Supporting Information

A hydrostable Zn^{2+} Coordination Polymer for Multifunction Detection of Inorganic and Organic Contaminants in Water

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Contents

Materials and Physical Measurements

All the reagents and $Zn(NO_3)_2 \cdot 6H_2O$ used were purchased from Aladdin Reagent (Shanghai)Co., Ltd. without further purification.

The relevant data of the elemental analysis described in this article was obtained through the Thermo Flash 2000 elemental analyzer. The infrared spectrum was measured on a Therrno Mattson FTIR spectrometer, and the wavenumber range was 4000~400 cm^{-1}. The powder X-ray diffraction (PXRD) patterns were determined on an X-ray diffractometer (Rigaku D/Max 2200PC) in the 2θ range of 5°~50°. The thermal analysis is performed from 30°C to 800°C at a heating rate of 10°C min^{-1}under N_2 atmosphere on a TGA/NETZSCH STA449C instrument. Mercury program version 3.10 was used to simulate the PXRD mode of Zn^{2+} complexe. F-7000 fluorescence spectrophotometer was used to obtain the luminescence of the solid powder and the suspension, and the wavelength range was 300~700 nm.

Crystallographic Data Collection and Refinement.

Single crystals of **ZnCP** with approximate dimensions of 0.35×0.30×0.10 mm^3 which were suitable for X-ray diffraction were obtained in moderate yield by solvothermal method. Crystal data of **ZnCP** was collected on a Bruker APEX-II CCD diffractometer (MoKα radiation, $\lambda = 0.71073$ Å) at 100 K. Structure was solved by direct methods and refined by a full matrix least-squares technique based on F2 using the SHELXL 2014 program.[1] In addition, the disordered crystalline water and DMF molecules in **ZnCP** are difficult to identify, correspondingly, solvate molecules were accounted for by using the program PLATON/SQUEEZE (Spek, 2009) in order to remove the contributions of disordered solvent.[2] For details about the squeezed material, see cif data in Supporting Information. Therefore, free water and DMF molecules which were determined on the basis of TGA and elemental microanalysis, and the data treated with the SQUEEZE routine within PLATON were added to the molecular formula of **ZnCP** respectively. Drawings of the molecules were performed with the program Diamond.[3] Crystallographic data as well as details of data collection and refinement for **ZnCP** is summarized in Table S1, important bond lengths are listed in Table S3. CCDC 2106760 contain the supplementary crystallographic data of **Zn-CP**, which can be obtained from the authors or the Cambridge Crystallographic Data Centre via www. ccdc.cam.ac.uk/data_request / cif.

Synthesis

The general procedure for preparation of **ZnCP**: A mixture of H_4L (0.01 mmol, 4.1 mg), $Zn(NO_3)_2 \cdot 6H_2O$ (0.01 mmol), 6mL DMF, 2 mL H_2O was heated at 150 °C for 3 days in a 10 mL Teflon-lined stainless steel, and then cooled at a rate of $6°C \cdot h^{-1}$ to room temperature. Colorless rhomboid single crystals were collected by filtration, washed with water for three times. Test samples except that for single crystal analysis were obtained from repeated experiments.[4, 5]

Chemical and Water Stability Experiment

The PXRD experiments and the fluorescence determination were performed to verify the chemical and water stability by soaking **ZnCP** in deionized water for two weeks, in aqueous solutions of different pH values (3~12) for 3 days, heated in water at 50°C and frozen in water at –20°C for 1 day respectively.

Details of DFT calculation

Geometry optimization and the time dependent density functional theory (TD-DFT) calculations of H_4L in a vacuum was carried out using the B3LYP hybrid function at the 6-31G (d, p) level and that for **ZnCP** was done by using the B3LYP hybrid function at the LANL2DZ level for Zn and 6-31G (d, p) level for C, H and O.[6] Visualization was done using GaussView 5.0.[7-9]

Table S1. Crystal data and structure refinement parameters for **ZnCP**.

Compound	**ZnCP**
Empirical formula	$C_{29}H_{30}N_4O_{13}Zn$
Temperature (K)	100(2)
Formula weight	706.11
Diffraction	Mo Kα (0.71073 Å)
Crystal system	Monoclinic
Space group	$P2_1/c$
Unit cell dimensions	a = 11.0213(5)Å; α=90° b =17.0939(8)Å; β=107.13(10)° c = 15.5201(7)Å; γ=90°
V/Å^3, Z	2794.2(2), 4
D_{calcd}/Mg m^{-3}	1.116
μ/mm^{-1}, F(000)	0.915, 944
θ range for date collection	2.271°~24.999°
index ranges, *hkl*	$-13 \leq h \leq 13$; $-20 \leq k \leq 20$; $-17 \leq l \leq 18$
Independent reflections (R_{int})	0.0887
Completeness	99.8%
Reflections unique / collected	4907 / 32630
Data / restraints / params	4907 / 2 / 280
Goodness–of–fit on F^2	1.147
Final R indices [$I > 2\sigma(I)$]	R_1 =0.0541, wR_2 =0.1323
R indices (all data)	R_1 = 0.0628, wR_2 = 0.1353

Table S2. Shape calculation results of Zn^{2+} in **ZnCP**.

Hexagon (HP-6)	0.2740
Pentagonal pyramid (PPY-6)	0.2261
Octahedron (OC-6)	0.0954
Trigonal prism (TPR-6)	0.1101
Johnson pentagonal pyramid J2 (JPPY-6)	0.2499

Table S3. Selected bond lengths (Å) and angles (˚) for **ZnCP**.

Zn1–O2	2.154(3)	Zn1–O3	2.213(3)	Zn1–O6	2.211(3)	Zn1–O7	2.177(3)
Zn1–N1	2.014(3)	Zn1–N2	2.019(3)				

O2–Zn1–O3	153.13(10)	O2–Zn1–O6	96.09(12)	O2–Zn1–O7	92.35(12)
O6–Zn1–O3	90.13(11)	O7–Zn1–O3	94.06(11)	O7–Zn1–O6	152.49(10)
N1–Zn1–O2	77.50(12)	N1–Zn1–O3	75.78(12)	N1–Zn1–O6	97.42(12)
N1–Zn1–O7	109.97(12)	N1–Zn1–N2	171.36(13)	N2–Zn1–O2	108.59(12)
N2–Zn1–O3	98.28(12)	N2–Zn1–O6	76.10(12)	N2–Zn1–O7	76.39(12)

Table S4. The H-bond parameters in **ZnCP**

D–H···A	d(D–H)	d(H···A)	d(D···A)	D–H···A
C10–H10···O3	0.0950(4)	2.4311(2)	3.2583(50)	145.443(287) ˚
C10–H10···O7	0.0950(4)	2.6924(9)	3.4408(52)	136.133(296) ˚
C12–H12···O1	0.9507(45)	2.6693(12)	3.3118(55)	125.383(294) ˚
C13–H13···O2	0.9501(40)	2.7381(8)	3.5482(50)	143.628(287) ˚
C13–H13···O6	0.9501(40)	2.6146(11)	3.3785(51)	137.717(287) ˚

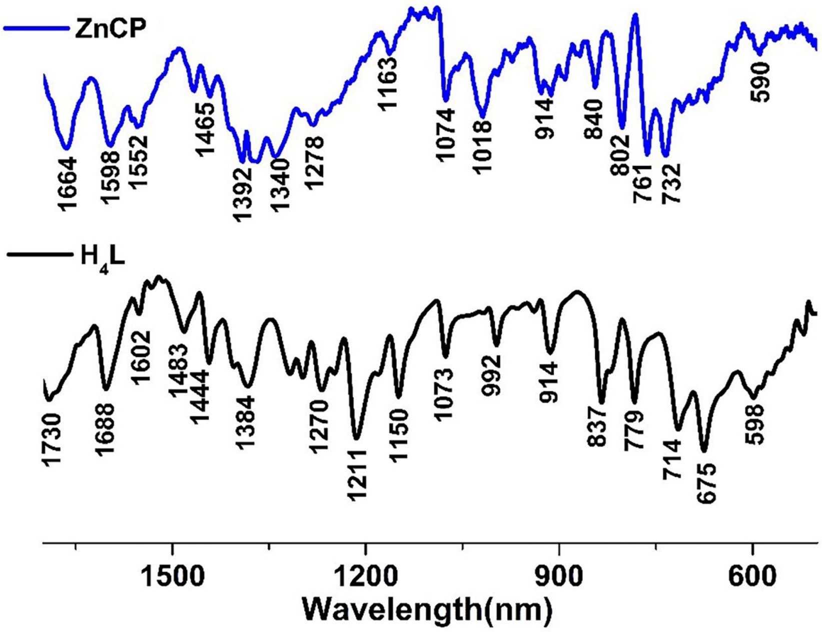

Fig. S1 IR spectra of H_4L, **ZnCP** in solid state with KBr discs.

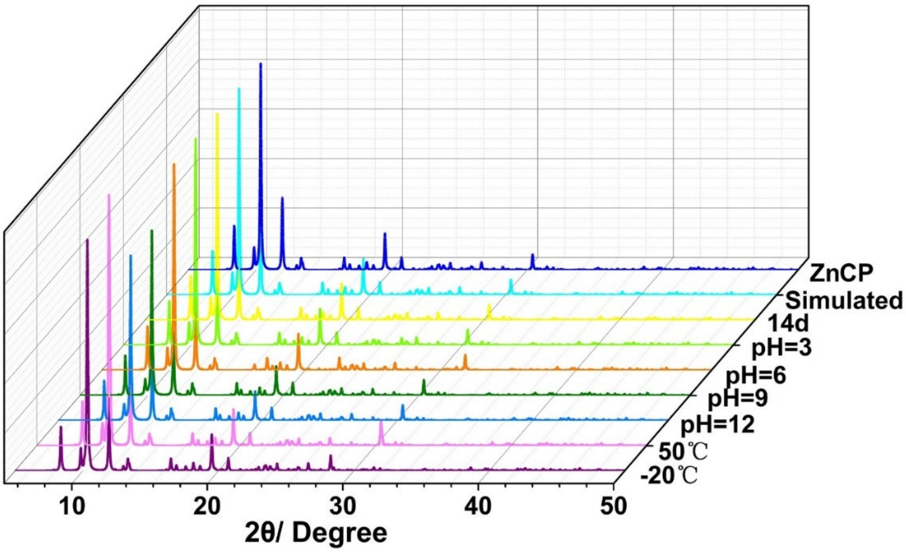

Fig. S2 PXRD patterns of **ZnCP** and that upon treated by aqueous solutions with pH values ranging from 3 to 12, after storage in water for 14 days, after frozen at –20°C and heated at 50°C in for 1 day.

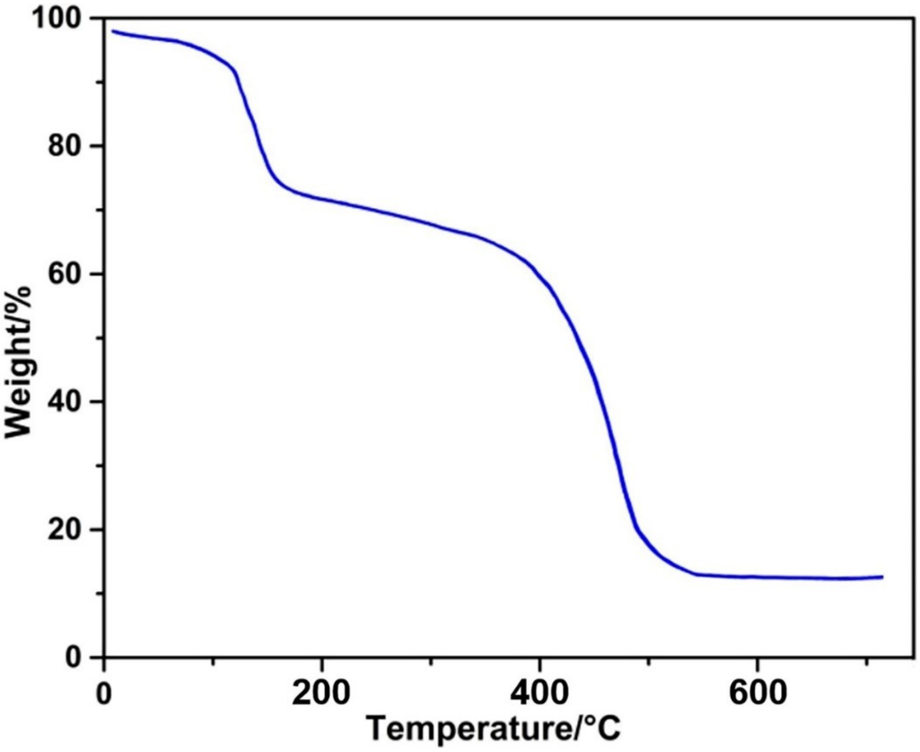

Fig. S3 TGA curves of **ZnCP** under N_2 atmosphere from 30 to 740 °C.

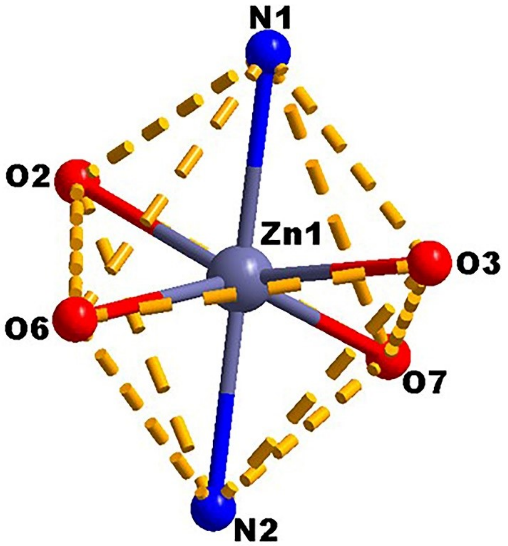

Fig. S4 The Coordination polyhedron of Zn^{2+} ion in **ZnCP**.

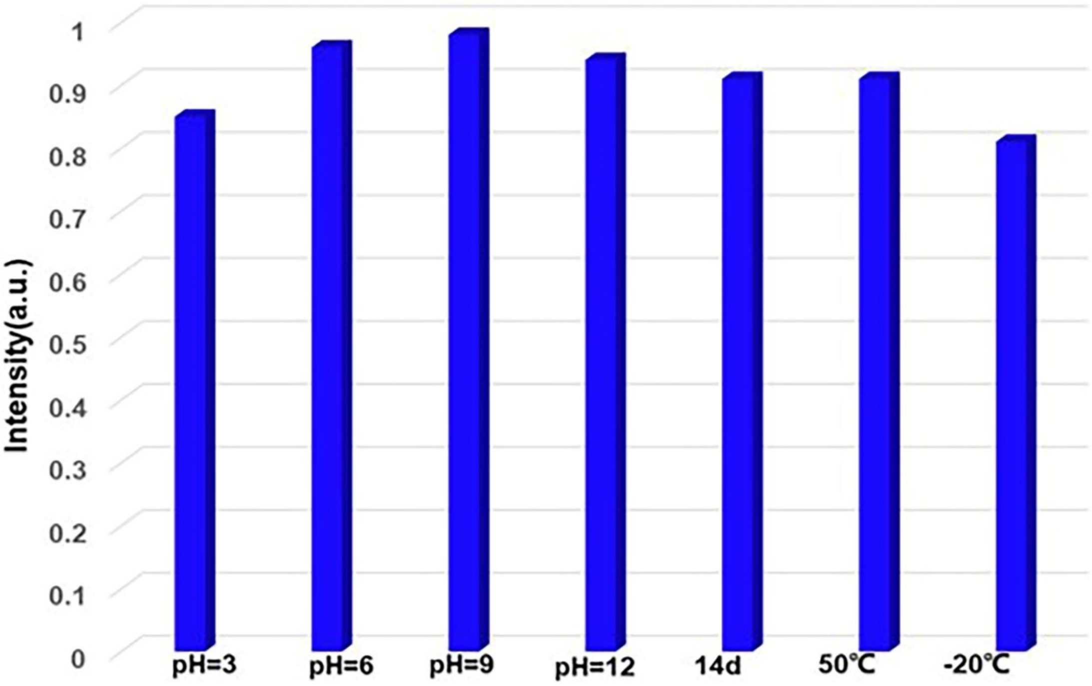

Fig. S5 The relative emission intensity of **ZnCP** at 441 nm upon treated with aqueous solutions with different pH values (3-12) and different temperatures.

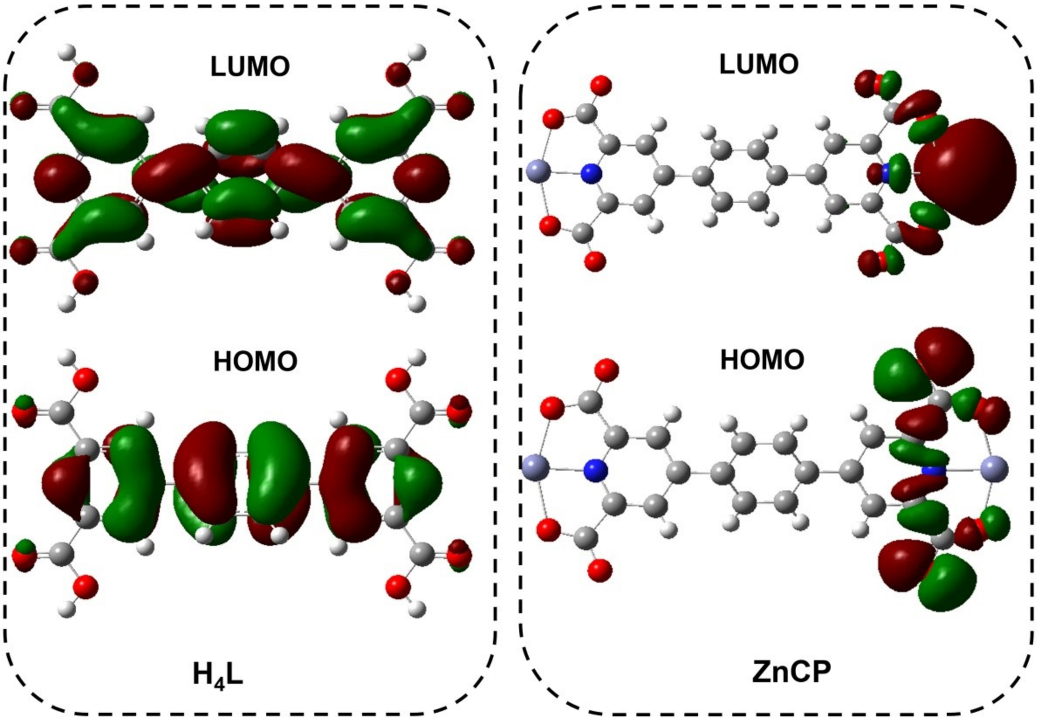

Fig. S6 Contour plots of the frontier orbitals of H_4L and **ZnCP**.

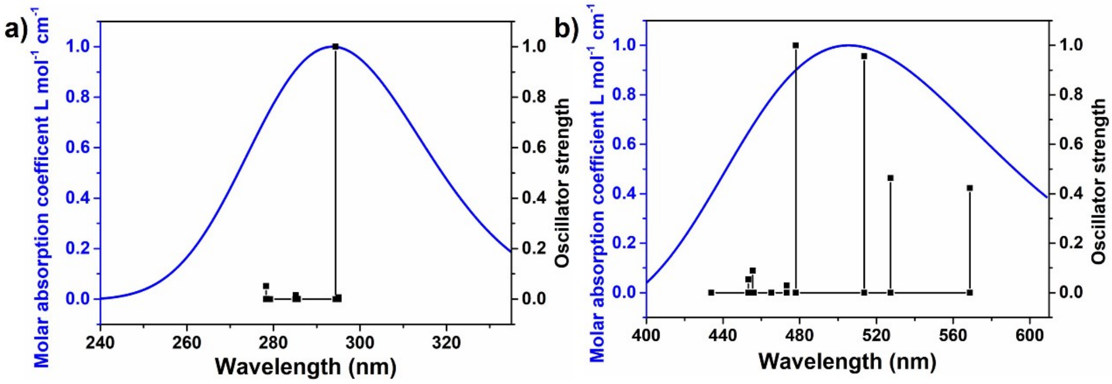

Fig. S7 The simulated fluorescence spectrum H_4L and **ZnCP** based on TD-DFT calculations.

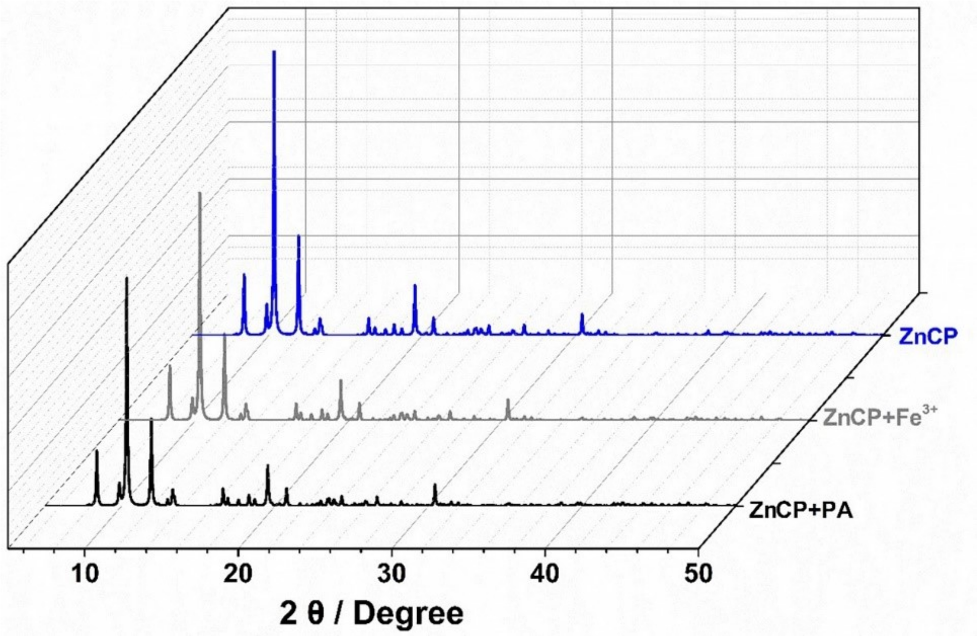

Fig. S8 PXRD patterns of **ZnCP** after immersed in PA aqueous solutions.

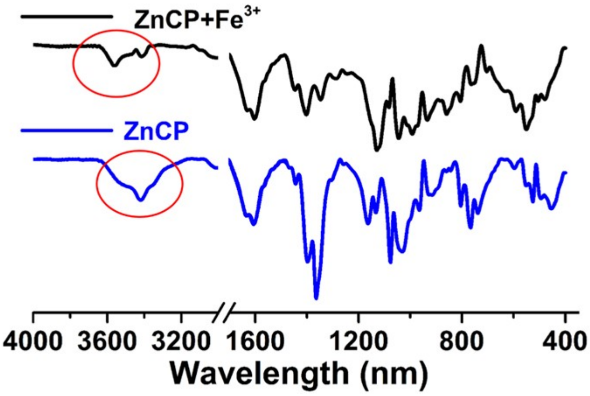

Fig. S9 FT-IR spectra of **ZnCP** and **ZnCP**@Fe^{3+}.

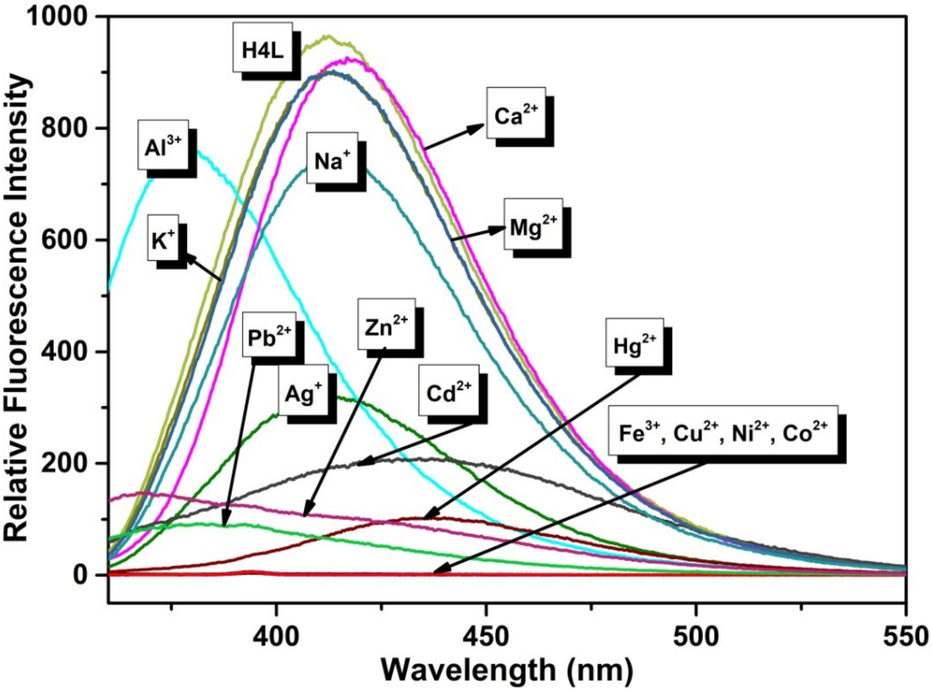

Fig. S10 Emission spectra of the water suspension of H_4L upon addition of 50 μM of different metal cations.

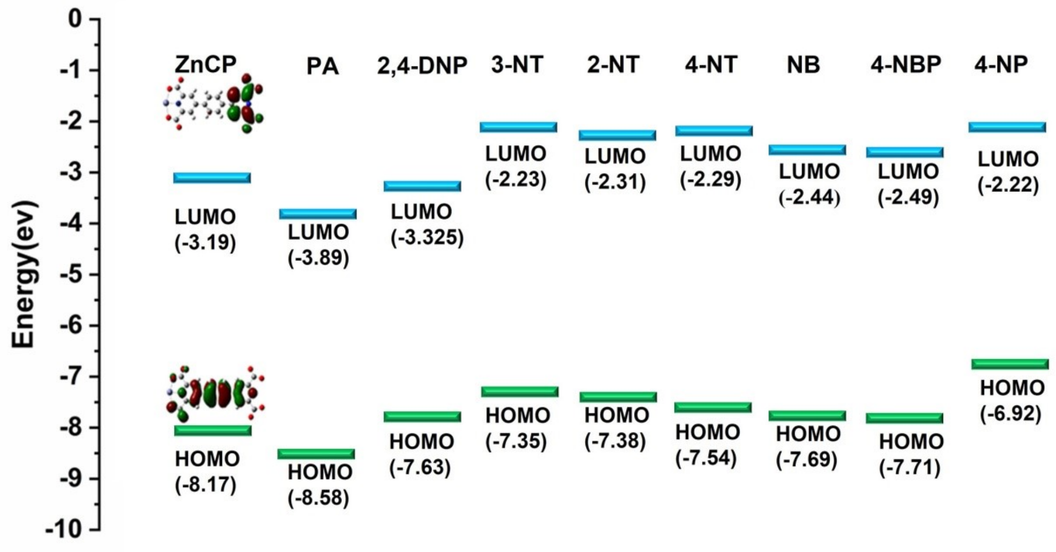

Fig. S11 Pictorial representation of the excited state electron transfer from the LUMO-HOMO.

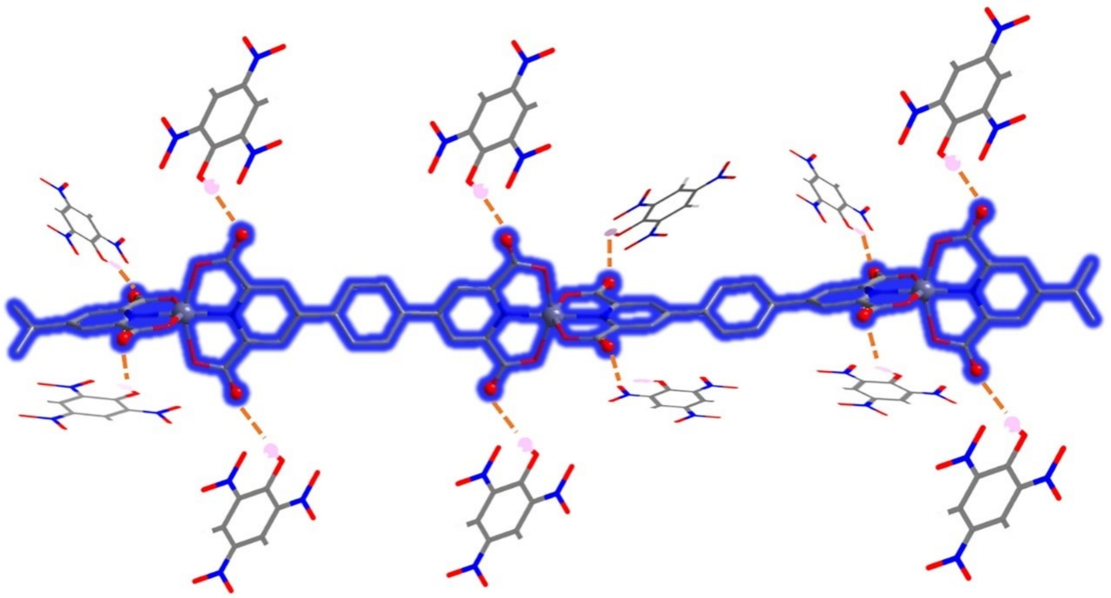

Fig. S12 The graphical representation showing proposed hydrogen bonding between of PA and **ZnCP**.

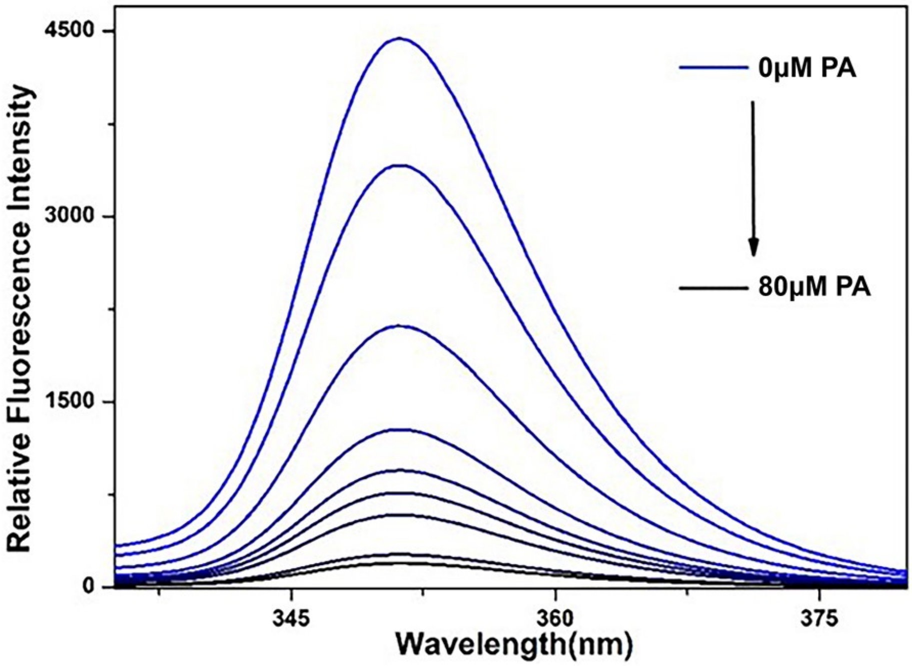

Fig. S13 The emission spectra of **ZnCP** suspensions at different concentrations of PA.

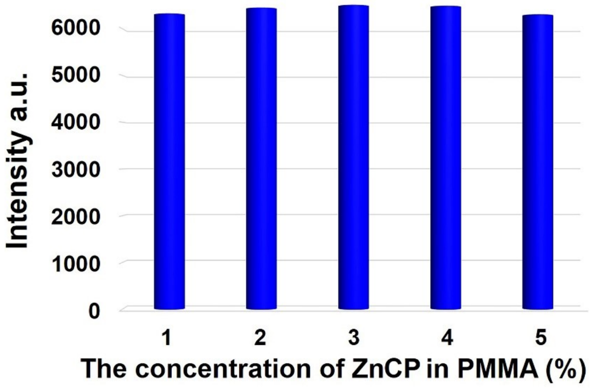

Fig. S14 The relative fluorescence intensity with the increase of concentration of **ZnCP** in PMMA.

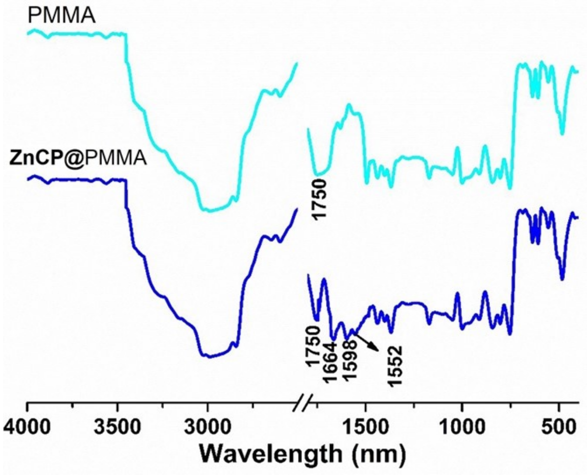

Fig. S15 IR spectra of **ZnCP**@PMMA.

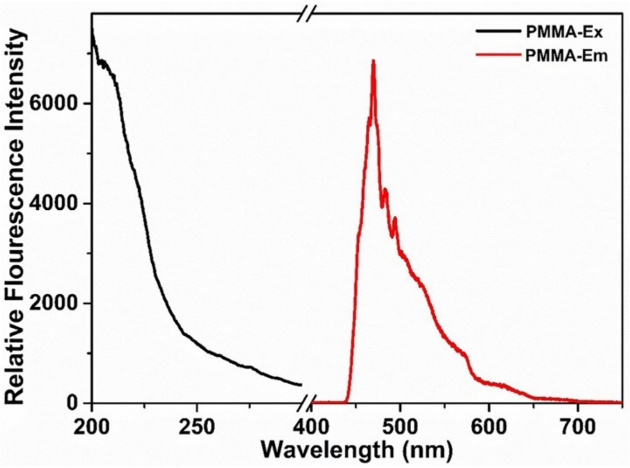

Fig. S16 Excitation and emission spectra of PMMA.

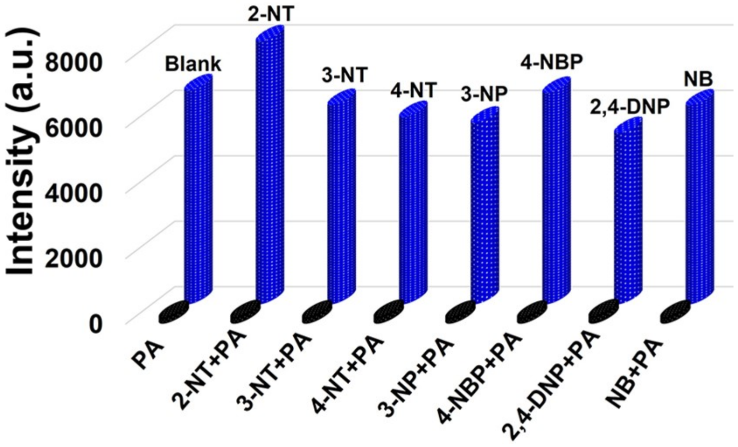

Fig. S17 The competition experiments of **ZnCP**@PMMA + PA in the presence of other nitroaromatics.

Reference

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