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## A naked-eye fluorescent sensor for copper(II) ions based on a naphthalene conjugate Bodipy dye†

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A novel naphthalene-Bodipy dye (N-Bodipy) was designed, prepared and characterized. N-Bodipy showed a selective and sensitive recognition toward Cu(II) ions as a fluorescent antenna group in acetonitrile/water over other metal cations. The complexation between Cu(II) ions and N-Bodipy gave a specific color change as well as caused fluorescence quenching under long-wavelength light (365 nm). The remarkable quenching effect in fluorescence intensity centered at 538 nm was only observed in the presence of copper(II) ions. Moreover, the orange color of N-Bodipy solution turned pale-yellow depending on the complexation effect in daylight. The complex stoichiometry was determined using a Job's plot and it was found to be 2 : 1 (ligand/metal). The binding constant was calculated with the Benesi–Hildebrand equation to be  $1.39 \times 10^{10} \text{ M}^{-1}$  and the detection limit was 1.28  $\mu\text{M}$  ( $\text{LOD} = 3\alpha/\text{slope}$ ,  $\alpha$  is the standard deviation) for Cu(II). The data proved that the binding between N-Bodipy and Cu(II) is chemically reversible.

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## Introduction

The selective detection of heavy metals is very important for environmental chemistry, medicinal chemistry and biochemistry. Copper is one of the most abundant among the essential transition metals in the human body. So, the copper ion has a crucial role in various physiological processes due to its catalytic and oxidative properties in living organisms.<sup>1</sup> However, the excess of copper ions can cause oxidative stress and neurodegenerative diseases including Alzheimer's, Parkinson's and Menkes. The copper ion can catalyze the formation of reactive oxygen species and its toxic nature damages the structures of lipids, nucleic acids, and proteins.<sup>1,2</sup> Moreover, copper ions can also cause pollution in drinking water. The highest level of copper contaminants allowed by the United States Environmental Protection Agency in drinking water is 1.3  $\text{mg L}^{-1}$  ( $\sim 1 \text{ ppm}$ ).<sup>3</sup> Therefore, the detection and removal of copper ions is a critical problem. Many detection methods have been used for this such as atomic absorption spectrometry,<sup>1–4</sup> voltammetric techniques,<sup>5</sup> inductively coupled plasma-atomic emission spectrometry (ICP-AES)<sup>6</sup> and fluorescence spectroscopy.<sup>7</sup> The standard instrumental techniques are expensive and not generally suitable for many applications,<sup>8–18</sup> and it becomes important to find alternative ways for determination of heavy-metal ions. The use of fluorescence spectroscopy is an

alternative method which has many advantages such as being low-cost, convenient, sensitive, having high selectivity for specific materials, having a broad analyte scope and simple operation.<sup>19,20</sup> Many reports based on fluorescence quenching sensors (turn-off sensors) for the detection of copper ions are available in the literature.<sup>21</sup>

A general view for the determination of metal ions using fluorescence sensors is based on the combination of metal ions and a fluorophore. When the metal ions interact with the donor atoms of the fluorophore it results in a change in fluorescence intensity or in the maximum peak wavelength of the fluorophore. The change in the fluorescence intensity may be either in the form of a decrease (quenching, turn off) or increase (turn-on) for fluorescence sensor processes. The quenching effect occurs generally by a charge or energy transfer between the quencher (copper(II) ion) and the fluorophore.

Boron-dipyrromethene (Bodipy) dyes have been generally chosen as an antenna group for fluorescence sensor studies due to several reasons such as their good quantum yields in non-polar solvents, remarkable molar absorption coefficients and clear fluorescence peaks.<sup>22</sup> Therefore, these substances are also widely used in anion determinations as pH indicators and metal sensors based on photoinduced electron transfer (PET) and intramolecular charge transfer (ICT) mechanisms.<sup>23</sup> There are various Bodipy-based fluorescent sensors for the detection of copper ions owing to the intrinsic fluorescence quenching property of Cu(II), and most of the research studies are based on fluorescence “on–off” behavior.<sup>2,24</sup>

This paper reports that the binding properties of metal ions [Ag(I), Ca(II), Cr(III), Co(II), Cu(II), Fe(II), Fe(III), Hg(II), K(I), Mg(II),

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Mn(II), Ni(II), Pb(II), and Zn(II)] were investigated toward N-Bodipy, but only the Cu(II) ion causes a remarkable quenching effect. This result can be explained with the photoinduced electron transfer (PET) mechanism from N-Bodipy to the Cu(II) ion. Thus, N-Bodipy can be considered as a selective and sensitive fluorescent probe for copper(II) ions.

## 2. Experimental

### 2.1. Materials and instruments

$^1\text{H}$ ,  $^{13}\text{C}$ -NMR,  $^{11}\text{B}$ -NMR  $^{19}\text{F}$ -NMR spectra were recorded at r.t. on Varian 400 MHz and Bruker 400 MHz spectrometers in  $\text{CDCl}_3$  (ESI $^\dagger$ ). The melting point of compounds was measured on a Gallenkamp apparatus. Infrared measurements were performed on a Bruker Fourier Transform Infrared FTIR (ATR). UV-vis curves were obtained by using a PerkinElmer Lambda 25 UV-vis spectrophotometer. The emission data (slits: 5 nm) were obtained on a PerkinElmer LS 55 fluorescence spectrophotometer in a fixed excitation. All measurements were carried out at 298 K. The elemental analyses results were obtained from a TruSpec elemental analyzer. Thin layer chromatography plates were supplied from Merck (silica gel 60 F254 on aluminum). The synthesis of all compounds was carried out under a nitrogen atmosphere. The solutions of metal ions were prepared by using their chloride salts. All chemicals were supplied from Fluka, Fisher Scientific (USA) and Acros Organics (USA), and Aldrich and used without purification.

### 2.2. Synthesis of compounds

**2.2.1. Synthesis of 8-{4-(chloromethyl)phenyl}-2,6-diethyl-4,4-difluoro-1,3,5,7-tetramethyl-4-bora-3a,4a-diaza-s-indacene (chloromethyl-Bodipy).** 4-(Chloromethyl)benzoyl chloride (3.750 g, 0.02 mol) was dissolved in dry dichloromethane (100 mL) and this solution was added dropwise to a dichloromethane solution of 2,4-dimethyl-3-ethylpyrrole (5.4 mL, 0.04 mol) at r. t. under  $\text{N}_2$ . The mixture was stirred at 60 °C for 2 h. Then, the solution was cooled to room temperature and triethylamine (TEA) (5 equiv.) was injected with a syringe. The mixture was stirred at r.t. for 30 min under  $\text{N}_2$  and then boron trifluoride diethyl etherate (7 equiv.) was dropwise added.<sup>22</sup> After the refluxing of the solution for 2 h and evaporating the solvent, the raw product was purified by column chromatography (petroleum ether-EtOAc in 8:1 ratio). A red solid (3.35 g, yield 40%). M.P.: 188 °C.  $^1\text{H}$  NMR [400 MHz,  $\text{CDCl}_3$ ]: 7.40 (d, PhH, 2H), 7.19 (d PhH, 2H), 4.61 (s,  $-\text{CH}_2$ , 2H), 2.42 (s,  $-\text{CH}_3$ , 6H), 2.20 (q,  $-\text{CH}_2$ , 4H), 1.26 (s,  $-\text{CH}_3$ , 6H), 0.91 (t,  $-\text{CH}_3$ , 6H).  $^{13}\text{C}$  NMR [100 MHz,  $\text{CDCl}_3$ ]:  $\delta$  (ppm); 154.01, 138.99, 138.21, 135.93, 135.44, 133.01, 130.98, 128.81, 129.11, 45.77, 16.92, 14.51, 12.73, 11.88. Anal. calc. for (%)  $\text{C}_{24}\text{H}_{28}\text{N}_2\text{F}_2\text{ClB}$ : C, 67.22; H, 6.57; N, 6.52; found: C, 66.87; H, 6.55; N, 6.33. MS for  $\text{C}_{24}\text{H}_{28}\text{N}_2\text{F}_2\text{ClB}$   $m/z$ : 428.1  $[\text{M} + \text{H}]^+$ .

**2.2.2. Synthesis of 8-{4-(azidomethyl)phenyl}-2,6-diethyl-4,4-difluoro-1,3,5,7-tetramethyl-4-bora-3a,4a-diaza-s-indacene (azidomethyl-Bodipy).** Chloromethyl-Bodipy (188 mg,

0.44 mmol), LiBr (174 mg, 0.44 mmol) and  $\text{NaN}_3$  (340 mg, 2.6 mmol) in DMF (10 mL) were mixed at r.t. for 24 h under  $\text{N}_2$ , and then  $\text{H}_2\text{O}$  (45 mL) was added. The aqueous layer was extracted with ethylacetate and the organic phase was dried with  $\text{MgSO}_4$ , filtered, and concentrated. Column chromatography ( $\text{SiO}_2$ ;  $\text{CH}_2\text{Cl}_2$ ) gave 7 (278 mg, 97%) as a dark-red solid that was used as received. M.P.: 140 °C.  $^1\text{H}$ -NMR [400 MHz,  $\text{CDCl}_3$ ]: 7.43 (d, PhH, 2H), 7.31 (d, PhH, 2H), 4.46 (s,  $-\text{CH}_2$ , 2H), 2.55 (s,  $-\text{CH}_3$ , 6H), 2.30 (q,  $-\text{CH}_2$ , 4H), 1.26 (s,  $-\text{CH}_3$ , 6H), 1.02 (t,  $-\text{CH}_3$ , 6H).  $^{13}\text{C}$  NMR [100 MHz,  $\text{CDCl}_3$ ]:  $\delta$  (ppm); 153.22, 139.33, 138.12, 136.17, 135.53, 132.81, 130.62, 128.32, 128.18, 55.19, 17.44, 15.14, 12.32, 11.99.

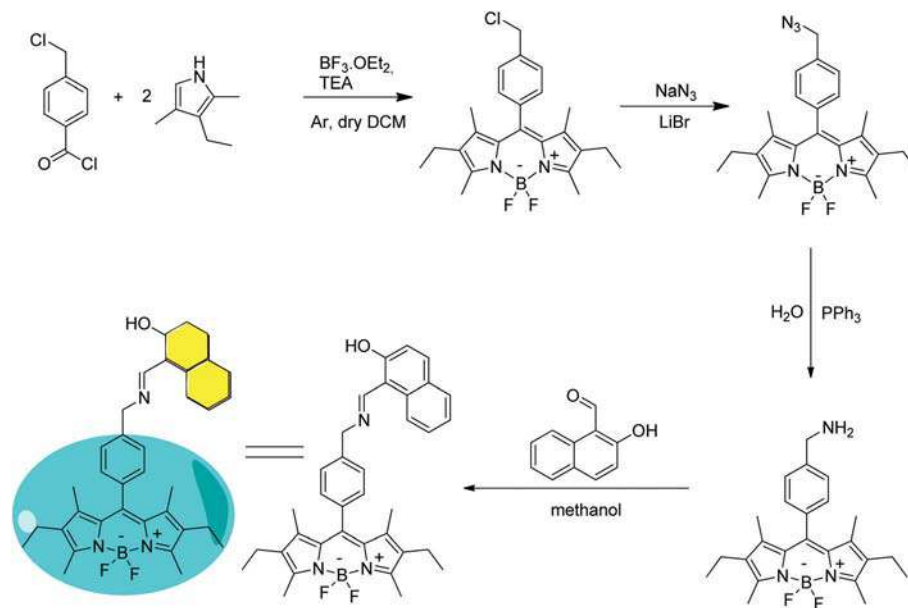
**2.2.3. Synthesis of 8-{4-(aminomethyl)phenyl}-2,6-diethyl-4,4-difluoro-1,3,5,7-tetramethyl-4-bora-3a,4a-diaza-s-indacene (aminomethyl-Bodipy).** A mixture of azidomethyl-Bodipy (435 mg, 1 mmol) and  $\text{PPh}_3$  (1 mmol, 262 mg) in dry THF (20 mL) was stirred for 5 h at room temperature under Ar, and then  $\text{H}_2\text{O}$  (2 drops) was added. This mixture was stirred overnight and the solvent was evaporated. Column chromatography ( $\text{SiO}_2$ ; DCM/MeOH: 10/1) offered aminomethyl-Bodipy (298 mg, 73%) as a red solid. M.P.:  $\approx 170$  °C.

$^1\text{H}$ -NMR [400 MHz,  $\text{CDCl}_3$ ]: 7.43 (d, PhH, 2H), 7.25 (d, PhH, 2H), 4.02 (s,  $-\text{CH}_2$ , 2H), 2.55 (s,  $-\text{CH}_3$ , 6H), 2.35 (q,  $-\text{CH}_2$ , 4H), 1.22 (s,  $-\text{CH}_3$ , 6H), 1.0 (t,  $-\text{CH}_3$ , 6H).  $^{13}\text{C}$  NMR [100 MHz,  $\text{CDCl}_3$ ]:  $\delta$  (ppm); 154.22, 142.33, 139.82, 137.17, 134.83, 132.99, 130.76, 128.32, 128.00, 46.22, 17.34, 14.84, 12.42, 12.02.

**2.2.4. Synthesis of 8-{4-((E)-1-((methylimino)methyl)naphthalen-2-ol)phenyl}-2,6-diethyl-4,4-difluoro-1,3,5,7-tetramethyl-4-bora-3a,4a-diaza-s-indacene (N-Bodipy).** Aminomethyl-Bodipy (0.409 g, 1 mmol) was dissolved in methanol (10 mL) and added dropwise to a solution of 2-hydroxy-1-naphthaldehyde (0.122 g, 1 mmol) in methanol (10 mL). The mixture was stirred at r.t. overnight. After the evaporation of the solvent, the raw product was purified on a column. An orange-red solid (516 mg, yield 92%). M.P.: 295 °C.  $^1\text{H}$ -NMR [400 MHz,  $\text{CDCl}_3$ ]: 11.55 (bs,  $-\text{OH}$ , 1H), 8.75 (s,  $\text{N}=\text{CH}$ , 1H), 7.45 (m, PhH, 4H), 7.28 (m, PhH, 4H), 7.18 (d, PhH, 2H), 4.70 (s,  $-\text{CH}_2$ , 2H), 2.55 (s,  $-\text{CH}_3$ , 6H), 2.35 (q,  $-\text{CH}_2$ , 4H), 1.22 (s,  $-\text{CH}_3$ , 6H), 1.0 (t,  $-\text{CH}_3$ , 6H).  $^{13}\text{C}$  NMR [100 MHz,  $\text{CDCl}_3$ ]:  $\delta$  (ppm): 165.21, 155.32, 141.98, 138.85, 137.61, 136.32, 136.19, 134.42, 132.96, 132.81, 131.55, 130.61, 128.02, 127.21, 125.11, 124.53, 62.22, 17.49, 14.77, 12.22, 11.99. Anal. calc. for (%)  $\text{C}_{35}\text{H}_{36}\text{BF}_2\text{N}_3\text{O}$ : C, 74.60; H, 6.44; N, 7.46; found: C, 74.97; H, 6.88; N, 7.32. MS for  $\text{C}_{35}\text{H}_{36}\text{BF}_2\text{N}_3\text{O}$   $m/z$ : 564.1  $[\text{M} + \text{H}]^+$ . MS for the N-Bodipy/Cu(II) complex  $\text{C}_{70}\text{H}_{70}\text{B}_2\text{F}_4\text{N}_6\text{O}_2$   $m/z$ : 1253.2  $[\text{M} + \text{H}]^+$  (Scheme 1).

## 3. Results and discussion

The changes in melting points can be explained with the increasing molecular weight and more intermolecular interactions. All changes in the melting point primarily prove the synthesis of the target compounds.



**Scheme 1** The synthesis procedure of N-Bodipy.

The design of the target compound (N-Bodipy) was firstly decided due to the cheaper practical synthesis, and high yield of aminomethyl-Bodipy through bridge-CH<sub>2</sub> units. However, bridge-CH<sub>2</sub> did not affect the fluorescence character of the target Bodipy and energy transfer. To the best of our knowledge, the obtained Bodipy derivative has some advantages such as usability as a metal-trap and the excellent ligand nature of Schiff bases. So, Cu(II) was easily encapsulated by the ligand due to its electron-donor groups and the best result was observed only in 3 minutes.

The NMR spectra of all compounds were given in the ESI.† The aliphatic protons (CH<sub>2</sub>'s and CH<sub>3</sub>'s) on the Bodipy core appeared between 2.5 and 1 ppm in the spectra of all compounds. The CH<sub>2</sub> protons around 4–5 ppm are crucial for the synthesis of chloromethyl-Bodipy, azidomethyl-Bodipy and aminomethyl-Bodipy. So, these protons were observed at 4.63, 4.46 and 4.02 ppm as singlets, respectively. The same peak was observed at 4.70 ppm in the <sup>1</sup>H-NMR of N-Bodipy and the CH proton of the Schiff base appeared at 8.75 ppm in the singlet form. Moreover, the aromatic protons overlapped in the multiplet form between 7 and 8 ppm. <sup>13</sup>C-NMR spectra of compounds show parallel results that the carbon signals of aliphatic groups appeared around 0–20 ppm while aromatic moieties' carbon gave a lot of peaks between 120 and 160 ppm. The bridge CH<sub>2</sub>' signals were observed at 45, 55, 46 and 62 ppm for chloromethyl-Bodipy, azidomethyl-Bodipy, aminomethyl-Bodipy and N-Bodipy, respectively. The most specific peak of N-Bodipy is the carbon signal of the C=N fragment occurred following Schiff base condensation which appeared at 165 ppm.

In the FT-IR spectrum of azidomethyl-Bodipy, the bands appeared at 2961 cm<sup>-1</sup>, 2868 cm<sup>-1</sup>, 1650 cm<sup>-1</sup>, 1542 cm<sup>-1</sup> and 1475 cm<sup>-1</sup> which can be attributed to aromatic νC–H, aliphatic

νC–H, imine νC=N, and alkene νC=C, respectively (ESI†). For azidomethyl-Bodipy, the most specific peak was observed at 2092 cm<sup>-1</sup> and the peak assigned to the N=N stretching of the azido fragment. This peak disappeared in the infrared spectrum of aminomethyl-Bodipy after the conversion of the azido unit. Instead of this stretching, the N–H vibration was observed at 3404 cm<sup>-1</sup> as a smaller peak. Other peaks slightly shifted to higher or lower frequencies. The FT-IR spectrum of N-Bodipy shows a new sharp band assigned C=N vibration at 1631 cm<sup>-1</sup>. As can be seen in the FT-IR spectrum, the N–H peak disappeared. Finally, the C=N band permanently shifted toward 1608 cm<sup>-1</sup> in the FT-IR spectrum of the N-Bodipy/Cu(II) complex.

The spectroscopic experiments of N-Bodipy are performed by UV-Vis and fluorescence spectroscopy. The UV-vis curves of N-Bodipy are obtained in the presence of some metal cations. The absorption spectra (Fig. 1) display that N-Bodipy has exhibited a specific major visible absorption band at 516 nm. When 20 equiv. of other metal cations were added, an important effect was not observed. However, the Cu(II) ion caused a crucial quenching in the absorption band of N-Bodipy as shown in Fig. 1. According to the absorption data, N-Bodipy has a good selectivity for the copper(II) ion over the other used metal ions.

The spectroscopic properties and the selective fluoroionophoric properties of N-Bodipy were initially investigated toward some transition metal ions such as Ag(I), Al(III), Cd(II), Co(II), Cr(III), Cu(II), Fe(III), Hg(II), Mn(II), Ni(II), Pb(II), Sn(II), Vo(II), and Zn(II). Upon increasing the amount of metal ions, the intensity of the emission band at ≈538 nm decreased (Fig. 2). As shown in Fig. 2, Cu(II) caused an important difference in the emission of N-Bodipy while no remarkable change was observed for the studied metal cations. By the interaction

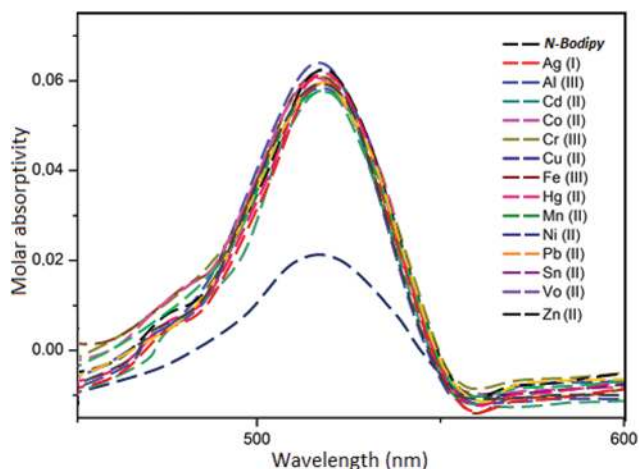


Fig. 1 The absorption spectra of N-Bodipy ( $5 \times 10^{-6}$  M in acetonitrile/ $\text{H}_2\text{O}$  (8 : 2)) in the presence of different metal ions (Ag(I), Al(III), Cd(II), Co(II), Cr(III), Cu(II), Fe(III), Hg(II), Mn(II), Ni(II), Pb(II), Sn(II), Vo(II), and Zn(II) (20 equiv.)) in acetonitrile/ $\text{H}_2\text{O}$  (8 : 2).

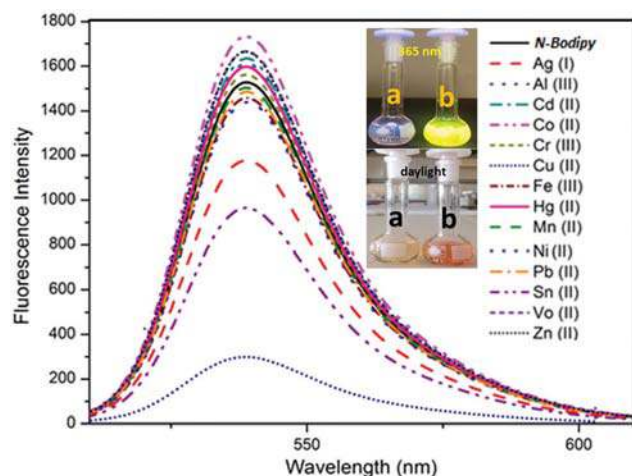


Fig. 2 The fluorescence intensities of N-Bodipy ( $5 \times 10^{-6}$  M in acetonitrile/ $\text{H}_2\text{O}$  (8 : 2)) in the presence of different metal ions (Ag(I), Al(III), Cd(II), Co(II), Cr(III), Cu(II), Fe(III), Hg(II), Mn(II), Ni(II), Pb(II), Sn(II), Vo(II), and Zn(II) (20 equiv.)) in acetonitrile,  $\lambda_{\text{ex}}$ : 470 nm, slit: 5 nm. (a) N-Bodipy/ $\text{Cu(II)}$  mixture and (b) N-Bodipy under long-wavelength 365 nm and daylight, respectively.

of the copper ion with N-Bodipy, the emission band appeared at 538 nm. The emission intensity reached a minimum with 20.0 equivalents of  $\text{Cu(II)}$ . These observations indicate that N-Bodipy is highly selective for the  $\text{Cu(II)}$  ion. The fluorescence quenching effect can be explained with a reversible PET (photoinduced electron transfer)<sup>25</sup> from the Schiff base based on Bodipy to the  $\text{Cu(II)}$  ion.<sup>26</sup>

In order to determine the metal–ligand ratio of the N-Bodipy/ $\text{Cu(II)}$  complex, the Job plotting method was used. The Job's graph shown in Fig. 3 for the N-Bodipy/ $\text{Cu(II)}$  complex that represented a maximum for the absorption

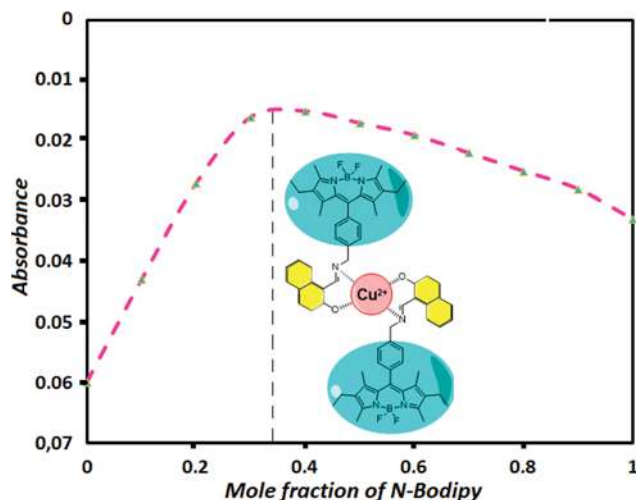


Fig. 3 Job plot of the N-Bodipy/ $\text{Cu(II)}$  complex in acetonitrile, keeping the total concentration of N-Bodipy and  $\text{Cu(II)}$  [acetonitrile/ $\text{H}_2\text{O}$  (8 : 2)].

bands around 0.33 mole fraction of  $\text{Cu(II)}$  to N-Bodipy indicated 2 : 1 formation for the ligand/metal ratio.

We have also investigated the concentration effect on the fluorescence intensity of N-Bodipy (Fig. 4). As seen in Fig. 4, the fluorescence intensity of N-Bodipy decreased with the increasing concentration of  $\text{Cu(II)}$  but there is no shift in the emission wavelength of N-Bodipy. The peak intensity is completely quenched when the maximum copper concentration is used. This quenching effect is achieved by the charge transfer between imine-nitrogen/oxygen atoms of N-Bodipy and the metal. The binding constant for the metal and the ligand (N-Bodipy) was calculated by using the graph shown in Fig. 5 and the Benesi–Hildebrand equation (eqn (1)):

$$1/(F - F_0) = 1/\{K(F_{\text{max}} - F_0) [\text{M}]^n\} + 1/[F_{\text{max}} - F_0] \quad (1)$$

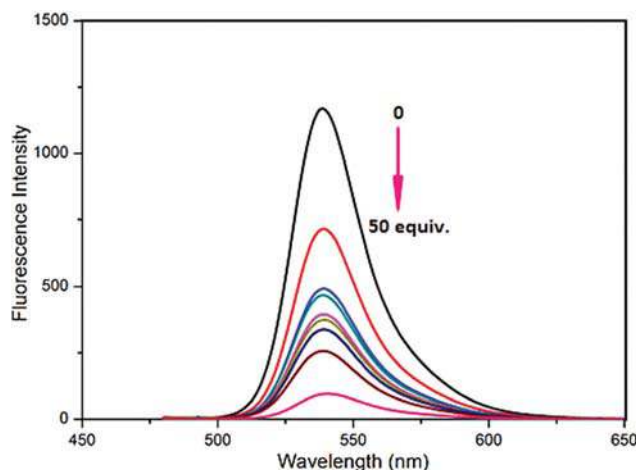
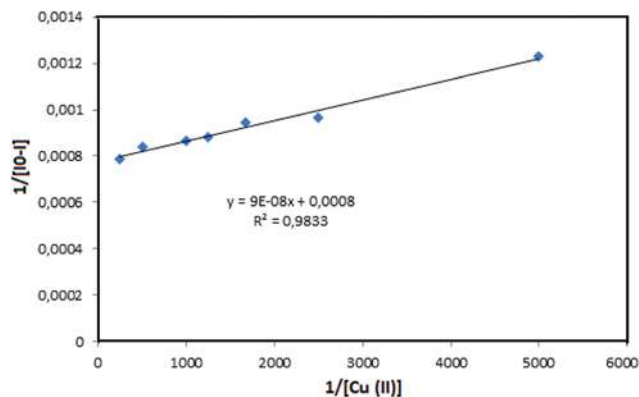


Fig. 4 The fluorescence intensities of N-Bodipy ( $5 \times 10^{-6}$  M) in the presence of different concentrations ( $1 \times 10^{-5}$ ,  $2 \times 10^{-5}$ ,  $3 \times 10^{-5}$ ,  $4 \times 10^{-5}$ ,  $5 \times 10^{-5}$ ,  $6 \times 10^{-5}$ ,  $1 \times 10^{-4}$ ,  $2.5 \times 10^{-4}$  M) of  $\text{Cu(II)}$  metal ions (20 equiv.) in acetonitrile/ $\text{H}_2\text{O}$  (8 : 2),  $\lambda_{\text{em}}$ : 538 nm, slit: 5 nm.



**Fig. 5** Benesi–Hildebrand plot of N-Bodipy with Cu(II) in acetonitrile. The excitation wavelength was 400 nm and the observed wavelength was 538 nm [acetonitrile/H<sub>2</sub>O (8 : 2)]. The binding constant was  $1.39 \times 10^{10}$  M for Cu(II) binding in N-Bodipy.

where  $F_0$  is the fluorescence intensity of the ligand in the absence of the metal ion and  $F$  is the fluorescence intensity in the presence of the metal ion.  $F_{\max}$  is the fluorescence intensity in the presence of added  $[M]_{\max}$  (max. metal concentration) and  $K$  is the association constant ( $M^{-2}$ ). The association constant ( $K_a$ ) could be determined from the slope of the linear graph of  $1/(F - F_0)$  against  $1/[M]^n$  (Fig. 5).

The binding constant ( $K$ ) was graphically calculated by plotting  $1/(I_0 - I)$  against  $1/[Cu(II)]$  (Fig. 5). The binding constant ( $K$ ) of Cu(II) binding in N-Bodipy was found to be  $1.39 \times 10^{10} M^{-2}$ .

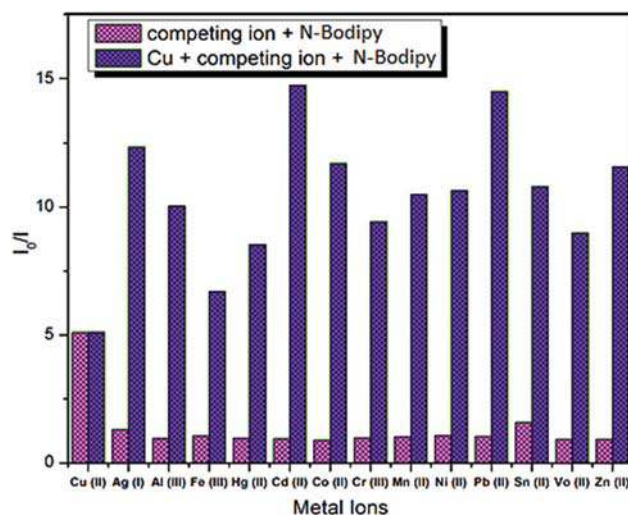
The limit of detection (LOD) of N-Bodipy for Cu(II) was determined from the following equation:

$$LOD = 3\alpha/K$$

where  $\alpha$  is the standard deviation of the blank solution;  $K$  is the slope of the calibration curve.

The detection limit of N-Bodipy towards the Cu(II) cation was found to be  $1.28 \mu M$ . This value is within the United States Environmental Protection Agency's copper limit for drinking water.

The experiments on the competing ions were performed in the presence of the Cu(II) ion ( $1 \times 10^{-4}$  M) mixed with Ag(I), Al(III), Cd(II), Co(II), Cr(III), Fe(III), Hg(II), Mn(II), Ni(II), Pb(II), Sn(II), Vo(II), and Zn(II) at  $1 \times 10^{-4}$  M concentration (Fig. 6). The competing ions have a similar effect on the fluorescence property that was caused by Cu(II) alone. The fluorescence change is observed only when Cu(II) was mixed with Fe(III), which indicates that Fe(III) competes with Cu(II) for binding with N-Bodipy. It is found that the other metal ions have no effect on the binding of N-Bodipy with Cu(II). Accordingly, these results confirm that N-Bodipy can behave as a selective fluorescent sensor towards the Cu(II) ion in the presence of most competing metal ions too.



**Fig. 6** The changes of the maximum fluorescence peaks of N-Bodipy ( $5 \times 10^{-6}$  M acetonitrile/H<sub>2</sub>O (8 : 2)) in the presence of both Cu(II) and the competing metal ions (20.0 equiv.),  $\lambda_{em}$ : 510 nm.

As is known, the response time for a lot of fluorescent chemosensors is one of the most important factors. A sensing response time of N-Bodipy was recorded for Cu(II) ions at various times (1, 2, 3, 4, 5, 6, 7, 8, 9, 10 and 20 minutes) and the fluorescence intensities (a.u.) are shown in Fig. 8 as a color wheel. By the addition of copper solution, the portions in the color wheel quickly decreased depending on the quenching in the fluorescence intensity of N-Bodipy. While the fluorescence intensity is higher in the free ligand form, the complexation effect caused a lower fluorescence intensity. The quenching effect almost stopped after three minutes, and the fluorescence intensity continued with a stable value through the increasing time. The response time experiment shows a perfect result for selective sensors that N-Bodipy may be used in the range of 1–5 min for the Cu(II) ion (Fig. 7).

Moreover, to determine the sensing level of N-Bodipy at the physiological level, the effect of pH of the free ligand and N-Bodipy complex on the fluorescence spectra was investigated at different pH values (5–10). As shown in Fig. 8, the fluorescence intensity of N-Bodipy quickly decreased in acidic medium (pH: 5–6) while no obvious fluorescence change was observed in higher pH values, indicating that the sensor was stable in a wide range of pH. The emission intensity of N-Bodipy in the presence of the Cu(II) ion was seen to change depending on the pH value, and the N-Bodipy/Cu(II) complex remains in a stable form in the pH range of 5.0–8.0. Then, basic medium caused the decomposition of the target complex and the fluorescence character of N-Bodipy re-emerged. In a highly basic medium, OH ions and N-Bodipy compete for the Cu(II) ion. It induces the metal ion precipitation; therefore, the emission intensity slightly re-increased. These results prove that N-Bodipy exhibits a satisfactory Cu(II) sensing ability in the physiological pH range.

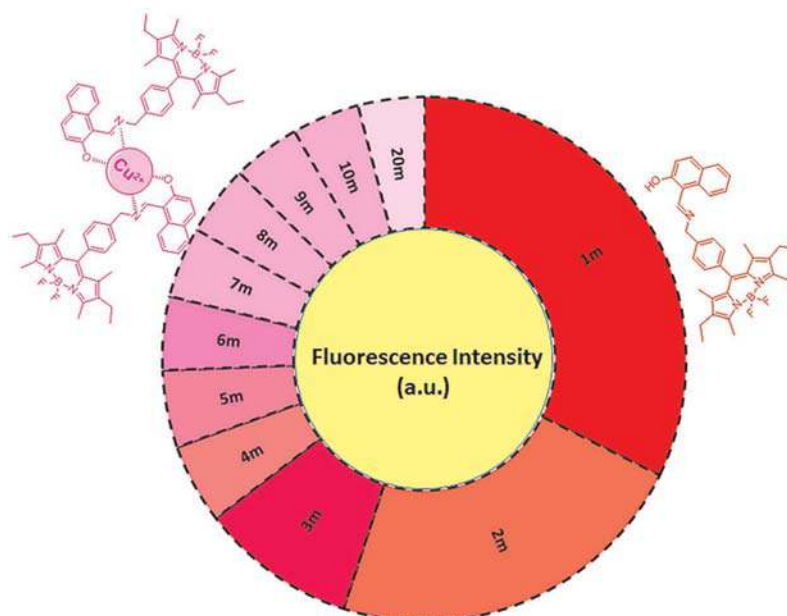


Fig. 7 The effect of the response time (1, 2, 3, 4, 5, 6, 7, 8, 9, 10 and 20 minutes) on the fluorescence intensity of N-Bodipy [ $5 \times 10^{-6}$  M in acetonitrile/ $\text{H}_2\text{O}$  (8 : 2)] by the addition of the Cu(II) ion [ $1 \times 10^{-4}$  M in acetonitrile/ $\text{H}_2\text{O}$  (8 : 2)] ( $\lambda_{\text{em, max}}$ : 538 nm).

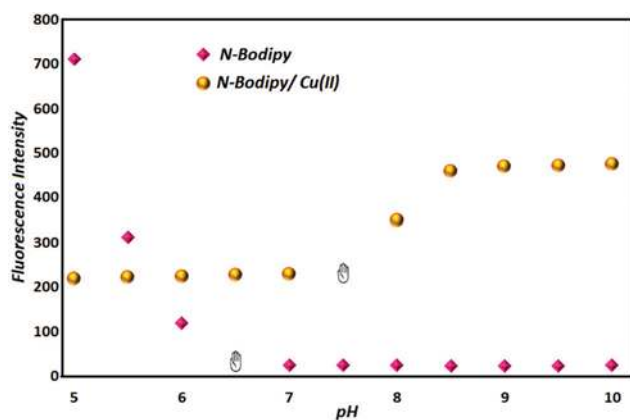


Fig. 8 The effect of pH (range of pH: 5–10) on the fluorescence intensity of N-Bodipy [ $5 \times 10^{-6}$  M in acetonitrile/ $\text{H}_2\text{O}$  (8 : 2)] by the addition of the Cu(II) ion [ $1 \times 10^{-4}$  M in acetonitrile/ $\text{H}_2\text{O}$  (8 : 2)] ( $\lambda_{\text{em}}$ : 538 nm).

## Conclusion

In conclusion, we have prepared and characterized a new fluorescent dye based on naphthalene and Bodipy that can achieve the detection of Cu(II) using appropriate donor atoms. The selective binding of N-Bodipy to Cu(II) caused immediate and remarkable fluorescence quenching without the change of the emission wavelength, which proved that N-Bodipy could serve as a sensitive and selective colorimetric/fluorometric sensor of Cu(II). The 2 : 1 complex stoichiometry between N-Bodipy and Cu(II) was proposed using a Job's plot and the association constant was  $1.39 \times 10^{10} \text{ M}^{-1}$  and the detection limit was  $1.28 \mu\text{M}$ . Furthermore, the colorimetric and fluorometric sensor,

N-Bodipy, can be used to detect Cu(II) in half-water samples with high accuracy in a lot of experiments, suggesting its quality and importance in removal and detection in the future.

## Conflicts of interest

There are no conflicts to declare.

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