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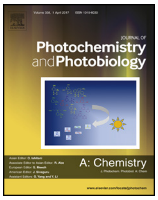

# A highly selective, fast-response and fluorescent turn on chemosensor for the detection of $Cu^{2+}$ ions and its potential applications

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ABSTRACT

In present report, a new **BDA** for $Cu^{2+}$ has been disclosed for the first time. The presence of $Cu^{2+}$ caused an obvious fluorescence enhancement at 407 nm upon excitation at 360 nm, which could be distinguished by the naked eye under a UV lamp. It was found to have acceptable detection limits (0.12 μM), high selectivity and reversibility/reusability. The photoluminescence measurement indicates that **BDA** with $Cu^{2+}$ presence, showed very strong blue emission bands with CIE chromaticity coordinates (0.1652, 0.0723). Besides, the designed probe has shown potential applications in the area of sample monitoring, photo-printing.

## 1. Introduction

Copper is an essential element in the human body, being required for enzymes involved in several key cellular activities, such as respiration, radical defense, neuronal myelination and angiogenesis. But on the other hand, copper is extremely toxic when excess copper is existed. For example, nausea [1], acute hemolysis [2] and renal tubular dysfunction [3]. Even more serious is that long-term over intake of copper is more likely to be the main cause of Alzheimer's Disease (AD) [4,5]. Besides, the disasters of anemia [6], osteoporosis [7], coronary heart disease [8], vitiligo [9] and other symptoms, would occur due to the lack of copper elements. Thus, WHO suggested that adults should take 0.03 mg of copper per kilogram of body weight per day to maintain health [10]. Up to now, many methods for detecting $Cu^{2+}$ involved atomic absorption spectroscopy, atomic emission spectrometry (AES) [11], and inductively coupled plasma mass spectrometry (ICP-MS) [12], electrochemical method and the colormetry. Among these methods, fluorescence analytical has received widespread attention for its advantages of operational simplicity, simple sample pretreatment and instrumentation, high sensitivity and selectivity, spatiotemporal resolution and non invasiveness [13]. So it is received much more attention for the construction of small fluorescent probes suitable for specific $Cu^{2+}$ detection in ecological environment and biological systems.

Recently, numerous fluorescent probes for $Cu^{2+}$ have been developed based on Rhodamine [14–18], Fluorescein [19–25], pyrene [26–28], 8-hydroxyquinoline [29–31], BODIPY derivatives [32], coumarin [33–35] and so on. These probes possessing large rigid π-conjugated system and the unique optical properties. Despite a large number of probes for $Cu^{2+}$ have been proposed, most of them can detect of $Cu^{2+}$ through only one channel, and some of them were used in organic solvent with high toxicity. Additionally, the probe which could be reversible for many times is worth to develop. So it is necessary to broaden the scope and to develop cost-effective probes that target $Cu^{2+}$ with high affinity, high sensitivity and selectivity.

In this work, we report a fluorescence probe, named 3,3′-[biphenyl-4,4′-diyldi(E)diazene-2,1-diyl]bis(4-aminonaphthalene) (**BDA**), (as shown in Fig. 1), which can be used as a selective probe for fast detect $Cu^{2+}$ through fluorescent and color when compared to other metal ions and anions. Despite its presence of donor N and O atoms in attached groups, this molecular system has never been explored for its metal sensing abilities. This work not only shed light on the different aspects of this particular sensing

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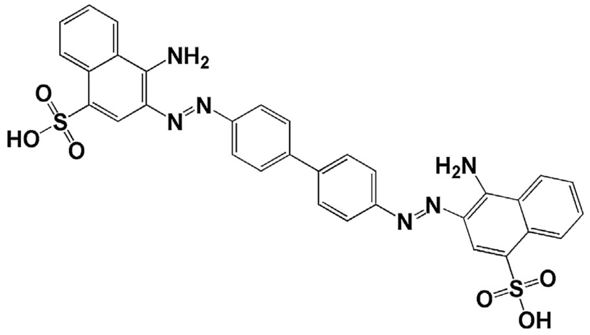

**Fig. 1.** The structure of **BDA**.

phenomenon but also explores the practical applicability of these newly disclosed systems in the realm of sample monitoring, membrane sensing and photo-printing.

## 2. Material and methods

### 2.1. Materials

Tris base was purchased from Sigma-Aldrich (St. Louis, MO). HCl (0.1 M) was added to aqueous Tris (25 mM) to adjust the pH to 7.20. The salts solutions of metal ions such as NaCl, KCl, $MgCl_2{\cdot}6H_2O$, $CaCl_2$, $BaCl_2$, $CrCl_3{\cdot}6H_2O$, $CoCl_2{\cdot}6H_2O$, $MnCl_2{\cdot}4H_2O$, $FeCl_3{\cdot}6H_2O$, $NiCl_2{\cdot}6H_2O$, $CuCl_2{\cdot}2H_2O$, $CdCl_2{\cdot}6H_2O$, $ZnCl_2$, SrCl, $AlCl_3$ and the salts solutions of anions such as $Na_3PO_4$, $Na_2CO_3$, NaAc, NaBr, $Na_2C_2O_4{\cdot}H_2O$, NaCl, NaF, $NaNO_3$, $NaNO_2$, $NaH_2PO_4$, $Na_2HPO_4$, $Na_2P_2O_7$, $Na_2B_4O_7$, $Na_2SO_4$, $NaClO_4$, NaCN, $NaHCO_3$, $NaHSO_4$ were purchased from Shanghai Experiment Reagent Co., Ltd (Shanghai, China). The filter membrane was purchased from Aladdin Reagent Co., Ltd (Shanghai, China). All other chemicals used were of analytical grade. Deionized water was used to prepare all aqueous solutions.

### 2.2. Instruments

$^1$H NMR and $^{13}$C NMR spectra were recorded on a Bruker DRX400 spectrometer with TMS as the internal standard. Electrospray ionization mass spectra (ESI–MS) were measured on a Finnigan LCQ system. Fluorescence spectra were recorded on RF-5301 spectrohotometer. Elemental analyses (EAs) were carried out with a VARI-EL elemental analyzer. FT-IR spectra (4000–400 cm$^{-1}$) were obtained on NICOLET380 FT-IR spectrometer in KBr disks. *pH* values of buffer solutions were measured using a PHS-3TC *pH* meter.

### 2.3. Fluorescent study

For fluorescence studies, stock solutions of the **BDA**, metal ions ($Na^+$, $K^+$, $Mg^{2+}$, $Ca^{2+}$, $Ba^{2+}$, $Cr^{3+}$, $Co^{2+}$, $Mn^{2+}$, $Fe^{3+}$, $Ni^{2+}$, $Cu^{2+}$, $Cd^{2+}$, $Zn^{2+}$, $Pb^{2+}$, $Al^{3+}$, $Hg^{2+}$, $Ag^+$) and anions ($NO_2^-$, $H_2PO_4^-$, $HPO_4^{2-}$, $P_2O_7^{2-}$, $PO_4^{3-}$, $SO_4^{2-}$, $C_2O_4^{2-}$, $B_4O_7^{2-}$, $CO_3^{2-}$, $ClO_4^-$, $NO_3^-$, $SCN^-$, $AC^-$, $F^-$, $Cl^-$, $Br^-$, $I^-$, $CN^-$, $HCO_3^-$, $HSO_4^-$) were prepared ($1.0 \times 10^{-3}$ M) in $CH_3CN$/Tris-HCl buffer ($v$:$v$ = 2:8, *pH* = 7.20). For spectral recordings, the stock solutions were further diluted to $1.0 \times 10^{-6}$ M. All fluorescence spectra were recorded from 380 to 600 nm in a quartz cell (1 cm path length) at room temperature (3.0 nm excitation and emission slit). Solutions were added through a Hamilton burette equipped with 1 mL syringe. For real time analysis was in $CH_3CN$/Tris-HCl buffer ($v$:$v$ = 2:8, *pH* = 7.20). The fluorescence intensity corrected for the inner filter effect was taken into account following the early report [36].

The binding constant was calculated from the emission intensity titration curve according to Eqs. (1) and (2) [37].

$$\frac{I_a - I_f}{I_b - I_f} = \frac{\left(b - (b^2 - 2K^2C_t[\mathrm{Cu}^{2+}]/s)^{1/2}\right)}{2KC_t} \qquad (1)$$

$$b = 1 + KC_t + K[\mathrm{Cu}^{2+}]/2s \qquad (2)$$

Where $I_a$ is the emission intensity observed at a given $Cu^{2+}$ concentration, $I_f$ is the emission intensity of free **BDA** in solution, $I_b$ is the emission intensity of **BDA** when fully bound to $Cu^{2+}$ (it is assumed that when further addition of $Cu^{2+}$ does not change the emission intensity), $K$ is the equilibrium binding constant, $C_t$ is the total **BDA** concentration, $[Cu^{2+}]$ is the $Cu^{2+}$ concentration, and $s$ is the binding ratio of [**BDA**]/$[Cu^{2+}]$. Both $K$ and $s$ are obtained from the best fit line.

## 3. Results and discussion

### 3.1. Structural characterization of **BDA**

As shown in Fig. 1, the structure of **BDA** was determined by $^1$H NMR, $^{13}$C NMR, Elemental analyses (EAs), Electrospray ionization mass spectra (ESI–MS), FT-IR spectra (IR) analysis (Figs. S1–S4). The elemental analysis data for **BDA** was consistent with the compositions of desired product. **BDA** showed absorption bands of infrared in 3483, 1609 for stretch vibrations of N—H, C—N, respectively. The $^1$H NMR and $^{13}$C NMR spectroscopy are the most precise method and a very convenient tool for determining the structure of the organic compounds. **Characterization**: $^1$H NMR (400 MHz, DMSO) $\delta$ 8.77 (dd, $J$ = 8.5, 1.0 Hz, 1H), 8.46 (d, $J$ = 8.4 Hz, 1H), 8.33 (s, 1H), 8.13 (d, $J$ = 8.6 Hz, 2H), 7.98 (d, $J$ = 8.7 Hz, 2H), 7.75 (s, 2H), 7.63–7.58 (m, 1H), 7.54–7.49 (m, 1H). $^{13}$C NMR (101 MHz, DMSO) $\delta$ 152.73 (s), 146.51 (s), 140.43 (s), 132.91 (s), 132.27 (s), 129.45 (s), 128.69 (d, $J$ = 9.1 Hz), 127.94 (s), 125.39 (s), 124.67 (s), 124.25 (s), 123.39 (s), 117.77 (s). Exact mass for **BDA**: 652.12, ESI–MS (positive mode) [**BDA** – 2H]$^{2-}$ ($m/z$, 325.2325).

### 3.2. Fluorescence studies of **BDA** with various metal ions and anions in different solvent systems

In present work, the selective recognition ability of **BDA** for metal ions and anions in different solvents system (including methanol, ethanol, tetrahydrofuran, dichloromethane, ethyl acetate, acetonitrile, Tris-HCl buffer *pH* = 2.0–11.0) were studied. The results showed that **BDA** can be used to recognize the $Cu^{2+}$ through the fluorescent emission in $CH_3CN$/Tris-HCl buffer ($v$:$v$ = 2:8, *pH* = 7.20). (Fig. 2). The emission spectrums of **BDA** were studied when various metals ions were added (10 equiv) in $CH_3CN$/Tris-HCl buffer ($v$:$v$ = 2:8, *pH* = 7.20), such as $Na^+$, $K^+$, $Mg^{2+}$, $Ca^{2+}$, $Ba^{2+}$, $Cr^{3+}$, $Co^{2+}$, $Mn^{2+}$, $Fe^{3+}$, $Ni^{2+}$, $Cu^{2+}$, $Cd^{2+}$, $Zn^{2+}$, $Pb^{2+}$, $Al^{3+}$, $Hg^{2+}$, $Ag^+$. It could be easily seen that the fluorescence intensity of **BDA** increased approximately by 15-fold at 407 nm ($\lambda_{ex}$ = 360 nm) with notable fluorescence changed from colorless to blue when $Cu^{2+}$ was added. The fluorescence emission intensity almost had no changes when other metal ions were added. In addition, the presence of other anions (up to 10 equiv.), such as $NO_2^-$, $H_2PO_4^-$, $HPO_4^{2-}$, $P_2O_7^{2-}$, $PO_4^{3-}$, $SO_4^{2-}$, $C_2O_4^{2-}$, $B_4O_7^{2-}$, $CO_3^{2-}$, $ClO_4^-$, $NO_3^-$, $SCN^-$, $AC^-$, $F^-$, $Cl^-$, $Br^-$, $I^-$, $CN^-$, $HCO_3^-$, $HSO_4^-$ shown no obvious fluorescence changes and could not interfere with the determination of $Cu^{2+}$ (Fig. S5). All the above results prove that the **BDA** exhibits a high selectivity for $Cu^{2+}$. This method represents an extremely easy way to qualitatively and quantitatively determine the presence of $Cu^{2+}$.