

A SIMPLE AND FACILE COLORIMETRIC CHEMOSENSOR FOR SELECTIVE DETECTION OF Cu^{2+} ION IN AQUEOUS SOLUTION

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ABSTRACT. In this paper the chemical sensing ability of aromatic salicylideneaniline Schiff-base (ASASB), synthesized solvent-free mechanochemically and characterized, was assessed *via* UV-Vis spectroscopic method together with naked-eye detection. Metal ions in aqueous medium from s, p and d-block elements were investigated based on chelation-induced colorimetric chemosensing. The result revealed that ASASB can be used as a new colorimetric chemosensor for selective detection of Cu^{2+} ion in aqueous solution.

KEY WORDS: Metal ion, Schiff-base, Colorimetric chemosensor, Mechanochemistry

INTRODUCTION

Metals are indispensable for life, as they are involved in many fundamental biological processes, including osmotic regulation, catalysis, metabolism, biomineralization, and signaling [1]. The important metals in living organisms fall into two classes: the transition metals (e.g. Fe, Zn, Cu, Mn, Co, Ni, Mo, V, and Se) and the alkali and alkaline earth metals (e.g. Na, K, Ca and Mg) [2]. The transition metals are present at much lower levels and often referred to as trace elements [1].

The selective sensing of metal ions is one of the most important areas of organic chemistry, supramolecular chemistry, drug delivery, and environmental chemistry because of its potential clinical applications [3, 4]. The toxicity of certain metal ions to human and other living organisms has also been a constant cause of environmental concern. Thus, the selective and sensitive detection of trace amounts of heavy metal ions in the environment is of utmost importance [5].

Cu^{2+} is an ion of ubiquitous presence in living systems with a prominent role in oxidative metabolism and homeostatic regulation [6]. The normal functioning of certain enzyme classes such as superoxide dismutase (SOD1), cytochrome-c-oxidase (Cyt-O), tyrosinase and ceruloplasmin rely on the $\text{Cu}^{\text{I}}/\text{Cu}^{2+}$ redox couple [6-10]. While under a normal state, this redox chemistry is essential for life, under “over expressed” or “mis-regulated” state, it becomes equally life threatening. It is believed that an excess amount of free Cu^{2+} triggers various serious diseases include amyotrophic lateral sclerosis [11], Alzheimer’s disease [12], Parkinson’s disease [13], Wilson’s disease [14,15] and Menkes syndrome [16,17]. Copper is widely used in piping for water supplies, refrigeration and air conditioning as well as in wires, electromagnets, electrical relays and switches. It is used in industry as an activator in froth floatation of sulfide ores, production of wood preservatives, electroplating, azo-dye manufacture, as a mordant for textile dyes, in petroleum refining and the manufacture of copper compounds. Due to the widespread application of Cu^{2+} ions in chemistry, medicine, biotechnology and industry, it has turn into one of the most important pollutants in environment when it exceeds the limit of

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tolerable concentration of Cu^{2+} ion in drinking water. Therefore, the detection of copper has been accepted as an important consideration.

Although a number of methods are available for determining the presence of metal ions in the environment, there is a growing need for rapid on-site analysis with chemosensors capable of detecting metal ions on a real-time basis. Consequently, a large number of papers involving colorimetric chemosensor [18-23], fluorescent chemosensor [24-29] and other techniques [30-35] have been published for metal ion detection. In recent themed issue series of *Chemical Society Reviews* on sensor targets and imaging agents also confined an exciting mix of reviews focusing on small organic or transition metal receptors. It also includes a selection of overview articles by leaders in the field, introducing issues; anions, cations, iomolecules/macromolecules, f-metal ion and materials [36-43]. However, still there has been an interest in the improvement of practical use of colorimetric chemosensors, such as the lack of aqueous solubility, designing of sensor toward specific metal ion detection, development of sensor probe *via* green synthesis protocol etc. Accordingly, developing new and practical sensing systems for metal ions is still a challenge.

In this work, we have focused on the development of a simple and facile colorimetric chemosensor, based on chelation-induced chemosensing for selective and sensitive recognition of Cu^{2+} from a wide variety of elements in the periodic table, *via* solvent-free mechanochemical synthesis. Mechanochemical processes are both solvent-free and less energy consuming than standard solution reactions and are rapidly becoming popular as green and sustainable alternative to conventional solution-based processes. The excellent conversion to products, with virtually zero workup, and isolation of species, which cannot be obtained in solution, make the mechanochemical approach a worthwhile *click* and *green* method for Schiff-base synthesis [44].

The design of ligands for the selective complexation of suitable guests such as metal cations and anions has been an important goal of simple organic and supramolecular chemistry [45-47]. In this regard, the ability to operate a naked-eye colorimetric response to the analyte is an attractive approach to the design of sensing molecules. Thus, we have developed a new ASASB ligand having ON chelating system, synthesized solvent-free mechanochemically, as a new colorimetric chemosensor for selective recognition of Cu^{2+} ion in aqueous solution. Metal ions were selected for this investigation was based on their biological importance and environmental impact as well as their differences in oxidation state.

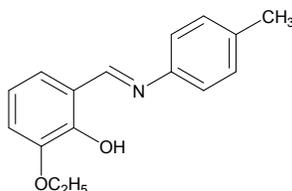


Figure 1. Structure of sensor probe ASASB (receptor).

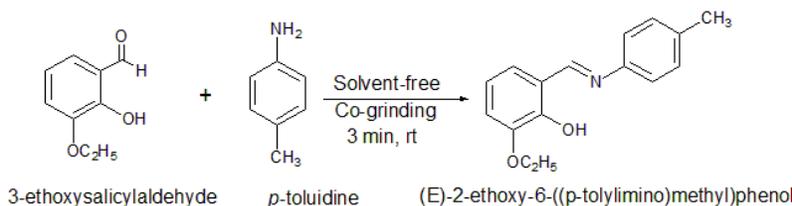
EXPERIMENTAL

Reagents

The probe (E)-2-ethoxy-6-((*p*-tolylimino)methyl)phenol was synthesized by the procedure mentioned below. *p*-toluidine and 3-ethoxysalicylaldehyde were from RDH and ALFA AESAR, respectively. Metal salts $\text{CrCl}_3 \cdot 6\text{H}_2\text{O}$, $\text{MnCl}_2 \cdot 4\text{H}_2\text{O}$, $\text{FeCl}_2 \cdot 4\text{H}_2\text{O}$, $\text{FeCl}_3 \cdot 6\text{H}_2\text{O}$, AlCl_3 were purchased from Sigma Aldrich, KBr , NaCl , $\text{MgCl}_2 \cdot 6\text{H}_2\text{O}$, $\text{CaCl}_2 \cdot 2\text{H}_2\text{O}$, $\text{SrCl}_2 \cdot 6\text{H}_2\text{O}$ were purchased from Mallinckrodt, $\text{CuCl}_2 \cdot 2\text{H}_2\text{O}$, ZnCl_2 were purchased from RDH, $\text{CoCl}_2 \cdot 6\text{H}_2\text{O}$, $\text{NiCl}_2 \cdot 6\text{H}_2\text{O}$ were purchased from Merck, $\text{AgC}_2\text{H}_3\text{O}_2$ and $\text{Hg}(\text{O}_2\text{CCH}_3)_2$ were purchased from Fluka Company.

Preparation

The solid reactant 3-ethoxysalicylaldehyde (0.1662 g, 1.0 mmol) and the solid *p*-toluidine (0.1072 g, 1.0 mmol) in mortar were ground with a pestle, separately at initial stages then together at later stages, at room temperature and without any solvents. As soon as the two reactants were mixed, there was fast color change, signifying that the dehydration reaction took place, and then the mixtures were ground further for 3 min prior to an investigation of the conversion to Schiff-base, without purification (Scheme 1). The progress of reaction was monitored with ¹H NMR spectroscopic method to make sure the quantitative conversion [44].



Scheme 1. Solvent-free mechanochemical synthesis of ASASB.

Characterization

Yield: 0.2531 g (99.1%); color: orange; m.p. 81 °C; ¹H NMR (400 MHz, CDCl₃, 27 °C, TMS): δ = 13.84 (s, 1H; OH), 8.61 (s, 1H; CH=N), 6.87–7.24 (m, 7H; Ar-H), 4.17 (q, ³J(H,H) = 8 Hz, 2H; CH₂), 2.32 (s, 3H; CH₃), 1.52 ppm (t, ³J(H,H) = 8 Hz, 3H; CH₃); ¹³C NMR (300 MHz; CDCl₃, 27 °C, TMS): δ = 161.6 (CH=N), 151.8, 147.8, 145.5, 137.0, 130.0, 123.8, 120.9, 119.4, 118.4, 116.3, 64.7 (CH₂), 21.1 (CH₃), 14.9 (CH₃) ppm; IR (KBr): ν = 1617 cm⁻¹ (C[dbond]N); HRMS (EI+): m/z calcd for C₁₆H₁₇NO₂+H⁺: 256.1338 [M+H]⁺; found: 256.1327 [44].

Instruments and method

¹H NMR and ¹³C NMR spectra were recorded using Bruker 400 and 300 MHz machines, with chemical shifts in δ units, downfield positive, and referenced to the residual peak of deuterated solvents (CDCl₃ δ d 7.24, CDCl₃ δ 77, correspondingly). Infrared spectra were recorded on a Perkin Elmer spectrum 100 FTIR spectrophotometer using the KBr pellet method. HR-ESI and EI+MS spectra were conducted on dual ionization ESCi® (ESI/APCi) source options Waters LCT Premier XE (Waters Corp., Manchester, UK) and a JMS-700 double focusing mass spectrometer (JEOL, Tokyo, Japan) with a resolution of 8000 (3000) (5% valley definition), respectively. Melting points were determined by using Perkin Elmer differential scanning calorimeter DSC 7 modules in sealed aluminum pans, heated in flowing nitrogen (20.0 mL/min) at 5 °C/min and a Fargo MP-2D melting point apparatus (uncorrected). UV-Vis spectra were recorded by a double-beam UV-S2000 UV-Visible spectrophotometer over a wavelengths scan of 200–800 nm with integration time of 45 ms, at normal pressure and room temperature. A 1 cm × 1 cm quartz cuvette was used for the spectroscopic analysis.

The spectral analyses were accomplished in un-buffered DI H₂O/ethanol 1:3 (v/v, mL) solution at room temperature. The concentration of ASASB for UV-Vis measurement was 50 μM. All the chloride and acetate salts were prepared in cold doubly ion-exchanged water. UV-Vis spectrophotometric titration was conducted directly in 2 mL cuvette by successive addition of corresponding chemical reagent using a microliter pipet. Upon addition of every aliquot, the solution was well mixed then the spectrum was measured.

RESULTS AND DISCUSSION

The receptor (Figure 1) used in this study was readily synthesized by a one-pot solvent-free mechanochemical reaction between *p*-toluidine and 3-ethoxysalicylaldehyde [44]. Experimentally the solvent-free mechanochemical conversion of *p*-toluidine and 3-ethoxysalicylaldehyde to the corresponding Schiff-base proceeded in a straight-forward manner. The Schiff-base product mixture was monitored by ¹H NMR spectroscopy in order to find the complete disappearance of the aldehyde and amine protons and the full emergence of the azomethine proton. At 100% conversion, the product spectra exhibited a singlet at δ 8.61 attributed to azomethine proton (CH=N) and no signal at ca. δ 10 attributed to aldehyde proton (-CH=O). The spectra also exhibit multiplets at δ 6.87–7.24, quartet at δ 4.17 and triplet at δ 1.52, are corresponding to aromatic ring protons, ethoxy -CH₂CH₃ and ethoxy -CH₂CH₃, respectively. It is worth mentioning that upon Schiff-base formation the signal of the azomethine hydrogen appears up field relative to the original signal of the aldehyde hydrogen (-CH=O). For this Schiff-bases the -OH proton signal of aldehyde originally at ca. δ 11 changed to that of Schiff-base at δ 13.84, the down field shift being attributed to the O-H···N intra-molecular H-bonding, as a common feature of *o*-hydroxysalicylidene systems [48]. The FT-IR and ESI-MS results were also further confirmed the successful conversion of aldehyde and primary aromatic amine to the corresponding Schiff base.

The receptor was chosen as the bidentate ON chelating ligand of phenolic OH and imine C=N are drastically bind with metal ion to form stable coordination compound, then change the UV-Vis absorption and change color of solution. Consequently, the selective recognition of the receptor towards Cu²⁺ ions in an aqueous medium has been demonstrated using UV/Vis absorption together with naked-eye detection.

Colorimetric chemosensing

The colorimetric sensing ability of probe ASASB toward different metal cations such as Na⁺, K⁺, Mg²⁺, Ca²⁺, Sr²⁺, Cr²⁺, Mn²⁺, Fe²⁺, Fe³⁺, Co²⁺, Ni²⁺, Cu²⁺, Zn²⁺, Al³⁺, Ag⁺ and Hg²⁺ were examined (Figure 2). Colorimetric titrations were carried out in DI H₂O/ethanol mixture. The color change was visualized by naked-eye analysis and optical response was studied by UV-Vis spectroscopy.



Figure 2. Color changes of (50 μM) concentration of receptor (ASASB) in H₂O: Ethanol 1:3 (v/v, mL) ratio upon addition of various metal ions (50 μM) in H₂O in 1:1 (v/v, mL) under day light.

The naked-eye analysis was aimed in aqueous medium, to suit for the physiological condition and real sample analysis. In the naked-eye experiments, visual inspection of solution of receptor ASASB in DI H₂O/ethanol 1:3 (v/v, mL) showed dramatic color change from colorless to yellow upon the addition of (1 equiv) of Cu²⁺ ion in DI H₂O. The change could easily be detected by the naked-eye during day light. The addition of other metal ion aqueous solutions such as Na⁺, K⁺, Mg²⁺, Ca²⁺, Sr²⁺, Cr²⁺, Mn²⁺, Fe²⁺, Fe³⁺, Co²⁺, Ni²⁺, Zn²⁺, Al³⁺, Ag⁺

and Hg²⁺ did not show any detectable color changes for a period of time. The color change can be attributed to the fast complex formation.

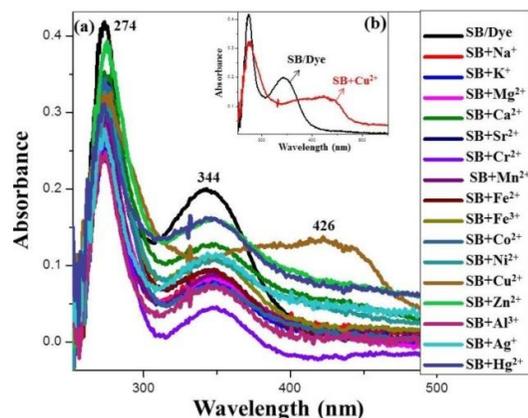


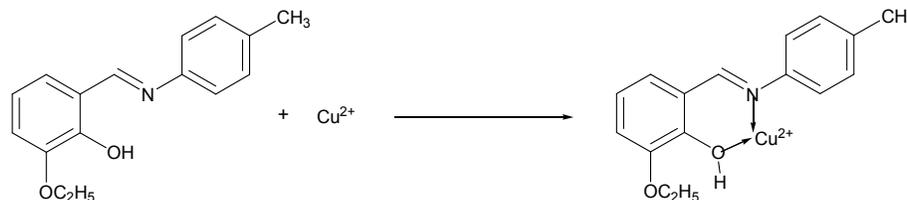
Figure 3. (a) UV-Vis spectra of receptor (ASASB) (50 μM) in H_2O : Ethanol 1:3 (v/v, mL) upon addition of Cl⁻ salts of Na⁺, K⁺, Mg²⁺, Ca²⁺, Sr²⁺, Cr²⁺, Mn²⁺, Fe²⁺, Fe³⁺, Co²⁺, Ni²⁺, Cu²⁺, Zn²⁺, Al³⁺ and acetate salt of Ag⁺ and Hg²⁺ (50 μM , respectively) in DI H₂O (b). Inset: UV-Vis spectra of receptor (ASASB) (50 μM) in H_2O : Ethanol 1:3 (v/v, mL) alone (Black) and with equivalent amount of Cl⁻ salts of Cu²⁺ in DI H₂O (Red).

UV-Vis analysis

The optical properties of probe ASASB (50 μM) were investigated in an Ethanol: H₂O (3:1) solution exhibited characteristic absorption bands at 274 and 344 nm attributed to: $\pi \rightarrow \pi^*$ and $n \rightarrow \pi^*$ transition respectively. However, complex formation would remove the electron density on the amine N-atom thereby reduces the intensity of $n \rightarrow \pi^*$ transition and consequently decreases the absorbance [49]. Accordingly, the absorption response of probe ASASB (50 μM) toward various metal ions was first explored and the results are shown in Figure 3. The free chemosensor probe ASASB (50 μM) remained colorless and did not exhibit apparent absorption above 400 nm in the aforementioned solution. Upon addition of 1.0 equiv. of Cu²⁺ to the colorless solution of probe ASASB (50 μM), decreases the absorbance of the ASASB at 344 nm and a new strong absorption band centered on 426 nm was formed, which likely attributed to the metal to ligand charge transfer (MLCT) band, accompanied with a distinct color change from colorless to yellow confirmed coordination of Cu²⁺ with ASASB. Addition of 1.0 equiv. of other metal ions such as Na⁺, K⁺, Mg²⁺, Ca²⁺, Sr²⁺, Cr²⁺, Fe²⁺, Fe³⁺, Co²⁺, Ni²⁺, Zn²⁺, Al³⁺, Ag⁺ and Hg²⁺ to the solution of probe ASASB (50 μM) did not induce significant absorption changes under the above conditions. This is presumably due to the fact that transition metal ions are the best candidate for formation of complexes as they have suitable vacant orbitals with optimum energy, being exist in variable oxidation state and have small size compared with the corresponding s and p block elements. Among the transition metals in this study Cu²⁺ ion probably has high affinity towards a pair of electrons in the donor atoms of ASASB and the greater this affinity, the faster the complex formation and the more stable the complex formed by the metal ion will be. Furthermore, the imine nitrogen of a Schiff-base shows pi-acceptor property and high affinity to transition metal Cu²⁺ ion to form stable coordination complex in aqueous medium. The results are in accordance with the literature values [50] and indicate sensor receptor ASASB has a remarkable selectivity to Cu²⁺ ion.

Structural analysis

Based on the results from UV–Vis and theoretical point of view the possible binding mode of the ligand/ASASB with copper ion is shown in Scheme 2. The ligand can act as a bidentate O, N-chelating system with the remaining coordination sites are possibly occupied by H₂O and/or Cl⁻. The detail structural investigation is underway with an aim to understand the mechanism of the interaction between Cu(II) ion and the receptor, ASASB.



Scheme 2. Proposed mechanism of Cu²⁺ ion sensing by (E)-2-ethoxy-6-((p-tolylimino)methyl)phenol (receptor) in water:ethanol.

CONCLUSIONS

A simple, highly selective colorimetric chemosensor for the detection of Cu²⁺ ion in an aqueous medium was developed. The bidentate ASASB ligand chelates with Cu²⁺ ions result in color change from colorless to yellow and showed a new strong non-ligand absorption band centered at 426 nm after the addition of Cu²⁺ ion independently, indicate ASASB can be used as a new colorimetric chemosensor for selective detection of Cu²⁺ ion in aqueous solution. We found that ASASB derivative responsive to environments together with easy mechanical synthesis, gives an enormous field of molecular design in order to engineer Schiff-bases to be used in chemosensing.

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