Application of P-Dimethylaminobenzaldehyde Benzoylthiourea as a Colorimetric Chemosensor for Detection of Cu²⁺ in Aqueous Solution

Sharizal Hasan, Nurul Asma Hamedan, and Hamizah Mohd Zaki

Abstract—**Design of a new specific colorimetric chemosensor for detection of Cu^{2+} is a challenge in the context of interference from coexisting metal ions in aqueous solution. Therefore, ortho (L1), meta (L2) and para (L3) bearing benzoyl thiourea moiety as binding site and *p*-dimethylaminobenzaldehyde moiety as signal group were designed and synthesized to apply as colorimetric chemosensors for detection of Cu^{2+}. The structure was confirmed by characterized the compound using Elemental analysis, Fourier Infrared (FTIR) and proton Nuclear Magnetic Resonance (^1H NMR) spectroscopy. Fuctional group of C=O, N-H, C=N and C=S was found at 1663 cm^{-1}, 3336 cm^{-1}, 1596 cm^{-1}, 1064 cm^{-1} respectively while ^1H NMR show peaks of alkane (CH_2), benzene (Ar-H), CONH, CSNH at 3.7 – 3.99, 7.05 – 7.79, 8.07, and 9.59 respectively. Elemental analysis for L1-L3 $C_{21}H_{26}N_5OSBr$ found was compatible with the expected theoretical calculation. For application, all of these three sensors showed excellent colorimetric specific selectivity and high sensitivity for Cu^{2+} in acetonitrile/water binary solutions so only L1 was selected for further studies towards sensitivity. When Cu^{2+} was added to the solution of L1, a dramatic color change from orange to brown, while other cations Fe^{2+}, Zn^{2+}, Ni^{2+}, Co^{2+}, Cr^{3+} and Mn^{2+} did not interfere with the recognition process for Cu^{2+}. The detection limits of L1 were 1.5×10^{-4} M and 1.7×10^{-5} M of Cu^{2+} using the visual color changes and Ultraviolet-visible spectroscopy changes respectively. Test strips based on L1 were fabricated, which could act as a convenient and efficient Cu^{2+} test kit.**

Index Terms—**Benzoyl thiourea, dimethylaminobenzaldehyde, copper (II) cation, colorimetric chemosensor, test strips.**

I. INTRODUCTION

The coordination chemistry of polyfunctional ligands that capable to realize different coordination modes with metal cations, is the utmost interest for the design and synthesis of new selective complexing agents and analytical reagents [1]. Compund with thiourea derivatives has gained considerable interest for the development of selective and sensitive sensors for toxic metal ions due to their main role in biological activities [2]-[4] and also found as chemosensors [5]-[7]. The receptors containing amide, urea, imine and thiourea groups act as cation sensors [8]-[10].

Due to high sensitivity, selectivity, low cost, and feasibility of in situ and real time monitoring, chemosensor has an attractive application prospect in detecting metal ions. Recently, a new chemosensor design concept of "single sensor for multiple analytes" gets more and more attention. The concept can be realized mainly by distinguishing different ions with different excitation wavelengths, detecting different ions indifferent solvents or recognizing different ions by UV–vis spectra. The development of novel sensors for multiple metal ions is of great significance because they are more efficient compared with sensors for single target. 4-Dimethylaminobenzaldehyde is widely used as fluorescent probe in chemosensors. It can modulate UV–vis absorption [7].

Copper is an essential trace element present in all living systems and is important for the function of many cellular enzymes [9]. However, excess copper can cause various intoxications [6], [11]. For example, the increasing concentration of copper cations in body causes imbalance in cellular processes resulting in pathogenesis Therefore, the rational design and synthesis of efficient sensors to selectively recognize copper cations is an important topic in supramolecular chemistry. Although previous work has involved the development of a wide variety of chemical and physical sensors for the detection of Cu^{2+}, so far, improving the detection selectivity in the context of interference from coexisting metal ions has been challenging.

In view of this requirement and as part of our research to ion recognition, an attempt was made to obtain efficient colorimetric sensors which could sense Cu^{2+} with specific selectivity and high sensitivity in aqueous solutions. This paper details the design and synthesis of a series of Cu^{2+} colorimetric sensors L1, L2 and L3 bearing benzoyl thiourea and dimethylaminobenzene groups. The strategies for the design of these sensors were as follows. Firstly, a symmetrical benzoyl thiourea group was introduced as the binding site. The C=S and C=O moiety on the benzoyl thiourea group possesses a high affinity with Cu^{2+}.

'Colorimetric chemosensors' are molecules that allow 'naked-eye' detection of cations without using any spectroscopic instrumentation [10] . Secondly, in order to achieve "naked-eye" colorimetric recognition, we introduced dimethylaminobenze moiety in terms of the suitability and performance as a fluorophore as the signal group [12].
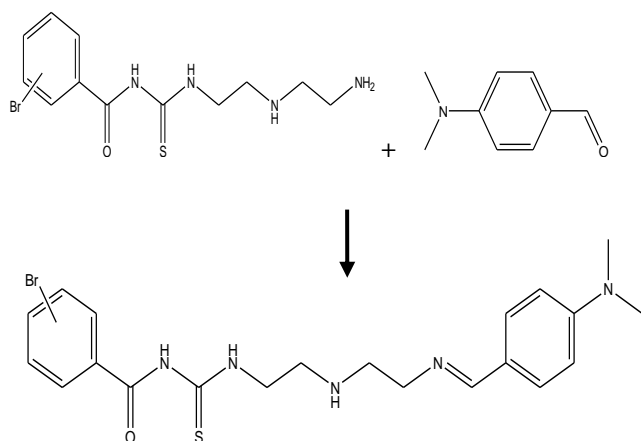
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Step 1:

'Half unit' ligand
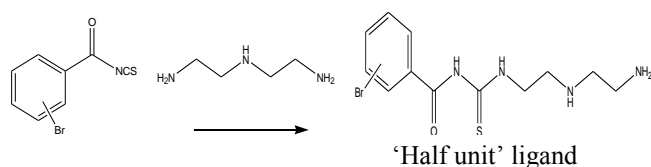
Step 2:

Scheme 1. Synthetic procedures for sensors L1-L3.

II. METHODS

A. Reagents and Physical Measurements

The inorganic salts $Fe(SO_4)_2.6H_2O$, $Mn(SO_4)_2$, $Cr(SO_4)_2XH_2O$, $Co(Cl_2)_2.6H_2O$, $Ni(NO_3)_2.6H_2O$, $Cu(NO_3)_2.3H_2O$ and $Zn(Cl_2)_2$ were purchased from Sigma Aldrich. All solvents and other reagents were of analytical grade. ^{1}H NMR spectra are recorded on a Bruker Avance III 300 Spectrometer at room temperature. ^{1}H chemical shifts are reported in ppm downfield from tetramethylsilane (TMS), d scale with the solvent resonances as internal standards). UV-vis spectra of compounds are recorded on a Perkin Elmer LAMBDA 25 UV-Vis spectrometer. Melting points were measured using BÜCHI Melting Point B-545 and the elemental analyses were conducted using CHNS Analyzer Flash EA 1112 series. The infrared spectra were performed using FTIR Perkin Elmer 100 Spectrophotometer in the spectral range of 4500-600 cm^{-1}.

B. General Procedure for UV-vis Spectroscopy

All the UV-vis experiments were carried out in Acetonitrile solution on a Perkin Elmer LAMBDA 25 UV-Vis spectrometer. Any changes in the UV-vis spectra of the synthesized compound were recorded on the addition of sulphate, chlorate and nitrate metal salts while the ligand concentration was kept constant in all experiments.

C. Binding Constant

The binding constant values for receptor towards Cu^{2+} were calculated from the UV–Vis titration results using Benesi–Hildebrand (B–H) Eq. (1).

$$\frac{1}{\Delta A} = \frac{1}{b\Delta\varepsilon[G_0][H_0]K_a} + \frac{1}{b\Delta\varepsilon[G_0]} \qquad (1)$$

where ΔA is the change in absorbance, $[G_0]$ is the concentration of the guest molecule, $[H_0]$ is the concentration of the host molecule and K_a is binding constant. Plot can be made with $1/\Delta A$ as a function of $1/[H_0]$. $\Delta\varepsilon$ can be derived from the intercept while K_a can be calculated from the slope.

D. Synthesis and Characterization of Sensors L1-L3

Preparation of 1-(2,3,4-Bromo-benzoyl)-3-(2-{2-[(4-dimethylamino-benzylidene)-amino]-ethylamino}-ethyl)-thiourea (L1-L3)

The 2,3,4-bromobenzoyl chloride (1.2 mL, 10 mmol) was added dropwise to a stirring acetone solution (40 mL) with ammonium thiocyanate (0.76 g, 10 mol). White precipitate of NH_4Cl was formed immediately and was filtered. The filtrate then was taken to be added dropwisely into diethylenetriamine (1 mL, 10 mmol) in 40 mL acetone then was put at reflux with constant stirring for 6 hours. After cooling, 4-dimethylaminobenzaldehyde (1.49 g, 10 mmol) in acetone was added to the solution for another half unit ligand. Reflux again for another 24 hours. By using rotavapor, the product was formed in an oily liquid but after evaporation a week, it leaves a solid form after scratched. The resulting precipitate was collected by filtration, washed several times with cold ethanol/water and purified by recrystallization from ethanol/dichloromethane mixture (1:1).

L1: Yield 60.9%; dark orange solid, m.p 87°C. IR (cm^{-1}): υ(C=O) 1663, υ(N-H) 3336, υ(C=N) 1596, υ(C=S) 1064. ^{1}H NMR (600 MHz, Acetone-d_6) δ 9.59 (s, 1H), 8.07 (d, J = 1.4 Hz, 1H), 7.79 (dd, J = 7.7, 1.8 Hz, 1H), 7.59 (dd, J = 9.7, 7.7 Hz, 1H), 7.56 – 7.05 (m, 15H), 6.67 – 6.55 (m, 1H), 3.99 – 3.89 (m, 4H), 3.70 (dd, J = 6.5, 5.4 Hz, 2H), 3.63 (d, J = 2.4 Hz, 1H), 3.64 – 3.53 (m, 3H), 3.52 – 3.42 (m, 3H), 2.97 (s, 2H), 2.93 – 2.86 (m, 3H), 2.83 – 2.69 (m, 3H). Anal. Calc. for $C_{21}H_{26}N_5OSBr$: C, 52.94; H, 5.50; N, 14.70. Found: C, 53.24; H, 5.17; N, 15.42.

L2: 51.9%; dark orange solid, m.p 98 °C. IR (cm^{-1}): υ(C=O) 1662, υ(N-H) 3319, υ(C=N) 1606, υ(C=S) 1060. ^{1}H NMR (600 MHz, Acetone-d_6) δ 8.11 (d, J = 1.9 Hz, 1H), 7.97 – 7.91 (m, 1H), 7.73 (ddd, J = 8.0, 2.1, 1.1 Hz, 3H), 7.46 (t, J = 7.9 Hz, 2H), 2.95 – 2.86 (m, 7H). Anal. Calc. for $C_{21}H_{26}N_5OSBr$: C, 52.94; H, 5.50; N, 14.70. Found: C, 58.23; H, 6.38; N, 13.69.

L3: 65%; dark red solid, m.p 145 °C. IR (cm^{-1}): υ(C=O) 1667, υ(N-H) 3361, υ(C=N) 1592, υ(C=S) 1024. ^{1}H NMR (600 MHz, Acetone-d_6) δ 8.03 – 7.95 (m, 1H), 7.53 – 7.44 (m, 2H), 7.43 – 7.33 (m, 1H), 3.80 – 3.74 (m, 1H), 3.67 (d, J = 6.6 Hz, 1H), 3.64 – 3.58 (m, 2H), 2.89 (d, J = 7.9 Hz, 2H), 2.79 (s, 1H), 2.75 (s, 1H), 1.16 (s, 1H). Anal. Calc. for $C_{21}H_{26}N_5OSBr$: C, 52.94; H, 5.50; N, 14.70. Found: C, 51.55; H, 4.91; N, 14.90.

III. RESULTS AND DISCUSSIONS

A. Absorption Studies of Receptors L1, L2 and L3 toward Various Cations

The cation binding abilities of the different receptors were investigated by UV-vis spectroscopic titration in ACN/ H_2O (10:1/v:v) at pH 7.0. The colorimetric sensing abilities were primarily investigated by adding various cations (Cu^{2+}, Mn^{2+}, Cr^{3+}, Fe^{2+}, Co^{2+}, Ni^{2+} and Zn^{2+} to the ACN/ H_2O (10:1/v:v, pH 7.0) solutions of sensor L1. Addition of Cu^{2+} to the solution of L1 (5.0×10^{-5} M), was responded sensor with dramatic color changes from orange to brown while other cation did not induce any changes (Fig. 1).

Fig. 1. Color changes observed upon the addition of various cations to the solutions of sensor L1 (1.5×10^{-3} M) in ACN/H_2O (10:1, v:v, pH 7.0) solutions. Left to right : free L1, Co^{2+}, Cu^{2+}, Cr^{3+}, Mn^{2+}, Zn^{2+}, Ni^{2+} and Fe^{2+}.
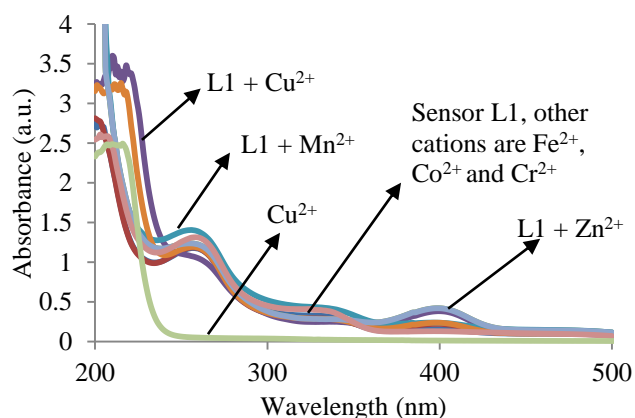

Fig. 2. UV-vis absorption spectra of L1 in the presence of of various cations in ACN/H_2O (10:1, v:v, pH 7.0) solution at room temperature.

In the corresponding UV-vis spectrum (see Fig. 2), the absorption peak of Cu^{2+} and Zn^{2+} were appeared at 400 nm. Meanwhile, a new peak appeared at 800 nm only for Cu^{2+}, which attributed to the color change from brown to green. However, when adding other cations Mn^{2+}, Cr^{3+}, Fe^{2+}, Co^{2+}, Ni^{2+} and Zn^{2+} into the ACN/ H_2O (10:1/ v:v, pH 7.0) solution of sensor L1 respectively, no significant color changes were observed. Therefore, in ACN/ H_2O solution, L1 showed specific colorimetric selectivity to Cu^{2+}. In order to exclude the possibility of these results being due to Cu^{2+} self absorption, a blank test were carried out via adding the same amount of Cu^{2+} to blank ACN/ H_2O solution (without containing L1), as a result, no color change was observed. In corresponding UV-vis spectra, there is no absorption peak appeared at the visible region (Fig. 2). It was confirmed that L1 could colorimetrically detect Cu^{2+} in ACN/ H_2O binary solution.

L2 and L3 show same result as L1 so only L1 was selected for further studies towards sensitivity to Cu^{2+}. A series of experiments was carried out to investigate the Cu^{2+} recognition capability and mechanism of L1.

To gain an insight into the stoichiometry of the L1-Cu^{2+} complex, the method of continuous variations (Job's method)

was used (see Fig. 3). When the molar fraction of sensor L1 was 0.63, the absorbance value approached a maximum, which demonstrated the formation of a 2:1 complex between the sensor L1 and Cu^{2+}.
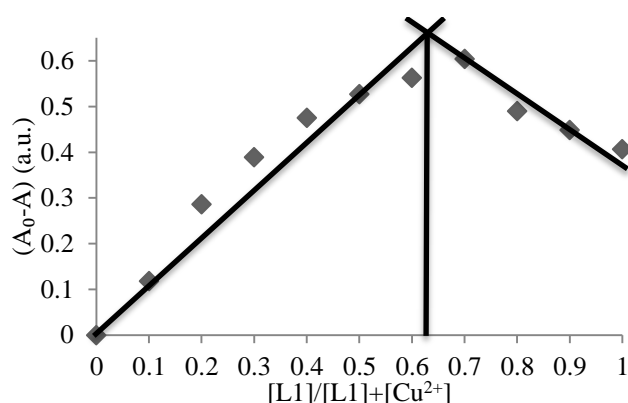

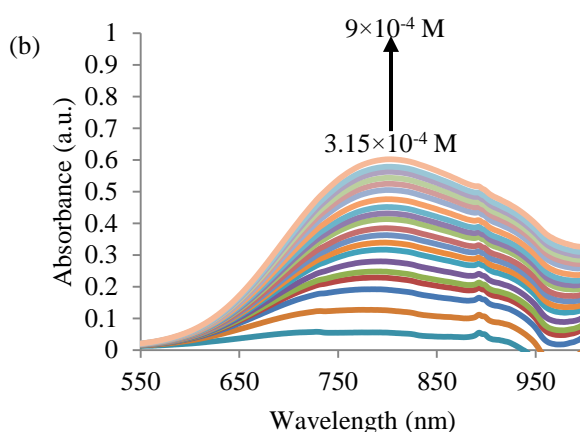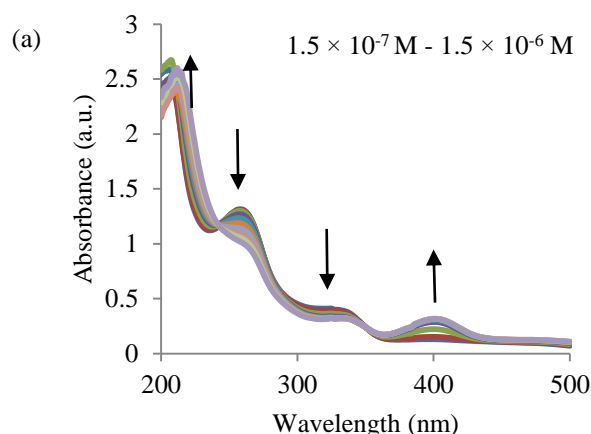Fig. 3. A Job plot of L1 and Cu^{2+}, which indicated that the stoichiometry of L1-Cu^{2+} complex was 2:1.

Fig. 4. (a) UV-vis spectral titration of sensor L1 (5×10^{-5} M) with Cu^{2+} (1.5×10^{-7} M - 1.5×10^{-6} M) in 10:1 ACN/H_2O (v/v) solution. (b) UV-vis spectral titration of sensor L1 (5×10^{-5} M) with Cu^{2+} (3.15×10^{-4} M - 9×10^{-4} M) in 10:1 ACN/H_2O (v/v) solution.

Fig. 4 (a) shows that the absorbance of L1 at UV spectra. The receptor with the low concentration of ion, it is found that the maximum wavelength for the compound within 256 and 400nm, there is no absorption band in the visible region, while the visible spectra was illustrated at 803nm by adding

more concentrated Cu^{2+} ions as shown in Fig. 4 (b). Three clear isosbestic points were observed (Fig. 4 (a)) at 244 and 351 nm, which indicated the formation of an L1-Cu^{2+} complex. Fig. 4 (b) illustrated the changes of UV-Vis spectra of L1 upon the addition of Cu^{2+} ions in 10:1 ACN/H_2O (v/v) solution. The absorption peak was increased with the increasing of Cu^{2+} concentration, meanwhile the spectral shape kept unchanged.
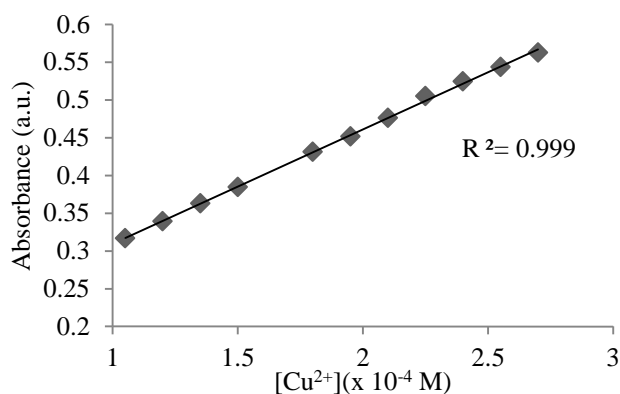

Fig. 5. Calibration curve was obtained from the plot of UV-Vis absorbance with the addition of Cu^{2+} concentration.

A calibration curve was obtained from the plot of UV-Vis absorbance with the addition of Cu^{2+} concentration. The curve equation as shown in Fig. 5 was $R^2=0.999$. The linear range of quantitative detection for Cu^{2+} was determined as 1.05×10^{-4} to 2.7×10^{-4} M with a detection limit of 1.7×10^{-5} M for Cu^{2+} from the curve in the used aqueous solution system. From the UV-Vis absorption measurements, the binding constant (K_a) of the copper complex of the receptor is calculated from the variation in the absorbance at 800nm, respectively and is found to be 2.35×10^3 M. This suggests that the receptor forms strong binding with Cu^{2+} ion [10].
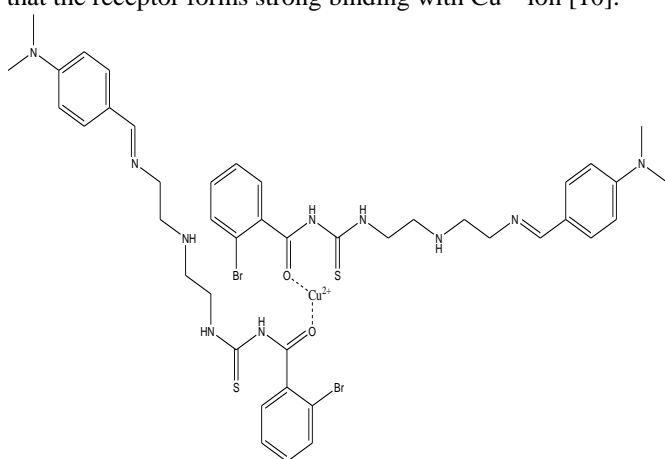
Scheme 2. The proposed reaction mechanism of the sensor L1 with Cu^{2+}.

The recognition mechanism of the sensor L1 with Cu^{2+} was investigated by IR spectra titration methods. Based on IR spectra of L1, the stretching vibration absobrption peaks of cyanide C=N, acyl C=O and thiourea C=S appeared at 1591, 1677 and 745 cm^{-1} respectively. However, when L1 coordinated with Cu^{2+}, the stretching vibration absorption peaks of acyl C=O were shifted to 1656 cm^{-1} while stretching vibration absorption peaks of cyanide C=N and

thiourea C=S didn't take place any shift, which indicated that L1 complexed with Cu^{2+} via Cu^{2+}- O coordination bond as shown in Scheme 2.
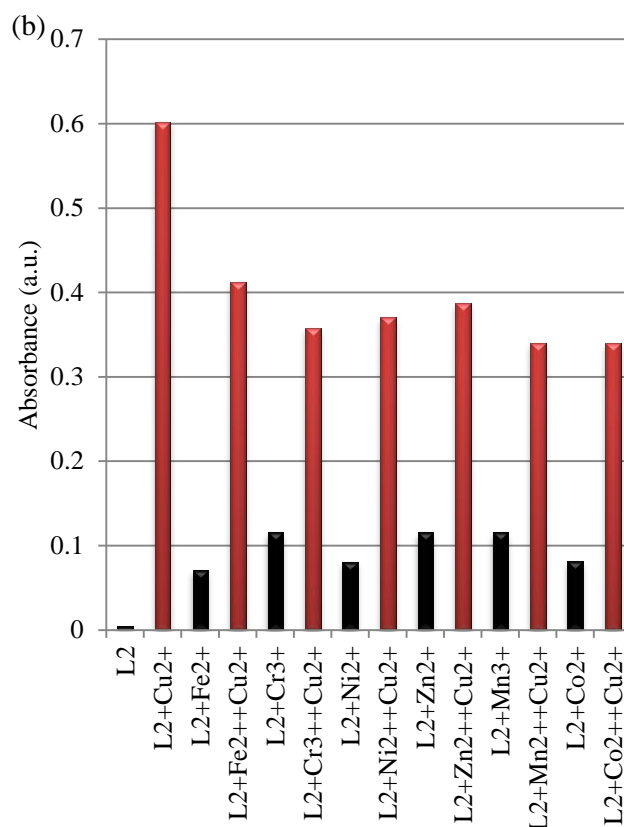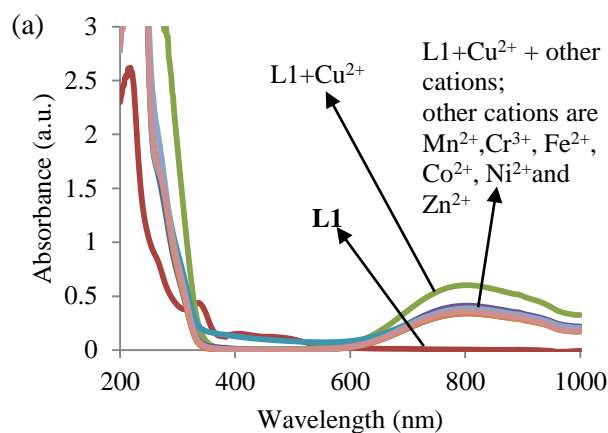
B. Sensing in the Presence of Competing Ions

Fig. 6. (a) UV-vis absorption spectra sensor L1 (5 x 10^{-5}M) in ACN/H_2O solutions in the presence of Cu^{2+} and the miscellaneous cations Fe^{2+}, Cr^{3+}, Ni^{2+}, Zn^{2+}, Mn^{2+} and Co^{2+}. (b) UV-vis absorption at 803nm of sensor L1 (5 $\times 10^{-5}$M) in ACN solutions in the presence of Cu^{2+} and the miscellaneous cations Fe^{2+}, Cr^{3+}, Ni^{2+}, Zn^{2+}, Mn^{2+} and Co^{2+}.

An important feature of the sensor is its high selectivity toward the analyte over other competitive species. The variations of UV- vis spectral and visual color changes of sensor L1 in ACN/H_2O binary solutions caused by the metal ions Mn^{2+},Cr^{3+}, Fe^{2+}, Co^{2+}, Ni^{2+} and Zn^{2+} were recorded in Fig. 6. It is noticeable that the miscellaneous competitive metal ions did not lead to any significant interference. In the presence of these ions, the Cu^{2+} still produced similar color and absorption changes (Fig. 7). These results shows that the

selectivity of sensor L1 toward Cu^{2+} was not affected by the presence of other cations and suggested that it could be used as a colorimetric chemosensor for Cu^{2+}.

C. Chromogenic Response in Aqueous Solutions

The colorimetric and UV-vis limits of sensor L1 for Cu^{2+} cation were also tested. As presented in Fig. 8, the detection limit using visual color changes is a concentration of 1.5×10^{-4} M of Cu^{2+} cation in 1.5×10^{-3} M solution of sensor L1. While, as shown in Fig. 4, with the gradual addition of Cu^{2+}, a sharp increase in the absorbance at 803 nm and an obvious decrease in the absorbance at 260 nm are observed. Simultaneously, the ratio of A803/A260 increases with the increasing in Cu^{2+} concentrations, which allowing the Cu^{2+} concentration to be determined ratiometrically. The detection limit of the UV-vis changes calculated is 1.7×10^{-5} M for Cu^{2+} cation, which pointing to the high detection sensitivity.
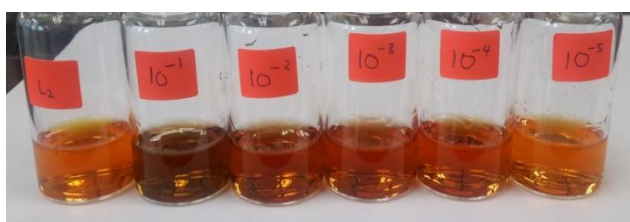

Fig. 7. Color changes observed upon the addition of varying quantities of Cu^{2+} (from left to right: free L1, 1.5×10^{-1}M, 1.5×10^{-2}M, 1.5×10^{-3}M, 1.5×10^{-4}M, 1.5×10^{-5}M) to the solutions of sensor L1 (1.5×10^{-3}M; ACN/H$_2$O, 10:1, v:v, pH 7.0).
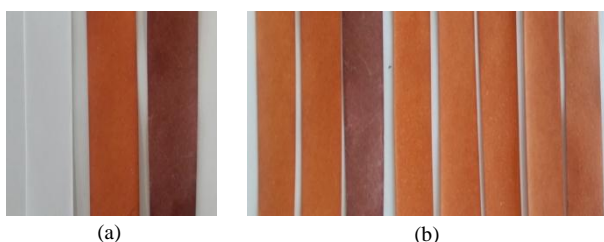

| (a) | (b) |

Fig. 8. Photographs of the L1 based test strips colorimetric detect Cu^{2+}. (a) Left to right: free test strip, test strips + ACN, test strip + ACN solution of Cu^{2+}. (b) After addition the ACN solutions of various metal cations respectively and dried them under room temperature. Left to right: free, Co^{2+}, Cu^{2+}, Ni^{2+}, Mn^{2+}, Zn^{2+}, Fe^{2+} and Cr^{3+}.

To investigate the practical application of chemosensor L1, test strips were prepared by immersing filter papers into ACN solution of L1 (0.1 M) and then drying in air. The test strips containing L1 were utilized to sense different cations. As shown in Fig. 8, when different cation solutions were immersed (5 minutes) on the test strips respectively, the obvious color change was observed only with Cu^{2+} solution. Therefore, the test strips could directly detect Cu^{2+} in ACN or ACN/H$_2$O binary solutions. In addition, the test strips also could detect Cu^{2+} in pure water. Before adding the pure water solution of Cu^{2+} to the test strip, one drop of ACN has been added to the test strip and the test strip was moistened by ACN. Then the purewater solution of Cu^{2+} was added to the ACN moistened test strip, the test strip carried out similar color changes just like the ACN/H$_2$O solution of Cu^{2+} added to the dry test strip. Therefore, the ACN

moistened test strip could conveniently detect the Cu^{2+} in pure water.

IV. CONCLUSION

In conclusion, L1-L3 bearing thiourea moiety as the binding site and *p*-dimethylaminobenzaldehyde moiety as the signal group was designed and synthesized to apply as colorimetric sensor for Cu^{2+} ion. This sensor showed specific selectivity for Cu^{2+} in ACN/H$_2$O binary solutions indicated that the aminobenzaldehyde moiety acted as a signal group and played a crucial role in the process of colorimetric recognition. Only sensor L1 was chosen for further studies due to the same selectivity towards metal of Cu^{2+} ion. Investigation of the recognition mechanism indicated that the sensor L1 recognized Cu^{2+} by forming a stable 2:1 L1- Cu^{2+}complex. The coexistence of other cations did not interfere with the Cu^{2+} recognition process. Moreover, the detection limit of the sensor L1 toward Cu^{2+} was 1.7×10^{-5} M, which indicated that the sensor L1 may be useful for preliminary detection of Cu^{2+} ions by simple solvent extraction in chemical and environmental applications. In addition, test strips based on L1 were fabricated, which also exhibits a good selectivity to Cu^{2+} as in solution. We believe the test strips could act as a convenient and efficient Cu^{2+} recognition in an early stage.

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