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Simple naked-eye ratiometric and colorimetric receptor for anions based on azo dye featuring with benzimidazole unit

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ABSTRACT

A simple, tailor made receptor **2** based on azo dye featuring with benzimidazole unit with hybrid –OH and –NH binding sites was synthesized and characterized. The addition of CN^- , AcO^- , F^- , and H_2PO_4^- in acetonitrile solution of **2** resulted in a large bathochromic shift from 315 nm to 470 nm allowing naked eye color change from colorless to orange. Anion sensing characteristics were determined using visual inspection, UV-vis and ^1H NMR spectroscopy pointing toward the improved chromogenic ability after introduction of –N=N– group in the azo dye **2**. The mechanism of anion binding with receptor **2** showed 1:2 (L/Anion) and the association constants were found in the order of $\text{AcO}^- > \text{CN}^- > \text{F}^- > \text{H}_2\text{PO}_4^-$.

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Introduction

The development of receptors which undergo a color change on addition of an analyte has attained great significance in the area of supramolecular chemistry.¹ The colorimetric-based sensing has shown unique merit, as it provides naked-eye detection of the analyte without resorting to any expensive equipment.² In general, the design of such receptors is based on the receptor-chromophore general binomial, which involves the binding of a specific analyte with receptor sites and a chromophore responsible for translating the binding of receptor–analyte into an optical signal.³ In colorimetric receptors, due to its interaction with the analyte, bathochromic or hypsochromic shift of absorption spectra or visual color change is affected by the respective increase or decrease in electron densities on the chromophore moiety.⁴

Owing to the ubiquity of anions and their importance as agricultural fertilizers and industrial raw materials, the development of anion sensing receptors received considerable attention.⁵ In recent years, the development of chromogenic anion sensors is mainly based on the anion induced polarization/deprotonation (in extreme cases) of OH in case of appropriately substituted phenols and NH in case of appropriately substituted anilides and aryl ureas.^{6–8} Anions particularly fluoride, cyanide, and phosphate are

not only released by industries but are also the degradation products (hydrolysis) of chemical warfare agents such as sarin, soman, and tabun, making them harmful to the environment as well as to human health.⁹ Among various anions, cyanide is an extremely toxic detrimental anion causing poisoning in biology; environment, and even relatively small amounts of this species are lethal to humans.¹⁰ Moreover, raw materials for synthetic fibers, resins, herbicides, and the gold-extraction process releases cyanide into the environment as a toxic contaminant. So, the colorimetric sensors for determination of anions are big challenges for investigators and they attract much interest.

It is well known that azo colorants are the largest chemical class of industrial colorants. They represent a robust group of synthetic dyes, which cover the full range of shades of colors. Their ease of preparation and economy of the reaction resulted in a large number of dyes.¹¹ Azo dyes possessing an aromatic heterocyclic moiety increased the chromophoric strength and thus, have been reviewed comprehensively.¹² Benzimidazole and its derivatives have been studied in anion and cation recognition systems that display color changes or fluorescence quenching or enhancement upon binding.¹³

This paper describes the design and synthesis of a new and simple anion receptor 2-(1-*H*-benzimidazol-2-yl)-4-(pyridine-3-ylazo)-phenol (**2**) containing both azo dye and benzimidazole and photophysical study of its anion recognition behaviors. In addition, the sensing processes can be realized by the ‘naked eye’ determination as it has a remarkable color response.

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Results and discussions

Synthesis of receptor 2

The preparation of receptor **2** based on the azo dye of benzimidazole **1** was carried out by diazo-coupling reaction as shown in Scheme 1. The chemical structure of the newly synthesized chemosensor was confirmed by ^1H NMR, ^{13}C NMR, and mass spectral data.

Sensing properties of receptor 1

To study the role of azo functionality in receptor **2**, the sensing abilities of **1** were primarily investigated by adding various anions such as CN^- , F^- , Cl^- , Br^- , I^- , AcO^- , H_2PO_4^- , and HSO_4^- (tetrabutyl ammonium was used as a counter anion) to its CH_3CN solution ($10\ \mu\text{M}$). The addition of 5 equiv of these anions did not cause any change in the absorption spectrum; however, further addition of these anions up to 50 equiv resulted in the emergence of a very weak charge transfer band at 374 nm with CN^- and F^- ions (Fig. 1), but the spectral changes were too small to calculate the corresponding association constants. Earlier results show that the addition of 5 equiv of F^- ions to a solution of receptor **1** in DMSO caused only a small bathochromic shift of 11 nm. Whereas, other anions did not induce any significant changes in the absorption spectra.¹⁴ However, by changing the polarity of the solvent from DMSO to CH_3CN , the small bathochromic shift observed with the addition of 5 equiv of F^- ion gets diminished and requires higher equivalents of anions to cause only a small red-shift.

Colorimetric signaling of (2)

As the presence of the $-\text{N}=\text{N}-$ group improves the chromogenic ability of the chemosensors, therefore, after introducing the azo functionality in the receptor **2**, both the colorimetric and absorption changes were greatly enhanced in CH_3CN itself. In naked-eye experiment (Fig. 2), receptor **2** ($10\ \mu\text{M}$) responded with a dramatic color change from colorless to dark yellow with the addition of 50 equiv of CN^- , F^- , AcO^- , and H_2PO_4^- , which indicates the formation of host-guest complex between these anions and **2**. However, no obvious color change was observed in the case of Cl^- , Br^- , I^- , and HSO_4^- ions, even when these anions were added in

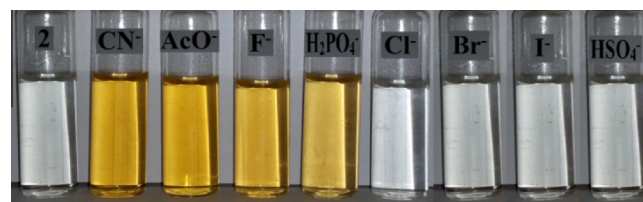


Figure 2. Naked-eye images of **1** in CH_3CN upon the addition of various anions (100 equiv).

excess, presumably due to weaker and insignificant interactions with the receptor.

UV-vis spectral studies

The qualitative anion sensing behavior of **2** was determined by recording the absorption spectra. In the UV-vis spectra of **2** ($10\ \mu\text{M}$) in acetonitrile media, the receptor peak is characterized by the appearance of a band centered at 315 nm with a shoulder near 365 nm. Upon interaction with CN^- , F^- , AcO^- , and H_2PO_4^- ions, a new intramolecular charge transfer band has been observed at 470 nm. UV-vis titrations were next carried out with increasing concentrations of CN^- , F^- , AcO^- , and H_2PO_4^- anions. Upon addition of CN^- ions to a solution of receptor **2** ($10\ \mu\text{M}$) in CH_3CN , a new band starts emerging at 470 nm with the addition of only 0.2 equiv of CN^- ions. However, after adding 3 equiv of CN^- ions, a sharp and gradual increase in intensity of the new band has been observed along with gradual decrease in absorbance of the 315 nm band (Fig. 3).

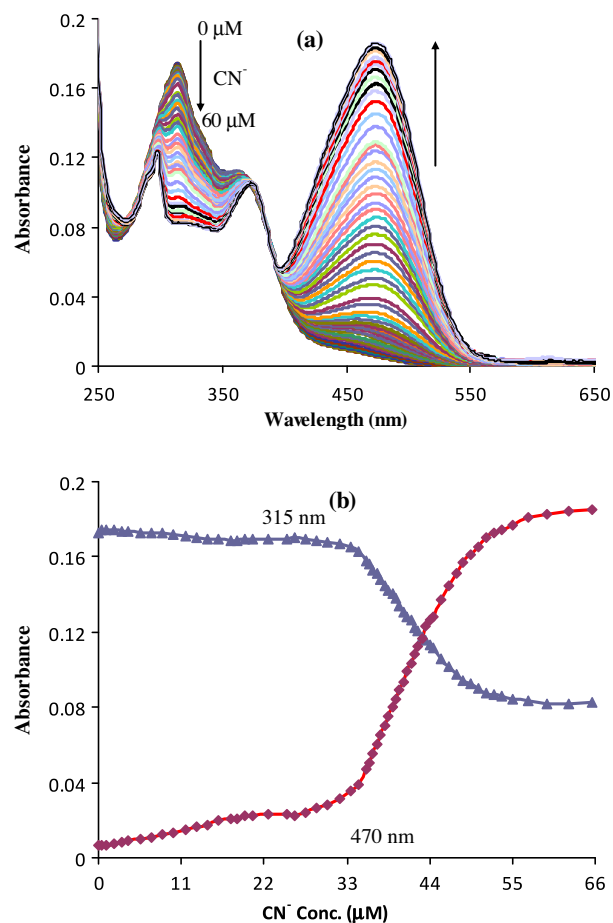
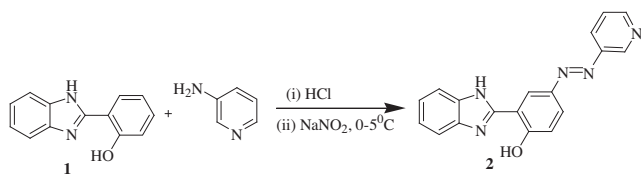


Figure 3. Evolution of the UV-vis spectrum of receptor **2** ($10\ \mu\text{M}$ in CH_3CN) during the titration of the CN^- ion; (b) plot of absorbances at 315 and 470 nm vs the concentration of CN^- added.



Scheme 1. Synthetic procedure for receptor **2**.

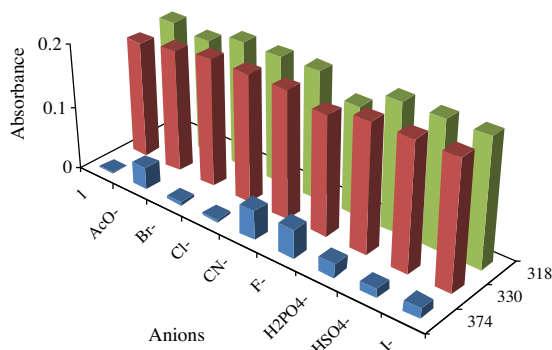


Figure 1. UV-vis absorbance of **1** ($10\ \mu\text{M}$) in the presence of 100 equiv of anions in CH_3CN .

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