



Recognition and Sensing of Cu^{2+} and Fe^{3+} utilizing Schiff base ligand of diaminoethane Receptor

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ABSTRACT

New Schiff based cation sensor compounds **L** was synthesized. Compound **L** acts as naked eye colorimetric sensor for the recognition of Fe^{3+} cation while generated distinguishable pattern for Cu^{2+} cations in the absorption titration experiments. The pattern generating behavior of small molecular systems have been exploited for mimicking the molecular level keypad lock in recent reports. Thus, this system presents a potential for research in the molecular level keypad which will open new arena for the application of such molecule in information systems.

Keywords: Sensors, colorimetric, copper cation sensors, Schiff base, "turn off" fluorescent

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INTRODUCTION

There is an increasing demand for small organic molecules with facile syntheses used in cation sensor systems[1]. Among these are Schiff bases derived from benzaldehyde and appropriate amine or hydrazide have shown promising sensing ability up to a limit of detection to micro molar level[2, 3] via effective chelation of metal cations[4, 5]. It has been reported that Hydrazone based molecular sensors are capable of sensing ions of biological importance and environmental importance[6,7]. On the other hand Pyrrole/indole and phenyl/hydroxyl based sensor systems have been applied in molecular switches[8, 9]. Also the calyz-4-pyrrole and thiosemicarbazone based sensors are explored for molecular level keypad locks, [10] and host-guest interaction in sensing application[11]. Our group has a long standing interest in the Schiff base ligands; their synthesis, and studies of their chemical, as well as their biological activities[12-14]. Our ligand is designed keeping in mind the potential of Schiff bases in cation sensing. In this paper, we describe the spectroscopic characterization of compound **L** and its cation-sensing potential. When analyzed spectroscopically, compound **L** showed sensitivity to all metal cations. A spectrometric titration method was used to study the formation of metal complexes, which demonstrated the isosbestic points of change between the ligand spectra and the ligand-metal complex spectra. Furthermore, Compound **L** have shown sensing towards Cu^{2+} and Fe^{3+} , with visible color change from colorless to pink for Fe^{3+} cation. These two cations have also generated distinct spectral pattern. Such distinct spectral pattern generation ability of small molecules has been explored for developing molecular level keypad lock systems using combinatorial methods. Similar approach is underway in our laboratory and will be reported in near future.

MATERIAL AND METHODS

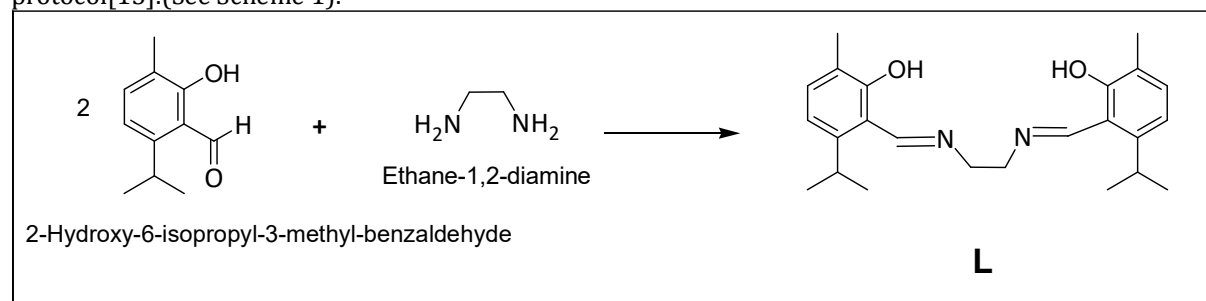
All the reactions were carried out at room temperature. All chemicals and solvents (HPLC grade) were procured from Merck and were used without further purification. All the chemicals were obtained commercially. The solutions of the metal ions used were prepared in methanol and deionized water from their chloride and nitrate salts. The solution of Fe^{3+} was prepared separately by dissolving in 0.1 M HCl. employed for colorimetric analyses were obtained from Sigma Aldrich and stored in fridge and desiccators

until use. Progress of reaction was followed by thin layer Chromatography. UV-Visible and fluorescence spectra were recorded using Shimadzu UV-1800. UV scanning was done between 200-800 nm. Absorbance was recorded in quartz cell (1-cm Width).

RESULTS AND DISCUSSION

SYNTHESIS

The synthesis of sensor compound **L** was carried out in two steps following our previously reported protocol [15]. (See Scheme 1).



Scheme 1. Synthesis of sensor compound L

NAKED EYE DETECTION: UV-visible absorption titrations were performed in water: methanol (v/v, 1:1) at room temperature. Freshly prepared solutions of sensor **L**, $100 \times 10^{-6} \text{ mol L}^{-1}$ and $100 \times 10^{-6} \text{ mol L}^{-1}$ of Co^{2+} , Fe^{3+} , Ni^{2+} , Cu^{2+} , Pb^{2+} , Hg^{2+} and Al^{3+} in a glass tubes. The color of each mixture was observed before and after addition of the cation solution. Figure 1 shows the change in color upon mixing the sensor and the cation solutions.

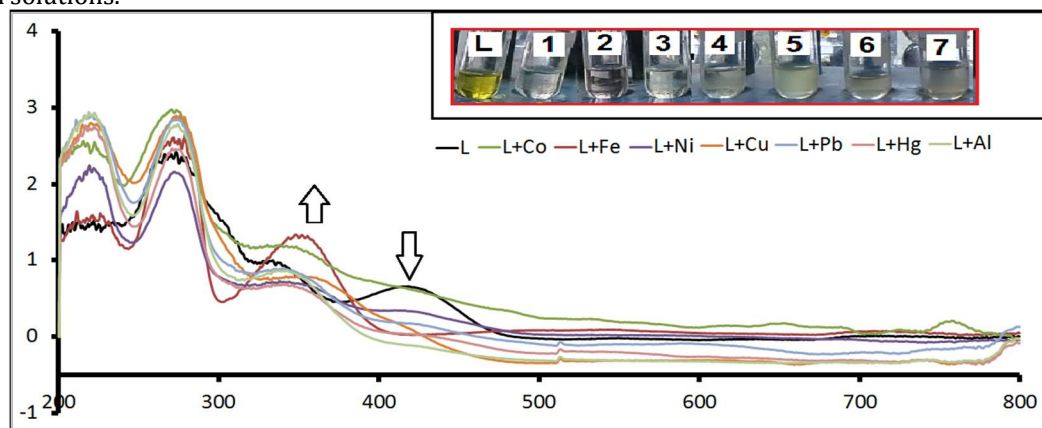


Figure 1. Absorption intensities of $100 \mu\text{M}$ sensor ligand to different metal ions ($100 \mu\text{M}$) in MeOH/H₂O (v/v, 1:1) and the Inset shows change in color of $100 \mu\text{M}$ sensor with the $100 \mu\text{M}$ cations tested, L = sensor ligand, 1, 2, 3, 4, 5, 6, 7, and 8 are after addition of Co^{2+} , Fe^{3+} , Ni^{2+} , Cu^{2+} , Pb^{2+} , Hg^{2+} and Al^{3+} respectively.

SPECTROPHOTOMETRIC EXPERIMENTS (UV/VISIBLE STUDIES)

SPECTROPHOTOMETRIC TITRATION

UV-visible spectroscopic studies of Sensor **L** carried out in methanol: water media showed absorbance maxima due to $\pi - \pi^*$ transitions in the two separate range groups as expected depending on electron-withdrawing effect of substituent as shown in scheme 1. In the spectrometric titration the variation in absorption in a fixed volume of Receptor 3ml ($100 \mu\text{M}$) was plotted against incremental addition of Fe cation ($10 \mu\text{M}$). The spectral response to incremental addition of cation showed reduction in the band at 410 nm and 328 nm with clear isosbestic points observed at 326 nm and 380 nm respectively, indicating a single compound formation as shown if figure 2a for Fe^{3+} . Similarly, isosbestic points at 342 nm and 386 nm was seen for incremental addition of Cu^{2+} as shown in figure 2b

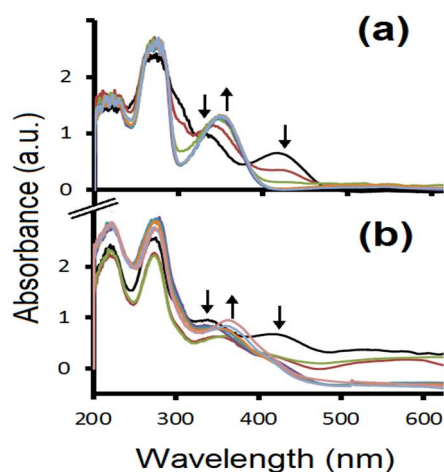


Figure 2. Absorption spectra for sensor compound **L** (3ml, 100 μ M) in Methanol: water solution plotted against incremental addition (0-100 μ M equiv.). (a) Fe^{3+} cation and (b) Cu^{2+} cation solutions

SPECTROSCOPIC PATTERN ANALYSIS

Compound **L** has shown cation recognition through spectral change for all the cations. However, for Fe cation and Cu cation it has shown distinct sensing at 352nm and 342nm respectively. A 352 nm and 342 nm absorption band can be produced in solution by sequential addition of Cu^{2+} and Fe^{3+} ; however, if the addition sequence is reversed, only 342 nm absorption band is seen (Figure 3a). This behavior of sensor compound **L** motivated us to generate a molecular keypad lock for molecular traffic signal with two inputs: input-1 and Input-2 being Fe^{3+} and Cu^{2+} , respectively. We observed that compound **L** has curved conformation as shown in Figure 3b. Similar thiosemicarbazone with curved conformation were reported recently[16]. This type of curved conformations are seen to limit the sensor/analyte interaction and also the size of the analyte as they vary it may create difference in approaching for the binding -N-H proton of thiosemicarbazone[17]. This could be one of the reasons for difference in interaction of the sensor compound **L** and cations Fe^{3+} and Cu^{2+} which could have led to distinct absorption pattern.

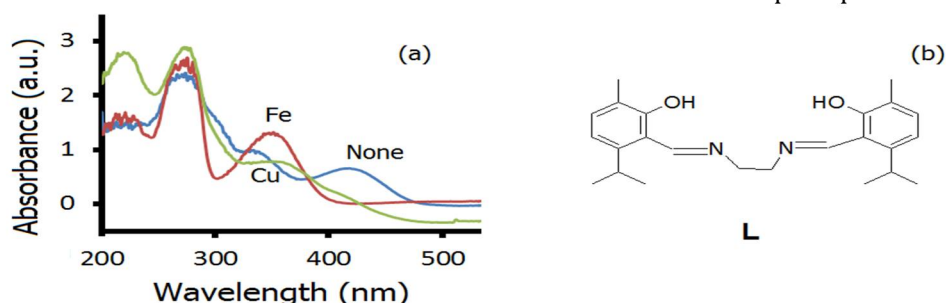


Figure 3. (a) Change in spectrum of sensor **L** (100 μ M) upon the addition of 50 μ M of cations (Cu) and (Fe). (b) Structure of sensor compound **L**

To generate a password the two inputs Cu^{2+} and Fe^{3+} were denoted by "N" and "S"; and the two spectral band thus produced at 352 nm and 342 nm respectively were denoted by "A" and "I" and the 'OPEN' state of the lock is denoted by "K". Now when the input "N" was added first followed by input "S", then both the absorption bands will be detected by the system, the lock will go in OPEN state and the password is created as "NASIK" (Figure 4). The star shows the zigzag key position. All the other sequences could not open the lock. So, this type of keypad lock system which requires a specific sequence to open may be applicable to protect information at molecular level.

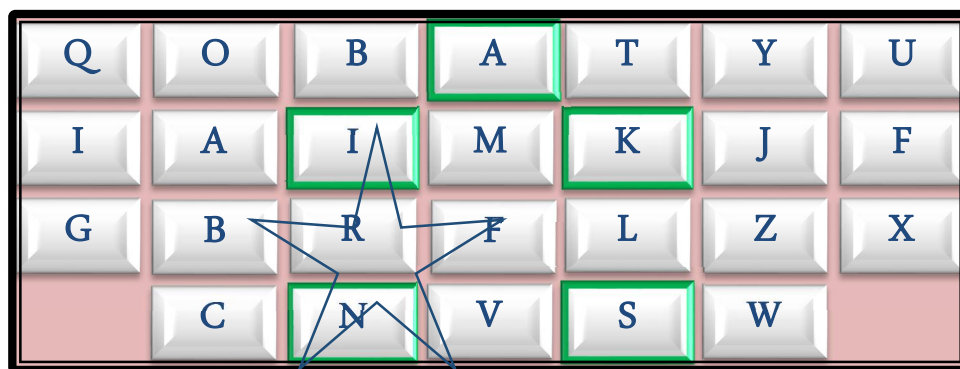


Figure 4. Schematic Keypad for accessing the password as will be generated by sequential chemical inputs of Cu^{2+} and Fe^{3+} resulting absorbance signal at 352 nm and 342 nm respectively

CONCLUSION

In Summary, we have developed a Schiff base sensor compound **L** which shows recognition and sensing for Cu^{2+} and Fe^{3+} at 252 nm and 242 nm respectively. Titrimetric analysis shows clear isosbestic points for formation of new compounds. A sequential chemical input method was used to explore the pattern generating ability of this compound. Our initial attempt for sequential input shows that this compound show two bands at 252nm and 242nm if the Cu^{2+} is added first followed by Fe^{3+} . However, if the sequence is reversed only 242nm band is generated. This type of combinatorial sensing is demonstrated as powerful tool for password protection at molecular level and hence maybe useful for future multifunctional logic devices.

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Conflict of interest: None.

ABBREVIATIONS:

UV – Ultra violet
 μM – Micrometer
 Cu - Copper

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