

## Highly selective sensing of $\text{ClO}_4^-$ in water with a simple cationic iridium(III) complex and its application in bioimaging



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### ABSTRACT

Anion sensing by optical sensors has gained considerable attention. Perchlorate ions readily exist in water medium. Sensing of  $\text{ClO}_4^-$  in water and living cells is still poorly studied. In this work, we demonstrate an efficient strategy for sensing of  $\text{ClO}_4^-$  in water and imaging  $\text{ClO}_4^-$  with red emission in cells by using a facilely synthesized cationic cyclometalated iridium(III) complex. Taking advantage of aggregation-induced emission enhancement (AIEE), this iridium(III)-based sensor with weak emission in water displayed clear emission enhancement in presence of  $\text{ClO}_4^-$ . It is also demonstrated that the sensing process in water would not be interfered by  $\text{Hg}^{2+}$  which is capable of quenching emission of the sensor in THF.

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### 1. Introduction

Various anions are involved in many physiological and environmental processes, and the sensing of these anions has received widespread attention in the past few decades [1–4]. Perchlorates are widely used in lithium batteries, gas generator, solid rocket fuels, explosives, rubber manufacture and automobile air bag inflators [5,6]. Perchlorates can also readily exist in water samples, foods and plants due to high solubility in water and become one of major environmental contaminants. In addition,  $\text{ClO}_4^-$  can disrupt thyroid iodine uptake for human body because of their comparable charge and ionic radius [7]. Hence, it is important to detect  $\text{ClO}_4^-$  in water and image it in cells. Optical sensing is thought to be one of the most promising methods due to simplicity, sensitivity and inexpensiveness [8,9]. Thus, various considerable optical sensors have been exploited for the sensing of ions [10,11]. However, there have been only several reported optical sensors for the sensing of  $\text{ClO}_4^-$ . These sensors are based on the organic dyes including imidazolium derivatives [12–14], and a rhodamine compound [15]. Although transition–metal complexes are widely used in bioimaging and biosensing due to their rich photophysical properties [16], transition–metal complexes as a luminescent sensor for detecting  $\text{ClO}_4^-$  are still poorly studied [17].

Usually, an optical sensor for anion sensing was designed on the basis of optimization of host–guest interaction through hydrogen

bonding, electrostatic attraction,  $\pi$ – $\pi$  donor–acceptor, etc. between the hosts (optical sensors) and guests (anions) [18–21]. Nevertheless, these non-covalent interactions might be interfered by water molecule or other ions in water in dispersed dilute state, which create difficulties for designing effective optical sensors. Aggregation-induced emission (AIE) has received a lot of attention as a promising sensing mechanism in the sensing of ions and small molecules since the first report by Tang et al. in 2001 [22–25]. These AIE-active sensors exhibited weak emission in aqueous solution due to intramolecular motion including rotation and vibration, while strong emission in aggregated state in presence of analytes because of restriction of intramolecular motion (RIM) as recently reviewed by Tang et al. [26] These sensors are structurally designed to show significant intramolecular motion such as the introduction of a tetraphenylethene (TPE) unit. The sensors based on AIE strategy are commonly limited to AIE luminogens taking advantage of restriction of intramolecular motion [27]. However, it is still important to find new AIE systems for bioimaging. Intermolecular interactions can also quench luminescence of luminogens such as solvent-induced emission quenching. Restriction of intermolecular interaction probably enhances emission of luminogens in aggregated state referring to general AIE luminogens. There are some luminogens which display weak emission in dilute solution not due to strong intramolecular motion. We wonder if such luminogens are capable of biosensing benefiting from AIE strategy, and this may amplify the obtainment of sensors utilizing AIE strategy. In this context, transition–metal complexes may be excellent candidates. First, they usually display rich photophysical properties especially long lifetimes superior to

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common organic dyes in time-resolved fluorescent imaging [28]. Next, transition-metal complexes with solid emission may be weakly emissive in water medium due to water-induced emission quenching [28]. Then, if they aggregate to form emissive nanoparticles in presence of analytes in water, emission will increase and the sensing system will be realized.

Cyclometalated iridium(III) complexes usually show excellent photophysical properties and they have been widely used in bioimaging such as luminescent sensors due to large Stokes shifts, good photostability, long-lived emission in the visible wavelength and variable emission properties towards molecular chemical environment [29–32]. There are several AIE-active iridium(III) complexes utilized as sensors for the sensing of  $\text{Cu}^{2+}$  [29],  $\text{Hg}^{2+}$  [33] and explosives [34]. It is possible that a cationic iridium(III) complex with weak emission in water is served as a luminescent sensor for the sensing of anions in water based on AIE strategy. For example, this cationic iridium(III) complex with strong solid emission shows weak emission in water, it may bind with anions by electrostatic attractions due to its positive charge. These species may further aggregate to form emissive nanoparticles due to low solubility in water and fulfill the sensing of anions [35].

Herein, we report an iridium(III)-based sensor **1** for selective sensing of  $\text{ClO}_4^-$  in water (1% DMSO) and cells based on the aggregation induced emission enhancement (AIEE) mechanism. This sensor exhibited luminescence turn-on response to  $\text{ClO}_4^-$  in HEPES buffer (10 mM, pH = 7.4, 1% DMSO) due to the aggregation of **1** in presence of  $\text{ClO}_4^-$  and the emissive nanoparticles in solution were confirmed by Dynamic Light Scattering (DLS) and scanning electron microscope (SEM) experiments. Although sensor **1** has a thioacetal group known as  $\text{Hg}^{2+}$ -promoted thioacetal deprotection reaction [36,37], the sensing of  $\text{ClO}_4^-$  was not interfered by  $\text{Hg}^{2+}$  in water.

## 2. Experimental

### 2.1. Materials and instruments

All materials were purchased from commercial suppliers and used as received.  $^1\text{H}$  NMR spectra were carried out using a Bruker Avance 500 MHz instrument with tetramethylsilane (TMS) as an internal standard. HRMS spectra were recorded using a Thermofisher Q-Exactive instrument. Emission spectra were measured by Lengguang Tech. Instruments (F97PRO) with Xe lamp as the light source. UV-vis absorption spectra were obtained on a PerkinElmer Lambda 950 spectrophotometer. The scanning electron microscope (SEM) images were carried out on a Hitachi S-4800 scanning electron microscope. The solid state quantum yield was measured using a calibrated integrating sphere on a

Quantaaurus-QY spectrophotometer. Particle size was determined with Malvern Nano ZS. Confocal Laser Scanning Microscope experiments were carried out with ZEISS LSM 510.

### 2.2. Synthesis of **1**

The mixture of compound **IrCHO** (63 mg, 0.074 mmol),  $\text{BF}_3 \cdot \text{Et}_2\text{O}$  (0.148 mmol) and 1, 3-propanedithiol (0.375 mmol) in dry  $\text{CH}_2\text{Cl}_2$  (10 mL) was stirred at room temperature for 24 h under an argon atmosphere. Then the reaction was quenched by saturated  $\text{NaHCO}_3$  aqueous solution (20 mL) and extracted with  $\text{CH}_2\text{Cl}_2$  ( $3 \times 30$  mL). The combined organic layer was washed with brine (100 mL) and dried over  $\text{MgSO}_4$ . Then the organic layer was evaporated to obtain crude product in vacuo. The crude product was purified by column chromatography ( $\text{SiO}_2$ ;  $\text{CH}_2\text{Cl}_2$ - $\text{Et}_3\text{N}$ , 200:1 v/v) and **1** was obtained as yellow solid (17.5 mg, yield: 25.5%).  $^1\text{H}$  NMR (500 MHz,  $\text{CD}_3\text{CN}$ ),  $\delta$  (ppm): 8.53 (d, 1H,  $J = 1.5$  Hz), 8.41 (s, 1H), 8.05 (d, 2H,  $J = 8.0$  Hz), 7.93 (d, 1H,  $J = 5.5$  Hz), 7.84 (m, 2H), 7.79 (m, 3H), 7.64 (d, 1H, 5.0 Hz), 7.57 (d, 1H,  $J = 6.0$  Hz), 7.54 (dd, 1H,  $J_1 = 4.0$  Hz,  $J_2 = 2.0$  Hz), 7.33 (d, 1H,  $J = 6.0$  Hz), 7.03 (m, 4H), 6.91 (m, 2H), 6.26 (m, 2H), 5.44 (s, 1H), 3.12 (m, 2H), 2.97 (m, 2H), 2.54 (s, 3H), 2.18 (m, 1H), 1.83 (m, 1H). HRMS calcd. for  $\text{C}_{37}\text{H}_{32}\text{IrN}_4\text{S}_2$  ( $[\text{M}-\text{PF}_6]^+$ ): 789.1698; Found: 789.1684.

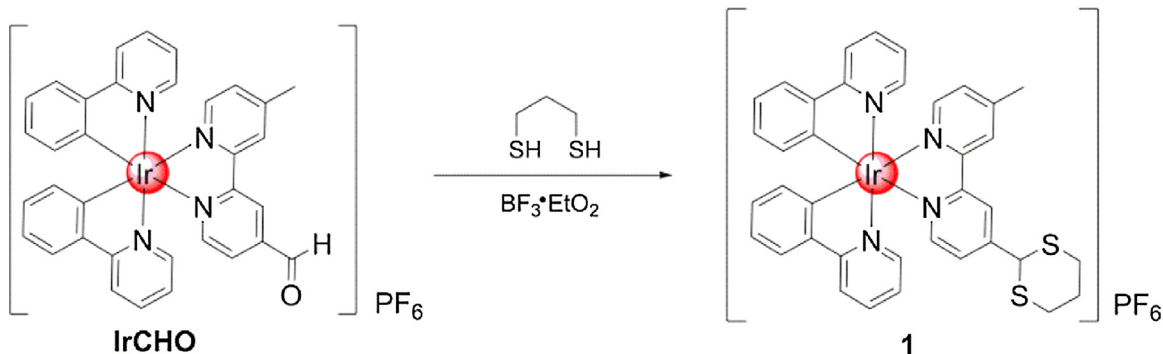
## 3. Results and discussion

### 3.1. Design and synthesis of sensor **1**

Sensor **1** bearing a thioacetal group was synthesized in a facile way (Scheme 1) and characterized through  $^1\text{H}$  NMR and HRMS spectra. The  $^1\text{H}$  NMR spectrum exhibits characteristic chemical shifts assigned to methyl (2.54 ppm) group and methylene groups of propanedithiol fragment (3.12 ppm, 2.97 ppm, 2.18 ppm and 1.83 ppm) (Fig. S1). The HRMS signal at  $m/z = 789.1684$  (calculated as 789.1698) is assigned to **1** (Fig. S2). Unlike weak emission of typical AIE luminogens in the good solvents [38–43], **1** dissolved well in air-equilibrated THF with a phosphorescence quantum yield of 1.92% while weak emission in water with a phosphorescence quantum yield of 0.16% at room temperature using  $[\text{Ru}(\text{bpy})_3]^{2+}$  (bpy = 2,2'-bipyridine) as a standard [44]. The weak emission of **1** in water was probably ascribed to water-induced phosphorescence quenching [35,45].

### 3.2. Optical response of **1** to $\text{ClO}_4^-$

First, we studied emission responses of sensor **1** towards  $\text{ClO}_4^-$  in HEPES buffer solution and the emission spectra are displayed in Fig. 1. As shown in Fig. 1, sensor **1** exhibits weak emission at 595 nm



Scheme 1. Synthetic procedure of **1**.

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