Electronic Supplementary Information (ESI)

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

Dan Li, ‡‡ Guangfu Li, ‡‡ Weilong Che, ‡ Dongxia Zhu,*a and Zhongmin Su,*a

*a Key Laboratory of Nanobiosensing and Nanobioanalysis at Universities of Jilin Province, Department of Chemistry, Northeast Normal University, 5268 Renmin Street, Changchun, Jilin Province 130024, P.R. China.

E-mail: zmsu@nenu.edu.cn; zhudx047@nenu.edu.cn.
Table of Contents

1. Experimental - general information .......................................................... S3
2. $^1$H NMR spectrum of complex 1 at room temperature ....................... S4
3. MS spectrum of complex 1 at room temperature .................................. S5
4. Photophysical properties ......................................................................... S5
5. Reference .................................................................................................. S8
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 C1 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 ºC for 5 hours under a nitrogen atmosphere. The suspension was dried and purified by silica gel column chromatography with ethyl acetate/acetonc (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 \([\text{Ir}(ppy)_2\text{Cl}]_2\)\(^{[3]}\) (0.1528 g, 0.2 mmol), Schiff base bridging ligand (0.1140 g, 0.4 mmol) and \(\text{Na}_2\text{CO}_3\) (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).

\[
\text{Ir}^{[3]}(ppy)_2\text{Cl} + \text{L} \xrightarrow{\text{Na}_2\text{CO}_3, 2\text{-ethoxyethanol, N}_2, 140 \degree\text{C, 8h}} \text{Complex 1}
\]

Scheme S2 Synthetic route for complex 1

2. \(^1\text{H NMR Spectrum of complex 1 at room temperature}\)

![1H NMR spectrum of complex 1 in DMSO-\(d_6\) at room temperature.](image)

**Fig. S1** \(^1\text{H NMR spectrum of complex 1 in DMSO-}d_6\text{ 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

<table>
<thead>
<tr>
<th>Absorption and emission at room temperature</th>
<th>Emission at 77 K</th>
</tr>
</thead>
<tbody>
<tr>
<td>$\lambda_{\text{em}} , ^a$ (nm)</td>
<td>$\lambda_{\text{em}} , ^b$ (nm)</td>
</tr>
<tr>
<td>404, 457</td>
<td>588</td>
</tr>
</tbody>
</table>

$^a$ Measured in DMSO (1.0×10⁻⁴ M) solution. $^b$ Measured in solid state ($\lambda_{\text{exc}} = 400$ nm; error for $\Phi_L \pm 5 \%$). $^c$ In DMSO solution.
Fig. S3 TEM image of nanoaggregates of complex 1 formed in DMSO–H₂O 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$_3$COOH 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