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Title: Design and Construction of a Luminescent and Highly Stable 3D Metal-Organic Framework with a

[Zn4(µ3-OH)2]6+ Core

Authors: Khan, S. (/jspui/browse?type=author&value=Khan%2C+S.)

Das, Prasenjit (/jspui/browse?type=author&value=Das%2C+Prasenjit) Mandal, S.K. (/jspui/browse?type=author&value=Mandal%2C+S.K.)

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Abstract: A highly stable and luminescent 3D metal–organic framework (MOF), {[Zn4(µ3-

OH)2(BTC)2(BBI4PY)2]·10H2O}n (Zn-MOF), with a rare [Zn4(µ3-OH)2]6+ core has been synthesized using a new rigid and functionalized pillar linker, 2,6-bis(pyridin-4-yl)-1,7dihydrobenzo[1,2-d:4,5-d']diimidazole (BBI4PY) in combination with Zn(OAc)2·2H2O and 1,3,5benzenetricarboxylic acid (H3BTC) under solvothermal conditions. Unlike other MOFs with the [Zn4(u3-OH)2]6+ core. Zn-MOF was synthesized without using an external base, as the intrinsic basicity of BBI4PY served the purpose. Furthermore, it retains crystallinity and phase purity up to 350 °C on the basis of TGA and in situ variable temperature PXRD, correlating with its solid-state structure. Using the dehydrated Zn-MOF, water sorption studies show uptake of 220 cm3 g-1 (corresponds to 10 water molecules). A large hysteresis in desorption isotherm signifies strong interactions between adsorbed water and Lewis basic sites present in the framework. The reversible nature of water sorption was further manifested by TGA and PXRD studies. As an example of its application, the highly fluorescent and electron-rich nature of Zn-MOF has been utilized for the selective sensing of Fe3+ and 2,4,6-trinitrophenol (TNP) in water with detection limits of 3.7 and 1.8 ppm, respectively. The mechanistic details for the turn-off quenching have been elucidated with the help of Stern-Volmer plots, spectral overlap, lifetime studies, and density functional theory calculations. This mechanistic evidence reveals that a combination of strong hydrogen bonding with resonance energy transfer and photoinduced electron transfer (PET) processes is synchronously responsible for the quenching of the fluorescence intensity of Zn-MOF.

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