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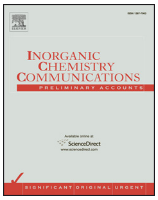

One diethylamine coumarin derivative with nitro substituted chalcone structure as chemosensor for cyanide and copper ions

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ABSTRACT

One diethylamine coumarin derivative with nitro substituted chalcone structure was synthesized via typical condensation reaction between 4-nitro-2-(hydroxyl)acetophenone with 7-(diethylamino)coumarinaldehyde in good yields. The investigation indicated that the compound exhibits quickly obvious UV–vis absorption, color change and fluorescence response to cyanide and copper ions in acetonitrile conditions. The bonding mechanism based on spectra change and in situ ^{1}H NMR suggested that cyanide is bonded to 4-position of coumarin and 1:2 complexation between compound and copper ion forms.

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For the past few years, due to the important roles in biological, industrial and environmental processes of cyanide and copper ions, the study of optical chemosensors for cyanide [1–10] and copper ions [11–16] has attracted more and more attention of many chemists. As we all know, cyanide is a highly toxic compound and the lethal to human is minimal [17]. Even though it has high toxicity, cyanide is really an important raw material in many industrial fields such as synthetic resin, pharmaceuticals, pesticides, insecticides, and fertilizers [18–20]. Copper, a very important element for hemopoiesis, metabolism, growth and immune system [21], has indispensable functions in various biological processes. But when the copper ion concentration is out of the required range, the normal activities of life system would be disrupted and the cells would be poisoned, which would cause severe copper metabolic disorders [22–24]. As a progress of our group in chalcone derivative as chemosensors for cyanide, one diethylamine coumarin derivative with nitro substituted chalcone structure was synthesized and its recognition properties for cyanide and copper ions were reported.

The title compound **1** was synthesized by condensation reaction between 7-(diethylamino)coumarinaldehyde and 4-nitro-2-(hydroxyl)acetophenone with a yield of 50% in ethanol (Scheme S1) and the compound was characterized by ^{1}H NMR, ^{13}C NMR and ESI-mass spectrometry [25]. A corresponding compound **R1** without nitro group was also synthesized. The molecular structures of compounds **1** and **R1** are shown in Fig. 1.

To examine the recognizing properties of the compounds for cyanide and copper ions, tetra (*n*-butyl)ammonium cyanide (TBACN) and copper (II) perchlorate hexahydrate ($Cu(ClO_4)_2 \cdot 6H_2O$) as cyanide and copper ion sources, respectively, were added to a solution of the compound in acetonitrile. The compound exhibits fast response to cyanide and copper ions (<5 s). As shown in Fig. 2a, with the increase of cyanide anions, the absorption peak of compound **1** at 489 nm ($\varepsilon = 3.19 \times 10^4\ M^{-1}\ cm^{-1}$) decreases gradually and is blue shifted to 469 nm with an isoabsorptive point at 481 nm. Obvious color change from red to yellow is observed. As shown in Fig. 2b, upon complexation with Cu^{2+}, the strong absorption peak at 489 nm gradually decreases, at the same time, a weak absorption band at 395 nm was formed. The compound also exhibits obvious color change from red to claret.

The fluorescence spectra changes of compound **1** upon the addition of CN^- and Cu^{2+} in acetonitrile were also detected. As shown in Fig. 3 and Fig. S1, red fluorescence at 669 nm was completely quenched and fluorescence change also can be observed by naked eye. Similar compound without nitro group **R1** also exhibits obvious response to cyanide anions, but the response rate is slow and sensitivity is less (Fig. S2a), which indicates that the import of nitro group is beneficial to the response for cyanide anions. Compound **R1** exhibits similar response to copper ions (Fig. S2b) with the original absorption peak (475 nm) decreasing gradually and disappearing at last, at the same time, a weak absorption peak at 395 nm appearing and increasing gradually.

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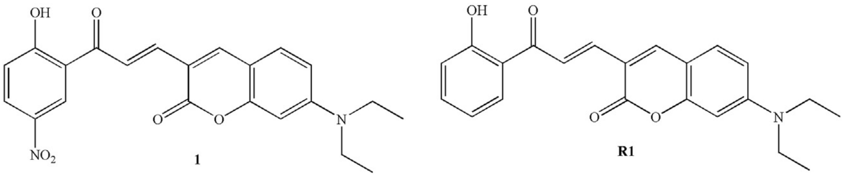

Fig. 1. The molecular structures of compounds **1** and **R1**.

What needs to be noted is that the absorption spectra of compounds **1** and **R1** are similar after complexing with copper ions, which indicates that the original main absorption peak is broken and the new absorption peak may be derived from diethylamine coumarin group.

Besides, job plots of the compound for cyanide and copper ions were also detected. As shown in Fig. 4(a), job plot data indicates that 1:1 reaction between the compound and cyanide anion occurs. Bonding mechanism of the compound for cyanide anions was investigated using the in situ ^{1}H NMR spectra of the compound before and after the interaction with CN^- in CD_3CN. As shown in Fig. S3, the proton signal of 4-coumarin group at 8.23 ppm disappeared and peaks related to vinylic protons (7.91(d, $J = 14.8$ Hz, 1H), 8.21(d, $J = 15.6$ Hz, 1H)) did not disappear and only the position changed (7.68(d, $J = 15.2$ Hz, 1H), 8.82(d, $J = 15.6$ Hz, 1H)), which indicates that the possible bonding mechanism is cyanide anions being bonded to 4-coumarin. The bonding of CN^- to 4-coumarin induces to the breaking of intramolecular charge tranfer and then results in the decrease of fluorescence.

Job plot data (Fig. 4(b)) indicate that 1:2 complex between the compound and copper ions forms. Compound **R1** also exhibits similar complexation to copper ions (Fig. S5), which indicates nitro group dose not take part in the complexation. The possible mechanism of the compound for copper ions is shown in Fig. S6. Hydroxyl and two carbonyl groups complex with two copper ions to form 1:2 complex. The decrease of fluorescence caused by Cu^{2+} may be derived from the intramolecular photoinduced electron transfer from the excited fluorophore to copper ion [26].

The detection (LOD) [27,28] and quantification (LOQ) limits of the compound for CN^- and Cu^{2+} in acetonitrile with absorption and fluorescence as detected signals are also examined (Table S1, Figs. S7 and S8). LODs with fluorescence as detected signal are 0.018 μM and 0.004 μM for CN^- and Cu^{2+}, respectively.

The influence of other cations and anions on the response of compound to copper ions and cyanide anions was examined. As shown in Fig. S9 and S10, the compound exhibits good selectivity. Other anions such as Cl^-, Br^-, I^-, SCN^-, and HSO_4^- and cations such as Na^+, Mg^{2+}, Co^{2+}, Ni^{2+}, Ca^{2+}, and Zn^{2+} induce negligible absorption changes to the compound, which indicates that the compound can recognize CN^- and Cu^{2+} from these anions and cations. Even Fe^{3+} can induce obvious change of absorption spectra, but the change is different to that of Cu^{2+}, which indicates that the compound can recognize Fe^{3+} and Cu^{2+} at the same time with absorption as detected signal. Fe^{3+} cannot cause obvious color change of the compound and then the compound can recognize Cu^{2+} with high selectivity using color change.

In summary, the effectiveness of one coumarin nitro substituted chalcone derivative as chemosensor for cyanide anions and copper ions was demonstrated. The results indicated that the compound exhibits obvious UV–vis absorption, color and fluorescence response in acetonitrile solution. Bonding mechanism investigation indicates that cyanide is bonded to 4-position of coumarin, hydroxyl and two carbonyl group complexes with two copper ions to form 1:2 complex.

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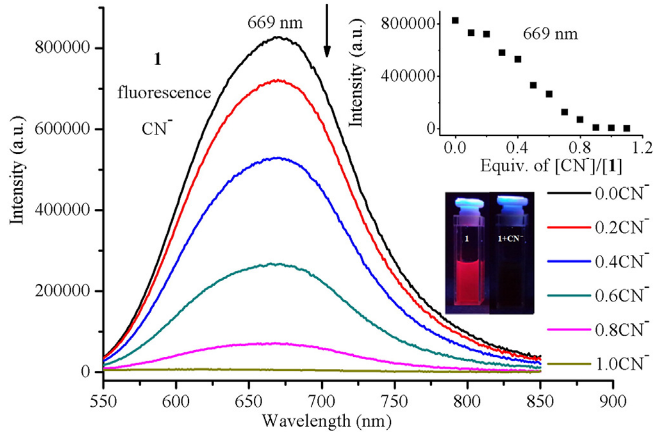

Fig. 3. Fluorescence ($C = 10$ μM) spectra change of compound **1** upon the addition of CN^- in acetonitrile.

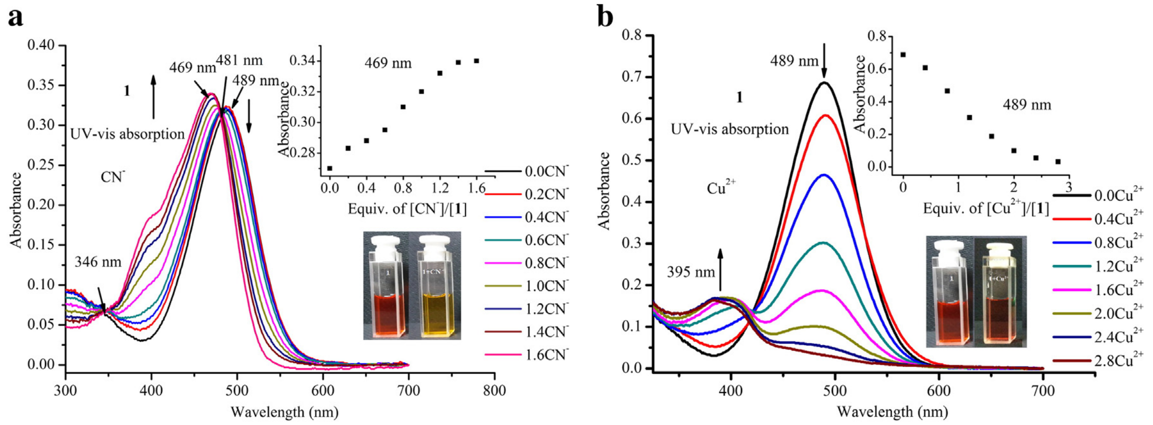

Fig. 2. UV–vis absorption spectra change of compound **1** upon the addition of CN^- (a, $C = 10$ μM) and Cu^{2+} (b, $C = 20$ μM) in acetonitrile. (For interpretation of the references to color in this figure, the reader is referred to the web version of this article.)

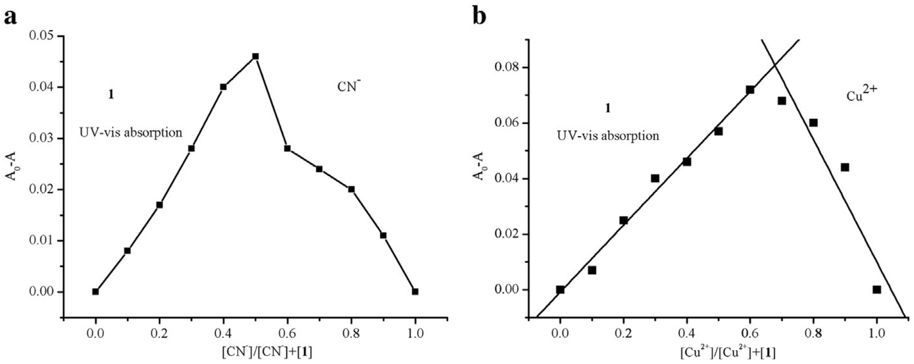

Fig. 4. Job's plots of the compounds for cyanide anions (a) and copper ions (b).

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Appendix A. Supplementary material

Supplementary data to this article can be found online at http://dx.doi.org/10.1016/j.inoche.2015.06.031.

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[25] **1**: ^{1}H NMR(400 Hz, $CDCl_3$), δ: 1.26(t, $J = 7.2$ Hz, 6H), 3.48(q, $J = 7.2$ Hz, 4H), 6.53(d, $J = 2.0$ Hz, 1H), 6.65(dd, $J = 8.8$ Hz, 2.0 Hz, 1H), 7.09(d, $J = 9.2$ Hz, 1H), 7.38(d, $J = 9.2$ Hz, 1H), 7.86(d, $J = 15.2$ Hz, 1H), 7.89(s, 1H), 8.29(d, $J = 14.8$ Hz, 1H), 8.35(dd, $J = 9.2$ Hz, 2.4 Hz, 1H), 8.94(d, $J = 2.4$ Hz, 1H), 13.86(s, 1H). ^{13}C NMR(100 Hz, $CDCl_3$), δ: 13.64, 45.33, 97.10, 109.13, 110.01, 114.09, 119.31, 119.47, 126.54, 130.71, 130.75, 139.66, 143.37, 147.62, 152.74, 157.24, 160.18, 168.59, 193.58. MS for $(M+H)^+$, Calcd exact mass: 409.4119, found 409.1335. **R1**: ^{1}H NMR(400 Hz, $CDCl_3$), δ:1.24 (t, $J = 7.2$ Hz, 6H), 3.46 (q, $J = 7.2$ Hz, 4H), 6.52 (d, $J = 2.4$ Hz, 1H), 6.63 (dd, $J = 8.8$, 2.4 Hz, 1H), 6.94 (t, $J = 7.2$ Hz, 1H), 7.00 (dd, $J = 8.4$, 0.8 Hz, 1H), 7.35 (d, $J = 8.8$ Hz, 1H), 7.48 (t, $J = 8.0$ Hz, 1H), 7.69 (d, $J = 15.2$ Hz, 1H), 7.80 (s, 1H), 8.03 (dd, $J = 8.0$, 1.6 Hz, 1H), 8.37 (d, $J = 15.2$ Hz, 1H), 13.03 (s, 1H).

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