



An azine based sensor for selective detection of Cu^{2+} ions and its copper complex for sensing of phosphate ions in physiological conditions and in living cells



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ABSTRACT

A simple and cost effective unsymmetrical azine based Schiff base, 5-diethylamino-2-[(2-hydroxy-benzylidene)hydrazonomethyl]-phenol (1) was synthesized which selectively detect Cu^{2+} ions in the presence of other competitive ions through “naked eye” in physiological conditions (EtOH–buffer (1:1, v/v, HEPES 10 mM, pH = 7.4)). The presence of Cu^{2+} induce color change from light yellow green to yellow with the appearance of a new band at 450 nm in UV–Vis spectra of Schiff base 1. The fluorescence of Schiff base 1 (10 μM) was quenched completely in the presence of 2.7 equiv. of Cu^{2+} ions. Sub-micromolar limit of detection (LOD = 3.4×10^{-7} M), efficient Stern–Volmer quenching constant ($K_{SV} = 1.8 \times 10^5 \text{ L mol}^{-1}$) and strong binding constant ($\log K_b = 5.92$) has been determined with the help of fluorescence titration profile. Further, 1 – Cu^{2+} complex was employed for the detection of phosphate ions (PO_4^{3-} , HPO_4^{2-} and H_2PO_4^-) at micromolar concentrations in EtOH–buffer of pH 7.4 based on fluorescence recovery due to the binding of Cu^{2+} with phosphate ions. Solubility at low concentration in aqueous medium, longer excitation (406 nm) and emission wavelength (537 nm), and biocompatibility of Schiff base 1 formulates its use in live cell imaging.

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1. Introduction

Copper is one of the most essential trace elements of importance for both physical and mental health and serve as a key factor for a wide variety of enzymes in living organisms [1]. However, its excess amount may lead to vomiting, lethargy, increased blood pressure and respiratory rates, acute hemolytic anemia, liver damage, neurotoxicity and neurodegenerative diseases [2,3]. Phosphate ions play essential roles in genetic information storage, gene regulation, energy transduction, signaling processing and muscle contraction [4,5]. Phosphate is a key unit of DNA, RNA and many chemotherapeutic and antiviral drugs [6,7]. In contrast, the over-use of phosphate can lead to excessive algal growth, followed by decomposition and depletion of dissolved oxygen, and finally, the eutrophication of aquatic ecosystems [8]. Hence, much attention has been paid to the development of highly selective and sensitive copper and phosphate sensors for biological and environmental applications.

Although, a number of papers have been published for the detection of copper and phosphate ions, however, there is still an urgent need for simple, biocompatible and cost effective synthetic compounds which may detect copper and phosphate ions with high affinity in competitive aqueous media at physiological conditions [9,10]. Aqueous medium is

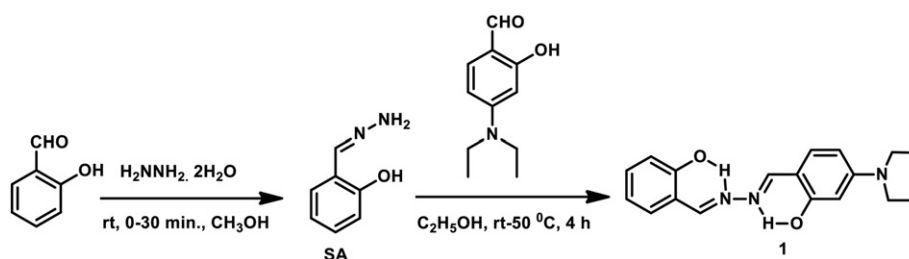
always interfering in the detection of ions due to their high degree of hydration in water [11,12]. Hence, synthesis of a novel receptor that can detect these ions selectively and sensitively in aqueous solution will be attention-grabbing due to their biological application in live cell imaging.

There are numerous reports in literature enlightening the photochemical behavior and sensing applications of azine based Schiff bases. For example, aldazine based chromo-fluorogenic sensor for fluoride ions in DMSO was developed by Li et al. [13]. Guchhait et al. have investigated spectral properties and sensing ability towards protic environment of a simple azine Schiff base [14]. This sensor is found to be nonfluorescent in aprotic solvents (MeCN and Dioxane) and become highly fluorescent in protic solvents (MeOH and H_2O) due to the formation of intermolecular hydrogen bonding between sensor and protic solvents. However, most of the reported azine based Schiff bases are symmetrical type ($\text{RHC}=\text{N}=\text{CHR}$) and shows aggregation induced emission (AIE) in aqueous solution [15]. A very small amount of research work in literature for unsymmetrical azine based Schiff bases ($\text{RHC}=\text{N}=\text{CHR}_1$) motivate us to synthesize these Schiff bases [16]. The designing and synthesis of novel unsymmetrical azine based Schiff base will be interesting because introduction of asymmetry may tune the photochemical properties of synthesized Schiff base.

In this work unsymmetrical azine based Schiff base, 5-diethylamino-2-[(2-hydroxy-benzylidene)hydrazonomethyl]-phenol (1) was synthesized in excellent yield from inexpensive and biocompatible starting

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Scheme 1. Synthesis of Schiff base 1.

materials having 2-hydroxysalicylaldehyde as main component. The Schiff base 1 possess both charge transfer and proton transfer group and was found to be highly fluorescent in both organic and aqueous solution. Coupled excited state intramolecular proton transfer (ESIPT) and intramolecular charge transfer (ICT) have been widely explored in the molecular systems possessing both charge transfer and proton transfer groups. However, there are a very small number of reports in literature, where one process is suppressed by other viz. Guchhait et al. have observed the ICT suppressed ESIPT single fluorescence at 527 nm for 4-(diethylamino)-2-hydroxybenzaldehyde [17]. In the case of Schiff base 1, ICT is suppressed and only ESIPT is observed because uneven intramolecular charge transfer facilitates ESIPT.

Most of the reported azine based Schiff base chromo-fluorogenic sensors for Cu^{2+} suffer from the interferences caused by Fe^{3+} , poor water solubility, use of organic solvents and poor detection limit [18, 19]. However, this chromo-fluorogenic Schiff base (1), synthesized by simple condensation reactions, is very efficient in selective detection of Cu^{2+} in EtOH-buffer solution (1:1, v/v, HEPES 10 mM, pH = 7.4) with LOD = 3.4×10^{-7} M. Further, 1 – Cu^{2+} complex was also utilized for sensing of phosphate ions in the same aqueous solution. Logic gate were constructed successfully by taking two input Cu^{2+} and EDTA in aqueous solution and a number of reversible cycles were observed upon alternative addition of Cu^{2+} and EDTA in EtOH-buffer (1:1, v/v, HEPES 10 mM, pH = 7.4) solution of Schiff base 1. To further evaluate the biological application of Schiff base 1, fluorescence has also been employed for detection of these ions in living cells.

2. Experimental

2.1. Materials and Methods

All analytical reagent grade chemicals were obtained from the commercial sources. Perchlorate salts of cations, tertbutylammonium salts of anions and HEPES buffer were purchased from Sigma-Aldrich

Chemicals, USA. Di sodium hydrogen phosphate dehydrate, Potassium dihydrogen orthophosphate, Aluminium(III) nitrate, tetrasodium EDTA (ethylene diamine tetra acetic acid) and all the solvents were obtained from Merck Chemicals, India. Absolute ethanol (Emsure grade) was purchased from Merck Germany. All the solvents were used after checking their purity thoroughly by UV-Vis and fluorescence spectral techniques. Double distilled water was prepared in lab using double distillation unit.

2.2. Synthesis of Schiff Base 1

The Schiff base, 5-diethylamino-2-[(2-hydroxy-benzylidene)hydrazonomethyl]-phenol (1) was synthesized by two step condensation reactions (Scheme 1). Synthetic methodology involved initial stirring of hydrazine hydrate with 2-hydroxybenzaldehyde in dry methanol at room temperature for 30 min to yield 2-hydrazone-methyl phenol (SA). The heating of SA with 4-diethylamino-2-hydroxybenzaldehyde in ethanol at 50 °C afforded the corresponding 5-diethylamino-2-[(2-hydroxy-benzylidene)hydrazonomethyl]-phenol (1) in excellent yield.

2.2.1. Analytical Data

$\text{C}_{18}\text{H}_{21}\text{N}_3\text{O}_2$: Physical state: Pale yellow solid, Yield 88%; M.p. 160 °C; found % for C, 69.51; H, 6.73; N, 13.55, Calc: C, 69.43; H, 6.80, N, 13.49; ^1H NMR (300 MHz, CDCl_3) δ 1.20 (t, $J = 6.9$ Hz, $-\text{CH}_3$); 3.40 (q, $J = 7.2$ Hz, 4H, $-\text{CH}_2$); 6.21 (d, $J = 2.4$ Hz, 1H, Ar-H); 6.27 (dd, $J = 8.7, 2.7$ Hz, 1H, Ar-H); 6.93 (dt, $J = 7.8, 1.2$ Hz, 1H, Ar-H); 7.00 (d, $J = 8.1$ Hz, 1H, Ar-H); 7.12 (d, $J = 8.7$ Hz, 1H, Ar-H); 7.29–7.35 (m, 2H, Ar-H); 8.52 (s, 1H, Iminic-H); 8.60 (s, 1H, Iminic-H), 11.64 (s, 1H, $-\text{OH}$, exchangeable with D_2O), 11.66 (s, 1H, $-\text{OH}$, exchangeable with D_2O) ^{13}C NMR (75 MHz, CDCl_3) δ 12.55, 44.47, 97.80, 104.30, 106.38, 116.91, 117.99, 119.59, 131.91, 132.51, 133.95, 152.00, 159.50, 161.16, 161.97, 163.91; HRMS Calc. $[\text{M} + \text{H}]^+$ 312.16 found 311.38 (100% abundance).

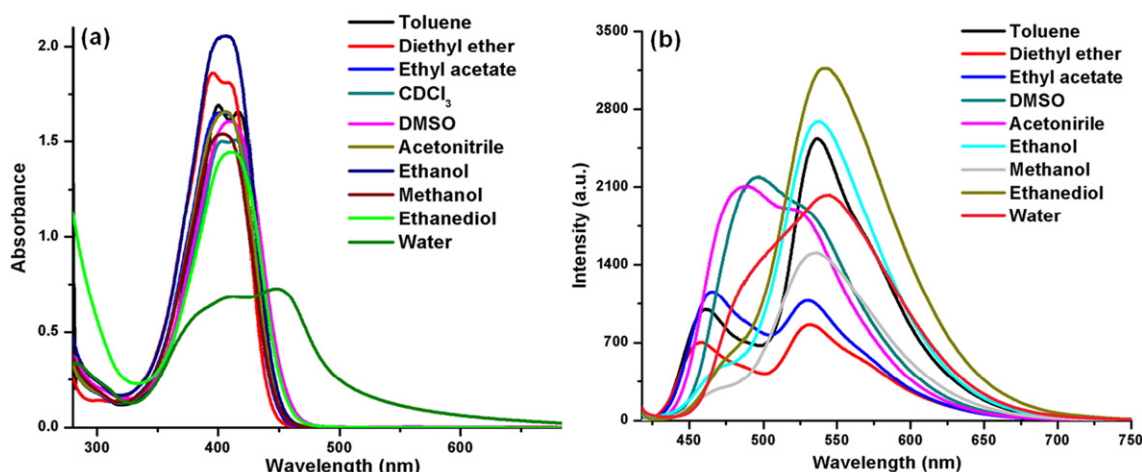


Fig. 1. Changes in UV-Vis spectra (a) and fluorescence spectra (b) of Schiff base 1 (30 μM) in different solvents with varying polarities and hydrogen bonding abilities.

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