



Two fluorescence turn-on coumarin Schiff's base chemosensors for cyanide anions



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ABSTRACT

Two novel diethylaminocoumarin Schiff's base chemosensors for cyanide with pyridine or thiophene as terminal group have been synthesized. Their photophysical properties as well as recognition properties for cyanide anions have also been examined. Both the compounds exhibit strong green fluorescence in all the solvents. Density functional theory calculation indicates that both the compounds exhibit intramolecular charge transfer from diethylaminocoumarin group to terminal pyridine or thiophene group. The compounds can recognize cyanide anions with fluorescence turn-on response based on copper ion complex displacement mechanism and obvious color change from red to yellow-green can be observed by naked eyes. The chemosensors exhibit a degree of repeatability and can be used repeatedly to recognize cyanide anions for several times.

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1. Introduction

Cyanide exists widely in our production and life, and plays an important role in industrial production. However, cyanide will attack human body's red blood cells and cause human to suffocate in very short time [1,2], then cyanide is seriously harmful to the organism and environment [3–5]. Therefore, cyanide detection is very important. The development of fluorescence chemosensors for cyanide appears to be particularly attractive because of their simplicity, high sensitivity, fast response, and inexpensive nature [2,3,6]. Recently, many fluorescence chemosensors for cyanide have been developed [7–20]. These chemosensors are mainly based on hydrogen bonding [7–9], nucleophilic addition [10–16] and metal complex ensemble displacement mechanism [17–20]. Among these, fluorescence turn-on chemosensors for cyanide anion (CN⁻) based on the copper ion displacement mechanism attract considerable interest in recent years [21–25]. Our group has been devoted to the investigation on chemosensors for CN⁻ for several years [4,26–28]. Two chemosensors for CN⁻ based on dipyrindylamine

and aurone moiety were developed in 2014 [28]. Here two novel diethylaminocoumarin Schiff's base chemosensors for cyanide based on copper ion complex displacement mechanism were obtained, which exhibit strong green fluorescence and can recognize CN⁻ with fluorescence turn-on response.

2. Experimental

2.1. Synthesis and characterization

The synthetic routes to compounds **1** and **2** are shown in Scheme 1. 7-Diethylaminocoumarin-3-aldehyde (**S**) was synthesized according to reference [29]. 2-Picolinyl hydrazide and 2-thiophenecarboxylic acid hydrazide were purchased from Aladdin Reagents. Other reagents were purchased from Shanghai Reagents. Solvents were dealt with according to standard procedures. NMR spectra were recorded on a Bruker Avance III 400 MHz spectrometer at room temperature. Mass spectra were recorded on an Agilent Q-TOF6510 spectrometer.

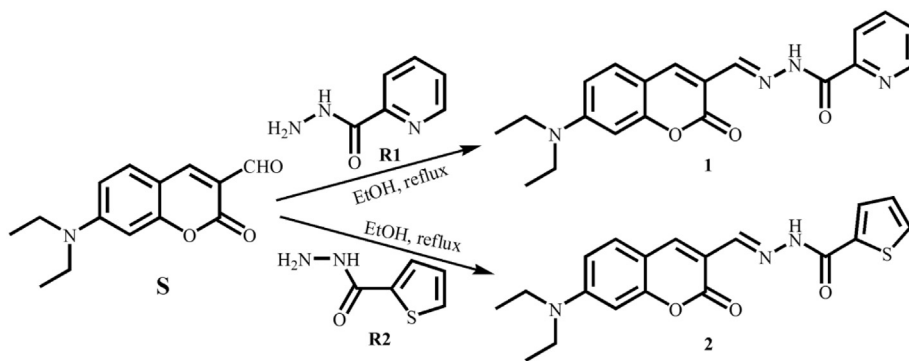
2.1.1. Synthesis of compound **1**

Compound **1** was synthesized via the condensation reaction between 7-diethylaminocoumarin-3-aldehyde (**S**) and 2-picolinyl

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

hydrazide (**R1**). The mixture of 0.49 g (0.002 mol) of **S** and 0.27 g (0.002 mol) of **R1** in 50 mL ethyl alcohol was heated under reflux for 8 h. After cooling to room temperature, yellow precipitate formed. The precipitate was filtered and repeatedly washed with dry ethyl alcohol for several times to get 0.52 g bright yellow solid **1** with yield 72%. $^1\text{H NMR}$ (400 MHz, CDCl_3), δ : 1.23 (t, $J = 7.1$ Hz, 6H), 3.44 (q, $J = 7.1$ Hz, 4H), 6.50 (d, $J = 2.2$ Hz, 1H), 6.63 (dd, $J = 8.9$ Hz, 2.4 Hz, 1H), 7.38 (d, $J = 8.9$ Hz, 1H), 7.48 (dd, $J = 7.6$ Hz, 1.1 Hz, 0.5H), 7.49 (dd, $J = 7.6$ Hz, 1.1 Hz, 0.5H), 7.89 (td, $J = 7.7$, 1.7 Hz, 1H), 8.30 (d, $J = 7.8$ Hz, 1H), 8.40 (s, 1H), 8.55 (s, 1H), 8.59 (d, $J = 4.4$ Hz, 1H), 11.07 (s, 1H). $^{13}\text{C NMR}$ (100 MHz, CDCl_3), δ : 12.57, 45.14, 97.26, 108.88, 109.78, 112.66, 122.96, 126.85, 130.63, 137.68, 140.25, 143.46, 148.29, 149.10, 151.74, 157.26, 160.00, 161.94. MS for $(\text{M} + \text{H})^+$, Calcd exact mass: 365.1614, found 365.1660.

2.1.2. Synthesis of compound **2**

The synthesis of compound **2** is similar to synthetic process of compound **1** with **S** and 2-thiophenecarboxylic acid hydrazide (**R2**) as the starting materials in 68% yield. $^1\text{H NMR}$ (400 MHz, CDCl_3), δ : 1.24 (t, $J = 7.1$ Hz, 6H), 3.45 (q, $J = 7.1$ Hz, 4H), 6.50 (s, 1H), 6.63 (dd, $J = 8.9$, 2.2 Hz, 1H), 7.18 (s, 1H), 7.41 (d, $J = 6.9$ Hz, 1H), 7.52–7.82 (m, 1H), 8.06–8.49 (m, 3H), 9.07 (s, 1H). $^{13}\text{C NMR}$ (100 MHz, DMSO), δ : 12.84, 44.72, 96.91, 108.53, 110.22, 112.97, 128.61, 129.35, 131.36, 132.29, 135.12, 139.12, 142.56, 151.84, 157.00, 161.35. $(\text{M} + \text{H})^+$, Calcd exact mass: 370.1225, found 370.1138.

2.2. Photophysical properties and response to cyanide anions

A spectroscopic grade of acetonitrile was used as the solvent for titration experiment. The titrations were carried out in 10 mm quartz cuvette at 25 °C on a Shimadzu UV2550 spectrophotometer and a Horiba Fluoromax-4 fluorescence spectrometer, respectively. The spectral changes were monitored upon the addition of a solution of Copper (II) perchlorate hexahydrate ($\text{Cu}(\text{ClO}_4)_2 \cdot 6\text{H}_2\text{O}$) and tetra (*n*-butyl)ammonium cyanide (TBACN) in acetonitrile as Cu^{2+} and CN^- source, respectively. The fluorescence quantum yields ϕ were measured by using a standard method [30] with coumarin 307 [31] as the standard.

2.3. Structure determination

Single crystal of compound **2** was obtained by slow evaporation of the compound in ethanol-dichloromethane solution. X-ray diffraction data of **2** was collected on a Bruker Smart APEX-II CCD X-ray single crystal diffractometer with a graphite-monochromated Mo $k\alpha$ radiation ($k = 0.71069$ Å) at 296(2) K. Crystal data, data collections and structure refinements of crystal **2** is shown in Table S1.

2.4. DFT and TDDFT calculations

Density functional theory (DFT) and time-dependent DFT (TDDFT) quantum chemical calculations on the compounds were carried out using Gaussian 09 program [32]. Geometry optimization on the ground state structures was performed at the B3LYP level of theory (Becke's three parameter hybrid functional [33] in conjunction with Lee, Yang, and Parr's correlation functional [34]). The optimized structures were confirmed as an energy minimum by following frequency calculations. The excited state calculation was performed with the time-dependent (TD) B3LYP method [35–37] based on the optimized ground state geometry. The first ten singlet excited states were solved in the TD/B3LYP calculations. Solvent (acetonitrile) effect on the ground state geometry and the excited state absorption spectra was modeled within the framework of polarizable continuum model with integral equation formalism (IEF-PCM) [38]. For C, H, O, N, and S atoms, 6-31 + G(d) [39] basis set was used. For Cu atom, LANL2DZ basis set and ECP were applied [40]. HOMO and LUMO of the compounds were obtained using the visualization package Gauss View.

3. Results and discussion

3.1. Synthesis and molecular structure

Compounds **1** and **2** were synthesized via two steps. Firstly, the intermediate 7-diethylaminocoumarin-3-aldehyde (**S**) was synthesized according to reference procedure [29]. Secondly, compounds **1** and **2** were synthesized by the condensation reaction between **S** and substituted amine **R1** and **R2**, respectively. Both the compounds were fully characterized by $^1\text{H NMR}$, $^{13}\text{C NMR}$, high-resolution MS and also structurally identified by single-crystal X-ray diffraction.

The crystal structure and packing diagram of compound **2** is shown in Fig. 1. Coumarin ring (C5–C13, O1) possesses high planarity with the largest deviation of all the non-hydrogen atoms from the least square plane being 0.096 Å (C12). The dihedral angle between thiophene and coumarin groups is 21.97°, which indicates that the molecular planarity is not good and there is a certain degree of distortion (Fig. 1b). Bond lengths of C12–C14 (1.450(6) Å), N2–N3 (1.387(5) Å) and C15–N3 (1.338(5) Å) are shorter than corresponding typical C–C, N–N and C–N single bond. The bond length of C14 = N2 (1.269(5) Å) is longer than typical C=N double bond length. These data indicate that there is a certain extent of conjugation between coumarin and thiophene groups. There is intermolecular hydrogen bond interaction between NH and O atom of carbonyl group. As shown in Fig. 1c, three molecules form an aggregate by N–H...O hydrogen bond action. Two aggregates form

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