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REGULAR ARTICLE

A DFT/TDDFT Study on the Luminescence Property and Adsorption Behaviors of a Luminescence MOFs as a Potential Probe for Detecting Formaldehyde

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Abstract: Density Functional Theory (DFT) and Time-Dependent Density Functional Theory (TDDFT) have been carried out to investigate luminescence property and adsorption behaviors of the MOFs, $Zn_3(BTC)_2(DMF)_3(H_2O)\bullet(DMF)(H_2O)$. Through the analysis of the binding energy and hydrogen bond complexes' structure, we proved that the MOFs can absorb formaldehyde and other small molecules. We pointed out that the luminescence mechanism of the MOFs is ligand-based luminescence by the analysis of frontier molecular orbitals (FMOs) and the corresponding electronic configurations of the MOFs and its hydrogen bond complexes. But when the CH_2O hydrogen bond complex is formed, the luminescence mechanism will change into dominating by the guest-induced luminescence. Accordingly, the MOFs have good potential for detecting formaldehyde in environment

AMS subject classifications: 74E70,78M50
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1. Introduction

Metal-Organic Frameworks (MOFs), a new fascinating class of porous materials, are synthesized via self-assembly with metal centers or clusters and organic linkers to form

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crystalline networks [1-3]. MOFs have an essentially infinite number of possible combinations of metal ions, organic linkers, and structural motifs, so MOFs exhibit extraordinary optoelectronic, ferroelectric, magnetic, adsorption, catalytic and luminescence properties [4-11]. In recent years, MOFs have attracted considerable interests for applications in a number of fields, especially in gas adsorption and Chemical Sensing [10-12].

Formaldehyde is widely used in construction such as wood processing, furniture, textiles, and carpeting [13], the effects of formaldehyde on human health have attracted great attention [14-17]. The conventional formaldehyde measurement systems are expensive and bulky, so a better one should be developed [18]. MOFs contain many hydrogen bond donors and acceptors, so formaldehyde will be adsorbed in MOFs by forming hydrogen bond complexes. Hydrogen bond plays an important role in many photophysical processes and photochemical reactions in the electronic excited state [19-33]. Luminescence properties of MOFs may be changed by absorbing formaldehyde, and therefore MOFs can be used as chemical sensor for detecting formaldehyde.

In 2006, a 3D chiral microporous MOFs, $Zn_3(BTC)_2(DMF)_3(H_2O)\bullet(DMF)(H_2O)$, was synthesized by Fang et al.. The solid-state excitation-emission spectra showed that the strongest excitation peaks is at 341 nm, and its emission spectra mainly showed strong peaks at 410 nm [34]. The MOFs also exhibit substantial adsorption behaviors for H_2O, CH_3OH and C_2H_5OH [34]. Due to the excellent luminescence property and good adsorption behaviors, the MOFs will be a potential chemical sensor for small molecules. In this work, we investigated the luminescence property and adsorption behaviors of the MOFs by using Density Functional Theory (DFT) and Time-Dependent Density Functional Theory (TDDFT). At first, We have intercepted the representative segment A ($Zn_2L_4(DMF)_2$，where L is benzoic acid) to study ground state geometric structure and excited energy of the MOFs. Furthermore, we considered hydrogen bond complexes which were formed by small molecules (H_2O, CH_3OH, C_2H_5OH and CH_2O) and A to study adsorption behaviors and luminescence properties of the MOFs. Through the analysis of the results, we predicted the possibility of using the MOFs as Luminescence-Based Chemical Sensor for detecting small molecules. In particular, we had more interesting in detecting formaldehyde in environment.

2. Computational details

MOFs are periodic crystalline material periodic structures. To avoid the complexity of periodic structures in the excited state, we truncated the $Zn_3(BTC)_2(DMF)_3(H_2O)\bullet(DMF)(H_2O)$ crystal structure into a representative segment A (see **Figure 1**). DFT and TDDFT were employed for ground state and excited state computations, respectively. The ground state and excited state computations of A was performed by using