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#### SPECIAL ISSUE PAPER

## Effect of long alkyl chains of aniline donor on the photovoltaic performance of D- $\pi$ -A zinc porphyrin for dye-sensitized solar cells

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#### Abstract

Three novel dyes of JJ1, JJ2, and JJ6 featured zinc porphyrin as a basic core structure; N, N-alkyl-4-(prop-1-yn-1-yl)aniline as an electron donor linked to meso-10-position; 4-(prop-1-yn-1-yl)benzoic acid as an electron acceptor linked to *meso*-20-position; and 2,6-bis(dodecyloxy)phenyl or 2,6-bis(octyloxy)phenyl respectively linked to meso-5 and meso-15-positions of zinc porphyrin have been synthesized and used for dye-sensitized solar cells. Porphyrin JJ6 featured the shortest alkyl group (-C<sub>4</sub>H<sub>9</sub>) on the donor, whereas JJ2 contained the longest alkyl groups (-C<sub>12</sub>H<sub>25</sub>), and JJ1 has a medium length of octyl groups. With these new porphyrin sensitizers, we observed that JJ6 has 7.55% power conversion efficiency under simulated one-sun illumination (AM 1.5 G, 100 mW/cm<sup>2</sup>) with  $J_{SC} = 18.64 \text{ mA/cm}^2$ ,  $V_{OC} = 0.66 \text{ V}$ , and fill factor (FF) = 0.61, which was higher than the other two; JJ1 (7.35%) with  $J_{SC} = 18.83 \text{ mA/cm}^2$ ,  $V_{OC} = 0.68 \text{ V}$ , and FF = 0.60; and JJ2 (6.33%) with  $J_{SC} = 15.69 \text{ mA/cm}^2$ ,  $V_{OC} = 0.62 \text{ V}$ , and FF = 0.65. The power conversion efficiency of JJ6 and JJ1 were higher than JJ2, demonstrating that the lengthy alkyl groups on the aniline cause a decrease in efficiency of the devices.

#### **KEYWORDS**

alkyl chain, dye, solar cells, zinc porphyrin

## **1 | INTRODUCTION**

The depletion of natural resources and the global warming crisis have come to the forefront because human beings have been overconsuming the petrochemical energy of Earth since the industrial revolution occurred in the 19th century. Thus, environmental protection awareness, development of renewable technology, and alternative energy are urgent issues. In addition to the fossil fuel, common alternative renewable energy sources, including wind power, marine energy, geothermal energy, hydroelectric energy and solar power, are all viable energy and eco-friendly.<sup>[1-3]</sup> Dye-sensitized solar 

cells (DSCs) have attracted much attention from scientists since being first reported by Michael Grätzel and coworkers in 1991.<sup>[4]</sup> For so many advantages of DSCs, such as simple manufacture, tunable optical properties, colorful and transparent features, and low cost, much exertion has been dedicated to improving the efficiency of DSCs and stability of the devices, which can be performed by appropriately modifying the dye structure.<sup>[5–15]</sup> In 2011, porphyrin dye **YD2-***o*-**C8**<sup>[16]</sup> achieved a record-high conversion efficiency of 11.9%, which is better than that of organic dyes and ruthenium dyes. In 2014, the structurally modified zinc porphyrin dyes GY50 and SM315 were provided with the highest

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power conversion efficiencies (PCEs) of 12.5 and 13.0%, respectively.<sup>[17,18]</sup> Therefore, understanding the structureproperty relationship of zinc porphyrin dyes is desirable for further improvement of the cell performance of DSCs. In 2016, we reported a series of porphyrin-based sensitizers, YD22-YD28, and YD24, among which the porphyrin dye featuring a triarylaminophenylethynyl with long carbon alkyl groups achieved a PCE of 9.19%. The introduction of long carbon alkyl groups into triarylamine functional groups significantly reduces molecular aggregation and contributes to the improved PCE.<sup>[19]</sup> Here, we developed and synthesized three zinc porphyrin dyes, JJ1, JJ2, and JJ6. All of them have zinc porphyrin as a core structure, with N, Nalkyl-substituted aniline as a donor and benzoic acid as an anchoring group. Implementation of aryl moieties with ortho-substituted alkoxy chains to meso-5, 15-positions of porphyrin ring (Scheme 1). Based on our previous studies, alkyl chains of the triphenylamine donor at meso-position can inhibit the electron transfer from TiO<sub>2</sub> conduction band to electrolyte and can lessen dye aggregation.<sup>[20,21]</sup> Here, we would like to elucidate the effects of the lengths of alkyl chains attached to the meso-phenyl and donor on their electrochemical, optical, and photovoltaic properties.

### 2 | RESULTS AND DISCUSSION

#### 2.1 | Synthesis and characterizations

The synthesis of the push–pull zinc porphyrin dyes with the donor and acceptor attached to meso-positions via ethynylene bridges has been described earlier.<sup>[19,22–24]</sup> The synthetic protocol for these **JJ**-series dyes were displayed in Scheme 2, the details of which are described in the Experimental Section. First, bis-protected, triisopropylsilyl-capped zinc porphyrin was desilylated by fluoride to obtain bis(ethynyl)-substituted zinc porphyrin, and was then reacted with N, N-dioctyl-, N, N-didodecyl-, or N, N-dibutyl-4-iodobenzamide and 4-iodobenzoic acid via Sonogashira cross-coupling reaction to



**SCHEME 1** Molecular structures of **JJ1**, **JJ2**, and **JJ6** 

obtain the desired products **JJ1**, **JJ2**, and **JJ6** in 24, 25, and 20% yields, respectively. These **JJ** series dyes are stable in air and easily soluble in common organic solvents such as  $CH_2Cl_2$ , ethanol (EtoH), and tetrahydrofuran (THF).

# 2.2 | Photophysical and electrochemical properties

The ultraviolet (UV)-vis absorption spectra for JJ series dyes in THF solution are displayed in Figure 1 and summarized in Table 1. All these dyes have an intense Soret band at ca. 455-458 nm and a weak Q band at ca. 658-670 nm; **J.I2** has the best molar absorptivity  $(\varepsilon)$  at Soret band, which is  $4.9 \times 10^5$  and  $0.7 \times 10^5$  M/cm at the Q band. For JJ1 and JJ6, their molar absorptivity of Soret band and Q band are  $2.7 \times 10^5$  and  $0.8 \times 10^5$  M/cm (JJ1) and  $2.3 \times 10^5$  and  $0.6 \times 10^5$  M/cm (**JJ6**), respectively. On the other hand, the optical bandgap ( $E_{0-0}$ ) of **JJ2** is slightly larger than **JJ1** and JJ6 (from 1.84 to 1.88 eV), which was measured from the intersection of emission and absorption spectra in the THF solution at room temperature, although blue-shifted absorption at Q band was observed for JJ2 compared to JJ1 and JJ6. To understand the electrochemical behavior of these porphyrin dyes, cyclic voltammetry measurements were taken in THF solution containing ferrocene/ferrocenium (Fc/Fc<sup>+</sup>) as an internal standard with 0.1 M tetrabutylammonium hexafluorophosphate (TBAPF<sub>6</sub>) as the supporting electrolyte. As shown in Figure 2 and collected data in Table 1, the potentials of Ehighest occupied molecular orbital (HOMO) were estimated from E1/2 for their first oxidation potential ( $E_{HOMO}$ ), +0.97 V for JJ2 that was anodically shifted as compared to JJ1 and JJ6. The excited-state oxidation potentials ( $E_{LUMO}$ ) were calculated from  $E_{\text{HOMO}} - E_{0-0}$ , in which  $E_{0-0}$  is the zero-zero excitation energy calculated from the crossing point of normalized emission and absorption spectra, respectively, -0.90, -1.08, and -1.09 V for JJ2, JJ1, and JJ6, respectively (Figure 3). The derivated  $E_{LUMO}$  potential for these dyes is all higher than the conduction-band level of TiO2, assuring an ample driving force for electron injection.<sup>[25–27]</sup> As the  $E_{LUMO}$  is lower than the oxidation potential of iodide/triiodide  $(I^{-}/I_{3}^{-})$  redox couple, this indicates that the effective regeneration of JJ series dyes in a DSC system is all thermodynamically favorable.

#### **2.3** | Photovoltaic performances

The DSC devices of zinc porphyrin-based dyes **JJ1**, **JJ2**, and **JJ6** using iodide/triiodide redox mediators in THF/C<sub>2</sub>H<sub>5</sub>OH (1:4) were studied. The current–voltage (*J-V*) characteristics of these porphyrin-sensitized devices under simulated one-sun illumination (AM 1.5 G, 100 mW/cm<sup>2</sup>) were displayed in Figure 4, and corresponding photovoltaic data were collected and are shown in Table 1. The solar-to-



**SCHEME 2** Synthetic procedure for **JJ1**, **JJ2**, and **JJ6**. (i) TBAF, THF. (ii) 4-iodobenzoic acid, N, N-dioctyl-4-iodobenzamide, cat. AsPh<sub>3</sub>, Pd<sub>2</sub>(dba)<sub>3</sub>, Et<sub>3</sub>N, THF. (iii) 4-iodobenzoic acid, N, Ndidodecyl-4-iodobenzamide, cat. AsPh<sub>3</sub>, Pd<sub>2</sub>(dba)<sub>3</sub>, Et<sub>3</sub>N, THF. (iv) 4-iodobenzoic acid, N, N-dibutyl-4-iodobenzamide, cat. AsPh<sub>3</sub>, Pd<sub>2</sub>(dba)<sub>3</sub>, Et<sub>3</sub>N, THF. The synthesis of compound **1** and compound **2** followed the procedure reported earlier<sup>[16,22–24]</sup>





**FIGURE 1** UV-vis absorption spectra of zinc porphyrin dyes, **JJ1, JJ2**, and **JJ6** in THF at 25°C

DSC devices with electric PCEs of 0.4 mM chenodeoxycholic acid (CDCA) as a coabsorbent additive were 7.35% for **JJ1** ( $J_{SC} = 18.83 \text{ mA/cm}^2$ ,  $V_{OC} = 0.68 \text{ V}$ , fill factor [FF] = 0.60), 6.33% for **JJ2** ( $J_{SC}$  = 15.69 mA/cm<sup>2</sup>,  $V_{\rm OC}$  = 0.62 V, FF = 0.65), and 7.55% for **JJ6**  $(J_{\rm SC} = 18.64 \text{ mA/cm}^2, V_{\rm OC} = 0.66 \text{ V}, \text{FF} = 0.61)$ . The  $V_{\rm oc}$ of the DSCs is decided by the potential difference between the quasi-Fermi level of the electrons at the TiO<sub>2</sub> film and the redox potential of electrolyte.<sup>[28]</sup> Based on the J-V curves, JJ2 has a lower  $V_{OC}$  value and short-circuit current  $(J_{\rm SC})$  than those of JJ1 and JJ6, leading to poorer cell performance. Most likely, the N, N-dodecyl chains on the aniline donor of JJ2 become aggregated due to hydrophobic interaction in the ionic medium.<sup>[29]</sup>

TABLE 1 Electrochemical, photophysical, and photovoltaic properties of JJ1, JJ2, and JJ6 sensitizers

	$\lambda_{\max} (\varepsilon)$ , <sup>a</sup> nm (10 <sup>5</sup> M/cm)	Emission $\lambda_{\max}^{,b}$ (nm)	E <sub>0-0</sub> , <sup>c</sup> (eV)	E <sub>HOMO</sub> d (V)	E <sub>LUMO</sub> <sup>e</sup> (V)	J <sub>SC</sub> (mA/cm <sup>2</sup> )	V <sub>OC</sub> (V)	FF	Efficiency (%)
JJ1	458 (2.7), 670 (0.8)	679	1.84	+0.76	-1.08	18.83	0.68	0.60	7.35
JJ2	455 (4.9), 659 (0.7)	667	1.88	+0.97	-0.90	15.69	0.62	0.65	6.33
JJ6	456 (2.3), 668 (0.6)	677	1.85	+0.76	-1.09	18.64	0.66	0.61	7.55

<sup>a</sup>Absorptions were measured in THF at 25°C.

<sup>b</sup>Measured in THF at 25°C.

<sup>c</sup>The optical bandgap ( $E_{0-0}$ ) was measured from the intersection of emission and absorption spectra in THF solution.

 $^{d}E_{\text{HOMO}}$  was determined in THF containing 0.1 M tetrabutylammonium hexafluorophosphate (TBAPF<sub>6</sub>) as a supporting electrolyte, which was calibrated with ferrocene/ferrocenium (Fc/Fc<sup>+</sup>) as an internal reference and converted to that versus NHE by addition of +0.64 V.

<sup>e</sup>Lowest-unoccupied molecular orbitals (LUMO) were obtained from HOMO and optical bandgap ( $E_{0.0}$ ) using the formula: LUMO = HOMO –  $E_{0.0}$ .



**FIGURE 2** Cyclic voltammograms of **JJ1**, **JJ2**, and **JJ6** in THF containing 0.1 M TBAPF<sub>6</sub> at 25°C



FIGURE 3 Schematic energy levels of JJ series porphyrin dyes



**FIGURE 4** *J-V* plots spectra of devices fabricated with **JJ** series dyes

#### **3** | EXPERIMENTAL

#### 3.1 | General information

We purchased all solvents and chemicals from commercial suppliers and used them without further purification unless specified. THF was refluxed with sodium/benzophenone ketyl to remove water and oxygen. CH2Cl2 was refluxed with CaH<sub>2</sub> to dry and was freshly distilled before use. Tetra(nbutyl)ammonium hexafluorophosphate ( $[(n-Bu)_4N]PF_6$ ) was recrystallized from absolute ethanol and further dried under vacuum for 2 days. Column chromatography was performed using silica gel from Merck (70–230 Mesh ASTM). <sup>1</sup>H NMR and <sup>13</sup>C NMR spectra were recorded on a Varian spectrometer operating at 400 MHz. The emission and UV-visible absorption spectra were measured using the JASCO FP-6000 spectrophotometer and Varian Cary 50 spectrofluorometer, respectively. Cyclic voltammetric experiments were determined with a three-electrode system, combined with CHI Instrument 750A potentiostat in the present of deoxygenated THF. The BAS glassy carbon (0.07 cm<sup>2</sup>) disk was used as the working electrode; the auxiliary and reference electrodes used platinum wire and Ag/AgCl (saturated), respectively. Potentials are compared with reference to ferrocene/ferrocenium (Fc/Fc<sup>+</sup>) at  $E_{1/2} = +0.63$  V versus normal hydrogen electrode (NHE) at 23°C in acetonitrile. Before use, the working electrode was polished with 0.03 µm aluminum on felt pads (Buehler), soaked in distilled water, and treated ultrasonically for 3 min. The current-voltage (J-V) characteristics of these JJ series-sensitized devices were measured with the one-sun illumination (AM 1.5 G, 100 mW/cm<sup>2</sup>) using a 700-W short-arc Xenon lamp equipped in the solar simulator machine (PEC-S20, Peccell Technologies, Inc. Yokohama, Japan) associated with the voltmeter (Keithley 2400C). The light intensity was calibrated by using a Si-KG3 filtered solar cell as a reference cell.

#### 3.2 | Synthesis of JJ1

To a solution of compound 1 (300 mg, 0.2 mmol) in dry THF (10 mL) was added tetra(n-butyl)ammonium fluoride (1 M in THF, 2.5 mL, 8.48 mmol). The solution was stirred for 30 min at room temperature under  $N_{2(g)}$ . The mixture was quenched with water and then extracted with CH<sub>2</sub>Cl<sub>2</sub>. The organic layer was dried over Na<sub>2</sub>SO<sub>4</sub>, and the solvent was removed by high-vacuum rotovapor. After that, N, Ndioctyl-4-iodobenzenamine (128 mg, 0.29 mmol) and 4-iodobenzoic acid (72 mg, 0.29 mmol) were added, catalyzed by tris(dibenzylideneacetone)dipalladium (22.98 mg, 0.022 mmol) and triphenylarsine (6.8 mg, 0.022 mmol), and then injected with dry THF (20 mL) and dry triethylamine (4 mL). Futhermore, after refluxing for 16 hr, the residue was purified by column chromatography using silica gel and CH<sub>2</sub>Cl<sub>2</sub>/CH<sub>3</sub>OH (15/1 vol/vol) as the eluent. Removal of the solvent under reduced pressure and recrystallization from CH<sub>2</sub>Cl<sub>2</sub>/CH<sub>3</sub>OH produced JJ1 as green crystals (81 mg, Yield 24%). <sup>1</sup>H NMR (400 MHz, CDCl3) δ 9.51 (dd, J = 8.9, 4.5 Hz, 4H), 8.73 (dd, J = 17.3, 4.4 Hz, 4H), 8.22 (d, J = 7.7 Hz, 2H), 7.94 (d, J = 7.8 Hz, 2H), 7.72 (d, J = 7.8 Hz, 2H), 7.8 Hz, J = 8.7 Hz, 2H), 7.63 (t, J = 8.4 Hz, 2H), 6.95 (d, J = 8.5 Hz, 4H), 6.68 (d, J = 8.5 Hz, 2H), 3.78 (t, J = 6.4 Hz, 8H), 1.58 (s, 6H), 1.34–1.14 (m, 22H), 0.93–0.78 (m, 22H), 0.66 (s, 9H), 0.52 (t, J = 7.3 Hz, 26H), 0.38 (s, 9H). <sup>13</sup>C NMR (101 MHz, CDCI3)  $\delta$  160.22 (s), 151.94 (s), 150.49 (s), 149.87 (s), 149.69 (d, J = 27.2 Hz), 149.28 (s), 135.84 (s), 135.59 (s), 135.35 (s), 133.00 (s), 131.13 (s), 130.15 (s), 129.68 (s), 123.58 (s), 123.33 (s), 123.08 (s), 114.98 (s), 111.70 (s), 105.44 (s), 68.81 (s), 51.28 (s), 32.03 (s), 31.64 (s), 29.61 (d, J = 18.1 Hz), 28.91 (d, J = 4.6 Hz), 27.46 (d, J = 14.2 Hz), 25.46 (s), 22.84 (s), 22.51 (s), 14.28 (s), 14.07 (s). high-resolution mass spectrometry-electrospray ionization (HRMS-ESI) (m/z) [M]<sup>+</sup> calcd for C<sub>97</sub>H<sub>125</sub>O<sub>6</sub>N<sub>5</sub>Zn, 1,519.8916, found 1,519.8904.

#### **3.3** | Synthesis of JJ2

To a solution of compound 2 (300 mg, 0.18 mmol) in dry state THF (10 mL) was added, obtaining tetra(n-butyl)ammonium fluoride (1 M in THF, 2.5 mL, 8.48 mmol). The solution was stirred at room temperature for 30 min under  $N_{2(g)}$ . The mixture was quenched with water and then extracted with CH<sub>2</sub>Cl<sub>2</sub>. The organic layer was dried over anhydrous Na<sub>2</sub>SO<sub>4</sub>, and the solvent was removed under vacuum. After that, N, Ndidodecyl-4-iodobenzenamine (124 mg, 0.22 mmol) and 4-iodobenzoic acid (55 mg, 0.22 mmol) were added, catalyzed by tris(dibenzylideneacetone)dipalladium (17 mg, 0.018 mmol) and triphenylarsine (6.78 mg, 0.019 mmol), and then injected with dry THF (10 mL) and dry triethylamine (2 mL). Futhermore, after refluxing for 10 hr, the residue was purified by column chromatography using silica gel and CH<sub>2</sub>Cl<sub>2</sub>/CH<sub>3</sub>OH (20/1 vol/vol) as the eluent. Removal of the solvent under reduced pressure and recrystallization from CH<sub>2</sub>Cl<sub>2</sub>/CH<sub>3</sub>OH provided JJ2 as green crystals (88 mg, Yield 25%). <sup>1</sup>H NMR (400 MHz, CDCl3)  $\delta$  9.53 (dd, J = 8.6, 4.5 Hz, 4H), 8.78 (d, J = 4.4 Hz, 4H), 8.24 (d, J = 8.1 Hz, 2H), 8.13 (d, J = 8.0 Hz, 2H), 7.95 (dd, J = 10.8, 8.4 Hz, 4H), 7.65 (t, J = 8.4 Hz, 2H), 6.96 (d, J = 8.6 Hz, 4H), 4.31 (t, J = 6.5 Hz, 2H), 3.81 (t, J = 6.4 Hz, 9H), 1.82-1.60 (m,4H), 1.50-1.16 (m, 21H), 1.17-0.53 (m, 78H), 0.40 (d, J = 51.2 Hz, 28H). <sup>13</sup>C NMR (101 MHz, CDCl3)  $\delta$  159.85 (s), 151.40 (s), 150.65 (d, J = 4.7 Hz), 131.69 (s), 130.98 (s), 129.79 (d, J = 27.9 Hz), 129.36-128.33 (m), 121.07 (s), 115.24 (s), 104.99 (s), 68.43 (s), 65.22 (s), 31.82 (d, J = 7.7 Hz), 30.15–28.00 (m), 26.02 (s), 25.23 (s), 22.62 (d, J = 4.8 Hz), 14.07 (d, J = 4.5 Hz). ESI-MS (m/z) calcd for  $C_{123}H_{179}O_6N_5Zn$ , 1886, found 1887,  $[M + H]^+$ .

#### 3.4 | Synthesis of JJ6

To a solution of compound 2 (400 mg, 0.25 mmol) in dry THF (10 mL) was added tetra(*n*-butyl)ammonium fluoride

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(1 M in THF, 2.5 mL, 8.48 mmol). The solution was stirred at room temperature for 30 min under  $N_{2(g)}$ . The mixture was quenched with water and then extracted with CH<sub>2</sub>Cl<sub>2</sub>. The organic layer was dried over anhydrous Na<sub>2</sub>SO<sub>4</sub>, and the solvent was removed under vacuum. After that, N, Ndibutyl-4-iodobenzenamine (106 mg, 0.32 mmol) and 4-iodobenzoic acid (86 mg, 0.35 mmol) were added, catalyzed by tris(dibenzylideneacetone)dipalladium (23 mg, 0.025 mmol) and triphenylarsine (8 mg, 0.026 mmol), and then injected with dry THF (15 mL) and dry triethylamine (3 mL). Futhermore, after refluxing for 16 hr, the residue was purified by column chromatography using silica gel and CH<sub>2</sub>Cl<sub>2</sub>/CH<sub>3</sub>OH (20/1 vol/vol) as the eluent. Removal of the solvent under reduced pressure and recrystallization from CH<sub>2</sub>Cl<sub>2</sub>/CH<sub>3</sub>OH provided JJ6 as green crystals (20 mg, Yield 20%). <sup>1</sup>H NMR (400 MHz, CDCl3)  $\delta$  9.53 (dd, J = 7.7, 4.5 Hz, 4H), 8.74 (dd, J = 17.4, 4.5 Hz, 4H), 8.24 (d, J = 8.4 Hz, 2H), 7.98 (d, J = 8.1 Hz, 2H), 7.75 (d, J = 8.1 Hz), 7.75J = 8.7 Hz, 2H), 7.66 (d, J = 8.4 Hz, 2H), 6.97 (d, J = 8.4 Hz, 4H), 6.71 (d, J = 8.7 Hz, 2H), 3.81 (t, J = 6.6 Hz, 8H), 3.32 (d, J = 8.0 Hz, 4H), 1.61 (s, 4H), 1.38 (d, J = 7.2 Hz, 4H), 1.23-0.83 (m, 58H), 0.77-0.67 (m, 58H)16H), 0.53 (s, 16H), 0.40 (s, 8H). <sup>13</sup>C NMR (101 MHz, CDCl3) & 159.94 (s), 149.52 (s), 149.25 (s), 148.97 (s), 135.63 (s), 135.38 (s), 135.14 (s), 132.76 (s), 130.87 (s), 129.92 (s), 123.34 (s), 123.09 (s), 122.84 (s), 111.39 (s), 105.14 (s), 77.39 (s), 77.07 (s), 76.75 (s), 68.54 (s), 50.73 (s), 31.79 (s), 29.66–28.97 (m), 28.71 (s), 25.22 (s), 22.59 (s), 20.32 (s), 14.03 (s). HRMS-ESI (m/z)  $[M + H]^+$  calcd for C<sub>105</sub>H<sub>142</sub>O<sub>6</sub>N<sub>5</sub>Zn, 1,633.02461, found 1,633.02473.

#### **3.5** | Device fabrication

All reagents were supplied by commercial resources, and approximately 99% were purified in the DSC fabrication process. Besides, all fabricating apparatus and materials were cleaned with detergent, deionized water, and ethanol sequentially by supersonication. The complete sandwichtyped cell was composed of the platinum-deposited counter electrode and dye-sensitized photoanode and sealed together by hot melt film (Surlyn, 30 µm) at 125°C. For the details, the photoanode was made by using a cleaned fluorine-doped tin oxide (FTO) glass (3.1 mm thick, 13  $\Omega$ /square, 8% haze) as substrate and then screen-printing the transparent layer with a TiO<sub>2</sub> particle size of 20 nm from Eternal Materials Ltd (Kaohsiung, Taiwan) and scattering layer with a TiO<sub>2</sub> particle size of 400 nm from CCIC (Osaka, Japan). Then, the TiO<sub>2</sub> film was sintered at progressive steps until 500°C under the air flow, and the thickness of the sintered film was, on average, 10-16 µm determined by using the portable roughness tester SURFCOM FLEX from ACCRETECH (Tokyo, Japan). After the thermal post-treatment with 40 mM TiCl<sub>4</sub> for half an hour at 70°C and annealing process at 450°C for 1 hr, the TiO<sub>2</sub> electrodes were soaked in 0.15 mM JJ series dyes solution and half concentration of CDCA as an additive in an equal volumetric ratio of THF and EtOH (vol/vol, 1:4) for 8-hr dve loading. For the photocathode, the platinum (Pt) counter electrode was manufactured by operating the two-step dip-coating process, interpreted such that the cleaned FTO glass (2.2 mm thick, 8  $\Omega$ /square) was subsequently dipping into the surfactant and H<sub>2</sub>PtCl<sub>6</sub> solution. The Pt counter was sintered for 1 hr at 325°C after rinsing with deionized water and was maintained in dry conditions. The preceding procedures for preparing the polyvinyl pyrrolidone (PVP)-Pt solution are described in the earlier reports.<sup>[30,31]</sup> The formulated electrolyte was injected through the drill hole on the cathode side of the aforementioned device. Concerning the durability and the leakage problem, the device should be encapsulated by sealing the drill hole with the surlyn sheet and thin cover glass at 120°C. For precise photovoltaic measurement, the shielding mask  $(0.36 \text{ cm}^2)$  was attached to the illuminating side of the device. The electrolyte included 0.5 M 4-tertbutyl pyridine, 0.1 M guanidinium thiocyanate, 0.05 M LiI, 0.03 M I<sub>2</sub>, and 1.0 M 1,3-dimethylimidazole iodide in acetonitrile/valeronitrile (85:15, vol/vol).<sup>[32]</sup>

#### 4 | CONCLUSIONS

This study reported the synthesis and the optical, electrochemical, and photovoltaic properties of zinc porphyrin dyes JJ1, JJ2, and JJ6. It was found that the JJ2 possesses the longest alkyl chain on donor and did not improve the PCE effectively compared to JJ1 and JJ6. Interestingly, JJ2 showed the highest molar absorptivity ( $\varepsilon$ ) at 455 nm for UV-Vis absorption. The photovoltaic studies showed that JJ6 was slightly higher than JJ1 and then JJ2, indicating that the introduction of alkyl chains to the dye molecules cannot assure better cell performance. Presumably, the long alkyl chains on the outer sphere of the TiO<sub>2</sub> surface caused more or less aggregation because of the hydrophobic interaction in the ionic environment. Therefore, lengthening of the alkyl group on aniline resulted in a decrease in efficiency. The work presented here would provide some insights for further modification of the structures of porphyrin dyes used in DSCs to increase the photon-to-current conversion efficiency.

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#### REFERENCES

- [1] A. Nasiri, S. A. Zabalawi, G. Mandic, *IEEE Trans. Ind. Electron.* 2009, 56, 4502.
- [2] M. Gorlatova, P. Kinget, I. Kymissis, D. Rubenstein, X. Wang, G. Zussman, *IEEE Wireless Commun.* 2010, 17, 18.
- [3] J. W. Matiko, N. J. Grabham, S. P. Beeby, M. J. Tudor, *Meas. Sci. Technol.* 2014, 25, 012002.
- [4] B. O'Regan, M. Grätzel, Nature 1991, 353, 737.
- [5] K. Kakiage, Y. Aoyama, T. Yano, K. Oya, T. Kyomen, M. Hanaya, *Chem. Commun.* **2015**, *51*, 6315.
- [6] K. Kakiage, Y. Aoyama, T. Yano, K. Oya, J. -I. Fujisawa, M. Hanaya, *Chem. Commun.* 2015, *51*, 15894.
- [7] M. Grätzel, Nature 2001, 414, 338.
- [8] M. Grätzel, J. Photochem. Photobiol. C. 2003, 4, 145.
- [9] M. K. Nazeeruddin, M. Grätzel, in *Comprehensive Coordination Chemistry II*, Vol. 9 (Eds: J. A. McCleverty, T. J. Meyer), Elsevier, Dordrecht, The Netherlands 2004, p. 719.
- [10] N. Robertson, Angew. Chem. Int. Ed. 2006, 45, 2338.
- [11] P. Docampo, S. Guldin, T. Leijtens, N. K. Noel, U. Steiner, H. J. Snaith, *Adv. Mater.* **2014**, *26*, 4013.
- [12] V. Sugathan, E. John, K. Sudhakar, *Renew. Sustain. Energy Rev.* 2015, 52, 54.
- [13] J. Wu, Z. Lan, J. Lin, M. Huang, Y. Huang, L. Fan, G. Luo, *Chem. Rev.* 2015, 115, 2136.
- [14] S. Yun, P. D. Lund, A. Hinsch, Energ. Environ. Sci. 2015, 8, 3495.
- [15] M. Freitag, J. Teuscher, Y. Saygili, X. Zhang, F. Giordano, P. Liska, J. Hua, S. M. Zakeeruddin, J. -E. Moser, M. Grätzel, A. Hagfeldt, *Nat. Photonics* **2017**, *11*, 372.
- [16] A. Yella, H.-W. Lee, H. N. Tsao, C. Yi, A. K. Chandiran, M. K. Nazeeruddin, E. W.-G. Diau, C.-Y. Yeh, S. M. Zakeeruddin, M. Gratzel, *Science* 2011, 334, 629.
- [17] S. Mathew, A. Yella, P. Gao, R. Humphry-Baker, B. F. Curchod, N. Ashari-Astani, I. Tavernelli, U. Rothlisberger, M. K. Nazeeruddin, M. Gratzel, *Nat. Chem.* **2014**, *6*, 242.
- [18] A. Yella, C. -L. Mai, S. M. Zakeeruddin, S. -N. Chang, C.-H. Hsieh, C.-Y. Yeh, M. Gratzel, *Angew. Chem. Int. Ed.* 2014, 53, 2973.
- [19] H. -H. Chou, K. S. K. Reddy, H. -P. Wu, B. -C. Guo, H. -W. Lee, E. W. G. Dia, C. P. Hsu, C. -Y. Yeh, ACS Appl. Mater. Interfaces 2016, 8, 3418.
- [20] N. Koumura, Z.-S. Wang, S. Mori, M. Miyashita, E. Suzuki, K. Hara, J. Am. Chem. Soc. 2006, 128, 14256.
- [21] Z.-S. Wang, N. Koumura, Y. Cui, M. Takahashi, H. Sekiguchi, A. Mori, T. Kubo, A. Furube, K. Hara, *Chem. Mater.* **2008**, *20*, 3993.
- [22] H. -P. Lu, C. -L. Mai, C. -Y. Tsia, S. -J. Hsu, C. -P. Hsieh, C. -L. Chiu, C. -Y. Yeh, E. -W. Diau, *Phys. Chem. Chem. Phys.* 2009, 11, 10270.
- [23] S.-L. Wu, H.-P. Lu, H.-T. Yu, S.-H. Chuang, C.-L. Chiu, C.-W. Lee, E. W.-G. Diau, C.-Y. Yeh, *Energ. Environ. Sci.* 2010, 3, 949.

- [24] C.-W. Lee, H.-P. Lu, N. M. Reddy, H.-W. Lee, E. W.- G. Diau, C.-Y. Yeh, *Dyes Pigm.* 2011, 91, 317.
- [25] D. P. Hagberg, J.-H. Yum, H. Lee, F. D. Angelis, T. Marinado, K. M. Karlsson, R. Humphry-Baker, L. Sun, A. Hagfeldt, M. Grätzel, M. K. Nazeeruddin, J. Am. Chem. Soc. 2008, 130, 6259.
- [26] K. Hara, T. Sato, R. Katoh, A. Furube, Y. Ohga, A. Shinpo, S. Suga, K. Sayama, H. Sugihara, H. Arakawa, J. Phys. Chem. B 2003, 107, 597.
- [27] J. K. Park, H. R. Lee, J. Chen, H. Shinokubo, A. Osuka, D. Kim, J. Phys. Chem. C 2008, 112, 16691.
- [28] M. Wang, P. Chen, R. Humphry-Baker, S. M. Zakeeruddin, M. Grätzel, *Chem. Phys. Chem.* **2009**, *10*, 290.
- [29] S. N. Mori, W. Kubo, T. Kanzaki, N. Masaki, Y. Wada, S. Yanagida, J. Phys. Chem. C 2007, 111, 3522.
- [30] J.-L. Lan, Y.-Y. Wang, C.-C. Wan, T.-C. Wei, H.-P. Feng, C. Peng, H.-P. Cheng, Y.-H. Chang, W.-C. Hsu, *Curr. Appl. Phys.* **2010**, *10*, S168.
- [31] T. C. Wei, C. C. Wan, Y. Y. Wang, Appl. Phys. Lett. 2006, 88, 103122.
- [32] Y. -C. Liu, H. -H. Chou, F. -Y. Ho, H. -J. Wei, T. -C. Wei, C. -Y. Yeh, J. Mater. Chem. A 2016, 4, 11878.

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