

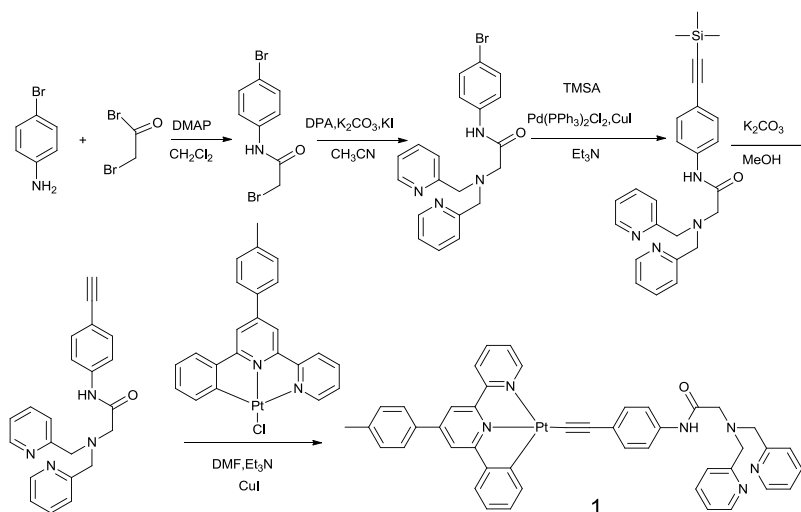
A Highly Selective and Sensitive Luminescent Chemosensor for Zn²⁺ Ion Based on Cyclometalated Platinum(II) Complexes

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Experimental Section

General Unless otherwise noted, materials were obtained from commercial suppliers and were used without further purification. CH₂Cl₂ and CH₃CN were distilled from CaH₂. ¹H NMR spectra were recorded on a Bruker Avance 400 spectrometer (400 MHz) using TMS as internal standard. Mass spectra were obtained in the positive ion mode (EI were recorded on a Waters GCT premier and ESI on LCMS-2010.) Infrared spectra were recorded with a Nicolet Avatar 360 FTIR spectrometer in the range of 4000-400 cm⁻¹ (KBr disk). Steady-state emission spectra were recorded at ambient temperature on a Hitachi F-4500 Spectrophotometer and UV/Vis spectra were recorded on a Shimadzu UV-1601 PC spectrophotometer. Time-resolved luminescent profiles were obtained by Edinburgh LP 920 using the third harmonic (355 nm) of a pulse Nd:YAG laser as the excitation source.

Synthesis 4-Tolyl-6-phenyl-2,2'-bipyridine (HC[^]N[^]N) was prepared via Kröhnke syntheses,¹ and the platinum(II) complex Pt(HC[^]N[^]N)Cl was made according to the literature method.²



Scheme 1 Synthesis of complex 1

Synthesis of 2-bromo-N-(4-bromophenyl)acetamide: A solution of 0.36 g (1.8 mmol) of 2-bromoacetyl bromide in 10 mL of dry CH₂Cl₂ was added dropwise to a solution of 0.26 g (1.5 mmol) 4-bromoaniline and 0.3 g (2.46 mmol) 4-dimethylaminopyridine(DMAP) in 60 mL of dry CH₂Cl₂ was stirred in an ice bath. After stirred 2 h at room temperature, the mixture was removed under reduced pressure to generate crude solid, which was purified by silica gel column chromatography (CH₂Cl₂:PE=1:1) to afford 2-bromo-N-(4-bromophenyl)acetamide as a white solid. Yield: 92%. ¹H NMR (400 MHz, CDCl₃, TMS) δ 8.11 (s, 1H), 7.58-7.33 (m, 4H), 4.01 (s, 2H). MS(EI): calcd. for C₈H₇Br₂NO [M]⁺ 292.887, found 292.872.

Synthesis of 2-(bis(pyridin-2-ylmethyl)amino)-N-(4-bromophenyl)acetamide: A mixture of 2-bromo-N-(4-bromo-

phenyl)acetamide (0.73 g, 2.5 mmol), di-(2-picolyl)amine (DPA) (1.0 g, 5mmol), potassium carbonate (0.83 g, 6mmol) and potassium iodide (1.0 g, 6 mmol) in acetonitrile (80 mL) was stirred at 80°C for 24 h. After cooling to room temperature, the mixture was extracted with CH₂Cl₂ and the combined organic layers were dried with Na₂SO₄ and concentrated under vacuum to obtain a brown oil, which was purified by silica gel column chromatography using ethyl acetate as eluent to afford 2-(bis(pyridine-2-ylmethyl)amino)-N-(4-bromophenyl)acetamide as a brown solid. Yield: 75%. ¹H NMR (400 MHz, DMSO, TMS) δ 10.72 (s, 1H), 8.58 (ddd, J = 4.8, 1.7, 0.8 Hz, 2H), 7.76 (td, J = 7.6, 1.8 Hz, 2H), 7.69-7.63 (m, 2H), 7.56-7.47 (m, 2H), 7.44 (d, J = 7.8 Hz, 2H), 7.28 (ddd, J = 7.5, 4.8, 1.1 Hz, 2H), 3.91 (s, 4H), 3.45 (s, 2H). MS(ESI): calcd. for C₂₀H₁₉BrN₄O [M+H]⁺ 411.1, found 411.1.

Synthesis of 2-(bis(pyridin-2-ylmethyl)amino)-N-(4-((trimethylsilyl)ethynyl)phenyl)acetamide: A mixture of 2-(bis(pyridin-2-ylmethyl)amino)-N-(4-bromophenyl)acetamide (0.41 g, 1mmol), bis(triphenylphosphine)palladium(II)chloride (35 mg, 0.05 mmol) and copper(I) iodide (19 mg, 0.1 mmol) in triethylamine(20 mL) was deaerated with nitrogen. (Trimethylsilyl)acetylene (0.15 g, 1.5 mmol) was then added to the reaction mixture and was stirred for 24 h at refluxing. After cooling to room temperature, the mixture was filtered and the filtrate was evaporated to dryness under reduced pressure to give a solid residue. The residue was then purified by column chromatography on silica gel using ethyl acetate as eluent to afford 2-(bis(pyridin-2-ylmethyl)amino)-N-(4-((trimethylsilyl)ethynyl)phenyl)acetamide as a yellow oil. Yield: 58%. ¹H NMR (400 MHz, DMSO-*d*₆, TMS) δ 10.75 (s, 1H), 8.57 (ddd, J = 4.8, 1.7, 0.9 Hz, 2H), 7.76 (td, J = 7.7, 1.8 Hz, 2H), 7.72-7.67 (m, 2H), 7.48-7.40 (m, 4H), 7.28 (ddd, J = 7.5, 4.9, 1.1 Hz, 2H), 3.92 (s, 4H), 3.46 (s, 2H), 0.22 (s, 9H). MS(ESI): calcd. for C₂₅H₂₈N₄OSi [M+H]⁺ 429.2, found 429.3, [M+Na]⁺ 451.2, found 451.3.

Synthesis of 2-(bis(pyridin-2-ylmethyl)amino)-N-(4-ethynylphenyl)acetamide: A mixture of 2-(bis(pyridin-2-ylmethyl)amino)-N-(4-((trimethylsilyl)ethynyl)phenyl)-acetamide (0.43 g, 1 mmol), potassium carbonate (0.41 g, 3 mmol) in methanol was stirred at room temperature for 3 h. Then the mixture was extracted with CH₂Cl₂ and the combined organic layers were dried with Na₂SO₄ and concentrated under vacuum to afford 2-(bis(pyridin-2-ylmethyl)amino)-N-(4-ethynylphenyl)acetamide as a yellow oil. Yield: 87%. ¹H NMR (400 MHz, DMSO-*d*₆, TMS) δ 10.77 (s, 1H), 8.58 (ddd, J = 4.8, 1.7, 0.9 Hz, 2H), 7.84-7.66 (m, 4H), 7.52-7.39 (m, 4H), 7.28 (ddd, J = 7.5, 4.9, 1.1 Hz, 2H), 4.10 (s, 1H), 3.92 (s, 4H), 3.46 (s, 2H). MS(ESI): calcd. for C₂₂H₂₀N₄O [M]⁺ 356.2, found 356.1.

Synthesis of complex 1: The mixture of 100 mg [Pt(C[^]N[^]N)Cl] (0.18 mmol), 10 mg CuI, 192 mg 2-(bis(pyridin-2-ylmethyl)amino)-N-(4-ethynylphenyl)acetamide (0.54 mmol), 4 mL DMF, and 3 mL Et₃N were

sonicated under nitrogen at room temperature for 8 h. Then 20 mL H₂O was added to the mixture to achieve the precipitate. The precipitate was filtered out and washed with diethyl ether and water. Recrystallization of the crude product by vapor diffusion of diethyl ether into a dichloromethane solution gave **1** as a reddish orange crystalline solid. Yield: 52%. ¹H NMR (400 MHz, DMSO-*d*₆, TMS) δ 10.59 (s, 1H), 9.09 (d, J = 4.9 Hz, 1H), 8.76 (d, J = 8.1 Hz, 1H), 8.67-8.50 (m, 3H), 8.41-8.28 (m, 2H), 8.05 (d, J = 7.9 Hz, 2H), 7.93-7.84 (m, 2H), 7.78 (t, J = 7.0 Hz, 3H), 7.62 (d, J = 8.3 Hz, 2H), 7.45 (dd, J = 17.2, 7.8 Hz, 4H), 7.36 (d, J = 8.4 Hz, 2H), 7.33-7.23 (m, 2H), 7.18-7.05 (m, 2H), 3.93 (s, 4H), 3.45 (s, 2H), 2.42 (s, 3H). IR (KBr disk ν/cm⁻¹): 2097(w), ν(C≡C); 1604(s), ν(C=O). MS(ESI): calcd. for C₄₅H₃₆N₆O⁺ [M+H]⁺ 872.3, found 872.6.

1 F. Kröhnke, *Synthesis* 1976, 1-24.

2 S. W. Lai, M. C. W. Chan, T. C. Cheung, S. M. Peng, C. M. Che, *Inorg. Chem.* 1999, **38**, 4046-4055.

Table S1 Photophysical properties of **1** and its Zinc complex

Entry	λ _{abs} (nm, log ε)	λ _{em} (nm) ^a	Φ _{em} ^b	τ(ns) ^c
Complex 1	290(4.78),434(3.94)	597	0.0045	53, 285
1 + Zn²⁺	290(4.75),431(3.98)	584	0.0295	302

a In degassed acetonitrile at 298 K. **b** The emission quantum yields were measured in degassed acetonitrile solutions at 298 K and estimated relative to [Ru(bpy)₃]Cl₂ in air-equilibrated aqueous solution as the standard (Φ_{em} = 0.028). **c** λ_{ex} = 434 nm and λ_{em} = 585 nm. Estimated uncertainty in τ was ± 15 %.

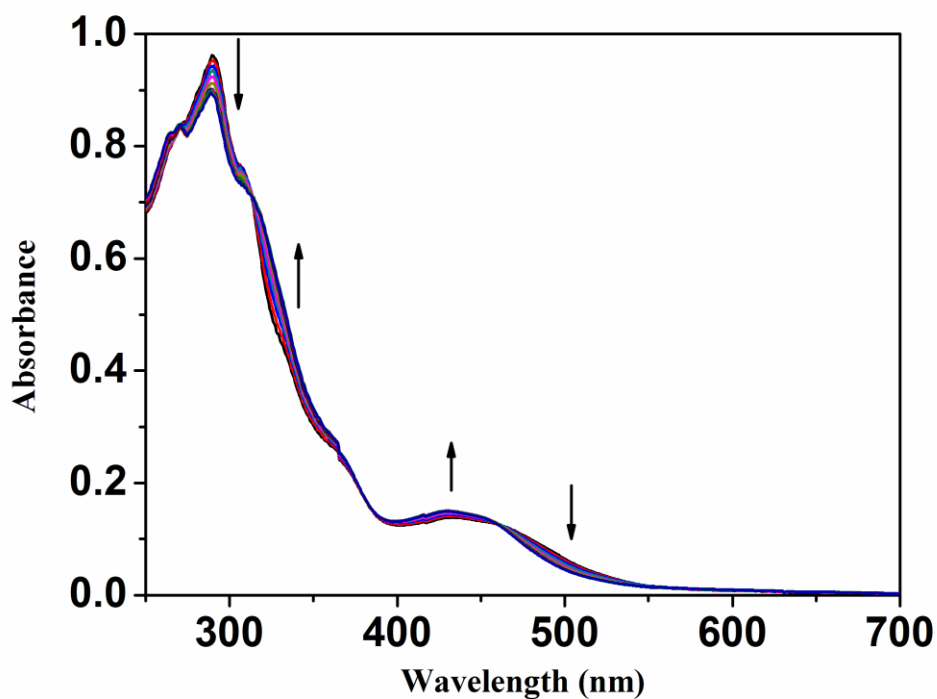


Fig. S1 The changes in absorption spectrum of complex 1 in CH₃CN upon addition of Zn²⁺ (0 to 3 equiv) .

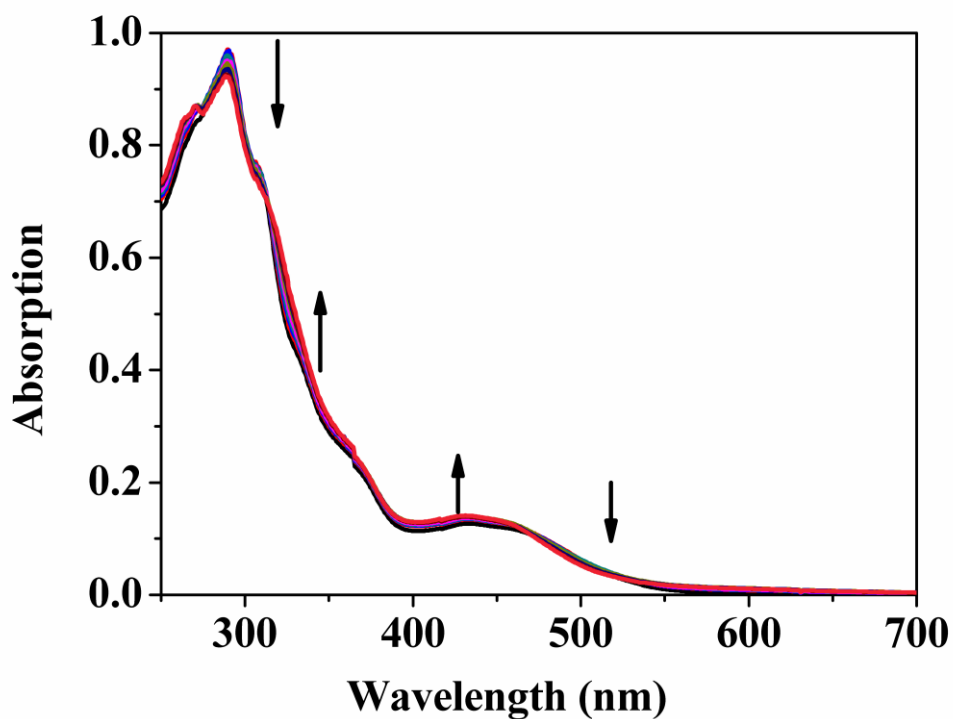


Fig. S2 The changes in absorption spectrum of complex 1 in CH₃CN upon addition of Cd²⁺ (0 to 3 equiv) .

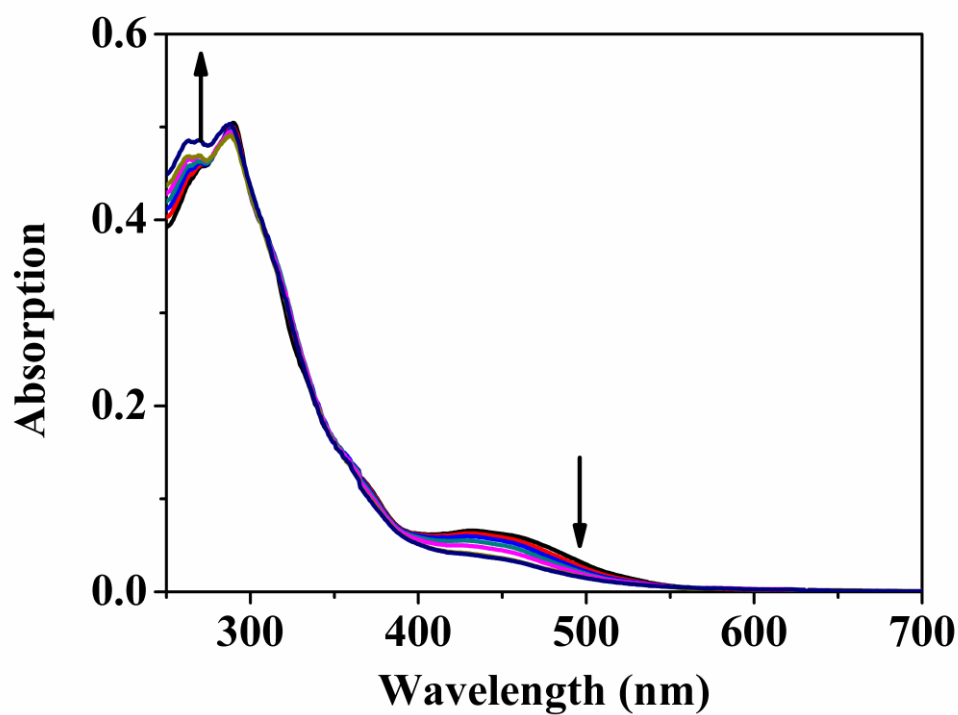


Fig. S3 The changes in absorption spectrum of complex **1** in CH₃CN upon addition of Cu²⁺ (0 to 3 equiv) .

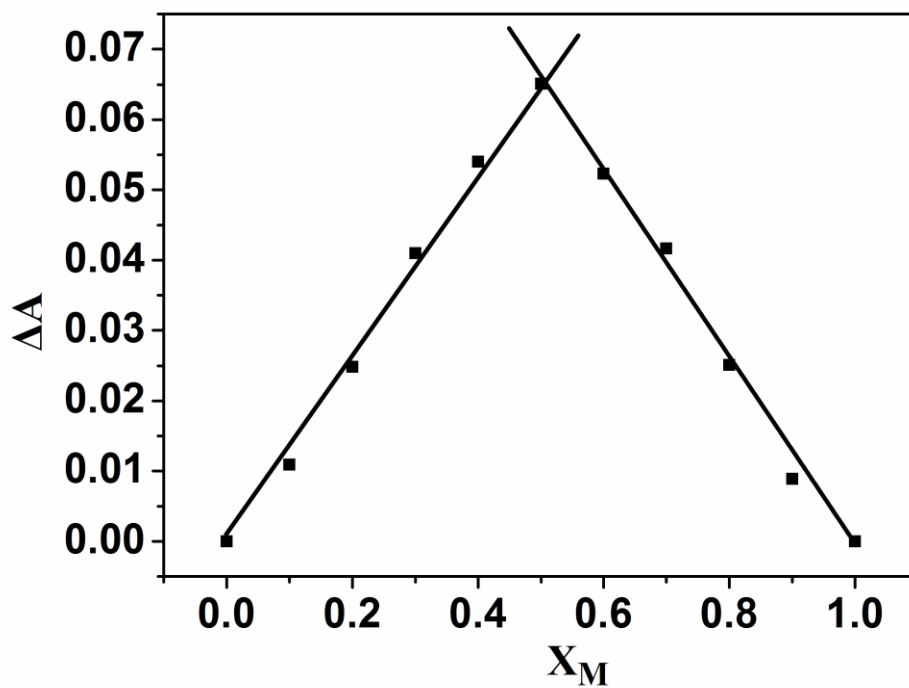


Fig. S4 The Job's plot for determining the stoichiometric ratio between complex **1** and Zn²⁺, where the variations of absorbance at 485 nm were measured as a function of molar ratio X_M ($[Zn^{2+}]/([Zn^{2+}]+[1])$).

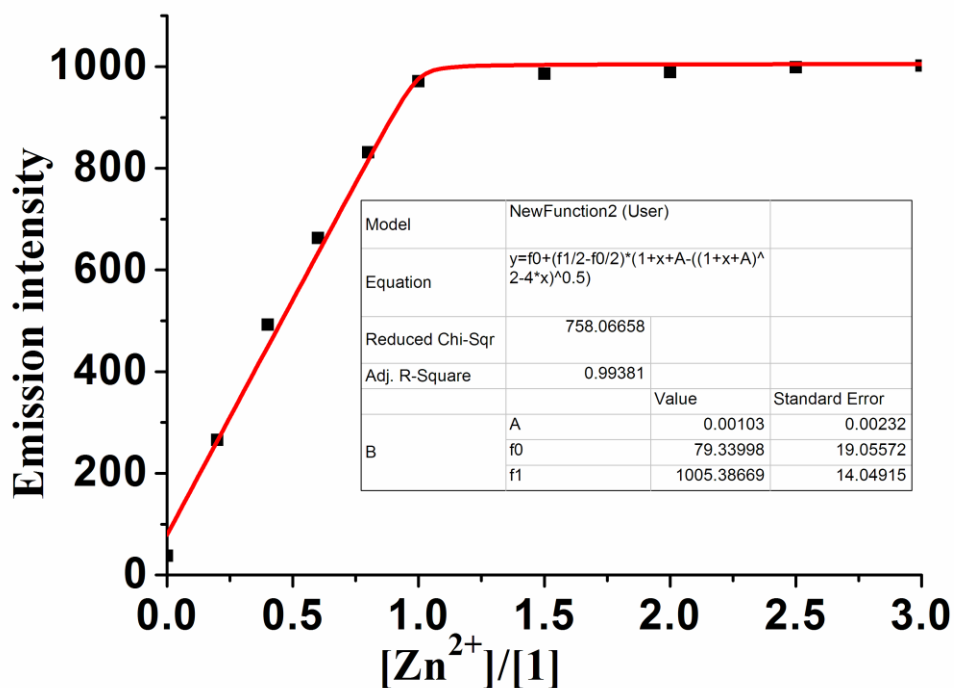


Fig. S5 A nonlinear curve fitting based on a 1:1 complex according to the equation:

$$F = F_0 + \frac{F_{\max} - F_0}{2} \left\{ 1 + \frac{C_M}{C_L} + \frac{1}{K_S C_L} - \left[\left(1 + \frac{C_M}{C_L} + \frac{1}{K_S C_L} \right)^2 - 4 \frac{C_M}{C_L} \right]^{1/2} \right\}$$

Where F and F_0 are the fluorescence intensities of complex **1** in the presence and absence of Zn^{2+} , C_M and C_L are the concentrations of Zn^{2+} and complex **1**, and K_S is the stability constant.

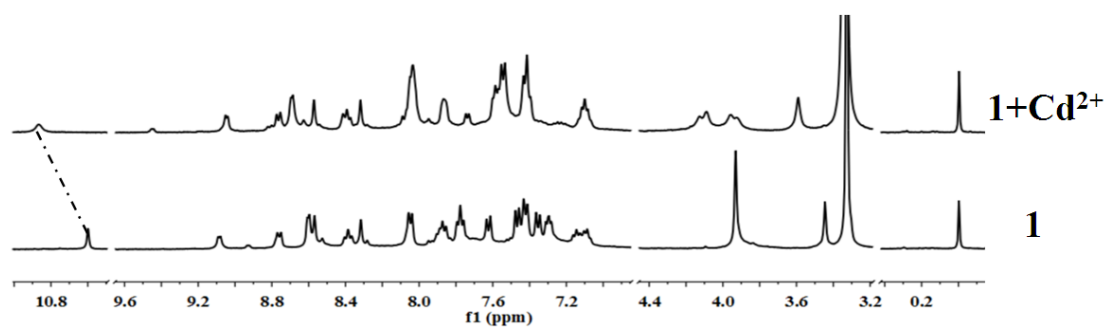
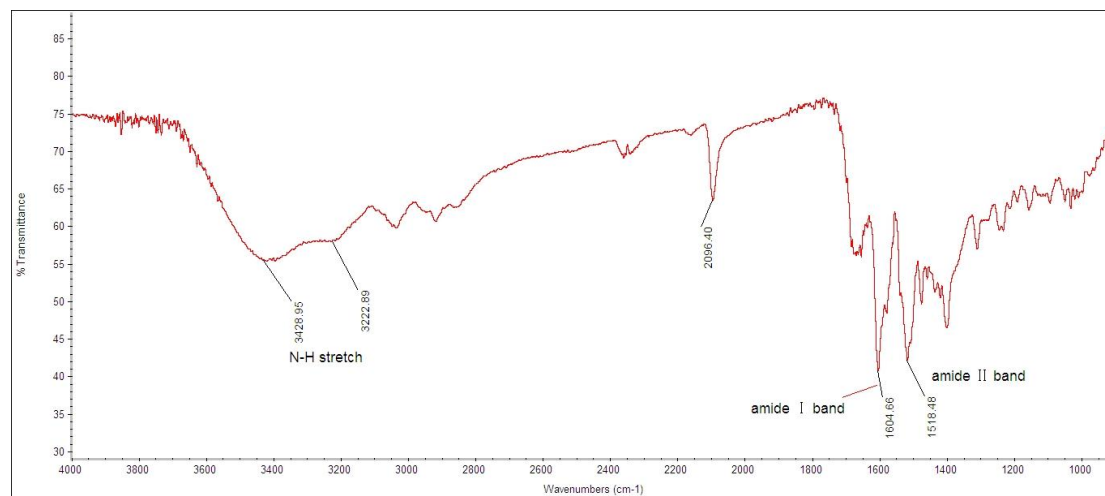


Fig. S6 1H NMR spectra of complex **1** in the absence and presence of Cd^{2+} in $DMSO-d_6$.

Complex 1



Zn²⁺-complex

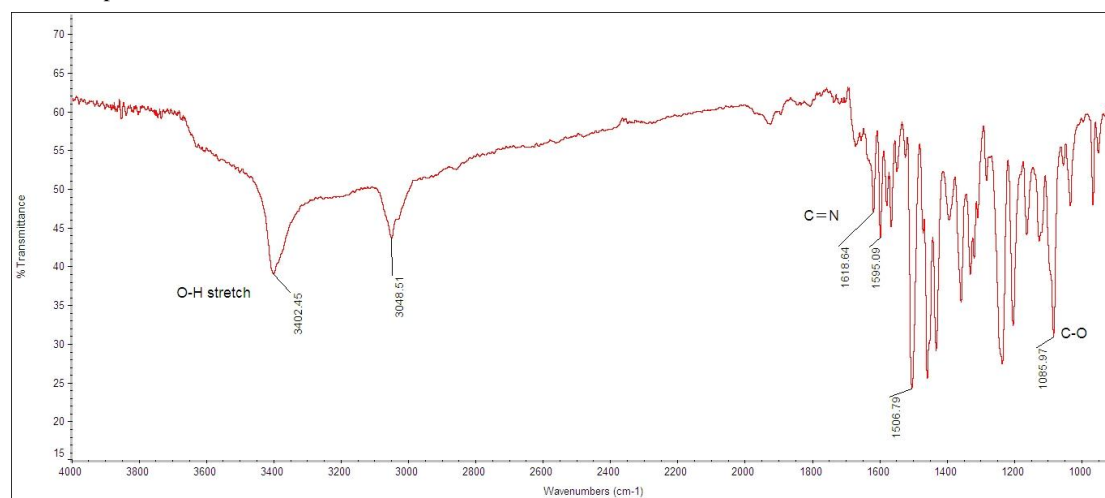


Fig. S7 IR spectra of complex 1 and its Zn²⁺-complex

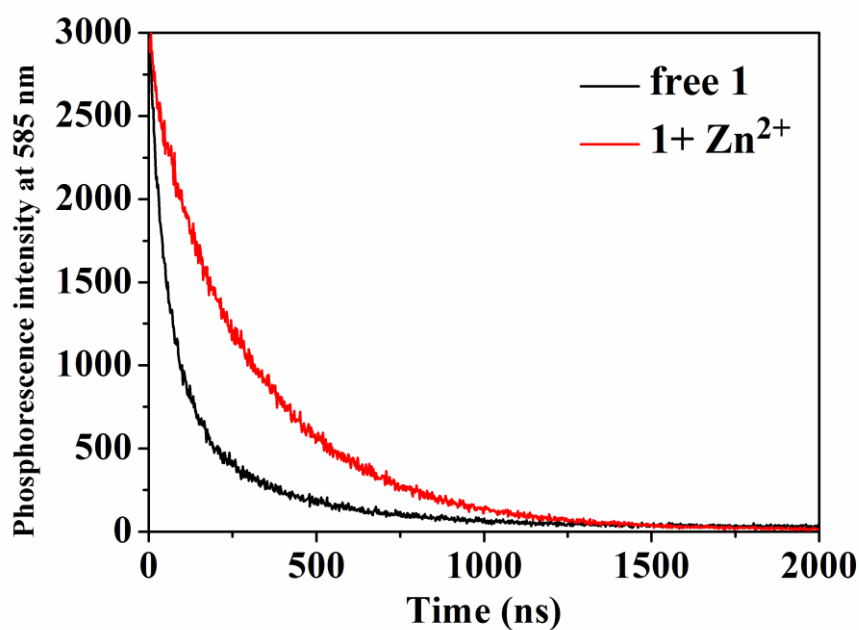


Fig. S8 Decay traces of **1** in the absence (black line) and presence (red line) of Zn^{2+} . The experiment was carried out in degassed CH_3CN . The excitation was 434 nm.

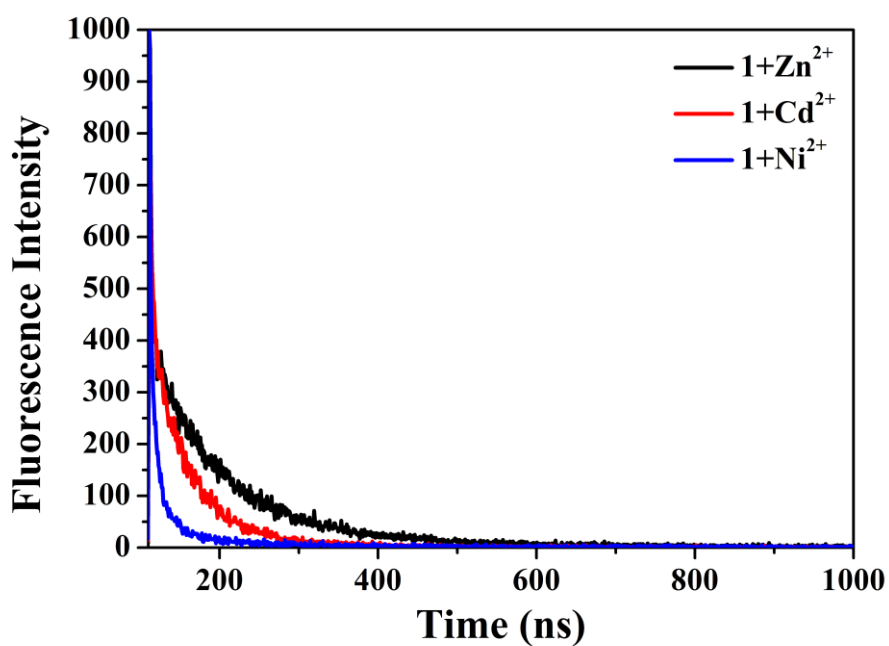


Fig. S9 Decay traces of **1** in the presence of Zn^{2+} (black line), Cd^{2+} (red line) and Ni^{2+} (blue line). The experiment was carried out in degassed $\text{CH}_3\text{CN-H}_2\text{O}$ (7:3, v/v). The excitation was 434 nm.