Commun. Comput. Chem.
doi: 10.4208/cicc.2013.v1.n3.6

Vol.**1**, No.**3**, pp.269-281
August 2013

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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Received 7 May 2013; Accepted (in revised version) 5 June 2013

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

binding mechanism for methanol sorption, which is responsible to the interesting two-step sorption behavior. On the other hand, the sorption performance, the chemical binding mechanism and the luminescent properties for methanal sorption are also depicted, which we believe will provide valuable insight into this novel material for luminescent detector of methanal.

2 Theoretical methods

The geometries for the ground-state structures of the monomers and complexes with methanol and methanal molecules have been optimized using the density functional theory (DFT). M06-2X functional is chosen because of its high performance for the study of noncovalent interactions [62-64]. All the calculations are carried out using Gaussian 09 program [65] suite with 6-31+G(d) basis set for nonmetallic elements as well as the pseudopotential LANL2DZ basis sets for Zn atom [66, 67]. The binding energies are also calculated with the basis set superposition error (BSSE) correction. All the local minima are confirmed by no imaginary mode from vibrational analysis calculations.

3 Results and Discussion

The central part of 1 is tetrahedral cluster Zn_4O as shown in **Figure 1a**. The clusters are bridged by two kinds of tetradentate ligand: 3,3′,5,5′-tetramethyl-4,4′-bipyrazolate (bpz) (**Figure 1b**) and 1,4-benzenedicarboxylate (bdc) (**Figure 1c**) to construct the framework. The cubelike cavity within 1 formed by eight tetranuclear clusters is shown in **Figure 1d**. It has been reported that the dimension of the cavity is 12.9×11.5×11.5 $Å^3$ by Chen and co-workers [61]. Since there are O atoms in the bdc ligand, hydrogen bond might play vital role in absorption of guest molecules containing hydroxyl, such as methanol. On the other hand, both bpz and bdc ligands have fine π conjugation systems, such as benzene and pyrazole structures. When guest molecules without hydroxyl are absorbed, the dominant factor will be π-π stacking and C-H···π interaction. Herein, the significant effects of these different interactions are clarified by investigation on the complex formed by the monomer of tetranuclear cluster and the guest molecules, such as methanol and methanol.

The tetranuclear cluster is the primary composition unit of 1. The optimized geometric structure of the cluster and complexes with methanol and methanal molecules are shown in **Figure 2**. In the monomer, the bond length of O_1-Zn_1, Zn_1-O_3, O_3-Zn_2 and Zn_2-O_2 are 2.004, 1.986, 1.986 and 2.004Å, respectively. The six-membered ring C_1-O_1-Zn_1-O_3-Zn_2-O_2 is planar with the dihedral angle of O_3-Zn_2-O_2-C_1 as 0°. In the dimer with one methanol molecule, the structure is changed, obviously. The bond length of O_3-Zn_2 and Zn_2-O_2 are changed to be 2.030 and 2.097Å. The dihedral angle of O_3-Zn_2-O_2-C_1 is changed to be -9.66°. There's no

hydrogen bond are formed between the molecule of methanol and the molecule of 1. Moreover, the distance between the O_4 atom of the methanol molecule and the Zn_2 atom of 1 molecule is 2.268Å. The binding energy is calculated to be 54.36 kJ/mol, which is beyond the hydrogen bonding energy [68, 69]. This interaction is assumed as coordination bond like. In the trimer complex with two methanol molecules, significant change of the structure is observed. The bond length of O_3-Zn_2 and Zn_2-O_2 are changed to be 2.044 and 2.164Å. The dihedral angle of O_3-Zn_2-O_2-C_1 is changed to be -40.45°. The distance between the O_4 atom of the methanol molecule and the Zn_2 atom of 1 molecule is shortened to be 2.167 Å, which indicates that the interaction is enhanced. On the other hand, two hydrogen bonds are formed, one is between two methanol molecules with the bond length as 1.631 Å, the other one is between the second methanol molecule and the 1 molecule with the bond length as 1.739 Å. The total binding energy of these two hydrogen bonds is calculated as 35.18 kJ/mol. The average value is 17.59 kJ/mol which is close to the binding energy of hydrogen bond O-H···O [68, 69]. It has been reported by Chen and co-workers the sorption behavior for methanol of 1 is separated into two steps [61]. Herein, two different interactions are observed corresponding to the different sorption mechanisms of the two-step sorption behavior. The strong coordination bond like interaction is corresponding to the first step in low pressure. The low sorption capability is ascribed to the low pressure and the large steric hindrance effect caused by the limited space and site for coordination of Zn atom in 1. Furthermore, the relatively weak interaction of hydrogen bond is proposed to be the dominant factor for the second step sorption in high pressure. Since the absorbed site is the O atom in the framework with large space and the main interaction is hydrogen bond with less saturated and steric hindrance feature, the second sorption step reveals very high sorption capability.

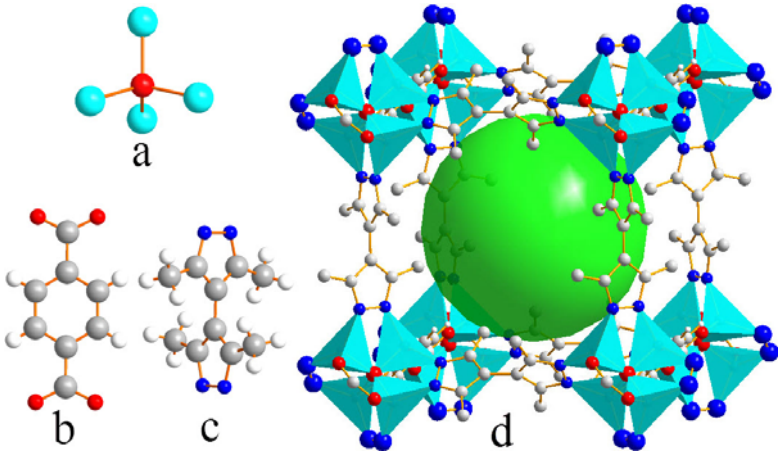

Figure 1: a) the tetranuclear cluster **b)** the 1,4-benzenedicarboxylate (bdc) ligand **c)** the 3,3′,5,5′-tetramethyl-4,4′-bipyrazolate (bpz) ligand d. cubelike cavity within 1 formed by eight tetranuclear clusters (Zn, cyan; N, blue; O, red; C, grey). The CCDC number of 1 is

683566. Hydrogen atoms are omitted for clarity.

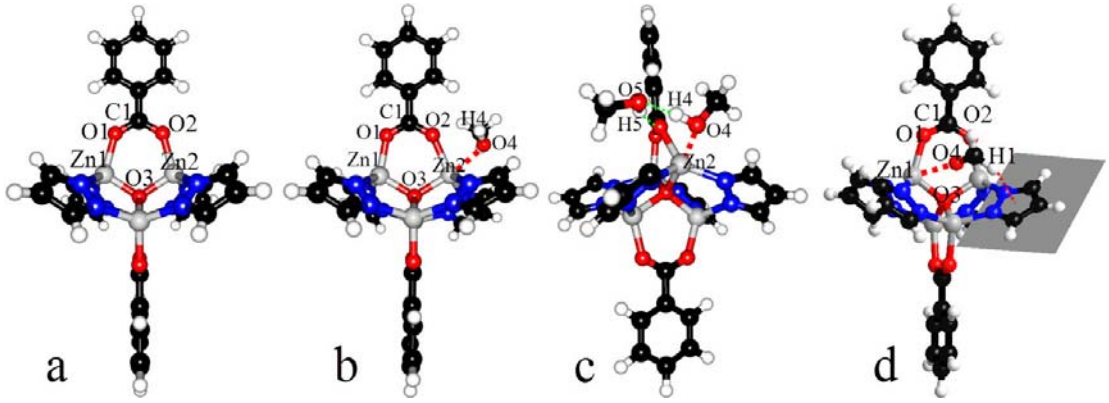

Figure 2: Optimized structure of the primary composition unit of 1 and complexes with 1 methanol, 2 methanols and 1 methanal molecule. The original monomer structure is cut from the crystal structure of 1, with the danging bonds saturated by hydrogen atoms. According to the little influence of methyl groups within the bpz ligands on the results, they are also replaced by hydrogen atoms in order to save computation time. a. the monomer structure b. the complex with one methanol molecule, the thick red dash line denotes the interaction between the O atom of methanol and the Zn2 atom c. the complex with two methanol molecules, two green dash line denote the hydrogen bond, the thick red dash line still denotes the interaction between the O atom of methanol and the Zn2 atom. d. the complex with one methanal molecule, the thick red dash line denotes the interaction between the O atom of methanal and the Zn atom, the thin red dash line denotes the vertical distance form the H atom of methanal to the plane of one pyrazole molecule in the bpz ligand. The grey plane denotes the plane of the pyrazole molecule. All the local minima are confirmed by no imaginary mode from vibrational analysis calculations. The optimized structure is consistent with the crystal structure of 1 very well.

In order to comparing with the methanol, the situation of methanal is also investigated. As shown in **Figure 2d,** methanal is located in the space formed by two bpz and one bdc ligands. The distance between the O_4 atom of methanal and the Zn_1 atom is 2.787 Å. That of the H_1 atom and the plane of bdc ligand is 2.428 Å. In addition, there is no hydrogen bond are formed. That is to say the primary factor for methanal association is the coordination bond like interaction and the C-H···π interaction. The total binding energy is calculated to be 94.55 kJ/mol, which is far large than hydrogen bond. Due to this strong interaction, the sorption behavior of methanal is proposed to be one-step, the same as those of benzene and toluene.[61] Therefore, 1 is also assumed to have high performance on absorption of methanal.

It has been reported that several Zn-MOFs exhibit potential application in luminescent sensors, due to the guest-dependent, such as organic solvents and lanthanide ions, luminescent properties [70-72]. Molecular orbital (MO) analysis can directly provide

insight into the nature of the electronically excited states [73–83]. The frontier molecular orbitals (MOs) of the monomer are shown in **Figure 3**. Herein, only HOMO-7, HOMO-8, LUMO and LUMO+1 are presented, since the excited state with the largest oscillation strength is mainly attributed to the transition of HOMO-7→LUMO+1 and HOMO-8→LUMO. As depicted in **Figure 3**, one can easily find that each transition mostly occurs on the ligand of benzene, which means this excited state is a local excited (LE) state. Metal-ligand charge transfer (MLCT) plays a significant role in luminescent properties of metal coordination complexes [59-60, 74]. However, it's clearly shown that there is no MLCT occurs, but little extent of ligand-ligand charge transfer (LLCT). According to the above analysis, since the absorbed sites for methanol are the Zn and O atoms in the central part of the molecule, but not the outside benzene ligand where the electronic transition occurs, it's rational to propose that sorption of methanol would have little influence on the luminescent properties of 1. On the contrary, it has been demonstrated that absorption of rigid guest molecules, such as benzene, toluene and p-xylene can induce the blue shift of the luminescent spectra [61]. Since methanal has similar absorption mechanism as the above rigid molecules, it's hypothesized that blue shifts will be observed for methanal adsorbed samples of 1. That also means 1 may be applied in luminescent detection for methanal molecules.

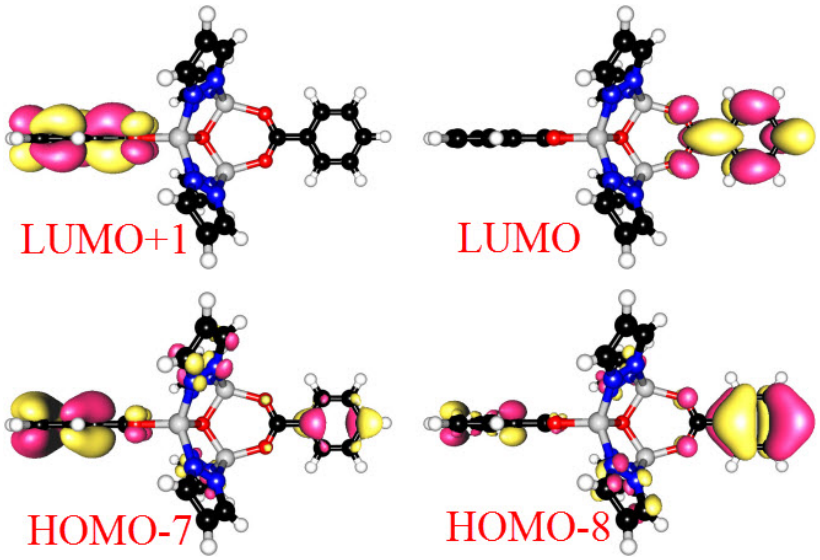

Figure 3: the frontie molecular orbitals.

4 Conclusions

In summary, we have presented a detailed investigation on the binding nature between a metal-organic framework (MOFs) (1) constructed by Zn_4O clusters and molecules of methanol

and mathanal using theoretical methods. We attribute the interesting two-step sorption behavior of methanol to two different interactions for the association of methanol molecules. One is the coordination bond like with large binding energy as 54.36 kJ/mol and the other one is hydrogen bond with small binding energy as 17.59 kJ/mol, which are corresponding to mechanisms for the first step in low pressure with low sorption capability and the second step in high pressure with high sorption capability, respectively. On the other hand, the dominant contribution for the absorption of methanal is demonstrated to be C-H···π interaction. The total binding energy between methanal molecule and the MOFs (1) molecule is very large as 94.55 kJ/mol, which indicates the strong interaction between them. The sorption behavior of methanal is proposed to be one-step, which is similar to that of other rigid guest molecules such as benzene and toluene. This MOFs (1) material has been indicated to be a promising luminescent detector for benzene [61]. Therefore, it is also proposed to have fine sorption capability for methanal as well as the high performance as luminescent detection for methanal. This study provides a comprehensive understanding about the sorption mechanism for this material with small organic molecules and paves new way on the synthesis and application of novel and stable MOFs.

Acknowledgments

This research was financed by the National Natural Science Foundation of China (grant nos. 21036006 and 21137001).

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