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Fluorescent sensor for selective detection of Al^{3+} based on quinoline–coumarin conjugate

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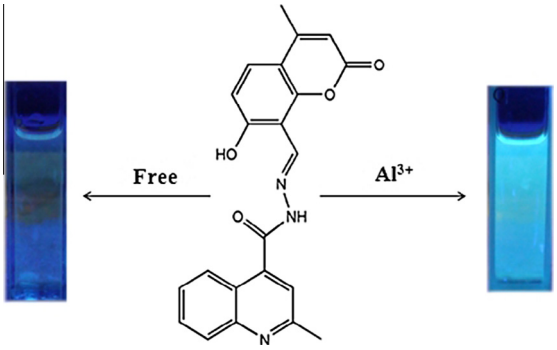
HIGHLIGHTS

- We have designed a new chemosensor for aluminum ions.
- 2-Methyl quinoline-4-carboxylic hydrazide was rarely synthesized.
- **L** shows a large fluorescence enhancement with turn-on over 200-fold in ethanol.
- It has lower detection limit.

GRAPHICAL ABSTRACT



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ABSTRACT

A fluorescence probe, 8-formyl-7-hydroxyl-4-methyl coumarin – (2′-methylquinoline-4-formyl) hydrazone (**L**) has been synthesized. The chemosensor is found preferential binding to Al^{3+} in presence of other competitive ions with associated changes in its optical and fluorescence spectra behavior. Upon addition of Al^{3+} to a solution of **L**, it shows 200-fold enhancement of fluorescence intensity which might be attributed to form a 2:1 stoichiometry of the binding mode of **L**—Al(III) and the chelation enhanced fluorescence (CHEF) process at 479 nm in ethanol. The lowest detection limit for Al^{3+} is determined as 8.2×10^{-7} M.

Introduction

As is known, the Al^{3+} ion existing in natural waters and most plants can enter the human body through water and foods [1]. WHO has listed aluminum ion as a source of food pollution and limited its drinking water concentration to 7.41 mM [2–4]. Accumulation of an excessive amount of the metal causes illnesses like Alzheimer's disease, Guamanian amyotrophic lateral sclerosis and Parkinsonism dementia. Therefore, it is crucial to develop some analytical methods for detecting and controlling the concentration levels of aluminum in the environment. In recent years, several methods are available for detection of Al^{3+}. In comparison to some conventional methods, fluorescent chemosensor have attracted considerable attention due to its easily detectable signals upon recognition metal ions with high sensitivity and selectivity [5–9].

On the other hand, because of the low coordination ability of Al^{3+}, the development of Al^{3+} sensors has been found to be comparatively more difficult than other metals. In general, as Al^{3+} is a hard-acid, it has been found that Al^{3+} prefers a coordination sphere containing N and O as hard-base donor sites. Schiff bases (imines) are known to be good ligands for metal ions [10–14]. The

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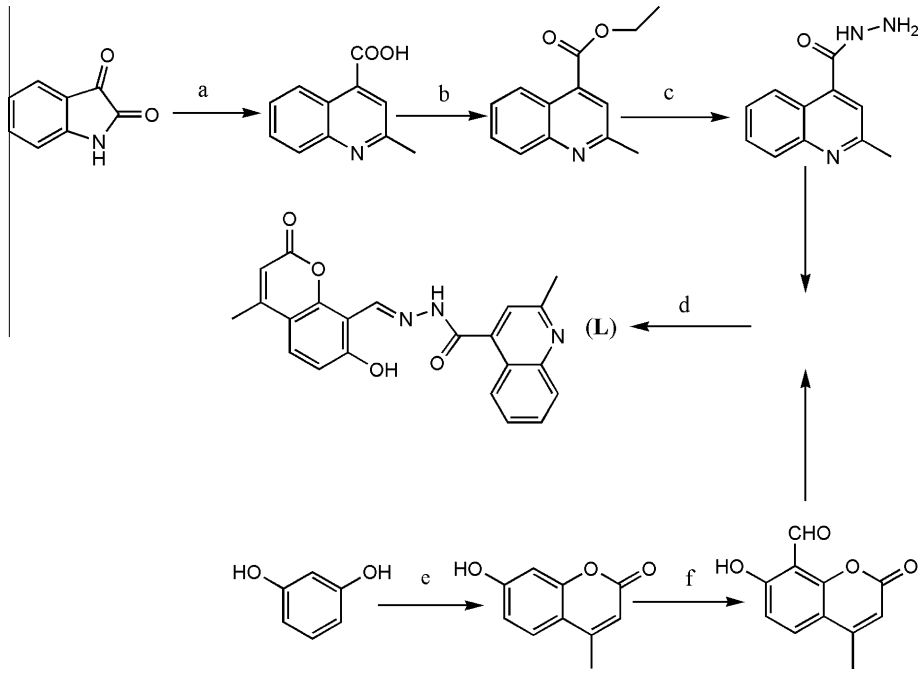

Scheme 1. Reagents and conditions: (a) (i) acetone, aq KOH, reflux, 15 h; (ii) conc HCl; (b) conc H_2SO_4, EtOH, reflux, 18 h; (c) EtOH, $N_2H_4{\cdot}H_2O$, 20 h; (d) EtOH, reflux, 10–12 h; (e) conc H_2SO_4, $CH_3COCH_2COOC_2H_5$, −5 °C; (f) HMT.

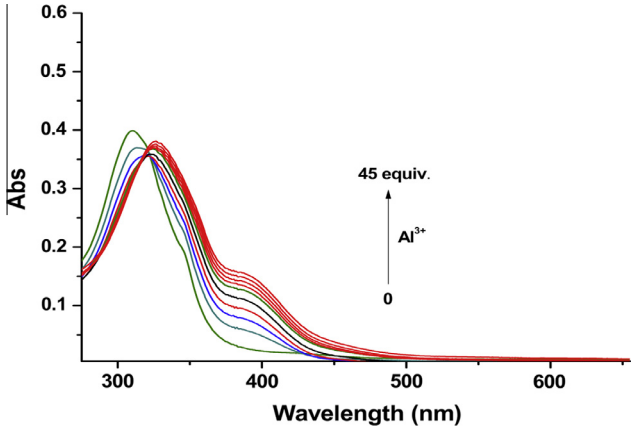

Fig. 1. Changes in the absorption spectra of **L** (10 μM) in ethanol at room temperature as a function of added Al^{3+} (0, 5, 10, 15, 20, 25, 30, 35, 40, 45 equiv.).

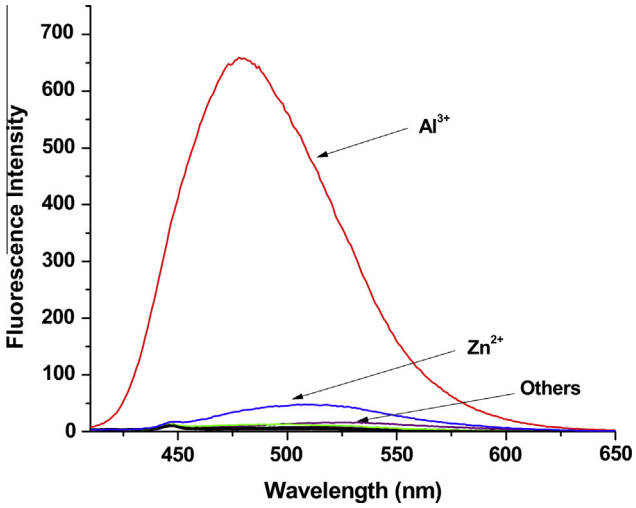

Fig. 2. Fluorescence spectra of **L** (10 μM) upon the addition of metal salts (1.0 equiv.) of Na^+, K^+, Mg^{2+}, Ca^{2+}, Pb^{2+}, Cr^{3+}, Mn^{2+}, Fe^{2+}, Ni^{2+}, Co^{2+}, Fe^{3+}, Ru^{3+}, Cu^{2+}, Ba^{2+}, Cd^{2+}, Hg^{2+}, $Zn^{2+}$and Al^{3+} in ethanol (λ_{ex} = 392 nm, slit widths: 5 nm/5 nm).

structures of Schiff bases contain nitrogen–oxygen-rich coordination environments which provide a hard-base environment for the hard-acid Al^{3+} [15]. More importantly, Schiff base derivatives equipped with a fluorescence moiety are attractive tools for the detection of metal cations. Keeping this in mind, we have designed a Schiff-base ligand, which was synthesized by condensing 2-methyl quinoline-4-carboxylic hydrazide with 8-formyl-7-hydroxyl-4-methyl coumarin. Thus far, to the best of our knowledge, there are no reports on the properties of the Schiff base.

Herein, we report a novel coumarin-based "turn-on" fluorescent probe for the determination of Al^{3+} in ethanol, which is attributed to a chelation-enhanced fluorescence (CHEF) process. It forms a 2:1 complex and the binding constants K_a is 3.3×10^6. The free chemosensor **L** shows weak fluorescence emission. Upon binding of Al^{3+} ions, a significant fluorescence enhancement over 200-fold is achieved in ethanol.

Experimental

General

All chemicals were obtained from commercial suppliers and used without further purification. ^{1}H NMR spectra were measured on the Bruker 400 MHz instruments using TMS as an internal standard. ESI-MS were determined on a Bruker esquire 6000 spectrometer. UV–vis absorption spectra were determined on a Shimadzu UV-240 spectrophotometer. Fluorescence spectra were recorded on a Hitachi RF-4500 spectrophotometer equipped with quartz cuvettes of 1 cm path length.