Electronic Supplementary Material

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Detection of Cd(II), Ni(II), and Cu(II) Using a Fluorescent Chemosensor Based on a 1,3-Alternate Pyrene–Thiosemicarbazone Calix[4]arene

Horacio Gómez-Machuca[*1], Cinthia Quiroga-Campano[2] and Claudio Saitz[1]

1. Departamento de Química Orgánica y Fisicoquímica, Facultad de Ciencias Químicas y Farmacéuticas, Universidad de Chile, Olivos 1007, Independencia, Santiago 8380494, Chile.

2. Centro de Estudios Para el Desarrollo de la Química (CEPEDEQ), Facultad de Ciencias Químicas y Farmacéuticas, Universidad de Chile, Santiago 8380494, Chile.

Horacio Gomez-Machuca

horacio.gomez@ciq.uchile.cl

https://orcid.org/0009-0003-8097-682X

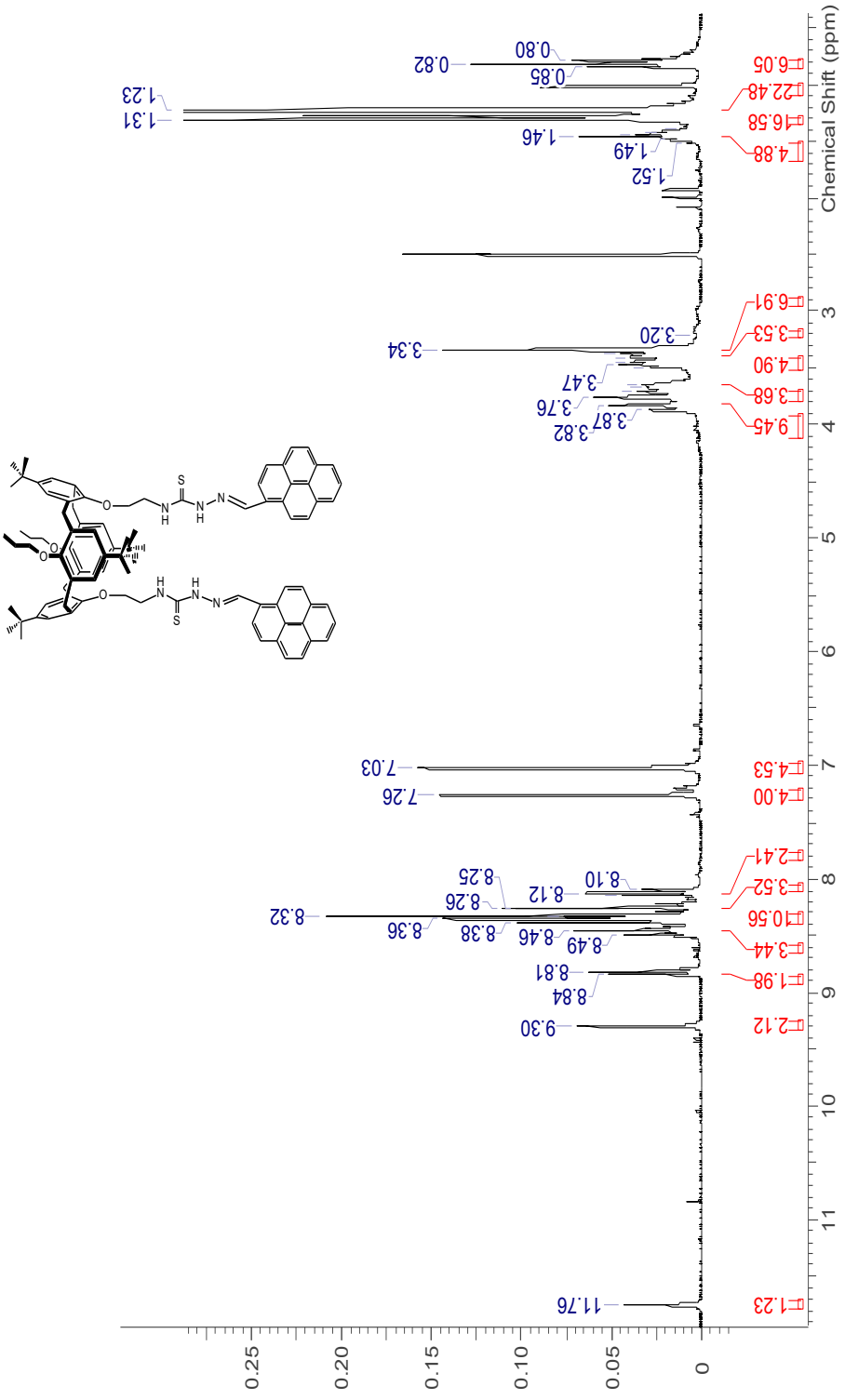
1. Synthesis of receptor I.

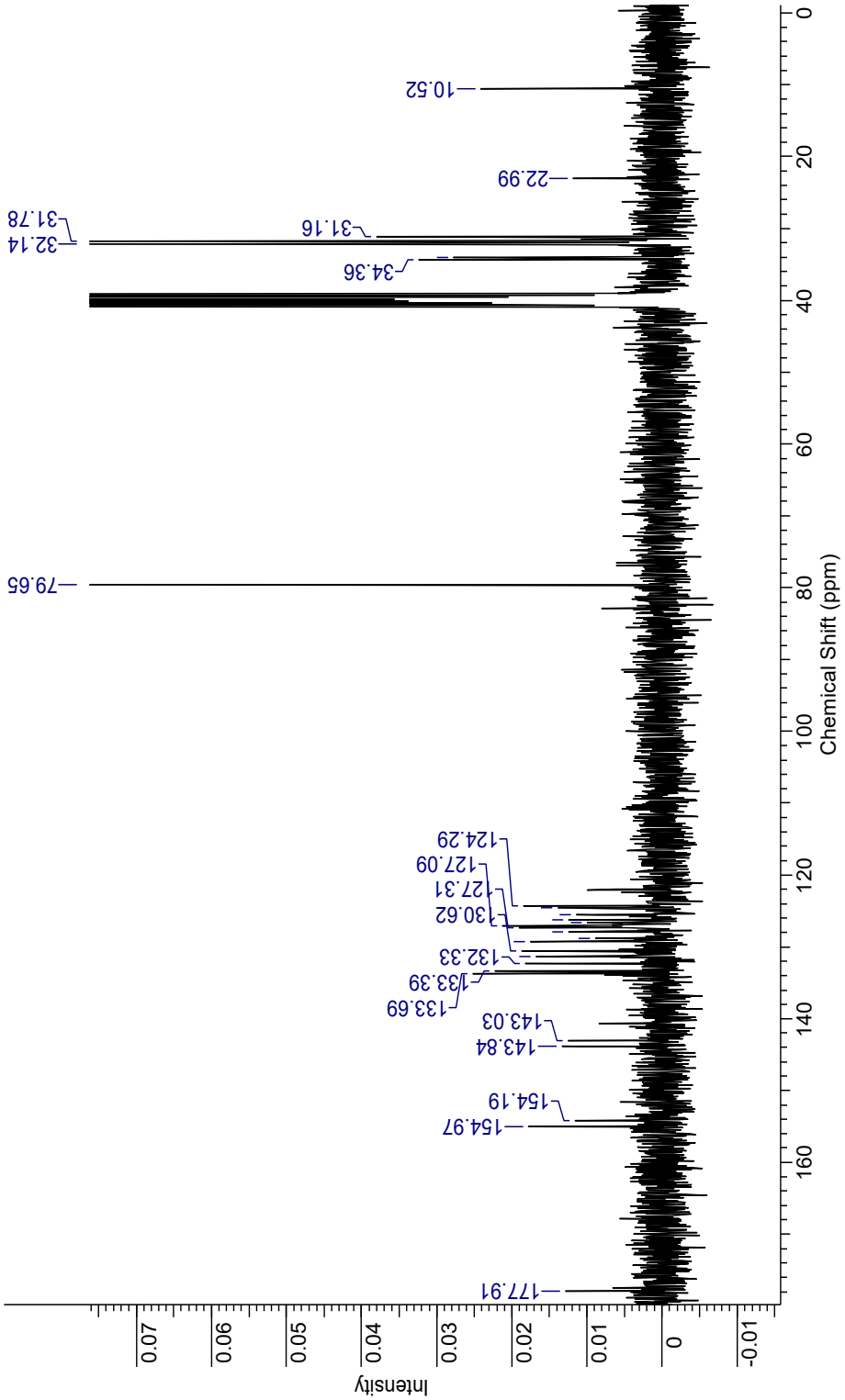
General procedure for the synthesis of receptor I. Hydrazine hydrate (80%, 16.2 mmol) was added to a stirred solution of the bis(isothiocyanate) calix[4]arene (1.1 mmol) in THF (50 mL), and the mixture was stirred vigorously for 24 h at room temperature. Ethyl acetate (30 mL) was then added, and the organic layer was washed with water (3 × 30 mL), dried over anhydrous Na_2SO_4, filtered, and concentrated to dryness. The resulting crude thiosemicarbazide was heated under reflux with 1-pyrenecarbaldehyde (300 mg, 1.9 mmol) in methanol (70 mL) for 24 h. After completion of the reaction, the precipitate was collected by filtration and purified by silica-gel column chromatography using hexane/ethyl acetate (3:1, v/v) as the eluent to afford receptor I as a yellow solid.

5,11,17,23-Tetra-tert-butyl-25,27-bis(1-pyrenyl-thiosemicarbazone-ethoxy)-26,28-dipropoxycalix[4]arene, 1,3-alternate (I). Yield: 59%; mp 270–274 °C. ^{1}H NMR (300 MHz, DMSO-d_6, TMS, 25 °C) δ: 11.76 (s, 2H, C=SNHN), 9.30 (s, 2H, N=CH), 8.82 (d, 2H, J = 8.2 Hz, pyrene-H), 8.50–8.42 (m, 4H, C=SNHCH$_2$, pyrene-H), 8.38–8.32 (m, 10H, pyrene-H), 8.25 (d, 2H, J = 3.8 Hz, pyrene-H), 8.12 (t, 2H, J = 7.7 Hz, pyrene-H), 7.26 (s, 4H, ArH), 7.03 (s, 4H, ArH), 3.85 (d, 4H, J = 15.0 Hz, ArCH$_2$Ar), 3.71 (d, 4H, J = 14.8 Hz, ArCH$_2$Ar), 3.66 (d, 4H, OCH$_2$CH$_2$N), 3.47 (t, 4H, J = 7.6 Hz, OCH$_2$CH$_2$CH$_3$), 3.39 (t, 4H, OCH$_2$CH$_2$N), 1.52–1.39 (m, 4H, J = 7.2 Hz, CH$_2$CH$_2$CH$_3$), 1.31 (s, 18H, C(CH$_3$)$_3$), 1.23 (s, 18H, C(CH$_3$)$_3$), 0.82 (t, 6H, J = 7.3 Hz, CH$_2$CH$_2$CH$_3$). ^{13}C NMR (75.47 MHz, DMSO-d_6, TMS, 25 °C) δ: 177.91, 154.97, 154.79, 143.84, 143.03, 142.39, 138.69, 133.69, 132.33, 130.62, 127.31, 126.99, 124.29, 34.36, 32.14, 31.78, 31.16, 22.99, 10.52. FT-IR (ATR, cm^{-1}): 3380, 3150 [ν(N–H)]; 2961–2873 [ν(C–H)]; 1540 [ν(C=N)]; 1481 [ν(C=C)]; 1201 [ν(C=S)]. UV–Vis (CH$_3$CN): λmax = 380 nm (ε = 7.27 × 10^4 M^{-1} cm^{-1}). Anal. calcd for $C_{90}H_{98}N_6O_4S_2$: C, 77.66; H, 7.10; N, 6.04; S, 4.61%. Found: C, 76.66; H, 7.24; N, 5.92; S, 4.52%.

2. Characterization of receptor I

Fig. S1 Characterization spectra of receptor I: (a) ^{1}H NMR, (b) ^{13}C NMR, and (c) FT-IR spectra

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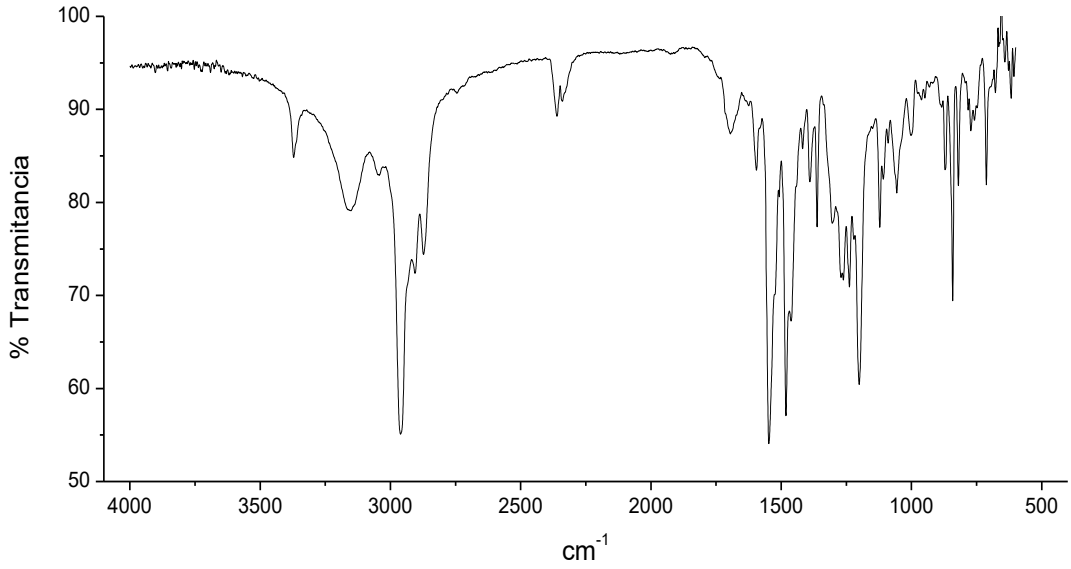
0.06
0.05
0.04
0.03
0.02
0.01
0
-0.01
Chemical Shift (ppm)
0
20
40
60
80
100
120
140
160
177.91
154.97
154.19
143.84
143.03
133.69
133.39
132.33
130.62
127.31
127.09
124.29
79.65
34.36
32.14
31.78
31.16
22.99
10.52


100
90
80
70
60
50
% Transmitancia
4000
3500
3000
2500
2000
1500
1000
500
cm-1

3. Photophysical characterization in solution

Fig. S2 Absorption spectra of receptor I at increasing concentrations in acetonitrile

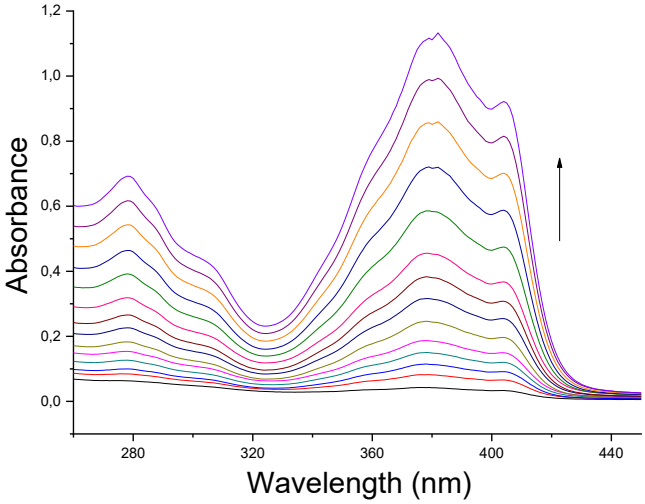


Fig. S3 Emission spectra of receptor I in acetonitrile over the concentration range 0.14–2.88 µM (λexc = 380 nm)

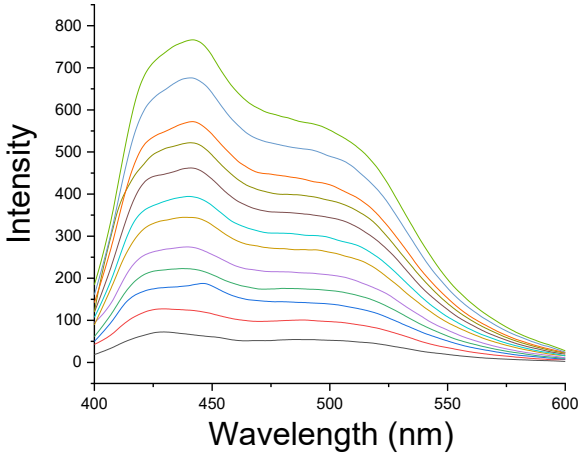


Fig S4 Fluorescence titration data for receptor I (0.5 µM) with Milli-Q Water from 0% to 20% in acetonitrile (λ_{exc} = 380 nm).

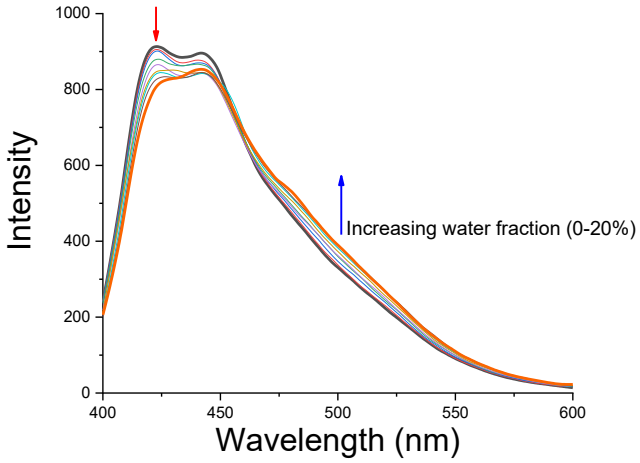


Fig. S5 Absorption spectra of receptor I (9.6 µM) in different solvents: (1) methanol, (2) acetonitrile, (3) isopropyl alcohol, (4) dimethyl sulfoxide, (5) tetrahydrofuran, (6) diethyl ether, (7) chloroform, (8) toluene, and (9) benzene

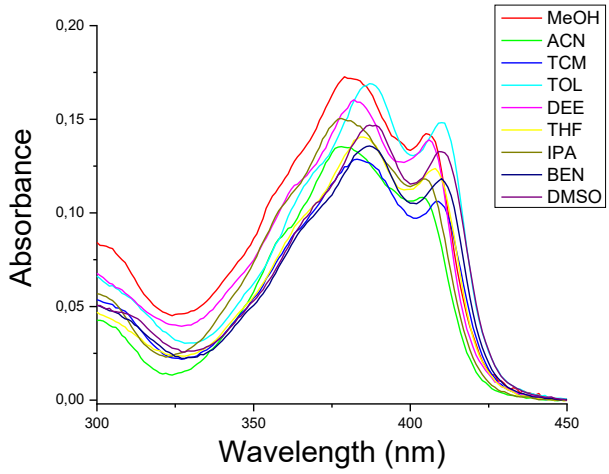


Fig. S6 Spectral phasor plot of the emission spectra and Lippert–Mataga plot of receptor I as a function of orientation polarizability (Δf): (1) methanol, (2) acetonitrile, (3) isopropyl alcohol, (4) dimethyl sulfoxide, (5) tetrahydrofuran, (6) diethyl ether, (7) chloroform, (8) toluene, and (9) benzene

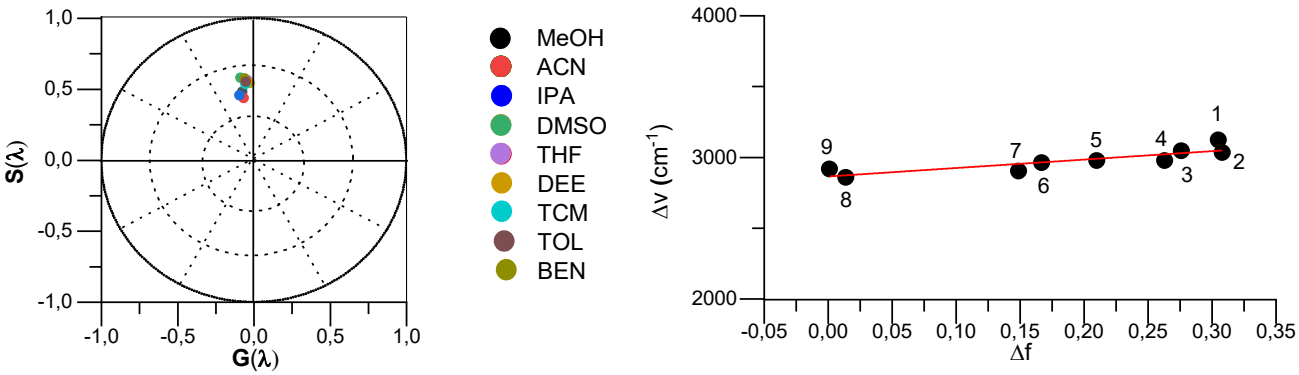
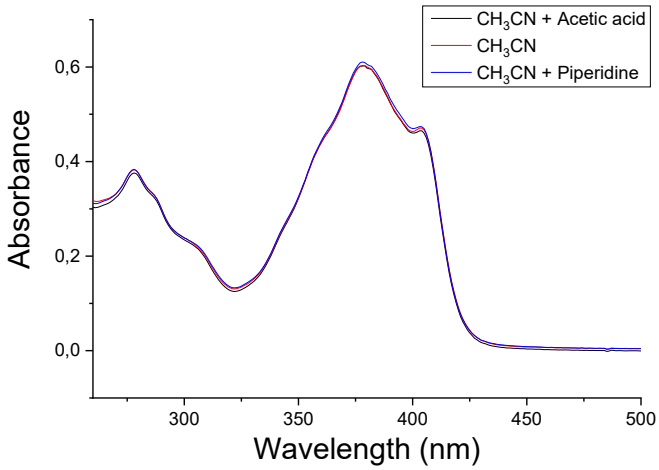


Fig. S7 Absorption spectra of receptor I (9.6 μM) with piperidine or acetic acid



4. Studies with metal ions

Table S1. Fluorescence lifetime components obtained from triexponential fitting of the time-resolved emission decays of the free receptor and its complexes with Cd^{2+}, Ni^{2+}, and Cu^{2+} in acetonitrile.

	τ_1 (ns)	τ_2 (ns)	τ_3 (ns)
I	13.0	4.11	1.20
Cd^{2+}	12.9	3.48	0.94
Ni^{2+}	12.6	3.23	0.87
Cu^{2+}	12.4	3.13	0.76

Fig. S8 Continuous-variation plots for receptor I obtained from fluorescence measurements at 500 nm in acetonitrile: (a) Cd^{2+}, (b) Cu^{2+}, and (c) Ni^{2+} (λexc = 380 nm)

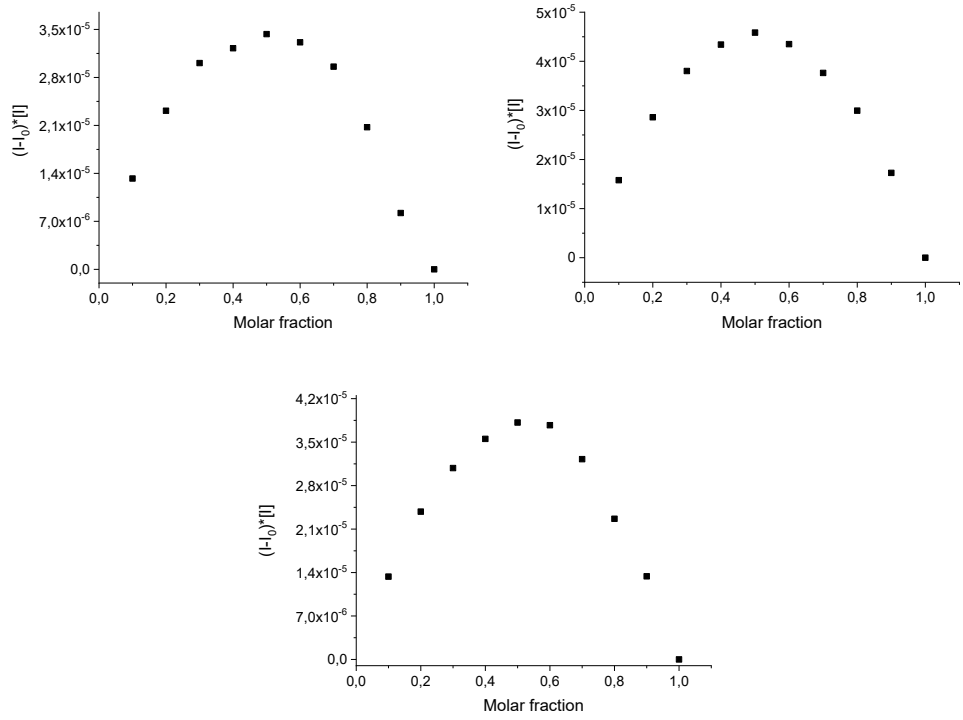
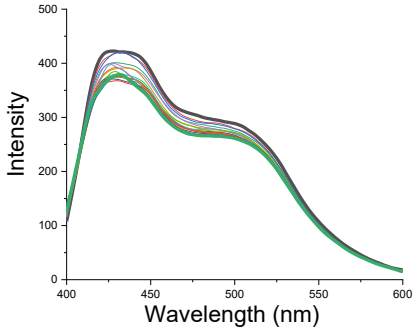


Fig. S9 Nonlinear fitting of fluorescence titration data for receptor I (0.5 μM) with (a) Cd^{2+}, (b) Cu^{2+}, and (c) Ni^{2+} in acetonitrile (λexc = 380 nm). Association constants were calculated using BindFit and a 1:1 host–guest binding model

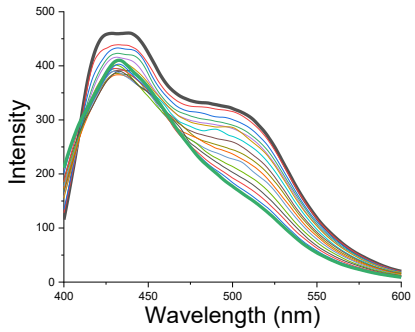


Details

Time to fit	1.3665 s
SSR	383215.3732
Fitted datapoints	6432
Fitted params	805

Parameters

Parameter (bounds)	Optimised	Error	Initial
K (0 → ∞)	841852.87 M^{-1}	± 0.6743 %	100.00 M^{-1}



Details

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Parameters

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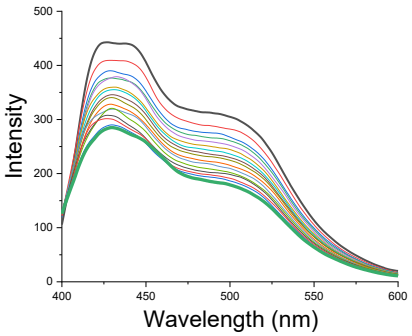

Details

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Parameters

Parameter (bounds)	Optimised	Error	Initial
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Fig. S10 Determination of the limits of detection (LOD) from linear fits of the fluorescence-titration data for Cd^{2+}, Cu^{2+}, and Ni^{2+} in acetonitrile

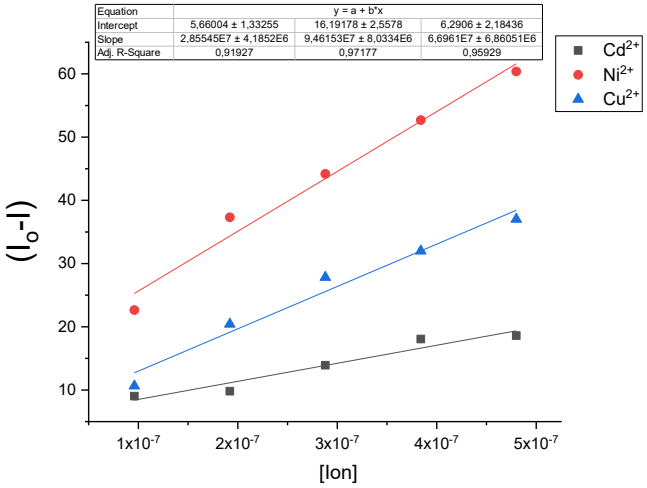

Fig. S11 ^{1}H NMR titration of receptor I (6 mM) in DMSO-d$_6$ upon addition of Cd^{2+}: (a) 0.0, (b) 0.2, (c) 0.4, (d) 0.6, (e) 0.8, (f) 1.0, and (g) 2.0 equiv

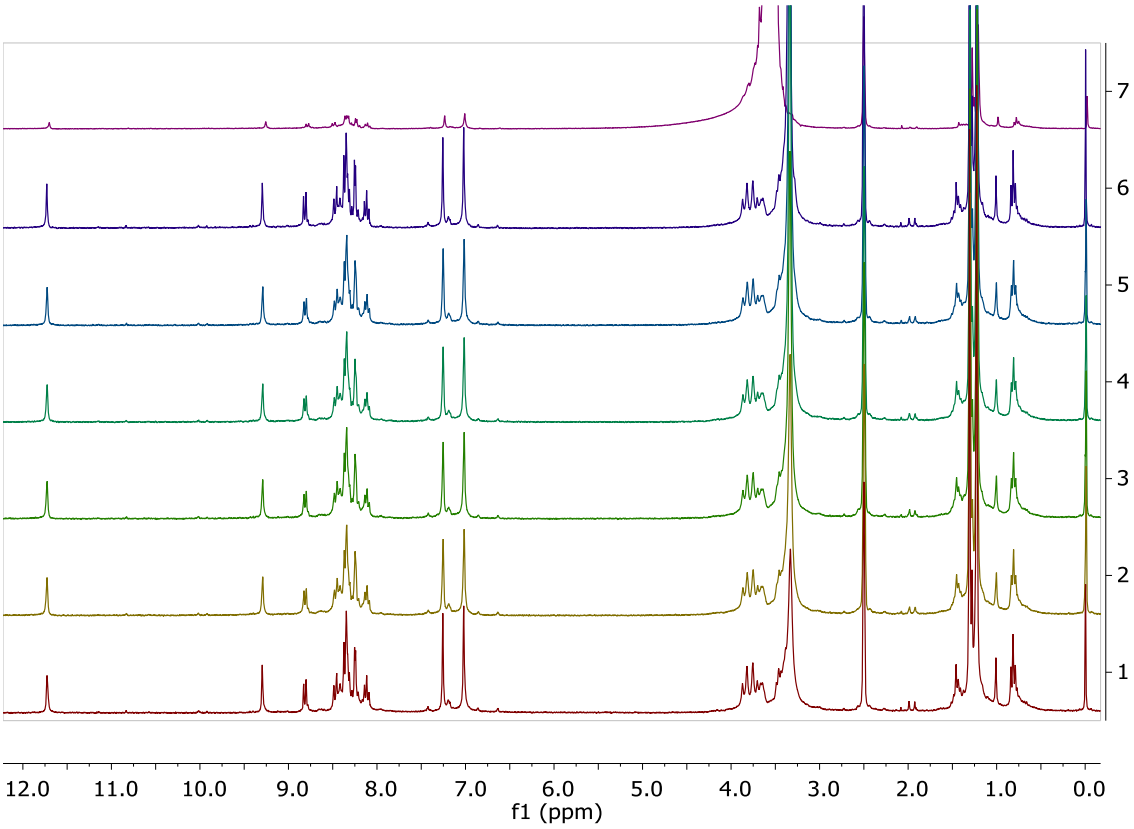

Fig. S12 ^{1}H NMR titration of receptor I (6 mM) in DMSO-d$_6$ upon addition of Ni^{2+}: (a) 0.0, (b) 0.2, (c) 0.4, (d) 0.6, (e) 0.8, (f) 1.0, and (g) 2.0 equiv

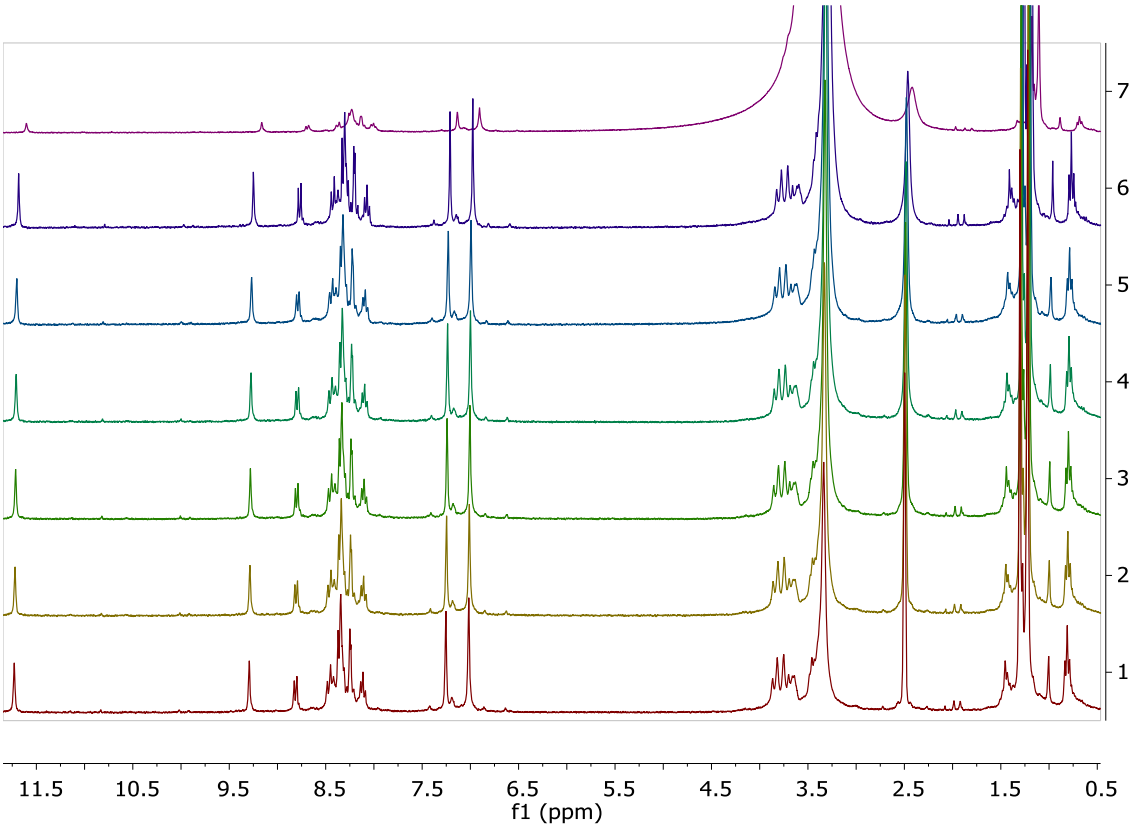

Fig. S13 ^{1}H NMR titration of receptor I (6 mM) in DMSO-d$_6$ upon addition of Cu^{2+}: (a) 0.0, (b) 0.2, (c) 0.4, (d) 0.6, (e) 0.8, (f) 1.0, and (g) 2.0 equiv

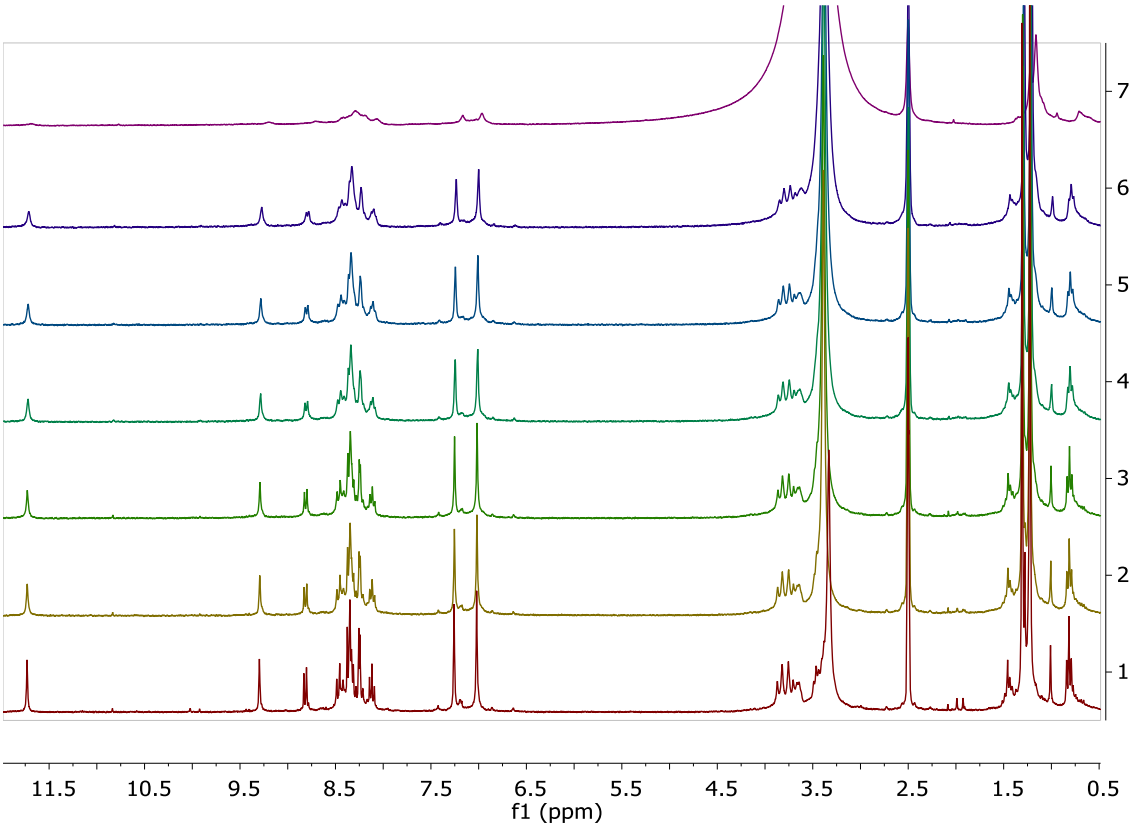

Fig. S14 the FT-IR spectra of (a) receptor I, (b) receptor I–Cd(II), (c) receptor I–Cu(II), and (d) receptor I–Ni(II)