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# Cyanide ion colorimetric chemosensor based on protonated merocyanine in EtOH

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#### ABSTRACT

This Letter aimed to develop an efficient method for the determination of cyanide ion (CN<sup>-</sup>). A novel colorimetric chemosensor 4-[(1*E*)-2-(4-hydroxyphenyl)ethenyl]-1-allylpyridinium bromide (HPEAPB) was synthesized. HPEAPB displayed good selectivity toward CN<sup>-</sup> over other competing anions in ethanol. A color change from yellow to red was immediately observed upon the addition of CN<sup>-</sup> and the limit of detection (LOD) was  $3.4 \times 10^{-6}$  mol L<sup>-1</sup>. The sensing mechanism was discussed by UV-vis, <sup>1</sup>H NMR titration, and a comparison study. Colorimetric test paper for CN<sup>-</sup> was prepared by attaching HPEAPB to a chromatography paper, which could be used to detect CN<sup>-</sup> in environmental samples as simply as a pH-indicator paper for pH value. The LOD of the test paper for CN<sup>-</sup> was  $2.0 \times 10^{-4}$  mol L<sup>-1</sup>. This detection method for CN<sup>-</sup> has potential applications in cyanide ion containing fields by combination of rapid and real-time advantages.

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#### Introduction

Cyanide is widely used as raw materials in chemical industry such as synthetic fibers, medicines, pesticides, and chemical fertilizers. Due to its excellent complexing ability, cyanide is also extensively used in gold mining, coking, and electroplating fields.<sup>1,2</sup> Unfortunately, cyanide is highly toxic to all aerobic organisms because it can disrupt the electron transport chain in the mitochondrial membrane and then prevent respiration. Hence, the widespread use of cyanide generates a major health risk to human beings, even a small amount of cyanide is lethal to living creatures.<sup>3–5</sup> Therefore, development of a detection method for trace cyanide ion in environmental monitoring and food analysis has attracted much research interest. A number of detecting strategies such as chromatography,<sup>6</sup> electrochemical methods,<sup>7,8</sup> atomic absorption spectrometry,<sup>9</sup> and flow injection analysis technique<sup>10</sup> have been adopted in cyanide ion recognition. Most of these methods not only need complex preprocessing, expensive equipment, and special operators, but also consume much time in detecting CN<sup>-</sup>. Furthermore, they cannot achieve real-time detection, which brings much inconvenience for cyanide ion detection. Colorimetric CN<sup>-</sup> sensing, which can detect CN<sup>-</sup> by the naked eye without expensive instruments, has attracted much research attentions. Receptors such as amides,<sup>11</sup> ureas,<sup>12</sup> thioureas,<sup>13–15</sup> imidazolium,<sup>16,17</sup> boranes,<sup>18</sup> naphthalene,<sup>19</sup> and coumarin-hemicyanine<sup>20</sup> have been reported, nevertheless, they suffer from several drawbacks such as complex structure, difficult synthesis, poor selectivity (especially in the presence of fluoride or acetate ions), and losing efficacy in protic solvents.<sup>15,16,21–23</sup> Therefore, development of an efficient, reliable, and selective method for the real-time determination of CN<sup>-</sup> is imperative.

In this work, a novel colorimetric cyanide receptor 4-[(1E)-2-(4-hydroxyphenyl)ethenyl]-1-allylpyridinium bromide (HPEAPB) was synthesized. The receptor showed good selectivity and fast response to CN<sup>-</sup>. A visually colorimetric test paper was prepared by attaching HPEAPB to a chromatography paper, which could be used for the detection of CN<sup>-</sup> concentration in real samples quickly and conveniently.

## Experimental

## Materials

4-Hydroxybenzaldehyde, 4-methylpyridine, acetic anhydride, allyl bromide, and all anions in the form of *tetra*-butylammonium salts were purchased from Aladdin Co., Shanghai, China. All solvents were of analytical reagent grade and commercially available, and used without further purification. Chromatography paper







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(specification:  $20 \times 20$  cm) was purchased from Whatman International Ltd., England.

<sup>1</sup>H NMR and <sup>13</sup>C NMR spectra were measured by a Bruker 300 MHz superconducting magnet high field NMR spectrometer using tetramethylsilane as an internal standard. Ultraviolet–visible (UV–vis) spectra were obtained on an UV-4802 spectrophotometer (UNICO(Shanghai) Instruments Co. Ltd., China). Mass spectra were recorded on a PE SCIEX API365 LC/MS/MS system. Elemental analysis was performed using a LECO CHN-900 CHN elemental analyzer.

## Synthesis of HPEAPB

HPEAPB was synthesized according to Ref. 24 with some modification (Fig. 1). Under a N<sub>2</sub> atmosphere, 4-methylpyridine (12.1 g, 0.13 mol) was added dropwise to a solution of 4-hydroxybenzaldehvde (16.0 g, 0.13 mol) and 30 mL of acetic anhvdride. and then refluxed for 24 h under electromagnetic stirring. After cooling to room temperature, the mixture was poured into 300 mL of ice water and then stirred for 1.5 h to hydrolyze the excess acetic anhydride. The resultant mixture was filtered, and the cake obtained was washed with ice water and recrystallized from ethanol. The obtained solid was introduced to an ethanolic solution (150 mL) of potassium hydroxide (7.0 g), and the mixture was refluxed for 90 min, yielding a dark solution. The pH of the solution was adjusted to 5-6 with acetic acid, and a pale yellow precipitate was formed. 4-[(E)-2-(4-Pyridinyl)ethenyl] phenol (13.1 g) was obtained as a pale yellow solid by filtration and dried in a freezedrier. 4-[(E)-2-(4-Pyridinyl)ethenyl]phenol (3.0 g, 15 mmol) and 25 mL of dry acetonitrile were introduced to a 100 mL flask. After heating to 60 °C under stirring, allyl bromide (2.8 g, 23 mmol) was added dropwise to the mixture within 10 min, and the resultant mixture was refluxed for 4 h, during which the color of the mixture changed from blood red to orange. The mixture was cooled to room temperature and filtered, and the solid was washed with acetonitrile and methanol. 4.0 g of HPEAPB as a yellow powder was obtained. Yield: 84.1%. MS-O1:(m/z) 238.1. <sup>1</sup>H NMR  $(300 \text{ MHz}, \text{DMSO-}d_6) \delta$  (ppm): 10.22 (s. broad 1H, OH), 8.83 (d. 2H, Py-H, *J* = 6.0), 8.18 (d, 2H, Py-H, *J* = 6.0), 7.98 (d, 1H, =CH-Py, *I* = 18.0), 7.63 (d, 2H, Ar-H, *I* = 9.0), 7.31 (d, 1H, =CH-Ar, *I* = 15.0), 6.88 (d, 2H, Ar-H, *J* = 9.0), 6.11–6.23 (m, 1H, =CH, *J* = 6.0–33.0), 5.42–5.45 (m, 2H, =CH<sub>2</sub>, I = 6.0-18.0), 5.13 (d, 2H, -CH<sub>2</sub>-, J = 6.0). <sup>13</sup>C NMR (75 MHz, DMSO- $d_6$ )  $\delta$  (ppm): 160.06, 153.73, 143.86, 141.57, 131.87, 130.25, 126.15, 123.14, 121.19, 119.53, 115.99, 60.10. Elemental Anal. Calcd: C, 60.39; H, 5.07; N, 4.40; found: C, 60.47; H, 5.06; N, 4.48.

#### **UV-vis detection**

UV-vis spectroscopic characterization of HPEAPB was performed in ethanol at 298 K. Air-tight screw-capped quartz cells of 1.0 cm optical path length was used in all experiments.

In a 50 mL volumetric flask, 59.5 mg HPEAPB was dissolved in ethanol to obtain HPEAPB solution with a concentration of  $1.0 \times 10^{-3}$  mol L<sup>-1</sup>. 60  $\mu$ L of HPEAPB solution was placed in a

3.0 mL cell, a series of anions in solution was then added. Ethanol was added to this mixture to a total volume of 3.0 mL. UV–vis spectra were measured after shaking for about 1 min.

#### Preparation of colorimetric test paper for cyanide ion

Colorimetric test paper for cyanide was prepared by immersing Whatman 1 chromatography paper and commercial filter paper in a methanolic solution of HPEAPB ( $3.0 \times 10^{-2} \text{ mol L}^{-1}$ ) for 30 min and then dried in air.

#### **Results and discussion**

It was reported by Zimmermann-Dimer and Machado<sup>25</sup> that a change in color could observed upon the addition of CN<sup>-</sup>, F<sup>-</sup>, and  $H_2PO_4^-$  to an acetonitrile solution of protonated merocyanine, in other words, protonated merocyanine was not a good colorimetric anionic chemosensor in acetonitrile. The response of HPEAPB to anions in different solvents has been investigated and found that in ethanol HPEAPB showed good selectivity and fast response to CN<sup>-</sup> over other interfering anions (F<sup>-</sup>, Cl<sup>-</sup>, Br<sup>-</sup>, I<sup>-</sup>, AcO<sup>-</sup>, H<sub>2</sub>PO<sub>4</sub><sup>-</sup>, and HSO<sub>4</sub>). Figure 2a illustrates the changes in UV-vis spectra, the absorbance at 414 nm decreased and a new absorbance at 531 nm appeared upon the addition of CN<sup>-</sup>. Other interfering anions (F<sup>-</sup>, Cl<sup>-</sup>, Br<sup>-</sup>, I<sup>-</sup>, AcO<sup>-</sup>, H<sub>2</sub>PO<sub>4</sub><sup>-</sup>, and HSO<sub>4</sub><sup>-</sup>) produced minimal change in the UV-vis spectra. At the same time, a color change from yellow to red was immediately observed (less than 2 s) upon the addition of CN<sup>-</sup> to the ethanolic solution of HPEAPB. Similarly, other interfering anions could not produce noticeable change in color (Fig. 2b). These results demonstrate that HPEAPB can distinguish CN<sup>-</sup> from halogen anions, AcO<sup>-</sup>, H<sub>2</sub>PO<sub>4</sub>, and HSO<sub>4</sub> with fast response and good selectivity, and can be detected by the naked eye.

UV-vis titration was conducted with CN<sup>-</sup> (Fig. 3a). It was found that the intensity of the absorbance at 414 nm decreased gradually and the absorbance at 531 nm increased gradually as CN<sup>-</sup> concentration increased, accompanied with the formation of an isosbestic point at 454 nm and a significant change in color from light yellow to dark red (Fig. 3c). The isosbestic point at 454 nm indicated the formation of a new complex between HPEAPB and CN<sup>-</sup>. The Job curve indicated that HPEAPB and CN- formed a 1:1 complex (Fig. 3b) (See ESI). According to Benesi-Hildebrand relation  $A = \frac{A_0 + A_1 K[X^-]^2 6}{1 + K[X^-]^2}$ , the association constant between HPEAPB and CN<sup>-</sup> was calculated to be  $3.2 \times 10^4$ . The limit of detection (LOD) for cyanide ion by UV-vis was determined to be  $3.4 \times 10^{-6}$  mol L<sup>-1</sup> according to  $DL = 3\sigma/K$ <sup>27</sup> The LOD for cyanide ion sensed by the naked eye was found to be  $8.0 \times 10^{-6}$  mol L<sup>-1</sup> (Fig. 4a). A linear relationship between the absorbance at 531 nm and CN<sup>-</sup> concentration in the range of  $2.0 \times 10^{-6}$  to  $2 \times 10^{-4}$  mol L<sup>-1</sup> (Fig. 4b) was obtained, illustrating that HPEAPB could be used to roughly measure CN<sup>-</sup> concentration in this concentration range.

Figure 5 shows the <sup>1</sup>H NMR spectra of HPEAPB in DMSO- $d_6$  (6.0 × 10<sup>-2</sup> mol L<sup>-1</sup>) upon the addition of CN<sup>-</sup>. The –OH signal that appeared at 10.20 in HPEAPB disappeared after the addition of



(a) (CH<sub>3</sub>CO)<sub>2</sub>, reflux 12h; (b) KOH, EtOH, reflux 1.5h; (c) Allyl bromide , Acetonitrile 3.5h



**Figure 2.** (a) UV-vis spectra of ethanolic solution of HPEAPB  $(2.0 \times 10^{-5} \text{ mol } \text{L}^{-1})$  upon the addition of 5 equiv of F<sup>-</sup>, Cl<sup>-</sup>, Br<sup>-</sup>, I<sup>-</sup>, AcO<sup>-</sup>, CN<sup>-</sup>, H<sub>2</sub>PO<sub>4</sub><sup>-</sup>, and HSO<sub>4</sub><sup>-</sup>. (b) Color changes observed in ethanolic solution of HPEAPB  $(2.0 \times 10^{-5} \text{ mol } \text{L}^{-1})$  upon the addition of various anions as *tetra*-butylammonium salts  $(1.0 \times 10^{-4} \text{ mol } \text{L}^{-1})$ .



**Figure 3.** (a) UV-vis spectra changes of HPEAPB ( $2.0 \times 10^{-5} \text{ mol } L^{-1}$  in ethanol) upon titration with CN<sup>-</sup>. (b) Job plot of HPEAPB with *tetra*-butylammonium cyanide determined by UV-vis in ethanol. (c) Photographs of HPEAPB in ethanol in the presence of increasing CN<sup>-</sup> concentrations.

0.01 equiv of CN<sup>-</sup>, indicating that CN<sup>-</sup> probably interacted with the hydroxyl group of HPEAPB through a hydrogen bond.<sup>25</sup> A noticeable upfield chemical shift was observed in the case of the aromatic ring probably due to this interaction.<sup>13</sup>

To further elucidate this point, the anionic response of 4-((E)-2-[(4-acetoxyphenyl)ethenyl-1-allyl pyridinium bromide (APEAPB)<sup>28</sup> and <math>4-((E)-2-[(4-sodium phenolate)ethenyl-1-allyl pyridinium bromide (SPEAPB) (Fig. 6a) was investigated. None of the anions caused obvious changes in both UV–vis spectra (Fig. 6b) and color (Fig. 6c) for ethanolic solution of APEAPB. However, CN<sup>-</sup> caused obvious changes in both UV–vis spectra and color for ethanolic solution of SPEAPB (Fig. 6d and e).<sup>29</sup> F<sup>-</sup>, HSO<sub>4</sub>, and AcO<sup>-</sup> also caused a little change in color. These results not only proved that CN<sup>-</sup> interacted with the hydroxyl group of HPEAPB through the

formation of a hydrogen bond, but also demonstrated HPEAPB was a better colorimetric sensor than SPEAPB.

The reversibility of the HPEAPB for CN<sup>-</sup> was studied through Cu<sup>2+</sup> displacement.<sup>30</sup> The reversibility was tested as follows: 60 µL of HPEAPB solution was added into a 3.0 mL cell, ethanol was subsequently added to a total volume of 3.0 mL, and UV-vis spectrum was detected. Then, 30 µL of  $1.0 \times 10^{-2}$  mol L<sup>-1</sup> CN<sup>-</sup> solution was added, and UV-vis was used to test the change in spectra. 6 µL of  $1.0 \times 10^{-2}$  mol L<sup>-1</sup> Cu<sup>2+</sup> solution was added, and UV-vis was used to test the change in spectra. The alternate addition of CN<sup>-</sup> and Cu<sup>2+</sup> cycle was repeated five times. Free HPEAPB in ethanol displayed a strong absorbance at 414 nm in UV-vis spectrum and yellow color. When 1.0 equiv CN<sup>-</sup> was introduced, the absorbance at 414 nm decreased (Fig. 7a), a color change from



Figure 4. (a) Photographs of ethanolic solution of HPEAPB ( $2.0 \times 10^{-5} \text{ mol } L^{-1}$ ) and upon the presence of  $CN^-$  ( $8.0 \times 10^{-6} \text{ mol } L^{-1}$ ). (b) Plot of relative absorbance at 531 nm versus  $CN^-$  concentration.



**Figure 5.** <sup>1</sup>H NMR spectra of HPEAPB in DMSO- $d_6$  (6.0 × 10<sup>-2</sup> mol L<sup>-1</sup>) upon the addition of CN<sup>-</sup> at 25 °C. From bottom to top: free, 0.0025, 0.005, 0.01, 0.05, 0.10, 0.50, and 1.0 equiv of CN<sup>-</sup>.

yellow to red was observed (Fig. 7b). Upon addition of  $Cu^{2+}$ ,  $CN^-$  was removed from HPEAPB- $CN^-$  complex to form a more stable complex  $[Cu(CN)_4]^{2-}$ , and the peak at 414 nm increased again. A color change from red to yellow was simultaneously observed.

Repeating the alternate addition of  $CN^-$  and  $Cu^{2+}$  cycle resulted in the similar result to those of the previous cycle, demonstrating the recognition of  $CN^-$  was reversible. This also demonstrates that the coexistence of  $Cu^{2+}$  would influence the accuracy, so the



**Figure 6.** (a) Chemical structure of HPEAPB, APEAPB, and SPEAPB. (b) UV-vis spectra of APEAPB  $(2.0 \times 10^{-5} \text{ mol } L^{-1})$  in ethanol after the addition of 5 equiv of F<sup>-</sup>, Cl<sup>-</sup>, Br<sup>-</sup>, I<sup>-</sup>, AcO<sup>-</sup>, CN<sup>-</sup>, H<sub>2</sub>PO<sub>4</sub>, and HSO<sub>4</sub>. (c) Photographs of APEAPB in ethanol solution  $(2.0 \times 10^{-5} \text{ mol } L^{-1})$  upon the addition of various anions as *tetra*-butylammonium salts  $(1.0 \times 10^{-4} \text{ mol } L^{-1})$ . (d) UV-vis spectra of SPEAPB  $(2.0 \times 10^{-5} \text{ mol } L^{-1})$  in ethanol after the addition of 5 equiv of F<sup>-</sup>, Cl<sup>-</sup>, Br<sup>-</sup>, I<sup>-</sup>, AcO<sup>-</sup>, CN<sup>-</sup>, H<sub>2</sub>PO<sub>4</sub>, and HSO<sub>4</sub>. (e) Photographs of SPEAPB in ethanol solution  $(2.0 \times 10^{-5} \text{ mol } L^{-1})$  upon the addition of 5 equiv of F<sup>-</sup>, Cl<sup>-</sup>, Br<sup>-</sup>, I<sup>-</sup>, AcO<sup>-</sup>, CN<sup>-</sup>, H<sub>2</sub>PO<sub>4</sub>, and HSO<sub>4</sub>. (e) Photographs of SPEAPB in ethanol solution  $(2.0 \times 10^{-5} \text{ mol } L^{-1})$  upon the addition of various anions as *tetra*-butylammonium salts  $(1.0 \times 10^{-4} \text{ mol } L^{-1})$ .



Figure 7. (a) Change in the absorbance at 413 nm of HPEAPB in ethanol upon alternate addition of  $CN^-$  and  $Cu^{2+}$ . (b) The corresponding change in color of ethanolic solution of HPEAPB upon alternate addition of  $CN^-$  and  $Cu^{2+}$ .



**Figure 8.** (a) Photographs of test paper for detecting various ions including  $F^-$ ,  $Cl^-$ ,  $Br^-$ ,  $I^-$ ,  $AcO^-$ ,  $CN^-$ ,  $H_2PQ_4^-$ , and  $HSQ_4^-$  ( $1.0 \times 10^{-3} \text{ mol } L^{-1}$ ). (b) Photographs of test paper for detecting  $CN^-$  with different concentrations, from left to right:  $0, 1.0 \times 10^{-4}, 2.0 \times 10^{-4}, 4.0 \times 10^{-4}, 5.0 \times 10^{-4}, 8.0 \times 10^{-4}, 1.0 \times 10^{-3}, 5.0 \times 10^{-3}$ , and  $1.0 \times 10^{-2} \text{ mol } L^{-1}$ . (c) Photographs of test paper for detecting  $CN^-$  in wastewater with different concentrations, from left to right:  $0, 2.0 \times 10^{-4}, 3.0 \times 10^{-4}, 4.0 \times 10^{-4}, 5.0 \times 10^{-4}, 6.0 \times 10^{-4}, 7.0 \times 10^{-4}, 8.0 \times 10^{-4}, and <math>1.0 \times 10^{-3} \text{ mol } L^{-1}$ .

removal of  $Cu^{2+}$  or exclusion of  $Cu^{2+}$  impact would be required if  $Cu^{2+}$  coexists in a real sample.

Inspired by a pH-indicator paper for pH value, visually colorimetric test paper was prepared, which made the detection of cyanide ion more conveniently. Both commercial filter paper and chromatography paper have been tested. It was found that the commercial filter paper could not absorb HPEAPB uniformly, and HPEAPB could be easily liberated from the paper by solution. However, the test paper made from chromatography paper possessed good properties. As shown in Figure 8a, a distinct change in color from yellow-green to red was immediately observed by dropping CN<sup>-</sup> ethanol solution to the test paper. However, other interfering anions (F<sup>-</sup>, Cl<sup>-</sup>, Br<sup>-</sup>, I<sup>-</sup>, AcO<sup>-</sup>, H<sub>2</sub>PO<sub>4</sub>, and HSO<sub>4</sub>) could not produce an obvious change in color. This indicated that the change in color on the test paper was caused by the interaction of HPEAPB and CN<sup>-</sup>, implying that the visually colorimetric test paper showed specific recognition to CN<sup>-</sup>. Furthermore, the detection of CN<sup>-</sup> with the test paper was as simple as the detection of pH using a pH-indicator paper. As the concentration of CN<sup>-</sup> increased, the color of the test paper gradually deepened and finally changed to scarlet (Fig. 8b). This illustrates that we can detect cyanide ion in real-time according to the test paper's color. The LOD was  $2.0 \times 10^{-4}$ mol  $L^{-1}$ . The test paper was used to make a qualitative analysis for wastewater, it also showed a similar change in color (Fig. 8c). Therefore, the visually colorimetric test paper can be used to detect the cyanide ion in wastewater as simply as a pH-indicator paper.

#### Conclusions

A novel cyanide ion receptor HPEAPB was synthesized. The receptor could recognize cyanide ion in ethanol with good selectivity, rapid response, good reversibility, and high sensitivity (LOD:  $3.4 \times 10^{-6}$  mol L<sup>-1</sup>). A visually colorimetric test paper was prepared by attaching HPEAPB to chromatography paper, which could be used for real-time qualitative analysis of the cyanide ion in wastewater. Although the LOD of the test paper was lower than the values in solution, we believe a test paper with higher LOD would be prepared in the near future.

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#### Supplementary data

Supplementary data associated with this article can be found, in the online version, at http://dx.doi.org/10.1016/j.tetlet.2014.03. 097.

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