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Two benzoyl coumarin amide fluorescence chemosensors for cyanide anions

Zian Wang^a, Qianqian Wu^a, Jiale Li^a, Shuang Qiu^a, Duxia Cao^{a, *}, Yongxiao Xu^a,

Zhiqiang Liu^b, Xueying Yu^a, Yatong Sun^a

^aSchool of Material Science and Engineering, University of Jinan, Jinan 250022,

Shandong, China

^bState Key Laboratory of Crystal Materials, Shandong University, Jinan 250100,

Shandong, China

*Corresponding author. E-mail address: duxiacao@ujn.edu.cn (D. X. Cao).

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Abstract

Two new benzoyl coumarin amide derivatives with ortho hydroxyl benzoyl as terminal group have been synthesized. Their photophysical properties and recognition properties for cyanide anions in acetonitrile have also been examined. The influence of electron donating diethylamino group in coumarin ring and hydroxyl in benzoyl groups on recognition properties was explored. The results indicate that the compounds can recognize cyanide anions with obvious absorption and fluorescence spectral change and high sensitivity. The import of diethylamine group increases smartly the absorption ability and fluorescence intensity of the compound, which allows the recognition for cyanide anions can be observed by naked eyes. The in situ hydrogen nuclear magnetic resonance spectra combining photophysical properties change and job's plot data confirm that Michael addition between the chemosensors and cyanide anions occurs. Molecular conjugation is interrupted, which leads to fluorescence quenching. At the same time, there is a certain extent hydrogen bond reaction between cyanide and hydroxyl group in the compounds, which is beneficial to the recognition.

Keywords: Coumarin amide; Cyanide anion; Chemosensor; Photophysical property; Michael addition

1. Introduction

For centuries, cyanide because of its extreme toxicity [1-4] has been used as a poison. In addition to direct ingestion, cyanide vapors and dusts can also enter the body through the respiratory tract or directly into the skin and produce great harm to organisms [5]. Cyanide also affects many functions in the human body, including blood vessels, vision, the central nervous system, heart, endocrine and metabolic systems. Despite its toxicity, cyanide is still widely applied as industrial materials in some fields such as synthetic fiber, synthetic resin, herbicide and the gold-extraction [6,7]. This enables the detection of trace cyanide to become an important part of human's health and social environment security [8-11]. So accurate and rapid determination of cyanide (cyanide anion) is of great significance to environmental monitoring and food safety.

At present, there are many methods to detect cyanide anions, such as spectral method, voltammetry, electrochemical method, ion chromatography and so on [12-18]. In recent years, people pay more attention to spectral method with the advantages of convenient, quick, low cost and high sensitivity [19-28]. Investigation indicates that hydrogen bonding often can promote the reaction between the Michael receptor and CN⁻, and electron withdrawing group is beneficial to Michael reaction [29,30]. Therefore, here two coumarin amide derivatives with hydroxyl benzoyl as terminal group were designed and synthesized. The original design is to introduce hydroxyl synergetic recognition role to cyanide anions. The introduction of diethylamine in coumarin ring can improve the fluorescence properties of the compound and

sensitivity of fluorescence recognition.

2. Experimental

2.1. Chemicals and instruments

2-hydroxy-benzamide and N,N-diethylaminesalicylaldehyde were purchased from Aladdin Reagents. Coumarin-3-carboxylic acid was purchased from Alfa Aesar company. Diethyl malonate was purchased from Tianjin Kermel Chemical Reagent Company Limited. Tetrabutylammonium cyanide was used as received from Shanghai Reagents. Coumarin-3-formyl chloride and 7-N,N-diethylaminecoumarin-3-formyl chloride obtained with coumarin-3-carboxylic acid were or 7-N,N-diethylaminocoumarin-3-carboxylic acid and thionyl chloride as the starting materials according to Ref. [31]. Magnetic resonance spectra were recorded on a MercuryPlus-400 spectrometer. Mass spectra were recorded on an Agilent Q-TOF6510 spectrometer.

2.2. Synthesis and characterization of the compounds

The synthetic routes to the title compounds **1** and **2** are shown in Scheme 1. The compounds were synthesized by the reaction between coumarin-3-formyl chloride or 7-N,N-diethylaminecoumarin-3-formyl chloride and 2-hydroxy-benzamide in anhydrous dichloromethane with triethylamine as catalyzer.

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

2.2.1. Synthesis of compound 1

Compound **1** was synthesized by the reaction between coumarin-3-formyl chloride and 2-hydroxy-benzamide. 0.21 g (0.001 mol) Of coumarin-3-formyl chloride, 0.14 g (0.001 mol) of 2-hydroxy-benzamide and 30 mL of anhydrous dichloromethane as solvent were put in a 50 mL round bottom flask. And then 0.7 mL triethylamine as catalyst was added. The mixture was stirred at room temperature for 8 hours and the reaction solution was treated by vacuum filtering. The precipitate was washed with dilute hydrochloric acid of 1% concentration, then washed with distilled water and dried to get 0.18g white solid compound **1** with 57.5% yield. ¹H NMR (400 MHz, DMSO), δ : 6.98 (t, *J* = 7.6 Hz, 1H), 7.03 (d, *J* = 7.6 Hz, 1H), 7.45 - 7.50 (m, 2H), 7.54 (d, *J* = 8.8 Hz, 1H), 7.80 (td, *J* = 8.0, 1.6 Hz, 1H), 7.85 (dd, *J* = 8.0, 1.6 Hz, 1H), 8.04 (dd, *J* = 8.0 Hz, 1.6 Hz, 1H), 8.94 (s, 1H), 11.57 (s, 1H), 12.44 (s, 1H). ¹³C NMR (100 MHz, DMSO), δ : 116.27, 117.05, 118.39, 118.48, 119.67, 120.10, 125.28, 130.59, 131.07, 134.64, 134.68, 148.73, 154.12, 157.00, 159.49, 160.87, 164.27. MS for (M+H)⁺. Calcd exact mass: 310.0637, found 310.0713.

2.2.2. Synthesis of compound 2

Compound 2 was synthesized similar to compound 1 with 7-N,N-diethylaminecoumarin-3-formyl chloride and 2-hydroxybenzamide as the starting materials with 34.1% yield, yellow solid. ¹H NMR (400 MHz, DMSO), δ : 1.28 (t, J = 7.2 Hz, 6H), 3.50 (q, J = 7.2 Hz, 4H), 6.54 (d, J = 2.4 Hz, 1H), 6.71 (dd, J = 9.2, 2.4 Hz, 1H), 6.98 (t, J = 7.6 Hz, 1H), 7.03 (d, J = 8.4 Hz, 1H), 7.48-7.53 (m, 2H), 7.83 (dd, J = 8.0, 1.2 Hz, 1H), 8.84 (s, 1H), 11.95 (s, 1H), 12.67 (s, 1H). ¹³C

NMR (100 MHz, CD₃Cl), δ: 12.59, 45.53, 96.81, 108.38, 108.93, 110.99, 114.27, 119.02, 119.57, 126.86, 132.25, 136.00, 150.60, 153.87, 158.40, 161.08, 163.24, 163.74, 169.68. MS for (M+H)⁺. Calcd exact mass: 381.1372, found: 381.1487.

2.3. Structure determination

Single crystal of compound **2** was obtained by slow evaporation of the compound in the mixed solution of dichloromethane and ethanol. X-ray diffraction data of a yellow single crystal (0.43 mm × 0.12 mm × 0.064 mm) was collected on a Bruker Smart APEX-II CCD X-ray single crystal diffractometer. The radiation source was Mo Ka. The crystal belongs to monoclinic, P2₁/a space group with a formula $C_{21}H_{20}N_2O_5$ and molecular weight 380.39. a = 13.8622(12) Å, b = 8.6531(7) Å, c =16.3572(13) Å, $\beta = 108.293(9)$, V = 1862.9(3) Å³, Z = 4, $\rho_{calc} = 1.356$ g cm⁻³, $\mu =$ 0.809 mm⁻¹, F(000) = 800.0, R1 = 0.0643, wR2 = 0.2081, T = 293.15 K.

2.4. Density functional theory (DFT) calculation

Density functional theory (DFT) calculation on compound **2** was carried out using Gaussian 09 program. B3LYP level of theory (Becke's three parameter hybrid functional [32] in conjunction with Lee, Yang, and Parr's correlation functional [33]) was used for the calculation. The frontier molecular orbitals (HOMO and LUMO) of the compound were obtained using the visualization package Gauss View.

2.5. Photophysical properties' measurement

UV-vis absorption and steady state fluorescence spectra of the compounds in acetonitrile with $C = 3.0 \times 10^{-5} \text{ mol} \cdot \text{L}^{-1}$ (1) or $1.0 \times 10^{-5} \text{ mol} \cdot \text{L}^{-1}$ (2) at room temperature were recorded on a Shimadzu UV2550 spectrophotometer and a Horiba Fluoromax-4 fluorescence spectrometer, respectively. To examine the

cyanide-recognizing properties of the compounds, tetrabutylammonium cyanide n-Bu₄NCN (TBACN) as a cyanide source was added to the solution of compounds **1** and **2** in acetonitrile.

3. Results and discussion

3.1. Crystal Structure

Molecular structure of compound **2** is shown in Fig. 1. The planarity of compound **2** is very good with the dihedral angle between the coumarin ring and benzene ring being only 3.77° , which will be beneficial to fluorescence properties. The bond lengths of N1-C8 (1.382(5) Å) is longer than that of N1-C7 (1.363(5) Å), but O3=C8 (1.212(4) Å) is shorter than that of C7=O2 (1.229(4) Å), which may be because benzoyl group possesses stronger electron accepting ability than diethylamine coumarin group. The frontier molecular orbitals (HOMO and LUMO) of the compound is shown in Fig. 2. From Fig. 2, we can see that charge transfer from diethylamine group to benzamide upon excitation from HOMO to LUMO.



Fig. 2. The electron density distribution of the frontier molecular orbitals of compound 2.

3.2. Photophysical properties of the compounds

UV-vis absorption and fluorescence spectra of the compounds in acetonitrile are

shown in Fig. 3. The compounds exhibit absorption in violet (**1**, 305 nm, $\varepsilon = 1.65 \times 10^4$ M⁻¹cm⁻¹; 336 nm, $\varepsilon = 1.38 \times 10^4$ M⁻¹cm⁻¹) or blue (**2**, 440 nm, $\varepsilon = 6.14 \times 10^4$ M⁻¹cm⁻¹) spectral region and fluorescence in blue spectral region (**1**, 417 nm; **2**, 483 nm). Compared with compound **1**, the absorption peak of compound **2** has 135 nm red-shift and molar absorptivity increases about three times. Similar to absorption properties, compound **2** also exhibits stronger fluorescence emission and longer fluorescence peak, which is due to the introduction of strong electron donating diethylamino group enhancing charge transfer of the molecule.

Fig. 3. UV-vis absorption and fluorescence spectra (1, $\lambda_{ex} = 305$ nm; 2, $\lambda_{ex} = 440$ nm) of the compounds in acetonitrile with $C = 3.0 \times 10^{-5}$ mol/L (1) and 1.0×10^{-5} mol/L (2).

3.3. Recognition of the compounds for cyanide anions

UV-vis absorption and fluorescence spectral changes upon the addition of CN^{-} to the compounds in acetonitrile are shown in Fig. 4. Both the compounds have sensitive response to cyanide in acetonitrile. As shown in Fig. 4a, we can see that with the increase of cyanide, the main absorption peak at 305 nm and 336 nm of compound **1** decrease gradually and three new absorption peaks at 272 nm, 316 nm and 387 nm are appeared. The complexation is saturated after 1.0 equiv. TBACN was added. Compound **2** also exhibits obvious spectral change upon the addition of cyanide anions with original absorption peak disappearing and new absorption peak in short

wavelength region appearing. Because of the longer absorption peak of compound 2, the compound exhibits obvious color change from yellow to colorless, which can be observed by naked eyes (insert of Fig. 4b). Based on the strong fluorescence emission of compound 2, the fluorescence response of 2 to CN^- was also investigated. As shown in Fig. 4c, because of the complexation with CN^- , the fluorescence peak of compound 2 at 483 nm gradually decreases to 18.0% of the original intensity at last, which can be observed by naked eye (insert of Fig. 4c).

Fig. 4. Changes in UV-vis absorption (a, b) and fluorescence (c, $\lambda_{ex} = 440$ nm) spectra of compounds 1 ($C = 3.0 \times 10^{-5}$ mol/L) and 2 ($C = 1.0 \times 10^{-5}$ mol/L) in acetonitrile upon the addition of cyanide anions.

The detection limits [34] of the compounds for cyanide anions were calculated. The detection limits with absorption as detected signal are 0.025 μ M (1) and 0.016 μ M (2), respectively. The detection limit of 2 with fluorescence as detected signal is 0.000047 μ M. Compound 2 has higher sensitivity relative to 1. Based on the fact that the spectral change of compound 2 can be observed by naked eyes because of the longer absorption and fluorescence peaks and stronger fluorescence emission, the import of diethylamine is helpful. But the previous reported work found that the import of diethylamine group decreases the electronegativity of C4 position of coumarin and then decreases the sensitivity. Most these compounds can recognize cyanide anions with lower sensitivity [31,35]. So even the compound with diethylamine group

possesses strong fluorescence and can recognize CN^- with fluorescence as detected signal and the change can be observed by naked eyes. But the low sensitivity limits their application. Here it is noted that compound **2** exhibits high sensitivity, which indicates that ortho hydroxyl benzoyl group is beneficial to the response.

It is generally accepted that high selectivity is a very important criterion for a desirable chemosensor. Therefore, the influence of other anions on the compounds was also examined. As shown in Fig. 5, other anions such as F^{-} , Cl^{-} , Br^{-} , I^{-} , $H_2PO_4^{-}$, HSO_4^{-} and SCN^{-} all induce negligible absorption changes.

Fig. 5. UV-vis spectral changes of compound 2 ($C = 1.0 \times 10^{-5} \text{ mol/L}$) in acetonitrile upon the addition of various anions ($C = 2.0 \times 10^{-5} \text{ mol/L}$).

3.3. Recognition mechanism

The recognition mechanism of the compounds to cyanide anions was investigated based on in situ ¹H NMR. From Fig. 6 we can see that ¹H NMR of compound **2** has single peaks at 8.86 ppm, 11.98 ppm and 12.69 ppm, which are attributed to proton in C4 of coumarin (Ha), hydroxyl (Hb) and amino (Hc). After the addition of TBACN, Ha and Hb peaks disappear and a new peak at 4.91 ppm is attended. Proton signal of Hc has a slight movement from 12.69 ppm to 13.58 ppm. The disappearance of proton signal at 8.86 ppm and the appearance of new peak at 4.91 ppm are due to the Michael addition between cyanide anions and compound **2** at C4 position, which leads to the double bond on coumarin ring of compound **2** opening

and cyanide group is added on the β position of the double bond. In addition, the peak at 11.98 ppm is disappeared after the addition of cyanide anion, which is because there is a certain extent hydrogen bond reaction between cyanide and hydroxyl group.

Fig. 6. ¹H NMR spectra of compound **2** in CD₃CN before and after the

addition of cyanide anions.

In order to clarify the reaction mechanism between the compounds and the cyanide anion, job-plot curves [36] were also tested. As shown in Fig. 7, the job's plot points of compounds **1** and **2** were between 0.6-0.7, which further proved there is a certain extent hydrogen bond reaction between cyanide anion and hydroxyl group.

Fig. 7. Job's plot curves of compounds 1 and 2 to cyanide anions.

¹H NMR and job's plot curves indicate that Michael addition reaction between the compounds and cyanide anions occurs. And at the same time, the presence of the hydroxyl group of compounds **1** and **2** makes the hydrogen bonding function simultaneously. Binding stoichiometry of both compounds with cyanide anion was calculated according to Ref. [37]. Binding stoichiometries between the compounds and CN⁻ are about 1:1, which means one molecule of the compounds bonding with one cyanide anions and the main reaction site is Michael reaction site C4 in coumarin group. Binding constants of both compounds with cyanide anion were also calculated

according to Refs. [37], which are $1.73 \times 10^5 \text{ M}^{-1}$ (1, absorption), $6.49 \times 10^5 \text{ M}^{-1}$ (2, absorption) and $2.23 \times 10^5 \text{ M}^{-1}$ (2, fluorescence), respectively. The recognition mechanism is shown in Fig. 8.

Fig. 8. Proposed bonding mechanism of compound 2 to CN⁻.

There is an interesting phenomenon that after the addition of cyanide anions, absorption band of compound 2 is similar to the long wavelength absorption band of 1. We think that before the addition of CN^{-} , the absorption spectra of the compounds are mainly from charge transfer. Diethylamine is a strong electron donating group. The import of this group in compound 2 increases the electron density of the molecule and leads to obvious charge transfer from diethylamine group to benzamide and then further leads to longer absorption and fluorescence band. After the addition of CN^{-} , the double bond on coumarin ring is broken and this charge transfer is blocked. The role of diethylamine group is weakened. So the main absorption spectra of the two compounds are similar.

4. Conclusion

Two benzoyl coumarin amide fluorescence chemosensors for cyanide anions have been synthesized. The compounds were characterized by nuclear magnetic resonance spectroscopy and mass spectrometry, and the crystal structure of compound 2 was obtained. Both the compounds exhibit obvious UV-vis absorption and

fluorescence response for cyanide anions in acetonitrile. Especially, compound **2** exhibits obvious color and fluorescence change, which can be observed by naked eye. Both the compounds can response cyanide anions with high sensitivity. Identification mechanism analysis shows that the compounds and cyanide anions have a Michael addition effect, and the conjugation of the molecules is interrupted, which leads to the fluorescence quenching. There is a certain extent hydrogen bond reaction between cyanide and hydroxyl group, which is beneficial to the recognition.

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Fig. 1.The molecular structure of compound 2.

CCC CCC ANA



2



Fig. 2. The electron density distribution of the frontier molecular orbitals of compound 2.



Fig. 3. UV-vis absorption and fluorescence spectra (1, $\lambda_{ex} = 305$ nm; 2, $\lambda_{ex} = 440$ nm) of the compounds in acetonitrile with $C = 3.0 \times 10^{-5}$ mol/L (1) and 1.0×10^{-5} mol/L

^{(2).}





Fig. 4. Changes in UV-vis absorption (a, b) and fluorescence (c, $\lambda_{ex} = 440$ nm) spectra of compounds 1 ($C = 3.0 \times 10^{-5}$ mol/L) and 2 ($C = 1.0 \times 10^{-5}$ mol/L) in acetonitrile upon the addition of cyanide anions.



Fig. 5. UV-vis spectral changes of compound 2 ($C = 1.0 \times 10^{-5} \text{ mol/L}$) in acetonitrile upon the addition of various anions ($C = 2.0 \times 10^{-5} \text{ mol/L}$).



Fig. 6. ¹H NMR spectra of compound **2** in CD₃CN before and after the addition of cyanide anions.

CCC CCC



Fig. 7. Job's plot curves of compounds 1 and 2 to cyanide anions.



Fig. 8. Proposed bonding mechanism of compound 2 to CN⁻.

SCR.



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

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300000 450000 2 250000 fluorescence () 250000 E 200000 400000 483 nm 483 nm 1 350000 150000 100000 300000 (1) 250000 -50000 0.00CN 0.25CN 0.0 2.0 0.5 1.0 1.5 Intensity 0.50CN Equiwalents of [CN]/[2] 200000 0.75CN 1.00CN 150000 2+C 1.25CN 100000 1.50CN 50000 - 1.75CN 2.00CN 460 480 500 520 540 560 580 600 620 640 Wavelength (nm) Chip and the second sec

Graphical Abstract

Highlights

- Two benzoyl coumarin amide derivatives with hydroxyl benzoyl group were synthesized.
- The compounds can recognize CN⁻ with obvious absorption and fluorescence spectral change.
- The change of the compound with diethylamine group can be observed by naked eyes.
- The recognition mechanism is Michael addition assisted by hydrogen bonding

reaction.

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