Supporting Information

Selective Colorimetric and Ratiometric Probe for Ni(II) in Quinoxaline Matrix with the Single Crystal X-ray Structure

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1. Experimental Section:

1.1 Materials and physical methods:

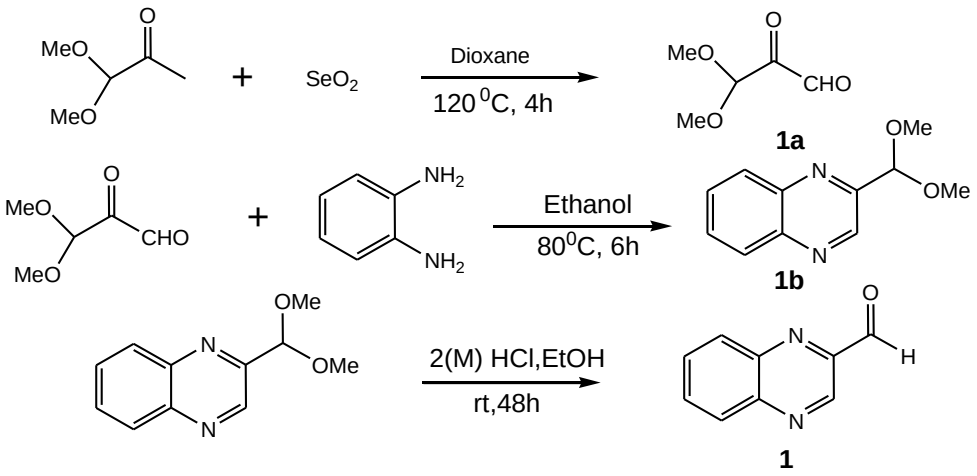
All chemicals and solvents were purchased from Sigma-Aldrich chemicals Private Limited and were used without further purification. Melting points were determined on a hot-plate melting point apparatus in an open-mouth capillary and are uncorrected. ^{1}H-NMR was recorded on a Brucker 400 MHz instrument. For NMR spectra, d_6-DMSO was used as a solvent using TMS as an internal standard. Chemical shifts are expressed in δ units and ^{1}H–^{1}H and ^{1}H–C coupling constants in Hz. UV-vis titration experiments were performed on a JASCO UV-V630 spectrophotometer. IR spectra were recorded on a JASCO FT/IR-460 plus spectrometer, using KBr discs. ^{13}C-NMR spectra were recorded on a JEOL 500 MHz instrument and fluorescence experiments were performed using a Perkin Elmer LS 55 fluorescence spectrophotometer with a fluorescence cell path of 10 mm.

1.2 General method of UV-vis titration:

For UV-vis titrations, stock solution of the sensor was prepared ($c = 1 \times 10^{-5}$ ML^{-1}) in CH_3CN. The solution of the guest cations using their salts in the order of 2×10^{-4} ML^{-1} was prepared in CH_3CN solvent. Solutions of various concentrations containing sensor and increasing concentrations of cations were prepared separately. Titration was carried out with 2 ml of ligand of concentration (1×10^{-5} ML^{-1}) with different cations of concentration (2×10^{-4} ML^{-1}). The spectra of these solutions were recorded by means of UV-vis methods.

1.3 Method for the preparation of quinoxaline aldehyde and the receptor (HQAP):

Synthesis of Quinoxaline Aldehyde (1) :



Scheme 1: Synthesis of the quinoxaline aldehyde(**1**)

Synthesis of 3,3 Dimethoxy 2-Oxo propanal (1a)

In a round bottom flask, pyruvaldehyde dimethyl acetal (5.5g, 46.5 mmol), selenium dioxide (6.1g, 55.8mmol) and 1,4-dioxan (20 ml) were taken and the reaction mixture was refluxed for 5h at 120^{o}C . After checking with TLC that the starting materials have been consumed, the reaction mixture was passed through celite bed and the filtrate was collected. The reaction mixture was washed with chloroform to get the crude compound**.** The crude compound was directly used for the next step reaction.

Synthesis of 2,2 Dimethoxy methyl Quinoxaline(1b)

The crude compound (6.1 g, 46.55 mmol) was dissolved in ethanol (50ml) and o-phenylene diamine (5g, 46.55 mmol) was added to it and the reaction mixture was refluxed for 12h at 80^{o}C. The reaction mixture was cooled and the ethanol was evaporated by a rotary evaporator and the crude material was purified by silica gel (100-

200 mesh) column chromatography using (90/10, v/v) ethyl acetate-pet ether to afford a brown color solid (7.1g, 74%).

($C_{11}H_{12}N_2O_2$): brown color solid.

Mp 85 °C.

^{1}H NMR ($CDCl_3$, 400 MHz): δ (ppm): 9.10 (s, 1H), 8.17-8.12 (m, 2H), 7.80-7.77 (m, 2H,), 5.56 (s, 1H,), 3.50 (s, 6H).

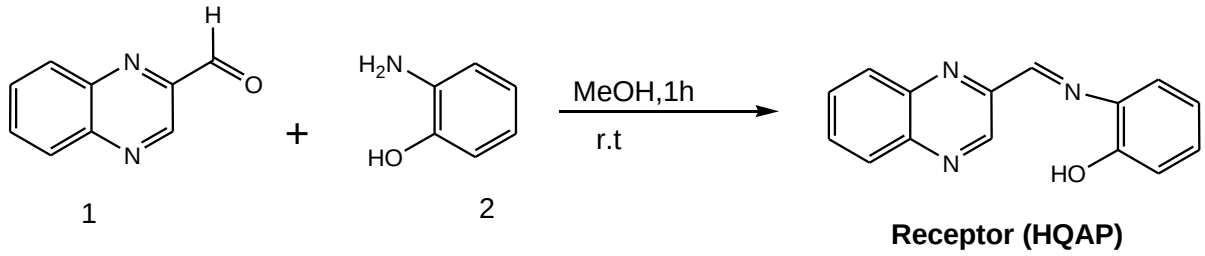
Synthesis of Quinoxaline aldehyde (1)

To the crude compound (4g, 19.60 mmol), 2(N) HCl (19ml) was added at 0^0C and the mixture was stirred for 48h at room temperature. The reaction mixture was quenched with saturated sodium carbonate solution and the mixture was extracted with ethyl acetate solution and finally purified by flash chromatography using 100-200 mesh silica-gel. The product was eluted in ethyl acetate-pet ether (95/5, v/v) to afford a light yellow solid (2.6g, 86%).

Mp-109 °C.

^{1}H NMR ($CDCl_3$, 400 MHz): δ (ppm): 10.19 (s, 1H), 9.36 (s, 1H), 8.31 (d, 1H, J=8.3Hz), 8.24 (d, 1H, J=8.3Hz), 7.89-7.82 (m, 2H).

Synthesis of the quioxaline ligand (HQAP):



Scheme 2: Synthesis of the receptor (**HQAP**)

To a stirred solution of quinoxaline aldehyde (**1**, 100mg, 0.63 mmol) in methanol solution (2ml), 2 amino phenol [**2**, (69mg, 0.63mmol) dissolved in 1 ml of ethanol] was added. A precipitate appeared instantaneously. The reaction mixture was stirred for another one hour. After TLC has shown that the completion of the reaction, the product was filtered and washed with a little amount of ethanol two times.

Yield 67%.

Yellow solid, Mp >280 °C.

^{1}H NMR (DMSO-d6 ,400 MHz): δ (ppm): 9.95 (s, 1H), 9.42 (s, 1H), 9.00 (s, 1H,), 8.18 (d, 2H, J=3.36), 7.94 (d, 2H, J=3.2) ,7.51(d, 1H, J=7.52), 7.21(t, 1H, J= 7.26), 6.96 (d,1H, J=7.88),6.90(t,1H,J=7.3).

MS : M^+ Calculated for $C_{15}H_{11}N_3O$ is 249.09; Found: 271.80$(M+Na)^+$.

^{13}C NMR (DMSO-d_6, 500 MHz): δ (ppm):157.30, 152.81, 149.63, 145.00, 142.63, 141.35, 136.28, 131.90, 131.46, 130.18, 129.87, 129.56, 120.33, 120.03, 117.21

2.4 Syntheses of the HQAP+Ni^{2+}complexes:

To a hot methanolic solution (1 ml) containing the quinoxaline ligand (**HQAP**, 1.0 mL), a methanolic solution containing $NiCl_2.6H_2O$ (28.0 mg, 0.12 mmol) was added. A dark deep violet precipitate appeared immediately. After stirring for 1.0 h, the deep violet complexes were filtered, collected and then washed for several times with hot methanol. The complexes were dried in a dessicator over anhydrous $CaCl_2$ under vacuum. The dried ligands and complexes were subjected to spectroscopic analyses. The complexes are air-stable, nonhygroscopic and soluble in H_2O, EtOH, MeOH, DMSO and DMF.

Yield 80%. Color: deep violet. mp >280 °C.

MS : M^+ Calculated for $C_{30}H_{20}N_6O_2Ni$ is 554.87; Found:555.10.

2. General procedure for drawing Job plot by UV–vis method:

Stock solution of same concentration of sensor and Ni were prepared in the order of ≈ 1.0 x 10^{-5} ML^{-1} CH_3CN. The absorbance 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 absorbance spectrum during titration and X_{host} is the mole fraction of the host in each case, respectively).

3. Determination of Detection Limit:

The detection limit DL of **HQAP** for Ni^{+2} was determined from the following equation [S1]:

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.

From the graph we get slope = 3990.8 , and Sb1 value is. 0.005534. Thus using the formula we get the Detection Limit = 4.16 µM i.e. HQAP can detect Ni^{2+} in this minimum concentration.

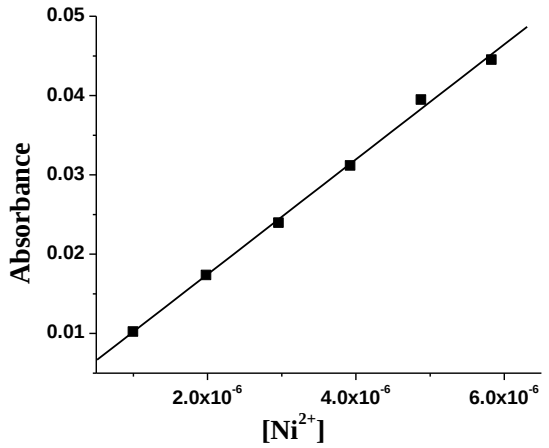


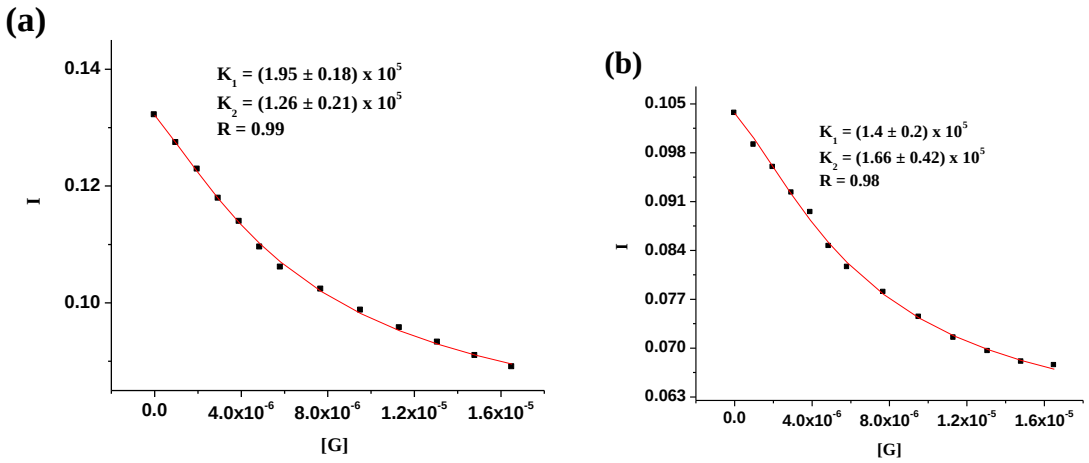
Figure S1: Absorbance vs Conentration plot of receptor **HQAP** (1x10^{-5}M) with Ni^{2+}.

4. Determination of Association constant:

The association constants were calculated based on the titration curve of the probes with metal ions. Association constants were determined by a nonlinear least squares fit of the data with the following equation. [S2]

$$I = (I_0 + K_1 \cdot C_G \cdot I\,[1{:}1] + K_1 \cdot K_2 \cdot I_{lim} \cdot C_{G2}) / (1 + K_1 \cdot C_G + K_1 \cdot K_2 \cdot C_{G2}) \qquad (1)$$

I represents the absorbance intensity, I_0 represents the intensity of pure host, and $I_{[1:1]}$ represents intensity at [G]/[H] = 1:1. C_G is the corresponding concentration of the guest and *K* is the association constant. The association constant and correlation coefficients (*R*) were obtained by a nonlinear least-square analysis of *I* vs. C_G.



(a) binding constant at 372 nm **(b) binding constant at 306 nm**

Figure S2: (a) Plots of absorbance at 372 nm of **HQAP** as a function of [G]. (b) Plots of absorbance at 306 nm of **HQAP** as a function of [G].

5. Absorbance vs. pH plot

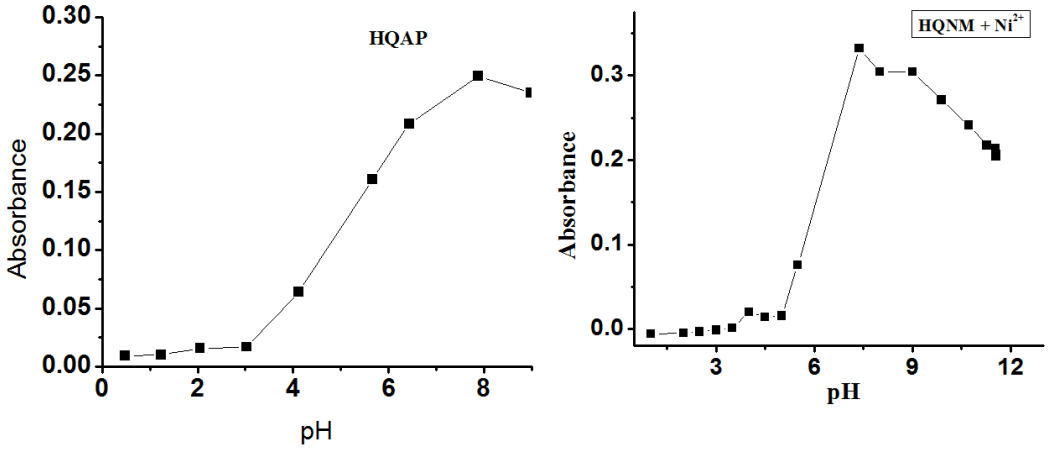
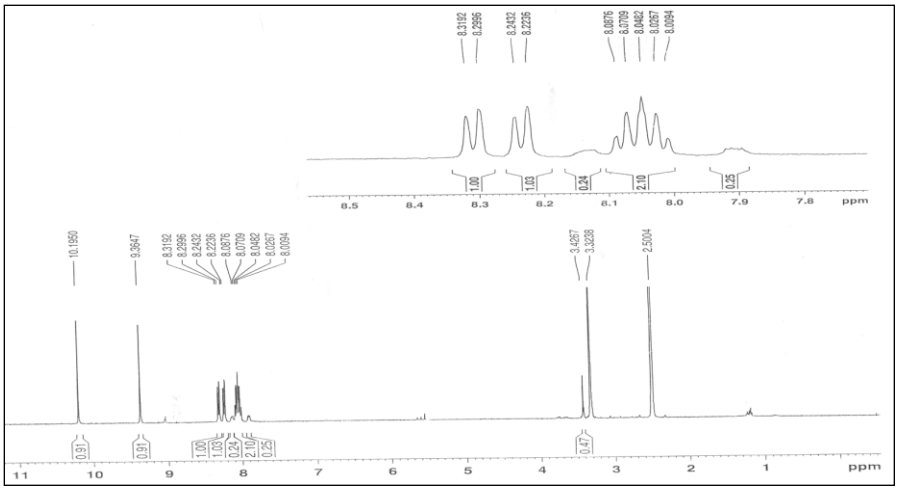


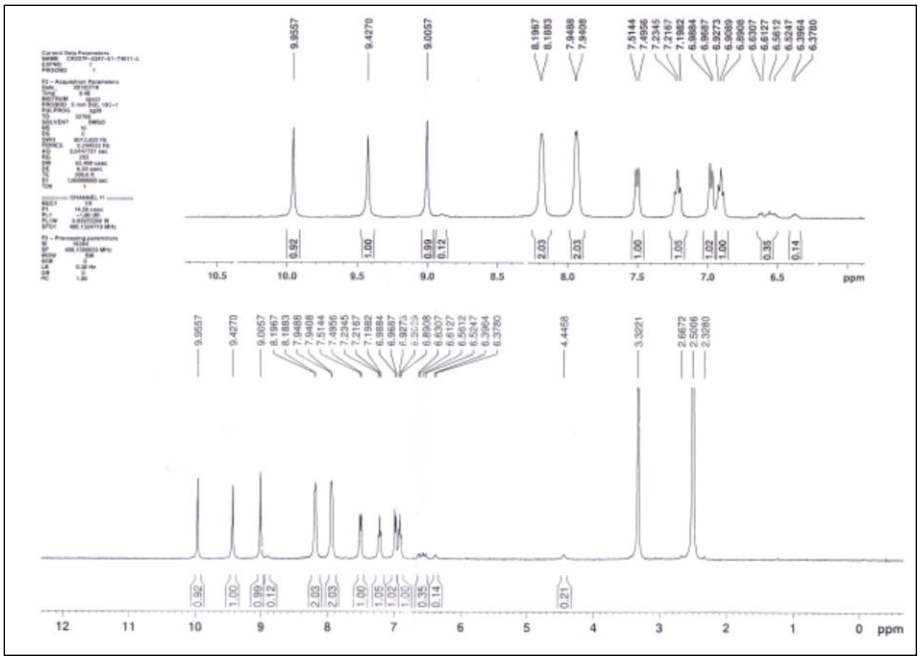
Figure S3: (a) Plots of absorbance at 372 nm of **HQAP** as a function of pH. The solid line is the best fit pH titration curve with **p*Ka*** 5.45. (b)Absobance intensity of **HQAP** (10 μM) at various pH values in CH_3CN-H_2O (9:1, v/v) medium in presence of Ni^{2+} (2.0 equiv., 2.0 x10^{-4} M)at 570 nm.

6. ^{1}H NMR, ESI MS and FT-IR spectra of Quinoxaline aldehyde, receptor and receptor + Ni:

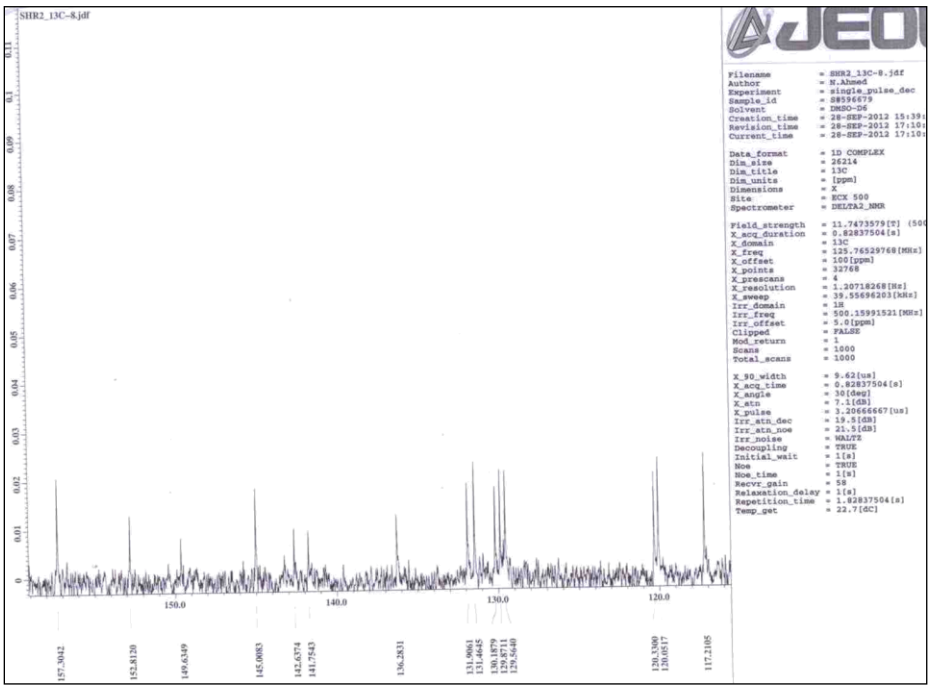
^{1}H NMR of quinoxaline aldehyde:



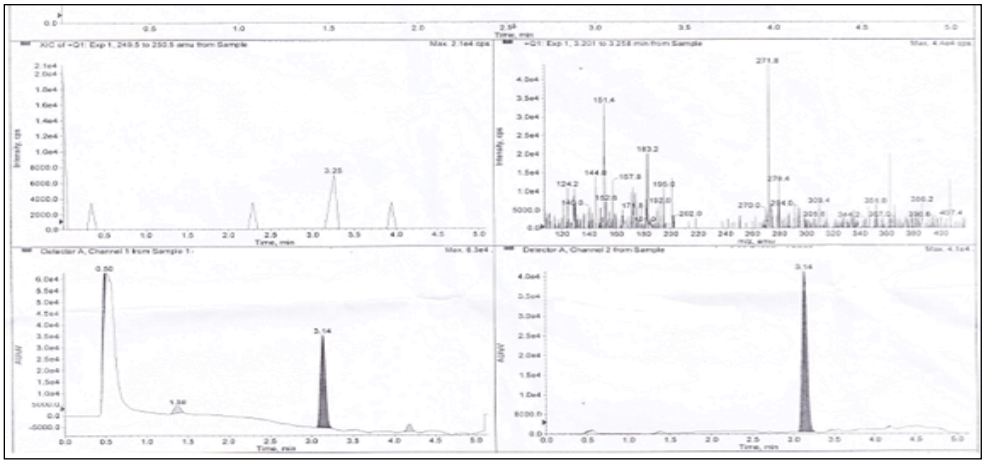
^{1}H NMR of Receptor:



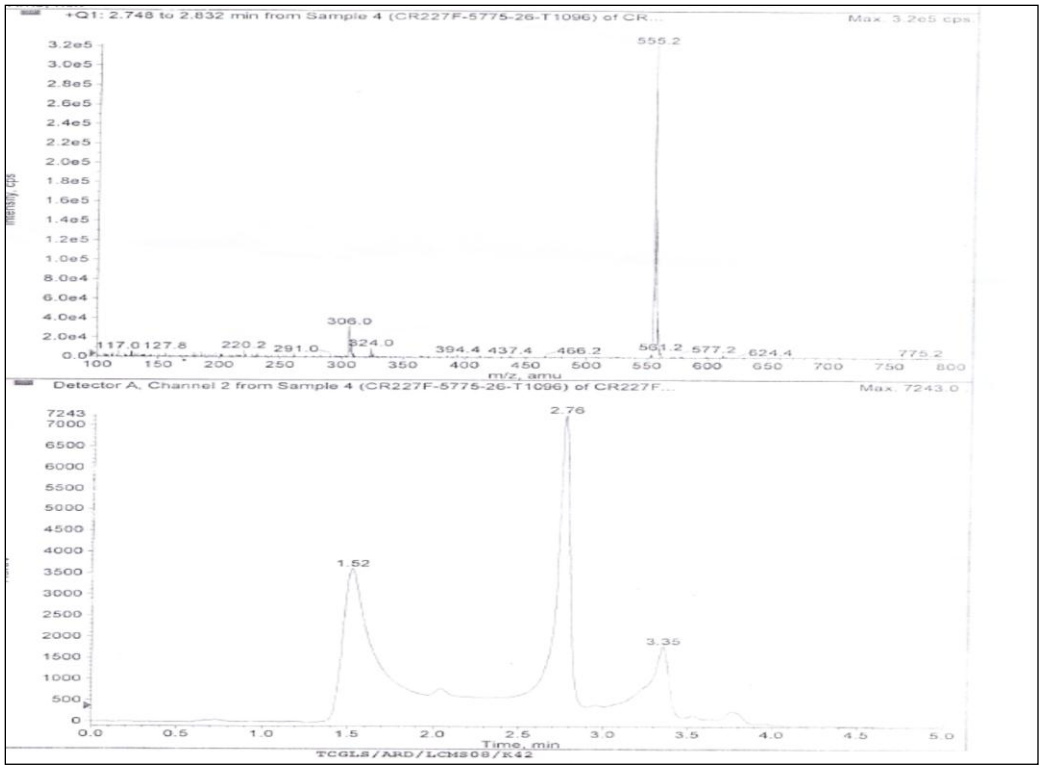
^{13}C NMR of Receptor:



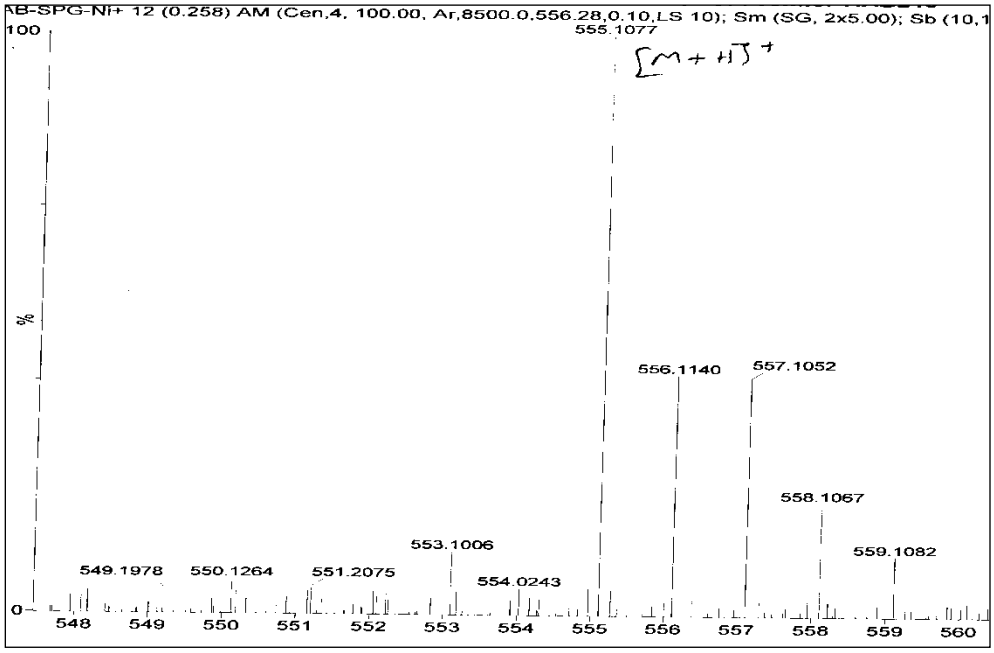
ESI LCMS spectra of Receptor:



ESI LCMS spectra of receptor +Ni:

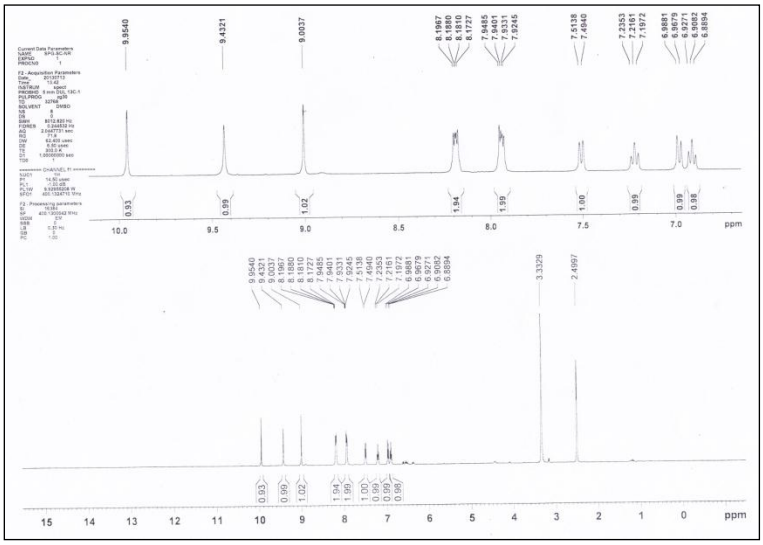


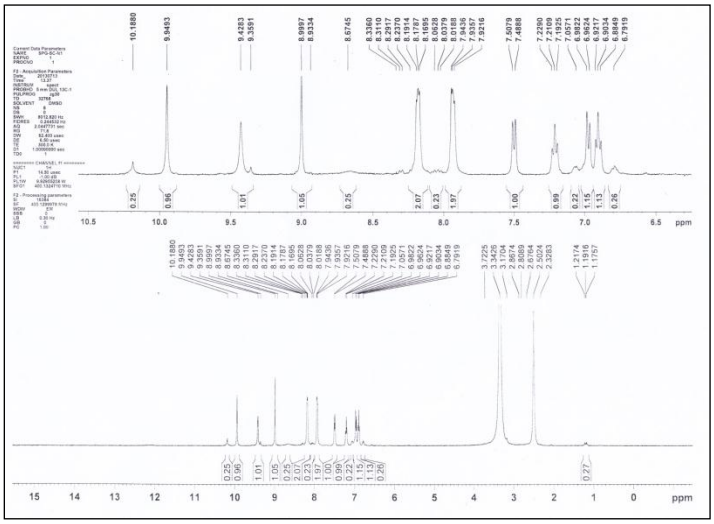
HRMS spectra receptor +Ni:

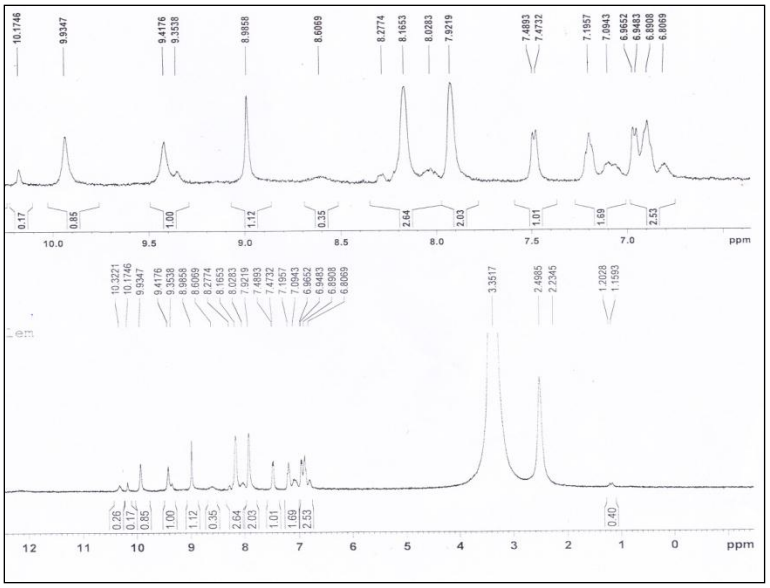


NMR Titration data of Receptor:

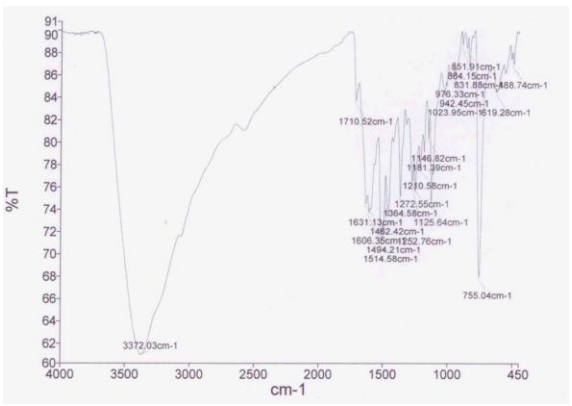
Partial ^{1}H NMR spectra (400MHz) of HQAP in DMSO-d_6 at 25°C and corresponding changes after the gradual addition of different equivalents of nickel chloride from .(a)HQAP (b) HQAP+0.2 equiv Ni^{2+} (c) HQAP+0.8 equiv Ni^{2+}

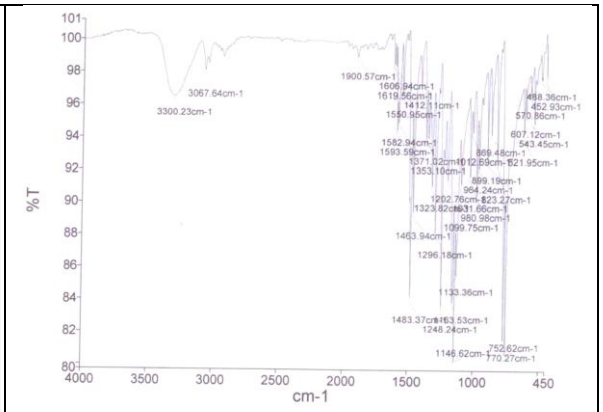






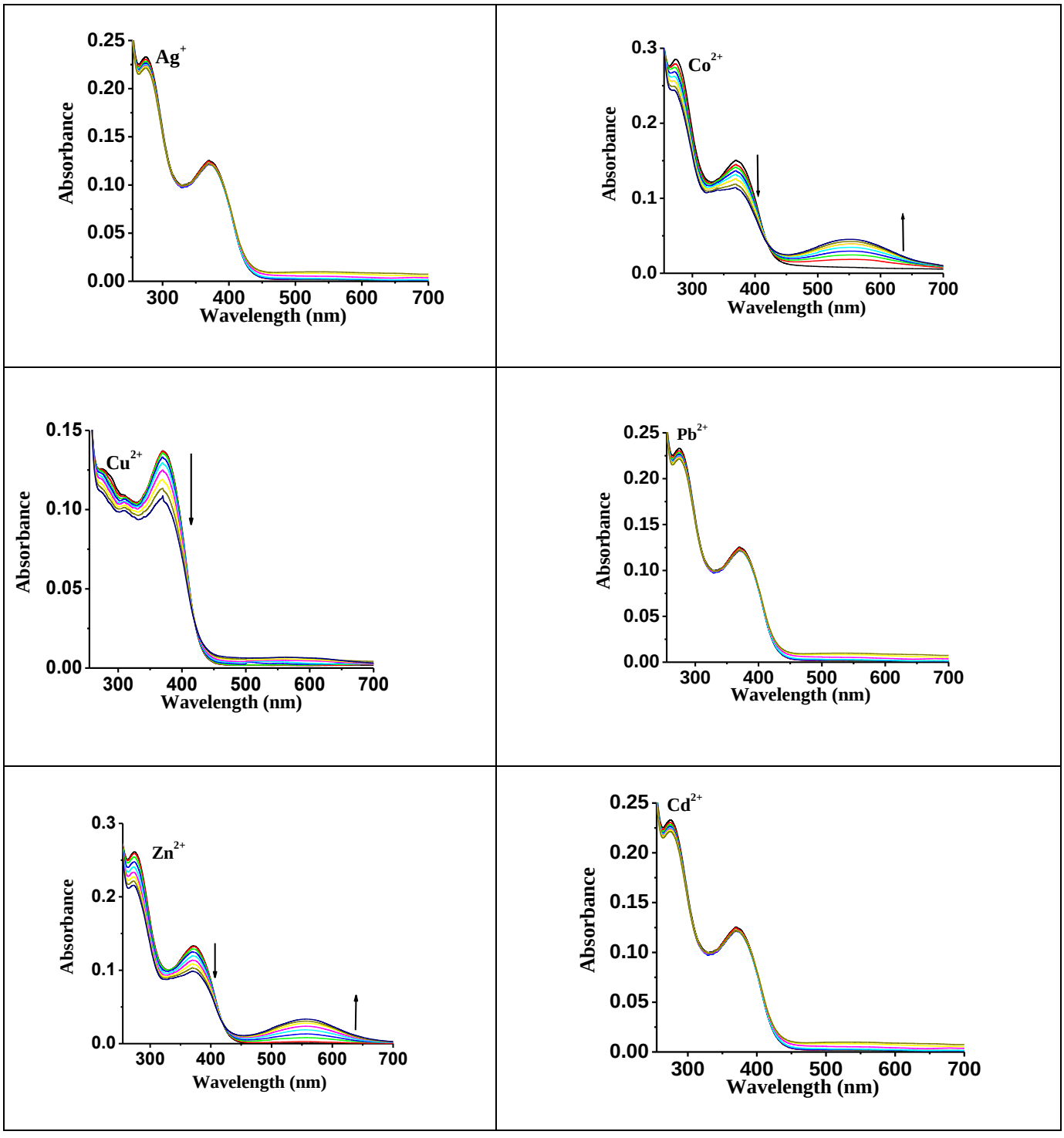
FT-IR data of (a) Receptor and its (b) Receptor +Ni

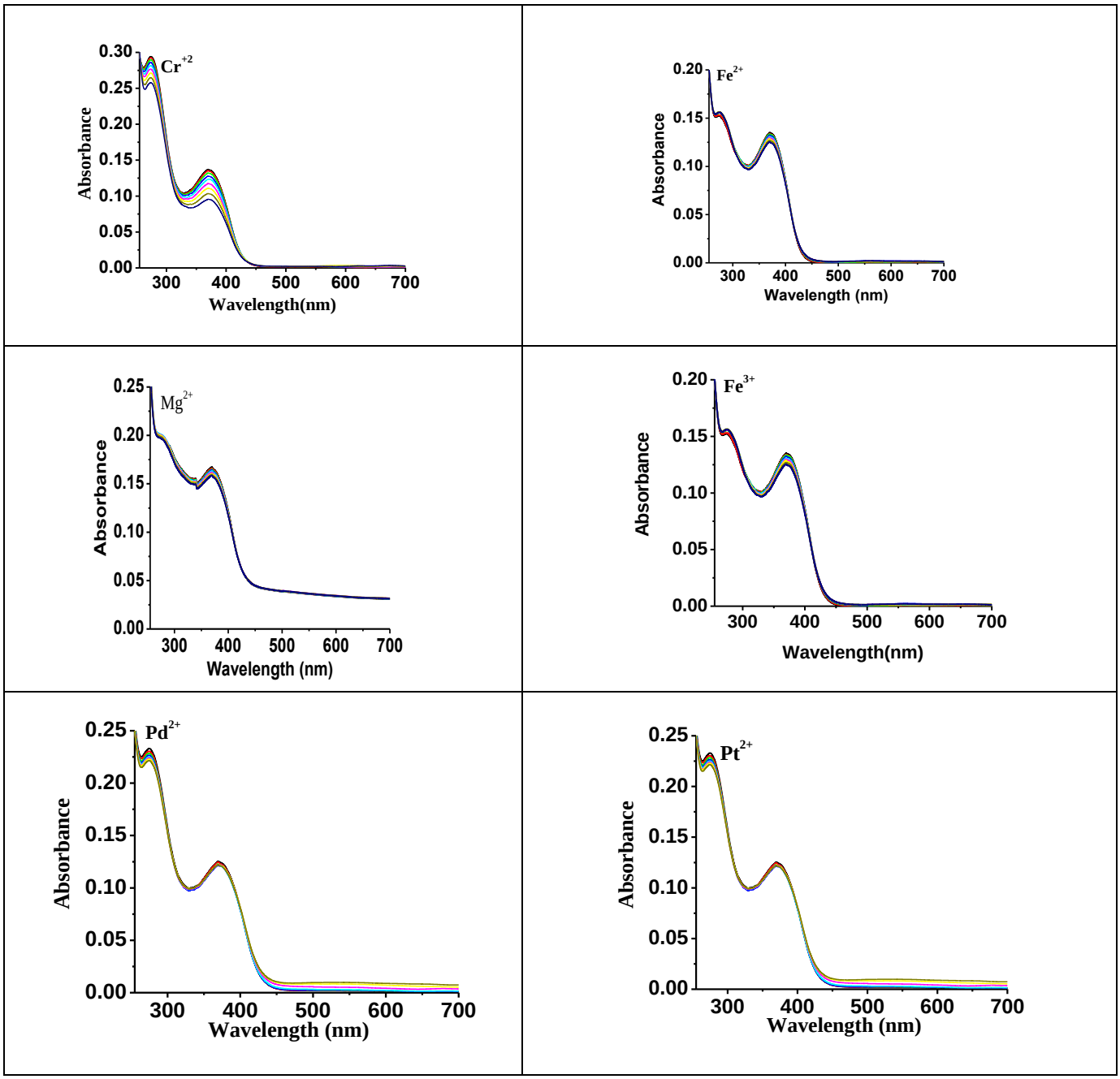


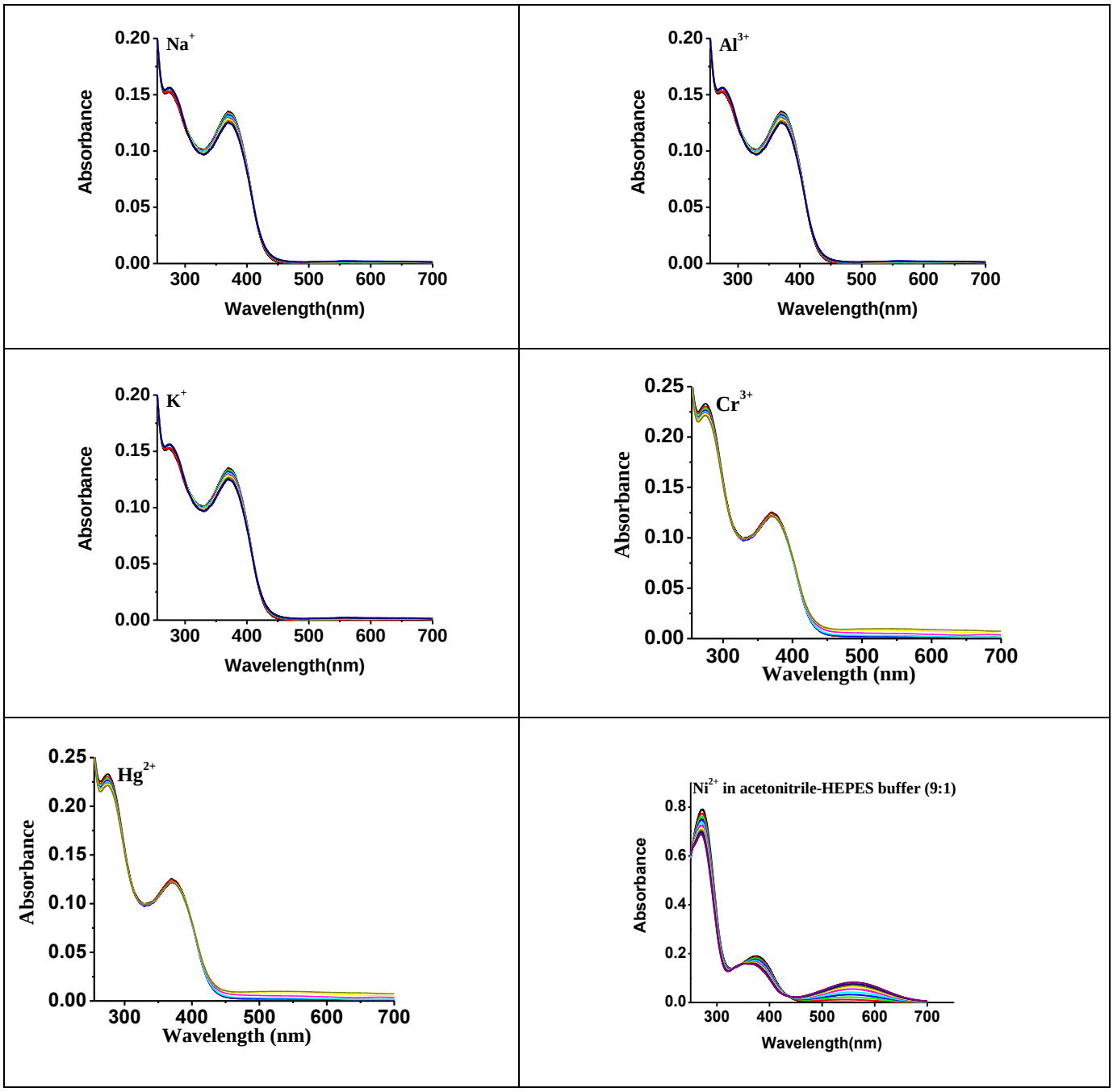


7. UV-vis spectra of receptor with different metals:

UV-vis titration spectra of receptor (c = 1.0 x 10^{-5} M) with another cations except Ni^{2+} i.e. (c = 2.0 x 10^{-4} M) in CH_3CN.

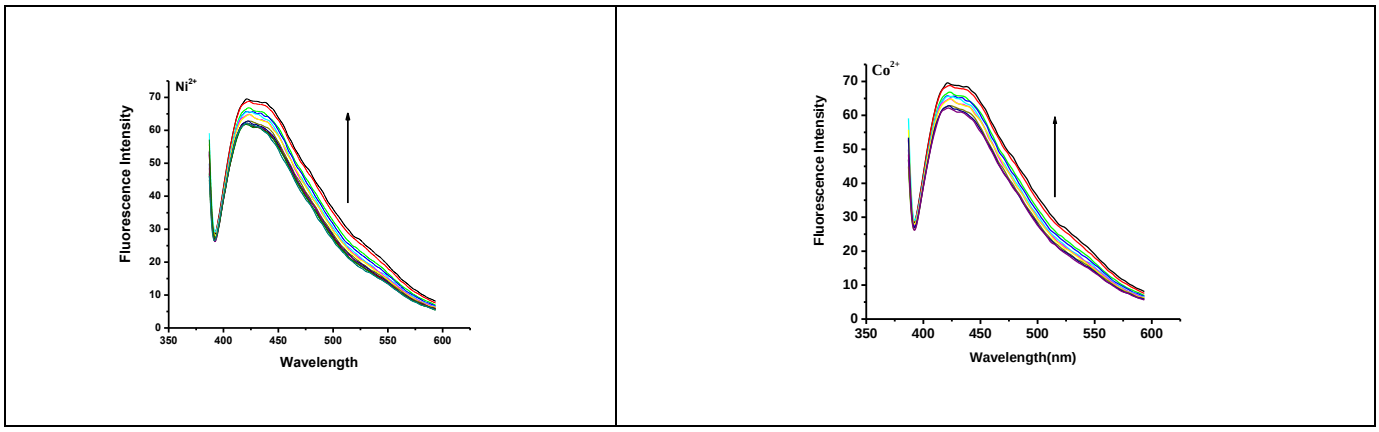

Ag+
Absorbance
Wavelength (nm)
Co2+
Absorbance
Wavelength (nm)
Cu2+
Absorbance
Wavelength (nm)
Pb2+
Absorbance
Wavelength (nm)
Zn2+
Absorbance
Wavelength (nm)
Cd2+
Absorbance
Wavelength (nm)


Cr+2
Absorbance
Wavelength(nm)
Fe2+
Absorbance
Wavelength (nm)
Mg2+
Absorbance
Wavelength (nm)
Fe3+
Absorbance
Wavelength(nm)
Pd2+
Absorbance
Wavelength (nm)
Pt2+
Absorbance
Wavelength (nm)



8. Fluorescence spectra of receptor with Ni^{2+} and Co^{2+}:

Fluorescence titration spectra of receptor (c = 1.0 x 10^{-5} M) with Ni^{2+} and Co^{2+} i.e. (c = 2.0 x 10^{-4} M) in CH_3CN.



9. X-ray Crystallography

Crystal structure of the nickel (II) complex was determined by single crystal X-ray diffraction from data collected at 100 K. A single crystal of 0.266 x 0.166 x 0.149 mm^3 in size was mounted on a glass fibre with epoxy cement for X-ray crystallographic study. The data were collected using a Bruker APEX2 DUO CCD diffractometer with the graphite monochromated MoKα radiation at a detector distance of 5cm and with APEX2 software. The collected data were reduced using SAINT program and the empirical absorption corrections were performed using the SADABS program. The structure were solved by direct methods and refined by least-squares using the SHELXTL software package. All non-hydrogen atoms were refined anisotropically whereas hydrogen atoms were refined isotropically. All hydrogen atoms were positioned geometrically with U_{iso} (H) = 1.2 U_{eq} (C). Crystallographic data for nickel (II) complex are presented in Table 1 and has been deposited with the Cambridge Crystallographic Data Center No. CCDC 964936.

The single crystal consists of a nickel (II) complex and a chloroform molecule in the asymmetric unit (Scheme 3). The two quinoxaline ligands exist in *trans* conformations with respect to the N1=C7 and N4=C22 bonds [1.278(7) and 1.292(8) Å]. The nickel (II) atom displays a distorted octahedral coordination geometry, provided by two N atoms [Ni—N = 2.025(5)- 2.219(5) Å] and one O atom [Ni—O = 2.047(4) and 2.055(4) Å] of each quinoxaline ligand. The dihedral angle between the mean planes of the two quinoxaline ligands is 79.81°, indicating that they are almost perpendicular to each other. The molecular structure is stabilized by an intramolecular C29—H29*A*···N1 hydrogen bond (Table 2). In the crystal (Fig. S3), the chloroform molecules are linked to the main molecules *via* C31—H31*A*···O2 hydrogen bonds (Table 2). These molecules are further linked by intermolecular C12—H12*A*···O2, C22—H22*A*···O1,

C24—H24*A*···O1 and C28—H28*A*···N2 hydrogen bonds (Table 2) and resulting in two-dimensional planes parallel to (010) (Fig. S4).

Table 1: X-ray crystallographic data

Compounds	FS279 (CCDC 964936)
Formula	$C_{30}H_{20}N_6NiO_2 \cdot CHCl_3$
Formula Weight	674.60
Crystal System	Triclinic
Space Group	*P*-1
T, K	100
Z	2
a,Å	9.6004 (9)
b,Å	10.577 (1)
c,Å	14.3427 (14)
α,deg	82.418 (2)
β,deg	81.231 (2)
γ,deg	80.012 (2)
V, $Å^3$	1409.2 (2)
d_{calcd} , g/cm^3	1.590
μ, mm^{-1}	1.02
Reflections with $I > 2\sigma(I)$	4482
Independent reflections	18626
θ range, deg	2.3–29.9
hkl range	$h = -11 \rightarrow 11$ $k = -12 \rightarrow 12$ $l = -16 \rightarrow 17$
GOF (F^2)	1.14
R_1 (wR_2), %	0.076, 0.197
Completeness (%)	98.5
T_{min}, T_{max}	0.774, 0.863

Table 2 Hydrogen-bond geometry (Å, º)

D—H···*A*	*D*—H	H···*A*	*D*···*A*	*D*—H···*A*
C12—H12*A*···O2^{i}	0.93	2.40	3.287 (7)	159
C22—H22*A*···O1^{ii}	0.93	2.29	3.052 (7)	139
C24—H24*A*···O1^{ii}	0.93	2.56	3.266 (7)	133
C28—H28*A*···N2^{iii}	0.93	2.60	3.282 (8)	131
C29—H29*A*···N1	0.93	2.61	3.463 (8)	152
C31—H31*A*···O2^{iv}	0.98	2.12	2.964 (9)	143

Symmetry codes: (i) *x*+1, *y*, *z*; (ii) −*x*+1, −*y*+1, −*z*+1; (iii) −*x*+2, −*y*+1, −*z*; (iv) −*x*+1, −*y*+2, −*z*+1.

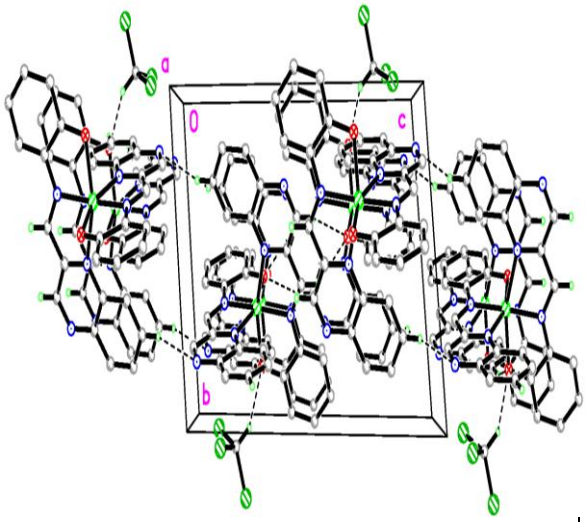


Figure S4: The crystal packing, viewed along the *a* axis, showing the chloroform molecules are linked to the main molecules *to* form two-dimensional planes.

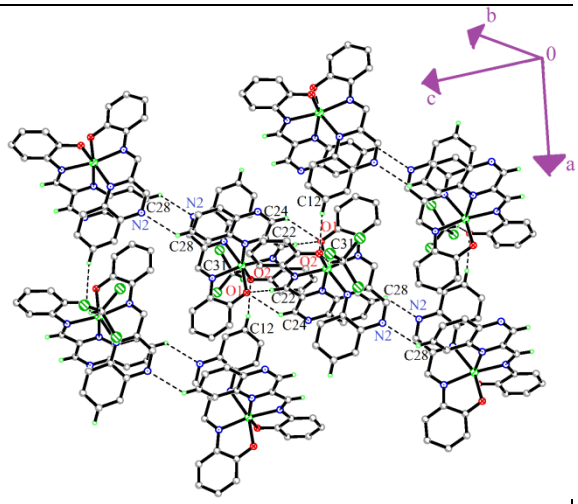


Figure S5: Part of the crystal packing showing the hydrogen-bonding network. Dashed lines indicate hydrogen bonds. H atoms not involved in the hydrogen bond interactions have been omitted for clarity.

10. References:

[S1]. M. Zhu, M. Yuan, X. Liu, J. Xu, J. Lv, C. Huang, H. Liu, Y. Li, S. Wang, D. Zhu, *Org. Lett*, **2008,** *10*, 1481.

[S2] S. Fukuzumi, Y. Kondo, S. Mochizuki, T. Tanaka, *J. Chem. Soc. Perkin Trans. 2*, **1989**, 1753.