Supporting Information

Charge Transfer Dynamics in Chlorophyll-Based Biosolar Cells

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Experimental section

Materials

Fluorine-doped tin oxide glass substrates (FTO, 8 Ω/cm²) were purchased from OPV Tech. TiO₂ nanoparticles (PST-18NR) were bought from JGC Catalysts and Chemicals Ltd. Titanium (IV) isopropoxide (97 wt%) was obtained from Sigma-Aldrich. Other chemicals and solvents were got from Sigma-Aldrich or Tokyo Chemical Industry and without further purification.

Methyl trans-3²-carboxy-pyropheophorbide-a (H₂Chl)¹ and zinc methyl 3-devinyl-3-hydroxymethyl-pyropheophorbide-a (ZnChl)² were synthesized according to previously reported procedures.

Fabrication of devices

The zinc powder and 3 mol/L HCl was used to etch FTO substrate, and the etched FTO was ultrasonically cleaned by deionized water, ethanol, acetone and chloroform (CF) for every 20 min. And then the cleaned substrate was processed by ultraviolet and ozone for 15 min. Titanium(IV) isopropoxide solution (100 μl/mL in ethanol) was spin-coated on the preprocessed FTO substrate at 4500 rpm for 30 s and then baked at 220 °C for 30 min. 0.39 g/mL TiO₂-18NR in ethanol was spin-coated at 1500 rpm for 30 s and sintered at 500 °C for 30 min in mufflen to form mesoporous layer. An aqueous TiCl₄ solution was used to impregnate the mesoporous TiO₂ film at
70 °C for 1 h. Then the substrate was sintered at 500 °C for 30 min again. When the temperature was cooled to 80 °C, the substrate was dipped into H₂Chl solution in ethanol (0.1 mg/mL) overnight in dark at room temperature and then rinsed with ethanol. ZnChl solution (10 mg/mL in the mixed solvents tetrahydrofuran and chloroform at the volume ratio of 4:1) was spin-coated on the top of H₂Chl-absorbed mesoporous TiO₂ film. Finally, a 100 mm Ag electrode was obtained on the (ZnChl)n film by thermally evaporated method to get the complete devices.

**Characterizations and measurements**

The ultraviolet–visible–near infrared (UV–Vis–NIR) spectra were acquired by a Shimadzu UV-3100 spectrophotometer. A Hitachi SU8020 field emission scanning electron microscope was used to measure the cross-sectional scanning electron microscope (SEM). And a computer-controlled Keithley 2400 source meter measurement system with an AM 1.5G filter under 100 mW/cm² illumination (determined by a standard silicon reference cell) was used to get the current density–voltage (J–V) characteristic of the solar cell. The CrowntechQTest Station 1000AD (SOFN INSTRUMENTS CO., LTO) equipped with a 100 W Xe arc lamp, filter wheel, and monochromator was used to get the incident photon-to-current conversion efficiency spectrum. Subpicosecond time-resolved absorption spectra (TAS) were measured with a conventional pump-probe method. Briefly, the light source was a femtosecond regenerative amplifier system (Spectra-Physics, Spitfire, 1 kHz, 80 fs, 800 nm) seeded by a mode-locked Ti:sapphire oscillator (Spectra-Physics, Tsunami).
The pump beam was a selected output from an optical parametric amplification (TOPAS, Light Conversion) with energies of 0.2 μJ/pulse. The probe beam was the supercontinuum white light by focusing the fundamental into a quartz cell filled with D₂O. The samples were put on an overlap position of the pump and probe beams. The transmitted probe beam was collected by an optical fiber and detected by a liquid nitrogen cooled CCD detector (Princeton Instruments, Spec-10) mounted on a grating monochromator (Acton Research, Spectra Pro 275). Finally, the TA signals were calculated by a logarithm of the intensity ratio of the probe beam as the pump beam off and on given by a 500 Hz chopper in close and open positions.

**Figure S1.** The device configuration of the fabricated Chl-based BSC.
Figure S2. The histograms of the photovoltaic parameters a) $V_{oc}$, b) $J_{sc}$, c) FF and d) PCE got through 30 devices of the solar cell.

Figure S3. The $J$–$V$ curve of a solar cell with FTO/compact TiO$_2$/TiO$_2$-H$_2$Chl/Ag.
Figure S4. Kinetic decay traces of TiO$_2$-H$_2$Chl at 610 nm and 680 nm.

IRF curve by a Gaussian function as shown above by nlf_GaussAmp(col(v),0,0.03,0.06,1) in origin, in which col(v) is the delay time point, 0 is baseline, 0.03 is time zero, 0.06 is the full width at half maximum.
**Figure S5.** The TAS of TiO$_2$-H$_2$Chl and TiO$_2$-H$_2$Chl/Spiro-OMeTAD at 0.04 ps delay time.

**Figure S6.** A kinetic decay trace of TiO$_2$-H$_2$Chl/Spiro-OMeTAD at 680 nm.
Figure S7. A kinetic decay trace of (ZnChl)$_n$ at 720 nm.

Table S1. The photovoltaic parameters of the solar cells with FTO/compact TiO$_2$/TiO$_2$-H$_2$Chl/Ag.

<table>
<thead>
<tr>
<th>$V_{oc}$ (V)</th>
<th>$J_{sc}$ (mA/cm$^2$)</th>
<th>FF</th>
<th>PCE (%)</th>
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<tbody>
<tr>
<td>0.42</td>
<td>0.46</td>
<td>0.41</td>
<td>0.079</td>
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References
