Quantitative Analysis Of F^- Ion Recognition By A New Chemosensor From The Flavon Group

R. Rahmawati[1*], Syarifa Wahidah Al-Idrus[1], Baiq Nila Sari[2], Bambang Purwono[3], Sabirin Matsjeh[3]

[1]Chemistry Education Division, Faculty of Teacher Training and Science Education, University of Mataram, Indonesia
[2]Department of Chemistry, Faculty of Science, Chulalongkorn University, Thailand.
[3]Department of Chemistry, Faculty of Matchematics and Natural Science, Univesitas Gadjah Mada, Indonesia

*Email: rahmawati_kimia@unram.ac.id

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ABSTRACT

A new chemosensor S8 compound from the flavon group that has been successfully synthesized. Test its ability as a chemosensor for F^- anion, providing positive results that it can recognize F^- anion with response to an increase in fluorescent solution. Titration of S8 solution in DMSO solvents was carried out with F^- anion at various concentrations and then measurements were made on fluorometry instruments. The fluorescent titration emission spectrum shows that the S8-F^- host-guest interaction quantitatively in the form of LOD and k_{ass}. LOD and K_{ass} values are 6.43×10^{-4} M and 2×10^6 M^{-1}, respectively.

Keywords: ion F^- recognition, fluorescence sensor, flavon.

INTRODUCTION

The sensor is a system that can experience intermolecular interactions with an analyte and produce stimulants due to changes in energy from lower levels to higher levels or vice versa. As a result of the interaction will result in changes in electronic properties to the signal side followed by changes in color, fluorescence, or electrochemistry in the system [1]. Two basic components of chemosensor design are: signal-site (fluorofore or chromofore) and recognition-site (receptors). Signal-site acts as a transducer that converts information (recognition events) into optical responses. Recognition-site is responsible for selectively and efficiently engaging with analytes. The ability of the sensor to detect analytes depends on the character of the ions and the molecular structure of the sensor, while still considering the solvent factor, pH, ionic strength, and its polarity [2].

In the process of recognizing sensor-specific interaction with the analyte, several photochemical mechanisms can be used, namely ICT (intermolecular charge transfer) and PET (photoinduced electron transfer). PET is based on the principle that in an excited state, the oxidative-reductive nature of the molecule increases and at that moment the electron transfer process occurs [3]. The recognition process of most analytes is a sensor-ion interaction (host-guest interaction) based on the selectivity of the host-guest complexation reaction [4]. The relationship between the sensor and the analyte can be seen as the interaction of the formation of a complex system of qualitative and quantitative host-guest chemosensors. The interpretation can be viewed mathematically from: (a) quantitative complex formation (determination of k_{ass}); (b) recognition quality (determination of detection limits). The calculation method is used as a criterion for evaluating the process of host-guest interaction based on its concentration. This method can be determined from UV-vis and 1H-NMR titration data [5].

In this project we will conduct a quantitative analysis of host-guest interactions that occur between the S8 sensor and the F ion ion during the recognition process.

EXPERIMENTAL

A total of 10 mmol of chalcone, 15 mL of DMSO, and 1 gram of I2 were added to the reaction flask. Then the mixture is refluxed for 1.5 hours, then the mixture is poured into 100 mL of cold distilled water. The precipitate formed is then recrystallized with ethanol. The solids obtained are determined by their melting point and characterized by FT-IR, mass spectra, 1H-NMR and 13C-NMR.

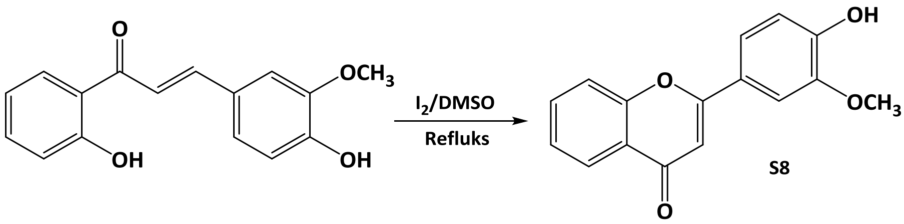


Figure 1. Pathway of synthesis of S8 compounds

A solvatochromic test is performed to observe the change in the color of the solution with respect to the solvent difference. A total of 0.134 g S8 was dissolved each with 5 mL of solvent: ethyl acetate, ethanol, and DMSO so that the concentration of each sensor in each solvent was 1×10^{-1} M. Then color changes were observed. Furthermore, each solution was diluted to obtain concentrations: 1×10^{-6} M, 1×10^{-7} M, and 1×10^{-8} M. Then absorbance was measured with a UV-vis spectrophotometer.

The ionochromic test was carried out by adding 3 drops of the saturated NaF solution to the S8/DMSO solution, then the color changes that occurred in the solution were observed and confirmed with a UV-vis spectrophotometer (in the range λ 200-800 nm) and spectrofluorometry. Host-Guest Interaction Analysis is done by titrating the S8/DMSO solution with NaF solution with a variety of concentrations, then the absorbance is measured.

RESULT AND DISCUSSION

The synthesized product is a creamy yellow powder with a yield of 74%, a molecular weight of 268 g/mol and a melting point of 189-192 ^{o}C. The S8 compound is completely dissolved in the DMSO solvent and gives a brownish yellow color. S8 compound at a concentration of 1×10^{-7} M gives absorption at λ 331 nm and produces a shoulder at λ 431 nm which proves the appearance of yellow in S8 / DMSO solution. Observation under UV light λ 366 nm shows the presence of fluorescent in S8 solution without anion (fluorescent 'on'), and fluorescent also observed in S8 solution added with F^- ions (fluorescent 'on') as in Figure 2.

The fluorescent treatment of S8/DMSO solution by titrating with F^- ions produced a titration solution under UV light λ 366 nm as shown in Figure 3.

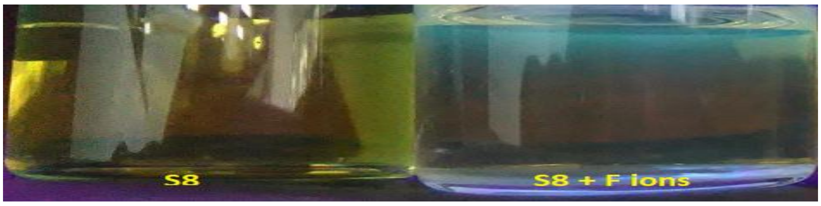


Figure 2. The response of S8 to F^- ions was observed under UV light λ 366

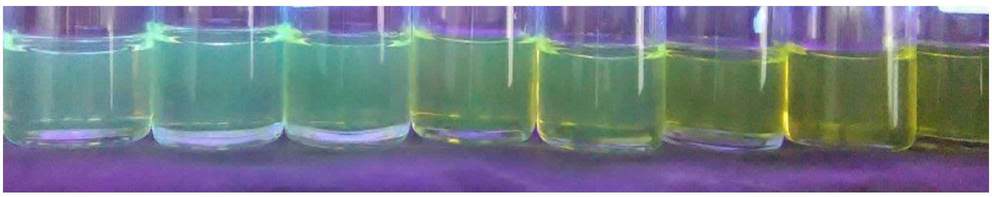


Figure 3. Visualization of S8 fluorescent titration with F^- ions

Quantitative analysis of the interaction of host-guest complex S8/F is carried out by measuring the intensity of fluorescence using a spectroflorometer instrument. The spectra of the measurement results are shown in Figure 4.

Without F^- ions, S8 experiences excitation at λ 400 nm and emissions at λ 450 nm with an intensity of 460000. The addition of 5×10^{-7} M ions (ek. 1) to 5×10^{-5} M (ek. 5) results in a decrease in fluorescent intensity, and the appearance of fluorescent intensity, and the appearance of the band at λ 710 nm indicates the electron transition π-π * from the chromophore [6].

Stoke's shift formed on a titration with CN^- of 80 nm and those formed on a titration with F^- of 280 nm indicates that the PET process has occurred in the S8-ion complex [7]. Large red shift on titration with F^- ions also causes the fluorescent to change color.

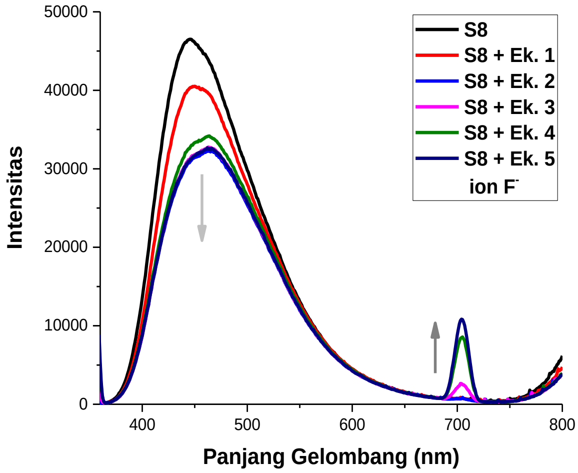


Figure 4. S8 fluorescent titration emission spectrum with ion F^-

Quantitative analysis of the formation of the S8/F^- host-guest complex is performed by calculating the LOD and k_{ass} values respectively and the complex interaction model based on fluorescent spectra data in Figure 4 and the Benesi-Hildebrand curve in Figure 5. Obtained LOD and k_{ass} values for the S8-F^- complex at a fluorescent titration are 6.43 × 10^{-4} M and 2 × 10^6 M^{-1}.

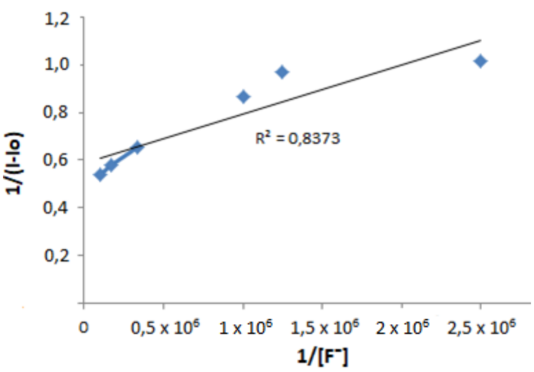


Figure 5. Benesi-Hildebrand curve of S8 titration with F fluorescent

Analysis of the S8/F^- complex host-guest interaction model is determined by calculating the stoichiometric ratio based on the Job's plot curve presented in Figure 6.

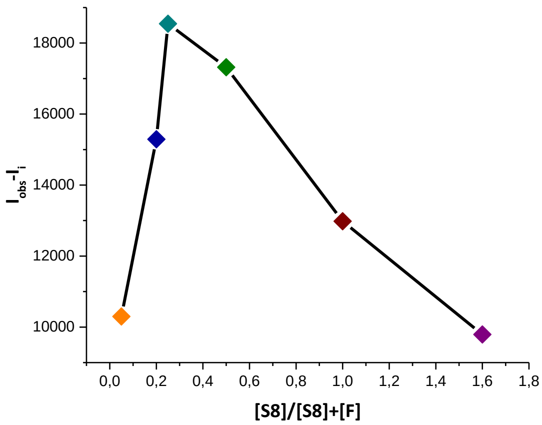


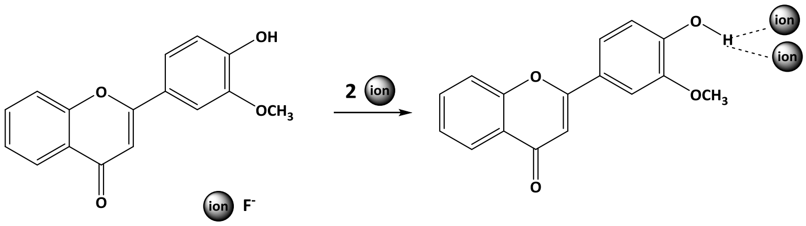
Figure 6. Job's curves plot S8 titration with F^- on fluorescent

Based on the curve in Figure 6, the interaction of the S8-F^- complex in fluorescent titration reaches its maximum intensity when fractionation is 0,25. The fractionimol 0.25 indicates that the host-guest interaction occurs when the S8/F^- stoichiometric ratio has a ratio of 1:2 [8-13].

The proposed interaction model of stoichiometric ratio is shown in Figure 6. The 1: 2 stoichiometric ratio shows that the interaction model occurs through the formation of hydrogen bonds by protons on the connective side of the -OH group of 1 S8 molecule with electrons of 2 Fon ion molecules so that the signal side provide a response in the form of complex fluorescent color changes.

CONCLUSION

The synthesized flavone derivative, S8, can recognize the presence of F ion ions in the S8/F^- ratio of 1: 2 with a response in the form of an increase in the fluorescent solution and the value of LOD and k_{ass} is 6.43 × 10^{-4} M and 2 × 10^6 M^{-1}



S8

Figure 7. The S8 host-guest interaction model with F¯ ions at a 1: 2 stoichiometric ratio

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References

[1] Bhatti, A. A., Oguz, M., & Yilmaz, M. (2020). New water soluble p-sulphonatocalix [4] arene chemosensor appended with rhodamine for selective detection of Hg2+ ion. *Journal of Molecular Structure*, *1203*, 127436.

[2] Aderinto, S. O., Xu, Y., Peng, H., Wang, F., Wu, H., & Fan, X. (2017). A highly selective fluorescent sensor for monitoring Cu 2+ ion: synthesis, characterization and photophysical properties. *Journal of fluorescence*, *27*(1), 79-87.

[3] Siraj, N., El-Zahab, B., Hamdan, S., Karam, T. E., Haber, L. H., Li, M., ... & Patonay, G. (2016). Fluorescence, phosphorescence, and chemiluminescence. *Analytical chemistry*, *88*(1), 170-202.

[4] Dybko, A., & Wroblewski, W. (2002). Analyte recognition and signal conversion in potentiometric and optical chemical sensors. *Polish Journal of Environmental Studies*, *11*(1), 5-10.

[5] Hirose, K. (2001). A practical guide for the determination of binding constants. *Journal of inclusion phenomena and macrocyclic chemistry*, *39*(3-4), 193-209.

[6] 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.

[7] Qin, J. C., Li, T. R., Wang, B. D., Yang, Z. Y., & Fan, L. (2014). A sensor for selective detection of Al3+ based on quinoline Schiff-base in aqueous media. *Synthetic metals*, *195*, 141-146.

[8] Tan, J., Wang, X., Zhang, Q., Zhou, H., Yang, J., Wu, J., ... & Zhang, X. (2018). Chalcone based ion-pair recognition towards nitrates and the application for the colorimetric and fluorescence turn-on determination of water content in organic solvents. *Sensors and Actuators B: Chemical*, *260*, 727-735.

[9] Sahana, A., Banerjee, A., Lohar, S., Banik, A., Mukhopadhyay, S. K., Safin, D. A., ... & Das, D. (2013). FRET based tri-color emissive rhodamine–pyrene conjugate as an Al 3+ selective colorimetric and fluorescence sensor for living cell imaging. *Dalton Transactions*, *42*(37), 13311-13314.

[10] Sivakumar, R., Reena, V., Ananthi, N., Babu, M., Anandan, S., & Velmathi, S. (2010). Colorimetric and fluorescence sensing of fluoride anions with potential salicylaldimine based schiff base receptors. *Spectrochimica Acta Part A: Molecular and Biomolecular Spectroscopy*, *75*(3), 1146-1151.

[11] Yue, G., Su, S., Li, N., Shuai, M., Lai, X., Astruc, D., & Zhao, P. (2016). Gold nanoparticles as sensors in the colorimetric and fluorescence detection of chemical warfare agents. *Coordination Chemistry Reviews*, *311*, 75-84.

[12] Rahmawati, R., Purwono, B., & Matsjeh, S. (2018). A Naked-Eye Colorimetric Receptor for Anions Based on Nitro Group Featuring with Benzimidazole Unit. *Asian Journal of Chemistry*, *30*(9), 1933-1936.

[13] Rahmawati, R., Purwono, B., & Matsjeh, S. (2017). A Novel 4-(1H-Benzimidazol-2-yl)-2-methoxy-phenol Derived Fluorescent Sensor for Determination of CN– Ion. *Asian Journal of Chemistry*, *29*(9), 1959-1962.