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Electronic Supplementary Information

A reaction-triggered luminescent Ce^{4+}/Tb^{3+} MOF probe for the detection of SO₂ and its derivatives

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2. Experimental

2.1. Chemicals and solutions

Ceric ammonium nitrate (99%, Ce⁴⁺ ion) was purchased from Sigma-Aldrich; Terbium nitrate (99.99%) was purchased from Baotou Rewin Rare Earth Metal Materials Co., Ltd.; m-phthalic acid (98%, PA), N-(2-Hydroxyethyl) piperazine-N'-2-ethanesulfonic acid (99.5%, HEPES), N, N-dimethylformamide (99.5%, DMF) and potassium ferricyanide (99.5%, FC) were purchased from Sangon Biotech. The solutions of Na_2SO_3 , NaHSO₃ and interfering substances including Na₂SO₄, NaNO₃, NaNO₂, Na₃PO₄, Na₂CO₃, NaClO, CuCl₂, CaCl₂, MgCl₂, FeSO₄, FeCl₃, Co(NO₃)₂, Cd(NO₃)₂, Pb(NO₃)₂, AgNO₃, Na₂S, glutathione (GSH), cysteine (Cys), ascorbic acid (AA), tyrosine (Tyr), glycine (Gly), alanine (Ala) and H_2O_2 were prepared by dissolving a certain amount of their compounds in ultrapure water, respectively. 3, 3', 5, 5'-tetramethylbenzidine (TMB) were purchased from Sigma-Aldrich. HEPES buffer (100 mM, pH 7) was prepared by dissolving 2.383 g of HEPES in 100 mL of ultrapure water. The HEPES buffers with different pH values were obtained by adjusting pH value with concentrated HCl or NaOH solution (1 M). Ultrapure water (18 M Ω cm; Milli-Q, Millipore) was used throughout all experiments. Unless otherwise stated, all chemicals are of analytical reagent grade and used without further purification.

2.2. Instruments and determinations

The morphology and size of nanoparticles were observed by a scanning electron microscopy (SEM) (Hitachi SU8010, Japan); Powder X-ray diffraction (XRD) was performed by a D8-Discover diffractometer (Bruker, Germany). Fourier transform infrared (FT-IR) spectra were recorded using an Avatar 360 FT-IR spectrometer (Nicolet, USA); UVvisible absorption spectra were obtained on a UV-2600 spectrophotometer (Shimadzu, Japan). Photoluminescence spectra were recorded with a LS55 fluorescence spectrophotometer (PerkinElmer, UK). The detection solution was placed in a standard quartz microcuvette (1-cm light path). A delay time of 0.05 ms and a gate time of 2 ms are used. The 250-nm excitation wavelength is used for the emission spectra. Excitation spectra were recorded by observing the emission intensity of Tb^{3+} at 545 nm. The XPS data were recorded with a PHI 5000 VersaProbe (Ulvac-PHI, Japan) X-ray photoelectron spectrometer equipped with Al-Ka X-ray source. Nitrogen adsorption and desorption isotherms were measured using a Tristar 3000 volumetric adsorption analyzer (Micromeritics Instrument Corporation, USA) at 77 K. The pH measurements carried out on a sartorius PB-18 pH meter. All the experiments were performed at room temperature. All data were measured three times equally, and the error is expressed by standard deviation (SD) for the triplicate measurements.

2.3. Preparation of Ce-PA-Tb MOF

Ce-PA-Tb MOF were prepared with a solvothermal method. Typically, 1 mL of Tb(NO₃)₃ aqueous solution (0.1 mM) and 1 mL of Ce(NH₄)₂(NO₃)₆ aqueous solution (0.1 mM) were added to 8 mL of DMF solution of PA (0.2 mM). The mixture was stirred for 20 min, then transferred to a Teflon-lined stainless steel autoclave and heated to 150 °C for 5 h. After cooled to room temperature, the precipitate was collected by centrifugation at 13,000 rpm (revolutions per minute) for 10 min, and then washed twice with ethanol and ultrapure water, respectively, for the removal of unreactants. The precipitate were dried (approximately 0.08025 g), and finally was dispersed in 1 mL of ultrapure water to form a Ce-PA-Tb suspension of 80.25 mg·mL⁻¹ for subsequent experiments. As a control, PA-Tb was synthesized under the same experimental steps and conditions except without Ce(NH₄)₂(NO₃)₆.

2.4. Luminescence response of Ce-PA-Tb MOF to sulfite ion

To 970 μ L of HEPES buffer (10 mM, pH 7), 20 μ L of Ce-PA-Tb suspension (1.6 mg·mL⁻¹) and different volumes of sulfite solutions (1-30 mM) and water were added, respectively, to make a series of sulfite solutions (1000 μ L) with concentrations of 0, 0.05, 0.1, 0.5, 1, 5, 20, 50, 100, 150, 200 and 300 μ M. After mixed well and reacting for 2 min, the luminescence spectra of these solutions were recorded at an excitation

wavelength of 248 nm.

For the selectivity test of Ce-PA-Tb to sulfite ion, 20 μ L of Ce-PA-Tb suspension (1.6 mg·mL⁻¹) and 10 μ L of interfering substance solution (20 mM) of anions (SO₄^{2–}, NO₃[–] NO₂[–], CO₃^{2–}, PO₄^{3–}, ClO[–] and S^{2–}), cations (Cu²⁺, Ca²⁺, Mg²⁺, Co²⁺, Fe²⁺, Cd²⁺, Ag⁺, Fe³⁺ and Pb²⁺) or possible coexisting glutathione (GSH), cysteine (Cys), ascorbic acid (AA), tyrosine (Tyr), glycine (Gly), alanine (Ala) and H₂O₂ were, respectively, added to 970 μ L of HEPES buffer (10 mM, pH 7) to form a 1000 μ L of test solution. The blank solution is composed of 20 μ L of Ce-PA-Tb and 980 μ L of HEPES buffer. After mixed well and reacting for 2 min, the luminescence intensities of these solutions were measured under the same conditions as the determination of sulfite solution.

2.5. Luminescent detection of sulfite in human serum

Fresh human serum was collected from healthy volunteers at Southeast University Hospital. After centrifuged at 10 000 rpm for 15 min, the supernatants of these serum as the samples were transferred to sterile tubes and stored at -20 °C for the use. These samples were diluted 50 times with 10 mM HEPES (pH = 7) buffer before the testing. A certain volume of sulfite solution (0-200 µM) and 20 µL of Ce-PA-Tb suspension (1.6 mg·mL⁻¹) were added to 960 µL of sample solution to make a sulfite test solution of 1000 µL with final concentration of 0, 0.5, 1, 10, 50, 100 and 200μ M, respectively. After incubated for 30 min at ambient temperature. The luminescence intensities of these solutions at 545 nm were recorded at an excitation wavelength of 250 nm.

2.6. Luminescent detection of SO₂ gas using Ce-PA-Tb MOF material

Standard SO₂ solution (1 μ g/mL) was prepared according to national standard method [1]. For the luminescence method using Ce-PA-Tb MOF, a series of 2 mL of standard SO₂ solutions (0, 0.05, 0.1, 0.2, 0.5, 0.8 and 1 μ g/mL) were prepared by diluting 1 μ g/mL of standard SO₂ solution with NH₄NH₂SO₃ mixed absorption solution (0.1 M) [2]. Then, the luminescence intensity of these solutions at 545 nm was determined. The calibration curve of the luminescence intensity versus the concentration of SO₂ was made.

For the test strip method using Ce-PA-Tb MOF, the test strip was prepared by dropping 100 μ L of Ce-PA-Tb MOF suspension (32 mg/mL) on a small strip of quantitative filter paper (Whatman), and then air-dried for use. The standard SO₂ solutions (0, 0.05, 0.1, 0.2, 0.5, 0.8 and 1 μ g/mL) were dropped on the test strip respectively. After reaction for 5 min, the color of the spots on the strip was photographed under a 302 nm UV lamp, and used as standard color for the colorimetric determination.

For formaldehyde absorbing pararosaniline (FAPA) spectrophotometry, a standard method for the determination of SO_2 in

ambient air in China [1], a series of 2 mL of standard SO₂ solutions (0, 0.05, 0.1, 0.2, 0.5, 0.8 and 1 μ g/mL) were prepared by diluting 1 μ g/mL of standard SO₂ solution with FAS absorption solution (2.7 section). Then, 0.1 mL of NaH₂NSO₃ solution and 0.1 mL of NaOH solution (1.5 M) were added. After mixed, 0.2 mL of PRA solution (2.7 section) was added quickly. After reaction for 5min, the absorbance at 577 nm was determined immediately. The calibration curve of the absorbance versus the concentration of SO₂ was made.

Gaseous SO_2 samples was prepared through a reaction of Na_2SO_3 with concentrated H_2SO_4 [3, 4].

$$Na_2SO_3 + H_2SO_4$$
 (conc.) $\rightarrow Na_2SO_4 + H_2O + SO_2$ (g)

To a 100 mL of three-necked flask containing sufficient amount of solid Na₂SO₃, 20, 50 and 100 μ L of concentrated H₂SO₄ (98%) were added to produce different concentrations of SO₂ gas, respectively. After reaction for 20 min, SO₂ gas was driven to a 200 mL of absorption solution by introducing N₂ gas. This solution was diluted 10 times and determined. Similarly, gaseous H₂S, NO₂, CO₂, NH₃ and N₂ were prepared through a reaction of sufficient Na₂S with H₂SO₄ (0.18 M, circa 1.6 mL), copper powder with HNO₃ (68%, circa 30 μ L), CaCO₃ with HCl (20%, circa 80 μ L) aqueous ammonia (25%, circa 45 μ L), and N₂ from a nitrogen cylinder, respectively.

2.7 Preparation of solutions for formaldehyde absorbing pararosaniline (FAPA) spectrophotometry

Formaldehyde absorption solution (FAS) was prepared by transferring 5.5 mL of formaldehyde solutions (36~38 %) and water to a 100 mL of volumetric flask. This solution was diluted 100 times with water when used. Pararosaniline hydrochloride solution (PRA, 0.005 g/mL) was prepared by adding 0.005 g of pararosaniline, 3 mL of concentrated phosphoric acid (85%), 1.2 mL of concentrated hydrochloric acid and water in 10 mL of brown volumetric flask, and spending 12 h in the dark for use. Sodium sulfamate solution (NaH₂NSO₃, 6.0 g/L) was prepared by adding 0.06 g of aminosulfonic acid (H₂NSO₃) and 0.4 mL of NaOH solution (1.5 mol/L) in 9.6 mL of water, stirring until completely dissolved. Sodium sulfite solution (Na₂SO₃, 1 g/L) was prepared by dissolving 0.1 g of Na₂SO₃ in 100 mL of Na₂EDTA solution (0.5 g/L), and calibrated with a standard Na₂S₂O₃ solution after standing for 2-3 h, 1 mL of this solution is equivalent to 320~400 μ g of SO₂. Standard SO₂ solution (1 μ g/mL) was prepared by transferring 2 mL of Na₂SO₃ solution (1 g/L) to a 100 mL of volumetric flask containing 40~50 mL of FAS, adding FAS until 100 mL to make a 20 μ g/mL solution. This solution was diluted with FAS to 1 $\mu g/mL$ when used.



Fig. S1. Energy dispersive spectrum (EDS) of Ce-PA-Tb.



Fig. S2. X-ray diffraction (XRD) spectrum of Ce-PA-Tb.



Fig. S3. N₂ adsorption (square) and desorption (circle) isotherms of the thermally activated of Ce-PA-Tb recorded at $-196 \text{ }^{\circ}\text{C}$ (at p/p₀ = 0.5). Inset is the pore volume (cm³/g) of Ce-PA-Tb.



Figure S4. Photos of Ce-PA-Tb and PA-Tb in daylight (left) and under a common 302 nm UV lamp (right).



Fig. S5. Luminescence response (at 545 nm) of Ce-PA-Tb (1.6 mg·mL⁻¹) to SO_3^{2-} .



Fig. S6. Luminescence stability of Ce-PA-Tb (1.6 mg·mL⁻¹) and PA-Tb (1.6 mg·mL⁻¹) in the HEPES buffer with pH 7.0 (a) and with different pH values (b).



Fig. S7. XPS spectra for Ce-PA-Tb before (a) and after (b) the addition of SO_3^{2-} ion.



Fig. 8. XPS analysis for Tb 4d of Ce-PA-Tb before (a) and after (b) the reaction with SO_3^{2-} .



Fig. 9. (a) Fluorescence spectra of Ce⁴⁺ (1 μ M) in the presence of PA (1 μ M) and SO₃²⁻ (10 μ m); (b) Fluorescence spectra of Ce³⁺ (1 μ M) in the presence of PA (1 μ M) and SO₃²⁻ (10 μ m).



Fig. S10. Luminescence lifetime of Ce-PA-Tb (square) and Ce-PA-Tb in the presence of SO_3^{2-} (100 μ M) (circle).



Fig. S11. UV-visible absorption spectra of Ce-PA-Tb (2 mg/mL), Ce-PA-Tb (2 mg/mL) + SO_3^{2-} (1 μ M), Ce⁴⁺ (1 μ M), Ce³⁺ (1 μ M) and SO_3^{2-} (0.1 mM).



Fig. S12. Determination of sulfite in human serum using Ce-PA-Tb material (2 mg/mL).



Fig. S13. Calibration curve of Ce-PA-Tb luminescence method measured by standard SO₂ solutions.



Fig. S14. Colors of the test strips of Ce-PA-Tb MOF exposed to different concentrations of SO₂ 0, 0.05 μ g/mL (3.5 ppm), 0.1 μ g/mL (7 ppm), 0.2 μ g/mL (14 ppm), 0.5 μ g/mL (35 ppm), 0.8 μ g/mL (56 ppm) and 1 μ g/mL (70 ppm) and different gases including SO₂, NH₃, H₂S, N₂, CO₂ and NO₂ (about 100 ppm), respectively.



Fig. S15. UV-vis absorption spectra (upper) and corresponding colors (lower) of pararosaniline solution in presence of different concentrations of SO_2 . The solution only without pararosaniline is used as a blank solution.

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$SO_2 (\mu g/mL)$	0	0.05	0.1	0.2	0.5	0.8	1	
А	0.099	0.114	0.128	0.145	0.221	0.274	0.312	
(A-A ₀)*	0	0.015	0.029	0.046	0.122	0.175	0.213	

Absorbance versus the corresponding concentration of SO₂

* A: absorbance; A₀: absorbance at a concentration of 0 μ g/mL



Fig. S16. Calibration curve of formaldehyde absorbing-pararosaniline spectrophotometry.

Table S1. XPS data of Ce-PA-Tb before and after the addition of SO_3^{2-} .

Sampla	Binding energy	Relative proportion			
Sample	Ce ⁴⁺	Ce ³⁺	Ce ⁴⁺	Ce ³⁺	
Ce-PA-Tb	882.68, 901.71	885.78	78.35 %	21.65 %	
	898.52, 916.83	904.08			
$Ce-PA-Tb + SO_3^{2-}$	882.79, 901.34 898.62, 916.89	885.98 904.26	48.36 %	51.64 %	

	•			
Human serum	Added	Detected	Recovery (%)	RSD (%) ^b
sample	$SO_{3^{2^{-}}}(\mu M)$	$SO_3^{2^2} (\mu M)^a$		
sample 1	5.0	5.43 ± 0.33	108	6.1
sample 2	10.0	10.41 ± 0.47	104.1	4.5
sample 3	50.0	49.57 ± 1.78	91.1	3.6
sample 4	100.0	98.48 ± 3.16	98.5	3.2

Table S2. Recovery test of SO_3^{2-} in human serum.

a: average value (n=3) \pm standard deviation; b: relative standard deviation

Tabl	e S3. A	comparison	of	luminescent	detect	ion (of SO	\mathcal{D}_2	gas
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Method	Detection of Limit	λex/λem (nm)	Response time	Refs
Graphene oxide	0.44 µM	370/470, 580	30 min	[5]
APTS-CdTe@SiO ₂ QDs	0.33 μM	340/425, 628	2 min	[3]
MOF-5-NH ₂	2.08 µM	399/450	15 s	[6]
Cyanine Dye-CDs	1.8 μM	365/450	4 min	[4]
Benzothiazole-cyanine	0.34 µM	390/560	15 min	[7]
Ce-PA-Tb MOF	0.093 µM	250/545, 355	30 s	This work

Table S4. Determination of SO_2 gas

SO ₂ gas	Ce-PA-Tb MOF	Ce-PA-Tb MOF	FAPA	RSD (%)
	luminescence	test strip	spectrophotometry	
Sample 1	$2.1\pm0.4~\text{ppm}$	not detected	$3.0 \pm 0.2 \text{ ppm}$	30
Sample 2	38.8± 1.2 ppm	$40 \pm 5 \text{ ppm}$	$34.1\pm0.8~\text{ppm}$	13.7
Sample 3	$70.4\pm0.8~\mathrm{ppm}$	$70 \pm 10 \text{ ppm}$	75.6 ± 1.1 ppm	6.8

a: average value (n=3) \pm standard deviation; b: relative standard deviation

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