Sensors and Actuators B 202 (2014) 779–787

Contents lists available at ScienceDirect

Sensors and Actuators B: Chemical

journal homepage: www.elsevier.com/locate/snb

# Synthesis of novel squaraine–bis(rhodamine-6G): A fluorescent chemosensor for the selective detection of $Hg^{2+}$

Hee-Soo So[a,1], Boddu Ananda Rao[a,1], Jiyong Hwang[a], Kada Yesudas[b], Young-A Son[a,*]

[a] Department of Advanced Organic Materials Engineering, Chungnam National University, Daejeon 305-764, Republic of Korea
[b] Department of Engineering Chemistry, GITAM University, Bangalore, Karnataka 561 203, India

ARTICLE INFO

*Article history:*
Received 30 April 2014
Received in revised form 31 May 2014
Accepted 4 June 2014
Available online 12 June 2014

*Keywords:*
Rhodamine
Squaraine
Mercury sensing
Fluorescent chemosensor
Molecular modeling
DFT studies

ABSTRACT

We report the design and synthesis of a novel squaraine–bis(rhodamine-6G) (SR)-based indicator for selective detection of $Hg^{2+}$ ion. Sensing behavior toward various metal ions (M = $Li^+$, $Na^+$, $Mg^{2+}$, $K^+$, $Fe^{3+}$, $Co^{2+}$, $Ni^{2+}$, $Cu^{2+}$, $Zn^{2+}$, $Ag^+$, $Cs^+$, $Hg^{2+}$, and $Pb^{2+}$) was investigated by UV–vis and fluorescence spectroscopy in acetonitrile solution. The indicator exhibited highly selective and sensitive colorimetric and "turn-on" fluorescent responses compared with the other investigated metal ions because of the soft-acid nature and large size of mercuric ion. The obvious change from colorless to pink upon the addition of $Hg^{2+}$ could make it a suitable "naked eye" indicator for $Hg^{2+}$. Finally, we proposed a reversible ring-opening mechanism (OFF–ON) of the rhodamine spirolactam induced by $Hg^{2+}$ binding and forming a 1:1 stoichiometric complex of SR–$Hg^{2+}$ which is supported by the density functional theory calculations. More significantly, the sensor displayed a remarkable blue-to-green fluorescence switch in the presence of $Hg^{2+}$ ions.

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## 1. Introduction

Mercury and most of its compounds are extremely toxic and thus very harmful to the human body and to the environment. The most toxic forms of mercury are its organic derivatives, such as dimethylmercury and methylmercury, which can easily enter the food chain and accumulate in high concentrations. These forms of mercury have been found to cause certain types of irreversible neurological damage [1]. The toxic nature of $Hg^{2+}$ ions causes severe health problems, such as central nervous system defects, pyrexy, and kidney damage [2,3]. Therefore, a convenient and rapid method for the analysis of $Hg^{2+}$ ions is highly desirable. Recently, numerous methods have been reported for the detection of these ions [4,5]. Toward this end, substantial advancements in spectroscopic sensing molecules for $Hg^{2+}$ ions have been reported [6]. In this respect, the use of fluorosensors provides distinct advantages in terms of sensitivity and response time [7]. Various fluorescence-based sensors have been recently described, including squaraines [8,9], fluorescein [10,11], rhodamine [12–14], quinolines [15–17], cholatefoldamers [18,19], calixarenes [20,21], porphyrins [22,23], oligonucleotides [24,25] and coumarin [26,27]. Among these sensors, a number of rhodamine (RH) [28–33] and squaraine (SQ)-based [34–42] chemosensors have been reported for the detection of $Hg^{2+}$ ions and have shown high sensitivity and selectivity. RH and fluorescein derivatives have been used as platforms for the construction of fluorescent probes because of their advantageous photophysical properties and the unique transformation of the non-fluorescent spirocyclic form to the fluorescent open-ring form upon coordination to $Hg^{2+}$ ion [3,43–46].

SQs are a class of organic dyes that exhibit substantial bond delocalization and possess resonance-stabilized zwitterionic structures. SQs also exhibit unique optical properties, such as intense light absorption and deeply colored, and efficient fluorescence emission in the visible-to-NIR region [47,48]. Thus, SQs have garnered considerable interest because of their tremendous photophysical properties and moderately efficient fluorescence emission, which make them highly suitable for a wide range of applications [49–51]. SQs are suitable for use in chemosensors because of their interesting optical properties, which can be perturbed by external factors such as change in polarity, temperature, pH of the medium or the addition of additives. Consequently, the mono-substituted RH derivative of SQ (aromatic squaric amide esters) has been synthesized and briefly described for the preparation of fluorescent moenomycin derivatives. SQ-RH possesses four potential binding sites: two from the oxygen atoms at the electron-deficient cyclobutene ring and two from the oxygen atoms of the spirolactam ring of the RH moieties. The coordination of these atoms with

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[*] Corresponding author. Tel.: +82 42 821 6620; fax: +82 42 821 8870.
*E-mail address:* yason@cnu.ac.kr (Y.-A. Son).
[1] These authors made equal contributions to this work.

http://dx.doi.org/10.1016/j.snb.2014.06.013
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metal ions can result in color modulation of the dyes, i.e., changes in their absorption spectra. For example, SQ consecutively binds to two protons or metal ions, causing a hypsochromic shift of the peak and then complete bleaching, respectively. This result has been reasonably inferred to indicate sequential coordination at the amide oxygen atoms [52].

In our previous study, we reported the synthesis and binding properties of a SQ [53] and iminium salt [54] chemosensors, which exhibited a high selectivity for cyanide anion. Very recently, we reported the cation sensing properties of our SQ chemosensor, which showed a selective change in absorption in the presence of mercury cations through "turn on" fluorescence intensity and a visual color change [55,56]. To the best of our knowledge, this sensor is one of the few SQ-based "turn on" fluorescent sensors [41,57,58], and the current work represents the first report on the use of a squaraine–rhodamine (SR) dye as a probe for the detection of mercury metal ion.

## 2. Experimental

### 2.1. Chemicals, materials and instruments

All the reagents and solvents, used for synthesis of SR, were purchased from Aldrich (St. Louis, USA) and used without further purification. Rhodamine 6G and squaric acid were purchased from the Sigma–Aldrich Company. Various metal ion solutions of $Hg(ClO_4)_2{\cdot}XH_2O$, $KClO_4$, $Mg(ClO_4)_2$, $Ni(ClO_4)_2{\cdot}6H_2O$, $Cu(ClO_4)_2{\cdot}6H_2O$, $AgClO_4$, $NaClO_4$, $Al(ClO_4)_3{\cdot}9H_2O$, $CsClO_4$, $Ca(ClO_4)_2{\cdot}XH_2O$, $LiClO_4$ and $Fe(ClO_4)_2{\cdot}XH_2O$ were purchased from Sigma–Aldrich, and $Zn(ClO_4)_2{\cdot}6H_2O$, $Pb(ClO_4)_2{\cdot}3H_2O$ and $Co(ClO_4)_2{\cdot}6H_2O$ were purchased from Alfa-Aesar Chemical Reagent Co. N-(rhodamine-6G) lactam-ethylenediamine (**1**) (m.p. 251–252 °C) was prepared by the reported procedures [59]. The IR spectra were recorded on a FTS-175C (Bio-laboratories, Cambridge, USA) infrared spectrometer. The electronic absorption spectra were recorded on an Agilent 8453 spectrophotometer. The fluorescence spectra were recorded on a Shimadzu RF-5301PC fluorescent spectrophotometer. $^1H$ NMR and $^{13}C$ NMR spectra were recorded on a JNM-AL400 spectrometer and AVANCE III 600 spectrometer operated at 600 MHz respectively. Mass spectra were recorded on a JEOL MStation [JMS-DX303]. High-resolution mass spectra (HRMS) were recorded on micrOTOF-QII-Model (Bruker Daltonik, Germany) mass spectrometers. All the melting points are uncorrected and were determined on a Barnstead electrothermal (UK) melting point apparatus. The quantum chemical calculations have been performed with Gaussian 09 program [60].

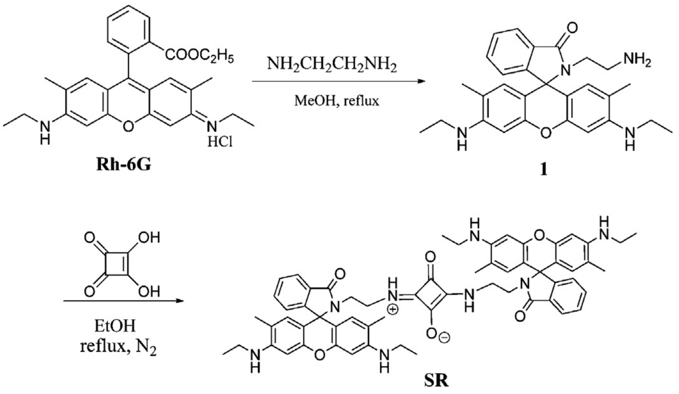
### 2.2. Preparation of the stock solutions

A 1000 μM solution of compound probe SR (49.5 mg, $4.9 \times 10^{-5}$ mol) was prepared in fresh $CH_3CN$ (50 mL) by diluting the concentrated stock solution to the required concentration. Metal ions were prepared by dissolving the salts in $CH_3CN$ to get the final concentrations of 100 μM. For the final concentration of the SR and metal ionic solutions, the mixtures were further diluted to 10 μM, $CH_3CN$ (8 mL), 1 mL (100 μM) SR and 1 mL (100 μM) metal ion. The $Hg^{2+}$ ion stock solution was prepared by dissolving $Hg(ClO_4)_2{\cdot}nH_2O$ to obtain a final concentration of 10 μM.

### 2.3. Synthetic procedures

#### 2.3.1. Synthesis of N-(rhodamine-6G)lactam-ethylenediamine (1)

Rhodamine 6G (958 mg, 2 mmol) was dissolved in 20 mL of hot ethanol, followed by addition of ethylenediamine (0.67 mL, 10 mmol). The reaction was refluxed for 6 h till the fluorescence of the solution was disappeared. The reaction was cooled to room temperature, and the precipitate was collected and washed with 10 mL of cold ethanol. Crude product was purified by recrystallization from acetonitrile yielded 721 mg of N-(rhodamine-6G) lactam-ethylenediamine as 75.3%. m.p.: 251–252 °C; $^1H$ NMR (600 MHz, $CDCl_3$): δ 1.31 (t, $J$ = 6.9 Hz, 6H), 1.89 (s, 6H), 2.04 (br, S, 2H), 2.41 (d, $J$ = 6.0 Hz, 2H), 3.16 (br, S, 2H), 3.20–3.21 (m, 4H), 3.51 (d, $J$ = 6.02 Hz, 2H), 6.14 (s, 2H), 6.33 (s, 2H), 7.05 (d, $J$ = 6.4 Hz, 1H), 7.45 (br, t, 2H), 7.91 (d, $J$ = 6.4 Hz, 1H); $^{13}C$ NMR (150 MHz, $CDCl_3$): δ 14.7, 16.7, 38.3, 40.7, 43.7, 65.1, 96.5, 106.0, 118.0, 122.8, 123.8, 128.0, 128.3, 131.1, 132.5, 147.4, 151.7, 153.5, 168.7; FAB-MS: calcd for $C_{28}H_{32}N_4O_2$ $m/z$ 456.58; found $m/z$ 457.



**Scheme 1.** Synthesis of the squaraine–rhodamine (SR) dye.

#### 2.3.2. Synthesis of squaraine–rhodamine (SR) dye

2.0 mmol (228 mg) of squaric acid dissolved in 10 mL of hot ethanol and to this solution 4.0 mmol (1.826 g) of **1** was added at 60 °C. The reaction mixture was refluxed for 5 h. The precipitate was filtered and washed with 10 mL of hot ethanol (4–5 times). Crude product was purified by soxhlet process extracting by methanol (100 mL × 4) solvent. The yield was (127 mg) 55.92%. m.p.: 220.5–222 °C; IR (KBr): $\nu_{max}$ 3433, 2967, 2930, 2873, 1688, 1619, 1579, 1514, 1421, 1371, 1269, 1215, 1133, 1013, 810, 746, 691 and 615 $cm^{-1}$; $^1H$ NMR (400 MHz, $CDCl_3$): δ 1.33 (br, t, 12H), 1.90 (s, 12H), 3.21–322 (m, 8H), 3.31–3.32 (br, s, 4H), 3.50 (br, s, 8H), 6.20 (s, 4H), 6.35 (s, 4H), 6.87 (br, s, 1H), 6.96 (br, s, 1H), 7.06 (br, s, 2H), 7.49 (br, s, 4H), 7.93 (s, 2H); $^{13}C$ NMR (150 MHz, $CDCl_3$): δ 14.7, 16.7, 29.7, 38.4, 44.6, 65.6, 96.6, 105.1, 105.2, 118.5, 123.0, 123.9, 127.8, 128.3, 130.5, 132.8, 147.7, 151.6, 153.5, 168.6, 169.4, 178.3; FAB-MS: calcd for $C_{60}H_{62}N_8O_6$ $m/z$ 991.18; found $m/z$ 991; HRMS (ESI) calcd for $C_{60}H_{62}N_8O_6$ ($[M+1]^+$): 991.18, found: 991.4864.

## 3. Results and discussion

### 3.1. Spectroscopic measurements

As shown in Scheme 1, the reaction of *N*-(rhodamine-6G) lactam-ethylenediamine (**1**) with squaric acid in ethanol solvent gave the disubstituted SR dye in quantitative yields. The structure of the SR was characterized by $^1H$ NMR, $^{13}C$ NMR, FAB-MS, FT-IR and HRMS (S1–S8, Supporting Information). To investigate the ability of SR to serve as a tridentate or tetradentate ligand and its potential use as a probe, we studied its interactions with various metal ions under different conditions. Neither the color nor the absorption and emission spectra of a solution of SR in acetonitrile changed upon the addition of various metal ions, M = $Li^+$, $Na^+$, $Mg^{2+}$, $K^+$, $Fe^{3+}$, $Co^{2+}$, $Ni^{2+}$, $Cu^{2+}$, $Zn^{2+}$, $Ag^+$, $Cs^+$, and $Pb^{2+}$ (perchlorate salts), to the solution, whereas a dramatic color change from colorless to pink was observed upon the addition of $Hg^{2+}$ ions (photographic images and fluorescence under a UV lamp at 365 nm are shown in Fig. S9, Supporting Information). The selectivity experiments for SR were

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