

Supporting Information

EXPERIMENTAL SECTION

Chemicals.

Zinc nitrate hexahydrate ($\text{Zn}(\text{NO}_3)_2 \cdot 6\text{H}_2\text{O}$), 2-amino-1,4-benzenedicarboxylate (BDC-NH₂) and was purchased at Shanghai Aladdin Reagent Co., Ltd.. Triethylamine (TEA) (99.0%, AR), sodium chloride (NaCl) and dichloromethane (CH_2Cl_2) (99.5%, AR) was purchased from Sinopharm Chemical Reagent Co., Ltd.. Sulfuric acid (98%) and sodium carbonate (Na_2CO_3) was purchased from Shanghai Ling Feng Reagent Co., Ltd.. N,N-dimethyl-formamide (DMF) was purchased from Nanjing Chemical Reagent Co., Ltd.. Sodium bisulfate (NaHSO_3), terbium nitrate hexahydrate ($\text{Tb}(\text{NO}_3)_3 \cdot 6\text{H}_2\text{O}$), sodium sulfate (Na_2SO_4) and ethanol (AR) were purchased from Shanghai Rhawn Technology Development Co. Ltd.. Single strand DNA (GGGTGGGTGGGTGGGTGGGT) sequences were synthesized by Shanghai Sangon Biotech company. TRIS (500 g) was purchased from Solarbio life science company. Water was prepared with a Milli-Q system (Billerica, MA, USA).

Apparatus and Characterization

The fluorescence intensity scan was performed by performed on a full-wavelength scanning multifunction reader (SPARK 10M, TECAN, Switzerland). TEM images were performed on a JEM-1200 EX with an accelerating voltage of 100 kV. High-angle annular dark field (HAADF) image and scanning transmission electron microscopy-energy dispersive spectroscopy (STEM-EDS) spectra were collected using a JEOL ARM-200F and Tecnai G2 F20 operating at 200 kV with an EDAX solid-state X-ray detector. UV-vis absorption measurements were performed on a UV-2401 spectrophotometer (Shimadzu). X-ray diffraction (XRD) measurements were performed on a Bruker D8 ADVANCE powder X-ray diffractometer, using Cu K α as the incident radiation.

Synthesis of MOF-5-NH₂.

MOF-5-NH₂ were firstly prepared at room temperature according to the previous report,^{S1} and a slight modification was made. In brief, Zinc nitrate hexahydrate ($\text{Zn}(\text{NO}_3)_2 \cdot 6\text{H}_2\text{O}$) (1.19 g) and 2-amino-1,4-benzenedicarboxylate (BDC-NH₂) (0.36 g) were added to 30 mL of N,N-dimethyl-formamide (DMF). After stirring 5 min, 0.88 mL of triethylamine (TEA) was added by drop to the solution, and white precipitation was formed soon, stirring at room temperature for another 120 min. After washings with ethanol (5×20 mL), the solid precipitation (MOF-5-NH₂) were immersed in dichloromethane (CH_2Cl_2) (25 mL) for one day to exchange the DMF guest molecules trapped in the framework. After centrifugation, the samples were dried in oven at 40 °C for 12 h to remove guest molecules and dry. Finally, the pale-yellow powder sample was collected in a container for subsequent use.

Synthesis of the DNA-Tb-MOF conjugates.

A single stranded DNA (ssDNA) was used to react with Tb³⁺. Briefly, the addition of

510 μL of Tris-HCl to ssDNA, obtained a 10 mM DNA sequence solution. And then 10 μM of Tb^{3+} was added the above solution. The mixture was incubated for 10 min at room temperature. Then, 1 $\text{mg}\cdot\text{mL}^{-1}$ of the prepared MOF-5- NH_2 suspension (ethanol solution) was mixed with the DNA- Tb^{3+} solution, and reacted for 10 min at room temperature. Finally, the sample was collected by centrifugal separation.

Luminescence detection of anions (HSO_3^-).

To detect anions, the PL spectra of the DNA-Tb-MOF conjugates suspension (1 $\text{mg}\cdot\text{mL}^{-1}$) were measured after addition of different anions such as Br^- , SO_4^{2-} , Cl^- , CO_3^{2-} , NO_3^- , PO_4^{3-} and HSO_3^- . The DNA-Tb-MOF conjugates were dispersed in ethanol by stirring to obtain the suspensions. The PL spectra were recorded by using a full-wavelength scanning multifunction reader (SPARK 10M, TECAN, Switzerland).

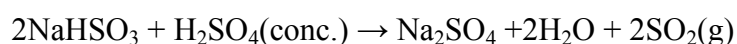
Preparation of luminescent test paper for detection of SO_2 .

The DNA-Tb-MOF materials were assembled into a test paper for portable detection applications. Blank neutral filter paper was dipped into the DNA-Tb-MOF conjugates suspension (2 $\text{mg}\cdot\text{mL}^{-1}$) for 2 min and then taken out with tweezers and dried for subsequent use. The prepared test paper exhibits luminescence emission under a UV lamp after exposure of SO_2 . All of the experimental conditions were consistent and carried out at room temperature.

Test paper for detection of SO_2 .

The test paper was exposed into SO_2 gas atmospheres, and then the PL changes in the test paper were observed under a UV lamp. The gas SO_2 was obtained using a Kipp's apparatus. The volume of the round-bottom flask was 500 mL, and the reaction equation was the following:

SO_2 gas:



During the detection process, the amount of SO_2 gas prepared was controlled by the number of the added acid, and the concentration of the SO_2 gas can be calculated by using this reaction equation. For example, to prepare SO_2 gas with a concentration of 1 ppm, 0.4 μL of concentrated H_2SO_4 was added into a Kipp's apparatus, which already contained a sufficient amount of NaHSO_3 .

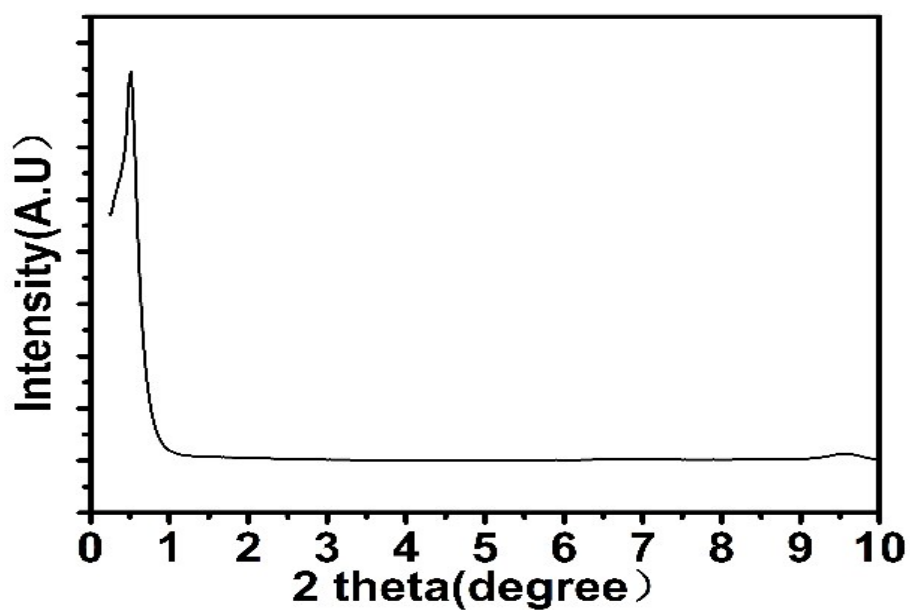


Figure S1. Small angle X-ray scattering pattern of the MOF nanoparticles.

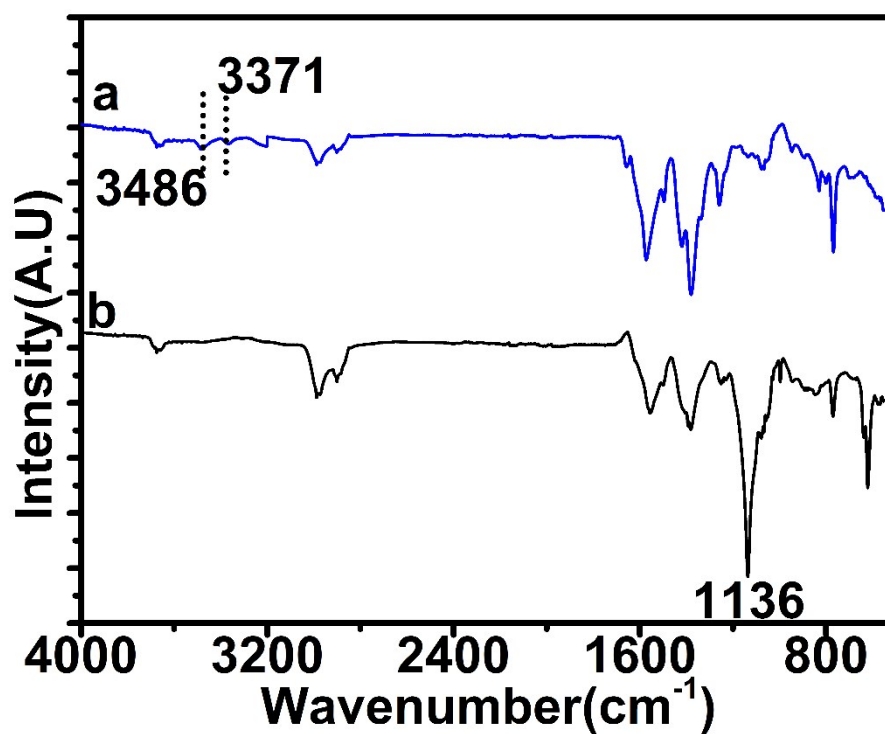


Figure S2. FT-IR spectra of the ammonia functionalized MOF-5 nanoparticles (a) and the corresponding FT-IR spectra of the nanoparticles after addition of HSO_3^- (b).

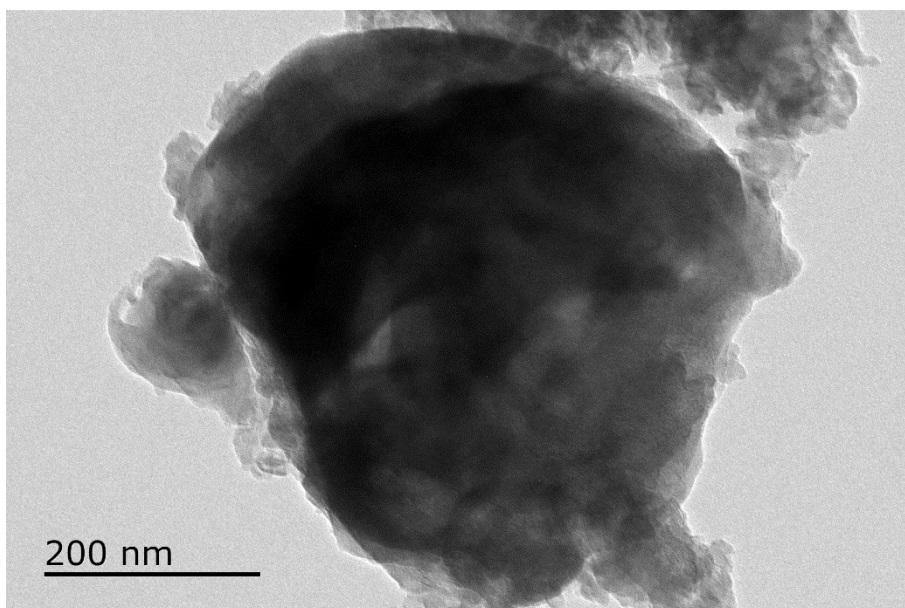


Figure S3. TEM of the DNA-Tb-MOF conjugates.

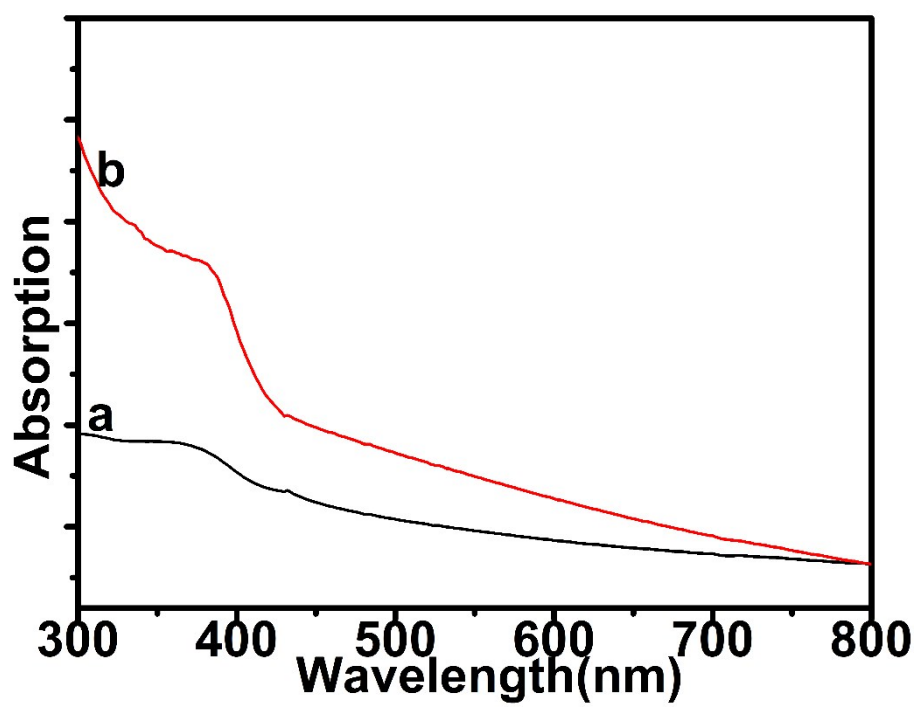


Figure S4. Absorption spectra of the DNA-Tb-MOF conjugates dispersions before and after adding HSO_3^- with concentration 0.03 M.

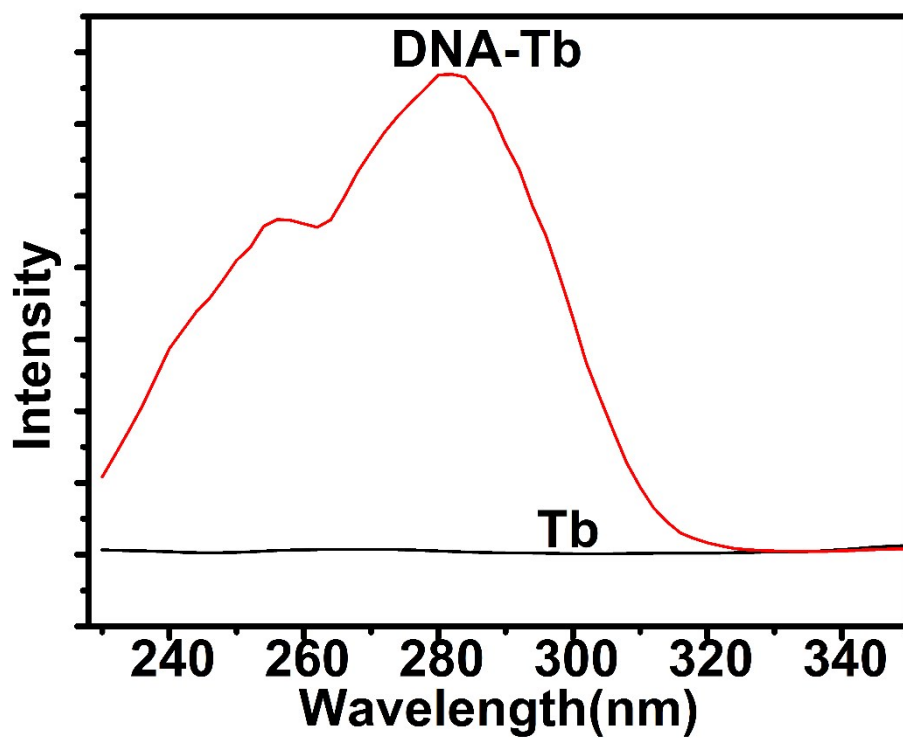


Figure S5. Excitation spectra (emission wavelength: 546 nm) of 25 μM Tb^{3+} in the absence and presence of 50 μM DNA.

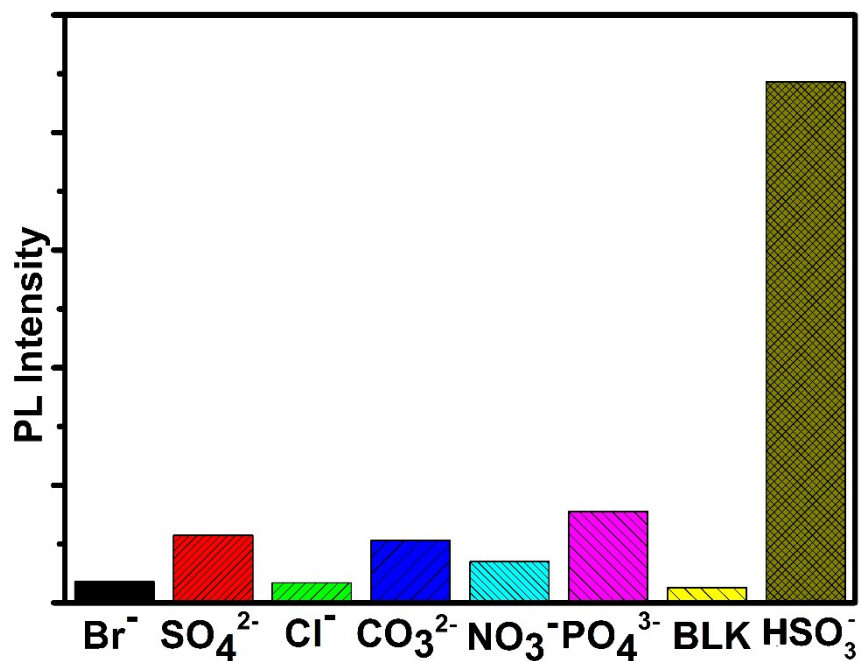


Figure S6. PL intensities of the DNA-Tb-MOF conjugates interacting with different anions at the same concentration ($0.5 \text{ mg}\cdot\text{mL}^{-1}$).

Table S1. Recoveries of the SO₂ in *Atractylodes Poria* samples by the DNA-Tb-MOF conjugate-based approach.

Spiked (ppm)	Detected (ppm)	Recoveries(%)
0	not detected	-----
0.8	0.95	118.8
1.2	0.99	82.5
1.4	1.26	90.0

S1. Kim, J.; Mcnamara, N. D.; Her, T. H.; Hicks, J. C. *ACS Appl. Mater. Interfaces* 2013, **5**, 11479–11487.