

Effect of Solvent Media and pH on the Detection of Fluoride Ions Using UiO-66-NH₂

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Abstract—Detection of fluoride ions in various solvent media and pH has been successfully carried out using UiO-66-NH₂ as the fluorescent probe. UiO-66-NH₂ was synthesized via the hydrothermal method using various modulators such as Acetic Acid (AA) Formic Acid (FA), Hydrogen Chloride (HCl), and Hydrogen Fluoride (HF). The success of the synthesis was proven by characterization using X-Ray Diffraction (XRD), Fourier Transform Infrared (FTIR), and Scanning Electron Microscope (SEM). The results showed that UiO-66-NH₂ synthesized using HF as a modulator provided higher %crystallinity values and fluorescence intensity at the maximum emission peak at 428 nm. In the detection of fluoride ions in various solvent media, it was seen that the water medium gave the highest fluorescence intensity compared to THF, ethanol, acetonitrile, DMSO, ethyl acetate, DMF, toluene, and acetone media. Varying pH detection (3–11) of fluoride ions did not give significantly different results, but pH 7 gave higher detection fluorescence intensity results. Overall it can be concluded that HF is a very suitable modulator in synthesizing UiO-66-NH₂. Detecting fluoride ions provides the best fluorescence intensity in water and pH 7. The Limit of Detection (LoD) value obtained is 0.036 ppm with a linear range of 0–10 ppm.

Keywords—fluorescent, fluoride ions, pH, solvent media

I. INTRODUCTION

Fluoride ion (F⁻) is one of the most important ions in the human body's and everyday life's physiological processes. Fluoride ions prevent osteoporosis, cure dental problems such as cavities, and strengthen tooth enamel [1]. Fluoride ions are generally used as additives which are often added to toothpaste, pharmaceutical ingredients, and drinking water [2]. According to the Environmental Protection Agency (EPA) in the United States, the mandatory standard for fluoride ions in drinking water is 2 mg L⁻¹, while based on the provisions of the World Health Organization (WHO) the maximum limit for fluoride ions in drinking water is 1.5 mg L⁻¹ [3].

Fluoride ions are easily absorbed by the body but are excreted slowly, as a result, excessive exposure to fluoride ions can cause metabolic, structural, and functional damage to organs such as the stomach, kidneys, liver, nervous system, endocrine glands and reproductive system which can trigger cancer, as well as causes fluorosis of bones and teeth [4]. Therefore, the detection of fluoride ions is very important, especially in food and drinking water for human health and monitoring or detecting the presence of fluoride ion emissions in the aquatic environment.

Fluorescence-based detection of fluoride ions can be carried out using materials such as graphene oxide [2], ionofluorochromic derivative nanoparticles [5], tryarylboron-acridine hybrid materials [6], graphitic Carbon Nitride Quantum Dots (g-

CNQDs) [7], 4,4-difluoro-4-bora-3a,4a-diaza-s-indacene (BODIPY) [8], and Metal Organic Frameworks (MOFs) based materials such as UiO-66 [9]. In this research, we focused on examining the effect of different modulators on the crystallinity of UiO-66-NH₂ and the effect of detection media such as various organic solvents as well as the effect of pH on the detection of fluoride ions.

II. LITERATURE REVIEW

Metal Organic Frameworks (MOFs) are porous solid crystal materials arranged in a lattice of metal Secondary Building Units (SBU) with organic ligands as connectors, which are formed through coordination bonds [10]. In the last decade, MOFs have become a trending research theme in the field of materials chemistry, because they have high surface area and crystallinity, low density, tunable pore structure and distribution, and very wide applications [11].

Zirconium (Zr)-based MOFs such as MOFs-801, MOFs-808, UiO-66, UiO-67, and UiO-68 are the most widely developed types of MOFs today. It is because zirconium (Zr) is an abundant metal in nature and has low toxicity that the development and application of Zr-MOFs are growing so rapidly. Among the above types of Zr-MOFs, UiO-66, and UiO-66-NH₂ are the most popular Zr-MOFs due to their good stability in aqueous, acidic, and alkaline media [12, 13].

UiO-66-NH₂ has very wide applications in the field of sensors such as for the detection of lysine and arginine [14], detection of phosphate ions with a detection limit of 5–150 μM [15], UiO-66-NH₂ modified with 1-ethynylpyrene for the detection of 2,4,6-trinitrophenol with a detection limit of 4.5×10⁻⁷ M [16], detection of formaldehyde compounds using UiO-66-NH₂ 4-bromo-1,8-naphthalic and hydrazine with a response time of 20 seconds and a detection limit of 0.167 μM [17] and detection of fluoride ions using UiO-66-NH₂ nanoparticle material and γ-AIO(OH) nanowire with a detection limit of 0.77 μM [18].

III. MATERIALS AND METHODS

A. Materials

The materials used in this study are ZrOCl₂·8H₂O, 2-aminoterephthalic acid (H₂BDC-NH₂), NaF, NaOH, and HCl obtained from Merck corporation, and solvents acetone, ethanol, DMF, DMSO, toluene, THF, n-hexane obtained from Sigma-Aldrich corporation.

B. Synthesis of UiO-66-NH₂

UiO-66-NH₂ was prepared by modifying the procedure

[19], 125.85 mg of $ZrOCl_2 \cdot 8H_2O$ and 72.46 mg of $H_2BDC-NH_2$ were dissolved into 15 mL of DMF and then sonicated for 15 minutes. After sonication, 1 mL of 6, 9M HF, HCl, AA, and FA were added. Next, it was transferred into a 25 mL duran bottle and heated for 24 hours at 110 °C. The UiO-66-NH₂ solid suspension after being cooled at room temperature was centrifuged and washed with ethanol (3×20 mL) and then soaked for 24 hours with 20 mL of ethanol. The solid was then dried at 80 C for 24 hours to obtain a yellow powder.

C. Characterization

The synthesized UiO-66-NH₂ was characterized by X-Ray Diffraction, Fourier Transform Infrared (FTIR), and Scanning Electron Microscope (SEM). Determination of the maximum absorbance value was measured using UV-Vis spectrophotometry and measurement of fluorescence intensity using a spectrofluorometer.

D. Fluorescent Sensing Measurement

20 mg UiO-66-NH₂ was suspended in 10 mL DI water and sonicated for 5 mins. 1 mL of UiO-66-NH₂ suspension ($2 \text{ mg} \cdot \text{mL}^{-1}$) was mixed with 10 mL of 1000 ppm fluoride ion solution at pH 3-13. For the detection media effect, 2 mg of UiO-66-NH₂ was suspended in 1 mL of different solvents, then mixed with 10 mL of 1,000 ppm fluoride ion solution in various solvents, and then the fluorescence intensity was measured.

IV. RESULT AND DISCUSSION

To obtain UiO-66-NH₂ with high %crystallinity, we used four variations of acid modulators namely Acetic Acid (AA), Formic Acid (FA), Hydrogen Chloride (HCl), and Hydrogen Fluoride (HF) with the same concentration of 6.9M. The results showed that the highest %crystallinity of UiO-66-NH₂ was obtained using HF as a modulator which was 72.3% while AA was 69.8%, FA 64.9%, and HCl 69.2%. The successful synthesis of UiO-66-NH₂ is indicated by the XRD diffractogram (Fig. 1(a)) with the appearance of characteristic peaks at 2θ 7.39, 8.52, and 26.77° which are the (111), (200), and (600) crystal planes [20].

Fig. 1(b) shows the FTIR spectra of UiO-66-NH₂ with various acid modulators. Overall, the difference in modulators did not significantly affect the spectra produced. Typical peaks that show UiO-66-NH₂ has been successfully synthesized are the appearance of absorption peaks at wave numbers 482 cm^{-1} which is the vibration of Zr-OH, 659, and 771 cm^{-1} belonging to the rocking vibration of Zr-O-Zr. The bands at 1257, and 1380 cm^{-1} are C-N stretching vibrations, while the band at 1434 cm^{-1} indicates the existence of the C-O bond. Besides, the band at 1571 cm^{-1} was caused by the skeleton vibration of the benzene ring skeleton [18]. Fig. 1(c) shows the SEM image of UiO-66-NH₂ with non-uniform morphology.

UiO-66-NH₂ synthesized using HF as a modulator, in addition to providing high %crystallinity also provides the highest fluorescence intensity in the detection of fluoride (F^-) ions (Fig. 2(a)), therefore this material is used subsequently for the detection of fluoride ions in various pH variations and media. Fig. 2(b) shows the excitation peak at $\lambda = 328 \text{ nm}$ and the emission peak at $\lambda = 428 \text{ nm}$ caused by the $\pi-\pi^*$

electronic transfer of aromatic nuclei in UiO-66-NH₂ [18, 21].

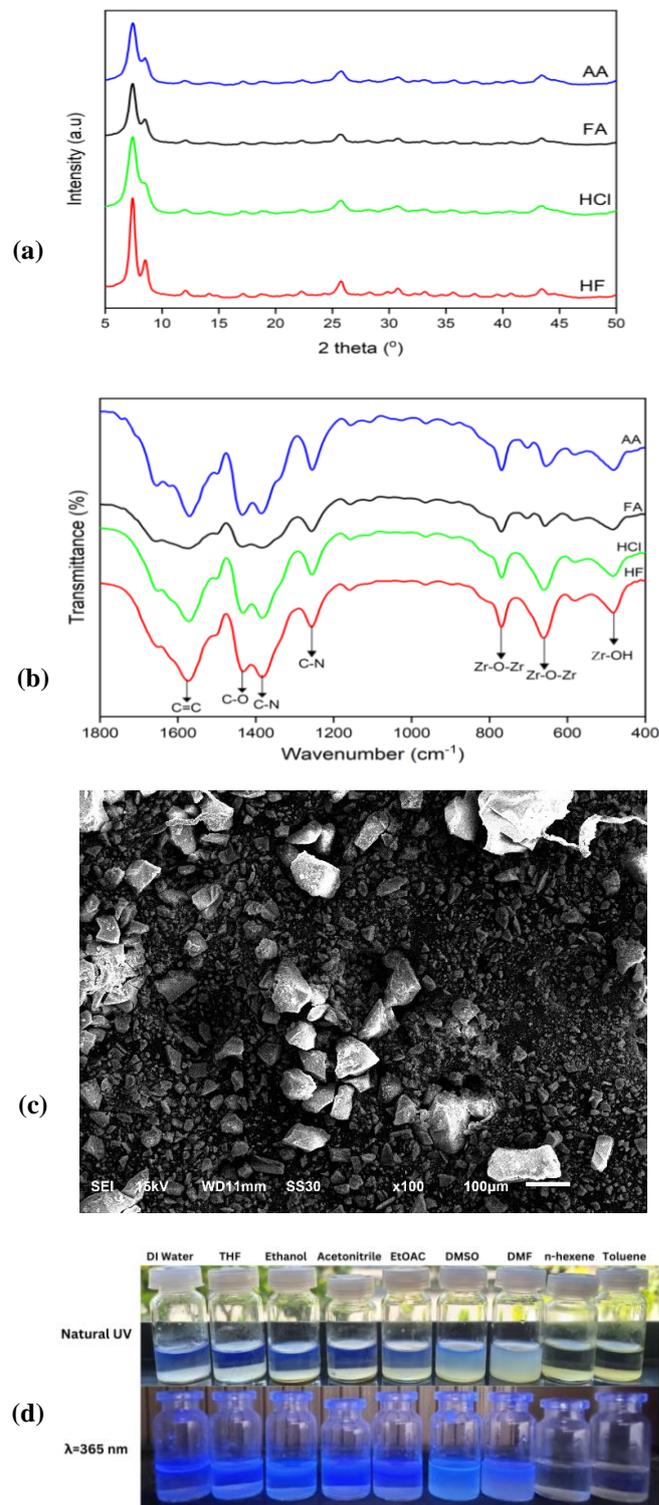


Fig. 1. (a) The XRD patterns of UiO-66-NH₂ with different acid modulators; (b) FTIR spectra of UiO-66-NH₂ with different acid modulators; (c) SEM image of UiO-66-NH₂; (d) Photoluminescence of fluoride ions in various media.

Fig. 2(c) shows the effect of solvent media on the detection of fluoride ions, based on the figure it can be seen that the detection of fluoride ions with water media has the highest fluorescence intensity, so it can be concluded that water media is a very suitable media for the detection of fluoride ions.

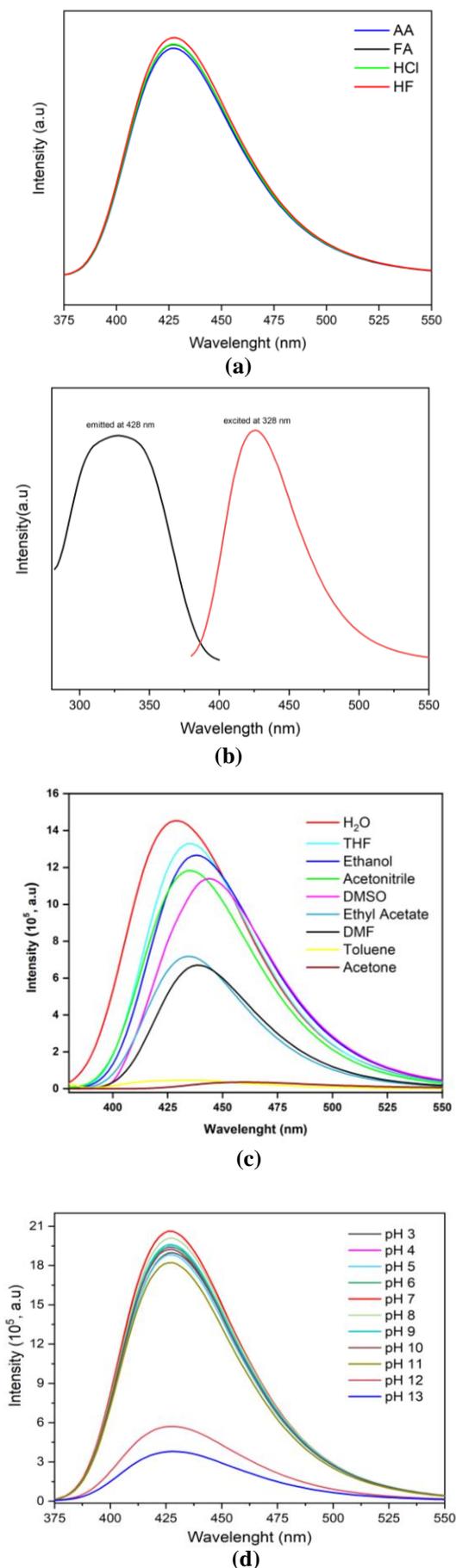


Fig. 2. (a) Fluorescence intensity of UiO-66-NH₂ with various acid modulators on F⁻ detection; (b) Excitation and emission of UiO-66-NH₂ after F⁻ addition; (c) The influence of solvent media on the detection of F⁻; (d) the effect of pH on the sensing performance of F⁻.

This phenomenon can be caused by two factors, namely the freedom of fluoride ions in the media, in this case, the solubility of NaF as a source of F⁻ in a medium, and the solubility of UiO-66-NH₂ in the media. Water has a very high polarity so it is very easy to dissolve NaF as a source of F⁻, on the other hand, UiO-66-NH₂ is also very easily suspended in water media so that the interaction between UiO-66-NH₂ with F⁻ in water media becomes very easy to occur. In contrast to toluene and acetone media which are non-polar solvents, making it difficult to dissolve NaF as a source of F⁻ and UiO-66-NH₂, as a result, the media does not provide fluorescence intensity as seen in Fig. 2(c) and does not provide a blue luminescence effect under natural UV light and UV lamp $\lambda = 365$. THF, ethanol, DMSO, acetonitrile, EtOAc, and DMF media also provide fluorescence intensity and blue luminescence (Fig. 3) so it can be said that these solvents can also dissolve NaF as a source of F⁻ and can suspend UiO-66-NH₂ so that the interaction of F⁻ and UiO-66-NH₂ in these media can occur.

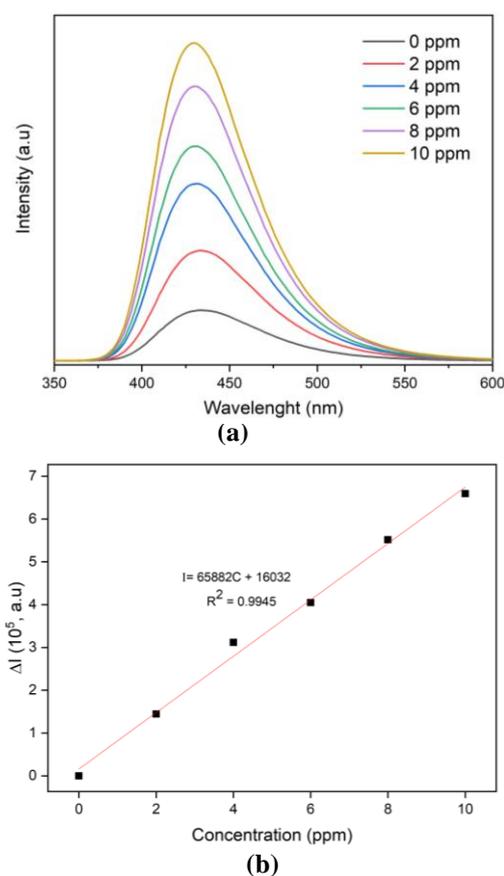


Fig. 3. (a) The fluorescence intensity of fluoride ions with different concentrations; (b) Linear plots of fluorescent intensity versus F⁻ ion concentration within 0–10 ppm.

The effect of pH on fluoride ion detection is shown in Fig. 2(d). From pH 3–11 the difference in fluorescence intensity is not significantly different, but the highest intensity where the pH is 7, so it can be concluded that under these conditions the stability of UiO-66-NH₂ is still stable. However, this is different when in very alkaline conditions (pH 12–13) there is a drastic decrease in fluorescence intensity, this can be caused by the amino groups in the UiO-66-NH₂ framework have been deprotonated and the abundance of OH⁻ ions in these conditions causes the movement of F⁻ ions in the media to be hindered, thus

reducing the interaction of F⁻ ions with UiO-66-NH₂.

The fluorescence intensity increases linearly with the increase of fluoride ion concentration in solution Fig. 3(a). The linearity relationship of intensity with fluoride ion concentration is shown in Fig. 3(b), it can be seen that the value of the regression coefficient ($R^2 = 0.9945$) shows a fairly good value. The linearity equation value is $I = 65882C + 16032$, where I is the emission intensity, and C is the fluoride ion concentration. Based on this value, the Limit of Detection (LoD) can be calculated using the equation ($LoD = 3\sigma/k$). σ is the standard deviation and k is the slope of the linear equation. The LoD value obtained is 0.036 ppm (0.036 mg·L⁻¹), a value much lower than the maximum limit of fluoride ions in drinking water determined by the World Health Organization (WHO) of 1.5 mg·L⁻¹ and the Environmental Protection Agency (EPA) of 2 mg·L⁻¹.

V. CONCLUSION

In this research, we focus on the synthesis of UiO-66-NH₂ with various acid modulators and the detection of fluoride ions in various media and pH. The synthesis of UiO-66-NH₂ using HF as a modulator gives higher % crystallinity and fluorescence intensity than other modulators. Water media and pH 7 are appropriate conditions for fluoride ion detection using UiO-66-NH₂. The LoD value obtained is 0.036 ppm which is much lower than the maximum limit for fluoride ions in drinking water determined by the World Health Organization (WHO) and the Environmental Protection Agency (EPA).

CONFLICT OF INTEREST

The authors declare no conflict of interest.

AUTHOR CONTRIBUTIONS

Muh Rizal B—Conducted the research, validation, formal analysis, investigation, and writing the original draft; Mudasir—Validation, formal analysis, writing-review and editing; Fajar Inggit Pambudi—Conceptualization, validation, formal analysis, writing-review, and editing.

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