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ARTICLE TYPE

A Highly Selective Ratiometric Chemosensor for Ni^{2+} in Quinoxaline Matrix

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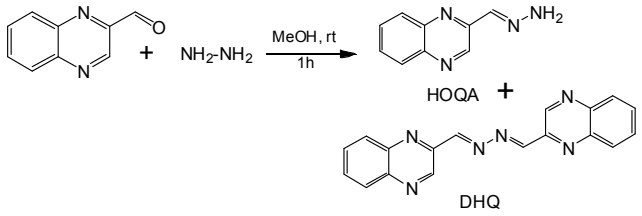
Abstract

The mono hydrazone of quinoxaline aldehyde (HOQA) is found to be a ratiometric and colorimetric probe for Ni^{2+}. HOQA shows a remarkable color change from colorless to yellow on specific and selective binding with nickel that can be identified even by naked eye detection. The cation recognition property of the receptor is monitored by the UV-vis and ^{1}H-NMR titrations and also by DFT(Density Functional Theory) and TD-DFT (Time Dependent Density Functional Theory) calculations.

Introduction

The design and synthesis of a chemosensor for the detection of a specific metal ion in aqueous or in non-aqueous medium is an active and fascinating area of present day investigation. Colorimetric sensors are promising due to their simplicity, real-time and on-line analysis, especially a significantly lower capital cost compared with the other closely related methods. Accordingly, the development of a novel colorimetric chemosensor for the rapid and convenient detection of Ni^{2+} is attractive. Ni^{2+} is used in a wide variety of metallurgical processes such as electroplating, rods for arc welding, pigments for paints, ceramics, surgical and dental prostheses, catalysts for hydrogenation and magnetic tapes of computers, alloy production as well as nickel–cadmium batteries. Ni^{2+} is an essential trace metal ion in biological systems in relevance with the biosynthesis and metabolism in certain microorganisms and plants. Beyond a concentration window, the presence of excess nickel causes pneumonitis, asthma and cancer in lungs and also causes disorder of respiratory and central nervous system in human.[1-6] Therefore its specific detection is very relevant for which the work described in this paper has been undertaken by designing a simple and highly sensitive sensor for nickel ion. Several methods such as atomic absorption spectrometry (AAS), flame atomic absorption spectrometry-electro thermal atomization (AAS-ETA),[7-8] ICP-AES and flame photometry[9] have been in use for the detection of nickel. However a selective and low cost method in monitoring Ni^{2+} under environment and in clinical analysis is needed.[10-13] Up to date, most of Ni^{2+} selective sensors are based on potentiometric methods.[14-15] Here we describe a facile and reliable Ni^{2+} colorimetric chemosensor based on a new quinoxaline Schiff base compound (**HOQA**) with one quinoxaline group and hydrazine moiety connected *via* an imine linkage[16-20] (Scheme 1). Addition of Ni^{2+} to CH_3CN solution of **HOQA** results in a rapid color change from colorless to bright yellow together with a red shift of the prominant band of the free **HOQA** from 324 to 385 nm and such cation binding property of **HOQA** has been investigated by means of UV-vis, and by ^{1}H nmr titration which show that **HOQA** selectively detects Ni^{2+} ion and this can be identified even by naked eyes over a large number of common alkali, alkaline earth, transition and rare earth metal ions avialable in the environment. The synthesized **HOQA** has been characterized by its single crystal X-ray structure and its bulk purity was established by different spectroscopic studies like ^{1}H-NMR, HRMS and FT-IR spectrocopy.



Scheme 1: Synthesis of the receptor (**HOQA**)

Experimental

1. General Experimental:

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. 1H-NMR was recorded on Brucker 400 MHz instruments. For NMR spectra, DMSO d^6 was used as solvent using TMS as an internal standard. Chemical shifts are expressed in δ units and 1H–1H and 1H–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 was recorded on a JEOL 500 MHz instrument.

General method of UV-vis titration:

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

Synthesis of monohydrazone of quinoxaline aldehyde (HOQA): To a stirred solution of quinoxaline aldehydes (50 mg, 0.31 mmol, supporting information) in 1 ml of methanol solution, the hydrazine hydrate [(20.2 mg, 0.63 mmol) dissolved in 0.5 ml of methanol] was added. A precipitate appeared instantaneously. The reaction mixture was stirred for another hour. TLC showed the presence of two different spots along with some left over starting material. The crude mixture was filtered and washed twice with little amount of ethanol . Then the relevant pure component was isolated from the crude mixture by column chromatography using silica-gel(100-200 mesh) in 5% EtOAC-hexane solution as eluting solvent and evaporating it under vacuum to yellow solid with the yield 67%. Analytical data (HOQA):($C_9H_8N_4$): mp >280 °C.
1H NMR (DMSO-d_6, 400 MHz): δ (ppm): 8.06 (s, 1H), 7.99 (s, 1H), 7.94 (m, 1H), 7.93 (d, 1H, J = 6.2), 7.82 (d, 2H, J = 7.9) ,6.10 (s, 2H)
13C NMR (DMSO-d_6, 500 MHz): δ (ppm): 157.3, 152.8, 149.6, 145.0, 142.6, 141.7, 136.3, 130.2, 120.3.

MS : M^+ Calculated for $C_9H_8N_4$ is 172.07 Found 173.2 $(MH)^+$.

Synthesis of the complex:

To a hot 1.0 ml methanolic solution containing 20 mg (0.11 mmol) of the ligand (L, **HOQA**), 1.0 mL of a methanolic solution containing 26 mg (0.11 mmol) of $NiCl_2.6H_2O$ was added. A yellow precipitate appears immediately. After stirring for 1.0 h the yellow complex was filtered, and washed with cold methanol for several times to remove any uncomplexed starting material. It was dried in a dessicator over anhydrous $CaCl_2$ under vacuum. The dry complex was subjected to spectroscopic analysis. The complex is air-stable, non-hygroscopic and soluble only in CH_3CN, DMSO-d^6 and DMF. Yield 80%. mp >280 °C. Single crystal suitable for X-ray structure could not be obtained for this compound using common solvents.
MS : M+ Calculated for $C_{18}H_{14}N_8Ni$, as $Ni(L)_2$ is 401.09 Found:401.1 $(2\ HOQA+Ni)^+$.

Results and Discussion

The binding behavior of the receptor (**HOQA**) with different cations was studied in CH_3CN. The titration was carried out in CH_3CN and CH_3CN-HEPES buffer (9:1, v/v, pH=7.4 at 1 × 10^{-5} M concentration of receptor HOQA upon addition of incremental amounts from 0-200 µl range of nickel chloride solution (2×10^{-4} M). This mono hydrazone (**HOQA**) of quinoxaline aldehyde is highly functional as an effective sensor for Ni^{2+} cation due to the coordination of free –NH_2 of hydrazone which easily chelates to Ni^{2+} along with quinoxaline ring nitrogen forming a stable six membered entity (scheme 2).

The UV-vis spectrum of the receptor (**HOQA**) is characterized by two absorption bands centered at 274 nm and around 345 nm (Figure 1). As shown in Figure 1, upon gradual increase of nickel ion concentration, the band at 274 gradually shifted to 263 nm and a new band appears around 385 nm with an isosbestic point at 363 nm, indicating the formation of a new complex between the receptor (**HOQA**) and nickel cation (Figure 1) which is also responsible for the generation of the yellow color after the addition of nickel chloride into the solution of the receptor. Figure 1 actually indicates the change of absorbance with the concentration of nickel. Furthermore the sensing ability of **HOQA** with nickel at different pH was also investigated.

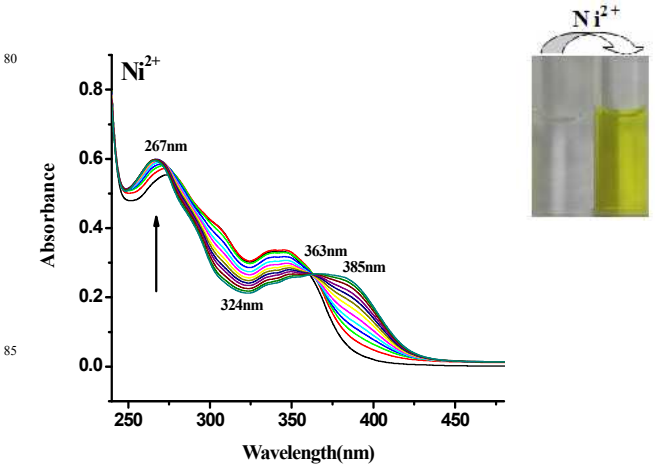


Figure 1: UV–vis absorption spectra of **HOQA** (1×10^{-5} M) in CH_3CN-HEPES buffer (9:1, v/v, pH=7.4) upon titration with nickel chloride ($NiCl_2.6H_2O$, 0.9 equiv). The arrow shows changes due to the increasing concentration of Ni^{2+}. Inset the change in colour on addition of Ni^{2+} .

At lower pH range, the sensor **HOQA** has a very low response to nickel in absorption spectroscopy due to protonation and at pH=7.4 the sensibility of the receptor **HOQA** is maximum and at higher pH the absorbance diminishes (supporting information) which may be due to the fact that the receptor **HOQA** is unstable at higher pH. This indicates that the probe may be suitable for bio-applications at the physiological pH. The free probe is highly stable under the assay conditions. Figure S2 shows plots of absorbance at 385 nm as a function of pH. This sigmoidal plot allowed us to determine the pKa value of **HOQA** to be 5.26. From the UV-visible titration data it is revealed that minimum 5.59 µM of nickel can be detected by using 10 µM of receptor HOQA using the equation DL = K × Sb1/S, where K = 3, Sb1 is the standard deviation of the blank solution and S is the slope of the calibration curve[14b](supporting information).

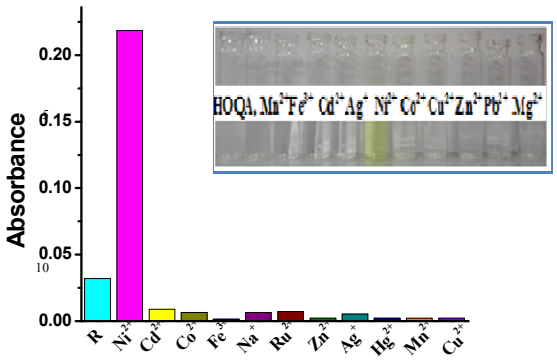
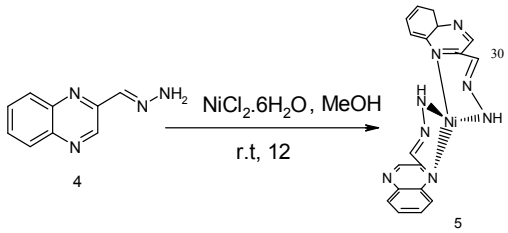


Figure 2: $(A-A_0)/A_0$ ratios of receptor **HOQA** (1×10^{-5} M) after the addition of 0.9 equivalents of each of the various cations in acetonitrile. Inset: Color changes of receptor **HOQA** (1×10^{-5} M) upon addition of 0.9 equivalents of each of the different guest cations.

On addition of 0.9 equivalent of nickel chloride the UV-visible absorption reaches a saturation level. Titrations were also carried out with various cations like Na^+, K^+, Fe^{3+}, Cu^{2+}, Mn^{2+}, Ag^+, Ca^{2+}, Zn^{2+}, Hg^{2+}, Cr^{3+}, Mg^{2+}, Pb^{2+} and Co^{2+} as their chloride salts (supporting information). Interestingly there is no obvious change observed in the UV spectra. From the experimental data, it can be concluded that the receptor



Scheme 2: Probable binding mode in solution phase

HOQA possesses high selectivity and sensitivity towards nickel in acetonitrile medium without any significant interference from other metals.[20c] The ligand may align as shown in scheme 2 to trap nickel ion to adopt a distorted tetrahedral geometry. The stability of the nickel ion in tetrahedral as well as in square planer environment may be responsible to form such complex. The other ions especially copper or cobalt should have responded to this ligand. It is known that cupric ion prefers square planar environment and as per scheme 2 such geometry is is not feasible. Therefore cupric ion would prefer to coordinate through the solvent molecule with its prefered geometry . The cobalt ion likes good donor as as CH_3CN to respond to octahedral coordination and therefore it adopts octahedral coordinartion using sovent molecules and may even refuse to add **HOQA** as its ligand simply. Figure 2 shows that this ligand has some preference for metal ions with prefered tetrahedral coordination like cadmium or cobalt but for metals with other common geometry this ligand does not coordinate. The color change is most probably due to the deprotonation of –NH group of receptor HOQA on the addition of nickel ion which is shown in scheme 2. To further explore the binding mechanism, the Job's plot of the UV–vis titrations of Ni^{2+} ion with a total volume of 2 ml was revealed. A maximum absorption was observed when the molar fraction reached 0.67, which is indicative of a 2:1 stoichiometric complexation between **HOQA** and Ni^{2+} ion for the newly formed species. The ESI mass spectrum of a mixture of **HOQA** and $NiCl_2.6H_2O$ also revealed the formation of a 2:1 ligand-metal complex through the metal coordination interaction, with a major signal at m/z=402.0 related to $(2\mathbf{HOQA}+Ni)^+$ ion. From the IR data the phenomenon is also well explained by the decreasing broadness of the –NH peak at 3372 cm^{-1} due to the insertion of nickel ion in **HOQA** (supporting information†).

These deprotonations followed with nickel ion coordination affect the electronic properties of the chromophore which results in change of color from colorless to yellow along with a new charge-transfer interaction between the nickel bound ligand. The deprotonation of –NH group of **HOQA** and nickel coordination could enhance π delocalization, which was expected to reduce the energy of the π-π* transition and therefore accounts for the appearance of a new absorption band near 385 nm resulting in the formation of a yellow color.[21] A well-defined isosbestic point at 363 nm emerged during the spectral titrations, which indicated the formation of the stable complex with a certain stoichiometric ratio between the receptor and the cation resulting a new ICT (internal charge transfer) band that appeared at 385 nm. The 2:1 stoichiometry for the complexation was elaborated by the profile of the intensities of the decreasing band centered at 385 nm and increasing band at 263 nm which was also confirmed by the Job plot analysis (Figure 3). The binding constant of **HOQA** with nickel is found to be 9.98 x 10^5 M^{-1} from nonlinear least squares fit analysis method at 385 nm(supporting information).[22] Furthermore, to examine the selectivity of the probe in a complex background of potentially competing species, the absorbance of **HOQA** with Ni^{2+} was investigated in the presence of other metal ions (6.0 equivalents). In contrast to other quinoxaline based nickel receptors, **HOQA** is very selective for nickel only.

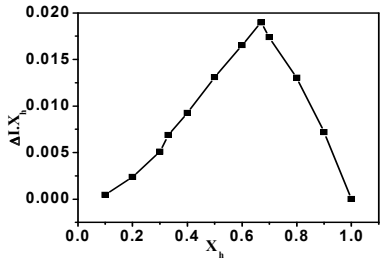


Figure 3*:* Jobs plot diagram of receptor **HOQA** for Ni^{2+} (where Xh is the mole fraction of host and ΔI indicates the change of the absorbance).

A background of competing metal ions did not interfere in the detection of Ni^{2+} by **HOQA** in acetonitrile (Figure 4).

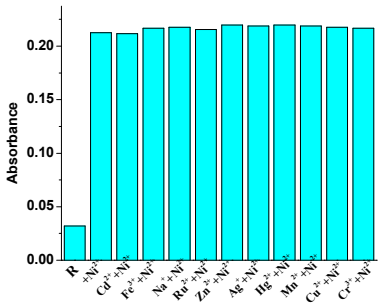
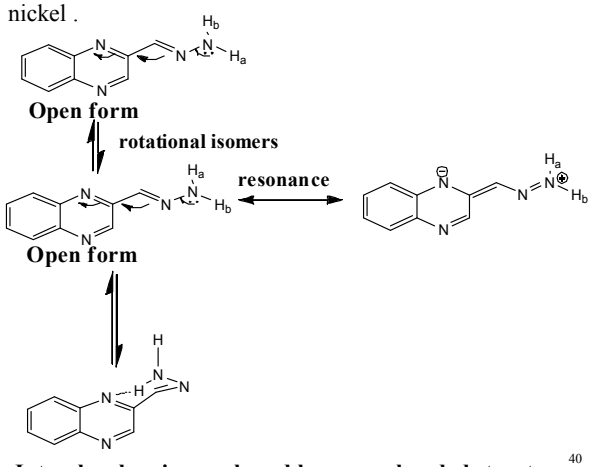


Figure 4: The metal ion sensitivity profile for **HOQA**: the change in the absorbance of **HOQA** + 6.0 equivalents of the investigated interfering M^{n+} + 2.0 equivalents of Ni^{2+}.

The binding of the receptor may be due to the enhanced acidity of the imine NH_2 of hydrazone (electron withdrawing resonance of quinoxaline moiety to the conjugated hydrazone part is shown in Figure 5) which undergoes deprotonation for complexation with nickel .



Intraolecular six membered hygrogen bonded structure[40]

Figure 5: Possible different forms of the receptor (**HOQA**) **.**

The selectivity here is greatly influenced based on charge-charge interactions, and the involvement of both N-H….Ni bonds. The unique binding motif can find a greater utility in the development of new cation receptors/sensors with enhanced binding affinity and substrate specificity, which is actively being investigated

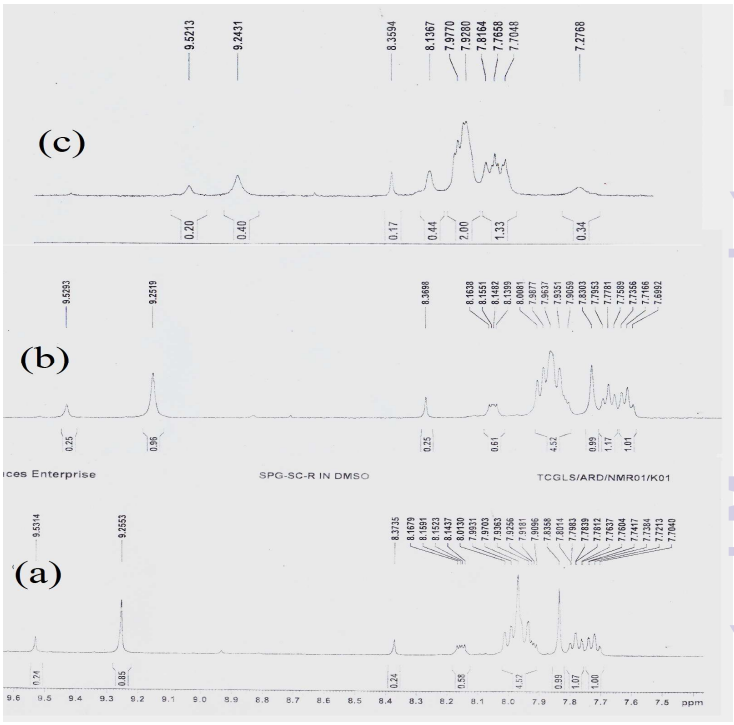


Figure 6: Partial 1H NMR spectra (400MHz) of **HOQA** in DMSO-d^6 at 25°C and corresponding changes after the gradual addition of different equivalents of nickel chloride from .(a)**HOQA** (b) **HOQA**+0.2 equiv Ni^{2+} (c) **HOQA**+0.5 equiv Ni^{2+}

From NMR study, we have investigated the molecular interaction between the receptor **HOQA** and nickel ion. The NMR titration curves (Figure 6) show that due to the complexation process, the –NH (H_b) proton of hydrazide undergoes an upfield shift from δ 9.255 ppm to δ 9.243 ppm because the cationic species induces an upfield chemical shift through diamagnetic shielding. Again noticeable up-field chemical shifts are also shown in the case of protons of quinoxaline -3CH of receptor **HOQA** from δ 8.373 ppm to δ 8.359 ppm because of the cation induced complexation after addition of 0.9 equivalents of nickel The NMR response of this nickel complex further suggests that the formed complex is diamagnetic in nature . Addition of HOQA into an acetonitrile solution containing Ni^{2+} ion does develop two weak d-d electronic transitions around 585 and 680 nm (see S5). These observation supports the structure of the yellow complex as distorted tetrahedral similar to the complexes with two bidentate nitrogen donor (N_2) like $[Ni(N_2)_2]$ reported earlier [23]

Crystallographic study:

Overall, the compound **HOQA** (Figure 7) is close to being planar (r.m.s. deviation for all the non-H atoms = 0.024 Å) and exists in *trans* conformations with respect to the N3═C9 bond (1.288(2) Å). In the crystal, molecules are linked into zig-zag chains (Fig. S5a, supporting information) along [001] *via* intermolecular N4—H1*N*4···N3 hydrogen bonds (Table 2, supporting information). Adjacent chains are crosslinked *via*

further N4—H2*N*4···N1 interactions into two-molecule-thick arrays lying parallel to (010). The crystal packing is further consolidated by π–π stacking interactions between symmetry-related pyrazine and benzene rings, with centroid-centroid separation of 3.5812(13) Å [symmetry code: x, 1+y, z]. The non-H atoms of the monohydrazone quinoxaline moieties in molecules *A* and *B* are nearly coplanar, with the *r.m.s.* deviations ranging from 0.026 to 0.067 Å. The dihedral angle between the two quinoxaline rings for molecules *A* and *B* is 9.22 (6) and 2.45 (6)º, respectively. In the crystal packing, adjacent molecules *A* are linked *via* intermolecular C10*A*—H10*A*···N6*A* hydrogen bonds (Table 2,supporting information) into chains propagating in [100]. In molecules *B*, the molecules are linked *via* intermolecular C3*B*—H3*BA*···N2*B* and C9*B*—H9*BA*···N1*B* interactions (Table 2, supporting information), forming R^2_2 (8) ring motifs, and together with intermolecular C10*B*—H10*B*···N6*B* interactions, assembled into chains propagating in [100].The molecules A and B are further linked together *via* C5*B*—H5*BA*···N6*A* interactions, forming *L*-shape columns. Molecules A and B are also stacked by π-π interactions between the pyrazine/pyrazine [centroid-centroid distances of 3.7043 (12) Å and 3.7439 (12) Å] and benzene/benzene [centroid-centroid distances of 3.7626 (13) Å] rings of adjacent sheets. There are no significant hydrogen bonds observed in the crystal structure. In the crystal structure, molecules are stacked along the *a* axis by way of weak aromatic π-π stacking interactions between the benzene rings in adjacent molecules with centroid-centroid distances of 3.748 Å.

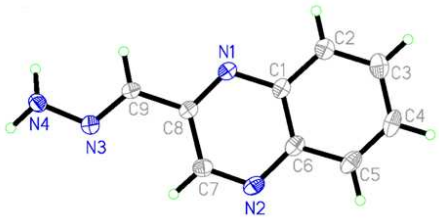


Figure 7: The molecular structures of Quinoxaline monohydrazine (HOQA) showing 50% probability displacement ellipsoids for non-H atoms and the atom-numbering scheme.

Computational Results:

In order to investigate the structural change occurred for the colorimetric response of **HOQA**-Ni, DFT (Density Functional Theory) calculations were carried out for **HOQA** and the **HOQA**-Ni using the DFT/B3LYP/6-311+G(d, p) basis set (Gaussian 03 program). (Revision B.04)[24] The significant difference in the π-conjunction between **HOQA** and **HOQA**–Ni is observed in the optimized structures of HOQA and HOQA-Ni (shown in Figure 8).

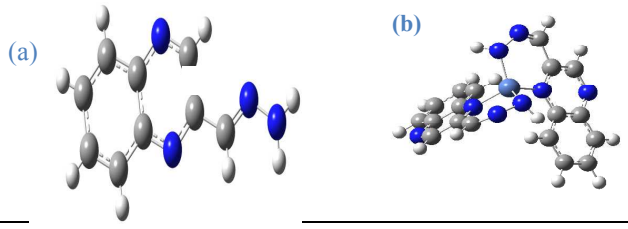


Figure 8. (a) HOQA and optimized structure of (b) HOQA-Ni

It clearly indicates the high degree of conjugation between the coplanar aromatic quinoxaline ring and the hydrazone moiety via a 'C=N' bond in **HOQA**-Ni complex (Figure 9a) than that in **HOQA** itself. The increased conjugation in **HOQA**-Ni (Fig. 9b) results from the addition of Ni at the hydrazone nitrogen of the quinoxaline ring which is responsible for observed bathochromic shift in the longer wavelength absorbance (ICT) of **HOQA** on forming the adduct. The HOMO–LUMO energy gap (Figure 9) in the calculated structures also supports the phenomenon.

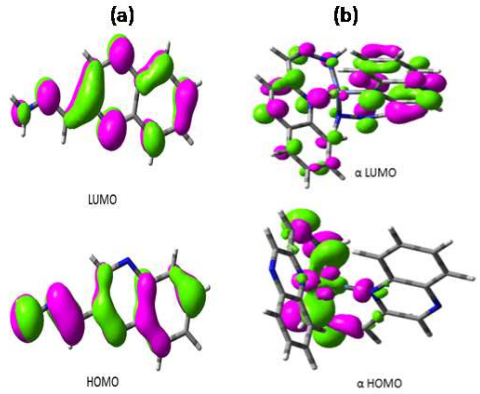


Figure 9: (a) HOMO and LUMO of Ligand with ISO Value Cutoff 0.04 (b) HOMO and LUMO of Complex

The electronic spectra of the free ligand (**HOQA**) and its complex with nickel ion (Figure 1) are similar with the TDDFT calculation in gas phase. The computed absorbtion for the free ligand at 327.08 and 275.03 nm exactly match with the experimental absorptions. For the complex the prominant absorption appears at 367.04 nm which is close to the observed absorption and the slight deviation may be due to solvent interaction.

Conclusions:

Herein we report a new receptor which selectively and successfully recognizes nickel cation to the limit of 5.59 μM over other interfering cations in CH_3CN solution. This receptor is unique as it preferentially recognises nickel over copper and cobalt ions especially in CH_3CN medium where the receptor as ligand provides a distorted tetrahedral arrangement for nickel ion. Its dramatic color change on the addition of nickel makes it an excellent chemosensor for detecting nickel cation even by naked-eye. This cost effective chemosensor can be used in large number of realistic applications in chemical and pathological laboratories to check nickel as biological and environmental contaminants.

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A Highly Selective Ratiometric Chemosensor for Ni^{2+} in Quinoxaline Matrix

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The monohydrazone of quinoxaline aldehyde (HOQA) is found to be a ratiometric and colorimetric probe for Ni^{2+}. HOQA shows a remarkable color change from colorless to yellow on specific and selective binding with nickel (easy naked eye detection). The cation recognition property of the receptor is monitored by the UV-vis, ^{1}H-NMR titrations and also by DFT (Density Functional Theory) calculations.