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A Unique Water-Tuning Dual-Channel Fluorescence-Enhanced Sensor for Aluminum Ions Based on a Hybrid Ligand from a 1,1′-Binaphthyl Scaffold and an Amino Acid**

Tian-Hua Ma, Ming Dong, Yu-Man Dong, Ya-Wen Wang,* and Yu Peng*[a]

Supramolecular chemistry based on host–guest interactions and self-organization first harnessed preorganization for the design of tailor-made molecular receptors effecting molecular recognition, catalysis, and transport on a variety of substrates, from metal ions to anions and chiral molecular substrates.[1] Guided by the above principle, fluorescent sensors are widely used as powerful tools to observe molecular recognition events owing to their high sensitivity, selectivity, versatility, and relatively simple handling.[2] To date, some of them are single-channel fluorescent sensors (SCF sensors), which exhibit changes of fluorescence intensity only at a single wavelength in the presence of an analyte. However, the fluorescence intensity is easily influenced by many factors, such as instrumental efficiency, environmental conditions, and the sensor concentration.[3] To this end, dual-channel fluorescent sensors (DCF sensors)[4] are more attractive because they provide internal calibration through dual-channel output for more precise measurement of an analyte. Therefore, considerable efforts have been devoted to the development of DCF sensors, most of which contain two chromophores[5] connected together with the analyte recognition site through a covalent bond. In contrast to successful developments of this kind of DCF sensors, DCF sensors with one fluorophore have rarely been developed so far, partly owing to the unpredictability of their photophysical behaviors. A common feature of DCF sensors is that substrate binding leads to enhancement of one emission channel at the expense of the other; dual-channel fluorescence-enhanced sensors are rare. Thus, the design of an efficient dual-channel fluorescence-enhanced sensor with only one fluorophore for specific analyte is still a huge challenge.

Aluminum is the most abundant metal in Earth's crust and is extensively used in modern life.[6] But it is neurotoxic to humans and induces many heath issues, such as Alzheimer's disease[7a] and Parkinson's disease.[7b] To this end, the development of sensors for the facile detection of Al^{3+} is of great importance in environmental monitoring and biological assays. However, owing to the weak coordination and strong hydration ability of Al^{III} in water, it is easily interfered with by the variation of the pH value of the solution and the coexistence of interfering ions. In comparison with transition-metal ions, scarce examples of fluorescence sensors have been reported for Al^{3+} so far and most of them have displayed limited sensitivity or selectivity.[8] In 2008, Lin et al.[8d] displayed the first example of a dual-channel fluorescence-enhanced Al^{3+} sensor with two fluorophores in mixed organic solvents. Very recently a new Al^{3+} SCF sensor based on anthraquinone has been reported by Kim and co-workers.[8a] Nevertheless, their dual optical and electrochemical sensor was operated only in CH_3CN, and was largely limited in its practical application. Therefore, it is highly desirable to develop more sophisticated and more selective Al^{3+} sensors that can be easily handled in both aqueous and nonaqueous solution.

Inspired by L-DOPA as an efficient treatment for Parkinson's disease,[9] herein, we present the design, synthesis, and characterization of a new water-soluble turn-on DCF aluminum sensor (*R*)-**1** with multiple binding sites of harder donors such as oxygen and nitrogen atoms and an efficient fluorophore (1,1′-binaphthyl)[10] in the molecular skeleton. The fluorescence behavior of (*R*)-**1** toward Al^{3+} was found to be strongly dependent on the nature of the employed medium (Figure 1). In CH_3OH, (*R*)-**1** is developed as a SCF sensor that can show selectivity toward Al^{3+}, whereas (*R*)-**1** becomes an efficient DCF-enhanced ratiometric sensor for

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[a] T.-H. Ma, M. Dong, Y.-M. Dong, Prof. Dr. Y.-W. Wang,
Prof. Dr. Y. Peng
Key Laboratory of Nonferrous Metal Chemistry
and Resources Utilization of Gansu Province
State Key Laboratory of Applied Organic Chemistry
and College of Chemistry and Chemical Engineering
Lanzhou University, Lanzhou 730000 (P.R. China)
Fax: (+86) 931-8912582
E-mail: ywwang@lzu.edu.cn
pengyu@lzu.edu.cn

[**] Tian-Hua Ma and Ming Dong contributed equally to this work.

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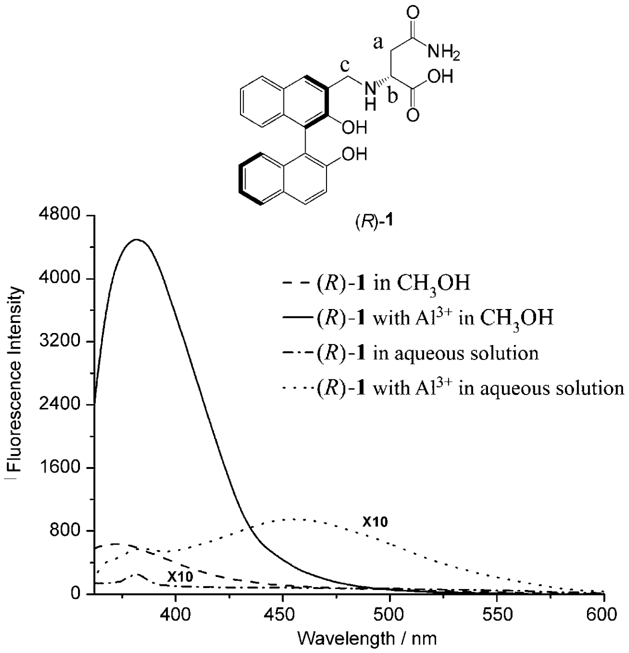

Figure 1. The sensor (*R*)-**1** (top) and fluorescence spectra of (*R*)-**1** or (*R*)-**1** with Al^{3+} in different solutions (bottom). ($\lambda_{ex}=337$ nm, slit = 5.0 nm/5.0 nm).

Al^{3+} in aqueous solution.[11] So this unique fluorescence behavior allows the efficient detection of Al^{3+} ions both in CH_3OH and aqueous solution. To the best of our knowledge, this is the first example of a dual-channel fluorescence-enhanced ratiometric aluminum sensor through cooperative recognition assisted by H_2O.

Sensor (*R*)-**1** was synthesized according to Scheme S1 (see the Supporting Information, which also contains the detailed experimental procedure and characterization data). Firstly the fluorescence properties of (*R*)-**1** were studied in pure CH_3OH solution. As shown in Figure 2a, when excited at 337 nm, free (*R*)-**1** exhibits weak, single fluorescence emission band at 379 nm. Upon the addition of Al^{3+}, a prominent fluorescence enhancement was observed with a slightly bathochromic shift from 379 to 383 nm denoted as CHEF (chelation-enhanced fluorescence).[12] The total fluorescence intensity of (*R*)-**1** was enhanced 6.3-fold when 1.0 equiv of Al^{3+} was present, and a further increase in Al^{3+} concentration led to slight fluorescence quenching. Moreover, a 1:1 stoichiometry complexation between (*R*)-**1** and Al^{3+} was obtained by using the Job's plot. The association constant *K* of the complex was then calculated to be $1.77\times10^{4}\,\text{M}^{-1}$ with a good linear relationship ($R=0.998$) by a 1:1 binding mode (see the Supporting Information, Figure S1).[13] Fluorescence measurements of (*R*)-**1** with various metal ions revealed excellent selectivity for Al^{3+} in Figure 2b. Alkali and alkaline-earth metal ions such as Li^+, Na^+, K^+, Mg^{2+}, Ca^{2+}, and Ba^{2+} hardly had any effect on the emission of (*R*)-**1**, and transition-metal and heavy-metal ions such as Mn^{2+}, Fe^{2+}, Fe^{3+}, Co^{2+}, Ni^{2+}, Cu^{2+}, Pb^{2+}, Ag^+, Cd^{2+}, Hg^{2+}, and Zn^{2+} quenched the fluorescence to different extents. These results indicated that (*R*)-**1** was highly selective for Al^{3+} in pure CH_3OH solution. The corresponding detection limit was found to be 0.80 μM (21.6 ppb) by plotting the fluorescence intensity at 383 nm versus the concentration of Al^{3+} (see the Supporting Information, Figure S4).[14]

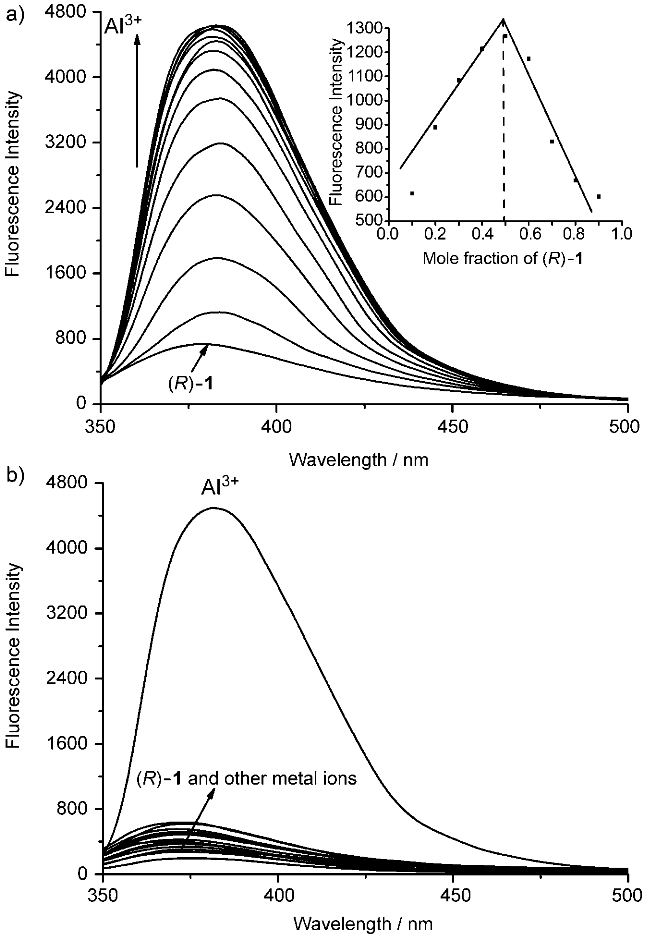

Figure 2. a) Fluorescent titrations of (*R*)-**1** (20 μM) with Al^{3+} (0.1, 0.2, 0.3, 0.4, 0.5, 0.6, 0.7, 0.8, 0.9, 1.0, 1.2, 1.5, 1.8, and 2.0 equiv) in CH_3OH. Inset: A Job's plot at 383 nm. b) Fluorescence spectra of (*R*)-**1** (20 μM) with various metal ions (Li^+, Na^+, K^+, Mg^{2+}, Ca^{2+}, Ba^{2+}, Al^{3+}, Mn^{2+}, Fe^{2+}, Fe^{3+}, Co^{2+}, Ni^{2+}, Cu^{2+}, Pb^{2+}, Ag^+, Cd^{2+}, Hg^{2+}, and Zn^{2+}; 1.0 equiv) in CH_3OH. ($\lambda_{ex}=337$ nm, slit = 5.0 nm/5.0 nm).

Considering the practical application, the fluorescence properties of (*R*)-**1** were further examined in aqueous solution. Owing to its low solubility in aqueous media, the fluorescent titrations of (*R*)-**1** with Al^{3+} proceeded in CH_3OH/H_2O (v/v = 1:99, pH 5.0) solution (Figure 3a). Compared to that in pure CH_3OH solution, the fluorescence intensity of free (*R*)-**1** was quenched up to 97% in CH_3OH/H_2O (v/v = 1:99, pH 5.0) solution. Surprisingly, intriguing dual emission signals in the range of 350–460 nm were observed upon the addition of Al^{3+} ions. The short-wavelength peak around 384 nm assigned to the monomer emission signal showed a 2.6-fold fluorescence enhancement owing to chelation-enhanced fluorescence, whereas a dramatic 11.8-fold fluorescence enhancement was observed in the long-wavelength

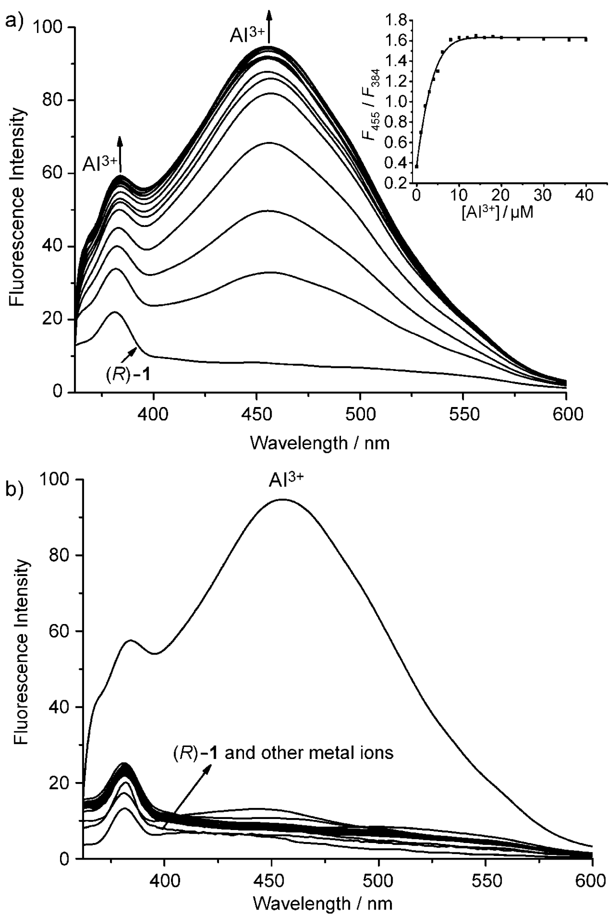

Figure 3. a) Fluorescent titrations of (*R*)-**1** (20 μм) with Al^{3+} (0.1, 0.2, 0.3, 0.4, 0.5, 0.6, 0.7, 0.8, 0.9, 1.0, 1.2, 1.5, 1.8, and 2.0 equiv) in CH_3OH/H_2O (v/v = 1:99, pH 5.0) solution. Inset: Ratiometric fluorescence intensity [F_{455}/F_{384}] as a function of [Al^{3+}]. b) Fluorescence spectra of (*R*)-**1** (20 μм) with various metal ions (Li^+, Na^+, K^+, Mg^{2+}, Ca^{2+}, Ba^{2+}, Al^{3+}, Mn^{2+}, Fe^{2+}, Fe^{3+}, Co^{2+}, Ni^{2+}, Cu^{2+}, Pb^{2+}, Ag^+, Cd^{2+}, Hg^{2+}, and Zn^{2+}; 1.0 equiv) in CH_3OH/H_2O (v/v = 1:99, pH 5.0) solution. (λ_{ex} = 337 nm, slit = 5.0 nm/5.0 nm).

emission at 455 nm as a result of the promotion of an emissive excimer channel formation.[15] Thus, sensor (*R*)-**1** displayed striking fluorescence amplification at two emission bands that is unprecedented in DCF sensors with one fluorophore.[16] The intensity ratio between 455 and 384 nm increased linearly and a 1.6-fold enhancement in the emission intensity ratio (F_{455}/F_{384}) was achieved with increasing Al^{3+} concentration. The effect of the concentration on the free (*R*)-**1** and (*R*)-**1** with Al^{3+} in CH_3OH/H_2O (v/v = 1:99, pH 5.0) solution was also studied (see the Supporting Information, Figures S7 and S8).[17] As the concentration of (*R*)-**1** with Al^{3+} increased from 2.0×10^{-6} to 2.0×10^{-4} м, the excimer emission at 455 nm increased significantly. At 2.0×10^{-6} м, (*R*)-**1** with Al^{3+} showed mainly the monomer emission. The free (*R*)-**1** exhibited only the monomer emission signal. These observations suggested that the long-wavelength emission should be attributed to the excimer emission of (*R*)-**1** with Al^{3+}. Moreover, the Job's plot method was employed by using emission changes at 455 nm as a function of the molar fraction of Al^{3+}, which revealed a 1:1 binding model between (*R*)-**1** and Al^{3+}. The same stoichiometry value was obtained by using the emission changes at 384 nm (see the Supporting Information, Figures S9 and S10). The association constant was estimated to be about 10^5 $м^{-1}$ by using the emission changes at both 455 nm and 384 nm (see the Supporting Information, Figures S2 and S3). The corresponding detection limits were both 0.80 μм (21.6 ppb) by plotting the fluorescence intensity at 384 nm or 455 nm versus the concentration of Al^{3+} (see the Supporting Information, Figure S5 and S6). In contrast, no significant fluorescence changes were observed when other metal ions (including Li^+, Na^+, K^+, Mg^{2+}, Ca^{2+}, Ba^{2+}, Mn^{2+}, Fe^{2+}, Fe^{3+}, Co^{2+}, Ni^{2+}, Cu^{2+}, Pb^{2+}, Ag^+, Cd^{2+}, Hg^{2+}, and Zn^{2+}) were added (Figure 3b). These results suggested that sensor (*R*)-**1** has a higher selectivity for Al^{3+} over other metal ions through substantial dual-channel fluorescence enhancements in CH_3OH/H_2O (v/v = 1:99, pH 5.0) solution. The pH dependence of the fluorescence intensity change of (*R*)-**1** (F_{455}/F_{381}) and (*R*)-**1** with Al^{3+} system (F_{455}/F_{384}) are shown in the Supporting Information (Figures S11–S13). The response of (*R*)-**1** with the Al^{3+} system was constant between pH 4.4 and 6.5. In this working pH range, only a small change was observed in the free (*R*)-**1** system. These results indicate that the dual-channel emission bands of (*R*)-**1** with Al^{3+} system were not produced by H^+. In subsequent experiments, a pH 5.0 solution was used as an ideal experimental condition. There was almost no change observed in the UV/vis spectra of (*R*)-**1** (277, 287 and 333 nm) upon the addition of Al^{3+} (see the Supporting Information, Figure S14).

To explore the effective applications of this sensor further, the fluorescence response of (*R*)-**1** to Al^{3+} in the presence of typical competing ions was studied both in methanol and aqueous solution. As shown in Figure 4, all competitive metal ions had no obvious interference with the detection of Al^{3+} ion. These results clearly indicated that (*R*)-**1** could be used as a potential Al^{3+}-selective fluorescent sensor. In addition, high sensitivity is also important for excellent sensors, which require a short response time. As shown in the Supporting Information (Figures S15 and S16), (*R*)-**1** displayed high sensitivity for Al^{3+} both in methanol or in aqueous solution. Thereby, sensor (*R*)-**1** is useful for selectively sensing Al^{3+} even under competition from other related metal ions, which will achieve the purpose of real-time monitoring.

As mentioned above, the photophysical properties revealed that a 1:1 complex was formed between (*R*)-**1** and Al^{3+}. Owing to the lack of an X-ray crystal structure of the complex, ^1H NMR titration experiments were carried out. As shown in Figure 5 and the Supporting Information (Figure S17), the signals of H_a, H_b, H_c, and Ar–H of (*R*)-**1** were downfield shifted upon the addition of Al^{3+} (1.0 equiv), which indicated a plausible interaction mode of (*R*)-**1**/Al^{3+} = 1:1. The binding sites of (*R*)-**1** with an aluminum ion may be OH, NH, and C=O of the carboxylic acid or the amide group. To elucidate the binding site further, the derivatives (*R*)-**2**, (*R*)-**3**, and (*R*)-**4** were synthesized by structural modi-

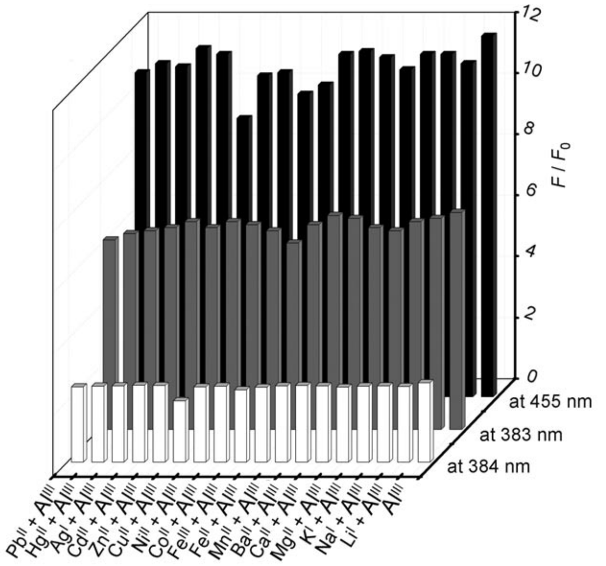

Figure 4. Metal-ion selectivity of (*R*)-**1** (20 μM). The white and black bars represent the fluorescence emission of (*R*)-**1** with the addition of 1.0 equivalent of the given ions in CH_3OH/H_2O (v/v = 1:99, pH 5.0) solution at 384 and 455 nm, respectively. The gray bars represent the fluorescence emission of (*R*)-**1** with addition of 1.0 equiv of the given ions in CH_3OH at 383 nm. All data (*F*) were normalized with respect to emission of the free sensor (*R*)-**1** (F_0).

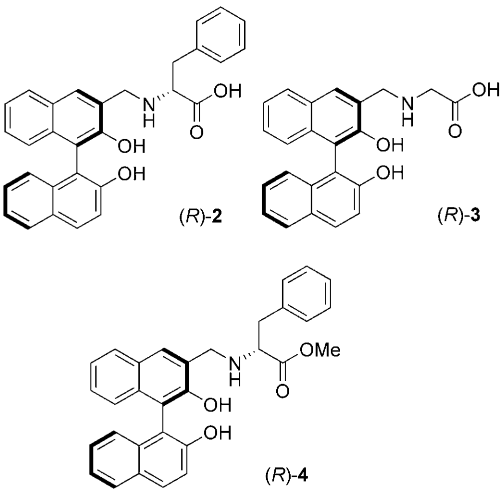

Figure 6. The structures of (*R*)-**2**, (*R*)-**3** and (*R*)-**4**.

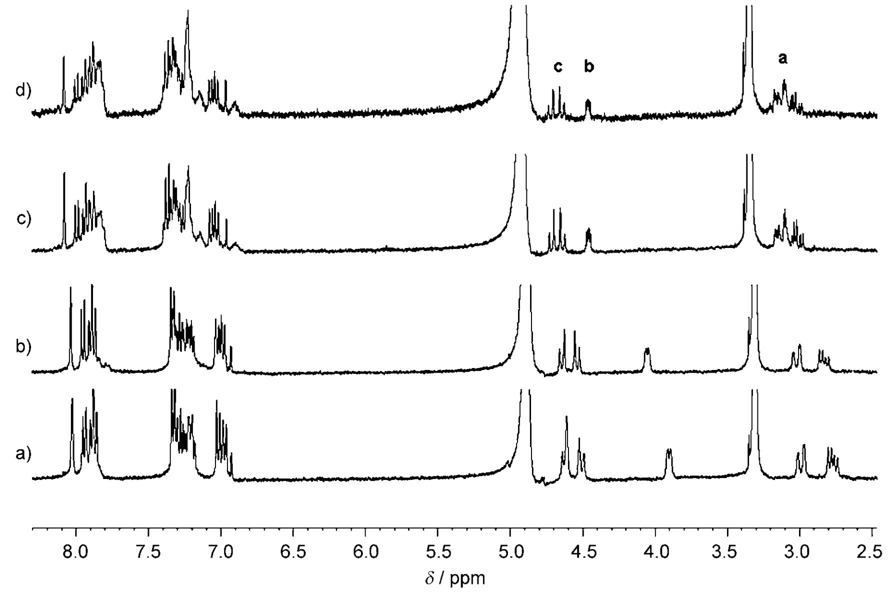

Figure 5. Partial ^1H NMR spectra (400 MHz) of sensor (*R*)-**1** (5.0 mM) with Al^{3+} in CD_3OD: a) (*R*)-**1** only, b) (*R*)-**1** + Al^{3+} (0.5 equiv), c) (*R*)-**1** + Al^{3+} (1.0 equiv), d) (*R*)-**1** + Al^{3+} (2.0 equiv).

fications of (*R*)-**1** (Figure 6). When (*R*)-**2** and (*R*)-**3** interacted with Al^{3+}, their fluorescent responses were indicative of high selectivity in CH_3OH, but no dual-channel fluorescent emission bands were observed in CH_3OH/H_2O (v/v = 1:99, pH 5.0) solution (see the Supporting Information, Figures S18–S20). These results showed that the −OH, −NH, and −COOH groups were the key binding sites for coordination with Al^{3+}. Considering the intramolecular protonation of the −NH group by the −COOH group, the ester derivative (*R*)-**4** was also synthesized and evaluated. In comparison with (*R*)-**2**–Al^{3+}, after the addition of Al^{3+} in the CH_3OH solution the ester derivative (*R*)-**4** did not show significant selectivity for Al^{3+} (see the Supporting Information, Figure S21). These results implied that the carbonyl oxygen in carboxylic group was the main binding site to show the significant selectivity for Al^{3+}. The Job's plot method for (*R*)-**2** and (*R*)-**3** (see the Supporting Information, Figures S16 and S17) and the ^1H NMR-titration experiments for (*R*)-**3** (see the Supporting Information, Figure S22) with Al^{3+} were also carried out, which implied that the three sensors, (*R*)-**1**, (*R*)-**2**, and (*R*)-**3**, were indeed associated with Al^{3+} in a 1:1 stoichiometry. The enhancement of the fluorescence intensity at about 383 nm of the sensors was presumably due to the chelation-enhanced fluorescence. The existence of the amide group of (*R*)-**1**, which was the good hydrogen-bond donor and acceptor, was the main factor in generating the dual-channel fluorescent emission change. Note that the above three sensors can be seen as new kind of metal-based amino acid receptor.[18]

To gain insight into the influence of H_2O and solvent effects for the dual-channel fluorescent emission change, the emission spectra of (*R*)-**1** in different solvents with different proportions of H_2O were measured. It only showed the monomer emission band of free (*R*)-**1** (~379 nm) in the range 0–99 % water and the fluorescence intensity was quenched severely (see Supporting Information, Figures S23–S25). As shown in Figure 7, in the presence of 1.0 equiv of Al^{3+}, (*R*)-**1** exhibited only the monomer emission signal at 383 nm in 100 % CH_3OH, whereas (*R*)-**1** displays both the monomer emission band at 384 nm and an excimer emission band at 455 nm in 99 % water. Moreover, with the addition of H_2O up to 60 % (v/v), a clear excimer emission at 455 nm was observed. The ratio of fluorescence emission intensity (F_{455}/F_{384}) increases with increasing the proportions of H_2O. Similar results were observed in C_2H_5OH or DMF systems (see the Supporting Information, Figures S26 and S27). These results indicated that the dual-channel fluorescence emission change was not generated by free (*R*)-**1** itself and was distinctively different from related previous reports.[4c,5a,c] Also, the emission change was not affected by organic solvents, but the synergistic influence of Al^{3+} and H_2O were the major factors, that is, the change was generated by the ternary system of (*R*)-**1**–Al^{3+}–H_2O because H_2O is an extremely good hydrogen-bond donor and acceptor compared with methanol. It may be proposed that further addition of H_2O induced the formation of intermolecular hydrogen-bonding[19] of the (*R*)-**1**–Al^{3+} complex, which allowed a new conformation to be adopted in which the binaphthyl units could come close and thus readily form an excimer to generate the dual-channel fluorescent emission change.

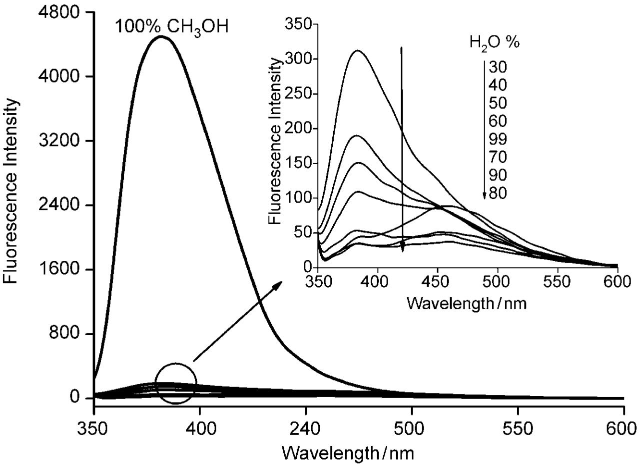

Figure 7. Fluorescence spectra of (*R*)-**1** (20 μM) with Al^{3+} (1.0 equiv) in CH_3OH with different proportions of H_2O. ($\lambda_{ex} = 337$ nm, slit = 5.0 nm/ 5.0 nm).

In conclusion, we have described the design, synthesis, and characterization of a new turn-on ratiometric fluorescent aluminum sensor (*R*)-**1**. The different fluorescence behavior of (*R*)-**1** toward Al^{3+} was found to be strongly dependent on the nature of the employed medium. In CH_3OH, (*R*)-**1** showed a single-channel fluorescent-enhanced sensor for Al^{3+} and an efficient dual-channel fluorescent-enhanced ratiometric sensor in aqueous solution, which was due to the cooperative recognition assisted by H_2O. Further studies on the accurate structure of the sensor–Al^{3+} complex are in progress in our laboratory. As a general design strategy, extension of the structural modifications of (*R*)-**1** may allow us to create a library[20] of fluorescent sensor candidates for Al^{3+} in the future and our research is ongoing.

Experimental Section

Details of synthesis for the sensors and the spectroscopic measures can be found in the Supporting Information.

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Keywords: aluminum · binol derivatives · chromophores · cooperative recognition · dual-channel sensor · fluorescence · sensors

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