

## A Naked-Eye Fluoride Ion Recognition Based Vanillin Derivative Chemosensors

R. Rahmawati<sup>1\*</sup>, Bambang Purwono<sup>2</sup>, Sabirin Mastjeh<sup>2</sup>

<sup>1</sup>Chemistry Education Division, Faculty of Teacher Training and Science Education, University of Mataram, Indonesia

<sup>2</sup>Department of Chemistry, Faculty of Mathematics and Natural Science, Universitas Gadjah Mada, Indonesia

\*Email: [rahmawati\\_kimia@unram.ac.id](mailto:rahmawati_kimia@unram.ac.id)

Received April 28, 2019; Accepted July 14, 2019

### ABSTRACT

Two new receptors S2 and S6 were designed and synthesized based on benzimidazole and azo-benzimidazole synthesized from vanillin for the colorimetric detection of fluoride ion. The presence of nitro group in S2 and azo in S6 makes -OH proton (binding site) acidic and therefore it could deprotonate with addition of basic anion such as fluoride. Hydroxyl (OH) functionality which detects basic fluoride ions via hydrogen-bonding mechanism which is mechanism involved in the color change of receptor R2 and R6, its mean that initial hydrogen bond formation of F<sup>-</sup> ion with -OH group.

Keywords: fluoride ion, recognition, chemosensor.

### INTRODUCTION

The fluoride anion (F<sup>-</sup>) is an important trace element in the human body [1]. F<sup>-</sup> is primarily obtained from food and drinking water. Most countries set strict limits on F<sup>-</sup> that is the permitted level of fluorine in foods [2]. It carries both benefits and dangers—a low concentration of F<sup>-</sup> can be effective in treating osteoporosis and the prevention of caries, but excess fluoride will cause dental and skeletal fluorosis, as well as urolithiasis and kidney and gastric disorders [3-6]. The content of F<sup>-</sup> in natural water is 0.3–0.5 mg/L and can reach 2.0–5.0 mg/L in groundwater with fluorine ore deposits [7]. Over 2.0 mg/L of F<sup>-</sup> in drinking water can cause damage to kidney and liver functions and over 4 mg/L will deform human bones and cause fluorosis [8-9].

In this work, two F<sup>-</sup> ratiometric fluorescent probes were developed for the sensitive detection of F<sup>-</sup> based. The two probes were prepared with nitro-benzimidazole (S2) and azo-nitro-benzimidazole (S6) as the chromophore side and Hydroxyl group as the reactive groups. The two probes could be used for the quantitative detection of F<sup>-</sup> in water.

### METHODOLOGY

#### Chemicals

vanillin, boric acid, distilled water, ethanol, o-phenylenediamine, aniline, 2-nitroaniline, ethanol. The anion used in the

sensor test comes from sodium fluoride (NaF) salt.

#### Method

S2 synthesis refers to the method of Karimi et al. (2012) with some modifications. A total of 10 mmol o-phenylenediamine and 4.8 mmol boric acid, each dissolved with 5 mL of warm distilled water at 45 °C then mixed in a beaker glass and stirred for 2 minutes. Then add 5-nitrovaniline 10 mmol which has been dissolved with distilled water temperature of 45 °C, then stirred for 3 minutes. The precipitate formed was recrystallized with ethanol, then the melting point was measured and characterized using FT-IR instruments, mass spectra, <sup>1</sup>H-NMR, and <sup>13</sup>C-NMR.

The synthesis of S6 compounds was carried out by adopting the method of Kaur et al. (2015) with some modifications. 4.2 mmol S1 synthesized and 2.8 mmol NaNO<sub>2</sub> were each dissolved with 1 mL THF. A total of 0.42 mL 2-nitroaniline was dissolved with 6 mL of distilled water and stirred in a beaker glass at 0-5 °C, then dropped with 1.2 mL of HCl 6 M and stirred for 15 minutes, then added a solution of NaNO<sub>2</sub> and S1 solution, condition pH by dripping with 2 M NaOH solution to reach pH 8-9. The mixture continues to be stirred for 2 hours, then neutralized the mixture by dripping a 1 M HCl solution. The precipitate formed is then filtered and recrystallized with ethanol. The solids obtained are then determined by their melting

point and characterized by FT-IR, mass spectra,  $^1\text{H-NMR}$  and  $^{13}\text{C-NMR}$ .

Solvatochromic test is carried out to observe the change in color of the solution towards the difference in the solvent. A total of 0.142 g S2 and 0.19 g S6 were dissolved with 5 mL of DMSO solvent so that the concentration of each sensor in each solvent was  $1 \times 10^{-1}$  M. Then color changes were observed. Furthermore, each solution was diluted to obtain concentrations:  $1 \times 10^{-6}$  M,  $1 \times 10^{-7}$  M, and  $1 \times 10^{-8}$  M. Then absorbance was measured with a UV-vis spectrophotometer.

Saturated anion solution made from NaF salt in distilled water. The ionochromic test is carried out by adding 3 drops of the saturated

anion solutions to each solution of the S2 and S6 compounds in the DMSO solvent. The color changes that occur in the solution were observed and then confirmed with a UV-vis spectrophotometer (in the range  $\lambda$  200-800 nm).

## RESULT AND DISCUSSION

S2 dissolves completely in the DMSO solvent, providing optimal absorbance at concentrations of  $1 \times 10^{-7}$  M with a  $\lambda_{\text{max}}$  of 470 nm, this is reinforced by the visual solution which shows a brownish yellow color.

S2 solution with a concentration of  $1 \times 10^{-7}$  M brownish yellow, the addition of  $\text{F}^-$  ions changes the color of the solution to amber color that can be seen with the naked eye (Figure 1).



Figure 1. Appearance of a solution of S2 before and after adding to the  $\text{F}^-$  ion



Figure 2. Visualization of color changes in the titration solution S2  $1 \times 10^{-7}$  M with  $\text{F}^-$  ions (consecutively concentrated from right to left: 0 eq., 1 eq., 2 eq., 3 eq., 4 eq., 5 eq., 6 eq.)



Figure 3. Visual response of the S6 solution in the presence of  $\text{F}^-$  ions.

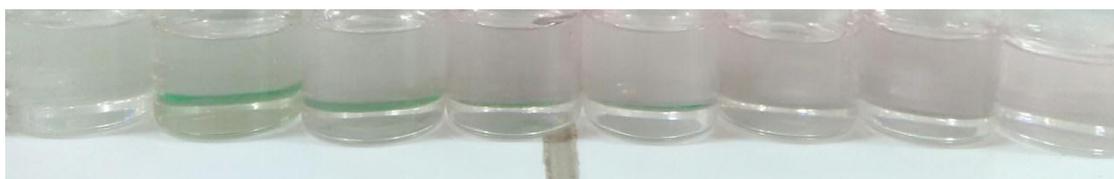


Figure 4. Visual titration of S6 with ion  $\text{F}^-$

Qualitative observations on the interaction of S2 with the F ions which show the color response in the ionochromic test are carried out by titration of the S2 / DMSO solution.

Figure 2 shows that with the increasing concentration of ions given, the color of the solution becomes more concentrated. At the addition of  $5 \times 10^{-7}$  M (eq. 1) the color of the solution is still similar to the color S2, starting from the addition of 2 equivalent colors gradually becomes amber, and the amber color becomes more concentrated on the addition of  $1.5 \times 10^{-4}$  M ions (eq. 6).

S6 dissolves completely only in DMSO solvents. The S6 compound in DMSO at a concentration of  $1 \times 10^{-6}$  M reveals a brownish solution. Measurements on the UV-Vis instrument (concentration  $1 \times 10^{-6}$  M) produce the optimal absorbance achieved at  $\lambda_{\max}$  435 nm, this corresponds to the brownish color that appears.

S6 in DMSO solvent with a concentration of  $5 \times 10^{-7}$  M revealed a brownish clear solution. Tests to determine the response of S6 to ions are carried out by dripping saturated ions ( $\text{CN}^-$ ,  $\text{F}^-$ ,  $\text{Br}^-$ ,  $\text{I}^-$ , and  $\text{H}_2\text{PO}_4^-$ ) 50  $\mu\text{L}$  into the S6 / DMSO solution. The test results are presented in Figure 3.

The sensor response S6 shows that there is a change in color to purple on the addition of  $\text{F}^-$  ions which can be seen directly with the naked eye. Then the S6 response with the F ion ion only shows the color change so that the S6 compound is color.

Qualitative analysis of the interaction of S6 with  $\text{F}^-$  ions was carried out by titrating a solution of S6 / DMSO  $1 \times 10^{-8}$  M using 50  $\mu\text{L}$   $\text{F}^-$  ions at several concentrations. Titration results are visually presented in Figure 4.

Measurement of S6- $\text{F}^-$  interaction strength was performed on the UV-Vis instrument whose measurement results in the form of absorbance spectra are presented in Figure 5. From Figure 5 UV-Vis spectra the titration results show that the absorbance of S6 / DMSO at  $\lambda$  320 nm with A value of 0.575 and shoulder on  $\lambda$  350 nm. Absorbance decreased immediately after  $5 \times 10^{-7}$  M (eq. 1)  $\text{F}^-$  ion was added, and at the same time the shoulder formed firmly at  $\lambda$  575 nm. These results indicate that there is an electron transition  $\pi$ - $\pi^*$  from chromophore. The gradual addition of ions to a concentration of  $5 \times 10^{-4}$  M causes the absorbance at  $\lambda_{\max}$  to continue to decrease and the absorbance at  $\lambda_{\text{shoulder}}$  continues to increase, but does not form an isosbestic point.

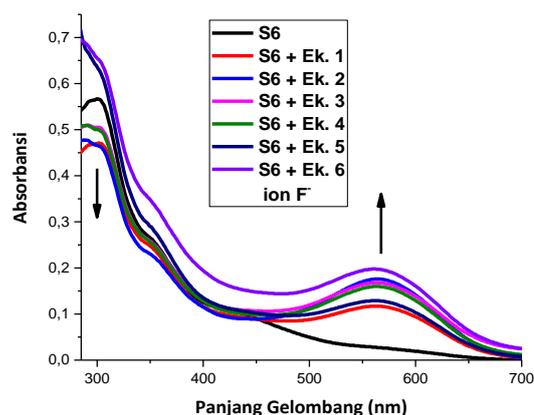


Figure 5. UV-Vis S6 titration spectra with  $\text{F}^-$

## CONCLUSION

S2 and S6 compounds can detect the presence of  $\text{F}^-$  ions with a response in the form of a change in the color of the solution that can be seen with the naked eye.

## References

- [1] Zhou, Y., Zhang, J. F., & Yoon, J. (2014). Fluorescence and colorimetric chemosensors for fluoride-ion detection. *Chemical reviews*, 114(10), 5511-5571.
- [2] Huang, D., Yang, J., Wei, X., Qin, J., Ou, S., Zhang, Z., & Zou, Y. (2017). Probabilistic risk assessment of Chinese residents' exposure to fluoride in improved drinking water in endemic fluorosis areas. *Environmental Pollution*, 222, 118-125.
- [3] Craig, L., Lutz, A., Berry, K. A., & Yang, W. (2015). Recommendations for fluoride limits in drinking water based on estimated daily fluoride intake in the Upper East Region, Ghana. *Science of the Total Environment*, 532, 127-137.
- [4] Xiong, X., Liu, J., He, W., Xia, T., He, P., Chen, X., ... & Wang, A. (2007). Dose-effect relationship between drinking water fluoride levels and damage to liver and kidney functions in children. *Environmental Research*, 103(1), 112-116.
- [5] Perumal, E., Paul, V., Govindarajan, V., & Panneerselvam, L. (2013). A brief review

- on experimental fluorosis. *Toxicology letters*, 223(2), 236-251.
- [6] Yu, X., Chen, J., Li, Y., Liu, H., Hou, C., Zeng, Q., ... & Pang, S. (2018). Threshold effects of moderately excessive fluoride exposure on children's health: a potential association between dental fluorosis and loss of excellent intelligence. *Environment international*, 118, 116-124.
- [7] Reddy, T. S., and Choi, M-S., Dicyanovinylcoumarin as A Turn-On Fluorescent Sensor for Cyanide Ion, *Journal of Photochemistry and Photobiology A: Chemistry*, **2018**, 351, 108-114.
- [8] Hakim, Y. Z., Yulizar, Y., Nurcahyo, A., & Surya, M. (2018). Green Synthesis of Carbon Nanotubes from Coconut Shell Waste for the Adsorption of Pb (II) Ions. *Acta Chimica Asiana*, 1(1), 6-10.
- [9] Reddy, T. S., & Choi, M. S. (2018). Dicyanovinylcoumarin as a turn-on fluorescent sensor for cyanide ion. *Journal of Photochemistry and Photobiology A: Chemistry*, 351, 108-114.