Dye-sensitized solar cells with napthol blue black as dye sensitizer

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Abstract. Nowadays, fossil fuel supply is decreasing over time. Thus, people are required to look for alternative energy sources that are renewable and environmentally friendly. Dye-Sensitized Solar Cells (DSSC) is one of the promising sources to overcome those problems. In this research, a DSSC with napthol blue-black (NBB) as dye sensitizer has been developed. In order to improve the performance of the DSSC, NBB was modified by inserting Fe to form Fe-NBB complex compound. Fe-NBB showed light harvesting characteristic through MLCT phenomenon (Metal to Ligand Charge Transfer) at 273 nm and metal-ligand bonding at 486.06 cm⁻¹ and 316.33 cm⁻¹. NBB and its derivatives (Fe-NBB) were applied as dye sensitizer in the DSSC. The obtained open circuit voltage, short circuit current, and efficiency for NBB were 0.218 V, 0.096 mA/cm² and 0.0083 %, respectively. While, Fe-NBB were 0.363 V, 0.567 mA/cm² and 0.0925%.

1. Introduction
Energy consumption in Indonesia mostly comes from fossil fuels where the demand is always increasing along with the increasing population in Indonesia [1]. On the other hand, the issue of liquid waste from textile industries such as Batik industries still demanding to be solved [2, 3]. However, the energy reserves is decreasing over time so looking for other alternative energy sources that are environmentally friendly become significant [4-6]. One of the sources of energy that is environmentally friendly and renewable is sunlight. Solar cells are a technology that produce electrical energy from solar energy conversion. The third generation of solar cell is DSSC (Dye Sensitized Solar Cell) is highly potential to be applied because it is cheaper to manufacture and is environmentally friendly [7]. Dye Sensitized Solar Cell consists of several components, namely a working electrode, dye (dye), a comparison electrode, semiconductor Titanium Dioxide (TiO₂) and electrolyte between the two electrodes [8]. The working electrode of DSSC consist of semiconductor and dye sensitizer which is usually an organic dye that absorbs sunlight [9, 10].

In Dye Sensitized Solar Cell (DSSC), the working electrode cannot work optimally without the dyes role. The dyes used in this study are synthetic dyes from the complex compound Fe(II)-naphtol blue black and for the rest will be wrote in Fe-NBB. This dye is synthesized from ferrous metal and naphtol blue black ligands. Iron metal was chosen because it has many (sub energy orbital) term symbols to produce sensitization from nano-crystalline TiO₂, and also has photo-physical properties similar to the
ruthenium complex [11, 12]. On the other hand, naphtol blue black was chosen because it has the ability to capture sunlight so that it potent to be applied as a dye sensitizer for DSSC. Naphtol blue black also has a chromophore group, has a conjugated double bond and has a maximum wavelength in the UV region so that it can capture sunlight wave energy [2, 6]. Another reason naphtol blue black was chosen because according to previous studies, ligands that are anionic have greater efficiency than cationic ligands [4].

In this study, NBB was modified by inserting Fe to the NBB structure through formation Fe-NBB complex compound. Furthermore, the synthesized Fe-NBB were characterized using a UV-Vis spectrophotometer, Fourier Transform Infrared (FTIR), and conductometer. The TiO₂ sol gel thin layer was used as the semiconductor and KI₃ as an electrolyte solution for the DSSC cells. The photovoltaic performance of complex Fe-NBB was determined from the measurement of the current and voltage by the multimeter.

2. Material and Methods

2.1 Synthesis of Fe-NBB complex

Weighed 0.3920 grams Mohr salt [(NH₄)₂Fe(SO₄)₂.6H₂O] and 1.8495 grams of Naphtol Blue Black powder then each was dissolved using ethanol, mixed and stirred for 15 minutes, then refluxed at 78 °C for 90 minutes. Then the solution was heated until a third of the remaining solution. Furthermore, the precipitate was filtered using a Buchner funnel, washed with heated ethanol and then dried [13].

2.2 Characterization of Fe-NBB complex

The solid Fe-NBB complex were analyze the absorption band characteristics using a UV-VIS spectrophotometer, FTIR spectrophotometer to analyze metal bonds with the NBB structure and a conductometer to analyze the electrical conductivity of complex compounds.

2.3 Photovoltaic assay of Fe-NBB complex

2.3.1 Preparation of sol-gel titanium dioxide as a semiconductor on DSSC. The TiO₂ sol gel was prepared according [14]. First, 5 mL of Triton X-100 solution was reacting with 12 mL of acetic acid. The solution then dissolved with 225 mL of ethanol and stirred for 3 minutes. On the other hand, 15 mL of TiO₂ precursor solution Titanium isopropoxide (TTIP) was mixed by 1 mL of HCl. Furthermore, Triton X-100 and TTIP solution were mixed and stirred for two hours until the sol is formed. The finished sol is ready to be coated on a glass plate.

2.3.2 Preparation of a working electrode on DSSC. The TiO₂-coated glass plate was then immersed in a 10⁻² M solution of the complex Fe-NBB in a petri dish for 24 hours until the complex Fe-NBB immersed homogenously [15]. For long-term use, after the coating process, the glass plate is stored in a closed dark bottle and as much as possible is avoided from scratches that can damage the TiO₂ layer.

2.3.3 Preparation of a counter electrode on DSSC. The surface of the glass plate was coated with graphite using a graphite pencil then the glass plate was evenly re-coated with carbon from wax smoke [4, 5].

2.3.4 Assembling of DSSC device. The working electrodes that have been made before were removed from the storage area, then the working electrode was attached with the counter electrode facing each other and are arranged in such a way that a layer of Fe-NBB on the top. Between the two electrodes was drooped by KI₃ electrolyte solution, an electrolyte is KI₃ that prepared from solution of I₂ in KI solution. Then the two electrodes were pressed against each other, then clamped at the edges using clamp clips, thus forming a series of solar cells. The DSSC circuit that has been assembled was connected to a multimeter where the (+) pole on the multimeter was connected to the counter electrode while the pole
(-) of the multimeter was connected to the working electrode then the maximum current and voltage were measured. Measurements were made in a bright place under the sun directly. The intensity of the incoming sunlight was measured by a light meter (luxmeter) [16].

3. Result and Discussion
In this research, napthol blue black was successfully applied as a dye sensitizer on DSSC. In order to increase their performance, the structure of NBB was modified by iron (Fe(II)) through complex compound formation Fe-NBB.

3.1 The result of synthesis Fe-NBB complex
The complex Fe-NBB was made by reacting Fe (II) as a metal from Mohr salt with naphtol blue black as a ligand. The resulting complex compound was a brown solid. Several factors that influence crystal growth were stirring process when mixing metal and ligand solutions, as well as the air condition around the solution. The complex compound that have been formed were characterized to determine their characteristics. The results of Fe-NBB complex is shown in Figure 1.

![Figure 1. The result of Fe-NBB synthesis](image)

3.2 The characterization of Fe-NBB

3.2.1 Characterization of Fe-NBB complex with a UV-Vis spectrophotometer. In this research, complex Fe-NBB has characterized its maximum wavelength and the characteristic bands of the Fe-NBB comparing with NBB ligand using a spectrophotometer. The result is shown in Table 1. Table 1 shows that overall the characteristic band NBB and Fe-NBB complex is similar. However, the complex compound shows the new band at 273.5 nm. This band represents a Metal to Ligand Charge Transfer (MLCT) phenomenon that only owned by the complex compound. The MLCT phenomenon will appear when a complex compound has ligand that has low energy π * orbitals and the metal has a low oxidation number. Besides, the MLCT phenomenon also appears on the complex which has abundant electrons in the d orbitals of metal and a huge number of ligands [17]. This MLCT phenomenon are good for dye sensitizer application because will optimize the dye when absorbing light from the sun. The d-d transition of complex compound is totally covered by the domination of the naphtol blue black ligand intensity and shown at 618 nm [18].

| Table 1. Characteristic bands of the NBB and Fe-NBB |
|-----------------------------------------------|
| Compound | Wavelength (nm) |
| NBB      | 228  | 399  | 448  | 619  |
| Fe-NBB   | 233  | 273.5| 399.5| 446.5| 618  |
3.2.2 Characterization of Fe-NBB complex using FTIR spectrophotometer. Fe-NBB complex compound was analysed using a FTIR spectrophotometer to investigate the functional groups and bonds formed between the metal (Fe) and the ligands (NBB). The results of FTIR characterization is shown in Figure 2 and described in Table 2. The results of characterization by FTIR spectrophotometer showed that the spectra of complex and ligand compounds were different. This indicates that a complex compound has been formed. Based on the Figure 2 and Table 2, it can be seen that there is a bond between Fe (II) metal and the blue black naphtol ligand, it can be seen from the appearance of the Fe-N and Fe-O bonds at 316.33 cm\(^{-1}\) and 486.06 cm\(^{-1}\). This bonding revealed that the complex Fe-NBB has been successfully synthesized.

![FTIR spectrum of ligand NBB and complex of Fe-NBB](image)

**Figure 2.** FTIR spectrum of ligand NBB and complex of Fe-NBB

| Functional Groups | Wavenumber (cm\(^{-1}\)) |
|-------------------|--------------------------|
| NBB               | Fe-NBB                   | Theoretical and reference |
| Fe-N              | -                        | 316.33                     | 400 – 300 [19] |
| Fe-O              | -                        | 486.06                     | 600 – 400 [19] |
| SO\(_3\)Na        | 1141.86                  | 1141.86                    | 1235 – 1070 [20] |
| N=N               | 1419.61                  | 1411.89                    | 1500 – 1400 [21] |
| NO\(_2\)          | 1489.05                  | 1489.05                    | 1550 – 1300 [21] |
| C=C aromatic      | 1573.91                  | 1573.91                    | 1607 – 1510     |
| OH                | 3441.01                  | 3425.58                    | 3639 – 3029     |
| NH\(_2\)          | 3749.62                  | 3749.62                    | 3800 – 3400 [21] |

3.2.3 Characterization of the electrical conductivity of the complex Fe-NBB with a conductometer. The electrical conductivity of complex compound was investigated using a conductometer. The conductance value is used to determine the type of complex compounds produced, namely molecular or ionic complex. The electrical conductivity of the complex Fe-NBB was measured and comparing with the solvent. If the conductivity value of the complex compound is higher than the solvent, it is a type of ionic complex compound, but if the conductivity value of the solvent is higher than the complex
It is a type of molecular complex compound [22]. The electrical conductivity of the solution is described in Table 3. From Table 3 we can conclude that the electrical conductivity of the complex Fe-NBB in aquabidest is greater than the aquabidest itself, so the Fe-NBB complex is an ionic complex. Ionic complex compounds are good for application in DSSC because they can ionize easily, so the electron transfer process can take place continuously. The advantages of using ionic complexes in DSSC include ionic complexes which have high boiling and melting points and have a crystalline structure so that they are more stable when used as dye sensitizers in DSSC. Ionic compounds are also water-soluble so they have good electrical conductivity [23].

| Compound                    | Conductance (µS) |
|-----------------------------|------------------|
| Aquabidest (solvent)        | 1.42             |
| Fe-NBB in aquabidest        | 59.6             |

3.3 Photovoltaic performance of Fe-NBB

3.3.1 The characterization of interaction semiconductor TiO₂ and Fe-NBB in working electrode. The interaction semiconductor TiO₂ and Fe-NBB as a dye sensitizer on DSSC is needed to be characterized to prove the presence of chemical bonds formed between Ti and Fe-NBB complex. The ligand functional group must have a lone pair to bind with TiO₂ [5]. Figure 3 shows that the interaction of TiO₂ with the Fe-NBB complex appear at wavelength 486.06 cm⁻¹. It means that Ti from TiO₂ making bond with O from the Fe-NBB and forming Ti-O bonding. This is in accordance with the literature that the Ti bond with the O group will appear at wave numbers 600–400 cm⁻¹ [19]. The chemical bond formed between dye sensitizer and semiconductor has advantages in the DSSC process, which is able to capture photons that are received to be injected into semiconductor which will then cause current and voltage.
3.3.2 Measurement of the DSSC power against the number of days. In this study, power measurement was carried out at 12 a.m in 5 different days and the results can be seen in Figure 4. For NBB, the power produced is increasing gradually from the first until the third day. However, on the fourth day, the power produced by NBB is decreased and steady on the fifth day. This result indicates that the regeneration electron on NBB is not stable. On the first day, the power produced by Fe-NBB is the largest because on the first day the dye and electrolyte is still new and the electron transfer is going well. On the second day, the power of Fe-NBB is drop because the intensity of sunlight is higher so that the electrolyte solution is more volatile. On the third day the power is still going down because on the sunlight intensity is smaller, namely 680 so that the received photons are also less. The fourth and the fifth days the power of Fe-NBB is increasing because light intensity of the sun is the highest. The intensity of sunlight affects the current output, the greater the intensity of sunlight, the greater the current output, the greater power is produced [16].

![Figure 4](image_url)

**Figure 4.** The result of power measurement against days

3.3.3 The result of photovoltaic performance assay. Based on Table 4, it shows that DSSC based on Fe-NBB complex has a fairly high efficiency value compared to the NBB alone. It can be explained that complex Fe-NBB is an ionic complex compound and experiences the Metal to Ligand Charge Transfer (MLCT) phenomenon which results in the Fe-NBB being "sunlight collector" so it can be used as a good sensitizer [18]. Some research also has proven that the presence of metal on the dye structure could improve the ability of dye in capturing the photon from the sunlight. Complex Fe-methyl orange had an efficiency of solar cell 1.37 % whereas the methyl orange only was 0.756% [5]. Metal complex Fe-congo red also showed the higher efficiency of solar cell namely 8.17 % whereas the congo red only 1.9 % [4]. Complex Fe-rhodamine B showed efficiency of solar cell 2.03 % while the rhodamine B only showed 0.0019 % [15]. Based on the previous research the efficiency of Fe-NBB is still lower than Fe-methyl orange, Fe-congo red, and Fe-rhodamine B. It can be explained that Fe-NBB has the lowest conductance value compared to Fe-congo red and Fe-rhodamine B. Therefore, the ability of Fe-NBB on generating electron cycle is weaker than the others and produce the lowest efficiency on the solar cell [4,15]. The captured photon by complex compound cause the electrons of complex compound were excited towards the TiO$_2$ conduction band. Then electrons were transferred to the counter electrode and undergo redox reaction that facilitated by the electrolyte solution KI. The movement of electrons will take place continuously in a cycle in the presence of sunlight that excites the electrons. This cycle will result in the current that appears to be used as a source of electricity [4].
### Table 4. The photovoltaic parameter of NBB and Fe-NBB

| Dye      | $V_{oc}$ (V) | $J_{sc}$ (mA/cm$^2$) | FF   | $\eta$ (%) |
|----------|--------------|----------------------|------|-------------|
| NBB      | 0.218        | 0.0240               | 0.7844 | 0.0083      |
| Fe-NBB   | 0.363        | 0.1418               | 0.8887 | 0.0925      |

4. Conclusion

The development of DSSC using NBB was successfully done. The napthol blue black (NBB) dye was modified through complex compound formation Fe-NBB to improve its photovoltaic performance. Complex Fe-NBB showed the presence of the MLCT phenomenon at wavelength of 273.50 nm. The FTIR spectra showed Fe-N vibrations at wavenumber 316.33 cm$^{-1}$ and Fe-O vibrations at 486.06 cm$^{-1}$. The electric conductivity assay showed that the Fe-NBB was an ionic complex compound. Fe-NBB complex was proven to be used as a dye sensitizer in DSSC and produce a short circuit current of 0.567 mA/cm$^2$, with a maximum voltage of 0.363 V and an efficiency value of 0.0925%.

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