Electronic Supporting Information

Extension of π-conjugation length along the Q_y axis of a chlorophyll *a* derivative for efficient dye-sensitized solar cells

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Table S-1 The TD-DFT (B3LYP/DGDZVP) with CPCM (ethanol) results for the transition energies (in nm) and the oscillation strengths (*f* in a.u.) for Chlorins-1–3 on Q bands.

Dye sensitizer	Main configurations (|C|>0.1)	nm	*f*
Chlorin-1	HOMO (150):LUMO (151)		
Q_y	0.61 (150→151)-0.31 (149→152)	616	0.28
Q_x	0.58 (149→151)+0.36 (150→152)	558	0.06
Chlorin-2	HOMO (157):LUMO (158)		
Q_y	0.62 (157→158)-0.29 (156→159)+0.12 (156→160)	622	0.36
Q_x	0.59 (156→158)+0.34 (157→159)-0.10 (157→160)	561	0.08
Chlorin-3	HOMO (163):LUMO (164)		
Q_y	0.63 (163→164)-0.23 (162→165)-0.152 (162→166)	650	0.33
Q_x	0.60 (162→164)+0.29 (163→165)+0.15 (163→166)	582	0.10

Table S-2 The shorter wavelength parts of the TD-DFT (B3LYP/DGDZVP) with CPCM (ethanol) results for the transition energies (in nm) and the oscillation strengths (*f*) for Chlorins-1–3.

Dye sensitizer	Main configurations (|C|>0.1)	nm	*f*
Chlorin-1	HOMO (150):LUMO (151)		
3	0.69 (148→151)	452	0.001
4	0.54 (150→152)-0.23 (149→151)+0.11 (149→154)	413	0.86
5	0.54 (149→152)+0.29 (148→152)+0.15 (150→151) +0.12 (149→153)	406	0.59
Chlorin-2	HOMO (157):LUMO (158)		
3	0.68 (155→158)	451	0.01
4	0.54 (157→159)-0.21 (156→158)+0.20 (157→160) -0.12 (156→161)+0.10 (155→158)+0.10 (156→160)	428	0.51
5	0.58 (156→159)+0.18 (155→159)+0.15 (157→158) +0.15 (156→160)	420	0.78
Chlorin-3	HOMO (163):LUMO (164)		
3	0.57 (163→165)-0.23(162→166) -0.22(163→166) -0.18(162→164)	488	0.16
4	0.62 (161→164)-0.26 (162→165)-0.17 (163→166)	468	0.05
5	0.54 (162→165)+0.30 (161→164)+0.21 (163→166) -0.14 (162→166)+0.11 (163→164)	456	0.33

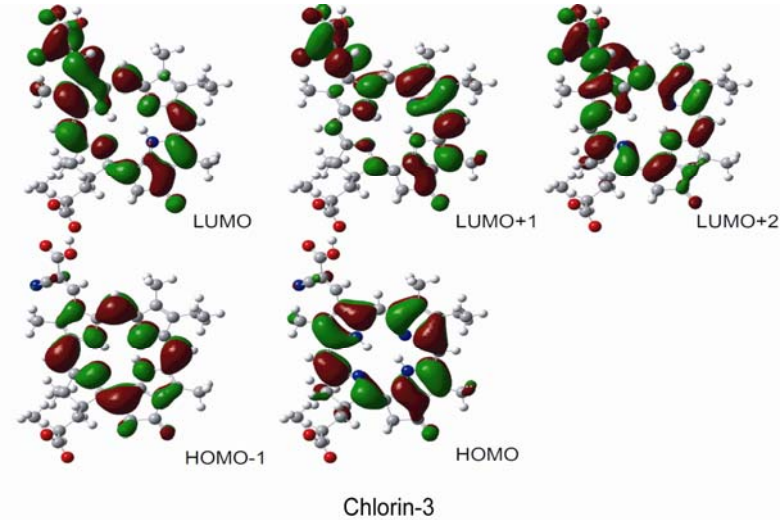

Fig. S-1 The result of the DFT calculation on Chlorin-3.

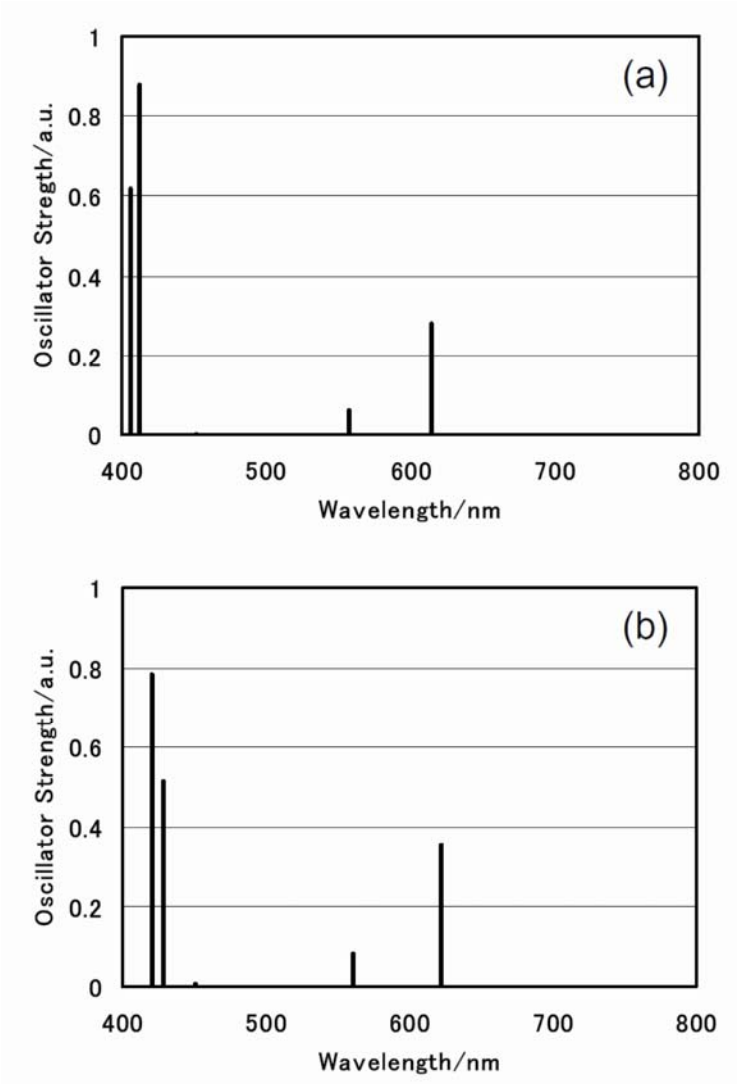

Fig. S-2 The results of TD-DFT calculation on Chlorin-1 (a) and Chlorin-2 (b).

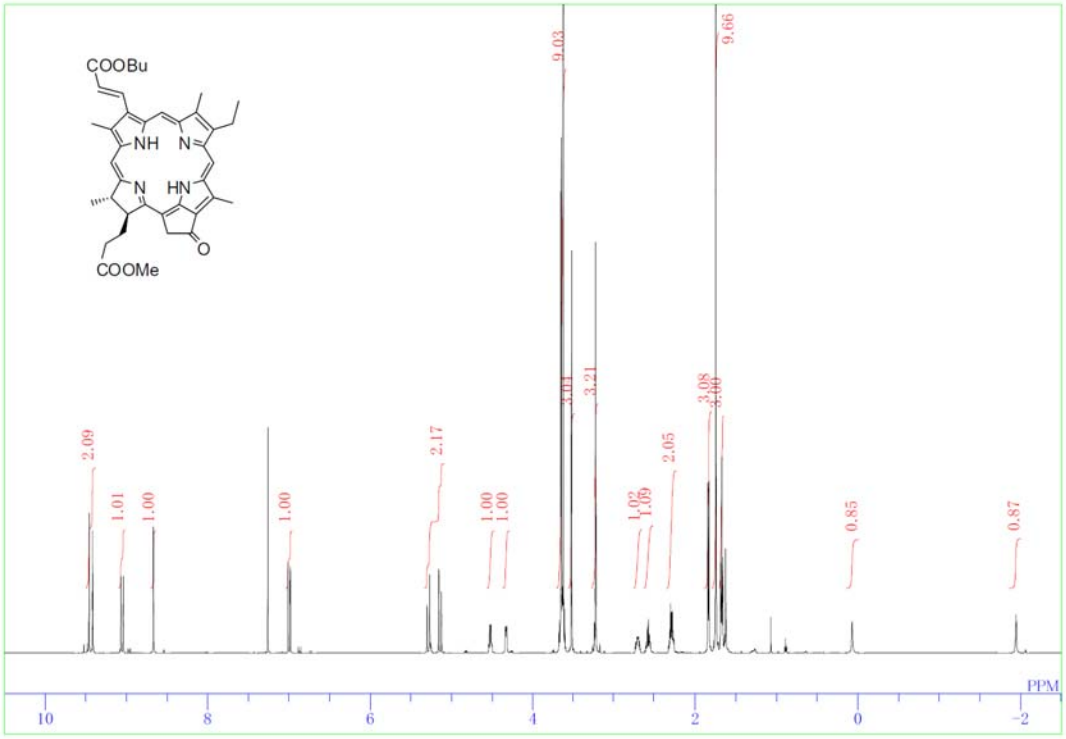

Fig. S-3 600 MHz ^{1}H-NMR spectrum of methyl *trans*-3^{2}-(*tert*-butoxycarbonyl)-pyropheophorbide-*a* in $CDCl_3$.

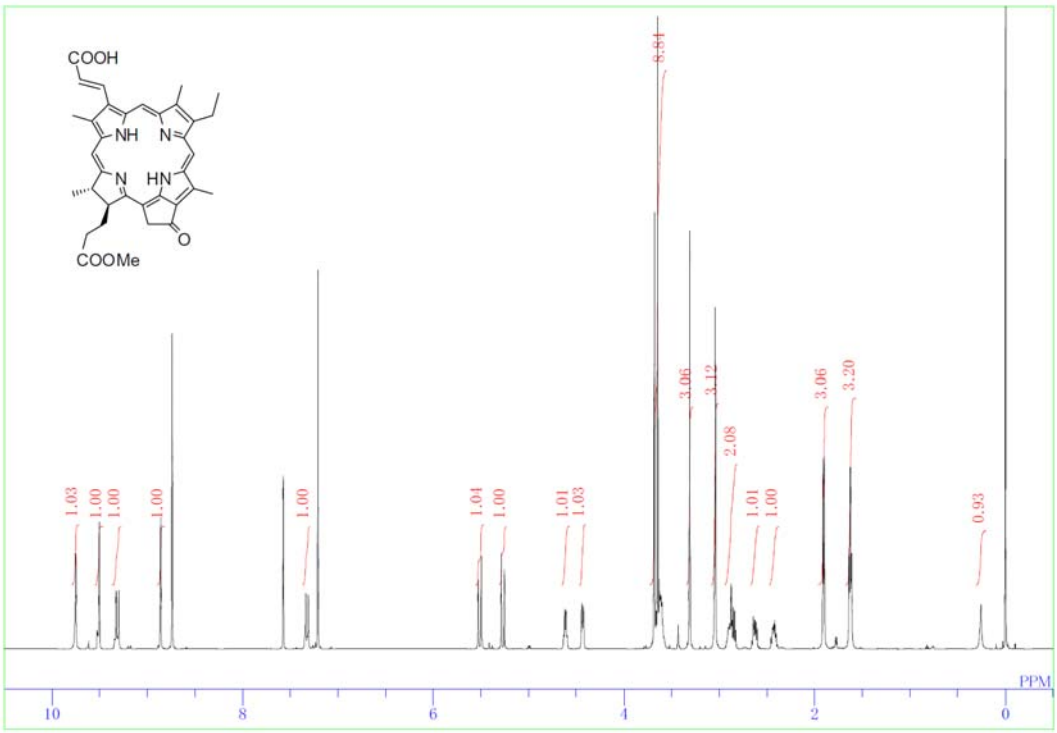

Fig. S-4 600 MHz ^{1}H-NMR spectrum of Chlorin-2 in pyridine-d_5.

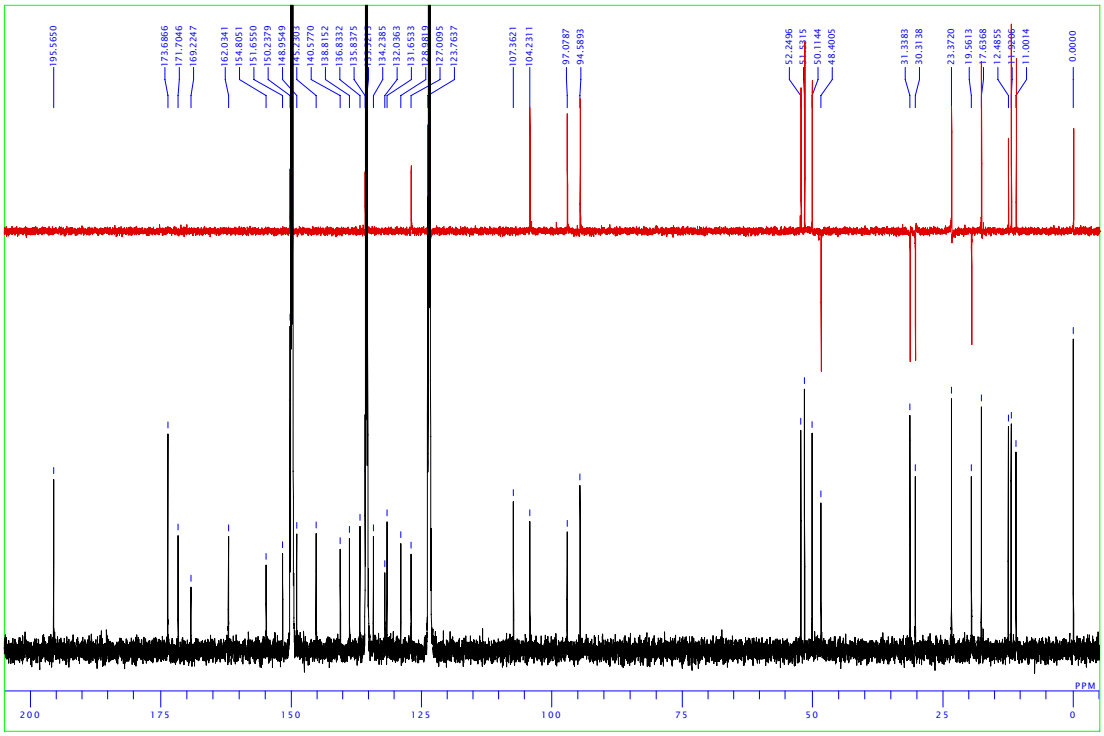

Fig. S-5 150 MHz ^{13}C-NMR spectrum of Chlorin-2 in pyridine-d_5 (lower, black). Primary and tertiary carbon signals are shown upwards while secondary ones appear downwards in the DEPT spectrum (upper, red).

Experimental

Synthesis of methyl *trans*-3^2-carboxy-pyropheophorbide-*a* (Chlorin-2). A mixture of methyl pyropheophorbide-*d* (165 mg, 0.30 mmol, see ref. S-2) and (*tert*-butoxycarbonylmethylene)triphenylphosphorane (339 mg, 0.90 mmol) in toluene (30 mL) was refluxed for 3 h. The mixture was cooled to room temperature, and subjected to silica gel chromatography (Et_2O-CH_2Cl_2, 1:19) to give methyl *trans*-3^2-(*tert*-butoxycarbonyl)-pyropheophorbide-*a* (185 mg, 95%) as a black solid: mp 140-142 °C; VIS (THF) λ_{max} 683 (relative intensity, 59%), 544 (11), 515 (13), 419 nm (100); ^{1}H-NMR ($CDCl_3$, 600 MHz) δ 9.46 (1H, s, 10-H), 9.41 (1H, s, 5-H), 9.05 (1H, d, J = 16 Hz, 3-CH), 8.67 (1H, s, 20-H), 7.00 (1H, d, J = 16 Hz, 3^1-CH), 5.28, 5.14 (each 1H, d, J = 19 Hz, 13^1-CH_2), 4.52 (1H, dq, J = 2, 7 Hz, 18-H), 4.33 (1H, br-d, J = 8 Hz, 17-H), 3.65 (3H, s, 12-CH_3), 3.64 (2H, q, J = 8 Hz, 8-CH_2), 3.62 (3H, s, $COOCH_3$), 3.52 (3H, s, 2-CH_3), 3.23 (3H, s, 7-CH_3), 2.71, 2.31 (each 1H, m, 17-CH_2), 2.58, 2.28 (each 1H, m, 17^1-CH_2), 1.84 (3H, d, J = 7 Hz, 18-CH_3), 1.75 (9H, s, $COOC(CH_3)_3$), 1.68 (3H, t, J = 8 Hz, 8^1-CH_3), 0.07, -1.94 (each 1H, s, NH×2); HRMS (FAB) *m/z*

649.3326 ($M+H^+$), calcd for $C_{39}H_{45}N_4O_5$ 649.3390.

The above *tert*-butyl ester (180 mg, 0.28 mmol) was dissolved in trifluoroacetic acid (10 mL) and the solution was stirred for 3 h at room temperature. The solution was then poured into water and extracted with CH_2Cl_2. The extract was concentrated and subjected to silica gel chromatography (MeOH-CH_2Cl_2, 1:19). The obtained product was dissolved in THF-CH_2Cl_2 (1:5, 10 mL), then hexane (100 mL) was added to form a precipitate, which was filtered and dried in vacuo to give Chlorin-2 (156 mg, 94%) as a black solid: mp 290 °C (dec.); VIS (THF) λ_{max} 682 (relative intensity, 58%), 544 (11), 514 (13), 419 nm (100); VIS (EtOH) λ_{max} 673 (ε, 61000), 615 (12900), 542 (15100), 510 (15800), 412 nm (126000); ^{1}H-NMR (pyridine-d_5, 600 MHz) δ 9.75 (1H, s, 10-H), 9.50 (1H, s, 5-H), 9.31 (1H, d, J = 16 Hz, 3-CH), 8.86 (1H, s, 20-H), 7.32 (1H, d, J = 16 Hz, 3^1-CH), 5.51, 5.27 (each 1H, d, J = 19 Hz, 13^1-CH_2), 4.61 (1H, q, J = 7 Hz, 18-H), 4.43 (1H, br-d, J = 10 Hz, 17-H), 3.68 (3H, s, 12-CH_3), 3.65 (3H, s, $COOCH_3$), 3.62 (2H, m, 8-CH_2), 3.31 (3H, s, 2-CH_3), 3.04 (3H, s, 7-CH_3), 2.89, 2.43 (each 1H, m, 17-CH_2), 2.85, 2.63 (each 1H, m, 17^1-CH_2), 1.91 (3H, d, J = 7 Hz, 18-CH_3), 1.63 (3H, t, J = 8 Hz, 8^1-CH_3) [the two inner NH protons could not be observed.]; ^{13}C-NMR (pyridine-d_5, 150 MHz) δ 195.6 ($C13^1$), 173.7, 171.7, 169.2, 162.0, 154.8, 151.7, 149.0, 145.2, 140.6, 138.8, 136.8, 134.2, 132.0, 131.7, 129.0, 107.4 (C1, 2, 3, 3^3, 4, 6, 7, 8, 9, 11, 12, 13, 14, 15, 16, 17^3, 19), 135.8 ($C3^1$), 127.0 ($C3^2$), 104.2 (C10), 97.1 (C5), 94.6 (C20), 52.2 (C17), 51.5 ($C17^5$), 50.1 (C18), 48.4 ($C13^2$), 31.3 ($C17^2$), 30.3 ($C17^1$), 23.4 ($C18^1$), 19.6 ($C8^1$), 17.6 ($C8^2$), 12.5 ($C2^1$), 11.9 ($C12^1$), 11.0 ($C7^1$) [one quaternary carbon peak was overlapped with a solvent peak at δ = 150.2, 135.5 or 123.8 ppm.]; HRMS (FAB) *m/z* 593.2755 ($M+H^+$), calcd for $C_{35}H_{37}N_4O_5$ 593.2764.

Cyclic Voltammetry. The solvent, dichloromethane (spectroscopic grade, Wako Chemicals, Japan), was purified by passing through an alumina column (Merck, Aluminum Oxide 90, activity II-III), and stored with a 3 Å molecular sieve (Kishida Chemicals, Japan) before use. The supporting electrolyte, tetrabutylammonium hexafluorophosphate (TBAHFP, polarographic grade, Sigma), was used without further purification. The concentration of TBAHFP was ~0.1 M and those of dyes were in the region of 10^{-3}-10^{-4} M. The solution was degassed with nitrogen before each measurement. Cyclic voltammetry was carried out by the use of a potentiostat (HA1010mM1A, Hokuto Denko, Japan). The working and counter electrodes were a platinum wire (0.5 mm in diameter), and the reference electrode was a Ag/AgCl

electrode. The scan rate was 100 mV/s.

Fabrication of Dye-Sensitized Solar Cell and Photovoltaic Measurements. The optically transparent electrode (OTE) with 0.25 cm working area contains 12 nm and 300 nm TiO_2 nanoparticles with thickness of 8 μm and 4 μm, for light-harvesting and light scattering, respectively. The details of fabrication of DSSCs were described before. Each DSSC that was fabricated by the use of this OTE, the counter electrode of Pt-sputtered FTO glass (Nippon Sheet Glass 10 $\Omega \cdot cm^{-2}$), and the electrolyte containing 0.1 M LiI, 0.05 M I_2, 0.6 M 1-propyl-3-methylimidazolium iodide, and 0.5 M *tert*-butylpyridine in a mixture of acetonitrile and valeronitrile (1 : 1, v/v). The IPCE profile of each DSSC was recorded under 5 $mW \cdot cm^{-2}$ monochromatic irradiation by the use of a setup for the IPCE measurement (Bunko-Keiki PV-25 DYE), which consisted of a 300 W halogen lump (Atago Bussan, XC-300), a monochrometer (Instruments S. A. Triax 180) and a potentiostat (Hokuto Denko HA-151). The conversion efficiency was determined under irradiation of AM 1.5 (100 $mW \cdot cm^{-2}$) by the use of a solar simulator (Yamashita Denso, YSS-80) equipped with a computer- controlled voltage-current source meter (Advantest, R6246).

References

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