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Highly Selective Turn-on Fluorescent Chemodosimeter for Al(III) Detection via Al(III)-Promoted Hydrolysis of Carbon-Nitrogen Double Bond in 8-Hydroxyquinoline Aldehyde Schiff Base

Jinmin Wang,^[a] Yuanyuan Li,^[b] Kai Li,*^[a] Xiangru Meng,^[a] and Hongwei Hou*^[a]

Abstract: Fluorescent chemodosimeters based on small organic molecules are widely used in the detection of various analytes. However, chemodosimeters for metal ions detections are still limited in a few transition metals like Hg (II), Cu (II), Fe (III), Au(III), etc. In this work, a fluorescent chemodosimeter of 5-chloro-7phenyliminomethyl-8-hydroxyquinoline (2) for the detection of Al(III) was reported. Chemodosimeter 2 exhibited a turn-on fluorescence response to AI(III) due to an AI(III)-promoted hydrolysis of carbonnitrogen double bond reaction. This reaction yielded a product of 1-Al complex which exhibited high fluorescence emission at 487 nm based on an inhibition of excited-state intramolecular proton transfer (ESIPT) mechanism. Because of the specific catalytic ability of Al(III), the selectivity of 2 to Al(III) is excellent both in aqueous solutions and in solid matrix. The fluorescence enhancement was as high as 582-fold and the turn-on fluorescence can be observed even by naked eye upon an irradiation of UV lamp. The detection limit of 2 for Al(III) sensing is 54 nmol/L and the linear range is 0-50 µmol/L. This work provided a new strategy for designing main group metal chemodosimeter based on small organic molecules.

Introduction

Chemodosimeters are a class of sensing system based on analyte-induced irreversible chemical reactions.^[1] Fluorescent chemodosimeters based on small organic molecules are widely used in detection and bioimaging of reactive oxygen species (ROS), amino acid, pH, metal ions, etc.^[2] They exhibited a lot of advantages such high selectivity, sensitivity, and relatively less influenced by the environment.^[3] Research on fluorescent organic chemodosimeters has been a hot topic in recent years. Nevertheless, the application of organic chemodosimeters is still limited, especially for metal ions detection. Most of the reported organic chemodosimeters for metal ions sensing are concentrated on a few transition metals, such as Hg (II), Cu (II), Fe (III), Au(III), etc.^[1b, 4] To the best of our knowledge, however, to date there is still lack of organic chemodosimeter for main group metals detection.

Aluminum is the most abundant metallic element in the earth's crust and extensively used in modern life. High levels of

J. Wang, Dr. K. Li, Prof. Dr. X. Meng, and Prof. Dr. H. Hou College of Chemistry and Molecular Engineering Zhengzhou University Henan 450001, P. R. China E-mail: likai@zzu.edu.cn or houhongw@zzu.edu.cn
Dr. Y. Li School of Chemistry and Chemical Engineering Henan University of Technology Henan 450001, P. R. China Supporting information for this article is given via a link at the end of the document. aluminum ions in human body can cause severe diseases including dialysis encephalopathy, Alzheimer's disease, and Parkinson's disease.^[5] Owing to its significant impact on human health, investigations on reliable methods for Al(III) detection have received intense attention in recent years. Compared with the traditional instrumental analysis methods for Al(III) such as atomic absorption spectrometry (AAS) and inductively coupled plasma mass spectrometry (ICP-MS),^[6] fluorescence sensing method has recently attracted widespread interest due to its quick response, non-destructive emission signals and capability of real-time detection in analysis.^[7]

Molecular design of new Al(III) sensor with high selectivity and sensitivity is the key issue for fluorescence sensing of Al(III). Most of the reported fluorescent sensors for Al(III) are based on chelating of the sensor molecules in the presence of Al(III).[8] In this work, a novel reaction-based fluorescent chemodosimeter of 5-chloro-7-phenyliminomethyl-8-hydroxyquinoline (2) for Al(III) detection was reported (Scheme 1). 2 showed a fluorescence turn-on response to Al(III) in an aqueous solution of 99% water/DMSO (v/v) with the fluorescence enhancement as high as 582-fold. It was proposed that AI(III) formed a complex with 2 at a ratio of 1:2 and promoted hydrolysis of carbon-nitrogen double bond in Schiff base moiety of 2, then yielded a complex of 1-AI with high fluorescence emission (Scheme 2). 2 featured good sensitivity with a detection limit of 54 nmol/L and a linear range of 0-50 µmol/L toward Al(III). Excellent selectivity of 2 for Al(III) was also achieved both in aqueous solution and in solid matrix, which was successfully used in the development of fluorescent test papers for rapid detection by naked eye. This work provided a new strategy for designing main group metal chemodosimeters based on small organic molecules.



Scheme 1. Synthetic pathway of 1-4.

Results and Discussion

The interaction between ${\bf 2}$ and Al(III) was firstly studied by fluorescence and absorption spectra. As shown in Figure 1A, ${\bf 2}$

exhibited a weak fluorescence peak at 550 nm in aqueous solution at pH 5.0. After the addition of Al(III), a new emission peak at 487 nm accompanied with a shoulder peak around 528 nm appeared, which gradually grew intense and reached to a maximum within 10 min. The fluorescence turn-on response can be observed by naked eye upon UV light irradiation. Interestingly, if adding excessive EDTA into the solution of 2 and Al(III), the fluorescence peaks almost disappeared and could not restore to the pattern of 2 (Figure 2A inset). These results suggested that there might not be a simple coordination reaction but an irreversible chemical reaction between 2 and Al(III). Analogous results could also be observed in absorption spectra (Figure 1B). In aqueous solution at pH 5.0, 2 showed two absorption bands at 314 nm and 456 nm. Upon the addition of Al(III), these two absorption bands decreased gradually, accompanied with a new absorption band at 381 nm emerged simultaneously. Two isobestic points at 361 nm and 403 nm could be found, suggesting the formation of new compounds. As had been found in the fluorescence spectra, the addition of excessive EDTA into the solution of 2 and Al(III) could not restore the absorption spectra to the original state of 2, which also implied that 2 and Al(III) might had underwent an irreversible chemical reaction.



Figure 1. A) Fluorescence spectra (left) and luminescence (right) changes of 2 before and after the addition of Al(III). B) Absorption spectra (left) and visible color (right) changes of 2 before and after the addition of Al(III). Conditions: 99% water/DMSO (*v/v*) buffered by 50 mmol/L NaAc-HAc at pH 5.0, the concentrations of 2 and EDTA were 50 μ mol/L and the concentration of Al(III) was 25 μ mol/L. Excitation for fluorescence spectra was performed at 403 nm.







Figure 2. HRMS spectrum of the purified reaction products of 2 and Al(III). Inset: calculated isotopic patterns.

To get insight into the reaction mechanism of 2 with Al(III), the reaction products of 2 and Al(III) were firstly investigated by high resolution mass spectrometry (HRMS). Details of the experiment can be seen in Experimental Section. As illustrated in Figure 2, the reaction products of 2 with AI(III) displayed two characteristic peaks at m/z 208.0164 and 210.0134 with a ratio of 3:1, which corresponded very well with the molecule weight of 5-Chloro-7carbaldehyde-8-hydroxyquinoline (1) ([1+H]+, calcd 208.0165 (100%) and 210.0136 (32%)). According to the literature, carbon-nitrogen double bond in Schiff base was metastable, which can be destroyed by hydrolysis reaction in the presence of catalysts such as protons and some metal ions.^[9] Therefore, a possible mechanism for the interaction between 2 and Al(III) was proposed (Scheme 2): Al(III) promoted hydrolysis of carbonnitrogen double bond in 2 by the formation of 2-AI complex, yielding a highly fluorescence product of 1-AI and aniline. Once Al(III) turned to 1-AI, it could not react with 2 anymore. As shown in Figure S1, 25 µmol/L Al(III) was added to 50 µmol/L 2 by 5 times. After each addition, the fluorescence intensity at 487 nm enhanced and reached to a stable value gradually in about 10 min. The gradual growing fluorescence intensity indicated that it was that the later added free Al(III) reacted with 2.



Scheme 2. Proposed mechanism for the interaction between 2 and Al(III).

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Besides the HRMS results, more evidences for the reaction products of **2** and Al(III) were obtained from comparative experiments using fluorescence and absorption spectra. As shown in Figure 3A, the shape and wavelength of fluorescence spectra of **2** and Al(III) were consistent with the mixed system of **1**, Al(III) and aniline. Analogous results could be obtained in absorption spectra, which proved that the reaction products of **2** and Al(III) are **1-AI** and aniline. Moreover, Job's plot analysis was carried out to evaluate the stoichiometry of **1-AI** (Figure 4). The result indicated that **1-AI** exhibited a 1:1 metal-to-ligand ratio.



Figure 3. A) Fluorescence and B) absorption spectra of the mixtures of 1, 2, aniline and Al(III). Conditions: 99% water/DMSO (ν/ν) buffered by 50 mmol/L NaAc-HAc at pH 5.0. The concentration of Al(III) was 500 μ mol/L, while that of 1, 2 and aniline were 50 μ mol/L, respectively. Excitation for fluorescence spectra was performed at 403 nm.



Figure 4. Job's plot data for evaluating the stoichiometry of **1-AI** complex. Conditions: 99% water/DMSO (ν/ν) buffered by 50 mmol/L NaAc-HAc at pH 5.0. The total concentrations of **1** and Al(III) were 50 μ mol/L. Excitation and Emission were performed at 403 nm and 487 nm, respectively.

The most direct evidence for the reaction products of 2 and Al(III) was gained from NMR spectra. As shown in Figure 5, ¹H NMR spectra of 1 and 2 before and after the addition of 1 equiv. Al(III) were measured in DMSO- d_6/D_2O (v:v = 9:1) at room temperature. The proton of aldehyde in 1 resonated at 10.5 ppm (Figure 5A, proton 1). After the addition of Al(III), a new signal was seen at 10.7 ppm (proton 2), which was attributed to the formation of 1-AI (Figure 5B, proton 2). For 2, the proton of Schiff base moiety showed a characteristic chemical shift of 14.1 ppm (Figure 5D, proton 3). When 1 equiv. Al(III) was added, the signal of proton 3 in 2 disappeared and two new signals at 10.7 ppm and 10.5 ppm were observed (Figure 5C, proton 1 and proton 2). These results were similar to that of 1 with Al(III) under the same conditions, which clearly showed that the reaction product of 2 with Al(III) was actually 1-Al. Although the addition of Al(III) in 1 or 2 made their NMR signals between 7.0-10.0 rough, similar shape and chemical shifts of the spectra in Figure 5B and Figure 5C were still detected. All of these results suggested that the reaction products of 2 and Al(III) were 1-AI and aniline.



Figure 5. ¹H NMR spectra of **1** and **2** in the absence and presence of Al(III) in DMSO-*d*₆. The concentrations of **1**, **2** and Al(III) were 50 μmol/L, respectively.

Generally, metal promotes hydrolysis of carbon-nitrogen double bond in Schiff base is accompanied by the formation of complex, which can effectively shorten the distance between the metal and Schiff base.^[10] Thus, we speculate that there might be a complex of 2-AI formed before the hydrolysis reaction. To confirm the formation of 2-AI complex, absorption spectra of 2 with Al(III) was recorded in anhydrous acetonitrile, where the hydrolysis reaction could be blocked and 2-AI could be stable once after the coordination reaction took placed. As shown in Figure 6, when Al(III) was added to 2, the absorption band at 452 nm decreased and new absorption band at 390 nm emerged simultaneously. Three isobestic points at 331 nm, 428 nm and 499 nm could be observed, suggesting the formation of complex 2-AI. The absorption ratio of A_{390}/A_{452} reached to its maximum when the amount of Al(III) was above 0.5 equiv., indicating a 1:2 metal-to-ligand ratio of 2-AI. Moreover, ESI-MS was measured to support the formation of complex 2-AI. As

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shown in Figure S2, a clear peak at m/z = 652.07 ([2M+Al+NO₃-H]⁺, calcd 652.07) could be observed in the presence of 0.5 equiv. Al(III), and the isotopic patterns corresponded very well with the calculated ones. This result supplied a more direct evidence for the 1:2 metal-to-ligand ratio of **2-Al**.



Figure 6. Absorption spectra of 50 μ mol/L **2** upon the addition of 0-50 μ mol/L Al(III) in acetonitrile. Inset: The absorbance ratio (A_{390}/A_{452}) as a function of Al(III) concentration.

Density functional theory (DFT) calculations were performed on 2 and 2-AI by the Gaussian 09 program to gain further insight into the Al(III)-promoted hydrolysis reaction mechanism. The geometries were optimized with M062X hybrid density function and the 6-31G (d,p) basis set. As shown in Figure 7, the HOMO and LUMO were evenly distributed on 2. This result was very different from that of 2-AI, whose HOMO and LUMO were localized at phenyliminomethyl and hydroxyquinoline part, respectively, suggesting the strong electron attracting of Al(III). More importantly, the Mulliken charge of the carbon atom in Schiff base moiety in 2-AI was 0.143 (Figure 8), which was much higher than that in 2 (0.115). According to the reports,[11] the negative regions in Schiff base are preferable sites for electrophilic attack whereas the positive regions are favored for nucleophilic attack. Therefore, as a nucleophilic addition process, the hydrolysis reaction was more likely to take place in 2-AI rather than 2.





Figure 8. Mulliken charge distribution of A) 2 and B) 2-AI.

To investigate whether free Al(III) in solution could also promote the hydrolysis reaction, a control compound of 4-chloro-2-phenyliminomethy-1-naphthol (4) was synthesized. Compared with 2, there was no quinoline N-binding site in 4, so the chelate ability of 4 with Al(III) should be much weaker than that of 2. As expected, the fluorescence spectra of 4 in the absence and presence of 1 equiv. Al(III) nearly overlapped with each other (Figure 9B). Meanwhile, no absorption change could be detected before and after the addition of Al(III) (Figure 9C). These results suggested that no complex was formed between 4 and Al(III). After stored the mixture for 10 min at room temperature, no fluorescence or absorption changes could be detected, suggesting that the hydrolysis reaction could not be promoted by the free Al(III) in solution. Hence, the chelation of 2 with AI(III) was essential for the AI(III)-promoted hydrolysis reaction.



Figure 9. A) The interaction between 4 and Al(III). B) Fluorescence and C) absorption spectra of 4 before and after the addition of Al(III). Conditions: 99% water/DMSO (ν/ν) buffered by 50 mmol/L NaAc-HAc at pH 5.0. The concentration of 4 was 50 μ mol/L. Excitation for fluorescence spectra was performed at 480 nm.

From all of the above studies, we can conclude that the fluorescence enhancement of **2** to Al(III) is based on an Al(III)promoted hydrolysis of carbon-nitrogen double bond reaction: Upon the addition of Al(III) to **2**, a complex of **2-AI** was formed and then hydrolyzed to **1-AI** and aniline, along with a significant fluorescence enhancement response (Scheme 2).

To investigate the effect of pH on the Al(III) detection, the fluorescence intensity of 2 at 487 nm in the absence and presence of 1 equiv. Al(III) were examined in a pH range from 3.0 to 9.0. As shown in Figure 10, the fluorescence intensity of 2 was very weak in this pH range. In contrast, the Al(III)-induced fluorescence enhancement reached to the maximum around pH 5.0. The reason should be that when pH < 5.0, the protonation of quinoline in 2 weakened its coordination ability to Al(III), hindering further hydrolysis reaction. While pH > 5.0, the formation of Al(OH)₃ precipitates significantly reduced the concentration of Al(III) in the solutions. The K_a of Al(III) is 1.0 x 10^{-5} and the K_{sp} of Al(OH)₃ is 1.3×10^{-33} ,^[12] which means that the maximum permissible AI(III) concentration in an aqueous solution of pH 6.5 is about 4×10⁻¹¹ mol/L. This concentration of Al(III) is too low to form 2-AI complex and can not promote the hydrolysis reaction. Higher pH will lead to a lower concentration of Al(III). Thus, no fluorescence response can be detected when pH > 6.5. In order to achieve the highest signal-to-noise ratio, pH 5.0 was employed for Al(III) detection when using 2 as the chemodosimeter.



Figure 10. Fluorescence intensity at 487 nm of **2** in the absence and presence of Al(III) at different pH. Conditions: 99% water/DMSO (*v*/*v*) buffered by 50 mmol/L NaAc-HAc and 50 mmol/L Tris-HCI. The concentrations of **2** and Al(III) were 50 μ mol/L, respectively. Excitation and Emission were performed at 403 nm and 487 nm, respectively.

As a fluorescent chemodosimeter, 2 revealed a remarkable selectivity to Al(III) over other metal ions. As illustrated in Figure 11A and Figure 11C, 1 equiv. different metal ions were added to the solution of 2, respectively. It was clear that only the addition of Al(III) induced an obvious fluorescence turn-on response.

As 8-hydroxyquinoline derivatives, there is a typical excitedstate intramolecular proton transfer (ESIPT) process in **2** due to its intramolecular H-bond between the hydroxy and nitrogen in quinoline moiety.^[13] The ESIPT process lead to a significant fluorescence quenching, so weak fluorescence was observed in **2** like most of the 8-hydroxyquinoline derivatives.^[13a, 14] According to the proposed mechanism (Scheme 2), the final product of the hydrolysis reaction of 2 and Al(III) is 1-Al complex. Thus, in order to study the cause of the high selective fluorescence enhancement of 2 toward Al(III), 1 was investigated as a control compound. The fluorescence of 1 is also very weak due to the ESIPT process mentioned above. After binding with Al(III), the intramolecular H-bond in 1 was broken, which inhibited the ESIPT process and resulted in a fluorescence turn-on response.^[14c, 15] In contrast, the fluorescence turn-on response of 1 could not be observed when adding other metal ions. There might be two reasons to illustrate the phenomenon. One is that the binding abilities of some metal ions (e.g. alkali metal and alkaline-earth metals) with 8hydroxyquinoline are rather weak, which could not form complexes and inhibite the ESIPT process. The other reason is that the paramagnetic nature of some metal ions (e.g. Cu(II), Ni(II), Co(II), Fe(III), etc.) will lead to fluorescence quenching after binding with fluorophore.[16] These two reasons partly explained the exellent selectivity of 2 to Al(III) over most of the metal ions. However, as shown in Figure 11A and Figure 11B. the fluorescence turn-on response was not only achieved in 1 with the addition of Al(III), but also with the addition of Zn(II) and Cd(II). This was apparently different from what was observed in 2. In order to find out the cause for the excellent selectivity of 2 to Al(III) over Zn(II) and Cd(II), dynamics of the hydrolysis reactions of 2 with these metal ions was investigated by studying the time-dependent fluorescence spectra at 487 nm. As can be seen in Figure 12, the fluorescence intensity of 2 was very stable without adding any metal ions or enhanced very slowly in the presence of Zn(II) or Cd(II), indicating the hydrolysis reactions of 2 barely took place. In contrast, apparent fluorescence enhancement at 487 nm was observed immediately after the addition of Al(III) and reached to its maximum in about 10 min. These results make it clear that the specific catalytic ability of Al(III) for the hydrolysis reaction is the primary cause for the high selectivity of 2.



Figure 11. A) Fluorescence intensity of 1 and 2 with 1 equiv. different metal ions. B) The photo of 1 with 1 equiv. different metal ions. C) The photo of 2 with 1 equiv. different metal ions. Ions: Al(III), Li(I), Na(I), K(I), Mg(II), Ca(II), Ba(II), Cr(III), Mn(II), Fe(III), Co(II), Ni(II), Cu(II), Ag(I), Zn(II), Cd(II), Hg(II), Pb(II). The photos were taken under irradiation of UV light (365 nm). Conditions: 99% water/DMSO (v/v) buffered by 50 mmol/L NaAc-HAc at pH 5.0. The concentrations of 1 and 2 were 50 μ mol/L, respectively. Excitation and Emission were performed at 403 nm and 487 nm, respectively.



Figure 12. Time-dependent fluorescence spectroscopy of 2 with 1 equiv. different metal ions. Conditions: 99% water/DMSO (v/v) buffered by 50 mmol/L NaAc-HAc at pH 5.0, the concentration of $\boldsymbol{2}$ was 50 $\mu \text{mol/L}.$ Excitation and Emission we performed at 403 nm and 487 nm, respectively.

Besides the better selectivity, chemodosimeter 2 exhibited a higher fluorescence enhancement ratio than that of the control compound 1. As can be seen in the inset of Figure 13, the fluorscence intensity of 1 at 487 nm is much higher than that of 2. Thus, though they produced the same product (1-AI) after reaction with Al(III), the maximum fluorescence enhancement of 1 combined with Al(III) was only 70-fold, whereas it was up to 582-fold in the same conditions when 2 reacted with Al(III). Furthermore, calibration curves for the determination of Al(III) by 2 was constructed. As shown in Figure 14, chemodosimeter 2 exhibited a linear range of 0-50 µmol/L with correlation coefficient of R²=0.996 (n=3). The detection limit was calculated as 54 nmol/L based on the definition by IUPAC ($C_{DL}=3S_b/m$) from ten blank solutions. As can be seen in Table S1, the content of Al(III) in drinking water sample and tap water sample were analyzed by the proposed method under optimized condition, which showed satisfactory recovery and R.S.D. values for all of the samples.



Figure 13. Fluorescence spectra of 1 and 2 before and after the addition of 10 equiv. Al(III). Conditions: 99% water/DMSO (v/v) buffered by 50 mmol/L NaAc-HAc at pH 5.0. The concentrations of 1 and 2 were 50 µmol/L, respectively. Excitation was performed at 403 nm.



Equation

ntercept

Slope

Adj. R-Sq 0.9958

Value Standard

13.890

5.8218

5.0586

0.11842

300

250

nm.

Due to the advantages of rapid detection and good selectivity, test papers based on 2 for Al(III) detection were successfully fabricated. 2 on filter paper itself was non-emissive under UV light irradiation, but its fluorescence intensity increased distinctly after exposure to AI(III) with certain concentrations (Figure 15). When the Al(III) concentration was higher than 100 µmol/L, strong fluorescence can be directly observed by naked eye upon UV light irradiation. More importantly, as illustrated in Figure 15B strong fluorescence was only observed with the addition of Al(III) which demonstrated that the test papers exhibited good selectivity to Al(III) over the other detected metal ions.



Figure 15. A) Images of test papers based on 2 for the detection of Al(III) at various concentrations under an irradiation of 365 nm UV lamp. B) Images of test papers based on 2 for the detection of different metal ions in aqueous solutions (5 mmol/L).

Conclusions

In conclusion, a fluorescent chemodosimeter based on small organic molecule for the detection of main group metal was reported. Chemodosimeter 2 exhibited very weak fluorescence

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emission without Al(III) in aqueous solution. After the addition of Al(III), an Al(III)-promoted hydrolysis of carbon-nitrogen double bond occured, producing a complex of **1-AI**. **1-AI** exhibited high fluorescence emission based on an inhibition of ESIPT mechanism. Because of the specific catalytic ability of Al(III), the selectivity of **2** to Al(III) was exellent both in aqueous solutions and in test papers. The fluorescence enhancement was as high as 582-fold and the turn-on fluorescence can be observed even by naked eye under an irradiation of UV lamp. This work provided a new strategy for designing main group metal chemodosimeter based on small organic molecules.

Experimental Section

Reagents

All the materials used in the experiments were of analytical grade. 5chloro-8-hydroxyquinoline, 4-chloro-1-naphthol, methenamine and aniline were purchased from J&K Chemical Co., Beijing, China. Unless otherwise noted, all the other materials were purchased from Sinopharm Chemical Reagent Beijing Co., Beijing, China. The solutions of all metal ions were prepared from their nitrate salts or perchlorate salts of analytical grade. Deionized water (distilled) were used throughout the experiment.

Apparatus

Fluorescence spectra were determined by a JASCO-FP-8300 fluorescence spectrophotometer. Absorption spectra were recorded using a JASCO-750 UV-vis spectrophotometer. All the pH measurements were carried out on a Mettler Toledo FE20/EL20 pH meter. ¹H and ¹³C NMR spectra were recorded by a Bruker 600 Avance NMR spectrometer operated at 600 MHz. HRMS were obtained on Shimadzu LCMS-IT/TOF Liquid Chromatograph Mass Spectrometer without using the LC part. The photos were taken using a Nikon D5500 camera.

Syntheses

Compound 1 and 3 were prepared through a reported procedure.^[17] **Syntheses of 5-chloro-7-phenyliminomethyl-8-hydroxyquinoline (2).** 208 mg compound 1 (1.0 mmol) was mixed with 20 mL absolute ethanol, stirred and heated to 85 °C till it was dissolved. After that, 93 mg aniline (1.0 mmol) was added and the mixture was stirred at 85 °C for 4 hours to form precipitate. The crude product was purified on a silica-gel column using CH₂Cl₂/CH₃OH (100/1 v/v) as eluent. Orange solid was obtained with a yield up to 90%. ¹H NMR (DMSO-d₆) δ (ppm): 14.09 (s, 1H), 9.07 (s, 1H), 8.95 (s, 1H), 8.42 (d, 1H, *J*=8.0 Hz), 7.80 (m, 2H), 7.52 (s, 4H), 7.33 (s, 1H). ¹³C NMR (DMSO-d₆) δ (ppm): 166.80, 157.36, 149.49, 144.38, 143.06, 132.82, 130.12, 129.61, 127.85, 127.21, 125.54, 120.54, 116.91, 114.56. HRMS spectrometry: *m*/*z* calcd for [M-H]: 281.0487; found: 281.0489.

Syntheses of 4-chloro-2-phenyliminomethy-1-naphthol (4). 207 mg compound 3 (1.0 mmol) was mixed with 20 mL absolute ethanol, stirred and heated to 85 °C till it was dissolved. After that, 93 mg aniline (1.0 mmol) was added and the mixture was stirred at 85 °C for 4 hours to form

precipitate. The resulting precipitate was filtrated and washed with 20 mL absolute ethanol for three times. After being dried under reduced pressure, orange solid were obtained in a yield of 85%. ¹H NMR (DMSO-d₆) δ (ppm): 14.62 (d, 1H, *J*=10.2 Hz), 8.95 (d, 1H, *J*=10.2 Hz), 8.40 (d, 1H, *J*=7.8 Hz), 7.95 (d, 1H, *J*=7.8 Hz), 7.80 (t, 1H, *J*=7.8 Hz), 7.57 (m, 3H), 7.49 (m, 3H), 7.31 (t, 1H, *J*=7.8 Hz). ¹³C NMR (DMSO-d₆) δ (ppm): 175.86, 155.38, 140.42, 134.26, 132.24, 130.77, 130.35, 128.48, 126.90, 126.84, 126.10, 124.34, 119.40, 116.61, 110.10. HRMS spectrometry: *m/z* calcd for [M-H]: 280.0535; found: 280.0536.

Analytical procedure

Stock solutions of **1**, **2** and **4** (5.0 mmol/L) were prepared in DMSO. Stock solutions (5.0 mmol/L) of the nitrate salts or perchlorate salts of Al(III), Li(I), Na(I), K(I), Mg(II), Ca(II), Ba(II), Cr(III), Mn(II), Fe(III), Co(II), Ni(II), Cu(II), Ag(I), Zn(II), Cd(II), Hg(II) and Pb(II) were prepared in deionized water. Absorption and fluorescence measurements were performed by adding a proper amount of stock solutions to the buffered solution of 50 mmol/L NaAc-Hac at pH 5.0 in a 1 cm cuvette. After being well mixed, the solutions were allowed to stand at 25 °C for 10 min. Then absorption or fluorescence spectra were recorded. For the timedependent fluorescence experiment, the fluorescence spectra were recorded immediately after the solution was well mixed.

Preparation of the reaction products of compound 2 and Al(III) for HRMS analysis

100 mL aqueous solution containing 1 mmol 2 and 1 mmol Al(III) were stirred for 2 hours at room temperature. Then excessive EDTA (2 mmol) was added into the system and continued stirring for 1 hour. After extracting with dichloromethane, the organic layer was collected and evaporated in vacuo. The resulting product was dissolved in methanol for HRMS analysis.

Preparation of test paper

Filter paper was put into a dichloromethane solution of 2 (50 mmol/L) for 10 min. Then the filter paper was dried in air for 30 min at room temperature. In this way a test paper was obtained.

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A reaction-based fluorescent chemodosimeter of 5-chloro-7phenyliminomethyl-8-hydroxyquinoline was reported, which exhibited excellent selectivity and sensitivity to Al(III) both in aqueous solutions and in solid matrix.



Jinmin Wang, Yuanyuan Li, Kai Li,* Xiangru Meng, and Hongwei Hou*

Page No. – Page No.

Highly Selective Turn-on Fluorescent Chemodosimeter for Al(III) Detection in Aqueous Solution via Novel Al(III)-Promoted Hydrolysis of Carbon-Nitrogen Double Bond in 8-Hydroxyquinoline Aldehyde Schiff Base