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

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ABSTRACT

A novel colorimetric chemodosimeter for cyanide (CN^-) 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^- over other competing anions in ethanol, a protic solvent, with a 1:1 binding stoichiometry and a detection limit of 1.7×10^{-6} mol L^{-1}. 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, ^1H 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^- in real water samples.

1. Introduction

Anions are extensively used in the environmental, industrial, biological, and medical fields [1–7]. Among important anions, cyanide (CN^-) is widely used in various areas, such as organic synthesis, fiber/resin synthesis, electroplating, and gold extraction; unfortunately, CN^- 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^{-1} of body weight. Thus, the development of efficient, selective, fast, and inexpensive detection methods to determine CN^- in the environment is of great importance.

Several methods to detect CN^- 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^- sensing, which allows CN^- detection by the 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^- sensing have been obtained, poor reversibility and lack of efficiency in protic media continue to present challenges to researchers. Therefore, the fabrication of CN^- 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^- receptor, 1-allyl-4-[2-(4-hydroxyphenyl)ethenyl]-quinolinium bromide (AHPEQB), was designed and synthesized. The receptor displayed good selectivity, fast response and good reversibility toward CN^- 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.

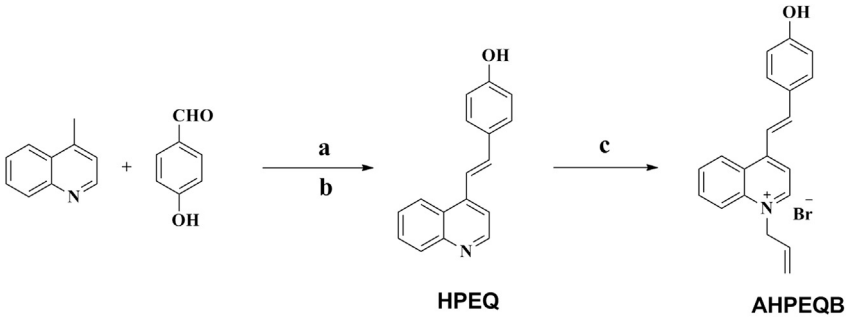
^{1}H NMR and ^{13}C NMR were recorded on a Bruker AV-300 NMR instrument using trimethylsilane as an internal standard. Ultraviolet–Visible spectroscopy (UV–Vis) spectra were obtained on a UV-4802 spectrophotometer [UNICO (Shanghai) Instruments Co. Ltd, China]. Elemental analysis was performed using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

2.2. Synthesis of AHPEQB

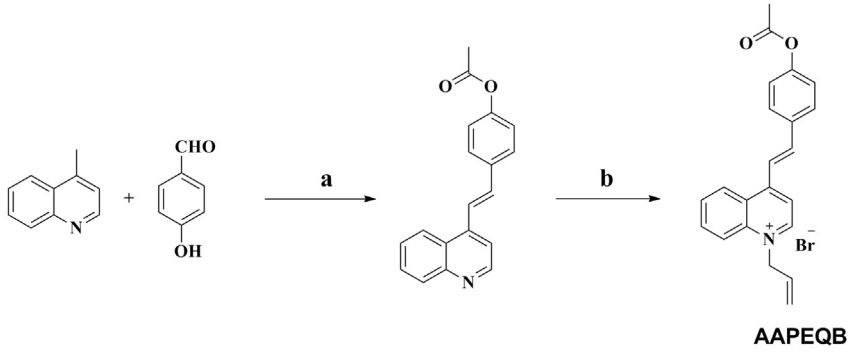
AHPEQB was synthesized via a two-step method (Fig. 1). The synthetic procedure is as follows: Under a N_2 atmosphere, 4-hydroxybenzaldehyde (8.54 g, 70.0 mmol) and 15.0 mL of acetic anhydride were added to a 50 mL flask. 4-Methylquinoline (10.02 g, 70.0 mol) was added dropwise to the mixture for 10 min 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 ^{1}H NMR and ^{13}C NMR (see Supporting information).

4-[2-(4-Hydroxyphenyl)ethenyl]quinoline (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% .^{1}H NMR (300 MHz, d_6-DMSO) δ (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, $J = 18.0$). ^{13}C NMR (75 MHz, d_6-DMSO) δ (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^- 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 ^{1}H NMR and ^{13}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.