SUPPORTING INFORMATION

Chinese Journal of Structural Chemistry

Two Bisligand-Coordinated Luminescent Zn(II)-Coordination Polymers for Sensing of Ions and Pesticides in Aqueous Solutions

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n EXPERIMENTAL

Synthesis of CP-1 and CP-2. $ZnSO_4 \cdot 7H_2O$ (2 eq., 0.0270 g, 0.096 mmol), DTP (1 eq., 0.0100 g, 0.048 mmol), a carboxylic group bearing ligand (1 eq., 0.048 mmol) and proper solvents were added and mixed in a Teflon-lined stainless-steel autoclave (25 mL). Afterwards, the autoclave was set at 80 ℃ for 3 days. Then the mixture was cooled to room temperature. The colorless crystalline materials were collected, filtered, and washed for several times with deionized water. The obtained solid was dried in open air for 3 days. Crystals suitable for single-crystal X-ray diffraction analysis were obtained from the synthesis process.

For **CP-1**, PTA (0.0078 g), DMF (5 mL) and water (5 mL) were used (0.0158 g, yield: 61% based on DTP ligand). Anal. Calcd. (%) for $C_{20}H_{22}N_8O_7Zn$: C, 43.53; H, 4.02; N, 20.31. Found (%): C, 43.23; H, 4.00; N, 20.15. IR (neat, cm^{-1}): 3129 (w), 1591 (s), 1560 (s), 1507 (s), 1374 (s), 1271 (s), 950 (s), 889 (s), 833 (s), 788 (s), 743 (s), 693 (s), 669 (s), 634 (s), 565 (s).

For **CP-2**, BTC (0.0058 g), acetonitrile (5 mL) and water (5 mL) were used (0.0192 g, yield: 71% based on DTP ligand). Anal. Calcd. (%) for $C_{42}H_{29}N_{17}O_{14}Zn_2$: C, 44.78; H, 2.59; N, 21.14. Found (%): C, 44.61; H, 2.50; N, 21.02. IR (neat, cm^{-1}): 3340 (bs), 1700 (s), 1621 (s), 1560 (s), 1508 (s), 1420 (s), 1342 (s), 1288 (s), 1226 (s), 1141 (s), 1081 (s), 990 (s), 889 (s), 786 (s), 762 (s), 714 (s), 693 (s), 669 (s), 634 (s), 557 (s), 537 (s).

Table S1. Selected Bond Lengths (Å) and Bond Angles (°) of **CP-1** and **CP-2**

CP-1	
Bond	Dist.
Zn(1)-O(1)	1.98(1)
Zn(1)-O(11)	1.98(1)
Zn(1)-O(1W)^{1}	2.16(1)
Zn(1)-O(1W)	2.16(1)
Zn(1)-N(1)	2.06(1)
Angle	(°)
O(1)-Zn(1)-O(1)^{1}	107.1(5)
O(1)^{1}-Zn(1)-O(1W)^{1}	86.9(4)
O(1)-Zn(1)-O(1W)	86.9(4)
O(1)-Zn(1)-O(1W)^{1}	91.7(4)
O(1)^{1}-Zn(1)-O(1W)	91.7(4)
O(1)-Zn(1)-N(1)	127.7(6)
O(1)^{1}-Zn(1)-N(1)	124.4(7)
O(1W)-Zn(1)-O(1W)^{1}	177.7(6)
N(1)-Zn(1)-O(1W)	98.8(6)
N(1)-Zn(1)-O(1W)^{1}	83.4(6)
C(1)-O(1)-Zn(1)	116.5(7)
Symmetry transformation: ^{1}1-*x*, *y*, 2.5-*z*; ^{2}0.5-*x*, -1.5-*y*, 3-*z*	
CP-2	
Bond	Dist.
Zn(1)-O(5)^{1}	1.999(5)
Zn(1)-O(1)	1.977(5)
Zn(1)-N(1)	2.019(6)
Zn(1)-N(7)^{2}	2.006(6)
O(5)-Zn(1)^{3}	1.999(5)
Angle	(°)
O(5)^{1}-Zn(1)-N(1)	101.4(2)
O(5)^{1}-Zn(1)-N(7)^{2}	119.2(2)
O(1)-Zn(1)-O(5)^{1}	97.3(2)
O(1)-Zn(1)-N(1)	109.7(2)
O(1)-Zn(1)-N(7)^{2}	110.7(2)
N(7)^{2}-Zn(1)-N(1)	116.5(3)
C(9)-O(5)-Zn(1)^{3}	105.7(5)
C(1)-O(1)-Zn(1)	108.8(5)
C(11)-N(1)-Zn(1)	123.4(5)
C(10)-N(1)-Zn(1)	132.8(5)
C(17)-N(7)-Zn(1)^{4}	130.2(5)
C(18)-N(7)-Zn(1)^{4}	125.6(5)
Symmetry transformation: ^{1}-1+*x*, *y*, *z*; ^{2}*x*, *y*,1+*z*; ^{3}1+*x*, *y*, *z*; ^{4}*x*, *y*, -1+*z*	

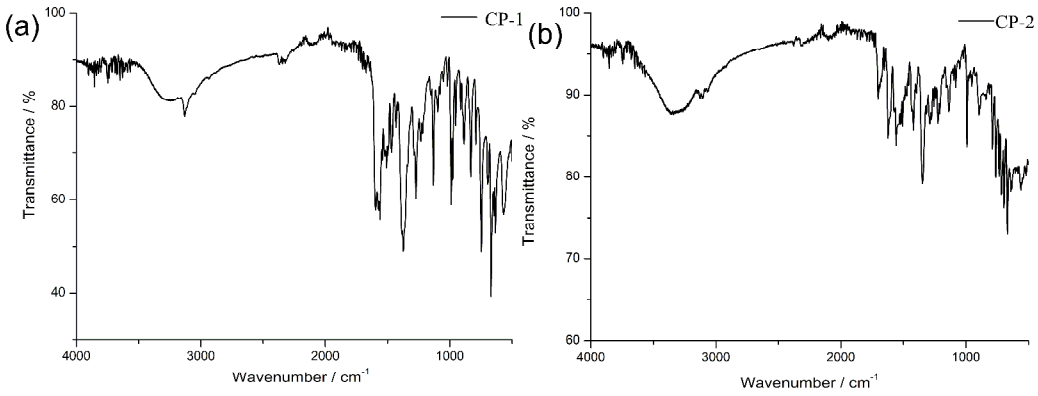


Figure S1. IR spectra of **CP-1** and **CP-2**.

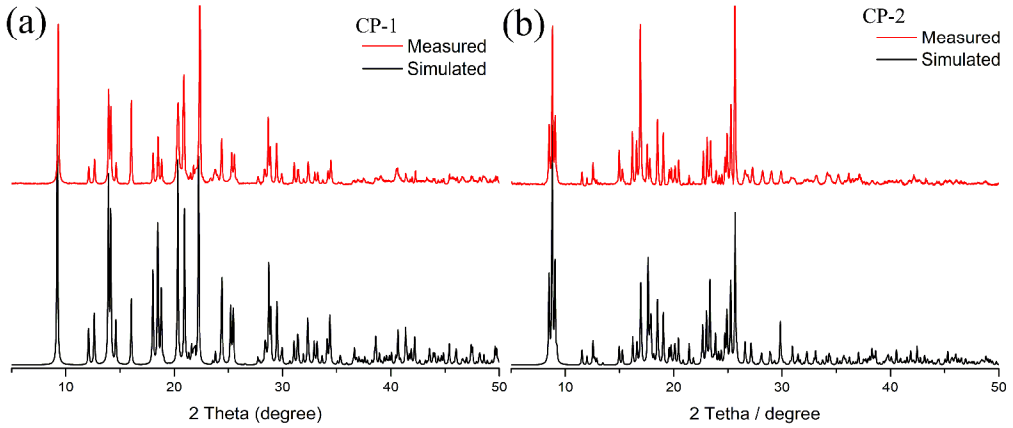


Figure S2. PXRD profiles for **CP-1** and **CP-2**. Simulated spectrum was calculated from the single crystal data.

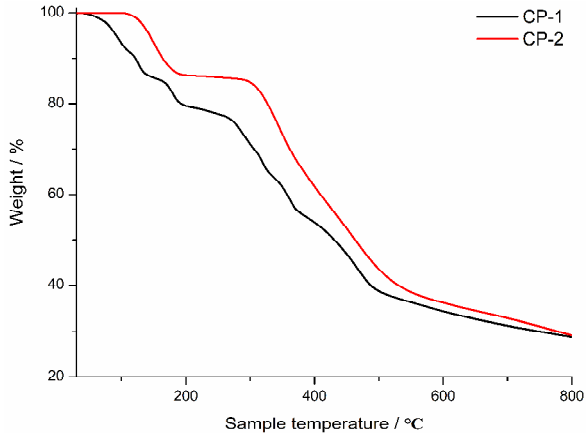


Figure S3. Thermogravimetric curves of **CP-1** and **CP-2** in the temperature range from r.t. to 800 °C under a N_2 atmosphere.

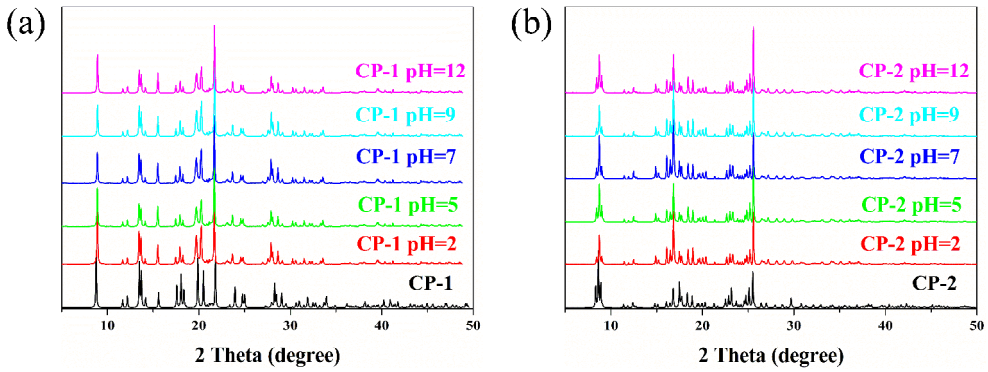


Figure S4. PXRD patterns of **CP-1** (a) and **CP-2** (b) in aqueous suspensions with the pH values ranging from 2 to 12.

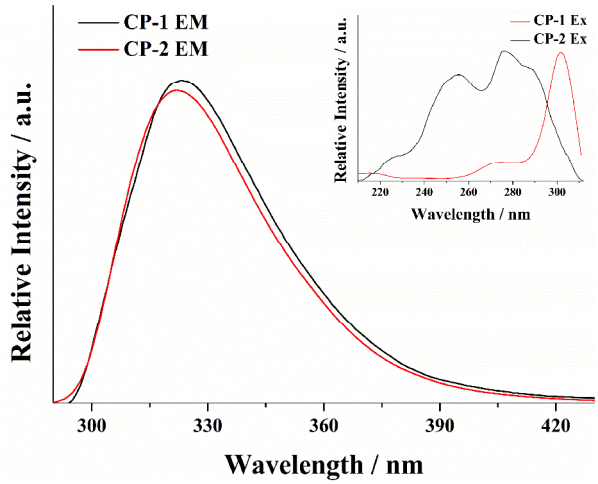


Figure S5. The photoluminescence spectra of **CP-1** and **CP-2** in solid state. Insert: the excitation spectra of **CP-1** and **CP-2**.

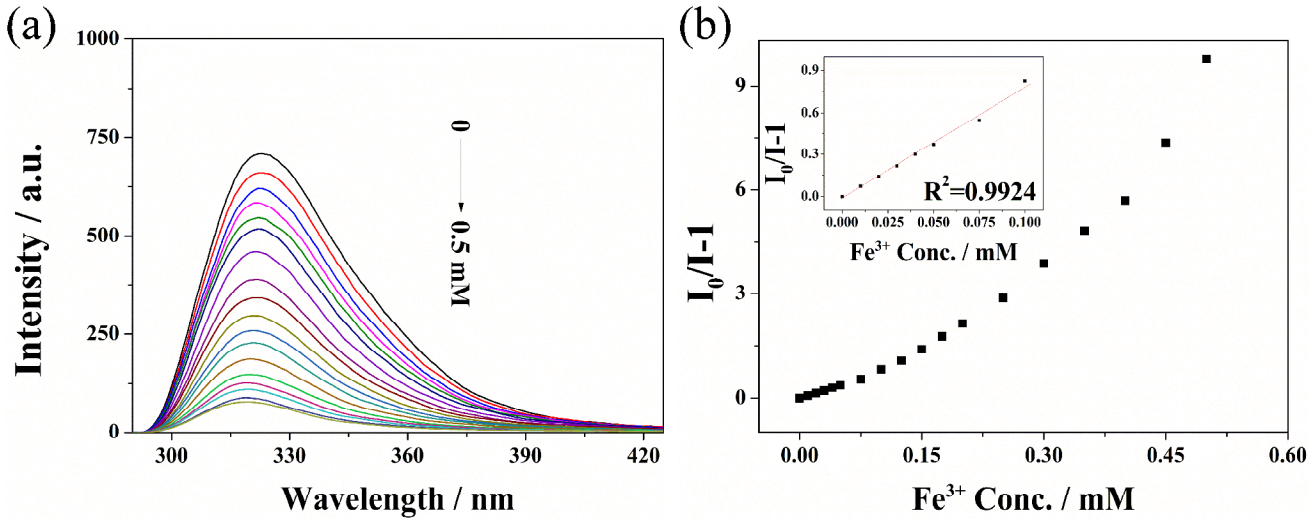


Figure S6. (a) Fluorescence intensities of **CP-1** dispersed in different concentrations of Fe^{3+}; (b) The plot of I_0/I - 1 of **CP-1** *vs*. concentration of Fe^{3+} in aqueous solution (Insert: The plot of I_0/I - 1 of the CP with the concentration over an Fe^{3+} concentration range from 0 to 0.1 mM in aqueous solution).

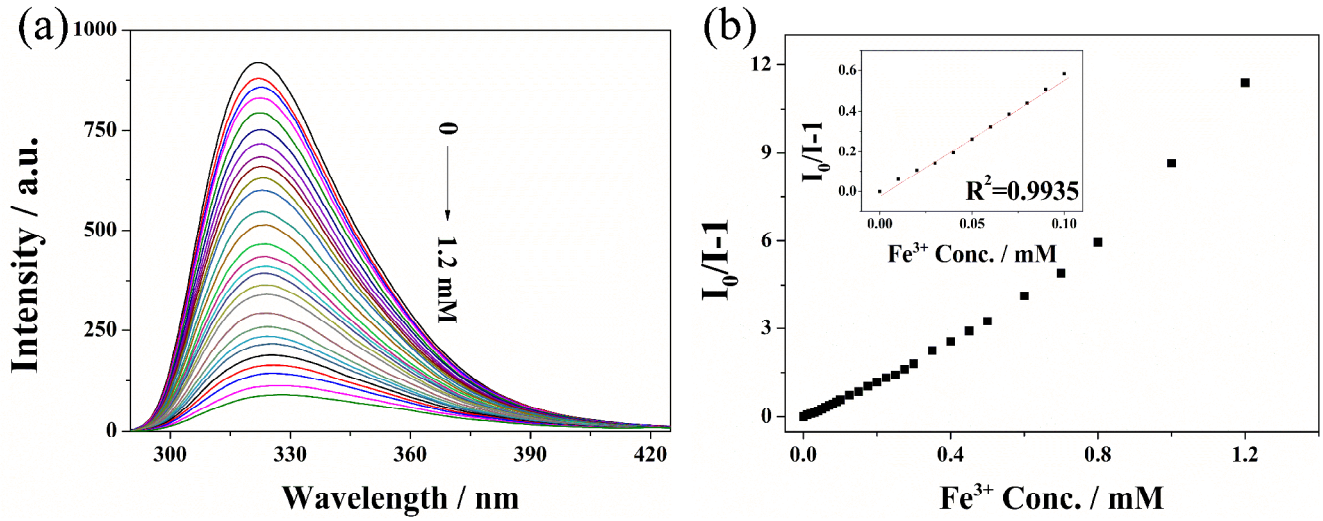


Figure S7. (a) Fluorescence intensities of **CP-2** dispersed in different concentrations of Fe^{3+}; (b)The plot of I_0/I - 1 of **CP-2** *vs*. the concentration of Fe^{3+} in aqueous solution (Insert: The plot of I_0/I - 1 of the CP with the concentration over an Fe^{3+} concentration range of 0-0.1 mM in aqueous solution).

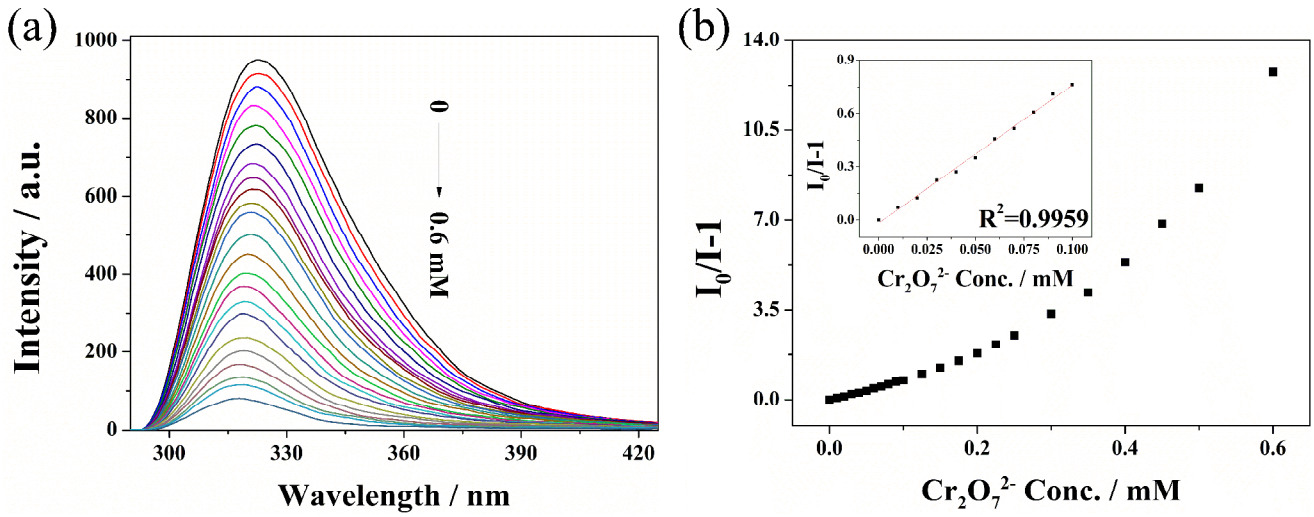


Figure S8. (a) Fluorescence intensities of **CP-1** dispersed in different concentrations of $Cr_2O_7^{2-}$; (b) The plot of I_0/I - 1 of **CP-1** *vs*. the concentration of $Cr_2O_7^{2-}$ in aqueous solution (Insert: The plot of I_0/I - 1 of the CP with the concentration over a $Cr_2O_7^{2-}$ concentration range from 0 to 0.1 mM in aqueous solution).

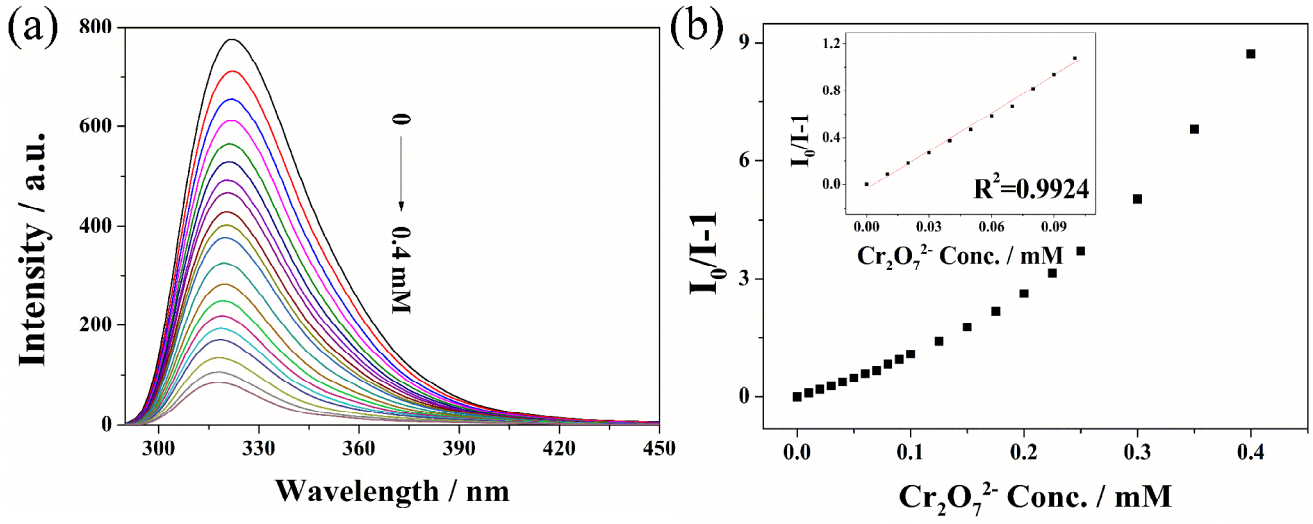


Figure S9. (a) Fluorescence intensities of **CP-2** dispersed in different concentrations of $Cr_2O_7^{2-}$; (b) The plot of I_0/I - 1 of **CP-2** *vs*. the concentration of $Cr_2O_7^{2-}$ in aqueous solution (Insert: The plot of I_0/I - 1 of the CP with the concentration over a $Cr_2O_7^{2-}$ concentration range of 0-0.1 mM in aqueous solution).

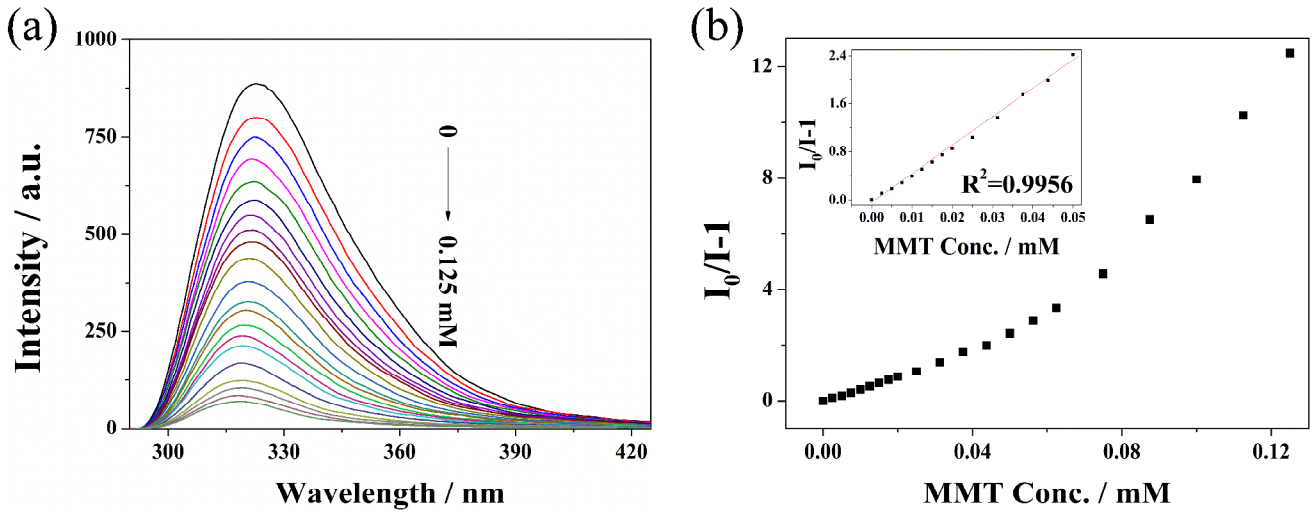


Figure S10. (a) Fluorescence intensities of **CP-1** dispersed in different concentrations of MMT; (b) The plot of I_0/I - 1 of **CP-1** *vs*. the concentration of MMT in aqueous solution (Insert: The plot of I_0/I - 1 of the CP with the concentration over a MMT concentration range from 0 to 0.05 mM in aqueous solution).

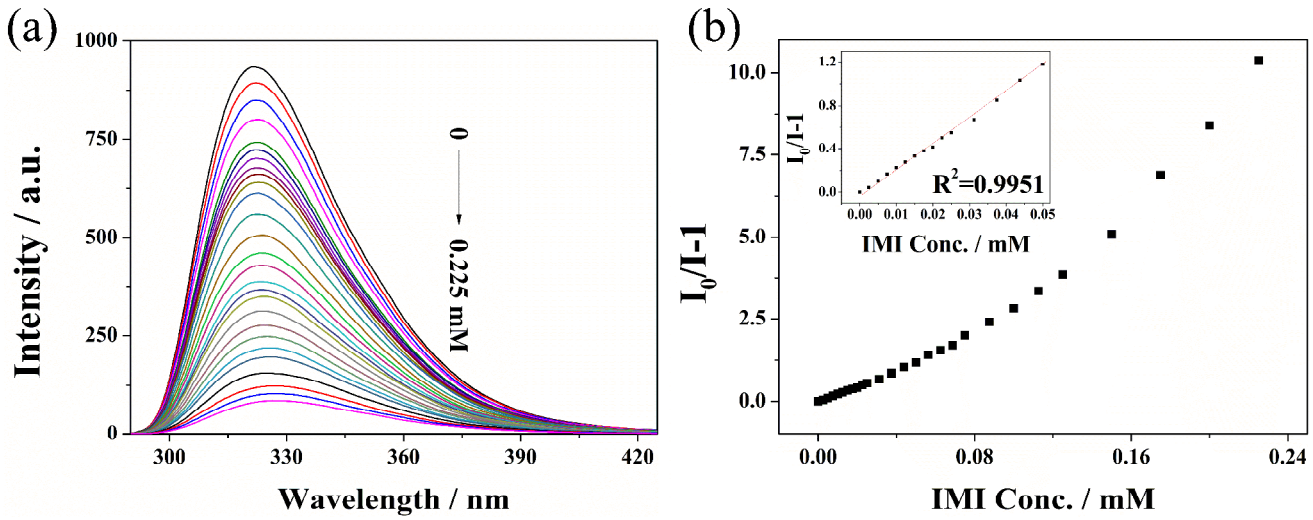
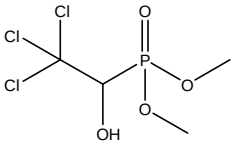
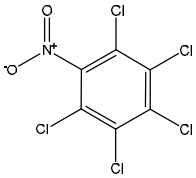
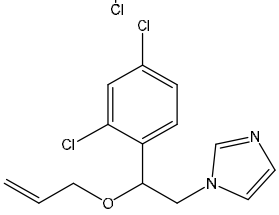
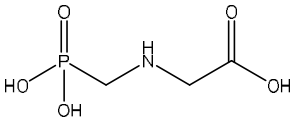
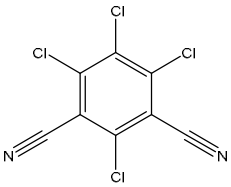
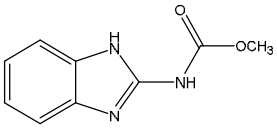
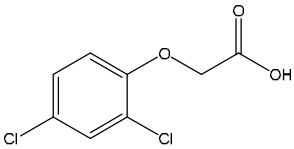
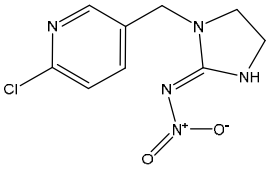
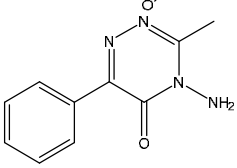
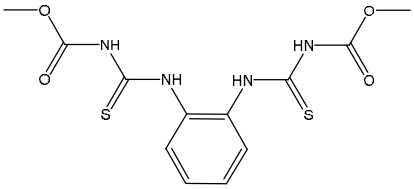


Figure S11. (a) Fluorescence intensities of **CP-2** dispersed in different concentrations of IMI; (b) The plot of I_0/I - 1 of **CP-2** *vs*. the concentration of IMI in aqueous solution (Insert: The plot of I_0/I - 1 of the CP with the concentration over an IMI concentration range from 0 to 0.05 mM in aqueous solution).

Table S2. Comparison of the Ksv and LOD Values of **CP-1** and **CP-2** for Ion Detection with the National Standards

Sensor	Analyte	Concentration/mg·mL^{-1}	Linearrange/μM	LOD/μM	Ksv×10^4/M^{-1}	National standards (China)[1]/μM
CP-1	Fe^{3+}	0.1	0-100	1.10	0.70	1846.15
CP-2	Fe^{3+}	0.1	0-100	0.94	0.81	
CP-1	$Cr_2O_7^{2-}$	0.1	0-100	0.98	0.78	85.03
CP-2	$Cr_2O_7^{2-}$	0.1	0-100	0.48	1.60	

Table S3. Chemical Structure of the Selected Pesticides

Name (abbreviation)	Chemical structure
dipterex (DIP)	
pentachloro-nitrobenzene (PCNB)	
imazalil (IMZ)	
glyphosate (GLY)	
chlorothalonil (TPN)	
carbendazim (CAR)	
2,4-dichlorophenoxyacetic acid (2,4-D)	
imidacloprid (IMI)	
metamitron (MMT)	
thiophanate-methyl (TPM)	

nitenpyram (NTP)

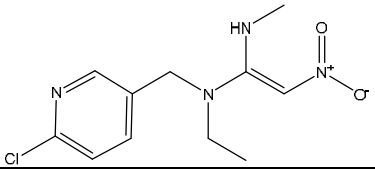


Table S4. Ksv and LOD Values for Recently Reported CP-Based Luminescence Probes for IMI and MMT

Sensor	Analyte	Concentration/mg·mL^{-1}	Linearrange/μM	LOD/μM	Ksv×10^4/M^{-1}	Ref.
CP-1	MMT	0.1	0-50	0.16	4.76	This work
CP-2	IMI	0.1	0-50	0.25	3.05	This work
Tb-MOF	IMI	1.0	0-100	0.26	3.01	[2]
Eu-MOF	IMI	1.0	0-100	0.29	2.63	[2]

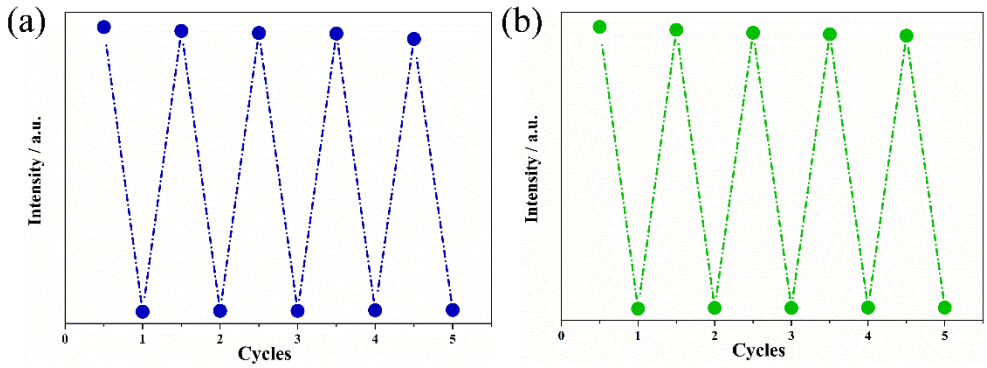


Figure S12. Recyclability of **CP-1** (a) implemented with 1 mM MMT aqueous solution and **CP-2** (b) implemented with 1 mM IMI aqueous solution.

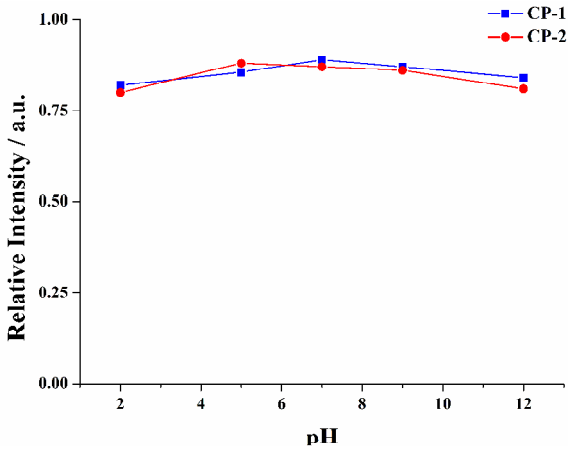


Figure S13. The fluorescence intensity of **CP-1** and **CP-2** under different pH conditions.

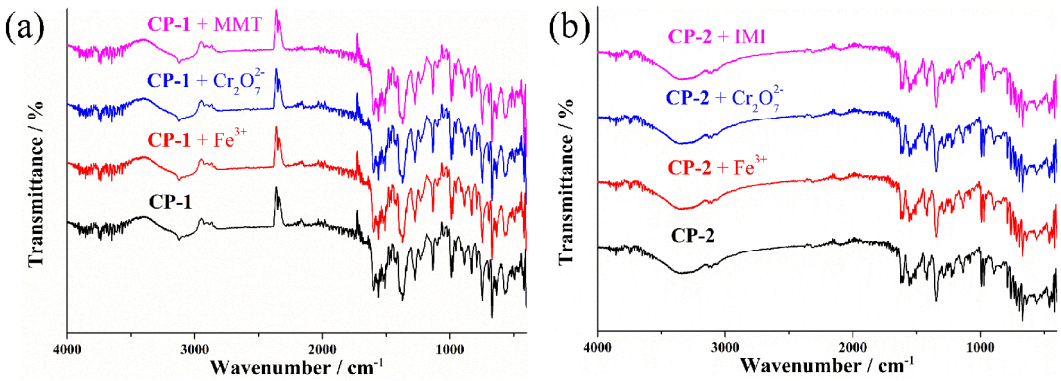


Figure S14. Comparison before and after adding the test substances of FT-IR spectra of **CP-1** (a) and **CP-2** (b).

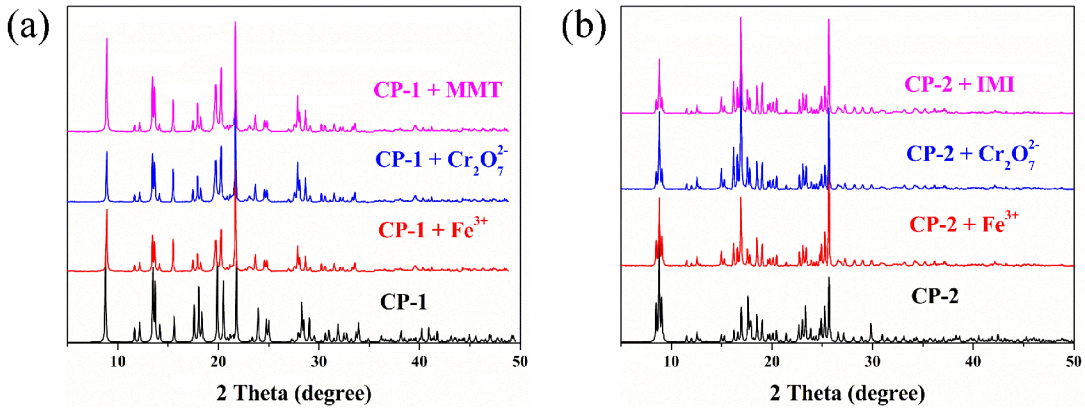


Figure S15. Comparison before and after adding the test substances of PXRD patterns of **CP-1** (a) and **CP-2** (b).

n REFERENCES

(1) General Administration of Quality Supervision, Inspection and Qurantine of the People's Republic of China. The Ministry of environmental protection, emission standards of pollutants for inorganic chemical industry. GB 31573-2015. Beijing. China Environmental Press **2015**.
(2) Zhou, Z. D.; Wang, C. Y.; Zhu, G. S.; Du, B.; Yu, B. Y.; Wang, C. C. Water-stable europium(III) and terbium(III)-metal organic frameworks as fluorescent sensors to detect ions, antibiotics and pesticides in aqueous solutions. *J. Mol. Struct*. **2022**, 1251, 132009.