Electronic Supplementary Material (ESI) for Chemical Communications.

Supporting Information

Metal–organic framework (MOF) as a unique turn-on fluorescent chemical sensor for ultra-sensitive detection of antibiotics

EXPERIMENTAL SECTION

Materials and methods. The reagents and chemicals were commercially available and used without further purification. Elemental analyses were performed by using an elemental analyzer (Elementar Vario EL III analyzer). UV-Vis absorption spectra were performed using a *Jingke L6S* spectrometer. Fourier transform infrared (FT-IR) spectra were carried out with KBr pellets. Thermogravimetric analysis (TGA) was carried out in N_2 atmosphere with a heating rate of 10 °C per minute (NETZSCH STA 449C). The fluorescence spectra were performed with a spectrophotometer (Hitachi F–4500). Powder X−ray diffraction (PXRD) were obtained from an X-ray diffractometer (Bruker D8 ADVANCE) with Cu−Kα radiation (λ = 1.5418 Å). The emission lifetimes were measured on an Edinburgh FLS-920 fluorescence spectrometer.

Synthesis and preparation of $\{[Zn_3(OH)(bmipia)(H_2O)_3]_4\cdot[Zn(H_2O)_{6.5}]_2\}_n$ (FCS-3). FCS-3 was synthesized by using a hydrothermal method. A mixture of H_6bmipia (27 mg), $Zn(NO_3)_2\cdot6H_2O$ (30 mg), NaOH (1 mg) and 10 mL deionized water was sealed in a autoclave and heated for 72 hours at 120 ºC, then finally cooled down to room temperature. **FCS-3** were obtained by filtration, washing and dried in ambient temperature. Yields: ca. 29% (based on Zn). Elemental analysis (EA) for $C_{104}N_4O_{77}H_{106}Zn_{14}$ (Mr = 3559.10): H 3.00%, C 35.09%, N 1.57%; found: C 35.75%, H 3.51%, N 2.28%. IR (KBr, cm^{-1}): 3403(w)，1633(s)，1564(vs)，1378(vs)，1232(w)，1170(w)，1054(w)，992(w)，791(m)，729(m).

Preparation antibiotics solutions. Specifically, 36.2 mg of ofloxacin (OFX) was added to 100 mL PBS solution (0.1 M, pH=8) and dissolved with vigorous stirring to obtain antibiotics stock solutions (1 mM).

Fluorescence properties. The fluorescence properties of **FCS-3** in aqueous suspension and solid state were performed at room temperature. 20 mg **FCS-3** was solved in deionized water (20 mL) and ultrasonicated for about 30 minutes, finally a stable emulsion was obtained to take the fluorescence measurements. For the fluorescence titration experiment, 2 mL of **FCS-3** emulsion was added into a quartz cuvette and measured in situ with the gradually increase of 1 mM antibiotics.

X–ray crystallographic study. By using a diffractometer (Agilent SuperNova), the single crystal X–ray data of **FCS-3** was obtained. With the usage of SHELXL software package, the structure was gotten by direct and developed method with difference Fourier techniques[1]. The location of H atoms attached to C were generated geometrically and all of the non-hydrogen atoms were handled anisotropically. In water molecules, the idealized locations of H atoms were deduced from Fourier difference maps and refined isotropically. The supplementary crystallographic data is presented in CCDC 1997504 for this paper, with a summary given in Table S3.

Calculation details of LUMO and HOMO of antibiotics. The LUMO and HOMO of fluoroquinolone antibiotics were calculated with Gaussian 09 software package (Gaussian, Inc., Pittsburgh, PA, 2009) on the Supercomputing Center of FJIRSM, CAS and other data were calculated according to the results reported[2] (Table S2). The geometry structures were optimized by using Density Functional Theory (DFT) method at the M062X/6-31G (d,p) level. The calculation of harmonic frequency was carried out to make sure that the structure obtained is the local minimal.

References:

1 G. Sheldrick, *Acta Crystallogr., Sect. A*, 2008, **64**, 112-122.

2 B. Wang, X.-L. Lv, D. Feng, L.-H. Xie, J. Zhang, M. Li, Y. Xie, J.-R. Li and H.-C. Zhou, *J. Am. Chem. Soc.*, 2016, **138**, 6204-6216.

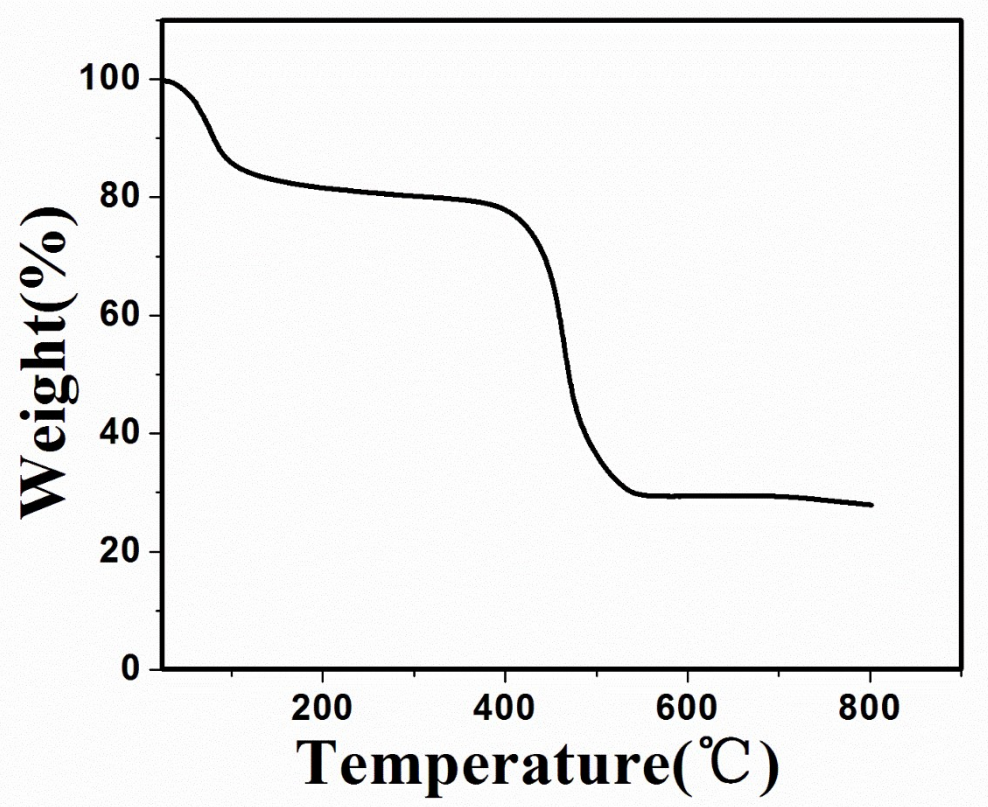

Fig. S1 TGA curve of **FCS-3**.

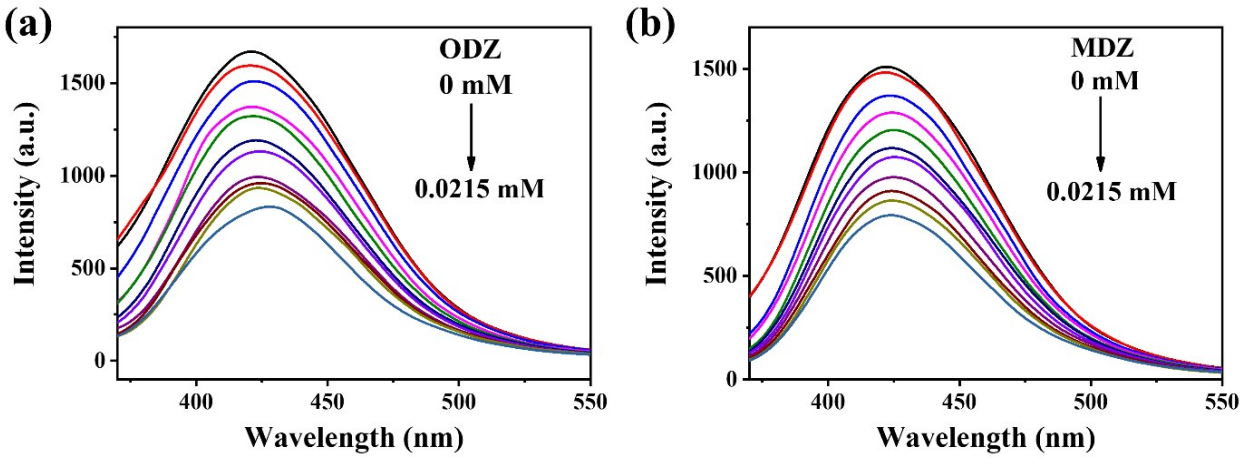

Fig. S2 The emission spectra of **FCS-3** in simulated wastewater with (a) ODZ and (b) MDZ.

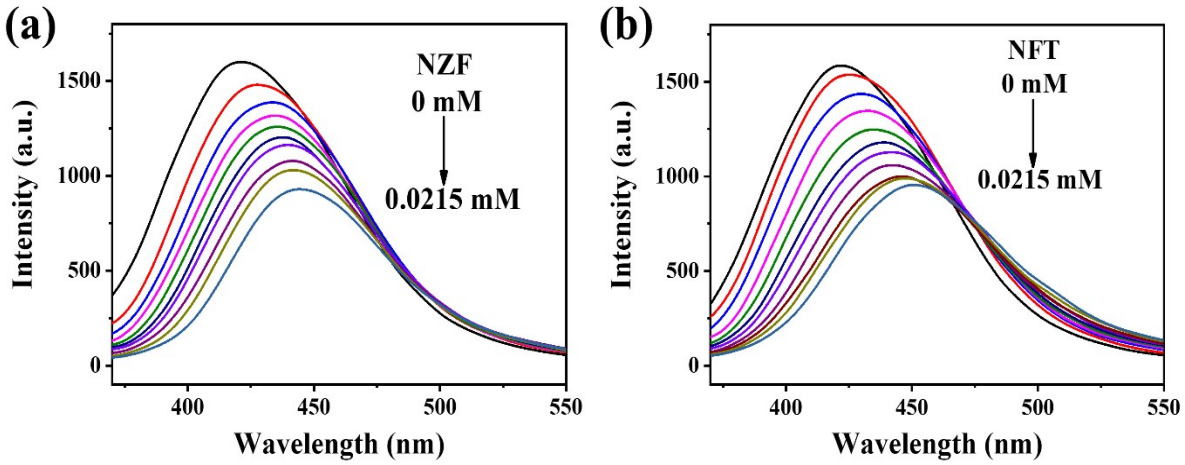

Fig. S3 The emission spectra of **FCS-3** in simulated wastewater with (a) NZF and (b) NFT.

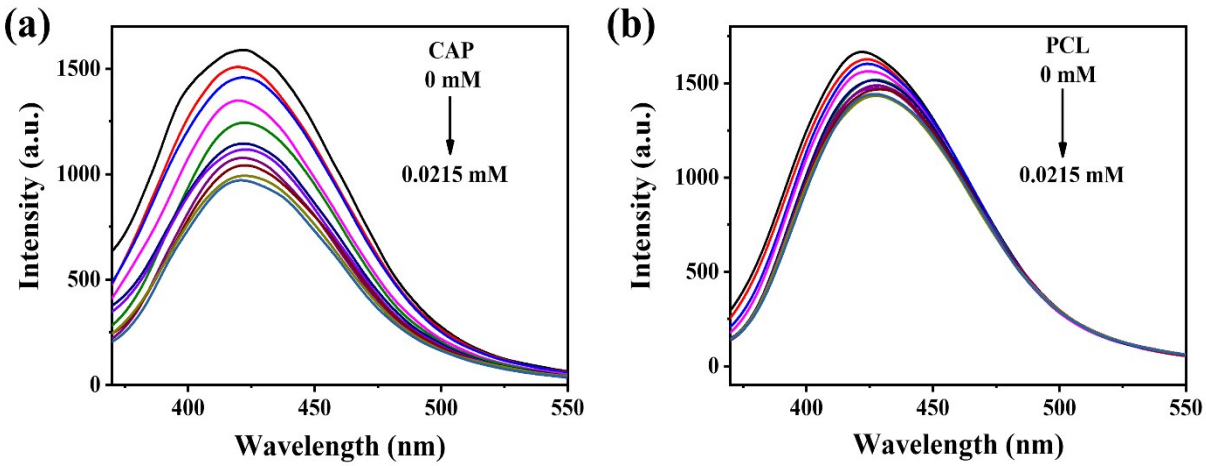

Fig. S4 The emission spectra of **FCS-3** in simulated wastewater with (a) CAP and (b) PCL.

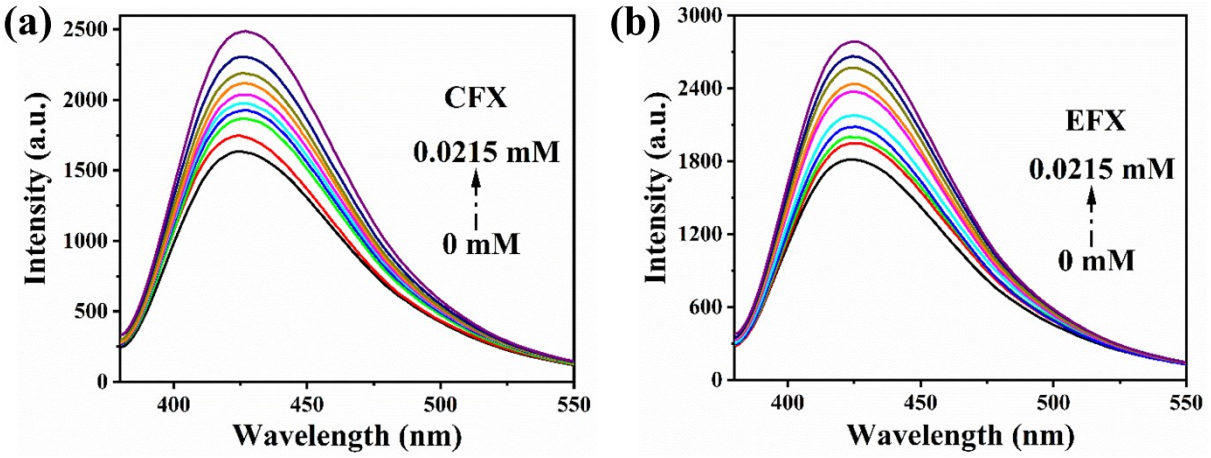

Fig. S5 The emission spectra of **FCS-3** in simulated wastewater with (a) CFX and (b) EFX.

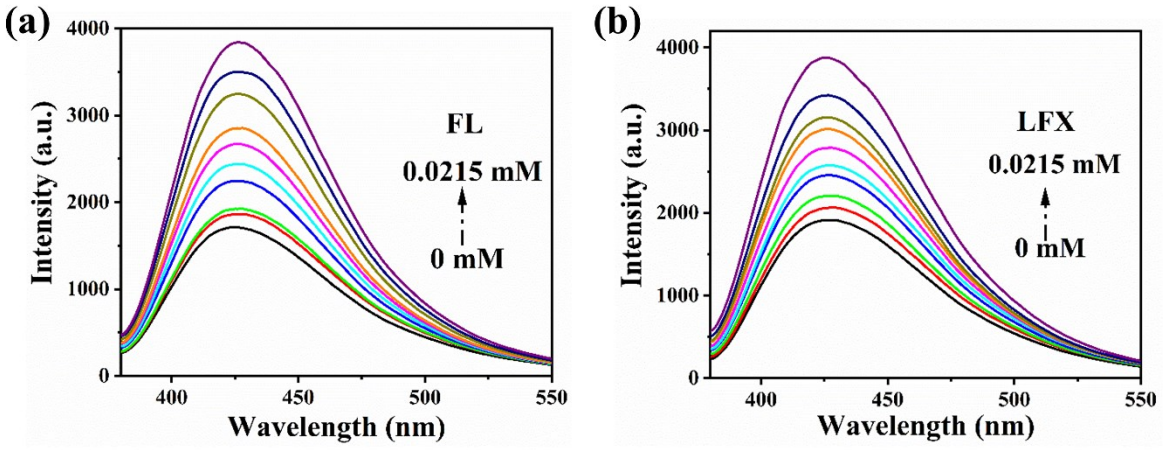

Fig. S6 The emission spectra of **FCS-3** in simulated wastewater with (a) FL and (b) LFX.

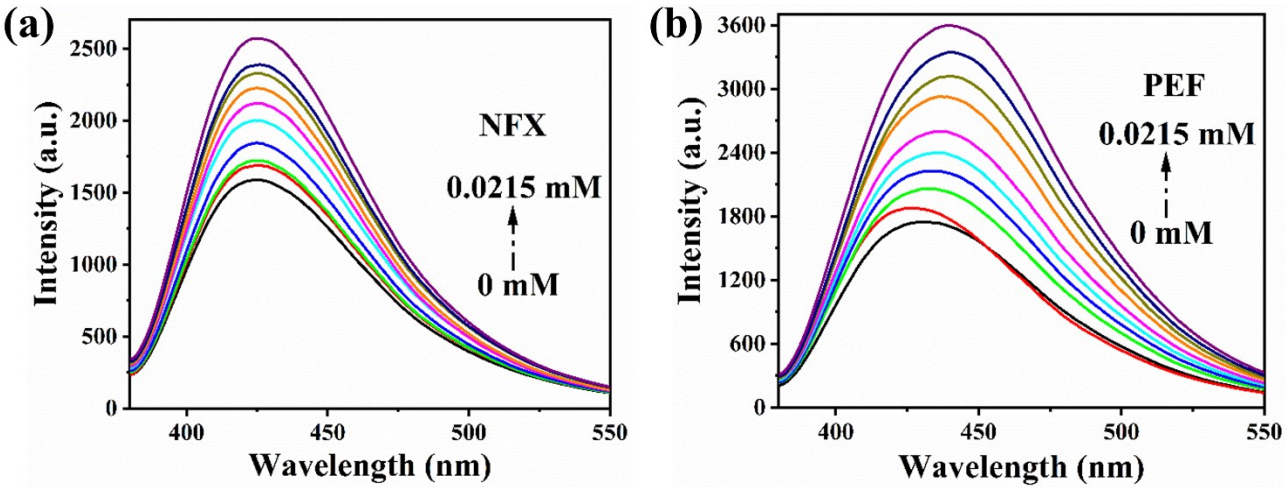

Fig. S7 The emission spectra of **FCS-3** in simulated wastewater with (a) NFX and (b) PEF.

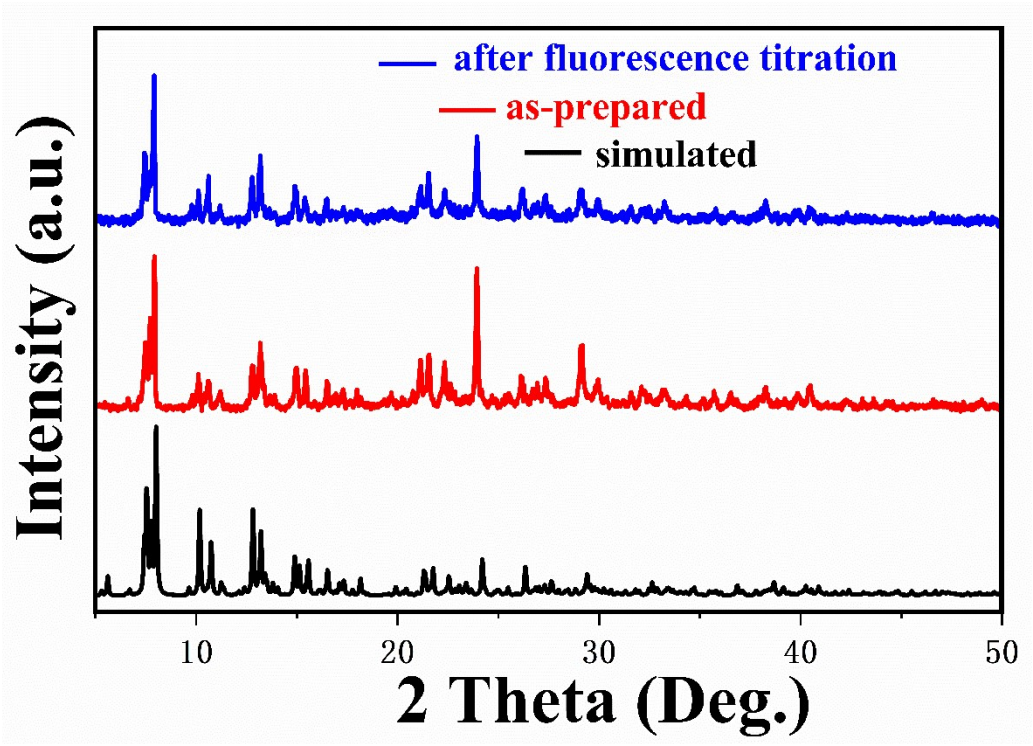

Fig. S8 Simulated and experimental PXRD patterns of **FCS-3** before and after the fluorescence titration experiments.

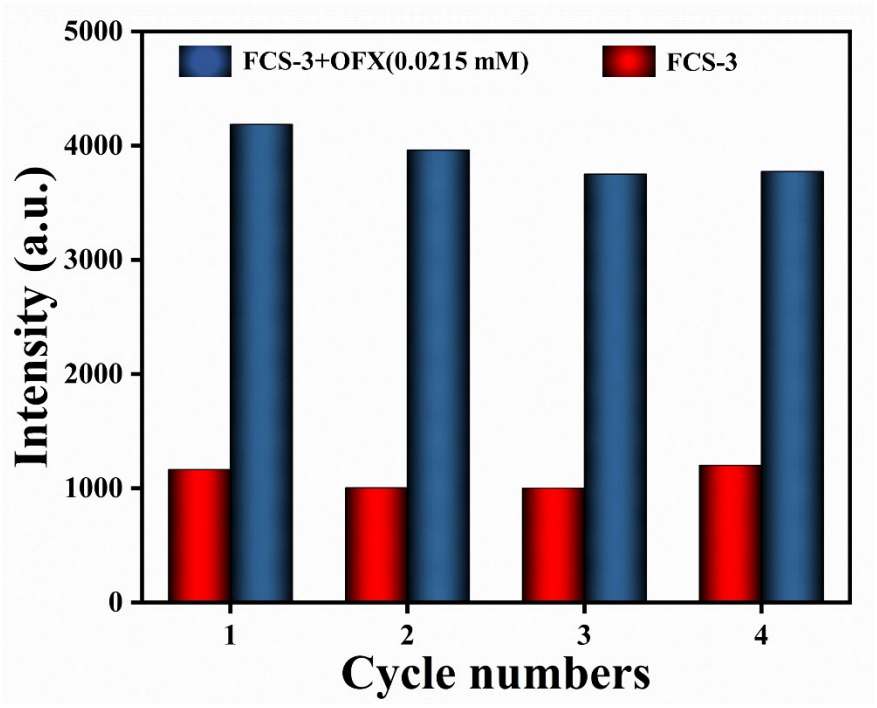

Fig. S9 Recyclability of **FCS-3** for the detection of OFX (0.0215 mM).

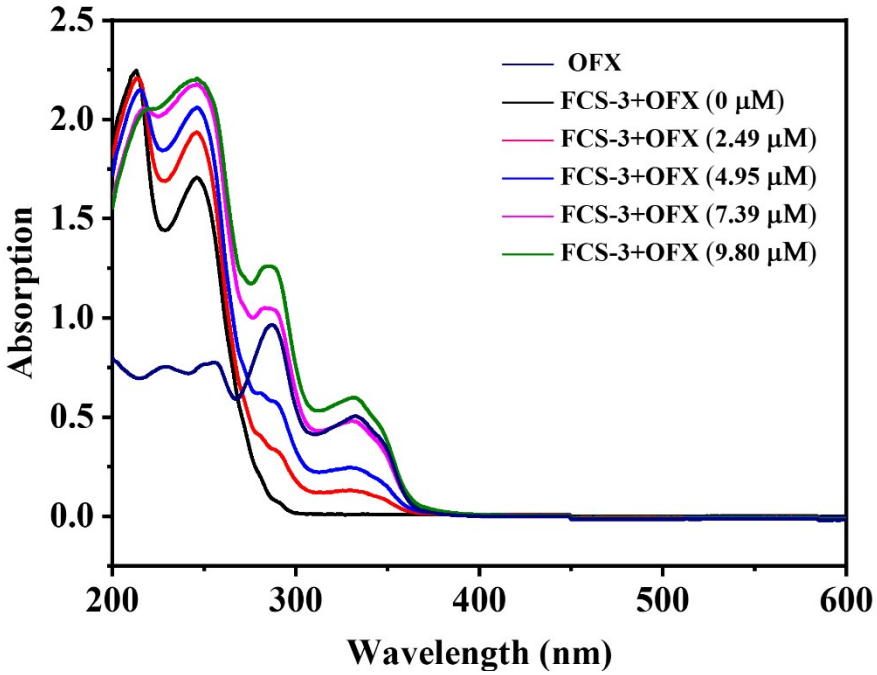

Fig. S10 UV-Vis spectra of **FCS-3** before and after the addition of OFX.

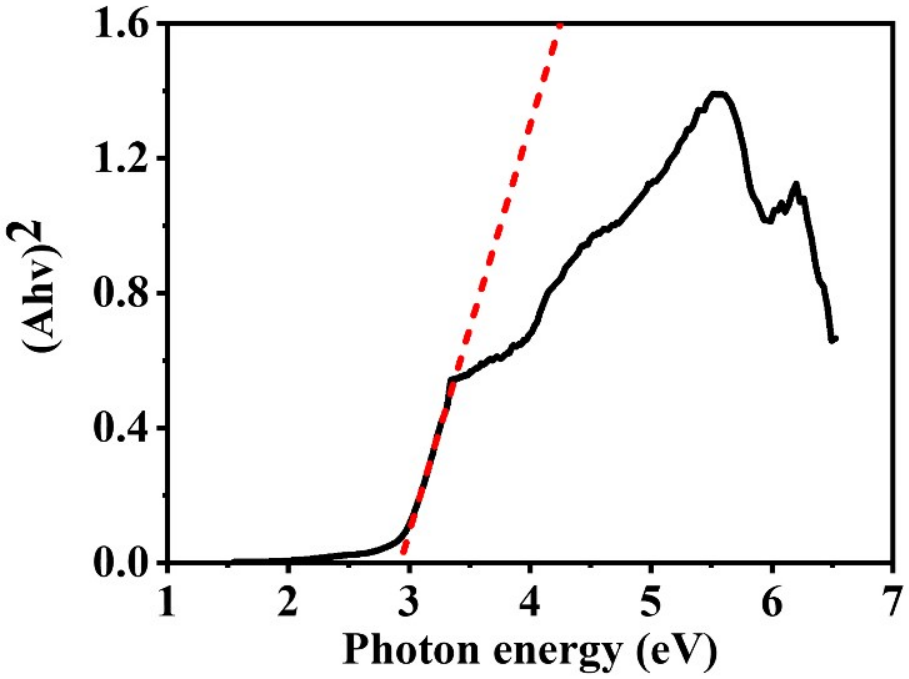

Fig. S11 Kubelka–Munk plot of **FCS-3**.

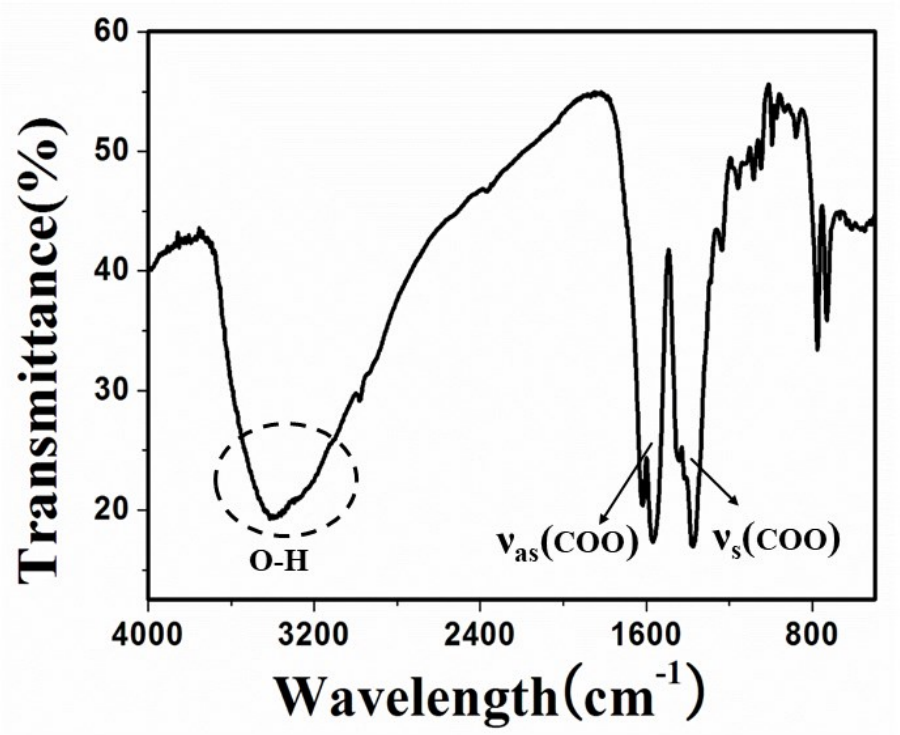

Fig. S12 IR spectrum of **FCS-3**.

Table S1. A comparison of enhancement (quenching) constant of various LMOFs used for detection of antibiotics in literature

MOF	Antibiotics used for detection	Detection method	Enhancement (quenching) constant	Ref.
$\{[Zn_2(bcob)(OH)(H_2O)]\cdot DMA\}_n$	tetracycline	Turn-off	2.7×10^4 M^{-1}	ACS Appl. Mater. Interfaces, 2020, 12, 8650-8662
$Zr_6O_4(OH)_8(H_2O)_4(CTTA)_{8/3}$	sulfadiazine	Turn-off	1.1×10^5 M^{-1}	J. Am. Chem. Soc. 2016, 138, 6204-6216
$\{(Me_2NH_2)[In(BCP)]\cdot 2.5DEF\}_n$	nitrofurazone	Turn-off	6.38×10^4 M^{-1}	Anal. Chem. 2018, 90, 1516-1519
$\{[Eu_2(BCA)_3(H_2O)(DMF)_3]\cdot 0.5DMF\cdot H_2O\}_n$	nitrofurazone	Turn-off	2.2×10^4 M^{-1}	Chem. Eur. J. 2017, 23, 10293-10300
$[TbL\bullet 2H_2O]_n$	nitrofurantoin	Turn-off	5.26×10^4 M^{-1}	Dalton Trans., 2019, 48, 12910-12917
Zn-PDC/Tb^{3+}	cefixime	Turn-off	1.1×10^5 M^{-1}	Inorg. Chem. 2018, 57, 3, 1417-1425
FCS-3	**ofloxacin**	**Turn-on**	**1.362×10^5 M^{-1}**	**This work**

Table S2. HOMO and LUMO energy levels of different antibiotics

Antibiotics	HOMO (eV)	LUMO (eV)
EFX	-7.07	-0.29
EL	-7.25	-0.41
CFX	-7.10	-0.33
LFX	-7.15	-0.34
NFX	-7.08	-0.41
OFX	-7.07	-0.30
PEF	-7.06	-0.28
NZF	-5.91	-3.62
NFT	-6.21	-3.86
ODZ	-6.28	-3.27
MDZ	-6.42	-3.43
CAP	-6.58	-3.69
PCL	-5.56	-1.78

Table S3. Crystal data and structure refinement of **FCS-3**

	FCS-3
Empirical formula	$C_{104}N_4O_{77}H_{106}Zn_{14}$
Molecular weight	3559.10
Crystal system	Monoclinic
Space group	$P2_1/n$
a (Å)	22.1643(14)
b (Å)	16.4288(10)
c (Å)	23.8287(15)
α (°)	90
β (°)	93.080(2)
γ (°)	90
***V* (Å^3)**	8664.3(9)
Z	2
D_{calc} (g·cm^{-3})	1.364
Reflections collected / independent	17042/16641
Goodness-of-fit on F^2	1.070
R_1[a] indices (I > 2σ(I))	0.0754
wR_2[b] indices (all data)	0.1998

[a] $R = \Sigma||Fo| - |Fc||/\Sigma|Fo|$. [b] $wR(F^2) = [\Sigma w(Fo^2 - Fc^2)^2/\Sigma w(Fo^2)^2]^{1/2}$.