Electronic Supplementary Information (ESI)

A Selective Fluorescent Ratiometric Chemodosimeter for Mercury Ion

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1. Experimental

¹H NMR spectra were obtained using a Brucker AM 500 spectrometer. Mass spectra (MS) were carried out on a MA1212 instrument using standard conditions. UV-vis absorption spectra were performed on a Varian Cary500 spectrophotometer. Fluorescence spectra were recorded on a Varian Cary Eclipse Fluorescence Spectrophotometer. Elemental analysis data were obtained on a Perkin-Elmer 240c instrument. Luminescence lifetime measurements were obtained using an Edinburgh Analytical Instruments (EAI) time-correlated single-photon counting apparatus (TCSPC) comprised of two model J-yA monochromators (emission and excitation), a single photon photomultiplier detection system model 5300, and a F900 nanosecond flashlamp (N₂ filled at 1.1 atm pressure, 40 kHz) interfaced with a personal computer via a Norland MCA card. Data correlation and manipulation was carried out using EAI F900 software version 5.1.3. Emission lifetimes were calculated using a single-exponential fitting function, Levenberg-Marquardt algorithm with iterative deconvolution (Edinburgh instruments F900 software). The reduced χ^2 and residual plots were used to judge the quality of the fits. The fluorescence decay were performed with 441 and 372 nm excitation wavelength and 530 and 475 nm emission wavelength for compound 1 and 2 respectively on Edinburgh F900 analytical instruments and were fitted to give the fluorescence lifetimes of compound 1 and 2. The χ^2 values of these fittings were kept as close to 1 as possible.



1.1. 4-Bromo-N-n-butyl-1,8-naphthalimide

5 g (18 mmol) 4-Bromo-1,8-naphthalic anhydride, 1.7 g (23.3 mmol) n-butylamine were refluxed with stirring for 6 h in 40 ml glacial acetic acid. The suspension was poured into 200 ml ice–water and filtered to give a brown solid (4.6 g, 77%). Recrystallization from chlorobenzene gave pale gray needles, m.p.109-110°C. TLC revealed the presence of a single component and the needles were used directly for the next reaction.

1.2. 4-(aminoethylene)amino-N-n-butyl-1,8-naphthlimide

1.0 g (3.0mmol) 4-Bromo-N-n-butyl-1,8-naphthalimide, 6.0 ml (90 mmol) ethylenediamine was dissolved in 15 ml DMF. Then 0.1 g $CuSO_4$ ·5H₂O were added. The resulting mixture was heated to reflux for 5 h with stirring. After cooling to room temperature, the solution was poured into 100 ml water, and the precipitate was collected by filtration, washed with water and dried to yield 0.6 g (64%) yellow powder. Recrystallization from chlorobenzene gave orange needles. m.p. 128-131°C.

1.3. 1-Benzoyl-3-[2-(2-butyl-1,3-dioxo-2,3-dihydro-1H-benzo[de]isoquinolin-6-

ylamino)-ethyl]-thiourea (1)

Benzoylisothiocyanate (0.52g, 3.2mol) was added dropwise to a solution of 4-(aminoethylene)amino-N-n-butyl-1,8-naphthlimide (1.0g, 3.2mmol) in 30 ml acetone which was stirred and heated to 45°C. The reaction mixyure was then stirred at that temperature for 45 minutes. After cooling the solution was filtered and washed with ethanol. The product was purified by chromatography using CH_2Cl_2 to yield 1 (1.2g, 78%)

m.p. 207-209°C. ¹H NMR (DMSO-d6) δ (ppm):0.90 (t, 3H), 1.32 (m, 2H), 1.57 (m, 2H), 3.70 (m, 2H), 4.00 (m, 4H, NCH₂CH₂N), 7.02 (d, 1H, J=8.65Hz), 7.49 (t, 2H, J=7.80Hz), 7.62 (t, 1H, J=7.47Hz), 7.88 (m, 3H), 7.93 (t, 1H, Ar-NH), 8.26 (d, 1H, J=8.51Hz), 8.43 (d, 1H, J=6.74Hz), 8.73 (d, 1H, J=8.27Hz), 11.07 (t, 1H, J=5.77Hz, -CS-NH), 11.40 (s, 1H, -CONH). EI-MS, *m/z*: 474 (M⁺). Anal. calcd. for C₂₆H₂₆N₄O₃S: C 65.80, H 5.52, N 11.81. Found: C 65.69, H 5.54, N 11.9%.

1.4. N-[1-(2-Butyl-1,3-dioxo-2,3-dihydro-1H-benzo[de]isoquinolin-6-yl)-4,5dihydro-1H-imidazol-2-yl]-benzamide (**2**)

To a solution of **1** (0.5g, 1mmol) in 20 ml acetonitrile was added HgAc₂ (2g, 6.2mmmol) with magnetic stirring at room temperature. The suspension became black after a few minutes and was left to react for 20 minutes. After this time the suspension was filtered. The filtrate was concentrated and the residue was purified by chromatography using CH₂Cl₂ to yield **2** (0.4 g, 91%). m.p. 233-235°C. ¹H NMR (DMSO-d6) δ (ppm): 0.85 (t, 3H), 1.39 (m, 2H), 1.65 (m, 2H), 3.93 (t, 2H), 4.11 (m, $-\sqrt{N-CH_2}$, 7.19 (t, 2H, J=7.74Hz), 7.33 (t, 1H, J=7.34Hz), 7.61 (d, 2H, J=8.42Hz), 7.86 (t, 1H, J=7.88Hz), 7.96 (d, 1H, J=7.87Hz), 8.51 (d, 1H, J=8.50Hz), 8.56 (d, 1H, J=7.28Hz), 8.58 (d, 1H, J=7.90Hz), 9.43 (s, 1H, -CONH). EI-MS, *m/z*: 440 (M⁺). Anal. calcd. for C₂₆H₂₄N₄O₃: C 70.89, H 5.49, N 12.72. Found: C 70.84, H 5.60, N 12.80%.



1

2



Figure S1. Absorption of **1** in ethanol $(1.0 \times 10^{-5} \text{ M})$.



Figure S2. Absorption of **1** in ethanol $(1.0 \times 10^{-5} \text{ M})$ in the presence of $\text{Co}^{2+} (1.0 \times 10^{-5} \text{ M})$



Figure S3. Absorption of **1** in ethanol $(1.0 \times 10^{-5} \text{ M})$ in the presence of Cu²⁺ $(1.0 \times 10^{-5} \text{ M})$



Figure S4. Absorption of **1** in ethanol $(1.0 \times 10^{-5} \text{ M})$ in the presence of Pb²⁺ $(1.0 \times 10^{-5} \text{ M})$



Figure S5. Absorption of **1** in ethanol $(1.0 \times 10^{-5} \text{ M})$ in the presence of Ni²⁺ $(1.0 \times 10^{-5} \text{ M})$



Figure S6. Absorption of **1** in ethanol $(1.0 \times 10^{-5} \text{ M})$ in the presence of $\text{Zn}^{2+} (1.0 \times 10^{-5} \text{ M})$



Figure S7. The plot of absorption spectra at 350 nm shows a linear relationship of $[A_0/(A-A_0)]$ vs $1/[Hg^{2+}]$, indicating the ~1:1 stoichiometry of Hg^{2+} and chemodosimeter 1.



Figure S8. An assay for Hg^{2+} , 0- 10µM. chemodosimeter 1 (3µM) in 80% aqueous solution of acetonotrile. Fluorescence was recorded every 5 min after adding Hg^{2+} : excitation wavelength (λ_{ex}), 435 nm; emission wavelength (λ_{em}), 529 nm.



Figure S9. An assay for Hg^{2+} , 0- 10µM. chemodosimeter 1 (3µM) in 80% aqueous solution of acetonotrile. Fluorescence was recorded every 5 min after adding Hg^{2+} : excitation wavelength (λ_{ex}), 350 nm; emission wavelength (λ_{em}), 475 nm.



Figure S10. Plot of the ratio of fluorescent emission of the chemodosimeter 1 at 529 and 475 nm as a function of added mercury ions.(excited at 290 nm).