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REGULAR ARTICLE

Theoretical Study on a Metal-Organic Framework Based on μ4-oxo Tetrazinc Clusters: the Sorption Mechanism for Small Molecules

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Abstract: The sorption features of a metal-organic framework (MOFs) constructed by Zn_4O clusters with bdc and bpz linkers with methanol and methanal molecules are investigated by theoretical methods. Two different interactions are presented for the association of methanol molecules. One is the coordination bond like with large binding energy and the other one is hydrogen bond with small binding energy. These two kinds of interactions are corresponding to the mechanisms of the intriguing two-step sorption behavior for methanol. On the other hand, the dominant contribution for the absorption of methanal is demonstrated to be C-H···π interaction. The strong interaction between methanal molecule and the MOFs molecule is indicated by the large total binding energy as 94.55 kJ/mol. This MOFs is proposed to have fine sorption capability as well as the high performance as luminescent detection for methanal. The findings in this paper provide a comprehensive understanding about the sorption mechanism for this kind of material with small organic molecules and shed light on the synthesis and application of novel and stable MOFs.

AMS subject classifications: 81V15

Key words: metal-organic framework, sorption mechanism, hydrogen bond, luminescent detection

1 Introduction

Porous metal-organic frameworks (MOFs) are widely regarded as promising materials for

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applications in catalysis1-4, separation [5-8], gas storage [9-12], molecular recognition [13-23], molecular magnets [23-28] and semiconductors [29-32]. Compared to classical microporous inorganic materials such as zeolites with limited components, these organic structures have the potential for more flexible rational design, which is provided by variety of metal ions, organic linkers, and structural motifs [1-34]. The first few porous MOFs with permanent porosity established by gas adsorption studies [11, 33-34], as exemplified by the most well-known material: MOF-5 with significantly high surface area of greater than 3000 m^2/g are reported in 1999, in which the oxide-centered Zn_4O tetrahedra as nodes linked by organic molecules. Since then, the research endeavors have been mainly focused on the realization of functional pores and thus their specific properties and applications [9, 35-43]. In early work by Eddaoudi and co-workers, the isoreticular MOF (IRMOF) series was synthesized utilizing the same Zn_4O corner with struts of varying size and chemical functionality [44, 45]. Several MOFs constructed by Zn_4O corner have high thermal stability and guest adsorption capacity, which are promising for industrial application [46-49].

Functional luminescent MOF materials can be developed by introduction of metal motifs or organic linkers which can provide the platforms to generate luminescence into the structure. In fact, a variety of luminescent MOFs have been realized for their diverse applications on chemical sensing, light-emitting devices, and biomedicine over the past two decades [13-23, 50-56]. The chemical bonding, electronic structure and optical properties of the metal-organic framework MOF-5 has been investigated by Yang et al., theoretically [57]. Weak interactions such as hydrogen bond, π-π stacking and C-H$\cdots\pi$ are indicated to play significant role in determination of the photochemical and photophysical properties of thess materials [57-60].

Many important properties of Zn_4O contained MOFs in various aspects has been invesigated, widely, such as electronic properties, electrostatic potential and charge density, mechanical properties including bulk moduli and elastic constants and even the possibility used as photocatalyst [1-4], quantum dot and semiconductor [29-32] materials. However, in order to optimize these MOFs for potential industrial applications, an improved and comprehensive understanding about many interesting properties of them is still desired. For example, a porous metal-organic framework based on μ4-oxo tetrazinc (Zn_4O) clusters connected by two kinds of tetradentate ligand: 3,3′,5,5′-tetramethyl-4,4′-bipyrazolate (bpz) (**Figure 1b**) and 1,4-benzenedicarboxylate (bdc) (**Figure 1c**) has been reported by Chen and co-workers,[61] which reveals guest-dependent luminescent properties and high sorption performance of methanol, benzene, toluene and xylene. However, the mechanism of the intriguing two-step sorption behavior for methanol and guest-dependent luminescent properties has not been clarified. In the present work, we have performed a computational study on these problems of this MOFs material (1) using density functional theory (DFT) calculations. A central feature of the paper is the detailed investigation of the chemical