



# A new triazole appended rhodamine chemosensor for selective detection of Cu<sup>2+</sup> ions and live-cell imaging

Narendra Reddy Chereddy<sup>a</sup>, Sathiah Thennarasu<sup>a,\*</sup>, Asit Baran Mandal<sup>b,\*</sup>

<sup>a</sup> Organic Chemistry Division, CSIR-Central Leather Research Institute, Adyar, Chennai 600020, India

<sup>b</sup> Chemical Laboratory, CSIR-Central Leather Research Institute, Adyar, Chennai 600020, India

## ARTICLE INFO

### Article history:

Received 6 December 2011

Received in revised form 25 March 2012

Accepted 27 March 2012

Available online 15 June 2012

### Keywords:

Rhodamine chemosensors

Chelation of triazole

Cu<sup>2+</sup> selective

Naked eye detection

Live cell imaging

## ABSTRACT

The size of the chelating ligand and nature of coordinating entities of the chelating moiety have been exploited to synthesize four rhodamine based chemosensors for selective recognition of metal ions. A triazole appended colorless chemosensor turns to pink upon complex formation only with Cu<sup>2+</sup> ions even in the presence of other competing metal ions at physiological pH, and enables naked-eye detection and imaging of live fibroblast cells exposed to Cu<sup>2+</sup> ions.

© 2012 Elsevier B.V. All rights reserved.

## 1. Introduction

Research for the development of chemical devices that selectively detect analytes has been attaining importance in recent years. Chemosensors for the detection of transition metals are more valuable because of the increasing demand for the detection of toxic heavy metal ions. Copper plays a vital role in several areas such as biological, environmental, and chemical systems. It is an essential trace element for both plants and animals, including humans. Cu<sup>2+</sup> ions are utilized in several physiological responses, and copper containing proteins are useful as redox catalysts in biological processes that involve electron transfer reactions and oxidation of various organic substrates [1,2]. Even though it is an essential element, surplus concentration of copper causing damage to infant liver has been reported in recent years. Excess intake of copper leads to both Indian childhood cirrhosis (ICC) [3], and non-Indian childhood cirrhosis (NICC) [4]. Excess concentrations of Cu<sup>2+</sup> can also lead to Alzheimer's [5,6] or Parkinson's disease [7]. Therefore, new methods for the selective and rapid detection of Cu<sup>2+</sup> in physiological samples will be of use in monitoring toxicological and environmental samples [8–12]. Several methods like atomic absorption spectrometry [13–15], inductively coupled plasma mass spectroscopy (ICP-MS) [16,17], inductively coupled plasma atomic

emission spectrometry (ICP-AES) [18,19] and voltammetry [20–22] have been developed for the detection of copper ions at trace quantity levels. But, these methods require sophisticated equipments, tedious sample preparation procedures, and trained operators. Therefore, chemosensors that allow “naked eye” detection would have advantages over other methods in being easy to perform, portable, and not requiring sophisticated instrumentation. Since Cu<sup>2+</sup> is paramagnetic in nature, the binding of the metal ion causes a quenching of the fluorescence emission [23] that leads to a “turn-off” signal [24–35]. Turn-on fluorescent chemosensors are much more advantageous compared to turn-off chemosensors in terms of sensitivity. Hence, the interest in design and synthesis of fluorescent chemosensors with a Cu<sup>2+</sup> induced “turn-on” fluorescence signal is increasing in recent years [36–49]. However, lack of metal specific ligands limits the development of target specific chemosensors. Hence, steps for chemical modification and screening of the currently available ligands are essential to attain selectivity for target metal ion.

The rhodamine fluorochrome has attracted considerable interest from chemists because of its excellent photophysical properties [50]. Rhodamine derivatives with closed spirolactam ring are non-fluorescent and colorless, but under strongly acidic conditions, opening of the spirolactam ring results in intense fluorescence emission and development of pink color [51]. Recent developments on rhodamine based chemosensors have been reviewed [52–54]. Rhodamine based chemosensors reported in the literature for the detection of Cu<sup>2+</sup> ions contain at least one potential coordination site for the metal ion [55–57]. But, some of them suffer from either

\* Corresponding author. Tel.: +91 44 24913289; fax: +91 44 24911589.

E-mail addresses: [thennarasu@gmail.com](mailto:thennarasu@gmail.com) (S. Thennarasu), [abmandal@hotmail.com](mailto:abmandal@hotmail.com) (A.B. Mandal).

poor sensitivity or cross reactivity towards other competitive metal ions, or longer response times [37,38,58]. Recently, a rhodamine triazole based fluorescent probe has been reported for the selective detection of  $\text{Pt}^{2+}$  ions in aqueous samples [59].

In the present study, we have explored the role of substituents in the chelating moiety and chelating ligand size on metal ion selectivity. We report the synthesis of a triazole appended  $\text{Cu}^{2+}$  specific chemosensor that displays excellent selectivity toward  $\text{Cu}^{2+}$  ions and stability at physiological pH. A possible application in the imaging of live fibroblast cells exposed to  $\text{Cu}^{2+}$  ions is also demonstrated.

## 2. Experimental

### 2.1. General

Dry acetonitrile and double distilled water were used in all experiments. All the materials for synthesis were purchased from commercial suppliers and used without further purification. The solutions of metal ions were prepared from the corresponding chloride salts. Absorption spectra were recorded on a Cary 50 Bio UV–visible spectrophotometer. Fluorescence measurements were performed on a Cary Eclipse fluorescence spectrophotometer. All pH measurements were made with a Systronics  $\mu\text{pH}$  System Model 361. NMR spectra were recorded using a JEOL-ECP500 MHz spectrometer operated at 500 MHz. ESI MS spectra were obtained on a

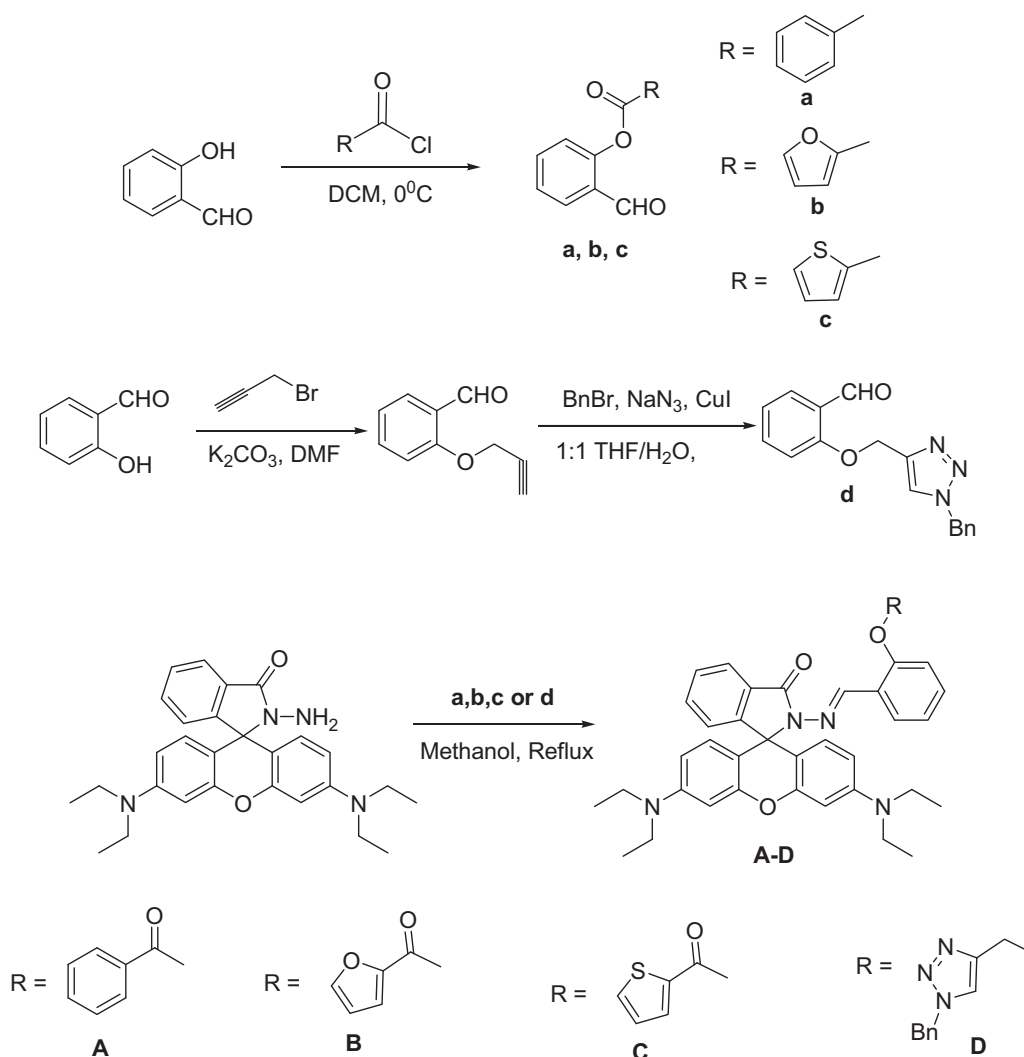
PE Sciex API3000 Mass Spectrometer. Fluorescence imaging experiments were performed using a Leica DM IRB microscope equipped with EBQ-100 UV-lamp. All measurements were carried out at room temperature ( $\sim 298\text{ K}$ ).

### 2.2. Synthesis of formylaryl esters (a, b, c)

Three formylaryl esters were synthesized as described below. Salicylaldehyde (0.61 g, 5 mmol) was dissolved in 20 mL DCM, and mixed with triethylamine (0.84 mL, 6 mmol). The resulting mixture was allowed to stir at ice-cold condition. Appropriate acid chloride (6 mmol) dissolved in 20 mL DCM, was added dropwise to this mixture and allowed to stir at room temp overnight. The solvent was evaporated under reduced pressure and the resulting mixture was subjected to column chromatography (silica gel 200 mesh) to get the desired compound in pure form. Yield (**a**, 0.90 g, 80%; **b**, 0.92 g, 85%; **c**, 0.93 g, 80%).

### 2.3. Synthesis of formylaryl triazole derivative d

Formylaryl triazole derivative was synthesized in a two-step procedure. To a solution of salicylaldehyde (0.61 g, 5 mmol) in DMF (20 mL) was added potassium carbonate (1.04 g, 7.5 mmol) and the solution was stirred at room temperature. Propargyl bromide (0.7 mL, 7.5 mmol) was added dropwise and the resulting mixture



**Scheme 1.** Scheme for the synthesis of chemosensors A–D.

Download English Version:

<https://daneshyari.com/en/article/745470>

Download Persian Version:

<https://daneshyari.com/article/745470>

[Daneshyari.com](https://daneshyari.com)