

Tailoring Structural, Thermal and Luminescent Properties of Solid-State MIL-53(Al) MOF via Fe³⁺ Cation Exchange

Authors : T. Ul Rehman, S. Agnello, F. M. Gelardi, M. M. Calvino, G. Lazzara, G. Buscarino, M. Cannas

Abstract : Metal-Organic Frameworks (MOFs) have emerged as promising candidates for detecting metal ions owing to their large surface area, customizable porosity, and diverse functionalities. In recent years, there has been a surge in research focused on MOFs with luminescent properties. These frameworks are constructed through coordinated bonding between metal ions and multi-dentate ligands, resulting in inherent fluorescent structures. Their luminescent behavior is influenced by factors like structural composition, surface morphology, pore volume, and interactions with target analytes, particularly metal ions. MOFs exhibit various sensing mechanisms, including photo-induced electron transfer (PET) and charge transfer processes such as ligand-to-metal (LMCT) and metal-to-ligand (MLCT) transitions. Among these, MIL-53(Al) stands out due to its flexibility, stability, and specific affinity towards certain metal ions, making it a promising platform for selective metal ion sensing. This study investigates the structural, thermal, and luminescent properties of MIL-53(Al) metal-organic framework (MOF) upon Fe³⁺ cation exchange. Two separate sets of samples were prepared to activate the MOF powder at different temperatures. The first set of samples, referred to as MIL-53(Al), activated (120°C), was prepared by activating the raw powder in a glass tube at 120°C for 12 hours and then sealing it. The second set of samples, referred to as MIL-53(Al), activated (300°C), was prepared by activating the MIL-53(Al) powder in a glass tube at 300°C for 70 hours. Additionally, 25 mg of MIL-53(Al) powder was dispersed in 5 mL of Fe³⁺ solution at various concentrations (0.1-100 mM) for the cation exchange experiment. The suspension was centrifuged for five minutes at 10,000 rpm to extract MIL-53(Al) powder. After three rounds of washing with ultrapure water, MIL-53(Al) powder was heated at 120°C for 12 hours. For PXRD and TGA analyses, a sample of the obtained MIL-53(Al) was used. We also activated the cation-exchanged samples for time-resolved photoluminescence (TRPL) measurements at two distinct temperatures (120 and 300°C) for comparative analysis. Powder X-ray diffraction patterns reveal amorphization in samples with higher Fe³⁺ concentrations, attributed to alterations in coordination environments and ion exchange dynamics. Thermal decomposition analysis shows reduced weight loss in Fe³⁺-exchanged MOFs, indicating enhanced stability due to stronger metal-ligand bonds and altered decomposition pathways. Raman spectroscopy demonstrates intensity decrease, shape disruption, and frequency shifts, indicative of structural perturbations induced by cation exchange. Photoluminescence spectra exhibit ligand-based emission (π - π^* or n - π^*) and ligand-to-metal charge transfer (LMCT), influenced by activation temperature and Fe³⁺ incorporation. Quenching of luminescence intensity and shorter lifetimes upon Fe³⁺ exchange result from structural distortions and Fe³⁺ binding to organic linkers. In a nutshell, this research underscores the complex interplay between composition, structure, and properties in MOFs, offering insights into their potential for diverse applications in catalysis, gas storage, and luminescent devices.

Keywords : Fe³⁺ cation exchange, luminescent metal-organic frameworks (LMOFs), MIL-53(Al), solid-state analysis

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