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Detection of Heavy Transition Metal Cations Using Novel Chemosensors

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Detection of Heavy Transition Metal Cations Using Novel Chemosensors

An Honors Thesis submitted in partial fulfillment of the requirements for Honors in Chemistry

By

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Under the mentorship of Dr. Shainaz Landge

ABSTRACT

Transition metals (TM) are found in the environment and living systems. When present in excess, these metals can trigger health problems, which include memory loss and cognitive functions. In this project, commercially-available compounds were used to aid in the making of novel mono- and di-triazole molecular sensors with a well-known reaction called "*click chemistry*". These sensors were used efficiently and selectively to attract a specific metal like iron III, copper, and zinc. Six sensors were tested via UV-spectroscopy, NMR, and fluorescence with the cations and selectivity increased as the sensors were altered.

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Honors Director:_____

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Introduction and Literature Overview

Heavy transition metal (HTM) ions are of major concern to human health and the environment.[1] Specifically, excess copper, zinc and aluminum will perpetuate the loss of memory and ability to perform cognitive functions in Alzheimer's disease.[2] Cations such as copper, zinc and aluminum are linked with Alzheimer's disease; silver has an adverse effect on the environment and platinum salts are considered as occupational hazards in industries. A report[1] on HTM's by the Social, Health and Family Affairs Committee (Council of Europe) states that there are a number of issues that need to be addressed:

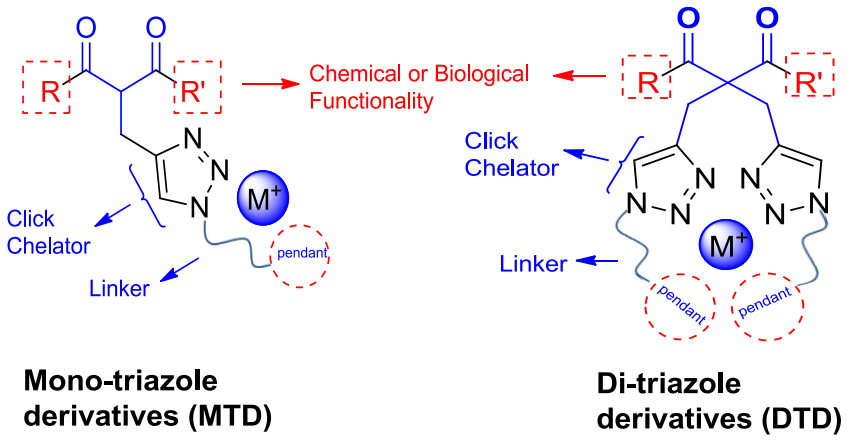
(i) detection and quantification of HTM's in the human body

(ii) the determination of concentration-levels of heavy metals in the body that necessitate medical treatment

(iii) the development of novel strategies to counteract the problem

With these concerns in mind, sophisticated and smart molecules are needed; which can be synthesized and utilized in the detection and quantification of HTM's. These molecules can be activated by external stimuli[3] for metal recognition using multidentate ligands to get the desired outcome. Our major goal of this project was to readily and effectively detect the HTM cations by novel molecular sensors. In this project, commercially-available compounds were used to aid in the making of novel mono- and di-triazole molecular sensors with a well-known reaction called "*click chemistry*". Our hypothesis was that 1,2,3-triazole derivatives (MTD and DTD), will recognize a HTM cation (M^+) at low

concentrations and deliver a "*visual signal*" such color/absorbance change or emit fluorescence which can be analytically measured (scheme 1).

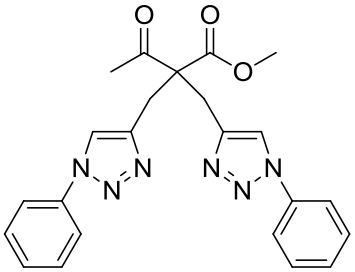


Scheme 1: Basic molecular scaffold of the molecular sensors

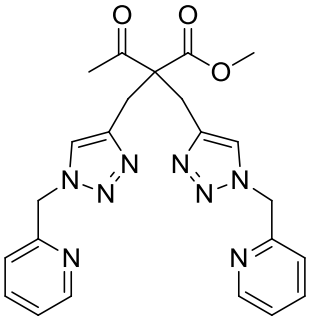
In scheme 1, the chemical or biological functionality is the location where binding to DNA, polymers, or carbon nanotubes (CNT) can occur. The chelator is the binding pocket for the metal, which is composed of a triazole unit (three linked nitrogen). Depending on the size of the metal, the "*linker"* will be adjusted by adding or taking away carbons. Attached to the linker is the "*pendant"*, which is the final molecule that encloses the pocket, and traps the metal inside. Sensors formed through this process can then be conjugated further with biological (protein/DNA) or chemical (polymer) groups allowing usage in real life applications. For this project, a total of 6 sensors were synthesized and the activity was tested by the use of UV-Vis and fluorimeter.

Results and Discussion

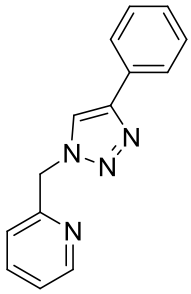
Chemosensors used in this study are depicted below:



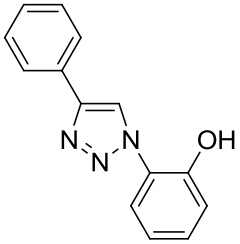
Sensor 1



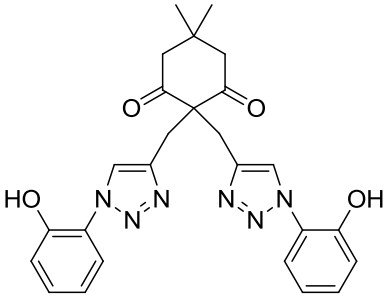
Sensor 2



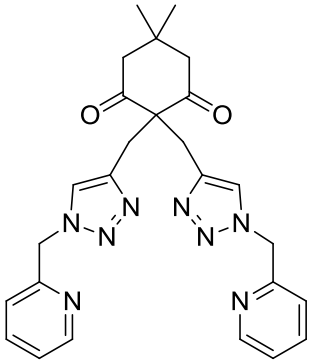
Sensor 3



Sensor 4

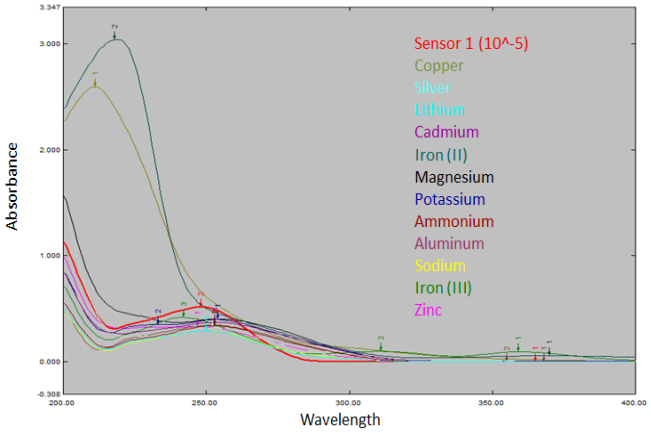


Sensor 5

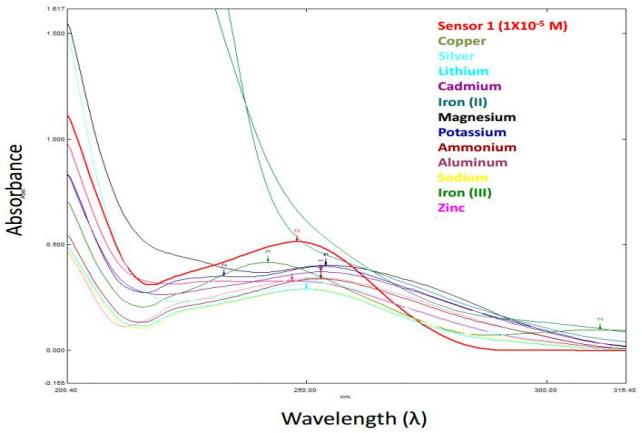


Sensor 6

During the longevity of this project, various concentrations and ratios of sensors and salts were tried and it was observed that a 1:1 ratio with equal concentrations of metal salt and sensor yielded the most accurate results (10^{-5} M) with the exception of copper and silver, which had a tenfold lower concentration (10^{-6} M). (The results below follow these concentration parameters.) The idea was to create a funneling affect in determining a sensor that would be selective to a specific metal.



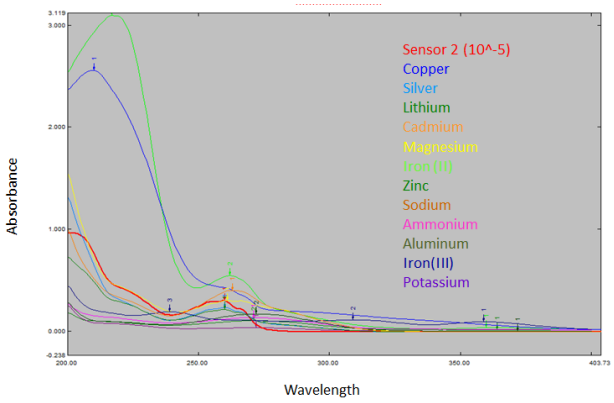
A



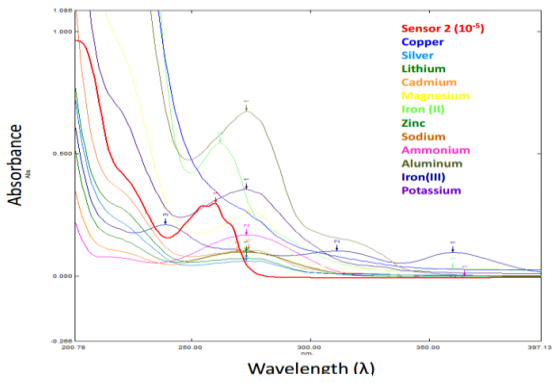
B

Figure 1. Sensor 1 and its interaction with various metals; B is the expansion of Figure 1A.

In Figure 1, you can see a red shift (right side) in the metals as compared to sensor 1 (shown in red), indicating binding occurred but there was no specific selectivity towards any metal. Also to be noted is the binding of copper and iron with the sensor showing huge absorbance band at ~220nm, which resulted due to the binding at the carbonyl region. Sensor 1 was then modified by changing the pendant group attached to the triazole ring.



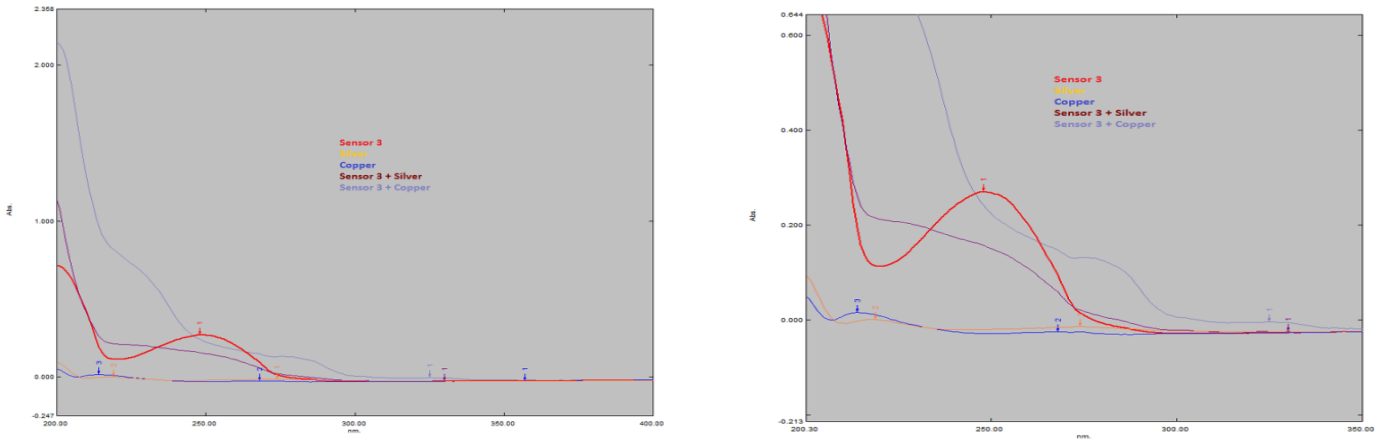
A



B

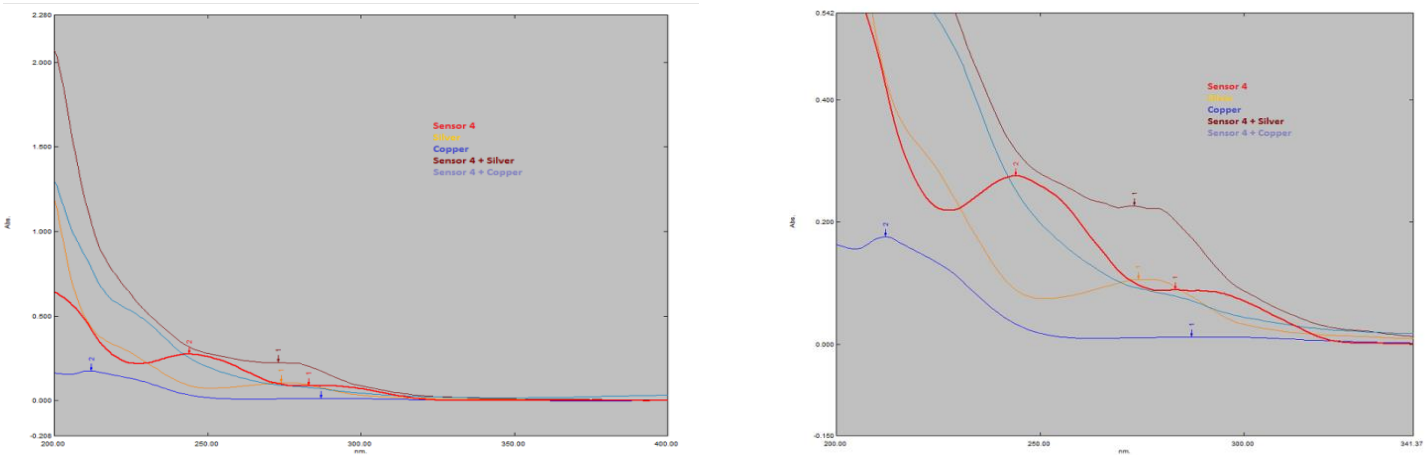
Figure 2. Sensor 2 and its interaction with various metals; B is the expansion of Figure 2A.

Sensor 2 was observed to be slightly more selective towards iron, copper, aluminum, and magnesium (Figure 2). After further observations were made, it was determined that binding was not only occurring in the triazole pocket, but with the dicarbonyl backbone as well. In an attempt to alleviate this problem, the sensor was modified to only have a cyclic ring as the backbone (Sensors 5 and 6). In the meanwhile, the monotriazole derivatives were tested with selected few metal salts (Sensors 3 and 4).



A B

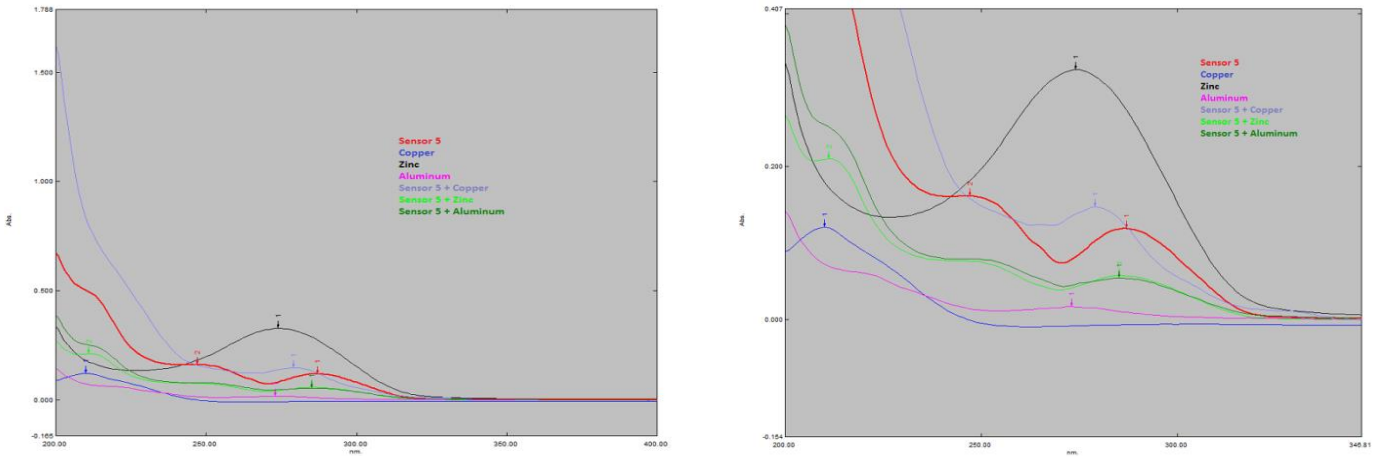
Figure 3. Sensor 3 and its interaction with various metals; B is an expansion of Figure 3A.



A B

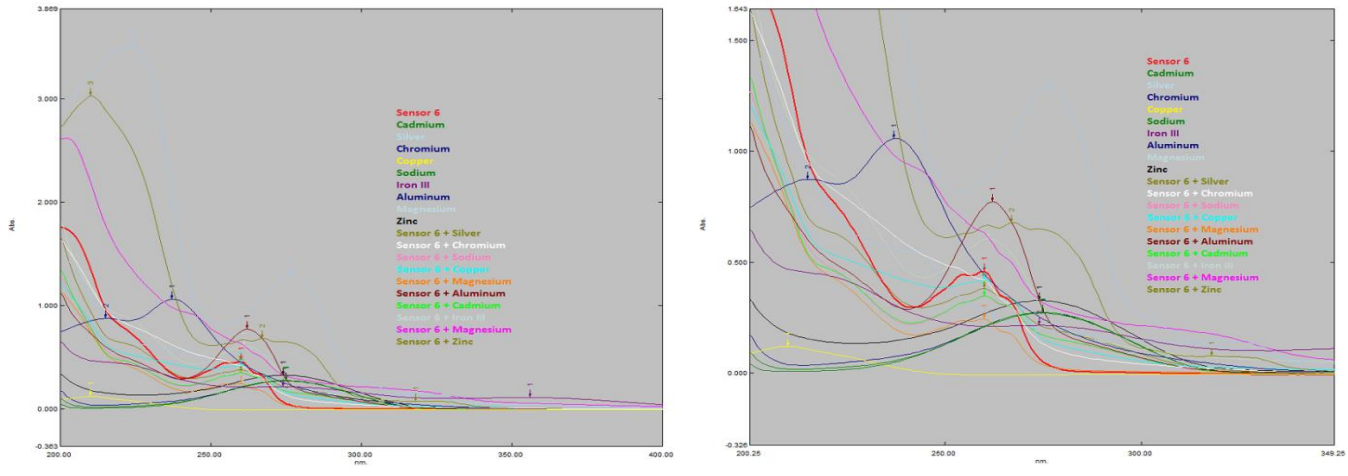
Figure 4. Sensor 4 and its interaction with various metals; B is an expansion of Figure 4A.

The monotriazole derivatives were tried to see if two molecules of sensors bind with one molecule of metal cations. Selectivity was seen to increase towards copper salts, but was not 100% selective to a particular metal. For sensors 5 and 6, the original dicarbonyl backbone was modified to cyclic dicarbonyl system to avoid the copper and iron from binding with the backbone.



A B

Figure 5. Sensor 5 and its interaction with various metals; B is an expansion of Figure 5A.



A B

Figure 6. Sensor 6 and its interaction with various metals; B is an expansion of Figure 6A.

Sensor 5 was selective towards copper and sensor 6 showed great sensing ability towards aluminum, zinc, and iron (III).

Materials and Method

Chemosensors were synthesized by Dr. Karelle Aiken and research group. Each sensor was dissolved in 100mL of acetonitrile and diluted by fractions of 10 to have a final concentration of 10^{-5} M. Twelve different perchlorate metal salts (copper, silver, zinc, iron (II), iron (III), magnesium, cadmium, sodium, chromium, lithium, aluminum, and potassium) were individually dissolved in 100mL of acetonitrile and diluted accordingly. All salts except for copper and silver were diluted to 10^{-5} M and the latter being 10^{-6} M. Carefully, 3.0mL of sensor was placed in a UV quartz cuvette and a UV-Vis absorbance spectrum was performed the sensor alone. This was replicated for all 6 sensors individually. An absorbance spectrum was also performed on each metal salt. Once both runs were completed, a 1:1 ratio of a particular sensor and salt were mixed together and left untouched for 5 minutes. UV-Vis spectrum was observed after 5 minutes. For example, 1.5 mL of sensor 1 in acetonitrile was combined with 1.5 mL of copper perchlorate salt in acetonitrile and let stand for 5 minutes; a UV spectrum was recorded after 5 minutes. This observation was repeated for all remaining sensors and salts.

Note: Cuvette was thoroughly cleaned with acetonitrile after every run was carried out.

Conclusion

In conclusion, we have observed a particular sensor being sensitive to various metals such as copper, zinc, silver, etc. but is not selective. Modifications were made for 6 different sensors in order to eliminate bonding in locations other than the triazole pocket. As this project progresses in the future, we have made a transition from using metal cations and testing interactions with the sensor to anions. Our aim is to observe how they interact and bind with the different sensors already in hand. The anion study is currently under progress.

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