

ABSTRACT

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Exploration of functionalities in some designed coordination polymers

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Chapter 1: This chapter consists of two sections: chapter 1A and chapter 1B.

Chapter 1A: This chapter contains short introduction about coordination polymers which contains history of CPs, different terminologies, various strategy of synthesis and role of variable factors for designing functional coordination polymers. Characterization techniques of coordination polymers, discussion on various functionalities, structural transformation and interpenetration in CPs are also here.

Chapter 1B: It illustrates the brief summary which has been discussed in the thesis.

Chapter 2: This chapter contains the synthesis of three new coordination complexes $[\text{Mn}(\text{L1})(\mu\text{-azide})(\text{azide})]_2 \cdot 4\text{H}_2\text{O}$ (1), $[\text{Mn}(\text{L1})(\text{fum})]_n$ (2) [$\text{L1} = 2\text{-methyl-N}^1, \text{N}^2\text{-bis(pyridin-2yl)propane-1,2-diamine}$, $\text{fum} = \text{fumaric acid}$] and $[\text{Co}(\text{L2})(\text{azide})]$ (3) [$\text{L2} = 6\text{-phenyl-1,3,5-triazine 2,4-diyl amino(pyridine-2yl)methanol}$]. All the complexes have been characterized by single crystal X-ray diffraction analysis. Complex 1, a dinuclear Mn(II) complex is formed by bridging azide ligand and other coordination sites are satisfied by tetradentate ligand L1 and terminal azide ligand. The overall structure is an incomplete supramolecular 3D cage structure, formed by intermolecular $\pi\text{-}\pi$ interaction of pyridyl ligand and hydrogen bonding. Complex 2 comprised of eight coordinated Mn(II) centre where ligand L1 and fumarate is bridged between the metal centers that leads to a one dimensional chain structure which further extended to a 3D structure by $\pi\text{-}\pi$ and $\text{C-H}\dots\pi$ interactions. The overall structure is further stabilized by hydrogen bonding with the guest water molecules. Complex 3, a six coordinated mononuclear Co(II) discrete complex is consist of pentadentate ligand L2 and azide act as a terminal ligand. This Mononuclear complex is connected by $\pi\text{-}\pi$, $\text{C-H}\dots\pi$ interactions and hydrogen bonding which ultimately leads to a supramolecular 2D architecture.

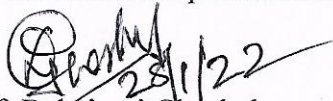
Chapter 3: This chapter is about the design and synthesis of interpenetrated metal organic frameworks (IMOFs). Interpenetrated metal organic frameworks (IMOFs) have occupied a top priority of interest in the last few decades due to their unexpected better potential applications in the various growing field. Like dynamic IMOFs, other IMOFs have also been important material due to their interesting structural phenomenon and inherent flexibility which is actually responsible for exhibition of different functionality even by a single framework. Interpenetrated framework is generally formed by coordination of metals with rigid ligands but flexible ligand shows more interesting results in some cases. It is well established that the length of used ligands, irrespective of flexibility and rigidity plays a vital role in making of these type of structures. In searching of IMOFs, three MOFs, $\{\text{Cd}(\text{bix})_{0.5}(\text{adp})_{0.5}(\text{H}_2\text{O})\}_n$ (1), $\{[\text{Cd}(\text{bix})(2,2'\text{-dmglu})] \cdot (\text{H}_2\text{O})\}_n$ (2) and $\{\text{Cd}(\text{bpmp})(2,2'\text{-dmglu})(\text{H}_2\text{O})\}_n$ (3) have been synthesized by using two different N,N-donor linkers bix {bix = 1,4-bis(imidazol-1-ylmethyl)-benzene}, bpmp {bpmp = 1,4-bis(4-pyridinylmethyl)piperazine} and two different substituted dicarboxylate adp {adp = adipate}, 2,2'-dmglu {2,2'-dmglu = 2,2'-dimethylglutarate}. Among the three complexes, three fold interpenetrated framework has been shown by complex 3 where long length more flexible N,N-donor ligand, bpmp { bpmp = 1,4-bis(4-pyridinylmethyl)piperazine}

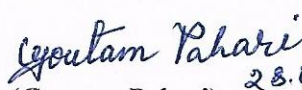
has been used. Gas sorption studies are performed with the three synthesized MOFs which substantially correlate with their framework.

Chapter 4: In this chapter anion exchange properties of coordination polymers have been explored. Anion exchange materials are important for their application in toxic anion control process. Coordination Polymers (CPs) with weakly coordinated anions and lattice anions may be practically useful in anion exchange process. To explore this anion exchange properties by coordination polymers (CPs) two water insoluble cationic CPs {[Mn(bix)₃(H₂O)₂].bix.(NO₃)₂]_n (1), {[Cd(bix)₂(NO₃)₂].(H₂O)₂]_n (2) have been synthesized by using N,N-donors linkers bix {bix = 1,4-bis(imidazol-1-ylmethyl)-benzene}. Structure of complex 1 is 1D and contains lattice NO₃⁻ anion and the complex 2 is 2D and contains weakly coordinated NO₃⁻ anion. Both these complexes along with another previously published structurally similar CP {[Cd(bix)₂(NO₃)₂]_n (3), response in anion exchange studies with foreign anions. All the anion exchange processes have monitored by FT-IR spectroscopy and PXRD measurements.

Chapter 5: This chapter contains the strategic design and synthesis of MOFs for CO₂ sorption at normal and high pressure. Metal organic frameworks with suitable void are promising materials for the execution of their exceptional functionalities. With the incorporation of proper void and modulating the structural flexibility, such frameworks have found very impressive for several applications. Accounting this phenomenon and to explore the structural diversity and sorption behavior of them, four metal organic frameworks namely {[Cu₃(3,3'-dmglut)₃(bte)].6(H₂O)]_n (1), {[Cu(3,3'-dmglut)(btp)_{0.5}].2(H₂O)]_n (2), [Zn(3,3'-dmglut)_{0.5}(bpe)_{0.5}]_n (3) and {[Mn₂(3,3'-dmglut)₂(bpe)₂(H₂O)₂].5(H₂O)]_n (4) have been synthesized. Here, three complexes exhibit 3D structure and one is 2D. All the complexes except 3, shows structural transformation upon activation. For the complexes 1 and 2, ligand flexibility plays a vital role for their sorption behavior. In complex 3, despite of low void space, it shows highest CO₂ sorption at high pressure, among all the complexes due to pore opening-closing phenomenon. In case of complex 4; dynamicity and additional adsorbate-adsorbent interaction force to exhibit an interesting carbon dioxide sorption at 1 bar pressure though it possesses 2D structure. High pressure carbon dioxide sorption of these complexes has also been studied and correlated with the structural transformations observed in the individual complexes.

Chapter 6: This chapter contains the synthesis of a two-fold interpenetrated 3D MOF {[Cd₂(bpe)₂(3,3-dmglu)₂]_n (1) by using trans-1,2-bis(4-pyridyl)ethylene ligand (bpe) and 3,3-dimethylglutarate (3,3-dmglu) with crystallographically two distinct C=C bonds, which undergoes [2+2] photo-cycloaddition and thermal reversible reaction, in a single-crystal-to-single crystal (SCSC) manner. The newly synthesized two-fold interpenetrated 3D MOF (1) has been reversibly converted into a 3D interpenetrated MOF {[Cd₂(rctt-tpcb)(3,3-dmglu)₂]_n (2), {where, tpcb = tetrakis(4-pyridyl)cyclobutane), in rctt, the r = reference substituent group, c = cis and t = trans for indicating the relative orientation of the substituent on the cyclobutane ring with regard to the reference group} in SCSC manner by the cycloaddition of two distinct C=C bonds with shorter and longer separations, simultaneously. The soft mechanical behaviour in these two crystals indicates that the molecular movements and flexible coordination cite in solid state is responsible for the reversible photochemical reactions in the molecular crystals of the said MOF.


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