ABSTRACT

The thesis entitled, "**Strategic Design of Functional Metal Organic Frameworks (MOFs) based on Various N, N-donor Spacers and Dicarboxylates for Their Potential Applications**" has been divided into six chapters.

Chapter **1** gives a brief account of the areas which are of relevance in this thesis, *viz.* MOFs, functional MOFs, their applications in various fields and the scope of the present work.

Chapter **2** is divided into two sections. Section **A** deals with the self-assembly of a V-shaped organic linker and a flexible N, N-donor spacer with different transitions metal ions leads to the formation of seven new complexes as 2D or 3D MOFs. Structural analysis, polymorphism, SC-SC transmetalation and gas sorption studies are presented. In section **B**, two new 2D MOFs based on bent carboxylates and an unexplored N, N-donor spacer which contains imine and amide functionality as well were achieved for preferential CO_2 uptake over N_2 and CH_4 at ambient conditions.

Chapter **3** is divided into two sections. Section **A** deals with selective separation of CO_2 from N_2 and CH_4 by Zn-MOF with polar pore surface. High separation selectivity supported with high loadings in the mixed gas phase were achieved through IAST calculations. In section **B**, a water stable two-fold interpenetrating microporous 2D Co-MOF is presented for preferential CO_2 uptake over N_2 and CH_4 at ambient conditions with high IAST selectivities.

Chapter **4** deals with the syntheses of three new Co(II)-MOFs with different architectures under diverse reaction conditions. Structural analysis, CO_2/N_2, CO_2/CH_4, C_2H_2/CH_4 separation selectivities and magnetic studies are presented.

Chapter **5** is divided into two sections. Section **A** deals with selective CO_2 sorption over N_2 and CH_4 by a permanently microporous two-fold interpenetrated 3D Co-MOF. CO_2 loading amounts in mixed gas phases are quite high as estimated through IAST calculation and experimentally validated through the dynamic breakthrough study. In section **B**, a strategic approach to induce moisture stability and high CO_2 binding affinity and hence separation selectivity exhibited by a 2D microporous Zn-MOF with polar -SO_2 functionality is presented. At ambient conditions, high CO_2/N_2 and CO_2/CH_4 gas mixture selectivities were achieved both from IAST method and real time dynamic breakthrough experiments with high CO_2 loadings in binary gas phases.

Chapter **6** describes a phosphate-based Ag-bipyridine 1D MOF with free phosphoric acid, its conjugate bases, and free water molecules into the crystal structure as superprotonic conductor. Crystallized dihydrogen phosphate anoins, free phosphoric acid, and water molecules are linked by extended hydrogen bonds, forming a 2D hydrogen-bonded network and exhibits the proton conductivity value of 3.3×10^{-3} S cm^{-1} at 80 °C and 95% RH.

The thesis ends with a summary and provides the scopes for the further research in these areas.

Keywords: *CO_2 separation, Gas sorption, Gas separation, Transmetalation, Magnetism, MOFs, Polymorphism, Proton Conduction.*