Synthesis and photophysical properties of Cu(I) complexes with bulky phosphine ligands

M.Sc. Thesis

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Synthesis and photophysical properties of Cu(I) complexes with bulky phosphine ligands

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Submitted in partial fulfillment of the requirement for the award of the degree

of

Master of Science

by

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DEPARTMENT OF CHEMISTRY INDIAN INSTITUTE OF TECHNOLOGY INDORE

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INDIAN INSTITUTE OF TECHNOLOGY INDORE <u>CANDIDATE'S DECLARATION</u>

I hereby certify that the work which is being presented in the thesis entitled **Synthesis and photophysical properties of Cu(I) complexes with bulky phosphine ligands,** 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 July 2023 to May 2024 under the supervision of **Dr. Abhinav Raghuvanshi,** Department of Chemistry, Indian Institute of Technology 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

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

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ABSTRACT

Luminescent materials are in high demand due to their wide-ranging various fields such OLEDs. applications across as LECs. photosensitizers in dye-sensitized solar cells, memory devices, anti-theft devices, and more. Cu(I) metal complexes offer a promising alternative for luminescent materials due to their high abundance, which impacts material cost, as well as their high luminescence efficiency and comparatively easy synthesis. This work aim is to synthesised cost effective and highly emissive material by using Cu(I) metal and nitrogen and phosphorous donor organic ligands. For that two-nitrogen donor organic ligands 9-(pyrimidin-5-yl)-9H-carbazole (L1) and 2-(pyridin-4yl) isoindoline-1,3-dione (L2) were synthesised. Then By the reaction between CuI metal and ligand (L1, L2) by varying metal ligand ration and different solvent condition we got four new 1D and 2D coordination polymers [Cu₄I₄(5-CzPm)(CH₃CN)₂] (CP1), [Cu₂I₂(5-CzPm)] (CP2), $[Cu_4I_4(5-CzPm)]$ (CP3), and (Cu₂I₂(2-Py.isoindoline)] (CP4) furthermore, bulky phosphine ligands (PPh₃, POP) were incorporated and explore the photophysical properties of the resulting coordination polymers/complexes. It is postulated that the incorporation of bulky phosphines will reduce distortions in the excited state and reduce nonradiative transitions, thereby yielding materials with enhanced quantum efficiency. Additionally, this work delved into the mechanochromism and thermochromism luminescent properties of these coordination polymers.

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5-CzPm	9-(pyrimidin-5-yl)-9H-carbazole
2-Pm. isoindoline	2-(pyridin-4-yl) isoindoline-1,3-dione
СР	Coordination polymer
C	Complex
CC	Cluster cantered
CDCl ₃	Chloroform-d
CHCl ₃	Chloroform
DCM	Dichloromethane
DMSO	Dimethyl sulfoxide
K_2CO_3	Potassium carbonate
LCMS	Liquid chromatography-mass spectrometry
МеОН	Methanol
NMR	Nuclear magnetic resonance
OLED	Organic light-emitting diode
POP	bis[2-(diphenylphosphino)phenyl] ether
PPh3	Triphenylphosphine
PXRD	Powder X-ray diffraction
SPhos	Dicyclohexyl(2',6'-dimethoxy-[1,1'-biphenyl]-2-yl)phosphane
TGA	Thermogravimetric analysis
TLC	Thin layer chromatography
UV	Ultra-violet
UV-Vis	Ultra-violet and visible
Х	Halide
TADF	Thermally activated delayed fluorescence
(M+X)LCT	Metal-halogen to ligand charge transfer
MC	Metal centre
CC	Cluster cantered
XMCT	Halide-to-metal charge-transfer
XLCT	Halide-to-ligand charge-transfer
MLCT	Metal-to-ligand charge-transfer
$^{13}C{^{1}H}$	Proton decoupled ¹³ C NMR

NOMENCLATURE

°C	Degree Celsius		
h	hour		
mL	Millilitre		
mg	Milligrams		
MHz	megahertz		
mmol	millimole		
nm	Nanometer		

CHAPTER 1

1.1 Objective

Highly luminescent materials are in great demand because of their use in various fields like light-emitting diodes, light electrochemical cells, anti-theft devices, etc. our main objective is to synthesize high luminescence coordination complex based on CuI with electron-rich nitrogen-containing ligands. The tunability of photoluminescent properties will be checked by varying metal ligand ration and by changing solvent conditions. However, these tetra-coordinated complexes/coordination polymers often suffer Jahn-Teller distortions in the excited state. To minimise the JTD we incorporate bulky phosphine ligand as an ancillary ligand. Such bulky groups are known to reduce the distortions and consequently help in to increase the overall photoluminescence yields.

1.2 Introduction

Several advancements are taking place in the field of synthesis of luminescence coordination compounds due to their interesting photophysical properties. In the beginning, luminescence compounds heavily relied on rare earth elements (REEs) like platinum (Pt), europium (Eu), and terbium (Tb), etc.¹⁻⁶ However, due to concerns regarding their limited availability, environmental impact, and low quantum efficiency, the research focus has shifted toward developing rare-earth elements free (REEs- free) luminescent materials.⁷ This transition underscores the importance of developing alternative materials that are not only more abundant but also possess improved luminescence properties. Luminescent complexes based upon CuX (where X= I, Br) are in high demand because of their exceptional photophysical properties due to no self-quenching in the excited state. Cu(I) complexes are commonly employed in various applications, including conversion solar energy systems, sensing. and electroluminescence devices like OLEDs and LECs etc.^{8–10} Especially, the emission wavelength of CuI based complexes can be tuned that can

cover the entire visible and IR range. This can be done by tuning the HOMO-LUMO gap by changing the inorganic framework (Cu_xI_y) or varying organic ligands.^{11–13}

Cu(I)-based metal complexes offer exceptional structural diversity, resulting in a wide range of accessible inorganic modules and organic ligands, as well as various coordination modes between CuI-based hybrids. These inorganic modules can have monomeric, dimeric, trimeric, or polymeric secondary building units (SBUs) leading to exceptional photophysical properties.⁷



Figure-1.1 Types of secondary building units in Cu(I) complexes. (taken from reference no.-7)

CuI-based organic-inorganic complexes have several excited state transitions that contribute to their luminescence. Inorganic-organic hybrid compounds typically emit fluorescence, phosphorescence, or TADF (thermally activated delayed fluorescence) from excited state MLCT, XLCT, and ³(M+X) LCT. Furthermore, if the Cu-Cu distance is less than 2.8Å (the total of the van der Wall radii), it can produce triplet clustered centered emission (3CC).^{14,15} The luminescence of the CuI complexes can also be affected by various stimuli such as temperature, mechanic force, and organic volatiles; the properties associated with these are known as thermochromism, vapochromism, and mechanochromism, respectively.

Thermochromism:

Thermochromism is a phenomenon where a substance undergoes a reversible change in color in response to variations in temperature. This means that the color of the substance shifts with temperature changes, and this alteration is often reversible when the temperature returns to its original state.¹⁶⁻¹⁹ For example, Hardt et al.,²⁰ demonstrated how temperature affects the way [CuI(py)]₄ emits light, in its state. They discovered that the emission color changes from blue to yellow when the temperature rises to room temperature from 77 K. The color change is due to changes in the intensity of two types of emissions. The first emission at 450 nm is a high energy (HE) emission caused by halide-tometal charge transfer (XMCT) and copper-centered $d \rightarrow s$, p transitions in ligand-containing systems. The second is a low energy (LE) emission in clusters with Cu---Cu distances smaller than 2.8 Å at room temperature, which appears as a yellow light at 600 nm. Both experimental data and density functional theory (DFT) calculations support the assumption that at room temperature luminescence largely emerges from the LE band, which originates from a [Cu₄I₄] clustercentered triplet excited state, regardless of the ligand characteristics. However, at lower temperatures, the LE band decreases dramatically, and the HE emission takes over due to a condition known as halidepyridine ligand charge transfer (XLCT). It is important to note that this XLCT band only manifests itself in clusters with ligands because it involves π^* orbitals of those ligands. Moreover, as the temperature decreases the LE band, in [CuI(py)]₄ experiences a shift, towards a higher wavelength. Specifically, it transitions from 580 nm at 298 K to 619 nm at 77 K. This fascinating phenomenon is directly linked to the Cu---Cu distances found within the cluster core of [Cu₄I₄].



Figure-1.2 Complex show thermochromism. (taken from reference no-20)

Mechanochromism:

Mechanochromism refers to the phenomenon where a material changes color in response to a mechanical stimulus. Mechanochromic Cu(I) complexes have attracted attention for their potential applications in mechanosensitive materials, sensors, and optoelectronic devices, where their color-changing behaviour can be utilized for various functional purposes like motion sensing devices, damage detector devices, memory devices and more.^{21–25} By subjecting specific complexes to mechanical forces via processes such as mechanical grinding, ball kneading, and ball milling, alterations in photophysical properties can be induced. These changes arise from modifications in structure, Van der Waals interactions, or variations in bond lengths, influencing the energy gap between the highest occupied molecular orbital (HOMO) and lowest unoccupied molecular orbitals (LUMO).

In the recent work done by Gangfeng Ouyang and co-works,²⁶ they study of the detailed structural changes after and before grinding by SC-XRD of their CuI(dmpz) polymer. After grinding the of 1D CuI(dmpz), the half ligand (dmpz) was detached and complex was converted in to new 2D CuI(dmpz) polymer. The structural changes lead to decrease the Cu---Cu distance because of that red shift in emission is observed.



Figure-1.3 (a) Crystal structure of CuI(dmpz) (b) Structure of CuI(dmpz)_{0.5} (c) Emission spectra of CuI(dmpz) and CuI(dmpz)_{0.5} (d) structure change after grinding from CuI(dmpz) greenish yellow to CuI(dmpz)_{0.5} orange red. (taken from reference no-26)

Recently, Sandrine Perruchas and coworkers²⁷ developed an energy diagram based on DFT calculations to describe the mechanism of the mechanochromism process, their $[Cu_4I_4(PPh_3)_4]$ complex show mechanochromism luminescence they concluded on the basis of DFT calculation, The HOMO is mostly made up of 3d and 5P orbitals of copper and iodide in the Cu₄I₄ core, and there are two types of LUMO: one that is localized on the ligand (primarily the π^* orbital of the phenyl ring) and another that has a high energy due to strong copper-copper interactions. Due to shortening in Cu---Cu distance after grinding leads to stabilized the energy of LUMO. The change in the energy level leads to higher wavelength emission after applying mechanical force.



Figure 1.4 Crystal structure at different pressure

(taken from reference no-27)



Figure 1.5 (a) Energy diagram to understand mechanochromic mechanism (b) Excitation and emission spectra of Complex 1b and 1a initially and after grinding (taken from reference no-27)

Based on these literature reviews, the primary goal of our research is to maximize photoluminescence efficiency via the TADF mechanism. To attain high quantum efficiency at ambient temperature in CuI complexes, The energy difference between the singlet (S1) and triplet (T1) for TADF emission should be less, between 0.5 and 1.0 eV. To achieve this, we create the organic ligand in a way that keeps the small energy gap (ΔE_{ST}) intact. It improves the reverse intersystem crossing from T1 to S1.^{28–36}

1.3 Scope of the work

- Our present research focuses on Cu(I) coordination complexes and polymers. Cu(I) coordination complexes have unique photoluminescence characteristics that make them useful for a variety of optoelectronic applications.
- Furthermore, they demonstrate interesting features like thermochromism, and mechanochromism dependent luminescence, which can also increase their use in practical applications.
- Cu(I) coordination complexes have a wide range of uses, including the creation of energy-storage technologies like supercapacitors and batteries.
- Additionally, these complexes are instrumental in sensing volatile organic compounds.



Figure-1.6 Applications of Cu(I) complex



Figure 1.7 Application of mechanochromism

CHAPTER-2

EXPERIMENTAL SECTION

2.1 MATERIALS AND INSTRUMENTATION

No additional purification was required for any of the compounds. Every reaction was carried out in a nitrogen atmosphere because of their sensitivity to oxygen or moisture. Using Merck 60 F254 pre-coated silica gel plates (0.25 mm thick), the reactions' progress was tracked using TLC, and the products were visible when exposed to UV light. A Bruker 400/500 spectrometer was used to record all ¹H, ¹³C{¹H}, and ³¹P{¹H} NMR spectra in CDCl₃ and DMSO-d6 at 400/500 MHz. Proton chemical shifts are expressed in delta (δ) units and reported in parts per million (ppm) in relation to tetramethyl silane (TMS). The internal standard was CDCl₃ and DMSO-d6, which peaks at 7.26 and 2.50 ppm. Mestre Nova was used to process the NMR data for the singlet (s), doublet (d), triplet (t), and multiplet (m) ¹H NMR splitting patterns.2.2

2.2. Synthesis of Ligands

2.2.1 Synthesis of 9-(pyrimidin-5-yl)-9H-carbazole / 5-CzPm (L1)



Scheme-1. Synthesis of ligand L1

5-Br.	Carbazole	CuI	1,10-	Base	Yield
pyrimidine			phenanthroline		
1	1	0.16	0.32	$K_2CO_3(2.5)$	13%
1	1	0.16	0.32	$Cs_2CO_3(2.5)$	15%
1	1	0.16	0.32	KOH (2.5)	14%
1.3	1	0.16	0.32	$K_2CO_3(5)$	35%
1.3	1	0.16	0.32	K ₂ CO ₃ (10)	82%

Table 1. Optimization table for ligand L1

Carbazole (2 g, 11.96 mmol) and K₂CO₃ (16.5 g, 119.61 mmol) were mixed in a two-neck round bottom flask with 15-20 mL of DMF solvent. The mixture was stirred at 145 °C for 30 minutes. Following that, 5-bromo pyrimidine (2.4g, 15.54 mmol), CuI (0.36g, 1.91 mmol), and 1,10-phenanthroline (0.75g, 3.82 mmol) were added, and the solution was constantly stirred for 72 hours at 140 °C. After the completion of the reaction, the solvent (DMF) was extracted under vacuum, followed by extraction with cold brine solution and EtOAc. The resultant solution was then dried using anhydrous sodium sulfate. The solvent was then evaporated using a rotary evaporator, and the crude product was purified using silica gel column chromatography with a solvent gradient ranging from 0.5% ethyl acetate/hexane. This process yielded a yellow solid product with an 82% yield.

¹H NMR (500 MHz, CDCl₃) δ 9.33 (s, 1H), 9.05 (s, 2H), 8.16 (d, *J* = 7.8 Hz, 2H), 7.46 (dd, *J* = 8.6, 6.8 Hz, 2H), 7.39 – 7.33 (m, 4H). ¹³C{¹H} NMR (126 MHz, CDCl₃) δ 157.07, 155.29, 140.28, 133.77, 126.73, 124.18, 121.39, 120.87, 109.05.

2.2.2 Synthesis of 2-(pyridin-4-yl) isoindoline-1,3-dione / 2-Py. isoindoline (L2)



Scheme-2. Synthesis of L2

In a two-neck round bottom flask, phthalic anhydride (3.37 mmol, 500 mg) and 4-aminopyridine (4.05 mmol, 382 mg) were dissolved in 15 mL of DMF. The resultant reaction mixture was agitated under nitrogen conditions at 140 °C for 48 hours. The reaction was monitored using thin-layer chromatography (TLC) with a solvent mixture of 1:9 hexaneethyl acetate. After completion, the reaction solvent (DMF) was evaporated under vacuum. Upon solvent evaporation, a white solid was produced, which was further purified using ethanol washing and crystallized in DMF solvent to yield a pure product. The product's production was confirmed by LCMS and NMR. LCMS m/z calculated $C_{13}H_9N_2O_2$ [M+H+CH₃OH] + 257.0921 found 257.0917.

. ¹H NMR (500 MHz, CDCl₃) δ 8.76 (s, 2H), 7.99 (dd, J = 5.6, 3.1 Hz, 2H), 7.83 (dd, J = 5.6, 3.0 Hz, 2H), 7.61 (d, J = 5.6 Hz, 2H). ¹³C{¹H} NMR (126 MHz, CDCl₃) δ 166.42, 150.94, 139.77, 135.09, 131.51, 124.27, 119.60.

2.3 Synthesis of Coordination polymers/ complexes

2.3.1 Synthesis of CP1



Scheme-3. Synthesis of CP1

In a test tube, dissolve copper iodide (16 mg, 0.08 mmol) in 3-4 mL of acetonitrile solvent. Following that, an acetonitrile solution of 5-CzPm (20 mg, 0.08 mmol) was added to the copper iodide solution at room temperature. Immediately, a light green precipitate formed. The resulting reaction mixture was stirred for 12 hours. Filtered and washed with dichloromethane (DCM) and acetonitrile (ACN) solvents to remove unreacted reactants.

2.3.2 Synthesis of CP2



Scheme-4. Synthesis of CP2.

Copper iodide (94 mg, 0.48 mmol) was dissolved in 3-4 mL of acetonitrile solvent in a test tube. Subsequently, an acetonitrile solution of 5-CzPm (20 mg, 0.08 mmol) was added to the copper iodide solution at room temperature. Instantly, a yellow precipitate appeared. The resulting reaction mixture was stirred for 12h, then filtered and washed with dichloromethane (DCM) and acetonitrile (ACN) solvents to remove unreacted reactants.

2.3.3 Synthesis of CP3



Scheme-5. Synthesis of CP3

Copper iodide (62 mg, 0.32 mmol) was dissolved in 3-4 mL of acetonitrile in a test tube. 5-CzPm (20 mg, 0.08 mmol) was dissolved in DCM solvent and mixed with the copper iodide solution at room temperature. Immediately, a yellow precipitate appeared. After a 12-hour stirring period, the reaction mixture was filtered and washed with solvents such as acetonitrile (ACN) and dichloromethane (DCM) to eliminate any unreacted reactants.

2.3.4 Synthesis of CP4



Schem-6. Synthesis of CP4

In a test tube, dissolve the CuI (0.089 mmol, 17mg) in ACN, then add the acetonitrile solution of 2-Py. isoindoline (0.089 mmol, 20mg). An orange precipitate appears instantly. The reaction is allowed to run for 12 hours at room temperature. After completion, the precipitate is filtered and washed with DCM and ACN 2-3 times to obtain the final pure product.

2.4 General Synthesis of Complexes C-1,2,3 and C-4

To the synthesis of Complex 1-4 the general procedure was followed in which in the MeOH + CHCl₃ (1:2) solvent, PPh₃ was dissolved then added CuX (where X= I, Br) and stirred the resulting reaction mixture for 30 min then Ligand (L1/L2) was added and continue the rection for 12h. The PPT was obtained washed it with 2-3 times by methanol to obtained final pure product

2.4.1 Complex-1 (C-1) Synthesis



Scheme-7. Complex-1(C-1) synthesis

In a Schlenk tube dissolved PPh₃ (0.163 mmol, 42.71 mg) in (5ml) CH₃OH + CHCl₃ (1:2) solvent then added CuI (0.081 mmol, 15.42 mg) solid and stirred the resultant mixture for 30 minutes, then the clear solution was obtained. Then added 9-(pyrimidine-5-yl)-9H-carbazole (0.081 mmol, 20mg) proceeded the reaction for 24h. the yellow colour ppt. was formed, and after completion, the precipitate was isolated through filtration and washed with 2-3 times MeOH to obtain the final pure product. ¹H NMR (500 MHz, CDCl₃) δ 9.35 (s, 1H), 9.08 (s, 2H), 8.16 (d, *J* = 7.9 Hz, 2H), 7.59 – 7.28 (m, 36H). ¹³C{¹H} NMR (126 MHz, CDCl₃) δ 157.03, 155.35, 134.44, 134.34, 129.70, 128.55, 128.47, 126.82, 121.47, 120.87, 109.13.

2.4.2 Complex-2 (C-2) synthesis



Scheme-8. Complex-2 (C-2) synthesis of

In a Schlenk tube, dissolve PPh₃ (0.165 mmol, 43 mg) in 5ml of CHCl₃+ MeOH (2:1) solvent, then add CuBr (0.082 mmol, 12 mg) solid and stir for 30 minutes until you get a clear solution. The reaction was then continued for 24 hours with the addition of 5-CzPm (L1) (0.082 mmol, 20 mg). The light-yellow ppt was generated, and after completion, the precipitate was separated via filtration and washed with 2-3 times MeOH to achieve the final pure product. ¹H NMR (500 MHz, DMSO- d₆) δ 9.41 (s, 1H), 9.27 (s, 2H), 8.28 (d, J = 7.6 Hz, 2H), 7.66 – 7.25 (m, 12H). ¹³C{¹H} NMR (126 MHz, DMSO-d₆) δ 156.99, 155.36, 139.92, 133.51, 129.92, 128.62, 126.61, 123.16, 120.86, 120.63, 109.49. ³¹P{¹H} NMR (202 MHz, DMSO-d₆) δ -6.07.

2.4.3 Complex-3 (C-3) synthesis



Scheme-9. Synthesis of complex-3 and possible structure

In a Schlenk tube, dissolve PPh₃ (0.178 mmol, 47 mg) in 5ml of CHCl₃+ MeOH (2:1) solvent, then add CuI (0.089 mmol, 17 mg) solid and stir for 30 minutes. 2-Py. isoindoline (0.089 mmol, 20mg) was added, and the reaction was continued for 24 hours. After that, a clear solution was produced, concentrated, and ether was added, and the precipitate was washed 2-3 times with MeOH before being dried under vacuum to provide the pure product. ¹H NMR (500 MHz, DMSO-d₆) δ 8.00 (d, *J* = 3.1 Hz, 2H), 7.94 (d, *J* = 3.1 Hz, 2H), 7.41 (dt, *J* = 25.0, 7.3 Hz, 19H). ¹³C{¹H} NMR (126 MHz, DMSO-d₆) δ 166.04, 135.05, 133.57, 133.45, 132.90, 132.66, 131.35, 129.99, 128.66, 128.58, 123.71. ³¹P{¹H} NMR (202 MHz, DMSO-d₆) δ -7.06.

2.4.4 Complex-4 (C-4) synthesis



Scheme-10. Complex-4 (C-4) Synthesis and possible structure

In a Schlenk tube, dissolve PPh₃ (0.44 mmol, 116 mg) in 10 mL of CHCl₃+ MeOH (2:1) solvent, then add CuBr (0.223 mmol, 32 mg) solid and stir for 30 minutes to create a clear solution. After adding 2-Py. isoindoline (0.223 mmol, 50 mg) and continuing the reaction for 24 hours, a clear solution was obtained. then concentrated it and added ether, to get PPT, once we had a PPT then rinsed it twice with MeOH and dried it under vacuum to obtain the pure product. ¹H NMR (500 MHz, DMSO-d₆) δ 9.41 (s, 2H), 9.27 (s, 3H), 8.28 (d, *J* = 7.6 Hz, 4H), 7.65 – 7.30 (m, 21H). ¹³C{¹H} NMR (126 MHz, DMSO-d₆) δ 156.99, 155.36, 139.92, 133.51, 129.92, 128.62, 126.61, 123.16, 120.86, 120.63, 109.49. ³¹P{¹H} NMR (202 MHz, DMSO-d₆) δ -6.07.

2.5 General synthesis Coordination polymer-5(CP5) and complex-6

A clear DCM solution of $[Cu(CH_3CN)_4]PF_6$ and bulky phosphine (SPhos, Bis[(2-diphenylphosphine)phenyl] ether) was stirred at r.t under nitrogen condition for 30 min. then added Ligand (L1/L2). After 3days the resulting clear solution was concentrated and add hexane to get PPT, washed it 2-3 times with ether to get pure product.

2.5.1 Synthesis of CP5



Scheme-11. Synthesis and possible structure of CP5

In a Schlenk tube with a magnetic bead, dissolve $[Cu(CH_3CN)_4PF_6]$ (45mg, 0.12 mmol) and Bis[(2-diphenylphosphine)phenyl] ether (72.06 mg, 0.13 mmol) in DCM solvent under nitrogen atmosphere. Stir the resulting reaction mixture for 30 minutes, then add 5-CzPm (30 mg, 0.13 mmol), continue the reaction for 72h, then concentrate it and add hexane. We obtained yellow-colored PPT and washed it with ether twice or three times to remove unreacted reactants.

2.5.2 Synthesis of Complex-6 (C-6)



Scheme-12. Synthesis of complex-6 (C-6)

In a Schlenk tube with a magnetic bead, dissolve $[Cu(CH_3CN)_4PF_6]$ (45mg, 0.12 mmol) and Bis[(2-diphenylphosphine)phenyl] ether (72.06 mg, 0.13 mmol) in DCM solvent under nitrogen atmosphere. Stir the

resulting reaction mixture for 30 minutes before adding 5-CzPm (30 mg, 0.13 mmol). Continue the process for 72h, then concentrate it and add hexane to get PPT, once we had PPT then washed it with ether to remove unreacted reactants. ¹H NMR (500 MHz, DMSO-d₆) δ 8.31 (s, 1H), 8.01 (dd, *J* = 5.5, 3.1 Hz, 7H), 7.94 (d, *J* = 5.5 Hz, 8H), 7.66 (s, 6H), 7.50 – 7.39 (m, 46H), 7.32 (dd, *J* = 21.4, 6.8 Hz, 39H), 7.09 – 7.01 (m, 15H), 6.65 (d, *J* = 8.1 Hz, 8H), 5.75 (s, 3H).¹³C{¹H} NMR (126 MHz, DMSO-d₆) δ 166.15, 157.40, 150.57, 135.09, 133.73, 133.33, 132.02, 131.38, 131.08, 130.30, 128.95, 124.93, 123.75, 120.25, 79.17, 54.91. ³¹P{¹H} NMR (202 MHz, DMSO-d₆) δ -18.86, -144.12.

CHAPTER 3

RESULT AND DISCUSSION

3.1 CHARACTERISATION OF LIGANDS

3.1.1 Characterization of ligand L1

The reaction between 4-bromopyrimidine and carbazole leads to give ligand L1 with 82% yield. The ligand was characterized using ¹H and ${}^{13}C{}^{1}H$ NMR. In proton NMR two singlet peaks at 9.33 and 9.05 ppm corresponding to one and two protons respectively confirm the presence of the pyrimidine unit, whereas one doublet and one doublet of a doublet at 7.46 and 6.8 of two protons and one multiplate of 4-proton in the range of 7.39-7.33 ppm confirming the carbazole unit. Also, in ${}^{13}C{}^{1}H$ NMR 9 peaks appear corresponding to 9 different carbon atoms present in ligand L1 confirming the formation of ligand L1.



Figure 3.1. ¹H NMR of 5-CzPm (L1)



Figure-3.2. ¹³C{¹H} NMR of 5-CzPm (L1)

3.1.2 Characterization of ligand L2

Ligand L2 was synthesized by a previously reported method, in which the phthalic anhydride and 4-aminopyridine reacted in DMF solvent at 140 °C leads to ligand L2 with 73% yield. The ligand L2 was characterized by the help of mass spectrometry and ¹H and ¹³C{¹H} NMR spectroscopy. The LCMS and NMR data exactly match with previously reported literature.



Figure-3.3. Mass spectrogram of 2-Py. isoindoline (L2)



Figure-3.4. ¹H NMR of 2- Pm. isoindoline (L2)



Figure-3.5. ¹³C{¹H} NMR spectrum of 2-Py. isoindoline (L2)

3.2 CHARACTERIZATION OF COORDINATION POLYMERS AND COMPLEXES

3.2.1 Characterization of CP1, CP2, CP3 and CP4

The stretching frequencies of C–N and C–C bonds of ligands L1 and L2 appears in the range of 1200-1600 cm⁻¹. Upon compression the IR spectra of free ligand to the considerable shift in the corresponding peaks from the free ligand indicates that the ligand coordinated with the metal center. Additionally in the IR spectra of CP2 absorbtion peak appear at 2270 cm⁻¹ corresponding stretching frequency of C-N triple bond of the acetonitrile molecule which is attached with the copper metal. By comparing the PXRD pattern to the simulated pattern generated from single-crystal X-ray diffraction (SC-XRD), the bulk identification of the material was confirmed.



Figure-3.6. CPs and the ligand IR spectra comparison.



Figure-3.7. Comparison of Simulated pattern of CPs with PXRD pattern

3.2.2 Characterization of Complexes C-1, C-2, C-3 and C-4

Complex-1 and complex-2 Using the general synthesis procedure, PPh₃, CuX (where X= I, Br), and ligand L1 were reacted in MeOH: CHCl₃ (1:1) for 2 days give complex-1 and complex-2, the complex was characterized by ¹H, ¹³C{¹H} and ³¹P{¹H} NMR. The NMR data confirm the presence of one 5-CzPm ligand and two PPh₃ molecules in the complex-1 and one ligand and one PPh3 in complex-2. However, predicting the possible structure remains challenging due to the utilization of the bidentate 5-CzPm ligand, which may result in the formation of a polymeric structure. To address this uncertainty, I am currently working to grow appropriate crystals for detailed structural analysis.



Figure-3.8. ¹H NMR of complex-1 (C-1)



Figure 3.9. ${}^{13}C{}^{1}H$ NMR of complex-1 (C-1)



Figure-3.10. ¹H NMR of complex-2 (C-2)



Figure-3.11. ¹³C{¹H} NMR of complex-2 (C-2)



AR-AK-117.6.1.1r

Figure-3.12. ³¹P{¹H} NMR of complex-2 (C-2)

Complex-3 and Complex-4: Using the general synthesis procedure, PPh₃, CuX (where X = I, Br), and ligand L2 were reacted in MeOH + CHCl₃ (1:1) for 2 days give complex-3 and complex-4, the NMR data of complex-3 confirm the presence of one 2-py. isoindoline ligand and one PPh₃, which indicates that the complex may contain one Cu₂I₂ unit. At which each copper is connected with one 2-Py. isoindoline ligand and one PPh₃. And two μ -2 iodides. While in the complex-4 The ${}^{1}H, {}^{13}C{}^{1}H$, and ${}^{31}P{}^{1}H$ NMR confirm the formation of the mononuclear complex in which copper is coordinated with two 2-Py. isoindoline ligand, one PPh3 and one bromide. Based on the NMR data the expected structure of complex-3 and complex-4 were proposed.



Figure-3.13. ¹H NMR of complex-3 (C-3)



Figure-3.14. ${}^{13}C{}^{1}H$ NMR of complex-3 (C-3)



Figure-3.15. ${}^{31}P{}^{1}H$ NMR of complex-3 (C-3)



Figure-3.16. ¹H NMR of complex-4 (C-4)



150 130 110 90 70 50 30 10 -10 -30 -50 -70 -90 -110 -130 -150 -170 -190 -210 -230 -25 fl(ppm)

Figure-3.18. ³¹P{¹H} NMR of complex-4 (C-4)

3.2.3 Characterization of CP5 and complex-6

One ligand and one Bis[(2-diphenylphosphine) phenyl] ether phosphine ligans are confirmed to be present in the complex by the NMR data of CP5. Based on this data the possible polymeric structure of CP5 was predicted. On the basis of NMR data of the complex-6, we are unable to predict the possible structure but to address this uncertainty, I am

currently working to grow appropriate crystals for detailed structural analysis.



Figure-3.20. $^{13}C{^{1}H}$ NMR of CP5



Figure-3.22.¹H NMR of complex-6 (C-6)

AR-AK-131.2.1.1r



210 200 190 180 170 160 150 140 130 120 110 100 90 80 70 60 50 40 30 20 10 0 -10 -; f1(ppm)

Figure-3.23. $^{13}C{^{1}H}$ NMR of complex-6 (C-6)



Figure-3.24. ${}^{31}P{}^{1}H$ NMR of complex-6 (C-6)

3.3 Crystal Structures of CPs

3.3.1 Crystal structure of CP1

The crystal structure of CP1 was determined using the SC-XRD method, and suitable crystals for X-ray analysis were grown by the slow evaporation of the saturated acetonitrile solution of CP1. The crystal structure reveals the formation of a 1D chain coordination polymer containing a Cu₂I₂ single chain as a secondary building unit (SBU). The asymmetric unit comprises one copper, one iodide, and one 5-CzPm ligand. The copper metal adopts a distorted tetrahedral geometry, connected to one nitrogen of the 5-CzPm ligand and µ₃-I. The Cu-Cu distance measures 2.713 Å, which is less than the sum of Van der Waals radii (i.e., 2.8 Å). Additionally, two types of interactions are observed in the coordination polymer. The first is a C-H--- π (2.821n Å) intramolecular interaction between the carbazole carbon of the 5-CzPm ligand and hydrogen of the pyrimidine ring of the 5-CzPm ligand. The second is an intermolecular N-H (2.671 Å) interaction between the uncoordinated pyrimidine nitrogen of the 5-CzPm ligand and the hydrogen of another pyrimidine ring of the 5-CbPm ligand.



Figure-3.25. Asymmetric unit of CP1



Figure-3.26. Crystal structure of CP1 showing Cu₂I₂ polymeric chain



Figure-3.27. Important bond length (Å) and bond angles (°) between copper and iodide atoms of CP1.



Figure-3.28. Crystal arrangement of CP1 showing N-H---C and C-H-- π interaction

3.3.2 Crystal structure of CP2

For SC-XRD examination, the saturated acetonitrile solution of CP2 slowly evaporated to grow an appropriate crystal. The creation of a 1Ddouble zig-zag chain-like structure, in which the 5-CzPm ligand acts as a bridging ligand between two zig-zag chains, is revealed by SCXRD investigations. CP2 formed in the triclinic P-1 space group, with the asymmetric unit containing four copper, four iodide, two acetonitrile, and one 5-Cz.Pm ligand. Interestingly, the acetonitrile solvent used for synthesis of CP2 is found coordinated with the copper metal. Because of the solvent coordination, two different types of arrangements are present around the copper center. In the first arrangement, the copper is coordinated to three iodides present in a μ -3 binding mode and one nitrogen of the pyrimidine ring of the 5-CzPm bidentate ligand. On the other hand, copper is attached to acetonitrile's nitrogen and three μ -3 iodides in another arrangement. In both configurations, the copper attains distorted tetrahedral geometry. The Cu---Cu distances in the CuI zig-zag chain of CP2 were different, the alternative Cu---Cu distances are 2.615, 3.304, 2.787, and 2.920 Å, this suggests that CP2 has a cuprophilic interaction, meaning that the Cu---Cu distance is smaller than the total of the Van der Waal radii (i.e., less than 2.8 Å). Furthermore, in CP2 two kinds of intermolecular π - π interactions appear between the two 5-CzPm ligands, which are connected by two separate CuI zig-zag chains. The first intermolecular π --- π interaction occurs between two different carbazole rings of the two 5-CzPm ligands. Both 5-CzPm ligands are coordinated with different CuI zig-zag chains, and the interaction distance is 3.381 Å. Additionally, there is a second π --- π interaction between the carbazole ring and the pyrimidine ring of the 5-CzPm ligand, with a distance of 3.375 Å between them.



Figure-3.29. Asymmetric unit of CP2



Figure-3.30. (a) CuI-Zig-zag chain of CP2 (b) Crystal structure of CP2 showing CuI double zig-zag chain.



Figure-3.31. Crystal Image of CP2 showing bridging behaviour of 5-CzPm ligand

SSS



Figure-3.32. Important bond lengths between the atoms of CP2



Figure-3.33. Crystal structure of CP2 showing intermolecular π --- π interactions.



Figure-3.34. Crystal packing of CP2 showing intermolecular π --- π interactions.

3.3.3 Crystal structure of CP3

The layering method was utilized to grow the appropriate crystal for SC-XRD analysis. First, 5-CzPm ligand was dissolved in dichloromethane solvent and positioned at the base of the test tube. Subsequently, the second layer was formed above the initial layer, utilizing a mixture of acetonitrile and dichloromethane solvents in a 1:1 ratio. Finally, the third layer was formed over the first two layers, utilizing an acetonitrile solution of CuI. After a couple of days, yellow color square shape crystal was obtained. SC-XRD on CP3 reveals the formation of 2Dcoordination polymer with orthorhombic Ima2 space group and the asymmetric unit contained three copper, three iodide, two 5-CzPm. ligand. And CP3 is contained Cu₄I₄ cubane tetramer secondary building unit. Interestingly, where in the CP2 the acetonitrile solvent is found to coordinate with the copper while in CP3 case the DCM solvent is found trapped in the vacant space of the crystal lattice.



Figure-3.35. Asymmetric unit of CP3



Figure 3.36 Important bond distances in CP3



Figure-3.37. Crystal structure of CP3

3.3.4 Crystal structure of CP4

The layering method was utilized to grow the appropriate crystal for SC-XRD analysis. First, 2-Py. isoindoline was dissolved in dichloromethane solvent and positioned at the base of the test tube. Subsequently, the second layer was formed above the initial layer, utilizing a mixture of ACN and DCM solvents in a 1:1 ratio. Finally, the third layer was formed over the first two layers, utilizing an acetonitrile solution of CuI. After a couple of days, crystals in the shape of yellow needles appeared. The crystal data show that CP4 crystallized in the monoclinic space group P21/c, with a 1D chain comprising a Cu₂I₂ double chain as a secondary building unit. The asymmetric unit contains one Cu, one iodide, and one 2-Py. isoindoline ligand. Each cooper adopts distorted tetrahedral geometry coordinated with one nitrogen od 2-Py. isoindoline

ligand and three μ_3 -bridging iodides. The polymer's Cu---Cu distance is 2.967 Å, larger than the total of the Van der Waal radii (2.80 Å), suggesting that there is no cuprophilic interaction. Additionally, there are two types of strong interaction present first in is the π --- π (3.200 Å) intramolecular interaction between carbon atoms of 5-membered rings of the two 2-Py. isoindoline ligand which are connected parallel to each other on the Cu₂I₂ double chain. Another interaction is present in between the oxygen atom of 2-Py. isoindoline ligand and carbon atom of another 5-membered ring of the 2-Py. isoindoline ligand and the distance of this intramolecular interaction is 3.200 and 3.107 Å.



Figure-3.38. Asymmetric unit of CP4



Figure-3.39. Crystal structure of CP4



Figure-3.40. Important bond lengths between atoms of CP4



Figure-3.41. Crystal image of CP4 showing inter and intramolecular interactions.

	CP1	CP2	CP3	CP4
Empirical formula	$C_{16}H_{11}CuIN_3$	$\begin{array}{ c c c c c c c c c c c c c c c c c c c$		C ₁₃ H ₈ CuIN ₂ O ₂
Formula weight	435.72	1089.15	2674.48	414.65
Temperature/K	298(2)	293(2)	197.00	197
Crystal system	monoclinic	Triclinic	Orthorhombic	Monoclinic
Space group	$P2_{1}/c$	P-1	Ima2	$P2_{1/c}$
a/Å	19.0792(4)	7.22420(10)	8.614(2)	15.0378(9)
b/Å	4.09690(10)	14.0153(2)	52.799(13)	4.2697(2)
c/Å	18.4704(4)	14.6303(3)	8.624(2)	20.1923(12)
α/°	90	111.341(2)	90	90
β/°	93.069(2)	92.351(2)	90	105.562(2)
γ/°	90	103.700(2)	90	90
Volume/Å ³	1441.68(6)	1327.17(4)	3922.3(18)	1248.43(12)
Ζ	4	2	2	4
$\rho_{calc}g/cm^3$	2.007	2.725	2.265	2.206
µ/mm ⁻¹	3.651	7.833	5.457	4.219
F(000)	840.0	1000.0	2504.0	792.0
Radiation	Μο Κα (λ=0.71073)	Μο Κα (λ=0.71073)	Μο Κα (λ=0.71073)	Μο Κα (λ=0.71073)
2θ range for data collection/°	4.276 to 54.74	3.476 to 54.984	4.628 to 55.8	7.544 to 56.588
Index ranges	$\begin{array}{l} -24 \leq h \leq 24, -5 \\ \leq k \leq 5, -23 \leq 1 \\ \leq 22 \end{array}$	$-9 \le h \le 9, -17 \le k \le 17, -18 \le 1 \le 18$	$-11 \le h \le 11, -69 \le k \le 69, -11 \le 11$	$-19 \le h \le 20, -5 \le k \le 5, -23 \le 1 \le 26$
Reflections collected	23597	31158	76766	7913
Independent reflections	$[R_{int} = 0.0406, R_{sigma} = 3149 \\ 0.0251]$	4917 [R _{int} = 0.1158, R _{sigma} = 0.0487]	$\begin{array}{l} 4978 \; [R_{int} = \\ 0.0731, \; R_{sigma} \\ = 0.0293] \end{array}$	2759 [$R_{int} =$ 0.0343, $R_{sigma} =$ 0.0372]
Goodness-of-fit on F ²	1.035	1.071	1.170	1.016
Final R indexes $[I \ge 2\sigma(I)]$	0.0275, 0.0644	0.0468, 0.1235	0.0390, 0.0889	0.0281, 0.0565
Final R indexes [all data]	0.0336, 0.0672	0.0563, 0.1316	0.0481, 0.0918	0.0441, 0.0624
Largest diff. peak/hole / e Å ⁻³	0.78/-0.57	1.28/-1.19	0.61/-0.65	0.49/-0.75

Table 2. Crystallographic Data for CP1, CP2, CP3 andCP4

3.4 Thermogravimetric analysis of CP1, CP2, CP3 and CP4

To evaluate the thermal stability. A thermogravimetric study was conducted with a temperature increase of 10 $^{\circ}$ C per minute and N₂ flow of 20 mL min⁻¹.

The TGA analysis reveals that weight loss of CP1 occurred in two different regions: 230-472 °C and 472-700 °C. The 5-CzPm ligand molecule in the CP1 crystal contributes to the first weight loss (52.59%) at 230-472 °C, suggesting that CP1 is stable up to 230 °C. The iodide molecule in the CP1 contributes for the second weight degradation (23.17%). While in the CP2 three weight degradation were observed first degradation is observed at 110 °C and the percentage of weight loss is approx. 4.3% which shows the dissociation of two acetonitrile molecules which coordinated to the Cu metal, the second decrement in weight % is observed at 243 °C corresponding to the complete dissociation of one ligand L1. The last weight degradation (38%) corresponds to the iodide molecule found in the CP2. Also in CP3 three weight degradation were observed first degradation is observed at 150 °C correspond to DCM solvent molecule which are trapped in crystal lattice. So according to TGA data CP1 CP2 CP3 and CP4 is stable up to 230, 110, 150, and 250 °C respectively.



Figure-3.42. TGA plots of CP1, CP2, CP3 and CP4

3.5 Photophysical Properties

3.5.1 Photophysical properties of CP1, CP2, CP3

The emission spectra of CP1, CP2, and CP3 in the solid state were measured at room temperature under excitation at $\lambda ex = 365$ nm, resulting in strong single-band emissions at 534nm, 500nm, and 532nm, respectively typically, luminescence in CuX-L complexes (where X represents a halogen and L a nitrogen donor ligand) is attributed to various charge transfer processes, MLCT, XLCT, ligand-to-ligand (LLCT), ligand-to-metal (LMCT), and by a unique case known as clustered centered emission (³CC), or the transition occurs within a CuI cluster and involves a combination of halide-to-metal (XMCT) and metal-cluster-centred (MCC) mechanisms. The MCC is caused by attraction interactions between the closed d-subshell d¹⁰ of the Cu atoms in the cluster, requiring Cu---Cu distances about or not much longer than 2.8 Å (Van der Waals radii of two copper atoms). To understand the origin of luminescence corresponding to these CPs, we compared the results of the emission spectra of these CPs with the free 5-CzPm ligand.

5-CzPm ligand shows a strong and sharp peak at 399nm due to π - π * transition, where CP1, CP2, and CP3 show emission with a strong single band at 534, 500, and 532nm respectively therefore, the observed emission band cannot be assigned to the ligand-centered (π - π *) transition. The emission of these CPs could be attributed to triplet clustered centered (³CC) and iodide-to-copper (M+X)LCT transitions. Because the Cu---Cu distance of these Cps is less than the sum of Van der Waal radii (i.e. less than 2.8 Å).



Figure-3.43. Excitation and emission spectra of (a) CP1, (b) CP2, and (c) CP3.

3.5.2 Photophysical properties of complex-1,2,6 and CP5

At normal temperature, the solid-state emission spectra of the coordination polymers C-1, 2, 6, and CP5 were measured. under excitation at $\lambda_{ex} = 365$ nm, resulting in strong single-band emissions. Comple-1,2 and 6 show emission at 582,600 and 542 nm respectively while CP5 show emission at 544nm. the complex-1,2 show emission because of the (M+X) LCT and complex-6 and CP5 show emission due to MLCT.



Figure-3.44. Solid state excitation and emission spectra of C-1,2,6 and CP5

3.6 Mechanochromic Behavior of CP1 and CP3 Mechanochromic materials have been found to be useful in optical recording/memory devices, damage detectors, security equipment, pressure or motion sensing systems as well as data storage equipment.^{26,37} Here, we explore the mechanochromic behavior of CP1 and CP3. Initially, CP1 under ultraviolet (UV) lamp excitation of ($\lambda_{max} = 365$ nm), show green emission [$\lambda_{max} = 500$ nm] but when we grind the CP1 with the help of mortar, The grounded sample exhibited green (500 nm) to orangishyellow (590 nm) emission color shifts along with mechanochromism luminescence. The grounded sample was able to return to its original green fluorescence (500 nm) by adding two to three drops of acetonitrile solvent. the PXRD data confirm that after grinding there is no structural change observe but due to grinding disruption of intramolecular C-H--- π and N-H---C interactions was observed. This disruption leads to a lowering of the energy level of the emitting excited state, resulting in a red-shifted emission at 590 nm. The first green emission was seen back, when the ground sample was exposed to two to three drops of acetonitrile, as a result of these interactions being restored.CP3 is also

show mechanochromic behaviour after grinding the emission color of CP3 change from greenish yellow ($\lambda_{max} = 532$ nm) to orange ($\lambda_{max} = 590$ nm), after adding the 2-3 drops of acetonitrile the emission color converts back in greenish yellow ($\lambda_{max} = 532$ nm. but the recover sample is the mixture of CP1 and CP2 which is confirm by matching the PXRD pattern of recover sample with CP1 and CP2.



Figure-3.45. Reversible mechanochromism by CP1



Figure-3.46. (a) Emission spectra of CP1 which show reversible mechanochromism (b) Change in emission intensity during reversible mechanochromism of CP1(c). Comparison of the PXRD data of CP1 initial, after grinding, and after recovery



Figure-3.47. Reversible mechanochromism by CP3



Figure-3.48. (a) Emission spectra of CP3 which show reversible mechanochromism (b) Change in emission intensity during reversible mechanochromism of CP3 (c). Comparison the CP3 PXRD data at initial, after grinding, and after recovery (d). Comparison the recover CP3 PXRD pattern with CP1 and CP2.

CHAPTER-4

CONCLUSION

In summary, three new 1D and 2D coordination polymers have been synthesised by the reaction between CuI and 5-CzPm ligand by varying the metal-ligand ratio and changing solvent conditions. The crystals of these CPs have been successfully synthesised and their complete crystal structures analysed by SXRD. Two CPs except CP2 shows mechanochromism behaviour because of the interruption in crystalline interaction after applying mechanic force which affect the Cu---Cu bond distance, this variation in crystal structure of these CPs induced change in emission. Apart from that reaction between CuI and 2-Py. isoindoline leads to give a new 1D coordination polymer-4 (CP4) the crystal structural was analysed by SXRD. The CP4 show thermochromism behaviour. Then moving forward develop high-luminescencent complex/coordination polymers, I have conducted the reaction of CuX (where X = I, Br) and ligand L1, L2 with commercially available bulky phosphines, because it is proposed that incorporating bulky phosphine will reduce distortions in the excited state and non-radiative transitions, resulting in high luminescence. So, I successfully synthesized Complex-1,2,3 and complex-4 using CuX (X= I, Br) ligands L1, L2, and triphenylphosphine (PPh₃), and analyzed them using NMR spectroscopy. and also described their photophysical properties. Then, I went on to bulkier phosphine (POP) and performed the reactions between POP, CuI, and ligands L1, and L2, from which I obtained complex-6 and CP5 and analyzed them using NMR spectroscopy. and also explored their photophysical properties. Alog with, I have checked the thermal stability of all the synthesized complexes/coordination polymers by thermogravimetric analysis (TGA).s

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