Rhodamine based biocompatible chemosensor for Al^{3+}, Cr^{3+} and Fe^{3+} ions: extraordinary fluorescence enhancement and precursor for future chemosensors

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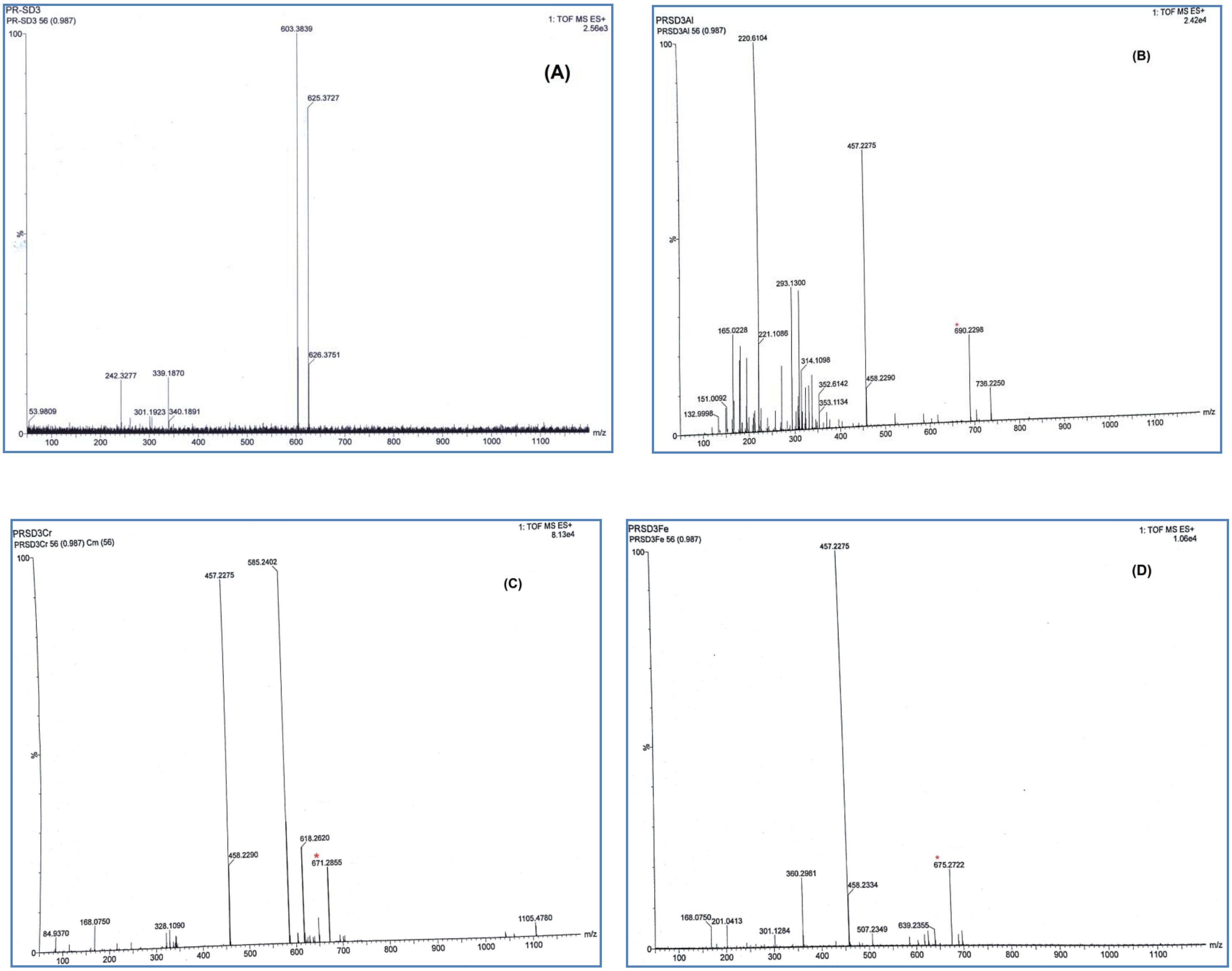


Fig. s1 ESI mass spectrum of (A) HL-CHO, (B) Al^{3+} complex of HL-CHO, (C) Cr^{3+} complex of HL-CHO and (D) Fe^{3+} complex of HL-CHO.

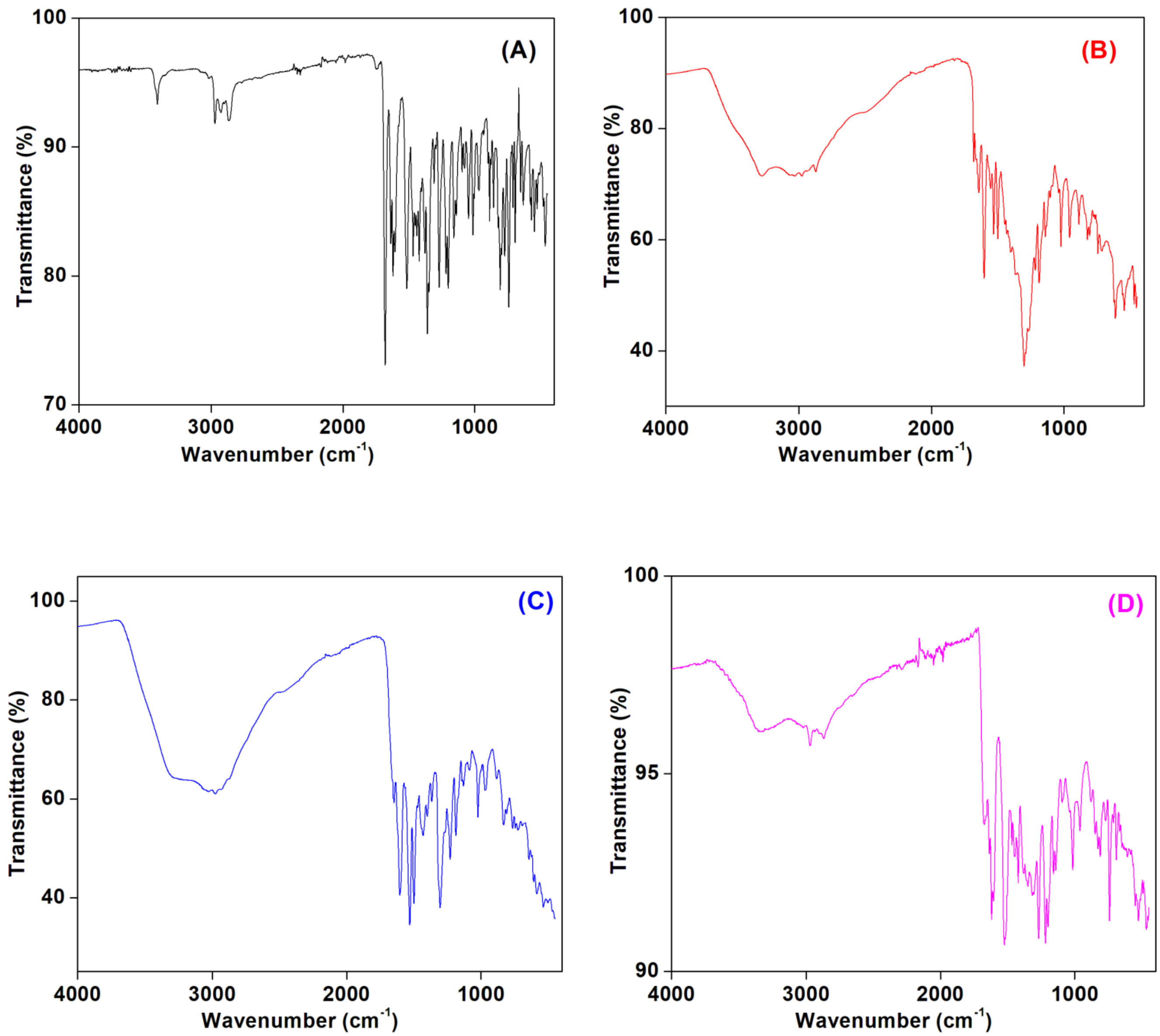


Fig. s2 FT-IR spectrum of (A) HL-CHO, (B) Al^{3+} complex of HL-CHO, (C) Cr^{3+} complex of HL-CHO and (D) Fe^{3+} complex of HL-CHO.

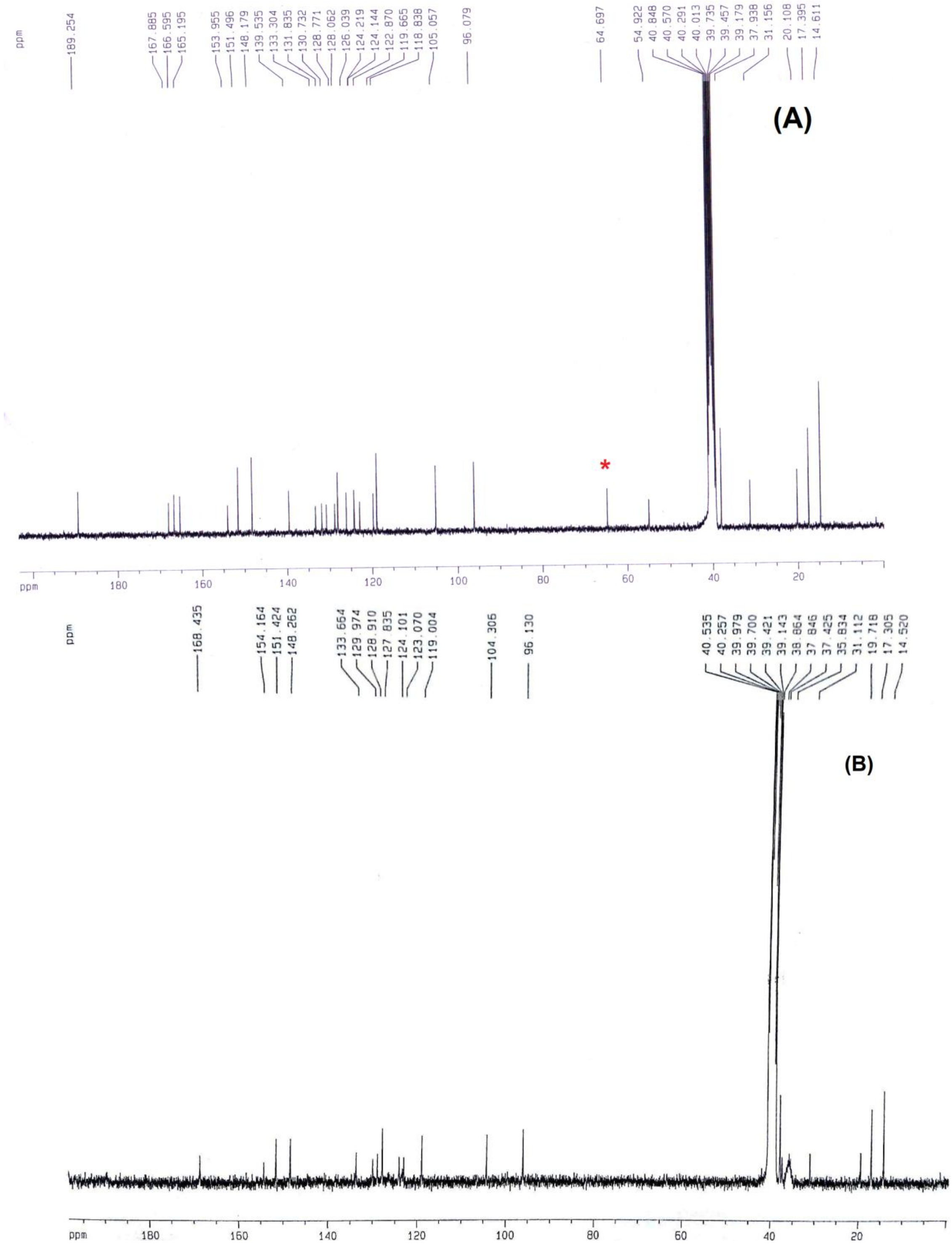
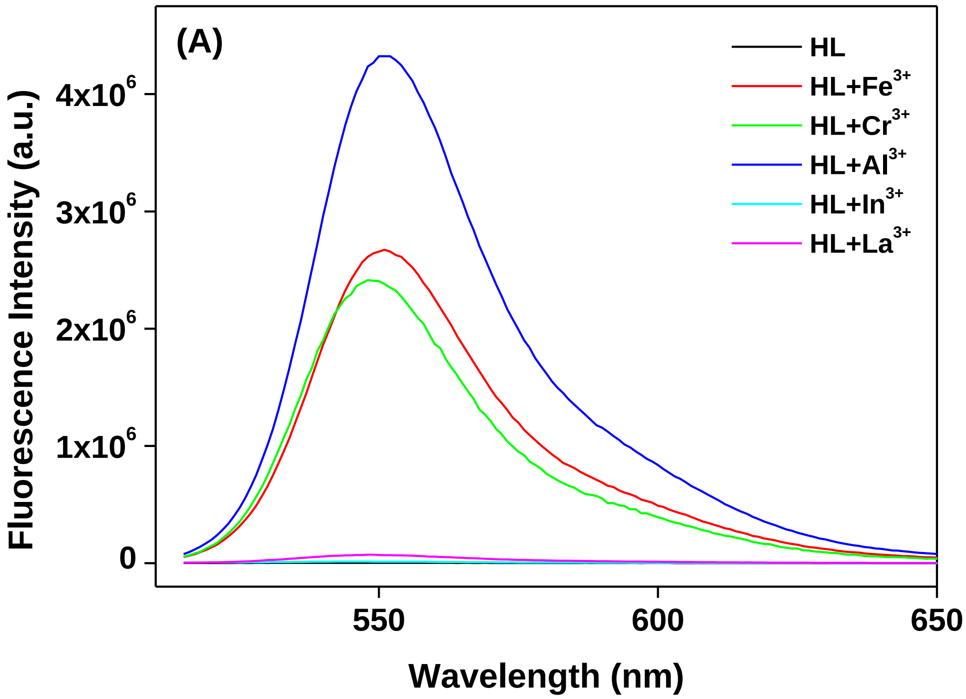


Fig. s3 ^{13}C NMR spectrum of (A) HL-CHO in DMSO-d_6 and (B) HL-CHO in the presence of Al^{3+} ion in DMSO-d_6.



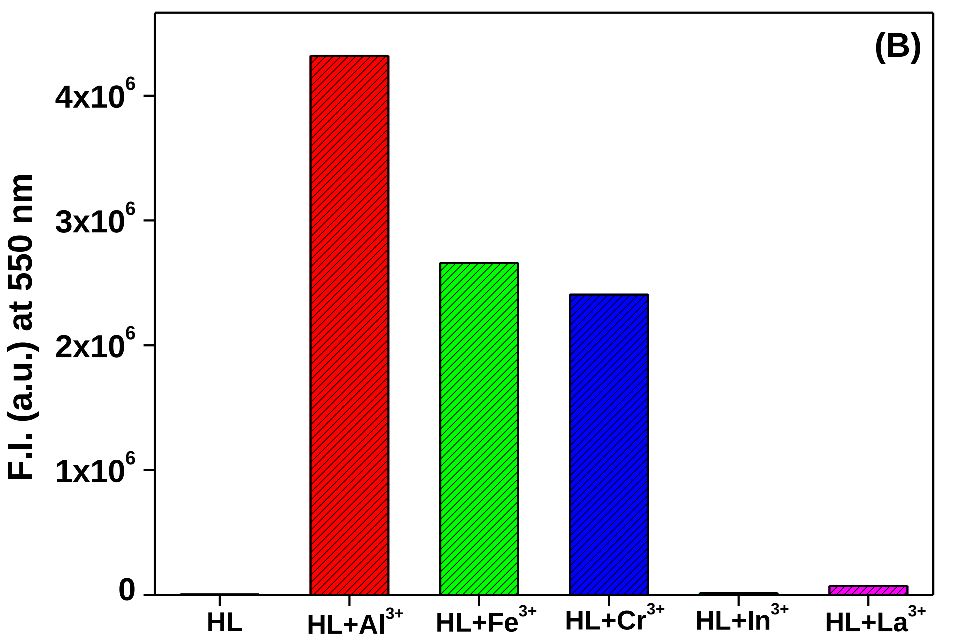


Fig. s4 (A) Fluorescence intensity of HL-CHO (40 μM) at 550 nm in the presence of one equivalent of different trivalent metal ions in 10 mM HEPES buffer in water:methanol (1:9) (pH 7.4) at room temperature; (B) Same result represented as bar diagram. Here, HL denotes HL-CHO.

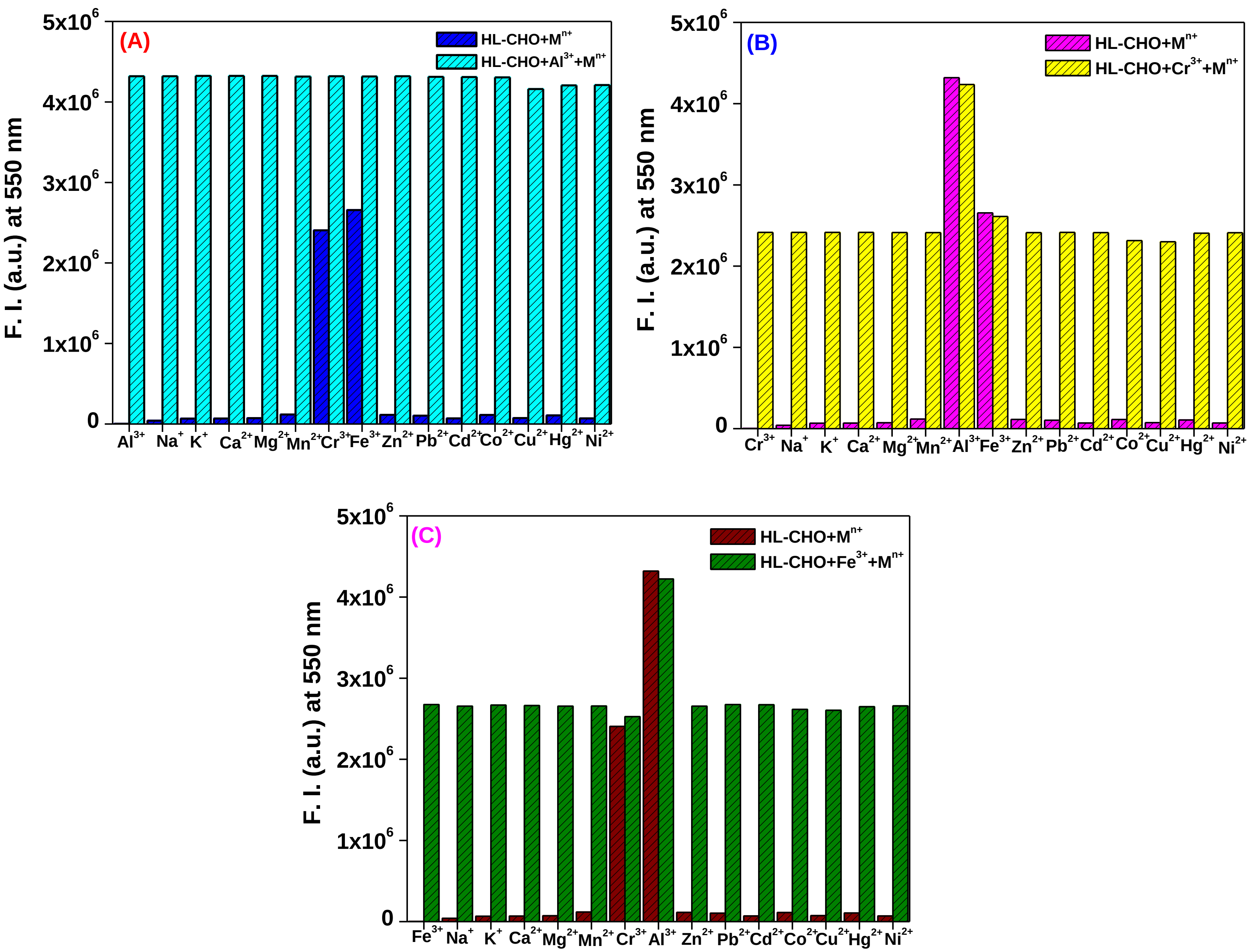


Fig. s5 Fluorescence intensity of HL-CHO with (A) Al^{3+}, (B) Cr^{3+} and (C) Fe^{3+} ions in the presence of five equivalent of other metal ions in 10 mM HEPES buffer.4 in H_2O:methanol (1:9, *v/v*) (pH 7) at room temperature.

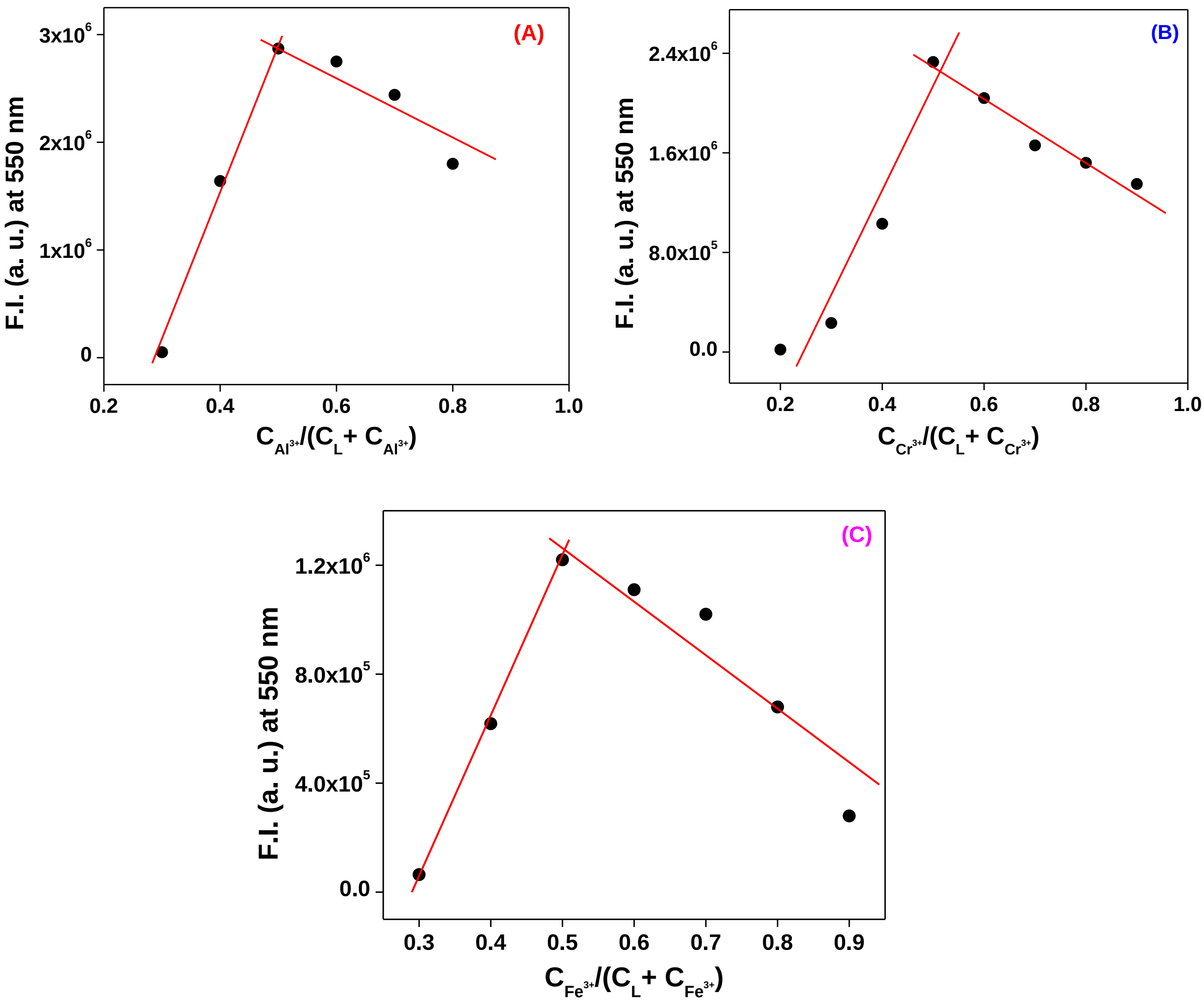


Fig. s6 Job's plot analysis with (A) Al^{3+}, (B) Cr^{3+} and (C) Fe^{3+} ions. Analysis shows 1:1 binding with HL-CHO. Here, L denotes HL-CHO.

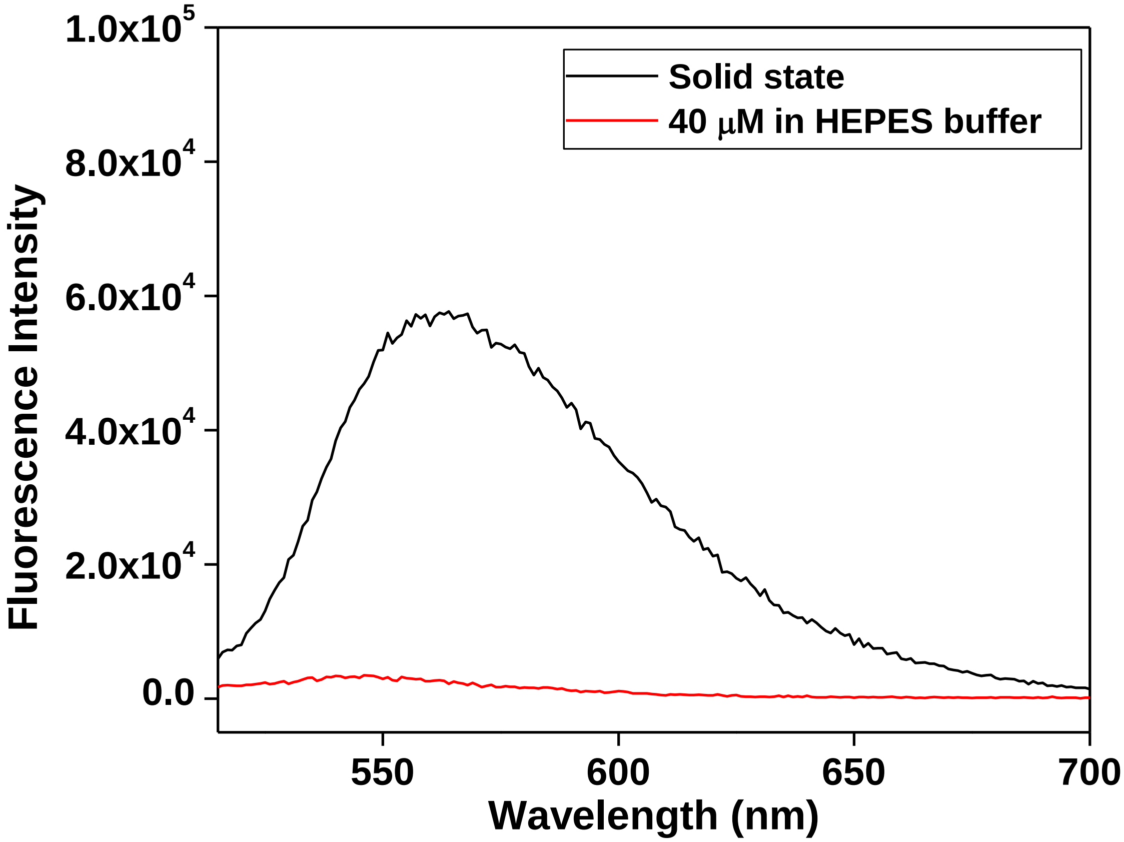


Fig. s7 Fluorescence spectrum of HL-CHO in solid state and in solution (HEPES buffer)

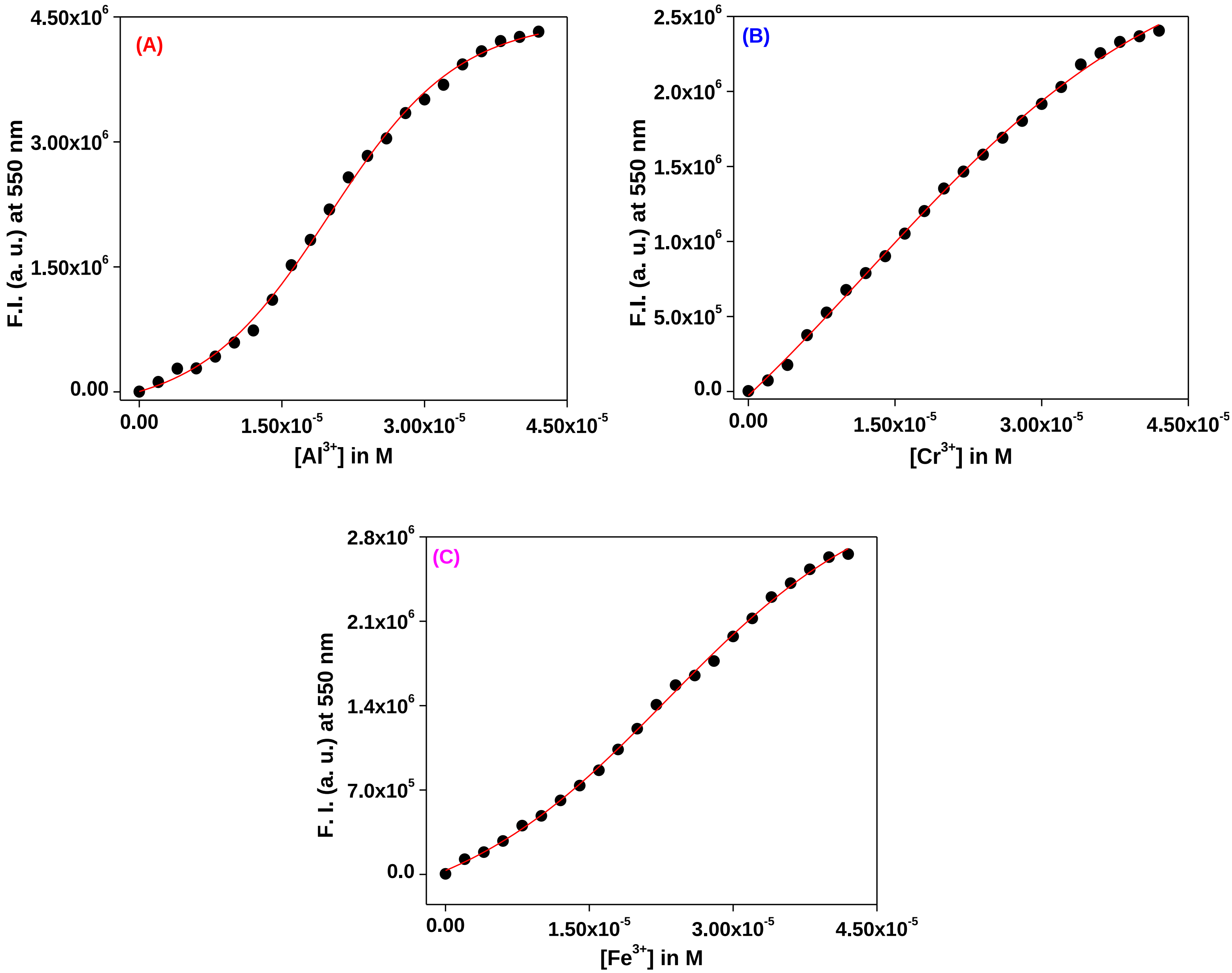


Fig. s8 Non-linear plot of fluorescence intensity (at 550 nm) vs. (A) [Al^{3+}], (B) [Cr^{3+}] and (C) [Fe^{3+}]

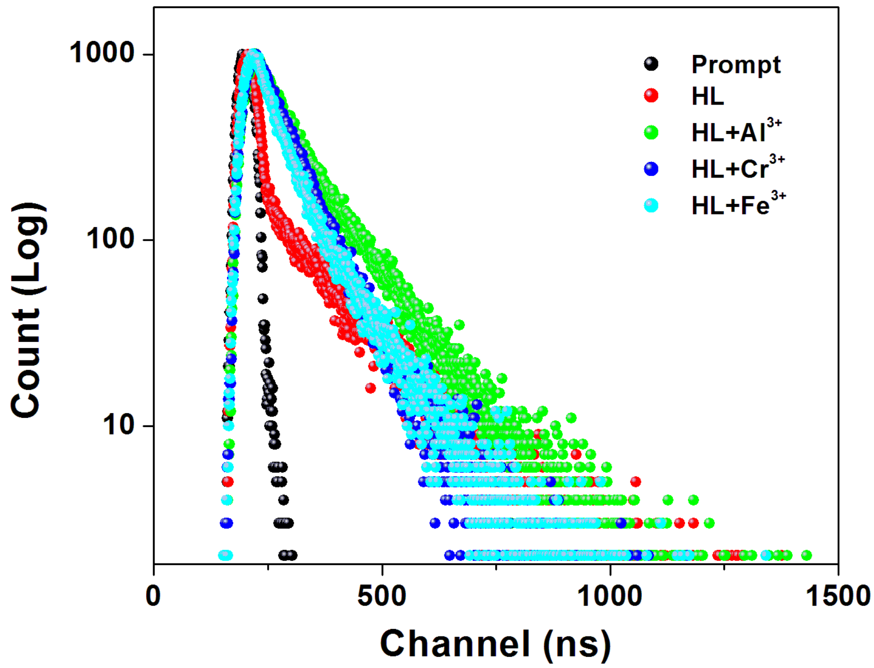


Fig. s9 Excited state fluorescence decay behavior of HL-CHO and its complex with Al^{3+}, Cr^{3+} and Fe^{3+} ions in 10 mM HEPES buffer.4 in H_2O:methanol (1:9, *v/v*) (pH 7) at room temperature. Here, HL denotes HL-CHO.

Determination of LOD of HL:

Limit of detection (LOD) for our probe has been determined by 3σ method by the following equation: DL = K* Sb1/S

where K = 2 or 3 (3 in this case); here Sb1 is the standard deviation of the blank HL-CHO solution; and S is the slope of the calibration curve obtained from Linear dynamic plot of F.I. vs [M^{3+}] in M. From the calculated high LOD values, it can be concluded that HL is a very good sensor for all the cations.

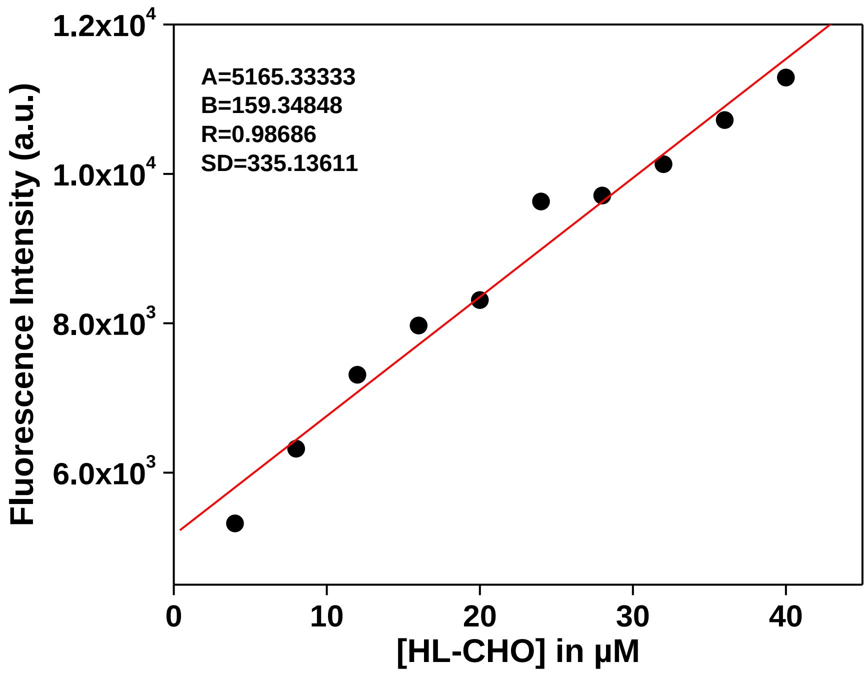


Fig. s10 Determination of Sb1 of the blank, HL-CHO solution.

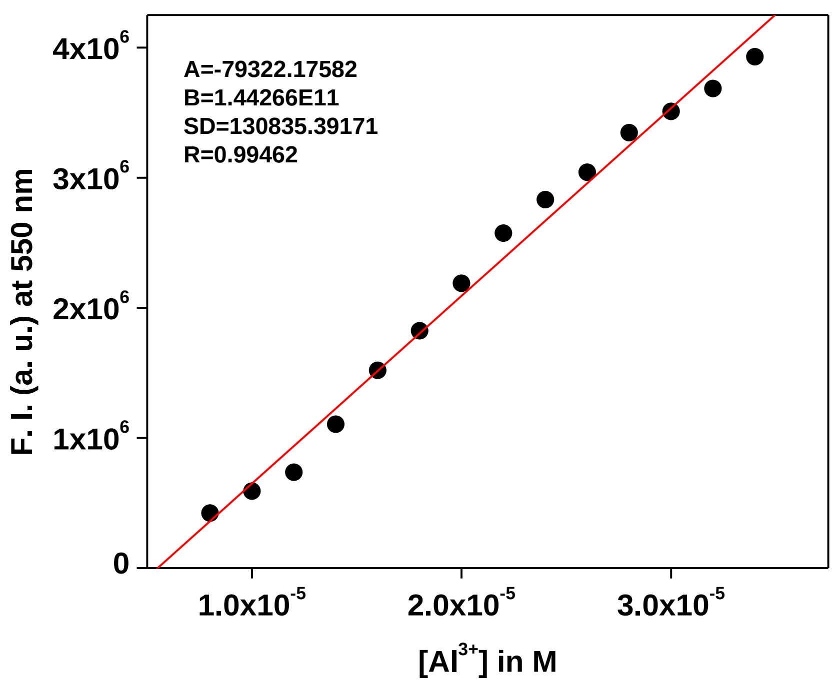


Fig. s11 Linear dynamic plot of F.I. (at 550 nm) vs. [Al^{3+}] for the determination of S (slope)

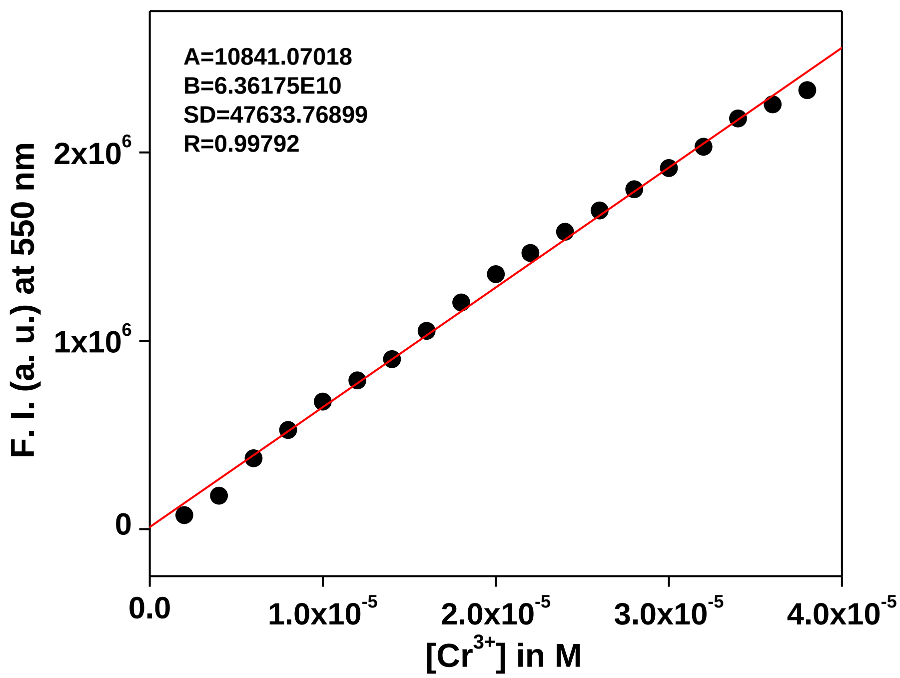


Fig. s12 Linear dynamic plot of F.I. (at 550 nm) vs. [Cr^{3+}] for the determination of S (slope)

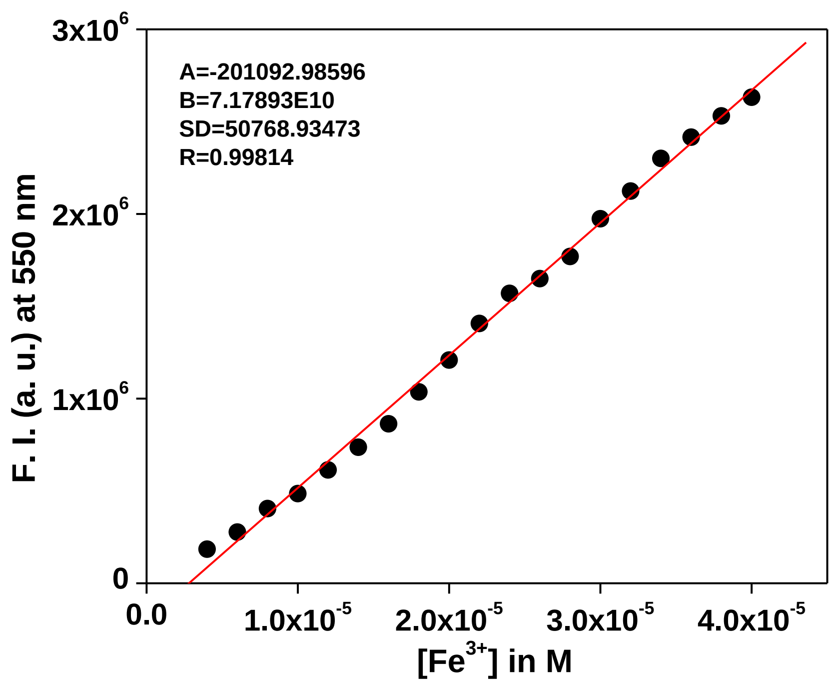


Fig. s13 Linear dynamic plot of F.I. (at 550 nm) vs. [Fe^{3+}] for the determination of S (slope)

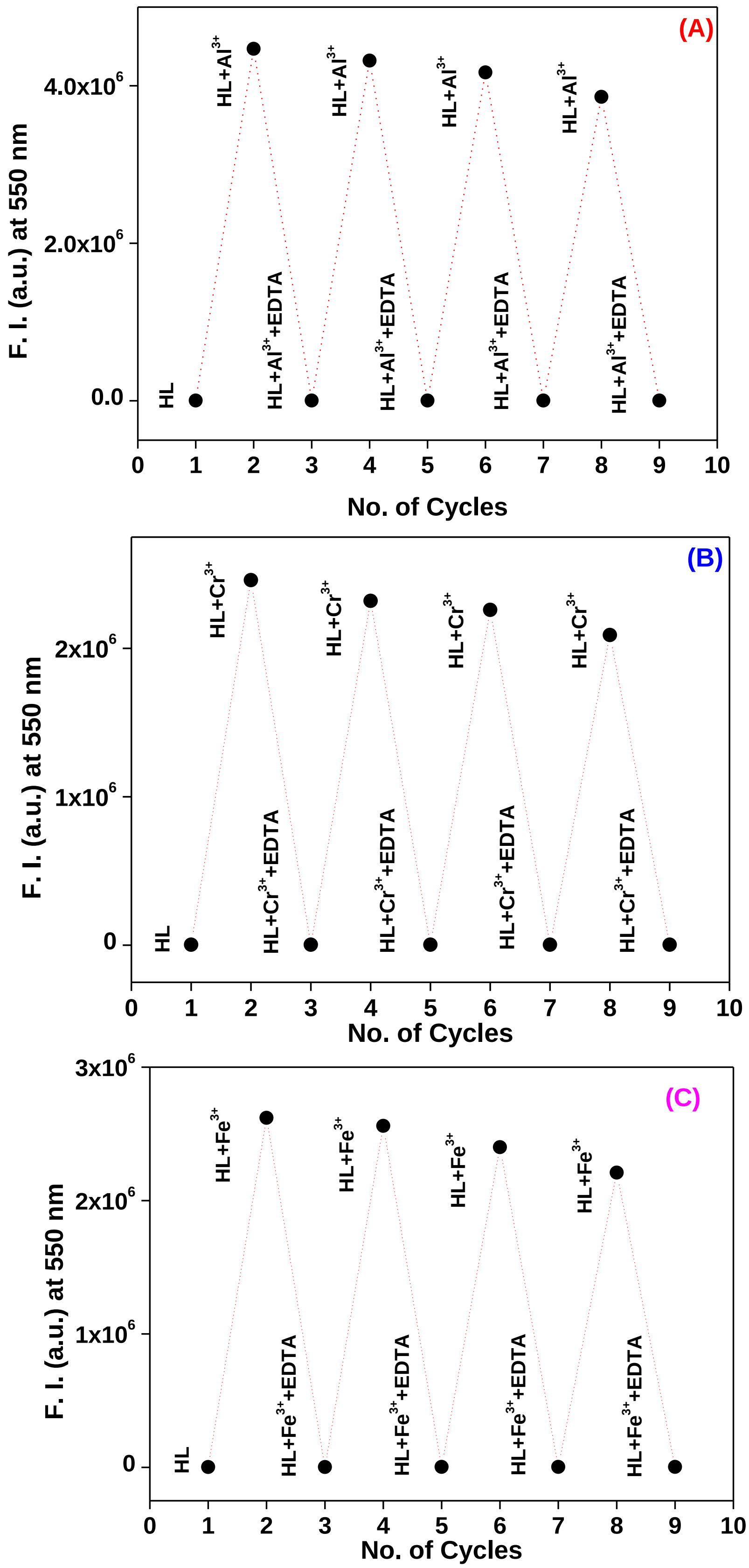


Fig. s14 Fluorescence intensities of HL-CHO + M^{3+} (1 : 1) in the presence of Na_2-EDTA for several cycles. Fluorescence spectra monitored at 550 nm. Here, HL denotes HL-CHO.

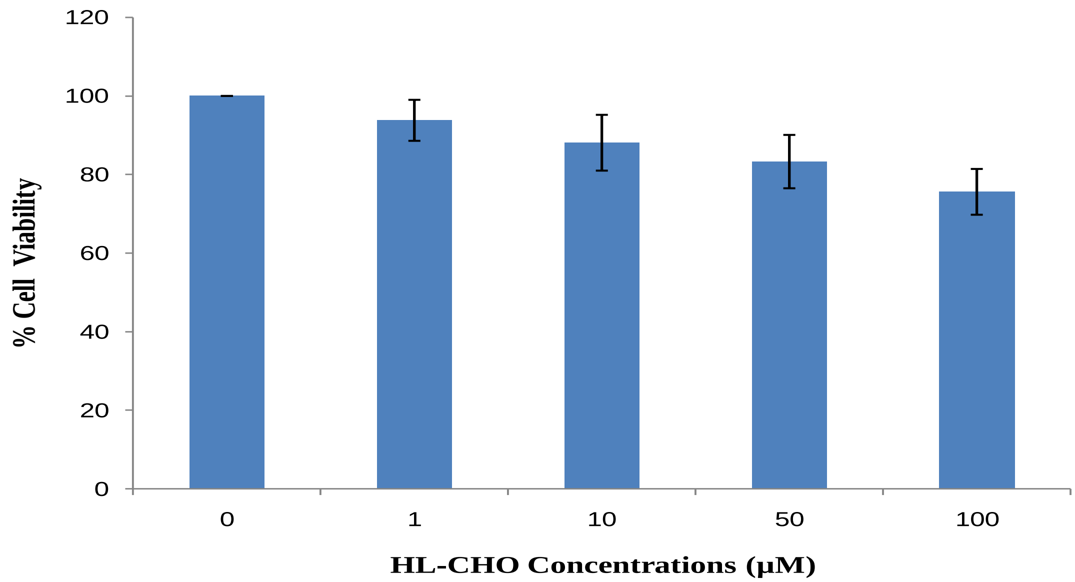
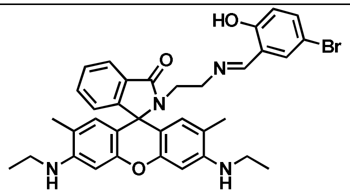
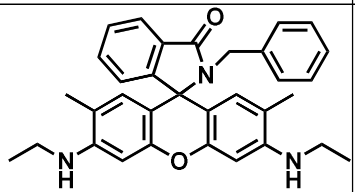
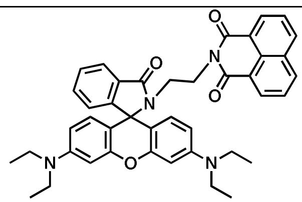
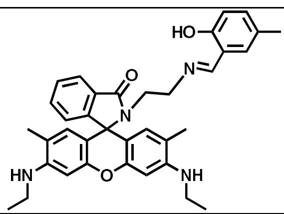
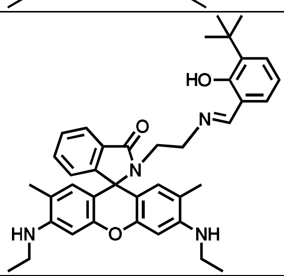


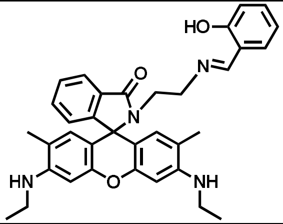
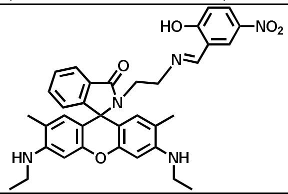
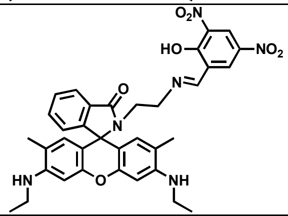
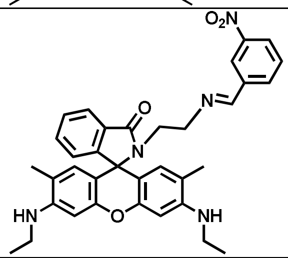
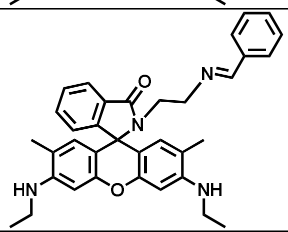
Fig. s15 % cell viability of human neuroblastoma SH-SY5Y cells incubated with different concentrations (1 µM-100 µM) of HL-CHO for 12 h as determined by MTT assay. Results are expressed as mean ± S.E of three independent experiments.

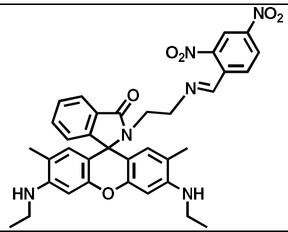
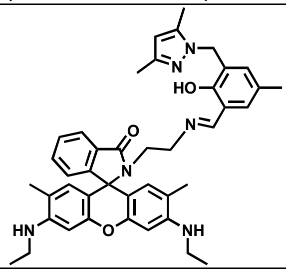
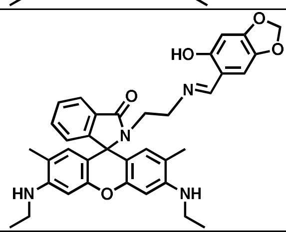
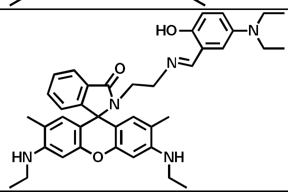
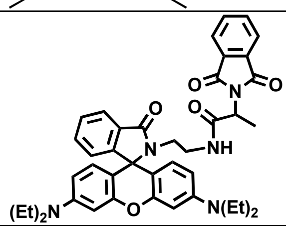
Table S1 Elemental analysis of HL-CHO and its complexes with Al^{3+}, Cr^{3+} and Fe^{3+}

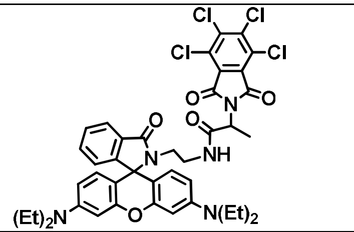
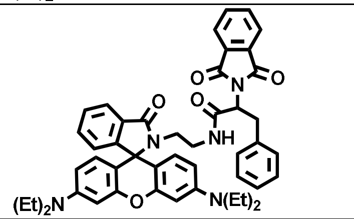
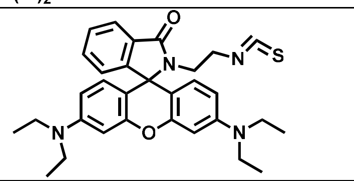
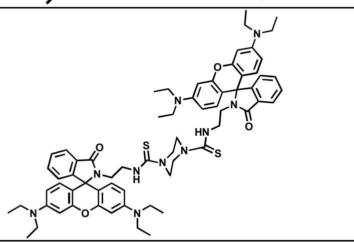
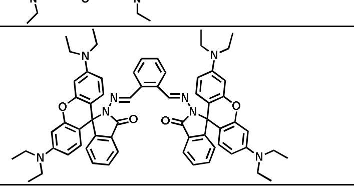
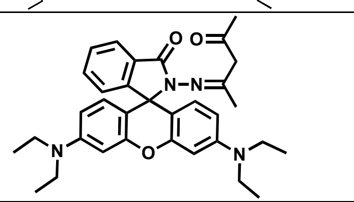
Species	Type	C	H	N
HL-CHO	Calculated	73.73	6.35	9.30
($C_{37}H_{38}N_4O_4$)	Found	73.65	6.26	9.23
HL-CHO + Al^{3+}	Calculated	64.53	5.12	10.17
([Al(L′)NO_3]) ($C_{37}H_{35}AlN_5O_7$)	Found	64.42	4.93	10.12
HL-CHO + Cr^{3+}	Calculated	60.73	5.10	9.57
([Cr(L′)(H_2O)]NO_3) ($C_{37}H_{37}CrN_5O_8$)	Found	60.66	5.02	9.45
HL-CHO + Fe^{3+}	Calculated	60.42	5.07	9.52
([Fe(L′)(H_2O)]NO_3)	Found	60.30	4.98	9.40
($C_{37}H_{37}FeN_5O_8$)				

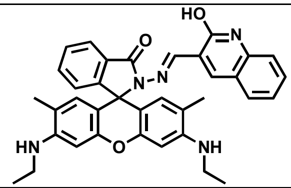
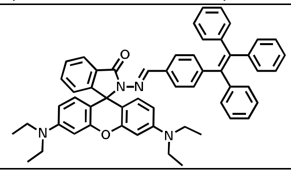
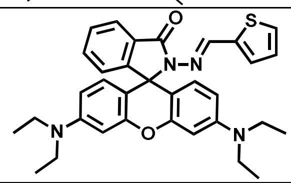
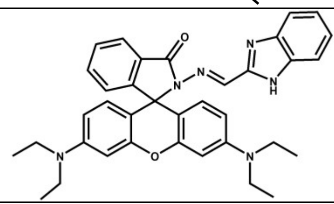
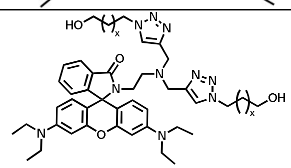
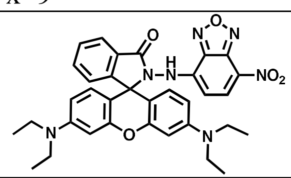
Table S2 Comparison of a few aspects of some recently published related rhodamine based chemosensors

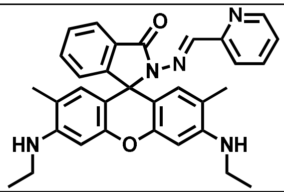
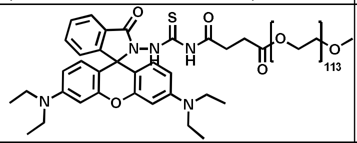
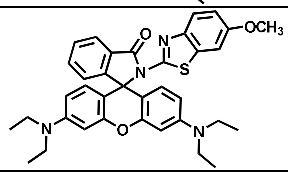
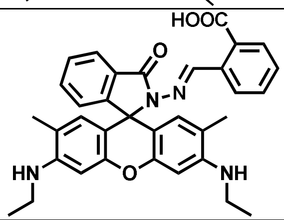
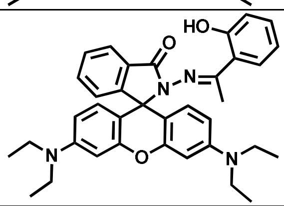
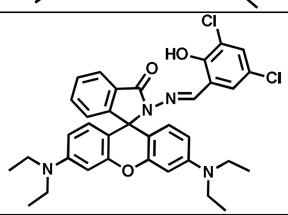
Entry	Probe	Excitation (nm)/ Emission (nm)	Fluorescence Enhancement (fold)	Concerned Cations	LOD	Binding Constant (K_a) or Dissociation Constant (K_d)	Cell Imaging	Ref.
1.		500/552	98 (Al^{3+}) 50 (Cr^{3+}) 38 (Fe^{3+})	Al^{3+}, Cr^{3+}, Fe^{3+}	1.18 nM (Al^{3+}), 1.80 nM (Cr^{3+}), 4.04 nM (Fe^{3+})	K_d= 5.20±0.39 μM (Al^{3+}) = 4.07±0.13 μM (Fe^{3+}) = 6.49±0.21 μM (Cr^{3+})	No	22
2.		502/558	31 (Al^{3+}) 26 (Cr^{3+}) 41 (Fe^{3+})	Al^{3+}, Cr^{3+}, Fe^{3+}	1.34 μM (Al^{3+}), 2.28 μM (Cr^{3+}), 1.28 μM (Fe^{3+})	K_a= (1.34±0.1)×10^4 M^{-1} (Al^{3+}) = (0.94±0.01)×10^4 M^{-1} (Fe^{3+}) = (0.87±0.01)×10^4 M^{-1} (Cr^{3+})	Yes	15c
3.		330/582 (Al^{3+}) 330/376 (Cr^{3+},Fe^{3+})	62 (Al^{3+}) 1.7 (Cr^{3+}) 1.47 (Fe^{3+})	Al^{3+}, Cr^{3+}, Fe^{3+}	1.74 nM (Al^{3+}), 2.36 μM (Cr^{3+}), 2.90 μM (Fe^{3+})	K_a= 1×10^4 M^{-1} (Al^{3+}) = 1.2×10^2 M^{-1} (Fe^{3+}) = 2.6×10^2 M^{-1} (Cr^{3+})	No	15a
4.		500/552	630	Al^{3+}	2.8 nM	K_d = 4.88 (±0.18) μM	Yes	23
5.		500/550 (Al^{3+}) 370/454 (Zn^{2+})	650 (Al^{3+}) 7 (Zn^{2+})	Al^{3+}, Zn^{2+}	10.98 nM (Al^{3+}) 76.92 nM (Zn^{2+})	K_a = 9.38×10^3 M^{-1} (Al^{3+}) = 4.75 × 10^4 M^{-1} (Zn^{2+})	Yes	24

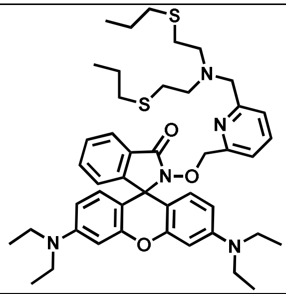
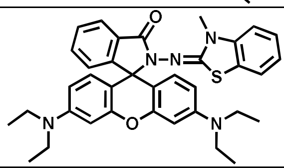
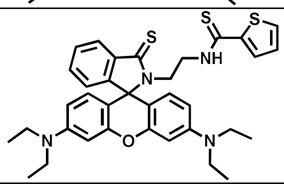
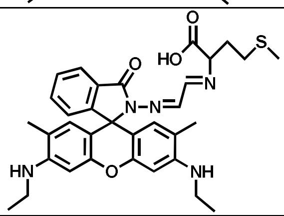
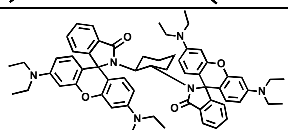
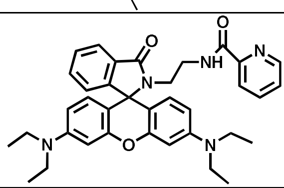
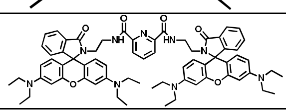
6.		528/552	-----	Fe^{3+}	-----	-----	Yes	19b
7.		528/552	-----	Fe^{3+}	-----	-----	Yes	19b
8.		528/552	-----	Fe^{3+}	-----	-----	Yes	19b
9.		528/552	-----	Fe^{3+}	-----	-----	Yes	19b
10.		528/552	-----	Fe^{3+}	-----	-----	Yes	19b

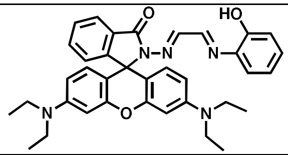
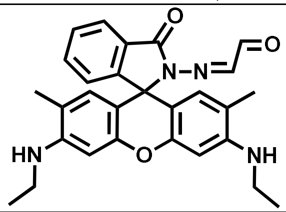
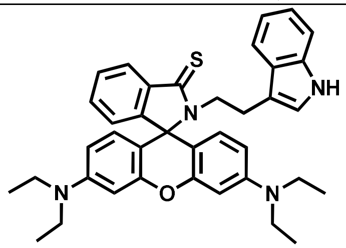
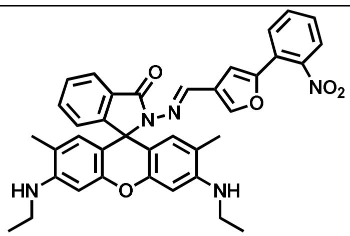
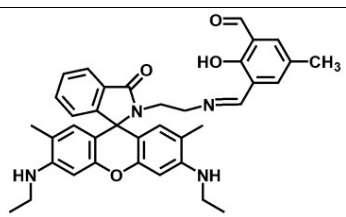
11.		528/552	-----	Fe^{3+}	-----	-----	Yes	19b
12.		510/555	14 (Al^{3+}) 10 (Cr^{3+}) 21 (Fe^{3+})	Al^{3+}, Cr^{3+}, Fe^{3}	0.34 µM (Al^{3+}), 0.31 µM (Cr^{3+}), 0.29 µM (Fe^{3+})	$K_a = 8.2\times10^4\ M^{-1}$ (Al^{3+}) $= 6.7\times10^4\ M^{-1}$ (Fe^{3+}) $= 6.0\times10^4\ M^{-1}$ (Cr^{3+})	Yes	15b
13.		525/556	18	Fe^{3+}	0.030 µM	-----	Yes	32a
14.		500/556	-----	Hg^{2+}	0.5-10 µM	3.5×10^6 (Stability Constant)	No	21
15.		525/581	-----	Hg^{2+}	2.5×10^{-8} M	$K_a = 2.1\times10^7\ M^{-1}$	Yes	32b

16.		525/581	-----	Hg^{2+}	4.2×10^{-8} M	$K_a = 4.4\times10^{5}\ M^{-1}$	Yes	32b
17.		525/581	-----	Al^{3+}	2.9×10^{-8} M	$K_a = 3.9\times10^{5}\ M^{-1}$	Yes	32b
18.		554/583	-----	Al^{3+}, Hg^{2+}	1.4×10^{-7} M (Hg^{2+}) 1.1×10^{-8} M (Al^{3+})	$K_a = 7.0\times10^{3}\ M^{-1}$ (Hg^{2+}) $= 4.5\times10^{4}\ M^{-1}$($Al^{3+}$)	No	32c
19.		554/583	-----	Al^{3+}, Hg^{2+}	1.89×10^{-8} M (Hg^{2+}) 1.64×10^{-7} M (Al^{3+})	$K_a = 1.49\times10^{10}\ M^{-2}$ (Hg^{2+}) $= 8.0\times10^{9}\ M^{-2}$ (Al^{3+})	No	32c
20.		520/570	13 (Fe^{3+}) 3 (Cu^{2+})	Cu^{2+} (Colorimetric), Fe^{3+} (Fluorimetric)	69 µM (Cu^{2+}) 100 µM (Fe^{3+})	$K_a = 1.65\times10^{3}\ M^{-1}$ (Cu^{2+}) $= 9.75\times10^{2}\ M^{-1}$ (Fe^{3+})	No	32d
21.		570/593	-----	Cu^{2+} (Colorimetric), Fe^{3+} (Fluorimetric)	48 nM (Cu^{2+}) 3.9 nM (Fe^{3+})	$K_a = 5.80\times10^{4}\ M^{-1}$ (Cu^{2+}) $= 6.50\times10^{4}\ M^{-1}$ (Fe^{3+})	No	32e

22.		510/572	-----	Cu^{2+} (Colorimetric), Fe^{3+} (Fluorimetric)	18 nM (Cu^{2+}) 33 nM (Fe^{3+})	$K_d = 13.99\times10^{-2}$ M (Cu^{2+}) $= 1.3\times10^{-2}$ M (Fe^{3+})	Yes	32f
23.		560/578	90 (Fe^{3+})	Cu^{2+} (Colorimetric), Fe^{3+} (Fluorimetric)	-----	-----	No	32g
24.		550/582	-----	Cu^{2+} (Colorimetric), Fe^{3+} (Fluorimetric)	38 nM (Cu^{2+}) 92 nM (Fe^{3+})	$K_a = 7.1\times10^{5}\ M^{-1}$ (Cu^{2+}) $= 7.4\times10^{4}\ M^{-1}$ (Fe^{3+})	No	32h
25.		530/582	1098 (Fe^{3+})	Cu^{2+} (Colorimetric), Fe^{3+} (Fluorimetric)	6.82×10^{-2} µmol/L (Cu^{2+}) 17 nmol/L (Fe^{3+})	$K_a = 7.1\times10^{5}\ M^{-1}$ (Cu^{2+}) $= 7.4\times10^{4}\ M^{-1}$ (Fe^{3+})	No	32i
26.	 x=9	515/572 (Cu^{2+}) 515/580 (Fe^{3+})	20 (Cu^{2+}) 14 (Fe^{3+})	Cu^{2+}, Fe^{3+}	-----	-----	No	32j
27.		500/573 (Cu^{2+}) 500/575 (Fe^{3+})	-----	Cu^{2+}, Fe^{3+}	10 nM (Cu^{2+}) 164 nM (Fe^{3+})	$K_a = 4.22\times10^{5}\ M^{-1}$ (Cu^{2+}) $= 2.94\times10^{3}\ M^{-1}$ (Fe^{3+})	No	32j

28.		500/552	-----	Cu^{2+} (Colorimetric), Fe^{3+} (Fluorimetric)	250 nM (Cu^{2+}) 90 nM (Fe^{3+})	$K_a = 1.9\times10^4\ M^{-1}$ (Cu^{2+}) $= 1.5\times10^5\ M^{-1}$ (Fe^{3+})	No	32l
29.		521/586	-----	Cu^{2+} (Colorimetric), Hg^{2+} (Fluorimetric)	5.92×10^{-7} M (Cu^{2+}) 2.85×10^{-6} M (Hg^{2+})	$K_a = 5.38\times10^4\ M^{-1}$ (Cu^{2+}) $= 1.63\times10^5\ M^{-1}$ (Hg^{2+})	No	32m
30.		550/580	-----	Fe^{3+}	5μM	$K_a = 4.52\times10^5\ M^{-1}$	Yes	32n
31.		500/554	90	Hg^{2+}	In ppb level	$K_a = 8.0\times10^5\pm0.1\ M^{-2}$	Yes	32o
32.		530/586	100 (Hg^{2+})	Cu^{2+} (Colorimetric), Hg^{2+} (Fluorimetric)	3.37 μM (Cu^{2+}) 150 nM (Hg^{2+})	$K_a = 2.2\times10^3\ M^{-1}$ (Cu^{2+}) $= 1.3\times10^4\ M^{-1}$ (Hg^{2+})	No	32p
33.		552/582	80 (Hg^{2+})	Cu^{2+} (Colorimetric), Hg^{2+} (Fluorimetric)	-----	-----	No	32q

34.		450/582	259 (Hg^{2+})	Cu^{2+} (Colorimetric), Hg^{2+} (Fluorimetric)	1.63 µM (Cu^{2+}) 2.36 µM (Hg^{2+})	$K_a = 1.61\times10^5\ M^{-1}$ (Cu^{2+}) $= 3.28\times10^5\ M^{-1}$ (Hg^{2+})	Yes	32r
35.		520/580	132	Cu^{2+}	1 nM	$K_a = 1.36\times10^5\ M^{-1}$	Yes	32s
36.		520/582	-----	Hg^{2+}	0.11 µM	$K_a = 3.03\times10^4\ M^{-1}$	Yes	32t
37.		500/545	27	Hg^{2+}	26.3 nM	$K_a = 3.39\times10^4\ M^{-1}$	Yes	32u
38.		520/580	100	Cr^{3+}	7.5 nM	$K_a = 3.4\times10^4\ M^{-1}$	Yes	4a
39.		560/582	100	Fe^{3+}	0.067 µM	$K_a = 2.70\times10^4\ M^{-1}$	Yes	32v
40.		560/582	100	Fe^{3+}	0.345 µM	$K_a = 1.97\times10^4\ M^{-1}$	Yes	32v

41.		540/578	-----	Al^{3+}	0.16 µM	$K_a = 6.9\times10^4\ M^{-1}$	Yes	3e
42.		530/561	-----	Fe^{3+}	0.29 µM	$K_a = 1.4\times10^{10}\ M^{-2}$	No	32w
43.		525/586	75	Hg^{2+}	2.1 nM	$K_a = 1.05\times10^5\ M^{-1}$	Yes	32x
44.		510/556	-----	Fe^{3+}	0.29 µM	$K_a = 1.17(\pm0.50)\times10^4\ M^{-1}$	No	32y
45		500/550	1465 (Al^{3+}) 588 (Cr^{3+}) 800 (Fe^{3+})	Al^{3+}, Cr^{3+}, Fe^{3+}	6.97 nM (Al^{3+}), 15.80 nM (Cr^{3+}), 14.00 nM (Fe^{3+})	$K_a = 1.47 \times 10^5\ M^{-1}$ (Al^{3+}) $= 6.24 \times 10^4\ M^{-1}$ (Cr^{3+}) $= 8.74 \times 10^4\ M^{-1}$ (Fe^{3+})	Yes	Present study