Functionalizing the Surface of CdSe-Based Nanoparticles

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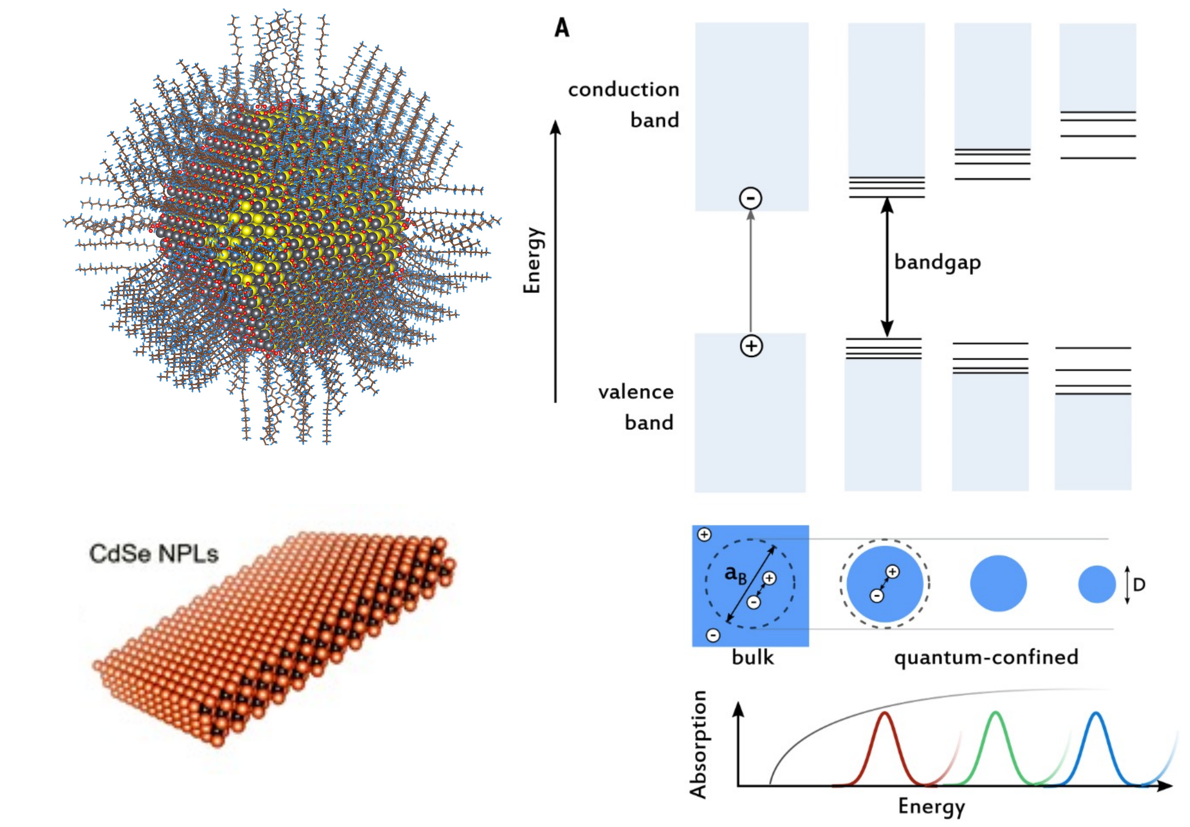
I. What are Nanoparticles?



Quantum Dots (QDs)

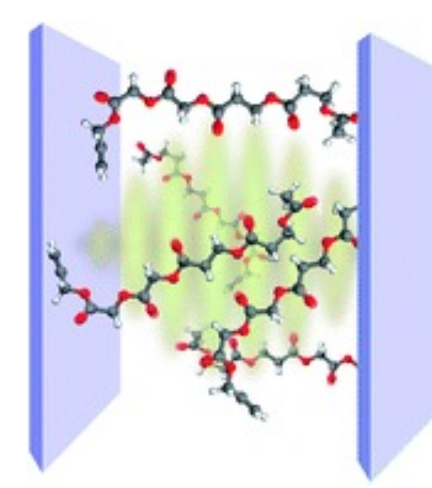
- Semiconducting metal core functionalized with organic ligands on the surface
- Size-tunable! QD diameter influences optical properties
- Wide range of applications, including:
  - Bioimaging
  - Computer displays
  - Energy harvesting: photovoltaic cells
  - Charge transport

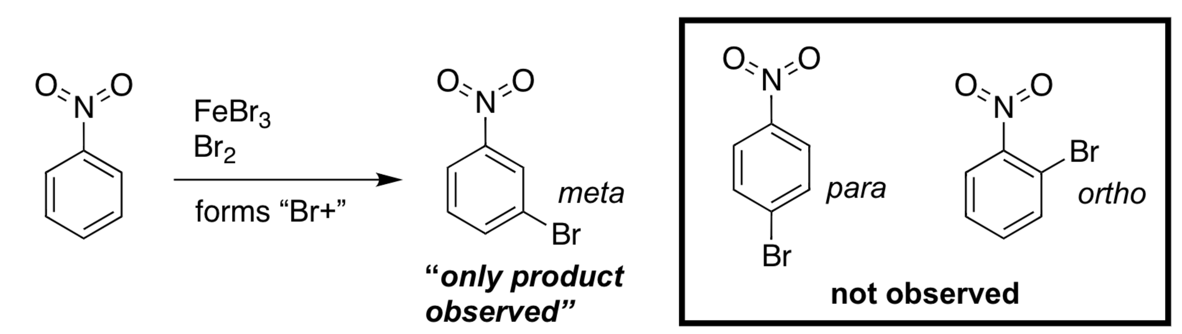
Nanoplatelets (NPLs)

- 2-dimensional representation of a QD
- More surface area provides more potential for surface modification
- Organized in monolayers/sheets
  - Somewhat predictable structural organization

II. CCI QuEST Project

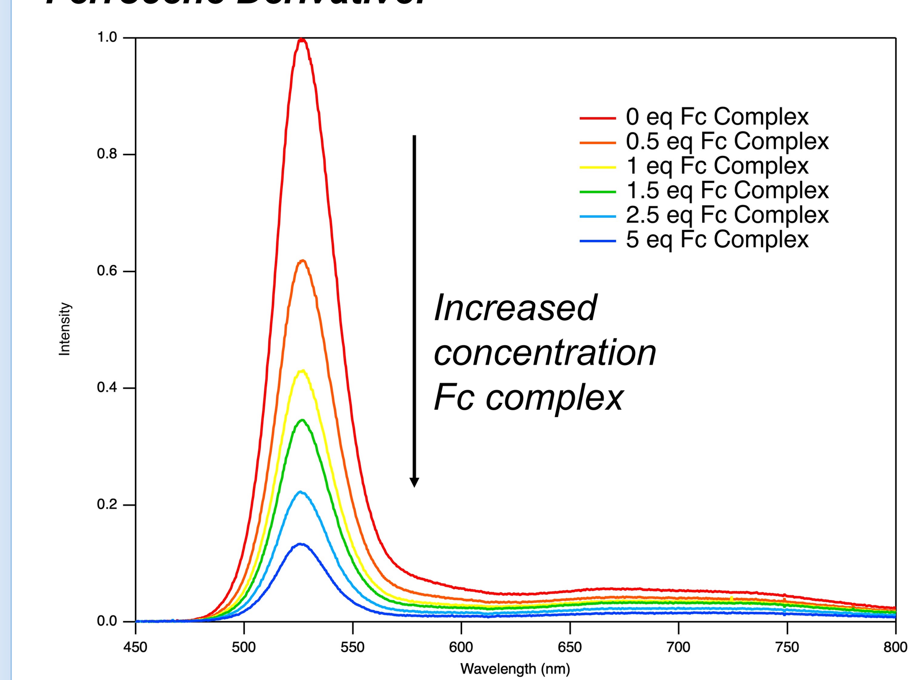
- Center for **Qu**antum **E**lectrodynamics for **S**elective **T**ransformations
- Motivating Idea:
  - Molecules coupled to an optical cavity can produce polaritons that can alter energy states of species within the cavity
    - Polariton: quasiparticle composed of a photon coupled to an exciton.
    - The ability to change energy states of molecules can alter the chemical reactivity of reactions performed within the cavity
- Attaching ligands with charge acceptor properties to cadmium selenide (CdSe) nanoplatelets (NPLs) allows for charge transfer reactions to occur, which can be monitored and possibly changed in an optical cavity



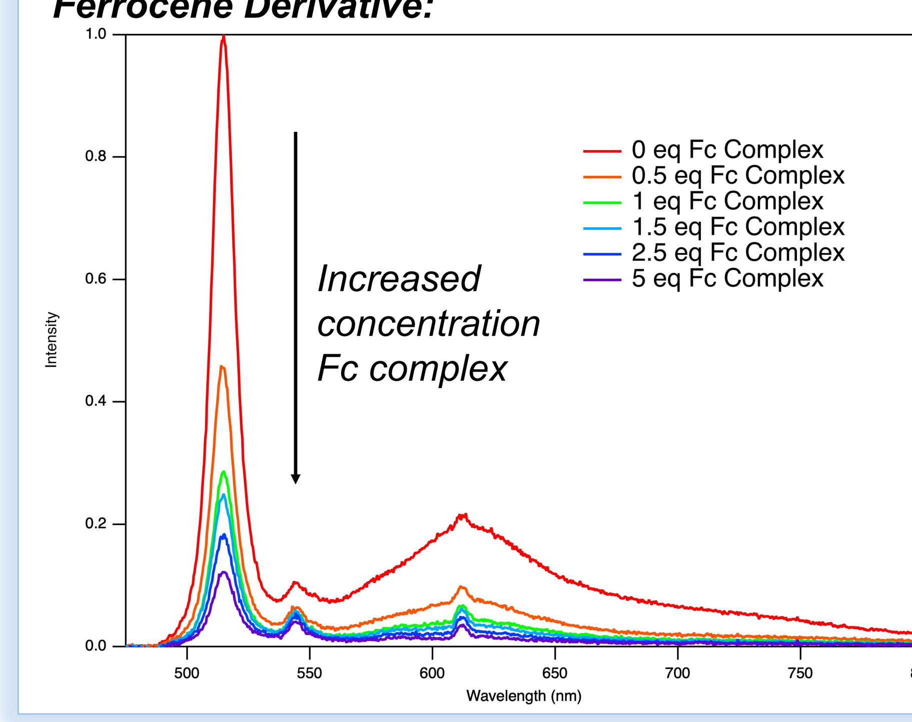


III. Using PL Spectroscopy to Probe the Surface of CdSe QDs and NPLs

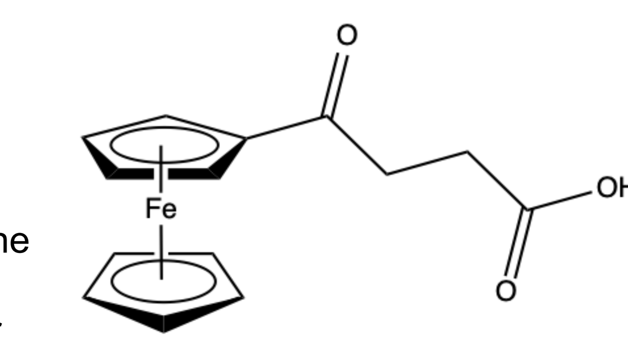
Photoluminescence Titration of CdSe QDs with a Ferrocene Derivative:



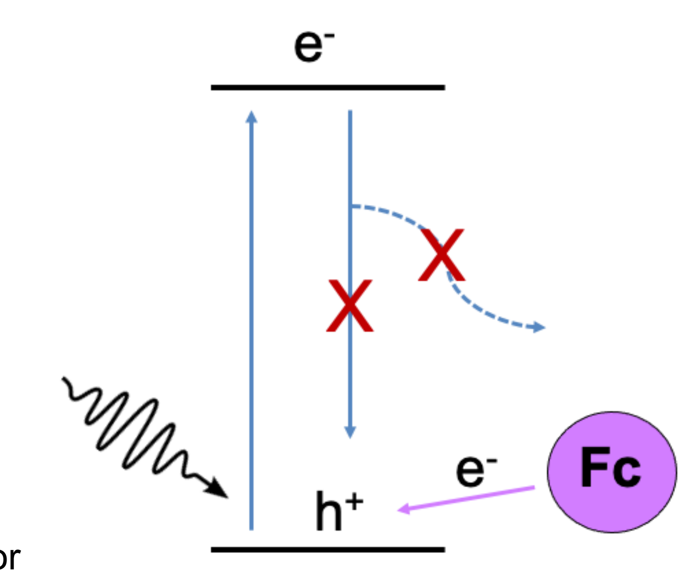
Photoluminescence Titration of CdSe NPLs with a Ferrocene Derivative:



- Photoluminescence (PL) spectroscopy was used to observe how the surface of **CdSe QDs** changes as increasing molar equivalents of a ferrocene (Fc) derivative were added
- Observed PL quenching with increasing equivalents of Fc
  - We hypothesize that the Fc is binding to the QD surface as this quenching is what we would expect for a bound charge acceptor
  - Further experiments are underway to confirm static or dynamic quenching
- Fc derivative is an electron donor, which can affect the charge-transfer capabilities when bound to the nanoparticle surface

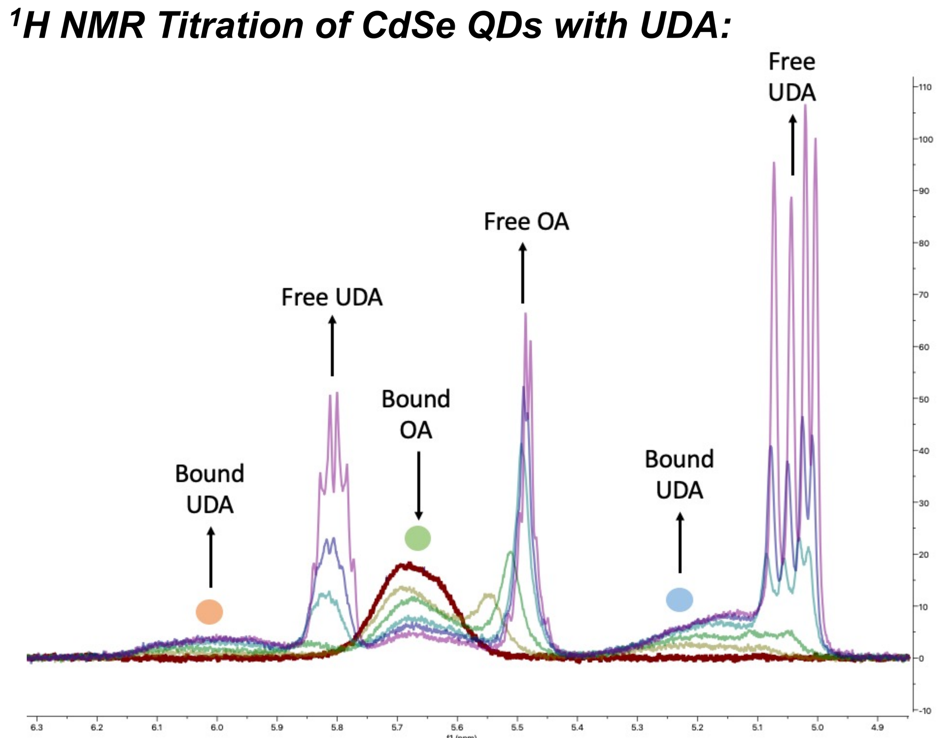


- PL spectroscopy was used to observe how the surface of **CdSe NPLs** changes as increasing molar equivalents of a Fc derivative were added
- Similarly to how the QDs responded, the NPLs also exhibited PL quenching upon addition of increased amounts of Fc
- Charge transfer between NPLs and a donor or acceptor can be explored in an optical cavity to see how charge transfer rates are impacted
  - Assuming the Fc complex is statically bound to the NPL surface

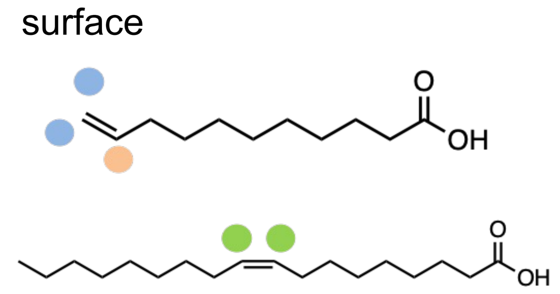


IV. Using ¹H NMR to Characterize the Surface of CdSe QDs and NPLs

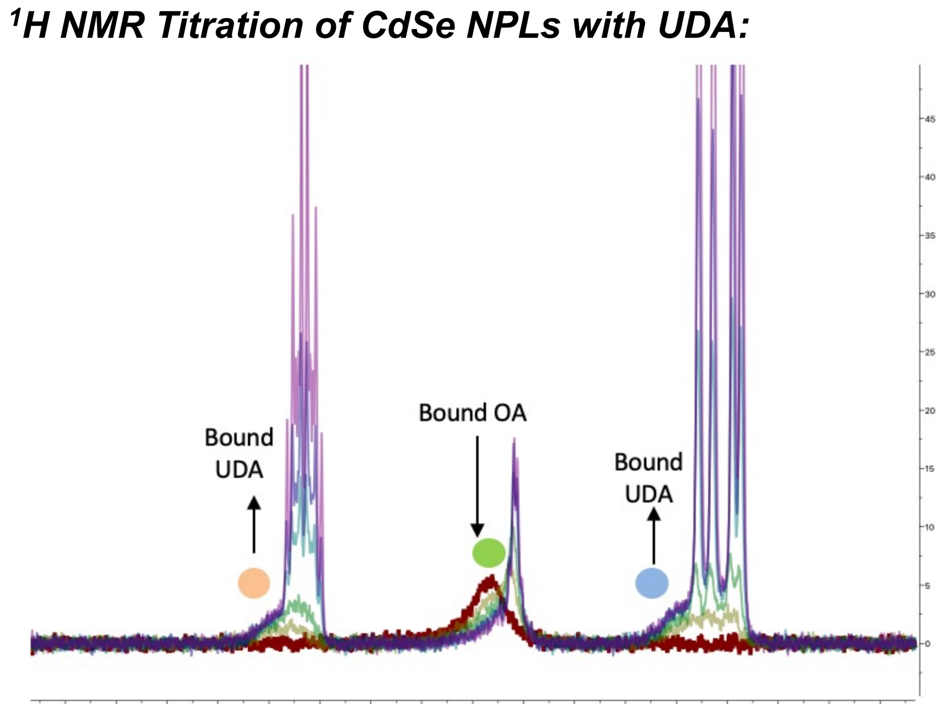
¹H NMR Titration of CdSe QDs with UDA:



- Increasing molar equivalents of undecylenic acid (UDA) added
- Successfully observed displacement of the native oleic acid (OA) ligand with the newly added UDA ligand
- Good peak separation allows for quantification of ligands on the surface



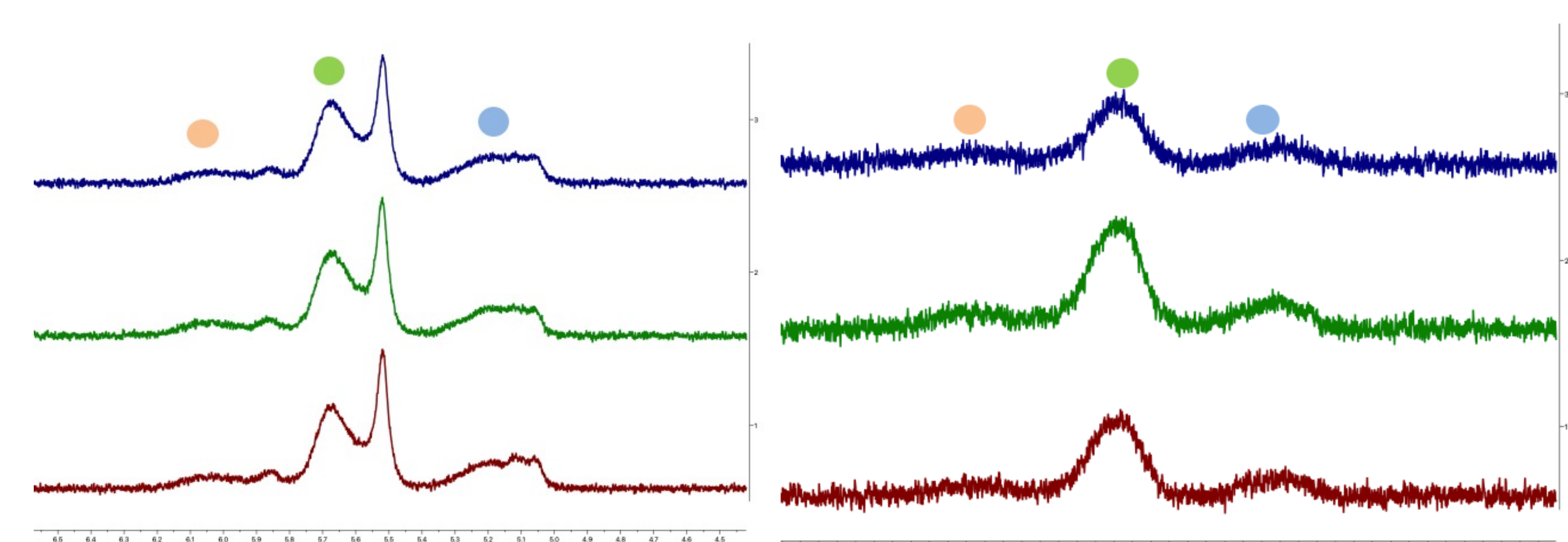
¹H NMR Titration of CdSe NPLs with UDA:



- Performed ¹H NMR titration with CdSe NPLs and UDA in hopes of observing similar behavior to QDs
- As expected, observed native OA ligand displacement as more UDA bound to NPL surface in situ
- Peak separation not as effective as QDs, but allows for fairly accurate resolution and quantification of bound vs. free ligands in solution
- CdSe NPLs exhibit similar affinity for surface modifications as QDs

Isolating Mixed-Shell CdSe(OA)$_{0.8}$(UDA)$_{0.2}$ QDs

Pre-Purification: ***Post-Purification:***



Sample
30 eq. UDA S1
30 eq. UDA S2
30 eq. UDA S3

	Pre-Purification	Post-Purification
Avg. % Bound OA	71% ± 3%	74% ± 5%
Avg. % Bound UDA	29% ± 3%	26% ± 5%

- ¹H NMR used to quantify the ligands present on the QD surface before and after washing away any free ligands
- Experiment performed in triplicates to obtain relative averages of ligand presence
- Successfully isolated mixed shell QDs at a ratio of approximately 70% oleic acid (OA) and 30% undecylenic acid (UDA)

V. Conclusions

- CdSe QDs and NPLs readily undergo ligand exchange reactions that can be probed using photoluminescence and ¹H NMR spectroscopic methods
- Mixed-shell QDs can be formed and quantified, which has the potential for exciting applications in predicting and tuning charge-transfer capabilities
- The quenching observed in the PL spectroscopy titrations indicates potential surface interaction between the Fc complex and the nanoparticles, but this could be due to either dynamic or static quenching
  - ¹H NMR can provide evidence of static surface binding. Further experiments can be conducted to confirm
- Successfully attaching a electron donor (Fc complex) or electron acceptor to CdSe NPLs has the potential to alter the rate of charge transfer
  - Charge-transfer kinetics can also be altered by coupling surface-modified NPLs to an optical cavity

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