Synthesis of 6,6’ - (1,2,5 - Oxadiazole - 3, 4 Diyl) Dipyridine-2,4-Dicarboxylic Acid: an Organic Dye for Dye-sensitized Solar Cell

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บทคัดย่อ

เซลล์แสงอาทิตย์ชนิดสีย้อมไวแสง ซึ่งเป็นอุปกรณ์เก็บเกี่ยวพลังงานที่เป็นทางเลือกที่มีจุดเด่นที่น่าสนใจ อาทิเช่น มีประสิทธิภาพในการแปลงพลังงานสูง ขณะที่ต้นทุนการผลิตต่ำ สีย้อมอินทรีย์เป็นองค์ประกอบหลักของเซลล์แสงอาทิตย์ชนิดสีย้อมไวแสง ทำหน้าที่เป็นวัสดุเก็บเกี่ยวแสง ซึ่งเป็นปัจจัยสำคัญที่มีผลต่อประสิทธิภาพของเซลล์แสงอาทิตย์ชนิดนี้ ปัจจุบันงานวิจัยต่าง ๆ ได้มุ่งเน้นการพัฒนาสีย้อมไวแสงที่ปราศจากโลหะให้ประสิทธิภาพเพิ่มขึ้นและเป็นมิตรกับสิ่งแวดล้อม งานวิจัยนี้ได้ประสบความสำเร็จในการสังเคราะห์ 6,6’-(1,2,5-Oxadiazole-3,4-Diyl) Dipyridine- 2,4-Dicarboxylic Acid เพื่อใช้เป็นสีย้อมอินทรีย์ไวแสง สารที่ทำการสังเคราะห์ทุกสารได้ทำการพิสูจน์เอกลักษณ์ด้วยสเปกโทรสโคปีต่อไปนี้ ^{1}H-NMR, IR และ MS การทดสอบประสิทธิภาพของการแปลงพลังงานแสงของสารประกอบดังกล่าว พบว่าให้ประสิทธิภาพเท่ากับ 1.19% (J_{SC} = 3.08 mAcm^{-2}, V_{OC} = 0.66 V และ FF = 0.58) ภายใต้สภาวะการทดลองเดียวกัน เมื่อใช้สารประกอบเชิงซ้อนของโลหะรูทิเนียม (N719) พบว่าให้ประสิทธิภาพเท่ากับ 3.56% (J_{SC} = 9.12 mAcm^{-2}, V_{OC} = 0.76 V และ FF = 0.67)

คำสำคัญ: สีย้อมอินทรีย์ไวแสง วัสดุเก็บเกี่ยวแสง เซลล์แสงอาทิตย์ชนิดดายเซนซิไทซ์ ออกซาไดอะโซล

Abstract

Dye-sensitized solar cell (DSSC), an alternate energy source harvester, has gained some attractive features such as high-energy conversion efficiency and low production cost. An organic dye which performs as light harvesting material is a key component of DSSC. The organic component has a major factor on the energy conversion efficiency. Currently, researchers are focusing on development of high efficiency, metal-free dye-sensitizers, which would be more environmental friendly. In this paper, we reported a successful synthesis of 6,6’ -(1,2,5-oxadiazole-3,4-diyl)dipyridine-2,4-dicarboxylic acid which was used as an organic sensitizer. All compounds were characterized by spectroscopic techniques (^{1}H-NMR, IR and mass spectroscopy). Investigation of light conversion efficiency (η) of

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the compound showed that it could reach 1.19% (J_{SC} = 3.08 mAcm^{-2}, V_{OC} = 0.66 V and FF = 0.58). Under the same conditions, the ruthenium complex (N719) gave the conversion efficiency as high as 3.56% (J_{SC} = 9.12 mAcm^{-2}, V_{OC} = 0.76 V and FF = 0.67).

Keywords: Organic Dye-sensitizer, Light Harvesting Material, Dye-sensitized Solar Cell, Oxadiazole

1. 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 it's inexhaustable, 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 [1] and Nazeeruddin et al. [2] 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 dues partly 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 [3], [4]. At present, several groups have been working on organic sensitizers to overcome the prohibitive issues of ruthenium complexes [5]. The possibility of using some oxadiazoles as orgnic dye sensitizers has been focused and investigation of their light harvesting efficeincy has been made to acheive in certain extent.

2. Materials and Methods

2.1 Materials

All chemicals were purchased from Sigma-Aldrich Company. 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. ^{1}H-NMR spectra were recorded in DMSO-d_6 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. Melting points were determined with an Electrothermal melting point apparatus.

2.2 Synthesis of 2-hydroxy-1,2-di(pyridin-2-yl) ethane-1-one (α-pyridoin)

Sodium cyanide (10 g, 200 mmol) was dissolved in water (100 mL) in a 250-mL round-bottomed flask. 2-Pyridine-carboxaldehyde (10 mL, 100 mmol) was slowly added dropwise into the above solution and vigorously stirred. The precipitates produced were extracted with dichloromethane. The organic layer was separated, dried over anhydrous sodium sulphate and evaporated under *vacuo*. The product was purified by recrystallization from ether to yield exclusively α-pyridoin in 10.0 g (93%) ; m.p. 135-138°C; (Found: C, 67.02; H, 4.86; N, 13.10; Calc. for $C_{12}H_{10}N_2O_2$: C, 67.28; H, 4.71; N, 13.08). IR(KBr) 3455 cm^{-1}, ν O-H(broad); 1591 cm^{-1}, ν C=N (pyridine ring); 1561 cm^{-1}, ν C=C (pyridine ring); 1182 cm^{-1}, ν C-O (sharp band); 783 and 733 cm^{-1}, ν C-H (out of plane). Positive-ion EI-MS Calc. m/z for $C_{12}H_{10}N_2O_2$ 214.07; found m/z 214.0 (M$^+$, 76%), 108.2 (pyCOH $^+$, 100%), 78.0(py$^+$, 22%). ^{1}H-NMR (DMSO-d_6) δ 13.10 ppm(s, 2H); δ 8.57 ppm(dd, J=4.8, 0.8 Hz, 2H); δ 8.00 ppm(dt, J= 7.6, 1.6 Hz, 2H); δ 7.79 ppm(d, J=7.6 Hz, 2H); δ 7.35-7.39 ppm (m, 2H).

2.3 Synthesis of 1,2-di(pyridin-2-yl)ethane-1,2-dione (2,2'-pyridil)

α-pyridoin (4.3 g, 20 mmol) was dissolved in ethyl acetate (25 mL) and filtered to give a yellowish solution which was then poured into a closed vessel and kept at room temperature for a week. The resulting yellow-brownish crystals were formed and were recrystallized from ether to afforda 2,2'-pyridil in 4.0 g (94%); m.p. 154-157 °C; (Found: C, 67.69; H, 4.07; N, 12.91; O, 15.33. Calc. for $C_{12}H_8N_2O_2$: C, 67.92; H, 3.80; N, 13.08; O, 15.08). IR (KBr) 3060 cm^{-1} ν C-H(py); 1713 and 1691 cm^{-1} ν C=O ketone (-CO-CO-); 1583 cm^{-1} C=C (pyridine ring); 897, 754 cm^{-1} ν CH(out of plane). Positive-ion EI-MS Calc. m/z for $C_{12}H_8N_2O_2$ 212.20; found m/z 212.0 (M$^+$, 30%), 156.0 (2py,100%), 78.0 (py$^+$, 10%). ^{1}H-NMR (DMSO-d_6) δ 8.65 ppm (d, J=4.4 Hz, 2H) ; δ 7.97 ppm (dt, J=8, 1.6Hz, 2H); δ 7.86 ppm (d, J=7.6 Hz, 2H); δ 7.51-7.54 ppm(m, 2H).

2.4 Synthesis of *N,N'*-(1,2-pyridin-2-yl) bis-(hydroxylamine); (α-pyridil dioxime)

A mixture of 2,2'-pyridil (2.12g, 10 mmol), hydroxylamine hydrochloride (4.17 g, 60 mmol), sodium acetate (8.16 g, 60 mmol) and methanol (25 mL) was refluxed for 8 hours. The suspension was then filtered and washed several times with hot methanol. The filtrate was dried over anhydrous sodium sulphate and filtered. After removal of solvents under *vacuo*, the residues were recrystallized from acetonitrile to give the white crystals 2.17 g (90%); mp. 235-236°C; (Found: C, 60.55; H, 3.64; N, 23.28. Calc. for $C_{12}H_8N_2O_2$: C, 59.50; H, 3.64; N, 23.13). IR (KBr) 3163 cm-^{1}, ν O-H (broad); 1624 cm^{-1}, ν C=N (oxime group); 1587 cm^{-1}, ν C=N (pyridine ring); 1566 cm^{-1}, ν C=C (pyridine ring). Positive-ion EI-MS: Calc. m/z for $C_{12}H_{10}N_4O_2$ 242.23; found m/z 242.0 (M$^+$, 2.61%), 224.0 (M$^+$-H_2O, 22%), 207.0 (M$^+$-2H_2O, 100%), 104.0 (PyCN$^+$, 10%), 78.0 (Py$^+$, 15%). ^{1}H-NMR (DMSO-d_6) δ 8.59 ppm (dd, J=4.8, 0.8 Hz, 2H,); δ 7.83 ppm (dt, J=7.6, 1.6 Hz, 2H); δ 7.47 ppm (d, J=7.6 Hz, 2H,); δ 7.32-7.36 ppm (m, 2H).

2.5 Synthesis of 3,4-di(pyridin-2-yl)-1,2,5-oxadiazole (1A)

A mixture of α-pyridil 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 the 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%); m.p. 120–122^{o}C; (Found: C, 64.45; H, 3.45; N, 25.23. Calc. for $C_{12}H_8N_4O$: C, 64.28; H, 3.60; N, 24.99). IR (KBr) 1588 cm^{-1}, ν C=N (pyridine ring); 1572 cm^{-1}, ν C=C (pyridine ring); 890 cm^{-1}, ν N-O. Positive-ion EI-MS: Calc. m/z for $C_{12}H_8N_4O$ 224.22; found m/z 224.0 (M^{+}, 20%), 104.0 (PyCN^{+}, 31%), 78.0 (Py^{+}, 100%). ^{1}H-NMR (DMSO-d_6) δ 8.57 ppm (dd, J=4.4, 0.8 Hz, 2H); δ 7.98 ppm (dt, J=7.6, 1.6 Hz, 2H,); δ 7.87 ppm (d, J=7.6 Hz, 2H,); δ 7.52-7.56 ppm (m, 2H).

2.6 Synthesis of 3,4-bis(4,6-diisopropylpyridin-2-yl)-1,2,5-oxadiazole (2A)

A mixture of **1A** (1.12 g, 5 mmol), isobutyric acid (2.5 mL, 25 mmol), silver nitrate (0.2 g, 1 mmol) and 60 mL of water : acetonitrile 1:1 as a co-sovent 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%); (Found: C, 73.20; H, 8.49; N, 14.50. Calc. for $C_{24}H_{32}N_4O$: C, 73.43; H, 8.22; N, 14.27). IR (KBr) 2966 cm^{-1}, ν C-H (methyl group stretching); 1603 cm^{-1}, ν C=N (pyridine ring); 1560 cm^{-1}, ν C=C (pyridine ring); 1465 cm^{-1}, ν C-H (methyl group deformation); 887 cm^{-1}, ν N-O. Positive-ion EI-MS: Calc. m/z for $C_{24}H_{32}N_4O$ 392.52; found m/z 392.2 (M^{+}, 10%), 377.1 (M^{+}-CH$_3$, 18%), 350.2 (M^{+}-C$_3$H$_7$, 50%), 350.2 (M^{+}-C$_3$H$_7$, -CH$_3$, 100%). ^{1}H-NMR (DMSO-d_6) δ 7.54 ppm (d, J=6.0 Hz, 2H); δ 7.09 ppm (d, J=4.5 Hz, 2H); δ 2.79-2.83 ppm (m, 2H); δ 2.67-2.71 ppm (m, 2H); δ 1.00-1.20 ppm (m, 24H).

2.7 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 time 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%); m.p. 93–94^{o}C; (Found: C, 47.51; H, 2.21; N, 14.18. Calc. for $C_{16}H_8N_4O_9$: C, 48.01; H, 2.01; N, 14.00). IR (KBr) 3550-3300 cm^{-1}, ν O-H(hydroxyl group); 1727 cm^{-1}, ν C=O (carbonyl group); 1609 cm^{-1}, ν C=N (pyridine ring); 1569 cm^{-1}, ν C=C (pyridine ring); 1243 cm-^{1}, ν C=C (aromatic substitution). Positive-ion EI-MS: Calc.

m/z for $C_{16}H_8N_4O_9$ 400.02; found m/z 400.13 (M^+, 12%), 355.1 (M^+-COOH, 40%). ^{1}H-NMR (DMSO-d_6) δ 8.82 ppm (d, J=4.5 Hz, 2H); δ 8.14 ppm (d, J=4.5 Hz, 2H).

2.8 Preparation of thin-film TiO_2 Working Electrode

TiO_2 nanoparticle powder 6.0 g, ethyl cellulose 2.0 g, polyethylene glycol 2.0 g and 0.1 mL of Triton X-100 were added into a mortar and ground to form a slurry [6]. Porous TiO_2 films were prepared by a screen printing technique spread onto fluorine-doped SnO_2 (FTO) conducting glass. The film was allowed to dry overnight in vacuum desiccators, this was then sintered at 450°C for 30 min at a heating rate of 5°C min^{-1}.

2.9 Preparation of Platinum Counter Electrode

Platinum counter electrode was prepared by deposition of a paste containing 5 mM H_2PtCl_6 in α-terpineol [7] using a screen printing technique on a previously cleaned fluorine-doped SnO_2 (FTO) conducting glass. After air-drying at room temperature, the plates were sintered in a furnace at 400°C for 30 min at a heating rate of 20°C min^{-1}.

2.10 Fabrication and Measurements of Dye-sensitized Solar Cells

The TiO_2 electrodes were immersed into the dye-sensitized solution (prepared in a 0.3 mM in absolute ethanol) overnight at room temperature. Counter electrode was directly placed on top of the dye-adsorbed TiO_2 electrode. Surlyn polymer sheet was used as a spacer. Electrolyte solution consisted of a solution of 0.5 M lithium iodide, 0.05 M iodine and 0.5 M 4-*tert*-butylpyridine in anhydrous acetonitrile as solvent [8] was filled to the cell. The current–voltage performance of the DSSC was measured by exposing with natural sunlight source at noon (at high noon on a cloudless day, the surface of the earth receives 1,000 watts of solar power per square meter [9]). In general, the current and voltage output can be determined by volt–amp meter as a variable loads and a measurement set-up [10]. The I–V curves generated by plot of short-circuit current density (J) against open circuit voltage (V). From the I–V curve it gave short-current density (J_{SC}), open-circuit voltage (V_{OC}) and fill-factor (FF), which had been calculated to give energy conversion efficiency (η).

3. Results and Discussion

A procedure of the synthetic route to the oxadiazole (3A) is outlined below (see Figure 1).

3.1 Synthesis and Characterizations of Organic Ligands used as Dye Sensitizers

Aqueous cyanide was essential for the condensation reaction of 2-pyridinecarboxal- dehyde; which afforded 2-hydroxy-1,2-di(pyridin-2-yl)ethane-1-one, (α-pyridoin) in 93% yield. The chemical shift of ^{1}H-NMR spectrum appeared as a singlet at 13.10 ppm corresponding to the intramolecular hydrogen bonding of the keto–enol α-pyridoin proton. The double doublets at 8.57 ppm was assigned to proton of the pyridine ring close to N atom. It is worth to note that when the reaction run by the reported procedure, which was heated at 140°C without solvent and catalyst, gave products in lower yield [11]. The α-pyridoin was further converted almost quantitatively to 1,2-di(pyridin-2-yl)ethane-1,2-dione (2,2’-pyridil) by dissolving in ethyl acetate and kept at RT for one

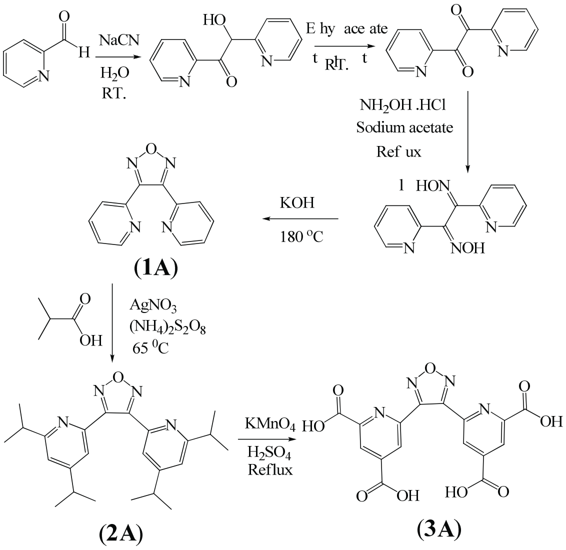

Figure 1 Schematic representation of the synthetic route to target molecule **(3A)**.

week. Presumably, a mild oxidation of α-pyridoin by trace oxygen had been taken place in ethyl acetate solution. ^{1}H-NMR spectrum showed four different signals of the pyridine protons as doublet at 8.56 and 7.86 ppm, double triplet at 7.97 ppm and multiplet at 7.53 ppm. The IR spectrum showed strong absorption bands around 1713 and 1691 cm^{-1} corresponding to the vibrational stretching of C=O groups of 2,2’-pyridil, which also agreed with the disappearance of the O–H vibrational stretching of α-pyridoin [12]. 2,2’-Pyridil was then converted to the corresponding oxime, *N,N’*-(1,2-pyridin-2-yl)bis (hydroxylamine) or α-pyridil-dioxime, in 90% yield. The reaction was done by reacting with an excess hydroxylamine in methanol at refluxing temperature [13]. ^{1}H-NMR revealed a singlet signal at 11.69 ppm of hydroxyl group, a low-field signal implyed a formation of an intermolecular hydrogen bond. IR spectrum showed a broad band at 3163 cm^{-1}, a weak band at 1624 cm^{-1}, and a sharp band at 1587 cm^{-1} which were assigned to the stretching vibration of OH, oximes and pyridine groups, respectively. The synthesis of **1A** was performed on heating of the α-pyridil dioxime in potassium hydroxide solution at 180°C for 18 hours; which induced the cyclodehydration yielding the expected product in 85% yield [14]. ^{1}H-NMR resonance peaks appeared at δ 8.57, δ 7.98, δ 7.87, δ 7.54 ppm which could be assigned to the contribution of pyridine ring protons. The **2A** were prepared from a free radical alkylation reaction of **1A** at α position [15] with isobutyric acid. Alkyl radical would be an electron rich species, therefore, attack at α position next to the electron withdrawing nitrogen. The mono-alkylated product so formed was then alkylated further at γ position to give dialkylated products. The β position would be highly steric for the introduction of second isopropyl group. By this way the alkylated products could be obtained as high as 67.3%. ^{1}H-NMR chemical shift at 7.54 and 7.09 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 1.00-1.20 ppm. A sharp IR peak at 2966 cm^{-1} was assigned to stretching vibration of methyl group (CH_3). 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. IR spectrum showed broad peak around 3431 cm^{-1}, which was assigned to the hydroxyl group (CO-OH). ^{1}H-NMR showed a doublet at 8.82 and 8.14 ppm which corresponding to the protons of pyridine ring.

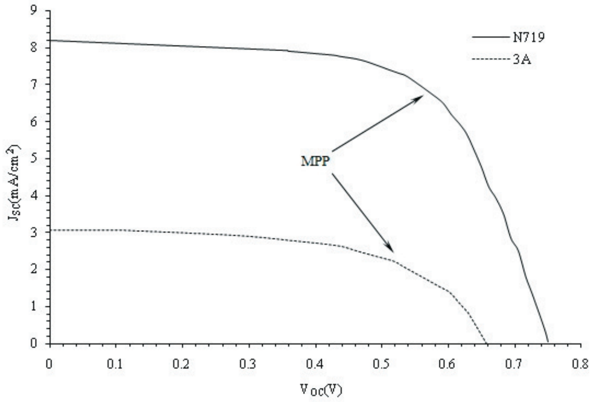

Figure 2 I-V curve from the measurements of a dye-sensitized solar cell.

3.2 Measurements of Dye-sensitized Solar Cell Efficiency

Dye-sensitized solar cell measurements, in general, were done by exposing with natural sunlight source at high noon (air mass 1.0, ~100 mWcm^{-2}) and recording current–voltage by volt–amp meter with a variable load. Results of the measurements were obtained as I–V curve by the plot of a short-circuit current density (J_{SC}) against an open circuit voltage (V_{OC}), which gave the maximum power point (MPP). The I–V curve of dye-sensitized solar cells using N719 and **3A** are shown in Figure 2.

The fill-factor (FF) and energy conversion efficiency (η) were calculated by the following equations [10], [11]

$$FF = \frac{V_{max} \cdot J_{max}}{V_{OC} \cdot J_{SC}}$$

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

Where J_{SC} is the short-circuit current density (mA cm^{-2}), V_{OC} is the open-circuit voltage (V), P_{in} is the intensity of the incident light (Wcm^{-2}), J_{max}(mA cm^{-2}) and V_{max}(V) are the current density and voltage at the point of maximum power output in the I–V curves, respectively. Performance measurements of the sensitized solar cells were studied as compared to the ruthenium dye, N719 as shown in Table 1

Table 1 Photovoltaic performance of dye-sensitized solar cells using difference dyes

Dye	J_{SC}(mAcm^{-2})	V_{OC}(V)	FF	η(%)
N719	9.12	0.76	0.67	3.56±0.12
3A	3.08	0.66	0.58	1.19±0.09
2A	0.05	0. 22	-	-
1A	0.04	0.24	-	-

The sensitized solar cell of N719 gave a J_{SC} of 9.12 mAcm^{-2}, V_{OC} of 0.76 V and a fill-factor of 0.67 with the corresponding conversion efficiency (η) of 3.56%. Under the same conditions, the conversion efficiency of sensitized solar cell using **3A** was obtained as 1.19% with J_{SC} of 8.81 mAcm^{-2}, V_{OC} of 0.66 and a fill-factor of 0.58. 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 (as seen from the light yellow color of the solution). The performances of sensitized solar cell using **1A** and **2A** were very low compared with **3A;** even though the three compounds have the same main structural features. Due to its lack of anchoring carboxyl groups, the transfer electrons from these dyes (**1A** and **2A**) to the TiO_2 electrode would be prohibited.

4. Conclusion

From our work many achievements have been made. Firstly, we have successfully modified a procedure for the synthesis of an organic ligand, 6,6'-(1,2,5-oxadiazole-3,4-diyl)-dipyridine-2,4-dicarboxylic acid **(3A)**. Secondly, the synthetic organic dye showed conversion efficiency which comparable with N719 without any metal complex.

The N719 gave conversion efficiency (η) of 3.56%, with a short-circuit current density (J_{SC}) of 9.12 mAcm^{-2}, an open-circuit voltage (V_{OC}) of 0.76 V and a fill-factor of 0.67. Under the same conditions, the sensitizer **(3A)** gave J_{SC} 3.08 mAcm^{-2}, V_{OC} 0.66 and a fill-factor 0.58 corresponding to η of 1.19%. The other two synthetic organic dyes (**1A** and **2A**) were found inactive in our studies.

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References

[1] B. O'Regan and M. Grätzel, "A low-cost, high-efficiency solar cell based on dye-sensitized colloidal TiO_2 films," *Nature*, vol.353, pp. 737 – 740, 1991.

[2] M. K. Nazeeruddin, A. Kay, I. Rodicio, R.Humpbry-Baker, E. Miiller, P. Liska, N. Vlachopoulos, and M. Grätzel, "Conversion of light to electricity by cis-X_2Bis(2,2′-bipyridyl-4,4′ dicarboxylate)ruthenium(II) charge-transfer sensitizers(X = C1-, Br-, I-, CN-, and SCN-) on Nanocrystalline TiO2 electrodes," *J. Am.Chem. Soc.*, vol. 115, pp. 6382-6390, 1993.

[3] S. Hwang, J. Ho Lee, C. Park, H. Lee, C., Kim, C. Park, M. H. Lee, W. Lee, J., Park, K. Kim, N. G. Park, and C. Kim, "A highly efficient organic sensitizer for dye-sensitized solar cells," *Chem. Commun*., pp. 4887-4889, 2007.

[4] K. Hara, Y. Tachibanaa, Y.,Ohgab, A. Shinpob, S. Sugab, K. Sayamaa, H. Sugiharaa ,and H. Arakawa, "Dye-sensitized nanocrystalline TiO_2 solar cells based on novel coumarin dyes," *Solar Energy Materials & Solar Cells*, vol. 77, pp. 89–103, 2003.

[5] A. Mishra, K. R. Fischer, and P. Büerle, "Metal free organic dyes for dye-sensitized solar cells: from structure: property relationships to design rules," *Angew. Chem. Int.*, vol. 48, pp. 2474-2499, 2009.

[6] Y. Wang, Y. Sun, B. Song, and J. Xi,"Ionic liquid electrolytes based on 1-vinyl-3-alkylimidazolium iodides for dye-sensitized solar cells," *Solar Energy Materials & Solar Cells*, vol. 92, pp. 660-666, 2008.

[7] R. Solarska J. Augustynski, and K. Sayama, "Viewing nanocrystalline TiO_2 photoelectrodes as three-dimensional electrodes: effect of the electrolyte upon the photocurrent efficiency," *Electrochimica Acta*, vol. 52, pp. 694-703, 2006.

[8] W. J. Lee, E. Ramasamy, D. Y. Lee, and J. S. Song, "Performance variation of carbon counter electrode based dye-sensitized solar cell," *Solar Energy Materials & Solar Cells*, vol. 92, pp.814-818, 2008.

[9] D. Dusabe, J. Munda, and A. Jimoh, "Modelling of cloudless solar radiation for PV module performance analysis," *Journal of Electrical Engineering*, vol. 60, pp. 192-197, 2009.

[10] G. P. Smestad, "Education and solar conversion: demonstrating electron transfer," *SolarEnergy*

Materials and Solar Cells, vol. 55, pp. 157-178, 1998.

[11] M. J. Percino, V. M.Chapela, S. Romero, C. Rodríguez-Barbarín, and F. J. Melendez-Bustamante, “Synthesis of 1,2-dimethoxy-1,2-di(pyridin-2-yl)-1,2-ethanediol: crystal and molecular structure determination,” *Journal of Chemical Crystallography*, vol. 36, pp. 303-308, 2006.

[12] W. S. Kim, B. J. Lee, N. M. Tuong, E. M. Son, K. S. Yang, and Y. S. Kwon, “Electro luminescence of co-ligated aluminum complex of α-pyridoin and 8-hydroxyquinoline,” *Current Applied Physics*, vol. 6, pp.596-600, 2006.

[13] M. Yadav, “Studies in 3,4-diaryl-1,2,5-oxadiazoles and their *N*-oxides: search forbetter COX-2 inhibitors,” *Acta Pharm*, vol.57, pp.13-30, 2007.

[14] C. Richardson, P. J. Steel, D. M. D’Alessandro, P. C. Junk, and F. R. Keeneand, “Mono- and di-nuclear complexes of the ligands 3,4-di (2-pyridyl)-1,2,5-oxadiazole and 3,4-di (2-pyridyl)-1,2,5-thiadiazole; new bridges allowing unusually strong metal–metal interactions,” *J. Chem. Soc. Dalton Trans*., pp.2775-2785, 2002.

[15] D. L. Comins, S. O′Connor, and R. S. Al-awar, *Comprehensive Heterocyclic Chemistry III A Review of the Literature,* volume 6, Indianapolis: Eli Lilly and Company, c2008.