***Supplementary data for***

**Carbazolyl-modified neutral Ir(III) complexes for efficient detection of picric acid in aqueous media**

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**Synthesis and characterization**

**Synthesis of ligands L1 and L2**

Cyclometalating ligands were synthesized with reference to the methods reported in the literature [1]. Brominated heterocyclic aromatic hydrocarbons (0.5 mmol), 4-(9-carbazolyl)phenylboronic acid (0.75 mmol, 215.35 mg), K2CO3 (1 mmol, 138.21 mg), and Pd(OAc)2 (1.5 mol%, 1.69 mg) were added to a mixture of 8 mL of anhydrous EtOH/H2O (3:1, V/V), and the reaction was carried out under air at 80℃ for 10-30 min. After the reaction, the cyclometalating ligands **L1** and **L2** were further purified by silica column chromatography using petroleum ether and ethyl acetate as eluents.



**Figure S1** Synthesis routes of the cyclometalating ligands **L1** and **L2**.



**Figure S2** Synthetic routes for complexes **1** and **2**.

**1**: Yield: 39%, a yellow solid. 1H NMR (400 MHz, CDCl3) *δ* 8.50 (d, *J* = 4.8 Hz, 2H), 8.02 (d, *J* = 7.6 Hz, 4H), 7.88-7.83 (m, 4H), 7.65-7.61 (m, 2H), 7.30-7.25 (m, 6H), 7.20-7.17 (m, 6H), 7.15-7.12 (m, 2H), 7.06 (d, *J* = 6.8 Hz, 2H), 6.46 (d, *J* =2.0 Hz, 2H), 5,34 (s, 1H), 1.88 (s, 6H). 13C NMR (100 MHz, CDCl3) *δ* 184.92, 167.63, 148.63, 148.26, 143.72, 140.36, 137.57, 137.37, 130.78, 125.51, 124.80, 123.19, 121.71, 119.91, 119.51, 118.70, 118.67, 110.51, 100.79, 28.88. MALDI-TOF-MS (*m*/*z*) calcd. for C51H37N4O2Ir [M]+: 930.2546, found: 930.2491.

**2**: Yield: 45%, a yellow solid. 1H NMR (400 MHz, CDCl3) *δ* 8.31 (d, *J* = 5.6 Hz, 2H), 8.02 (d, *J* = 7.6 Hz, 4H), 7.80 (d, *J* = 8.0 Hz, 2H), 7.66 (s, 2H), 7.29-7.25 (m, 6H), 7.19-7.16 (m, 6H), 7.12-7.09 (m, 2H), 6.88 (d, *J* = 6.0 Hz, 2H), 6.46 (d, *J* = 2.0 Hz, 2H), 5.31 (s, 1H), 2.45 (s, 6H), 1.87 (s, 6H). 13C NMR (100 MHz, CDCl3) *δ* 184.80, 164.91, 148.02, 147.80, 143.99, 140.38, 138.17, 137.03, 131.54, 130.77, 125.44, 124.22, 123.12, 119.86, 119.42, 118.53, 118.24, 110.54, 100.79, 28.96, 18.51. MALDI-TOF-MS (*m*/*z*) calcd. for C53H41N4O2Ir [M]+: 958.2859, found: 958.2875.

**Photophysical and AIPE properties**





**Figure S3** UV-Vis absorption and normalized emission spectra of **1** and **2**.



**Fig. S4** Phosphorescence decay traces of (ppy)2Ir(acac) (a), **1** (b), and **2** (c) in deoxygenated CH2Cl2 (10 μM).

**Table S1** Photophysical data of complexes **1** and **2**.

|  |  |  |  |  |
| --- | --- | --- | --- | --- |
| Complexes | *λ*abs *a* (nm) | *λ*em *b* (nm) | *Ф*PL *c* | *τ* *d* (μs) |
| **1** | **278** (2.60)  344 (0.36) | **517** | 0.18 | 2.60 |
| **2** | **278** (2.59)  334 (0.34) | **516** | 0.27 | 3.44 |

*a* Measured in CH2Cl2 at a concentration of 10 μM and extinction coefficients (104 M-1 cm-1) are shown in parentheses. *b* The maximum emission values are bold. *c* The quantum yields (*Ф*solution) in deoxygenated CH2Cl2 were measured with [Ir(ppy)2(acac)] (*Ф*PL = 0.34) as a standard. *d* In deoxygenated CH2Cl2.

**Figure S5** shows the UV-Vis absorption spectra of **1** and **2** in THF/H2O with various water fractions (*c* = 10 μM). The spectra indicate a peak at 278 nm for **1** and **2** in the range of 0-60% water fraction. As the water fraction increases, the absorbance gradually decreases, but the absorption wavelength remains constant. The absorption spectra do not show significant changes beyond 300 nm. At the 70% water fraction, the absorbances of **1** and **2** decrease continuously at 278 nm, and there are no significant changes in the absorption spectra of **1** and **2** beyond 300 nm. However, at 80% and 90% water fractions, the absorption spectra of **1** and **2** change significantly, resulting in a red shift at different degrees and increased absorbances beyond 300 nm. It is worth noting that the absorption spectra of **1** and **2** change significantly only at 80% and 90% water fractions. The changes in the absorption spectra can be attributed to the aggregation of the complex monomers and increased scattering as the increase of water proportions.





**Figure S5** UV-Vis absorption spectra of **1** and **2** at 10 μM in THF/H2O with various water fractions.

**Theoretical calculations**

DFT calculations were employed to analyze the electronic distributions of **1** and **2**. The highest occupied molecular orbitals (HOMOs) of both complexes are primarily located on the iridium centers and the phenyl and carbazolyl moieties of the cyclometalating ligands, whereas the lowest unoccupied molecular orbitals (LUMOs) are primarily distributed on the aryl and pyridine rings of the cyclometalating ligands. As shown in **Figure S5**, the energy gaps (*E*g) of **1** and **2** are 3.43 and 3.41 eV, respectively. It is evident that introducing a methyl group results in a small elevation of HOMO and LUMO levels of the complexes.



**Figure** **S6** Calculated energy level diagrams of **1** and **2**.

**Sensing of PA**



**Figure S7** The emission spectra of **2** in 11 blank samples in THF/H2O (*f*w = 90%, 10 μM).



**Figure S8** The linear graph of the emission intensity of **2** *vs*. the concentrations of PA.

The value of *σ* for **2** was calculated according to the following equation:

X*i* (i = 1, 2, 3…11) represents the emission intensity of each blank sample, X represents the mean value of the emission intensity, *n* represents the number of blank samples.



**Figure S9** Photos of the mixtures of **2** in THF/H2O with various ionic compounds under 365 nm UV light.

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**Figure S10** The normalized emission spectra of **2** in THF/H2O after addition of different concentrations of PA.

**NMR spectra and HRMS of 1 and 2**



**Figure S11** 1H NMR spectrum of **1** in CDCl3.



**Figure S12** 13C NMR spectrum of **1** in CDCl3.



**Figure S13** 1H NMR spectrum of **2** in CDCl3.



**Figure S14** 13C NMR spectrum of **2** in CDCl3.



**Figure S15** The HRMS of **1**.



**Figure S16** The HRMS of **2**.

**Reference**

[1] Liu, C.; Rao, X.; Lv, X.; Qiu, J.; Jin, Z. Substituent effects on the photophysical and electrochemical properties of iridium(III) complexes containing an arylcarbazolyl moiety. *Dyes Pigm.* **2014**, *109*, 13-20.