

# SYNTHESIS OF A HIGHLY SELECTIVE AND SENSITIVE ALUMINUM SENSOR IN A WEAK ACID AQUEOUS MEDIUM.

**Middlesex County College, Edison, NJ**

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**CHM-240**

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## Abstract:

*The purpose of this research project was to replicate the synthesis and test for the effectiveness of an  $Al^{3+}$  chemical sensor under weak, acidic, aqueous conditions. Aluminum has been shown to effectively bind to two sites on the sensor, 4-(8'-hydroxyquinolin-5'-yl)methyleneimino-1-phenyl-2,3-dimethyl-5-pyazole, in order to draw the lone pair of electrons on the nitrogen away from the chromophore sites to release luminescent emission energy that is then measured to detect the presence of  $Al^{3+}$ . This chemical sensor's viability was then tested under various conditions, including different concentrations of ions and under the presence of different metal ions with varying charges. Findings were consistent with the proposed chelation enhanced luminescence phenomena that was reported in the literature. Measurable quantitative differences were found upon the addition of  $Al^{3+}$ , no matter which ion was contaminating the solution at the time. All work was completed, synthesized, and tested at Middlesex County College's chemistry laboratories. This includes the use of various measurement devices, including Nuclear Magnetic Resonance Spectroscopy, Ultraviolet Visible Spectroscopy, Fluorescent Emission Spectroscopy, and of course, other devices used to prepare the sensor, including a rotary evaporator and the use of column chromatography. This experiment was first conducted by X. Jiang, B. W. et. Al. (2011). 8-hydroxyquinoline-5-carbaldehyde schiff-base as a highly selective and sensitive  $Al^{3+}$  sensor in weak acid aqueous medium. *Inorganic Chemistry Communications* 14, 1224-1227*

## Introduction:

Aluminum is one of the **most** abundant elements in the earth's crust. It has an extremely wide range of various applications, including, but not limited to, beverage cans, foil, auto parts, home construction, sewage cleanup, and electrical wires. During 2009, there were 3.4 million tons of aluminum generated in the United States **alone**<sup>1</sup>. Because of this, Aluminum waste can be found all over the environment, including ground soil, bodies of water, even acid rain. Aluminum pollution is hazardous to human health as it has severe toxicity in the central nervous system and greatly affects the enzyme activity of the gastrointestinal tract<sup>23</sup>.

According to the World Health Organization, an average daily intake of 7mg/kg of  $Al^{3+}$  and the tolerable weekly dietary intake of 7mg/kg can be ingested. Concentrations of  $Al^{3+}$  that

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<sup>1</sup> (Keep America Beautiful, Inc., 2013)

<sup>2</sup> (D.G. Weller, 2010)

<sup>3</sup> (D. P. Perl, 1980)

exceeds the WHO recommendations can cause renal failure, idiopathic Parkinson's disease, impairment of memory, Alzheimer's disease, bone softening, vitamin deficiencies, cancer, and smoking related illnesses<sup>4567</sup>. Humans are not the only species that are affected by aluminum toxicity. Toxicity also endangers freshwater fish and influences agricultural production in acidic soil with a pH of less than 5.5<sup>8910</sup>. Because Aluminum is highly soluble in acidic mediums, it was found to be even more toxic due to increased concentration of Al<sup>3+</sup> ions<sup>11</sup>.

The emergence of Al<sup>3+</sup>, its health hazards, and its vital role in civilization requires effective monitoring of possible pollution sites and it requires faster methods of identifying toxicity in order to expedite treatment. In order to complete these two tasks effectively, a chemical "sensor" needs to be synthesized that is able to detect minute Aluminum ion concentrations in a medium that is analogous to ground soil. Luminescent molecules are preferred chemical sensors due to their ability to change an inherent observable property in the presence of their substrate metal ion. This observable property, or luminescence, is relatively harmless to humans as well as to other species such as fish, plants, and other animals. Quantitative analysis of the sensor's ability to detect Al<sup>3+</sup> is to be measured through the altered intensity of luminescence in the presence of varying concentrations of Al<sup>3+</sup>.

Luminescent sensors are generally based on a few phenomenon. These include intramolecular charge transfer (ICT)<sup>12</sup>, photo-induced electron transfer (PET)<sup>13</sup>, chelation-enhanced luminescence (CHEL)<sup>14</sup>, luminescence resonance energy transfer (FRET)<sup>15</sup>, and excited state intramolecular proton transfer (ESIPT)<sup>16</sup>. A single method of luminescence cannot meet the requirements needed to create an effective, selective, and specific sensor for Aluminum that varies in intensity based solely on concentration. Therefore, the sensor that was synthesized utilizes photo-induced electron transfer as well as chelation enhanced luminescence to detect the presence of aluminum.

Due to the photo-induced electron transfer phenomenon, or PET, the sensor molecule **4-(8'-hydroxyquinolin-5'-yl)methyleneimino-1-phenyl-2,3-dimethyl-5-pyazole** has a natural

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<sup>4</sup> (Polizzi, 2006)

<sup>5</sup> (Walton, 2006)

<sup>6</sup> (Altschuler, 1999)

<sup>7</sup> (B. Wang, 2010)

<sup>8</sup> (L. V. Kochian, 2004)

<sup>9</sup> (Yang, 2006)

<sup>10</sup> (Witters, 1996)

<sup>11</sup> (Poléo, 1997)

<sup>12</sup> (W. Y. Lin, 2009)

<sup>13</sup> (Y. Fujikawa, 2008)

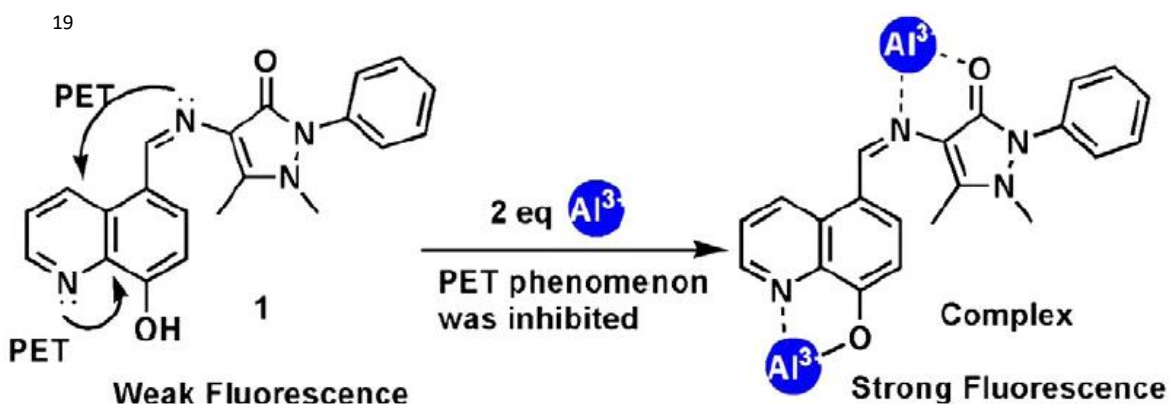
<sup>14</sup> (N. C. Lim, 2005)

<sup>15</sup> (C.Y. Li, 2013)

<sup>16</sup> (K.C. Tang, 2011)

luminescence that is effectively quenched due to the presence of lone pairs of electrons on the Nitrogen atoms which are able to transfer to the two chromophore sites in order to lock away the emission energy of the molecule. There is still some luminescence produced, but the net effect is a decrease in natural luminescence. This molecular state is necessary, and by extension, this phenomena is necessary to prevent maximum luminescence without the presence of its substrate<sup>17</sup>.

When the sensor is in the presence of  $Al^{3+}$ , it is able to undergo the Chelation Enhanced Luminescence. In this case, the  $Al^{3+}$  acts as a lewis acid and draws the electron density away from the specific chromophore site it has bonded to, and it places the electron density onto itself to free up the emission energy of the sensor molecule. This allows the luminescent intensity of the molecule to increase and the emission energy to be freely emitted.<sup>18</sup>



In order to show the presence of aluminum, the sensor has to be hit with light in the ultraviolet region. This energy rich light excites the electrons of the chromophore and propels them from the highest occupied molecular orbital ( $n$ ) into the lowest unoccupied molecular orbital ( $n+1$ ). As the electrons revert back into their original orbital (HOMO or  $n$ ), they emit a photon with a longer wavelength and lower energy that places it into the visible light region, allowing us to view it as luminescence. The reason why nitrogen's lone pair of electrons are required to stay away from the site in order to unlock the sensor's emission energy is because the extra electrons would be occupying the next orbital, or  $n+1$  orbital, the same orbital that the electrons in HOMO would be traveling to (LUMO). Because the  $n+1$  orbital is occupied, the

<sup>17</sup> (X. Jiang, 2011)

<sup>18</sup> (X. Jiang, 2011)

<sup>19</sup> (X. Jiang, 2011)

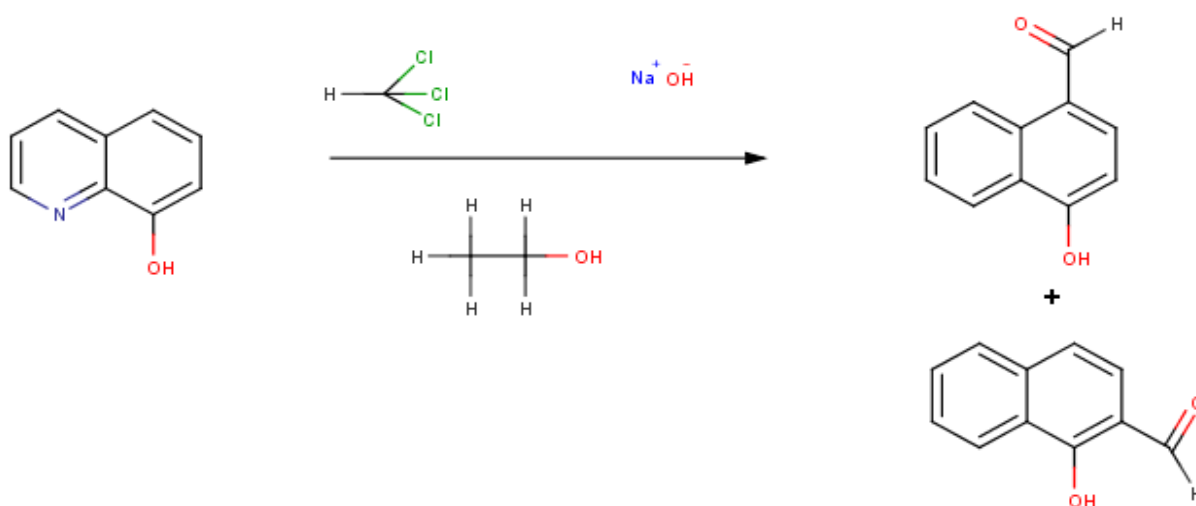
electrons in HOMO would need **even more** energy to reach the  $n+2$  orbital, than it would need to reach the  $n+1$  had the  $n+1$  orbital been empty. Light in the UV region is not able to provide that amount of energy that is required by the electrons to jump to  $n+2$ , therefore the electrons never go into a higher orbital, and as a result they cannot lose energy in order to emit any photons. Thus we have a quenched molecule with limited luminescent ability.

## Synthesis:

### Materials:

All chemicals were purchased from Sigma-Aldrich and used without further purification. The metal ions were dissolved in their salt forms. Distilled water was used throughout the experimentation.  $^1\text{H}$  NMR spectra was gathered using the in house NMR spectrometer. A UV-vis spectrum was gathered using the in house spectrophotometer using quartz cuvettes of 1 cm path length. Fluorescence spectrum was gathered using an in house oil plate fluorescent spectrometer.

## Synthesis: Part I HQ5A (8-hydroxyquinoline-5-carbaldehyde)



The method with which to synthesize the 8-hydroxyquinoline-5-carbaldehyde was to utilize the classic Reimer-Tiemann reaction<sup>20</sup> and react the 8-hydroxyquinoline with NaOH and chloroform to formulate an aldehyde group in the ortho or para position to the hydroxyl group on the 8-HQ.<sup>21</sup>

1. 14.5g (0.1 mol) of 8-Hydroxyquinoline was gathered and placed in a 250-ml three-necked round bottomed flask and was dissolved in 60mL of EtOH.
2. 35g of NaOH was dissolved in 60mL of water and was added to the round bottomed flask. A yellow precipitate began to appear.
3. The solution was heated in order to dissolve the precipitate.
4. The solution was then refluxed while 32mL of chloroform was added drop-wise over 1 hour and it was refluxed continuously for 8 hours at 100°C.
5. The EtOH and any excess chloroform was distilled off. The remains were diluted with 200mL of water and poured into a 500mL beaker.
6. The solution was acidified slowly with 1M HCl to a pH of 4.1. A mass of brown precipitate formed.
7. This was then filtered, dried, and extracted with ether and ethyl acetate 1:1. The ether and ethyl acetate was then distilled off to get the crude product.

<sup>20</sup> (X. Jiang, 2011)

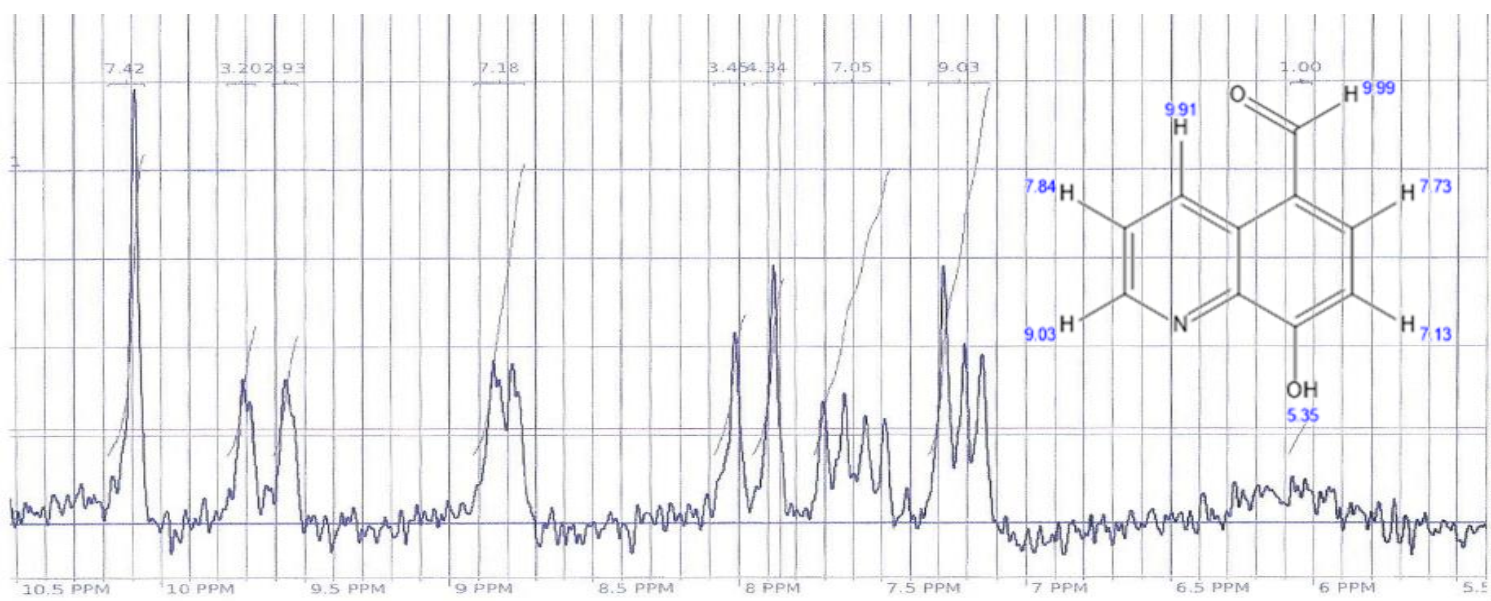
<sup>21</sup> (X. Jiang, 2011)

- This was then purified by column chromatography with dichloromethane to obtain the intermediate product, 8-hydroxyquinolin-5-carbaldehyde.
- The intermediate product was crystallized from dichloromethane and anhydrous methanol.<sup>22</sup>

HQ5A: Melting Point: 178-179°C, 1.12g, yield 6.49%.

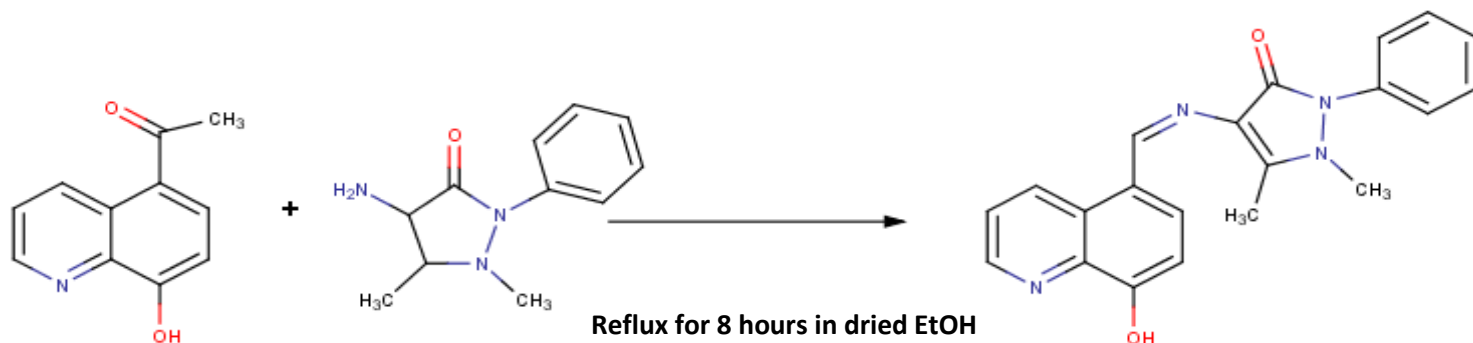
HQ7A: Melting Point: N/A, 0.0g, yield 0.00%.

### <sup>1</sup>H NMR Spectrum:



<sup>22</sup> (X. Jiang, 2011)

## Synthesis: Part II Sensor (4-(8'-hydroxyquinolin-5'-yl)methyleneimio-1-phenyl-2,3-dimethyl-5-pyazole)

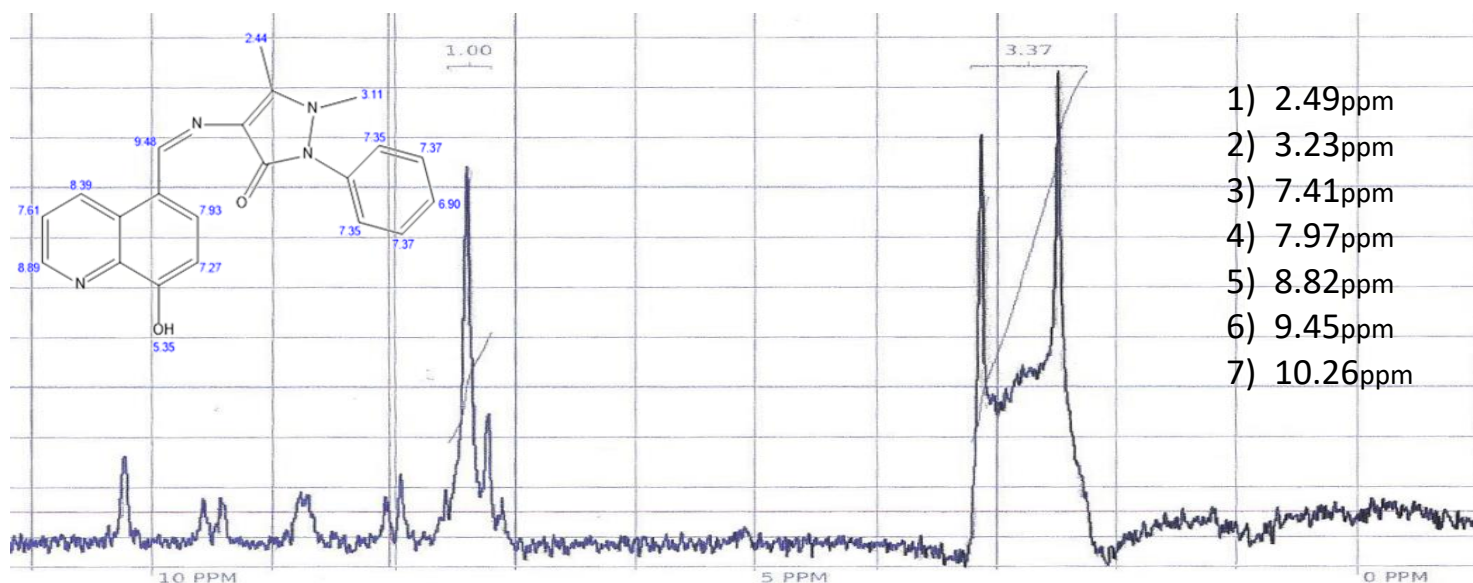


The mechanism used to synthesize the sensor 4-(8'-hydroxyquinolin-5'-yl)methyleneimio-1-phenyl-2,3-dimethyl-5-pyazole was by Schiff-base condensation of 8-hydroxyquinoline-5-carbaldehyde and 4-aminoantipyrine to couple the aldehyde on HQ5A with the amino group on the 4-aminoantipyrine. This reaction formulates the final molecule which will be our sensor.

1. 0.509g of 8-hydroxyquinoline-5-carbaldehyde was dissolved in 15mL of hot EtOH
2. 0.503g of 4-aminoantipyrine was dissolved in 5mL of EtOH.
3. The two solutions were then mixed together and refluxed for 8 hours with stirring.
4. Light yellow precipitate formed.
5. Mixture was filtered and dried under vacuum to obtain the final product.

Melting Point: 256-257°C, 0.401g, yield 46.62%

### <sup>1</sup>H NMR Spectrum:





## Testing Preparation:

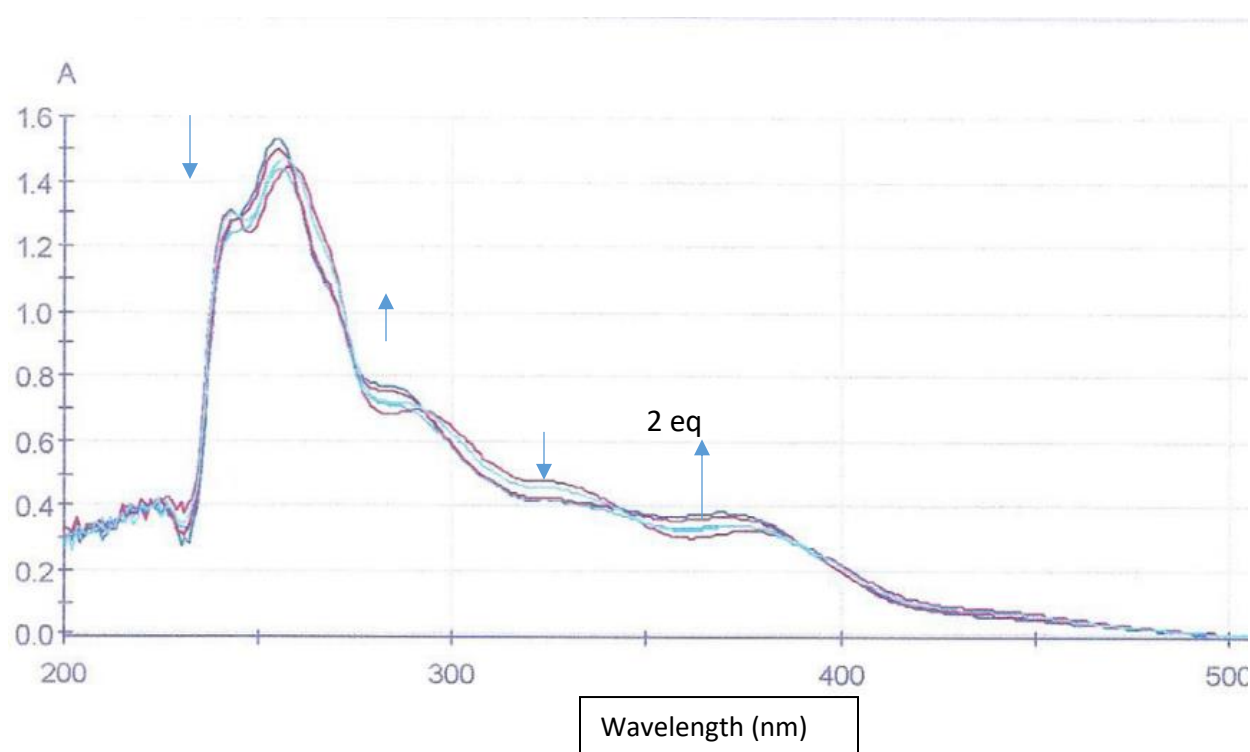
A 4.5 pH Acetate Buffer was first synthesized using Acetic Acid and Sodium Acetate. Using the Henderson-Hasselbalch equation, the buffer required 18.7g of NaOAc and 14.6mL of 6M HOAc to create a 250mL 4.5pH Acetate Buffer in water. This was used to simulate the weak acidic condition that is found in ground soil.

A 40uM of sensor in 1:9 MeOH and Acetate Buffer solution was created by first dissolving 5.6mg of the sensor in 10mL of MeOH, then extracting 6.39mL out of that solution and adding it to 8.61mL of MeOH, and adding 135mL of Acetate Buffer to make 150mL of 40uM sensor in 1:9 MeOH and OAc Buffer.

0.04M stock solutions of  $\text{Al}^{3+}$ ,  $\text{In}^{3+}$ ,  $\text{Zn}^{2+}$ , and  $\text{Fe}^{3+}$  in 1:9 MeOH and OAc Buffer were generated.

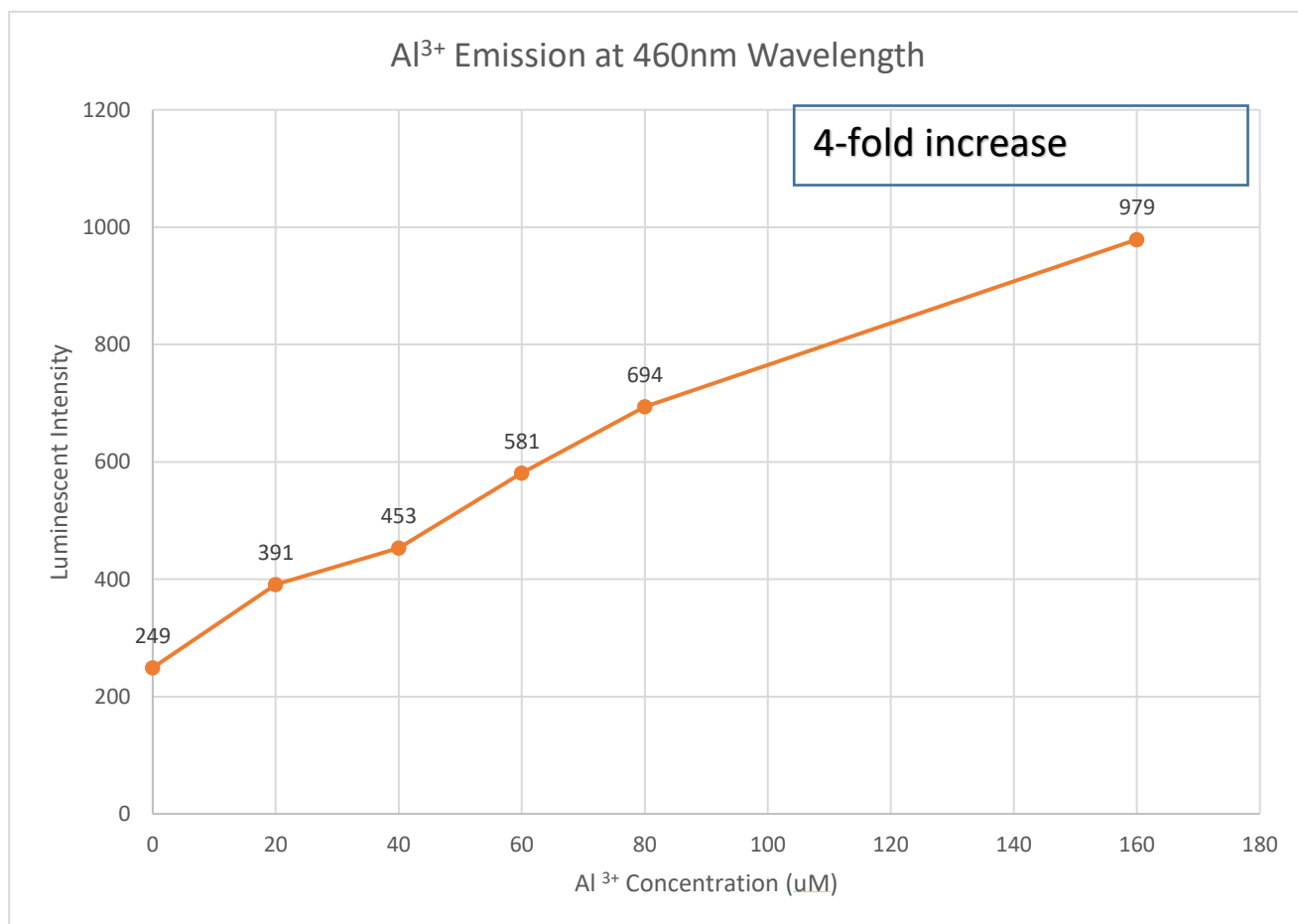
## Analysis:

The very first analysis that was performed was a UV-visible spectrum regarding the binding properties of the sensor with varying concentrations of  $\text{Al}^{3+}$  in a weak acidic and aqueous solution.



This spectrum was taken with a sensor solution at 40uM concentration and 5 varying concentrations of Al<sup>3+</sup>: 0.0eq (0uM), 0.5eq (20uM), 1.0eq (40uM), 1.5eq (60uM), and 2.0eq (80uM). According to the data, the absorbance bands at 270 nm, 287nm and 368 nm were enhanced and at 232nm, they were decreased in the UV-vis spectra. These findings are expected of any HQ-derived molecules when the hydroxyl group is deprotonated in order to allow the Al<sup>3+</sup>/sensor complex to exist<sup>23</sup>. The five isobestic points found at 242nm, 258nm, 271nm, 293nm, and 340nm indicate that a single complex exists in equilibrium. This spectrum also confirms the presence of a 1:2 complex of sensor and aluminum.<sup>24</sup>

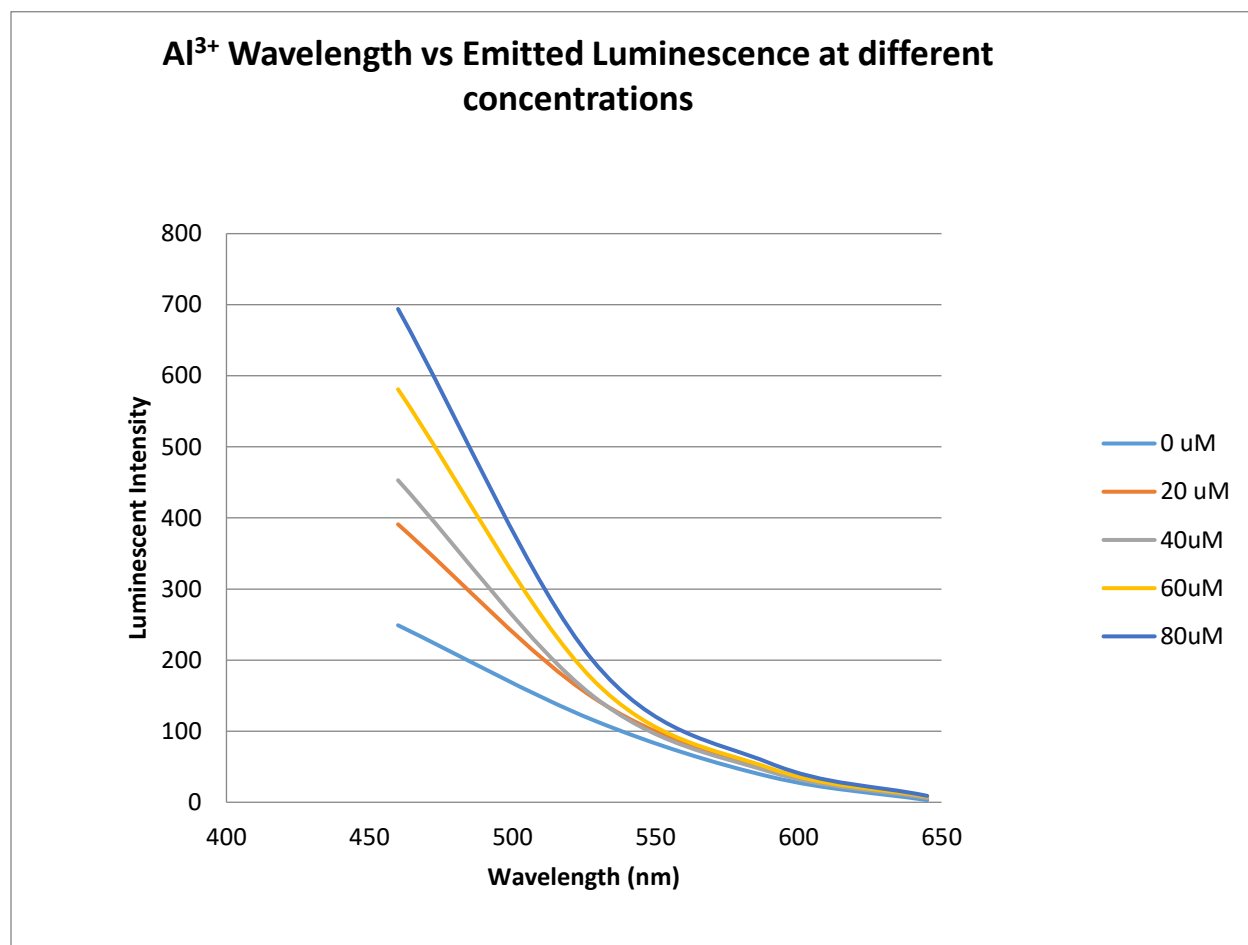
Fluorescence spectra was measured in an oil-plate fluorescent emission spectrometer with respect to the same 5 concentrations of Aluminum in the presence of 40uM of the sensor, as well as a saturated concentration of aluminum (160uM) in 40uM of sensor solution. Throughout all of the next emission spectrum tests, the molecule was excited at the 360 nm wavelength. For this first test, emission spectra was recorded at the 460 nm wavelength.



<sup>23</sup> (L. Xue, 2008)

<sup>24</sup> (X. Jiang, 2011)

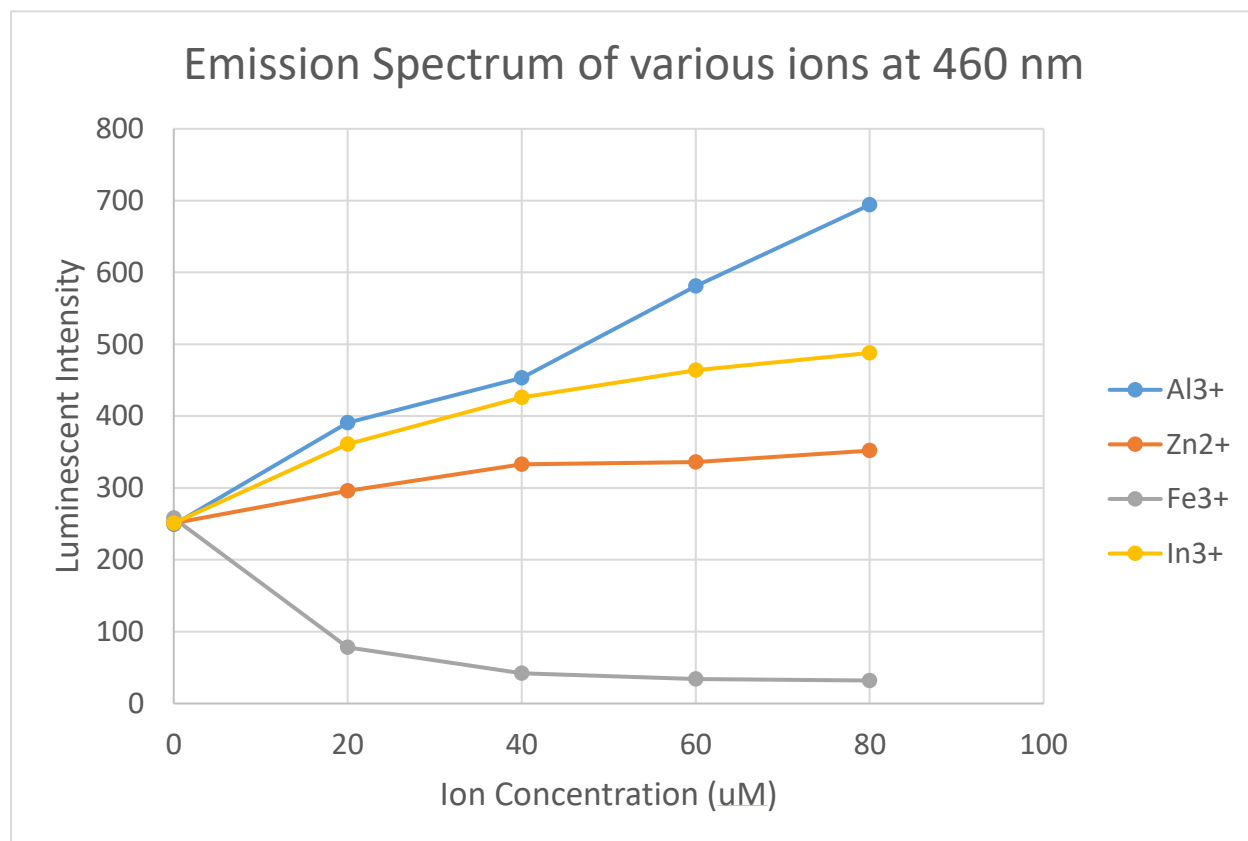
The luminescent intensity spectra shows what was expected all along. The increasing presence of  $\text{Al}^{3+}$  increases the luminescence intensity of the molecule almost 4-fold as the sensor becomes saturated with  $\text{Al}^{3+}$ . It is likely that 2 eq (80 $\mu\text{M}$ ) concentration of  $\text{Al}^{3+}$  was not enough to increase the luminescent intensity to its maximum potential because there may not have been enough time for all the  $\text{Al}^{3+}$  ions to bind to all of the available sites of the sensor. This hypothesis would need to be tested during any further experimentation. This same trend was also observed when measuring 528nm, 590nm and 645nm emission wavelength (suppl. 1-3).



The effect of different concentrations of  $\text{Al}^{3+}$  on the sensor's emission at different wavelengths were all measured to show that the most intense luminescence was observed at the 460nm wavelength. The nature of the graph suggests that 460nm emission is not the absolute most intense, only that it is the most intense that was able to be measured, given the tools at our disposal. It is very likely that the true wavelength in which the sensor gives off the

most intense luminescence is near the 400nm region according to this graph. This cannot be proven or tested without a fluorescence spectrometer that can measure emissions at wavelengths lower than 460nm. According to the literature, peak excitation was also reported to be 378nm. This is not an option at the Middlesex County College laboratories as the oil-plate fluorescent spectrometer device is only able to excite the molecule at 360nm.

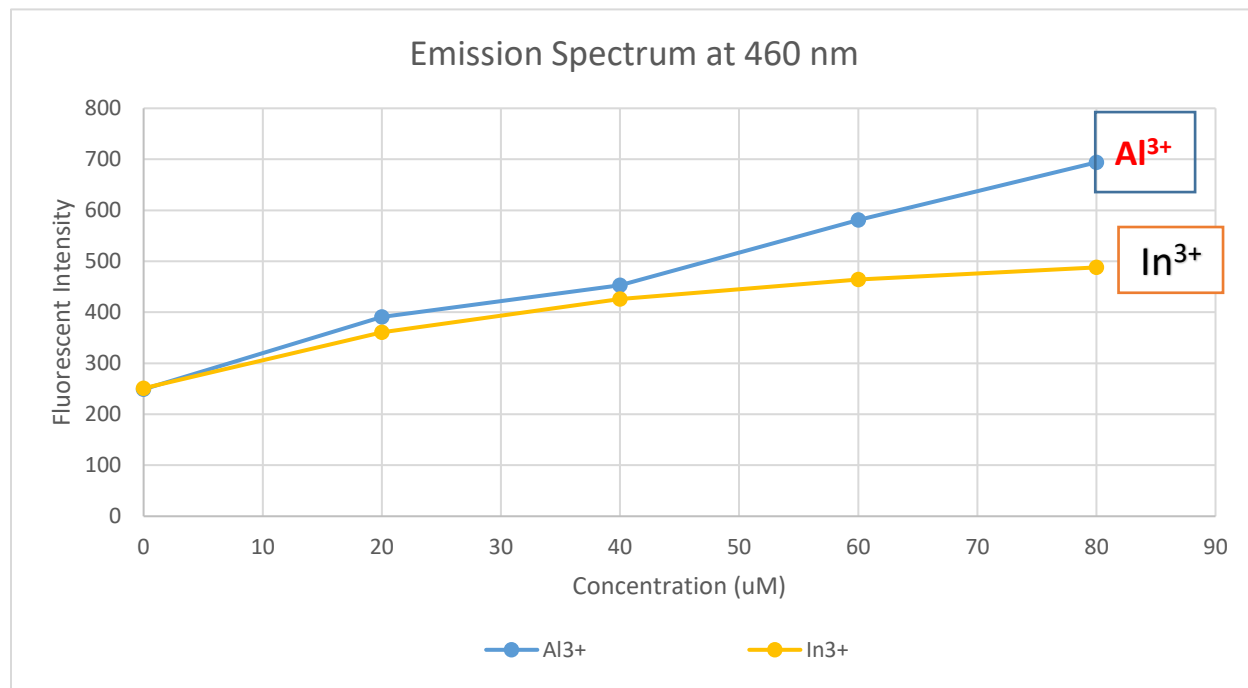
The specificity of the sensor was also measured. A sensor that is equally susceptible to ions other than aluminum would have little benefit in detecting aluminum in the environment.  $Zn^{2+}$ ,  $Fe^{3+}$ , and  $In^{3+}$  were all measured up against  $Al^{3+}$  to determine if the sensor can render a false positive due to the effect of another ion.



According to the data, it is clear that  $Al^{3+}$  is able to demand the most intense luminescence out of the sensor.  $Fe^{3+}$  quenches the sensor even more than the sensor was quenching itself. It is clearly acting more as a lewis base, quite possibly due to metal-to-ligand charge transfer phenomena. Its partially filled D orbital may also wish to get rid of its own electrons, thus pushing more electrons into the sensor's chromophores and locking away any emission energy.  $Zn^{2+}$ , on the other hand, seems to be able to increase the luminescence of the molecule by almost 2x at 2eq (80uM) concentration. This can be due to its full D orbital

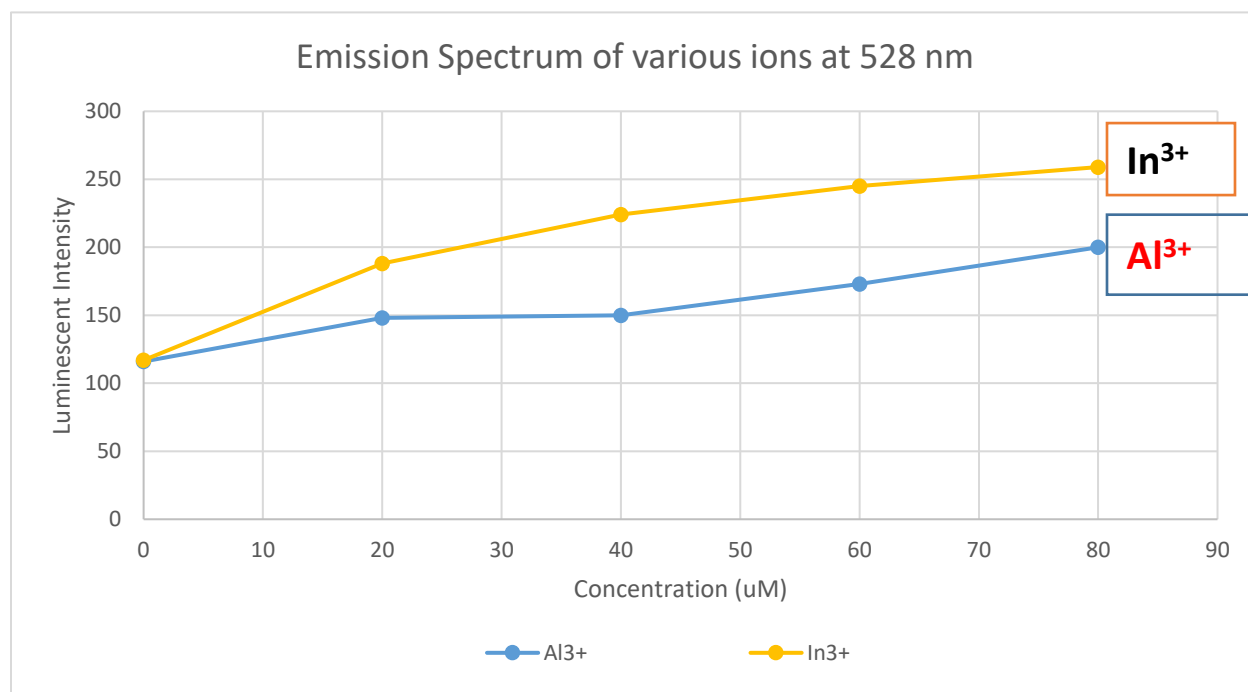
preventing the ion from giving away any electrons and its +2 charge which will naturally draw the electron density toward itself, but it still doesn't have as big an effect as the aluminum's +3 charge.

Due to its location on the periodic table (same group as  $\text{Al}^{3+}$ ), Indium was expected to have similar characteristics to Aluminum.



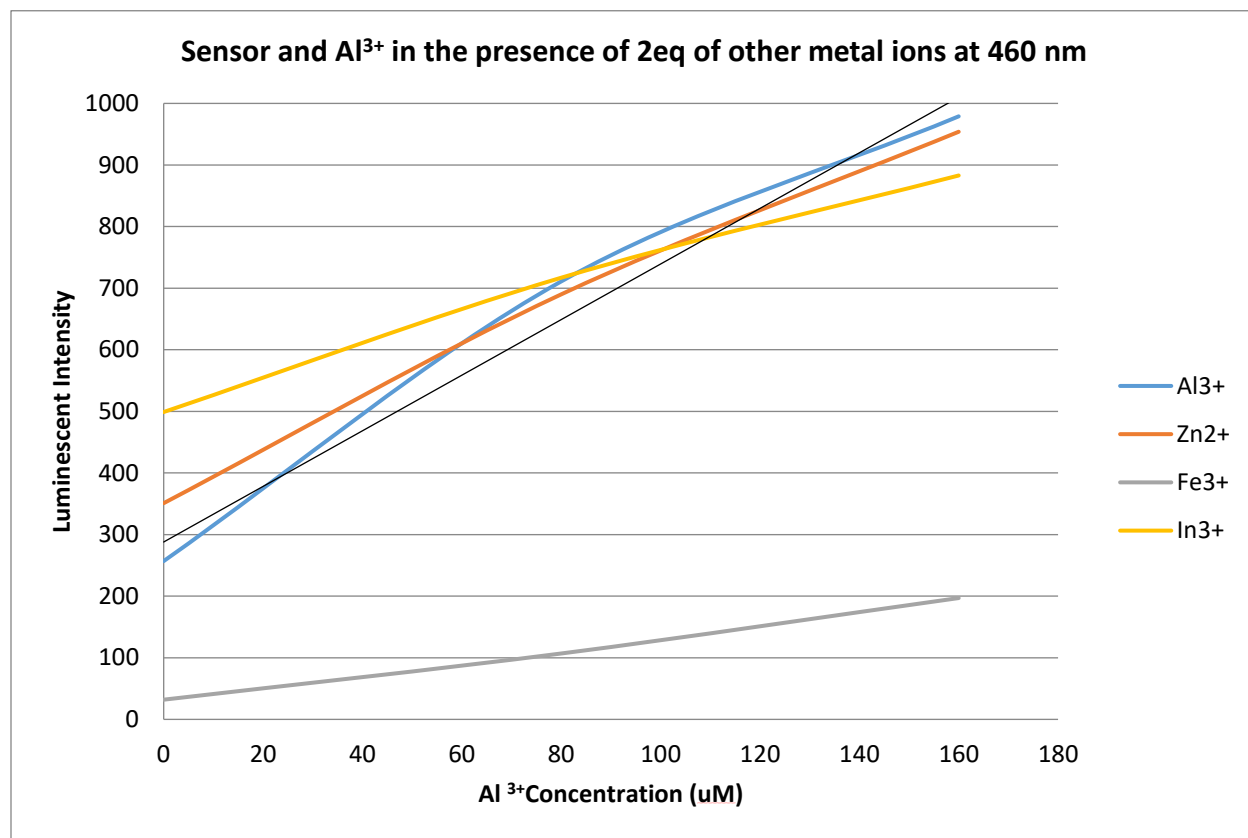
According to the data collected,  $\text{In}^{3+}$  is able to increase the luminescent property of the sensor by an amount comparable to the aluminum's effect on the sensor. This is because it is also a +3 charged ion AND it has the added benefit of having a full D orbital. Like  $\text{Zn}^{2+}$ , it will have no intention of getting rid of any electrons if it has a full D orbital. Unlike  $\text{Zn}^{2+}$  however, it has a +3 charge. It will want to pull the electron density toward itself in order to relieve the +3 charge it is retaining. At the 460nm wavelength emission, while the  $\text{In}^{3+}$  ion is increasing the sensor's luminescence comparably to the  $\text{Al}^{3+}$ , the  $\text{Al}^{3+}$  ion is still able to generate the most luminescence from the sensor.

The next spectrum was taken at 528 nm emission wavelength in order to see how the luminescence intensity changes relative to each ion.



Looking at the 528nm wavelength emission spectrum, it is clear that Indium is able to generate more luminescence than Aluminum is. This spectrum shows that In<sup>3+</sup>, even though it was expected to be less of a Lewis acid than Aluminum, proves to be able to emit a more intense luminescence at higher emission wavelengths. This effect would need to be investigated further to gather any meaningful conclusion out of this data, however, it is safe to say that, while Indium is able to generate a false positive at certain wavelengths of emission, it is not expected to be a common occurrence due to the scarcity of Indium, as well as the lack of any known Indium toxicities in patients.

The effect of Aluminum on the sensor in the presence of one other metal ion was also tested to ensure that the sensor is able to function and detect aluminum effectively, despite any further metal contamination. It would not be a very effective sensor in real world scenarios if it is unable to differentiate and discriminate between aluminum and another charged metal ion.



Despite the presence of the 2eq (80uM) concentration of another metal ion, the sensor is still able to detect the aluminum and increase its luminescence as though the second metal ion was not affecting it during each of the instances. Solutions containing Zn<sup>2+</sup>, Fe<sup>3+</sup>, and In<sup>3+</sup> in the presence of varying concentrations of aluminum were all able to increase luminescence comparably to each other, indicating limited effect from the added metal ions. At 2eq (80uM) of Al<sup>3+</sup>, the luminescence intensity of the sensor in the presence of 2eq (80uM) of all other ions as well existed in a narrow range of 650 to 725. This data indicates that the sensor is extremely proficient at detecting aluminum no matter which additional contaminant is included. Even in regards to the Fe<sup>3+</sup>, which is possibly the strongest lewis base, the ferric ion was unable to continue quenching the molecule and the luminescence begins to increase as Aluminum concentration begins to increase.

## Conclusion:

This research project was able to complete its required research goal and experimentation to synthesize and test a highly sensitive and selective chemical sensor for detecting the presence of aluminum ions via luminescent intensity. This sensor's novelty stems from the fact that it is one of the few sensors that is able to function in acidic aqueous mediums. The data collected shows that the sensor is highly sensitive to Aluminum. While the literature was able to prove sensitivity to Aluminum in the 2.5uM range, the instruments provided to us by Middlesex County College were not sensitive enough to prove this. We were able to show that the 40uM sensor is sensitive to 20uM<sup>25</sup>. This is still an extremely small amount of aluminum that is able to be detected by the sensor. Any concentration below 20uM requires new, highly sensitive measuring equipment, including a new UV-visible spectrophotometer machine.

The data suggests that different metal ions were unable to have a great effect on the sensor's luminescence as compared to Aluminum. During each of the tests, Aluminum was able to generate the most luminescence at the 490 nm emission spectrum. This shows that the sensor is highly selective to Aluminum.

The last characteristic of this sensor that was confirmed was its ability to differentiate between aluminum and other metal ions. The data shows that the sensor is able to detect Aluminum while also in the presence of most other metal ions.

All of the data gathered during this experiment gives confidence in the sensor's ability to detect aluminum, despite any foreseeable problems that may arise, including too low a concentration or secondary metal contamination.

The original literature included, not only many more concentrations of metal ion solutions, but it also included many more types of charged metal ions to instill further confidence into the sensor's ability to detect Aluminum ions<sup>26</sup>. The original literature was also able to document a 30-fold increase upon titration of 2eq Al<sup>3+</sup> while our experimentation was only able to reproduce a 4-fold increase. This is likely due to the wavelength in which the molecule was excited. The authors of the article had the resources to excite the molecule at 378nm while we were limited to excitation at 360nm. The authors were also able to detect emissions at lower wavelengths while we were limited to only 460nm and bigger. Experimentation on the numerous different concentrations of sensor solution as, experimentation of the many different types of charged metal ions, excitation at 378nm,

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<sup>25</sup> (X. Jiang, 2011)

<sup>26</sup> (X. Jiang, 2011)



emission detection at less than 460nm were unable to be replicated due to constraints in resources and time. However, the data seen in this research project aims to create a foundation upon which other researchers can build in order to finally bring a chemical sensor that detects  $\text{Al}^{3+}$  pollution or toxicity in acidic mediums into the hands of members of society.

## **Acknowledgements:**

Special thanks goes out to many many members of not only Middlesex County College, but of other organizations that were able to provide support in numerous ways toward the initiation and completion of this research project.

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