A Zn based two-dimensional metal-organic framework as a dual ion sensor in aqueous media.

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ABSTRACT

Excess and shortage of some metal ions like Fe^{3+} ions in drinking water away from permissible levels can cause severe health threat. Similarly, chromium is found chiefly in a hexavalent form that also poses a threat to human health. Human beings and other living organisms are at greater risk of exposure to these toxic ions and other chemicals. Development of new, effective and fast sensors is the need of time. MOFs are nanoporous materials which have quite fast detection time and effective in sensing of various metal ions and hazardous chemicals. A Zn based two-dimensional is synthesized and applied for the sensing of Fe^{3+} and $Cr_2O_7^{2-}$ ions. Due to the presence of free oxygen and nitrogen atoms, this MOF showed quite high sensitivity with Ksv value of 1.8×10^4 and 6.5×10^4 with a limit of detection (LOD) 2.5μM and 0.15μM for Fe^{3+} and $Cr_2O_7^{2-}$ions respectively. This study proved the two-dimensional MOF as excellent sensor for the detection of Fe^{3+} and $Cr_2O_7^{2-}$ ions. This can be used as colorimetric sensor for these ions due to color changes visible to the naked eye.

Keywords: Luminescent MOF, metal ion sensing, Post-synthetic modification.

INTRODUCTION

A large number of world’s population has no excess to clean water due to water pollution. Effluents from industrial, agricultural, and domestic activities carrying various toxic chemical waste are discharged directly to water streams which affect aquatic and human life (Ohe *et al.*, 2004). In developing countries most of the diseases are directly related to polluted water. In recent years, researchers have paid more and more attention for detecting pollutants such as toxic metal ions. Excess and lack of metal ions from allowed levels can lead to severe disorders (Boretti & Rosa, 2019, Rasheed *et al.*, 2019). Anionic forms of chromium ($Cr_2O_4^{2-}$ and $Cr_2O_7^{2-}$) are significant source of water pollution. These ions are added directly into fresh water through effluents from paint and leather industries(Zayed & Terry, 2003). For the detection of presence of minute amount of these ions in water, efficient and cost effective methods with low LODs are required. In this scenario luminescent sensors are appropriate materials for sensing the presence of cations/anions in water because of their ease to use, high sensitivity and selectivity. (Li *et al.*, 2019).

Metal-organic frameworks (MOFs) being nano-porous crystalline hybrid materials containing organic-inorganic moieties (Li *et al.*, 2009, Bai *et al.*, 2016) are potential candidates for diversified applications such as in gas storage, separation (Yu *et al.*, 2017), adsorption (Li *et al.*, 2013), chemical sensing(Wang *et al.*, 2016), drug delivery (Horcajada *et al.*, 2010). MOFs have proved to be good material for detection of various metal ions and other pollutants (Cui *et al.*, 2011) by virtue of their various advantages such as their molecular sieving, host-guest interactions, selectivity that can be make better by modification of pore and aperture size. The MOFs containing metals like zinc in combination with organic linkers such as dicarboxylates and tetrazolates can be good candidate for detection of cations/anions. (Senthilkumar *et al.*, 2018). Due to the presence of multiple binding sites, N, N containing aminotetrazole has been selected as organic linker in combination with zinc metal. The multiple binding sites can be helpful in detection/ sensing of metal ions. (Zhang *et al.*, 2016). A two-dimensional named as BUT-25 [Zn (ATZ)HCO_2] (BUT = Beijing University of Technology) having pillar-layered structure was developed and used for the sensing of Fe^{3+} and $Cr_2O_7^{2-}$. BUT-25 selectively detected Fe^{3+} and $Cr_2O_7^{2-}$ with a LOD (limit of detection) of 0.25μM and 0.15μM for Fe^{3+} and $Cr_2O_7^{2-}$, respectively. These LODs of Fe^{3+} and $Cr_2O_7^{2-}$ in portable water are lower than the minimum standard values put by US-EPA and WHO (15.7μM and 2 μM (0.1mg/L respectively)(Wang *et al.*, 2017, Swaidan *et al.*, 2019).

Materials and Methods

Zn based 2D MOF BUT-25 was synthesized by the reported method (Talha *et al.*, 2020) with little modification, i.e. Zn(NO3)2 (29.7mg), 5-aminotetrazole(8.5mg) and thiophene-2,5-dicarboxylic acid (34.5mg) mixed together in a mixture of DMF and water with ratio of 1.5 : 1in 4mL glass vial. This mixture was ultrasonicated for few minutes to obtain a clear solution. The vials were placed in an oven at 100^{o}C. Vials were taken out after 36hrs and cooled down. The crystals were collected, filtered and washed with DMF. For comparison, BUT-26 and 27 were also prepared by the earlier method (Talha et al., 2020, Alamgir *et al.*, 2021). For fluorescence experiments, a 20mg sample of BUT-25 was grinded into fine powder and added into equal amount of water. The mixture was sonicated to form a uniform suspension.

Result and Discussion

The Structures of BUT-26, 27 has all ready been published (Talha et al., 2020, Alamgir et al., 2021). In BUT-25 the Zn atom is tetrahedrally coordinated to three nitrogen atoms from three different aminotetrazolates and one oxygen atom. A honeycomb-shaped two dimensional layer is shown in figure 1, in which two Zn atoms are connected with each other by aminotetrazolate while formate ions are present on same side of this layer. In addition, a bilayer is formed by joining two neighboring layers by formate ions. The hydrogen bonding stabilizes the framework. BUT-26 and BUT-27 for comparison were formed by sequential addition of dicarboxylates to BUT-25 i.e. isophthalic acid (H_2IPA) and thiophene-2,5-dicarboxylic acid (H_2TDC). When H_2TDC (thiophene-2,5dicarboxylic acid with a bond angle of 148^0 between the arms) was introduced into BUT-25, the pillars were replaced via self-assembly. To accommodate the longer linker i.e. H_2TDC the honeycomb-shaped layers moved a little bit longer distance without producing any change to the structure of honeycomb-shaped layers. On the other side, when a different dicarboxylate, i.e. isophthalic acid (H_2IPA with a bond angle 120^0 between the arms), was added, it did not replace any linker instead it added and adjusted itself to give a unique structure similar to zeolites LTA topology. BUT-27 and BUT-26 both are formed under similar conditions with only difference of angle between the arms of dicarboxylate that leads to two different structures.

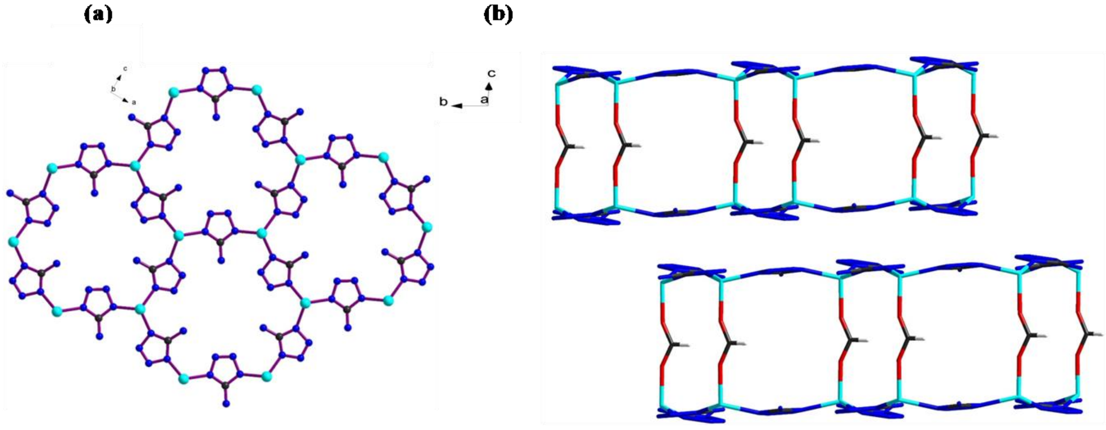

Figure**1.** (a) 2D-Honeycomb-shaped layer (b) Adjacent layers joined by $HCOO^-$in BUT-25

The luminescence of MOFs can be due to the organic linker containing nitrogen and oxygen atoms (Sie *et al.*, 2012). Figure 2 shows the fluorescence quenching of BUT-25 by Fe^{3+} and $Cr_2O_7^{2-}$ that is 80% and 90% respectively while other ions have lower percentage of quenching. Response time BUT-25 towards detection of both ions is quite fast. The metal ion solutions were prepared with a variety of concentrations to find out the LOD. The solutions of metal ions were added in BUT-25 suspension and decrease in intensity was observed as shown in figure 3b and 3e.The Stern-Volmer equation ($I_0/I = 1 + K_{sv}[M]$) was applied to calculate the sensitivity of the MOF. The S-V plots as shown in figure 3c and 3f depicts a linear correlation (R2= 0.994, 0.993 for Fe^{3+} and $Cr_2O_7^{2-}$ respectively).The calculated values of K_{sv}= 1.8×10^4 and 6.5×10^4 with LOD 2.5μM and 0.19μM for Fe^{3+} and $Cr_2O_7^{2-}$ ions respectively.

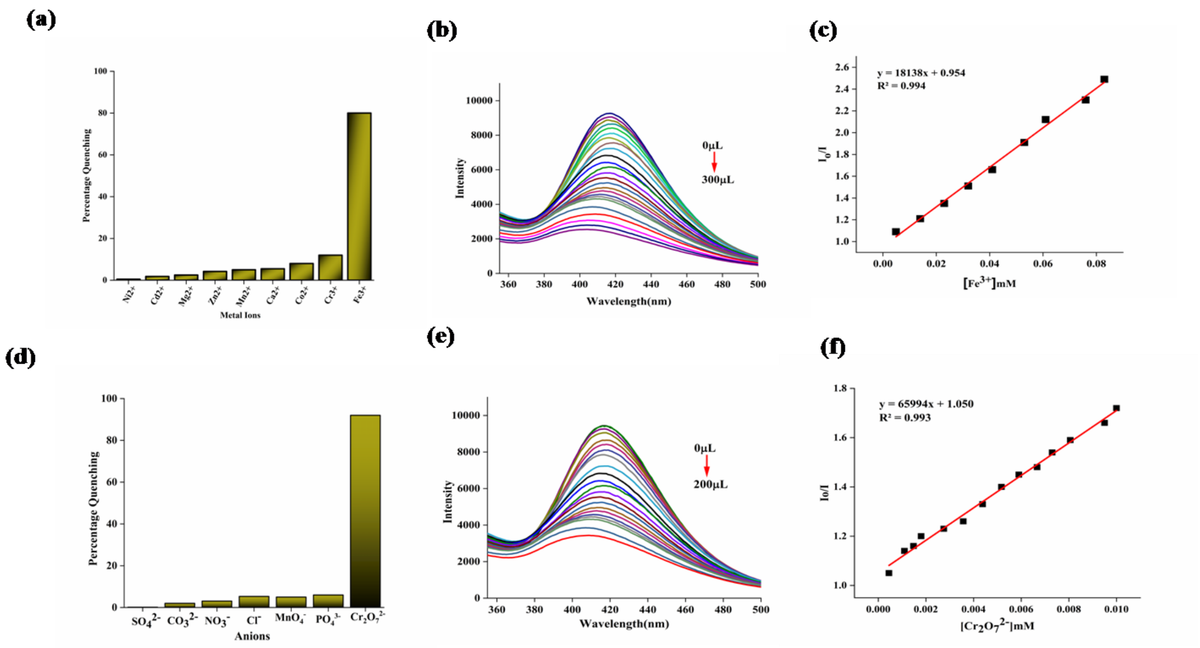

Figure 2. Fluorescence quenching percentage of BUT-25 by selected **(a)**cations**(d)** anions. Fluorescent spectra of BUT-25 suspensions after treating with varying amounts of **(b)**$Fe^{3+}$and**(e)**$Cr_2O_7^{2-}$ions.Fitting of S-V plot for the fluorescence quenching of BUT-25 by **(c)** $Fe^{3+}$and**(f)** $Cr_2O_7^{2-}$.

Mechanism

It is clear from the PXRD of BUT-25 that detection of ions is not due to detection of ions is not due to the structural collapse and crystallinity remained intact during detection process as shown in figure 5(c). (Zhang *et al.*, 2018). One of the commonly reported mechanisms of detection by MOFs is host-guest interactions through energy transfer. For this purpose absorption spectra of various ions were observed as shown in figure 5(a) and 5(b). The UV-Vis absorption spectrum of $Cr_2O_7^{2-}$ was observed in the 200-600nm range and that of Fe^{3+} ions in 250-425nm. The absorption spectrum of dichromate ions covers the excitation and emission spectrum of BUT-25.Due to this resonance energy transfer was observed that lead to the florescence quenching of MOF. (Lv *et al.*, 2016). However, rest of the anions didn't show such kind of overlap. The strong host-guest interactions among free oxygen and nitrogen atoms in the framework and $Cr_2O_7^{2-}$ anions make the energy transfer more efficient. It was observed that the absorption spectrum of Fe^{3+} ion covers the excitation wavelength of BUT-25 indicating competitive absorption between MOF and Fe^{3+} (Hou *et al.*, 2016). The empty orbital of Fe^{3+} ions makes it an acceptor for electrons and free O and N atoms act as good electron donors resulting in energy transfer and luminescence quenching (Zhao *et al.*, 2016). The overlapping of excitation wavelength and absorption spectrum of Fe^{3+} ions leads to the weaker fluorescence of BUT-25 in the presence of Fe^{3+} ions. (Lustig *et al.*, 2017).

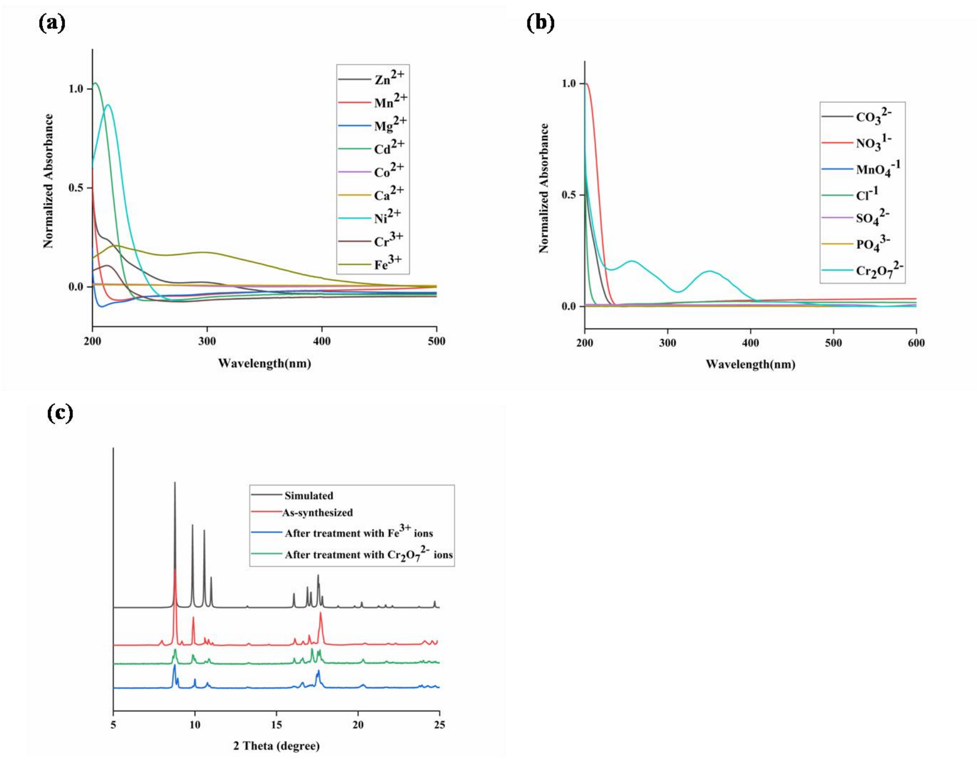

Figure 5. UV-Vis Absorption Spectra of **(a)** Cations **(b)** Anions (c) PXRD of BUT-25

Conclusions

A two-dimensional honeycomb bilayered MOF BUT-25 in which two layers combined together by formate ions proved to be an efficient material for its use in sensitive and selective detection of Fe^{3+} and $Cr_2O_7^{2-}$ ions in water. In this work, we presented a comprehensive comparative study of MOFs with two 3D structures. The development of 3D-MOFs by post-synthetic modification of 2D-MOF provides a way to speed up the synthesis of new structures with different linkers and functionalities for their use in catalysis, sensing and much more.

Conflicts of interest

There are no conflicts to declare.

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Reviewers Remarks

This article is well written and well presented

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