

Supporting Information

Dependence of Photocurrent and Conversion Efficiency of Titania-Based Solar Cell on the Q_y Absorption and One Electron-Oxidation Potential of Pheophorbide Sensitizer

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S-1. Preparation of 3-devinyl-3-ethyl-8-deethyl-8-carboxy-pyropheophorbide a (Phe x)

To a solution of methyl 3-devinyl-3-ethyl-8-deethyl-8-formyl-pyropheophorbide *a* (110 mg, 0.20 mmol) in THF (15 mL) and 2-methyl-2-butene (8 mL) added was a solution of $\text{NH}_2\text{SO}_3\text{H}$ (120 mg, 1.2 mmol) in H_2O (1.5 mL), and the mixture was stirred for 5 min at room temperature. NaClO_2 (100 mg, 1.1 mmol) in H_2O (1 mL) was added dropwise and the disappearance of 8-formyl-chlorin was checked by TLC. The mixture was poured into H_2O , extracted with CH_2Cl_2 , and concentrated in vacuo. The product was purified by silica-gel chromatography ($\text{MeOH}-\text{CH}_2\text{Cl}_2$, 1:9) followed by GPC column (CHCl_3) and HPLC (acetone/1,2-dichloroethane = 1:5, t_R 11 min) to give Phe *x* (16 mg, 14%) as a black solid: VIS (CH_2Cl_2) λ_{max} 655 (relative intensity, 25%), 601 (5), 564 (4), 517 (5), 427 nm (100); $^1\text{H-NMR}$ δ = 10.09 (1H, s, 10-H), 9.05 (1H, s, 5-H), 8.49 (1H, s, 20-H), 5.18, 5.04 (each 1H, d, J = 18 Hz, 13^1-CH_2), 4.47 (1H, dq, J = 2, 8 Hz, 18-H), 4.25 (1H, br-d, J = 10 Hz, 17-H), 3.72 (2H, q, J = 8 Hz, 3- CH_2), 3.66 (3H, s, COOCH_3), 3.54 (3H, s, 7- CH_3), 3.47 (3H, s, 12- CH_3), 3.28 (3H, s, 2- CH_3), 2.71, 2.26 (each 1H, m, 17- CH_2), 2.61, 2.36 (each 1H, m, 17^1-CH_2), 1.89 (3H, d, J = 8 Hz, 18- CH_3), 1.70 (3H, t, J = 8 Hz, 3^1-CH_3), -0.54, -2.33 (each 1H, s, NH); $^{13}\text{C-NMR}$ δ = 196.0, 173.5, 172.2, 171.1, 162.3, 150.0, 149.5, 149.0, 147.5, 142.8, 142.4, 138.2, 135.3, 131.8, 130.8, 130.7, 127.2, 108.4, 105.0, 97.0, 92.5, 51.9, 51.8, 49.8, 47.9, 31.1, 29.7, 23.1, 19.3, 16.9, 13.8, 12.1, 10.9; HRMS (FAB) found m/z 567.2628. Calcd for $\text{C}_{33}\text{H}_{35}\text{N}_4\text{O}_5$: MH^+ , 567.2607.

S-2. Electronic-Absorption Spectra of Sensitizers in Solution and Bound to TiO_2

Figure S-1 shows the electronic-absorption spectra of BPhe *a*, Phe *a*, Phe *x*, Phe *b*, Phe *c*₁ and Phe *c*₂ in tetrahydrofuran (THF) solution, the ordinate scale being the molar extinction coefficient (ϵ). The spectra can be characterized as follows: (i) The spectral profiles of BPhe *a*, Phe *a*, Phe *c*₁ and Phe *c*₂ are broader than those of Phe *x* and Phe *b*. We suspect that the former pheophorbides may be dimeric and the latter ones monomeric in THF solution, because the pheophorbide molecules having conjugated macrocycles can aggregate even in such a polar solvent. (ii) The relative intensity of the Soret vs. Q_y absorption is rather comparable in BPhe *a* and Phe *a*, but the former absorption is much higher than the latter in Phe *x*, Phe *b*, Phe *c*₁ and Phe *c*₂: The higher relative intensity in Phe *x* and Phe *b* may be ascribable to the chlorin skeleton having slightly lower symmetry

(pseudo C_{2h}). In Phe c_1 and c_2 , the relative intensity becomes much larger because of the porphyrin ring having approximate D_{4h} symmetry. (iii) The Q_y absorption of BPhe a is substantially shifted to the near-infrared region in comparison to those of Phe a , Phe x , Phe b , Phe c_1 and Phe c_2 . This is ascribable to the bacteriochlorin macrocycle. (iv) All the observed single (or split) peaks can be assigned to the Soret, Q_x and Q_y absorptions, appearing systematically from the shorter- to the longer-wavelength region.

Figure S-2 exhibits the electronic-absorption spectra of BPhe a , Phe a , Phe x , Phe b , Phe c_1 and Phe c_2 that are adsorbed on the TiO_2 layer. They can be characterized as follows: (i) In the shortest-wavelength region, weak shoulders on the strong TiO_2 absorption in the spectra of BPhe a and Phe a (416 and 408 nm) as well as distinct strong peaks partially overlapped with the TiO_2 absorption in the spectra of Phe x , Phe b , Phe c_1 and Phe c_2 (406, 402, 422 and 421 nm, respectively) can be assigned to the Soret absorption of pheophorbides. The relative intensities of the Soret, Q_x and Q_y absorption bands roughly correspond to those in the spectra free in solution (Figure S-1). Unique difference originates from the very strong contributions of the TiO_2 absorption in the shortest-wavelength region. (ii) All the Q_y absorptions become much broader when bound to the TiO_2 layer, suggesting that the aggregates of pheophorbides are formed on the surface of the TiO_2 layer. (iii) The relative intensities of the split Q_y absorptions are changed in BPhe a possibly due to partial degradation upon binding to TiO_2 . The relative intensities between the Soret and the Q_y absorption vary depending on the structure of sensitizers just like in solution.

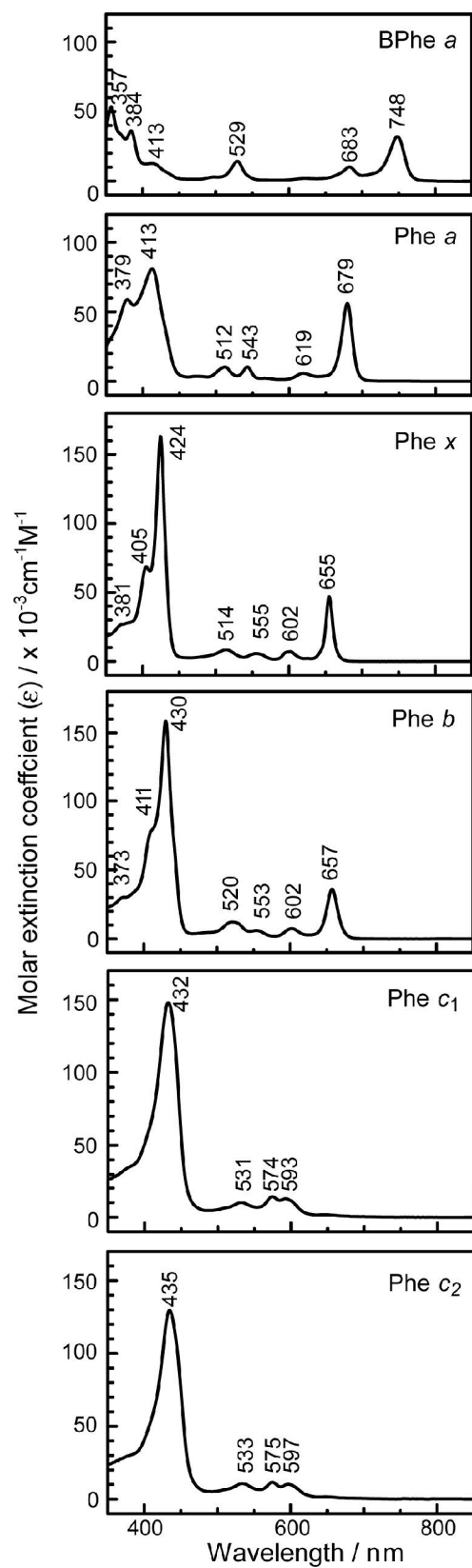


Figure S-1. Electronic-absorption spectra of BPhe *a*, Phe *a*, Phe *x*, Phe *b*, Phe *c*₁ and Phe *c*₂ in THF solution.

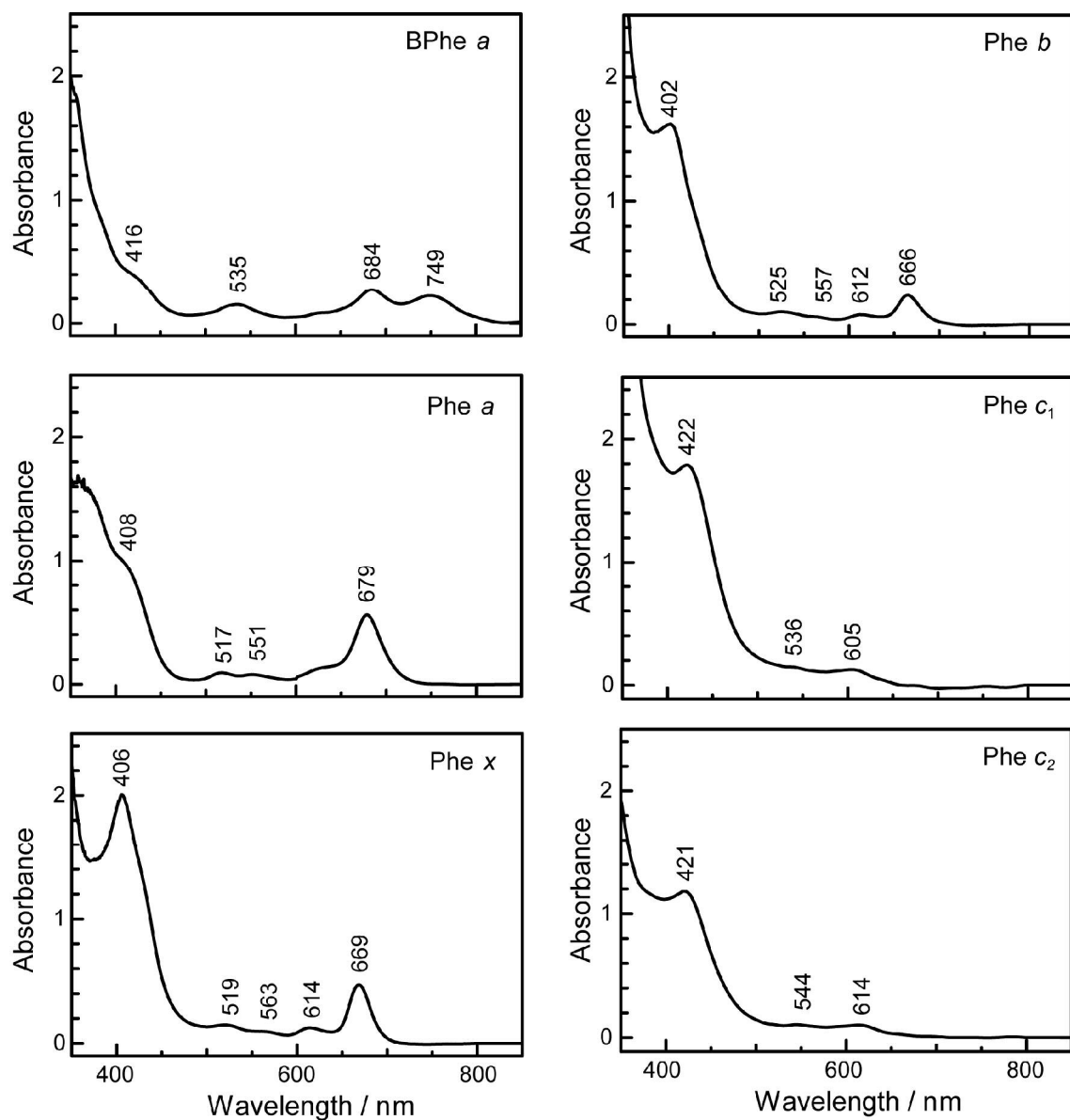


Figure S-2. Electronic-absorption spectra of BPhe *a*, Phe *a*, Phe *x*, Phe *b*, Phe c_1 and Phe c_2 adsorbed on the TiO_2 layer.

S-3. Dependence of $\int IPCE d\bar{\nu}$, J_{sc} and η on the Q_y absorption and E_{ox}

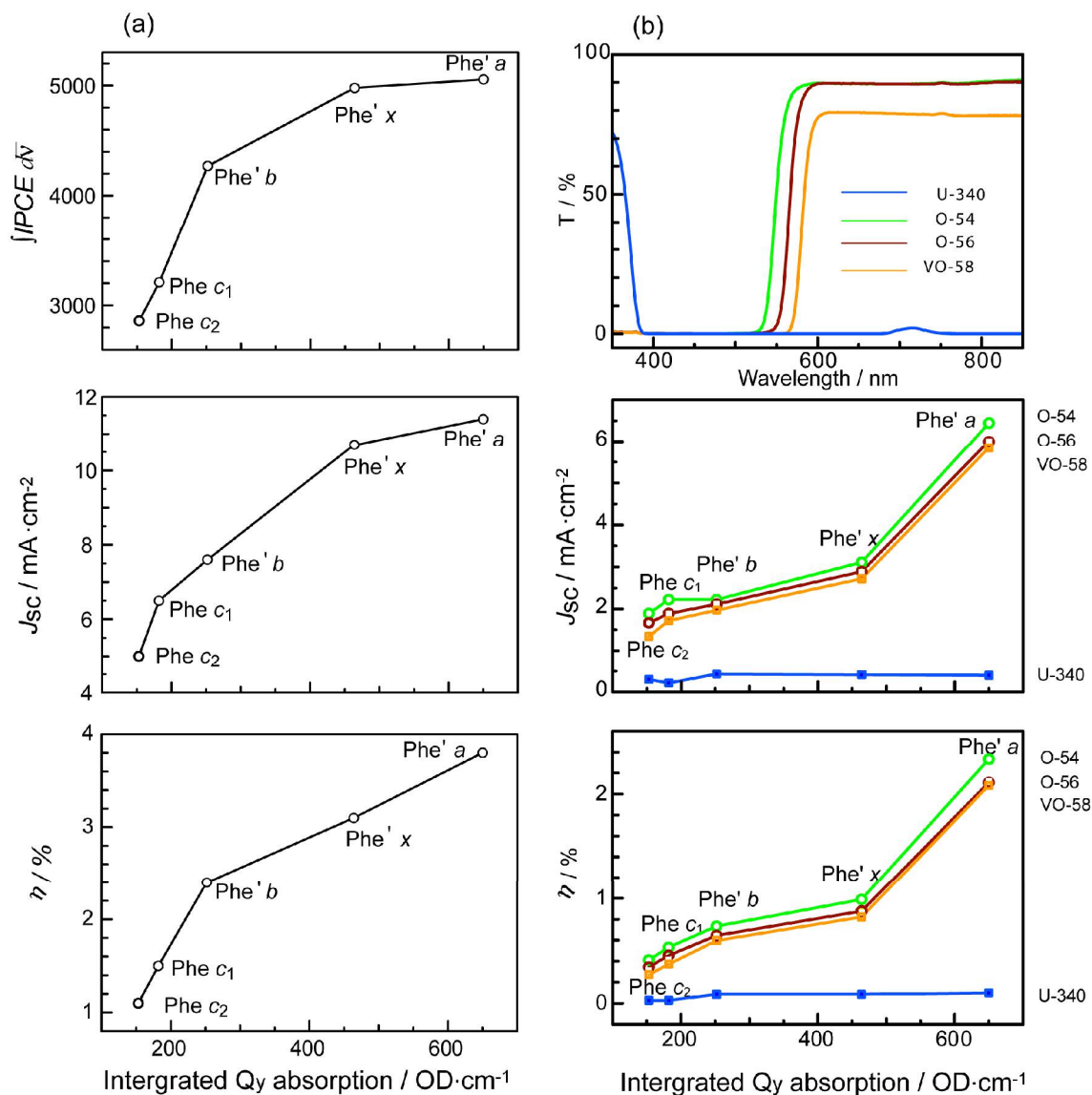


Figure S-3. (a) Correlations between the values of $\int IPCE d\bar{\nu}$, J_{sc} and η of DSSCs and the values of the integrated Q_y absorption for the sensitizers including BPhe *a*, Phe *a*, Phe *x*, Phe *b*, Phe *c*₁ and Phe *c*₂. (b) The J_{sc} and η values when the UV absorption of TiO₂ or the Q_y absorption of each pheophorbide sensitizer was selectively excited by the use of filters whose spectra are shown in the top panel.

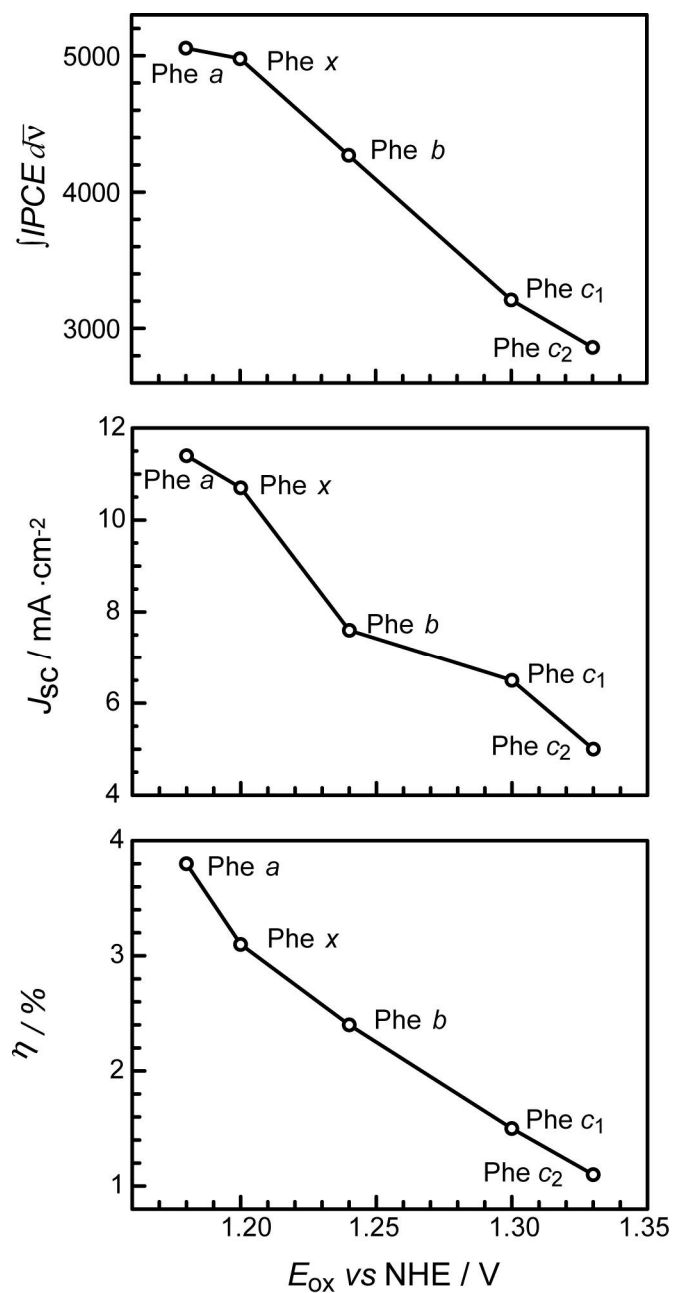


Figure S-4. Correlations between the values of $\int IPCE d\nu$, J_{sc} and η of DSSCs and the E_{ox} values of the sensitizers including Phe *a*, Phe *x*, Phe *b*, Phe *c*₁ and Phe *c*₂, (see also Table 1 in the text).

S-4. The Results of Fitting Trials to Photocurrent (J_{sc}) as Functions of Q_y Absorption and One Electron-Oxidation Potential

TABLE S-1: Fitting Results for an Empirical Equation Assuming Different Models: Photocurrent (J_{sc}) as a Function of the Q_y Absorption and the One Electron-Oxidation Potential

(a) $J_{sc} = A + B = 0.0046Q_y \text{ absorption} + 16.7982 \exp\left[-\frac{\{2.05 - (2.86 - E_{ox})\}^2}{2.05 \times 0.1}\right]$				
Pheophorbide sensitizer	Obs	Fit	Δ	$2\Delta/\text{Obs}+\text{Fit}$ (%)
Phe <i>a</i>	11.4	11.7	0.3	3
Phe <i>x</i>	10.7	10.2	-0.5	5
Phe <i>b</i>	7.6	8.0	0.4	5
Phe <i>c</i> ₁	6.5	6.1	-0.4	6
Phe <i>c</i> ₂	5.0	5.2	0.2	4
(b) $\eta = A + B = 0.00495Q_y \varepsilon + 0.04849 \exp[1.7166 \times (2.86 - E_{ox})]$				
Pheophorbide sensitizer	Obs	Fit	Δ	$2\Delta/\text{Obs}+\text{Fit}$ (%)
Phe <i>a</i>	3.8	3.6	-0.2	5
Phe <i>x</i>	3.1	3.2	0.1	3
Phe <i>b</i>	2.4	2.6	0.2	8
Phe <i>c</i> ₁	1.5	1.3	-0.2	14
Phe <i>c</i> ₂	1.1	1.2	0.1	9
(c) $J_{sc} = 0.05005 \exp\left\{\frac{-[1.06094 - (E_{ox} - 0.44)]^2}{0.1 \times 1.06094}\right\} \times Q_y \text{ absorption}$				
Pheophorbide sensitizer	Obs	Fit	Δ	$2\Delta/\text{Obs}+\text{Fit}$ (%)
Phe <i>a</i>	11.4	12.3	0.9	8
Phe <i>x</i>	10.7	9.9	-0.8	8
Phe <i>b</i>	7.6	6.6	-1.0	14
Phe <i>c</i> ₁	6.5	6.2	-0.3	5
Phe <i>c</i> ₂	5.0	5.8	0.8	15
(d) $J_{sc} = 0.082971 \exp[(-0.050965) \times E_{ox} \times \sqrt{Q_y \text{ absorption}}] \times Q_y \text{ absorption}$				
Pheophorbide sensitizer	Obs	Fit	Δ	$2\Delta/\text{Obs}+\text{Fit}$ (%)
Phe <i>a</i>	11.4	11.6	0.2	2
Phe <i>x</i>	10.7	10.3	-0.4	4
Phe <i>b</i>	7.6	7.7	0.1	1
Phe <i>c</i> ₁	6.5	6.2	-0.3	5
Phe <i>c</i> ₂	5.0	5.5	0.5	10

S-5. Possible Correlations of Two Physical Parameters, i.e., Q_y Absorption vs. One Electron-Oxidation Potential

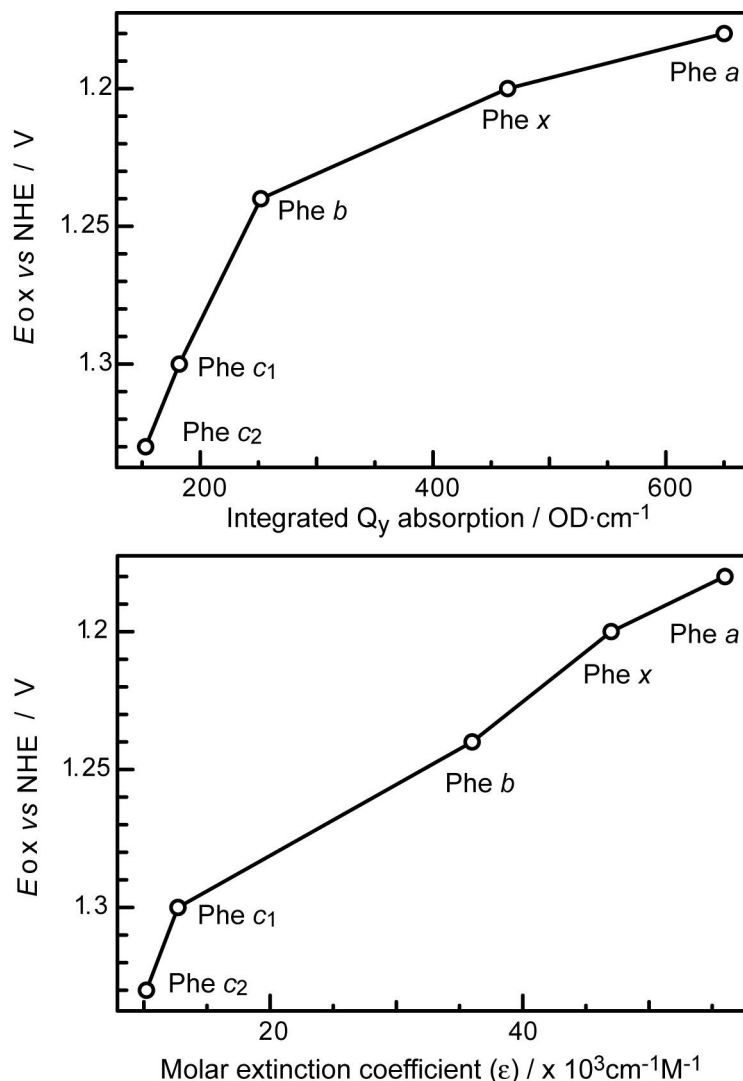


Figure S-5. Correlation of the one electron-oxidation potential (E_{ox}) with the integrated Q_y absorption and molar-extinction coefficient for pheophytins bound to TiO₂ and free in solution, respectively.

S-6. Determination of the Surface Coverage of Phe a sensitizer on TiO₂ Surface

One of the reviewers encouraged us to determine the surface coverage: The monolayer structure of the dye on the TiO₂ surface can be defined by the dye sensitizer which is chemically bound to the TiO₂ surface through the carboxyl group. We prepared a TiO₂ film on a glass plate by the doctor blade method, and cut into a piece

with 0.8×0.8 cm area. The average thickness of such a film measured by a profiler (Sloan Dektak 3, Japan) was ~ 8 μm , and the density of the TiO_2 film ($1.7 \text{ g}\cdot\text{cm}^{-3}$) was calculated by measuring the weight (0.8 mg) of the TiO_2 film (size $0.64 \text{ cm}^2 \times 8 \mu\text{m}$). The surface area of the TiO_2 layer used in our experiment (solaronix Ti-nanooxide T) has a standard value of $\sim 120 \text{ m}^2/\text{g}$. Such a film was then dipped into a Phe *a* solution in THF for 3 hours, and washed with EtOH to remove free Phe *a* on the surface. The film with deposited dye was dipped into 5ml 1mM KOH aqueous solution, and left to stand until the color of the TiO_2 film becomes unchanged. Then, the absorption spectrum of the KOH solution of Phe *a* was measured.

The coverage (Γ) was determined by a standard method (Masatoshi Yanagida et al. Inorg. Chim. Acta, 351 (2003) 283-290) to be $3 \times 10^{-8} \text{ mol}\cdot\text{cm}^{-2}$. Thus, apparently a 20% of the surface of TiO_2 particles was covered (a minimum value).

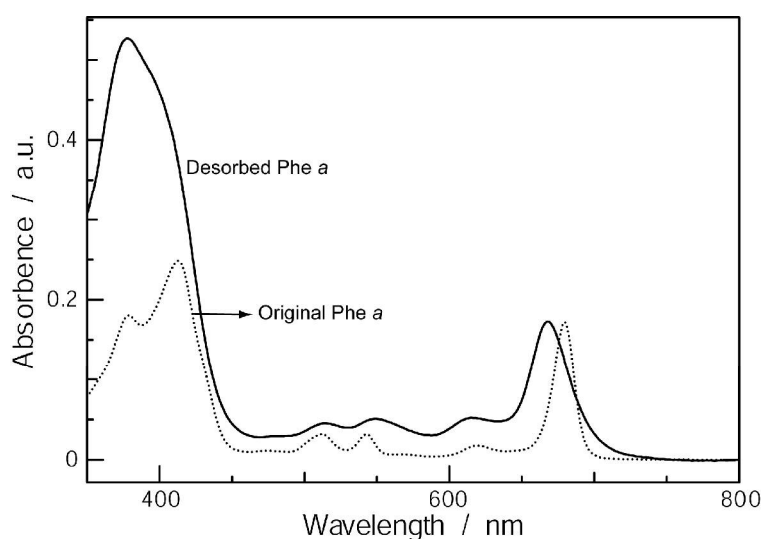


Figure S-6. The absorption spectrum of Phe *a* in KOH solution desorbed from TiO_2 film and in THF solution. The Q_y peaks were normalized.

S-7. Stability of Sensitizer Phe a and Durability of Phe a-Sensitized Solar Cell.

Two of the reviewers addressed questions concerning the stability and durability of our sensitizer and DSSC: We performed a preliminary experiments to answer these questions by the use of Phe *a* giving rise to the highest conversion efficiency among the set of Phe sensitizers. (a) *Stability of the sensitizer.* We dipped a plate with the TiO_2 film into a THF solution of Phe *a* for 3h and dried it as a test sample. In the dark, the Q_y

absorption of this test sample decreased into 91% in 24 h, while in the light (AM 1.5 full sunlight illumination), decreased into 73% in 30 min and 56% in 60 min. The degradation of the sensitizer is obviously due to electron injection into TiO_2 and the resultant oxidation. (b) *Durability of the Phe a-sensitized solar cell.* We dipped the TiO_2 plate into the Phe *a* THF solution for 3 h, and fabricated a DSSC by the use of it. After 24 h, the J_{sc} and η values reduced to 70% and 76%, respectively. A control experiment was performed by the use of a Ru-complex N719, instead; after 24 h, the J_{sc} and η values reduced to 92 and 89%, respectively. Even under the condition of constant supply of electrons in the DSSCs, our Phe *a* sensitizer is less stable than the Ru-complex (~80%).