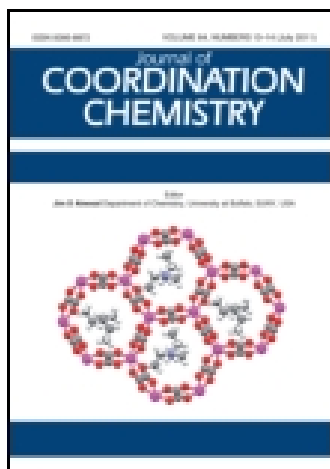


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A highly selective and sensitive fluorescent turn-on chemosensor for Al^{3+} based on a chromone Schiff base

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A Schiff-base fluorescent sensor, 7-methoxychromone-3-carbaldehyde-(3',4'-dimethyl)pyrrole hydrazone (MCPH), was synthesized. The new sensor showed high selectivity for Al^{3+} over other metal ions examined in acetonitrile. Upon binding Al^{3+} , a significant fluorescence enhancement with a turn-on ratio over 101-fold was triggered. The detection limit of MCPH for Al^{3+} was $2.5 \times 10^{-7} \text{ mol L}^{-1}$.

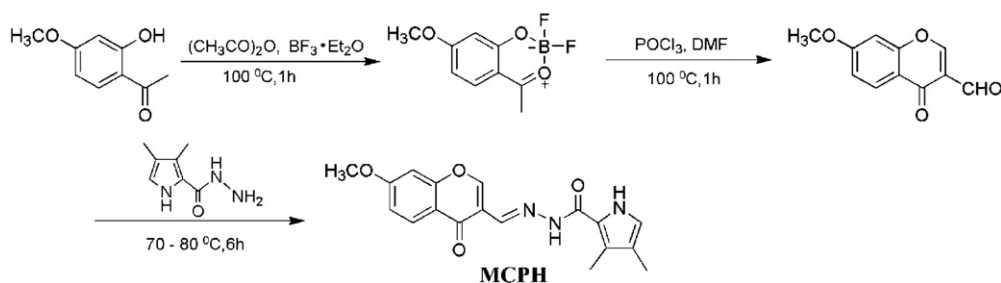
Keywords: Fluorescence sensor; Chromone; Aluminum ion

1. Introduction

Aluminum is the third most prevalent element and most abundant metal in the earth's crust. It has been widely used in many industrial fields, including the manufacturing of cars and computers [1–3]. Conversely, Al^{3+} has gained prominence through a possible biochemical link to Alzheimer's disease by its toxicity. According to a World Health Organization report, the average human intake of aluminum is 3–10 mg per day [4]. Due to the potential impact of Al^{3+} on human health and the environment, highly selective and sensitive chemosensors for Al^{3+} are needed.

Standard techniques, such as atomic absorption or inductively coupled plasma atomic emission spectrometry, are expensive and time-consuming in practice. Advances of molecular fluorescence for sensing and switching include high sensitivity of detection down to the single molecule, “on-off” switchability, feasibility of human-molecule communication, subnanometer spatial resolution with submicron visualization, and submillisecond temporal resolution [5]. Owing to weak coordination and strong hydration of Al^{3+} in water, coexistence of interfering ions is a problem [6–9]. Therefore, design of a highly selective chemosensor for Al^{3+} with “turn-on” type fluorescence changes remains desirable. In 2011, Lu *et al.* displayed a photoinduced electron transfer (PET)-based chemosensor possessing dual PET processes by simultaneously

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Scheme 1. Synthesis of MCPH.

introducing both nitrogen and sulfur donors [10]. Very recently a new Al^{3+} sensor based on salicylimine has been reported by Soojin Kim and co-workers [11]. This article reports a fluorescent Al^{3+} chemosensor, 7-methoxychromone-3-carbaldehyde-(3',4'-dimethyl)pyrrole hydrazone (MCPH), which was synthesized by Schiff-base condensation of 7-methoxychromone-3-carbaldehyde and 3,4-dimethylpyrrole hydrazone (scheme 1). MCPH has been chosen because of its availability by classical organic syntheses and low detection limit; free MCPH shows no fluorescence. Upon binding of Al^{3+} , a significant fluorescence enhancement with turn-on ratios over 101-fold was achieved in CH_3CN .

2. Experimental

2.1. Materials and instrumentation

All chemicals were obtained from commercial suppliers and used without purification. ^1H NMR spectra were measured on a Bruker 400 MHz instrument using TMS as an internal standard. Electrospray ionization mass spectra (ESI-MS) were determined on a Bruker Esquire 6000 spectrometer. UV-Vis absorption spectra were recorded 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. Elemental analyses were carried out on an Elemental Vario EL analyzer.

2.2. Synthesis

7-Methoxychromone-3-carbaldehyde was obtained according to literature procedures [12]. Synthesis of MCPH was based on the following method: a methanol solution (10 mL) which contained 3,4-dimethylpyrrole hydrazone (0.153 g, 1 mmol) was added dropwise to 7-methoxychromone-3-carbaldehyde (0.204 g, 1 mmol) ethanol solution (20 mL). With stirring at 70–80 °C for 6 h, white precipitates were collected then recrystallized from DMF/methanol (1:1, V/V), m.p. 181–183 °C, yield: 48.3%. ^1H NMR ($\text{DMSO}-d_6$, 400 MHz): δ 11.16 (s, 1H), 8.75 (s, 1H), 8.06 (d, 1H), 7.22 (d, 1H), 7.12 (m, 1H), 6.79 (s, 1H), 3.91 (s, 3H), 2.24 (s, 3H), 1.96 (s, 3H).

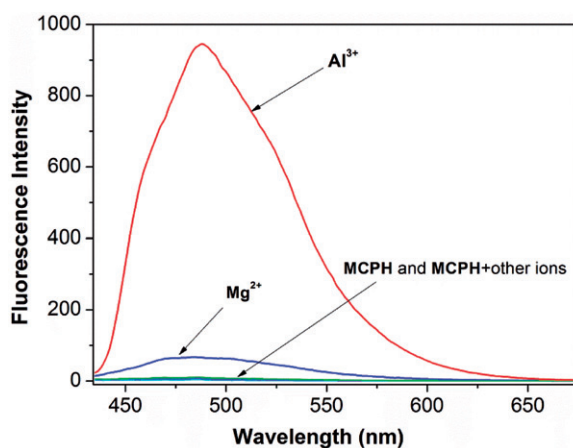


Figure 1. Fluorescence responses of MCPH ($50.0 \mu\text{mol L}^{-1}$) in CH_3CN with $500.0 \mu\text{mol L}^{-1}$ of Ni^{2+} , Na^+ , Mg^{2+} , K^+ , Fe^{3+} , Cu^{2+} , Cr^{3+} , Co^{2+} , Cd^{2+} , Ca^{2+} , and $50.0 \mu\text{mol L}^{-1}$ of Al^{3+} . Excitation wavelength was at 425 nm.

2.3. Analysis

Stock solutions (5 mmol L^{-1}) of the nitrate salts of Ni^{2+} , Na^+ , Mg^{2+} , K^+ , Fe^{3+} , Cu^{2+} , Cr^{3+} , Co^{2+} , Cd^{2+} , Ca^{2+} , and Al^{3+} in CH_3CN were prepared. Stock solutions of MCPH (5 mmol L^{-1}) were prepared in CH_3CN . Test solutions were prepared by placing $20 \mu\text{L}$ of the probe stock solution into cuvettes, adding an appropriate aliquot of each ion stock, and diluting the solution to 2 mL with CH_3CN . Both the excitation and emission slit widths were 5.0 nm .

3. Results and discussion

MCPH forms colorless and non-fluorescent solutions in either aqueous media or organic solvents, including DMF, THF, DMSO, ethanol, methanol, or CH_3CN . Addition of aluminum ions to MCPH in ethanol, methanol, and CH_3CN leads to yellow-green color and yellow-green fluorescence (figure S1).

The photophysical properties of MCPH were investigated by monitoring the fluorescence behavior upon addition of several metal ions in CH_3CN . At 425 nm excitation, MCPH alone did not show any fluorescence. The addition of Ni^{2+} , Na^+ , Mg^{2+} , K^+ , Fe^{3+} , Cu^{2+} , Cr^{3+} , Co^{2+} , Cd^{2+} , and Ca^{2+} respond with very little enhancement in the fluorescence intensity. In contrast, addition of Al^{3+} results in a great enhancement of the emission intensity positioned around 484 nm as shown in figure 1.

The lone pair electrons from the Schiff-base nitrogen contributed to PET phenomenon, which quenched fluorescence emission of MCPH. The quenched fluorescence could increase dramatically upon chelating the metal ion by a highly efficient chelation-enhanced fluorescence (CHEF) effect [13–17]. In the emission spectrum, the fluorescence intensity of MCPH ($\Phi F=0.140$) increased remarkably at 485 nm ($\Phi F=0.366$) upon addition of Al^{3+} , as shown in figure 2.

The changes in UV-Vis absorption spectra are shown in figure S2. Upon addition of Al^{3+} , absorbances at 390 nm and 450 nm were enhanced and decreased at 290 nm of the

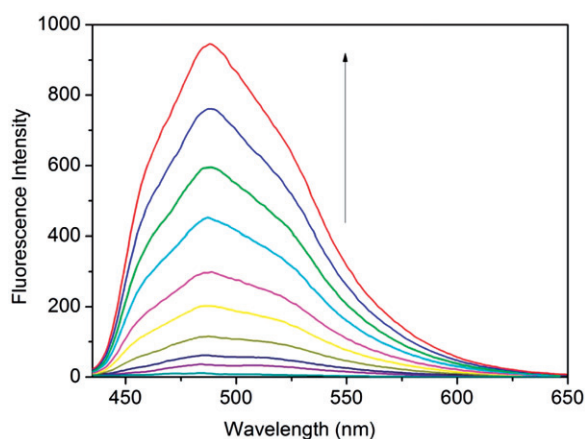


Figure 2. Fluorescence emission spectra of MCPH ($50.0 \mu\text{mol L}^{-1}$) in CH_3CN upon addition of Al^{3+} (0, 0.1, 0.2, 0.3, 0.4, 0.5, 0.6, 0.7, 0.8, 0.9 equiv.) with an excitation of 425 nm.

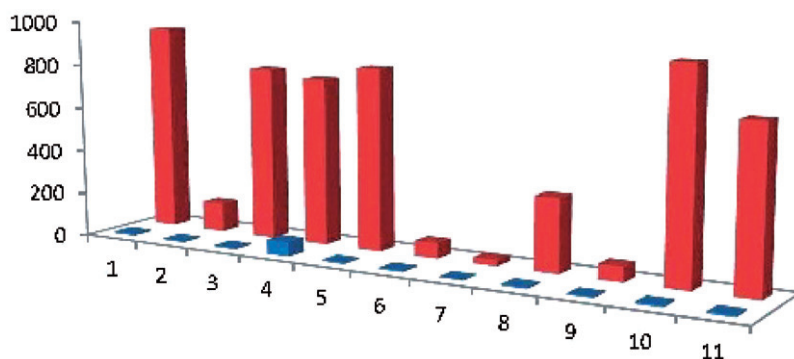


Figure 3. Relative fluorescence of MCPH and its complexation with Al^{3+} in the presence of various metal ions. Front bar: MCPH ($50.0 \mu\text{mol L}^{-1}$) and MCPH with 10 equiv. of Ni^{2+} , Na^+ , Mg^{2+} , K^+ , Fe^{3+} , Cu^{2+} ,

UV-Vis spectra. A clear isosbestic point was observed at 325 nm when spectra were recorded with varying concentrations of Al^{3+} .

To explore the possibility of using MCPH as a practical ion selective fluorescent chemosensor for Al^{3+} , competition experiments were carried out. For this purpose, MCPH was treated with 2 equiv. of Al^{3+} in the presence of 10 equiv. of other metal ions. Relatively low interference was observed for detection of Al^{3+} in the presence of other metal ions (figure 3). MCPH response for Al^{3+} in the presence of Ni^{2+} , Fe^{3+} , Cu^{2+} , and Co^{2+} are relatively low but clearly detectable. Therefore, MCPH is a promising selective fluorescent sensor for Al^{3+} in the presence of competing metal ions.

As shown in figure S3, the association constant K_a of the complex was then calculated to be $3.05 \times 10^4 (\text{mol L}^{-1})^{-1}$ with a linear relationship by Benesi–Hildebrand method (equation (1)) [18].

$$\frac{1}{F - F_{\min}} = \frac{1}{K(F_{\max} - F_{\min})[\text{Al}^{3+}]} + \frac{1}{F_{\max} - F_{\min}}. \quad (1)$$

From the changes in Al^{3+} -dependent fluorescence intensity (figure S4), the detection limit was estimated to be $2.5 \times 10^{-7} \text{ mol L}^{-1}$ [19–22].

Reversibility is a prerequisite in developing chemosensors for practical application. The reversibility of recognition of MCPH was studied by adding an Al^{3+} binding agent, EDTANa_2 . The addition of EDTANa_2 to a mixture of MCPH and Al^{3+} resulted in diminution of the fluorescence intensity at 485 nm, which indicated regeneration of free MCPH (figure S5). Such reversibility and regeneration are important for fabrication of devices to sense Al^{3+} .

NMR spectroscopy was used to ascertain the binding mode of the ligand and Al^{3+} . ^1H NMR spectra of MCPH were recorded in CD_3CN upon addition of Al^{3+} (figure S6). H_a undergoes a downfield shift of 0.21 ppm upon addition of Al^{3+} , signals of H_b , H_c , and H_d were downfield shifted, and signals of the other protons remained nearly unchanged. This indicated direct involvement of carbonyl of chromone, nitrogen of $-\text{C}=\text{N}$, and the carbonyl of pyrrole hydrazone in coordinating to Al^{3+} .

A Job plot obtained from UV-Vis absorption showed 2:1 stoichiometric complexation between MCPH and Al^{3+} (figure S7). The 2:1 binding stoichiometry was further confirmed by elemental analysis data: Anal. Found (Calcd for $\text{C}_{36}\text{H}_{32}\text{AlN}_7\text{O}_{11}$, 765.25): C, 56.39 (56.47); H, 4.15 (4.21); N, 12.73 (12.81), which match with the 2:1 complex of MCPH-Al. The ESI-MS also provided additional evidence for the formation of a 2:1 complex of MCPH-Al with a peak of $[\text{2MCPH-Al}]^+$ at m/z 703.4 (figure S8).

IR spectra of MCPH and its Al(III) complex are presented in figure S9. For the complex, $\nu_{(\text{hydrazonic})} \text{C}=\text{O}$, $\nu_{(\text{carbonyl})} \text{C}=\text{O}$, and $\nu_{\text{C}=\text{N}}$ vibrations were at 1618, 1662, and 1577 cm^{-1} , respectively. For free ligand, these peaks were at 1653, 1625, and 1606 cm^{-1} , respectively. The $\nu_{(\text{ligand-complex})}$ was 35, 37, and 29 cm^{-1} , respectively, demonstrating that these three groups coordinate to Al^{3+} . The peak of $\nu_{(\text{hydrazonic})} \text{C}=\text{O}$ in the complex was weak, maybe because of hydrazide carbonyl enolization. The six coordination of Al^{3+} can be satisfied by two MCPH molecules. Enhancement of fluorescence intensity of MCPH is due to metal binding to $-\text{C}=\text{N}$ moiety followed by PET suppression.

4. Conclusion

We have developed a chemosensor based on PET and CHEF mechanism which exhibited high selectivity for Al^{3+} over other metal ions with 101-fold fluorescence enhancement and high sensitivity with the detection limit reaching $10^{-7} \text{ mol L}^{-1}$ in CH_3CN . MCPH could serve as an excellent chemosensor for the highly toxic aluminum ion.

Acknowledgments

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