

Supporting Information

The fluorescence distinction of chiral compounds: a Zn coordination polymer sensor for the detection of cinchonine and cinchonidine

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1. Experimental

1.1 Reagents and Instrumentation

5-(5-Pyrimindinyl)-1,3-benzenedicarboxylic acid (H₂PT) is supplied by Jinan Henghua. All other chemicals were also purchased and used commercially without further purification, and the reagents used in the experiments were of analytical purity. The single crystal data was obtained on the Bruker SMART APEX II CCD X-ray single crystal diffractometer, The infrared spectrum in the 400-4000 cm⁻¹ region was recorded on the VERTEX70 spectrometer. Thermogravimetric analysis (TGA) was performed on a STA449 FJupiter analyzer heated from 30 °C to 1400 °C in a nitrogen atmosphere. Powder X-ray diffraction (PXRD) was used to characterize the crystal structure on Empyrean using Cu K α radiation measured at room temperature in the 2 θ range of 5°-50°. Fluorescence spectra were measured by FLS920 spectrophotometer. Ultraviolet-visible spectroscopy was recorded on the Hitachi U-3900 spectrophotometer. The ¹HNMR spectroscopy data were measured on AVANCE NEO.

1.2 Synthesis of IMU-Zn1

29.8 mg (0.10 mmol) Zn(NO₃)₂·6H₂O and 24.4 mg (0.10 mmol) H₂PT were dissolved in the mixed solvent of 3.0 mL dimethylacetamide (DMA) and 5.0 mL H₂O. A well-mixed suspension was obtained after stirring thoroughly for 30 min, and transferred to a 25 mL polytetrafluoroethylene reactor. The mixture was heated at 120 °C for 4 days and then cooled down to 30 °C at a cooling rate of 5 °C h⁻¹. Finally, pale yellowish flake crystals of **IMU-Zn1** were obtained. The crystals were washed several times with a mixture of DMA and deionized water and dried in 20.4 % yield. Elemental analysis: the composition of **IMU-Zn1**: C₁₂H₁₀N₂O₆Zn, theoretical values (%): C, 41.95; N, 8.15; H, 2.91; experimental values (%): C, 41.66; N, 8.01; H, 2.85. IR data (KBr pellet,

cm⁻¹): 3388(s), 1616(s), 1569(s), 1447(m), 1407(s), 1380(m), 1299(s), 1174(s), 1106(s), 865(s), 765(s), 705(m), 655(m), 458(m).

1.3 Crystallographic data collection and refinement

The total number of runs and images was based on the strategy calculation from the program. The maximum resolution that was achieved was $\theta = 0.79$. The collected diffraction patterns were indexed and corrected by APEX 4. Finally, the structure of the complex was analyzed using the SHELX program in Olex 2, and the anisotropy of all non-hydrogen atoms was refined and refined using the full matrix least square method (XL) in F^2 of SHELX-2018 program. Theoretical hydrogenation and various in-phase refinements were carried out.

1.4 Fluorescence measurements

1.1 mg **IMU-Zn1** powder was dissolved in 2.7 mL ionized water and ultrasonically stirred for 15 min. It was then prepared into a suspension with a concentration of 1.0×10^{-3} M. The solutions of +Ccn and -Ccn with concentrations of 1.0×10^{-2} M were prepared using ethanol. The analytes were slowly added to the suspension and their fluorescence spectra were measured at the room temperature. The emission spectra of the suspension for **IMU-Zn1** were collected in the wavelength range of 350 - 650 nm.

1.5 The test method of liquid nuclear magnetic resonance hydrogen spectrometry

A solution with a concentration of 0.05 mol/L was prepared by mixing 8.8 mg powder sample of +Ccn or -Ccn with 600 μ L of DMSO, respectively. The 7.4 mg powder sample of H₂PT ligand was mixed with 600 μ L of DMSO to prepare a solution with a concentration of 0.05 mol/L. The samples with the above concentration were tested by ¹HNMR. The interaction between the analytes and H₂PT ligand, were determined by ¹HNMR after mixing 600 μ L H₂PT with 150 μ L +Ccn / -Ccn for 2 days.

1.6 Computational method

To further understand the fluorescence sensing mechanism and the nature of **IMU-Zn1**, The DFT calculations based on the B3LYP motif group were performed using Gaussian 09 to investigate the optimal geometry of the probe. The analysis was accomplished using the Multiwfn program and VMD software¹⁻².

1.7 Cycling Experiment

The powder of 20.4 mg **IMU-Zn1** was dispersed into 100 ml ethanol solution of two analytes (concentration 1.0×10^{-2} M) to form a suspension for testing its fluorescence intensity, respectively, then the suspension was centrifuged. The solid sample after the centrifugation was firstly washed with ethanol, and ultrasonically dispersed in 100 ml of ethanol solution to examine its fluorescence intensity once again. The above steps were repeated several times.

2.Supporting Figures

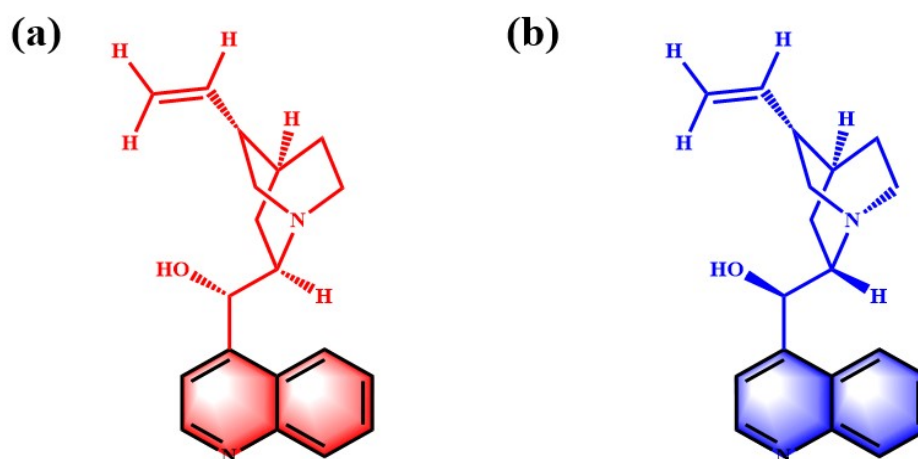


Fig. S1 (a) The structure of +Ccn; (b) The structure of -Ccn.

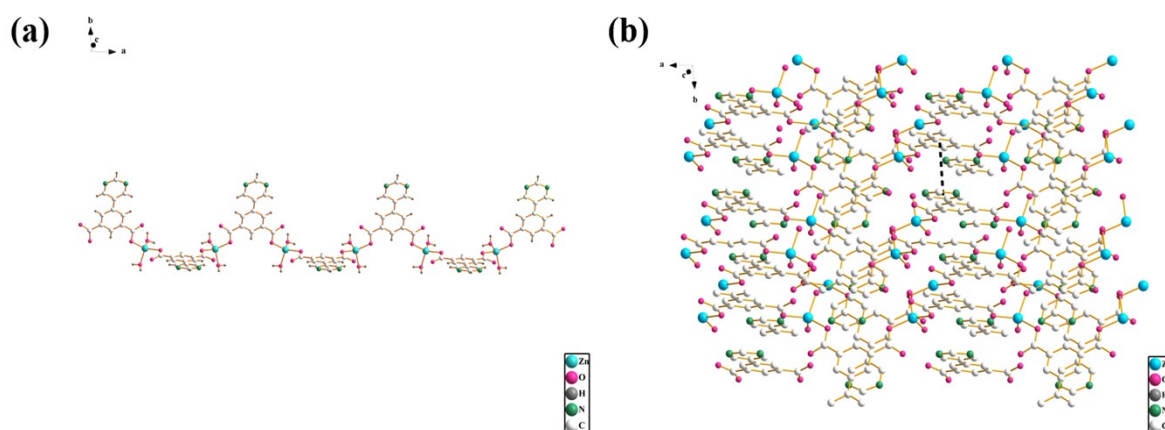


Fig. S2 (a) One-dimensional chain structure of **IMU-Zn1**; (b) The $\pi \cdots \pi$ interaction between layers.

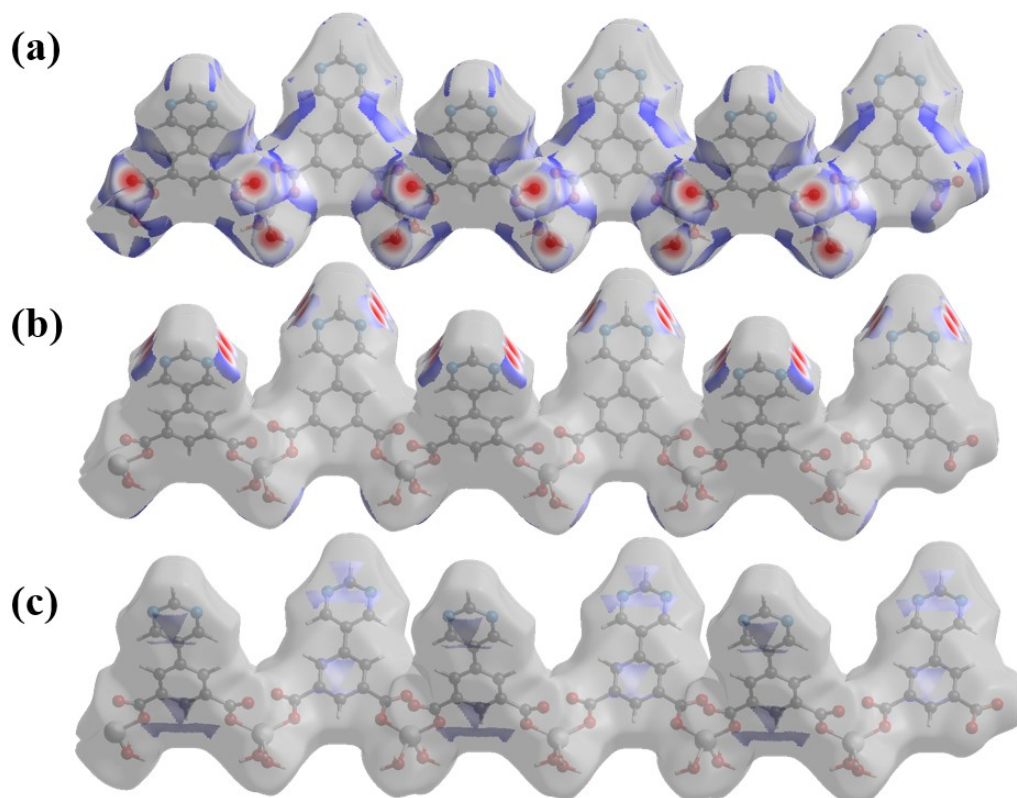


Fig. S3 Surface distribution of d_{norm} plots for probe **IMU-Zn1** (a) $\text{O}\cdots\text{H}/\text{H}\cdots\text{O}$ interactions, (b) $\text{N}\cdots\text{H}/\text{H}\cdots\text{N}$ interactions and $\pi\cdots\pi$ interactions (c).

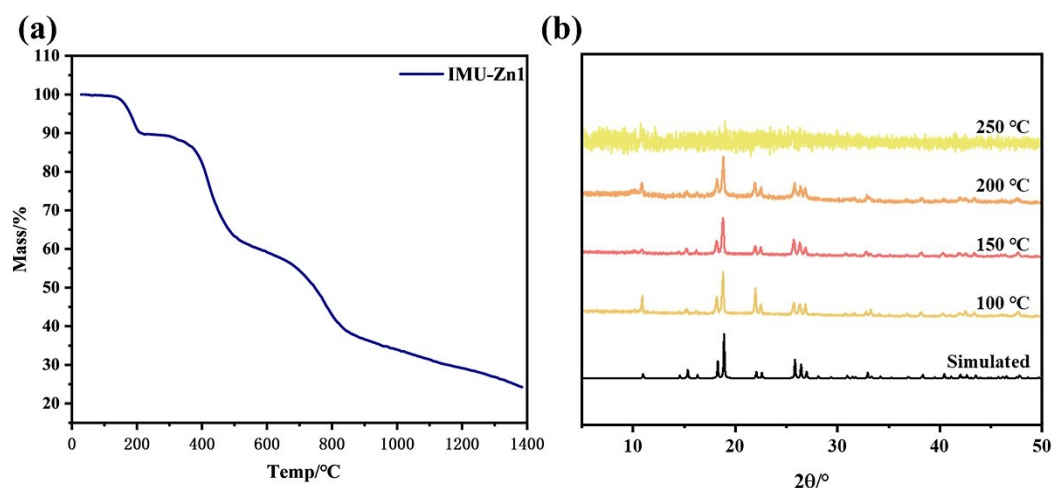


Fig. S4 (a) The TGA curves of **MOF 1**; (b) PXRD patterns of **IMU-Zn1** in different temperature.

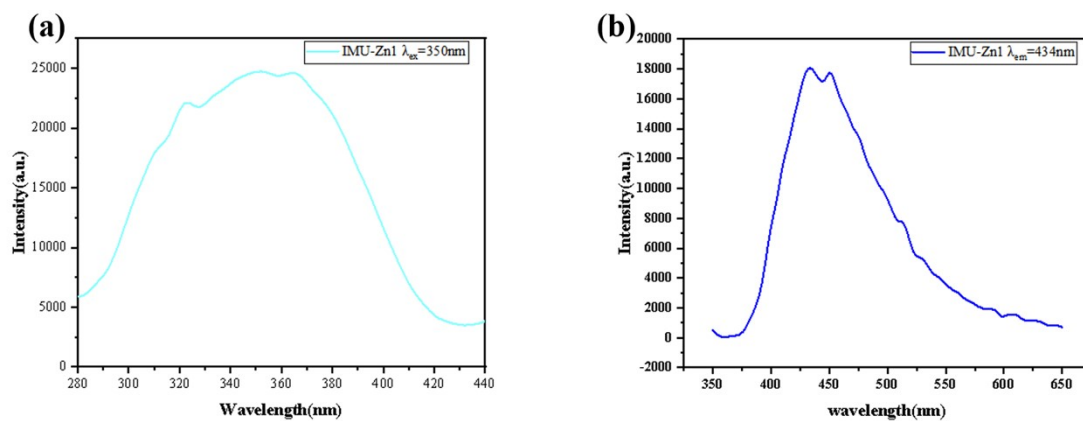


Fig. S5 (a) Excitation spectrum and (b) Fluorescence emission spectrum of IMU-Zn1.

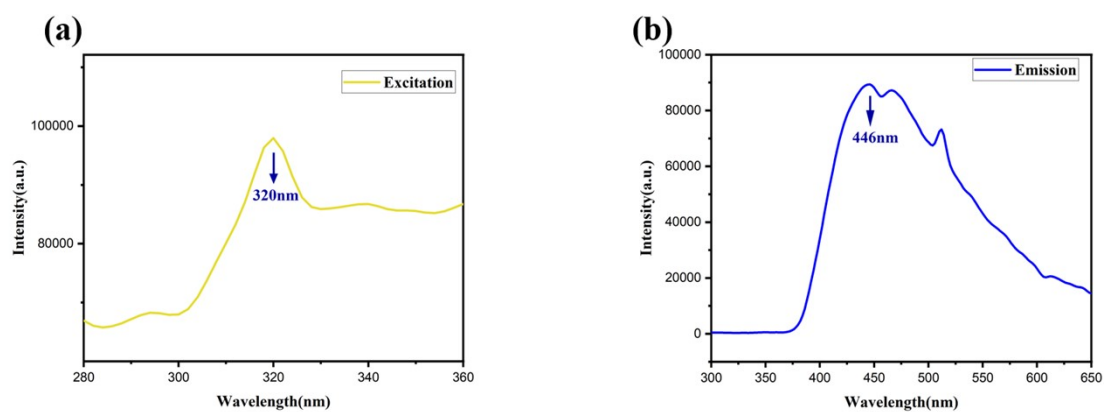


Fig. S6 (a) Excitation spectrum and (b) Emission spectrum of H₂PT ligand.

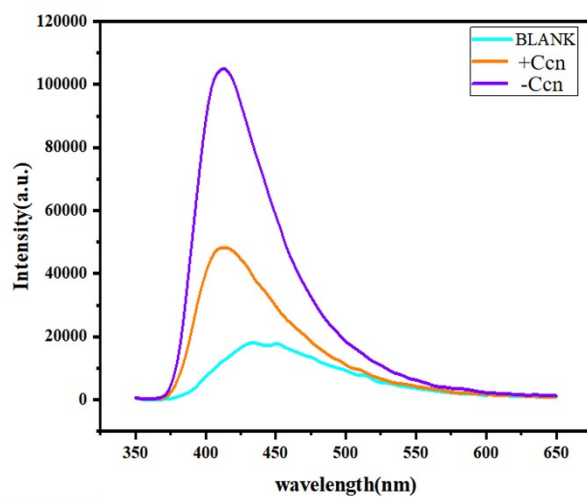


Fig. S7 Fluorescence spectra of IMU-Zn1 in +Ccn and -Ccn.

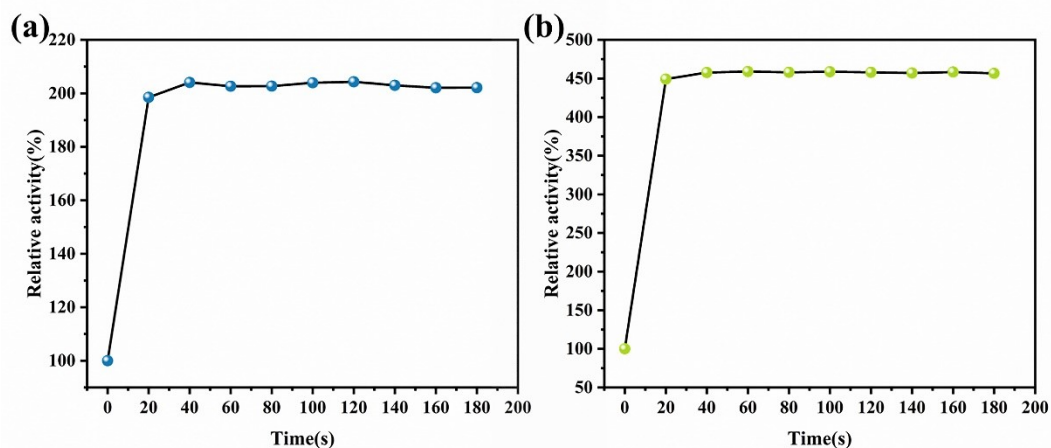


Fig. S8 (a) Time response of IMU-Zn1 to +Ccn; (b) Time response of IMU-Zn1 to -Ccn.

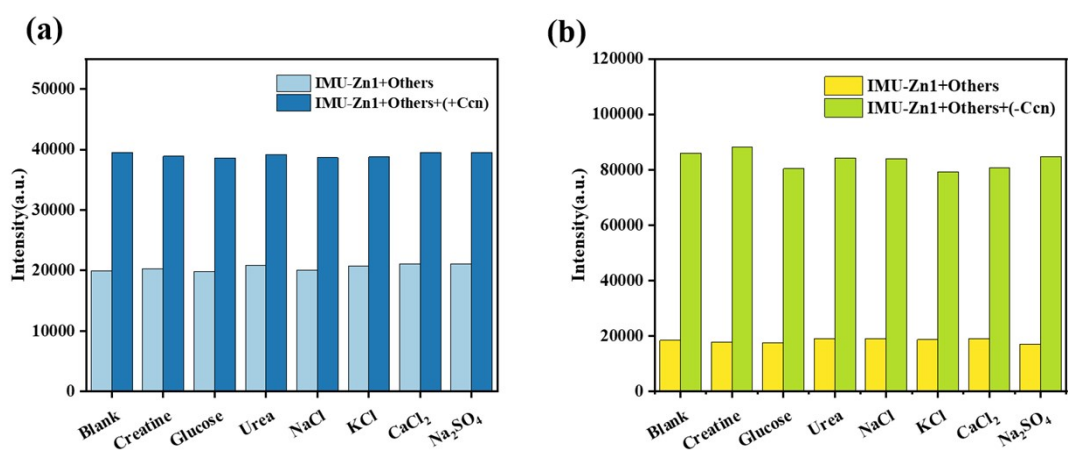


Fig. S9 The anti-interference of IMU-Zn1.

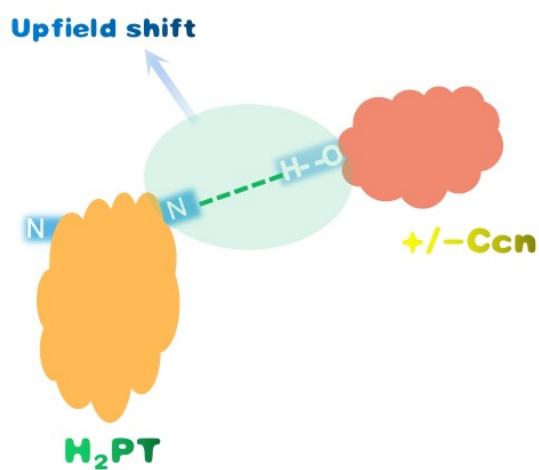


Fig. S10 Diagram of interaction between H₂PT and analytes.

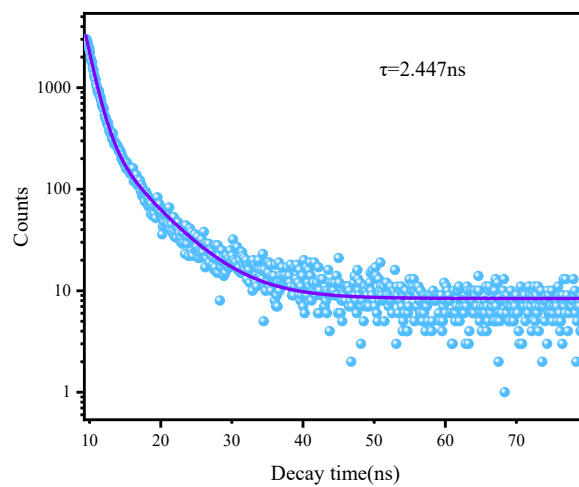


Fig. S11 Attenuation and fitting curves of fluorescence lifetime of **IMU-Zn1**.

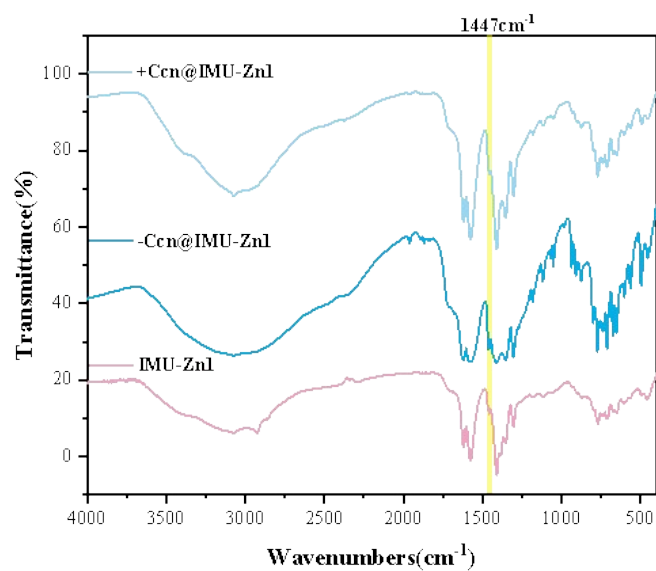


Fig. S12 IR spectra of +Ccn@IMU-Zn1 and -Ccn@IMU-Zn1.

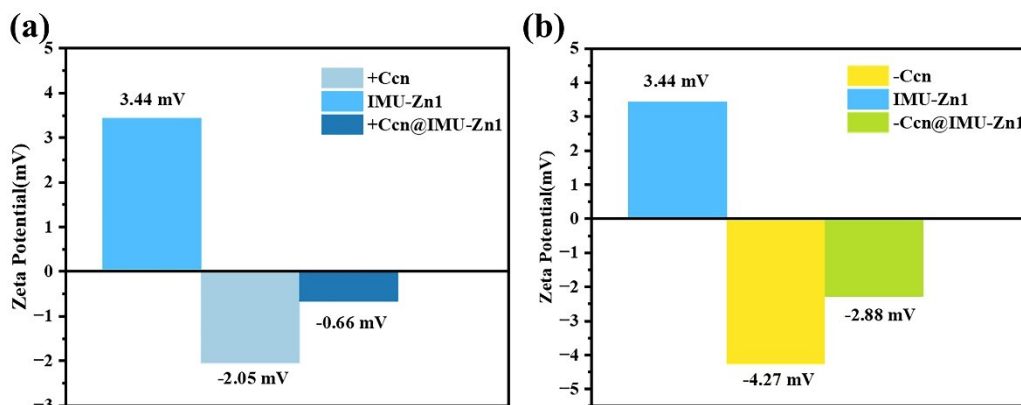


Fig. S13 (a) Zeta potential of +Ccn and **IMU-Zn1**; **(b)** Zeta potential of -Ccn and **IMU-Zn1**.

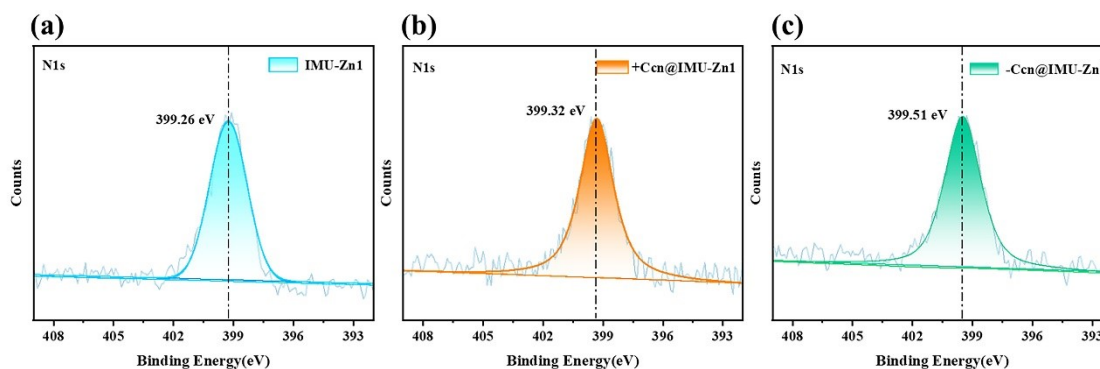


Fig. S14 3d XPS peak of N1s in **IMU-Zn1**, **+Ccn@IMU-Zn1** and **-Ccn@IMU-Zn1**

3. Supporting Tables

Table S1 Crystallographic parameters of the **IMU-Zn1** complex.

Compound	IMU-Zn1
CCDC number	2361371
Empirical formula	$C_{12}H_{10}N_2O_6Zn$
Formula weight	343.6008
Temperature [K]	273.15
Crystal system	orthorhombic
Space group	<i>Ama2</i>
<i>a</i> [Å]	16.115(7)
<i>b</i> [Å]	12.152(6)
<i>c</i> [Å]	6.558(3)
α [°]	90
β [°]	90
γ [°]	90
Volume/Å ³	1284.2(10)
<i>Z</i>	4

ρ_{calc} [gcm ⁻³]	1.777
μ [mm ⁻¹]	1.943
$F(000)$	696.0
Radiation	MoK $_{\alpha}$ ($\lambda=0.71073$ Å)
2 θ range [°]	5.06 to 53.47 (0.79 Å)
Index ranges	-17 \leq h \leq 20, -15 \leq k \leq 6, -7 \leq l \leq 8
Reflections collected	2293
Independent reflections	1189 [$R_{\text{int}} = 0.0403$, $R_{\text{sigma}} = 0.0565$]
Data/restraints/parameters	1189/1/103
Goodness-of-fit on F^2	1.070
Final R indexes [$I \geq 2\sigma(I)$]	$R_1 = 0.0439$, $wR_2 = 0.1158$
Final R indexes [all data]	$R_1 = 0.0539$, $wR_2 = 0.1214$
Largest peak/hole [eÅ ⁻³]	0.63/-0.62
Flack parameter	0.06(3)
^a $R_1 = \sum F_o - F_c / \sum F_o $. ^b $wR_2 = [\sum [\omega(F_o^2 - F_c^2)^2] / \sum \omega(F_o^2)^2]^{1/2}$.	

Table S2. Selected bond lengths [Å] and angles [°] for IMU-Zn1.

IMU-Zn1.			
Zn1–O1	1.977(6)	Zn1–O3	1.917(5)
Zn1–O1 A	1.977(6)	Zn1–O3 A	1.917(5)
O1–Zn1–O1A	94.9(4)	O3–Zn1–O1A	108.0(3)
O1–Zn1–O3	105.7(2)	O3–Zn1–O3A	129.3(4)
O1–Zn1–O3A	108.0(3)	O3A–Zn1–O1A	105.7(2)

Symmetry transformations used to generate equivalent atoms:

#1: 1.5-X, +Y, +Z; #2: 1-X, 1-Y, +Z;

Table S3. Hydrogen bonds for IMU-Zn1 [Å and °].

D-H...A	d(D-H)	d(H...A)	d(D...A)	<(DHA)
O1-H1A...O2A	0.85	1.994	2.718(8)	142.3
O1-H1B...N1A	0.85	1.923	2.748(8)	162.9

Symmetry transformations used to generate equivalent atoms:

#1: +X, -0.5+Y, -0.5+Z; #2: +X, -0.5+Y, -1.5+Z.

Table S4. Comparison of detection methods for cinchonine and cinchonidine.

Materials	$K_{\text{SV}} / K_{\text{EC}}$ (M ⁻¹)	Analytes (LOD) (M)		Ref.
		Cinchonine	Cinchonidine	
Schiff-base Zn ^{II} complex 1		4.38×10^{-7}	–	3
Zn-MOF-C-Tb	$K_{\text{SV}} = 4.66 \times 10^3$ (Cinchonine) $K_{\text{SV}} = 3.45 \times 10^3$	–	–	4

	(Cinchonidine)			
IMU-Zn1	$K_{EC} = 3.08 \times 10^3$ (Cinchonine)	2.10×10^{-6}	1.89×10^{-6}	This Work
	$K_{EC} = 6.83 \times 10^3$ (Cinchonidine)			

4. Reference

1. T. Lu and F. Chen, *J. Comput. Chem.*, 2012, **33**, 580-592.
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3. I. P. Oliveri and S. Di Bella, *Tetrahedron*, 2011, **67**, 9446-9449.
4. Z. Han, K. Wang, Y. Guo, W. Chen, J. Zhang, X. Zhang, G. Siligardi, S. Yang, Z. Zhou, P. Sun, W. Shi and P. Cheng, *Nat. Commun.*, 2019, **10**, 5117.