



Visual & reversible sensing of cyanide in real samples by an effective ratiometric colorimetric probe & logic gate application



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HIGHLIGHTS

- Novel multidentate probe 3 was synthesized and characterized.
- Ratiometric & colorimetric sensing of CN^- ion by ICT phenomena.
- UV–vis and NMR studies were performed.
- A CGE for CN^- ion based on probe 3 as ionophore was prepared.
- Real sample analysis and logic gate applications.

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ABSTRACT

A novel anion probe 3 (2,4-di-*tert*-butyl-6-((2,4-dinitrophenyl) hydrazono) methyl) phenol) has been unveiled as an effective ratiometric and colorimetric sensor for selective and rapid detection of cyanide. The sensing behavior was demonstrated by UV–vis experiments and NMR studies. This sensory system exhibited prominent visual color change toward cyanide ion over other testing anions in DMSO (90%) solvent, with a 1:1 binding stoichiometry and a detection limit down to $3.6 \times 10^{-8} \text{ mol L}^{-1}$. Sensor reveals specific anti-jamming activity and reversible in the presence of Cu^{2+} ions. This concept has been applied to design a logic gate circuit at the molecular level. Further we developed coated graphite electrode using probe 3 as ionophore and studied the performance characteristics of electrode. The sensitivity of ratiometric-based colorimetric assay is below the $1.9 \mu\text{M}$, accepted by the World Health Organization as the highest permissible cyanide concentration in drinking water. So it can be applied for both quantitative determination and qualitative supervising of cyanide concentrations in real samples.

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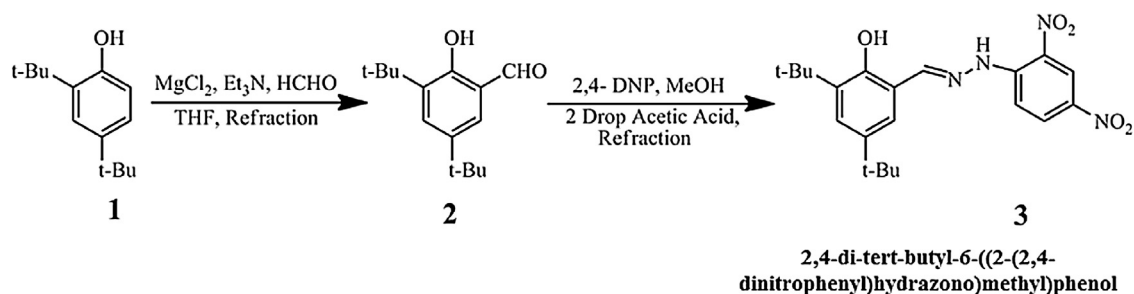
1. Introduction

Cyanide is extremely hazardous and one of the most toxic material to the environment and human health [1,2]. It directly affects all aerobic organisms by breaking up the electron transport chain in the mitochondria membrane and prevents respiration [3]. Chronic exposure to cyanide leads to many diseases including the nervous system [3], cardiac, vascular, endocrine, visual and metabolic systems [4,5]. Repeated exposure to low concentrations of cyanides over a long period causes nausea, muscle cramps, weakness, memory deficits loss of appetite and paralysis of the arms and legs [6]. Cyanide ion is an extremely toxic and fast-acting poison with a lethal concentration of 23–26 mM in human blood and a lethal dose of 0.5–3.5 mg/kg in human body [7]. According to the World

Health Organization, cyanide concentrations less than $1.9 \mu\text{M}$ are acceptable in drinking water. Nevertheless, cyanide compounds are still widely used in various fields such as synthetic fibres, resins, electroplating, metallurgy [8], herbicide, chelating agents for water treatment and pharmaceuticals, the gold-extraction process and X-ray film recovery trades [9]. Unfortunately, accidental leaching of cyanide into the environment happens and raises a number of environmental concerns specifically in terms of widespread human exposure. In nature cyanide occurs in many food materials like; cassava, bamboo shoots, sorghum, and bitter almonds [10]. Certain fungi, algae, and bacteria also act as a potential contamination source of cyanide particularly in drinking water sources. For these reasons, an efficient sensor for cyanide to monitor cyanide concentration from contaminate are highly desirable.

Various methods have been developed for the determination of cyanide ion at small concentration ranges, using different experimental protocols and detection techniques, such as ion-selective electrode [11], amperometric [12], chromatography [13],

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Scheme 1. Synthetic route to hydrazine based probe (3), 2,4-di-tert-butyl-6-((2-(2,4-dinitrophenyl) hydrazono) methyl) phenol.

fluorimetry, spectrophotometry [14,15], surface enhanced Raman scattering (SERS) method [16], atomic absorption spectroscopy, and flow injection analysis technique [17] etc. However, these methods are time consuming; require complex pre-processing, relatively expensive equipment and large infrastructure back up, special operators, and long detection times. Selective analytical methodology, which is easily operated and involve harmless reagents, cost effective equipment, have therefore been proposed as alternative to these standard methods. Colorimetric sensing, which allows cyanide detection by the naked eye without any expensive equipment, has appealed great attention in recent years [18–20]. To increase the sensitivity and selectivity, ratiometric measurements are used, which involve the observation of varies in the ratio of the intensities of the absorption at two wavelengths [21,22]. These ratiometric measurements provide a built-in correction for environmental factors and enhance the dynamic range of absorption measurements. Hence, sensors displaying both ratiometric and colorimetric responses to cyanide are able to offer efficient quantitative information thru their internal calibration of dual absorption and simultaneously exclusive response toward cyanide ion via the color alteration.

In this connection we have designed and synthesized a novel ratiometric colorimetric sensor toward cyanide by using internal charge charge transfer (ICT) as a signalling mechanism for the naked eye detection of cyanide ion in DMSO:H₂O (90%) with high selectivity. This sensor reacts with cyanide in a 1:1 stoichiometric manner, a process which causes a large enhancement in absorption intensity and a marked color changes from yellow to magenta in DMSO–H₂O (90%) at room temperature.

2. Experimental

2.1. Materials and instrumentation

All reagents practised for the synthesis work were bought from Sigma–Aldrich chemical. These reagents were stacked away under vacuum condition and were utilized without further refining. All the anions were taken in the form of sodium salts. DMSO used for the preparation of stalk solutions of different concentrations were dried by the help of drying agent and distilled under reduced pressure.

IR spectra were taken with PerkinElmer FT-IR 1000 spectrophotometer as films between KBr. The UV–vis titration experiments were executed on Specord S600 PC single beam spectrophotometer with quartz cuvette featuring path length 1 cm. ¹H NMR spectra along with titration experiments were performed on a Bruker DRX 500 MHz spectrophotometer by applying tetramethylsilane (TMS) as an internal standard.

2.2. Synthesis of 2,4-di-tert-butyl-6-((2(2,4-dinitrophenyl)hydrazono) methyl) phenol and characterisation

As shown in Scheme 1 5 mmol solution of 3,5-di-tert-butyl-2-hydroxybenzaldehyde 2, [23] (0.99 g) and 5 mmol of 2,4-DNP (1.17 g) in methanol was refluxed for 3 h in presence of catalytic amount of glacial acetic acid. After cooling, the red colored precipitate was obtained, washed with hot methanol several times, and

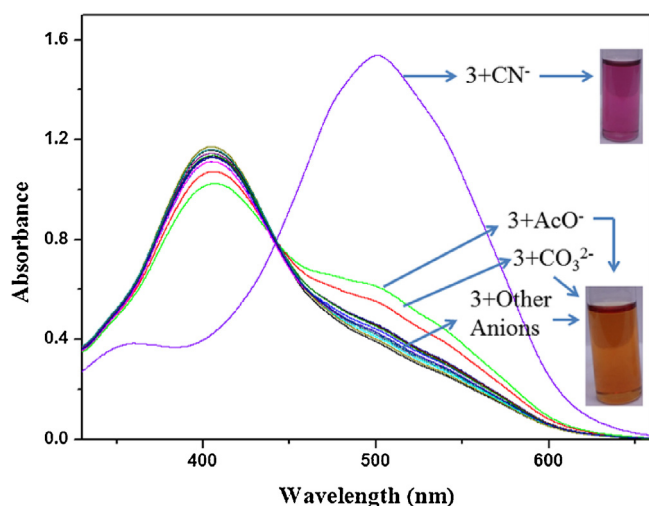


Fig. 1. The absorption spectra of probe 3 ($5.0 \times 10^{-5} \text{ mol L}^{-1}$) after addition of 10 equivalents of different anions in DMSO (90%) solution and corresponding color changes.

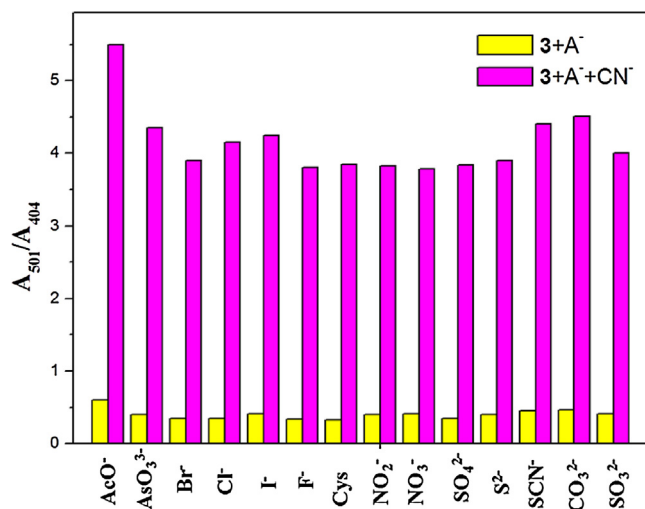


Fig. 2. Competition graph; showing selectivity of 3, yellow bar indicates absorption intensity ratio of probe 3 in the presence of other competitive anions, magenta bar indicate absorption intensity ratio of ratio 3 & CN⁻ in the presence of other competitive anions. (For interpretation of the references to color in this figure legend, the reader is referred to the web version of this article.)

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