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# 1,8-Naphthalimide derived dual-functioning fluorescent probe for "turn-off" and ratiometric detection of $Cu^{2+}$ based on two distinct mechanisms in different concentration ranges

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## ABSTRACT

In this study, a novel 1,8-naphthalimide derived compound bearing the coumarin moiety called 7-Diethylaminocoumarin-3-aceone (*N*-hydroxyethyl-1',8'-naphthalimide-4'-) hydrazone (**1**) has been designed, synthesized and evaluated as a dual-functioning fluorescent probe for "turn-off" and ratiometric detection of $Cu^{2+}$ based on two distinct mechanisms in different concentration ranges in aqueous solution. This probe **1** showed high selectivity and sensitivity for $Cu^{2+}$ over other common metal ions, for the limit of detection (LOD) could reach $3.90 \times 10^{-8}$ M and $3.26 \times 10^{-7}$ M for "turn-off" and ratiometric detection respectively. Moreover, in $Cu^{2+}$ equivalence range of 0–0.5, a decrease in fluorescence emission intensity at 441 nm was observed upon addition of $Cu^{2+}$, but in $Cu^{2+}$ equivalence range of over 0.5, a new emission band centered at 462 nm appeared with increasing intensity accompanied by a decrease in fluorescence emission intensity at 570 nm, which provided ratiometric fluorescence detection of $Cu^{2+}$. The sensing mechanisms for the responses of **1** to $Cu^{2+}$ were chelation-quenched fluorescence (CHQF) and chemical reaction between **1** and $Cu^{2+}$ over $Cu^{2+}$ equivalence range of 0–0.5 and more than 0.5, respectively. Thus, this probe **1** could be utilized for sensing and monitoring $Cu^{2+}$ in environmental and biological systems in different concentration ranges.

## 1. Introduction

It is well known that copper is the third most abundant transition metal element (after iron and zinc) in human body and widely distributed in the environment [1]. As generally found to be divalent state, $Cu^{2+}$ plays a vital role in a variety of physiological, pathological and toxicological processes in organisms ranging from bacterials to mammal animals, such as neurotransmission [2], membrane depolarization [3], transportation of $O_2$ [4] and redox processes [5]. $Cu^{2+}$ can also act as a key cofactor for various metalloenzymes and proteins in living organisms [6,7]. Thus, it is important to keep the $Cu^{2+}$ level in a good manner for physical and mental health in human body [8,9]. However, Copper element is identified as a significant environmental pollutant for its wide use in the fields of industry [10], agriculture [11], biochemistry [12], analytical chemistry [13] and medicine [14]. When it is exposed to high concentration of $Cu^{2+}$ that exceeds the needs of cells and tissues, the biological systems can suffer from the toxicity and the overload of $Cu^{2+}$ in human bodies is associated with neurodegenerative diseases, such as Alzheimer's disease [15], Parkinson's disease [16], Menkes disease [17] and Wilson's disease [18]. The maximum acceptable level of $Cu^{2+}$ in drinking water is set as about 20 μM by the U.S. Environmental Protection Agency (EPA) [19]. Considering these factors, developing a simple, efficient, highly selective and sensitive method for rapid detection of $Cu^{2+}$ is of great significance for human health and environmental protection [20,21].

Many available methods like atomic absorption spectrometry (AAS) [22], inductively coupled plasma atomic emission spectrometry (ICP-AES) [23], inductively coupled plasma mass spectroscopy (ICP-MS) [24], voltammetry [25], electrochemical techniques [26] and colorimetric method [27] have been applied for the trace quantification of $Cu^{2+}$, but the requirements of expensive apparatus, tedious sample preparation procedures and trained operators limit their applications in environmental and biological systems [28]. Up to date, fluorescence detection has been one of the hottest topics of great concern among scientists because of its simplicity, rapidity, good selectivity, high sensitivity and non-destructivity to the substrates [29–34]. A great many fluorescent probes have been designed and synthesized for the detection and recognition of $Cu^{2+}$, and most of them are based on the changes in fluorescence emission intensity at a single wavelength in the presence of $Cu^{2+}$ like fluorescence quenching or enhancement [35–42].

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Especially, the “turn-off” fluorescent probes for $Cu^{2+}$ have been an overwhelming concern [43], which is attributed to the paramagnetic property of $Cu^{2+}$ related to the electron or charge transfer process from photoinduced metal to fluorophore, and this phenomenon is called chelation-quenched fluorescence (CHQF) [44–47]. Nevertheless, these fluorescence intensity measurements can be influenced from various factors like microenvironment (pH, temperature, polarity, and so forth), the concentration of probe molecule and instrumental efficiency, which is due to the lack of background signal [48]. These disadvantages can be circumvented by using ratiometric fluorescent probes that can provide built-in correction for these factors by measuring the changes of fluorescence emission ratio at two different wavelengths, which makes quantitative detection of a specific analyte more accurate [49–56]. The mechanisms for the ratiometric fluorescent probes are always based on intramolecular charge transfer (ICT) [57], fluorescence resonance energy transfer (FRET) [58] and monomer-excimer dual fluorescence [59], but the reaction-based ratiometric fluorescent probes for detecting and recognizing metal ions are relatively few [60]. Therefore, it is a great challenge to develop $Cu^{2+}$ fluorescent probes on a basis of chemical reaction mechanisms.

Among various fluorophores, 1,8-naphthalimide and its derivatives have been extensively applied for designing fluorescent probes due to their excellent optical properties like high fluorescence quantum yield, large Stokes’ shift and good photostability [61–63]. On the other hand, coumarin is also a good fluorophore that can be used for developing probes for the detection of metal ions, anions and biomolecules [64–66]. The studies of $Cu^{2+}$ fluorescent probes based on chelation-quenched fluorescence (CHQF) [67] and chemical reactions [68] have been reported respectively. However, to the best of our knowledge, there are no fluorescent probes for “turn-off” and ratiometric detection of $Cu^{2+}$ based on these two distinct mechanisms in different concentration ranges. As a result, the development of fluorescent probes based on two distinct mechanisms is highly desirable and becoming more and more appealing for the quantitative detection of $Cu^{2+}$ in environmental and biological systems [69].

With these factors in mind, we have designed and synthesized a novel 1,8-naphthalimide derived dual-functioning fluorescent probe bearing the coumarin moiety called 7-Diethylaminocoumarin-3-aceone (*N*-hydroxyethyl-1’,8’-naphthalimide-4’-) hydrazone (**1**) (Scheme 1), which could be utilized as a “turn-off” and ratiometric fluorescent probe for $Cu^{2+}$ based on chelation-quenched fluorescence (CHQF) and chemical reaction mechanisms in different concentration ranges, respectively. This probe **1** showed high selectivity and sensitivity towards $Cu^{2+}$ over other common metal ions, which broadened its applications in environmental and biological fields.

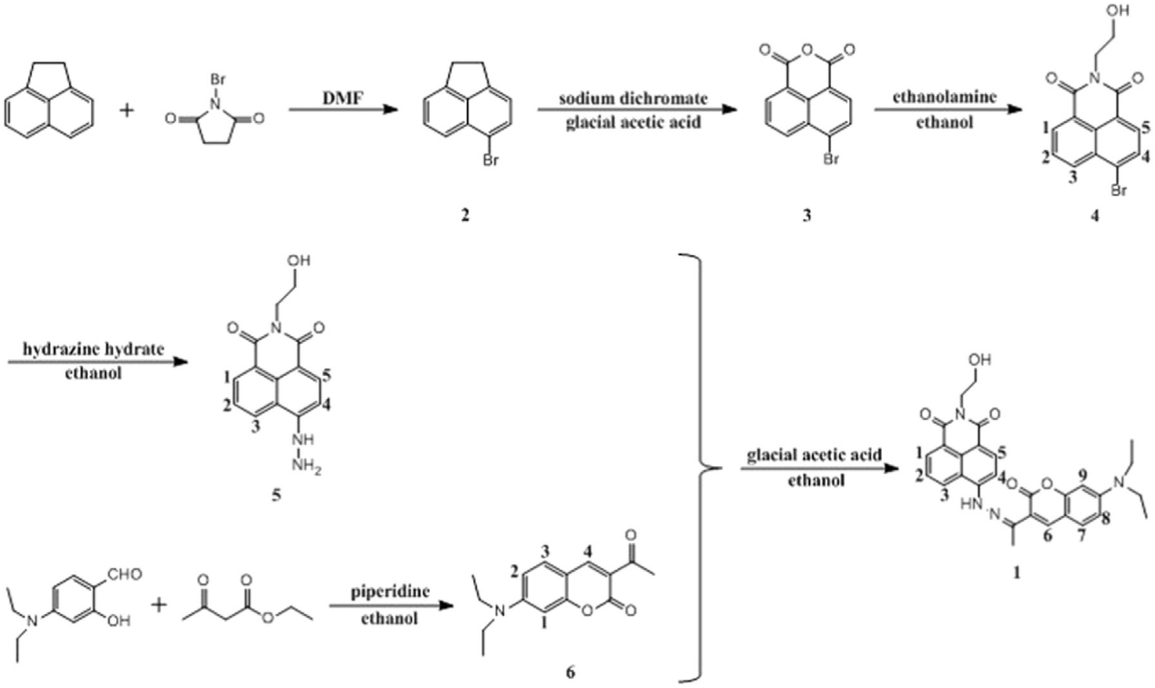
## 2. Experimental

### 2.1. Materials

Acenaphthene, *N*-bromosuccinimide, sodium dichromate, glacial acetic acid, ethanolamine, hydrazine hydrate, dichloromethane, 4-diethylaminosalicylaldehyde, ethyl acetoacetate, piperidine, absolute ethanol, absolute methanol, acetonitrile, tetrahydrofuran (THF), *N*,*N*-dimethyl formamide (DMF), dimethyl sulfoxide (DMSO) and cationic salts such as $CuCl_2$, $Al(NO_3)_3$, $Ba(OAc)_2$, $Ca(NO_3)_2$, $Cd(OAc)_2$, $Co(OAc)_2$, $Cr(NO_3)_3$, $Fe(NO_3)_2$, $Fe(NO_3)_3$, K(OAc), $Mg(NO_3)_2$, $Mn(NO_3)_2$, $NaClO_4$, $Ni(NO_3)_2$, $Pb(OAc)_2$ and $Zn(NO_3)_2$ were obtained from commercial suppliers, and used as received without further purification. Stock solutions of compound **1** (10 mM) and compound **6** (10 mM) were prepared in DMSO, and stock solutions (10 mM) of the cationic salts of $Cu^{2+}$, $Al^{3+}$, $Ba^{2+}$, $Ca^{2+}$, $Cd^{2+}$, $Co^{2+}$, $Cr^{3+}$, $Fe^{2+}$, $Fe^{3+}$, $K^{+}$, $Mg^{2+}$, $Mn^{2+}$, $Na^{+}$, $Ni^{2+}$, $Pb^{2+}$ and $Zn^{2+}$ in absolute ethanol were also prepared. Distilled water was used throughout all experiments.

### 2.2. Apparatus

$^1H$ NMR spectra were recorded on the JNM-ECS 400 MHz instruments spectrometers in $CDCl_3$ or DMSO-$d_6$ solution using TMS (tetramethylsilane) as an internal standard. The ESI-MS data were obtained in ethanol from a Bruke Esquire 6000 spectrometer. UV–vis absorption spectra were collected on a Shimadzu UV-240 spectrophotometer at 298 K. All fluorescence measurements were recorded on a Hitachi RF-5301 spectrophotometer equipped with quartz cuvettes of 1 cm path length at 298 K. Melting points were determined on a Beijing XT4-100× microscopic melting point apparatus without correction.



**Scheme 1.** The synthetic route of compound **1**.

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