

## PREFACE

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Investigations on coordination polymers and metal organic frameworks have always been interesting from the analytical, structural and technical point of view. A variety of coordination polymers of different compositions and stereochemistries are attainable even with the same ligand and metal ion just by changing the experimental conditions. A slight modification in solvent and temperature may display remarkable effect on the morphology and structure of isolated coordination polymers. The polydentate thiol ligands yield highly thermal stable and insoluble chelates on reaction with noble metal ions. Heterocyclic ligands derived from mercapto–thiadiazole have a number of N and S active donor sites that can bind to the metal ions in a particular fashion. These materials thus can act as potential linkers and are able to form structurally diversified interesting polymers with noble metal ions.

The past one decade has witnessed a rapid role of coordination complexes in the field of life sciences, environment sustainability and pharmaceutical industries. The formation of metal–enzyme complexes is universal in nature and many reactions in living systems occur *via* metal–complex formation with such large molecules. The aim of this work is to explore the coordination behaviour of organic ligand derived from 2–mercapto–1,3,4–thiadiazole system towards noble metal ions (Gold and Silver) and to achieve the probable structures of the infinite arrayed coordination polymers on the basis of spectroscopic studies and X–ray diffraction. The electro–activity of these compounds generally depends on type of ligands, coordination sites and metal ions. It is expected that the assembly of infinite arrayed coordination polymers synthesized here should be more useful for various application including device fabrication and sensing.

Several lifesaving drugs which are commonly used in our daily life are hazardous for human health when the dose exceed from a certain limit. Therefore it is

necessary to quantify the drug dose in the pharmaceutical formulation as well as in biological fluids. There are a number of techniques available for the quantification of drugs such as HPLC, spectrophotometry, spectro-fluorimetry and Ion chromatography etc., but they are of limited applicability due to sophisticated instrumentation and high cost while electrochemical detection is a simple, cheap, highly sensitive and reliable approach for the assay of drugs. In view of these advantages various electro-active materials are developed for electrochemical assay but they are suffering from electrode fouling, lesser stability at electrode and electrode poisoning. The designed coordination polymers circumvent these limitations of available electrode modifier. The fabricated assembly highlights highly sensitive and ultra-trace detection of drugs.

The study of the infinite arrayed coordination polymers could develop into a very wide field but the present investigation is restricted to 2-mercapto-1,3,4-thiadiazole system and Au/Ag ions. The reactions have been carried out in ethanolic, media by stirring at room temperature without using any initiator. The polymeric assemblies have been characterized by FT-IR, Raman, XPS, UV-Vis, CV and thermal studies. The structural architecture of the synthesized assembly has been determined by X-ray diffraction technique. The developed polymeric assembly is utilized for the modification of electrode in the voltammetric assay of drugs, resorcinol, Atropine sulphate and Ciprofloxacin hydrochloride.

The whole work has been presented in the form of five chapters. The introductory chapter (**Chapter-1**), after outlining briefly about the fabrication, organization, dimensionality, of coordination polymers, and their potential applications, gives a brief preview of the literature on synthetic, magnetic, spectral and structural studies of infinite arrayed coordination polymers. **Chapter-2** deals with the development of coordination polymer derived from 2,5-dimercapto-1,3,4-thiadiazole

system and gold chloride (DMTD–Au) and investigated by using several analytical tools (spectroscopic and diffraction techniques). Thereafter, based on these studies, the possible structural network of DMTD–Au is proposed that is in accordance with the results obtained. Further, it is utilized for the electro detection of Resorcinol in aqueous media. The **chapter–3** illustrates the fabrication of nano–porous coordination polymer DMTD–Ag. The developed assembly is characterized for the structural confirmation and then structural network is proposed that is in consistent with the results. Thereafter it demonstrates the effective use of DMTD–Ag in the voltammetric detection of anticholinergic drug, Atropine sulphate. In this series, **chapter–4** highlights the fabrication of nano–crystalline coordination polymer (AMT–Ag) constructed from 2–amino–5–mercapto–1,3,4–thiadiazole and silver nitrate. The structural assembly of AMT–Ag is thoroughly studied by several analytical characterizations and then the structural network of AMT–Ag is proposed. These assemblies of nano–crystallites are employed in the voltammetric detection of Ciprofloxacin hydrochloride along with their commercial formulation and biological fluids. Each chapter separately organized with different sections the introduction, experimental, and results. All the results have been thoroughly discussed to reach a logical conclusion, **chapter–5** complies a chapter wise summary of the work. The lists of references are included at the end.