Synthesis and Characterization of Modified Carbon Dots to Investigate Fluorescence Sensing Properties

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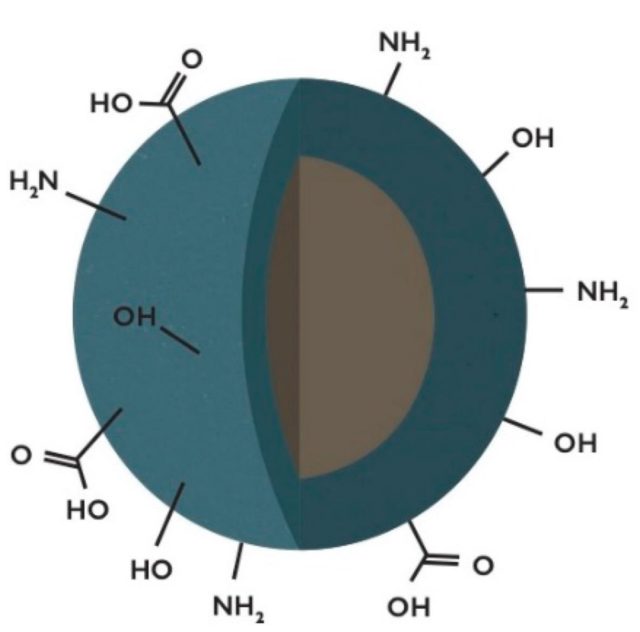
Project Overview

Carbon-based nanoparticles, or carbon dots (CDs), were synthesized and modified using various starting materials. The CDs were characterized using UV-Vis, fluorescence, IR, and NMR spectroscopy to consider their structural and functional properties. These adjustments were analyzed to determine the effects on stability and fluorescence for future applications as biological and chemical sensors. pH studies were performed, and it was noted that the wavelength of absorption and intensity of fluorescence was stable in, and well beyond, the physiological pH range. Additionally, CDs synthesized from different carbon sources containing thiol functional groups were studied and cross-linked with catechol, 2-butyne-1,4-diol (BDL), and phloroglucinol dihydrate (PGL). CDs made from mercaptosuccinic acid (MSA) were most stable in solution and showed strong absorption and fluorescent properties after synthesis and cross linking modification. Studies comparing the cross-linking behavior of MSA and citric acid carbon dots were also carried out.

What are Carbon Dots?

Carbon dots (CDs) are nanometer-scale materials primarily composed of carbon atoms with different functional groups, such as carboxylic acids, alcohols, and amines, on the surface. We synthesize the CDs by combining a carbon source (e.g., citric acid) with a nitrogen source (e.g., urea) and subjecting the resulting water-soluble mixture to microwave irradiation for a short time period (e.g., 5 min). The CDs have fluorescent properties similar to other materials (such as biological dyes and semiconductor quantum dots), but they have the advantage of having a lower toxicity.



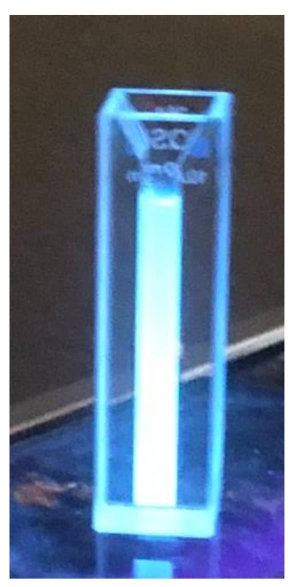


Image (left): Jorns, M.; Pappas, D. *Nanomaterials* **2021**, *11*(6), 1448.

Why Are We Studying CDs?

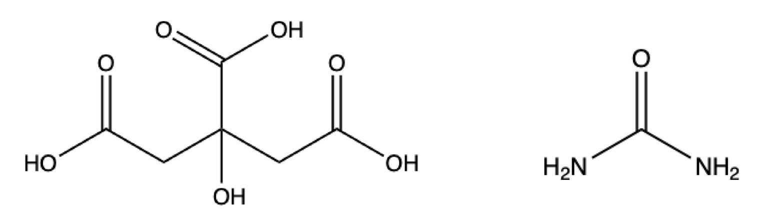
We are interested in these nanomaterials for a number of reasons. Our goals include modifying the nanoparticle surface to investigate interesting chemistry and incorporate sensing capabilities. More specifically, we would like to use our modified CDs as sensors for metal ions in solutions. Similar CD versions have been used as sensors for the following metal ions: Fe^{3+}, Hg^{2+}, Zn^{2+}, Cu^{2+}, Au^{3+}, Co^{2+}, Ni^{2+}, Pd^{2+}, Pb^{2+}, Mn^{2+}, Bi^{3+}, Al^{3+}, K^{+}, Sn^{2+}, Cr^{6+}, and Ag^{+}.* These previous studies do not involve any specific surface modification. However, we want to modify the surface in an attempt to enhance the sensing ability of the CDs for metal ions. For example, modifying the surface with crown ether molecules should have an impact on the sensing of alkali metal ions.

*M. Li et al. *ACS Sens.* **2019**, *4*, 1732-1748.

Spectroscopic Characterization

For our initial recipe for the CD synthesis, we used citric acid (CA) as the carbon source and urea as the nitrogen source. After the CD preparation, we used UV-vis spectroscopy and fluorescence spectroscopy to characterize the unique spectral properties of the CDs.

Starting Materials:



citric acid urea

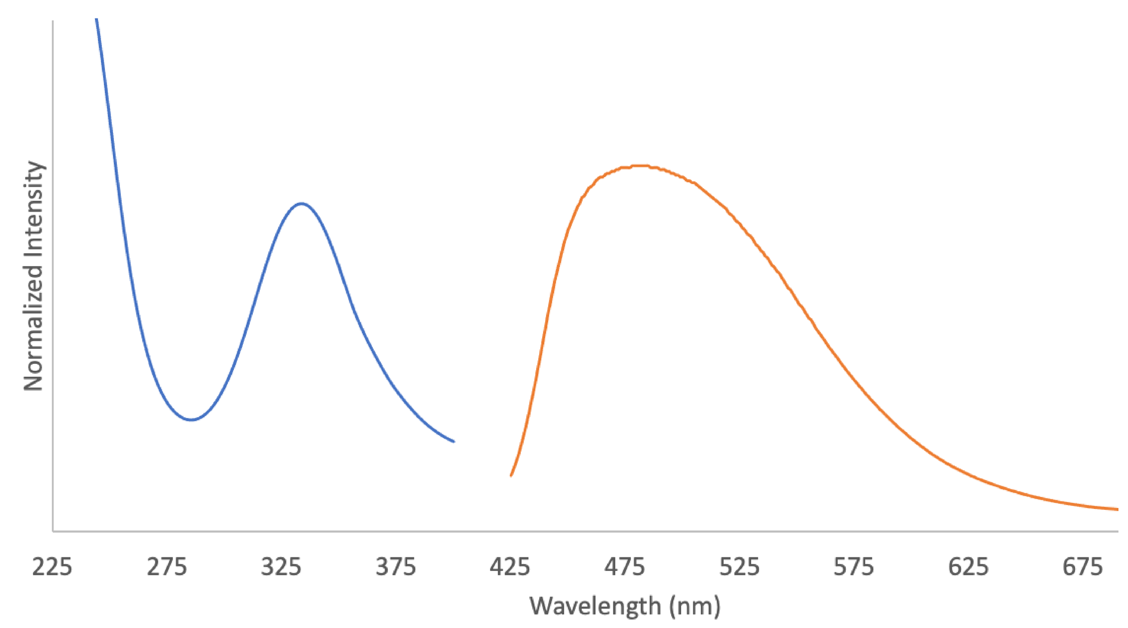
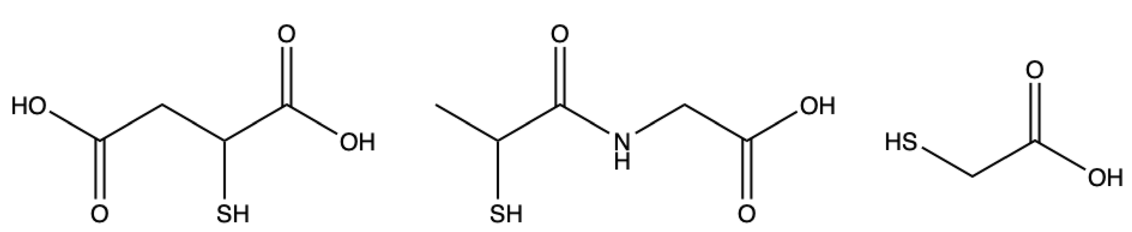
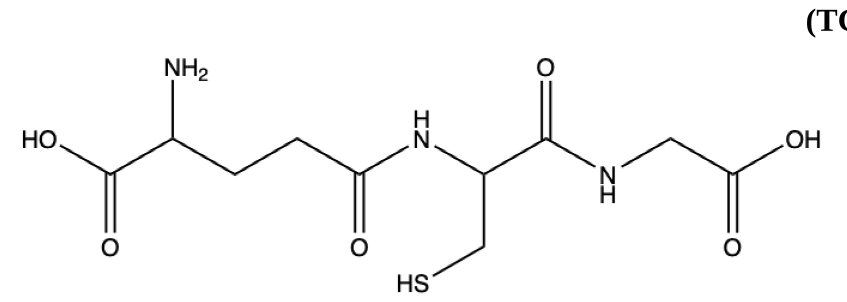


Figure. UV-vis (blue) and fluorescence (orange, λ_{EXC} = 360 nm) spectra of CA-CDs (nitrogen source = urea).

We investigated what would happen if we used water-soluble thiols as the carbon source for the CD synthesis.



mercaptosuccinic acid (MSA) tiopronin (TIO) thioglycolic acid (TGA)



glutathione (GLU)

Thiol	Abs. λ_{MAX}	Em. λ_{MAX}
MSA	281 nm	494 nm
GLU	319 nm	480 nm
TIO	321 nm	473 nm
TGA	324 nm	493 nm

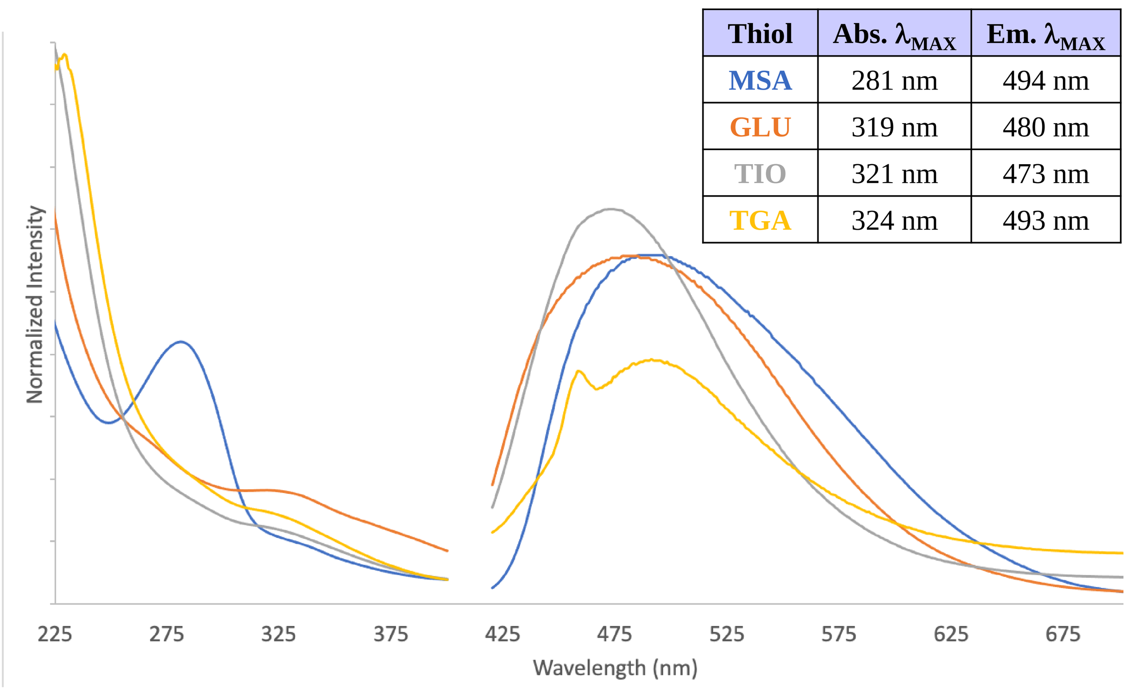


Figure. UV-vis (left) and fluorescence (right, λ_{EXC} = 360 nm) spectra of CDs prepared from urea and water-soluble thiols (MSA = blue, GLU = orange, TIO = gray, TGA = gold).

The absorbance and emission spectra of the thiol-based CDs show differing spectroscopic properties based on the thiol carbon source used. MSA- and TGA-CDs show a notable red-shift in the wavelength of maximum emission in comparison to the GLU- and TIO-CDs. We believe this shift to decrease the likelihood of self-quenching, which strengthens the fluorescence properties of the CDs. Also, the MSA-CDs displayed stronger absorption and fluorescence properties in comparison with the other thiol-based CDs.

Infrared Spectroscopy

We used attenuated total reflectance Fourier Transform infrared (ATR-FTIR) spectroscopy to characterize the CD surface. The types of functional groups that are present on the CD surface can be determined using this analytical technique.

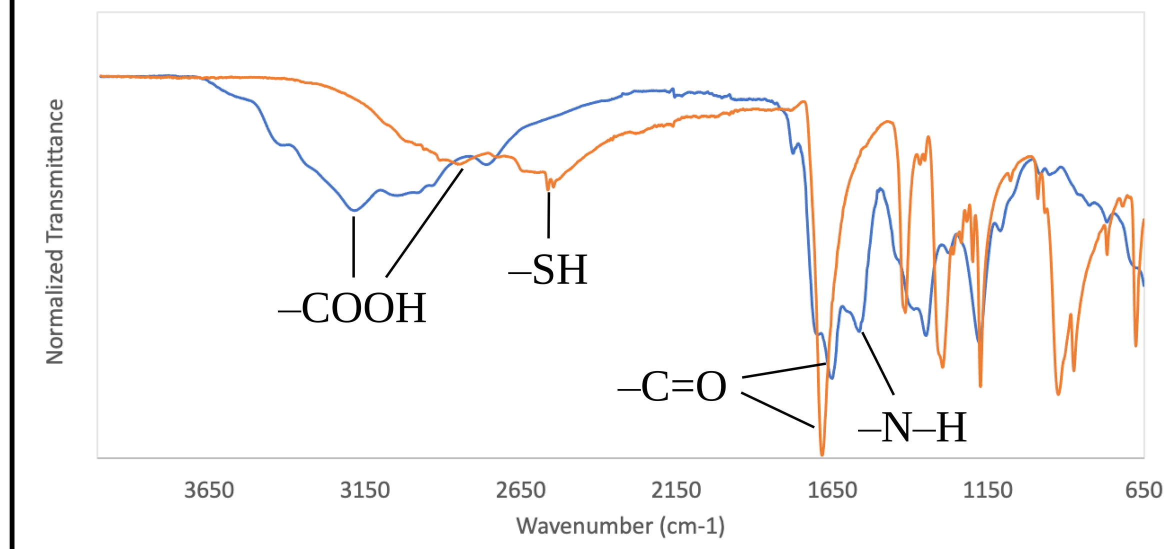


Figure. ATR-FTIR spectra of MSA-CDs (blue) and MSA (orange), annotated with functional group assignments.

Investigations Based on pH

We are interested in knowing how CDs behave under different pH conditions. In particular, how they perform at the physiological pH range (7.35-7.45) is of interest to us for sensing capabilities. The CDs have stable fluorescence properties in the pH range of 3-12. A significant decrease in fluorescence was observed outside of this pH range.

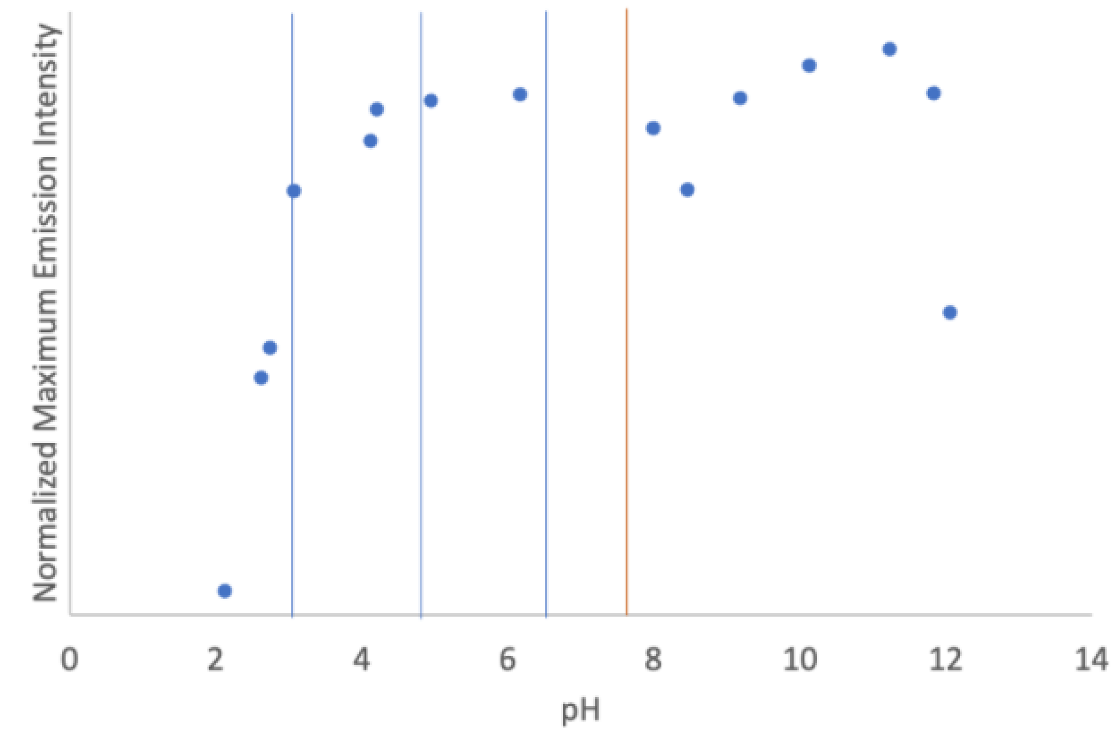


Figure. Impact of pH on fluorescence properties of CA-CDs (nitrogen source = ethylenediamine). Blue lines are pK_a values for citric acid; the orange line is physiological pH.

Further analysis of the CDs with respect to pH shows that at acidic pH values, the wavelength of maximum emission red-shifts with increasing acidity. We observed changes in spectral properties based on a change in the pH of the CDs. Thus, we see that these CDs have the ability to behave as pH sensors (to some degree).

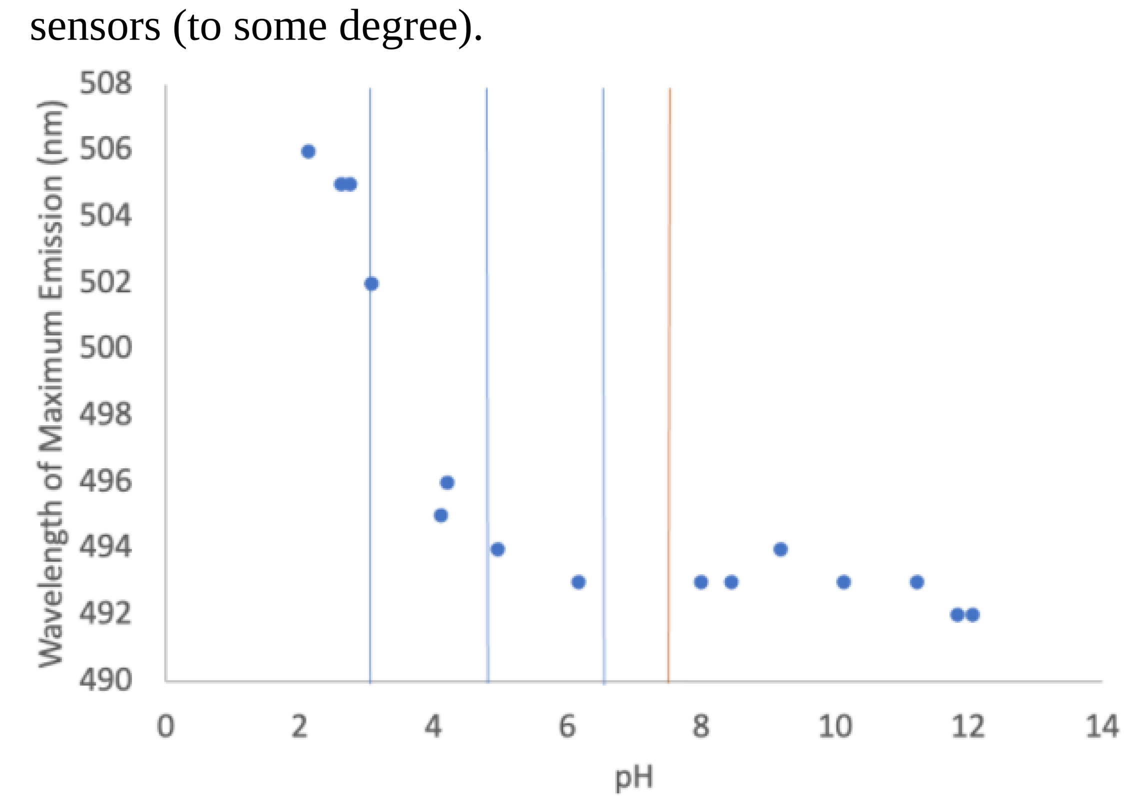
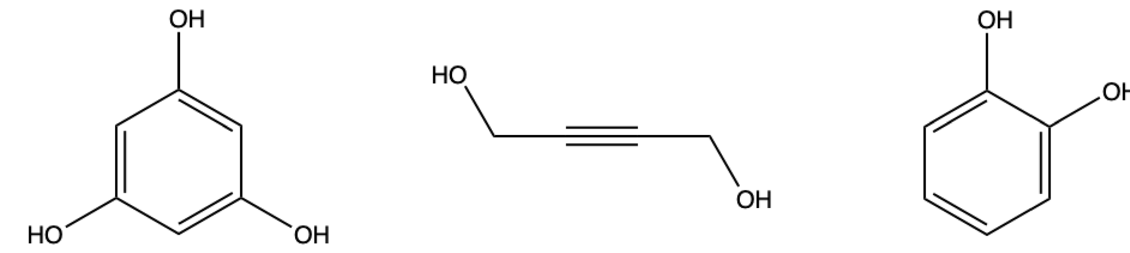


Figure. CA-CDs behaving as a pH sensor.

Cross-Linking of CDs

We attached different molecules to the CD surface by using simple amide and ester coupling chemistry. We made attempts to cross-link the CDs using alcohol-containing molecules with some degree of planarity and/or rigidity.



phloroglucinol (PGL) 2-butyne-1,4-diol (BDL) catechol

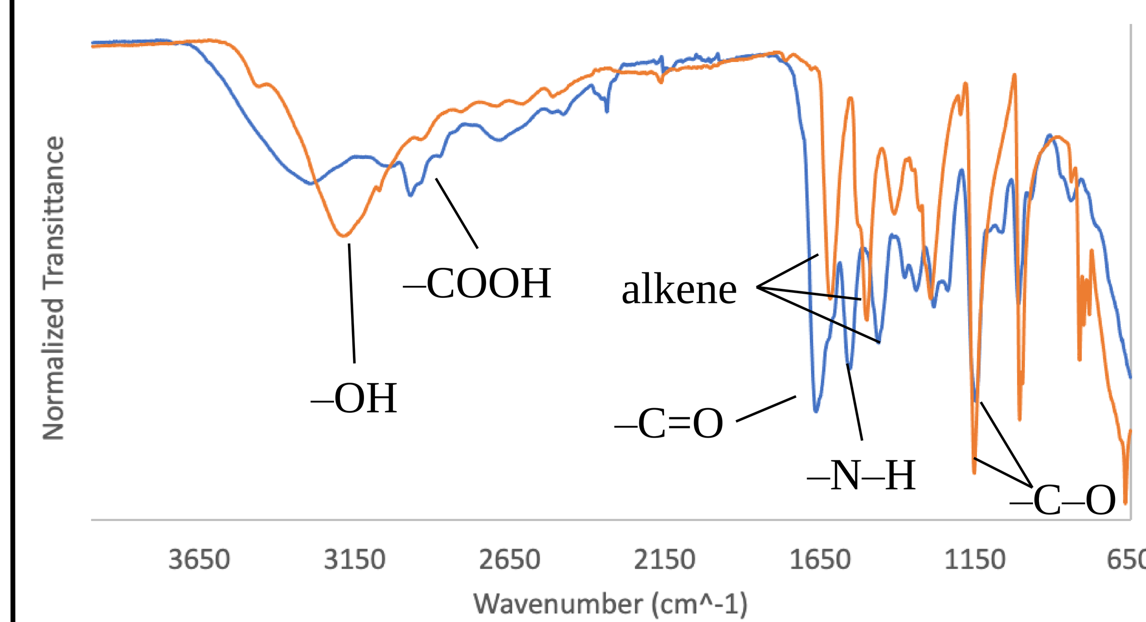


Figure. ATR-FTIR spectra of cross-linked MSA-CDs with PGL (blue) and free PGL (orange).

The cross-linked CDs were characterized using UV-vis and fluorescence spectroscopy to determine what impact the modification had on the spectral properties of the CDs. From the spectral analysis, it appears that the modification has enhanced the spectral clarity of the CDs (i.e., the emission peaks are narrower).

Cross-linker	Abs. λ_{MAX}	Em. λ_{MAX}
catechol	271 nm	500 nm
PGL	243 nm	499 nm
BDL	287 nm	493 nm
none	281 nm	490 nm

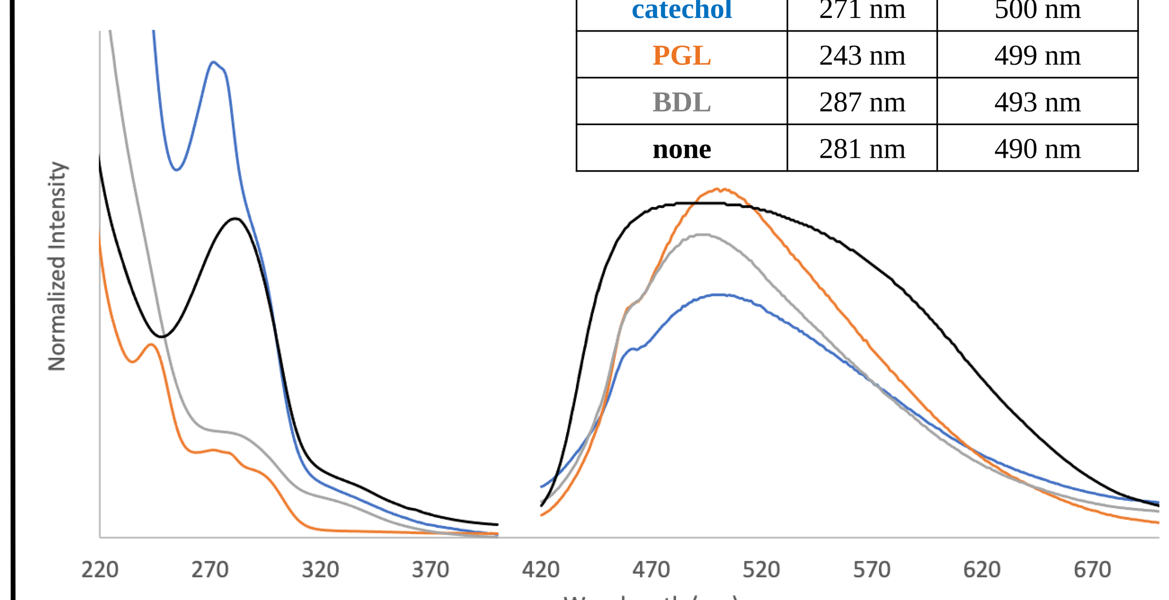


Figure. UV-vis (left) and fluorescence (right, λ_{EXC} = 360 nm) spectra of cross-linked MSA-CDs (catechol = blue, PGL = orange, BDL = gray, no cross-linker = black).

Future Directions

Our future research plans for this project include:

- Refining our surface modification process
- Refining our characterization of the nanomaterials
- Investigating the sensing properties for metal ions
- Investigating the electrochemical properties of the CDs

Acknowledgments & Group Members

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