

Electronic Supplementary Material (ESI) for Dalton Transactions.

Electronic Supplementary Information

A reaction-based luminescent switch-on sensor for the detection of OH⁻ ion in simulated wastewater

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Experimental

Material

Unless specified, all the reagents were purchased from Sigma Aldrich (St. Louis, MO) and used as received without further purification, and all aqueous solutions were prepared with Milli-Q water ($18.2 \text{ M}\Omega \text{ cm}^{-1}$) unless specified. Iridium chloride hydrate ($\text{IrCl}_3 \cdot x\text{H}_2\text{O}$) was purchased from Precious Metals Online (Australia). Specifically, all hydroxide (OH^-) ions were applied as solutions of sodium hydroxide (NaOH) at the indicated concentrations in this work.

General Experiment

Mass spectrometry was performed in the Mass Spectroscopy Unit at Department of Chemistry, Hong Kong Baptist University, Hong Kong (China). Deuterated solvents for NMR purposes were obtained from Armar and used as received. ^1H and ^{13}C NMR were recorded on a Bruker Avance 400 spectrometer operating at 400 MHz (^1H) and 100 MHz (^{13}C). ^1H and ^{13}C chemical shifts were referenced internally to solvent shift (DMSO-*d*₆: ^1H , 2.50, ^{13}C , 39.52). Chemical shifts are quoted in ppm, the downfield direction being defined as positive. Uncertainties in chemical shifts are typically ± 0.01 ppm for ^1H and ± 0.05 for ^{13}C . Coupling constants are typically ± 0.1 Hz for ^1H - ^1H and ± 0.5 Hz for ^1H - ^{13}C couplings. The following abbreviations are used for convenience in reporting the multiplicity of NMR resonances: s, singlet; d, doublet; t, triplet; q, quartet; m, multiplet; br, broad. All NMR data was acquired and processed using standard Bruker software (Topspin).

Synthesis

Complex **1** were prepared according to modified literature methods.^{1,2} Briefly, 136 mg of 3-methyl-2-phenylpyridine and 140 mg of $\text{IrCl}_3 \cdot x\text{H}_2\text{O}$ were mixed together and

further heated overnight at 120 °C in 12 mL of 2-methoxyethanol/H₂O (3/1). Afterwards, the mixture was filtered and washed by excessive deionized water and then diethyl ether for three times respectively to generate the dichloro-bridged dimer [Ir(F₂ppy)₂Cl]₂. The oven-dried dimer was treated with 2.1 equivalents of 4, 4'-dibromo-2, 2'-bipyridine in dichloromethane (4 mL) and methanol (4 mL) at 65 °C for 10 h. Then, an excess of solid NH₄PF₆ was added and the reaction was stirred for another 20 min at room temperature. The orange powder thus obtained was isolated and filtrated by removing the solvent under reduced pressure, and the residue was purified by silica gel column chromatography employing dichloromethane and methanol as solvent. Yield: 67%.

Complex **1** ¹H NMR (400 MHz, DMSO): δ 9.23 (s, 1H), 7.97 (d, J = 8.6 Hz, 1H), 7.92 – 7.87 (m, 1H), 7.77 (s, 1H), 7.70 – 7.60 (m, 2H), 7.55 – 7.44 (m, 2H), 7.08 – 6.97 (m, 2H), 6.90 – 6.80 (m, 2H), 6.06 (d, J = 7.7 Hz, 2H), 2.75 (s, 1H). ¹³C NMR (101 MHz, DMSO): δ 164.72, 156.03, 151.86, 150.43, 148.39, 145.70, 143.06, 136.21, 132.83, 131.38, 128.28, 123.78, 122.61, 23.12. HRMS: Calcd. for C₃₄H₂₆Br₂N₄IrPF₆ [M-PF₆]⁺: 843.0133 Found: 843.0108. Anal. (C₃₄H₂₆Br₂N₄IrPF₆ + 1.5 H₂O) C, H, N: calcd 40.25, 2.88, 5.52 Found 40.07, 2.68, 5.59.

Complex **2** Reported³

Complex **3** Reported³

Complex **4** Reported⁴

Complex **5** Reported⁵

Complex **6** Reported⁶

Complex **7** Reported⁷

Complex **8** Reported⁸

Photophysical measurement

Emission spectra and lifetime measurements for complex **1** were performed on a PTI TimeMaster C720 Spectrometer (Nitrogen laser: pulse output 335 nm) fitted with a 395 nm filter. Error limits were estimated: λ (± 1 nm); τ (± 10 %); ϕ (± 10 %). All solvents used for the lifetime measurements were degassed using three cycles of freeze-vac-thaw. Luminescence quantum yields were determined using the method of Demas and Crosby with $[\text{Ru}(\text{bpy})_3][\text{PF}_6]_2$ in degassed acetonitrile as a standard reference solution ($\Phi_r = 0.062$) and were calculated according to the following reported equation (1):

$$\Phi_s = \Phi_r(B_r/B_s)(n_s/n_r)^2(D_s/D_r) \quad (1)$$

Where the subscripts s and r refer to the sample and reference standard solution respectively, n is the refractive index of the solvents, D is the integrated intensity, and Φ is the luminescence quantum yield. The quantity B was calculated by $B = 1 - 10^{-AL}$, where A is the absorbance at excitation wavelength and L is the optical path length.

Stability analysis of complex 1

Complex **1** was stored in DMSO-*d*₆/D₂O (9:1; 5 mM) at 298 K for seven days for ¹H NMR spectroscopy measurement. ¹H NMR experiments were performed with a Bruker Avance 400 spectrometer (Bruker Avance-III, UltraShield Magnet). Alternatively, the complex was stored in acetonitrile/H₂O (9:1; 50 μ M) at 298 K for seven days for UV-vis absorption spectroscopy measurement. Absorption spectra were recorded on a UV-Visible Spectrophotometer (Cary UV-100).

OH⁻ detection

A stock solution of complex **1** (0.5 mM) was prepared in dimethyl sulfoxide (DMSO) for further use. The complex was diluted in DMSO/H₂O (9:1, v/v) to a final concentration of 2.5 μ M for 1.5 mL. After that, 50 μ L of OH⁻ (as NaOH) was added

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to the cuvette and the resulting spectra were recorded at 25 °C on a PTI QM-1 spectrofluorometer (Photo Technology International, Birmingham, NJ). A double-beam spectrophotometer (Cary UV-300) was used for recording UV-vis absorption spectra and a 400 MHz Bruker spectrometer was used for recording NMR spectra.

Filter paper detection

20 μL of complex **1** stock solution (0.5 mM) was initially diluted with 3580 μL of DMSO in a 10 mL tube as a stock solution. Then 450 μL of the stock solution was added into two tubes, with the further addition of 50 μL of Milli-Q water in tube 1 as luminescent ink **1** and 50 μL of NaOH solution (1 M) in tube 2 as luminescent ink **1**-OH⁻. Then, plastic droppers were employed as pens and stuffed with degreasing cotton to control the flow velocity of luminescent inks. Then the initials of Hong Kong Baptist University, namely the letters “HKBU” were written by the using of luminescent ink **1** and **1**-OH⁻ respectively on two filter papers, which were finally recorded under ambient light and UV light at 365 nm.

Application of complex 1 in simulated wastewater

Four kinds of entity water were collected separately from Tseung Kwan O (TKO, pH = 3.21), Lung Kwu Tan (LKT, pH = 5.17), Tsim Sha Tsui (TST, pH = 7.80) and Shing Mun River (SMR, pH = 7.32) in Hong Kong, China. Herewith, both TKO and LKT were wastewater, while TST and SMR were seawater. The entity waters themselves were used as control in this part, also, further addition of NaOH solid (0.3999 g) into different entity waters (10 mL) were prepared to simulate industrial wastewaters. Instead of the 50 μL of Milli-Q water or 50 μL of NaOH solution (1M) applied for OH⁻ detection, 50 μL of the four different kinds of entity water, with or without the further dissolution of NaOH solid, were added into the sensing system

with 2.5 μL of complex **1** stock solution and 447.5 μL of DMSO in each tube. Finally, the luminescent intensity for different sensing systems was investigated by the same PTI QM-1 spectrofluorometer mentioned above.

Table S1 Photophysical properties of complex **1** (2.5 μM).

Complex	Quantum yield / %	λ_{ex} / nm	λ_{em} / nm	Lifetime / μs	UV-vis absorption λ_{abs} / nm (ϵ / $\text{dm}^3\text{mol}^{-1}\text{cm}^{-1}$)
1	9.33	310	630	3.925	220 (1.25×10^4), 253 (1.15×10^4)

Table S2. Comparison of complex **1** with fluorescent dyes for hydroxide sensing.

Ref in ESI	Signal output	Lifetime	pH detection range	Application environment	Selectivity over ions
9	Switch-on	N/A	10.24–10.96	N/A	N/A
10	Switch-on	N/A	2–12	N/A	N/A
10	Switch-off	N/A	10–12	N/A	N/A
This work	Switch-on	3.925 μs	12–14	Simulated wastewater	I^- , $\text{S}_2\text{O}_3^{2-}$, SO_4^{2-} , Cl^- , F^- , Br^- , ClO_4^- , CO_3^{2-} , NO_3^-

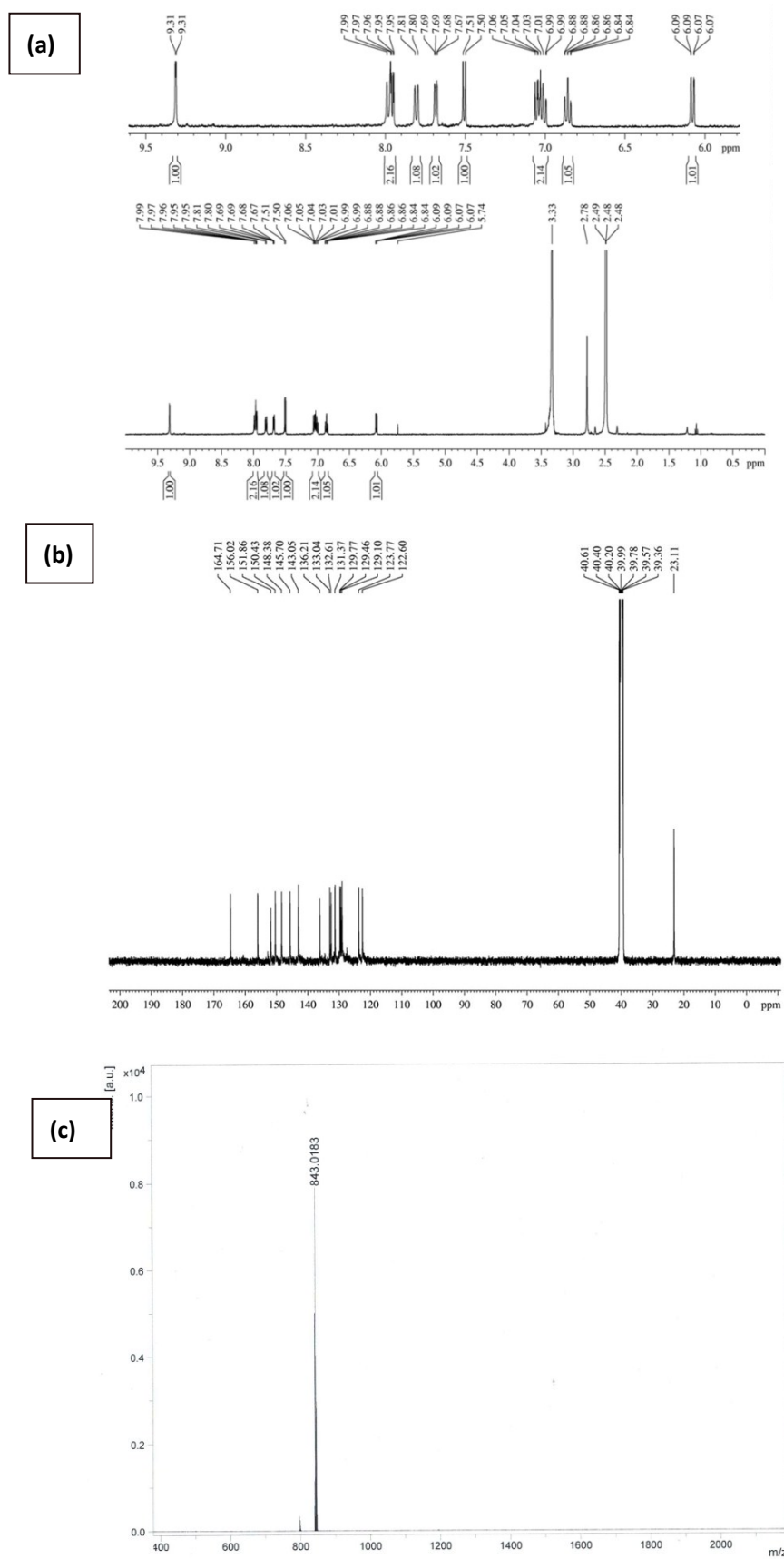


Fig. S1 (a) ^1H NMR spectra for complex 1; **(b)** ^{13}C NMR spectra for complex 1; **(c)** HRMS spectra for complex 1.

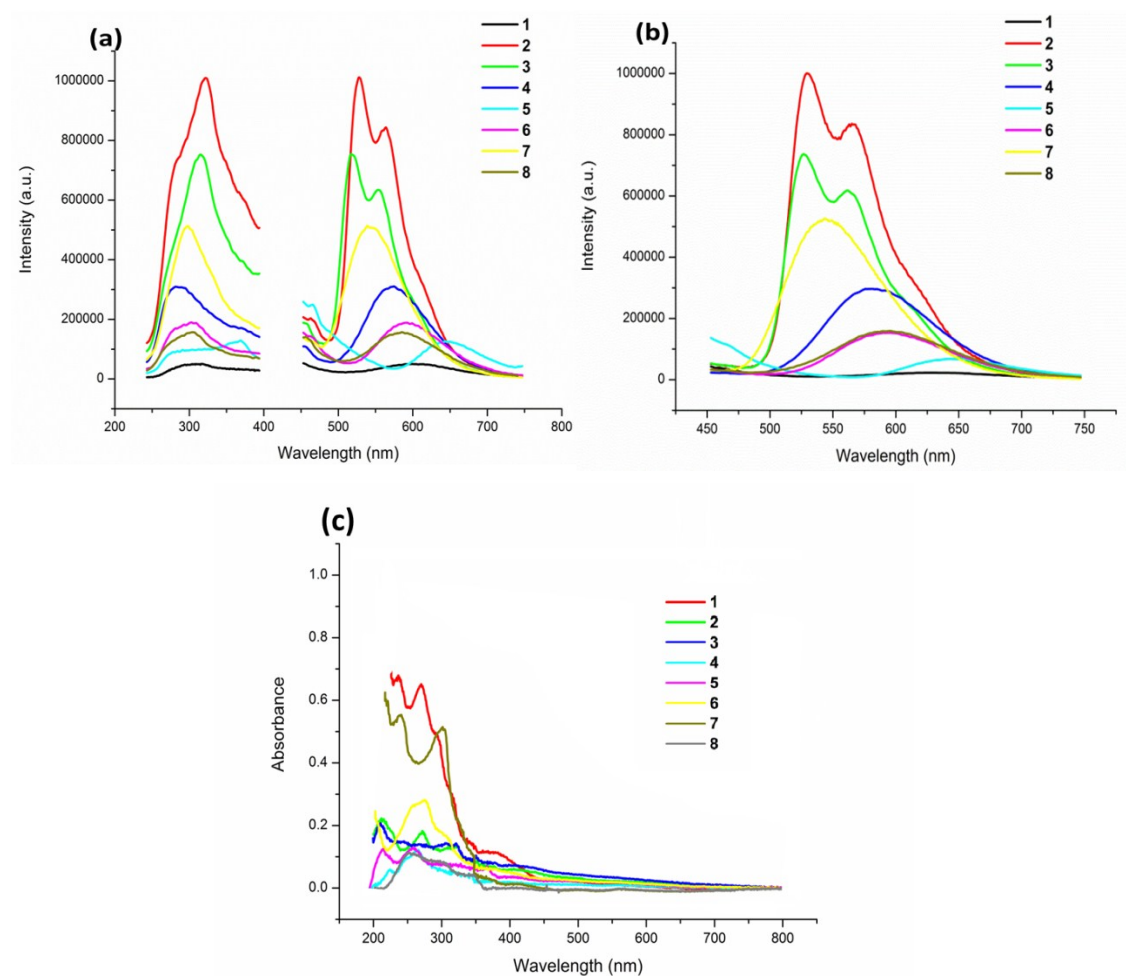


Fig. S2 (a) Excitation spectra of complexes **1–8** (2.5 μM) in DMSO. (b) Emission spectra of complexes **1–8** (2.5 μM) in DMSO with the excitation wavelength at 310 nm. (c) Absorption spectra of complexes **1–8** (2.5 μM) in acetonitrile.

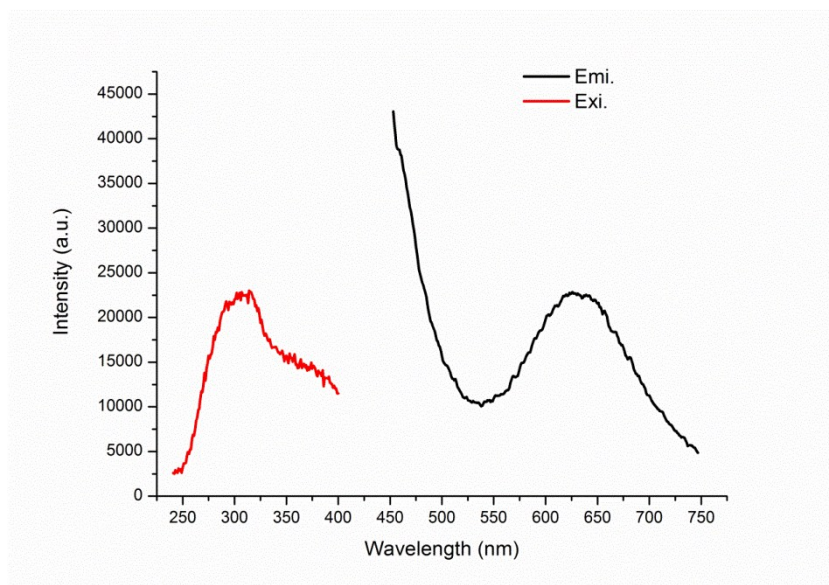


Fig. S3 Excitation spectra and emission spectra of complex **1** in DMSO with excitation wavelength at 310 nm.

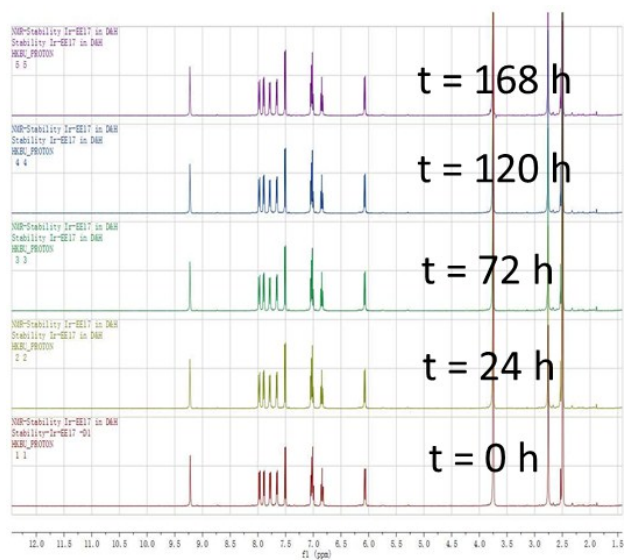


Fig. S4 ^1H NMR spectra of complex **1** (5 mM) in DMSO- d_6 /D $_2$ O (9:1) at $t = 0$ h and after incubation for 0, 24, 72, 120 and 168 h at 298 K.

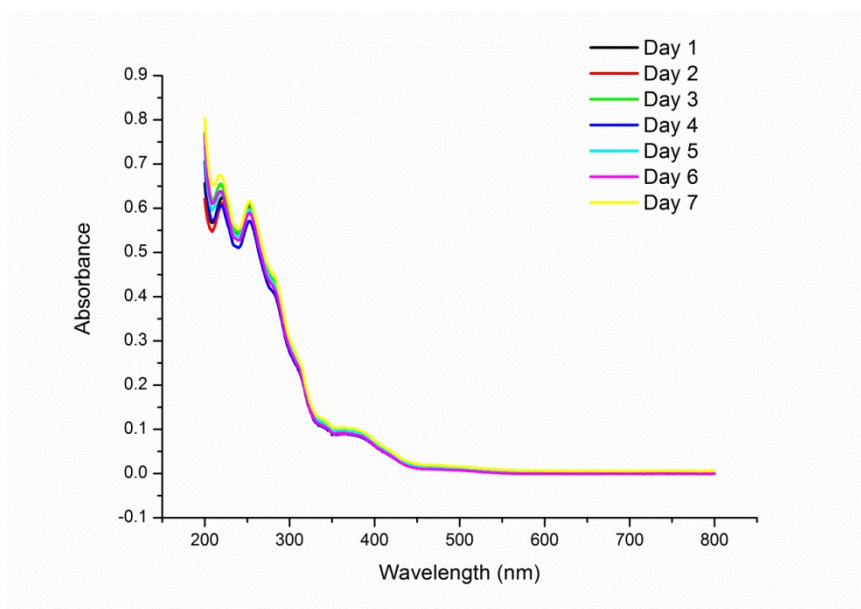


Fig. S5 UV/Vis absorption of complex **1** (2.5 μM) in acetonitrile/H $_2$ O (9:1) at $t = 0$ h and after incubation for 1, 2, 3, 4, 5, 6 and 7 days at 298 K.

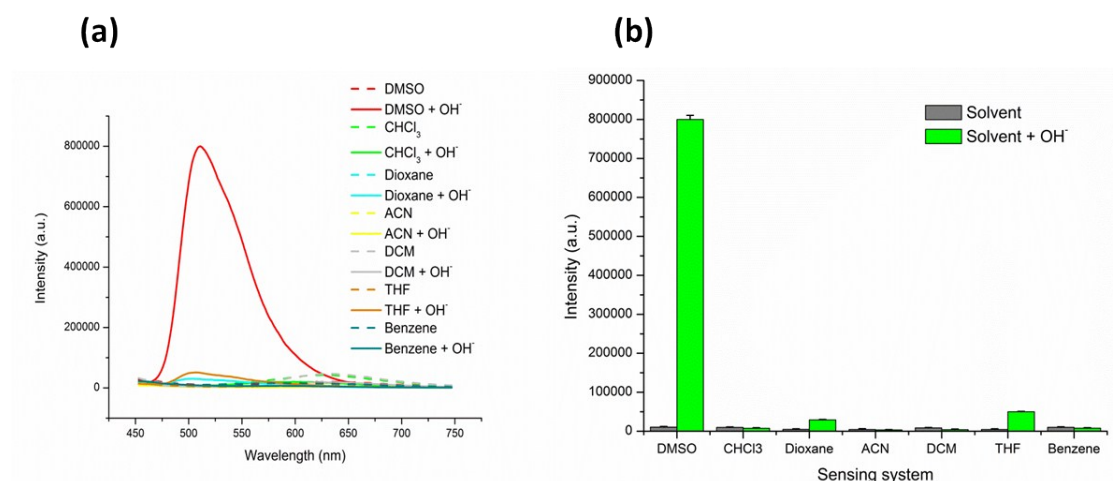


Fig. S6 (a) Emission spectra for complex **1** (2.5 μM) in the absence and presence of OH⁻ (100 mM) in different solvents (solvent/H₂O = 9:1). **(b)** Bar chart for complex **1** (2.5 μM) in the absence and presence of OH⁻ (100 mM) in different solvents (solvent/H₂O = 9:1).

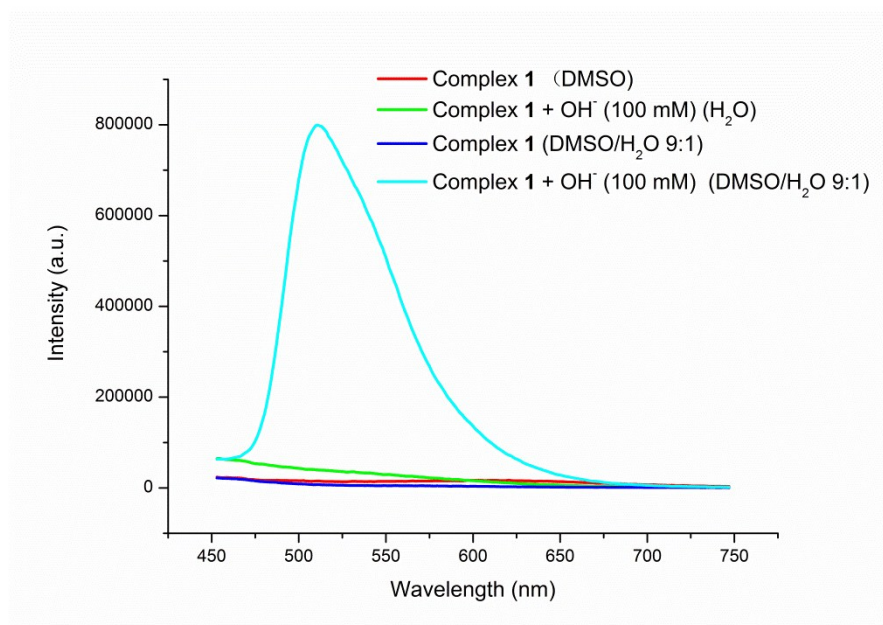


Fig. S7 Emission spectra of complex **1** (2.5 μM) in DMSO, OH⁻ solution (containing 0.5% DMSO), DMSO/H₂O (9:1), and DMSO/H₂O (9:1) with OH⁻ (100 mM).

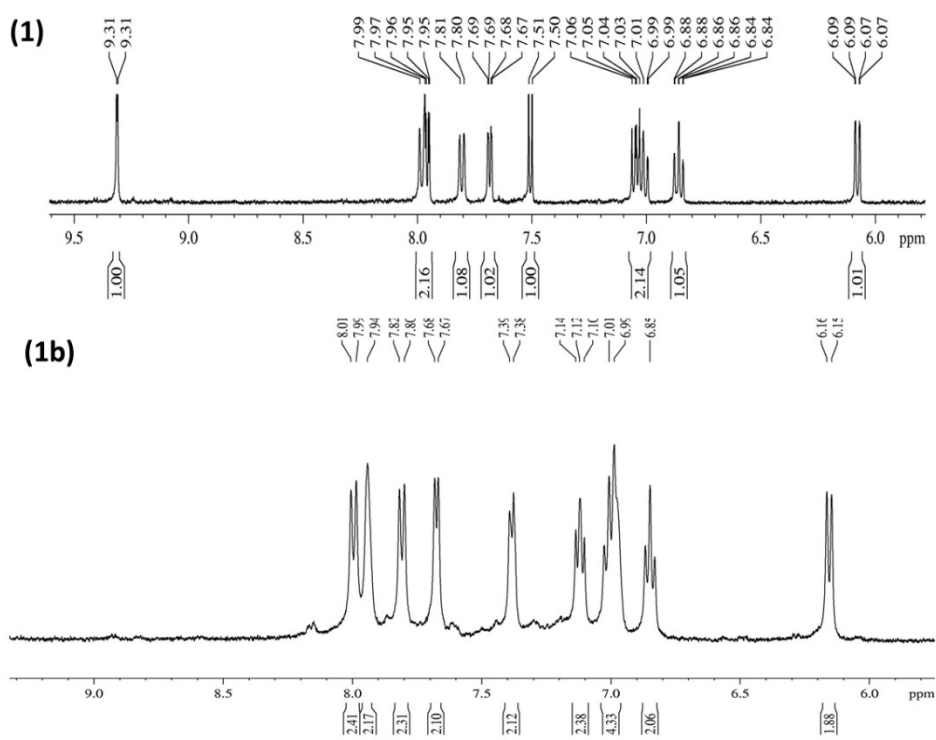
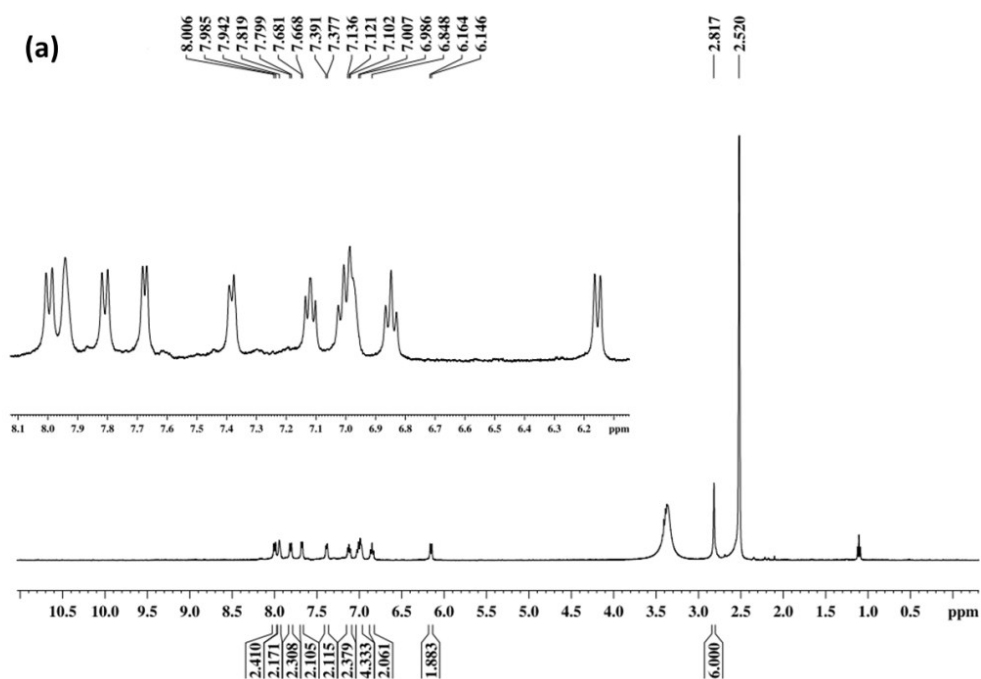
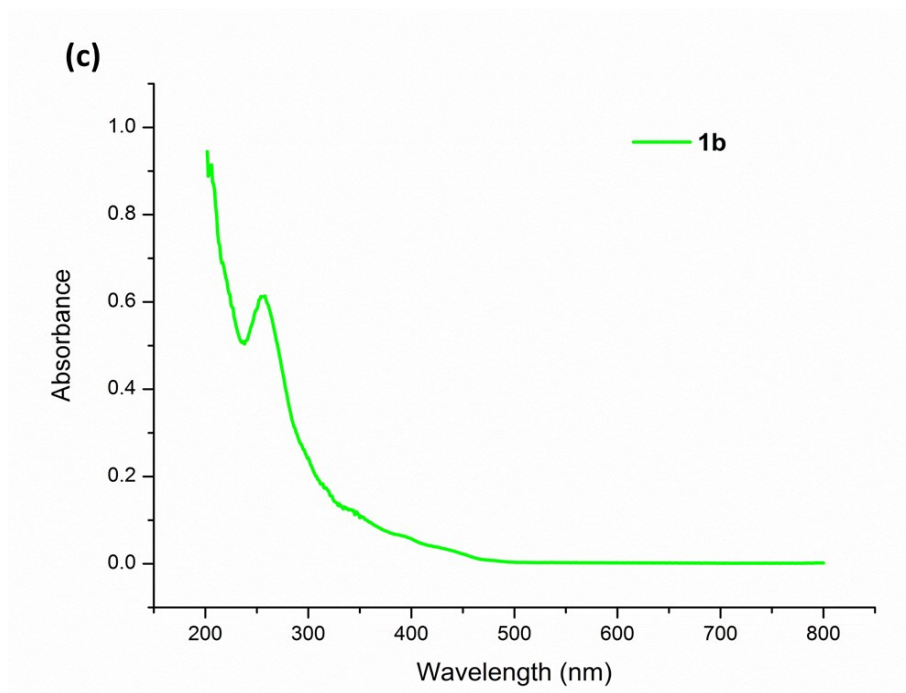
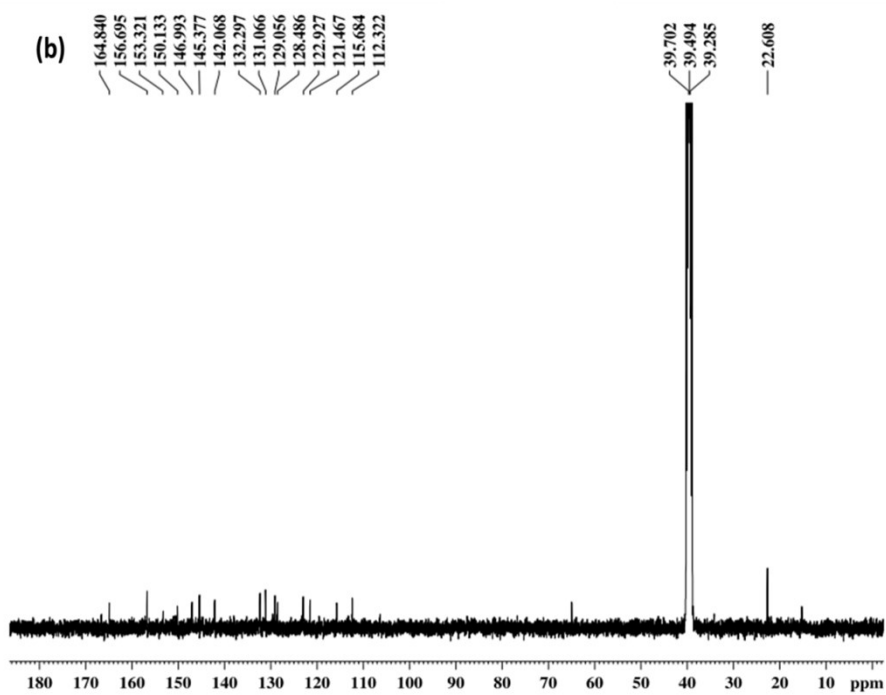


Fig. S8 ^1H NMR spectra for the aromatic region of complex **1** ($2.5\ \mu\text{M}$) with the **(1)** absence and **(1b)** presence of OH^- ($100\ \text{mM}$) in $\text{DMSO}/\text{H}_2\text{O}$ (9:1).





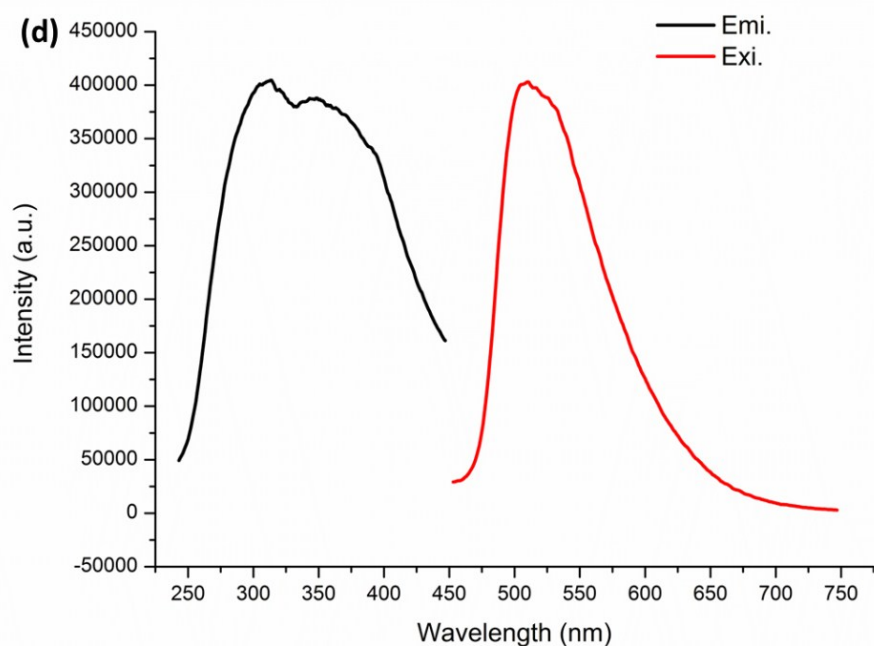


Fig. S9 (a) ^1H NMR spectra for **1b**; (b) ^{13}C NMR spectra for **1b**; (c) UV/Vis absorption of complex **1b** ($2.5\ \mu\text{M}$) in acetonitrile; (d) Excitation spectra and emission spectra of complex **1b** ($2.5\ \mu\text{M}$) in DMSO with emission and excitation wavelength at 517 nm and 310 nm, respectively.

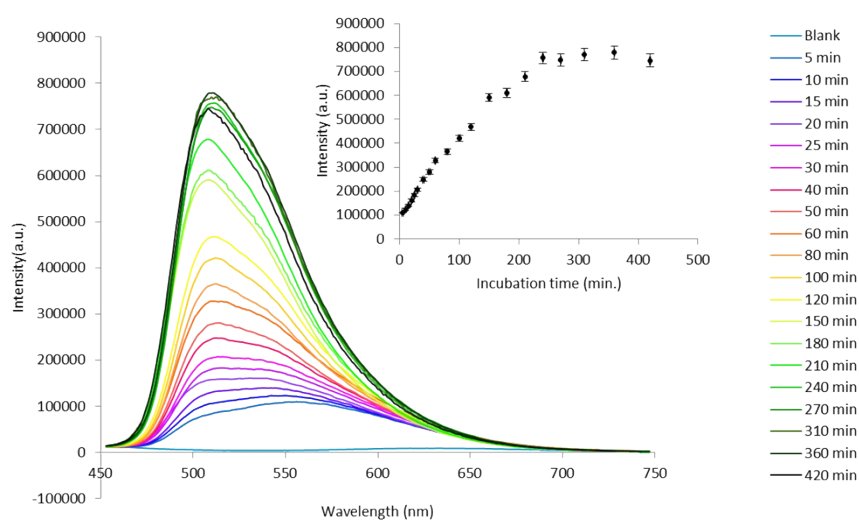


Fig. S10 Emission spectra of complex **1** ($2.5\ \mu\text{M}$) with OH^- ($100\ \text{mM}$) in DMSO/ H_2O (9:1) at different incubation times. Inset: Plot of intensity against incubation time under 517 nm.

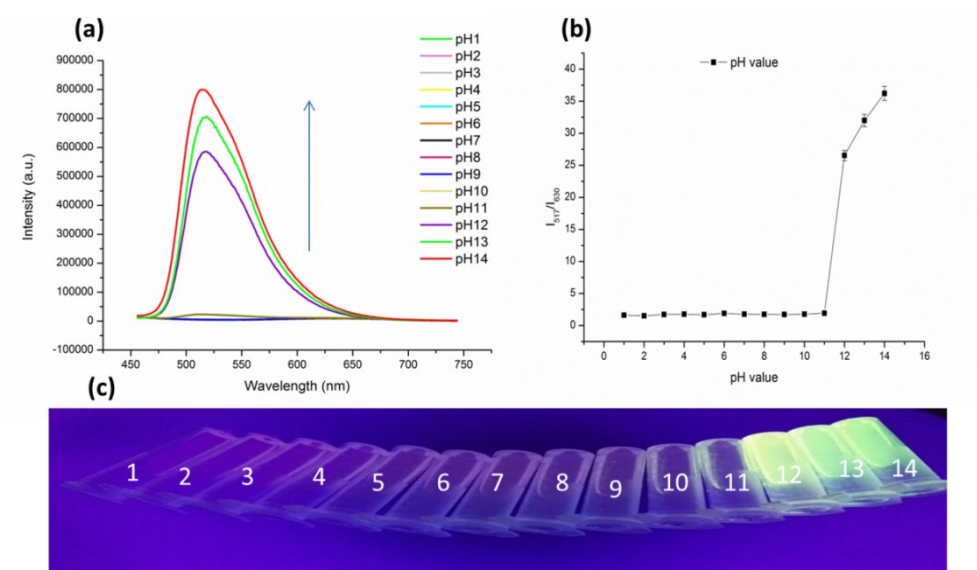


Fig. S11 (a) Emission spectra of complex **1** (2.5 μ M) in DMSO/H₂O (9:1) with the addition of solutions at different pH values. (b) Plot of I_{517}/I_{630} ratio of **1** at different pH values.

References

1. J.-B. Liu, L.-J. Liu, Z.-Z. Dong, G.-J. Yang, C.-H. Leung and D.-L. Ma, *Scientific Reports*, 2016, **6**, 36509.
2. T.-S. Kang, Z. Mao, C.-T. Ng, M. Wang, W. Wang, C. Wang, S. M.-Y. Lee, Y. Wang, C.-H. Leung and D.-L. Ma, *Journal of Medicinal Chemistry*, 2016, **59**, 4026-4031.
3. L.-J. Liu, L. Lu, H.-J. Zhong, B. He, D. W. J. Kwong, D.-L. Ma and C.-H. Leung, *Journal of Medicinal Chemistry*, 2015, **58**, 6697-6703.
4. D.-L. Ma, S. Lin, L. Lu, M. Wang, C. Hu, L.-J. Liu, K. Ren and C.-H. Leung, *Journal of Materials Chemistry B*, 2015, **3**, 4780-4785.
5. D.-L. Ma, L.-J. Liu, K.-H. Leung, Y.-T. Chen, H.-J. Zhong, D. S.-H. Chan, H.-M. D. Wang and C.-H. Leung, *Angewandte Chemie International Edition*, 2014, **53**, 9178-9182.
6. D. Hanss, J. C. Freys, G. Bernardinelli and O. S. Wenger, *European Journal of Inorganic Chemistry*, 2009, **9**, 4850-4859.
7. S. Lin, W. Gao, Z. Tian, C. Yang, L. Lu, J.-L. Mergny, C.-H. Leung and D.-L. Ma, *Chemical Science*, 2015, **6**, 4284-4290.
8. F. Garces, K. King and R. Watts, *Inorganic Chemistry*, 1988, **27**, 3464-3471.
9. Y. Tian, C.-Y. Chen, C.-C. Yang, A. C. Young, S.-H. Jang, W.-C. Chen and A. K. Y. Jen, *Chemistry of Materials*, 2008, **20**, 1977-1987.

10. H. Lu, B. Xu, Y. Dong, F. Chen, Y. Li, Z. Li, J. He, H. Li and W. Tian, *Langmuir*, 2010, **26**, 6838-6844.