

Supporting Information for

Photocurrent generation system incorporated with antenna function

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Materials and Preparation. All chemicals used in this study were of reagent grade. Gold electrodes were prepared by a vacuum deposition technique with chromium (50 Å, 0.1 Å/s) and gold (200 Å, 0.1 Å/s) in a sequence onto Pyrex slide glass (IWAKI) held at 300 °C (5.5×10^{-6} - 6.5×10^{-6} Torr) and cut into small pieces (1 cm x 3 cm), rinsed with dilute hydrochloric acid, Milli-Q water, and ethanol and dried with a stream of nitrogen gas before being soaked in a thiol solution.¹ The gold electrodes were dipped into 1 M CH₂Cl₂ solution of **1** at room temperature for 24 h under nitrogen. The solution was shielded from light during the modification. After soaking, electrodes were rinsed well with CH₂Cl₂ and dried with a stream of nitrogen. The molecule on the gold substrate was monitored using a UV-visible absorption spectroscopy to confirm the complete formation of the monolayer. The surface-bound porphyrins were metalated in 5 mL of CHCl₃ solution containing a few drops of MeOH solution saturated with Zn(OAc)₂ at 50 °C for 2 h under argon atmosphere. The resulting electrode was washed copiously

with CH₂Cl₂ and MeOH, and dried with a stream of nitrogen. The complete metalation was confirmed by disappearance of the absorption band of free base porphyrin at 500 nm, cyclic voltammetry ($\Gamma = 3.1 \times 10^{-11} \text{ mol cm}^{-2}$), and fluorescence spectra.

Elongation of Porphyrin on Au electrodes. First, multi-porphyrin array of **2** was dissolved (0.1 mM or 1 mM) in nitrobenzene-pyridine in a 1:1 molar ratio to dissociate the molecule into the monomeric unit **2** by competitive coordination of pyridine. An aliquot (0.2 mL) of this solution was added dropwise onto the whole Au electrode surface of SAM **3** and pyridine with a smaller portion of nitrobenzene was evaporated slowly at 50 °C in an air stream for 10 minutes. Porphyrin solution was applied again on the electrode and evaporated. This series of solution application and evaporation was repeated, and electrodes were finally washed with CH₂Cl₂, treated with ultrasonic and dried under a stream of nitrogen.

More concentrated solution of **2** (10 mM) was also tried, but it was not effective for the extension. In the case that **2** was dissolved (0.1 mM or 1 mM) in nitrobenzene containing pyridine in a 9:1 molar ratio, no improvement of elongation could be achieved. No more optimization was tried about concentration of **2** or ratio of nitrobenzene to pyridine.

Synthetic Procedures. Synthetic routes of **1** were shown in Scheme S1. The starting materials including 5-mesityldipyrromethane **4**, *p*-[(6-acetylthio)hexoxy]benzaldehyde **5**² and *N*-methylimidazolecarboxyaldehyde **6** were synthesized by using reported methods.

Treatment of **4** (2.07 g, 7.84 mmol), **5** (3.3 g, 11.8 mmol) and **6** (431 mg, 3.92 mmol) with trifluoroacetic acid (TFA, 1.78 g, 15.6 mmol) in chloroform under N₂ afforded corresponding free-base porphyrin **7** and isolated by column chromatography on silica gel (CHCl₃/acetone). Free-base porphyrin **7** was dissolved in CHCl₃ (20 mL) and metalated with 8 mL of Zn(OAc)₂-MeOH solution, extracted with CHCl₃ and recrystallized from CHCl₃-MeOH. The ω-mercaptoacetate group in **8** was hydrolyzed to afford thiol porphyrin, followed by demetalation with hydrochloric acid to yield 229 mg of **1** (yield = 7%). When **7** was directly subjected to the hydrolysis, appreciable decomposition was observed.

8: mp >300 °C (uncorrected); IR (KBr) 3443, 2924, 2857, 1690, 1606, 1473, 1333, 1284, 1244, 1173, 993, 794, 719 cm⁻¹; MALDI-TOF *m/z* (M+H⁺), 939.5, Calcd 939.3; λ_{abs} (Chloroform) 417.5, 435, 524.5, 564.5, 611 nm; ¹H NMR (270 MHz, CDCl₃) δ 8.92 (d, *J* = 4.5 Hz, 2H), 8.62 (d, *J* = 4.5 Hz, 2H), 8.47 (d, *J* = 7.8 Hz, 1H), 8.10-8.03 (m, 3H), 7.45 (s, 2H), 7.36 (d, *J* = 7.8 Hz, 1H), 7.25 (d, *J* = 7.8 Hz, 1H), 7.09 (s, 2H), 5.60 (d, *J* = 4.5 Hz, 2H), 5.51 (s, 1H), 4.29 (t, *J* = 5.9 Hz, 2H), 2.98 (t, *J* = 6.7 Hz, 2H), 2.69 (s, 6H), 2.61 (s, 6H), 2.37 (s, 3H), 2.28 (s, 1H), 2.07-1.96 (m, 2H), 1.66 (s, 3H), 1.71-1.26 (m, 6H), 1.20 (s, 6H). Anal. Calcd for C₅₆H₅₄N₆O₂SZn·H₂O: C, 70.17; H, 5.89; N, 8.77. Found: C, 69.79; H, 5.63; N, 8.38.

1: mp >300 °C (uncorrected); IR (KBr) 3429, 2924, 2856, 1606, 1465, 1344, 1281, 1244, 1178, 802, 734 cm⁻¹; HR-FAB MS *m/z* (M+H⁺), Calcd 835.4158. Found 835.4151; λ_{abs} (Chloroform) 419.5, 515, 551, 589, 644 nm; ¹H NMR (270 MHz, CDCl₃) δ 8.83 (d, *J* = 4.8 Hz, 2H), 8.74-8.67 (m, 6H), 8.14 (d, *J* = 8.4 Hz, 1H), 8.06 (d, *J* = 8.4 Hz, 1H), 7.63 (d, *J* = 1.4 Hz, 1H), 7.44 (d, *J* = 1.4 Hz, 1H), 7.29-7.23 (m, 6H),

4.24 (t, $J = 6.3$ Hz, 2H), 3.49 (s, 3H), 2.67-2.57 (m, 8H), 2.00-1.93 (m, 2H), 1.90 (s, 6H), 1.76 (s, 6H), 1.84-1.58 (m, 6H), 1.39 (t, $J = 7.7$ Hz, 1H), -2.60 (s, 2H).

Photocurrent Measurements. UV-vis spectra were obtained on a Shimadzu UV3100-PC spectrometer. All electrochemical studies were performed on a Bioanalytical Systems, Inc. CV-50W voltammetric analyzer using a standard three-electrode cell with a modified Au working electrode (0.5 cm^2), a platinum wire counter electrode, and an Ag/AgCl (saturated KCl) reference electrode. The adsorbed amount of SAM **3** on gold electrode was calculated from the charge of the anodic peak.

Photoelectrochemical measurements were undertaken in Pyrex cell (5 mL) under N_2 atmosphere. The cell was illuminated with 150 W Xe lamp (HAMAMATSU L-2273) through an IR cut-off filter or excitation light passed through a monochromator (Shimazu SPG-100-ST) using the same 150 W Xe lamp on the SAM of 0.5 cm^2 . An N_2 -saturated aqueous electrolyte solution contained 0.1 M Na_2SO_4 and 5 mM methyl viologen (MV^{2+}). The photocurrent was measured in a three-electrode arrangement, a modified gold working electrode, a platinum wire counter electrode, and an Ag/AgCl (saturated KCl) reference. The light intensity was monitored by an ADVANTEST. Q-8221 optical power meter. All the measurements were carried out at room temperature.

References

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