



Potency Complex Compound Mn(II)-TMPyP as a Dye Sensitizer on DSSC

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Abstract. Both the increasing human population and energy consumption are the main factors which cause energy crises. In this situation, we need new alternative energy source. DSSC (Dye Sensitized Solar Cells) has great potential to develop because the dye as a light catcher can be directly applied in daily life. In this research, Mn(II)-TMPyP complex compound has been synthesized as a dye sensitizer from $\text{MnCl}_2 \cdot 4\text{H}_2\text{O}$ and the derivatives of porphyrin (TMPyP), (5,10,15,20-Tetrakis(1- methyl-4-pyridinio)porphyrin, and tetra(p-toluenesulfonate). Mn(II)-TMPyP complex compound has been characterized using a UV-Vis spectrophotometer and showed a wavelength of 439.50 nm and 461 nm, and the vibration of Mn-N at a wavenumber of 300.90 cm^{-1} . The performance of Mn(II)-TMPyP complex compound as photosensitizer respectively obtained the value of short-circuit current (J_{sc}) at 5 mA/cm^2 , with an open circuit voltage (V_{oc}) at 0.40 V and the value of efficiency at 3.64%.

Keywords: Mn(II)-TMPyP · complexes · dye-sensitizer · renewable · Solar-Cell

1 Introduction

Energy is a vital source which is needed by all countries all around the world. Currently, energy necessities are increasing and resulting energy crisis. The limited resources of fossil fuels causing renewable energy resources are expected to be a new alternative. One of the alternative resources of renewable energy is by utilizing sunlight. Solar cells work using solar energy that is converted into electrical energy [1].

Dye Sensitized Solar Cell (DSSC) is a third-generation solar cell as a substitute for silicon solar cells or commonly called Grätzel cells. DSSC as a material has a huge potential to be developed because dye as a light catcher can be easily applied. DSSC was chosen because the production costs are relatively low and environmentally friendly. Thus, DSSC is very promising to be developed into a future power plant. DSSC uses simple electrochemical principles to capture solar energy, then converts it into electrical

energy. DSSC consists of several components, such as a dye, an electrode, an electrolyte, and a semiconductor [2, 3].

One of the most important components in DSSC is a dye. Dye is a component in DSSC that has a sensitizing effect as a sunlight catcher. Several dyes such as fluorescent dyes, platinum complexes, Ruthenium(II) complexes, and phthalocyanine [2, 3] are widely used as sensitizers in DSSC. These dyes still have many inadequacies such as materials that are difficult to obtain, expensive prices, and can damage the environment. Based on, these problems, many researchers have developed new ideas to obtain dyes that are cheaper, easier to obtain, less damage to environment and higher efficiency [4]. In previous studies, it has been known that Mn(II)-porphyrin derivatives that have a chromophore group can absorb more photons than porphyrin derivatives that do not have a chromophore group [5]. The chromophore group of porphyrin derivatives causes a shift towards a longer wave number. The nature of porphyrin derivatives has low solubility in water, it is necessary to make a modification that increases solubility performance in the water. The presence of a sulfonate group that is easy to solute in water that binds to TMPyP is expected to increase the solubility of TMPyP in water. Therefore, this research aim is to investigate the potential of Mn- TMPyP as a dye sensitizer on DSSCs which are responsible for the light harvesting mechanism [2, 6].

Mn metal was chosen as a substance to react with TMPyP because the metal is both easily reacted and is widely available in nature [7]. A study using Mn- TeNPs compounds produced an efficiency of 0.12% [8]. It can be proved that Mn can be used as a photosensitizer. It is relatively new in DSSC research, to use Mn as a substance to react with ligands in DSSC. Hence, Mn metal has high novelty and potential to be developed.

In this study, the dye was coated on the surface of TiO₂ using a modified dip coating method. This technique is simple and easy. The modification technique of the dip coating method is the TiO₂ suspension coating method where FTO glass is dipped in TiO₂ suspension and then leveled evenly. The sensitizer properties of the Mn(II)-TMPyP complex will be tested using current and voltage measurements produced by a multimeter when exposed to direct sunlight. The results of the synthesis of Mn(II)-TMPyP complex will be characterized using UV-Vis and Fourier Transform Infrared (FTIR).

2 Experimental

2.1 Synthesis of Mn(II)-TMPyP Complex

The Mn(II)-TMPyP complex was synthesized by reacting MnCl₂·4H₂O and TMPyP in a mole ratio of 1:1. The synthesis was carried out by mixing 10 ml of 10⁻³ M Mn²⁺ solution and 10 ml of 10⁻³ M TMPyP solution, then the solution was put into a 50 ml round bottom flask and added boiling stone to prevent bumping occurs. Next, the solution was refluxed at a temperature of 60–70 °C for 4–5 h. The results of the synthesis of the Mn(II)-TMPyP complex compound were evaporated to remove residual solvent, and after being evaporated the compound was left overnight until a precipitate formed [9, 10].

2.2 Preparation of Dye-Sensitized Solar Cells

2.2.1 TiO₂ coating on Glass Plates

Firstly, the FTO glass was sanded and washed with ethanol so that there would be no dirt when the FTO glass was used, then the FTO glass was dried. Secondly, 0.25 g of TiO₂ anatase Degussa P25 was suspended in 25 ml of 98% methanol to form a suspension. Thirdly, FTO glass measured by 2.5cm x 2.5cm x 0.01cm is immersed in TiO₂ suspension and then flattened on the part until the thickness is equal. Even distribution is assisted by scotch tape on the side of the glass which has a resistivity so that an area of 2 x 2 cm² is formed. The scotch tape serves to control the thickness of the TiO₂ suspension. TiO₂ suspension is coated on semiconductor glass by using a modified dip coating method, leveling the TiO₂ suspension by immersing the FTO glass in the TiO₂ suspension then leveling it by shaking the glass vertically and horizontally until it reaches a certain thickness and then placing it on a flat surface so that the flatness is maintained. Next, the FTO glass is left outside then dried using an oven.

Fourthly, the coating was carried out 3 times in the same way to obtain an even thickness of the TiO₂ suspension layer. Lastly, the glass plate was weighed before and after TiO₂ coating [11]. The thickness uniformity of the TiO₂ suspension layer was measured using a screw micrometer. Measurements were made at 5 points from the FTO glass section, then the average thickness was taken to prove the thickness of the TiO₂ layer.

2.2.2 Preparation of KI₃ as an Electrolyte Solution

The preparation of the electrolyte solution is to make a comparison of the salt concentration between 0.5 M KI and 0.05 M I₂. Prepared 2 beakers, for the first beaker 0.498 g of KI was poured and dissolved in 6 mL of acetonitrile in a beaker which was soluble in water. 5 min. In the second beaker, 0.076 g of I₂ and 6 mL of acetonitrile were added, then stirred until completely dissolved, the dissolution time was 3 h. After the solution in the two beakers is homogeneous, then the solution in the two beakers is mixed and stirred.

2.2.3 Preparation of Working Electrode

FTO glass that has been coated with TiO₂ suspension is then immersed in a 10–4 M Mn(II)-TMPyP complex solution for 3x24 hours and stored in a dark room to avoid sunlight. So that FTO glass can be used for a long time, the glass is stored in a closed dark bottle which is useful to avoid damage to the TiO₂ layer [12].

2.2.4 Preparation of Counter Electrode

The sanded FTO glass is then tapered and coated using a graphite pencil on a rough surface, then the glass is given carbon by burning the surface of the FTO glass coated with graphite pencil with wax until an even thickness of carbon is obtained [13]. Coating aims to speed up the reaction on the DSSC.

2.2.5 Fabrication of DSSC Cell

The working electrode is assembled by attaching the working electrode at the top with the comparison electrode opposite and dripping electrolyte KI_3 between the two electrodes. Then the uncoated edges of the two electrodes are clamped using binder clips to form a series of DSSC cells.

2.2.6 The Measurement of DSSC Current and Voltage with Direct Sunlight

First, the DSSC cell is connected by multimeter wires on both sides of the FTO glass with the reference electrode on the positive pole and the working electrode on the negative pole. Second, the DSSC cell that has been connected to a multimeter cable is then irradiated by the sun with the working electrode in the upper position. Last, the maximum current and voltage are measured.

2.2.7 The Measurement of Photovoltaic Performance of DSSC Using a Potentiometer (I- V Curve)

Photovoltaic performance was carried out by connecting DSSC cells with a potentiometer 100 K Ω . Next, the potentiometer was minimized and maximized to determine the current and voltage characteristics.

3 Results and Discussion

The Mn(II)-TMPyP complex was synthesized using a modified Adler method [14]. Adler's method is a method used to synthesize porphyrin compounds and porphyrin derivatives by reacting porphyrins with metals using dimethylformamide (DMF) solvent and refluxing it for 6–8 h. In this study, the modification of the Adler method was used because it used ethanol as a solvent which had a lower boiling point than DMF. The result of Mn(II)-TMPyP complex was evaporated and then left overnight to form a precipitate [14]. The obtained Mn(II)-TMPyP complex is reddish brown in color. The precipitate results were further characterized using UV-Vis spectrophotometer and FTIR.

The results of the characterization using UV-Vis spectrophotometer can be seen in Table 1. From Table 1, we can compare the maximum wavelength in the Q band region and the maximum wavelength in the Soret band region of the Mn(II)-TMPyP complex compound and TMPyP as a ligand. In the Mn(II)-TMPyP, there has been a shift in wavelength, which is marked by a shift from the maximum wavelength of TMPyP of 424.50 nm to 439.50 and 461 nm. In the Mn(II)-TMPyP, the decreasing intensity of the Q band happens when Mn(II) metal ions are inserted into the TMPyP compound.

On the other hand, the Soret band will experience a red shift from 424.50 nm (TMPyP) to 461.00 nm (Mn-TMPyP) where the phenomenon characteristic of the complex compound formed [14]. The appearance of a peak at a wavelength of 439.50 nm proves that the Mn(II)-TMPyP complex undergoes a charge transfer phenomenon characterized by the formation of a new peak in the UV region. The TMPyP compound has a low energy π^* orbital so the phenomenon of charge transfer can occur. Compounds that

experience a charge transfer phenomenon will absorb photons more optimally producing higher current and voltage in compounds that do not experience the charge transfer phenomenon.

Characterization using FTIR was used to determine the functional groups formed in the Mn(II)-TMPyP complex compound and to determine the bond between Mn(II) metal and TMPyP compounds. The results of the FTIR spectra of the TMPyP compound and the Mn(II)-TMPyP complex were different, indicating the formation of a new compound, but the spectra differences between TMPyP and Mn(II)-TMPyP were not significant. The FTIR results for TMPyP compounds and Mn(II)-TMPyP complexes and the descriptions of functional groups can be seen in Fig. 1 and Table 2.

Based on the FTIR spectral image of the functional group information from the table above, it can be seen that there is a bond between Mn(II) metal and TMPyP. The formation of Mn-N bonds detected at a wavenumber of 300.90 cm^{-1} , can be concluded that the Mn(II)-TMPyP complex has been formed. In accordance with the literature, the Mn-N bond will appear at wavenumbers of $300\text{--}400\text{ cm}^{-1}$ (Nakamoto, 2009). Mn(II) metal can bond to the N in the middle of the porphyrin ring because the N in the middle of the porphyrin ring has a greater density than the N at the outside of the porphyrin ring making Mn(II) metal easily enters the porphyrin ring. The theoretical prediction of the bond between Mn(II) and TMPyP can be seen in Fig. 2.

Table 1. Characterization results for complex Mn(II)- TMPyP and TMPyP.

Compound	λ_{maks} (nm)		
	Sort bands	Q bands	
Mn(II)-TMPyP	439.50; 461	768	707.50
TMPyP	424.50	648	708.50

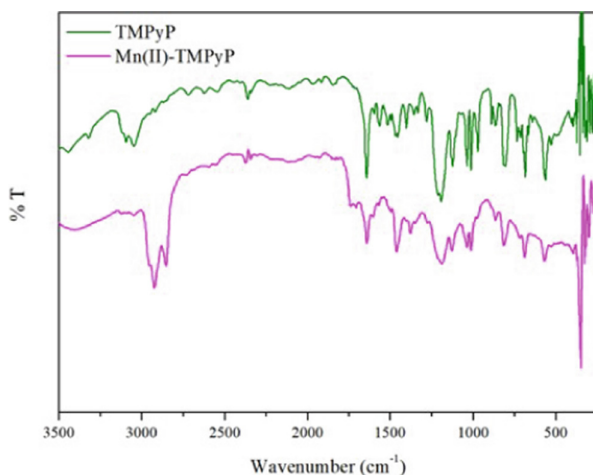
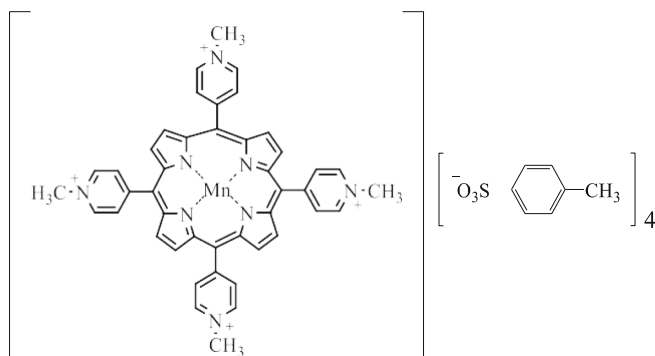


Fig. 1. The FTIR spectra of Mn(II)-TMPyP complex

Table 2. Identification of functional groups of complex Mn(II)-TMPyP and TMPyP.

Functional Group	Wavenumber (cm^{-1})		
	TMPyP	Mn(II)-TMPyP	Theory
Mn-N	-	300.90	400–300
SO ₃ H	1192.01	1188.15	1330–1050
C = N	1564.27	1460.11	1580–1450
C-H	3047.53	3090	3100–3000
N-CH ₃	1280.73	1365.60	1400–1000
C-N	1124.50	1128.36	1235–1070
N-H	3442.94	3425.58	3800–3400
C = C aromatics	1641.42	1639.49	1640–1607

[15–17].

**Fig. 2.** Bonding prediction between Mn and TMPyP.**Table 3.** The measurement result of short circuit current (I_{sc})

Day	Short Circuit Current (I_{sc}) (mA)			
	TiO ₂	TMPyP	Mn(II)-TMPyP	Lux
1	18	22	26	51.034
2	18	20	24	50.797
3	16	18	24	50.481
4	14	18	20	50.955
5	12	14	22	49.375

Table 4. Cost of Using Agroforestry Agricultural Medicines in Research Area 2021

Day	Short Circuit Voltage (Voc) (mV)			
	TiO ₂	TMPyP	Mn(II)-TMPyP	Lux
1	240	260	540	51.034
2	220	360	440	50.797
3	220	300	360	50.481
4	200	240	340	50.955
5	180	220	240	49.375

The photovoltaic performance of Mn(II)- complex was analyzed by applying the complex as a dye sensitizer on DSSC cell. The first analysis was current measurements were carried out for 5 days. DSSC current measurement is by varying the sample with TiO₂, TMPyP, Mn(II)-TMPyP complex. The results of current measurements can be seen in Table 3 and Fig. 3. Whereas the result of voltage measurements can be seen in Table 4 and Fig. 4.

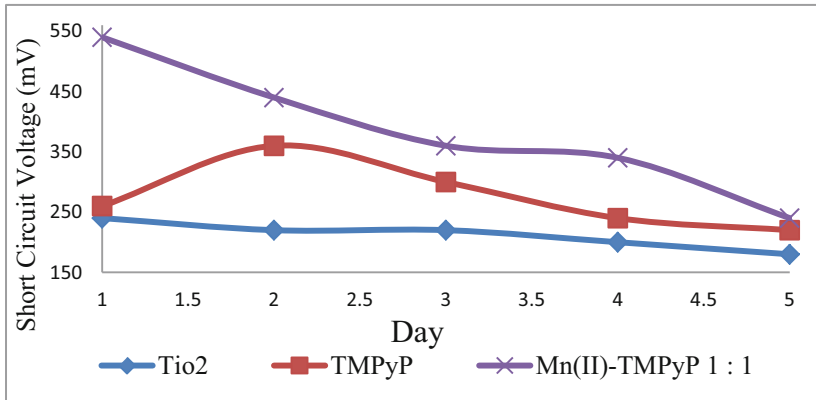
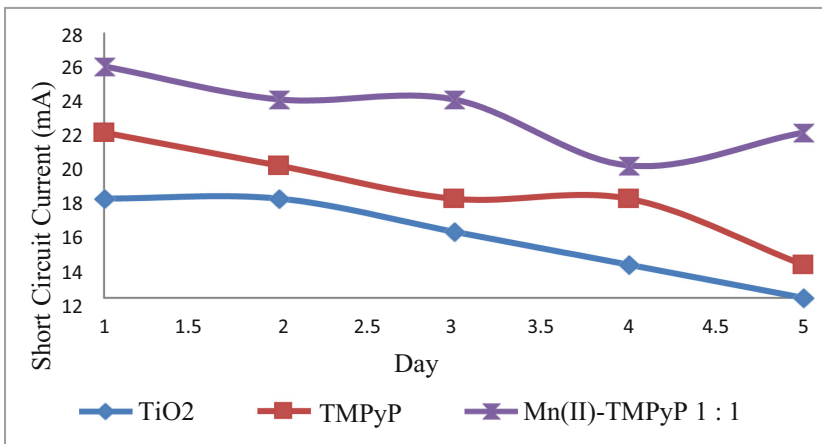
Based on Fig. 3, shows that the Mn(II)-TMPyP complex has higher currents than TiO₂, TMPyP. This is because there is a chemical bond between Mn and TMPyP compound so it can increase the ability of the photosensitizer. In complex compounds, Mn(II)- TMPyP, a charge transfer phenomenon occurs so that the absorbed light will be higher causing higher as well as the current value. In addition, the Mn(II)- TMPyP complex compound has conjugate bonds and lone pairs of electrons. As a consequence, the measured current is greater because it is easier to excite electrons. The measured DSSC cell current are decreasing as time goes by, this is because of the differences in the intensity of light. The lower the intensity of the light absorbed, the lower the current generated [18].

In Fig. 4, it can be seen that Mn(II)-TMPyP complex compound has a higher voltage than TiO₂, and TMPyP due to chemical interactions that occur. As a result, Mn(II)-TMPyP complex compound has a higher voltage. Therefore, the addition of dye can improve the performance of DSSC cells.

The ability of DSSC cells to conduct electricity can be done by determining the I to V curve by measuring using a potentiometer. Based on Table 5, the short circuit current (Isc) of TiO₂, TMPyP and complex Mn(II)-TMPyP is 28 mA; 22 mA; 20 mA, where the Isc obtained in this study is higher than the Isc in chlorophyll which is included in the porphyrin derivatives, namely 8 mA, 14 mA, 8 mA, and 16 mA [12, 19]. The value of open circuit Voltage (Voc) Iis also obtained by 0.24 V; 0.36 V; and 0.4 V. Based on data, the efficiency values of TiO₂, TMPyP, and complex Mn(II)-TMPyP are 2.46%; 3.22% and 3.64%. The Mn(II)-TMPyP complex compound produce the highest efficiency values compared to other compounds in this study. It happens because the Mn(II)-TMPyP complex compound experiences a charge transfer phenomenon, where the complex compound experiences a charge transfer phenomenon that will absorb sunlight optimally and produce a higher values of currents, voltages, and efficiency.

Table 5. Cost of Agroforestry Agricultural Labor Wages in Research Areas in 2021

Compound	Voc (V)	Isc (mA)	Jsc	FF	η (%)
TiO ₂	0.24	28	7	0.77	2.46
TMPyP	0.36	22	5.5	0.83	3.22
Mn(II)-TMPyP	0.40	20	5	0.90	3.64

**Fig. 3.** Graph of the relationship of short circuit current against the day**Fig. 4.** Graph of the relationship of open circuit voltage against the day

4 Conclusion

Based on the results that have been obtained, it can be concluded that the characteristics of complex compounds are formed. When Mn metal is reacted with TMPyP, it shows a maximum wavelength shift of 439.50 nm and 461.00 nm, there is a bond between metal and ligand at a wave number of 300.90 cm^{-1} which is an Mn-N vibration. The effect of Mn on the performance of TMPyP can increase the efficiency of TMPyP by 3.23% to 3.64%.

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Authors’ Contributions. **Handoko Darmokoesoemo:** Conceptualization, Data curation.

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Irmina Kris Murwani: Writing – review & editing.

Evi Triana Putri: Investigation.

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