# A 4-(1*H*-Benzo[*d*]oxazole-2-yl)-2-methoxyphenol as Dual Selective Sensor for Cyanide Ion Detection

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A dual sensor based on benzoxazole containing moiety **S3** was successfully synthesized and applied for detection of $CN^-$ ion. The **S3** molecule changed its colour for dark brown to dark green on addition of the $CN^-$ ion only in DMSO solvent. The limit of detection (LOD) and association constant ($K_{ass}$) values was $0.4 \times 10^{-6}$ M and $1.0 \times 10^7$ $M^{-1}$; and $0.46 \times 10^{-4}$ M and $1.0 \times 10^5$ $M^{-1}$ determined by UV-visible spectroscopic titration and fluorescence titration, respectively.

**Keywords: Dual selective sensor, Benzoxazole, Cyanide ion.**

## INTRODUCTION

Environmental pollution by organic chemicals continues to be one of the world's leading challenges to sustainable development [1]. In recent years, the developments of optical chemosensors for selective detection of environmentally important ionic (pollution) species, such as cyanide ion, have gained attentions in research community [2].

Cyanide as one of the most toxic anions exists in many natural sources [3] and its known as one of the most rapidly acting and powerful poisons, various industrial processes release of cyanide to the environment. Therefore, recognition and detection of cyanide have also received considerable attention [4]. The rational synthesis design of highly selective and sensitive efficient chemosensors for $CN^-$ anion detection have attracted great attention due to their operational simplicity, good convenience, low cost, and excellent selectivity and high sensitivity [5].

In previous study, we designed a chemosensor compound derived from benzimidazole (S1) [6] which is active as fluorescence receptor and selectively to detect $CN^-$ ion. However, S1 molecule suffers from several parameters like long response time, low detection limit, *etc.* hence in this study, a new chemosensor compound (**S3**) based on benzoxazole molecule is designed and tested for optical properties for detecting the presence of $CN^-$ ion.

## EXPERIMENTAL

Melting point was measured using a Electrothermal-9100, the IR spectra measured using a FTIR Shimadzu Prestige-21, Mass spectra were analyzed by using gas chromatograph-mass spectrometer (GCMS-QP2010S), ^{1}H and ^{13}C NMR were measured using a JOEL JNM ECA-500 MHz while fluorescent was conducted using a SpectroFlourophotometer Shimadzu RF-6000.

All the solvents and materials obtained commercially (Merck) in this work were of analytical purity grade quality and used without further purification. The anions were added in the form of sodium cyanide, sodium flouride, sodium iodide, sodium dihydrogenphosphate and sodium bromide

**Synthesis:** The synthetic procedure for **S3** molecule is adopted from Reyes *et al.* method [7] with some modifications. Vanillin (1.6 g), 2-aminophenol (1.1 g) and alumina (0.75 g) in 25 mL acetonitryl were stirred at room temperature for 5 h. The progres of the reaction was checked with TLC, then the mixture was poured into 300 mL cold distilled water and left the solution at room temperature for 24 h. The precipitate formed was recrystallized with methanol and then characterized (**Scheme-I**). Greenish-brown powder, Yield: 71 %, m.p 178-180 ºC. FT-IR (KBr, $\nu_{max}$, $cm^{-1}$): 3441.01 (O-H from phenol), 2931.8 (C-H methyl), 2337.72 (C=N imidazole), 1612.49
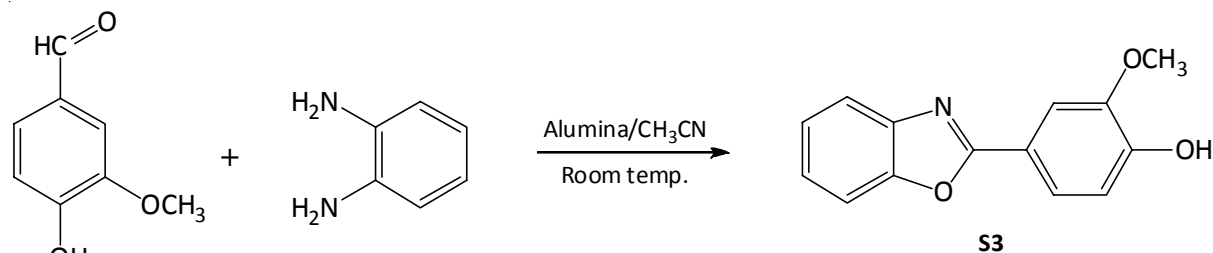
**Scheme-I:** Synthesis of benzoxazole containing compound (**S3**)

(C=C arom.), (3093.82 C-H *sp²*), 1512.19 (C=O oxazole), 1280.73 (C-O-C ether). ¹H NMR (500 MHz, CDCl₃) δ: 9.982 (s, 1H), 9.568 (s, 1H), 8.950 (d, 1H), 7.679 (m, 1H), 7.364 (m, 1H), 6.887 (t, 1H), 6.710 (m, 1H), 5.569 (t, 1H), 3.342 (s, 3H); ¹³C NMR (500 MHz, CDCl₃) δ: 55.684, 100.644, 110.655, 119.06, 121.85, 125.00, 130.01, 147.42, 166.21, 191.87. MS % (EI): *m/z* 241(M⁺, 20), 149 (M⁺, 100), 80 (M⁺, 80).

## RESULTS AND DISCUSSION

**Ionochromic test:** Initial test of molecule **S3** sensor activity was performed at concentration of $1 \times 10^{-1}$ M DMSO in the presence of several anions (CN⁻, F⁻, Br⁻, I⁻ and H₂PO₄⁻). The addition of 50 μL CN⁻ ions in **S3**-DMSO solution causes color change to green. Furthermore, fluorescence occurs only in **S3**-CN⁻ solutions as indicated by UV spectrum at λ 366 nm, which means that molecule **S3** has a high selectivity for CN⁻ ion.

**UV-visible spectroscopic titration:** The **S3** solution in DMSO at the concentration of $1 \times 10^{-6}$ M was brownish clear solution in the absence of ions. Titration of CN⁻ ions with the **S3**-DMSO solution was performed at the equivalent concentration of the ion and sensor. It is found that the discolouration of **S3**-DMSO solution after the addition of 50 μL CN⁻ ions was occured. The enhancement in colour contrast occurred as the concentration of CN⁻ ions increase.

The determination of **S3**-CN⁻ interaction was quantitatively preceded by measuring the absorbance of complex solutions using UV-visible spectroscopy. The UV-visible spectra of **S3** titration with CN⁻ ions is presented in Fig. 1. The **S3** solution shows the absorbance at λ 320 nm having a peak at 390 nm in
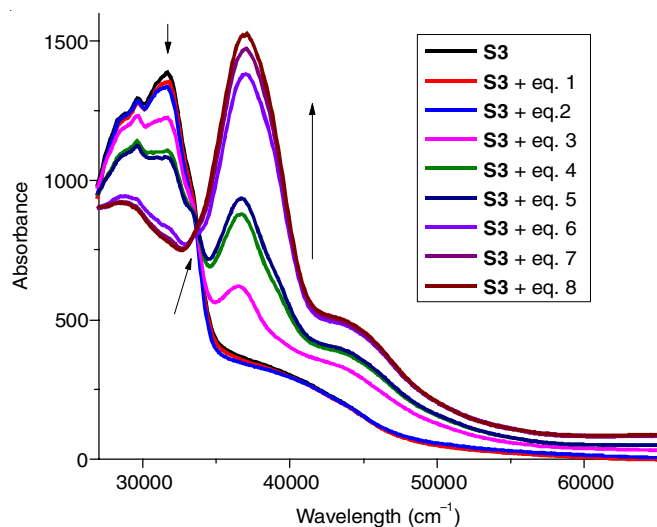
absence of CN⁻ ion. The addition of CN⁻ ions caused the absorbance spectra to gradually decrease, it means that the interaction of **S3** with CN⁻ occurs. The colour of the solution being turned to green-yellow was indicated by the appearance of a new peak at λ 420 nm. The isosbestic point formed at 340 nm indicated a chemical interaction between **S3** and CN⁻ [8].

**Fluorometry titration:** The fluorescent titrations were carried at a concentration of $1 \times 10^{-6}$ M solution yielded poorly spectral results. So further dilute solution was recommended ($1 \times 10^{-7}$ M) for performing the fluorescent titration,

The colour of **S3** solution was clear brown colour solution in absence of ions and it absorbed the light at λ_max 410 nm. Titrations of CN⁻ ions with **S3**-DMSO solution were performed at the equivalent concentration of ion and sensor. It is found that the fluorescence colour of **S3** solution changed after the addition of 50 μL CN⁻ ions. Thus, more the concentration of CN⁻ ion added, the more intense of fluorescent strength. The titration spectra of UV-visible shown in Fig. 2. The **S3** emitted light at λ 365 nm with an intensity of 224000. The addition of CN⁻ ions to the 3rd equivalent ($2 \times 10^{-5}$ M) results in decreased emission intensity, and from the addition of 4th equivalent ($4 \times 10^{-5}$ M) λ shifted to λ 431 nm with the value of Stoke's shift 66 nm.
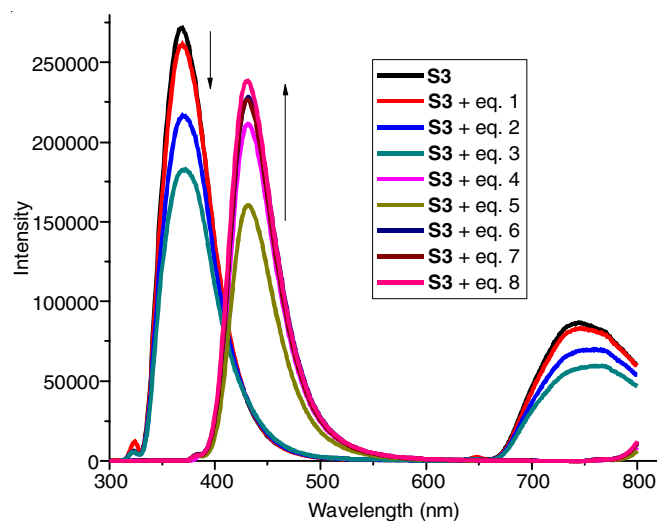


Fig. 2. Spectrophotometric fluorescent titration of **S3** with CN⁻ ions

**Host-guest interaction:** The quantitative analysis of host-guest interaction of complex **S3**-CN⁻ was done by measuring the LOD and K_ass values; and determining their interaction mechanisms. The LOD of **S3**-CN⁻ complex was calculated using 3σ/K equation [2]. On the basis of their stoichiometry ratio, the corresponding K_ass of **S3**-CN⁻ complex were calculated



Fig. 1. UV-visible spectra of **S3** titration with CN⁻ ions

based on UV-visible and fluorescent titration experiments. For a complex with 1:1 (H:G) stoichiometry ratio, the association constant with non-linear relationship could be determined by titration curves (Fig. 3) of Benesi-Hilderbrand method [9] according to the eqn 1 [10,11] for UV-visible titration and eqn 2 [12,13] for fluorescent titrations data.

$$A = A_o + (A - A_o) \times \frac{\frac{CH + CG1}{K} - \left(\frac{CH + CG1}{K} - 4CH \times CG\right)^{1/2}}{2CH} \quad (1)$$

$$1/[I - I_o] = \left(\frac{1}{K[I - I_o][CG]}\right) + \left(\frac{1}{[I - I_o]}\right) \quad (2)$$

The UV-visible titration results showed that LOD value of **S3**-CN⁻ complex was $0.4 \times 10^{-6}$ M and its $K_{ass}$ value was $2 \times 10^7$ M⁻¹. Whereas, fluorometric titration indicated that the LOD value of LOD **S3**-CN complex and $K_{ass}$ value were $0.46 \times 10^{-6}$ M and $2.6 \times 10^7$ M⁻¹, respectively. The interaction mechanism of **S3**-CN⁻ complex host-guest was determined based on the Job's plot curve (Fig. 4). The **S3**-CN⁻ complex indicated the absorption value and maximum emission intensity

at the mole fraction of 0.5, which indicated that the interaction of **S3**/CN⁻ complex takes place on 1:1 stoichiometric ratio [14].

The schematic representation of 1:1 host-guest complex interaction ratio formed on **S3**-CN⁻ complex can be predicted by the mechanism as depicted in Fig. 5. The interaction of the **S3**-CN⁻ complex and CN⁻ ion was 1:1 stoichiometric ratio. The binding mechanism can be explained in term of colour and fluorescence changes when the proton of hydroxyl group (OH) from **S3** single molecule binds with electrons from a single molecule of CN⁻ ion to form a hydrogen bond.

## Conclusion

In conclusion, benzoxazole moiety containing **S3** compound is used as a dual sensor for colour and as fluoroscent. The **S3** sensor is highly sensitive toward CN⁻ ions only.
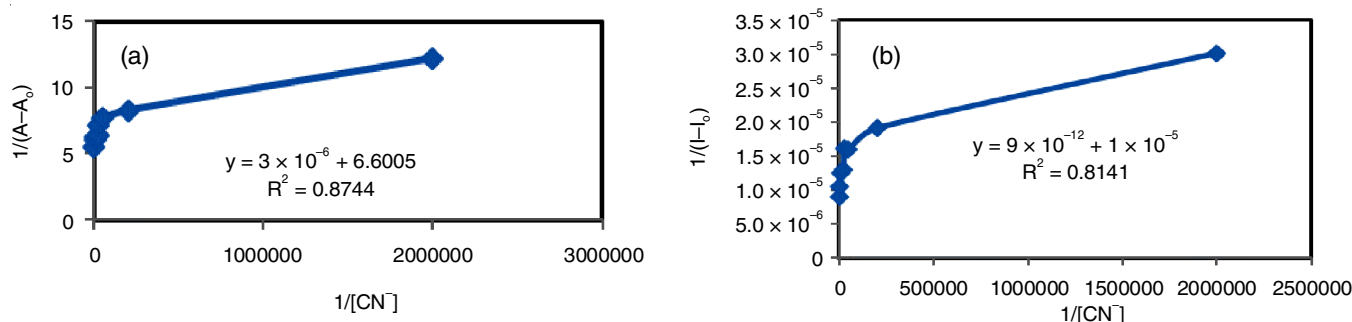
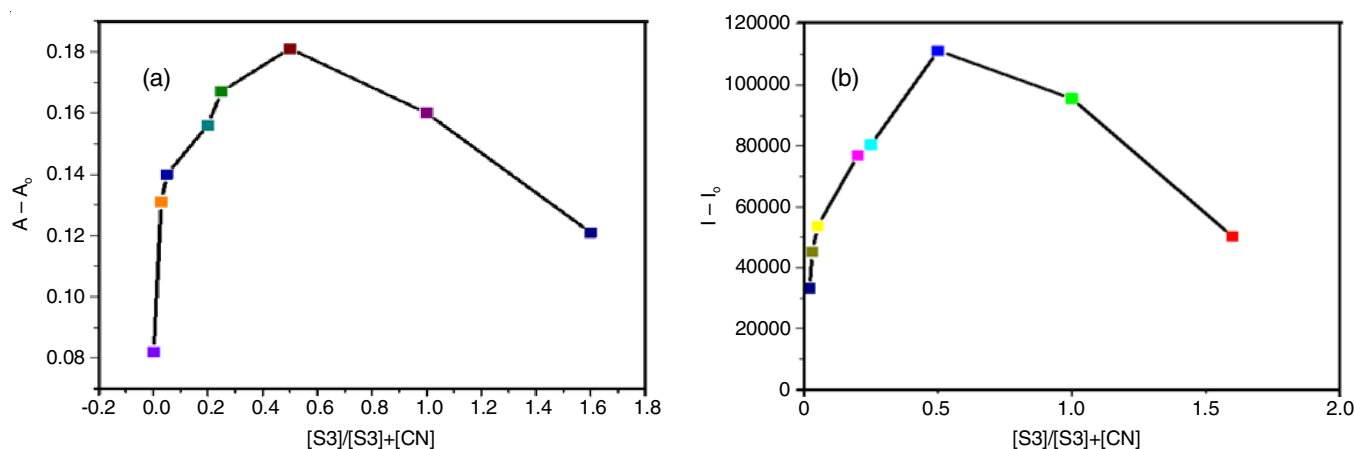Fig. 3. Benesi-Hilderbrand curve of **S3**-CN⁻ complex on titration: (a) UV-visible and (b) fluorescent



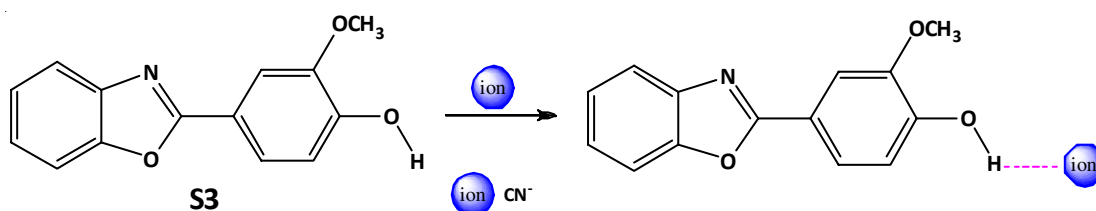Fig. 4. Job's plotted curve titration of **S3**-CN⁻ on: (a) UV-visible and (b) fluorescent



Fig. 5. Proposed host-guest interaction mechanism of **S3**-CN⁻ complex

## CONFLICT OF INTEREST

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

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