Synthesis of All-In-One Cu(I) Complexes

M.Sc. Research Thesis

By

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DEPARTMENT OF CHEMISTRY
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Synthesis of All-In-One Cu(I) complexes

A THESIS

Submitted in the fulfillment of the

Requirements of the award of the degree

of

Master of Science

by

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DEPARTMENT OF CHEMISTRY

INDIAN INSTITUTE OF TECHNOLOGY

MAY 2026

INDIAN INSTITUTE OF TECHNOLOGY INDORE

CANDIDATE'S DECLARATION

I hereby certify that the work being presented in the thesis entitled **"Synthesis of All In One Cu(I) Complexes"** in the partial fulfilment of the requirements for the award of the degree of **MASTER OF SCIENCE** and submitted to the **Department of Chemistry, Indian Institute of Technology Indore**, is an authentic record of my work carried out during the period from July 2025 to May 2026 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.

Vishal Kumar
10/05/2026

Vishal Kumar

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

Abhinav

Dr. Abhinav Raghuvanschi

Vishal Kumar has successfully given his M.Sc. oral examination held on **11/05/2026.**

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M.Sc. Second Year

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DEDICATE TO MY FAMILY……

ABSTRACT

Recently, researchers have been concentrating on fabricating optoelectronic devices using cost-effective and environmentally friendly materials. Cu(I) complexes and hybrid materials are promising candidates and are used as emitters in optoelectronic devices (WLEDs, OLEDs, LEECs, etc.), as photocatalysts for organic transformations, and for gas and volatile organic sensing. Organic-inorganic hybrid materials are important due to their potential across various fields, including optoelectronics, anti-counterfeiting, and white-light-emitting diodes. This project aims to synthesize and characterize ionic ligands and their all-in-one Cu(I) complexes.

The present study involves the synthesis of N and S-donor ionic ligands. These ligands were confirmed by Mass spectrometry and NMR spectroscopy. Ligands were treated with Copper sources to obtain a suitable single crystal. Crystal structure was confirmed by SCXRD and further characterized by PXRD, TGA, FE-SEM, and EDS.

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ACRONYMS

$CDCl_3$	Chloroform-d
ACN	Acetonitrile
DCM	Dichloromethane
MeOH	Methanol
EA	Ethyl Acetate
LCMS Spectrometry	Liquid Chromatography Mass
HRMS Spectrometry	High Resolution Mass
NMR	Nuclear Magnetic Resonance
TLC	Thin Layer Chromatography
CP	Coordination Polymer
Ppm	Part Per Million

NOMENCLATURE

Mg	Milligram
Mmol	Millimole
µl	Microliter
ml	Milliliter
°C	Degree Celsius
rt	Room Temperature
δ	Chemical shift

Chapter 1: INTRODUCTION

1.1 Copper (I) complexes

The viable use of Cu(I) complexes for real-world implementation, particularly in the fields of light initiation by electroluminescence, including optoelectronic devices such as Light-Emitting Diodes (LEDs) and Light-Emitting Electrochemical Cells (LEECs), along with in the field of thermosensing, and as photocatalysts, has focused significant scientific and primary studies over the past few years.[1] These studies have not only LED to advances in the clarification of the optical and chemical characteristics of the Cu(I) complexes but also enabled evolution of numerous new materials with significantly improved properties, for example, as OLED emitters.[2] Furthermore, design and strategies of materials could be developed to engineer very effective emitters, and different emission mechanisms could be introduced.

Metal complexes of first-row transition metals have significant technological applications due to their lower cost compared to those of other similar metals.[3,4] Specifically, Cu(I) complexes exhibit variable emission properties that can be tuned over different regions of visible light based on the ligand's coordination mode to the copper metal.[5] Moreover, multinuclear Cu(I) complexes exhibit good optical characteristics other than the mononuclear complexes.[6] General utilization for Cu(I) complexes includes OLEDs, bioimaging, catalysis, salvochromic, and vapochromic sensors.[7-10]

In recent times, Cu(I) based hybrid coordination materials have emerged as a crucial set of systems due to structural diversity, moisture stability, and strong, tunable luminescence.[11] It can form monomers, dimers (Cu_2I_2), trimers (Cu_3I_3), and tetramers (Cu_4I_4), which have structures ranging from zero-dimensional to three-dimensional.[12] The photoluminescence properties that are generated from various types of charge transfer exhibit a higher photoluminescence quantum yield than other phosphors. [13]

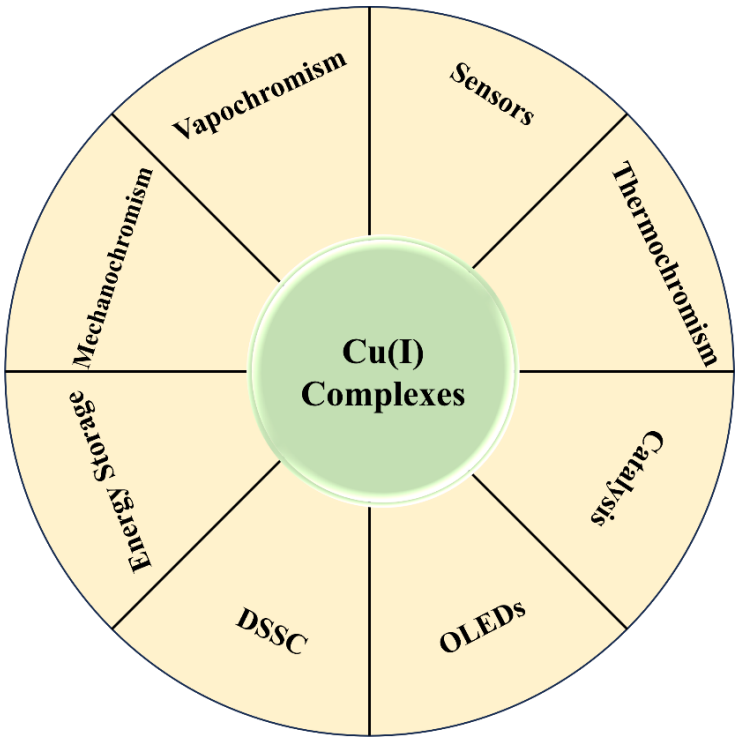


Figure 1: Properties and applications of Cu(I) complexes

1.2 Copper (I) hybrid materials

Copper (I) halide-based inorganic organic hybrid semiconductor exhibits a crucial class of crystalline materials. These hybrid materials exhibit intrinsic features, involving structural versatility, optical photophysical behavior, and environmental stability.

Over the past few years, these hybrid materials have gained significant attention due to their potential application in rare earth elements (REE) and solid state lighting (SSL). These hybrids can also exist as electro-neutral compounds, which may adopt zero-dimensional (0D) clusters, one-dimensional (1D) extended chains, two-dimensional (2D) architectures, three-dimensional (3D) coordination frameworks, and so on. This structural diversity demonstrates a significant role in their photophysical property, which makes them highly fascinating for advanced optoelectronic devices.[14]

The result of this is the tunable luminescence properties of these hybrid materials are associated with electronic transitions, particularly interligand charge transfer (ILCT), ligand-to-metal charge transfer (LMCT), metal to ligand charge transfer (MLCT), halide to ligand charge transfer (XLCT), and cluster-centered (CC) or an association of the following charge transfers. The prevalent structural unit of the hybrid materials is CuI monomeric unit, rhomboid Cu_2I_2 dimer, Cu_3I_3 trimer, and Cu_4I_4 tetramer (cubane structure). This structural diversity plays a significant role in determining their photophysical properties. Although the two major limitations of these materials are low blue-light excitability and lower solubility. Due to these limitations, hybrid materials are less applicable to white-light-emitting diode (WLED) and solution-based devices.

To resolve this issue, a synthetic approach has evolved in which cation-anion pairs are covalently bonded, which are commonly known as an all in one (AIO) type structure. This approach enhanced their stability and solubility due to the intense association between the ionic ligands and the metal center.[15]

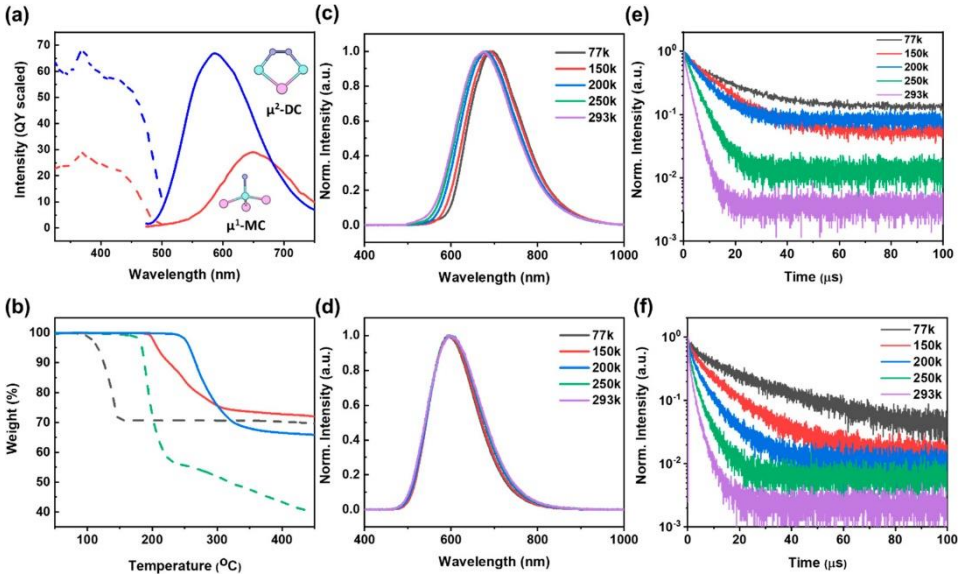


Figure 2: (a) excitation and emission spectra. (b) TGA plot. (c,d) Normalized emission spectra at variable temperature. (e,f) Luminescence decay profile at variable temperature. (fig from ref no 15)

1.3 All-in-one (AIO) type Cu(I) complexes

Most reported metal-halide (CuI)- based hybrid materials are assembled by the formation of a coordinate bond between the metal and neutral ligands or neutral organic ligands. Formed structures are Cu_2I_2 dimer, Cu_4I_4 tetramer, 1D chain, and 2D layer.[16] These types of hybrid materials are known as type I compounds. Type II hybrid structures are formed by cationic systems and anionic motifs. In this type of structure, there are no coordination bonds; the organic and inorganic modules are connected through electrostatic forces. The only drawbacks of this material are its low excitability and poor solution processability. To resolve this challenge, an AIO-type material design is used, featuring both ionic and coordinate bonds within a single molecule. These are the combination of I and II type materials.[17,18] These types of compounds are showing better thermal stability than both.

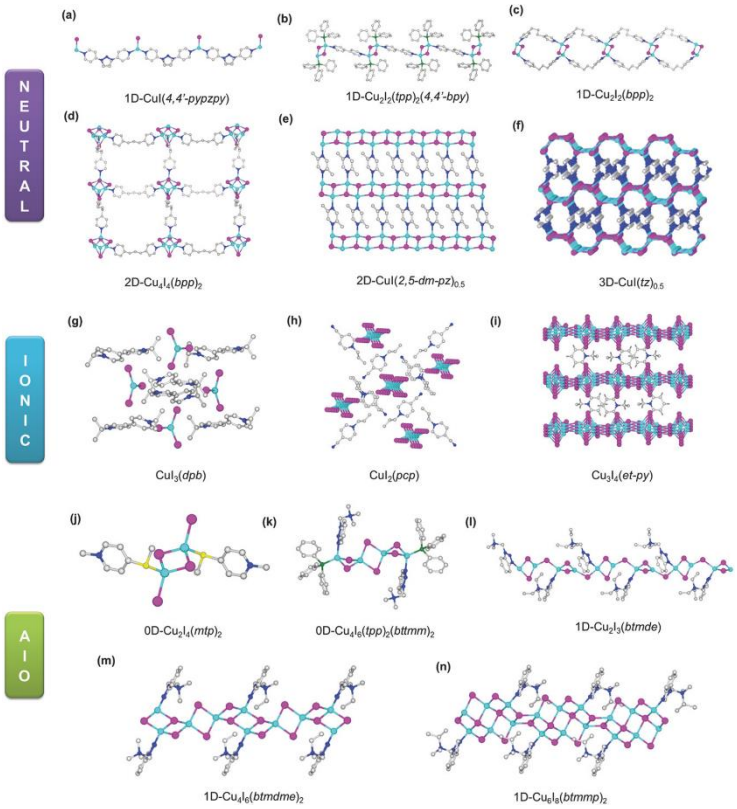


Figure 3. (a–n) Structure Types of I, II, and III compounds. Color palette: Cu, cyan; I, purple; N, blue; C, gray; S, yellow; P, green. (fig from ref 17)

Chapter 2: EXPERIMENTAL SECTION

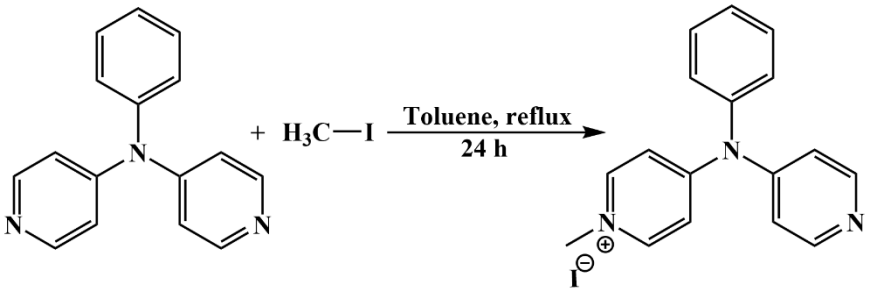
2.1 Material and Instrumentation

All chemicals were purchased and used without further purification. TLC was used to monitor reaction progress on a Merck 60 F254 precoated silica gel plate (0.25 mm thickness), and the products were visualized in a UV chamber. All ^{1}H and $^{13}C\{^{1}H\}$ NMR spectra were collected using a Bruker 400/500 spectrometer in $CDCl_3$ and DMSO-d_6 at 400/500 MHz for ^{1}H and $^{13}C\{^{1}H\}$ NMR. Data for proton NMR chemical shifts are shown in ppm downfield from tetramethyl silane and are mentioned in delta (δ) units. $CDCl_3$ is used as an internal standard, which shows a peak at 7.26 ppm. The ^{1}H NMR splitting patterns are singlet (s), doublet (d), and multiplet (m), and the NMR data were analyzed using Mestre Nova.

2.2 Synthesis of cationic ligand

2.2.1 Synthesis of *1-methyl-4-(phenyl(pyridin-4-yl)amino)pyridin-1-ium iodide* (L1)

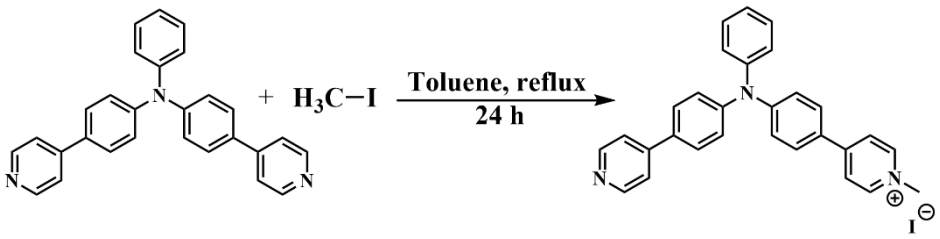
In a dry oven, a pressure tube was added phenyl dipyridine (100 mg, 0.4 mmol), which was dissolved in toluene. After complete dissolution, methyl iodide (251 µL, 4.04 mmol) was subsequently introduced, and the reaction mixture was stirred at 110 °C for 24 hours. Filtered reaction mixture, followed by washing with toluene and ether, then dried under vacuum. The obtained product was a yellow solid with 61 % yield. **LCMS** (ESI) *m/z* calculated for $\mathbf{C}_{17}H_{16}N_3$ 262.1344, obtained 262.1355.



Scheme 1: synthesis of L1

2.2.2 synthesis of *1-methyl-4-(4-(phenyl(4-(pyridin-4-yl)phenyl)amino) phenyl)pyridin-1-ium* (L2)

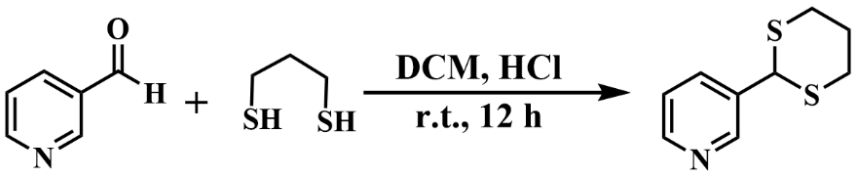
Took di pyridine triphenyl amine (50 mg, 0.125 mmol) in a dried oven pressure tube and dissolved it in toluene. After complete dissolution, methyl iodide (10 µL, 1 mmol) was introduced, and the reaction mixture was stirred at 110 °C for 24 hours. Filter the reaction mixture, followed by washing with toluene and ether, then dried under vacuum. The obtained product was a reddish solid with 77 % yield. **LCMS** (ESI) *m/z* calculated for C29H24N3 214.2002. Obtain 214.2014.



Scheme 2: synthesis of L2

2.2.3 Synthesis of *propane-1,3-dithiol--3-(1,3-dithian-2-yl) pyridine* (P1)

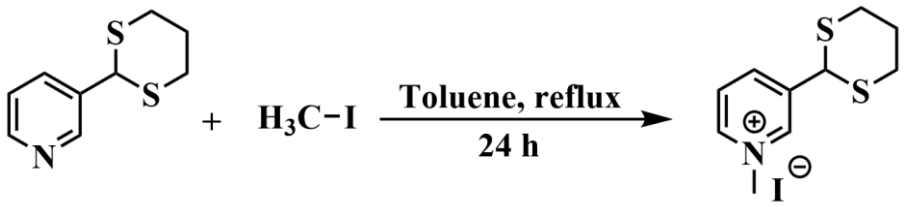
I have synthesized a ligand with a previously reported procedure with some modifications. In a clean, dry two-neck round-bottom flask, 3-pyridine carboxaldehyde (0.56 ml, 0.0046 mol) and propane-1,3-dithiol (0.591 ml, 0.005 mmol) were dissolved in dichloroethane. Subsequently, hydrochloric acid (2 ml) was introduced to the reaction mixture, and the reaction mixture was stirred for 12 hours. The reaction was neutralized with 10 % aqueous NaOH solution. The layer was separated, and the organic layer was isolated and washed with water and brine solution. The organic solvent was dried using magnesium sulphate ($MgSO_4$).[19] The solvent was evaporated, and the product was isolated by column chromatography. The obtained product was a light-yellow solid (800 mg, 76% yield). HRMS (ESI) m/z calculated for $C_9H_{11}NS_2$ [M + H] $^+$ 198.0411, found 198.0434. **^{1}H NMR (500 MHz, $CDCl_3$)** δ 8.67 (d, *J* = 2.6 Hz, 1H), δ 8.53 (s, 1H), δ 7.81 (dt, J = 7.9, 2.1 Hz, 1H), δ 7.27 (dd, J = 8.1, 4.6 Hz, 1H), δ 5.16 (s, 1H), δ 3.08 (t, 2H), δ 3.02 (t, 2H), δ 2.17 (t, 1H), δ 1.97 (d, 1H). **^{13}C NMR (126 MHz, $CDCl_3$)** δ 149.74, 148.91, 135.19, 134.85, 123.35, 48.16, 31.96, 24.48.



Scheme 3: synthesis of P1

2.2.3.1 Synthesis of *3-(1,3-dithian-2-yl)-1-methylpyridin-1-ium* (L3)

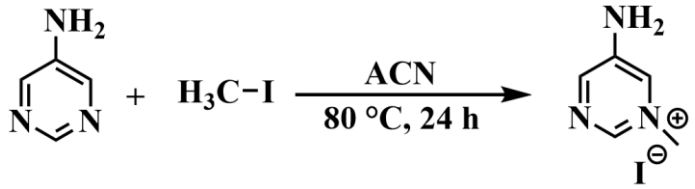
Took 3-(1,3-dithian-yl)-pyridine (200 mg, 1.015 mmol) in a dried oven pressure tube and dissolved in toluene. After complete dissolution, methyl iodide (10 mmol) was introduced, and the reaction mixture was heated at 110 °C for 24 hours. Filter the reaction mixture, wash it three times with toluene and ether, and dry it under vacuum. The obtained product was a brown solid (305 mg, 85% yield). HRMS (ESI) m/z calculated for $C_{10}H_{14}NS_2$ 212.0568, found 212.0575. **^{1}H NMR (500 MHz, DMSO)** δ 9.09 (s, 1H), 8.96 (s, 1H), 8.62 (d, *J* = 12.6 Hz, 1H), 8.20 – 8.08 (m, 1H), 5.72 (s, 1H), 4.38 (s, 3H), 3.09 (s, 2H), 3.02 (s, 2H), 2.18 (s, 1H), 1.82 (s, 1H). **^{13}C NMR (126 MHz, DMSO)** δ 145.54, 144.32, 143.88, 139.83, 128.01, 48.25, 44.74, 29.98, 24.11.



Scheme 4: synthesis of L3

2.2.4 Synthesis of *5-amino-1-methylpyrimidin-1-ium iodide* (L4)

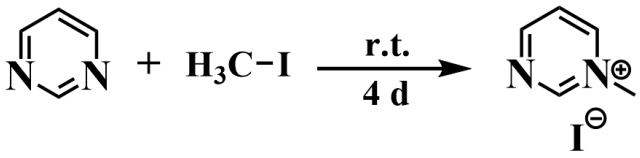
Took 5-amino pyrimidine (100 mg, 1.05 mmol) in a dried oven pressure tube and dissolved it in acetonitrile. After complete dissolution, methyl iodide (10 mmol) was introduced, and the reaction continued at 82 °C for 24 hours. Filter the reaction mixture, wash it three times with ether and ACN, and dry it under vacuum, off white slod product was obtained. (354 mg, 70% yield). HRMS (ESI) m/z calculated for $C_5H_8N_3$ 110.0718, found 110.0727. **^{1}H NMR (500 MHz, DMSO)** δ 8.88 (s, 1H), 8.60 (s, 1H), 8.30 (s, 1H), 6.88 (s, 2H), 4.14 (s, 3H), 3.33 (s, 2H). **^{13}C NMR (126 MHz, DMSO)** δ 147.37, 144.31, 140.89, 143.41, 44.81.



Scheme 5: synthesis of L4

2.2.5 Synthesis of 1-methylpyrimidin-1-ium iodide (L5)

Took pyrimidine (200 mg, 1.05 mmol) in a dried oven pressure tube and dissolved it in acetonitrile. After complete dissolution, methyl iodide (2 mL) was added, and the reaction mixture was continued at ambient temperature for 4 days. Filter the reaction mixture, wash it three times with ether, and dry it under vacuum. The product was obtained as a yellow solid (381 mg, 41 % yield). **^{1}H NMR (500 MHz, DMSO)** δ 9.79 (s, 1H), 9.44 (d, 1H), 9.36 (d, 1H), 8.29 (t, 1H), 4.27 (s, 3H). **^{13}C NMR (126 MHz, DMSO)** δ 164.07, 154.53, 153.11, 123.31, 45.27.

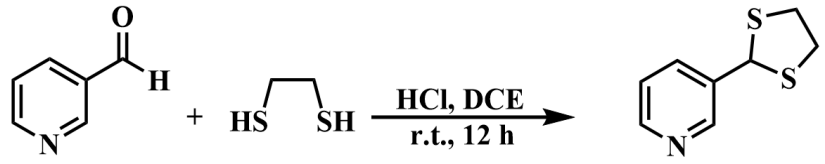


Scheme 6: synthesis of L5

2.2.6 Synthesis of *3-(1,3-dithiolan-2-yl) pyridine* (P2)

I have synthesized a ligand with a previously reported procedure with some modifications. In a clean, dry two-neck round-bottom flask, 3-pyridine carboxaldehyde (2 ml, 0.018 mol) and ethane-1,2-dithiol (1.93 ml, 0.020 mmol) were dissolved in dichloroethane. Subsequently, hydrochloric acid (6 ml) was introduced to the reaction mixture, and the reaction mixture was continued for 12 hours. The reaction was neutralized with a 10 % aqueous NaOH solution.

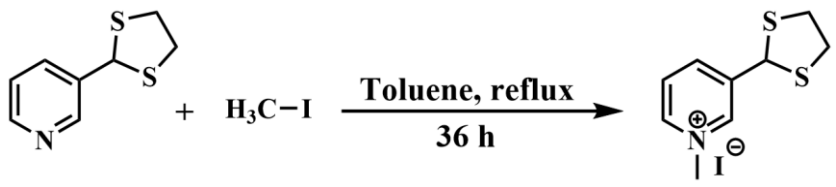
The layer was separated, and the organic phase was isolated and washed with water and brine solution. The solvent was dried using anhydrous magnesium sulfate ($MgSO_4$). The obtained product was as a Pale-yellow liquid (3 ml, 87 % yield). HRMS (ESI) m/z calculated for $C_9H_{11}NS_2$ [M + H] $^+$ 184.0252, found 184.0255.



Scheme 7: synthesis of P2

2.2.6.1 Synthesis of *3-(1,3-dithiolan-2-yl)-1-methylpyridin-1-ium iodide* (L6)

Took 3-(1,3-dithian-yl)-pyridine (1000 mg, 5.46 mmol) in a dried oven pressure tube and dissolved in toluene. After complete dissolution, methyl iodide (54.6 mmol) was introduced, and the reaction was continued at 110 ℃ for 24 hours. Filter the reaction mixture, wash it three times with toluene and ether, and vacuum dry. The obtained product was a yellow solid (1180 mg, 66 % yield). HRMS (ESI) m/z calculated for $C_{10}H_{14}NS_2$ 198.0411, found 1998.0412. **^{1}H NMR (500 MHz, DMSO)** ^{1}H NMR (500 MHz, DMSO) δ 9.08 (s,1H) δ 8.89 (d, *J* = 6.0 Hz, 1H), 8.67 (s, 1H), 8.10 (d, *J* = 8.2 Hz, 1H), 5.97 (s, 1H), 4.35 (s, 3H), 3.62 – 3.53 (m, 2H), 3.45 (d, *J* = 11.4 Hz, 2H). **^{13}C NMR (12 MHz, DMSO)** δ 144.63, 144.21, 144.07, 144.01, 127.49, 50.03, 48.13, 40.03.



Scheme 8: synthesis of L6

2.3 Synthesis of coordination complexes (CPs)

2.3.1 Synthesis of CP1

The ligand (10 mg, 0.038 mmol) was dissolved in methanol in a clean test tube. Separately, CuI (7.2 mg, 0.024 mmol) was weighed and dissolved in acetonitrile (ACN). Both solutions were combined, yielding a light-yellow solid. The resulting mixture was stirred at room temperature for 5 hours. Upon completion of the reaction, filtered the mixture, and the residue was washed 2–3 times with MeOH and ACN to remove unreacted ligand and CuI, respectively.

This product was then dissolved in different solvents to get crystals. Layering, autoclave synthesis, and slow evaporation were performed to obtain crystals; however, no crystals were observed in any of the cases.

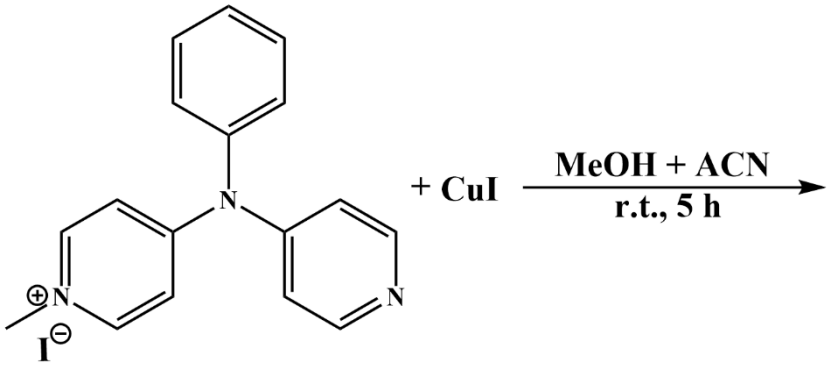


Figure 4: synthesis of CP1

2.3.2 Synthesis of CP2

The ligand (5 mg, 0.012 mmol) was dissolved in a clean test tube in methanol. Separately, CuI (5 mg, 0.024 mmol) was weighed and dissolved in acetonitrile (ACN). Both solutions were combined, resulting in a light red solid. The resulting mixture was then stirred at room temperature for 5 hours.

Upon completion of the reaction, filtered the mixture, and the residue was washed 2–3 times with MeOH and ACN to remove unreacted ligand and CuI, respectively.

This product was then dissolved in different solvents to get crystals. Layering, autoclave synthesis, and slow evaporation were performed to obtain crystals; however, no crystals were observed in any of the cases.

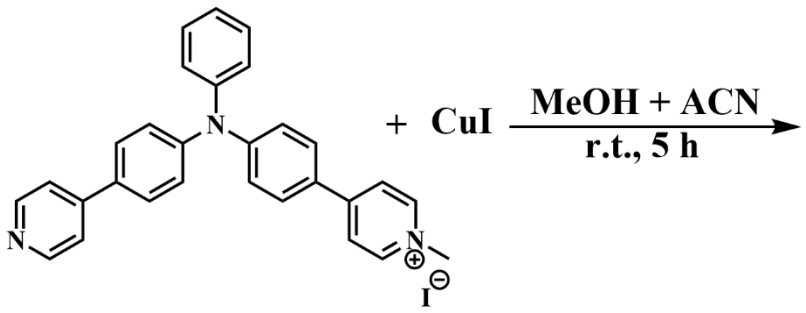


Figure 5: synthesis of CP2

2.3.3 Synthesis of CP3

The ligand (10 mg, 0.029 mmol) was dissolved in methanol in a clean test tube. Separately, CuI (11.02 mg, 0.056 mmol) was weighed and dissolved in acetonitrile (ACN). Both solutions were combined, yielding an orange solid. The resulting mixture was then continued at room temperature for 5 hours. Upon completion of the reaction, filtered the mixture, and the residue was washed 2–3 times with MeOH and ACN to remove unreacted ligand and CuI, respectively.

The obtained solid was dissolved in acetonitrile through sonication and heating. The clear solution was kept at room temperature to afford suitable crystals for single-crystal X-ray analysis.

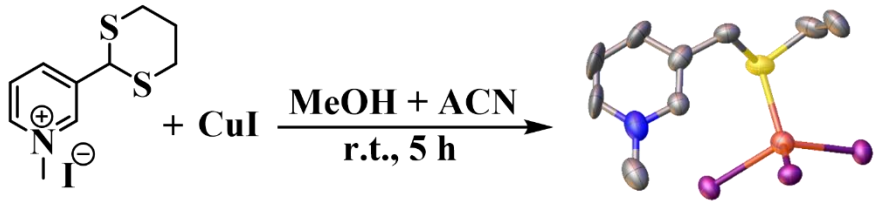


Figure 6: synthesis of CP3

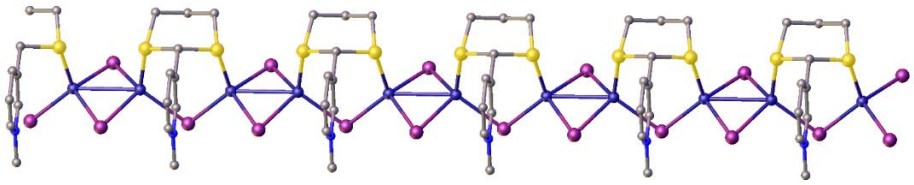


Figure 7: 1D Polymer

2.3.4 Synthesis of CP4

The ligand (10 mg, 0.047 mmol) was dissolved in methanol in a clean test tube. Separately, CuI (9 mg, 0.047 mmol) was weighed and dissolved in acetonitrile (ACN). Both solutions were combined, yielding a Brown solid. The resulting mixture was then continued at room temperature for 5 hours. Upon completion of the reaction, filtered the mixture, and the residue was washed 2–3 times with MeOH and ACN to remove unreacted ligand and CuI, respectively. This product was then dissolved in different solvents to get crystals. Layering, autoclave synthesis, and slow evaporation were performed to obtain crystals; however, no crystals were observed in any of the cases.

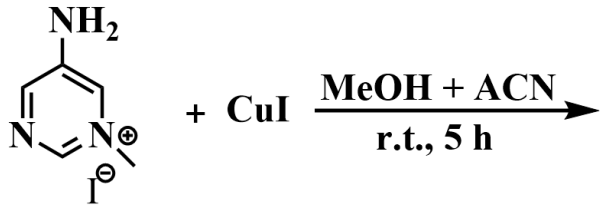


Figure 8: synthesis of CP4

2.3.5 Synthesis of CP5

The ligand (10 mg, 0.045 mmol) was dissolved in methanol in a clean test tube. Separately, CuI (17.11 mg, 0.09 mmol) was weighed and dissolved in acetonitrile (ACN). Both solutions were combined, yielding a green solid. The resulting mixture was then continued at room temperature for 5 hours. Upon completion of the reaction, filtered the mixture, and the residue was washed 2–3 times with MeOH and ACN to remove unreacted ligand and CuI, respectively. The obtained solid was dissolved in acetonitrile, then sonicated and heated. The solution was kept at room temperature for the crystals. This product was then dissolved in different solvents to get crystals. Layering, autoclave synthesis, and slow evaporation were performed to obtain crystals; however, no crystals were observed in any of the cases

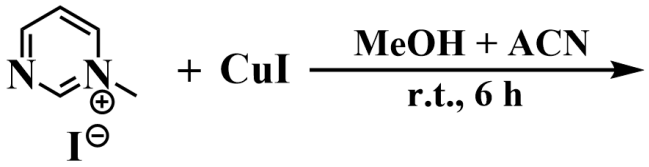


Figure 9: synthesis of CP5

2.2.6 Synthesis of CP6

The ligand (10 mg, 0.0307 mmol) was dissolved in a clean test tube in methanol. Separately, CuI (11 mg, 0.615 mmol) was weighed and dissolved in acetonitrile (ACN). Both solutions were combined, resulting in an orange solid. The mixture was then continued at room temperature for 5 hours. Upon completion of the reaction, filtered the mixture, and the residue was washed 2–3 times with MeOH and ACN to remove unreacted ligand and CuI, respectively.

This product was then dissolved in different solvents to get crystals. Layering, autoclave synthesis, and slow evaporation were performed to obtain crystals; however, no crystals were observed in any of the cases.

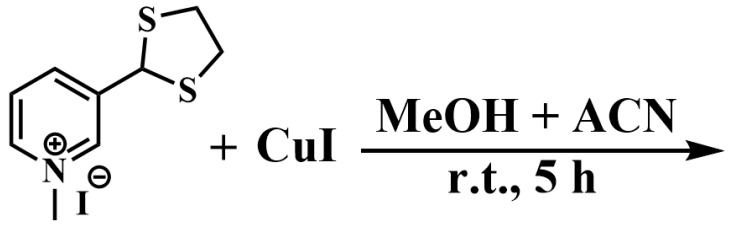


Figure 10: synthesis of CP6

2.3 Synthesis of complexes

2.3.1 Synthesis of C1

In a nitrogen-rinsed Schlenk tube, copper iodide (9.7 mg, 0.051 mmol) and triphenyl phosphene (26.97 mg, 0.102 mmol) were dissolved in a two-solvent system in methanol and chloroform (1:3). The reaction was allowed to stir at ambient temperature until converted into a clear solution in a nitrogen atmosphere. Added ligand L1 and stirred the reaction at ambient conditions for 24 hours. During this process, the mixture was converted from transparent to light yellow.

Upon completion of the reaction, the solvent was evaporated under reduced pressure, and a yellow solid was obtained. The product was washed with dichloromethane and hexane and dried under vacuum.

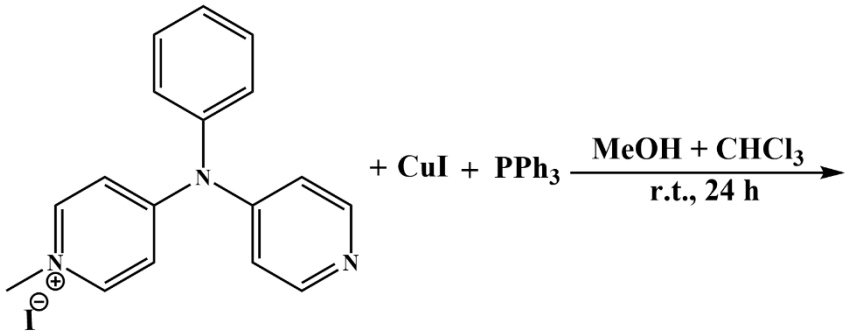


Figure 11: synthesis of C1

2.3.2 Synthesis of C2

In a nitrogen-rinsed Schlenk tube, copper iodide (7 mg, 0.036 mmol) and triphenyl phosphine (19 mg, 0.073 mmol) were dissolved in a two-solvent system of methanol and chloroform (1:3). The reaction was allowed to stir at ambient temperature until converted into a clear solution in a nitrogen atmosphere. Added ligand L2 and stirred the reaction at ambient conditions for 24 hours. During this process, the reaction mixture turned from transparent to light yellow.

After the reaction was completed, the solvent was evaporated under reduced pressure, and a yellow solid was obtained. The product was washed with dichloromethane and hexane and dried under vacuum.

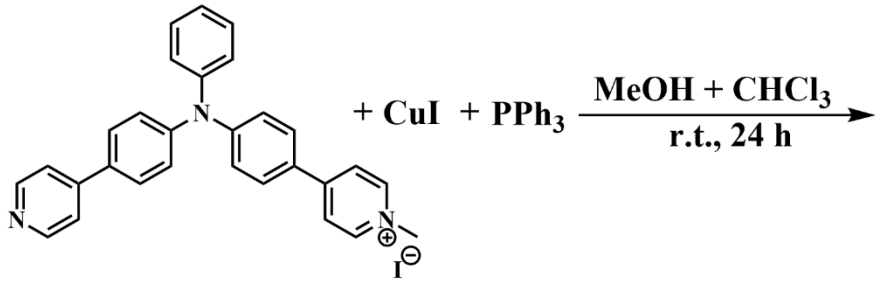


Figure 12: synthesis of C2

2.3.3 Synthesis of C3

In a nitrogen-rinsed Schlenk tube, copper iodide (11.02 mg, 0.058 mmol) and triphenyl phosphene (30.24 mg, 0.116 mmol) were dissolved in a two-solvent system of methanol and chloroform (1:3). The reaction was allowed to stir at ambient temperature until converted into a clear solution in a nitrogen atmosphere. Added ligand L3 and stirred the reaction at ambient conditions for 24 hours. During this process, the reaction mixture turned from transparent to light yellow. After the reaction was completed, the solvent was evaporated under reduced pressure, and a yellow solid was obtained. The product was washed with dichloromethane and hexane and dried under vacuum.

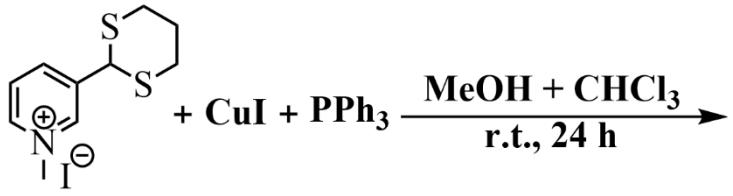


Figure 13: synthesis of C3

2.3.4 Synthesis of C4

In a nitrogen-rinsed Schlenk tube, copper iodide (24.05 mg, 0.126 mmol) and triphenyl phosphene (66.30 mg, 0.253 mmol) were dissolved in a two-solvent system of methanol and chloroform (1:3). The reaction was allowed to stir at ambient temperature until converted into a clear solution in a nitrogen atmosphere. Added ligand L4 and stirred the reaction at ambient conditions for 24 hours. During this process, the reaction turned from transparent to light yellow. After reaction was complete, filter the reaction mixture, wash with methanol and acetonitrile, and obtain a white solid.

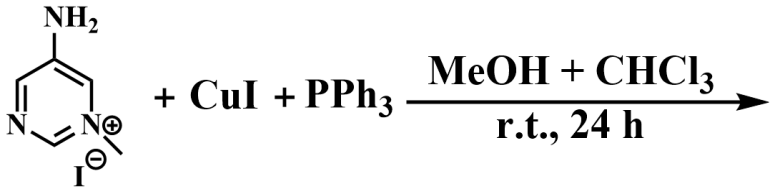


Figure 14: synthesis of C4

2.3.5 Synthesis of C5

In a nitrogen-rinsed Schlenk tube, copper iodide (85 mg, 0.450 mmol) and triphenyl phosphine (236 mg, 0.90 mmol) were dissolved in a two-solvent system of methanol and chloroform (1:3). The reaction was allowed to stir at ambient temperature until converted into a clear solution in a nitrogen atmosphere. Added ligand L1 and stirred the reaction at ambient conditions for 24 hours. During this process, the reaction turned from transparent to light yellow.

After the reaction was completed, the solvent was evaporated under reduced pressure, and a yellow solid was obtained. The product was washed with dichloromethane and hexane, and dried under vacuum.

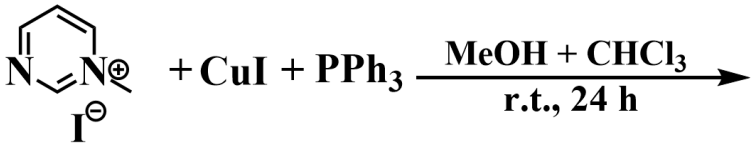


Figure 15: synthesis of C5

2.3.6 Synthesis of C6

In a nitrogen-rinsed Schlenk tube, copper iodide (23.38 mg, 0.123 mmol) and triphenyl phosphene (64.56 mg, 0.246 mmol) were dissolved in a two-solvent system of methanol and chloroform (1:3). The reaction was allowed to stir at ambient temperature until converted into a clear solution in a nitrogen atmosphere. Added ligand L5 and stirred the reaction at ambient conditions for 24 hours. During this process, the reaction turned from transparent to light yellow. After the reaction was completed, the solvent was evaporated under reduced pressure, and a yellow solid was obtained. The product was washed with dichloromethane and hexane and dried under vacuum.

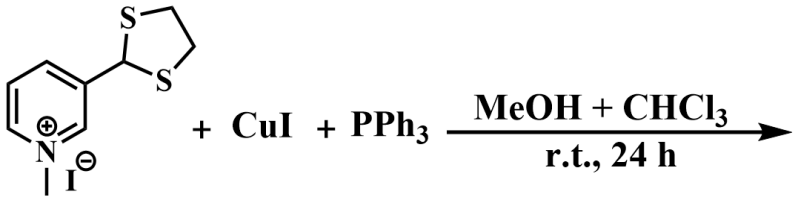


Figure 16: synthesis of C6

Chapter 3: RESULTS AND DISCUSSION

3.1 Characterization

3.1.1 Characterization of ligands

3.1.1.1 Characterization of L1

L1 was synthesized according to Scheme 1. In this reaction, toluene was used as a solvent. The yellow solid product was isolated with 61 % yield. The product was characterized by mass spectrometry.

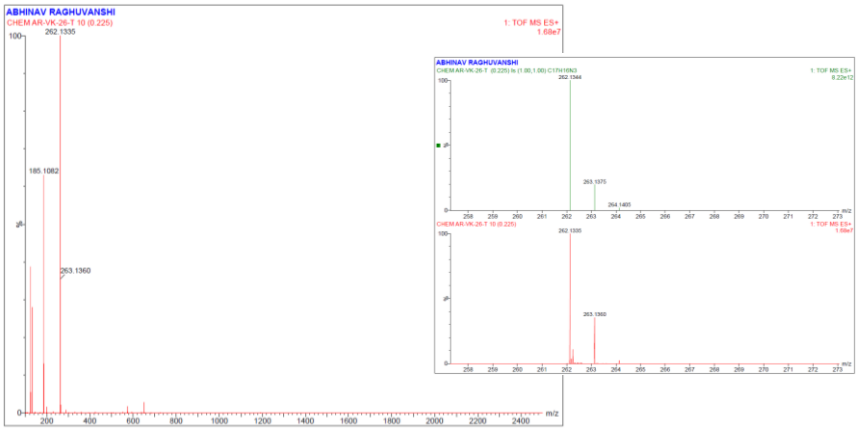


Figure 17: Mass spectrogram of L1

3.1.1.2 Characterization of L2

L2 was synthesized according to Scheme 2. In this reaction, toluene was used as a solvent. A light red solid product was isolated in 77% yield. The product was characterized by mass spectrometry.

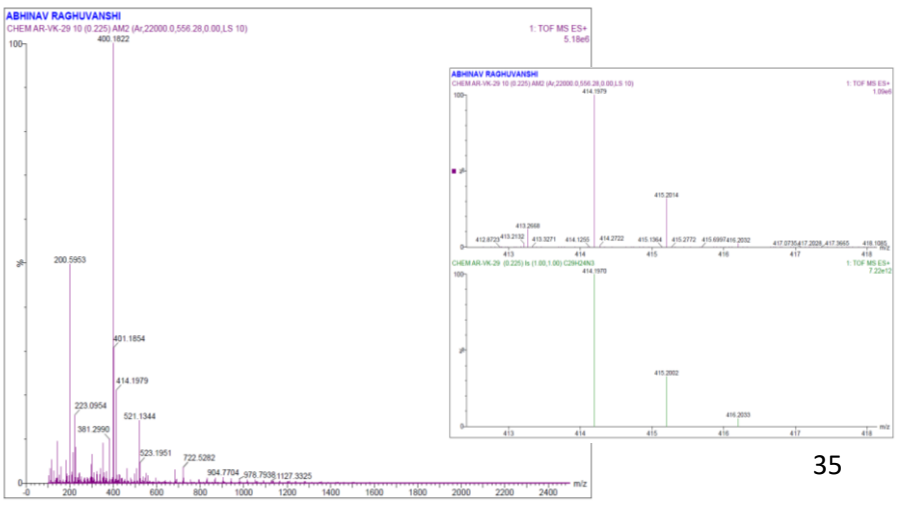


Figure 18: Mass spectrogram of L2

3.1.1.3 Characterization of L3

L3 was synthesized according to Scheme 4. In this reaction, toluene was used as a solvent. The brown solid product was isolated with 85 % yield. The isolated product was characterized by mass spectrometry and ^{1}H and $^{13}C\{^{1}H\}$ NMR spectroscopy.

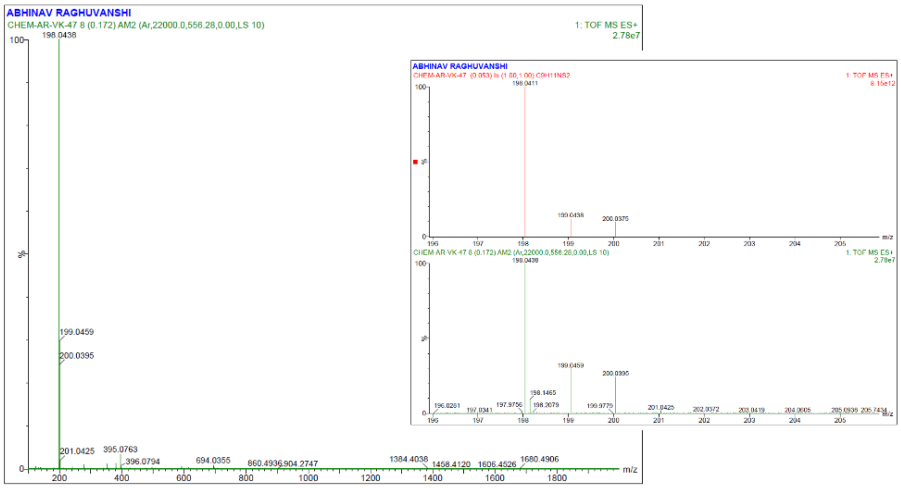


Figure 19: Mass spectrogram of L3

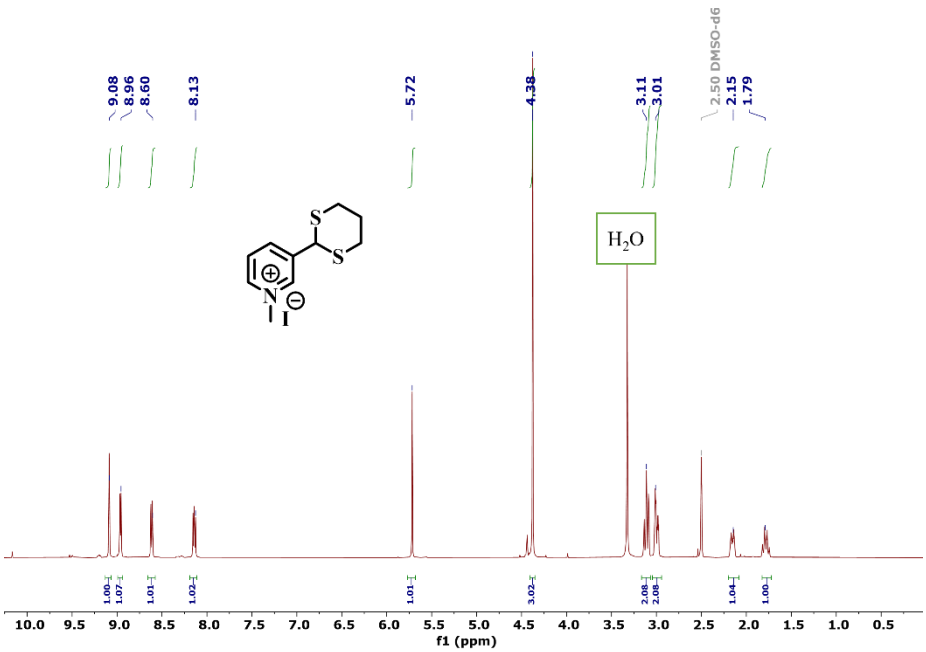


Figure 20: ^{1}H NMR spectra of L3

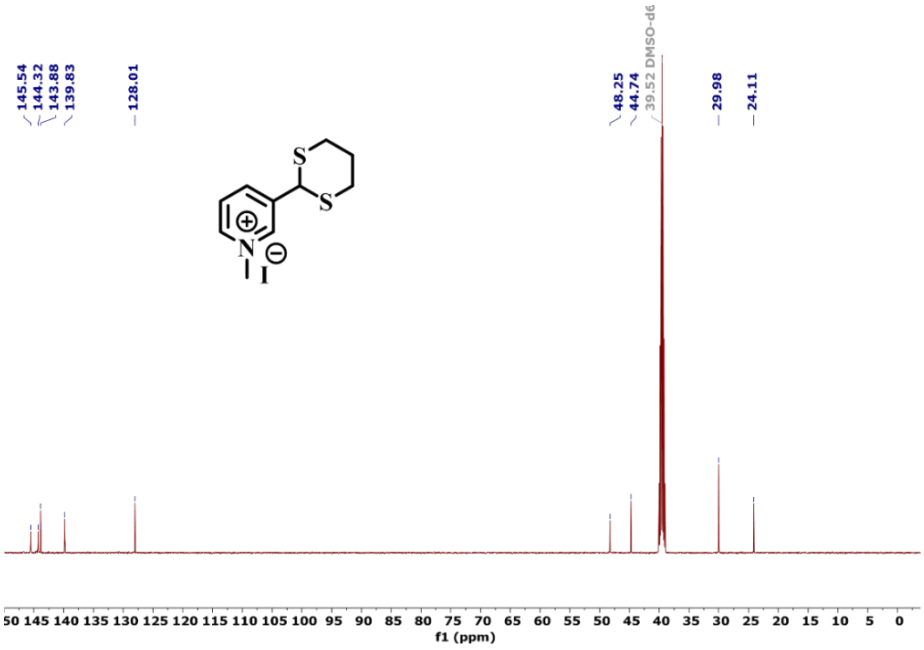


Figure 21: $^{13}C\{^{1}H\}$ NMR spectra of L3

3.1.1.4 Characterization of L4

L4 was synthesized according to Scheme 5. In this reaction, acetonitrile was used as a solvent. An off-white solid product was isolated with 70 % yield. The isolated product was characterized by mass spectrometry and ^{1}H and $^{13}C\{^{1}H\}$ NMR spectroscopy.

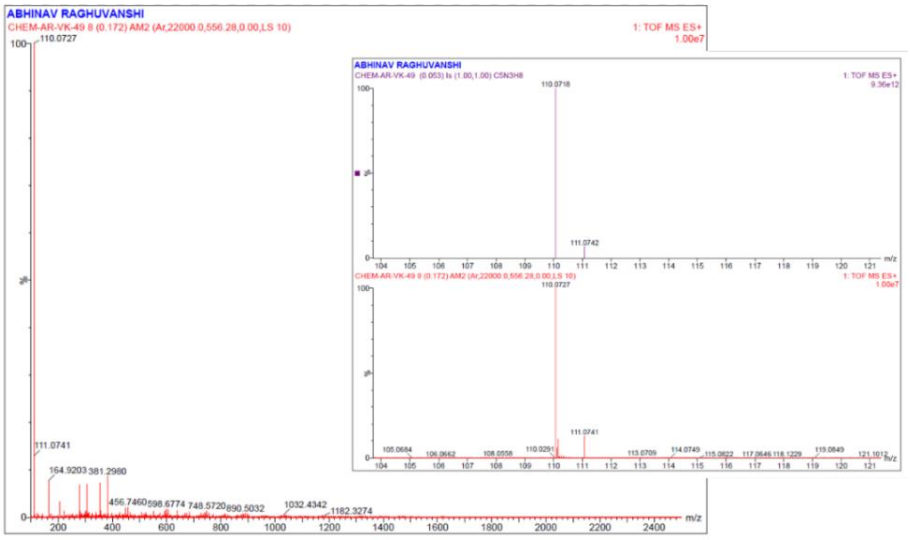


Figure 22: Mass spectrogram of L4

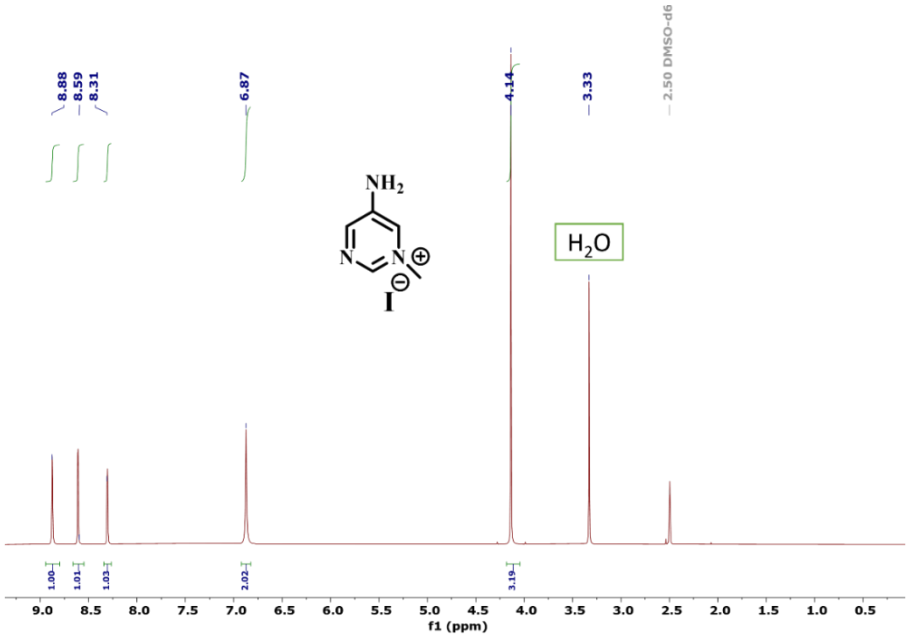


Figure 23: ^{1}H NMR spectra of L4

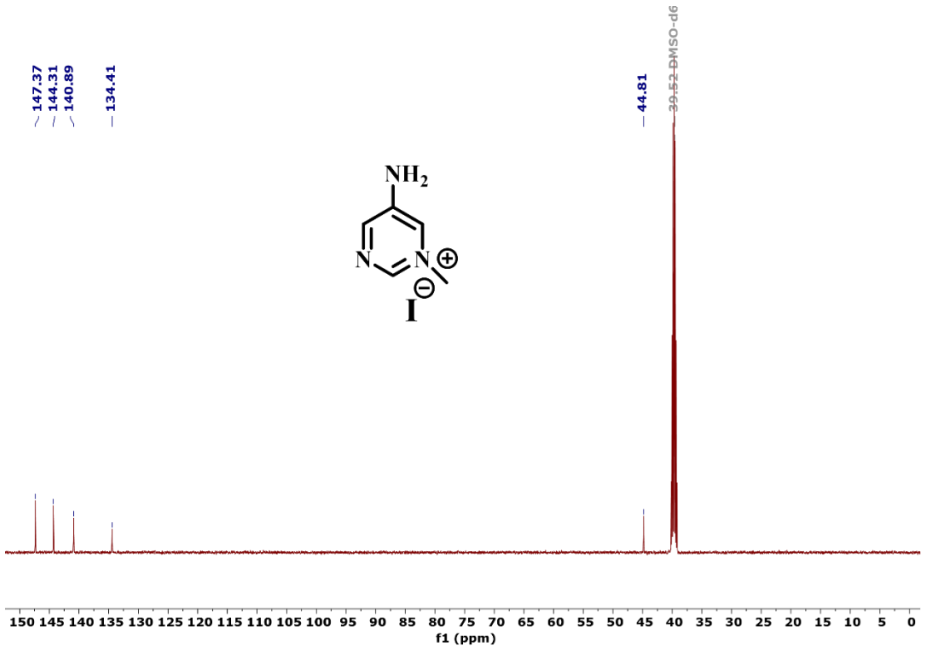


Figure 24: $^{13}C\{^{1}H\}$ NMR spectra of L4

3.1.1.1 Characterization of L5

L4 was synthesized according to Scheme 6. In this reaction, toluene was used as a solvent. The yellow solid product was isolated with 41 % yield. The isolated product was characterized by ^{1}H and $^{13}C\{^{1}H\}$ NMR spectroscopy.

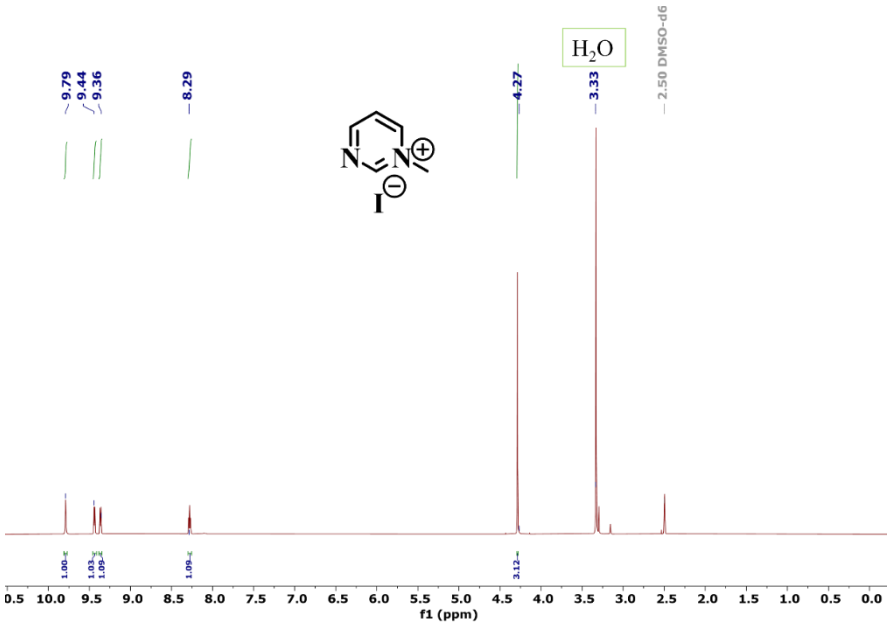


Figure 25: ^{1}H NMR spectra of L5

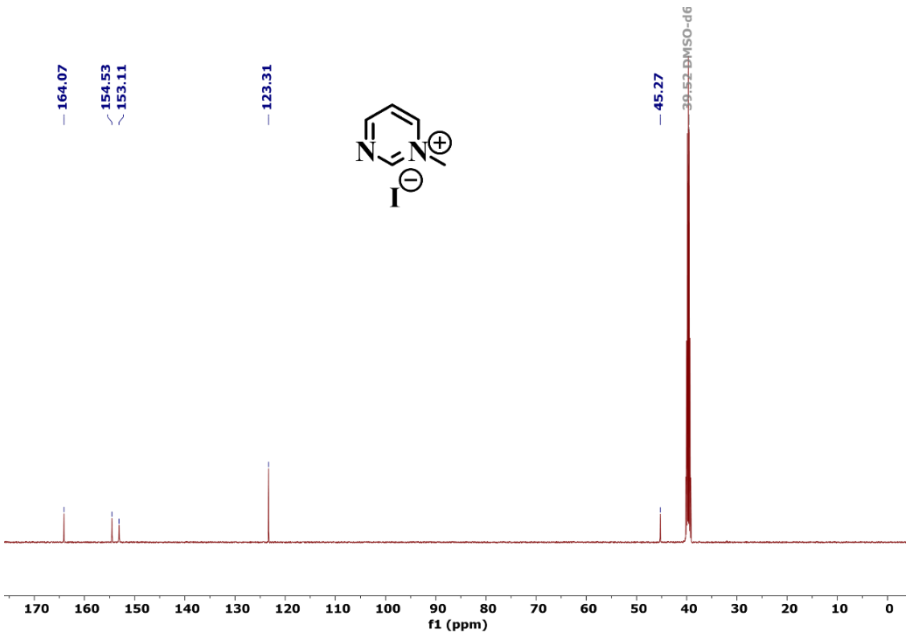


Figure 26: $^{13}C\{^{1}H\}$ NMR spectra of L5

3.1.1.2 Characterization of L6

L5 was synthesized according to Scheme 7. In this reaction, acetonitrile was used as a solvent. The yellow solid product was isolated with 66 % yield. The isolated product was characterized by mass spectrometry and ^{1}H and $^{13}C\{^{1}H\}$ NMR spectroscopy.

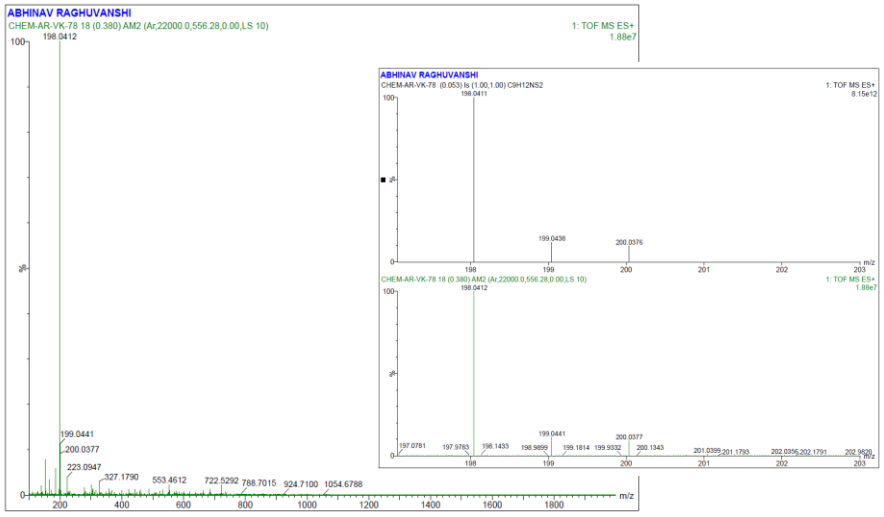


Figure 27: Mass spectrogram of L6

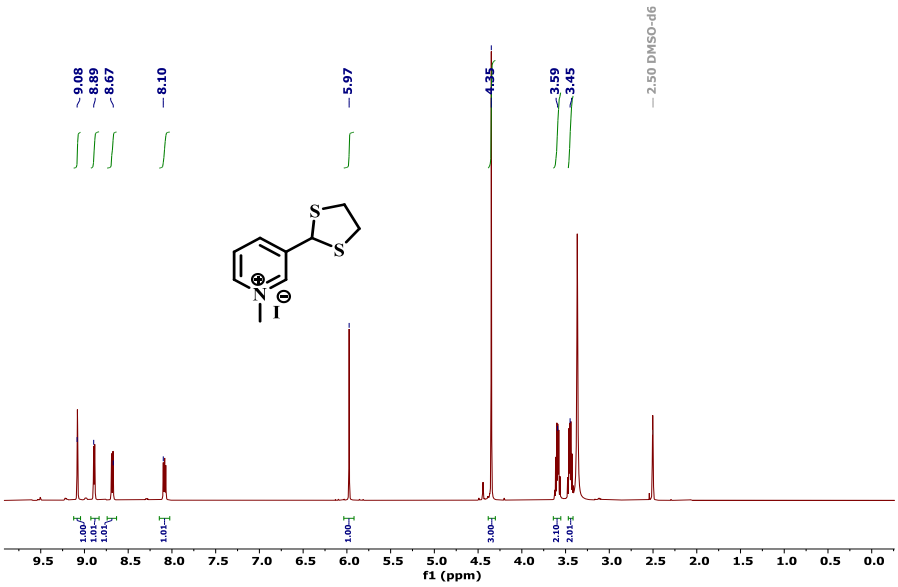


Figure 28: ^{1}H NMR spectra of L6

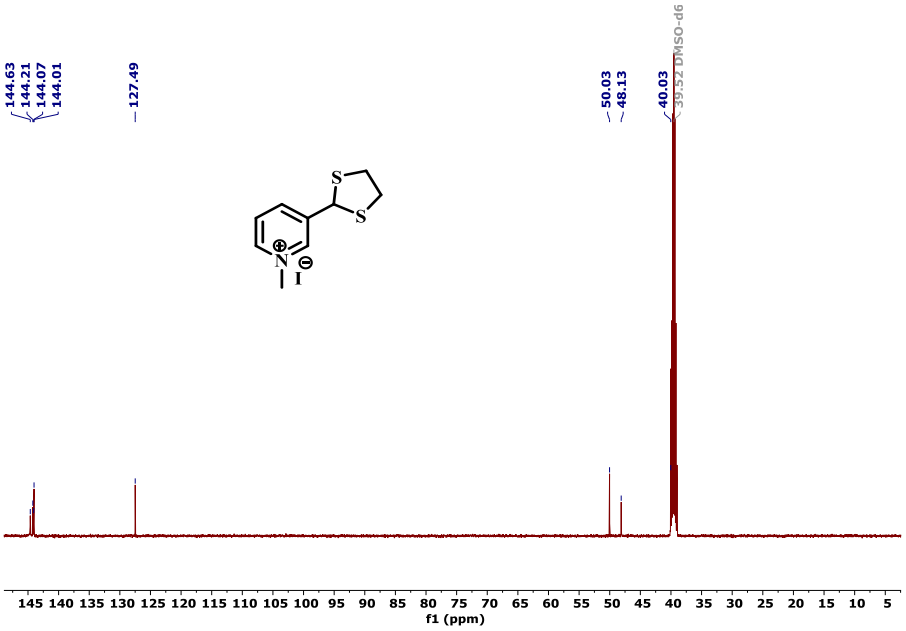


Figure 29: $^{13}C\{^{1}H\}$ NMR spectra of L6

3.1.2 Characterization of Complexes

3.1.2.1 Characterization of CP3

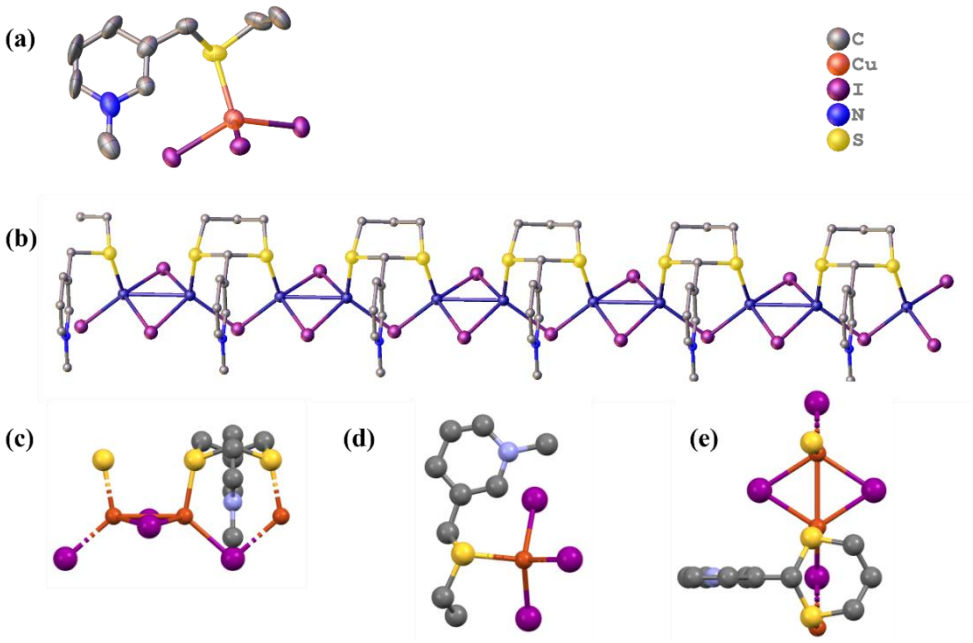


Figure 30: (a) Asymmetric unit of CP3, (b) Grown structure of CP3, (c) Crystal structure in a, b, and c directions

Suitable crystals for single-crystal X-ray diffraction (SC-XRD) analysis were acquired by dissolving products in boiling acetonitrile. The needle-like crystals of CP3 were obtained by keeping acetonitrile solutions undisturbed at room temperature. The asymmetric unit contains one copper atom, three iodine atoms, and a ligand unit. Further, the grown structure suggests the fabrication of a one-dimensional (1D) coordination polymer with the molecular formula $Cu_2(\mu2\text{-}I)_3L3$, featuring a $Cu_2I_3^-$ secondary building unit (SBU) in which the valency of the respective Cu- atom is satisfied by three iodine atoms and one sulfur atom from the ligand unit. All three iodine atoms are coordinated in μ2-mode.

The geometry of the Cu atom is a distorted tetrahedral. The distortion geometry can be confirmed by calculating the bond angle and bond distance around the Cu atom. Where Cu-S distance is 2.332 Å.

Cu-I is 2.606 Å, 2.710 Å, 2.640 Å, and Cu-Cu distance is 2.886 Å. The bond angle is S-Cu-I is 120.82°, 99.39 °, 104.00 °, and I-Cu-I is 113.20°.

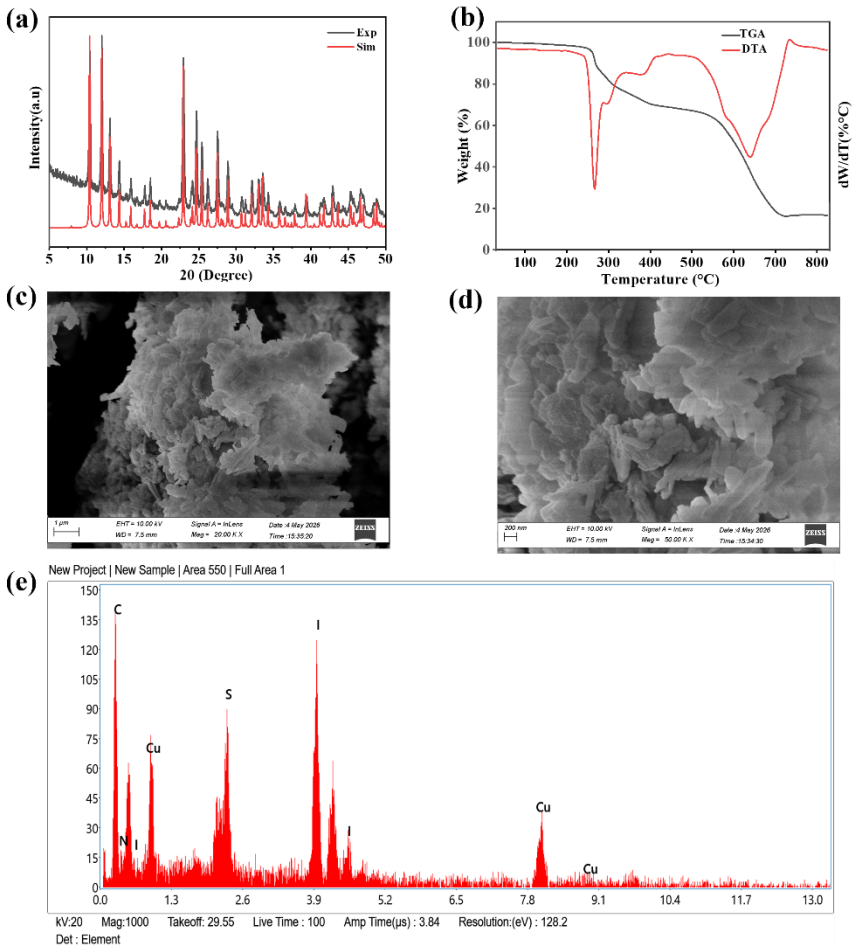


Figure 31: (a) PXRD of CP3, (b) TGA curve of CP3, (c, d) FESEM images of CP3, (e) EDS spectra of CP3.

The bulk purity and crystallinity of the polymer were demonstrated by powder X-ray diffraction over the 2θ range of 5−50°.

The PXRD pattern of the polymer matched perfectly with their simulated one obtained from the SC-XRD. The sharp peaks in the PXRD spectra indicate the polymer's high crystallinity.

Thermogravimetric analysis (TGA) was conducted to investigate the thermal stability of the polymer. The TGA curve shows the polymer is stable up to 250 °C.

To examine the polymer surface morphology, we performed FESEM analysis. The SEM image shows that the polymer's surface morphology is flower-like, with structures appearing as several thin nanosheets.

To investigate the elemental composition of the polymer, we conducted Energy-Dispersive X-ray Spectroscopy (EDS) analysis. EDS data confirmed the presence of C, N, Cu, S, and I in the polymer structure.

3.1.3 FT-IR Spectra of Complexes

Copper complexes show weak bands in the FT-IR spectra in the low-frequency region, generally attributed to 400–500 cm^{-1}, ν(Cu-N).[20]

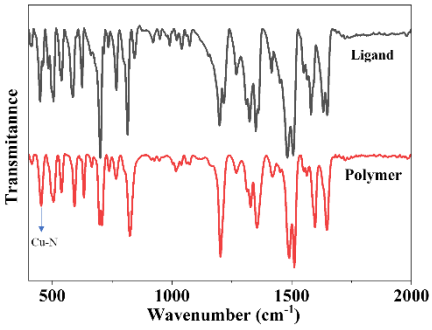


Figure 32: FT-IR data of CP1

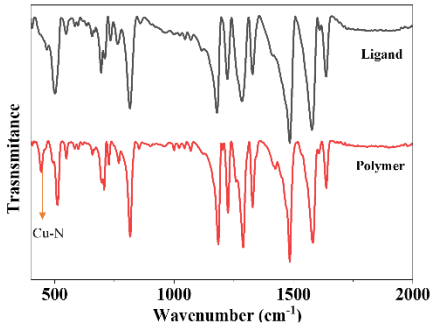


Figure 33: FT-IR data of CP2

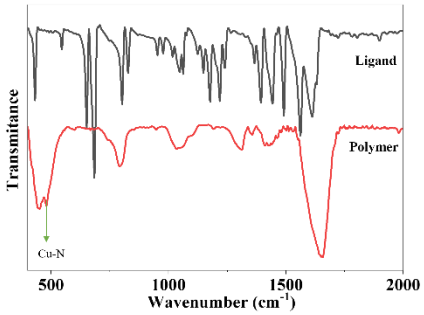


Figure 34: FT-IR data of CP3

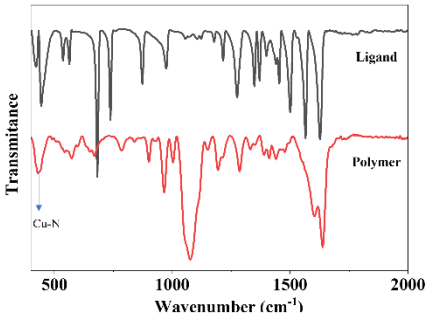


Figure 35: FT-IR data of CP4

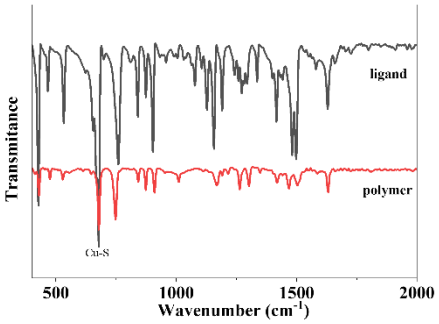


Figure 36: FT-IR data of CP5

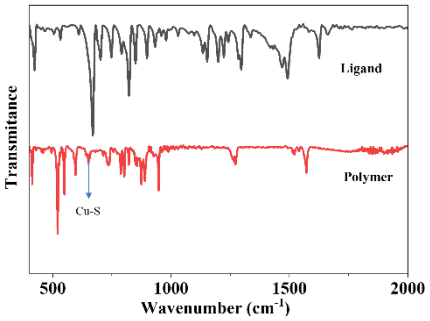


Figure 37: FT-IR data of CP6

Chapter 4: CONCLUSIONS

To conclude, we synthesized and characterized five N- and S-donor ionic ligands. Further, these ligands were analyzed by mass spectrometry and NMR spectroscopy. All synthesized ligands were treated with CuI salt, out of which only the CP3 crystal was obtained, which was further characterized by SC-XRD, and a very unique structure was obtained from the previously reported structure. The structure obtained was a 1D polymer containing $Cu_2I_3^-$ SBU, which was also characterized by PXRD, TGA, FESEM, and EDS analysis. In addition, these ligands were treated with CuI and triphenylphosphine under suitable reaction conditions, yielding phosphine-Cu (I) complexes.

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