Research Article

Harsasi Setyawati*, Handoko Darmokoesoemo, Irminda Kris Murwani, Ahmadi Jaya Permana, Faidur Rochman

Functionalization of Congo red dye as a light harvester on solar cell

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Abstract: The demands of ecofriendly technologies to produce a reliable supply of renewable energy on a large scale remains a challenge. A solar cell based on DSSC (Dye-Sensitized Solar Cell) technology is environmentally friendly and holds the promise of a high efficiency in converting sunlight into electricity. This manuscript describes the development of a light harvester system as a main part of a DSSC. Congo red dye has been functionalized with metals (Fe, Co, Ni), forming a series of complexes that serve as a novel light harvester on the solar cell. Metal-congo red complexes have been characterized by UV-VIS and FTIR spectroscopy, and elemental analyses. The performance of metal complexes in capturing photons from sunlight has been investigated in a solar cell device. The incorporation of metals to congo red successfully improved of the congo red efficiency as follows: Fe(II)-congo red, Co(II)-congo red and Ni(II)-congo red had efficiencies of 8.17%, 6.13% and 2.65%, respectively. This research also discusses the effect of metal ions on the ability of congo red to capture energy from sunlight.

Keywords: Functionalization; congo red; metal; light-harvester; ecofriendly.

1 Introduction

The increasing demand for renewable energy has prompted many researchers to investigate new sources to produce renewable energy. Sunlight is an abundant energy source which can be converted into electricity. A solar cell, in particular DSSC (Dye Sensitizer Solar Cell), is one of the best technologies to obtain clean energy from sunlight [1–8]. A dye sensitizer, commonly known as a light harvester, is the main part of the DSSC device. A light harvester has a significant role in capturing energy from the sun, and the electron produced is used in photochemical pathways on the solar cell [9]. Much research has been focused on developing a light harvester material to obtain a high-efficiency solar cell [1,2,4,5,7–11]

On the other hand, in Indonesia, the growth of the economy has been driven by the development of the garment/ textile industry, in particular, the Batik industry. In order to keep down the industrial costs, many industries tend to use synthetic dyes such as rhodamine B, congo red, naphthol blue black and methyl orange for their dyeing processes. Because of the lack of waste treatment technology, many industries dispose of dye waste directly into the environment. Hence, in this research, we focus on how to reduce dye waste and convert them into a component of solar cell technology.

In earlier work, waste dyes such as rhodamine B, congo red, naphthol blue black and methyl orange were successfully used as a light harvesters in solar cells [9]. In that study, congo red proved to have the highest efficiency of 1.01%. Therefore, in this study, congo red was chosen as a candidate for a light harvester on the solar cell. A promising way to improve the efficiency of solar cells in *via* the addition of metal ions. In this context, congo red is considered as a ligand. The metal-ligand interaction in metal complexes produces new functional materials that provide a wide application in many scientific fields. For example, the presence of iron on the rhodamine B structure has been shown to improve the efficiency of a solar cell from 0.0019% (rhodamine B) to 2.03%

*Corresponding author: Harsasi Setyawati, Department of Chemistry, Faculty of Science and Technology, Airlangga University, Surabaya 60119, Indonesia, E-mail: harsasi-s@fst.unair.ac.id
Handoko Darmokoesoemo, Ahmadi Jaya Permana, Faidur Rochman, Department of Chemistry, Faculty of Science and Technology, Airlangga University, Surabaya 60119, Indonesia
Irminda Kris Murwani, Department of Chemistry, Institut Teknologi Sepuluh Nopember Surabaya 60111, Indonesia

(Fe-rhodamine B) [12,13]. The presence of iron (as a metal complex) on an antibiotic structure has proven to enhance the antibacterial activity [14]. Incorporation metal-ligand complexes yields excellent electronic properties in the molecular electronics field [15,16].

In the current research, a series of complexes were prepared by reacting congo red dye with Fe(II), Co(II) and Ni(II) ions. All compounds were characterized by UV-Vis and FTIR spectrophotometry, EDX (Energy-Dispersive X-ray) elemental analysis, and conductometry. The performance of all complexes as a light harvester on a solar cell device was analyzed and compared to the performance of congo red. In this study, the solar cell device consisted of a thin layer of titanium dioxide (TiO_2) as a semiconductor, graphite as a counter electrode, potassium tri-iodide (KI_3) solution as an electrolyte solution and FTO (Fluorine-doped tin oxide) glass as solar cell body.

2 Experimental

2.1 Material

All chemicals were purchased from commercial sources (Sigma Aldrich) and used without further purification. Materials for synthesis of complexes were Mohr salt $[(\text{NH}_4)_2\text{Fe}(\text{SO}_4)_2 \cdot 6\text{H}_2\text{O}]$, cobalt chloride ($\text{CoCl}_2 \cdot 6\text{H}_2\text{O}$), nickel sulphate ($\text{NiSO}_4 \cdot 7\text{H}_2\text{O}$), congo red ($\text{C}_{32}\text{H}_{22}\text{N}_6\text{Na}_2\text{O}_6\text{S}_2$) and ethanol ($\text{CH}_3\text{CH}_2\text{OH}$). Material for preparation of the DSSC cell were conductive glass plates i.e. FTO (*Fluorine doped Tin Oxide*) glass from *Latech scientific supply Pte. Ltd Singapore* (10 Ω , 25 x 25 x 3.2 mm), counter electrode i.e., graphite, titanium dioxide anatase, iodine (I_2), potassium iodide (KI), acetic acid (CH_3COOH), hydrochloric acid (HCl), ethanol ($\text{CH}_3\text{CH}_2\text{OH}$), aquabidest and ether.

2.2 Congo red complexes characterization

The absorption spectra of complexes (as solutions) were measured using a UV-Vis spectrophotometer (Shimadzu 1800). Infrared spectra were recorded with a FTIR spectrophotometer (Jasco FTIR 5300). Elemental analyses of complexes were performed using a EDX Carl Zeiss EVO MA 10. Electrical conductivity was analyzed with a EUTECH Conductometer. The structure of thin layer TiO_2 was characterized by X'pert PRO Diffractometer.

2.3 Determination of ratio mole metal to ligand

The number of ligands which bind to the metal was calculated by determining the mole ratio of metal and ligand using mole ratio methods, [17], as follows: Stoichiometry of metal complexes is determined by the mole ratio method, using the wavelength of maximum absorbance of the congo red ligand. A solution of the appropriate metal ion was made with a constant number of moles, while solutions of congo red were made with a variation of the number of moles. Eight volumetric flasks (10 mL) were prepared. A solution of the appropriate metal ion (5×10^{-5} M) in a fixed mole (1 mL) was transferred to the flask and congo red 5×10^{-5} M with a variation mole (1 mL; 2 mL; 3 mL; 4 mL; 5 mL; 6 mL; 7 mL; 8 mL) was added. Furthermore, the solution is diluted with aquabidest. 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.

2.4 Preparation of the complexes

A series of complexes were synthesized by reacting a metal ion and congo red ligand. The appropriate metal salt and ligand were weighed, based on the mole ratio determination; one mole of metal and three mole of ligand congo red. Then, each compound was dissolved in ethanol. The solutions were mixed and heated at 100°C under reflux system. After one third of the solution remained, the solution was left for two weeks at room temperature until complexes crystallised. Subsequently, the complexes were washed with hot ethanol (40°C), then dried [12,13]. The ionic character of complex compound was determined by conductance analysis.

2.5 Preparation of DSSC cell

Photo anode or working electrode were prepared by superimposing a thin layer of TiO_2 sol on FTO glasses following the procedure described in our previous work [12]. For a working-electrode, a glass plate with a size of 2.5 cm x 2.5 cm with 1 mm of thickness was sanded to obtain a rough-surface. Then, the glass plate was soaked with ethanol for 24 hours. Furthermore, the glass plate was coated by sol-gel titanium dioxide to obtain a thin layer of titanium dioxide. A sol-gel solution of TiO_2 was dropped on the glass plate surface and flattened using

Figure 1: The diagram of DSSC cells, together with the structure of congo red and the three metal ions used to make complexes.

a stirring rod until a homogenous coating was obtained. Then, a coated glass plate was calcined at a temperature of 450 °C for 30 minutes. The obtained titanium dioxide was characterized by X-ray diffraction. Subsequently, the adsorption of dyes from congo red complexes onto FTO glasses-TiO₂ were done by immersing the electrodes in the complexes of congo red solution (0.1 mmol.L⁻¹) for 24 hours at room temperature and then dried. Three complexes of congo red, and a solution of congo red were immersed with TiO₂ glasses, respectively.

Counter electrodes were prepared by coating carbon on the conducting side using a graphite pencil until evenly distributed. Furthermore, FTO glass slides were heated at 450°C for 30 min and then washed with ethanol and dried. Electrolyte solution was prepared by dissolving iodine (I₂) in potassium iodide (KI) solution until KI₃ solution was obtained. The light harvester solar cells were assembled by sandwiched TiO₂-dye as working electrode and graphite as counter electrodes as described in Figure 1. An electrolyte solution of KI₃ was dropped between the two electrodes. Then, the two electrodes were clamped with clips and connected to a multimeter and potentiometer 100 kΩ. The solar cell circuit was connected to a multimeter cable where the positive pole was connected to the counter electrode and the negative pole was connected to the working electrode. Then, the solar cell device was irradiated for 2 weeks by direct sunlight and every day the maximum current and voltage were measured. The intensity of the sunlight was also measured using a lux meter.

Ethical approval: The conducted research is not related to either human or animal use.

3 Results and discussion

In this research, functionalization of congo red was achieved by the formation of Fe(II), Co(II) and Ni(II) complexes. The result of the mole ratio of metal to ligand determination is shown in Figure 2. Through this step, the formation of complexes can be formed effectively [12].

Figure 2 shows the mole ratio metal to the ligand of all congo red complexes are 0.27. All complexes show that the mole ratio almost 0.3. This result means that all of the complexes stable synthesized on mole ratio metal to ligand 1:3. One metal could bind 3 ligands and form an octahedral structure which has a six coordination numbers. This suggests that congo red is a bidentate ligand which can donate two pairs of electrons to the metal ions [18].

After synthesis, all complexes were characterized by UV-Vis spectrophotometry, with selected data shown in Table 1. It is apparent that all complexes show d-d transition band on wavelength close to 498 nm. These results show that the d-d transitions of metal complexes is highly influenced by the very intense color of the ligand. The electronic absorption spectra of complexes give different characteristic bands such as intra-ligand transition, charge transfer (MLCT or LMCT), and d-d transition. All synthesized congo-red complexes indicate the octahedral structure. Based on orbital selection rule and Laporte forbidden rule, the complex compound with an inversion center like octahedral structure will have a weak d-d transition that caused the low in intensity. If the complex has a ligand with a very intense color such as congo red, it will be hard to determine the d-d transition

Figure 2: The determination of mole ratio of metal to ligand for the congo red complexes.

of a complex compound because of the color of ligand and LMCT phenomenon masking its d-d transition [19,20]. In this research, all complexes show charge transfer (CT) bands. It is beneficial to implement the metal complexes as a light harvester on solar cells because charge transfer phenomenon highly support generating electron transfer on solar cell device [9,13,18].

All synthesized metal complexes in this research were non-hygroscopic, non-deliquescent and stable at room temperature. In order to characterize their elemental composition, all complexes were analyzed by Energy Dispersive X-Ray (EDX). EDX is a chemical microanalysis technique which can be used for qualitative (the type of elements) as well as quantitative (the percentage of each element of the sample) studies. This analysis detects the x-rays emitted from the sample following the bombardment of the sample with an electron beam to

Table 1: Characteristic bands of the complexes in deionized water in UV-Vis spectra [$\lambda_{\max}$, in nm].

Compound	IL ^a bands and CT ^b bands		d-d bands
Congo red	238	345.5	498-
Fe-congo red	239	339	508
Co-congo red	213	-	502
Ni-congo red	239	339.5	498.5

a = intra-ligand band; b = charge transfer band

characterize the elemental composition. The data that is generated by EDX analysis consists of spectra with peaks corresponding to all the different elements that are present in the sample. An advantage of the EDX technique is that it is a non-destructive characterization technique, which

Table 2: The result of elemental analysis of congo red complexes.

Compound		Element				
		C	N	O	S	Metal
Fe(II)-congo red	Wt found/ Wt calc. (%)	43.01/42.65	8.75/8.74	36.89/36.89	8.62/9.22	2.73/2.50
	At found/ At calc. (%)	52.44/59.50	9.15/13.02	33.77/14.88	3.94/9.92	0.71/2.68
Co(II)-congo red	Wt found/ Wt calc. (%)	44.47/44.53	9.27/8.89	33.88/33.57	8.47/9.08	3.91/3.93
	At found/ At calc. (%)	59.44/54.58	13.00/9.36	14.86/30.91	9.91/4.71	2.79/0.98
Ni(II)-congo red	Wt found/ Wt calc. (%)	51.28/51.39	5.79/5.93	33.73/33.89	6.43/6.02	2.77/2.76
	At found/ At calc. (%)	60.62/59.38	5.89/12.99	29.97/14.85	2.85/9.89	0.67/2.89

Table 3: Conductance analysis of complex compounds.

Compound	Conductance (μmho)
Water (H_2O)	1.93
Fe(II)-congo red in water	67.23
Co(II)-congo red in water	87.60
Ni(II)-congo red in water	75.57

requires little or no sample preparation [21]. EDX has also been used to determine elemental composition [22–25].

In this research, EDX characterization was used in qualitative purposed such as proving the presence of metal in the complex compound. The result of the elemental determination of complexes is shown in Table 2. Table 2 shows that each synthesized complex contains an expected metal.

As a dye sensitizer, a complex compound must have character ionic in order to facilitate redox reaction in a DSSC cells. In order to ensure the ionic character on complex compounds, the conductance of each solution of congo red complex was determined by conductometry. The molar conductivities of the synthesized complexes were measured in water. Based on Table 3, the conductance of metal complexes is in a range 67.23 μmho – 87.60 μmho . This result revealed that all complexes were ionic with being 1:1 electrolyte, whereas the water showed conductance 1.93 μmho that correlate with nonelectrolytic [19,26]

The incorporation of metal in the complex compound leads to a change of ligand characteristics. When a metal coordinates with the ligand, some changes will occur in stretching frequencies of the ligand. Based on Table 4, the azo ($\text{N}=\text{N}$) bands in each complex compound shifted from 1612.49 cm^{-1} to 1604.77 and 1512.19 cm^{-1} , which indicates the coordination of N on azo group to the metal center [21]. The result of FTIR characterization of complexes is

Figure 3: The determination of functional groups of congo red complexes using FTIR.

shown in Figure 3, Figure 4 and Table 4. In general, the characteristic of FTIR spectra of complexes was similar to the ligand (congo red). This suggests that most a functional groups of complexes are broadly similar to those of the free ligand. However, based on Figure 4, there were significant differences spectra in the far-infrared area (under 500 cm^{-1}). This peak indicates the coordination of ligand to metal has been formed. Coordination Fe-N appears at 362.62 cm^{-1} ; coordination Co-N appears at 347.19 cm^{-1} and coordination Ni-N appears at 354.9 cm^{-1} . [12,13,27].

In investigating the performance of complexes as light harvesters, the photovoltaic performance of each complex was analyzed on a solar cell device. Each complex was dispersed on semiconductor titanium dioxide (TiO_2) that formed a working electrode. The interaction of metal complexes with TiO_2 was characterized by FTIR spectrophotometry and the results are shown in Figure 5. This shows that bonding between Ti and metal complexes is indicated by the appearance of peaks in the range of

Table 4: The functional group and metal ligand bonding of congo red complexes.

Functional Groups	Congo red	Fe-congo red	Co-congo red	Ni-congo red
Metal-NH ₂	-	362.62	347.19	354.9
C-N	1049.28	1049.28	1049.28	1172
R-SO ₃ ⁻	1180.44	1118.71	1180.44	1180.44
N=N	1612.49	1604.77	1604.77	1512.19
NH ₂	3448.72	3464.15	3456.44	3448.72

References : [27][28][18]

Figure 4: The determination of metal-ligand bonding of congo red complexes using FTIR. **Figure 5:** The determination of TiO₂ bonding with congo red complexes using FTIR spectrophotometry.

400-500 cm⁻¹. This peak indicates the bonding of Ti and O from the sulfonate group of ligand congo red. The incorporation of Ti and dye through bonding highly support the electron flow that occurred on the solar cell device. This condition is beneficial in increasing the electron flow [29-31].

The photovoltaic performance of each metal complex has been investigated and compared with the ligand congo red. The results (Table 5) show the terms of short-circuit current (J_{sc}), open-circuit voltage (V_{oc}), maximum current density (J_{max}), maximum voltage (V_{max}), fill factor (FF) and energy conversion efficiency (η) for the four solar cell systems investigated.

Table 5 shows that the efficiency of metal complexes is higher than the ligand itself (congo red). It means that the functionalization of congo red using metal ions is proven to increase their performance as a light harvester [12,13]. The highest photovoltaic performance was reached by Fe(II)-congo red complex (8.17%) and the lowest photovoltaic performance was reached by the Ni(II)-congo red complex (2.65%). The Fe(II) complex has the highest efficiency because the electron configuration of Fe(II) has more electrons than Co(II) and Ni(II) in their d orbitals. This means that iron(II) (d⁶) has more energy levels (Term Symbol : ⁵D, ¹S, ¹D, ¹G, ³P, ³F, ³P, ³D, ³F, ³G, ³H, ¹S, ¹D, ¹F, ¹G, ¹I) which can absorb photon energy [20]. The more energy levels available, the higher electron flow can be generated by light harvester, and the greater amount of electricity that can be obtained [30,32]. The Fe(II) complex obtained the highest Open Circuit Voltage (V_{oc}) comparing with the Co(II) and Ni(II) complex which are 0.872 V (Fe(II)), 0.268 V (Co(II)) and 0.445 V (Ni(II)).

Based on Table 5 and Table 6 we can see that there is a correlation between the efficiency of the metal complex and the metal atomic number. The higher of metal atomic number, the decrease in efficiency of solar cells. It can be explained that the higher metal atomic number cause the higher of effective nuclear charge of the metal. This

Table 5: The photovoltaic performance of congo red complexes.

Dye	J_{sc} (mAcm ⁻²)	V_{oc} (V)	J_{max} (mAcm ⁻²)	V_{max} (V)	FF	η (%)
Congo red	14	0.176	3	0.167	0.203	1.90
Fe-congo red	3	0.872	2.5	0.860	0.822	8.17
Co-congo red	12.5	0.268	8	0.202	0.481	6.13
Ni-congo red	2.5	0.445	1.6	0.435	0.626	2.65

Sunlight Intensity: 26.307 mWcm⁻²; Area: 4 cm²

Table 6: The effective nuclear charge (Z_{eff}) of metal complexes [20].

Metal ion	Shielding Constant (S)*	Atomic Number (Z)	Effective Nuclear Charge (Z_{eff})**
Fe ²⁺	19.75	26	6.25
Co ²⁺	20.10	27	6.90
Ni ²⁺	20.45	28	7.55

* Shielding Constant (S) was calculated by Slater's rule

** Effective Nuclear Charge (Z_{eff}) was calculated by Z minus S

condition will cause the electron density of the ligand to become more attracted to the metal. As a result, the electrons transferred by the dye to the semiconductor are reduced partially. This causes the electron cycle in the solar cell to decrease so that the electricity produced decreases.

4 Conclusions

The use of three metal ions to the synthetic dye, congo red, to improve its photovoltaic performance (through the formation of complexes) has been investigated. This research successfully proves that the addition of metals ion to congo red structure can improve efficiency of the solar cell. The addition of Fe(II) to congo red structure obtained the highest efficiency i.e. 8.17%. The larger an atomic number metal ion, the greater the effective nuclear charge of the metal so that the electron density of the ligand that will be donated to the photovoltaic process will be reduced because it is attracted to the metal. This condition causes a decrease in solar cell efficiency.

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