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A novel C_{3v}-symmetric completely water soluble turn-on chemo sensor for Cd^{2+} and the resultant complex for iodide anion in aqueous medium

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ABSTRACT

A novel simple C_{3v}-symmetric, completely water soluble quinoline based guanidinium Schiff's base system have been reported for the selective detection of Cd^{2+} in physiological environment through a turn-on fluorescence response. The cadmium complex is found to be highly selective toward iodide by turning off the fluorescence through the sequestration of Cd^{2+} from $\mathbf{L_1}$-Cd by the precipitation of CdI_2. Detection limit for Cd^{2+} and iodide are found to be 51 ppb and 1 ppb, respectively. $\mathbf{L_1}$ is reversible toward Cd^{2+} and iodide and can be recycled. The receptor was used for the detection of Cd^{2+} in complex natural samples (tap, lake and river water).

1. Introduction

Selective sensing and recognition of metal ions is of considerable current interest for a broad range of biological and environmental applications [1,2]. Highly sensitive and selective methods for the detection of metal ions not only can provide insight into the physiological activity of metal ions but also are in great demand for waste management and food safety screening. Cadmium is used in numerous processes such as electroplating, metallurgy, agriculture, war industry, Ni–Cd batteries, phosphate fertilizers, pigments, and semiconducting quantum dots and rods [3–5]. For its use in these various fields lead to cadmium exposure, and as a result in certain areas cadmium content is increasing in food, which poses severe harm for human health and the environment [6]. Toxicity of Cd^{2+} affects reproduction, bones, kidneys, nerve system, and tissues, subsequently resulting in renal dysfunction, calcium metabolism disorders, and an increased incidence of certain forms of cancers [3]. Therefore development of reliable chemo-sensors for detection and monitoring of cadmium in environment and biology is still in demand. However, numerous numbers of fluorescent sensors have been reported to detect and analyze different kinds of heavy toxic metal ions because of their simplicity, high sensitivity, and real-time detection [7,8] but there are only a few reports of fluorescent sensors for cadmium ion [9–14], and even rare examples are available in living cells [15–20]. The paramount challenge in the detection of Cd^{2+} is the interference of other transition metal ions, in particular Zn^{2+}, which have similar properties to those of Cd^{2+} because they are in the same group of the periodic table. As a result, they show similar spectral changes with fluorescent sensors [21–23]. Recently, some groups have reported Cd^{2+}-selective fluorescent chemo-sensors, which can distinguish Cd^{2+} from Zn^{2+} to some extent [24,25]. Thus, there is a still great need for developing Cd^{2+}-selective sensors that can distinguish Cd^{2+} from Zn^{2+} with high sensitivity and selectivity under physiological conditions.

On the other hand, nowadays anion recognition is of prime interest in the field of chemistry and biochemistry due to their various important roles in biology, environment, and industry [26–29]. Among the range of biologically important anions, iodide is of particular interest due to its essential role for thyroid gland function. As a result, the iodide content of urine and milk is often required for nutritional, metabolic, and epidemiological studies of thyroid disorders [30–32]. So, deficiency of iodide can cause severe diseases [33,34]. To prevent iodine deficiency, addition of iodide into food (salt) is being a regular practice for years. Though, it is still a public health problem in some countries [35]. Moreover iodine is important in chemical synthesis, elemental iodine is used in synthesizing some organic chemicals, in manufacturing dyes. Again the radioactive isotope of iodine is used in medicine and in

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analytical chemistry [36–39]. On the other hand due to these human activities the amount of iodine and its derivatives especially its dangerous radioactive isotopes are increasing in the biosphere [40,41]. Therefore development of receptors for the selective sensing and binding of iodide anion are highly desired. Although a lot of studies concerning other anions have been published but there are a few reports available regarding the estimation of iodide.

Fluorescent sensors are nowadays renowned as powerful tools for monitoring cations, anions, and small molecules due to their high sensitivity, simplistic operation, and real time and online detection [42–46]. Iodide has large ionic radius, low charge density, and low hydrogen-bonding ability, due to these infamous properties it is very difficult to design receptors for iodide anions. However, only a few iodide sensors have been reported in the literature due to the above difficulties faced in designing receptors for iodide [47–49]. Again, the receptors for iodide based on hydrogen-bonding suffer from the competition of water molecules in aqueous media.

Recently metal based anion sensing is in consideration to chemists for the successful development of sensors for F^- [50], CN^- [51,52], PPi [53–56] S^{2-} [57,58], I^- [59,60]. This process is also highly sensitive and also these systems have lower detection limit which are very much important in sensing of analytes. Metal based anion sensing is mainly dependent on the cation–anion cooperative interaction or precipitation [44,61]. As CdI_2 have low solubility in water, so we predicted that a cadmium complex or sensor could be utilized for sensing iodide anion through sequestrating Cd^{2+} from the complex by means of formation of CdI_2 precipitates in aqueous media. This process would liberate sensor from cadmium complex and consequently induces a significant fluorescence signal output.

Herein, we report the synthesis, characterization and sensing behavior of a novel completely water soluble quinoline based tripodal receptor for the selective recognition of cadmium in aqueous medium in physiological condition. The in situ formed complex has been exploited for the sensing of iodide over other important anions in aqueous medium. We envisaged that the N-atom of the quinoline ring in $\mathbf{L_1}$ is responsible for the sensing behavior, which was further validated by employing a control compound $\mathbf{L_2}$.

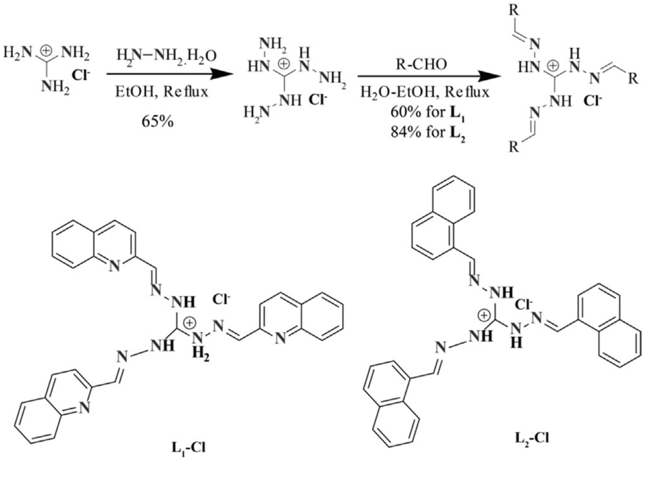
2. Experimental

2.1. General information and materials

All the materials used for synthesis were purchased from commercial suppliers and used without further purification.

2.2. Synthesis of $\mathbf{L_1}$

Triaminoguanidinium chloride was prepared by literature methods [62]. Triaminoguanidinium chloride (2.0 mmol) was dissolved in a hot mixture of H_2O (3 mL) and ethanol (20 mL). A mixed solution of 2-quinolinecarboxaldehyde (6 mmol) and ethanol (3 mL) was slowly added to the above hot mixture (Scheme 1). After stirring and heating under reflux for 4 h, the resulting mixture was cooled to room temperature. A large body of amorphous yellow powder was obtained when some amount of diethyl ether added into the reaction mixture. Then the desired product $\mathbf{L_1}$ was collected, washed with diethyl ether and dried under reduced pressure. Yield: 60%. ^1H NMR [600 MHz, CD_3Cl, δ (ppm)]: 9.44 (3H, s), 8.50 (3H, d, J = 6.6 Hz), 8.34 (3H, d, J = 7.2 Hz), 7.74 (3H, d, J = 6.6 Hz), 7.66 (3H, d, J = 7.8 Hz), 7.38 (6H, s). ^{13}C NMR [150 MHz, CD_3Cl, δ (ppm)]: 149.3, 147.5, 133.3, 131.2, 131.1, 128.5, 127.1, 126.9, 125.9, 125.7, 123.2. ESI-MS (positive mode, m/z) calculated $[\mathbf{L_1}]^+$ = 522.2155, found 522.2286.



Scheme 1. Synthetic route for $\mathbf{L_1}$ and $\mathbf{L_2}$.

2.3. Synthesis of $\mathbf{L_2}$

Triaminoguanidinium chloride (2.0 mmol) was dissolved in a hot mixture of H_2O (3 mL) and ethanol (20 mL). A mixed solution of 1-naphthalenecarboxaldehyde (6 mmol) and ethanol (3 mL) was slowly added to the above hot mixture. After heating under reflux for 4 h, the resulting mixture was cooled to room temperature. The obtained precipitate was collected and washed with cold methanol and dried under reduced pressure. Yield: 84%. ^1H NMR [600 MHz, CD_3Cl, δ (ppm)]: 9.34 (3H, s), 8.48 (3H, d, J = 6 Hz), 8.32 (3H, d, J = 7.2 Hz), 7.72 (3H, d, J = 4.2 Hz), 7.56 (6H, d, J = 4.2 Hz), 7.35 (3H, d, J = 6 Hz), 6.83 (3H, d, J = 6 Hz). ^{13}C NMR [150 MHz, CD_3Cl, δ (ppm)]: 149.0, 147.1, 133.3, 131.2, 131.1, 128.4, 127.7, 127.0, 126.6, 125.8, 123.1. ESI-MS (positive mode, m/z) calculated $[\mathbf{L_2}]^+$ = 519.2297, found 519.2399.

2.4. UV–vis and fluorescence spectroscopic studies

Stock solutions of various ions (1×10^{-3} mol L^{-1}) were prepared in deionized water. Perchlorate, chloride or nitrate salts of metal ions were used to prepare metal stock solutions. Tetra butyl, tetraethyl or sodium salts of the corresponding anions were used for anion sensing experiments. The solution of $\mathbf{L_1}$ was then diluted to 1×10^{-6} mol L^{-1} with MeOH: aqueous HEPES buffer (1 mM, pH 7.4; 2:3 v/v). All the spectroscopic experiments have been performed in a mixed solvent MeOH: aqueous HEPES buffer (1 mM, pH 7.4; 2:3 v/v). In titration experiments, a solution of $\mathbf{L_1}$ (1×10^{-6} mol L^{-1}) was filled in a quartz optical cell of 1.0 cm optical path length, and the ion stock solutions were added gradually by using a micropipette to achieve a concentration of 1×10^{-5} mol L^{-1}. In selectivity experiments, the test samples were prepared by interacting appropriate amounts of the anions/cations stock into 2 mL of $\mathbf{L_1}$ solution (2×10^{-5} mol L^{-1}). For all the samples, the spectra were recorded following 1 min of the addition of the ions. For fluorescence measurements, excitation was set at 420 nm and emission was recorded from 450 nm to 650 nm. The selective binding of $\mathbf{L_1}$ with Cd^{2+} among all other metal ions was also studied by fluorescence emission spectroscopy of the solution of $\mathbf{L_1}$ (10.0×10^{-6} mol L^{-1}) in the absence and presence of an excess (10 equiv.) of each of the metal ions in mixed solvent. Reversible behavior of $\mathbf{L_1}$ upon the sequential addition of Cd^{2+} and iodide was carried out in the same mixed solvent.

2.5. Detection limit for Cd^{2+} ion and iodide

The detection limit was calculated on the basis of the fluorescence titration. The fluorescence emission spectrum of $\mathbf{L_1}$ was