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# Visual and reversible detection of cyanide ions in protic solvents by a novel colorimetric receptor



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#### A R T I C L E I N F O

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# 1. Introduction

Anions are extensively used in the environmental, industrial, biological, and medical fields [1–7]. Among important anions, cy-anide (CN<sup>-</sup>) is widely used in various areas, such as organic synthesis, fiber/resin synthesis, electroplating, and gold extraction; unfortunately, CN<sup>-</sup> use has led to leaching of the anion into the environment and widespread human exposure [8–11]. Cyanide is lethal to humans at concentrations of 0.5–3.5 mg kg<sup>-1</sup> of body weight. Thus, the development of efficient, selective, fast, and inexpensive detection methods to determine CN<sup>-</sup> in the environment is of great importance.

Several methods to detect CN<sup>-</sup> have been developed using various experimental protocols and detection techniques, such as chromatography [12], spectrophotography [13], electrochemical methods [14,15], and flow injection analysis technique [16]. However, these methods require complex preprocessing, expensive equipments, special operators, and long detection times. Colorimetric CN<sup>-</sup> sensing, which allows CN<sup>-</sup> detection by the

#### ABSTRACT

A novel colorimetric chemodosimeter for cyanide (CN<sup>-</sup>) and 1-allyl-4-[2-(4-hydroxyphenyl)ethenyl)]quinolinium bromide (AHPEQB) was designed and synthesized by condensation and terminal N alkyl reaction. AHPEQB exhibited highly selective and sensitive recognition properties toward CN<sup>-</sup> over other competing anions in ethanol, a protic solvent, with a 1:1 binding stoichiometry and a detection limit of  $1.7 \times 10^{-6}$  mol L<sup>-1</sup>. AHPEQB also displayed rapid colorimetric response that could be readily observed by the naked eye and good reversibility. The sensing mechanism of the proposed chemodosimeter was studied by UV–Vis, <sup>1</sup>H NMR titration, and comparison 1-allyl-4-[2-(4-acetoxyphenyl)ethenyl)]-quinolinium bromide (AAPEQB). The colorimetric chemodosimeter showed high accuracy in determining the concentration of CN<sup>-</sup> in real water samples.

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naked eye without expensive instruments, has attracted considerable attention in the past decade [17–32]. Receptors such as amide [17], urea [18], thiourea [19–21], imidazolium [22,23], borane [24], naphthalene [25], coumarin—hemicyanine [26], diarylethene derivatives [29], oxazine [30], and heptamethine cyanine dye [32] have been reported. While remarkable achievements in colorimetric CN<sup>-</sup> sensing have been obtained, poor reversibility and lack of efficiency in protic media continue to present challenges to researchers. Therefore, the fabrication of CN<sup>-</sup> receptors with simple design, rapid response, good reliability and reversibility, and high selectivity in protic solvents or aqueous environments is necessary.

In this work, a novel colorimetric CN<sup>-</sup> receptor, 1-allyl-4-[2-(4hydroxyphenyl)ethenyl]-quinolinium bromide (AHPEQB), was designed and synthesized. The receptor displayed good selectivity, fast response and good reversibility toward CN<sup>-</sup> in ethanol, a protic solvent.

#### 2. Experimental

# 2.1. Reagents and apparatus

4-Methylquinoline (98%), 4-hydroxybenzaldehyde (98%), acetic anhydride (98%), and allyl bromide (98%) were purchased from





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Aladdin Co., Shanghai, China. All anions in the form of *tetra*butylammonium salts were purchased from Aladdin Co., Shanghai, China. All chemical reagents and solvents used were purchased from commercial suppliers and used without further purification.

<sup>1</sup>H NMR and <sup>13</sup>C NMR were recorded on a Bruker AV-300 NMR instrument using trimethylsilane as an internal standard. Ultraviolet–Visible spectroscopy (UV–Vis) spectra were obtained on a UV-4802 spectrophotometer [UNICO (Shanghai) Instruments Co. Ltd, China]. Elemental analysis was performed using a Leco CHN-900 micro carbon–hydrogen–nitrogen analyzer. The concentration of CN<sup>-</sup> was measured using a CNO150X Cyanide electrode (Van London-pHoenix Co., USA).

#### 2.2. Synthesis of AHPEQB

AHPEQB was synthesized via a two-step method (Fig. 1). The synthetic procedure is as follows: Under a  $N_2$  atmosphere, 4-hydroxybenzaldehyde (8.54 g, 70.0 mmol) and 15.0 mL of acetic anhydride were added to a 50 mL flask. 4-Methylquinoline (10.02 g, 70.0 mol) was added dropwise to the mixture for 10 min and then refluxed for 24 h, yielding a black oil mixture. After cooling to room temperature, the mixture was poured into 100 mL of ice water and then stirred for 30 min to hydrolyze the excess acetic anhydride. The resultant mixture was filtered, and the cake obtained was washed with ice water and recrystallized in ethanol. The obtained solid was introduced to an ethanolic solution (80 mL) of KOH (5.00 g). The mixture was heated to reflux for 150 min, resulting in a dark solution. The pH of the solution was adjusted to 5–6 with acetic acid, and a pale yellow precipitate was formed. 4-[2-(4-

Hydroxyphenyl)ethenyl]quinoline as a light yellow powder was obtained by filtration and dried over in a freeze-drier (11.58 g, yield: 70.0%). The structure of 4-[2-(4-hydroxyphenyl)ethenyl]quinoline was confirmed by <sup>1</sup>H NMR and <sup>13</sup>C NMR (see Supporting information).

4-[2-(4-Hvdroxyphenyl)ethenyllquinoline (1.50 g, 6.0 mmol) and 15.0 mL of dry acetonitrile were dispensed to a 50 mL flask. After heating to 60 °C under stirring, allyl bromide (0.74 g. 6.1 mmol) acetonitrile solution (5.0 mL) was added dropwise to the mixture within 5 min; the resultant mixture was refluxed for 6 h, during which the color of the mixture changed from red to orange. The mixture was cooled to room temperature and filtered, and the solid was washed with acetonitrile and methanol, producing 1.41 g of AHPVEB as an orange powder. Yield: 71.3% .<sup>1</sup>H NMR (300 MHz,  $d_6$ -DMSO)  $\delta$  (ppm): 10.31 (s, broad, 1H), 9.34 (d, 1H, J = 9.0), 9.08 (d, 1H, J = 6.0), 8.52 (d, 1H, J = 9.0), 8.42 (t, 1H, J = 9.0), 8.24 (t, 1H, J = 6.0), 8.19 (d, 2H, J = 6.0), 8.02 (t, 1H, J = 15.0), 7.92 (d, 2H, J = 9.0), 6.94(d, 2H, J = 9.0), 6.22 (m, 1H, J = 3.0-33.0), 5.64 (d, 2H, J = 3.0), 5.38 (m, 1H, J = 12.0), 5.27(d, 1H, J = 18.0). <sup>13</sup>C NMR (75 MHz,  $d_6$ -DMSO)  $\delta$  (ppm): 161.00, 154.11, 147.59, 144.64, 138.42, 135.36, 132.15, 131.78, 129.33, 127.21, 127.16, 126.85, 120.12, 119.80, 116.46, 116.35, 115.97, 58.44. Elemental analysis cal. (%): C 64.68, H 5.43, N 3.72; found (%): C 64.62, H 5.42, N 3.74. M.p. 213.5-214.0 °C.

To investigate the CN<sup>-</sup> recognition mechanism, 1-allyl-4-[2-(4-acetoxyphenyl)ethenyl]-quinolinium bromide (AAPEQB) was synthesized (Supporting Information: S. Fig. 1) according to a previously reported method [27]. The detailed synthesis procedure and <sup>1</sup>H NMR and <sup>13</sup>C NMR information of this compound are described in Supporting information.



**Reaction condiation:** a)  $(AcO)_2O$ , reflux 24 h; b) KOH, EtOH, reflux 2.5 h; c) allyl bromide , Acetonitrile reflux 6h



Reaction condiation: a)  $(AcO)_2O$ , reflux 24 h; b) allyl bromide , Acetonitrile reflux 6h

Fig. 1. Synthetic route of AHPEQB and AAPEQB.

#### 2.3. General procedure for anion response

A stock solution of AHPEQB ( $1.0 \times 10^{-3} \text{ mol } \text{L}^{-1}$ ) was prepared by dissolving 3.70 mg of AHPEQB in 10 mL of ethanol. Solutions of various anions (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>;  $1.0 \times 10^{-3} \text{ mol } \text{L}^{-1}$ ) were prepared by dissolving the corresponding *tetra*-butylammonium salts in ethanol.

Approximately 60  $\mu$ L of AHPEQB solution and 300  $\mu$ L of anion solution were placed in a 3.0 mL cuvette. Ethanol was added to this mixture to a total volume of 3.0 mL. Characterization was conducted via UV–Vis spectroscopy.

#### 2.4. Titration of CN<sup>-</sup>

Titration experiments were carried out at 25 °C. Approximately 60  $\mu$ L of AHPEQB solution and different volumes of CN<sup>-</sup> solution were place in a 3.0 mL cuvette. Ethanol was added to this mixture to a total volume of 3.0 mL. Characterization was performed by UV– Vis spectroscopy.

# 2.5. Analytical applications for the detection of cyanide in water samples

Four real water samples (distilled water, river water, domestic sewage, and industrial wastewater) were used. Approximately 60  $\mu$ L of AHPEQB solution and 300  $\mu$ L of the water sample were placed in a 3.0 mL cuvette. Ethanol was added to this mixture to a total volume of 3.0 mL. Sample spectra were obtained by UV–Vis spectroscopy.

#### 3. Results and discussion

#### 3.1. Selectivity of AHPEQB

Changes in the UV-Vis spectra and colors of the receptors toward anions are highly solvent sensitive [33,34]. Therefore, the response of AHPEQB to anions (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  $HSO_{4}^{-}$ ) in different solvents (DMSO, acetonitrile, THF, methanol, methanol, H<sub>2</sub>O, CHCl<sub>3</sub>, and toluene) was investigated. AHPEQB showed poor solubility in THF, toluene, and CHCl<sub>3</sub>, whereas the anions showed low selectivity in acetonitrile, methanol and water. Therefore, these solvents cannot be used for anion detection. Ethanol was finally selected as the solvent; in its solvent, AHPEQB showed high selectivity and CN<sup>-</sup> displayed good selectivity over other interfering anions, as evidenced by the rapid color and obvious UV-Vis spectral changes observed. As shown in Fig. 2(A), a color change from pale yellow to blue was readily observed after addition of CN<sup>-</sup> to an ethanolic solution of AHPEQB; the response time was 2 s. Other 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 changes in color. CN<sup>-</sup> also caused a significant change in the UV-Vis absorption spectrum of AHPEQB. As shown in Fig. 2(B), the UV–Vis spectrum of AHPEQB is characterized by one band centered at 464 nm. Upon addition of CN- to the AHPEQBethanol solution, the band at 464 nm weakened and a new band appeared at 610 nm, which indicates that a new complex had formed between AHPEQB and CN<sup>-</sup>. This new complex was also responsible for the color change in Fig. 2(A). Other interfering anions could not produce any obvious change in the UV-Vis spectrum of AHPEQB. The anti-jamming ability of AHPEQB was evaluated using UV-Vis competition experiments, and results illustrated that coexistence with other anions cannot induce significant interferences in CN<sup>-</sup> recognition (Supporting Information: S. Fig. 2).

The interaction of AHPVQB with CN<sup>-</sup> was also investigated by fluorospectro-photometer. The fluorescence spectrum of AHPVQB ( $2.0 \times 10^{-5}$  mol L<sup>-1</sup>) exhibited a strong fluorescence emission at



**Fig. 2.** (A) Color changes in ethanol solutions of AHPEQB ( $2.0 \times 10^{-5}$  mol L<sup>-1</sup>) in the presence of various anions (5 equiv.). Added anions from left to right: none, F<sup>-</sup>, Cl<sup>-</sup>, Br<sup>-</sup>, l<sup>-</sup>, AcO<sup>-</sup>, CN<sup>-</sup>, H<sub>2</sub>PO<sup>-</sup>\_4, and HSO<sup>-</sup>\_4. (B) UV–Vis spectra of AHPEQB ( $2.0 \times 10^{-5}$  mol L<sup>-1</sup>) in ethanol upon addition of various anion salts (5 equiv.). (For interpretation of the references to color in this figure legend, the reader is referred to the web version of this article.)

560 nm in ethanol which could be ascribed to the quinoline skeleton. Upon the addition of CN<sup>-</sup>, the original fluorescence emission of AHPVQB was quenched sharply (Supporting Information: S. Fig. 3). The emission change could also be readily distinguished by the naked eye. And no significant change was observed in the emission spectrum of AHPVQB upon the addition of other interfering anions.

These results indicate that AHPEQB is an excellent CN<sup>-</sup> colorimetric receptor in ethanol with fast responses and good selectivity over other interfering anions.

### 3.2. Mechanism studies for CN<sup>-</sup> recognition

UV–Vis titration was conducted with  $CN^-$  (Fig. 3). As the concentration of  $CN^-$  gradually increased, the absorption peak at 464 nm gradually decreased, a new peak at 610 nm gradually increased, and the spectra showed a clear isosbestic point at 515 nm, which indicates the formation of a new complex between AHPEQB and  $CN^-$ . After addition of 7 equiv. of  $CN^-$ , it reached a saturation level (Fig. 3(A)). A color change from pale yellow to green to blue during titration was also observed by the naked eye (Fig. 3(B)).

The stoichiometry between AHPEQB and CN<sup>-</sup> was determined from the UV–Vis titration data. The measured absorbance variation at 610 nm ( $A = A_{abs} - A_i$ ) reached maximum values when the molar fraction of ([AHPEQB]/[CN<sup>-</sup>] + [AHPEQB]) was 0.5, which indicates that AHPEQB and CN<sup>-</sup> form a 1:1 complexes [19] (Fig. 3(C)). Benesi–Hildebrand plots [35–37] yield an association constant of 1.69 × 10<sup>4</sup> (Fig. 3(D)), which is greater than that obtained in previous reports [34,38]. The limit of detection of AHPEQB for CN<sup>-</sup> in ethanol was determined to be 1.7 × 10<sup>-6</sup> mol L<sup>-1</sup> in ethanol



**Fig. 3.** (A) UV–Vis titration spectra of AHPEQB in ethanol  $(2.0 \times 10^{-5} \text{ mol L}^{-1})$  after addition of various amounts of CN<sup>-</sup> (0, 0.5, 1.5, 2.0, 2.5, 3.0, 3.5, 4.0, 4.5, 5.0, 6.0, and 7.0 equiv.). (B) Color changes in the AHPEQB–ethanol solution with increasing CN<sup>-</sup> concentration. (C) Job plot of AHPEQB with *tetra*-butylammonium cyanide determined by UV–Vis in ethanol. (D) Plot of relative absorbance at 610 nm versus CN<sup>-</sup> concentration. (For interpretation of the references to color in this figure legend, the reader is referred to the web version of this article.)



**Fig. 4.** <sup>1</sup>H NMR titration of AHPEQB in DMSO– $d_6$ .



**Fig. 5.** (A)Color change in ethanol solutions of AAPEQB  $(2.0 \times 10^{-5} \text{ mol L}^{-1})$  in the presence of various anions (5 equiv.). Added anions from left to right: none, 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) UV–vis spectra of AAPEQB  $(2.0 \times 10^{-5} \text{ mol L}^{-1})$  in ethanol upon addition of various anion salts (5 equiv.). (For interpretation of the references to color in this figure legend, the reader is referred to the web version of this article.)



Fig. 6. Sensing mechanism of AHPEQB for CN<sup>-</sup>.

according to  $DL = 3\sigma/K$  [39–42], which is lower than the upper limit of 1.9 × 10<sup>-6</sup> mol L<sup>-1</sup> for CN<sup>-</sup> in drinking water set by the World Health Organization [43].

<sup>1</sup>H NMR titration was carried out to further elucidate the intermolecular interaction between AHPEQB and  $CN^-$ . As shown in Fig. 4, the –OH signal in the receptor that appears at 10.31 in AHPEQB disappeared after addition of 0.05 equiv. of  $CN^-$ , illustrating a hydrogen bonding interaction between AHPEQB and  $CN^-$  at a small quantities of  $CN^-$  [11,39]. This also demonstrated that APHEQB was a highly sensitive colorimetric chemosensor for  $CN^-$ . A noticeable upfield chemical shift was observed in the case of benzene protons as well as in the quinolinium ring because of this complexation. This result could be ascribed to the delocalization of electrons in the benzene ring [19,34].

The anionic response of AAPEQB (which does not contain –OH group) was investigated to verify our assumption. None of the anions caused obvious changes in both color and UV–Vis spectra (Fig. 5), which demonstrates that CN<sup>-</sup> interacts with the –OH group of AHPEQB to form the AHPEQB–CN<sup>-</sup> complex.

As illustrated in Fig. 6, the relevant reaction mechanism can be reasonably explained by the interaction of  $CN^-$  anion with the



Fig. 8. Changes in absorbance at 603 nm as a function of CN<sup>-</sup> concentration.

hydrogen of -OH. This interaction increases the separation between H and O, and the electron-rich O increases the conjugation of AHPEQB. Obvious spectral and color changes may then be observed.

### 3.3. Reversibility of AHPEQB

The reversibility of the AHPEQB sensor for  $CN^-$  was studied through  $Cu^{2+}$  displacement [23,42,44]. The UV–Vis spectrum of free AHPEQB in ethanol displayed strong absorbance at 464 nm and a pale yellow color. When 1.0 equiv.  $CN^-$  was introduced to AHPEQB, a new absorbance peak at 610 nm appeared because of the



**Fig. 7.** (A) UV–Vis spectrum of AHPEQB in ethanol and corresponding spectral changes upon alternate addition of  $CN^-$  and  $Cu^{2+}$  and (B) the absorbance at 464 nm. (C) Photograph of free AHPEQB–ethanol solution and corresponding color changes upon alternate addition of  $CN^-$  and  $Cu^{2+}$ . (For interpretation of the references to color in this figure legend, the reader is referred to the web version of this article.)

Determination of CN-	concentration in water samples.

Table 1

Water samples	A <sub>at 603 nm</sub>	Addition of $CN^{-}$ (mol $L^{-1}$ )	A <sub>at 603 nm</sub> after CN <sup>-</sup> addition	Detected $CN^-$ concentration (mol $L^{-1}$ )	Deduced $CN^-$ concentration (mol $L^{-1}$ )	$CN^{-}$ concentration detected by selective electrode (mol $L^{-1}$ )
Distilled water	0.00675	2.00E-5	0.08493	2.00E-05	Null	Null
River water	0.00915	2.00E-5	0.08582	2.03E-05	0.03 E-05	Null
Domestic sewage	0.03185	1.00E-5	0.07395	1.47E-05	0.47 E-05	0.50 E-05
Industrial wastewater	0.05617	1.00E-5	0.09175	2.20E-05	2.20 E-05	2.33 E-05

formation of AHPEQB– $CN^-$  complex and a color change from yellow to blue was observed. Upon addition of  $Cu^{2+}$ ,  $CN^-$  was removed from AHPEQB– $CN^-$  complex to form a more stable complex [ $Cu(CN)_4$ ]<sup>2-</sup>; here, the peak at 610 nm disappears and the peak at 464 nm is restored to the original value obtained from the AHPEQB–ethanol solution (Fig. 7(A) and (B)). A color change from blue to yellow was simultaneously observed (Fig. 7(C)). Alternate addition of  $CN^-$  and  $Cu^{2+}$  resulted in results similar to those observed in previous cycles, which demonstrates that the recognition of  $CN^-$  is reversible.

# 3.4. Analytical application

As described above, AHPEQB is a colorimetric receptor for CN<sup>-</sup> with good selectivity and reversibility, high sensitivity, rapid response, and convenient detection. Therefore, AHPEQB should have broad applications in fields containing CN<sup>-</sup>. In the present study, the application of AHPEQB for the ultrasensitive determination of CN<sup>-</sup> in four water samples was studied. These water samples included distilled water (as the blank), river water, domestic sewage, and industrial wastewater; these samples were spiked with CN<sup>-</sup> at concentrations of  $2.0 \times 10^{-5}$ ,  $2.0 \times 10^{-5}$ ,  $1.0 \times 10^{-5}$ , and  $1.0 \times 10^{-5}$  mo L<sup>-1</sup>. To determine CN<sup>-</sup> in water samples, a calibration cure was first plotted via UV–Vis titration (Fig. 8).

The CN<sup>-</sup> determination procedure was similar to the UV-Vis titration procedure described in Section 2.4, except that the solvent used for CN<sup>-</sup> determination was a mixture of ethanol and water with a volume ratio of 9:1. Approximately 10.00 mL of river water. domestic sewage, and industrial wastewater was placed in a test tube for centrifugal separation, and the aqueous solution was neutralized to pH 7 with Na<sub>2</sub>CO<sub>3</sub> (10%) and HCl (0.01 mol  $L^{-1}$ ). The experiments were repeated six times. The average concentration of CN<sup>-</sup> in the three water samples can be deduced from the curve of the absorbance at 603 nm versus the concentration of CN<sup>-</sup> after deduction of the blank. Determination results are shown in Table 1. Industrial wastewater contained the highest CN<sup>-</sup> concentration. For comparison, the CN<sup>-</sup> concentration of four water samples without CN<sup>-</sup> spiking was detected by a CN<sup>-</sup>-selective electrode. As shown in Table 1, the CN<sup>-</sup> concentration in industrial wastewater and domestic sewage measured by AHPEQB was comparable with the data measured by the CN<sup>-</sup> selective electrode with a relative standard deviation of approximately 5% and an accuracy of approximately 94.6%. The CN<sup>-</sup> concentrations in distilled water and river water could not be detected because they were far below the limit of detection of our proposed CN--selective electrode (0.1 ppm). This result illustrates that the colorimetric chemodosimeter developed in this work could be used for the ultrasensitive detection of CN<sup>-</sup>.

#### 4. Conclusions

A colorimetric chemodosimeter for CN<sup>-</sup> based on quinolinium with rapid responses and good sensitivity and selectivity over other anions in ethanol was developed. The receptor-ethanol solution immediately showed obvious changes in color from yellow to blue after introduction of CN<sup>-</sup>, which allows rapid detection of CN<sup>-</sup> in ethanol. This receptor was used for the ultrasensitive determination of CN<sup>-</sup> in real samples by UV–Vis. Results implied that the receptor has broad applications in fields requiring CN<sup>-</sup> determination. The receptor also displayed good reversibility toward CN<sup>-</sup> through Cu<sup>2+</sup> displacement.

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#### Appendix A. Supplementary data

Supplementary data related to this article can be found at http://dx.doi.org/10.1016/j.dyepig.2014.02.020.

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