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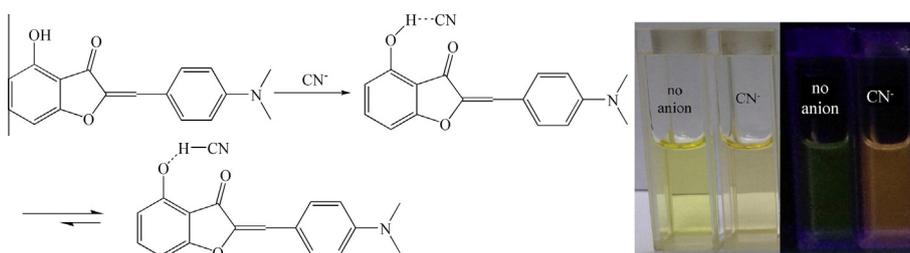
Three hydroxy aurone compounds as chemosensors for cyanide anions

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HIGHLIGHTS

- Three 4-hydroxy aurone compounds were synthesized.
- The compounds can recognize cyanide anions with obvious color and fluorescence change.
- The compounds allow naked eye detection of cyanide anions.

GRAPHICAL ABSTRACT



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ABSTRACT

Three new 4-hydroxy aurone compounds **1–3** with dimethylamino (**1**), bromine (**2**) and cyano (**3**) as terminal group have been synthesized. Their photophysical properties as well as recognition properties for cyanide anions in acetonitrile and aqueous solution have also been examined. These compounds exhibit remarkable response to cyanide anions with obvious color and fluorescence change owing to hydrogen bonding reaction between cyanide anions and the O–H moiety of the sensors, which allows naked eye detection of cyanide anions.

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Introduction

It is well known that cyanide anions are extremely toxic to living organism and a small amount of cyanide anions will lead to vomiting, convulsions, loss of consciousness, and even eventual death [1]. Despite their toxicity, cyanides are still widely applied to various processes as raw materials for synthetic fiber, synthetic resin, herbicide, and the gold-extraction process [1–3], which releases cyanide into the environment as a toxic contaminant. According to the standard of World Health Organization, cyanide

concentrations in drinking water cannot be more than 1.9 μM [4,5]. Therefore, highly selective probes for cyanide anions are of considerable interest due to their applicability to environmental cyanide detection and to the pathological bioimaging of the anions.

In recent years, the optical chemosensors for cyanide anions, especially sensors exhibiting obvious color and/or fluorescence change easily observed by the naked eye directly have attracted considerable attention because of their simplicity, low cost, and rapid measurement [6–25]. Our group is devoted to the research on chemosensors for cyanides for several years [26–28].

Here three new 4-hydroxy aurone receptors with high sensitivity and selectivity for cyanide anions through hydrogen bonding were synthesized and the recognition properties to cyanide anions were investigated. These compounds exhibit remarkable response

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to cyanide anions with obvious color and fluorescence changes, which allows naked eye detection of cyanide anions.

Experimental

Chemical and instruments

2',6'-Dihydroxyacetophenone, p-dimethylaminobenzaldehyde, p-bromobenzaldehyde and 4-formylbenzonitrile 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 ambient temperature. Mass spectra were recorded on an Agilent Q-TOF6510 spectrometer. Elemental analyses were carried out on a PE 2400 autoanalyzer.

Synthesis and characterization

The synthetic routes to compounds **1–3** is outlined in Scheme S1. The compounds were synthesized via four steps [29]. Firstly, one hydroxyl group in 2',6'-dihydroxyacetophenone was protected using methoxymethoxy group by the reaction of 2',6'-dihydroxyacetophenone with methyl chloromethyl ether in acetone to afford 2'-hydroxy-6'-methoxymethoxy acetophenone (**S-1**) as colorless oil with a high yield (83%). Secondly, **S-1** reacts with the aldehydes to afford the corresponding 2'-hydroxy-6'-methoxymethoxy chalcone compounds (**S-2**). Thirdly, 4-methoxymethoxy aurone compounds (**1'–3'**) were obtained by the cyclization of chalcones using mercury (II) acetate in pyridine according to Ref. [30]. Finally, the methoxymethoxy group in **1'–3'** was deprotected to afford the 4-hydroxy products **1–3** with high yield.

4'-N,N-Dimethylamino-4-hydroxy-aurone (1) Compound **1** was red solid in 92% yield. ^1H NMR (CDCl_3 , 400 MHz), δ (ppm): 3.07(s, 6H), 6.58 (d, $J = 8.2$ Hz, 1H), 6.76(d, $J = 8.9$ Hz, 2H), 6.77(d, $J = 8.1$ Hz, 1H), 6.85(s, 1H), 7.46 (t, $J = 8.2$ Hz, 1H), 7.83(d, $J = 8.9$ Hz, 2H), 7.97 (s, 1H). ^{13}C NMR (CDCl_3 , 100 MHz), δ (ppm): 40.18, 103.60, 109.16, 110.47, 112.10, 115.55, 119.90, 133.89, 138.18, 144.62, 151.65, 156.69, 164.36, 185.00. MS for $(\text{M} + \text{H})^+$, Calcd exact mass: 282.1130, found 282.1119. Anal. Calcd for $\text{C}_{17}\text{H}_{15}\text{NO}_3$: C, 72.58; H, 5.37; N, 4.98. Found C, 72.71; H, 5.39; N, 4.99.

4'-Bromide-4-hydroxy-aurone (2). Compound **2** was yellow solid in 97% yield. ^1H NMR (CDCl_3 , 400 MHz), δ (ppm): 6.64(d, $J = 8.4$ Hz, 1H), 6.76(s, 1H), 6.81(d, $J = 8.4$ Hz, 1H), 7.54(t, $J = 8.4$ Hz, 1H), 7.59(d, $J = 8.8$ Hz, 2H), 7.77(d, $J = 8.8$ Hz, 2H), 7.78 (s, 1H). ^{13}C NMR (CDCl_3 , 100 MHz), δ (ppm): 103.78, 109.56, 110.31, 111.80, 124.72, 131.06, 132.36, 132.96, 139.60, 146.98, 156.84, 164.94, 185.63. MS for $(\text{M} + \text{H})^+$, Calcd exact mass: 316.9813, found 316.9825. Anal. Calcd for $\text{C}_{15}\text{H}_9\text{BrO}_3$: C, 56.81; H, 2.86. Found C, 56.92; H, 2.87.

4'-Cyano-4-hydroxy-aurone (3) Compound **3** was yellow solid in 96% yield. ^1H NMR (CDCl_3 , 400 MHz), δ (ppm): 6.67(d, $J = 8.4$ Hz, 1H), 6.78(s, 1H), 6.82(d, $J = 8.0$ Hz, 1H), 7.57(t, $J = 8.0$ Hz, 1H), 7.73(d, $J = 8.4$ Hz, 2H), 7.75(s, 1H), 7.98(d, $J = 8.4$ Hz, 2H). ^{13}C NMR (CDCl_3 , 100 MHz), δ (ppm): 103.72, 109.11, 110.00, 110.72, 112.82, 118.50, 131.57, 132.52, 136.47, 139.94, 148.05, 156.86, 164.91, 185.36. Anal. Calcd for $\text{C}_{16}\text{H}_9\text{NO}_3$: C, 73.00; H, 3.45; N, 5.32. Found C, 73.16; H, 3.46; N, 5.31.

Photophysical properties and response to cyanide anions

Solutions of compounds **1–3** with 10 μM in acetonitrile (CH_3CN) or $\text{CH}_3\text{CN}-\text{H}_2\text{O}$ solution were prepared for photophysical measurements. UV-vis absorption and steady-state fluorescence spectra were recorded on a Shimadzu UV2550 spectrophotometer and an

Edinburgh FLS 920 spectrometer, respectively. The compounds were titrated with cyanide anions by addition of a solution TBACN in acetonitrile.

Structure determination

Single crystal of compound **1** was obtained by slow diffusion of the compound in dichloromethane. X-ray diffraction of a red single crystal of **1** (0.5 mm \times 0.5 mm \times 0.2 mm) was collected on a Bruker Smart APEX-II CCD X-ray single crystal diffractometer. The crystal belongs to the monoclinic system, $P 2_1/n$ space group, with formula $\text{C}_{17}\text{H}_{15}\text{NO}_3$ and molecular weight 281.30; $T = 296.0$ (2) K, $a = 7.5419$ (2) \AA , $b = 23.7783$ (8) \AA , $c = 8.4789$ (2) \AA , $\beta = 110.193$ (2) $^\circ$, $V = 1427.09$ (9) \AA^3 , $Z = 4$, $F(000) = 592$, $\mu = 0.090$ mm^{-1} , $d_{\text{calcd.}} = 1.309$ Mg m^{-3} , $R_1 = 0.0439$, $wR_2 = 0.1483$.

Results and discussion

Synthesis and crystal structure

The hydroxyl aurone compounds **1–3** were synthesized via four steps with 2',6'-dihydroxyacetophenone and p-substituted benzaldehyde as the starting materials with high yield. All the new compounds were fully characterized by NMR, mass spectra and elemental analyses.

The molecular structure of compound **1** along with the atom labeling is shown in Fig. 1. Benzofuran group possesses perfect planarity with the maximum deviation for the non-hydrogen atoms being 0.017 \AA for O1. Atoms O1 and O2 are also almost in benzofuran plane with the deviations are 0.006 \AA (O1) and 0.019 \AA (O2), respectively. The molecular backbone exhibits perfect planarity with the dihedral angle between benzofuran and benzene group being 7.62° , which is much larger than that of aurone without hydroxyl group (5.80°) [30]. That means that the import of hydroxyl group slightly decreases the molecular planarity.

Linear absorption and steady fluorescence properties

Linear absorption and steady fluorescence properties of the compounds in acetonitrile are shown in Table 1 and the spectra are shown in Fig. 2. Compound **1** can be classified as D- π -A type of molecule with dimethylamino and benzofuran as electron-donating and withdrawing groups, respectively. But compounds **2** and **3** can be classified as A- π -A' type of molecules with two electron-withdrawing groups (**2**: bromide and benzofuran; **3**: cyano and benzofuran). From Fig. 2, we can see that compound **1** exhibits strong linear absorption in blue region with the main absorption peak at 449 nm, which can be ascribed to charge transfer from dimethylamino to benzofuran. Compounds **2** and **3** possess similar absorption spectra with the main absorption peak at 389 nm, which also can be ascribed to intramolecular charge transfer and

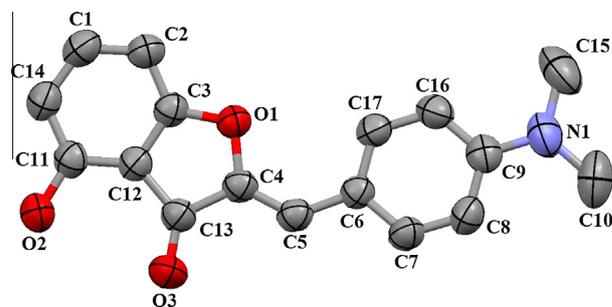


Fig. 1. The molecular structure of compound **1**.

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