Two Regioisomeric and Exclusively Selective Hg(II) Sensor Molecules Composed of A Naphthalimide Fluorophore and An *o*-Phenylenediamine Derived Triamide Receptor

Jiaobing Wang^a and Xuhong Qian^{*a,b}

^aState Key Laboratory of Fine Chemicals, Dalian University of Technology, PO Box 89, Zhongshan Road 158, Dalian 116012, China, ^bShanghai Key Laboratory of Chemical Biology, School of Pharmacy, East China University of Science and Technology, Shanghai 200237, China

Email Address (xhqian@ecust.edu.cn)

Supporting Information

Materials. All the solvents were of analytic grade. ¹H-NMR were measured on a Bruker AV-400 spectrometer with chemical shifts reported as ppm (in D₂O, CDCl₃ or DMSO-d6, TMS as internal standard). Mass spectra were measured on a HP 1100 LC-MS spectrometer. Melting points were determined by using an X-6 micro-melting point apparatus and were uncorrected. All pH measurements were made with a Sartorius basic pH-Meter PB-20. Fluorescence spectra were determined on a Hitachi F-4500. Absorption spectra were determined on a PGENERAL TU-1901 UV-VIS Spectrophotometer.

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^aKey: (a) ethanol; (b) 2-(2-aminoethoxy)-ethanol, DMF; (c) SnCl₂, acetonitril/ethanol;

(d) ethyl bromoacetate, N'N-diisopropylethylamine, acetonitrile; (e) 2-aminoethanol, acetonitril.

3: A solution of 4-nitro-1,8-naphthalic anhydride **1** (0.243 g, 1 mmol), N'-(2-nitro-phenyl)-ethane-1,2diamine **2**^[1] (0.181 g, 1 mmol) in 40 mL ethanol was refluxed for 1 hour, then cooled and filtered out the dark yellow precipitate **3** (0.31 g, 75%). m.p. 245-247 °C; ¹H NMR (400 MHz, DMSO-d6): δ 8.71 (d, *J* = 8.8 Hz, 1 H), 8.63 (d, *J* = 8 Hz, 1 H), 8.58 (d, *J* = 8.8 Hz, 1 H), 8.55 (d, *J* = 7.6 Hz, 1 H), 8.10 (t, *J* = 8.4 Hz, 1 H), 8.05 (d, *J* = 8.4 Hz, 1 H), 7.56 (t, *J* = 7.6 Hz, 1 H), 7.29 (d, *J* = 9.2 Hz, 1 H), 6.69 (t, *J* = 7.6 Hz, 1 H), 4.32 (t, *J* = 6 Hz, 2 H), 3.72 (t, *J* = 6 Hz, 2 H), MS (APCI) Calcd for ([M+H])⁺, 407; Found, 407.

4: To a solution of 50 ml DMF was added 0.21 g (0.5 mmol) of **3** and 1 g (9.5 mmol) of 2-(2-aminoethoxy)-ethanol. The solution was stirred for 24 h at room temperature. The mixture was poured into 150 mL cold water, then filtered out the yellow precipitate and chromatographed on silica gel using dichloromethane/methanol 100: 10 (v/v) as eluant to afford 0.15 g (0.33 mmol, 65%) **4** as

yellow solid. mp: 88-89 °C. ¹H (400 MHz, DMSO-d6): δ 8.70 (d, J = 8.4 Hz, 1 H), 8.45 (d, J = 7.2 Hz, 1 H), 8.23 (d, J = 8.4 Hz, 1 H), 8.04 (d, J = 8.1 Hz, 1 H), 7.69 (t, J = 8 Hz, 1 H), 7.55 (t, J = 8 Hz, 1 H), 7.30 (d, J = 8.8 Hz, 1 H), 6.84 (d, J = 8.8 Hz, 1 H), 6.68 (t, J = 8 Hz, 1 H), 4.31 (t, J = 6 Hz, 2 H), 3.74 (t, J = 6 Hz, 2 H), 3.65 (t, J = 6 Hz, 2 H), 3.58 (t, J = 6 Hz, 2 H), 3.51 (m, 4 H); MS (APCI) Calcd for ([M+H])⁺, 465; Found, 465.

5: To a solution of 40 mL acetonitrile and 30 mL absolute ethanol was added 0.13 g (0.28 mmol) of 4 and 1.5 g (6.5 mmol) of SnCl₂-2H₂O. The mixture was refluxed for 7 h under N₂ atmosphere. Then neutralized with 150 ml saturated sodium carbonate and extracted with 100 mL dichloromethane 5 times. The organic phase was dried over sodium sulfate and evaporated to dryness. The residue was chromatographed on silica gel and eluted with dichloromethane/methanol 100: 7 (v/v) to afford 85 mg (0.19 mmol, 70%) 4 as yellow solid. mp: 183-185 °C. ¹H (400 MHz, DMSO-d6): δ 8.70 (d, *J* = 8 Hz, 1 H), 8.49 (d, *J* = 6.4 Hz, 1 H), 8.31 (d, *J* = 8.4 Hz, 1 H), 7.71 (t, *J* = 8 Hz, 1 H), 6.87 (d, *J* = 8.4 Hz, 1 H), 6.77 (d, *J* = 7.6 Hz, 1 H), 6.55 (m, 2 H), 6.44 (t, *J* = 7.2 Hz, 1 H), 4.22 (t, *J* = 5.6 Hz, 2 H), 3.73 (t, *J* = 5.6 Hz, 2 H), 3.59 (t, *J* = 5.6 Hz, 2 H), 3.51 (m, 4 H), 3.30 (t, *J* = 5.6 Hz, 2 H); MS (APCI) Calcd for ([M+H])⁺, 435; Found, 435.

6: A solution of **4** (70 mg, 0.156 mmol), ethyl bromoacetate (2 mL, 18 mmol), sodium iodide (0.51 g, 3.4 mmol) and diisopropylethylamine (1.1 mL, 6.67 mmol) in 30 mL acetonitrile was refluxed under nitrogen for 7 hours, then cooled and poured into 100 mL water. The resulting mixture was extracted with dichloromethane (3×150 mL). The extract was dried over sodium sulfate and was concentrated to give a brown oil, which was purified by flash chromatography using hexane/ethyl acetate (8: 2, v/v) as eluant to give 33 mg (0.047 mmol, 30%) of **5** as a brown viscous oil. ¹H NMR (400 MHz, CDCl₃) δ 8.49 (d, *J* = 6.4 Hz, 1 H), 8.38 (d, *J* = 8.4 Hz, 1 H), 8.22 (br, 1 H), 7.59 (br, 1 H), 7.44 (br, 1 H), 7.01 (br, 2 H), 6.95 (br, 1 H), 6.68 (d, *J* = 8.4 Hz, 1 H), 4.57 (br, 2 H), 4.36 (br, 2 H), 4.14 (s, 4 H), 4.07 (q, *J* = 6.8 Hz, 2 H), 3.99 (q, *J* = 6.8 Hz, 4 H), 3.93 (br, 2 H), 3.85 (br, 2 H), 3.79 (br, 2 H), 3.72 (br, 2 H), 3.59 (br, 2 H), 1.18 (t, *J* = 6.8 Hz, 3 H), 1.12 (t, *J* = 6.8 Hz, 6 H); MS (APCI) Calcd for ([M+H])⁺, 693; Found, 693.

RS1: A solution of **5** (30 mg, 0.043 mmol) in 3 mL acetonitrile and 3 mL 2-aminoethanol was refluxed under nitrogen for 10 hours, and then cooled down. The mixture, without further disposal, was chromatographed twice using dichloromethane/methanol 100: 25 (v/v) as eluant to give 22 mg (0.03 mmol, 70%) of **RS1** as a yellow solid, which decomposed at 277 °C; ¹H NMR (400 MHz, D₂O) δ 7.57 (d, *J* = 8 Hz, 1 H), 7.48 (d, *J* = 7.6 Hz, 1 H), 7.32 (d, *J* = 7.6 Hz, 1 H), 6.94 (t, *J* = 7.2 Hz, 1 H), 6.75 (d, *J* = 7.2 Hz, 1 H), 6.55 (d, *J* = 8 Hz, 1 H), 6.47 (m, 2 H), 6.06 (d, *J* = 7.6 Hz, 1 H), 3.86 (s, 2 H), 3.71 (s, 4 H), 3.62 (m, 8 H), 3.54 (t, *J* = 5.6 Hz, 2 H), 3.46 (t, *J* = 5.6 Hz, 2 H), 3.38 (t, *J* = 5.6 Hz, 2 H), 3.32 (t, *J* = 5.6 Hz, 4 H), 3.13 (t, *J* = 5.6 Hz, 2 H), 3.03 (t, *J* = 5.6 Hz, 4 H); FTIR (ethanol, cm⁻¹) 3336, 2920, 1658, 1640, 1631, 1580, 1550, 1396, 1366, 1067; HRMS (ES+), Calcd for ([M+H])⁺, 738.3463; Found, 738.3467.





^aKey: (a) 2-methoxy-ethanol; (b) SnCl₂, acetonitril/ethanol; (c) ethyl bromoacetate,

N'N-diisopropylethylamine, acetonitrile; (d) 2-aminoethanol, acetonitril.

8: A solution of $7^{[2]}$ (1.81 g, 5 mmol), *N*⁻(2-nitro-phenyl)-ethane-1,2-diamine **2** (2.72 g, 15 mmol) in 80 mL 2-methoxy-ethanol was refluxed under N₂ for 40 hours, then cooled and poured into 200 ml water. The pH was adjusted by HCl to 3. The mixture was extracted with 150 mL dichloromethane 5 times. The extract was dried over sodium sulfate and was concentrated to give a brown oil, which was purified by flash chromatography on silica gel using dichloromethane/methanol 100: 8 (v/v) as eluant to afford 0.4 g (0.86 mmol, 17%) **8** as a dark yellow solid. m.p. 212-213 °C; ¹H NMR (400 MHz, DMSO-d6): δ 8.45 (d, J = 8.4 Hz, 1 H), 8.38 (d, J = 6.4 Hz, 1 H), 8.40 (d, J = 8.4 Hz, 1 H), 7.99 (d, J = 7.6 Hz, 1 H), 7.46 (t, J = 7.6 Hz, 1 H), 7.31 (t, J = 7.6 Hz, 1 H), 6.86 (d, J = 8 Hz, 1 H), 6.60 (d, J = 8.8 Hz, 1 H), 6.53 (t, J = 7.6 Hz, 1 H), 7.31 (t, J = 7.6 Hz, 1 H), 6.86 (d, J = 8 Hz, 1 H), 6.60 (d, J = 8.8 Hz, 1 H), 6.53 (t, J = 7.6 Hz, 1 H), 6.53 (t, J = 7.6 Hz, 1 H), 6.53 (t, J = 7.6 Hz, 1 H), 6.54 (t, J = 7.6 Hz, 1 H), 6.55 (t,

7.6 Hz, 1 H), 4.23 (t, J = 6 Hz, 2 H), 3.70 (br, 2 H), 3.64 (t, J = 6.4 Hz, 2 H), 3.59 (br, 2 H), 3.50 (m, 4 H) MS (APCI) Calcd for ([M+H])⁺, 465; Found, 465.

9, 10, and RS2 were similarly prepared from 5, 6, and RS1 in 68%, 65%, and 73% yield, respectively.

9: m.p. 140-142 °C; ¹H NMR (400 MHz, DMSO-d6) δ 8.59 (d, J = 8.4 Hz, 1 H), 8.46 (d, J = 7.2 Hz, 1 H), 8.32 (d, J = 8.8 Hz, 1 H), 7.57 (t, J = 8 Hz, 1 H), 7.42 (br, 1 H), 6.69 (m, 3 H), 6.58 (t, J = 7.2 Hz, 1 H), 4.34 (t, J = 6 Hz, 2 H), 3.76 (t, J = 6 Hz, 2 H), 3.70 (br, 2 H), 3.61 (m, 4 H), 3.52 (t, J = 6 Hz, 2 H); MS (APCI) Calcd for ([M+H])⁺, 435; Found, 435.

10: 10 was obtained as a brown viscous oil; ¹H NMR (400 MHz, CDCl₃) δ 8.57 (d, J = 7.2 Hz, 2 H), 8.39 (d, J = 8.8 Hz, 1 H), 7.61 (t, J = 8 Hz, 1 H), 7.16 (br, 2 H), 7.01 (br, 2 H), 6.52 (d, J = 8.8 Hz, 1 H), 4.41 (t, J = 5.6 Hz, 2 H), 4.30 (br, 4 H), 4.16 (s, 4 H), 3.87 (m, 6 H), 3.84 (br, 2 H), 3.68 (br, 4 H), 3.45 (br, 2 H), 1.32 (t, J = 6.4 Hz, 3 H), 0.9 (t, J = 6.4 Hz, 6 H); MS (APCI) Calcd for ([M+H])⁺, 693; Found, 693.

RS2: RS2 was obtained as a yellow solid, which decomposed at 282 °C; ¹H NMR (400 MHz, D₂O) δ 7.67 (d, J = 6.8 Hz, 1 H), 7.29 (m, 2 H), 6.90 (m, 1 H), 6.73 (t, J = 6.8 Hz, 1 H), 6.64 (m, 3 H), 5.74 (d, J = 8.4 Hz, 1 H), 3.86 (m, 4 H), 3.63 (s, 4 H), 3.59 (t, J = 5.2 Hz, 2 H), 3.46 (m, 8 H), 3.34 (t, J = 5.6 Hz, 2 H), 3.21 (t, J = 5.6 Hz, 4 H), 3.10 (t, J = 5.6 Hz, 2 H), 2.9 (m, 4 H); FTIR (ethanol, cm⁻¹) 3349, 2920, 1636, 1578, 1549, 1497, 1396, 1362, 1112, 1065; HRMS (ES+), Calcd for ([M+H])⁺, 738.3463; Found, 738.3470.

Reference

- [1] Compound **2** was synthesized following the literature method. Linsker, F.; Evans, R. L. J. Org. Chem. **1945**, *10*, 283.
- [2] Compound **7** was synthesized following the literature method. Guo, X.; Qian, X.; Jia, L. J. Am. Chem. Soc. **2004**, *126*, 2272.

Spectroscopic Data



Figure S1. Job's plot for **RS1** and Hg(II) ([**RS1**] + [Hg(II)] = 10 μ M) in phosphate (0.1M) solution (pH = 7.5, 23 °C).



Figure S2. Job's plot for **RS2** and Hg(II) ([**RS2**] + [Hg(II)] = 10 μ M) in phosphate (0.1M) solution (pH = 7.5, 23 °C).



Figure S3. Time course measurement of fluorescence intensity for **RS1** ([**RS1**] = [Hg(II)] = 10 μ M) in phosphate (0.1M) solution (pH = 7.5, 23 °C).



Figure S4. Time course measurement of fluorescence intensity for **RS2** ([**RS2**] = [Hg(II)] = 10 μ M) in phosphate (0.1M) solution (pH = 7.5, 23 °C).



Figure S5. pH titration profiles of the unbound **RS1** (triangles) and **RS1**-Hg(II) complex (circles, $[RS1] = [Hg(II)] = 10 \ \mu M$) in water solution.



Figure S6. Emission spectra change of the **RS1**-Hg(II) complex ([**RS1**] = [Hg(II)] = 10 μ M) when 1 equiv of TPEN was added.



Figure S7. Emission spectra change of the **RS2**-Hg(II) complex ([**RS2**] = [Hg(II)] = 10 μ M) when 1 equiv of TPEN was added.



Figure S8. A typical emission spectra of **RS1** ([**RS1**] = 10 μ M, 0.1M sodium phosphate, pH = 7.5, 23 °C) recorded in the competition experiment. 2 eq. of Hg(II) or Cu(II) was added. The spectra were recorded from 520 to 600 nm. The spectra for other detected cations are just similar and not listed.



Figure S9. A typical emission spectra of **RS2** ([**RS2**] = 10 μ M, 0.1M sodium phosphate, pH = 7.5, 23 °C) recorded in the competition experiment. 2 eq. of Hg(II) or Cd(II) was added. The spectra were recorded from 520 to 600 nm. The spectra for other detected cations are just similar and not listed.