

Short communication

Novel 4,5-diazafluorene-based Schiff base derivatives as Al³⁺ ions fluorescence turn-on sensorsShu Jiang Zhang^{a,*}, Hui Li^{a,b}, Chen Liang Gong^a, Jian Zhi Wang^b, Zhong Ying Wu^a, Feng Wang^{b,*}^a College of Chemistry and Chemical Engineering, Lanzhou University, Lanzhou 730000, PR China^b Key Laboratory for Green Chemical Process of Ministry of Education, School of Chemical Engineering and Pharmacy, Wuhan Institute of Technology, Wuhan 430073, PR China

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ABSTRACT

A new 4,5-diazafluorene-based fluorescent chemosensor has been synthesized by Schiff base condensation of 9,9-bis(3-methyl-4-aminophenyl)-4,5-diazafluorene with salicylaldehyde. The interaction of Schiff base with different metal ions has been studied over UV–vis absorption spectra and photofluorescent spectra. The results were indicated that Schiff base exhibited turn-on fluorescent behavior with Al³⁺ ions in ethanol. Such fluorescent responses could be detected by naked eye under UV-lamp. The limit of detection was calculated to be 4.2 ppm by titration method.

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1. Introduction

In recent years, fluorescent chemosensors have attracted significant interest because of their potential applications in medicinal and environmental research. Due to the fluorescence quenching effects of biologically important ions, the development of fluorescence turn-on sensors still remains a challenging task. Thus, many fluorescent chemosensors specific for Hg²⁺, Cu²⁺, Zn²⁺ or other transition metals have been developed. Compared to these transition metal ions, only a few fluorescent chemosensors have been reported for detection of Al³⁺ [1–24].

Aluminum is one of the most frequently found compounds in the earth's crust. It forms approximately 8% of earth mass [17]. Al³⁺ ions existing in natural waters and most plants can enter the human body through foods and water [25]. The normal concentration range for aluminum ions in biological systems is narrow, with both deficiency and excess causing many pathological states, such as Alzheimer's disease, Parkinson's disease, chronic renal failure, bone softening and smoking related diseases [26–30]. Since there is a close association between Al³⁺ and human health, developing fluorescent chemosensors with high selectivity and sensitivity for detecting trace amounts of Al³⁺ has attracted

increasing attention. In the past several years, considerable efforts have been made to develop fluorescent chemosensors for Al³⁺ ions based on hydrazones [31–34], Schiff based [35–37], coumarin [3,38], pyrrolidine [1,2], calixarene [39,40], hydroxyflavone [41,42], 8-hydroxyquinoline [43], oxazoline and imidazoline [44] derivatives have been synthesized and used for this purpose. However, the detection of Al³⁺ has always been problematic due to the lack of spectroscopic characteristics and poor coordination ability [21]. Therefore, for practical applications, it is still desirable to develop simple Al³⁺ sensors with good selectivity and sensitivity. The 4,5-diazafluorene derivatives have been chosen as an ideal component of a fluorescent chemosensor due to its large π -system and bidentate coordination ability with various transition [45]. The present study is aimed to serve these purposes to develop the specific sensory materials for Al³⁺ ion detections with optical turn-on responses.

Herein, we report the synthesis and characterization of a Schiff base ligand (L) as Al³⁺ turn-on sensors. The interaction of Schiff base with different metal ions has been studied over UV–vis absorption spectra and photofluorescent spectra.

2. Experiment

2.1. Materials and instrumentation

The reactants 4,5-diazafluorene-9-one (1) [46] was prepared according to the literature. 2-Methylaniline (Tianjin Guangfu) was

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purified by distillation prior to use. All organic solvents were of analytical reagent grade. Nitrate and chloride salt of all cations used were of high purity and used without any purification.

The ^1H NMR and ^{13}C NMR spectra were measured on a JEOL EX-400 spectrometer using Acetone- d_6 or DMSO- d_6 as solvent and tetramethylsilane as the internal reference. UV–vis spectra were examined on a Pgeneral TU-1810 spectrophotometer and fluorescence recorded on a F96PRO spectrofluorophotometer with excitation slit at 10.0 nm and emission at 20.0 nm.

The stock solution for **L** were prepared in DMSO (5 mM), stock solution for nitrate and chloride salt of different metals of Ag^+ , Al^{3+} , Ba^{2+} , Ca^{2+} , Cd^{2+} , Co^{2+} , Cr^{3+} , Cu^{2+} , Fe^{2+} , Fe^{3+} , Hg^{2+} , K^+ , Mn^{2+} , Na^+ , Ni^{2+} and Pb^{2+} were prepared in ethanol. All the metal ion solutions for the study were prepared in distilled water.

2.2. Monomer synthesis

2.2.1. Synthesis of 9,9-bis(3-methyl-4-aminophenyl)-4,5-diazafluorene (**2**)

9,9-bis(3-methyl-4-aminophenyl)-4,5-diazafluorene was synthesized by accordingly to describe the method in Scheme 1. Trifluoromethanesulfonic acid (4.08 g, 27.2 mmol) was slowly added to the 2-Methylaniline (14.9 g, 139.49 mmol) was placed in a 100 ml three-necked flask with magnetic stirring and a nitrogen inlet. Then, 4,5-diazafluorene-9-one (3.62 g, 19.92 mmol) was added. The mixture was heated to 165 °C for 24 h under an atmosphere of nitrogen with continuous stirring. The solution was cooled below 80 °C followed by neutralization with a solution of 5% sodium hydroxide. The precipitate was filtered and washed with water. The crude product was purified by recrystallization to give a white powder (4.48 g, yield: 59.49%), M.p.: 312–314 °C.

IR (KBr, cm^{-1}): 3369 (NH), 1500 cm^{-1} (C=N); ^1H NMR (400 MHz, Acetone- d_6 , δ , ppm, TMS, Fig. 1): 2.01 (s, 6H, $-\text{CH}_3$), 4.29 (s, 4H, $-\text{NH}_2$), 6.54 (dd, H^7 , 2H), 6.76 (t, H^4 , H^6 , 4H), 7.30 (dd, H^{11} , 2H), 7.83 (dd, H^{10} , 2H), 8.61 (dd, H^{12} , 2H); ^{13}C NMR (100 MHz, Acetone- d_6 , δ , ppm, TMS, Fig. 1): 17.7 (C^2), 61.0 (C^8), 115.2 (C^7), 122.4

(C^{11}), 123.9 (C^6), 127.2 (C^3), 130.4 (C^4), 133.6 (C^9), 134.5 (C^{10}), 146.1 (C^5), 148.5 (C^1), 150.2 (C^{12}), 158.7 (C^{13}).

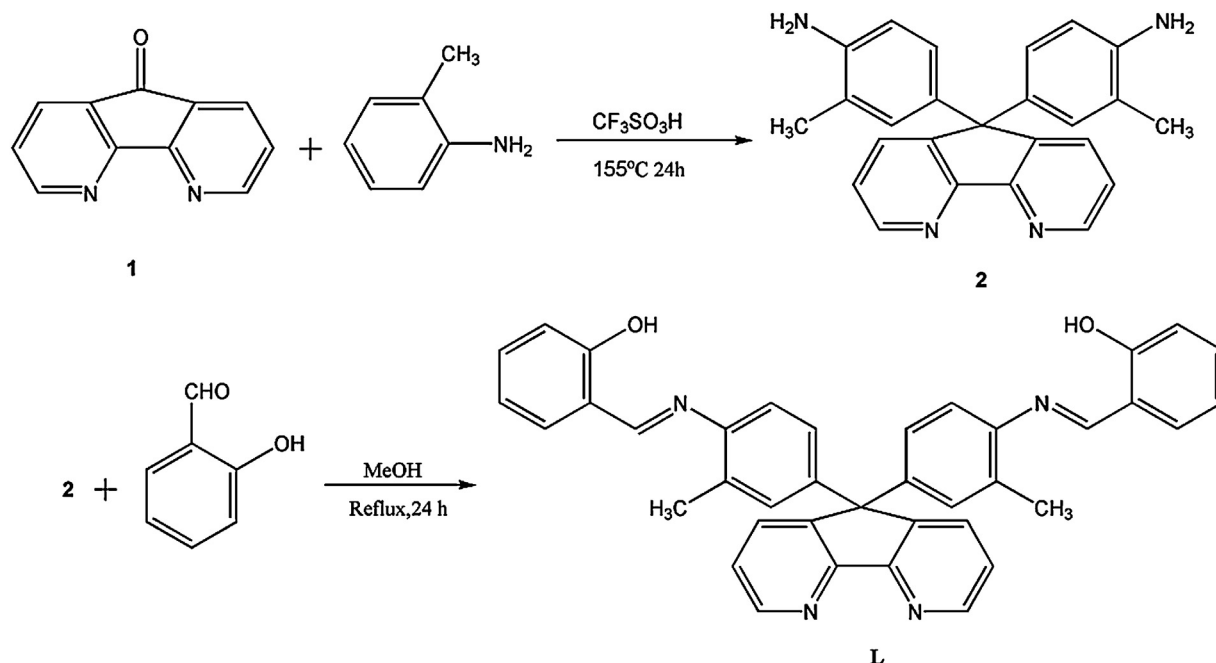
2.2.2. Synthesis of 4,5-diazafluorene Schiff bases (**L**)

9,9-bis(3-methyl-4-aminophenyl)-4,5-diazafluorene (0.152 g, 0.4 mmol) was placed into a 100 ml round-bottom flask which was fitted with condenser, thermometer and magnetic stirrer. methanol (50 ml) was added into the flask and reaction mixture was heated up to 80 °C. A solution of salicylaldehyde (0.146 g, 1.2 mol) in 20 ml methanol was added into the flask. Reactions were maintained for 24 h under reflux. The precipitated monomers were filtered hot and dried in a vacuum desiccator. (0.23 g, yield: 98.1%). ^1H NMR (DMSO- d_6 , δ , ppm, TMS, Fig. 2): 8.84 (s, H^7 , 1H), 8.73 (d, H^{19} , 1H), 8.08 (d, H^{17} , 1H), 7.62 (d, H^5 , 1H), 7.46 (dd, H^3 , 1H), 7.41 (t, H^{18} , 1H), 7.26 (d, H^2 , 1H), 7.10 (m, H^9 , H^{10} , 2H), 6.94–6.99 (m, H^4 , H^{12} , 2H), 3.53 (s, $-\text{OH}$), 2.23 (s, $-\text{CH}_3$). ^{13}C NMR (DMSO- d_6 , δ , ppm, TMS, Fig. 2): 191.6 (C^1), 167.7 (C^7), 160.2 (C^{20}), 156.7 (C^8), 149.9 (C^{19}), 147.1 (C^{11}), 145.6 (C^{17}), 140.0 (C^3), 136.2 (C^{13}), 134.2 (C^{16}), 133.4 (C^{12}), 132.4 (C^5), 128.2 (C^{10}), 127.3 (C^9), 123.9 (C^4), 119.1 (C^{18}), 118.9 (C^6), 60.0 (C^{15}), 18.3 (C^{14}).

3. Result and discussion

In order to perform the fluorescence characterization of the **L**, the emission spectra of **L** in the presence of 1.0 equiv. of Al^{3+} were recorded in different solvents. As shown in Fig. 3, on the addition of 1.0 equiv. of Al^{3+} , the fluorescence intensity of **L** increased in EtOH and MeOH, there was no obvious change in THF, CH_3CN and DMSO. Since the highest fluorescence intensity of **L** was observed in EtOH, so the EtOH was choose as the test solvent.

The chemosensor behavior of receptor **L** with the following 16 metal ions: Al^{3+} , Ag^+ , Ba^{2+} , Ca^{2+} , Cd^{2+} , Co^{2+} , Cr^{3+} , Cu^{2+} , Fe^{2+} , Fe^{3+} , Hg^{2+} , K^+ , Mn^{2+} , Na^+ , Ni^{2+} and Pb^{2+} in EtOH was investigated by UV–vis and fluorescence measurements. As seen in Fig. 4, the absorption spectrum of receptor **L** exhibited three absorbance peak. The intense absorption band in high energy region at 232 nm was assigned to $\pi \rightarrow \pi^*$ transitions, and a small hump at 258 nm



Scheme 1. Synthesis of the Schiff base **L**.

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