Supporting Information

For

A Ratiometric and Highly Selective Fluorescent Sensor for Cadmium under Physiological pH Range: a New Strategy to Discriminate Cadmium from Zinc

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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 NaClO₄, KClO₄, MgCl₂·6H₂O, CaCl₂, Fe(NO₃)₃, CoCl₂·6H₂O, NiCl₂·6H₂O, Zn(NO₃)₂·6H₂O, Cd(NO₃)₂·4H₂O, 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/ CD₃OD- d₄, TMS as internal standard). HRMS were measured on a Micomass HPLC-Q-Tof MS (Micro) spectrometer. 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. 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. Compound 2 was synthesized according to the published procedures.¹
(a) CH₃OCH₂CH₂OH, HR, heated; (b) CH₃CN, 2-aminoethanol, reflux; (c) CH₂Cl₂, PBr₃, rt; (d) CH₃CN, DPA, KI, K₂CO₃, reflux.

5a:
2-(aminomethyl)pyridine (350 µL, 3.4 mmol) was added dropwise to a solution of N-buty1-4-bromo-5-nitro-1,8-napthalimide 2 (1.0 g, 2.66 mmol) in 12 mL 2-methoxyethanol, and then the mixture was moderately heated 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 crude product was then chromatographed on silica gel (100-200 mesh). Elution of the column with a mixture of ethyl acetate and dichloromethane (1:2) gave 932 mg (80 %) of 5a. Mp: 194.6~196.8°C. ¹H-NMR (CDCl₃, 400 MHz) δ 0.97 (t, J = 7.2 Hz, 3H), 1.43 (m, J = 7.2 Hz, 2H), 1.69 (m, J = 7.2 Hz, 2H), 4.13 (t, J = 7.2 Hz, 2H), 4.71 (s, 2H), 6.74 (d, J = 8.4 Hz, 1H), 7.29 (t, J = 7.6 Hz, 1H), 7.38 (d, J = 8.0 Hz, 1H), 7.74 (t, J = 7.6 Hz, 1H), 7.85 (d, J = 8.0 Hz, 1H), 8.33 (d, J = 8.0 Hz, 1H), 8.47 (d, J = 8.4 Hz, 1H), 8.66 (d, J = 7.6 Hz, 1H), 8.94 (s, N-H). ¹³C-NMR (CDCl₃, 100 MHz) δ 14.05, 20.60, 30.37, 40.27, 49.36, 106.76, 110.53, 118.40, 121. 89, 122.78, 122.96, 125.10, 131.35, 132.20, 132.69, 135.09, 137.27, 149.33, 150.02, 155.42, 163.76, 164.32. MS (APCI) [M+H]⁺ 438.
$^1$H NMR of 5a

$^{13}$C NMR of 5a
3a:
To a solution of 5a (250 mg, 0.57 mmol) in acetonitrile were added 2-aminoethanol (680 µL, 11.4 mmol). The mixture was then refluxed for 24 h. After the reaction was completed, the solvent was removed under reduced pressure. The crude product was then chromatographed on silica gel (100-200 mesh). Elution of the column with a mixture of methanol and dichloromethane (1:10) gave 160 mg (67 %) of 3a. Mp: 201.0–202.7 °C. 1H-NMR (DMSO, 400 MHz) δ 0.91 (t, J = 7.6 Hz, 3H), 1.31 (m, J = 7.6 Hz, 2H), 1.54 (m, J = 7.6 Hz, 2H), 3.39 (t, J = 6.0 Hz, 2H), 3.80 (t, J = 6.0 Hz, 2H), 3.98 (t, J = 7.6, 2H), 4.67 (s, 2H), 4.92 (t, O-H), 6.78 (d, J = 8.4 Hz, 1H), 6.89 (d, J = 8.8 Hz, 1H), 7.35 (t, J = 7.6 Hz, 1H), 7.52 (d, J = 8.4 Hz, 1H), 7.82 (t, J = 7.6 Hz, 1H), 8.17 (d, J = 7.6 Hz, 1H), 8.23 (d, J = 7.6 Hz, 1H), 8.65 (d, J = 7.6 Hz, 1H). 13C-NMR (DMSO, 100 MHz) δ 13.74, 19.81, 29.88, 38.60, 46.51, 48.43, 58.98, 106.56, 109.69, 110.17, 121.85, 122.48, 131.85, 133.13, 136.94, 148.76, 152.10, 153.05, 156.78, 163.28. IR (KBr, cm⁻¹): 3425, 3330, 3222, 2930, 2723, 1668, 1619, 1576, 1460, 1376, 1345, 804, 776, 747. MS (APCI) [M+H]⁺ 419.

1H NMR of 3a
**13C NMR of 3a**

4a:
To an ice cold solution 3a (250 mg, 0.60 mmol) in dichloromethane (20 mL) was dropwise added ca. 5 mL PBr3. After that, the reaction mixture was further stirred at room temperature for an additional period of 3 h. The reaction was quenched with ice-cold water and the pH was adjusted to 7-8. The organic portion was extracted with dichloromethane and the solvent was removed under vacuum. The crude product was chromatographed on silica gel (100-200 mesh). Elution of the column with a mixture of methanol and dichloromethane (1:20) gave 124 mg (43%) of 4a. Mp: 183.7–184.9℃. 1H-NMR (DMSO, 400 MHz) δ 0.91 (t, J = 7.2 Hz, 3H), 1.30 (m, J = 7.2 Hz, 2H), 1.56 (m, J = 7.2 Hz, 2H), 3.74 (t, J = 6.0 Hz, 2H), 3.83 (t, J = 6.0 Hz, 2H), 3.98 (t, J = 7.2, 2H), 4.69 (s, 2H), 6.79 (d, J = 8.8 Hz, 1H), 6.96 (d, J = 8.8 Hz, 1H), 7.36 (t, J = 7.6 Hz, 1H), 7.40 (d, J = 8.4 Hz, 1H), 7.53 (d, J = 8.0 Hz, 1H), 7.84 (t, J = 8.0 Hz, 1H), 8.18 (d, J = 4.4 Hz, 1H). 13C-NMR (DMSO, 100 MHz) δ 13.66, 19.73, 29.79, 31.66, 38.58, 45.53, 48.23, 122.13, 122.69, 131.74, 132.95, 133.12, 137.51, 148.37, 151.84, 151.91, 156.47, 163.16, 163.21. IR (KBr, cm⁻¹): 3336, 2955, 2931, 2871, 1675, 1632, 1594, 1433, 1406, 1360, 810, 751. MS (APCI) [M+H]⁺ 481.
$^1$H NMR of 4a

$^{13}$C NMR of 4a
1a:
To a solution of 4a (50 mg, 0.10 mmol) in acetonitrile were added 2 equiv of KI (35 mg), 2 equiv of K₂CO₃ (29 mg), and 2 equiv of DPA (37 µL). After the reaction mixture had been moderately heated and refluxed for over 6 h, all the volatile components were evaporated and the residue was partitioned between dichloromethane and water. The organic phase was washed with water (3 × 50 mL), then dried in Na₂SO₄. Flash chromatographic purification (dichloromethane–methanol = 20 : 1) afforded 1a (46 mg, 74% yield). Mp: 122.6~124.4. ¹H-NMR (CD₃OD, 500 MHz) δ 0.97 (t, J = 7.6 Hz, 3H), 1.40 (m, J = 7.6 Hz, 2H), 1.64 (m, J = 7.6 Hz, 2H), 3.04 (t, J = 6.0 Hz, 2H), 3.37 (t, J = 6.0 Hz, 2H), 3.80 (s, 4H), 4.06 (t, J = 7.2, 2H), 4.63 (s, 2H), 6.58 (d, J = 8.5 Hz, 2H), 6.73 (d, J = 8.5 Hz, 2H), 7.04 (t, J = 6 Hz, 2H), 7.27 (t, J = 6 Hz, 1H), 7.35 (d, J = 7.6 Hz, 2H), 7.45 (t, J = 8.0 Hz, 3H), 7.73 (t, J = 7.6 Hz, 1H), 8.13 (d, J = 8.5 Hz, 1H), 8.24 (t, J = 4.5 Hz, 3H), 8.51 (d, J = 4.8 Hz, 2H). ¹³C-NMR (DMSO, 100 MHz) δ 13.81, 19.87, 29.94, 41.39, 48.35, 52.03, 59.47, 106.28, 106.49, 109.50, 109.62, 110.08, 121.72, 122.07, 122.46, 122.84, 131.84, 133.13, 136.88, 137.58, 148.72, 152.12, 152.85, 156.65, 158.74, 163.33. IR (KBr, cm⁻¹): 3322, 2954, 2924, 2853, 2816, 1673, 1631, 1587, 1405, 1355, 1310, 1145, 1089, 995, 968, 832, 811, 750. MS (APCI) [M+H]+ 600. HRMS (ES+), calcd. for C₃₆H₃₇N₇O₂ [M+H]+ 600.3087, found 600.3080.

¹H NMR of 1a
5b:
Using the method described for the preparation of 5a, the crude compound was purified by column chromatography on silica gel (1:2 ethyl acetate/dichloromethane) to afford a yellow solid (82%). Note: in this reaction, 3-(aminomethyl)pyridine was used instead of 2-(aminomethyl) pyridine.

^1H-NMR (CDCl3, 400 MHz) δ 0.95 (t, J = 7.2 Hz, 3H), 1.41 (m, J = 7.2 Hz, 2H), 1.69 (m, J = 7.2 Hz, 2H), 4.13 (t, J = 7.2 Hz, 2H), 4.65 (s, 2H), 6.74 (d, J = 8.8 Hz, 1H), 7.40 (s, 1H), 7.79 (d, J = 8.0 Hz, 1H), 7.91 (t, J = 8.0 Hz, 1H), 8.35 (d, J = 8.0 Hz, 1H), 8.46 (d, J = 8.0 Hz, 1H), 8.85 (d, J = 8.0 Hz, 1H).

3b:
Using the method described for the preparation of 3a, the crude compound was purified by column chromatography on silica gel (1:10 methanol/dichloromethane) to afford a yellow solid (60%).

^1H-NMR (CDCl3, 400 MHz) δ 0.90 (t, J = 7.2 Hz, 3H), 1.30 (m, J = 7.2 Hz, 2H), 1.55 (m, J = 7.2 Hz, 2H), 3.37 (t, J = 5.6 Hz, 2H), 3.73 (t, J = 5.6 Hz, 2H), 4.00 (t, J = 6.8, 2H), 4.56 (s, 2H), 6.79 (d, J = 8.4 Hz, 1H), 6.86 (d, J = 8.4 Hz, 1H), 7.39 (t, J = 6.8 Hz, 1H), 7.91 (d, J = 6.8 Hz, 1H), 8.16 (d, J = 8.4 Hz, 1H), 8.23 (d, J = 8.4 Hz, 1H), 8.49 (d, J = 8.4 Hz, 1H), 8.69 (s, N-H).

4b:
Using the method described for the preparation of 4a, the crude compound was purified by column chromatography on silica gel (1:20 methanol/dichloromethane) to afford a yellow solid (40%).

^1H-NMR (DMSO, 400 MHz) δ 0.90 (t, J = 7.2 Hz, 3H), 1.31 (m, J = 7.2 Hz, 2H), 1.55 (m, J = 7.2 Hz, 2H), 3.37 (t, J = 5.6 Hz, 2H), 3.73 (t, J = 5.6 Hz, 2H), 4.00 (t, J = 6.8, 2H), 4.56 (s, 2H), 6.79 (d, J = 8.4 Hz, 1H), 6.86 (d, J = 8.4 Hz, 1H), 7.39 (t, J = 6.8 Hz, 1H), 7.91 (d, J = 6.8 Hz, 1H), 8.16 (d, J = 8.4 Hz, 1H), 8.23 (d, J = 8.4 Hz, 1H), 8.49 (d, J = 8.4 Hz, 1H), 8.69 (s, N-H).
Hz, 2H), 3.69 (t, J = 5.6 Hz, 2H), 3.78 (t, J = 5.6 Hz, 2H), 3.97 (t, J = 7.2, 2H), 4.60 (s, 2H), 6.79 (d, J = 8.4 Hz, 1H), 6.93 (d, J = 8.4 Hz, 1H), 7.39 (t, J = 6.0 Hz, 1H), 7.90 (d, J = 8.0 Hz, 1H), 8.18 (d, J = 8.4 Hz, 1H), 8.25 (d, J = 8.4 Hz, 1H), 8.25 (d, J = 8.4 Hz, 1H), 8.50 (s, 1H), 8.72 (s, 1H). MS (APCI) [M+H]+ 481.

1b:
Using the method described for the preparation of 1a the crude compound was purified by flash column chromatography (1:20 methanol/dichloromethane) to afford a yellow solid (80%).

$^1\text{H}$-NMR (DMSO, 400 MHz) $\delta$ 0.90 (t, J = 7.2 Hz, 3H), 1.31 (m, J = 7.2 Hz, 2H), 1.55 (m, J = 7.2 Hz, 2H), 2.92 (t, J = 5.6 Hz, 2H), 3.37 (t, J = 5.6 Hz, 2H), 3.83 (s, 4H), 3.98 (t, J = 7.2, 2H), 4.60 (s, 2H), 6.68 (d, J = 8.8 Hz, 1H), 6.76 (d, J = 8.8 Hz, 1H), 7.14 (t, J = 6.0 Hz, 2H), 7.31 (dd, J = 4.4 Hz, 1H), 7.40 (d, J = 7.6 Hz, 2H), 7.57 (t, J = 7.6 Hz, 2H), 7.83 (d, J = 7.6 Hz, 1H), 8.16 (t, J = 8.8 Hz, 2H), 8.34 (d, J = 4.0 Hz, 2H), 8.46 (d, J = 4.0 Hz, 1H), 8.68 (s, 1H). $^{13}\text{C}$-NMR (DMSO, 100 MHz) $\delta$ 13.95, 20.01, 30.07, 41.02, 45.01, 51.62, 55.03, 59.46, 106.06, 107.42, 109.03, 110.24, 110.52, 122.33, 123.26, 123.71, 131.98, 133.02, 133.47, 133.96, 135.24, 136.61, 148.38, 148.90, 148.97, 152.36, 152.68, 158.57, 163.50, 163.56. HRMS (ES+), calcd. for C$_{36}$H$_{37}$N$_7$O$_2$ [M+H]$^+$ 600.3087, found 600.3093.

$^1\text{H}$ NMR of 1b
Using the method described for the preparation of 5a, the crude compound was purified by column chromatography on silica gel (1:2 ethyl acetate/dichloromethane) to afford a yellow solid (85%). Note: in this reaction, 2-(aminoethyl)pyridine was used instead of 2-(aminomethyl) pyridine. 

$^1$H-NMR (CDCl$_3$, 400 MHz) $\delta$ 0.96 (t, $J = 7.2$ Hz, 3H), 1.43 (m, $J = 7.2$ Hz, 2H), 1.69 (m, $J = 7.2$ Hz, 2H), 3.31 (t, $J = 6.4$ Hz, 2H), 3.85 (t, $J = 6.4$ Hz, 2H), 4.13 (t, $J = 7.2$ Hz, 2H), 6.81 (d, $J = 8.8$ Hz, 1H), 7.22 (t, $J = 6.0$ Hz, 1H), 7.67 (t, $J = 7.6$ Hz, 1H), 7.77 (t, $J = 8.0$ Hz, 1H), 7.91 (s,1H), 8.29 (d, $J =8.0$ Hz,1H), 8.47 (d, $J = 8.8$ Hz, 1H), 8.60 (s, 1H).

Using the method described for the preparation of 3a, the crude compound was purified by column chromatography on silica gel (1:10 methanol/dichloromethane) to afford a yellow solid (62%). 

$^1$H-NMR (DMSO, 400 MHz) $\delta$ 0.91 (t, $J = 7.2$ Hz, 3H), 1.31 (m, $J = 7.2$ Hz, 2H), 1.55 (m, $J = 7.2$ Hz, 2H), 3.19 (t, $J = 6.8$ Hz, 2H), 3.36 (t, $J = 5.6$ Hz, 2H), 3.59 (t, $J = 6.8$ Hz, 2H), 3.70 (t, $J = 5.6$ Hz, 2H), 3.97 (t, $J = 7.2$ Hz, 2H), 6.83 (d, $J = 8.4$ Hz, 1H), 6.88 (d, $J = 8.4$ Hz, 1H), 7.28 (t, $J = 6.0$ Hz, 1H), 7.41 (t, $J = 7.8$ Hz, 1H), 7.77 (t, $J = 7.8$ Hz, 1H), 7.91 (s,1H), 8.21 (dd, $J = 5.6$ Hz, 2H), 8.54 (d, $J = 4.0$ Hz, 1H).

Using the method described for the preparation of 4a, the crude compound was purified by column chromatography on silica gel (1:20 methanol/dichloromethane) to afford a yellow solid (45%).

$^1$H-NMR (CDCl$_3$, 400 MHz) $\delta$ 0.95 (t, $J = 7.2$ Hz, 3H), 1.42 (m, $J = 7.2$ Hz, 2H), 1.69 (m, $J = 7.2$ Hz, 2H), 3.35 (t, $J = 7.2$ Hz, 2H), 3.85 (t, $J = 7.2$ Hz, 2H), 4.14 (t, $J = 7.2$ Hz, 2H), 6.82 (d, $J = 8.4$ Hz, 1H), 7.32 (t, $J = 7.2$ Hz, 2H), 7.41 (t, $J = 7.8$ Hz, 1H), 7.77 (t, $J = 7.8$ Hz, 1H), 7.92 (s,1H), 8.20 (dd, $J = 5.6$ Hz, 2H), 8.53 (d, $J = 4.0$ Hz, 1H).
Hz, 2H), 3.30 (t, J = 5.6 Hz, 2H), 3.70 (m, 6H), 4.13 (t, J = 7.2, 2H), 6.73 (dd, J = 8.8 Hz, 2H), 6.88 (s, 1H), 7.04 (s, N-H), 7.23 (t, J = 6.5 Hz, 1H), 7.29 (d, J = 7.6 Hz, 1H), 7.69 (d, J = 7.6 Hz, 1H), 8.40 (dd, J = 7.6 Hz, 2H), 8.50 (s, 1H). MS (APCI) [M+H]$^+$ 495.

1c:
Using the method described for the preparation of 1a, the crude compound was purified by flash column chromatography (1:20 methanol/dichloromethane) to afford a yellow solid (82%).

$^1$H-NMR (DMSO, 500 MHz) δ 0.91 (t, J = 7.2 Hz, 3H), 1.30 (m, J = 7.2 Hz, 2H), 1.56 (m, J = 7.2 Hz, 2H), 2.87 (t, J = 6.8 Hz, 2H), 3.11 (t, J = 5.6 Hz, 2H), 3.38 (t, J = 6.8, 2H), 3.61 (t, J = 5.6 Hz, 2H), 3.85 (s, 4H), 3.98 (t, J = 7.2 Hz, 2H), 6.65 (d, J = 8.4 Hz, 1H), 6.92 (d, J = 8.4 Hz, 1H), 7.19 (m, 3H), 7.28 (d, J = 7.6 Hz, 1H), 7.44 (d, J = 7.8 Hz, 2H), 7.47 (N-H, 2H), 7.64 (t, J = 7.6 Hz, 2H), 7.69 (t, J = 7.6 Hz, 1H), 8.10 (d, J = 8.0 Hz, 1H), 8.23 (d, J = 8.4 Hz, 1H), 8.40 (d, J = 4.0 Hz, 2H), 8.46 (d, J = 4.0 Hz, 1H). $^{13}$C-NMR (DMSO, 100 MHz) δ 13.96, 20.01, 30.09, 35.92, 41.14, 43.63, 51.60, 59.50, 105.91, 106.53, 109.00, 109.94, 121.93, 122.35, 123.15, 123.51, 132.05, 133.34, 136.65, 137.02, 148.91, 149.17, 152.69, 152.73, 158.79, 159.31, 163.52, 163.59. HRMS (ES+), calcd. for C$_{36}$H$_{37}$N$_7$O$_2$ [M+H]$^+$ 614.3243, found 614.3236.

$^1$H NMR of 1c
$^{13}$C NMR of 1c
**Spectroscopic Data**

**Figure S1.** Influence of pH on the fluorescence of 1a (10 µM) in ethanol-water solutions (1:9, v/v), $\lambda_{ex} = 460$ nm. pH value was adjusted by HClO$_4$ and tetramethylammonium hydroxide.

**Figure S2.** Changes in the fluorescence emission spectra of 1a (2 µM) upon titration of Cd$^{2+}$, $\lambda_{ex} = 420$ nm. Inset: Ratiometric calibration curve $I_{487}/I_{531}$ as a function of Cd$^{2+}$ concentration. Condition: ethanol-water solutions (1:9, v/v, 50 mM HEPES buffer, pH = 7.2).
**Figure S3.** Influence of pH on the fluorescence of 1a + Cd²⁺ adduct (1:1, [1a] = [Cd²⁺] = 10 µM) in ethanol-water solutions (1:9, v/v): (a) the influence of pH on the ratio of fluorescence intensity (I₄₈⁷/I₅₃₁); (b) the influence of pH on the fluorescent intensity (I₄₈⁷), λₑₓ = 420 nm.

**Figure S4.** Selectivity of 1a for Cd²⁺ over other metal ions. All data were obtained in ethanol-water solutions (1:9, v/v, 50 mM HEPES buffer, pH = 7.2), λₑₓ = 420 nm, and were expressed as fluorescence ratio (487 nm/531 nm). The blank bars represented the emission of 1 in the presence of cations of interest: 1, control; 2, Zn²⁺; 3, Hg²⁺; 4, Ni²⁺; 5, Pb²⁺; 6, Ag⁺; 7, Fe³⁺ (respectively 10 µM) and 8, Ca²⁺; 9, Mg²⁺; 10, Na⁺; 11, K⁺ (respectively 5 mM) were added to 1a (10 µM). The solid bars represented the fluorescence change that occurred when Cd²⁺ (10 µM) was added to each solution.
Figure S5. Titration of 1a with Cd$^{2+}$ ions in the presence of 1 equiv of Zn$^{2+}$ ([1a] = [Zn$^{2+}$] = 10 µM) in ethanol-water solutions (1:9, v/v, 50 mM HEPES buffer, pH = 7.2), $\lambda_{ex}$ = 420 nm; [Cd$^{2+}$] = 0–20 µM.

Figure S6. (a) Changes in the absorption spectra of 1b (10 µM) upon titration of Zn$^{2+}$; (b) Changes in the absorption spectra of 1b (10 µM) upon titration of Cd$^{2+}$; (c) Changes in the absorption spectra of 1c (10 µM) upon titration of Zn$^{2+}$; (d) Changes in the absorption spectra of 1c (10 µM) upon titration of Cd$^{2+}$. All data were obtained in ethanol-water solutions (1:9, v/v, 50 mM HEPES buffer, pH = 7.2).
Figure S7. (a) Changes in the fluorescence emission spectra of 1b (10 µM) upon titration of Zn$^{2+}$; (b) Changes in the fluorescence emission spectra of 1b (10 µM) upon titration of Cd$^{2+}$; (c) Changes in the fluorescence emission spectra of 1c (10 µM) upon titration of Zn$^{2+}$; (d) Changes in the fluorescence emission spectra of 1c (10 µM) upon titration of Cd$^{2+}$. All data were obtained in ethanol-water solutions (1:9, v/v, 50 mM HEPES buffer, pH = 7.2), $\lambda_{ex} = 460$ nm.
Figure S8. Partial $^1$H-NMR spectra (500 MHz) of 1a (10 mM) in DMSO (top): (a) 1a + 1.0 equiv Zn$^{2+}$; (b) 1a + 1.0 equiv Cd$^{2+}$; (c) free 1a. Partial $^1$H-NMR spectra (500 MHz) of 1b (10 mM) in DMSO (middle): (a) 1b + 1.0 equiv Zn$^{2+}$; (b) 1b + 1.0 equiv Cd$^{2+}$; (c) free 1b and Partial $^1$H-NMR spectra (500 MHz) of 1c (10 mM) in DMSO (bottom): (a) 1c + 1.0 equiv Zn$^{2+}$; (b) 1c + 1.0 equiv Cd$^{2+}$; (c) free 1c.$^{52}$
H-H COSY of free 1a

H-H COSY of 1a + 1.0 equiv Zn$^{2+}$
H-H COSY of 1a + 1.0 equiv Cd²⁺

Notes and references


S2 The peaks were assigned to the protons according to the H-H COSY spectra. ¹H-NMR spectra study was failed to get satisfactory result under CD₃OH-D₂O (1:1) and [1a] = 10 mM because of precipitation. Although further test under 20 mM of 1a in CD₃OD got well discernible ¹H-NMR spectra (see ¹H NMR of 1a), addition of Zn²⁺ also resulted in precipitation.