Electronic Supplementary Material (ESI) for RSC Advances

Supporting Information

A Naphthalimide-Quinoline based probe for selective, fluorescence ratiometric sensing of trivalent ions

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1. General procedure for drawing Job plot by fluorescence method:

Stock solution of same concentration of sensor and M^{3+} (where M = Fe^{3+}, Al^{3+} and Cr^{3+}) were prepared in the order of 20μM in [CH_3CN/ H_2O, 40/60, v/v] (at 25 °C) at pH 7.4 in HEPES buffer. The emission spectrum in each case with different *host–guest* ratio but equal in volume was recorded. Job plots were drawn by plotting $\Delta I.X_{host}$ *vs* X_{host} (ΔI = change of intensity of the emission spectrum at 390 nm during titration and X_{host} is the mole fraction of the host in each case, respectively).

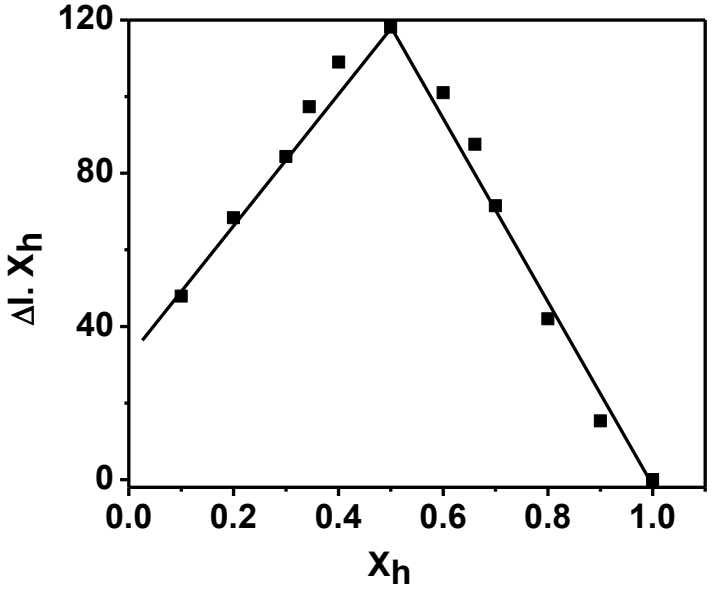


Figure S1: Job's plot diagram of receptor for Fe^{3+} ion (where X_h is the mole fraction of the host and ΔI indicates the change of emission intensity at 390 nm)

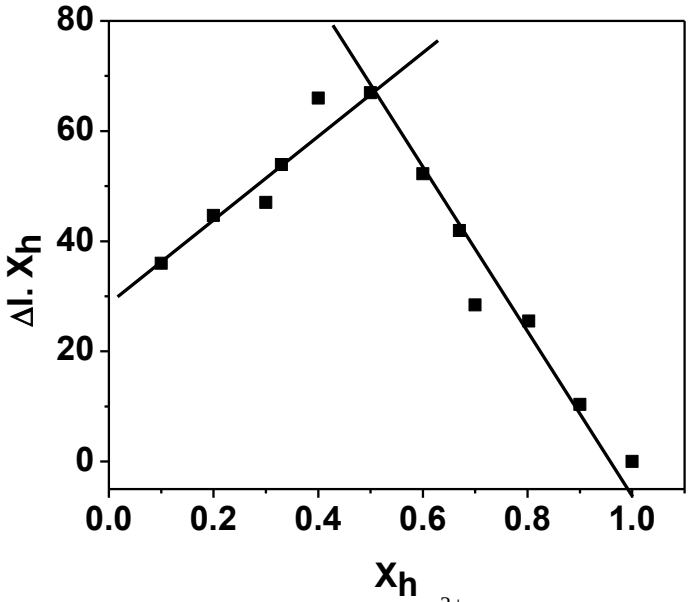


Figure S2: Job's plot diagram of receptor for Al^{3+} ion (where X_h is the mole fraction of the host and ΔI indicates the change of emission intensity at 390 nm)

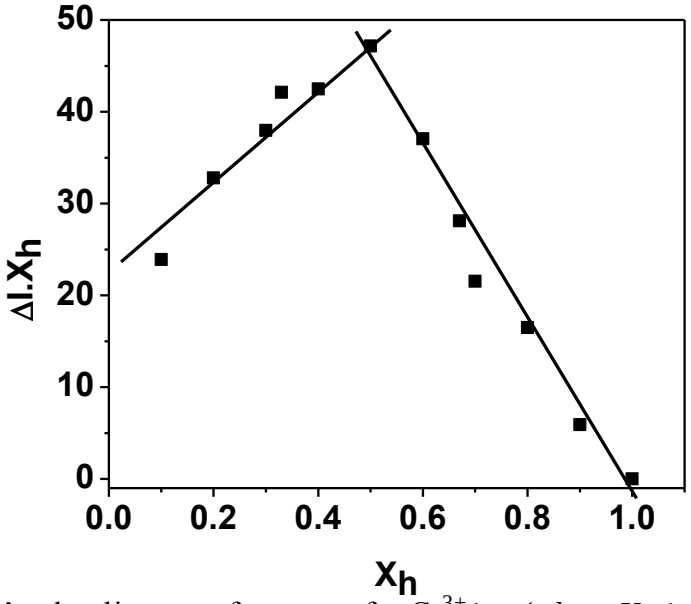


Figure S3: Job's plot diagram of receptor for Cr^{3+} ion (where X_h is the mole fraction of the host and ΔI indicates the change of emission intensity at 390 nm)

2. Association constant determination:

The binding constant value of M^{3+} (where M = Fe^{3+}, Al^{3+} and Cr^{3+}) with sensor has been determined from the emission intensity data following the modified Benesi–Hildebrand equation[1], $1/\Delta I = 1/\Delta I_{max} + (1/K[C])\ (1/\Delta I_{max})$. Here $\Delta I = (I-I_{min})$ and $\Delta I_{max} = (I_{max}-I_{min})$, where I_{min}, I, and I_{max} are the emission intensities of sensor considered in the absence of M^{3+}, at an intermediate M^{3+} concentration, and at a concentration of complete saturation where K is the binding constant and [C] is the M^{3+} concentration respectively. From the plot of $1/ (I-I_{min})$ against $[C]^{-1}$ for sensor, the value of K has been determined from the ratio of intercept and slope of Benesi-Hildebrand plot. As the plot of $1/ (I-I_{min})$ vs 1/[C] gives a straight line, indicates the 1:1 complexation of the sensor with M^{3+}. The association constant (K_a) as determined by fluorescence titration method for sensor with Fe^{3+} , Al^{3+} and Cr^{3+} are found to be $1.0852 \times 10^4\ M^{-1}$, $8.770 \times 10^3\ M^{-1}$and $5.676 \times 10^3\ M^{-1}$ respectively (error ± 10%).

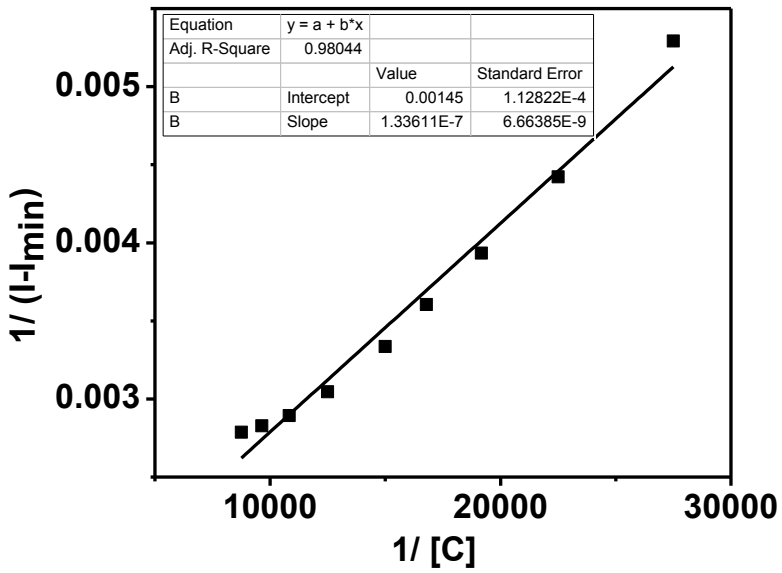


Figure S4: Benesi–Hildebrand plot from fluorescence titration data of receptor (20 μM) with Fe^{3+}.

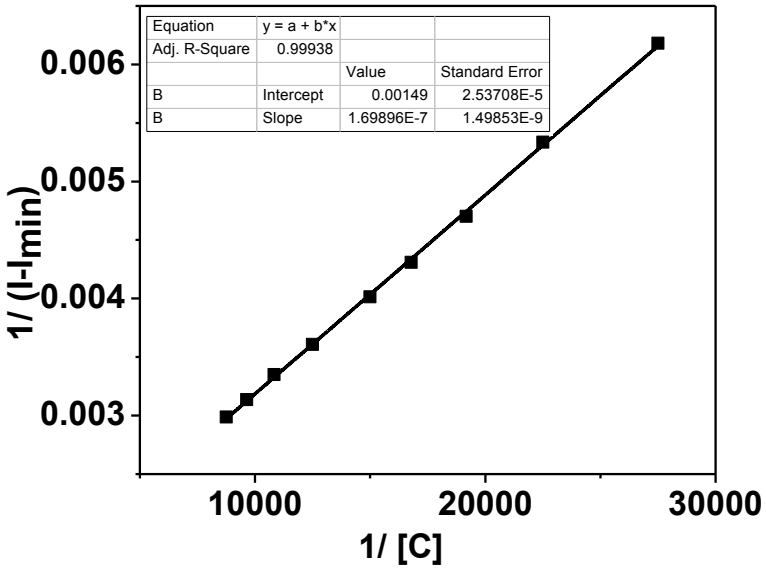


Figure S5: Benesi–Hildebrand plot from fluorescence titration data of receptor (20 μM) with Al^{3+}.

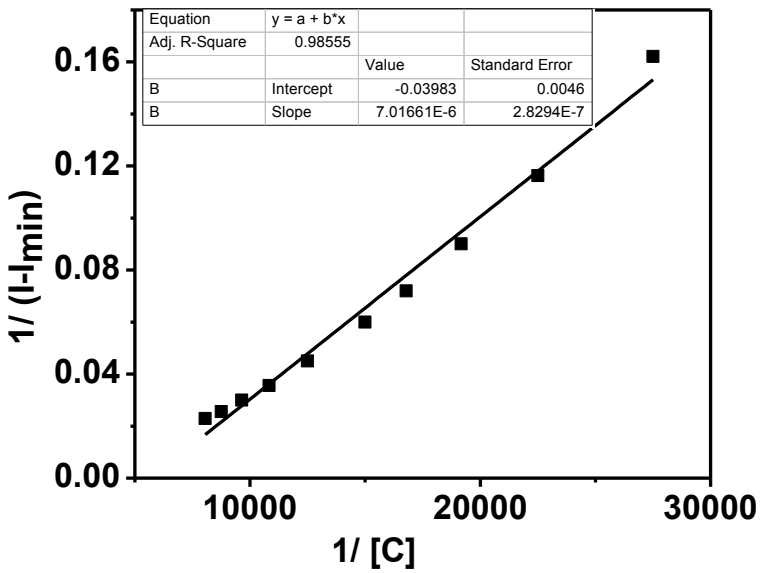


Figure S6: Benesi–Hildebrand plot from fluorescence titration data of receptor (20 µM) with Cr^{3+}.

3. Determination of detection limit:

The detection limit (DL) of **NAQ** for Fe^{3+}, Al^{3+} and Cr^{3+} were determined from the following equation:
DL = K* Sb1/S
Where K = 2 or 3 (we take 3 in this case); Sb1 is the standard deviation of the blank solution; S is the slope of the calibration curve.

For Fe^{3+}:
From the graph we get slope = 16700.99, and Sb1 value is 0.115058
Thus using the formula we get the Detection Limit = 20 µM i.e. NAQ can detect Fe^{3+} in this minimum concentration.

For Al^{3+}:
From the graph we get slope = 7.53E+03, and Sb1 value is 0.059735
Thus using the formula we get the Detection Limit = 23 µM i.e. NAQ can detect Al^{3+} in this minimum concentration.

For Cr^{3+}:
From the graph we get slope = 2662.453, and Sb1 value is 0.022587
Thus using the formula we get the Detection Limit = 25 µM i.e. NAQ can detect Cr^{3+} in this minimum concentration.

4. Metal ion selectivity profile of the sensor :

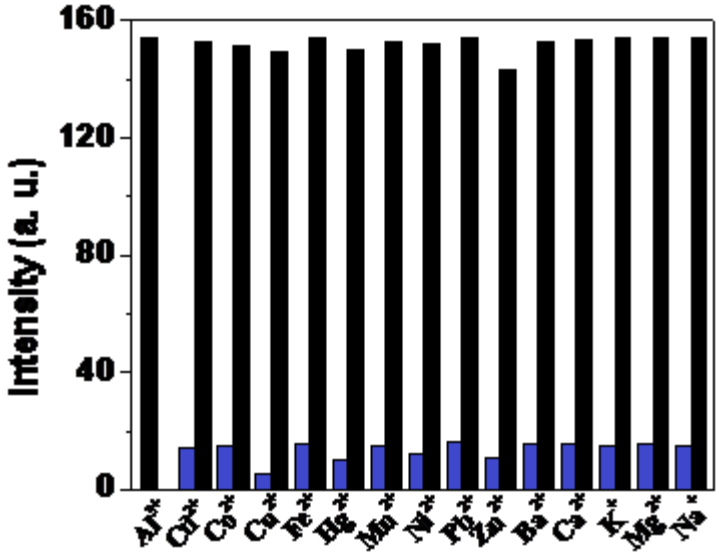


Figure S7: Metal ion selectivity profile of the receptor (20 μM): (black bars) change of emission intensity of receptor + 10 equiv M^{n+}; (blue bars) change of emission intensity of receptor + 10 equiv M^{n+}, followed by 3 equiv Al^{3+} at 484 nm

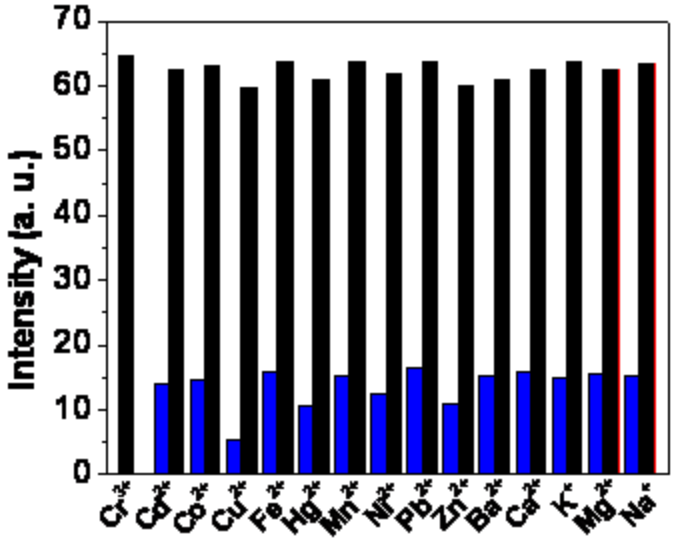
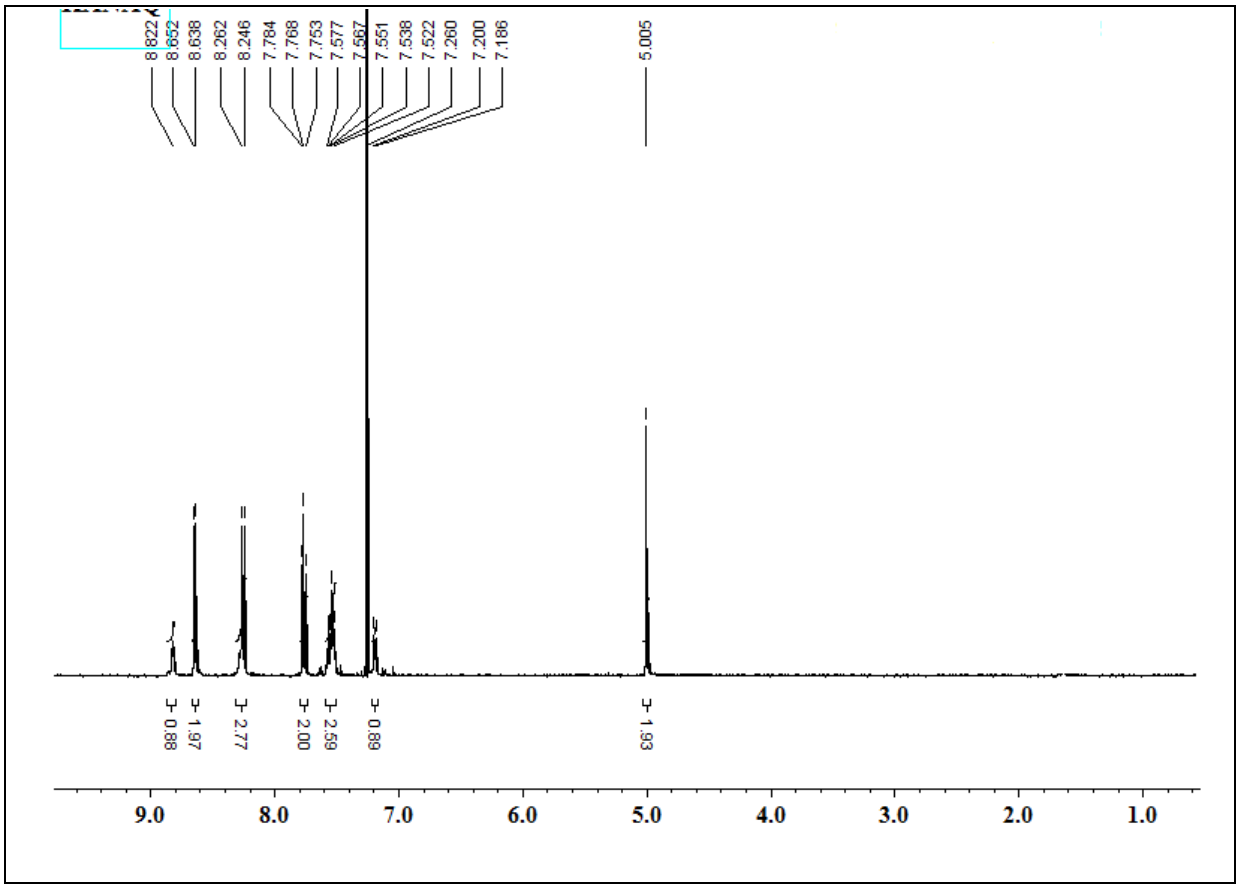
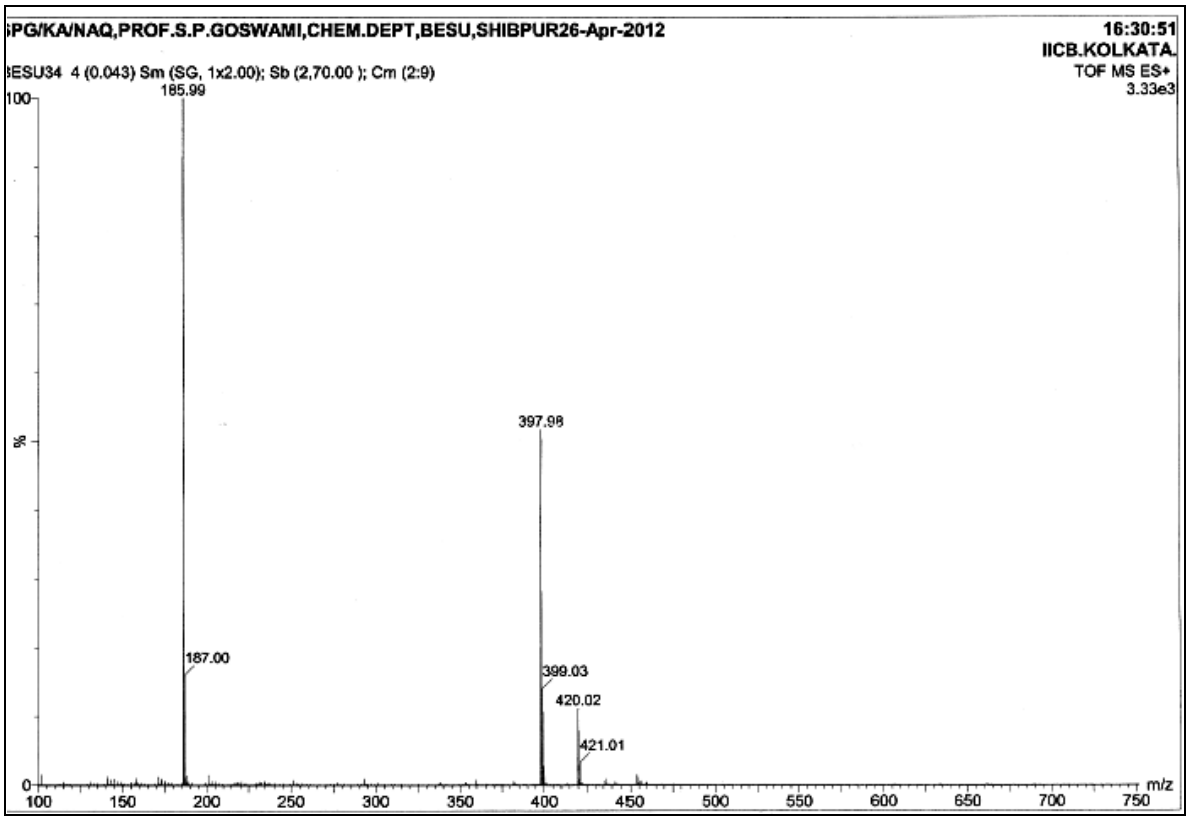


Figure S8: Metal ion selectivity profile of the receptor (20 μM): (black bars) change of emission intensity of receptor + 10 equiv M^{n+}; (blue bars) change of emission intensity of receptor + 10 equiv M^{n+}, followed by 3 equiv Cr^{3+} at 484 nm

5.

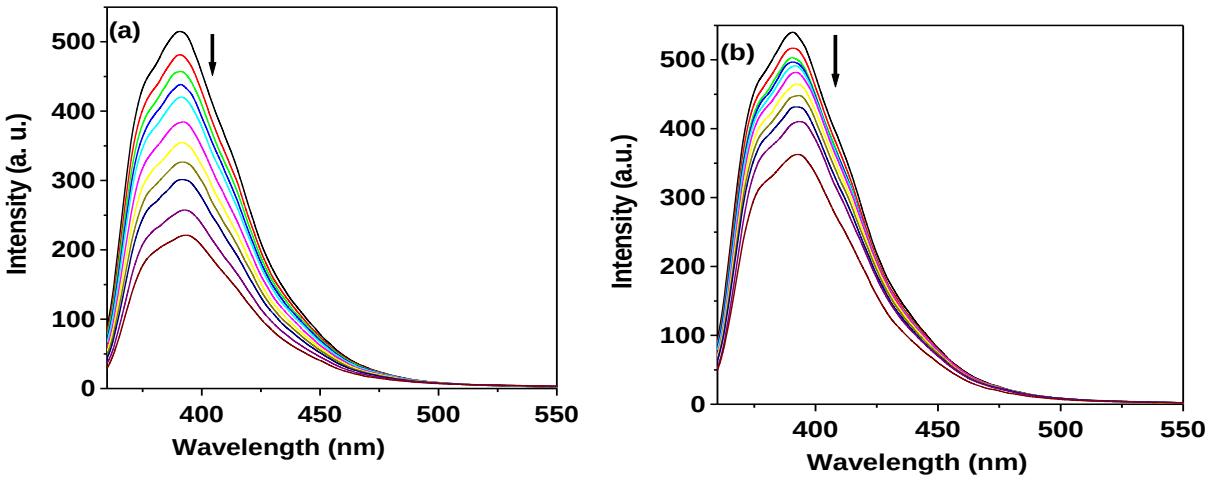


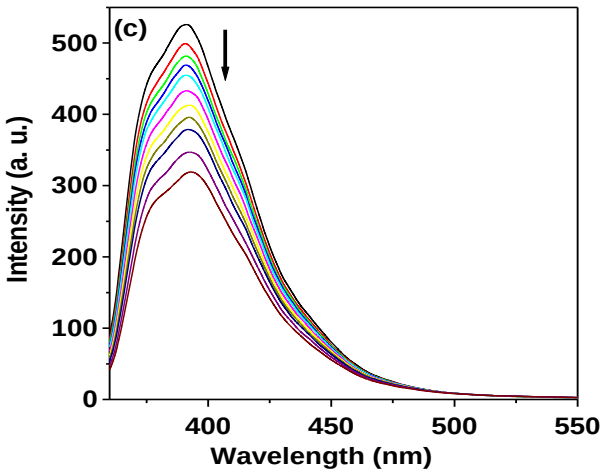
S9: 1H NMR spectrum of NAQ

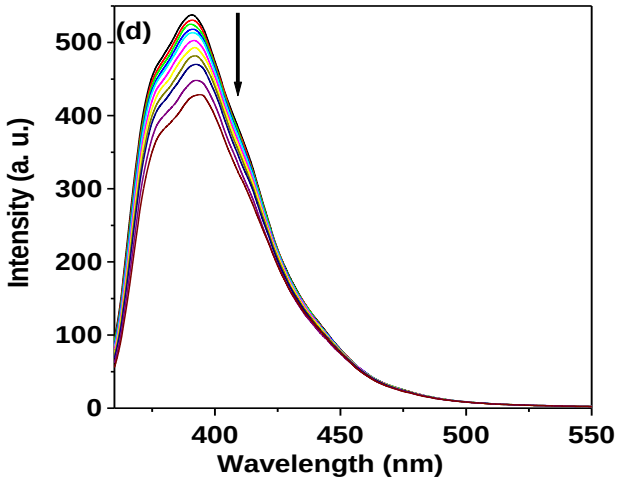


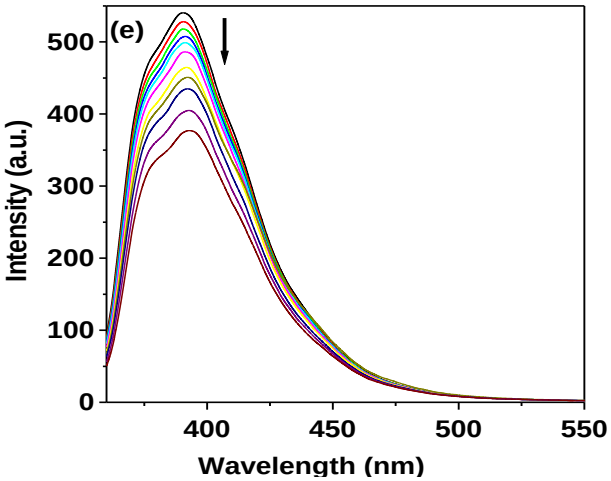
S10: Mass spectrum of NAQ.

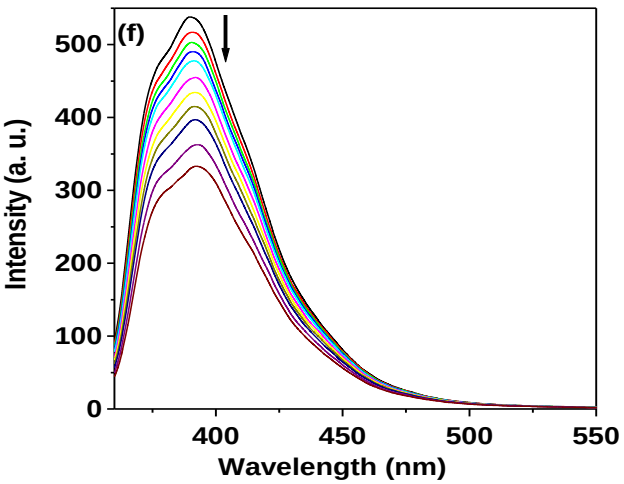
6. Fluorescence titration spectra of receptor with different guest cations:

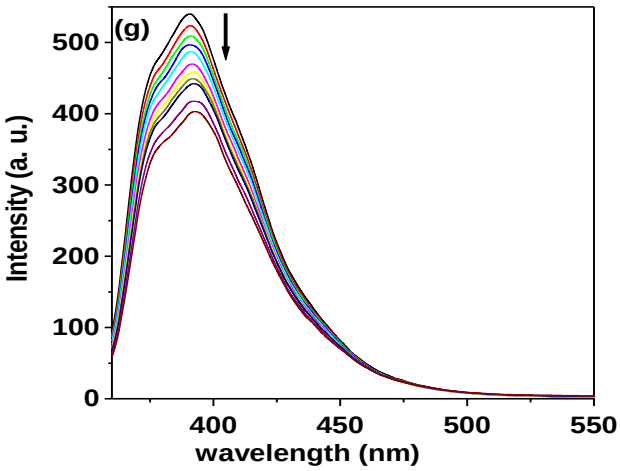


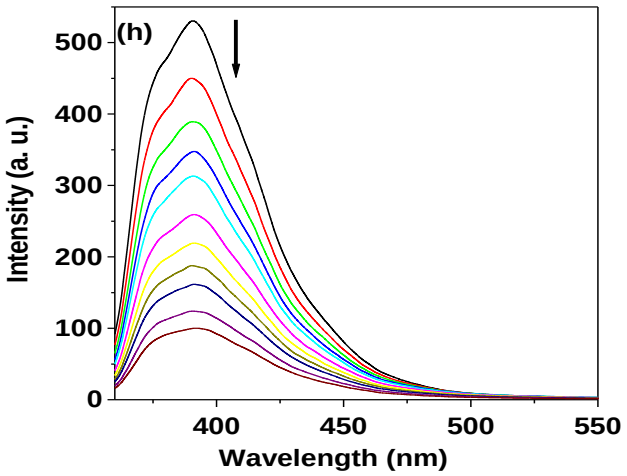












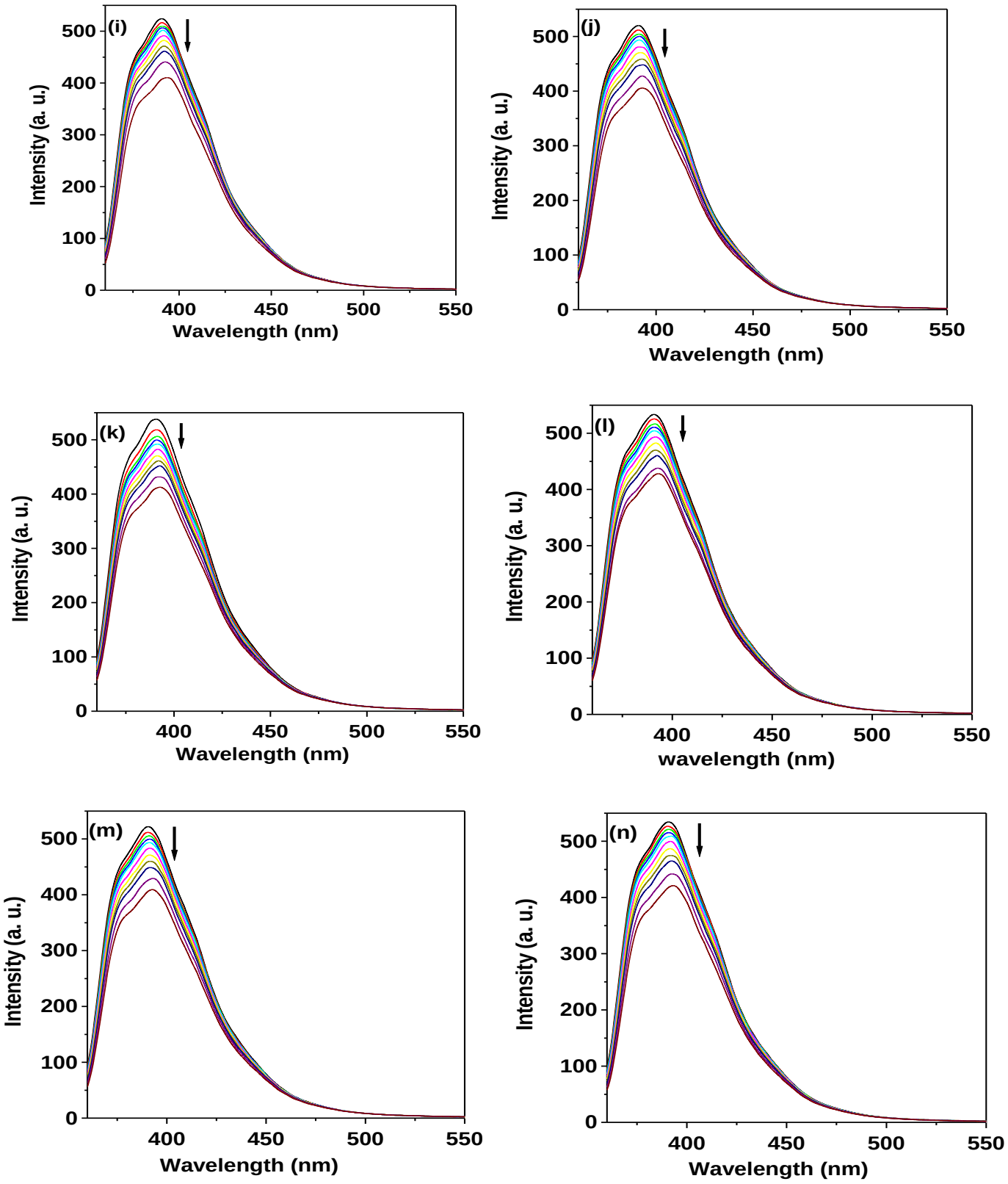


Figure S11: Fluorescence titration spectra of receptor (20 μM in CH_3CN/ H_2O, 40/60, v/v, HEPES buffer solution) with (0- 10 equiv.) of (a) Zn^{2+}, (b) Hg^{2+}, (c) Cd^{2+}, (d) Fe^{2+},

(e) Co^{2+}, (f) Ni^{2+}, (g) Pb^{2+}, (h) Cu^{2+}, (i) Mn^{2+}, (j) Ba^{2+}, (k) Ca^{2+}, (l) K^{+}, (m) Mg^{2+}, (n) Na^{+} respectively.

7. UV-vis titration spectra of the sensor with Fe^{3+}, Al^{3+} and Cr^{3+}:

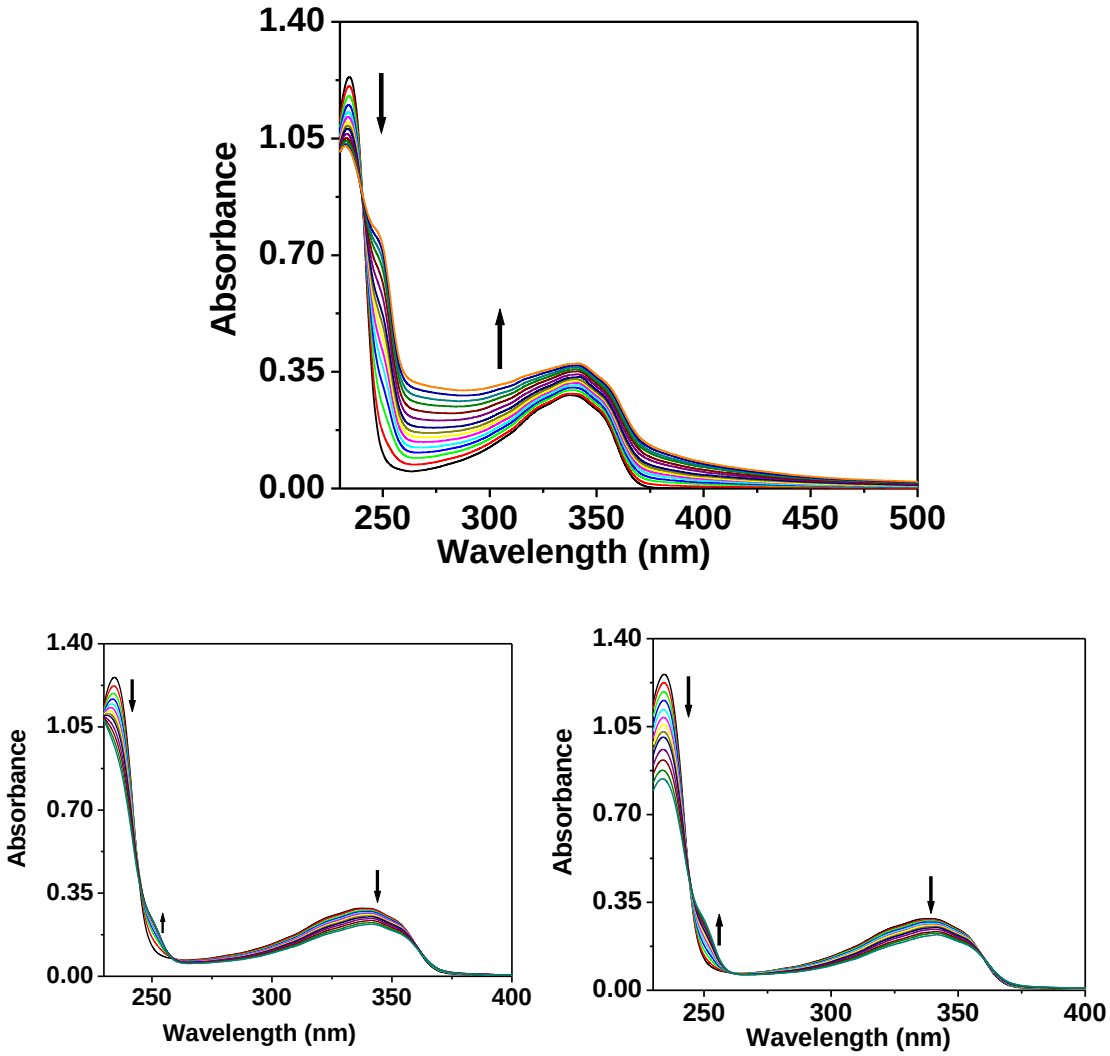


Figure S12: UV-vis titration spectra of NAQ with (a) Fe^{3+}, (b) Al^{3+} and (c) Cr^{3+} (0 to 10 equivalents) in CH_3CN / H_2O (40/ 60, *v/v*, pH=7.4) solutions.

9. Crystallographic data and details of the structure determination of receptor (NAQ):

The data were collected using a Bruker-APEX II SMART CCD diffractometer with the graphite monochromated Mo-Kα radiation (λ = 0.71073) at a detector distance of 5 cm and with APEX2 software. For data processing and absorption correction the packages SAINT[1] and SADABS[2] were used. The structures were solved by direct and Fourier methods and refined by full-matrix least squares based on F2 using SHELXTL[3] and SHELXL-97[4] packages. The crystallographic data and hydrogen bond geometry are

presented in Tables 1 and 2, respectively. Crystallographic data for receptor **NAQ** has been deposited with the Cambridge Crystallographic Data Center No. CCDC 888916.

Table 1:

CCDC No.	888916
Empirical Formula	$C_{23}H_{15}N_3O_4$
Formula weight	397.38
Crystal system	
Space group	P b c a
T [K]	296 K
a [Å]	15.1430(4)
b [Å]	13.8141(4)
c [Å]	17.0179(5)
α [deg]	90
β [deg]	90
γ [deg]	90
Z	8
V [Å^3]	3559.92(17)
*D*calc [g/cm^3]	1.483
F [000]	1648.0
Crystal size [mm]	0.10 x 0.20 x 0.30
Theta min-max [deg]	2.3, 27.1
μ [mm^{-1}]	0.104
Reflections collected	34767
Unique reflections	3918
Observed reflections	2982
R [$F^2 > 2\sigma(F^2)$]	0.0394
wR(F^2)	0.1561

References:

(1) APEX-II, SAINT-Plus, and TWINABS; Bruker-Nonius AXS, Inc.: Madison, WI, 2004
(2) Sheldrick, G. M. SAINT, version 6.02 and SADABS, version 2.03; Bruker AXS, Inc.: Madison, WI, 2002.
(3) SHELXTL, version 6.10; Bruker AXS, Inc.: Madison, WI, 2002.
(4) Sheldrick, G. M. SHELXL-97, Crystal Structure Refinement Program; University of G€ottingen: Germany, 1997.