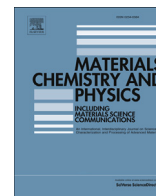




Contents lists available at ScienceDirect

Materials Chemistry and Physics

journal homepage: www.elsevier.com/locate/matchemphys

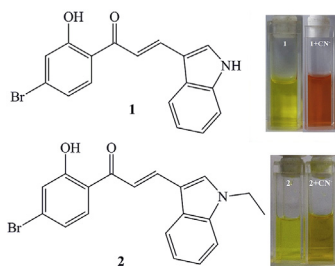
Two indole chalcone derivatives as chemosensor for cyanide anions

Yanyan Shan ^a, Qianqian Wu ^a, Ning Sun ^a, Yunhui Sun ^b, Duxia Cao ^{a,*}, Zhiqiang Liu ^{c,**}, Ruifang Guan ^a, Yongxiao Xu ^a, Xueying Yu ^a^a School of Material Science and Engineering, Shandong Provincial Key Laboratory of Preparation and Measurement of Building Materials, University of Jinan, Jinan, 250022, Shandong, China^b Zhejiang Province Comprehensive Utilization Institute of Alunite, Wenzhou, 325028, Zhejiang, China^c State Key Laboratory of Crystal Materials, Shandong University, Jinan, 250100, Shandong, China

HIGHLIGHTS

- Two bromine substituted indole chalcone derivatives were synthesized.
- The compounds exhibit fluorescence turn-on response to cyanide anions.
- Bonding mechanism of indole compound hydrogen bonding reaction between CN⁻ and N–H.
- Bonding mechanism of the corresponding N-ethylindole compound is Michael reaction.

GRAPHICAL ABSTRACT



ARTICLE INFO

Article history:

Received 2 December 2015

Received in revised form

14 October 2016

Accepted 30 October 2016

Available online xxx

Keywords:

Chalcone derivative

Hydrogen bonding

Cyanide anion

Chemosensor

Michael reaction

ABSTRACT

Two bromine substituted indole chalcone derivatives were synthesized via typical condensation reaction between 2-(hydroxyl)-4-bromine acetophenone and 3-indolealdehyde (**1**) or N-ethyl-3-indolealdehyde (**2**) in good yields. Their recognition properties for cyanide anions were investigated. The results indicate that the compounds exhibit quick and obvious color and fluorescence turn-on changes to cyanide anions with color changes from yellow to red (**1**) or from light yellow to deep yellow (**2**). Mechanism studies suggest that hydrogen bonding reaction between cyanide anions and N–H moiety of compound **1** occurs, which leads to the red shift of absorption spectra and the deepening of color. To compound **2**, bonding mechanism is typical Michael reaction mechanism.

© 2016 Elsevier B.V. All rights reserved.

1. Introduction

Cyanide has so formidable toxicity that once the tongue licks it a bit, the organism will be poisoned. Thus, cyanide is known as the “murder poison”. The World Health Organization allows that the

maximum permissible level of cyanide in drinking water is 1.9 μM [1,2]. Cyanide is ingested by the respiratory and digestive tract, which will release cyanide anion in the body quickly. Cyanide anions will combined with ferric ions in cytochrome and the enzyme activity will be inhibited and then the organism will loss of consciousness, dilated pupils and rapid death [3–5]. However, cyanide plays an important role in many industrial productions [6–9], such as electroplating industry, mining industry and the manufacture of various resin monomers. Therefore, the study of cyanide anion chemosensors aroused the interest of many scholars [10–22]. Our

* Corresponding author.

** Corresponding author.

E-mail addresses: duxiaocao@ujn.edu.cn (D. Cao), zqliu@sdu.edu.cn (Z. Liu).

group has reported series of chalcone derivatives with single reaction site [23–26], which show remarkable fluorescence response to CN^- based on Michael reaction mechanism. Here, two chalcone derivatives containing indole group as chemosensors for cyanide were reported and the reaction mechanism was analyzed. The compound with 3-indolealdehyde as the starting material possesses two different reaction sites.

2. Experimental section

2.1. Chemicals and instruments

The synthetic routes to the title compounds **1** and **2** are shown in Scheme 1. 2-(Hydroxyl)-4-bromine acetophenone and 3-indolealdehyde were purchased from Energy Chemical and tetra(*n*-butyl)ammonium cyanide was purchased from Aladdin Reagents. *N*-ethyl-indolealdehyde was synthesized according to literature procedure [27]. Magnetic resonance spectra were recorded on a MercuryPlus-400 spectrometer. Mass spectra were recorded on an Agilent Q-TOF6510 spectrometer.

2.2. Synthesis and characterizations

2.2.1. Synthesis of compound 1

0.73 g (5.0 mmol) of 3-indolealdehyde, 1.07 g (5.0 mmol) of 2-(hydroxyl)-4-bromine acetophenone and 0.4 mL (5.0 mmol) of pyrrolidine were dissolved in 20 mL of ethanol. The mixture was stirred 8 h at room temperature to afford yellow precipitates. The precipitates were filtered, washed with ethanol and dried. 1.30 g yellow solid was obtained with yield 76%. ^1H NMR (400 MHz, CDCl_3) δ 6.94 (d, $J = 8.9$ Hz, 1H), 7.34–7.41 (m, 2H), 7.48 (dd, $J = 6.6, 2.0$ Hz, 1H), 7.56 (dd, $J = 8.9, 2.5$ Hz, 1H), 7.58 (d, $J = 15.2$ Hz, 1H), 7.72 (d, $J = 2.9$ Hz, 1H), 8.02–8.05 (m, 2H), 8.25 (d, $J = 15.2$ Hz, 1H), 8.63 (s, 1H), 13.18 (s, 1H). ^{13}C NMR (100 MHz, CDCl_3) δ : 110.40, 112.22, 114.78, 114.94, 120.69, 120.84, 121.74, 122.46, 124.12, 125.46, 131.30, 131.74, 137.35, 138.44, 140.69, 162.58, 192.86. MS for $(\text{M}+\text{H})^+$, Calcd exact mass: 342.0130, found 342.0109.

2.2.2. Synthesis of compound 2

Compound **2** was synthesized similar to **1** with 2-(hydroxyl)-4-bromine acetophenone and *N*-ethyl-3-indolealdehyde as the starting materials. Yellow solid, 70%. ^1H NMR (400 MHz, CDCl_3) δ 1.56 (t, $J = 7.3$ Hz, 3H), 4.25 (q, $J = 7.3$ Hz, 2H), 6.93 (d, $J = 8.9$ Hz, 1H), 7.36–7.39 (m, 2H), 7.43–7.45 (m, 1H), 7.51 (d, $J = 15.4$ Hz, 1H), 7.54 (dd, $J = 8.8$ Hz, 2.4 Hz, 1H), 7.64 (s, 1H), 8.00–8.03 (m, 1H), 8.04 (d, $J = 2.4$ Hz, 1H), 8.24 (d, $J = 15.1$ Hz, 1H), 13.25 (s, 1H). ^{13}C NMR

(100 Hz, CDCl_3) δ : 15.33, 41.84, 110.32, 110.57, 113.32, 113.64, 120.64, 121.00, 121.84, 122.25, 123.60, 126.52, 131.64, 134.04, 137.61, 138.22, 140.68, 162.55, 192.64. MS for $(\text{M}+\text{H})^+$, Calcd exact mass: 370.0443, found 370.0469.

2.3. Photophysical properties' measurement

UV-vis absorption and steady-state fluorescence spectra of the compounds in acetonitrile with $C = 10 \mu\text{M}$ at room temperature were recorded on a Shimadzu UV2550 spectrophotometer and Edinburgh FLS920 fluorescence spectrometer, respectively. The spectral changes were monitored with the addition of a solution of tetra (*n*-butyl)ammonium cyanide (TBACN) in acetonitrile as CN^- source.

3. Results and discussion

3.1. UV-vis absorption spectral response to cyanide anions

The spectral responses of the compounds to cyanide were investigated firstly with absorption spectra as detected signal. UV-vis absorption spectral changes upon addition of CN^- to compounds **1** and **2** in acetonitrile are shown in Fig. 1. The compounds exhibit strong absorption in blue region. Compared with that of compound **1** (408 nm, $\epsilon = 5.9 \times 10^4 \text{ mol}^{-1} \text{ L cm}^{-1} \text{ M}^{-1} \text{ cm}^{-1}$), the absorption peak of compound **2** (419 nm, $\epsilon = 4.3 \times 10^4 \text{ mol}^{-1} \text{ L cm}^{-1} \text{ M}^{-1} \text{ cm}^{-1}$) is red-shifted 11 nm.

Both the compounds exhibit obvious response to cyanide in

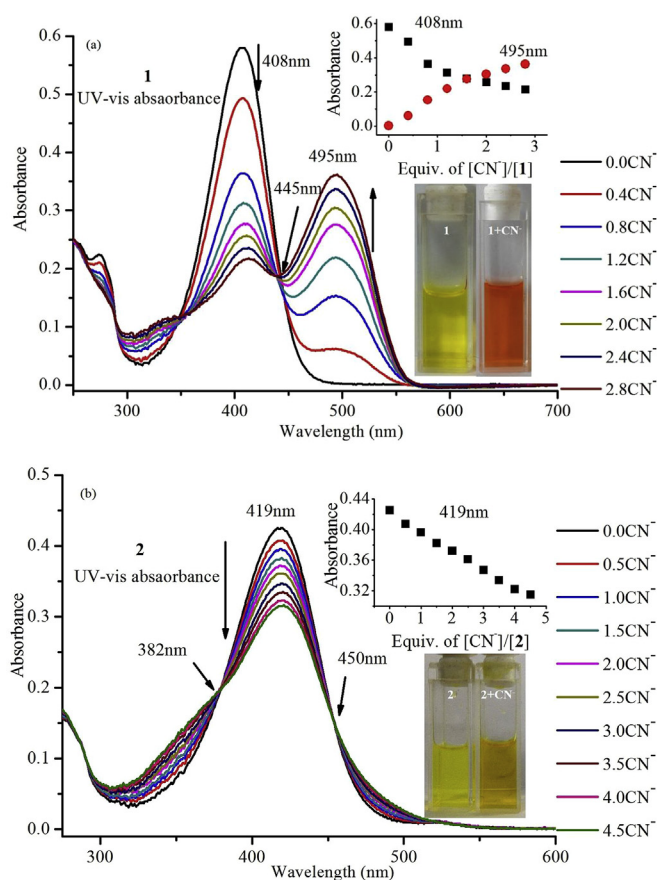


Fig. 1. Changes in UV-vis absorption spectra of compounds **1** (a) and **2** (b) in acetonitrile ($C = 10 \mu\text{M}$) upon the addition of different concentration of TBACN with equilibrium time being 10 s.

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

Download English Version:

<https://daneshyari.com/en/article/5448493>

Download Persian Version:

<https://daneshyari.com/article/5448493>

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