SYNTHESIS AND SUPRAMOLECULAR CHEMISTRY OF BILE ACID-BASED ANION-RECEPTORS, POLYMERS AND SELF-ASSEMBLY SYSTEMS

by

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DOCTOR OF PHILOSOPHY

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This thesis is

Dedicated to my

Grandmother

CERTIFICATE

This is to certify that the thesis entitled "**Synthesis and Supramolecular Chemistry of Bile Acid-Based Anion-Receptors, Polymers and Self-Assembly Systems**" being submitted by Mr. Rajesh Kumar Chhatra to the Department of Chemistry, 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. Rajesh Kumar Chhatra has worked under my guidance and supervision and has fulfilled the requirements for the submission of this thesis, which to my knowledge has reached the requisite standard. The results contained in this thesis have not been submitted in part or in full to any other University or Institute for the award of any degree or diploma.

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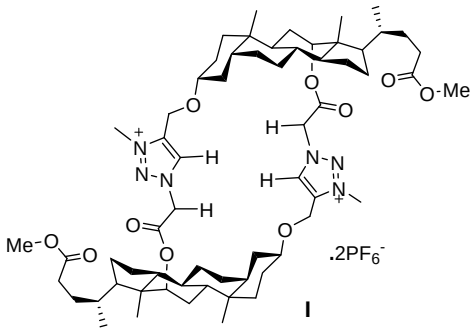
ABSTRACT

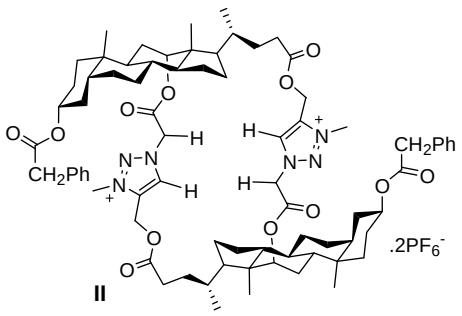
The application of click chemistry developed by Meldal and Sharpless involving the Cu(1)-catalyzed 1,3-dipolar cycloaddition reaction of azide and terminal alkyne to synthesize 1,4-disubstituted 1,2,3-triazole rings is constantly growing in the field of anion recognition due to the hydrogen-bond donor ability of its polarized C(5) hydrogen. This property makes them suitable candidates for the synthesis of anion binding receptors. The present thesis deals with the synthesis of 1,2,3-triazole and 1,2,3-triazolium receptors containing bile acid framework for anion recognition. The synthesis of main-chain bile acid-based polymers linked with 1,2,3-triazole rings *via* click reaction including metal-free solid state click reaction and their applications towards the stabilization of silver nanoparticles and ion sensing behaviour have also been described. In addition, the self-assembly behaviour of bile acid-based conjugates containing uracil and 2,6-diaminopyridine derivatives has also been discussed. The present thesis has been divided into four chapters.

Chapter 1 presents a brief literature survey on the recent developments in the anion recognition properties of 1,2,3-triazole and 1,2,3-triazolium receptors, bile acid-based polymers as well as self-aseembly systems.

Chapter 2 describes the synthesis and anion binding properties of steroidal and non-steroidal receptors having 1,2,3-triazolium and 1,2,3 triazole moieties. The binding properties of all the receptors with anions were examined by ^{1}H NMR titration in $CDCl_3$ using WinEQNMR software. Receptor **I** showed the highest affinity for chloride ion with an association constant of 3700 M^{-1}. Receptor **II** with larger and flexible cavity size also showed the affinity for chloride ion with a binding constant of 1600 M^{-1}.

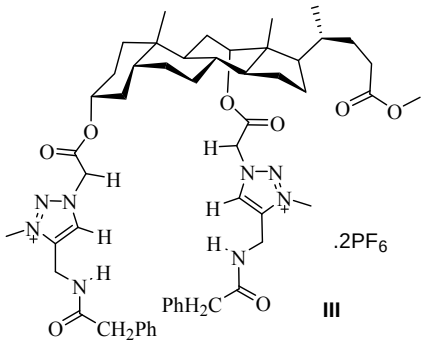


I



II

This chapter also describes the synthesis and anion binding properties of receptor **III** containing 1,2,3-triazolium and amide moieties. Receptors **III** showed very high affinity and selectivity for fluoride ion with association constant of 1.25 x 10^5 M^{-1}. The synthesis and anion binding properties of non-steroidal 1,2,3-triazolium receptors **IV** and **V** have also been studied. The *meta*-substituted receptor **V** showed the highest affinity for acetate ion (1 x 10^4 M^{-1}). However, *ortho*-substituted receptor **IV** showed the highest affinity for hydrogen sulphate ion (800 M^{-1}). The *meta*-substituted receptor **V** also showed high precipitation behavior with $H_2PO_4^-$ ion in polar solvents compared to *ortho*-substituted receptor **IV**.



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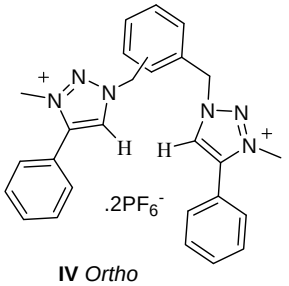
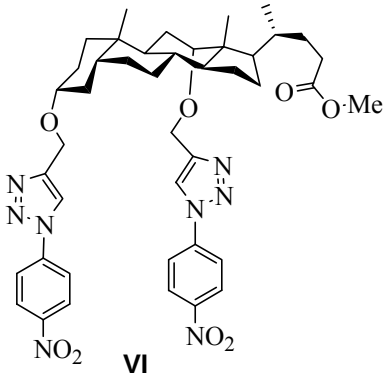


IV *Ortho*

V *Meta*

Further, deoxycholic acid-based acyclic 1,2,3-triazole bearing receptors **VI** and **VII** containing electron withdrawing groups attached to triazole rings have also been synthesized in view of exploring the effect of these substituents on the binding ability of the triazole rings. Receptor **VI**

showed colorimetric change with F^- and $H_2PO_4^-$ ions whereas receptor **VII** showed colorimetric change with F^- ion.



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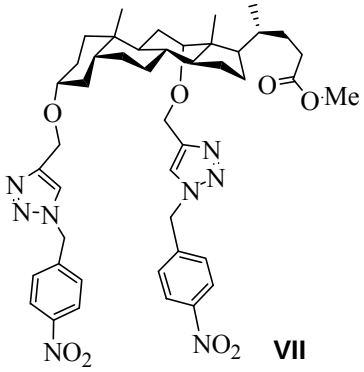
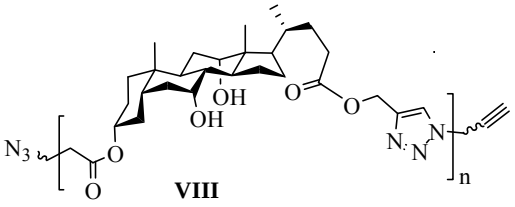
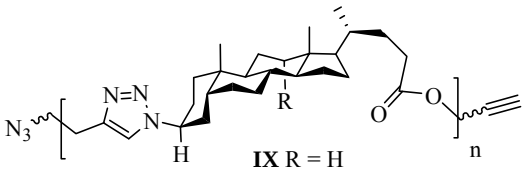


VII

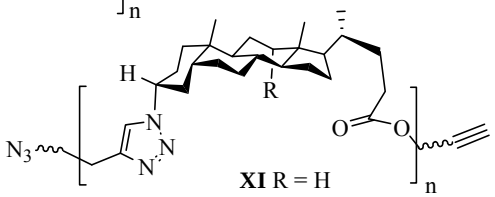
Chapter 3 deals with the synthesis of main-chain bile acids-based polymers **VIII- XVI** linked by 3α- and 3β-1,2,3-triazole rings *via* click reaction as well as metal-free solid state click reaction.



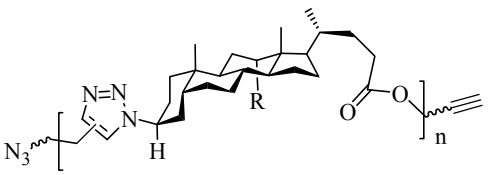
VIII



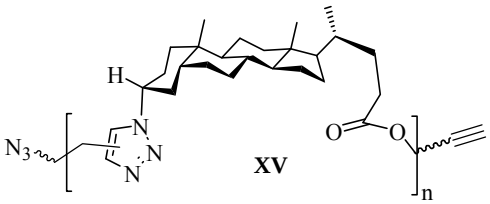
IX R = H
X R = OH



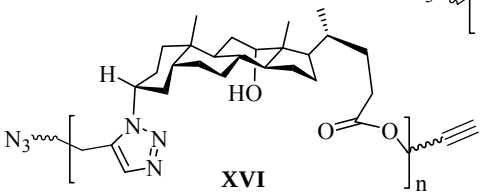
XI R = H
XII R = OH



XIII R = H
XIV R= OH



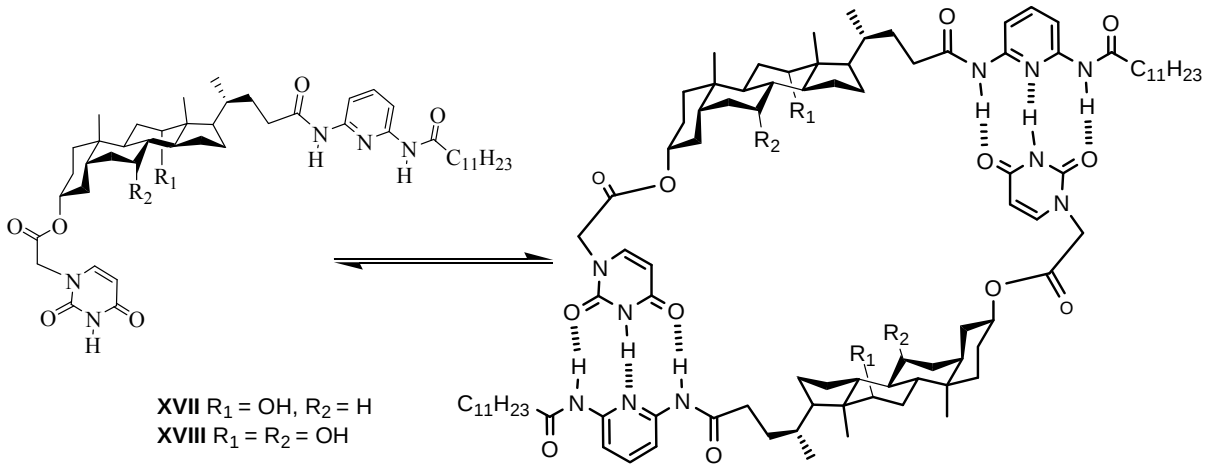
XV



XVI

Interestingly, pure 1,5-disubstituted 1,2,3-triazole-linked bile acid polymer **XVI** was obtained through crystal-lattice controlled azide-alkyne metal-free solid state click reaction. These polymers have been used as capping agent for the stabilization of silver nanoparticles. These silver nanoparticles showed highly selective colorimetric sensing for Hg^{2+} and iodide ions.

Chapter 4 deals with the synthesis of deoxycholic acid and cholic acid-based derivatives containing 2,6-diaminopyridine and uracil units and studied their self-assembly behaviour in view of investigating the effect of hydroxyl groups in the self-assembly process. The dimerization constants for deoxycholic and cholic acid conjugates were found to be $1x10^5$ M^{-1} and $3x10^5$ M^{-1}, respectively.



XVII R_1 = OH, R_2 = H
XVIII R_1 = R_2 = OH

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