Fluorinated ZnFeIII Hollow Metal–Organic Framework as a 19F NMR Probe for Highly Sensitive and Selective Detection of Hydrogen Sulfide

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ABSTRACT: Hydrogen sulfide (H2S) is considered as a highly toxic environmental pollutant and an important signal transmitter in physiological processes, and the selective and reliable detection of H2S is of great concern and remains challenging. Herein, we report a smart sensitive “off–on” 19F NMR sensor for H2S by partially introducing a fluorinated ligand to construct a hollow dual metal–organic framework (MOF) nanosystem, F-ZnFeIII HMOF, in which the fluorinated ligand acts as the 19F signal source but is initially quenched due to the strong paramagnetic relaxation enhancement (PRE) effect from neighboring FeIII nodes. Upon exposure to sulfide ions, reduction of FeIII to FeII is specifically triggered, which attenuates PRE efficiency, thus turning on the 19F NMR signal. The unique hollow MOF architecture benefits the mobility of 19F atoms, thereby improving the response sensitivity. Meanwhile, the desirable H2S-sorption feature and appropriate redox potential of FeIII/FeII account for the favorable selectivity. The increase in the 19F signal is linear with the concentration of sulfide in the range of 20 to 150 μM with a detection limit of 2.8 μM. The probe is well demonstrated by analyzing H2S in complex matrixes such as biological and foodstuff samples.

INTRODUCTION

Hydrogen sulfide (H2S) is a poisonous, corrosive, and flammable chemical with a distinctive foul odor of rotten eggs, having drawn widespread attention as a typical environmental contaminant and harmful gas for a long time.1 It is frequently discharged from various industrial and daily activities and natural calamities such as petroleum refining, waste disposal, and forest fire, bringing risks to human health.2–4 Even exposure to a low level of H2S (e.g., 300 ppb) may cause irreversible harm to respiratory and central nervous systems.5–6 On the other hand, in recent years, H2S has also been found as one of the important signal transmitters involved in many physiological/pathological processes.7–9 Therefore, in all these situations, there is an extensive demand to develop sensitive, selective, and reliable methods for H2S quantification, especially with regard to complex matrixes.

To date, a variety of analytical approaches have been developed for detection of H2S, including conventional chromatography (GC/HPLC), inductively coupled plasma-optical emission spectroscopy (ICP-OES), electrochemistry, and fluorometry and colorimetry methods.10–17 Among them, GC and ICP-OES often require tedious and complicated procedures of sample pretreatment due to the non-static type of detection in which samples pass through the core parts of the instrument. Although electrochemical sensors for sulfide are considered as a highly sensitive strategy, they suffer from relatively low stability for quantification because the reactions occurring on electrodes are sensitive to ambient temperature, humidity, or pH values. In addition, the vast majority of optical approaches based on organic dyes18–20 and nanoparticle sensors21–23 exhibit really high sensitivity for sulfide analysis, while the colored interferents and opaque solution of matrixes may frequently compromise the detection performance.

In general, the fluorine element is absent in biological systems, environmental media, foodstuff, and so forth. Thus, the 19F nuclear magnetic resonance (NMR) signal response can serve as an ideal readout for complex matrix analysis, avoiding background interference.24 Moreover, 19F possesses a natural abundance of 100% and spin quantum number of 1/2, which renders 19F NMR desirable sensitivity (0.83 relative to proton NMR).25 Meanwhile, 19F NMR analysis almost has no or low requirement on sample preparation due to its static detection mode and negligible influence from the color and opacity of matrix solution. In the past few decades, 19F NMR/MRI probes based on fluorine-containing organic metal complexes,26 polymers,27–29 and fluorinated nanosystems30–32 have been extensively exploited for sensing and bioimaging applications. For examples, the Ye group3 constructed a redox-activatable self-assembled fluorescent 19F NMR/1H MRI multifunctional nanoprobe for specific detection of reductive biothiols and imaging of redox status, in which the reducing biological environment triggered disassembly to
produce turn-on of fluorescence and \(^{19}\text{F}\) NMR signal. The Que group exploited fluorinated copper complexes as \(^{19}\text{F}\) MRI contrast agents for monitoring cellular hypoxia, in which the trifluorinated Cu(II) complex with an appropriate redox potential was able to be selectively reduced to Cu(I) in cells grown under hypoxic conditions, yielding an “off–on” \(^{19}\text{F}\) signal.\(^{32}\) Recently, they also reported \(^{19}\text{F}\) PARASHIFT probes for detection of hydrogen peroxide and peroxidase activity based on a large \(^{19}\text{F}\) chemical shift resulting from oxidation of the fluorinated Co(II) complex to its Co(III) counterpart.\(^{35}\) In these pioneering works, the paramagnetic relaxation enhancement (PRE) mechanism has been frequently utilized for probe design; that is, the PRE effect from the paramagnetic transition-metal ions shortens the transverse relaxation time \((T_2)\) of adjacent \(^{19}\text{F}/^{1}\text{H}\) nuclei, attenuating their NMR/MRI signal or resulting in large chemical shifts. Meanwhile, upon exposure to a stimulus like reduction/oxidation, the transition-metal ions might be converted to a diamagnetic state or destructed, thus restoring the NMR signal. In addition to Cu and Co ions, other metals including Gd,\(^{36}\) Fe,\(^{37}\) Mn,\(^{38}\) and Cu\(^{39}\) complexes with desired PRE capability have been exploited as contrast agents or NMR sensors.

In most cases, PRE-based probes including organic molecular,\(^{40,41}\) polymeric,\(^{42}\) and nanoprobes\(^{33,43}\) are required to explore and synthesize suitable and specific ligands with functional groups to chelate with paramagnetic metal ions, which may involve complicated organic synthesis and post-treatment processes. In another aspect, metal–organic frameworks (MOFs) are generally fabricated in facile strategies, possessing desirable properties of high surface areas, tailorable sizes, great diversity, and flexibility of modification, which have been extensively explored and shown great potential in a variety of important applications.\(^{24,45–48}\) Especially, most of the MOFs utilized transition metals as nodes, which may allow MOF to be a good candidate for construction of smart \(^{19}\text{F}\) nanoprobes by incorporation of the PRE effect into the MOF structure together with the fluorinated moiety. Moreover, in recent years, rational design and synthesis of nanoscale MOFs with hollow features have attracted intensive attention since it is expected to enhance the inherent properties such as loading capacity, gas-sorption capability, and controllable molecular-size selectivity and endow the materials with novel functionalities.\(^{49–51}\)

Herein, we report a novel fluorinated hollow nano-MOF probe for selective H\(_2\)S detection. Based on the controllable synthesis and flexibility of functionalization for MOFs, the corresponding fluorinated ligand, trifluoromethyl-substituted 1,4-benzenedicarboxylic acid (denoted as F-H\(_2\)BDC), was partially introduced to construct the Zn/Fe dual metal hollow MOF nanoprobe, F-ZnFe\(_{III}\) hMOF, of which the F-H\(_2\)BDC ligand can serve as a desirable \(^{19}\text{F}\) signal response moiety. The sensing principle depends on the fact that the \(^{19}\text{F}\) NMR signal was initially quenched due to the strong PRE effect from adjacent Fe\(^{3+}\) ions, while H\(_2\)S triggered reduction of Fe\(^{3+}\) to Fe\(^{2+}\), attenuating the PRE effect, thus turning the \(^{19}\text{F}\) signal on (Scheme 1). The dual metal composition was beneficial to adjust the PRE efficiency on neighboring \(^{19}\text{F}\) nuclei by changing the Zn/Fe ratios; meanwhile, the hollow architecture facilitates the mobility of \(^{19}\text{F}\) atoms, which improves the \(^{19}\text{F}\) NMR signal, thereby attaining an optimal detection limit and a wide range of response. The satisfactory selectivity toward H\(_2\)S over other ions, thiols, and amino acids might be ascribed to the appropriate redox potential of Fe\(^{2+}/\text{Fe}^{3+}\), as well as the desired H\(_2\)S-sorption capability of these hollow nano-MOFs. The practicality of the designed nanoprobe was further validated by detecting H\(_2\)S in biological and foodstuff samples.

**RESULTS AND DISCUSSION**

**Fabrication and Characterization of F-ZnFe\(_{III}\) hMOF Nanoprobe.** The F-ZnFe\(_{III}\) hMOF was successfully prepared via a solvothermal method in the presence of metallic precursors (zinc/ferric ions) and organic ligands including 1,4-benzenedicarboxylic acid (H\(_2\)BDC) and fluorinated H\(_2\)BDC (F-H\(_2\)BDC), where F-H\(_2\)BDC also served as the \(^{19}\text{F}\) signal source (Scheme 1). The transmission electron microscopy (TEM) image of the as-prepared F-ZnFe\(_{III}\) hMOF showed that the product appears to have a hollow and octahedral shape with an average size of 200 nm (Figure 1A). The powder X-ray diffraction (PXRD) pattern (Figure 1C) suggested that the product has an amorphous structure, which is consistent with the MOM hollow octahedral nanostucture reported previously.\(^{52}\) Furthermore, scanning electron microscopy (SEM) and elemental mapping results revealed the homogeneous distribution of elements Zn, Fe, and F in the uniform F-ZnFe\(_{III}\) hMOF nanostructures (Figure 1B). As expected, Fe was observed to be fewer than other elements due to the low feeding ratio of Fe/Zn, which is consistent with...
the EDS result (Figure S2). In addition, FT-IR spectra (Figure 1C,D) verified the presence of the C–F bond in F-ZnFeIII hMOF with the stretching vibration of C–F (∼1050 cm⁻¹) and the coordination of the carboxylate groups to metal ions, as evidenced by the red shift of carboxylate stretching vibration from 1680 and 1705 (for uncoordinated H₂BDC and F-H₂BDC, respectively) to 1591 cm⁻¹. This red shift occurring for H₂BDC is consistent with the previous reports, and for F-H₂BDC, it can also be verified by the IR spectrum of the product synthesized with only F-H₂BDC as the organic ligand, although it was not a hollow structure under this condition (denoted as F-ZnFeIII MOF) (Figure S3). 19F NMR spectra of the F-ZnFeIII hMOF nanoprobe before and after exposure to H₂S displayed an obvious off–on effect, suggesting the potential feasibility for sulfide sensing (Figure 1E).

In order to attain the most efficient responsiveness of the nanoprobe, the related factors including reaction time (Figure S4), dosages of the ferric iron precursor (Figure S5), and feed ratios of the two ligands (H₂BDC:F-H₂BDC) (Figure S6) have been optimized. Taken together, crystallinity evolution and shape conversion of the nanostructure may occur with changes of the above conditions. Generally, the hollow MOF structure with good integrity was beneficial for retaining the mobility of 19F moieties, thus giving rise to desirable 19F NMR responses. As suggested in Figure S4, with fixed feeding ratios of metal precursors and organic ligands, when extending the reaction time, F-ZnFeIII hMOFs gradually turned into solid structures, of which the corresponding 19F SINO decreased with maximal intensity at a reaction time of 8 h. As for the iron precursor, when the iron precursor was less than 5 mg, disordered nanostructures was formed (Figure S5). With increase of the iron precursor, gradually, F-ZnFeIII hMOFs were obtained. Finally, a dosage of 10 mg was adopted. On the other hand, it was not expected that more F-H₂BDC ligands certainly contribute more to the 19F NMR response. As shown in Figure S6, at higher dosages of F-H₂BDC (larger than 50%), solid nanostructures were obtained, and accordingly, 19F SINO decreased due to the restriction of 19F mobility; therefore, an optimal feed ratio of 1:1 was applied.

19F NMR Off–On Sensing Mechanism. As designed for the F-ZnFeIII hMOF nanostructure, Fe(III) nodes act as efficient quenchers to the 19F NMR signal originating from the coordinated fluorine ligands (F-H₂BDC) due to the strong PRE effect of Fe(III) and an appropriate proximity to 19F moieties. Upon exposure to hydrogen sulfide, Fe(III) was reduced to Fe(II), greatly attenuating the PRE effect on the adjacent 19F nuclei and thus leading to off–on of the 19F NMR signal. As can be seen in Figure 2A,B, TEM and SEM images of F-ZnFeIII hMOF after reaction with sulfide (1 mM) showed that its morphology and structure were well retained, indicating the fine stability of the probe. The color of the reaction solution changing from orange yellow to bright yellow also suggested that mild reduction occurred under such a level of analyte (1 mM), generating ferrous iron and sulfur (yellow), while at a much higher level of sulfide (10 mM), ferrous iron could further react with sulfide ions to produce FeS (black) (Figure S7). Moreover, the reduction of Fe³⁺ to Fe²⁺ by sulfide could be reversibly switched back. As displayed in Figure 2C, the 19F NMR intensity of the F-ZnFeIII hMOF nanoprobe system treated with sulfide decreased by bubbling oxygen into the solution due to the recovery of the PRE effect by oxidizing Fe(II) into Fe(III), indicating that the hollow MOF nanostructure remained intact in this redox process. With

the prerequisite of stability and hollow feature for the F-ZnFeIII hMOF probe, to maximize the change in the signal between the “off” and “on” states was also dependent on the dosage of ferric iron. As a comparison, F-FeIII MOF was synthesized under the same conditions as F-ZnFeIII hMOF without introduction of the Zn precursor (Figure S8). It was clearly seen in Figure 2D that F-FeIII MOF demonstrated extremely lower recovery of the 19F NMR signal upon addition of sulfide than that for F-ZnFeIII hMOF, owing to the redundant Fe(III) and a solid structure. Therefore, both the hollow structure and optimal doping of ferric iron for the as-prepared F-ZnFeIII hMOF probe account for the highly sensitive response to sulfide.

Analytical Performance of the H₂S Sensor. The as-fabricated F-ZnFeIII hMOF probe can be well dispersed in an aqueous medium and shows excellent stability. As can be manifested in Figure S9, the 19F NMR intensity (SINO) of the nanoprobe colloidal solution remained almost unchanged for a period of 1 week, while upon exposure to H₂S (1 mM), significant enhancement of the NMR signal was observed, similar to that of freshly prepared probe solution. Subsequently, we investigated the feasibility of quantitative detection of H₂S with this F-ZnFeIII hMOF probe based on activation of the 19F NMR signal. Various concentrations of NaHS were added to the solutions of F-ZnFeIII hMOF (1.2 mg/mL) to evaluate the efficiency of the probe. As shown in Figure 3A, a good linear correlation (R² = 0.993) between the 19F NMR signal changes (ΔSINO) and concentrations of the added NaHS was observed. The limit of detection (LOD) was further found to be 2.8 μM, with a linear range covering from 20 to 150 μM, which were comparable to or better than those previously reported probes (Table S1). Moreover, this new nanoprobe avoids complicated sample pretreatment and possesses a fast response time, within 10 min (Figure S10), suggesting that the favorable reaction rate/response time and the proper detection window might bring great convenience and efficiency for practical applications.

To investigate whether the “turn on” of the 19F NMR signal induced by H₂S is specific, the 19F NMR spectra of F-ZnFeIII hMOF upon addition of various potential interferents, including inorganic ions like Fe³⁺, Ca²⁺, K⁺, Cl⁻, SO₄²⁻, HPO₄²⁻, and H₂PO₄⁻, biological thiols like GSH and Cys, amino acids such as Val, Tyr, and His, glucose (Glu), and
The hollow structure of the F-ZnFeIII hMOF was crucial for decreasing the PRE effect and immediately turning on the 19F NMR signal-to-noise ratio increase ($\Delta SINO$) of F-ZnFeIII hMOF and the concentration of sulfide at pH 7.0. (B) normalized 19F NMR intensity increase of F-ZnFeIII hMOF toward sulfide and various interfering species at a concentration of 5-fold to that of sulfide.

Table 1. Detection Results of H2S in Different Real Samples (Mean ± SD, n = 3)

| sample               | added (μM) | observed (μM) | recovery (%) |
|----------------------|------------|---------------|--------------|
| fetal calf serum     | 20         | 19.0 ± 0.3    | 95.0 ± 1.2   |
| fetal calf serum     | 40         | 39.4 ± 0.7    | 98.5 ± 1.8   |
| milk                 | 20         | 19.6 ± 2.0    | 98.0 ± 7.4   |
| milk                 | 40         | 38.3 ± 2.1    | 95.8 ± 5.9   |
| fresh egg white      | 20         | 20.2 ± 1.2    | 101.0 ± 5.3  |
| fresh egg white      | 40         | 41.6 ± 1.9    | 104.0 ± 4.8  |

95.0 and 98.5% were obtained for the biological sample (fetal calf serum) at both spiking levels. For the foodstuff samples like milk and fresh egg white, favorable recoveries within 95.8 to 104.0% were also achieved. These results demonstrated that the laudable selectivity of the F-ZnFeIII hMOF nanoprobe toward H2S is well applicable for analyzing complex matrices, such as biological and food samples.

**CONCLUSIONS**

In summary, we have designed and prepared a new 19F NMR off-on sensor for selective detection of H2S by partially introducing a fluorinated ligand to construct a hollow ZnFeIII dual metal MOF nanostructure, F-ZnFeIII hMOF. The fluorinated ligand of the MOF structure acts as the 19F signal response source, which was initially quenched by adjacent Fe3+ nodes due to the PRE effect. Meanwhile, the presence of H2S would specifically trigger the reduction of Fe3+ to Fe2+, decreasing the PRE effect and immediately turning on the 19F signal. The hollow structure of the F-ZnFeIII hMOF was crucial in achieving highly specific detection of H2S as such a structure allowed for enough mobility of fluorine atoms as well as sufficient reaction of sulfide ions with Fe3+. With a concise sample treatment protocol and fast response time (10 min), the developed method was successfully used to analyze H2S in complex matrices such as biological and foodstuff samples, which demonstrated desirable applicability of the as-prepared nanoprobes. This novel strategy based on the MOF structure and PRE effect of its metal nodes may pave new avenues for the design of MOF-based nanosensors for other analytes in the analytical and related fields.

**EXPERIMENTAL SECTION**

**Chemicals and Reagents.** Iron acetylacetonate (Fe(acac)3) was obtained from Scientific Research Special (Japan). Polyvinylpyrrolidone (PVP, MW ~30000 Da) was purchased from Shanghai Yuan-ye Biotechnology Co., Ltd. Zinc nitrate ($\text{Zn(NO}_3\text{)}_2\cdot\text{6H}_2\text{O}$) and 1,4-benzenedicarboxylic acid (denoted as H2BDC) were supplied by Tianjin Guang-fu Fine Chemical Research Institution, and 2-(trifluoromethyl)-1,4-benzenedicarboxylic acid (denoted as F-H2BDC) was bought from Shanghài Bi-de Pharmaceutical Technology Co., Ltd. Sodium hydrosulfide (NaHS) was purchased from Beijing Yi-nuo-kai Technology Co., Ltd. Sodium chloride (NaCl), potassium chloride (KCl), calcium chloride (CaCl2), ferric chloride (FeCl3), potassium sulfate (K2SO4), dipotassium hydrogen phosphate (KH2PO4), potassium dihydrogen phosphate (KH2PO4), glucose (Glu), ethanol (EtOH), and N,N-dimethylformamide (DMF) were purchased from Beijing Chemical Factory. Cysteine (Cys), glutathione (GSH), valine (Val), ascorbic acid (AA), tyrosine (Tyr), and histidine (His) were from Beijing Ao-bo-xing Biotechnology Co., Ltd. Fetal calf serum (FBS) was supplied by Hangzhou Si-ji-qing Bioengineering Materials Co., Ltd. Eggs and milk were bought from a local supermarket in Beijing. All of the above chemicals were of analytical grade and were used without further purification.

**Characterization.** The transmission electron microscopy (TEM) images were collected on a JEOL JEM-1200EX (200 kV) transmission electron microscope. Scanning electron microscopy (SEM) images and elemental mapping tests were performed using a JEOL JSM-7800F scanning electron microscope. The IR spectra were measured on a Nicolet Nexus 670 Fourier transform infrared (FT-IR) spectrometer. The powder X-ray diffraction (PXRD) patterns were acquired on a Bruker AXS D8-Advanced X-ray diffractometer. 19F nuclear magnetic resonance (NMR) experiments were carried out on a Bruker AVANCE III 400 spectrometer at 376.47 MHz. All 19F NMR spectra were measured using a “single-pulse” sequence (Bruker “zg” pulse sequence) without decoupling of 1H. The D2O coaxially capillary was used for locking the field. To attain reliable quantification with 19F NMR, the other major parameters were set as follows: spectral width 56.47 KHz; data points (size) of spectrum 64 K; pulse angle 90°; relaxation delay 0.8 s; and scan number 256. The total experiment time was about 6 min.

**Preparation of F-ZnFeIII hMOF.** The synthetic procedure of F-ZnFeIII hMOF was referred to previously reported methods with modification. Typically, iron(III) acetylacetonate (Fe(acac)3, 10 mg), Zn(NO3)2·6H2O (46.4 mg), H2BDC (4.8 mg), F-H2BDC (6.8 mg), and PVP (MW ~30000, 200 mg) were dissolved in a DMF/EtOH mixture (DMF:EtOH = 16:9.6 mL) under magnetic stirring for 10 min at room temperature. The resultant mixture solution was transferred into a 50 mL Teflon-lined autoclave and sealed, which was...
then put in an oven and heated at 100 °C for 8 h. After cooling to room temperature, the raw products were collected via centrifugation at 8000 rpm for 10 min and then washed with DMF and EtOH successively. The resulting product was dispersed in 5 mL of ethanol for further use. The F-FeIII MOF nanoparticles were prepared under the same conditions as F-ZnFeII hMOF without introduction of the Zn precursor, but a hollow structure was not formed.

19F NMR Detection of H2S. To quantify H2S in solution, the corresponding calibration curve was established (for convenience, NaHS was used as the source of H2S here). First, a series of different concentrations of NaHS solution were prepared. Then 50 μL of the NaHS solutions (corresponding to the final concentrations of 20, 40, 60, 80, 100, 125, and 150 μM), 100 μL of F-ZnFeIII hMOF probe solution (the final concentration was 1.2 mg/mL), and 350 μL of solvent were mixed in a standard NMR tube. The resulting mixture was then incubated at 37 °C for 10 min. Finally, 19F NMR was performed, and the signal-to-noise ratios (denoted as SINO) were recorded to establish the standard curve. For the anti-interference investigations, the interfering species were utilized at a 5-fold concentration to that of NaHS.

Real Sample Assay. Detection of H2S in several real samples with the complex matrix was performed with the developed method. The fetal calf serum was diluted 10 times with DI water without further pretreatment prior to 19F NMR detection. The milk samples were only centrifuged at 15000 rpm for 5 min before the detection. The fresh egg white samples were obtained from eggs by centrifuging the protein part at 15000 rpm for 5 min after 10-fold dilution. After the simple pretreatment, 350 μL of the real sample was mixed with 100 μL of the F-ZnFeIII hMOF probe solution (the final concentration was 1.2 mg/mL) in an NMR tube, and 50 μL of NaHS solution with different concentration levels was spiked to carry out 19F NMR detections.

ASSOCIATED CONTENT

Supporting Information

XRD pattern of F-ZnFeIII hMOF (Figure S1); energy dispersive spectrum F-ZnFeIII hMOF (Figure S2); IR spectrum and TEM image of F-ZnFeIII MOF (not a hollow structure) (Figure S3); influence of reaction time on morphologies of F-ZnFeIII hMOFs and their 19F NMR responses (Figure S4); influence of iron precursor dosages on morphologies of F-ZnFeIII hMOFs and their 19F NMR responses (Figure S5); influence of feed ratios of the ligands on morphologies of F-ZnFeIII MOFs and their 19F NMR responses (Figure S6); photographs of F-ZnFeIII hMOF aqueous solutions before and after reaction with sulfide (Figure S7); TEM image of F-FeIII MOF (Figure S8); stability of F-ZnFeIII hMOF aqueous solution at pH 7.0 (Figure S9); 19F NMR intensity (SINO) of F-ZnFeIII hMOF (at pH 7.0) versus the incubation (at 37 °C) time with sulfide (Figure S10); comparison of the linear range, LOD, and response time with previously developed methods (Table S1) (PDF).

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Notes

The authors declare no competing financial interest.

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