Journal of Photochemistry and Photobiology A: Chemistry 282 (2014) 41–46

Contents lists available at ScienceDirect

Journal of Photochemistry and Photobiology A: Chemistry

journal homepage: www.elsevier.com/locate/jphotochem

A BODIPY-based fluorescent chemosensor for Cu^{2+} and biological thiols, and its application as a Cu^{2+} probe in live cell imaging

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ARTICLE INFO

Article history:
Received 12 December 2013
Received in revised form 6 March 2014
Accepted 11 March 2014
Available online 21 March 2014

Keywords:
BODIPY
Fluorescence quenching
Cu^{2+} Sensor
Biothiols sensor
Cell images

ABSTRACT

A new fluorescent boron dipyrromethene (Bodipy) derivative **1** containing a di(2-picolyl)amine group as a binding site for Cu^{2+} was synthesized and characterized. Compound **1** behaves as an "on–off" fluorescent sensor for highly selective and sensitive detection of Cu^{2+} ions. The selective interaction between compound **1** and Cu^{2+} leads to formation of a **1**·Cu^{2+} complex, associated with quenching of the fluorescence of **1**. An investigation into the detection of biothiols shows that the **1**·Cu^{2+} complex has better recognition for glutathione than cysteine and homocysteine in CH_3OH–HEPES (1:1, v/v) buffer solution at pH 7.4 (HEPES = 4-(2-hydroxyethyl)-1-piperazineethanesulfonic acid). In addition, fluorescence images obtained *via* confocal microscopy reveal that compound **1** exhibits excellent selectivity and high sensitivity for Cu^{2+} under physiological conditions and in living cells.

1. Introduction

Metal ions and biological thiols (biothiols) containing peptides and amino acids play essential roles in many antioxidant defense mechanisms of biological systems. For this reason the design of selective and sensitive sensors for the detection and recognition of important biological metal ions and amino acids has attracted considerable attention [1–3]. In particular, glutathione (GSH), is a particularly abundant biothiol and a basal endogenous antioxidant, which plays an important role in defending cells against toxins and free radicals [4]. Cellular deficiency of GSH has been linked to ailments such as cancer, premature aging, and cardiovascular diseases [5,6]. Changes in the level of expression of cysteine (Cys)/homocysteine (Hcy) amino acids are involved in many diseases [7,8]. Thus, the significant biological role of biothiols, especially GSH, motivates efforts to find efficient methods for the detection of GSH both *in vitro* and *in vivo* [9–15]. Boron dipyrromethene (Bodipy)-based dyes are useful materials that have many properties, such as relatively high fluorescence quantum yields and molar absorption coefficients, narrow emission bandwidths with high peak intensities, good solubility, excellent stability toward light and chemicals, and excitation/emission wavelengths in the visible spectral region (≥500 nm) [16]. Bodipy dyes are therefore well suited for applications in fluorescence based biological sensing.

Although there are some reports of Bodipy dyes used for biothiol sensing, most detection methods are based on covalent interactions between the fluorophore and biothiols [17–21], which feature long response times. However, for real-time detection of biothiols, non-covalent interactions may be more effective in these sensing platforms. Owing to the strong affinity of biothiols for Cu^{2+}, the addition of biothiols into a non-emissive system containing a fluorophore–Cu^{2+} complex may induce a change in the binding interaction of Cu^{2+} within the complex [22]. This interaction may release free fluorophores, and induce changes in the fluorescence intensity and/or color of the complex [3]. In this context, we report a Bodipy-based compound consisting of a Bodipy fluorophore and a di(2-picolyl)amine (DPA) binding moiety, and its application as a metal ion sensor. The compound exhibits a rapid "on–off" type spectroscopic response: non-emissive in the presence of Cu^{2+} ions, switching on through recovery of fluorescence in the presence of biothiol-containing amino acids and peptides. The most interesting

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http://dx.doi.org/10.1016/j.jphotochem.2014.03.009
1010-6030/

aspect of this new compound is that it exhibits a high selectivity and sensitivity for Cu^{2+} under physiological conditions and in living cells.

2. Experimental

2.1. General information

All start materials were obtained from commercial sources, and used as-received without further purification unless otherwise stated. The ^1H NMR spectra were measured on a Bruker instrument operating at a ^1H frequency of 400 MHz at 298 K. Chemical shifts (δ, ppm) were referenced to tetramethylsilane for ^1H. The ESI-MS data were obtained with an APEX II Model FT-ICR mass spectrograph. Absorption spectra were recorded using a Hitachi U-3010 scanning spectrophotometer, and the emission spectra of the solutions were measured using a Hitachi F-4500 fluorescence spectrophotometer at room temperature. The fluorescence quantum yield in solution was measured by a relative method against quinine sulfate in a sulfuric acid aqueous solution (λ_{ex} = 345 nm, Φ_s = 0.546) at room temperature.

2.2. Determination of dissociation constant

The dissociation constant K_d was determined based on the fluorometric titration curve of the complex between **1** and Cu^{2+} in 10 mM of CH_3OH-HEPES (1:1, v/v) buffer solution at pH 7.4 at 25 °C. The dissociation constant, K_d, was calculated by nonlinear fitting of Eq. (1) to the fluorescence data as a function of the [Cu^{2+}] yield values of F, F_{max}, and F_{min} [23].

$$K_d = \frac{(F_{max} - F)[Cu^{2+}]}{(F - F_{max})} \quad (1)$$

In Eq. (1), F is the fluorescence signal of [Cu^{2+}], and F_{min} and F_{max} denote the fluorescence signals at minimal and maximal [Cu^{2+}], respectively.

2.3. Fluorescence bioimaging

The sensitivity of **1** to Cu^{2+} in human lung adenocarcinoma epithelial cells was investigated using confocal microscopy. Fluorescence images were recorded with excitation by a 488-nm diode laser, using a Spinhole aperture, an oil-objective lens with 60 times magnification, 1.40 NA, and 100% detector gain. The A549 cells were incubated with compound **1** (5.0 μM) in phosphate-buffered saline (PBS) for 30 min at 37 °C. Experiments for Cu^{2+} uptake were carried out over 30 min in the same medium, supplemented with 25 μM of $Cu(ClO_4)_2$.

2.4. Synthesis and characterization

2.4.1. Synthesis of compound 2

4,4-Difluoro-8-(4-aminophenyl)-1,3,5,7-tetramethyl-2,6-diethyl-4-bora-3a,4a-diaza-s-indacene (**3**) was prepared by procedures given in the literature [24]. A solution of **3** (0.514 g, 1.3 mmol) with potassium carbonate (0.1 g, 0.7 mmol) in CH_2Cl_2 (50 mL) was stirred for 15 min in an ice bath, at which point chloroacetyl chloride (0.17 g, 1.5 mmol) was added dropwise, and the solution was stirred at room temperature for 24 h. The resulting reaction mixture was filtrated to remove potassium carbonate. The organic layer was dried over Na_2SO_4 and filtered. The solvent was evaporated to give the crude product, which was purified by column chromatography over a silica gel column using petroleum ether (boiling range 60–90 °C) and ethyl acetate (5:1, v/v) as the eluent. Recrystallization of the product from a dichloromethane/diethyl ether solution afforded a pale yellow solid powder crystal. Yield: 0.37 g (60%). ^1H NMR (400 MHz, DMSO): δ 10.53 (s, 1H), 7.79 (d, 2H, J = 8.4 Hz), 7.31 (d, 2H, J = 8.4 Hz), 4.30 (s, 2H), 2.43 (s, 6H), 2.29 (q, 4H, J = 7.4 Hz), 1.30 (s, 6H), 0.94 (t, 6H, J = 7.5 Hz).

2.4.2. Synthesis of compound 1

Compound **2** (0.471 g, 1.0 mmol) with potassium carbonate (0.138 g, 1.0 mmol), potassium iodide (0.166 g, 1.0 mmol) in THF (50 mL) was stirred for 15 min, then dipicolylamine (0.242 g, 2.4 mmol) was added dropwise under a nitrogen atmosphere. The reaction mixture was refluxed for 24 h. The resulting solution was filtered and evaporated in vacuum to produce the Bodipy-DPA crude product, which was purified by column chromatography over a silica gel column using petroleum ether and ethyl acetate (1:1, v/v) as the eluent. Recrystallization of the product from a dichloromethane/diethyl ether solution afforded red prismatic crystals. Yield: 0.37 g (50%). ^1H NMR (400 MHz, DMSO): δ 10.73 (s, 1H), 8.58 (d, 2H, J = 4.4 Hz), 7.86 (d, 2H, J = 8.4 Hz), 7.76 (td, 2H, J = 7.6, 1.5 Hz), 7.48 (d, 2H, J = 7.7 Hz), 7.29 (dd, 4H, J = 10.5, 4.3 Hz), 3.96 (s, 4H), 3.51 (s, 2H), 2.43 (s, 6H), 2.30 (q, 4H, J = 7.3 Hz), 1.32 (s, 6H), 0.94 (t, 6H, J = 7.5 Hz). ^{13}C NMR (101 MHz, DMSO-d_6) δ 169.72, 158.43, 152.99, 148.98, 140.49, 139.43, 138.10, 136.67, 132.40, 130.22, 129.22, 128.59, 123.13, 122.30, 119.22, 59.61, 57.97, 16.38, 14.48, 12.19, 11.53. ^{19}F NMR (376 MHz, DMSO-d_6) δ −142.84, −143.01.

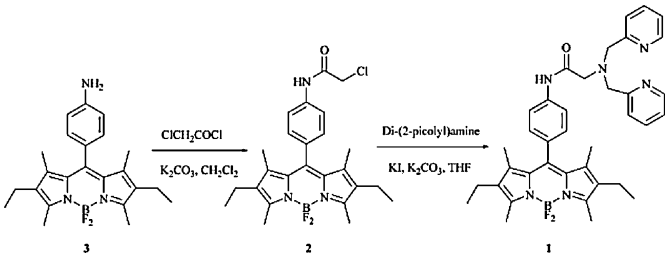
2.5. X-ray crystallography

A crystal of compound **1** suitable for X-ray structure analysis was obtained by slow evaporation of diethyl ether into a solution of complex **1** in dichloromethane. The diffraction data were collected on a Rigaku Saturn diffractometer using a graphite monochromator with Mo-Kα radiation (λ = 0.071073 nm) at 113 K. The structure was solved by direct methods and refined by full-matrix least-squares methods on all F2 data (SHELX-97) [25].

3. Result and discussion

3.1. Synthesis and characterization

The Bodipy-based derivative **1** was obtained from 5-(chloroacetamido)-Bodipy-based **2**, which was prepared by reacting 4,4-difluoro-8-(4-aminophenyl)-1,3,5,7-tetramethyl-2,6-diethyl-4-bora-3a,4a-diaza-s-indacene and chloroacetyl chloride, with the DPA moiety used as a metal ion sensor (Scheme 1) [26,27]. Compounds **1** and **2** were characterized by ^1H nuclear magnetic resonance (NMR), ^{13}C NMR and ^{19}F NMR spectroscopy, and electrospray ionization mass spectrometry (ESI-MS) (see Supporting Information). A previous report demonstrated that a compound similar to compound **1**, without a carbonyl group, could be used as a fluorescence probe for Zn^{2+} [28]. In the present study, the introduction of a carbonyl group into the molecule of **1** may enhance the binding selectivity for Cu^{2+} [29].



Scheme 1. Preparation of compound **1**.

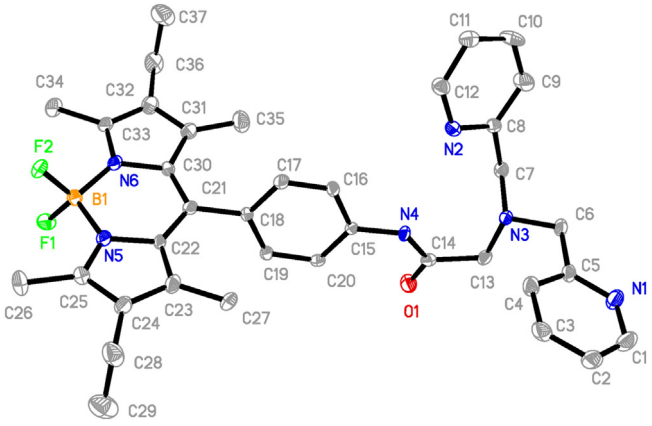


Fig. 1. Perspective view of compound **1** with atom-labeling scheme. Hydrogen atoms and solvent molecules are omitted for clarity.

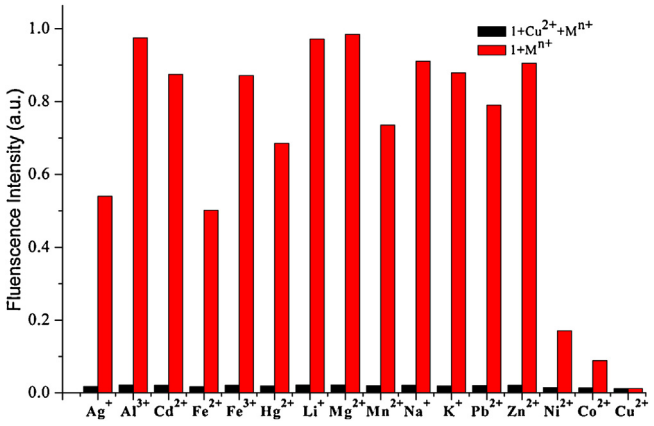


Fig. 3. Fluorescence spectra of compound **1** (5.0 μM) in the presence of various metal ions with or without Cu^{2+} in 10 mM of CH_3OH–HEPES (1:1, v/v) buffer solution at pH 7.4 (λ_{ex} = 526 nm).

The X-ray structural analysis of **1** is shown in Fig. 1. Full crystallographic data and details on data collection and refinement can be found in the Electronic Supporting Information. The X-ray crystallographic analysis of the compound reveals that the Bodipy moiety exhibits a planar arrangement of the dipyrrin group, and the boron center adopts a slightly distorted tetrahedral coordination. The average B–N and B–F distances of 1.534(7) and 1.399(6) Å, respectively, fall within normal limits. The corresponding F(1)—B(1)—F(2), N(5)—B(1)—N(6), and N(5)—B(1)—F(1) bond angles are 108.8(4)°, 107.7(3)°, and 110.1(4)°, respectively.

3.2. Photoluminescence

Compound **1** exhibits a strong visible absorption band with λ_{max} at 522 nm (ε = 76,958 M^{-1} cm^{-1}) in 10 mM of CH_3OH–HEPES (1:1, v/v) buffer solution at pH 7.4, and displays a bright green fluorescence in solution with an emission peak at 539 nm upon excitation at 526 nm (Φ_F = 0.42). In the presence of 10 equiv. of metal ions such as Zn^{2+}, Pb^{2+}, Na^+, Mn^{2+}, Mg^{2+}, Li^+, Hg^{2+}, Fe^{3+}, Fe^{2+}, Cd^{2+}, Al^{3+}, and Ag^{2+}, slight changes in the fluorescence emission intensity were observed except in the cases of Ni^{2+} and Co^{2+} (Fig. 2). However, Cu^{2+} ions, cause the greatest fluorescence quenching of compound **1**. At a 1:1 molar ratio of **1** and Cu^{2+}, the fluorescence of compound **1** was almost completely quenched by the Cu^{2+}, with a quenching efficiency of 0.98 ($(I_0 - I)/I_0 \times 100\% = 98\%$). The selective recognition of compound **1** toward Cu^{2+} is not affected by the presence of other interfering cations.

The fluorescent behavior indicates that the interaction **1** with Cu^{2+} is more effective for quenching the excited state than with other interfering cations (Fig. 3) [30–42]. It is particularly important to ensure there is no disruption of the detection of Cu^{2+}, by Mg^{2+}, Na^+, and K^+, because these three metal ions exist in high concentrations under physiological conditions. The results of the titration of **1** at increasing concentrations of Cu^{2+} in a CH_3OH-HEPES solution demonstrate that the fluorescence intensity gradually decreases and then remains constant after addition of 1 equiv. of Cu^{2+} (Fig. 4), indicating the formation of a **1**·Cu^{2+} complex. In addition, investigations using electrospray ionization mass spectrometry showed the system containing compound **1** emits two ESI/MS signals at m/z = 348.7 and 796.1, which can be ascribed to $[\mathbf{1}+Cu]^{2+}$ and $[\mathbf{1}+Cu+(ClO_4)]^+$, respectively (Fig. S1). This is consistent with the formation of a 1:1 stoichiometric **1**·Cu^{2+} complex in 10 mM of CH_3OH–HEPES (1:1, v/v) buffer solution at pH 7.4. The dissociation constant K_d is calculated as 7.56×10^{-6} M from the changes of the fluorescence intensity *via* nonlinear fitting of the fluorometric titration data shown in Fig. 4.

Using ethylenediaminetetraacetate (EDTA) as a chelator of metal ions, Cu^{2+} ions can be bound away from **1**·Cu^{2+} complex to release compound **1**. When EDTA is added to the **1**·Cu^{2+} solution complex, it is found that the fluorescence intensity is significantly

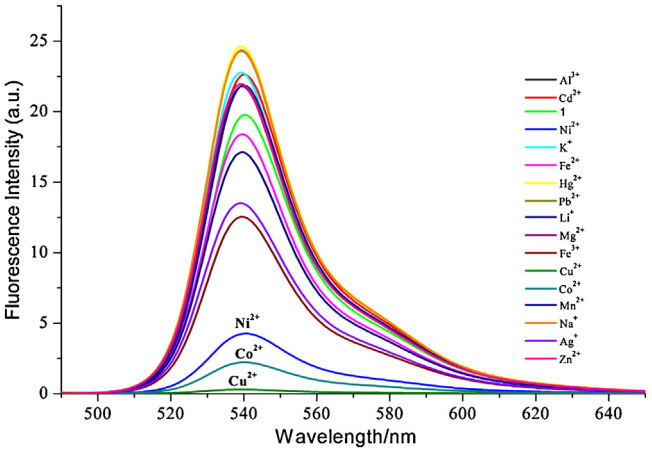


Fig. 2. Fluorescence spectra of compound **1** (5.0×10^{-6} M) with addition of various metal ions in 10 mM of CH_3OH–HEPES (1:1, v/v) buffer solution at pH 7.4 (λ_{ex} = 526 nm).

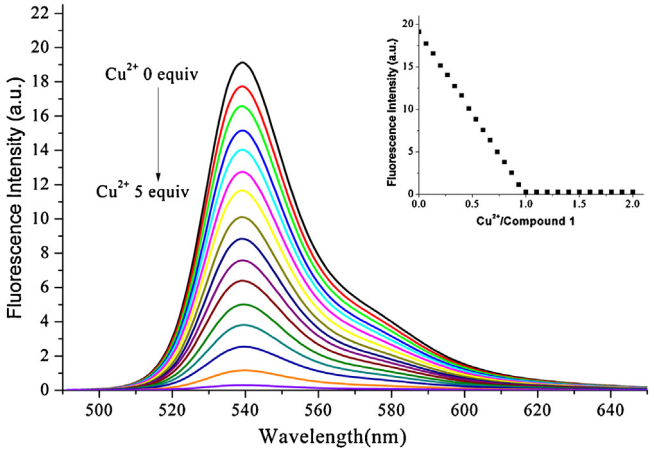


Fig. 4. Fluorescence titration of **1** with various concentrations of Cu^{2+} ions in 10 mM of CH_3OH–HEPES buffer solution at pH 7.4 ([1] = 5.0 μM, λ_{ex} = 526 nm).

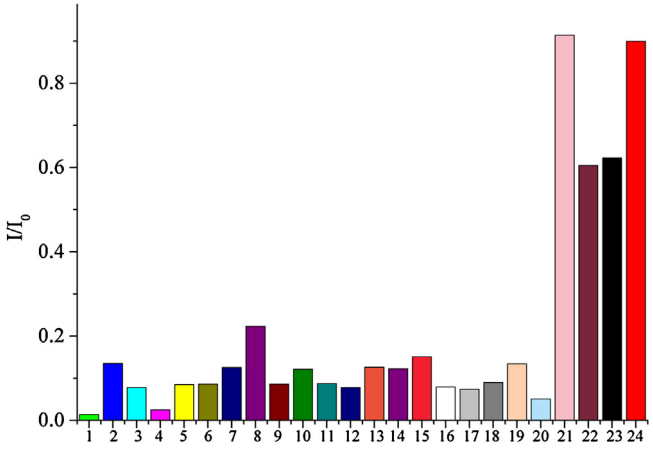


Fig. 5. Fluorescence intensity changes I/I_0 of the **1**·**Cu**$^{2+}$ complex (5.0 μM) in 10 mM of CH_3OH–HEPES (1:1, v/v) buffer solution at pH 7.4 after the addition of 100 μM of various amino acids (λ_{ex} = 526 nm): 1. None; 2. Phe; 3. Ala; 4. Gly; 5. Glu; 6. Gln; 7. Met; 8. Arg; 9. Lys; 10. Tyr; 11. Leu; 12. Pro; 13. Trp; 14. Ser; 15. Thr; 16. Asp; 17. Asn; 18. Val; 19. Ile; 20. His; 21. Na_2S; 22. Cys; 23. Hcy; 24. GSH.

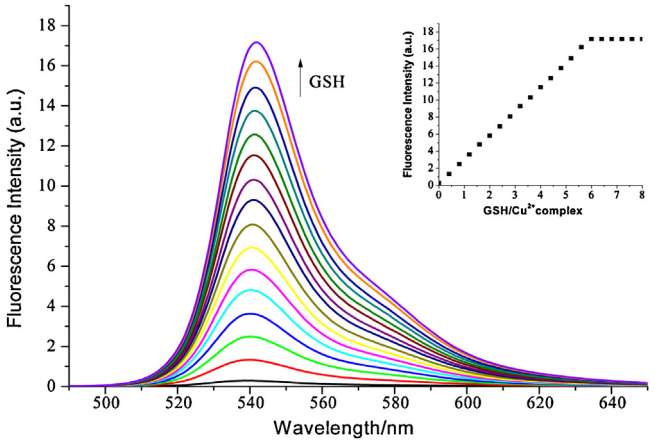


Fig. 6. Fluorescence titration of the **1**·**Cu**$^{2+}$ complex with various concentrations of GSH in 10 mM of CH_3OH–HEPES (1:1, v/v) buffer solution at pH 7.4 ([**1**·**Cu**$^{2+}$] = 5.0 μM, λ_{ex} = 526 nm).

enhanced and is recovered to 90% of its initial intensity (Fig. S2). Additionally, in the presence of sulfide ions, the **1**·**Cu**$^{2+}$ complex also displays a remarkable fluorescence-enhancing behavior due to the formation of CuS, whose existence is ascertained by NMR spectral measurements of compound **1** (Fig. S3).

There have also been reports on the use of metal ion (Cu^{2+} or Hg^{2+}) complexes as sensors for thiol-containing peptides and amino acid based on the high affinity of biothiols for metal ions [43–45]. In the present study, the **1**·**Cu**$^{2+}$ complex can potentially lose Cu^{2+}, and recover its fluorescence through regeneration of compound **1**. To investigate the potential of the **1**·**Cu**$^{2+}$ complex as a thiol-containing peptide and amino acid sensor in buffer solution, we examined the changes in the fluorescence spectra of solutions containing the **1**·**Cu**$^{2+}$ complex after the addition of various thiol-containing peptides and amino acids (GSH, Hcy, Cys, Met) as well as non-thiol-containing amino acids (Ala, Arg, Asn, Asp, Gln, Glu, Gly, His, Ile, Leu, Lys, Phe, Pro, Ser, Thr, Trp, Tyr, Val).

The **1**·**Cu**$^{2+}$ complex in 10 mM of CH_3OH-HEPES with various thiol-containing peptides and amino acids showed some changes in fluorescence, as illustrated in Fig. 5. Remarkably, recovery of fluorescence was observed upon addition of GSH or S^{2-}. Compared with GSH, the addition of Cys and Hcy leads to only partial recovery of fluorescence intensity, while other amino acids cause no obvious changes in emissive intensity. Notably the **1**·**Cu**$^{2+}$ complex has better recognition for GSH than Cys and Hcy. A titration of the **1**·**Cu**$^{2+}$ complex (5.0 μM) with GSH, while monitoring fluorescence showed that the fluorescence intensity displayed a steady increase for increasing concentrations of GSH (0–30.0 μM) (Fig. 6), and the fluorescence intensity changes are linear with [GSH] in the range 0–30 μM, for [S^{2-}] 0–5 μM. Recovery of 90% of the fluorescence signal could be attributed to the release of compound **1** from interactions between Cu^{2+} and S^{2-} or mercapto groups (Figs. S4 and S5).

3.3. Fluorescence bioimaging

Additionally, we examined the sensitivity of **1** to Cu^{2+} in human lung adenocarcinoma epithelial cells (A549) by confocal microscopy. Fluorescence images were recorded by excitation with a 488-nm diode laser, using a Spinhole aperture, an oil-objective lens with 60 times magnification, 1.40 NA (numerical aperture), at 100% detector gain. After the A549 cells were incubated with compound **1** (5.0 μM) in PBS for 30 min at 37 °C, significant green fluorescence was observed (Fig. 7a). However, 10 min after the addition of 25 μM of Cu^{2+} to the same system, the fluorescence was almost completely quenched (Fig. 7b). The fluorescence quenching could be attributed to the association of compound **1** with Cu^{2+}. As shown in Fig. 8, the overlays of fluorescence and brightfield images reveal that the fluorescence signals are localized in the perinuclear region of the cytosol. These results confirm that compound **1** is cell permeable and can respond to variations in intracellular Cu^{2+}.

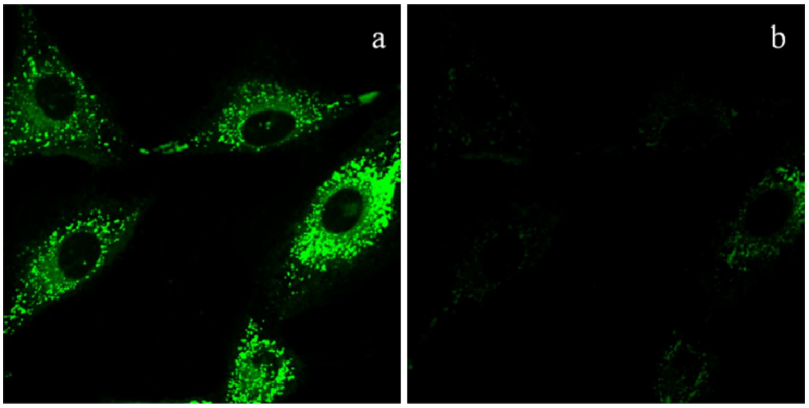


Fig. 7. Fluorescence image of compound **1** in living cells at 37 °C. (a) A549 cells incubated with 5.0 μM of compound **1** in 10^{-3} mM, 1 mL PBS for 30 min. (b) A549 cells incubated with 5.0 μM of compound **1** treated with 25 μM of Cu^{2+} aqueous solution with each of 125 μM Na^+, Mg^{2+}, K^+, for 10 min.

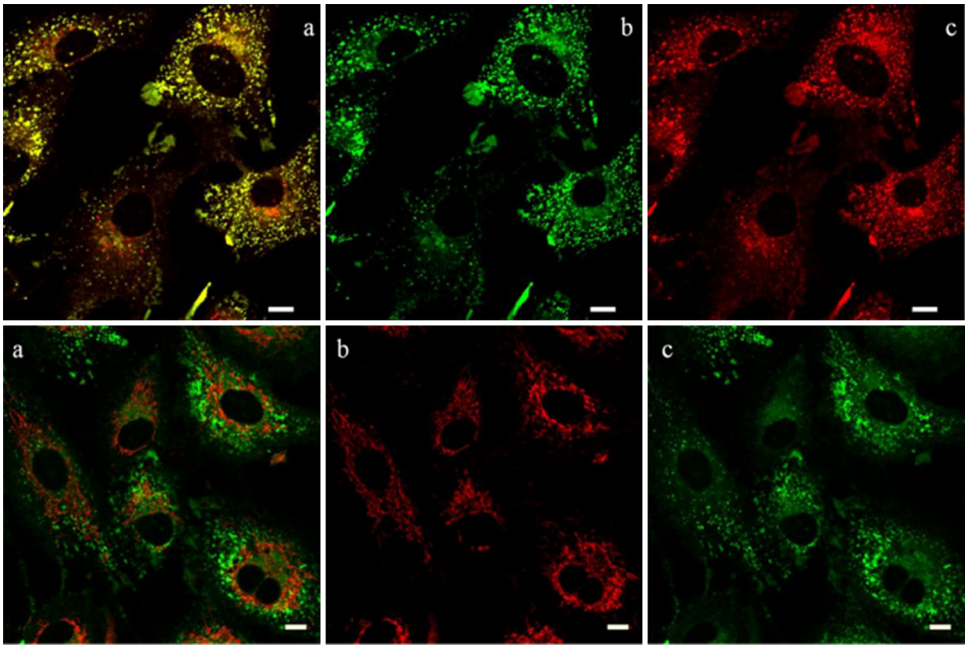


Fig. 8. Co-staining fluorescence images of compound **1** with LysoTracker or MitoTracker in living cells at 37 °C: (top) (a) The overlay of a fluorescence image of compound **1** with LysoTracker; fluorescence images of compound **1** (b) and LysoTracker (c). (bottom) (a) An overlay of a fluorescence image of compound **1** with MitoTracker; the fluorescence images of MitoTracker (b) and compound **1** (c).

4. Conclusions

We synthesized a new Bodipy-based compound containing a Bodipy signaling fluorophore and a DPA binding moiety for selective sensing of Cu^{2+} ions and biothiols. The compound features higher selectivity for detection of GSH than Cys and Hcy. In the presence of Cu^{2+} ions, the compound displays "on–off" type emissive behavior. With the addition of biothiols, especially GSH, a fast fluorescent "off–on" response occurs owing to the strong affinity of biothiols to coordinate Cu^{2+}. This promotes the removal of Cu^{2+} from the **1**·Cu^{2+} complex to release the fluorophore, and give fluorescence recovery. Compound **1** can be used as a fluorescence probe to recognize Cu^{2+} under physiological conditions and in living cells, and its Cu(II) complex can be used for sensing biothiols in biological systems.

Acknowledgements

This work was financially supported by the Ministry of Science and Technology (2013CB834804 and 2012DFH40090). We thank the Natural Science Foundation of China (NSFC Grant Nos. 21071123, 21273257 and U1137606), Yunnan Key Project (2010CC007) and Program for Changjiang Scholars and Innovative Research Team in University (IRT0979) for financial support.

Appendix A. Supplementary data

Supplementary data associated with this article can be found, in the online version, at http://dx.doi.org/10.1016/j.jphotochem.2014.03.009.

References

[1] D.T. Quang, J.S. Kim, Chem. Rev. 110 (2010) 6280–6301.
[2] A. Bencini, V. Lippolis, Coord. Chem. Rev. 256 (2012) 149–169.
[3] Y. Zhou, J.Y. Yoon, Chem. Soc. Rev. 41 (2012) 52–67.
[4] A. Meister, J. Biol. Chem. 263 (1988) 17205–17208.
[5] H. Refsum, P.M. Ueland, O. Nygard, S.E. Vollset, Annu. Rev. Med. 49 (1998) 31–62.
[6] S.C. Lu, Mol. Aspects Med. 30 (2009) 42–59.
[7] S. Seshadri, A. Beiser, J. Selhub, P.F. Jacques, I.H. Rosenberg, R.B. D'Agostino, P.W.F. Wilson, N. Engl. J. Med. 346 (2002) 476–483.
[8] S. Shahrokhian, Anal. Chem. 73 (2001) 5972–5978.
[9] S. Na, N. Shao, J.Y. Jin, H. Wang, J. Zheng, R.H. Yang, W.H. Chan, Z. Abliz, J. Am. Chem. Soc. 132 (2010) 725–736.
[10] Y. Guo, H. Wang, Y. Sun, B. Qu, Chem. Commun. 48 (2012) 3221–3223.
[11] B.K. McMahon, T. Gunnlaugsson, J. Am. Chem. Soc. 134 (2012) 10725–10728.
[12] Y. Li, P. Wu, H. Xu, H. Zhang, X. Zhong, Analyst 136 (2010) 196–200.
[13] G.-J. Kim, K. Lee, H. Kwon, H.-J. Kim, Org. Lett. 13 (2011) 2799–2801.
[14] R.R. Deng, X.J. Xie, M. Vendrell, Y.-T. Chang, X.G. Liu, J. Am. Chem. Soc. 133 (2011) 20168–20171.
[15] B. Zhu, X. Zhang, Y. Li, P. Wang, H. Zhang, X. Zhuang, Chem. Commun. 46 (2010) 5710–5712.
[16] N. Boens, V. Leen, W. Dehaen, Chem. Soc. Rev. 41 (2012) 1130–1172.
[17] J. Shao, H. Guo, S. Ji, J. Zhao, Biosens. Bioelectron. 26 (2011) 3012–3017.
[18] H.M. Guo, Y.Y. Jing, X.L. Yuan, S.M. Ji, J.Z. Zhao, X.H. Li, Y.Y. Kan, Org. Biomol. Chem. 9 (2011) 3844–3853.
[19] J. Shao, H. Sun, H. Guo, S. Ji, J. Zhao, W. Wu, X. Yuan, C. Zhang, T.D. James, Chem. Sci. 3 (2012) 1049–1061.
[20] J. Lu, C. Sun, W. Chen, H. Ma, W. Shi, X. Li, Talanta 83 (2011) 1050–1056.
[21] Y. Yue, Y. Guo, J. Xu, S. Shao, New J. Chem. 35 (2011) 61–64.
[22] O.G. Tsay, K.M. Lee, D.G. Churchill, New J. Chem. 36 (2012) 1949–1952.
[23] S.H. Yin, W.L. Yuan, J.L. Huang, D.B. Xie, B. Lin, K.Z. Jiang, H.Y. Qiu, Spectrochim. Acta A: Mol. Biomol. Spectrosc. 96 (2012) 82–88.
[24] M.L. Li, H. Wang, X. Zhang, H.-S. Zhang, Spectrochim. Acta A 60 (2004) 987–993.
[25] G.M. Sheldrich, SHELX-97, Program for the Refinement of Crystal Structures, University of Göttingen, Germany, 1997.
[26] H.-W. Rhee, C.-R. Lee, S.-H. Cho, M.-R. Song, M. Cashel, H.E. Choy, Y.-J. Seok, J.-I. Hong, J. Am. Chem. Soc. 130 (2008) 784–785.
[27] C.C. Woodroofe, S.J. Lippard, J. Am. Chem. Soc. 125 (2003) 11458–11459.
[28] H. Koutaka, J.-I. Kosuge, N. Fukasaku, T. Hirano, K. Kikuchi, Y. Urano, H. Kojima, T. Nagano, Chem. Pharm. Bull. 52 (2004) 700–703.
[29] M.G. Choi, S.Y. Cha, H.Y. Lee, H.L. Jeon, S.-K. Chang, Chem. Commun. (2009) 7390–7392.
[30] M.H. Lim, B.A. Wong, W.H. Pitcock Jr., D. Mokshagundam, M.-H. Baik, S.J. Lippard, J. Am. Chem. Soc. 128 (2006) 14364–14373.
[31] S.H. Kim, J.S. Kim, S.M. Park, S.K. Chang, Org. Lett. 8 (2006) 371–374.
[32] M.M. Zhang, K.L. Zhu, F.H. Huang, Chem. Commun. 46 (2010) 8131–8141.
[33] S.C. Wang, G.W. Men, L.Y. Zhao, Q.F. Hou, S.M. Jiang, Sens. Actuators B 145 (2010) 826–831.
[34] X.J. Xie, Y. Qin, Sens. Actuators B 156 (2011) 213–217.
[35] Z.T. Jiang, R.R. Deng, L. Tang, P. Lu, Sens. Actuators B 135 (2008) 128–132.
[36] H.S. Jung, P.S. Kwon, J.W. Lee, J.I. Kim, C.S. Hong, J.W. Kim, S.H. Yan, J.Y. Lee, J.H. Lee, T.H. Joo, J.S. Kim, J. Am. Chem. Soc. 131 (2009) 2008–2012.
[37] A. Helal, M.H.O. Rashid, C.H. Choi, H.S. Kim, Tetrahedron 67 (2011) 2794–2802.
[38] R. Pandey, P. Kumar, A.K. Singh, M. Shahid, P.Z. Li, S.K. Singh, Q. Xu, A. Misra, D.S. Pandey, Inorg. Chem. 50 (2011) 3189–3197.
[39] W.B. Chen, X.J. Tu, X.Q. Guo, Chem. Commun. (2009) 1736–1738.

[40] J.H. Jung, M.H. Lee, H.J. Kim, H.S. Jung, S.Y. Lee, N.R. Shin, K. No, J.S. Kim, Tetrahedron Lett. 50 (2009) 2013–2016.
[41] Y.J. Zhang, X.P. He, M. Hu, Z. Li, X.X. Shi, G.R. Chen, Dyes Pigments 88 (2011) 391–395.
[42] D. Maity, A.K. Manna, D. Karthigeyan, T.K. Kundu, S.K. Pati, T. Govindaraju, Chem. Eur. J. 17 (2011) 11152–11161.
[43] Y.B. Ruan, A.F. Li, J.S. Zhao, J.S. Shen, Y.B. Jiang, Chem. Commun. 46 (2010) 4938–4940.
[44] N. Shao, J.Y. Jin, S.M. Cheung, R.H. Yang, W.H. Chan, T. Mo, Angew. Chem. Int. Ed. 45 (2006) 4944–4948.
[45] Y.K. Yang, S. Shim, J. Tae, Chem. Commun. 46 (2010) 7766–7768.