ABSTRACT

TITLE: DESIGN OF MULTIFUNCTIONAL METAL-ORGANIC FRAMEWORK (MOF) FOR THE NEXT GENERATION APPLICATIONS

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Chapter 1. This chapter is divided into two sections: Chapter **1A** focuses on a brief survey regarding metal organic frameworks and their multifunctional behavior, while Chapter **1B** provides a summary of various research works.

Chapter 2. This chapter explores into a series of mixed-ligand Zn(II) coordination polymers $\{[Zn_2(\mu_2\text{-}OH)(azbpy)(btc)(H_2O)].(H_2O)(MeOH)\}_n$ (**1**), $\{[Zn_2(\mu_3\text{-}OH)(azbpy)_{1.5}(btc)(H_2O)].(azbpy)_{0.5}(H_2O)_4\}n$ (**2**), and $\{[Zn_{2.5}(azbpy)(Hbtc)_2(\mu_2\text{-}OH)(H_2O)_2].(H_2O)_{3.5}(MeOH)\}n$ (**3**) formed by altering the relative ratio of two ligands. Comprehensive characterization using single crystal X-ray diffraction (SCXRD), elemental analysis, infrared (IR) spectroscopy, thermogravimetric (TG) analysis, UV-visible spectroscopy, and powder X-ray diffraction (PXRD) has been conducted for all CPs **1**, **2**, and **3**. The gas sorption and luminescence have been done for all the CPs.

Chapter 3. The chapter delves into two d^{10} metal complexes, $\{Zn_2(fum)_2(dim)_2(MeOH)\}_n$ (**1**) and $\{Cd_2(fum)_2(dim)_2(H_2O)\}_n$ (**2**), synthesized. The single crystal of complex **1** demonstrates a reversible SCSC transformation, selective elimination of lattice methanol at room temperature. However, complex **2** showcases (DRST) through slow evaporation of methanol molecules. The selective solvent-induced reversible SCSC transformation of complex **1** and the reversible DRST of complex **2** at room temperature have been confirmed through PXRD and luminescence studies. Revealing a higher hydrogen uptake in the polycatenated framework of complex **2**.

Chapter 4. This work focuses on modifying ligands to synthesize a pair of mixed-ligand d^{10} MOFs. The original compound, a Zn(II)-MOF, $\{[Zn(4\text{-}bpdh)(H_2dht)]\cdot(MeOH)(H_2O)\}_n$ (**1**) modified by Cd(II), resulting in a rigid compound with the same framework formula as the base material but lacking interpenetration. The second modification involved substituting the 4,4'-coordinating N,N′-donor ligand with an isomeric 3,3'-coordinating N,N′-donor linker, rejuvenating the dynamism within the compound, confirmed by PXRD studies. These 3D MOFs exhibit excited-state intramolecular proton transfer (ESIPT) phenomena and demonstrate water-sensing properties in various organic solvents.

Chapter 5. Here, the growing demand for advanced switches and sensors has been addressed, specifically, exploring alterations in the photophysical properties of materials, particularly in solid-state. Solid-state ESIPT phenomena are not novel in material chemistry, especially in organic molecules, its observation within coordination polymers (CPs) has been unprecedented. Introduced the pioneering solid-state, solvent-free, and solvent-independent ESIPT-active coordination polymer (CP). Remarkably, this CP displays temperature-dependent ESIPT on-off behaviour, highlighting its potential as an innovative material in the realm of cutting-edge switches and sensors.

Chapter 6. Detection and sensing of amine through enhanced fluorescence emission is always challenging in aqueous solution. Designed a 2D+2D→3D inclined polycatenated $-NO_2$ functionalized flexible metal organic framework (MOF) for selective fluorescence enhancement segregation of electron rich aromatic primary amines from fluorescence quenching electron deficient amines in aqueous solution showing different emission behaviour.. The above findings are also supported by time resolved fluorescence spectroscopy as well. The respective fluorescence enhancement and quenching have been explained by the interaction between the CB of MOF and LUMO of amines.

Chapter 7. This work presents incorporation of potassium ions in a structurally flexible Co(II)-MOF) for OER application. Therefore, maintaining proper orientation potassium ions in such bimetallic MOFs, their structural stability can be maintained in alkaline medium as well as their electrocatalytic OER activity can also be tuned. Here it has been demonstrated that how the potassium ion introduction in $\{K_2[Co(H_2O)_2(CO_3)_2]\}_n$ (**2**) and $\{K_2[Co(2,6\text{-dcp})_2](H_2O)_7\}_n$ (**3**) 3D MOFs. Compound **3** shows a low overpotential of 292 mV (at 10 mA cm^{-2}) and a small Tafel slope of 50 mV dec^{-1}; with a remarkable long-term electrochemical stability for the OER. The turn over frequency (TOF) of compound **3** has the value of 1.96 s^{-1}.

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