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A highly sensitive and selective turn-on fluorescent chemodosimeter for Cu^{2+} based on BODIPY and its application in bioimaging†

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A BODIPY-based turn-on fluorescent probe 1 has been designed and synthesized for fluorescence detection of Cu^{2+} in aqueous media and imaging in living cells. The C=N bonds are selectively hydrolyzed by the reaction with Cu^{2+} to generate formyl-BODIPY. The favorable features of probe 1 towards Cu^{2+} include significant fluorescence enhancement (over 290-fold), high selectivity and low detection limit (0.1 μM).

The development of highly sensitive and selective fluorescent probes for the sensing and recognition of environmentally and biologically important ionic species, especially metal ions, has been of great interest in recent years.[1] Among the metal ions, the design and synthesis of sensitive and selective probes for the detection of Cu^{2+} has attracted much attention, as it is the third most abundant essential trace element after iron and zinc in biological systems and plays a vital role in a variety of fundamental physiological processes in organisms ranging from bacteria to mammals.[2,3] In addition, excessive levels of copper could do harm to organisms and copper is closely connected with some neurodegenerative diseases, such as Menkes[4] and Wilson's diseases,[5] familial amyotropic lateral sclerosis, and Alzheimer's disease owing to the aberrant oxidative and nitrosative stress induced by Cu^{2+}.[6,7] In the past few years, more and more Cu^{2+} fluorescent probes have been reported based on different detecting mechanisms.[2,3] Recently, reaction-based Cu^{2+} probes that called chemodosimeters have attracted intense attention, as an important alternative to the classical chelation-based probes. So far, a large number of examples of chemodosimeters for Cu^{2+} *via* chemical reactions, include those by Cu^{2+}-promoted hydrolysis of amides,[8a] esters,[8b–e] hydrazone,[8f] lactams[8g,h] and lactone,[3a] oxidation of dihydrorosamine,[3g] phenothiazine,[9a] catechol,[9b] phenol[9c] and DNA,[9d] *etc.* have been developed. However, many of these suffer from the limitations, such as act only in pure organic solvents or solutions with very small amounts of water,[8a,9a–c,10] require specific reaction conditions,[3a,b,8b,c,f,10b] show low Cu^{2+} sensitivity or selectivity in the presence of other metal cations.[3j,8a,e,g,h,9d,10b,11] Thus, it is still of great interest to develop new fluorescent sensor for Cu^{2+} ions with high selectivity, and sensitivity.

Over the past decade, various fluorophores have been used in the design of fluorescent probes for the detection of Cu^{2+}, including coumarin,[2s,3a–c,f,8f] fluorescein,[3i] naphthalimide,[2c,f,t] rhodamine,[2e,3d,10c] luminescent transition metal complexes,[12] and borondipyrromethenes (BODIPY).[2g,h,3b,c,8e] Among these fluorophores, BODIPY has played a pivotal role in fluorescent probe development, and it is one of the most exploited fluorophores due to its excellent photophysical properties and recently the development of the BODIPY-based fluorescent probes with high sensitivity and selectivity attracted increasing attention.[13] Herein, we present that the Cu^{2+}-promoted hydrolysis of a new hydrazone derivative of BODIPY allows selective and sensitive chemodosimetric detection of Cu^{2+} in aqueous solution with neutral pH at room temperature.

It was know that the hydrolysis of hydrazone of ketone can be catalyzed by Cu^{2+} to act as a new fluorescence detective method for Cu^{2+} (ref. 8f) and the hydrazone derives show the selective coordination property binding to Cu^{2+} which can be displaced by Hg^{2+}.[2g,14] In addition, the hydrazone derivatives have been employed as highly selective fluorescent probes of Cu^{2+} and/or Hg^{2+}.[15] With all this in mind, we design and synthesis a new turn-on Cu^{2+} fluorogenic probe **1** that emits a green fluorescence by incorporating 2-hydroxynaphthylhydrazone fragment to BODIPY fluorescent core.

As shown in Scheme 1, probe **1** was synthesis from the condensation of readily available 2-formyl BODIPY **2** (ref. 16a) with 2-hydroxynaphthylhydrazone **3** straightforwardly. The chemical structure of compound **1** was characterized by ^1H

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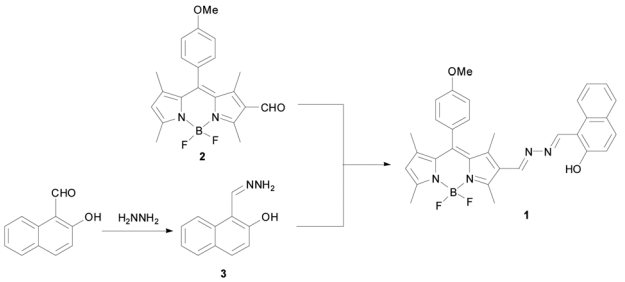

Scheme 1 Synthesis of chemodosimeter **1**.

NMR, ^{13}C NMR and MS analysis (Fig. S9–11, ESI†). The compound **1** is weakly fluorescent, but Cu^{2+} addition shows a strong fluorescence enhancement (Fig. S1, ESI†). This enhancement was promoted *via* a coordination of Cu^{2+} with **1** followed by hydrolysis C=N bond near BODIPY structure leading to the formation of fluorescent 2-formyl-BODIPY molecule.

We commenced our investigation by first examining the parameters of the sensing media. Among various solvent systems tested, a combination of CH_3CN–H_2O (1 : 1, v/v) proved to be highly efficient for the sensing process for Cu^{2+} (Fig. S1, ESI†). A solution of 10 μM **1** in CH_3CN–H_2O (v/v, 1 : 1) exhibited an absorption band at 525 nm and was very weakly fluorescent. However, addition of Cu^{2+} induced significant changes in both the absorption and emission spectra (Fig. S2, ESI†). Then, Cu^{2+}-titration and spectral responses were investigated in detail. Firstly, the absorption spectral changes of **1** upon addition of various cations was measured to evaluate its sensing ability. As shown in Fig. 1, probe **1** (10 μM) in CH_3CN–H_2O (1 : 1, v/v) exhibited a clear absorbance at 525 nm. With the addition of Cu^{2+}, a new absorption peak centered at 490 nm was appeared at the expense of the original absorption peak at 525 nm, and the color of the solution changed from red-purple to pale yellow. No obvious responses could be observed upon the addition of Li^+, Ba^{2+}, Na^+, Pb^{2+}, K^+, Cu^+, Co^{2+}, Al^{3+}, Ag^+, Hg^{2+}, Mg^{2+}, Ni^{2+}, Cd^{2+}, Ca^{2+}, Fe^{3+}, Mn^{2+}, Cr^{3+}, and Zn^{2+}, initially indicating the special selectivity towards Cu^{2+} (Fig. S3, ESI†). Furthermore, an

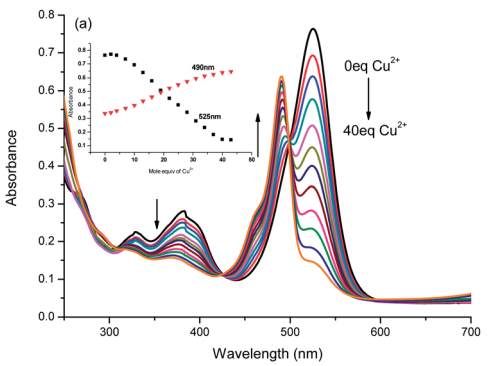

Fig. 1 Absorbance spectra of compound **1** (10 μM) towards Cu^{2+} ions (0 to 40 equiv.) in H_2O–CH_3CN (1 : 1, v/v) medium. The inset shows the absorbance of **1** at 525 nm and 490 nm as the functions of Cu^{2+} concentration respectively.

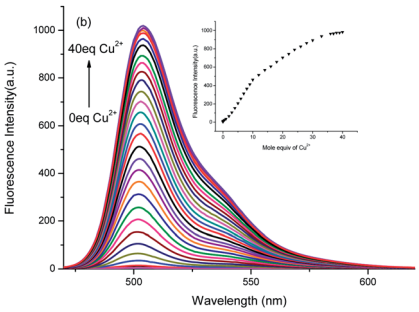

Fig. 2 Fluorescence spectra of compound **1** (10 μM) towards Cu^{2+} ions (0, 0.01, 0.02, 0.04, 0.1, 1, 2, 3, 4, 5, 6, 7, 8, 9, 10, 12, 14, 16, 18, 20, 22, 24, 26, 28, 30, 33, 36, 37, 38, 39, 40 equiv.) in H_2O–CH_3CN (1 : 1, v/v) medium (λ_{ex}: 460 nm). The inset shows fluorescence intensity change as a function of Cu^{2+} concentration.

isosbestic point at 500 nm was observed, which indicated the formation of a new compound.

Next, the fluorescence titration experiments for **1** (10 μM) with different concentrations of Cu^{2+} was carried out (Fig. 2). Significant enhancement in the featured emission of formyl-BODIPY at 507 nm was observed upon gradual addition of Cu^{2+}. The emission intensity reached its maximum when 40 equiv. of Cu^{2+} was added, with an enhancement factor over 290-fold. There was the linear dependence of the fluorescence intensity on the Cu^{2+} concentration from 0.1 μM to 0.1 mM, and from 0.1 mM to 0.3 mM, respectively (Fig. S4b, ESI†). The detection limit for Cu^{2+} was determined as 0.1 μM under the experimental conditions (ESI†), which is sufficiently low to allow the fluorogenic detection of micromolar concentrations of Cu^{2+} in drinking water and living systems.

The pH titration was also investigated on the pH-dependence of probe **1** in the detection of Cu^{2+} (Fig. S5, ESI†). Probe **1** was stable and weakly fluorescent over a wide pH range (pH = 6.0 to 10.0). On the other hand, the fluorescence response of the probe **1** towards the addition of Cu^{2+} was indeed pH dependent. Probe **1** displayed an efficient fluorescence response to Cu^{2+} in the pH range of 6.0–8.0. Notably, the fluorescence enhancement was significantly greater at physiological pH (pH = 7.2), which suggests that probe **1** can work in the biological pH range without influence.

The applicability of the developed chemodosimeter **1** to the analysis of Cu^{2+} ions in a practical sample was also investigated. The fluorescence titration of probe **1** with various metal ions was conducted to examine the selectivity. The weak fluorescence of probe **1** was only marginally increased upon addition of representative cations such as Li^+, Na^+, K^+, Mg^{2+}, Ca^{2+}, Ba^{2+}, Al^{3+}, Pb^{2+}, Cr^{3+}, Mn^{2+}, Fe^{3+}, Co^{2+}, Ni^{2+}, Cu^+, Ag^+, Zn^{2+}, Cd^{2+}, Hg^{2+} (Fig. S3b, ESI†). Only when Cu^{2+} was added the unique fluorescent characteristic of formyl-BODIPY was detected.[16] It is noted that the unique absorbance and fluorescence bands resulting from the addition of the Cu^{2+} ions were not influenced by other cations. We further examined the fluorescence response of probe **1** toward Cu^{2+} in the presence of other potentially competing ions. Fluorescence spectra of solutions of **1** (10 μM) recorded 5 min after the addition of Cu^{2+} (4 equiv.) to

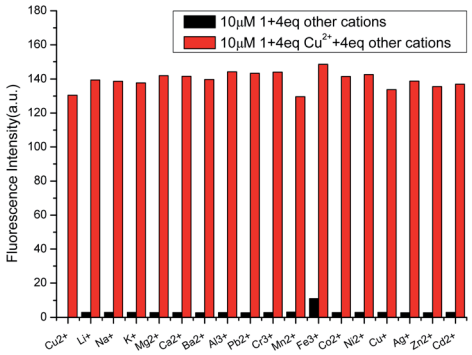

Fig. 3 Fluorescence responses of **1** (10 μM) to various cations in H_2O–CH_3CN (1 : 1, v/v) medium. The black bars represent the emission intensities of **1** in the presence of 40 μM of alkali (IA) and alkaline earth (IIA) metals and for other cations of interest. The red bars represent the change of the emission that occurs upon the subsequent addition of 40 μM of Cu^{2+} to the above solution. The intensities were recorded at 507 nm, excitation at 460 nm.

a CH_3CN–H_2O (1 : 1, v/v) solution containing **1** and 4 equiv. of the other metal ions are shown in Fig. 3. The fluorescence intensity changes caused by the addition of Cu^{2+} are not influenced by the presence of the other metal ions, which may be attributed to reason that the hydrazone moiety was not cleaved by other metal ions. All of these results indicate that the selectivity of probe **1** for the Cu^{2+} ion over other competitive cations in aqueous medium is remarkably high.

The significant emission enhancement and the properties of high sensitivity and selectivity of probe **1** is due to the hydrolysis of hydrazone promoted by Cu^{2+} ion. The sensing mechanism of probe **1** toward Cu^{2+} was postulated as follows: probe **1** coordinated with Cu^{2+} ion due to its high affinity for various amine and hydroxy ligands. Subsequently, the hydrolysis of the hydrazone bond near BODIPY occurred promoted by Cu^{2+} ion to produce formyl-BODIPY which allow the strong green fluorescence emission (Fig. 4).

In an effort to gain more detailed information on better understanding the sensing mechanism, ^{1}H NMR spectroscopy was employed. The reaction of probe **1** with Cu^{2+} was carried out in CD_3CN for 10 min, and then a ^{1}H NMR spectrum of the resulting solution was recorded (Fig. 4). The ^{1}H NMR spectrum shows the disappearance of two singlet peaks at 8.79 ppm (H_a) and 9.67 ppm (H_b) corresponding to the protons on the CH=N moieties in dihydrazone unit of probe **1** respectively. Meanwhile, the singlet peak at 10.03 ppm (H_c) corresponding to the proton of the CHO moiety in the one of the hydrolysis products fomyl-BODIPY and the singlet peak at 10.85 ppm (H_d) corresponding to the proton of the CHO moiety in another hydrolysis product 2-hydroxynaphthyl aldehyde. In addition, the singlet peak at 13.37 ppm corresponding to the proton of OH on probe **1** disappeared, followed by the arising of broad singlet peak at 13.13 ppm corresponding to the proton of OH on 2-hydroxynaphthyl aldehyde. This result clearly further confirms that probe **1** was hydrolyzed effectively in the presence of Cu^{2+} generating highly fluorescent product, fomyl-BODIPY.

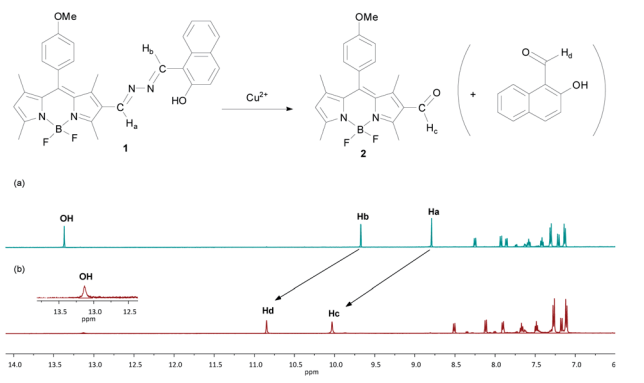

Fig. 4 Proposed sensing mechanism and partial ^{1}H NMR spectra of **1** (1 mM) in CD_3CN upon addition of (a) 0, (b) 1 equiv. of Cu^{2+}.

The potential applications of probe **1** for fluorescence imaging of Cu^{2+} in living HeLa cells was further assessed (Fig. 5). Incubation of HeLa cells with 10 μM of probe **1** for 30 min at assessed 37 °C gave almost no intracellular fluorescence. When the incubated HeLa cells were pretreated with 20 μM of Cu^{2+}, fluorescence became from clearly visible to remarkable enhancement in the cytoplasm of HeLa cells with the same treatment with the probe **1** after 1 hour and 3 hours. These results demonstrate that probe **1** is cell membrane permeable and can be used as a possible sensor to detect Cu^{2+} within living cells.

In conclusion, we have developed a "turn-on" type fluorescent probe that shows significant fluorescence emission enhancement in response to Cu^{2+} with high sensitivity and selectivity over other metal ions. This novel probe operates through an irreversible chemical reaction and thus can be classified as a chemodosimeter. Beside the low detection limit and efficient operation under physiological conditions, this probe can also be applied for the imaging of Cu^{2+} in living cells. The interesting reaction properties of **1** may be extended to the development of other BODIPY-based chemodosimeters.

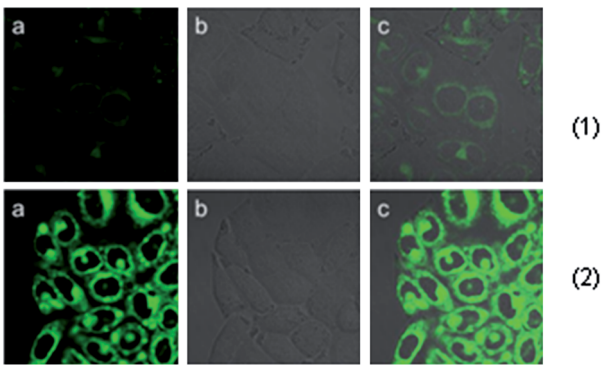

Fig. 5 Confocal fluorescence images of living HeLa cells (1a) cells loaded with 10 μM probe **1** at 25 °C for 30 min (λ_{ex} = 488 nm; band path: 490–650 nm); (1b) bright field image of (1a). (1c) Overlaid images of panels (1a and b). (2a) Probe **1** loaded cells with 20 μM Cu^{2+} at 25 °C for 3 h (λ_{ex} = 488 nm; band path: 490–650 nm); (2b) bright field image of 2a. (2c) Overlaid images of panels (2a and b).

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