APPLICATIONS OF COPPER(I)-CATALYZED AZIDE-ALKYNE CLICK REACTION IN SUPRAMOLECULAR CHEMISTRY

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APPLICATIONS OF COPPER(I)-CATALYZED AZIDE-ALKYNE CLICK REACTION IN SUPRAMOLECULAR CHEMISTRY

by

ANJUL KUMAR

Department of Chemistry

Submitted

in fulfillment of the requirements of the degree of

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to the

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This thesis is dedicated to my parents

CERTIFICATE

This is to certify that the thesis entitled, **"Applications of Copper(I)-Catalyzed Azide-Alkyne Click Reaction in Supramolecular Chemistry"**, being submitted by Mr. Anjul Kumar, 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 him. Mr. Anjul Kumar 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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INDIA

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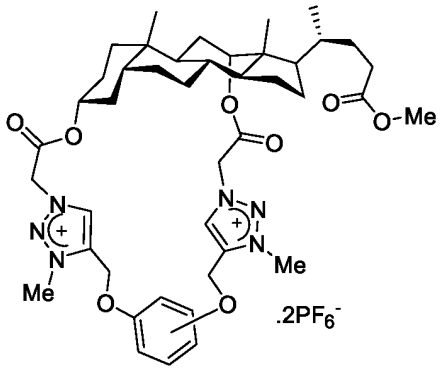
ABSTRACT

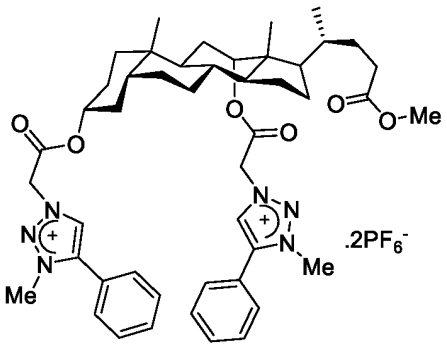
The click reaction involving Cu(I)-catalyzed 1,3-dipolar cycloaddition reaction between an azide and a terminal alkyne has become a versatile tool in conjugate chemistry and has found wide applications in the synthesis of a variety of polymers, biomaterials and peptides having interesting properties. Besides, the unique properties of 1,2,3-triazole in terms of its ability to act as a hydrogen bond acceptor as well as a hydrogen bond donor make it even more interesting. Recently, the role of 1,2,3-triazole moiety in the recognition of metal ions and anions has been realized.

The present thesis deals with the synthesis of steroidal and non-steroidal receptors using click reaction and studies of their anion and metal ion binding properties. It also focuses on the design and synthesis of main-chain bile acid-based 1,2,3-triazole linked polymers and studies of their precipitation behaviour with metal ions. The thesis has been divided into five chapters. The first chapter presents a brief literature survey on application of azide-alkyne click reaction in various fields.

Chapter 2 describes the synthesis and anion binding properties of steroidal and non-steroidal receptors having 1,2,3-triazolium moieties. Bile acid framework has been well recognized for the design of receptors for anion recognition. We have synthesized deoxycholic acid-based cyclic and acyclic receptors **I-III** having 1,2,3-triazolium units for anion binding.



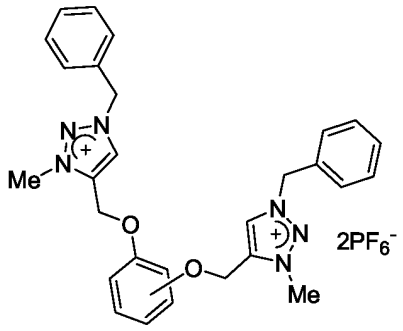
meta, **I**
para, **II**



III

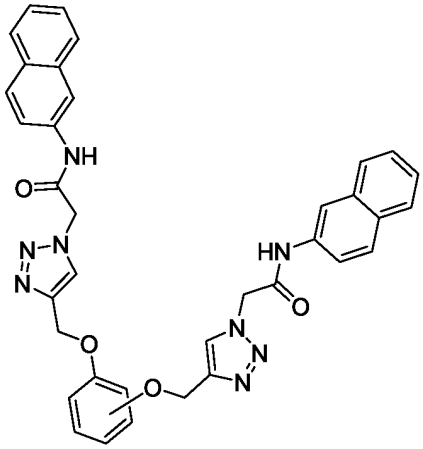
The binding properties of the 1,2,3-triazolium receptors **I, II** and **III** with anions were examined by ^{1}H NMR spectroscopy. The association constants were determined from their titration curves by monitoring chemical shift changes of C(5)-H proton of 1,2,3-triazolium units using WinEQNMR software. Receptor **5a** showed the highest affinity for fluoride ion with an association constant of 560 M^{-1}. Receptor **II** with larger cavity size showed the highest affinity for $H_2PO_4^-$ ion with a binding constant of 1100 M^{-1}. Interestingly, the acyclic receptor **II** was found to show much higher affinity and selectivity towards $H_2PO_4^-$ ion as compared to the cyclic receptor **II**, having a binding constant of 1920 M^{-1}.

We have also synthesized and studied the anion binding properties of non-steroidal 1,2,3-triazolium receptors **IV** and **V**. These compounds **IV** and **V** showed considerable selectivity for fluoride (3500 M^{-1}) and chloride (2800 M^{-1}) ions, respectively

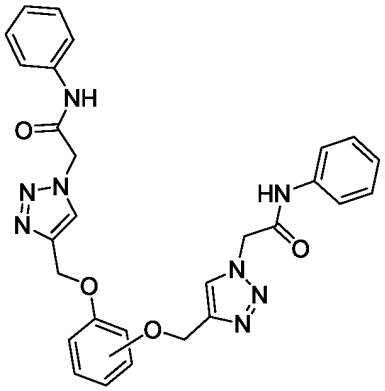


ortho, **IV**
meta, **V**

This chapter also describes the synthesis and anion binding properties of receptors **VI-IX**, containing 1,2,3-triazole as well as amide moieties. Receptors **VI-IX** showed very high affinity and selectivity for dihydrogen phosphate ion. The *meta*-substituted receptors **VII** and **IX** showed relatively low affinity for dihydrogen phosphate ion compared to *ortho*-substituted receptors **VI** and **VIII**.



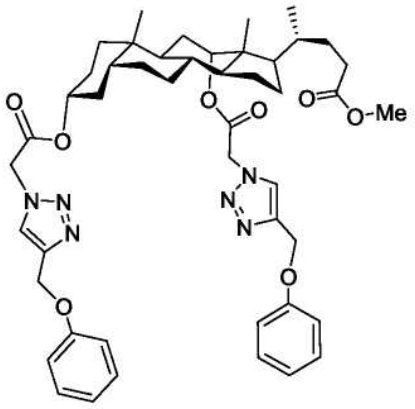
ortho, **VI**
meta, **VII**



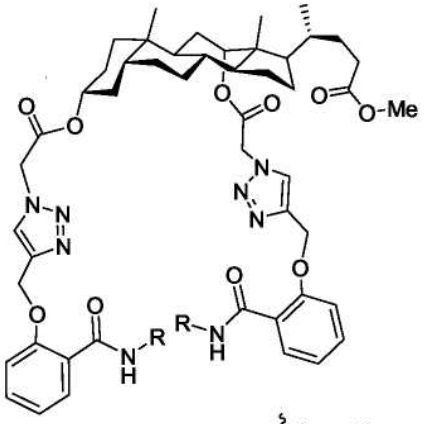
ortho, **VIII**
meta, **IX**

Chapter 3 deals with the synthesis of deoxycholic acid-based 1,2,3-triazole receptors **X-XIII** and studies of their recognition properties towards various metal ions. The binding behaviour of these receptors **X-XIII** towards metal ions was studied by UV-Vis titration.

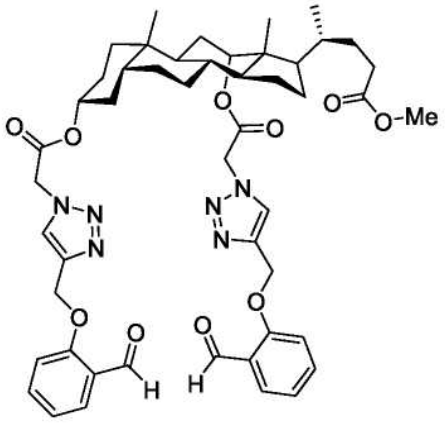
Receptors **X** and **XI** were found to be selective for Cu^{2+} and Pb^{2+} metal ions, respectively. Whereas, receptors **XII** and **XIII** showed high selectivity for Hg^{2+} ion. Mercury and lead are highly toxic elements and environmental pollutants that are continuously released to the environment from different sources. Therefore, routine detection of mercury and lead salts is essential for the monitoring of environment and natural food materials.



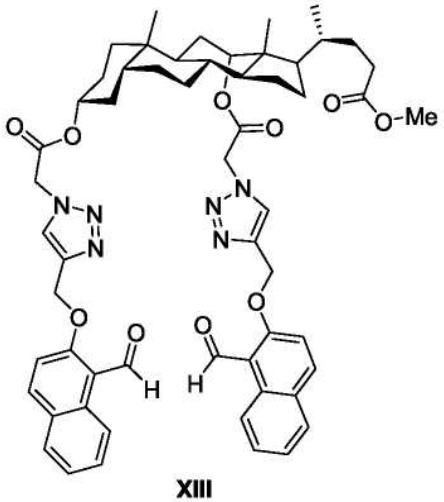
X



XI



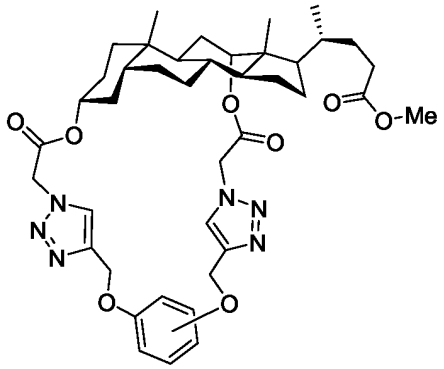
XII



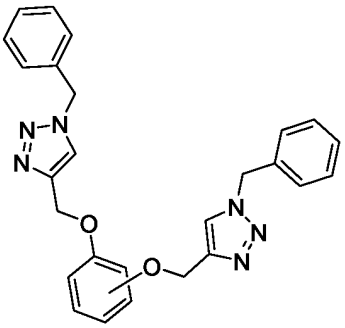
XIII

The synthesis of transition metal nanoparticles is important in view of their applications in catalysis, materials science and supramolecular chemistry. Recently, metal nanoparticle-based sensing of ions has received considerable attention, because it shows

much enhanced sensitivity and provides their fast colorimetric detection even at low concentration. Chapter 4 deals with the synthesis of silver nanoparticles stabilized with 1,2,3-triazole-containing compounds **X-XVII**. The AgNPs were synthesized by the reduction of $AgNO_3$ by visible light in the presence of 1,2,3-triazole compounds. These silver nanoparticles showed colorimetric sensing for Hg^{2+} metal ion (except in the case of **XI**). Some of these nanoparticles (stabilized with compounds **XV** and **XVII**) showed highly selective colorimetric sensing for iodide ion.

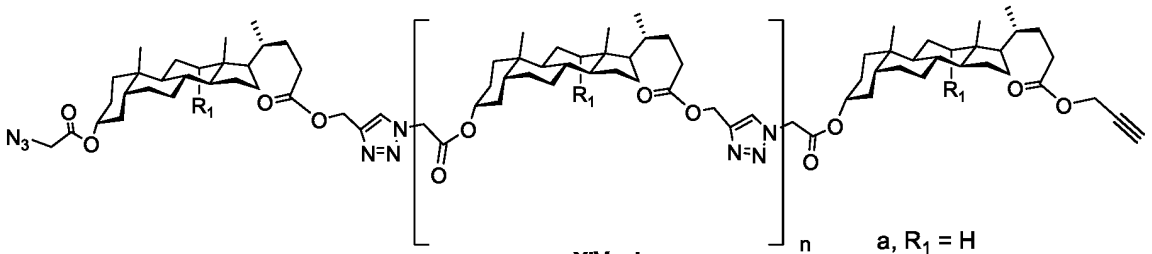


meta, **XIV**
para, **XV**



ortho, **XVI**
meta, **XVII**

Chapter 5 deals with the synthesis of main-chain bile acids-based polymers **XIVa** and **XIVb** using Cu(I)-catalyzed 1,3-dipolar cycloaddition reaction of monomers having both azide and alkyne functionalities. These bile acid-based polymers showed selective precipitation behaviour towards Hg^{2+} ion.



XIVa, b

a, R_1 = H
b, R_1 = OH

CONTENTS