Electronic Supplementary Information (ESI)

Remarkable phosphorescent sensor for acid-base vapours based on AIPE-active Ir(III) complex

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Table of Contents

1. Experimental - general information

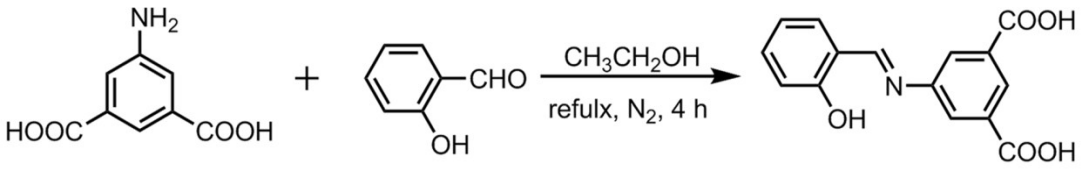
Materials obtained from commercial suppliers were used without further purification unless otherwise stated. All glassware, syringes, magnetic stirring bars, and needles were thoroughly dried in a convection oven. Reactions were monitored using thin layer chromatography (TLC). Commercial TLC plates were used and the spots were visualized under UV light at 254 and 365 nm. ^{1}H NMR spectra were recorded at 25 ºC on a Varian 500 MHz spectrometer and were referenced internally to the residual proton resonance in DMSO-d_6 (δ 2.5 ppm). Transmission electron microscopy (TEM) and electron diffraction analyses of the samples were obtained using a TECNAI F20 microscope. The samples were prepared by placing microdrops of the solution on a holey carbon copper grid. UV-vis absorption spectra were recorded on a Shimadzu UV-3100 spectrophotometer. Photoluminescence spectra were collected on an Edinburgh FLS920 spectrophotometer.

Theoretical calculations

The calculations reported here were performed using the Gaussian 09 software package.[1] The geometrical structures for iridium(III) complexes were fully optimized with *C*1 symmetry constraints by using b3LYP methods with the LANL2DZ basis set for the Ir atom and 6-31G* for the rest of the atoms.[2]

Synthesis of Schiff base (Scheme S1)

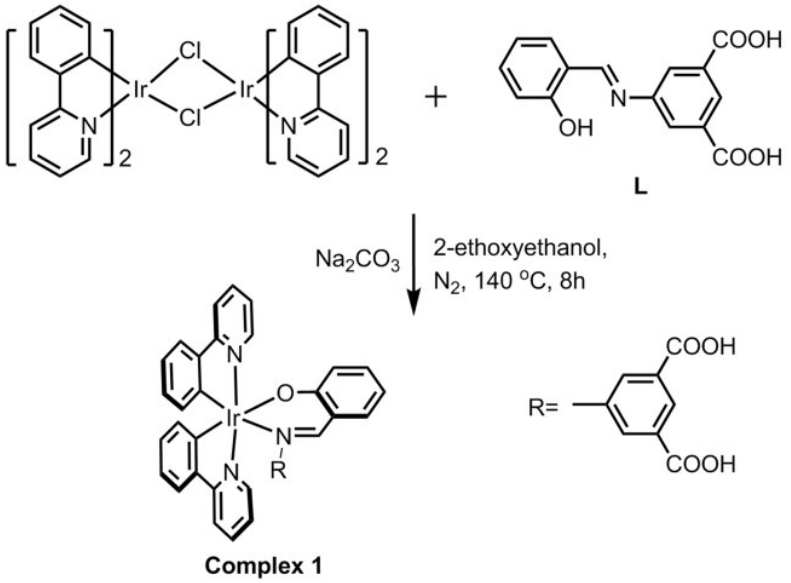
0.3622g (2 mmol) of 3,5-Diaminobenzoic acid and 0.20g (1.63 mmol) of Salicylaldehyde were refluxed in Ethanol (20 mL) at 78℃ for 5 hours under a nitrogen atmosphere. The suspension was dried and purified by silica gel column chromatography with ethyl acetate/acetone (5:1 v/v) as eluent. The Schiff base was obtained as an orange solid in 80% yield (0.37g).



Scheme S1 Synthetic route for Schiff base ligand

Synthesis of complex 1

A yellow suspension of the dichloro-bridged diiridium complex $[Ir(ppy)_2Cl]_2$ [3] (0.1528 g, 0.2 mmol), Schiff base bridging ligand (0.1140 g, 0.4 mmol) and Na_2CO_3 (0.212 g, 2 mmol) in 2-ethoxyethanol was stirred at 140 °C for 8 hours under a nitrogen atmosphere and the suspension was dried and purified by silica gel column chromatography with ethyl acetate/acetone (1:3 v/v) as eluent. The complex was obtained as an orange solid in 48% yield (0.152 g).



Scheme S2 Synthetic route for complex **1**

2. ^{1}H NMR Spectrum of complex 1 at room temperature

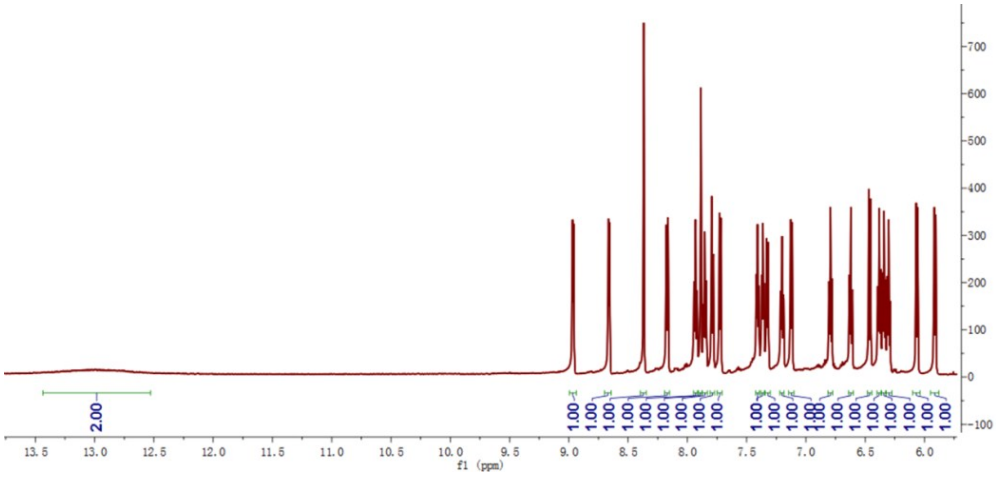


Fig. S1 ^{1}H NMR spectrum of complex **1** in DMSO-d_6 at room temperature.

3. MS Spectrum of complex 1 at room temperature

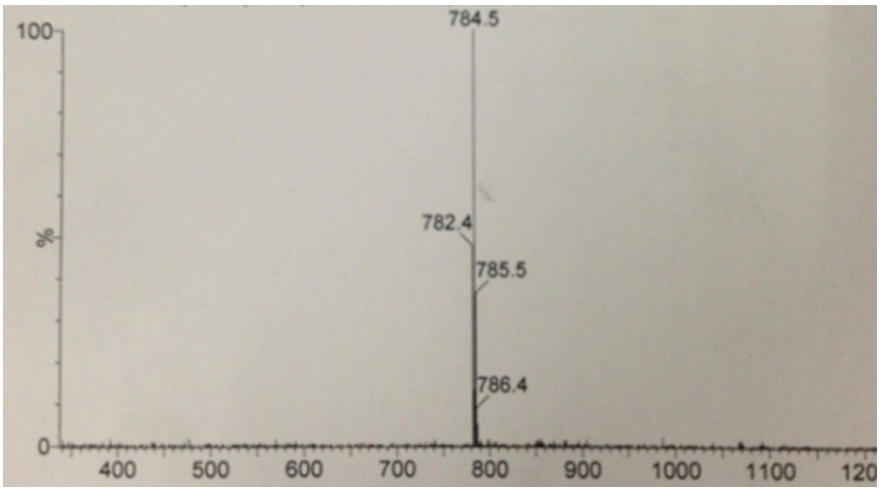


Fig. S2 MS spectrum of complex **1** at room temperature.

4. Photophysical properties

Table S1 Photophysical characteristics of complex **1**

Absorption and emission at room temperature			Emission at 77 K
$\lambda_{abs}{}^{a}$ (nm)	$\lambda_{em}{}^{b}$ (nm)	$\Phi_{em}{}^{b}$ (τ^{b}[μs])	$\lambda_{em}{}^{c}$ (nm)
404, 457	588	0.19 (0.50)	579

[a] Measured in DMSO (1.0×10^{-4} M) solution. [b] Measured in solid state (λ_{exc} = 400 nm; error for Φ_L ± 5 %). [c] In DMSO solution.

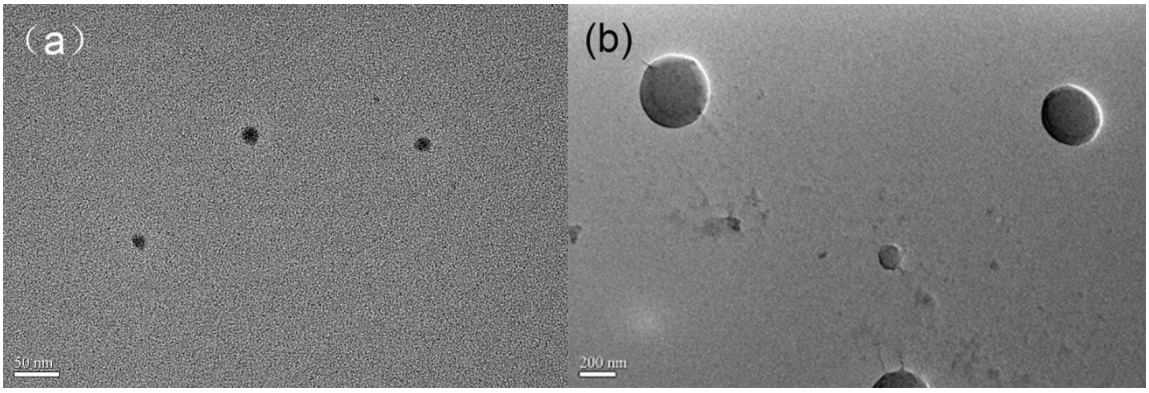


Fig. S3 TEM image of nanoaggregates of complex **1** formed in DMSO–H_2O mixtures with 0% (a) and 90% (b) water fraction.

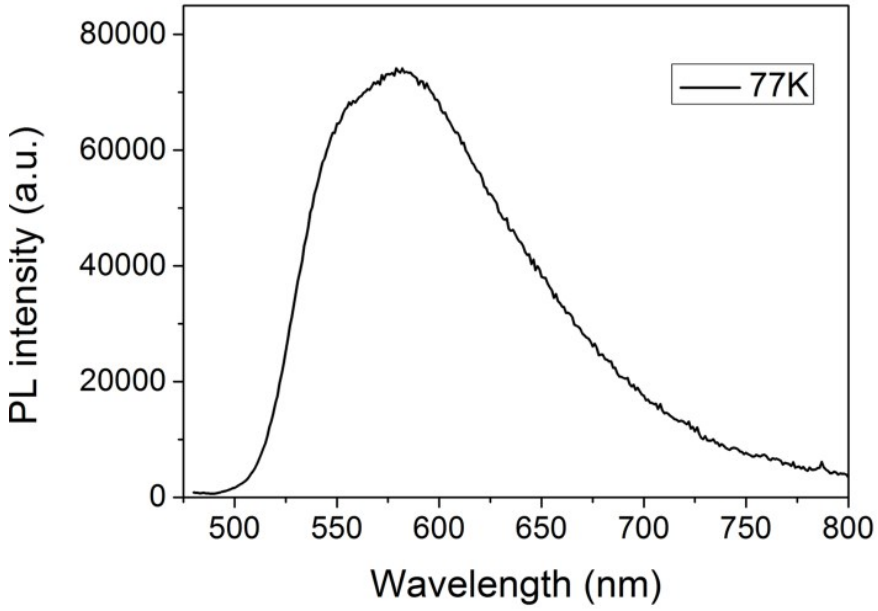


Fig. S4 Emission spectrum of complex **1** in DMSO solution (10^{-5} M) at 77 K.

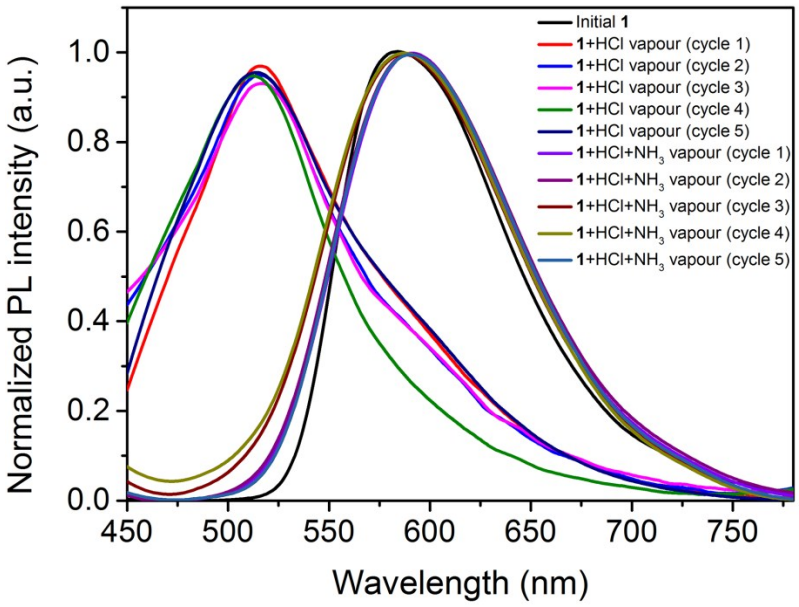


Fig. S5 The normalized PL spectra of the complex **1** powder repeated fuming with HCl and NH_3 vapours.

Fig. S6 Photographs of pH test strips fuming with TFA, HCl, HCOOH, CH_3COOH vapours.

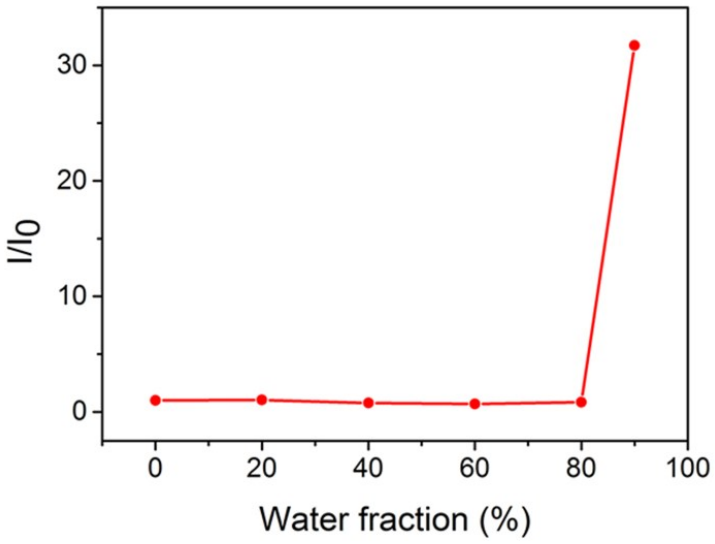


Fig. S7 Variations of the relative emission intensity (I/I_0) with the increasing f_w.

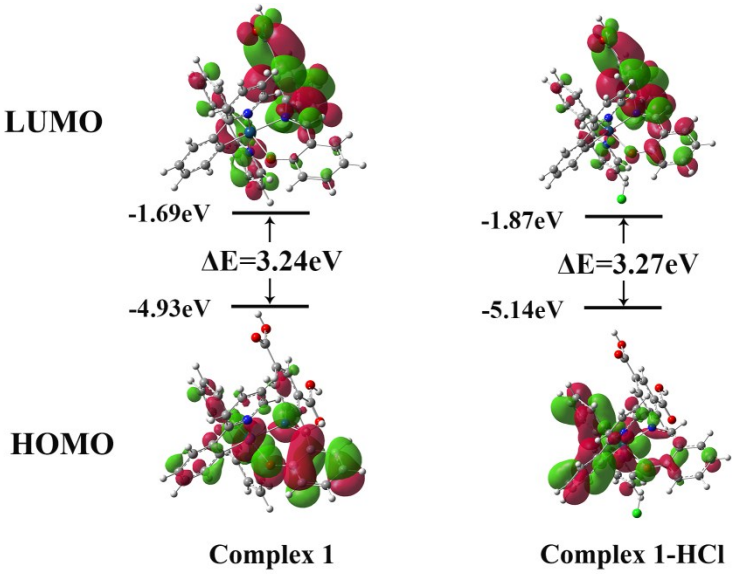


Fig. S8 Theoretically calculated frontier orbitals of complex **1** and complex **1**-HCl.

5. Reference

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