



Highly reactive (<1 min) ratiometric probe for selective 'naked-eye' detection of cyanide in aqueous media

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ARTICLE INFO

Article history:

Received 15 September 2012

Revised 19 December 2012

Accepted 22 December 2012

Available online 5 January 2013

Keywords:

Sensor

Cyanide

Ratiometric

Naked-eye detection

Triphenylamine

Benzothiazole

ABSTRACT

We have designed and synthesized a triphenyl aminebenzothiazole coupled receptor (TBH) that exhibits a selective, sensitive, colorimetric, and ratiometric rapid response toward cyanide anion in aqueous media. The sensing event is explained by spectroscopy along with DFT calculation and CV diagram. Sensor displays a very fast response (<1 min) toward cyanide at room temperature with a 'naked-eye' change over F^- and AcO^- in aqueous media.

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The development of optical chemosensors for anions of biological, environmental, and clinical concerns is currently under active investigation.¹ Among the toxic anions acting as severe environmental pollutants and consequently having adverse health effects, cyanide is one of the most-concerning anions. It can directly lead to the death of human beings² as well as aquatic life,³ even at low concentration, by binding to 3 cytochromes, inhibiting the electron transport chain in mitochondria and by depressing the central nervous system.⁴ Due to this, it is lethal to human at concentrations of 0.5–3.5 mg/kg of body weight.⁵ Despite its toxicity, its application in various areas as raw materials for synthetic fibers, resins, herbicides, and the gold extraction process is inevitable, which release cyanide into the environment as a toxic contaminant^{6,7} and it can lead to serious contamination of the ground and/or drinking water.⁸ Thus, there is a need for an efficient sensing system for cyanide to monitor cyanide concentration from contaminant sources.

In past few years, a variety of colorimetric and fluorescent probes for cyanide have been reported. One of the common approaches is utilizing cyanide complexes or addition with Zn^{2+} -porphyrin,^{9a} Ru^{2+} -pyridine,^{9b} boronic acid derivatives,^{9c} and CdSe quantum dots.^{9d} Other strategies were also involved, such as hydrogen bonding interactions,¹⁰ copper–cyanide affinity,¹¹ and

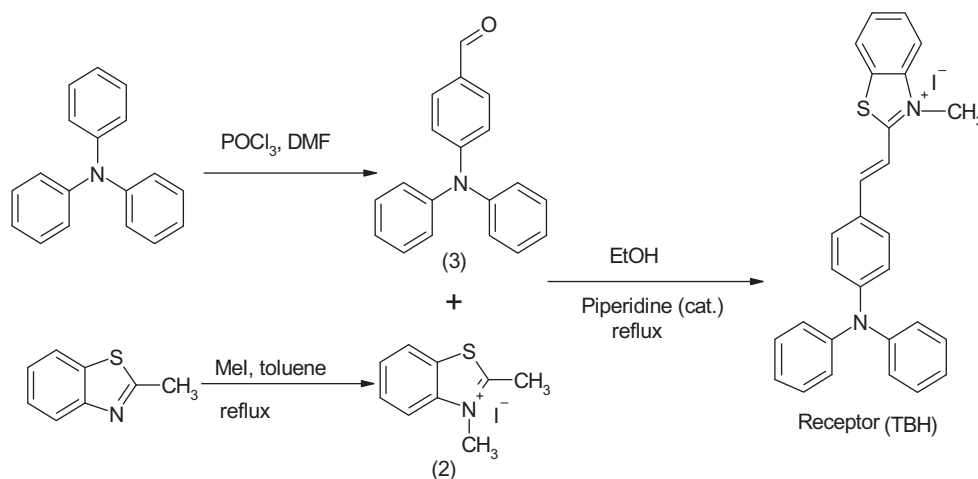
single-electron transfer reaction.¹² Recently, nucleophilic addition of cyanide has also been adopted for sensing cyanide. Based on this idea, nucleophilic addition of cyanide to oxazine, pyrylium, squarane, trifluoroacetophenone, acyltriazene, acridinium, salicylaldehyde, and carboxamide has been reported.¹³

In spite of these developments, there are still relatively few examples of selective and sensitive probe for cyanide anion especially those that display limited inference in the presence of other anions particularly with F^- , AcO^- , and $H_2PO_4^-$. Moreover, the receptors based on these approaches have very complex structures. This requires multiple step synthesis with relatively low overall yields. As a result, developed chemosensors cannot be prepared on a large scale. Furthermore, most of the sensors/receptors have limitations in analytical and bio analytical applications due to poor sensing of cyanide in aqueous media and most of the chemo dosimeter type sensors for CN^- are time consuming, that is, the nucleophilic attack of cyanide to the sensor is really slow. Therefore, it is highly desirable to develop sensitive, selective, and easy-to-prepare chemical sensor for cyanide even in water medium with a rapid response.

With these considerations in mind, we report here the design and synthesis of a simple receptor, triphenylamine benzothiazole hybrid (TBH) that exhibits a selective, sensitive, colorimetric, and ratiometric response toward cyanide anion in aqueous acetonitrile solution. Importantly, TBH displays a very fast response (<1 min) to cyanide at room temperature, and 'naked-eye' detection is possible in the presence of only 1 equiv of cyanide.

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Scheme 1. Synthesis of the receptor (TBH).

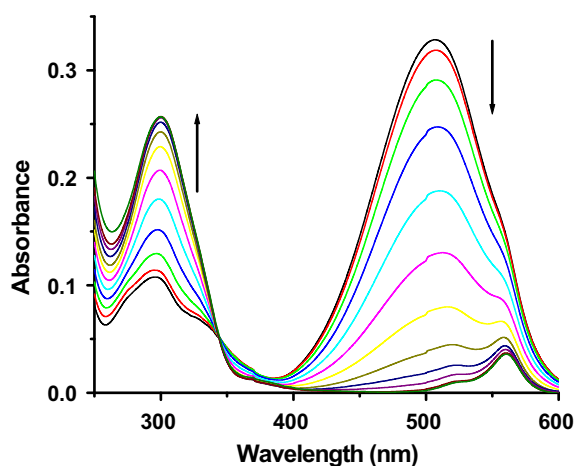


Figure 1. UV-vis absorption titration spectra of TBH ($c = 2.0 \times 10^{-6}$ M) in the presence of CN^- ($c = 2.0 \times 10^{-5}$ M) at pH 7.1 in $\text{CH}_3\text{CN}/\text{H}_2\text{O} = 1:1$.

The synthesis of the sensor is shown in Scheme 1. The precursor mono aldehyde of triphenylamine (**3**) is prepared from the corresponding amine maintaining the Vilsmeier–Haack condition according to the literature procedure.¹⁴ When benzothiazole is treated with MeI in toluene as a solvent corresponding salt (**2**) is obtained. In the presence of piperidine, **2** and **3** are coupled in absolute ethanol to form the desired receptor (i.e., TBH) in 90% yield. The purity of TBH was confirmed by ¹H NMR, ¹³C NMR, and ESI-MS spectra (Supplementary data).

The behavior of TBH toward a variety of anions was explored with UV-vis absorption spectrometry. The various anions tested are AcO^- , Cl^- , Br^- , I^- , F^- , and PhO^- as their tetra butyl salts; SH^- , H_2PO_4^- , PO_4^{3-} , S^{2-} , N_3^- , $\text{P}_2\text{O}_7^{4-}$, and SCN^- as their sodium salts;

CN^- and ADP as their potassium salts in solution. In UV-vis absorption spectrometry, only CN^- was found to perturb the electronic behavior of TBH to a significant extent. The absorption spectrum of TBH (2×10^{-6} M, in $\text{CH}_3\text{CN}/\text{H}_2\text{O}$ as 1:1) is characterized by an intense absorption band (a twin band) centered at 507 nm attributed to intramolecular charge-transfer (ICT) transition, in combination with the less intense $\pi \rightarrow \pi^*$ transitions at 300 nm. The ICT band is responsible for the reddish pink color of TBH. Upon incremental addition of CN^- solution (2×10^{-5} M, in HEPES solution), a complete reduction in the intensity of 507 nm bands accompanied by ratiometric (isosbestic point at 343 nm) increase of intensity at 300 nm was observed which achieved saturation after the addition of 1 equiv solution of CN^- ions (Figs. 1 and 3). The visual color change is shown in Figure 2. In emission spectroscopy there is a negligible change observed in 440 nm range upon addition of 1 equiv cyanide ion (Supplementary data).

This indicated the minimum required amount of CN^- which was used at this point of saturation for the formation of the visual colorless solution. The large hypsochromic shift in the ICT band resulted in the observed complete bleaching of the original reddish pink color of the receptor.

We envisaged that the observed bleaching of the color in the presence of CN^- may arise from the nucleophilic addition reaction of CN^- at the benzothiazole ring carbon adjacent to the quaternary nitrogen atom to give a neutral structure and thus rupturing the electronic delocalization with the concurrent disappearance of the low energy band, resulting in the formation of colorless species (Scheme 2).

This was confirmed by ¹H NMR spectra which show the δ value downfield shift (0.61 ppm) from 1.45 to 2.06 ppm of methyl protons adjacent to quaternary 'N' to tertiary 'N' (Supplementary data). From the IR data the phenomenon is also well explained by the appearance of a new peak at 2250 cm^{-1} due to the insertion of the cyano group in TBH (Supplementary data). The mass spec-

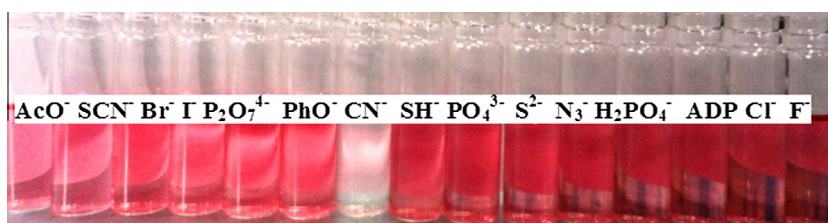


Figure 2. Visual changes of TBH ($c = 2.0 \times 10^{-6}$ M) with addition of 1.0 equiv of each anion ($c = 2.0 \times 10^{-5}$ M) at pH 7.1 in $\text{CH}_3\text{CN}/\text{H}_2\text{O}$ (1:1, V/V).

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