Supporting Information for

# Phosphorescent chemosensor for Hg<sup>2+</sup> and acetonitrile based on iridium(III) complex

Qun-bo Mei, \* <sup>*a*</sup> Yuan-hui Guo, <sup>*a*</sup> Bi-hai Tong, <sup>*b*</sup> Jie-Na Weng, <sup>*a*</sup> Bin Zhang , <sup>*a*</sup> and Wei Huang<sup>\**a*</sup>

<sup>a</sup>Key Laboratory for Organic Electronics & Information Displays (KLOEID), Institute of Advanced Materials (IAM), Nanjing University of Posts and Telecommunications (NUPT), Nanjing 210046, China

<sup>b</sup> College of Metallurgy and Resources, Anhui University of Technology, Ma'anshan, Anhui 243002, P. R. China;

\* Corresponding author. e-mail: iamqbmei@njupt.edu.cn; iamwhuang@njupt.edu.cn

## **Table of Contents**

**1. Materials and Methods** 

2. Metal cation titration of Ir1 and solvent titration of Ir2

3. Detection limit of Ir(dpp)<sub>2</sub>(dtc) in THF or in MeCN

4. Computational Details

5. GC-MS, <sup>1</sup>H-NMR, <sup>13</sup>C NMR Spectra and EI-MS spectra

6. Titration curve of Ir(dpp)<sub>2</sub>(dtc) with Hg<sup>2+</sup> in MeCN

7. Electrochemical response of Ir(dpp)<sub>2</sub>(dtc) to Hg<sup>2+</sup>(dissolved in MeCN)

8. UV-Visable absorption and emission spectra of addition different mental ions(dissolved in MeCN) to Ir1

9. Selective luminescence response of Ir2 to various solvents

10. Structures and orbital properties of Ir(dpp)<sub>2</sub>(dtc) and Ir(dpp)<sub>2</sub>(MeCN)<sub>2</sub><sup>+</sup>

#### 1. Materials and Methods

All chemicals and solvents were purchased from commercial suppliers and treated according to the literature. <sup>1</sup>H NMR spectra were recorded with a Varian spectrometer at 400 MHz. Mass spectra were obtained on a Shimadzu matrix-assisted laser desorption/ionization time-of-flight mass spectrometer (MALDI-TOF-MS) or LCQ Fleet ESI mass spectrometer. UV-Vis absorption spectra were measured on an UV-3600 Shimadzu UV/Vis spectrophotometer. Emission experiments at room temperature were measured on an Edinburgh Instruments Xe-920 spectrometer. Electrochemical measurements were performed with an Eco Chemie Autolab at room temperature in DMF containing 0.1M tetrabutyl ammonium hexafluorophosphate (Bu<sub>4</sub>NPF<sub>6</sub>). All measurements were carried out in a one-compartment cell under N<sub>2</sub> gas, equipped with a glassy-carbon working electrode, a platinum wire counter electrode, and a Ag/AgNO<sub>3</sub> reference electrode. The scan rate was 50 mV/s. All solutions were deoxygenared by argon bubbling for at least 10 min.

#### 2. Metal cation titration of Ir1 and solvent titration of Ir2

Spectrosphotometric titrations were performed on  $20\mu$ M of Ir(dpp)<sub>2</sub>(dtc)(Ir1) in DCM for both UV-Vis absorption and emission spectra. The solution(2.5mL) was added into a quartz cuvette, the UV-Vis absorption and emission spectra of samples were recorded upon addition of aliquots of fresh mercury(II), respectively. Furthermore, eight other kind of cations were tested for selectivity using the same methods.

The Ir2(2.5mL,  $20\mu$ M) was obtained by adding 1.2 equiv of mercury(II) to Ir1(2.5mL,  $20\mu$ M) in presence of DCM and THF, the emission spectra of samples were recorded upon addition of various solvents, respectively. Furthermore, eight other kind of solvents were tested for selectivity using the same methods.

#### 3. Detection limit of Ir(dpp)<sub>2</sub>(dtc) in THF or in MeCN

The detection limit was determined from the fluorescence titration data based on a reported method.<sup>1</sup> The fluorescence spectrum of sensor  $Ir(dpp)_2(dtc)$  was measured by five times and the standard deviation of blank measurement was achieved. To gain the slop, the fluorescent intensity data at 568 nm was plotted as a concentration of  $Hg^{2+}$ . So the detection limit was calculated with the following equation:

Detection limit=3o/K

$$\sigma = \sqrt{\frac{\sum (x_i - \bar{x})^2}{N - 1}}.$$

Where  $\sigma$  is the standard deviation of blank measurement, N is the number of tests, and K is the slop between the fluorescence versus Hg<sup>2+</sup> concentration.

## (1) Detection limit of Ir(dpp)<sub>2</sub>(dtc) in THF



**Figure S1**. Normalized response of fluorescence signal of  $Ir(dpp)_2(dtc)$  in THF  $(2.0 \times 10^{-5} \text{ M})$  in the presence of increasing amount of Hg<sup>2+</sup> (0-1.0 equiv.) predissolved in DCM solution ( $\lambda_{em}$ =568nm).

Detection limit=3o/K=3.33/49.67=0.067µM

The sensor allow determination of  $Hg^{2+}$  in THF in the working range of 4.0  $\mu M$ —16.0  $\mu M$  with a detection limit of 0.067  $\mu M.$ 

(2) Detection limit of Ir(dpp)<sub>2</sub>(dtc) in MeCN



**Figure S2**. Normalized response of fluorescence signal of  $Ir(dpp)_2(dtc)$  in THF  $(2.0 \times 10^{-5} \text{ M})$  in the presence of increasing amount of Hg<sup>2+</sup> (0-1.0 equiv.) predissolved in MeCN solution ( $\lambda_{em}$ =568nm).

Detection limit=3o/K=3.27/46.63=0.071µM

The sensor allow determination of  $Hg^{2+}$  in MeCN in the working range of 2.0  $\mu$ M-16.0  $\mu$ M with a detection limit of 0.071 $\mu$ M.

## **4.** Computational Details

The structures and orbital properties were studied by performing density functional theory calculation using the Beck's three parameterized Lee-Yang-Parr exchange functional (B3LYP) using a suite of Gaussian 03 program. The split valance 6-31G\* basis sets were used except iridium metal for which the LanL2DZ effective core potential was used.



Figure S3. The calculated model molecule of iridium(III) complexes.



## 5. GC-MS, <sup>1</sup>H-NMR, <sup>13</sup>C NMR Spectra and EI-MS spectra





Figure S6. <sup>13</sup>C NMR of 4, 6-Diphenyl-pyrimidine in CDCl<sub>3</sub>.



**Figure S8**. <sup>13</sup>C NMR of Ir(dpp)<sub>2</sub>(dtc) in CDCl<sub>3</sub>



Figure S10. EI-MS of [Ir(dpp)<sub>2</sub>(MeCN)<sub>2</sub><sup>+</sup>]ClO<sub>4</sub><sup>-</sup>

# 6. Titration curve of Ir(dpp)<sub>2</sub>(dtc) with Hg<sup>2+</sup> in MeCN



Figure S11. Titration curve of Ir1 with  $Hg^{2+}$  (dissolved in MeCN) (obtained from Fig. 3)

## 7. Electrochemical response of Ir(dpp)<sub>2</sub>(dtc) to Hg<sup>2+</sup>(dissolved in MeCN)



**Figure S12**. Electrochemical response of **Ir1** to Hg<sup>2+</sup>(dissolved in MeCN)

# 8. UV-Visable absorption and emission spectra of addition different mental ions(dissolved in MeCN) to Ir1



Figure S13.UV-Visable absorption and emission spectra of addition different mental ions in MeCN to Ir1 in DCM







intensity after addition of  $MeCN(1\mu L)$  to the above solutions. (1, n-hexane; 2, DMF; 3, petroleum ether; 4, water; 5, ethyl acetate; 6, acetic acid; 7, ethanol; 8, DMSO; 9, MeCN; 10, blank).



## 10. Structures and orbital properties of Ir(dpp)<sub>2</sub>(dtc) and Ir(dpp)<sub>2</sub>(MeCN)<sub>2</sub><sup>+</sup>

Figure S15. Computed isodensity surface of the HOMO and LUMO obitals of iridium(III) complexes

## **References:**

(a) Yamin Li, Y.M.; Zhang, X.L.; Zhu, B.C.; Yan, J.L.; Xu, W.P. Analytical Sciences 2010, 26, 1077; (b) Yang, X.F.; Wang, L.P.; Xu, H.M.; Zhao, M.L. Analytica Chimica Acta 2009, 631, 91; (c) Yang, Y.; Jiang, J.H.; Shen, G.L.; Yu, R.Q. Analytica Chimica Acta 2009, 636, 83; (d) Ma, Q.J.; Zhang, X.B.; Zhao, X.H.; Jin, Z.; Mao, G.J.; Shen, G.L.; Yu, R.Q. Analytica Chimica Acta 2010, 663, 85.