



Full paper/Mémoire

Naked-eye detection of cyanide ions in aqueous media based on an azo-azomethine chemosensor



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ABSTRACT

The optical and colorimetric properties of a new chemosensor 4-((2,4-dichlorophenyl) diazenyl)-2-(3-hydroxypropylimino)methylphenol (**L**) for cyanide ions were investigated by the naked-eye detection and UV–vis spectroscopy. This receptor reveals visual changes toward CN^- anions in aqueous media. No significant color changes were observed upon the addition of any other anions. The cyanide recognition properties of the receptor through proton-transfer were monitored by UV–vis titration and ^1H NMR spectroscopy. The binding constant (K_a) and stoichiometry of the formed host–guest complex were calculated by the Benesi–Hildebrand (B–H) plot and Job's plot method, respectively. The detection limit of the probe towards CN^- was $1.03 \times 10^{-6} \text{ mol L}^{-1}$, which is lower than the maximum value of cyanide ($1.9 \times 10^{-6} \text{ mol L}^{-1}$) permitted by the World Health Organization in drinking water. Thus, this chemosensor was sensitive enough to detect cyanide in aqueous solutions. ^1H NMR experiments were conducted to investigate the nature of interaction between the receptor and CN^- anions. Notably, the designed sensor can be applied for the rapid detection of cyanide anions in the basic pH range and also under physiological conditions, for practical purposes for a long duration. The sensing behavior of the receptor was further emphasized by computational studies. Quantum-chemical calculations and molecular studies via Density Functional Theory (DFT) were carried out to supplement the experimental results.

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1. Introduction

Cyanide is an extremely lethal anion that can affect several functions of human health, involving the visual, vascular, cardiac, central nervous, endocrine, and metabolic systems [1–10]. Cyanide could be absorbed through the skin, gastrointestinal tract and lungs, causing convulsion, vomiting, loss of consciousness, and eventual death [1,9]. Its toxicity arises from its ability to bind to the iron in cytochrome *c* oxidase, interfering with electron transport and resulting in hypoxia [10–15]. Despite its toxicity, cyanide is

generally employed in various chemical processes such as raw material for synthetic fibers, herbicides, resins, tanning, metallurgy and the gold extraction process [16–19]. Due to its serious toxicity and general utility, developments of reliable and efficient probes are quite necessary to monitor the presence of cyanide from contaminant sources. The most difficult fact in the anion sensing in aqueous environment is that water is a highly competitive solvent and interferes with the detection process of anions by intervening in the interaction between associates [20,21]. One of the greatest challenges for detecting cyanide arises from the interference of other anions, most especially, fluoride and acetate, working only in organic media [22,25]. The higher solvation energy of cyanide ions in aqueous media is known to negatively affect the hydrogen-bonded adduct formation between the receptor unit and the CN^-

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[26,27]. With these considerations in mind, it is evident that the development of highly selective and operative sensors, capable of detecting cyanide in aqueous media, is an important target for real-life applications. So far, most chemo-dosimeters for cyanide are based on hydrogen bonding [20,28,29], complexation to Lewis acids [30–32], time-gated fluorescence [33], quantum dots [34], Au nanoparticle [35], sensing on Al_2O_3 -based thin-film matrix [36] dyes equipped with a metal binding unit [21] or covalent bond formation [37–43]. Hence, receptors with chromogenic subunits are interesting as naked eye detection systems, which have been actively studied over the past 10 years because of their high sensitivity, ease of operation, rapid response rates and relatively low costs [14,43,44]. Based on our previous works [45–47], in this study, we present a chromogenic chemosensor **L** based on azo-azomethine receptors, for the rapid detection and colorimetric sensing of cyanide anions. Above all, it is worthy of note that sensor **L** could clearly detect cyanide from other interfering anions by color change from yellow to reddish orange through naked-eye detection in aqueous media. To the best of our knowledge, this is the first unsymmetrical azo-azomethine receptor derived from 2-amino-1-propanol for the qualitative and quantitative detection of toxic cyanide anions in water and other samples. Colorimetric receptor **L** possessing two phenolic and alcoholic OH binds to cyanide ions by involving azomethine cyanide reaction sites and phenolic OH via hydrogen bonding interaction. To gain a deeper insight into the mechanism and structure in addition to the spectral aspects of the complex, quantum-chemical calculations were performed using Density Functional Theory (DFT) to supplement the experimental results.

2. Experimental

2.1. Materials and equipment

All chemicals were purchased from Sigma–Aldrich and Merck and were used without further purification. Electronic spectral measurements were performed utilizing an Optizen 3220 UV spectrophotometer in the range of 200–900 nm at room temperature. ^1H NMR spectra were recorded on a Bruker AV 300 MHz spectrometer and chemical shifts were recorded in ppm. The sensor **L** was synthesized based on our previous reported procedure [48]. Fourier transform infrared (FT-IR) spectra were recorded as pressed KBr discs utilizing a Unicom Galaxy Series FT-IR 5000 spectrophotometer within the region of 400–4000 cm^{-1} .

2.2. Results and discussion

2.2.1. Colorimetric and spectral response of **L** toward CN^-

With seldom exceptions [20,49,50], the sensing of cyanide was limited to only tetrabutylammonium (TBA) as the counter ion within pure organic media since the solvation of KCN/NaCN in aqueous/mixed aqueous systems generally leads to sensing silence as a result of competitive and interfering problems of solubility in water. From this point, at first, the sensing behavior of the receptor **L** toward

various anions such as F^- , Cl^- , Br^- , AcO^- , H_2PO_4^- , HSO_4^- , ClO_4^- , N_3^- , NO_2^- , SCN^- and CN^- , as their inorganic sodium salts, was probed qualitatively by naked-eye colorimetric examination and then, absorption spectral studies were conducted on sensor **L** ($5 \times 10^{-5} \text{ mol L}^{-1}$) in $\text{DMSO}/\text{H}_2\text{O}$ (95:5, v/v) upon the addition of 10 equivalent of typical anions in water in order to survey the selectivity of receptor **L** as a colorimetric sensor. As illustrated in Fig. 1, sensor **L** was yellow in color and displayed a broad band with a maximum absorption wavelength, centered at about 400 nm in the UV–vis spectrum, corresponding to $\pi \rightarrow \pi^*$ transition of azo and azo-methane chromophores and intra-molecular charge transfer (ICT) transition [51–53]. Upon the addition of different anions to the solution of **L**, only CN^- caused a remarkable color change from yellow to reddish orange instantly (Fig. 1a) and demonstrated a bathochromic shift (from 400 to 505 nm) in absorption spectra (Fig. 1b), while other anions demonstrated almost no change in color and UV–vis spectra under identical conditions.

In order to inspect the further detailed response of the designed receptor **L** toward CN^- ions, we conducted UV–vis spectroscopic titrations by adding 10 equivalents of cyanide anions in water into the diluted solution of **L** ($2 \times 10^{-5} \text{ mol L}^{-1}$) in $\text{DMSO}/\text{H}_2\text{O}$ (95:5). As shown in Fig. 2, with incremental addition of cyanide ions, the absorption band at 400 nm was gradually reduced and a new band centered at 505 nm progressively appeared with an obvious isosbestic point at 460 nm, indicating the formation of new species. The extinction coefficient of the chemosensor **L** at 400 nm is $24,250 \text{ M}^{-1} \text{ cm}^{-1}$ and $10,338 \text{ M}^{-1} \text{ cm}^{-1}$ at 505 nm for the $\text{L}-\text{CN}^-$ adduct. Consequentially, these distinct changes can be attributed to the charge transfer interactions due to the complexation between cyanide ions and reactant sites of **L** at high concentrations. The conclusive stoichiometric ratio between **L** and CN^- was inferred to be 1:2 with the aid of Job's plot

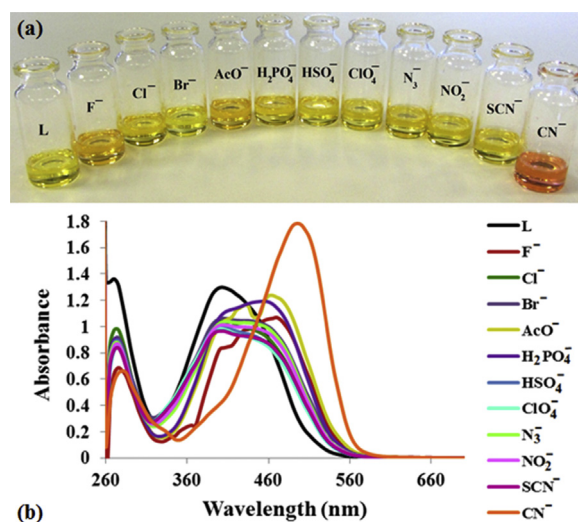


Fig. 1. Color changes (a) and UV–vis absorption spectra (b) of receptor **L** ($5 \times 10^{-5} \text{ mol L}^{-1}$) in $\text{DMSO}/\text{H}_2\text{O}$ (95:5) in the presence of 10 equiv. of different anions.

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