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# Chalcone derivatives as fluorescence turn-on chemosensors for cyanide anions

Yunhui Sun<sup>a</sup>, Huihui Chen<sup>a</sup>, Duxia Cao<sup>a,b,\*</sup>, Zhiqiang Liu<sup>b,\*\*</sup>, Hongyu Chen<sup>c</sup>, Yunlong Deng<sup>a</sup>, Qi Fang<sup>b</sup>

<sup>a</sup> School of Material Science and Engineering, Shandong Provincial Key Laboratory of Preparation and Measurement of Building Materials, University of Jinan, Jinan 250022, Shandong, China

<sup>b</sup> State Key Laboratory of Crystal Materials, Shandong University, Jinan 250100, Shandong, China

<sup>c</sup> Faculty of Chemistry and Chemical Engineering, Taishan Medical University, Taian 271016, Shandong, China

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### 1. Introduction

It is well known that cyanide anions (CN<sup>-</sup>) are extremely toxic to living organisms, and trace scale intake of cyanides may result in the death. However, cyanides are still widely used as irreplace-able industrial materials in some fields including synthetic resin, medicine, pesticide, fertilizer, gold and silver extraction [1–3]. World Health Organization sets the maximum permissive level of cyanide in drinking water is at  $1.9 \,\mu$ M [4,5]. So, cyanide detection is very important to environmental concern, food analysis and even anti-terrorism [6,7].

Over the past ten years, optical chemosensors for cyanide anion, in which a change in color, fluorescence intensity or spectral position corresponding to the chemical interaction between sensor and cyanide is monitored, have attracted growing interests due to their simple, inexpensive, and rapid implementation [3,8–13]. Generally, optical chemosensors for cyanides are designed based on the characteristic properties of cyanide anion, such as its strong nucleophilicity, high binding affinity and similarity with halogen anion ( $CN^-$  is also called pseudohalogen). For example, most of chemodosimeter approaches are based on the exceptional

## ABSTRACT

Three o-hydroxy chalcone derivatives **1–3** with carbazolyl (**1**), pyrene (**2**) and 4-nitrobenzene (**3**) as terminal group have been synthesized. Their crystal structures, photophysical properties in CH<sub>3</sub>CN and recognition properties for cyanide anions have also been examined. The research indicates that the stronger electroaffinity of the chalcone derivative's  $\beta$ -unit is beneficial to Michael reaction and can improve the response rate of the compound to cyanide anions. These compounds are found to be able to recognize cyanide anions with fluorescence turn-on response. Especially, compound **3** with strong electron accepting group exhibits remarkable response to cyanide anions in CH<sub>3</sub>CN–H<sub>2</sub>O (1:1, v/v) solution with a ca. 40-fold intensity enhancement.

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nucleophilicity of cyanides to the carbon cation [5,14–27]. Recently, Kim group discovered a chalcone derivative (2'-hydroxyl-4"dimethylamino-chalcone (**0**)), which showed a highly fluorescence turn-on response for the cyanide anion [28]. The *o*-hydroxy group is believed to play an important role in activating this chalcone compound as Michael acceptor to react with cyanide anion.



Our group is devoted to the research on chalcone derivatives for several years [29,30]. During the course of our ongoing efforts toward developing novel chemosensor for cyanides [31,32], chalcone derivatives were also examined. In this paper, three chalcone derivatives **1–3** with carbazolyl (**1**), pyrene (**2**) and 4-nitrobenzene (**3**) as terminal group, have been synthesized and their crystal structures and recognition properties for cyanide anions have also been examined. Varied electron donating or accepting group were introduced to tune the intramolecular hydrogen bond and then affect responsibility to cyanide anions.

## 2. Experimental

## 2.1. Synthesis and characterization

The synthetic routes of chalcone derivatives **1–3** and corresponding cyanide bonding compounds **1-CN** and **2-CN** are shown

<sup>\*</sup> Corresponding author at: School of Material Science and Engineering, Shandong Provincial Key Laboratory of Preparation and Measurement of Building Materials, University of Jinan, Jinan 250022, Shandong, China. Tel.: +86 531 8973 6751; fax: +86 531 8797 4453.

<sup>\*\*</sup> Corresponding author Tel.: +86 531 8836 2782; fax: +86 531 8836 2782. E-mail addresses: duxiacao@ujn.edu.cn (D. Cao), zqliu@sdu.edu.cn (Z. Liu).

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Scheme 1. Synthetic routes of compounds 1-3.

in Scheme 1. 2-(Hydroxy)acetophenone, pyrrolidine, pyrene-1carboxaldehyde and p-nitrobenzaldehyde were purchased from Aladdin Reagents. N-ethyl-carbazole-3-aldehyde, tetrabutylammonium cyanide and other chemicals were used as received from Shanghai Reagents. 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 of 1 [29]. 0.6 mL (5.0 mmol) 2-(hydroxy)acetophenone, 1.12g (5.0 mmol) N-ethyl-carbazole-3-aldehyde and 0.4 mL (5.0 mmol) pyrrolidine were dissolved in 15 mL ethanol. The mixture was stirred overnight at room temperature to afford compound 1 as yellow precipitates. The solid was filtered, washed twice with ethanol and dried in vacuum (1.31 g, yield 77%). <sup>1</sup>H NMR (CDCl<sub>3</sub>, 400 MHz),  $\delta$  (ppm): 1.47 (t, J=7.2 Hz, 3H), 4.39 (q, J=7.2 Hz, 2H), 6.97 (t, J=7.6 Hz, 1H), 7.04 (d, J=8.4 Hz, 1H), 7.30 (t, J=7.4 Hz, 1H), 7.42 (d, J=4.0 Hz, 1H), 7.45 (d, J=4.0 Hz, 1H), 7.49 (d, J=7.2 Hz, 1H), 7.53 (d, J=8.4 Hz, 1H), 7.71 (d, J=15.2 Hz, 1H), 7.81 (d, J=8.4 Hz, 1H), 8.02 (d, J=8.0 Hz, 1H), 8.16 (d, J = 7.6 Hz, 1H), 8.17 (d, J = 15.2 Hz, 1H), 8.40 (s, 1H), 13.11 (s, 1H). <sup>13</sup>C NMR (CDCl<sub>3</sub>, 100 MHz),  $\delta$  (ppm): 13.85, 37.84, 108.99, 116.78, 118.58, 118.70, 119.88, 120.33, 120.69, 121.98, 122.87, 123.61, 125.71, 126.48, 126.66, 129.56, 135.95, 140.55, 141.75, 147.20, 163.61, 193.65. MS for (M+H)<sup>+</sup>, Calcd exact mass: 342.1494, found 342.1486. Anal. Calcd for C23H19NO2: C, 80.92; H, 5.61; N, 4.10; Found C, 80.66; H, 5.63; N, 4.12.

Synthesis of 1-CN. 0.34g (1.0 mmol) of 1 and 10 equiv. tetrabutylammonium cyanide (TBACN) were dissolved in 50 mL CH<sub>3</sub>CN in a flask. The mixture was stirred overnight at room temperature and then the solvent was removed under reduced pressure and the residue was extracted with dichloromethane ( $50 \text{ mL} \times 3$ ) from acidic aqueous solvent and separated by column chromatography using dichloromethane as the eluent to afford the desired 1-CN as a light yellow solid (0.34 g, yield 92%). <sup>1</sup>H NMR (CDCl<sub>3</sub>, 400 MHz),  $\delta$  (ppm): 1.43 (t, J=7.2 Hz, 3H), 3.64 (dd, J=5.6 Hz, J=18 Hz, 1H), 3.86 (dd, J=8.4 Hz, J=18 Hz, 1H), 4.37 (q, J=7.2 Hz, 2H), 4.71 (dd, J = 6.0 Hz, J = 5.6 Hz, 1H, 6.88 (t, J = 7.8 Hz, 1H), 7.00 (d, J = 8.4 Hz, 1H),7.26 (t, J=7.6 Hz, 1H), 7.42 (dd, J=8.4 Hz, J=3.2 Hz, 2H), 7.46–7.52 (m, 3H), 7.65 (d, J=8.0Hz, 1H), 8.11 (d, J=7.6Hz, 1H), 8.15 (s, 1H), 11.92 (s, 1H). <sup>13</sup>C NMR (CDCl<sub>3</sub>, 100 MHz),  $\delta$  (ppm): 13.79, 31.82, 37.70, 44.83, 108.74, 109.21, 118.78, 118.82, 119.22, 119.30, 119.48, 120.62, 121.08, 122.37, 123.53, 124.76, 125.03, 126.33, 129.42, 137.06, 139.65, 140.47, 162.57, 200.58. MS for (M+H)<sup>+</sup>,

Calcd exact mass: 369.1603, found 369.1616. Anal. Calcd for  $C_{24}H_{20}N_2O_2$ : C, 78.24; H, 5.47; N, 7.60; Found C, 78.18; H, 5.52; N, 7.64.

Synthesis of **2**. Compound **2** was synthesized similar to compound **1** using pyrene-1-carboxaldehyde and 2-(hydroxy)acetophenone as the starting materials. Orange solid (0.25 g, yield 68%). <sup>1</sup>H NMR (CDCl<sub>3</sub>, 400 MHz),  $\delta$  (ppm): 7.00 (t, J=7.6 Hz, 1H), 7.08 (d, J=8.4 Hz, 1H), 7.55 (t, J=7.8 Hz, 1H), 7.96 (d, J=15.2 Hz, 1H), 8.04–8.08 (m, 2H), 8.07 (d, J=7.6 Hz, 1H), 8.10 (d, J=8.8 Hz, 1H), 8.17 (d, J=8.8 Hz, 1H), 8.22 (d, J=8.8 Hz, 1H), 8.25–8.28 (m, 2H), 8.46 (d, J=8.0 Hz, 1H), 8.61 (d, J=9.2 Hz, 1H), 9.13 (d, J=15.2 Hz, 1H), 12.99 (s, 1H). <sup>13</sup>C NMR (CDCl<sub>3</sub>, 100 MHz),  $\delta$  (ppm): 118.74, 118.92, 120.24, 122.05, 122.53, 124.35, 124.63, 125.07, 125.10, 126.13, 126.28, 126.44, 127.35, 128.44, 128.99, 129.03, 129.73, 130.64, 130.76, 131.35, 133.30, 136.41, 142.12, 163.78, 193.51. MS for (M+H)<sup>+</sup>, Calcd exact mass: 349.1229, found 349.1231. Anal. Calcd for C<sub>25</sub>H<sub>16</sub>O<sub>2</sub>: C, 86.19; H, 4.63; Found C, 86.08; H, 4.68.

Synthesis of **2-CN**. Compound **2-CN** was synthesized similar to **1-CN**. Pale-yellow solid (0.17 g, yield 86%) <sup>1</sup>H NMR (CDCl<sub>3</sub>, 400 MHz),  $\delta$  (ppm): 3.72 (dd, *J*=4.0 Hz, *J*=18 Hz, 1H), 4.05 (dd, *J*=9.6 Hz, *J*=18 Hz, 1H), 5.60 (dd, *J*=4.4 Hz, *J*=9.6 Hz, 1H), 6.85 (t, *J*=7.6 Hz, 1H), 7.03 (d, *J*=8.4 Hz, 1H), 7.49 (t, *J*=7.8 Hz, 1H), 7.61 (d, *J*=8.0 Hz, 1H), 8.07 (t, *J*=7.6 Hz, 1H), 8.09 (d, *J*=8.8 Hz, 1H), 8.14 (d, *J*=8.8 Hz, 1H), 8.18 (d, *J*=9.6 Hz, 1H), 8.23 (d, *J*=9.6 Hz, 1H), 8.25 (d, *J*=7.6 Hz, 3H), 8.30 (d, *J*=8.4 Hz, 1H), 11.94 (s, 1H). <sup>13</sup>C NMR (CDCl<sub>3</sub>, 100 MHz),  $\delta$  (ppm): 29.13, 43.91, 118.67, 118.92, 119.28, 120.68, 120.98, 124.69, 125.28, 125.31, 125.53, 125.82, 126.13, 126.51, 127.30, 127.52, 128.23, 129.27, 129.39, 130.51, 131.33, 131.67, 137.25, 162.68, 200.40. MS for (M+H)<sup>+</sup>, Calcd exact mass: 376.1338, found 376.1298. Anal. Calcd for C<sub>26</sub>H<sub>17</sub>NO<sub>2</sub>: C, 83.18; H, 4.56; N, 3.73; Found C, 83.06; H, 4.58; N, 3.76.

Synthesis of **3**. Compound **3** [33] was synthesized similar to **1** with p-nitrobenzaldehyde and 2-(hydroxy)acetophenone as the starting materials. Yellow solid (0.62 g, 46% yield): <sup>1</sup>H NMR (CDCl<sub>3</sub>, 400 MHz),  $\delta$  (ppm): 6.98 (t, *J* = 7.6 Hz, 1H), 7.06 (d, *J* = 8.4 Hz, 1H), 7.54 (t, *J* = 7.8 Hz, 1H), 7.76 (d, *J* = 15.6 Hz, 1H), 7.81 (d, *J* = 8.8 Hz, 2H), 7.91 (d, *J* = 9.0 Hz, 1H), 7.93 (d, *J* = 15.4 Hz, 1H), 8.30 (d, *J* = 8.8 Hz, 2H), 12.56 (s, 1H). <sup>13</sup>C NMR (CDCl<sub>3</sub>, 100 MHz),  $\delta$  (ppm): 118.88, 119.11, 119.80, 124.18, 124.30, 129.14, 129.68, 137.03, 140.72, 142.11, 148.80, 163.78, 193.01. MS for (M+H)<sup>+</sup>, Calcd exact mass: 270.0766, found 270.0735. Anal. Calcd for C<sub>15</sub>H<sub>11</sub>NO<sub>4</sub>: C, 66.91; H, 4.12; N, 5.20; Found C, 66.98; H, 4.10; N, 5.17.

#### Table 1

Crystal data, data collections, and structure refinements of compounds 2 and 3.

Crystal data	2	3	
Empirical formula	$C_{25}H_{16}O_2$	C <sub>15</sub> H <sub>11</sub> NO <sub>4</sub>	
Formula mass	348.38	269.25	
Crystal system	Orthorhombic	Monoclinic	
Space group	P21 21 21	$P2_1/c$	
a [Å]	4.964(5)	7.431(2)	
b [Å]	13.019(5)	12.954(4)	
c [Å]	26.727(5)	13.270(4)	
β[°]	90.00	94.463(4)	
V [Å <sup>3</sup> ]	1727.3(19)	1273.5(7)	
Ζ	4	4	
$\rho_{\rm calc}  [{ m g}  { m cm}^{-3}]$	1.34	1.404	
$\mu$ [mm <sup>-1</sup> ]	0.084	0.103	
F(000)	728	560	
Crystal size [mm]	$0.15 \times 0.12 \times 0.10$	$0.24 \times 0.09 \times 0.07$	
$\theta_{\min} - \theta_{\max}$ [°]	3.05-26.00	2.20-27.48	
T [K]	293(2)	296(2)	
Scan mode	ω, φ	ω, φ	
Index range	$-6 \le h \le 6$	$-9 \le h \le 9$	
	$-16 \le k \le 14$	$-13 \le k \le 16$	
	$-32 \le l \le 32$	$-16 \le l \le 17$	
Collected reflections	5987	7676	
Unique reflections	3135	2895	
Refined parameters	246	183	
$R_1$ , $wR_2$	0.0909, 0.2813	0.0666, 0.1960	
$ ho_{ m fin}$ (max., min.) [e Å <sup>-3</sup> ]	0.286, -0.270	0.170, -0.202	

Several efforts to get pure compound **3-CN** were failed because of the poor stability.

## 2.2. Photophysical properties and response to cyanide anions

Solutions of compounds **1–3** with 10  $\mu$ M in CH<sub>3</sub>CN or CH<sub>3</sub>CN–H<sub>2</sub>O (1:1, v/v) were prepared for photophysical measurements. UV–vis absorption and steady-state fluorescence spectra were recorded at room temperature on a Shimadzu UV2550 spectrophotometer and an Edinburgh FLS 920 spectrometer, respectively. The compounds were titrated with cyanide anions by the addition of a solution TBACN in CH<sub>3</sub>CN. The spectral changes were monitored with the varied equivalent of CN<sup>–</sup> and reaction time. The fluorescence quantum yields  $\Phi$  were measured by using a standard method with quinine sulfate as the standard [34].

#### 2.3. Structure determination

Single crystal of compound **2** was obtained by slow diffusion of *n*-hexane into a solution of the compound in chloroform (CHCl<sub>3</sub>). X-ray diffraction data of an orange single crystal of **2** (0.15 mm  $\times$  0.12 mm  $\times$  0.10 mm) was collected on a Gemini CCD X-ray single crystal diffractometer. Single crystal of compound **3** was obtained by slow evaporation of a solution of the compound in CHCl<sub>3</sub>. X-ray diffraction data of a yellow single crystal of compound **3** (0.24 mm  $\times$  0.08 mm  $\times$  0.04 mm) was collected on a Bruker Smart APEX-II CCD X-ray single crystal diffractometer. Crystal data, data collections and structure refinements of compounds **2** and **3** are shown in Table 1.

#### 3. Results and discussion

#### 3.1. Synthesis and molecular structures

All these chalcone derivatives **1–3** were synthesized by ordinary condensation reaction of the 2-(hydroxy)acetophenone with different aryl-aldehydes in good yields as the routes in Scheme 1. These compounds were fully characterized by NMR, mass spectra and elemental analyses. The coupling constant of vinylic protons of compounds **1–3** is nearly 15 Hz, which clearly indicates that these



Fig. 1. The molecular structures of compound 2 (a) and compound 3 (b).

compounds are trans-conformation and this was also proved by the single crystal diffraction results. No cis-isomers were detected [35]. To investigate the reactive site of Michael addition, corresponding cyanide bonding compounds were also prepared and purified. Compared with that of compound 1, the <sup>1</sup>H NMR spectrum of compound 1-CN is obviously different resulting from the Michael addition of the cyanide anions to the enone of 1. For example, the signal of vinylic protons in **1** (8.17 and 7.71 ppm, with I = 15.2 Hz) disappeared and three groups of new peaks appear at 3.64, 3.86, and 4.71 ppm, which should be corresponding to the protons bonding to C8 and C9. The fine structures in <sup>1</sup>H NMR of 1-CN also seem indicating the chiral carbon center of C9 after the Michael addition. Furtherly, <sup>13</sup>C NMR of **1-CN** also clearly shows the difference. Two aliphatic peaks at 44.83 and 31.82 ppm indicate the product of the Michael addition. Similar to that of compound 1-CN, the NMR spectra of compound 2-CN also clearly show three groups of new peaks at 5.60, 4.05 and 3.72 ppm in <sup>1</sup>H NMR and two aliphatic peaks at 43.91 and 29.13 ppm in <sup>13</sup>C NMR. Furtherly, the mass spectra and elemental analyses also support the assumed Michael addition product. What should be pointed out, although 1-CN and 2-CN can be obtained successfully, the nitro-substituted compound is failed. This compound seems quite unstable during the column chromatography process and acidic workshop.

The crystal structures of compounds **0** and **1** had been published by us previously [29,30], and the single crystal structures of 2 and 3 (Fig. 1 and Table 1) were also obtained recently. Unfortunately, all the efforts to grow the single crystal of 1-CN and 2-CN are failed. The dihedral angles between benzoyl groups and the phenyl rings of the aniline (0 and 1), pyrene ring (2) or nitrobenzene ring (3) are shown in Table 2. Although the dihedral angles between benzoyl group and the phenyl ring vary with different terminal groups, these compounds are generally planar. For compound 1, the dihedral angle is similar to that of compound **0**. But the dihedral angle of compound **2** is obviously bigger than that of **0** and **1**. The planarity of compound **3** is the best with the dihedral angle being only 3.08°. There are also some noticeable conjugation in the C10-C9=C8-C7 bridge of compounds **0–3** between the benzoyl groups and the phenyl rings, as indicated by the stretched C8 = C9 double bond and shrank C7-C8 and C9-C10 single bonds.

	C1—O1 (Å)	C1—C6 (Å)	C6—C7 (Å)	C7—O2 (Å)	C7—C8 (Å)	C8—C9 (Å)	C9—C10 (Å)	Dihedral angle $\alpha$ , (°) <sup>a</sup>
0	1.352(4)	1.410(4)	1.472(4)	1.254(4)	1.447 (4)	1.344 (4)	1.431 (4)	10.28
1	1.347(3)	1.397(3)	1.471(3)	1.250(3)	1.457(3)	1.328(3)	1.454(3)	11.12
2	1.343(10)	1.389(13)	1.441(12)	1.268(9)	1.459(12)	1.335(10)	1.425(11)	24.62
3	1.345(4)	1.403(4)	1.457(4)	1.239(3)	1.468(4)	1.320(4)	1.463(4)	3.08

 Table 2

 Selected geometric parameters (Å,°) of the crystal structures.

<sup>a</sup> The dihedral angles of benzoyl group and the phenyl ring (C10-C15).

## 3.2. Spectral response to cyanide anion complexation

Linear absorption spectra of compounds **1–3** in CH<sub>3</sub>CN are shown in Fig. 2. Compounds **0–3** are chalcone derivatives with similar molecular structures and different electron donor or acceptor groups. The accepting electron ability of terminal group is in a sequence nitrobenzene > pyrene > carbazolyl > dimethylamino. Compound 1 exhibits strong linear absorption at 405 nm with  $\varepsilon = 5.61 \times 10^4 \, \text{M}^{-1} \, \text{cm}^{-1}$ . Compound **2** exhibits vibrated structure at 392 nm ( $\varepsilon = 2.71 \times 10^4 \text{ M}^{-1} \text{ cm}^{-1}$ ) and 424 nm $(\varepsilon = 2.82 \times 10^4 \text{ M}^{-1} \text{ cm}^{-1})$ . Even though **2** possesses weaker charge transfer compared to 1 because of the weaker electron donating ability of pyrene group, its absorption peak exhibits slight red shift, which may be derived from larger conjugated structure of pyrene group. Compared to other two compounds, compound **3** exhibits shorter absorption peak with  $\lambda_{max}$  319 nm  $(\varepsilon = 3.42 \times 10^4 \,\mathrm{M^{-1} \, cm^{-1}})$ , which may be derived from the strong electron accepting ability of nitro group and then it is a  $A-\pi-A'$ type of molecule.

To examine the cyanide-recognizing properties of these compounds, tetrabutylammonium cyanide n-Bu<sub>4</sub>NCN (TBACN) as a cyanide source was added to a solution of compounds **0–3** in CH<sub>3</sub>CN. Time-dependent UV–vis spectral changes upon addition of CN<sup>-</sup> to compounds **1–3** in acetonitrile are shown in Fig. 3. As shown in Fig. 3(a), upon complexation with CN<sup>-</sup>, the characteristic intense charge-transfer absorption band of compound **1** at 405 nm gradually decreases and after 13 h, **1** bonds with cyanide anions completely. Compound **2** exhibits similar spectra response (Fig. 3(b)) to cyanide anions with **1**, the absorption band at 424 nm gradually decreases and new bands at 265 nm, 276 nm, 326 nm and 342 nm are attended and gradually increase and after 8.0 h, the complexation is finished.

Spectral experiments also indicate that different compounds show greatly different response rate to the addition of cyanide anions. The kinetic analysis gave the rate constants  $k(1) = 7.2 \times 10^{-5} \text{ s}^{-1}$ ,  $k(2) = 6.7 \times 10^{-4} \text{ s}^{-1}$  and  $k(3) = 1.8 \times 10^{-3} \text{ s}^{-1}$ 



**Fig. 2.** Linear absorption spectra of compounds **1–3** in CH<sub>3</sub>CN with  $C = 10 \mu$ M.

under the pseudo first-order reaction conditions [25]. These data clearly indicate that compound **3** exhibit stronger bonding interaction with cyanide anions than other compounds. So, it seems that the stronger electroaffinity of the chalcone-derivative's  $\beta$ -unit is beneficial to Michael reaction and can improve the response rate of the compound to cyanide anions.

What should be more interesting, further investigation indicates that compound **3** can response to cyanide anions in aqueous system. As shown in Fig. 4, upon the addition of cyanide anion, a new absorption band appeared at 256 nm and increased by time, with the simultaneous gradual disappearance of the band at 322 nm. The complexation is saturated after 2 h with an isoabsorptive point at 277 nm. The influence of other anions such as  $F^-$ ,  $Cl^-$ ,  $Br^-$ ,  $I^-$ ,  $HSO_4^-$ ,  $NO_3^-$ ,  $H_2PO_4^-$ ,  $AcO^-$ , and  $SCN^-$  have also been examined. These anions induced negligible absorption changes, therefore the compounds exhibit excellent selectivity to cyanide anions.

The pH range within which compound **3** remains stable was investigated. The absorbance of compound **3** at 322 nm was



**Fig. 3.** Time-dependent UV-vis spectral changes upon addition of 30 equiv.  $CN^-$  to **1** (a, 10  $\mu$ M in CH<sub>3</sub>CN) and 5 equiv.  $CN^-$  to **2** (b, 20  $\mu$ M in CH<sub>3</sub>CN). Insert: plot of absorption intensity at 405 nm (**1**) and 342 nm, 424 nm (**2**) versus time.



**Fig. 4.** Time-dependent UV-vis spectral changes upon addition of 30 equiv.  $CN^-$  to compound **3** (10  $\mu$ M in CH<sub>3</sub>CN—H<sub>2</sub>O (1:1, v/v)). Insert: plot of absorption intensity at 322 nm versus time.

monitored as a function of pH. As shown in Fig. S11, compound **3** remains stable with pH value changing from 5.0 to 10.0, but when pH value is larger than 10.3, the absorbance at 322 nm decreases and exhibit similar spectra change with the addition of cyanide. After 30 equiv. CN<sup>-</sup> was added to compound **3** solution in water, the pH is 9.4, which indicates that compound **3** should be stable without the addition of cyanide in this pH environment. pH-dependence for the CN<sup>-</sup> response was also investigated. From Fig. S12, we can see the compound exhibit similar response to CN<sup>-</sup> in pH range 6.0–10.0.

The detection limits [28,36,37] for  $CN^-$  are also provided. Fluorescence changes by increasing the amount of cyanide was measured (Fig. S13). The detection limit of compounds **1–3** are ca. 2.1  $\mu$ M (**1** in CH<sub>3</sub>CN), 0.8  $\mu$ M (**2** in CH<sub>3</sub>CN) and 7.2  $\mu$ M (**3** in CH<sub>3</sub>CN–H<sub>2</sub>O (1:1, v/v)).

Fluorescence spectral response of the compounds to cyanide anion complexation was also investigated. Excitation spectra of compounds **1–3** before and after the addition of TBACN are shown in Fig. S14. According to excitation spectra, the excitation wavelengths are 360 nm (**1**), 350 nm (**2**) and 280 nm (**3**), respectively. As shown in Fig. 5, compounds **1–3** exhibit weak fluorescence emission and the quantum yields of the compounds **1–3** are very low with the values being 0.00075 (**1**), 0.0035 (**2**) and 0.0018



**Fig. 5.** Fluorescence spectra change of solutions **1** and **2** in  $CH_3CN$ , **3** in  $CH_3CN$ — $H_2O$  (1:1, v/v) before and after addition of TBACN to **1** (30 equiv., 15 h), **2** (10 equiv., 10 h) and **3** (30 equiv., 3 h) with  $C = 10 \mu M$ .

(3). The weak fluorescence emission and low quantum yields of the compounds 1-3 are maybe due to the ultrafast intramolecular hydrogen atom transfer and/or ultrafast deactivation processes such as intersystem crossing and internal conversion through the hydrogen bonding [30,33,35]. However, their fluorescence intensity and quantum yields increase smartly with the addition of cyanide anion with quantum yields being 0.1 (1 added cyanide anions), 0.05 (2 added cyanide anions) and 0.041 (3 added cyanide anions). That is to say, the compounds are able to recognize cyanide anions with fluorescence turn-on response. After the addition of cyanide anions, compound 1 in CH<sub>3</sub>CN solution shows strong blue fluorescence emission with  $\lambda_{max}$  468 nm and the fluorescence intensity exhibits 80-fold enhancement with 17 nm red shift. Compound 2 exhibits similar spectral response with 10-fold intensity enhancement upon the addition of cyanide anions. Especially, compound 3 can recognize cyanide anions in CH<sub>3</sub>CN-H<sub>2</sub>O (1:1, v/v) solution with a ca. 40-fold intensity enhancement.

## 4. Conclusion

In summary, the effectiveness of three chalcone derivatives as chemosensor for cyanide anions were demonstrated. The chalcone derivative **3** with nitrobenzene as terminal electron acceptor group can recognize cyanide anions in  $CH_3CN-H_2O(1:1, v/v)$  solution. The further investigation following this way should be possible to find more efficient cyanide sensor for ground application.

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#### Appendix A. Supplementary data

Supplementary data associated with this article can be found, in the online version, at http://dx.doi.org/10.1016/j.jphotochem.2012.06.012.

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