Supporting Information

Fabrication of a dual-emitting RhB@Zn-1 Composite as a recyclable luminescent sensor for sensitive detection of nitrofuran antibiotics

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S1. General methods

FT-IR spectra were recorded on a Nicolet NEXUS 670 spectrophotometer using KBr pellets in the range of 500–4000 cm^{-1}. Thermogravimetric analyses (TGA) were carried out on a Mettler Toledo TGA/SDTA851 instrument with a heating rate of 5 °C/min under nitrogen atmosphere. Powder X-ray diffraction (PXRD) patterns were collected on a Rigaku ULTIMA IV diffractometer equipped with Cu Kα in a 2θ range of 5–40°. Elemental analyses (C, H and N) were performed on an Elementar Vario ELIII analyzer. Fluorescence spectra were recorded at room temperature with an Edinburgh FLS980 fluorescence spectrophotometer. UV-visible absorption spectra were measured on a Cary 100 Bio UV-visible Spectrophotometer.

S2. X-ray Crystallography.

Diffraction intensity data for **Zn-1** was collected on a Bruker Apex II CCD area detector equipped with graphite-monochromated Mo-Kα radiation (λ = 0.71073 Å) at 293K. Empirical absorption correction was applied using the SADABS program. The structure was solved by direct methods and refined by the full-matrix least-squares based on F^2 using SHELXTL. The non-hydrogen atoms were refined anisotropically, and the hydrogen atoms of the ligands were placed in calculated positions and refined using a riding model. The $[(CH_3)_2NH_2]^+$ ions and other solvent molecules in the channels are highly disordered and could not be modeled correctly, so the residual electron densities resulting from them were removed by the SQUEEZE function in PLATON, and the resultant new file was used to further refine the structure.

S3. Explanation for Alerts B in the CheckCIF report

PLAT990_ALERT_1_B Deprecated .res/.hkl Input Style SQUEEZE Job ... ! Note

Explanation: This alert comes from the use of squeeze program of Platon software.

Table S1. Crystal data and structural refinements for **Zn-1**.

Complex	**Zn-1***
Formula	$Zn_3C_{42}H_{62}O_{26}N_4S_2$
Fw	1299.25
Crystal system	Orthorhombic
Space group	*Pnma*
a (Å)	16.93290(10)
b (Å)	16.73970(10)
c (Å)	24.8806(2)
V (Å3)	7052.45(8)
Z	31
ρ_{calc} (g m^{-3})	0.814
μ (mm^{-1})	2.053
F(000)	1720
reflections collected	79647
unique reflections	6524
R_{int}	0.0459
GOF	1.067
R_1 [I>2σ(I)]	0.0347
wR_2 (all data)	0.0974

*The refinement results were obtained from squeeze data.

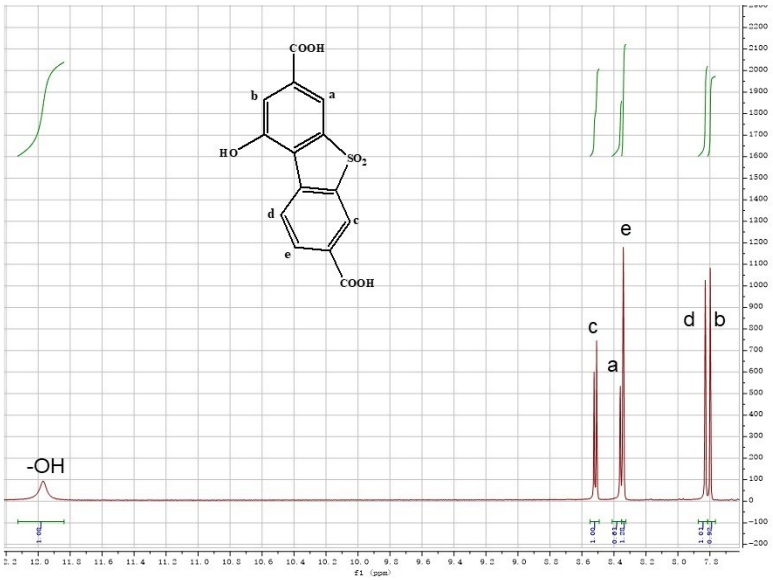

Figure S1. ^{1}H-NMR (DMSO) spectrum of H_2L.

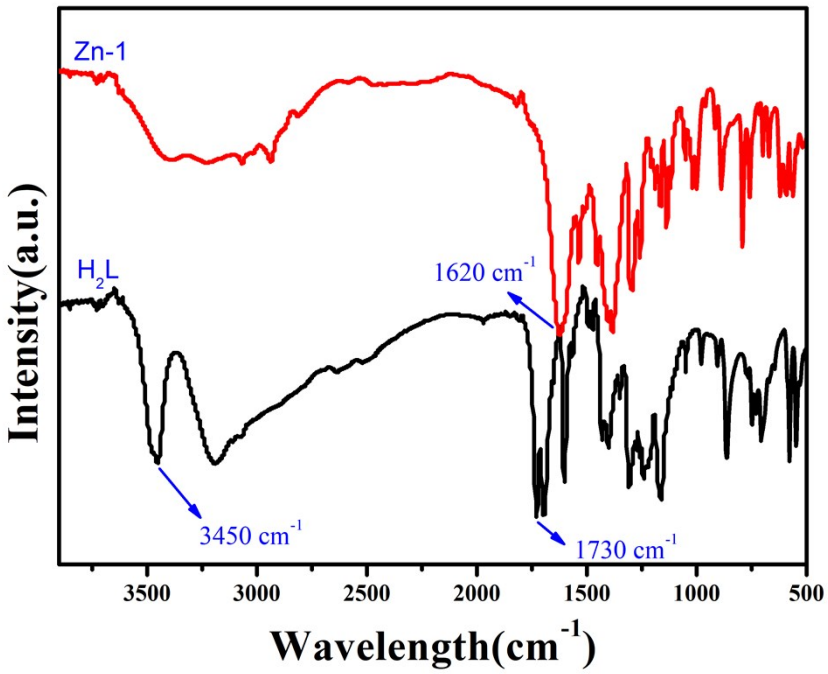

Figure S2. IR spectra of H_2L ligand and complex **Zn-1**.

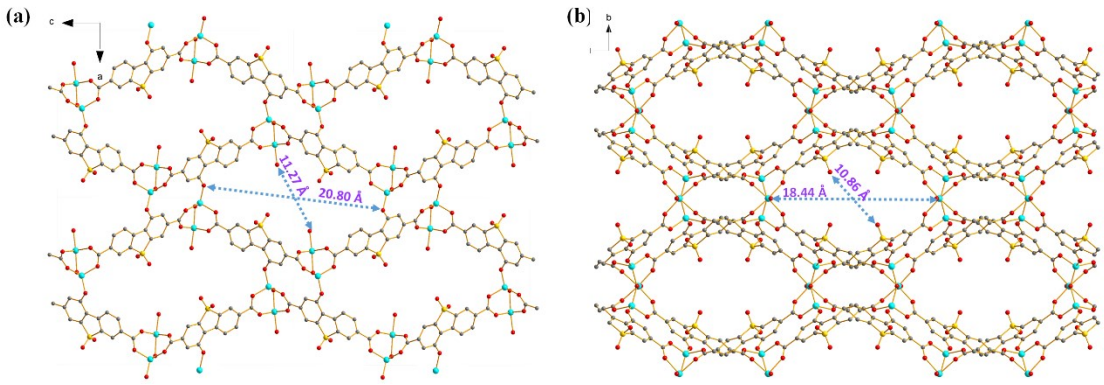

Figure S3. Three dimensional frameworks of **Zn-1** with 1D channels viewed along the *a* and *b* axises.

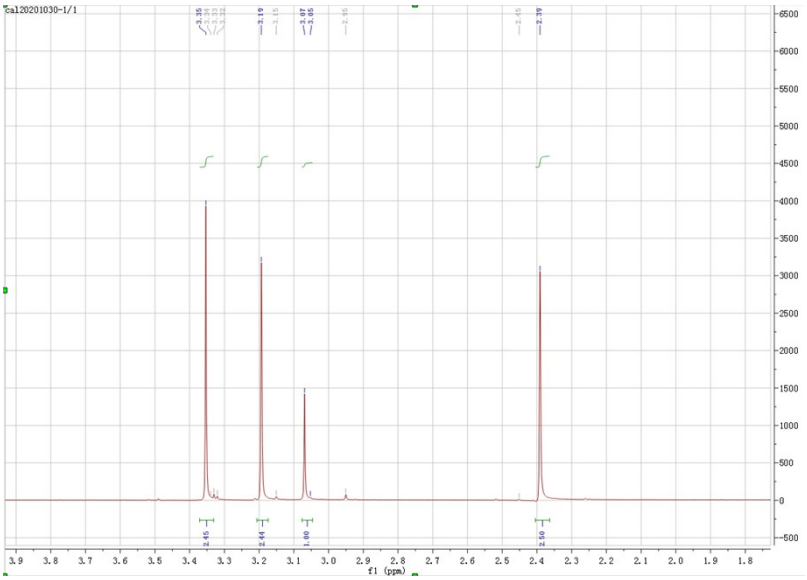

Figure S4. ^{1}H-NMR (D_2O) spectrum of the NaCl solution after soaking Zn-1. (DMA molecules also release from the framework owing to the partial collapse of **Zn-1** in water.) δ: 2.39 (-OC-CH3), 3.07 (-N-CH3), 3.10 (-CO-N-CH3), 3.35 (-CO-N-CH3)

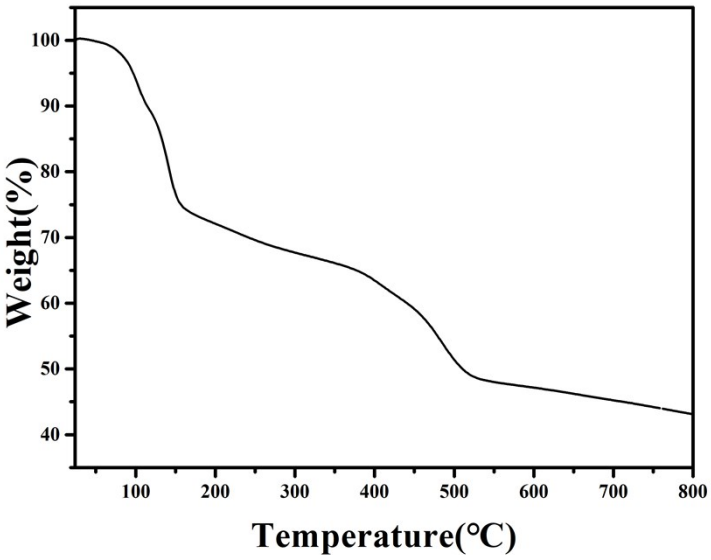

Figure S5. TGA curve of complex **Zn-1**.

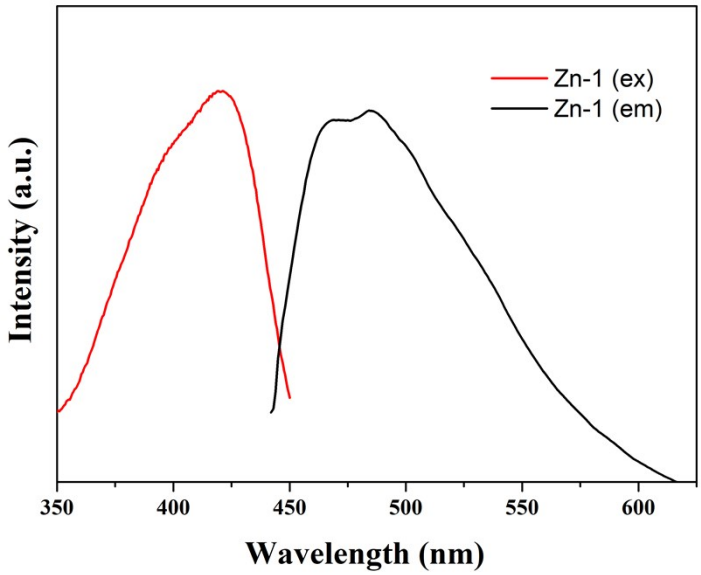

Figure S6. The solid state excitation and emission spectra of **Zn-1**.

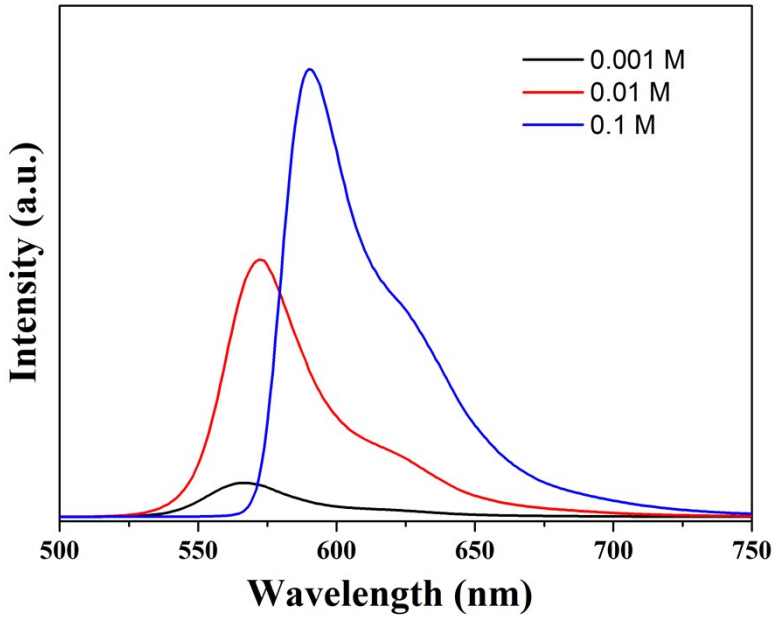

Figure S7. The fluorescent emission spectra of EtOH solution of RhB with different concentrations.

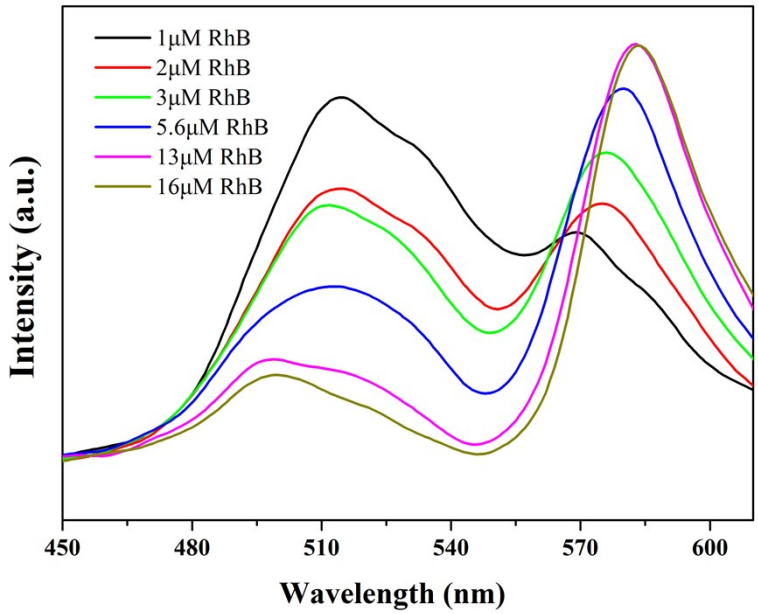

Figure S8. The fluorescent emission spectra of EtOH solution of H_2L with different amounts of RhB.

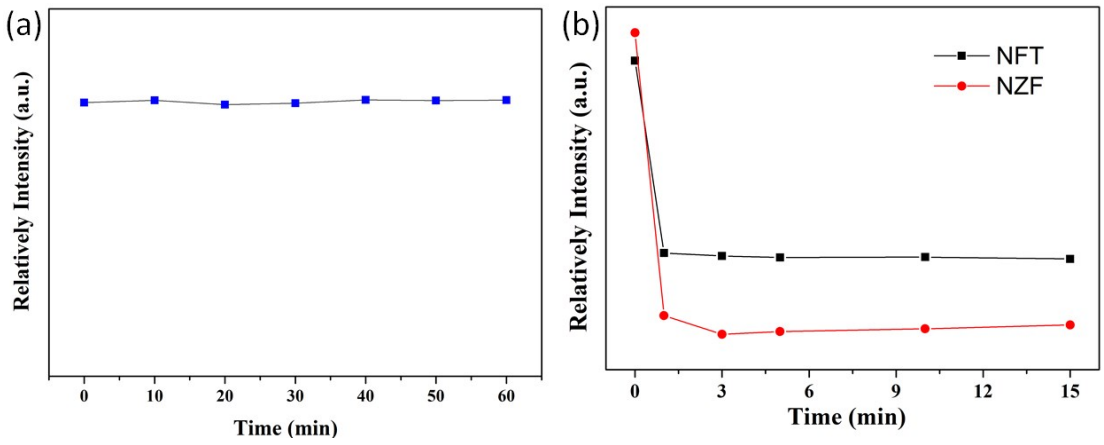

Figure S9. (a) Luminescent stability of suspension of **RhB@Zn-1** in EtOH within 60 min (b)Response times of **RhB@Zn-1** towards NFT and NZF.

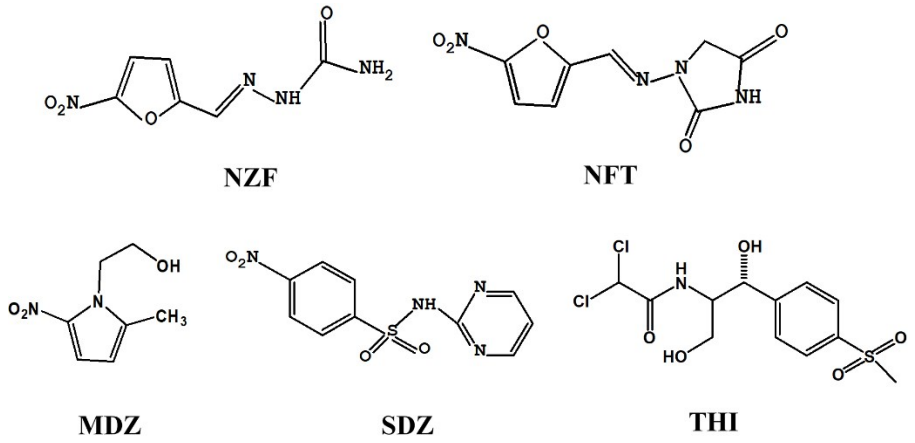

Figure S10. Molecule structures of the antibiotics.

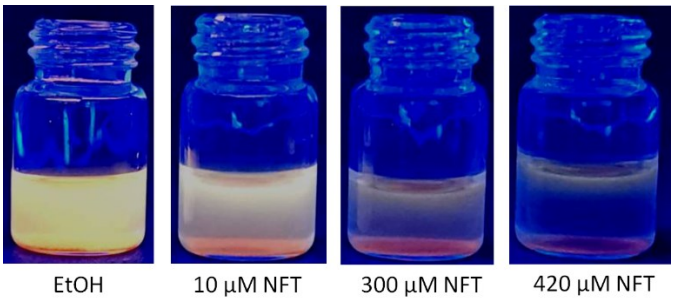

Figure S11. Color changes of **RhB@Zn-1** suspension upon incremental addition of NFT under a UV lamp.

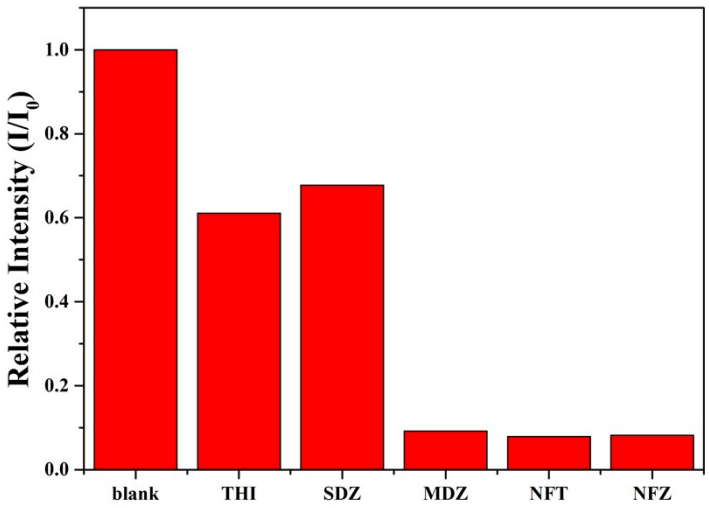

Figure S12. The luminescence intensities of **Zn-1** in EtOH containing various antibiotics (600 μM).

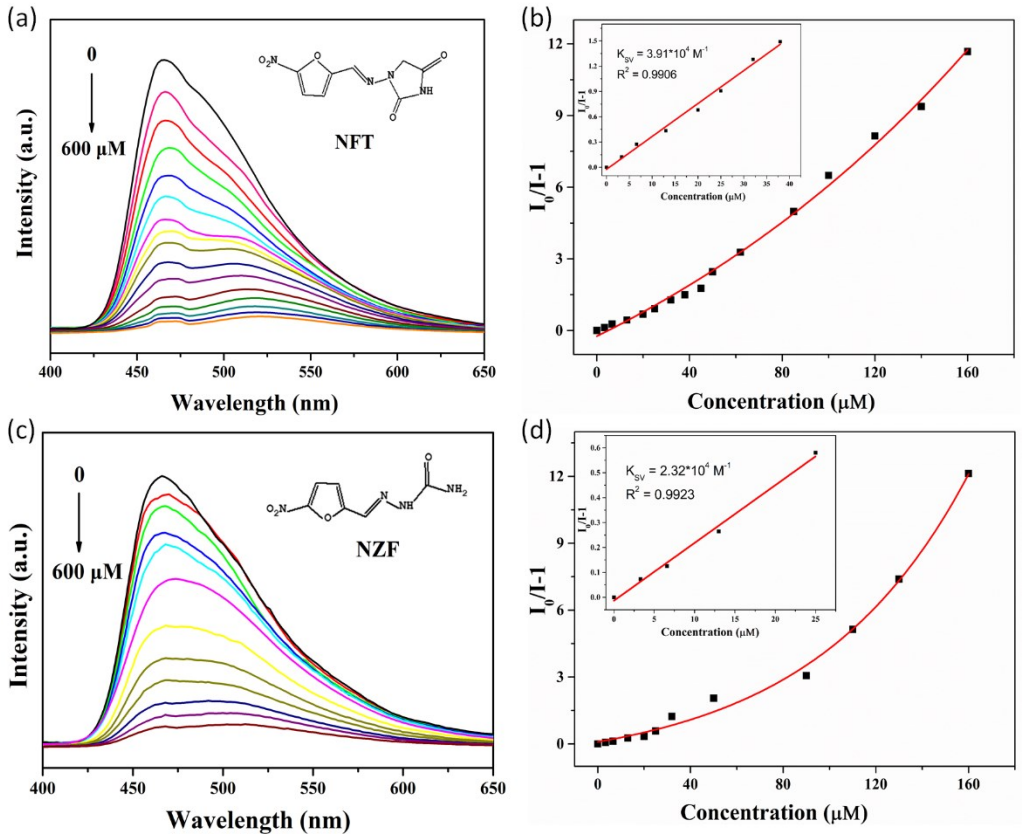

Figure S13. Emission spectra of **Zn-1** upon incremental addition of NFT (a) and NFZ (c); The Stern−Volume plots of **Zn-1** for NFT (b) and NFZ (d). Inset: Linear relationship of the SV plots at low concentration.

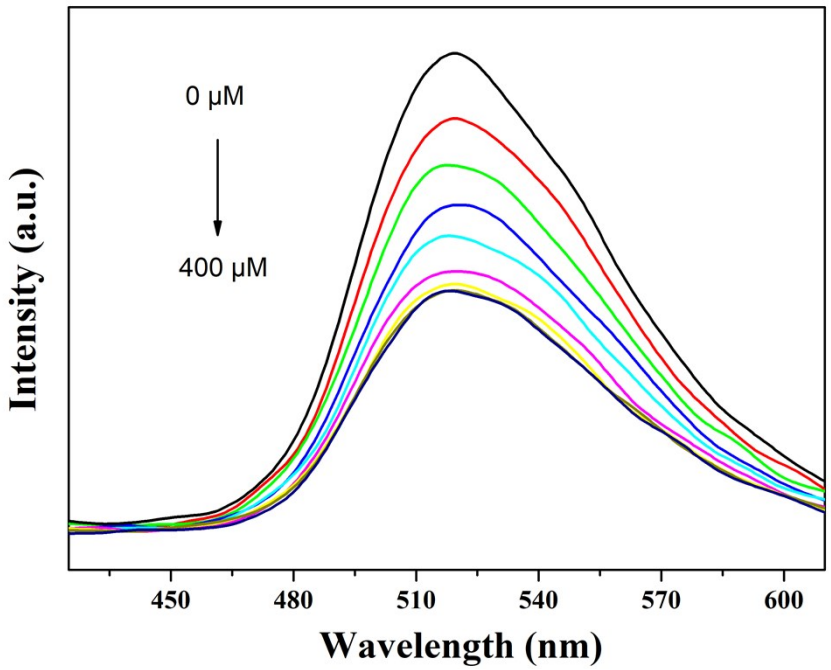

Figure S14. Emission spectra of H_2L in EtOH upon incremental addition of NFT.

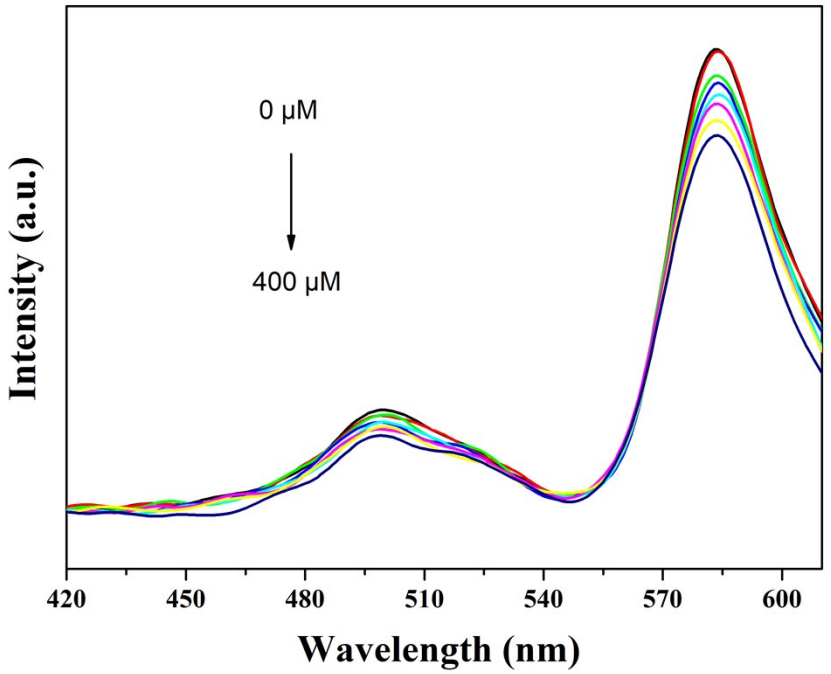

Figure S15. Emission spectra of H_2L in EtOH upon incremental addition of NFT in the presence of RhB.

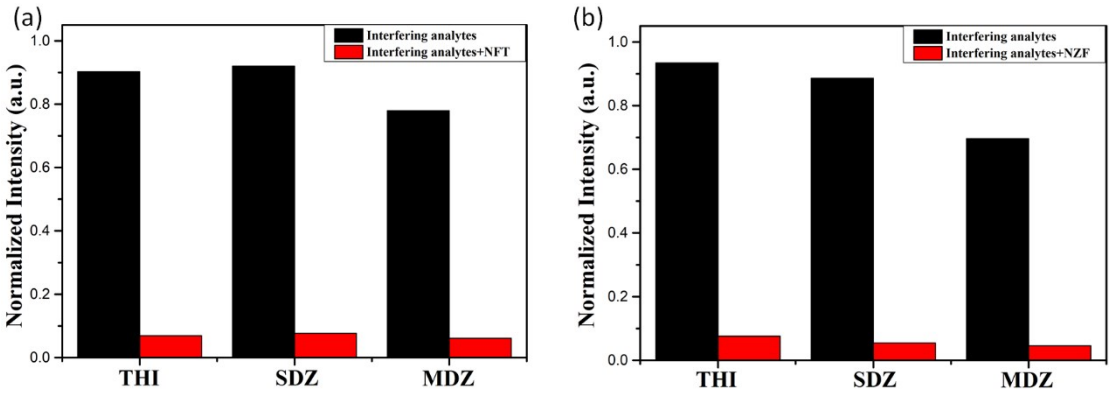

Figure S16. Anti-inference of **RhB@Zn-1** towards NFT (a) and NZF(b)

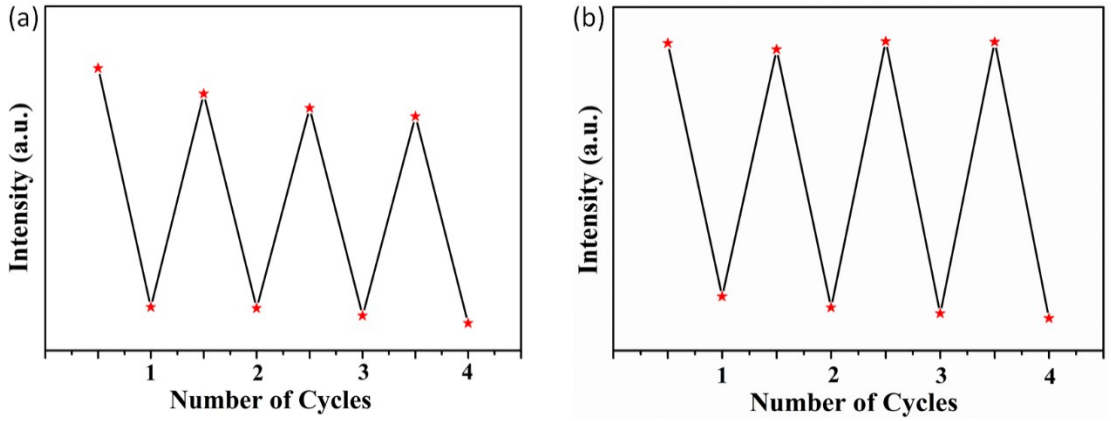

Figure S17. Fluorescence intensities of **Zn-1** in four recyclable experiments for sensing NFT (a) and NFZ (c) in EtOH.

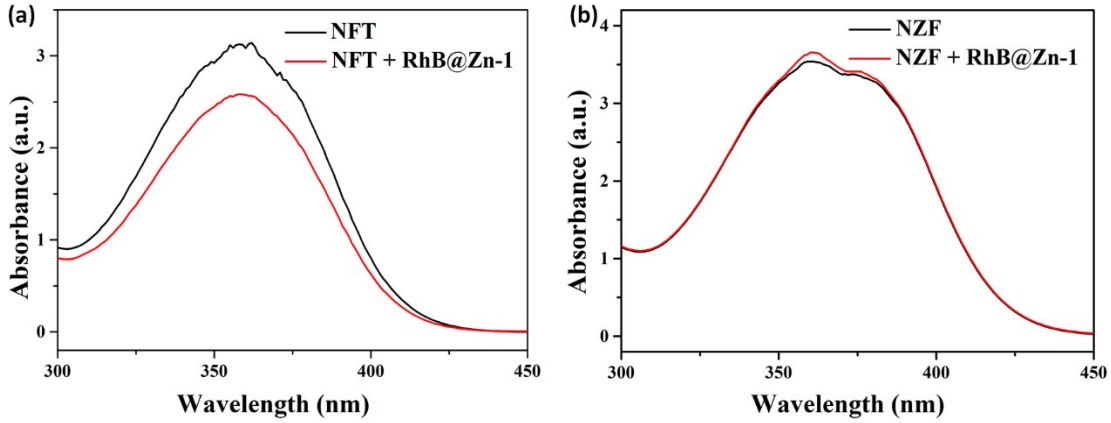

Figure S18. UV-vis spectra of EtOH solutions of NFT (a) and NZF (b) before and after adding **RhB@Zn-1**.

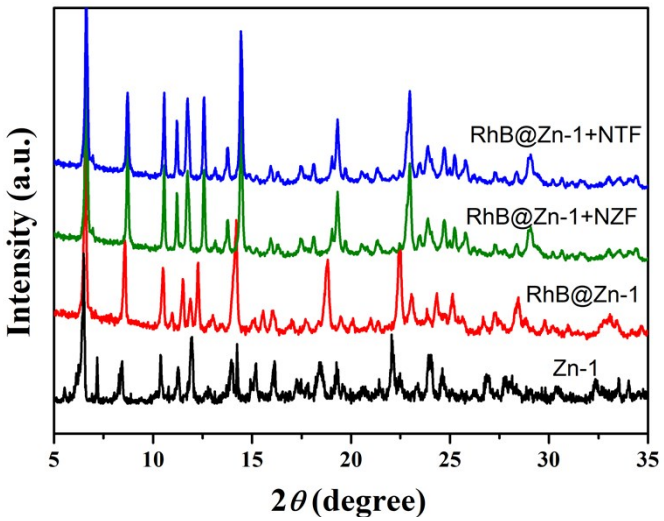

Figure S19. X-ray diffraction of **RhB@Zn-1** before and after sensing NFT/NZF.

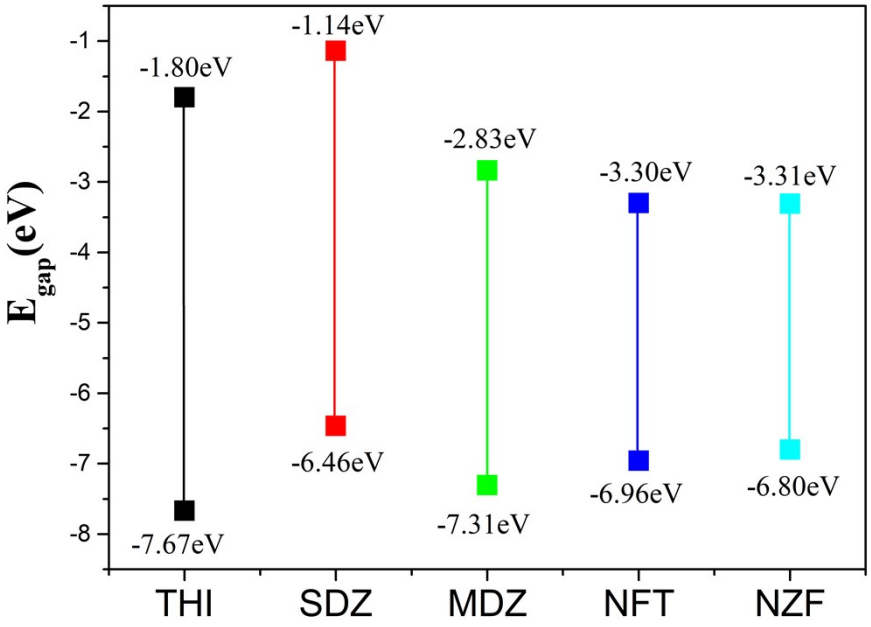

Figure S20. HOMO and LUMO energy levels of the selected antibiotics calculated by density functional theory (DFT) with B3LYP/6-31+G* basis set.

Table S1. The K_{SV} and LOD values of **RhB@Zn-1** and **Zn-1** towards NZF/NFT.

MOFs	NFs	K_{SV} ($\times 10^4$ M^{-1})	LOD (μM)	solvent	Ref.
RhB@Zn-1	NFT	5.61	0.73	EtOH	This work
RhB@Zn-1	NZF	4.73	0.86	EtOH	This work
Zn-1	NFT	3.91	1.24	EtOH	This work
Zn-1	NZF	2.32	2.10	EtOH	This work
$[Zn_2(Py_2TTz)_2(BDC)_2]\cdot 2DMF\cdot 0.5H_2O$	NZF	1.726	0.91	H_2O	1
$[Eu_2(BCA)_3(H_2O)(DMF)_3]\cdot 0.5DMF\cdot H_2O$	NFT	1.6	0.16	H_2O	2
$[Eu_2(BCA)_3(H_2O)(DMF)_3]\cdot 0.5DMF\cdot H_2O$	NZF	2.2	0.21	H_2O	2
$Zr_6O_4(OH)_8(H_2O)_4(CTTA)_{8/3}$	NFT	3.8	---	H_2O	3
$\{[Tb(TATMA)(H_2O)\cdot 2H_2O\}_n$	NFT	3.35	---	H_2O	4
$\{[Tb(TATMA)(H_2O)\cdot 2H_2O\}_n$	NZF	3.00	---	H_2O	4
$[Cd_7(SO_4)_6(tppe)_2]$ 2DMF·$2H_2O$	NZF	0.174	---	H_2O	5
$\{[NH_2(CH_3)_2]_4[Zn_3(HBDPO)_2(SO_4)_2]\}_n$	NFT	4.5	---	DMF	6

References:

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2. F. Zhang, H. Yao, T. S. Chu, G. W. Zhang, Y. Wang and Y. Y. Yang, *Chem.-Eur. J.*, 2017, **23**, 10293-10300.
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6. H. He, Q.-Q. Zhu, F. Sun and G. Zhu, *Cryst. Growth Des.*, 2018, **18**, 5573-5581.