Supporting Information

For

A Colorimetric and Ratiometric Fluorescent Chemosensor with a Large Red-shift in Emission: Cu(II)-only Sensing by Deprotonation of Secondary Amines as Receptor Conjugated to Naphthalimide Fluorophore

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Materials and Methods. All the solvents were of analytic grade and used as received. The solutions of metal ions were prepared from LiClO₄·3H₂O, NaClO₄, KClO₄, MgCl₂·6H₂O, CaCl₂, Fe(NO₃)₃, CoCl₂·6H₂O, NiCl₂·6H₂O, ZnCl₂, CdCl₂·2½H₂O, CuCl₂·2H₂O, HgCl₂, AgNO₃, Pb(NO₃)₂, respectively, and were dissolved in distilled water. ¹H-NMR were measured on a Bruker AV-400 spectrometer with chemical shifts reported as ppm (in CDCl₃/DMSO-d₆, TMS as internal standard). Mass spectra were measured on a HP 1100 LC-MS spectrometer. Melting points were determined by an X-6 micro-melting point apparatus and are uncorrected. IR spectra were recorded on a Nicolet Nexus 770 spectrometer. 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. The fluorescence quantum yields (Φₚ) were estimated with N-butyl-4-butylamino-1,8-naphthalimide in absolute ethanol as a standard (Φₚ = 0.81).
Synthesis and Characteristics of Compounds 1 and 2.

Compound 6 was synthesized according to the published procedures. \(^{S2}\)

**N-butyl-4-bromo-5-nitro-1,8-naphthalimide (7).**

To a solution of 400 mg (1.24 mmol) 4-bromo-5-nitro-1,8-naphthalic anhydride in 40 mL ethanol was added dropwise 90 mg (1.24 mmol) butylamine in 12 mL ethanol. The mixture was then heated at reflux for 40 min and monitored by TLC. After the reaction was completed, the solvent was removed under reduced pressure. The crude product was then purified by chromatography on a silica gel column (CHCl\(_3\)) to give 7 as a white solid in 40% yield (188 mg). Mp: 175.8-176.2 °C. \(^1\)H-NMR (CDCl\(_3\), 400 MHz) \(\delta\) 0.99 (t, \(J = 7.2\) Hz, 3H), 1.45 (m, \(J = 7.2\) Hz, 2H), 1.71 (m, \(J = 7.2\) Hz, 2H), 4.18 (t, \(J = 7.2\) Hz, 2H), 7.93 (d, \(J = 8.0\) Hz, 1H), 8.21 (d, \(J = 8.0\) Hz, 1H), 8.51 (d, \(J = 8.0\) Hz, 1H), 8.71 (d, \(J = 8.0\) Hz, 1H). \(^1^3\)C-NMR (CDCl\(_3\), 100 MHz) \(\delta\) 13.95, 20.49, 30.21, 40.92, 122.69, 123.72, 124.26, 125.99, 131.37, 132.49, 136.14, 162.21, 162.98. IR (KBr, cm\(^{-1}\)) : 3057, 2963, 2935, 2912, 2860, 1706, 1568, 1541, 1230, 658, 586. HRMS (EI) calcd for C\(_{16}\)H\(_{13}\)BrN\(_2\)O\(_4\) [M+] 376.0059, found 376.0075.

**N-butyl-4,5-di[2-(phenylamino)ethylamino]-1,8-naphthalimide (1).**

0.3 mL (2.10 mmol) N-Phenylethylenediamine was added dropwise to a solution of 100 mg (0.266 mmol) N-butyl-4-bromo-5-nitro-1,8-naphthalimide 7 in 3.00 mL 2-methoxyethanol, and then the mixture was heated to reflux for 3 h and monitored by TLC. After the reaction was completed, the solution was cooled at room temperature to give yellow needle crystals. The product was filtered off, washed with 2-methoxyethanol, and then dried in the air. The product was then purified by chromatography on a silica gel column (CH\(_2\)Cl\(_2\)/EtoAC, 1:1, v/v) to give 1 as a yellow crystal in 87% yield (120 mg). Mp: 203.5-204.1 °C. \(^1\)H-NMR (CDCl\(_3\), 400 MHz) \(\delta\) 0.94 (t, \(J = 7.2\) Hz, 3H), 1.41 (m, \(J = 7.2\) Hz, 2H), 1.67 (m, \(J = 7.2\) Hz, 2H), 3.37 (s, 4H), 3.43 (s, 4H), 4.10 (t, \(J = 7.2\) Hz, 2H), 6.23 (s, N-H), 6.56 (d, \(J = 8.4\) Hz, 2H), 6.67 (d, \(J = 7.2\) Hz, 4H), 6.77 (t, \(J = 7.6\) Hz, 2H), 7.19 (t, \(J = 7.6\) Hz, 4H), 8.28 (d, \(J = 8.4\) Hz, 2H). \(^1^3\)C-NMR (CDCl\(_3\), 100 MHz) \(\delta\) 14.06, 20.67, 30.61, 40.03, 40.47, 44.04, 107.25, 110.4, 112.75, 113.59, 119.01, 129.80, 132.26, 133.62, 147.89, 152.21, 164.66. IR (KBr, cm\(^{-1}\)) : 3328, 3058, 2961, 2934, 1673, 1626, 1603, 1513, 1499, 1310, 996. HRMS (EI) calcd for C\(_{32}\)H\(_{35}\)N\(_5\)O\(_2\) [M+] 521.2791, found 521.2779.
**N-butyl-4-[2-(phenylamino)ethylamino]-1,8-naphthalimide (2).**

Compound 2 was prepared by standard methods from 4-bromo-1,8-naphthalic anhydride by reaction with firstly butylamine and then N-Phenylethlenediamine.

Mp: 146.3-147.1 °C. $^1$H-NMR (CDCl$_3$, 400 MHz) $\delta$ 0.91 (t, $J = 7.2$ Hz, 3H), 1.31 (m, $J = 7.2$ Hz, 2H), 1.57 (m, $J = 7.2$ Hz, 2H), 3.40 (s, 4H), 4.11 (t, $J = 7.2$ Hz, 2H), 5.76 (s, N-H), 6.53 (t, $J = 7.2$ Hz, 1H), 6.61 (d, $J = 8.0$ Hz, 2H), 6.81 (d, $J = 8.4$ Hz, 1H), 7.07 (t, $J = 8.0$ Hz, 2H), 7.67 (t, $J = 8.0$ Hz, 1H), 8.24 (d, $J = 8.4$ Hz, 1H), 8.42 (d, $J = 7.6$ Hz, 1H), 8.66 (d, $J = 8.4$ Hz, 1H). $^{13}$C-NMR (CDCl$_3$, 100 MHz) $\delta$ 14.03, 20.57, 30.45, 40.14, 42.88, 43.09, 104.44, 110.66, 113.50, 118.70, 120.36, 123.00, 124.83, 126.15, 129.60, 129.66, 131.16, 134.27, 147.78, 149.34, 164.20, 164.68. IR (KBr, cm$^{-1}$): 3328, 3043, 2953, 2869, 1673, 1633. HRMS (El) calcd for C$_{24}$H$_{25}$N$_3$O$_2$ [M$^+$] 387.1947, found 387.2738.

Reference.
Figure S1. a) Color change of the ethanol-water (60:40, v/v, 50 mM HEPES buffer, pH 7.2) solutions of compound 1 on addition of different metal ions. [1] = 10 µM, and the concentration of each metal ion was 50 µM. b) Visible emission observed from the solution of 1 and Cu(II). left, excited at 420 nm; right, excited at 510 nm.

Figure S2. UV-Vis absorption response of 1 to various metal ions in ethanol-water solutions (60:40, v/v, 50 mM HEPES buffer, pH 7.2). [1] = 10 µM, and the concentration of each metal ion was 50 µM. The blue (left) bars represent absorption at 419 nm. The black (right) bars represent absorption at 509 nm.
Figure S3. Fluorescence response of 1 to various metal ions in ethanol-water solutions (60:40, v/v, 50 mM HEPES buffer, pH 7.2). [1] = 10 µM, and the concentration of each metal ion was 50 µM. The blue (left) bars represent emission at 518 nm (excited at 420 nm). The black (right) bars represent emission at 592 nm (excited at 510 nm).