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Hemicyanine-based colorimetric chemosensors: Different recognition mechanisms for CN⁻ sensing

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HIGHLIGHTS

G R A P H I C A L A B S T R A C T

- Simple hemicyanine dyes were synthesized by a condensation reaction.
- Different sensing mechanisms of the dyes towards cyanide ion were confirmed by ¹H NMR studies.
- ► These dyes show no colorimetric response towards the other anions investigated.



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Introduction

The field of anion recognition has made remarkable progress over the past three decades. Anions play a fundamental role in many biological and chemical processes [1]. Among various anions, cyanide is one of the most toxic materials and extremely harmful

ABSTRACT

Simple hemicyanine dyes were synthesized by a classical condensation reaction. The structures of these dyes were characterized by ¹H NMR spectroscopy, elemental analysis, and FAB-Mass spectrometry. The sensing behavior of the hemicyanines towards a selection of anions was investigated by UV-vis absorption spectroscopy. These structurally simple dyes displayed a rapid response and high selectivity for cyanide ion over other common anions in the DMSO/H₂O solution. Different sensing mechanism of the dyes to cyanide ion were confirmed by ¹H NMR studies, together with theoretical calculations based on DFT and PPP-MO methods. These dyes show no colorimetric response for other anions investigated.

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to the environment and human health [2]. Nevertheless, a large number of cyanides are extensively utilized in industries such as mining, metallurgy, photographic processing, and the production of nitriles, nylon and acrylic plastics, which raise a number of environment concerns, particularly in terms of its retention in leech circuits, recovery and potential for contamination. This scenario has necessitated the development of cyanide ion probes. Many analytical techniques such as potentiometry, chromatography, and flow injection have been adopted for cyanide detection [3]. However, these methods often require extensive and timeconsuming procedures that involve the use of sophisticated instru-

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mentation with high detection limits. Optical sensors for cyanide, in which a change in color and/or fluorescence intensity is monitored, have been studied actively over the past ten years due to their simple, inexpensive, and rapid implementation. With these considerations, a number of promising chemodosimeters and fluorescent chemosensors have been reported as optical sensors for cyanide ions [4]. Indoles have been used as chromogenic receptors for anions because they contain single NH group that could act as anion binding moiety. Until now, some ratiometric anion chemosensors containing functionalized indoles have been reported [5-10]. In all cases, a bathochromic shift was observed, suggesting an increase in the donor strength of the indole NH group upon anion coordination. A number of other groups have reported the ability of aromatic-OH---anion interactions to supplement an anion binding process [11–14]. In all cases, the phenol group was connected through a conjugated system with the acceptor moiety. In the presence of certain anions, coordination with the aromatic-OH or deprotonation of the phenolic group was observed. With either coordination or deprotonation, the outcome was an enhancement of the donor character of the phenolic oxygen resulting in a bathochromic shift of the charge-transfer band. We report herein the synthesis and cyanide binding properties of hemicyanine dyes containing two phenolic OH groups.

Experimental

Materials and methods

2,5-Dihydroxybenzaldehyde, 2,3,3-trimethylindolenine, and 2methylbenzothiazole were purchased from Sigma–Aldrich. All kinds of anions, tetrabutylammonium bromide (Br⁻), tetrabutylammonium chloride (Cl⁻), tetrabutylammonium fluoride (F⁻), tetrabutylammonium nitrate (NO₃⁻), tetrabutylammonium phosphate monobasic (H₂PO₄⁻), Tetrabutylammonium perchlorate (ClO₄⁻), tetrabutylammonium cyanide (CN⁻), and tetrabutylammonium hydrogensulfate (HSO₄⁻), were also purchased from Sigma–Aldrich. The rest of chemicals were commercially available with high grade and were used without further purification. 2,3-Dimethylbenzothiazolium iodide **2** and 1,2,3,3-tetramethylindolenium iodide **3** were obtained by synthesis according to the literature methods [15].

Instruments

Melting points were determined using an Electrothermal IA900 apparatus and were uncorrected. Elemental analyses were recorded on a Carlo Elba Model 1106 analyzer. Mass spectra were recorded on a JMS-700 high resolution mass spectrometer using an FAB ion source. ¹H NMR spectra were recorded on Varian Unity Inova 400 MHz FT-NMR spectrophotometer with TMS as internal standard. The UV–Vis absorption spectra were measured on an Agilent 8453 spectrophotometer. Calculation of the LUMO electron density was carried out with PiSystems XTE ver. 6.2 package.

Synthesis of dye 1 and 2

A mixture of 2,5-dihydroxybenzaldehyde **1** (0.3 g, 2.17 mmol), 2,3-dimethylbenzothiazolium iodide **2** (0.6 g, 2.12 mmol), and absolute ethanol (20 mL) was refluxed for 4 h under a nitrogen atmosphere. After cooling, the crude product was filtered and recrystallized from ethanol. Yield: 10%. ¹H NMR (400 MHz, DMSO-d₆): δ 4.30 (s, 3H), 6.84 (d, *J* = 8.8 Hz, 1H), 6.91 (d, *J* = 8.8 Hz, 1H), 7.36 (s, 1H), 7.76 (t, *J* = 8.0 Hz, 1H), 7.84–7.91 (m, 2H), 8.18–8.25 (m, 2H), 8.36 (d, *J* = 7.84 Hz, 1H), 9.15 (s, 1H, -OH), 10.21 (s, 1H, -OH) ppm. EA: Anal. Calcd. for C₁₆H₁₄INO₂S: C,

46.73; H, 3.43; N 3.41; S, 7.80. Found: C, 46.39; H, 3.42; N, 3.70; S, 7.77%. [M]⁺ – I = 284.3. mp: 281–282 °C.

Dye **2** was obtained by using similar procedure. The crude product was filtered and washed with hot ethanol. Yield: 16%. ¹H NMR (400 MHz, DMSO-d₆): δ 1.75 (s, 6H), 4.09 (s, 3H), 6.90 (d, *J* = 8.84 Hz, 1H), 7.00 (d, *J* = 8.84 Hz, 1H), 7.47 (s, 1H), 7.65–7.75 (m, 3H), 7.90–7.85 (m, 2H), 8.47 (d, *J* = 16.4 Hz, 1H), 9.19 (br s, 1H, -OH), 10.39 (s, 1H, -OH) ppm. EA: Anal. Calcd. for C₁₉H₂₀INO₂: C, 54.17; H, 4.79; N, 3.32; Found: C, 53.94; H, 4.83; N, 3.29%. [M]⁺ − I = 294.3. mp: 266–268 °C.

Results and discussion

In our design and synthesis strategy, we took the following points into consideration. At first, 2,3-dimethylbenzothiazolium iodide **2** and 1,2,3,3-tetramethylindolenium iodide **3** can be easily capable of condensing with a wide range of aromatic aldehydes to form all kinds of hemicyanine dyes. Second, these hemicyanine dyes are exceptionally bright with high tinctorial ability and fine solubility in all organic solvents. The synthesis of the dye **1** and **2** was performed by condensation reaction as shown in Scheme 1, the key intermediates 2,3-dimethylbenzothiazolium iodide **2** and 1,2,3,3-tetramethylindolenium iodide **3** were synthesized by the reaction of methyl iodide with 2-methylbenzothiazole and 2,3,3-trimethylindolenine, respectively.

These key intermediates were subsequently reacted with 2,5dihydroxybenzaldehyde **1** by condensation reaction. The chemical structures of all the intermediates, dye **1** and dye **2** are characterized by ¹H NMR spectroscopy, FAB-Mass spectrometry and elemental analysis. For the interpretation of the chromophoric system of dye **1** and **2**, the quantum chemical DMol³ approach was used. All the theoretical calculations were performed by DMol³ program in the Materials Studio 4.4 package [16–18] which is the quantum mechanical code using density functional theory. Perdew–Wang 1991 (PW91) function of generalized gradient approximation (GGA) level [19] was used to calculate the energy level of the frontier molecular orbital. Fig. 1 shows the electron distribution of the HOMO and LUMO energy level of dye **1** and **2**.

Comparison of the electron distribution in the frontier MOs reveals that the HOMO-LUMO excitation moves the electron distribution from dihydroxybenzene moiety to the acceptor, which showed a strong migration of intramolecular charge transfer character of dye 1 and 2. The dihydroxybenzene part of these dyes has two OH fragments that can form intermolecular proton transfer complexes with the guest anions. This was investigated by adding various anions $(Br^-, Cl^-, F^-, NO_3^-, H_2PO_4^-, ClO_4^-, CN^-andHSO_4^-)$ to a 5×10^{-5} M solution of dye **1** in DMSO/H₂O (1:1, v/v) and recording the changes in absorption spectra that occurred during the titration of the solution of dye 1. As Fig. 2 shows, upon the addition of cyanide ion to the solution of dye 1, the absorption band at 360 and 442 nm progressively decreased in intensity and a new peak at 589 nm appeared; an isosbestic point at 502 nm also developed. The appearance of this isosbestic point suggests that at least one stable dye- cyanide ion species is present in solution and is indicative that a stable complex formed between dye 1 and cyanide ion. However, none of the other anions investigated, namely Br⁻, Cl⁻, F⁻, NO₃⁻, H₂PO₄⁻, ClO₄⁻ and HSO₄⁻ had any noticeable effect on absorption, as shown in Fig. 3.

To confirm the nature of the intermolecular proton transfer between dye **1** and cyanide anion, the ¹H NMR spectrum of dye **1** was recorded in the absence and presence of cyanide ion (Fig. 4(a)). It was noticed that original OH proton signal, appearing at 9.15 and 10.21 ppm, disappeared upon addition of $[Bu_4N]^+$ CN⁻. With addition of cyanide, the olefinic and aromatic protons showed an upfield shift due to the OH… CN⁻ bond formation which increased



Fig. 1. Electron distribution of the HOMO and LUMO energy levels of dye **1** and dye **2**.

Dye 1

Dye 2



Fig. 2. The changes in the absorption spectra of dye 1 $(5 \times 10^{-5} \text{ mol } L^{-1})$ uponFig. 3. Referencetitration with CN⁻ in DMSO/H₂O (1:1, v/v).589 nm.

the electron density of the olefinic and phenyl ring. These results indicate that an intermolecular proton transfer between dye **1** and cyanide ion is formed.



Fig. 3. Responses of dye 1 in DMSO/H₂O (1:1, v/v). The absorbance was measured at 589 nm. The concentration of dye 1 was 5×10^{-5} mol L⁻¹.

The interaction of dye **2** with anions was investigated in DMSO/ H_2O (1:1, v/v) solution through spectrophotometric titration experiments. Fig. 5 showed the UV-vis absorption spectral changes



Fig. 4. ¹H NMR spectra of dye 1 (a) and dye 2 (b) in the absence and the presence of 1 equiv. CN⁻.



Fig. 5. The changes in the absorption spectra of dye $2~(5\times 10^{-5}\,mol\,L^{-1})$ upon titration with CN^- in $DMSO/H_2O~(1:1,\,v/v).$

of dye **2** with cyanide ion. Upon addition of cyanide ion to the dye **2** solution, the band at 374 and 462 nm decreased drastically. The color changed from yellow to colorless. However, addition of other anions such as Br^- , Cl^- , F^- , NO_3^- , $H_2PO_4^-$, ClO_4^- and HSO_4^- under similar condition does not have any significant effect on the absorption spectrum of dye **2**.

To explain this finding, it is recommended to consider CN⁻ interaction behavior, namely nucleophilic addition reaction with dye **2** chromophore. The nucleophile of CN⁻ attacks α -carbon position of dye **2** molecule having lower electron density in LUMO (LUMO of dye **2** in Fig. 1(b)), which results in a carbanion adduct. π -Electron density of LUMO of dye **2** was also calculated using Par-



Fig. 6. π -Electron density values of LUMO of dye **2**.

iser–Parr–Pople (PPP) MO method. Fig. 6 represents the π -electron density values of LUMO of dye **2**. It clearly shows that α -carbon position of dye **2** is the lowest value of 0.034 and where the resulting interaction with CN⁻ can be proposed.

¹H NMR studies provide evidence consistent with the above analysis. When the chromogenic dye **2** was treated with amount of 1 equiv. CN^- (as Bu_4N^+ salt) in $DMSO/H_2O$ (1:1, v/v), all its aromatic protons were shifted to the upfield region (Fig. 4(b)). Also the hydroxyl OH peak at 9.19 and 10.39 ppm disappeared as adduct formed. An olefinic proton at 6.90 and 7.00 ppm of dye **2** was highly upfield shifted to 5.71 ppm, while the other proton is slightly upfield shifted. These ¹H NMR studies indicate that the CN^- was added to the olefinic bridge region via a simple addition reaction of the CN^- to dye **2**.

Conclusions

In summary, this investigation has led to the development of a rapid response and highly selective cyanide probe dye **1** and **2** in

DMSO/H₂O (1:1, v/v) solution. Hemicyanine dye **1** and **2** based on dihydroxybenzene as the donor unit exhibited marked changes in UV–vis absorption peak upon the addition of cyanide anion. Other anions did not impart noticeable color changes. These two chemosensors provide a different sensing mechanism. We have investigated the sensing mechanisms by UV–vis, ¹H NMR, and DFT/PPP-MO calculation. The interaction mode of dye **1** with CN⁻ can be understood as proton transfer complex. However, dye **2** undergoes a nucleophilic addition reaction of CN⁻ to olefinic α -carbon of dye molecule.

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