Spring 5-2016

A Chemical Sensor for Cyanide

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A Chemical Sensor for Cyanide

by

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A Thesis
Submitted to the Honors College of
The University of Southern Mississippi
in Partial Fulfillment
of the Requirements for the Degree of
Bachelor of Science
in the Department of Chemistry and Biochemistry

May 2016

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Abstract

The cyanide ion and its gaseous form, hydrogen cyanide, are extremely toxic. Cyanide impairs cellular respiration by inhibiting cytochrome c oxidase, an enzyme in the electron transport chain, leading to cell death.

In a previous study, we synthesized an optical sensor that detects cyanide selectively. The aim of this project is to increase the sensitivity of this sensor. This can be achieved by utilizing the unique spectroscopic properties of lanthanide ions.

The lanthanide metal (europium or terbium) was added to a coumarin-glycine chemodosimeter in a DMSO solvent system. The sensor was titrated with several monodentate analytes including, nitrate, octylamine, 1-pentanethiol, tetrafluoroborate, thiocyanate, azide, cyanide, and the halides, and several bidentate analytes including, acetate, phosphate monobasic, sulfate, ethylene diamine, 1,10-phenanthroline, carbonate, and citrate, using fluorescence and phosphorescence techniques.

The results from the fluorescence and phosphorescence studies show that the anions are not only coordinating to the coumarin sensor side of the molecule but are also directly coordinating to the lanthanide ion. This is problematic because it affects the sensitivity of the molecular probe. Thus, we carried out a series of studies by "blocking" the coordination environment of the lanthanide ion with different functional groups (aliphatic and aromatic amines) in order to force the cyanide ion to coordinate only to the coumarin molecule. Aliphatic amines initiate a lanthanide emission, but aromatic amines continue to quench the system.

Keywords: Cyanide detection, coumarin, fluorescence, lanthanide ions, europium

Acknowledgements

I would first like to thank my thesis advisor, Dr. Karl Wallace, for giving me the opportunity to experience research and his help and guidance over the past four years. I would also like to express my gratitude to Aaron Davis and Ashley Johnson, my graduate student mentors, for their support, advice, and patience. I am endlessly grateful for everyone from the Wallace research group and the Department of Chemistry and Biochemistry who have guided me through my undergraduate career.

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List of Abbreviations

DFB	3,3'-difluorobenzaldazine
DMSO	dimethyl sulfoxide
DNA	deoxyribonucleic acid
$EuCl_3$	europium (III) chloride
FRET	fluorescence resonance energy transfer
HCN	hydrogen cyanide
KCN	potassium cyanide
$NaBF_4$	sodium tetrafluoroborate
NaCN	sodium cyanide
NH_4ClO_4	ammonium perchlorate
$(NH_4)_2CO_3$	ammonium carbonate
$(NH_4)_2HC_6H_5O_7$	ammonium citrate dibasic
NH_4NCS	ammonium thiocyanate
NH_4OH	ammonium hydroxide
TBABr	tetrabutylammonium bromide
TBACl	tetrabutylammonium chloride
TBAF	tetrabutylammonium fluoride
$TBAH_2PO_4$	tetrabutylammonium phosphate monobasic
$TBAHSO_4$	tetrabutylammonium bisulfate
TBAI	tetrabutylammonium iodide
$TBANO_3$	tetrabutylammonium nitrate
TBAOAc	tetrabutylammonium acetate
TEACN	tetraethylammonium cyanide
UV-Vis	ultraviolet and visible spectroscopy

Chapter 1: Introduction

The cyanide ion and its protonated form, hydrogen cyanide (HCN), are extremely toxic. Cyanide impairs cellular respiration by inhibiting cytochrome c oxidase, an enzyme in the electron transport chain. Impairment of respiration causes cell death and suffocation and is a cause for concern in ecosystems in which concentrated cyanide accumulates. Additionally, cyanide exposure can cause adverse effects in the nervous, vascular, and endocrine systems of humans.[1]

The cyanide ion is required for many industrial processes, such as the production of different chemicals, metals, and medicines.[2] For example, in the gold mining industry, HCN is released into the environment and is often found in waste water.[3] Additionally, the miners themselves can encounter gaseous hydrogen cyanide in the mines.[2] Gaseous cyanide can also be encountered during a house fire, in which burning materials release the chemical to the air.[4]

The environment also naturally produces hydrogen cyanide. Certain foods, such as apples, contain a small amount of cyanide in their seeds, and several strains of bacteria also produce cyanide gas. Normally, these sources of cyanide are not significant enough to affect humans. However, immunocompromised patients, such as sufferers of cystic fibrosis, can contract infections of cyanide producing bacteria, such as *Pseudomonas aeruginosa*.[5] These infections can raise the amount of cyanide in their blood.[2]

Thus, detection of cyanide presence in water reservoirs and in biomedical applications has become a widespread cause of concern. Traditional methods of cyanide detection, such as titrimetric methods or potentiometric methods, are expensive and require relatively long amounts of time to complete. However, optical sensor

compounds[1] or chromogenic sensors,[2] which can bind to cyanide and display a visual color or fluorescence change, can quickly and inexpensively detect the quantity of cyanide in solution, such as a water or blood sample.[1] In a previous study, we synthesized a chromogenic sensor that selects for cyanide over several different common analytes in solution. The aim of this project is to increase the sensitivity of this sensor by coordinating it to a lanthanide ion.

Chapter 2: Literature Review

Many chromogenic sensors for cyanide have been synthesized.[1] These sensors normally contain large conjugated systems, which cause a visible color change as their electrons move across the π system.[6] One type of optical sensor for cyanide ions is a chemodosimeter, which relies on cyanide's high potential to undergo a nucleophilic attack on an organic scaffold. A chemodosimeter interacts with the analyte through covalent bonding, whereas other sensors may solely rely on hydrogen bonding to interact with the analyte.[1]

In a previous study, two coumarin based sensors, which selectively detected cyanide ions in a DMSO solution, were synthesized. These molecules are chemodosimeters because they undergo a Michael addition with the cyanide anion at the C9 carbon of the molecule, Figure 1. The cyanide ion is negatively charged and can attack an electron deficient region of the chemodosimeter, forming a covalent bond.[1] The cyanide ion attacks the molecule, forming a new carbon-carbon bond and changing the hybridization of the carbon atom from sp^2 to sp^3. This change in hybridization disturbs the planarity of the molecule. The sensors exhibit both visible absorbance and fluorescence changes, being initially yellow in solution and becoming clear upon the addition of cyanide.[7]

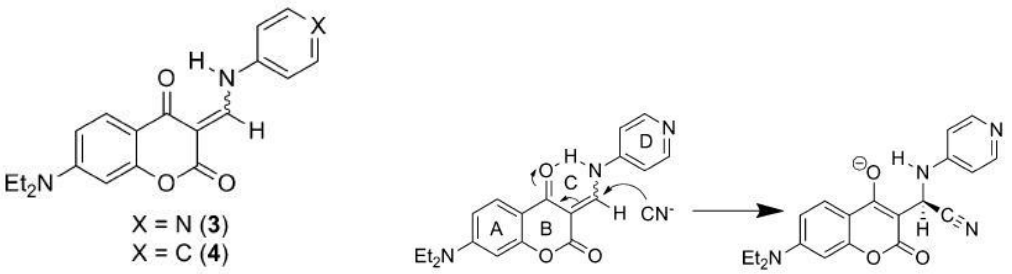


Figure 1. The structure of the previously synthesized coumarin-enamine sensors (coumarin-aniline and coumarin-4-aminopyridine) for cyanide and the mechanism of the Michael addition.[7]

One way to increase the sensitivity (detection of cyanide at low concentrations) is to utilize a lanthanide metal as part of the molecular probe design. The lanthanide series consists of lanthanum and the fourteen other members of the first row of the *f*-block of the periodic table. All the elements in the lanthanide series have similar properties.[8] They are known to absorb and emit light in the visible and near infrared regions of the electromagnetic spectrum, and they possess unique emission spectra.[9] Europium and Terbium have become the most studied lanthanides because they emit light in the visible region.[10] In solution, the lanthanide ions are found in the +3 oxidation state. Their electronic configurations allow their spectroscopic qualities to be nearly unaffected by the environment. Thus, detection using lanthanides is constant under different conditions.[11]

Unfortunately, solitary lanthanide ions are difficult to excite due to their weak ability to transfer energy between their *f*-orbitals. However, this problem can be thwarted by associating the lanthanide with a ligand, or chromophore, which can then indirectly excite the lanthanide, in a process known as sensitization.[10] When the chromophore is

excited, the energy that it absorbs can be transferred to the lanthanide's energy state at which it releases light energy, known as the lanthanide's emissive state. This energy transfer mechanism is known as the antenna effect, with the chromophore acting as an antenna for the lanthanide.[9]

Thus, sensors involving lanthanides are composed of a complex involving the lanthanide metal ion and an antenna. The analyte to be detected does not directly interact with the lanthanide, but, instead, interacts with the antenna.[10] Ideally, the antenna's excited state should be greater than 2.0×10^3 nm^{-1} above the emissive state of the lanthanide. Energy can be lost if the two states are too close together or the excited state is lower than the emissive state.[12] The luminescence spectrum of the lanthanide can also be negatively affected if the metal interacts directly with its solution, especially aqueous solutions and solvents containing hydroxyl groups.[11] In order to shield the lanthanide from the solution, a coordinating agent must also be part of the complex.[8] The coordination complex completely surrounds the lanthanide and may or may not include the actual antenna.[10]

Another modification which could increase the sensitivity of a chromogenic sensor is to associate the sensor with a quantum dot. Quantum dots are semiconductor nanocrystals, which have a smaller physical size than the excitation radius of the elements of which they are composed. With these properties, quantum dots acquire discrete energy levels.[13] Thus, quantum dots absorb energies of specific values and absorb large quantities of energy per mole in the ultraviolet and visible regions of light. Quantum dots are made of more than one element, such as cadmium and sulfur, and they can emit intense energy as photons, which form characteristic spectral profiles that can

fall between the infrared and ultraviolet regions.[14] Quantum dots have already been used as fluorescent probes in many biological molecules, such as DNA and peptides.[17] Lanthanides can also be associated with quantum dots. Through fluorescence resonance energy transfer (FRET), the lanthanide can transfer energy to the quantum dot. Chromophores can also transfer energy to the quantum dot through the FRET process.[15]

The focus of this study will be to increase the sensitivity of the coumarin based cyanide sensor by coupling its reaction with that of a lanthanide. In the future, we hope to also add a quantum dot to the complex to further increase sensitivity of the sensor and to use our sensor for biomedical cyanide detection.

Chapter 3 Methodology

Synthesis

The following synthesis was pre-established in the lab and the literature before the current study began. The initial coumarin sensor (coumarin-glycine) was synthesized by refluxing 7-(diethylamino)-4-hydroxycoumarin, glycine, and triethylorthoformate in 2-propanol for two hours, Figure 2. The 4-aminopyridine and aniline groups attached to the organic scaffold (Figure 1) were replaced with glycine to encourage better coordination with a lanthanide ion. The reaction was, then, allowed to cool, and the solid was isolated by vacuum filtration. The 7-(diethylamino)-4-hydroxycoumarin must be synthesized for use in this reaction by refluxing bis-2,4,6-trichlorophenylmalonate, 3-diethylaminophenol, and anhydrous toluene for three hours. The bis-2,4,6-trichlorophenylmalonate must also be synthesized by refluxing 2,4,6-trichlorophenol, malonic acid, and phosphorus (V) oxychloride for three hours. The product was precipitated and dissolved with deionized water, and the pH was adjusted to 7 by adding sodium bicarbonate. The product, then, was vacuum filtered and recrystallized.[7]

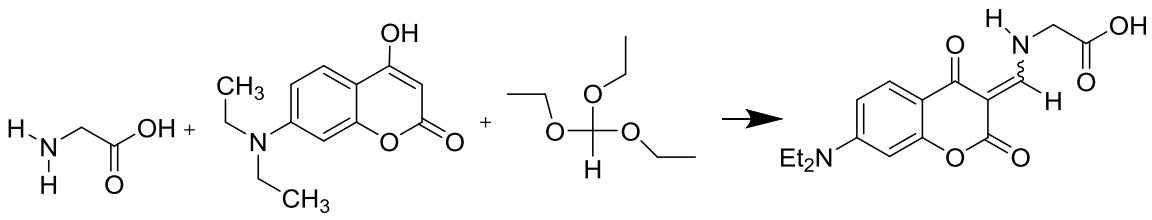


Figure 2. Reaction of 7-(diethylamino)-4-hydroxycoumarin and triethylorthoformate with glycine

Spectroscopic Analysis of Coumarin-glycine Selectivity

DMSO was used as the solvent due to its mundane spectroscopic qualities based on the previous study.[7] The coumarin-glycine sensor was mixed in a one-to-one ratio with $EuCl_3$ in DMSO. A 100 µL sample of 3.1 x 10^{-4}M coumarin-glycine was added to 10 µL of 3.1 x 10^{-3}M $EuCl_3$ and 1890 µL of DMSO in a quartz fluorescence cuvette. All salts and solvents were obtained from Sigma Aldrich supplier.

Fluorescence

The coumarin-glycine solution was titrated with the solutions from Table 1. Half-equivalent increments of the solutions were added to the ligand until the solution contained five equivalents of the analyte. After each addition, the solution was stirred for one minute with a stir bar; then, its fluorescence spectrum was recorded on the PTI QuantaMasterTM 40 intensity based spectrofluorometer from 370-720 nm wavelengths after being excited at 360 nm with slit widths open to 0.35 mm. The solutions listed in Table 2 were added in 0.25 equivalent increments.

Table 1. Solutions Titrated in 0.5 equivalent increments

Analyte	*Concentration (M)*
adenine	0.0031
TBACl	0.0031
$TBANO_3$	0.0031
TBABr	0.0031
$TBAHSO_4$	0.0031
TBAI	0.0031
$TBAH_2PO_4$	0.0031
$(NH_4)_2HC_6H_5O_7$	0.0031
NH_4ClO_4	0.0031
NH_4NCS	0.0031
$NaBF_4$	0.0031
1-pentanethiol	0.0031
NH_4OH	0.0031

Table 2. Solutions Titrated in 0.25 equivalent increments

Analyte	*Concentration (M)*
$(NH_4)_2CO_3$	0.0031
TBAF	0.0031
NaCN	0.0031
KCN	0.0031
octylamine	0.0031
TBAOAc	0.0031

Phosphorescence

The same starting solution of coumarin-glycine and $EuCl_3$ was used to test steady state phosphorescence. The solutions in Table 3 were titrated by making additions of half-equivalents until five equivalents were reached. The phosphorescence of the solution after each addition was recorded on the spectrofluorometer from 550-750 nm wavelengths after being excited at 360 nm with slit widths open to 2.50 mm. The titration with TEACN was performed in 0.2 equivalent increments until 4 increments were reached then, 1 equivalent increments until 10 equivalents were reached, and the slit widths were open to 0.6 mm.

Table 3. Analytes Measured with Phosphorescence

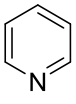
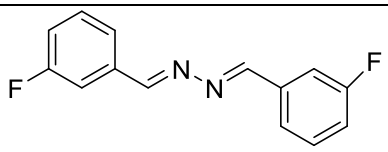
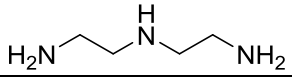
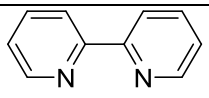
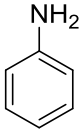
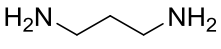
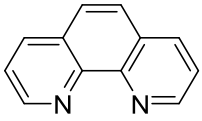
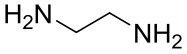
Analyte	*Concentration (M)*
TBACl	0.0031
TBABr	0.0031
TBAI	0.0031
TBAF	0.0031
$TBANO_3$	0.0031
$TBAH_2PO_4$	0.0031
$NaBF_4$	0.0031
$(NH_4)_2CO_3$	0.0031
NaN_3	0.0031
NH_4ClO_4	0.0031
1-pentanethiol	0.0031
octylNH_2	0.0031
NH_4NCS	0.0031
NH_4OH	0.0031
$(NH_4)_2HC_6H_5O_7$	0.0031
TBAOAc	0.0031
octylamine	0.0031
TEACN	0.0031
NaCN	0.0031

Spectroscopic Analysis of Lanthanide Protecting Groups

Fluorescence

The same fluorescence procedure was repeated, but the titrations were performed with molecules, such as aliphatic and aromatic amines, that could potentially serve to protect the lanthanide from water molecules in solution. These solutions are listed in Table 4. Pyridine, DFB, aniline, and 2,2-bipyridil were titrated in one equivalent increments until five equivalents were reached. Ethylene diamine, diethylene triamine, and diaminopropane were titrated in 0.25 equivalent increments until seven equivalents were reached.

Table 4. Concentrations of Potential Protecting Groups

Analyte	*Concentration (M)*
pyridine 	0.003098124
DFB 	0.00311231
diethylene triamine 	0.003247068
2,2-bipyridyl 	0.003105391
aniline 	0.003113927
1,3-diaminopropane 	0.003103076
1,10 phenanthroline 	0.003112306
ethylene diamine 	0.003112306

Phosphorescence

The same phosphorescence procedure was repeated with the analytes from Table 4 except that the slit width was open to 0.50 mm. Both diethylene triamine and diaminopropane titrations of 0.25 increment additions to reach 7 equivalents were recorded using phosphorescence.

Chapter 4: Results and Discussion

Analysis of Selectivity of Coumarin-glycine

The fluorescence spectrum of NaCN, as seen in Figure 3, showed three bands at 603 nm, 610 nm, and 696 nm, respectively. The titration with KCN produced similar results. The fluorescence spectrum of TBAF, as shown in Figure 4, showed bands at 604 nm, 607 nm, and 693 nm. The spectrum of octylamine showed small bands at 604 nm, 611 nm, and 696 nm. The spectrum of acetate showed bands at 604 nm, 610 nm, and 696 nm. The spectra of the remaining tested anions lacked bands in these areas, which indicates that they did not cause a unique europium emission. Figure 7 shows the spectrum of TBACl, an example of a spectrum without these bands. Thus, NaCN, octylamine, acetate and TBAF are interacting with the sensor in some way to cause an emission. Either they are directly coordinating to the europium ion to block the water molecules that are quenching it in solution, or they are directly interacting with the coumarin-glycine molecule to sensitize the lanthanide ion. Acording to the previous study, TBAF, octylamine, and acetate could be undergoing an acid-base or hydrogen bonding interaction with the coumarin molecule disturbing the original hydrogen bond at the enamine functional group.[7] Thus, they could be able to cause a fluorescence change in the sensor without undergoing the same addition mechanism as cyanide. The remaining tested anions are either unable to interact with the complex or are serving to quench the lanthanide ion along with water molecules in solution.

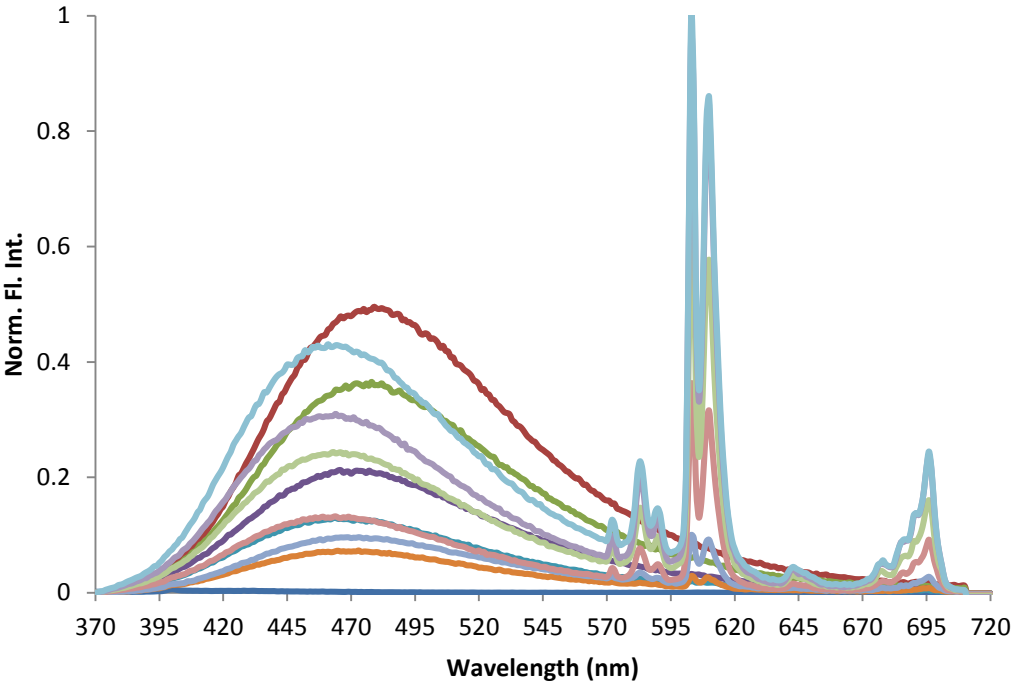


Figure 3. Fluorescence spectrum of titration with NaCN

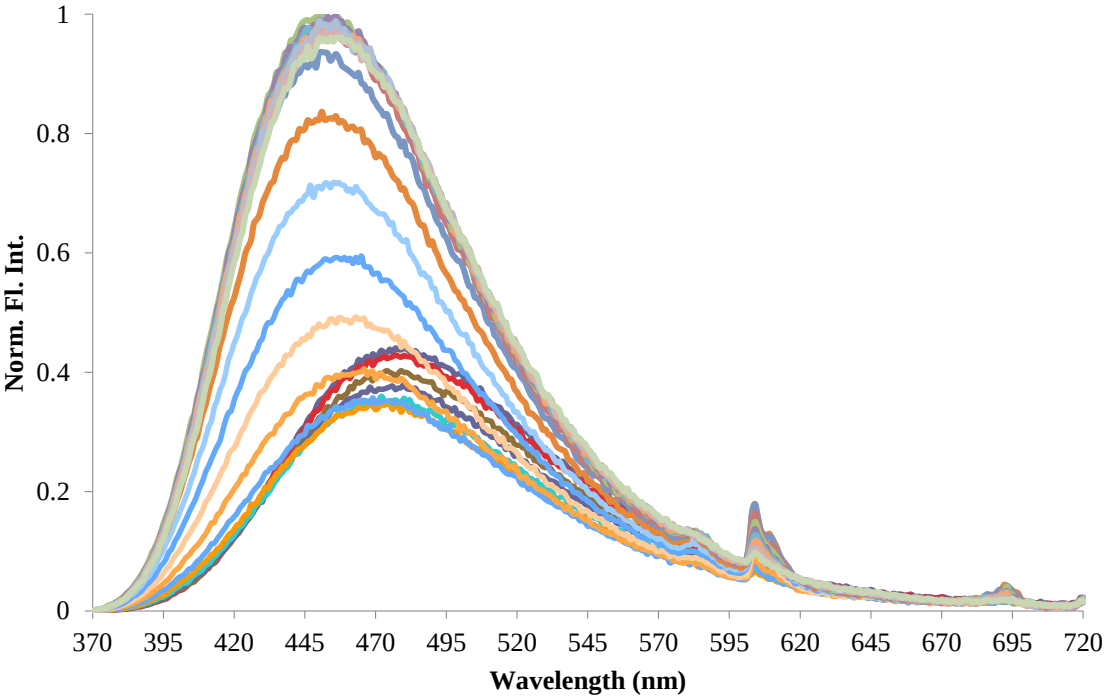


Figure 4. Fluorescence spectrum with TBAF

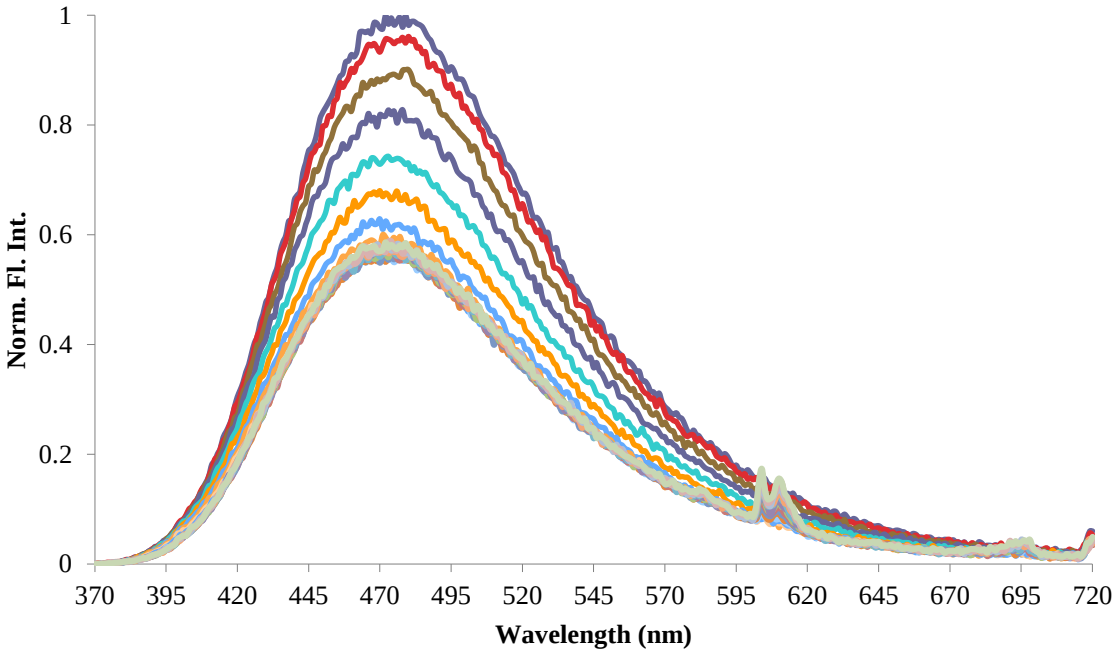


Figure 5. Fluorescence spectrum with octylamine

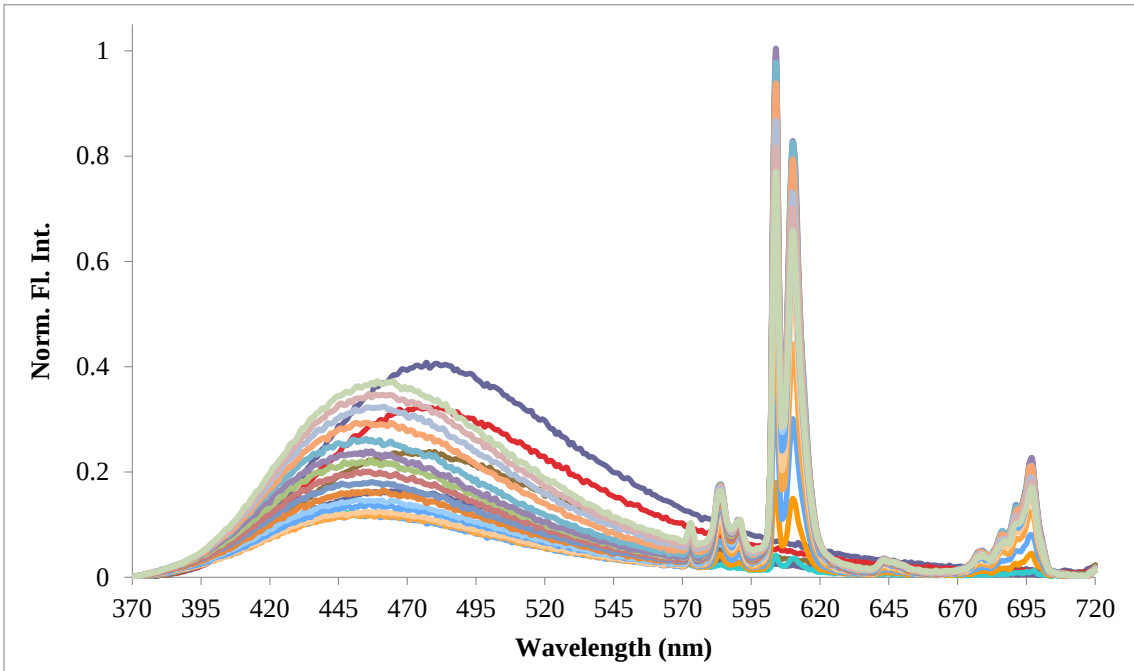


Figure 6. Fluorescence spectrum with TBAOAc

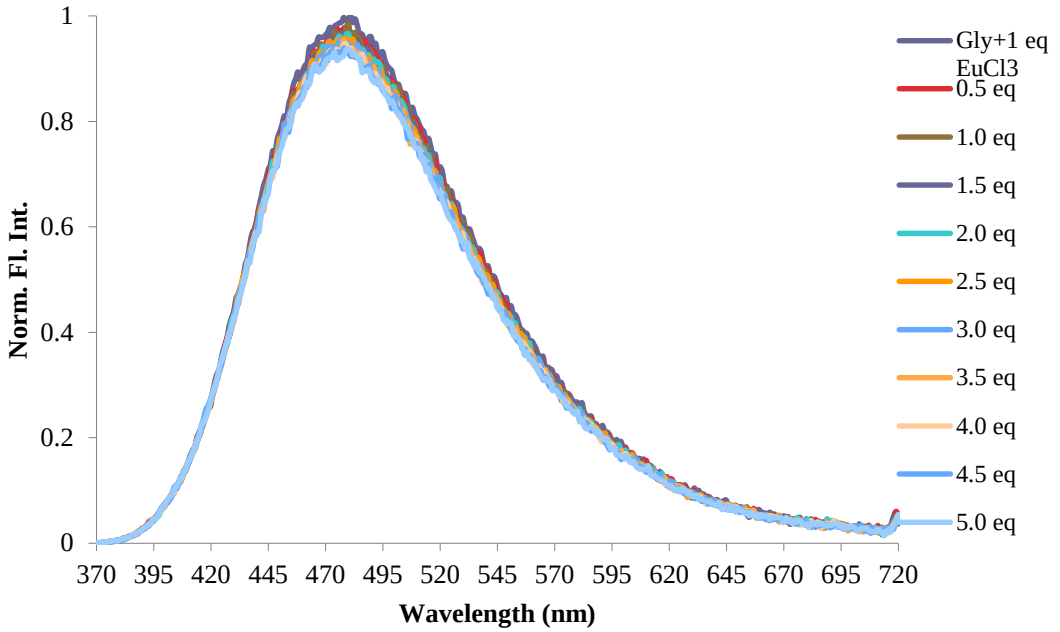


Figure 7. Fluorescence spectrum with TBACl

The interaction of NaCN, acetate, octylamine, and TBAF with the complex was expected based on previous studies in the Wallace group.[7] However, the acetate induced europium emission was greater than expected. Acetate's resonance distributed negative charge and bidentate coordination could be causing this emission response comparable to that of the titration with NaCN.

The intensity changes at the three bands of the fluorescence spectrum of the NaCN titration became apparent at 3 equivalents, as can be seen from the isothermal graph in Figure 8. Also, at values above 7 equivalents of NaCN, the signals begin to decrease, and the maximum signal during this titration was recorded at 6.5 equivalents. In Figure 9, the maximum signal from the TBAF titration occurs at 3 equivalents but quickly diminishes beyond 3.5 equivalents. Thus, TBAF interacts with the complex to produce a smaller signal over a shorter range than the interaction with NaCN. The isothermal plots of octylamine and acetate, in Figures 10 and 11 respectively, resemble that of cyanide. Octylamine's isotherm shows low intensities, similar to TBAF. The

isothermal plot of TBAOAc shows large intensities that begin at a smaller number of equivalents due to acetate's bidentate coordination interactions.

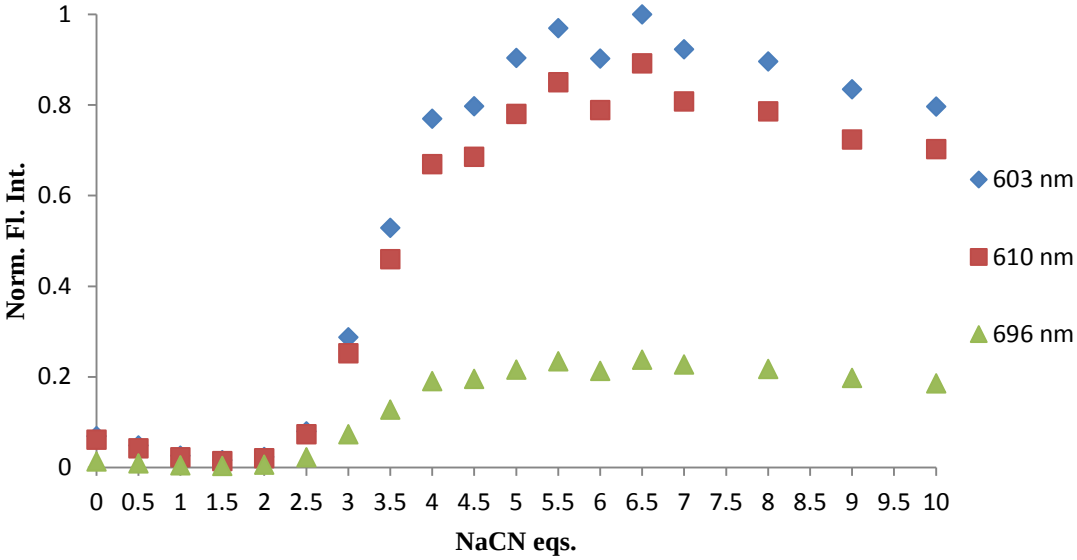


Figure 8. Isothermal plot of NaCN equivalents to normalized fluorescence signal

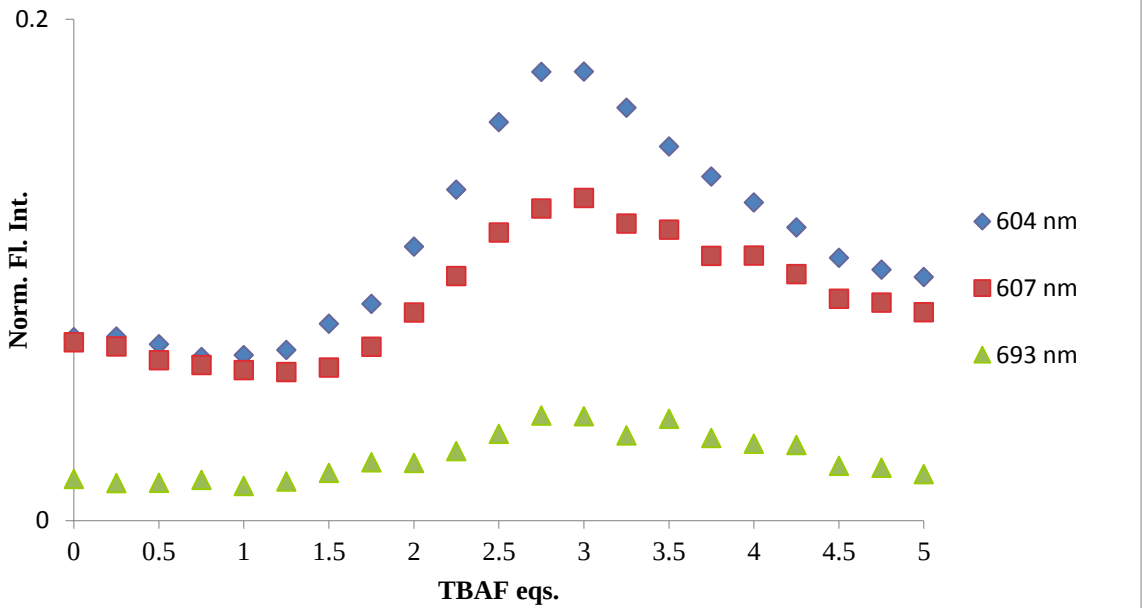


Figure 9. Isothermal plot of TBAF equivalents to normalized fluorescence signal

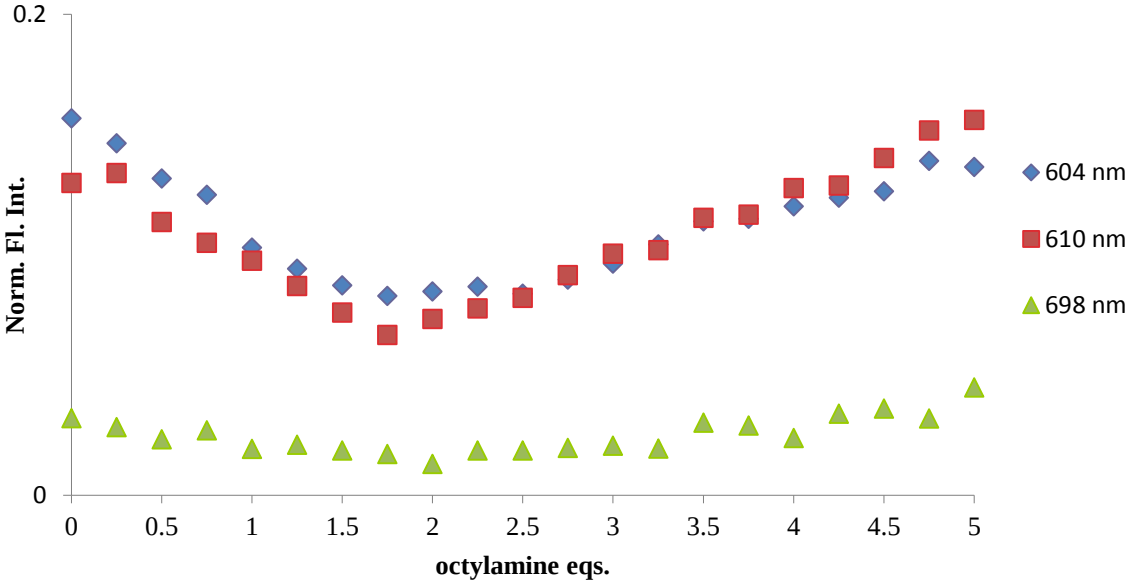


Figure 10. Isothermal plot of octylamine equivalents to normalized fluorescence signal

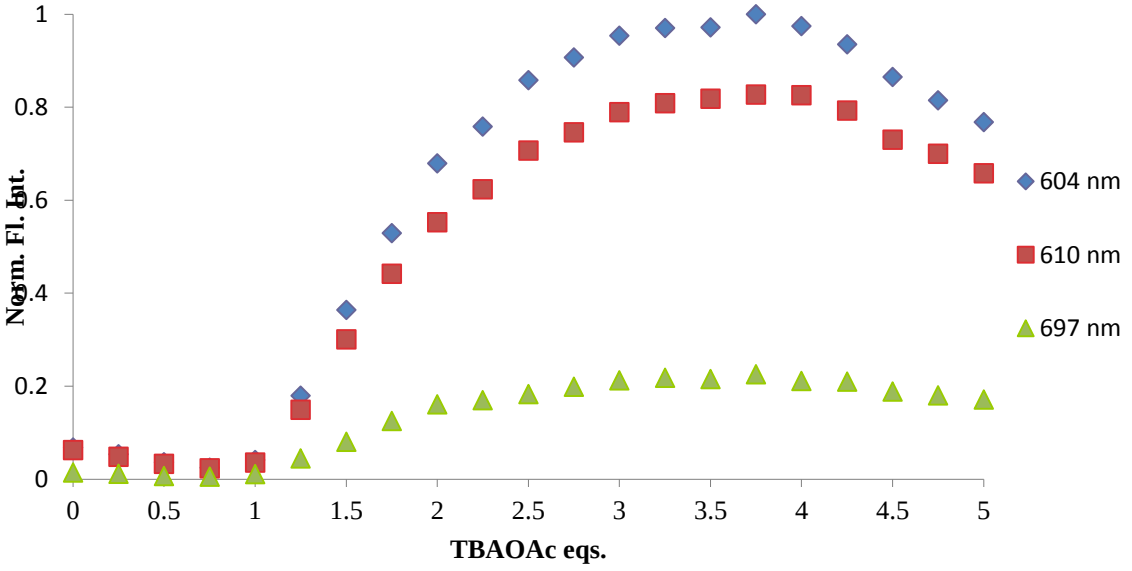


Figure 11. Isothermal plot of TBAOAc equivalents to normalized fluorescence intensity

The phosphorescence studies produced similar results. The phosphorescence spectrum of NaCN, which can be seen in Figure 12, produced peaks at 595 nm, 620 nm, and 705 nm. The titration with TEACN produced similar results. These same peaks

were produced in the spectra of TBAF, octylamine and TBAOAc, which can be seen in Figures 13, 14, and 15, respectively.

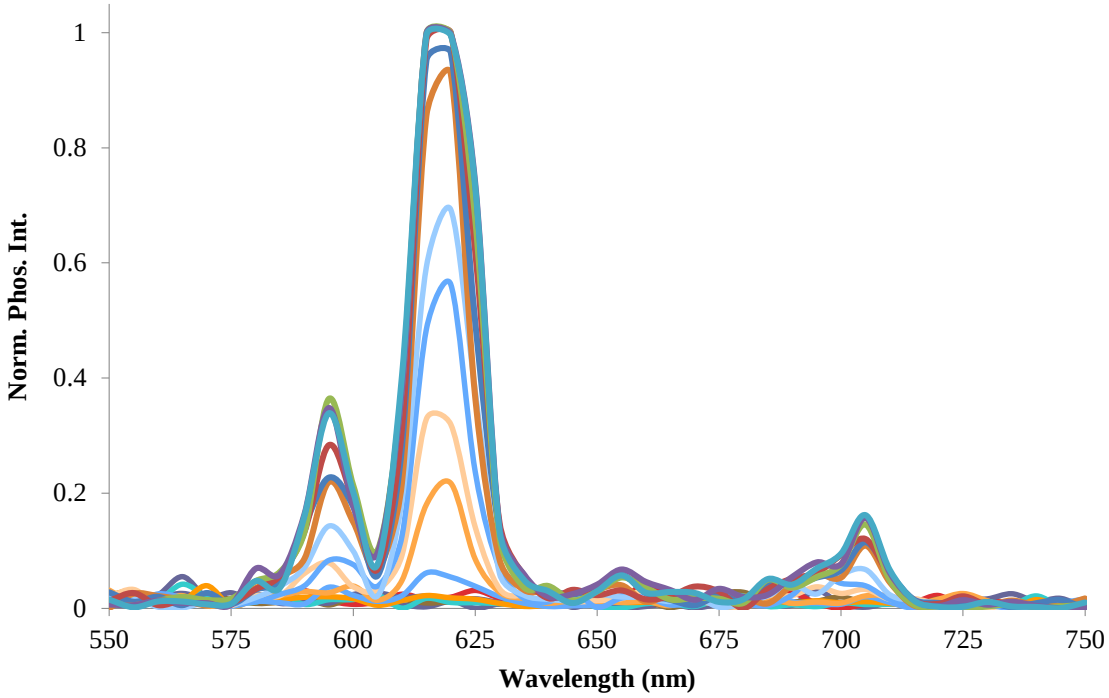


Figure 12. Normalized phosphorescence spectrum of the titration with NaCN

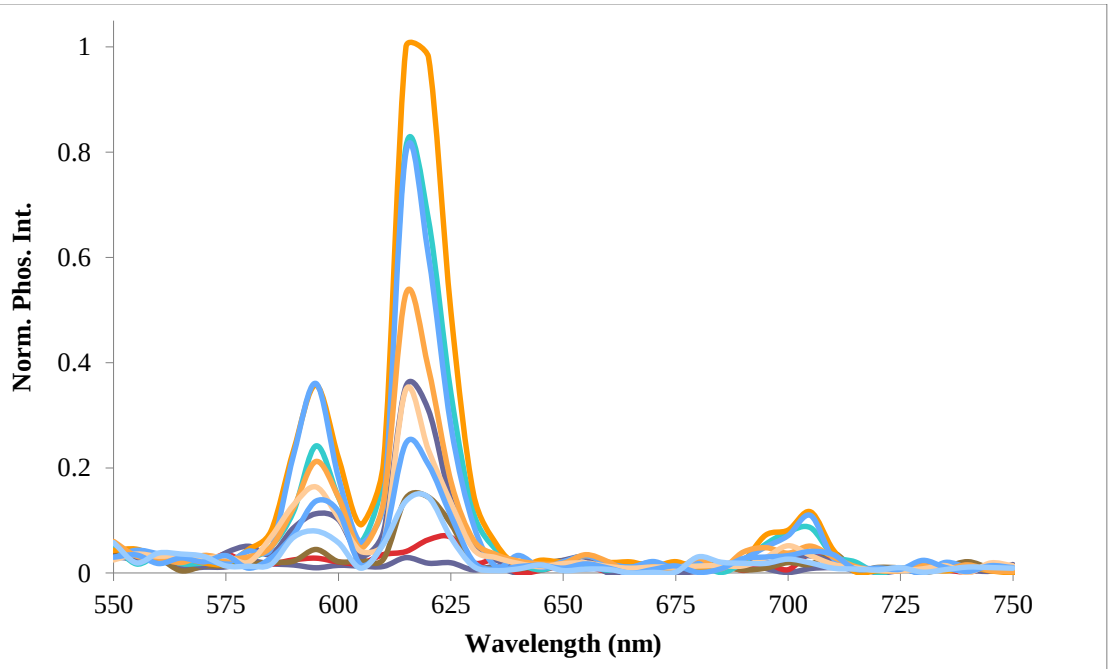


Figure 13. Normalized phophorescence spectrum of the titration with TBAF

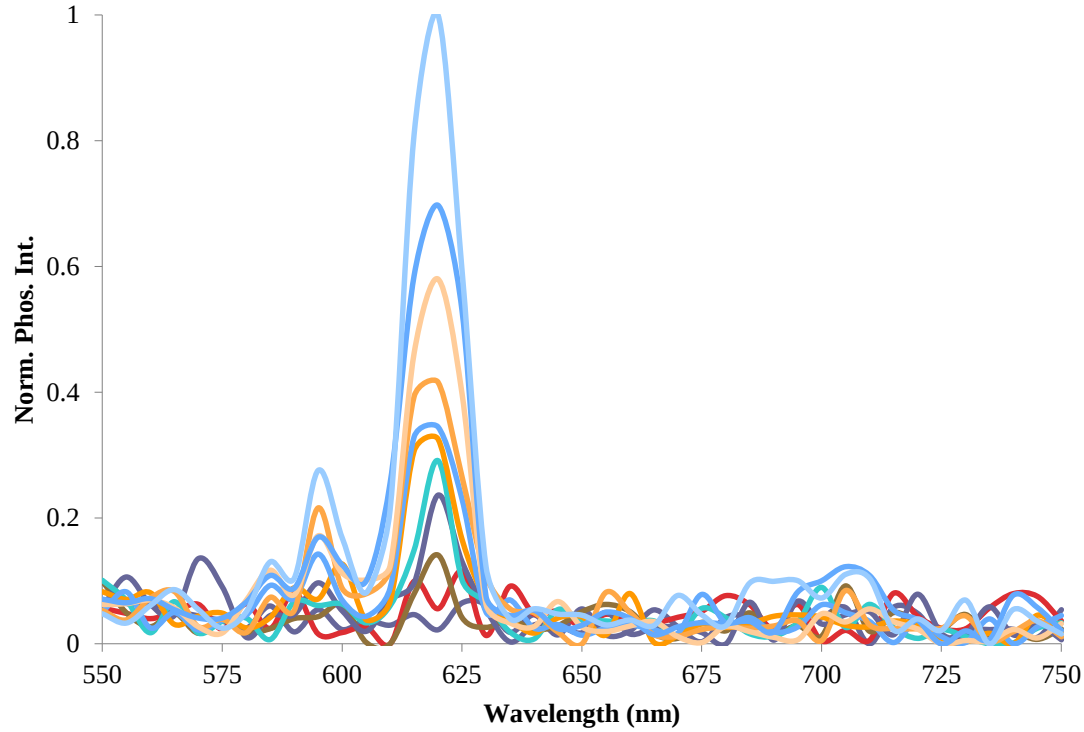


Figure 14. Normalized fluorescence spectrum of the titration with octylamine

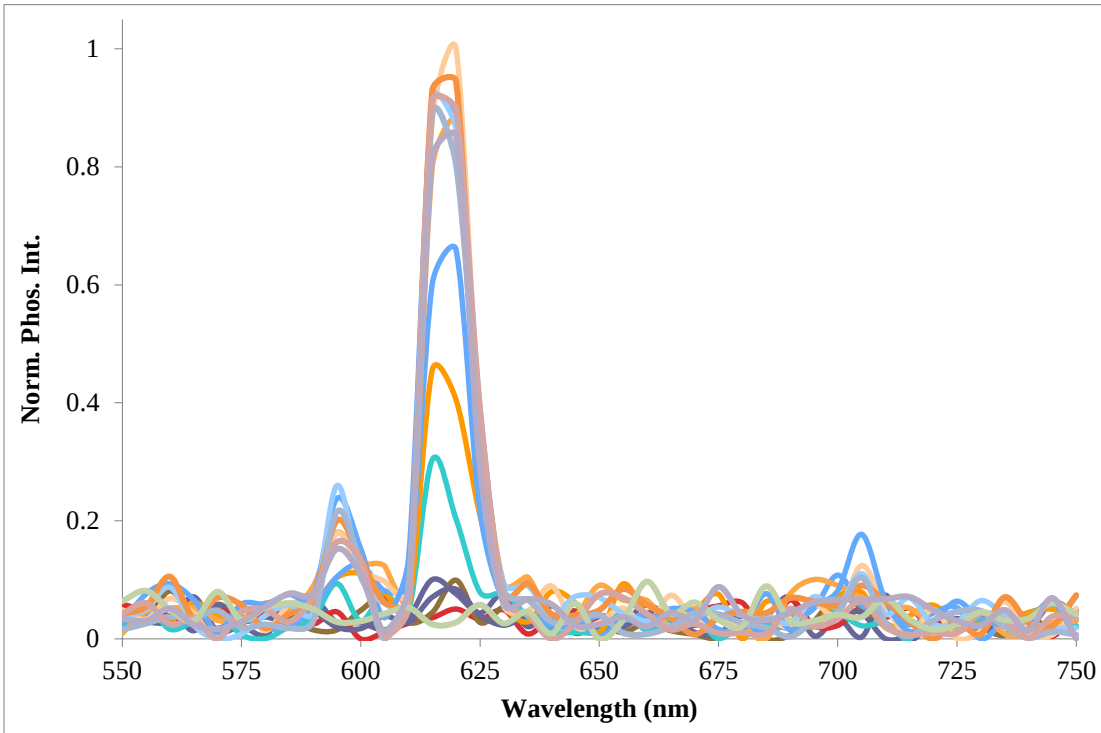


Figure 15. Normalized phosphorescence spectrum of the titration with TBAOAc

The following isothermal graph in Figure 16 shows that the signal in the titration with TBAF becomes apparent at 1 equivalent but dies off at 3 equivalents, and both the signal in the titration with TBAOAc and TEACN becomes apparent at 2 equivalents. These results are similar to the fluorescence results in that the titration with TBAF produced a maximum signal between 2 and 3 equivalents that diminishes quickly, while the titrations of TEACN and TBAOAc produced a maximum signal between 3.5-4 equivalents. The titration with octylamine does not produce a maximum signal until 5 equivalents are added. However, the intensities of the maximum bands in these studies cannot be compared because the slit width was changed to maximize the readings for each titration.

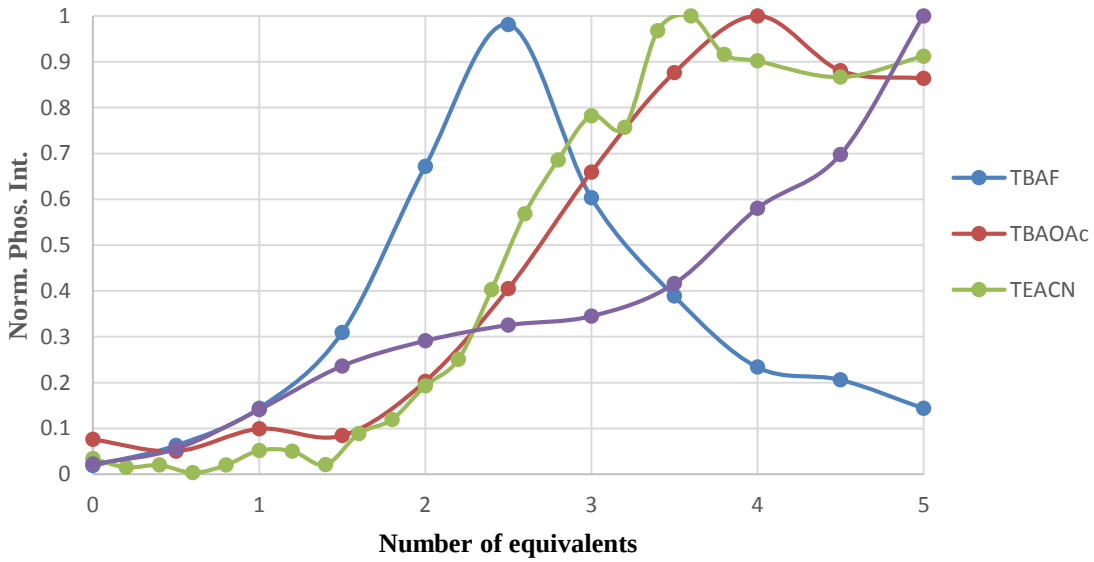


Figure 16. Isothermal comparison of normalized intensities of addition of TEACN, TBAOAc, and TBAF at 620 nm

Spectroscopic Analysis of Lanthanide Protecting Groups

The fluorescence titrations of aliphatic amines, including diethylene triamine, diaminopropane, and ethylene diamine, produced large bands at 584 nm, 604 nm, 610

nm, and 697 nm. The spectra of these titrations appear similar to that of NaCN in Figure 3. The remaining titrations of the aromatic compounds, including 2,2-bipyridyl, aniline, DFB, pyridine, and 1,10-phenanthroline, did not produce any similar bands (similar to titration of TBACl, Figure 7). The isothermal plots were affected based on whether the analyte was bidentate or tridentate. As seen in Figures 17 and 18, the emission intensity of the titration with diethylene triamine, a tridentate analyte, reaches a maximum at 3.5-4 equivalents, while the intensity of the titration with ethylene diamine, a bidentate analyte, does not reach a maximum until 4.5-5 equivalents are added.

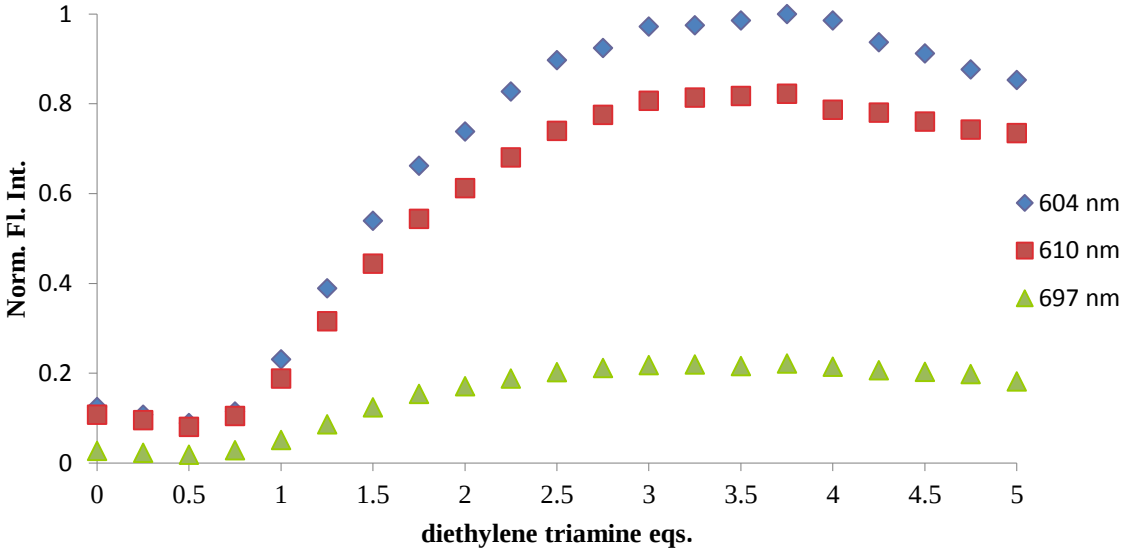


Figure 17. Isothermal plot of diethylene triamine equivalents to normalized fluorescence intensity

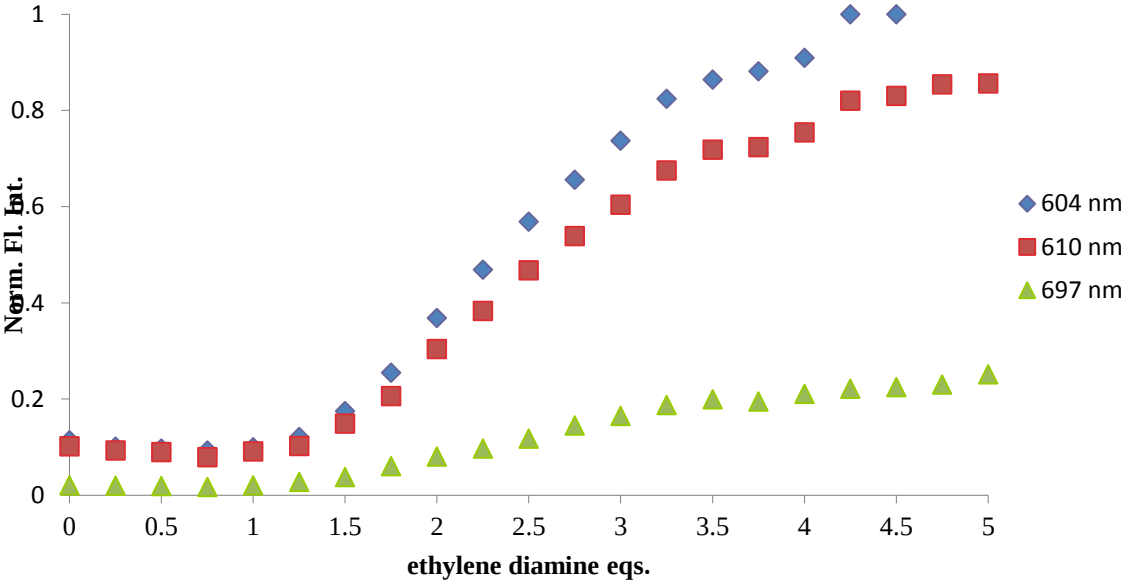


Figure 18. Isothermal plot of ethylene diamine equivalents to normalized fluorescence intensity

The phosphorescence titrations of ethylene diamine and diethylene triamine produced bands at 595 nm, 620 nm, and 705 nm. The titration with 1,10-phenanthroline did not produce any significant bands.

Thus, the aliphatic compounds were able to induce the lanthanide signal while the aromatic compounds were not. To cause the signal, the aliphatic amines could be coordinating around the positively charged europium (III) ion. This behavior would protect the ion from the solution, blocking the water molecules from quenching the emission. The aromatic compounds are either not interacting with the complex or, more likely, are also coordinating around the lanthanide ion. If the aromatic compounds are coordinating to the lanthanide, they are not causing a europium emission.

Chapter 5: Conclusion

The fluorescence studies show that the coumarin-glycine europium (III) sensor produces bands at 603 nm, 610 nm, and 696 nm upon addition of at least 3 equivalents of cyanide. These bands are close to the bands reported in the literature for europium (III).[10] The addition of TBAF and octylamine also produced similar but much smaller peaks, supporting the results obtained in the Wallace et al. study of the coumarin-aniline and coumarin-4-amionpyridine sensors.[7] That study showed that the cyanide induced signal was six times greater than the fluoride induced signal.[7] The acetate titration produced similar emissions as the cyanide titration. However, because acetate did not show this behavior in the original study[7], it is not believed to interacting with the coumarin molecule in the same way as cyanide. Instead, it could be strongly coordinating to the europium ion due to its bidentate coordination. The phosphorescence studies produced similar results for cyanide, fluoride, octylamine, and acetate with peaks at approximately 595 nm, 620 nm, and 705 nm, corresponding to the literature values of europium (III) emissions.[16] Thus, the sensor was able to produce the characteristic europium fluorescence and phosphorescence emissions.

However, these results also indicate that a noticeable signal was not produced by the sensor until at least three equivalents of cyanide were added to the solution. Thus, two or three analyte molecules are required to interact with the sensor to produce a signal instead of the single molecule required if the expected Michael addition occurs between the sensor and the analyte.[7] This inconsistency indicates that the titrated molecules are coordinating around the lanthanide ion in addition to directly interacting with the coumarin antenna. Alternatively, the titrated molecules could be completely filling the

coordination spots on the lanthanide ion. The need to protect the lanthanide ion from the other molecules in solution led to the testing of various aliphatic and aromatic amines as protecting groups.

The aliphatic titrations, including those of ethylene diamine, diethylene triamine, and diaminopropane, all produced the europium (III) peaks in both fluorescence and phosphorescence, noticeable at two equivalents for the diamines and one equivalent for the triamine. Thus, the aliphatic compounds were able to interact with the europium ion in solution. However, none of the titrations with the aromatic compounds, such as aniline and pyridine, produced a signal. These results could indicate that the aromatic compounds are either not interacting with the sensor or are protecting the lanthanide but also not causing an emission. Their aromatic bonds could allow them to affect the emission, whereas the aliphatic amines are unable to do so.

A future study could include titrating cyanide with several equivalents of one of these aromatic compounds in solution with the coumarin-glycine europium sensor. If cyanide is able to induce a signal in this solution at one equivalent, it could indicate that the aromatic compound has successfully protected europium (III). Other future studies of this sensor could include isolating the coumarin-glycine europium complex from solution. This isolation would allow structural studies to be performed on the complex. The properties of coumarin-glycine could also be studied with terbium instead of europium. The terbium specific emissions have been utilized in many biomedical applications, which could allow a similar sensor with terbium to be used in such applications.[16]

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