

## 염료감응 태양전지를 위한 무금속 유기염료의 합성

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## Synthesis of Metal-free Organic Dye for Dye-sensitized Solar Cell

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**요 약.** 염료감응 태양전지(DSSC)는 대체에너지 집적제로서 낮은 생산단가로 고에너지 전환 효과를 볼 수 있다. 친환경적이며 효과가 큰 무금속 염료감응제의 개발이 중요하다. 본 연구에서 유기 감광제로 6,6'-(1,2,5-oxadiazole-3,4-diyl)dipyridine-2,4-dicarboxylic acid(3A)을 합성하였다. 이 감광제를 사용하여 광전환효율( $\eta$ )이 1.00%를 달성함을 발견하였다. 같은 조건에서 루테늄착물(N719)은 4.02%의 광전환효율을 나타내었다.

**주제어:** 유기염료 감응제, 집광 소재, 염료감응 태양전지

**ABSTRACT.** Dye-sensitized solar cell (DSSC); an alternate energy source harvester has gained some attractive features such as high-energy conversion efficiency low production cost. Dye-sensitizer is a basic component of DSSC, which affecting the performance of the energy conversion efficiency. Current research has been focusing on development of high efficiency, metal-free dye-sensitizers, which would be more environmental friendly. We had successfully explored synthetic route to 6,6'-(1,2,5-oxadiazole-3,4-diyl)dipyridine-2,4-dicarboxylic acid (3A) which has been used as organic sensitizer. Investigation of light conversion efficiency ( $\eta$ ) of the compound uses standard measurement condition (one sun simulated irradiation, AM 1.5, 100 mW/cm<sup>2</sup>) showed that it could reach 1.00% ( $J_{SC}=2.63 \text{ mAcm}^{-2}$ ,  $V_{OC}=0.64 \text{ V}$  and  $FF=0.59$ ). Under the same conditions, the ruthenium complex (N719) gave the conversion efficiency as high as 4.02% ( $J_{SC}=10.50 \text{ mAcm}^{-2}$ ,  $V_{OC}=0.67 \text{ V}$  and  $FF=0.57$ ).

**Keywords:** Organic dye-sensitizer, Light harvesting material, Dye-sensitize Solar Cell

## INTRODUCTION

The rising price of fuels and the pollution concerns have led to an investigation for alternative energy sources. Solar energy is interesting energy source due to its inexhaustible, clean and environmental friendly characteristics. It can be converted directly into electrical power by photovoltaic (PV) cell devices, commonly called solar cells. At present, silicon-based solar cells have gained more interest and highly developed. In the last decade the new molecular photovoltaic (PV) materials had emerged and could be

alternative low-cost solar cells in the near future. Dye-sensitized solar cells (DSSC) are designed for light harvesting; which enable of using a dye-sensitizer (DS) on semiconductor. DSSC are composed mainly of non-toxic materials and inexpensive technology for high efficient solar cells. The light harvesting material in DSSC, a dye sensitizers, acts as the solar energy absorbers; of which the proprieties of the materials play an important role on the conversion efficiency. Dye sensitizers used in DSSC were mainly metal complexes containing ruthenium as a metal center and complexing organic ligands. At present, organic

dyes, natural and synthetic organic dyes, have been increasing interest due to their simple and lower synthetic cost. DSSC had gained interest in the first time after O'Regan and Grätzel<sup>1</sup> and Nazeeruddin *et al.*<sup>2</sup> reported high solar energy for electricity conversion; which has efficiency up to 11% with ruthenium bipyridyl dyes. However, the ruthenium complex-based DSSCs are quite expensive for cost-conversion efficiency. This is partly due to the limited resources of noble metal, ruthenium, and the synthetic processes of those complexes, which are very complicated and difficult to achieve their purities. Furthermore, ruthenium complexes containing heavy metals are not environmentally friendly. Therefore, organic dyes would be the choice for further development of DSSC for future energy sources.<sup>3,4</sup> At present, several groups have been working on organic sensitizers to overcome the prohibitive issues of ruthenium complexes.<sup>5</sup> The possibility of using some oxadiazoles as organic dye sensitizers has been focused and investigation of their light harvesting efficiency has been made to achieve in certain extent.

## EXPERIMENTAL

### Instrumentation

IR spectra were recorded in KBr on a Nicolet 6700 FT-IR spectrophotometer. Elemental analyses were carried out in a Perkin-Elmer Series 2 CHNS/O analyzer 2400. <sup>1</sup>H-NMR spectra were recorded in DMSO-*d*<sub>6</sub> on a Bruker AVANCE-400 MHz NMR spectrometer using TMS as internal standard. Electron impact mass spectra were obtained at 70 eV using a Finnigan Mat GCQ spectrometer.

### Reagents

All chemicals were purchased from Sigma-Aldrich Company.

**Synthesis of 3,4-di(pyridin-2-yl)-1,2,5-oxadiazole (1A):** A mixture of  $\alpha$ -pyridyl dioxime (2.42 g, 10 mmol) and 1 M potassium hydroxide (2 mL) were placed in a moderate pressure vessel and placed in an oil bath preheating to 180 °C and maintained at this temperature for 18 hours. The vessel was then allowed to cool to room temperature. The residuals were extracted with 100 mL of dichloromethane and dried over anhydrous sodium sulphate. Solvents were reduced to about 20 mL and poured into 100 mL of hexane, the light yellow precipitates were formed. The residue was recrystallized from ethyl acetate to afford product 1.98 g (85%).

**Synthesis of 3,4-bis(4,6-diisopropylpyridin-2-yl)-1,2,5-oxadiazole (2A):** A mixture of 1A (1.12 g, 5 mmol), isobu-

tyric acid (2.5 mL, 25 mmol), silver nitrate (0.2 g, 1 mmol) and 60 mL of water : acetonitrile 1:1 as a co-solvent was placed into a three-necked flask (250 mL) fitting with a 50-mL graduated funnel containing a solution of ammonium peroxydisulfate (7 g, 30 mmol) in 40 mL of water and it was slowly added to the reaction mixture. After complete addition, the reaction mixture was stirred for further 30 minutes at 65 °C, then cooled to room temperature. The reaction mixture was extracted with 50 mL dichloromethane. The organic layer was separated and dried over anhydrous sodium sulphate, the solvent was reduced in *vacuo*. Hexane was added up to ten times to the solution for precipitating out the starting material. The filtrate was evaporated in *vacuo* to give a dark yellow oil 1.32g (67.3%).

**Synthesis of 6,6'-(1,2,5-oxadiazole-3,4-diyl) dipyridine-2,4-dicarboxylic acid (3A):** Potassium permanganate (8 g, 50 mmol) was dissolved in 100 mL of 10% sulfuric acid in a flask (250 mL). The solution was poured into a round-bottomed flask containing of 2A (2 g, 5 mmol). The mixture was refluxed with stirring until the purple color disappeared. The solution was filtered, and the residue was washed with 50 mL of hot water. The mixture was then extracted five times with 10 mL of ethyl acetate. The organic layers were combined and dried over anhydrous sodium sulphate, the solvent was evaporated under *vacuo*. The residue was recrystallized from ethyl acetate affording 3A as a yellow crystals in 0.9g (45%).

### Preparation of electrodes

The thin-film TiO<sub>2</sub> working electrode (TiO<sub>2</sub> nanoparticle powder 6.0 g, ethyl cellulose 2.0 g, polyethylene glycol 2.0 g and 0.1mL of Triton X-100<sup>6</sup>) and platinum counter electrode (5 mM H<sub>2</sub>PtCl<sub>6</sub> in  $\alpha$ -terpineol<sup>7</sup>) were prepared by a screen printing technique spread onto a previously cleaned fluorine-doped SnO<sub>2</sub> (FTO) conducting glass. Porous TiO<sub>2</sub> films were sintered at 450 °C for 30 min at a heating rate of 5 °C.min<sup>-1</sup>. The platinum counter electrode plates were sintered in a furnace at 400 °C for 30 min at a heating rate of 20 °C.min<sup>-1</sup>.

### Fabrication and measurements of dye-sensitized solar cells

The TiO<sub>2</sub> electrodes were immersed into the dye-sensitized solution (0.3 mM in absolute ethanol) overnight at room temperature. Counter electrode was directly placed on top of the dye-adsorbed TiO<sub>2</sub> electrode. Surlyn polymer sheet was used as a spacer. Electrolyte solution consisted of a solution of 0.1M Lithium iodide, 0.05M Iodine and 0.5 M 4-*tert*-butylpyridine in anhydrous acetonitrile as solvent<sup>8</sup>

was filled to the cell. The current–voltage performance of the DSSC was measured by exposing with simulated AM 1.5 irradiation with an incident power density of 100 mW/cm<sup>2</sup> using a 1000 W Xe arc lamp solar simulator.

## RESULTS AND DISCUSSION

A procedure of the synthetic route to the oxadiazole (3A) has been outlined below (see Fig. 1).

### Results of synthesis and characterizations of organic dye used as dye sensitizers

The synthesis of 3,4-di(pyridin-2-yl)-1,2,5-oxadiazoles (1A) was performed on heating of the  $\alpha$ -pyridil dioxime in potassium hydroxide solution at 185 °C for 18 hours; which effected the cyclodehydration yielding the expected product in 85% yield.<sup>9</sup> <sup>1</sup>H-NMR resonance peaks appeared at  $\delta$  8.57,  $\delta$  7.98,  $\delta$  7.87,  $\delta$  7.54 ppm could be assigned to the contribution of pyridine ring protons. The elemental analysis was in good agreement with those calculated values for the expected molecular formula C<sub>12</sub>H<sub>8</sub>N<sub>4</sub>O: C, 64.28; H, 3.60; N, 24.99; O, 7.14. Mass spectra showed the molecular ion peak at m/z 224.0 (M<sup>+</sup>, 20%), together with m/z at 104.0 (PyCN<sup>+</sup>, 31%) and 78.0 (Py<sup>+</sup>, 100%), which agreed with the proposed structure. Isobutyric acid was used to generate isopropyl radical for alkylation of the pyridine ring of (1A) at  $\alpha$  position. Alkyl radical would be an electron rich species, therefore, attack at  $\alpha$  position next to the electron withdrawing nitrogen. The monoalkylated product so formed was then alkylated further at  $\gamma$  position to give dialkylated product. The  $\beta$  position would be highly steric for the introduction of second isopropyl group. By

this way the alkylated product could be obtained as high as 67.3%. <sup>1</sup>H-NMR chemical shift at 7.540 and 7.092 ppm could be assigned to protons of pyridine ring. The strong multiplet was assigned to protons of methyl group as its chemical shift shown at 1.071 ppm. A sharp IR peak at 2966 cm<sup>-1</sup> was assigned to stretching vibration of methyl group (CH<sub>3</sub>). Calculation of m/z for C<sub>24</sub>H<sub>32</sub>N<sub>4</sub>O was 392.52 which agreed with the found molecular ion at m/z 392.2. Elemental analysis obtained for C, H, N, and O were 73.20, 8.49, 14.50 and 3.81%, respectively. The values agreed very well with the molecular formula C<sub>24</sub>H<sub>32</sub>N<sub>4</sub>O (C, 73.43%; H, 8.22%; N, 14.27%; O, 4.08%). The alkyl side chains of 2A were smoothly oxidized with hot aqueous potassium permanganate to give carboxylic acid moiety attaching to the pyridine rings. The oxidative product 3A, containing four carboxylic groups, was obtained in 45% yield with melting point at 93-94 °C. Elemental analysis was found for C, H, N, and O: 47.51, 2.21, 14.18 and 35.90%, respectively. The result agreed nicely with the calculation for C<sub>16</sub>H<sub>8</sub>N<sub>4</sub>O<sub>9</sub> (C, 48.01%; H, 2.01%; N, 14.00%; O, 35.98%). IR spectra showed broad peak around 3431 cm<sup>-1</sup>, which was assigned to the hydroxyl group (O-H). A sharp peak at 1727 cm<sup>-1</sup> was assigned for the carboxyl group. MS showed the molecular ion at m/z 400.13, which corresponding to the proposed structure. <sup>1</sup>H-NMR showed a doublet at 8.825 and 8.143 ppm which corresponding to the protons of pyridine ring.

### Measurements of dye-sensitized solar cell efficiency

The dye-sensitized solar cell measurements were done by exposing with simulated AM 1.5 irradiation with an incident power density of 100 mW/cm<sup>2</sup>(P<sub>in</sub>). The results were obtained as J–V curve by the plot of a short-circuit current density (J) against an open circuit voltage (V), which gave the maximum power point (MPP). The I–V curve of dye-sensitized solar cells using N719 and 3A were shown in Fig. 2.

The fill factor (FF) and energy conversion efficiency ( $\eta$ ) had been calculated by the following equations Eq. 1 - Eq. 2<sup>10,11</sup>

$$FF = \frac{V_{max} \cdot J_{max}}{V_{OC} \cdot J_{SC}} \quad (1)$$

$$\eta(\%) = \frac{V_{OC} \cdot J_{SC} \cdot FF}{P_{in}} \cdot 100 \quad (2)$$

Performance measurements of the sensitized solar cells were studied as compared to the ruthenium dye, N719 as shown in Table 1.

The sensitized solar cell of N719 gave a J<sub>SC</sub> of 10.50

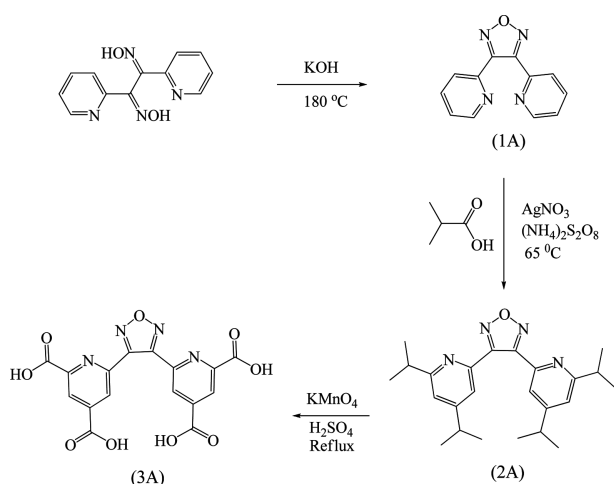
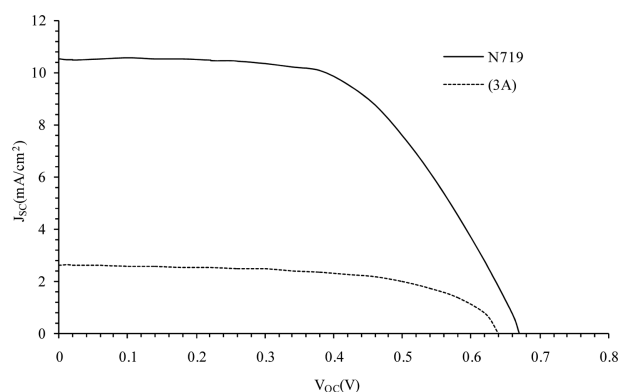


Fig. 1. Schematic representation of the synthetic route to the target molecule (3A).



**Fig. 2.** I-V curve from the measurements of a dye-sensitized solar cell.

**Table 1.** Photovoltaic performance of dye-sensitized solar cells using difference dyes under simulated irradiation source (AM 1.5 100 mW/cm<sup>2</sup>)

Dye	J <sub>SC</sub> (mAcm <sup>-2</sup> )	V <sub>OC</sub> (V)	FF	η(%)
N719	10.50	0.67	0.57	4.02±0.04
3A	2.63	0.64	0.59	1.00±0.06

mAcm<sup>-2</sup>, V<sub>OC</sub> of 0.67 V and a fill factor of 0.57 with the corresponding conversion efficiency (η) of 4.02%. Under the same conditions, the conversion efficiency of sensitized solar cell using 3A was obtained as 1.00% with J<sub>SC</sub> of 2.63 mAcm<sup>-2</sup>, V<sub>OC</sub> of 0.64 V and a fill factor of 0.59. However, one of the main reasons for the lower efficiency of 3A compared with N719 was due to its light absorption close to the ultraviolet region.

## CONCLUSION

We have successfully modified a procedure for the synthesis of an organic dye (6,6'-(1,2,5-oxadiazole-3,4-diyl)-dipyridine-2,4-dicarboxylic acid (3A)) used as a dye-sensitized solar cell without metal complexes. The conversion efficiency of the sensitized cells using the synthetic

organic dye (3A) was compared with N719 ruthenium complex sensitized cells. The performance of dye-sensitized solar cells of N719 using standard measurement condition under simulated irradiation source (AM 1.5 100 mW/cm<sup>2</sup>) gave a J<sub>SC</sub> of 10.50 mAcm<sup>-2</sup>, V<sub>OC</sub> of 0.67 V and a fill factor of 0.57 with the corresponding conversion efficiency (η) of 4.02 %. Under the same condition, the conversion efficiency of sensitized solar cell using the synthetic organic dye (3A) was obtained as 1.00% with J<sub>SC</sub> of 2.63 mAcm<sup>-2</sup>, V<sub>OC</sub> of 0.64 and a fill factor of 0.59.

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