# BILE ACID-BASED 1,2,3-TRIAZOLE LIGANDS: SYNTHESIS AND APPLICATION IN ION SENSING AND CATALYSIS

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by

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Department of Chemistry

Submitted

in fulfillment of the requirements of the degree of

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to the

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***Dedicated to my parents***

# CERTIFICATE

This is to certify that the thesis entitled, **"BILE ACID-BASED 1,2,3-TRIAZOLE LIGANDS: SYNTHESIS AND APPLICATION IN ION SENSING AND CATALYSIS"**, being submitted by Ms. Aradhana Nayal, to the Indian Institute of Technology Delhi, for the award of the degree of 'Doctor of Philosophy in Chemistry', is a record of bonafide research work carried out by her. Ms. Aradhana Nayal has worked under my guidance and supervision and has fulfilled all the requirements for the submission of this thesis, which to my knowledge has reached the requisite standard. The results embodied in this thesis have not been submitted in part or in full, to any other University or Institute for award of any degree or diploma.

**(Pramod S. Pandey)**

Thesis Supervisor

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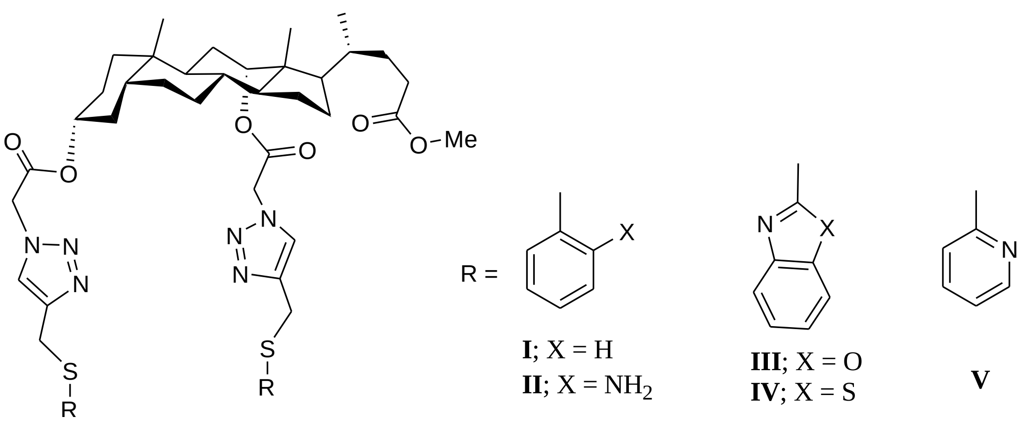
# ABSTRACT

The present thesis deals with the design, synthesis and application of bile acid-based 1,2,3-triazole ligands for ion sensing and stabilization of Pd, Ag, Au nanoparticles. These nanoparticles have been explored for their application in colorimetric sensing of metal ions as well as anions and catalytic reduction of nitroarenes. It also deals with the design of bile acid-based ligands suitable to stabilize Cu(I) state, which has been used as catalyst for click reaction. The present thesis has been divided into six chapters.

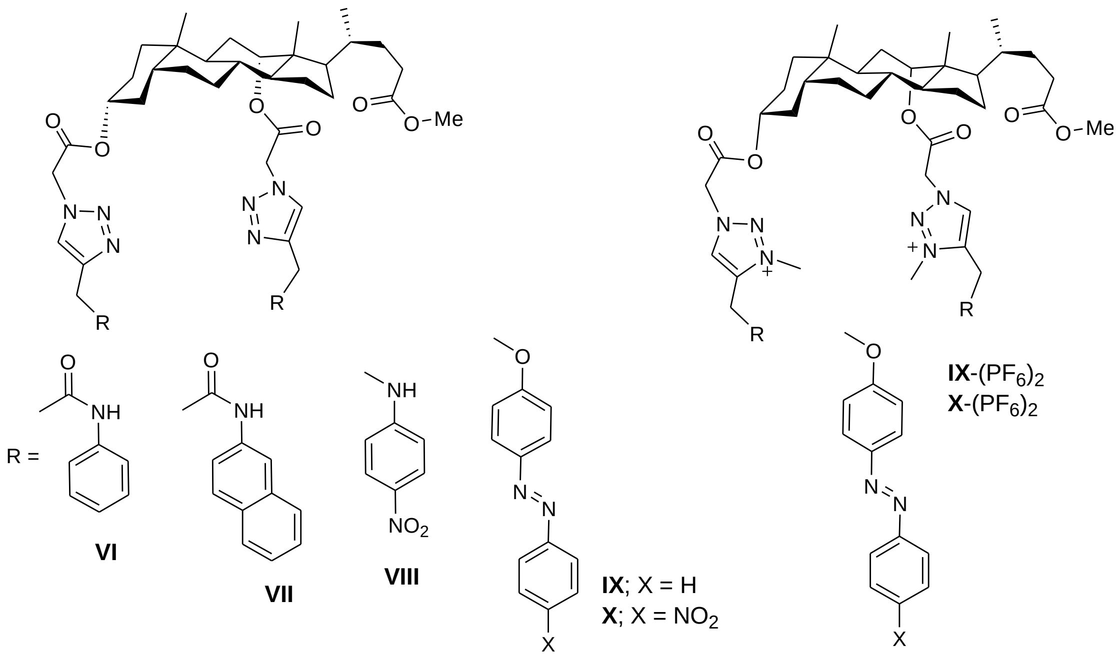
The first chapter describes the important applications of click reaction in various areas. It also contains a brief literature survey on the role of bile acid-based receptors for molecular recognition.

Chapter 2 deals with the synthesis of deoxycholic acid-based 1,2,3-triazole receptors **I**–**V** using Cu(I)-catalyzed click reaction of methyl 3α,12α-bis-(azidoacetyl)deoxy-cholate with various terminal alkynes. The metal ion binding property of receptors **I**−**V** was investigated by UV-Vis titration. UV-Vis studies revealed that all of these receptors show significant binding affinity for $Hg^{2+}$ ion. Receptors **II**, **III** and **V** showed the highest binding affinity for $Cd^{2+}$ ion, whereas receptors **I** and **IV** showed the highest affinity for $Pb^{2+}$ and $Hg^{2+}$ ions, respectively.



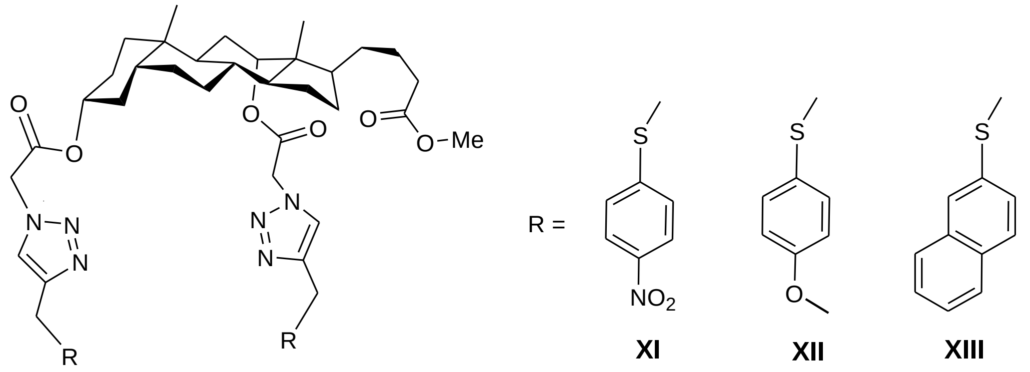
Job's plot analysis showed the 1:1 ligand-metal complexes formation between receptors **I**–**V** with all metal ions.

Chapter 3 describes the synthesis and anion recognition properties of various bile acid based 1,2,3-triazole and triazolium receptors **VI**−**X**-($PF_6$)$_2$.



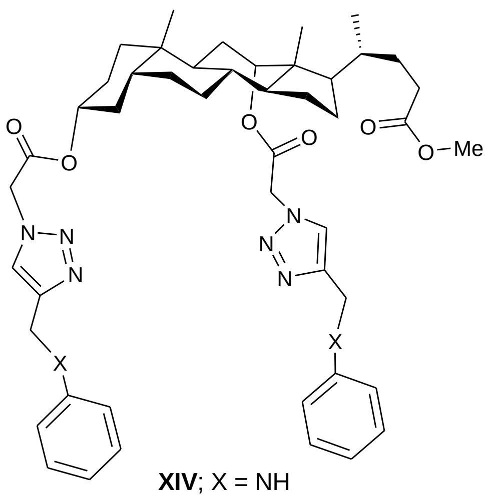

Receptors **VI** and **VII** have been found to show considerable binding affinity towards $Br^-$ and $I^-$ ions, respectively. Receptor **VIII** showed colorimetric recognition of $H_2PO_4^-$ and highest binding affinity for $F^-$ ion. Receptor **X** showed the highest selectivity and binding affinity for $CH_3COO^-$ ion. The methylation followed by anion exchange of receptors **IX** and **X** resulted in 1,2,3-triazolium receptors, **IX**-($PF_6$)$_2$ and **X**-($PF_6$)$_2$. These Receptors showed the highest affinity for $CH_3COO^-$ ion. The **X**-($PF_6$)$_2$ also showed colorimetric detection of $CH_3COO^-$, $F^-$ and $H_2PO_4^-$ ions.

The naked-eye sensing has been of considerable interest in recent years. Thus in Chapter 4, the ligands **I**, **II**, **V**, **XI**, **XII** and **XIII** have been used for stabilizing AuNPs, whereas ligands **I** and **II** have been examined for stabilization of AgNPs.

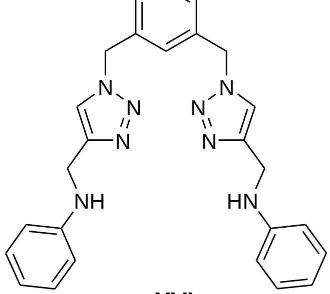



The size of AuNPs stabilized with these ligands was found to be in the range of 2−8 nm, whereas the average size of AgNPs was ~10 nm (as revealed by TEM studied). The AuNPs stabilized with **I**, **V**, **XI**, **XII**, **XIII** and AgNPs stabilized with **I** and **II** showed remarkably selective colorimetric sensing for $Hg^{2+}$. AgNPs stabilized with **I**, **II** and AuNPs stabilized with **II**, **XI**, **XII** and **XIII** also showed highly sensitive colorimetric response to $I^{-}$ ion. However, AuNPs stabilized with ligand **I** and **V** showed colorimetric responses for iodide as well as bromide ions.

In Chapter 5, the role of three bile acid-based ligands **I**, **XIV** and **XV** in stabilization of Pd, Ag and Au NPs and their application as catalysts in reduction of nitroarenes have been described. To compare the role of bile acid framework, a non-steroidal ligand **XVI** has also been synthesized. The formation of highly monodispersed Pd NPs of average diameter of 3 and 4 nm was observed when steroidal ligands **XIV** and



**XIV**; X = NH
**XV**; X = O



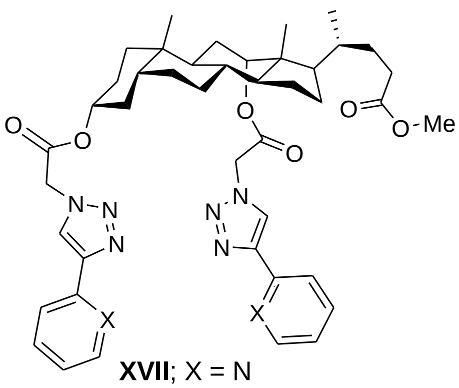
**XVI**

**XV** were used as capping agents. However, when ligand **XVI** was used, the aggregation of PdNPs occurred which resulted in their precipitation from solution. This observation suggests that the bile acid framework plays a significant role in the synthesis of uniformly dispersed NPs of palladium.

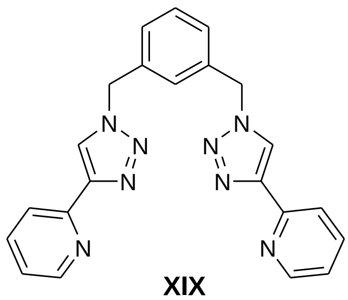
The PdNPs stabilized with ligands **XIV** and **XV** show similar activity as almost same time (~7 minutes) are required for complete conversion of 4-nitrophenol to 4-aminophenol at similar catalyst loading. However, 20 minutes are required for the complete conversion of 4-nitrophenol to 4-aminophenol when ligand **XVI** stabilized PdNPs were used at similar catalyst loading. The aggregation of NPs stabilized with ligand **XVI** appears to be responsible for its lower catalytic activity.

The Ag and Au NPs stabilized with ligand **I**, **XIV**, **XV** and **XVI** have also been studied for the reduction of 4-nitrophenol. These showed almost similar activity as obtained for PdNPs. These NPs have also been studied for their reactivity towards other nitro compounds such as 2- and 3-nitrophenol and 2-, 3- and 4-nitroaniline.

One of the significant important aspects of the designing of ligands is to stabilize the metal in various oxidation states and facilitate the organic reactions in their presence. Thus, Chapter 6 describes the role of bile acid-based triazole ligands **XVII** and **XVIII** in Cu(I)-catalyzed click reaction. The analogous ligand **XIX** (without bile acid backbone) has also been synthesized.



**XVII**; X = N
**XVIII**; X = C



**XIX**

The possibility of these systems to act as catalyst for Cu(I)-catalyzed click reactions of various azides with terminal alkynes has been examined. The ligand **XVI** has been found to catalyze click reaction of a number of alkynes and azides in presence of $Cu(CH_3CN)_4.BF_4$ at very low catalyst loading {1 mol % of Cu(I) and 1 mol % of **XVI**} and under milder reaction conditions. Reactions are very clean and in many cases column chromatography is not required. However, **XVIII** and **XIX** do not show significant activity for this reaction under optimum reaction conditions.

# CONTENTS

**CHAPTER 3: Bile acid-based triazole and triazolium receptors for anion recognition**



**CHAPTER 4: Gold and silver nanoparticles stabilized with bile acid-based triazole ligands as visual sensors for metal ions and anions**

**CHAPTER 5: Palladium, silver and gold nanoparticles stabilized with bile acid-based triazole ligands as efficient catalysts for reduction of nitroarenes**



**CHAPTER 6: Bile acid-based triazole ligands for Cu(I)-stabilization and catalysis in azide-alkyne click reaction**