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A novel optical sensor for copper ions based on phthalocyanine tetrasulfonic acid

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ABSTRACT

Phthalocyanine tetrasulfonic acid (PCTS) performed as a optical probe for selective detection of Cu^{2+} in DMSO solution over other metal ions used. The complexation behavior of chemodosimeter toward various metal ions has been studied via UV–vis absorption and fluorescence emission spectra. Induced changes were found to be observable from naked eye. The association constant (K_a) and low limit of detection were found to be 8.80×10^5 M^{-1} and 5.53×10^{-7} M, respectively. The optode showed excellent selectivity behavior in the environmental pH range.

1. Introduction

Copper is the third most plentiful transition element in living organisms, which naturally occurs in soil, rock, water, sediment and air [1]. This higher occurrence along with its distinct thermo-electric properties makes it very indispensable for different industries including alloy, machine parts, batteries, electric wires, fertilizers etc. Likewise it play a vital role in many biological processes such as regulation of metabolism, construction of connective tissues by fixing calcium in bones, protection from fungal and yeast infections. Furthermore, it is required to maintain the estrogen metabolism in women during fertility and pregnancy, production of cellular energy, etc. [2]. It is also very crucial in ferrous–ferric redox transformation and resultant heamoglobin synthesis. The availability of copper is found in many foods like as seafood, nuts, seeds, wheat bran cereals, grain products, organ meats and cocoa products. Copper is an active ingredient of many drugs particulary useful during copper deficiency. Copper based medication has been suggested during certain physical condition such as patients with intestinal bypass surgery, anemia, for improving wound healing, brittle bones (osteoporosis) and osteoarthritis [3–5]. On the other hand, its high concentration also is regarded potentially toxic, as it can cause of vomiting, diarrhea, stomach cramps, depression, anxiety, bipolar disorder, memory loss and Alzheimer disease (especially in young people), hypothyroidism and Hashimoto's disease, premenstrual syndrome, infertility, miscarriages, pelvic inflammatory disease, and fibrocystic breast disease [6–9].

Thus, there is a high-up demand for the development of highly selective, sensitive and facile method for the Cu^{2+} detection, in both physiological and non-physiological condition. Many techniques are previously applied for copper detection such as atomic absorption spectrometry [10], inductively coupled plasma mass spectroscopy (ICP-MS) [11], ion selective membrane electrode [12–16], voltammetry [17,18], but fluorescence has provided high selective, sensitive, low-cost and rapid implementation method for detection of metal ions in last decades [19–24]. Various fluorescent chemosensors for Cu^{2+} have been designed by using different fluorophores [25–36], which exhibited good selectivity and sensitivity toward copper ions but the utility of many of them is limited that are needed complex multistep synthesis procedure and higher interference with Ni^{2+}, Co^{2+}, and Fe^{3+} ions.

In this paper, we describe phthalocyanine tetrasulfonic acid as a colorimetric and fluorescent sensor. Here, copper metal ions are bonded with 4 N-site of PCTS via coordination bond, this effect was intensively studied by UV–vis absorption and fluorescent techniques. The quenching of fluorescence emission in DMSO solution is quite observable upon the addition of Cu(II) and a visible color

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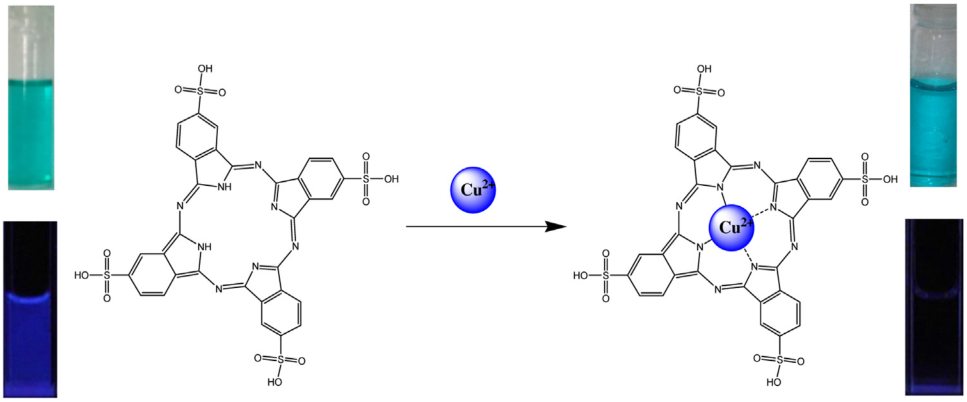

Fig. 1. Colorimetric and fluorescent effect with Cu(II).

change can be seen with naked eyes without the need for expensive equipment (Fig. 1). Accordingly to the results, the compound **PCTS** is highly selective and sensitive for detection of Cu(II) as a "turn-off" fluorescence and colorimetric sensor.

2. Experimental

2.1. Materials and instrumentation

Different metal salt aluminum (III) nitrate, silver (I) nitrate, copper (II) chloride, calcium (II) chloride, cobalt (II) chloride, iron (III) chloride, iron (II) chloride, cadmium (II) acetate, nickel (II) chloride, chromium (III) chloride, lead (II) acetate, mercury (II) nitrate, potassium (I) chloride, lithium (I) chloride, manganese (II) acetate, magnesium (II) chloride, gadolinium (III) chloride, zinc (II) acetate, uranyl (II) nitrate and neodymium (III) nitrate were purchased from Sigma–Aldrich and SD-Fine chemicals used without further purification.

The UV–vis absorbance spectra were recorded on Shimadzu UV-2450 spectrophotometer and fluorescence emission spectra collected on a Shimadzu RF-5301 PC spectrofluorophotometer (Japan) with excitation and emission slit width at 5.0 nm. Differential pulse voltammetry (DPV) was performed with a CHI760E electrochemical workstation (USA) model and all pH value measured with Eutech pH-510.

The stock solution for chemosensor **PCTS** (1.0×10^{-3} M) and different metal salt (1.0×10^{-2} M) of Ag^+, Al^{3+}, Ca^{2+}, Co^{2+}, Cr^{3+}, Cd^{2+}, Cu^{2+}, Fe^{2+}, Fe^{3+}, Gd^{3+}, Hg^{2+}, K^+, Li^+, Mg^{2+}, Mn^{2+}, $UO_2{}^{2+}$, Nd^{3+}, Ni^{2+}, Pb^{2+}, and Zn^{2+} were prepared in DMSO. pH adjustment was made with dil. HCl and NaOH.

3. Results and discussion

3.1. UV–vis studies of chemodosimeter with various metal ions

UV–vis absorption spectra of chemodosimeter (**PCTS**) were performed on the Shimadzu UV-2450 spectrophotometer in the presence of various metal ions Ag^+, Al^{3+}, Ca^{2+}, Cd^{2+}, Co^{2+}, Cr^{3+}, Cu^{2+}, Fe^{2+}, Fe^{3+}, Gd^{3+}, Hg^{2+}, K^+, Li^+, Mg^{2+}, Mn^{2+}, Nd^{3+}, Ni^{2+}, Pb^{2+}, $UO_2{}^{2+}$ and Zn^{2+} in DMSO solution. The chemodosimeter illustrated five absorption bands in the absorption spectrum (Fig. 2), a broad band at 340 nm, two weak bands at 613 nm and 638 nm, and two strong bands at 668 nm and 692 nm. The strongest absorption bands were assigned to the Q band, that can be attributed to the π–π^* allowed transition [37]. In the presence of various metal ions other than Cu^{2+} investigated, the absorption spectra remained unaffected, but surprisingly copper showed noticeable difference in the absorption band at 674 nm emerged toward higher intensity. Consequently, a significant color change from green to blue was apparent from bare eye (Fig. 3). Therefore, Copper ions could be easily identified among all other cations on the basis of color change. Furthermore, the interference of other metal ions was also investigated by competitive experiments, no changes were apparent on the addition of other metal ions. This result is an added evidence for the high selectivity of the Cu(II) ion sensing.

3.2. Fluorescence studies of chemodosimeter

The fluorescence studies of **PCTS** were investigated with excitation and emission slit width at 5.0 nm. As shown in result, when excited at 670 nm a broad emission band appear at λ_{max} 720 nm for phthalocyanine tetrasulfonic acid. After the addition of appropriate amount of different metals Ag^+, Al^{3+}, Ca^{2+}, Cd^{2+}, Co^{2+}, Cr^{3+}, Fe^{2+}, Fe^{3+}, Gd^{3+}, Hg^{2+}, K^+, Li^+, Mg^{2+}, Mn^{2+}, Nd^{3+}, Ni^{2+}, Pb^{2+}, $UO_2{}^{2+}$ and Zn^{2+} ions observed no any significant changes in fluorescence intensity but in case of Cu^{2+} ion emission band peak at 720 nm exhibited a quenching (Fig. 4). Furthermore, the sensitivity of **PCTS** was examined by the titration between **PCTS** and different concentration (0.0–3.0 equiv.) of copper ions at 720 nm (Fig. 5). As expected, the strong fluorescence emission intensity was gradually quenched in a linear manner ($R^2 = 0.992$) for copper ions, that indicate **PCTS** could be used for the quantitative determination of Cu^{2+} ions. Finally, limit of detection (LOD)

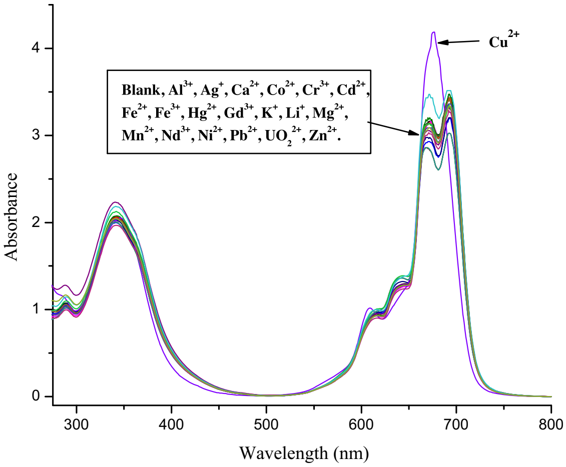

Fig. 2. UV–vis absorption spectra of chemodosimeter **PCTS** (25 μM) in the absence and presence of different metal ions (25 μM) in DMSO at 25 °C.