

# Promising Dye Sensitizer on Solar Cell From Complexes of Metal and Rhodamine B

Harsasi Setyawati<sup>‡</sup>, Handoko Darmokoesoemo, Hamami, Faidur Rochman, Ahmadi Jaya Permana

Department of Chemistry, Faculty of Science and Technology, Airlangga University, 60115

(harsasi85@gmail.com, handoko-d@fst.unair.ac.id, hamami.@fst.unair.ac.id, faidur-r@fst.unair.ac.id, ahmadi-j-permana@fst.unair.ac.id)

<sup>‡</sup>Corresponding Author; Harsasi Setyawati, Department of Chemistry, Faculty of Science and Technology, Airlangga University, 60115, Tel: +62-31 5922427, Fax: +62-31 5922427, harsasi85@gmail.com

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**Abstract-** Herein a series of complexes from metals (Fe, Co, Ni) and rhodamine B as ligand were synthesized, characterized and applied as promising dye sensitizer on solar cell. Complexes were obtained from the reaction of Fe(II), Co(II), Ni(II) salts and rhodamine B with mole ratio 1:3. UV-Visible spectroscopy confirms all of complexes showing Metal Ligand Charge Transfer (MLCT) absorption band at 258 nm and stability constant (log K) of complexes were 23.47 for Fe-Rb and Ni-Rb and 23.76 for Co-Rb. Infrared spectroscopy confirms metal-ligand coordination through carbonyl (CO) and methoxy (CH<sub>3</sub>O) groups. Electrical conductivity analysis indicates that all of complexes are ionic complexes. All of complexes can be utilized as promising dye sensitizer with efficiency 2.03% (Fe), 0.59% (Co), and 0.12% (Ni). Goal of this research is to help solve dye waste problem and energy crisis.

**Keywords:** Metal, rhodamine B, complexes, dye sensitizer, solar cell, waste

## 1. Introduction

The increasing human population led the increase in energy demand. However, energy supply from fossil fuel cannot fully accommodate it. Such situation leads scientists to seek alternative renewable green energy to minimize negative impacts on the environment [1, 4]. One of alternatives, among which does not produce pollutants is by empowering sunlight energy using Dye Sensitized Solar Cell (DSSC).[14] DSSC has several components, i.e. semiconductor glass, an electrolyte solution, electrode comparator and dye sensitizer. Dye sensitizer plays an important role in DSSC because it can capture photons from sunlight and improve solar cell performance [11, 13]. Rhodamine B is a potential dye which can be used as dye sensitizer because its chemical properties are not easily degradable; it has a conjugated double bond; its maximum wavelengths is more than 500 nm; and its aromatic ring has a chromophore group [2, 14]. In addition, rhodamine B is a textile waste that causes environmental damage. Therefore, the usage of rhodamine B as dye sensitizer is expected to reduce the negative impact of dye waste on environment. In this research, pure rhodamine B was complexed with various transition metals [Fe(II), Co(II), Ni(II)] to enhance the performance and stability of rhodamine B as dye sensitizer [2, 3, 5, 8, 13, 19]. A series of complex compounds were characterized using UV-VIS spectrophotometer, Fourier Transform Infrared (FTIR) spectrophotometer, Energy

Dispersive X-Ray (EDX), Stability Constant analysis and Electrical Conductivity Analysis. The application of complexes as dye sensitizer on solar cell is then extensively explored.

## 2. Experiment

### 2.1. Material and Methods

All chemicals were purchased from commercial sources (Sigma Aldrich) without further purifications. Materials for synthesis of complexes were rhodamine B (C<sub>28</sub>H<sub>31</sub>Cl.N<sub>2</sub>O<sub>3</sub>) as ligand, Mohr salt [(NH<sub>4</sub>)<sub>2</sub>Fe(SO<sub>4</sub>)<sub>2</sub>.6H<sub>2</sub>O], cobalt chloride (CoCl<sub>2</sub>.6H<sub>2</sub>O), nickel sulphate (NiSO<sub>4</sub>.7H<sub>2</sub>O), deionized water, barium hydroxide (Ba(OH)<sub>2</sub>) and ether. Material for preparation of DSSC cell were titanium(IV)isopropoxide (Ti(OC<sub>3</sub>H<sub>7</sub>)<sub>4</sub>) (TTIP), 4-(1,1,3,3-tetramethylbutyl) phenylpolyethylene glycol (Triton X-100), iodine (I<sub>2</sub>), potassium iodide (KI), acetic acid (CH<sub>3</sub>COOH), ethanol (CH<sub>2</sub>CH<sub>3</sub>OH), hydrochloric acid (HCl), and ether. The conductive glass plate was used, i.e. FTO (Fluorine doped Tin Oxide) glass from Latech scientific supply Pte. Ltd Singapore (10Ω, 25 x 25 x 3.2 mm). Graphite was used in a counter electrode.

Spectra and stability constant of the complexes were measured by UV-VIS Shimadzu 1800 while infrared spectra were recorded by Jasco FTIR 5300. Elemental analysis was performed by EDX Carl Zeiss EVO MA 10 while electrical

conductivity was analyzed by EUTECH Conductometer. Thin layer TiO<sub>2</sub> was characterized by X<sup>3</sup>pert PRO diffractometer. Photovoltaic tests of DSSC cells using complexes of rhodamine B were performed by measuring current density- voltage curves under solar irradiation in real condition (outdoor) as long as five days. The voltage and current density of the cell were measured by multimeter Dekko using potentiometer circuit while intensity of light was measured by Light Meter Krisbow KW06-288.

## 2.2. Determination of Ratio Mole Metal: Ligand and Stability Constant of Complexes

Previously, mole ratio of metal and ligand was determined to predict the number of ligand which is bind to the metal. Three series of metal solutions Fe(II), Co(II), Ni(II) with fixed mole were reacted with various mole of rhodamine B. Hereafter, the mole ratio of metal to ligand was determined by intersection between the straight line equation of curve between a mole ratio of metals to ligand and absorbance of ligand. The result of determination of mole ratio was used to measure the stability constant of complexes using equation [18] :

$$K = \frac{(A_{ekst}/A)C}{(C_m - (A_{ekst}/A)C) (C_l - (A_{ekst}/A)C)^3}$$

A<sub>ekst</sub> : the absorbance extrapolation located close to the equivalent point

A : The average value of the actual absorbance

C : Metal concentrations

C<sub>m</sub> : Total concentration of metals

C<sub>l</sub> : Total concentration of ligand

## 2.3. Preparation of the Complexes

Complexes of rhodamine B were prepared by reacting metal salt and ligand based on the mole ratio determination. Then the mixture was heated at 100 °C. After the third solution remained, the solution was added by Ba(OH)<sub>2</sub> solution to bind ion pairs of metal salts remaining. The precipitate formed was filtered in hot condition and the filtrate was separated. The filtrate was left for one week until rhodamine B complexes were formed. Subsequently, the complex compounds were washed with ether and then dried.

## 2.4. Chemical Analyses Values

Anal.Calc. for [Fe-rhodamine B] C, 63.29; N, 4.99; O, 31.42; Fe, 0.29. Found: C, 63.32; N, 4.98; O, 31.41; Fe, 0.29%. Anal. Calc.for [Co-rhodamine B] C, 58.34; N, 4.0; O, 32.03; Co, 5.62. Found: C, 58.89; N, 3.59; O, 31.86; Co, 5.66%. Anal.Calc.for [Ni-rhodamine B] C, 65.44; N, 2.70; O, 31.36, Ni, 0.49. Found: C, 65.49; N, 2.69; O, 33.20; Ni, 0.5%.

## 2.5. Preparation of DSSC Cell

### 2.5.1. Preparation of TiO<sub>2</sub>-dye electrode (Photo anode) as working electrode

Photo anode were prepared with a thin layer of TiO<sub>2</sub> sol. TiO<sub>2</sub> sol was prepared by adding 5 ml of Triton X-100 to 12 mL of acetic acid solution. Then the mixture was diluted with 225 mL of ethanol and stirred until homogenous. Subsequently, the solution was added 15 mL of TiO<sub>2</sub>

precursor (TTIP) and 1 mL of hydrochloric acid and then stirred again at room temperature for 2 hours.

FTO glasses were washed with deionized water and dried at 80 °C for 10 minutes. Subsequently, FTO glasses were coated with TiO<sub>2</sub> sol 3 times. Then each FTO glass was dried at 80 °C for 10 minutes. In the last coating, FTO glasses were calcined at 450 °C for 2 hours. The adsorption of dyes from rhodamine B complexes onto FTO glasses-TiO<sub>2</sub> were done by immersing the electrodes in the complexes of rhodamine B solution (0.1 mmolL<sup>-1</sup>) for 24 hours at room temperature and then dried. Three complexes of rhodamine B, and rhodamine B were immersed with TiO<sub>2</sub> glasses.

### 2.5.2. Preparation of graphite coated as counter electrode

FTO glasses were coated with carbon on the conducting side using a graphite pencil until evenly distributed. Subsequently, FTO glasses were heated at 450 °C for 30 min and then washed with ethanol and dried before the device was assembled.

### 2.5.3. Preparation of graphite coated as counter electrode

Electrolyte solution was used was KI<sub>3</sub>. Iodine (I<sub>2</sub>) was dissolved by potassium iodide (KI) solution until KI<sub>3</sub> solution was obtained.

### 2.5.4. Assembly of DSSC cells

The dye sensitizer solar cells were assembled by sandwiched TiO<sub>2</sub>-dye electrode as working electrode and carbon as counter electrodes, respectively. The structure of the dye sensitized solar cell device was shown in Figure. 1.

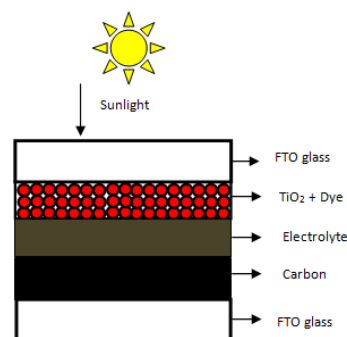
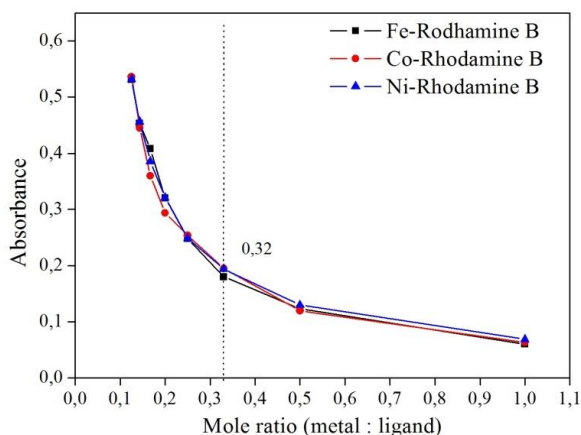


Fig. 1. Structure of DSSC device from rhodamine B complexes

## 3. Results and Discussion

### 3.1. Synthesis of Rhodamine B Complexes

Synthesis of rhodamine B complexes was started with determining of the stoichiometric of the complexes with mole ratio method. Mole ratio method was performed by reacting a series of fixed moles of metal ion with variation ligand mole [18]. The absorbance of the mixtures was measured using UV-VIS spectrophotometer to plot a curve between a mole ratio of metals to ligand and absorbance of ligand. Figure 2 shows the mole ratio of three rhodamine B complexes were 0.32. This result means that one mole of metal can bind three moles of rhodamine B. Based on the stoichiometric, it is expected that the rhodamine B ligand is bidentate ligand because it can donate two pairs of electrons to the metals to form octahedral complexes [10].



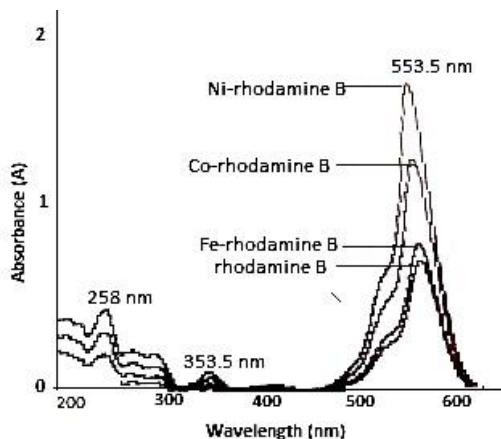
**Fig. 2.** Mole ratio of rhodamine B complexes

Stability constant of metals-rhodamine B complexes was determined using mole ratio method. Stability constants of complexes were 23.47 for Fe-rhodamine B; 23.76 for Co-rhodamine B; and 23.47 for Ni-rhodamine B. Overall, all of the complexes have high stability constant and indicate forming a chelate with rhodamine B ligand. This is advantageous because one of the requirements of good sensitizer is stable [5].

### 3.2. Characterization of Rhodamine B Complexes

#### 3.2.1. Absorption Spectra of Rhodamine B complexes

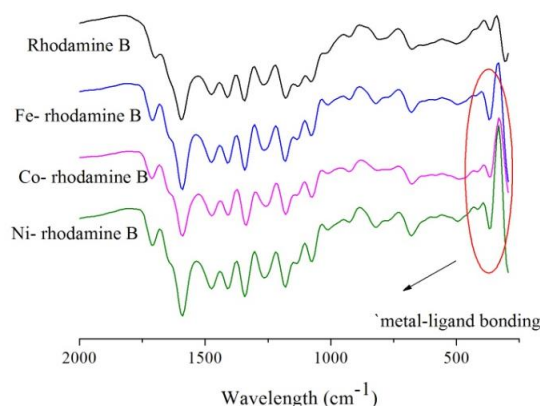
Figure 3 shows the UV-VIS absorption spectra for rhodamine B and rhodamine B complexes. The maximum wavelength of rhodamine B complexes coincides with the maximum wavelength of rhodamine B because rhodamine B gives high intensity colored and may cause the d-d transition of the complexes to be completely overwhelmed and essentially impossible to observe. Presence of rhodamine B complexes was proved by intense absorption band at 258 nm, showing the complexes exhibit strong charge transfer absorption, i.e MLCT (Metal to Ligand Charge Transfer). These complexes show MLCT because the complexes have  $\pi$ -acceptor ligand. The empty  $\pi^*$  orbital on the ligand becomes the acceptor orbital on light absorption. It is very beneficial that complex compounds with MLCT absorptions will play an important role in solar energy application because these complexes act as light harvester [10].



**Fig. 3.** Absorption spectra of rhodamine B and rhodamine B complexes

#### 3.2.2. Infrared spectra of Rhodamine B complexes

Infrared spectra of rhodamine B complexes were recorded to identify the functional groups in the rhodamine B complexes and the bond between metals with rhodamine B ligand. Determination of metal-ligand bonding was shown by a different peak of rhodamine B ligand from that of rhodamine B complexes. Figure 4 shows that the functional groups of complex compounds with ligand were broadly similar. Chloride functional group appears at wave number 795-540  $\text{cm}^{-1}$ ; the vibration of C-O-C ether groups appears at wave numbers 1300-1000  $\text{cm}^{-1}$ ; the vibration of CN group appears in the wave number 1350-1000  $\text{cm}^{-1}$ ; vibration  $-\text{CH}_3$  appears at wave number 1450-1375  $\text{cm}^{-1}$ ; C=C bonds in aromatic compounds appears at wave number 1600-1400  $\text{cm}^{-1}$ ; and the carbonyl group C = O appears at wave number 1800-1680  $\text{cm}^{-1}$ . The indication of coordination of ligand to the metal ions is shown in Table 1.



**Fig. 4.** Infrared spectra of rhodamine B and rhodamine B complexes

**Table 1.** Metals-ligand bonding on the rhodamine B complexes

Coordination ligand and metal ions	Wavenumber ( $\text{cm}^{-1}$ ) [references]
Fe-O methoxy	362.62 [12]
Fe-O carbonyl	316.33 [12]
Co-O methoxy	354.90 [7, 16]
Co-N	478.35 [7, 16]
Ni-O methoxy	354.90 [12]
Ni-O carbonyl	678.94 [12]

#### 3.2.3. Infrared spectra of Rhodamine B complexes

The electrical conductivities of rhodamine B complexes was analyzed to determine the ionic or molecular properties of complexes. The complexes are molecular compound if the electrical conductivity of complex is close to the value of electrical conductivity of the solvent. However, if the electrical conductivity of complex is greater than the electrical conductivity of the solvent, the complex is an ionic compound. Table 3 shows the electrical conductivities of rhodamine B complexes in deionized water were greater than the electrical conductivity of solvent. It indicates that the complex compounds were not molecular but ionic compound. Ionic compound is more advantageous for sensitizer, as it forms ions in the solvent and easily

delivers the electrons in the complex charge transfer, than molecular compounds.[1]

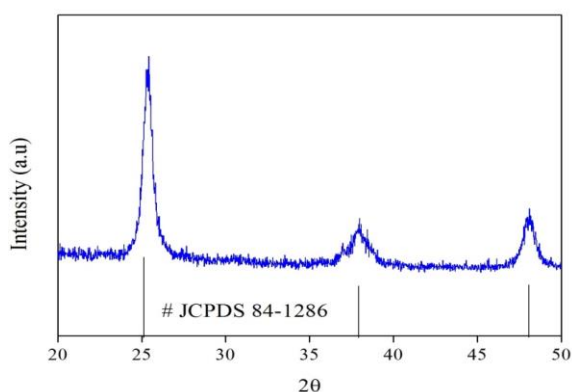
**Table 3.** The electrical conductivities of rhodamine B complexes

Solution	Electrical Conductivity ( $\mu\text{S}$ )
Deionized water	1.93
Fe-rhodamine B	119.07
Co-rhodamine B	74.23
Ni-rhodamine B	70.50

### 3.3. Complexes Characterization of $\text{TiO}_2$ -dye as Working Electrode

#### 3.3.1. XRD patterns of $\text{TiO}_2$ thin films

The XRD patterns of  $\text{TiO}_2$  thin films are shown in Figure. 5.



**Fig. 5.** The XRD patterns of  $\text{TiO}_2$  thin films

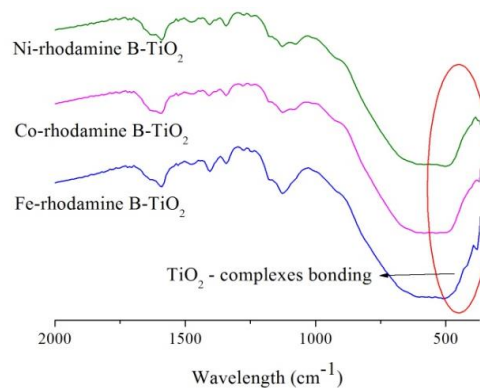
The diffractogram patterns of  $\text{TiO}_2$  thin films shows peaks (25.29; 37.92; 48.19) indicating that the  $\text{TiO}_2$  thin films were anatase. As semiconductor in DSSC, anatase has more advantages than rutile because the bandgap is wider, i.e.  $\sim 3.02$  eV for anatase and  $\sim 3.0$  eV for rutile [15]. This diffractogram pattern is according to [9] and interpretation data card JCPDS number 84-1286.

#### 3.3.2 Infrared spectra of $\text{TiO}_2$ - Rhodamine B complexes

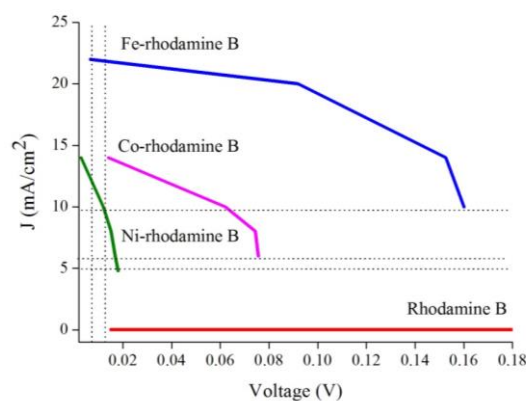
The characterization of  $\text{TiO}_2$ -dye was observed by recorded infrared spectra of the rhodamine B complexes. Figure. 6 shows the presence of  $\text{TiO}_2$  bind to the carboxylate group of complexes at 509.21 for Fe-rhodamine B and Co-rhodamine B, and 501.49 for Ni-rhodamine B [12]. Dye molecules can bind onto the surface of  $\text{TiO}_2$  via interaction between hydroxyl groups on  $\text{TiO}_2$  surface and carboxyl or hydroxyl on dye molecules. All of rhodamine B complexes show promising performance as dye sensitizer in DSSC because  $\text{TiO}_2$ -dye bonding can act as favorable electronic pathways [17].

#### 3.4. Photovoltaic Properties of Rhodamine B Complexes

Figure 7 and Table 4 present the performance of the rhodamine B as sensitizer in DSSC in terms of short-circuit current ( $J_{sc}$ ), open-circuit voltage ( $V_{oc}$ ), fill factor (FF) and energy conversion efficiency ( $\eta$ ) for four solar cell systems.



**Fig. 6.** Infrared spectra of  $\text{TiO}_2$ -rhodamine B complexes



**Fig. 7.** Current density-voltage curve of rhodamine B and rhodamine B complexes

**Table 4.** Photovoltaic performance of rhodamine B complexes as dye sensitizer

Dye	$J_{sc}$ ( $\text{mAcm}^{-2}$ )	$V_{oc}$ (mV)	FF	$\eta$ (%)
Rhodamine B	0.01	454	0.1125	0.0019
Fe-rhodamine B	5.5	160	0.6069	2.03
Co-rhodamine B	3.5	75.6	0.5858	0.59
Ni-rhodamine B	3.5	18	0.4825	0.12

Sunlight Intensity : 26. 307  $\text{mWcm}^{-2}$ ; Area : 4  $\text{cm}^2$

Table 4 shows the efficiency of complex compounds is higher than the efficiency of rhodamine B. This result proves that rhodamine B complexed with transition metals (Fe, Co, Ni) has better ability as sensitizer because it has better ability to harvest light. Light harvesting ability is strongly affected by complexes MLCT absorption [10]. The efficiency of complex compounds from high to low are Fe-rhodamine B, Co-rhodamine B, and Ni-rhodamine B. Fe-rhodamine B shows promising photoelectrochemical performance, i.e.  $J_{sc} = 5.5 \text{ mAcm}^{-2}$ ,  $V_{oc} = 160 \text{ mV}$ ,  $FF = 0.6069$  and  $\eta = 2.03 \%$ . Fe-rhodamine B has the highest efficiency because its electron configuration has lone pair electrons more than Co and Ni. So the electronic structure of Fe is more diverse meaning that more levels of solar energy can be absorbed by Fe. The more levels of solar energy can be absorbed, the higher electron flow can be generated so that resulting current will be greater. On the other hand, the efficiency of complexes is still below the required standard of industrial scale application because high concentration of complexes

causes the aggregation of molecule of complexes on the surface area semiconductor. It may cause the dye molecules not to be absorbed effectively so the flow of electrons from the working electrode to counter electrode is not smooth and the electric current generated becomes low [6, 17].

#### 4. Conclusion

In this work we have reported an investigation on metals (Fe, Co, Ni)-rhodamine B complexes as dye sensitizer on DSSC and compared their photoelectrochemical activities with free rhodamine B and its complexes. Rhodamine B complexes showed better photosensitizer ability than rhodamine B because these complexes have MLCT absorption which act as light harvester. The application of metals-rhodamine B complexes obtained efficiencies ranging between 0.12 and 2.03 %, open circuit voltage ( $V_{oc}$ ) ranging between 18 and 454 mV and short-circuit photocurrents ( $J_{sc}$ ) varied from 0.01 until 5.5 mAcm<sup>-2</sup>. Though energy conversion efficiencies of these complexes are still below the requirements for large scale applications, this result is expected to be smart solution to solve the negative impact of dye waste on environment by using the waste (e.g. rhodamine B) as dye sensitizer on solar cell to produce electrical energy. So we can name our finding as “clean technology” because it can reduce dye waste on environment and produce energy without producing any waste. The application of complexes based on metals and another waste (congoed, naphthol blue black) as dye sensitizer on DSSC are currently being further explored in our laboratory and will be published in forthcoming article.

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