



# A highly selective quinaldine–indole based spiropyran with intramolecular H-bonding for visual detection of Cu(II) ions

Haribhau S. Kumbhar, Balu L. Gadilohar, Ganapati S. Shankarling\*

Dyestuff Technology Department, Institute of Chemical Technology, Matunga, Mumbai 400 019, India

## ARTICLE INFO

### Article history:

Received 30 December 2014

Received in revised form 5 August 2015

Accepted 7 August 2015

Available online 10 August 2015

### Keywords:

Spiropyran  
Copper ion  
Chemosensor  
Visual detection

## ABSTRACT

A novel quinaldine–indole based spiropyran (**QSP**) with stabilized merocyanine form has been developed for colorimetric detection of Cu<sup>2+</sup> ions. Chemosensor **QSP** shows high sensitivity and selectivity for Cu<sup>2+</sup> ions amongst other metal ions (Na<sup>+</sup>, Mg<sup>2+</sup>, K<sup>+</sup>, Ca<sup>2+</sup>, Al<sup>3+</sup>, Co<sup>2+</sup>, Ni<sup>2+</sup>, Zn<sup>2+</sup>, Cd<sup>2+</sup>, Ba<sup>2+</sup>, La<sup>3+</sup>, Hg<sup>2+</sup>, Pb<sup>2+</sup>). The stoichiometry of QSP–Cu<sup>2+</sup> complex determined by Jobs plot was found to be 1:1. The association constant for QSP–Cu<sup>2+</sup> complex determined from Benesi–Hildbrand plot was  $1.9 \times 10^5 \text{ M}^{-1}$  with a limit of detection  $6.3 \times 10^{-7} \text{ M}$ . Applicability of **QSP** to detect Cu<sup>2+</sup> ions in tap water has been demonstrated, thus indicating the potential use of **QSP** as viable probe for visual detection of Cu<sup>2+</sup> ions.

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## 1. Introduction

Spiroyrans are well-known for their photo and thermochromic properties and are applied for hi-tech applications such as data recording and storage, optical switching, displays and nonlinear optics [1,2]. The cyclic spiropyran absorbs in the UV region, whereas the open merocyanine absorbs in the visible region. The open merocyanine form absorption in visible region is found to be sensitive towards solvents of different polarity, dielectric constant and refractive indices, that indicate a zwitterionic structure [3]. The reversible spiropyran isomerization is stimulated by different solvents, metal ions, acids and bases, temperature, redox potential, and mechanical force [2,4]. Spiropyran provides synthetic feasibility for structural variation and task-oriented tuned properties which deals with the various application [5,6]. The interaction in open merocyanine form of spiropyran is feasible because of naphthalonate oxygen atom [7], however additional binding site leads to much more stabilized merocyanine form [8] and helps in quantitative and qualitative detection of metal ions. Spiropyran and its various derivatives have been reported for sensing of several metal ions such as Zn<sup>2+</sup>, Cd<sup>2+</sup>, Al<sup>3+</sup>, Fe<sup>3+</sup>, Ca<sup>2+</sup>, Cu<sup>2+</sup>, Tb<sup>3+</sup>, Eu<sup>3+</sup>, Sm<sup>3+</sup> and Pb<sup>2+</sup> ions [8].

The detection of Cu<sup>2+</sup> is studied thoroughly since Cu<sup>2+</sup> ions serve as essential micronutrient for many of biological systems as co-component of the metalloenzymes [9], but the excess of

the Cu<sup>2+</sup> ions causes, neurodegenerative diseases, such as Menkes, Wilson [10,11] Alzheimer's and Parkinson's [12], also excess Cu<sup>2+</sup> ions generates reactive oxygen species (ROS) which disturbs cellular metabolism [13,14]. Several analytical methods [15–17] and probes [18–20] have been developed to detect selectively Cu<sup>2+</sup> ions, although these method mostly requires the use of sophisticated instruments and can't be applied in environmental medium or on site analysis. Hence, researchers have focused toward the development of organic optical probes for easy detection of Cu<sup>2+</sup> ions colorimetrically [21,22] and fluorimetrically [23].

In present work we have designed and synthesized quinaldine–indole based spiropyran (**QSP**) colorimetric sensor for the detection of Cu<sup>2+</sup> ions. The **QSP** shows stabilization of merocyanine form through intramolecular hydrogen bonding between the naphthalonate of spiro with the adjacent carboxylate group and serve as the binding site for Cu<sup>2+</sup> ions. **QSP** showed naked eye detection in the micro-molar range.

## 2. Experimental

### 2.1. Materials and methods

All chemicals and reagents of analytical grade were procured from SD Fine Chemical Ltd and some from Finar Ltd. (Mumbai, India) and were used without further purification. Nuclear magnetic resonance spectra were recorded on Bruker 400 and 500 MHz instrument with TMS as an internal standard. ESI-MS analysis was performed on Varian mass spectrometer. UV–visible spectra were

\* Corresponding author. Tel.: +91 2233612708; fax: +91 22 33611020.  
E-mail address: [gsshankarling@gmail.com](mailto:gsshankarling@gmail.com) (G.S. Shankarling).

recorded on with a Perkin-Elmer Lamda-25 spectrophotometer at room temperature.

## 2.2. Synthesis

The 8-hydrazinyl-2-methylquinoline (**2**) was synthesized according to previously reported method [24] in two steps by carrying out diazotization of the 8-amino-2-methyl quinoline followed by reduction by using  $\text{SnCl}_2/\text{HCl}$ .

## 2.3. Synthesis of 2,3,3,8-tetramethyl-3H-pyrrolo[3,2-h]quinoline (**4**)

In 5 ml of 4 M aq. HCl 8-hydrazinyl-2-methylquinoline **2** (0.173 g, 100 mmol) and 3-methylbutan-2-one **3** (0.103 g, 120 mmol) was added. The reaction mass was heated for next 5 h. After 5 h cool the reaction mass to room temperature, extract with 10 ml diethyl ether. Further aqueous layer was neutralized with 1 M aq. NaOH and extracted with ethyl acetate, organic layer was separated. Dried over sodium sulphate and solvent was evaporated under reduced pressure. Crude product was then purified by column chromatography to get pale yellow solid (Yield 55%). (*m.p.* 140–142 °C)  $^1\text{H}$  NMR (400 MHz,  $\text{CDCl}_3$ )  $\delta$  8.03 (d,  $J=8.5$  Hz, 1H), 7.62 (d,  $J=8.1$  Hz, 1H), 7.42 (d,  $J=8.1$  Hz, 1H), 7.25 (d,  $J=8.5$  Hz, 1H), 2.83 (s, 3H), 2.41 (s, 3H), 1.35 (s, 6H).  $^{13}\text{C}$  NMR (101 MHz,  $\text{CDCl}_3$ )  $\delta$  188.74, 159.67, 148.68, 146.07, 140.75, 136.10, 126.70, 125.00, 121.66, 119.06, 54.95, 25.63, 22.51, 15.49.

## 2.4. Synthesis of

### 1,2,3,3,8-pentamethyl-3H-pyrrolo[3,2-h]quinolin-1-ium iodide (**5**)

In 5 ml of dichloromethane, 2,3,3,8-tetramethyl-3H-pyrrolo[3,2-h]quinoline **4** (0.224 g, 100 mmol) was dissolved and then methyl iodide (0.288 g, 200 mmol) was added slowly under stirring. The reaction mass was heated to reflux for next 10 h. The reaction mass was then cooled to room temperature and the solvent was evaporated under vacuum. The crude product obtained was recrystallized from methanol to give purified product **5**. Yield: 54%, *m.p.* 258–260 °C,  $^1\text{H}$  NMR (400 MHz, DMSO)  $\delta$  8.51 (d,  $J=8.6$  Hz, 1H), 8.23 (d,  $J=8.3$  Hz, 1H), 8.01 (d,  $J=8.2$  Hz, 1H), 7.65 (d,  $J=8.5$  Hz, 1H), 4.69 (s, 3H), 2.85 (s, 3H), 2.79 (s, 3H), 1.62 (s, 6H).  $^{13}\text{C}$  NMR (101 MHz, DMSO)  $\delta$  196.50, 160.48, 144.66, 137.55, 137.41, 134.51, 130.17, 127.01, 122.97, 119.83, 54.23, 25.25, 21.14, 14.24. Mass (EI):  $\text{C}_{16}\text{H}_{19}\text{N}_2$  calculated 239.33( $\text{M}^+$ ), found 241.3 ( $\text{M}+2$ ).

## 2.5. Synthesis of quinaldine spiropyran (**QSP**)

1,2,3,3,8-Pentamethyl-3H-pyrrolo[3,2-h]quinolin-1-ium iodide **5** (0.366 mg, 100 mmol), 4-formyl-3-hydroxy-2-naphthoic acid **6** (0.216 mg, 100 mmol), and triethylamine (0.250 ml, 200 mmol) were added to the 5 ml of the ethanol. Reaction mass was refluxed for next 5 h. After 5 h reaction mass was cooled to room temperature and filtered to get the solid, which was recrystallized from ethanol to obtain green colored solid (Yield 43%, *m.p.* 258–260 °C).  $^1\text{H}$  NMR (500 MHz,  $\text{CDCl}_3$ )  $\delta$  17.60 (s, 1H), 8.93 (d,  $J=14.4$  Hz, 1H), 8.80 (s, 1H), 8.69 (d,  $J=14.5$  Hz, 1H), 8.14 (d,  $J=8.5$  Hz, 1H), 7.92 (d,  $J=8.3$  Hz, 2H), 7.80–7.71 (m, 1H), 7.59 (t,  $J=7.0$  Hz, 1H), 7.56 (d,  $J=8.2$  Hz, 1H), 7.39 (d,  $J=8.5$  Hz, 1H), 7.32 (t,  $J=7.5$  Hz, 1H), 4.73 (s, 3H), 2.80 (s, 3H), 1.91 (s, 6H). Mass (EI):  $\text{C}_{28}\text{H}_{24}\text{N}_2\text{O}_3$  calculated 436.18 ( $\text{M}^+$ ), found 437.13 ( $\text{M}+1$ ).

## 2.6. UV-visible experiments

UV-visible spectra were recorded on a Perkin Elmer Lamda-25 UV-visible spectrophotometer using freshly prepared solutions.

The absorption spectra were recorded using quartz cell of 1 cm path length. All the experimental parameters were kept constant throughout, in order to have precision and accuracy. Stock solutions of the cations ( $2 \times 10^{-3}$  M) and chemosensor **QSP** ( $2 \times 10^{-5}$  M) were prepared in methanol/water (9:1, v/v) solutions. Titration experiment was carried out by taking fixed concentration of **QSP** directly into the cuvette by adding incremental amount of cations ( $\text{Cu}^{2+} = 2 \times 10^{-3}$  M) with the help of micropipette. The changes in absorbance at 518 and 585 nm were plotted against  $\text{Cu}^{2+}$  ion concentration. Job's plot was plotted using equimolar concentration of **QSP** and  $\text{Cu}^{2+}$  ion by keeping total concentration of **QSP** and  $[\text{Cu}^{2+}]$  was kept constant.

## 2.7. Detection of $\text{Cu}^{2+}$ ions in tap water

Laboratory tap water analysis was also done by spiking method. The tap water sample were spiked with 10 and 20  $\mu\text{M}$  of  $\text{Cu}^{2+}$  ion, and analyzed by proposed method.

## 3. Result and discussion

### 3.1. Synthesis of **QSP**

The **QSP** was synthesized by simple approach shown in Scheme 1. The synthesis of **QSP** starts from 8-aminoquinaldine to get quaternized quinaldine-indole (**5**) in three successive steps, diazotization followed by reduction to get 8-hydrazinoquinaldine and cyclization to get compound (**4**). Further condensation with 4-formyl-3-hydroxy-2-naphthoic acid to get desire chemosensor **QSP**.

### 3.2. Absorption properties

The absorption spectra of the **QSP** exhibits an absorption peak at 518 nm with extinction coefficient ( $\epsilon$ )  $2.8 \times 10^4 \text{ M}^{-1} \text{ cm}^{-1}$  for open merocyanine form which attributes intramolecular charge transfer (ICT), while at 249 nm for the cyclic spiro form. The strong absorption band at 500–600 nm with high extinction coefficient is due to the hydrogen bonding with adjacent carboxylate group results in stabilization of merocyanine form of **QSP** (Scheme 2). This stabilized merocyanine form of **QSP** offers the binding or chelation sites for the metal ions. The conversion of spiropyran in to merocyanine was used for metal ion sensing and for that the spiropyran necessarily should be in thermo-/photostable merocyanine from [2]. Moreover **QSP** does not shows photochemical isomerization upon UV irradiation. This is may be due to intramolecular hydrogen bonding stabilization of open merocyanine form, which does not allow reversible cyclization (Fig. S1).

Sensing property and selectivity of **QSP** toward metal ions was investigated in methanol:water (9:1) system with various metal chlorides salts of  $\text{Na}^+$ ,  $\text{Mg}^{2+}$ ,  $\text{K}^+$ ,  $\text{Ca}^{2+}$ ,  $\text{Al}^{3+}$ ,  $\text{Co}^{2+}$ ,  $\text{Ni}^{2+}$ ,  $\text{Cu}^{2+}$ ,  $\text{Zn}^{2+}$ ,  $\text{Cd}^{2+}$ ,  $\text{Ba}^{2+}$ ,  $\text{La}^{3+}$ ,  $\text{Hg}^{2+}$ ,  $\text{Pb}^{2+}$  (10 equiv.). In presence of  $\text{Cu}^{2+}$  ions, chemosensor **QSP** displayed distinct change in absorption spectra. The absorption maxima of **QSP** shifted from 518 nm to 585 nm on chelation with  $\text{Cu}^{2+}$  ions. The chemosensor **QSP** displayed visual color change from purple to cyan on addition of  $\text{Cu}^{2+}$  ions, which is very well depicted in Fig. 1. The hydrogen bonding in open merocyanine form offers two partially negatively charged oxygen while a nitrogen from quinoline part act as chelating center owing to which a remarkable bathochromic shift is observed for  $\text{Cu}^{2+}$  ions.

The selectivity and sensitivity of **QSP** toward  $\text{Cu}^{2+}$  ions was tested competitively. The selectivity of **QSP** for  $\text{Cu}^{2+}$  ions remains unchanged in presence of other metal ions. Figs. 2 and 3 illustrate no significance interference, which establishes the selectivity of **QSP** for  $\text{Cu}^{2+}$  ions amongst the other metal ions. The effect of counter

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