

## Research Article

# Incorporation of Kojic Acid-Azo Dyes on TiO<sub>2</sub> Thin Films for Dye Sensitized Solar Cells Applications

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Sensitization of heavy metal free organic dyes onto TiO<sub>2</sub> thin films has gained much attention in dye sensitized solar cells (DSSCs). A series of new kojic acid based organic dyes **KA1–4** were synthesized *via* nucleophilic substitution of azobenzene bearing different vinyl chains **A1–4** with kojyl chloride **4**. Azo dyes **KA1–4** were characterized for photophysical properties employing absorption spectrometry and photovoltaic characteristic in TiO<sub>2</sub> thin film. The presence of vinyl chain in **A1–4** improved the photovoltaic performance from 0.20 to 0.60%. The introduction of kojic acid obtained from sago waste further increases the efficiency to 0.82–1.54%. Based on photovoltaic performance, **KA4** achieved the highest solar to electrical energy conversion efficiency ( $\eta = 1.54\%$ ) in the series.

## 1. Introduction

Dye sensitized solar cells (DSSCs), a third-generation solar cell discovered in early 1990s, have gained intensive attention and been considered as promising alternative for fossil fuel energy [1, 2]. DSSCs offer advantages over the conventional silicon based solar cell due to cost effectiveness, flexibility in shape, easy accessibility of dye resources, and noteworthy performance [3, 4]. DSSCs convert sunlight into electrical energy mimicking the photosynthesis process employing synthetic or natural dye as light harvesting pigments [5]. Sensitizer in the cell absorbs photons and induces excitation of electron to the wide bandgap semiconductor, dyes, and electrolyte [6]. Ruthenium complex is one of the most effective light harvesting sensitizers reported in DSSCs; however, the drawbacks of these ruthenium sensitizers are complicated procedure, limited source, and being expensive, environmentally unsafe, and carcinogenic [7–9].

Over the years, tremendous efforts have been made to explore natural and organic dye as DSSCs sensitizer due to being nontoxic and environmentally friendly, low cost, and easy modification for functionalization. Extracted

natural dye, however, has low yields of extract and scarce resources [10]. Organic dye such as azobenzene has outstanding chromophores with strong absorption in visible region and intrinsic advantages of good photo and thermal stability [11, 12]. Azobenzene is a reactive precursor for functional group conversion and attachment such as vinyl and alkoxy chain with enhanced optical properties [13, 14].

Development of natural and organic dyes as sensitizer on TiO<sub>2</sub> thin film for DSSC performance has been widely reported [15–17]. Anthocyanin in natural dye which has carbonyl and hydroxyl groups has been reported for its anchoring ability to TiO<sub>2</sub> surface in DSSC applications [18–20]. Binding of C=O and OH groups to the TiO<sub>2</sub> surface promotes better electron transfer mechanism to the conduction band of TiO<sub>2</sub>. Kojic acid [21, 22], a natural pyrone which carries one C=O and two OH groups, is envisaged to have similar properties of natural anthocyanins dyes for its ability to bind with TiO<sub>2</sub>. Kojic acid is a nonhazardous and biodegradable natural product, which was earlier reported for tyrosinase inhibition and colorimetric determination [23–26]. To the best of our knowledge, no studies reported on the applications of kojic acid derivatives as DSSCs sensitizer.

In this current study, we report on the synthesis of heavy metal free photosensitizer of organic dye azobenzene, which consists of vinyl chain as spacer and kojic acid anchoring group for DSSCs application. Kojic acid was obtained from fermentation of sago biomass was incorporated with azobenzene organic dye **A1–4** via esterification and formed novel dyes **KA1–4**. The effect of anchoring group and spacer on the performance of the DSSCs was also studied.

## 2. Experimental

**2.1. Materials.** Commercially available reagent grade chemicals were used without further purification. All solvents were of analytical grade and used as received unless specified as dry, in which case they were dried and distilled before being used under oxygen free nitrogen as follows: acetone was distilled over magnesium sulphate anhydrous and stored over 4 Å molecular sieves.

*Sago hampas* (an abundant agricultural waste in Sarawak, Malaysia) was collected from Herdson Sago Mill in Pusa, Sarawak. The substrate was oven dried and ground before use. ITO-coated (Indium-doped tin oxide) conductive glass slides (surface resistivity 15 Ω/sq, thickness 2.2 mm) obtained from China were used as substrates for preparing TiO<sub>2</sub> thin film electrode and platinum counter electrode.

**2.2. Measurements.** <sup>1</sup>H and <sup>13</sup>C NMR spectra were recorded on a JEOL ECA 500 spectrometer at 500 MHz (<sup>1</sup>H) and 125 MHz (<sup>13</sup>C) with the chemical shifts δ (ppm) reported relative to DMSO-d<sub>6</sub> as standard. Tetramethylsilane (TMS) was used as the internal reference. Infrared (IR) spectra (ν cm<sup>-1</sup>) were recorded as KBr pellets on a Perkin Elmer 1605 FTIR spectrophotometer. The coupling constants (*J*) are given in Hertz (Hz). The current to voltage characterization was carried out by varying the value of load resistance under the light source of 120 W/240 V and was used and illuminate at 120 W/m<sup>2</sup>. The electrical characteristics of DSSCs were measured on two-wire current-voltage analyzer using National Instrument Educational Laboratory Virtual Instrumentation Suite NI ELVIS II+ 100 MS/s Oscilloscope. The CHNS elemental analyses were using Thermo Scientific™ FLASH 2000 CHNS/O Analyzer. Supplementary data for FTIR, <sup>1</sup>H NMR, <sup>13</sup>C NMR, and UV spectra and photovoltaic measurement of synthesized compounds are available online (in Supplementary Material available online at <https://doi.org/10.1155/2017/2760301>).

**2.3. Preparation of Kojic Acid (1) [27].** *Sago hampas* (5 g) was supplemented with 3% (w/v) urea and 10% mineral salts solution containing KH<sub>2</sub>PO<sub>4</sub>, (w/v) MgSO<sub>4</sub>·7H<sub>2</sub>O and yeast. Mixed strains of *Aspergillus Flavus NSH9* and *Aspergillus Flavus Link 44-1* were employed for fermentation. The culture was incubated at 30 ± 2 °C in static condition for 18 days. The slurry suspension culture (40 mL) was extracted with ethyl acetate (2 × 15 mL). The organic layer was evaporated in *vacuo* to form crude brown solid and recrystallized from ethanol to afford **1** as yellowish needle like crystal (0.15 g, 30%): IR (KBr Pellet) ν<sub>max</sub> in cm<sup>-1</sup>: 3173 (OH), 2919 (C=C), 1661 (C=O), 1228 (C-O); <sup>1</sup>H NMR (500 MHz, DMSO-D<sub>6</sub>): δ 9.04 (s, 1H),

8.02 (s, 1H), 6.34 (s, 1H), 5.67 (s, 1H), 4.29 (s, 1H); <sup>13</sup>C NMR (125 MHz, DMSO-D<sub>6</sub>): δ 174.4, 168.6, 146.2, 139.8, 110.4, 60.0.

### 2.4. Synthesis Azo Dyes [28]

**2.4.1. Ethyl 4-[E-(4-Hydroxyphenyl)azo]benzoate (2).** A solution of 4-aminobenzoate (5 g, 30.0 mmol) in methanol (50 mL) was cooled in an ice bath (0–5 °C) and HCl (8 M, 100 mL) was added dropwise to the solution at such a rate that the reaction temperature was maintained below 5 °C. A solution of sodium nitrite (3.1 g, 45.0 mmol) in distilled water (10 mL) and phenol (3.4 g, 36 mmol) in methanol (50 mL) were cooled to 0–5 °C and added dropwise to the reaction mixture. NaOH solution (1 M, 100 mL) was cooled in ice bath and added dropwise to pH 8.5–9.5. The reaction mixture was stirred for 4 h under nitrogen atmosphere. Methanol (50 mL) and ice (20 mL) were added to the reaction mixture and were acidified with HCl (8 M, 50 mL) until yellow precipitate formed. The solid formed was filtered, washed, and recrystallized from ethanol to give **2**, an orange colored solid (6.7 g, 83%); ν<sub>max</sub> (KBr, cm<sup>-1</sup>) 3399 (OH), 2959 (CH<sub>2</sub>CH<sub>3</sub>), 1696 (C=O), 1596 (aromatic), 1431 (N=N), 1228 (C-O), 1133 (C-N); <sup>1</sup>H NMR (500 MHz, DMSO-D<sub>6</sub>): δ 8.11 (d, *J* 8.4 Hz, 2H), 7.88 (d, *J* 8.4 Hz, 2H), 7.84 (d, *J* 8.5 Hz, 2H), 6.96 (d, *J* 9.2 Hz, 2H), 4.34 (q, 2H), 1.34 (t, 3H); <sup>13</sup>C NMR (125 MHz, DMSO-D<sub>6</sub>): δ 166.3, 165.8, 162.3, 155.3, 145.8, 131.4, 125.9, 122.8, 116.7, 61.6, 52.9.

**2.4.2. 4-[(E)-(4-Hydroxyphenyl)azo]benzoic Acid (3).** KOH (0.13 g, 2.4 mmol) was added to the solution of **2** (0.2 g, 0.8 mmol) in methanol (50 mL) and refluxed for 4 h under nitrogen. The reaction was monitored by TLC analysis. Water (30 mL) and crushed ice (10 mL) were added and the reaction mixture was acidified with acetic acid (8 M) until precipitate formed. The crude product was filtered and recrystallized from ethanol to give **3** (0.12 g, 62%) as bright yellow solid; ν<sub>max</sub> (KBr, cm<sup>-1</sup>) 3208 (OH), 1686 (COO), 1594 (aromatic), 1198 (C-O), 1140 (C-N). <sup>1</sup>H NMR (500 MHz, DMSO-D<sub>6</sub>): δ 8.10 (d, *J* 8.6 Hz, 2H), 7.88 (d, *J* 8.6 Hz, 2H), 7.84 (d, *J* 8.6 Hz, 2H), 6.96 (d, *J* 9.15 Hz, 2H); <sup>13</sup>C NMR (125 MHz, DMSO-D<sub>6</sub>): δ 167.2, 162.0, 155.1, 145.9, 132.6, 131.1, 125.8, 122.6, 116.6.

**2.5. General Procedure for the Synthesis of A1–4 [29].** Azo precursor **3** was added to the solution of bromoalkene derivatives, t-BuOK, and KI in dried acetone. The reaction mixture was refluxed for 48 h under nitrogen and the reaction was monitored using TLC analysis. DCM (50 mL) and water (30 mL) were added and the layers separated. The aqueous layer was extracted with DCM (2 × 30 mL) and the combined organic layers were dried and evaporated under reduced pressure to give the *title compounds*.

**2.5.1. 4-[E-(4-But-3-enoxyphenyl)azo]benzoic Acid (A1).** Azo precursor **3** (1.5 g, 5 mmol) was added to the solution of 4-bromobutene (0.68 g, 0.51 mL, and 5.0 mmol), tBuOK (0.62 g, 5.0 mmol), and KI (20 mg) in dried acetone (100 mL). The reaction mixture was refluxed under nitrogen for 48 h and worked up according to the general procedure. The crude product was recrystallized from ethanol to give **A1** (1.03 g,

70%) as orange colored solid;  $\nu_{\max}$  (KBr,  $\text{cm}^{-1}$ ) 3073 (C=CH), 2947 ( $\text{CH}_2$ ), 1677 (C=O), 1599 (Aromatic), 1425 (N=N), 1243 (C-O), 1139 (C-N).  $^1\text{H}$  NMR (500 MHz,  $\text{DMSO-D}_6$ ):  $\delta$  8.10 (d,  $J$  8.6 Hz, 2H), 7.87 (m, 4H), 6.96 (d,  $J$  9.16 Hz, 2H), 5.92 (m, 1H), 5.15 (dd,  $J$  10.9 Hz, 2H), 4.16 (t, 2H), 1.22 (s, 2H);  $^{13}\text{C}$  NMR (125 MHz,  $\text{DMSO-D}_6$ ):  $\delta$  167.4, 162.2, 155.1, 145.9, 131.1, 125.8, 125.5, 122.7, 122.6, 116.6, 115.6, 67.8, 50.2.

**2.5.2. 4-[E-(4-Pent-4-enoxyphenyl)azo]benzoic Acid (A2).** Azo precursor **3** (1.5 g, 5 mmol) was added to the solution of 5-bromopentene (0.83 g, 0.72 mL, and 5.0 mmol), *t*BuOK (0.62 g, 5.0 mmol), and KI (20 mg) in dried acetone (100 mL). The reaction mixture was refluxed under nitrogen for 48 h and worked up according to the general procedure. The crude product was recrystallized from ethanol to give **A2** (1.0 g, 65%) as brown colored solid;  $\nu_{\max}$  (KBr,  $\text{cm}^{-1}$ ) 3080 (C=CH), 2943 ( $\text{CH}_2\text{CH}_3$ ), 1591 (Aromatic), 1380 (N=N), 1245 (C-O), 1149 (C-N).  $^1\text{H}$  NMR (500 MHz,  $\text{DMSO-D}_6$ ):  $\delta$  7.96 (d,  $J$  8.4 Hz, 2H), 7.87 (d,  $J$  8.4 Hz, 2H), 7.71 (d,  $J$  8.0 Hz, 2H), 7.12 (d,  $J$  8.4 Hz, 2H), 6.84 (s, 1H), 5.88 (m, 1H), 5.04 (dd,  $J$  11.4 Hz, 2H), 4.09 (t, 2H), 2.20 (m, 2H), 1.85 (m, 2H);  $^{13}\text{C}$  NMR (125 MHz,  $\text{DMSO-D}_6$ ):  $\delta$  167.4, 162.5, 155.0, 146.6, 138.4, 132.6, 131.1, 125.6, 122.8, 115.9, 115.7, 67.9, 30.0, 28.2.

**2.5.3. 4-[E-(4-Hept-6-enoxyphenyl)azo]benzoic Acid (A3).** Azo precursor **3** (1.5 g, 5 mmol) was added to the solution of 7-bromoheptene (0.98 g, 0.84 mL, and 5.0 mmol), *t*BuOK (0.62 g, 5.0 mmol), and KI (20 mg) in dried acetone (100 mL). The reaction mixture was refluxed under nitrogen for 48 h and worked up according to the general procedure. The crude product was recrystallized from ethanol to give **A3** (1.15 g, 68%) as brown colored solid;  $\nu_{\max}$  (KBr,  $\text{cm}^{-1}$ ) 3382 (OH), 2954 ( $\text{CH}_2\text{CH}_3$ ), 1596 (Aromatic), 1239 (C-O), 1147 (C-N).  $^1\text{H}$  NMR (500 MHz,  $\text{DMSO-D}_6$ ):  $\delta$  8.11 (d,  $J$  8.55 Hz, 2H), 7.92 (d,  $J$  9.15 Hz, 2H), 7.90 (d,  $J$  8.6 Hz, 2H), 7.14 (d,  $J$  9.2 Hz, 2H), 5.81 (m, 1H), 4.99 (dd,  $J$  13.75 Hz, 2H), 4.09 (t, 2H), 2.06 (m, 2H), 1.77 (m, 2H), 1.43 (m, 4H);  $^{13}\text{C}$  NMR (125 MHz,  $\text{DMSO-D}_6$ ):  $\delta$  167.6, 162.6, 154.9, 146.5, 139.2, 133.0, 131.1, 125.6, 122.7, 115.7, 115.5, 68.6, 33.6, 28.9, 28.4, 25.5.

**2.5.4. 4-[E-(4-Oct-7-enoxyphenyl)azo]benzoic Acid (A4).** Azo precursor **3** (1.5 g, 5 mmol) was added to the solution of 8-bromooctene (1.06 g, 0.93 mL, and 5.0 mmol), *t*BuOK (0.62 g, 5.0 mmol), and KI (20 mg) in dried acetone (100 mL). The reaction mixture was refluxed under nitrogen for 48 h and worked up according to the general procedure. The crude product was recrystallized from ethanol to give **A4** (1.4 g, 80%) as brown colored solid;  $\nu_{\max}$  (KBr,  $\text{cm}^{-1}$ ) 2925 ( $\text{CH}_2\text{CH}_3$ ), 1677 (C=O), 1600 (Aromatic), 1418 (N=N), 1246 (C-O), 1141 (C-N).  $^1\text{H}$  NMR (500 MHz,  $\text{DMSO-D}_6$ ):  $\delta$  8.11 (d,  $J$  8.45 Hz, 2H), 7.91 (t, 4H), 7.14 (d,  $J$  8.4 Hz, 2H), 5.80 (m, 1H), 4.97 (dd,  $J$  13.4 Hz, 2H), 4.08 (t, 2H), 2.03 (m, 2H), 1.75 (m, 2H), 1.36 (m, 6H);  $^{13}\text{C}$  NMR (125 MHz,  $\text{DMSO-D}_6$ ):  $\delta$  172.4, 168.5, 162.3, 153.9, 146.6, 139.4, 130.8, 125.3, 122.2, 115.6, 71.9, 68.5, 40.2, 33.6, 29.0, 28.7, 25.8.

**2.6. 2-(Chloromethyl)-5-hydroxy-pyran-4-one (4) [30].** Thi-onyl chloride (0.036 g, 0.3 mmol) was added to the solution

of **1** (0.014 g, 0.1 mmol) in DMF (20 mL) and refluxed for 4 h. The reaction mixture was extracted with DCM (2  $\times$  15 mL). The organic layer was dried, filtered, and concentrated under reduced pressure. Compound **5** was recrystallized from ethanol to give yellowish needle solid (0.012 g, 70%).

**2.7. General Procedure for the Synthesis of KAI-4.** Azo intermediate **A1-4** was added to the solution of **4** in dried acetone with TEA and refluxed for 24 h. The reaction mixture was washed with dilute HCl (1M, 2  $\times$  20 mL). The organic layer was dried, filtered, and concentrated under reduced pressure to give title compound.

**2.7.1. (5-Hydroxy-4-oxo-pyran-2-yl)methyl-4-[(E)-(4-but-3-enoxyphenyl)azo]benzoate (KA1).** Azo intermediate **A1** (0.14 g, 0.5 mmol) was added to the solution of **4** (0.1 g, 0.6 mmol) in dried acetone (20 mL) with TEA (0.015 g, 0.15 mmol) refluxed for 24 h. The reaction mixture was worked up according to the general procedure. Crude product was recrystallized from ethanol to afford **KA1** as yellow solid (0.15 g, 70%);  $\nu_{\max}$  (KBr,  $\text{cm}^{-1}$ ) 3223 (C=CH), 1713 (C=O ester), 1651 (C=O), 1620 (Aromatic), 1453 (N=N), 1243 (C-O), 1140 (C-N);  $^1\text{H}$  NMR (500 MHz,  $\text{DMSO-d}_6$ ):  $\delta$  8.19 (d,  $J$  8.05 Hz, 2H), 8.13 (s, 1H), 7.95 (d,  $J$  8.55 Hz, 2H), 7.94 (d,  $J$  8.6 Hz, 2H), 7.16 (dd,  $J$  8.88 Hz, 2H), 6.60 (s, 1H), 5.90 (m, 1H), 5.26 (s, 2H), 5.15 (dd,  $J$  13.74 Hz, 2H), 4.16 (t, 2H), 1.21 (s, 2H);  $^{13}\text{C}$  NMR (125 MHz,  $\text{DMSO-d}_6$ ):  $\delta$  174.4, 165.1, 163.3, 162.0, 155.4, 146.7, 146.5, 140.7, 135.1, 131.4, 130.4, 125.7, 123.0, 115.7, 115.3, 113.3, 67.7, 56.3, 33.34.

**2.7.2. (5-Hydroxy-4-oxo-pyran-2-yl)methyl-4-[(E)-(4-pent-4-enoxyphenyl)azo]benzoate (KA2).** Azo intermediate **A2** (0.16 g, 0.5 mmol) was added to the solution of **4** (0.1 g, 0.6 mmol) in dried acetone (30 mL) with TEA (0.015 g, 0.15 mmol) and refluxed for 24 h. The reaction mixture was worked up according to the general procedure. Crude product was recrystallized from ethanol to afford **KA2** as orange solid (0.19 g, 87%);  $\nu_{\max}$  (KBr,  $\text{cm}^{-1}$ ) 3219 (C=CH), 1712 (C=O ester), 1651 (C=O), 1619 (Aromatic), 1453 (N=N), 1236 (C-O), 1139 (C-N);  $^1\text{H}$  NMR (500 MHz,  $\text{DMSO-d}_6$ ):  $\delta$  8.18 (d,  $J$  8.55 Hz, 2H), 8.13 (s, 1H), 7.95 (d,  $J$  6.3 Hz, 2H), 7.93 (d,  $J$  6.85 Hz, 2H), 7.15 (d,  $J$  8.6 Hz, 2H), 6.60 (s, 1H), 5.87 (m, 1H), 5.25 (s, 2H), 5.03 (dd,  $J$  13.75 Hz, 2H), 4.10 (t, 2H), 2.20 (m, 2H), 1.85 (m, 2H);  $^{13}\text{C}$  NMR (125 MHz,  $\text{DMSO-d}_6$ ):  $\delta$  174.3, 168.9, 165.1, 162.8, 162.0, 155.3, 146.5, 140.7, 138.4, 131.4, 130.3, 125.7, 123.0, 115.9, 115.7, 113.3, 68.0, 62.7, 30.0, 28.2.

**2.7.3. (5-Hydroxy-4-oxo-pyran-2-yl)methyl-4-[(E)-(4-hept-6-enoxyphenyl)azo]benzoate (KA3).** Azo intermediate **A3** (0.17 g, 0.5 mmol) was added to the solution of **4** (0.1 g, 0.6 mmol) in dried acetone (30 mL) with TEA (0.015 g, 0.15 mmol) and refluxed for 24 h. The reaction mixture was worked up according to the general procedure. Crude product was recrystallized from ethanol to afford **KA3** as orange solid (0.19 g, 82%);  $\nu_{\max}$  (KBr,  $\text{cm}^{-1}$ ) 3218 (C=CH), 2938 ( $\text{CH}_2$ ), 1711 (C=O ester), 1651 (C=O), 1620 (Aromatic), 1451 (N=N), 1234 (C-O), 1140 (C-N);  $^1\text{H}$  NMR (500 MHz,  $\text{DMSO-d}_6$ ):  $\delta$  8.19 (d,  $J$  8.4 Hz, 2H), 8.13 (s, 1H), 7.94 (t, 4H),

7.14 (d,  $J$  9.15 Hz, 2H), 6.60 (s, 1H), 5.81 (m, 1H), 5.25 (s, 2H), 4.98 (dd,  $J$  13.35 Hz, 2H), 4.10 (t, 2H), 2.05 (m, 2H), 1.75 (m, 2H), 1.43 (m, 4H);  $^{13}\text{C}$  NMR (125 MHz, DMSO- $d_6$ ):  $\delta$  174.2, 165.1, 162.8, 161.9, 155.4, 146.6, 140.6, 139.2, 131.4, 130.2, 125.7, 123.0, 115.7, 115.4, 113.8, 113.3, 68.6, 62.8, 33.7, 29.0, 28.5, 25.1.

**2.7.4. (5-Hydroxy-4-oxo-pyran-2-yl)methyl-4-[(E)-(4-oct-7-enoxyphenyl)azo]benzoate (KA4).** Azo intermediate **A4** (0.18 g, 0.5 mmol) was added to the solution of **4** (0.1 g, 0.6 mmol) with TEA (0.015 g, 0.15 mmol) in dried acetone (20 mL) and refluxed for 24 h. The reaction mixture was worked up according to the general procedure. Crude product was recrystallized from ethanol to afford **KA4** as yellow solid (0.019 g, 78%);  $\nu_{\text{max}}$  (KBr,  $\text{cm}^{-1}$ ) 3220 (C=CH), 2934 ( $\text{CH}_2$ ), 1708 (C=O ester), 1654 (C=O), 1606 (Aromatic), 1454 (N=N), 1212 (C-O), 1120 (C-N);  $^1\text{H}$  NMR (500 MHz, DMSO- $d_6$ ):  $\delta$  8.17 (d,  $J$  7.65 Hz, 2H, Ar), 8.11 (s, 1H), 7.93 (t, 4H), 7.13 (d,  $J$  9.2 Hz, 2H), 6.58 (s, 1H), 5.78 (m, 1H), 5.24 (s, 2H), 4.95 (dd,  $J$  13.4 Hz, 2H), 4.06 (t, 2H), 2.01 (m, 2H), 1.73 (m, 2H), 1.35 (m, 6H);  $^{13}\text{C}$  NMR (125 MHz, DMSO- $d_6$ ):  $\delta$  173.7, 164.4, 162.2, 161.4, 154.8, 146.0, 140.1, 138.7, 130.8, 130.6, 125.2, 122.5, 115.1, 114.7, 112.7, 68.0, 62.1, 41.8, 33.4, 28.4, 28.1, 25.2.

**2.8. Fabrication of DSSCs.** Indium Tin Oxide (ITO) substrate was cleaned with deionized water and treated in water bath for 10 min to remove ionic impurities. The ITO was soaked in methanol for 5 min and dried. Scotch tape was used to cover two corners of the conducting side of ITO. 3  $\text{cm}^2$  of area was used for  $\text{TiO}_2$  film.  $\text{TiO}_2$  (1.0 g) was transferred into a crucible and annealed at 450°C in a furnace for 2 h and cooled to room temperature.  $\text{TiO}_2$  electrode was prepared by mixing dried  $\text{TiO}_2$  (1.0 g) with acetic acid (1 mL) and Triton X-100 (0.5 mL) at room temperature for 5 min. The  $\text{TiO}_2$  paste was applied onto ITO and coated using spin coater (1000 rpm) for 15 sec, heated at 250°C for 30 min and immersed in 0.5 mM of **A1-4** and **KA1-4** dyes solution and rinsed with ethanol after 24 hr. The conducting side of another ITO glass was coated with graphite and clamped tightly in a sandwich pattern so that the dyed  $\text{TiO}_2$  is facing down onto the coated graphite anode. A solution of iodide/tri-iodide (5 mL) in acetonitrile acted as electrolyte was added to the cell. The fabricated DSSCs were stored in dark for 24 h prior to testing.

**2.9. Photovoltaic Measurement.** A voltage and current measurement of DSSC **A1-4** and **KA1-4** were applied via connection of anode and cathode to DUT+ and DUT- of The National Instruments Educational Laboratory Virtual Instrumentation Suite (NI ELVIS), respectively. LabVIEW was used to display the current and voltage during a voltage sweep from 0 to 5 V. The voltage spacing was set to 0.04 V. The electrical properties of the DSSC were determined via the potential difference between both electrodes in DSSC. The percentage efficiency ( $\eta$ ) of DSSC is the ratio of power output ( $P_{\text{out}}$ ) versus power input ( $P_{\text{in}}$ ), where  $P_{\text{in}}$  is the total radiant energy incident on the active area of the cell calculated by (1).  $P_{\text{in}}$  for efficiency measurement using 3  $\text{cm}^2$  is 120  $\text{W}/\text{m}^2$ .

$$\text{FF} = \frac{V_{\text{max}} \times I_{\text{max}}}{V_{\text{oc}} \times I_{\text{sc}}}$$

$$\eta = \frac{P_{\text{out}}}{P_{\text{in}}}$$

$$\eta (\%) = \frac{V_{\text{oc}} \times I_{\text{sc}} \times \text{FF}}{P_{\text{in}}} \times 100\%$$

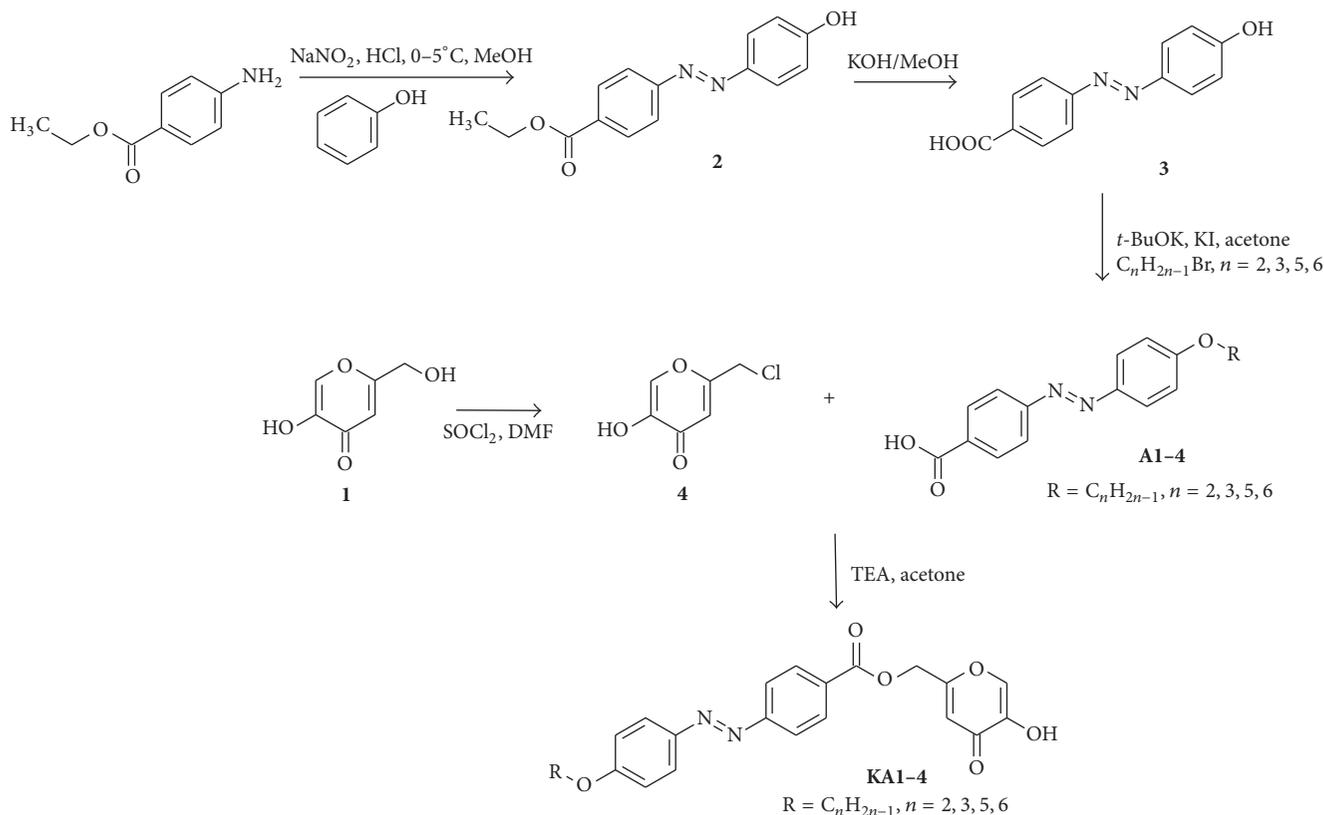
(1)

### 3. Results and Discussion

**3.1. Preparation of Kojic Acid (1).** Kojic acid **1** was prepared via fermentation of *sago hampas* employing mixed strains of *Aspergillus Flavus* NSH9 and *Aspergillus Flavus* Link 44-1. The optimum parameters were from a combination of 3% (w/v) urea and 10% mineral salts solution containing  $\text{KH}_2\text{PO}_4$ , (w/v)  $\text{MgSO}_4 \cdot 7\text{H}_2\text{O}$  and yeast.  $\text{KH}_2\text{PO}_4$  and  $\text{MgSO}_4$  were employed to support the growth of bacteria strain and to boost the production of kojic acid [31]. *Aspergillus Flavus* was used for a higher yield of **1** [32]. Yeast acted as a nitrogen source to enhance kojic acid production through metabolic activation. It also contains high levels of essential components to support growth and fermentation such as vitamins and oligoelements [33]. Extraction with ethyl acetate afforded **1** with 30% yield. Low yield obtained was due to the properties of kojic acid which is soluble in both water and ethyl acetate [34, 35]. The NMR and IR spectra corresponded to structure of kojic acid.

**3.2. Synthesis.** The synthesis pathway of kojic acid based organic dye is shown in Scheme 1. Ethyl 4-aminobenzoate underwent diazotization with sodium nitrite in the presence of hydrochloric acid and coupled with phenol to afford azobenzene dye **2** [28]. Hydrolysis of ester bond in **2** with strong base KOH was performed to give **3**. Introduction of vinyl group gives optical properties [29]. The alkylation of **3** with series of bromoalkenes was carried out in the presence of *t*BuOK and a catalytic amount of KI in refluxing acetone to afford **A1-4**. Compound **1** was treated with thionyl chloride to obtain kojyl chloride **4** [30] followed by nucleophilic substitution of **A1-4** with **4** in TEA to afford organic dye **KA1-4**.

**3.3. Characterization.** Characterization of **KA1-4** was performed using FTIR,  $^1\text{H}$ , and  $^{13}\text{C}$ -NMR spectroscopies. FTIR showed the absorption band for olefinic group at 3223–3218  $\text{cm}^{-1}$ . IR spectra revealed a strong band at 1713–1708  $\text{cm}^{-1}$  attributed to the presence of ester group and a sharp band at 1654–1651  $\text{cm}^{-1}$  corresponded to C=O of **1**. The absorption band at 1620–1606  $\text{cm}^{-1}$  is attributed to the aromatic group. The synthesized **KA1-4** was further characterized using  $^1\text{H}$  NMR spectroscopy. The  $^1\text{H}$  NMR showed two singlets at  $\delta$  8.13–8.11 ppm and  $\delta$  6.60–6.58 ppm representing olefinic protons of **1**. The presences of four doublets peaks at  $\delta$  8.19–7.13 ppm were attributed to eight protons in aromatic ring. The peak of oxymethyl proton of **1** was observed at  $\delta$  5.26–5.24 ppm as singlet indicated 7-O-substituent **1** [36]. The CH=C resonated at  $\delta$  5.90–5.78 ppm as multiplet and C=CH<sub>2</sub> proton of vinyl chain was observed as doublet of doublet at  $\delta$  5.15–4.95 ppm. The OCH<sub>2</sub> of



SCHEME 1: Synthesis of kojic acid based organic dyes.

vinyl chain resonated as doublet at  $\delta$  4.16–4.06 ppm as triplet. The  $^{13}\text{C}$  NMR spectra showed all the important peaks supported to the formation of the desired product. The  $^{13}\text{C}$ -NMR spectrum displayed two deshielded carbon signals at  $\delta$  174.4–173.7 ppm and  $\delta$  168.9–164.4 ppm indicated for C=O of kojic acid and ester group. The aromatic carbons and vinyl group were represented by absorption peak at  $\delta$  163.3–112.7 ppm. The signals at  $\delta$  68.6–67.7 ppm and  $\delta$  62.8–56.3 ppm were designated as  $\text{OCH}_2$  of **1** and vinyl chain, respectively.

**3.4. UV-Vis Absorption Spectra.** The UV-vis spectra of **A1-4** and **KA1-4** in ethanol are shown in Figure 1. Absorption spectra of **A1-4** exhibit an absorption band at 358–363 nm while **KA1-4** exhibited two distinct absorption bands. The absorption band at 346–392 nm in the UV region was attributed to the  $\pi$ - $\pi^*$  transition and another strong absorption band at 489–494 nm in the visible region was due to the  $n$ - $\pi^*$  transition [37]. The red shift in maximum absorption for **KA1-4** compared to **A1-4** is due to expansion of overall  $\pi$  conjugation systems after incorporation of kojic acid moieties and suggested some increased electron delocalization [38, 39]. The corresponding data are presented in Table 1. The bandgap ( $E_g$ ) is estimated from the onset of absorption edge for **A1-4** did not have significant difference, indicating that the length of vinyl chain only showed slight influence on

TABLE 1: Absorption properties of the dyes.

Dyes	Absorption	
	$\lambda_{\text{max}}^a$ (nm)	$E_g^b$ (eV)
<b>A1</b>	358	3.05
<b>A2</b>	360	3.12
<b>A3</b>	360	3.04
<b>A4</b>	363	3.02
<b>KA1</b>	496	2.21
<b>KA2</b>	494	2.20
<b>KA3</b>	489	2.32
<b>KA4</b>	495	2.25

<sup>a</sup>Absorption maxima of **A1-4** and **KA1-4** in ethanol. <sup>b</sup>The bandgap estimated from absorption edge.

the absorption. Introduction of kojic acid (**KA1-4**) to **A1-4** significantly lowered the bandgap energy to 2.2–2.3 eV.

**3.5. Photovoltaic Performance of DSSCs.** The current density-voltage ( $J$ - $V$ ) characteristic and power-voltage characteristic of the dyes on  $\text{TiO}_2$  are shown in Figures 2 and 3, respectively. Photovoltaic performances of solar cell employing **A1-4** and **KA1-4** as organic sensitizer were characterized using the

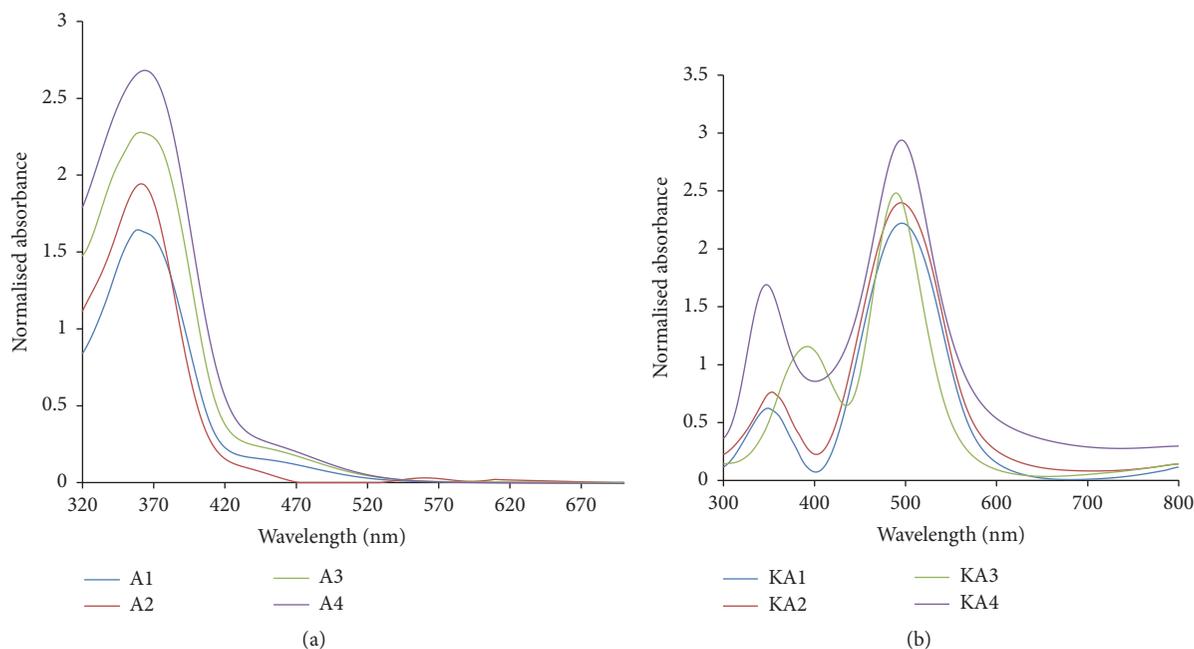


FIGURE 1: UV-vis absorption spectra of (a) **A1-4** and (b) **KA1-4** in ethanol.

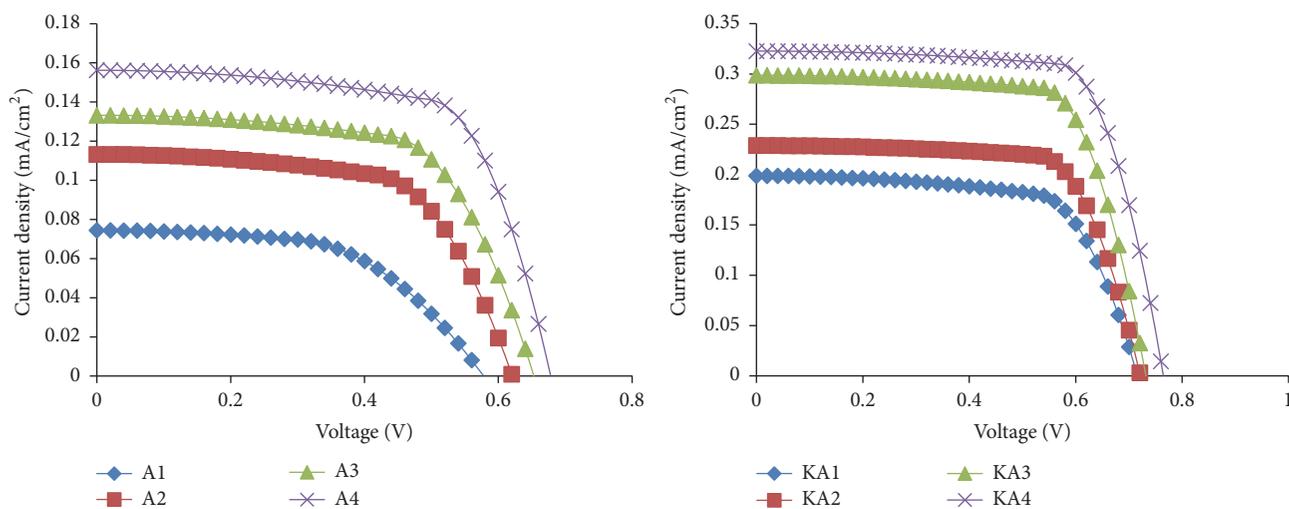


FIGURE 2: Current density-voltage ( $J$ - $V$ ) characteristic of **A1-4** and **KA1-4**.

National Instruments Educational Laboratory Virtual Instrumentation Suite (NI ELVIS) under irradiation  $120 \text{ W/m}^2$ . The photovoltaic properties of the dyes are summarized in Table 2.

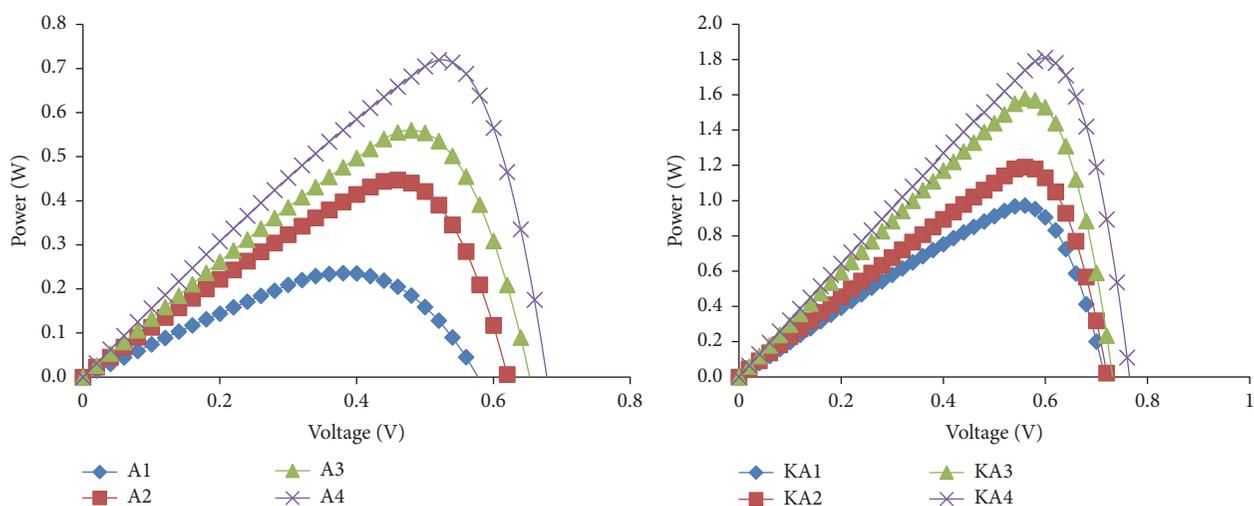
The kojic acid-azo dye, **KA1-4**, exhibits enhancements in efficiency,  $\eta$  (0.82–1.54%) compared to **A1-4** (0.20–0.60%). The **KA1-4** based DSSCs showed higher open circuit voltage and current density with fill factor 68–75%. The high fill factor is comparable to typical first-generation silicon based solar cell [40]. This phenomenon is ascribed to the anchoring ability of kojic acid moieties to the  $\text{TiO}_2$  photoanode. The carbonyl and hydroxyl group of **1** acted as chemical binding anchors by either monodentate or bidentate bridging to the

$\text{TiO}_2$  surface which enhanced the binding of **KA1-4** to the substrate [41]. Anchoring ability of dye is critical for DSSCs sunlight harvesting where the efficiency is dependent on dye deposition [42]. Incorporation of **1** also expands the  $\pi$ -conjugation in **KA1-4** and promotes better electron transfer mechanism to the conduction band of  $\text{TiO}_2$ , resulting in higher absorption in the visible region [21].

In addition, the presence of vinyl hydrocarbon chain has increased the open circuit voltage and solar energy to electricity conversion efficiency in both **A1-4** and **KA1-4**. Both open circuit voltage and solar energy to electricity conversion efficiency were increased as the vinyl chain increased. Azo

TABLE 2: Photovoltaic performance of DSSCs based on **A1-4** and **KA1-4**.

Dye	$V_{oc}$ (V)	$J_{sc}$ (mA/cm <sup>2</sup> )	$V_{max}$ (V)	$J_{max}$ (mA/cm <sup>2</sup> )	FF (%)	Power output (W/m <sup>2</sup> )	Efficiency (%)
<b>A1</b>	0.577	0.074	0.386	0.062	56	0.23932	0.20
<b>A2</b>	0.621	0.114	0.461	0.097	63	0.44717	0.37
<b>A3</b>	0.653	0.133	0.48	0.117	65	0.5616	0.46
<b>A4</b>	0.678	0.156	0.522	0.138	68	0.72036	0.60
<b>KA1</b>	0.716	0.199	0.562	0.174	68	0.97788	0.82
<b>KA2</b>	0.722	0.228	0.565	0.213	73	1.20345	1.00
<b>KA3</b>	0.732	0.301	0.573	0.282	73	1.61586	1.35
<b>KA4</b>	0.764	0.322	0.614	0.301	75	1.84814	1.54

FIGURE 3: Power-voltage characteristic of **A1-4** and **KA1-4**.

dye bearing the longest vinyl chain demonstrated the highest efficiency due to increase of electron life time in  $TiO_2$  conduction band. Longer vinyl chains may reduce the recombination ability at  $TiO_2$ /electrolyte interface, which prevent electron leakage from nanocrystalline  $TiO_2$  to the iodine/iodide redox electrolyte [14, 43, 44]. Moreover, photosensitivity of vinyl group to light in visible region increased the light harvesting ability of the DSSCs [45, 46].

Molecular design of **KA1-4** consisted of an extended  $\pi$ -conjugation, spacer, and anchoring group. The proposed binding of **KA1-4** is illustrated in Figure 4. The best photovoltaic performance with highest efficiency (1.54%) was obtained when **KA4** was used as organic sensitizer. **KA4** affords an open circuit voltage ( $V_{OC}$ ) of 0.76 V and a short circuit density of 0.32 mA/cm<sup>2</sup> under stimulated power input of 120 W/m<sup>2</sup>. The efficiency of semisynthetic sensitizer **KA1-4** is comparable with reported natural dye such as chlorophyll and anthocyanin dye [47–49] and higher than other heavy metal dyes [39] as well as metal free organic dye [40].

## 4. Conclusions

A series of kojic acid based organic dyes **KA1-4** were demonstrated for dye sensitized solar cell. Kojic acid fermented from sago biomass was acted as an anchoring group in the dye and proven based on photovoltaic performance. The incorporation of kojic acid shifted the absorption band to the visible region and improved the photovoltaic performance compared to azobenzene organic dye **A1-4** in DSSCs. Kojic acid was proven as a promising anchoring group in enhancing the device efficiency. The presence of vinyl chain improved the performance of DSSCs where **KA4**-based DSSC gave the highest open circuit voltage, current density, and efficiency.

## Conflicts of Interest

The authors declare that there are no conflicts of interest regarding the publication of this paper.

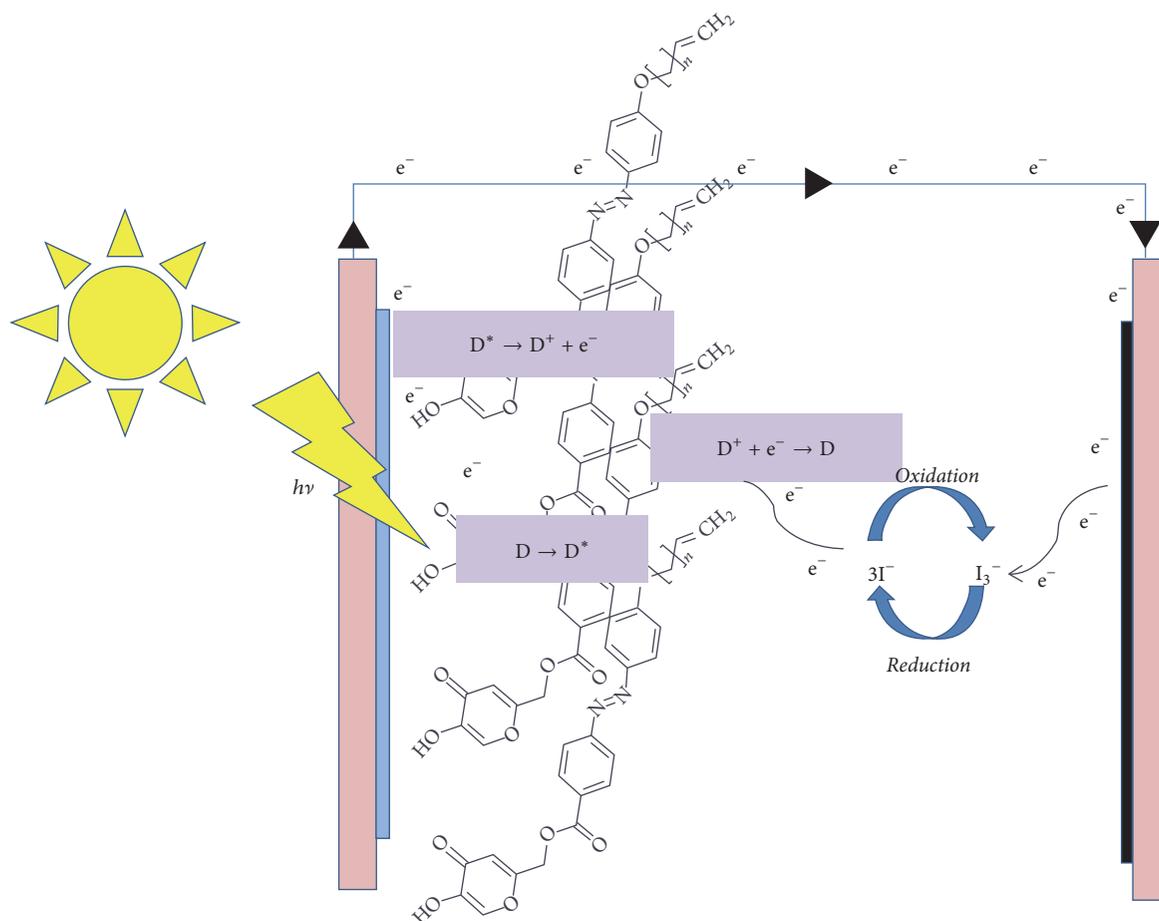


FIGURE 4: Proposed binding mechanism of KAI-4 to TiO<sub>2</sub> photoanode.

## Acknowledgments

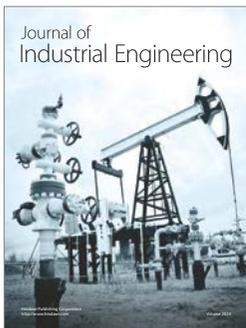
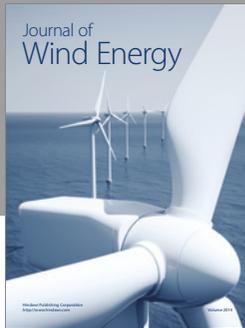
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