Luminescent Iridium(III) Chemosensor for Tandem Detection of F⁻ and Al³⁺

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Supporting Information

ABSTRACT: A new highly sensitive luminescent iridium(III) chemosensor, I, was designed and synthesized for tandem detection of fluoride ions (F⁻) and aluminum ions (Al³⁺). This sensor I exhibited obvious luminescence quenching by hydrogen bond interactions with F⁻. In addition, the resulting 1-F complex can be further used to detect Al³⁺ through a luminescence enhancement. The detection limit (0.02 μM) of 1-F for Al³⁺ is far lower than the World Health Organization concentration for drinking water (7.41 μM). Importantly, chemosensor 1-F could be used to detect and quantify F⁻ and Al³⁺ reversibly. This sensor achieved rapid detection of two ions, which relies on only one probe.

1. INTRODUCTION

Fluoride ions (F⁻) are important in a number of medical and biological processes. F⁻ plays an essential role in dental health¹ and may help in preventing osteoporosis.² However, over-exposure to F⁻ can cause kidney problems and acute gastric disorders.³ Consequently, the detection of F⁻ is an important goal for scientists.⁴ Meanwhile, the extensive use of aluminum in various industrial activities can cause the release of free aluminum ions (Al³⁺) into the biosphere. At high concentrations, Al³⁺ is a neurotoxin and can cause organ damage, Parkinson’s disease, or Alzheimer’s disease.⁵,⁶ The World Health Organization has set the permissible level of the Al³⁺ concentration in drinking water to be 7.41 μM.

Traditional instrument-based detection methods for the detection of F⁻ and/or Al³⁺ (¹⁹F NMR analysis for F⁻ and absorption spectroscopy⁷ and inductively coupled plasma mass spectrometry⁸ for Al³⁺) require expensive instrumentation and/or time-consuming sample preparation.⁹ Recently, the development of rapid and accurate sensitive probes for the monitoring of F⁻ and Al³⁺ ions has received considerable interest.¹⁰

Numerous organic dyes have been reported for Al³⁺ detection, whereas relatively fewer transition metal complex chemosensors for Al³⁺ have been described.¹²⁻²⁰ Compared with organic dyes, metal complexes are attractive scaffolds for chemosensors owing to their large Stokes shift and long-lived luminescence.²¹⁻²³ In a preliminary investigation, we have reported a novel iridium(III) complex equipped with o-phenolsalicilimine (an Al³⁺ receptor) in the N’N donor ligand as an Al³⁺ chemosensor.²⁴ However, the synthesis of this iridium(III) complex required a relatively complicated synthetic route, resulting in a low yield. Therefore, it is worthwhile to develop transition metal complex chemosensors with a relatively simple synthetic route and high sensitivity for Al³⁺ detection.

Developing methods for detection of two ions by only one probe is meaningful and useful. A tandem F⁻- and metal ion-selective sensor has been reported by scientists. However, there is no investigation found in tandem F⁻–Al³⁺ monitoring.¹⁵⁻²⁰ In addition, we recently reported a novel iridium(III)-based probe for the in vitro and in vivo detection of iron(III) and sulfide ions in a switch “on–off–on” mode.³⁰ Herein, we present a novel luminescent iridium(III) complex, I, containing two 2-phenylbenzimidazole (pbim) C’N ligands and a dimethylphenanthroline N’N donor ligand as a tandem F⁻ and Al³⁺ chemosensor (Scheme 1).

The emission parameters of iridium(III) complexes are sensitive to both the surrounding environment and the characteristics of their N’N and C’N ligands. Through its imidazole motif, complex 1 serves as a hydrogen bond donor with F⁻, which can deprotonate the N—H group contributed by the formation of the highly stable HF₂⁻ anions. This results in increased photoinduced electron transfer, thereby quenching the emission in the 1-F complex.³¹ Subsequently, Al³⁺ can

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coordinate to anionic Pbim, which results in the change of the metal-to-ligand charge-transfer state of the complex, causing a substantial recovery in the emission of 1,32,33 Therefore, this complex can be used as a luminescent chemosensor in tandem sensing of F\(^-\) and Al\(^{3+}\).

2. RESULTS AND DISCUSSION

2.1. Optimization of Chemosensors. Previous studies by the Liu group have reported the hydrogen-bonding interaction of iridium(III) complexes containing an imidazole group with F\(^-\), causing a significant change in the emissive characteristics of the complex.25 In the present work, four iridium(III) complexes (1–4) with a range of C\(^\wedge\)N and N\(^\wedge\)N ligands were tested for their capability to be quenched by the F\(^-\) (Figure 1a). Complexes 1 and 2, both containing imidazole motifs in the C\(^\wedge\)N ligands, were significantly quenched by F\(^-\) (Figures 1b and S5). The slightly weaker quenching response of 2 could possibly be due to its sterically bulky N\(^\wedge\)N ligand, which hinders the access of F\(^-\) to the acidic proton. On the other hand, complex 3 lacking an imidazole ring and complex 4 bearing a thiazole ring in place of imidazole both showed minimal response to F\(^-\) (Figures 1b and S5). These results suggest that quenching is associated with interactions at the imidazole sites. Considering that complex 1 gave the maximum response (15-fold reduction), we selected 1 as the lead sensor for F\(^-\) detection.

2.2. Luminescence Emission Response of 1 toward F\(^-\). We initially examined the luminescence response of 1 to F\(^-\). Without F\(^-\), 1 displayed strong luminescence intensity in solvent system DMSO/H\(_2\)O (9:1, v/v). However, when F\(^-\) was added, the luminescence intensity of 1 was quenched significantly (Figure 2). We next examined the use of other organic solvents (in combination with 10% H\(_2\)O), including N,N-dimethylformamide (DMF), acetonitrile (ACN), acetone, and ethanol (EtOH). The results showed that DMSO provided the best probe performance to F\(^-\) (Figure S6). Moreover, the optimal ratio of DMSO and H\(_2\)O was determined to be 9:1 (v/v), with higher amounts of H\(_2\)O leading to a lower quenching response (Figure S7). In emission titration experiments, complex 1 (10 \(\mu\)M) showed gradually reduced luminescence intensity with increasing concentrations of F\(^-\). The luminescence intensity reached its minimum at 40 molar equiv of F\(^-\), with a 15-fold reduction (Figure 2a). A linear relationship (\(R^2 = 0.991\)) was established from 2 to 10 \(\mu\)M F\(^-\), and a detection limit (S/N = 3) of 0.75 \(\mu\)M was recorded (Figure 2b).

2.3. Selectivity Studies of Anions to 1. The selectivity of sensor 1 for F\(^-\) over other potential interfering anions was examined. The luminescence response of 1 (10 \(\mu\)M) in the presence of 0.4 mM anions, such as I\(^-\), Br\(^-\), Cl\(^-\), SO\(_4^{2-}\), S\(_2\)O\(_3^{2-}\), NO\(_2\), NO\(_3\), N\(_3\), and SCN\(^-\), was recorded (Figure 3). The results showed that only F\(^-\) led to obvious changes in luminescence response, whereas the rest of the anions caused no significant response under the same conditions. To further demonstrate the specificity of the sensor to F\(^-\), we performed competition studies by adding F\(^-\) (0.4 mM) to complex 1 (10 \(\mu\)M) in the presence of other anions (0.4 mM). The result
showed no significant change in luminescence emission, indicating that 1 has the ability to selectively detect F\(^-\) even when these other common interfering anions were present.

### 2.4. Detection of Al\(^{3+}\) by 1-F

As a tandem detection strategy for both fluoride and aluminum ions, we then examined the luminescence signal of complex 1-F to Al\(^{3+}\). To achieve this, complex 1-F was prepared from 10 \(\mu\)M 1 with a 1:40 molar equiv ratio of 1:F\(^-\) in solvent system DMSO/H\(_2\)O (9:1, v/v) and the resulting solution was treated with increasing concentrations of aluminum ions (0.2−5 \(\mu\)M). The luminescence intensity of 1 went up linearly with the increasing concentrations of Al\(^{3+}\), with a maximal ca. 15-fold luminescence enhancement at [Al \(^{3+}\)] = 5 \(\mu\)M (Figure 4a). A linear relationship \((R^2 = 0.999)\) was established from 0 to 1.4 \(\mu\)M Al\(^{3+}\), and a detection limit of 0.2 \(\mu\)M was recorded (Figure 4b).

Interestingly, 0.5 molar equiv of Al\(^{3+}\) was sufficient for full luminescence recovery, which could be ascribed to Al\(^{3+}\) multicoordination with 1-F. To verify the tandem interaction among 1, F\(^-\), and Al\(^{3+}\), the reactions were monitored by \(^1\)H NMR spectroscopy (Figure S8). The pbim (H at 8.01 ppm) proton signal of 1 was downfield-shifted, suggesting the presence of hydrogen bond interactions. Moreover, the luminescence on−off−on of sensor 1 in tandem response to F\(^-\) and Al\(^{3+}\) could be easily visualized by eye under UV illumination (Figure 5).

### 2.5. Selectivity Studies of Metal Ions to 1-F

To investigate the selectivity of this Al\(^{3+}\) detection method, common metal ions were added into the 1-F mixture in DMSO/H\(_2\)O (9:1, v/v). Upon addition of 1 equiv of various metal ions to 1 (10 \(\mu\)M), including Zn\(^{2+}\), Ni\(^{2+}\), Cd\(^{2+}\), Ba\(^{2+}\), Fe\(^{3+}\), Cu\(^{2+}\), Mg\(^{2+}\), Cr\(^{3+}\), Ca\(^{2+}\), Pb\(^{2+}\), K\(^+\), Ag\(^+\), Mn\(^{3+}\), and Ce\(^{3+}\), the enhancement of luminescent response of 1-F was negligible in comparison to the response for 0.4 equiv of Al\(^{3+}\) (Figure 6). This shows that the probe has excellent selectivity toward Al\(^{3+}\) (Figure 6). We believe that this is because Al\(^{3+}\) binds fluoride with great affinity than other metal cations.

### 2.6. Reversibility of Sensor 1

Finally, we explored the reversibility of the tandem detection method for F\(^-\) and Al\(^{3+}\). Complex 1 (10 \(\mu\)M) was treated with 40 equiv of F\(^-\), which induced luminescence quenching. Five minutes later, the solution was treated with 0.4 equiv of Al\(^{3+}\), leading to

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**Figure 2.** (a) Luminescence spectra of 1 (10 \(\mu\)M) with increasing concentration of F\(^-\) (0−50 molar equiv, sodium fluoride aqueous solution) in DMSO/H\(_2\)O (9:1, v/v), \(\lambda_\text{ex} = 300\) nm. (b) Relationship between luminescence intensity and F\(^-\) concentration.

**Figure 3.** Luminescence response of 1 (10 \(\mu\)M) to different anions. The black bars represent the addition of 0.4 mM different anions to the solution of 1. The red bars represent the subsequent addition of 0.4 mM F\(^-\) to the solution, \(\lambda_\text{ex} = 300\) nm.

**Figure 4.** (a) Luminescence spectra of 1-F (10 \(\mu\)M, 1:40 molar equiv ratio) with increasing concentration of Al\(^{3+}\) (0−5.5 \(\mu\)M) in DMSO/H\(_2\)O (9:1, v/v). (b) Relationship between luminescence intensity and Al\(^{3+}\) concentration, \(\lambda_\text{ex} = 300\) nm.
restoration of luminescence. After luminescence returned to the initial levels, another 80 equiv of F\(^-\) was introduced into the solution and luminescence of the solution was quenched again. Five minutes later, the solution was treated with a further 0.8 equiv of Al\(^{3+}\), restoring the luminescence a second time. Continuing in similar fashion, the on–off cycle could be repeated at least three times (Figure 7). Furthermore, this hydrogen bond interaction cycle could be reversed several times without a decrease in the maximum luminescence. This result suggests that probe 1 can be used for the reversible tandem measurement of F\(^-\) and Al\(^{3+}\) in solution.

3. CONCLUSIONS

We have reported a new luminescent chemosensor, 1, for tandem F\(^-\) and Al\(^{3+}\) detection via hydrogen bond interactions. The results show that the luminescence of complex 1 can be readily quenched by F\(^-\), forming complex 1-F, and upon addition of Al\(^{3+}\), its luminescence can be restored. On the basis of the above results, a luminescent switch on–off–on tandem sensor for F\(^-\) and Al\(^{3+}\) was developed. Moreover, 1-F showed a linear response to Al\(^{3+}\) from 0.2 to 1.4 \(\mu\text{M}\) and showed an excellent selectivity to Al\(^{3+}\). Moreover, the reversibility of the on–off–on sensor to tandemly monitor F\(^-\) and Al\(^{3+}\) was demonstrated. We anticipate that this probe could be further optimized to generate an on–off–on sensor that could be used in biological systems.

4. MATERIALS AND METHODS

4.1. F\(^-\) and Al\(^{3+}\) Detection. The stock solution of 2.5 mM complex 1 was prepared in acetonitrile (ACN). The complex was then added into dimethyl sulfoxide (DMSO)/water (H\(_2\)O) (9:1, v/v) to a final concentration of 10 \(\mu\text{M}\). Different concentrations of F\(^-\) were then added to the DMSO/H\(_2\)O mixture with complex 1 (10 \(\mu\text{M}\)) in a cuvette. As for the tandem detection of Al\(^{3+}\), 0.4 mM F\(^-\) and 10 \(\mu\text{M}\) 1 were mixed in DMSO/H\(_2\)O in a cuvette and then different concentrations of Al\(^{3+}\) were then added to the solution. Luminescence emission spectra were recorded on a Cary UV-300 spectrophotometer (double beam).

4.2. Synthesis of Complexes 1–4. A solution of the N\(^2\)N ligand (0.12 mmol) and dichloro-bridged [Ir(C\(^2\)N\(_2\))\(_2\)Cl\(_2\)] (0.056 mmol) in dichloromethane (3 mL) and methanol (3 mL) was stirred at 60 °C overnight. After the reaction completed, an excess of ammonium hexafluorophosphate (NH\(_4\)PF\(_6\)) solid was added and the reaction mixture was stirred for another 0.5 h at room temperature. The solvent was removed under reduced pressure, and the residue was purified by silica gel column chromatography (eluent, methanol/dichloromethane, 1/20, v/v) to yield complexes 1–4.

ASSOCIATED CONTENT

Supporting Information

The Supporting Information is available free of charge on the ACS Publications website at DOI: 10.1021/acsomega.7b01646. General experimental procedures, materials, photophysical properties, UV–vis absorption spectra, solvent screening experiments, and partial \(^1\)H NMR spectra details (PDF)

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**Notes**

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