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A Thiourea-Containing Fluorescent Chemosensor for Detecting Ga³⁺

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Abstract

A thiourea-based fluorescent chemosensor NADA, (E)-2-(4-(diethylamino)-2-hydroxybenzylidene)-N-(naphthalen-1-yl)hydrazine-1-carbothioamide, has been designed and synthesized. NADA could detect Ga³⁺ through a fluorescent turn-on with a low detection limit (0.29 μ M). Importantly, NADA could effectively discriminate Ga³⁺ from Al³⁺ and In³⁺. The binding mechanism of NADA with Ga³⁺ was identified by ESI-mass, NMR titration, and DFT calculations.

Keywords Ga^{3+} · Thiourea · Chemosensor · Calculations · Fluorescence

Introduction

Gallium, one of the group 13 elements, is uncommon element found in little amounts in the soil. Nevertheless, it has an imperative impact on our daily life [1, 2]. Due to its unique optical and electrical properties, gallium and its derivatives are broadly applied to energy storage of solar cell, catalysis and the manufacture of microelectronic product such as LEDs [3, 4]. As the scale of the electronics industry is growing, the consumption of gallium is getting increased. Therefore, we are easily exposed to gallium ions. Gallium ions are known to be carcinogenic and highly noxious to humans and animals [5–7]. For example, visual, auditory toxicities and microcytic anemia may materialize in patients medicated with gallium nitrate. In addition, Gabased substances that are absorbed in the body through food cause severe diseases including asthenia, vertigo, anemia and skin cancer [8, 9]. Therefore, dependable methods are required for the detection of gallium ion [10]. However, it has been challenging to distinguish Ga³⁺ from Al³⁺ and In³⁺ due to the similar properties of group 13 elements [11, 12].

Some approaches have been developed to detect gallium ions including titrimetric method, absorption, ion exchange and atomic spectrometry [13, 14]. However, these methods demand high-cost instruments or complex preparation procedures [15, 16]. Therefore, it is imperative to develop new, low-cost and convenient methods for detecting gallium ions [17, 18]. Fluorescent methods have attracted lots of attention because they have easy operational advantage, fast response times, convenience, high sensitivity and selectivity [19–21]. Some fluorescent chemosensors for detecting Ga³⁺ have been reported, but they are less effective due to the inhibition of Al³⁺ or In³⁺ [22–25].

The naphthyl moiety, one of the fluorophores, can act as an ideal signal part because of high fluorescence quantum yield and good sensitivity [26, 27] In addition, another effective fluorophore, N,N-diethylaminophenol group may enhance the ICT (intramolecular charge transfer), resulting in a large bathochromic shift in emission [28–30]. On the other hand, the thiourea moiety can easily chelate metal ions with two nitrogen atoms and one sulfur atom, and be used as a linker [31–34]. Therefore, a thiourea-based sensor with naphthyl moiety and diethylaminophenol group can efficiently bind to transition metal ions with a unique and strong fluorescence.

Herein, we report a thiourea-based fluorescent sensor **NADA** with the diethylaminophenol and naphthyl groups. **NADA** selectively detected gallium ions with a low detection limit. The binding mechanism of gallium ion to **NADA** was explained by fluorescent and UV-vis experiments, Job plot analysis, ESI-mass, ¹H NMR titration, DFT calculation.

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Experimental Section

Materials and Equipment

4-(Diethylamino)-2-hydroxybenzaldehyde (98%), 1-naphthyl isothiocyanate (98%), hydrazine (80%) and gallium(III) nitrate hydrate (Ga(NO₃)₃·xH₂O, 99.9%) were acquired commercially from TCI (located in Tokyo, Japan) and Sigma-Aldrich (located in St. Louis, USA). A Varian 400 MHz spectrometer was used to afford ¹³C and ¹H NMR spectra. With Perkin Elmer spectrometers (Lambda 365 for UV-vis and LS 45 for fluorescence), absorption and emission data were provided. A Thermo Finnigan LCQTM Advantage MAX quadrupole ion trap instrument was employed to collect ESI-MS spectra.

Synthesis of Sensor NADA

Compound NH (N-(naphthalen-1-yl) hydrazine carbothioamide) was synthesized through the nucleophilic addition of 1-naphthyl isothiocyanate with hydrazine. 4 mmol of 1-naphthyl isothiocyanate and 5 mmol of hydrazine monohydrate were dissolved in 15 mL of ethanol (EtOH). The reaction mixture was stirred until a white-colored powder was formed, and the resultant powder was filtered and washed with ether. ¹H NMR (deuterated DMSO) δ (ppm): 9.2 (s, 1H), 7.9 (m, 2H), 7.7 (d, 1H, J= 8 Hz), 7.6 (s, 1H), 7.5 (m, 4H) 4.9 (s, 2H).

NADA was synthesized by the reaction of NH (217.29 mg, 1 mmol) and 4-(diethylamino)-2-hydroxybenzaldehyde (231.9 mg, 1.2 mmol) in EtOH (5 mL). The solution was stirred for 16 h at 24 °C. Pale yellow powder was formed, filtered and washed with ether. NADA was soluble in DMSO, DMF and THF, and stable for 6 h in the solvents

NADA + Ga³ 600 NADA NADA+G ADA, NADA +other metal ions $NADA + Al^{3+}$, $NADA + In^{3}$ NADA+ Pb²

800

400

200

I_F (a.u.)

Fig. 1 Fluorescent changes of NADA $(2 \times 10^{-6} \text{ M})$ with varied cations (12 equiv.; Co^{2+} , K^+ , Cu^{2+} , Pb^{2+} , Ca^{2+} , Zn^{2+} , Na^+ , Al^{3+} , Mn^{2+} , Fe^{2+} , Cr^{3+} , Ni^{2+} , Fe^{3+} , Mg^{2+} , Cd^{2+} and In^{3+} and Ga^{3+}) ($\lambda_{ex} = 400 \text{ nm}$)

500

 λ (nm)

(Fig. S1). ¹H NMR (DMF- d_7): δ 11.54 (s, 1H), 10.18 (s, 1H), 9.79 (s, 1H), 8.62 (s, 1H), 8.0 (m, 2H) 7.91 (d, 1H), 7.72 (m, 2H), 7.55 (t, 3H), 6.33 (d, 1H), 6.25 (s, 1H), 3.40 (m, 4H). 1.15 (t, 6H). ¹³C NMR (deuterated DMSO): δ (ppm): 12.5 (3C), 43.8 (3C), 97.3 (1C), 104.00 (1C), 107.5 (1C), 123.3 (1C), 125.4 (1C) 125.9 (3C), 126.1 (1C), 126.4 (1C), 127.8 (1C), 130.5 (1C), 133.7 (1C), 142.4 (1C), 150.2 (1C), 158.2 (1C). ESI-mass: calcd (calculated) for $C_{22}H_{25}N_4OS +$ H⁺ ([**NADA** + H⁺])⁺: 393.17 found 393.33.

Fluorescent and UV-Visible Titrations

4**5**0

Compound NADA (0.39 mg, 1×10^{-3} mmol) was dissolved in 1.0 mL of DMSO. 6 μ L (1 × 10⁻³ M) of the NADA was diluted in 2.994 mL MeOH to make 2×10^{-6} M. 0.3–3.6 µL (or 0.3–3.3 μ L for UV-vis titration) of Ga(NO₃)₃ (2 × 10⁻² M)

Scheme 1 Synthesis of NADA





550

dissolved in MeOH were added to sensor **NADA** $(2 \times 10^{-6} \text{ M}, 3.0 \text{ mL})$. After mixing them in a minute, fluorescence spectra (or UV-visible spectra) were taken.

Quantum Yields

With quinine as a standard fluorophore ($\Phi_F = 0.54$ in 1×10^{-1} M H₂SO₄), quantum yield (Φ) was provided. The equation is as follows [35]:

$$\Phi_{\mathrm{F}(\mathrm{x})} = \Phi_{\mathrm{F}(\mathrm{s})} \left(\mathrm{A}_{\mathrm{S}} \mathrm{F}_{\mathrm{X}} / \mathrm{A}_{\mathrm{X}} \mathrm{F} \right) \left(\mathrm{n}_{\mathrm{x}} / \mathrm{n}_{\mathrm{s}} \right)^{2}$$

 $(\Phi_F:$ fluorescent quantum yield; A: absorbance; F: area of fluorescence emission curve; s: standard; x: unknown; n: refractive index of the solvent).

Job Plot

A stock solution of sensor **NADA** $(1 \times 10^{-3} \text{ M})$ was given in 1.0 mL of DMSO. Ga³⁺ solution $(1 \times 10^{-3} \text{ M})$ was provided with its nitrate salt in MeOH (1.0 mL). 0.27–0.03 mL of the **NADA** was transferred to several quartz cuvettes. 0.03–0.27 mL of Ga³⁺ solution was added to diluted **NADA**. Each quartz cuvette was filled with 3 ml of MeOH. The solutions were well blended, and their fluorescence spectra were taken.

Competition Experiments

Sensor **NADA** (0.39 mg, 1×10^{-3} mmol) was dissolved in DMSO (100 µL). Stock solutions (0.6 mmol) of Ga(NO₃)₃, KNO₃, Cr(NO₃)₃, Fe(NO₃)₃, Cd(NO₃)₂, Al(NO₃)₃, Ni(NO₃)₂, Ca(NO₃)₂, NaNO₃, Co(NO₃)₂, Mn(NO₃)₂, In(NO₃)₃, Cu(NO₃)₂, Fe(NO₃)₂, Pb(NO₃)₂, and Mg(NO₃)₂, were dissolved in 3.0 mL MeOH. 3.6 µL of each metal (2×10^{-2} M) was added into 3.0 mL MeOH to make 12



Fig. 2 Fluorescent spectra of NADA (2×10^{-6} M) with the variation of concentrations of Ga³⁺ (0–12 equiv)



Fig. 3 UV-vis changes of probe NADA $(2 \times 10^{-6} \text{ M})$ with different concentrations of Ga³⁺ (0–11 equiv)

equiv. 5.25 μ L (2 × 10⁻² M) of Ga³⁺ ion was added into the solutions to afford 3.5 equiv. 6 μ L of **NADA** (1 × 10⁻³ M) was added into the blended solutions. The solutions were well blended, and their fluorescence spectra were taken.

¹H NMR Titration

Four NMR tubes of **NADA** (3.9 mg, 1×10^{-2} mmol) dissolved in deuterated dimethylformamide (0.7 mL) were afforded, and diverse equivalents (0, 0.5, 1.0 and 2.0 equiv) of Ga(NO₃)₃ dissolved in dimethylformamide (0.3 mL) were transferred separately to the solutions of **NADA**. ¹H NMR data were gained after blending the solutions for 30 s.

Calculations

All theoretical calculations for **NADA** and **NADA**-Ga³⁺ were made using the gaussian 16 W program [36]. DFT calculations for geometry optimization were performed by applying the basis of B3LYP/6-311G to C, O, N, H and S atoms, and



Fig. 4 Job plot for the binding of NADA with Ga³⁺





LANL2DZ to Ga^{3+} [37–43]. The integral equation formalism polarizable continuum model was employed to consider the effect of the solvent, methanol [44, 45]. The energy level and transition state of **NADA** and **NADA**-Ga³⁺ were analyzed through time-dependence DFT calculation.

Results and Discussion

The intermediate compound **NH** was produced via the nucleophilic addition of 1-naphthyl isothiocyanate with hydrazine. Sensor **NADA** was produced via the condensation reaction of **NH** with 4-(diethylamino)-2-hydroxybenzaldehyde (Scheme 1), and verified by ¹³C NMR, ¹H NMR and ESI-mass.

To check out the fluorescent behavior of **NADA**, the fluorescent emission change was measured with varied cations $(Co^{2+}, K^+, Cu^{2+}, Pb^{2+}, Ca^{2+}, Zn^{2+}, Na^+, Al^{3+}, Mn^{2+}, Fe^{2+}, Cr^{3+}, Ni^{2+}, Fe^{3+}, Mg^{2+}, Cd^{2+} and In^{3+})$ in MeOH. As exhibited in Fig. 1, **NADA** ($\Phi = 0.01$) and **NADA** with most cations displayed little fluorescence band at 457 nm ($\lambda_{ex} = 400$ nm). Al³⁺, In³⁺ and Pb²⁺ increased slightly the band. However, the addition of Ga³⁺ showed a dramatic increment of fluorescence at 457 nm ($\Phi = 0.134$) within 2 min (Fig. S2). Therefore, **NADA** may be employed as a sensor for the selective fluorescent detection of Ga³⁺. Importantly, **NADA** could effectively discriminate Ga³⁺ from In³⁺ and Al³⁺.

To know the photophysical character of **NADA** to Ga³⁺, fluorescent and UV-vis titrations were achieved (Figs. 2 and 3). In the fluorescent titration, the fluorescence emission of **NADA** at







457 nm increased constantly until the amount of Ga³⁺ reached up to 12 equiv. On addition of Ga³⁺ into **NADA** for UV-vis titration (Fig. 3), the absorbance of 380 nm constantly decreased, and the absorbance of 400 nm increased consistently until the amount of Ga³⁺ reached up to 11 equiv. An explicit isosbestic point displayed at 390 nm suggested that the reaction of **NADA** with Ga³⁺ afforded one species. The detection limit of Ga³⁺ with **NADA** was calculated to be 0.287 μ M (3 σ /k) through fluorescence titration (R² = 0.9941) (Fig. S3) [46]. Interestingly, **NADA** has the lowest detection limit compared to other naphthyl derivative sensors (Table S1).

For the purpose of studying the complexation ratio of NADA with Ga³⁺, Job plot experiment was accomplished and resulted in the highest value at a molar fraction of 0.5 (Fig. 4). It indicated that one Ga^{3+} combined with one NADA. It was further supported by ESI-mass analysis (Fig. S4). The peak of m/z: 537.16 was proposed to be [NADA(- $2H^+$) + Ga³⁺ + DMSO]⁺ (calcd, 537.09) in positive-ion spectrum. Moreover, the proton NMR titration was implemented to analyze how to bind NADA with Ga^{3+} (Fig. S5). With the addition of diverse concentrations of Ga^{3+} (0.5, 1.0 and 2.0 equiv) into NADA, the proton H₉ of -NH and proton H₂ of -OH disappeared. The proton H_8 of -NH and proton H_1 of the imine were shifted to down field (0.082 and 0.195 ppm, respectively). These results led us to assume that Ga³⁺ would coordinate to two nitrogen atoms and one oxygen one of NADA. Summarizing the results of Job plot, ESI-mass and ¹H NMR titration, the appropriate structure of NADA-Ga³⁺ was proposed (Scheme 2).

The binding constant of NADA-Ga³⁺ complex was given to be 1.2×10^5 M⁻¹ from Benesi-Hildebrand equation (Fig. S6) [47]. Competition experiment was accomplished to know if NADA could effectively bind to Ga³⁺ with the coexisting other cations (Fig. S7). Most cations did not inhibit the binding of NADA with Ga³⁺. However, Cu²⁺ showed fluorescence quenching of NADA-Ga³⁺, and In³⁺, Fe²⁺ and Ag⁺ did some fluorescence quenching (30–60%).

To get insights into detection mechanism of **NADA** toward Ga³⁺, theoretical calculations were conducted. The energyminimized patterns of **NADA** and **NADA**-Ga³⁺ were exhibited in Fig. 5. The structure of **NADA** was slightly distorted by the rotation of the naphthyl ring (10, 2 N, 3 N, 4 N = 129.61°), whereas **NADA**-Ga³⁺ showed a more flattened structure (10, 2 N, 3 N, 4 N = -0.43°) with restricted rotation of the naphthyl ring in the complex formation process.

To understand molecular orbital transitions and possible transition states, TD-DFT calculations were executed. The main absorption of **NADA** was observed at 373.98 nm, affected by HOMO \rightarrow LUMO and HOMO-1 \rightarrow LUMO transitions (Fig. S8). The major absorption of **NADA**-Ga³⁺ appeared at 418.48 nm through HOMO \rightarrow LUMO and HOMO-1 \rightarrow LUMO+1 transitions (Fig. S9). Because of showing the apparent transition of the molecular orbital, the characteristics of

major absorptions of **NADA** and **NADA**-Ga³⁺ were ICT (Fig. S10). Given the similar orbital movement in two molecules and the formation of a more rigid structure in the complex, the fluorescence turn-on process for **NADA**-Ga³⁺ could be CHEF (chelation enhanced fluorescence) effect. Non-radiative transitions like rotation and vibration were limited during complex formation, while radiative transition like fluorescence emission increased. The reduced HOMO-LUMO energy gap was consistent with bathochromic shift in UV-vis spectra. Considering various experimental results and theoretical calculations, plausible detection mechanism for **NADA**-Ga³⁺ was suggested in Scheme 2.

Conclusion

We represented the thiourea-based fluorescent chemosensor NADA that can selectively detect Ga³⁺ by a fluorescence turnon mechanism. NADA had very low detection limit (0.287 μ M) and high binding constant (1.2 × 10⁵ M⁻¹) for Ga³⁺. Importantly, NADA showed the lowest detection limit compared to other naphthyl derivative sensors. In addition, NADA could effectively discriminate Ga³⁺ from Al³⁺ and In³⁺. Binding mechanism of NADA to Ga³⁺ could be explained by ESI-mass, NMR titration, UV-vis and fluorescent titration.

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