

Electronic Supplementary Material

Tb³⁺-doped Ag-MOFs for fluorescent detection of formaldehyde in a novel smartphone platform and its removal applications in milk products and wastewater

Mengwen Li^a; Ao Shen ^a; Man Du ^{b*}; Xiaohui Hao^a; Hongquan Wang ^{c*}; Xiaoyu Du ^a; Shufeng Ma ^a; Jiaxin Yuan^a; Yunxu Yang^{a*}

^a *Department of Chemistry and Chemical Engineering, School of Chemistry and Biological Engineering, University of Science and Technology Beijing, Beijing 100083, China.*

^b *School of Chemical and Pharmaceutical Engineering, Hebei University of Science and Technology, Shijiazhuang, 050018, China.*

^c *State key laboratory of pathogen and biosecurity, Beijing institute of microbiology and epidemiology, Beijing, 100071, China.*

Corresponding Author: Yang Yunxu^a; Du man^b; Wang Hongquan^c.

E-mail addresses: yxyang@ustb.edu.cn (Yang yunxu);

mandu@hebust.edu.cn (Du man);

bjwanghq@163.com (Wang Hongquan).

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Table S1. Comparison of the results of various formaldehyde sensors.

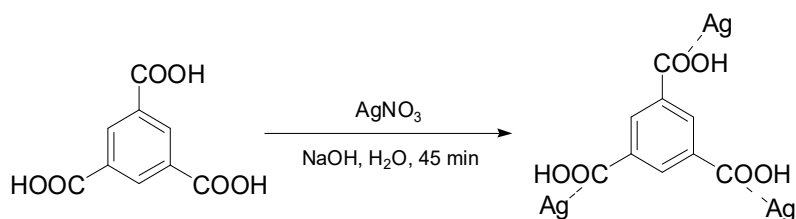
Ref.	Sensor Material	Type of Material	Response Time (s)	Detection Limit	Sensing Mode
22	Al-MIL-53-NHNH ₂	MOF	60	8.37 μ M	turn-on
23	Zr-UiO-66-NH ₂		120	4.0 μ M	turn-off
24	Eu/Zr-UiO-66-NH ₂		-	6.7 μ M	turn-on
25	Ag ⁺ /Eu ³⁺ -UiO-66		360	1.7 μ M	turn-on
26	ZIF-90-LW		28	2.3 μ M	turn-on
8	AnB	organic molecule	-	165 nM	turn-on
9	compound 1		480	0.78 μ M	turn-on
10	FAP-1		7200	5 μ M	turn-on
11	Na-FA		1800	7.1 $\times 10^{-7}$ M	turn-on
12	FP1		10800	0.01 mM	turn-on
13	FAP		7200	0.5 μ M	turn-on
14	RFAP		7200	0.3 μ M	turn-on
15	probe 1		-	900 nM	turn-on
	Tb ³⁺ @Ag-BTC	MOF	180	1.9 μ M	turn-on

Materials and reagents. 1,3,5-benzenetricarboxylic acid (BTC) and polyacrylonitrile (PAN) were purchased from Beijing Ouhe Technology Co., Ltd; silver nitrate (AgNO_3) and sodium hydroxide (NaOH) were purchased from Aladdin; terbium chloride (TbCl_3) was purchased from Shanghai Macklin Biochemical Technology Co., Ltd; trichloroacetic acid was purchased from Beijing Innochem Co., Ltd. All the other reagents obtained from commercial sources were analytical pure and used without further purification. The water was purified by Millipore filtration system.

Instruments. X-Ray Diffracter data (XRD) were obtained with Ultima IV multipurpose X-ray diffraction system (Japan). Fluorescence emission studies were carried out with a Hitachi F-4500 Fluorescence Spectrophotometer. Fourier transform infrared (FT-IR) spectra were recorded in the region of $440\text{--}4000\text{ cm}^{-1}$ with a FTIR-8400s Fourier Transform Infrared Spectrometer (Shimadzu). The scanning electron microscope (SEM) was used Ultra-high Resolution Scanning Electron Microscope SU8010. Thermogravimetric Analysis data (TG) were obtained by a METTLER TOLEDO TGA/DSC1 Synchronous Thermal Analyzer. XPS studies were performed on a Physical Electronics spectrometer (PHI Versa Probe II Scanning XPS Microprobe) with scanning monochromatic X-ray $\text{Al K}\alpha$ radiation ($100\text{ }\mu\text{m}$, 100 W , 20 kV , $1,486.6\text{ eV}$) as the excitation source and with a dual-beam charge neutralizer. The Brunauer–Emmette–Teller (BET) surface area and pore size measurements of the prepared samples were recorded by N_2 adsorption/desorption analysis using an ASAP 2020 Micromeritics (USA). ^1H NMR spectra were measured on a Varian Gemin-400 MHz spectrometer with chemical shifts reported in ppm (TMS as internal standard). Electrosprayionization (ESI) mass spectra were collected on Bruker Daltonics Inc. Pgeneral TU-1901 and Hitachi F-4500 fluorescence spectrometers were used in performing fluorescence spectra at $25\text{ }^\circ\text{C}$. Spectrophotometer CS-520 and iPhone 12 pro max were used to construct the smart sensing platform.

Gas Chromatography. SHIMADZU GC-2014 and flame ionization detector (FID) were used for gas chromatograph (GC) analysis. DM-5MS type glass capillary column ($30\text{ m} \times 0.25\text{ mm}$) was used for separation. Injection volume was $1\text{ }\mu\text{L}$ by a split injector (1/100). The inlet temperature was $200\text{ }^\circ\text{C}$ and the detector temperature was $240\text{ }^\circ\text{C}$. High-purity nitrogen was used as the carrier gas and the flow rate was 1.2 mL/min . Column temperature was kept at $50\text{ }^\circ\text{C}$ for 5 min , then programmed to $100\text{ }^\circ\text{C}$ at $5\text{ }^\circ\text{C/min}$ and kept at $100\text{ }^\circ\text{C}$ for 15 min .

Synthesis of Ag-BTC



Scheme S1. Synthesis of Ag-BTC.

Ag-BTC was synthesized according to the reported literature.³⁸ To prepare Ag-BTC, a solution of NaOH (1 M) was added drop-wise to a suspension of BTC (1.007 g, 4.8 mmol) in 75 mL of distilled water until the pH reached 7.0. To this solution, a solution of silver nitrate (2.840 g, 16.8 mmol) in 12.5 mL of distilled water was also added drop-wise with simultaneous mechanical stirring. After 45 min of stirring of the mixture at room temperature, the product was recovered by filtration, and washed first with distilled water and then with ethanol and, finally, air-dried.

The PXRD patterns of the synthesized Ag-BTC and $\text{Tb}^{3+}@\text{Ag-BTC}$ were shown in Fig. S1. As shown Fig. S1, the synthesized Ag-BTC was consistent with the simulated pattern, and all the main diffraction peaks of them at 5.2° , 6.5° , 7.6° , 15.2° , 25.9° , 28.1° and 31.8° showed great similarity.

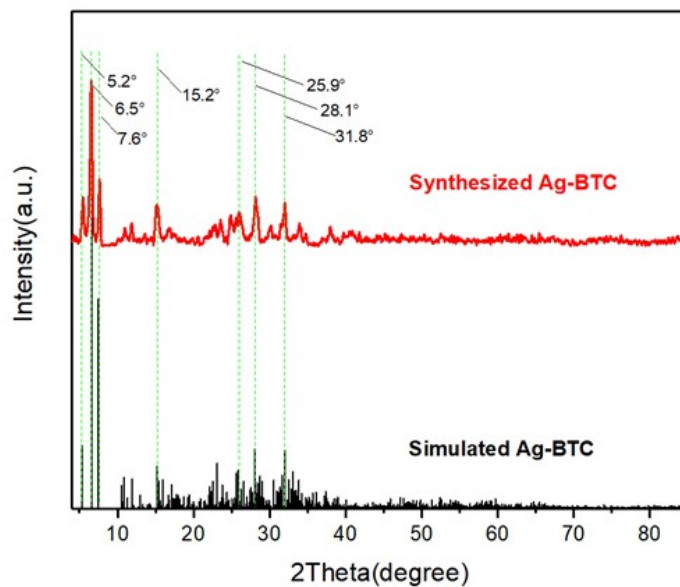


Fig. S1. PXRD pattern of the synthesized Ag-BTC and the simulated Ag-BTC.

For the purpose of determining the chemical composition and element state of $\text{Tb}^{3+}@\text{Ag-BTC}$ composites, XPS was performed as shown in Fig. S2a - S2e. In the XPS experiment, the samples were exposed to monochromatic X-radiation, and the properties of inner-shell electrons were to be probed. According to the XPS survey spectrum of $\text{Tb}^{3+}@\text{Ag-BTC}$ sample (Fig. S2a), kinds of elements (C, O, Ag and Tb) were detected in the sample.

The C 1s emission spectrum could be divided into four main peaks as shown in Fig. S2b. The binding energy at 284.2 eV obtained in the XPS analysis was standardized for specimen charging using C 1s as the reference. The peak at 287.6 eV was attributed from the carboxylate carbon in $\text{O}=\text{C}-\text{OH}$, while the peaks at 284.0 and 284.7 eV were associated with the aryl carbon from benzene ring. The O 1s emission spectrum (Fig. S2c) could be divided into three main peaks by Gaussian fitting method. The peak at 530.1 eV was metal-oxygen ($\text{Ag}-\text{O}$) bonds, and 530.7 eV came from $\text{C}=\text{O}$ bonds in the organic ligand, while the peak 532.7 eV could be attributed from the $-\text{OH}$ groups from $-\text{COOH}$. Fig. S2d displayed the Ag 3d level spectrum. The Ag $3d_{3/2}$ and Ag $3d_{5/2}$ spin-orbital photoelectrons were located at 367.9 eV and 373.9 eV, respectively. In Fig. S2e, the peak at 151.6 eV was typical of Tb $4d_{5/2}$.

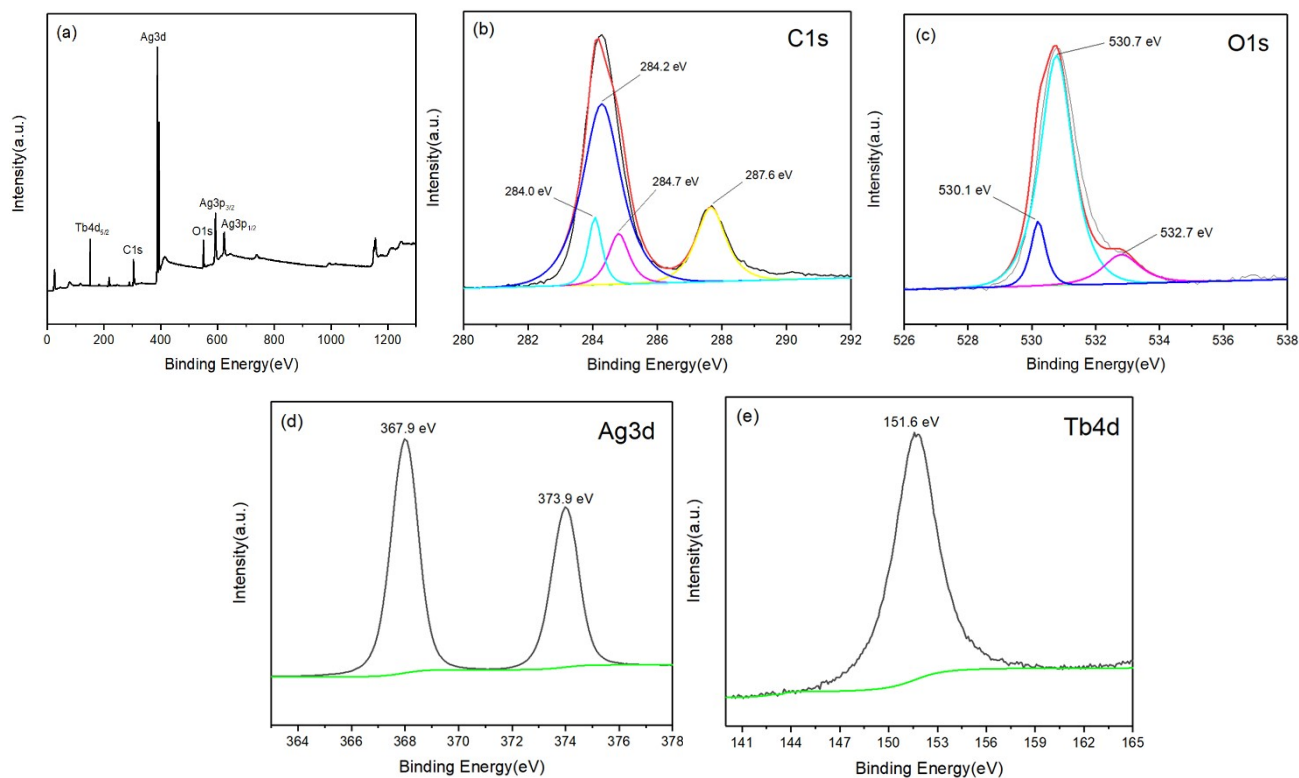


Fig. S2. XPS spectra of $\text{Tb}^{3+}@\text{Ag-BTC}$: (a) the survey scan; (b) C 1s; (c) O 1s; (d) Ag 3d; and (e) Tb 4d.

Kinetic studies:

The reaction of **Tb³⁺@Ag-BTC** (4 mM, 1.7 mg/mL) with 1 mM FA was monitored using the fluorescence intensity. The reaction was carried out at 25 °C. The *pseudo*-first-order rate constant for the reaction was determined by fitting the fluorescence intensities of the samples to the *pseudo*-first-order equation:

$$\ln [(F_{\max} - F_t) / F_{\max}] = -k't$$

Where $F_{\max}$ and F_t are the fluorescence intensities at 547 nm at time t and the maximum value obtained after the reaction was complete. k' is the *pseudo*-first-order rate constant. The *pseudo*-first-order plots for the reaction of **Tb³⁺@Ag-BTC** with FA is shown in Fig. S2, the *pseudo*-first-order rate constant $k' = 1/t_l = 0.66 \text{ min}^{-1}$.

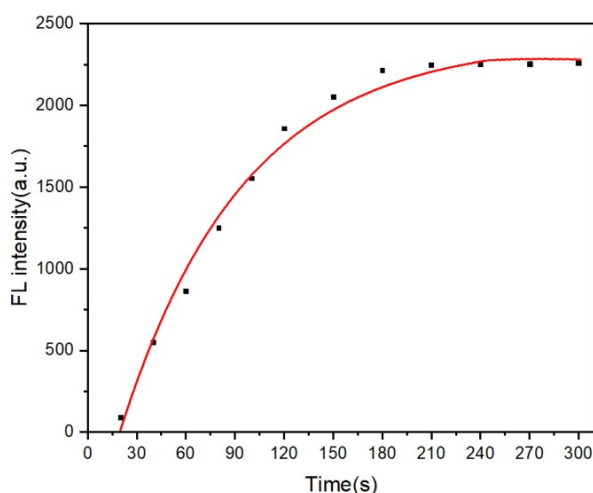


Fig. S3. Time course of the signaling of probe by FA. **Tb³⁺@Ag-BTC** was 4 mM (1.7 mg/mL), FA was 1 mM, in a mixture of DMF and Tris buffer solution (7 : 3, v/v), pH = 7.0. $\lambda_{\text{ex}} = 365 \text{ nm}$.

Research on the influence of temperature:

In order to eliminate the interference of temperature, we have made the following supplements and explanations:

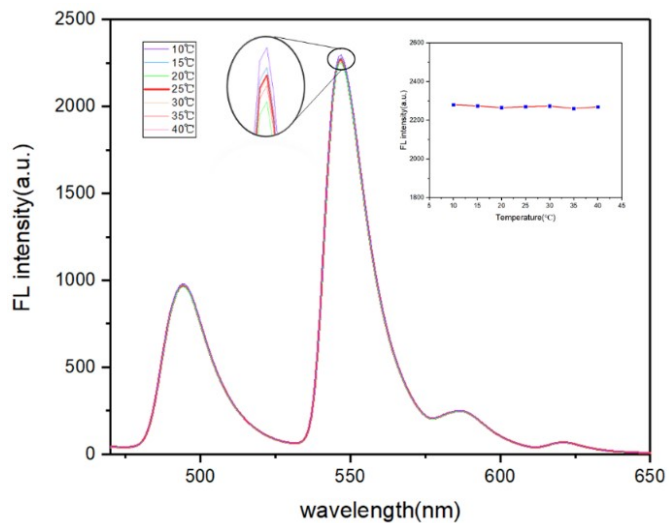


Fig. S4. The fluorescence intensity of $\text{Tb}^{3+}@\text{Ag-BTC}$ response to FA in different temperatures. $\text{Tb}^{3+}@\text{Ag-BTC}$ was 4 mM (1.7 mg/mL), FA was 1 mM, in DMF and Tris buffer solution (7 : 3, v/v), $\lambda_{\text{ex}} = 365$ nm.

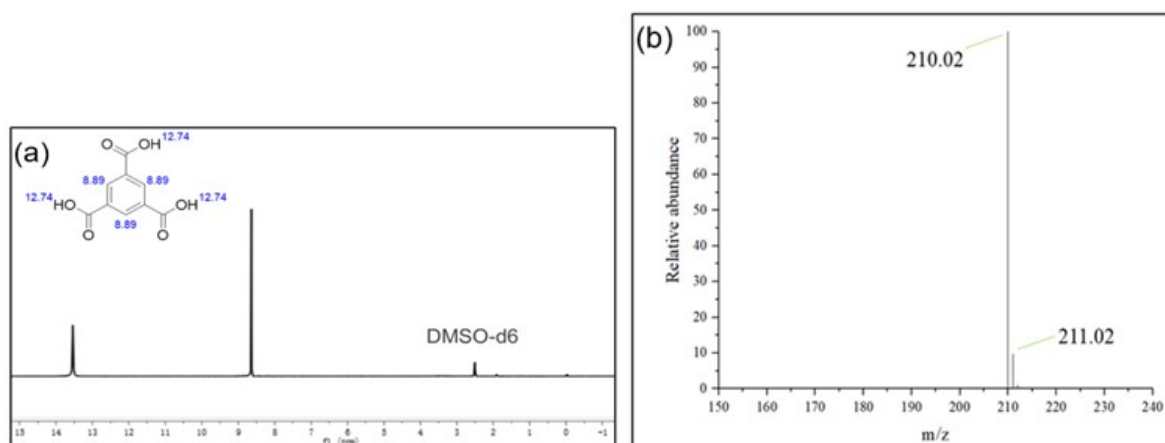


Fig S5. (a) ^1H NMR and (b) ESI mass spectra of released BTC ligand.

^1H NMR (400 MHz, DMSO- d_6) δ (TMS, ppm): 8.89 (s, 3H), 12.74 (s, 3H).

ESI (+)-HRMS (m/z): for TBC: calcd., 210.08, found: [M], 210.02, $[\text{M}+\text{H}]^+$, 211.02.

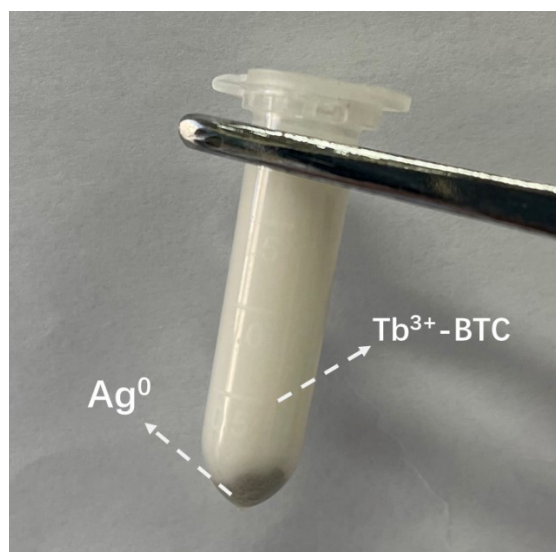


Fig. S6. With the naked eye to observe the reaction of $\text{Tb}^{3+}@\text{Ag-BTC}$ with FA (the precipitated of Ag at the bottom at the test tube, and Tb^{3+} and BTC formed the fluorescent substance.)

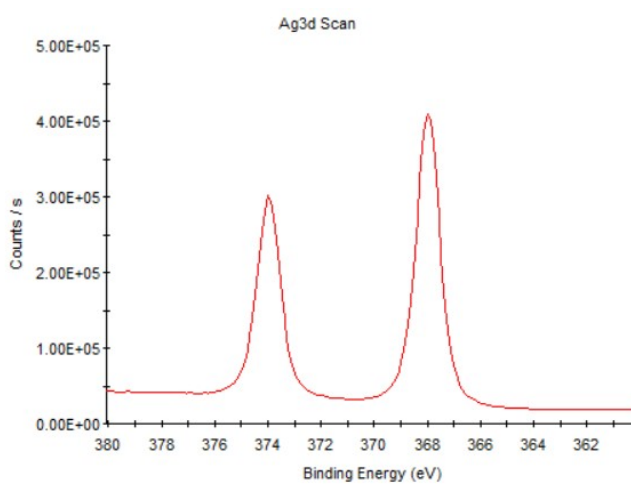


Fig. S7. XPS spectra of Ag 3d.

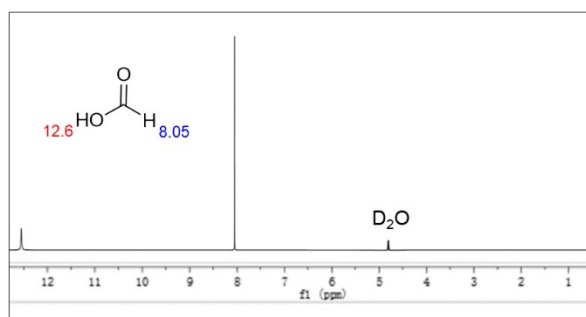


Fig. S8. ^1H NMR spectra of formic acid. ^1H NMR (400 MHz, CDCl_3) d (TMS, ppm): 8.05 (s, 1H), 12.6 (s, 1H).

Fluorescence sensing of FA in milk and wastewater:

10 mL milk and 10 mL wastewater were pre-treated as the same methods in chapter 2.7. The stock solutions of FA with different concentrations (0.1 – 1.2 mM) were prepared in deionized water, and 25 mL stock solution of $\text{Tb}^{3+}@\text{Ag-BTC}$ (4 mM, 1.7 mg/mL) was prepared in DMF and Tris buffer (7 : 3, v/v). Excitation wavelength was 365 nm and emission slit widths was 5.0 nm and 10.0 nm separately. The fluorescence spectra were scanned and collected from 450 nm to 650 nm at 1200 nm/min.

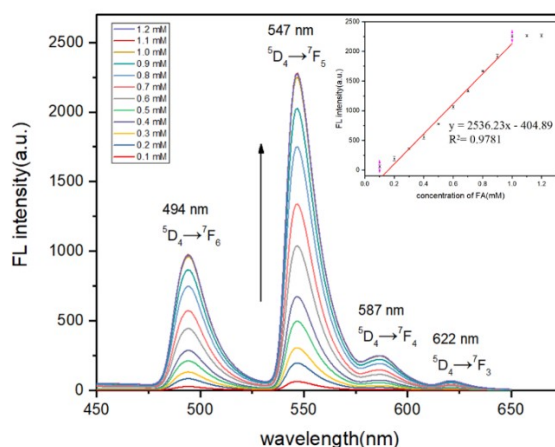


Fig. S9. The fluorescence intensity of $\text{Tb}^{3+}@\text{Ag-BTC}$ in different FA concentrations in milk sample. Insert: The linear fit of the fluorescence intensity upon FA concentrations ($R^2 = 0.9781$). $\text{Tb}^{3+}@\text{Ag-BTC}$ was 4 mM (1.7 mg/mL), FA was 0.1 – 1.2 mM, in DMF and Tris buffer (7 : 3, v/v), pH = 7.0, $\lambda_{\text{ex}} = 365$ nm.

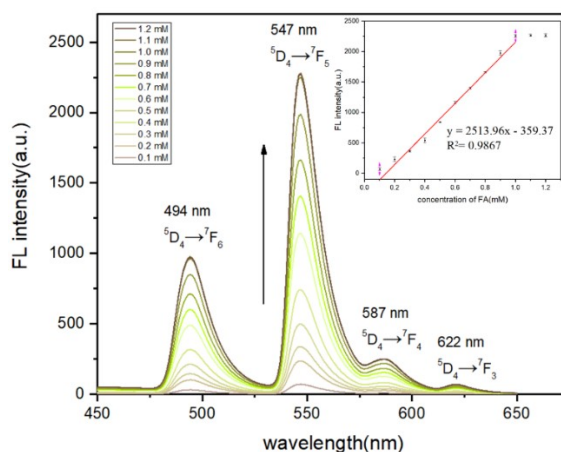


Fig. S10. The fluorescence intensity of $\text{Tb}^{3+}@\text{Ag-BTC}$ in different FA concentrations in wastewater sample. Insert: The linear fit of the fluorescence intensity upon FA concentrations ($R^2 = 0.9867$). $\text{Tb}^{3+}@\text{Ag-BTC}$ was 4 mM (1.7 mg/mL), FA was 0.1 – 1.2 mM, in DMF and Tris buffer (7 : 3, v/v), pH = 7.0, $\lambda_{\text{ex}} = 365$ nm.

In Table S2, the content of FA in pure milk was 37.77% at first. After the treatment of **Tb³⁺@Ag-BTC@PAN** film, it reduced to 0.56%. The removal rate of FA could be calculated in this way:

$$\text{Removal rate} = (37.77\% - 0.56\%) / 37.77\% = 98.52\%$$

Similarly, the removal rate of FA in factory wastewater was:

$$\text{Removal rate} = (22.77\% - 1.05\%) / 22.77\% = 95.38\%$$

Table S2. Retention time (RT, min), peak area (Q), peak height (H), concentration (C, %) of FA in real samples.

real sample	RT	Q		H		C	
		initial	final	initial	final	initial	final
pure milk	2.172	3.23×10 ⁶	0.08×10 ⁶	7.44×10 ⁵	0.59×10 ⁵	37.77	0.56
wastewater	2.170	1.77×10 ⁶	0.13×10 ⁶	5.76×10 ⁵	0.91×10 ⁵	22.77	1.05

Table S3. Removal efficiency of FA in pure milk and factory wastewater samples by HPGC analysis.

real sample	removal rate (%)	concentration of FA (μM)	
		initial	final
pure milk	98.52	100	1.48
wastewater	95.38	100	4.62

Optimization of the ratio of FA concentration and the volume of $\text{Tb}^{3+}@\text{Ag-BTC}@\text{PAN}$ film:

(1) In removal applications, according to the water flux (F) calculation formula of the film:

$$F = Q/(Vt)$$

“Q” is the penetration amount of water, 0.05 L; “V” is the film volume, $9.9 \times 10^{-3} \text{ m}^3$; “t” is the test time, 5.1 h.

When we made the film according to the designed ratio (1.5 g PAN and 0.5 g $\text{Tb}^{3+}@\text{Ag-BTC}$ and the film was 5 cm in diameter and 0.5 cm in thick), F reached the maximum value of 99.0%. So, we chose this volume of $\text{Tb}^{3+}@\text{Ag-BTC}@\text{PAN}$ for removal applications.

(2) On the basis of the definite volume of $\text{Tb}^{3+}@\text{Ag-BTC}@\text{PAN}$ film, we explored the effect of samples containing different FA concentrations on the removal rate. Different concentrations (0.1 – 1.0 mM) of FA aqueous solution (10 mL) were add into 10 mL processed milk and 10 mL wastewater respectively. The residual amount of FA was monitored by gas chromatography and the removal rate was calculated. As shown in Fig. S11 and Fig. S12, the removal rate was not affected by the concentration of FA and always remained stable.

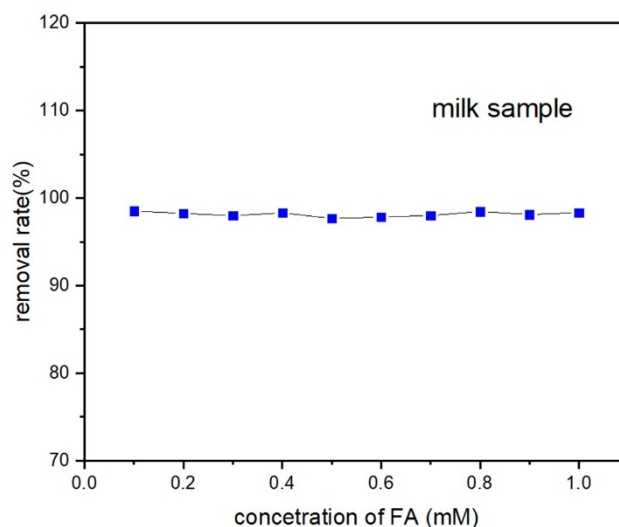


Fig. S11. The removal rate of FA in milk sample with different FA concentrations. The volume of $\text{Tb}^{3+}@\text{Ag-BTC}@\text{PAN}$ film was $9.9 \times 10^{-3} \text{ m}^3$, FA was 0.1 – 1.0 mM (10 mL).

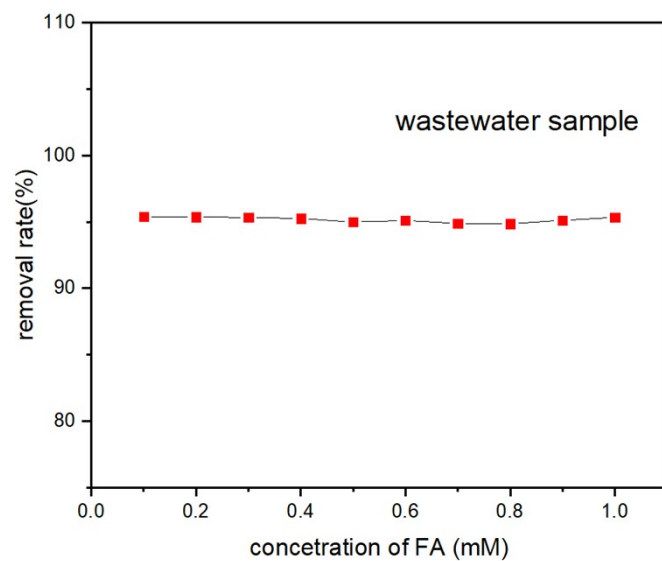


Fig. S12. The removal rate of FA in wastewater sample with different FA concentrations. The volume of $\text{Tb}^{3+}@\text{Ag-BTC}@\text{PAN}$ film was $9.9 \times 10^{-3} \text{ m}^3$, FA was 0.1 – 1.0 mM (10 mL).