

ELECTRONIC SUPPLEMENTARY INFORMATION (ESI)

**A Novel Dansyl Appended Bile Acid Receptor for
Preferential Recognition of Hg²⁺**

Pradeep K. Muwal, Shubha Pandey and Pramod S. Pandey*

*Department of Chemistry, Indian Institute of Technology Delhi, Hauz Khas,
New Delhi 110016, India.*

* To whom the correspondence should be addressed.

E-mail: pramod@chemistry.iitd.ac.in (PS Pandey); Tel: +91 11 26591506;

Fax: +91 11 26582037

Table of contents

	Page No.
Synthesis of the compound 4 and 5	3
Characterization of compound 5	3-4
¹ H and ¹³ C NMR of Compound 5	4
Mass Spectrum of 5	5
Calibration plot for the detection limit	5
Change in Uv-vis spectra of 5 in the presence of Cu ²⁺	6
Competitive experiment of 5 in the presence of Hg ²⁺ + other metal ions	7
Calibration plot showing stoichiometry and binding constant	8

General Synthesis:

Compounds **1** and **2** were synthesized according to the reported literature procedures.¹ The propargyl dansyl amide (**4**) was synthesized by the reaction of dansyl-chloride with propargyl amine in the presence of triethylamine in dichloromethane according to the literature procedure.² Afterwards receptor **5** was synthesized by the coupling of diazido derivative of deoxycholic acid (**2**) with propargyl dansyl amide (**4**) using click reaction.

1. (a) Kumar, A.; Pandey, *tetrahedron Lett.* **2009**, *50*, 5842-5845. (b) Chhatra, R. K.; Kumar, A.; Pandey, P. S. *J.Org. Chem.* **2011**, *76*, 9086.
2. Sarez, A. I.; Braden, M. R.; Gerdes, J. M.; Thompson, C. M. *Bioorg. Med. Chem. Letts.* **2010**, *20*, 194.

Synthesis of compound **5**:

To a solution of 3 β , 12 β -bis-(azidoacetyl)deoxycholate (**2**) (800 mg, 1.39 mmol) in 80 ml of *t*-BuOH, propargyl dansylamide (**4**) (845 mg, 2.93 mmol) was added. To this solution, CuSO₄·5H₂O (10 mol %) and sodium ascorbate (20 mol %) were added in 8.0 ml of H₂O. This reaction mixture was stirred at 50 °C for 10 hours followed by evaporation under vacuum. The residue was dissolved in 50 ml of CHCl₃ and washed with H₂O (40 ml) twice. Afterwards chloroform layer was dried over anhydrous Na₂SO₄, filtered and evaporated completely. The crude product was purified by column chromatography over basic alumina (2% methanol in chloroform) to give pure **5**. Yield: 80 %, **M.P.**: 70-71 °C.

¹H NMR (300 MHz, CDCl₃, TMS) δ 0.69 (s, 3H, 18-Me), 0.80 (d, 3H, J = 5.1 Hz, 21-Me), 0.91 (s, 3H, 19-Me), 0.95-2.32 (26H, steroidal H), 2.88 (6H, -NCH₃ \times 6), 3.67 (s, 3H, -OCH₃), 4.14 (s, 2H, -NHCH₂), 4.25 (s, 2H, -NHCH₂), 4.70 (m, 1H, 3 β -H), 5.07-5.29 (m, 5H, 12 β -H, -OCOCH₂ \times 2), 6.03 (b, 2H, -NH \times 2), 7.14 (1H, Ar-H), 7.17 (1H, Ar-H), 7.51 (m, 4H, Ar-H), 7.68 (2H, Triazole-H), 8.26 (m, 4H, Ar-H), 8.11 (d, 1H, J = 6.0 Hz, Ar-H), 8.5 (d, 1H, J = 7.2, Ar-H); ¹³C NMR (300 MHz, CDCl₃, TMS) δ 12.14, 14.05, 17.56, 22.69, 23.20, 25.12, 25.73, 25.86, 26.50, 27.12, 28.88, 29.08, 29.28, 29.43, 29.54, 29.61, 30.67, 30.69, 30.90, 31.42, 31.57, 31.85, 33.73, 33.90, 34.49, 34.57, 35.29, 38.49, 38.50, 41.51, 44.96, 45.35, 47.27, 49.16, 51.26, 51.50, 76.88, 77.21, 78.39, 113.99, 115.22, 115.25, 123.11, 128.42, 129.29, 129.37, 129.48, 129.53, 129.76, 129.81, 130.41, 134.58, 134.73, 139.18, 151.78, 165.25, 165.76, 174.69.

IR ν_{\max} (KBr) 3447.92, 2930.92, 2867.81, 1741.04, 1636.46, 1456.64, 1326.58, 1224.24, 1144.88 cm⁻¹.

HRMS (ESI, MS) m/z : calcd for $C_{59}H_{76}N_{10}O_{10}NaS_2$ 1171.5085, found 1171.5087, (M + Na).

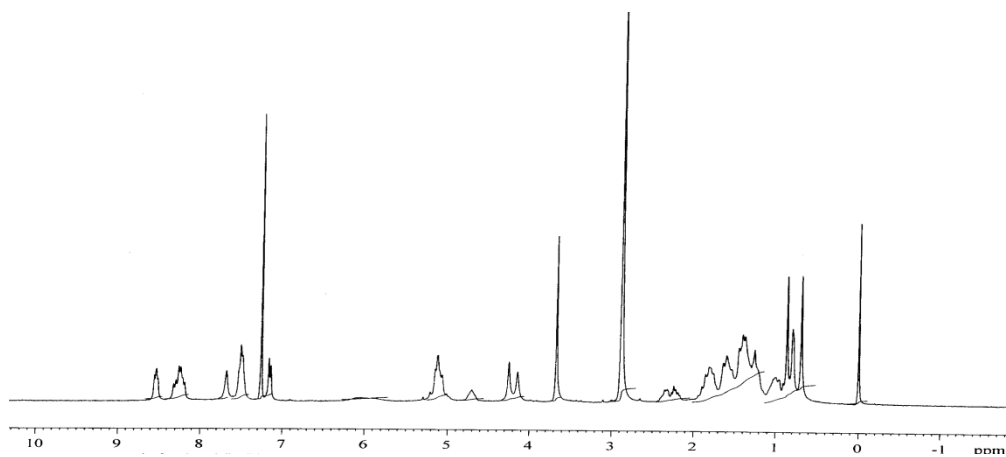


Figure S1a: 1H NMR (300 MHz, $CDCl_3$, δ in ppm) spectrum of compound **5**.

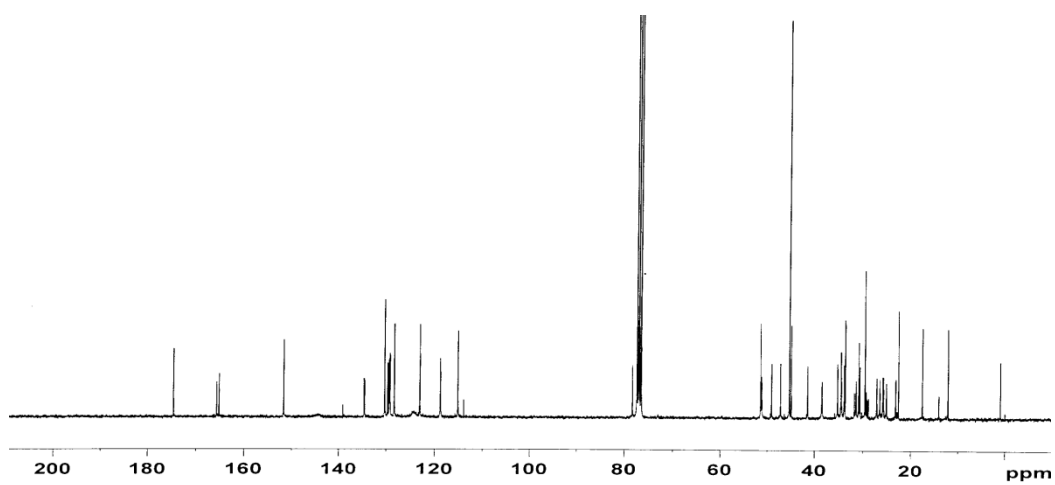


Figure S1b: ^{13}C NMR spectrum of compound **5**.

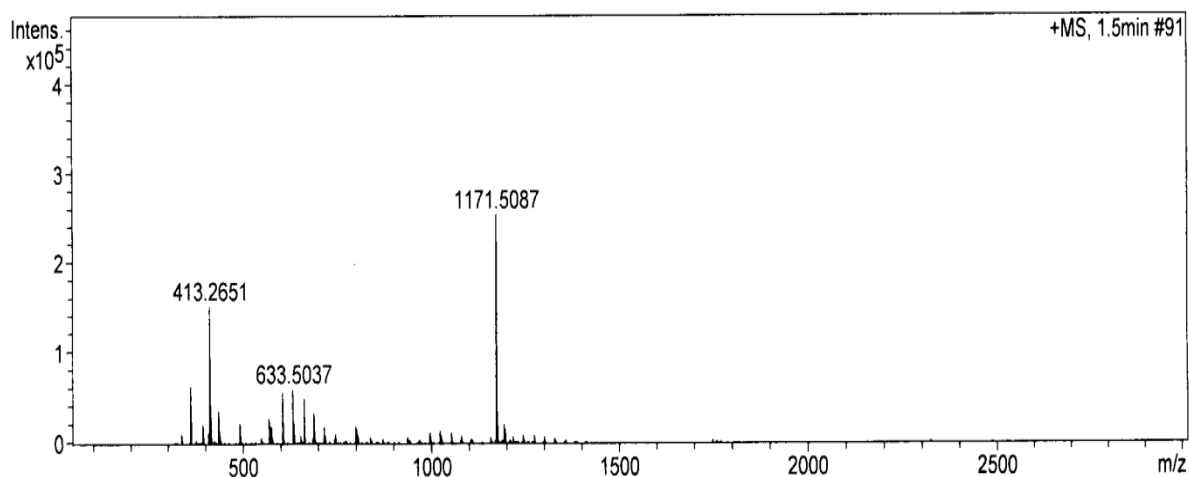


Figure S2: Mass spectrum of compound 5.

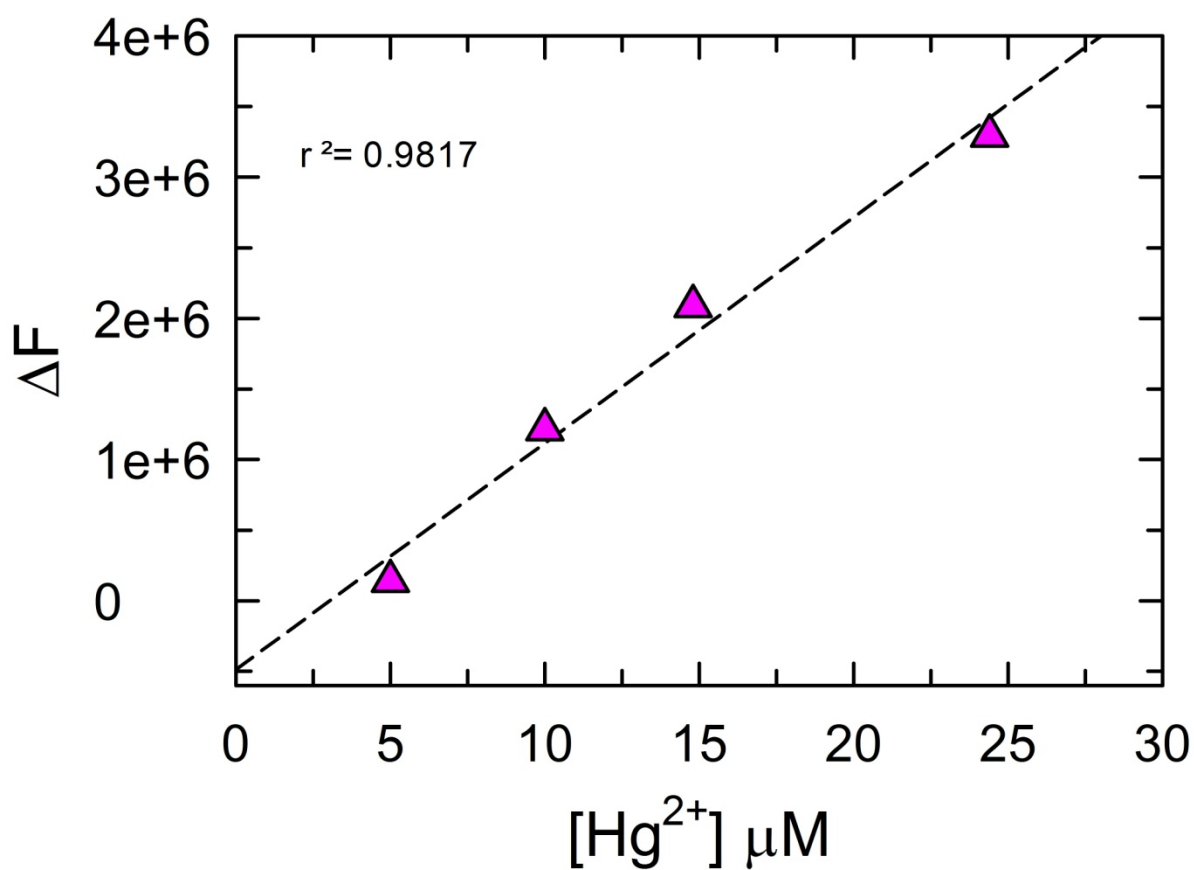


Figure S3. Change in fluorescence intensity of 5 upon addition of Hg^{2+} for $0 \leq [\text{Hg}^{2+}] \leq 25 \mu\text{M}$ (calibration plot for the calculation of detection limit).

Detection Limit:

Fluorescence intensity of **5** was varied linearly with $[\text{Hg}^{2+}]$ upto $25\mu\text{M}$ and limit of detection for Hg^{2+} by **5** could be calculated by using calibration sensitivity (m) of relative fluorescence intensity versus $[\text{Hg}^{2+}]$ in the aforementioned range. To calculate LOD, minimum change in the fluorescence intensity due to the presence of $[\text{Hg}^{2+}]$ was taken to be $3 \times s_0$ where s_0 represents standard deviation of F_0 for 12 replicate measurements. Thus, the LOD is calculated using the formula $\text{LOD } [\text{Hg}^{2+}] = 3 \times s_0 / m$, and it was found to be $\sim 2 \mu\text{M}$.

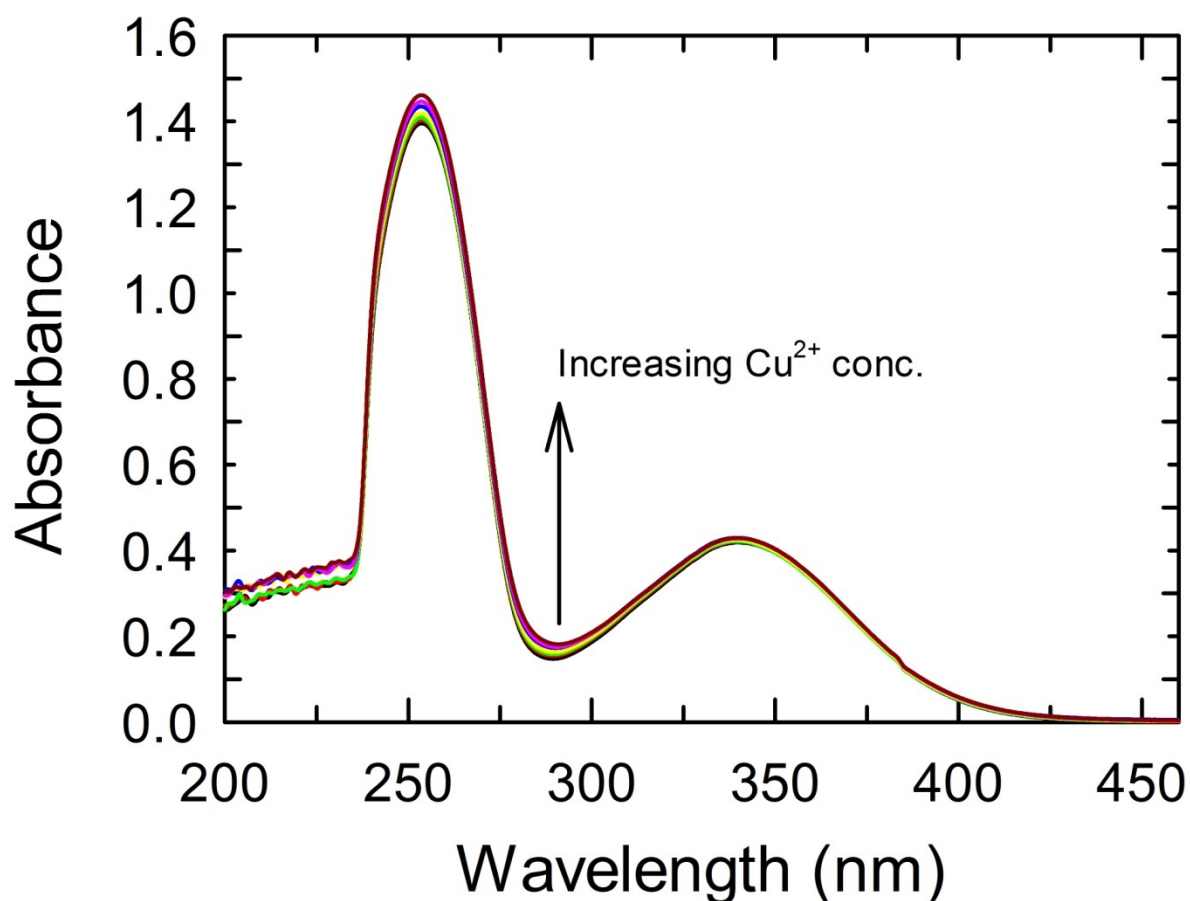


Fig S4. Change in UV-Vis spectra of receptor **5** ($100 \mu\text{M}$) upon addition of Cu^{2+} in $\text{CHCl}_3:\text{MeOH}$ (7:3, v/v).

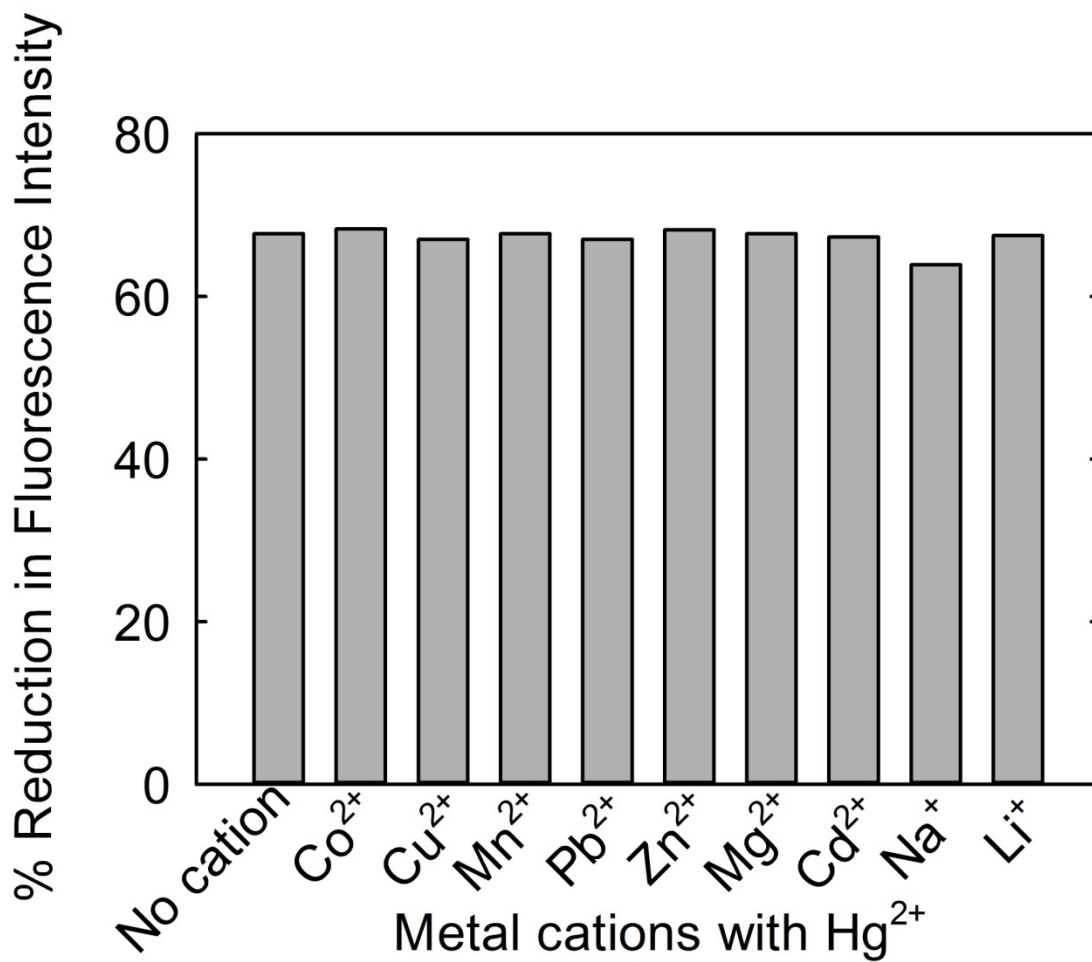


Fig S5. % reduction in the fluorescence intensity of **5** (25 μM) in the presence of 100 μM each of M_n^+ and Hg^{2+} in $\text{CHCl}_3:\text{MeOH}$ (7:3, v/v) at ambient conditions ($\lambda_{\text{excitation}} = 351 \text{ nm}$).

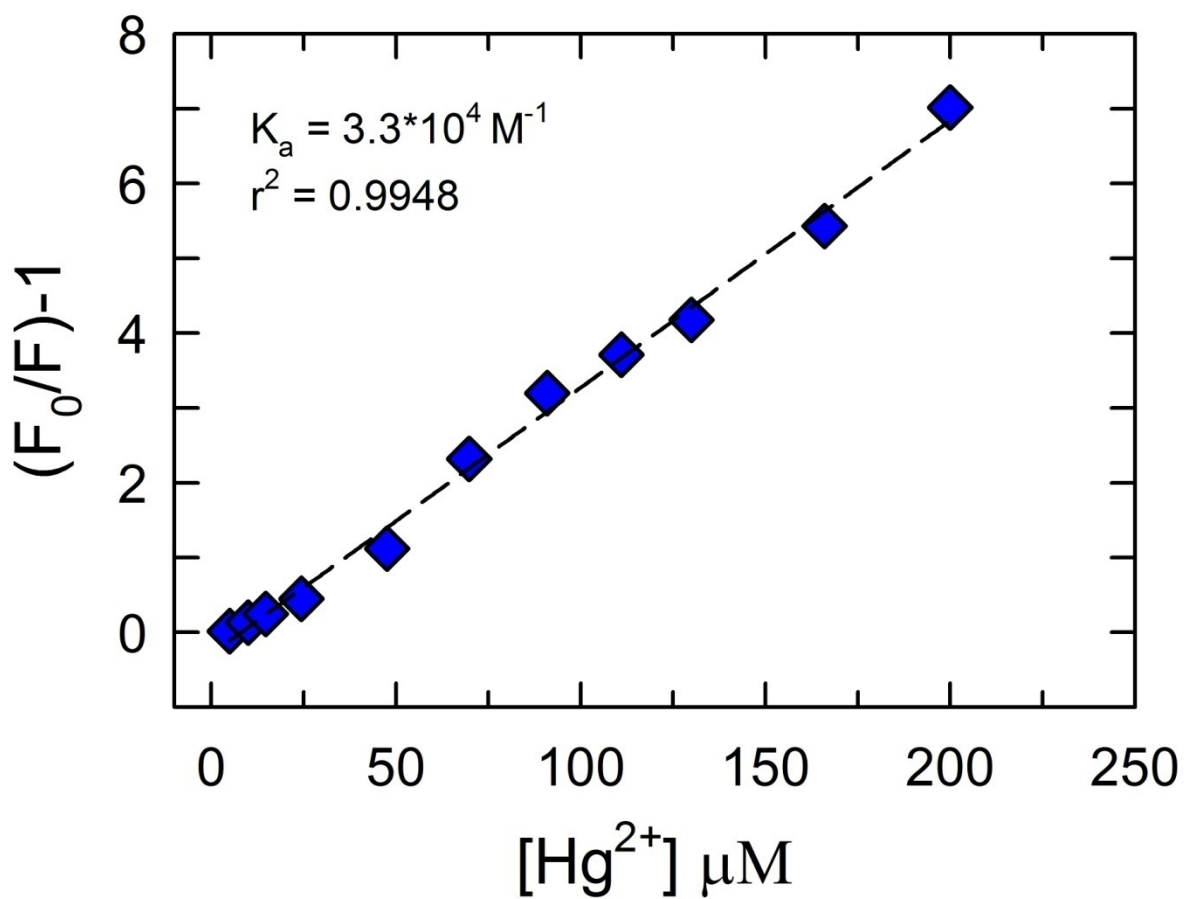


Figure S6. Change in fluorescence upon addition of Hg^{2+} for $0 \leq [\text{Hg}] \leq 200 \mu\text{M}$.