Novel Amino-pillar[5]arene as a Fluorescent Probe for Highly Selective Detection of Au\textsuperscript{3+} Ions

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Supporting Information

ABSTRACT: A novel fluorescent probe, amino-pillar[5]arene (APA), was prepared via a green, effective, and convenient synthetic method, which was characterized by nuclear magnetic resonance (NMR), infrared (IR), and high-resolution mass spectrometry. The fluorescence sensing behavior of the APA probe toward 22 metal ions in aqueous solutions were studied by fluorescence spectroscopy. The results showed that APA could be used as a selective fluorescent probe for the specificity detection of Au\textsuperscript{3+} ions. Moreover, the detection characteristics were investigated by fluorescence spectral titration, pH effect, fluorescence competitive experiments, Job’s plot analysis, \textsuperscript{1}H NMR, and IR. The results indicated that detection of Au\textsuperscript{3+} ions by the APA probe could be achieved in the range of pH 1−13.5 and that other coexisting metal ions did not cause any marked interference. The titration analysis results indicated that the fluorescence intensity decreased as the concentration of Au\textsuperscript{3+} ions increased, with an excellent correlation ($R^2 = 0.9942$). The detection limit was as low as 7.59 × 10\textsuperscript{-8} mol L\textsuperscript{-1}, and the binding ratio of the APA probe with Au\textsuperscript{3+} ions was 2:1. Therefore, the APA probe has potential applications for detecting Au\textsuperscript{3+} ions in the environment and in living organisms.

1. INTRODUCTION

Au\textsuperscript{3+} ions, a notable heavy metal, have received great attention in chemistry and biology during recent decades and have been widely used in gold plating,\textsuperscript{1} environmental studies,\textsuperscript{2} anticancer agents,\textsuperscript{3} nanomaterials, efficient catalysts, biological sensors, and drug/gene delivery systems based on their unique chemical properties and high biocompatibility.\textsuperscript{4−7} In addition, these ions have also been developed for application in the jewelry industry.\textsuperscript{8} Studies have shown that Au\textsuperscript{3+} ions can be used to prepare reduced graphene oxide/Au nanoparticles (NPs), drugs, and catalysts to detect dopamine, ascorbic acid, and uric acid; to treat tuberculosis and rheumatoid arthritis; and to activate carbon−carbon triple bonds.\textsuperscript{9−11} Although Au\textsuperscript{3+} ions have versatile roles in materials science and biological systems, studies have demonstrated that Au\textsuperscript{3+} ion-based drugs exhibit potential toxicity at certain concentrations.\textsuperscript{12} Alternatively, the Au\textsuperscript{3+} ions may be broken down and cause damage to the liver, kidney, and nervous system when bound to proteins and DNA\textsuperscript{13,14} Therefore, it was essential to explore a fast, operationally simple, and capable method to detect metabolic processes in living organisms, in view of the medically, physiologically, and environmentally important research value of gold derivatives.

Recently, fluorescent probes are the most effective methods in the field of ion detection because of their instant response,\textsuperscript{15} operational simplicity,\textsuperscript{16,17} and high sensitivity.\textsuperscript{18−20} In recent years, the synthesis of macrocyclic compounds and their functionalization for applications in fluorescent probes have attracted the interest of many researchers. Pillararene was the only highly symmetrical tubular molecule found after the investigation of other macrocyclic molecules, such as crown ethers, cyclodextrin, calixarene, and cucurbituril\textsuperscript{21} and has been widely applied in biology, drug delivery,\textsuperscript{22} separation process,\textsuperscript{23} functional materials,\textsuperscript{24,25} and the environment since 2008 owing to its unique rigid structural characteristics and good host−guest recognition performance.\textsuperscript{26−28} To date, many researchers have successfully applied pillararenes to ion detection.\textsuperscript{29−31} For example, Huang’s research group reported a fluorescent chemosensor anthracene-appended 2:3 copillar[5]arene to detect Fe\textsuperscript{3+}.\textsuperscript{32} Yuan and Feng et al. reported a nonsymmetric pillar[5]arene bearing triazole-linked 8-oxyquinolines, which was applied as a sequential fluorescence sensor for thorium(IV) followed by fluoride ions with high sensitivity and selectivity.\textsuperscript{33} Xia and Wang et al. developed a host−guest system between pillar[5]arene and a rhodamine B-containing amphiphile as a Cu(II) ion sensor in aqueous media.\textsuperscript{34} In addition, the Stoddart et al. has reported gold recovery from gold-bearing raw materials by α-cyclodextrin.\textsuperscript{35}

In this paper, we synthesized a novel fluorescent probe, amino-pillar[5]arene (APA), bearing water-soluble amino groups. The amino groups were successfully modified on the
Au³⁺ ions have been found in the literature. Therefore, the reports concerning APA as an experiments were carried out. To the best of our knowledge, no primary aim of this work was to synthesize a novel Na⁺, Pb²⁺, Sb²⁺, Sn²⁺, Sr²⁺, Ni²⁺, and Au³⁺ (Ba²⁺, Bi⁺, Ca²⁺, Cd²⁺, Co³⁺, Cs⁺, Cu²⁺, Fe²⁺, Fe³⁺, Hg²⁺, K⁺, Li⁺, Mg²⁺, Na⁺, Pb²⁺, Sb²⁺, Sn²⁺, Sr²⁺, Ni²⁺, and Au³⁺ (λₑ = 323 nm).

2. RESULTS AND DISCUSSION

2.1. APA Fluorescence Performance Measurement. The APA probe showed yellow-white fluorescence (Figure 1a) under a UV lamp at 365 nm, as observed by the naked eye, and a sharp peak (Figure 1b) was detected at 323 nm in the fluorescence spectrum of aqueous APA. The experimental results and pictures show that APA can not only produce yellow-white light in solid form but also detect a strong fluorescence peak in aqueous solution. Although the emission peak of the APA aqueous solution was in the UV emission range and different from the solid-state luminescence performance, due to the luminescent properties of substance were not only related to itself and form. Moreover, different solvents also affect the luminescence properties. Therefore, the luminescent properties of the substances in different forms were independent of each other. Therefore, APA could be used as a fluorescence probe to study the recognition of the host–guest system of metal ions.

2.2. Detection of Metal Ions. The fluorescence spectra (Figure 2) showed an obvious decrease in fluorescence intensity from 703 to 20 au after adding 3 equiv of Au³⁺, but other metal ions did not show major changes. The results showed that the APA probe had high selectivity for Au³⁺ ions in aqueous solution and could thus be used as a fluorescence probe to detect Au³⁺ ions. The APA aqueous solution was in the UV emission range and different forms were independent of each other. Therefore, APA could be used as a fluorescent probe for detecting Au³⁺ ions in the environment and living organisms.

2.3. Fluorescence Spectral Titration. To further study the interaction between Au³⁺ ions and APA, fluorescence spectral titration experiments were carried out. A series of APA (2 × 10⁻⁵ mol·L⁻¹) and Au³⁺ ion solutions were prepared. The concentrations of Au³⁺ ions ranged from 0 to 6 equiv (0, 0.2, 0.4, 0.6, 0.8, 1.0, 1.2, 1.4, 1.6, 1.8, 2.0, 2.2, 2.4, 2.6, 2.8, and 3.0). The fluorescence spectrum measurement method was the same as described in Section 4.3.1. The results are shown in Figure 3. The fluorescence intensity gradually decreased with increasing concentrations of Au³⁺ ions, and the APA fluorescence was almost completely quenched when 4 equiv of Au³⁺ ions was added. Furthermore, there was a good linear curve fitting between the fluorescence intensity and Au³⁺ ion concentration over a range of concentrations. As shown in Figure 3b, the linear equation was y = 659.93 − 209.40X, R² = 0.99365.

The lowest detection limit was calculated by the following formula

\[ \text{LOD} = \frac{3\delta}{S} \]

where LOD (mol·L⁻¹): detection limit, \( \delta \) (mol·L⁻¹): standard deviation of 10 blank measurements, \( S = 209.40 \); the slope of a linear fitting curve from fluorescence spectral titration experiments.

\[ \delta = \sqrt{\frac{1}{N-1} \sum_{i=1}^{N} (F_i - \bar{F})^2} = 0.53 \]

The lowest detection limit obtained from formula 1 was 7.59 × 10⁻⁸ mol·L⁻¹. The results showed that the APA probe had a high sensitivity to detect Au³⁺ ions and that APA could be used as a fluorescence probe to detect Au³⁺ ions quantitatively in aqueous solution.

2.4. Job’s Plot. The stoichiometry of APA and Au³⁺ ions was determined by the Job method. The total molar concentrations of APA and Au³⁺ ions were maintained at 2 × 10⁻⁵ mol·L⁻¹ in aqueous solution. The molar fraction of Au³⁺ ions ([Au³⁺]/([Au³⁺] + [A])) varied from 0 to 1.0. Then, the fluorescence intensity was recorded at 323 nm by a fluorescence spectrometer at room temperature. A Job plot (Figure 4a) was generated by taking the molar fraction of Au³⁺ ions as the X-coordinate and the fluorescence intensity multiplied by the molar fraction as the Y-coordinate. The binding stoichiometry of the APA probe with Au³⁺ ions was determined from the highest.
point of the Job plot. If the highest point of the Job plot corresponds to the \( X \)-coordinates of 0.33, 0.5, and 0.67, the binding stoichiometries of the APA probe with Au\(^{3+}\) ions were 2:1, 1:1, and 1:2, respectively. It can be seen from Figure 4a that the highest point corresponding to the \( X \)-coordinate was 0.33, from which it could be inferred that the binding ratio of APA to Au\(^{3+}\) ion was 2:1.

**2.5. pH Effect Studies.** In general, pH was also a significant factor affecting ion fluorescence, which determined the sensitivity of detecting ions. In this work, the pH effect was investigated by adding Au\(^{3+}\) ion (2 equiv) to the solution of APA probe (2 \( \times \) 10\(^{-5}\) mol \( \cdot \) L\(^{-1}\)). The pH range of 1–13.5 was regulated by using 0.1 mol \( \cdot \) L\(^{-1}\) HCl and 0.1 mol \( \cdot \) L\(^{-1}\) NaOH. The APA fluorescence intensity increased as the pH increased (Figure 5). In a strong acid environment, the fluorescence intensity of APA was relatively weak, which could be explained by protonation of the amino group. The APA fluorescence was relatively strong in neutral and alkaline environments, and the maximum intensity was 744.356 au. Minor changes were observed in the pH range of 1–13.5 when the Au\(^{3+}\) ion solution was added, which indicated that the APA fluorescent probe was not significantly affected by the detection of Au\(^{3+}\) ions in this pH range. APA showed very stable fluorescence characteristics in the pH range of 1–13.5. Therefore, this fluorescent probe could be used for detecting Au\(^{3+}\) ions in subsequent research in acidic, neutral, and alkaline environments.

**2.6. Competition with Other Metal Ions.** For a good fluorescent probe, the most important factor is that the detected ions are not affected by the addition of competitive ions. In this research, the detectability of Au\(^{3+}\) ions by APA was evaluated by fluorescence competitive experiments, which were carried out by adding Au\(^{3+}\) ions (2 equiv) to the APA (2 \( \times \) 10\(^{-5}\) mol \( \cdot \) L\(^{-1}\)) solution with Ag\(^{+}\), Al\(^{3+}\), Ba\(^{2+}\), Bi\(^{3+}\), Ca\(^{2+}\), Cd\(^{2+}\), Co\(^{3+}\), Cs\(^{+}\), Cu\(^{2+}\), Fe\(^{2+}\), Fe\(^{3+}\), Hg\(^{2+}\), K\(^{+}\), Li\(^{+}\), Mg\(^{2+}\), Na\(^{+}\), Pb\(^{2+}\), Sb\(^{3+}\), Sn\(^{2+}\), Sr\(^{2+}\), and Ni\(^{2+}\) (2 equiv) cations and Br\(^{-}\), I\(^{-}\), PO\(_4\)\(^{3-}\), PO\(_4\)\(^{2-}\), Cl\(^{-}\), HSO\(_4\)\(^{-}\), CO\(_3\)\(^{2-}\), HCO\(_3\)\(^{-}\), SO\(_4\)\(^{2-}\), NO\(_3\)\(^{-}\), NO\(_2\)\(^{-}\), and F\(^{-}\) (2 equiv) anions, the results are shown in Figure 6. It was found that other coexisting metal ions did not cause any marked interference. Therefore, APA had good selectivity for the detection of Au\(^{3+}\) ions.

**2.7. \(^1\)H NMR and infrared Spectra.** To confirm the binding mode and mechanism of the fluorescent probe APA with Au\(^{3+}\) ions, the \(^1\)H NMR spectra of APA and different equivalents of Au\(^{3+}\) ions were measured in D\(_2\)O. Figure 7 showed that the obvious gradually disappeared APA peaks at 6.89 ppm (1), 4.54 ppm (3), and 3.88 ppm (5) when the concentration of Au\(^{3+}\) ions...
increased. Meanwhile, the obvious low-field shifts of APA peaks at 3.16 ppm (6) and 2.80 ppm (7) after addition of Au^{3+} ions. However, there were no significant changes at other peaks. Therefore, it inferred that the interaction between Au^{3+} ions with N signal peak (5) of APA, and at signals peaks 1, 2, and 3 disappearance of APA due to the electron cloud was shielded, which demonstrated again that APA and Au^{3+} ions formed a complex compound.

To further infer the binding mode and mechanism of the fluorescent probe APA and Au^{3+} ions, the infrared (IR) spectra of APA and complex compound were measured. The result is shown in Figure 8a; by comparing the IR spectra of APA with the complex, it can be clearly observed from Figure 8a that the peak intensity and peak shape at 3400 (N), 1650 (C=O), and 1150 (C−O−C) all have changed after Au^{3+} was complexed with APA. However, there was no significant change in the peak position corresponding to the benzene ring (1600, 1580, and 1500). Therefore, it can be inferred that Au^{3+} interacted with the N branch of the APA and without interacting with the benzene ring. On the basis of the findings of the above results, we inferred that the binding mode of APA with the Au^{3+} ions was shown in Figure 8b.

3. CONCLUSIONS

In summary, the fluorescent probe APA was successfully synthesized and characterized by nuclear magnetic resonance (NMR), IR, and high-resolution mass spectrometry (HRMS). Fluorescence spectroscopy showed that APA can be used as a probe to detect Au^{3+} ions. APA exhibited stable fluorescence characteristics in the pH range of 1−13.5, and other coexisting ions did not cause any marked interference. The binding mode was further confirmed by Job’s plot analysis, 1H NMR, and IR, showing that the binding ratio of APA to Au^{3+} ions was 2:1. Therefore, the fluorescent probe APA may open new prospects.
for the design and metabolism of gold-based drugs in living organisms.

4. EXPERIMENTAL SECTION

4.1. Materials. 1,4-Diethoxybenzene, paraformaldehyde, 1,2-dichloroethane, boron trifluoride etherate, chloroform, boron tribromide, ethanol, potassium carbonate, anhydrous acetonitrile, methyl chloroacetate, dichloromethane, anhydrous sodium sulfate, methanol, ethylenediamine, n-hexane, and hydrochloric acid were obtained from Aladdin Reagent Co. Ltd. Ag⁺, Al³⁺, Ba²⁺, Bi⁺, Ca²⁺, Cd²⁺, Co³⁺, Cs⁺, Cu²⁺, Fe²⁺, Fe³⁺, Hg²⁺, K⁺, Li⁺, Mg²⁺, Na⁺, Pb²⁺, Sb²⁺, Sn²⁺, Sr²⁺, Ni²⁺, Au³⁺, Br⁻, I⁻, PO₄³⁻, HPO₄²⁻, Cl⁻, H₂PO₄⁻, CO₃²⁻, HCO₃⁻, SO₄²⁻, NO₃⁻, NO₂⁻, F⁻ (AgNO₃, Al(NO₃)₃·9H₂O, BaCl₂·2HO₂, Bi(NO₃)₃·5H₂O, CaCl₂, CdCl₂, CoCl₂·6H₂O, Cs₂CO₃, CuSO₄·5H₂O, FeSO₄·7H₂O, FeCl₃·6H₂O, HgCl₂, KCl, LiF, MgSO₄·7H₂O, Na₂SO₄, Pb(NO₃)₂, SnCl₂·2H₂O, SrCl₂·6H₂O, NiCl₂·6H₂O, HAuCl₄, NaBr, NaI, Na₃PO₄, Na₃HPO₄, NaCl, NaHSO₄, Na₂CO₃, NaHCO₃, NaNO₃, NaNO₂, and NaF) metal ions were purchased from Sinopharm Chemical Reagent Co. Ltd. Deionized water was used throughout all experiments.

4.2. Syntheses of the APA Probe. The synthetic route to fluorescent probe E is depicted in Figure 9. First, compound B was obtained in one step by a Lewis acid-catalyzed condensation reaction of commercial starting material A and paraformaldehyde. Subsequently, deprotection of compound B with boron tribromide in chloroform produced compound C, which was further applied in the substitution reaction with methyl chloroacetate to achieve compound D. Finally, the desired product E was obtained via amidation of compound D with ethylenediamine.

4.2.1. Synthesis of Compound B. Paraformaldehyde (2.8 g, 0.09 mol) was added to a solution of 1,4-dioethoxy-benzene (5.0 g, 0.03 mol) in dry ClCH₂CH₂Cl (150 mL) under a nitrogen atmosphere at 25 °C. Next, BF₃·OEt₂ (4.2 mL) was added to the mixture, and the reaction was then stirred at 25 °C for 90 min. The mixture was then quenched with ethanol (20 mL). After stirring for 7 min, the filtrate was collected. The filtrate was extracted three times with deionized water, and the organic phase was then subjected to evaporation to an oil. The resulting oil was dissolved in CH₂Cl₂ (30 mL) and precipitated in EtOAc. The solid was recrystallized from CH₂Cl₂ and n-hexane to obtain a white solid B (2.8 g, yield: 52%).

1H NMR (400 MHz, CDCl₃): δ (ppm): 6.74 (s, 10H), 3.86 (q, J = 6.8 Hz, 20H), 3.77 (s, 10H), 1.28 (t, J = 6.8 Hz, 30H).

4.2.2. Synthesis of Compound C. Boron tribromide (4.5 mL, 0.044 mol) was slowly added to a solution of compound B (2.0 g, 0.022 mol) in CHCl₃ (100 mL) under a nitrogen atmosphere at −12 °C. The reaction was then stirred at 25 °C for 24 h. The mixture was then quenched by ice water (50 mL) and stirred for 30 min. Finally, the solid was collected by filtration and washed by hydrochloric acid (36%). Then, the samples were washed three times with CHCl₃ and dried to get a white solid C (1.42 g, yield: 90%). 1H NMR (400 MHz, DMSO): δ (ppm): 8.44 (s, 10H), 6.57 (s, 10H), 3.43 (s, 10H). 13C NMR (100 MHz, DMSO): δ (ppm): 146.5, 126.8, 117.7, 29.5.

4.2.3. Synthesis of Compound D. Potassium carbonate (10 g, 0.1 mol) and methyl chloroacetate (10 mL, 0.1 mol) were sequentially added to a solution of compound C (1.5 g, 0.0025 mol) in anhydrous CH₃CN (60 mL) under a nitrogen atmosphere. The reaction was stirred at 85 °C for 36 h. After washing with dichloromethane, the filtrate was collected. Then, the solvent was removed, and the solid was recrystallized from CH₂Cl₂ and MeOH to obtain a white solid D (1.87 g, yield: 56%). 1H NMR (400 MHz, CDCl₃): δ (ppm): 6.98 (s, 10H), 4.55 (s, 20H), 3.85 (s, 10H), 3.53 (s, 30H). 13C NMR (100 MHz, DMSO): δ (ppm): 169.7, 148.8, 128.4, 114.4, 65.4, 51.9, 29.2.
4.2.4. Synthesis of Compound E. Compound D (1.33 g, 0.001 mol) was dissolved in ethylenediamine (5 mL) under a nitrogen atmosphere. The reaction was stirred at 110 °C for 12 h. Then, the solvent was removed, and the residue was dissolved in deionized water (15 mL) and finally extracted three times with CHCl₃. The combined organic phase was washed with water, brined, dried by Na₂SO₄ filtered, and concentrated under reduced pressure to get a light-yellow solid E (1.4 g, yield: 87%). mp 126–127 °C. IR ν max (cm⁻¹): 3.357, 2.931, 1.666, 1.541, 1.496, 1.438, 1.403, 1.206, 1.062, 934, 582. ¹H NMR (400 MHz, D₂O): δ: 6.88 (s, 10H), 4.54 (s, 2OH), 3.88 (s, 1OH), 3.53–3.16 (m, 2OH), 2.97–2.40 (m, 2OH). ¹³C NMR (100 MHz, DMSO): δ (ppm): 168.3, 149.4, 128.4, 115.1, 68.2, 42.0, 41.2, 29.3. HRMS (ESI) m/z calc for C₂₃H₃₅N₂O₂ [M + H]⁺, 316.2309; found, 316.2307.

3.16 (m, 20H), 2.97 – 2.40 (m, 2OH).

3.53–3.16 (m, 2OH).

3.53; 1611.8279; found, 1611.8277.

Fluorescence Characteristics of APA. A stock solution of APA was prepared, which was further diluted to the appropriate concentration (2 × 10⁻⁵ mol L⁻¹). The emission spectrum was carried out using an excitation wavelength of 240 nm. The emission wavelength was adjusted to 10 nm, and the emission wavelength was adjusted to 10 nm. The excitation slit was adjusted to 10 nm, and the emission wavelength was adjusted to 10 nm.

3.2. Detection of Metal Ions. First, different metal ion solutions, including Ag⁺, Al³⁺, Ba²⁺, Bi³⁺, Ca²⁺, Cd²⁺, Co³⁺, Cs⁺, Cu²⁺, Fe³⁺, Fe⁶⁺, Hg²⁺, K⁺, Li⁺, Mg²⁺, Na⁺, Pb²⁺, Sn²⁺, Sr²⁺, Ni²⁺, and Au³⁺, were prepared. Then, different metal ions (5 equiv) were added to the APA solution (2 × 10⁻⁵ mol L⁻¹), and fluorescence spectra were measured and recorded under the conditions described in Section 3.2.1.

ASSOCIATED CONTENT

Supporting Information
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Synthetic route of fluorescent probe APA (PDF)

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Notes
The authors declare no competing financial interest.

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