Development of a bisphenol A based chemosensor for Al^{3+} and its application in cell imaging as well as in plant root imaging

Sibshankar Bari,[a] Dinesh Maity,[b] Deepanjan Mridha,[c] Tarit Roychowdhury,[c] Pritam Ghosh[d] and Partha Roy[a]

[a] Department of Chemistry, Jadavpur University, Kolkata, 700032, India

Email address: partha.roy@jadavpuruniversity.in

[b] Department of Chemistry, Government General Degree College, Mangalkote, Purba Bardhaman 713132, India

[c] School of Environmental Studies, Jadavpur University, Kolkata, 700032, India

[d] Department of Chemistry, Humboldt-Universität zu Berlin, Brook-Taylor-Straße 2, Berlin 12489, Germany

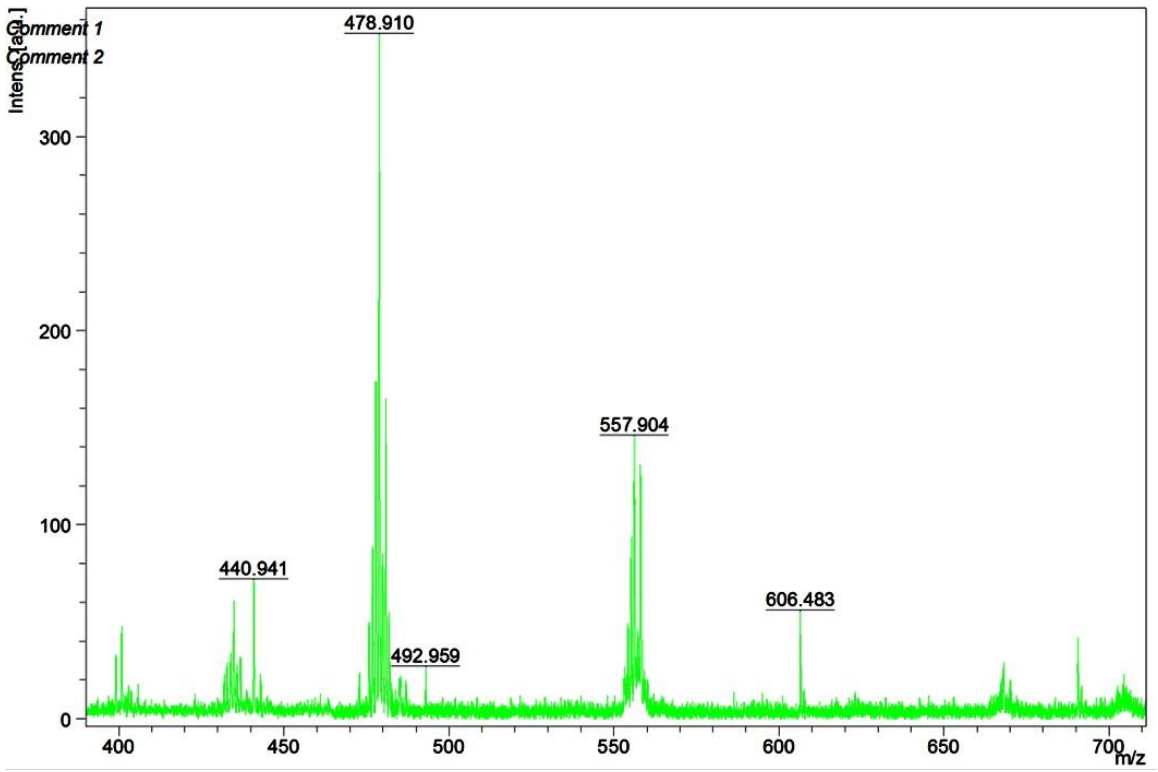


Fig. S1 ESI mass spectrum of NO_2-H_4L in methanol.

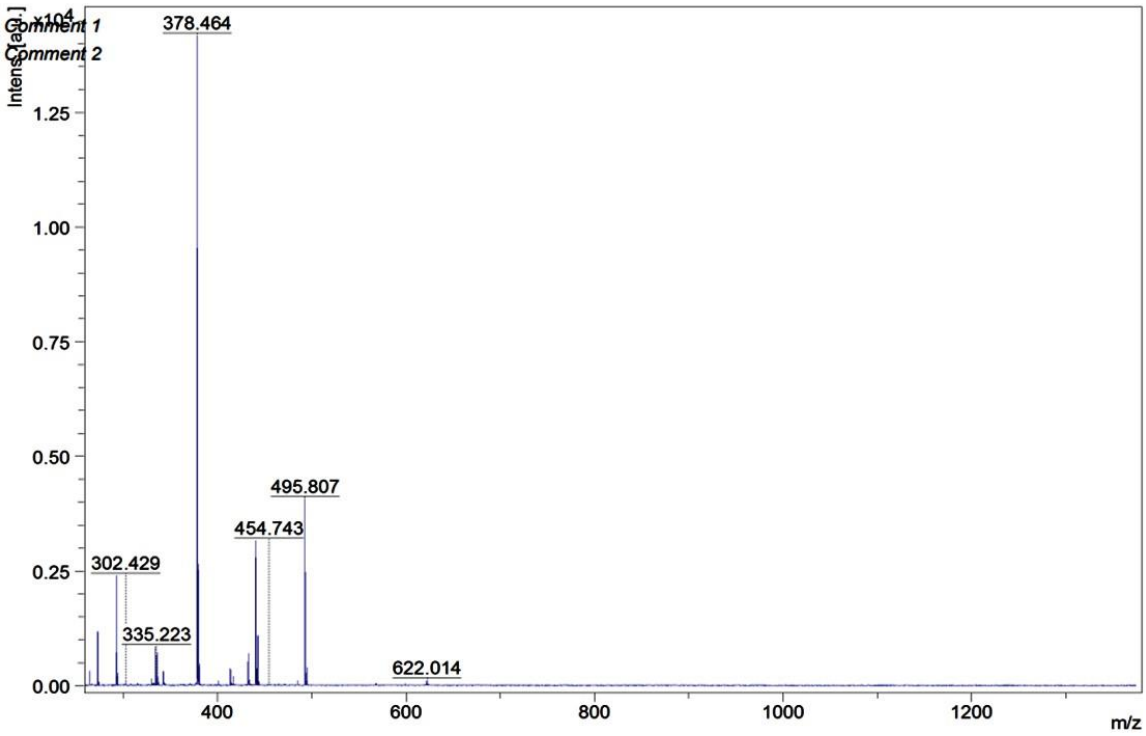


Fig. S2 ESI mass spectrum of Me-H_4L in methanol.

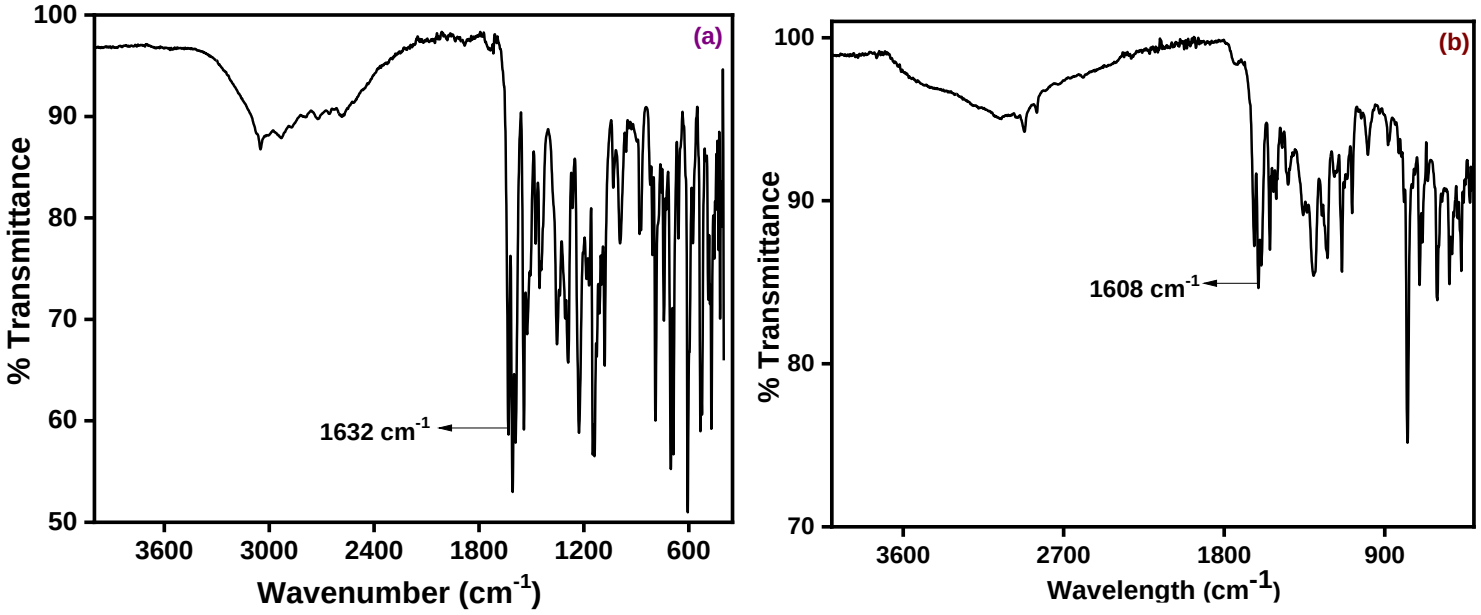


Fig. S3 FT-IR spectra of (a) Me-H_4L and (b) its complex with Al^{3+}.

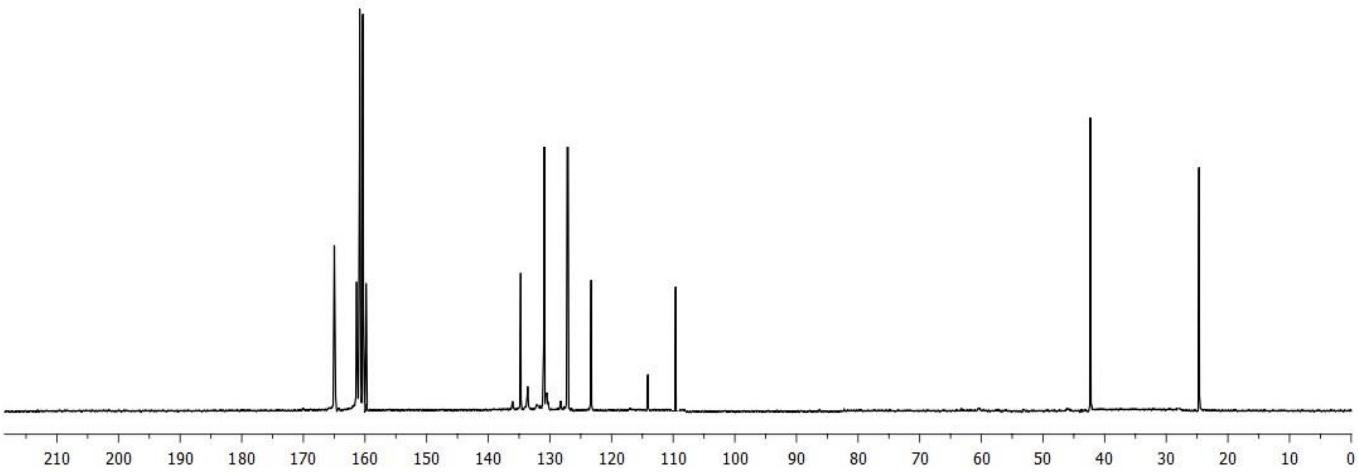


Fig. S4 ^{13}C NMR spectrum of Me-H_4L in DMSO-d_6.

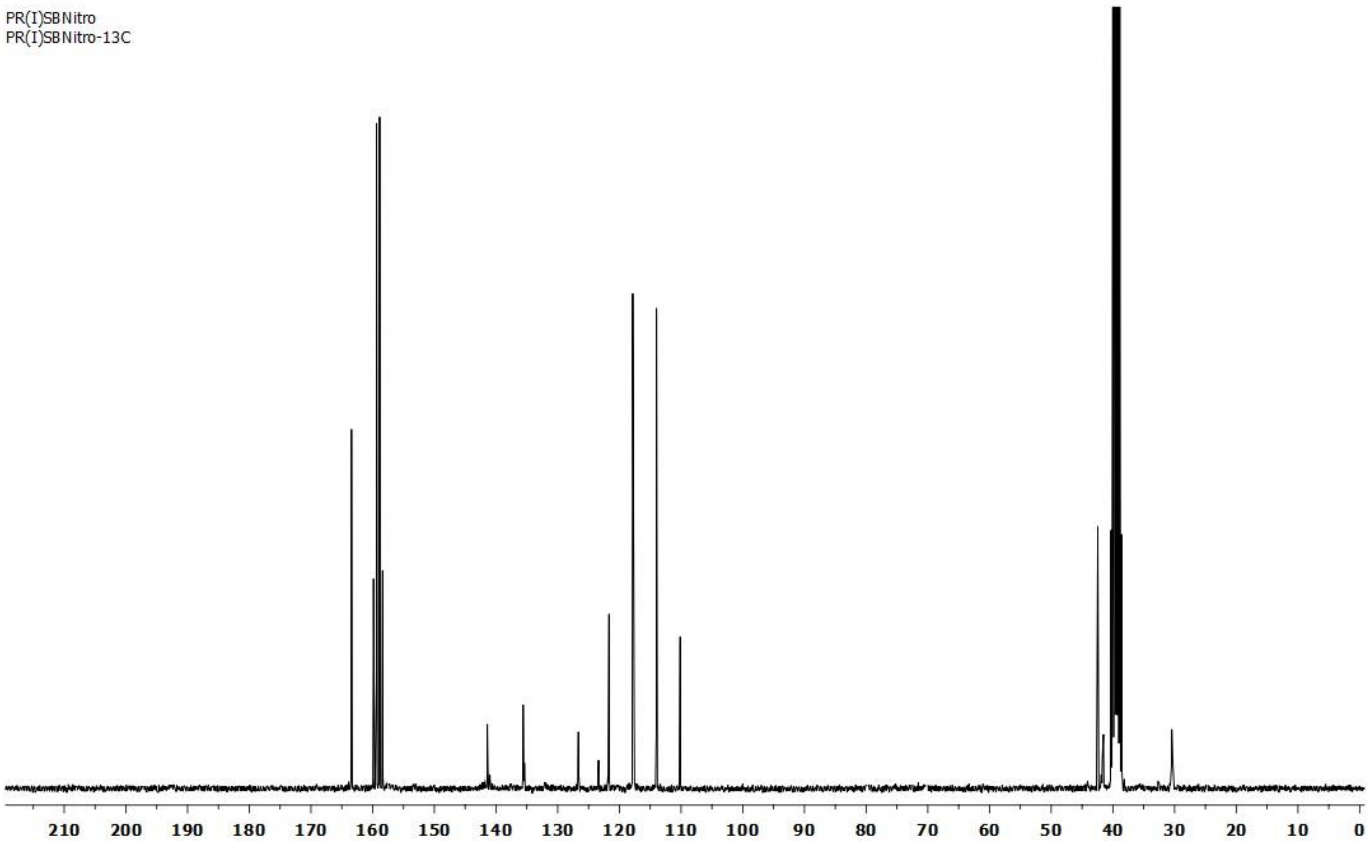


Fig. S5 ^{13}C NMR spectrum of NO_2-H_4L in DMSO-d_6.

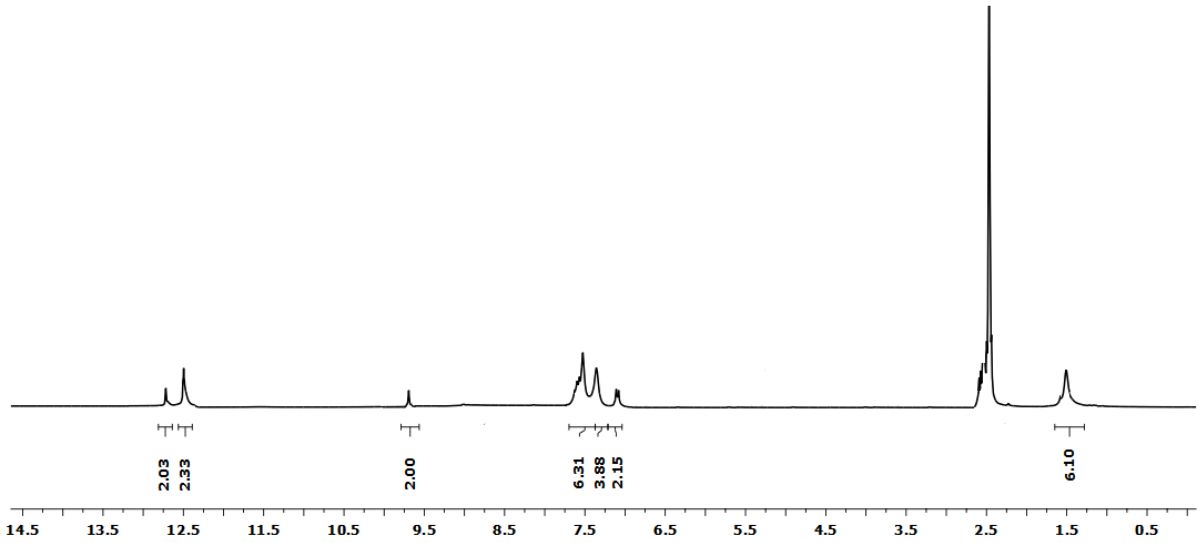


Fig. S6 ^{1}H NMR spectrum of NO_2-H_4L in DMSO-d_6

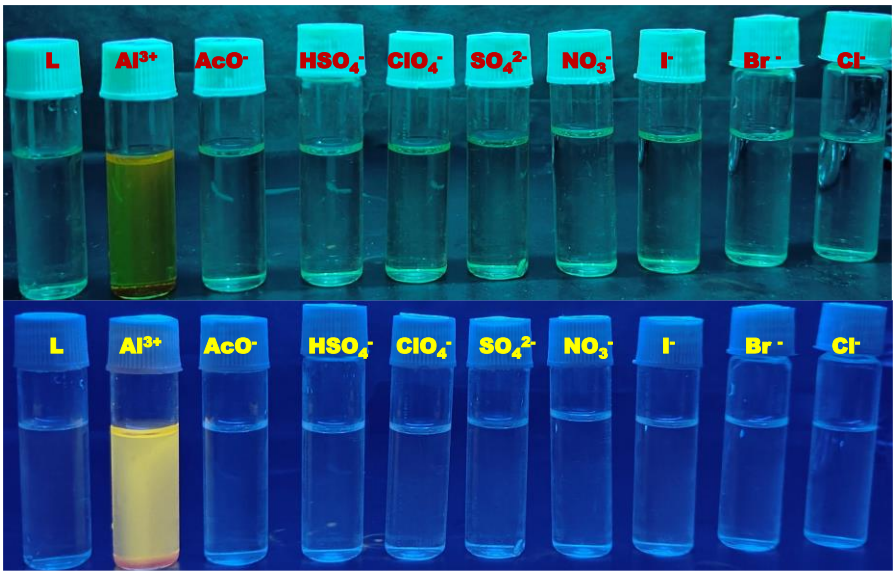


Fig. S7 Color of Me-H_4L in in the presence of various anions viewed under normal light (upper row) and UV light (lower row). L in the picture denotes Me-H_4L.

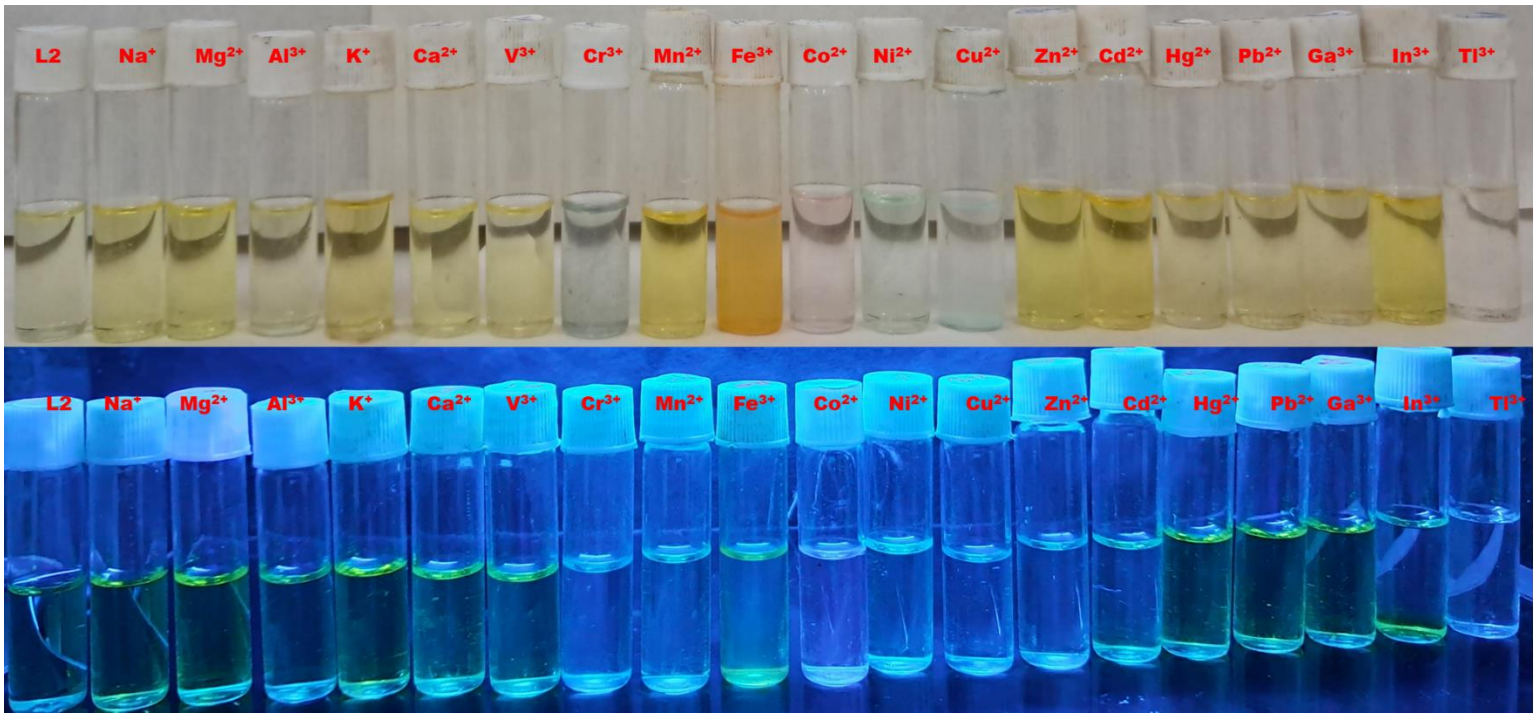


Fig. S8 Color of NO_2-H_4L in absence and in the presence of various metal ions viewed under normal light (upper row) and UV light (lower row). L2 in the picture denotes NO_2-H_4L.

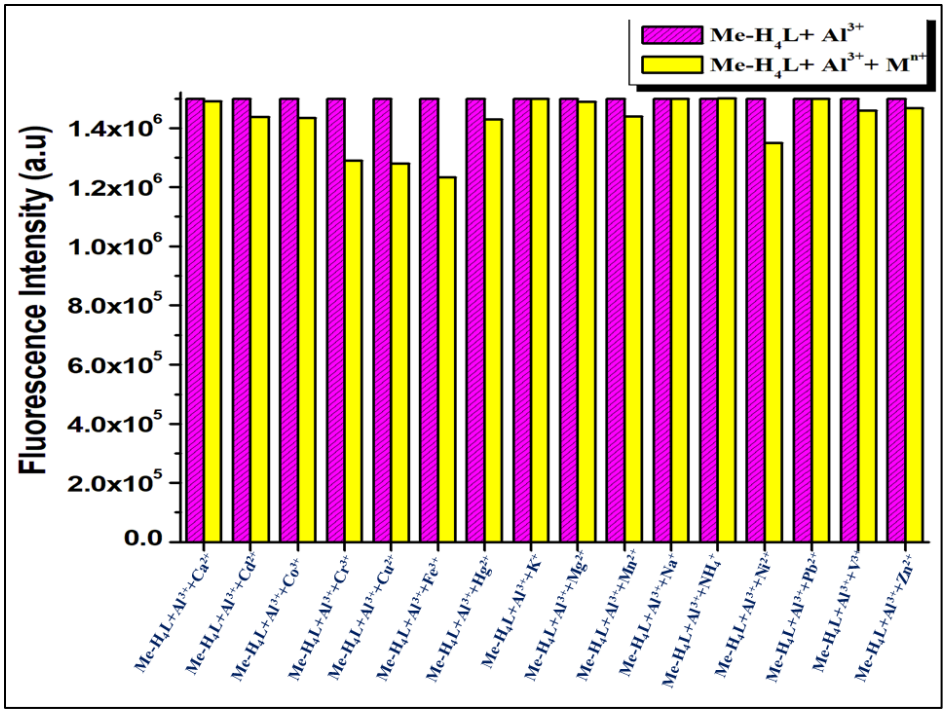


Fig. S9 Fluorescence intensity of Me-H_4L (40 μM) + Al^{3+} (80 μM) at 535 nm in the presence of different metal ions (3 eqv.) in 10 mM HEPES buffer in H_2O/DMF = 4:1 (v/v) (pH 7.4) at room temperature.

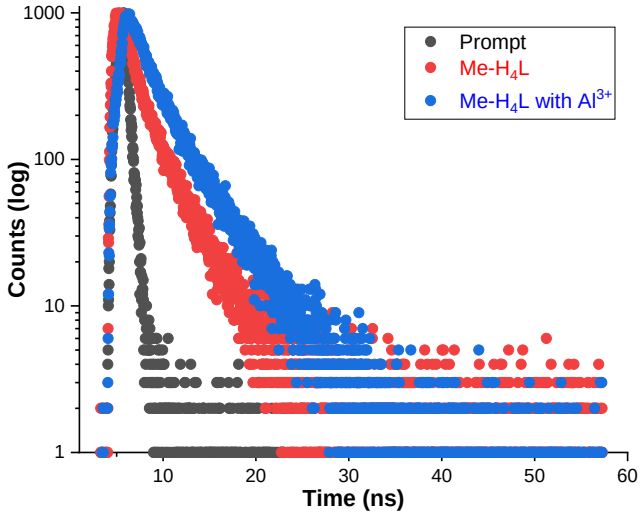


Fig. S10 Fluorescence excited state decay behavior of Me-H_4L and its complex with Al^{3+}

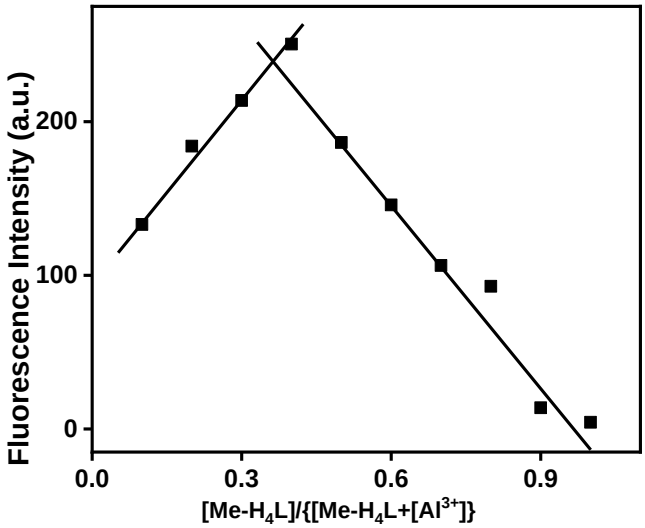


Fig. S11 Job's plot analysis indicating 1:2 (L/M) stoichiometry.

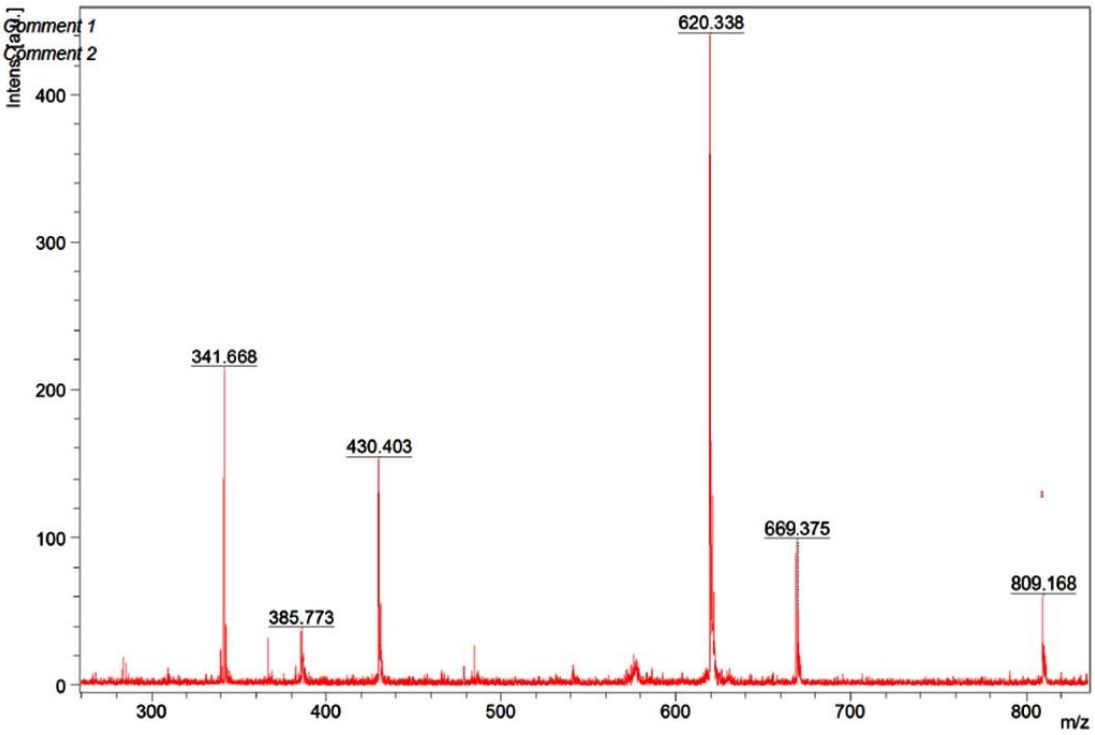
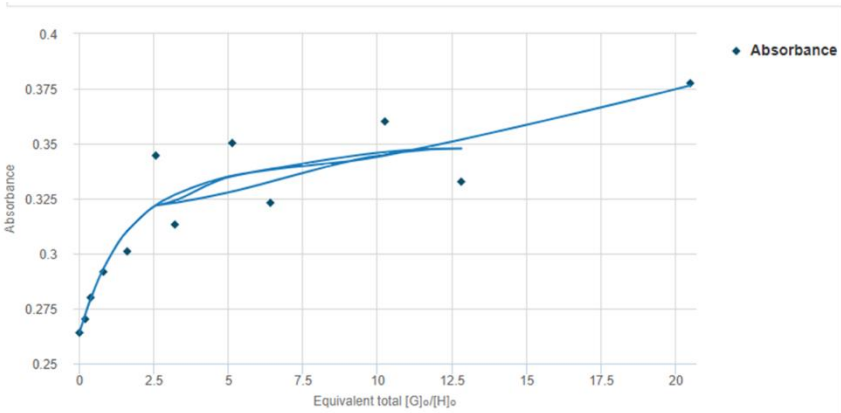


Fig. S12 ESI mass spectrum of Al-probe complex of Me-H_4L.



Details

Time to fit	1.0593 s
SSR	1.7260e-3
Fitted datapoints	12
Fitted params	4

Parameters

Parameter (bounds)	Optimised	Error	Initial
K_{11} (0 → ∞)	26786.89 M^{-1}	± 90.0632 %	1000.00 M^{-1}
K_{12} (0 → ∞)	-878.82 M^{-1}	± -90.0632 %	100.00 M^{-1}

Fig. S13 A plot of absorbance of Me-H_4L at 445 nm against $[G]_o/[H]_o$.Here $[G]_o$ denotes concentration of guest i.e. concentration of Al^{3+} and $[H]_o$ denotes concentration of host i.e. concentration of Me-H_4L. Association constant has been determined as 2.68×10^4 M^{-2} by using a software found at http://app.supramolecular.org/.

Limit of detection (LOD) for Me-H_4L 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 Me-H_4L solution; and S is the slope of the calibration curve obtained from Linear dynamic plot of F.I. vs [Al^{3+}] in M. The LOD of Me-H_4L has been calculated to be 9.65×10^{-6} M for Al^{3+} .

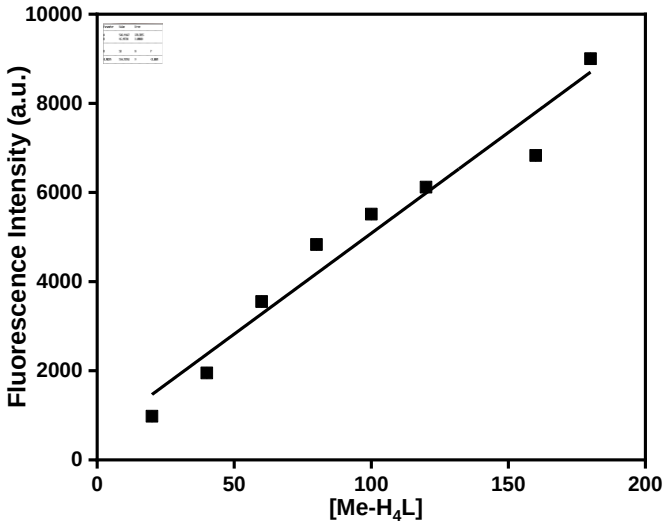


Fig. S14 Determination of Sb1 of the blank, Me-H_4L solution.

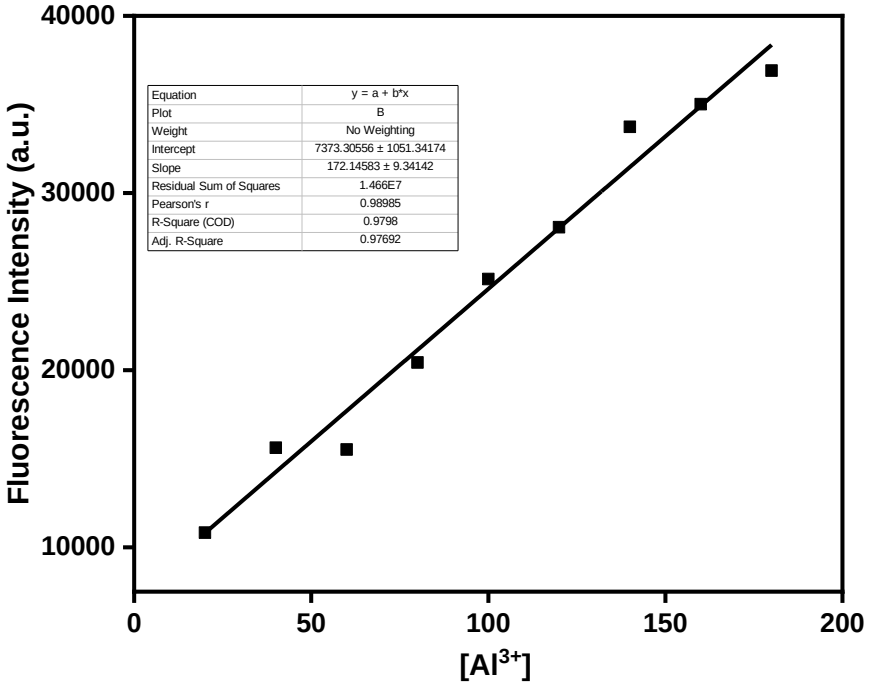


Fig. S15 Linear dynamic plot of F.I. vs. [Al^{3+}] for the determination of S (slope); [Me-H_4L] = 40 μM

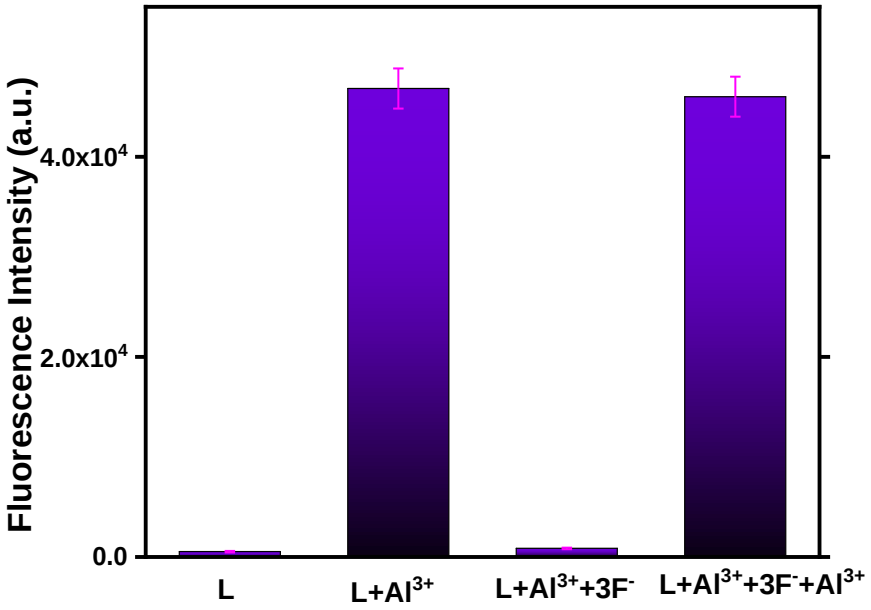


Fig. S16 Fluorescence Intensity of Me-H_4L at 535 nm after sequential addition of Al^{3+} and F^{-} indicating the reversible character of the probe.

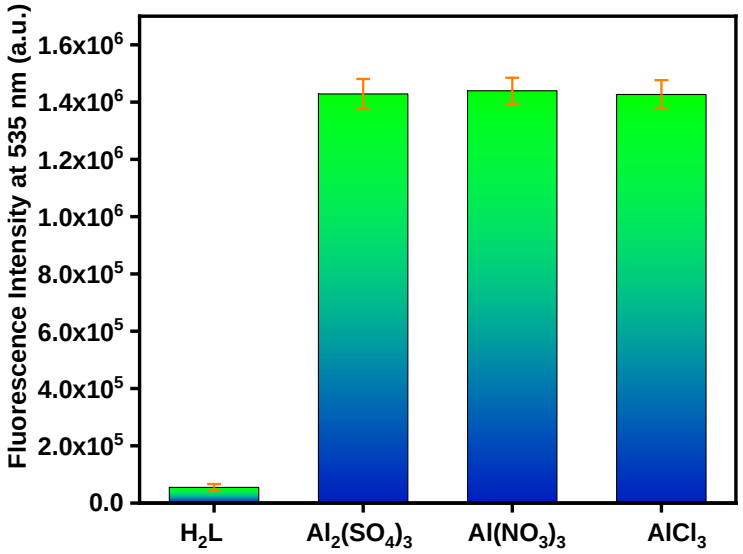


Fig. S17 Fluorescence Intensity of Me-H_4L at 535 nm in the presence of various salts of Al^{3+}.

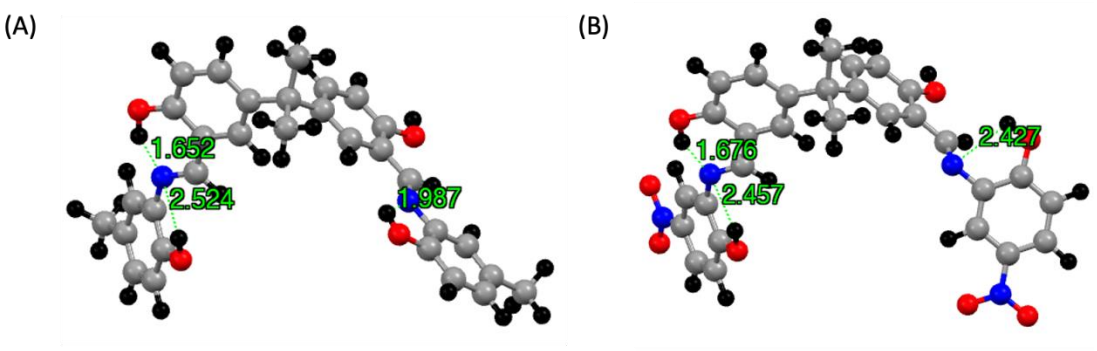


Fig. S18 Hydrogen bonding within the probes between phenolic -OH and Schiff base nitrogen (a) Me-H_4L and (b) NO_2-H_4L.

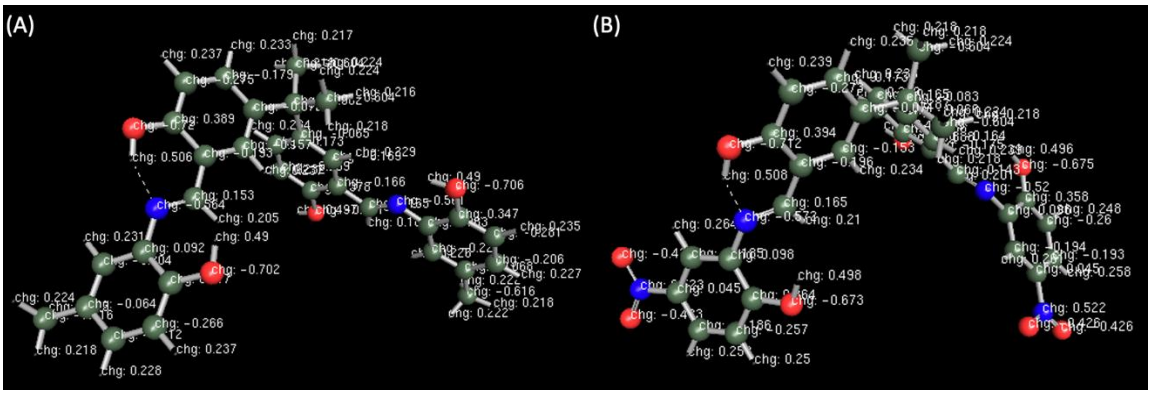


Fig. S19 NBO population data of (a) Me-H_4L and (b) NO_2-H_4L.

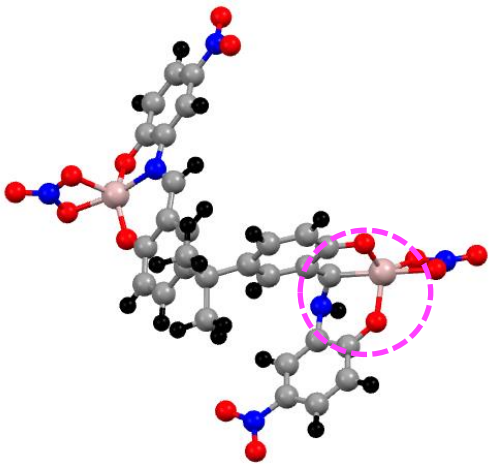


Fig. S20 Al^{3+} complex with NO_2-H_4L, the purple circle showed Al-carbon bond formation instead of Al-nitrogen of Schiff base.

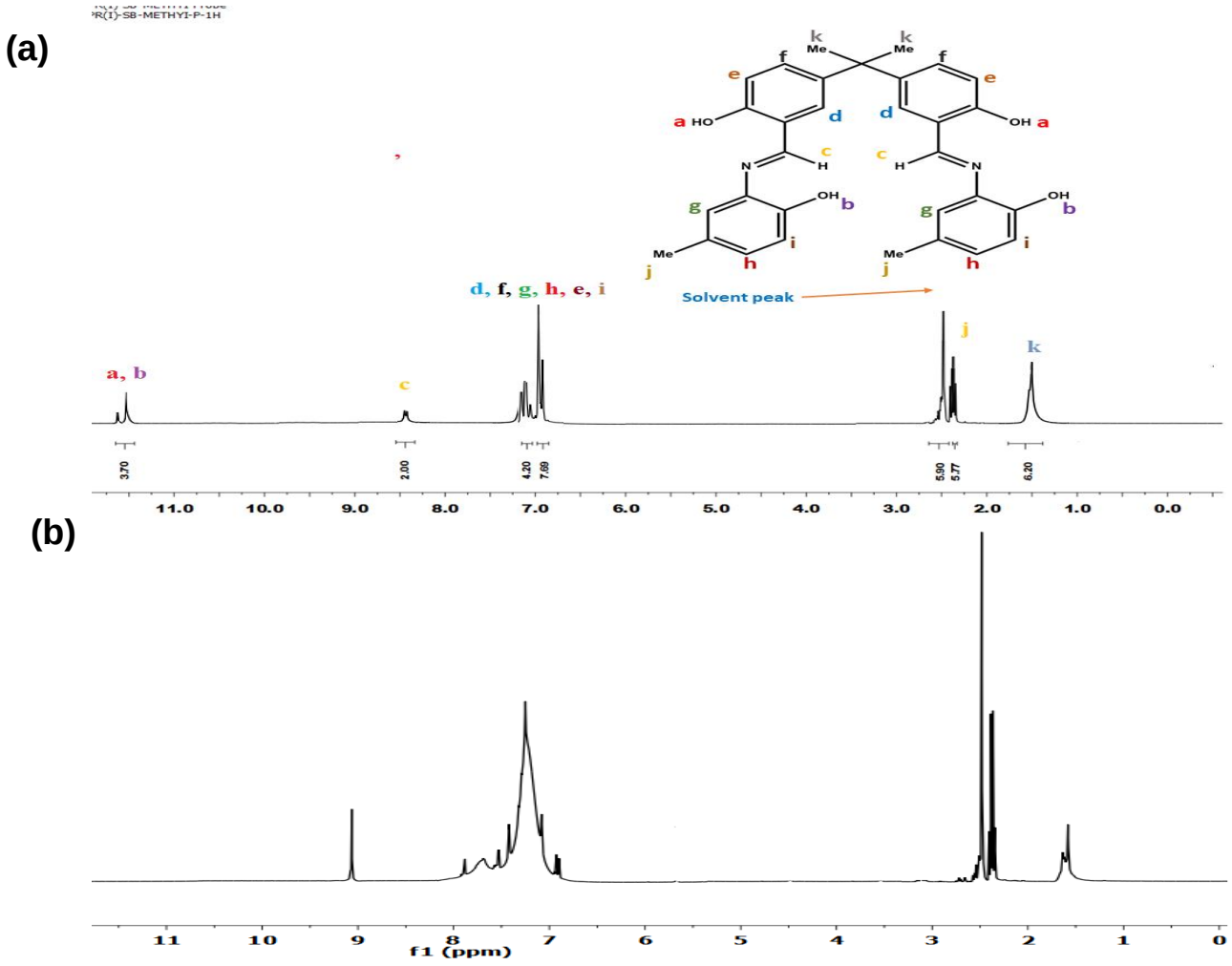


Fig. S20 ^{1}H NMR spectra of (a) Me-H_4L and (b) Me-H_4L with Al^{3+} in DMSO-d_6.

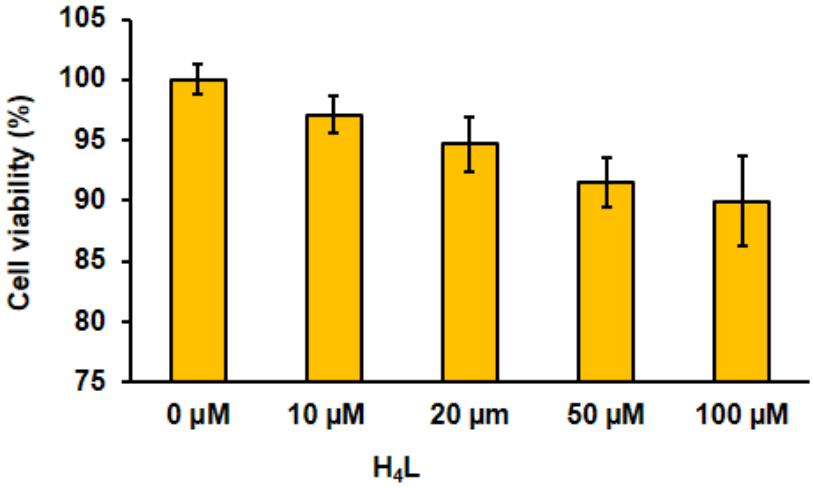


Fig. S21 Cell viability (%) of HepG2 cells treated with different concentrations (10-100 µM) of Me-H_4L for 6 h determined by MTT assay. Here H_4L denotes concentration of Me-H_4L.

Table S1 Me-H_4L optimized coordinates.

total energy = -1607.75067560487 Hartree

67

C	-4.0519227	2.1574225	2.7621872
C	-3.2826824	1.0072417	3.0006150
C	-3.8902461	-0.2653463	2.9133234
C	-5.2622222	-0.3414774	2.5885422
C	-6.0382102	0.7882810	2.3492258
C	-5.4007632	2.0443926	2.4416545
C	-7.5367686	0.7275081	2.0158120
C	-7.7922598	1.5080243	0.7150197
C	-6.9721743	1.2892932	-0.3935222
C	-7.1838255	1.9342995	-1.6264692
C	-8.2702381	2.8482196	-1.7601700
C	-9.0951995	3.0753098	-0.6493312
C	-8.8568930	2.4166359	0.5576959
C	-8.0253557	-0.7210534	1.7992462
C	-8.3142985	1.3165249	3.2134655
O	-1.9656093	1.0752111	3.3111153
O	-8.5039454	3.4897245	-2.9121025
C	-6.2868092	1.6842484	-2.7393313
C	-3.0984800	-1.4684525	3.1527414
N	-3.6020044	-2.6504464	3.0994010
N	-6.4580057	2.2597642	-3.8857171
C	-2.8647930	-3.8190789	3.3163891
C	-5.6089711	2.0604522	-4.9880061

C	-3.6522913	-4.9999237	3.2527282
C	-3.0577896	-6.2491933	3.4480193
C	-1.6856295	-6.3285640	3.7037175
C	-0.8793515	-5.1772400	3.7693465
C	-1.4881816	-3.9303315	3.5729550
C	-5.2634626	3.1832382	-5.7579396
C	-4.4115692	3.0993934	-6.8662532
C	-3.9252672	1.8305730	-7.2199140
C	-4.2914574	0.6912628	-6.4992388
C	-5.1304440	0.7864891	-5.3847682
O	-5.4597841	-0.3688916	-4.7388627
C	-4.0415714	4.3374397	-7.6487299
O	-4.9754001	-4.8856899	3.0035700
C	0.6052027	-5.2721833	4.0373836
H	-3.5786679	3.1412062	2.8260868
H	-5.6913955	-1.3398334	2.5280639
H	-5.9715605	2.9552326	2.2461577
H	-6.1261974	0.6012670	-0.3149623
H	-9.9238795	3.7795252	-0.7485374
H	-9.5254962	2.6261411	1.3933125
H	-9.0923467	-0.7108740	1.5229546
H	-7.4709729	-1.2202853	0.9881237
H	-7.9195227	-1.3229187	2.7173583
H	-9.4036141	1.2251857	3.0703856
H	-8.0751327	2.3802124	3.3748907
H	-8.0485374	0.7645421	4.1298248
H	-1.6717705	2.0033466	3.3367069
H	-7.7909828	3.1823221	-3.5669557
H	-5.4405057	1.0036127	-2.5503642

H -2.0361511 -1.3019003 3.3838579

H -3.6760394 -7.1480324 3.3978511

H -1.2294209 -7.3108809 3.8549333

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H -3.2613974 1.7258491 -8.0822838

H -3.9345324 -0.2984588 -6.7927613

H -6.2437590 -0.2377089 -4.1769296

H -4.9377138 4.8351963 -8.0603072

H -3.5264234 5.0776624 -7.0108174

H -3.3735177 4.0929981 -8.4901401

H -5.1230777 -3.9135809 2.9053221

H 0.9135402 -6.3150626 4.2151499

H 1.1938631 -4.8874047 3.1850582

H 0.8941299 -4.6776418 4.9223019

Table S2 NO_2-H_4L optimized coordinates.

total energy = -1937.78092466458 Hartree

65

C 8.7228491 -15.3289658 -2.0681475

C 9.3195331 -14.0678168 -1.9041252

C 10.6391221 -13.8644799 -2.3629607

C 11.3285688 -14.9357383 -2.9714930

C 10.7489579 -16.1877559 -3.1455851

C 9.4265946 -16.3601872 -2.6798081

C 11.4724390 -17.3697201 -3.8079045

C 10.6228978 -17.8735269 -4.9878063

C 10.0800943 -16.9576377 -5.8891779

C 9.3382885 -17.3600129 -7.0168858

C 9.1260464 -18.7493631 -7.2569483

C 9.6655497 -19.6747033 -6.3517966

C 10.3962674 -19.2403924 -5.2458730

C 12.8549180 -16.9653179 -4.3634284

C 11.6907510 -18.4604648 -2.7363864

O 8.6706315 -13.0338508 -1.3218268

O 8.4220914 -19.1790603 -8.3110753

C 8.7782381 -16.3615278 -7.9035979

C 11.2648349 -12.5527911 -2.2260182

N 12.4675882 -12.3155656 -2.6172758

N 8.0936085 -16.6903263 -8.9524314

C 13.0271492 -11.0400661 -2.4637333

C 7.5396809 -15.7284274 -9.8128546

C 13.5754529 -10.3984862 -3.5773406

C 14.1481860 -9.1312438 -3.4444532

C 14.2214771 -8.4838108 -2.2058370

C 13.7151389 -9.1320163 -1.0860845

C 13.1220410 -10.4001635 -1.1953867

C 6.1894817 -15.8308593 -10.1548142

C 5.6118065 -14.8859763 -11.0045349

C 6.3598964 -13.8385137 -11.5543379

C 7.7122259 -13.7542546 -11.2499932

C 8.3171666 -14.6875892 -10.3917709

O 12.6733531 -10.9782553 -0.0630352

O 9.6387082 -14.5557996 -10.1659250

N 14.6936190 -8.4761686 -4.6260575

O 15.1865578 -7.3609911 -4.4961072

O 14.6364353 -9.0676986 -5.6985407

N 4.1955907 -15.0018277 -11.3303914

O 3.7002028 -14.1576170 -12.0678732

O 3.5639348 -15.9373276 -10.8527816

H 7.6994576 -15.4880137 -1.7176871

H 12.3417371 -14.7271736 -3.3115630

H 8.9299950 -17.3243688 -2.8121751

H 10.2195784 -15.8860073 -5.7252321

H 9.4987086 -20.7389445 -6.5297770

H 10.7959992 -19.9975133 -4.5704588

H 13.3196558 -17.8338765 -4.8579201

H 12.7735552 -16.1565090 -5.1073743

H 13.5294695 -16.6315622 -3.5573225

H 12.2845220 -19.3003558 -3.1328513

H 10.7369734 -18.8616689 -2.3569671

H 12.2437438 -18.0317816 -1.8846755

H 7.7715203 -13.3008761 -1.0588744

H 8.1210992 -18.3612822 -8.8227198

H 8.9412268 -15.3054801 -7.6293262

H 10.6334488 -11.7608328 -1.7902416

H 13.5385519 -10.8879121 -4.5483506

H 14.6779104 -7.4986372 -2.1284152

H 13.7697591 -8.6698329 -0.0989376

H 5.5904461 -16.6393882 -9.7408031

H 5.8861049 -13.1160908 -12.2166457

H 8.3343493 -12.9653234 -11.6758224

H 12.4193662 -11.9061394 -0.2251923

H 9.9998464 -15.3381319 -9.7092623

Table S3 Al- Me-H_4L complex optimized coordinates.

total energy = -2650.65235020479 Hartree

73

C -5.3454951 1.5231757 3.1993514

C -4.3804220 0.5077346 3.3456524

C -4.6765223 -0.7796922 2.8031081

C -5.9110350 -0.9916607 2.1358690

C -6.8472861 0.0176740 1.9743505

C -6.5337276 1.2833805 2.5250355

C -8.1947076 -0.1778029 1.2655653

C -8.3285369 0.8864797 0.1634776

C -7.2791760 1.0911486 -0.7274568

C -7.3475384 2.0302621 -1.7806409

C -8.5410443 2.7997590 -1.9588142

C -9.6049511 2.5756420 -1.0704156

C -9.4964254 1.6503232 -0.0346441

C -8.3077347 -1.5656831 0.5987768

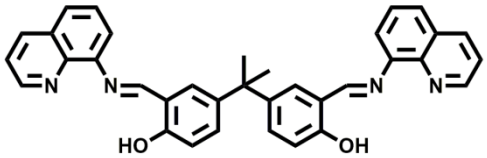
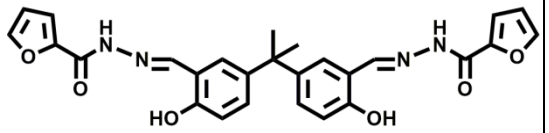
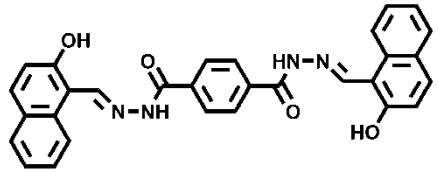
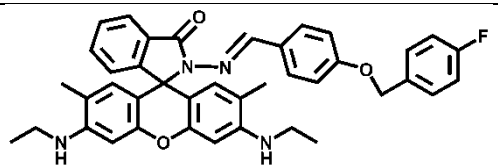
C -9.3125232 -0.0660045 2.3258612

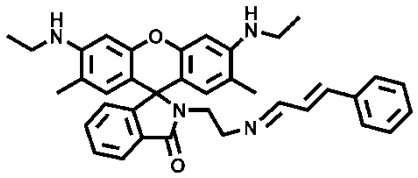
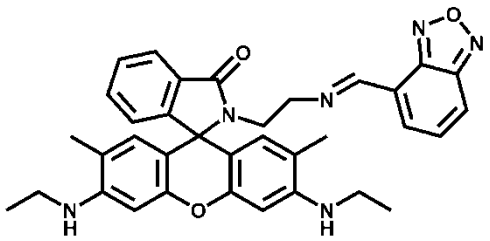
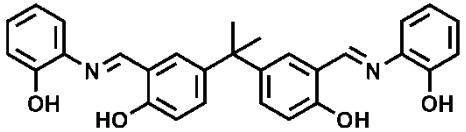
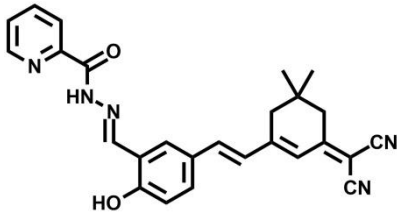
O -3.2479758 0.7825337 3.9857195

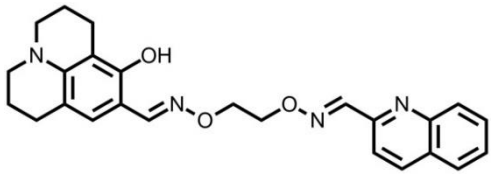
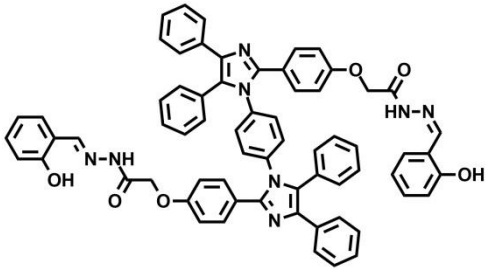
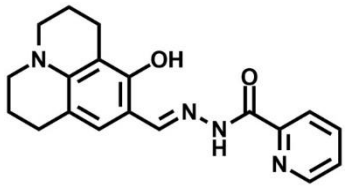
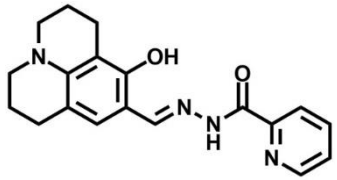
O	-8.6826611	3.7003108	-2.9287565
C	-6.2435195	2.1070379	-2.6977585
C	-3.8070373	-1.9056218	2.9958540
N	-2.6183961	-1.8039822	3.5199157
N	-6.1733067	2.9924949	-3.6494840
C	-1.7989500	-2.8660134	3.9443321
C	-5.2542267	3.0034296	-4.7146442
C	-0.7663082	-2.4052867	4.8000097
C	0.1172421	-3.3406011	5.3522299
C	-0.0297377	-4.6940074	5.0411703
C	-1.0475801	-5.1599821	4.1828853
C	-1.9369004	-4.2250035	3.6406108
C	-4.0663248	2.2718356	-4.8241223
C	-3.2833725	2.3728405	-5.9796633
C	-3.7311122	3.2163631	-7.0181105
C	-4.9148222	3.9504831	-6.9204852
C	-5.6915737	3.8569070	-5.7591067
O	-6.8423164	4.5320999	-5.5790363
C	-1.9829224	1.6157878	-6.1122934
O	-0.6945323	-1.0826642	5.0422754
C	-1.1567358	-6.6289287	3.8477583
H	-5.1258659	2.5072211	3.6181702
H	-6.0989817	-1.9933796	1.7483555
H	-7.2440223	2.1061922	2.4124142
H	-6.3563602	0.5156491	-0.6205333
H	-10.5200755	3.1556441	-1.2054075
H	-10.3515453	1.5274713	0.6307598
H	-9.2712545	-1.6417818	0.0687618
H	-7.5040717	-1.7331395	-0.1365402

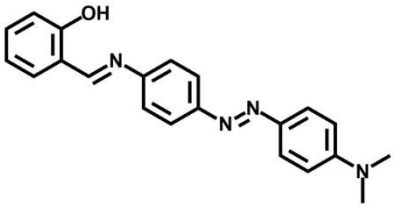
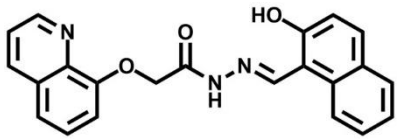
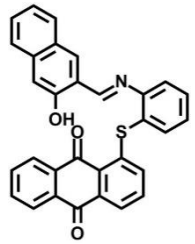
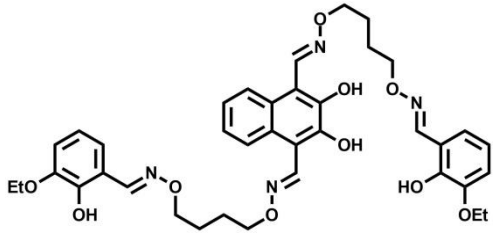
H	-8.2697352	-2.3751762	1.3469426
H	-10.3033346	-0.2729598	1.8888264
H	-9.3430654	0.9328711	2.7907782
H	-9.1370170	-0.8065909	3.1232780
H	-5.4616676	1.3420969	-2.6104851
H	-4.1995408	-2.8963574	2.7341832
H	0.9108302	-2.9965852	6.0189071
H	0.6690577	-5.4147134	5.4758666
H	-2.7345489	-4.5601648	2.9736614
H	-3.7423814	1.6255615	-4.0051263
H	-3.1310474	3.3007450	-7.9288769
H	-5.2468560	4.5988296	-7.7340868
H	-1.1153279	2.3002374	-6.0798250
H	-1.8600351	0.8820651	-5.2994331
H	-1.9295886	1.0745980	-7.0730834
H	-1.1156338	-7.2525412	4.7577605
H	-2.0990447	-6.8527162	3.3221685
H	-0.3247833	-6.9545792	3.1964524
Al	-7.4385559	4.4338534	-3.9156653
Al	-1.7582545	-0.1376262	3.9904805
N	-7.5214833	6.6984196	-3.2548573
O	-7.5236666	7.8334231	-2.8968604
O	-8.3929509	6.1728559	-4.0278549
O	-6.6187162	5.8343249	-2.8991532
N	-0.2585441	1.3183508	2.8930740
O	0.4934434	2.0256448	2.3009190
O	-0.8130478	0.2641031	2.3740620
O	-0.6246782	1.4905180	4.1052480

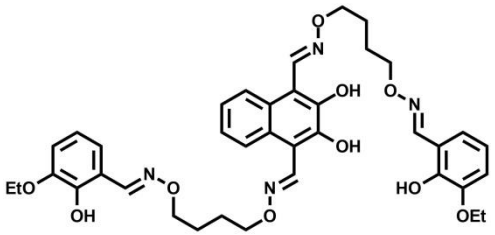
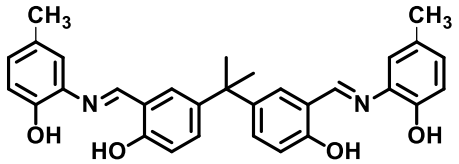
Table S4 Different parameters of recently published chemosensors for Al^{3+}

Entry no.	Probes	Sensor for	Solvent	Excitation (nm)/Emission (nm)	LOD for Al^{3+} (M)	Binding constant (K_a) with Al^{3+}	Application	Ref
1		Zn^{2+}, Al^{3+} F^-	EtOH-H_2O (v/v, 9/1)	395/560 (Zn^{+2}) 395/530 (Al^{+3}) 420/610 (F^-)	$3.68 (\pm 0.21) \times 10^{-6}$	$(1.53 \pm 0.18) \times 10^{10}$ M^{-2}	NA	59
2		Al^{3+} CN^-	CH_3CN: HEPES (80:20, v:v)	382/462 (Al^{+3}) 355/516 (CN^-)	2.66×10^{-9}	0.607×10^{10} M^{-2}	Test paper strip	60
3		Al^{3+}	DMF	365/514	4.22×10^{-8}	4.82×10^4 M^{-1}	Logic gate and real sample analysis	61
4		Al^{3+} Ga^{3+} In^{3+} Tl^{3+}	HEPES buffer in (1:9, v/v) water:ethanol (pH 7.4)	495/555 (for all)	2.66×10^{-9}	5.01×10^4 M^{-1}	Real sample	62

5		Al^{3+} Ga^{3+} In^{3+} Tl^{3+}	HEPES buffer in (1:9, v/v) water:ethanol (pH 7.4)	495/558 (for all)	2.8×10^{-8}	---	Test paper strip, real sample	32
6		Al^{3+} Hg^{2+}	HEPES buffer in (1:9, v/v) water:ethanol (pH 7.4)	500/550 (for all)	6.54×10^{-9}	$4.44 \times 10^{4}\ M^{-1}$	Test paper strip, real sample, logic gate	63
7		Al^{3+}	HEPES buffer/DMF (4:1 (v/v, pH 7.4)	430/519	4.6×10^{-7}	$6.95 \times 10^{8}\ M^{-2}$	Plant root	35
8		Al^{3+}	DMF/H_2O (v/v, 3/7)	430/620	4.01×10^{-8}	$1.83 \times 10^{4}\ M^{-1}$	Cell imaging	64

9		Al^{3+} Zn^{2+}	DMSO/H_2O (9/1, v/v, HEPES, pH = 7.4)	350/426 350/451	2.1×10^{-7} 9.7×10^{-8}	1.07×10^{5} M^{-1}	---	65
10		Al^{3+}	DMF	340/434	1.56×10^{-8}	1.07×10^{6} M^{-1}	Test papers and sample of stomach tablets	66
11		Al^{3+} $H_2PO_4^-$	HEPES buffer	365/550	5.7×10^{-8} 1.48×10^{-7}	---	Food samples, and cell imaging	67
12		Al^{3+} Zn^{2+}	DMSO/H_2O (9/1, v/v, HEPES, pH = 7.4)	354/493 354/434	3.99×10^{-8} 1.33×10^{-8}	2.08×10^{7} M^{-1}	Latent fingerprint analysis	68

13		Al^{3+}	HEPES buffer/DMSO solution (2/8 v/v)	380/512	1.53×10^{-7}	$2.36 \times 10^{4}\ M^{-1}$	Cell imaging	69
14		Al^{3+} Hg^{2+}	DMSO/H_2O (v/v = 4:6)	……..	4.34×10^{-9} 5.70×10^{-8}	……	Test kit preparation	70
15		Al^{3+}	Methanol/urotropine buffer medium (1:1, v/v, pH 4.5).	385/459	31.6×10^{-9}	$8.87 \times 10^{4}\ M^{-2}$	Zebrafish imaging	71
16		Al^{3+}	DMF:H_2O (9:1, v/v)	260/446	8.64×10^{-8} M	$7.19 \times 10^{4}\ M^{-1}$	Testing of actual water samples	72

17		Al^{3+}	H_2O	400/460	2.20×10^{-8}	$7.74 \times 10^{6}\ M^{-1}$	Cytotoxicity toward hepatocytes	73
18		Al^{3+}	HEPES buffer in water/DMF (4:1 (v/v, pH 7.4)	445/535	9.65×10^{-6}	$2.68 \times 10^{4}\ M^{-2}$	Cell imaging and plant root imaging	Present work