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# Synthesis and Characterization of Fe(II) Complex Compounds with Schiff Base Ligands of 4-Dimethylamino Benzaldehyde and Aniline as Dye Sensitized in Dye Sensitized Solar Cell (DSSC)

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## ABSTRAK
Sintesis dan karakterisasi kompleks Fe(II) dengan ligan basa Schiff 4-dimetilamino benzaldehida dan anilin telah dilakukan dengan perbandingan konsentrasi 1:1. Kristal dasar Schiff yang dihasilkan berwarna jingga dengan rendemen 78%. Sintesis senyawa kompleks Fe(II) menghasilkan kristal kuning dengan rendemen 86%. Analisis menggunakan spektrofotometer UV-Vis menunjukkan panjang gelombang maksimum pada daerah transisi π* dari gugus azometina dasar Schiff sebesar 355 hingga 565 nm setelah pengkompleksan. Analisis DTA TGA menunjukkan tiga kali kehilangan berat, kehilangan massa pertama terjadi pada suhu 200-276,7oC sebesar 10,09%, kehilangan massa kedua terjadi pada suhu 276,7-379oC sebesar 85%, dan kehilangan massa terjadi pada suhu 389,4 – 600,4oC sebesar 15% yang kehilangan satu molekul Fe2O3 yang merupakan residu sebesar 17,29% , hasil pengujian DSSC diperoleh arus kuat dan tegangan memiliki efisiensi tertinggi sebesar 2,086%.

Kata kunci : Sintesis, karakterisasi, kompleks Fe(II), azometin, kristal.

## ABSTRACT
Synthesis and characterization of Fe(II) complex with Schiff base ligand of 4-dimethylamino benzaldehyde and aniline has been carried out with a concentration ratio of 1:1. The resulting Schiff base crystal is orange with a yield of 78%. The synthesis of Fe(II) complex compound producing yellow crystals with a yield of 86%. Analysis using UV-Vis spectrophotometer showed a maximum wavelength in the transition region π* from basic azometina group of Schiff by 355 to 565 nm after complexing. DTA TGA analysis showed three times the weight loss, the first mass loss at a temperature of 200-276.7$^{o}$C of 10.09%, the second mass loss occurs at a temperature of 276.7-379$^{o}$C by 85% which, and mass loss occurs at a temperature of 389.4 – 600.4$^{o}$C by 15% which loses one molecule of $Fe_2O_3$ which is a residue of 17.29% , DSSC test results obtained strong current and the voltage has the highest efficiency of 2.086%.

Keyword: Synthesis, characterization, Fe(II) complex, azomethine, crystal.

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**INTRODUCTION**

Electrical energy is one of the most important energies in human life, ranging from basic to commercial needs, most of this energy need is met by natural energy sources, namely from fossil fuels, but its availability is decreasing and cannot be renewed, so energy is still a problem. Sustainable until now (Hadi, 2016). Sunlight is the most effectively used in Indonesia because Indonesia is a tropical country (Gong et al., 2015). The solar cell technology is called Dye sensitized solar cell (Kalyanasundaram, 2010). DSSC is a solar cell coated with a dye to increase the efficiency of sunlight conversion. DSSC consists of several components, namely working electrode, electrolyte, semiconductor, dye or dye sensitized, and reference electrode. DSSC efficiency is influenced by its constituent components, one of the most important components in DSSC is dye sensitized or dyes to absorb photons from sunlight and convert them into electrical energy (Al-Barody, 2018).

*Dye sensitized* using a ruthenium complex compound can produce an efficiency of up to 11%, but the ruthenium complex requires a complex synthesis process and high costs because it belongs to the noble metal group (Shalini et al., 2018). Other complex compounds are widely used to replace ruthenium complexes because they have several advantages, namely more chemical and thermal stability, lower costs, and easier synthesis processes (Chadijah, 2012). Complex compounds synthesized from ferrous metal have been applied to DSSC in several studies such as those conducted (Mardiana, 2014) using Fe(II)-congo red which resulted in an efficiency of 3.32% and using Fe(II) -bipyridyl produces an efficiency of 3.96% on a variation of the gel electrolyte with a concentration of 0.15 M, in addition, synthetic organic dyes as dye sensitized in DSSC have been widely used, one of which is using Schiff base (Soliman, 2020). Many previous researchers have succeeded in synthesizing Schiff base compounds through condensation reactions, based on the results of reports of several researchers, the condensation method is used because the process is relatively faster and simpler (Sembiring et al., 2013).

Research conducted (Ghann et al., 2017) have synthesized Schiff base from salicylaldehyde with ethylenediamine and applied it as dye sensitized in dye sensitized solar cell (DSSC), the results of performance measurements on DSSC showed that the use of Schiff base resulted in an efficiency of 0.14% (Ghann et al., 2017). Naik et al. (2018) has succeeded in synthesizing metal-free organic dyes in the form of Schiff base from 4-dimethylaminobenzaldehyde and para-aminobenzoic acid. The synthesis was carried out using the reflux method in methanol for 5 hours.

## EXPERIMENTAL

The materials use include Aniline pa Merck, 4-(dimethylamino) benzaldehyde pa Merck, acetic acid, alcohol 96%, $TiO_2$ powder, Whatman Paper 42, polyethylene glycol (PEG) 6000, acetonitrile pa Merck, potassium iodide, iodine ($I_2$), Indium Tin Oxide (ITO) glass measuring 2 x 2 cm x 1 mm, aquabides and Mohr's salt $(NH_4)_2 Fe(SO_4)_2.6H_2O$, multimeter Zotek ZT111, UV-Vis spectrophotometer, IR spectrophotometer Agilent Cary 660 and Differential Thermal Analysis-Thermogravimetry Analysis (DTA/TGA).

### Schiff Base Compound Synthesis

Schiff base compound was synthesized by mixing two ingredients, namely aniline and 4-dimethylamino benzaldehyde using a mole ratio [1:1], as much as 0.92 mL (1 x $10^{-2}$ mol ) of aniline is dissolved in 10 mL of ethanol, then the resulting solution is mixed with 4-dimethylamino benzaldehyde as much as 1.4919 grams (1 x $10^{-2}$ mo1) which has been dissolved in 10 mL of ethanol. 4-dimethylamino benzaldehyde solution and aniline solution were mixed in a 50 mL round bottom flask and added 4 drops of acetic acid then refluxed for 45 minutes at 78°C using a hot plate, then cooled in a desiccator at room temperature until crystals formed. The crystals formed were washed using 10 mL of distilled water, filtered with Whatman 42 filter paper, then dried again in a desiccator and weighed until a constant weight was obtained.

### Synthesis of Schiff Base Fe(II) Complex Compounds

Before synthesizing the Fe(II) complex with a Schiff base, the stoichiometry of the Fe(II) complex with a Schiff base was calculated. Determination of stoichiometry of complex compounds was carried out by mixing Schiff base ligands with Fe(II) metal ions based on variations in Schiff base concentration as presented in Table 1.

**Table 1.**Stoichiometric comparison of complex compounds with Schiff base

| No | Fe(II) ($10^{-2}$ mol) | Schiff Base ($10^{-2}$ mol) |
|---|---|---|
| 1 | 1 | 1 |
| 2 | 1 | 2 |
| 3 | 1 | 3 |

The formation of complex compounds from each variation was carried out by a reflux process for 2 hours at a temperature of 78°– 80°C using a magnetic stirrer. The complex compound formed was washed using distilled water, filtered with Whatman 42 filter paper and dried in a desiccator to constant weight. The complex compounds formed were then characterized using UV-Vis spectrophotometer, IR spectrophotometer and DTA/TGA.

### Dye Sensitized Solar Cell (DSSC) Fabrication

### $TiO_2$ Paste Manufacturing

$TiO_2$ paste made from 0.5 grams of $TiO_2$ powder which was ground, sieved, and put into a beaker, then added 2 mL of ethanol and stirred for 15 minutes. $TiO_2$ paste has been formed mixed with 0.25 grams of Schiff base compound then stirred for 15 minutes, then both are stored in a closed bottle.

### Gel Electrolyte Manufacturing

Gel electrolyte was made from a mixture of 0.5 M KI solution, 0.05 M $I_2$, and 0.1 M PEG 6000, as much as 0.498 grams of KI was dissolved in 6 mL of acetonitrile, then the solution formed was mixed with 0.076 grams of $I_2$ which had been dissolved into 6 mL of acetonitrile. The mixture was added 2.4 grams of PEG 6000 and stirred with a magnetic stirrer until homogeneous.

**Reference Electrode Preparation**

The preparation of the reference electrode was carried out on the conductive side of the ITO glass with candle flame soot. 3 pairs of ITO glass were washed with 96% alcohol, then dried, then tested using a digital multimeter to determine the conductive side. The conductive side of the ITO glass is covered with scotch tape at the edges, leaving a size of 1 x 1 cm. The ITO glass is then burned using soot from a candle flame.

**DSSC Component Assembling**

Solar cells assembled with preparing three cleaned ITO glasses, the three ITO glasses measuring 2 x 2 cm were formed in an area where a mixture of $TiO_2$ with a Schiff base Fe(II) complex compound was deposited and deposited with the help of tape on the conductive glass to form an area of 1 x 1 cm. The layer was dried for 10 minutes and heated at a temperature of 200ºC for 10 minutes, then the three variations of the polymer gel electrolyte were dripped each on the surface of the three glasses contained. a mixture of $TiO_2$ paste with a Schiff base Fe(II) complex. Pin the first glass dripping with 0.025 M electrolyte gel solution, the second glass with 0.05 M electrolyte gel solution, and the third glass with 0.1 M electrolyte gel solution, then each glass is covered with a counter electrode so that it forms a sandwich structure , then so that the cell structure is firmly clamped with a paperclip. The three solar cells that have been assembled were tested for voltage with a Zotek ZT111 digital multimeter. The light source used is direct sunlight when bright irradiation.

## RESULTS AND DISCUSSION

**Schiff base compound**

Schiff base compound obtained from the synthesis in the form of yellowish brown crystals as much as 1.7480 g with a yield of 78% is shown in figure 1. Schiff base compounds were characterized using UV-Vis spectrophotometer, and infrared (IR) spectrophotometer to determine the maximum wavelength and functional groups of the synthesized Schiff base.

**Figure 1.**Synthesized Schiff base crystall solid

The UV-Vis spectrum shown in Figure 2 shows the presence of 3 absorption peaks of the Schiff base compound. The absorption at a wavelength of 202 nm and an absorbance of 0.321 was formed due to the influence of the solvent used. Absorption at a wavelength of 237 nm with an absorbance of 0.153 indicates the presence of a chromophore of benzene which has a transition π→π*, because benzene absorbs at a wavelength between 230-270 nm. The wavelength of the synthesized Schiff base is formed at a wavelength of 355 nm with an absorbance of 0.348 and has a transition of n→π*.

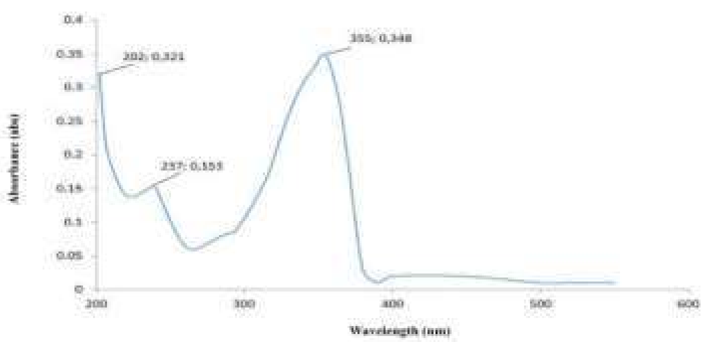


**Figure 2.** UV-Vis spectrum of Schiff base synthesis

The data on the wavelength of the synthesized Schiff base and its constituent compounds are shown in Table 2. Table 2 shows that the compound 4-(dimethylamino) benzaldehyde has a maximum wavelength of 340 nm, and aniline with a maximum wavelength of 285 nm.

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**Table 2.**Schiff base wavelength data and its constituent compounds

| compounds | $\lambda_1$ (nm) | $\lambda_2$ (nm) | $\lambda_{max}$ (nm) | Reference |
|---|---|---|---|---|
| 4-DMAB | 245 | - | 340 | NIST Standard Reference Data, 2019 |
| Aniline | 205 | 232 | 285 | Kumar, 2006 |
| Schiff Base | 202 | 237 | 355 | - |

The IR spectrum of the synthesized Schiff base is shown in Figure 3.

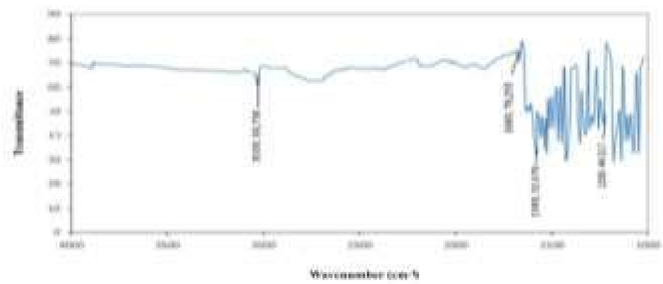

**Figure 3.**Synthesized Schiff base IR spectrum

The IR spectrum of the synthesized Schiff base in Figure 3 shows the azomethine absorption peak (-C=N-) that appears in the 1660 $cm^{-1}$ area, the absorption is in accordance with the research of Tai et al. (2003) which states that the Schiff base generally forms absorption in the wave number region of 1600-1660 $cm^{-1}$. Absorption band (C-N) bound to the aromatic ring is characterized by the appearance of a peak at the absorption 1150-1350 $cm^{-1}$. The wavenumber data obtained from each particular functional group bond is shown in Table 3.

**Table 3.**Schiff base IR spectrum data and its formation compounds

| | *v* (C=N) | *v(* N-H) | *v* (C=O) | *v* (C=C) | *v* (C-N) | *v* (C-H) |
|---|---|---|---|---|---|---|
| 4-DMAB | - | - | 1694 | 1552 | 1240 | 2906 |
| Aniline | - | 3358 | - | 1497 | 1275 | 2924 |
| Schiff Base | 1660 | - | - | 1580 | 1230 | 3028 |

The results of the analysis indicate that the Schiff base has been successfully synthesized due to the absence of absorption of the carbonyl and amine groups, as well as the appearance of the azomethine group which is a typical group of Schiff base compounds.

**Schiff Base Fe(II) Complex Compounds**

The synthesis of the Schiff base Fe(II) complex produced dark yellow crystals as much as 0.92 g with a yield of 86%.

**Figure 4**. Crystall solid compound Fe(II) synthesized base Schiff

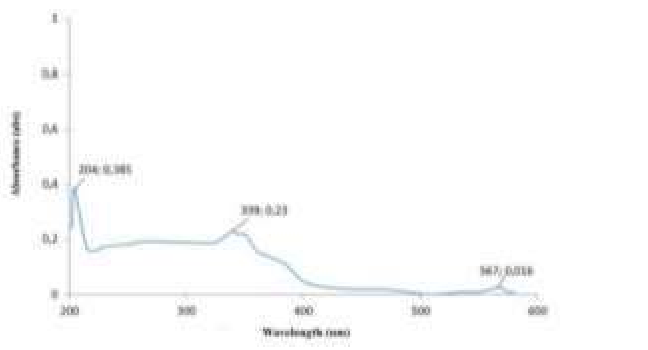

**Figure 5.** UV-Vis spectrum of the synthesized Fe(II) base Schiff complex

Based on Figure 5, it is known that a new compound has been formed, in terms ofthe presence of a chromophore in the azomethin group which undergoes an $n \rightarrow \pi^*$ transition and causes a shift in the maximum wavelength of 355 to 565. After being characterized using a UV-Vis Spectrophotometer, then characterized using a Spectrophotometer IR, IR spectrum of the Schiff base Fe(II) complex is shown in Figure 6.

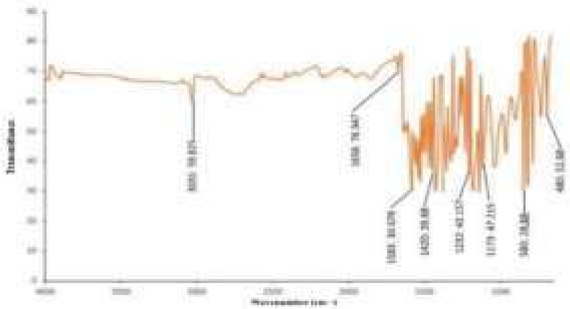

**Figure 6.** IR spectrum of synthesized Schiff base Fe(II) complex compound

The wave number data obtained from the synthesized Fe(II) Schiff base complex is shown in Table 4.

**Table 4.** Data on the IR spectrum of the Schiff base Fe(II) complex and its constituent compounds

| Compounds | *v* (Fe-N) | *v* (C=N) | *v( C=C)* | *v* (C-N) | *v* (C-H) |
|---|---|---|---|---|---|
| Ligand | - | 1660 | 1580 | 1230 | 3028 |
| complex compound | 580 | 1658 | 1583 | 1232 | 3031 |

The absorption band that appears does not show a significant shift. Additional vibrations appear in the 580 $cm^{-1}$ region on the infrared spectrum of complex compounds indicating the presence of Fe bonds with N and indicating that the synthesized complex compounds have been formed, then at wave number 1173 $cm^{-1}$ indicates the presence of $SO_4^{2-}$ groups and when reacted with ligands Schiff base ligand substitution occurs so that the $SO_4^{2-}$ ion is replaced with a stronger ligand, the Schiff base ligand (Nakamoto, 2009).

***Differential Thermal Analysis- Thermogravimetric Analysis (*****DTA-TGA)**

The DTA-TGA thermogram of the synthesized Schiff base complex is shown in Figure 7. In the DTA-TGA thermogram, there are two curves, namely the DTA curve which shows the heat involved in each mass change process and the TGA curve which shows the change in mass of the Schiff base Fe(II) complex.

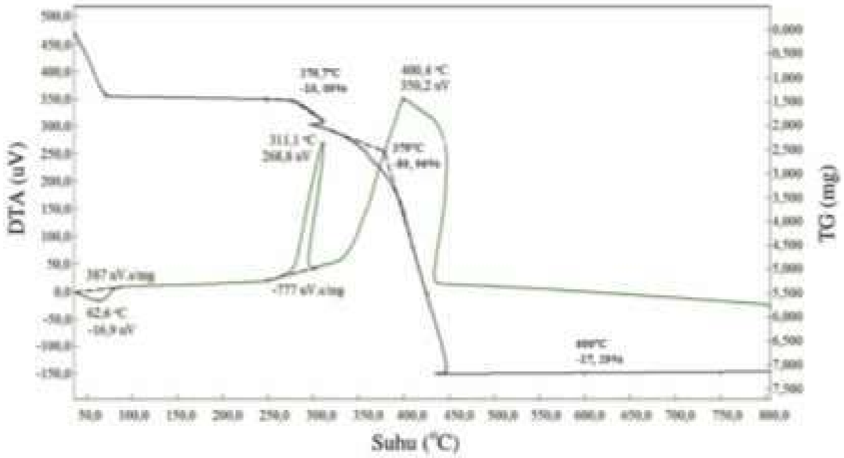


**Figure 7.** Thermogram of DTA-TGA complex Fe(II) base Schiff

The DTA curve in Figure 7 shows the presence of an endothermic peak at a temperature of 62.6°C which means that heat absorption occurs by the sample which is characterized by a decrease in the temperature of the sample so that the DTA curve obtained as a minimum peak, there are two exothermic peaks at a temperature of 311.1°C and 400.4°C indicates the occurrence of heat release by the sample which is characterized by an increase in temperature of the sample so that the DTA curve obtained is the maximum peak.

**Application of Schiff Base Fe(II) Complex Compounds on Dye Sensitized Solar Cell (DSSC)**

The Dye Sensitized solar cell that has formed the sandwich is clamped with plastic clamps so it doesn't move easily. Candle flame soot was chosen for the preparation of DSSC on the carbon electrode because in previous studies other variations have been used, but the most optimum efficiency results are those using candle flame soot. then tested the energy conversion ability with illumination from sunlight using a digital multimeter as shown in Figure 8.

**Figure 8**. Testing process under the sun

The solar cell has succeeded in converting sunlight energy into electricity as indicated by the values of voltage, current, and efficiency in Table 5.

**Table 5.** Data from measurement of voltage (mV), current strength (mA), and efficiency (Ƞ) DSSC

| PEG electrolyte concentration (M) | (mV) | (mA) | Ƞ (%) |
|---|---|---|---|
| 0.025 | 650 | 0.6 | 0.39 |
| 0.05 | 1120 | 0.9 | 1.008 |
| 0.1 | 1710 | 1.22 | 2.086 |

The maximum efficiency of converting solar energy into electrical energy is obtained at 0.1 M PEG electrolyte concentration, which is 2.086% with a voltage of 1710 mV and a maximum current generated of 1.22 mA.

## CONCLUSION

Based on the results of the research and discussion, the conclusions obtained from this research are the Schiff base ligands synthesized from Schiff's base ligand was synthesized from 4-dimethylaminobenzaldehyde and aniline with acetic acid as an orange solid with a yield of 78%, the synthesized compound Fe(II) base Schiff is a brownish yellow crystalline solid with a yield of 86%, characterization results with UV-Vis, IR and DTA-TGA showed that the complex compound with the synthesized Schiff base ligand could be used as a sensitizer in DSSC. DSSC measurements showed a maximum efficiency of 2.086% on a variation of 0.1 M PEG gel electrolyte with a voltage of 1710 mV and a current of 1.22 mA.

## ACKNOWLEDGMENTS

Based on the research that has been done, it is recommended that further research needs to be characterized using SEM-EDX to determine the morphology and composition of the compound, and it is recommended to add variations in the concentration of the gel electrolyte so that the data obtained is more complete and the DSSC efficiency value will be greater.

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