CHAPTER–2

Materials and methods

Materials and Methods

2.1. Introduction

This chapter highlights the details of materials and experimental techniques used in synthesis as well as characterization of organic ligands, their metal complexes, coordination polymers (CPs) and Metal-Organic Frameworks (MOFs). The current chapter also describes the details of different techniques used for obtaining single crystals of organic ligands, CPs and MOFs. Various analytical methods, which are used to characterize and analyse the structure and properties of the compounds are described. Software used for data interpretation are listed and details of theoretical studies performed for some of the compounds are also included in this chapter.

2.1.1. Instrumental details

Elemental Analysis (**EA**), Fourier Transform Infrared (**FTIR**), Nuclear Magnetic Resonance (**NMR**), High Resolution Mass Spectrometry (**HRMS**), Powder X-ray Diffraction (**PXRD**), and Single Crystal X-ray Diffraction (**SCXRD**) studies were used for characterization of synthesised organic ligands, metal complexes, CPs, and MOFs. Atomic Absorption Spectroscopy (**AAS**) and Electron Dispersive X-ray Spectroscopy (**EDX/EDS**) were used for quantitative and qualitative measurements of the constituents present in a compound, respectively.

Field Emission Scanning Electron Microscope (**FE-SEM**) was used for morphology study. Thermal Gravimetric Analysis (**TGA**) was performed to determine the thermal stability of compounds. UV-Visible Spectrophotometer and Fluorometer were utilized for photophysical studies. Instrument Quanta-phi, which is a part of fluorometer, was used for measuring the absolute quantum yield of the compounds in solid and solution states. Time Correlated Single Photon Count (**TCSPC**) was used for excited state lifetime measurements.

Impedance Analyser (**IA**) and Superconducting Quantum Interference Device (**SQUID**) were used for conductivity and magnetic measurements, respectively. High Pressure Reactor Autoclave (**HPRA**) was used to synthesise MOFs.

Primary lab equipment such as magnetic stirrer, rotary evaporator, hotplate, centrifuge, sonicator, pH meter, microscope etc., were used for routine research purpose. The instrumentation details including the parameters applied to characterize the organic ligands, metal complexes, CPs, and MOFs are documented in this chapter. Table 2.1 shows the summary of instrumentation details.

Table 2.1: Instrumentation details

Instrument(s)	Model Number (Make)	Purpose	Department (BITS/Others)
1. FTIR	MB-3000 (ABB) IRAffinity 1S (Shimadzu)	Functional group characterization	Department of Chemistry, BITS Pilani, Pilani Campus
2. NMR	AVANCE III 400 MHz (Bruker)	^1H, ^{13}C spectra and 2D NMR	Central Facility, Pilani Campus
3. HRMS	6545 Q-TOF LC/MS (Agilent)	Mass spectra	Department of Chemistry, BITS Pilani, Pilani Campus
4. UV-Visible Spectrophotometer	V-650 (Jasco) UV-2450 (Shimadzu)	Absorption spectra of compounds in solution or solid state	
5. Fluorometer	Fluorimax-4 (Horiba)	Fluorescence	
6. Quanta-phi	Quanta-phi	Quantum yield measurements	
7. TCSPC	Fluorocube -01-NL(Horiba)	Excited state lifetime	
8. AAS	AA-7000 (Shimadzu)	Atomic Concentration	Department of Chemical Engineering, BITS Pilani, Pilani Campus
9. TGA	TGA4000 (Perkin Elmer)	Thermal stability	
10. TGA	TGA-50 (Shimadzu)	Thermal stability	Central Analytical Laboratory, Pilani Campus
11. Elemental Analyzer	Vario Elemental Analyzer	Elemental analysis, percentage of C, N, O	
12. EDX 13. SEM	Apreo LoVac (Leica Ultra Microtome) EMUC7, 127 eV on Mn-Kα	Atomic Concentration and Morphology	Central Facility, Pilani Campus
14. PXRD	Rigaku miniflex 11, λ =1.54 Å, Cu Kα	Crystallinity, Purity, diffraction angle, plane	Department of Physics, BITS Pilani, Pilani Campus
15. Impedance	IM3570-HIOKI	Conductivity	
16. SCXRD	Bruker Kappa APEX II diffractometer MoKα	Crystal Structure	IISER Mohali
17. SCXRD	Bruker AXS D8 QUEST ECO (MoKα)		Ramakrishna Mission Kolkata
18. SQUID	MPMS ever cool magnetometer	Magnetism	IIT Roorkee
Lab equipment(s)			
1. High Pressure Autoclave Reactor	Autoclave Engineering	Hydrothermal/Solvothermal reactions	Department of Chemistry, BITS Pilani, Pilani Campus
2. Hotplate	Macro Scientific Pvt.Ltd	Reactions	
3. Centrifuge	Myfuge Mini micro Centrifuge	Separation	
4. pH meter	Systronics 335	To measure acidity and basicity	
5. Rotary evaporator	Heidolph	Evaporation,	
6. Sonicator	Leela Electronics	Dissolution	
7. Microscope	Zeiss Optical Microscope	To check crystal quality and for Imaging	

2.1.2. Details of software used for data analysis

The following licensed and free software were used for data analysis and interpretation:

1. OriginPro 9
2. Chemdraw 19.0
3. MestReNova 10.0
4. Endnote X7

5. Gaussian-09
6. Mercury-4.0.0
7. ORTEP-3, Windows Ver. 2014.1
8. HighScore plus

IR, UV-visible, Fluorescence, PXRD, lifetime, magnetic and impedance data were plotted using OriginPro software. Chemdraw was used for drawing molecular structures, schemes and figures. NMR data was processed and reported using MestRenova software. All references in this thesis were added using EndNote reference manager. Gaussian-09 was used for density functional theory (DFT) calculations. Crystal structure images were generated using mercury software. ORTEP-3 software was used to generate Oak Ridge Thermal Ellipsoid Plots (ORTEP). Highscore plus was used for PXRD data analysis.

2.2. Purchased chemicals, reagents and solvents

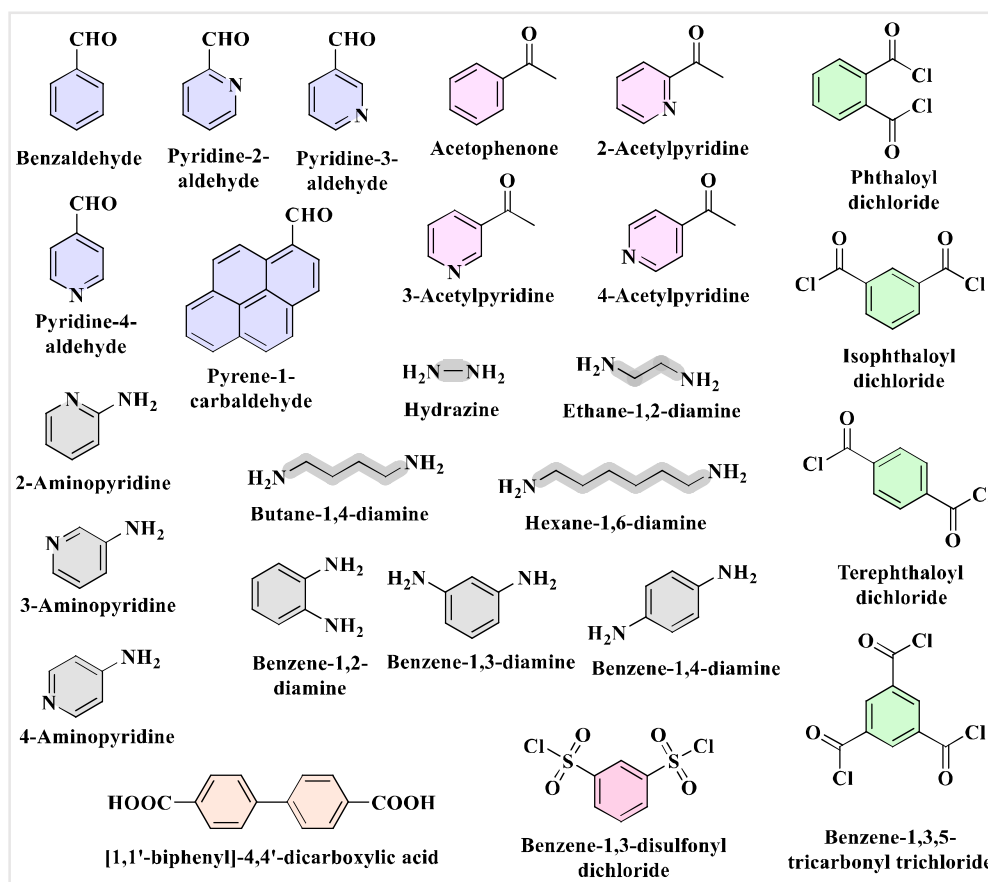Various organic chemicals used as precursors for synthesis of organic ligands are shown in Figure 2.1.

Figure 2.1: Purchased chemicals which were used as precursors for the synthesis of organic ligands

Metal salts used for the synthesis of metal complexes, CPs, and MOFs

1. Sodium(I) chloride
2. Potassium(I) chloride
3. Calcium(II) chloride
4. Magnesium(II) nitrate
5. Barium(II) chloride
6. Strontium(II) nitrate
7. Manganese(II) chloride
8. Chromium(III) chloride
9. Iron(II) sulphate
10. Iron(III) nitrate
11. Iron(III) chloride
12. Cobalt(II) nitrate trihydrate
13. Cobalt(II) nitrate hexahydrate
14. Nickel(II) nitrate hexahydrate
15. Nickel(II) chloride hexahydrate
16. Copper(II) nitrate hexahydrate
17. Copper(II) nitrate trihydrate
18. Copper(I) iodide
19. Copper(II) perchlorate hexahydrate
20. Copper(II) sulphate
21. Zinc(II) nitrate hexahydrate
22. Lead(II) nitrate
23. Mercury(II) nitrate
24. Cadmium(II) nitrate tetrahydrate
25. Cadmium(II) chloride
26. Silver(I) nitrate
27. Potassium(I) thiocyanate
28. Sodium(I) azide

Other chemicals used in the thesis work include:

1. Organic dyes

   a. Methylene blue
   b. Rhodamine B
   c. Methyl orange
   d. Malachite green

2. For guest inclusion studies in CPs/MOFs:

   a. Iodine
   b. Benzotriazole
   c. Benzene
   d. Naphthalene
   e. Pyrene
   f. Anthracene
   g. Benzonitrile
   h. Nitrobenzene
   i. o-/m-/p-Xylene
   j. Toluene

3. Quinine sulphate was used as reference for quantum yield measurements

4. Solvents:

   a. Methanol
   b. Chloroform
   c. Dichloromethane
   d. Tetrahydrofuran
   e. Hexane
   f. Ethyl acetate
   g. Acetonitrile
   h. Acetone
   i. 1,4-Dioxane
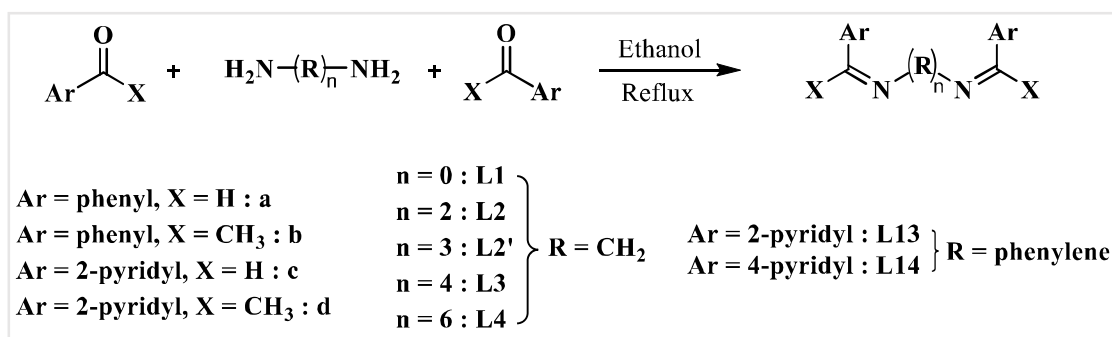   j. Dimethylformamide
   k. Dimethylsulfoxide

2.3. Synthesis of organic ligands

Various imine, amide and sulfonamide functionalised ligands have been synthesised during this thesis work, which were further utilized in preparing metal complexes, CPs and MOFs. The organic ligands synthesized in this thesis are listed in Table 2.2 and details of their synthesis are given in the respective chapters.

| Chapter	Ligand class	Organic ligands
	Table 2.2: List of synthesised organic ligands	
3A	Bis(aryl)-di-imine	**L1a**, **L1b**, **L2a**, **L2b**, **L3a**, **L3b**, **L4a**, **L4b**
3B	Bis(pyrenyl)-di-imine	**L5a**, **L6a**, **L7a**, **L8a**, **L9a**
3C	Bis(pyridyl)-disulfonamide	**L10b**, **L11b**, **L12b**
4A	Bis(pyridyl)-di-imine	**L3c**, **L2′c**, **L4c**, **L13c**
4B	Bis(pyridyl)-di-imine	**L2c**
5	Bis(pyridyl)-diamide	**L15b**
6	Bis(pyridyl)-di-imine	**L14c**

2.3.1. Synthesis of ligands with imine groups in the spacer

These ligands were synthesised according to the literature procedure[1] by condensation of aldehyde or ketone with diamine as shown in Scheme 2.1. An ethanolic solution of diamine was added dropwise to an ethanolic solution of aldehyde or ketone followed by refluxing the reaction mixture for 5-6 hours. Acetic acid (2-3 drops) was used as catalyst in the synthesis of ligands **L13c** and **L14c**. The compounds **L1a** to **L4b** were isolated by evaporating of solvent and followed by recrystallisation from methanol.

Ar = phenyl, X = H : a
Ar = phenyl, X = CH$_3$: b
Ar = 2-pyridyl, X = H : c
Ar = 2-pyridyl, X = CH$_3$: d

n = 0 : L1
n = 2 : L2
n = 3 : L2'
n = 4 : L3
n = 6 : L4

R = CH$_2$

Ar = 2-pyridyl : L13
Ar = 4-pyridyl : L14

R = phenylene

**Scheme 2.1:** Aryl based imine spacer ligands

L2c, L2′c, L3c, **L4c, L13c**, and **L14c** were recrystallised from hexane. **L6a–L9a** were prepared by condensation of pyrene aldehyde with diamine spacers as shown in Scheme 2.2.[2] Diamine was added dropwise to an ethanolic solution of 1–pyrenecarboxaldehyde, followed by addition of catalytic amount of trifluoroacetic acid (TFA) (2-3 drops). The mixture was stirred for 24 hours under refluxing condition. Synthesis of **L5a** was carried out by following the same procedure, however, dimethylacetamide (DMA) instead of ethanol, was used as solvent and temperature was set at 90 °C. Synthesis and characterization details are provided in the subsequent chapters.
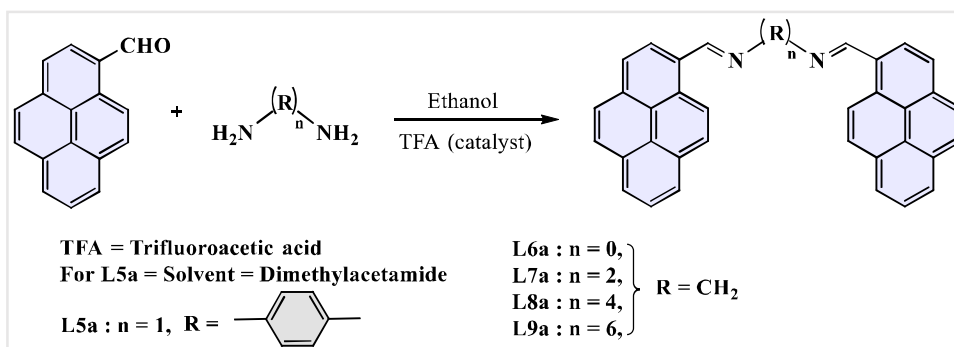
Scheme 2.2: Pyrene based imine spacer ligands

2.3.2. Synthesis of ligands with amide groups in the spacer

Diamide ligand **L15b** has been synthesised according to the literature procedure.[3] Solution of diacyl chloride in THF (15 mL) was added dropwise into solution of aminopyridine in THF (15 mL) which is kept at 0 °C (Scheme 2.3). To the above mixture, triethylamine (TEA) was added and stirred for 15 minutes while maintaining the temperature at 0 °C. Further, the reaction mixture was stirred for overnight at room temperature and filtered. The white precipitate obtained was washed with 50% ethanol-water mixture and dried under vacuum.
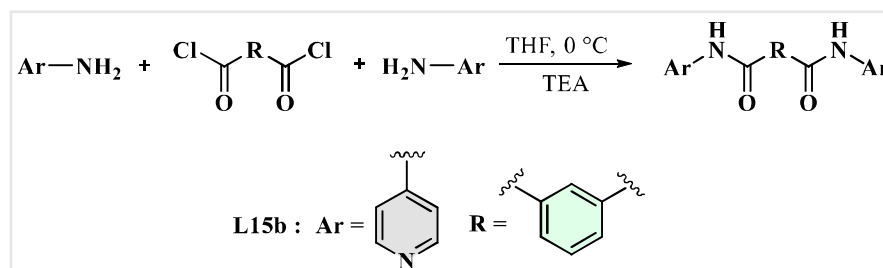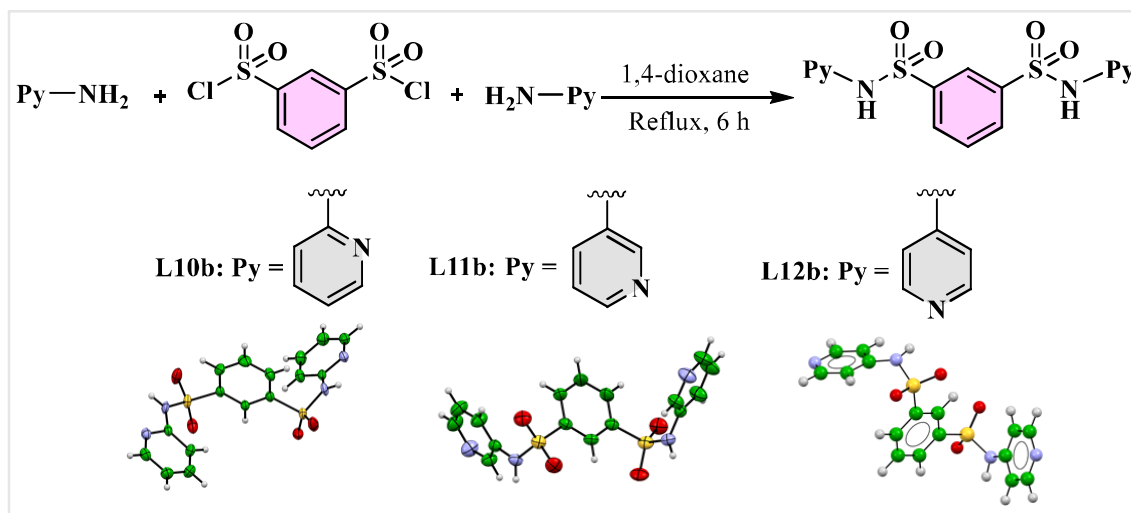

Scheme 2.3: Synthesis of ligands-based on amide spacers

2.3.3. Synthesis of ligands with sulfonamide groups in the spacer

L10b, L11b and **L12b** have been synthesised according to the literature procedure.[4] Aminopyridine was added to solution of disulfonyl dichloride in 1,4-dioxane in 2:1 molar ratio and refluxed for 6 hours (Scheme 2.4). The white solid residue formed was washed with cold water and recrystallised from ethanol. The synthesis details are given in Chapter 3C.

2.3.4. Synthesis of CPs/MOFs

Generally, CPs are synthesised by linking of organic ligands with metal ions in presence of solvent(s) using various techniques. Crystallization of CPs and MOFs will be influenced by various parameters (ligand to metal ratio, solubility, temperature, pressure, solvents, guest molecules).

Scheme 2.4: Synthesis of ligands based on sulfonamide spacers

Direct mixing of ligand and metal ion gives powder form of CPs due to rapid polymerization. Rate of reaction/polymerization is diminished by reducing the mixing time through various techniques, which results in the formation of crystalline nuclei. Further, these nuclei are kept under undisturbed condition until they grow into crystals, suitable for the Single crystal X-ray Diffraction (SCXRD) analysis. In this thesis, the following techniques/methods were used to synthesise the CPs/MOFs:

2.3.4.1. Layering technique[5]

In this technique, suitable solvents are chosen to dissolve the ligands and metal ions such that the ligand solution is denser than the metal ion solution or vice versa. Solution having higher density (ligand solution in this case) is kept at bottom side of the culture tube (Figure 2.2) and then, slowly less dense blank solvent was layered over the ligand solution to reduce the mixing time of ligand and metal ion solutions. Less dense metal ion solution is slowly layered on the blank solvent alongside the wall of culture tube. After that, culture tube is covered tightly by lid/aluminium foil and solution is left in undisturbed condition to allow slow diffusion of the

Figure 2.2: Synthesis of CPs in crystalline form through slow diffusion

components of lower density solvent into the higher density solvent. In this thesis, to synthesise amide group containing CPs, DMF was used for dissolving the amide ligands whereas ethanol/acetonitrile was used for dissolving the metal ions, and blank solvent was methanol. This technique also provides the CP crystal via in situ reactions like anion exchange, cation exchange etc.

2.3.4.2. Solvothermal technique[6]

In this technique, autoclave was used to synthesise the MOFs/CPs in crystalline form at high pressure and high temperature (Figure 2.3). The instrument contains a sealed teflon-lined autoclave vessel where the reaction mixture is kept and it is connected to temperature and pressure regulators. Reaction mixture includes ligand and metal salt in a solvent in some particular ratio and then the reaction was proceeded for 2-3 days in sealed tube. The parameters such as, pressure, temperature, solvent, concentration, time, and pH depend on the type of reaction.[7] Premixing and dispersion of the compounds in solvent were achieved through mechanochemical process and ultrasonication, respectively. In mechanochemical process, ligand and metal salt were grinded with 2-3 drops of solvent using a mortar-pestle for 15 minutes. The resulting mass was washed with solvent to remove the unreacted material and transferred into teflon-lined container along with minimum amount of solvent. This reaction mixture was kept at temperature 120 °C under N_2 atmosphere for 48-72 hours. After that, it was cooled to room temperature as slowly as possible like 5 °C/h or 10 °C/h. In this thesis,
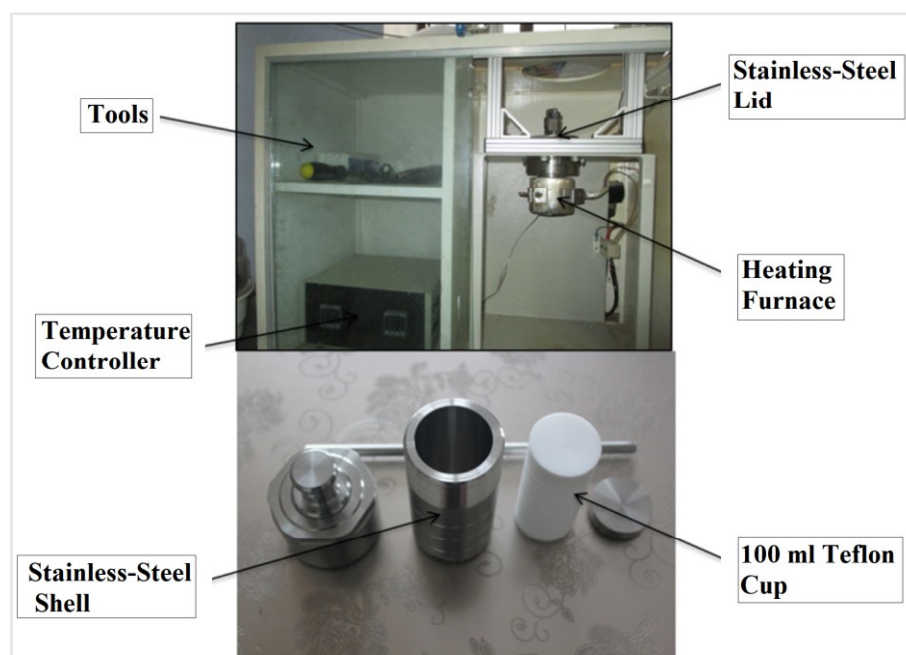

Figure 2.3: High pressure autoclave reactor for solvothermal synthesis of MOFs

mixed functionality (imine and dicarboxylate) based MOFs were synthesised under the solvothermal condition in DMF at 50 bar and 150 °C.

2.3.4.3. Conventional heating method

MOFs were synthesised mechanochemically then it was kept on hotplate for crystallisation. Ligands and metal salts were grinded in mortar-pestle for 15-20 minutes with 2-3 drops of solvent and then washed with solvent to remove the unreacted material. It was then transferred into 15 mL culture tube and 8 mL of solvent was added. The culture tube was covered with cotton ball and kept on hot plate at some particular temperature for 2-3 days in undisturbed condition, which resulted in the formation of crystals. In this thesis, mixed functionalised imine and dicarboxylate based MOFs were synthesised using this process in DMF at 150 °C.

2.3.4.4. Precipitation method

CPs are required in bulk amounts for analysis purpose. So, CPs were synthesised in powder form through the direct mixing technique. Ligand and metal salt solutions were prepared separately in large amounts according to their metal to ligand ratio and directly mixed by glass rod to get immediate precipitation of the CPs. In this thesis, several times we have synthesised powder form of the CPs and PXRD were matched with the parent crystals before analysis.

2.4. Instrumentation parameters and sample preparation methods

Choosing appropriate instrumentation parameters and sample preparation methods is important for characterisation of ligands/CPs/MOFs and analysis of their properties. Parameters selected for each instrument along with sample preparation techniques are described below:

2.4.1. Fourier transform infrared spectroscopy

IR spectra of ligands/complexes/CPs/MOFs required for qualitative analysis as well as functional group characterization were obtained from either ABB-Bomen AB-3000 or Shimadzu IRAffinity 1S FTIR instruments. These instruments have two types of sample mounting options, one is KBr pellet mount and another one is Attenuated total reflectance (ATR) mount. In KBr method, 2-3 mg of sample was grinded with 100 mg of dry KBr into a fine powder using mortar-pestle and then transferred into KBr pellet die to make pellet using KBr Press (Model MP-15) at pressure 2 ton. In ATR method, 1-2 mg of sample (powdered solid/liquid) is used directly for data collection. Percentage transmittance (%T) values for each wavenumber ($\bar{\upsilon}$) of incident IR radiation was recorded in the range of 400-4000 cm^{-1} and

corrected from the background data collected for either air (ATR method) or KBr (pellet method). Average spectrum of minimum 20 scans was processed through baseline correction and peak peaking. The peaks were labelled as very strong (vs), strong (s), medium (m) and weak (w) based on their intensity.

2.4.2. Nuclear magnetic resonance (NMR) spectroscopy

^1H, ^{13}C, COSY (Correlation Spectroscopy), NOESY (Nuclear Overhauser Effect Spectroscopy) and Selective NOE were carried out on 400 MHz NMR spectrometer (Bruker AVANCE III). This spectrometer is equipped with BBFO probe and auto sampler. Sample (5-12 mg) was dissolved in 0.6 mL of $CDCl_3$/ DMSO-d_6 and transferred into NMR tube. NMR tube was mounted on an autosampler holder and the spectra were recorded either in automation or manual mode. Before acquiring NMR data for the sample, the following steps were performed in order: solvent locking; tuning & matching (to set the magnetic field at 400 MHz); shimming (to distribute the magnetic field homogeneously); gaining (to adjust amplification of receiving signal) for better peak shape and resolution. All the data were processed using Bruker topspin software. Data is represented in terms of chemical shift (δ) in parts per million (ppm), multiplicity (s = singlet, d = doublet, t = triplet), coupling constant (J) and peak integration was done through MestReNova software.

2.4.2.1. Sample preparation for concentration dependent aggregation and complexation studies through NMR analysis

For concentration dependent NMR, a stock solution of ligand (1 M) was prepared in 0.5 mL of deuterated solvent. Further, 0.1 M solution was prepared by pipetting out 0.1 mL of stock solution and diluting it 10 times with same solvent (0.9 mL). Similarly, 0.1 M ligand solution was diluted 10 times to make 0.01 M solution. Finally, NMR spectra were recorded for the prepared ligand solutions (1 M, 0.1 M, 0.01 M).

For complexation NMR, stock solutions (0.1 M) of metal and ligand were prepared separately in 0.6 mL of deuterated solvent. Then these two solutions were mixed in different ratio (ligand:metal) such as 1:1, 1:2, etc. NMR spectra of above mixtures were recorded and compared with NMR spectrum of ligand.

2.4.3. High resolution mass spectrometry (HRMS)

Agilent LC-QTOF 6545 equipped with Electron Spray Ionisation (ESI)/Atmospheric Pressure Chemical Ionisation (APCI) source was used to mass analysis of the synthesised ligands and

complexes. The calculated m/z value of molecular ion was matched with experimentally found values.

2.4.4. Elemental analysis

The elemental composition in terms of weight% of carbon, nitrogen and hydrogen was obtained from CHN analyser and was matched with quantitatively calculated values. In this thesis, the CHN elemental analysis was done by Vario Micro V2 2.0 system.

2.4.5. Ultraviolet-Visible (UV-Vis) spectroscopy

UV-visible spectrophotometer gives information about amount of energy absorbed by a molecular chromophore when it goes from electronic ground state to excited state. Sample concentration, solvent polarity, solution pH, higher conjugation and complexation affect the absorbance as well as λ_{max} value. The instrument (Jasco V-650 UV-visible spectrophotometer) has deuterium lamp (D_2-lamp) and tungsten lamp for covering the range 190 - 350 nm and 350 - 1100 nm, respectively. The solution spectra were recorded in the range of 190 - 900 nm. The spectral data were acquired through the spectra manager software. Before analysis, all the parameters such as, photometric mode (absorbance/transmittance), measurement range (190-900 nm), scan speed (fast/medium/slow), etc., were set as per requirement. For solid sample, Shimadzu UV-2450 was used to record the spectra in the range of 190 to 800 nm. Here, 5 mg of solid sample was mixed with 500 mg of $BaSO_4$ and spectra were recorded whereas $BaSO_4$ act as reference. Different qualitative and quantitative experiments performed by using the UV-visible analysis are listed below:

2.4.5.1. Calibration method for determining the unknown concentration of guest molecule

Calibration plot was obtained by taking five standard solutions of a compound (guest molecule) having different concentrations. Absorbance was recorded using UV-visible spectrophotometer. Absorbance vs concentration graph was plotted at λ_{max} of corresponding compound (guest molecule). The unknown concentration of guest molecule was determined from calibration curve.

2.4.5.2. Mole ratio method[8] and Yoe-Jones method[9]

Among the various methods, the mole ratio (ligand: metal) and Yoe Jones (Figure 2.4) methods were used to determine the stoichiometry and stability constant of the complexes respectively.

In mole ratio method, ligand (or metal salt) solution of fixed concentration is titrated with metal salt (or ligand) solution and absorbance of solution at selected λ_{max} value was monitored. In this thesis, the concentration of ligand solution was kept constant, and concentration of metal ion solution was varied. Then absorbance vs mole ratio was plotted and from the graph the maximum absorbance point represents the binding ratio. The non-linear least square fit plot was drawn from titration data using origin software (Figure 2.4). In Yoe-Jones method, the straight lines tangential to experimental curve were extrapolated, and the intersection point is denoted as **A₀** which is maximum absorbance of complexation when degree of dissociation (α) of complex is zero (Figure 2.4). Binding constant (**K**) was determined by using equation 1 (Figure 2.5)
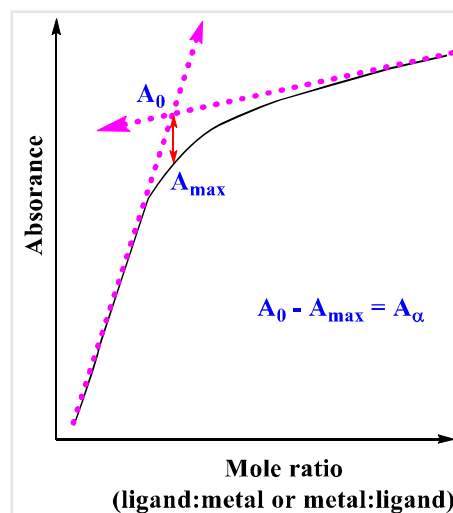

Figure 2.4: Yoe-Jones Method

$$M_mL_n \rightleftharpoons mM + nL$$

C	0	0	(initial)
$(1-\alpha)C$	$n\alpha C$	$m\alpha C$	(at equilibrium)

$$K = \frac{(1-\alpha)C}{(m\alpha C)^m \times (n\alpha C)^n} \quad \dashrightarrow \quad (1)$$

$$A_\alpha = \varepsilon b(\alpha C) \quad \dashrightarrow \quad (2)$$

$$\alpha = \frac{A_\alpha}{\varepsilon bC} \quad \dashrightarrow \quad (3)$$

$$A_\alpha = A_0 - A_{max} \quad \dashrightarrow \quad (4)$$

M = metal ion
L = ligand
m,n = stoichiometric coeffecients of metal and ligand, respectively
C = Initial concentration of complex
α = degree of dissociation
b = path length
ε = molar extinction coefficienct
K = stability constant
A_0, A_{max} = maximum absorbance of complex theoretical and experimental, respectively
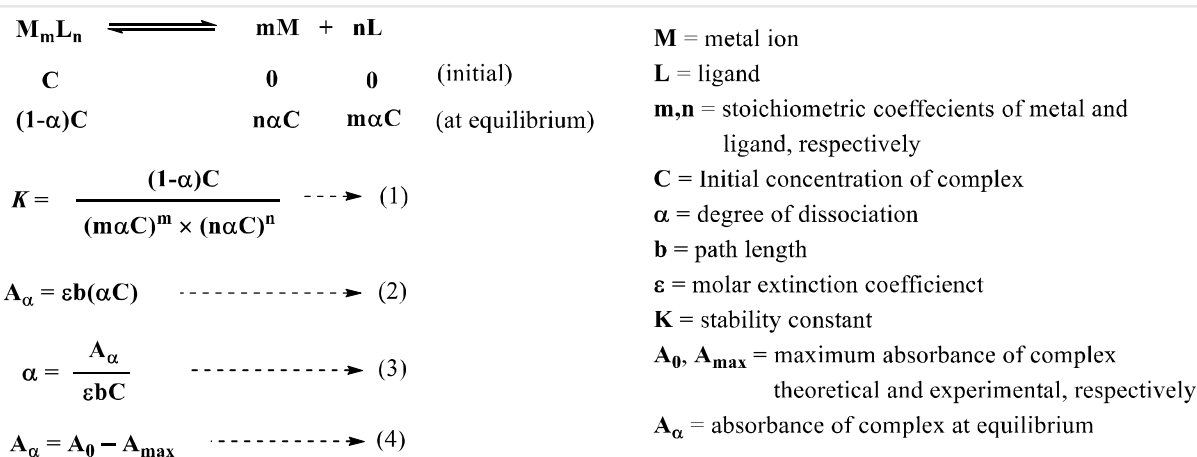A_α = absorbance of complex at equilibrium

Figure 2.5: Mathematical calculation for Yoe-Jones Method

2.4.5.3. Limit of detection (LOD) method

Efficiency of a sensor is measured in terms of LOD. According to the International Organisation for Standardisation, LOD is defined as 'the lowest quantity of a substance that can be distinguished from the absence of substance (blank value) within a stated confidence level'. For metal ion sensor, this indicates how much amount of metal ion that can be detected using minimum concentration of sensor.[10]

2.4.6. Fluorescence spectroscopy

Horiba Jobin Yvon Fluoromax 4 spectrofluorometer was used to record all the fluorescence experiments. Both qualitative and quantitative analyses of fluorescent molecule were carried

out. Before the analysis, the instrument was initiated and then connected to fluorescence software. Sample was irradiated by the excitation wavelength (λ_{ex}) wherein the starting and ending range of emission wavelength (λ_{em}) were given by the operator, the starting λ_{em} range should be 5/10 nm higher than the λ_{ex}. The λ_{ex} was decided from the λ_{max} of UV-visible spectra of corresponding molecule. Slit width was also changed to 2-7 nm according to the emission spectra. During excitation, sample absorbs the light and then emits the fluorescence that is collected by monochromator and the intensity was detected by the photomultiplier tube of the instrument (Figure 2.6). The quartz cuvette was used to take solution spectra and sample cell was used to take solid state spectra.
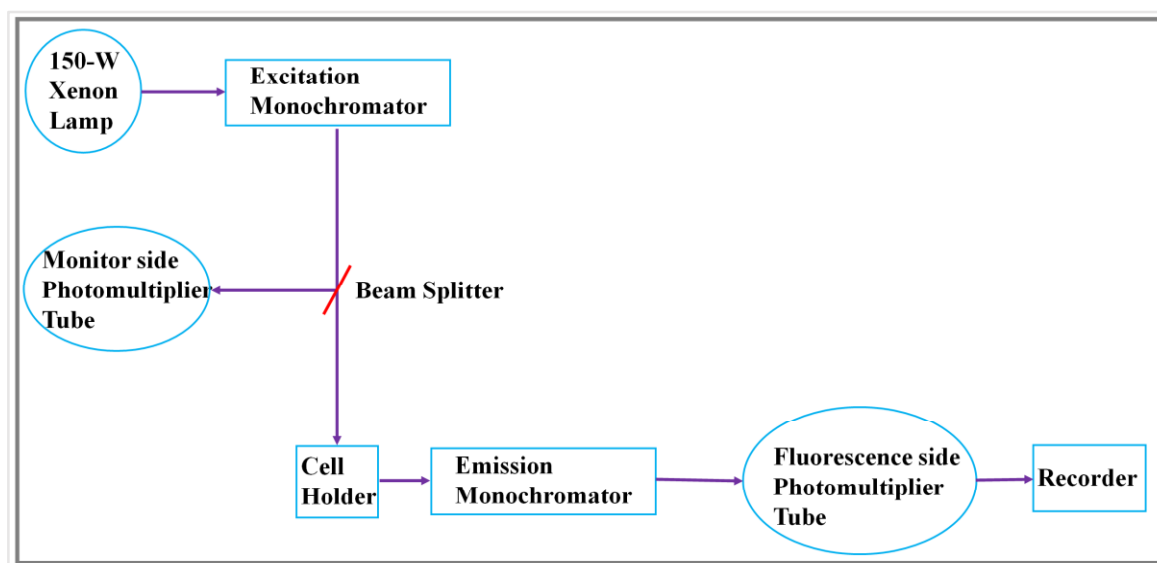

Figure 2.6: Schematic representation of instrumentation part of spectrofluorometer

2.4.6.1. Quantum yield calculation

Quantum yield is the fluorescence efficiency and is measured as number photons emitted divided by number photons absorbed. Fluorescence quantum yield was determined using optically matching solutions of quinine sulfate[11] ($\Phi_f = 0.546$ in 0.5 M H_2SO_4) as standard at an excitation wavelength of 345 nm. In solid state, the sample was kept directly in sample holder cup and then absolute quantum yield was recorded. Both solution and solid-state quantum yields were determined by assembling the quanta phi with the main instrument (Horiba Jobin Yvon Fluoremax-4).

2.4.6.2. Time correlated single photon counting (TCSPC) techniques

TCSPC technique was performed by the time resolved spectrofluorometer of Horiba Jobin Yvon fluorocube 01-NL to measure the lifetime of excited singlet state in picoseconds from

intensity decays. Picosecond diode laser of 375 nm (nanoLED 375L IBH UK) and 300 nm nanoLED, (nanoLED 300 nm IBH, UK) were used as light sources. Lifetime decay profile data was collected for each sample by setting wavelength to its emission λ_{max} and data for the prompt and sample plotted with respect to time (in nanosecond). The exponential time decay equation ($I(t) = \alpha_1 e^{-t/\tau_1}$, where $I(t)$ = intensity decay time, α_1 = pre-exponential factor and τ_1 = lifetime) is generated by the software automatically which decides the excited state lifetime of species.

2.4.7. Scanning electron microscope (SEM) and electron diffraction X-ray (EDX) spectroscopy

SEM and EDX analyses were performed by Apreo LoVac (Leica Ultra Microtome) EMUC7 model with 127 eV on Mn-Kα radiation. The morphology study was performed before and after complexation through the SEM analysis. EDX was performed to determine the atomic percentage of the metal in the sample. In this technique, X-ray source interacts with the sample to produce electron beam that can be used for the determination of the abundance of specific elements in the sample.

2.4.8. Atomic absorption spectroscopy (AAS)

AAS was carried out using AA-7000 (Shimadzu) instrument. Air/N_2O Acetylene flame was used for ignition purpose. In this thesis, AAS analysis was performed to determine the nickel and cadmium concentrations at ppm level in the real time samples. First, the instrument was calibrated for metal ion under analysis using internal standard. The relation between the absorbance vs concentration was established by means of external standard solutions, wherein, five different standard solutions (ppm) of nickel and cadmium metal ion were prepared for calibration. In case of analysing elemental compositions in CPs and MOFs, sample pre-treatment involving metal digestion process was carried out to break of the network of CPs/MOFs. During metal digestion, sample was treated with 1-2 mL of concentrated HNO_3 and the mixture was gently boiled until dense fumes appeared. Then the residue was diluted with milli-Q water to obtain specified concentration required for AAS.

2.4.9. X-ray diffraction (XRD)

X-ray diffraction techniques are used for the determination of molecular structure of crystalline solids. The ligands/complexes/CPs/MOFs are characterized using SCXRD and PXRD.

2.4.9.1. Single crystal X-ray diffraction (SCXRD)

Transparent and optically clear crystal is chosen with the help of microscope and it is mounted on diffractometer. X-ray beam interacted with the matter and resulted a 3D picture of electron density as dots. Positions of the atoms, chemical bond between the atoms and disorder in the crystalline solid are determined. The unit cell and cell parameters of the lattice structure of crystal are determined.

The single crystal XRD analysis of **CP1** and **CP2** was done at IISER Mohali, Punjab, using a Bruker Kappa APEX II diffractometer equipped with a CCD detector and sealed tube monochromated Mo-Kα radiation. The structures were solved by using the APEX2 program. By using the program SAINT for the integration of the data, reflection profiles were fitted, and values of F^2 and $\sigma(F^2)$ for each reflection were obtained. Data were also corrected for Lorentz and polarization effects. The subroutine XPREP was used for the processing of data that includes determination of space group, application of an absorption correction (SADABS), merging of data, and generation of files necessary for solution and refinement.[12] The structure was solved by direct methods and refined by least square methods on F^2 using SHELX-97.[13] Non-hydrogen atoms were refined anisotropically and hydrogen atoms were fixed at calculated positions and refined using a riding model. The single crystal structural information was deposited in the Cambridge Crystallographic Data Centre (CCDC numbers for **CP1** and **CP2** are 1981911 and 1981912, respectively).

The single crystal XRD analysis of **L5a**, **L10b**, **L11b** and **Zn-MOF** was done at Narendrapur Ramakrishna Mission, Kolkata, using a Bruker AXS D8 QUEST ECO diffractometer equipped with monochromatic Mo-target rotating anode X-ray and graphite monochromator α radiation with $\lambda = 0.71073$ Å by ω and φ scan technique. The integrated diffraction data, unit cell and data correction were performed by using Bruker SAINT system, SMART and SADABS respectively. The structure was solved by SHELXS-97 through direct method and refined by full matrix least squares based on F^2 through SHELXS-2018/3.[14] The hydrogen atoms were added at determined positions as riding atoms and non-H atoms were refined anisotropically.

2.4.9.2. Powder X-ray diffraction (PXRD)

PXRD were recorded with a Rigaku Miniflex II (Cu-Kα, $\lambda = 1.54$ Å) at room temperature. First, around 20 mg crystalline sample was dried, and grounded into powder using mortar-pestle. Then sample was transferred and homogeneously distributed on the sample holder. Finally, the

sample plate was placed into the instrument and intensity of diffracted X-rays was recorded for each 2θ value in the range 5-60° with scan speed 2°/min. Intensity vs 2θ plot represents the diffraction pattern. Sharp peak pattern is obtained for the crystalline sample where intensity represents the planar density and peak position refer to the planes. Also, other parameters such as planes (d_{hkl}), particle size (from full width at half maxima values for each peak), etc., are calculated. In this thesis, the experimental PXRD pattern of powder sample was matched with the theoretical PXRD which is generated from SCXRD data (using mercury software) and planes were determined by using the HighScore plus software.

2.4.10. Thermogravimetric analysis (TGA)

TGA 4000 Perkin Elmer and TGA-50 Shimadzu were used to analyse the thermal stability of the compounds. Around 10 mg of sample was taken in a platinum crucible and heated at a rate of 10 °C/min under N_2 atmosphere up to 800°C. First, sample weight was measured in inert weighing balance and then all the parameters such as heating rate, atmosphere and temperature range are given to the instrument. The corresponding weight loss was recorded with respect to temperature coefficient in TGA curve. In this thesis, % weight loss vs temperature TGA curve was used to determine the stability of the compound as well as composition of the decomposed solvent, guest, and ligand molecules from the CPs/MOFs. First derivative plot "derivative of weight % per minute vs temperature" was used to identify the different stages of decomposition.

2.4.11. Superconducting quantum interference device (SQUID) analysis

The magnetic measurements of **CP1** were performed at IIT Roorkee using MPMS ever cool SQUID magnetometer at constant magnetic field (1000 oersted) in the temperature range 1.9 – 400K. The SQUID is a very sensitive magnetometer used for measuring the magnetic property of the sample directly. In this device, two super conductors are separated by thin layers of insulator to form parallel Josephson junctions. The electrical current density depends on the phase difference ($\Delta\varphi$) between wave functions of two superconductors. This $\Delta\varphi$ value is manipulated by applying magnetic flux through the superconducting ring. This arrangement converts the magnetic flux into the electrical voltage. The basic working principle helps to understand the magnetic measurement. The pellet of polycrystalline sample (100 mg) was taken and recorded the magnetic susceptibility with respect to temperature. Magnetic field vs magnetic moment (emu) data were plotted in origin software. $\chi_m T$ vs magnetic field and $1/\chi_m$

vs magnetic field are plotted by conversion of magnetic moment value to χ_m in per Oersted (Oe) per mol.

2.4.12. Impedance analyser

The impedance measurements were carried out by placing a pellet of the sample between the silver electrodes at room temperature (25°C) and under wide frequency range 4 Hz–5 MHz using computer-interfaced HIOKI impedance analyser (Model IM3570). An impedance analyser is used to measure the complex electrical impedance as a function of frequency. Impedance (Z) is the resistance to the flow of an alternate current at a given frequency. Impedance is the complex quantity which is represented on a vector plane. This vector is the combination of the real
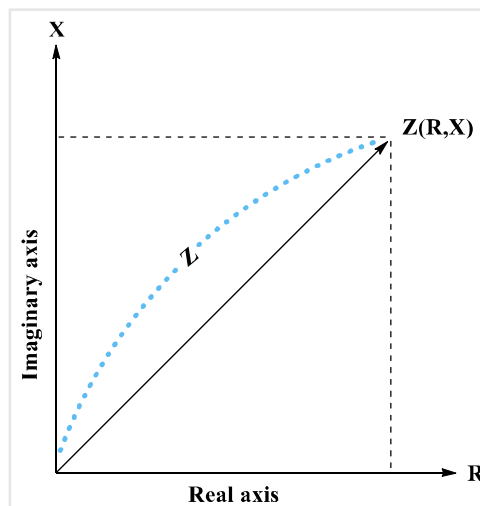

Figure 2.7: Representation of impedance complex quantity

part (Resistance, R) and the imaginary part (Reactance, X), as shown in the Figure 2.7. Basically, the impedance analyser creates frequencies at applied voltage and then measure the reproduced current in Ohms. Nyquist plot and Cole-Cole plot are used for the data analysis. These two plots are incorporated with real part and imaginary part in the graph. Nyquist plot is related to the frequency response parametric plot whereas Cole-Cole plot deals with polarisation of the component which is represented as imaginary part vs real part.

2.5. References

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