INDIAN INSTITUTE OF TECHNOLOGY GUWAHATI
SHORT ABSTRACT OF THESIS

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Programme of Study : Ph.D.

Thesis Title: Studies on supramolecular assemblies, metal complexes of aromatic oxime derivatives for molecular and ions recognition.

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Thesis Submitted to the Department : Chemistry

Date of completion of Thesis Viva-Voce : 28.08.2018

Key words for description of Thesis Work : Oxime; Self-assembly; Physicochemical property; Metal Complex; Recognition; Cocrystal and Salt.

SHORT ABSTRACT

Different self-assemblies of oxime derivatives, some of their cocrystals and ionic salts are studied through crystal engineering approach. Properties of oximes as well as their different adducts in solid state are compared with the properties observed in solution. The formation and stability of self-assemblies of hydroxy-aromatic aldoximes with different tetrabutylammonium fluoride salts are essentially guided by the intrinsic acidity of fluoride ions. Different oxime derivatives and transition metal aldoxime complexes showed selectively detect fluoride ions in the presence of other anions. The role of metal ion in the complexes on the recognition process is ascertained. The inclusion of a dihydroxy-aromatic aldoxime in cadmium coordination polymer is compared with corresponding inclusion complex with the parent aldehyde to show the stability of the oxime derivative in confined conditions. Recognition of oxime derivatives by nitrogen containing compounds in solution and solid state are demonstrated. Competition between different types of acid-oxime interactions is investigated and various synthons in the cocrystals are described. Pre-designed non-covalent synthesis and the domain expansions of the sub-assemblies are elucidated. Photophysical and thermal properties of picrate salts of aromatic amine or heterocyclic linked oxime derivatives are studied and a unique example protonation at oxime nitrogen atom by picric acid was identified and their physicochemical properties are established. The thesis has improvised the scope of pre-designed non-covalent synthesis utilizing interplay of the weak interactions of oximes to generate new supramolecular assemblies with interesting optical properties in solid or solution state for molecular and ion recognitions.

The thesis entitled “**Studies on supramolecular assemblies, metal complexes of aromatic oxime derivatives for molecular and ions recognition**” deals with various non-covalently linked self-assemblies of oxime derivatives to establish their molecular and ions recognition abilities. The content of the thesis is divided into six chapters.

Chapter 1: Introduction

Self-assemblies of oxime containing compounds are well studied, and necessary supramolecular features of oxime derivatives to form non-covalently linked self-assembly are brought forward in the introductory chapter. This chapter contains discussions on pharmaceutical applications, molecular or ion recognition properties, coordination chemistry and biological activities of oxime derivatives and their metal complexes.

Chapter 2 (Part A): Anion Assisted Supramolecular Assemblies of Oxime Derivatives and Recognition of Fluoride ion

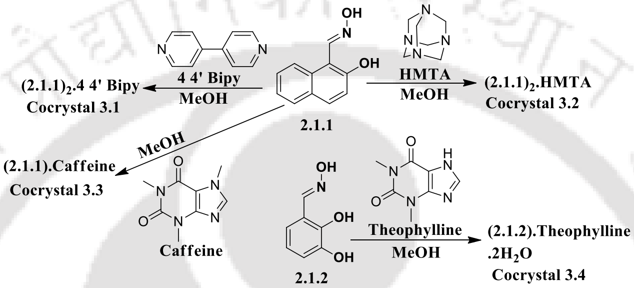
In this chapter we have discussed the role of hydroxyl-group together with oxime functional group on the self-assemblies of hydroxyaromaticaldoximes. Additionally, we have discussed on the role of deprotonating oxime or hydroxy functional group of oxime derivatives by fluoride ions to form new supramolecular architecture. Also solution and solid state studies presented in this chapter have suggested that fluoride ion can be distinguished from other anions through characteristic changes in absorption and emission spectra.

Chapter 2 (Part B): Anion Assisted Conformationally Guided Dendrimer-like Self-assemblies of Multi-component Cocrystals of Dioxime

Oximes having ability to remain as syn-syn or syn-anti conformation provides wide scope to study such effects in self-assemblies. These effects are shown in different self-assemblies of salts and cocrystals as well as in the parent aromatic dialdoximes. This chapter contains discussions on anion assisted conformational guided self-assemblies of dioxime in different cocrystals and salts of different tetrabutylammonium salts. The effects of hydration, conformational changes, multicomponent cocrystal formation are discussed. Role of hydrogen bonding ability of anions, hydrations and intrinsic basicity of anions anchored as tetrabutylammonium salt are presented. FT-IR and Raman spectra of oxime are used to distinguish different conformers.

Chapter 3: Recognition of Aggregation Induced Emission Active Oxime Derivatives by Nitrogen Containing Compounds in Solid and Solution State

The third chapter contains results obtained on selective crystallization of different cocrystals and signal transductions caused by nitrogen containing compounds upon interactions with aromatic hydroxyaldoximes and their cocrystals shown in the scheme 1. These oxime derivatives showed aggregation induced emission enhancement in dimethylsulfoxide solution with different water fractions. The packing pattern of the cocrystals with 4,4'-bipyridine, hexamethylenetetramine, caffeine and theophylline are investigated to correlate and is suggested the role of C-H…π interactions and π-π interactions in emission of solid samples.

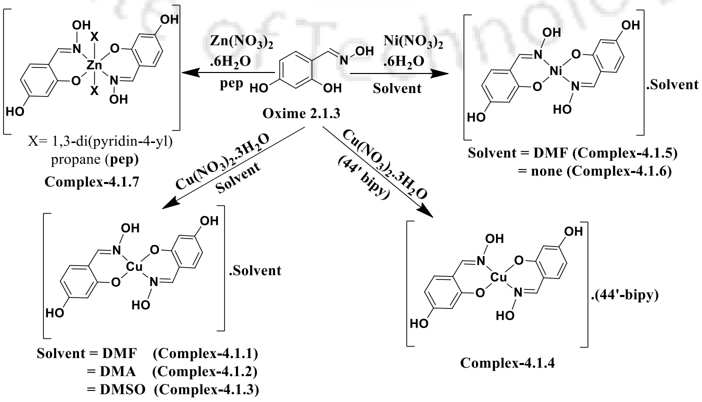


Scheme 1: Synthesis of different cocrystals of oxime derivatives

The differences in fluorescence emission found in solid and solution have suggested that the wide variations of emission properties in solid and solution phase. This also enabled to establish molecular recognition differently in solution and in solid state.

Chapter 4 (Part A): Transition Metal Complexes of Hydroxyaromaticaldoximes and Their Interactions with Fluoride ion

The self-assemblies of copper, nickel and zinc chelated metal complexes of hydroxyaromaticaldoximes are presented (Scheme 2). The roles of solvated molecules contributing to packing are discussed.



Scheme 2: Synthesis of transition metal complexes of 2,4-dihydroxybenzaldoxime.

Three different solvates from independent solvent of the copper complexes are discussed to suggest the directional properties of free hydroxyl group of the complex in guiding the respective self-assemblies of complexes**.** The role of free hydroxy functional group of these metal complexes on detection of fluoride ion in presence of other anions and the role of the metal ions in the complex to shift the emission patterns upon interactions with fluorides are presented. The advantage of using the zinc complex among copper and nickel complexes in the fluoride detection is demonstrated.

Chapter 4 (Part B): Inclusion of Aldehyde or Oxime in Cadmium Coordination Polymer and Conversion of Aldehyde to Oxime

The synthesis of different cadmium coordination polymers of 1,3-di(pyridin-4-yl)propane ligand encapsulating an oxime or aldehyde to understand possible reaction due to formation of inclusion complex is presented in this chapter. The association ability of the oxime with the parent cadmium complex is higher than aldehyde, facilitated conversion of aldehyde to oxime by the cadmium coordination polymer.

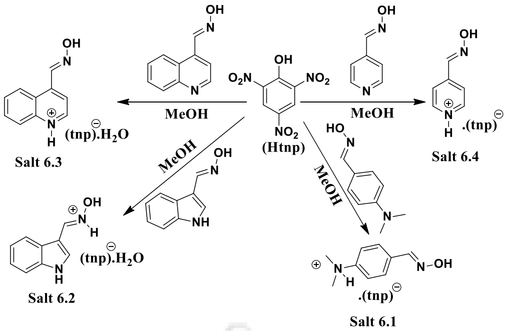
Chapter 5: Supramoleular Aspects of Quinoline-4-carbaldoxime with Aliphatic Dicarboxylic or Mineral or Aromatic Carboxylic Acids

The acid-oxime interactions are observed in quinoline-4-carbaldoxime cocrystals or crystalline salts with aliphatic dicarboxylic or mineral or aromatic carboxylic acids. Quinoline-4-carbaldoxime forms cocrystals with adipic acid, succinic acid, fumaric acid and 2-methylbenzoic acid whereas it formed salts with maleic acid, oxalic acid, nitric acid, hydrochloric acid, 2-hydroxybenzoic acid, 3-nitrobenzoic acid, 4-nitrobenzoic acid, 2,3-dihydroxybenzoic acid or 2,4-dihydroxybenzoic acid. Furthermore, in this chapter deprotonation, complementing hydrogen bond formation and competition between oxime-oxime, oxime-carboxylic acid, and carboxylic acid-carboxylic acid interactions are established to show that predesign synthesis is possible in systems having less competitive hydrogen bond factors to form different synthons.

Chapter 6: Self-assemblies, Absorption and Emission Properties of Picrate Salts of Aromatic Amine or Heterocycle Linked Oxime Derivatives

In this chapter we discussed on the self-assemblies, photo physical and thermal properties of picrate salts of aromatic amine or heterocycle linked oxime derivatives. Several oximes (scheme 3) are used for preparation of salts with different nitro-aromatic phenols. In this chapter the various aspects such as protonation at specific positions, the change of oxime-

oxime synthons on salt formation, charge transfer interactions are presented. The relevance of such interactions in solution is discussed.



Scheme 3: Synthesis of different picrate salts of oxime derivatives with different protonation sites.

The extent of protonation of oxime derivatives by picric acid is found to be different in each case. Solid state UV-vis studies revels that picrate salt of indole-3-carbaldoxime has charge-transfer interactions between protonated oxime and picrate anion. Thermal properties observed in differential scanning calorimetry of the picrate salts are also described in this chapter. Furthermore, in this chapter it is shown that hydrogen bond donor-acceptor properties associated the heterocyclic amines makes different self-assemblies of salts that are having close structural relationship when independently considered. It is also shown that charge-transfer adducts of picric acids are observed only in specific cases.

The thesis is concluded with brief conclusions deliberating the major findings on different self-assemblies and the difference in solution properties from solid state properties. The major findings are attributed to the understanding on competitive hydrogen bond formation and conformational guidance to form specific types of architectures and to utilize them in molecular and ion recognitions. The synthon expansion and specificity in formation of charge transfer complexes are depicted. And also certain series of cocrystals and salts that are isostructural suggesting a step towards predesigned non-covalent synthesis. Certain spectra and crystallographic table for each compound is given at the end. The crystallographic information files are also included. And detail structural description, synthetic procedure and spectroscopic characterization of each oxime derivatives, cocrystals and salts are available in the experimental section which is included at the end of each chapter.