



A Novel Fluorescent Chemosensor for Cu (II) Ion: Click Synthesis of Dual-Bodipy Including the Triazole Groups and Bioimaging of Yeast Cells

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Abstract

A fluorescent chemosensor including dual Bodipy units (*d-BODIPY*) was improved for selective copper (II) sensing in half-aqueous samples. The sensor *d-BODIPY* has a highly selective and sensitive detection towards Cu (II) over the studied competing for metal cations. The interaction among solutions of Cu (II) and *d-BODIPY* caused a crucial quenching effect in fluorescence maxima at 548 nm ($\lambda_{\text{ex}} = 470$ nm) owing to the electronic trap occurring between the amide and triazole units. The quenching effect without any change in wavelength can be explained by a photoinduced electron transfer (PET) process. The binding constant (K_a) of *d-BODIPY* with Cu (II) was calculated and also the limit of detection of *d-BODIPY* for Cu (II) was 1.2×10^{-8} M. In addition, the bio-imaging in the yeast cells suggested that *d-BODIPY* had an excellent potential to be used to investigate Cu (II).

Keywords Bodipy · Fluorescent · Click · Copper · Yeast

Introduction

Chemists and biochemists focused on chemosensors owing to the visible selective/sensitive detection of various transition metals [1–3] and biological ions in the aqueous or half-aqueous medium [4–9]. Therefore, various analytical methods have been developed for the sensitivity experiments of metal cations. The using of fluorescent materials gained importance in the detection and removal of metal cations and anions in aqueous medium [10–12]. There are many studies for the development of fluorescent chemosensors, which can detect copper and other metal ions [13–18]. Although the synthesized chemosensors can selectively recognize to the metal ion, the detection of Cu^{2+} ions is still one of the biggest problems to be overcome. For the development of an effective fluorescent sensor used in the identification of metal ions, photoinduced electron transfer (PET) and the intramolecular charge transfer (ICT) system-based fluorescence signaling

mechanisms are proposed [19–21]. Some experimental data indicate that photoinduced electron transfer plays a key role in the photophysical properties of donor-acceptor compounds. Photoinduced electron transfer is the electron transfer process in the excited-state. Here, the excited electron is transferred from the donor to the acceptor. A lot of fluorescent sensors were proposed by scientists working on rhodamine [22, 23], fluorescein, Bodipy [24, 25], coumarin [26] dansyl chloride [27] have been fabricated for the detection and removal of heavy metal ions. Among these fluorescent compounds, Bodipys are important substances having high quantum-yielding that they are highly resistant to light and chemicals, absorbing rays in the visible region range. Owing to these properties, Bodipy compounds are preferred for a lot of applications [28–31]. These compounds are used in intelligent circuit switches, light picking systems, energy transfer cassettes, color-sensitive solar cells, polymers, laser dyes and, OLED applications [32, 33].

Herein, we report the design and preparing of a fluorescent material for the selective detection of Cu (II) ion. After the synthesis of Bodipy including methylene chloride, a Bodipy derivative having azido terminal was prepared for a click reaction with aromatic compound concluding dual alkyne terminals. The prepared compound was used for the sensitivity of metal ions. The results show that the chemosensor, *d-*

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BODIPY, can be used for copper (II) ion in the half-water medium. The sensitivity and selectivity studies were supported by bio-imaging of yeast cells.

Experimental Section

Materials, Methods, and Instruments

All chemicals were analytical grade and they were used as received without any further purification. Elemental analyses and melting points of compounds were carried out by using a Gallenkamp and a TruSpec, respectively. ^1H and ^{13}C -NMR spectral measurements were taken in CDCl_3 on a Varian 400 MHz spectrometer at room temperature. The FT-IR data were carried out on a Bruker Vertex 70 spectrophotometer. The emission and absorption spectra were taken on a PerkinElmer LS 55 and Shimadzu 1280 apparatus, respectively (the emission slits were set as 5 nm in the fixed excitation). The dried dichloromethane was used for the synthesis of Bodipy including chlorine terminal. Merck plates (silica gel 60 F254 on aluminum) were used for TLC (thin layer chromatography) observations. The spectroscopic measurements were carried out by metal chloride in half aqueous medium. For all the microscope images, an Olympus (BX51/BX2-FLB3-000) microscope was used. Microscope images were collected using a CCD camera (DP70 12.5 million-pixel resolution). The microscope has a different magnification lens: 4 \times , 10 \times , 20 \times , 50 \times and 100 \times . The capture of images is possible with software: DP Manager. For the fluorescence light, an FTIC filter was used, otherwise, for all the other images, a transmitted light was used.

The Preparing of Compounds

The Synthesis of Compound 3

8-{4-(chloromethyl)phenyl}-2,6-diethyl-4,4-difluoro-1,3,5,7-tetramethyl-4-bora-3a,4a-diaza-s-indacene was prepared just as the synthesis procedure in our previous papers [31]. *p*-(chloromethyl)benzoyl chloride (7.5 g, 0.04 mol) was bitten by bit added to a solution (in DCM, 200 mL) of Kryptopyrrole (10.8 mL, 0.08 mol) in Ar atmosphere at room temperature. Then, the stirring of the solution was allowed for 4 h. Following cooling of the solution, 10 mL of triethylamine was added to the mixture, it was stirred at r. t. for half-hour and boron trifluoride diethyl etherate (8 mL) was injected by syringe. The mixture was heated to 65 °C for 3 h and the residue was purified by a solution of ethylacetate-cyclohexane in 1:8 ratio (3.47 g, Yield 40%). Melting point: 189 °C. ^1H NMR [400 MHz, CDCl_3]: 7.42 (PhH, d, 2H), 7.20 (PhH, d, 2H), 4.65 (CH_2 , s, 2H), 2.46 (CH_3 , s, 6H) 2.23 (CH_2 , q, 4H) 1.29 (CH_3 , s, 6H) 0.91 (CH_3 , t, 6H). ^{13}C NMR

[100 MHz, CDCl_3]: δ (ppm); 154.03, 139.49, 138.66, 135.88, 136.11, 133.02, 130.77, 128.99, 128.38, 45.66, 16.98, 14.66, 12.54, 11.66. Analytical Cal. for (%) $\text{C}_{24}\text{H}_{28}\text{N}_2\text{F}_2\text{ClB}$: H, 6.58; C, 67.22; N, 6.53; Found: H, 6.97; C, 66.98; N, 6.13. MS for $\text{C}_{24}\text{H}_{28}\text{N}_2\text{F}_2\text{ClB}$: 428 $[\text{M} + \text{H}]^+$.

The Synthesis of Compound 4 (8-{4-(Azidomethyl)Phenyl}-2,6-Diethyl-4,4-Difluoro-1,3,5,7-Tetra Methyl-4-Bora-3a,4a-Diaza-5-Indacene)

Compound 1 (0.44 mmol) and NaN_3 (0.344 g, 0.53 mol) were dissolved in *N,N*-dimethylformamide (20 mL) and mixed for 24 h at room temperature under inert atmosphere. The residue was extracted with water/chloroform. The organic phases were collected, dried with Na_2SO_4 . Following evaporation of chloroform, raw product was purified in column (only dichloromethane) (0.56 g, 96%). Caution: Compound 4 must be handled with special care due to its explosive character, Melting point: 140 °C. ^1H -NMR [400 MHz, CDCl_3]: 7.45 (PhH, d, 2H), 7.33 (PhH, d, 2H), 4.48 (CH_2 , s, 2H), 2.57 (CH_3 , s, 6H) 2.32 (CH_2 , q, 4H), 1.28 (CH_3 , s, 6H), 0.99 (CH_3 , t, 6H). ^{13}C NMR [100 MHz, CDCl_3]: δ (ppm); 154.04, 138.99, 138.03, 135.98, 135.62, 132.95, 130.81, 128.29, 129.03, 55.34, 17.44, 15.02, 12.32, 11.99. Analytical Cal. for (%) $\text{C}_{24}\text{H}_{28}\text{BF}_2\text{N}_5$: H, 6.48; C, 66.22; N, 16.09; Found: H, 6.67; C, 66.38; N, 16.15.

The Synthesis of Compound 7 (N^1, N^3 -di(Prop-2-Ynyl) Isophthalamide) (Compound 7)

0.5 mL of triethylamine was added to a solution of isophthaloyl dichloride (167.0 mg, 1 mmol) in dichloromethane at -5 °C (salt-ice). Then, 0.4 mL of propargylamine (Compound 6) was added dropwise to this solution at room temperature and stirred for 48 h. The mixture was extracted in a DCM-water mixture (*v/v* ratio: 1/3) and the crude product was extracted into the organic phase. The organic phase was dried with MgSO_4 and the solvent was evaporated in vacuo. The crude product was purified by column (Petroleum ether 40–60% / EtOAc; 1: 1). A white solid was obtained. Yield: 81%. m.p. 177 °C.

^1H -NMR [400 MHz, CDCl_3]: 9.08 (NH, t, 2H), 8.35 (PhH, t, 1H), 8.02–7.95 (PhH, m, 2H), 7.56 (PhH, t, 1H), 4.10–4.08 (CH_2 , m, 4H), 3.15 (CH, t, 2H); ^{13}C NMR [100 MHz, CDCl_3]: δ (ppm); 165.7, 133.9, 129.8, 128.2, 126.2, 80.8, 72.5, 28.1.

The Synthesis of *d*-BODIPY

0.870 g of Compound 4 and 0.240 g of Compound 7 were added to a mixture solvent including chloroform:methanol:water in a ratio of 10: 1: 1, respectively.

Subsequently, copper (II) sulphate and sodium ascorbate (0.3 eq.) were added as catalysts and stirred rapidly in a magnetic stirrer for 72 h. The solvent was evaporated, and the residue was extracted three times in a mixture of chloroform: water. The solvent of the organic phase was evaporated, and the residue was purified by column chromatography (ethylacetate/cyclohexane:1/1). A red solid was obtained 0.444 g, Yield: 40%.

$^1\text{H-NMR}$ [400 MHz, CDCl_3]: 8.80 (NH, s, 2H), 8.52 (PhH, s, 1H), (8.22 (PhH, d, 2H), 7.70 (PhH, t, 1H), 7.33–7.10 (PhH, m, 10H), 5.28 (CH_2 , s, 4H), 4.22 (CH_2 , s, 4H), 2.52 (CH_3 , s, 12H) 2.36 (CH_2 , q, 8H), 1.26 (CH_3 , s, 12H), 1.09 (CH_3 , t, 12H). $^{13}\text{C NMR}$ [100 MHz, CDCl_3]: δ (ppm); 167.02, 144.22, 142.24, 141.37, 139.21, 137.39, 136.53, 135.98, 135.62, 132.45, 130.19, 129.14, 129.03, 125.35, 124.47, 123.33, 120.11, 119.35, 57.24, 42.22, 18.45, 17.44, 15.34, 12.46, 10.87. Analytical Cal. for (%) $\text{C}_{62}\text{H}_{68}\text{B}_2\text{F}_4\text{N}_{12}\text{O}_2$: H, 6.17; C, 67.03; N, 15.13; Found: H, 6.48; C, 66.90; N, 14.95. MS $\text{C}_{62}\text{H}_{68}\text{B}_2\text{F}_4\text{N}_{12}\text{O}_2$ [H^+]; m/z : 1111, 57 (Scheme 1).

Yeast Cell Culture for Fluorescence Imaging

In this study, native *Saccharomyces cerevisiae* was purchased from a local supermarket and used as received after re-hydration in water at an approximate weight concentration of 30 mg mL⁻¹. Since the hydrated *S. cerevisiae* in the water and BODIPY molecules are both negatively charged, yeast cells were coated with a polyelectrolyte using deposition of PAH (from 10 mg mL⁻¹ solution in 0.5 M NaCl) adhering to the surface of the cells. Briefly, 300 μL of the yeast cell suspension was combined with 1 mL of PAH aqueous solution during constant shaking, incubated during 10 min and then centrifuged. The remaining excess polyelectrolyte was removed, and the cells were re-dispersed and washed three times with Milli-Q water. In the same way, the coated cells were introduced into the suspension of BODIPY molecules, incubated for 15 min and then centrifuged. The remaining excess BODIPY molecules were removed; the cells were washed with water for three times and examined with fluorescence microscopy.

Results and Discussion

Synthesis and Characterization of *d*-BODIPY

The principal aim of this study was the design and synthesis of a new fluorescent chemosensor including dual Bodipy units, and this material was performed for the detection of Cu (II) ions in half-aqueous media. The synthesized compounds have been characterized through $^1\text{H NMR}$, FT-IR, and $^{13}\text{C NMR}$, elemental analysis, melting point techniques.

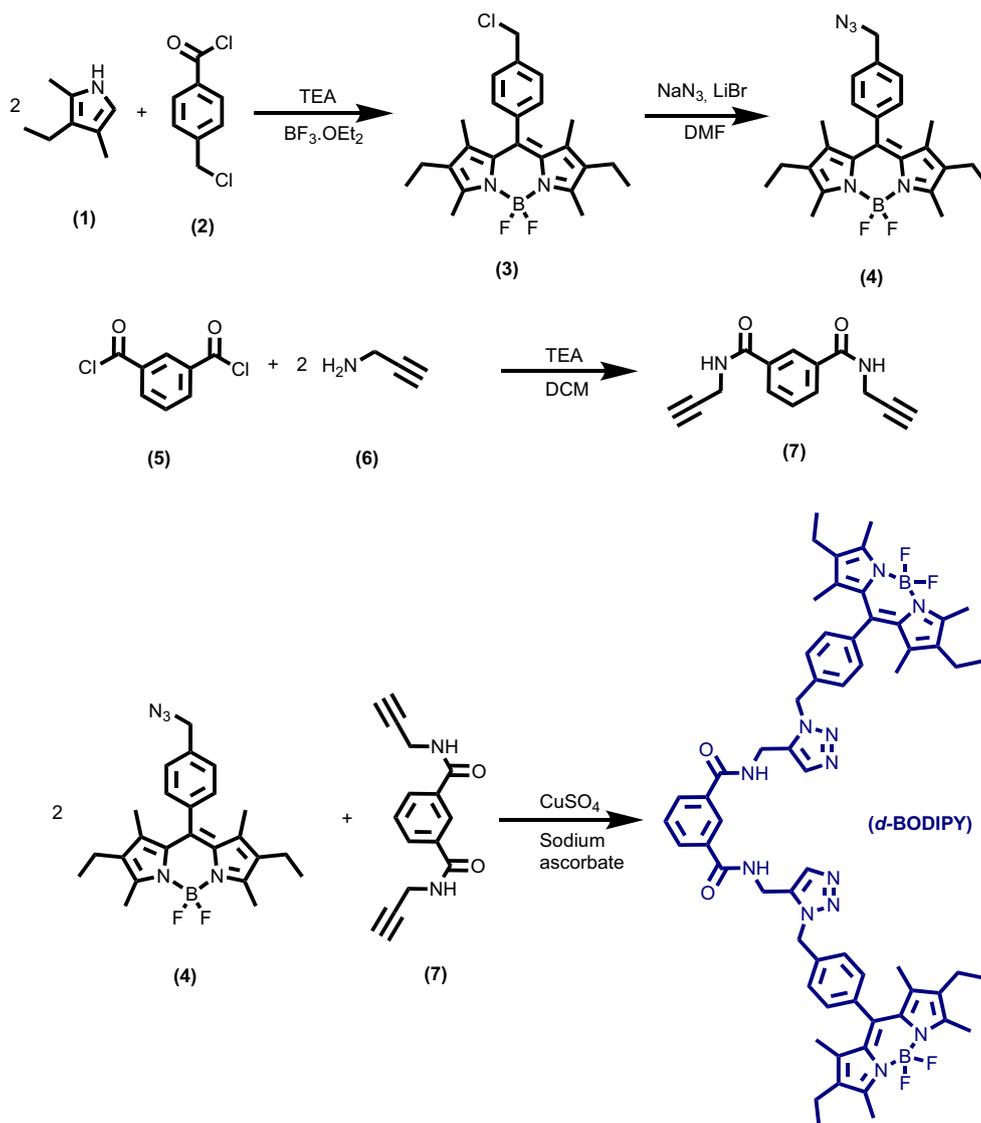
All spectral data (NMR-FTIR) of Compound 3, 4, 7 and *d*-BODIPY were present in Supporting Info. The proton peaks of CH_2 and CH_3 units on kryptopyrroles in Compound 3, 4 and *d*-BODIPY were observed between 2.70–0.90 ppm like given Supp. info. The proton peaks of methylene bound to benzene rings in compound 3, 4 and *d*-BODIPY raised at 4.65, 4.48 and 5.32 ppm in singlet form, respectively. The protons of aromatic groups on benzene units centered in an overlapping form between 7 and 8 ppm. The carbon signals of methylene bound to benzene rings appeared at 45.66, 55.34 and 42.22 ppm for compound 3, 4 and *d*-BODIPY, respectively.

In the infrared spectrum of compound 3, the bands appeared at 2868 and 2963, 1474, 1542, 1652 cm^{-1} , which can be referred to, aromatic and aliphatic C-H, aromatic C=C stretching's, C=N imine fragments, respectively. For compound 4, the most unique and sharp band was observed at 2091 cm^{-1} and the peak was ascribed to the N=N stretching of N_3 fragment. This peak vanishes in the FT-IR curve of *d*-BODIPY following the triazole cycling reaction.

Spectroscopic Studies of *d*-BODIPY with Metal Ions

The sensitivity ability of *d*-BODIPY towards metal ions was examined by the emission and absorption measurements in a solution of $\text{CH}_3\text{OH}/\text{H}_2\text{O}$ (9:1, v/v). To this aim, some metal cations were used such as Li (I), Cr Fe (II), (III), Mn (II), Hg (II), Co (II), Zn (II), Ni (II), Cu (II), Al (III), Ga (III), Ag (I), Cd (II). The free *d*-BODIPY (1.10^{-6} M, $\lambda_{\text{ex}} = 470$ nm) has a sharp emission intensity at 548 nm that it did not significantly change in the presence of metal cations except Cu (II) ions. As seen in Fig. 1, an effective quenching in the fluorescence intensity at 548 nm was improved upon the interaction of *d*-BODIPY with Cu (II) cation while other cations were not showing any effect. The chemosensor *d*-BODIPY exhibited an 15-fold decrease in emission intensity at 458 nm with the addition of 20.0 equivalents of Cu (II).

When the absorption spectrum of *d*-BODIPY was examined, three bands indicating π - π^* and n - π^* transitions between aromatic groups at 250 nm, 280 nm, and 350 nm were observed (Fig. 2). However, the sharp band indicating the classical Bodipy band appeared around 525 nm. After the addition of metal ion solutions to the individual *d*-BODIPY solution, no significant change was observed in the absorption spectrum of the other ions ligand studied except for the Cu (II) ion. With the addition of Cu (II) ions, the bands, especially around 250 nm and 280 nm, expanded. This change in the absorption spectrum in the presence of copper ions has been a preliminary idea for the Cu (II) ion sensitivity of *d*-BODIPY. Namely, it gave a complex reaction with the nitrogen's in the two triazole groups in the compound and resulted in the suppression of the PET mechanism. Besides, hard-soft acid-base interaction plays an important role that the increased charge of copper gains to a harder acid character for itself.



Scheme 1 The synthetic route of *d-BODIPY*

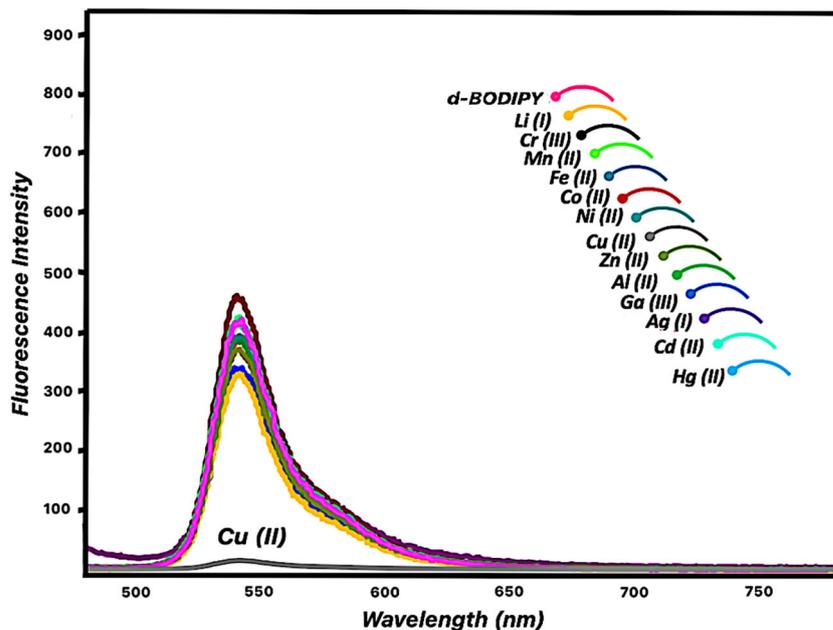
To support the selectivity performance of *d-BODIPY*, the competing ion tests were carried out with the studied competing ions (Li (I), Cr (III), Zn (II), Mn (II), Co (II), Ni (II), Fe (II), Ag (I), Cu (II), Al (III), Cd (II), Ga (III), Hg (II)). As seen in Fig. 3, these competitive ions did not affect the main emission intensity and wavelength of *d-BODIPY*/Cu (II) mixture in the studied concentration range. So, the results approve that *d-BODIPY* can be a good selectivity Cu (II) sensor.

One of the most important factors for fluorescent chemosensors is fast response time. To examine the good photostability and fast response of chemosensor *d-BODIPY*, the time-dependent fluorescence experiment was composed. The time-dependence fluorescence quenching of the chemosensor *d-BODIPY* was evaluated in the presence of Cu (II) in CH₃OH/H₂O (9:1, v/v) over for 20 min (Fig. 4). The results showed that in the presence of Cu (II), the

fluorescence intensity of chemosensor *d-BODIPY* reached a crucial quenching to their minimum value within the first 8 min. Following 8 min, it reached almost constant up to 20 min. Thus, the change in fluorescence intensity approved that 8 min reaction time is required to form the complex between the metal ions with ligands. So, *d-BODIPY* worked successfully for a complex reaction in 8 min and this duration is especially crucial for the practical real-time detection of a metal ion.

The metal/ligand ratio of the complex occurred between *d-BODIPY* and Cu (II) was determined by the changes in the emission intensities with various Cu (II) concentrations. The fluorescence intensity reached a minimum level in the ratio of metal/ligand is fifty/fifty. This situation revealed that the complex stoichiometry between *d-BODIPY* and Cu (II) cation is 1:2 such as shown in Fig. 5.

Fig. 1 Fluorescence spectral changes of *d*-BODIPY upon addition of various metal ions (Li (I), Cr (III), Zn (II), Mn (II), Ga (III), Fe (II), Co (II), Ni (II), Hg (II), Cu (II), Al (III), Ag (I), Cd (II)) ($\lambda_{\text{ex}} = 470 \text{ nm}$)



The binding constant in the complex was calculated by using the Stern-Volmer equation. For this, the fluorescence intensity maxima of *d*-BODIPY/Cu (II) solutions were taken.

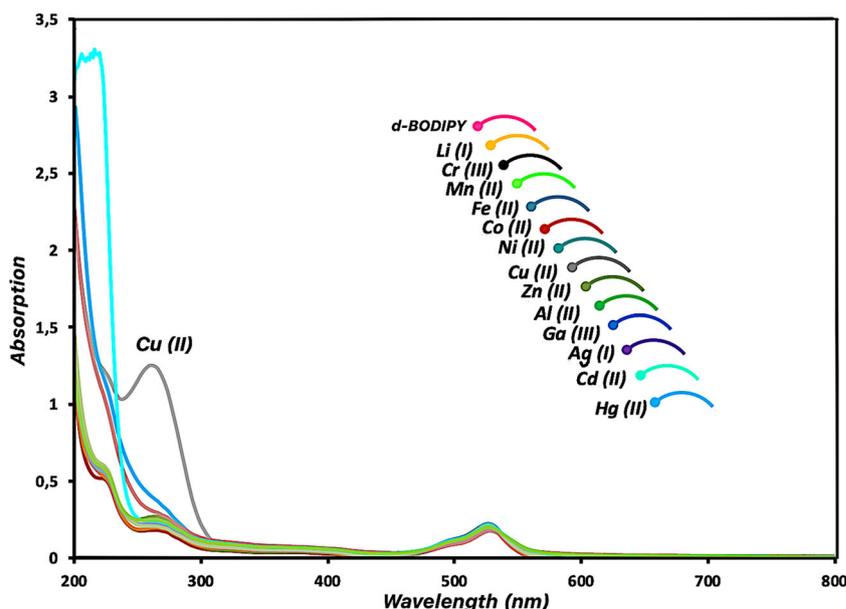
$$F_0/F = 1 + K_{\text{sv}} [Q]$$

Here F_0 ; Fluorescence intensity of *d*-BODIPY in the absence of Cu (II) ion, F ; the emission intensity in the presence of Cu (II) ion, Q ; Cu (II) ion concentration and K is the binding constant. As it is understood from the graph, the linear and ascending curve of F_0/F ratio at different concentrations appeared (Fig. 6). The

quenching constant from the equation was calculated as $K_{\text{sv}}: -6. \times 10^5$.

The limit of detection (LOD) for the interaction of copper (II) ions with *d*-BODIPY was calculated by using emission data. The titration process was carried out by the addition of various concentrations of copper solutions ($1 \times 10^{-8} \text{ M}$ to 1×10^{-6}) to the *d*-BODIPY solution and then allowed to interact for 15 min. Following these experiments, the calibration curve/slope was obtained, the limit of detection was calculated using *Limit of Detection* = $K (\alpha/s)$ formula (where α ; standard deviation, K ; 3, s ; slope). The fluorescence intensity of *d*-BODIPY

Fig. 2 Absorption spectral changes of *d*-BODIPY upon addition of various metal ions (Li (I), Cr (III), Mn (II), Fe (II), Co (II), Ni (II), Cu (II), Zn (II), Al (III), Ga (III), Ag (I), Cd (II), Hg (II))



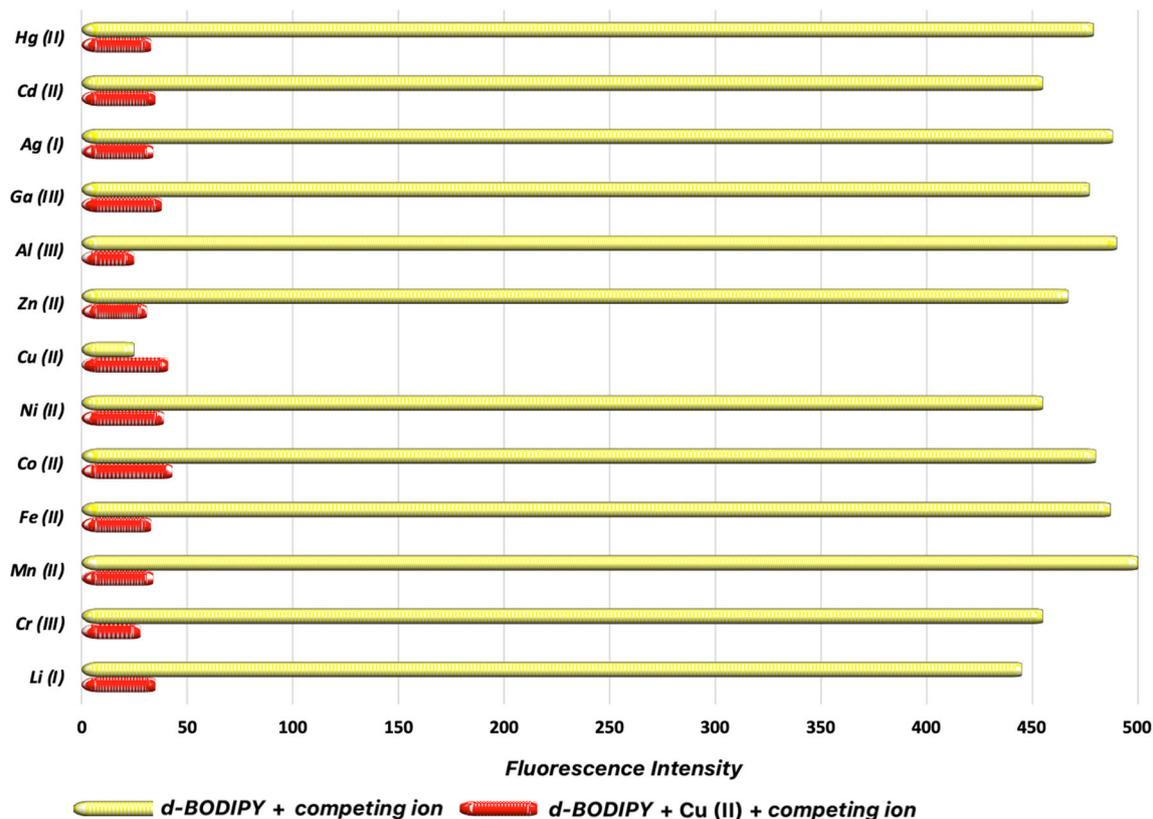


Fig. 3 Fluorescence intensities around 548 nm of *d*-BODIPY&Cu (II) ion mixture in the presence of a series of metal ions (Li (I), Ga (III), Cr (III), Mn (II), Fe (II), Al (III), Cu (II), Co (II), Ni (II), Zn (II), Ag (I), Cd (II), Hg (II))

was quenched upon the addition of various concentrations of Cu (II) ion. The LOD was calculated as 1.2×10^{-8} M by using the emission intensities in Fig. 7. The U.S. defined maximum contaminant level for copper ions in tap water is 20 μ M, therefore, the chemosensor *d*-BODIPY is suitable for the detection of Cu (II) ions in practical applications.

As shown in Table 1, the sensing of *d*-BODIPY is comparable to those of some Bodipy-based fluorescent sensors having PET principle and turn-off mechanism for copper ions [34–37], that indicate that *d*-BODIPY has more advantages. PET is often the cause of fluorescence quenching, when the PET process is followed by a nonluminescent process returning to the ground state [37]. The fluorescence intense

Fig. 4 Effect of response time on *d*-BODIPY/Cu(II) complexation in the half-aqueous system ($\lambda_{em_{max}} = 548$ nm)

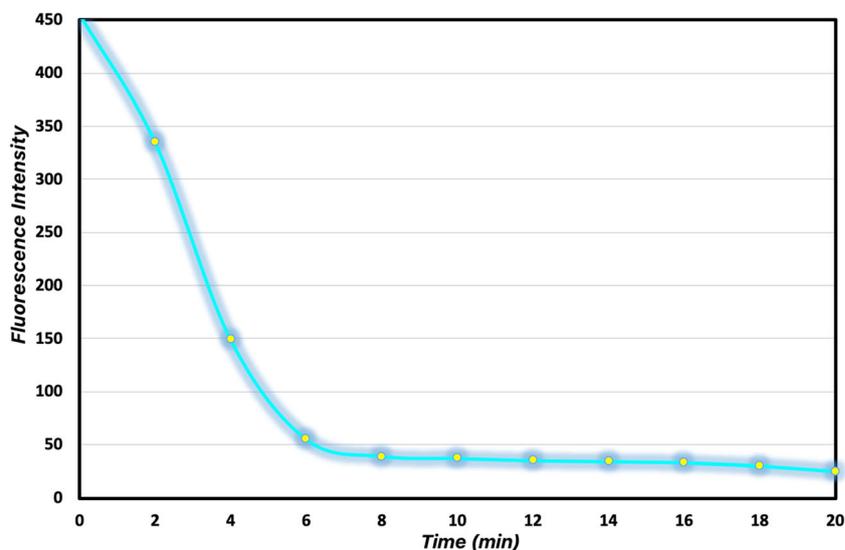
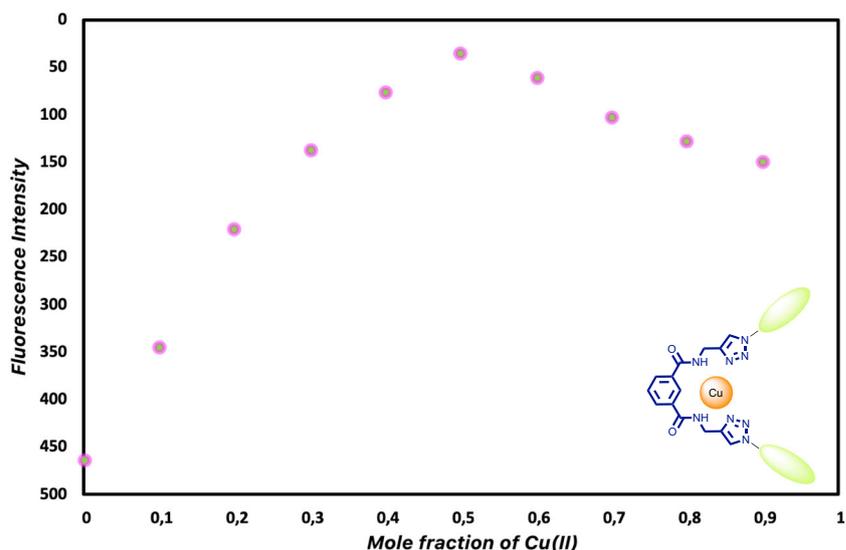


Fig. 5 Job's plots of the complex occurred between *d-BODIPY* with Cu (II)



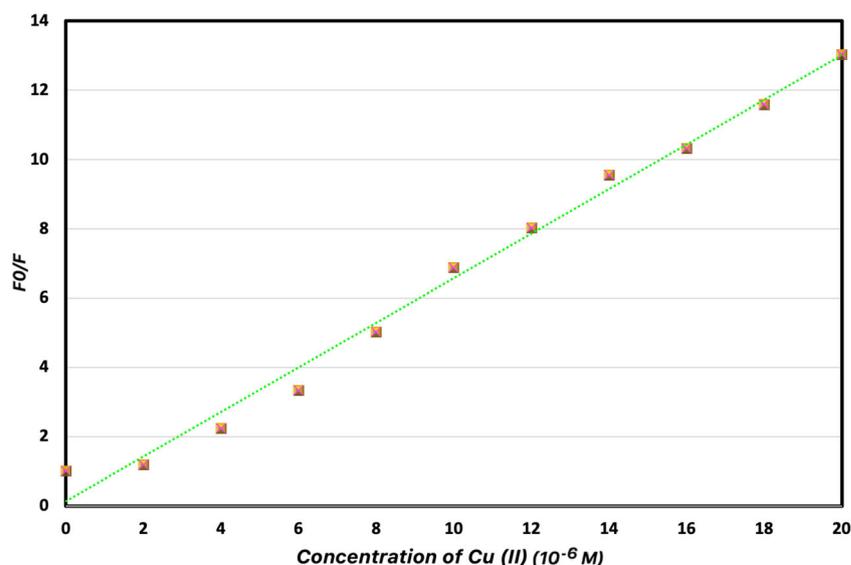
of *d-BODIPY* is quenched by oxidative PET from the excited-state fluorophore, two Bodipy units, to the triazole moiety coordinated with Cu(II) ion. Multi-donor atoms, nitrogen and oxygen, captured to Cu (II) ions and energy transfer process carried out.

Table 1 Comparison of alternative Bodipy sensors for Cu (II) in previous studies.

Fluorescence Imaging on Yeast Cells

The bright-field optical microscopy images of yeast cells are shown in Fig. 7 (a). After positive polyelectrolyte coating, the cells were treated with fluorescent *d-BODIPY* molecules and examined under fluorescence microscopy. As can be seen from Fig. 7 (b) positively charged yeast cells interact with negatively charged *d-BODIPY*. The image presented in Fig.

Fig. 6 The fluorescence intensities ratio (F_0/F) around 548 nm plotted against copper (II) cation concentrations (1.10^{-6} - 2.5×10^{-5} M) ($\lambda_{em_{max}} = 548$ nm)

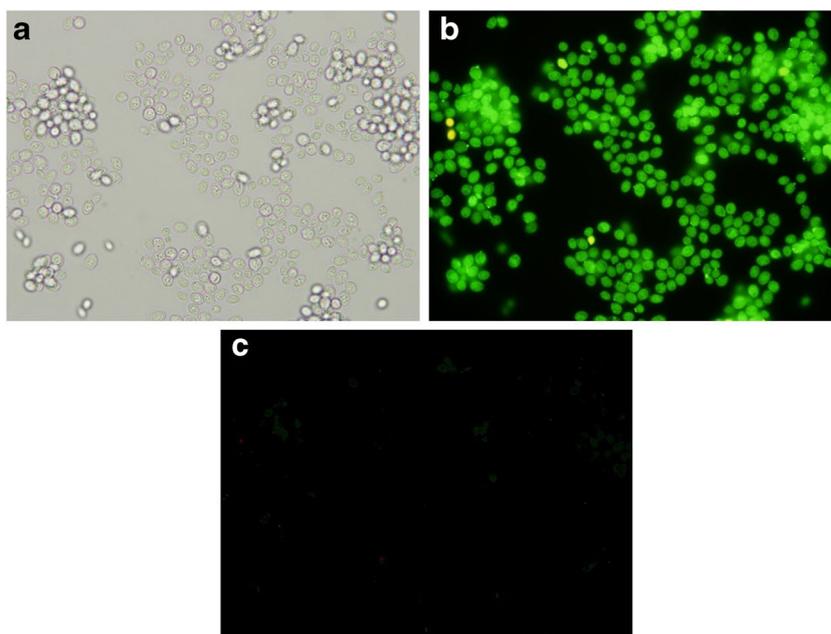


7 (c) confirmed that Cu ions were quenched the fluorescence intensity of *d-BODIPY*.

Conclusion

A new fluorescent chemosensor concluding double triazole and Bodipy working with the photoinduced electron transfer process and triazole conjugated systems were designed and prepared for the detection of Cu (II). The experimental data approve that *d-BODIPY* can possess for high selectivity for Cu (II) over the studied metal ions with the LOD reaching 1.2×10^{-8} M level and high sensitivity with a good fluorescence quenching in methanol/water. The fluorescence imaging tests showed that the chemosensor *d-BODIPY* is applicable for monitoring Cu (II) in yeast cells. Thus, the competing

Fig. 7 Bright-field optical microscopy image of (a) yeast cells and fluorescence microscopy image of (b) yeast cells with *d*-BODIPY. When Cu solution was also added to the *d*-BODIPY-treated cells (c) no fluorescence was detected



ion and response time tests confirmed that the knowledge *d*-BODIPY can be used as a fluorescent sensor for sensing studies of Cu (II) ions in living cells. To the best of our knowledge, this report will pioneer useful methods in the sensing detection of copper ions in living cells.

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