Supporting Information

Development of two fluorescent chemosensors for selective detection of Zn²⁺

and Al³⁺ ions in quinoline platform by tuning of substituent in the receptor

part: Elucidation of structures of metal bound chemosensors and biological

studies

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Scheme S1 Route to the synthesis of chemosensors (HL_1 and HL_2).



Scheme S2 Enhancement of ROS in presence of complexes 1 and 2.



Fig. S1 ESI-MS spectrum of HL₁.



Fig. S2 ESI-MS spectrum of HL₂.



Fig. S3 FT-IR spectrum of HL₁.



Fig. S4 FT-IR spectrum of HL₂.



Fig. S5 ESI-MS spectrum of complex 1.



Fig. S6 ESI-MS spectrum of complex 2.



Fig. S7 FT-IR spectrum of complex 1.



Fig. S8 FT-IR spectrum of complex 2.



Fig. S9 Thermo Gravimetric Analysis of (a) HL_1 , (b) HL_2 , (c) complex 1 and (d) complex 2 under nitrogen atmosphere.



Fig. S10a $\pi \cdots \pi$ interactions of complex **1** along the ab plane (a= 3.484Å and b=3.512 Å).



Fig. S10b Halogen… π and halogen…halogen interactions of complex 1 along the a axis (a= 3.525Å and b=3.639Å).



Fig. S11 Different supramolecular interactions of complex **2** along the c axis (a= 3.569Å; b=3.842 Å and c= 2.909Å).





Fig. S12(b) Expanded view of ¹H NMR spectrum of HL_1 in DMSO- d_6 solvent.



Fig. S13(a) ¹H NMR spectrum of HL_2 in DMSO- d_6 solvent.



Fig. S13(b) Expanded view of ¹H NMR spectrum of HL_2 in DMSO- d_6 solvent.



Fig. S14(a) ¹H-NMR spectrum of the free ligand **HL**₁ and with the addition of 0.125, 0.25 and 0.50 equivalent of Zn^{2+} ion in DMSO- d_6 solvent.



Fig. S14(b) ¹H-NMR spectrum of the free ligand **HL**₂ and with the addition of 0.125, 0.25 and 0.50 equivalent of Al^{3+} ion in DMSO- d_6 solvent.



Fig. S15(b) Expanded view of ¹H NMR spectrum of complex 1 in DMSO- d_6 solvent.



Fig. S16(a) ¹H NMR spectrum of complex 2 in DMSO- d_6 solvent.



Fig. S16(b) Expanded view of ¹H NMR spectrum of complex 2 in DMSO- d_6 solvent.



Fig. S17 ¹³C NMR spectrum of HL_1 in DMSO- d_6 solvent.



Fig. S18 ¹³C NMR spectrum of HL_2 in DMSO- d_6 solvent.



Fig. S19 ¹³C NMR spectrum of complex 1 in DMSO- d_6 solvent.



Fig. S20 ¹³C NMR spectrum of complex **2** in DMSO- d_6 solvent.



Fig. S21 1:2 binding stoichiometry of Zn^{2+} ions to the probe HL₁, shown by Job's plot. Symbols

and solid lines represent the experimental and simulated profiles, respectively.



Fig. S22 1:2 binding stoichiometry of Al^{3+} ions to the probe HL_2 , shown by Job's plot. Symbols and solid lines represent the experimental and simulated profiles, respectively.



Fig. S23 Non-linear least square curve fitting for complex 1 by using UV-Vis titration plot of HL_1 in presence of Zn^{2+} ions.



Fig. S24 Non-linear least square curve fitting for complex 2 by using UV-Vis titration plot of HL_2 in presence of Al^{3+} ions.



Fig. S25 Variation of fluorescence intensity of HL_1 (10 μ M) in presence of different common metal ions (5 μ M) in 10 mM HEPES buffer solution at pH 7.4.



Fig. S26 Variation of fluorescence intensity of HL_2 (10 μ M) in presence of different common metal ions (5 μ M) in 10 mM HEPES buffer solution at pH 7.4.



Fig. S27 Variation of fluorescence intensity of HL_1 (10 μ M) in presence of different common anions (5 μ M) in 10 mM HEPES buffer solution at pH 7.4.



Fig. S28 Variation of fluorescence intensity of HL_2 (10 μ M) in presence of different common anions (5 μ M) in 10 mM HEPES buffer solution at pH 7.4.



Fig. S29 Relative fluorescence intensity profile of $[(L_2)_2-Al^{3+}]$ system in the presence of different common cations in 10 mM HEPES buffer at pH 7.4. Here, $[HL_2]= 10 \ \mu$ M; $[Al^{3+}]= 5 \ \mu$ M; [other cations]= 50 μ M.



Fig. S30 Relative fluorescence intensity profile of $[(L_1)_2-Zn^{2+}]$ system in the presence of different common anions in 10 mM HEPES buffer at pH 7.4. Here, $[HL_1]$ 10 μ M; $[Zn^{2+}]=5 \mu$ M; [anions]= 50 μ M.



Fig. S31 Relative fluorescence intensity profile of $[(L_2)_2-Al^{3+}]$ system in the presence of different common anions in 10 mM HEPES buffer at pH 7.4. Here, $[HL_2]= 10 \ \mu\text{M}$; $[Al^{3+}]= 5 \ \mu\text{M}$; $[anions]= 50 \ \mu\text{M}$.



Fig. S32 Non-linear least square curve fitting for complex 1 by using fluorescence titration plot of HL_1 in presence of Zn^{2+} ions.



Fig. S33 Non-linear least square curve fitting for complex 2 by using fluorescence titration plot of HL_2 in presence of Al^{3+} ions.



Fig. S34 Visual colour changes in reversibility experiments in 10mM HEPES buffer (pH 7.4) medium. Here, $A = HL_1 (10\mu M)$, $B = HL_1 (10\mu M) + Zn^{2+} (5 \mu M)$, $C = HL_1 (10\mu M) + Zn^{2+} (5 \mu M)$ + EDTA²⁻ (5 μ M), $D = HL_2 (10\mu M)$, $E = HL_2 (10\mu M) + Al^{3+} (5 \mu M)$ and $F = HL_2 (10\mu M) + Al^{3+} (5 \mu M)$ + EDTA²⁻ (5 μ M). Above images are taken under normal light and below images are taken under UV lamp.



Fig. S35(a) Fluorescence reversibility experiment of HL₁ between pH 4 and 10.



Fig. S35(b) Fluorescence reversibility experiment of HL₂ between pH 4 and 10.



Fig. S36 Fluorescence intensity of HL_2 (10 μ M) in the absence and presence of Al³⁺ ions (5 μ M) at various pH values in 10 mM HEPES buffer.



Fig. S37 Reactive oxygen species (ROS) generation using *MDA-MB* 468 cell lines after 12h in presence of complexes 1 and 2.



Fig. S38 DFT optimized structure of HL₁.



Fig. S39 DFT optimized structure of HL₂.

	HL ₁	HL ₂
LUMO+2		
LUMO+1		
LUMO		
НОМО		
HOMO-1		
HOMO-2		





Fig. S41 Pictorial representation of key transitions of chemosensor HL₂.

 Table S1 Crystallographic parameters and refinement details of complexes 1 and 2.

Complex	1	2
Empirical formula	C ₃₃ H _{18.50} Br ₄ Cl ₃ N ₄ O ₂ Zn	C ₃₂ H ₂₀ AlN ₇ O ₉
Formula weight	994.38	673.53
Temperature (K)	273(2)	273(2)
Crystal system	triclinic	monoclinic
Space group	P -1	$P 2_l/n$
<i>a</i> (Å)	11.5856(9)	12.5503(9)
<i>b</i> (Å)	12.9455(10)	14.1977(10)
<i>c</i> (Å)	13.6796(10)	16.8800(12)
$\alpha(^{\circ})$	80.891(3)	90
β(°)	66.130(3)	101.622(2)
$\gamma(^{\circ})$	63.965(3)	90
Volume (Å ³)	1685.3(2)	2946.1(4)
Ζ	2	4
D_{calc} (g cm ⁻³)	1.959	1.519
Absorption	5.747	0.141
coefficient (mm ⁻¹)		
F(000)	963	1384
θ Range for data	1.751-27.202	1.89-27.11
collection (°)		
Reflections	52107	42415
collected		
Independent	3548/0.2031	5168/ 0.0277
reflection / R _{int}		
Data / restraints /	7292/0/424	6465/0/ 450
parameters		
Goodness-of-fit	1.159	1.510
on F^2		
Final <i>R</i> indices	R1 = 0.1150;	R1 = 0.0936;
[I>2σ(I)]	wR2 = 0.1490	wR2 = 0.3187
D 11	D.1 0.0011	D 4 0 F 4
R indices (all	KI = 0.2214;	KI = 0.107/1;
data)	WK2 = 0.1/81	WK2 = 0.3438
Largest diff. peak	0.825/ -0.809	1.888/-0.590
/ nole (e A ⁻³)		

 Table S2 Binding constant and LOD values of complexes 1 and 2.

	Binding constant (k)		
	From UV-Vis study	Limit of detection	
		study	(LOD)(M)
Complex 1	$(1.33\pm0.04) \times 10^4$	$(1.49\pm0.01) \times 10^4$	1.39 × 10 ⁻⁷
Complex 2	$(1.65\pm0.008) \times 10^4$	$(1.74\pm0.01) \times 10^4$	1.50×10^{-7}

 Table S3 Life time and quantum yield values of chemosensors and complexes 1 and 2.

	Life time (ns)	χ^2	Quantum Yield (Φ)
HL ₁	3.15	1.15	0.019
HL ₂	1.45	1.02	0.054
Complex 1	3.91	1.10	0.170
Complex 2	1.50	0.98	0.210

Table S4 LD 50 values of complexes 1 and 2.

Complex	MDA-MB 468	SiHa
1	88±2.8	86±2.7
2	92±2.3	95±1.8

	HL ₁	HL ₂
LUMO+5	0.35	0.56
LUMO+4	0.1	0.04
LUMO+3	-0.06	-1.08
LUMO+2	-0.94	-1.6
LUMO+1	-1.59	-1.8
LUMO	-2.51	-2.72
НОМО	-5.4	-5.83
HOMO-1	-6.4	-6.69
HOMO-2	-6.68	-6.72
HOMO-3	-7.08	-7.44
HOMO-4	-7.37	-7.53
HOMO-5	-7.39	-7.64

Table S5 Energy (eV) of selected M.O.s of chemosensors (HL_1 and HL_2).

 Table S6 Electronic transition calculated by TDDFT using B3LYP/CPCM method in methanol

 solvent of chemosensors (HL1 and HL2).

	E _{excitation}	$\lambda_{\text{excitation}}$	Osc. Strength	Key transition	Transition
	(ev)	(nm)	(f)		assigned
HL1	2.61	474	0.3115	HOMO \rightarrow LUMO (99%)	n→π*
	3.50	353	0.3617	HOMO-1 \rightarrow LUMO (93%)	$\pi \rightarrow \pi^*$
HL2	2.80	442	0.4338	$HOMO \longrightarrow LUMO (99\%)$	n→π*
				HOMO-3 →LUMO (48%)	$\pi \rightarrow \pi^*$
				HOMO-3 →LUMO+1 (24%)	
	3.68	336	0.4495	HOMO-3 →LUMO+2 (16%)	

Chart S1 Previously reported quinoline based different chemosensing probes								
Probe	Crystal Structure	Sensing of metal ion(s)	Excitation(nm)/ Emission(nm)	Sensing Media	Binding constant	Limit of detection (LOD)	Biological study	Refs.
HL	-	Al ³⁺ , Zn ²⁺ and F^-	416/500, 416/530, -	EtOH-H ₂ O solution ($v/v = 4/1$, 0.01 M, Tris-HCl buffer, pH = 7.30)	$\begin{array}{r} 6.83 \ \times \ 10^4 \\ M^{-1}, \ 2.06 \ \times \\ 10^4 \ M^{-1} \\ \text{-} \end{array}$	23.5 nM, 11.5 nM and 86.0 nM	Yes	55a
4-methyl-2-((quinolin-6-ylimino)methyl)phenol (6-QMP)	-	Al^{3+} and Zn^{2+}	415/543 and 415/525	10 mM HEPES buffer in water :methanol (1 : 9, v/v) (pH 7.4)	$\begin{array}{c} 3.4{\times}10^{4} \\ M^{-1}, \ 8.8 \times \\ 10^{4} \ M^{-1} \end{array}$	23.4 nM and 53.7 nM	Yes	55b
4-methyl-2-((quinolin-2-ylimino)methyl)phenol (2-QMP)	-	Al^{3+} and Zn^{2+}	330/376 and 435/550	10 mM HEPES buffer in water :methanol (1 : 9, v/v) (pH 7.4)	$\begin{array}{c} 3.86 \ \times \ 10^4 \\ M^{-1}, \ 8.18 \ \times \\ 10^4 \ M^{-1} \end{array}$	3.79 μM and 136.3 nM	Yes	55b
N-(quinoline-8-yl)pyridine-2-carboxamide (Hbpq)	Yes	Zn^{2+} and Co^{2+}	370/481 and 401/-	CH ₃ CN	$\begin{array}{c} 7.0 \times 10^{11} \\ M^{-2} and \\ 4.0 \times 10^{11} \\ M^{-2} \end{array}$	7.93×10 ⁻⁷ M and 2.20×10 ⁻⁶ M	Yes	55c
AQZ-2COOH	Yes	Zn ²⁺	350/510	Tris-HCl buffer	3.6×10^9 M ⁻¹	0.10 μΜ	Yes	55d
2-amino-(quinolin-8-yl)acetamide (1)	Yes	Zn^{2+} and Cd^{2+}	300/504	Tris-HCl aqueous buffer pH 7.4 solution containing methanol (1% v/v) and Ethanol	$\begin{array}{rrrr} 1.41 \ \times \ 10^6 \\ M^{-1} & and \\ 8.45 \ \times \ 10^6 \\ M^{-1} \end{array}$	1.6 μM, -	Yes	55e
((E)-2-methoxy-N-((quinolin-2- yl)methylene)aniline) (MQA)	Yes	Zn^{2+} and Hg^{2+}	350/565 and 350/530	DMSO/water mixture (1/99 v/v)	$\begin{array}{cccc} 1.52 \ \times \ 10^4 \\ M^{-1} & and \\ 1.41 \ \times \ 10^5 \\ M^{-1} \end{array}$	0.011 μM and 0.040 μM	-	55f
L ₁	-	Zn^{2+} and $H_2PO_4^-$	390/525 and 390/430	$DMSO/H_2O$ $(v/v = 8:2)$	1.94×10 ⁴ M ⁻¹ ,	41.0 nM, -	Yes	55g
N-(quinoline-8-yl)pyrazine-2-carboxamide (Hqpzc)	-	Zn ²⁺ and Cu ²⁺	360/476 and 378/-	acetonitrile	$\begin{array}{c} 3.837{\times}10^{4} \\ M^{-1} & and \\ 7.352 \times 10^{7} \\ M^{-1} \end{array}$	$\begin{array}{ccc} 1.11 \times 10^{-6} \\ M & \text{and} \\ 1.48 \times 10^{-5} \\ M \end{array}$	-	55h
1-((quinolin-3-ylimino)methyl)naphthalen-2-ol (HL)	-	Al^{3+} and F^{-}	350/464 and 350/412	methanol	$\begin{array}{c c} 7.784 \overline{\times 10^8} \\ M^{-1} \end{array}$	75.19 nM, -	-	55i

					-			
L2	-	Zn^{2+} and F^{-}	400/500 and 400/475	DMSO	-	2.1×10 ⁻⁷ M,	-	55j
HL	-	Zn ²⁺	420/483	MeOH/H ₂ O (4:1; pH=7.4)	1.69×10 ⁴ M ⁻¹	5.81×10 ⁻⁶ M	-	55k
L1	-	Zn ²⁺	360/500	H_2O/e thanol (8 : 2, v/v)	-	0.65 μΜ	Yes	551
HAQT	Yes	Zn ²⁺	342/488	Tris buffer (pH = 7.40, CH ₃ OH–H ₂ O = 4:1, v/v)	5.18×10 ⁵ M ⁻¹	2.56 ×10 ⁻⁷ M	-	55m
1	-	Zn ²⁺	350/536	10 mM bis-tris, pH 7.0	1.4×10 ⁴ M ⁻¹	4.48 μM	-	55n
2-methoxy-6-((quinolin-8-ylimino)methyl)phenol (HL)	Yes	Zn ²⁺	461/594	9:1 v/v MeCN/H ₂ O in Tris–HCl buffer at pH 7.2	1.05 ×10 ⁴ M ⁻¹	1.3×10 ⁻⁷ M	Yes	550
2,4-dichloro-6-(quinolin-8- ylimino)methyl)phenol (HL)	Yes	Zn ²⁺	454/553	1:1, v/v CH ₃ CN:H ₂ O in HEPES buffer at pH = 7.2	3.10×10 ⁵ M ⁻²	5.0×10 ⁻⁹ M	Yes	55p
BFQ	-	Zn ²⁺ , Al ³⁺ and F-	395/560, 395/530 and 420/610	EtOH–H2O(v/v =9/1) and MeCN	$\begin{array}{c} (8.51\pm0.25)\\ \times10^{10} \ \ M^{-2},\\ (1.53\pm0.18)\\ \times10^{10} \ \ M^{-2}\\ \text{and}\\ (8.37\pm0.17\\ \times10^8 \ \ M^{-2} \end{array}$	$\begin{array}{c} (3.56{\pm}0.14) \\ \times 10^{-6} M, \\ (1.14{\pm}0.11) \\ \times 10^{-6} M \\ \text{and} \\ (3.68{\pm}0.21) \\ \times 10^{-6} M \end{array}$	-	55q
2,4-Dibromo-6-((quinolin-8- ylimino)methyl)phenol (HL ₄)	Yes	Zn ²⁺	440/540	10 mM HEPES buffer at pH 7.4	(1.33 ± 0.04) × 10 ⁴ M ⁻¹	1.39×10 ⁻⁷	Yes	This work
4-Nitro-2-((quinolin-8-ylimino)methyl)phenol) (HL ₂)	Yes	Al ³⁺	400/475	10 mM HEPES buffer at pH 7.4	(1.65 ± 0.00) 8)× 10 ⁴ M ⁻¹	1.50×10 ⁻⁷ M	Yes	This work