Luminescent Cu(I) Coordination Polymers from Triphenylamine based S-donor ligands

M.Sc. Thesis

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DEPARTMENT OF CHEMISTRY INDIAN INSTITUTE OF TECHNOLOGY

INDORE

MAY 2022

Luminescent Cu(I) Coordination Polymers from Triphenylamine based S-donor ligands A THESIS

Submitted in partial fulfilment of the requirement for the award of the

degree

of

Master of Science

by

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MAY 2022



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CANDIDATE'S DECLARATION

I hereby commit that the work which is being proposed in the thesis entitled **Luminescent Cu(I) Coordination Polymers from Triphenylamine based S-donor ligands** in the partial fulfillment of the requirements for the award of the degree of **MASTER OF SCIENCE** and submitted in the **DEPARTMENT OF CHEMISTRY, Indian Institute of Technology Indore**, is an authentic record of my own work done during the time period from September 2021 to May 2022 under the supervision of Dr. Abhinav Raghuvanshi, Assistant Professor, Department of Chemistry, IIT Indore. The matter presented in this thesis has not been submitted by me for the award of any other degree of this or any other institute.

Signature of the student with date

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This is to confirm that the above statement made by the candidate is right to the best of my/our knowledge.

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ACKNOWLEDGEMENTS

This report could not have been accomplished without a great deal of guidance and support. I would like to sincerely thank those people who provided me with everything I needed during these months. I wish to express my feeling to those whose support and motivation made it possible to present my research work in the form of a dissertation.

First of all, I would like to thank my thesis supervisor **Dr. Abhinav Raghuvanshi** for valuable guidance, suggestions and supervision, and constant encouragement throughout my research work. Further, I would like to thank my PSPC members, **Prof. Apurba K. Das** and **Prof. Sampak Samanta**, for their valuable suggestions and support. I am highly obliged in taking the opportunity to sincerely thank all the faculty members, seniors (research scholars), SIC staff of **IIT INDORE** for their help and cooperation during this dissertation work. I wish to express my special thanks to the lab mates (**Mr. Dilip Pandey, Mr. Kharabe Laxman, & Mr. Shivendu Mishra**). Despite your own project, you never hesitated to answer my questions to help me out with the project's motto. All the things that you were willing to share with me were highly inspiring, not only for this specific project but also for the communication practice in general as well. I want to extend my thanks to my batch mates who were always there and never let me down during these M.Sc. days. Last but not the least, I would

never let me down during these M.Sc. days. Last but not the least, I would like to pay sincere thanks to my loving parents for their continuous help and moral support.

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DEDICATED TO

MY BELOVED FAMILY

ABSTRACT

The aim of this project is to synthesize and characterize triphenylamine based S-donor ligands, their Cu(I) coordination polymers and explore the applications of the synthesized complexes. Cu(I) coordination polymers are known to emit light in the UV-visible range upon excitation and this makes them usable as emitters in the optoelectronic devices or they can be used in many other fields like sensing, separation, adsorption and photocatalysis. For this work, efforts were made to the synthesis of triphenylamine based Sdonor ligands for Cu(I) Coordination Polymers. For which, I have made four ligands. These four ligands are N-(4-(1,3-dithiolan-2-yl)phenyl)-4-(1,3dithiolan-2-yl)-N-phenylaniline (1), N-(4-(1,3-dithian-2-yl)phenyl)-4-(1,3dithian-2-yl)-N-phenylaniline (2), tris-(4-(1,3-dithiolan-2-yl)phenyl)amine (3), tris-(4-(1,3-dithian-2-yl)phenylamine (4). Different coordination polymers with Cu₂X₂ rhomboids were obtained from the reaction of ligand 1 and 2 with Cu(I) halides. In case of ligand 2 & CuI, a 3D coordination polymer was obtained while in other cases, formation of 1D CPs were observed. These CPs are insoluble in most of the organic solvents. All the coordination polymers were found to be luminescent and show emission in 450-500 nm range. In addition, some of the CPs show solvatochromism while some show mechanochromic behaviour. All the synthesized ligands were characterized by the Mass Spectrometry, ¹H NMR Spectroscopy & ¹³C NMR Spectroscopy. All the coordination polymers are characterized by the SCXRD and PXRD.

TABLE OF CONTENTS

LIST OF FIGURES	x-xi
LIST OF TABLES	xii
LIST OF SCHEMES	xiii-xiv
ACRONYMS	XV
NOMENCLATURE	xvi
CHAPTER 1: INTRODUCTION	1-11
1.1 General Introduction	1-3
1.2 Properties of Cu(I) coordination polymers	3-6
1.3 S-Donor ligand based Cu(I) coordination polymers	7-9
1.4 TPA as a starting material for S-donor ligand	9-10
CHAPTER 2: EXPERIMENTAL SECTION	12-19
2.1. Materials and Instrumentation	12
2.2 . Synthesis of S-donor ligands	12-15
2.3 . Metalation of Copper(I) halides with ligands	16-19
CHAPTER 3: RESULTS AND DISCUSSION	20-44
3.1. Characterization of ligands	20-28
3.2. Characterization of Cu(I) coordination polymers	29-44
CHAPTER 4: CONCLUSION	45
REFERENCES	46-49

LIST OF FIGURES

Figure 1.1 Structural Diversity of Cu(I) halide clusters

Figure 1.2 Applications of Cu(I) halide-based MOFs

Figure 1.3 Solvatochromism in Copper(I) Coordination Polymers

Figure 1.4 Emission Spectrum of Copper(I) Coordination polymers at 298K & 77K

Figure 1.5 Emission Spectrum of the solid sample and ground sample

Figure 1.6 Structural diversity of Sulphur donor ligand-based Cu(I) coordination polymers

Figure 1.7 Molecular structure of TPA showing conformational flexibility

Figure 1.8 Crystal Structure of ligand 2

Figure 3.1 Mass spectrogram of ligand 1

Figure 3.2 ¹H NMR spectrum of ligand 1

Figure 3.3 Mass spectrogram of ligand 2

Figure 3.4 ¹H NMR Spectrum of ligand 2

Figure 3.5 ¹³C NMR Spectrum of ligand 2

Figure 3.6 Crystal structure of ligand 2

Figure 3.7 Flourescence Spectrum of ligand 1 & 2 in different solvents at a excitation wavelength of 365 nm

Figure 3.8 Mass spectrogram of ligand 3

Figure 3.9 ¹H NMR Spectrum of ligand 3

Figure 3.10 Mass spectrogram of ligand 4

Figure 3.11 ¹H NMR Spectrum of ligand 4

Figure 3.12 Crystal Structure of CPs from the ligand 1 & ligand 2 with the CuBr and CuCl.

Figure 3.13 Crystal Structure of CPs from the ligand 2 & ligand 3 with the CuI and CuBr respectively

Figure 3.14 PXRD pattern of CPs

Figure 3.15 TGA Spectrum of CPs

Figure 3.16 Photos of CPs at a excitation wavelength of 365 nm, under ambient light and under UV light.

Figure 3.17 Flourescence Spectrum of CPs with the ground sample at a excitation wavelength of 385 nm

Figure 3.18 Flourescence Spectrum of CPs in the presence of different solvents at a excitation wavelength of 385 nm

LIST OF TABLES

Table 1. Crystallographic data of Ligand 2

Table 2. Crystallographic data of CP1 and CP2

 Table 3. Crystallographic data of CP3

Table 4. Crystallographic data of CP4 & CP5

Table 5. Crystallographic data of CP6

LIST OF SCHEMES

Scheme 1. Synthesis of N-(4-(1,3-dithiolan-2-yl)phenyl)-4-(1,3-dithiolan-2-yl)-N-phenylaniline ligand

Scheme 2. Synthesis of N-(4-(1,3-dithian-2-yl)phenyl)-4-(1,3-dithian-2-yl)-N-phenylaniline ligand

Scheme 3. Synthesis of Tris(4-(1,3-dithiolan-2-yl)phenyl)amine ligand

Scheme 4. Synthesis of Tris(4-(1,3-dithian-2-yl)phenyl)amine ligand

Scheme 5. Synthesis of N-(4-(1,3-dithiolan-2-yl)phenyl)-4-(1,3-dithiolan-2-yl)-N-phenylaniline ligand based coordination polymer with the copper(I) bromide

Scheme 6. Synthesis of N-(4-(1,3-dithiolan-2-yl)phenyl)-4-(1,3-dithiolan-2-yl)-N-phenylaniline ligand based coordination polymer with the copper(I) chloride

Scheme 7. Synthesis of N-(4-(1,3-dithian-2-yl)phenyl)-4-(1,3-dithian-2-yl)-N-phenylaniline ligand based coordination polymer with the copper(I) iodide

Scheme 8. Synthesis of N-(4-(1,3-dithian-2-yl)phenyl)-4-(1,3-dithian-2-yl)-N-phenylaniline ligand based coordination polymer with the copper(I) bromide

Scheme 9. Synthesis of N-(4-(1,3-dithian-2-yl)phenyl)-4-(1,3-dithian-2-yl)-N-phenylaniline ligand based coordination polymer with the copper(I) chloride

Scheme 10. Synthesis of Tris(4-(1,3-dithian-2-yl)phenyl)amine ligand based coordination polymer with the Copper(I) bromide

Scheme 11. Synthesis of CP1 and CP2

Scheme 12. Synthesis of CP3, CP4 and CP5

Scheme 13. Synthesis of CP6

ACRONYMS

CH ₃ CN	Acetonitrile
CDCl ₃	Chloroform-D
EtOAc	Ethyl Acetate
LCMS	Liquid Chromatography Mass Spectrometry
СН ₃ ОН	Methanol
М	Molar
NMR	Nuclear Magnetic Resonance Spectroscopy
ррт	Parts per million
H ₂ SO ₄	Sulfuric acid

NOMENCLATURE

cm	Centimeter
δ	Chemical shift
° C	Degree Celsius
mL	Milliliter
mmol	Millimole
nm	Nanometer
π	Pi
rt	Room temperature

CHAPTER 1 INTRODUCTION

1.1 General Introduction

In recent years, Copper(I) complexes have attracted great scientific attention. These compounds have been found suitable in chemical, material and biological applications.¹⁻³ Copper has very rich coordination chemistry, it can combine both organic ligands and inorganic motifs, which shows a large structural diversity as shown in Figure 1.1.⁴



Figure 1.1 Structural Diversity of Cu(I) halide clusters (taken from reference no. 2).

Complexes formed by CuX depend on the different structural combinations of the Copper halide with the organic ligands in which the coordinating atoms can be Nitrogen, Oxygen, Phosphorus, Arsenic, Sulphur, & Selenium. Due to structural diversity, their structures can range from discrete molecular complexes to a broad coordination network.⁵ All these types of structures show a wide range of photophysical & chemical properties. Some of the coordination polymers have separation and adsorption properties due to its porous nature. They can adsorb the small gas molecules by the pores that are present in high nuclearity coordination polymers. By these pores, they can

separate the small gas molecules from the large gas molecules. In many reactions, CPs are also used as a photocatalyst. Some of CPs can tune their emission based on the excitation wavelength and some CPs can sense the external stimuli like temperature, pressure, solvent, etc.⁵⁻¹²



Figure 1.2 Applications of Cu(I) halide-based MOFs (taken from reference no. 2).

Among all the Copper(I) coordination compounds, those compounds which are based on CuI clusters attract the scientific community because these types of complexes have interesting luminescence and high quantum yield. If the distance between the two adjacent copper centers, in polynuclear Copper iodide entities is less than 2.8 Å (less than the sum of Van der Waals radii of Cu), then it shows cuprophilic interactions which can strongly affect the emissive nature of the Copper(I) coordination polymers at low temperature.

Due to this type of luminescence properties of CuI clusters, these complexes are particularly perfect for the application in optoelectronic devices, which includes OLEDs and optical sensors. Along with these properties, the most important thing is the processability of the complexes, which plays a significant role in the devices. Different multi-functional compounds have been made in the form of the fibers, coatings, gels & films, or the form of the composites where CuI complexes have been used as basic units.¹²⁻¹⁵

The emissive CuI complexes sometimes show additional properties, which are porosity, catalytic behavior & conductivity which further enhance the applicability of these complexes in various fields. Furthermore, the emission of these coordination polymers can be changed by the structure & the composition, and the material phase can also affect their emission. Sometimes luminescence changes because of physical stimuli which is temperature & pressure, so by changing the temperature and pressure, luminescence of the complexes can change, and the processes are called thermochromism and mechanochromism, respectively. Some complexes show different type of luminescence properties due to the interaction with solvent molecules, this process is called solvatochromism.¹⁵⁻¹⁹

1.2 Properties of Copper(I) Coordination Polymers

Solvatochromism in Copper(I) Coordination Polymers

Some of the Cu(I) coordination polymers, in which the solvent molecules enter in the moieties of the coordination polymer, and due to this, the emission behavior of Copper(I) complexes changes. Recently, an example is reported by Yunfang et,al. where two compounds were obtained by same reactants under different solvents i.e. DEF and DMF. The main difference between the two compounds is the presence of solvent guest molecules. It was observed that in the case of DEF and DMF solvent, the emission behaviour of the compound was different because both the solvent molecules have different sizes. The hydrogen-bond and Van der Waals interaction present between all the solvent molecules & one of the amidogens of ligand. N–H---O distances in the polymers are 2.7593 & 2.7297 Å for 1 & 2 respectively. If the sizes of the guests's solvent molecules are different, then the cage sizes are also different. The size of the solvent molecules influence the length of the cage through the c axis.¹⁹⁻²⁴



Figure 1.3 Solvatochromism of CPs (taken from reference no. 20).

Thermochromism in Copper(I) Coordination Polymers

In recent years, it was found that Cu(I) Coordination Polymer can have different luminescent properties at different temperatures. These Cu(I) clusters can also be used as luminescent probes. These luminescent clusters, which show thermochromism, their changes in luminescence with temperature variation are easily detectable (i.e., by the naked eye and the movable instruments). Upon cooling and heating, it shows a large shift & fast response, so it has high sensitivity. These thermochromic luminescent materials also have large temperature ranges, great photo sustainability & long lifetimes.

Cu(I) complexes having secondary building units consists of cubane Cu₄I₄L₄ units with N or P donor ligands, mostly exhibit thermochromic behaviour. This type of complexes show two type of emission band, one is a high energy band & second is a low energy band, which originates from the two excited states of the similar energies. At the room temperature, the Cu(I) clusters which have the distance between the Cu···Cu lower than the Van der Waals radius, which is 2.8 Å for Cu---Cu, the luminescence is influenced by the Low Energy band. DFT calculations show that this is because of the combination of an XMCT & the Copper centered d to s & p transitions, which are designated as the cluster centered and it involves the triplet excited state of the [Cu₄I₄] cluster. At the low temperature, the low energy band is very weak & the emission is influenced by the high energy

band, which was due to the XLCT (where X is halide & L is the pyridine ligand) excited state. At the low temperature, the emission spectra were observed only for the clusters incorporating-unsaturated ligands because the ligand orbitals participate in the XLCT band.²⁴⁻²⁷

On decreasing the temperature from 298K to 77K, the Low Energy band exhibit bathochromic shift (in which wavelength increase from 580 nm to 619 nm respectively) for the [CuIpy]₄ complex & this type of behaviour was due to the distance between the Cu···Cu in the [Cu₄I₄] cluster core. In the lowest unoccupied molecular orbitals (LUMO) excited state, the Cu--- Cu bonds have the bonding character. On decreasing the temperature, the distance between the Cu···Cu becomes smaller so it stabilizes the ³CC excited state & copper cluster emission spectra shifts to the bathochromic shift, which is also known as redshift. If there is no change in the phase of the materials which shows thermochromism, then these thermochromic materials show a completely reversible behaviour. These types of luminescent materials show different behaviours.²⁷⁻³⁰



Figure 1.4 Structure of [CuIpy]₄ clusters on the left side & on the right side its emission spectrum at 298K (orange line) & at 77K (blue line) (taken from reference no. 26).

Mechanochromism in Copper(I) Coordination Polymers

Copper(I) CPs show luminescence mechanochromism. Generally, the $[Cu_2I_2L_2]_n$ type of Copper(I) coordination polymers have this type of properties. On grinding the sample, they change their luminescence from some wavelength to another wavelength. An example reported by Kim et al. where a CP shows mechanochromism, in which the color was changed from greenish blue to yellow color upon applying the pressure. It was observed by the PXRD & Raman studies that the main reason for mechanochromism is the bond lengths of the crystalline CP, which change upon applying the pressure. This entire process is fully reversible i.e., if a few drops of ACN are added to the ground sample, then the yellow color is converted to the original greenish-blue color. Sometimes the color changes were observed due to the conversion of the crystalline form to the amorphous form. In some cases, the structure of the CP converted to another form like after grinding the sample, the cubane form converts to the chair form.³⁰⁻³⁵



Figure 1.5 Emission spectra of the solid sample and ground sample (taken from reference no. 31).

1.3 Sulphur-Donor Ligand Based Cu(I) Coordination Polymers

Nowadays, scientists are interested in the formation of different CPs based on organosulphur ligands, which can be mono or dithioether ligands. On reacting the Cu(I) halides or any other Cu(I) salts with these ligands give coordination polymers with different dimensionality.³⁶ The dimensionality of these type of coordination polymers depends on the different factors like the donor atom on the ligands, substituents on the ligands, the nature of halides,³⁷ the metal &ligand ratio, and the reaction conditions like solvent, temperature, etc.³⁸ it is found that the coordination polymer based on organsulphur ligand have many types of applications like it can be used as a catalyst³⁹ and also it can be used in sensing as they can sense the external stimuli. Specially the porous 3D coordination polymers can play an important role in the sensing application.⁴⁰

Rheingold et al. reported the formation of a 1D coordination polymer by the reaction of tridentate thioether ligand MeSi(CH₂SMe)₃ with the copper halide.⁴¹ It was also observed that when the metal & ligand ratio was increased then two-dimensional or three-dimensional structure was obtained.⁴² When the cyclophane derivative 2,11,20,29tetrathiadodecahydro[3.3.3.3]cyclophane was reacted with the copper iodide in the acetonitrile solvent a three-dimensional coordination polymer with a rhomboid dimer as secondary building units was achieved.⁴³ Knorr et al. has recently reported the coordination polymer based on the octadentate thioether-decorated octasilsesquioxanes, when this ligand reacts with copper iodide then it generates a 3D POSS-based coordination polymer with dinuclear or closed-cubane-type secondary building units.⁴⁴

In the past, there is a history of using five, six & seven-membered dithiaheterocycles ligand⁴⁵⁻⁴⁷ for the metalation with different metal salts like AgNO₃, AgBF₄, and it can also react with $[Cu(MeCN)_4]BF_4$. When $[Cu(MeCN)_4]BF_4$ reacted with the dithiaheterocycle then four coordination network was formed, which depends on the metal & ligand ratio & the solvent conditions.⁴⁷⁻⁴⁹ A series of different dimensionality coordination

polymer was found if 1,3-dithiane and derivatives of 1,3-dithiane were used.⁵⁰ It was also observed that when μ_2 -2-methyl-1,3-dithiane reacted with Copper iodide then three-dimensional CP [{Cu₈(μ_3 -I)_8} (μ_2 -2- methyl-1,3-dithiane)₄]_n was found with a Cu₈I₈S₈ clusters core as a SBUs. These CPs also show good luminescent behaviour.⁵¹

Recently, several coordination polymers are reported where several 1,3dithiane and 1,3-dithiolane has been used as a ligand. The reason behind that is to increase the number of sulphur donor sites in the ligand which can provide more coordination sites and leads to various interesting CPs which can show good photophysical properties. This type of ligand can also bind with the other soft metal salts, which can be HgBr₂, and HgCl₂.⁵¹⁻⁵⁴ A recent example reported by Knorr et al. where they used 2,2-ethylenebis-(1,3dithiane) as a ligand to obtain several CPs. Different CPs were obtained when different ratio of CuI is used for the reaction (Figure 1.6).⁵²



2D CP3 [{Cu(μ₄-l)(μ₂-l)Cu}₂(μ₄-L1)]_n

Figure 1.6 Structural diversity of Sulphur donor ligand-based Cu(I) coordination polymers (taken from reference no. 52).

1.4 Triphenylamine as a starting material for Sulphur-donor ligands

Triphenylamine (TPA) has a non-planar, flexible propeller-shaped structure that has some weak intermolecular interactions in the solid state (Figure 1.7). Studies show that TPA has a very good mechanochromic response due to their non-planarity. It was observed that on applying the mechanical force, TPA derivatives show some conformational changes due to this behaviour, and the change in the solid-state fluorescence was observed. On grinding the TPA derivatives, the crystalline form converts into the disordered form due to this a blue shift with a decrease in intensity was observed. It was also confirmed by the PXRD pattern that this was due to the conversion of the crystalline form to the amorphous form. But another result was observed, which was against the above result. When high pressure (1.9 GPa) was applied, a redshift with an increase in intensity was obtained in the emission spectra, the reason behind this is the high pressure, TPA becomes more planar that the restriction of intramolecular rotation takes place, due to less intramolecular rotation TPA will have lower energy which cause redshift in the emission spectra.⁵⁴⁻⁶²



Figure 1.7 Molecular structure of TPA showing conformational flexibility (taken from reference no. 56).

Considering the structural properties of TPA ligands and rich coordination property of 1,3-dithiane and 1,3-dithiolane ligand, in this project, I have combined both these and synthesized four ligands. The coordination behaviour of these ligands towards Cu(I) salts have been studied. Further, the solvatochromic and thermochromic behaviour of these CPs has been studied.



Figure 1.8 Ligands used in the thesis for construction of CPs.

CHAPTER 2

EXPERIMENTAL SECTION

2.1 MATERIALS AND INSTRUMENTATION

All the chemicals were used as received if not mentioned somewhere. Many reactions were performed under the nitrogen environment because of moisture or oxygen sensitive, while others were performed under air and checked by TLC using Merck 60 F254 pre-coated silica gel plate (0.25 mm thickness) and the product was judged under UV chamber. Mass spectra were obtained through Bruker Daltonik High Performance LCMS spectrometer. All the ¹H & ¹³C NMR spectra were obtained on Bruker 500 spectrometer in CDCl₃ or in d₆-DMSO operating at 500 MHz for ¹H NMR. Data for proton NMR Chemical shifts are mentioned in delta (δ) units, showed in ppm downfield from tetramethyl silane (TMS). CDCl₃ is used as an internal standard, which showing peak at 7.26 ppm. The ¹H NMR splitting patterns have been mentioned as singlet(s), double(d), triplet(t) & multiplet(m). Compounds were named by using Chem draw Ultra 16.0 and NMR data processed by Mestre Nova.

2.2 SYNTHESIS OF LIGANDS

2.2.1 Synthesis of N-(4-(1,3-dithiolan-2-yl)phenyl)-4-(1,3-dithiolan-2-yl)-N-phenylaniline ligand (1)

Into a RB, bis(4-formylphenyl)phenylamine (0.1 g, 0.33 mmol) was dissolved in DCM (1-2 mL) & HCl (1 mL) was also added after that 1,2ethanedithiol (0.065 g, 0.696 mmol) was added in the above reaction mixture. This reaction mixture was stirred for 6h at room temp. The resulted product was extracted with DCM, then the solvent was passed through anhydrous Na₂SO₄ & evaporated by rotary evaporator. The obtained crude was purified by the column chromatography [C_6H_{14} : EtOAc—98 : 2]



Scheme 1. Synthesis of ligand 1

Yellow solid; yield 65%; LCMS (ESI) m/z calculated for $C_{24}H_{23}NS_4[M+H]^+$ 454.0728, found 454.0786. ¹H NMR (500 MHz, CDCl₃) δ 7.38 (d, *J* = 8.5 Hz, 4H), 7.27 – 7.22 (m, 2H), 7.08 (d, *J* = 7.3 Hz, 2H), 7.02 – 6.98 (m, 4H), 5.63 (s, 2H), 5.29 (s, 1H), 3.54 – 3.47 (m, 4H), 3.38 – 3.31 (m, 4H)ppm.

2.2.2 Synthesis of N-(4-(1,3-dithian-2-yl)phenyl)-4-(1,3-dithian-2-yl)-N-phenylaniline ligand (2)

Into a RB, bis(4-formylphenyl)phenylamine (0.1 g, 0.33 mmol) was dissolved in DCM (1-2 mL) & HCl (1 mL) was also added after that 1,3-propanedithiol (0.071 g, 0.66 mmol) was added in the above reaction mixture. This reaction mixture was stirred for 6h at room temp. The resulted product was extracted with DCM, then the solvent was passed through anhydrous Na_2SO_4 & evaporated by rotary evaporator. The product was precipitate out with minimum amount of dichloromethane with hexane.



Scheme 2. Synthesis of ligand 2

White crystalline solid; yield 90.70%; LCMS (ESI) m/z calculated for $C_{26}H_{27}NS_4 [M+H]^+ 482.0990$, found 482.1099.

¹H NMR (500 MHz, CDCl₃) δ 7.31 (d, J = 8.5 Hz, 4H), 7.27 – 7.22 (m, 3H), 7.08 (d, J = 8.5 Hz, 2H), 7.01 (d, J = 8.7 Hz, 4H), 5.13 (s, 2H), 3.06 (t, J =

12.3 Hz, 4H), 2.91 (d, *J* = 15.7 Hz, 4H), 2.16 (d, *J* = 9.5 Hz, 2H), 1.99 – 1.88 (m, 2H)ppm. ¹³C NMR (126 MHz, CDCl₃) δ 147.72, 147.36, 133.19, 129.46, 128.74, 125.15, 123.89, 123.58, 51.09, 32.32, 25.20 ppm.

2.2.3 Synthesis of Tris(4-(1,3-dithiolan-2-yl)phenyl)amine ligand (3)

Into a RB, tris(4-formylphenyl)amine (0.15 g, 0.455 mmol) was dissolved in dichloromethane (2-3 mL) & HCl (1 mL) was also added after that 1,2ethanedithiol (0.137 g, 1.45 mmol) was added in the above reaction mixture. This reaction mixture was stirred for 6h at room temp. The resulted product was extracted with DCM, then the solvent was passed through anhydrous Na_2SO_4 & evaporated by rotary evaporator. The product was precipitate out with minimum amount of dichloromethane with hexane.



Scheme 3. Synthesis of ligand 3

Pink colour ppt; yield 78.74%; LCMS (ESI) m/z calculated for $C_{27}H_{27}NS_6$ [M]⁺ 557.0260, found 557.0462. ¹H NMR (500 MHz, CDCl₃) δ 7.38 (d, J = 8.7 Hz, 6H), 7.00 (d, J = 8.7 Hz, 6H), 5.62 (s, 3H), 3.54 – 3.47 (m, 6H), 3.39 – 3.32 (m, 6H)ppm.

2.2.4 Synthesis of Tris(4-(1,3-dithian-2-yl)phenyl)amine ligand (4)

Into a RB, tris(4-formylphenyl)amine (0.15 g, 0.455 mmol) was dissolved in dichloromethane (2-3 mL) & HCl (1 mL) was also added after that 1,3-propanedithiol (0.156 g, 1.45 mmol) was added in the above reaction mixture. This reaction mixture was stirred for 6h at room temp. The resulted product was extracted with DCM, then the solvent was passed through anhydrous Na_2SO_4 & evaporated by rotary evaporator. The product was precipitate out with minimum amount of dichloromethane with hexane.



Scheme 4. Synthesis of ligand 4

Brown colour ppt; yield 76.76%; LCMS (ESI) m/z calculated for $C_{30}H_{33}NS_6$ $[M+H]^+$ 600.0757, found 600.1010.

¹H NMR (500 MHz, CDCl₃) δ 7.32 (d, J = 8.7 Hz, 6H), 7.01 (d, J = 8.5 Hz, 6H), 5.13 (s, 3H), 3.06 (t, J = 12.1 Hz, 6H), 2.91 (d, J = 18.0 Hz, 6H), 2.16 (d, J = 14.0 Hz, 3H), 1.97 – 1.87 (m, 3H)ppm.

2.3 SYNTHESIS OF COORDINATION POLYMERS:

2.3.1 Synthesis of N-(4-(1,3-dithiolan-2-yl)phenyl)-4-(1,3-dithiolan-2-yl)-N-phenylaniline ligand based coordination polymer with the copper(I) bromide

Into a schlenk under N_2 condition, ligand (0.050 g, 0.11 mmol) was dissolved in acetonitrile and CuBr (0.126 g, 0.88 mmol) was separately dissolved in acetonitrile, 1-2 ml methanol was also added in the CuBr solution to avoid the oxidation of copper. After that this CuBr solution was added in the ligand solution & the reaction mixture was stirred for 6 h at room temp. After 6 h, a pink colour ppt was observed, this ppt was washed with DCM (1-2 mL, 2-3 times) for removing the unreacted ligand. The yield of the final compounds is 83.5%.



Scheme 5. Synthesis of coordination polymer 1

2.3.2 Synthesis of N-(4-(1,3-dithiolan-2-yl)phenyl)-4-(1,3-dithiolan-2-yl)-N-phenylaniline ligand based coordination polymer with the copper(I) chloride

Into a schlenk under N_2 condition, ligand (0.050 g, 0.11 mmol) was dissolved in acetonitrile and CuCl (0.087 g, 0.0883 mmol) was separately dissolved in acetonitrile, methanol (1-2 mL) was also added in the CuCl solution to avoid the oxidation of copper. After that this CuCl solution was added in the ligand solution & the reaction mixture was stirred for 6 h at room temp. After 6 h, a light pink colour ppt was observed, this ppt was washed with DCM (1-2 mL, 2-3 times) for removing the unreacted ligand. The yield of the final compound is 79%.



Scheme 6. Synthesis of coordination polymer 2

2.3.3 Synthesis of N-(4-(1,3-dithian-2-yl)phenyl)-4-(1,3-dithian-2-yl)-N-phenylaniline ligand based coordination polymer with the copper(I) iodide

Into a schlenk, ligand (0.050 g, 0.1039 mmol) was dissolved in ACN & CuI (0.157 g, 0.831 mmol) was separately dissolved in acetonitrile. After that this CuI solution was added in the ligand solution & the reaction mixture was stirred for 6 h at room temp. After 6 h, an off white colour ppt was observed, this ppt was washed with DCM (1-2 mL, 2-3 times) for removing the unreacted ligand. The yield of the final compounds is 81.8%.



Scheme 7. Synthesis of coordination polymer 3

2.3.4 Synthesis of N-(4-(1,3-dithian-2-yl)phenyl)-4-(1,3-dithian-2-yl)-N-phenylaniline ligand based coordination polymer with the copper(I) bromide

Into a schlenk under N_2 condition, ligand (0.060 g, 0.124 mmol) was dissolved in acetonitrile and CuBr (0.143 g, 0.997 mmol) was separately dissolved in acetonitrile, methanol (1-2 mL) was also added in the CuBr solution to avoid the oxidation of copper. After that this CuBr solution was added in the ligand solution & the reaction mixture was stirred for 6 h at room temp. After 6 h, a white colour ppt was observed, this ppt was washed with DCM (1-2 mL, 2-3 times) for removing the unreacted ligand. The yield of the final compounds is 69.3%.



Scheme 8. Synthesis of coordination polymer 4

2.3.5 Synthesis of N-(4-(1,3-dithian-2-yl)phenyl)-4-(1,3-dithian-2-yl)-N-phenylaniline ligand based coordination polymer with the copper(I) chloride

Into a schlenk under N_2 condition, ligand (0.050 g, 0.103 mmol) was dissolved in acetonitrile and CuCl (0.082 g, 0.831 mmol) was separately dissolved in acetonitrile, methanol (1-2 mL) was also added in the CuCl solution to avoid the oxidation of copper. After that this CuCl solution was added in the ligand solution & the reaction mixture was stirred for 6 h at room temp. After 6 h, a off white colour ppt was observed, this ppt was washed with DCM (1-2 mL, 2-3 times) for removing the unreacted ligand. The yield of the final compounds is 31%.



Scheme 9. Synthesis of coordination polymer 5

2.3.6 Synthesis of Tris(4-(1,3-dithian-2-yl)phenyl)amine ligand based coordination polymer with the Copper(I) bromide

Into a schlenk under N_2 condition, ligand (0.015 g, 0.0269 mmol) was dissolved in dichloromethane (2 mL) and CuBr (0.0386 g, 0.269 mmol) was separately dissolved in acetonitrile (2 mL), methanol (1 mL) was also added in the CuBr solution to avoid the oxidation of Copper. After that this CuBr solution was added in the ligand solution & the reaction mixture was stirred for 6 h at room temp. After 6 h, a off white colour ppt was observed, this ppt was washed with DCM (1-2 mL, 2-3 times) for removing the unreacted ligand. The yield of the final compounds is 79%.



Scheme 10. Synthesis of coordination polymer 6

CHAPTER 3

RESULTS AND DISCUSSION

3.1 CHARACTERIZATION OF LIGANDS

3.1.1 Characterization of ligand 1

Ligand 1 was synthesized by stirring bis(4-formylphenyl)phenylamine and 1,2-ethanedithiol at the room temp. under acidic medium, which is shown in the scheme 1. The final product was a yellow solid product which was observed with 65 % yields. The obtained solid product was characterized by Mass spectometry and ¹H NMR spectroscopy. Two multiplets around 3.5 ppm for four hydrogens each, two singlets around 5.5 ppm for one hydrogen each confirm the presence of dithiane unit, whereas the presence of multiplets in the range of 7.00-7.40 ppm for 13 protons confirms the presence of TPA unit.



Scheme 1. Synthesis of ligand 1



Figure 3.1 Mass spectrogram of ligand 1



Figure 3.2 ¹H NMR spectrum of ligand 1

3.1.2 Characterization of ligand 2

Ligand 2 was synthesized by stirring bis(4-formylphenyl)phenylamine and 1,3-propanedithiol at the room temp. under acidic medium which is shown in the scheme 2. The final product was a white crystalline solid which was observed with 90.70 % yields. The obtained solid product was characterized by Mass spectrometry, ¹H NMR spectroscopy, ¹³C NMR spectroscopy and by the SXRD. Two multiplets in the range of 2.50-3.00 ppm for four hydrogens each, one triplet around 3.2 ppm for four hydrogens, one singlet around 5.2 ppm for two hydrogens confirm the presence of dithiane unit, whereas the presence of multiplets in the range of 7.00-7.40 ppm for 13 protons confirms the presence of TPA unit.



Scheme 4. Synthesis of ligand 2



Figure 3.3 Mass spectrogram of ligand 2



Figure 3.4 ¹H NMR spectrum of ligand 2



Figure 3.5 ¹³C NMR spectrum of ligand 2

3.1.2.1 Crystal Structure

Crystal Structure of Ligand 2 was obtained by slow evaporation of dichloromethane solution (Figure 3.6). The compound crystallizes in $P2_1/c$ space group. The TPA unit arranged in a propeller like arrangement where angle between the three planes are 89, 47 & 81 degrees. Two of the three benzene rings are substituted with 1,3-dithiolane units at 4th position and both 1,3-dithiolane units is arranged in a more stable chair configuration.



Figure 3.6 Crystal structure of ligand **2**. Color code; S, yellow; N, blue and C, grey.

3.1.2.2 Flourescence spectrum of ligand 1 & ligand 2

Liquid state fluorescence was taken for the ligand 1 & ligand 2 in different solvents, namely DCM, CHCl₃, THF, ACN, and DMF. For ligand 1, Emission spectra was observed at 435 nm, 480 nm, 492 nm, 504 nm, and 529 nm for the solvents DMF, THF, CHCl₃, DCM, and ACN respectively (Fig. 3.7a). For ligand 2, Emission spectra was observed at 464 nm, 478 nm, 488 nm, 499 nm, and 525 nm for the solvents THF, CHCl₃, DCM, DMF and ACN respectively (Fig. 3.7b).



Figure 3.7 Flourescence Spectrum of ligand 1 & 2 in different solvents at a excitation wavelength of 365 nm (a) Emission spectra of ligand 1 (b) Emission spectra of ligand 2.

3.1.3 Characterization of ligand 3

Ligand 3 was synthesized by stirring tris(4-formylphenyl)amine and 1,2ethanedithiol at the room temp. under acidic medium, which is shown in the scheme 3. The final product was a pink colour solid product which was observed with 78.74 % yields. The obtained solid product was characterized by Mass spectrometry, ¹H NMR spectroscopy. Two multiplets around 3.5 ppm for six hydrogens each, one singlets around 5.6 ppm for three hydrogen confirm the presence of dithiane unit, whereas the presence of multiplets in the range of 7.00-7.40 ppm for 12 protons confirms the presence of TPA unit.



Scheme 5. Synthesis of ligand 3



Figure 3.8 Mass spectrogram of ligand 3



Figure 3.9 ¹H NMR spectrum of ligand 3

3.1.4 Characterization of ligand 4

Ligand 4 was synthesized by stirring tris(4-formylphenyl)amine and 1,3propanedithiol at the room temperature, which is shown in the scheme 4. The final product was a brown colour solid product which was observed with 76.76 % yields. The obtained solid product was characterized by Mass spectrometry, ¹H NMR spectroscopy. Two multiplets around 1.9-2.9 ppm for six hydrogens each, one triplet around 3.1 ppm for six hydrogen, one singlet around 5.1 ppm for three hydrogen confirm the presence of dithiane unit, whereas the presence of multiplets in the range of 7.00-7.40 ppm for 12 protons confirms the presence of TPA unit.



Scheme 6. Synthesis of ligand 4



Figure 3.10 Mass spectrogram of ligand 4



Figure 3.11 ¹H NMR spectrum of ligand 4

3.2 CHARACTERIZATION OF COORDINATION POLYMERS

CP1 & CP2 were synthesized by reacting the ligand 1 with the CuBr & CuCl respectively in 1:8 ratio. The product remains the same even when different ratio of reactants was taken. The final compound was a pink coloured ppt with 83.5% yield in case of CP 1 and 78.8% yield in case of CP2 (Scheme 11). CP3, CP4, and CP5 was synthesized by reacting the ligand 2 with the CuI, CuBr & CuCl respectively in 1:8 ratio. The final compound were an off white colour ppt with 81.8%, 69.3%, and 31 % yields in case of CP3, CP4, and CP5 respectively (Scheme 12). CP6 was synthesized by reacting the ligand 3 with the CuBr in 1:10 ratio. The final compound was a off white coloured ppt with 79 % yields (Scheme 13). CuX can form different type of rhombic cores like Cu₂I₂, Cu₄I₄ staircase & cubane form and Cu₈I₈ etc. but here, all the CPs have only Cu₂I₂ rhombic core. The obtained precipitate of all the compound was insoluble in most of the organic solvents (partially soluble in acetonitrile, propionitrile and DMF), so all the precipitate (except CP3) was dissolved in ACN by heating. When the solvent was evaporated, hexagon shape yellow colour crystal in case of CP1, CP2, CP5, & CP6 and plate shape white colour crystal for CP4 was obtained. The crystal of CP3 was obtained by layering method, firstly a ligand layer in DCM (4 mL) then a neutral layer of DCM & ACN (4-4 mL) and in the upper layer CuI in ACN (4 mL) was taken. After 2-4 days, when solvent was evaporated, needle shaped white colour crystal was obtained. Other than this, I have also tried 1:2 & 1:4 ratio, but in all the cases same result was observed. In 1:8 ratio, I have observed maximum yields.



Scheme 11. Synthesis of CP1 and CP2.



Scheme 12. Synthesis of CP3, CP4 and CP5.



Scheme 13. Synthesis of CP6

3.2.1 Crystal Structure

All the crystals were obtained in the acetonitrile. In the CPs of ligand **1** & ligand **2** with CuBr & CuCl, a 1D-chain was observed with a Cu₂I₂ rhombic core (Fig. 3.12). In case of CuI with ligand 2 and CuBr with ligand 3, a 3D & 2D polymer was observed respectively with a Cu₂I₂ rhombic core, these CPs have voids in their structures (Fig. 3.13). The Cu---Cu, Cu---X, and Cu---S distances in the CP1 & CP2 are 2.97, 2.45, 2.28 Å and 2.92, 2.34, 2.30 Å respectively. The Cu---Cu, Cu---X, and Cu---S distances in the CP3, CP4 & CP5 are 2.85, 2.64, 2.33 Å, 2.98, 2.52, 2.32 Å and 2.92, 2.21, 2.27 respectively while the Cu---Cu, Cu---X, and Cu---S distances in the CP6 are 2.72, 2.50, and 2.32 Å. Out of all the CPs, CP3 has voids in their structure which have a diameter of 21.678 Å.





Figure 3.12 Crystal Structure of CPs of the ligand **1** & ligand **2** with the CuBr and CuCl (a) CP1 (b) CP2 (c) CP4 (d) CP5. Color code; Cu, orange; Br, brown; Cl, green; S, yellow; N, blue; C, grey.



Figure 3.13 Crystal Structure of (a) CP3 (b) CP3 with voids (c) CP6 (d) CP6 with voids. Color code; Cu, orange; I, violet; Br, brown; S, yellow; N, blue; C, grey.

3.2.2 Powder X-ray diffraction pattern

PXRD studies were performed to check the purity of the samples. The simulated patterns obtained from the SCXRD data matches with the experimental pattern confirming the purity of the bulk samples.



Figure 3.14 Simulated and experimentally observed PXRD pattern of CPs (a) CP1 (b) CP2 (c) CP4 (d) CP5

3.2.3 Thermogravimetric Analysis Spectrum

TGA was performed for all the compounds which confirms the stability upto 200 $^{\circ}$ C, 204 $^{\circ}$ C, 218 $^{\circ}$ C and 226 $^{\circ}$ C for CP1, CP2, CP3 and CP4, respectively.



Figure 3.15 TGA Spectrum of CPs (a) CP1 (b) CP2 (c) CP3 (d) CP4

3.2.4 Photophysical Studies

I have checked the photophysical studies of the compounds. The compounds was a off white colour or pink colour precipitate under ambient light, which shows bluish-cyan luminescence under UV light (365 nm) as shown in the following figure (Fig. 3.16). All the compounds exhibit good mechanochromism and solvatochromism behaviour.



Figure 3.16 Photos of CPs at a excitation wavelength of 365 nm, under ambient light and under UV light. (a) CP1 (b) CP2 (c) CP3 (d) CP4 (e) CP5 (f) CP6.

Mechanochromism

Solid-state fluorescence was performed for all the CPs, which show good mechanochromism. Strong grinding of CP1 & CP2 showed a small blue shift from 452 nm to 446 nm and 448 nm to 463 nm with a large increase in the intensity (Figure 3.17a & 3.17b). CP4 & CP5 showed a red shift from 426 nm to 448 nm in both CPs with a increase in intensity in CP4 and decrease in intensity in CP5 (Figure 3.17c & 3.18d). This change in the emission spectra was observed due to the structure of the propeller shaped TPA substituted S-donor ligand. In case of CP1 & CP2, the angle between the plane of the phenyl ring of TPA were about 85°, 57°, and 86° while in the CP4 & CP5, the angle was 89°, 47°, and 81°. After grinding the sample, the emission band was observed at 448 nm for all the CPs. So it can be the reason that after grinding both type of samples, which show blue shift & red shift becomes more planar which may be have a angle between the plane of the phenyl rings somewhere in between which can be 86°, 52° and 84°.



Figure 3.17 Flourescence Spectrum of CPs with the ground sample at a excitation wavelength of 385 nm (a) emission spectra of CP1 (b) emission spectra of CP2 (c) emission spectra of CP4 (d) emission spectra of CP5.

Solvatochromism

Fig. 3.18 shows the fluorescence spectra of CPs in different solvents, namely Chloroform, Acetone, ACN, DCM, THF, Propionitrile, MeOH, and DMF. With the increasing solvent polarity from Chloroform to DMF, the maximum emission wavelength of CP1 shows an red-shift from 444 nm to 469 nm, gradually changing from bluish to cyan-yellow (Fig. 3.18a). In case of CP2, no change was observed in the emission band position (465 nm), but the emission intensity was increased gradually in different solvents (Fig. 3.18b). CP4 shows a emission band at 428 nm which exhibits a very small red shift from 428 nm to 435 nm in acetonitrile and acetone solvents, and the emission intensity also increases in different solvents (Fig. 3.18c). In case of CP5, a slight red shift was observed in DCM from 426 nm to 432 nm, the emission intensity of the compound was also increased in different solvents (3.18d). As the polarity of the solvent increases from Chloroform to DMF, intensity of the emission spectra increases, it may be due to the dipole-dipole interactions between the solute & solvent molecules. Some of the solvents are not following this pattern, so till now, we don't know the exact reason behind this emission intensity change that, why is it happening, we are still finding the exact reason behind this.



Figure 3.18 Flourescence Spectrum of CPs in the presence of different solvents at a excitation wavelength of 385 nm (a) emission spectra of CP1 (b) emission spectra of CP2 (c) emission spectra of CP4 (d) emission spectra of CP5.

Table 1 Crystallographic data of Ligand 2	
Compound	Ligand 2
Formula	$C_{26}H_{27}NS_4$
Formula Weight	642.30
Wavelength	0.71073 Å
Crystal System	monoclinic
Space group	P2₁/c
a/Å	11.4824(7)
b/ Å	19.6385(9)
c/ Å	11.7588(8)
α /°	90
β/°	111.691(7)
γ/°	90
V/ Å ³	2463.8(3)
Ζ	4
\mathcal{P}_{calcd} (g/cm ³)	1.299
Temperature/K	293.00
GOF	1.049
20 range for data collection	6.582 to 50
Reflections collected	20559
Independent reflections	$4320[R_{int} = 0.017]$
Completeness to $\theta = 25.242$	99.9
Final R indices [I > 2σ(I)]	$R_1 = 0.05027, wR_2 = 0.1268$
Final R indices [all data]	$R_1 = 0.0862, wR_2 = 0.1477$
Largest diff. peak /hol/ e Å ⁻³	0.43/-0.37

Table 2 Crystallographic data of CP 1 and CP 2		
Compound	1-CuBr	1-CuCl
Formula	C ₂₄ H ₂₃ BrCuNS ₄	$C_{48}H_{46}Cl_{2}Cu_{2}N_{2}S_{8}$
Formulaweight	597.12	1105.33
Wavelength	0.71073 Å	0.71073 Å
Crystal system	triclinic	triclinic
Space group	P-1	P-1
a/Å	9.1864(5)	9.1410(5)
b/Å	10.4799(10)	10.4411(9)
c/Å	13.0998(10)	13.0328(8)
a/o	99.642(7)	100.066(6)
β/°	103.110(5)	103.938(5)
γ/°	97.023(6)	95.714(6)
V/ Å ³	1193.94(16)	1175.54(14)
Z	2	1
P _{calcd} (g/cm ³)	1.661	1.561
Temperature	293.00	293.00
GOF	1.005	0.968
2θ range for		
data collection	6.28 to 49.992	6.35 to 49.998
Reflections collec	Reflections collected92068170	
Independent		
reflections	$4204[R_{int} = 0.0747]$	$4094 [R_{int} = 0.1140]$
Completeness to		
$\theta = 25.242$	99.7	99.7
Final R indices		
I>2σ(I)]	R ₁ =0.0502, wR ₂ =0.1254	$R_1 = 0.0640, wR_2 = 0.1598$
Final R indices		
[all data]	R ₁ =0.0682, wR ₂ =0.1343	$R_1 = 0.1045, wR_2 = 0.1890$
Largest diff.		
peak/hol/ eÅ ⁻³	0.95/-0.77	0.69/-0.64

Table 3 Crystallographic data of CP 3		
Compound	2-CuI	
Formula	$C_{39}H_{41}I_3Cu_3N_2S_6O$	
Formula Weight	1304.87	
Wavelength	0.71073 Å	
Crystal System	trigonal	
Space group	P321	
a/Å	36.7865(12)	
b/ Å	36.7865(12)	
c/ Å	7.9698(2)	
α /°	90	
β/°	90	
γ/°	120	
$V/ Å^3$	9340.2(7)	
Ζ	6	
p_{calcd} (g/cm ³)	1.392	
Temperature/K	293.00	
GOF	0.991	
20 range for data collection	5.86 to 49.992	
Reflections collected	10989	
Independent reflections	$10989[R_{int} = 0.017]$	
Completeness to $\theta = 25.242$	99.7	
Final R indices $[I > 2\sigma(I)]$	$R_1 = 0.1067, wR_2 = 0.2778$	
Final R indices [all data]	$R_1 = 0.1302, wR_2 = 0.2972$	
Largest diff. peak /hol/ e Å ⁻³	6.16/-1.15	

Table 4 Crystallographic data of CP 4 and CP 5			
Compound	2-CuBr	2-CuCl	
Formula	$C_{104}H_{89}Br_4Cu_4N_4S_{16}\\$	C ₂₆ H ₂₇ ClCuNS ₄	
Formula Weight	907.88	1100.96	
Wavelength	0.71073 Å	0.71073 Å	
Crystal System	monoclinic	monoclinic	
Space group	Cc	$P2_1/n$	
a/Å	20.2286(9)	10.1508(3)	
b/ Å	20.0135(7) 10.0144(3)		
c/ Å	27.0851(12) 25.8556(6)		
α /°	90 90		
β/°	104.830(4)	96.520(2)	
γ/°	90	90	
$V/ Å^3$	10600.0(8)	2611.33(13)	
Z	11	4	
P _{calcd} (g/cm ³)	1.564	2.100	
Temperature/K	293.00	293.00	
GOF	1.080	1.093	
20 range for			
data collection	6.082 to 49.998	5.824 to 49.994	
Reflections collector	Reflections collected6486318333		
Independent			
reflections	2458 [R _{int} =0.1288]	$4573 [R_{int} = 0.0554]$	
Completeness to			
θ=25.242	99.8	99.8	
Final R indices			
[I>2σ(I)]	R ₁ =0.1037,wR ₂ =0.2260	R ₁ =0.0716,wR=0.2048	
Final R indices			
[all data]	R ₁ =0.2056,wR ₂ =0.2842	R ₁ =0.1044,wR ₂ =0.2276	
Largest diff.			
peak/hol/ e Å ⁻³	3.48/-0.7	1.85/-0.68	

Table 5 Crystallographic data of CP 6	
Compound	3-CuBr
Formula	$C_{54}H_{54}Br_2Cu_2N_2S_{12}$
Formula Weight	1402.61
Wavelength	0.71073 Å
Crystal System	monoclinic
Space group	$P2_1/n$
a/Å	13.2337(4)
b/ Å	22.3187(6)
c/ Å	19.6316(5)
α /°	90
β/°	98.239(3)
γ/°	90
V/ Å ³	5738.5(3)
Ζ	4
P _{calcd} (g/cm ³)	1.623
Temperature/K	293.00
GOF	1.027
20 range for data collection	6.07 to 49.998
Reflections collected	55303
Independent reflections	$10079[R_{int} = 0.0939]$
Completeness to $\theta = 25.242$	99.8
Final R indices [I > 2σ(I)]	$R_1 = 0.0710, wR_2 = 0.1960$
Final R indices [all data]	$R_1 = 0.1145, wR_2 = 0.2273$
Largest diff. peak /hol/ e Å ⁻³	1.29/-0.94

CHAPTER 4

CONCLUSION

I have synthesized four sulphur-donor ligands. The sulphur-donor ligands were designed on the TPA backbone. Six new Copper(I) coordination polymers were synthesized by reacting the CuX with the TPA based sulphurdonor ligands. CPs are characterized by the SCXRD, PXRD, & Thermogravimetric analysis (TGA). Out of the Six CPs, 4 CPs are 1D, one CP is 2D and one CP is 3D. All the CPs show bluish-cyan colour under UV light. In the mechanochromic behaviour of CPs, two contrast results were obtained. In case of CP1 & CP2, a blue shift in the emission spectrum with a increase in the intensity were observed while in case of CP4 & CP5, a red shift in the emission spectrum with increase in the intensity of CP4 & decrease in the intensity of CP5 were observed. All the coordination polymers show the good solvatochromic behaviour. In the different solvents, the emission intensity of the compound was increased and in some solvent, the emission band shifting was also observed. By these results, we can say that these CPs have good stimuli-responses, so these can be used in the sensing and in many other applications.

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