**Electronic Supplementary Information _ESI**

A highly selective and ratiometric fluorescent sensor for relay recognition of zinc(II) and sulfide ions based on modulation of excited-state intramolecular proton transfer

Lijun Tang*, Mingjun Cai, Pei Zhou, Jia Zhao, Keli Zhong, Shuhua Hou, and Yanjiang Bian

*Department of Chemistry, Liaoning Provincial Key Laboratory for the Synthesis and Application of Functional Compounds, Bohai University, Jinzhou 121013, China

E-mail: ljtang@bhu.edu.cn

**Table of contents**

<table>
<thead>
<tr>
<th>Fig.</th>
<th>Description</th>
<th>Page</th>
</tr>
</thead>
<tbody>
<tr>
<td>S1</td>
<td>Fluorescence spectra of BMD in different solvents</td>
<td>S3</td>
</tr>
<tr>
<td>S2</td>
<td>Job’s plot for BMD with Zn(^{2+})</td>
<td>S3</td>
</tr>
<tr>
<td>S3</td>
<td>HRMS spectrum of BMD solution in the presence of Zn(^{2+})</td>
<td>S4</td>
</tr>
<tr>
<td>S4</td>
<td>Hill plot for binding of BMD (10 (\mu)M) with Zn(^{2+})</td>
<td>S4</td>
</tr>
<tr>
<td>S5</td>
<td>Linear dependence of intensity ratio ((F_{424\ nm}/F_{502\ nm})) of probe BMD (10 (\mu)M) was related to the concentration of Zn(^{2+}) (1.0 to 4.25 (\mu)M) in CH(_3)CN/H(_2)O (2:8, v/v, HEPES 10 mM, pH = 7.4)</td>
<td>S5</td>
</tr>
<tr>
<td>S6</td>
<td>pH effects on intensity ratio ((F_{424\ nm}/F_{502\ nm})) of BMD-Zn(^{2+})</td>
<td>S5</td>
</tr>
<tr>
<td>S7</td>
<td>HRMS spectrum of BMD solution in the presence of 0.5 equiv of Cd(^{2+})</td>
<td>S6</td>
</tr>
<tr>
<td>S8</td>
<td>HRMS spectrum of BMD solution in the presence of 1.0 equiv of Cd(^{2+})</td>
<td>S6</td>
</tr>
</tbody>
</table>
Fig. S9. HRMS spectrum of BMD-Zn\textsuperscript{2+} solution in the presence of Na\textsubscript{2}S......... S7

Fig. S10. The intensity ratio ($F_{424 \text{ nm}}/F_{502 \text{ nm}}$) of sensor BMD-Zn\textsuperscript{2+} (10 µM) was linearly related to the concentration of $S^{2-}$ (50-140 µM).......................... S7

Fig. S11. Linear dependence of intensity ratio($F_{424 \text{ nm}}/F_{502 \text{ nm}}$) of BMD (10 µM) on Zn\textsuperscript{2+} concentration (0-6 µM) in three natural water samples............................ S8

Fig. S12. Linear dependence of intensity ratio($F_{424 \text{ nm}}/F_{502 \text{ nm}}$) of BMD-Zn\textsuperscript{2+} (10 µM) on $S^{2-}$ concentration (50-500 µM) in three natural water samples............................ S8

Fig. S13. $^1$H NMR spectra of sensor BMD. ............................................................. S9

Fig. S14. $^{13}$C NMR spectra of sensor BMD............................................................. S9

Fig. S15. HRMS (positive) spectrum of sensor of BMD. ....................................... S10
Fig. S1. Fluorescence spectrum of BMD in different solvents.

Fig. S2. Job’s plot for BMD with Zn$^{2+}$ in CH$_3$CN/H$_2$O (2:8, v/v, HEPES 10 mM, pH = 7.4).
Fig. S3. HRMS spectrum of BMD solution in the presence of Zn$^{2+}$.

Fig. S4. Fluorescence intensity at 424nm (F$_{424}$) of BMD (10 μM) versus increasing concentration of Log[Zn$^{2+}$]. The fluorescence response fits to a Hill coefficient of 1.01281, which is consistent with the 1:1 binding stoichiometry for the BMD-Zn$^{2+}$ complex.
Fig. S5. Linear dependence of intensity ratio ($F_{424\text{ nm}}/F_{502\text{ nm}}$) of probe BMD (10 µM) on the concentration of Zn$^{2+}$ (1.0 to 4.25 µM) in CH$_3$CN/H$_2$O (2:8, v/v, HEPES 10 mM, pH = 7.4).

The detection limit is calculated with the equation: detection limit = $3s/\rho$, where $s$ is the standard deviation of blank measurements, $\rho$ is the slope between intensity ratio ($F_{424\text{ nm}}/F_{502\text{ nm}}$) versus Zn$^{2+}$ concentration.

Fig. S6. pH effects on intensity ratio ($F_{424\text{ nm}}/F_{502\text{ nm}}$) of BMD-Zn$^{2+}$ in CH$_3$CN/H$_2$O (2:8, v/v).
Fig. S7. HRMS (positive) spectrum of BMD solution in the presence of 0.5 equiv of Cd$^{2+}$.

Fig. S8. HRMS (positive) spectrum of BMD solution in the presence of 1.0 equiv of Cd$^{2+}$. 
Fig. S9 HRMS (positive) spectrum of BMD-Zn$^{2+}$ solution in the presence of Na$_2$S.

Fig. S10. The intensity ratio ($F_{424\text{ nm}}/F_{502\text{ nm}}$) of probe BMD-Zn$^{2+}$ (10uM) was linearly related to the concentration of S$^{2-}$ (50–140 µM) in CH$_3$CN/H$_2$O (2:8, v/v, HEPES10 mM, pH = 7.4).
Fig. S11. Linear dependence of intensity ratio \( \frac{F_{424 \text{ nm}}}{F_{502 \text{ nm}}} \) of BMD (10 μM) on \( \text{Zn}^{2+} \) concentration (0-6 μM) in three natural water samples.

Fig. S12. Linear dependence of intensity ratio \( \frac{F_{424 \text{ nm}}}{F_{502 \text{ nm}}} \) of BMD-\( \text{Zn}^{2+} \) (10 μM) on \( \text{S}^{2-} \) concentration (50-500 μM) in three natural water samples.
**Fig. S13.** $^1$H NMR spectrum of sensor BMD in DMSO-$d_6$.

**Fig. S14.** $^{13}$C NMR spectrum of sensor BMD in DMSO-$d_6$. 
**Fig. S15.** HRMS (positive) spectrum of sensor of BMD.

**X-ray Crystallographic Details.**

Diffraction intensities for BMD were collected using a Bruker APEX–II CCD diffractometer equipped with graphite-monochromated Mo-Kα radiation with radiation wavelength 0.71073 Å by using the φ−ω scan technique at 296(2) K. The structures were solved by the direct method and refined by the Full-matrix least-squares on $F^2$ using the SHELXL software.¹ Non-hydrogen atoms were refined with anisotropic temperature parameters. The hydrogen atoms of organic ligands were generated geometrically and refined isotropically. CCDC 919147 contain the supplementary crystallographic data in this paper. These data can be obtained free of charge from The Cambridge Crystallographic Data Centre via [www.ccdc.cam.ac.uk/data_request/cif](http://www.ccdc.cam.ac.uk/data_request/cif).

Reference