



## Two new fluorescence turn-on chemosensors for cyanide based on dipyridylamine and aurone moiety



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### ABSTRACT

Two new fluorescence turn-on chemosensors for cyanide based on dipyridylamine substituted aurone moiety have been synthesized. The strong yellow-green fluorescence of the compounds were completely quenched after the addition of Cu(II) ions because of the complexation between the compounds and Cu(II) ions and were almost recovered after the addition of cyanide owing to the strong bonding ability between cyanide and Cu(II) ions, which lead to the removal of copper ions from the complexes. The chemosensors exhibit good repeatability.

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## 1. Introduction

Cyanide is a well-known highly toxic substance [1,2], but it is still indispensable in some industrial using such as gold mining, electroplating and plastic production [3–5]. Although regulations are established to limit the use of cyanide, its accidental release is unavoidable and may lead to disastrous consequences. Therefore, it is very important to develop efficient and fast-response way to track trace of cyanide. Up to now, fluorescent probe has drawn much attention due to its high sensitivity and selectivity [6–12]. Several strategies of designing cyanide probes have been developed, including hydrogen-bonding [13–15], nucleophilic addition [16–19] and metal complex ensemble displacement [20–23]. Among these, “turn-on” fluorescent CN<sup>-</sup> probes based on Cu<sup>2+</sup> ensembles have been greatly developed in recent years [20–22]. Aurones, which are the structurally isomers of flavonoids and are mainly found from natural sources, have been investigated focusing on their biological or medical activities but seldom concerned for their fluorescent virtue [24–26]. Herein, we present the synthesis, structures and CN<sup>-</sup> sensing fluorescence “turn-on” properties of two dipyridylamine substituted aurone moieties.

## 2. Experimental

### 2.1. Synthesis and characterization

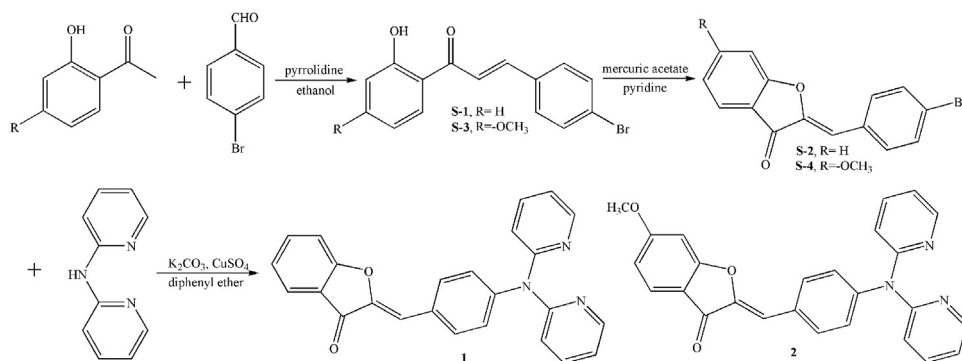
The synthetic routes to compounds **1** and **2** are shown in Scheme 1. 2-(Hydroxy)acetophenone, 2-hydroxy-4-methoxyacetophenone, *p*-bromo benzaldehyde, 2,2'-dipyridylamine and mercuric acetate (Hg(OAc)<sub>2</sub>) were purchased from Aladdin Reagents. Other reagents were purchased from Shanghai Reagents and were used as received directly without further purification. NMR spectra were recorded on a Bruker Avance III 400 MHz spectrometer at room temperature. Mass spectra were recorded on an Agilent Q-TOF6510 spectrometer. Elemental analyses were carried out on a PE 2400 autoanalyzer.

#### 2.1.1. Synthesis of 2'-hydroxy-4-bromo chalcone (**S-1**)

0.74 g (5.4 mmol) of 2-(hydroxy)acetophenone, 1.0 g (5.4 mmol) of *p*-bromo benzaldehyde and 0.2 mL (5.4 mmol) of pyrrolidine were dissolved in 20 mL ethanol. The reaction mixture was stirred at room temperature for 12 h and finally gave a yellow precipitate. The precipitate was filtered out and repeatedly washed with ethanol to afford 0.91 g of compound **S-1** as a yellow solid, yield 56%. <sup>1</sup>H NMR (400 MHz, CDCl<sub>3</sub>), δ: 6.96 (t, *J* = 7.6 Hz, 1H), 7.04 (d, *J* = 8.4 Hz, 1H), 7.52 (t, *J* = 8.0 Hz, 1H), 7.53 (d, *J* = 8.8 Hz, 2H), 7.58 (d, *J* = 8.4 Hz, 2H), 7.65 (d, *J* = 15.2 Hz, 1H), 7.86 (d, *J* = 15.2 Hz, 1H), 7.91 (d, *J* = 8.0 Hz, 1H), 12.76 (s, 1H).

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Scheme 1. Synthetic routes to compounds **1** and **2**.

### 2.1.2. Synthesis of 4-bromo aurone (S-2)

0.91 g (3.0 mmol) of **S-1**, 0.96 g (3.0 mmol) of mercuric acetate ( $\text{Hg}(\text{OAc})_2$ ) and 20 mL of pyridine were added in a 50 mL flask. The mixture was heated under reflux for 3 h. After cooling to room temperature, it was poured into ice water (150 mL) and acidified with dilute HCl. The precipitate was filtered and repeatedly washed with ethanol to afford 0.82 g of **S-2** as a yellow solid, yield 91%.  $^1\text{H}$  NMR (400 MHz,  $\text{CDCl}_3$ ),  $\delta$ : 6.82 (s, 1H), 7.24 (t,  $J=7.2$  Hz, 1H), 7.34 (d,  $J=8.4$  Hz, 1H), 7.59 (d,  $J=8.4$  Hz, 2H), 7.68 (t,  $J=8.0$  Hz, 1H), 7.79 (d,  $J=8.8$  Hz, 2H), 7.82 (d,  $J=8.0$  Hz, 1H).

### 2.1.3. Synthesis of 4-2,2'-dipyridylamine aurone (1)

0.50 g (2.9 mmol) of 2,2'-dipyridylamine, 0.36 g (1.2 mmol) of **S-2**, 0.66 g (4.8 mmol) of  $\text{K}_2\text{CO}_3$ , 0.032 g (0.2 mmol) of  $\text{CuSO}_4$  and 1.0 mL of diphenyl ether were added to a Schlenk tube. The mixture was degassed and heated to reflux (200 °C) for 3 days under nitrogen. After cooling to room temperature, it was dissolved in water and extracted with dichloromethane. The organic phase was repeatedly washed with water and dried over  $\text{MgSO}_4$ . The solvent was removed using a rotary evaporator and the residue was separated by column chromatography using dichloromethane/acetone (1:1) as the eluent to afford compound **1** as a yellow solid, then it was recrystallized from ethanol-dichloromethane to give orange crystal (0.25 g, yield 53%).  $^1\text{H}$  NMR (400 MHz,  $\text{CDCl}_3$ ),  $\delta$ : 6.90 (s, 1H), 7.00 (d,  $J=8.0$  Hz, 1H), 7.01 (d,  $J=7.2$  Hz, 1H), 7.07 (d,  $J=8.4$  Hz, 2H), 7.22 (t,  $J=7.2$  Hz, 1H), 7.23 (d,  $J=8.4$  Hz, 2H), 7.30 (d,  $J=8.4$  Hz, 1H), 7.60–7.67 (m, 3H), 7.81 (d,  $J=7.6$  Hz, 1H), 7.91 (d,  $J=8.8$  Hz, 2H), 8.38 (d,  $J=4.8$  Hz, 2H).  $^{13}\text{C}$  NMR (100 MHz,  $\text{CDCl}_3$ ),  $\delta$ : 113.02, 113.04, 118.02, 119.20, 121.96, 123.54, 124.77, 125.99, 128.77, 133.06, 136.84, 138.00, 146.70, 149.08, 157.91, 166.07, 184.78. MS for ( $\text{M}+\text{H}$ ) $^+$ : Calcd exact mass 392.1399; found 392.1430. Anal. calcd for  $\text{C}_{25}\text{H}_{17}\text{N}_3\text{O}_2$ : C 76.71, H 4.38, N 10.74; found C 76.48, H 4.39, N 10.73.

### 2.1.4. Synthesis of 2'-hydroxy-4'-methoxy-4-bromo chalcone (S-3)

**S-3** was synthesized similarly to **S-1** as yellow needles (58%)  $^1\text{H}$  NMR (400 MHz,  $\text{CDCl}_3$ ),  $\delta$ : 3.87 (s, 3H), 6.49 (d,  $J=8.8$  Hz, 2H), 7.51 (d,  $J=8.8$  Hz, 2H), 7.56 (d,  $J=15.2$  Hz, 1H), 7.57 (d,  $J=8.8$  Hz, 2H), 7.81 (d,  $J=15.6$  Hz, 1H), 7.81 (d,  $J=8.4$  Hz, 1H), 13.38 (s, 1H).

### 2.1.5. Synthesis of 2-methoxy-4'-bromo aurone (S-4)

**S-4** was synthesized similarly to compound **S-2** as yellow needles (94%).  $^1\text{H}$  NMR (400 MHz,  $\text{CDCl}_3$ ),  $\delta$ : 3.94 (s, 3H), 6.74 (s, 1H), 6.77 (d,  $J=7.6$  Hz, 1H), 6.78 (s, 1H), 7.57 (d,  $J=8.8$  Hz, 2H), 7.71 (d,  $J=8.8$  Hz, 1H), 7.75 (d,  $J=8.8$  Hz, 2H).

### 2.1.6. Synthesis of 4'-2,2'-dipyridylamine-6-methoxy aurone (2)

Compound **2** was synthesized similarly to compound **1** as red crystal (55%).  $^1\text{H}$  NMR (400 MHz,  $\text{CDCl}_3$ ),  $\delta$ : 3.92 (s, 3H), 6.75

(d,  $J=8.4$  Hz, 2H), 6.81 (s, 1H), 7.01 (t,  $J=7.6$  Hz, 2H), 7.05 (d,  $J=8.4$  Hz, 2H), 7.21 (d,  $J=8.8$  Hz, 2H), 7.61 (t,  $J=8.0$  Hz, 2H), 7.71 (d,  $J=8.8$  Hz, 1H), 7.88 (d,  $J=8.4$  Hz, 2H), 8.38 (d,  $J=4.8$  Hz, 2H).  $^{13}\text{C}$  NMR (100 MHz,  $\text{CDCl}_3$ ),  $\delta$ : 56.16, 96.75, 111.79, 112.24, 115.14, 117.92, 119.10, 125.92, 126.11, 129.00, 132.81, 137.96, 146.41, 147.64, 149.03, 157.94, 167.45, 168.48, 183.07. MS for ( $\text{M}+\text{H}$ ) $^+$ : Calcd exact mass 422.1505; found 422.1509. Anal. calcd for  $\text{C}_{26}\text{H}_{19}\text{N}_3\text{O}_3$ : C 74.10, H 4.54, N 9.97; found C 74.25, H 4.55, N 9.95.

## 2.2. Photophysical properties and response to cyanide anions

UV–vis absorption (with  $C=10.0\ \mu\text{M}$ ) and steady-state fluorescence spectra (with  $C=5.0\ \mu\text{M}$ ) of compounds **1** and **2** in acetonitrile were recorded at room temperature on a Shimadzu UV2550 spectrophotometer and an Edinburgh FLS 920 spectrometer, respectively. The spectral changes were monitored with the addition of a solution of Copper (II) perchlorate hexahydrate ( $\text{Cu}(\text{ClO}_4)_2 \cdot 6\text{H}_2\text{O}$ ) and tetra (*n*-butyl)ammonium cyanide (TBACN) in acetonitrile as  $\text{Cu}^{2+}$  and  $\text{CN}^-$  source, respectively. The fluorescence quantum yields  $\Phi$  were measured by using a standard method [27] with Coumarin 307 as the standard [28].

## 2.3. Structure determination

Single crystals of compounds **1** and **2** were grown by slow evaporation of the solutions of the corresponding compounds in ethanol-dichloromethane. X-ray diffraction data of **1** and **2** were collected on a Bruker Smart APEX-II CCD X-ray single crystal diffractometer with a graphite-monochromated Mo  $\text{K}\alpha$  radiation ( $k=0.71069\ \text{\AA}$ ) at 296(2) K. The CIF files of **1** and **2** have been deposited with the Cambridge structure database and assigned the following numbers: CCDC 966886 and 966887. Crystal data, data collections and structure refinements of crystals **1** and **2** are shown in Table S1.

## 3. Results and discussion

### 3.1. Synthesis and molecular structures

As shown in Scheme 1, compounds **1** and **2** were synthesized via three steps. Firstly, 2'-hydroxy-chalcones **S-1** and **S-3** were synthesized via the Claisen–Schmidt condensation reaction between appropriately substituted 2'-hydroxy-acetophenones and benzaldehydes in basic conditions [29]. Secondly, bromo aurone derivatives **S-2** and **S-4** were prepared via the oxidative cyclization methodology using mercury(II) acetate in pyridine with satisfactory yield [15]. Finally, compounds **1** and **2** were synthesized from 2,2'-dipyridylamine and bromo aurone derivatives via a typical Cu catalyzed Ullmann reaction [30]. All these compounds were fully characterized by  $^1\text{H}$  NMR,  $^{13}\text{C}$  NMR (Figs. S1 and S2),

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