Tetrahedron Letters 58 (2017) 3868–3874

Contents lists available at ScienceDirect

Tetrahedron Letters

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

Quinoline-based highly selective and sensitive fluorescent probe specific for Cd^{2+} detection in mixed aqueous media

Xiaohu Ding, Feifei Zhang, Yinjuan Bai *, Junxia Zhao, Xia Chen, Man Ge, Wei Sun

Key Laboratory of Synthetic and Natural Functional Molecule Chemistry of Ministry of Education, College of Chemistry and Materials Science, Northwest University, Xi'an, Shannxi 710127, PR China

ARTICLE INFO

Article history:
Received 22 May 2017
Revised 24 August 2017
Accepted 28 August 2017
Available online 30 August 2017

Keywords:
Fluorescent probe
Quinoline
Cadmium(II) ions
Recognition
Density functional theory calculations

ABSTRACT

Quinoline-based fluorescent probe as a recognition unit was designed and synthesized in this study. The probe **R1** displayed excellent selectivity and sensitivity for cadmium ions (Cd^{2+}) over a wide range of metal ions in acetonitrile-water (MeCN-H_2O) mixed solution. In order to better understand the recognition mechanism between probe and Cd^{2+}, the density functional theory calculations were performed. Finally, the colorimetric experiment result was observed and conveniently monitored by the naked eye, and a visual detection limit of 4×10^{-6} mol L^{-1} was achieved. These experimental results indicated the promising potential of the probe to detect Cd^{2+} in biological system. Furthermore, the probe **R1** was successfully used for the highly sensitive detection of Cd^{2+} in living cells.

Introduction

Pollution caused by heavy metal ions has become a serious and urgent problem because it causes potential damage to the environment and poses serious health hazards to the human and animal life even at low concentrations.[1] Among them cadmium ions (Cd^{2+}) are the most toxic and hazardous ions that are known to lack any vital or beneficial effects on humans.[2] Cd is widely used in many fields including military affairs, agriculture, and industry. When accumulated in the kidney, thyroid gland, spleen, and so on, Cd can cause serious illness, such as lung cancer, renal dysfunction, calcium metabolism disorders, prostate disorder, oxidative stress, and high blood pressure even at very low concentrations.[3,4] Therefore, rapid and efficient detection of Cd^{2+} is highly desirable and necessary in order to control its concentration levels in the biosphere and its direct impact on human health. Though various methods such as atomic emission spectroscopy, ion-coupled plasma emission-mass spectroscopy, and X-ray fluorescence spectroscopy[5,6] are available for the detection of content of Cd^{2+}, use of fluorescent probe to recognize Cd^{2+} is the most common one. Although these conventional methods provide an extremely sensitive and rapid analysis approach, they need sophisticated sample-pretreatment procedures, complicated instrumentation, and rigorous experimental conditions, which limit their use. In recent years, the fluorescence method has been developed for analysis of Cd^{2+} and the colorimetric technique has frequently been applied.[7,8]

Till date, fluorescent probes capable of detecting heavy-metal ions have attracted significant attention in virtue of their operational simplicity, high sensitivity, high selectivity, low detection limit, easy operational procedure, and high response speed.[9] The construction of single fluorescent probes capable of simultaneous detection of multiple targets has drawn increasing interest due to their cost-effective and real-time applications.[10] However, recognition of multiple analytes is a great challenge. Presently, among these, a few recent quinoline-based fluorescent probes as a recognition unit have been reported. Liu et al. reported a novel and efficient quinoline-based fluorescent sensor for zinc(II) ion (Zn^{2+}) and its application in live-cell imaging.[11] Mehdi et al. reported a selective "On–Off" switching behavior of a small fluorogenic molecule, *N*-(quinolin-8-yl)quinoline-2-carboxamide in acetonitrile (MeCN) solution for detection of Zn^{2+}.[12] Zhu et al. reported a ratiometric Al^{3+} ion probe based on the coumarin-quinoline fluorescence resonance energy transfer system.[13] Montalti et al. reported a fluorescent behavior of 8-hydroxyquinoline containing chemosensors.[14] However, many of the reported quinoline-based fluorescent probes have limitations, such as low selectivity and requirement for long response time and specific reaction conditions such as high temperature and acidic or basic environment. Moreover, quinoline-based fluorescent probes for detection of Cd^{2+} have rarely been reported. Pamuk and Algi reported synthesis of a novel on/off fluorescent Cd^{2+} probe.[15] However, extensive research efforts are required to be devoted to the

* Corresponding author.
E-mail address: 13649246460@163.com (Y. Bai).

http://dx.doi.org/10.1016/j.tetlet.2017.08.068
0040-4039/

quinolone-based fluorescent probes for the rapid and highly selective and sensitive detection of Cd^{2+} at room temperature in mixed aqueous media.

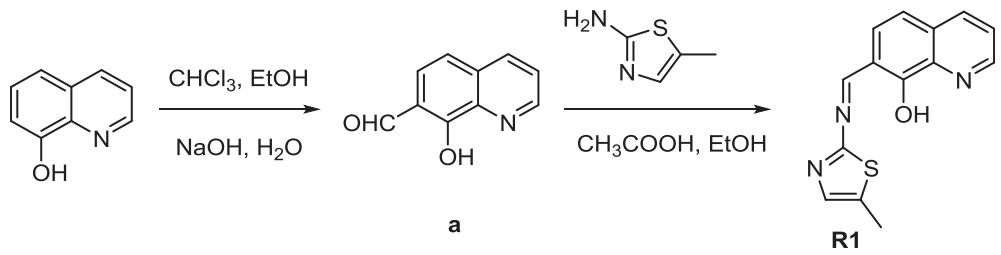
To address the above mentioned problem herein, a quinoline-based fluorescent probe **R1** was designed and synthesized. The new fluorescent probe **R1** displayed an excellent selectivity for Cd^{2+} over a wide range of metal ions in MeCN-H_2O systems. Probe **R1** displayed strong fluorescence enhancement with Cd^{2+} and other metal ions could not enhance the fluorescence intensity. Moreover, the colorimetric experiment result was observed and conveniently monitored by the naked eye and a visual detection limit of 4×10^{-6} mol L^{-1} was achieved. Finally, the quinoline-based fluorescent probe was successfully used for detecting Cd^{2+} in biological system.

Results and discussions

The synthesis of **R1** is outlined in Scheme 1. It was characterized by ^1H NMR, ^{13}C NMR, and high resolution mass spectroscopy (HRMS), and the corresponding spectra are provided in Supplementary materials.

The solvent affects the fluorescent intensity of the probe in the process of detection of Cd^{2+}. Therefore, some experiments were conducted to investigate and discuss the effect of solvent and select an optimal solvent system for the effective detection of Cd^{2+}. Fig. 1a shows that **R1** displays a strong fluorescent emission peak in an aprotic polar solvent dimethylformamide (DMF), and this peak becomes faint in MeCN under no any ions circumstance. Therefore, in order to reduce the fluorescence response of the solvent itself compared to the probe **R1**, MeCN was selected as an optimized solvent. However, whether in nature or in the body to detect metal ions are inseparable the water, and to improve the usability of the probe, we selected MeCN-H_2O as the optimized solvent system. In order to reduce the interference of external environment during the detection of Cd^{2+} by using probe **R1**, accurate judgment of the solvent ratio for probe **R1** testing was required; therefore, we tested the probe in solvent systems with different ratios for detecting the fluorescence response of Cd^{2+}. Fig. 1b exhibits that **R1** with Cd^{2+} shows weak fluorescence intensity in water alone. Upon gradual addition of MeCN solvent, an obvious enhancement of fluorescence intensity is observed, and the fluorescence intensity no longer increases when the MeCN and water ratio reaches 1:1. Thus, the above mentioned results indicate that the best ratio for MeCN-H_2O solvent system is 1:1.

For an ideal probe, a high selectivity for the analyte is a matter of necessity. Related metal ions, including Ag^+, Al^{3+}, Ba^{2+}, Ca^{2+}, Cd^{2+}, Cr^{3+}, Co^{2+}, Cu^{2+}, Fe^{3+}, Hg^{2+}, K^+, Li^+, Mg^{2+}, Mn^{2+}, Na^+, Ni^{2+}, Pd^{2+}, and Zn^{2+} were used to monitor the binding abilities of **R1** with the metal ions in the MeCN-H_2O (1:1, v/v) solution by fluorescence spectroscopy (Fig. 2a). Upon addition of probe **R1**, the fluorescent intensity of metal ions other than Cd^{2+} did not alter noticeably. Only Cd^{2+} significantly affected the fluorescent intensity of **R1** even in the presence of other interfering metal ions. This result indicates high selectivity and sensitivity of **R1** toward Cd^{2+}. To verify the effect of **R1** on the complexation of Cd^{2+}, following competitive experiment was conducted: the fluorescence emission of **R1** was analyzed upon adding different metal ions. Fig. 2b demonstrates that the fluorescence of **R1** enhances with the addition of Cd^{2+} to the mixture of **R1** with other interfering ions. Thus, the result reveals that selectivity of **R1** toward Cd^{2+} is not significantly



Scheme 1. The synthetic route to **R1**.

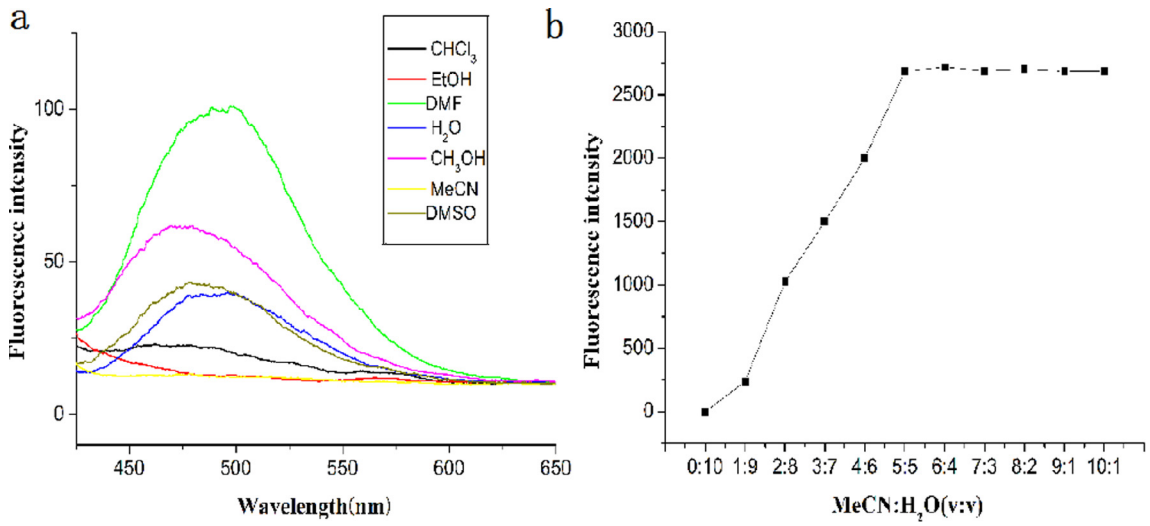


Fig. 1. (a) Fluorescence spectra of probe **R1** (10 μM) in the presence of various solvents (λ_{ex} = 375 nm). (b) Fluorescence probe in response of **R1** with Cd^{2+} under the same solvent conditions in different proportions.