Abstract

[Index No: 26/19/Chem./26]

Title: Coordination Polymer: Synthesis, Characterization and Structure-Property Correlation for Sensing and Electrical Conductivity

Coordination Polymers (CPs) or Metal-Organic Frameworks (MOF) have extensive role in the field of sensing, electrical conductivity, gas absorption, magnetism, water splitting, environmental management, drug delivery and other biological applications. Structural diversity plays important role to exhibit different property with diverse applications. The coordination polymers are synthesized using the different metal nodes with the combination of bridging ligands. Transition metal CPs with N-heterocyclic bridgers and/or aromatic or aliphatic carboxylate (linker) serve as efficient magnetic materials. Many methods (like, slow evaporation, hydrothermal etc.) are followed to synthesize the CPs and characterised by using different spectroscopic methods (SXRD, TGA, PXRD, IR etc.). Coordination polymers are assembled via C-Cl···π, π···π, C-H···π and H-bonding. The CPs are also used for the selective detection of environmentally important metal ions, anions and small molecules. Extended π-conjugation, structural flexibility, π···π interaction and metal nodes are the reason for electrical conductivity in the dark/light condition and these materials are used to fabricate the Schottky diode. The CPs are also used in the field of biology to derive microbiologically potential drugs. A short review and motivation of this research is delineated in the **Chapter 1**.

In **Chapter 2** the design, synthesis and structural characterization of two Zn(II) based 1D coordination polymers, [Zn(adc)(4-Cltpy)(H_2O)] (CP**1**) and [Zn(*trans*-muca)(4-Cltpy)] (CP**2**) (4-Cltpy = 4′-Chloro-2,2′:6′,2″-terpyridine, H_2adc = Acetylene-dicarboxylic acid, *trans*-H_2muca = *trans*, *trans*-muconic acid) are described. Both CPs have selectively detected Cu^{2+} in aqueous medium with limit of detection 0.14 μM (CP**1**) and 0.06 μM (CP**2**). Also these CPs have shown internalization within HepG2 cells and subsequent microscopic cell images are collected.

In **Chapter 3** Zn(II) based 1D coordination polymer, {[Zn(2,6-NDC)(4-Cltpy)](H_2O)$_4$} (4-Cltpy = 4′-chloro-[2,2′;6′,2″]terpyridine and 2,6-NDC = 2,6-Naphthalene dicarboxylic acid) is spectroscopically characterized and has been confirmed by the Single Crystal X-Ray

Professor of Chemistry
Department of Chemistry
Jadavpur University
Kolkata-700 032
16/2/23

Suprava Bhunia
16/02/23

diffraction measurements. Here, 1D chains are assembled via Cl···π, π···π and H-bonding and have formed 3D geometry. This CP was used to detect the $Fe^{2+/3+}$ by Absorption spectroscopic studies. Zn(II) coordinated metal centre was substituted by Fe and color of CP was changed from colorless to pink in aqueous medium. Limit of detection (LOD) are 0.11 μM (Fe^{2+}) and 0.15 μM (Fe^{3+}). The Zn-CP also exhibits microscopic cell imaging using MDA-MB 231 cells.

In **Chapter 4** the design and synthesis of Cd(II) based 2D coordination polymer, $\{[Cd(HAIPA)(tppz)(OH)].3H_2O\}_n$ (2,3,5,6-Tetrakis(2-pyridyl)pyrazine (tppz), and 5-Aminoisophthalic acid (H_2AIPA)) is reported. Single crystal X-ray diffraction data had helped to evaluate the structure. In presence of different secondary interaction, a 2D network was assembled. The 2D-CP uses selectively and specifically to detect Pd^{2+} in aqueous medium with a limit of detection is 0.08 μM even in presence of large number of cations. The CP shows exhibited electrical conductivity in light and dark condition and upon incorporation of Pd^{2+} in the CP the electrical conductivity is increased.

The **Chapter 5** reports three Cd(II) based 3D coordination polymers, [Cd(tppz)(adc)(MeOH)] (**1**), [Cd(tppz)(trep)] (**2**) and [Cd(tppz)(2,6-ndc)] (**3**) (tppz = 2,3,5,6-Tetrakis(2-pyridyl)pyrazine, acetylene dicarboxylic acid (H_2adc), terephthalic acid (H_2trep) and 2,6 naphthalene dicarboxylic acid (2,6 H_2ndc)). Different spectral techniques have helped to characterise these CPs. The CPs **1** and **2** form 2D network and compound **3** forms 1D chain. DFT computational study of CPs helped to evaluate the band gap that supported the electrical conductivity results.

In **Chapter 6** one coordination complex, $[CdI_2(4\text{-nvp})_2]$ (**1**) (CdI_2 = Cadmium iodide and 4-nvp = 4-(1-naphthylvinyl)pyridine)) has been reported. Single crystal X-ray diffraction study confirms the formation of complex (**1**). Different secondary interactions help to assemble the complex. This complex is very much selective and sensitive towards the detection of TNP (trinitrophenol) in acetonitrile. DFT computational study helps to determine the band gap and mechanistic aspect of sensing.

Suprava Bhunia
16/02/2023

Sinha
16/2/23
Professor of Chemistry
Department of Chemistry
Jadavpur University
Kolkata-700 032