

A Naked-Eye Colorimetric Receptor for Anions Based on Nitro Group Featuring with Benzimidazole Unit

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A novel receptor based on nitro group featuring with benzimidazole unit (**S2**) was successfully synthesized and applied to the anion (CN^- , F^- and H_2PO_4^-) recognition. The **S2** changed its colour for light yellow to dark yellow on addition of the anions in DMSO solvent. The LOD and K_{ass} values determined by UV-visible titration was $2.8 \times 10^{-6} \text{ M}$ and $1.2 (\pm 0.25) \times 10^6 \text{ M}^{-1}$ for CN^- ion; $1.14 \times 10^{-6} \text{ M}$ and $2.5 (\pm 0.25) \times 10^6 \text{ M}^{-1}$ for F^- ion; and $1.23 \times 10^{-5} \text{ M}$ and $6.25 (\pm 0.177) \times 10^6 \text{ M}^{-1}$ for H_2PO_4^- ion, respectively.

Keywords: Colorimetric, Nitro group, Benzimidazole.

INTRODUCTION

The development of sensors and receptors capable of binding and sensing for anions selectively has received a great attention from chemist due to the key roles played by anions during the chemical, biological and environmental processes [1]. The anion can be recognized either by H-bonding or by the deprotonation of proton in the receptor in organic solvent [2]. Especially, the colorimetric and ratiometric chemosensors appear to be particularly attractive due to their simplicity, high sensitivity and high selectivity. Colorimetric sensing possesses huge advantages in practical application as it can rapidly provide qualitative information about the analyte without any expensive instrument [3,4].

Among the chemosensors for the detections of anions, the colorimetric chemosensor have attracted considerable attention since they provide immediate qualitative signal, which allows direct naked-eye detection of anion because of a specific colour change of solution upon anion complexation [5]. Binding of anions such as AcO^- , F^- and H_2PO_4^- results in a note worthy change in the visible region of spectrum (approximately 100 nm red shift), which can be detected by the 'naked-eye' [6].

A large numbers of anion receptors containing NO_2^- subunits have been designed, synthesized and tested for anion

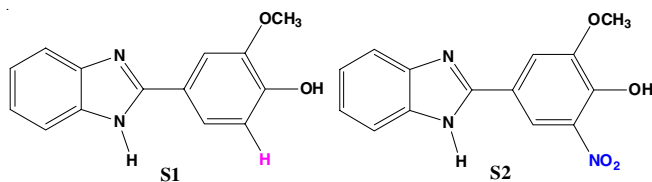
recognition and sensing during the past decades [7]. A nitro group functionality was introduced into benzimidazole moieties, which were anticipated to be responsible for colour changes and also to increase hydrogen bond donor tendency. Incorporating the nitro group resulted shifting the wavelength absorbance of sensor, facilitating the occurrence of deprotonation and resulted strong colour of sensor [5].

In the previous study, we designed a chemosensors compound derived from benzimidazole (**S1**) [8] which are active as fluorescence receptor and selectively to detect CN^- ion. Sensor **S1** are synthesized from vanillin by keeping OH group as a binding site. In this project, we design a new chemosensor compound by adding with nitro group at the fifth position on vanillin ring structure, to produce the 5-nitro vanillin. We made a new chemosensor (**S2**) which are derived from benzimidazole which are bearing by nitro group (Fig. 1).

The nitro group was introduced on **S2** to affects the change of LOD value, K_{ass} value and colour mode of the original compound (**S1**).

EXPERIMENTAL

Melting point was measured using a Electrothermal-9100, the IR spectra measured using a FTIR Shimadzu Prestige-21, Mass spectra were taken by gas chromatograph-mass spectrometer (Shimadzu-QP2010S), ^1H and ^{13}C NMR were measured

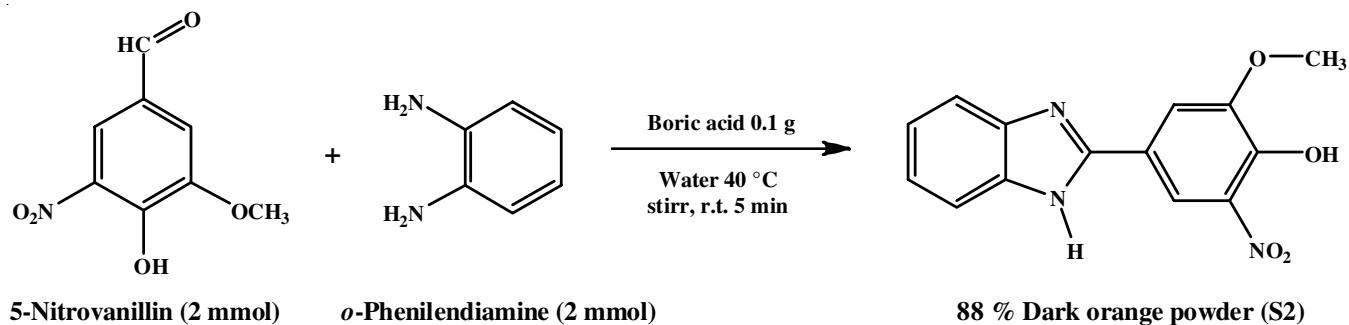
Fig. 1. Structures of **S1** and **S2** compounds

using a JOEL JNM ECA-500 MHz, fluorescent were measured using a Spectro Fluorophotometer Shimadzu RF-6000.

All the reagents obtained commercially were used without further purification: DMSO, DCM, water, ethanol. The material synthesis: vanillin, *o*-phenyldiamine, boric acid. The anion were added in the form of sodium cyanide, sodium fluoride and sodium dihydrogen phosphate. All the materials for synthesis is p.a quality Merck.

Method: The method on synthesis of **S2** is applied by Karimi's method [9]. This synthesis used 5-nitrovanillin as a carbonyl sources, using hot water (40 °C) to dilute the reactans and the synthesis was conducted at room temperature. A 5-nitrovanillin (0.32 g), *o*-phenyldiamine (0.21 g) and boric acid (0.1 g), were mixed in 5 mL of hot water. A mixture was stirred directly at room temperature for 5 min (the progress of reaction was monitored by TLC). After completion of reaction, the obtained solid was collected by filtration and purified by recrystallization from boiled ethanol (Fig. 2). Colour dark orange powder, 88 % yield, m.p. 207.7-208.5 °C; FTIR (KBr, $\nu_{\max}$, cm^{-1}): 3441.01 O-H from phenol N-H, 2931.8 C-H methyl, 2337.72 C=N imidazole, 1612.49 C=C aromatics (3093.82 C-H sp^2), 1543.05 NO_2 , 1280.73 cm^{-1} C-O-C ether; ^1H NMR (500 MHz, CDCl_3): 8.307 (s, 1H), 8.021 (s, 1H), 7.764 (d, 1H), 7.554 (m, 1H), 7.074 (s, 2H), 5.573 (s, 2H), 3.869 (s, 3H); ^{13}C NMR (500 MHz, CDCl_3): 56.778, 110.991, 113.487, 114.572, 116.856, 119.314, 123.115, 127.588, 137.157, 141.986, 150.02, 151.579; MS (EI) : m/z 285 (M^+ , 75 %), 122 (M^+ , 100 %).

The 5-nitrovanillin compound was synthesized from Vanillin by Yadav method [10] with some modifications. A vanillin (0.07 mol) was dissolved in 55 mL of dichloromethane, squirted by 12 mL of HNO_3 , then stirred for 20 min at room temperature, added 25 mL of ice water then leave it for 2 h, the solid formed was recrystallized with ethanol. The melting point of synthesized product was determined and characterized by FTIR instrument. The synthesized 5-nitrovanillin is light yellow powder, 64 % yield, m.p 175-177 °C (reference, 176 °C); FTIR (KBr, $\nu_{\max}$, cm^{-1}): 1560.77 due to NO_2 group.

Fig. 2. Scheme of synthesis the sensor compound (**S2**)

RESULTS AND DISCUSSION

The **S1** compound in DMSO solvent shows a colourless solution, absorbed at $\lambda_{\max} = 295$ nm. Addition of anions to the **S1** solution did not any colour change and observation under 366 nm UV lamp shows a fluorescence response only toward CN^- ion (selective). The inclusion of nitro group into **S2** indicated a change in properties and response to anions. The **S2** in DMSO solvent is a yellow colour, its means the **S2** is a colorimetric responsive response and observation under 366 nm UV lamp shows non-fluorescence response. The **S2** absorbed at $\lambda_{\max} = 450$ nm (visible region), not selective to certain anions because **S2** responds positively to anions. Addition of anions to the **S2**/DMSO solution causes the colour change along with the increase of anions concentration, from yellow to Amber colour, shifted absorbance wavelength to $\lambda_{\max} = 470$ nm. Titrations of anions does not change the colour and $\lambda_{\max}$ caused only more strong colour and increase the absorbance value.

Compared with **S1** sensor that are fluorescent and selective against CN^- ion with LOD 8.8×10^{-6} M and K_{ass} $2.5 (\pm 0.26) \times 10^6 \text{ M}^{-1}$, the **S2** not only responds as a colorimetric sensor and is not selective towards CN^- ion, but also it can detect F^- and H_2PO_4^- ions. With the inclusion of nitro group, the **S2** [LOD value 2.8×10^{-6} and K_{ass} value $6.25 (\pm 0.177) \times 10^6 \text{ M}^{-1}$] sensor becomes more sensitive than the **S1**.

Naked eye detection of anions: The anion binding study of receptor **S2** (1×10^{-7} M) have been investigated by 'naked-eye' in DMSO solution. Visual inspection of receptor **S2** showed a clear colour change from light yellow to dark orange upon addition of CN^- , F^- and H_2PO_4^- ions (1×10^{-4} M). On the other hand, addition of Br^- and I^- into the solution did not result in any colour change (Fig. 3).

UV-visible spectroscopy titration: A solution of **S2** (1×10^{-7} M) changed from light yellow to dark yellow upon the addition of 40 eq. (2×10^{-5} M) of CN^- or F^- or H_2PO_4^- . The colouration of the solution was intensified with increasing anion concentration (Fig. 4).

The ability of **S2** to recognize CN^- , F^- and H_2PO_4^- was investigated by monitoring UV-visible spectroscopy. Fig. 5 shows the change in UV-visible spectra of **S2** during titration with anions.

In absence of anion, **S2** absorbed light at $\lambda_{\max} = 455$ nm with absorbance value (A) 0.156. As a concentration of anions (CN^- , F^- and H_2PO_4^-) was added, the wavelength shifted to $\lambda_{\max}$ 470 nm and absorbance increase. The increasing of anions concentration does not cause any wavelength shifted but just caused increasing of the absorbance (A) intensity.

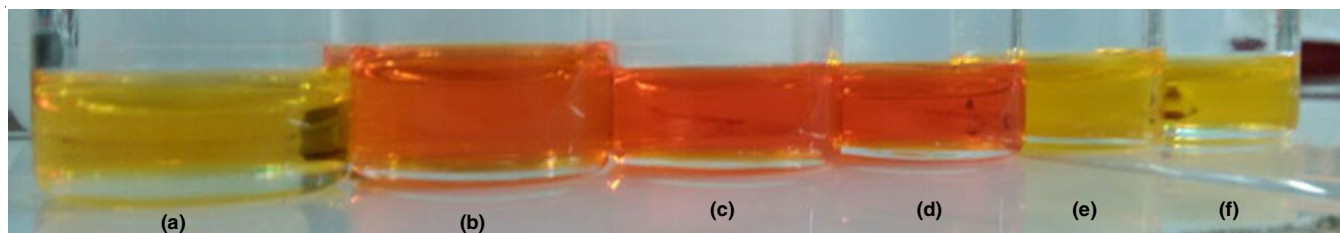


Fig. 3. Visual colour solution (a) **S2**, (b) **S2**+F⁻, (c) **S2**+CN⁻, (d) **S2**+ H₂PO₄⁻, (e) **S2**+I⁻, (f) **S2**+Br⁻

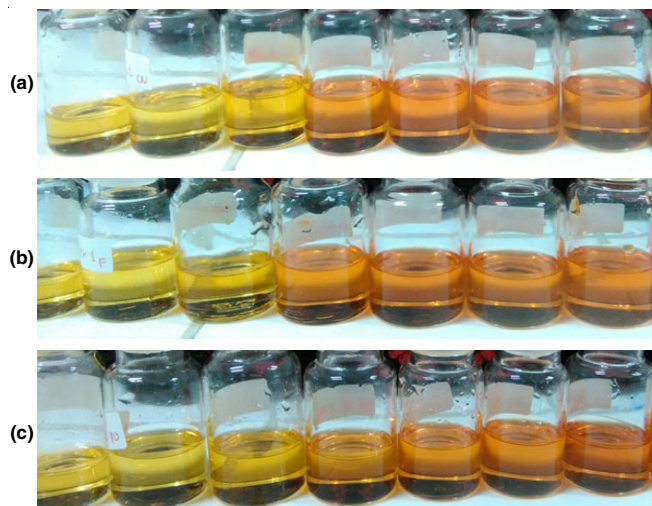


Fig. 4. Colour change of **S2** upon addition increasing concentration of anion : (a) CN⁻, (b) F⁻ and (c) H₂PO₄⁻

The spectra showed isosbestic point at λ 370 nm (λ 390 nm), λ 375 nm and λ 380 nm for CN⁻, F⁻, H₂PO₄⁻, respectively, indicated that **S2** reacted with ions form ion complex and the hydrogen-bonding [11]. Meanwhile, for F⁻ and H₂PO₄⁻, an isosbestic point was observed during the titration process. Suryanti *et al.* [12] hypothesized that the anion sensing process first involved hydrogen bonding interaction and then followed by the protonations upon further addition of ions.

In order to determine the stoichiometric ratio between **S2** and anion guest, the method of continuous variation (Job's plot) [7] was used. The **S2**-anions (CN⁻, F⁻ and H₂PO₄⁻) complex concentration approaches a maximum when the mole fraction of **S2** is 0.5, 0.5, 1.0, respectively. This indicated that **S2** and anions form 1:1, 1:1, 2:1 complexes (stoichiometry ratio), respectively (Fig. 6).

Figs. 7 and 8 show the probability scheme of interaction of **S2**-ions complex.

Determination of LOD and K_{ass}: The colorimetric detection limit of **S2** for anions (CN⁻, F⁻ and H₂PO₄⁻) were also calculated by using UV-visible data and gave the value of 2.8×10^{-6} M, 1.14×10^{-5} M and 1.23×10^{-5} M, respectively.

On the basis of their stoichiometry ratio, the corresponding binding constant (K_{ass}) of **S2** for anions (CN⁻, F⁻ and H₂PO₄⁻) were calculated based on the UV-visible titration experiments. For a complex with 1:1 (H:G) stoichiometry ratio, the binding constant could be determined by non-linear fitting analysis of the titration curves according to eqn. 1 and for complex 2:1 (H:G) the binding constant could be obtained according to the eqn. 2 [6].

$$A = A_o + (A + A_o) \times \frac{\frac{CH + CG + 1}{K} - \left(\frac{CH + CG + 1}{K} - 4CH \times CG \right)^{1/2}}{2CH} \quad (1)$$

$$(A - A_o) = [(\epsilon - \epsilon_o) \times CH \times K \times CG^2]^{-1} + [(\epsilon - \epsilon_o)CH]^{-1} \quad (2)$$

The A is intensity of absorbance of host when guest is added; A_o is intensity of absorbance of host only; ϵ is extinction coefficient host-guest; ϵ_o is extinction coefficient host only; CH and CG is concentration of host and guest, respectively; K is binding constant. The K_{ass} result is $1.2 (\pm 0.25) \times 10^6$ M⁻¹ for **S2**-CN⁻, $2.5 (\pm 0.25) \times 10^6$ M⁻¹ for **S2**-F⁻ and $6.25 (\pm 0.177) \times 10^6$ M⁻¹ for **S2**-H₂PO₄⁻.

Conclusion

In summary, we have synthesized a 'naked-eye' colourimetric anion receptor **S2** based on nitro group and its shows colorimetric sensitivity for CN⁻, F⁻ and H₂PO₄⁻ ions in DMSO solution. The presence of Nitro group resulted in the change of nature and character of the original compound (**S1** sensor): the fluorescence changed to colourimetric activity, LOD value decreased and K_{ass} value increased.

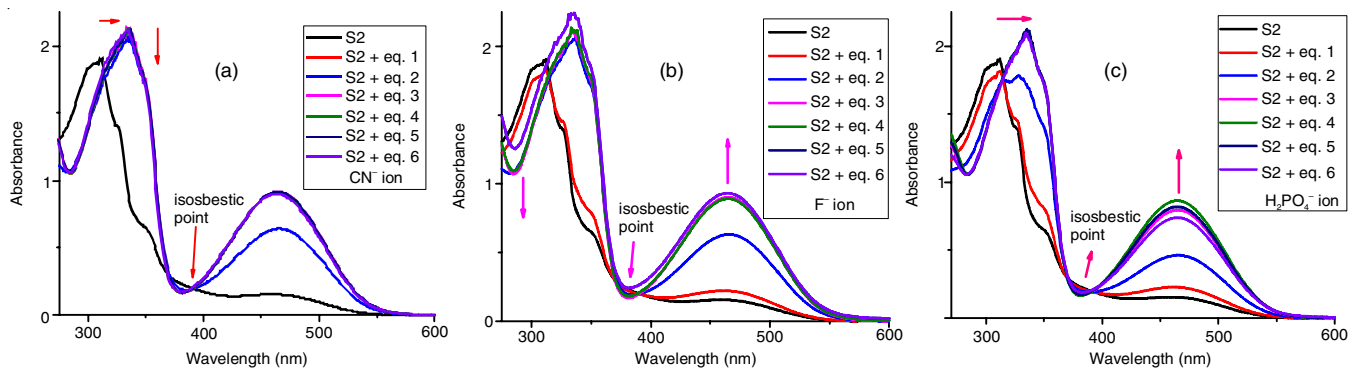


Fig. 5. Change of UV-visible spectral of **S2** upon titration of anion (a) CN⁻, (b) F⁻ and (c) H₂PO₄⁻

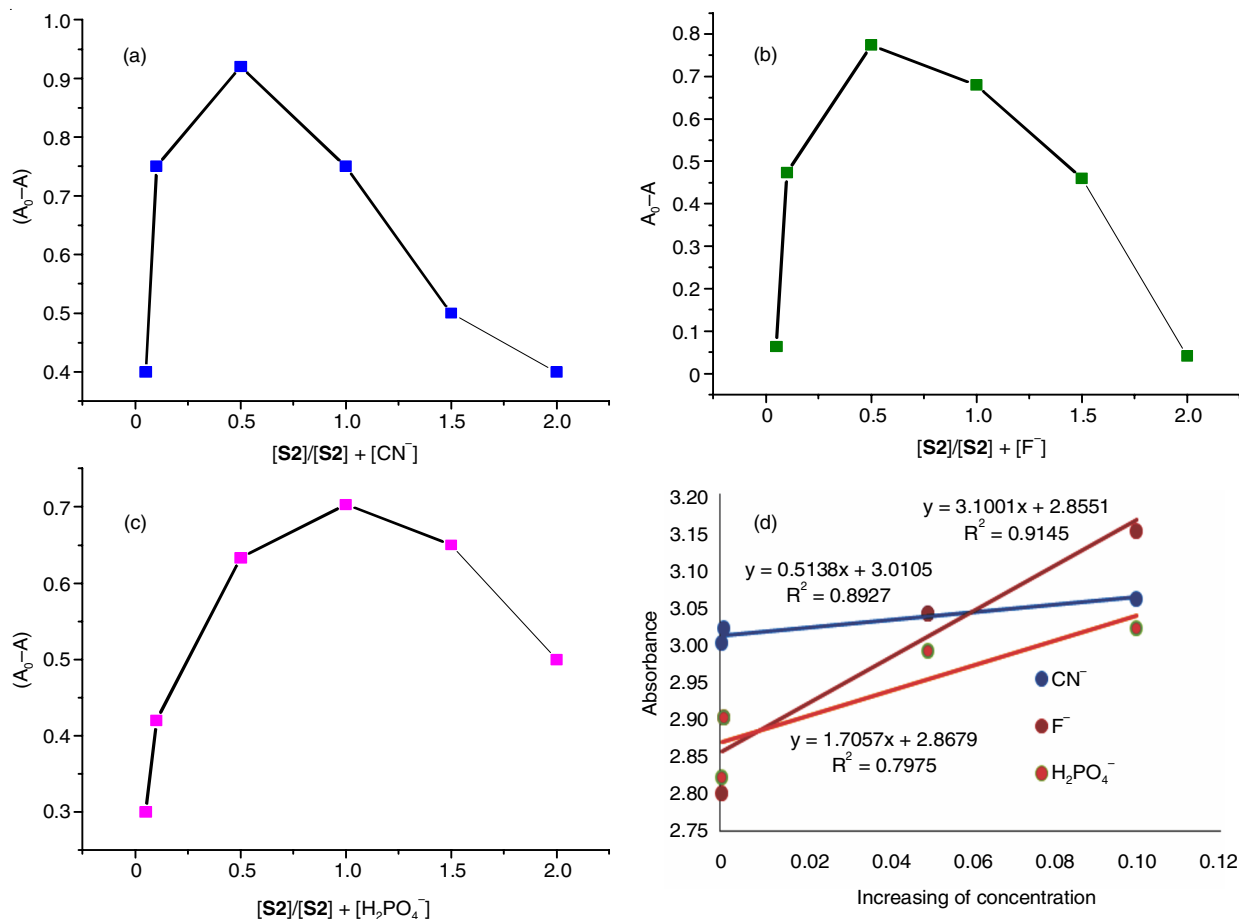


Fig. 6. Job's plot of S2 ions (a) CN^- , (b) F^- , (c) H_2PO_4^- . (d) Linear regression curve of ions

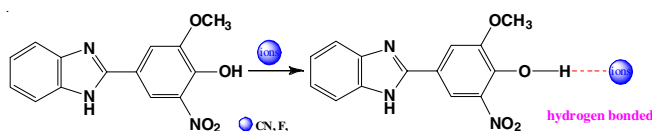


Fig. 7. Scheme of host-guest interaction between S2-ion with 1:1 stoichiometry ratio

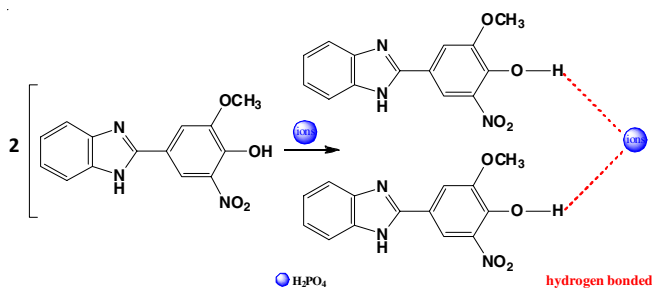


Fig. 8. Scheme of host-guest interaction between S2-ion with 2:1 stoichiometry ratio [Ref. 13]

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CONFLICT OF INTEREST

The authors declare that there is no conflict of interests regarding the publication of this article.

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