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SHORT COMMUNICATION

A Quinoline Derivative as an Efficient Sensor to Detect Selectively Al^{3+} ion

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Abstract A quinoline-based Schiff base 1 has been utilized as a fluorescence chemosensor for the selective detection of Al^{3+}. The receptor 1 exhibited a high association constant (3.67×10^5 M^{-1}) with submicromolar detection limit (0.18 ppm) towards Al^{3+} in CH_3CN solution.

Keywords Chemosensor · Fluorescence · Turn-On · Quinoline

In recent years, fluorescent chemosensors have attracted significant interest because of their potential application in medicinal and environmental research. Thus, many fluorescent chemosensors specific for Hg^{2+}, Cu^{2+}, Zn^{2+} or other transition metals have been developed. Compared to these transition metal ions, only a few fluorescent chemosensors have been reported for detection of Al^{3+} [1–21]. Al^{3+} most widely exists in the environment due to acidic rain and human activities. Its toxicity not only hampers plant growth but also damages the human nervous system to induce Alzheimer's disease, Parkinson's disease, amyotrophic lateral sclerosis, etc. [1, 4, 22–25]. Therefore, detection of Al^{3+} is crucial in controlling its concentration levels in the biosphere and its direct impact on human health. The detection of Al^{3+} has always been problematic due to the lack of spectroscopic characteristics and poor coordination ability [26]. In addition, the majorities of the reported Al^{3+} has limitations such as requiring complicated synthesis and are insoluble in polar solutions. For practical applications, it is necessary to develop Al^{3+} sensors that are easily prepared, and possess selective and sensitive signaling mechanisms.

Most of the fluorescent sensors structures for Al^{3+} contain nitrogen–oxygen-rich coordination environments which could provide a hard-base environment for the hard-acid Al^{3+}. Recently, 8-hydroxyquinoline and its derivatives are efficient candidates for many metal ions recognition and are widely used by many researchers for the synthesis of sensors for selective detection many metal ions [27–30]. The well-known 8-hydroxyquinoline derivative 1 (receptor 1) has been synthesized by previous reports [31, 32]; however, its chemosening behavior towards metal ions has not been investigated yet. Here, we reported receptor 1 exhibited a highly selective detection towards Al^{3+} among a series of metal ions. In addition, the receptor 1 exhibited a high association constant with submicromolar detection limit towards Al^{3+} in CH_3CN solution (Scheme 1).

The chemosensor behavior of receptor 1 with the following 15 metal ions (as perchlorate salts): Li^+, Na^+, K^+, Ca^{2+}, Mn^{2+}, Hg^{2+}, Fe^{2+}, Fe^{3+}, Co^{2+}, Ni^{2+}, Cu^{2+}, Pb^{2+}, Cd^{2+}, Zn^{2+} and Al^{3+} in CH_3CN, was investigated by UV–vis and fluorescence measurements. Receptor 1 shows significant variations of the absorption spectrum in the 300–470 nm range (Fig. S2) for all the added metal ions. However, from the fluorescence spectra of receptor 1 (Fig. 1), receptor 1 alone and other cations all displayed very weak single fluorescence emission band at 480 nm when it was excited at 346 nm except for Al^{3+}. Upon addition of Al^{3+}, receptor 1 exhibited a prominent fluorescence enhancement with the quantum yield of 0.024 and accompanied a red shift of 27 nm from 450 to 477 nm. Based on the use of a UV lamp, in the presence of Al^{3+}, the solution of receptor 1 showed a dramatic color change from dark blue to light blue which could easily be detected by the naked-eye. (Fig. 2). In addition, the fluorescent enhancement efficiency observed at 477 nm was 570-fold greater than the

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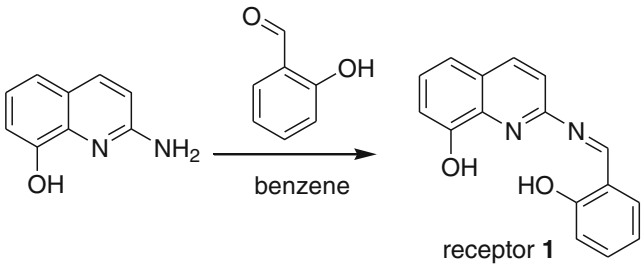

Scheme 1 Synthesis of receptor 1

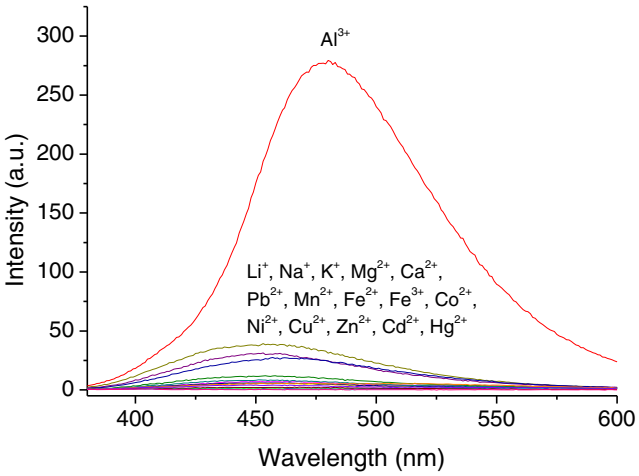

Fig. 1 Fluorescence emission spectra ($\lambda_{ex.}$ = 346 nm) of 1 (30 μM) in the presence of 10.0 equiv. of various cations in CH_3CN

control in the absence of Al^{3+} (Fig. 3). The observed fluorescent enhancement may be attributed to the formation of a rigid system after binding with Al^{3+}, causing the chelation-enhanced fluorescence (CHEF) effect [33, 34]. This unique selectivity of receptor 1 towards Al^{3+} could be interpreted in terms of the smaller ionic radius and higher charge density of the Al^{3+}.

To further investigate the chemosensing properties of receptor 1, fluorescence titration of receptor 1 with Al^{3+} were performed. From the fluorescence titration profiles (Fig. 4),

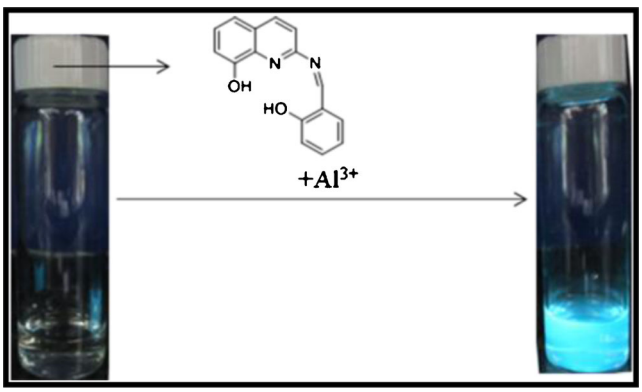

Fig. 2 Fluorescence changes excited by UV lamp ($\lambda_{ex.}$ = 365 nm) of 1 upon addition of 10 equiv. of Al^{3+}

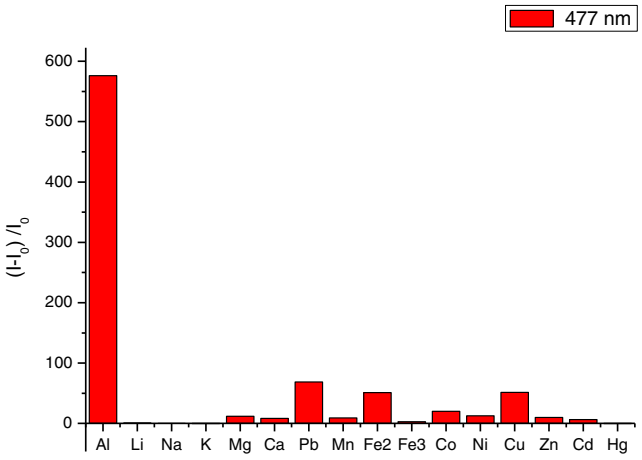

Fig. 3 Variation of the fluorescence intensity at 477 nm ($\lambda_{ex.}$ = 346 nm) of 1 (30 μM) in the presence of 10.0 equiv. of various cations in CH_3CN

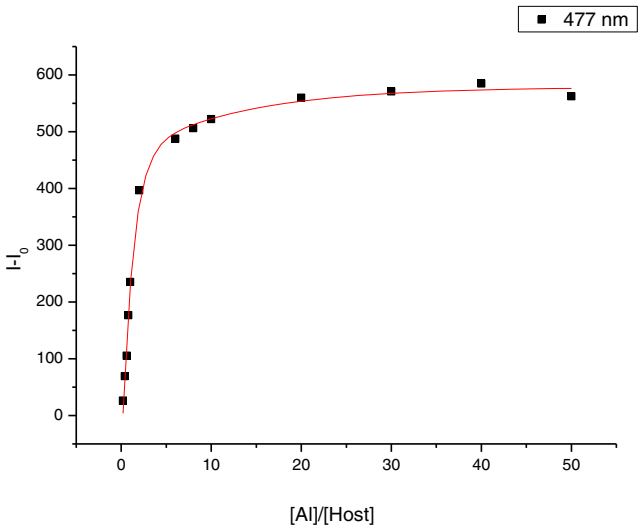

Fig. 4 Fluorescence titration of 1 (30 μM) in CH_3CN upon addition of increasing concentrations Al^{3+}

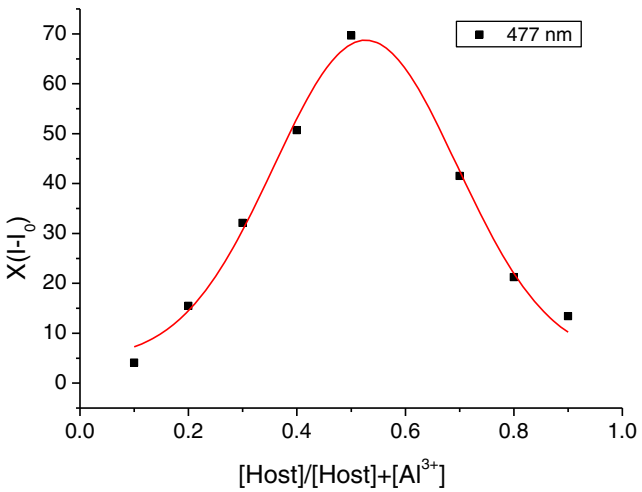

Fig. 5 Job plot

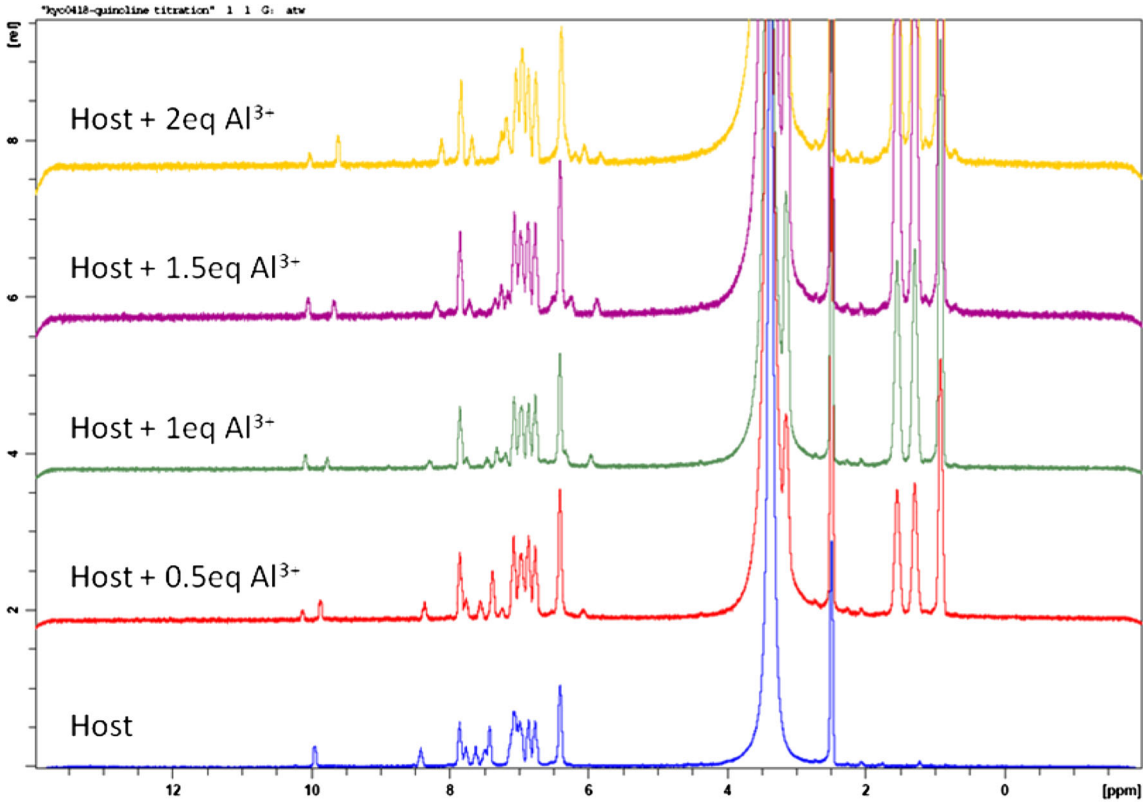

Fig. 6 ^{1}H NMR titration plots of 1 with Al^{3+} in CD_3CN

the association constant for 1-Al^{3+} in CH_3CN was determined as 3.67×10^5 M^{-1} by a Hill plot (Fig. S3). A Job plot indicated a 1:1 stoichiometric complexation of receptor 1 with Al^{3+} (Fig. 5). In addition, the formation of 1:1 complex between 1 and Al^{3+} was further confirmed by the appearance of a peak at m/z 607, assignable to [receptor $1+Al^{3+}+H_2O+3ClO_4^-$] in the ESI/MS (Fig. S4). By using above-mentioned fluorescence titration results, the detection limit for Al^{3+} was determined as 0.18 ppm. The detection limit is sufficiently low to detect submicromolar concentration of the Al^{3+}, which belongs the range found in many chemical and biological systems.

The selectivity towards Al^{3+} was further ascertained by the competition experiment. Receptor 1 was treated with 10.0 eq. of Al^{3+} in the presence of other metal ions of the same concentration. Relatively low interference was observed for the detection of Al^{3+} in the presence of other metal ions except Fe^{2+} and Fe^{3+} (Fig. S5). The receptor 1 responses for Al^{3+} in the presence of Fe^{2+} and Fe^{3+} were relatively low but clearly detectable. To our reason, receptor 1 may form a complex with Al^{3+} and then this complex may further interact with Fe^{2+} or Fe^{3+}, leading to the quenching of Al^{3+}-1 complex. However, the receptor 1 still can be used as a selective fluorescent sensor for Al^{3+} in the presence of most competing metal ions.

To better understand the complexation behavior of receptor 1 with Al^{3+}, ^{1}H NMR titration experiments were carried out in CD_3CN. The spectral differences were depicted in Fig. 6. The imine proton of receptor 1 at around 8.45 ppm was shifted upfield towards 8.25 ppm upon the addition of Al^{3+}. In addition, two protons of phenol were showed at around 10.18 and 9.81 ppm, respectively. These observations obviously indicated that the phenolic O-H and the nitrogen atom of the imine were participated in the interaction with Al^{3+}.

In summary, we prepared simple receptor 1 for the detection of selected metal ions. Receptor 1 displayed dramatic change in enhanced fluorescence intensity selectively for Al^{3+} over other ions in CH_3CN. More importantly, the detection limit was sufficiently low to detect submicromolar concentration of the Al^{3+}. Thus, we trust that receptor 1 has an ability to serve as a practical sensor for Al^{3+} detection in biological system and environment.

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