

Electronic Supplementary Information

Metal-organic framework based fluorescent sensing of tetracycline type antibiotics applicable to environmental and food analysis

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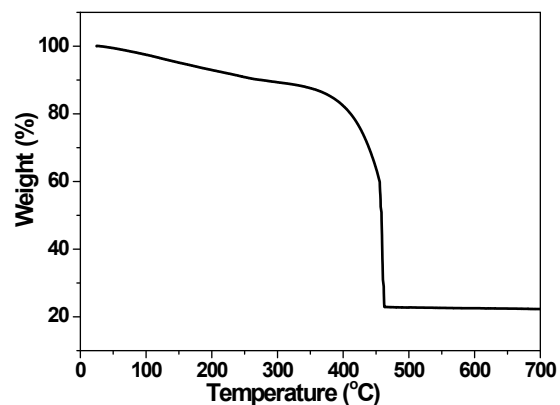


Fig. S1 Thermogravimetric curve of as-prepared In-sbdc. The overall weight loss from room temperature to 700 °C was 77.51%, which is in good consistence with the calculated value of 77.70% for the removal of all lattice H₂O molecules and organic components based on the formula of [In₂(sbdc)₃(H₂O)₄](H₂O)₈.

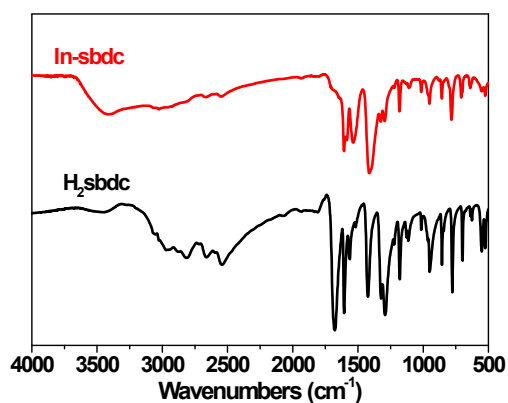
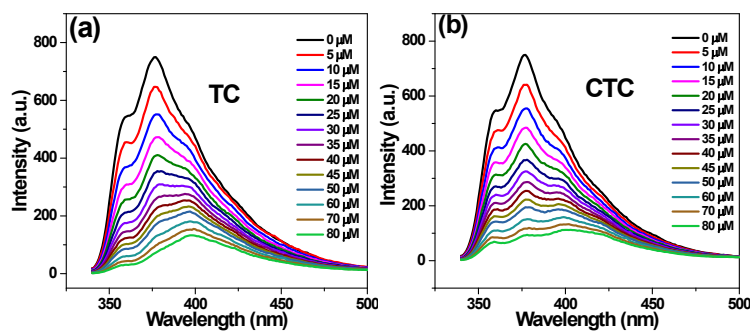


Fig. S2 FT-IR spectra of In-sbdc and free H₂sbdc ligand. In the spectrum of In-sbdc, the peaks corresponding to the stretching vibration of carboxyl groups appeared at 1606 and 1410 cm⁻¹, indicating that the H₂sbdc ligand is completely deprotonated upon the formation of MOF structure.



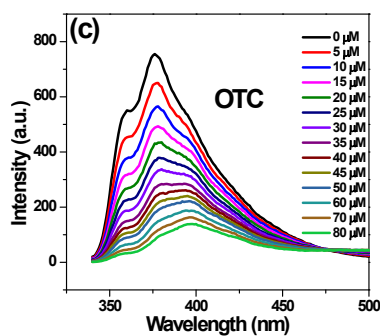


Fig. S3 Fluorescent spectra of the suspension of In-sbdc (15 mg L⁻¹) after the addition of different concentrations of (a) TC, (b) CTC and (c) OTC.

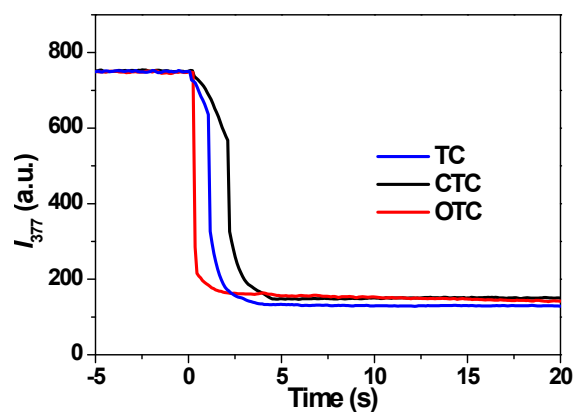


Fig. S4 Fluorescent intensity change of In-sbdc suspension after the addition of TC antibiotics. 15 mg L⁻¹ In-sbdc, 60 μM TC antibiotics.

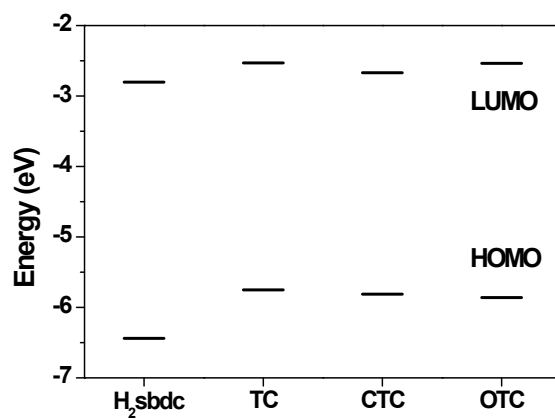


Fig. S5 Frontier orbital levels of TC antibiotics and H₂sbdc ligand, calculated at B3LYP/6-311++G(2df,2p)//B3LYP/6-31+G(d) level.

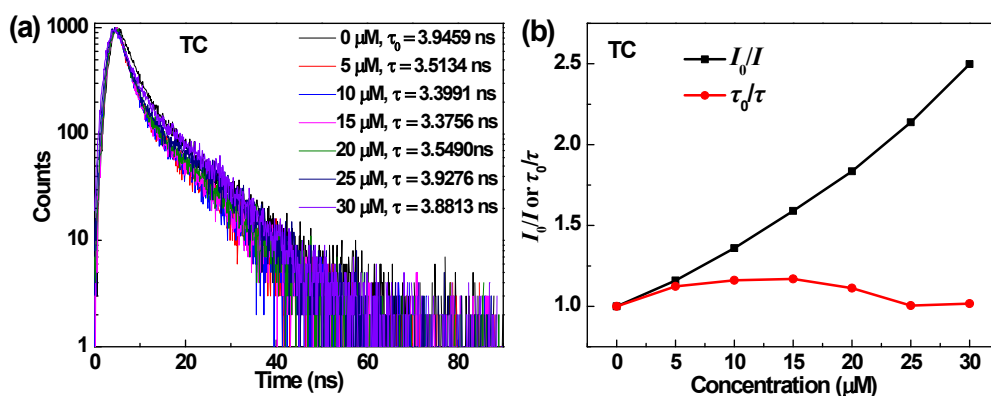


Fig. S6 (a) Fluorescence decay transients of In-sbdc suspension with different concentrations of TC. (b) Steady-state (I_0/I) and time-resolved (τ_0/τ) Stern-Volmer plots of TC.

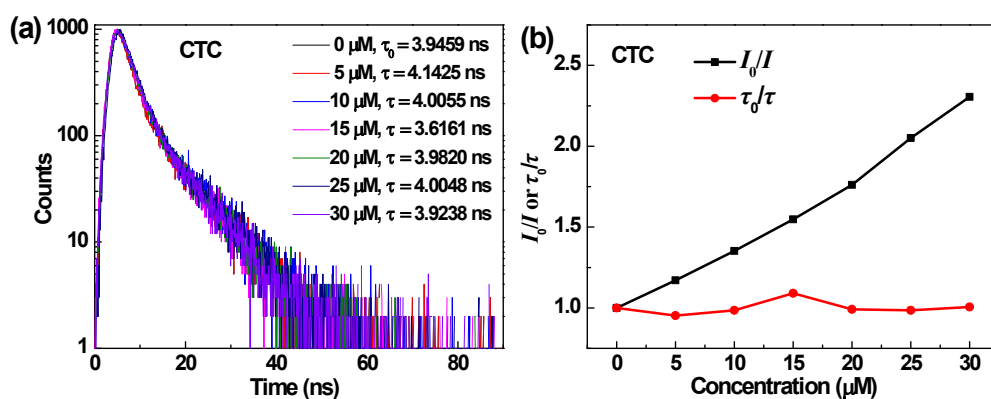


Fig. S7 (a) Fluorescence decay transients of In-sbdc suspension with different concentrations of CTC. (b) Steady-state (I_0/I) and time-resolved (τ_0/τ) Stern-Volmer plots of CTC.

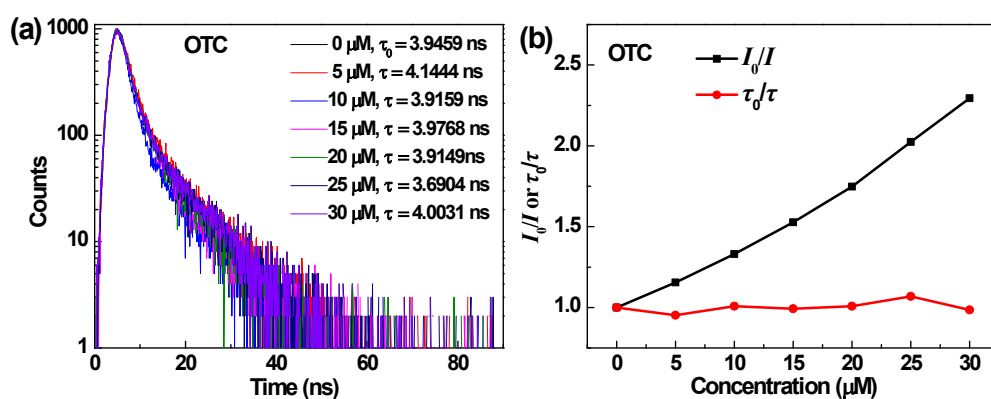


Fig. S8 (a) Fluorescence decay transients of In-sbdc suspension with different concentrations of OTC. (b) Steady-state (I_0/I) and time-resolved (τ_0/τ) Stern-Volmer plots of OTC.

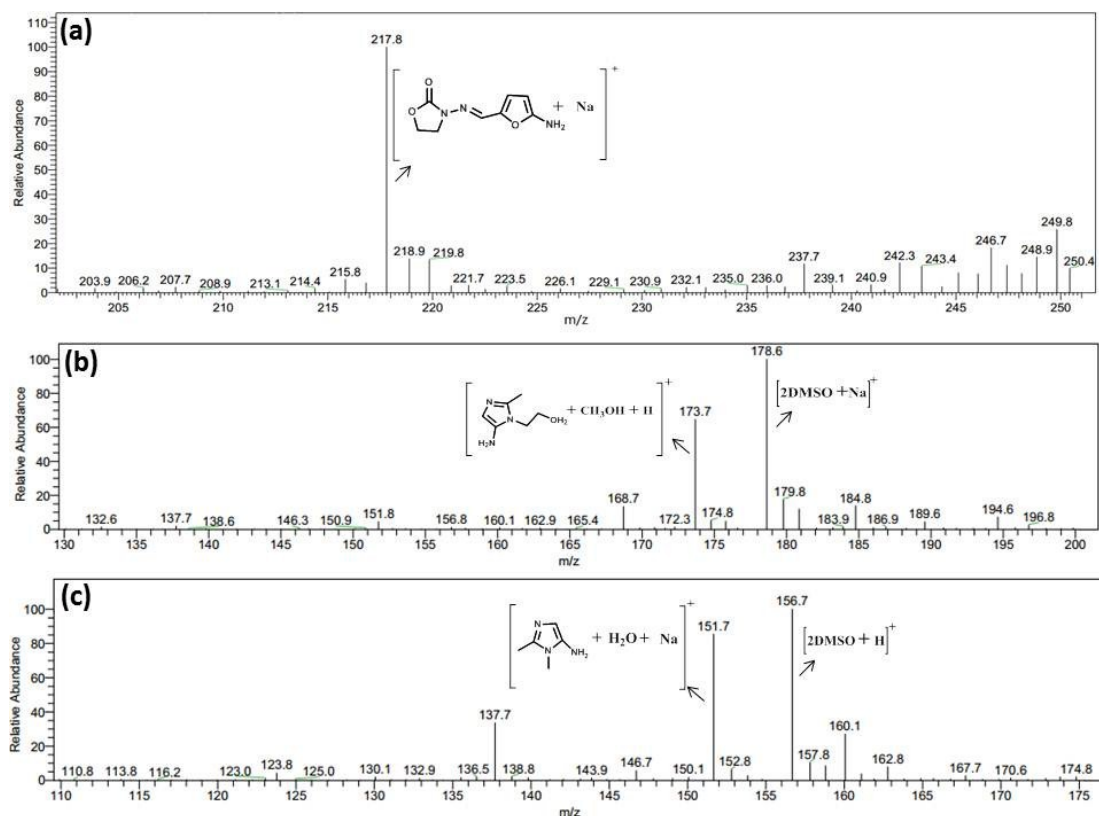


Fig. S9 ESI-MS spectra of the reduction products of (a) FZD, (b) MNZ and (c) DMZ. To enhance the solubility of reactants, the reactions were carried out in DMSO. Methanol was used as the mobile phase in ESI-MS measurement.

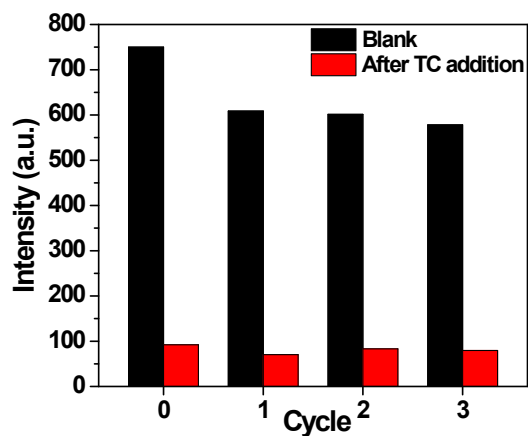


Fig. S10 Fluorescent responses of In-sbdc to TC (80 μ M) in four consecutive cycles.

Table S1 Selectivity of reported MOF based sensing systems for antibiotics

Entry	Analyte	Response induced by other antibiotic		Ref.
		$\frac{\text{Response induced by other antibiotic}}{\text{Response induced by equal amount of analyte}} \times 100\%$		
1	Nitrofurazone, nitrofurantoin	5 – 72%		1
2	Nitrofurazone, nitrofurantoin	8 – 15%		2
3	Nitrofurazone, nitrofurantoin	10 – 18%		3
4	Nitrofurazone, nitrofurantoin, FZD	21 – 84%		4
5	Ronidazole	5 – 20%		5
6	Ornidazole	5 – 14%		6
7	Cefixime	3 – 20%		7
8	TC	10 – 17%		8
9	TC, CTC, OTC	0 – 10%		This work

Table S2 Analytical results of TCs in pure milk^a

Antibiotic	Spiked (μM)	Found (μM)	Recovery (%)
TC	0	–	–
	5	4.894±0.071	97.88
	10	9.972±0.205	101.56
	15	14.906±0.109	98.69
	20	19.986±0.184	101.60
CTC	0	–	–
	5	5.072±0.255	101.44
	10	10.043±0.544	99.42
	15	14.934±0.241	97.81
	20	20.062±0.059	102.57
OTC	0	–	–
	5	5.078±0.074	101.56
	10	10.009±0.184	98.62
	15	15.044±0.152	100.70
	20	20.133±0.0482	101.77

^a The milk sample was diluted with Bis-Tris-HCl buffer by 3×10^3 times before measurement.

Table S3 Analytical results of TCs in pork^a

Antibiotic	Spiked (μM)	Found (μM)	Recovery (%)
TC	0	–	–
	5	5.005 \pm 0.032	100.11
	10	9.954 \pm 0.058	98.97
	15	14.929 \pm 0.090	99.49
	20	19.967 \pm 0.196	100.77
CTC	0	–	–
	5	4.954 \pm 0.029	99.08
	10	10.070 \pm 0.184	102.33
	15	15.074 \pm 0.387	100.06
	20	20.009 \pm 0.094	98.71
OTC	0	–	–
	5	5.080 \pm 0.082	101.60
	10	10.021 \pm 0.182	98.82
	15	15.149 \pm 0.114	102.56
	20	20.109 \pm 0.034	99.20

^a 1 g of pork sample was ground and extracted with 5 mL acetonitrile. The extraction was filtered and diluted with Bis-Tris-HCl buffer by 3×10^3 times before measurement.

Table S4 Analytical results of TCs in fish^a

Antibiotic	Spiked (μM)	Found (μM)	Recovery (%)
TC	0	–	–
	5	4.946 \pm 0.081	98.92
	10	9.934 \pm 0.186	99.76
	15	14.948 \pm 0.068	100.28
	20	19.930 \pm 0.105	99.94
CTC	0	–	–
	5	4.977 \pm 0.189	99.53
	10	10.098 \pm 0.272	102.43
	15	15.070 \pm 0.157	99.44
	20	19.932 \pm 0.391	97.25
OTC	0	–	–
	5	5.086 \pm 0.057	101.72
	10	10.210 \pm 0.231	102.48
	15	15.028 \pm 0.199	96.35
	20	20.137 \pm 0.054	102.18

^a 1 g of fish sample was ground and extracted with 5 mL acetonitrile. The extraction was filtered and diluted with Bis-Tris-HCl buffer by 3×10^3 times before measurement.

References

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