

ABSTRACT

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Title of the Thesis: Some Metal-Organic Framework Compounds: Synthesis, Structure and Studies on Physico-chemical Property

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The thesis entitled “**Some Metal-Organic Framework Compounds: Synthesis, Structure and Studies on Physico-chemical Property**” presents a glimpse of recent advances in the field of metal-organic framework (MOF) for their large applicability in a fundamental and industrial perspective. The work includes the synthesis of different carboxylate linker or mixed-linker based MOF, their characterization and application in gas storage and separations, heterogeneous catalysis and luminescence sensing.

The thesis comprises of seven (7) chapters as follows:

Chapter 1 introduces the general discussion on the multiple features of metal-organic frameworks (MOFs), numerous practices to design diverse functional MOFs, key role of the various carboxylate linkers in the adaptability of MOFs, involvement of transition metals to design carboxylate based and mixed-linker based MOFs while a variety of spacer has been used, application of MOFs in heterogeneous catalysis and the role of MOF solids in heterogeneous catalytic condensation reactions and epoxidation reactions; selective gas adsorption studies, luminescence properties etc. Scope of the current research and the summary of the research works have also been presented.

Chapter 2 accounts synthesis of a hydrogen-bonded 3D supramolecular network constructed by two-dimensional cadmium(II) layer. Two-dimensional cadmium(II) based coordination polymer $[Cd(abb)H_2O]_n$ (**1**) [$abb = 3,3'$ -azobis(benzoate)] has been synthesized by hydrothermal method. Notably, $[Cd(abb)H_2O]_n$ exhibited unprecedented high uptake of hydrogen and also displayed moderate uptake capacity of other small gas molecules like CO_2 , N_2 etc. In addition, photoluminescence property of $[Cd(abb)H_2O]_n$ also has been explored.

Chapter 3 discloses synthesis of quinoline derivative containing monomeric and polymeric metal carboxylates that displayed gas sorption over a 2D layered framework. Supramolecular metal-carboxylate framework $[Co(mqc)_2]_n$ (**2**), and another monomeric compound $[Zn(mqc)_2(H_2O)]$ (**3**) ($mqc = 4$ -methoxy-2-quinolinicarboxylate) have been synthesized solvothermally and characterized by single crystal X-ray diffraction. Compound **2** is a 2D coordination polymer, further extended to a 3D

porous supramolecular network having void space in between each 2D layers. Compound **2** displayed noticeable gas uptake capacity of both CO₂ and H₂ compared to other gas molecules. While compound **3** is a simple monomer, extended to a one-dimensional chain like structure through strong intermolecular hydrogen-bonding.

Chapter 4 deals with the structural diversity and inter-conversion among four hydrothermally synthesized metal carboxylate compounds, $\{[\text{Mg}(\text{H}_2\text{O})_6][\text{Cu}(\text{pdc})_2]\cdot 2\text{H}_2\text{O}\}_n$ (**4**), $\{[\text{CuMg}(\text{pdc})_2(\text{H}_2\text{O})_4]\cdot 2\text{H}_2\text{O}\}_n$ (**5**), $\{2(\text{Him})\cdot [\text{Cu}(\text{pdc})_2]\}_n$ (**6**), and $\{[\text{Cu}(\text{pdc})(\text{im})_2]\cdot 2\text{H}_2\text{O}\}_n$ (**7**) (pdc = pyridine-2,5-dicarboxylate and im = imidazole). Compounds **4-7** were synthesized respectively from 1, 2, 3 and 4 mmol of imidazole. Compound **6** revealed a polymeric ribbon like 1D chain structure and catalyzes olefin epoxidation reaction in heterogeneous condition. In catalytic study, H₂O₂ acts as an oxidizing agent. Notably, cyclooctene was effectively converted to epoxy-cyclooctane with *ca.* 100% selectivity and conversion.

Chapter 5 reports a three-dimensional mixed-linker zinc-based porous MOF, $[\text{Zn}_2(\text{H}_2\text{O})(\text{nic})(\text{pzdc})]_n \cdot n\text{H}_2\text{O}$ (**8**), (pzdc = pyrazole-3,5-dicarboxylate and Hnic = isonicotinic acid) which has been synthesized by availing hydrothermal route. The as-synthesized MOF has large solvent accessible void space (~ 15.9%) which is enhanced to ~ 34.1% upon dehydration. The framework compound and its dehydrated product both displayed highly selective CO₂ adsorption over other small gas molecules at low partial pressure. The selectivity of CO₂ adsorption is well interpreted by computational methods, molecular dynamics and grand canonical Monte Carlo simulations. The adsorption capacity of MOF has been calculated theoretically that follows the order: MOF-CO₂>MOF-CH₄>MOF-N₂>MOF-H₂.

Chapter 6 describes the synthesis of two structurally diverse 3D mixed-linker cadmium-based metal-organic frameworks (MOFs), $[\text{Cd}_2(\text{pzdc})_2(\text{azpy})_{0.5}(\text{H}_2\text{O})]_n$ (**9**) and $\{[\text{Cd}_3(\text{pzedc})_2(\text{azpy})_2]\cdot \text{H}_2\text{O}\}_n$ (**10**) (pzdc = pyrazole-3,5-dicarboxylate, pzedc = pyrazolate-3,5-dicarboxylate and azpy = 4,4'-azopyridine) through solvothermal method. Both the frameworks (**9**) and (**10**) showed a pillared-layer structure. Photoluminescence properties of both the MOFs have been investigated in solid state as well as in different solvent medium and both displayed “turn on” and turn off” type of responses in specific solvent with selectivity.

Chapter 7 reports the noteworthy attainments of the effort embodied in the present thesis.

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