

Abstract

The goal of this research was to determine whether functionalized gold nanoparticles can be useful as a sensitive residential fluorescent sensor for lead contamination in drinking water. In the future, such nanoparticles could be dispersed into a membrane visible through a window inside a household tap filter. A large body of work exists in the literature concerning use of gold nanoparticles to detect lead. Almost all of these depend on a visible color shift, which is less sensitive compared to fluorescence and can confuse the consumer.

Background and Motivations

Gold Nanoparticles were chosen as sensors because of:

1. Surface Plasmon Resonance

Electrons on GNP surface oscillate in resonance with incident light. Wavelength of oscillations subject to change do to changes in:

- The dielectric constant of the solvent
- The diameter of the nanoparticles
- Aggregation

2. Fluorescent Capabilities

5 and 10 nm citrate coated GNPs shown to fluoresce [1]

Literature Motivations

MUA-GNPs have been shown to exhibit a colorimetric response when exposed to lead in water, as shown by Kim et al. [2]

This method yields a color change from red to purple upon addition of lead, and is reversible with the addition of Ethylenediaminetetraacetic acid (EDTA)

MUA-GNPs have also been shown by Huang et al to exhibit a fluorimetric response upon addition of mercury II. [3] This method is highly selective towards Hg^{2+} with the addition of pyridine-2,6-dicarboxylic acid (PDCA).

Methods

3D excitation emission matrix spectroscopy (EEMS) were used to analyze and compare samples of MUA-GNPs at varying concentrations with samples of MUA-GNPs with varying concentrations of Pb^{2+} .

All samples were corrected for the Raman spectrum of water and Inner Filtering Effects (IFE) via a MatLab script. Tucker et al [4] provides a method for correcting for IFE via equations 1 and 2.

$$f_{prim} = \frac{F_{corr}}{F_{obs}} = \frac{2.303A(y-x)}{10^{-Ax} - 10^{-Ay}} \quad (1)$$

$$f_{sec} = \frac{F_{corr}}{F_{obs}} = \frac{(v-u)/\left(\frac{1}{b}\right)\ln(T)}{T_{at v} - T_{at u}} \quad (2)$$

Where u and v are the dimensions of the interrogation zone, and T is the transmittance of the sample, obtained from UV-Vis.

EEMs and 2D

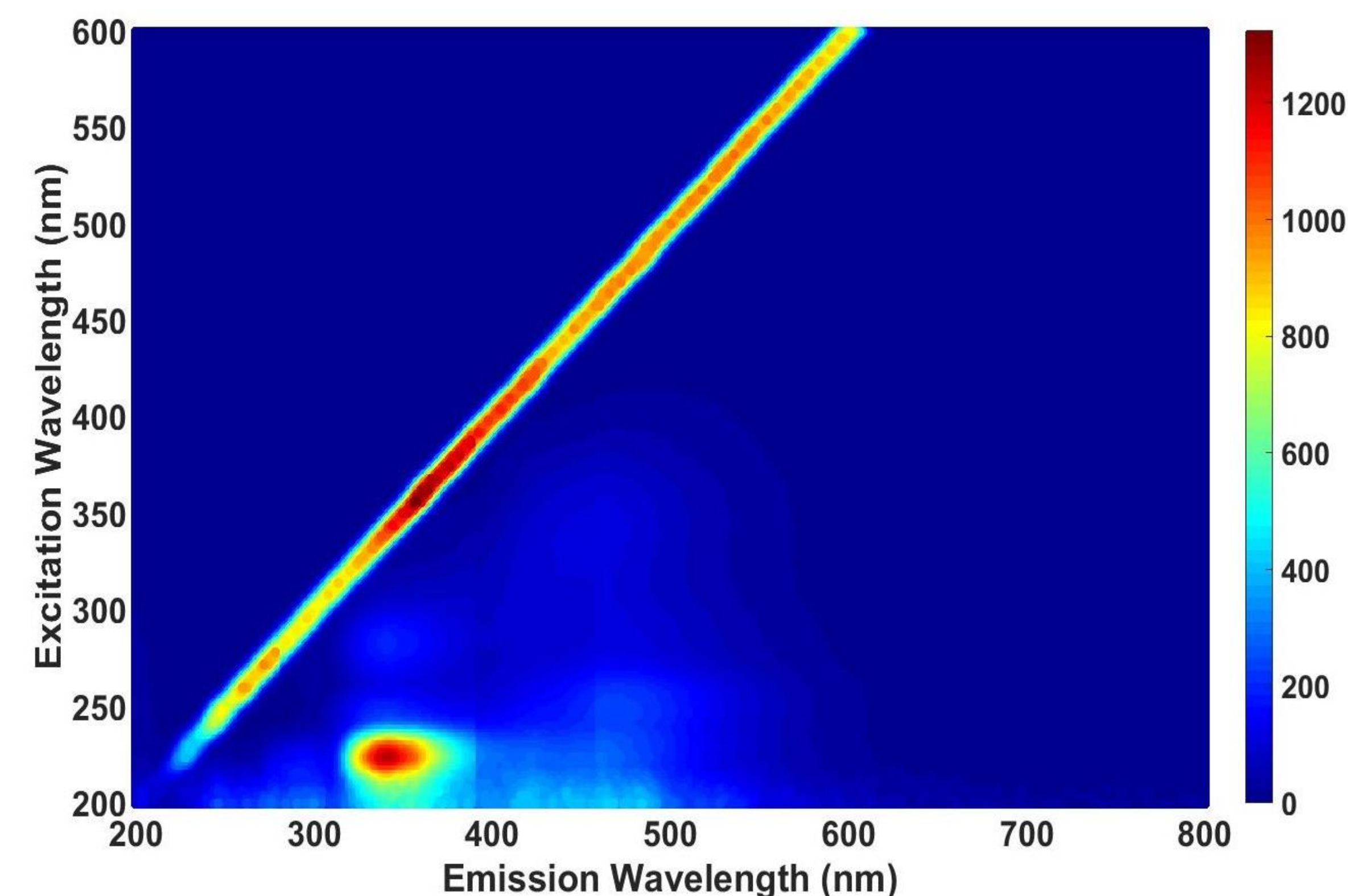


Figure 1: 5 nm MUA-GNPs at a concentration of 11.375 $\mu\text{g/mL}$

Because determination of enhancement/quenching proved difficult from the 3D maps, 2D spectra of the MUA-GNPs with Pb^{2+} were obtained from the 3D maps and compared to a predicted intensity spectrum to determine whether the sample was quenched or enhanced. Predicted spectra are obtained via the following equation:

$$\text{Predicted Intensity} = \text{Intensity}_{\text{MUA-GNP}} + \text{Intensity}_{\text{Pb}^{2+}}$$

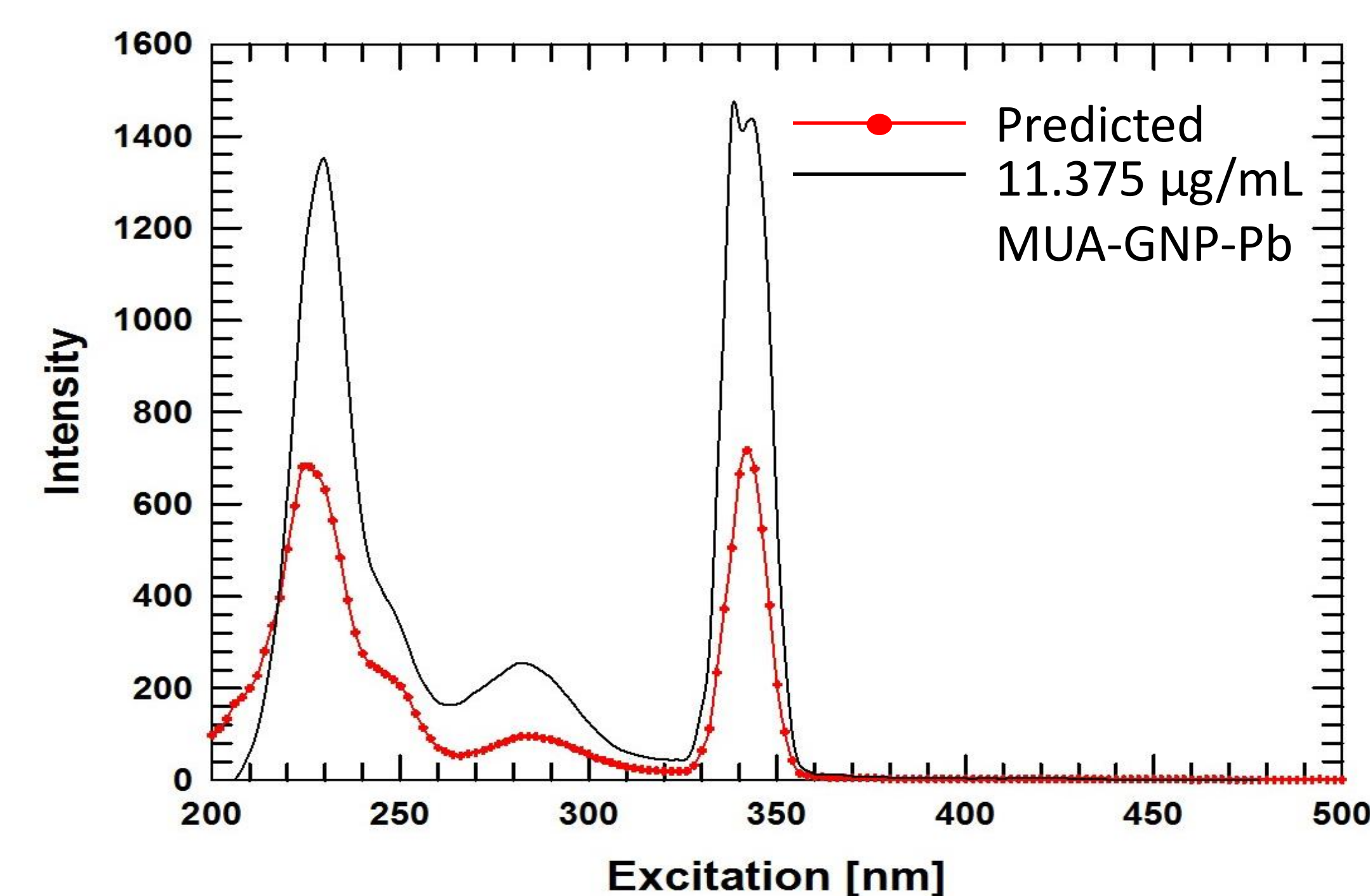
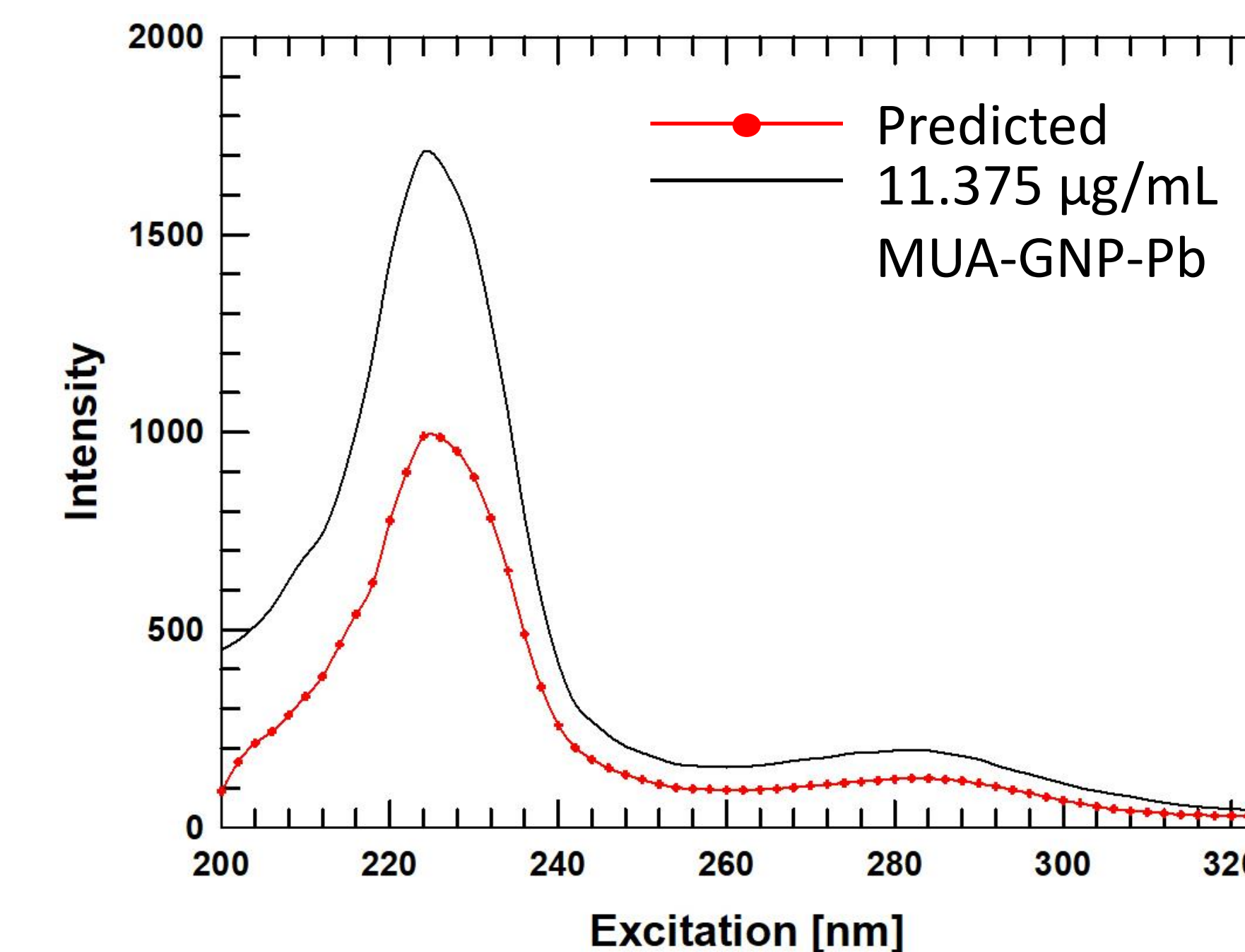
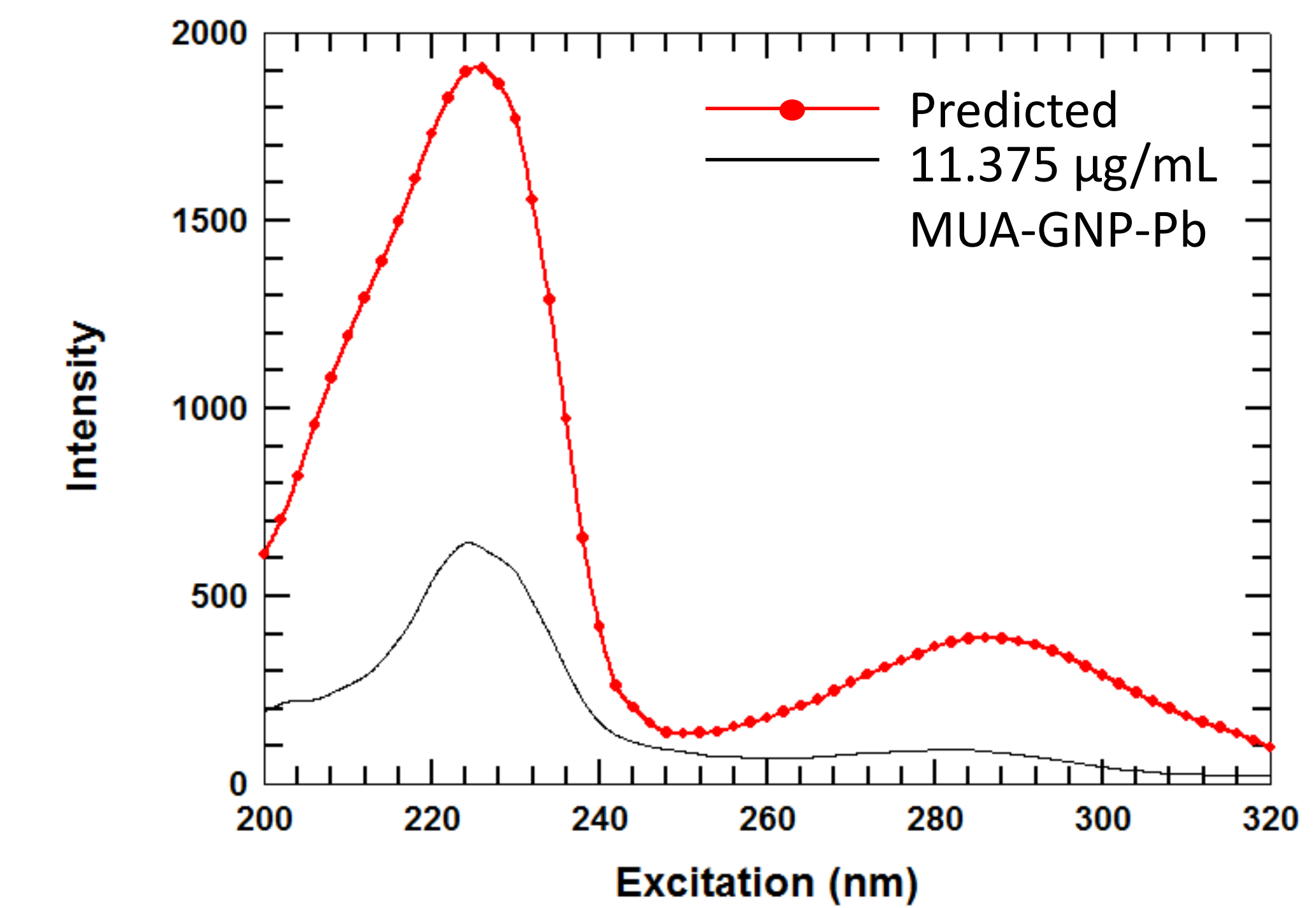
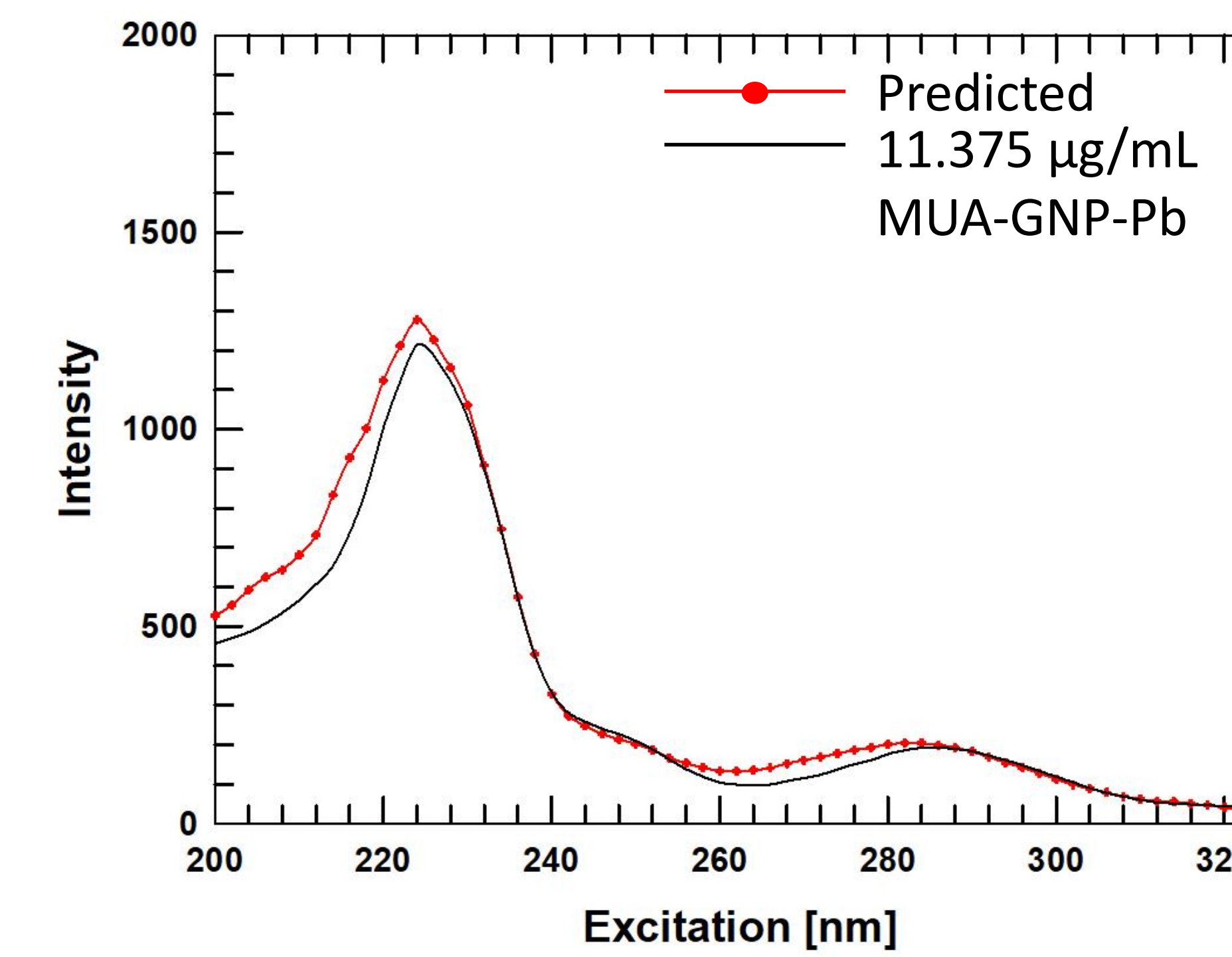


Fig 2: 2D Map (EX = 342 nm) of MUA-GNPs at 11.375 $\mu\text{g/mL}$ with 15 $\mu\text{g/L}$ Pb^{2+}



These tests were all done with a concentration of 11.375 $\mu\text{g/mL}$ MUA-GNP in a solution with 100 $\mu\text{g/mL}$ Pb^{2+} . These graphs show a “predicted” curve, which would be the fluorescent intensity in the case that lead and MUA-GNP’s did not interact, and a “MUA-GNP-Pb” curve, which is the experimental fluorescence results obtained. The three graphs show all three possible outcomes of fluorescence: enhancing, quenching, and no change.

Conclusion and Future Work

From the 2D spectra, it appears that functionalized gold nanoparticles can interact with the lead ions in water, and cause a change in the predicted fluorescence. Other concentrations of MUA-GNP’s were tested, and received similar results to the above graphs. We believe the intensity differences could result from the lead ions changing the state of aggregation of the GNPs, and therefore could affect the distance at which the ion itself is adsorbed to the surface. It’s possible that the MUA-GNP’s aggregated differently between the tests, which could lead to different fluorescent results, even when testing the same concentration. Further testing is being done using dynamic light scattering (DLS) to study how differences in aggregation could possibly affect the fluorescence of the gold nanoparticles before and after interaction with lead, and if aggregates are forming in a time-dependent manner. Further testing will also be done to find an optimum concentration of MUA-GNP and Pb^{2+} such that the intensity which results from addition of lead can be predicted. Once this is achieved, selectivity testing needs to be conducted, as well as nanoparticle incorporation into a membrane.

References:

- 1) Esfahani, Milad Rabbani, Vasanta L. Pallem, Holly A. Stretz, and Martha J. M. Wells. “Extinction, Emission, and Scattering Spectroscopy of 5–50 Nm Citrate-Coated Gold Nanoparticles: An Argument for Curvature Effects on Aggregation.” v
- 2) Kim, Youngjin, Robert C. Johnson, and Joseph T. Hupp. “Gold Nanoparticle-Based Sensing of ‘Spectroscopically Silent’ Heavy Metal Ions.”
- 3) Huang, Chih-Ching, Zusing Yang, Kun-Hong Lee, and Huan-Tsung Chang. “Synthesis of Highly Fluorescent Gold Nanoparticles for Sensing Mercury(II).”
- 4) Tucker, Sheryl A., Vicki L. Amszi, and William E. Acree. “Primary and Secondary Inner Filtering. Effect of $K_2Cr_2O_7$ on Fluorescence Emission Intensities of Quinine Sulfate.”