

# Fluorescent Ratiometric Cu<sup>2+</sup> Probe Based on FRET by Naphthalimide-Appended Rhodamine Derivative

Chunwei Yu,<sup>a</sup> Yingying Wen,<sup>a</sup> Xi Qin<sup>\*,b</sup> and Jun Zhang<sup>\*,a</sup>

<sup>a</sup> *Laboratory of Environmental Monitoring, School of Tropical and Laboratory Medicine, Hainan Medical University, Haikou, 571101, China*

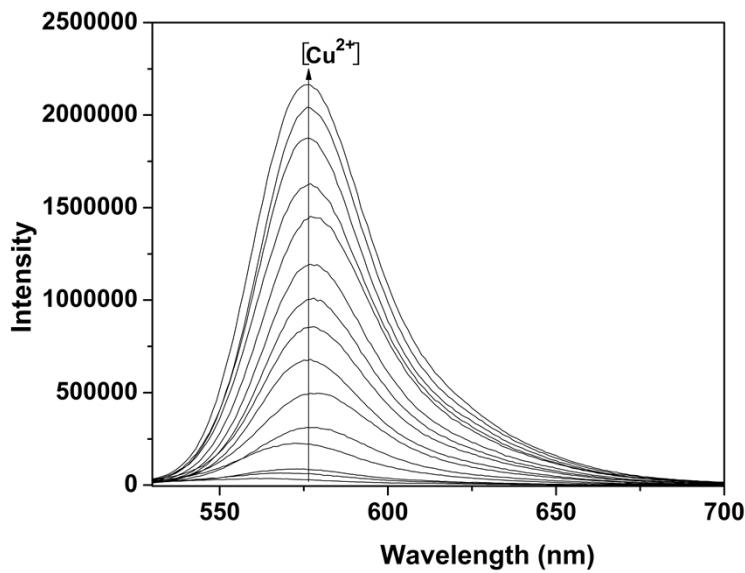
<sup>b</sup> *Department of Clinical Laboratory, Affiliated Hospital of Hainan Medical University, Haikou 570102, China*

\*Corresponding author. Tel.: +86 898 66973190; Fax: +86 898 66989173.

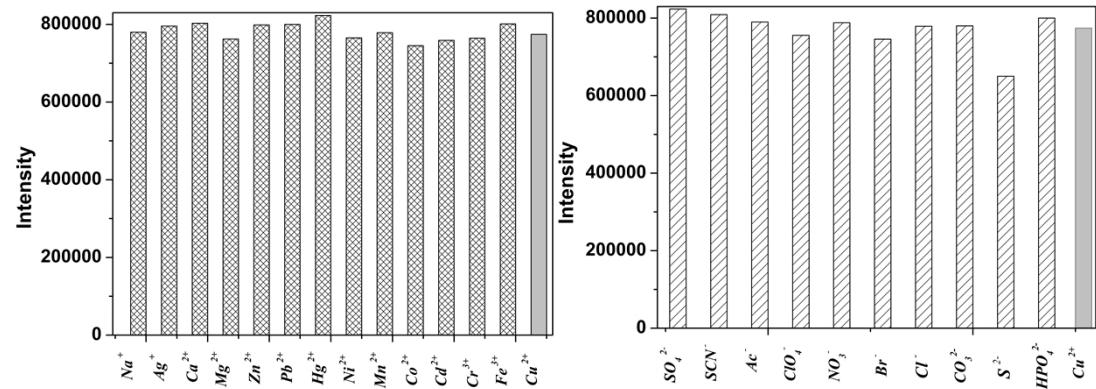
\*\*Corresponding author. E-mail address: [qinxi99@21cn.com](mailto:qinxi99@21cn.com) (X. Qin),  
[jun\\_zh1979@163.com](mailto:jun_zh1979@163.com) (J. Zhang)

## Contents

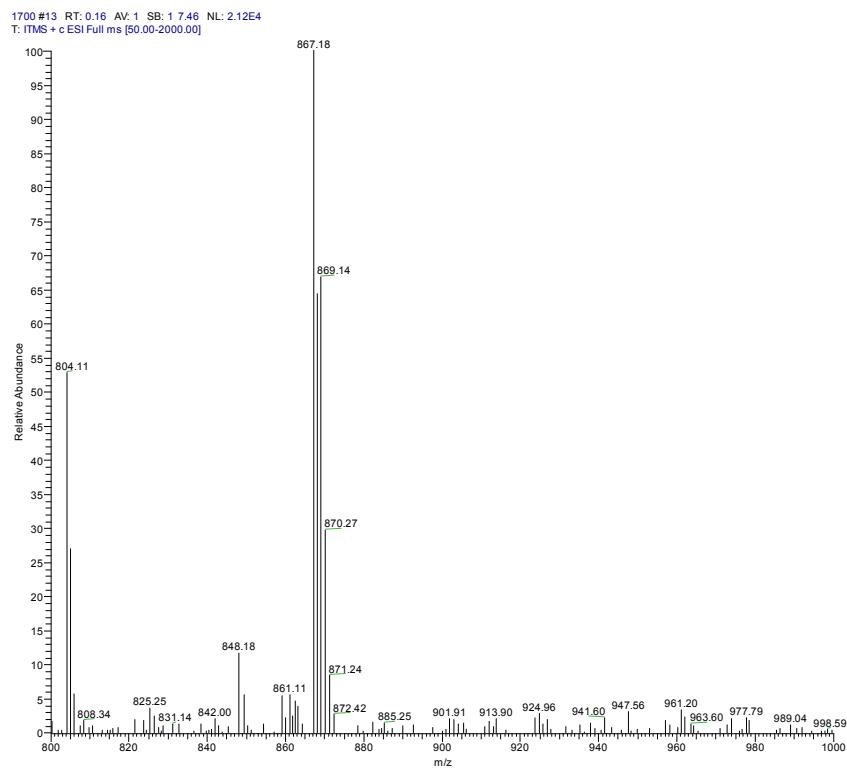
<b>Fig. S1.</b> Fluorescence titration spectra of L (2 $\mu$ M) in ethanol/water solution (1:9 ,v/v, 50 mM HEPES, pH 7.4) upon gradual addition of Cu <sup>2+</sup> (0-20 $\mu$ M). Ex=520 nm.....	3
<b>Fig. S2.</b> Fluorescence spectra response of L (2 $\mu$ M) to Cu <sup>2+</sup> (10 $\mu$ M) containing various metal ions and anions (50 $\mu$ M) in ethanol-water solution (1:9, v:v. 50 mM HEPES, pH 7.4) .....	3
<b>Fig. S3.</b> Partial ESI-MS mass spectrum of a mixture of L and 1 equiv Cu <sup>2+</sup> in ethanol solution.....	4
<b>Fig. S4.</b> ESI-MS mass spectrum of L .....	4
<b>Fig. S5.</b> <sup>1</sup> H NMR spectrum of L .....	5
<b>Fig. S6.</b> <sup>13</sup> C NMR spectrum of L .....	5
<b>Table S1.</b> Performances comparison of various fluorescent probes for Cu <sup>2+</sup> ion based on FRET .....	6



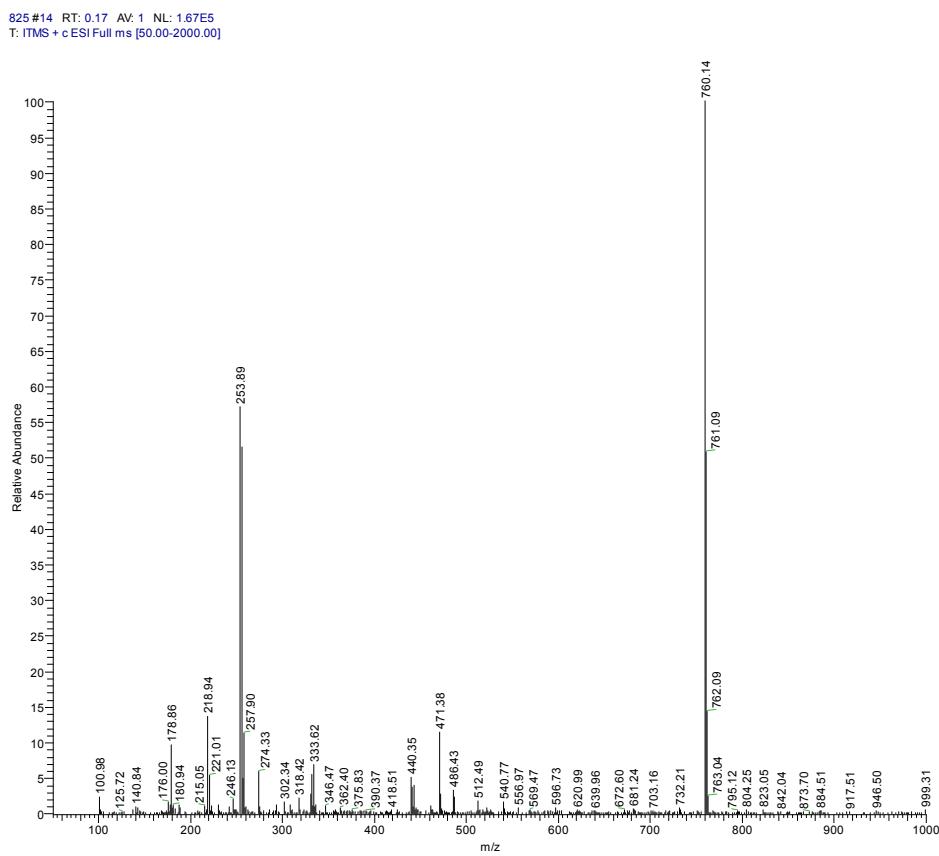
**Fig. S1.** Fluorescence titration spectra of **L** (2  $\mu$ M) in ethanol/water solution (1:9 ,v/v, 50 mM HEPES, pH 7.4) upon gradual addition of  $\text{Cu}^{2+}$  (0-20  $\mu$ M). Ex=520 nm.



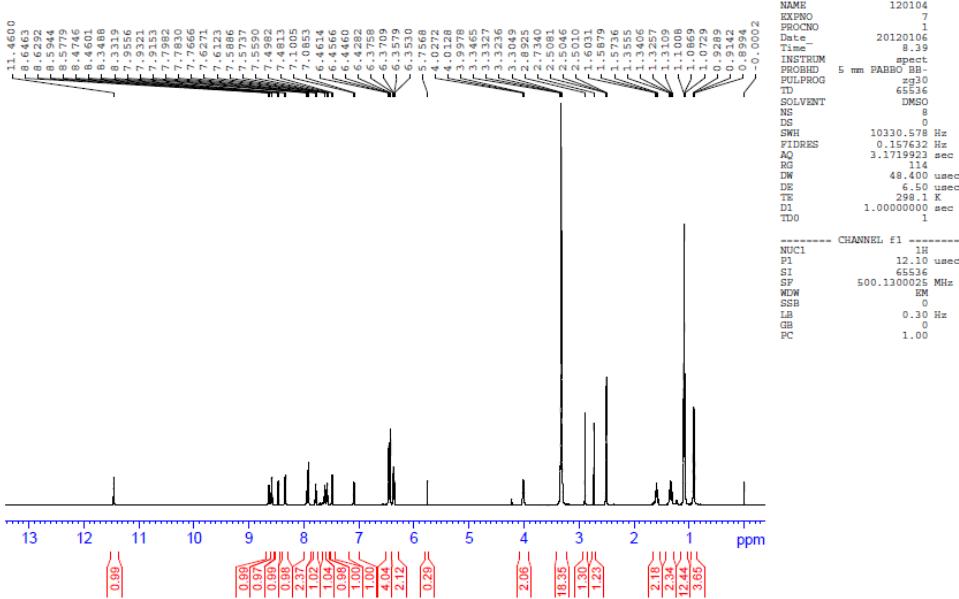
**Fig. S2.** Fluorescence spectra response of **L** (2  $\mu$ M) to  $\text{Cu}^{2+}$  (10  $\mu$ M) containing various metal ions and anions (50  $\mu$ M) in ethanol-water solution (1:9, v:v. 50 mM HEPES, pH 7.4).



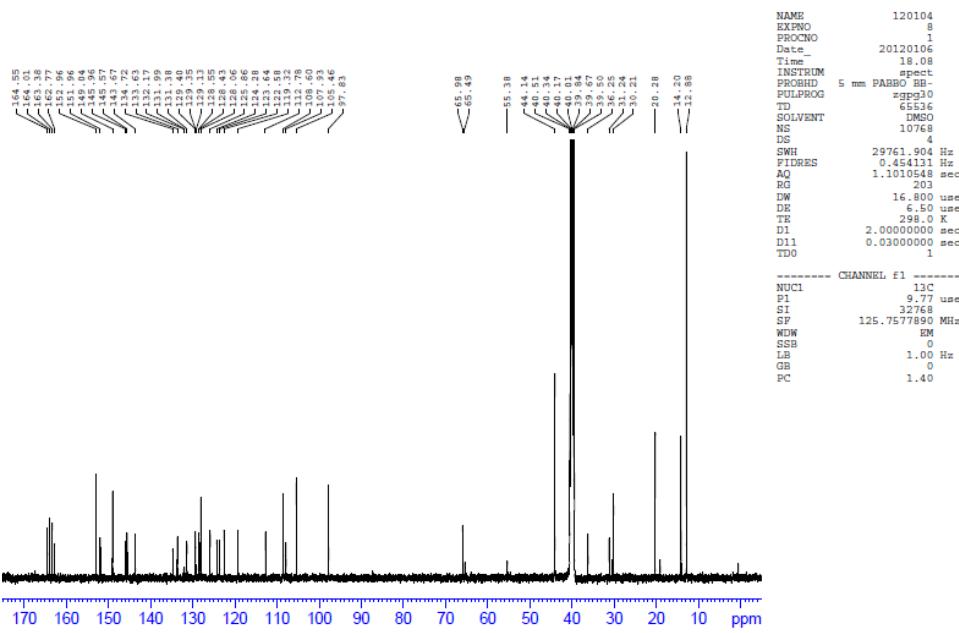
**Fig. S3.** Partial ESI-MS (ES+) mass spectrum of **L** in the presence of 1.0 equiv. of  $\text{Cu}^{2+}$  in ethanol.



**Fig. S4.** ESI-MS mass spectrum of **L**.



**Fig. S5.**  $^1\text{H}$  NMR spectrum of **L**.



**Fig. S6.**  $^{13}\text{C}$  NMR spectrum of **L**.

Table S1

Energy donor/acceptor	Testing media	Applications	Reproducibility	Linear range (nM)	LOD (nM)	Ref.
Naphthalene/Pyrene unit	CH <sub>3</sub> CN	NA <sup>a</sup>	NA	NA	NA	[1]
Coumarin/Fluorescein	H <sub>2</sub> O/DMSO solution (9:1, v/v)	NA	NA	NA	NA	[2]
Dansyl/Rhodamine	H <sub>2</sub> O/CH <sub>3</sub> CN (1:9, v/v, pH 7.0, Tris -HCl buffer)	NA	NA	NA	NA	[3]
Naphthalimide/dansyl	Acetonitrile containing neutral micelles TX-100 (2 mM)	NA	Reversible	NA	NA	[4]
Coumarin/Rhodamine	H <sub>2</sub> O/CH <sub>3</sub> CN solution (4:1, v/v, pH 7.0, HEPES buffer)	HeLa cells	NA	0.08-30 μM	NA	[5]
Coumarin/4-amino-7-sulfamoyl benzoxadiazole	H <sub>2</sub> O/CH <sub>3</sub> CN solution (9:1, v/v pH 7.4, Tris-HCl buffer)	MCF-7 cells	Reversible	NA	3 mM	[6]
Indole/Rhodamine	H <sub>2</sub> O/CH <sub>3</sub> CN solution (4:1, v/v, pH 7.3, HEPES buffer)	HeLa cells	NA	NA	3.6 ppb	[7]
Coumarin/Rhodamine	H <sub>2</sub> O/CH <sub>3</sub> CN solution (4:1, v/v, pH 7.0, HEPES buffer)	MCF-7 cells	NA	NA	NA	[8]
Dansyl/Rhodamine	H <sub>2</sub> O/CH <sub>3</sub> CN solution (1:1, v/v, pH 7.4, HEPES buffer)	HeLa cells	NA	10 to 50 mM	0.12 mM	[9]
Naphthalimide/Rhodamine	H <sub>2</sub> O/Ethanol solution (1:9, v/v, pH 7.4, HEPES buffer)	RAW cells	Reversible	0.5–1.5 μM	0.25 μM	This work

<sup>a</sup> NA: Not Available.

## References

- [1] H. J. Kim, S. Y. Park, S. Yoon and J. S. Kim, *Tetrahedron*, 2008, **64**, 1294.
- [2] S. Y. Lee, H. J. Kim, J. S. Wu, K. No and J. S. Lim, *Tetrahedron Lett.*, 2008, **49**, 6141.
- [3] M. H. Lee, H. J. Kim, S. Yoon, N. Park and J. S. Kim, *Org. Lett.*, 2008, **10**, 213.
- [4] V. S. Jisha, A. J. Thomas, and D. J. Ramaiah, *J. Org. Chem.*, 2009, **74**, 6667.
- [5] L. Yuan, W. Y. Lin, B. Chen and Y. N. Xie, *Org. Lett.*, 2012, **14**, 432.
- [6] Y. C. Chen, C. C. Zhu, J. J. Cen, J. Li, W. J. He, Y. Jiao and Z. J. Guo, *Chem. Commun.*, 2013, **49**, 7632.
- [7] C. Kar, M. D. Adhikari, A. Ramesh and G. Das, *Inorg. Chem.*, 2013, **52**, 743.
- [8] X. Y. Guan, W. Y. Lin and W. M. Huang, *Org. Biomol. Chem.*, 2014, **12**, 3944.
- [9] Z. J. Hu, J. W. Hu, Y. Cui, G. N. Wang, X. J. Zhang, K. Uvdalb and H. W. Gao, *J. Mater. Chem. B*, 2014, **2**, 4467.