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Short communication

High sensitive luminescence metal-organic framework sensor for hydrogen sulfide in aqueous solution: A trial of novel turn-on mechanism

Yuan-Yuan Cao[a,b,1], Xiao-Feng Guo[a,b,1], Hong Wang[a,*]

[a] Key Laboratory of Analytical Chemistry for Biology and Medicine (Ministry of Education), College of Chemistry and Molecular Sciences, Wuhan University, Wuhan 430072, China
[b] Suzhou Institute of Wuhan University, Suzhou 215123, China

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ABSTRACT

Metal-organic framework (MOF) is a class of crystalline porous solid materials which could be designed as sensors for bioactive molecules. In this study, we illustrated a novel turn-on mechanism based on collapse of MOF structure for luminescence MOF sensors. Taking H_2S as an analyte, we validated our mechanism using a specially selected MOF material Fe^{III}-MIL-88-NH_2 for H_2S sensing. The detection limit towards H_2S is about 10 μM, which is lower than the reported MOF sensors for H_2S designing with other turn-on mechanism.

1. Introduction

Hydrogen sulfide (H_2S), with an unpleasant odor of rotten egg, was traditionally considered as a toxicant [1,2]. Despite of its acute toxicity as air pollutants, H_2S has recently attracted more and more attention as the endogenous gaseous signaling molecule along with nitric oxide (NO) and carbon monoxide (CO) [3,4]. Endogenous H_2S participates in several physiological processes, like K_{ATP} channel-mediated hyperpolarization of vascular smooth muscle, antioxidant and anti-apoptotic signaling effects to cardioprotection, therapeutic benefit in the treatment of ischemia-induced heart failure and so on [5–9]. Also, H_2S plays a role in the respiratory system, central nervous system, endocrine system, and gastrointestinal system [4,10–12]. Normally, endogenous H_2S concentration in mammals is at micromolar levels (10–100 μM) [3,5,13,14], and the abnormal H_2S level is supposed to be related to some diseases, such as arterial and pulmonary hypertension [15], cardiovascular disease [16], Alzheimer's [17,18], Parkinson's [6] and even cancer [19]. Therefore, sensitive and selective detection of H_2S is desired.

Till now, several techniques have been applied for determination of H_2S, including colorimetry [20–22], electrochemical analysis [23–25], gas chromatography [26] and fluorescence [27–29]. Considering the high volatility and reactivity of H_2S, fluorescence based methods have obvious advantages like high selectivity and sensitivity, short trapping time, easy to achieve in-situ and real time imaging [30,31]. In these methods, fluorescence turn-on probes and ratiometric probes are more preferable because they can effectively avoid false response and have a better signal-to-noise ratio in dark background [32–36]. By far, several kinds of turn-on and ratiometric fluorescent probes have been reported for H_2S detection, such as small-molecule fluorescent probes, quantum dots, nanoparticles [37–41].

Metal-organic framework (MOF) is a class of crystalline porous solid materials, in which metal ions are linked by polyfunctional organic ligands to form the porous periodic network with great specific surface area and large pore volume [42,43]. As novel functional materials, MOFs have been widely applied in gas storage, separation, catalysis, chemical sensing, biomedicine, etc [44–48]. As chemical sensors, MOFs have some other particular advantages comparing with other kinds of sensors, like flexibility of functionalization for MOFs, introduction of different active metal centers and ligand for improving selectivity and pre-concentration of the analytes, and so on [49–54]. Up till now, there are several luminescent MOFs have been reported as sensors with luminescence

* Corresponding author.
E-mail address: hongwang@whu.edu.cn (H. Wang).
[1] These authors contributed equally.

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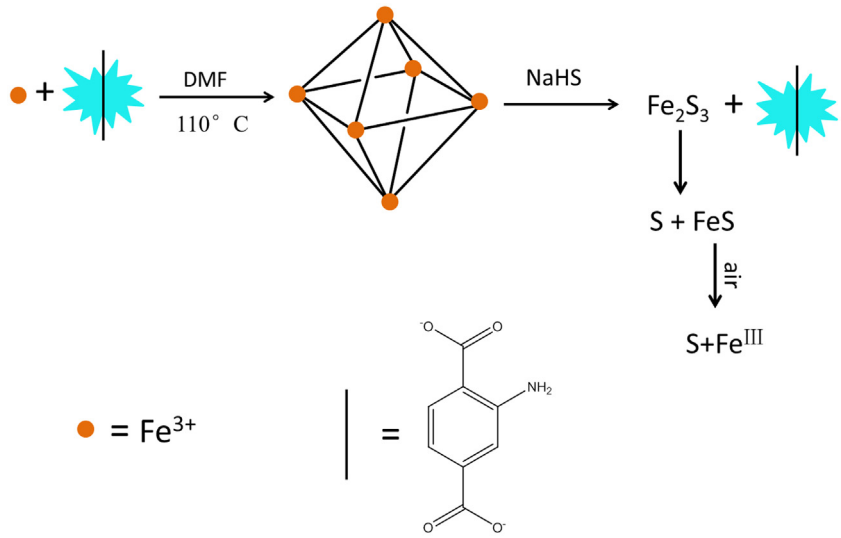

Scheme 1. Schematic illustration of the synthesis and the turn-on function of Fe^{III}-MIL-88-NH_2.

detection. For instance, UIO-66 MOFs have been used to probe H_2S under physiological pH conditions based on the reaction of H_2S and $-N_3$/-NO_2 (UIO-66@-N_3 and UIO-66@-NO_2) [55,56], MIL-88 MOFs have been adopted as sensors for 6-mercaptopurine (Fe-MIL-88-NH_2)[57] and biothiols (Fe-MIL-88/H_2O_2) [58], UiO-67 and MIL-100 have been applied to O_2 detection [59,60]. In these MOF sensors, turn-on and turn-off fluorescence are commonly used designing strategy. The turn-on or turn-off mechanisms of them are based on the reaction between analytes and functional groups of ligands or metal ions adsorbed on the MOFs (not metal ion vertexes). However, the sensitivity of such mechanism is not satisfied (about mM magnitude).

In this study, we proposed a novel turn-on mechanism for MOFs sensors based on the collapse of MOF structure and release of fluorescent ligand in the presence of analyte. To fufill this purpose, the ligands of MOFs should be fluorescent because the turn-on fluorescence is coming from released free ligands. Meanwhile, the MOFs sensors should have no intrinsic fluorescence, thus the paramagnetic metal ions are preferred to be vertexes of MOFs which can quench the fluorescence of ligands. We call these MOFs paramagnetic ion quenched MOFs (PIQ MOFs). In addition, all the functional groups on ligand of MOFs sensors should not react with analytes to avoid unnecessary interference. We tried to validate this mechanism using a specially selected MOF material for H_2S detection. Fe^{III}-MIL-88 is typical MOFs and has been used as sensors for several analytes like 6-mercaptopurine (Fe-MIL-88-NH_2) and biothiols (Fe-MIL-88/H_2O_2) [57,58]. As shown in Scheme 1, Fe^{III}-MIL-88-NH_2 is an ideal model to evaluate our mechanism with fluorescent 2-aminoterephthalic acid (NH_2-H_2BDC) as the ligand and paramagnetic Fe^{III} ions as the vertexes. Fe^{III} vertexes of Fe^{III}-MIL-88-NH_2 will be seized by H_2S with the addition of H_2S easily and rapidly since the ultra high affinity between S^{2-} and Fe^{3+} (ultra small solubility product constant of Fe_2S_3, 1.4×10^{-88}). At the same time, the MOF collapses and fluorescent ligands are released accompanying with the appearance of fluorescence. The sensitivity of such PIQ MOF sensor based on its collapse should be improved obviously comparing with the reported MOF sensors for H_2S because of the following reasons. First, the reaction between H_2S and Fe^{III} is easier and faster than those between H_2S and functional groups on organic ligands. Second, Fe_2S_3 is the direct resulting product of the reaction, and this product could convert to FeS and S rapidly, and FeS would further convert to Fe^{III} in the presence of air. According to thermodynamic equilibrium theory, such conversion is significantly beneficial to the completion of the reaction of the analyte and MOF sensor. Third, MOFs have potential on gas storage, which might adsorb and enrich gas molecules. With the processing of the reaction, the size of MOF dots is decreasing, and the specific surface area is increasing, which is also favorable to the reaction.

2. Materials and methods

The synthesis of Fe^{III}-MIL-88-NH_2 was performed under solvothermal condition from NH_2-H_2BDC and $FeCl_3 \cdot 6H_2O$ in DMF [61,62]. The reaction product was recovered by filtration. The unreacted raw materials and occluded guest molecule in Fe^{III}-MIL-88-NH_2 were firstly removed by washing with DMF for several times. The DMF was secondly removed by exchanging with ethyl alcohol for 2 days (Soxhlet extraction), and the volatile ethanol was then removed under vacuum at 100 °C for 12 h. The IR spectrum was recorded on an iS10 FT-IR spectrophotometer using KBr pellet in 400–4000 cm^{-1} range. Powder X-ray diffraction pattern (PXRD) was performed on the X'Pert Pro X-Ray diffractometer in 5°–40° 2θ range. Thermal gravity analysis (TGA) was performed on a simultaneous thermal analyzer STA 449C from 20 °C to 600 °C (10 °C/min, N_2 atmosphere). Scanning electron microscope (SEM) pictures were recorded on the SIGMA FE-SEM microscope. Fluorescence measurement was carried out using the F-4600 Fluorescence Spectrophotometer with a 1 cm × 1 cm quartz cell.

3. Results and discussion

The powder X-ray diffraction (PXRD) patterns of as-synthesized Fe^{III}-MIL-88-NH_2 and Fe^{III}-MIL-88-NH_2 soaked in water for 30 min both agree well with the simulated one (Fig. S1 and Fig. S2), which indicates the stability of Fe^{III}-MIL-88-NH_2 in aqueous solution during our experiment. The thermogravimetric analysis of as synthesized Fe^{III}-MIL-88-NH_2 shows that the Fe^{III}-MIL-88-NH_2 loses its occluded solvent molecules on heating (Fig. S3). Two absorption peaks at 3360 and 3465 cm^{-1} in the FT-IR spectrum reveals the existent of $-NH_2$ (Fig. S4). The sizes of Fe^{III}-MIL-88-NH_2 particles (Fig. S5) in aqueous solution were measured by dynamic light scattering (DLS) system and the result showed that the sizes mostly hovered at 750 nm (Fig. S6).

The reaction between Fe^{III}-MIL-88-NH_2 and H_2S was studied using NaHS as H_2S donor according to references [63,64]. After the NaHS solution has been added to the MOF suspension, black pre-