Metal-organic framework film for fluorescence turn-on H_2S gas sensing and anti-counterfeiting patterns

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ABSTRACT Hydrogen sulphide (H_2S) is a common air pollutant, which is produced in various industry processes. Therefore, it is of crucial importance to detect H_2S in real time. Many fluorescent sensors were reported aiming at detecting H_2S in solution; however, the fluorescence sensing of gaseous H_2S has not yet been reported. In this work, we utilized the post-functionalized fluorescent film, MIL-100(In) $@\text{Eu}^{3+}/\text{Cu}^{2+}$ film, realizing fluorescence turn-on sensing of gaseous H_2S at room temperature for the first time with the limit of detection as low as 0.535 ppm, which is comparable to some reported fluorescent probes for S^{2-} ions and semiconductor based gaseous H_2S sensors. The sensor was designed due to the strong affinity of H_2S with Cu^{2+} . With the formation of CuS , the “antenna effect” between the ligand and Eu^{3+} recovered, resulting in the fluorescence turn-on of Eu^{3+} emission. Additionally, we proposed a new method to realize multi-colour anti-counterfeiting patterns with lanthanide ions ink, taking advantage of the extraordinary smooth surface and uncoordinated carboxylate groups within the MIL-100(In) film.

Keywords: H_2S gas, fluorescence sensing, film, anti-counterfeiting

INTRODUCTION

Various harmful and toxic gases such as H_2S , NO_2 , SO_2 , NH_3 have severely damaged our life and environment [1]. It is an ongoing topic to detect and control these gases. Among them, H_2S is one of the most toxic gases, which is produced in sewage plants, oil, coalmines and natural gas industries [2,3]. The exposure to H_2S would cause acute symptoms and severe adverse effect, such as eye irritation, fluid in the lungs, cortical pseudolaminar necrosis, cerebral edema and even death [4]. In this regard, the Oc-

cupational Safety and Health Act of the United States (OSHA) set the occupational exposure limit for gaseous H_2S to be 10 ppm for 8 h [5]. Therefore, it is urgent to detect gaseous H_2S at such low levels. In past decades, many efforts have been made in developing semiconductor based H_2S sensors [5–8]. However, these sensors are vulnerable to the electromagnetic environment and suffer from the poor anti-disturbing to interference gases [9,10]. As a result, enormous research attention has been aroused to develop alternative methods to detect H_2S . Fluorescence-based H_2S sensing owns many advantages, including good sensitivity, real-time response, noninvasive sensing, which has become a hot research topic recently. Traditionally, there are three ways to realize fluorescence turn-on H_2S sensing in solution: (1) utilize the strong reducibility of H_2S to reduce electron-receptors to electron-donors [11,12]. (2) Utilize the nucleophilicity of H_2S to drop off the fluorophore [13,14]. (3) Utilize the precipitation reaction of H_2S with some metal ions [3,15]. Although many fluorescence turn-on type H_2S sensors have been reported based on the above methods recently, few are aimed to detect gaseous H_2S , because these mechanisms usually do not work in the absence of water.

Metal-organic frameworks (MOFs), which have emerged as exciting inorganic-organic hybrid porous material, can be self-assembled from inorganic metal ions with organic linkers [9,16–19]. Due to the hybrid nature, MOFs may exhibit the properties of both inorganic and organic photonic units. Benefitting from the fruitful energy transfer processes among photonic units and analytes, MOFs show significant potential as fluorescent sensors. In the past decade, MOFs have been largely investigated as sensors for metal ions, anions, pH, small molecules, nitroaromatic

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explosives and temperature [20–27], but the sensors for gases are rarely reported [22]. There are some challenges in realizing MOF-based fluorescent sensors for gases, for example, gaseous H_2S : (1) MOFs must be fabricated in film samples since the powder cannot stand the blast of gas flux [28,29]. (2) Most of the sensing routines work in solutions but very ineffective in gases.

In our previous work, we developed a luminescent metal-organic framework film through post functionalization of porous MIL-100(In) [30], revealing excellent post-functionalizing ability of this film. As shown in Scheme 1a, b, Eu^{3+} and Cu^{2+} ions can be simultaneously post-functionalized on the extra carboxylate acid of MIL-100(In) film. Cu^{2+} ions have been found to be able to quench the emission of Eu^{3+} ions which is due to the obstruction of “antenna effect” between the organic ligand and lanthanide ions [9]. As a result, the emission of Eu^{3+} ions in this film is at off state. However, Cu^{2+} ions may drop from the coordination site with the presence of S^{2-} because of the strong affinity between them, resulting in the fluorescence turn-on of Eu^{3+} ions (Scheme 1b). Inspired by this mechanism, we incorporated Eu^{3+} and Cu^{2+} ions into MIL-100(In) film to form a MIL-100(In)@ $\text{Eu}^{3+}/\text{Cu}^{2+}$ film in luminescent turn-off state. We found that the reaction of Cu^{2+} and H_2S could also take place in the absence of water, and therefore, with the presence of gaseous H_2S , the characteristic emission of Eu^{3+} ions in MIL-100(In)@ $\text{Eu}^{3+}/\text{Cu}^{2+}$ would turn on with the recovery of “antenna effect” (Scheme 1c). In this contribution, we realized the fluorescence sensing of gaseous H_2S for the first time.

EXPERIMENTAL SECTION

Preparation of ITO

The indium-tin oxide (ITO) coated glass was cut into

small pieces (20 mm × 20 mm), and cleaned with acetone and ethanol in an ultrasonic bath for several times. After that, the ITO pieces were dried with N_2 .

Synthesis of MIL-100(In) film

Homogenized mixture of InCl_3 (0.30 mmol, 66.4 mg), 1,3,5-benzenetricarboxylic acid (BTC, 0.30 mmol, 63.0 mg), *N,N*-dimethylformamide (DMF, 5.25 mL), ethanol (5.25 mL), and H_2O (1.5 mL) was sealed in a 25-mL Teflon-lined bottle. Afterwards, the pre-cleaned ITO glass slide was vertically put into the above solution. The mixture was heated at 120°C for 24 h. After the solvothermal reaction, the MIL-100(In) film was soaked in anhydrous methanol for 8 h at 60°C for three times, and during each time the extract was replaced by fresh methanol. Then the film was treated with acetone similarly for another five times. After the removal of acetone, the film was dried under dynamic vacuum at 60°C to yield the final product.

Preparation of MIL-100(In)@ $\text{Eu}^{3+}/\text{Cu}^{2+}$

MIL-100(In) film was put into 0.1 mol L^{-1} $\text{Eu}(\text{NO}_3)_3$ and 1 mmol L^{-1} $\text{Cu}(\text{NO}_3)_2$ mixture, and then heated at 60°C for 1 day. After that, the film was washed three times with methanol followed by exchanging it with acetone over three times. During each time, the extract was replaced by fresh acetone. Then the post-functionalized film was dried under vacuum at 60°C.

Film characterization

The X-ray diffraction (XRD) patterns of films were collected on a Shimadzu XRD7000 X-ray diffractometer in the $2\theta = 3^\circ$ – 30° range with the recording rate of 3° min^{-1} at room temperature. The surface and cross-section morphology and the energy spectra of films were performed with a field emission scanning electron micro-

Scheme 1 Schematic diagram of the fluorescence turn-on sensor for H_2S gas of MIL-100(In)@ $\text{Eu}^{3+}/\text{Cu}^{2+}$ film. (a) The supertetrahedra of MIL-100(In) film and the coordinated BTC ligands; fluorescence state of MIL-100(In)@ $\text{Eu}^{3+}/\text{Cu}^{2+}$ film in (b) absence and (c) presence of H_2S .

scope (FE-SEM, Hitachi S4800). Fourier transform infrared (FT-IR) spectrum was performed on Thermo Fisher Nicolet iS10 spectrometer using KBr pallets in the 4000–400 cm^{-1} range. The binding state of Eu^{3+} and Cu^{2+} were studied by X-ray photoelectron spectroscopy (XPS; Axis Supra, Kratos Analytical Ltd) and the data were calibrated with reference to the C 1s signal at 285 eV. Inductively coupled plasma mass spectrometry (ICP-MS) was performed on a Thermo Scientific XSERIES 2 ICP-MS system. Nitrogen adsorption/desorption isotherms were investigated at 77 K using a Micromeritics ASAP 2020 surface area analyzer and pore size analyzer.

Luminescence sensing experiments

A home-made gas mixture was used to control the temperature and concentration of gases. As shown in Fig. S1, the mixture gases were introduced into a sensing chamber, which was precisely controlled by the mass flowmeters. The films were placed on a heater whose temperature was controlled by the extra temperature-controlled system. The sensing chamber was placed in the photoluminescence measure chamber with the heater in it. Luminescence spectra were collected on a Hitachi F-4600 fluorescence spectrometer. All error bars represent standard deviations from three repeated experiments.

RESULTS AND DISCUSSION

Characterization of films

As shown in Fig. S2, MIL-100(In) is characterized by the MTN zeolite-type structure with two types of cavities with free diameters of around 25 and 29 Å. The secondary building units (SBUs) of MIL-100(In) are μ_3 -oxo-centered trinuclear units (In_3O), which locate at each corner and interconnect through the ligands to form the framework. Each In atom is bonded to four carboxylates from the ligand and exhibits a terminal position occupied by other guest molecules. The In trimer is further combined with trimesic acids to form supertetrahedra, which assembles by regular repetition into a crystalline MTN zeolite-type structure. The IR spectrum of MIL-100(In) exhibits a shoulder at 1683 cm^{-1} assigned to the $\nu(\text{C}=\text{O})$ mode of uncoordinated carboxyl groups of the ligand (Fig. S3), providing the sites for post functionalization, which matches well with our previous report [30]. To demonstrate the crystallinity of the synthesized MIL-100(In) film, XRD experiments have been conducted under ambient conditions and room temperature. As shown in Fig. 1, the XRD patterns of MIL-100(In) film matches well with the simulated MIL-100(Al). Some of the peaks

Figure 1 XRD patterns of the films. (a) Simulated MIL-100(Al). (b) As-synthesized MIL-100(In) film. (c) MIL-100(In)@ $\text{Eu}^{3+}/\text{Cu}^{2+}$ film. (d) MIL-100(In)@ $\text{Eu}^{3+}/\text{Cu}^{2+}$ film after heating to 100°C. (e) MIL-100(In)@ $\text{Eu}^{3+}/\text{Cu}^{2+}$ film after exposure to H_2S gas at 100°C. (f) MIL-100(In)@ $\text{Eu}^{3+}/\text{Cu}^{2+}$ film after putting into air for two months.

move slightly to lower angle, which is due to the difference of ionic radius between In^{3+} and Al^{3+} . The porosity of the prepared MIL-100(In) was determined in powder sample by N_2 sorption isotherm after guest removal, which exhibits Brunauer-Emmett-Teller (BET) surface areas of 1104.11 $\text{m}^2 \text{g}^{-1}$ (Fig. S4).

Inspired by the reactive nature of the uncoordinated carboxyl groups and the permanent porosity of the MIL-100(In) film, we modified the film with metal cations in DMF at 60°C for 24 h, giving the sensing material, MIL-100(In)@ $\text{Eu}^{3+}/\text{Cu}^{2+}$ film. The XRD patterns confirm that the modifications of MIL-100(In) barely change the structure of the film (Fig. 1c). The Eu 4d and Cu 2p XPS core level spectra were recorded to study the chemical state of europium and copper ions in MIL-100(In)@ $\text{Eu}^{3+}/\text{Cu}^{2+}$ film. As shown in Fig. S5, the Eu 4d peak of MIL-100(In)@ $\text{Eu}^{3+}/\text{Cu}^{2+}$ is similar to that of $\text{Eu}(\text{NO}_3)_3$ while its peak positions at 142.7 and 137.1 eV are 1 eV lower than that of $\text{Eu}(\text{NO}_3)_3$, which is due to the coordinate covalent bond of $\text{Eu}-\text{O}$ between Eu^{3+} and carboxylate acid in the film. Similarly, the Cu 2p peak position of MIL-100(In)@ $\text{Eu}^{3+}/\text{Cu}^{2+}$ is about 1 eV lower than that of $\text{Cu}(\text{NO}_3)_2$, arising from the coordinate covalent bond of $\text{Cu}-\text{O}$. The metal cations loading level of MIL-100(In)@ $\text{Eu}^{3+}/\text{Cu}^{2+}$ were quantified by ICP-MS measurement, which showed the molar ratio of In:Eu:Cu was 19.18:2.16:1. Moreover, the MIL-100(In)@ $\text{Eu}^{3+}/\text{Cu}^{2+}$ demonstrates analogous N_2 sorption behavior to MIL-100(In), yet the BET surface area of MIL-100(In)@ $\text{Eu}^{3+}/\text{Cu}^{2+}$ (1052.24 $\text{m}^2 \text{g}^{-1}$) is slightly lower than that of MIL-100(In) (Fig. S4), which is due to the steric hindrance effect

of the metal ions within pores.

The surface and cross-section morphology of MIL-100(In) $@\text{Eu}^{3+}/\text{Cu}^{2+}$ film was investigated to examine whether the metallization reaction would damage the film. As shown in Fig. 2a, b, the film maintains continuous and well adhered to the ITO surface. It can be estimated that the thickness of MIL-100(In) $@\text{Eu}^{3+}/\text{Cu}^{2+}$ is approximate 2 μm . Energy spectrum analysis also demonstrated the coexistence of Eu and Cu (Fig. 2c, d).

H_2S sensing properties

The emission and excitation spectra of MIL-100(In) $@\text{Eu}^{3+}$ film were firstly investigated, as shown in Fig. S6. When excited at 298 nm under N_2 atmosphere at room tem-

perature, MIL-100(In) $@\text{Eu}^{3+}$ film shows the strong characteristic transitions of Eu^{3+} ($^5\text{D}_0 \rightarrow ^7\text{F}_2$, $J = 1, 2, 4$) at 594, 619, and 699 nm. However, in the MIL-100(In) $@\text{Eu}^{3+}/\text{Cu}^{2+}$ film, the $^5\text{D}_0 \rightarrow ^7\text{F}_2$ transition of Eu^{3+} at 619 nm shows very weak fluorescence emission, which is due to the quenching effect caused by Cu^{2+} ions. When H_2S gas (1% v/v diluted with N_2) was induced into the measurement chamber, the characteristic emission of Eu^{3+} at 619 nm exhibited significant enhancement. Considering that the reaction between H_2S and Cu^{2+} would be affected by temperature, we investigated the fluorescence intensity at different temperatures. As shown in Fig. S7, the enhancement fold of emission intensity increases from 9.38 at 20°C to 10.93 at 40°C, because higher tem-

Figure 2 SEM images of (a) top view and (b) cross section of MIL-100(In) $@\text{Eu}^{3+}/\text{Cu}^{2+}$ film. (c, d) Energy-dispersive X-ray spectroscopy of MIL-100(In) $@\text{Eu}^{3+}/\text{Cu}^{2+}$ film. SEM images of (e) top view and (f) cross section of MIL-100(In) $@\text{Eu}^{3+}/\text{Cu}^{2+}$ film after exposure to H_2S at 40°C. (g, h) Energy-dispersive X-ray spectroscopy of MIL-100(In) $@\text{Eu}^{3+}/\text{Cu}^{2+}$ film after exposure to H_2S at 40°C.

perature promotes the reaction between H_2S and Cu^{2+} ions. However, when the temperature continually increased from 40 to 100°C , the enhancement fold of emission intensity decreased from 10.93 to 7.29, due to that high temperature hindered the energy transfer efficiency between Eu^{3+} ions and ligands [31]. After the sensing process, we investigated the morphology and energy spectrum of the film. As shown in Fig. 2e, f, the film remains continuous and well adhered to the ITO, and the XRD pattern also demonstrates the intact crystalline structure (Fig. 1d, e). The energy spectrum of the film exhibits the existence of S element (Fig. 2h, g), which affirms the reaction between Cu^{2+} and H_2S .

Based on the above results, all the following fluorescent measurements were carried out at 40°C . Fluorescence response of the films were examined in different gases: N_2 , CO_2 , O_2 , CH_4 , C_2H_6 , C_2H_4 , C_2H_2 , SO_2 , NH_3 , NO_2 , and H_2S (all the gases were diluted to 1% v/v with N_2). As shown in Fig. 3, most gases showed limited quenching or enhancing effect to the fluorescence intensity of the film. In contrast, H_2S gas induced a large increase on the fluorescence intensity of Eu^{3+} emission, which effectively differentiated the H_2S from other gases.

The fluorescence response of $\text{MIL-100}(\text{In})@\text{Eu}^{3+}/\text{Cu}^{2+}$ film to different concentrations of H_2S was further studied for three times. As shown in Fig. 4a, when the concentration of H_2S increased from 3 to 115 ppm, the fluorescence intensity of $\text{MIL-100}(\text{In})@\text{Eu}^{3+}/\text{Cu}^{2+}$ film was gradually enhanced. In Fig. 4b, the enhancing curve at lower H_2S concentrations displays a good linear relationship with the function of $I = 17.184C_{\text{H}_2\text{S}} + 794.54$ ($R^2 = 0.99945$), suggesting that the H_2S can be detected quantitatively using this film. The limit of detection (LOD) of $\text{MIL-100}(\text{In})@\text{Eu}^{3+}/\text{Cu}^{2+}$ film to H_2S was calculated according to the 3σ IUPAC criteria [28,32], $\text{LOD} = 3\sigma/K$, where σ is the standard deviation calculated from the 30 replicating fluorescence measurements of blank values and K is the slope of the fitting curve. The LOD was estimated as 0.535 ppm. Table 1 lists some recent representative work of the H_2S sensors. Most of the fluorescence based H_2S sensors work in solutions, while semiconductor or cataluminescence based H_2S sensors need very high temperature. This work presents the first example of a fluorescence sensor for detecting gaseous H_2S with the comparable LOD to some other reported fluorescent probes for H_2S in solution.

Applications for anti-counterfeiting

Anti-counterfeiting materials are in great demand for labelling and bioanalytical assays, causing enormous

Figure 3 The enhancement fold of the emission intensity of ${}^5\text{D}_0 \rightarrow {}^7\text{F}_2$ transition of Eu^{3+} of $\text{MIL-100}(\text{In})@\text{Eu}^{3+}/\text{Cu}^{2+}$ film towards various gases (1% v/v diluted with N_2) at 40°C .

Figure 4 Emission spectra (a) and K_{SV} curve (b) of $\text{MIL-100}(\text{In})@\text{Eu}^{3+}/\text{Cu}^{2+}$ film in the presence of different concentration of H_2S at 40°C .

economic and security implications for government, industry and consumers [45]. Optical functionality is considered to be an ideal anti-counterfeiting system due to the features of being hard to copy and easy to read [9]. Anti-counterfeiting materials should also be stable,

Table 1 Comparison of the sensing properties of various H₂S sensors

Material	Method	Sensing medium	Detection limit		Temperature (°C)	Ref.
			Test conc. (ppm)	LOD (ppm)		
MIL-100(In)@Eu ³⁺ /Cu ²⁺ film	Luminescence	Gas	3	0.535	40	This work
DUT-52-(NO ₂) ₂	Luminescence	HEPES buffer	3.41	0.682	37	[33]
CD-MONT-2	Luminescence	DMSO	0.0341	0.002	RT	[34]
Al-MIL-101-N ₃	Luminescence	HBSS	0.130	0.130	37	[35]
Ce-UiO-66-N ₃	Luminescence	HEPES buffer	~11.935	0.416	RT	[36]
Ce-UiO-66-NO ₂	Luminescence	HEPES buffer	~11.935	1.186	RT	[36]
Fe-MIL-88-NH ₂	Luminescence	Water	2.046	0.341	RT	[37]
[CuL[AlOH] ₂] _n	Luminescence	BBS butter	0.0017	0.000546	RT	[38]
Zr-UiO-66-NO ₂	Luminescence	HEPES buffer	25.92	6.411	RT	[39]
Al-MIL-53-N ₃	Luminescence	HEPES buffer	0.0068	0.0030	RT	[40]
Al-MIL-53-NO ₂ MMM	Luminescence	Water	0.0105	0.0032	RT	[41]
MN-ZIF-90	Luminescence	Water	0.273	—	RT	[42]
Co ₃ O ₄	Cataluminescent	Gas	2.38	0.72	241	[43]
Zn ₃ (BTC) ₂ ·12H ₂ O	Cataluminescent	Gas	~5	4.4	250	[5]
ZIF-8	Cataluminescent	Gas	~6	3	250	[5]
Fe ₂ O ₃ nanoboxes	Semiconductor	Gas	5	5	50	[8]
Au:Fe ₂ O ₃	Semiconductor	Gas	10	10	250	[44]

available in large scale, easy to be fabricated, and highly reproducible [46–48]. Due to their narrow emission characteristic bands, large Stokes shifts, high color purity and non-overlapping spectra, lanthanide-based anti-counterfeiting materials have aroused significant attention [9]. Every Ln(III) cation has its characteristic emission peaks, which facilitates the application of Ln(III)-based luminescent anti-counterfeiting materials in various situations [49]. However, most Ln(III)-based MOF anti-counterfeiting materials are hard to be nanoscaled, easy to fall off and have high roughness. In contrast, MIL-100(In) film provides an excellent platform for anti-counterfeiting due to its good robustness, easiness for fabrication in large scale and unique antenna effect with lanthanide ions. More importantly, the smooth surface of this film sample makes the pattern-writing process very convenient.

Different from the traditional methods that utilized Ln(III)-based luminescent material as ink, we utilized lanthanide ions solutions as ink and MIL-100(In) film as pad. Firstly, 1 mmol L⁻¹ solutions of Eu³⁺, Tb³⁺ and Dy³⁺ in ethanol were prepared. When the lanthanide ions solutions were dropped onto MIL-100(In) film, the characteristic emissions of lanthanide ions immediately appeared upon the excitation of 285 nm due to the antenna effect between the organic ligand and lanthanide

ions. Fig. 5a presents the patterns (the logo of Zhejiang University and Letters) written by using the lanthanide ions ink on MIL-100(In) film, and the high-quality pattern in three color can be easily identified upon the excitation of 285 nm. This means the fluorescent barcoded signal is successfully marked on the film. In order to inspect the reliability of this barcode system, we put the films with pattern into water and heat it at 90°C for 24 h. It can be seen in Fig. 5b that the pattern almost remains the original shape and intensity, indicating the good stability of this system. Fig. S8 displays the SEM images of the film (top view and cross section) after the writing of anti-counterfeiting patterns and heating at 90°C for 24 h, which confirms the contact of the film. Meanwhile, PXRD patterns confirm the stability of the MIL-100(In) film for two months (Fig. 1f), which makes it promising for the practical application. Our work demonstrated a solution ink along with film pad, which can easily seal various patterns on the smooth surface of the film pad, providing a new method for luminescent barcoding.

CONCLUSIONS

In summary, we presented the first example of fluorescent sensing for gaseous H₂S based on MIL-100(In)@Eu³⁺/Cu²⁺ film, and realized a promising anti-counterfeiting material. Because of the uncoordinated carboxyl groups

Figure 5 Photographs of the patterns written by the lanthanide ions ink on MIL-100(In) film pad under nature light (a1) and UV excitation (a2–a5); Photographs of the patterns after immersed in hot water under nature light (b1) and UV excitation (b2–b5). a2: Eu^{3+} ink; a3: Tb^{3+} ink; a4: Dy^{3+} ink.

in the channels of MIL-100(In) film, we functionalized this film with Eu^{3+} and Cu^{2+} ions simultaneously. We found that H_2S in gas state also showed high affinity for Cu^{2+} ions, which could strongly enhance the fluorescence of Eu^{3+} . This work expands the fluorescence sensing of H_2S to the gas state, which may inspire researchers to further find more mechanisms to realize gaseous H_2S fluorescent sensing. Moreover, we demonstrated a promising anti-counterfeiting method that utilizing MIL-100 (In) film as pad along with lanthanide ions solutions as ink, which provided a new insight for realizing luminescent anti-counterfeiting application.

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基于金属有机框架薄膜材料的硫化氢气体荧光增强型探针和图案防伪

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摘要 硫化氢气体是一种常见的工业气体, 也是一种大气污染物, 因此对硫化氢气体的实时检测具有十分重要的意义. 当前报道的硫化氢荧光探针大多是在溶液中进行探测的, 能检测硫化氢气体的荧光探针还鲜有报道. 本文利用后修饰的具有荧光发光潜力的薄膜, MIL-100(In)@Eu³⁺/Cu²⁺, 在室温下首次实现了对硫化氢气体的荧光增强型检测, 检测限可达0.535 ppm. 此探针的设计是基于硫化氢气体与Cu²⁺的强结合力. 当形成CuS之后, 有机配体与Eu³⁺之间的“天线效应”恢复, 使得Eu³⁺的荧光发射增强. 这个荧光探针的性能可以与溶液中检测硫化氢的荧光探针相媲美, 并且不输于传统的半导体型硫化氢气体探针. 此外, 由于MIL-100(In)薄膜表面平整度高且具有未配位的羧基基团, 我们利用稀土离子溶液在其表面上实现了多色防伪图案.