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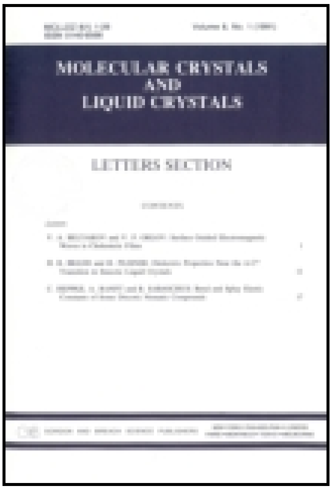

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A Highly Selective Rhodamine Based Colorimetric Sensor Toward Cu^{2+}

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A probe for recognition of Cu^{2+} was developed based on rhodamine B. The probe was synthesized by condensation between rhodamine B and quinoline-2-carbaldehyde. The probe exhibits highly selectivity toward Cu^{2+} detection. It binds Cu^{2+} in a 1:1 stoichiometry in acetonitrile solution. Distinct color change can be observed upon the addition of Cu^{2+} and little interference with other biologically relevant metal ions. Only Fe^{3+} addition shows a little disturbance in absorption enhancement. In addition, the limit of detection toward Cu^{2+} is about 235 times lower than the World Health Organization (WHO) recommended level in drinking water.

Keywords rhodamine B; Cu^{2+}; highly selectivity; detection limit

Introduction

The framework of rhodamine is an ideal model for the construction of chelating, which may increase/decrease the emission intensity or reversibly shift the emission wavelength with "on-off" or "off-on" switch model [1, 2]. In recent years, rhodamine has been attracted a great deal of attention due to its excellent properties, such as good photostability, high extinction coefficients, high fluorescence quantum yields, and longer-wavelength absorptions and emissions [3–7]. Rhodamine spirolactam or spirolactone derivatives are nonfluorescent and colorless, whereas ring-opening of the corresponding spirolactam/lactone gives rise to strong fluorescence emission and a pink color. Based on the distinguished difference in color and electronic spectra, most of rhodamine sensors were deigned according to this ring-open and ring-close reaction [8–10]. In general, attaching appropriate ligand on a spirolactam ring can induce a color change as well as a fluorescence change upon addition

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of metal ions, even though this process is somewhat dependent on the solvent system. Therefore, a rapidly developments of fluorescent chemo-sensors for heavy and transition metals (**HTM**) cations have been opened up and many rhodamine derivatives have been actively synthesized and utilized as the fluorescent or colorimetric chemodosimeters for detection of **HTM** cations [11], such as Fe^{3+} [12, 13], Cu^{2+} [14, 15], Hg^{2+} [16, 17], Cr^{3+} [17], Pb^{2+} [18], Pt^{2+} [19].

A larger number of publications about rhodamine based chemosensors have been well documented in recent decades. Herein, a new rhodamine B-based derivative being condensed between rhodamine B and quinoline-2-carbaldehyde was developed, which exhibited higher selectivity toward Cu^{2+} over other metal cations in CH_3CN solutions.

Experimental

General Procedures and Materials

All the solvents used in the reaction were carefully dried according to the standard procedure and stored over 4Å molecular sieve. All the reagent-grade chemicals were purchased from Sigma-Aldrich CO. LLC. (South Korea) and used without further purification. Melting points were determined on a Mel-Temp® IA9200 digital melting point apparatus in a glass capillary and were uncorrected. All the synthesized compounds were routinely characterized by TLC and ^{1}H NMR. TLC was performed on aluminum-backed silica gel plates (Merck DC. Alufolien Kieselgel 60 F254).

^{1}H and ^{13}C NMR Spectroscopy

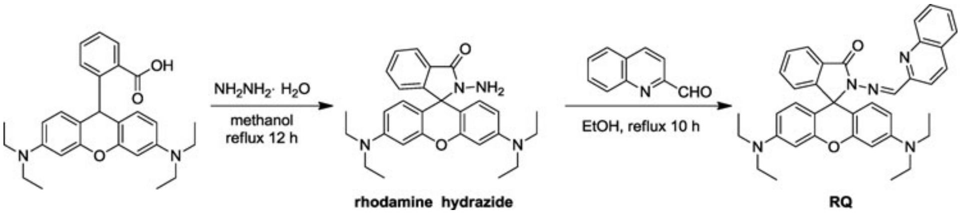
^{1}H and ^{13}C nuclear magnetic resonance (NMR) spectra were recorded on a Brucker AM-400 spectrometer operating at frequencies of 400 MHz for proton 100 MHz for carbon in DMSO-d_6. Proton chemical shifts (δ) are relative to tetramethylsilane (TMS, $\delta = 0$) as internal standard and expressed in parts per million. Spin multiplicities are given as *s* (singlet), *d* (doublet), *t* (triplet), and *m* (multiplet) as well as *b* (broad). Coupling constants (*J*) are given in Hertz.

Mass and High Resolution Mass Spectra (HRMS)

Mass spectra measured on a LC-MS (Waters UPLC-TQD) mass spectrometer. High resolution mass spectra (HRMS) were measured on a Brucker microOTOF II Focus instrument.

UV-Vis Spectra

The absorption spectra were measured with a PERSEE TU-1900 and an Agilent 8453 spectrophotometer. The solvents used in photochemical measurement were spectroscopic grade and were purified by distillation. The stock solution of compounds (2×10^{-3} M) was prepared in THF, and a fixed amount of these concentrated solutions were added to each experimental solution. All the experiments were done repeatedly, and reproducible results were obtained. Prior to the spectroscopic measurements, solutions were deoxygenated by bubbling nitrogen through them.



Scheme 1. Synthesis of 2-((2-rhodaminehydrazono)methyl)quinoline (**RQ**).

Theoretical Calculations

For the theoretical study of excited state photo-physics of the compound, the *DMol*^{3} program packaged in *Material Studio* (*Accelrys Software Inc., US*) was used [20, 21]. The ground state geometries and the frontier molecular orbital of the compound were calculated using the density function theory (DFT) with the B3LYP hybrid functional and the double numerical plus *d*-functions (DND) atomic orbital basis set.

Synthesis

The synthesis of the target rhodamine sensor, 2-((2-rhodaminehydrazono)methyl)quinoline (**RQ**), was outlined in Scheme 1. Rhodamine hydrazide was synthesized according to the published procedure [22]. **RQ** was obtained by the condensation between rhodamine hydrazide and quinoline-2-carbaldehyde.

Rhodamine hydrazide (200 mg, 0.44 mmol) and quinoline-2-carbaldehyde (76 mg, 0.48 mmol) dissolved in ethanol (30 mL). The mixture was refluxed for 10 h with the color of mixture changed from light red to deep red. The reaction process was monitored by TLC. The solvent was evaporated until the rhodamine hydrazide was disappeared on TLC. The crude product was recrystallized from ethanol yielding the red powder 190 mg (73%).

^{1}H NMR (400 MHz, $CDCl_3$, δ) 8.70 (*s*, 1H), 8.13 (*d*, $J = 8.7$ Hz, 1H), 8.06–7.97 (m, 3H), 7.73 (*d*, $J = 8.3$ Hz, 1H), 7.63 (*t*, $J = 7.7$ Hz, 1H), 7.54–7.43 (*m*, 3H), 7.14 (*d*, $J = 7.2$ Hz, 1H), 6.57 (*d*, $J = 8.8$ Hz, 2H), 6.49 (*d*, $J = 2.5$ Hz, 2H), 6.24 (*dd*, $J = 8.9$, 2.5 Hz, 2H), 3.31 (q, $J = 7.0$ Hz, 8H), 1.15 (t, $J = 7.0$ Hz, 12H); ^{13}C NMR (100 MHz, $CDCl_3$, δ) 165.4, 155.0, 153.0, 152.2, 148.9, 147.7, 146.7, 135.7, 133.7, 129.1, 128.3, 128.2, 128.1, 127.6, 127.5, 126.7, 123.7, 123.6, 118.2, 107.9, 105.7, 98.1, 66.0, 44.2, 12.6; EI$^+$/MS m/z 595 (M$^+$); HRMS (EI$^+$) calcd for $C_{38}H_{37}N_5O_2$ 595.2947, found 595.2943.

Result and Discussion

RQ showed very weak absorption in the visible region (Fig. 1). Upon addition of Cu^{2+}, the solution color changed from colorless to red color. The effects of Cu^{2+} on the colorimetric and chemosensing properties of a 1.0×10^{-5} M solution of **RQ** in CH_3CN were investigated. A detailed study on the recognition characteristics of **RQ** toward Cu^{2+} was carried out. The absorption spectra of **RQ** in the presence of varying Cu^{2+} concentrations were recorded in Fig. 1. As shown in Fig. 1, the solution of **RQ** (1.0×10^{-5} M) exhibited very weak absorption band above 350 nm. Upon addition of Cu^{2+}, the main absorption peak at 320 nm decreased gradually, and a new absorption band appeared at 555 nm dramatically with the isosbestic point at 352 nm, which can be ascribed to the delocalized xanthene moiety of rhodamine. The absorbance of **RQ** at 555 nm increased more than 563-fold on

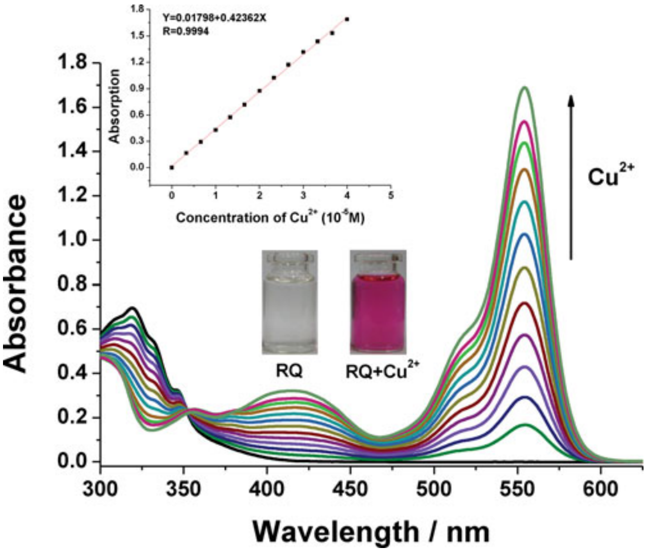


Figure 1. Changes in the UV-Vis absorption spectra of **RQ** in CH_3CN with various amounts of Cu^{2+} (0-4eq) (inset: dependence of absorption in intensity at 555nm with respect to concentrations of Cu^{2+} ion in CH_3CN; color picture of **RQ** with and without Cu^{2+}).

increasing the concentration of Cu^{2+} from 0 to 4 μM. A satisfactory linear relationship between the absorption intensity and Cu^{2+} concentration was observed with the correlation coefficient as high as 0.9994. The titration experiments were repeated 10 times. Excellent linear relationship of the absorption intensity against [Cu^{2+}] reproduced. The detection limit of Cu^{2+} for **RQ** in CH_3CN was as low as 0.2 μM (ca. 8.5 μg/L) based on the S/N test method and serial dilution method. The relative standard deviation of eleven cycles was estimated to be 2.8%. The detection limit of **RQ** to Cu^{2+} is 235 times lower than the recommended water quality standard of Cu^{2+} (2 mg/L) for drinking water by WHO [23], EU [24], and Australia [25]. Therefore, Cu^{2+} can be satisfactorily detected by sensor **RQ**. In addition, the absorption behavior changes the color of the resultant solution from colorless "off" to red color "on," allowing "naked-eye" detection. **RQ** is different from the rhodamine derivatives published as fluorescent "on-off" or "off-on" type probe [26–29]. The fluorescence quantum yield of **RQ** is lower than 0.01 and no observable fluorescence enhance was observed upon addition of Cu^{2+}.

The selectivity of **RQ** between Cu^{2+} and other 17 metal ions was also investigated. Each of the 17 metal ions was pre-incubated with **RQ** before Cu^{2+} added. Then, the absorbance was recorded. As shown in Fig. 2, the absorbance of **RQ** with Cu^{2+} was not affected significantly in the presence of other tested metal ions, demonstrating little interferences from the other metal ions. Only the addition of Fe^{3+} induced a light absorption increase at 555 nm. The absorption enhancement at 555 nm induced by the same amount (10 μM) of Cu^{2+} was estimated to be 4.7-fold (Fe^{3+}). For other metal ions, there is more than 35-fold of absorption enhancement induced by Cu^{2+}, indicating the highly selectivity of **RQ** over most of the metal ions. To the best of our knowledge, only seldom rhodamine derivatives exhibit highly selective toward one metal ion over 17 disturbing metal ions.

The binding stoichiometry between **RQ** and Cu^{2+} was confirmed by Job's plot (Fig. 3). Job's plot was preformed by continuous variation with a total concentration of 10 μM. The

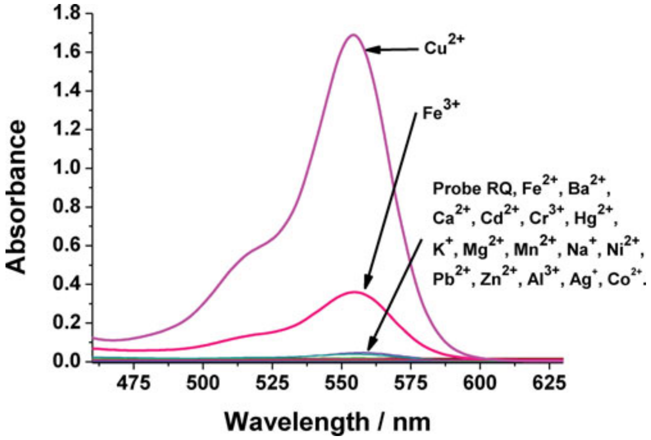


Figure 2. Changes in the absorption spectra of **RQ** (10μM) in the presence of different metal ions (10μM for Fe^{3+}, Fe^{2+}, Ba^{2+}, Ca^{2+}, Cd^{2+}, Cr^{3+}, Hg^{2+}, K^+, Mg^{2+}, Mn^{2+}, Na^+, Ni^{2+}, Pb^{2+}, Zn^{2+}, Al^{3+}, and Ag^+) in CH_3CN.

maximum absorbance was obtained at 555 nm when the molecular fraction of Cu^{2+} and **RQ** was close to 1:1, suggesting 1:1 stoichiometry for the binding of **RQ** and Cu^{2+}. A likely sensing mechanism based on metal ions triggered spiro ring-opening process is proposed in scheme 2 [19, 30–32]. To determine the association constant *K*ass, Benesi-Hildebrand method was used [33]. According to the 1:1 stoichiometry supported by the job plot, the function can be given as follows. Where A_i and A_0 denote the absorbance of **RQ** in the presence and absence of Cu^{2+} respectively; A_∞ stands for the absorbance measured when excess amount of Cu^{2+} added; K_{ass} is the association constant, and $[Cu^{2+}]$ is the concentration of cooper ion added to the solution. The association constant K_{ass} is

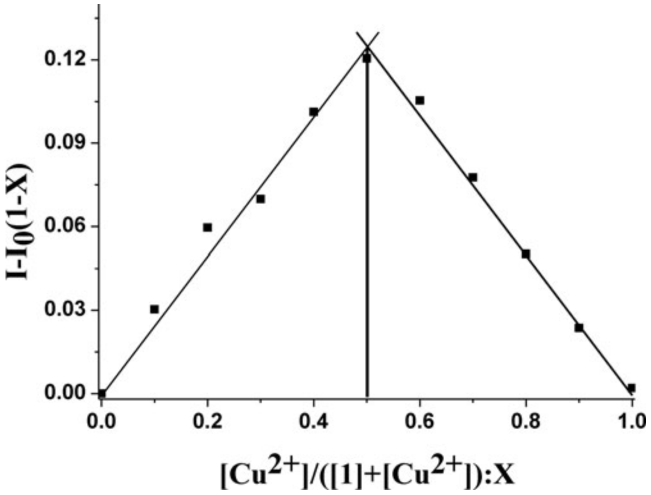
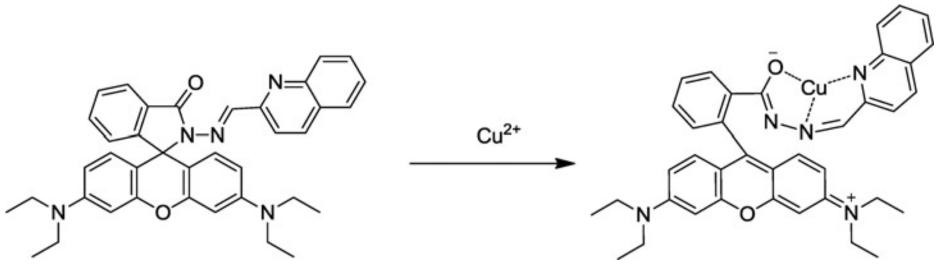


Figure 3. Job's plot of **RQ** and Cu^{2+} in CH_3CN solution. The absorbance was collected at 555 nm.



Scheme 2. Proposed mechanism for the color change of **RQ** upon the addition of Cu^{2+}.

calculated to be 2.96×10^4 M^{-1}.

$$\frac{1}{A_i - A_0} = \frac{1}{K_{ass}(A_\infty - A_0)[Cu^{2+}]} + \frac{1}{A_\infty - A_0}$$

To better comprehend the geometrical, electronic, and optical properties of **RQ/RQ-Cu**, we undertook a comprehensive computational investigation using Material Studio. To reduce the run times in the first instance, the ground-state energy-minimized structures were calculated using DFT and LDA/DN basis set. Further refinement and optimization on structures were undertaken using DND/B3LYP basis set.

The calculated electron density distributions in the frontier molecular orbitals (FMOs) of **RQ** are shown in Fig. 4. According to the analysis of optimized structure, the attached quinoline moiety is highly twisted with framework of rhodamine. Therefore, a donor-acceptor construction formed. It is not difficult to predict that the HOMO distribution spread over rhodamine moiety, whereas the LUMO distribution delocalized away from rhodamine to quinoline moiety. The calculation results showing in Fig. 4 clearly indicates the above

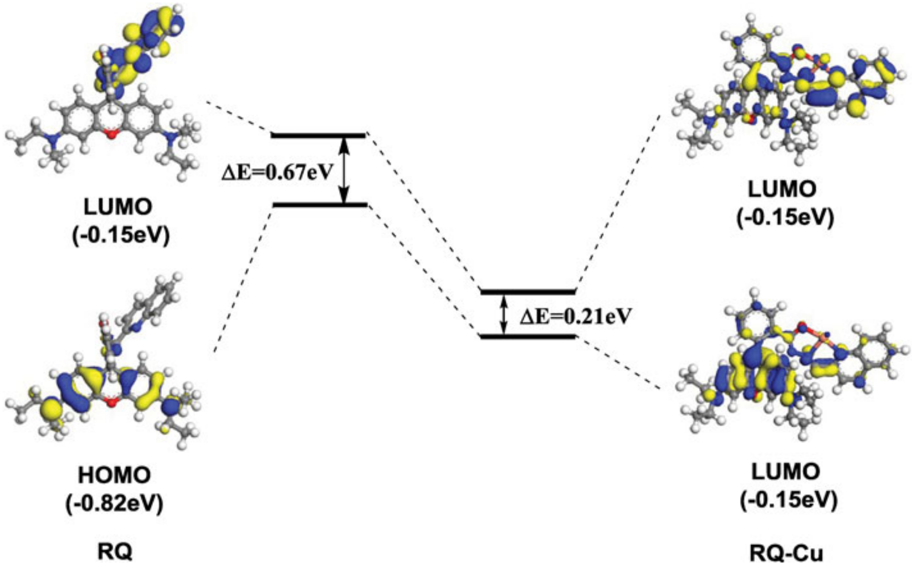


Figure 4. Electron distributions of HOMO/LUMO and energy levels.

mentioned distribution trend of HOMO and LUMO of **RQ**. This is a typical character of effect electron migration. After binding with Cu^{2+}, the effect electron migration was weakened significantly, which will influence the energy potential levels of HOMO/LUMO significantly also. The energy potential values of HOMO/LUMO in **RQ** are indicated in Fig. 4 and the energy gap between HOMO and LUMO is estimated to be 0.67 eV. The energy gap was lowered significantly to 0.21 eV in **RQ**-Cu. It can lead to the red shift of longest maximum absorption corresponding to the lowered HOMO/LUMO energy gap. This is also in agreement with the experimental results of color changing from colorless (UV region) to red (555 nm).

Conclusions

In summary, a new probe by condensation of rhodamine B and quinoline-2-carbaldehyde was synthesized and characterized. Distinct color change was observed upon addition of Cu^{2+}, which can attribute to the Cu^{2+} chelating with **RQ**. **RQ** harbors a Cu^{2+}-receptor moiety and binds in a 1:1 stoichiometry, which was supported by the Job plots. A good linear relationship was established for the Cu^{2+} titration with the correlation coefficient as high as 0.9994. The detection limit is about 235 times lower than the WHO recommended value for Cu^{2+} (2.0mg/L). It is likely that the experimental results of this study will provide a new basis for the design of interesting spiro-rhodamine-based chemosensors, and further studies including the design of new analogs of **RQ** as various chemosensors are still underway.

Acknowledgments

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