ABSTRACT

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Title of the Thesis: **Investigation into Some Metal-Organic Frameworks: Synthesis, Structural Studies and Exploration of Catalytic Property**

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The thesis entitled **"Investigation into Some Metal-Organic Frameworks: Synthesis, Structural Studies and Exploration of Catalytic Property"** presents a glimpse of recent advances in the field of heterogeneous catalysis by lanthanide-based metal organic frameworks. The major emphasis is given on the synthesis, structural characterization of framework compounds, and catalytic C–heteroatom bond forming reaction under heterogeneous condition.

The thesis comprises of six (6) chapters as follows:

Chapter 1 introduces the general discussion on the diverse features of metal-organic frameworks (MOFs), numerous synthetic procedure to design diverse functional MOFs, key role of the different carboxylate linkers in the adaptability of MOFs, involvement of transition metals to design carboxylate based MOFs while a variety of spacer has been used; application of MOFs in catalysis and the role of MOF solids in catalytic reactions such as C-heteroatom, C-N bond forming reactions; selective gas adsorption studies, luminescence properties, proton conductivity etc. Apart from transition metal based MOFs, vast application of different lanthanide or rare-earth based MOFs (Ln/RE-MOFs) in catalysis has been briefly discussed. Scope of the current research and the summary of the research works have also been presented shortly.

Chapter 2 discloses synthesis of a robust and thermally stable three dimensional Gd-MOF, $\{[Gd_4(NDC)_6(H_2O)_6]\cdot 2H_2O\}_n$ **(**MOF-**1)**. This 3D Gd-MOF has been synthesized by hydrothermal route and different physical characterization have been described. Attractively, this $\{[Gd_4(NDC)_6(H_2O)_6]\cdot 2H_2O\}_n$ is capable of catalyzing the O-arylation reaction efficiently between substituted phenol and bromoarene under heterogeneous condition at 80°C to afford unsymmetrical diarylethers. In addition, thermogravimetric analysis demonstrates that the mass of MOF-**1** remains constant until ~530°C after its dehydration under nitrogen atmosphere which is in agrement with the robust character of this Gd-MOF.

Chapter 3 reports the synthesis of novel lanthanide based two-dimensional metal-organic framework (MOF) compound $[Dy(NDC)(NO_3)(DMA)_2]_n$ (MOF-**2**) [H_2NDC=2,6-naphthalenedicarboxylic acid and DMA = N,N-dimethylacetamide]. MOF-**2** has been synthesized by solvothermal route and the structure has been solved through single-crystal X-ray diffraction study. Structural analysis reveals that MOF-**2** possesses a two-dimensional framework system. A "Paddle-wheel" like unit represents the core of the 2D network structure. Such type Paddle-wheel core unit is scarcely found amongst

rare-earth MOFs. The morphology of the MOFs as well as different types of weak interactions possessed by the framework have been assessed using Hirshfeld surface analysis and fingerprint plots have been drawn to understand various interactions. Notably, $[Dy(NDC)(NO_3)(DMA)_2]_n$ (MOF-**2**) catalyzes C–N coupling reaction between aryl-halides and amines under heterogeneous condition.

Chapter 4 deals with the synthesis of two novel lanthanide MOFs with formula $[Tb(NDC)(NO_3)(DMA)_2]_n$ (MOF-**3**) and $[Ho(NDC)(NO_3)(DMA)_2]_n$ (MOF-**4**) [where NDC= dinegative 2,6-naphthalenedicarboxylate ligand and DMA = N,N-dimethylacetamide]. Both of these two MOFs have been synthesized by solvothermal process with subtle change in synthesis procedure. SC-XRD analysis reveals that structure of these two MOFs are largely the same and morphology of the two and different types of weak interactions possessed by the framework have been confirmed using Hirshfeld surface analysis (HS) and subsequent supplementary pseudo-mirror 2D fingerprint plot. MOF-**3** and MOF-4 have been tested as heterogeneous catalysts for O–arylation reaction that affords unsymmetrical diarylethers. Both of them are capable of catalyzing O–arylation reaction efficiently between substituted phenols and different substituted bromobenzene under heterogeneous condition at 95°C. The product yield obtained for MOF-**3** is higher than MOF-**4** catalyst.

Chapter 5 describes an unprecendentent in situ decarboxylation-hydroxylation reaction of 3-hydroxy-2-quinoxalinecarboxylic acid catalyzed by lanthanide metal in hydrothermal condition under autogeneous pressure in teflon lined Parr-acid digestion bomb. 3-hydroxy-2-quinoxalinecarboxylic acid is converted into 1,4-dihydroquinoxaline-2,3-dione (DQD). Apart from spectral characterization like IR and NMR spectroscopic and HRMS analysis the authenticity of hydroxylated derivative has been established by single crystal X-ray structure solution of the ligand. Besides, *in-situ* generated hydroxylated ligand affords lanthanide metal-organic framework compounds of Gd, Ho, Er and Yb (MOF-**5**, MOF-**6**, MOF-7 and MOF-**8** respectively). All these four MOFs have been characterized by single-crystal X-ray diffraction and their structures have been established. Notably, this work represents an unusual reaction (decarboxylation-hydroxylation catalyzed by lanthanides) and this is the first example of Ln-catalyzed decarboxylation hydroxylation.

Chapter 6 reports the noteworthy attainments of the effort embodied in the present thesis.

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