Final Technical Report for: **Chemical Control of Charge Trapping and Charge Transfer Processes at the Organic-Inorganic Interface within Quantum Dot-Organic Complexes**

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Executive Summary: Within the research program funded through the Early Career Research Award we designed complexes of colloidal semiconductor quantum dots (QDs) and organic molecules in which the interfacial chemistry controls the electronic structure and dynamics of the excitonic state of the QD. The program included two main projects: **(1)** investigation of the mechanisms by which organic surfactants control the quantum confinement of excitonic charge carriers, and **(2)** development of models for electron transfer between QDs and adsorbed molecules as a function of interfacial chemistry. This project was extremely successful in that our achievements in those two areas addressed the great majority of questions we outlined in the original proposal *and* answered questions I did not think to ask in that original proposal. Our work led to the discovery of "exciton delocalizing ligands", which change the electronic structure of colloidal semiconductor nanocrystals by altering, with small synthetic modifications to their surfaces, their most defining characteristic – the quantum confinement of their excited states. It also led to detailed, quantitative descriptions of how the surface chemistry of a QD dictates, thermodynamically and kinetically, the probability of exchange of electrons between the QD and a small molecule. We used two of the three major techniques in the proposal (transient photoluminescence and transient absorption). Electrogenerated chemiluminescence was also proposed, but was too technically difficult with these systems to be useful. Instead, NMR spectroscopy emerged as a major analytical tool in our studies. With the fundamental advancements we made with this project, we believe that we can design QDs to be the next great class of visible-light photocatalysts.

Below, I highlight the accomplishments from the two general areas of research funded by this award.

Project 1. Quantum Dots and Molecules in the "Strong Coupling" Regime. This project explores how organic molecules – in particular phenyldithiocarbamates (PTC), **Fig. 1** and thiophenolates – change the confinement potential for excitonic carriers (electrons and holes) within QDs, and thereby change the energy, dynamics, and pathway for decay of the exciton and provide a means of coupling of the exciton to the surrounding medium. This demonstration of ligand-induced delocalization of charge carriers is a first step toward eliminating current-limiting resistive interfaces at organic/inorganic junctions within solid-state hybrid devices. Facilitating electronic coupling across heterogeneous interfaces is especially important for nanostructured devices, which comprise a high density of such interfaces.

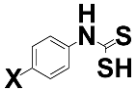

Fig.1 Chemical structure of a *para*-substituted phenyldithiocarbamate (PTC).

We first demonstrated unprecedented bathochromic shifts (up to 970 meV) of the optical band gaps of CdS, CdSe, and PbS QDs upon adsorption of PTC, and the use of PTC to map the quantum confinement of specific charge carriers within the QDs as a function of their radius. For a given QD material and physical radius, R, the magnitude of the increase in apparent excitonic radius (ΔR) upon delocalization by PTC directly reflects the degree of quantum confinement of

one or both charge carriers. The plots of ΔR vs R for CdSe and CdS show that exciton delocalization by PTC occurs specifically through the excitonic hole. Further-more, the plot for CdSe, which spans a range of R over multiple confinement regimes for the hole, identifies the radius (R∼1.9 nm) at which the hole transitions between regimes of strong and intermediate confinement. We then described a method to control the quantum confinement, and therefore the energy, of excitonic holes in CdSe QDs through *para*-substitutions of the phenyl ring of PTC with electron-donating or -withdrawing groups. These substitutions control hole delocalization in the QDs through the energetic alignment of the highest occupied orbitals of PTC with the highest density-of-states region of the CdSe valence band, to which PTC couples selectively. We also demonstrated the enhancement of the quantum yield of photoluminescence (PL) of CdSe QDs upon the adsorption phenyldithiocarbamate. Increasing the apparent excitonic radius by only 10% increases the value of the radiative rate constant by a factor of 1.8 and the PL quantum yield by a factor of 2.4. Ligand exchange therefore simultaneously perturbs the confinement energy of charge carriers and enhances the probability of band-edge transitions. We also measured the dependence of ΔR on the surface coverage of hexyl-substituted PTC (C6-PTC) by ^{1}H nuclear magnetic resonance (NMR) spectroscopy. This dependence is non-linear. Calculations of the excitonic energy of a CdS QD upon displacement of native insulating ligands with exciton delocalizing ligands using a 3D spherical potential well model show that this response includes the contributions to ΔR from both isolated, bound C6-PTC ligands and from groups of adjacent C6-PTC ligands. Fits to the experimental plots of ΔR vs. surface coverage of C6-PTC with a statistical model that includes the probability of formation of clusters of bound C6-PTC on the QD surface allow for the extraction of the height of the confinement barrier presented by a single, isolated C6-PTC molecule to the excitonic hole. We measured this barrier height to be less than 0.6 eV for QDs with a radius of 1.9 nm and between 0.6 and 1.2 eV for QDs with a radius of 2.5 nm. Finally, we described the use of a phenyl *bis*-dithiocarbamate (PBTC) linker to enhance the quantum yield of photoinduced electron transfer (eT) from a zinc porphyrin (ZnP) molecule (donor) to a CdSe quantum dot (QD) (acceptor), where quantum yield is defined as the fraction of photoexcited ZnP molecules in the sample that donate an electron to the QD. The PBTC ligand links the ZnP to the QD by coordinating to Cd^{2+} on the surface of the QD and the Zn metal center in ZnP via its dithiocarbamate groups. Compared with the donor-acceptor complex formed in the absence of PBTC linkers, where the ZnP molecule adsorbs to the QD through its carboxylate moiety, the PBTC linkage increases the binding affinity between ZnP molecules and QDs by an order of magnitude, from $1.0 \times 10^{5} \pm (0.7\times10^{4})$ M^{-1} to $1.0 \times 10^{6} \pm (1.0\times10^{5})$ M^{-1}, and thereby increases the eT quantum yield by, for example, a factor of four (from 8% to 38%) within mixtures where the molar ratio ZnP:QD = 1:1.

We also demonstrated exciton delocalization with thiophenolate ligands, and used this delocalization to analyze the modes by which thiophenolate binds to QDs. Displacement of native octylphosphonate (OPA) ligands for methylthiophenolate (CH_3-TP) on the surfaces of CdSe quantum dots (QDs) causes a moderate (up to 50 meV) decrease in the band gap of the QD. Plots of the corresponding increase in apparent excitonic radius, ΔR, of the QDs vs. the surface coverage of CH_3-TP, measured by ^{1}H NMR, for several sizes of QDs reveal that this ligand adsorbs in two distinct binding modes, (i) a tightly bound mode ($K_a = 1.0\pm0.3 \times 10^{4}$ M^{-1}) capable of exciton delocalization, and (ii) a more weakly bound mode ($K_a = 8.3\pm9.9 \times 10^{2}$ M^{-1}) that has no discernable effect on exciton confinement. For tightly bound CH_3-TP, the degree of delocalization induced in the QD is approximately linearly related to the fractional surface area

occupied by the ligand for all sizes of QDs. Comparison of the dependence of ΔR on surface coverage of CH_3-TP over a range of physical radii of the QDs, R = 1.1 nm to 2.4 nm, to analogous plots simulated using a 3D spherical potential well model yield a value for the confinement barrier presented to the excitonic hole by tightly bound CH_3-TP of ~1 eV. We also examined the dependence of the interfacial chemical and electronic structure of CdSe QDs on the *para*-substituent of the thiophenolate (X-TP, X= NH_2, CH_3O, CH_3, Cl, NO_2). ^{1}H NMR spectra of mixtures of CdSe QDs and X-TPs yield the number of X-TPs bound to the surface of each QD. The binding data, in combination with the shift in the energy of the first excitonic peak of the QDs as a function of the surface coverage of X-TP and Raman and NMR analysis of the mixtures indicate that X-TP binds to CdSe QDs in at least three modes, two modes that are responsible for exciton delocalization, and a third mode that does not affect the excitonic energy. The first two modes involve displacement of OPA from the QD core, whereas the third mode forms cadmium-thiophenolate complexes that are not electronically coupled to the QD core. Fits to the data using the dual-mode binding model also yield the values of Δr_1, the average radius of exciton delocalization due to binding of the X-TP in modes 1 and 2. A 3D parameterized particle-in-a-sphere model enables the conversion of the measured value of Δr_1 for each X-TP to the height of the potential barrier that the ligand presents for tunneling of excitonic hole into the interfacial region. The height of this barrier increases from 0.3 eV to 0.9 eV as the substituent, X, becomes more electron-withdrawing.

Project 2. The Dependence of the Rate and Yield of Interfacial Electron Transfer between Colloidal QDs and Molecules on the Surface Chemistry of the QDs. The objective of this project is to determine the chemical factors that influence the rates of charge separation and charge recombination across the interfaces between semiconductor nanocrystals and adsorbed (or transiently adsorbed) small molecules.

We realized early in the project the influence of the intermolecular ordering of ligands on the surface of QDs on interfacial electron transfer. We first studied the structure of tight-binding octylphosphonate ligands on the surface of colloidal CdSeQDs within solid state films, and the dependence of this order on the size of the QDs. The order of the organic ligands, as probed by vibrational sum frequency generation (SFG) spectroscopy, decreases as the radius of the QDs decreases; this decrease is correlated with an decrease in the order of underlying Cd^{2+}, as detected by X-ray photoelectron spectroscopy (XPS) linewidth measurements, for radii of the QDs, R > 2.4 nm, and is independent of the disorder of the Cd^{2+} for R < 2.4 nm. We believe that, for R < 2.4, the decreasing order of the ligands with decreasing size is due to an increase in the curvature of the QD surfaces. Disorder in the Cd^{2+} results from the presence of a shell of Cd^{2+}-surfactant complexes that form during synthesis, so this work demonstrates the possibility for chemical control over molecular order within films of colloidal QDs by changing the surfactant mixture.

We then applied transient absorption (TA) spectroscopy to study solution-phase mixtures of colloidal CdS quantum dots (QDs) with acid-derivatized viologen molecules, N-[1-heptyl],N'-[3-carboxypropyl]-4,4'-bipyridinium dihexafluorophosphate (V^{2+}), and showed that electron transfer occurs from the conduction band of the QD to the LUMO of V^{2+} after photoexcitation of a band-edge exciton in the QD. We figured out how to analyze the magnitude of the ground state bleach of the QD as a function of the molar ratio QD:V^{2+} to obtain the QD-ligand adsorption

constant. We used this value of K_a, together with the measured rates of (i) formation of the $V^{+\bullet}$ electron transfer product and (ii) recovery of the ground state bleach of the QD, to determine the *intrinsic* rate constant for charge separation, $k_{CS,int} \sim 1.7\times10^{10}$ s^{-1}, the rate for a single QD-V^{2+} donor-acceptor pair. A further study of the adsorption equilibrium of solution-phase CdS QDs and the acid-derivatized V^{2+} revealed that the structure of the surfaces of the QDs depends on their concentration. We monitor the adsorption equilibrium is monitored through quenching of the photoluminescence of the QDs by V^{2+} upon photoinduced electron transfer. When modeled with a simple Langmuir isotherm, the equilibrium constant for QD-V^{2+} adsorption, K_a, increases from 6.7×10^5 M^{-1} to 8.6×10^6 M^{-1} upon decreasing the absolute concentration of the QDs from 1.4×10^{-6} M to 5.1×10^{-8} M. The apparent increase in K_a upon dilution results from an increase in the mean number of available adsorption sites per QD from 1.1 (for [QD] = 1.4×10^{-6} M) to 37 (for [QD] = 5.1×10^{-8} M) through desorption of native ligands from the surfaces of the QDs and through disaggregation of soluble QD clusters. A new model based on the Langmuir isotherm that treats both the number of adsorbed ligands per QD and the number of available binding sites per QD as binomially-distributed quantities is described. This model yields a concentration-independent value of K_a of 8.7×10^5 M^{-1} for the QD-V^{2+} system and provides a convenient means for quantitative analysis of QD-ligand adsorption in the presence of competing surface processes. Ultrafast transient absorption measurements also revealed that the rate constant for photoinduced electron transfer from colloidal CdS quantum dots (QDs) to alkylcarboxylate-functionalized viologens is independent of the number of methylene groups in the alkyl chain (n). The rate constant for PET is $(1.2 \pm 0.3) \times 10^{10}$ s^{-1} for n = 1, 2, and 3, and for n = 0 (methylviologen). The insensitivity of the electron transfer rate constant to the length of the functional groups on the viologen suggests that a "through-space" pathway, where the electron bypasses the alkylcarboxylate and tunnels instead through only the orbitals of the QD and of the bipyridinium core, is the dominant PET pathway.

We also described the mechanisms of charge recombination on both the nanosecond and microsecond timescales in a donor-acceptor system comprising thiol-modified bis(diarylamino)4,4'-biphenyl (TPD) molecules attached to a CdS QD via the thiolate linker. Transient absorption measurements, in conjunction with EPR and magnetic field effect studies, demonstrate that recombination on the nanosecond timescale is mediated by radical pair intersystem crossing (RP-ISC), as evidenced by the observation of a spin correlated radical ion pair, the formation of the localized ^{3*}TPD state upon charge recombination, and the sensitivity of the yield of ^{3*}TPD to an applied magnetic field. These experiments show that the radical spins of the donor-acceptor system have weak magnetic exchange coupling ($|2J|$<10 mT), and that the electron donated to the QD is trapped in a surface state rather than delocalized within the QD lattice. The microsecond-timescale recombination is probably gated by diffusion of the trapped electron among QD surface states. This study demonstrated that magneto-optical studies are useful for characterizing the charge-separated states of molecule-QD hybrid systems, despite the heterogeneity in the donor-acceptor geometry and the chemical environment of the radical spins that is inherent to these systems.

Finally, we demonstrated an increase in the yield of collisionally gated photoinduced electron transfer (electron transfer events per collision) from oleate-capped PbS QDs to benzoquinone (BQ) with increasing temperature (from 0 °C to 50 °C), due to increased permeability of the oleate adlayer of the QDs to BQ. The same changes in intermolecular structure of the adlayer

that increase its permeability to BQ also increase its permeability to the solvent, toluene, resulting in a decrease in viscous drag and an apparent increase in the diffusion coefficient of the QDs, as measured by diffusion-ordered spectroscopy (DOSY) NMR. Comparison of NMR and transient absorption spectra of QDs capped with flexible oleate with those capped with rigid methylthiolate provides evidence that the temperature dependence of the permeability of the oleate ligand shell is due to formation of transient gaps in the adlayer through conformational fluctuations of the ligands.

DOE Solar Photochemistry-Sponsored Publications 2010-2015

16. Harris, R.D.; Amin, V.A.; Lau, B.; Weiss, E.A. The Role of Inter-ligand Coupling in Determining the Interfacial Electronic Structure of Colloidal CdS Quantum Dots, *submitted*.

15. Aruda, K.O.; Amin, V.A.; Lau, B.; **Weiss, E.A.** A Description of the Adsorption and Exciton Delocalizing Properties of *p*-Substituted Thiophenols on CdSe Quantum Dots, *submitted*.

14. Amin, V.A.; Aruda, K.O.; Lau, B.; Rasmussen, A.M.; Edme, K.; **Weiss, E.A.** The Dependence of the Bandgap of CdSe Quantum Dots on the Surface Coverage and Binding Mode of an Exciton-Delocalizing Ligand, Methylthiophenolate, *J. Phys. Chem. C*, 119, 19423-19429 **(2015)**.

13. Aruda, K.O.; Bohlmann Kunz, M.; Tagliazucchi, M.; **Weiss, E.A.** Temperature-Dependent Permeability of the Ligand Shell of PbS Quantum Dots Probed by Electron Transfer to Benzoquinone, *J. Phys. Chem. Lett.*, 6 , 2841–2846 **(2015)**.

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11. Weinberg, D.J.; Dyar, S.M.; Khademi, Z.; Malicki, M.; **Marder, S.**; **Wasielewski, M.R.**; **Weiss, E.A.** Spin-Selective Charge Recombination in Complexes of CdS Quantum Dots and Organic Hole Acceptors, *J. Am. Chem. Soc.*,136, 14513-14518 **(2014).**

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8. Frederick, M.T.; Amin, V.A. Swenson, N.K.; Ho, A.Y.; **Weiss, E.A.** Control of Exciton Confinement in Quantum Dot-Organic Complexes through Modulation of the Energetic Alignment of Interfacial Orbitals, *Nano Lett.*, 13, 287-292 (**2013**).

7. Morris-Cohen, A.J.; Peterson, M.D.; Kamm, J.; Frederick, M.T.; **Weiss, E.A.** Evidence for a Through-Space Path for Electron Transfer from Quantum Dots to Carboxylate-Functionalized Viologens, *J. Phys. Chem. Lett.*, 3, 2840-2844 (**2012**).

6. Morris-Cohen, A.J.; Malicki, M.; Peterson, M.D.; Slavin, J.J.W.; **Weiss, E.A.** Chemical, Structural, and Quantitative Analysis of the Ligand Shells of Colloidal Quantum Dots, *Chem. Mater.*, 25, 1155-1165 (**2013**).

5. Morris-Cohen, A.J.; Vasilenko, V.; Amin, V.A.; Reuter, M.; **Weiss, E.A.** A Model for Adsorption of Ligands to Colloidal Quantum Dots with Concentration-Dependent Surface Structure, *ACS Nano*, 6, 557-565 (**2012**).

4. Frederick, M.T.; Cass, L.C.; Amin, V.A.; **Weiss, E.A.** A Molecule to Detect and Perturb the Confinement of Charge Carriers in Quantum Dots, *Nano Lett.*, 11, 5455-5460 (**2011**).

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Personnel. The following table lists the graduate students and postdocs who received salary from this grant between 4/2010 and 4/2015.

Amin,Victor
Aruda,Kenneth O
Edme,Kedy
Evans,Christopher M
Frederick,Matthew Thomas
Harris,Rachel Dory
Jin,Shengye
Knowles,Kathryn Eileen
Lian,Shichen
Malicki,Michal
Mathew,Nathan A
Morris-Cohen,Adam Joshua
Nepomnyashchii,Alexander Borisovich
Peterson,Mark David
Sung,Kimberly
Weinberg,David Joseph