Abstract of the Ph.D. thesis

Role of Supramolecular Interactions in the Construction of Coordination Polymers and their Applications

Faruk Ahmed

Roll No. 2012Ph.Da.CHM03

Department of Chemistry

Aliah University

Newtown, Kolkata-700 156

Supervisors: Dr. Md. Hedayetullah Mir and Dr. Seikh Mafiz Alam

Abstract

This thesis describes the synthesis and structural characterization of Cu(II), Zn(II) and Cd(II) metal coordination polymers (CPs). The PhD dissertation study focuses on (i) synthesizing CPs of interesting topologies, (ii) investigating the role of supramolecular interactions in the construction of CPs and (iii) Finding out the physical significance of the supramolecular interactions in terms of their application in gas adsorption and conductivity study. The thesis has been divided into 6 Chapters.

The chapter **1** provides the background research literature briefly to understand the rest of the chapters in the thesis, reviews the recent developments in CPs, and in crystal engineering and also to understand the aspects of supramolecular chemistry and the nature of various supramolecular interactions.

The role of halogen···halogen interactions in the construction of higher dimensional coordination polymers (CPs) and their impacts on sorption behavior has been revealed in chapter **2**. It has been observed that 2D sheet of CPs when fabricate 3D supramolecular architecture through type-I halogen···halogen interactions give rise to considerable amount of voids for exhibiting gas adsorption properties. For the first time, halogen···halogen interactions have been used as a tool in the construction of high-dimensional CPs for sorption studies.

Chapter **3** describes metal ion dependent charge transport properties in a series of linear isotypical 1D CPs based on Zn(II), Cd(II) and Cu(II) This chapter is divided into two sections. Section **1** discusses the cation dependent charge transport mechanism comparison between Zn(II) and Cd(II) based isotypical 1D CPs. The analysis indicates that the Cd(II) compound has higher mobility and diffusion length in comparison to the compound Zn(II) compound. Cd(II) compound, with larger cation and shorter H-bonding distance, shows the higher electrical conductivity and photosensitivity as compared to the Zn(II) compound.

For better performance of the device, Cu(II) based 1D CP was synthesized keeping the redox inactive ligand system almost same .This is discussed in section **2**. This material exhibits Schottky diode behavior and shows better electrical conductivity and charge transport property as compare to the above Zn(II) and Cd(II) compound for the application in active electronic device. This is may be due to the presence of square-pyramidal d^9 Cu(II) centres possessing loosely bound electrons.

Chapter **4** describes the formation of a Zn(II) based 2D Layer-Stacked CP and its application in photosensitive electronic device. Analysis of crystal structure and nucleus-independent chemical shifts (NICS) calculations revealed that the chelate ring can be a hydrogen acceptor in the C-H$\cdots\pi$ interactions and exhibit aromatic character. To the best of our knowledge, aromaticity of 14-member chelate ring is elusive. Interestingly, this compound exhibits photosensitivity with appreciable on-off ratio.

In chapter **5** encapsulation of Z-Shaped acyclic water tetramer and electrical conductivity of a Cu(II) based 2D CP is evaluated. This compound exhibits semiconductor nature and showing photosensitive Schottky diode behavior in the metal- CP junction.

Finally, the thesis ends with an overall conclusion and offers scopes for further investigations in this particular area of research.