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

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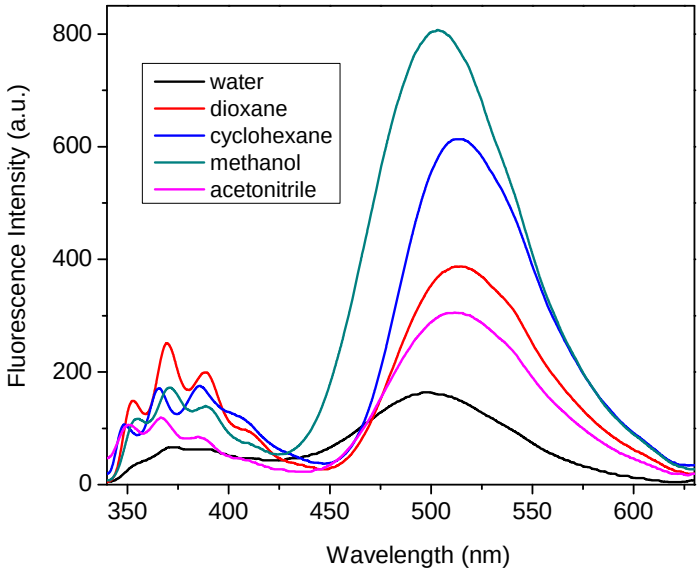

Fig. S1. Fluorescence spectrum of **BMD** in different solvents.

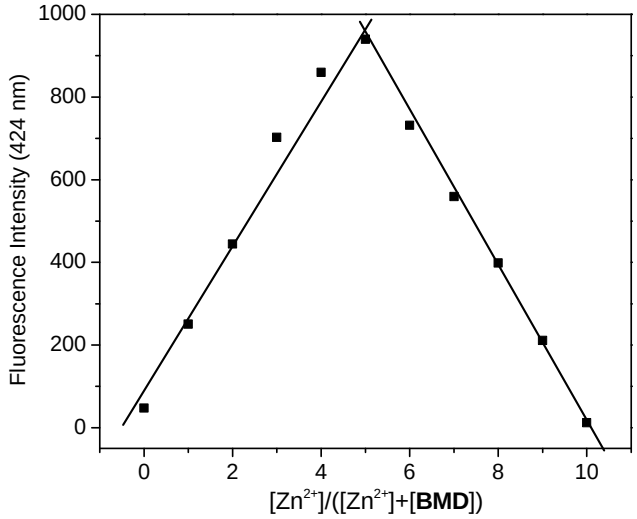

Fig. S2. Job's plot for **BMD** with Zn^{2+} in CH_3CN/H_2O (2:8, v/v, HEPES 10 mM, pH = 7.4).

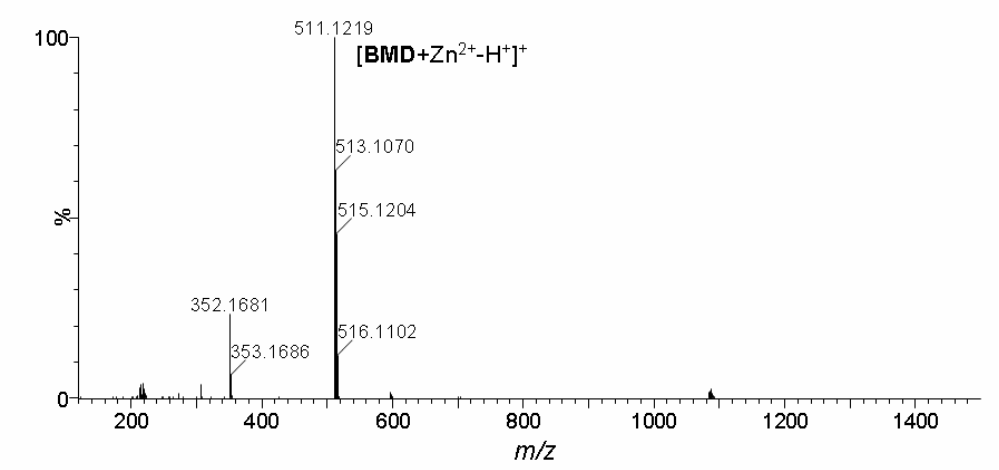

Fig. S3. HRMS spectrum of **BMD** solution in the presence of Zn^{2+}.

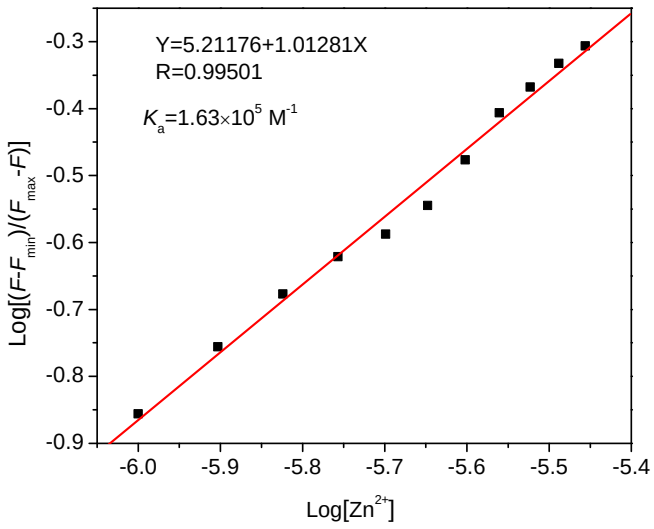

Fig. S4. Fluorescence intensity at 424nm (F_{424}) of **BMD** (10 μM) versus increasing concentration of Log[Zn^{2+}]. The fluorescence response fits to a Hill coefficient of 1.01281, which is consistent with the 1:1 binding stoichiometry for the **BMD**-Zn^{2+} complex.

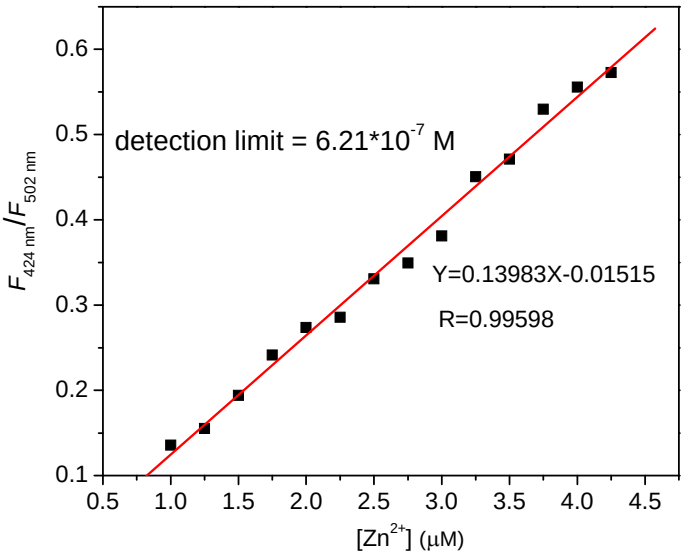

Fig. S5. Linear dependence of intensity ratio ($F_{424\ nm}/F_{502\ nm}$) of probe **BMD** (10 μM) on the concentration of Zn^{2+} (1.0 to 4.25 μM) in CH_3CN/H_2O (2:8, v/v, HEPES 10 mM, pH = 7.4).

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

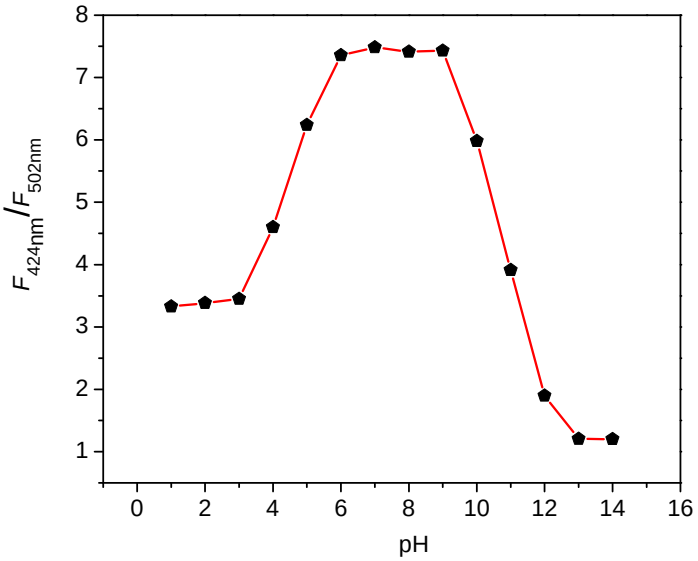

Fig. S6. pH effects on intensity ratio ($F_{424\ nm}/F_{502\ nm}$) of **BMD**-Zn^{2+} in CH_3CN/H_2O (2:8, v/v).

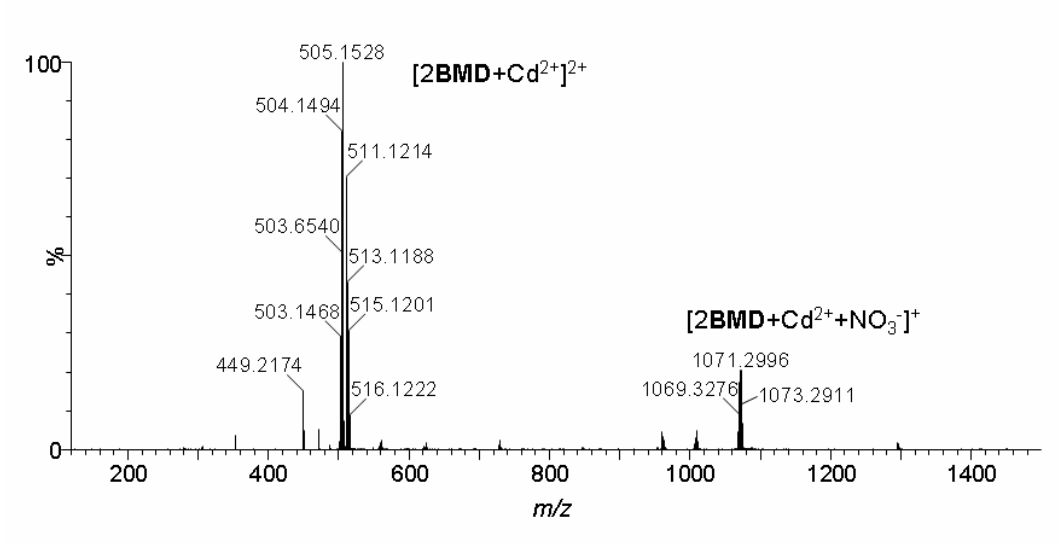

Fig. S7. HRMS (positive) spectrum of **BMD** solution in the presence of 0.5 equiv of $\mathbf{Cd^{2+}}$.

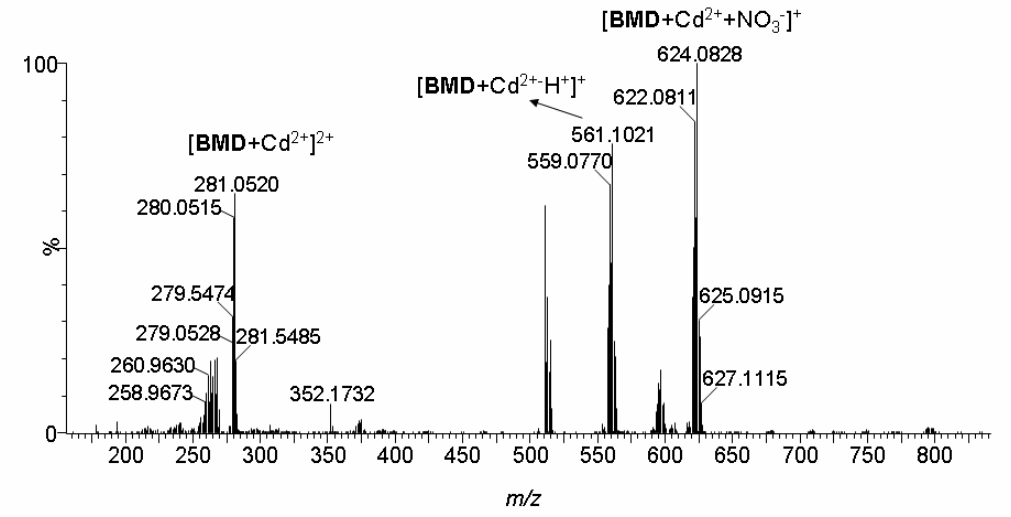

Fig. S8. HRMS (positive) spectrum of **BMD** solution in the presence of 1.0 equiv of $\mathbf{Cd^{2+}}$.

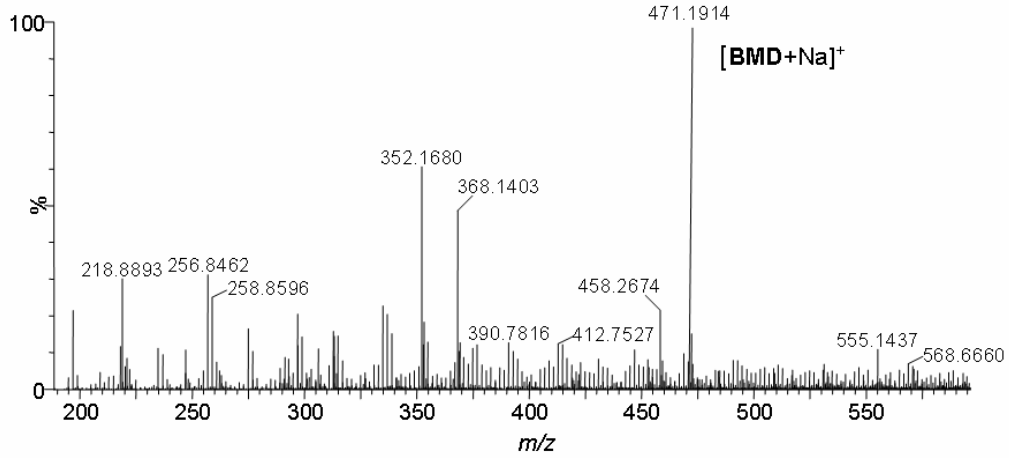

Fig. S9 HRMS (positive) spectrum of **BMD**-Zn^{2+} solution in the presence of Na_2S.

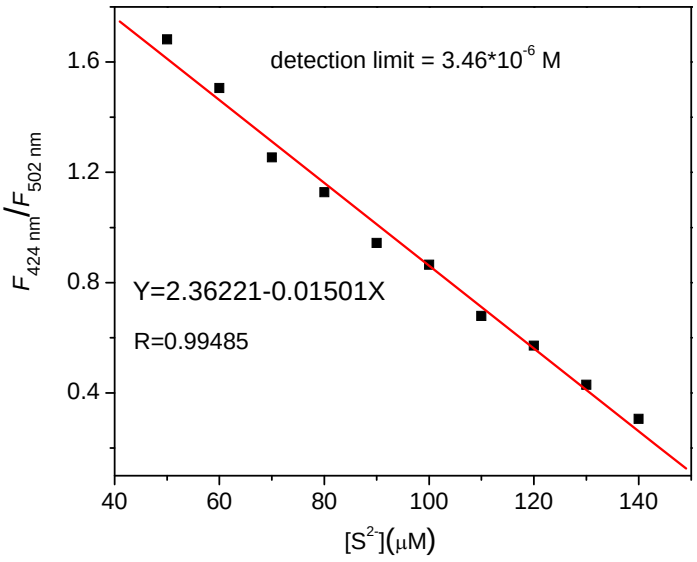

Fig. S10. The intensity ratio ($F_{424\ nm}/F_{502\ nm}$) of probe **BMD**-Zn^{2+} (10uM) was linearly related to the concentration of S^{2-} (50−140 μM) in CH_3CN/H_2O (2:8, v/v, HEPES10 mM, pH = 7.4).

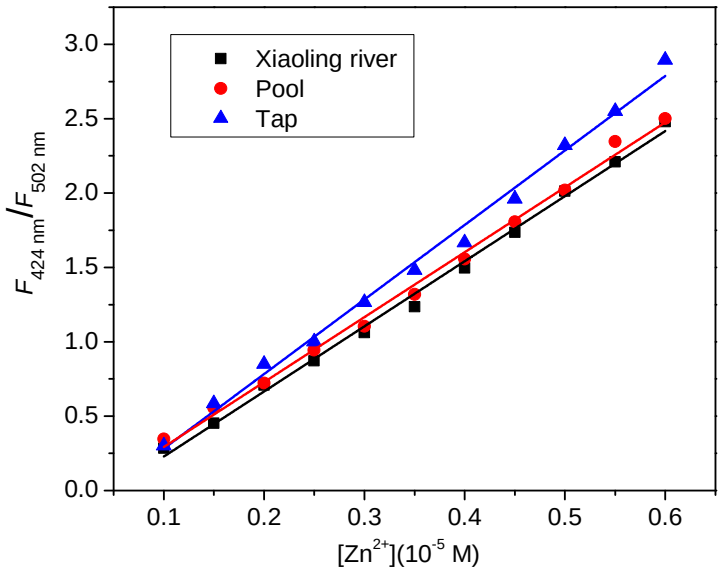

Fig. S11. Linear dependence of intensity ratio($F_{424\ nm}/F_{502\ nm}$) of **BMD** (10 μM) on Zn^{2+} concentration (0-6 μM) in three natural water samples.

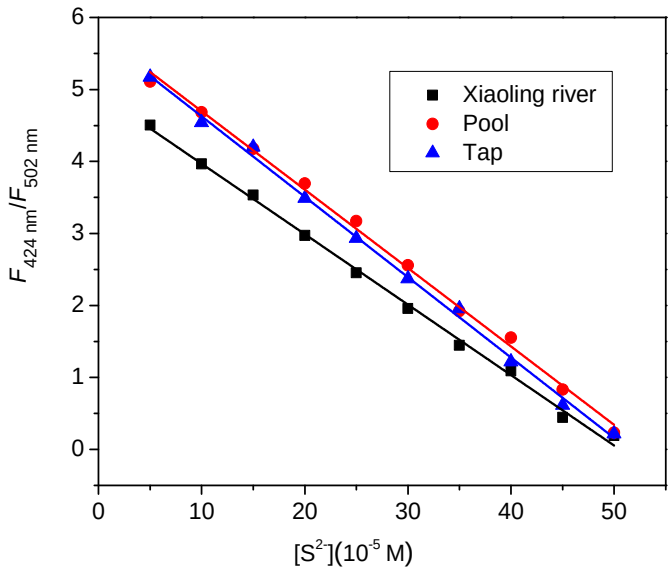

Fig. S12. Linear dependence of intensity ratio($F_{424\ nm}/F_{502\ nm}$) of **BMD**-Zn^{2+} (10 μM) on S^{2-} concentration (50-500 μM) in three natural water samples.

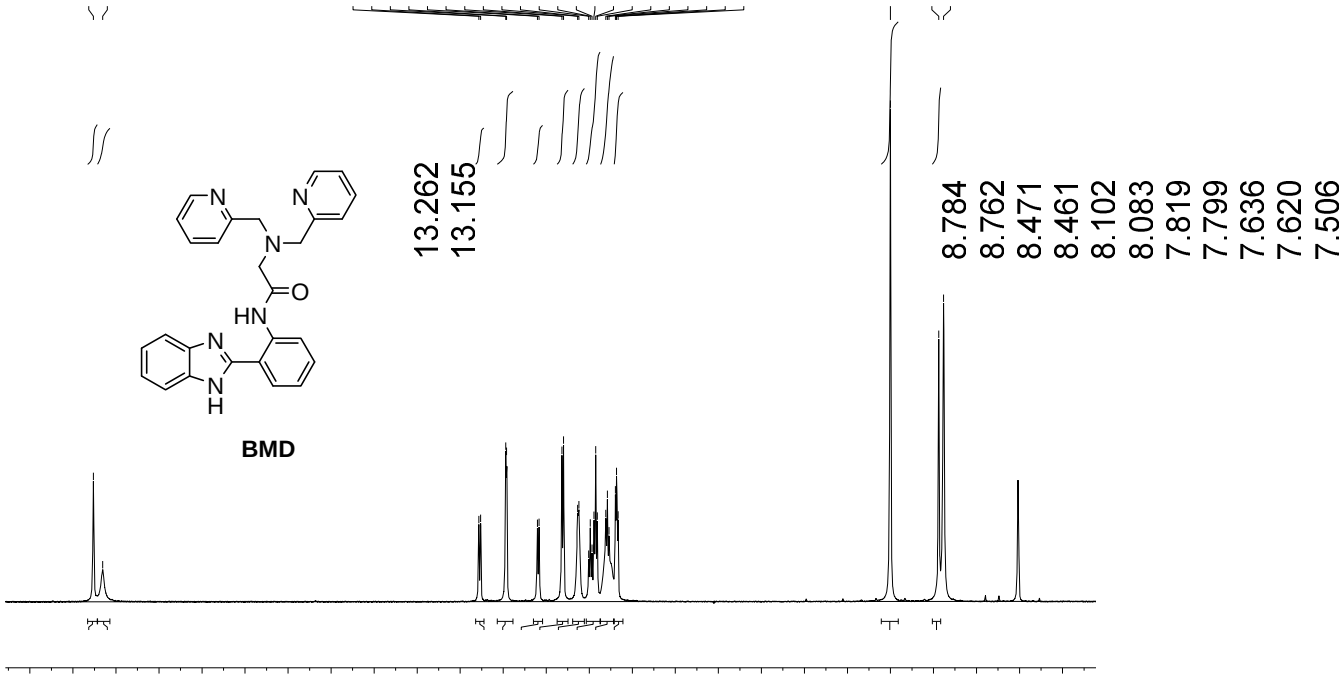

Fig. S13. ^{1}H NMR spectrum of sensor **BMD** in DMSO-d_6.

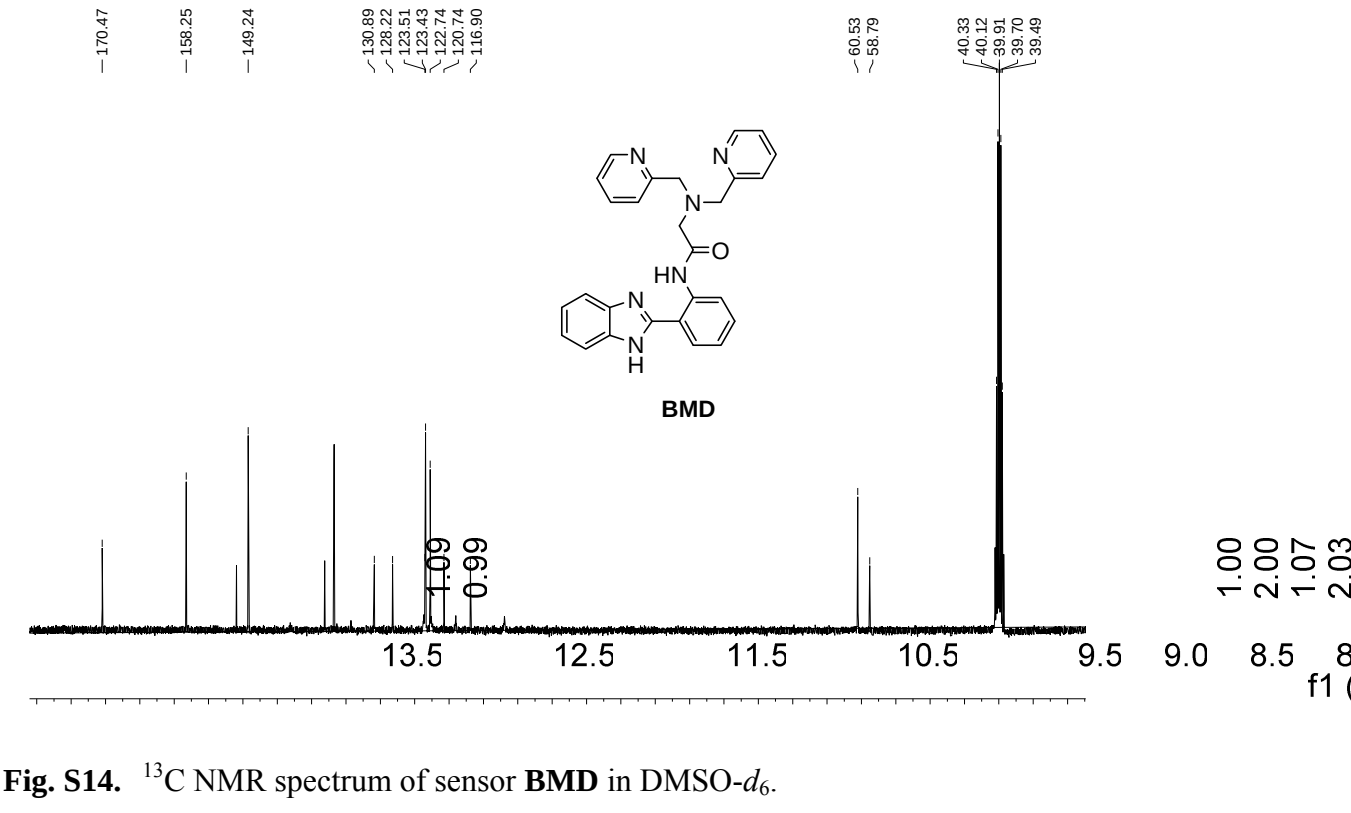

Fig. S14. ^{13}C NMR spectrum of sensor **BMD** in DMSO-d_6.

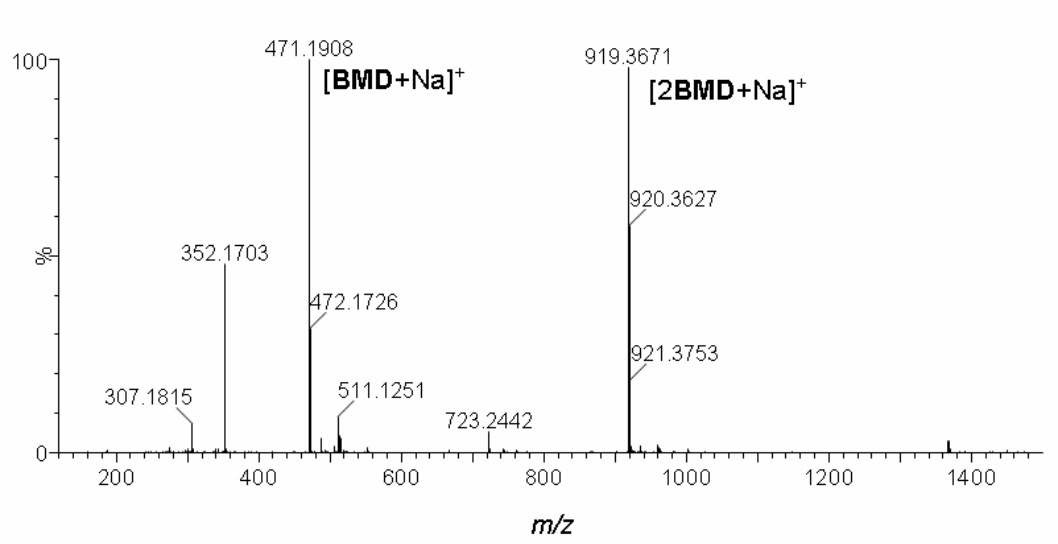

Fig. S15. HRMS (positive) spectrum of sensor of **BMD**.

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 $\varphi-\omega$ 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.

Reference

1. Sheldrick, G. M., *Acta Crystallogr. A.,* 2008**, 64**, 112-122.