ABSTRACT

Title of the dissertation: **Crystal Structure of Transition Metal Coordination Polymers and Their Applications**

Submitted by: **Srikanta Jana** Index No.: **74/18/Chem./25**

This dissertation describes the design, synthesis and structural characterization of d-block metal-based carboxylato coordination polymers and their applications. The thesis has been divided into seven chapters. The study is focused on (i) Design and synthesis of coordination polymers with interesting topologies, (ii) Exploration the role of different supramolecular interactions in the construction of coordination polymers, (iii) Evaluating the physical significance of the supramolecular interactions in terms of their application in efficient electrochemical catalysis, reduction of water pollutants and inclusion of electrical conductivity, magnetic response (iv) Estimating photo-responsive and super capacitive behaviour in the coordination polymers. In this thesis work, various ditopic carboxylato bridging linkers along with mono/di-dentate heterocyclic-N donor ligands have been engaged to assemble a wide dimensional range of coordination polymers.

In this contest, in the Chapter-2, two cu-based electro-conductive 0D, 1D coordination polymers $[Cu_2(DABA)_4(4,4'\text{-}BPY)]_n$ (**1**) and $[Cu_4(DABA)_8(PYZ)(H_2O)_2]$ (**2**) (HDABA = 4-Diallylamino-benzoic acid) have been synthesized by varying axial linkers, 4,4′-Bipyridine (4,4′-BPY) and Pyrazine (PYZ). Upon light irradiation the thin film of the compounds increases the electrical conductivity with respect to the dark phase and the conductivity of **1** is ~150 times higher than **2**. Compound **1** exhibits ferromagnetic behavior and compound **2** is antiferromagnetic at 300 K and the effective magnetic moment at 300 K, is 1.94 and 0.93 BM, respectively. In this Chapter-3, a 1D Cu(II) coordination polymer with encapsulated antiferromagnetically coupled binuclear Cu(II) has been synthesized by using 5-nitroisophthalic acid (5-N-IPA) and 4-aminopyridine (4-APY) $[Cu_2(5\text{-}N\text{-}IPA)_2(4\text{-}APY)_4]_n$ (**1**). This complexe have the potential to form higher dimensional structures throughout H-bonding (2.865–3.3.320 Å) and Supramoleculer (aromatic π….π) interactions (3.869–4.148 Å). The charge transfer mechanism and dielectric relaxation throughout the CP have been established. The shape of the $\chi_M T$ *vs* T curve indicates dominant antiferromagnetic coupling, which results from the interaction between the copper(II) atoms. In Chapter-4, tetranuclear (0D) $[Zn_4(\mu_4\text{-}O)(DABA)_6]$ (**1**) and polynuclear (1D) $[Zn_2(DABA)_4(4,4'\text{-}BPY)]_n$ (**2**), in one pot (HDABA = 4-Diallylamino-benzoic acid and 4,4′-BPY = 4,4′-Bipyridine) complexes have been synthesized and characterized by single crystal X-ray diffraction measurements and other spectroscopic data. The tetranuclear Zn(II) complex (**1**) shows Zn···Zn separation in the range 3.122-3.186 Å, and the μ_4-O ---- Zn distance lies in the range 1.927-1.944 Å (Figure 4.4). The structure analysis of **2** shows that a carboxylato bridged Zn(II) paddle wheel $[Zn_2(DABA)_4]$ unit is connected by the 4, 4′-bipyridine at the axial coordination position and helps to form 1D polymeric chain. This research discovered the high efficiency and selectivity in electrocatalytic CO_2 reduction to methanol, formaldehyde and formic acid. Also due to the polymeric nature of compound **2** (1D), the conductivity based on diode derived from J-V characteristics has promisingly increased by 10^4 times than tetranuclear complex. In the successive chapters we have successfully studied the role of supramolecular interactions in the construction of a 1D coordination polymer, $[Cu_2(\mu_2\text{-}OH)_2(DABA)_2]_n$ (**1**), (HDABA = 4-Diallylamino-benzoic acid) and this was extended in the 3D array by hydrogen bonds (bonding) and π•••π interactions along with weak C−H•••π interactions. **1** shows catalytic performance in the reduction of toxic nitrophenols to corresponding aminophenols by $NaBH_4$. The susceptibility measurements ($\chi_M T$) of Cu(II) coordination polymer indicates the presence of a very weak antiferromagnetic coupling between the metal centres. In this chapter (Chapter-6), a Cu based metal−organic framework, $\{[Cu_4(BTC)_6(4\text{-}APy)_2(\mu_3\text{-}OH)_2](CH_3OH)(H_2O)\}n$, (Cu-MOF) ($H_3BTC$ = 1,3,5-benzenetricarboxylic acid; 4-APy = 4-Aminopyridine) has been synthesized. The hybrid material, Cu-MOF exhibits very high specific capacitance, 547 F g^{-1} at the scan rate of 2 mV s^{-1} with excellent recycling stability (retains 97.4% after 5000 cycles). The $\chi_M T$ value for CuMOF at 300 K is 1.735 cm^3 mol^{-1} K for four copper(II) ions which is as expected for four isolated copper(II) ion with g = 2.15.

Ssinha

Signature of Supervisor

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Professor of Chemistry
Department of Chemistry
Jadavpur University
Kolkata-700 032

Srikanta Jana

Signature of the Candidate

08/02/2022