Supporting Information

Four MOFs with isomer ligands as fluorescent probe for highly selective, sensitive and stable detection of antibiotics in water

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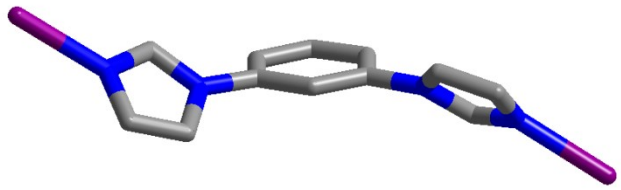
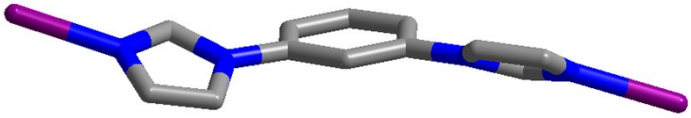
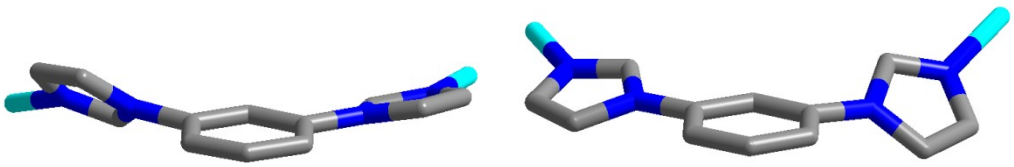


(1)

(2)



(3)



(4)

Fig. S1 Coordination modes and conformations of bis(1-imidazoly)benzene (bib) ligands in complexes **1**-**4**.

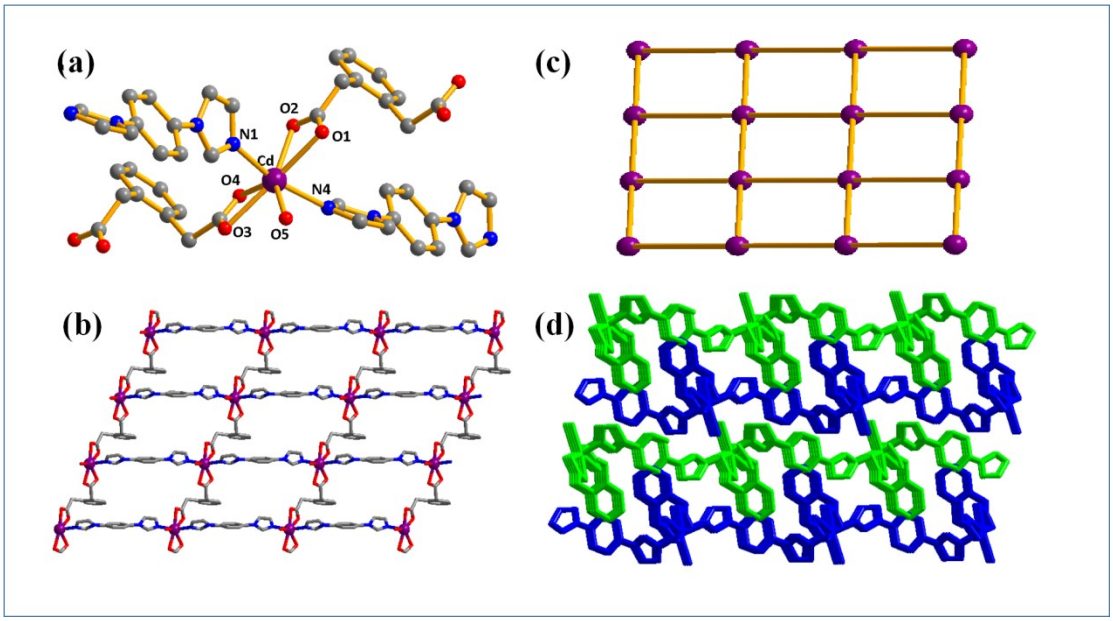


Fig. S2 (a) Coordination environment of Cd(II) atom in complex **2**. All hydrogen atoms are omitted for clarity; Symmetry code: #1: *x*+1, *y*, *z*-1; #2: *x*-1, *y*, *z*; #3: *x*+1, *y*, *z*; #4: *x*-1, *y*, *z*+1. (b) and (c) Ball-and-stick view of 2D (4,4) layer in **2**. (d) View of the 3D network of **2** extended by the 2D layers in an offset stacking fashion.

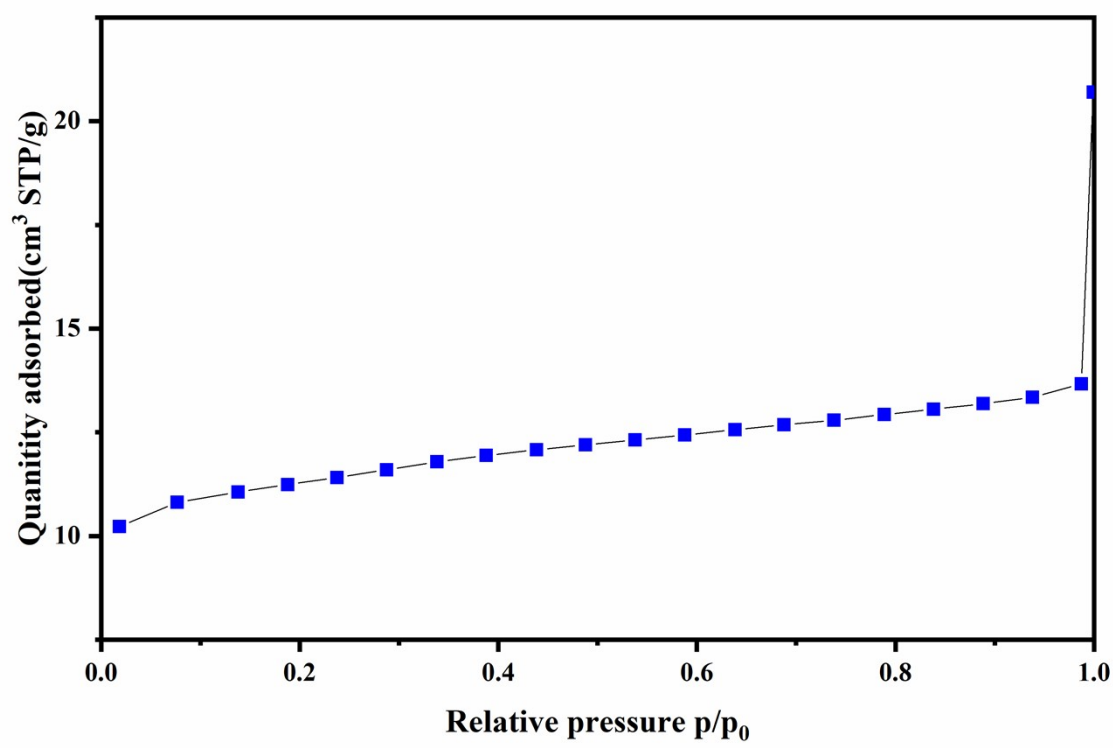


Fig. S3 The N_2 adsorption-desorption isotherms of complex **4** sample.

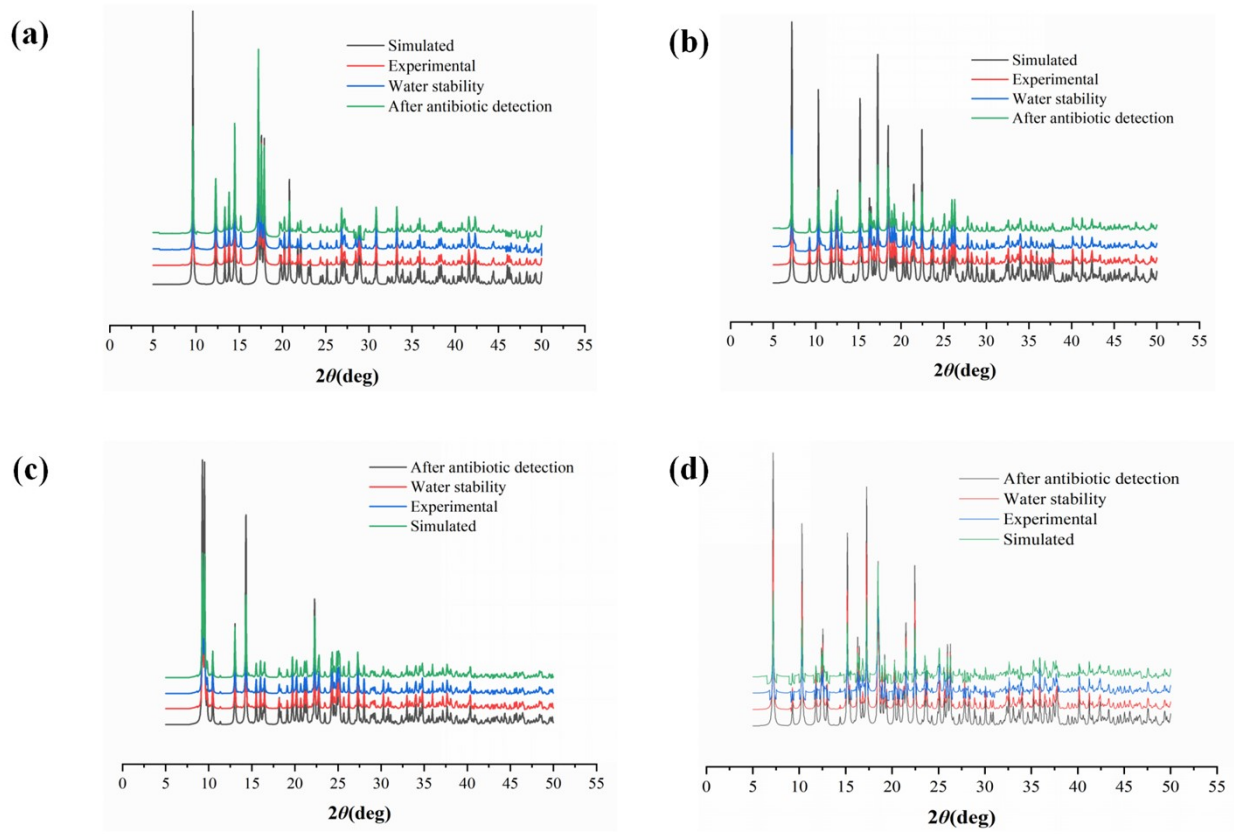
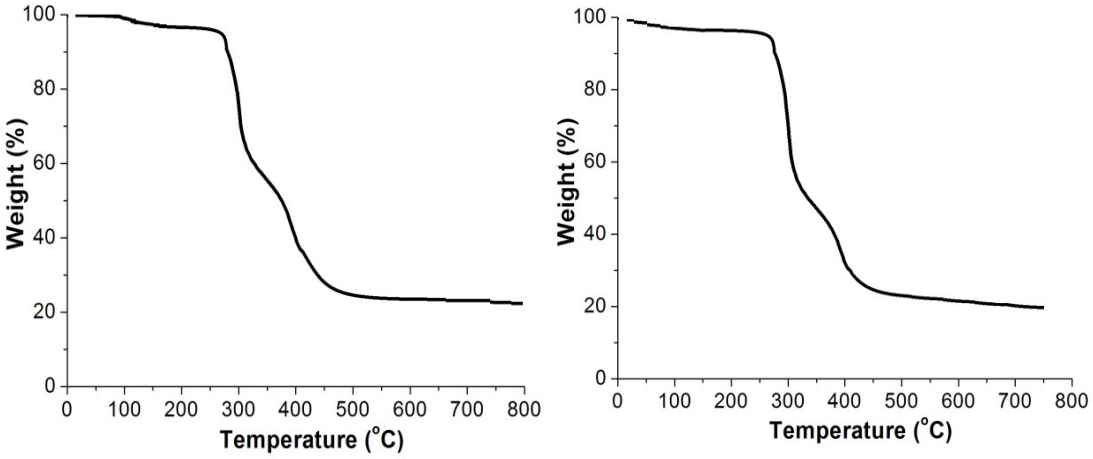
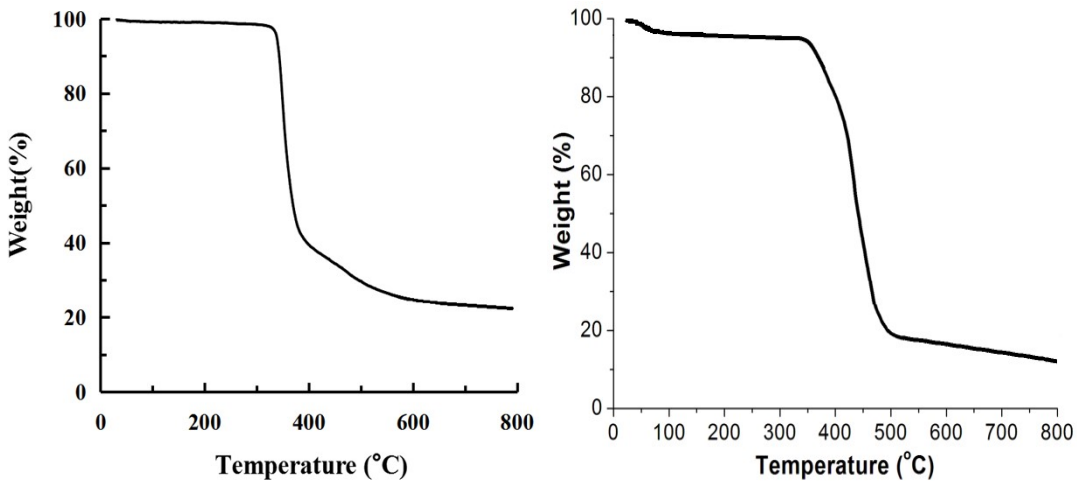


Fig. S4 PXRD patterns of complexes **1-4**.



(1) (2)



(3) (4)

Fig. S5 Thermal gravimetric analysis (TGA) curves of complexes **1**-**4**.

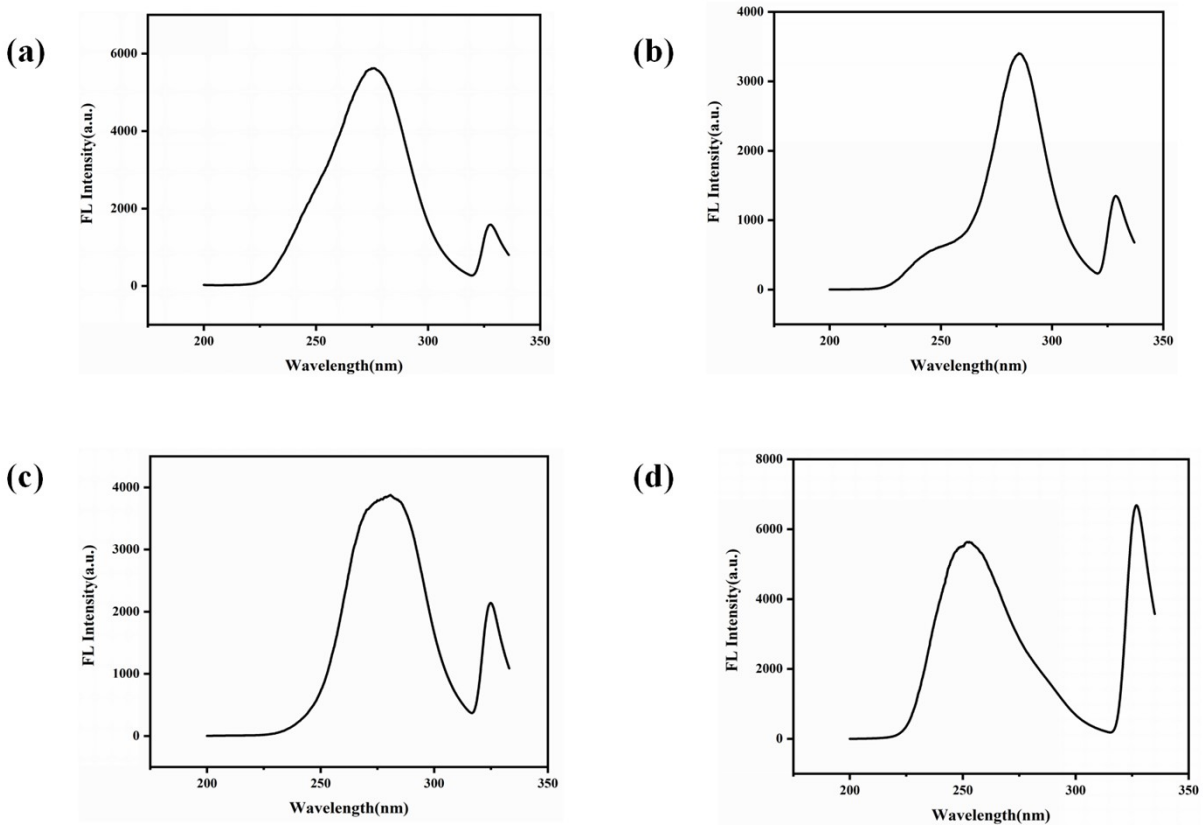
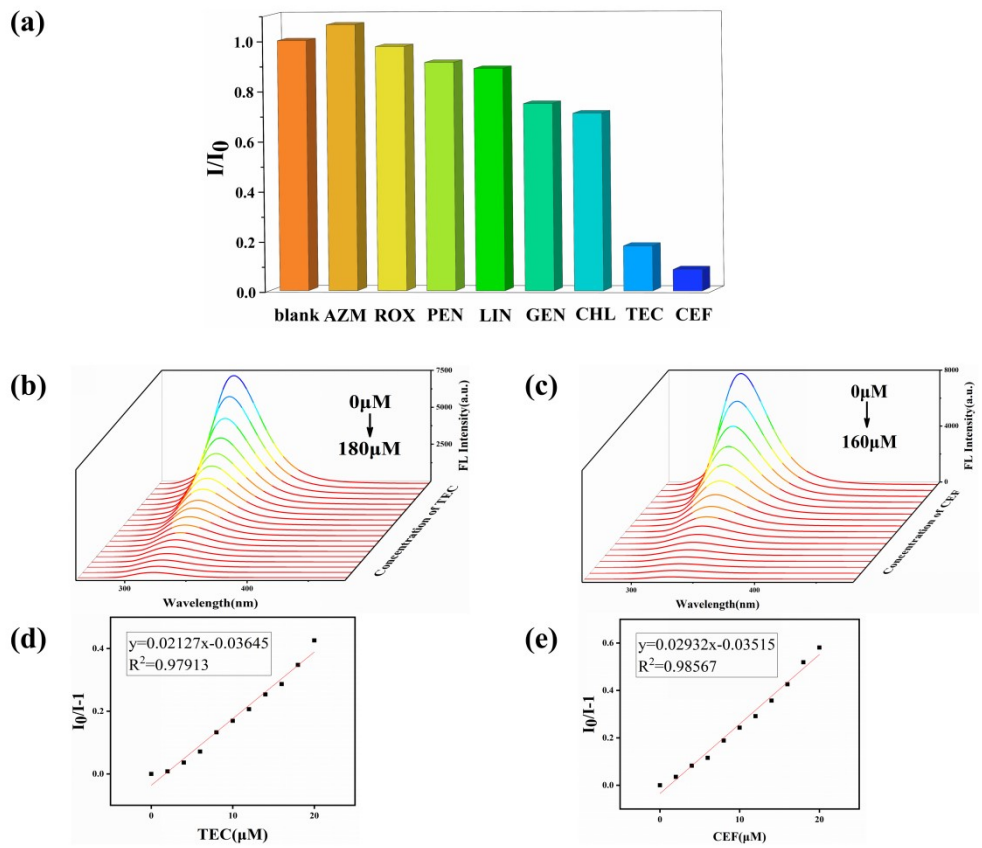
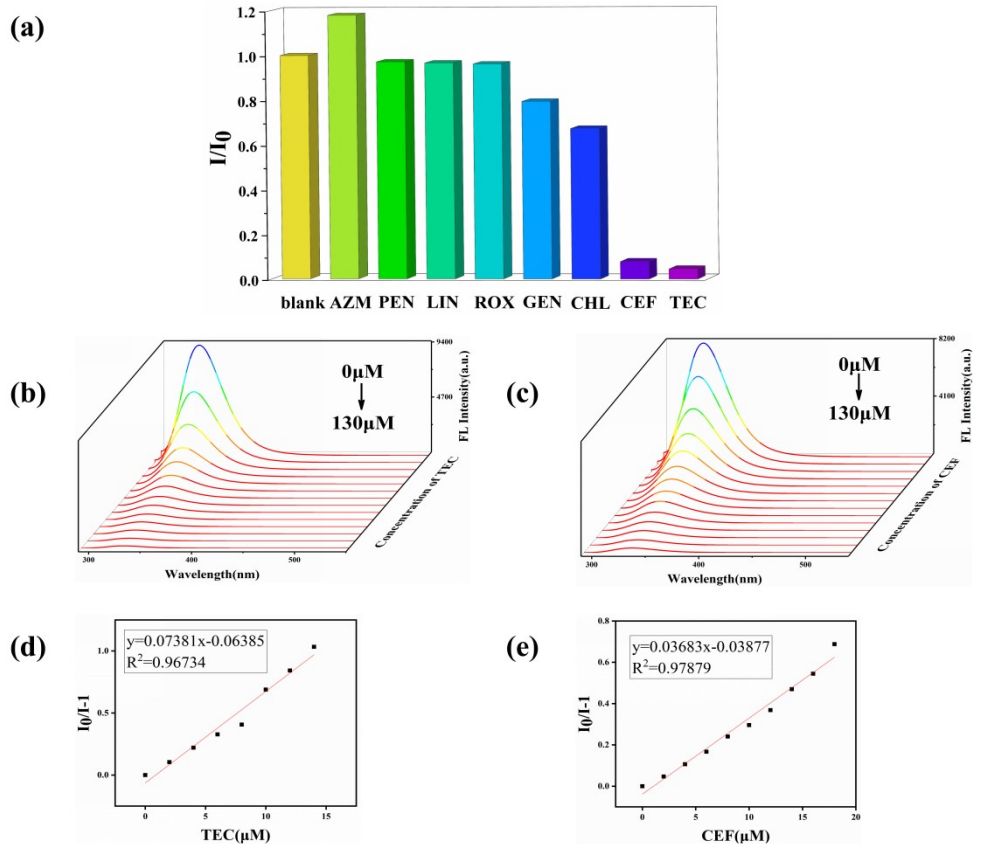


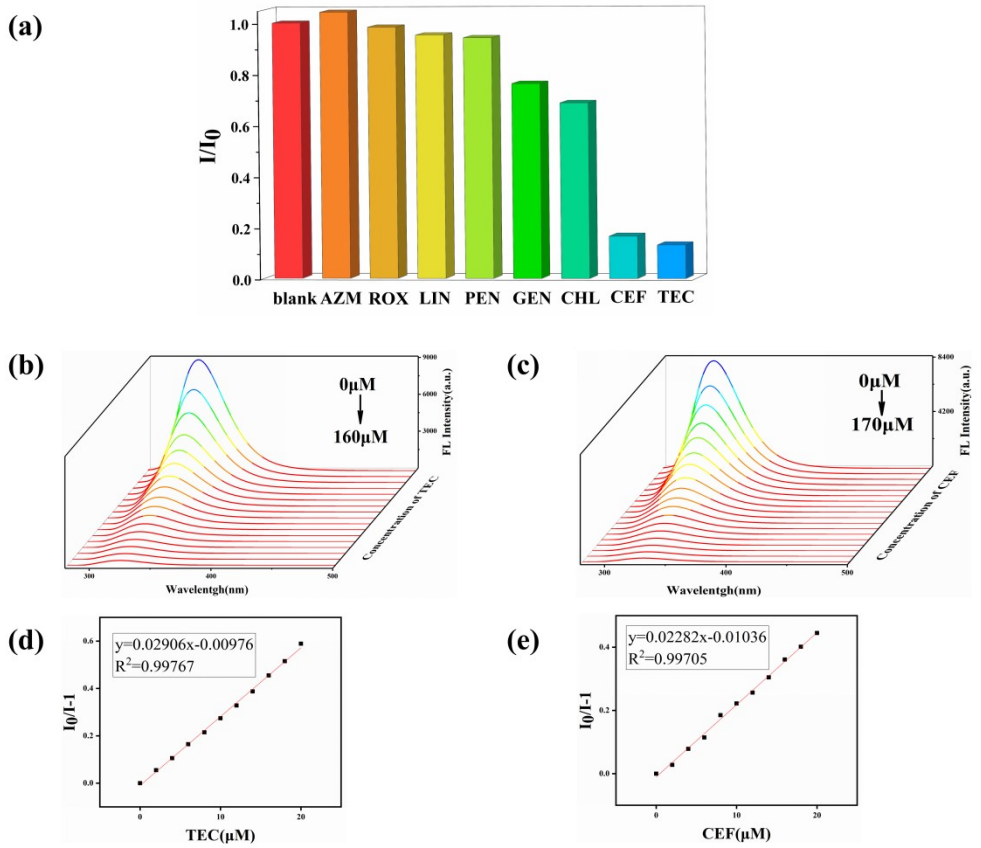
Fig. S6 Excitation spectra of complexes **1-4**


(a)
I/I0
blank AZM ROX PEN LIN GEN CHL TEC CEF
(b)
0μM
180μM
FL Intensity(a.u.)
Concentration of TEC
Wavelength(nm)
(c)
0μM
160μM
FL Intensity(a.u.)
Concentration of CEF
Wavelength(nm)
(d)
y=0.02127x-0.03645
R2=0.97913
I0/I-1
TEC(μM)
(e)
y=0.02932x-0.03515
R2=0.98567
I0/I-1
CEF(μM)

Complex 1


(a)
I/I0
blank AZM PEN LIN ROX GEN CHL CEF TEC
(b)
0μM
130μM
FL Intensity(a.u.)
Concentration of TEC
Wavelength(nm)
(c)
0μM
130μM
FL Intensity(a.u.)
Concentration of CEF
Wavelength(nm)
(d)
y=0.07381x-0.06385
R2=0.96734
I0/I-1
TEC(μM)
(e)
y=0.03683x-0.03877
R2=0.97879
I0/I-1
CEF(μM)

Complex 2



Complex 3

Fig. S7(a) Luminous intensity of complex **1-3** (2 mL, prepared solution) in aqueous solutions with different antibiotic (0.001 M). (b) and (c) Concentration-dependent luminescence quenching of complex **1-3** suspension in water by tetracycline(TEC) and cefoxime (CEF) (excited at 270nm and 270nm). (d) and (e) Stern−Volmer plot of complex **1-3** suspension quenched by tetracycline(TEC) and cefoxime (CEF).

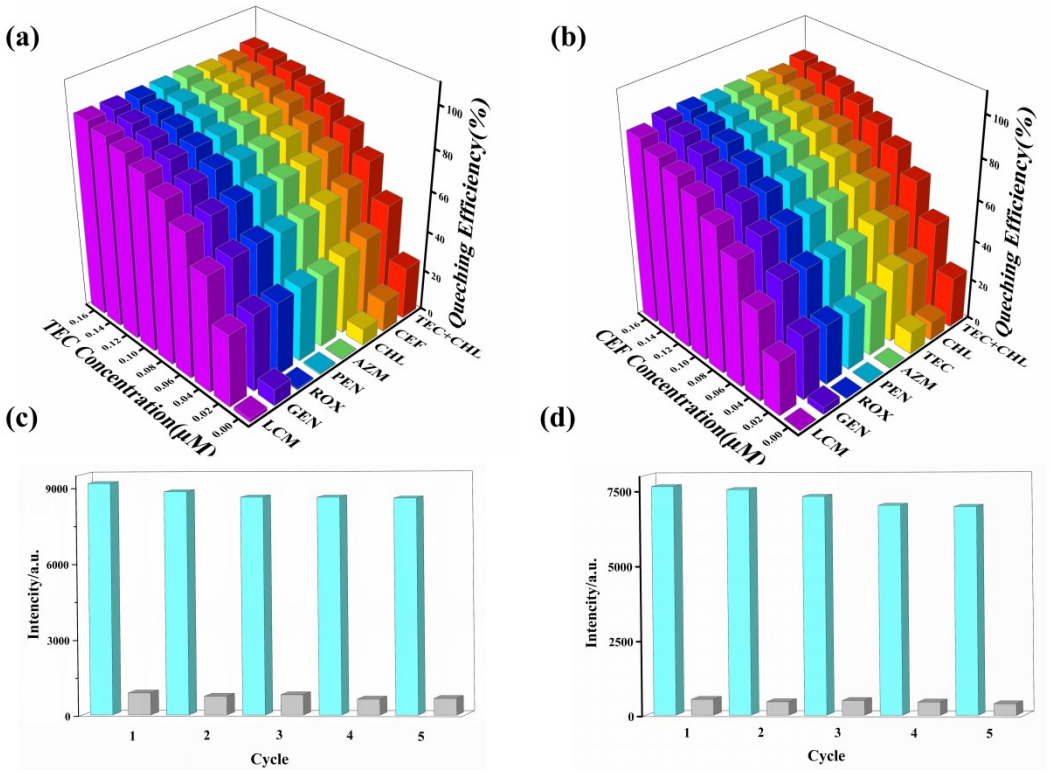


Fig. S8 Luminescence quenching efficiency of complex **3** with 1 mM antibiotic aqueous solution upon adding different concentrations of TEC(a) and CEF(b).The cycle stability of complex **3** fluorescent probe for the detection of TEC(c) and CEF(d)

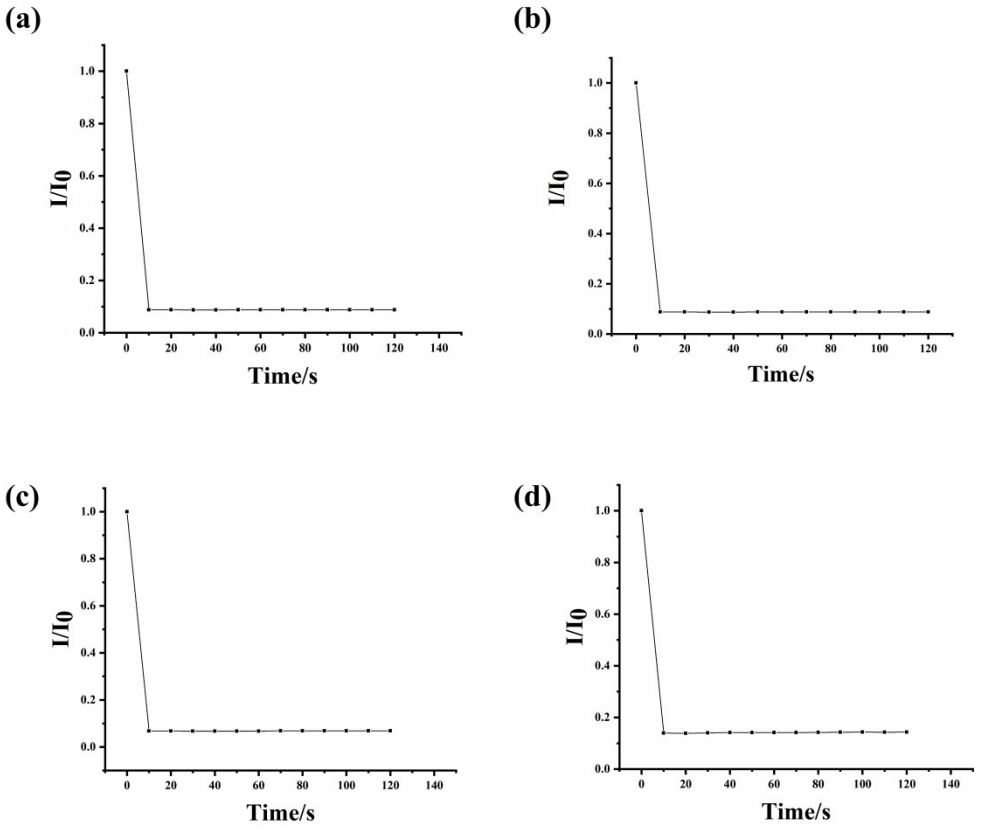


Fig. S9 The fluorescence intensity changes of the present probe with the duration after introducing 100 μL TEC(picture a and c) and CEF(picture b and d), (a) (b) for complex **2** and (c) (d) for complex **4**.

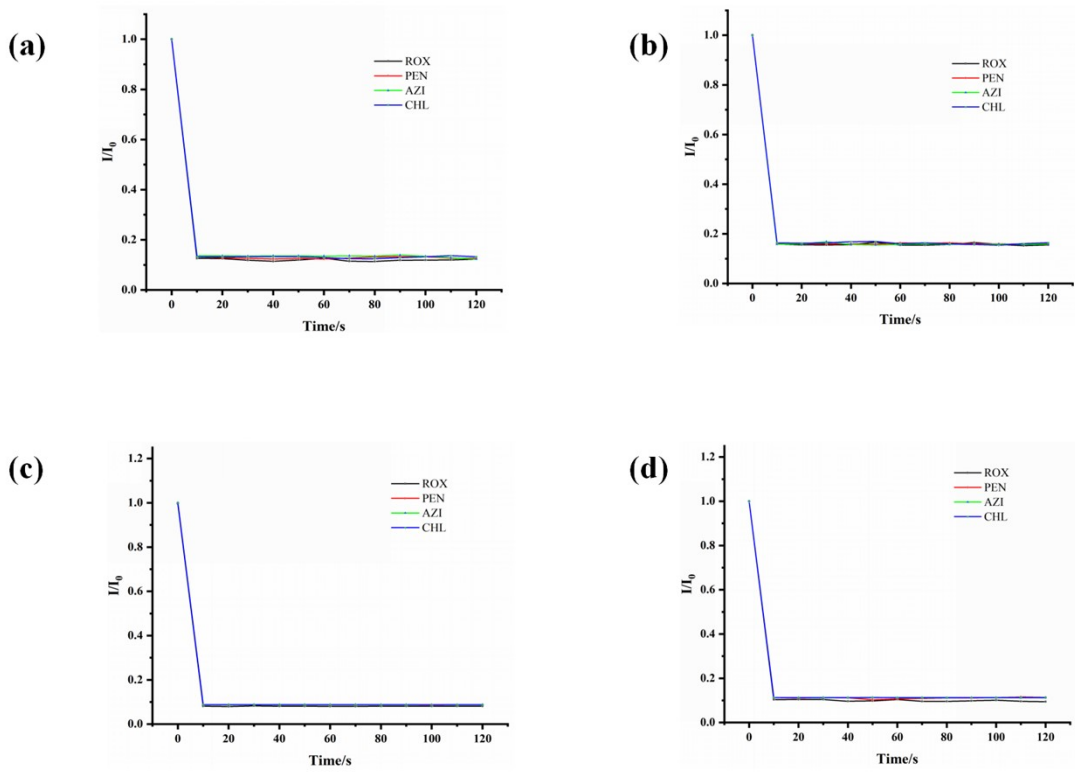


Fig. S10 The fluorescence intensity changes of the present probe with the duration after introducing 100 μL TEC(picture a and c) and CEF(picture b and d) mixed with other antibiotics, (a) (b) for complex **2** and (c) (d) for complex **4**.

Table S1. Selected Bond Lengths (Å) and Bond Angles (º) for Complexes **1**-**4**.

Bond	Dist.	Bond	Dist.	Bond	Dist.
Cd(1)-O(3)	2.324(3)	Cd(1)-N(1)#1	2.3119(19)	Cd(1)-N(1)	2.3119(19)
Cd(1)-O(1)#1	2.3747(17)	Cd(1)-O(1)	2.3747(17)	Cd(1)-O(2)	2.5239(18)
Cd(1)-O(2)#1	2.099(2)				
Angle	(°)	Angle	(°)	Angle	(°)
O(3)-Cd(1)-O(1)#1	136.06(4)	O(3)-Cd(1)-O(1)	136.06(4)	O(3)-Cd(1)-O(2)#1	82.89(4)
O(3)-Cd(1)-O(2)	82.90(4)	N(1)-Cd(1)-O(3)	91.80(5)	N(1)#1-Cd(1)-O(3)	91.80(5)
N(1)#1-Cd(1)-N(1)	176.40(10)	N(1)#1-Cd(1)-O(1)	84.55(7)	N(1)#1-Cd(1)-O(1)#1	92.85(7)
N(1)-Cd(1)-O(1)	92.85(7)	N(1)-Cd(1)-O(1)#1	84.55(7)	N(1)#1-Cd(1)-O(2)	85.84(7)
N(1)-Cd(1)-O(2)#1	85.84(7)	N(1)-Cd(1)-O(2)	94.61(7)	N(1)#1-Cd(1)-O(2)#1	94.61(7)
O(1)-Cd(1)-O(1)#1	87.88(8)	O(1)-Cd(1)-O(2)	53.18(6)	O(1)#1-Cd(1)-O(2)#1	53.18(6)
O(1)#1-Cd(1)-O(2)	141.02(6)	O(1)-Cd(1)-O(2)#1	141.03(6)	O(2)-Cd(1)-O(2)#1	165.79(8)
2					
Bond	Dist.	Bond	Dist.	Bond	Dist.
Cd(1)-N(1)	2.300(3)	Cd(1)-O(5)	2.318(3)	Cd(1)-N(4)#1	2.320(3)
Cd(1)-O(2)	2.394(2)	Cd(1)-O(4)#2	2.401(3)	Cd(1)-O(3)#2	2.456(3)
Cd(1)-O(1)	2.496(3)				
Angle	(°)	Angle	(°)	Angle	(°)
N(1)-Cd(1)-O(5)	90.82(11)	N(1)-Cd(1)-N(4)#1	164.06(11)	O(5)-Cd(1)-N(4)#1	84.88(11)
N(1)-Cd(1)-O(2)	90.24(10)	O(5)-Cd(1)-O(2)	146.37(10)	N(4)#1-Cd(1)-O(2)	85.00(10)
N(1)-Cd(1)-O(4)#2	103.61(11)	O(5)-Cd(1)-O(4)#2	128.04(10)	N(4)#1-Cd(1)-O(4)#2	91.05(10)
O(2)-Cd(1)-O(4)#2	84.11(8)	N(1)-Cd(1)-O(3)#2	88.60(10)	O(5)-Cd(1)-O(3)#2	78.03(10)
N(4)#1-Cd(1)-O(3)#2	105.43(10)	O(2)-Cd(1)-O(3)#2	135.59(9)	O(4)#2-Cd(1)-O(3)#2	53.29(8)
N(1)-Cd(1)-O(1)	84.60(10)	O(5)-Cd(1)-O(1)	93.54(10)	N(4)#1-Cd(1)-O(1)	80.37(10)
O(2)-Cd(1)-O(1)	53.13(8)	O(4)#2-Cd(1)-O(1)	136.78(8)	O(3)#2-Cd(1)-O(1)	169.11(8)
3					
Bond	Dist.	Bond	Dist.	Bond	Dist.
Cd(1)-O(4)#1	2.415(3)	Cd(1)-O(1)#2	2.363(3)	Cd(1)-O(1)	2.411(3)
Cd(1)-N(1)	2.318(3)	Cd(1)-O(2)	2.516(3)	Cd(1)-O(3)#1	2.421(3)
Cd(1)-N(4)#3	2.304(3)	Cd(1)-C(10)#1	2.753(4)		
Angle	(°)	Angle	(°)	Angle	(°)

O(4)#1-Cd(1)-O(2)	145.05(10)	O(4)#1-Cd(1)-	54.13(11)	O(4)#1-Cd(1)-C(10)#1	27.07(11)
O(1)-Cd(1)-O(4)#1	157.96(11)	O(1)#2-Cd(1)-	89.04(10)	O(1)#2-Cd(1)-O(1)	71.64(10)
O(1)-Cd(1)-O(2)	52.96(9)	O(1)#2-Cd(1)-O(2)	124.60(9)	O(1)#2-Cd(1)-O(3)#1	142.93(10)
O(1)-Cd(1)-O(3)#1	143.03(9)	O(1)#2-Cd(1)-	115.86(12)	O(1)-Cd(1)-C(10)#1	164.58(10)
N(1)-Cd(1)-O(4)#1	86.04(11)	N(1)-Cd(1)-O(1)	81.90(11)	N(1)-Cd(1)-O(1)#2	84.99(11)
N(1)-Cd(1)-O(2)	87.70(11)	N(1)-Cd(1)-O(3)#1	88.06(11)	N(1)-Cd(1)-C(10)#1	85.32(11)
O(2)-Cd(1)-C(10)#1	118.11(12)	O(3)#1-Cd(1)-O(2)	91.34(10)	O(3)#1-Cd(1)-C(10)#1	27.12(11)
N(4)#3-Cd(1)-O(4)#1	97.76(11)	N(4)#3-Cd(1)-O(1)	96.79(11)	N(4)#3-Cd(1)-O(1)#2	102.65(11)
N(4)#3-Cd(1)-N(1)	171.47(10)	N(4)#3-Cd(1)-O(2)	84.82(10)	N(4)#3-Cd(1)-O(3)#1	88.01(11)
N(4)#3-Cd(1)-C(10)#1	94.58(10)				

4

Bond	Dist.	Bond	Dist.	Bond	Dist.
Zn(1)-O(1)	1.944(2)	Zn(1)-O(5)	1.960(2)	Zn(1)-N(1)	2.007(3)
Zn(1)-N(8)#1	2.038(3)	Zn(2)-N(5)	2.042(3)	Zn(2)-N(4)	2.069(3)
Zn(2)-O(8)	2.105(3)	Zn(2)-O(4)	2.156(3)	Zn(2)-O(3)	2.277(3)
Zn(2)-O(7)	2.365(3)	Zn(2)-C(1)	2.556(4)	Zn(2)-C(20)	2.582(4)
Angle	(°)	Angle	(°)	Angle	(°)
O(1)-Zn(1)-O(5)	104.50(11)	O(1)-Zn(1)-N(1)	111.89(11)	O(5)-Zn(1)-N(1)	118.02(11)
O(1)-Zn(1)-N(8)#1	120.41(10)	O(5)-Zn(1)-N(8)#1	96.70(11)	N(1)-Zn(1)-N(8)#1	105.15(11)
N(5)-Zn(2)-N(4)	99.39(11)	N(5)-Zn(2)-O(8)	96.05(13)	N(4)-Zn(2)-O(8)	145.46(11)
N(5)-Zn(2)-O(4)	149.24(11)	N(4)-Zn(2)-O(4)	90.37(13)	O(8)-Zn(2)-O(4)	91.90(14)
N(5)-Zn(2)-O(3)	91.37(10)	N(4)-Zn(2)-O(3)	102.06(11)	O(8)-Zn(2)-O(3)	108.28(11)
O(4)-Zn(2)-O(3)	57.98(10)	N(5)-Zn(2)-O(7)	102.94(11)	N(4)-Zn(2)-O(7)	89.64(10)
O(8)-Zn(2)-O(7)	56.72(11)	O(4)-Zn(2)-O(7)	106.24(11)	O(3)-Zn(2)-O(7)	159.87(11)

Symmetry code:

1 #1: *x*, -*y*-1/2, -*z*+1/2; #2: *x*, -*y*-3/2, -*z*+3/2; #3: *x*, -*y*+1/2, -*z*+1/2.

2 #1: *x*+1, *y*, *z*-1; #2: *x*-1, *y*, *z*; #3: *x*+1, *y*, *z*; #4: *x*-1, *y*, *z*+1.

3 #1: -*x*+2, -*y*+3, -*z*; #2: -*x*+3, -*y*+3, -*z*; #3: *x*+1, *y*+1, z; #4: *x*-1, *y*-1, *z*.

4 #1: -*x*+1/2, *y*-1/2, -*z*+1/2; #2 -*x*+1/2, *y*+1/2, -*z*+1/2.

Table S2. Surface area, pore size and pore volume parameters of complex **4**.

Samples	Surface area[a] (m^2g^{-1})	Pore size[b] (nm)	V_t[c] (m^3g^{-1})
Complex 4	38.76	2.68	0.02358

a Measured using N2 adsorption with the Brunauer–Emmett–Teller (BET) method.

b Pore size in diameter calculated by the desorption data using Barrett–Joyner–Halenda (BJH) method.

c Total pore volume determined at P/P0= 0.99.

Table S3.The quantum yield and fluorescence lifetime for complexes 1-4 with and without TEC

samples	τ_1(ns)	%	τ_2(ns)	%	Fluorescence lifetime(ns)
Complex 1	0.08	99.39	20.00	0.61	0.201512
+TEC	0.07	96.15	19.78	0.60	0.185985
Complex 2	0.09	99.82	10.55	0.18	0.108828
+TEC	0.09	98.37	10.49	0.17	0.103633
Complex 3	0.08	99.60	11.00	0.40	0.12368
+TEC	0.07	98.76	10.56	0.39	0.110316
Complex 4	0.06	99.39	11.00	0.61	0.126734
+TEC	0.06	98.75	10.72	0.60	0.12357