



Contents lists available at ScienceDirect

Chinese Chemical Letters

journal homepage: [www.elsevier.com/locate/cclet](http://www.elsevier.com/locate/cclet)

Original article

## A coumarin-based colorimetric and fluorescent probe for the highly selective detection of Au<sup>3+</sup> ions

Qi Wang, Yan Feng\*, Jun Jiang, Wen-Juan Wang, Jiu-You Chen, Hong-Ting Sheng, Xiang-Ming Meng, Man-Zhou Zhu

School of Chemistry and Chemical Engineering &amp; Center for Atomic Engineering of Advanced Materials, Anhui University, Hefei 230039, China

## ARTICLE INFO

## Article history:

Received 4 January 2016  
Received in revised form 28 January 2016  
Accepted 23 February 2016  
Available online xxx

## Keywords:

Coumarin  
Alkyne  
Au<sup>3+</sup>  
Colorimetric  
Fluorescent probe

## ABSTRACT

We develop a novel coumarin-alkyne derivative (**NC7-AL**), which can specifically react with Au<sup>3+</sup> and give a colorimetric and fluorescent “turn-on” response toward Au<sup>3+</sup>. Notably, other alkynophilic metal species such as Au<sup>+</sup>, Ag<sup>+</sup>, Pd<sup>2+</sup>, Ni<sup>2+</sup>, Cu<sup>2+</sup>, and Hg<sup>2+</sup> do not produce an interfering signal. A good linear relationship between emission intensity at 420 nm and Au<sup>3+</sup> concentration from 0 to 2 equivalent is observed, and the detection limit (3σ/k) is estimated to be ca. 3.58 nmol/L. Harnessing the Au<sup>3+</sup>-induced color change from light yellow to colorless, we find that **NC7-AL**-based modified TLC plate can be used for convenient naked-eye detection of Au<sup>3+</sup>.

© 2016 Chinese Chemical Society and Institute of Materia Medica, Chinese Academy of Medical Sciences. Published by Elsevier B.V. All rights reserved.

### 1. Introduction

The noble metal gold (Au) and its salts have attracted intense attention owing to their potentials in catalysis [1,2] and biomedical applications [3–5]. Gold ions are known to activate alkynes for nucleophilic addition, and a series of organic transformations has been carried out according to the characteristic alkynophilicity of gold ions [6–10]. Also, gold-based drugs have been widely used in the treatment of rheumatoid arthritis and tuberculosis [11–13]. However, gold salts such as gold chloride are also highly toxic because they can damage the liver, kidneys, and nervous systems [14–16]. Furthermore, Au<sup>3+</sup> ions have strong affinity to DNA, which could lead to the serious damage of DNA via the catalytic cleavage [17–19]. Therefore, it is highly desirable to develop effective methods for the specific, rapid, and real-time monitoring of Au<sup>3+</sup> ions in the environment, agrochemicals, and potentially living systems.

Fluorescence sensing has become a preferable approach for Au<sup>3+</sup> detection because of its high sensitivity and selectivity, versatility, and ease of use [20,21]. Alkynes are often used as the recognition moiety for gold ions, due to their well-acknowledged alkynophilicity. Therefore, introducing a reactive alkyne moiety to the fluorophore could provide an efficient route to developing Au<sup>3+</sup>-selective fluorescent probes. Representative examples are Au<sup>3+</sup>-induced

intramolecular cyclization of the rhodamine-based alkynes to yield oxazolecarbaldehyde derivatives [22–25]. Additionally, several alkyne-containing compounds as fluorescent probes for Au<sup>3+</sup> ions based on fluorescein [26,27], BODIPY [28], 1,8-naphthalimide [29], and coumarin [30,31] fluorophores are also successfully designed and reported in the literature. However, the most prominent drawback of this sensing mechanism is the cross affinity with other alkynophilic metal species such as Au<sup>+</sup>, Ag<sup>+</sup>, Pd<sup>2+</sup>, Ni<sup>2+</sup>, Cu<sup>2+</sup> and Hg<sup>2+</sup>, which interferes with the detection of Au<sup>3+</sup> ions. Hence, there is an urgent need to develop a fluorescent probe for Au<sup>3+</sup> free from the cross-sensitivity of other alkynophilic metal species.

Herein, we present a colorimetric and fluorescent probe (**NC7-AL**) for the detection of Au<sup>3+</sup> utilizing the characteristic alkynophilicity of gold ions with low detection limit, large Stokes shift, and rapid response. Probe **NC7-AL** shows a remarkable fluorescence “turn-on” response only toward Au<sup>3+</sup> ions over Au<sup>+</sup>, Ag<sup>+</sup>, Pd<sup>2+</sup>, Ni<sup>2+</sup>, Cu<sup>2+</sup>, and Hg<sup>2+</sup>. Upon addition of Au<sup>3+</sup> ions, color changes from light yellow to colorless could be observed with the naked eye, and the **NC7-AL**-based modified TLC plates is an easy and convenient testing method that can be used for Au<sup>3+</sup> detection.

### 2. Experimental

#### 2.1. Materials and equipments

All solvents were purchased and dried according to standard procedures before use. <sup>1</sup>H-NMR and <sup>13</sup>C-NMR spectra were recorded

\* Corresponding author.  
E-mail address: [fy70@163.com](mailto:fy70@163.com) (Y. Feng).

on a Bruker Avance II spectrometer at 400 MHz and 100 MHz, respectively. ESI-TOF spectra were recorded over a Waters xevo G2 QT mass spectrometer. UV-vis absorption spectra were recorded on a Shimadzu UV-1800 spectrophotometer. Fluorescence spectra were obtained using a Hitachi F-7000 Fluorescence spectrometer. The fluorescence quantum yields were measured with HORIBA FluoroMax-4P.

### 2.2. Synthesis of 7-((4-(dimethylamino)phenyl)ethynyl)-2-oxo-N-(prop-2-yn-1-yl)-2H-chromene-3-carboxamide (NC7-AL)

A solution of **NC7** (0.333 g, 1 mmol), 1-hydroxybenzotriazole (HOBT, 0.203 g, 1.5 mmol), 1-(3-dimethylaminopropyl)-3-ethylcarbodiimide hydrochloride (EDC-HCl, 0.211 g, 1.1 mmol), ethyldiisopropylamine (DIPEA, 0.496 mL, 3 mmol), and propargylamine (0.192 mL, 3 mmol) in anhydrous DMF (10 mL) was stirred at r.t. under N<sub>2</sub> atmosphere for 24 h. The crude product was extracted with CH<sub>2</sub>Cl<sub>2</sub>, washed with brine and purified by column chromatography on silica gel (CH<sub>2</sub>Cl<sub>2</sub>:petroleum ether = 1:1, v/v) to afford 0.136 g of **NC7-AL** as a yellow solid in a 37% yield. <sup>1</sup>H NMR (400 MHz, DMSO-*d*<sub>6</sub>): δ 8.91 (t, 1H, *J* = 5.6 Hz), 8.87 (s, 1H), 7.98 (d, 1H, *J* = 8.1 Hz), 7.58 (s, 1H), 7.50 (d, 1H, *J* = 7.8 Hz), 7.42 (d, 2H, *J* = 8.6 Hz), 6.74 (d, 2H, *J* = 8.7 Hz), 4.13 (d, 2H, *J* = 3.2 Hz), 3.16 (s, 1H), 2.98 (s, 6H). <sup>13</sup>C NMR (100 MHz, DMSO-*d*<sub>6</sub>): δ 160.97, 160.08, 153.95, 150.60, 147.16, 132.94, 130.47, 128.92, 127.45, 118.06, 117.81, 117.52, 111.79, 107.12, 96.39, 86.99, 80.70, 73.26, 39.61, 28.70. HRMS (ESI-TOF): *m/z*: calcd. For [C<sub>23</sub>H<sub>18</sub>N<sub>2</sub>O<sub>3</sub> + H]<sup>+</sup>: 371.1317, found: 371.1396.

### 2.3. Preparation of test solution

In this paper, a solution of **NC7-AL** at 5 μmol/L in CH<sub>3</sub>CN was used for testing. The solutions of various testing species were prepared in doubly distilled water, and CH<sub>3</sub>CN-doubly distilled water (1:1, v/v) was used for Au<sup>3+</sup> due to solubility problems. Various ions were prepared from AuCl, AuCl<sub>3</sub>, Ce(NO<sub>3</sub>)<sub>3</sub>·6H<sub>2</sub>O, Cs<sub>2</sub>CO<sub>3</sub>, NaCl, ZnCl<sub>2</sub>, NiSO<sub>4</sub>·6H<sub>2</sub>O, CrCl<sub>3</sub>·6H<sub>2</sub>O, CoCl<sub>2</sub>, MnCl<sub>2</sub>·4H<sub>2</sub>O, CaCl<sub>2</sub>, MgSO<sub>4</sub>, BaCl<sub>2</sub>, KCl, CuCl<sub>2</sub>, CuI, FeCl<sub>2</sub>·4H<sub>2</sub>O, FeCl<sub>3</sub>, AgNO<sub>3</sub>, HgCl<sub>2</sub>, PdCl<sub>2</sub>, and *n*-Bu<sub>4</sub>N<sup>+</sup>CN<sup>-</sup>.

## 3. Results and discussion

### 3.1. Synthesis of probe NC7-AL

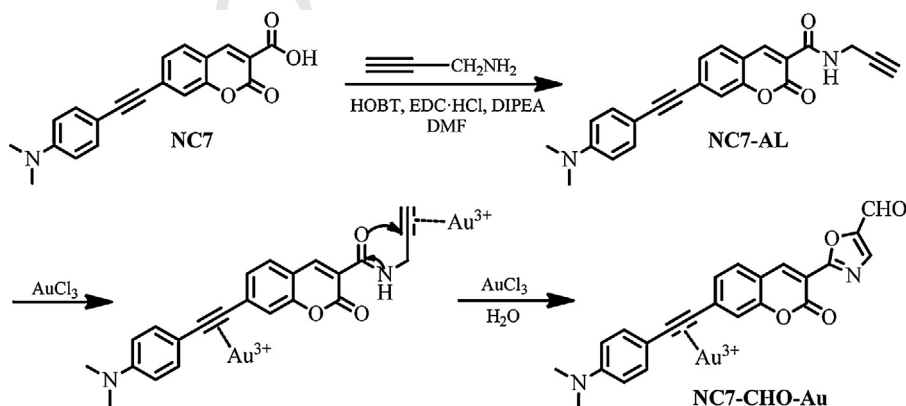
Compound **NC7** was synthesized from salicylaldehyde following literature procedures [32,33]. Condensation of **NC7** with propargylamine afforded **NC7-AL** as a yellow powder in a 37% yield (Scheme 1). The structure of **NC7-AL** was confirmed by <sup>1</sup>H NMR, <sup>13</sup>C NMR, and HR-MS.

### 3.2. Spectroscopic properties

The UV-vis and fluorescence spectra of **NC7-AL** (5 μmol/L) were investigated in CH<sub>3</sub>CN. As shown in Fig. 1, the **NC7-AL** solution displayed almost no fluorescence. Addition of Au<sup>3+</sup> to this solution resulted in enhancement of an emission band at 420 nm upon excitation at 360 nm. The emission intensity reached its maximum with ca. 6 equivalent of Au<sup>3+</sup>. An approximate 200-fold fluorescence enhancement could be observed accompanied by a quantum yield increase from <0.1% to 18.5%. The UV-vis spectra of **NC7-AL** displayed a similar sensing behavior toward the addition of Au<sup>3+</sup>. **NC7-AL** showed two absorption bands at 300 nm and 422 nm. With the addition of Au<sup>3+</sup> (10 equivalent), the absorption band at 422 nm diminished, and a new absorption band with a maximum at 330 nm gradually increased. Concomitantly, the solution color changed from light yellow to colorless, facilitating direct observation by the naked eyes. A well-defined isosbestic point at 378 nm was found indicating a desired one-to-one type clean conversion. The Stokes shift was as large as 90 nm, which could minimize self-quenching.

We studied the kinetics of the fluorescence enhancement resulting from the addition of Au<sup>3+</sup> (6 equivalent) to the solution of probe **NC7-AL**. As shown in Fig. S1 in Supporting information, the fluorescence intensity reached its maximum in ca. 20 s. Thus, all testing of UV-vis absorption and fluorescence were performed after 1 min. Moreover, a good linear relationship between the dosage of Au<sup>3+</sup> (from 0 to 2 equivalent) and the emission intensity was observed (Fig. S2 in Supporting information), and the detection limit (3σ/*k*) [34] was as low as 3.58 nmol/L. These results show that probe **NC7-AL** has a rapid response and good detection sensitivity toward Au<sup>3+</sup>.

We further investigated the selectivity profile of **NC7-AL** against other metal ions, such as Cu<sup>2+</sup>, Cu<sup>+</sup>, Ba<sup>2+</sup>, Mn<sup>2+</sup>, Ni<sup>2+</sup>, Pd<sup>2+</sup>, Ca<sup>2+</sup>, Cs<sup>+</sup>, Mg<sup>2+</sup>, Co<sup>2+</sup>, Ce<sup>3+</sup>, Cr<sup>3+</sup>, Na<sup>+</sup>, K<sup>+</sup>, Zn<sup>2+</sup>, Fe<sup>2+</sup>, Fe<sup>3+</sup>, Hg<sup>2+</sup>, Ag<sup>+</sup>, and Au<sup>+</sup>. The fluorescence intensity changes of the probe **NC7-AL** upon addition of various other metal ions are shown in Fig. 2a. It can be seen that the fluorescence of **NC7-AL** showed no obvious changes after the addition of metal ions except Au<sup>3+</sup> ions. Remarkably, commonly coexistent alkynophilic metal ions, such as Au<sup>+</sup>, Ag<sup>+</sup>, Pd<sup>2+</sup>, Ni<sup>2+</sup>, Cu<sup>2+</sup>, and Hg<sup>2+</sup> have no interference on **NC7-AL**. This is a notable advantage of **NC7-AL** compared to the existing probes for Au<sup>3+</sup>. As shown in Fig. 2b, bar graphs of **NC7-AL** toward various other metal ions (60 equivalent) both in the absence and presence of Au<sup>3+</sup> (6 equivalent) were carried out to investigate the selectivity of **NC7-AL** to Au<sup>3+</sup> in the presence of other metal ions. The fluorescence was activated when Au<sup>3+</sup> ions were added to the solutions of **NC7-AL** and those metal ions, which indicated that the coexistence of other metal ions had little effect on the detection of



Scheme 1. Synthetic route and possible Au<sup>3+</sup>-induced reaction mechanism of probe **NC7-AL**.

Download English Version:

<https://daneshyari.com/en/article/5143218>

Download Persian Version:

<https://daneshyari.com/article/5143218>

[Daneshyari.com](https://daneshyari.com)