Executive Summary of the Ph.D. Thesis

Novel Metallomacrocyclic Dithiocarbamate Complexes and Their Potential Applications in Host-Guest Binding Study

A Thesis Submitted to

THE MAHARAJA SAYAJIRAO UNIVERSITY OF BARODA

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DOCTOR OF PHILOSOPHY

IN

CHEMISTRY

By

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Brief Research methodology

Materials and measurements

All reactions and manipulations throughout the work were carried out in an inert atmosphere of nitrogen. Solvents were purchased from the commercial sources and were freshly distilled prior to use. Chemicals used in this work were of laboratory grade available at various commercial sources and used without further purification. Thin Layer Chromatography was performed on Merck 60 F254 aluminium coated plates. FT-IR (KBr pellets) spectra were recorded in the 4000-400 cm^{-1} range using a Perkin-Elmer FT-IR spectrometer. The NMR experiments were carried out on a Bruker AV-III 400 MHz spectrometer in $CDCl_3$ solvents as per the solubility and chemical shifts are reported in parts per million (ppm). UV-visible absorption spectra were recorded on a JASCO V-730 UV-visible spectrophotometer whereas fluorescence spectral studies were carried out on JASCO make spectrofluorometer model FP-8200. TGA/DTA plots were obtained using SII TG/DTA 6300 in flowing N_2 with a heating rate of 10 °C min^{-1}. All the geometry optimizations were performed with the Gaussian 16 program and molecular orbitals were generated using Gauss View 6.0 program.

X-ray Crystallography and Data Collection

Intensity data for *R,R*-**BI-1** and *S,S*-**BI-2** were collected on 'X-calibur, Eos, Gemini' X-ray diffractometer equipped with Eos CCD detector at 298 K. Monochromatic MoKα (λ = 0.71073 radiations were used for the measurements. Data was collected and reduced by using the ''CrysAlispro'' program (Version 1.171.37.33 Agilent Technologies, 2014) [1]. The structures were solved by the direct methods, and the refinement was carried out by full-matrix least squares against F^2 using SHELXL program package [2] and Olex2 (version 1.2.5) program package [3]. All non-hydrogen atoms were refined anisotropically.

Molecular docking study

Ligand preparation

The 3D structures of certain ligands were extracted from optimized structure in Gaussian 16.0 in PDB format and they were assigned charges and torsions and converted to PDBQT in autodock vina.

Protein preparation and Grid Parameters

The protein Tumor Necrosis Factor Alpha with PDB ID: 1TNF and 2AZ5 is downloaded from RCSB Protein Data Bank. The protein was prepared by Discovery Studio Client 21. The grid co-ordinates were assigned within the 3D space of ligand for 1TNF and 2AZ5 by autodock vina. The docking protocol is validated by re-docking the ligand onto the active site of receptor pocket.[4] The binding site of the protein was predicted by Discovery Studio Visualizer 21. The assigned Grid Co-ordinates of the active site X: 34.948322 Y: 58.626136 Z: 47.521359, the ligands were also blind docked with complete Chain-A of 1TNF and 2AZ5 as binding pocket.

Validation of Docking

The docking of ligands onto the binding site of protein is executed and docking was performed using autodock vina. The ligands were screened for their efficient fitting into the receptor (minimized) grid. The ligands were screened with all possible minimum energy confirmations. The non-bonding interactions within 6 Å of active site of receptor pocket is explored using Discover Studio Visualizer 21.[5] Visualization of residues Interaction. Non-bonding interactions of all ligands with protein were elucidated using Discovery Studio Client 21. The binding interactions of ligands with active site of protein were compared with that of ligand with binding energy.

Synthesis

Several amine functionalized ligand precursors and their ensuing binuclear transition metal dithiocarbamate macrocyclic complexes have been synthesized by using an effective and straightforward synthetic methodology. [6-8]

Key findings

Researchers have taken due interest 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. 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.

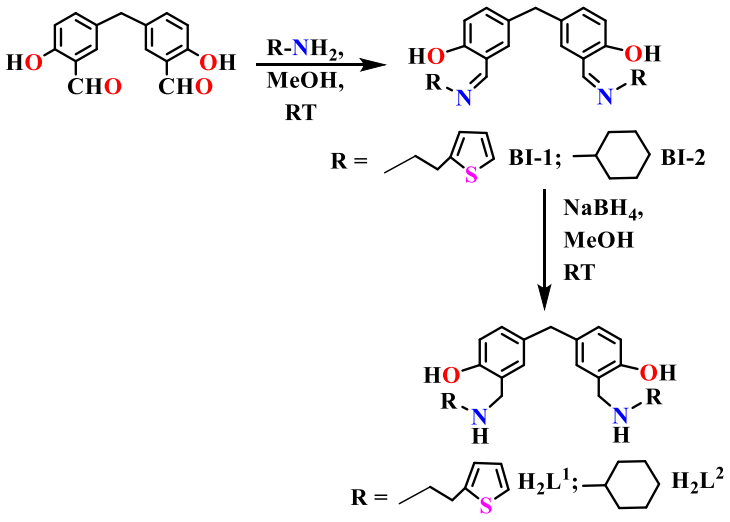
The work presented in this thesis is focuses mainly on the synthesis, spectral, crystallographic characterization, computational investigation and Host-guest binding studies of several series of sulphure rich metal complexes derived through metal directed self-assembly of new amine precursors bearing functionalized backbone, CS_2 and metal ions fragments. A number of chiral/ achiral amine precursors have been designed and synthesized for the purpose of developing new library of sulphure-rich metallomacrocyclic complexes. The overall work is summarized into five chapters. The chapter-wise key findings are summarized below:

Chapter 1: A detailed literature review on functionalized diamine precursors holding varied spacers and their importance in the development of novel 1,1-dithiocarbamate ligand systems and their transition/ non-transition metal dithiocarbamate complexes that display an array of applications in the area of medicinal, material and in the supramolecular chemistry has been included in this chapter. The reactivity of newly synthesized metallomacrocyclic molecules towards various guest species have been further emphasized. The foremost objectives of the present investigation are also

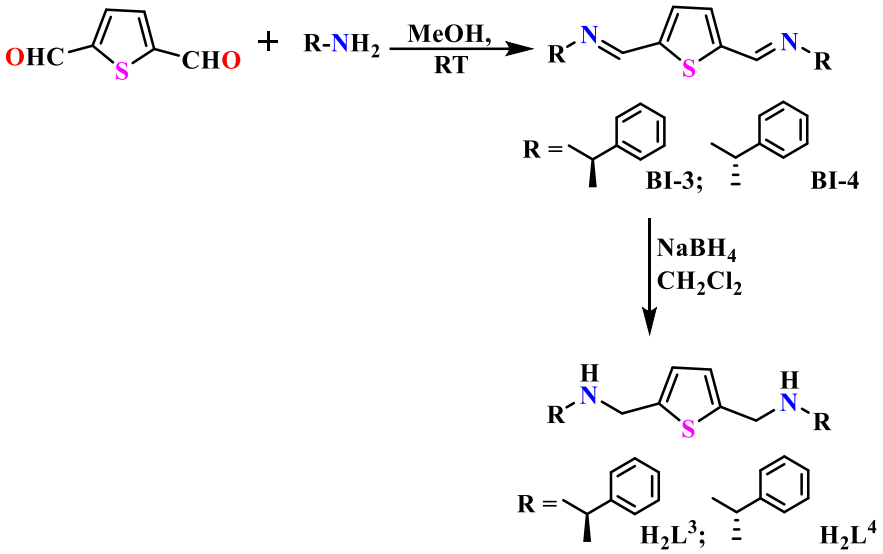
described in this chapter.

Chapter 2 includes the design and synthesis of several diamine ligand precursors (H_2L^1-H_2L^6) holding either diphenylmethane, thiophene or piperazine moieties in the spacers as per the **Scheme 1-3**. All of the functionalized organic diamines were characterized thoroughly by elemental analysis, NMR (^1H and ^{13}C), UV-visible, FTIR, TGA/DTA and single crystal X-ray diffraction (SCXRD) techniques. The optical properties of these molecules have been further investigated by using UV-visible spectral data and the results are well supported by theoretical calculations.

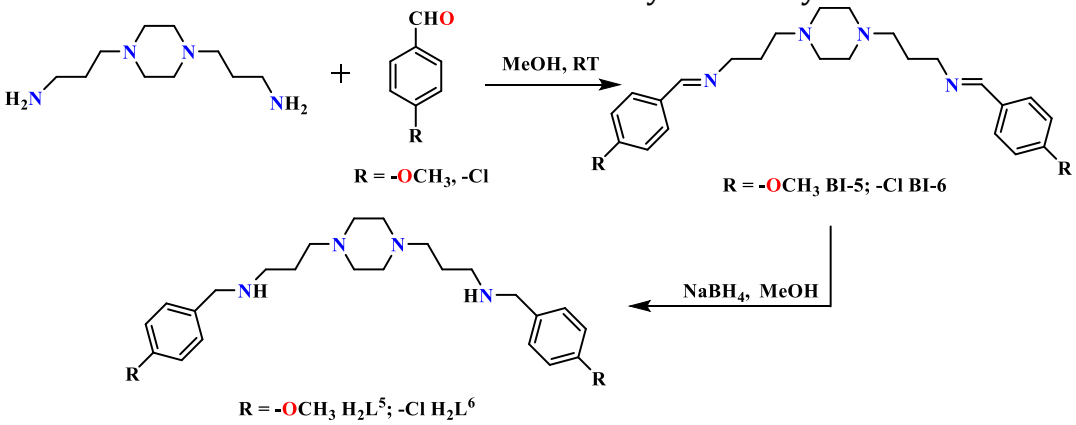
Single crystals of the organic precursors H_2L^1, BI-3 and BI-4 suitable for single crystal X-ray diffraction study were grown by slow evaporation of these compounds in CH_2Cl_2. The unprecedented molecular structures of H_2L^1, BI-3 and BI-4 are shown in Fig. 1, Fig. 2 and Fig. 3, respectively.



Scheme 1: Synthesis of new organic diamines (H_2L^1- H_2L^2) bearing diphenylmethane in the linker framework with N-thiophenylethyl-/ cyclohexyl substituents.



Scheme 2. Synthesis of new organic diamines (H_2L^3- H_2L^4) bearing thiophene in the linker framework that holds chirality at N-benzylic carbons.



Scheme 3: Preparation of diamines holding piperazine in the linker framework with *p*-methoxybenzyl/ *p*-chlorobenzyl *N*-substituents at peripheral positions.

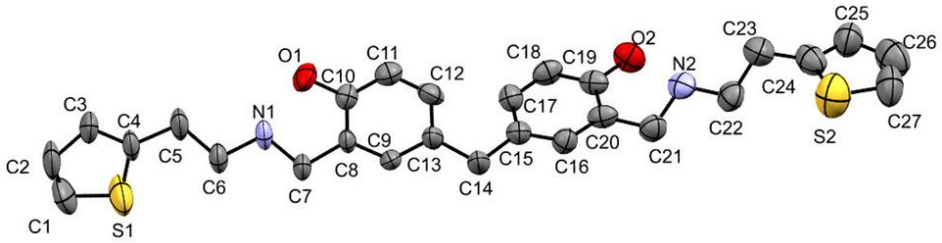


Fig. 1. Molecular structure of **H_2L^1** (hydrogens are omitted for clarity).

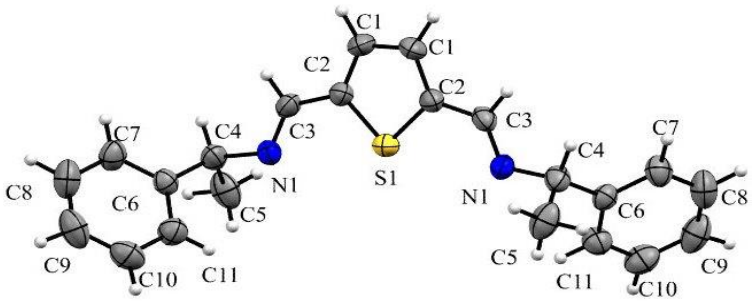


Fig. 2. Molecular structure of **BI-3**.

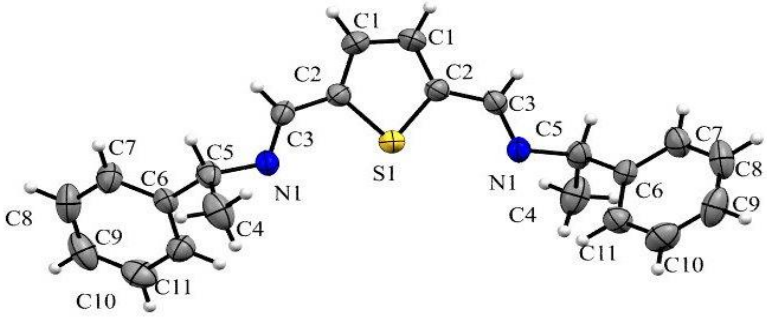
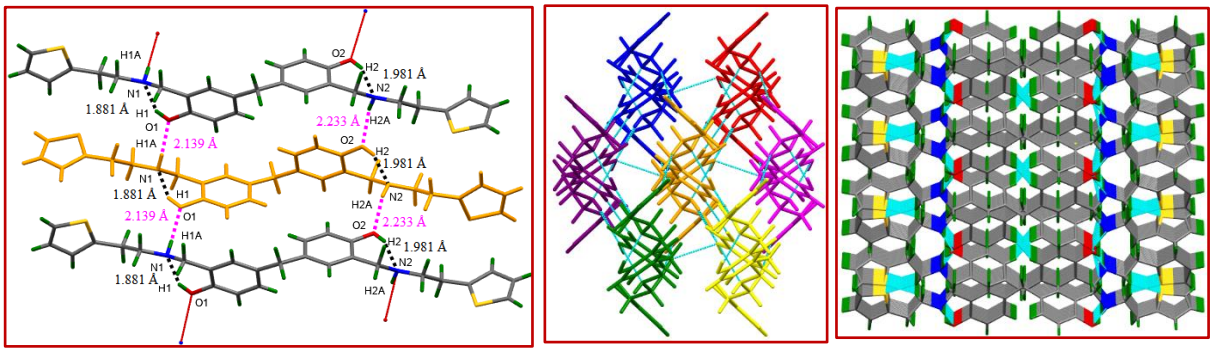


Fig. 3. Molecular structure of **BI-4**.

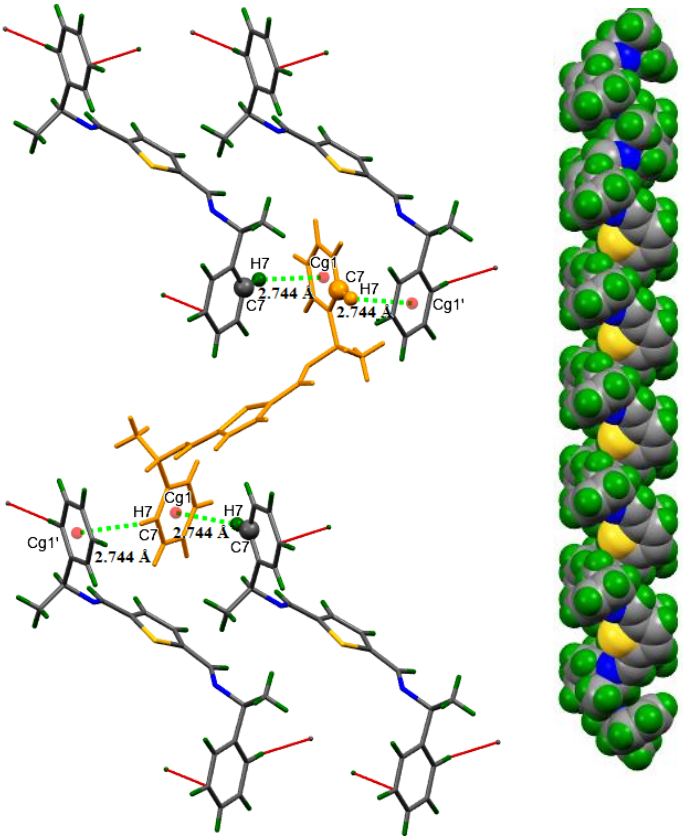
The molecules of **H_2L^1** have shown the propensity to form intra- and intermolecular H-bonding interactions O-H…N (1.881 Å) and N-H…O (2.139 Å) in the solid state, forming a 2D sheet like supramolecular structure in bc-plane as shown in Fig. 4.



(a) (b) (c)

Fig. 4. Asymmetric molecule of H_2L^1 forming (a) intra- and intermolecular H-bonding interactions, arranges the molecules along *c*-axis (tilted down), (b) supramolecular aggregate consists of **7** molecules in the *bc*-plane (c) 2D sheet like supramolecular structure in bc-plane.

However, the molecules of BI-3 and BI-4 holding *S*- and *R*-chirality at benzylic carbons are sustained primarily through intermolecular C-H…π (2.744 Å) interactions as shown in Fig. 5 (a).



(a) (b)

Fig. 5. Asymmetric molecule of **BI-3** primarily forms (a) C-H… π intermolecular contacts, arranges the molecules along *c*-axis, leading to a supramolecular aggregate consists of 5 molecules. (b) Spacefill model illustrating the formation of 2D drill screw like architecture (view along c-axis).

Each peripheral phenyl groups of **BI-3** offering C-H…π (2.774 Å; Cg1= Cg1' = C6C7C8C9C10C11) donor-acceptor contacts, connecting four molecules anti-parallelly along c-axis. These contacts are extended two dimensionally and forming a fascinating 2D drill screw like architecture as shown in Fig. 5(b).

Moreover, frontier molecular orbitals of bis-imine precursors BI-3-BI-6 and their reduced products H_2L^3-H_2L^6 were derived from DFT calculation at B3LYP/6-31G level (Fig. 6 and Fig. 7) which clearly suggests that Homo and Lumo molecular orbitals are mainly localized at central thiophenyl group in BI-3-BI-4 and H_2L^3-H_2L^4 (Fig. 6) whereas in BI-5-BI-6 and H_2L^5-H_2L^6 holding piperazine in the spacer, the

highest occupied molecular orbitals (Homo) are mainly localized at the central piperazine but lowest occupied molecular orbitals (Lumo) are localized at one of the peripheral phenyl rings (Fig. 7).

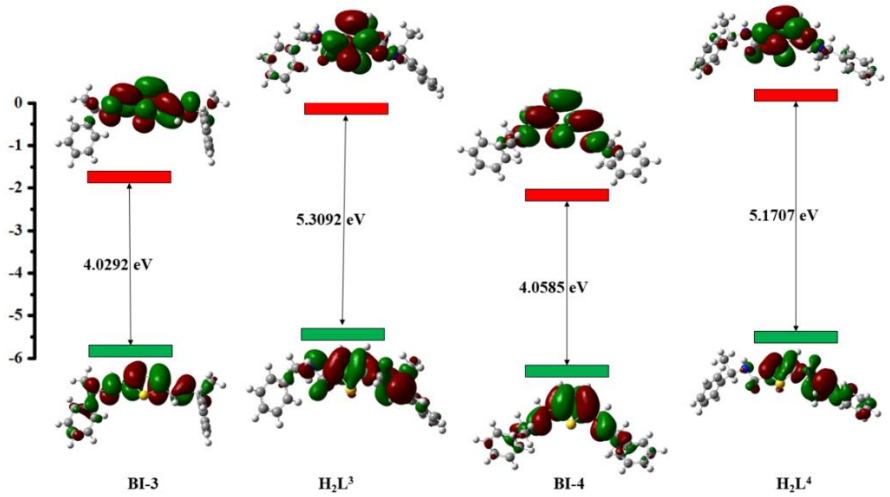


Fig. 6. Frontier molecular orbitals derived from DFT calculation at B3LYP/6-31G level.

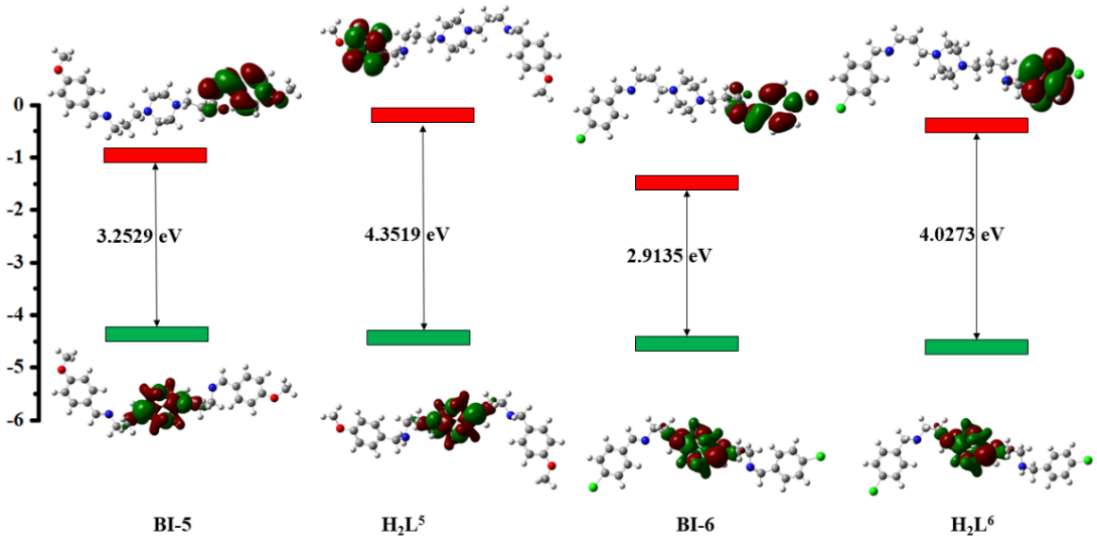


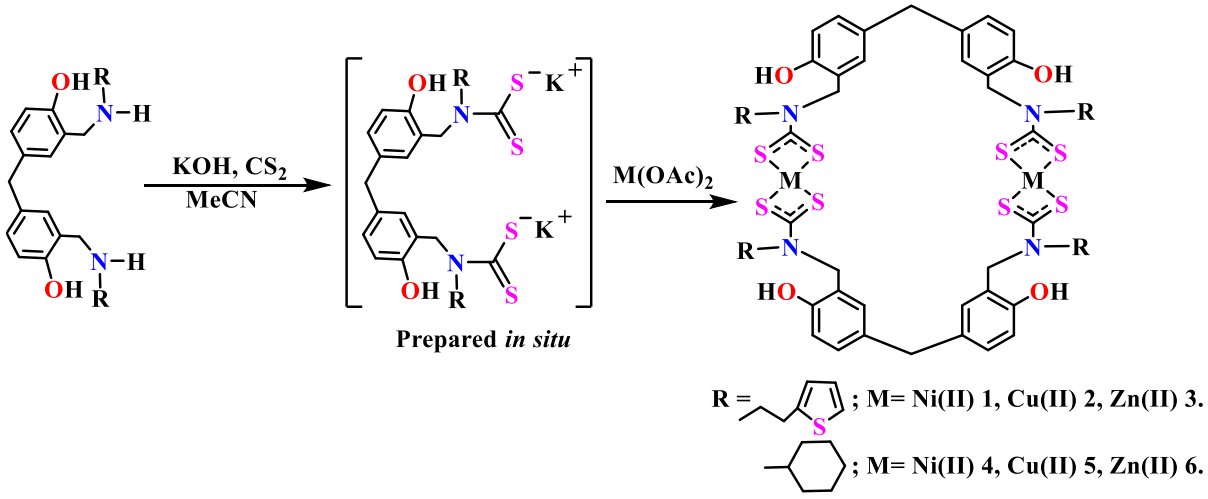
Fig. 7. Frontier molecular orbitals derived from DFT calculation at B3LYP/6-31G level.

Table.3. Summary of computational study

Entry	HOMO (eV)	LUMO (eV)	Band Gap (eV)	Entry	HOMO (eV)	LUMO (eV)	Band Gap (eV)
BI-3	-5.9658	-1.9366	3.4724	**BI-5**	-4.2458	-0.9929	3.2529
H_2L^3	-5.6518	-0.3426	5.3092	**H_2L^5**	-4.3707	-0.0188	4.3519
BI-4	-6.1378	-2.0792	4.0585	**BI-6**	-4.4512	-1.5377	2.9135
H_2L^4	-5.5470	-0.3763	5.1707	**H_2L^6**	-4.5288	-0.5015	4.0273

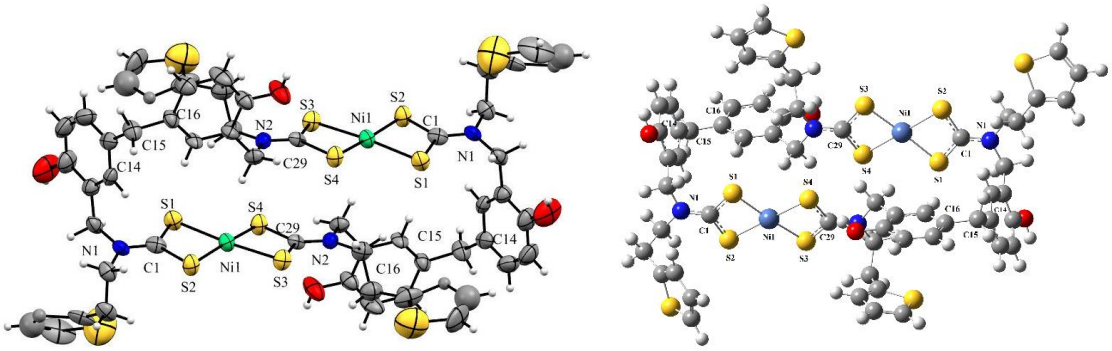
The calculated Homo-Lumo band gaps fall in the range of 2.9-5.3 eV suggesting non-semiconducting nature of these organic molecules which indeed well supported by experimentally. The diamine precursors H_2L^1-H_2L^6 have been further studied for their utility to form corresponding dithiocarbamate ligands and their ensuing metal complexes and the results are elaborated in the coming chapters.

Chapter 3: In this chapter, metal directed self-assembly of diamine precursors H_2L^1-H_2L^2 with CS_2 and Ni^{II}, Cu^{II} or Zn^{II} ions (**Scheme 4**) leading to a new series of binuclear metallomacrocyclic dithiocarbamate complexes **1-6** holding pendent phenolic and thiophenyl groups at the peripheral position of macrocycle is summarized. The compounds were characterized by microanalysis, NMR (^1H, ^{13}C), HRMS, UV-visible, FTIR, thermogravimetric and crystallographic techniques.



Scheme 4: Synthesis of binuclear metallomacrocyclic dithiocarbamate complexes **1-6** holding pendent phenolic and thiophenyl groups at the peripheral position of macrocycle.

The unambiguous structure of nickel(II) dithiocarbamate complex 1 (Fig. 8a) has been determined by means of SCXRD which is found to be consistent with its theoretically optimized structure (Fig. 8b)



(a) (b)

Fig.8. (a) X-ray structure (b) optimized structure of nickel(II) complex **1**.

The geometry of all the complexes 1-6 has been optimized by a DFT level calculations and the structural parameters obtained theoretically are well compared with experimentally determined structural parameters. Notably, the molecules of complex **1** are stabilized by a good number of C-H….S intermolecular contacts forming an attractive 3D multiple open tubular supramolecular assembly as shown by spacefill model (Fig. 9).

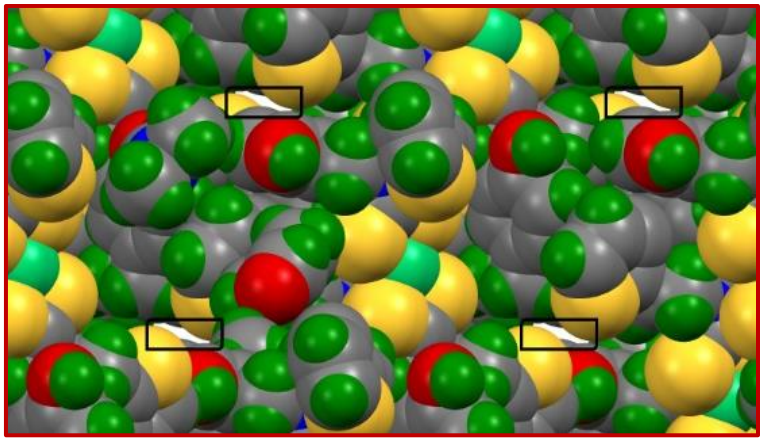
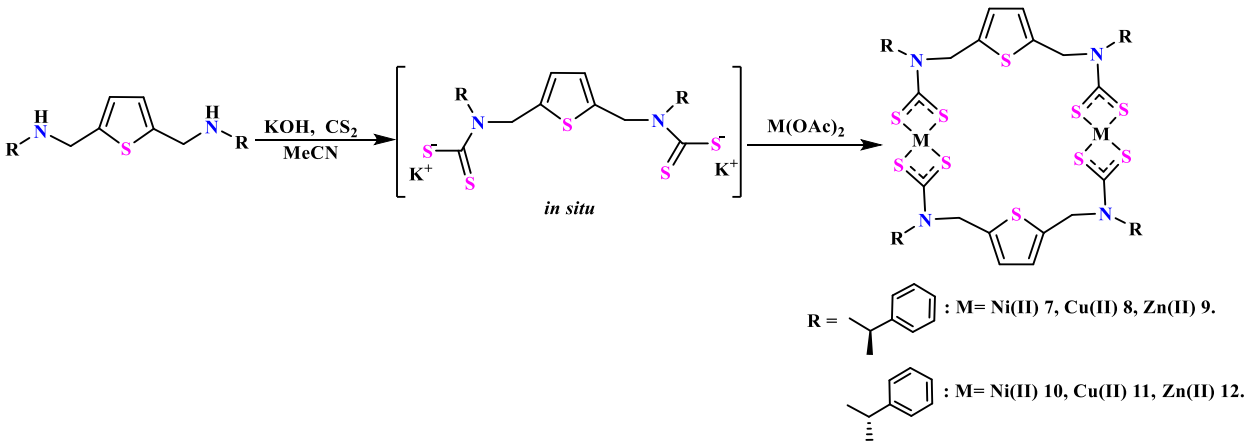


Fig. 9. Molecules of complex **1** forming an attractive 3D multiple open tubular supramolecular assembly through a number of C-H….S intermolecular contacts.

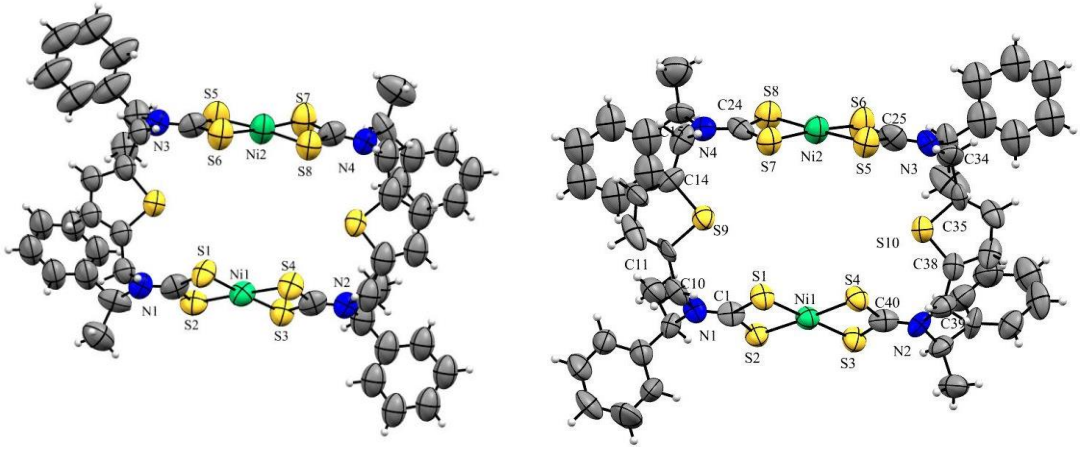
Complexes holding thiophenyl groups are found to be thermally more stable as their degradation start at ~200ºC which is much higher than the degradation temperature of other complexes **4-6** holding cyclohexyl groups. Interestingly, the band gaps calculated theoretically for all the complexes 1-6 suggests that copper (II) dithiocarbamate complexes with band gaps of 1.86 eV (for **2**) and 1.89 eV (for **5**) are semiconducting in nature. Further, binuclear metallomacrocyclic dithiocarbamate Ni^{II} complex **1** and Zn^{II} complex **3** have shown the ability to bind environmentally hazardous organic dyes "Acid orange (II)" and "Bromocresol green" in 3:1 and 1:2 stoichiometric ratio, respectively.

In Chapter 4, the chiral secondary amines (H_2L^3-H_2L^4) holding thiophene spacer synthesized in the previous chapter, were taken for the development of new binuclear dithiocarbamates macrocyclic complexes of Ni^{II}, Cu^{II} and Zn^{II} (7-12) as per the following Scheme 5.



Scheme 5: Synthesis of binuclear dithiocarbamate macrocyclic complexes **7-12** holding thiophene in the spacer.

The compounds were characterized by microanalysis, NMR (^1H, ^{13}C), HRMS, UV-visible, magnetic moment, FTIR, thermogravimetric and crystallographic techniques. The UV-visible data along with magnetic moment data reveals square planar geometry around Ni^{II}, Cu^{II} ions and tetrahedral geometry around Zn^{II} ions in their respective compounds. Further, the geometry around these metal centres were confirmed by SCXRD study.



(a) (b)

Fig. 10. Molecular structure of (a) complex 7 and (b) complex 10.

The structural parameters obtained experimentally are well supported by theoretical calculations.

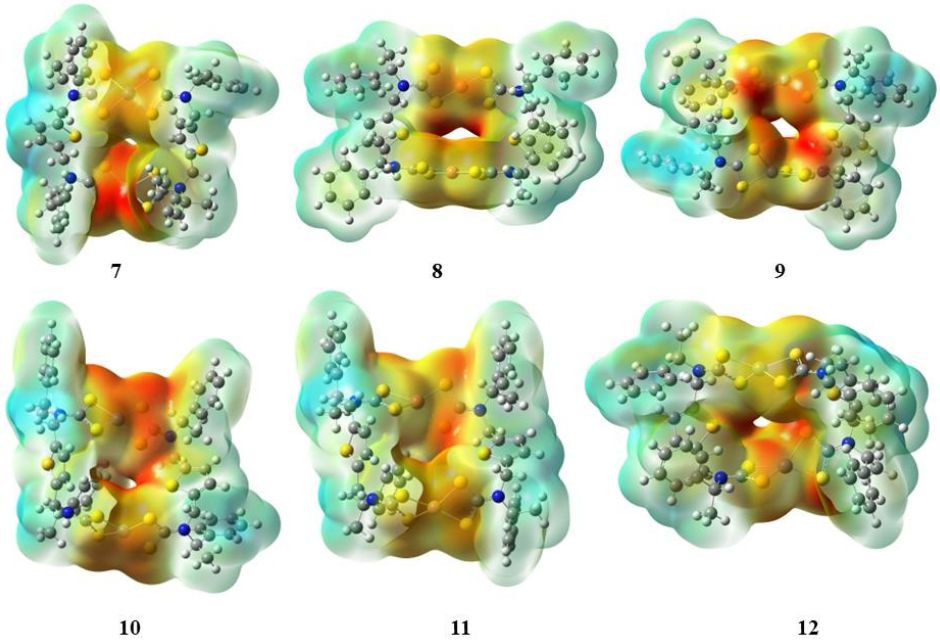


Fig. 11. *MESP* diagrams for the metallomacrocyclic complexes 7-12.

The molecular electrostatic potentials of 7-12 were determined theoretically, suggesting localization of negative potential around chelate rings and positive potentials around C-H groups and confirms the ability of these molecules to offer donor-acceptors intermolecular contacts in the solid state which is indeed verified experimentally. For instance, molecules of complex **7** evidently offer intermolecular

CH….S, $\pi_{aromatic}$… $\pi_{chelate}$ and CH…pi contacts, arranges the molecules three dimensionally and forming a fascinating supramolecular assembly displaying 3D pores of (5 × 18) Å^2 dimensions in the solid state as shown in Fig. 12.

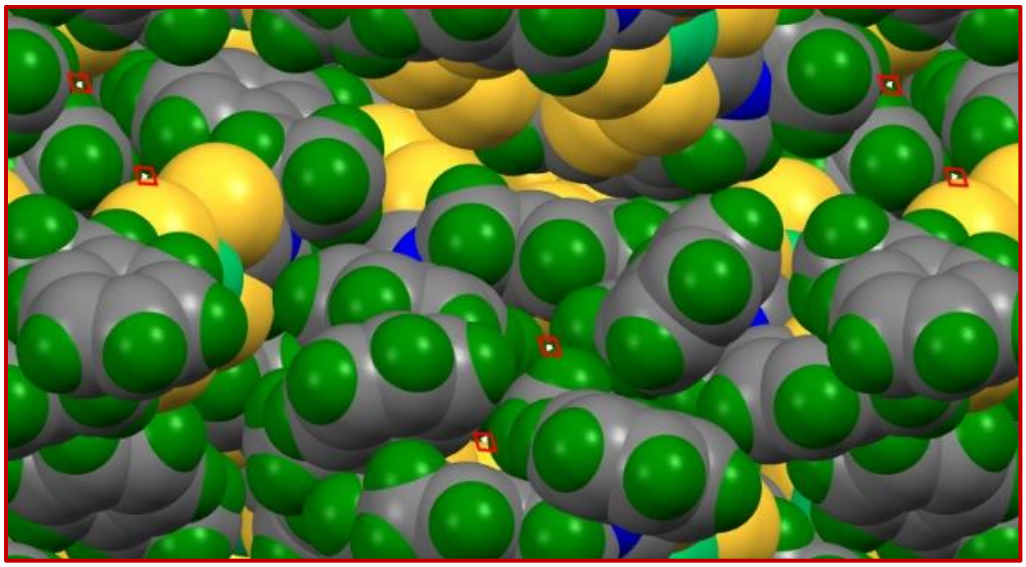
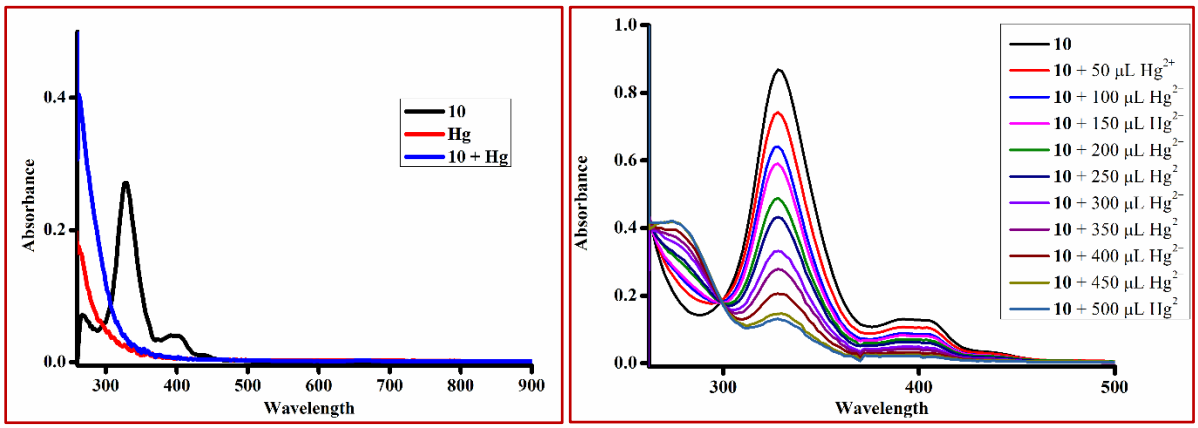


Fig. 12. Supramolecular assembly formed by complex **7** displaying 3D pores of dimension (5 × 18) Å^2 shown by the spacefill model.

Similar to the nature of copper(II) complexes **2** and **5** included in chapter 4, the band gaps calculated theoretically for all the complexes 7-12 suggests that copper(II) dithiocarbamate complexes with band gaps of 2.08 eV (for **8**) and 1.84 eV (for **11**) are semiconducting in nature. Further, binuclear metallomacrocyclic dithiocarbamate complexes **10-12** were further investigated for their ability to bind with environmentally hazardous heavy metal ions viz.

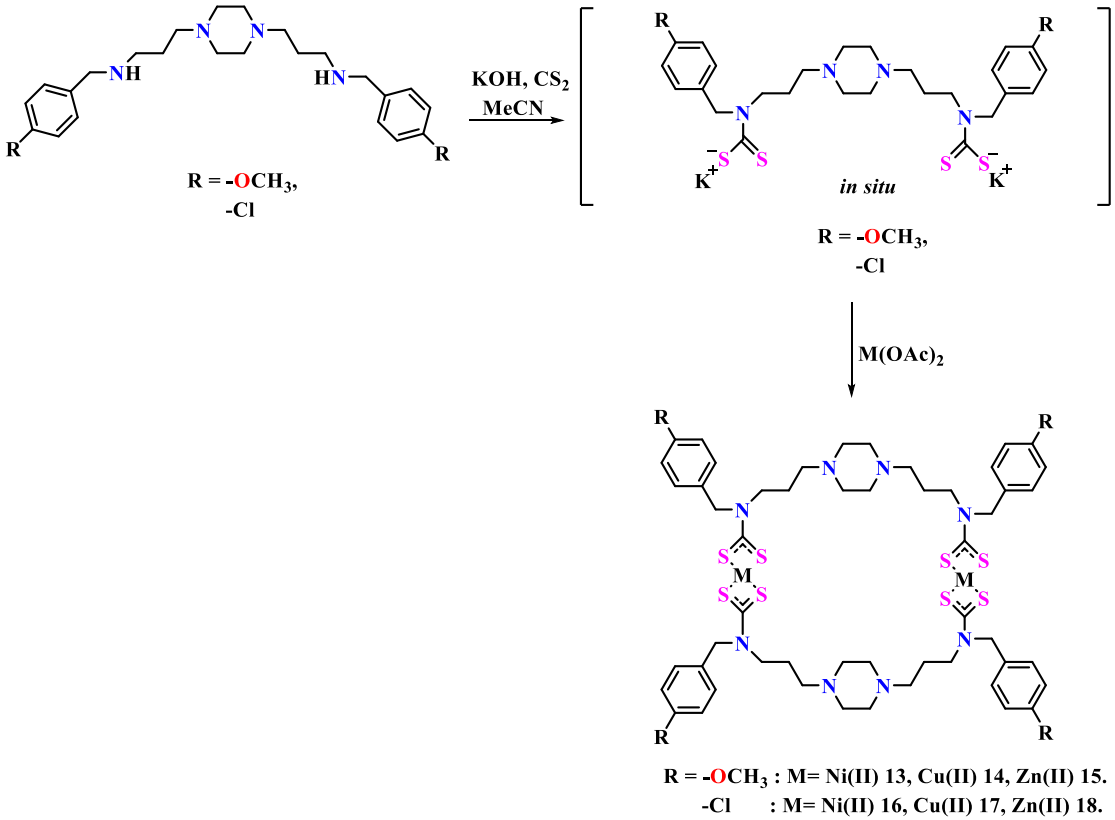


(a) **(b)**

Fig. 13. (a) Sensing study of complex **10** with Hg^{2+} (b) UV-visible titration of complex **10** with Hg^{2+}.

Cd^{2+}, Pb^{2+}, As^{3+}, As^{5+}, Hg^{2+}, Ag^{+} and the results suggests that binuclear metallomacrocyclic dithiocarbamate complexes **10-12** can sense Hg^{2+} and Pb^{2+} invariably as intra-ligand n→π* transition apparently associated with thiophene disappears in the presence of Hg^{2+} (Fig. 13). However, the effort to find out the exact stoichiometry of Host-Guest interaction and to establish the exact mode of binding of these metal ions are on the way.

Chapter 5: In this chapter, piperazine based diamine precursors **H_2L^5** and **H_2L^6** have been successfully utilized in the synthesis of a new series of bimetallic bis-dithiocarbamate complexes **13-18** holding functionalized linker framework. All the compounds have been characterized by elemental analysis, relevant spectroscopic (NMR, IR, UV-visible, HRMS), thermogravimetric techniques.



Scheme 6: Synthesis of Piperazine Based Metallomacrocyclic Dithiocarbamate Complexes **13-18**.

The appearance of expected number of sharp NMR signals (*ca* Fig. 14), macroanalysis and HRMS data (ca Fig. 15) confirmed the purity and composition of these complexes. The magnetic moment data along with UV-visible spectral data indicates square planar geometry around Ni^{II} and Cu^{II} centers and tetrahedral environment around Zn^{II} centers in their respective homo bimetallic dithiocarbamate complexes 13-18.

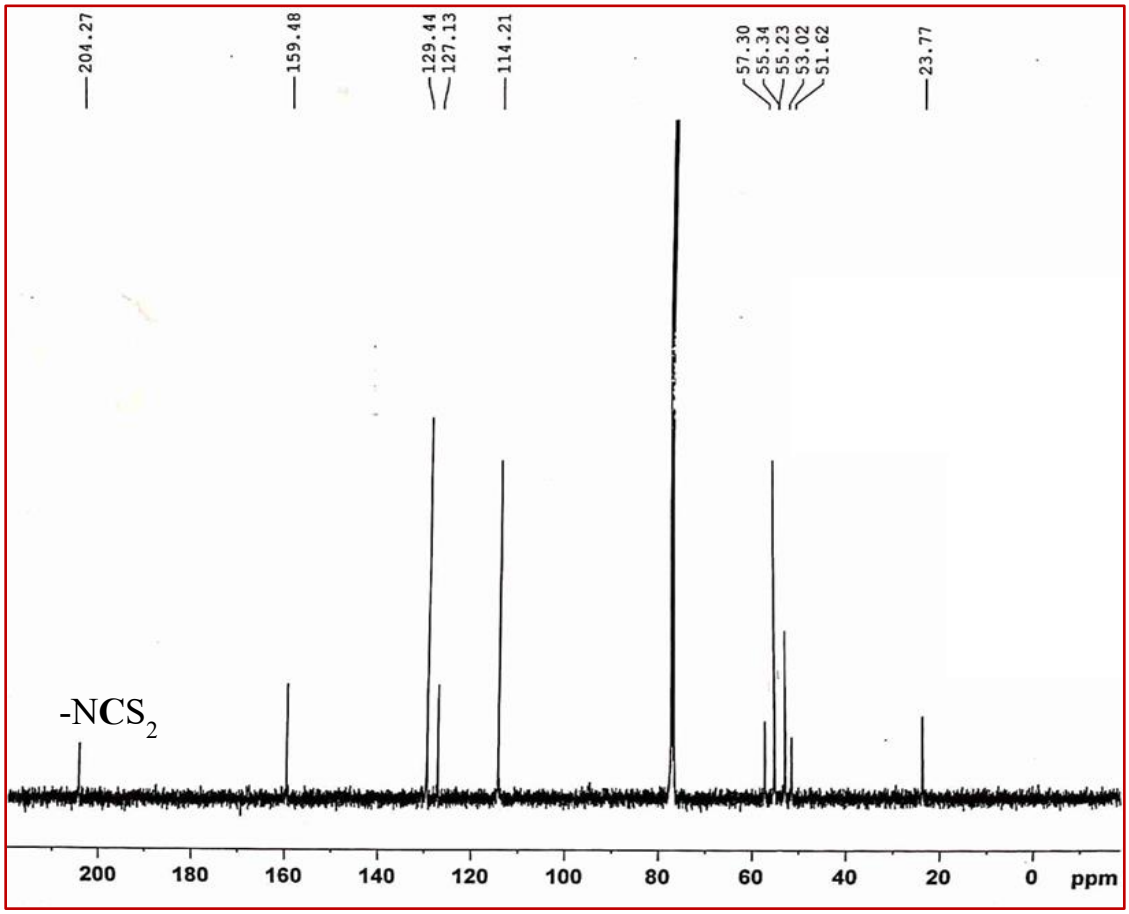


Fig.14. ^{13}C NMR specrun of Zn^{II} dithiocarbamate complex **15.**

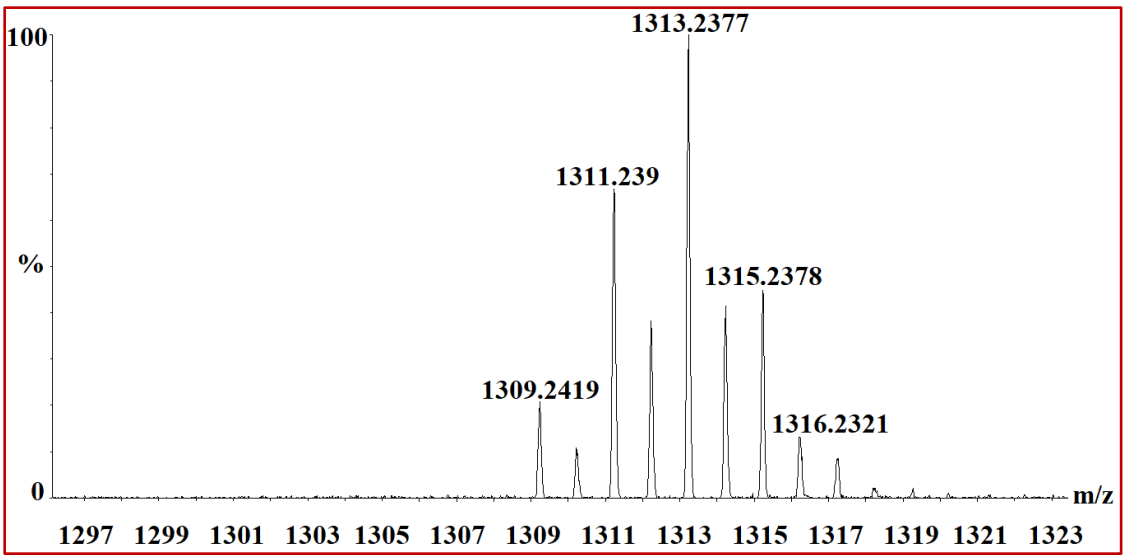


Fig.15. HRMS specrun of Zn^{II} dithiocarbamate complex **15.**

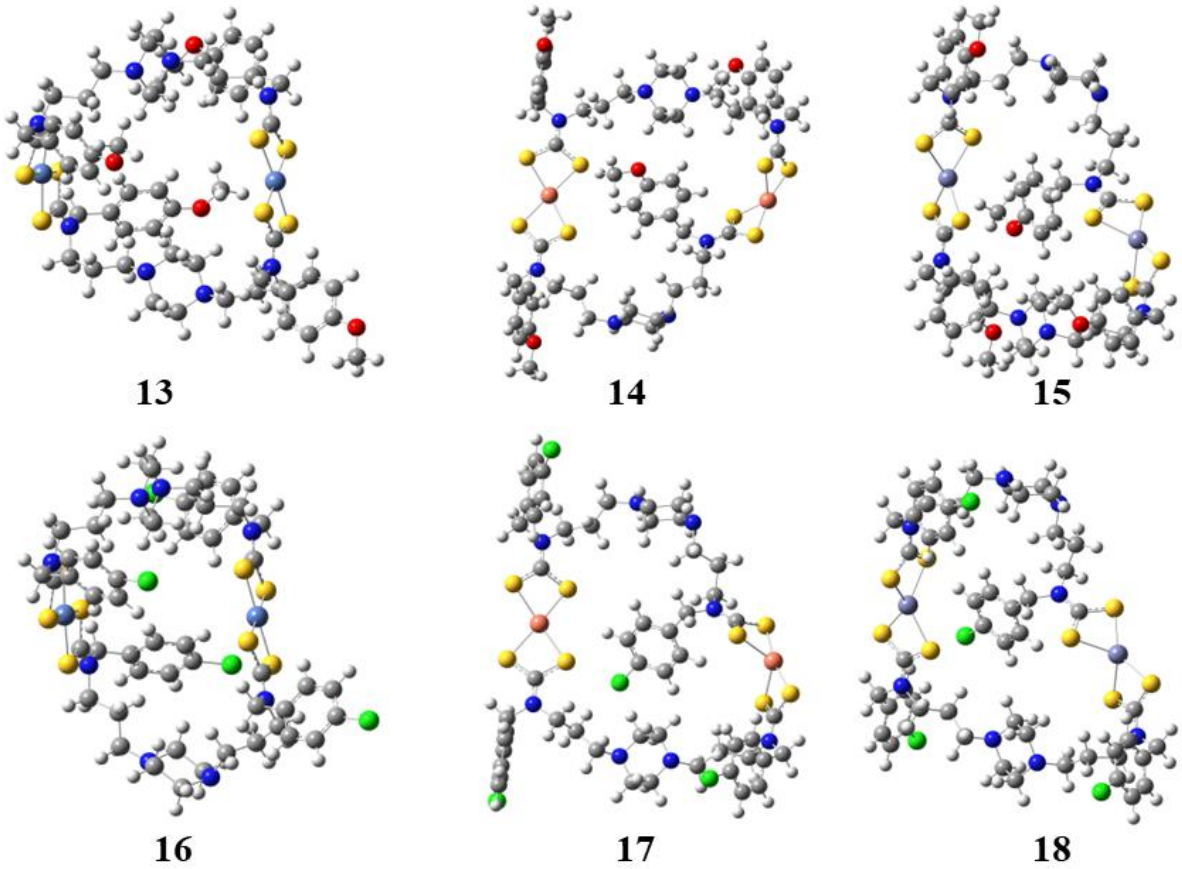


Fig.16. Optimized geometry for the minimum energy conformation of macrocyclic dithiocarbamate complexes **13-18** at B3LYP/LanL2DZ basis set.

The HOMO-LUMO band gaps obtained theoretically for Ni^{II} (**13** and **16**) and Cu^{II} (**14** and **17**) complexes falls in the range of 1.0-2.8 eV (Table 4) and suggests the semiconducting nature of these complexes.

Table.4: Energy of Homo-Lumo and energy band gaps

Entry	HOMO (eV)	LUMO (eV)	Band gap (eV)	Entry	HOMO (eV)	LUMO (eV)	Band gap (eV)
13	-4.7073	-1.8541	2.8532	**16**	-4.8107	-2.0501	2.7606
14	-4.7040	-3.3693	1.3347	**17**	-4.8929	-3.7013	1.1916
15	-4.6447	-0.9483	3.6964	**18**	-4.8472	-1.2754	3.5718

The potentials of all these complexes as a Host for a range of guest species including environmentally hazardous heavy metal ions are yet to be examined.

Conclusions

In conclusion, a number of novel diamino ligand precursors such as 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 functionalized linker framework were designed and synthesized under a mild reaction conditions. All the synthesized compounds were suitably characterized by microanalysis, ^1H, ^{13}C NMR, FTIR studies. The geometry of all the molecules has been optimized by using a density functional theory calculation and the theoretical data were compared well with the experimental outcomes. The non-conducting nature of these compounds are ascertained by their HOMO-LUMO band gaps falls in the range of 2.91-5.30 eV. Furthermore, a molecular docking study was employed to virtually screen these nitrogenous compounds in order to suggest possible biologically essential molecules. All diamino precursors were suitably utilized in the development of several new series of metallomacrocyclic dithiocarbamate compounds useful in in the host-guest binding study.

For instance, a new series of 32-membered homobimetallic dithiocarbamate macrocyclic complexes [M(II)$_2$-μ^2-bis-{κ^2*S*^*S*-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**) were competently synthesized through single pot reaction involving 4,4'-methylenebis-2-((2-thiophen-2-yl)ethylamino)methylphenol (**H_2L^1**) or 4,4'-methylenebis-2-(cyclohexylamino)methylphenol (**H_2L^2**), CS_2 and transition metal ions. A number of analytical tools and density functional theory calculations were used to verify the composition and purity of the products. Notably, the analysis of single crystal X-ray diffraction (SCXRD) data of Ni(II)-dithiocarbamate macrocyclic complex **1** reveals that complex **1** has the potential to form a fascinating 3D supramolecular structure possessing multiple opening of dimension: ~ 8.890 × 35.213 Å^2 in the solid state which opens a scope for macrocyclic complex **1** and its analogues to be investigated as a potential host in the host-guest supramolecular chemistry to sense/ bind hazardous organic dyes. Evidently, Ni(II)-dithiocarbamate macrocyclic complex **1** shown the ability to sense Acid Orange (II) selectively with considerable blue shifting of absorption bands whereas Cu(II) / Zn(II)-dithiocarbamate macrocyclic complexes **2** and **3** have shown the ability to sense Bromocresol green, selectively with significant red shifting of absorption bands. The ^{1}H NMR titration study reveals the formation of 3:1 host-guest stochiometric complex between **1** and Acid Orange (II) (G-1). The presence of Lewis acidic metal centers, hydrophobic cavity and several polar substituents at the peripheral positions in our macrocycles are found to be crucial in the recognition as a potential host to sense/ bind hazardous organic dyes. The main driving forces in facilitating host-guest interactions are apparently hydrophobic, electrostatic and π–π stacking interactions between the host and guest. The present study exposes a new strategy to construct and utilize new homobimetallic dithiocarbamate macrocyclic complexes for binding/ sensing of organic pollutants.

Further, the secondary diamino precursors viz. *S,S*-(Thiophene-2,5-diyl)bis(N-(1-phenylethyl)methanamine) **H_2L^3** and *R,R*-(Thiophene-2,5-diyl)bis(N-(1-phenylethyl)methanamine) **H_2L^4** holding thiophene spacers prepared in chapter 2 have been successfully utilized to derive a new series of binuclear metallomacrocyclic dithiocarbamate complexes [M(II)$_2$-μ^2-bis-{(κ^2*S,S*-S_2CN(CH(*S*-

CH_3)Ph)CH_2)$_2$thiophene}]; M = Ni(II) **7**, Cu(II) **8**, Zn(II) **9** and [M(II)$_2$-μ^2-bis-{(κ^2*S,S*-S_2CN(CH(*R*-CH_3)Ph)CH_2)$_2$thiophene}]; M = Ni(II) **10**, Cu(II) **11**, Zn(II) **12**. The formation and purity of all the binuclear metallomacrocyclic dithiocarbamate complexes were verified by microanalysis and standard spectroscopic methods such as HRMS, NMR, IR and UV-visible absorption spectroscopy and supported by SCXRD study 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.

Moreover, a new series of *N,N'*-bis(3-dithiocarbamatopropyl) piperazine bridged metallomacrocyclic complexes [M(II)$_2$-μ^2-bis-{(κ^2*S,S*-S_2CN(R)C_3H_6)$_2$piperazine}] (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**) can be conveniently synthesized by using a single pot-multi component reaction protocol. The phase purity and formulation of these were thoroughly verified by microanalysis, relevant spectroscopies, validated by density functional theory calculations. Interestingly, critical analysis of TG curves indicates the potentials of compounds **14**, **15** and **17** to form high purity metal sulphides (MS) nanoparticle that can form a new class of resources for energy conversion and/or storage applications whereas the analysis of HOMO-LUMO band gaps indicates the semiconducting nature Cu(II)-dithiocarbamate **14** and **17**. It is worth noting that the use of soft sulphur donor atoms in the chelating unit of metallomacrocycles **13-18** evidently increase their affinity and selectivity for Hg(II) ions over Pb(II) and Cd(II). A comprehensive literature survey reveals that dithiocarbamate complex based UV-visible/ fluorescent chemosensors have not yet been described for heavy metal ions except for Li^+, Na^+, K^+, Cs^+, neutral organic or anionic guest species such as halides, $H_2PO_4^-$, CH_3COO^-, and $C_6H_5COO^-$. Thus, our explorations on the use of sulphur rich metallomacrocyclic compounds as small-molecule probe for optical read-outs of environmentally hazardous heavy metal ions, preferably

Hg(II) ions over Pb(II) and Cd(II) add merit to this work. The results further suggest that such transition metal dithiocarbamate based molecular probe can be suitably designed as an analysis tools, optical devices or profitable indicators to assist rapid detections of hazardous metal ions in the laboratory.

Recommendations/Suggestions: The candidate Ms Komal Kolte has authors a number of publications during her PhD work and also she has participated actively and presented his work in various National and regional level conferences/ seminars as listed below.

List of Publications:

1. **Synthesis, X-ray crystallographic, Hirshfeld, DFT study and interactions with TNFα receptors of chiral bisimines and diamines holding thiophene spacers,** Komal Kolte, Shailykumari K. Patel, Vinay K. Singh, Journal of Molecular Structure **2023** 1300 137165.
2. **Macrocyclic Ni^{II}-Xanthate [Ni^{II}_2-μ^2-bis-{(κ^2S,S-$S_2COCH_2CH_2)_2N(Ts)$}] Complex and a Cyclic Thiocarbonate Monomer: Synthesis, Crystallography, Photophysical, TD-DFT and Investigation of Thermochromism**, Rahul Kadu, Komal Kolte, Chirag Savani, Sanjio S. Zade, Anvarhusein A. Isab, Atresh Kumar Singh, Vinay K. Singh, Journal of Molecular Structure **2023** 1287 135657.
3. **New series of M^{II}-dithiocarbamate complexes (M = Cu^{II}, Ni^{II} and Zn^{II}) holding pendant *N,O*-Schiff base moieties: Synthesis, characterization, photophysical, crystallographic, anti-microbial and DFT study**, Shailykumari K. Patel, Komal Kolte, Chirag J. Savani, Pallepogu Raghavaiah, Dhruti Dave, Anvarhusein A. Isab, Disha Mistry, Devesh Suthar, Vinay K. Singh, Inorganica Chimica Acta **2022** 543 121139.

❖ **List of papers under communication**

1. *N,N'*-bis(3-dithiocarbamatopropyl) piperazine bridged metallomacrocyclic complexes of Ni(II), Cu(II) and Zn(II): synthesis, characterization, photophysical, in-silic o study and their potential utility in heavy metal ion sensing, Komal Kolte,

Alka Singla, Arun Kumar Das, Vinay K. Singh (*Under review by Inorganic Chemistry*)

2. Employment of novel Binuclear Metallomacrocyclic Dithiocarbamate Hosts of Ni^{II}, Cu^{II} and Zn^{II} for Selective binding with Environmentally Hazardous Dyes: Synthesis, Characterization and in- Silico Study, Komal Kolte, Priyanka Mathur, Arpita Desai, Vinay K. Singh (*Under Communication*)
3. Synthesis, characterization and metal ion sensing study of novel Metallomacrocylcic dithiocarbamate complexes holding thiophenyl groups in the macrocyclic framework, Komal Kolte and Vinay Kumar Singh (Under Manuscript Preparation)

Papers presented at National /State Level Seminars / Conferences –

1. **Presented Oral Presentation** in VIII All Gujarat Research Scholar's Meet at The Maharaja Sayajirao University of Baroda, Vadodara, **February 2023.**
2. **Participated** in National Seminar on Decadal Trends in Chemistry Research: The Perspective of Women Scientist (**W-CHEM-2020)** at The Maharaja Sayajirao University of Baroda, Vadodara, **March 2020.**
3. **Participated** in National Seminar on Advances in Chemistry of bioactive Molecules (ACBAM-2020) at The Maharaja Sayajirao University of Baroda, Vadodara, **January 2020.**
4. **Participated** in National workshop on Advanced Analytical Techniques for Elemental Analysis (AAT-2019) at The Maharaja Sayajirao University of Baroda, Vadodara, **December 2019.**
5. **Presented Poster Presentation** in International Conference on Advanced Functional Materials of Energy, Environment and Health Care (AFMEEHC) at University of Mysore, **March 2019.**
6. **Participated** in National Symposium on Advances in Chemical Research (ACR-2019) at The Maharaja Sayajirao University of Baroda, Vadodara, **February 2019.**
7. **Participated** in VII All Gujarat Research Scholars' Meet at The Maharaja Sayajirao University of Baroda, Vadodara, **February 2018.**

8. **Participated** in National Conference on Chirality (NCC-2017) at The Maharaja Sayajirao University of Baroda, Vadodara, **November 2017.**

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