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Metal-regulated d^{10} coordination polymers constructed from bis(pyridyl)-bis(amide) ligands with different spacers as high-efficiency fluorescence sensors for identifying chlortetracycline and furaltadone

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Section 1 Experimental section

I. Materials and general methods

The reagents were obtained from commercial resources and used directly without further purification. The powder X−ray diffraction (PXRD) data were carried out by using a Rigaku Ultima IV diffractometer at room temperature. FT−IR spectra were collected on a Varian 640 FT−IR spectrometer with KBr pellets. The fluorescent spectra were recorded on a Hitachi F-4500 luminescence spectrometer. Fluorescence lifetime data was obtained on the FLS1000 transient steady-state fluorescence spectrometer. UV-vis absorption spectra were carried out on SP-1901. For the synthesis of CPs **1-3**, the autoclave was cooled to room temperature with cooling rate of 1 °C every 6 minutes and washed with ethanol, and the suitable crystals were manually picked from the precipitation.

II. X-ray crystallography.

Data collection was performed on a Bruker Smart APEX II diffractometer with Kα (λ = 0.71073 Å) by θ and ω scan mode at room temperature. The crystal structures of CPs **1**-**3** were solved by the direct method using the SHELXT program of the Olex 2 crystallographic software package and refined on F^2 by full-matrix least-squares methods.[1] Anisotropic thermal parameters were utilized in all non-hydrogen atoms. CCDC are No. 2240924, 2240925 and 2240926. Selected bond lengths and angles were shown in Table S1 for CPs **1-3**. Hydrogen bonding interactions were listed in

Table S2.

III. Luminescent sensing experiments

During the sensing experiments, CPs **1-3** (3 mg) were ground in the air, dispersed in 4 mL of water, and sonicated for 30 min to form a dispersed solution. Then, the analyte to be tested is added to the suspension to perform the fluorescence titration experiments, and the fluorescence intensity is detected by a fluorescence spectrometer. In the recycling experiment, the original fluorescence intensity of the samples was first tested, and then the analyte solution was added to record the fluorescence intensity. The samples at the end of the experiments were centrifuged, washed with ethanol, centrifuged again and dried, and then water was added to repeat the previous detection method for cyclic detection.

Table S1. Selected bond distances (Å) and angles (°) for CPs **1-3**.

CP **1**			
Cd(1)-O(3)#1	2.221(2)	N(1)-Cd(1)-O(4)#1	83.57(9)
Cd(1)-O(4)#1	2.755(2)	N(1)-Cd(1)-O(6)#2	83.44(10)
Cd(1)-O(1)	2.186(2)	N(1)-Cd(1)-O(5)#2	116.34(14)
Cd(1)-N(1)	2.284(3)	O(6)#2-Cd(1)-O(4)#1	166.98(9)
Cd(1)-O(6)#2	2.451(3)	O(5)#2-Cd(1)-O(4)#1	135.24(9)
Cd(1)-O(5)#2	2.304(3)	O(5)#2-Cd(1)-O(6)#2	53.10(9)
Cd(2)-O(2)W	2.267(3)	O(2)W-Cd(2)-O(2)W#3	180.0
Cd(2)-O(2)W#3	2.267(3)	O(2)W-Cd(2)-O(1)W#3	91.06(11)
Cd(2)-O(1)W#3	2.298(2)	O(2)W-Cd(2)-O(1)W	88.94(11)
Cd(2)-O(1)W	2.298(2)	O(2)W#3-Cd(2)-O(1)W#3	88.94(11)
Cd(2)-O(3)W	2.264(2)	O(2)W#3-Cd(2)-O(1)W	91.06(11)
Cd(2)-O(3)W#3	2.264(2)	O(1)W-Cd(2)-O(1)W#3	180.0
O(3)#1-Cd(1)-O(4)#1	51.17(7)	O(3)W-Cd(2)-O(2)W#3	93.82(10)
O(3)#1-Cd(1)-N(1)	111.61(9)	O(3)W-Cd(2)-O(2)W	86.18(10)
O(3)#1-Cd(1)-O(6)#2	136.03(9)	O(3)W#3-Cd(2)-O(2)W#3	86.18(10)
O(3)#1-Cd(1)-O(5)#2	84.11(9)	O(3)W#3-Cd(2)-O(2)W	93.82(10)

O(1)-Cd(1)-O(3)#1	122.59(9)	O(3)W-Cd(2)-O(1)W#3	80.65(10)
O(1)-Cd(1)-O(4)#1	94.84(9)	O(3)W#3-Cd(2)-O(1)	80.65(10)
O(1)-Cd(1)-N(1)	107.16(10)	O(3)W#3-Cd(2)-O(1)W#3	99.35(10)
O(1)-Cd(1)-O(6)#2	88.17(11)	O(3)W-Cd(2)-O(1)W	99.35(10)
O(1)-Cd(1)-O(5)#2	114.11(14)	O(3)W#3-Cd(2)-O(3)W	180.0

Symmetry Code: #1 –X, –Y, 2–Z; #2 1–X, –Y, 2–Z; #3–X, 1-Y, –Z; #4–X, 2–Y, 1–Z

CP **2**

Zn(1)-O(1)#2	1.984(3)	O(1)#1-Zn(1)-N(1)#2	105.13(9)
Zn(1)-O(2)	1.964(3)	O(2)-Zn(1)-O(1)#1	103.90(13)
Zn(1)-N(1)#2	2.059(3)	O(2)-Zn(1)-N(1)#2	107.74(8)
Zn(1)-N(1)	2.059(3)	O(2)-Zn(1)-N(1)	107.74(8)
O(1)#1-Zn(1)-N(1)	105.13(9)	N(1)#2-Zn(1)-N(1)	125.25(15)

Symmetry Code: #1 +X, +Y, –1+Z; #2 +X, 1/2–Y, +Z; #3 +X, +Y, 1+Z; #4 3–X, 1–Y, –Z

CP **3**

Cd(1)-O(6)#1	2.212(18)	O(4)#2-Cd(1)-O(5)#1	167.28(7)
Cd(1)-O(5)#1	2.711(2)	N(1)-Cd(1)-O(5)#1	84.25(8)
Cd(1)-O(1)	2.183(2)	N(1)-Cd(1)-O(4)#2	83.07(8)
Cd(1)-O(4)#2	2.456(2)	N(1)-Cd(1)-O(3)#2	116.66(11)
Cd(1)-N(1)	2.274(2)	O(3)#2-Cd(1)-O(5)#1	135.11(7)
Cd(1)-O(3)#2	2.300(2)	O(3)#2-Cd(1)-O(4)#2	53.24(8)
Cd(2)-O(3)W	2.261(2)	O(3)W-Cd(2)-O(3)W#3	180.0
Cd(2)-O(3)W#3	2.261(2)	O(3)W-Cd(2)-O(1)W	80.49(9)
Cd(2)-O(1)W	2.280(2)	O(3)W-Cd(2)-O(1)W#3	99.51(9)
Cd(2)-O(1)W#3	2.280(2)	O(3)W#3-Cd(2)-O(1)W#3	80.49(9)
Cd(2)-O(2)W#3	2.266(2)	O(3)W#3-Cd(2)-O(1)W	99.51(9)
Cd(2)-O(2)W	2.266(2)	O(3)W-Cd(2)-O(2)W	93.84(8)
O(6)#1-Cd(1)-O(5)#1	51.63(6)	O(3)W#3-Cd(2)-O(2)W	86.16(8)
O(6)#1-Cd(1)-O(4)#2	135.70(8)	O(3)W#3-Cd(2)-O(2)W#3	93.83(8)
O(6)#1-Cd(1)-N(1)	113.04(8)	O(3)W-Cd(2)-O(2)W#3	86.17(8)
O(6)#1-Cd(1)-O(3)#2	83.53(8)	O(1)W-Cd(2)-O(1)W#3	180.00(11)

O(1)-Cd(1)-O(6)#1	122.42(8)	O(2)W#3-Cd(2)-O(1)W	91.21(9)
O(1)-Cd(1)-O(5)#1	95.76(8)	O(2)W-Cd(2)-O(1)W	88.79(9)
O(1)-Cd(1)-O(4)#2	87.20(9)	O(2)W#3-Cd(2)-O(1)W#3	88.79(9)
O(1)-Cd(1)-N(1)	107.46(8)	O(2)W-Cd(2)-O(1)W#3	91.21(9)
O(1)-Cd(1)-O(3)#2	112.60(11)	O(2)W#3-Cd(2)-O(2)W	180.0

Symmetry Code: #1 2–X, –Y, 2–Z; #2 1–X, –Y, 2–Z; #3 2–X, 1–Y, –Z; #4 2–X,2–Y,1–Z

Table S2. Selected hydrogen-bonding distances (Å) and angles (°) for CPs **1-3**.

CP **1**				
D-H···A	D-H	H···A	D···A	D-H···A
O2W-H2WB···O7	0.93	2.27	2.830(5)	118
CP **2**				
D-H···A	D-H	H···A	D···A	D-H···A
N2-H2···O7	0.86	2.06	2.728(7)	134
CP 3				
D-H···A	D-H	H···A	D···A	D-H···A
O2W-H2WB···O7	0.89	1.88	2.702(3)	153

Section 2 Results discussion section

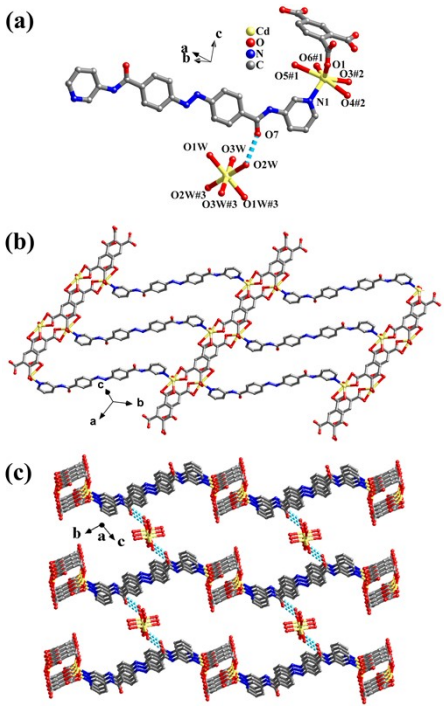


Fig. S1 (a) The coordination environment of the Cd^{2+} ions in CP **3**; (b) View of the 2D layer; (c) The 3D supramolecular framework of CP **3**.

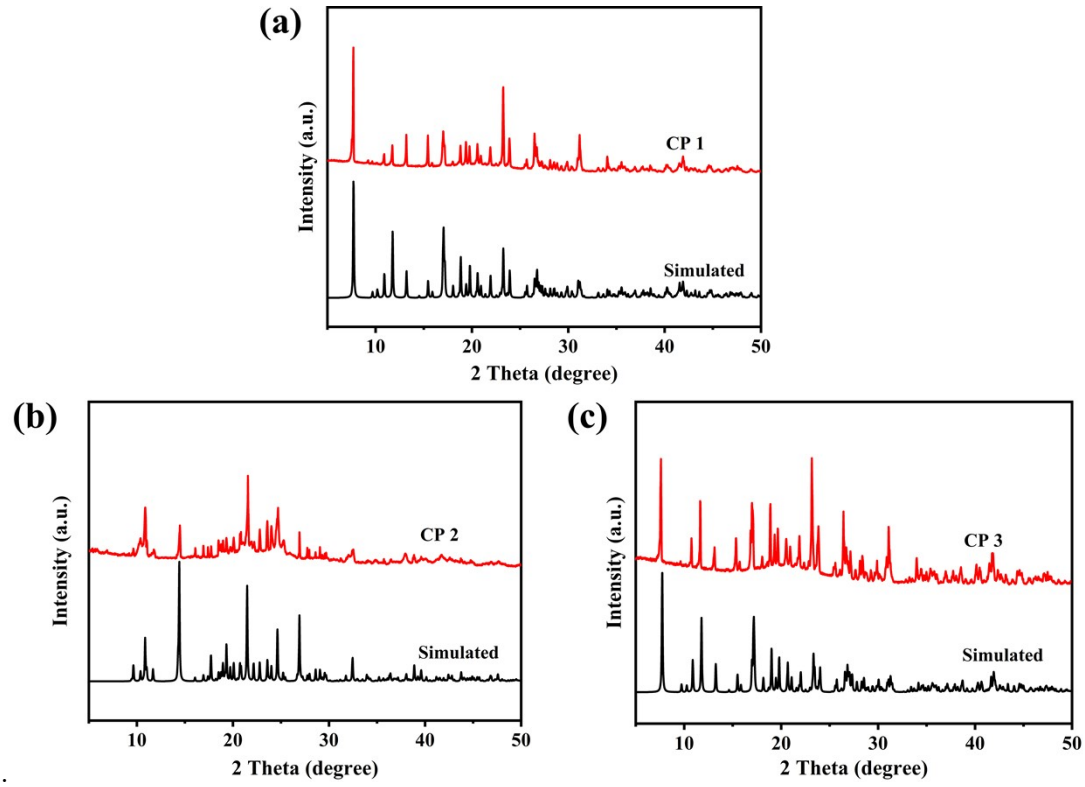


Fig. S2 (a-c) The PXRD patterns of CPs **1-3**.

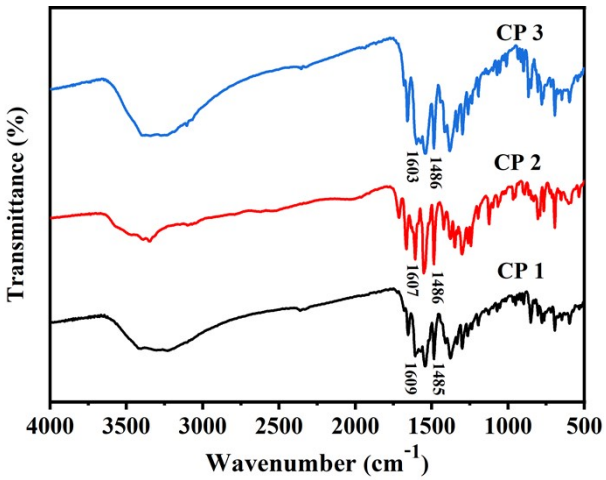


Fig. S3 FT-IR spectra of CPs **1-3**.

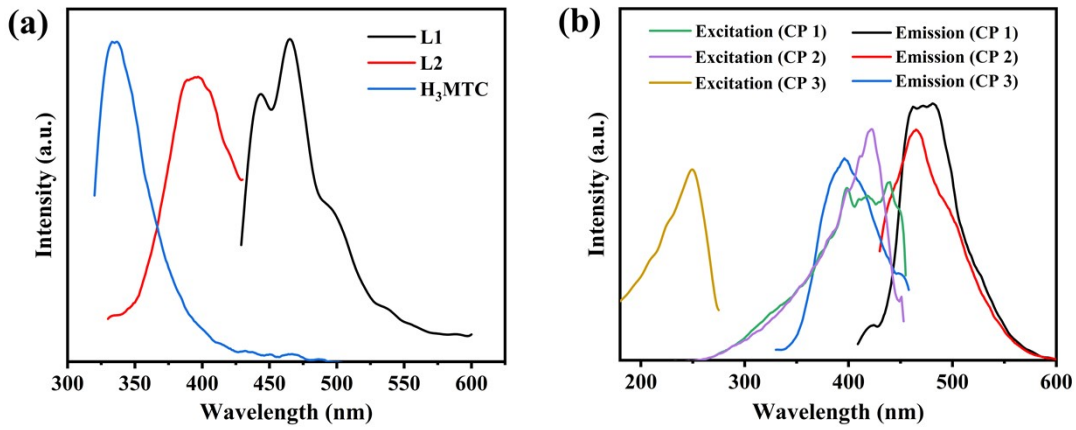


Fig. S4 (a) The emission spectra of solid-state L1 and L2 ligands, and H_3MTC; (b) The solid-state excitation and emission spectra of CPs **1-3**.

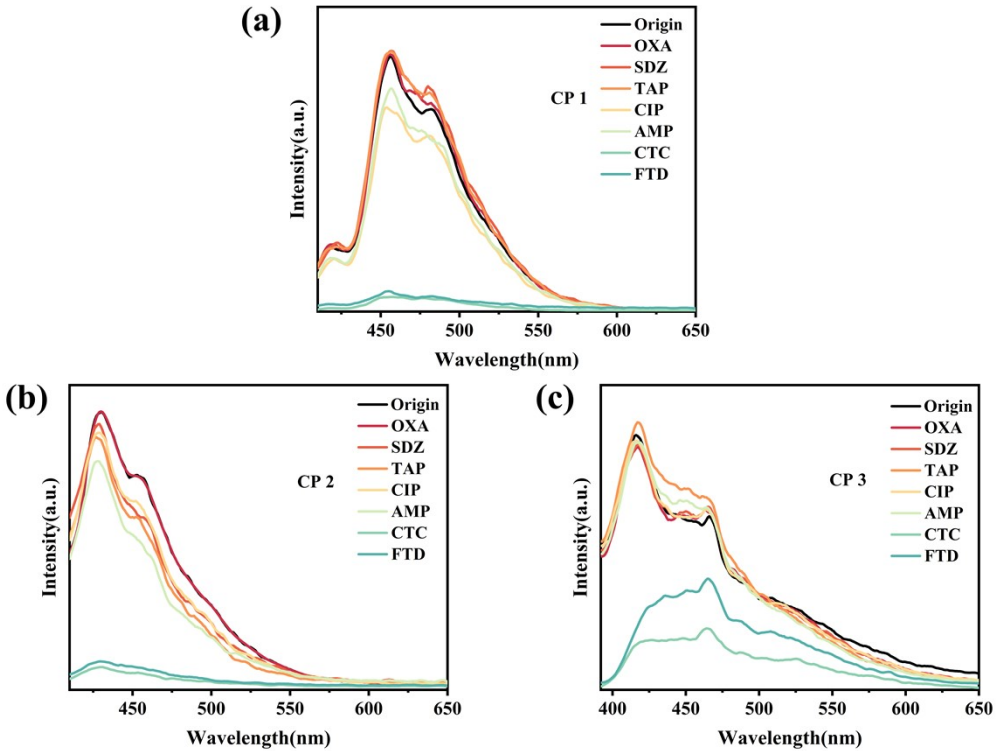
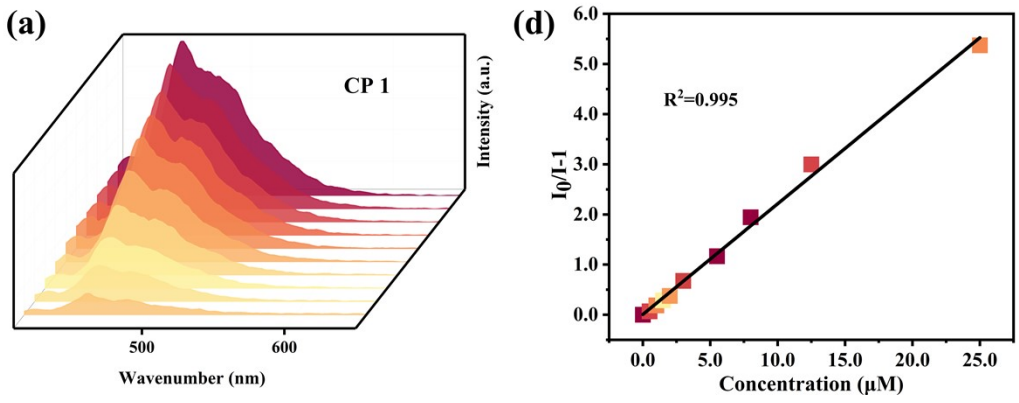


Fig. S5 Sensing selectivity of antibiotics by CPs **1-3**.



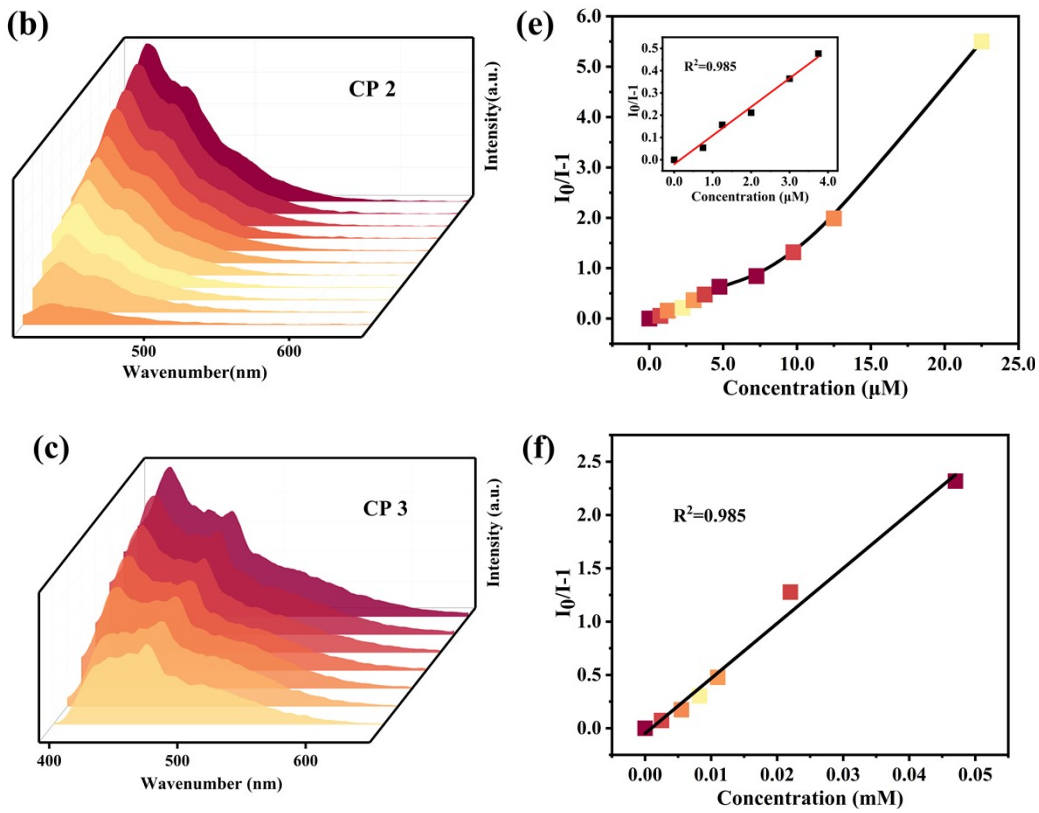


Fig. S6 Emission fluorescence spectra of CP **1** (a); CP **2** (b); CP **3** (c) with the gradual addition of FTD aqueous solution of different volumes, respectively; S−V plots of CP **1** (d); CP **2** (e); CP **3** (f) with the addition of FTD aqueous solution.

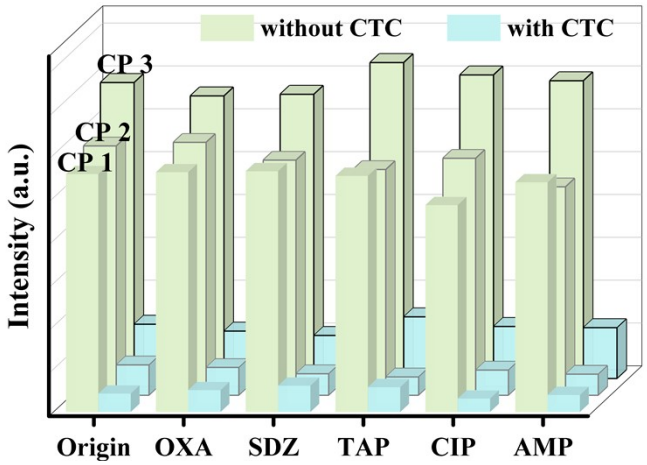


Fig. S7 Fluorescence emission intensity of CPs **1-3** to other antibiotics without CTC and with CTC.

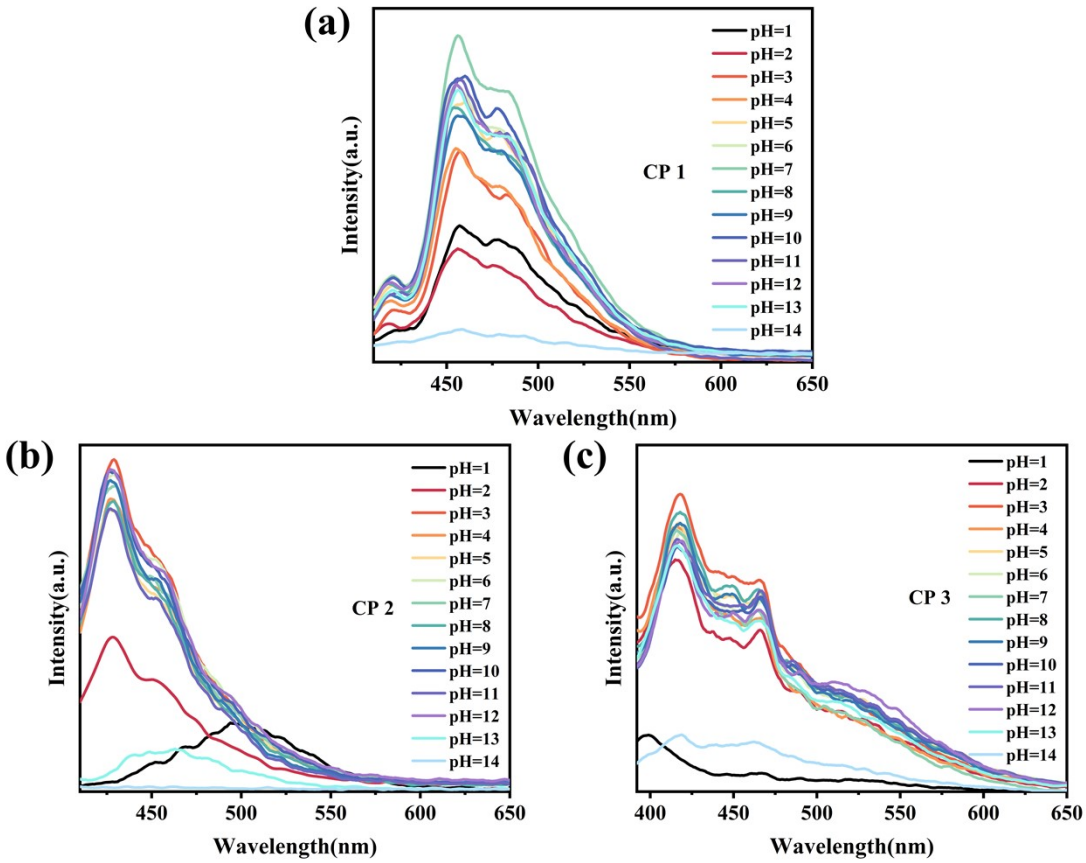


Fig. S8 Emission intensity of CPs **1-3** suspensions in different pH values.

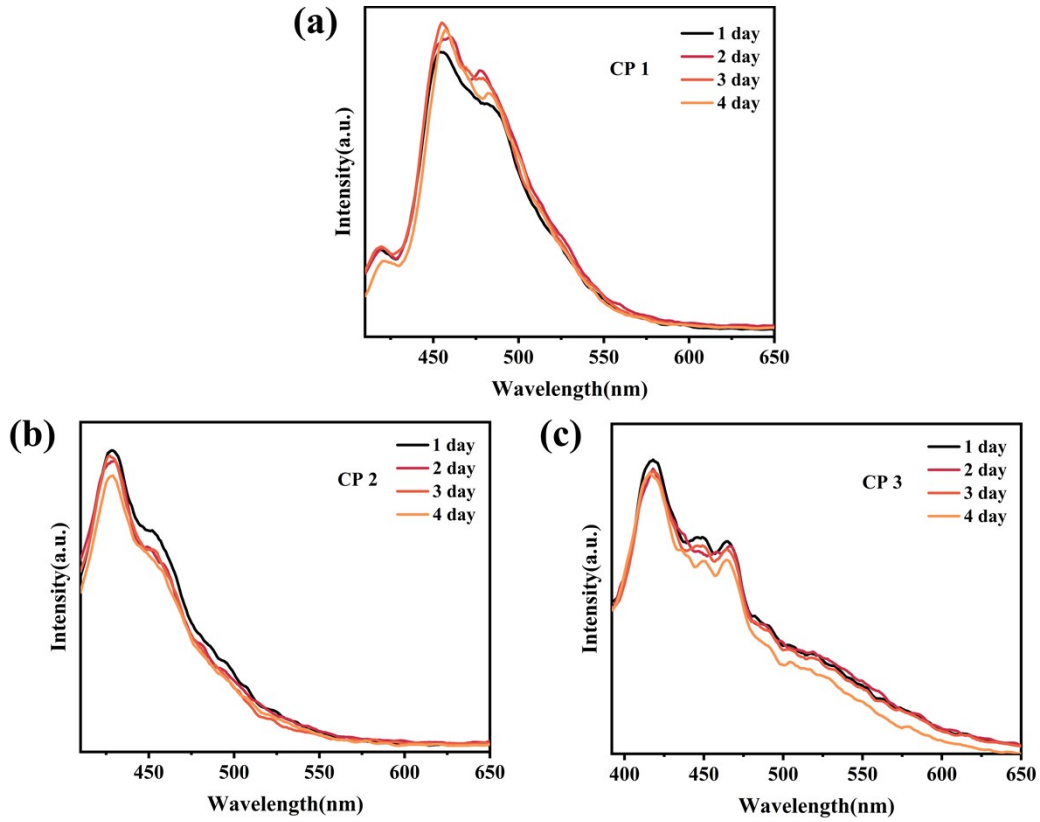


Fig. S9 Fluorescence intensity spectra of CPs **1-3** within four days.

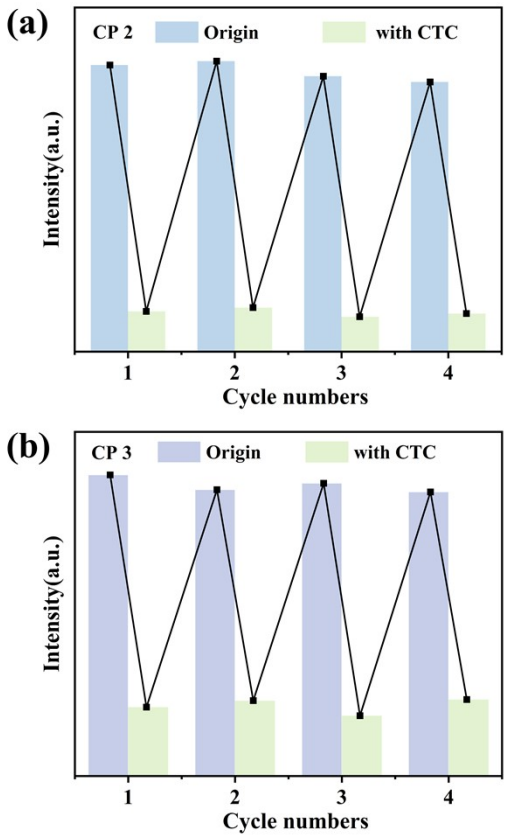


Fig. S10 Reproducibility of the fluorescence intensity of CP **2** (a); CP **3** (b) with four cycles.

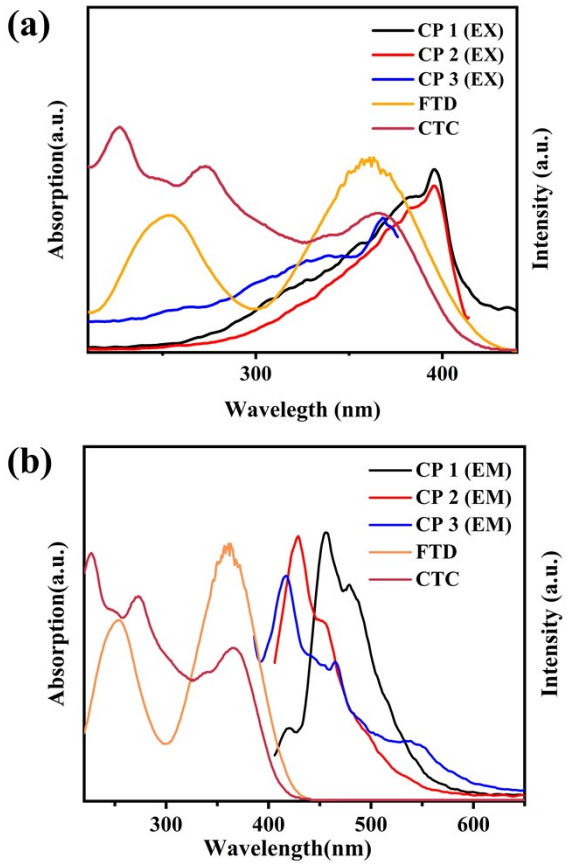


Fig. S11 The UV−vis absorption spectra of FTD and CTC, and excitation (a); emission (b) spectra of CPs **1-3**.

Table S3 Comparison of the LODs for CTC and FTD using different methods.

Methods/Sensors	Analyte	LOD	References
HPLC	CTC	6.93×10^{-6}	Du et al.[2]
CuNCs@His	CTC	8.76×10^{-7}	Wang et al.[3]
OVA-AuNCs	CTC	1.88×10^{-7}	Zhang et al.[4]
ELISA/ICA	CTC	1.20×10^{-7}	Long et al.[5]
CdTe QDs@ZIF-8	CTC	3.70×10^{-8}	Yang et al.[6]
Fluorescence	CTC (AM)	4.48×10^{-7}	Liu et al.[7]
Fluorescence	CTC (AM)	6.23×10^{-8}	Liu et al.[7]
HPLC	FTD	0.18 ng/g	Díaz et al.[8]
Fluorescence	FTD	8.50×10^{-8}	zhang et al.[9]
ELISA	FTD	4 ppb	Jester et al.[10]
CP **1**	CTC	5.12×10^{-8}	Present work
CP **1**	FTD	9.41×10^{-8}	Present work
CP **2**	CTC	1.04×10^{-7}	Present work
CP **2**	FTD	1.81×10^{-7}	Present work
CP **3**	CTC	8.04×10^{-7}	Present work
CP **3**	FTD	3.83×10^{-7}	Present work

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