Supplementary Information

Photovoltaic Properties and Long-term Durability of Porphyrin-Sensitized Solar Cells with Silicon-based Anchoring Groups
Tomohiro Higashino, Shimpei Nimura, Kenichi Sugiura, Yuma Kurumisawa, Yukihiro Tsuji, Hiroshi Imahori*

Department of Molecular Engineering, Graduate School of Engineering, Kyoto University, Nishikyo-ku, Kyoto 615-8510, Japan
Institute for Integrated Cell-Material Sciences (WPI-iCeMS), Kyoto University, Sakyo-ku, Kyoto 606-8501, Japan

E-mail: imahori@scl.kyoto-u.ac.jp

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1. Experimental Section

Instrumentation and Materials.

Commercially available solvents and reagents were used without further purification unless otherwise mentioned. Silica-gel column chromatography was performed with UltraPure Silica Gel (230-400 mesh, SiliCycle) unless otherwise noted. Thin-layer chromatography (TLC) was performed with Silica gel 60 F254 (Merck). Size exclusion gel permeation chromatography (GPC) was performed by Bio-beads S-X1 (Bio-rad). UV/Vis/NIR absorption spectra of solutions and films were measured with a Perkin-Elmer Lambda 900 UV/vis/NIR spectrometer. Steady-state fluorescence spectra were obtained by a HORIBA Nanolog spectrometer. $^1$H and $^{13}$C NMR spectra were recorded with a JEOL EX-400 spectrometer (operating at 400 MHz for $^1$H and 100 MHz for $^{13}$C) by using the residual solvent as the internal reference for $^1$H (CDCl$_3$: δ = 7.26 ppm or CD$_2$Cl$_2$: δ = 5.32 ppm) and $^{13}$C (CDCl$_3$: δ = 77.16 ppm). High-resolution mass spectra (HR-MS) were measured on a Thermo Fischer Scientific EXACTIVE spectrometer for ESI measurements. Attenuated total reflectance-Fourier transform infrared (ATR-FTIR) spectra were taken with the golden gate diamond anvil ATR accessory (NICOLET 6700, Thermo scientific), using typically 64 scans at a resolution of 2 cm$^{-1}$. All samples were placed in contact with the diamond window using the same mechanical force.

Electrochemical Measurements.

Electrochemical measurements were made using an ALS 630a electrochemical analyzer. Redox potentials were determined by differential pulse voltammetry (DPV) in THF containing 0.1 M tetrabutylammonium hexafluorophosphate (Bu$_4$NPF$_6$). A glassy carbon (3 mm diameter) working electrode, Ag/AgNO$_3$ reference electrode, and Pt wire counter electrode were employed. Ferrocene (+0.642 V vs NHE) was used as an internal standard for the DPV measurements.

Density Functional Theory (DFT) Calculations.

All calculations were carried out using the Gaussian 09 program.$^{51}$ All structures of porphyrins were fully optimized without any symmetry restriction. The calculations were performed by the density functional theory (DFT) method with restricted B3LYP (Becke’s three-parameter hybrid exchange functionals and the Lee-Yang-Parr correlation functional) level, employing a basis set 6-31G(d) for C, H, N, O, Si and Zn.

Preparation of Porphyrin-Sensitized TiO$_2$ Electrode and Photovoltaic Measurements.

The preparation of TiO$_2$ electrodes and the fabrication of the sealed cells for photovoltaic measurements were performed according to literature.$^{52,53}$ We used two types of TiO$_2$ pastes, one composed of nanocrystalline TiO$_2$ particles (30 nm, PST30NR-D, Dyesol) and another containing submicrocrystalline TiO$_2$ particles (400 nm, CCIC:PST400C, JGC-C&C), to form the transparent
and the light-scattering layers of the photoanode, respectively. To prepare the working electrodes, FTO glasses (solar 4mm thickness, 10 Ω/□, Nippon Sheet Glass) were first cleaned in a detergent solution using an ultrasonic bath for 10 min and then rinsed with distilled water and ethanol. After UV-O₃ irradiation for 18 min, the FTO glass plates were immersed into a 40 mM aqueous TiCl₄ solution at 70 °C for 30 min and then washed with distilled water and ethanol. A nanocrystalline TiO₂ layer of 12 µm was coated on the FTO glass plate by a screen-printing method, kept in a clean box for a few minutes, and then dried over 6 min at 125 °C. After drying the films at 125 °C, a layer of the submicrocrystalline TiO₂ paste was further deposited by screen-printing in the same method as the fabrication of the nanocrystalline TiO₂ layer, resulting in formation of a light-scattering TiO₂ film of 4 µm on the transparent TiO₂ film of 1/2 µm. Finally, the electrodes coated with the TiO₂ pastes were gradually heated under an airflow at 325 °C for 5 min, at 375 °C for 5 min, at 450 °C for 15 min, and at 500 °C for 15 min. The thickness of the films was determined using a surface profiler (SURFCOM 130A, ACCRETECH). The size of the TiO₂ film was 0.16 cm² (4 × 4 mm). The TiO₂ electrode was treated again with 40 mM TiCl₄ solution at 70 °C for 30 min and then rinsed with distilled water and ethanol, sintered at 500 °C for 30 min, and cooled to 70 °C before dipping into the dye solution. For ZnP₃₁, ZnP₃₂, and ZnP₃₃, the TiO₂ electrode was immersed into a toluene and acetonitrile solution (v/v = 9/1) of the porphyrins (0.30 mM) at 25 °C. Then, the porphyrin-adsorbed TiO₂ electrode was further immersed into an ethanol solution of chenodeoxycholic acid (CDCA) for 2 h. For YD₂-o-C₈, the TiO₂ electrode was immersed into an ethanol solution of the porphyrin (0.30 mM) at 25 °C without CDCA. The porphyrin surface coverage adsorbed on the TiO₂ film (Γ, mol cm⁻²) was determined by measuring the porphyrin absorbance at 639 nm on TiO₂ electrode to that of YD₂-o-C₈. The surface coverage of YD₂-o-C₈ on TiO₂ was determined by measuring the absorbance of the porphyrin that was detached from porphyrin-stained TiO₂ film into 0.1 M NaOH solution of 1:1 mixture of THF and water.

The counter electrode was prepared by drilling a small hole in an FTO glass (solar 1 mm thickness, 10 Ω/□, Nippon Sheet Glass), rinsing with distilled water and ethanol followed by treatment with 0.1 M HCl solution in 2-propanol using an ultrasonic bath for 15 min. After heating in air for 15 min at 400 °C, the platinum was deposited on the FTO glass by coating with a drop of H₂PtCl₆ solution (2 mg in 1 mL of ethanol) twice. Finally, the FTO glass was heated at 400 °C for 15 min to obtain the counter Pt-electrode.

A sandwich cell was prepared by using the dye-anchored TiO₂ film as a working electrode and a counter Pt-electrode, which were assembled with a hotmelt-ionomer film Surlyn polymer gasket (DuPont, 50 µm), and the superimposed electrodes were tightly held and heated at 110 °C to seal the two electrodes. The aperture of the Surlyn frame was 2 mm larger than that of the area of the TiO₂ film, and its width was 1 mm. The hole in the counter Pt-electrode was sealed by a film of Surlyn. A hole was then made in the film of Surlyn covering the hole with a needle. A drop of an electrolyte was put on the hole in the back of the counter Pt-electrode. It was introduced into the
cell via vacuum backfilling. Finally, the hole was sealed using Surlyn film and a cover glass (0.13–0.17 mm thickness). A solder was applied on each edge of the FTO electrodes. The electrolyte solution was composed of 1.0 M 1,3-dimethylimidazolium iodide, 0.03 M I₂, 0.05 M LiI, 0.01 M guadinium thiocyanate, and 0.5 M 4-tert-butylpyridine in acetonitrile/valeronitrile mixture.

Incident photon-to-current efficiency (IPCE) and photocurrent-voltage (I-V) performance were measured on an action spectrum measurement setup (CEP-2000RR, BUNKOUKEIKI) and a solar simulator (PEC-L10, Peccell Technologies) with a simulated sunlight of AM 1.5 (100 mW cm⁻²), respectively: IPCE (%) = \(100 \times \frac{1240 \times i}{W_{in} \times \lambda}\), where \(i\) is the photocurrent density (A cm⁻²) \(W_{in}\) is the incident light intensity (W cm⁻²), and \(\lambda\) is the excitation wavelength (nm). During the photovoltaic measurements, a black plastic tape was attached on the back of the TiO₂ electrode except for the TiO₂ film region to reduce scattering light. The convolution of the spectral response in the photocurrent action spectrum with the photon flux of the AM 1.5G spectrum provided the estimated \(J_{sc}\)-value, which is in good agreement with the \(J_{sc}\)-value obtained from the I-V performance.
2. Synthesis

[5-Bis(4-hexylphenyl)amino-15-ethynyl-10,20-bis(2,6-dioctyloxy-phenyl)porphyrinato]zinc(II) (1)

and YD2-o-C8 were prepared according to literature.⁴

[5-Bis(4-hexylphenyl)amino-15-triethoxysilyl-ethynyl-10,20-bis(2,6-dioctyloxyphenyl)-porphyrinato]zinc(II) (ZnPSi1).

A solution of LDA was prepared from n-BuLi (2.7 mL, 0.61 mmol) and diisopropylamine (0.84 mL, 0.61 mmol) in THF (4.0 mL). To a solution of porphyrin 1 in dry THF (0.6 mL) was added the LDA solution (0.50 mL, 11 µmol) and the mixture was stirred at –78 °C for 1.5 h under argon atmosphere. Chlorotriethoxysilane (69 µL, 380 µmol) was slowly added to the mixture, and the resulting mixture was stirred at room temperature for 2 h. After the solvent was removed under reduced pressure, the residue was purified by GPC using toluene as eluent to give ZnPSi1.

Re precipitation from CH₂Cl₂ and acetonitrile gave a green solid of ZnPSi1 (30.2 mg, 19.4 µmol, 84%).

¹H NMR (400 MHz, CDCl₃): δ = 9.59 (d, J = 4.4 Hz, 2H), 9.18 (d, J = 4.9 Hz, 2H), 8.86 (d, J = 4.9 Hz, 2H), 8.68 (d, J = 4.9 Hz, 2H), 7.64 (t, J = 8.4 Hz, 2H), 7.20 (d, J = 8.8 Hz, 4H), 6.97 (m, 8H), 4.27 (m, 6H), 3.87 (t, J = 6.0 Hz, 8H), 2.45 (t, J = 7.6 Hz, 4H), 1.52-0.35 (m, 91H) ppm; ¹³C NMR (100 MHz, CDCl₃): δ = 160.0, 152.5, 152.0, 150.7, 150.3, 134.7, 134.7, 132.3, 132.2, 130.6, 129.9, 128.8, 122.1, 120.9, 114.3, 105.3, 68.7, 59.5, 35.3, 31.8, 31.6, 29.2, 28.7, 28.6, 28.5, 25.2, 22.7, 18.5, 14.2, 13.9 ppm. UV/Vis (ethanol/THF (v/v = 4/1)): λ (ε, M⁻¹ cm⁻¹) = 430 (157000), 573 (12000), 632 (15000) nm. Fluorescence (ethanol/THF (v/v = 4/1), λₑx = 430 nm): λₑmax = 659 nm. HR-MS (ESI, positive): m/z calcd for C₉₆H₁₃₂N₅O₇SiZn [M+H]: 1558.9182; found 1558.9175. FT-IR (ATR) νmax: 2922, 2853, 1586, 1506, 1454, 1335, 1246, 1096, 999, 795, 713, 492, 407 cm⁻¹.

[5-Bis(4-hexylphenyl)amino-15-(4-iodophenyl)ethynyl-10,20-bis(2,6-dioctyloxyphenyl)-porphyrinato]zinc(II) (2).

A solution of porphyrin 1 in dry THF (20 mL) and triethylamine (5.0 mL) was degassed with argon for 20 min. 1,4-Diiodobenzene (70.0 mg, 212 µmol), Pd(PPh₃)₄ (7.0 mg, 6.1 µmol), and CuI (1.5 mg, 7.9 µmol) were added to the mixture and the mixture was stirred at room temperature for 1 h under argon atmosphere. The reaction was quenched with water and the product was extracted with CH₂Cl₂. The organic layer was dried over anhydrous Na₂SO₄ and the solvent was removed under reduced pressure. The residue was purified by GPC using toluene as eluent to give 2 (40.1 mg, 25.1 µmol, 63%) as a green solid.

¹H NMR (400 MHz, CD₂Cl₂): δ = 9.62 (d, J = 4.4 Hz, 2H), 9.18 (d, J = 4.9 Hz, 2H), 8.86 (d, J = 4.9 Hz, 2H), 8.68 (d, J = 4.9 Hz, 2H), 7.88 (d, J = 8.3 Hz, 2H), 7.72 (d, J = 8.4 Hz, 2H), 7.65 (t, J = 8.3 Hz, 2H), 7.20 (d, J = 8.8 Hz, 4H), 6.94 (m, 8H), 3.83 (t, J = 6.0 Hz, 8H), 2.45 (t, J = 7.6 Hz, 4H), 1.52-0.35 (m,
82H) ppm; $^{13}$C NMR (100 MHz, CDCl$_3$): $\delta$ = 159.9, 152.1, 151.9, 150.5, 150.3, 137.8, 134.7, 133.0, 132.2, 130.6, 130.3, 129.9, 128.8, 122.0, 120.8, 114.5, 105.2, 98.6, 68.7, 35.3, 31.8, 31.6, 31.5, 29.2, 28.7, 28.6, 28.5, 25.2, 22.7, 22.3, 14.2, 13.9 ppm. UV/Vis (ethanol/THF (v/v = 4/1)): $\lambda$ (ε, M$^{-1}$ cm$^{-1}$) = 444 (213000), 585 (6000), 642 (24000) nm. Fluorescence (ethanol/THF (v/v = 4/1), $\lambda$$_{ex}$ = 430 nm): $\lambda$$_{max}$ = 664 nm. HR-MS (ESI, positive): $m/z$ calcd for C$_{96}$H$_{121}$N$_5$O$_4$IZn [M+H]+: 1598.7749; found 1598.7745. FT-IR (ATR) $\nu$$_{max}$: 2923, 2854, 1591, 1506, 1455, 1338, 1249, 1098, 999, 795, 713, 541, 448 cm$^{-1}$.

[5-Bis(4-hexylphenyl)amino-15-(4-triethoxysilylphenyl)ethynyl-10,20-bis(2,6-dioctyloxyphenyl)porphyrinato]zinc(II) (ZnP$_{2}$Si$_2$).

A solution of porphyrin 2 (149 mg, 91.2 $\mu$mol) in dry THF (5 mL) and diisopropylethylamine (0.7 mL) was degassed with argon for 20 min. Pd$_2$(dba)$_3$ (15.0 mg, 16.4 $\mu$mol), and 2-(di-tert-butylphosphino)biphenyl (15.0 mg, 50.3 $\mu$mol) were added to the mixture. The solution was stirred at room temperature for 1 h under argon atmosphere. The reaction was quenched with water and the product was extracted with CH$_2$Cl$_2$. The organic layer was dried over anhydrous Na$_2$SO$_4$ and the solvent was removed under reduced pressure. The residue was purified by GPC using toluene as eluent to give ZnPSi$_2$. Re-precipitation from CH$_2$Cl$_2$ and acetonitrile gave a green solid of ZnPSi$_2$ (60.3 mg, 36.9 $\mu$mol, 39%).

$^1$H NMR (400 MHz, CD$_2$Cl$_2$): $\delta$ = 9.62 (d, $J$ = 4.4 Hz, 2H), 9.18 (d, $J$ = 4.9 Hz, 2H), 8.86 (d, $J$ = 4.9 Hz, 2H), 8.68 (d, $J$ = 4.9 Hz, 2H), 7.88 (d, $J$ = 8.3 Hz, 2H), 7.72 (d, $J$ = 8.4 Hz, 2H), 7.65 (t, $J$ = 8.3 Hz, 2H), 7.20 (d, $J$ = 8.8 Hz, 4H), 6.94 (m, 8H), 3.83 (t, $J$ = 6.0 Hz, 8H), 2.45 (t, $J$ = 7.6 Hz, 4H), 1.52-0.35 (m, 83H) ppm; $^{13}$C NMR (100 MHz, CDCl$_3$): $\delta$ = 159.9, 152.0, 152.0, 150.5, 150.0, 135.0, 134.7, 132.1, 130.1, 130.0, 128.8, 122.0, 120.9, 114.5, 105.2, 99.0, 68.7, 59.0, 35.3, 31.8, 31.6, 29.2, 28.7, 28.6, 28.5, 25.2, 22.7, 18.4, 14.2, 13.9 ppm. UV/Vis (ethanol/THF (v/v = 4/1)): $\lambda$ (ε, M$^{-1}$ cm$^{-1}$) = 443 (207000), 587 (12000), 638 (31000) nm. Fluorescence (ethanol/THF (v/v = 4/1), $\lambda$$_{ex}$ = 430 nm): $\lambda$$_{max}$ = 664 nm. HR-MS (ESI-MS) $m/z$ calcd for C$_{102}$H$_{135}$N$_5$O$_7$SiZn [M+H$^+$]: 1633.9417; found 1633.9455. FT-IR (ATR) $\nu$$_{max}$: 2925, 2850, 1591, 1506, 1455, 1338, 1249, 1098, 999, 795, 713, 541, 448 cm$^{-1}$.

[5-Bis(4-hexylphenyl)amino-15-[4-(4-triethoxysilylphenyl)carbamoylphenyl]ethynyl-10,20-bis(2,6-dioctyloxyphenyl)porphyrinato]zinc(II) (ZnP$_3$Si$_3$).

2-Chloro-1-methyl-pyridinium iodide (11.8 mg, 9.3 $\mu$mol) was added to a mixture of YD2-o-C8 (20.9 mg, 13.8 $\mu$mol), 4-triethoxysilylaniline (35.0 mg, 141 $\mu$mol) and triethylamine (15 $\mu$L) in dry THF (6 mL) and the mixture was stirred at room temperature for 15 h. After the solvent was removed under reduced pressure, the residue was purified by GPC using toluene as eluent to give ZnPSi$_3$. Reprecipitation from CH$_2$Cl$_2$ and acetonitrile gave a green solid of ZnPSi$_3$ (20.2 mg, 11.5 $\mu$mol, 83%).
$^1$H NMR (400 MHz, CD$_2$Cl$_2$): $\delta = 9.69$ (d, $J = 4.4$ Hz, 2H), 9.15 (d, $J = 4.9$ Hz, 2H), 8.88 (d, $J = 4.9$ Hz, 2H), 8.67 (d, $J = 4.9$ Hz, 2H), 8.13 (d, $J = 8.3$ Hz, 2H), 8.03 (m, 3H), 7.69 (m, 6H), 7.18 (d, $J = 8.8$ Hz, 4H), 6.99 (m, 8H), 3.87 (m, 14H), 2.47 (t, $J = 7.6$ Hz, 4H), 1.26-0.52 (m, 91H) ppm; $^{13}$C NMR (100 MHz, CDCl$_3$): $\delta = 196.1, 159.9, 152.2, 152.1, 150.6, 150.4, 136.1, 132.3, 132.2, 131.8, 130.7, 129.9, 128.9, 127.4, 122.1, 120.8, 119.4, 105.2, 68.6, 58.9, 35.3, 31.8, 31.6, 31.4, 29.2, 28.7, 28.5, 25.2, 22.7, 22.3, 18.3, 14.1, 13.9 ppm. UV/Vis (ethanol/THF (v/v = 4/1)): $\lambda$ ($\varepsilon$, M$^{-1}$ cm$^{-1}$) = 447 (232000), 582 (13000), 644 (35000) nm. Fluorescence (ethanol/THF (v/v = 4/1), $\lambda_{\text{ex}}$ = 430 nm): $\lambda_{\text{max}}$ = 670 nm. HR-MS (ESI, positive): $m/z$ calcd for C$_{109}$H$_{141}$N$_6$O$_8$SiZn [M+H]$^+$: 1753.9866; found 1753.9880. FT-IR (ATR) $\nu_{\text{max}}$: 2925, 2854, 1587, 1506, 1455, 1338, 1249, 1099, 998, 792, 725, 480, 446 cm$^{-1}$. 

S7
3. High-Resolution ESI-MS

Figure S1. Observed (top) and simulated (bottom) high-resolution ESI-MS of (a) ZnPSi1, (b) 2, (c) ZnPSi2, and (d) ZnPSi3.
4. NMR Spectra

Figure S2. (a) $^1$H and (b) $^{13}$C NMR spectra of ZnPSi1 at 25 °C in CDCl$_3$. Peaks marked with * arise from residual solvents.
**Figure S3.** (a) $^1$H and (b) $^{13}$C NMR spectra of 2 at 25 °C in CDCl$_3$. Peaks marked with * arise from residual solvents.
Figure S4. (a) $^1$H and (b) $^{13}$C NMR spectra of ZnPSi2 at 25 °C in CDCl₃. Peaks marked with * arise from residual solvents.
Figure S5. (a) $^1$H NMR spectrum in CD$_2$Cl$_2$ and (b) $^{13}$C NMR spectrum in CDCl$_3$ of ZnPSi3 at 25 °C. Peaks marked with * arise from residual solvents.
5. Fluorescence Spectra

Figure S6. Normalized fluorescence spectra of ZnPSi1 (blue), ZnPSi2 (red), ZnPSi3 (green), and YD2-o-C8 (black) in ethanol/THF (v/v = 4/1). The samples were excited at 430 nm.
6. DPV curves

Figure S7. Differential pulse voltammetry (DPV) curves of ZnPSi1 (blue), ZnPSi2 (red), ZnPSi3 (green), and YD2-o-C8 (black). The sweeps are shown in (a) oxidation and (b) reduction regions with a sweep rate of 40 mV s⁻¹.
7. CDCA Effect for YD2-o-C8

Figure S8. Plots of the power conversion efficiency ($\eta$) as a function of the amount of CDCA for the DSSCs based on YD2-o-C8.
8. Adsorption Geometry

Figure S9. Schematic representations of the plausible adsorption geometry of ZnPSi1, ZnPSi2, and ZnPSi3 on TiO₂. With increasing the spacer length, the tilt angle (θ) of the porphyrins increases in the following order: ZnPSi1 < ZnPSi2 < ZnPSi3. Nevertheless, the through-space distance (R) for ZnPSi2 between the porphyrin and TiO₂ is larger than those for ZnPSi1 and ZnPSi3. The longer through-space distance leads to the weaker electronic coupling and slower CR process.
9. References

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