

ABSTRACT

The thesis entitled “**Crystal engineering of bis(aryl)-di-imines, bis(pyridyl)-diamides, bis(pyridyl)-disulfonamides and their metal-organic-frameworks (MOFs): Analysis of their photophysical properties, metal-ion sensing and application of MOFs in catalysis**” has been fragmented into seven chapters and deals with the synthesis of flexible as well as rigid type bis(aryl)-di-imine and bis(pyridyl)-diamide molecules containing alkylene to phenylene spacer wherein aryl is phenyl, 2-/3-/4-pyridyl and pyrene. It also includes the engineering of their metal-organic-frameworks (MOFs)/coordination polymers (CPs) with metal ions like Co(II), Cu(II) and Zn(II) in the crystalline form to study the detailed structural features by using the single-crystal X-ray diffraction technique.

Chapter 1 portrays a detailed study of the literature reports on the structure of MOFs/CPs and their properties based on networks. Basic understanding of supramolecular chemistry followed by illustration of crystal engineering was done in the chapter. This chapter describes use of crystal engineering in pre-designing the materials with desired properties and involvement of various non-covalent interactions in assembling the molecules into different types of MOF networks there by influencing their properties. Applications of MOFs/CPs such as gas adsorption, sensing, catalysis, etc. have been discussed and finally, aim of present thesis work has been stated in the end of this chapter.

Chapter 2 lists all the chemicals, instruments, laboratory equipment and software used for completing this thesis work. This chapter describes the procedures used for synthesis of ligands. It also contains the details of various crystallization techniques, qualitative and quantitative analysis methods that were being followed in this thesis work.

Chapter 3 has been further sub divided into three parts where correlation between the non-covalent interactions and photophysical properties of bis(phenyl)-di-imines (chapter 3A), bis(pyrenyl)-di-imines (chapter 3B) and bis(pyridyl)-disulfonamides (chapter 3C) has been explored.

Bis(phenyl)-di-imine molecules with alkylene spacer [ethylene (**L2a**, **L2b**), 1,4-butylene (**L3a**, **L3b**) and 1,6-hexylene (**L4a**, **L4b**)] have showed aggregation enhanced light-emission property in solid-state, while quenching was observed for bis(phenyl)-di-imine with hydrazine spacer (**L1a** and **L1b**). The photoluminescence spectra and the crystal structure have been

compared with bis(pyridyl)-ethylene-di-imine (**L2c**) and bis(pyridyl)-butylene-di-imine (**L3c**). The crystal structure analysis of the compounds has rationalized the observed results. The concentration-dependent ^1H NMR and NOESY spectra have supported the aggregation behaviour of the ligands.

In chapter 3B, the photophysical properties of bis(pyrenyl)-di-imines have been investigated in solution as well as solid-state. The light-emitting property has been controlled by tuning the length of alkylene spacer [ethylene (**L7a**), butylene (**L8a**), and hexylene (**L9a**)] in bis(pyrenyl)-di-imines. The aggregation-induced emission (AIE) has been observed at higher concentrations as well as in solid state in case of the compounds with alkylene spacer whereas no spacer (hydrazine group) (**L6a**) and phenylene (**L5a**) spacer have not shown any emission in solid-state like traditional pyrene excimer. The crystal structure analysis of **L5a** has explained its non-emissive nature in the solid-state. The aggregation caused quenching (ACQ) is turned into AIE *via* incorporation of flexible alkylene spacer in bis(pyrenyl)-di-imines. Further, formation of J-type aggregation has been supported by both the crystal structure analysis and bathochromic shift in UV-visible spectra.

In chapter 3C, the three new disulfonamides N^1, N^{β} -di(pyridin-2-yl)benzene-1,3-disulfonamide (**L10b**), N^1, N^{β} -di(pyridin-3-yl)benzene-1,3-disulfonamide (**L11b**) and N^1, N^{β} -di(pyridin-4-yl)benzene-1,3-disulfonamide (**L12b**) have been synthesised and their photophysical properties were studied. The photophysical properties of disulfonamide ligands and correlation of the structure-property relationship with their crystal structure have been discussed. Among three compounds, **L10b** and **L12b** have showed the ACQ effect, while interesting AIE phenomenon has been observed in **L11b** which is explained by the breakdown of ACQ effect due to its unique geometry.

Chapter 4 deals with metal-ligand interaction studies of bis(pyridyl)-di-imine derivatives (**L3c**, chapter 4A; **L2c**, chapter 4B) and application in metal-ion sensing in real samples.

In chapter 4A, the pyridyl based Schiff base compound, (1E,1'E)-N,N'-(butane-1,4-diyl)bis(1-(pyridin-2-yl)methanimine) (**L3c**) has been established as a highly selective and sensitive ratiometric chemosensor for Ni^{2+} and Cd^{2+} ions. Using Mole ratio and Yoe Jone's methods binding ratio of metal ions (Ni^{2+} and Cd^{2+}) with **L3c** has been found as 1:1, while binding constants for Ni^{2+} and Cd^{2+} of have been determined as 26.88×10^6 L/mol and 4.29×10^6 L/mol, respectively. The limit of detection of **L3c** in sensing Ni^{2+} and Cd^{2+} was observed to be 3.08 μM and 1.4688 μM , respectively. Further, interference of various other metal ions while

detecting Cd^{2+} and Ni^{2+} using **L3c** has also been studied with the help competitive reaction analysis. The sensor, **L3c**, has been applied in real-time application for the detection of nickel ion in river water samples.

In chapter 4B, the pyridyl based Schiff based compound, (1E,1'E)-N,N'-(ethane-1,2-diy)bis(1-(pyridin-2-yl)methanimine) (**L2c**) has shown as convenient colorimetric sensor (colourless to purple) for Fe^{+2} detection among a series of metal ions. Photoluminance studies have revealed quenching of fluorescence by the Fe^{+2} ion with appearance new peaks. Experimentally, binding ratio of **L2c** and Fe^{2+} has been determined as 1:2 with help of mole ratio method, and the binding constant of complexation has been calculated as $7.2 \times 10^{10} \text{ M}^{-2}$ using Yoe Jone's method. Limit of detection of **L2c** using colorimetric naked eye method is $25 \mu\text{M}$ and this method has also been applied for real samples analysis like tap water and river water. NMR analysis of Fe(II)-L2c complex supported the low spin of Fe(II) in complex. Structure of Fe(II)-L2c complex was optimized using Gaussian09 software through the B3LYP method with the charge state 4 and the spin multiplicity 1 by taking Fe(II) in low spin state. From these results, electronic properties were evaluated between Fe(II) and **L2c** by investigating energies of frontier molecular orbitals.

In chapter 5, a one-dimensional looped chain coordination polymer (**CP1**) has been synthesized by the reaction of Co(II) with N^{α},N^{β} -di(pyridine-4-yl)isophthalamide. Transmetalation reaction of **CP1** with Cu(II) showed single-crystal-to-single-crystal (SC-SC) transformation to form **CP2**, which is also a 1D looped chain. Both **CP1** and **CP2** showed the presence of DMF as guest molecules near the loops of the 1D chains. **CP1** and **CP2** were found to have band gaps of 2.41 eV and 1.30 eV, respectively, which were calculated by Tauc plot. The difference observed in the optical band gaps of **CP1** 2.41 eV and **CP2** 1.30 eV is reflected in photocatalytic dye degradation studies. It was observed that **CP2** showed much greater efficiency in degrading the dyes (Methylene blue, Methyl orange, and Rhodamine B) as compared to that of **CP1**. The polar nature of the loops of the chains in **CP1** and **CP2** due to the presence of DMF was exploited to study the adsorption and desorption of I_2 . Adsorption of I_2 in **CP1** and **CP2** was found to follow first-order kinetics with a rate constant of $8.32 \times 10^{-5} \text{ s}^{-1}$ for **CP1** and $9.71 \times 10^{-5} \text{ s}^{-1}$ for **CP2**. Guest inclusion reaction was performed to incorporate benzotriazole in the **CP1**. Impedance measurements showed a higher conductivity in the benzotriazole incorporated **CP1**.

Construction and structure analysis of a new 3-fold interpenetrated Zn-MOF $[C_{62}H_{38}N_4O_{14}Zn_3]_n$ using (1E,1'E)-*N,N'*-(1,4-phenylene)bis(1-(pyridin-4-yl)methanimine) (**L14c**) as pillar ligand and [1,1'-biphenyl]-4,4'-dicarboxylic acid (**4,4'-bp**) as co-ligand has been described in Chapter 6. The crystal structure analysis has revealed two types of coordination environments for three Zn atoms, in which one of them adopted octahedral (O_6) geometry, and the other two fitted in tetrahedral (N_1O_3) coordination environment. The metal core of **Zn(II)-MOF** has been surrounded by six molecules of **4,4'-bp** and two molecules of **L14c** resulting a paddle-wheel shaped secondary building unit (SBU). These SBUs have constructed a 2D triangle-and square-tessellated layers in a hex net which represents a pinwheel structure. A pinwheel is pillared by **L14c** and resulted in a 3D framework. This **Zn(II)-MOF** has also been established as a prominent catalyst for the Knoevenagel condensation reaction between an aldehyde and active methylene compound malononitrile where more than 90% conversion (with respect to malononitrile) has been observed within half an hour as monitored by gas chromatography.

Chapter 7 discusses the overall outcome of this thesis and gives overview of possible directions in which the present work can be extended in future.