



A colorimetric and fluorometric dual-modal chemosensor for cyanide in water

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ABSTRACT

We have developed a new class of benzothiazolium hemicyanine Cu(II) complex based colorimetric and fluorometric dual-modal chemosensor for the toxic cyanide anion in 100% water solution. This dual-modal response was achieved by the removal of Cu(II) ions from sensor complex in the presence of cyanide to recover the internal charge transfer (ICT) character of the hemicyanine dye. The novel sensor shows good sensitivity with μM -level detection limit, and displays high selectivity to cyanide in the presence of other common interference anions.

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1. Introduction

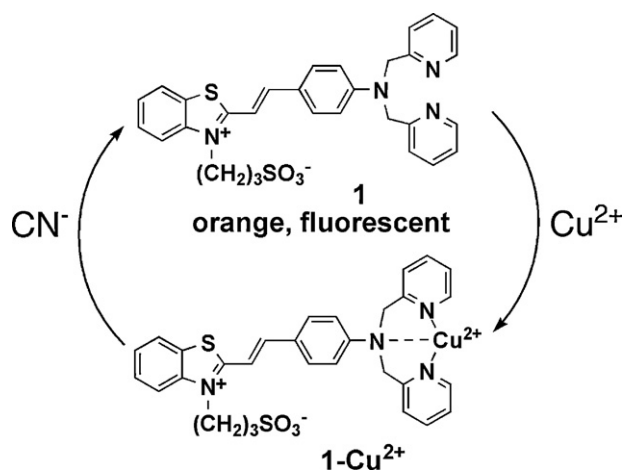
Cyanide is highly toxic and harmful to human health since cyanide binds to the ferric form of cytochrome-c and inhibits the mitochondrial electron-transport chain [1,2]. The World Health Organization has set an upper limit of $1.9 \mu\text{M}$ for cyanide in drinking water [3]. However, cyanide salts is widely used in the chemical industry (1.5 million tons/year) such as synthesis of nitriles, nylon and acrylic polymers, and in electroplating and gold mining [1]. Therefore, it is greatly desirable to develop sensitive, selective and highly convenient methods to monitor cyanide concentration from contaminant sources and drinking water. Although several chemical and physiochemical methods (chromatography, electrochemical analysis, etc.) have been used for the detection of cyanide, the applications of such examples have been restricted due to their tedious sample preparation, complicated measurement and low sensitivity [2]. The optical chemosensors for cyanide have attracted considerable attention in recent decades because of their simplicity, low cost, and rapid measurement [4–32]. For example, colorimetric or fluorometric sensors for detecting and measuring cyanide based on the traditional host–guest interaction have been reported [4–6]. However, these sensors show moderate selectivity and most of them only work in organic solvent due to high solvation

energy of the cyanide ion in aqueous environments. An alternative approach for detection of cyanide in aqueous solution is based on the chemodosimetric methodology [2,7–19]. The changes of photophysical properties are induced by the chemical reactions, most of which rely on the nucleophilic property of cyanide anion. Those methods which have successfully used to detect cyanide in aqueous solution, still have certain limitations such as a lack of reversibility, or the use of elevated reaction temperature.

The drawbacks mentioned above could be overcome by the chemosensors based on strong copper-cyanide affinity [20–25]. In such sensor systems, complexation of cyanide with copper(II) induces a change in the photophysical properties of the chromophores. Despite the increasing number of proof-of-principle molecular prototypes, only a few examples of cyanide detection systems worked in genuine aqueous environment with colorimetric and fluorescence turn-on dual-modal response. To date, there is still a demand for new colorimetric chemosensors that can achieve “naked-eye” detection in the visible wavelength region without the requirement of equipment. We aim at the design and synthesis of a novel colorimetric and fluorescence turn-on dual-modal chemosensor to selectively detect the presence of cyanide over a wide range of other anions in aqueous solution.

Herein we designed and synthesized benzothiazolium hemicyanine dye based sensor precursor **1**, in which di-(2-picolyl)amine (DPA) was chosen as a Cu^{2+} receptor and an electron-donating group (Scheme 1). The hemicyanine dyes have a typical D- π -A structure with an absorption band in the visible wavelength region

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Scheme 1. The conversion of **1** in the presence of Cu^{2+} and CN^- .

is of internal charge transfer (ICT) character. The color and fluorescence variations of our sensor system were achieved by the removal of Cu(II) ions in the presence of CN^- , which could strongly change the electron-donating ability of the electron donor in DPA and the photophysical properties of the chromophore (Scheme 1). The hemicyanine dye was selected as an optical reporting chromophore because of its large molar extinction coefficient, good fluorescence quantum yield, photostability and solubility in aqueous solutions [33,34]. Although the hemicyanine dyes have been widely used in nonlinear optical, photo voltage, and photoelectrical materials due to their rich photophysical properties, rare examples have been reported for the application of sensors [33–37].

2. Experimental

2.1. Instruments and reagents

Unless otherwise noted, materials were obtained from commercial suppliers and were used without further purification. ^1H NMR spectra were recorded on Advance Bruker 400M. Mass spectra were obtained using a Bruker Daltonik Microflex Mass Spectrometer. Fluorescence spectra were measured on a Hitachi 4500 Spectrophotometer. UV/vis spectra were recorded on a Shimadzu

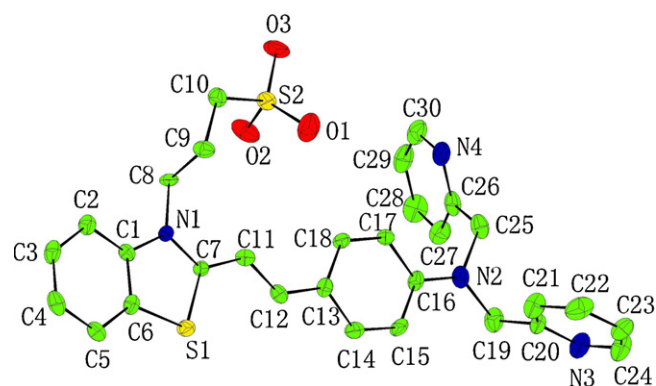


Fig. 1. Single crystal X-ray crystallography of compound **1**. H atoms and solvent molecule are omitted for clarity.

UV-1601PC Spectrophotometer. Crystallographic measurements were performed on a Rigaku MM007HF Saturn724+ diffractometer.

2.2. Synthesis

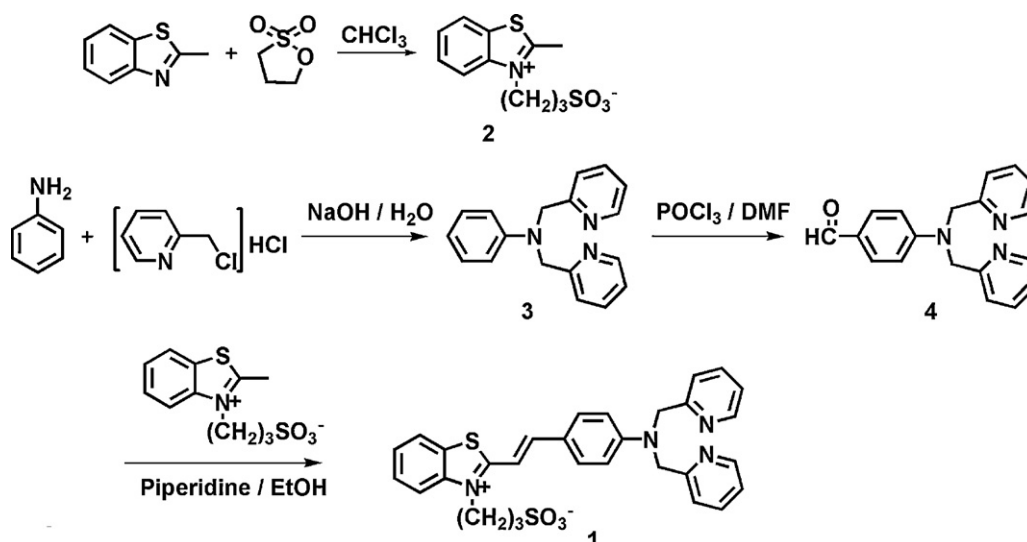
Our target molecule **1** was synthesized in good yields by condensation of aldehyde with benzothiazolium according to the procedure reported previously (Scheme 2) [34]. New compound **1** was well characterized by UV-vis, NMR and MS. The structure of **1** was further characterized with single crystal X-ray crystallography (Fig. 1).

2.2.1. Synthesis of compound 2

2-Methylbenzo[d]thiazole (2.7 g, 18 mmol), 1,3-propane sulfone (3.0 g, 24.6 mmol) were dissolved in CHCl_3 (20 mL). The resulting mixture was refluxed for 48 h. Upon cooling to r.t., the precipitate was collected and washed with CH_2Cl_2 and acetone to afford 2.45 g of product as a pale yellow solid. Yield: 50%. ^1H NMR (DMSO- d_6 , 400 MHz): δ 8.43 (t, 2H, $J=7.2$ Hz), 7.89 (t, 1H, $J=7.6$ Hz), 7.79 (t, 1H, $J=7.6$ Hz), 4.91 (t, 2H, $J=8.0$ Hz), 3.20 (s, 3H), 2.63 (t, 2H, $J=6.4$ Hz), 2.15 (quint, 2H, $J=7.6$ Hz).

2.2.2. Synthesis of compound 3

Aniline (0.46 g, 5 mmol), 2-(chloromethyl)pyridine hydrochloride (2.05 g, 12.5 mmol, 2.5 equiv.) and hexadecyl trimethyl ammonium bromide (20 mg) were dissolved in 20 mL NaOH



Scheme 2. Synthesis of compound **1**.

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