



Short communication

## A fluorescence turn-on probe for iodide based on the redox reaction between cupric and iodide

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## ABSTRACT

We have successfully introduced a novel strategy for the rational design of a fluorescence turn-on probe for iodide, which is a notorious fluorescence quencher due to the heavy atom effect. The strategy is based on the redox reaction between  $\text{Cu}^{2+}$  and iodide. The probe exhibited a 20-fold fluorescence enhancement in the presence of 4 equiv. of iodide. The probe developed herein represents the first fluorescence amplified probe for iodide. We believe that it will find interesting use in environment.

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### 1. Introduction

Halogen containing compounds have been widely used in many areas such as plastics, pesticides, food, and photography. However excessive halide levels may cause pollution in environment [1,2]. Thus, the development of fluorescent probes for halide ions is important in environmental monitoring [1,3–8]. Researchers have developed many fluoride probes [9–16]. By contrast, the fluorescent iodide probes are relatively fewer, although it is necessary to detect iodide in environmental samples as iodide deficiency in natural resources is implicated in the occurrence of endemic goitre in mammals [1,17,18].

Only a very few small-molecule fluorescence “turn-off” iodide probes are known, including bis-imidazolium and benzimidazole derivatives [19,20]. Furthermore, Leclerc and Valiyaveetil, respectively, reported thiophene- and carbazole-containing polymers as colorimetric and fluorescence quenching probes for iodide [21,22], and Corma reported pyrene covalently anchored on zeolite as a fluorescence turn-off sensor for iodide [23]. Very recently, Li's group has devised a cadmium selenide quantum dots based sensor which displayed a fluorescent quenching response to iodide [24], and Okamoto group has studied the fluorescence properties of 4-trifluoroacetylaminophthalimide in the presence of iodide upon photolysis at 254 nm in acetonitrile [25]. However, the major lim-

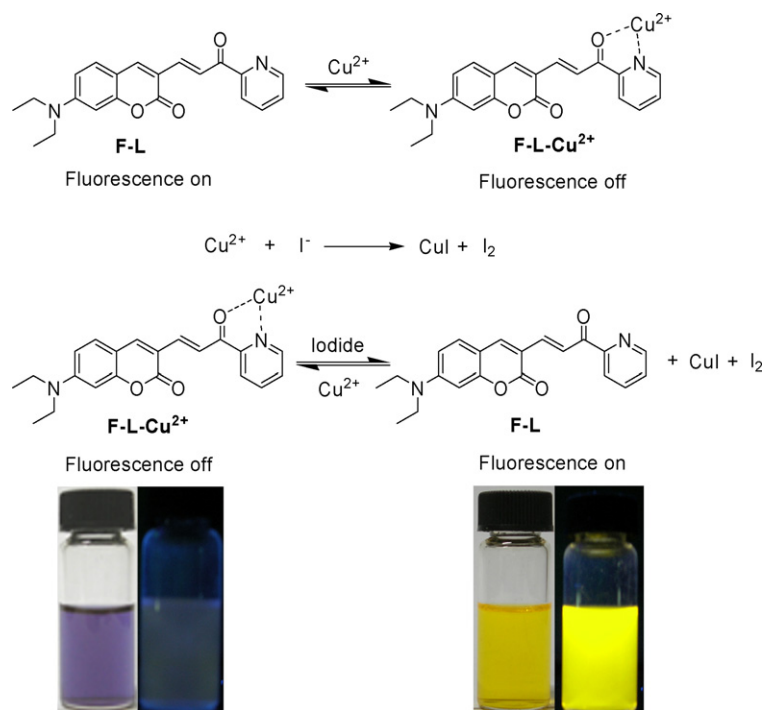
itation of the known iodide probes is that they only showed a fluorescence quenching signal upon treatment with iodide. The fluorescence quenching response usually results in low signal-to-noise ratio [26,27]. In addition, fluorescent quenching probes may provide false positive data by other fluorescent quenchers in real samples. Thus, from the analytical point of view, it is much more desirable to detect iodide by an enhanced fluorescence signal.

However, to design fluorescence turn-on iodide probes based on iodide coordination chemistry, it must face a difficult hurdle. Iodide has the intrinsic fluorescence quenching nature due to the heavy atom effect [2,4,28,29], which is believed to be the main reason for the fluorescence quenching response in the iodide probes. Clearly, it is a great challenging task to construct probes which can exhibit a fluorescence amplified signal in response to iodide.

To the best of our knowledge, the iodide-specific fluorescence amplified probes have not been reported yet. In this work, to circumvent the intrinsic fluorescence quenching effect of iodide, we employed a novel strategy based on the redox reaction between iodide and  $\text{Cu}^{2+}$  to develop a novel type of fluorescence turn-on iodide probes. As part of our ongoing studies on fluorescent probes [30–35], we have recently constructed colorimetric probe **F-L** (Scheme 1) for  $\text{Cu}^{2+}$  based on intramolecular charge transfer (ICT), and the binding mode has been studied in detail [30]. Importantly, upon binding to  $\text{Cu}^{2+}$ , the emission of compound **F-L** is almost completely quenched due to the intrinsic fluorescence quenching character of paramagnetic  $\text{Cu}^{2+}$  [30].

In the preliminary studies of this work, we noted that the UV–vis spectrum of compound **F-L** exhibited no visible changes upon addition of  $\text{Cu}^+$  (Supplementary data, Fig. S1), implying that  $\text{Cu}^+$  does not

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**Scheme 1.** The design concept of a fluorescence turn-on probe for iodide.

complex with compound **F-L** otherwise a significant red-shift in the absorption spectrum should be observed due to ICT [30]. The different binding behaviors of compound **F-L** toward paramagnetic  $\text{Cu}^{2+}$  and diamagnetic  $\text{Cu}^+$  may be explained due to the distinct binding geometry preference of cupric and cuprous ions.  $\text{Cu}^{2+}$  complexes tend to be in square planar geometry. By contrast,  $\text{Cu}^+$  favors tetrahedral coordination [36]. On the other hand, it is well known that iodide can reduce  $\text{Cu}^{2+}$  into  $\text{Cu}^+$  at ambient temperature (Scheme 1) [37]. This redox reaction has been broadly applied in determination of  $\text{Cu}^{2+}$  known as the iodometric method [38–40]. However, the reaction has not been exploited in design of fluorescent probes for iodide.

On the basis of the binding and fluorescence quenching response of compound **F-L** to  $\text{Cu}^{2+}$  and the redox reaction between  $\text{Cu}^{2+}$  and iodide, we envisioned that compound **F-L** could serve as an interesting platform for fluorescence turn-on sensing of iodide. As described in Scheme 1, compound **F-L** is in the fluorescence “on” state, and it turns into the fluorescence “off” state in **F-L-Cu<sup>2+</sup>** upon coordination with  $\text{Cu}^{2+}$ . However, further treatment of iodide with **F-L-Cu<sup>2+</sup>**,  $\text{Cu}^{2+}$  is reduced into  $\text{Cu}^+$  accompanied with the release of free compound **F-L**. Thus the fluorescence is on again. Conceivably, in this system, the fluorescence could be switched off–on by the addition of  $\text{Cu}^{2+}$  or iodide.

## 2. Experimental

### 2.1. Materials and measurements

Unless otherwise stated, all chemical reagents were obtained from commercial suppliers and used without further purification. Solvents used were purified and dried by standard methods prior to use. Twice-distilled water was used throughout all the experiments. Electronic absorption spectra were recorded with a SHIMADZU UV-2450 spectrometer. The emission spectra were recorded on a HITACHI F4500 fluorescence spectrophotometer. Fluorescence quantum yield was determined in spectroscopic grade  $\text{CH}_3\text{CN}$  using

quinine sulfate ( $\Phi_r = 0.546$  in 1N  $\text{H}_2\text{SO}_4$ ) as standard and it was calculated using a reported method (Supporting Information) [41,42]. The detection limit was determined from the fluorescence titration data based on a reported method (Supporting Information) [43,44].

### 2.2. Spectral measurements

$\text{Na}_2\text{SO}_3$ ,  $\text{Na}_2\text{SO}_4$ ,  $\text{Na}_2\text{CO}_3$ ,  $\text{NaHCO}_3$ ,  $\text{K}_2\text{HPO}_4$ ,  $\text{NaBF}_4$ ,  $\text{KNO}_3$ ,  $(\text{Bu})_4\text{NCl}$ ,  $(\text{Bu})_4\text{NF}$ ,  $(\text{Bu})_4\text{NBr}$ ,  $\text{KI}$ , and  $\text{NaClO}_3$  stock solutions were prepared in a small amount of twice-distilled water and then diluted with acetonitrile.  $\text{CuCl}_2$  and compound **F-L** were dissolved in acetonitrile to afford the corresponding stock solutions. Test solutions were prepared by placing 0.5 mL of the compound **F-L** stock solution (0.25 mM), 0.4 mL  $\text{CuCl}_2$  stock solution (1.25 mM), and 0.005–0.2 mL of  $\text{KI}$  stock solution (2.5 mM) into a 5 mL volumetric flask, and then adding acetonitrile to the final volume of 5 mL. The resulting solution was shaken well and the absorption and emission spectra of the metal complexed were recorded immediately. Unless otherwise noted, for all measurements, the excitation wavelength was at 463 nm, and both the excitation and emission slit widths were 2.5 nm.

## 3. Results and discussion

### 3.1. Synthesis of coumarin 1

The synthesis of compound **F-L** was reported by us previously [30].

### 3.2. UV-vis and fluorescence spectra of **F-L-Cu<sup>2+</sup>** titrated with iodide ions

Firstly, we examined the changes in the optical properties of compound **F-L** (25  $\mu\text{M}$ ) in acetonitrile upon addition of 4 equiv. of  $\text{Cu}^{2+}$ . A large red-shift from 463 to 585 nm in UV-vis absorption spectra due to ICT was observed, while the fluorescence emission

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