

A Zinc Porphyrin Sensitizer Modified with Donor and Acceptor Groups for Dye-Sensitized Solar Cells

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In this article, we have designed and synthesized a novel donor- π -acceptor (D- π -A) type porphyrin-based sensitizer (denoted *UI-5*), in which a carboxyl anchoring group and a 9,9-dimethyl fluorene were introduced at the *meso*-positions of porphyrin ring *via* phenylethynyl and ethynyl bridging units, respectively. Long alkoxy chains in *ortho*-positions of the phenyls were supposed to reduce the degree of dye aggregation, which tends to affect electron injection yield in a photovoltaic cell. The cyclic voltammetry was employed to determine the band gap of *UI-5* to be 1.41 eV based on the HOMO and LUMO energy levels, which were estimated by the onset oxidation and reduction potentials. The incident monochromatic photon-to-current conversion efficiency of the *UI-5* DSSC assembled with double-layer (20 nm-sized TiO₂/400 nm-sized TiO₂) film electrodes appeared lower upon overall ranges of the excitation wavelengths, but exhibited a higher value over the NIR ranges ($\lambda = 650$ -700 nm) compared to the common reference sensitizer N719. The *UI-5*-sensitized cell yielded a relatively poor device performance with an overall conversion efficiency of 0.74% with a short circuit photocurrent density of 3.05 mA/cm², an open circuit voltage of 0.54 mV and a fill factor of 0.44 under the standard global air mass (AM 1.5) solar conditions. However, our report about the synthesis and the photovoltaic characteristics of a porphyrin-based sensitizer in a D- π -A structure demonstrated a significant complex relationship between the sensitizer structure and the cell performance.

Key Words : Zinc porphyrin, Donor- π -Acceptor Dye, Electrochemical properties, Dye-sensitized solar cells, Photovoltaics

Introduction

Owing to the rapid economic expansion, increase in world population, and ever-increasing human reliance on energy-based appliances, the global energy consumption has been accelerating at an alarming rate. Accordingly, the research and development of sustainable energy conversion technology has attracted a great deal of interest. The solar cell has been considered to be a green and effective technology to address today's energy conversion and environment issues.¹ Although conventional solar cells based on silicon and other inorganic materials have come to commercialization, there are still some challenging issues related to the high cost, limited flexibility, and environmental issues.²⁻⁴ Organic photovoltaics have been regarded as one of the promising alternatives to overcome those shortcomings.⁵

Dye-sensitized solar cells (DSSCs) have attracted considerable attention as a possible candidate for low-cost photovoltaic cells. The heart of this cell is a photoanode, consisting of a nanoporous TiO₂ film covered by a monolayer of photosensitizer.⁶ Considerable effort has been devoted to the development of new and efficient sensitizers suitable for practical use, such as coumarin,⁷⁻⁹ indoline,¹⁰⁻¹² oligoene,^{13,14} thiophene,¹⁵⁻¹⁷ triarylamine,¹⁸⁻²⁰ perylene,²¹⁻²³ cyanine,²⁴⁻²⁶ phthalocyanine,²⁷ and hemicyanine derivatives.^{28,29} Inspired by the efficient energy transfer in naturally occurring photosynthetic reaction centers, porphyrins are considered as one of promising sensitizers for DSSC applications.³⁰⁻³⁸

Officer and co-workers firstly achieved above 7% in the overall efficiency of DSSC comprising a side-anchoring, fully conjugated porphyrin dye.³⁹ Recently, a push-pull porphyrin co-sensitized with an organic dye has been also reported as the best performing dye of DSSC using a cobalt-based electrolyte to yield the conversion efficiency of 12.3%.⁴⁰ The efficiency of push-pull porphyrin sensitizer in DSSC strongly relies on the types and combination of the donor and acceptor groups tethered to the porphyrin ring.^{39,41-43} Thus, a variety of sensitizers with a systematic variation of the structure should be designed in order to figure out the reliance complexity between the dye structure and the device performance.

In this article, we described the synthesis of a donor- π -acceptor (D- π -A) type porphyrin dye (denoted *UI-5*) modified with the 9,9-dimethyl fluorene group (donor) and the phenylethynyl-bridged carboxyl anchoring group (acceptor). The push group was introduced at the *meso*-position of the porphyrin ring, which was elongated with ethynyl bridging unit in order to improve the donor effect. Additionally, long alkoxy chains were introduced in the *ortho*-positions of the phenyls at the *meso*-position of the porphyrin ring in order to reduce the degree of dye aggregation, which counted as the major factor in decreasing the efficiency of sensitized photocurrent generation.^{44,45} Moreover, we fabricated solar cells with *UI-5*, and examined incident photons to the current efficiency (IPCE) and the photon conversion efficiency (η).

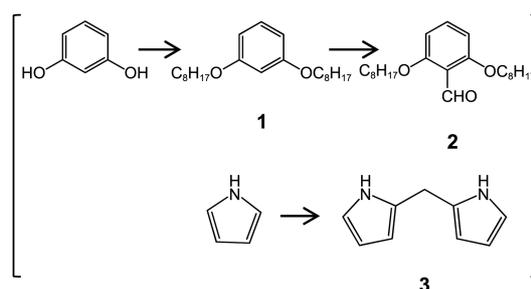
Experimental Section

Materials. 1,3-Bis(hydroxyl)benzene, *n*-bromohexane, paraformaldehyde, pyrrole, fluorene, iodomethane, *N*-bromosuccinimide, zinc acetate dihydrate, (triisopropylsilyl)acetylene, 4-iodobenzoic acid, tetrabutylammonium perchlorate, *tert*-butyl pyridine and toluene were purchased from Sigma-Aldrich and used as received. Acetone, ethyl alcohol, methyl alcohol, tetrahydrofuran, acetonitrile and methylene chloride were purchased from Samchun chemicals. Dimethylformamide (DMF), valeronitrile, trifluoroacetic acid, chloroform-*d* and dimethylsulfoxide-*d* were also purchased from Sigma-Aldrich. F-doped tin oxide (FTO glass, 8 Ω/cm, *d* = 100 μm) and thermoplastic film (Surlyn, *d* = 100 μm) were purchased from Libby Owens Ford, and DuPont, respectively. 1-Hexyl-2,3-dimethylimidazolium iodide > 98% (C-TRI), 1-butyl-3-methylimidazolium iodide 98% (C-TRI), 3-propyl-1,2-dimethylimidazolium iodide (C-TRI), iodine (Sigma-Aldrich), lithium iodide (Sigma-Aldrich) TiO₂ paste 20 (Solaronix), Ti-Nanoxide 400 (Solaronix), and Pt-catalyst T/SP (Solaronix) were purchased and used as received.

Synthesis of 1,4-Bis(octyloxy)benzene (1). 1,3-Bis(hydroxy)benzene (2 g, 18.2 mmol) and *n*-bromohexane (10 mL, 60.6 mmol) were successively added to a stirred suspension of potassium hydroxide (8 g, 142.5 mmol) in 32 mL of dimethyl sulfoxide (DMSO). The reaction was stirred overnight at RT and was then quenched with pouring into 50 mL of water. The product was extracted with methylene chloride, dried over magnesium sulfate (MgSO₄), and concentrated under reduced pressure. The product was purified by flash column chromatography as eluent of DCM to obtain **1** (the chemical structure in Scheme 1) as white crystal in 4.1 g, 72% yield. ¹H NMR (CDCl₃, 400 MHz) δ_H 7.15 (t, *J* = 8.4 Hz, 1H), 6.48 (m, 3H), 3.92 (t, *J* = 6.4 Hz, 4H), 1.76 (m, 4H), 1.44 (m, 4H), 1.33-1.29 (m, 16H), 0.90 (t, *J* = 7.6 Hz, 6H). MS (GC-mass): *m/z* 334.4 [M⁺]; C₂₂H₃₈O₂ (334.3).

Synthesis of 2,6-Bis(octyloxy)benzaldehyde (2). A three-neck flask was equipped with an additional funnel and charged with compound **1** (3 g, 10 mmol) and tetramethylethylenediamine (0.39 mL, 4.3 mmol) in 28 mL of THF. The solution was degassed with nitrogen (N₂) for 15 min and cooled to 0 °C, and then mixed dropwise with 1.6 M *n*-butyllithium in hexane (7.46 mL, 12 mmol) over 20 min, and allowed to stir for 3 h. After warming to RT, DMF (1.46 mL, 20 mmol) was added dropwise into the reaction mixture, which was stirred for an additional 2 h. The reaction was quenched with pouring into water, and the mixture was extracted with ether (3 × 80 mL), dried over anhydrous MgSO₄. The solvent was removed under reduced pressure. The product was recrystallized from hexane to yield a white solid (2.72 g, 75% yield) (the chemical structure in Scheme 1). ¹H NMR (CDCl₃, 400 MHz) δ_H 10.47 (s, 1H), 7.31 (t, *J* = 8.4 Hz, 1H), 6.47 (d, *J* = 8.4 Hz, 2H), 3.95 (t, *J* = 6.4 Hz, 4H), 1.77-1.71 (m, 4H), 1.39 (m, 4H), 1.25-1.21 (m, 16H), 0.81 (t, *J* = 7.2 Hz, 6H). MS (GC-mass): *m/z* 362.3 [M⁺]; C₂₃H₃₈O₃ (362.3).

Synthesis of Dipyrrromethane (3). Paraformaldehyde (0.6



Scheme 1. The synthesis route to 2,6-bis(octyloxy)benzaldehyde and dipyrrromethane.

g, 20 mmol) and pyrrole (50 mL, 720 mmol) were dissolved in a mixture of AcOH (150 mL) and MeOH (50 mL). The solution was stirred for 20 h at 25 °C. Then the reaction mixture was washed with water (100 mL × 2) and aqueous KOH solution (0.1 M; 100 mL × 2). The product was purified by flash column chromatography as eluent of DCM to obtain **3** (the chemical structure in Scheme 1) as dark green crystal in 34.8% yield (1.02 g). ¹H NMR (CDCl₃, 400 MHz) δ_H 8.9 (s, 2H), 6.62 (d, *J* = 8.4 Hz, 2H), 6.01 (t, *J* = 8.4 Hz, 2H), 5.58 (d, *J* = 8.4 Hz, 2H), 3.90 (s, 2H), MS (GC-mass): *m/z* 146.1 [M⁺]; C₉H₁₀N₂ (145.1).

Synthesis of 5,15-Bis(2,6-dioctoxyphenyl)porphyrin (4). To a degassed solution of dipyrrromethane (0.5 g, 3.43 mmol) and compound **2** (1.24 g, 3.43 mmol) in DCM (500 mL) was added trifluoroacetic acid (0.23 mL, 37.3 mmol). The solution was stirred under nitrogen atmosphere at 23 °C for 4 h, and charged with DDQ (1.17 g, 5.14 mmol). Then, the mixture was stirred for an additional 1 h. The mixture was basified with Et₃N (0.58 mL) and filtered through silica. After the solvent was removed under reduced pressure, the residue was purified by column chromatography (silica gel) using DCM/hexane = 1/2 as eluent. The product was recrystallized from MeOH/DCM to give the product (1.02 g, 30%) as a purple powder. ¹H NMR (CDCl₃, 400 MHz) δ_H 10.13 (s, 2H), 9.26 (d, *J* = 4.8 Hz, 4H), 8.96 (d, *J* = 4.8 Hz, 4H), 7.71 (t, *J* = 8.4 Hz, 2H), 7.02 (d, *J* = 8.4 Hz, 4H), 3.83 (t, *J* = 6.4 Hz, 8H), 0.93-0.88 (m, 8H), 0.87-0.80 (m, 8H), 0.67-0.60 (m, 8H), 0.58-0.50 (m, 28H), 0.47-0.40 (m, 8H), -3.02 (s, 2H). ¹³C NMR (CDCl₃, 100 MHz) δ_C 160.7, 148.2, 145.5, 131.3, 130.9, 130.5, 120.6, 112.0, 105.9, 104.4, 69.2, 31.8, 29.1, 25.8, 22.8, 14.3. MS (MALDI-TOF): *m/z* 974.9 [M⁺]; C₆₄H₈₆N₄O₄ (974.7).

Synthesis of 5,15-Dibromo-10,20-bis(2,6-dioctoxyphenyl)porphyrin (5). To a stirred solution of compound **4** (0.35 g, 0.36 mmol) in DCM (150 mL) was slowly added a solution of NBS (0.13 g, 0.75 mmol) in DCM (50 mL) in a period of 6 h at 0 °C under inert condition. The reaction was quenched with adding acetone (30 mL). After the solvent was removed under reduced pressure, the residue was purified by column chromatography (silica gel) using DCM/hexane = 1/2 as eluent. Recrystallization from MeOH/DCM gave the product (0.32 g, 81%) as a purple powder. ¹H NMR (CDCl₃, 400 MHz) δ_H 9.51 (d, *J* = 4.8 Hz, 4H), 8.80 (d, *J* = 4.8 Hz, 4H), 7.70 (t, *J* = 8.4 Hz, 2H), 6.99 (d, *J* = 8.4 Hz,

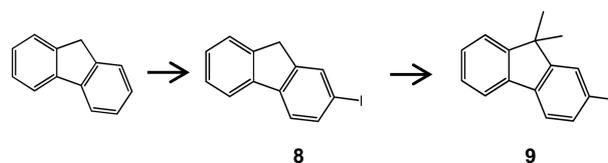
4H), 3.84 (t, $J = 6.4$ Hz, 8H), 0.97-0.95 (m, 8H), 0.82-0.80 (m, 8H), 0.64-0.60 (m, 8H), 0.54-0.51 (m, 28H), 0.44-0.40 (m, 8H), -2.59 (s, 2H). MS (MALDI-TOF): m/z 1132.3 [M^+]; $C_{64}H_{84}Br_2N_4O_4$ (1132.5).

Synthesis of [5,15-Dibromo-10,20-bis(2,6-dioctoxyphenyl)porphinato] zinc (II) (6). A suspension of the compound **5** (0.23 g, 0.22 mmol) and $Zn(OAc)_2 \cdot 2H_2O$ (40.44 g, 0.4 mmol) in a mixture of DCM (45 mL) and MeOH (22 mL) was stirred at 23 °C for 3 h. The reaction was quenched with adding water (10 mL), and the mixture was extracted with DCM (3 × 10 mL). The combined extracts were washed with water and dried over anhydrous $MgSO_4$. The solvent was removed under reduce pressure to give the product (0.25 g, 96%). 1H NMR ($CDCl_3$, 400 MHz) δ_H 9.62 (d, $J = 4.8$ Hz, 4H), 8.89 (d, $J = 4.8$ Hz, 4H), 7.69 (t, $J = 8.4$ Hz, 2H), 6.99 (d, $J = 8.4$ Hz, 4H), 3.84 (t, $J = 6.4$ Hz, 8H), 0.98-0.90 (m, 8H), 0.83-0.75 (m, 8H), 0.62-0.41 (m, 44H), 0.39-0.33 (m, 8H). MS (MALDI-TOF): m/z 1196.5 [M^+]; $C_{64}H_{82}Br_2N_4O_4Zn$ (1196.4)

Synthesis of [5,15-Di(trisopropylsilyl)ethynyl-10,20-bis(2,6-dioctoxyphenyl)porphinato] zinc(II) (7). The compound **6** (0.5 g, 418 μ mol), anhydrous toluene (10 mL), (trisopropylsilyl)acetylene (0.19 mL, 850 μ mol), and copper(I) iodide (6.66 mg, 35 μ mol) in a round-bottom flask were stirred under nitrogen. Triethylamine (1 mL) was then added into the mixture, which was then degassed by N_2 bubbling. After the addition of bis(triphenylphosphine)palladium(II) dichloride (24.5 mg, 35 μ mol), the solution was heated at 85 °C overnight. The solvent was removed under vacuum, and the residue was purified by column chromatography (silica gel) using methylene chloride/hexane (1/3) as eluent. Solvent were removed to afford compound **7** (0.26 mg, 87%) as dark purple solid. 1H NMR ($CDCl_3$, 400 MHz) δ_H 9.65 (d, $J = 4.8$ Hz, 4H), 8.87 (d, $J = 4.8$ Hz, 4H), 7.66 (t, $J = 8.4$ Hz, 2H), 6.97 (d, $J = 8.4$ Hz, 4H), 3.81 (t, $J = 6.4$ Hz, 8H), 1.43-1.39 (m, 42H), 0.96-0.90 (m, 8H), 0.77-0.70 (m, 8H), 0.54-0.39 (m, 44H), 0.38-0.34 (m, 8H). MS (MALDI-TOF): m/z 1398.9 [M^+]; $C_{86}H_{124}N_4O_4Si_2Zn$ (1397.8).

Synthesis of 2-Iodofluorene (8). 2-Iodofluorene was synthesized by iodination of fluorene (1 g, 6.02 mmol) with iodine (0.8 g, 3.2 mmol) in the presence of *ortho*-periodic acid (H_3IO_6) (20 g, 0.88 mmol) in 80% acetic acid aqueous solution (20 mL) at 80 °C for 4 h under nitrogen atmosphere. After cooling, the solvent was removed by decantation, and a brown solid was obtained. This was dissolved in toluene and washed with 5% $NaHSO_3$ aqueous solution to remove the remaining iodine. Then, the resulting solid was purified by alumina column chromatography using toluene as an eluent, to obtain **8** (the chemical structure in Scheme 2). Yield: 1.05 g (60%). 1H NMR ($CDCl_3$, 400 MHz) δ_H 7.89 (s, 1H), 7.76 (d, $J = 8.4$ Hz, 2H), 7.70 (d, $J = 8.4$ Hz, 2H), 7.73 (d, $J = 8.4$ Hz, 2H), 7.38-7.35 (m, 2H), 3.87 (s, 2H), MS (GC-mass): m/z 292.0 [M^+]; $C_{13}H_9I$ (292.1).

Synthesis of 9,9-Dimethyl-2-iodofluorene (9). 1 g (3.44 mmol) of 2-iodofluorene and 100 mL of dimethylsulfoxide were put into a 500 mL three-neck round-bottom flask. Subsequently, 0.04 g (0.22 mmol) of benzytrimethyl-



Scheme 2. The synthetic route to 9,9-dimethyl-2-iodofluorene.

ammonium chloride and 1 mL of 50% sodium hydroxide aqueous solution were added to the mixture. This mixture was stirred at RT for 3 h. Thereafter, 0.76 g (5.2 mmol) of iodomethane was added into the reaction mixture, which was stirred at RT for an additional 3 h. After completion of the reaction, the reaction solution was washed with 1.0 mol/L hydrochloric acid; a water layer was extracted three times with ethyl acetate. The collected organic layer was washed with saturated saline, and then dried with magnesium sulfate. After drying, the mixture was subjected to suction filtration, and the filtrate was concentrated. An obtained residue was purified by silica gel column chromatography (hexane as eluent), and an obtained solution was concentrated. The residue solid was recrystallized with a mixed solvent of chloroform and hexane to yield 0.7 g of a white, powdery solid of 2-iodo-9,9-dimethylfluorene (64% yield) (the chemical structure in Scheme 2). 1H NMR ($CDCl_3$, 400 MHz) δ_H 7.92 (s, 1H), 7.70 (d, $J = 8.4$ Hz, 1H), 7.66 (d, $J = 8.4$ Hz, 1H), 7.60 (d, $J = 8.4$ Hz, 1H), 7.47 (d, $J = 8.4$ Hz, 1H), 1.37 (s, 6H), MS (GC-mass): m/z 320.0 [M^+]; $C_{15}H_{13}I$ (320.1).

Synthesis of UI-5. To a solution of the compound **7** (100 mg, 0.071 mmol) in THF (5 mL) was added tetra-*n*-butylammonium fluoride (0.715 mL, 0.71 mmol) at RT. Prior to the addition of water, the mixture was stirred for 1 h. Then, the solution was extracted with methylene chloride. The green organic layer was collected, and the solvent was evaporated under reduced pressure to get the deprotected intermediate. To a solution of the deprotected intermediate in a degassed mixture of THF (20 mL) and NEt_3 (3 mL) was added 4-iodobenzoic acid (21.8 mg, 85 μ mol), and compound **9** (27 mg, 85 μ mol), $Pd_2(dba)_3$ (3.25 mg, 3.55 μ mol), and $AsPh_3$ (43 mg, 142 μ mol). The mixture was stirred at 85 °C for 5 h. The solvent was removed under vacuum and the residue was purified by column chromatography (silica gel) using CH_2Cl_2/CH_3OH (19/1) as eluent. Recrystallization from CH_2Cl_2/CH_3OH gave UI-5 (29.7 mg, 30%). 1H NMR ($CDCl_3$, 400 MHz) δ_H 9.74 (d, $J = 4.8$ Hz, 4H), 8.90 (d, $J = 4.8$ Hz, 4H), 8.05-8.02 (m, $J = 8.4$ Hz, 4H), 7.91-7.84 (m, $J = 8.4$ Hz, 4H), 7.72 (t, $J = 8.4$ Hz, 2H), 7.53 (m, $J = 8.4$ Hz, 2H), 7.40 (td, $J = 8.4$ Hz, 3H), 3.87 (t, $J = 6.4$ Hz, 8H), 1.26 (m, 6H), 0.99 (m, 6H), 0.82 (m, 8H), 0.50 (m, 44H), MS (MALDI-TOF): m/z 1398.9 [M^+]; $C_{90}H_{100}N_4O_6Zn$ (1397.7).

Fabrication of DSSC. For the DSSC, a screen-printed double-layer film of interconnected TiO_2 particles was used as the mesoporous anode. First, an 8 μ m thick film of 20-nm-sized TiO_2 particles (Solaronix) was printed on the fluorine-doped SnO_2 conducting glass electrode (FTO, 8 Ω/sq), which was pretreated with 40 mM $TiCl_4$ aqueous solu-

tion referring to the earlier report of Grätzel group.⁴⁶ Subsequently, a 4 μm thick second layer of 400-nm-sized light-scattering anatase particles (CCIC) was coated further on the first layer. The TiO_2 electrode was stained by immersing it into the dye solution containing 0.5 mM *UI-5* in a mixture of anhydrous alcohols at RT for 24 h. The sensitized titanium electrode was assembled with a conducting Pt-counter electrode which was prepared by heating a FTO glass plate coated with two drops of 5 mM H_2PtCl_6 ethanol solution by means of a hot steam of air (400 $^\circ\text{C}$) for 20 min. The electrolyte composed of 0.6 M 1-butyl-3-methylimidazolium iodide, 0.05 M I_2 , 0.1 M LiI, and 0.5 M *tert*-butyl pyridine in a mixture of acetonitrile/valeronitrile (v/v = 1/1), was introduced into the sandwiched cell with an architecture of FTO/20 nm- TiO_2 /400 nm- TiO_2 /*UI-5*/Pt-FTO.

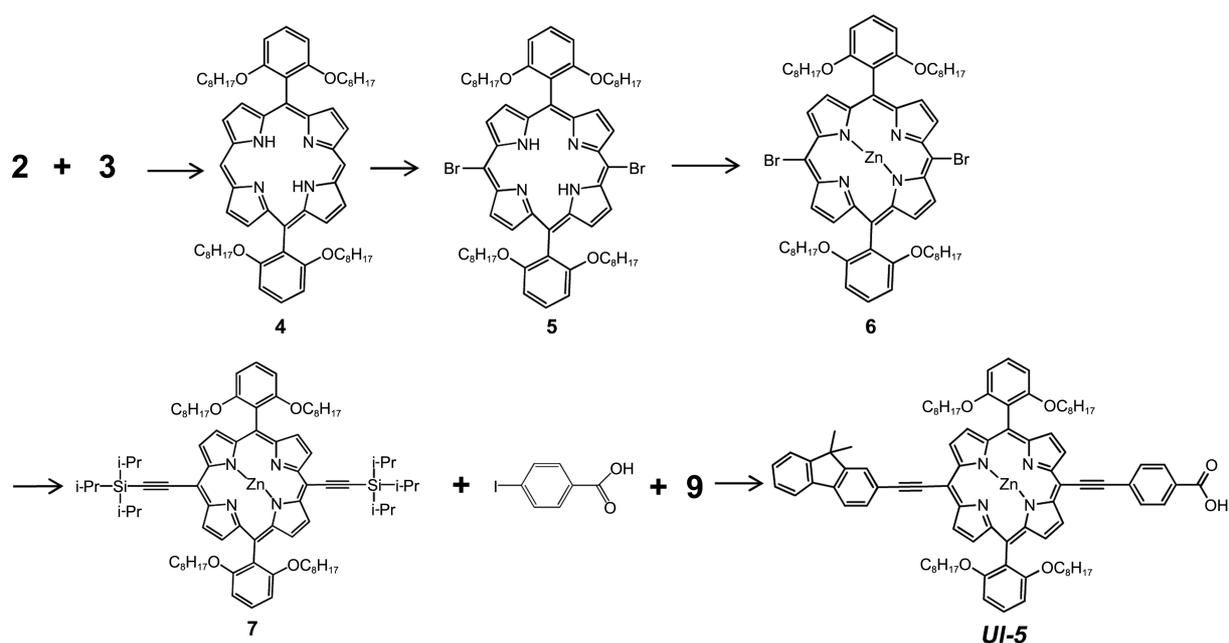
Photovoltaic Characterization. The *UI-5*-sensitized solar cells were assessed employing a solar simulator equipped with a 400 W xenon lamp (Oriel), appropriate filters, and a digital source meter (Keithley model 2400) connected to a personal computer, which allows to determine photocurrents and photovoltages. The solar simulator was calibrated under global standard air mass (AM 1.5, 100 mW/cm^2) condition by employing KG5 filtered Si reference solar cell.

These measurements were carried out for dry film electrodes, and no corrections were made for optical effects due to the presence of the electrolyte. Photocurrent action spectra and photocurrent-photovoltage characteristics of the dye-sensitized TiO_2 electrodes were measured with sandwich-type cells. The working electrode of the dye-sensitized TiO_2 film on conducting glass was squeezed together with a platinized conducting glass using a thermoplastic film and illuminated from the substrate side. The electrolyte, typically 0.5 M LiI/0.5 M I_2 in acetonitrile and valeronitrile, was attracted into the cavities of the dye-sensitized TiO_2 electrode by capillary forces. A 400 W xenon lamp with a mono-

chromator was used as light source for the photocurrent action spectra measurements. The cell was operated in the short-circuit mode.

Incident Photon-to-current Conversion Efficiency. The incident photon-to-current conversion efficiency (IPCE) spectra were measured as a function of wavelength from 300 to 900 nm using a specially designed IPCE system (PV Measurements Inc.) for DSSCs. A similar data acquisition system was used to control the IPCE measurement. Under full computer control, the light from a 400 W xenon lamp (ILC Technology) was focused through a Gemini-180 double monochromator (Jobin Yvon Ltd.) onto the photovoltaic cell under test. The monochromator was incremented through the visible spectrum to generate the IPCE (λ) as defined by $\text{IPCE}(\lambda) = 1240 (I_{sc}/\lambda\phi)$, where λ is the wavelength, I_{sc} is the short-circuit photocurrent density (mA/cm^2), and ϕ is the incident radiative flux (mW/cm^2). The photovoltaic performance was measured by using a metal mask with an aperture area of 0.159 cm^2 . Solar cells covered with a 50 mm thick of polyester film (Preservation Equipment Ltd., UK) as a 400 nm UV cut off filter were irradiated at open circuit under a Sun test CPS plus lamp (ATLAS GmbH, 100 mW/cm^2) in ambient air at 60 $^\circ\text{C}$. The photovoltaic measurements were carried out at RT after allowing the cells to cool down and equilibrate during 2 h.

Electrochemical Measurements. The electrochemical experiments were performed in a conventional electrode cell with separate compartments for counter and reference electrodes at room temperature using an IVIUM compactstat. Glassy carbon acted as the working electrode, a saturated calomel electrode (SCE) as the reference, and a platinum wire as the counter electrode, respectively. The glassy carbon electrode was polished on abrasive Al_2O_3 paper (0.05 μm), and sonicated in ethanol and twice-distilled water for 5 min prior to each measurement. The electrolyte was 0.1 M tetra-



Scheme 3. The synthetic route to zinc porphyrin dye *UI-5*.

butylammonium perchlorate in dry THF. The concentration of the dye in the electrolyte was 0.5 mM. Scans are initiated at 0 V *versus* SCE in negative direction at the rates 50 mV/s. The solutions were purged with nitrogen and stirred over 15 min prior to the measurements.

Other Methods. UV/visible absorbance and emission spectra of *UI-5* were recorded using a Parkin-Elmer Lambda 40 spectrophotometer and fluorescence spectrometer (Shimadzu RF-5000), respectively. Nuclear magnetic resonance (NMR) spectra were obtained from a VARIAN UNITY INOVA 400 instrument. Infrared spectra were taken using FT-IR Spectrophotometer (Nicolet). MALDI-TOF Mass analysis was carried out employing an instrument (Voyager DE-STR, Applied Biosystems) in a reflector mode with a matrix of 3,5-dimethoxy-4-hydroxy-trans-cinnamic acid (sinapinic acid) in all cases.

Results and Discussion

Synthesis of *UI-5*. The synthesis of *UI-5* was carried out using the reaction route outlined in Scheme 3. The free base porphyrin derivative was synthesized according to a common method using the stoichiometric reaction between dipyrromethane and functionalized benzaldehyde with the help of DDQ and trifluoroacetic acid.⁴⁷ The long alkyl chains in the middle phenyl ring were supposed to considerably increase the solubility of the chromophores in common solvents. The free base porphyrin was metalated using zinc acetate after the bromination with NBS. The completeness of the reaction was confirmed on the basis of the disappearance of a characteristic absorption band of the free base porphyrin at 515 nm. The synthetic approach to this ethynyl-bridged porphyrin (denoted *UI-5*) with 9,9-dimethyl fluorene (donor) and phenylethynyl-bridged carboxylate dye (acceptor) was achieved by Sonogashira coupling reaction.^{48,49}

The chemical structure of *UI-5* was determined using ¹H NMR, IR, and MALDI-TOF-Mass spectroscopy (see supporting information SI). Above all, the chemical structure of *UI-5* was clearly identified using MALDI-TOF-Mass spectroscopy, as shown in Figure 1.

UV/visible Absorption and Fluorescence Spectra. Representative absorption and emission spectra of *UI-5* (Figure 2) in dichloromethane/methanol mixture were not significantly different from the parent porphyrins prior to the introduction

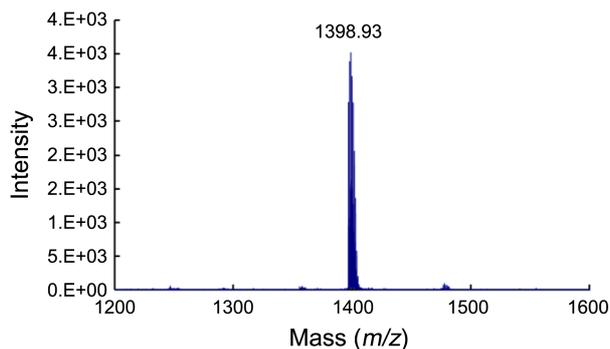


Figure 1. MALDI-TOF-Mass spectrum of *UI-5*.

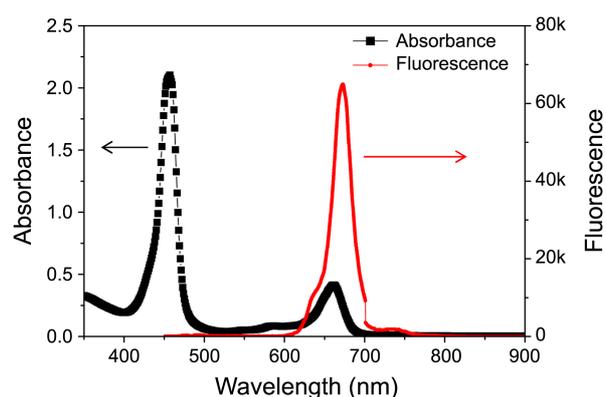


Figure 2. Optical absorption and emission spectra of *UI-5*.

of the donor and acceptor groups. The UV/visible spectra of *UI-5* in solution exhibited the typical absorption feature of a porphyrin ring; well-resolved intense Q band in the visible region (550-750 nm) and even more intense (about 10 times) Soret band (400-500 nm). As expected, the electronic absorption bands of porphyrins are sensitive to substituents on the periphery of the porphyrin ring. Soret band peak position was shifted from 394 to 457 nm due to substituents on the periphery of the porphyrin ring.⁵⁰ The fluorescence spectra of *UI-5* ($\lambda_{\text{ex}} = 450$ nm) displayed a broad and strong emission near 673 nm with a shoulder band at 740 nm (Figure 2).

Electrochemical Properties. Cyclic voltammetry was employed to determine the HOMO and LUMO energy levels of *UI-5* by using a three-electrode cell composed of glassy carbon acted as the working electrode, SCE as the reference, and a platinum wire as the counter electrode with 0.1 M tetrabutylammonium perchlorate in anhydrous THF as the supporting electrolyte, as shown in Figure 3. Note that the SCE was calibrated using a ferrocene-ferrocenium (Fc/Fc⁺) redox couple ($E_{\text{HOMO}} = 4.8$ eV below the vacuum level) as an external standard.⁵¹ Electrochemical analysis of *UI-5* using cyclic voltammetry showed an onset oxidation potential of 0.61 V and onset reduction potential of -0.78 V. The HOMO and LUMO energy level of *UI-5* were estimated

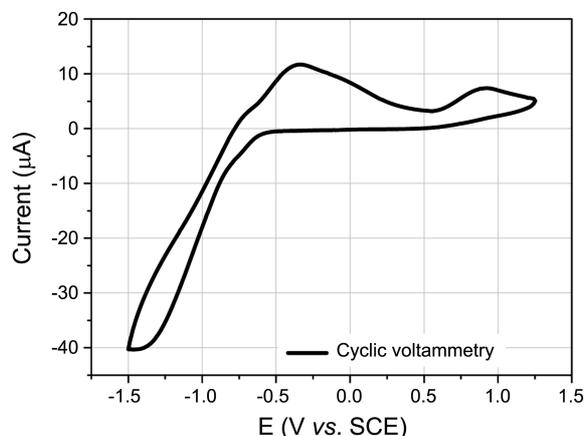


Figure 3. Cyclic voltammogram of 0.5 mM *UI-5* dye (scan rate = 50 mV/s). 0.1 M tetrabutylammonium perchlorate in dry THF was used as supporting electrolyte. The solutions were stirred under purging nitrogen over 15 min prior to the measurements.

based on onset oxidation and reduction potentials to be 5.41 and 4.0 eV respectively.⁵¹ The band gap of *UI-5* was calculated to 1.41 eV.

Photovoltaic Studies. The performance of the sensitizer *UI-5* was evaluated in a typical DSSC fabricated with screen-printed and double-layer films composed of an 8 μm 20-nm-sized TiO_2 transparent layer and a 4 μm 400-nm-sized TiO_2 scattering layer, as described previously.⁶ Figure 4 shows a comparison of *UI-5* and a reference sensitizer N719 in the photocurrent action spectra obtained from a sandwich cell using an electrolyte containing 0.6 M 1-butyl-3-methylimidazolium iodide, 0.05 M iodine, 0.1 M LiI, and 0.5 M *tert*-butyl pyridine in a 50:50 (v/v) mixture of valeronitrile and acetonitrile. The photocurrent action spectra of *UI-5* (Figure 4(a)) tend to agree well with the UV/visible absorbances (Figure 2). The incident monochromatic photon-to-current conversion efficiency (IPCE) of *UI-5* appeared lower over the whole range of 300-800 nm compared to N719 (based on our cell manufacturing skill). However, the IPCE of *UI-5* was higher over NIR range of 650-700 nm compared to N719. In addition, we have achieved an overall conversion efficiency of 0.74% under standard global air mass (AM 1.5) solar conditions with a short-circuit photocurrent density (I_{sc}) of 3.05 mA/cm^2 , an open-circuit voltage (V_{oc}) of 0.54 mV, and a fill factor of 0.44, which were

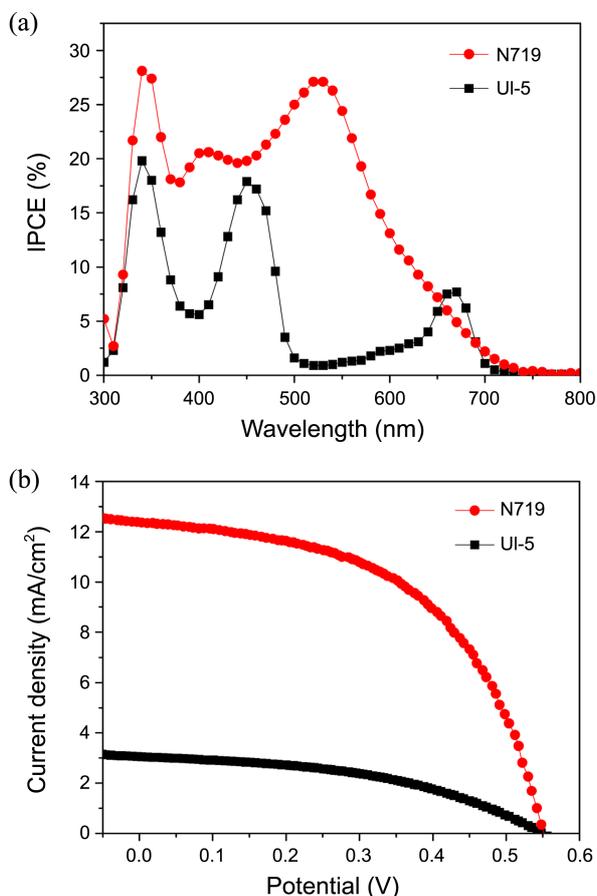


Figure 4. (a) Photocurrent action spectra. (b) photocurrent-photovoltage characteristics of sandwich solar cells based on a *UI-5*- TiO_2 film electrode using iodide/triiodide electrolyte.

Table 1. The photovoltaic parameters of *UI-5* and N719 dyes

Dye	I_{sc} mA/cm^2	V_{oc} mV	FF	η (%)
<i>UI-5</i>	3.05	0.54	0.44	0.74
N719	12.4	0.73	0.52	4.73

determined from the current-voltage characteristics of the *UI-5*-sensitized cell (Figure 4(b)). It is noteworthy that the photovoltaic data for a standard sensitizer N719 (Table 1) showed overall conversion efficiency 4.73% versus a record cell efficiency of 11% by Grätzel,⁶ indicating the level of cell manufacturing skill.

Conclusion

We have designed and synthesized a novel porphyrin-based sensitizer (*UI-5*) in a D- π -A structure, in which the carboxyl anchoring group was connected to the porphyrin ring via a phenylethynyl bridging unit at a *meso*-position. Simultaneously, 9,9-dimethyl fluorene was also connected at a *meso*-position of the porphyrin ring via ethynyl bridging unit to elongate the donor effect of a sensitizer in DSSCs.

The band gap of *UI-5* was determined to be 1.41 eV based on the HOMO and LUMO energy levels, which were estimated by onset oxidation and reduction potentials in the cyclic voltammogram. The performance of the sensitizer *UI-5* was evaluated in a typical DSSC assembled with double-layer film electrodes; a transparent 20 nm-sized TiO_2 layer ($d = 8 \mu\text{m}$) and a 400 nm-sized TiO_2 scattering layer ($d = 4 \mu\text{m}$). The IPCE of *UI-5* reflected for the most part the UV/visible absorbances of the sensitizer, which was featured with an intense absorbance in the range of 550 to 750 nm (Q band) and even more intense Soret band in the range of 400-500 nm. It is noteworthy that IPCE of *UI-5* with a maximum value of 18% appeared lower upon overall ranges of the excitation wavelengths compared to the reference sensitizer N719, but exhibited a higher value over the NIR ranges ($\lambda = 650\text{-}700 \text{ nm}$). The *UI-5*-sensitized cell yielded a relatively poor device performance with an overall conversion efficiency of 0.74% under the standard global air mass (AM 1.5) solar conditions. However, our report about the synthesis and the photovoltaic characteristics of a porphyrin-based sensitizer in a D- π -A structure would be significantly contributed to the design of new and highly efficient sensitizers for DSSCs, as the complex relationship between the sensitizer structure and the cell performance is considered.

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