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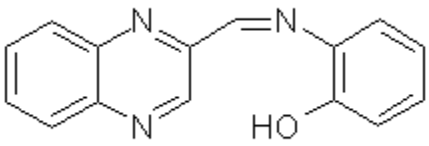

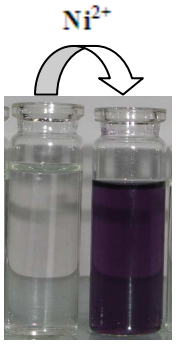

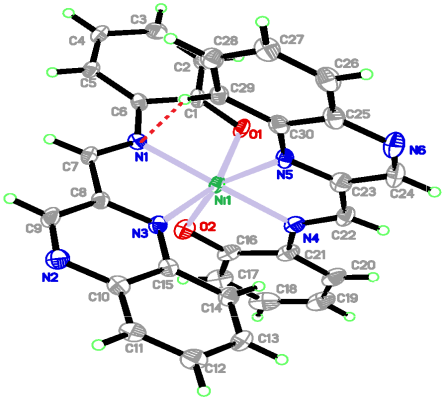

Cite this: DOI: 10.1039/c0xx00000x

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ARTICLE TYPE

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

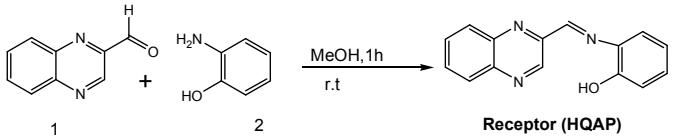
Shyamaprosad Goswami*, Shampa Chakraborty [a], Avijit Kumar Das [a], Abhishek Manna [a], Aditya Bhattacharyya [b], Ching Kheng Quah [c] & Hoong-Kun Fun [c, d].

Received (in XXX, XXX) Xth XXXXXXXXX 20XX, Accepted Xth XXXXXXXXX 20XX
DOI: 10.1039/b000000x

A quinoxaline based colorimetric nickel sensor, HQAP [2-(quinoxalin-2-ylmethyleneamine)phenol] with high selectivity and sensitivity toward Ni^{2+} ion is shown to be potential for practical use. The absorption maximum of HQAP shows a large ratiometric shift from 306 to 570 nm (ΔI= 264 nm) in the presence of Ni^{2+} ion, and the color changes from colorless to deep violet only upon addition of Ni^{2+} which is very easily observed by the naked eye (the detection limit of Ni^{2+} is as low as 4.16 µM in solution). The predicted binding mode (2:1) from spectral analysis and Job's plot was confirmed by the single crystal X-ray structure of the complex.

Nickel is widely used in various industrial applications such as in Ni–Cd batteries, electroplating, rods for arc welding, pigments for paints, ceramics, surgical and dental prostheses, catalysts for hydrogenation and as magnetic tapes of computers. Enzymes of some microorganisms and plants contain nickel as an active site, which makes the metal an essential nutrient for them. On the other hand, it is also a toxic metal and known to cause pneumonitis, asthma and cancer of lungs and also cause disorder of respiratory and central nervous system.[1-6] Number of methods, such as atomic absorption spectrometry (AAS), flame atomic absorption spectrometry-electro thermal atomization (AAS-ETA),[7,8] ICP-AES and flame photometry[9] can be used for the determination of nickel. These methods provide accurate results but are not very appropriate for analysis of a large number of environmental samples because they require appropriate expertise and good infrastructure. On the other hand, selective metal ion sensors are very useful for the monitoring of heavy metals in large number of samples as they are cheaper, convenient and easy to operate and generally they require no sample pre-treatment. There is a requirement to impart selectivity to the ion sensor for a material that the material has a strong affinity for a particular metal ion but has poor sensitivity to others. However in reality such good sensors for nickel are very rare, particularly in quinoxaline matrix.[10, 11]

Ratiometric colorimetric probes can enable the measurement of absorption intensities at two different wavelengths, providing a built-in correction for environmental effects and increase the dynamic range of absorption measurement. This was considered as a good approach to overcome the major limitation of intensity based probes, in which variations in the environmental sample and probe distribution were problematic for quantitative measurements. However, so far, the ratiometric and colorimetric probes for Ni (II) are still very rare.[12-18]



1 2 **Receptor (HQAP)**

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

We report here a remarkably simple but very efficient chemosensor **HQAP**[19] for nickel by the simple condensation reaction between quinoxaline aldehyde[20] and 2-aminophenol in dry methanol at room temperature (Scheme-1). Here, we use quinoxaline as the key moiety of the receptor as electron withdrawing part of **HQAP** and 2-aminophenol due to its electron-donating hydroxyl group which provides a suitable cavity for the binding of metal ion.The sensing properties of receptor was investigated by monitoring the UV–vis absorption spectral behavior upon addition of various metal ions such as Na^+, K^+, Fe^{3+}, Cu^{2+}, Mn^{2+}, Ag^+, Ca^{2+}, Zn^{2+}, Hg^{2+}, Cr^{3+}, Mg^{2+}, Pb^{2+} and Ni^{2+} ions.

The spectroscopic studies of **HQAP** (1×10^{-5}M) were carried out in acetonitrile by using different interfering metal ions having 2×10^{-4} M strength. As shown in Fig. 1, the UV- vis spectrum of the receptor (**HQAP**) is characterized by the two characteristic bands centered at 341 and 372 nm. Upon gradual increasing nickel ion concentration, the bands at 341 and 372 nm gradually disappear and a new band appears at 570 nm with an isosbestic point at 432 nm, indicating the formation of a complex[20] between the receptor and nickel (Figure 1).
which is also responsible for the generation of a deep violet color after the addition of nickel chloride into the solution of the receptor. Figure 2 actually indicates the change of absorbance with the concentration of nickel. From the UV-vis titration data, it is revealed that minimum 4.16 µM of Ni2+

can be detected by using 10 μM of receptor HQAP 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 [21] (supporting information).

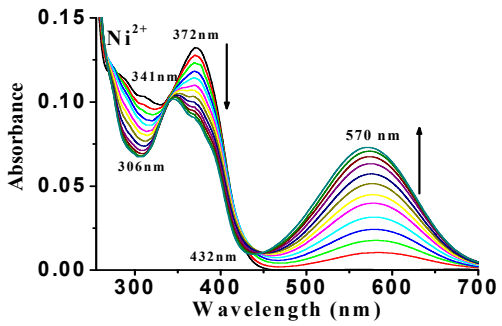


Figure 1: UV–vis absorption spectra of **HQAP** (1×10^{-5} M) in CH_3CN upon titration with nickel chloride ($2x10^{-4}$M). The arrows show changes due to the increasing concentration of Ni^{2+}, binding isotherms were recorded at 250 to 700 nm with Ni^2

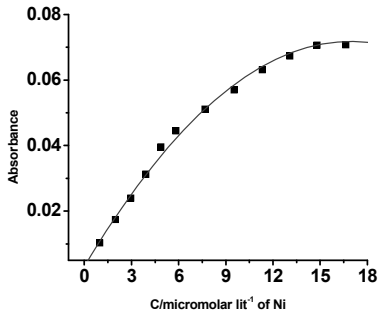


Figure 2: The change of absorbance as a function of [Ni^{2+}] at 570 nm.

After addition of 1.6 equivalents of nickel chloride, it 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+},Pt^{2+},Pd^{2+} and Co^{2+} as their chloride salts. Interestingly, there is no obvious change observed in the UV-vis spectra except with Co^{2+} which shows a slight interference (supporting information). Little appearance of a new peak at 557 nm indicates that the receptor (**HQAP**) has a slight response to cobalt and zinc ions due to their similar size and charge. The cavity of **HQAP** binds selectively to Ni^{2+} over Co^{2+} probably because the size of the cation perfectly fits.

Figure 3 actually shows the selectivity for nickel over other cations which is shown by the sky blue bar. The slight interference of cobalt is shown by the grey bar but the Co^{2+} ion is not clearly detectable in naked eye which is shown in Figure 4. From the experimental data, it can be concluded that the receptor **HQAP** possesses high selectivity and sensitivity towards nickel in acetonitrile medium as well as in 9:1 acetonitrile-HEPES buffer medium (supporting information). The other cations except cobalt and zinc had no practical significant influence. The color changes are most probably due to the formation of coordination bonds or deprotonation of –OH group of receptor **HQAP** on the addition of nickel ion which is shown in Scheme 2.

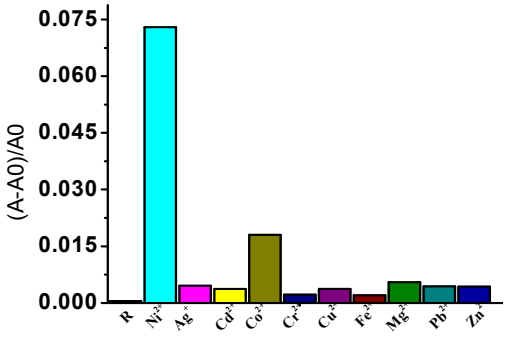


Figure 3: $(A-A_0)/A_0$ ratios of receptor **HQAP** (1×10^{-5} M) after the addition of 1.6 equivalents of each of the various cations having concentration 2×10^{-4}M in acetonitrile.

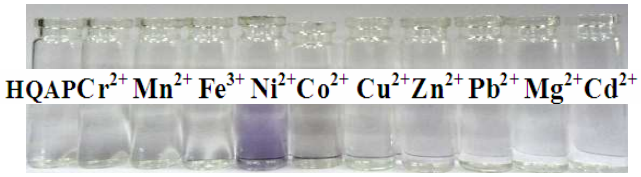


Figure 4: Color changes of receptor **HQAP** (1×10^{-5} M) upon addition of 0.8 equivalents of each of the different guest cations (2×10^{-4}M).

These results suggest that **HQAP** could be exploited as a colorimetric "naked eye" sensor for Ni^{2+} ion amongst the various typical transition-metal ions such as Cu^{2+}, Pb^{2+}, and Hg^{2+} which are normally difficult to differentiate.

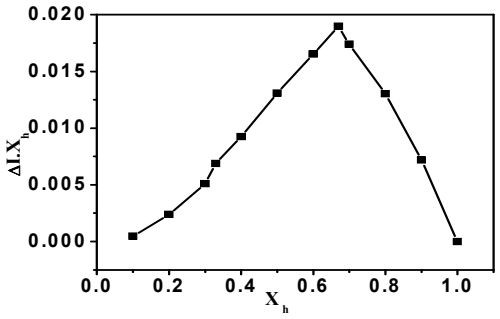
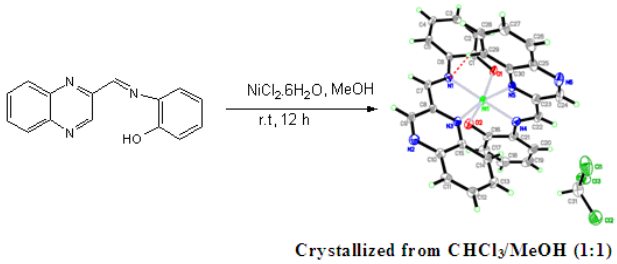


Figure 5: Job's plot diagram of receptor **HQAP** for Ni^{2+} cation (where Xh is the mole fraction of host and ΔI indicates the change of the absorbance).

These coordination bonds or de-protonations affect the electronic properties of the chromophore which results in the change of color from colorless to deep violet, along with a new charge-transfer interaction between the nickel bound -OH moiety and the electron deficient quinoxaline moiety. A well-defined isosbestic point at 432 nm emerged during the spectral titrations, which indicated the formation of the stable complex with a certain stoichiometric ratio between the host and guest via internal charge transfer (ICT) with a new band which appeared at 570 nm. The 2:1 stoichiometry for the host–guest complexation was elaborated by the profile of the intensities

of the decreasing band centered at 372 nm and increasing band at 570 nm which was also confirmed by the Job's plot analysis (Figure 5). Crystal structure of the nickel (II) complex was determined by the single crystal X-ray diffraction and the crystallographic data has been deposited with the Cambridge Crystallographic Data Center No. CCDC 964936.



Scheme 2: The molecular structure of the nickel (II) complex showing 50% probability displacement ellipsoids for non-H atoms and the atom-numbering scheme. Intramolecular interaction is shown as dashed line.

Yusuff et.al reported the synthesis of several metal complexes[20] of HQAP by refluxing in ethanol with metal diacetate (or chloride for Fe^{3+}) in more than gram scale. However in our UV-vis titration experiments, when concentration of HQAP was 10^{-5} M we observed the sensing selectivity of Ni^{2+} with some interference from Co^{2+} and Zn^{2+} (less than Co^{2+}) but no interference from other metal ions in that concentration.

The first single crystal X-ray structural proof of the nickel-HQAP is demonstrated which shows the participation of quinoxaline nitrogen in favor of six membered ring along with the five membered one formed from imino phenol moiety previously[20] suggested by other spectral studies. The single crystal consists of a nickel (II) complex and a chloroform molecule in the asymmetric unit (Scheme 2). 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 binding constant of **HQAP** with nickel is found to be 1.26 x 10^5 M^{-1} from nonlinear least squares fit analysis method at 372 nm(supporting information). 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 obtained. A maximum absorption was observed when the molar fraction reached 0.67, which is indicative of a 2:1 stoichiometric complexation between **HQAP** and Ni^{2+} ion. The ESI mass spectrum of a mixture of **HQA**P and $NiCl_2.7H_2O$ also revealed the formation of a 2:1 ligand-metal complex through the metal coordination interaction, with a major signal at m/z=555.0 [for $(2M+Ni)^+$ ions]. From the IR data, the phenomenon is also well explained by the decreasing broadness of the –OH peak at 3372 cm^{-1} due to the insertion of nickel metal in **HQAP** (Supporting information†).

Furthermore, to examine the selectivity of the probe in a complex background of potentially competing species, the absorbance of **HQAP** with Ni^{2+} was investigated in the presence of other metal ions. The experiment is performed by adding the species under investigation i.e. Ni^{2+} (2.0 equivalents) to the sensor in the presence of commonly employed interfering species i.e. metal ions (6.0 equivalents). With the exception of Co^{2+} and Zn^{2+} a background of competing metal ions did not interfere in the detection of Ni^{2+} by **HQAP** in acetonitrile(Figure 6).

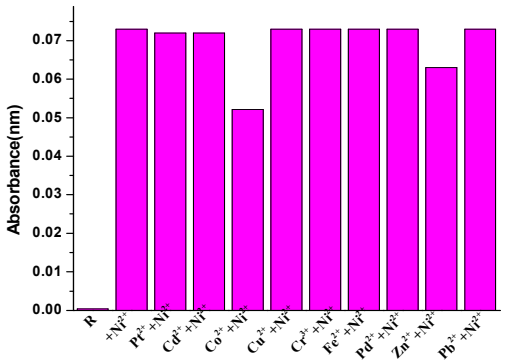


Figure 6: The metal ion sensitivity profile for **HQAP**: the change in the absorbance of **HQAP** + 6.0 equivalents of the investigated interfering M^{n+} + 2.0 equivalents of Ni^{2+}.

In the complex of HQAP and Ni2+ ion, the metal ion coordinates with the nitrogen atoms of 2 aminophenol and C=N Schiff group as well as the hydroxyl oxygen atom of the phenol moiety. On the basis of this binding mode, the ratiometric shift in the absorption spectra upon addition of the metal ion can be rationalized by ICT.

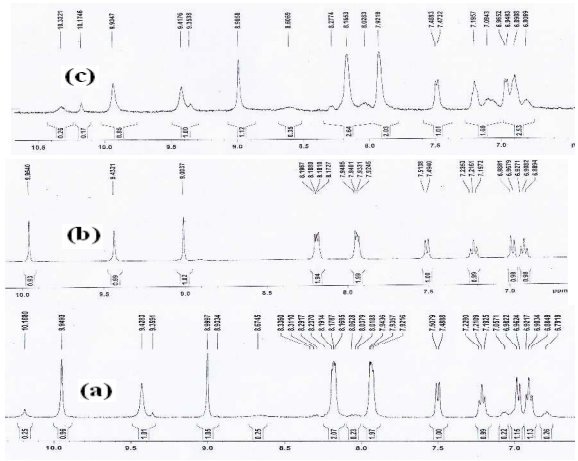


Figure 7: Partial ^1H NMR spectra (400MHz) of HQAP in DMSO-d_6 at 25°C and corresponding changes after the gradual addition of different equivalents of nickel chloride from .(a)HQAP (b) HQAP+0.2 equiv Ni^{2+} (c) HQAP+1.6 equiv Ni^{2+}

The coordination of a metal ion to the nitrogen and oxygen atom of phenol and C=N Schiff moiety increases its electron-withdrawing character, which leads to a stronger ICT from the electron-donating hydroxyl group to the metal-complexed moiety. At the same time, due to complexation process, the –OH proton of 2- aminophenol undergoes a downfield shift from δ 9.9540 ppm to δ 10.1746 ppm because the cationic species induces a downfield chemical shift through diamagnetic deshielding. Again noticeable downfield

chemical shifts are also shown in the case of protons of quinoxaline -3CH and the immine proton of receptor **HQAP** from δ 9.4321 ppm to δ 9.9347 ppm and δ 9.0037 ppm to δ 9.4176 ppm respectively which are induced due to complexation after addition of 1.6 equivalents of nickel which is shown in NMR titration curves (Figure 7 and supporting information).

From NMR study, we have investigated the molecular interaction between the receptor **HQAP** and nickel ion. The peak at slightly downfield (δ 10.3221 ppm) probably belongs to --OH of 2-amino phenol which decreased and the intensity of all the protons of the **HQAP** have gradually increased after addition of 0.5 equivalent of nickel ion indicating that there is a complex formation (2:1) between -OH group of 2-aminophenol moiety and nickel ion (Figure 7). The selectivity of the receptor may be due to enhanced acidity of the -OH of 2-aminophenol. The selectivity here is greatly influenced based on charge-transfer interaction between metal and ligand and the involvement of both O-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.

In summary, we have developed a simple practically useful colorimetric chemosensor **HQAP** based on quinoxaline moiety which exhibits highly selective and sensitive recognition toward Ni^{2+} ion in solution. The recognition of Ni^{2+} ion gave rise to dramatic color change from colorless to deep violet in acetonitrile-methanol which was clearly visible to the naked eye. The detection limit of Ni^{2+} ion is as low as 4.16 μM in solution by the "naked eye" without resort to any spectroscopic instrumentation. We believe that this economic chemosensor, with sensitive and selective naked eye responses can be used for many practical applications in chemical (laboratory practicals), environmental and biological systems. We also first proved the complex structure by the single crystal X-ray diffraction.

Acknowledgements:

We acknowledge the Department of Science and Technology (DST/SR/S1/OC-58/2010) and the Council of Scientific and Industrial Research (CSIR), Government of India, for financial support. S.C thanks TCG Life sciences Ltd for their overall support. The authors extend their appreciation to The Deanship of Scientific Research at King Saud University for funding the work through research group project no. RGP-VPP-207.

References and notes

[a] Department of Chemistry, Bengal Engineering and Science University, Shibpur, Howrah 711103, West Bengal, India E-mail: spgoswamical@yahoo.com; Fax: +91-3326682916.

[b] Department of Chemistry, Indian Institute of Technology, Kanpur 208016, India

[c] X-ray Crystallography Unit, School of Physics, Universiti Sains Malaysia, 11800 USM, Penang, Malaysia. E-mail: ckquah@usm.my, hkfun@usm.my

[d] Department of Pharmaceutical Chemistry, College of Pharmacy, King Saud University, P.O. Box 2457, Riyadh 11451, Saudi Arabia.

E-mail: hfun.c@ksu.edu.sa

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