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RPPR Final Report

as of 24-Apr-2019

Agency Code:

Proposal Number: 56779CHPCS

Agreement Number: W911NF-11-1-0075

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EIN: 362167817

Report Date: 09-May-2016

Date Received: 08-Jan-2019

Final Report for Period Beginning 10-Feb-2011 and Ending 09-Feb-2016

Title: PECASE: Organic Ligands as Tools to Analyze and Control Electronic Relaxation in Fluorescent Quantum Dots

Begin Performance Period: 10-Feb-2011

End Performance Period: 09-Feb-2016

Report Term: 0-Other

Submitted By: Emily Weiss

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STEM Degrees: 10

STEM Participants: 2

Major Goals: The major goals of this study are: i) identify general categories of nonradiative decay processes from both the lowest-energy “band-edge” excited state and higher-lying states present in CdSe QDs; ii) identify the rates and specific mechanisms by which these processes dephase or relax the excited states of the QD; iii) identify the physical and chemical features of the QD surfaces that promote or enable each decay process; and iv) decrease the contribution of nonradiative decay and, thereby increase PL quantum yield, by synthetically altering the surface chemistry of the QDs. To achieve these objectives, we will use the ligands themselves as probes: we will produce a series of solution-phase CdSe QD-ligand systems, where the electronic and chemical properties of the ligands, and the percent of surface sites covered by the ligands, vary systematically.

Accomplishments: 1. We used a combination of FT-IR, ¹H NMR, nuclear Overhauser effect (NOESY), and diffusion-ordered (DOSY) NMR spectroscopies shows that samples of oleate-coated PbS quantum dots (QDs) with core radii ranging from 1.6 nm to 2.4 nm, and purified by washing with acetone, contain two species of oleate, characterized by the stretching frequencies of their carboxylate groups, the chemical shifts of their protons, and their diffusion coefficients. One of these oleate species exists primarily on the surfaces of the QDs, and either chelates a Pb²⁺ ion, or bridges two Pb²⁺ ions. The ratio of bridging oleates to chelating oleates on the surfaces of the QDs is approximately 1:1 for all sizes of the QDs we studied. The second oleate species in these samples bridges two Pb²⁺ ions within clusters or oligomers of lead oleate (with a hydrodynamic radius of ~1.4 nm), which are byproducts of the QD synthesis. This work quantitatively characterizes the distribution of binding geometries at the inorganic/organic interface of the nanocrystals, and demonstrates the utility of using organic ligands as probes for the composition of a colloidal QD sample as a function of preparation procedure.

2. We used visible, near-infrared, and mid-infrared steady-state optical spectroscopy to study the geometries in which tetracyanoquinodimethane (TCNQ) adsorbs to the surfaces of highly cadmium enriched and near-stoichiometric CdSe quantum dots (QDs) in the formation of QD-TCNQ charge transfer (CT) complexes. Several TCNQ molecules are spontaneously reduced by chalcogenides on the surface of each CdSe QDs. The degree of CT depends on the geometry with which the TCNQ adsorbs, the degree of charge transfer upon adsorption, and the degree of distortion of TCNQ's geometry upon adsorption. This study provides a framework for determining the range of adsorption geometries of small molecules on QD surfaces, and for optimizing QD surfaces to adsorb molecules in configurations with maximal electronic coupling between the QD and the adsorbate.

3. We controlled the competition between step-growth and living chain-growth polymerization mechanisms in the formation of cadmium chalcogenide colloidal quantum dots (QDs) from CdSe(S) clusters by varying the concentration of anionic surfactant in the synthetic reaction mixture. The growth of the particles proceeds by step-addition from initially nucleated clusters in the absence of excess anionic ligand, and proceeds indirectly by

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dissolution of clusters, and subsequent chain-addition of monomers to stable clusters (Ostwald ripening) in the presence of excess anionic ligand. Fusion of clusters by step-growth polymerization is an explanation for the consistent observation of so-called “magic-sized” clusters in QD growth reactions. Living chain-addition (chain addition with no explicit termination step) produces QDs over a larger range of sizes with better size dispersity than step-addition. Tuning the molar ratio of surfactant to Se^{2-} (S^{2-}), the limiting ionic reagent, within the living chain-addition polymerization allows for stoichiometric control of QD radius without relying on reaction time.

4. We use of cadmium sulfide quantum dots (CdS QDs) as visible-light photocatalysts for the reduction of nitrobenzene to aniline through six sequential photoinduced, proton-coupled electron transfers. At pH = 3.6-4.3 the internal quantum yield of photons-to-reducing electrons is 37.1% over 54 hours of illumination, with no apparent decrease in catalyst activity. Monitoring of the QD exciton by transient absorption reveals that, for each step in the catalytic cycle, the sacrificial reductant, 3-mercaptopropionic acid, scavenges the excitonic hole in ~ 5 ps to form $\text{QD}^{\bullet-}$; electron transfer to nitrobenzene or the intermediates nitrosobenzene and phenylhydroxylamine then occurs on the nanosecond timescale. The rate constants for the single-electron transfer reactions are correlated with the driving forces for the corresponding proton-coupled electron transfers. This result suggests, but does not prove, that electron transfer, not proton transfer is rate-limiting for these reactions.

5. We described the changes in surface chemistry that occur in oleate-capped CdS QDs upon dilution from NMR-relevant concentrations (10 μM) to photoluminescence (PL)-relevant concentrations (0.1 μM), and the consequences these changes have on the relative probabilities of radiative and non-radiative decay of the QD exciton. Characterization of the QD surface by nuclear magnetic resonance (NMR) spectroscopy reveals that, upon dilution in three solvents: C_6D_6 , C_6D_{12} and CDCl_3 , oleate ligands, in the form of cadmium oleate and Cd_xO_y clusters, desorb. Changes in the ligand coverage by 30% - 40% do not impact the solubility of the QDs, do not have measurable influence on the absorption or PL linewidths, produce small non-monotonic changes in the relative PL quantum yield, and produce small, non-monotonic changes the relative partitioning between band-edge and “trapped” exciton emission. Desorption of surface ligands as a result of dilution of the QDs does, however, make the QDs more redox-active with respect to a small molecule photo-oxidant, benzoquinone (BQ). This study directly correlates the surface composition of the QDs to their photophysical properties.

6. We performed density functional theory (DFT)-based calculations of the rate constants for radiative (k_R) and nonradiative (k_{NR}) decay from the lowest singlet excited state (S_1) to the ground state (S_0) of a $\text{Cd}_{16}\text{Se}_{13}$ cluster ligated with various molecules in various binding geometries. The value of k_R is suppressed by ligands whose localized orbitals, as a result of their binding geometry, become the cluster's frontier orbitals, and thereby decrease the overlap of the electron densities of the HOMO and LUMO necessary for efficient dipole coupling. This work suggests that the photoluminescence quantum yield of CdSe nanoparticles can be maximized by ensuring that the bridging binding mode is the dominant binding mode of the ligands; bridging modes decrease the nonradiative decay rate and eliminate mid-bandgap trap states in all cases studied, except for dithioate ligands.

7. We performed density-functional-theory- (DFT-) based computations of resonance Raman (RR) spectra of ligand molecules adsorbed to the surface of a $\text{Cd}_{16}\text{Se}_{13}$ cluster. Signals from asymmetric vibrational modes of ligand binding groups, such as the asymmetric O-C-O stretching modes of carboxylates, are enhanced relative to the symmetric vibrational modes when the excitation energy is on-resonance with the excitonic energy of the cluster. Certain ligand molecules have frontier orbitals with the correct energies and symmetries to mix with the orbitals of the CdSe cluster, and as a result, the wavefunctions of the electron and the hole delocalize from the cluster onto the ligand molecules. This work suggests that the use of exciton-delocalizing ligands to optimize electronic coupling between neighboring CdSe nanoparticles may, at the same time, enhance the rates of nonradiative exciton decay by coupling the exciton and ligand vibrational modes.

8. We described the pH dependence of the excitonic energies and dynamics of CdS quantum dots (QDs) capped with phosphonopropionate (PPA) in water. QDs capped with PPA carry a negative charge on their surfaces upon deprotonation of PPA above pH ~ 8.5 ; the resultant electric field induces large changes in the QD's optical properties. Between pH 5.6 and 12.0, an increase in pH is accompanied by a 47-meV bathochromic shift in the bandgap of the QDs and a decrease in the Stokes shift by ~ 4.3 meV/pH unit. An increase in the radiative recombination rate by a factor of 20.9 occurs on increasing the pH from 5.6 to 9.4. These observations are attributed to a shifting of the energy levels within the first exciton manifold, and are simulated using time-dependent density functional theory calculations on model $\text{Cd}_{29}\text{S}_{29}$ clusters.

Training Opportunities: Three graduate students and five postdocs were supported by this grant during the reporting period.

Results Dissemination: Ten peer-reviewed publications were published as a result of the work performed under this grant. The PI also reported this research in the form of invited talks at Universities and conferences (on the order of 25 talks on this particular research).

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Honors and Awards: Dow Chemical Company Research Professorship, Northwestern University
2016

Distinguished Women in Science Seminar Speaker, Stanford University	2016
Phi Lambda Upsilon Distinguished Speaker, Kansas State University	2015
Harry B. Gray Award for Creative Work in Inorganic Chemistry by a Young Investigator	2015
Camille Dreyfus Teacher-Scholar Award, The Dreyfus Foundation	2014
Kavli Emerging Leader in Chemistry, The Kavli Foundation	2014
Distinguished Teaching Award, Northwestern Undergraduate Chemistry Council	2013
Irving M. Klotz Research Professorship, Northwestern University	2012
Kavli Fellow of the National Academy of Sciences, The Kavli Foundation	2011
NU-Argonne Early Career Investigator Award for Energy Research	2011
A.P. Sloan Foundation Research Fellowship, The Sloan Foundation	2011
Packard Fellowship for Science and Engineering, The Packard Foundation	2010

Protocol Activity Status:

Technology Transfer: Jensen, SA; Wasielewski, MR; Weiss, EA. Cadmium sulfide quantum dots for the photoreduction of nitrobenzene to phenylhydroxylamine and aniline, US Patent pending, submitted 2015. Synopsis: The surface chemistry of cadmium sulfide quantum dots is formulated (in terms of surface charge density and solubility) to efficiently perform the 6-electron, 6-proton reduction of nitrobenzene to aniline in water/methanol dispersion.

PARTICIPANTS:

Participant Type: PD/PI

Participant: Emily A Weiss

Person Months Worked: 10.00

Funding Support:

Project Contribution:

International Collaboration:

International Travel:

National Academy Member: N

Other Collaborators:

Participant Type: PD/PI

Participant: Christopher Thompson

Person Months Worked: 15.00

Funding Support:

Project Contribution:

International Collaboration:

International Travel:

National Academy Member: N

Other Collaborators:

Participant Type: PD/PI

Participant: Stephen Jensen

Person Months Worked: 15.00

Funding Support:

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Project Contribution:
International Collaboration:
International Travel:
National Academy Member: N
Other Collaborators:

Participant Type: PD/PI

Participant: Alexander Nepomnyaschii

Person Months Worked: 15.00

Funding Support:

Project Contribution:
International Collaboration:
International Travel:
National Academy Member: N
Other Collaborators:

Participant Type: PD/PI

Participant: Michal Malicki

Person Months Worked: 15.00

Funding Support:

Project Contribution:
International Collaboration:
International Travel:
National Academy Member: N
Other Collaborators:

Participant Type: PD/PI

Participant: Christopher Evans

Person Months Worked: 15.00

Funding Support:

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ARTICLES:

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Publication Identifier: 10.1021/ja3079576

Volume: 134

Issue: 0

First Page #: 17298

Date Submitted: 1/6/19 12:00AM

Date Published:

Publication Location:

Article Title: Semiconductor Clusters Polymerize to Quantum Dots through Competing Step-Growth Mechanisms

Authors: Christopher Evans, Alyssa Love, Emily A. Weiss

Keywords: quantum dot, magic-sized cluster, step-growth polymerization

Abstract: This paper introduces step-growth polymerization as a useful mechanistic description of the formation of CdSe colloidal quantum dots (QDs) from CdSe clusters. Step-growth proceeds directly from initially nucleated clusters in the absence of excess anionic ligand (for Cd²⁺), and proceeds indirectly by dissolution of clusters and subsequent step-addition of monomers to stable clusters (Ostwald ripening) in the presence of excess ligand. Combination of clusters by direct step-growth polymerization explains the consistent observation of so-called "magic-sized" clusters in QD growth reactions. Tuning the ratio of Cd²⁺ to Se²⁻ within an indirect step-growth polymerization provides the first example of stoichiometric control of QD radius. Controlling the competition between direct and indirect step-growth is the key to expanding the range of QD sizes that can be synthesized with optimal monodispersity.

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Article Title: Surfactant-Controlled Polymerization of Semiconductor Clusters to Quantum Dots through Competing Step-Growth and Living Chain-Growth Mechanisms

Authors:

Keywords: semiconductor cluster, polymerization, ligands

Abstract: This article reports control of the competition between step-growth and living chain-growth polymerization mechanisms in the formation of cadmium chalcogenide colloidal quantum dots (QDs) from CdSe (S) clusters by varying the concentration of anionic surfactant in the synthetic reaction mixture. The growth of the particles proceeds by step-addition from initially nucleated clusters in the absence of excess phosphinic or carboxylic acids, which adsorb as their anionic conjugate bases, and proceeds indirectly by dissolution of clusters, and subsequent chain-addition of monomers to stable clusters (Ostwald ripening) in the presence of excess phosphinic or carboxylic acid. Fusion of clusters by step-growth polymerization is an explanation for the consistent observation of so-called "magic-sized" clusters in QD growth reactions. Living chain-addition (chain addition with no explicit termination step) produces QDs over a larger range of sizes with better size dispersity than step-addition. Tuning

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Journal: Journal of Coordination Chemistry

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Publication Identifier: 10.1080/00958972.2012.695019

Volume: 65

Issue: 0

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Publication Location:

Article Title: Review of the synthesis and properties of colloidal quantum dots: the evolving role of coordinating surface ligands

Authors: Christopher Evans, Laura Cass, Kathryn Knowles, Daniel Tice, Robert P.H. Chang, Emily A. Weiss

Keywords: Quantum dot; Photoluminescence; Metal chalcogenide; Passivation

Abstract: This review highlights the developments in synthetic methods for colloidal quantum dots that have expanded the range of achievable sizes, shapes, materials, and surface chemistries over the past 30 years, and how these methods have enabled optimization of properties like photoluminescence quantum yield, monodisperse size distributions, and conductivity in the solid state.

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Journal: Anal. Chemistry

Publication Identifier Type:

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Volume: 0

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Date Submitted:

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Publication Location:

Article Title: The Chemical Environments of Oleate Species within Samples of Oleate-Coated PbS Quantum Dots

Authors:

Keywords: PbS quantum dot, FTIR, Diffusion-ordered spectroscopy NMR, carboxylate

Abstract: A combination of FT-IR, ^1H NMR, nuclear Overhauser effect (NOESY), and diffusion-ordered (DOSY) NMR spectroscopies shows that samples of oleate-coated PbS quantum dots (QDs) with core radii ranging from 1.6 to 2.4 nm, and purified by washing with acetone, contain two species of oleate characterized by the stretching frequencies of their carboxylate groups, the chemical shifts of their protons, and their diffusion coefficients. One of these oleate species exists primarily on the surfaces of the QDs and either chelates a Pb^{2+} ion or bridges two Pb^{2+} ions. The ratio of bridging oleates to chelating oleates on the surfaces of the QDs is approximately 1:1 for all sizes of the QDs we studied. The second oleate species in these samples bridges two Pb^{2+} ions within clusters or oligomers of lead oleate (with a hydrodynamic radius of ~ 1.4 nm), which are byproducts of the QD synthesis. The concentration of these clusters increases with increasing size of the QDs because larger QDs are produced.

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Publication Identifier Type: DOI **Publication Identifier:** 10.1146/annurev-physchem-040513-103649
Volume: 65 **Issue:** 1 **First Page #:** 317
Date Submitted: **Date Published:**
Publication Location:
Article Title: The Role of Ligands in Determining the Exciton Relaxation Dynamics in Semiconductor Quantum Dots
Authors:
Keywords: surface chemistry, transient absorption, Auger relaxation, electron-to-vibrational energy transfer, charge trapping
Abstract: This article reviews the mechanisms through which molecules adsorbed to the surfaces of semiconductor nanocrystals, quantum dots (QDs), influence the pathways for and dynamics of intra- and interband exciton relaxation in these nanostructures. In many cases, the surface chemistry of the QDs determines the competition between Auger relaxation and electronic-to-vibrational energy transfer in the intraband cooling of hot carriers, and between electron or hole-trapping processes and radiative recombination in relaxation of band-edge excitons. The latter competition determines the photoluminescence quantum yield of the nanocrystals, which is predictable through a set of mostly phenomenological models that link the surface coverage of ligands with specific chemical properties to the rate constants for nonradiative exciton decay.
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Volume: 118 **Issue:** 31 **First Page #:** 18263
Date Submitted: **Date Published:**
Publication Location:
Article Title: Electronic and Vibrational Structure of Complexes of Tetracyanoquinodimethane with Cadmium Chalcogenide Quantum Dots
Authors:
Keywords: TCNQ, charge transfer complex, vibrational signatures
Abstract: This paper describes the use of visible, near-infrared, and mid-infrared steady-state optical spectroscopy to study the geometries in which tetracyanoquinodimethane (TCNQ) adsorbs to the surfaces of highly cadmium enriched and near-stoichiometric CdSe quantum dots (QDs) in the formation of QD-TCNQ charge transfer (CT) complexes. Several TCNQ molecules are spontaneously reduced by chalcogenides on the surface of each CdSe QD. The degree of CT depends on the geometry with which the TCNQ adsorbs and the degree of distortion of TCNQ's geometry upon adsorption. Comparison of the electronic and vibrational spectra of CdSe QD-TCNQ complexes with those of CT complexes of TCNQ with molecular reductants (including molecular chalcogenides) and computer simulations of the geometries and vibrational spectra of the TCNQ-chalcogenide CT complexes show that (i) the Cd-enriched CdSe QDs reduce a factor of 7.4 more TCNQ molecules per QD than nearly stoichiometric CdSe QDs because surface selenides are m
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Article Title: Direct Visible-light, Room-Temperature Photocatalytic Reduction of Nitrobenzene to Aniline by Quantum Dots

Authors: Stephen Jensen, Stephanie Homan, Emily A. Weiss

Keywords: photocatalysis, cadmium sulfide, electron transfer

Abstract: This paper describes the visible-light photocatalysis of the proton-coupled six-electron reduction of nitrobenzene to aniline at room temperature within dispersions of CdS quantum dots (QDs) in 80:20 water: methanol. The QDs act as direct photocatalysts – there is no intervening molecular catalyst present. Over 54 hours of illumination with visible light at pH 2.6, each QD transfers 4.5×10^6 electrons to reduce 8.3×10^5 nitrobenzene molecules to aniline and the other isolable intermediate, phenylhydroxylamine. 3-mercaptopropionic acid serves as (i) a solubilizing ligand for the QDs, (ii) the terminal reductant that regenerates the QD catalyst and (iii) the proton donor in each reduction step. If left unprotonated, aniline adsorbs to the QD surface and limits the reaction rate and yield by inhibiting electron transfer to nitrobenzene. The activity (electrons transferred \times g catalyst $^{-1}$ \times J photons $^{-1}$) of the high-surface-area QDs used in this study is a factor of 4.6×10^3 greater than that of

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Article Title: Electrostatic Control of Excitonic Energies and Dynamics in a CdS Quantum Dot through Reversible Protonation of Its Ligands

Authors: Christopher M. Thompson, Mohamad Kodaimati, Dana Westmoreland, Raul Calzada, Emily A. Weiss

Keywords: phosphonopropionate, pH-dependence, ligand

Abstract: This paper describes the pH dependence of the excitonic energies and dynamics of CdS quantum dots (QDs) capped with phosphonopropionate (PPA) in water. QDs capped with PPA carry a negative charge on their surfaces upon deprotonation of PPA above pH \approx 8.5; the resultant electric field induces large changes in the QD's optical properties. Between pH 5.6 and 12.0, an increase in pH is accompanied by a 47-meV bathochromic shift in the bandgap of the QDs and a decrease in the Stokes shift by \approx 4.3 meV/pH unit. An increase in the radiative recombination rate by a factor of 20.9 occurs on increasing the pH from 5.6 to 9.4. These observations are attributed to a shifting of the energy levels within the first exciton manifold, and are simulated using time-dependent density functional theory calculations on model Cd₂₉S₂₉ clusters surrounded by point charges.

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Date Submitted: 1/7/19 12:00AM

Date Published: 8/1/16 5:00AM

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Article Title: Electronic Processes within Quantum Dot-Molecule Complexes

Authors: Rachel D. Harris, Stephanie Bettis Homan, Mohamad Kodaimati, Chen He, Alexander B. Nepomnyashchii

Keywords: quantum dots, surface states, exciton

Abstract: The subject of this review is the colloidal quantum dot (QD) and specifically the interaction of the QD with proximate molecules. It covers various functions of these molecules, including (i) ligands for the QDs, coupled electronically or vibrationally to localized surface states or to the delocalized states of the QD core, (ii) energy or electron donors or acceptors for the QDs, and (iii) structural components of QD assemblies that dictate QD–QD or QD–molecule interactions. Research on interactions of ligands with colloidal QDs has revealed that ligands determine not only the excited state dynamics of the QD but also, in some cases, its ground state electronic structure. Specifically, the article discusses (i) measurement of the electronic structure of colloidal QDs and the influence of their surface chemistry, in particular, dipolar ligands and exciton-delocalizing ligands, on their electronic energies; (ii) the role of molecules in interfacial electron and energy transfer processes

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Publication Location:

Article Title: Composition and Permeability of Oleate Adlayers of CdS Quantum Dots upon Dilution to Photoluminescence-Relevant Concentrations

Authors: Alexander B. Nepomnyashchii, Rachel D. Harris, Emily A. Weiss

Keywords: quantum dot, ligand shell, NMR

Abstract: This paper describes the changes in surface chemistry that occur in oleate-capped CdS quantum dots (QDs) upon dilution from NMR-relevant concentrations (10⁻⁴ M) to photoluminescence (PL)-relevant concentrations (0.1⁻⁴ M) and the consequences these changes have on the relative probabilities of radiative and nonradiative decay of the QD exciton. Characterization of the QD surface by nuclear magnetic resonance (NMR) spectroscopy reveals that upon dilution in three solvents, C₆D₆, C₆D₁₂, and CDCl₃, oleate ligands, in the form of cadmium oleate and Cd_xO_y clusters, desorb. Changes in the ligand coverage by 30–40% do not impact the solubility of the QDs, do not have measurable influence on the absorption or PL line widths, produce small (±0.05), nonmonotonic changes in the relative PL quantum yield, and produce small, nonmonotonic changes the relative partitioning between band-edge and “trapped” exciton emission.

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Article Title: Computational Study of the Resonance Enhancement of Raman Signals of Ligands Adsorbed to CdSe Clusters through Photoexcitation of the Cluster

Authors: Nathaniel K. Swenson, Mark A. Ratner, Emily A. Weiss

Keywords: DFT, CdSe cluster, Raman spectra

Abstract: This paper describes density-functional-theory-based computations of resonance Raman (RR) spectra of ligand molecules adsorbed to the surface of a Cd₁₆Se₁₃ cluster. Signals from asymmetric vibrational modes of ligand binding groups, such as the asymmetric O–C–O stretching modes of carboxylates, are enhanced relative to the symmetric vibrational modes when the excitation energy is on-resonance with the excitonic energy of the cluster. Certain ligand molecules have frontier orbitals with the correct energies and symmetries to mix with the orbitals of the CdSe cluster, and as a result, the wave functions of the electron and the hole delocalize from the cluster onto the ligand molecules; experimentally, this delocalization results in a bathochromic shift of the band edge excitonic absorption. Increased excitonic delocalization results in greater vibronic coupling between the exciton and the ligand vibrations and, on average, preferential enhancements in the RR signals of those vibrations.

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Abstract: This article describes density-functional-theory- (DFT-) based calculations of the rate constants for radiative (k_R) and nonradiative (k_{NR}) decay from the lowest singlet excited state (S₁) to the ground state (S₀) of a Cd₁₆Se₁₃ cluster ligated with various molecules in various binding geometries. The value of k_R is suppressed by ligands whose localized orbitals, as a result of their binding geometry, become the cluster's frontier orbitals and, thereby, decrease the overlap of the electron densities of the HOMO and LUMO necessary for efficient dipole coupling. Thiolate ligands in a monodentate geometry and dithioate ligands in a bridging geometry decrease k_R in this manner. The value of k_{NR} is also sensitive to the binding geometries of the ligands: binding geometries that are less rigid yield a greater change in nuclear coordinates between the S₁ and S₀ electronic states, which, in turn, increases the rate of nonradiative decay by maximizing the vibronic coupling between the band-edge

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