

A New Colorimetric Sensor Responding CN- Anion based on Hydrazone Compound in Acetonitrile Solution

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Abstract: A new hydrazone compound 2-methoxy-6-((*E*)-phenyldiazenyl)-4-((*E*)-(2-phenylhydrazineylidene)methyl)phenol (receptor R) based on vanillin has been synthesized and applied to cyanide anion detection in acetonitrile solvent. Color of the receptor solution turned from yellow to purple in the presence of cyanide anion and other anions like H₂PO₄⁻, Br⁻, CN⁻, SO₄²⁻, Cl⁻, I⁻, CH₃COO⁻ and F⁻ could not effect color of receptor. Changing in the maximum wavelength of the receptor after addition of cyanide anion was confirmed by UV-Vis spectrophotometer. In the presence of cyanide, wavelength of the receptor changed from 347 nm to 510 nm. Detection limit of the receptor were also observed by UV-Vis spectrophotometer. Based on the UV-Vis titration, the receptor detected cyanide anions with limit of detection 4mM in the acetonitrile solvent.

1 INTRODUCTION

The anion waste produced from natural processes or industries like gold mining, electroplating, metal and pesticides industries cause health and environmental problems (Ghanavati et al., 2014). Some anions waste like cyanide have toxic properties and a lethal effect (Mourzina et al., 2003; Nezamzadeh-ejhieh and Esmailian, 2012) even exposure to large amount of cyanide through both Inhalation or oral exposure cause death and systemic effect (respiratory, cardiovascular, gastrointestinal, neurological, haematological) on living organisms (Research Triangle Institute, 1997). WHO has established level of cyanide in drinking-water 0.5 mg/L (WHO, 2011). The toxic effect of cyanide can be described from its ability to inhibit enzyme cytochrome oxidase on step of oxidative phosphorylation of respiration process (Gupta, 2009). Cyanide anion can form complex phenomenon with a part of enzymatic structure that can inhibit function and cellular growth (Mekuto et al., 2016).

Several methods have been widely used to detect the presence of anions waste in the environment including potentiometric (Mourzina et al., 2003; Nezamzadeh-ejhieh & Esmailian, 2012; Cuartero et al., 2013), ion chromatography (Silveira

et al., 2014) and electrochemical analysis (Pulkka et al., 2014). They are less practical methods that sample preparation is required. In addition, the analysis of anion by the methods require high cost and a long time for analysis. Therefore we need more practical method for detecting these anions. Colorimetric chemosensor method, a method developed for the detection of anions, is more efficient method which is not require sample preparation and the specific instrument. Furthermore, analysis with this method is directly observed by naked eye. It uses sensor compounds called chemosensor which generally consists of two parts: The binding site like -NH or -OH groups plays as fragment that can interact with anions and signaling subunit like chromophore groups is act as a signal transducer (Martinez-Manez & Sancenon, 2003). Both binding site and signaling sub unit are important part in the colorimetric sensor which gives effect to its selectivity and sensitivity to anion.

Organic materials have been widely used as chemosensor. Recently, researcher have been reported the colorimetric anion based chalcone, azo and hydrazone derivatives. Azo derivative was used as sensor of H₂PO₄⁻, F⁻ and acetate anion with the amine group as the binding site (Shao et al, 2009). Hydrazone derivative was also used as sensor of acetate anion by amine group on the synthesized

compound as binding site that interact with the acetate anion through hydrogen bonds (Qiao, 2009). The color change of the synthesized compound solution in DMSO solvent from yellow to green was occurred after addition of acetate anion. In addition, azo-hydrazone derivative such as 4-phenylazo-2-hydroxy-benzaldehyde phenylhydrazone compound from salicylaldehyde was used as compound sensor by the change of color from yellow to red after the addition of acetate, F⁻ and H₂PO₄⁻ anions (Li et al., 2010).

In this study, we synthesized receptors 2-methoxy-6-((*E*)-phenyldiazenyl)-4-((*E*)-(2-phenylhydrazineylidene)methyl)phenol (receptor R). We also present the solvent (solvatochromic) and electron-withdrawing group like azo effect to UV-Vis electronic absorption and sensitivity of receptors R to cyanide anion.

2 EXPERIMENTAL SECTION

2.1 General

Vanillin, NaOH, methanol, acetic acid, H₂SO₄ 98% , ethanol, NaNO₂, CHCl₃, phenylhydrazine, DMSO, acetonitrile, acetone, silica gel 60 (0.040-0.063 mm), NaF, NaCl, NaI, NaBr, Na₂CO₃, Na₂SO₄, NaH₂PO₄, CH₃COONa, NaCN. All materials were purchased from Merck. Infrared spectra were recorded using Shimadzu Prestige-21 FT-IR Spectrophotometer. The spectra of ¹H-NMR and ¹³C-NMR were evaluated on JEOL JNM ECA-500, Mass spectra were performed on Shimadzu QP-QP-5000 and 2010. Melting point was measured using uncorrected Electrothermal-9100

2.2 Synthetic Procedure of 4-hydroxy-3-methoxy-5-(phenyldiazenyl)benzaldehyde

Solution I (aniline 0.03 mol, water (7.5 mL) and H₂SO₄ 7.5 mL) was added into sodium nitrite solution (0.03 mol, water 12 mL) and stirred for 1 h. Solution II (NaOH 3.6 g in water 90 mL and vanillin 0.03 mol, 0-5 °C) was dropwisely into the solution I. The solution was stirred for 3 h at temperature 0-5 °C. The precipitate was filtered (Radchatawedchakoon et al., 2014). Product was obtained as dark red solid and yield 72%. IR cm⁻¹: 3425 (O-H); 3062 (Csp²-H), 2931 and 2864 (Csp³-H); 1681 (C=O); 1604 (C=C aromatic); 1458 (N=N); 1411(-CH₃); 1280 (C-N); 1141 and 1072 (C-O-C). ¹H-NMR (CDCl₃):

δ/ppm 14.23 (O-H, s, 1H); 9.94 (CHO, s, 1H); 7.88 (m, 2H); 7.56-7.52 (m, 3H); 7.48 (s, 1H), 4.00 (OCH₃, s, 3H). EI-MS (m/z): 256.

2.3 Synthetic Procedure of Receptor R

The compound of 4-hydroxy-3-methoxy-5-(phenyldiazenyl)benzaldehyde (1 mmol) in ethanol (100 mL) was introduced into the base-round three neck flask capacity 250 mL with a condenser. Phenylhydrazine (1 mmol) and four drop of acetic acid were dropwisely into the solution. The solution stirred and refluxed for 3 h. The precipitate was filtered. Product was produced as dark brown solid, yield 81%, m.p. 141-141.8 °C. IR (cm⁻¹): 3425 (O-H); 3309 (N-H); 3055 (Csp²-H); 2931 and 2854 (Csp³-H); 1597 (C=N); 1496 (N=N); 1265 (C-N); 1149 and 1072 (C-O-C). ¹H-NMR (DMSO-d₆; δ/ppm): 13.66 (NH, s, 1H); 7.78 (aromatic, d, J = 1.95 Hz, 2H); 7.74 (CH=N, s, 1H); 7.63 (OH, s, 1H); 7.56-7.48 (m, 5H); 7.3-7.28 (m, 2H); 7.14 (s, 2H); 6.88 (s, 1H); 4.03 (-OCH₃, s, 3H). ¹³C-NMR (DMSO-d₆; δ/ppm): 149.9; 149.6; 145.4; 136.8; 131.4; 129.7; 129.6; 129.5; 127.0; 123.6; 122.5; 122.2; 120.3; 112.9; 110.5; 56.6. EI-MS (m/z): 346 (M⁺).

2.4 Solvatochromic Study of Receptor R

Solvatochromic studies of receptors R were used various solvent such as ethanol, DMSO, acetonitrile and acetone. 4.0 mg of Receptor was dissolved in solvents. The color change and the UV-Vis absorptions were recorded.

2.5 Selectivity Study of Receptor R

Selectivity studies of receptor R were carried out in acetonitrile solution at concentration level 2 x 10⁻⁵ M. The solution of receptor was added by 10 μL of NaF, NaCl, NaBr, NaI, NaCN, Na₂SO₄, Na₂CO₃, CH₃COONa and NaH₂PO₄ solution, respectively. The color change and the UV-Vis absorption were recorded.

2.6 UV-Vis Titration of Receptor R with CN⁻

The titration of UV-Vis was carried out in acetonitrile solution at concentration level of 5 x 10⁻⁵ M for receptor R and (1-10) x 10⁻² and (1-10) x 10⁻³ M for CN⁻. The solution of receptor was added by 50 μL of CN⁻ solution. The UV-Vis absorptions were

recorded by spectrophotometer UV-Vis at 200-700 nm.

3 RESULT AND DISCUSSION

The receptor R was synthesized by condensation reaction between 1 mmol of 4-hydroxy-3-methoxy-5-(phenyldiazonyl) benzaldehyde and 1 mmol of Phenylhydrazine in 100 mL ethanol solvent (Fig. 1). The chemical structure of receptor R were confirmed by GC-MS, FT-IR, ^{13}C -NMR and ^1H -NMR.

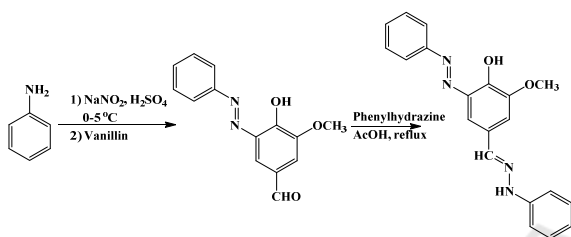


Figure 1: Synthesis of receptor R.

3.1 Solvatochromic Study

Solvatochromic studies of receptor R carried out with variety of protic and non-protic solvents. Table 1 shows the maximum wavelength of receptor R in various solvents and Fig. 2 shows solvatochromic absorbance spectra of receptor.

Table 1: λ_{max} values of receptor 1, 2 and 3 in various solvents.

Receptor	λ_{max} (nm)			
	DMSO	acetonitrile	Acetone	Ethanol
R	355	347	348	351

Table 2: ET(30) and normalized EN/T value.

Solvent	ET (30) (Kcal mol $^{-1}$)	$\frac{N}{E_T}$
Ethanol	51.9	0.654
DMSO	45.1	0.444
Acetonitrile	45.6	0.460
Acetone	42.2	0.355

Based on Table 1 showed that polar solvent such as DMSO and ethanol caused bathochromic shift compared to less polar solvent such as acetonitrile and acetone. Solvent polarity causes the different of maximum wavelength of receptor R. Based on the UV-Vis electronic absorption, maximum wavelength of receptor in DMSO solvent was 355 nm, while in acetonitrile solvent was 390 nm. Hypsochromic shift occurred at acetone (λ_{max} 348 nm and acetonitrile

(λ_{max} 347 nm) solvent. The difference of solvent polarity affects electronic transition energy of the ground state to the excited state. More polar solvents such as DMSO stabilizes the electron in the excited state (π^*) that causes the transition energy becomes smaller so maximum wavelength will be greater. In addition, protic (DMSO) and aprotic (ethanol) solvent affect maximum wavelength of receptor. Based on normalized E_{T}^{N} and ET (30) value, ethanol solvent is more polar than solvent DMSO (see Table 2). However, maximum wavelength of receptor in ethanol solvent is smaller than the DMSO solvent. Transition energy of the ground state to the excited state is influenced by the ability of the solvent to form hydrogen bond with receptor. Protic solvent such as ethanol can form hydrogen bonds with the receptor that causes free electrons in the ground state is more stabilized than the excited state. Therefore, the energy transition will be greater and maximum wavelength will be smaller (Reichardt, 1994).

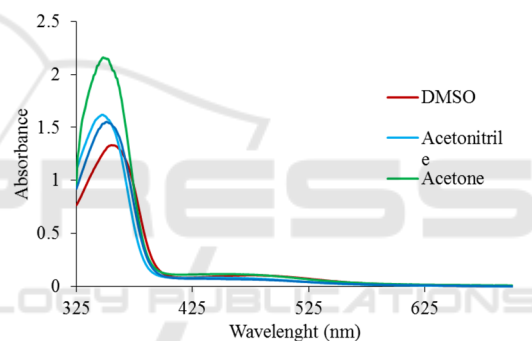


Figure 2: Solvatochromic UV-Vis spectra of receptor R.

Figure 2 shows the UV-Vis spectra of receptors R. Table 1 and Fig. 2 shows that the substituent at aromatic ring affect the λ_{max} value between receptor R. Electron-withdrawing group such as azo group increases delocalization of electron which it caused the electron more conjugated and bathochromic shift (Huang et al., 2012). It is attested by the presences of azo group at receptor increased the intensity of color change and wavelength shift of receptor.

3.2 Selectivity Study of Receptor R

The selectivity of receptor was evaluated by adding anions like H_2PO_4^- , CO_3^{2-} , Br^- , CN^- , SO_4^{2-} , Cl^- , I^- , CH_3COO^- and F^- to acetonitrile solution of receptors R. It was observed that the addition of CO_3^{2-} and CN^- anions to receptor solution, the receptor solution color changed from bright yellow to purple (Fig. 3). Other anions such as H_2PO_4^- , Br^- , SO_4^{2-} , Cl^- , I^- ,

CH₃COO⁻, F⁻ did not provide color change of receptor solution. In addition, the absorbance spectra were determined by UV-Vis spectrophotometer. Out of all anions examined, the presence of CN⁻ in solution appeared new band at 510 nm. New band appeared at 522 nm after addition CO₃²⁻ but the absorbance intensity of CN⁻ were greater than CO₃²⁻ (Fig. 4). Based on the study, we concluded that the receptor could be used as a colorimetric sensor for CN⁻ in acetonitrile solvent.



Figure 3: The color change of receptor 3 in CH₃CN after addition of anions: 1) Receptor, 2) F⁻, 3) Cl⁻, 4) Br⁻, 5) I⁻, 6) H₂PO₄⁻, 7) CH₃COO⁻, 8) SO₄²⁻, 9) CO₃²⁻, 10) CN⁻.

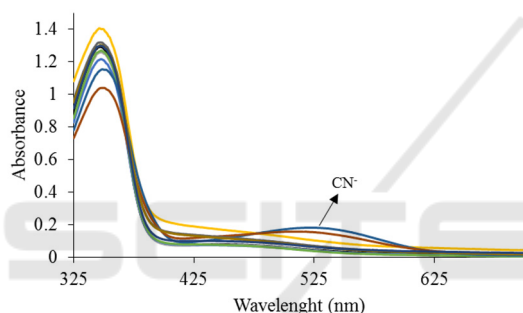


Figure 4: Titration of UV-Vis of receptor R with Cyanide.

The color change caused by the presence of CN⁻ in solution proves that there is an interaction between receptor and CN⁻. We suggested three possible mechanisms. The first interaction is the hydrogen bond between CN⁻ with O-H or N-H group. The second interaction is deprotonation of H atom at hydroxyl or amine group (Mondal et al., 2018). The last possible mechanism is chomodisimeter: CN⁻, which is a strong nucleophile, attacks C=N to form a new C-C bond (Cao & Wang, 2013).

3.3 UV-Vis Titration of Receptor R with CN⁻

UV-Vis titration receptors R were carried out in acetonitrile solution at a concentration level 2×10^{-5} M. the ability of anion to form bond with receptor R was evaluated by adding solution of sodium cyanide salt. The addition of CN⁻ anion also affected UV-Vis spectra of receptor 3 (Fig. 5). The addition of CN-

anion to receptor caused absorbance at 347 nm decreased gradually and new band appeared at 510 nm. In addition, the change of color from yellow to purple occurred after addition of cyanide anion to receptor (Fig. 3). The color change and wavelength shift after the addition of CN⁻ anion indicated that the receptors reacted with CN⁻ anion. We concluded that receptor could be used to cyanide detection by naked eye.

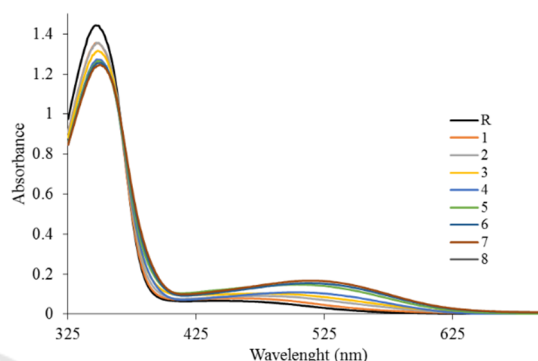


Figure 5: UV-Vis titration of R with Cyanide.

Receptor R have two active sites part i.e. amine and hydroxyl groups. However, the ability of amine group to form hydrogen bond with cyanide anion was better than hydroxyl group. The presence of azo group on the receptor caused the proton on the amine group is more acid than the hydroxyl group (Shang and Xu, 2009). Thus, Interaction occurs between -NH at receptor with CN⁻ anion. The presence of chromophore group such as azo group affect the sensitivity of the receptor to the CN⁻ anion. It is attested by detection limit of receptor. Based on Fig. 5, the color change at receptor occurred after the addition of 4 mM of CN⁻ anion.

4 CONCLUSIONS

Receptor R show the solvatochromic properties in protic and aprotic solvents. In aprotic solvents, bathochromic shift of receptors occur in more polar solvents, while protic solvent such as ethanol can form H-bonds with binding site of receptor that can stabilize the electron in the ground state. It causes the λ_{max} value of receptor in ethanol is smaller than the DMSO. The presence of electron withdrawing-group like azo group can increase sensitivity of receptor to cyanide anion. It is evidenced by the limit of detection of receptor was 4 mM.

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