## Supplementary Information

## For

## A Novel Fluorescent 'Off-On-Off' Probe for Relay Recognition of Zn<sup>2+</sup> and Cu<sup>2+</sup> Derived from *N*,*N*-Bis(2-pyridylmethyl)amine

Yameng Liu, Qiang Fei, Hongyan Shan, Minghui Cui, Qing Liu, Guodong Feng, and Yanfu Huan\* College of Chemistry, Jilin University, Changchun 130023, People's Republic of China <u>yfhuan@jlu.edu.cn</u>

## Table of contents

Table of contents	
1. Supplementary spectral data	
Figure S-1	2
Figure S-2	3
Figure S-3	4
Figure S-4	5
Figure S-5	6
Figure S-6	7
Figure S-7	8
Figure S-8	9
Figure S-9	10
2. The characterization data of comp	bound 1, 2, NBPA
Mass spectrum for compound 1	11
Mass spectrum for compound 2	12
Mass spectrum for NBPA	13
<sup>1</sup> HNMR spectra coppies of 1	14
<sup>1</sup> HNMR spectra coppies of 2	15
<sup>1</sup> HNMR spectra coppies of NBPA	16
<sup>13</sup> CNMR spectra coppies of NBPA	17
	1



1. Supplementary spectral data

Figure S-1. ESI-MS of NBPA-Zn<sup>2+</sup> in  $CH_3OH$ 



Figure S-2. ESI-MS of NBPA-Zn<sup>2+</sup>-Cu<sup>2+</sup> in  $CH_3OH$ 



**Figure S-3.** The fluorescence spectra of compound NBPA ( $10 \,\mu$ M) before (black line) and after (red line) addition of 1.0 equiv of Zn<sup>2+</sup> in different solvent /H<sub>2</sub>O(1:1, v/v). a) acetonitrile, b)DMF, c) THF, d) ethanol; entrance slit, 2.5 nm; exit slit, 5 nm; t, 10 min.



**Figure S-4.** a) Effect of different ratios of  $CH_3CN$  to  $H_2O$  solvents on the fluorescence intensity of NBPA (black line) and NBPA- $Zn^{2+}$  (red line); b) Effect of pH on the fluorescence intensity of NBPA (black line) and NBPA- $Zn^{2+}$  (red line); pH, 2.30-10.30; c) Effect of different buffer solutions on the fluorescence intensity of NBPA and NBPA- $Zn^{2+}$ ; pH value of buffer solutions, 6.30.



**Figure S-5.** The fluorescence spectra of compound NBPA (10  $\mu$ M) before (black line) and after (red line) addition of 1.0 equiv of Zn<sup>2+</sup> at different temperatures in CH<sub>3</sub>CN /H<sub>2</sub>O(1:1, v/v); entrance slit, 2.5 nm; exit slit, 2.5 nm; t, 10 min.



Figure S-6. Stern-Volmer plot to estimate fluorescence quenching for complex NBPA-Zn<sup>2+</sup> in the presence of Cu<sup>2+</sup>.



**Figure S-7.** Fluorescence spectra of NBPA and the addition of various ions to NBPA in CH<sub>3</sub>CN- buffer solution (1:1, v/v); NBPA,  $1.0 \times 10^{-5}$  M; metal ions,  $1.0 \times 10^{-5}$  M; Buffer solution (HAc-NaAc), 0.10 M; entrance slit, 2.5 nm; exit slit, 5 nm; t, 10 min.



**Figure S-8.** Fluorescence spectra of NBPA-Zn<sup>2+</sup> and the addition of various ions to NBPA-Zn<sup>2+</sup> in CH<sub>3</sub>CN-buffer solution (1:1, v/v); NBPA-Zn<sup>2+</sup>,  $1.0 \times 10^{-5}$  M; metal ions,  $1.0 \times 10^{-5}$  M; Buffer solution (HAc-NaAc), 0.10 M; entrance slit, 2.5 nm; exit slit, 5 nm; t, 10 min.



Figure S-9. Fluorescence decay curves for NBPA in presence of (a)  $Zn^{2+}$  (b)  $Cu^{2+}$  and (c)  $Zn^{2+}/Cu^{2+}$  (excitation at 353 nm, emission at 443 nm)





Figure S-10. ESI-MS of 1 in CH<sub>3</sub>OH



Figure S-11. ESI-MS of 2 in CH<sub>3</sub>OH



Figure S-12. ESI-MS of NBPA in CH<sub>3</sub>OH





Figure S-14. The <sup>1</sup>H NMR spectra of 2 in CDCl<sub>3</sub>



Figure S-15. The <sup>1</sup>H NMR spectra of NBPA in CDCl<sub>3</sub>



Figure S-16. The <sup>13</sup>C NMR spectra of sensor NBPA in CDCl<sub>3</sub>