Synthesis of three-coordinate luminescent copper(I) complexes

M.Sc. Thesis

By

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DEPARTMENT OF CHEMISTRY
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A THESIS

Submitted in partial fulfillment of the requirements
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by

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DEPARTMENT OF CHEMISTRY

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CANDIDATE DECLARATION

I hereby certify that the work which is being presented in the thesis entitled **Synthesis of three- coordinate luminescent copper(I) complexes** 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 August 2020 to June 2021 under the supervision of Dr. Abhinav Raghuvanshi, Assistant Professor, 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.

Aasha
01/06/2021

Signature of the student with date

This is to certify that the above statement made by the candidate is right to the best of my/ourknowledge.

Abhinav 03/06/2021

Signature of the Supervisor of M.Sc. thesis

Dr. Abhinav Raghuvanshi

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Date: 09/06/2021	Date: 09/06/2021

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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 least, I would like to pay sincere gratitude to my loving parents for their continuous help and moral support throughout my project work.

Dedicated to….

My Family

ABSTRACT

The overall aim of this project is to synthesize and characterize Cu(I) complexes that emit light in the UV-visible range upon excitation and this makes them usable as emitters in the optoelectronic devices. For this work, efforts were made to the synthesis of three-coordinate copper(I) complexes bearing bulky and rigid ligands. A bidentate N^N ligand and a bulky monodentate N-heterocyclic carbene ligand is proposed for the synthesis of copper(I) complexes. Here, N-heterocyclic carbene ligand will have a sigma donor property and phenazine-2,3-dicarbonitrilo has acceptor property. The synthesized complexes were characterized by various spectroscopic techniques.

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ACRONYMS

$CDCl_3$	Chloroform-D
H_2SO_4	Sulfuric acid
CH_3CN	Acetonitrile
CH_3OH	Methanol
EtOAc	Ethyl acetate
LCMS	Liquid chromatography mass Spectrometry
NMR	Nuclear magnetic resonance spectroscopy
M	Molar
ppm	Parts per million

NOMENCLATURE

π	pi
δ	Chemical shift
cm	Centimetre
nm	Nanometre
^{o} C	Degree Celsius
mmol	Millimole
mL	Millilitre
rt	Room temperature

CHAPTER 1 INTRODUCTION

1.1.General Introduction

The increasing population demands more electrical energy, leading to the search for new and better lighting systems. The prominent chemist Albert Hofmann said that we people are "beings of light" and need energy for our existence. Copper has been constantly used in illumination since the electricity-powered first time. Volta lamp was invented first by Alessandro Giuseppe Antonio Anastasio. It was the device that employed a glowing copper wire. As a large amount of energy is wasted as heat in volta lamps, such systems' efficiency is not good. So new technologies were adapted to reduce the consumption of energy. This drew the attention towards LECs and OLEDs. The typical working principle of both OLEDs and LECs is electroluminescence. In this process, there is the direct conversion of electrical energy into light. In the application of solid-state lighting devices like LECs, OLEDs, LEDs, the only working principle involved is electroluminescence.

Development of advanced photoactive materials have been a hot research topic as they have wide applications in organic light-emitting diodes (OLEDs)[1,2], light-emitting electrochemical cells (LEECs)[3,4], photosensitizers in dye-sensitized solar cells (DSSCs)[5,6], sensor or for bioimaging[7,8], as electron transfer agents in photocatalytic reactions[9,10]. There are two types of photoactive compounds known: organic and transition metal compounds (figure1). The significant distinction between them lies in the property of complexes of transition metals which can assist intersystem crossing to populate excited triplet state due to spin orbit couplingand release photons by phosphorescence effectively. This mechanism is not prevalent in case of the organic compounds.

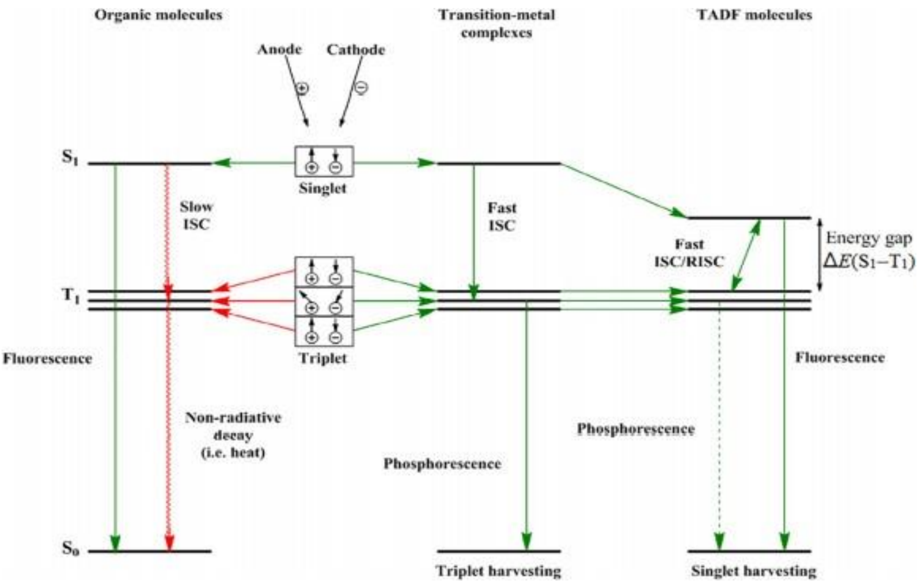


Figure 1. Difference between organic and organometallic photoactive compounds

The various applications lead to the enhancement of such energy-saving research or new technologies that demand emissive materials that do not lead to the degradation of natural resources. This motivated researchers to look for new combinations of 3d transition metals and ligands. The other substitute to luminescent processes, fluorescence and phosphorescence, has been established in past 12-15 years, termed thermally activated delayed fluorescence (TADF). In TADF, thermal equilibrium is observed between singlet and triplet states at high temperature with emission from S_1 at very high temperature[12,13]. The reverse intersystem crossing (rISC) is a procedure where triplet exciton can be converted into singlet exciton when the energy gap between triplet and first singlet excited singlet state is less. When there is a long lifetime of excited triplet state, and there is less energy gap between singlet and triplet state, rISC can occur at room temperature. This leads to populate S_1 from T_1 and finally $S_1 \rightarrow S_0$ transition leads to emission, this process is termed as TADF[14]. For efficient phosphorescence, greater atomic mass and spin-orbit coupling were necessary. So, heavy transition metals complexes of 4d and 5d, mainly $\mathrm{Ru^{II}}$, $\mathrm{Re^{I}}$, $\mathrm{Os^{II}}$, $\mathrm{Ir^{III}}$ and $\mathrm{Pt^{II}}$ are used for phosphorescent emitters. However, TADF emission mechanism does not have such restrictions.

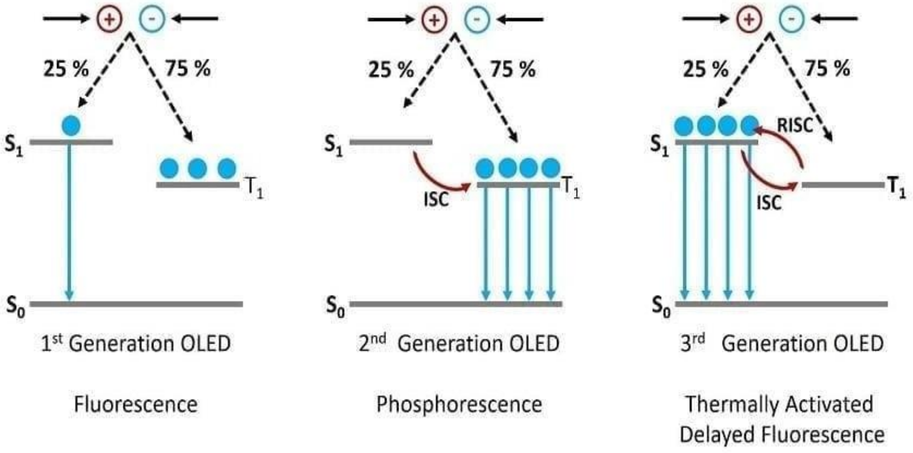


Figure 2. Three generations of OLEDs

The difference between different emission mechanisms leads to internal quantum efficiency (IQE) that is achieved by the transformation of all excitons, which are developed by the electron-hole combination[15] (figure2). The first generation of OLEDs incorporated emitters following the fluorescence process that could achieve only 25% of the internal quantum efficiency (IQE)[16]. The second generation emitters involve the phosphorescence process. This process could achieve 100% IQE. However, these emitters require the presence of heavy metals like platinum, iridium etc. for efficient phosphorescence[17]. A high atomic mass and spin orbit coupling is necessary for efficient intersystem crossing. Due to the cost of noble metals and limited resources, third-generation emitters were introduced. It was found that TADF complexes can be made by using donor and acceptor units with a large separation to avoid mixing. Most of the organic TADF systems involve either a long bridging ligand or twisted π-systems[18-20]. While in transition metals compound, there is no such requirement because of the nature of different types of orbitals involved in donor and acceptor unit(figure 3).

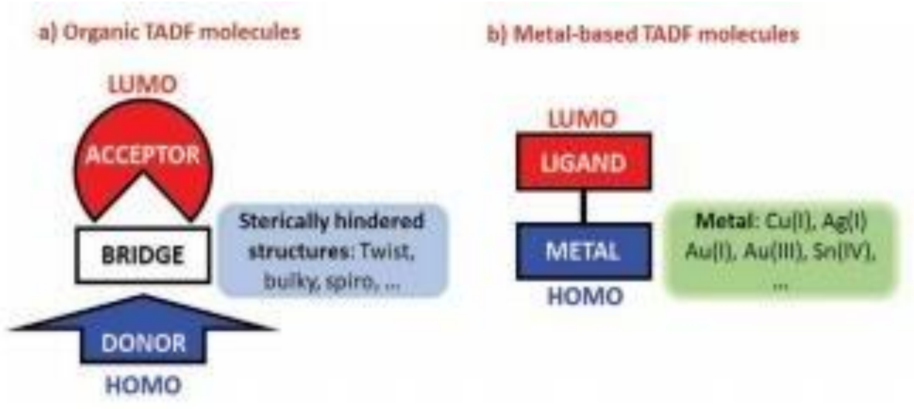


Figure 3. Organic and metal-based TADF molecules

Among the photoactive materials of 3d metals, copper holds a particular position. In the organometallic compounds Cu(I) having d^{10} configration is preferred rather than Cu(II), which reduces the non-radiative decay due to metal centred d-d transition. Also, Cu(I) is very flexible and can show geometries like tetrahedral, trigonal planar, and linear is also presented with good photophysical properties. Also, it has been observed that TADF is mainly seen in photoactive Cu(I) complexes which are heteroleptic in nature[21]. Further, according to the selection of various metals ions and metal complexes the delayed fluorescence complexes have been divided into four broad categories (figure 4):

(a) This category included TADF complexes showing only delayed fluorescence process. For that k(ISC) must be greater than that of k(F).

(b) This category included TADF compounds showing both delayed fluorescence and fluorescence processes. For this, both k(ISC) and k(F) must be larger.

(c) This category included metal assisted delayed fluorescent compounds showing both delayed fluorescence and phosphorescence for which k(ISC) must be greater and k(F) and k(RISC) have similar values.

(d) This category included TADF compounds showing delayed fluorescence and phosphorescence and fluorescence processes.

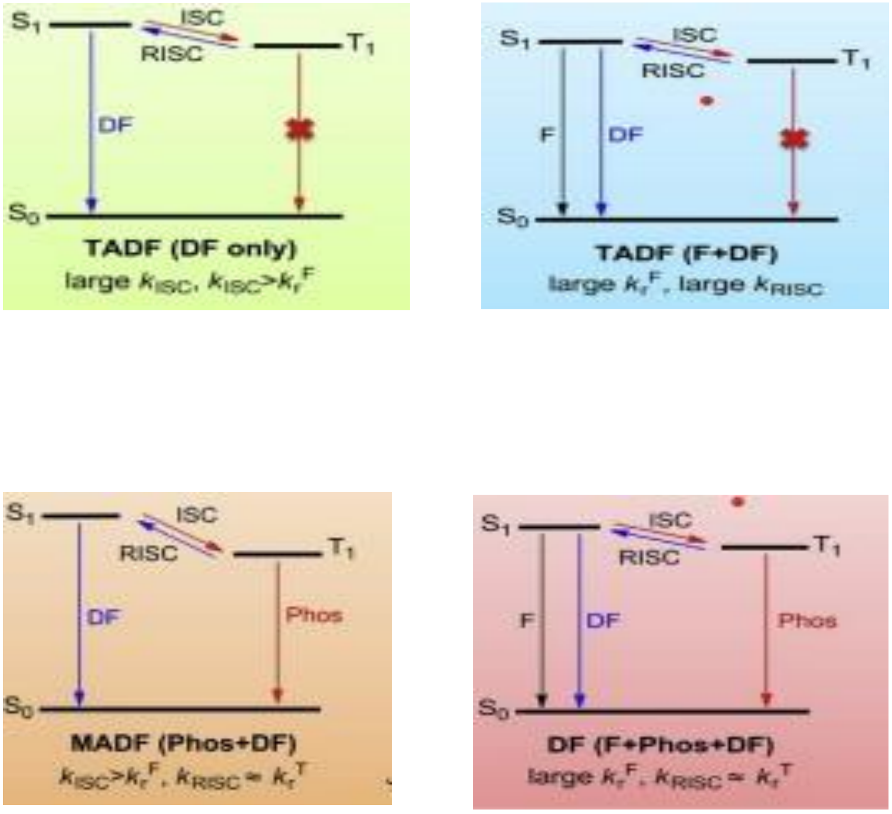


Figure 4. Categories of Delayed fluorescence complexes

Considering all these aspects, developing complexes based on Cu(I) is the current field of interest. The development was strongly inspired by the lower cost, low toxicity and abundanceof copper in contrast to other noble metals and rare earth metals.

LITERATURE SURVEY:

Solid-state lighting devices like OLEDs having less demanding fabrication conditions are becoming favourable technology for this generation. Complexes of Pt (II) and Ir (III) were usedas light-emitting devices because they help to achieve 100% internal quantum efficiency (IQE) through phosphorescence[22,23]. Due to their relatively low abundance and expensive, scientists started looking for other metal complexes that fulfill the desires of availability. In order to maintain sustainability, strategies like TADF was invented. The two demands for a complex ora material to show TADF is a low energy gap between singlet and first excited triplet state, reverse intersystem crossing. Two methods, vacuum deposition and solution processing were established for OLEDs. Vacuum deposition operates at high temperature and low pressure to sublime materials. However, only a few articles reported the vacuum thermal deposition process because most Cu(I) complexes are not stable thermally. As a result, solution processing was used for OLEDs. All the above research by the scientists towards the investigation and the development of low-cost more efficient complexes using copper metal.

Sauvage and McMillin discovered the first Cu(I) complex $[Cu(dmp)_2]^+$ (dmp=2,9-dimethyl- 1,10-phenanthroline) which showed luminescence at room temperature [24,25]. Due to the fullyfilled configuration of Cu(I) complexes and due to weak spin-orbit coupling for copper, transitions of the first excited triplet state to singlet ground state and singlet to the first excited triplet state are forbidden. So, a lack of luminescent properties, especially in mononuclear counterparts were observed. So in the charge recombination process, difficulty in gathering triplet excitons existed. Also, device stability through photochemical reactions and strong saturation effect was hampered by phosphorescence decay which took a longer time[26]. Then instead of mononuclear Cu(I) complexes, the study was focused on multinuclear complexes, and an increase in their luminescent properties were dedicated to strong metal-metal interactions and ligand to metal-metal charge transfer (LMMCT) [27]. The first tetranuclear Cu(I) complex $[Cu_4(C{=}CPh)_4L_2]$ (L=1,8-bis(diphenylphosphino)-3,6-dioxaoctane) was synthesized by Che and Ma as the OLED emitter. But limited brightness and less quantum efficiency of 0.1% were obtained as a result [28,29]. Another intrinsic problem in the complex $[Cu(dmp)_2]^+$ was non-emissive decay lead through Jahn-teller flattening distortion after excitation of metal to ligand charge transfer (MLCT) state and instability of complex. Cu(I) has d^{10} configuration, which gives rise to the distribution of symmetrical electron density, which in fact favours the tetrahedral geometry to remove repulsions [30,31]. Upon photoexcitation, oxidation of tetrahedral Cu(I) into Cu(II) square planar occurs due to metal to ligand charge transfer excitation (MLCT) from the 3d orbitals of Cu to antibonding π^* of ligands. Jahn teller distortion could also be observed if the lifetime of the complex is enough. This lead to quenching, and the process of electron transfer gets further slow[32,33]. The MLCT flattening factor was removed by using bulky ligands. In addition, increase in rigidity helps in improving the quantum yield.

On-demand of stearic factor, PPh_3 was introduced in $[Cu(dmp)_2]^+$. Then longer lifetime was observed for this complex in a deoxygenated solvent condition[34,35], but complex still showed quenching in the solvent methanol. As a result, bidentate phosphine ligands were incorporated in $[Cu(dmp)(DPEphos)]^+$ (DPEphos = bis[2-(diphenyl phosphine)phenyl]ether[36,37]. Also, the more donor character of phosphine ligand resulted in increment of emission lifetime at room temperature. On the opposite side, the efficiency of the Cu(I) based OLEDs can be affected bydevice fabrication conditions. In 2004, a first Cu(I) based OLED that was four coordinated wasreported, shifting the focus on research to this side. For green colour OLED applications, the complexes $[Cu(N^\wedge N)(PPh_3)_2]BF_4$ and $[Cu(N^\wedge N)(DPEphos)]BF_4$ that were mononuclear were documented by Wang[38]. Wang had shown a colour changement plan from orange-red to red that is achieved through increasing the π conjugation in nitrogen-based bidentate ligands in [Cu(N^N)(DPEphos)]BF_4 that was red coloured OLEDs[39].

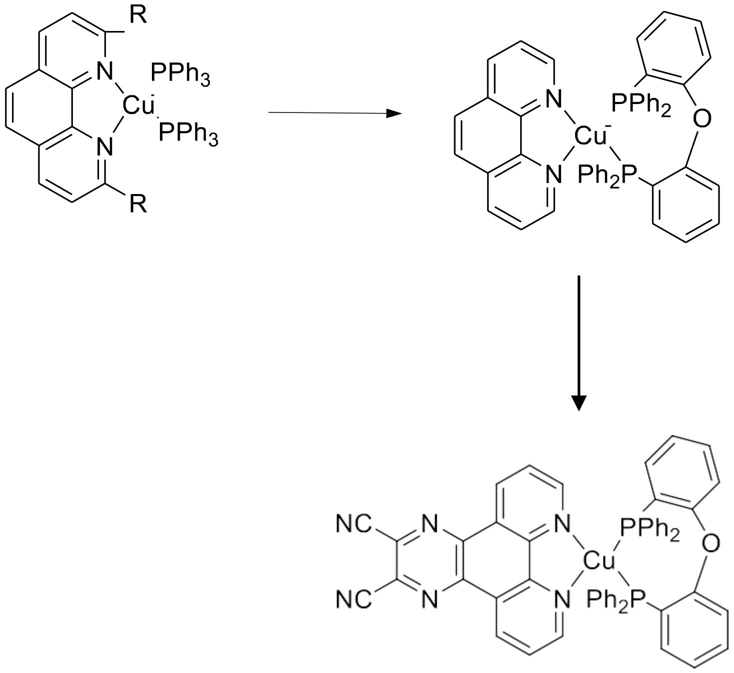


Figure 5. Modifications in bidentate N^N ligand

Li et al., in their study, have presented color changement from green-yellow to orange range using dicyanopyrazine group in phenanthroline ligand. In the phenanthroline ligand, an electron-withdrawing group was introduced, which was 2,3-dicyanopyrazine group[40]. Polarization effects between the copper(I) complexes were used to change colors. By introducing electron-donating and electron-withdrawing chromophores, the colour of emission can be tuned. On the other side, another change is observed due to rigidity, which increases with the number of nitrogen atoms in a N^N bidentate ligand. In a recently published work, more efficient Cu(I) complex was obtained by using tridentate phosphine ligand 2,2'- (phenylphosphinediyl)bis(2,1-phenylene)bis(diphenylphosphine)[41]. For the four coordinated compounds, the approach made to decrease the structural changes or reestablishment in the structure was by inserting bulky ligands around Cu(I) center. This issue can also be tackled by using a sterically congested bidentate N^N or P^P ligand with a monodentate anionic ligand (carbene (NHC), halide, thiol). Furthermore, Steffen et al. has synthesize $[Cu(CAAC)_2]^+$ and Cu(CAAC)X (X=halide) complexes with the use of CAAC ligands 1-(2,6-di-iso- propylphenyl)-3,3,5,5-tetramethyl-2-pyrrolidineylidene[42]. CAAC ligand was obtained to be a good π-chromophore. Also, by substituting with bulky ligands, rigidity was not that much increased, so the focus was done on multinuclear compounds.

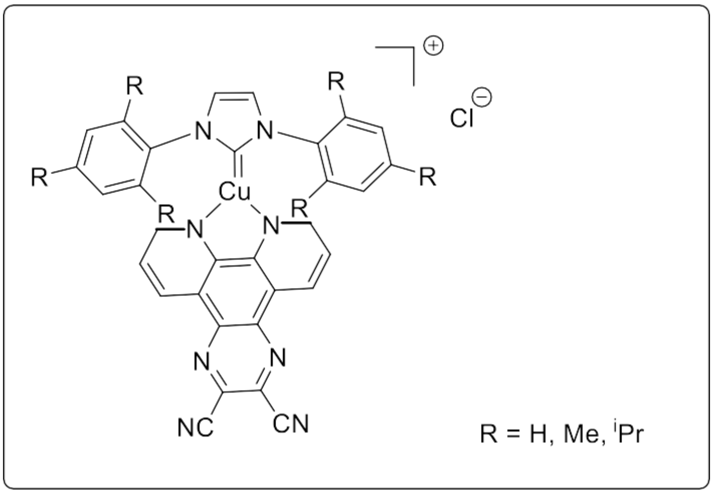
The main reason to use a multinuclear compound was to enhance the rigidity in the structure. Due to this, the possibility of structural reorganization was reduced, and this increased the emissive properties. The first binuclear Cu(I) compound involves bridges of nitrogen. In 2005, a binuclear complex bis(bis(di-iso-butylphenyl phosphine)amido)dicopper(I) was presented which had a PLQY of 68% in cyclohexane at 298K[43]. Apart from N/P bridging ligands, due to high structural diversity, high emission efficiency, halide atoms can be employed as the bridging ligands. PLQY were generally low for monodentate phosphine ligands. Also, by substitution on phosphine ligands changes the solubility of complexes can be changed from polar to non-polar solvent, with PLQYs ranging from 28% to 99%. When binuclear complexes substituted by nanoclusters then both rigidity and thermal and photostability of copper(I) complexes gets enhanced. Recently, a Cu_4I_4 cluster employing the 2,9-di(diphenyl phosphine)-dibenzofuran ligand has been reported by Xie and Xu. As tetranuclear complexes showed poor quantum efficiency, their relationship of structure-property must be studied in light-emitting devices but then focus was done on mononuclear compounds.

The study from four-coordinate mononuclear compounds was focused to three and two- coordinate mononuclear compounds to reduce the structural rearrangements. For strongly photoemissive properties, two-coordinate complex (L)MX (L=Carbene, M=Cu, X=anionic ligand) with linear geometry have previously played a significant role[44]. Depending on the nature carbene ligand can exhibit both strong electron donor and π acceptor properties. The anionic ligand that is halide atom X favours charge transfer in the acceptor orbital of carbene. CAAC complexes of copper[45] are found to be very stable thermally, and these are also resistant to the rearrangement of ligands. In the case of CAAC copper halides, a photoluminescence quantum yield of 96% is observed. In further research, anion X was taken as arylamide to give carbazolate. The HOMO was located on carbazole, while LUMO comprises mainly $C_{carbene}$ p-orbital. TADF mechanism is shown through emission from CMA complexes. On warming, a characteristic blue shift is obtained from the TADF process. Also, a temperature-dependent red shift is displayed by CMAs. To maintain structural rigidity, amide N is locked into a rigid 6,7- membered ring. The wavelengths in the visible spectrum can be changed from blue to deep red by varying electron-donor properties of amido ligands. Then thefurther focus was done on using aryl halides with amines rather than aryl amides.

Ullmann reported a cross-coupling reaction between amines and the aryl halides that lead to the formation of bonds between carbon and nitrogen[46]. But then problem of high stoichiometric copper metal loadings, high reaction temperature, and long reaction times occurred for cross-coupling aryl halides and amines. In new recent research, it was observed that by incorporating bidentate ligands such as 1,10-phenanthroline; these reactions can be performed at lower reaction temperature (<110°C) with lower copper loading (<10%).

OBJECTIVE

TARGET COMPOUND



In this work, synthesis of three coordinate copper complex is proposed. In the three coordinate mononuclear copper complex, IMes carbene is one of the ligands which acts as sigma donor and 2,3-dicarbonitrilophenazine(1,10)phenanthroline is another bidentate ligand as acceptor property. Our main objective is to study photophysical properties of this complex and compareit with previously synthesized complexes to evaluate the steric and electronic effects. In previous reports, it has been observed that colour can be changed from green yellow to orange red by inserting electron withdrawing groups in phenanthroline ligand. So, by inserting electron withdrawing and electron acceptor groups colour tuning can be done. Also to increase rigidity, π conjugation is extended in phenanthroline ligand and thus bidentate ligand chosen for project work is 2,3-dicarbonitrilophenazine(1,10)phenanthroline. Also according to recent reports, a sigma-donor and a pi-acceptor ligand on Cu helps to get better results. As carbene has strong σ donor properties and its metal complexes are air and moisture stable so substituted carbeneligand was proposed for the project work.

CHAPTER 2

EXPERIMENTAL SECTION

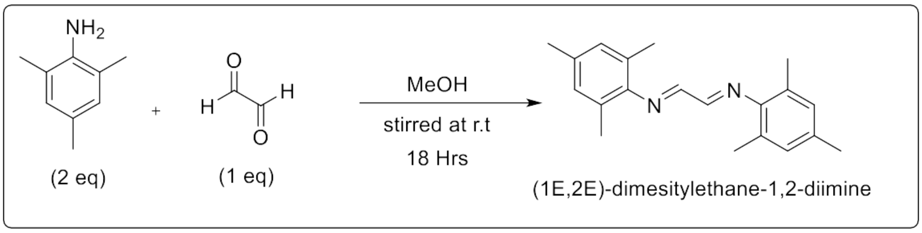
2.1. MATERIALS AND INSTRUMENTATION:

Chemicals were used as received unless otherwise indicated. All reactions were performed under nitrogen atmosphere 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. All the NMR spectra were obtained on a Bruker 400 spectrometer in $CDCl_3$ or d_6-DMSO operating at 400 MHz for ^{1}H NMR. Data for proton NMR Chemical shifts are mentioned in delta (δ) units, showed in parts per million (ppm) downfield from tetramethyl silane (TMS). The residual protonated solvent as an internal standard is $CDCl_3$ showing peak at7.26 ppm. The ^{1}H NMR splitting patterns have been mentioned as ‘s’, singlet, ‘d’, doublet; ‘t’, triplet, and ‘m’, multiplet.”. Compounds were named by using Chem draw Ultra 16.0 and NMR data processed by Mestre Nova.

2.2. GENERAL PROCEDURE FOR SYNTHESIS OF PRECURSORS:

2.2.1. Synthesis of (1E,2E)-dimesitylethane-1,2-diimine

Synthesized according to literature procedure[47]: 2,4,6-trimethylaniline (0.280 mL, 2mmol) was added in methanol solvent (4.5 mL). The above prepared solution was added into 40% glyoxal aqueous solution (0.115 mL, 1 mmol) at room temperature. At room temperature, the reaction mixture was stirred for about 18 hours. The resulted suspension was filtered off and washed with cold methanol to give (1E,2E)-dimesitylethane-1,2-diimine as yellow needles.

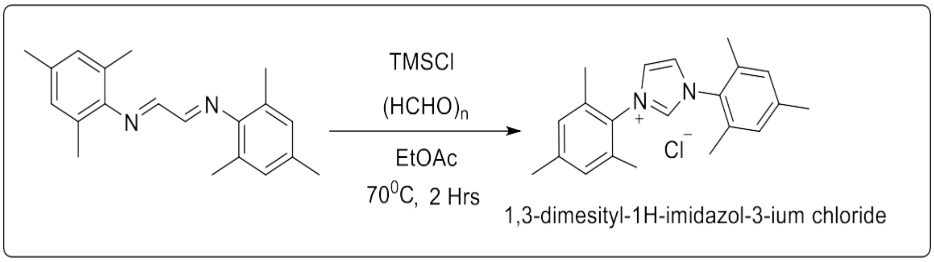


Scheme 1. Synthesis of (1E,2E)-dimesitylethane-1,2-diimine

Yellow needles; yield 52.34% (102.6 mg); ^{1}H NMR (400 MHz, $CDCl_3$) δ 8.10 (s, 2H), 6.91 (s, 4H), 2.29 (s, 6H), 2.16 (s, 12H)ppm; LCMS (ESI) m/z calculated for $C_{20}H_{24}N_2$ $[M+Na]^+$ 315.2038, found 315.1832.

2.2.2. Synthesis of 1,3-dimesityl-1H-imidazole-3-ium chloride (2a)

Synthesized according to literature procedure[47]: a solution of (1E,2E)-dimesitylethane-1,2- diimine (2 g, 6.84 mol) and paraformaldehyde (0.2114 mL, 7.044 mol) in ethyl acetate (40 mL) was heated at 70 ^{0}C and stirred till most of paraformaldehyde dissolved. Then, a solution of tetramethyl silyl chloride (0.9920 mL, 7.044 mol) in ethyl acetate (18 mL) was dissolved into the reaction mixture dropwise with vigorous stirring. The reaction mixture was stirred further at 70 ^{0}C for 2 hours under protection of N_2 atmosphere. Then, solution was let to cool in a ice-bath and filtered and then washed with cold ethyl acetate and ether. Then product was dried to suction to obtain the pale-yellow product 1,3-dimesityl-1H-imidazole-3-ium chloride.

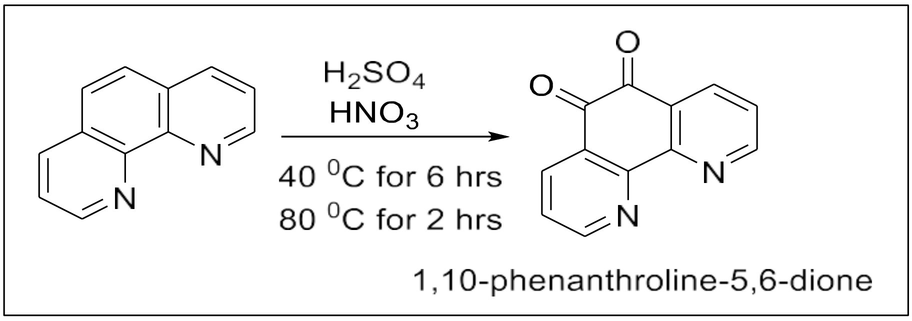


Scheme 2. Synthesis of 1,3-dimesityl-1H-imidazol-3-ium chloride

Pale yellow powder; yield 36.22% (843.9 mg); LCMS (ESI) m/z calculated for $C_{21}H_{25}N_2^+Cl^-[M-Cl]^+$ 305.2185, found 305.2012.

Synthesis of 1,10-phenanthroline-5,6-dione (3a)

Synthesized according to literature procedure[48]: 1,10-phenanthroline (100 mg) and potassium bromide (150 mg) were mixed together and then the mixture was put into an ice-cooled flask having 1 mL of H_2SO_4 (98%). The solution was cooled sufficiently for about 30 minutes. Then 0.5 mL of dense HNO_3 was mixed into the reaction mixture dropwise within a time period of 2 minutes. Then, the solution was heated in reflux condition at 40 ^{0}C for 6 hours and then further at 80 ^{0}C for another 2 hours. When the reaction happened, the Br_2 was removed from the flask by letting it open for some time in hood. The residue cool mixture was put into ice cold water. Then aqueous solution of NaOH was added to make the pH neutral around 6-7. Then extraction was done with chloroform and crude product was obtained by rotary evaporator. The mixture was recrystallized from ethanol to obtain the product.



Scheme 3. Synthesis of 1,10-phenanthroline-5,6-dione

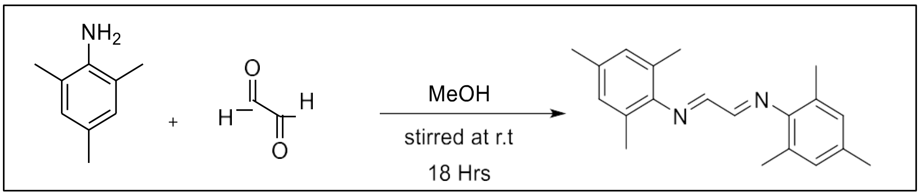
Yellow orange powder; yield 96% (88.06 mg); ^{1}H NMR (400 MHz, $CDCl_3$) δ 8.91 (dd, 2H),8.01 (dd, 2H), 7.39 (dd, 2H)ppm.

CHAPTER 3

3.1. RESULTS AND DISCUSSION

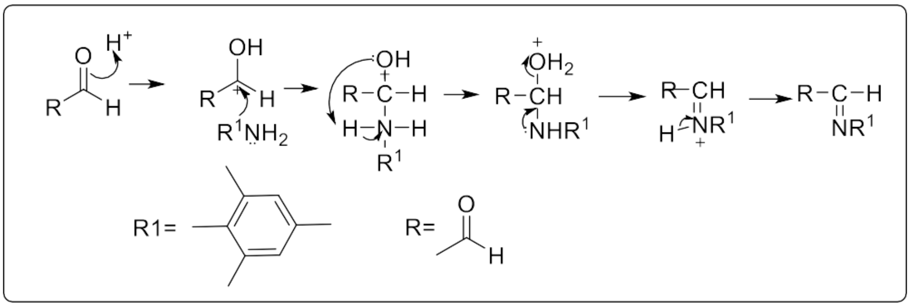
Synthesis of ligand 1a and characterization

1a was synthesized by stirring glyoxal and 2,4,6-trimethylaniline at room temperature as shown in Scheme 1. The final product was obtained in 52% yield. Obtained solid was characterized by ^{1}H NMR spectroscopy and mass spectrometry.



Scheme 1. Synthesis of 1a

Plausible mechanism of reaction



Firstly, aldehyde group takes proton from solvent methanol with subsequent nucleophilic attack of amine on aldehydic carbon. Then proton transfer occurs to neutralize amine nitrogen. Then lone pair of nitrogen attacks occurs on aldehydic carbon with loss of water. Then deprotonation takes place to yield imine as product.

Figure 1 showing the ^1H NMR spectrum of 1a from where we can see that a singlet at 8.10 ppm for 2 protons and singlet at 6.91 ppm for 4 protons in aromatic region and singlet at 2.29 ppm for 6 methyl protons and singlet at 2.16 ppm for 12 methyl protons. Thus, from the spectra it is clear that solid obtained is (1E,2E)-dimesitylethane-1,2-diimine.

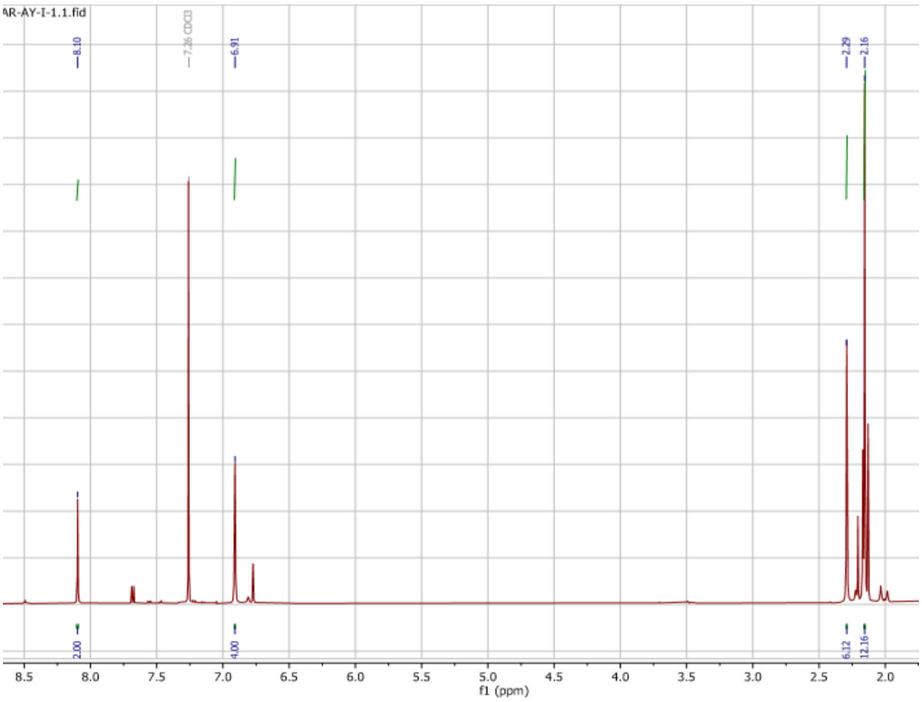


Figure 1. ^1H NMR spectrum of 1a

Figure 2 showing the mass spectrum of 1a which clearly indicated molecular weight of compound and the resulting fragmentation pattern provided information for elucidating the structure of ligand 1a. The electron impact mass spectra of ligand was recorded and showed a well-defined base peak m/z 315.1832 $[M+Na]^+$. This could be attributed to $C_{20}H_{24}N_2$.

LCMS (ESI) m/z solved for $C_{20}H_{24}N_2$ $[M+Na]^+$ 315.2038, obtained 315.1832.

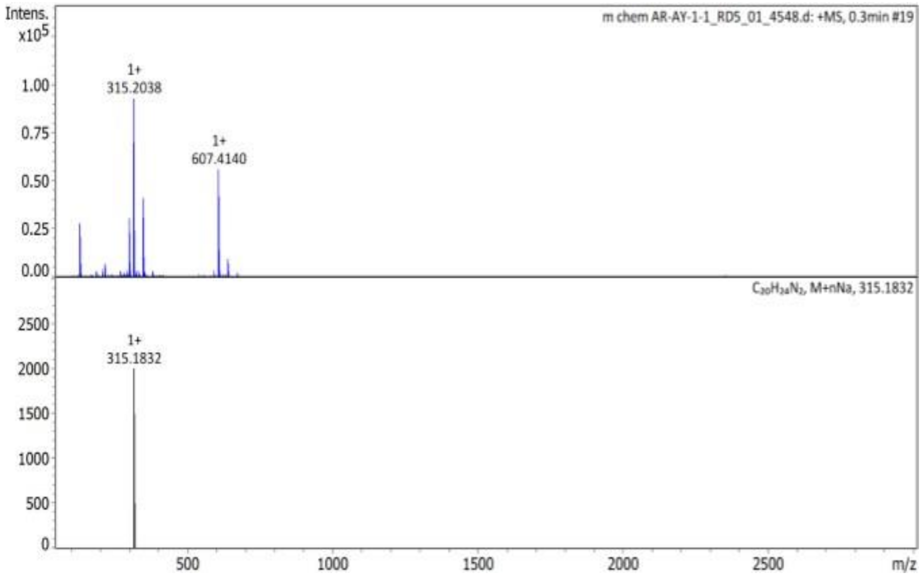
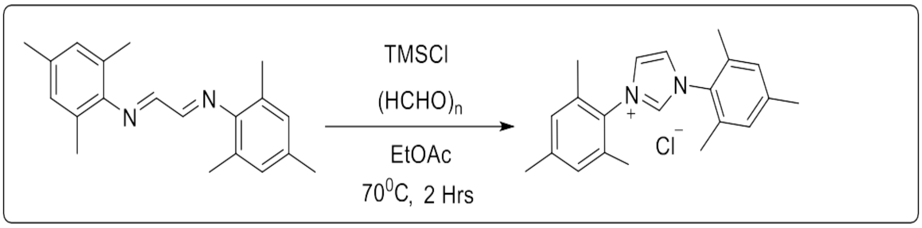


Figure 2. Mass spectrogram of 1a

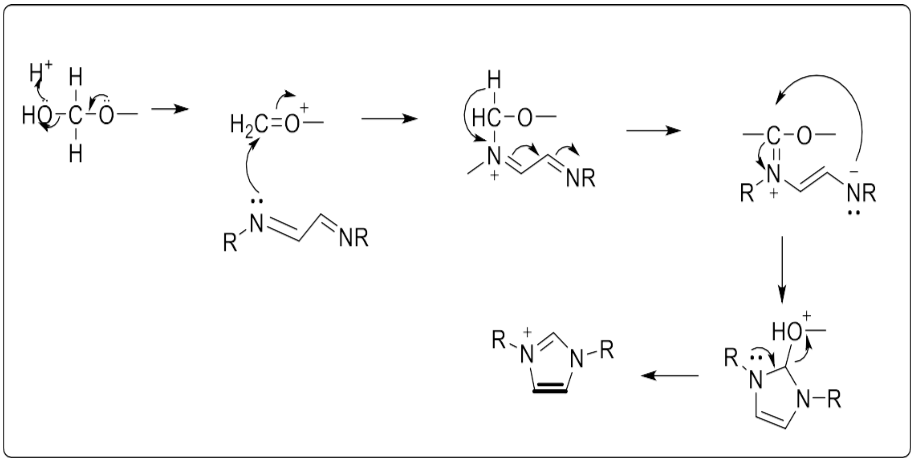
Synthesis of ligand 2a and characterization

Ligand 2a was synthesized by heating (1E,2E)-dimesitylethane-1,2-diimine withparaformaldehyde and tetramethyl silyl chloride as shown in Scheme 2. The final product wasobtained in 36.22% yield. Obtained solid was characterized by mass spectrometry.



Scheme 2. Synthesis of 2a

Plausible mechanism of reaction



Firstly, protonation of alcoholic group of paraformaldehyde occurs. Then nucleophilic attack of nitrogen of dimesitylethane-1,2-diimine takes place onto carbon of paraformaldehydeneutralizing oxygen. Then proton transfer takes place with subsequent attack of nitrogen to form a five membered ring. Then lone pair of nitrogen attacks to remove oxygen carbocation to give cyclic five membered ring as product.

Figure 3 showing the mass spectrum of 2a which clearly indicated the molecular weight of the compound and the resulting fragmentation pattern provided information for elucidating the structure of the ligand 1a. The electron impact mass spectra of ligand 2a was recorded and showed a well-defined base peak m/z 305.2012 [M-Cl]$^+$. This could be attributed to for $C_{21}H_{25}N_2^+Cl^-$.

LCMS (ESI) m/z solved for $C_{21}H_{25}N_2^+Cl^-$ [M-Cl]$^+$ 305.2185, obtained 305.2012.

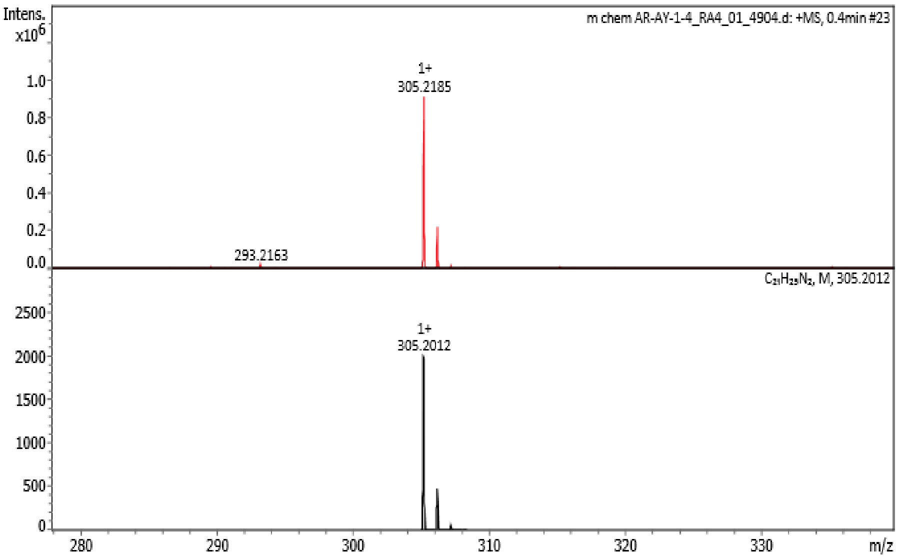
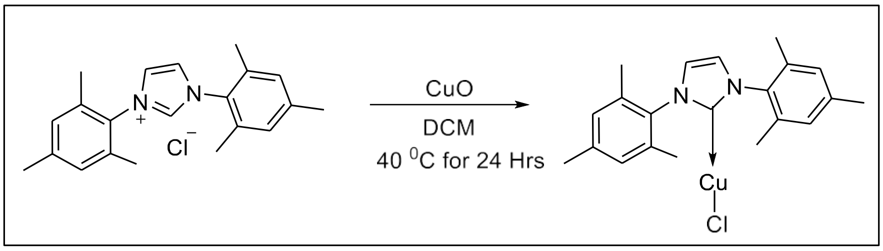
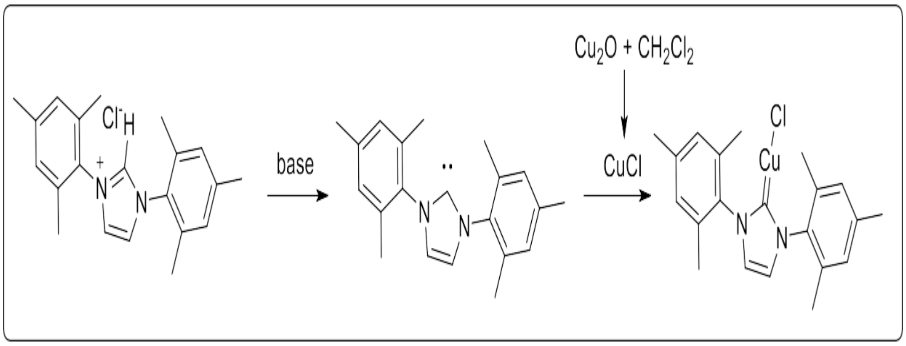


Figure 3. Mass spectrogram of 2a

Synthesis of mesityl carbene copper chloride



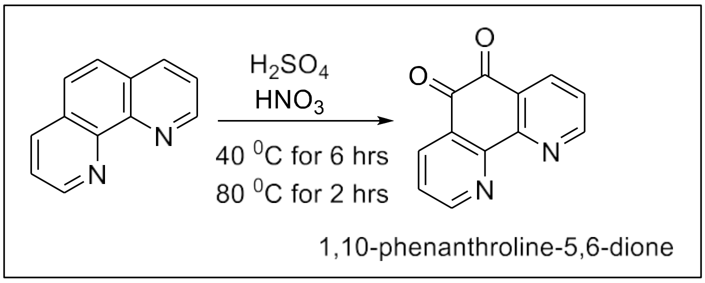
Plausible mechanism of reaction



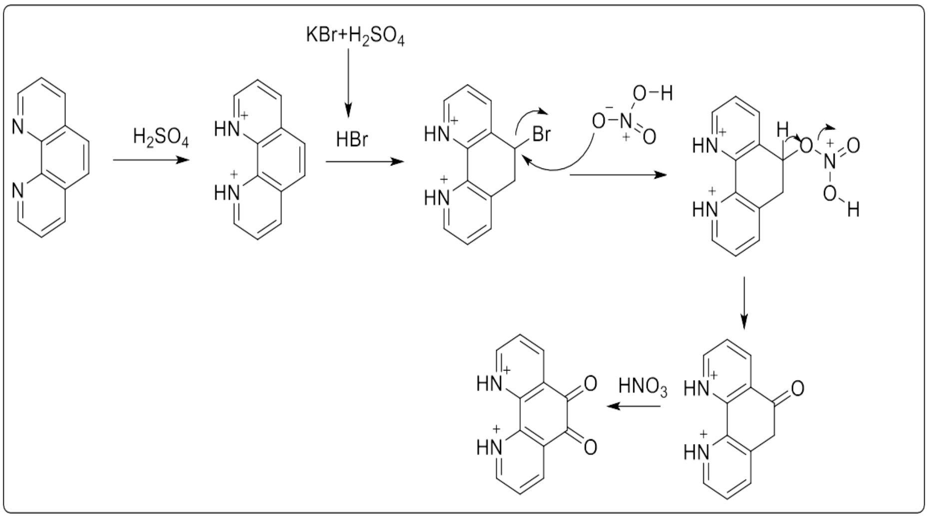
Firstly, base attacks on proton to form carbene. Then copper oxide and dichloromethane forms copper chloride which attacks on carbene to form copper carbene chloride.

Synthesis of ligand 2,3-Dicarbonitrilopyrazino(1,10)phenanthroline

Synthesis of 1,10-phenanthroline-5,6-dione

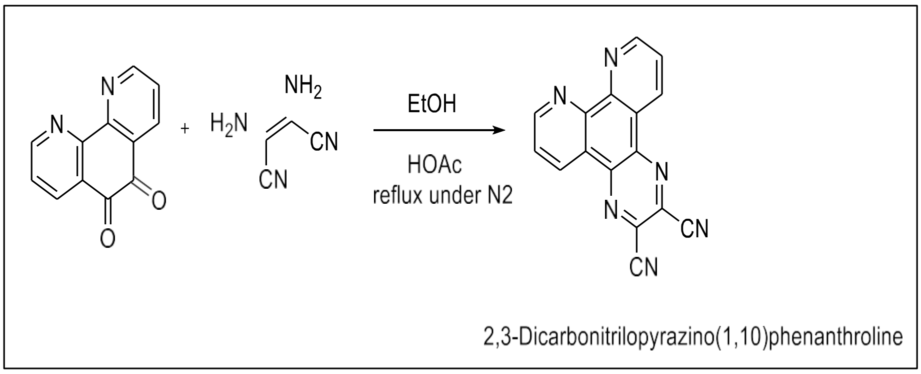


Plausible mechanism of reaction

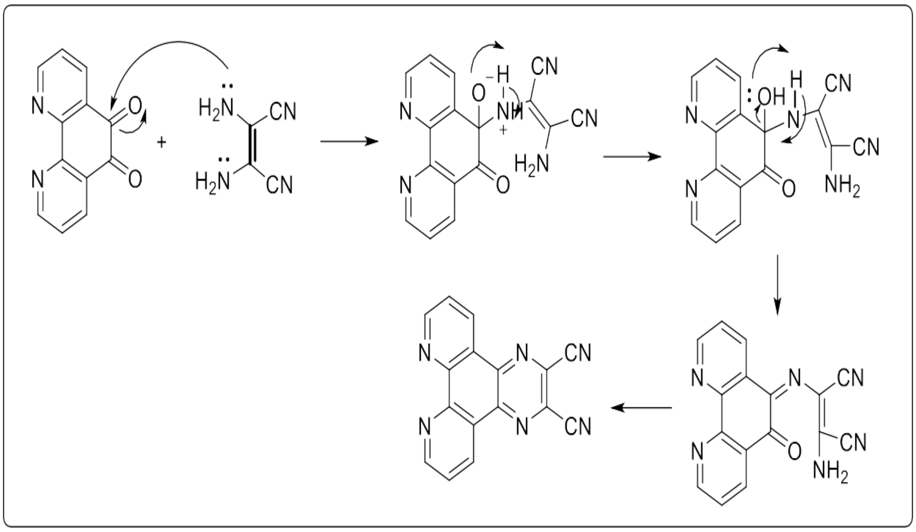


Firstly, protonation of both nitrogen takes place in the presence of acid. Then bromo addition occurs in presence of potassium bromide. Then nucleophilic attack of oxygen of nitric acid removes bromine. And in the last step, proton removal occurs to form Dione. Then, with another molecule of nitric acid phenanthroline-5,6-dione is formed.

Synthesis of 2,3-Dicarbonitrilopyrazino(1,10)phenanthroline

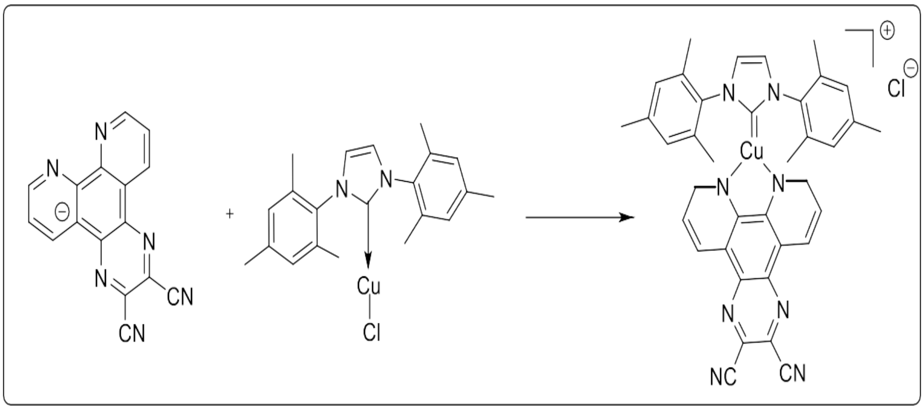


Plausible mechanism of reaction



Firstly, nucleophilic attack from lone pair of nitrogen of diaminomalenonitrile occurs to Dionegroup. Then proton transfer takes place for neutralization. In the next step, protonation occurs. Then with the removal of water, formation of imine occurs. Then following same procedure for another imine group, yields product.

Synthesis of target compound



CHAPTER 4

CONCLUSION

For the application of light-emitting devices, various range of accessible materials can be designed through conformational flexibility. So, by varying the group from an electron donor to an electron acceptor, various wavelengths can be achieved to the range of the complete visible spectrum. From that way, various colour lighting devices OLEDs can be observed. In the current work, we were working on developing luminescent three-coordinate copper(I) complex with an N-heterocyclic ligand and another was 2,3-dicarbonitrilophenazine(1,10)- phenanthroline. The mesityl (IMes) substituted carbene ligand was chosen for the three- coordinate complex. The synthesized complexes were characterized successfully by mass spectrometry and nuclear magnetic resonance spectroscopy. The fruitful results will be documented in due course of time.

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