

## Supporting information

### Modulating the Selectivity of Near Infrared Fluorescent Probe Toward Various Metal Ions by Judicious Choice of Aqueous Buffer Solutions

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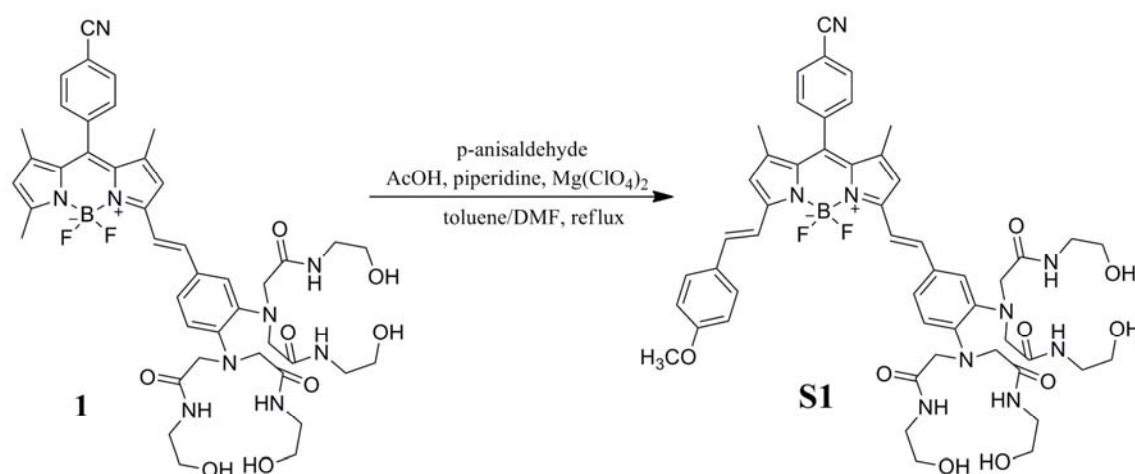
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## 1. Materials and instruments

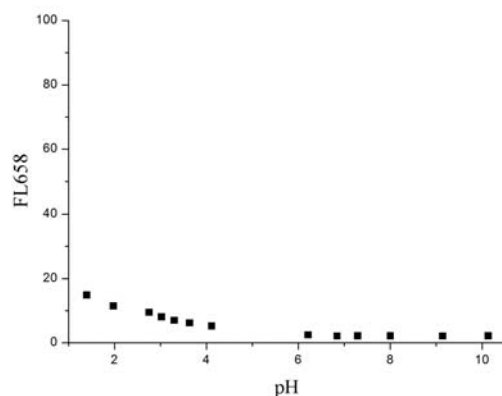
All the solvents were of analytic grade. The salts used in stock solutions of metal ions were  $\text{Hg}(\text{ClO}_4)_2 \cdot 3\text{H}_2\text{O}$ ,  $\text{Pb}(\text{ClO}_4)_2 \cdot 3\text{H}_2\text{O}$ ,  $\text{Zn}(\text{ClO}_4)_2 \cdot 6\text{H}_2\text{O}$ ,  $\text{Cr}(\text{ClO}_4)_3 \cdot 6\text{H}_2\text{O}$ ,  $\text{FeSO}_4 \cdot 7\text{H}_2\text{O}$ ,  $\text{FeCl}_3 \cdot 6\text{H}_2\text{O}$ ,  $\text{Ba}(\text{ClO}_4)_2 \cdot 3\text{H}_2\text{O}$ ,  $\text{Co}(\text{ClO}_4)_2 \cdot 6\text{H}_2\text{O}$ ,  $\text{Mn}(\text{ClO}_4)_2 \cdot 6\text{H}_2\text{O}$ ,  $\text{Cu}(\text{ClO}_4)_2 \cdot 6\text{H}_2\text{O}$ ,  $\text{Ca}(\text{ClO}_4)_2 \cdot 4\text{H}_2\text{O}$ ,  $\text{Ni}(\text{ClO}_4)_2 \cdot 6\text{H}_2\text{O}$ ,  $\text{LiClO}_4$ ,  $\text{NaClO}_4 \cdot \text{H}_2\text{O}$ ,  $\text{KClO}_4$ ,  $\text{CsClO}_4$ ,  $\text{AgClO}_4 \cdot \text{H}_2\text{O}$ ,  $\text{Cd}(\text{ClO}_4)_2 \cdot 6\text{H}_2\text{O}$ .  $^1\text{H}$ -NMR and  $^{13}\text{C}$ -NMR were measured on a Bruker Avance-400 spectrometer with chemical shifts reported in ppm (in  $\text{DMSO}-d_6$ ; TMS as internal standard). Mass spectra were measured on a HP 1100 LC-MS spectrometer. All pH measurements were made with a Sartorius PB-10 basic pH meter. Fluorescence spectra were determined on a Varian Cary Eclipse Fluorescence spectrophotometer. Absorption spectra were determined on a Varian Cary 100 Bio UV-Visible spectrophotometer.

## 2. Synthesis of probe S1



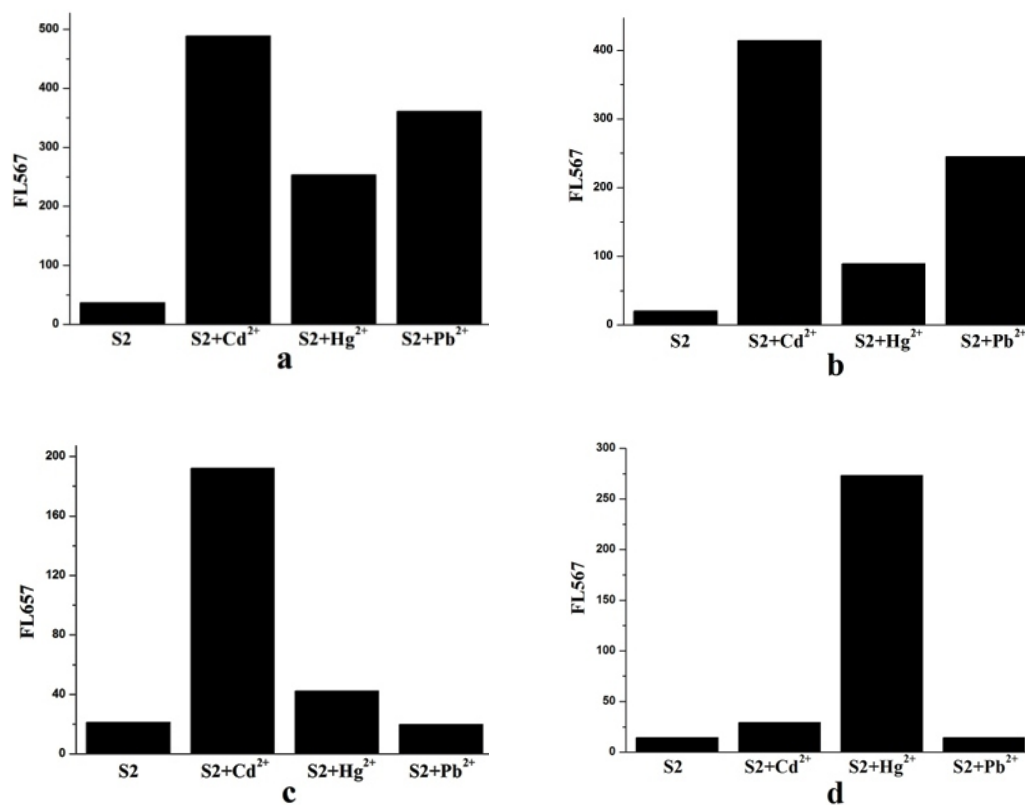
**1** (0.05 mmol) and 4-methoxybenzaldehyde (0.5 mmol) were dissolved in toluene (15 mL) and DMF (5 mL) with piperidine (0.12 mL), glacial acetic acid (0.1 mL), and catalytic amount of  $\text{Mg}(\text{ClO}_4)_2$ . The resulting mixture was refluxed, and the water formed during the reaction was removed azeotropically by heating in a Dean-Stark apparatus for about 2 hours. The solvent was removed under vacuum, and the residue was purified by silica column chromatography ( $\text{CH}_2\text{Cl}_2/\text{CH}_3\text{OH}$ , 9/1 to 7/1, v/v). The desired product **S1** was obtained as black solid in 37% yield.  $^1\text{H}$  NMR (400 MHz,  $\text{DMSO}-d_6$ )  $\delta$ : 1.40 (s, 6H), 3.10-3.11 (m, 8H), 3.32-3.33 (m, 8H), 3.83 (s, 3H), 4.03 (s, 4H), 4.09 (s, 4H), 4.61-4.65 (m, 4H), 6.93-6.97 (m, 3H), 7.05 (d,  $J = 8.4$  Hz, 2H), 7.12 (s, 1H), 7.18 (d,  $J = 8.0$  Hz, 1H), 7.35 (d,  $J = 16.4$  Hz, 1H), 7.43-7.46 (m, 2H), 7.55 (d,  $J = 16.4$  Hz, 1H), 7.63 (d,  $J = 8.8$  Hz, 2H), 7.73 (d,  $J = 8.0$  Hz, 2H), 8.07 (d,  $J = 8.0$  Hz, 2H);  $^{13}\text{C}$  NMR (100 MHz,  $\text{DMSO}-d_6$ )  $\delta$ : 14.9, 14.9, 41.8, 41.8, 54.7, 55.0, 55.8, 60.1, 60.2, 112.6, 115.1, 116.0, 116.4, 118.8, 119.0, 119.0, 121.0, 121.4, 121.5, 129.3, 129.5, 130.0, 130.5, 132.3, 132.5, 133.6, 135.8, 137.3, 138.5, 139.8, 141.2, 141.6, 143.6, 152.7, 153.4, 160.9, 170.3, 170.3; HRMS (ES<sup>+</sup>,  $[\text{M} + \text{H}]^+$ ): Calcd for  $\text{C}_{51}\text{H}_{58}\text{BF}_2\text{N}_9\text{O}_9$  990.4497; found, 990.4487.

## 3. pH titration



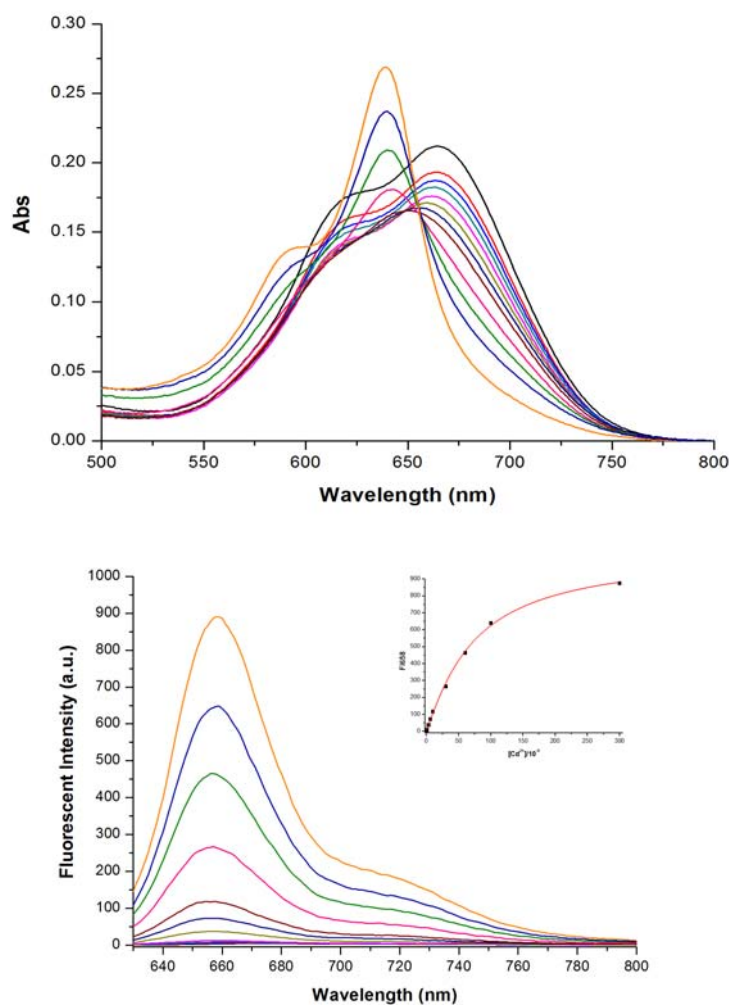
**Fig. S1.** The fluorescence Intensity of **S1** ( $5 \mu\text{M}$ ) at 658 nm as a function of pH in water solution (10% DMSO) (pH was adjusted by 75%  $\text{HClO}_4$  and NaOH). The samples were excited at 620 nm. Excitation and emission slit widths were both 5 nm.

#### 4. The selectivity of **S2** for $\text{Cd}^{2+}$ , $\text{Hg}^{2+}$ and $\text{Pb}^{2+}$



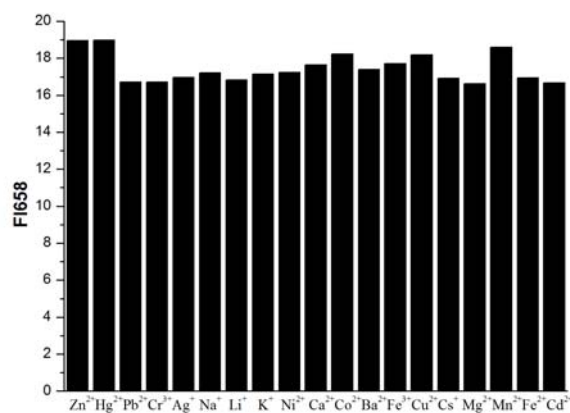
**Fig. S2** The fluorescent intensity of **S2** ( $4 \mu\text{M}$ ) in the absence and presence of  $\text{Cd}^{2+}$ ,  $\text{Hg}^{2+}$  or  $\text{Pb}^{2+}$  ( $20 \mu\text{M}$ ) emitted at 567 nm. (a) in 3-Morpholinopropanesulfonic Acid (MOPS) buffer solution (50 mM, 10% DMSO, pH = 7.0); (b) in HEPES buffer solution (10 mM, 10% DMSO, pH= 7.2, 10 mM NaCl); (c) in Tris-HCl (20 mM) buffer solution (containing 10% DMSO, 0.1 mM sodium phosphate, pH = 7.5); (d) in 50 mM citrate-phosphate buffer solution (pH = 7.0, 10% DMSO). The samples were excited at 555 nm. Excitation and emission slit widths were 2.5 nm and 5 nm.

## 5. Cadmium titration



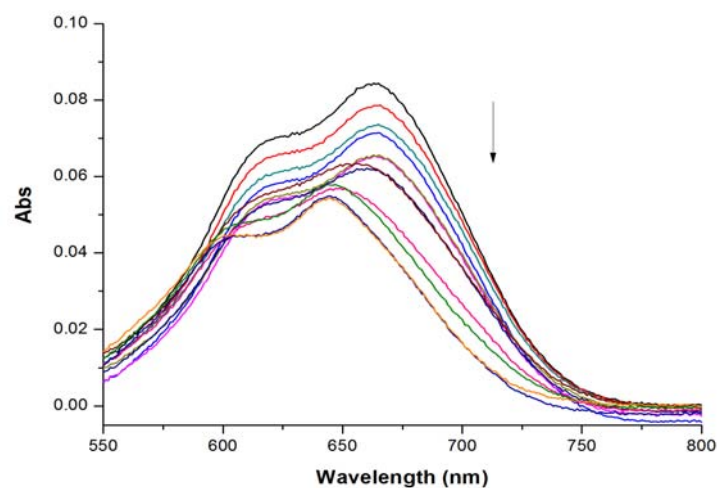
**Fig. S3.** The absorption (top) and emission (bottom) spectra of **S1** (5 μM) upon addition of Cd<sup>2+</sup> from 0 to 3 mM in Tris-HCl (0.02 M) solution (containing 10% DMSO, 0.1 mM sodium phosphate, pH=7.5). The samples were excited at 620 nm. Excitation and emission slit widths were both 5 nm. Inset: Curve of fluorescence intensity of **S1** at 658 nm versus the concentration of Cd<sup>2+</sup>.

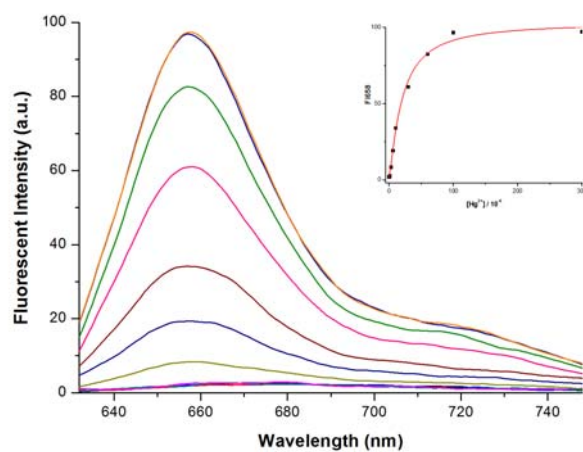
## 6. Competition experiments of cadmium



**Fig. S4.** The fluorescent intensity of **S1** ( $5 \mu\text{M}$ ) at  $658 \text{ nm}$  with  $5 \text{ equiv } \text{M}^{\text{n}+}$ , followed by  $3 \text{ equiv } \text{Cd}^{2+}$  in Tris-HCl ( $0.02 \text{ M}$ ) solution (containing  $10\% \text{ DMSO}$ ,  $0.1 \text{ mM}$  sodium phosphate,  $\text{pH}=7.5$ ). The samples were excited at  $620 \text{ nm}$ . Excitation and emission slit widths were both  $5 \text{ nm}$ .

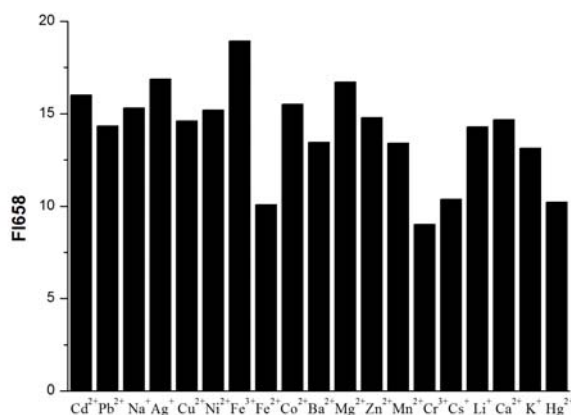
## 7. Mercury titration





**Fig. S5.** The absorption (top) and emission (bottom) spectra of **S1** ( $2 \mu\text{M}$ ) upon addition of  $\text{Hg}^{2+}$  from 0 to 0.3 mM in citrate-phosphate buffer (0.05 M, 10% DMSO, pH= 7.0). The samples were excited at 620 nm. Excitation and emission slit widths were both 5 nm. Inset: Curve of fluorescence intensity of **S1** at 658 nm versus the concentration of  $\text{Hg}^{2+}$ .

## 8. Competition experiments of mercury



**Fig. S6.** The fluorescent intensity of **S1** (2  $\mu$ M) at 658 nm with 5 equiv  $M^{n+}$ , followed by 2.5 equiv  $Cd^{2+}$  in citrate-phosphate buffer (0.05 M, 10% DMSO, pH= 7.0). The samples were excited at 620 nm. Excitation and emission slit widths were both 5 nm.

## 9. Determination of quantum yield

The quantum yield of **S1** and **S1**- $Cd^{2+}$  were determined according to the literature<sup>2</sup>.

$$\Phi_S = \frac{\Phi_B I_S A_B \lambda_{exB} \eta_S}{I_B A_S \lambda_{exS} \eta_B}$$

Where  $\Phi$  is quantum yield;  $I$  is integrated area under the corrected emission spectra;  $A$  is absorbance at the excitation wavelength;  $\lambda_{ex}$  is the excitation wavelength;  $\eta$  is the refractive index of the solution; the  $S$  and  $B$  refer to the sample and the standard, respectively. We chose Rhodamine B with trifluoroacetic acid in absolute ethanol as standard, which has the quantum yield of 0.49.

## 10. Determination of association constant

$K_s$  was determined by a nonlinear least-squares analysis of  $Y$  versus  $c_M$  using the following equation<sup>3</sup>:

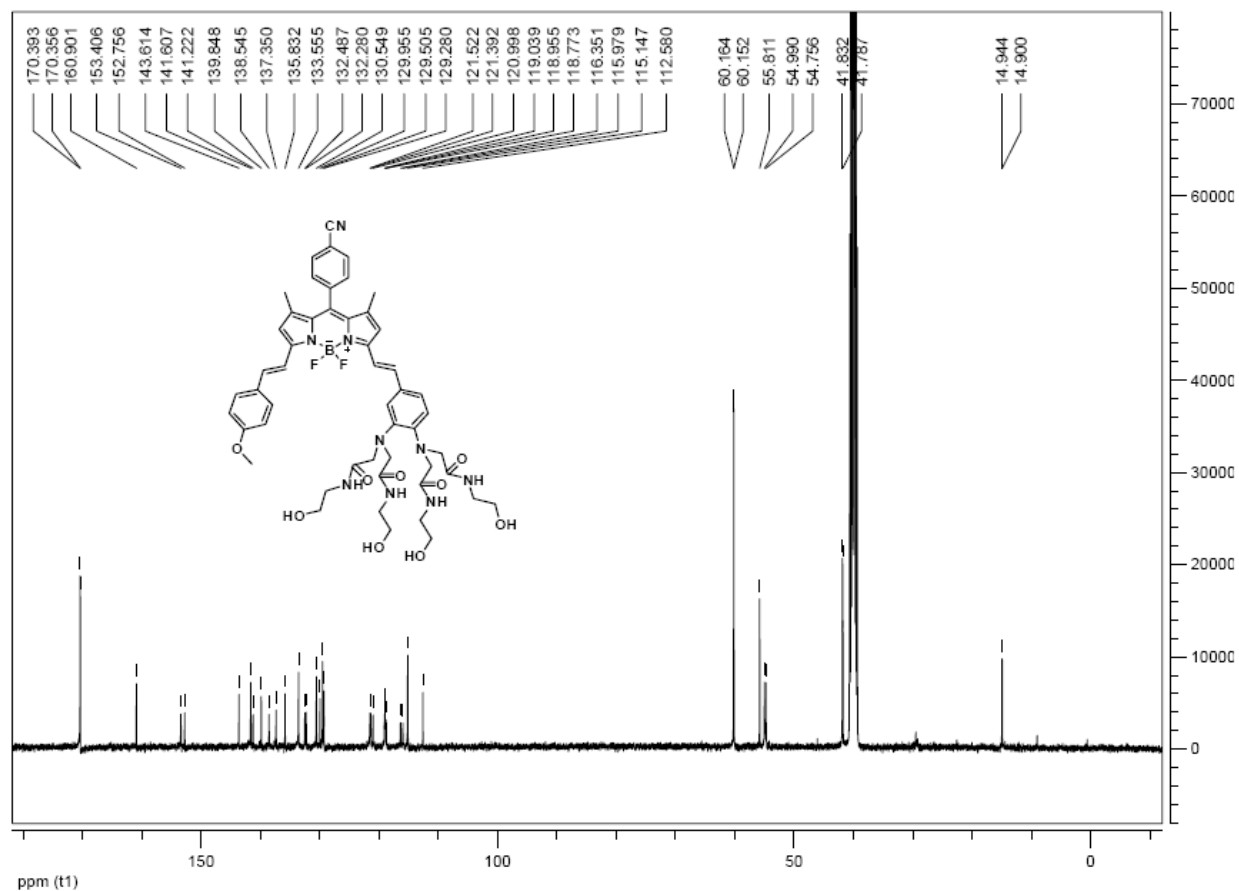
$$Y = \frac{Y_0 + c_M \Phi K_{11} [M] + Y_{lim} \beta_{21} [M]^2}{1 + K_{11} [M] + \beta_{21} [M]^2}$$

Where  $\beta_{21} = K_{11} K_{21}$ ,  $[M] \approx c_M$  is  $Cd^{2+}$  ion concentration,  $Y_0$  or  $Y$  is integrated emission in the absence or presence of  $Cd^{2+}$  ion,  $\Phi$  is the quantum yield of the sensor- $Cd^{2+}$  complex in 1:1 stoichiometry.

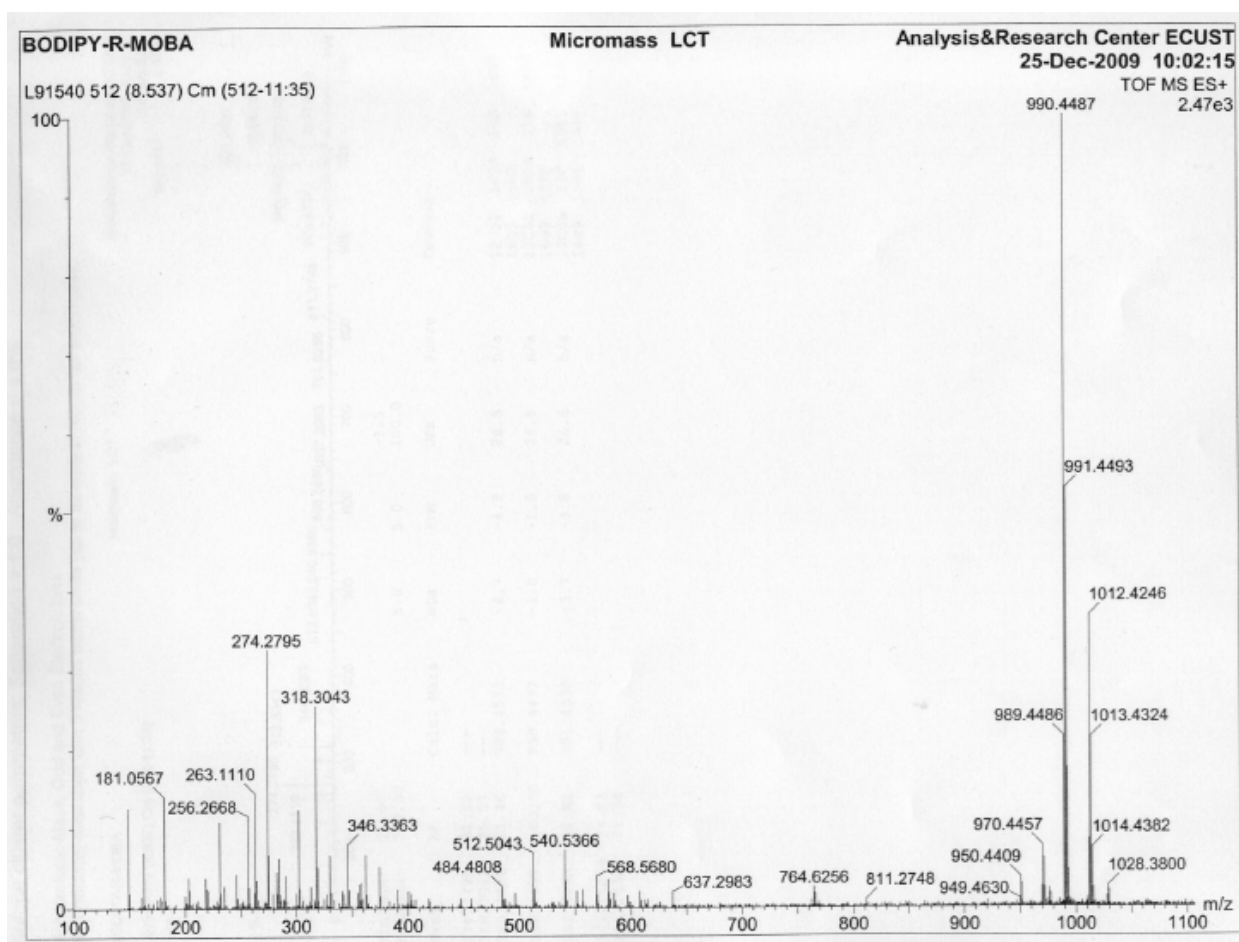




### $^{13}\text{C}$ NMR of **S1**



### HRMS spectrum of **S1**



## 12. References

1. Cheng, T.; Xu, Y.; Zhang, S.; Zhu, W.; Qian, X.; Duan, L., *J. Am. Chem. Soc.* **2008**, *130*, 16160–16161.
2. Casey, K. G.; Quitevis, E. L., *J. Phys. Chem.* **1988**, *92*, 6590-6594.
3. Valeur, B., *Molecular Fluorescence: Principles and Applications*. Wiley-VCH: Weinheim, 2002.