

Electronic Supplementary Information

**A Photosensing System Composed of Photosystem I, Molecular wire,
Gold Nanoparticle, and Double Surfactants in Water**

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Synthesis.

General. Hexanethiol protected Au nanoparticle ($\text{Au}_x(\text{SC}_6\text{H}_{13})_y$) was prepared by reference to Brust method.¹ $\text{Au}_x(\text{SC}_6\text{H}_{13})_y(\text{S}(\text{OEt})_3\text{CH}_3)_z$ was prepared according to the literature.² The compound **3** was prepared according to the literature.³ ^1H NMR spectra were recorded with a Bruker DRX500 spectrometer. Transmission electron microscopy (TEM) images were recorded at 200 kV using a Hitachi HF-2000 equipped with an AMT-CCD camera. TEM samples of Au nanoparticles were prepared at room temperature by depositing THF-dispersed particles onto a carbon film supported by a carbon grid. The size distribution of the nanoparticles was obtained by manually measuring the diameters of more than 200 particles.

Synthesis of $\text{Au}_x(\text{C}_6\text{H}_{13}\text{S})_y$. HAuCl_4 (1.00 g, 2.43 mmol) in water (80 cm^3) bubbled with N_2 for 30 min was added to toluene solution (700 cm^3) of tetra-*n*-octylammonium bromide (5.61g, 10.3 mmol) bubbled with N_2 for 30 min. The mixture was vigorously stirred for 3 h under N_2 . Organic phase was separated from aqueous phase. Hexanethiol (1.1 cm^3 , 7.8 mmol) was added into the organic phase and stirred under air at 0 °C for 1 h. The aqueous solution (80 cm^3) of sodium borohydrate (1.04 g, 27.6 mmol) was slowly dropped into the toluene solution and stirred under air overnight. Organic phase was separated from aqueous phase. The mixture was concentrated until ca. 10 cm^3 *in vacuo*. EtOH (1 dm^3) was added to into the toluene solution to afford to $\text{Au}_x(\text{SC}_6\text{H}_{13})_y$ (369 mg).

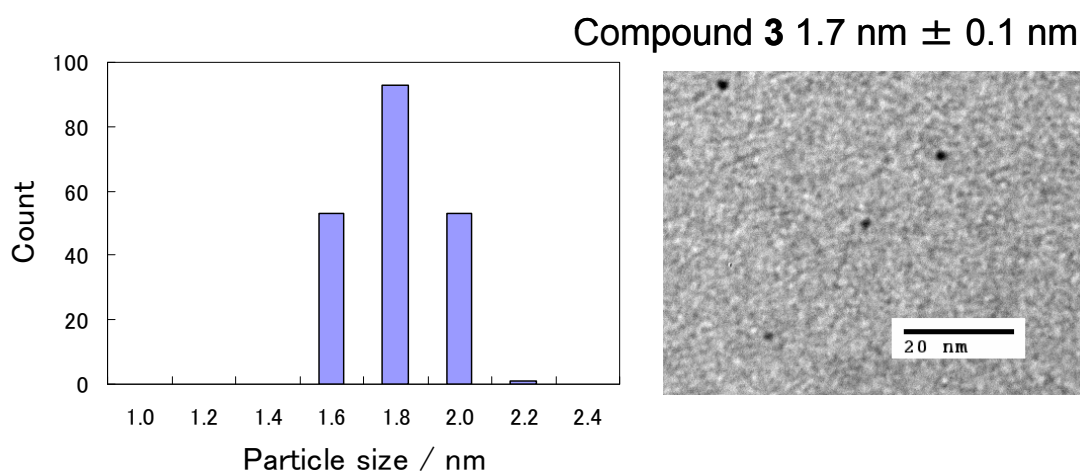


Fig. S1. TEM image and size distribution of compound **3**.

Preparation and immobilization of PSI. The procedures used for the preparation and immobilization of PSI by reconstitution are illustrated in Figure 1. First, VK₁ was extracted from PSI to obtain PSI(-VK₁). The PSI samples were suspended in a 50% water-saturated diethyl ether solution (1 mg dried PSI/5 cm³ diethyl ether) for 10 min at 4 °C. Diethyl ether was removed by centrifugation. This extraction was applied twice, to obtain VK₁-free PSI. Second, the molecular wire **3** was conjugated to the SAM formed by **1**. A gold electrode was immersed into a 10 mmol dm⁻³ ethanol solution of **1** for two days at 25 °C to allow thiolation of the electrode surface, washed with ethanol, and dried with stream of nitrogen to provide the modified electrode with **1**. Subsequently, the SAM-modified electrode was immersed in a 1 μmol dm⁻³ ethanol solution of **3** for one day at 25 °C, washed with ethanol, and dried, enabling thiol substitution at the surface of **3**, which immobilized **3** onto the electrode. Finally, reconstitution of PSI was carried out by immersing the modified electrode into a

solution of PSI(-VK₁) in MES-NaOH buffer (MES = 2-(N-morpholino)ethanesulfonic acid) for 4–5 days at 4 °C, washed with MES-NaOH buffer, to obtain the PSI-functionalized Au electrode.

Photodetection Measurements. Photodetection measurements were carried out using an Au electrode immobilized with an Au nanoparticle functionalized PSI, and an Ag/AgCl reference electrode (3 mol dm⁻³ NaCl(aq.)). The electrolyte composition was sodium ascorbate (NaAsc; 0.25 mol dm⁻³), 2,6-dichloroindophenol (DCIP) (2.5 mmol dm⁻³), NaClO₄ (0.1 mol dm⁻³), and MES-NaOH buffer (pH 6.4). Applied potential to Ag/AgCl reference electrode was 0 V. An acrylic plastic cell was used for this study, and the Au electrode was exposed to the electrolyte through a rectangular -shaped hole of the cell. Photodetection measurements were performed with a parameter analyzer (Agilent HP4142B). A halogen lamp (Mitutoyo MEGALIGHT 100) was used for the light source, and monochromatic light, which was obtained through monochromator, was focused on the area of the Au electrode using optical lens and a fiber. All experiments were carried out under air at 25 °C.

Image of Au electrode. The Au electrode was originally developed for this study. Figure S2 shows the microscope image of the electrode (a) and the schematic illustration of the electrode (b). The effective area of the Au electrode was $16.7 \times 16.7 \mu\text{m}^2$, and rest of the Au area was covered with a resist (SU-8) in order not to be exposed to the electrolyte.

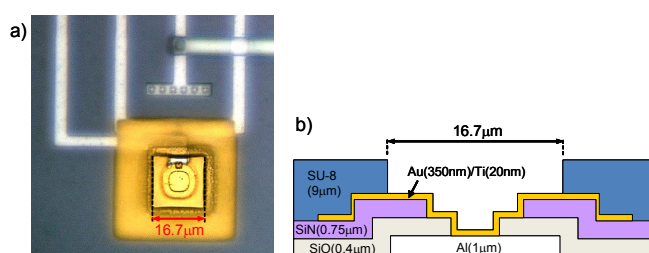


Fig. S2. a) The microscope image of the Au electrode. b) The schematic illustration of the electrode.

Gradation of photodetection. E_{rest} changes of PSI-AuNP-Au electrode depended on the irradiation intensity of light. The result was shown in Figure S3.

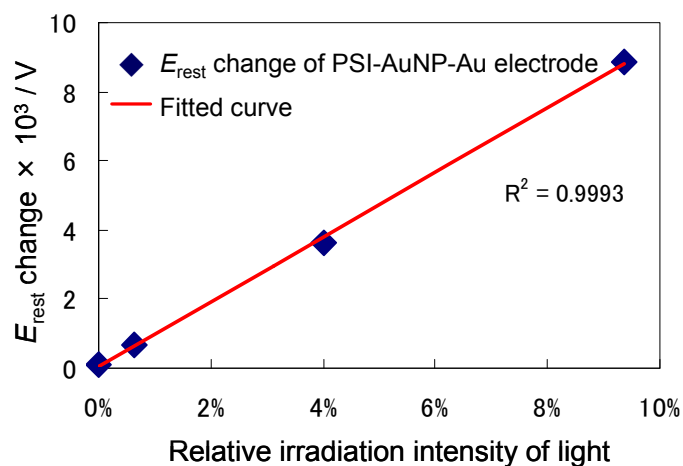


Fig. S3. Gradation of photodetection of PSI-AuNP-Au electrode.

Photodetection measurement with clean Au electrode (control). Control measurement of photodetection was carried out using a clean Au electrode. The result was shown in Fig. S4. A halogen lamp was used for the light source without monochromator. The electrolyte composition was sodium ascorbate (NaAsc; 0.25 mol dm⁻³), 2,6-dichloroindophenol (DCIP) (2.5 mmol dm⁻³), NaClO₄ (0.1 mol dm⁻³), and MES-NaOH buffer (pH 6.4). E_{rest} was measured with a parameter analyzer through a voltage follower circuit which we originally developed with an intention to increase the sensitivity of the photodetection.⁴ The effective area of the Au electrode was 2.6 × 2.6 μm². Photo response was not observed.

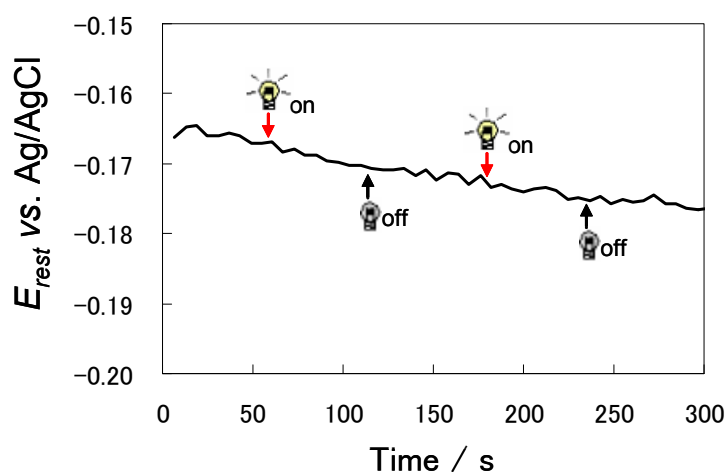


Fig. S4. E_{rest} change of clean Au electrode.

References

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