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Supporting Information

Aqueous media ultra-sensitive detection of antibiotics via highly stable luminescent 3D Cadmium-based MOF

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i. Materials and methods

All the chemical reagents and solvents were purchased of analytical grade from certified sellers and used without any further refinement. X-ray diffraction (PXRD) patterns were obtained with monochromatized Cu Kα (λ = 1.540598 Å) on a Rigaku D/Max-2500PC diffractometer at ambient temperature. FT-IR spectra were recorded with wavelength range 4000-400 cm^{-1} using BRUKER ALPHA II spectrophotometer. TGA analysis was conducted via TA Q50 thermal analyzer with range of 30–800 °C at the rate of 10 °C min^{-1} under ambient environment. Scanning electron microscopic (SEM) study was investigated with Zeiss Sigma 500 microscope. UV-visible spectroscopy was performed via Hitachi UH4150 spectrophotometer. DFT calculations were carried out using Gaussian 09w package with B3LYP function and 6-31+G* basis set. Elemental analyses (EA) were carried out with a Perkin-Elmer 240 elemental analyzer. Photoluminescence emission and excitation spectra were recorded at ambient temperature with a HORIBA FluoroLog-3 fluorescence spectrometer, while time-resolved decay measurements were carried on HORIBA FluoroLog-3 fluorescence spectrometer equipped with a laser of 370 nm working in time-correlated single-photon counting mode (TCSPC) with a time resolution of 100 ns.

ii. Crystallographic data collection and structural refinement

Single crystal X-ray diffraction (SC-XRD) measurement for Cd-based MOF (**1**) was performed at 200 K on a Rigaku XtaLAB Pro diffractometer with Cu-Kα radiation (λ= 1.54184 Å). All the structures were solved with direct methods (SHELXS)[1] and refined by full-matrix least-squares on F^2 using OLEX2,[2] which utilizes the SHELXL-2015 module[3]. The imposed restraints and constraints (ISOR, DFIX, DELU, TRIA, etc.) in the least-squares refinement of each structure were commented in the corresponding crystallographic CIF files. The crystal structures are visualized by DIAMOND3.2. Detailed information about the X-ray crystallography data, intensity collection procedure, and refinement results for the compound are summarized in Table S1.

iii. Table S1 Crystal data for Compound 1

Empirical formula	$C_{93}H_{77}Cd_2N_7O_{11}$
Formula weight	846.71
Temperature/K	200.00(10)
Crystal system	Monoclinic
Space group	P2/c
a/Å	14.4126(2)
b/Å	20.6834(4)
c/Å	16.4770(3)
α/°	90
β/°	104.140(2)
γ/°	90
Volume/Å^3	4763.00(15)
Z	2
ρ_{calc}g/cm^3	1.181
μ/mm^{-1}	4.030
F(000)	1736.0
Crystal size/mm^3	0.03 × 0.03 × 0.02
Radiation	CuKα (λ = 1.54184)
2Θ range for data collection/°	6.324 to 145.55
Index ranges	-17 ≤ h ≤ 17, -24 ≤ k ≤ 23, -20 ≤ l ≤ 18
Reflections collected	31299
Independent reflections	9196 [R_{int} = 0.0516, R_{sigma} = 0.0572]
Data/restraints/parameters	9196/95/536
Goodness-of-fit on F^2	1.050
Final R indexes [I>=2σ (I)]	R_1 = 0.0574, wR_2 = 0.1523
Final R indexes [all data]	R_1 = 0.0798, wR_2 = 0.1626
Largest diff. peak/hole / e Å^{-3}	1.13/-1.07

iv. Table S2. Selected Bond lengths for 1

Atom	Atom	Length/Å
Cd1	N1[3]	2.300(5)
Cd1	N2	2.312(5)
Cd1	O1	2.451(3)
Cd1	O1[4]	2.399(3)
Cd1	O2	2.373(4)
Cd1	O3	2.493(3)
Cd1	O4	2.302(4)
N1	Cd1[5]	2.300(5)
O1	Cd1[4]	2.399(3)

[1]2-X,+Y,3/2-Z; [2]-X,+Y,1/2-Z; [3]+X,1+Y,+Z; [4]1-X,+Y,1/2-Z; [5]+X,-1+Y,+Z

Table S3. Selected Bond angles for 1

Atom	Atom	Atom	Angle/˚
N1[3]	Cd1	O1	93.03(14)
N1[3]	Cd1	O3	86.78(14)
N2	Cd1	O1	86.38(15)
N2	Cd1	O1[4]	90.19(15)
N2	Cd1	O2	87.57(17)
N2	Cd1	O3	95.73(15)
O1[4]	Cd1	O1	74.25(12)
O1[4]	Cd1	O3	145.01(11)
O1	Cd1	O3	140.43(11)
O2	Cd1	O1	54.22(11)
O2	Cd1	O1[4]	128.46(11)
O2	Cd1	O3	86.32(11)
O4	Cd1	N2	87.40(17)
O4	Cd1	O1[4]	91.33(12)
O4	Cd1	O1	164.25(12)
O4	Cd1	O2	139.89(12)
O4	Cd1	O3	54.70(12)
Cd1[4]	O1	Cd1	105.46(12)

[1]2-X,+Y,3/2-Z; [2]-X,+Y,1/2-Z; [3]+X,1+Y,+Z; [4]1-X,+Y,1/2-Z; [5]+X,-1+Y,+Z

v. The thermal stability test of 1

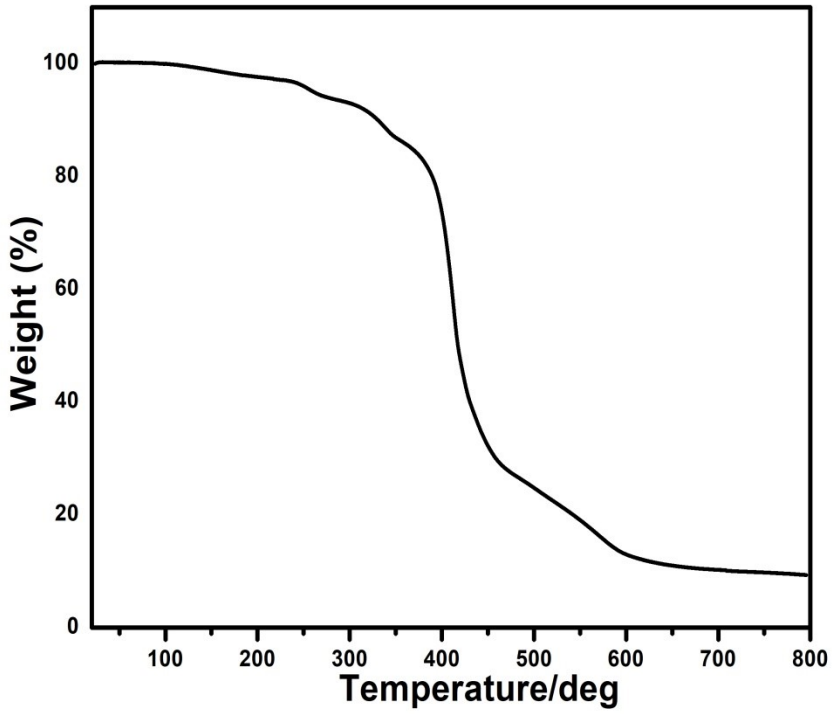

Fig. S1 Thermal stability test (TGA) of **1**

vi. SEM and Mapping

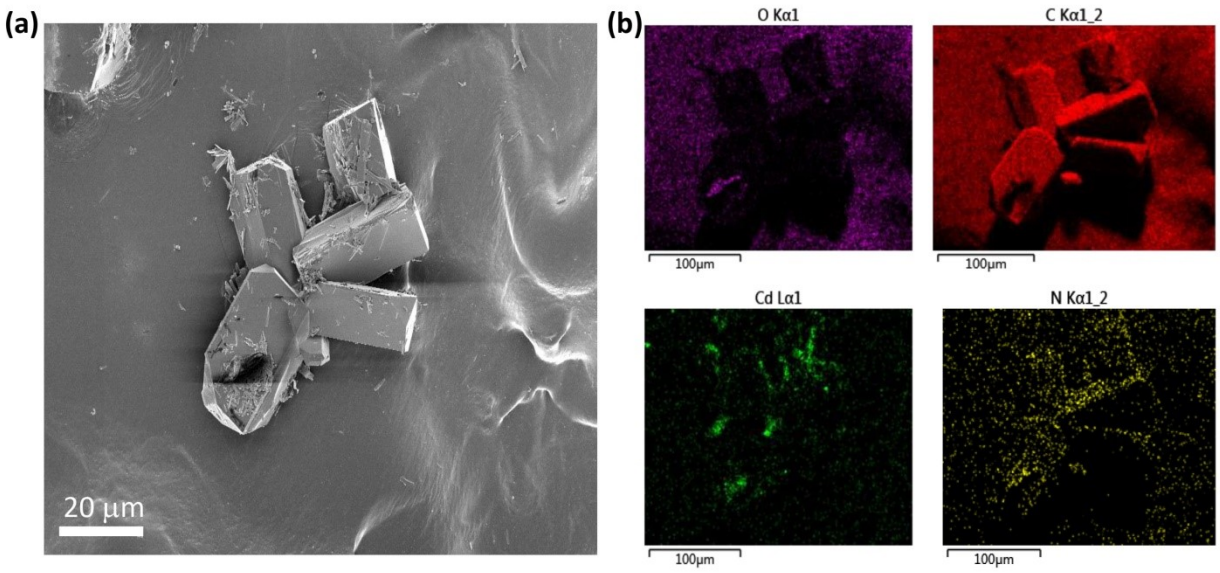

Fig. S2 (a) SEM image of **1** (b) Elemental mapping images of **1**.

vii. Quenching and LoD calculations for antibiotics

Standard Deviation (σ) calculation:

Blank Readings	FL Intensity
Reading 1	2.53358
Reading 2	2.53358
Reading 3	2.47324
Reading 4	2.35596
Reading 5	2.29437
Standard Deviation (σ)	0.108251

(i)

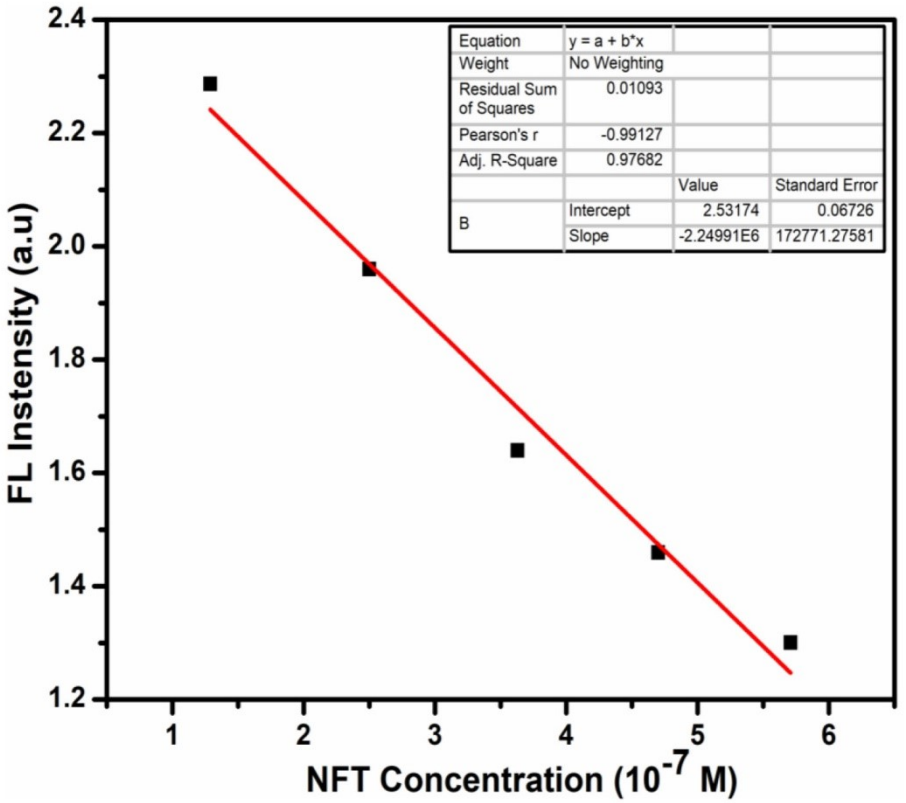

Fig. S3 LoD calculation for NFT antibiotic

Calculation of Detection limit (LOD) for NFT:

Slope (m)	2.24991E+6
Standard deviation (σ)	0.108251
Limit of detection (3σ/m)	0.14 µM

(ii)

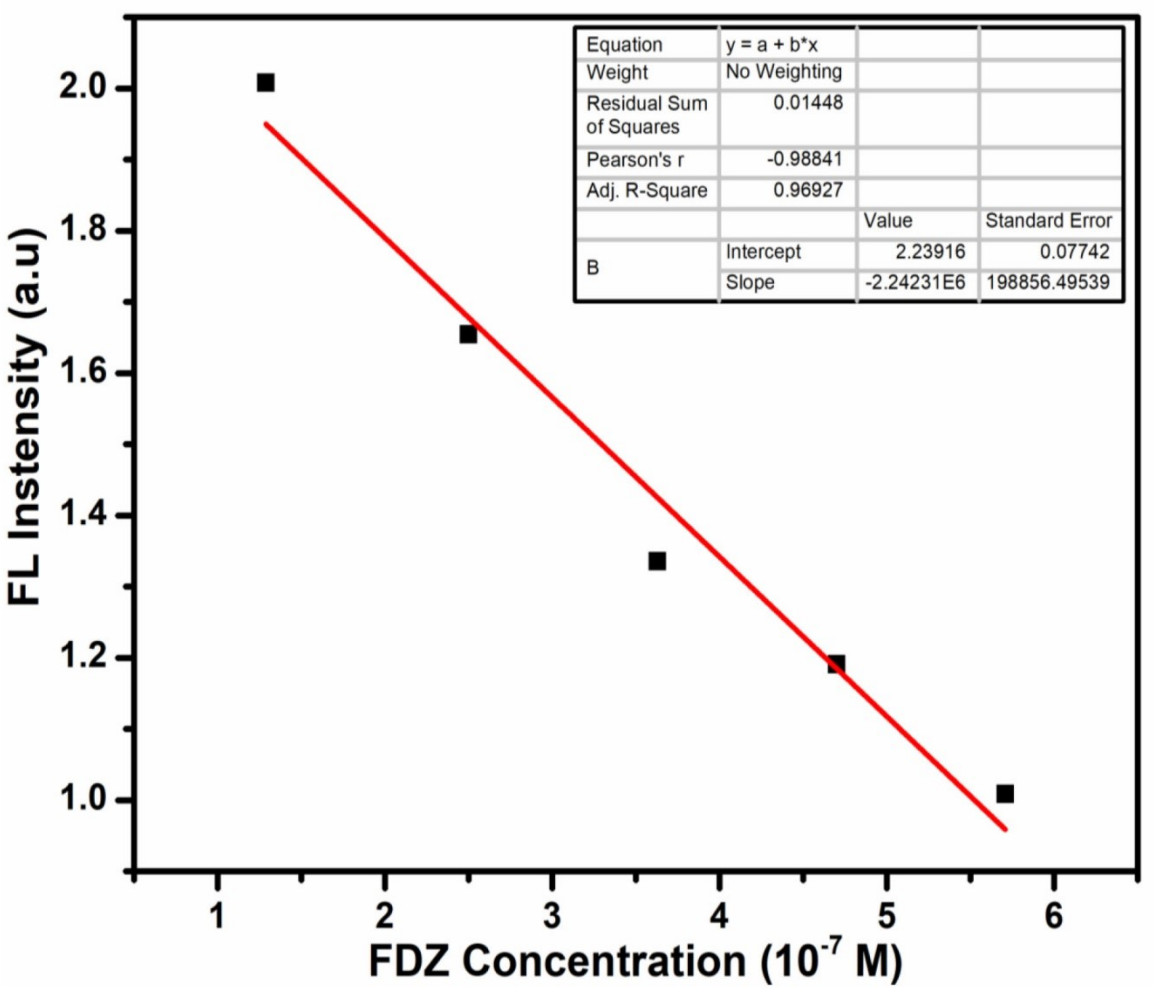

Fig. S4 LoD calculation for FDZ antibiotic

Calculation of Detection limit (LOD) for FDZ:

Slope (m)	2.24231E+6
Standard deviation (σ)	0.108251
Limit of detection (3σ/m)	0.14 µM

(iii)

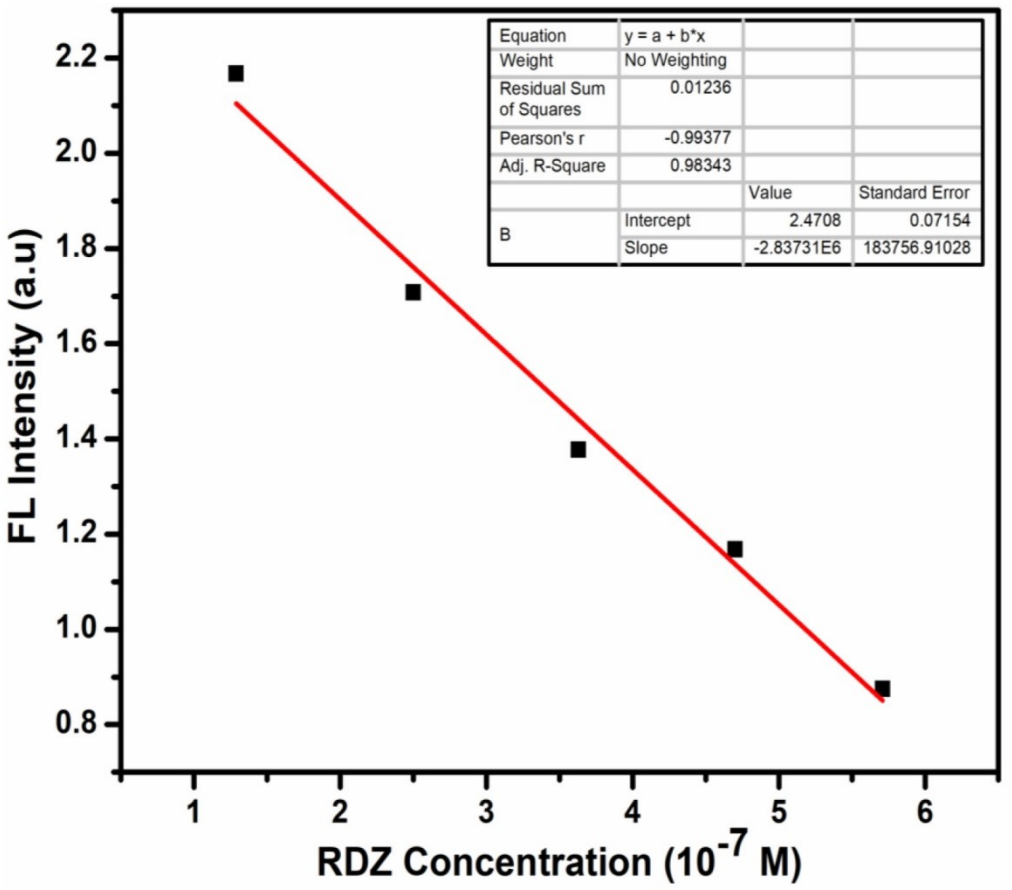

Fig. S5 LoD calculation for RDZ antibitic

Calculation of Detection limit (LOD) for RDZ:

Slope (m)	2.83731E+6
Standard deviation (σ)	0.108251
Limit of detection (3σ/m)	0.11 µM

(iv)

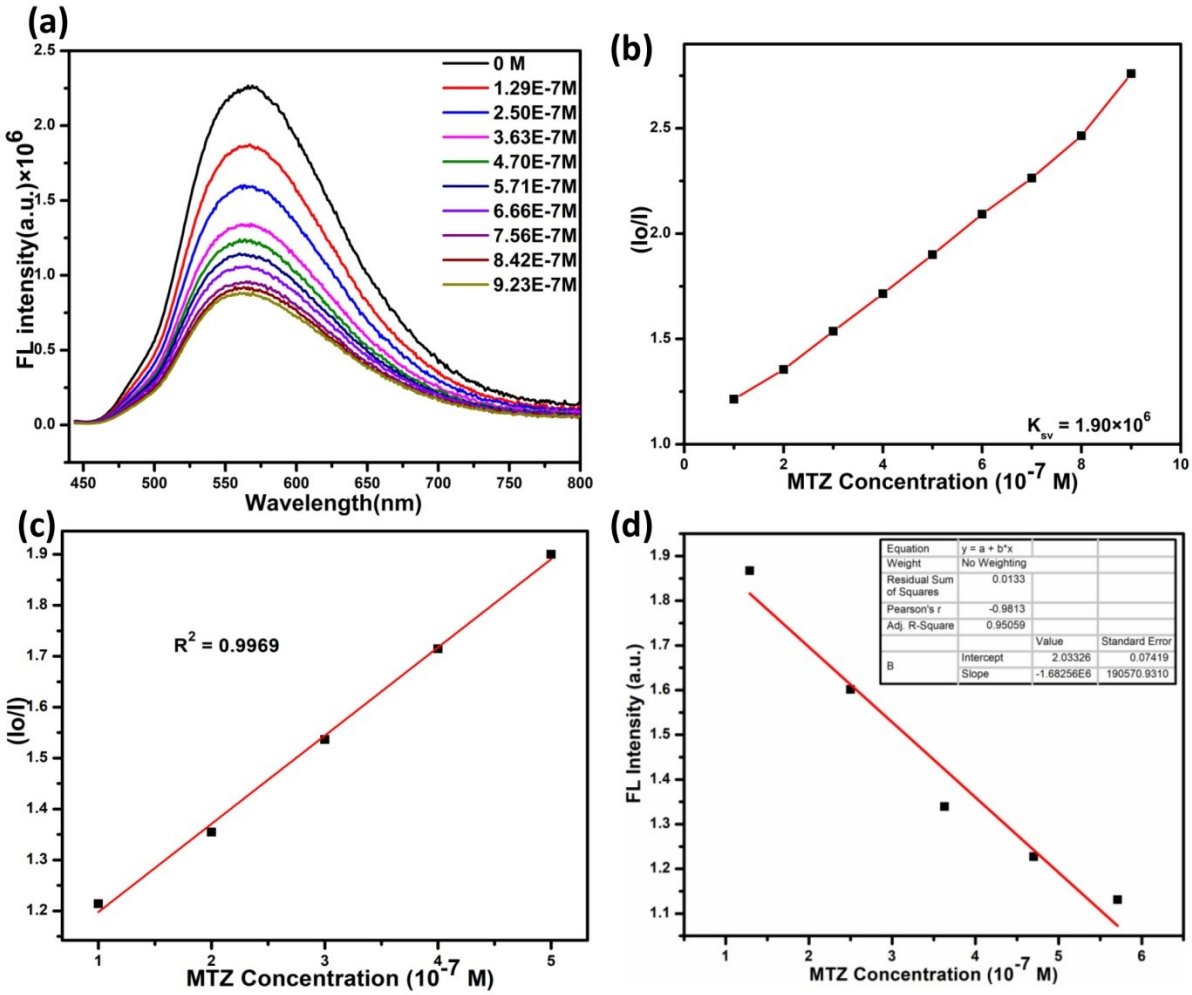

Fig. S6 Quenching titration graph and LoD calculation for MTZ antibiotic

Calculation of Detection limit (LOD) for MTZ:

Slope (m)	1.68256E+6
Standard deviation (σ)	0.108251
Limit of detection (3σ/m)	0.19 µM

(V)

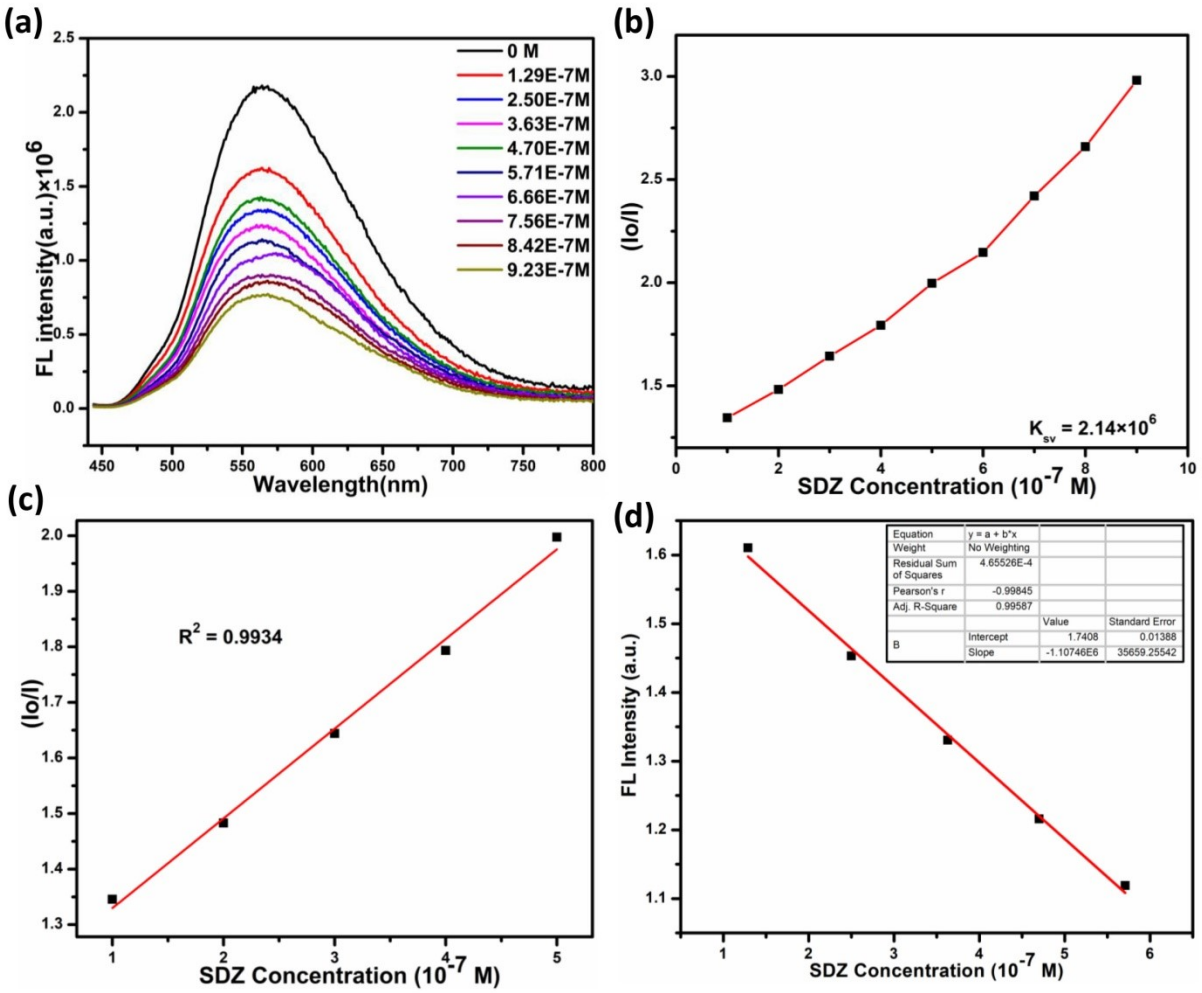

Fig. S7 Quenching titration graph and LoD calculation for SDZ antibiotic

Calculation of Detection limit (LOD) for SDZ:

Slope (m)	1.10746E+6
Standard deviation (σ)	0.108251
Limit of detection (3σ/m)	0.29 µM

(vi)

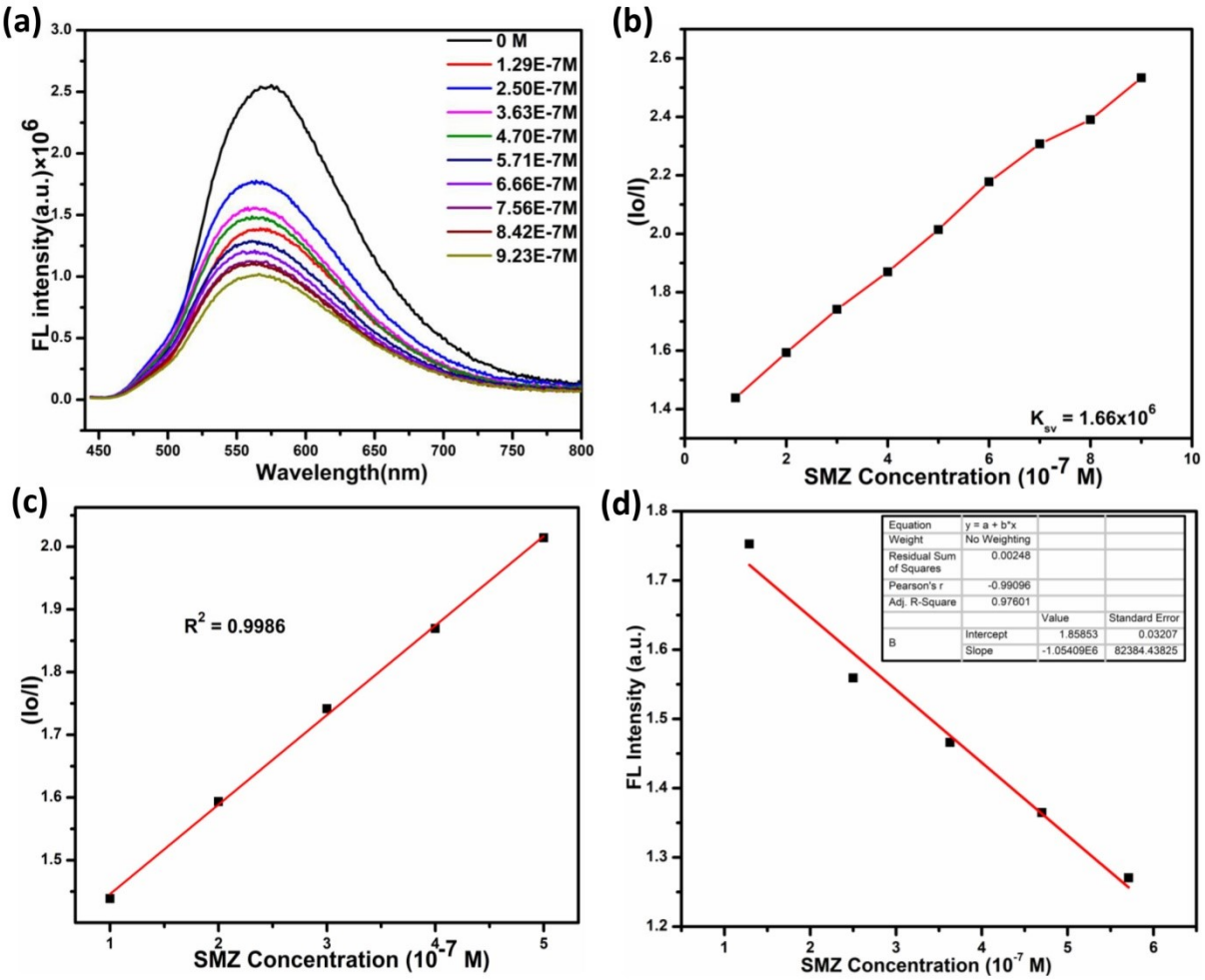

Fig. S8 Quenching titration graph and LoD calculation for SMZ antibiotic

Calculation of Detection limit (LOD) for SMZ:

Slope (m)	1.05409E+6
Standard deviation (σ)	0.108251
Limit of detection (3σ/m)	0.30 µM

(vii)

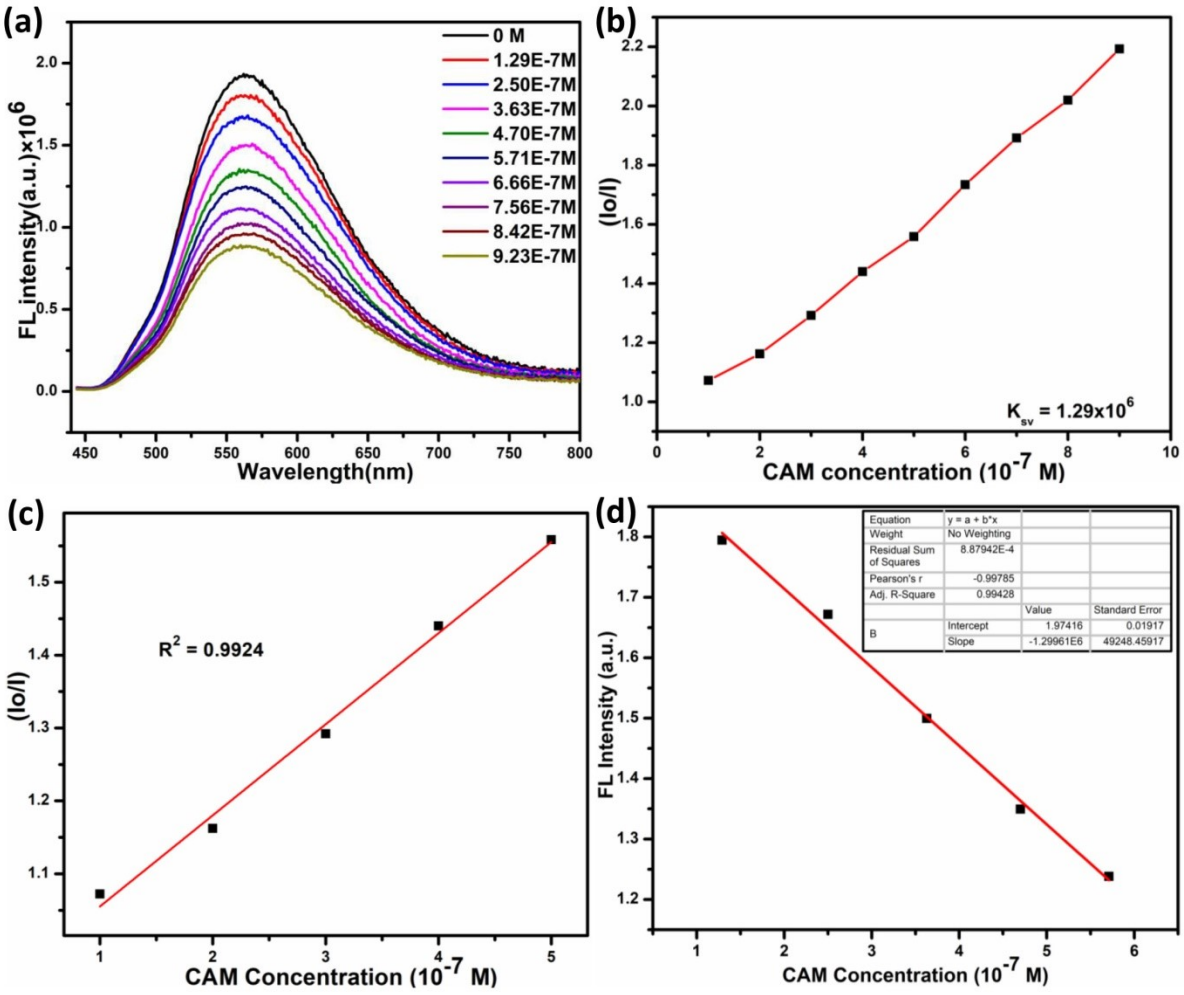

Fig. S9 Quenching titration graph and LoD calculation for CAM antibiotic

Calculation of Detection limit (LOD) for CAM:

Slope (m)	1.29961E+6
Standard deviation (σ)	0.108251
Limit of detection (3σ/m)	0.24 µM

(viii)

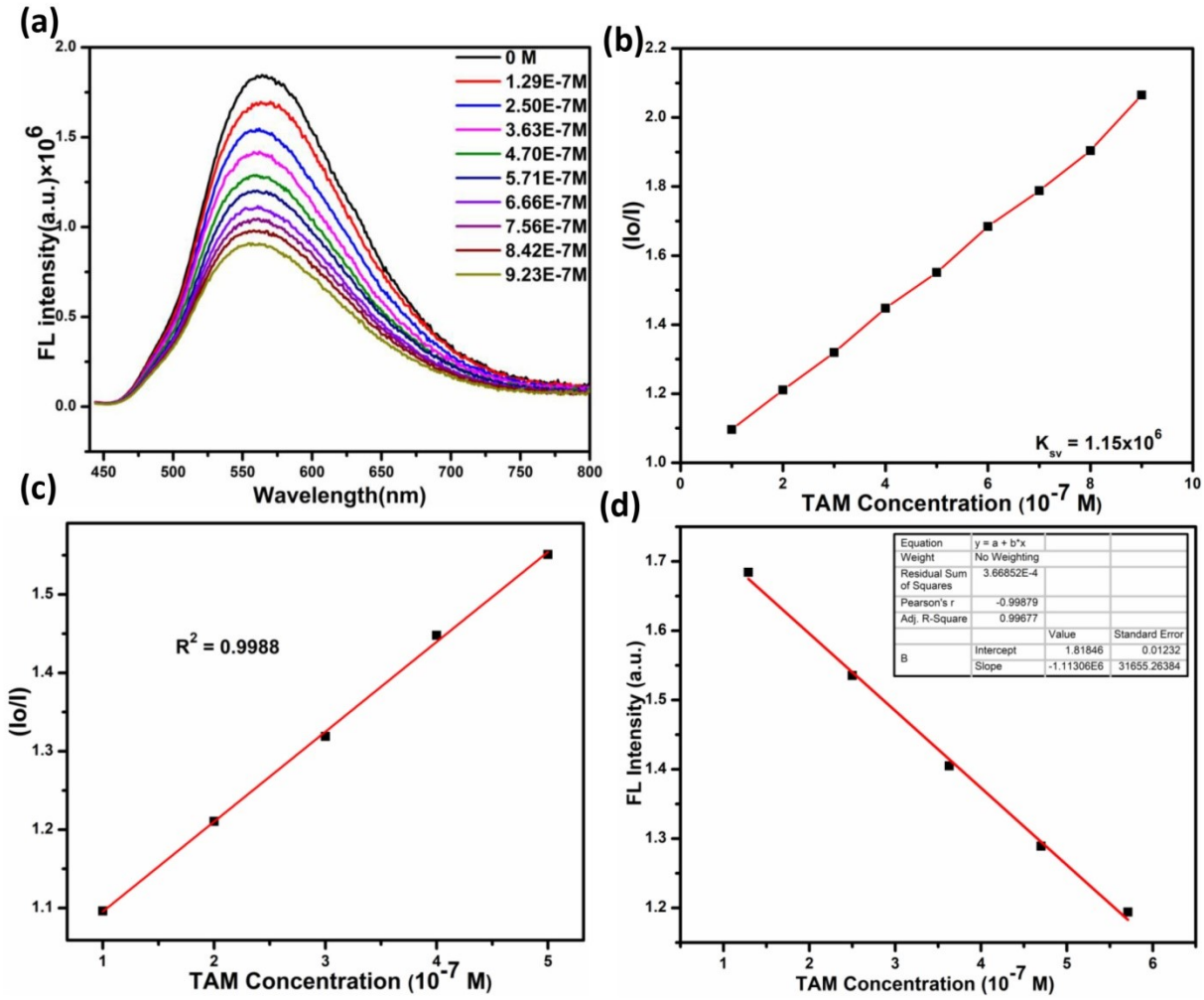

Fig. S10 Quenching titration graph and LoD calculation for TAM antibiotic

Calculation of Detection limit (LOD) for TAM:

Slope (m)	1.11306E+6
Standard deviation (σ)	0.108251
Limit of detection (3σ/m)	0.29 µM

viii. Table. S4 Calculated K_{sv} K_q and LoD values for common antibiotics

Selected analytes	Ksv (M^{-1})	K_q ($M^{-1}S^{-1}$)	Detection limits (µM)
Nitrofuratoin(NFT)	2.92×10^6	0.19×10^{15}	0.14
Furazolidone (FDZ)	3.57×10^6	0.23×10^{15}	0.14
Ronidazole (RDZ)	5.16×10^6	0.33×10^{15}	0.11
Metronidazole (MTZ)	1.91×10^6	0.12×10^{15}	0.19
Sulfadiazine (SDZ)	2.14×10^6	0.14×10^{15}	0.29
Sulfamethazine (SMZ)	1.66×10^6	0.10×10^{15}	0.30
Chloramphenicol(CAM)	1.29×10^6	0.84×10^{14}	0.24
Thiamphenicol (TAM)	1.15×10^6	0.75×10^{14}	0.29

ix. Recyclability study

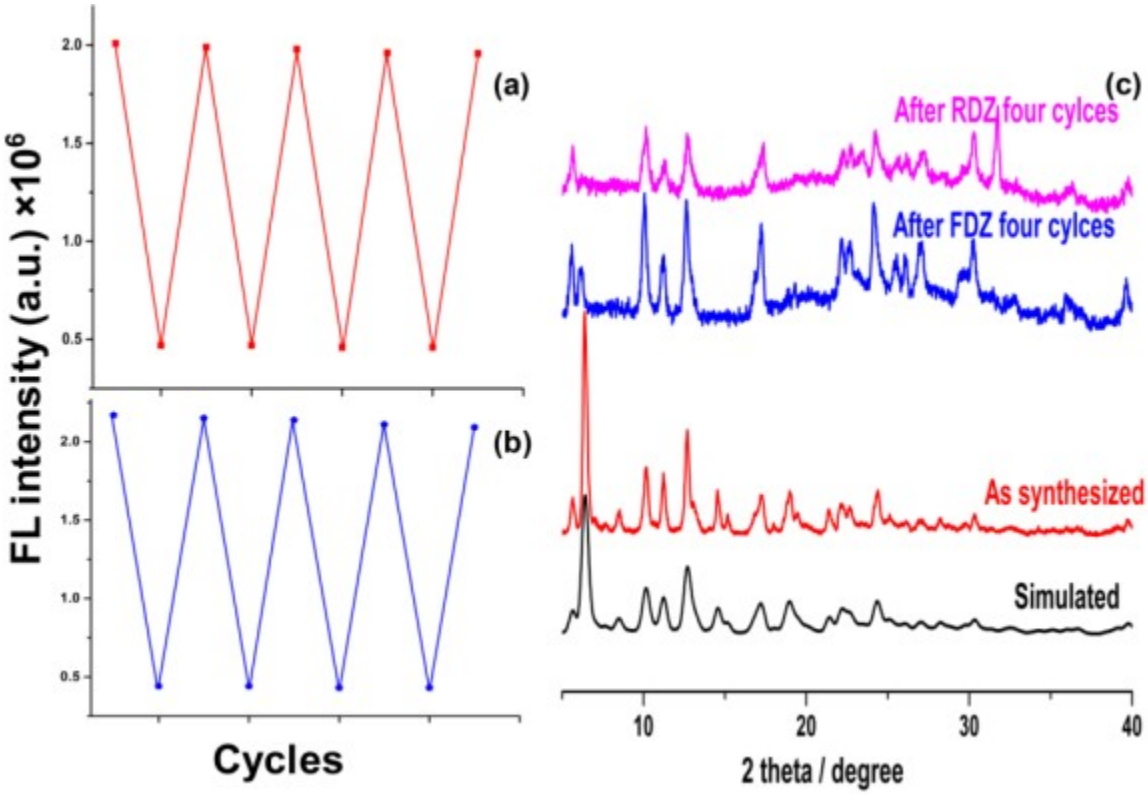

Fig. S11 Fluorescence intensity of **1** after four cycles detection of (a) FDZ, (b) RDZ and (c) P-XRD patterns of **1** after 4 cycles sensing of FDZ and RDZ compared with the simulated and as-synthesized.

x. Uv-visible spectroscopy

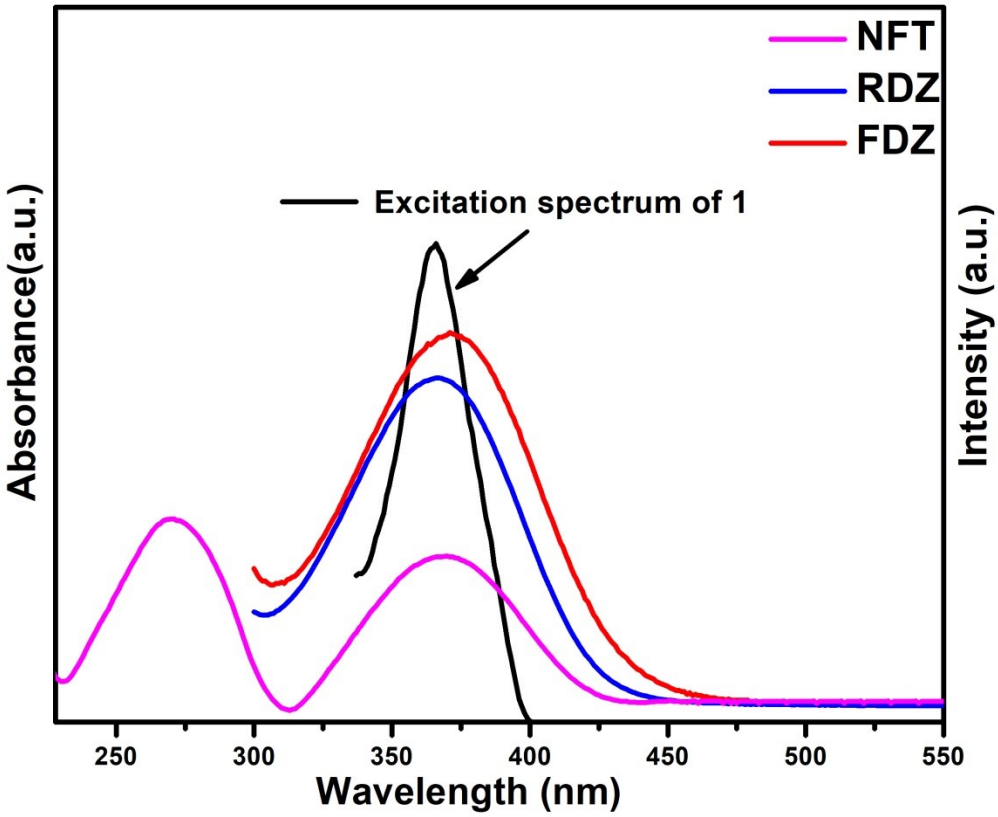

Fig. S12 UV-vis spectra of NFT, RDZ, and FDZ, and excitation spectra of **1**

xi. TCSPC calculation for 1 and different antibiotics

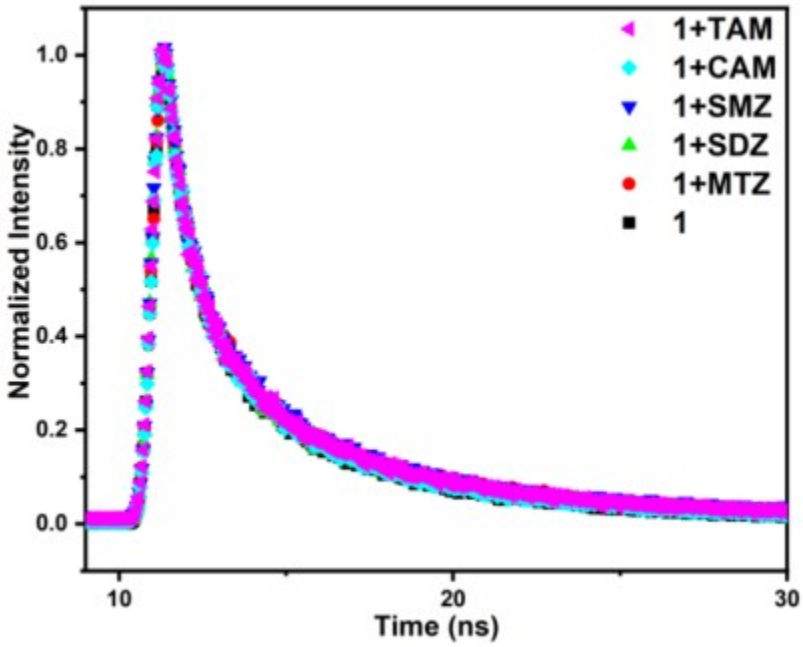

Fig. S13 Time-resolved fluorescence decay profile for **1** and different antibiotics.

Table. S5 Decay life-time calculations for 1 and antibiotics

Samples	T1 (ns)	T2 (ns)	B1	B2	(T1×B1+T2×B2) (ns)
1	19.5985	5.586098	0.6877	0.3123	15.22
1+NFT	7.10502	20.48647	0.3125	0.6875	16.30
1+FDZ	6.43309	19.7718	0.2546	0.7454	16.37
1+RDZ	21.53541	8.148406	0.6784	32.16	17.23
1+ MTZ	7.18421	20.3890	30.45	69.55	16.36
1+SDZ	6.30467	19.6943	0.2793	0.7207	15.95
1+SMZ	19.82028	6.30224	0.7100	0.2900	15.90
1+CAM	6.25478	20.07246	0.3073	0.6927	15.82
1+TAM	5.81566	19.47863	0.3038	0.6962	15.32

xii. DFT calculations

All the DFT calculations were performed to find HOMO-LUMO bandgap for **1** and different antibiotics. All theoretical calculations were carried out using Gaussian 09w package with B3LYP function and 6-31+G* basis set [4-6].

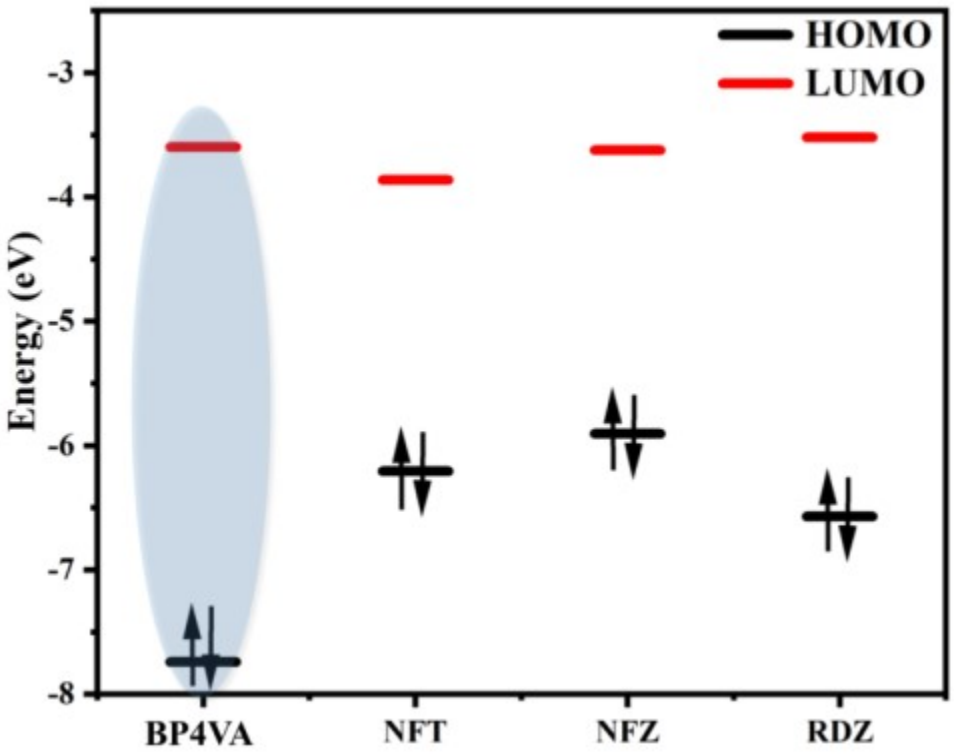

Fig. S14 Theoretically calculated HOMO and LUMO energies for ligand and different antibiotics.

Table. S6 Theoretically calculated HOMO-LUMO energy levels for different antibiotics

Analytes	HOMO (eV)	LUMO (eV)	Band gap
BP_4V_4	-7.7419	-3.599	-4.1429
NFT	-6.205	-3.864	-2.341
NFZ	-5.905	-3.624	-2.281
RDZ	-6.57	-3.52	-3.05
SDZ	-7.564	0.0163	-7.547
MTZ	-6.42	-3.43	-2.99
SMZ	-5.457	-1.898	-3.559
CAM	-6.58	-3.69	-2.89
TAM	-7.09	-1.52	-5.57

xiii. References

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