Electronic Supplementary Information

A novel fluorescent peptidyl probe for highly sensitive and selective ratiometric detection of Cd(II) in aqueous and bio-samples via metal ion-mediated self-assembly

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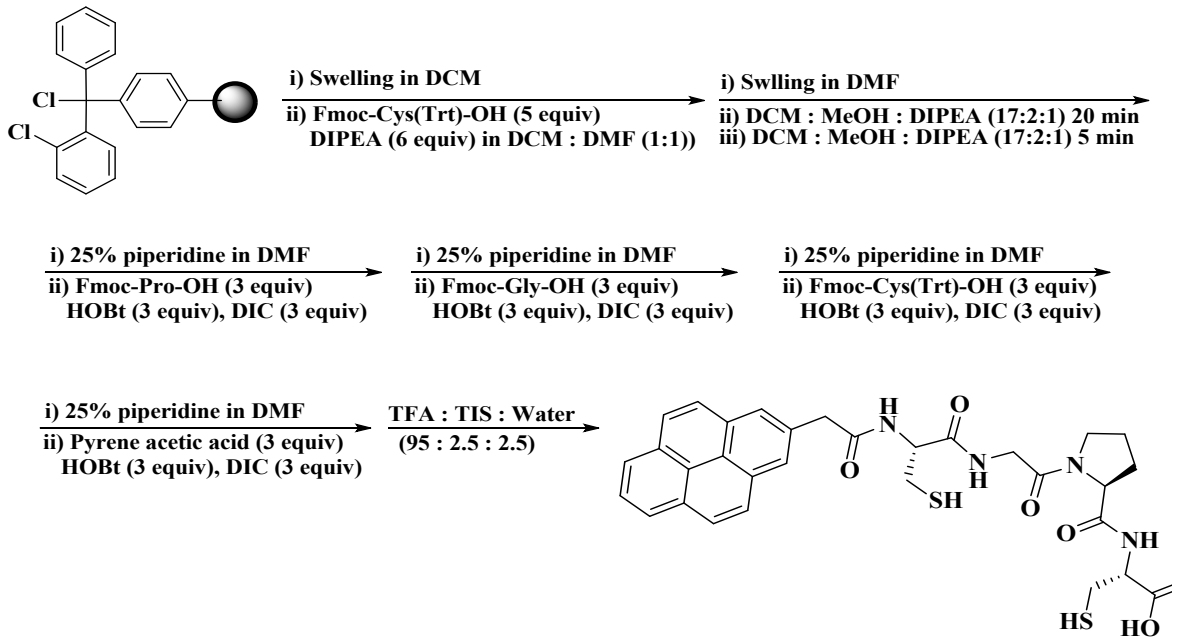


Scheme S1. Synthetic scheme of **1**.

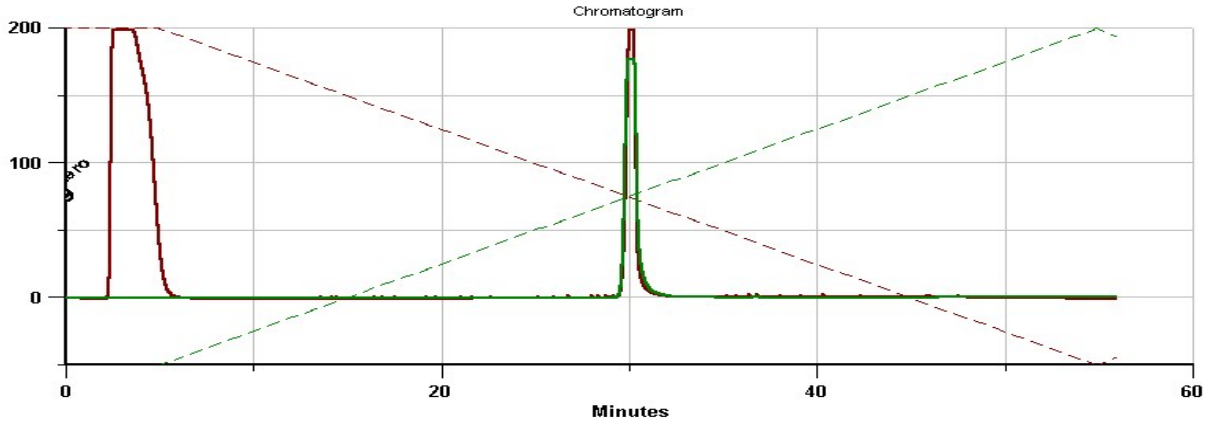


Figure S1. HPLC chromatogram of **1**.

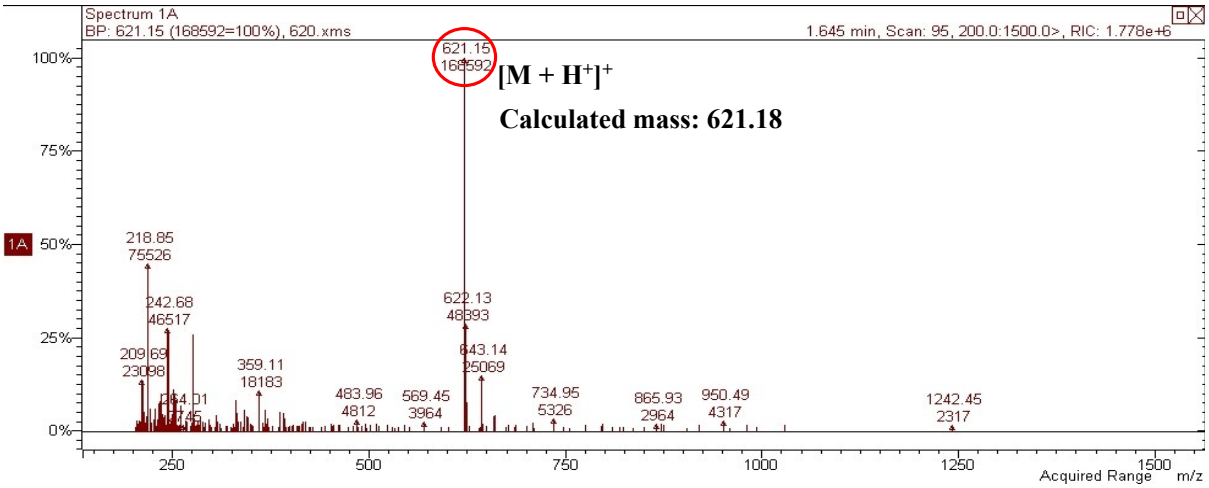


Figure S2. ESI-Mass spectrum of **1**.

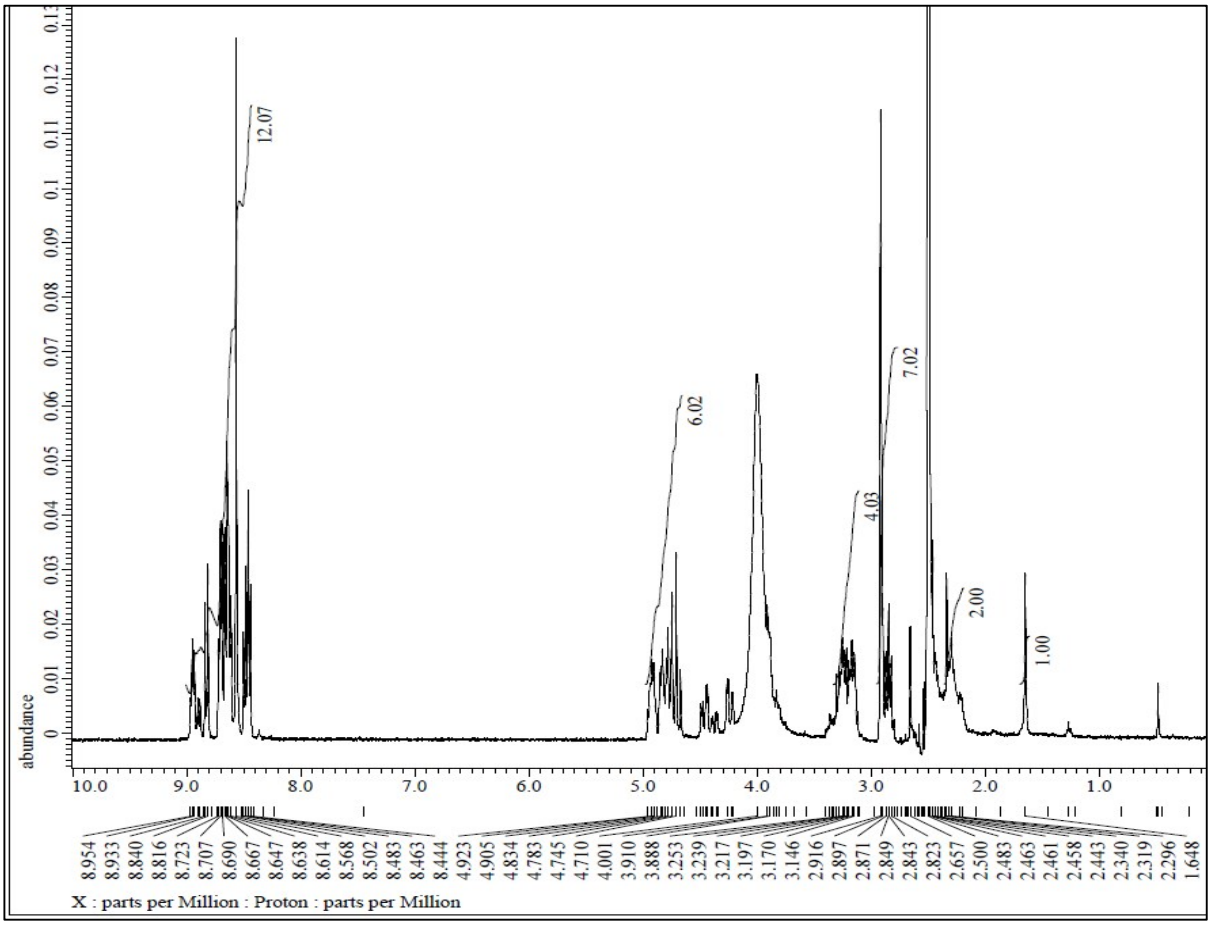


Figure S3. ^{1}H NMR of **1**.

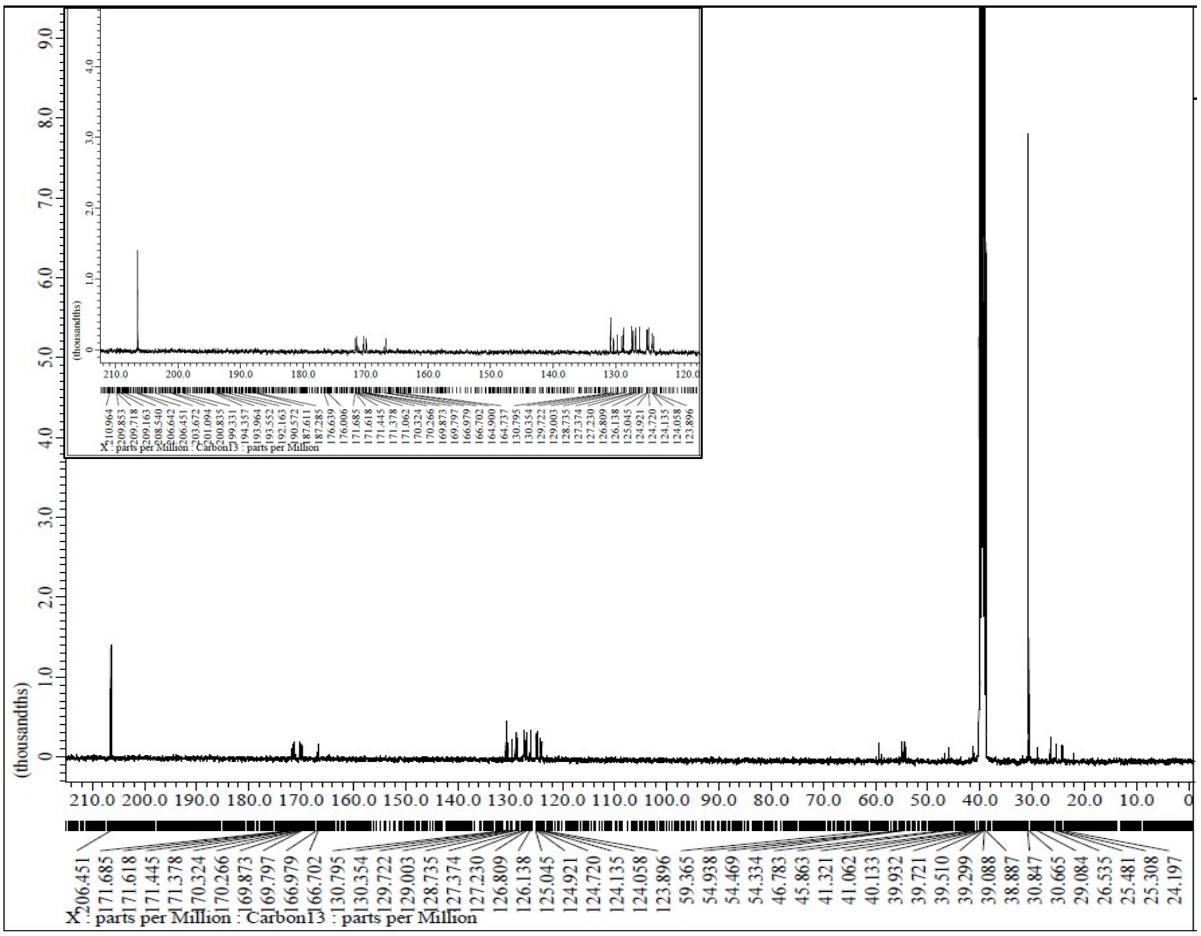


Figure S4. ^{13}C NMR of **1**.

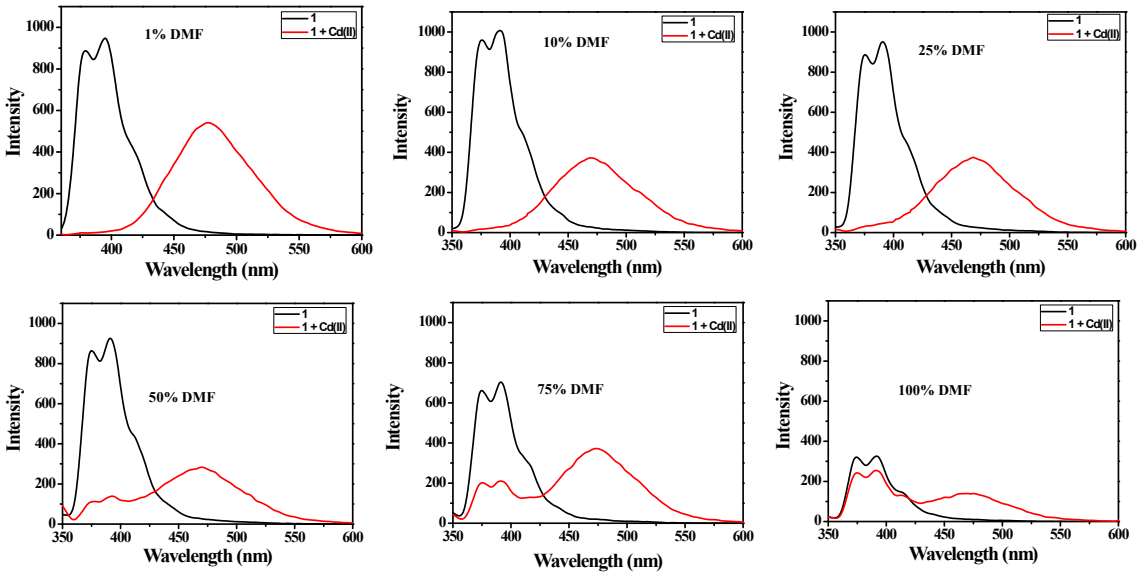


Figure S5. Fluorescence emission spectra of **1** (15 μM) with Cd^{2+} (15 μM) in aqueous buffered solutions (10 mM, HEPES, pH 7.4) containing various volume of DMF.

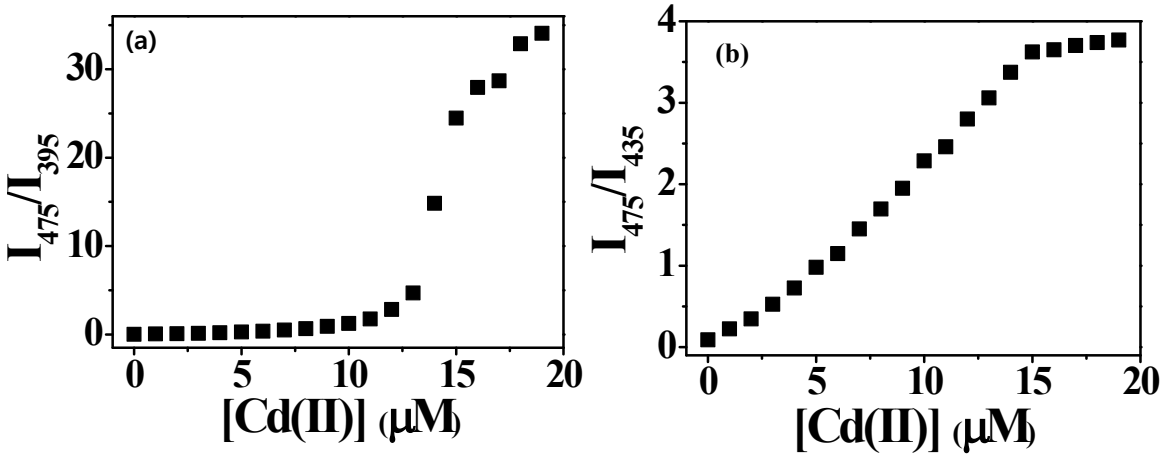


Figure S6. Intensity ratio change (a, I_{475}/I_{395}; b, I_{475}/I_{433}) of **1** (15 μM) as a function of Cd^{2+} in aqueous buffered solution (10 mM HEPES, pH 7.4) containing 1% DMF (λ_{ex} = 342 nm).

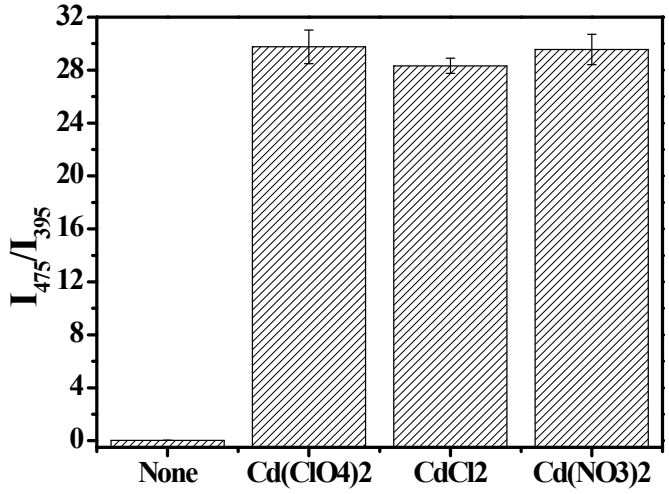


Figure S7. Emission intensity ratio of **1** (10 μM) induced by various sources of Cd^{2+} (1 equiv) in aqueous buffered solution (10mM HEPES, pH 7.4) containing 1% DMF .

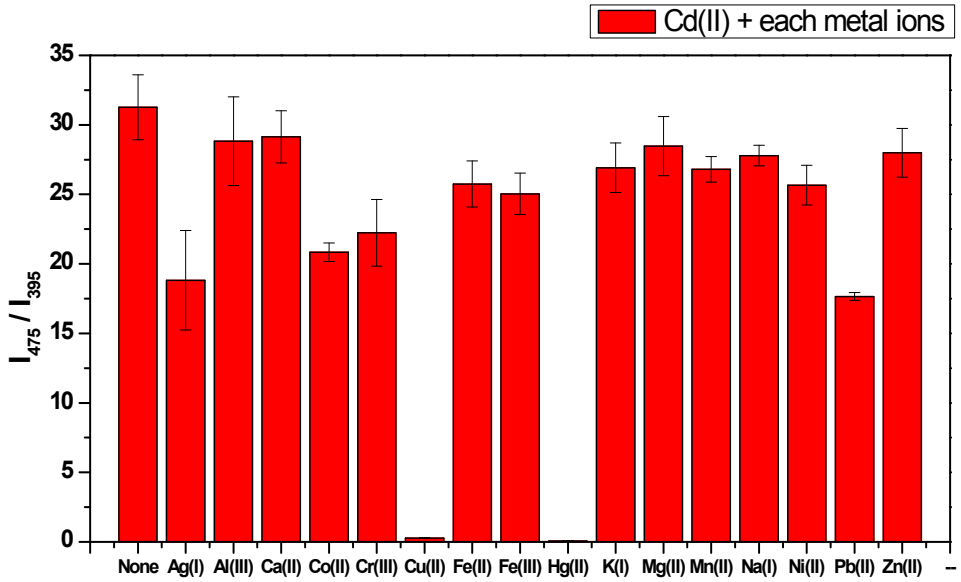


Figure S8. Emission intensity ratio of **1** (15 μM) in the presence of Cd^{2+} (1 equiv) and various metal ions (5 equiv) in aqueous buffered solution (10mM HEPES, pH 7.4) containing 1% DMF.

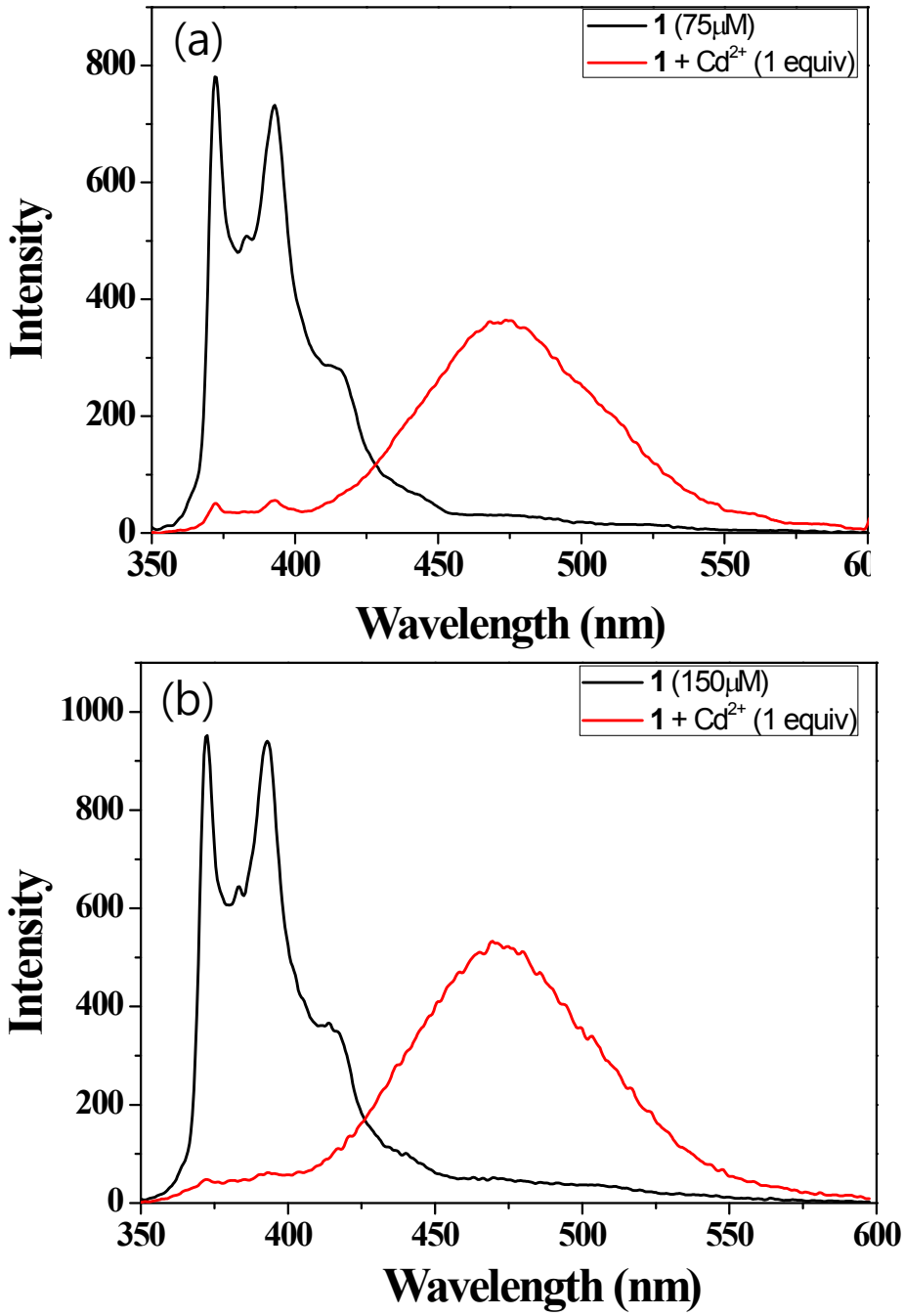


Figure S9. Fluorescence emission spectra of **1** (a; 75 μM, b; 150 μM) in the absence and presence of Cd^{2+} (1 equiv) in aqueous buffered solutions (2 mM, HEPES, pH 7.4) containing 3% DMF (λ_{ex} = 342 nm).

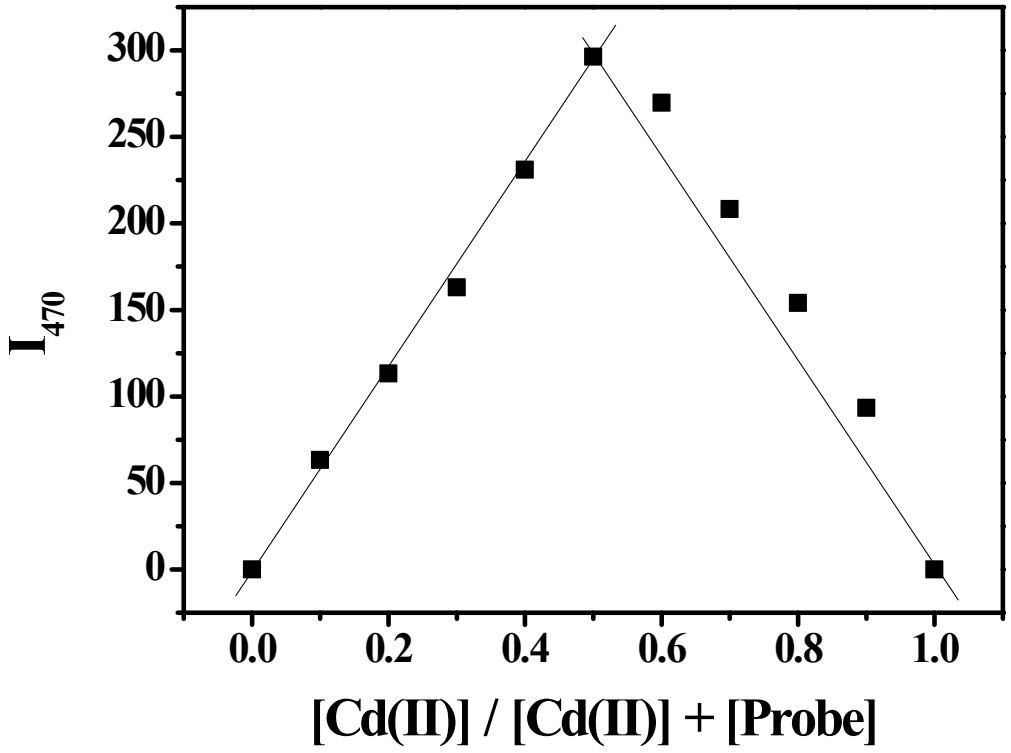


Figure S10. Job's plot for **1** with Cd^{2+} in aqueous buffered solution (10 mM HEPES, pH 7.4) containing 1% DMF; total concentration = 15 μM, slit 15/12 nm, 1% attenuator (λ_{ex} = 342 nm).

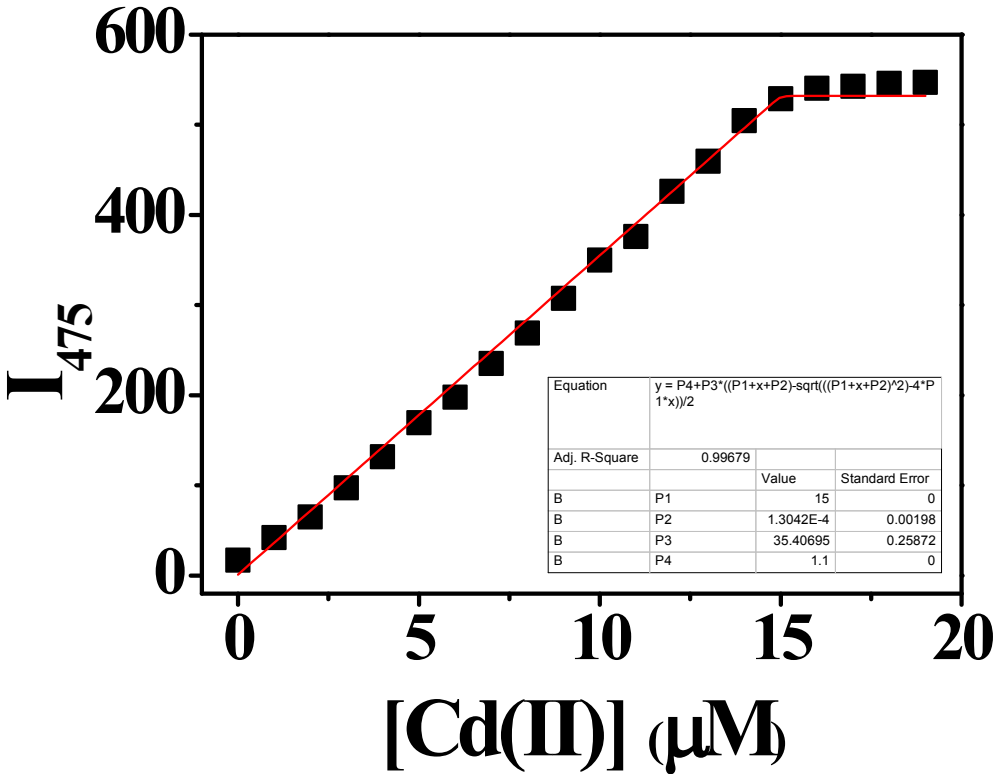


Figure S11. Non-linear least square fitting of the emission intenisty of **1** (15 μM) as a fucntion of cocentration of Cd^{2+} by a 1:1 complex model.

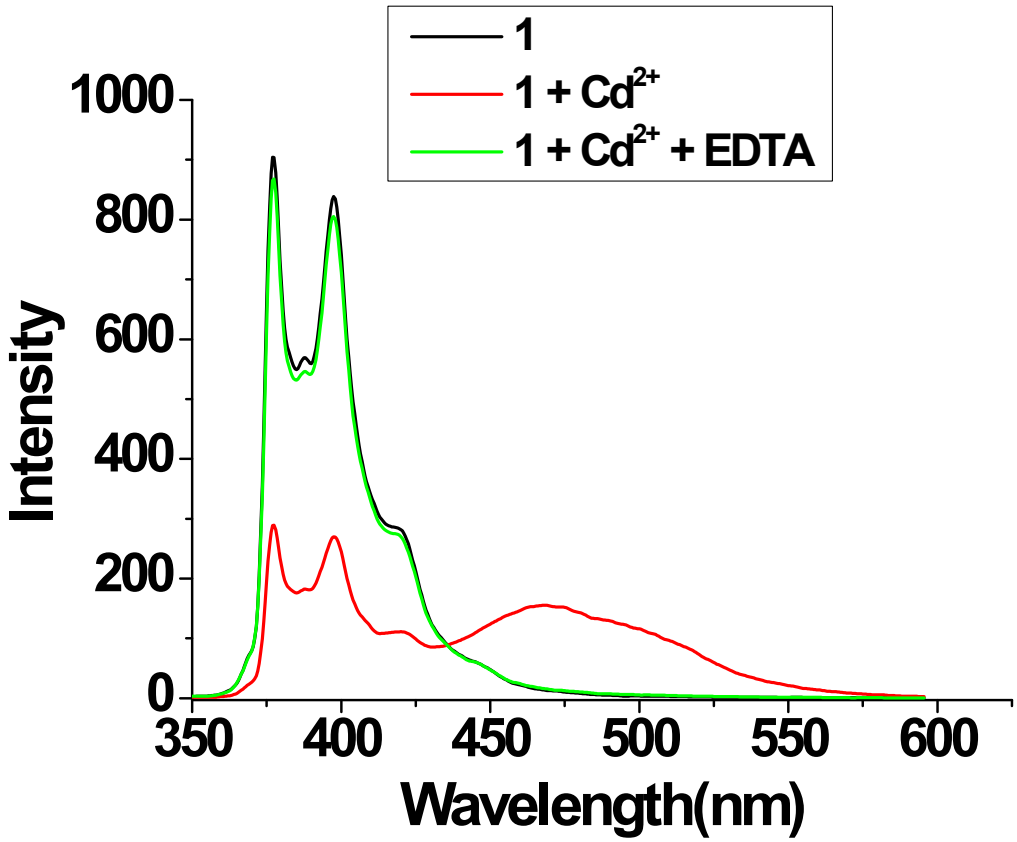


Figure S12. Fluorescence emission spectra of **1** (10 μM) in the absence and presence of Cd^{2+} (1 equiv) and EDTA (1 equiv) in aqueous buffered solutions (10 mM, HEPES, pH 7.4) containing 1% DMF (λ_{ex} = 342 nm).

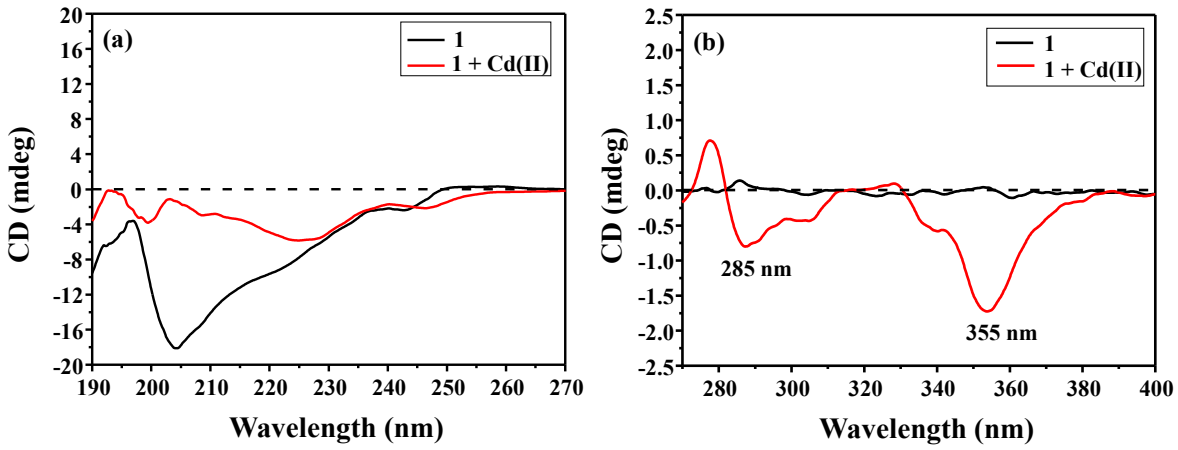


Figure S13. (a) Far- and (b) Near-UV CD Spectra of **1** (75 μM) in the absence or presence of Cd^{2+} (75 μM) in aqueous buffered solutions (10 mM PBS, pH 7.4) containing 5% (v/v) 2,2,2-trifluoroethanol.

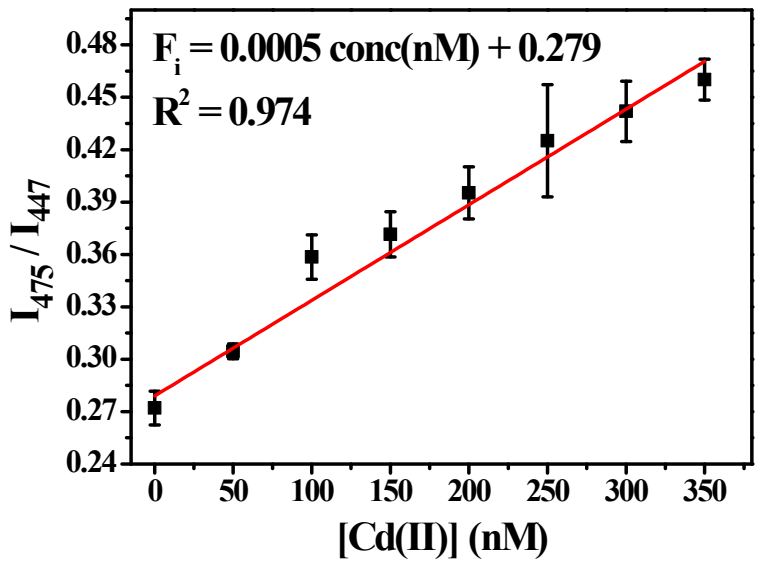


Figure S14. Linear curve fitting of emission intensity ratio change of **1** (15 μM) as a function of the concentration of Cd^{2+} in aqueous buffered solutions (10 mM, HEPES, pH 7.4) containing urine samples.

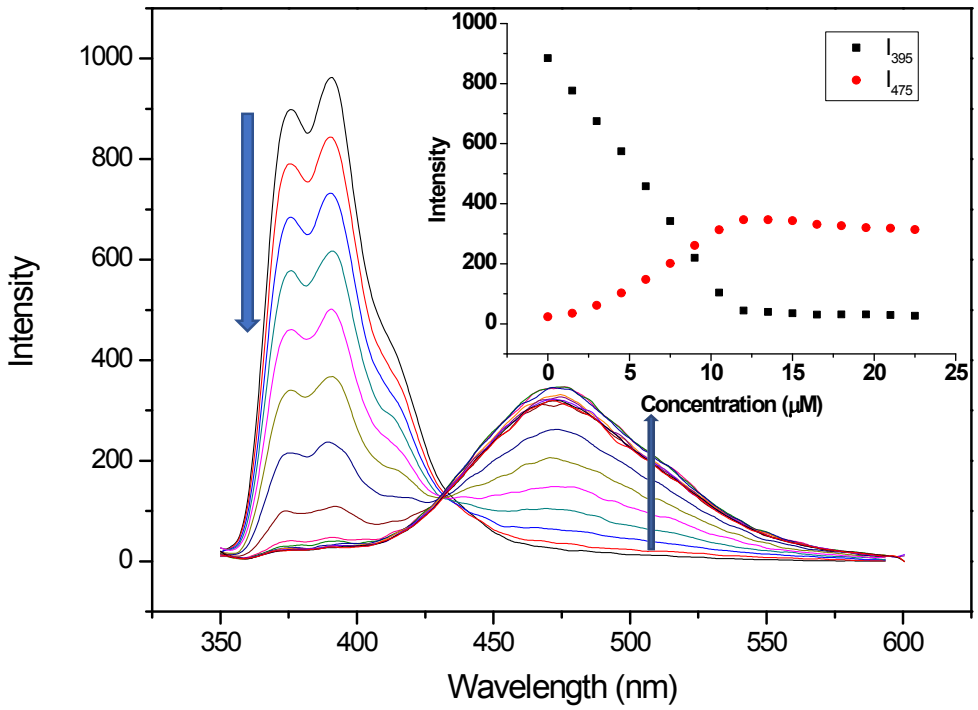
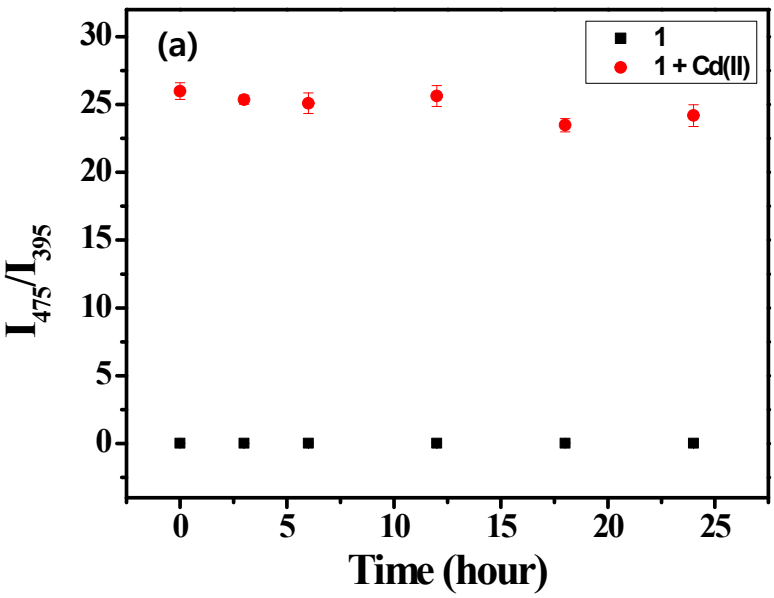


Figure S15. Emission spectra of **1** (15 μM) with increasing concentration of Cd^{2+} in aqueous buffered solutions (10 mM HEPES, pH 7.4) containing ground waters.



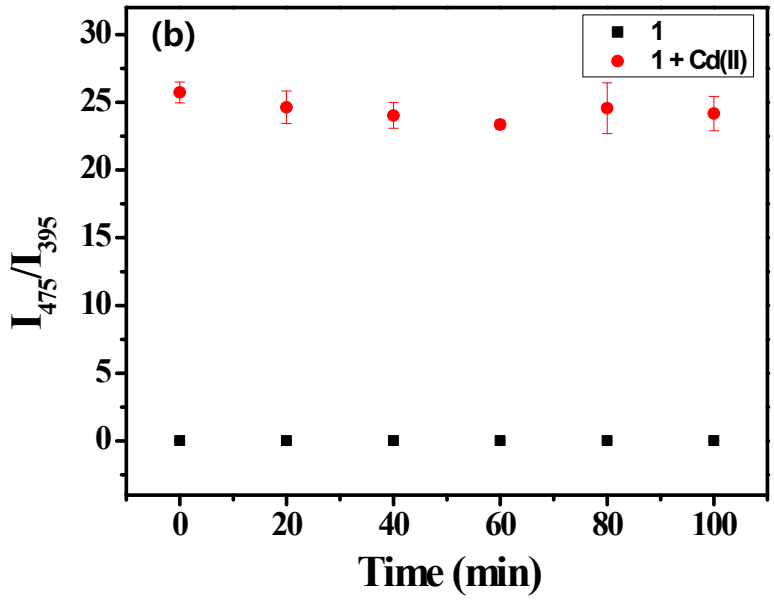


Figure S16. (a) Incubation of stock solution of **1** at room temperature for 24 hrs and emission intensity ratio of **1** (15 μM) by Cd^{2+} (15 μM) (b) Upon addition of Cd^{2+} into the solution containing **1**, emission intesnity ratio induced by Cd^{2+} for 100 mins in aqueous buffered solutions (10 mM, HEPES, pH 7.4) containing 1% DMF.

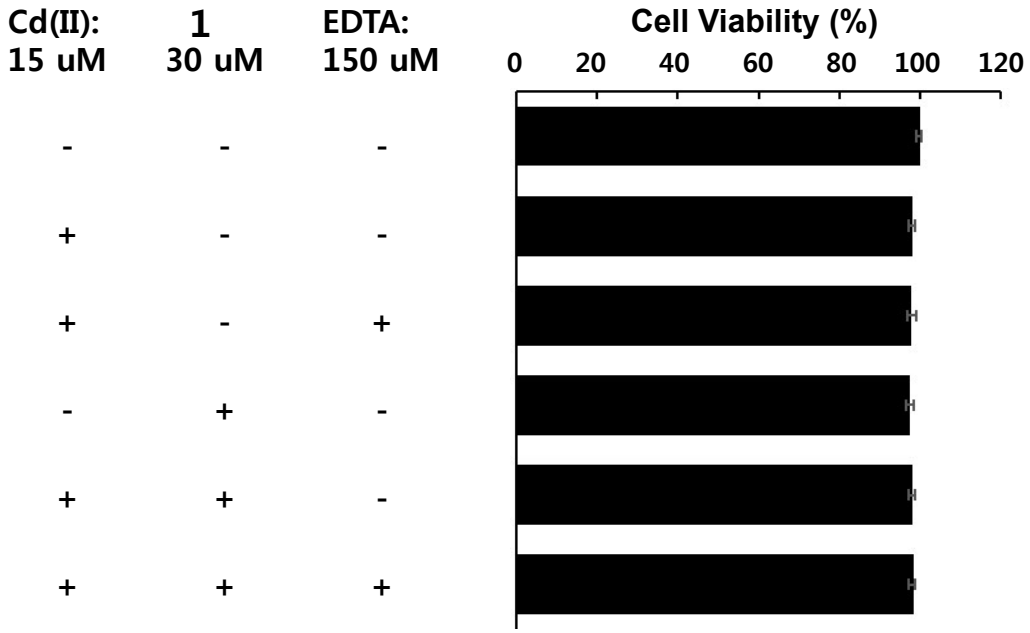


Figure S17. MTS assay for the viability of MDA-MB-231 cells in DMEM 10% FBS treated with **1**, **1** + $Cd(ClO_4)_2$, and **1** + $Cd(ClO_4)_2$ + EDTA for 24 h.

Table S1 Comparison of the properties of ratiometric fluorescent probes for Cd(II) in aqueous solution.[1-11]

Fluorophore(s)	Organic cosolvent	Emission bands (nm)	Change (fold)	LOD	Response	Application
Dansyl Trp	0%	350 to 500	9	0.9 μM	Hg(II), Zn(II), Ag(I)	No cell image
Dansyl Trp	0%	350 to 500	4	0.3 μM	Cu(II), Zn(II)	No cell image
5-Dimethylamino-2-(2-pyridinyl)-benzoimidazole)	0%	493 to 587	8	0.3 pM	Zn(II)	Cell image
Coumarin	0%	328 to 368	3.5	40 pM	Zn(II)	Cell image
4,5-Diamino-1,8-naphthalimide	10% EtOH	487 to 531	3	0.1 μM	Zn(II)	No cell image
Boradiazaindacene (BODIPY)	90% Acetone	550 to 800	13	ND[a]	Cr(III), Ni(II), Cu(II)	Cell image
8-Hydroxyquinoline norbornene	50% Methanol	330 to 600	2	1.6 nM	Zn(II)	Paper strip
8-Hydroxyquinoline	80% Ethanol	350 to 650	4.5	23.6 nM	Zn(II)	Cell image
8-Hydroxy-2-methyl quinoline	80% Dioxane	400 to 700	92	20 nM	Cu(II), Zn(II)	No cell image
4-Isobutoxy-6-(dimethylamino)-8-methoxyquinaldine	0%	400 to 700	3	9.6 pM	Mn(II),Fe(II),Co(II),Ni(II), Cu(II), Hg(II), Pb(II), Zn(II)	Cell image
Phenanthro[9,10-d]oxazole	50% DMF	400 to 600	ND[a]	ND[a]	Fe(III), Hg(II), Pb(II),Cu(II)	Paper strip
Pyrene (Present work)	1% DMF	395 to 475	28	22 nM	Only Cd(II)	Cell image, Urine

[a]ND means not determined.

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