Supporting information

An “off–on–off” sensor for sequential detection of Cu$^{2+}$ and hydrogen sulfide based on naphthalimide-rhodamine B derivative and its application in dual-channel cell imaging

Shuai Wang, Haichang Ding, Yuesong Wang, Congbin Fan, Yayi Tu, Gang Liu*, Shouzhi Pu*

Jiangxi Key Laboratory of Organic Chemistry, Jiangxi Science & Technology Normal University, Nanchang 330013, PR China

*Corresponding author: E-mail address: liugang0926@163.com (G. Liu); pushouzhi@tsinghua.org.cn (S. Pu), Tel. & Fax: +86-791-83831996.

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Table. 1. Comparison of the analytical performance of the sensors for copper/sulfide determination.

Fig. S1. $^1$H NMR spectrum of 1 in CD$_2$Cl$_2$.

Fig. S2. $^{13}$C NMR spectrum of sensor 1 in CD$_2$Cl$_2$.

Fig. S3. The ESI-MS spectrum of 1.

Fig. S4. Nonlinear curve fitting of the ratio change of absorbance ($A_{564}/A_{425}$) from 0 to 35 μM for 1 with Cu$^{2+}$ in CH$_3$CN–H$_2$O (9/1, v/v) solution at room temperature.

Fig. S5. The limit of detection (LOD) of the ratio change of absorbance ($A_{564}/A_{425}$) of sensor 1 towards Cu$^{2+}$ by UV-vis measured.

Fig. S6. Nonlinear curve fitting of the fluorescence titration data from 0 to 40 μM for 1 with Cu$^{2+}$ at 610 nm in CH$_3$CN–H$_2$O (9/1, v/v) solution at room temperature.

Fig. S7. The limit of detection (LOD) of 1 towards Cu$^{2+}$ by fluorescence measured at 610 nm.

Fig. S8. Nonlinear curve fitting of the ratio change of absorbance ($A_{564}/A_{425}$) from 0 to 35 μM for 1 with Cu$^{2+}$ in CH$_3$CN–H$_2$O (9/1, v/v) solution at room temperature.

Fig. S9. The limit of detection (LOD) of the ratio change of absorbance ($A_{564}/A_{425}$) of sensor 1 towards Cu$^{2+}$ by UV-vis measured.

Fig. S10. Nonlinear curve fitting of the fluorescence titration data from 0 to 40 μM for 1-Cu$^{2+}$ complex towards H$_2$S at 610 nm in CH$_3$CN–H$_2$O (7/3, v/v) solution at room temperature.

Fig. S11. The limit of detection (LOD) of 1-Cu$^{2+}$ complex towards H$_2$S by fluorescence measured at 610 nm.

Fig. S12. Normalized spectral overlap of fluorescence spectrum of naphthalimide (green) and absorption spectrum of rhodamine B (pink) in CH$_3$CN–H$_2$O (9/1, v/v) solution.
| Sensor      | $\lambda_{ex}/\lambda_{em}$ (nm) | Selectivity | Approaches         | LOD      | Ref.                  |
|-------------|----------------------------------|-------------|---------------------|----------|-----------------------|
| Cu$^{2+}$   | 470/517                          |             | Fluorescence quench | $1.0 \times 10^{-7}$ M | Chem. Commun., 2009, 0, 7390–7392 |
| S$^{2-}$    |                                  |             | Fluorescence increase | $4.2 \times 10^{-7}$ M |          |
| Cu$^{2+}$   | 494/523                          |             | Fluorescence quench | $1.08 \times 10^{-5}$ M | Dalton Trans., 2012, 41, 5799–5804 |
| H$_2$S      |                                  |             | Fluorescence increase | $1.7 \times 10^{-6}$ M |          |
| Cu$^{2+}$   | 540/600                          |             | Fluorescence quench | no data | Chem. Commun., 2013, 49, 7510–7512 |
| HS$^{-1}$   |                                  |             | Fluorescence increase | $1.0 \times 10^{-6}$ M |          |
| Cu$^{2+}$   | 243/436                          |             | Fluorescence quench | $2.77 \times 10^{-6}$ M | Dalton Trans., 2014, 43, 5815–5822 |
| S$^{2-}$    |                                  |             | Fluorescence increase | $2.51 \times 10^{-6}$ M |          |
| Cu$^{2+}$   | 510/604                          |             | Fluorescence quench | $8.95 \times 10^{-8}$ M | J. Mater. Chem. B, 2017, 5, 8957–8966 |
| S$^{2-}$    |                                  |             | Fluorescence increase | $1.36 \times 10^{-7}$ M |          |
| Cu$^{2+}$   | 530/581                          |             | Fluorescence increase | $2.43 \times 10^{-8}$ M | RSC Adv., 2014, 4, 5718–5725 |
| S$^{2-}$    |                                  |             | colorimetric         | no data |          |
| Cu$^{2+}$   | 325/528,610                     | H$_2$S      | Fluorescence quench | $2.3 \times 10^{-7}$ M | This work |

Table 1.
Fig. S2.
Fig. S3.
Fig. S4.

\[ Y = 0.52887 \times X - 0.44648 \]

\[ R = 0.99571 \]
Fig. S5.

\[ Y = 0.37398 \times X - 0.02661 \]

\[ R = 0.99579 \]

\[ \text{LOD} = 3 \sigma / k \]

\[ = 3 \times 0.03298 / 0.37398 \]

\[ = 0.26456 \mu M \]}
Fig. S6.

\[ Y = 60.5712 \times X + 109.64832 \]

\[ R = 0.9876 \]
Fig. S7.

Emission Intensity (a.u.) vs. $[\text{Cu}^{2+}] / \text{I} (\mu\text{M})$

Y = 79.28338 * X - 46.16081
R = 0.99277
LOD = $3 \sigma / k$

$= 3 \times \frac{4.560702}{79.28338}$

$= 0.172572 \mu\text{M}$
Fig. S8.

\[ Y = -0.1638 \times X + 16.31734 \]

\[ R^2 = 0.97723 \]
Fig. S9.

The graph shows a linear relationship between $A_{564}/A_{425}$ and [Cu$^{2+}$]1 (µM). The equation of the line is:

$$Y = -0.27333 \times X + 17.62838$$

The $R^2$ value is 0.9774. The LOD (Limit of Detection) is calculated as:

$$\text{LOD} = 3 \sigma / k = 3 \times 0.03635 / 0.27333$$

$$= 0.39897 \text{ µM}$$
Fig. S10.

The graph shows the relationship between emission intensity (a.u.) and the concentration of Cu$^{2+}$, with the equation

$$Y = -39.5825 \times X + 1920.65909$$

$$R^2 = 0.99854$$
Fig. S11.

\[ Y = -40.66429 \times X + 1925.80952 \]

\[ R^2 = 0.99524 \]

\[ \text{LOD} = 3 \, \sigma / k \]

\[ = 3 \times 3.139964 / 40.66429 \]

\[ = 0.23165 \, \mu M \]
