Abstract

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Title: Synthesis and Structural Characterization of Coordination Frameworks and Their Potential Applications

Chapter 1 introduces Coordination Polymers (CPs) and Metal-Organic Frameworks (MOFs) as structurally tunable materials with diverse functional attributes. Constructed through the coordination of π-rich organic ligands with inorganic secondary building units (SBUs), these frameworks exhibit enhanced robustness, porosity, and chemical stability. The rational design of CPs/MOFs enables precise control over their structural and electronic properties, positioning them as promising candidates for applications in gas storage, ion exchange, drug delivery, catalysis, molecular magnetism, sensing, and energy devices.

The chapter outlines key synthetic methodologies, including slow diffusion and hydrothermal techniques, and highlights advanced characterization tools-SCXRD, PXRD, TGA, and IR spectroscopy-that confirm structural fidelity and compositional purity. Non-covalent interactions such as $\pi\cdots\pi$ stacking, C-H$\cdots\pi$ interactions, and hydrogen bonding are discussed for their pivotal roles in framework assembly, stability, and function.

Finally, the **chapter 1** defines the research scope, emphasizing its methodological improvement, contribution to bridging existing knowledge gaps, and relevance to the advancement of CP/MOF-based functional materials.

Chapter 2 reports the synthesis and structural elucidation of a one-dimensional cadmium(II)-based coordination polymer, $[Cd(glu)_2(pbiq)_2(H_2O)]_n$ (**1**), assembled from glutaric acid (H_2glu) and 4-(6-(pyridin-4-yl)benzo[4,5]imidazo[1,2-*c*]quinazoline) (**pbiq**). Hydrogen bonding and $\pi\cdots\pi$ stacking drive the formation of a three-dimensional supramolecular framework, which exhibits strong photoluminescence at 416 nm in acetonitrile. The emission is selectively quenched by nitroaromatic compounds, particularly trinitrophenol (TNP), with a detection limit of 1.51×10^{-7} M. The material also demonstrates semiconducting properties (band gap: 3.31 eV) and was integrated into an electronic device, showing non-ohmic *I-V* characteristics ($\Lambda = 1.10 \times 10^{-3}$ S·m^{-1}, $\Phi_B = 0.69$ eV).

Chapter 3 presents the synthesis of a novel two-dimensional cadmium(II)-based metal-organic framework, $\{[Cd_2(5\text{-nip})_2(pdiq)_2(H_2O)_2(CH_3OH)]\cdot H_2O\}_n$ (CP **1**), constructed from 5-nitroisophthalic acid (H_2nip) and a pyridylimidazoquinazoline ligand (**pdiq**). Non-covalent C-H$\cdots\pi$ and $\pi\cdots\pi$ interactions guide the assembly into a three-dimensional supramolecular structure. CP **1** exhibits strong luminescence, selectively quenched by trinitrophenol (TNP) with a detection limit of 2.75×10^{-7} M, even in the presence of other nitroaromatic analytes. Additionally, CP **1** demonstrates enhanced semiconducting behavior, with electrical conductivity increasing from 1.12×10^{-3} S·m^{-1} (dark) to 6.33×10^{-3} S·m^{-1} under illumination, and a corresponding reduction in energy barrier from 0.53 eV to 0.42 eV, highlighting its potential for optoelectronic applications.

Chapter 4 describes the successful synthesis of a robust three-dimensional Zn(II)-based luminescent coordination polymer, $[Zn_2(tdc)_4(pdiq)_3]$ (**1**), constructed from 2,5-thiophenedicarboxylic acid (H_2 tdc) and pyridyl-imidazoquinazoline (**pdiq**). Structural stability is reinforced by $\pi\cdots\pi$ interactions between imidazolium and phenyl moieties. The polymer exhibits excellent dispersibility in acetonitrile, enhancing its fluorescence response for highly selective and sensitive ratiometric detection of Al^{3+} ions (LOD: 1.39×10^{-7} M). Additionally, the fluorescence is efficiently quenched by trinitrophenol (TNP), with a detection limit of 1.54×10^{-7} M, confirming its dual sensing capability. The material displays semiconducting behavior (band gap: 3.33 eV) and a marked increase in conductivity under illumination (from 1.14×10^{-3} to 5.35×10^{-3} S·m^{-1}).

Chapter 5 details the synthesis of a redox-active cobalt-based coordination polymer (Co-CP), constructed using (*E*)-N-(pyridin-4-ylmethylene)-4*H*-1,2,4-triazol-4-amine as a bridging ligand and capped with 2,5-thiophenedicarboxylate. Designed for electrocatalytic applications, Co-CP exhibits promising activity toward the oxygen evolution reaction (OER) in alkaline media. Incorporation of Ni^{2+} ions at varying concentrations yields Ni@Co-CP composites with enhanced performance. The optimized Ni-2@Co-CP, featuring an amorphous framework, delivers outstanding OER activity with a low overpotential of 290 mV at 10 mA·cm^{-2}, a Tafel slope of 35 mV·dec^{-1}, and a charge transfer resistance of 6.97 Ω, accentuating its potential in energy conversion catalysis.