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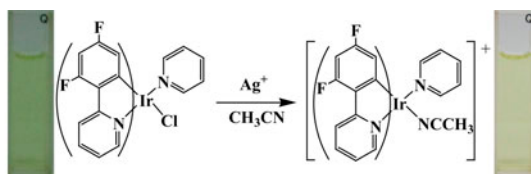
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## Synthesis, crystal structure, and application as a $\text{Ag}^+$ chemodosimeter of phosphorescent iridium complexes

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A Selective Phosphorescent and Chromogenic Chemodosimeter was prepared for silver ion due to the interaction between chloride anion and silver ion.

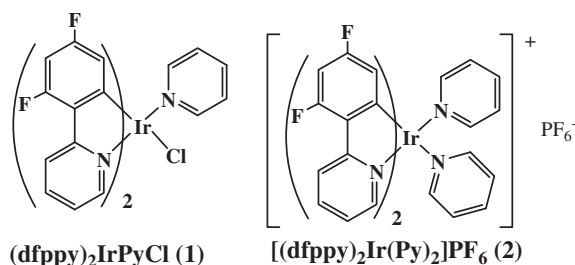
The syntheses and crystal structures of two iridium complexes,  $(\text{dfppy})_2\text{IrPyCl}$  (**1**) and  $[(\text{dfppy})_2\text{Ir}(\text{Py})_2]\text{PF}_6$  (**2**), are reported. **1** can selectively detect  $\text{Ag}^+$  with UV–vis absorption and emission spectra. In the presence of  $\text{Ag}^+$ , the obvious decrease of the luminescence intensity at 476 nm was observed, which could be monitored by the naked eyes. The phosphorescence quantum yield decreases from 0.024 to 0.012. No obvious changes of the luminescence intensity were observed upon addition of a large excess of other transition metal ions. Due to the strong interaction between chloride and  $\text{Ag}^+$ , the special chemical reaction induced by  $\text{Ag}^+$  is responsible for the significant change of absorption and luminescence spectra.

*Keywords:* Iridium complex; Chemodosimeter; Silver ions; Phosphorescence

### 1. Introduction

Fluorescent chemosensors for cations have received attention by scientists because of their unique properties such as selectivity, sensitivity, and potential application in biological systems [1, 2]. Phosphorescent iridium complexes based on metal-to-ligand charge transfer

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Scheme 1. The chemical structure of iridium complexes.

transition ( $^3MLCT$ ) exhibit many advantageous photophysical properties, such as large Stokes shifts and tunable emission wavelengths, and high quantum yield. With the advantages they have, iridium complexes have been applied in organic light-emitting diodes [3], catalysts [4], chemosensors [5, 6], and bioimaging in living cells [6].

Design and synthesis of chemosensors for detecting  $Ag^+$  have attracted attention because excess  $Ag^+$  leads to serious environmental pollution [7]. As  $Ag^+$  has a strong oxidation, it can also cause symptoms of internal organs oedema in humans. Because the human body does not have the mechanism of metabolism of  $Ag^+$ , there is no effective antidote for  $Ag^+$  poisoning [8]. Therefore, quick and efficient detection of  $Ag^+$  is an important issue in environmental science, biochemistry, and medicine. Traditional methods for detection of  $Ag^+$  include graphite furnace atomic absorption spectrometry, flame atomic absorption spectrometry, coupled plasma absorption atomic emission spectrometry, and inductively coupled plasma mass spectrometry [9]. However, the disadvantage of pre-treatment for the sample brings trouble for detection. During the past few years, a number of  $Ag^+$ -selective chemosensors based on organic small molecules [10], polymers [11], and nanoparticles [12] have been investigated by utilizing their chromogenic and fluorogenic property. Compared to relatively well-developed chemosensors, the design for chemical reaction-based chemodosimeters with short equilibrium time appears necessary. In this article, we reported the synthesis and crystal structure of two iridium complexes,  $(dfppy)_2IrPyCl$  (1) and  $[(dfppy)_2Ir(Py)_2]PF_6$  (2) (scheme 1). 1 can be used as a fluorogenic and chromogenic chemodosimeter for detection of  $Ag^+$ . The mechanism of this detection process was also explored, which is due to the strong chemical interaction between  $Ag^+$  and chloride.

## 2. Experimental

### 2.1. General

Iridium trichloride hydrate was purchased from Shanghai Jiuyue Chemical Company. 2-(4',6'-Difluorophenyl)pyridine (dfppy) was purchased from Shanghai Ruiyi Medical Tech. Co., Ltd and 2-Ethoxyethanol was obtained from Acros. Other reagents were obtained from Sinopharm Chemical Reagent Co., Ltd. Commercially available chemical reagents were used without purification.  $^1H$  NMR spectra were recorded with a Bruker DMX400. Electrospray ionization mass spectra (ESI-MS) were measured on a Micromass LCTTM system. The absorption and emission spectra were recorded using a UV-7502PC Xinmao spectrophotometer and a Varian Cary Eclipse Fluorescence Spectrophotometer (America),

respectively. Luminescence quantum yields of these complexes in aerated  $\text{CH}_3\text{CN}$  solution were measured using an aerated aqueous solution of  $[\text{Ru}(\text{bpy})_3]\text{Cl}_2$  ( $\phi = 0.028$ ) as the standard solution.

Spectrophotometric titrations of **1** (20  $\mu\text{M}$ ) were assayed in  $\text{CH}_3\text{CN}$ . Typically, aliquots of fresh cations of nitrates ( $\text{Ag}^+$ ,  $\text{Ca}^{2+}$ ,  $\text{Cd}^{2+}$ ,  $\text{Co}^{2+}$ ,  $\text{Cr}^{3+}$ ,  $\text{Cu}^{2+}$ ,  $\text{K}^+$ ,  $\text{Mg}^{2+}$ ,  $\text{Na}^+$ ,  $\text{Ni}^{2+}$ ,  $\text{Pb}^{2+}$ ,  $\text{Fe}^{3+}$ , and  $\text{Mn}^{2+}$ ) were added. The solution was incubated for 5 min. The UV-vis absorption and fluorescent spectra of the samples were recorded.

## 2.2. Synthesis of **1** and **2**

The chloride-bridged dimer  $[(\text{dfppy})_2\text{Ir}(\mu\text{-Cl})_2(\text{dfppy})_2]$  was synthesized according to previous literature [13]. The chloride-bridged dimer (304 mg) was dissolved in  $\text{CH}_2\text{Cl}_2/\text{CH}_3\text{OH}$  (48 mL, 2 : 1 v/v) under nitrogen. To this solution, two equivalents and five equivalents of pyridine were added, respectively. The reaction mixture was refluxed with stirring for 10 h. For **2**, excess  $\text{KPF}_6$  was added into the flask and stirred for 2 h. Then the solvent was removed under vacuum to yield yellow oil crude product. The pure complexes were obtained in 68% yield for **1** and 80% for **2** by alumina column chromatography using gradient elution of  $\text{CH}_2\text{Cl}_2/\text{methanol}$ .  $^1\text{H}$  NMR for **1**:  $^1\text{H}$  NMR (400 MHz,  $\text{DMSO-d}_6$ , 298 K),  $\delta$  (ppm): 5.72 (d,  $J = 8.4$ , Hz, 2H), 7.53 (t,  $J = 6.4$  Hz, 2H), 7.65 (d,  $J = 6.0$  Hz, 3H), 8.05 (t,  $J = 7.6$  Hz, 2H), 8.14 (d,  $J = 8.8$  Hz, 2H), 8.40 (d,  $J = 6.0$  Hz, 4H), 8.75 (d,  $J = 5.6$  Hz, 2H).  $^1\text{H}$  NMR for **2**: (400 MHz,  $\text{DMSO-d}_6$ , 298 K):  $\delta$  (ppm) 5.73 (dd,  $J = 2.0$ , 6.4 Hz, 2 H), 6.84 (td,  $J = 2.0$ , 9.6 Hz, 2 H), 7.51 (t,  $J = 6.8$  Hz, 4 H), 7.57 (t,  $J = 6.0$  Hz, 2H), 8.03 (t,  $J = 8.0$  Hz, 2H), 8.10 (t,  $J = 8.0$  Hz, 2H), 8.18 (d,  $J = 8.5$  Hz, 2H), 8.49 (d,  $J = 5.2$  Hz, 4H), 8.80 (d,  $J = 5.6$  Hz, 2H).

## 3. Results and discussion

### 3.1. The structural characterization of **1** and **2**

Iridium complexes **1** and **2** have been characterized by X-ray crystallography analysis. Single crystals were grown from mixed solution of dichloromethane/diethyl ether by slow evaporation at room temperature. ORTEP drawings, crystallographic refinement parameters,

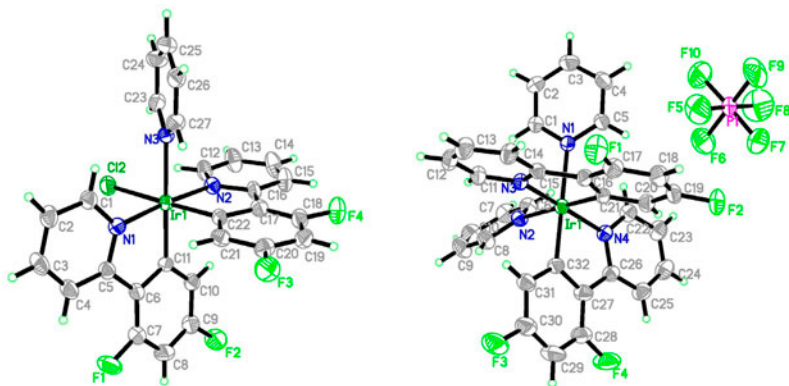


Figure 1. The perspective view of **1** (left) and **2** (right).

and selected bond parameters are depicted in figure 1, tables S1 and S2 (see online supplemental material at <http://dx.doi.org/10.1080/00958972.2014.913136>). Iridium centers in **1** and **2** both exhibit distorted octahedral coordination geometry. Distances of Ir–C ( $\sim 2.00$  Å) and Ir–N (C<sup>^</sup>N ligand) ( $\sim 2.04$  Å) in **1** and **2** (table S2) are very similar to those of Ir(ppy)<sub>2</sub>(bpy) [14]. The Ir–N (pyridine ligand) distances are much longer than that of Ir–N (N<sup>^</sup>N ligand) in Ir(ppy)<sub>2</sub>(bpy), which indicates weaker coordination interaction between iridium and pyridine of **1** than that of **2**.

### 3.2. Photophysical properties of **1** and **2**

**1** and **2** in CH<sub>3</sub>CN at room temperature showed similar photophysical properties (figure 2). Intense absorption at 250–350 nm ( $\epsilon \approx 2.0 \times 10^4$  M<sup>-1</sup> L cm<sup>-1</sup>) is attributed to spin-allowed intraligand ( $\pi \rightarrow \pi^*$ ) transition. Weak absorption at 350–450 nm is assigned to mixed singlet and triplet metal-to-ligand charge-transfer (<sup>1</sup>MLCT and <sup>3</sup>MLCT) states with the previous report of related cyclometalated iridium complexes [15], corresponding to yellow color of the solution. Upon excitation at 365 nm under ambient conditions, **1** in CH<sub>3</sub>CN solution has broad and featureless luminescence emission centered at 476 nm in the blue–green region, while **2** in CH<sub>3</sub>CN solution exhibited intense emissions with fine structure at 457 and 486 nm. The emission with the fine structure for **2** is perhaps due to <sup>3</sup>LC ( $\pi$ C<sup>^</sup>N $\rightarrow$  $\pi^*$ C<sup>^</sup>N) and [ $d\pi(\text{Ir}) \rightarrow \pi^*$ C<sup>^</sup>N] <sup>3</sup>MLCT transitions [16]. The phosphorescence quantum yield in CH<sub>3</sub>CN is ca. 0.024 for **1** and 0.087 for **2**, in which an aerated aqueous solution of [Ru(bpy)<sub>3</sub>]Cl<sub>2</sub> ( $\phi = 0.028$ ) was used as the standard solution [17].

### 3.3. The changes of optical properties of **1** for Ag<sup>+</sup>

As shown in figure 3(a), upon addition of Ag<sup>+</sup> to solution of **1**, the absorption in the visible region disappeared progressively until addition of two equivalents. The solution turned colorless accordingly. Luminescent emission spectra of **1** in CH<sub>3</sub>CN in the presence of different equivalent of Ag<sup>+</sup> were also investigated. The addition of two equivalents of Ag<sup>+</sup> resulted in decrease of luminescence intensity ( $\phi = 0.012$ ). Under UV light irradiation, the photoluminescence of **1** changes to low intensity.

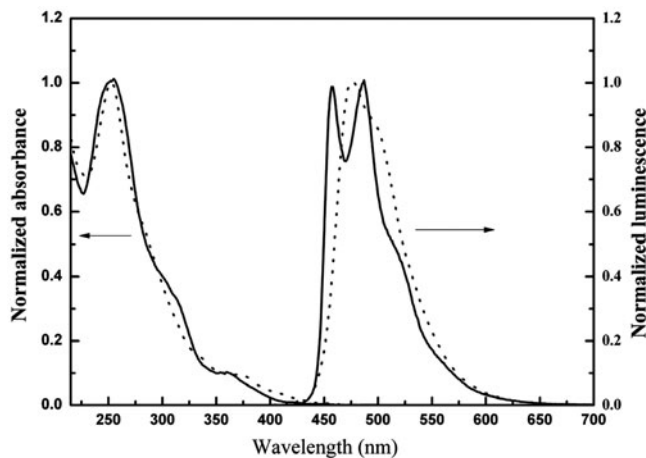


Figure 2. Absorption and luminescence spectra of **1** (dot) and **2** (solid) in CH<sub>3</sub>CN solution.

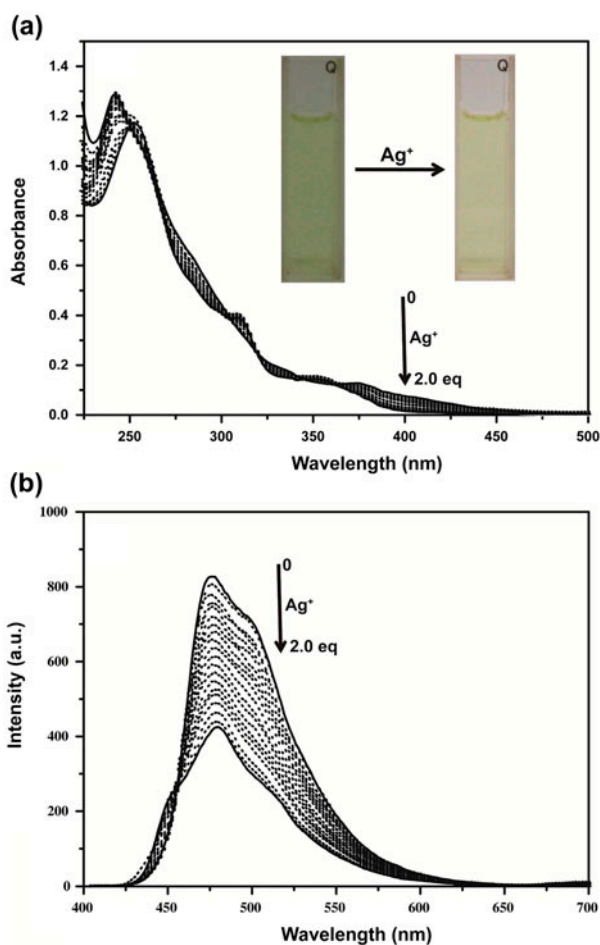
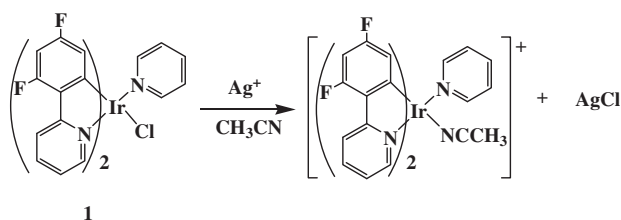


Figure 3. Changes in the UV-vis absorption spectra (a) and luminescence spectra (b) of **1** (20 μM) in CH<sub>3</sub>CN as a function of Ag<sup>+</sup> (0–40 μM), λ<sub>ex</sub> = 370 nm. Inset: (a) The photograph of color responses of **1** upon addition of 40 μM Ag<sup>+</sup>.

To confirm the interaction between Ag<sup>+</sup> and **1**, ESI-MS spectrum of **1** upon addition of two equivalents of Ag<sup>+</sup> was studied (figure S1). The peak at 693.1 (Calcd 693.1) is assigned to [Ir(dfppy)<sub>2</sub>(NCCH<sub>3</sub>)Py]<sup>+</sup>, probably due to Ag<sup>+</sup> and Cl<sup>-</sup> combining to precipitate AgCl (scheme 2). Chloride in Ir(dfppy)<sub>2</sub>PyCl is replaced by acetonitrile due to the strong interaction between Ag<sup>+</sup> and chloride, responsible for the significant change of absorption and luminescence spectra. No response to Ag<sup>+</sup> of **2** further confirms this mechanism (figures S2 and S3). This idea will be extended to the similar system to develop a new chemodosimeter for Ag<sup>+</sup>.

### 3.4. Selective luminescent response of **1** to various metal ions

The phosphorescent response of **1** towards a large excess of other metal ions (Ca<sup>2+</sup>, Cd<sup>2+</sup>, Co<sup>2+</sup>, Cr<sup>3+</sup>, Cu<sup>2+</sup>, K<sup>+</sup>, Mg<sup>2+</sup>, Na<sup>+</sup>, Pb<sup>2+</sup>, Fe<sup>3+</sup>, and Mn<sup>2+</sup>) was also examined. As presented



Scheme 2. The mechanism of **1** for  $\text{Ag}^+$ .

in figure 4, only the addition of  $\text{Ag}^+$  gave remarkable luminescence intensity changes; the other metal ions caused only slight luminescence intensity change (figure S4). At the same time, the presence of  $\text{Ag}^+$  changed the solution color from green to nearly colorless. These results confirmed that **1** displayed a high selectivity to  $\text{Ag}^+$ . We could easily monitor

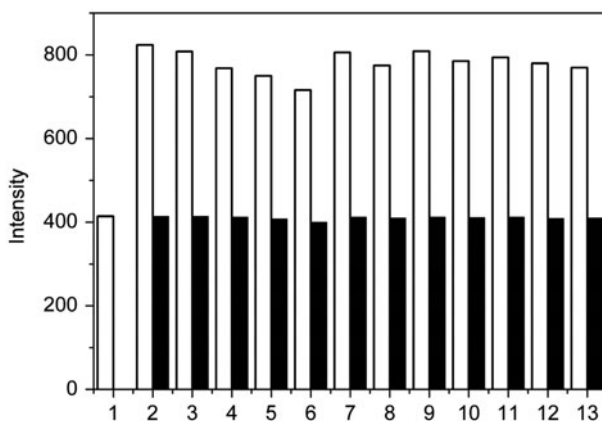


Figure 4. Luminescent response of **1** ( $20\ \mu\text{M}$ ) to various metal ions ( $20\ \mu\text{M}$ ) in  $\text{CH}_3\text{CN}$  solution. Bars represent the luminescence intensity of the peak located at  $476\ \text{nm}$ . White bars represent the addition of one fold of various metal ions to a  $20\ \mu\text{M}$  solution of **1**. Black bars represent the addition of  $\text{Ag}^+$  ( $20\ \mu\text{M}$ ) to the above solution, respectively. 1,  $\text{Ag}^+$ ; 2,  $\text{Ca}^{2+}$ ; 3,  $\text{Cd}^{2+}$ ; 4,  $\text{Co}^{2+}$ ; 5,  $\text{Cr}^{3+}$ ; 6,  $\text{Cu}^{2+}$ ; 7,  $\text{K}^+$ ; 8,  $\text{Mg}^{2+}$ ; 9,  $\text{Na}^+$ ; 10,  $\text{Ni}^{2+}$ ; 11,  $\text{Pb}^{2+}$ ; 12,  $\text{Fe}^{3+}$ ; 13,  $\text{Mn}^{2+}$ .

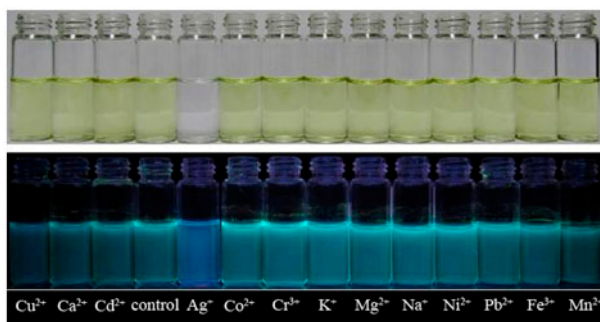


Figure 5. Color and phosphorescent emission observed from the solutions of **1** ( $20\ \mu\text{M}$ ) in the presence of different cations ( $20\ \mu\text{M}$ ). Excitation wavelength was  $365\ \text{nm}$  from a portable lamp.



interaction of **1** and  $\text{Ag}^+$  with our naked eyes (figure 5). To further explore the utility of **1** as a probe for  $\text{Ag}^+$ , a competition experiment was performed. The result is shown in figure 4. Regardless of the presence or absence of other metal ions,  $\text{Ag}^+$  evoked similar luminescence changes. All these results indicate that the selectivity of **1** for  $\text{Ag}^+$  over other cations is remarkably high.

#### 4. Conclusion

We have reported two blue phosphorescent iridium complexes with X-ray crystal structures. **1** is a highly selective phosphorescent and chromogenic chemodosimeter for  $\text{Ag}^+$ . The selective chemical reaction between  $\text{Ag}^+$  and chloride is responsible for the significant changes of optical properties. This strategy will be extended to similar systems to develop a new chemodosimeter for  $\text{Ag}^+$ .

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