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Several hemicyanine dyes as fluorescence chemosensors for cyanide anions

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ABSTRACT

Four hemicyanine dyes as chemosensors for cyanide anions were synthesized easily. Their photophysical properties and recognition properties for cyanide anions were investigated. The results indicate that all the dyes can recognize cyanide anions with obvious color, absorption and fluorescence change. The recognition mechanism analysis basing on in situ ¹H NMR and Job plot data indicates that to the compounds with hydroxyl group, the recognition mechanism is intramolecular hydrogen bonding interaction. However, to the compounds without hydroxyl group, cyanide anion is bonded to carbon–carbon double bond in conjugated bridge and induces N⁺ CH₃ to neutral NCH₃. Fluorescence of the compounds is almost quenched upon the addition of cyanide anions.

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1. Introduction

As we all know, cyanide has extreme toxicity [1]. A small amount of cyanide can cause acute symptoms of poisoning, such as vomiting, convulsion, loss of consciousness, and even eventual death [2]. Despite its toxicity, cyanide is an important raw material of synthetic resin, pharmaceuticals, pesticides and other industrial areas. In the meanwhile, cyanide is used to dissolve gold and silver ores in the mining industry, and also used in electroplating, plastics and other industrial production [1,3,4]. Thus, chemists have paid more and more attention to compose quickly and highly selective chemosensors for cyanide anions.

In recent decades, optical sensors for cyanide, in which a change in color, fluorescence intensity, or emission wavelength is monitored [5–15], have been paid more attention by scholars due to their simple operation, high sensitivity and low cost. Our group is devoted to the research on chemosensors for cyanides for several years [16–20].

Here four hemicyanine dyes as fluorescence chemosensors for CN^- were synthesized. These compounds exhibit remarkable response to CN^- with obvious color and fluorescence changes, which allows naked eye detection.

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2. Experimental

2.1. Chemical and instruments

5-Bromosalicylaldehyde, p-nitrobenzaldehyde, N-ethyl-3carbazolecarboxaldehyde, 4-(diethylamino)salicylaldehyde, 4methylpyridine and 2-methylpyridine were purchased from Aladdin Reagents. Other reagents were purchased from Shanghai Reagents and used as received directly without further purification. NMR spectra were recorded on a Bruker Avance III 400 MHz spectrometer at room temperature.

2.2. Synthesis and characterization

The molecular structures of compounds **1–4** are shown in Fig. 1. Compounds **1–4** (Table S1) were synthesized by the condensation reaction between the substituted aldehyde and 4-methyl-Nmethylpyridinium iodide (S1) or 2-methyl-N-methylpyridinium iodide (S2) [21–23]. The raw materials were put into 50 mL flask with a stirrer and condenser, and then an amount of ethanol and 3 drops of piperidine were added in turn. The mixture was heated under reflux for 4 h. After cooling to room temperature, precipitate of compounds **1**, **3** and **4** was filtered and washed by dichloromethane to afford the products. But the product of compound **2** is an oil-like object, which was recrystallized from a mixed solution of dichloromethane and ethanol to give green crystals.









Fig. 1. The molecular structures of compounds 1-4.

2.3. Photophysical property measurement

3.1. UV–vis absorption and fluorescence properties

3. Results and discussion

UV–vis absorption and fluorescence spectra of the compounds in acetonitrile were recorded at room temperature on a Shimadzu UV2550 spectrophotometer and a Horiba Fluoromax-4 fluorescence spectrometer with $C = 1.0 \times 10^{-5}$ M at room temperature, respectively. The spectral changes were monitored with the addition of a solution of tetra (*n*-butyl)ammonium cyanide (TBACN) in acetonitrile as CN⁻ source at room temperature.



Fig. 2. UV-vis absorption (a) and fluorescence spectra (b) of compounds **1–4** in acetonitrile with $C = 1.0 \times 10^{-5}$ M at room temperature.

UV-vis absorption, fluorescence emission spectra and excitation

spectra of the compounds in acetonitrile are shown in Fig. 2 and Fig. S1. From Fig. 2a, we can see that compound **1** exhibits linear absorption in violet region with the absorption peaks at 374 nm ($\varepsilon = 1.41 \times 10^4 \text{ M}^{-1} \text{ cm}^{-1}$). The absorption peaks of compounds **2-4** are 490 nm (**2**, $\varepsilon = 2.65 \times 10^4 \text{ M}^{-1} \text{ cm}^{-1}$), 336 nm (**3**, $\varepsilon =$ $3.58 \times 10^4 \text{ M}^{-1} \text{ cm}^{-1}$) and 417 nm (**4**, $\varepsilon = 3.18 \times 10^4 \text{ M}^{-1} \text{ cm}^{-1}$), respectively, and they exhibit much stronger linear absorption than compound **1**. The shorter absorption wavelength of compound **3** relative to compound **4** may be derived from stronger electron accepting ability of nitro group. (For interpretation of the references to color in this figure, the reader is referred to the web version of this article.)

As shown in Fig. S1, excitation and absorption spectra of all the compounds are very similar. The fluorescence spectra were obtained with the excitation wavelengths at 370 nm (1), 490 nm (2), 340 nm (3) and 420 nm (4). Compounds 1 and 4 exhibit stronger fluorescence compared with other compounds (Fig. 2b). The fluorescence intensity of compound 3 is lower than other compounds significantly, perhaps because it contains nitro group and nitro group has fluorescence quenching effect. The fluorescence peak of compound 2 at 607 nm is the longest, which may be because it has a strong electron donating group diethylamino.

3.2. Response to cyanide anions

As shown in Fig. 3(a), compound **1** has two absorption peaks in acetonitrile at 323 nm and 374 nm. When cyanide anions are added, a new absorption peak at 577 nm appears and increases gradually, which is accompanied by the decrease at 323 nm and 374 nm, at the same time, a new absorption peak at 353 nm appears. Three isosbestic points at 287 nm, 348 nm and 448 nm are observed. Compound **1** also exhibits fluorescence spectral response to cyanide anions. From the Fig. 3(b), we can see that the fluorescence intensity at 533 nm decreases and is almost quenched completely when 1.4 equiv. cyanide anions are added.

Upon the addition of cyanide anions, compound **2** also exhibits obvious UV–vis absorption change with the original absorption peak (490 nm) decreasing and new absorption peak in long wavelength region (589 nm) appearing (Fig. S2). The fluorescence at 607 nm of compound **2** decreases and fluorescence intensity finally decreases to 7% of the original fluorescence and fluorescence peak has a 21 nm red shift. (For interpretation of the references to color in this figure, the reader is referred to the web version of this article.)

The detection limits [24,25] of compounds **1** and **2** for cyanide anions with UV–vis absorption and fluorescence as detected signal are also investigated. From Figs. S3 and S4, the detection limits of compounds **1**



Fig. 3. UV-vis absorption (a) and fluorescence (b, $\lambda_{ex}=370$ nm) spectra of 1 $(1.0\times10^{-5}\,M)$ in acetonitrile at room temperature upon the addition of CN⁻.

and **2** for cyanide anions are 0.38 μ M (**1**, DL_{abs}), 0.21 μ M (**2**, DL_{abs}), 0.00082 μ M (**1**, DL_{fluo}) and 0.0016 μ M (**2**, DL_{fluo}).

Compound **3** also exhibits obvious response to CN^- (Fig. S5). As shown in Fig. S5, with the addition of CN^- , absorption peak of compound **3** at 336 nm decreases gradually, while new peaks at 425 nm and 568 nm appear and an isosbestic point at 373 nm is observed. The detection limit of compound **3** for cyanide anions with absorption as the detected signal is 2.7 μ M (**3**, DL_{abs}).

As shown in Fig. 4(a), upon the addition of cyanide anion to an acetonitrile solution of compound **4**, the peak at 417 nm decreases gradually and an isosbestic point at 300 nm is observed and finally is saturated when 3 equiv. cyanide anions are added. As for Fig. 4(b), we can see that with excitation at 490 nm, the fluorescence intensity at 570 nm of compound **4** has a decrease when cyanide anions are added. Fluorescence intensity finally decreased to 11% of the original fluorescence with 6 nm blue shift. From Figs. S6 and S7, the detection limits of compound **4** for cyanide anions are 0.75 μ M (DL_{abs}), 0.0004 μ M (DL_{fluo}). (For interpretation of the references to color in this figure legend, the reader is referred to the web version of this article.)

From the fluorescence titration spectra of compounds **1**, **2**, and **4**, we can see that the compounds exhibit turn-off response to cyanide anions.

From Figs. S8, Job's plots indicates that the complexation between the compounds and cyanide anions is 1:1. Based on ¹H NMR spectrum of compound **4** in $(CD_3)_2SO$ before and after the addition of cyanide



Fig. 4. UV-vis absorption (a) and fluorescence (b, $\lambda_{ex}=420$ nm) spectra of 4 $(1.0\times 10^{-5}\,M)$ in acetonitrile at room temperature upon the addition of CN⁻.

anions, the reaction mechanism was investigated. From Fig. 5, we can see that upon the addition of cyanide anions, the two hydrogens of double bonds in 8.20 ppm (d, J = 16.0 Hz) and 7.62 ppm (d, J = 16.0 Hz) disappear, and two sets of new peaks in 3.76 ppm (d, J = 8.8 Hz) and 5.20 ppm (d, J = 8.8 Hz) appear, which may be because the double bond of compound **4** changes to single bond by Michael addition reaction, in which cyanide is added to carbon–carbon double bond. Hydrogen proton signal of NCH₃ is up field shifted from 4.42 ppm to 2.96 ppm, which may be corresponding to the change from N⁺CH₃ to neutral NCH₃. The mechanism of the reaction is also shown in Fig. 5. The fluorescence decrease of the compounds upon the addition of cyanide anions is because cyanide anion is bonded to the CC in conjugated bridge, which induced to the breaking of charge transfer.

To compounds **1** and **2**, after the addition of cyanide anions, the original main absorption peaks in short wavelength region decrease, at the same time, a absorption peak in long wavelength region appears. These spectral changes are different to that of compound **4**. Compared with compounds **1** and **2**, there is no hydroxyl in compound **4**. So the absorption peak in long wavelength region may be derived from hydroxyl bond interaction between hydroxyl group of the compounds and CN^- . The in situ ¹H NMR spectrum of compound **1** in CD_3CN before and after the addition of cyanide anions indicates that CC double bond dose not disappear. We think that the reaction mechanism of compounds **1** and **2** to cyanide anions is intermolecular hydrogen bond interaction (Fig. S9).



Fig. 5. The ¹H NMR spectrum of compound 4 in (CD₃)₂SO before and after the addition of cyanide anions at room temperature and reaction mechanism.

3.3. Selective detection of cyanide anion

High selectivity for a chemosensor is very important. The influence of other anions on the response of the compounds to cyanide anions in acetonitrile was examined. The selective response of compounds **1–4** towards cyanide anions was evaluated by adding 5 equiv. of various anions in acetonitrile such as CN⁻ (TBACN), F⁻ (NaF), Cl⁻

(NaCl), Br⁻ (KBr), I⁻ (NaI), HPO₄⁻ (KHPO₄), SCN⁻ (KSCN), HSO₄⁻ (NaHSO₄) and CO₃²⁻ (Na₂CO₃). From Fig. S10, for compounds **2–4**, no significant absorption spectral change upon the addition of other anions is observed. As expected, compounds **2–4** have pretty well selective detection for cyanide anion. To compound **1**, upon the addition of CO₃²⁻ and F⁻, the absorption spectra also change obviously, but the change is different to that induced by CN⁻, which means that the selectivity



natural light

365nm UV-light

Fig. 6. Photographs showing the color change of compounds **1–4** before (a) and after (b) the addition of cyanide anions in acetonitrile in natural light and 365 nm UV-light. (For interpretation of the references to color in this figure legend, the reader is referred to the web version of this article.)

of compound **1** is also very good. At the same time, the selectivity of compound **2** (Fig. S11) in test paper was tested. From Fig. S11, we found that the color of compound **2** with cyanide is obviously different from that with other anions, so the selective detection of cyanide can be realized by the change of color in test paper. When cyanide is added, the color of **2** changes from red to purple.

3.4. 'Naked-eye' detection of cyanide anions

The color changes of the compounds in acetonitrile upon the addition of cyanide anions were also researched (Fig. 6). To compounds **1** and **3**, upon the addition of cyanide anions, the color changes from colorless to blue (**1**) and light yellow (**3**) in nature light. Color of compound **2** changes from red to blue. In 365 nm UV-light, compounds **1** and **4** exhibit stronger fluorescence compared with other compounds and the green (**1**) or yellow (**4**) fluorescence are almost quenched upon the addition of cyanide anions.

4. Conclusion

In summary, the effectiveness of four compounds as chemosensors for cyanide anions was demonstrated. The results indicate that the compounds exhibit obvious UV–vis absorption and fluorescence change response in acetonitrile solution. Especially, all the compounds allow for 'naked-eye' detection of cyanide anions with high selectivity and sensitivity. Bonding mechanism analysis indicates that to the compounds **1** and **2** with hydroxyl group, recognition mechanism is intramolecular hydrogen bond interaction. However, to the compounds **3** and **4** without hydroxyl group, cyanide anion is bonded to CC of conjugated bridge and induces N⁺ CH₃ to neutral NCH₃, which breaks the intramolecular charge transfer and induced to fluorescence decrease.

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Appendix A. Supplementary data

Supplementary data to this article can be found online at http://dx. doi.org/10.1016/j.saa.2016.02.008.

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