systematic studies to quantify ligand displacement reactions. We quantified carboxylate ligand exchange

reactions on CdSe and PbS nanocrystals by exploiting ligands with unique NMR handles that can inform relative bound and free populations (Chart 1). We learned these exchange reactions occur with a 1:1 stoichiometry when both the native and exchange ligand binding groups are carboxylates (UDA and OA, Chart 1); the reactions are under equilibrium, and a K_{eq} can be determined (Figure 1). These studies provide key insight to the dynamic nature of nanocrystal surfaces.

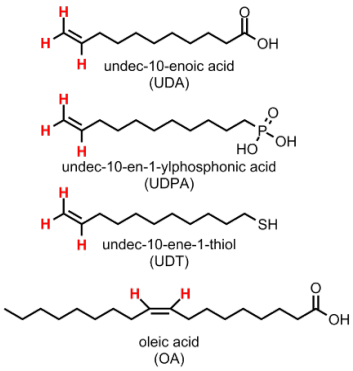

Chart 1. The alkenyl protons (red) of both the native oleate ligands and the exchange ligands (UDA, UDPA and UDT) provide spectroscopic handles to quantify both the free and surface-bound forms of these ligands.

The reactivity of carboxylate-capped CdSe nanocrystals with phosphonic acid (UDPA) and thiol-terminated (UDT) ligands was also studied. These studies revealed that phosphonic acid-terminated ligands irreversibly displace native oleates in a 1:1 ratio, while thiols both coordinate as L-type ligands to open coordination sites and undergo irreversible X-type exchange reactions with oleates (coordinating as thiolates). These studies provided broad understanding of how to control the integration of functionalized ligands and nanocrystals and how to intentionally remove or add specific ligands in order to control nanocrystal surface composition.

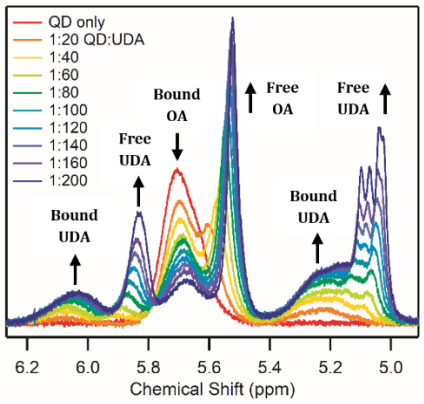

Figure 1. ^{1}H NMR of 50 μM PbS QDs (3.05 nm) titrated with undec-10-enoic acid (UDA) in benzene-d_6.

Unlike CdSe, where the thiol-terminated ligand undec-10-ene thiol (UDT) was found to irreversibly displace oleate, we observe that thiol-terminated ligands are in exchange with oleic acid for PbS. However, the exchange ratio is non-stoichiometric and changes over the course of the titration, suggesting that 1) thiols bind open coordination sites, 2) thiols can engage in X-type exchange reactions with native oleates, and 3), thiols can help promote the displacement of Z-type Pb(oleate)$_2$ from the surface of PbS. To more deeply

understand these surface reactions, we have designed and validated a method to map out the native surface population and quantify these three parallel reaction mechanisms. Specifically, we quantify the surface coverage of the PbS nanocrystals via ^{1}H NMR, react the nanocrystals with either UDT or tetramethylethylenediamine (TMEDA), then isolate the reacted nanoparticles. The surface chemistry of the isolated nanocyrstals post exchange is quantified by ^{1}H NMR, and the supernatant is examined via ICP-MS to quantify the loss of Z-type Pb(oleate)$_2$ ligands. TMEDA is known to help displace Z-type ligands without also binding to the nanocrystal surface and helps to deconvolute the multiple reactive modes of UDT. These studies are ongoing.

Changes in nanocrystal surfaces upon the introduction of charge carriers

Quantum dot surfaces are redox active and are known to influence the electronic properties of nanocrystals, yet the molecular-level changes in surface chemistry that occur upon addition of charge are not well understood. Where do charge carriers localize when added to nanocrystals and what structural changes occur upon charging? To answer this question, we have explored how the addition of charge carriers perturbs the surface composition of semiconductor nanocrystals.

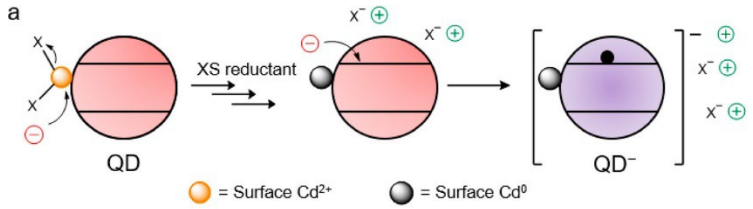

Figure 2. Electrons added to CdSe quantum dot (QD) with a chemical reductant initially localize on Cd^{2+} surface states to form Cd^0 moieties before reducing the conduction band. Reduction of Cd^{2+} is accompanied by the loss of anionic oleate ligands (X^-).

These studies showed that addition of charge carriers (electrons) via outer sphere reductants to CdSe and PbS nanocrystals (remote chemical doping) is accompanied by changes to the surface coordination chemistry when these charge carriers localize in surface trap states (Figure 2).[43] For example, we found that a subpopulation of electrons added to CdSe and PbS nanocrystals localize in cation-based surface states (Cd^{2+} and Pb^{2+}) and promote loss of native oleate ligands for charge balance as Cd^0 and Pb^0 is formed (Figure 2). The liberation of oleate from the surface provides a direct handle for quantifying electrons in these specific trap states via ^{1}H NMR spectroscopy (Figure 3). Notably, the Cd^0 species formed has recently been invoked as a critical site of reactivity in nanocrystal-catalyzed substrate reduction reactions.

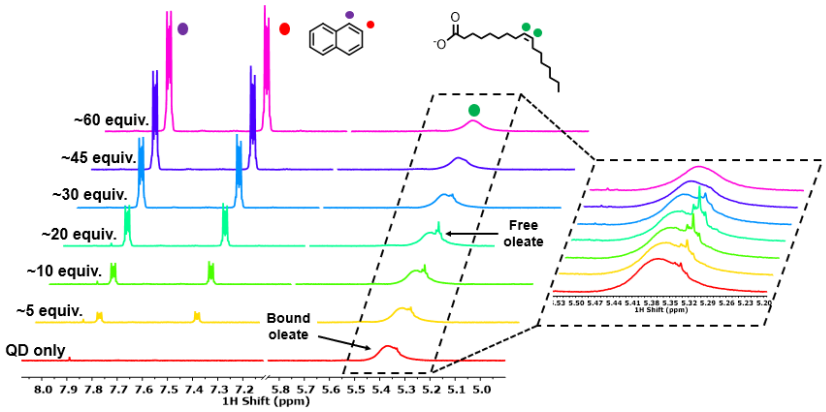

Figure 3. ^{1}H NMR spectra of oleate-capped CdSe nanocrystals upon titration of sodium napthalenide, a strong chemical reductant. Over the course the titration, a signal for free oleate grows in, indicating oleate is liberated from the nanocrystal surface upon reduction.

Based on these findings, more recent work has focused on how changes to the nanocrystal surface are coupled to electronic changes in the material both by loss of passivating ligands and by filling of electron-deficient trap sites. These studies expand our understanding of the effects of varying nanocrystal size and reductant strength on the surface reduction phenomenon in PbS nanocrystals. Complementary techniques allow us to comprehensively probe changes in surface chemistry in these systems: NMR distinguishes between bound and free (and liberated) ligands, Fourier transform infrared (FTIR) informs us about the binding modes of the ligands, X-ray photoelectron (XPS) spectroscopies XPS to report on X-type ligand loss by confirming nanocrystal stoichiometry doesn't change, and UV-Vis-NIR absorption spectroscopy detects changes in nanocrystal size, conduction band filling, or wavefunction overlap into the ligand shell. We have also employed a chemical method based on phosphine oxidation to quantify the presence of disulfides on the PbS surface, another potential trap state for charge carriers. By comparing across nanocrystal size and adding a mild reductant (cobaltocene), for example, we are able to vary both the driving force for band edge electron injection as well as the available surface area for reduction (Figure 4). Importantly, these studies have revealed that even nanocrystals anticipated to have unfavorable band edge offsets with the redox potential of the reductants used still undergo electron-promoted X-type ligand loss, demonstrating the important reactivity of redox active surface trap states and suggesting the direct reduction of surface Pb^{2+} cations. Insight to the changes in electronic structure and surface chemistry induced by the addition of charge carriers broadly impact our understanding of energy and electron flow through arrays of nanocrystals. Our ability to probe — and interpret — the molecular changes that occur at nanocrystal surfaces upon carrier trapping will enable us to evaluate the role of these states in electron transfer pathways at nanocrystal interfaces.

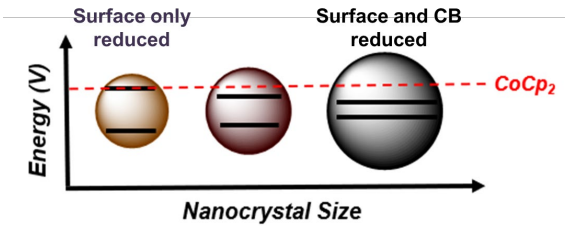

Figure 4. Variations in the nanocrystal size allow us to tune the relative driving force for conduction band reduction (which is nanocrystal size-dependent) without impacting driving force for reduction of surface states (which are predicted to be size-independent).

Mapping the Surface Topology of PbS Nanocrystals

The shapes of nanocrystals inform us about the different crystal facets, along with the edges between different facets, present in a nanomaterial. These details are critical for establishing a comprehensive and molecular-level picture of nanocrystal surfaces. PbS nanocrystals have been predicted to exhibit size-dependent shapes, with smaller nanocrystals having an octahedral shape and larger nanocrystals exhibiting a cuboctahedral morphology (Figure 5). Experimental evidence for size-dependent topology has been inferred from comparison of X-ray photoelectron spectroscopic measurements of Pb:S ratios with ideal morphologies as well as from Wulff ratios of nanocrystals extracted from high-resolution transmission electron microscopy images.

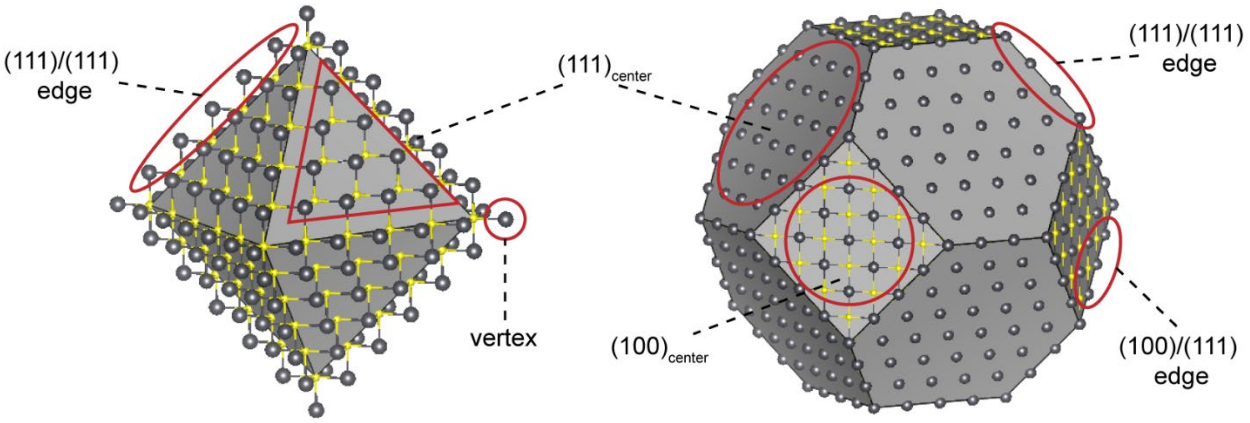

Figure 5. Octahedral model ca. 3 nm in diameter (left) and truncated octahedral model ca. 4 nm in diameter (right). Pb ions are gray spheres and S ions are yellow spheres; (111) lattice planes are drawn to visualize the coordination of surface Pb ions and ligands are omitted for clarity.

Eager to gain more direct evidence for these size-dependent topologies, we exploited chemical reactivity at the nanocrystal surface as a tool to probe surface composition and effectively “image” the nanocrystal shape as a function of size. Specifically, we reacted N,N,N′,N′-tetramethylethane-1,2-diamine (TMEDA) into oleate-capped PbS nanocrystals. TMEDA liberates (κ_2-TMEDA)Pb(OA)$_2$ (OA = oleate), which is readily distinguished from bound oleate via nuclear magnetic resonance (NMR) spectroscopy (see above). Separately, we confirmed the stoichiometry of these liberated fragments by combining oleate integrations from ^{1}H NMR spectra with Pb quantitation from inductively coupled plasma mass spectrometry. By monitoring the displacement of (κ_2-TMEDA)Pb(OA) as a function of TMEDA added, we generated displacement isotherms that revealed a distribution of binding sites for these Z-type ligands, each with its own equilibrium constant (Figure 6). The displacement isotherms were distinct for small and large PbS particles, and correlated with size-specific models of octahedron and cuboctahedron, respectively (Figure 7). These distinct topological differences between small and large nanocrystals provides explicit evidence for truncation at octahedral vertices, forming (100) facets as the nanocrystal diameter increases (Figure 5). Further, this work provides the roadmap needed to selectively control the relative subpopulations of surface-based trap states, providing a key foundation for to examine the role of specific trap states in carrier trapping and charge transfer dynamics.

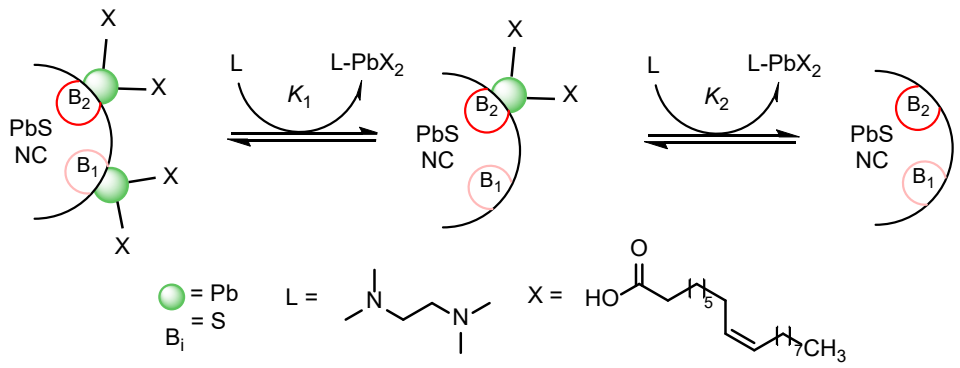

Figure 6. Equilibrium processes describing L-type promoted $Pb(OA)_2$ displacement from distinct Lewis basic sites on the PbS NC surface. PbX_2 complexes bound to the surface are depicted to show the stoichiometry of the dissociated complex, but the oleates could bridge two Pb ions when bound to the nanocrystal.

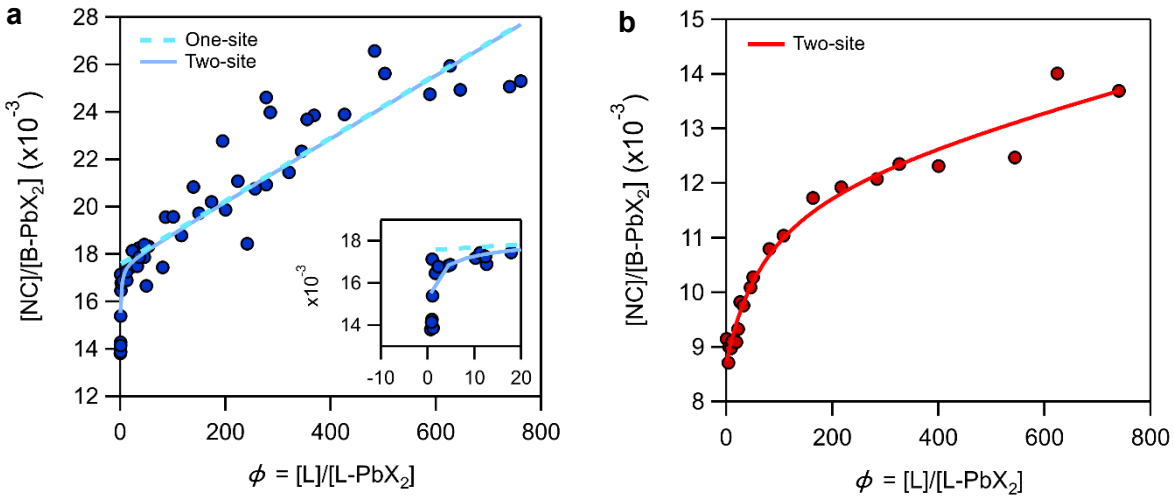

Figure 7. (a) TMEDA additions to 2.8 nm PbS NCs fit to one-site isotherm (dashed line) and a two-site isotherm (solid line). Inset is zoomed in on low values of φ. (b) TMEDA additions to 3.9 nm PbS NCs fit a two-site isotherm.

Publications to-date on this project (3 additional research and 1 perspective article expected to cite this award):

Kessler, Melody L.; Dempsey, J. L. Mapping the Topology of PbS Nanocrystals through Displacement Isotherms of Surface-Bound Metal Oleate Complexes. Chem. Mater. **2020**, *32*, 2561–2571.

Hartley, C. L.; Dempsey, J. L. Electron-Promoted X-Type Ligand Displacement at CdSe Quantum Dot Surfaces. *Nano Letters* **2019**, *19*, 1151–1157.

Kessler, M. L.; Starr, H, E.; Knauf, R. R.; Rountree, K. J.; Dempsey, J. L. Exchange Equilibria of Carboxylate-Terminated Ligands at PbS Nanocrystal Surfaces. *Physical Chemistry Chemical Physics* **2018***, 20,* 23649–23655.

Knauf, R. R.; Lennox, C. J.; Dempsey, J. L. Quantifying Ligand Exchange Reactions at CdSe Nanocrystal Surfaces. *Chemistry of Materials* **2016**, *28*, 4762-4770 (published July 2016, acknowledges 1 year seed grant FA-9550-15-1-0227, which overlapped with this grant cycle).