

SYNOPSIS

The thesis consists of ten chapters. Chapter 1 reviews about the crystal engineering strategies in designing functional materials with predefined properties by the utilization of coordinate bonds as well as hydrogen bonds. The aim of this thesis is to apply the supramolecular synthon approach to assemble the coordination frameworks by introducing amide functionalities. For this purpose, exobidentate pyridyl based ligands with amide moieties as the spacers were selected. In these molecules, the pyridyl groups are expected to propagate coordination frameworks whereas the amide groups are expected to assemble these networks *via* N-H \cdots O hydrogen bond synthons. The interaction interference between amide and pyridyl functionalities was studied by analyzing crystal structures of pyridyl and amide containing moieties. These studies are discussed in Chapter 2. The synthesis of coordination networks of these ligands and the anion and guest exchange properties of the complexes are discussed in the subsequent chapters, with Chapters 3, 4-5 and 6 dealing with the 1D, open 2D- and 2D-interpenetrated networks respectively. The anion and guest exchange properties of materials that are described in chapters 3-6 are discussed in Chapter 7. The utilization of secondary building units in the construction of MOF's for this family of ligands are discussed in Chapter 8. Apart from the studies on the amide based ligands, the Ag(I) coordination networks of diamino-alkanes and exo bidentate ligands with imine groups as spacer are described in chapter 9. Rationalization of the overall results is described in chapter 10.

Chapter 1:

Introduction

Crystal engineering deals with the design of novel materials of specified architectures and properties. A thorough understanding of the intermolecular interactions, which controls the crystal packing, is the foremost goal in this context. Hydrogen bond with its combined effects of directionality and strength is an

indispensable tool in the supramolecular assembly. Strong hydrogen bonds like O–H···O, N–H···O, O–H···N and N–H···N play the major role in arranging the molecules in the crystal. Also the much weaker C–H···O and C–H···N interactions are important in determining the supramolecular architecture. The judicious use of the structure directing nature of hydrogen bonds can lead to varied novel frameworks.

Crystal engineering of metal-organic hybrid materials is relatively young area of research compared to the engineering of materials based on purely organic molecules. Metal-organic hybrid materials have several potential applications in the areas such as catalysis, conductivity, porosity, chirality, luminescence, magnetism, spin-transition and non-linear optics. Coordination polymers or metal-organic frameworks constitute the major share of these materials. Although the term coordination polymer was coined in 1964, the principles of “crystal engineering” for designing coordination polymers were not applied until 1995.

Although there are several studies on metal-organic hybrid materials that are purely based on coordination bonds and organic materials that are purely based on hydrogen bonds, the studies combining these two types of interactions are relatively rare. The combination of these two aspects are expected to achieve the more control over the network geometries in three-dimensions. This can be achieved by the design of the ligands containing functional groups capable of hydrogen bonds and coordination bonds. This chapter provides a brief overview on various types of hydrogen bonded synthons with a particular attention on amide-to-amide hydrogen bonds. Further, some of the existing metal-organic frameworks containing hydrogen-bonded synthons are discussed.

Chapter 2:

Structural Features of Bis(pyridylcarboxamido)alkanes: Effect of Pyridyl Groups in the Occurrence of Amide-to-Amide Hydrogen Bonds

A combination of various possible intermolecular interactions between the molecules results in their definite arrangements in the crystal packing. The key to