

---

## Supplementary Material

### **Decoding and Quantitative Detection of Antibiotics by a Luminescent Mixed-Lanthanide-Organic Framework**

*Yuping Wang<sup>a</sup>, Jing Xia<sup>b</sup>, Yanxin Gao<sup>a\*</sup>*

a. Department of Environmental Science and Engineering, Fuzhou University, Minhou, Fujian 350108, China

b. State Environmental Protection Key Laboratory of Environmental Risk Assessment and Control on Chemical Process, School of Resources and Environmental Engineering, East China University of Science and Technology, Shanghai 200237, China

\* Corresponding author.

E-mail: [gaoyx20@fzu.edu.cn](mailto:gaoyx20@fzu.edu.cn)

---

## S1. Quantum yield measurements

The quantum yields ( $\Phi$ ) were determined by employing the method developed by Bril *et al.* The  $\Phi$  value of a sample was calculated by a direct comparison with a standard phosphor whose  $\Phi$  value was previously determined by absolute measurement (Bril and de Jager-Veenis, 1976). In this work, the quantum yield  $\Phi_x$  was determined by:

$$\Phi_x = \left( \frac{1 - R_{ST}}{1 - R_x} \right) \left( \frac{\Delta\Phi_x}{\Delta\Phi_{ST}} \right) \Phi_{ST}$$

Where  $R_{ST}$  and  $R_x$  are the amounts of exciting radiations reflected by the standard phosphor and the sample, respectively.  $\Phi_{ST}$  is the quantum yield of the standard phosphor. The terms of  $\Delta\Phi_{ST}$  and  $\Delta\Phi_x$  correspond to the respective integrated photon fluxes ( $\text{photo}\cdot\text{s}^{-1}$ ) for the standard phosphor and the sample, respectively. The standard phosphor was sodium salicylate, whose  $\Phi_{ST}$  is 55% at room temperature as reported in previous literature (Malta *et al.*, 1998).

## S2. Limit of detection (LOD)

For a variety of optical analysis methods, measurable minimum analysis signal  $S_L$  is determined by the following equation:

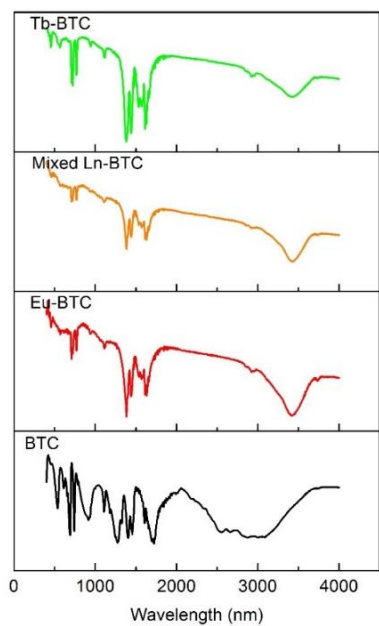
$$S_L = S_b + aD_b$$

Where  $S_b$  is the average blank signal;  $D_b$  is the standard deviation of the blank signal;  $k$  is a coefficient determined based on a certain confidence level. The International Union of Pure and Applied Chemistry (IUPAC) recommended  $a = 3$  for spectral chemical analysis, the confidence level corresponding to  $a = 3$  is about 90%.

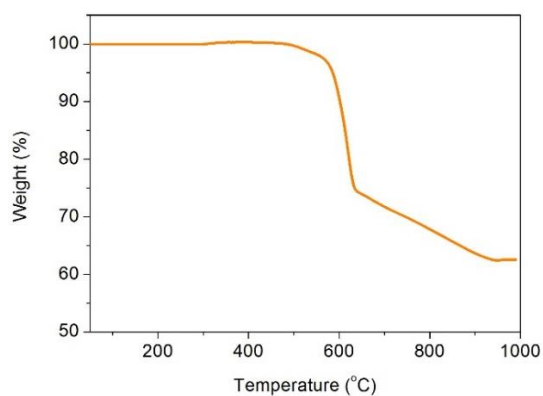
The concentration or amount corresponding to  $S_L - S_b$  ( $aD_b$ ) is the limit of detection.

$$LOD = \frac{S_L - S_b}{k} = \frac{aD_b}{k} = \frac{3D_b}{k}$$

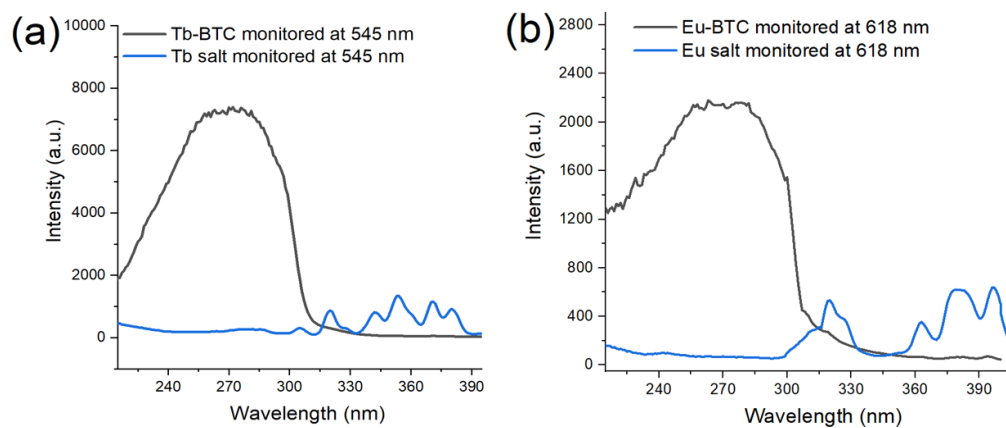
Where  $k$  is the sensitivity (the slope of the calibration curve).



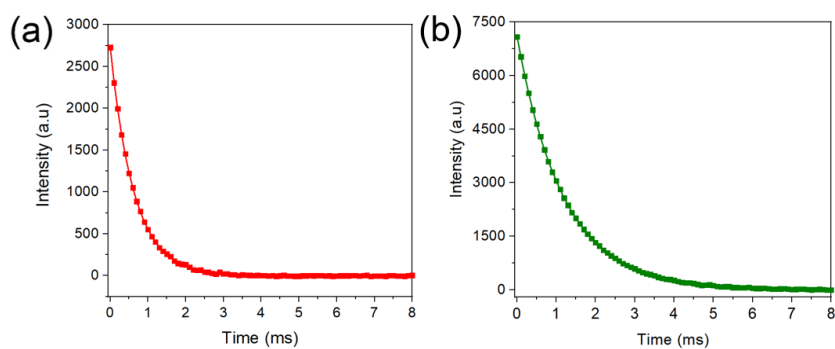
**Figure S1.** FT-IR spectra of BTC and Ln-BTC.



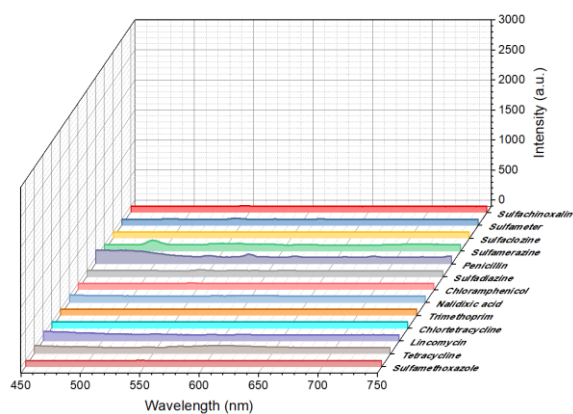
**Figure S2.** TGA spectra of Ln-BTC



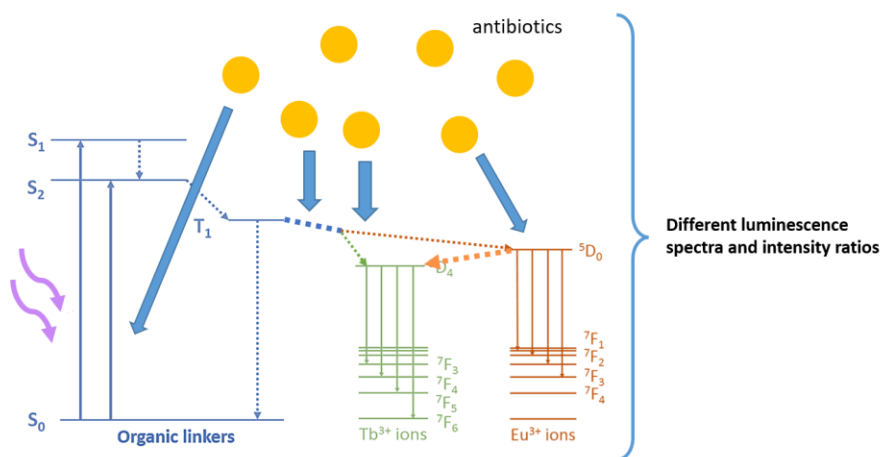
**Figure S3.** Excitation spectra for (a)  $\text{Tb}(\text{NO}_3)_3 \cdot 6\text{H}_2\text{O}$  and Tb-BTC, (b)  $\text{Eu}(\text{NO}_3)_3 \cdot 6\text{H}_2\text{O}$  and Eu-BTC



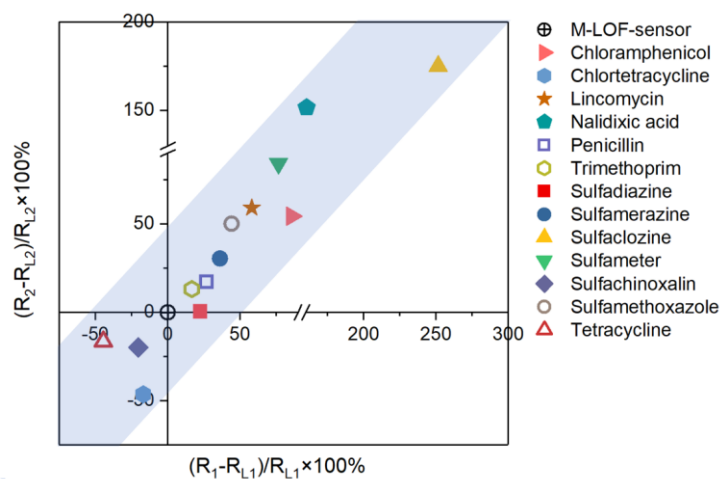
**Figure S4.** Photoluminescence decay curve of (a) Eu-BTC (monitored at 618 nm) and (b) Tb-BTC (monitored at 545 nm) under 286 nm excitation.



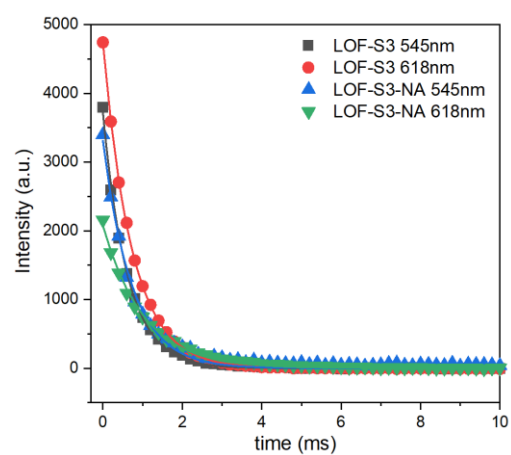
**Figure S5.** Luminescence spectra of antibiotics



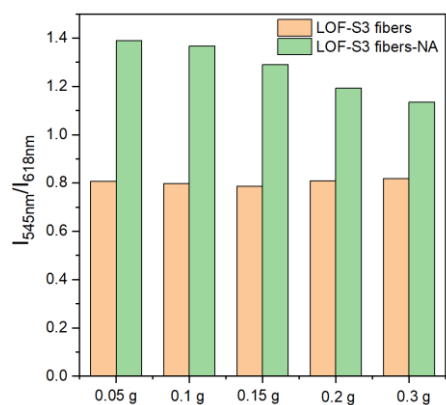
**Scheme S1.** Schematic representation of the main energy flow paths during the sensitization of lanthanide ions luminescence and the possible mechanism of mixed LOF for decoding and sensing antibiotics (antibiotics can modulate the energy transfer pathway and efficiency from organic parts to Ln ions, the energy allocation between Eu and Tb, and the transitions of Ln ions).



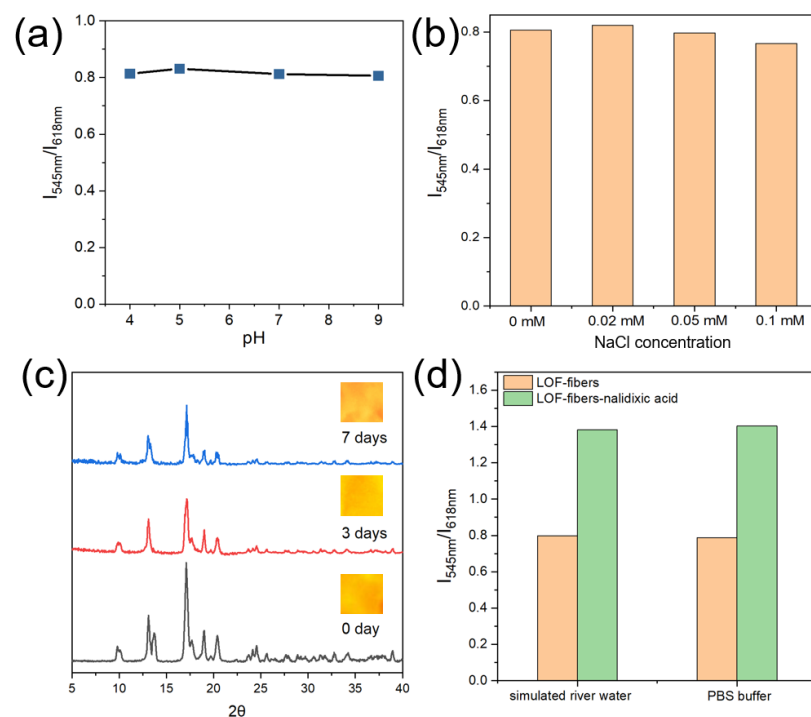
**Figure S6.** Decoded map for different antibiotics of LOF-S3 sensor (200  $\mu$ M antibiotics,  $\lambda_{ex} = 286$  nm,  $R_1 = I_{545\text{ nm}}/I_{618\text{ nm}}$  of the antibiotic,  $R_2 = I_{592\text{ nm}}/I_{488\text{ nm}}$  of the antibiotic,  $R_{L1} = I_{545\text{ nm}}/I_{618\text{ nm}}$  of LOF-S3,  $R_{L2} = I_{592\text{ nm}}/I_{488\text{ nm}}$  of LOF-S3)



**Figure S7.** Photoluminescence decay curves of LOF-S3 before/after the detection of nalidixic acid ( $\lambda_{ex} = 286$  nm)



**Figure S8.** Intensity ratios ( $I_{545nm}/I_{618nm}$ ) of LOF-S3 fibers with different amounts of Ln-BTC added into DMF during synthesis (adsorbate: NA (nalidixic acid), 100  $\mu$ M).



**Figure S9.** (a) Intensity ratios ( $I_{545nm}/I_{618nm}$ ) of LOF-S3 fibers in solutions of different pH and (b) different ionic strength (NaCl); (c) XRD patterns of LOF-S3 fibers after exposure to different storage time in water. (d) Intensity ratios ( $I_{545nm}/I_{618nm}$ ) of LOF-S3 fibers before and after the detection of nalidixic acid (100  $\mu$ M) in simulated natural samples.

Simulated river water:

Salts	NaCl	$KH_2PO_4$	$NaNO_3$	$Na_2SO_4$
<b>Concentration (mg/L)</b>	63.5	2.64	54.0	96.4

**Table S1.** Elemental composition of LOF-S3 obtained by EDX.

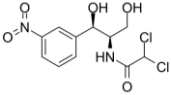
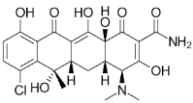
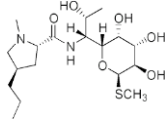
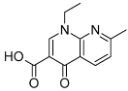
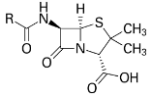
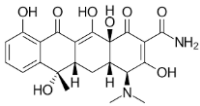
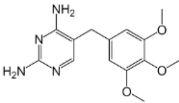
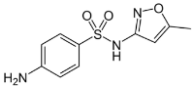
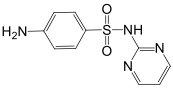
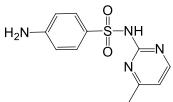
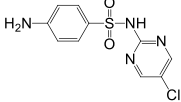
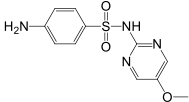
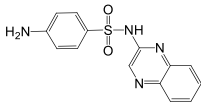
Elements	Weight percentage	Atomic percentage
<b>C</b>	47.74	71.86
<b>O</b>	21.73	24.56
<b>Mg</b>	0.41	0.31
<b>Eu</b>	1.59	0.19
<b>Tb</b>	20.90	2.38
<b>Pt</b>	7.64	0.71
<b>Total</b>	100.00	

**Table S2.** Previously published methods for the luminescent detection of antibiotics

Material	Method applied	Antibiotics	Reference
Carbon dots	Fluorescent quenching	tetracycline	(Feng et al., 2015)
CdTe quantum dots	Fluorescent quenching	tetracycline	(Yang et al., 2016)
silver nanoparticles	Metal-enhanced fluorescence effect	fluoroquinolone	(Yin et al., 2017)
Zn-PDC/Tb <sup>3+</sup>	Fluorescent quenching	cefixime	(Pan et al., 2018)
{Eu(BTB)DMF} <sub>n</sub>	Fluorescent quenching	sulfamethazine	(Ren et al., 2019)
RhB@Tb-dcppt	luminescence color and intensity	nitrofurazone and nitrofurantoin	(Yu et al., 2019)
[Eu(cppa)(OH)]	luminescent intensity	ornidazole and nitrofurantoin	(Li et al., 2020a)
[Tb(HL)L(H <sub>2</sub> O)] <sub>n</sub>	luminescent intensity	oxytetracycline and tetracycline	(Li et al., 2020b)
Eu(TATB)	luminescent intensity	sulfamethazine	(Yan et al., 2022)
{[Eu <sub>2</sub> (FDA) <sub>3</sub> (H <sub>2</sub> O) <sub>3</sub> (DMF)·DMF·2H <sub>2</sub> O]} <sub>n</sub>	luminescent intensity	nitrofurans, nitroimidazole and sulfonamides	(Li et al., 2022)

**Table S3.** The structure and LOD of antibiotics

Name	Molecular weight (g/mol)	Structural formula	LOD $\mu$ M
------	--------------------------	--------------------	-------------

<b>chloramphenicol</b>	323.13		0.66
<b>chlortetracycline</b>	478.88		3.76
<b>lincomycin</b>	406.54		0.97
<b>nalidixic acid</b>	232.24		0.29
<b>penicillin</b>	243.26		2.12
<b>tetracycline</b>	444.44		1.37
<b>trimethoprim</b>	290.32		3.22
<b>sulfamethoxazole</b>	253.28		1.39
<b>sulfadiazine</b>	250.28		2.67
<b>sulfamerazine</b>	264.30		1.58
<b>sulfaclozine</b>	284.73		0.25
<b>sulfameter</b>	280.31		0.75
<b>sulfachinoxalin</b>	300.34		3.00

---

**Table S4.** Fitting results of photoluminescence decay curves ( $\lambda_{\text{ex}} = 286 \text{ nm}$ ,  $\tau$ : ms)

	<b>Tb-BTC</b>	<b>Eu-BTC</b>	<b>EuTb-BTC</b>	<b>EuTb-BTC</b>	<b>LOF-S3-NA</b>	<b>LOF-S3-NA</b>
	<b>545 nm</b>	<b>618 nm</b>	<b>545 nm</b>	<b>618 nm</b>	<b>545 nm</b>	<b>618 nm</b>
<b>A<sub>1</sub></b>	887	2597	581	4707	2576	1011
<b><math>\tau_1</math></b>	0.814	0.616	0.189	0.724	0.516	0.565
<b>A<sub>2</sub></b>	6221	136	3214	34	791	1140
<b><math>\tau_2</math></b>	1.246	0.914	0.6882	2.208	1.349	1.442
<b><math>\tau_{\text{av}}</math></b>	1.209	0.637	0.664	0.756	0.887	1.216
<b>R<sup>2</sup></b>	0.999	0.999	0.999	0.999	0.998	0.999

---

---

Bril A, De Jager-Veenis A W (1976). Some Methods of Luminescence Efficiency Measurements. Journal of research of the National Bureau of Standards. Section A, Physics and chemistry, 80A(3): 401-407

Feng Y, Zhong D, Miao H, Yang X (2015). Carbon dots derived from rose flowers for tetracycline sensing. TALANTA, 140: 128-133

Li B, Jiang Y-Y, Sun Y-Y, Wang Y-J, Han M-L, Wu Y-P, Ma L-F, Li D-S (2020a). The highly selective detecting of antibiotics and support of noble metal catalysts by a multifunctional Eu-MOF. DALTON TRANSACTIONS, 49(42): 14854-14862

Li C, Zeng C, Chen Z, Jiang Y, Yao H, Yang Y, Wong W-T (2020b). Luminescent lanthanide metal-organic framework test strip for immediate detection of tetracycline antibiotics in water. JOURNAL OF HAZARDOUS MATERIALS, 384

Li L, Zou J-Y, Zhang L, You S-Y, Xie X, Chen G-H (2022). Sensitive detection of the antibiotic pollutants by a solvent-stable luminescent sensor based on a europium(III) metal-organic framework. JOURNAL OF SOLID STATE CHEMISTRY, 305

Malta O L, Brito H F, Menezes J F S, Silva F, Donega C D, Alves S (1998). Experimental and theoretical emission quantum yield in the compound Eu(thenoyltrifluoroacetate)(3).2(dibenzyl sulfoxide). CHEMICAL PHYSICS LETTERS, 282(3-4): 233-238

Pan H, Wang S, Dao X, Ni Y (2018). Fluorescent Zn-PDC/Tb<sup>3+</sup> Coordination Polymer Nanostructure: A Candidate for Highly Selective Detections of Cefixime Antibiotic and Acetone in Aqueous System. INORGANIC CHEMISTRY, 57(3): 1417-1425

Ren K, Wu S-H, Guo X-F, Wang H (2019). Lanthanide Organic Framework as a Reversible Luminescent Sensor for Sulfamethazine Antibiotics. INORGANIC CHEMISTRY, 58(7): 4223-4229

Yan J, Zhang J, Zhang M, Shi G (2022). Lanthanide metal-organic framework as a paper strip sensor for visual detection of sulfonamide with smartphone-based point-of-care platform. TALANTA, 237

Yang Y, Niu H, Zhang H (2016). Direct and Highly Selective Drug Optosensing in Real, Undiluted Biological Samples with Quantum-Dot-Labeled Hydrophilic Molecularly Imprinted Polymer Microparticles. ACS APPLIED MATERIALS & INTERFACES, 8(24SI): 15741-15749

Yin S-N, Yao T, Wu T-H, Zhang Y, Wang P (2017). Novel metal nanoparticle-enhanced fluorescence for determination of trace amounts of fluoroquinolone in aqueous solutions. TALANTA, 174: 14-20

Yu M, Xie Y, Wang X, Li Y, Li G (2019). Highly Water-Stable Dye@Ln-MOFs for Sensitive and Selective Detection toward Antibiotics in Water. ACS APPLIED MATERIALS & INTERFACES, 11(23): 21201-21210