Electronic Supplementary information

A water-stable lanthanide coordination polymer as multiresponsive luminescence sensor for Fe^{3+}, Cr(VI) and 4-nitrophenol

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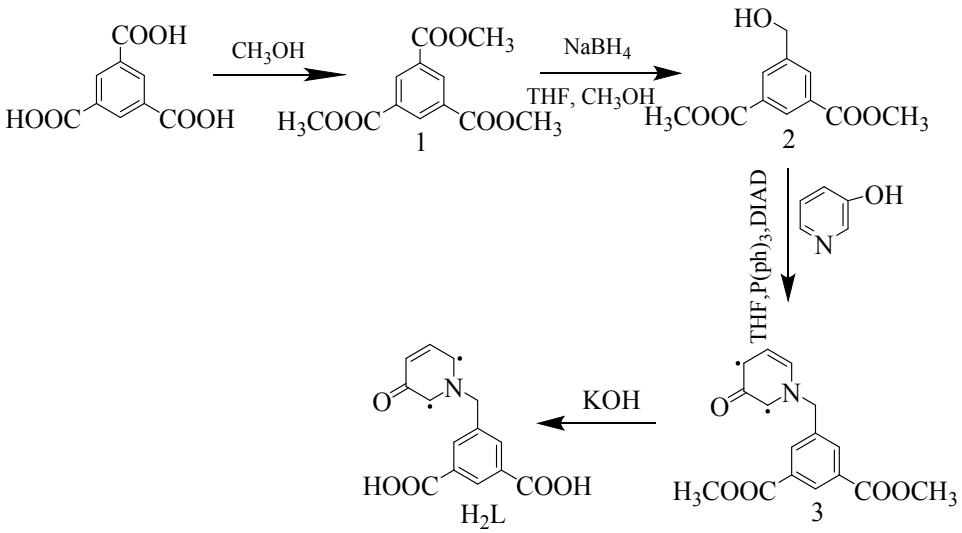
Synthesis of isomer of 5-((pyridin-3-yloxy)methyl)isophthalic acid (H_2L)



Scheme S1 Synthetic procedure for H_2L.

Trimethyl 1,3,5-benzenetricarboxylate (1).

Benzenetricarboxylic acid (10.5 g, 50 mmol) was dissolved in methanol (150 mL). Concentrated sulfuric acid (2 mL) was added. The solution was refluxed for 24 h. Solvent was removed under reduced pressure, the residue was dissolved in chloroform (150 mL) and washed with saturated bicarbonate (200 mL), and the solvent was removed under reduced pressure to give the desired product **1** as a white powder (11 g, 88%).

Dimethyl 5-hydroxymethylbenzene-1,3-dicarboxylate (2).

Trimethyl-1,3,5-tricarboxybenzoate (12.6 g, 50 mmol) was placed, along with a stirring bar, in a two-neck 250 ml flask equipped with a reflux condenser and a 50 ml addition funnel. While maintaining a dry nitrogen atmosphere, anhydrous THF (40 ml) was added to the reaction flask causing dissolution of the white solid. $NaBH_4$ (2.3 g, 60 mmol) was then added to this solution thus forming a suspension which was stirred continuously at room temperature. While stirring, a mixture of THF/MeOH (25 ml / 7.4 ml) was added dropwise via the addition funnel. The reaction mixture was then refluxed for 80 min; during this time the reaction mixture changed from a transparent solution to a light yellow and back to transparent again. After cooling, the reaction was quenched with 35 ml of 1 N HCl slowly. The product was then extracted with EtOAc (3 x 35 ml). The organic phase was dried over Na_2SO_4 and the solvent was removed in vacuo giving white solid of **2** (7.8g, 69%).

Dimethyl 5-((pyridin-3-yloxy)methyl)isophthalate (3).

Trihydroxypyridine (2.355 g, 24.78 mmol), triphenylphosphine (6.507 g, 24.807 mmol) and diisopropyl azodicarboxylate (DIAD) (4.884 mL, 25.263 mmol) were added into a 250 mL round bottom flask with 150 mL anhydrous tetrahydrofuran stirred at room temperature for 1 h. Then, the mixed solution turned to orange. **2** (6 g, 26.784 mmol) was added into the mixture. The reactant was stirred for 2d at room temperature. The solution turned to yellowish. The solution was almost clear despite of some undissolved substance. The solvent was removed under reduced pressure. The crude mixture was purified by silica gel column chromatography with dichloromethane: methanol = 10: 0.1. **3** was obtained with 1.8 g (22%) as yellow solid. ^{1}H NMR

(DMSO-d_6, 400 MHz, ppm) δ 8.42 (m, 1H), 8.32 (m, 1H), 7.70 (t, 1H), 7.68 (m, 1H), 7.31(m, 1H), 6.9 (t, 1H), 5.52 (s, 2H), 3.85 (s, 6H) (**Fig. S11**). ESI-MS: m/z = 301.9 $[M + H]^+$ (**Fig. S13**).

The isomer of 5-((pyridin-3-yloxy)methyl)isophthalic acid (H_2L).

3 (3 g, 10 mmol) was dissolved in methanol (90 mL) being clear yellow solution. Aqueous solution of KOH (0.223 g, 1 mL) was added into above mixture, heating at 75 °C for 5 h. After cooling to room temperature, solvent was removed under reduced pressure to give a yellow solid. The solid was dissolved into water (35 mL). Dilute hydrochloric acid was added dropwise to the aqueous with stirring. Lots of yellow particles appeared when the pH value of solution is about 3. Yellow solid H_2L (2.5 g, 93%) was obtained by filtration. ^{1}H NMR (DMSO-d_6, 400 MHz, ppm) : δ 8.80 (s, 1H), 8.67 (s, 1H), 8.48 (s, 1H), 8.38 (t, 1H), 7.93(m, 2H), 5.87 (s, 2H) (**Fig. S12**). ESI-MS: m/z = 273.9 $[M + H]^+$ (**Fig. S14**).

Table. S1 Crystal data and structure refinements for **Eu-CP**

Compound	Eu-CP
Empirical formula	$C_{15}H_{10}EuNO_7\cdot(H_2O)$
Formula weight	486.23
Crystal system	Monoclinic
Space group	$P2_1/c$
a(Å)	9.5090 (5)
b(Å)	8.4050 (3)
c(Å)	19.1014 (7)
β(˚)	95.170 (4)
V(Å^3)	1520.44 (11)
T(K)	293
Z	4
$Dcalc$(Mg/m^3)	2.124
μ(Mo Kα), mm^{-1}	4.17
F000	944.0
F000’	943.85
h,k,l_{max}	13,11,26
T_{min},T_{max}	0.612,0.716
$T_{min'}$	0.600
S	1.09
R_1, $wR_2[I>2\text{sigma}(I)]$	0.0381, 0.0700
CCDC number	1812540

$w = 1/[\sigma^2(F_o^2) + (0.078P)^2]$, where $P = (F_o^2 + 2F_c^2)/3$

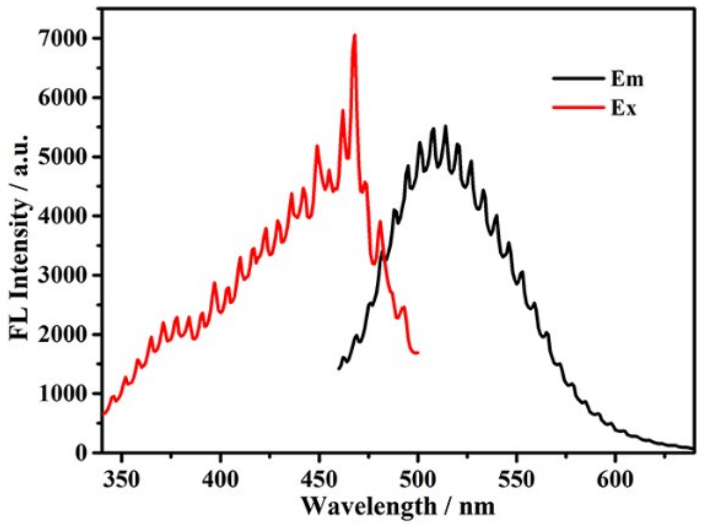


Fig. S1 Solid-state emission spectra of **H_2L** at room temperature (λ_{ex} = 450 nm)

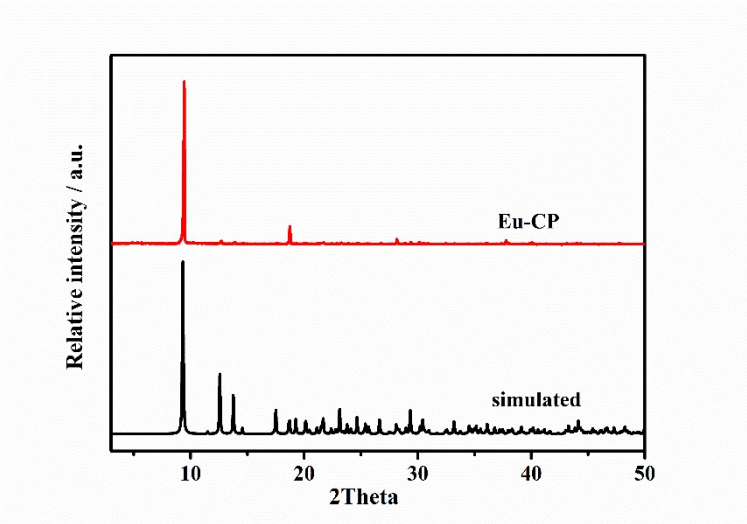


Fig. S2 PXRD patterns of **Eu-CP**

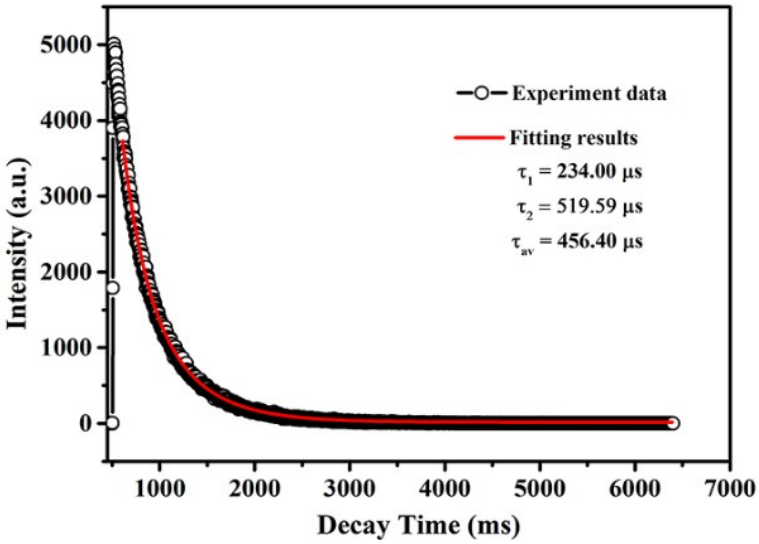


Fig. S3 Decay time of **Eu-CP**

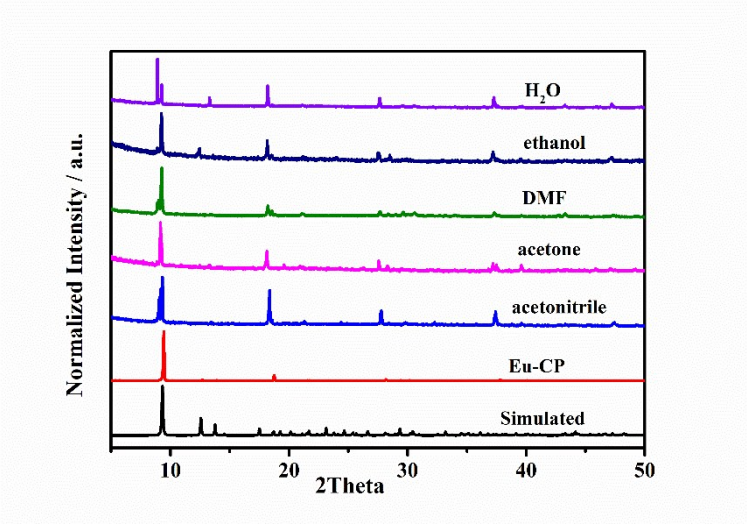


Fig. S4 PXRD patterns of **Eu-CP** in different solvents

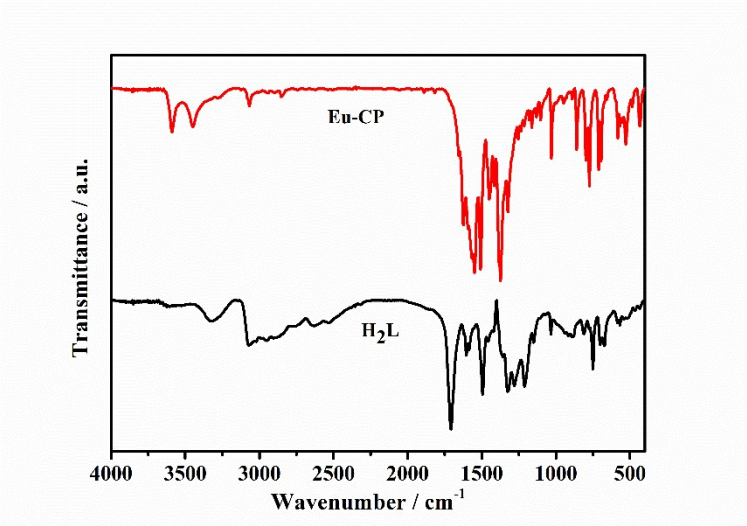


Fig. S5 IR spectrum of **Eu-CP**

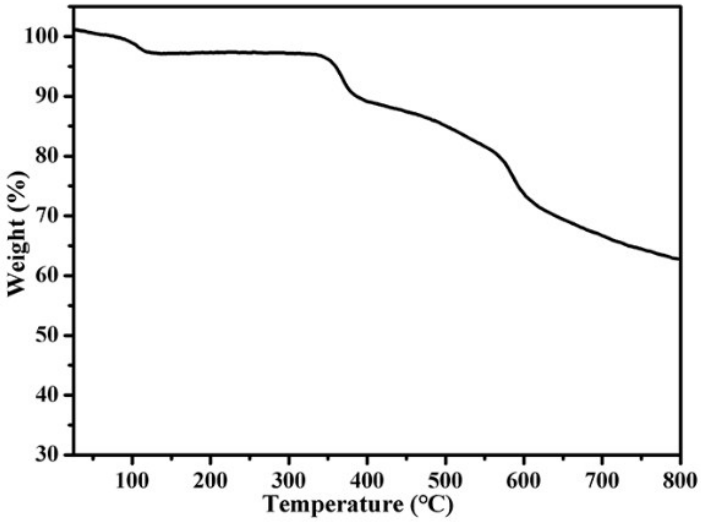


Fig. S6 TGA curve of **Eu-CP**

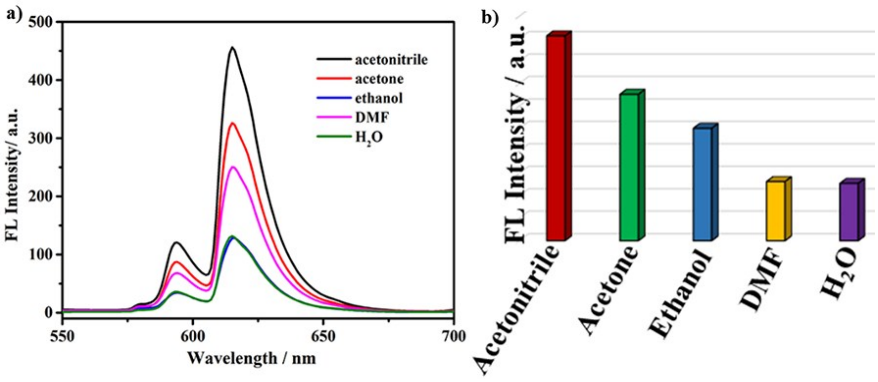


Fig. S7 Luminescence intensities at 615 nm of **Eu-CP** in different solvents

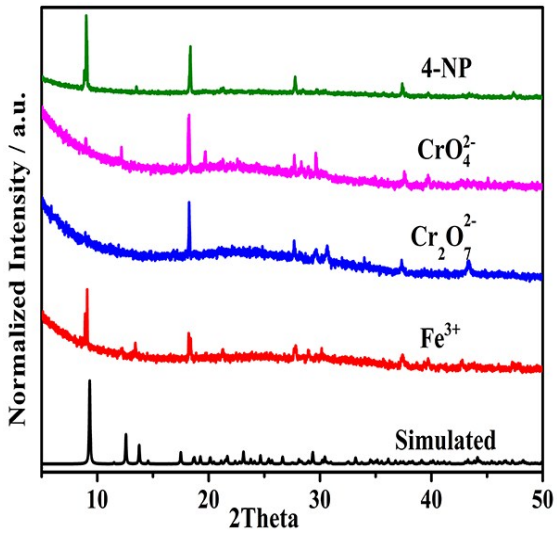


Fig. S8 PXRD patterns of **Eu-CP** in aqueous solutions of toxic substance

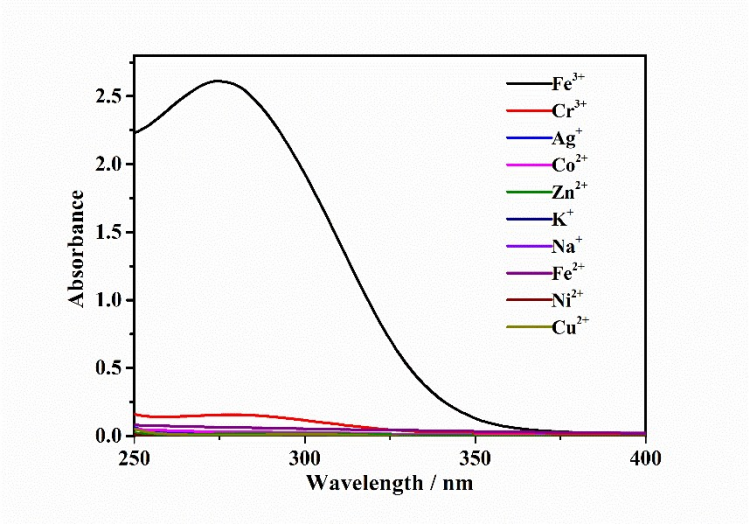


Fig. S9 UV-Vis spectra of different metal ions in aqueous solutions

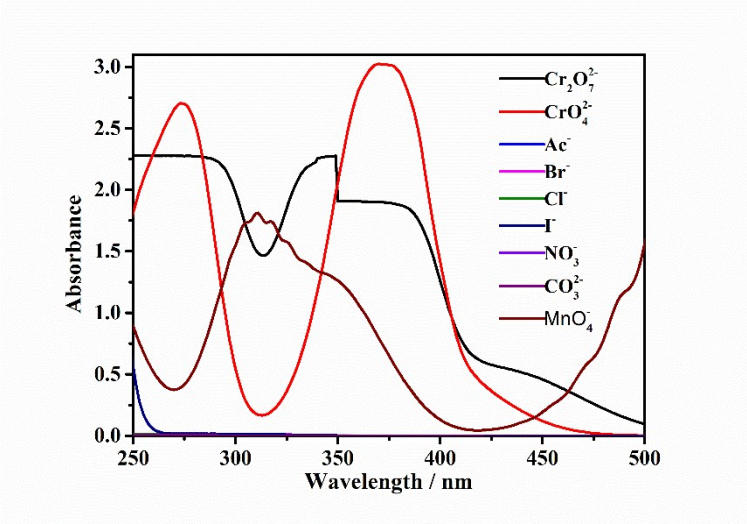


Fig. S10 UV-Vis spectra of different anions in aqueous solutions

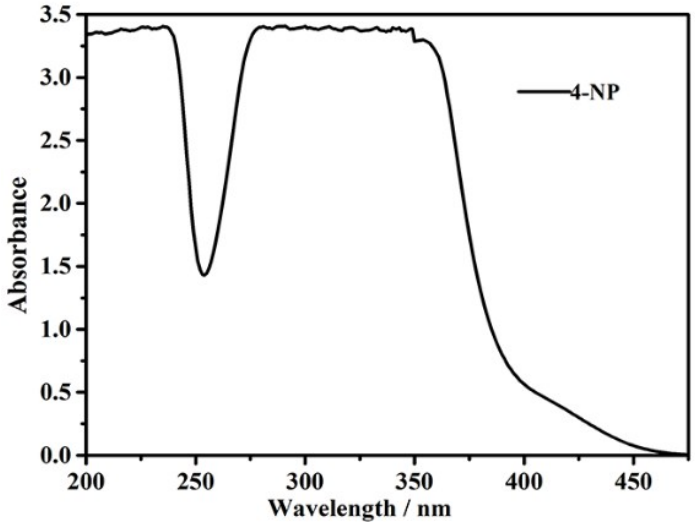


Fig. S11 UV-Vis spectra of 4-NP in aqueous solution

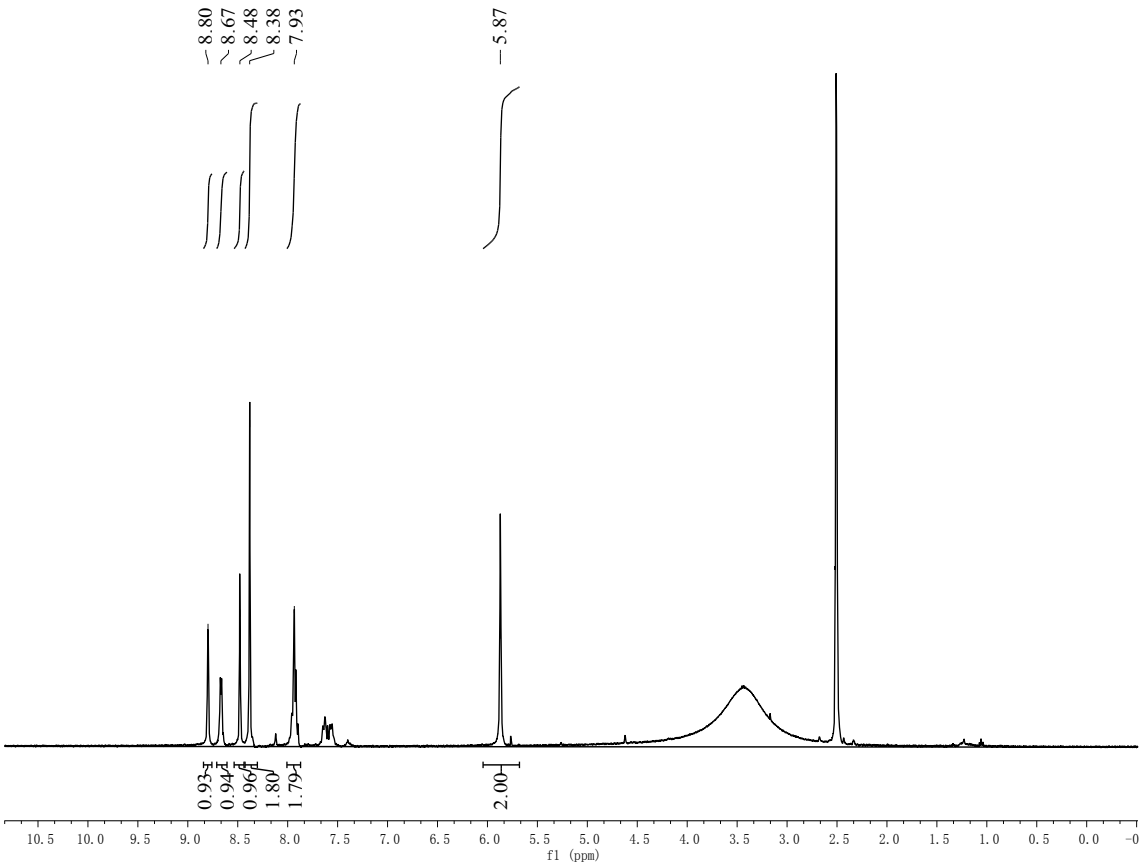


Fig. S12 ^{1}H NMR spectrum of **3** in DMSO-d_6

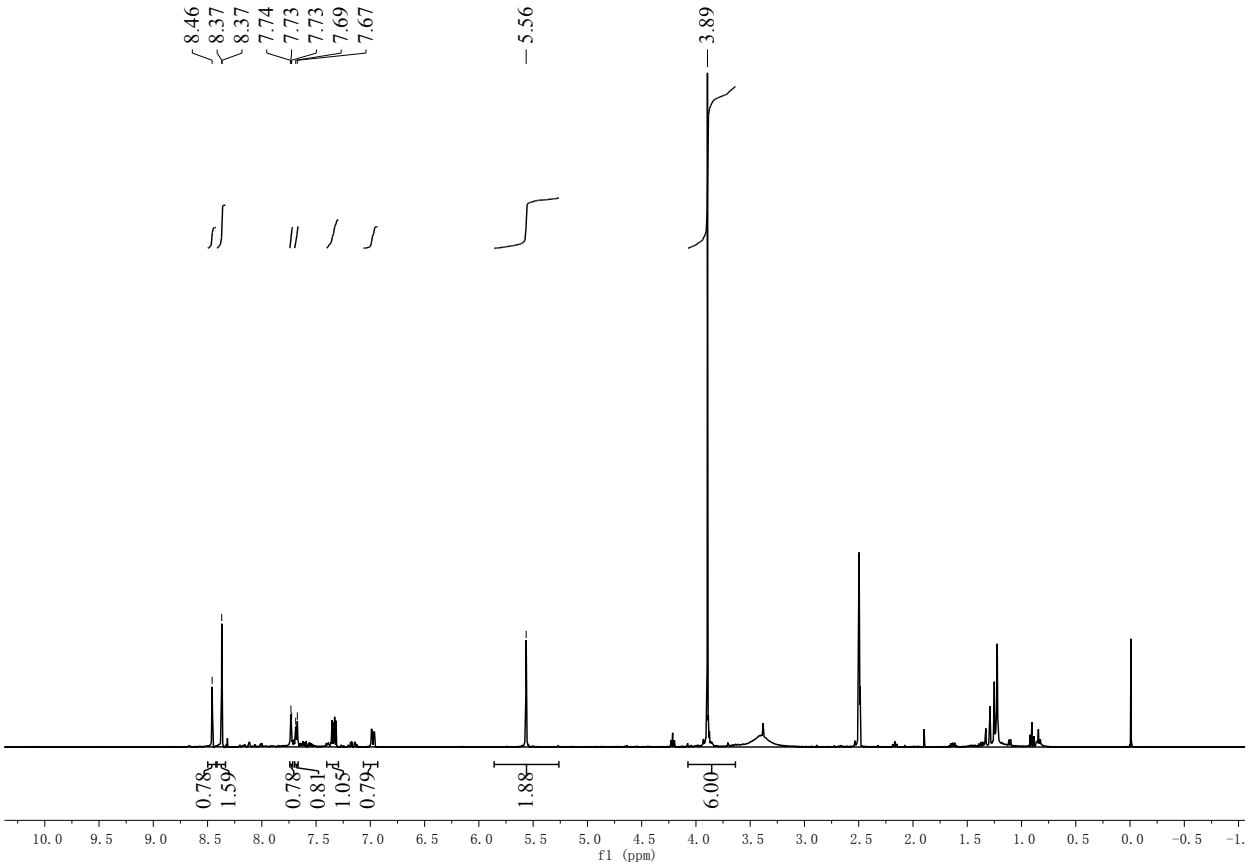


Fig. S12 ^{1}H NMR spectrum of **H_2L** in DMSO-d_6

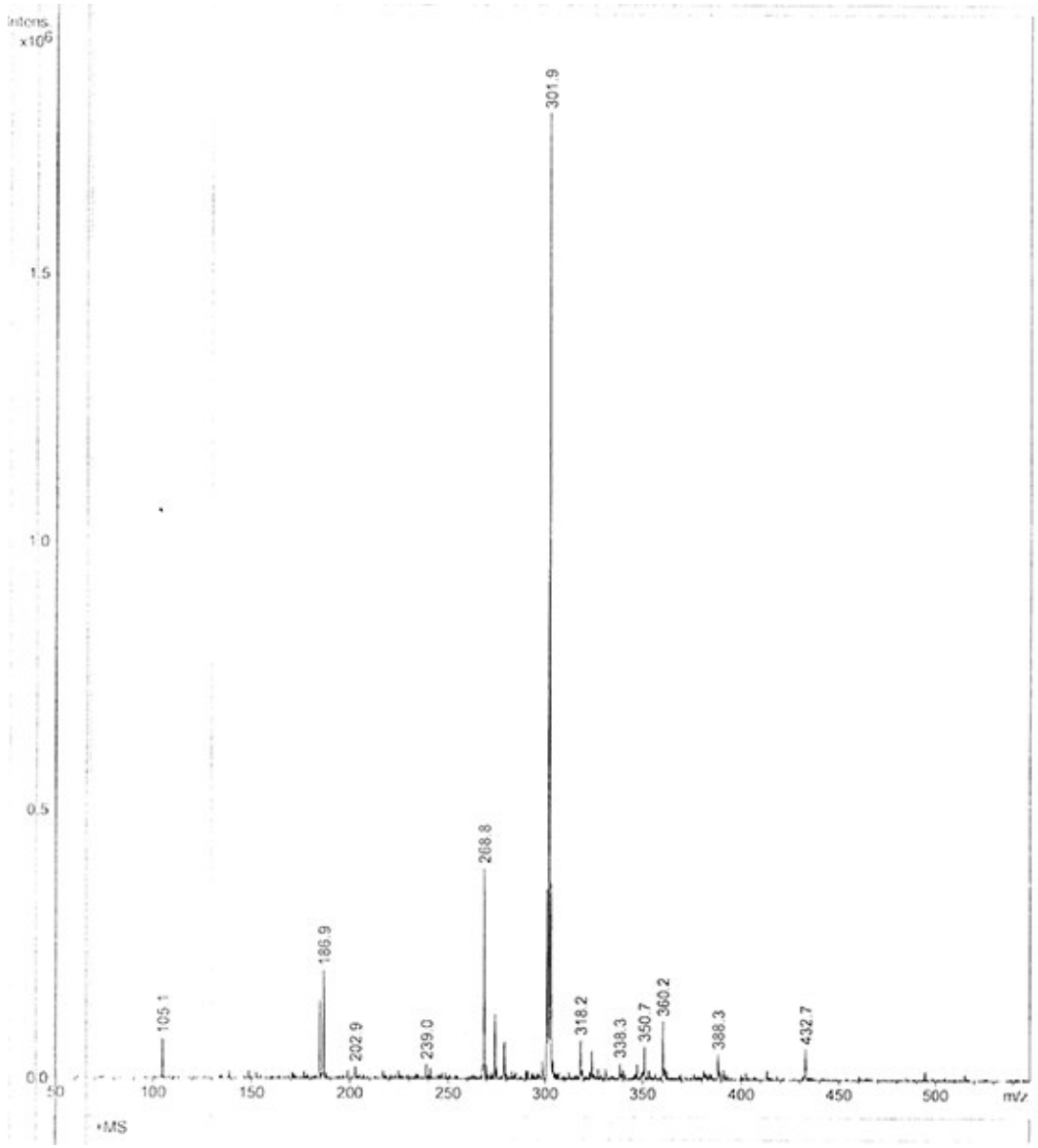


Fig. S13 ESI-MS of **3**

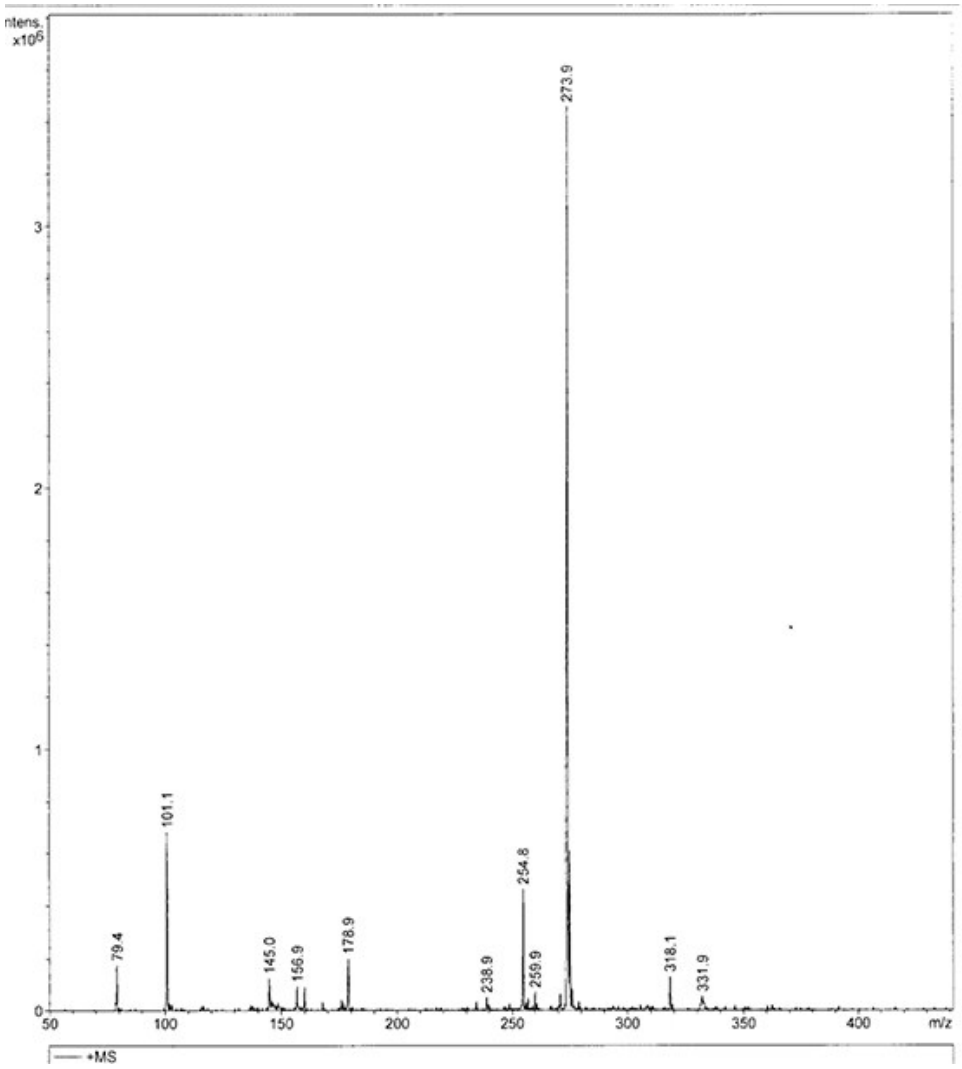


Fig. S14 ESI-MS of **H_2L**