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3-Amidocoumarins as chemodosimeters to trap cyanide through both Michael and intramolecular cyclization reaction

Yunhui Sun[a], Yuanyuan Wang[b], Duxia Cao[a,b,*], Huihui Chen[a], Zhiqiang Liu[b,**], Qi Fang[b]

[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] State Key Laboratory of Crystal Materials, Shandong University, Jinan 250100, Shandong, China

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ABSTRACT

Two 3-amidocoumarin derivatives have been utilized as doubly activated Michael acceptors to selectively and sensitively trap cyanide with remarkable colorimetric and fluorescent response. Single-crystal structures of the cyanide adducts clearly confirm Michael additions taking place at the 4-position of coumarin, then an unexpected intramolecular cyclization reaction between the cyano and amido groups occurring.

1. Introduction

Although the cyanide anion (CN^-) is well known for its extreme toxicity [1], it is still widely used in many industrial fields including synthetic resin, medicine, pesticide and fertilizer manufacture, as well as gold and silver extraction [2]. Thus, human exposure to cyanide may arise from dietary, industrial, environmental and other sources. Therefore, the development of CN^- sensor, which is cheap, simple, highly selective and sensitive, would be of great significance [3].

Generally, a successful strategy to design colorimetric and/or fluorescent probes for CN^- must be based around the characteristic chemical properties of cyanide, such as its high binding affinity to several metal ions [4], similarity to halogen anions (CN^- is known as pseudohalogen) [5], as well as strong nucleophilicity [6]. However, in many cases, cyanide-sensing probes have been proposed based on spectral techniques but lack clear structural evidence. The actual sensing mechanism is often quite difficult to be determined, especially for multi-activated or multi-site sensors. For example, Kim and co-workers have recently reported that some coumarin derivatives can work as efficient probes to detect the cyanide anion and/or biothiol, but the postulated binding sites are different in different papers due to different mechanisms being proposed [7].

Considering both intramolecular hydrogen bond activated enones [8] and coumarinyl aldehydes have been reported to function as Michael acceptors for cyanide, and that the coumarin group has been extensively studied as unit for fluorescent signaling, we decided to examine the CN^- sensing properties of two easily prepared 3-amidocoumarin derivatives **1** [9] and **2** [10] (see Scheme 1). Since the 4-position of coumarin is known as a site for Michael addition [7b,7c], compounds **1** and **2** could be assumed to be doubly activated Michael acceptors due to the presence of an intramolecular hydrogen bond.

2. Experimental

2.1. Synthesis and characterization

The synthetic routes to compounds **1** and **2**, and the corresponding cyanide-bound compounds **1-CN** and **2-CN** are shown in Scheme 1. Compounds **1** and **2** can be easily prepared according to the literature procedure by one-step reaction from coumarin-3-carboxylic acid and the appropriate amine under mild conditions [11]. Both of them are quite stable to the air in solution. Coumarin-3-carboxylic acid, benzylamine, aniline, triphenylphosphite and pyridine were obtained as analytical reagents from Shanghai Reagents. NMR spectra of the compounds were recorded on a Bruker Avance III 400 MHz spectrometer at ambient temperature. High-resolution mass spectra were recorded on an Agilent

* 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 8973 6751.
** 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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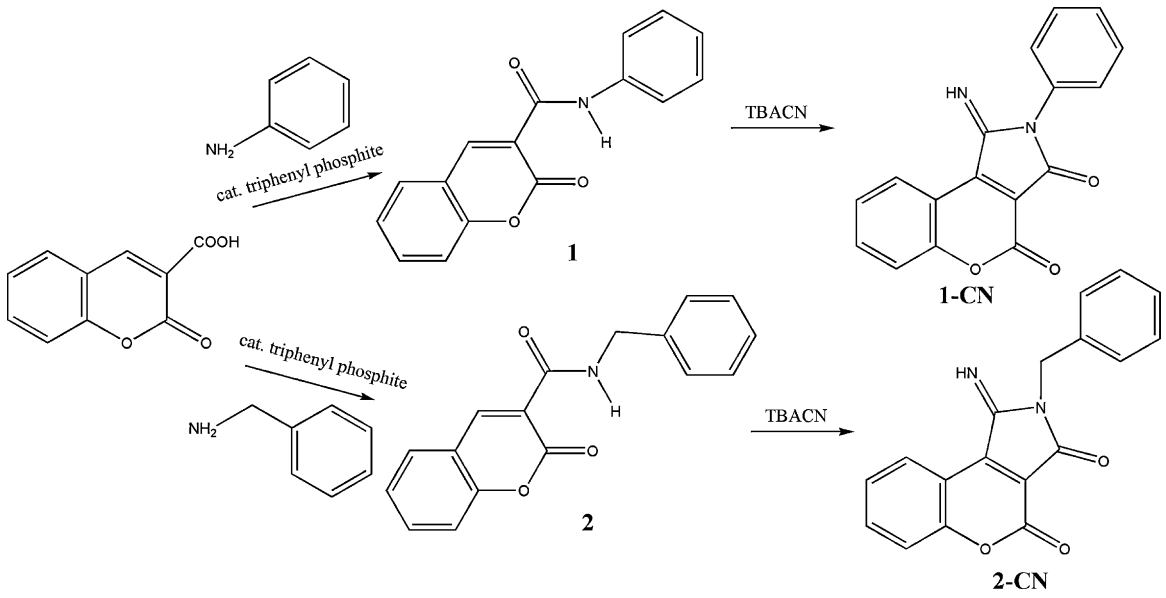

Scheme 1. Synthetic routes to compounds **1**, **2**, **1-CN** and **2-CN**.

Q-TOF6510 spectrometer. Elemental analyses were carried out on a PE 2400 autoanalyzer.

Synthesis of N-[(2-Oxo-2*H*-1-benzopyran-3-yl)carboxyl]-aniline (**1**). Aniline (0.93 g, 10 mmol) in pyridine (10 mL) was added to solution of coumarin-3-carboxylic acid (1.90 g, 10 mmol) in pyridine (30 mL). The mixture was stirred for 10 min, during which a white precipitate was formed. The mixture was heated at reflux and triphenylphosphite (3.10 g, 10 mmol) was added slowly over a period of 15 min. The resultant solution was then heated with stirring at reflux for 8 h. After the mixture had cooled to room temperature, distilled water (200 mL) was added, and a pale precipitate formed immediately. The separated precipitate was repeatedly recrystallized from chloroform to give small, light-yellow needles. (0.82 g, 31%). ^{1}H NMR ($CDCl_3$, 400 MHz): 7.17 (t, J = 7.6 Hz, 1H), 7.36–7.46 (m, 4H), 7.69 (d, J = 8.0 Hz, 1H), 7.74 (d, J = 7.6 Hz, 3H), 9.03 (s, 1H), 10.84 (s, 1H).

Synthesis of N-[(2-Oxo-2*H*-1-benzopyran-3-yl)carboxyl]-benzylamine (**2**). Compound **2** was synthesized similarly to compound **1** to give white platelets (0.45 g, 16%). ^{1}H NMR ($CDCl_3$, 400 MHz): 4.60 (d, J = 6.0 Hz, 2H), 7.08–7.33 (m, 7H), 7.57–7.63 (m, 2H), 8.88 (s, 1H), 9.11 (s, 1H).

Synthesis of compound **1-CN**. Compound **1** (128 mg, 0.48 mmol) and TBACN (5 equiv.) were dissolved in CH_3CN (25 mL) in a flask. The reaction mixture was stirred 1 h at room temperature and then the solvent was removed under the reduced pressure and the residue was extracted with CH_2Cl_2 (25 mL × 3) from aqueous solvent and purified by column chromatography using CH_2Cl_2 to afford **1-CN** as a yellow solid (68.7 mg, 49%). ^{1}H NMR ($CDCl_3$, 400 MHz): 7.31 (d, J = 7.6 Hz, 2H), 7.42–7.50 (m, 2H), 7.53 (d, J = 7.6 Hz, 1H), 7.60 (t, J = 7.6 Hz, 2H), 7.76 (t, J = 8.0 Hz, 1H), 8.93 (d, J = 7.6 Hz, 1H), 9.11 (s, 1H). ^{13}C NMR ($CDCl_3$, 100 MHz): 114.37, 115.86, 117.40, 125.54, 127.96, 128.27, 129.47 130.32, 130.45, 135.28, 149.30, 154.14, 156.09, 157.20, 162.72. MS for $(M+H)^+$: Calcd exact mass: 291.0770; found 291.0772. Anal. calcd for $C_{17}H_{10}N_2O_3$: C 70.34, H 3.47, N 9.65; found C 70.46, H 3.45, N 9.68.

Synthesis of compound **2-CN**. Compound **2-CN** was synthesized similarly to **1-CN** to give the product as a light-yellow solid (81.4 mg, 56%).^{1}H NMR ($CDCl_3$, 400 MHz): 4.91 (s, 2H), 7.28–7.33 (m, 3H), 7.36 (d, J = 7.2 Hz, 2H), 7.39 (d, J = 7.8 Hz, 1H), 7.44 (d, J = 8.0 Hz, 1H), 7.71 (t, J = 7.8 Hz, 1H), 8.82 (d, J = 8.0 Hz, 1H), 8.89 (s, 1H). ^{13}C NMR ($CDCl_3$, 100 MHz): 41.76, 114.35, 115.94, 117.33, 125.43, 127.23, 128.15, 128.35, 129.23, 134.69, 135.17, 149.77, 154.15, 156.18, 157.12, 163.57. MS for $(M+H)^+$: Calcd exact mass 305.0926; found 305.0921. Anal. calcd for $C_{18}H_{12}N_2O_3$: C 71.05, H 3.97, N 9.21; found C 71.28, H 3.95, N 9.18.

2.2. Photophysical properties and response to cyanide anions

Solutions of compounds **1** and **2** with 3.0×10^{-5} M or 1.0×10^{-5} M in CH_3CN 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 addition of a solution tetra(*n*-butyl)ammonium cyanide (TBACN) in CH_3CN. The spectral changes were monitored with the varied equivalent of CN^-. The fluorescence quantum yields Φ were measured by using a standard method with quinine sulfate as the standard [12].

2.3. Structure determination

Single crystals of compounds **2**, **1-CN** and **2-CN** were obtained by slow evaporation of the solutions of the compounds in chloroform. X-ray diffraction data of compounds **2**, **1-CN** and **2-CN** were collected on a Bruker Smart APEX-II CCD X-ray single crystal diffractometer with a graphite-monochromated MoKa radiation (λ = 0.71069 Å) at 296(2)K. By SHELXTL-97 program, the structures were solved by direct methods, which successfully located most of the nonhydrogen atoms and refined by full-matrix least-squares method on F^2 using the allowed location of the remaining nonhydrogen atoms. All H atoms were geometrically fixed and allowed to ride on their attached atoms. The CIF files have been deposited with the Cambridge structure database and assigned the following numbers: CCDC 855868–855870. Crystal data, data collections and structure refinements of compounds **2, 1-CN** and **2-CN** are shown in Table 1.

3. Results and discussion

The interaction of **1** and **2** with tetra(*n*-butyl)ammonium cyanide (TBACN) was firstly examined by UV–vis absorption spectroscopy. As expected, compounds **1** and **2** can react with