A Novel Fluorescens Sensor from Flavone Derivative: 2-(4-Hydroxy-3-Methoxicyclohexyl)4h-Chrom-4-on for Anions Recognition

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A NOVEL FLUORESCENS SENSOR FROM FLAVONE DERIVATIVE: 2-(4-hydroxy-3-methoxicyclohexyl)-4*H*-chrom-4-on FOR ANIONS RECOGNITION

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ABSTRACT

A novel chemosensor compound from flavone derivative (named: FS) has been successfully synthesized. FS activity as a chemosensor was tested by dripping FS/DMSO solution $1x10^{-1}$ M with CN^{-}, Cl^{-}, Br^{-}, I^{-}, and F^{-} ions. Naked-eye observations show that there is a change in the color of the solution from clear to light brown only in solutions that are dropped with CN^{-} ion. Observation under UV light λ366 nm showed that the FS/DMSO solution glowed in a solution dripped with CN^{-} and F^{-}, indicating that FS was fluorescent. Quantitative analysis was performed to see the quantity of FS host-guest interactions with ions, in the form of LOD, k_{ass}, and stoichiometric ratios. Performed by titrating the FS/DMSO $1x10^{-7}$ M solution with 50 μL of CN^{-}, F^{-} and I^{-} ions then measured on a UV-Vis instrument for colored solutions and fluorometry for fluorescent solutions. In the UV-Vis titration measurement, the LOD value of the complex FS-CN^{-} is 1.2×10^{-6} M and the k_{ass} is 2×10^{6} M^{-1}, in the fluorometric titration measurement the LOD value is 3.15×10^{-4} M and the k_{ass} is 1×10^{5} M^{-1}.

Keywords: chemosensor, fluorescent, flavone derivative.

INTRODUCTION

Environmental pollutants such as CN^{-} anions come from chemicals from industrial processes which can be bad because they can damage the environment, and in the long run this condition if left unchecked will threaten human life (Santi, 2004). So as to deal with or prevent the effects of pollution, deep detection is needed qualitatively and quantitatively.

In recent years, the development of research on optical chemosensors to detect important ionic species (pollutants), such as the CN^{-} anion, has received great attention from many researchers. Required material that can interact with pollutants so that it can detect the identity of pollutants. The observed physical changes due to chemosensory interactions with the analyte can be a change in color due to changes in absorption at a specific wavelength (λ) (color) or fluorescent changes.

In this work, the new chemosensor compound from flavone as receptor to detect ion anions has been synthesized. The advantages of this receptor are namely its simple structure. It has the substituent of OH group from its vanillin skeletons used as a binding site that forms hydrogen bonds with the anions, and has a high flourometri sensitivity to recognise anion with a low detection limit value. The behavior of this new compound towards anions was investigated by fluorescence spectroscopy in DMSO.

MATERIALS AND METHOD

Materials

All reagents for synthesis obtained commercially were used without further purification, its DMSO, aquadest, ethanol. The material synthesis : vanillin, 2-hydroxyacetofenone, alumina as a chatalys, DMSO and iodine. The anion were added in the form of sodium cyanide (NaCN salt) and sodium fluoride (NaF salt). All materials for synthesis is p.a quality Merck.

Method

Flavone Sensor synthesis is carried out using the Theja (2011) method with several modifications. A chalcone 10 mmol and 1 gram I_2 were dilute in 15 mL DMSO. A mixture was refluxed at the solvent boiling point for 1.5 hours (the progress of reaction was monitored by TLC), and then mixture was poured into 100 mL cold aquadest. After completion of reaction, the obtained solid was collected by filtration and purified by recrystalization from boiled ethanol, calculated its melting point, and characterized using FT-IR, MS, ^{1}H-NMR dan ^{13}C-NMR instrument.

Ion test is done by adding 3 drops of each saturated anion solution into each solution of the compound synthesized 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 of λ 200-800 nm) and spectrofluorometry. Data from the absorbance obtained were made by Benesi-Hildebrand curve and then the LOD and k_{ass} values were calculated.

RESULT AND DISCUSSION

The synthesized FS compound is a creamy yellow powder with a yield of 74%, a molecular weight of 268 g/mol and a melting point of 189-192 °C, completely dissolved in the DMSO solvent and gives a yellowish brown color, as shown in Figure 1. While in other FS solvents does not dissolve completely. The FS 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 the FS/DMSO solution.

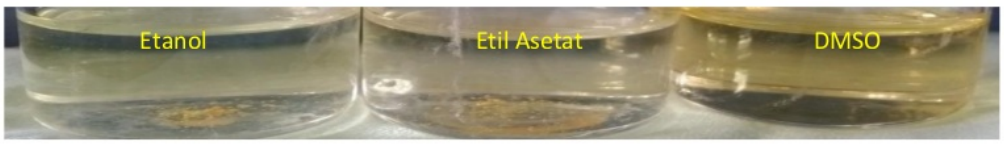


Figure 1. Solubility of FS in several solvents.

The FS sensor activity test was carried out at a concentration of 1×10^{-7} M which was added with 50 μL of saturated solution of ions: CN^-, F^-, Br^-, I^-, and $H_2PO_4^-$. The results of this ionochromic test are: there is a change in color to light brown on the addition of CN^- and no change in color on the addition of other ions. Observations under UV light λ 366 nm showed the presence of fluorescence in FS solutions without anions (fluorescent 'on'), and fluorescents were also observed in FS solutions added with ions of CN^- and F^- (fluorescent 'on'). Therefore FS is dual sensor, as a selective colori sensor for CN^- ions as well as an "on-on" fluorescent sensor for CN^- and F^- ions.

(a)

(b)

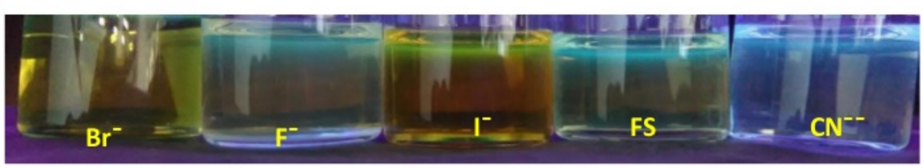


Figure 2. FS response to ions: (a) naked-eye observation; (b) observations under UV lamps λ 366.

UV-Vis Titration

The titration treatment takes place at a concentration of FS / DMSO solution 1×10^{-7} M, using 50 μL of CN ion ion solution with several variations of concentration. Figure 3 displays the results of FS titration with CN^- ions.

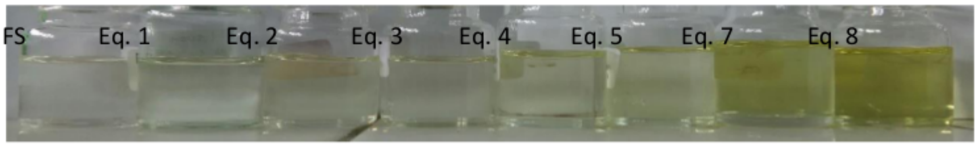
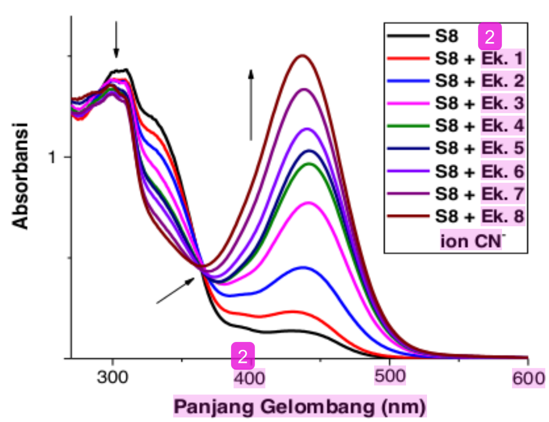


Figure 3. Visual results of FS titration with CN^-.

Qualitative analysis of FS/DMSO solution titration with CN^- ions was performed by UV-Vis spectroscopy and the measurement spectra are shown in Figure 4. Without the addition of CN ions the FS solution absorbs at λ 331 nm (A value 1.4) with a shoulder at λ 441 nm. The addition of 5×10^{-7} M (eq. 1) CN^- ions results in decreased absorbance and absorbance in the shoulder being increased, indicating that there has been an electron transition π-π * from chromophores (Reddy and Choi, 2018). The decrease in absorbance at λ 331 nm continues until the addition of 5×10^{-4} M (eq. 8) is followed by the continued increase in absorbance at λshoulder (441 nm) due to the n-π * transition (Singh et al, 2018) and at the same time formed isosbestic point at λ 370 nm. A batochromic shift of 109 nm occurred and isosbestic points formed showed that there was an interaction between FS and CN^- to form one type of active complex namely FS-CN^- (Singh et al, 2018).

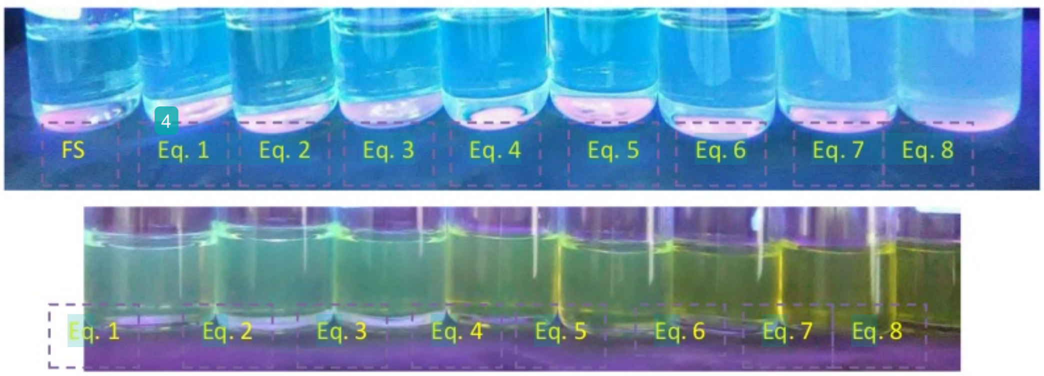


Gambar 4. Spectra titrasi UV-Vis FS dengan ion CN^- .

Fluorescent Titration

Fluorescent treatment of FS/DMSO solution by titration using CN^- menggunakan and F^- ion ions produced a titration solution under UV light λ 366 nm as shown in Figure 5.

Fluorescent FS compounds are light blue, with fluorescent color CN^- ions becoming thicker (deep blue) and with fluorescent F^- ions turning greenish. Addition of CN^- dan and F^- ions with a concentration of 5×10^{-7} M (eq. 1) to a concentration of 5×10^{-4} M (eq. 8) gradually produces a stronger intensity of fluorescent color. On the addition of F^- ions, the greeny fluorescent color on the addition of 5×10^{-7} M (eq. 1) ions becomes greeny yellow on the addition of 5×10^{-4} M (eq. 8).

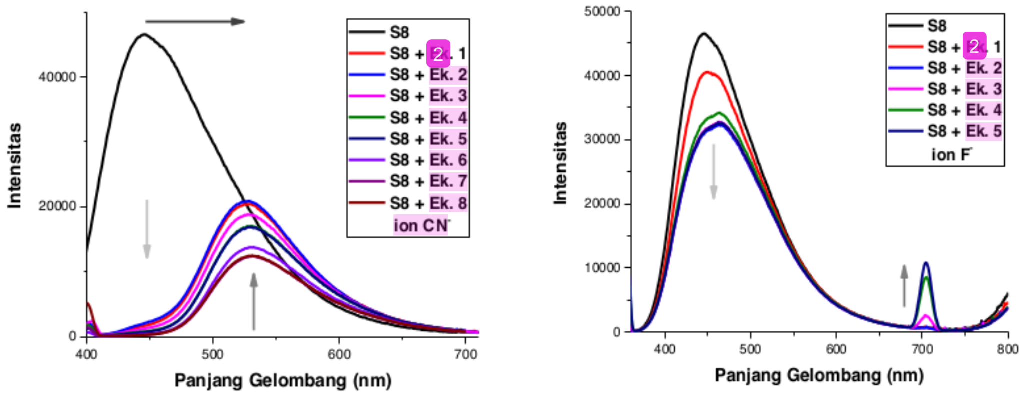


a

b

Figure 5. Visualization of fluorescent of FS titration with (a) CN ions and (b) F^- ions.

Quantitative analysis of the interaction of host CN-FS complexes was carried out by measuring the intensity of fluorescents using a spectrophotometer instrument. The spectra of the measurement results are shown in Figure 6.



(b)

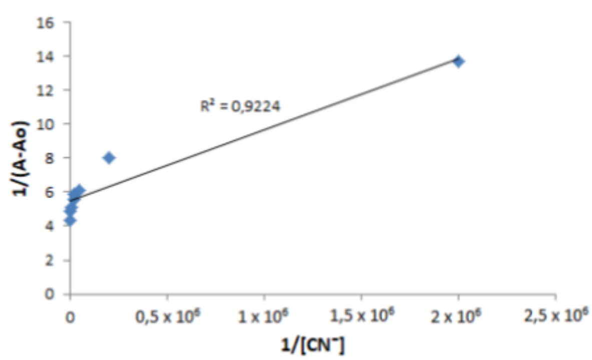
(a)

Figure 6. Spectra emission of FS fluorescents with (a) CN ions and (b) F^- ions.

Host-guest Interaction Analysis

Quantitative analysis of the formation of the FS-CN^-/F^- host-guest complex was carried out by calculating the LOD and k_{ass} values respectively and the complex interaction model based on UV-Vis and fluorescent spectra data and the Benesi-Hildebrand curve in Figure 7.

(a)



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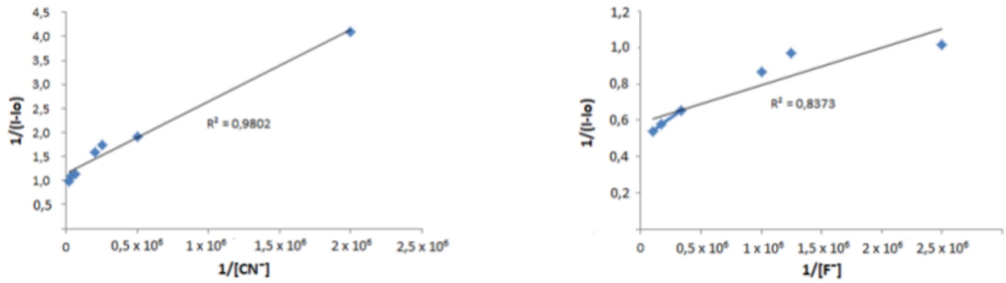

Figure 7. Benesi-Hildebrand curve of titration FS with CN ˉ and Fˉ on (a) UV-Vis and (b) fluorescent.

Obtained calculation results, the LOD and kass values for the FS-CN^- complex on UV-Vis titration are 1.2 × 10^{-6} M and 2 × 106 M^{-1}, the LOD and kass values for the FS-CN^- complex on fluorescent titration are 3.15 × 10^{-}4 M and 1 × 105 M^{-1}, and the LOD and kass values for the FS-F^- complex in fluorescent titration are 6.43 × 10^{-4} M and 2 × 106 M^{-1}.

CONCLUTION

This Flavone compounds group (FS) can be used as chemosensor to detect CN anions and F anions. The sensor response forms are colory with CN anion and fluorescent with CN anion and F anion.

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