ABSTRACT **Index No. 185/16/Phys./25**

Title of the Thesis: Design, synthesis and study of functional properties of some novel metal organic materials using crystal engineering approach

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The present thesis depicts the design and synthesis of some novel transition or lanthanide metal-based metal organic materials exploiting the covalent and noncovalent interactions through crystal engineering approach and in-depth study of their crystal structure, catalytic activity, magnetic property, host-guest behavior and enzymatic activity as per the functional properties expected to be evolved according to their structure-property relationship. This thesis deals with the following new functional metal organic materials.

(i) Design and synthesis of a novel two dimensional MOF, $\{[Ni^{II}(squarate)(2,2'\text{-bipy})(H_2O)]\cdot H_2O\}_n$, [squarate = 3,4-dihydroxycyclobut-3-ene-1,2-dionate, 2,2′-bipy = 2,2′-bipyridine] exhibiting a very rare μ-$_{1,2,3}$ squarato bridging has been presented. The study of structural, thermal, magnetic and optical properties of the sample was performed. This framework exhibits antiferromagnetic behavior and photo-luminescent activity and also can act as a metal-organic supramolecular host (MOSH).

(ii) The design, synthesis, crystal and supramolecular structure of a Pr (III)-complex, $\{[Pr(1,10\ phen)_2\ (H_2O)_5]\ Cl_3(H_2O)\ (CH_3OH)\}$, incorporating a 2D water-chloride-methanolic supramolecular sheet has been reported. The coordination tendency of the Pr(III) ion and the self-assembling tendency of water-chloride and methanol stabilize the system, making strong affinity of the host towards the guest molecules. Thus, the supramolecular metal-organic polymer (SMOP) can behave as a dynamic supramolecular metal-organic host with expulsion and absorption of water molecules upon heating and cooling. The breathing nature of the system had been established by powder X-ray diffraction method.

(iii) Thermal, redox, photoluminescence behavior and catalytic activity of newly synthesized oxalato bridged binuclear Cu (II)-complex: $[Cu_2(oxalate)(1,10phen)_2Cl_2]$ has been studied. This sample exhibits high product selective catalytic activity towards the corresponding epoxide in the oxidation of a series of alkenes in presence of green oxidant H_2O_2.

(iv) The design, synthesis, structure and exploration of a metamagnetic behavior of a mononuclear Mn(III)-Schiff base complex :$[Mn(L)(H_2O)Cl]$ and a trinuclear Mn_2Fe complex:$\{[Mn(L)(H_2O)]_2Fe(CN)_6\}^2$ (L= Schiff base ligand) has been done. This report presents

a unique example of an inorganic reaction where a selective metal-ligand bond undergoes dissociation assisted by the formation of intermolecular π-π and H-bonding interactions leading to the formation of the trimeric metamagnetic complex from a monomeric metamagnetic precursor for the first time.

(v) The design, synthesis, magnetic properties and bio-catalytic activity of a flying bee-like double phenoxido bridged dimeric Mn^{III}-Schiff base complex decorated with double dicyanamide (dca^-) ligands and formulated as: $[Mn_2(L)_2(dca)_2]$ (where H_2L = 2,2′ -((1E,1′E)(ethane-1,2-diylbis(azanylylidene))-bis(ethan-1-yl-ylidene)) diphenol) has been reported. This complex is the first reported dimeric Mn^{III} complex of a Schiff base ligand having two terminal dca^- ligands. The present study reveals that in presence of tetradentate Schiff base ligands, the use of a 1:2 Mn: dca^- ratio leads to formation of a dimeric Mn^{III} complex in contrast to the discrete mononuclear complexes or 1D structures previously obtained for the Mn:dca^- ratio of 1:1. The AC susceptibility measurements indicate that the complex behaves as a field-induced single-molecule magnet (SMM), with a high energy barrier of 73(4) K. Moreover, the present complex exhibits a high solvent selective catechol-oxidase-like activity for the model substrate 3,5-DTBC in acetonitrile medium. The present thesis has been written on the basis of following publications:

[1] Inorganica Chimica Acta. **2014**, 410, 111–117

[2] Inorganica Chimica Acta. **2014**, 423, 123–132

[3] Inorganica Chimica Acta. **2019**, 486, 352–360

[4] Inorg. Chem. **2020**, 59,12, 8487-8497

[5] Inorganica Chimica Acta. **2023,** 550, 121370-121379.

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