PREFACE

Interests in metal directed self-assembly, its wide array of applications in numerous aspects of material chemistry, specifically the use of new sulphur rich binuclear macrocyclic complexes as effective hosts to bind hazardous heavy metal ions, organic molecules as well as toxic dyes has been contained. The exceptional stereoelectronic features of metal ions and dithiocarbamate ligands in metal-directed self-assembly direct to the formation of distinct supramolecular frameworks with interesting physicochemical properties and their application in medicinal, magnetism, electrical conductivity, optoelectronic properties and supramolecular chemistry. In recent years new strategies in ligand modifications and judicious selection of metal ions presented great opportunities for significant adjustments of molecular units in the resulting self-assembled structures with fascinating electronic properties, required for various applications. The results presented in this thesis is based on the synthesis, spectral characterization, photophysical, single crystal X-ray diffraction (SCXRD) and in-silico study of some homonuclear bimetallic bis-dithiocarbamate macrocyclic complexes based on new diamino ligand precursors holding functionalized linker framework. The efficient and straightforward procedures have been employed in the synthesis of these complexes. Majorly, these complexes have been further investigated as a potential host to bind/ sense a number of environmentally hazardous heavy metal ions and toxic organic dyes as well. The thesis is mainly divided into five chapters.

Chapter 1 presents an overview of self-assembly, its wide array of applications in numerous aspects of material chemistry, molecular magnetism, electrical conductivity, optoelectronic properties and specifically in host-guest binding Study. The importance of the development of metal-directed self-assembled molecular architectures has been hilighted in this chapter. In particular, emphasis has been made on the novel dithiocarbamate ligand system and its versatile coordination chemistry with transition metals as well as organometallic fragments that display a wide range of applications. The use of various organic and inorganic macrocyclic compounds including bimetallic bis-dithiocarbamate macrocyclic complexes in the host-guest reactivity studies, as well as specific objectives of the present study, are also described in this chapter.

Chapter 2 deals with **t**he synthesis of a number of secondary diamine precursors *viz.* 4,4'-methylenebis-2-((2-thiophen-2-yl)ethylamino)methylphenol (**H_2L^1**), 4,4'-methylenebis-2-(cyclohexylamino)methylphenol (**H_2L^2**), S,S-(Thiophene-2,5-diyl)bis(N-(1-phenylethyl)methanamine) (**H_2L^3**), R,R-(Thiophene-2,5-diyl)bis(N-(1-phenylethyl)methanamine) (**H_2L^4**), *N*,*N'*-bis{3-(*p*-methoxybenzylamino)propyl}piperazine (**H_2L^5**) and *N*,*N'*-bis{3-(p-chlorobenzylamino)propyl}piperazine (**H_2L^6**) holding diversified linkers. The formation and purity of all the compounds were verified by microanalysis and standard spectroscopic methods such as NMR, IR, SCXRD and supported by density functional theory calculations. The unambiguous molecular structure of some of the representative compounds determined means of single crystal XRD and their crystal packing patterns were explored. The photophysical properties of these precursors were also investigated before utilizing them for further derivatization in succeeding chapters.

Chapter 3 is devoted on the use of newly synthesized secondary diamino precursors 4,4'-methylenebis-2-((2-thiophen-2-yl)ethylamino)methylphenol (H_2L^1) and 4,4'-methylenebis-2-(cyclohexylamino)methylphenol (H_2L^2) in the synthesis of a new series of 32-membered homobimetallic dithiocarbamate macrocyclic complexes $[M_2\text{-}\mu^2\text{-bis-}\{\kappa^2S\text{\^{}}S\text{-}S_2CN(R)CH_2C_6H_3(OH)\}_2CH_2]$ (R = 2-thiophenylethyl; Ni^{II} **1**, Cu^{II} **2**, Zn^{II} **3;** R = cyclohexyl; Ni^{II} **4**, Cu^{II} **5**, Zn^{II} **6**). A number of analytical tools (elemental analysis, HRMS, IR, NMR, UV-visible TGA/DTA) have used to confirm the formation of products. Further, molecular structures of Ni^{II}-dithiocarbamate macrocyclic complex **1** have been determined by SCXRD method. The geometries of all the M^{II}-dithiocarbamate macrocyclic complexes **1-6** have been optimized by a density functional theory calculation with B3LYP/LanL2DZ basis sets to corroborate the experimental results. Ccomplexes **1-3** were further investigated for their potentials as a molecular probe in sensing/ binding of environmentally hazardous dyes such as Acid Orange (II), Bromocresol green, Bromophenol blue, Bromothymol blue, Crystal violet, Methylene blue by means of UV-visible and ^1H NMR tools and the outcomes of this study are elaborated in this chapter.

Chapter 4 is dedicated to the synthesis of a new series of binuclear metallomacrocyclic dithiocarbamate complexes $[M(II)_2\text{-}\mu^2\text{-bis-}\{(\kappa^2S,S\text{-}S_2CN(CH(S\text{-}CH_3)Ph)CH_2)_2\text{thiophene}\}]$; M = Ni(II) **7**, Cu(II) **8**, Zn(II) **9** and $[M(II)_2\text{-}\mu^2\text{-bis-}\{(\kappa^2S,S\text{-}S_2CN(CH(R\text{-}CH_3)Ph)CH_2)_2\text{thiophene}\}]$; M = Ni(II) **10**, Cu(II) **11**, Zn(II) **12** by using a metal directed self-assembling process involving secondary diamino precursors *S,S*-(Thiophene-2,5-diyl)bis(N-(1-phenylethyl)methanamine) $\mathbf{H_2L^3}$ or *R,R*-(Thiophene-2,5-diyl)bis(N-(1-phenylethyl)methanamine) $\mathbf{H_2L^4}$, carbon disulfide and transition metal ion in a single pot reaction. All the compounds have been characterized by various spectral and crystallographic techniques as well as density functional theory calculations. The experimental and theoretical calculations suggest square planar/distorted square planar environment around nickel(II)/ copper(II) and tetrahedral/distorted tetrahedral environment around zinc(II) centres in **7-12**. Notably, the calculated HOMO-LUMO gaps (1.84-2.08 eV) for Cu(II)-dithiocarbamate **8** and

11 indicates their semiconducting nature. The potentials of these binuclear metallomacrocycles as a molecular probe for optical sensing of environmentally hazardous heavy metal ions *ca* Pb(II), Cd(II) and Hg(II) were further examined by using UV-visible.

Chapter 5 encompasses the explorations on the use of secondary diamines precursors *N,N'*-bis{3-(*p*-methoxybenzylamino)propyl}piperazine (**H_2L^5**) and *N,N'*-bis{3-(p-chlorobenzylamino)propyl}piperazine (**H_2L^6**) holding *N,N'*-bispropylpiperazine linkers in the development of another series of *N,N'*-bis(3-dithiocarbamatopropyl) piperazine bridged metallomacrocyclic complexes [$M(II)_2$-μ^2-bis-{($\kappa^2 S,S$-$S_2CN(R)C_3H_6)_2$piperazine}] wherein R = *p*-methoxybenzyl, M = Ni(II) **13**, Cu(II) **14**, Zn(II) **15**; R = *p*-chlorobenzyl, M = Ni(II) **16**, Cu(II) **17**, Zn(II) **18**. The composition of all the complexes and their phase purity were verified by microanalysis and standard spectroscopies HRMS, NMR, IR, corroborated by density functional theory calculations. The experimental (magnetic susceptibility and UV-visible) and theoretical calculations suggest square planar/distorted square planar environment around nickel(II)/ copper(II) and tetrahedral/distorted tetrahedral environment around zinc(II) centres in **13-18**. Thermogravimetric study was carried out on **13-18** to study their thermal stability and degradation behaviour. Interestingly, TG curves of compounds **14**, **15** and **17** gave a stable residual mass corresponding to corresponding metal sulphides (MS) and suggest their potential utility as single source precursors for the synthesis of high purity MS nanoparticle as a new class of resources for energy conversion and/or storage applications. Moreover, the calculated HOMO-LUMO gaps (1.19-1.33 eV) for Cu(II)-dithiocarbamate **14** and **17** indicates their semiconducting nature. The potentials of these binuclear metallomacrocycles as a molecular probe for optical sensing of environmentally hazardous heavy metal ions *ca* Pb(II), Cd(II) and Hg(II) were further examined by using UV-visible.