

Abstract

In the last two decades, self-assembled Metal Organic Materials (MOMs) with intriguing structures and properties have become a hot topic for scientists in various fields for their potential applications in gas sorption and storage, catalysis, magnetism, sensing, drug delivery, etc. Discrete Metal Organic Cages (MOCs) and Coordination Polymers (CPs) are the two major subclasses of MOMs. These materials are strategically designed for various applications based on the choice of ligands/linkers and diverse coordination chemistry offered by numerous metal ions. Although several synthetic methods have been reported in the literature, the room temperature self-assembly method is desired for its simplicity, cost-effectiveness and easy to scale-up.

The most important aspect of this research was to find the strategic combination of ligand and linker for the structural diversity (nuclearity and dimensionality) and hence the properties of MOCs and CPs. In combination with various di/tricarboxylic acids, several flexible and spanning bis(tridentate) polypyridyl ligands with variable spacer were used to explore their chemistry. A series of MOCs and CPs have been successfully synthesized under ambient conditions and in good yields. These have been extensively characterized by various analytical techniques including elemental analysis, FT-IR and UV-Vis spectroscopy, TGA, single crystal and powder X-ray diffraction. The first part of this work focuses on mostly MOCs (and few CPs) using various magnetically active cores, like $\{\text{Mn}_2(\mu\text{-O})(\mu\text{-O}_2\text{CR})_2\}_{2+}$, $\{\text{Fe}_2(\mu\text{-O})(\mu\text{-O}_2\text{CR})_2\}_{2+}$ and $\{\text{Mn}_2(\mu\text{-O})_2(\mu\text{-O}_2\text{CR})\}_{2+}$ for demonstrating their magnetic properties. Both tetranuclear and unprecedented octanuclear MOCs have been obtained, where both flexibility and methylene chain length of bis(tridentate) polypyridyl ligands and dicarboxylates play a huge role in the structural diversity and magnetic properties of these compounds. Their magnetic behaviour was according to expected ferro- and antiferro-interactions within as well as between the cages. In the second part, a rich and diverse chemistry of four different divalent metal ions (Mn^{2+} , Co^{2+} , Ni^{2+} and Cd^{2+}) was unveiled through a systematic combination of (a) rigid carboxylates and semirigid spanning ligands, (b) flexible carboxylates and semirigid spanning ligands, (c) a heterocyclic dicarboxylate and all spanning ligands, and (d) a semirigid dicarboxylate and semirigid spanning ligands. In addition to their spectroscopic and thermal properties, and structural elucidation, examples of heterogeneous catalysts for the Knoevenagel condensation reaction are demonstrated utilizing the open metal sites as Lewis acidic centers.