Fluorescent Quantum Dots for Sensing Applications
Eric L. Coats, Raissa V. Hang, Elizabeth R. Sherman and David B. Cordes
Department of CHEMISTRY | Pacific University | 2043 College Way | Forest Grove, OR 97116 | cordes@pacificu.edu

Abstract: We have explored the preparation of specifically modified fluorescent quantum dots (QDs) for various sensing applications. Originally, our goal had been to prepare QDs as sensors for metal ions. In the course of our studies, however, we became focused instead on using QDs as the basis of a carbohydrate detection system. A variety of QD core and shell combinations were investigated and several different strategies for surface modification were applied. Preliminary results with CdTe/ZnS QDs modified with carboxylic and boronic acids show a considerable increase in fluorescence intensity as concentration of carbohydrate is increased. With further modifications we hope to achieve improved brightness, solubility, and analyte sensitivity.

Background:
Quantum dots (QDs) are nanometer-sized crystals composed of semiconducting materials such as CdSe or ZnS. The optical properties of these fluorescent nanomaterials can be tuned by careful control of QD size and surface chemistry. Interest in fluorescent QDs derived from their broad absorption, narrow emission, intense brightness, and good photostability relative to organic dyes. Widely used in a variety of applications, QDs truly constitute a unique class of nanomaterials. Often, additional coatings of materials such as ZnS or silica are added to provide improved photostability and to provide a scaffold for the installation of additional functional groups at the surface.

Fluorescence QDs are quite small, the optical properties of QDs are quite sensitive to changes in the surface chemistry that occur when new molecules or ions bind to the surface. This sensitivity makes them excellent candidates as fluorescent sensors. To achieve a specific sensitivity to a particular analyte, we are investigating the attachment of particular ligands with specific attractions for different analytes.

Experimental Methods:
General:
Previously we had used the method depicted in Scheme 1 to prepare ZnS-MoS2-doped QDs. The QDs used in our current research consist of a CdTe core coated with a two-layer ZnS shell as shown in Scheme 2. Using coordinating solvents such as trioctylphosphine (TOP) or tetradecylphosphonic acid (TDPA), a tellurium with a two-layer ZnS shell as shown in Scheme 2 doped QDs. The QDs used in our current research consist of a CdTe core coated with a two-layer ZnS shell as shown in Scheme 2 doped QDs. To achieve a specific sensitivity to a particular analyte, we are investigating the attachment of particular ligands with specific attractions for different analytes.

Core Modification:
Although our research focused on using CdTe as the core material, two other cores were examined for fluorescence properties. CdSe and a CdTeSe mix were evaluated against CdTe. To synthesize these QDs the same method was used, the difference being the precursor (either Te, Se, or SeTe) that were transferred into the Cd solution. Fluorescence spectra were recorded for all three cores (See figure below.). The CdTe QDs had an emission wavelength of 616 nm while those composed of CdSe had a more blue-shifted emission at 568 nm. Lastly, the mixed CdTeSe had a red-shifted emission at 636 nm.

Quenching Study:
To better understand how binding events at the surface affect the fluorescence of the QDs, we conducted a study to determine the sensitivity of these QDs to methyl viologen (MVI2+), a well-known fluorescence quencher. MVI2+ was used to quench CdTe/ZnS QDs modified with β-mercaptoethanol (BME), L-cysteine (Cys), and mercaptopropionic acid (MPA). The results are quantified through determination of static (Ksv) and dynamic (V) quenching constants and suggest that the QDs probably interact with the quencher via an electrostatic attraction. Understanding how these QDs are quenched provides information as to how other binding events affect the fluorescence of the system. Characteristic binding data collected at pH 7.4 and pH 10 are shown below.

Boric Acid Modification:
Boronic acids are common sugar-sensing compounds as they easily bind to sugars. Under appropriate circumstances, this sugar binding can also induce electronic changes to the boronic acid. We suspected that boronic acid sugar binding at the surface of the QD would likely perturb the fluorescence of the QD. To test the hypothesis, we prepared CdTe/ZnS QDs with good solubility by co-functionalizing them with mercaptopropionic acid (MPA), β-mercaptoethanol (BME) and mercaptobenzylic acid (BA). Ultimately, we found that we could prepare highly carbohydrate-sensitive, fluorescent QDs using a 1:1 ratio of MPA to BA. These QDs behave like an "ON" sensor and become increasingly fluorescent with increasing concentrations of simple carbohydrates such as ethylene glycol, glucose, galactose, and fructose. A generic binding scheme is shown for ethylene glycol and binding curves are shown for the sugars: glucose and fructose.

Other Functionalizations:
Using similar chemistry for surface attachment, other functional groups were attached at the surface. As depicted in the figure below, various fluorescent QDs were prepared using carboxylic acid, amine, alcohol, and boronic acid functional groups.

Acknowledgments:
Pacific University Chemistry Department; Murdock Charitable Trust; Pacific University Research Institute for Science and Mathematics

Table of quenching constants collected at pH 7.4 and pH 10:

<table>
<thead>
<tr>
<th>pH 7.4</th>
<th>MPA</th>
<th>L-Cys</th>
<th>BME</th>
</tr>
</thead>
<tbody>
<tr>
<td>Ksv</td>
<td>0.00</td>
<td>0.00</td>
<td>0.00</td>
</tr>
<tr>
<td>V</td>
<td>0.00</td>
<td>0.00</td>
<td>0.00</td>
</tr>
<tr>
<td>pH 10</td>
<td>MPA</td>
<td>L-Cys</td>
<td>BME</td>
</tr>
<tr>
<td>Ksv</td>
<td>0.00</td>
<td>0.00</td>
<td>0.00</td>
</tr>
<tr>
<td>V</td>
<td>0.00</td>
<td>0.00</td>
<td>0.00</td>
</tr>
</tbody>
</table>

Future Work:
- Optimize the quantum dots with the silica shell.
- Functionalize CdTe/ZnS/Silica quantum dots with carboxylic acid for sugar sensing
- Functionalize the CdTe/ZnS/Silica quantum dots with ligands for metal sensing

Fluorescent intensity as concentration of carbohydrate is increased. Using similar chemistry for surface attachment, other functional groups were attached to the surface. As depicted in the figure below, various fluorescent QDs were prepared using carboxylic acid, amine, alcohol, and boronic acid functional groups.