Supporting Information

Creation of anaerobic microenvironments by Photosystem I in porous glass nanopores enables photoinduced H_2 evolution under aerobic conditions

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[Solution of the Kinetic Model for the P700$^+$ State]

The time dependence of the total PSI population in the P700$^+$ state was obtained by solving the following revised coupled rate equations for $[P700^+ - F_B^-]$, $[P700^+ - F_B]$ and $[P700 - F_B^-]$.

$$\frac{d[P700^+ - F_B^-]}{dt} = -(k_1 + k_2 + k_3)[P700^+ - F_B^-] \quad \text{(S1)}$$

$$\frac{d[P700^+ - F_B]}{dt} = -k_3[P700^+ - F_B] + k_2[P700^+ - F_B^-] \quad \text{(S2)}$$

$$\frac{d[P700 - F_B^-]}{dt} = -k_2[P700 - F_B^-] + k_3[P700^+ - F_B^-] \quad \text{(S3)}$$

With $t = 0$, Equation. S1 gives

$$[P700^+ - F_B^-] = [P700^+ - F_B^-]_0 \, e^{-(k_1 + k_2 + k_3)t} \quad \text{(S4)}$$

Substitution of Equation. S4 into Equation. S2 and solution by an integrating factor $e^{k_3 t}$ yields

$$[P700^+ - F_B] = \frac{k_2[P700^+ - F_B^-]_0}{k_1 + k_2}\left(e^{-k_3 t} - e^{-(k_1 + k_2 + k_3)t}\right) \quad \text{(S5)}$$

The state $[P700 - F_B^-]$ is obtained by integrating Equation S3:

$$[P700 - F_B^-] = \frac{k_3[P700^+ - F_B^-]_0}{k_1 + k_3}\left(e^{-k_2 t} - e^{-(k_1 + k_2 + k_3)t}\right) \quad \text{(S6)}$$

Because $[P700 - F_B^-]$ does not contain oxidized P700, this state does not contribute to the P700$^+$ absorption signal and is therefore not included in the total P700$^+$ population.

$$[P700^+] = [P700^+ - F_B^-] + [P700^+ - F_B] \quad \text{(S7)}$$

and thus

$$[P700^+] = [P700^+ - F_B^-]_0\left(\frac{k_1}{k_1 + k_2}e^{-(k_1 + k_2 + k_3)t} + \frac{k_2}{k_1 + k_2}e^{-k_3 t}\right) \quad \text{(S8)}$$

which is identical to Equation 5 in the main text.

[Definitions of TON and O_2 Tolerance]

$$TON = \frac{n_{H_2}}{n_{PSI}} \text{ (S9)}$$

where n_{H_2} is the amount of H_2 evolved during illumination (mol), and n_{PSI} is the amount of PSI present in the reaction system (mol).

$$O_2\ tolerance\ (\%) = 100 \times \frac{TON_{aerobic}}{TON_{anaerobic}} \text{ (S10)}$$

where $TON_{aerobic}$ and $TON_{anaerobic}$ are TON values measured under aerobic and anaerobic conditions, respectively.

Table S1. Rate constant k_3 obtained by fitting the transient absorption time courses of PSI in solution and PGP-immobilized PSI.

		rate constant (s^{-1})	
		k_3	
condition	Pre-irradiation time (min)	solution	PGP
aerobic	0	0.49	0.34
	1	0.50	0.36
	2	—	0.57
	3	0.50	0.74
	5	0.51	0.96
	7	—	0.60
	10	0.51	0.56
anaerobic		0.60	0.40

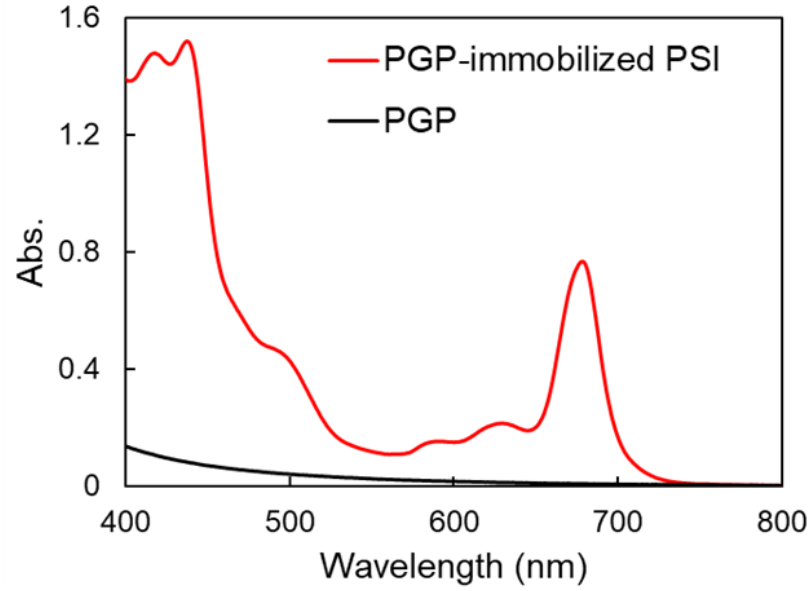

Figure S1. UV–vis absorption spectra of porous glass plate (PGP) (black) and PGP-immobilized photosystem I (PSI) (red).

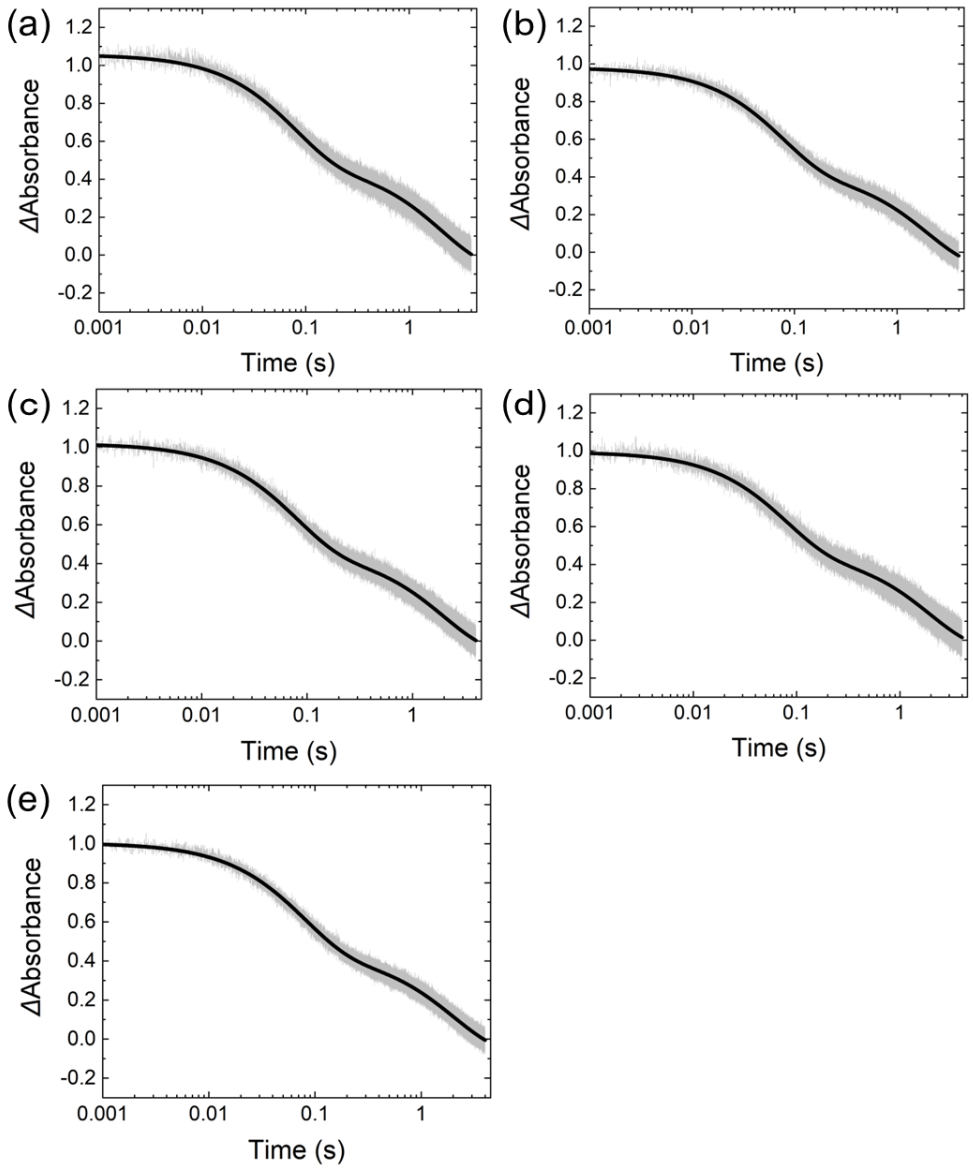

Figure S2. Pre-irradiation time dependence of transient absorption decay in PSI. Transient absorption decay time courses of PSI in solution recorded after (a) 0, (b) 1, (c) 3, (d) 5 and (e) 10 min of pre-irradiation. Colored lines represent the best-fit curves obtained using Equation. 5.

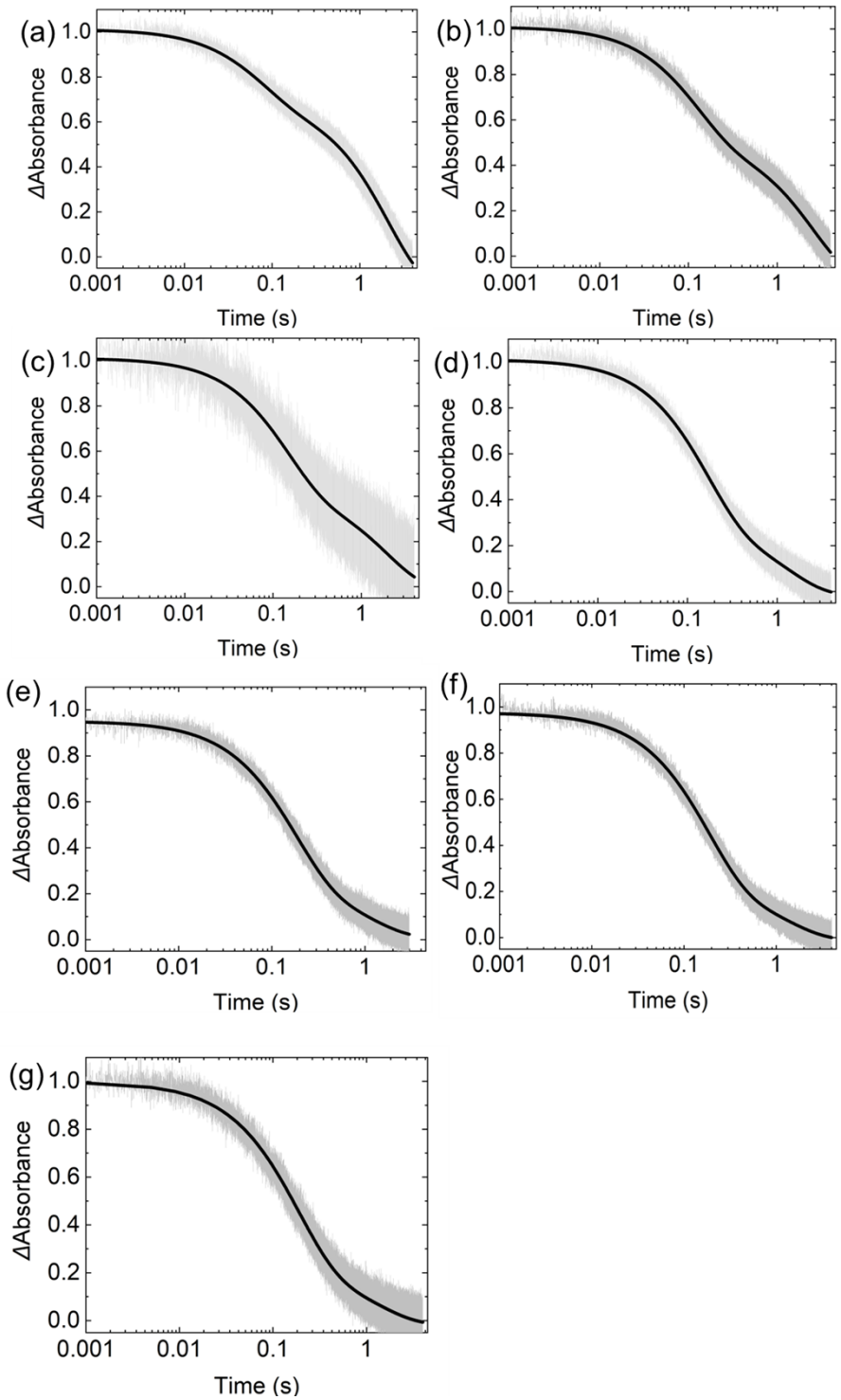

Figure S3. Pre-irradiation time dependence of transient absorption decay in PSI. Transient absorption decay time courses for PGP-immobilized PSI recorded after (a) 0, (b) 1, (c) 2, (d) 3, (e) 5, (f) 7 and (g) 10 min of pre-irradiation. Gray lines show experimental results. Colored lines represent the best-fit curves obtained using Equation. 5.

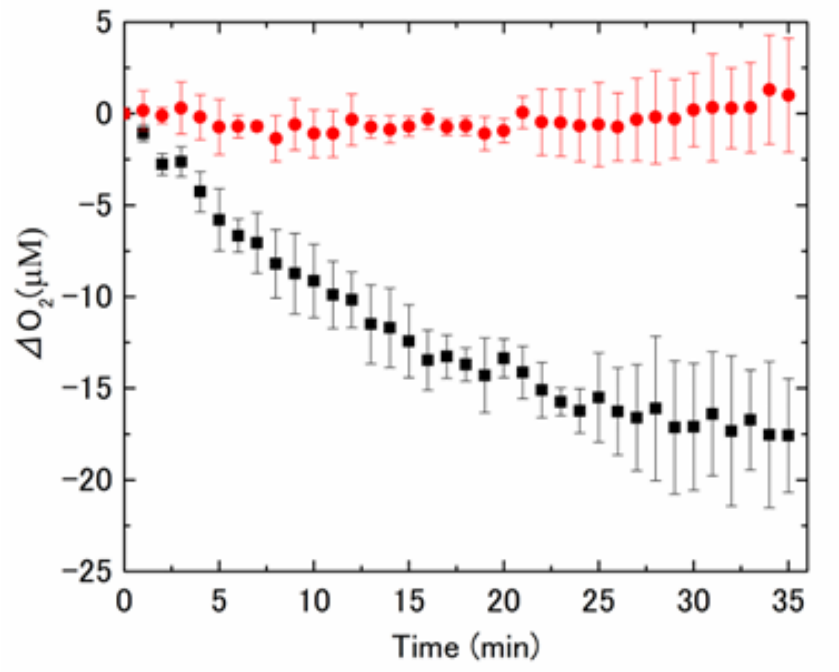

Figure S4. Time course of dissolved O_2 concentration in PSI solution under aerobic conditions. Dissolved O_2 concentration was monitored using a NeoFox-GT oxygen monitor equipped with a standard sensor probe (Ocean Optics). The PSI solution was prepared under the same solution conditions as those used for TAS measurements: 180 nmol L^{-1} PSI in 40 mmol L^{-1} HEPES–NaOH buffer (pH 7.8) containing 50 mmol L^{-1} NaCl, 10 mmol L^{-1} ascorbic acid, 0.1 mmol L^{-1} DCIP, and 0.03% (w/v) DM. The irradiation conditions were the same as those used for the light-driven H_2 evolution experiments. Black squares: under light irradiation; red circles: without light irradiation.

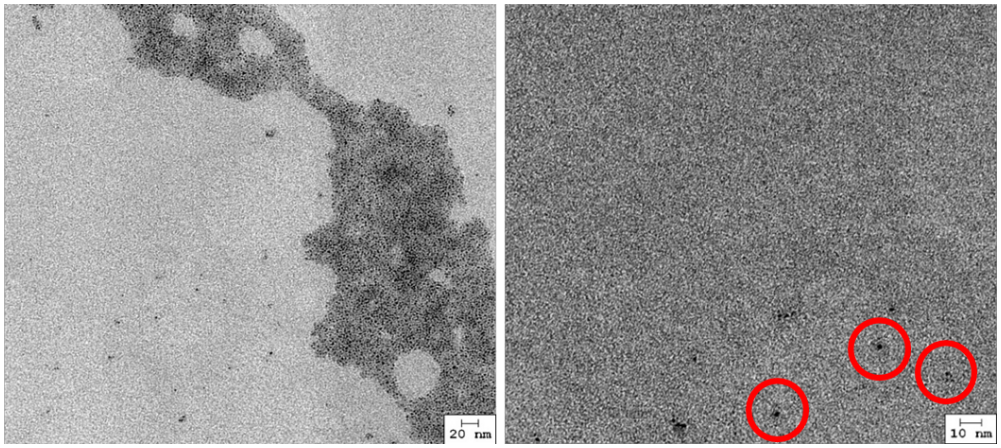

Figure S5. TEM images of Pt nanoparticles (PtNPs) at magnifications of ×4,000 (left) and ×10,000 (right). The particle diameter estimated from the TEM images was approximately 2 nm.

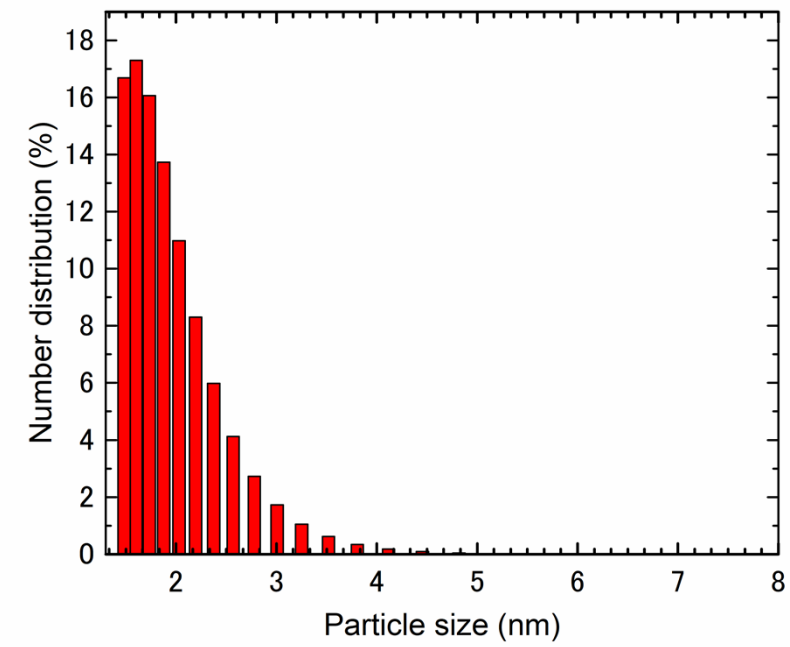

Figure S6. Particle size distribution of the synthesized PtNPs measured by DLS. The mean particle diameter was 1.8 ± 0.6 nm.

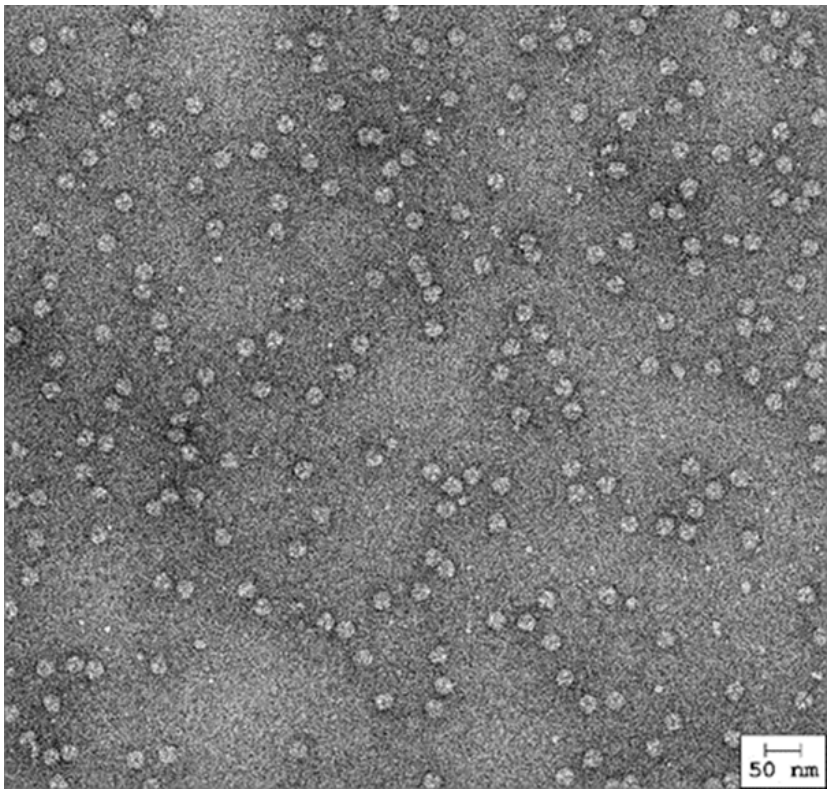

Figure S7. TEM image of PSI (magnification: ×20,000).

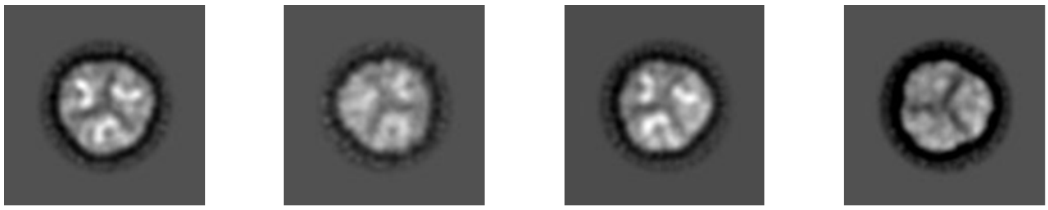

Figure S8. Negative-stain TEM 2D class averages of PSI. Numbers in parentheses indicate the number of particles contributing to each class-average image. In total, 4,676 particle images obtained from 65 micrographs were classified into four classes, followed by 2D class averaging.

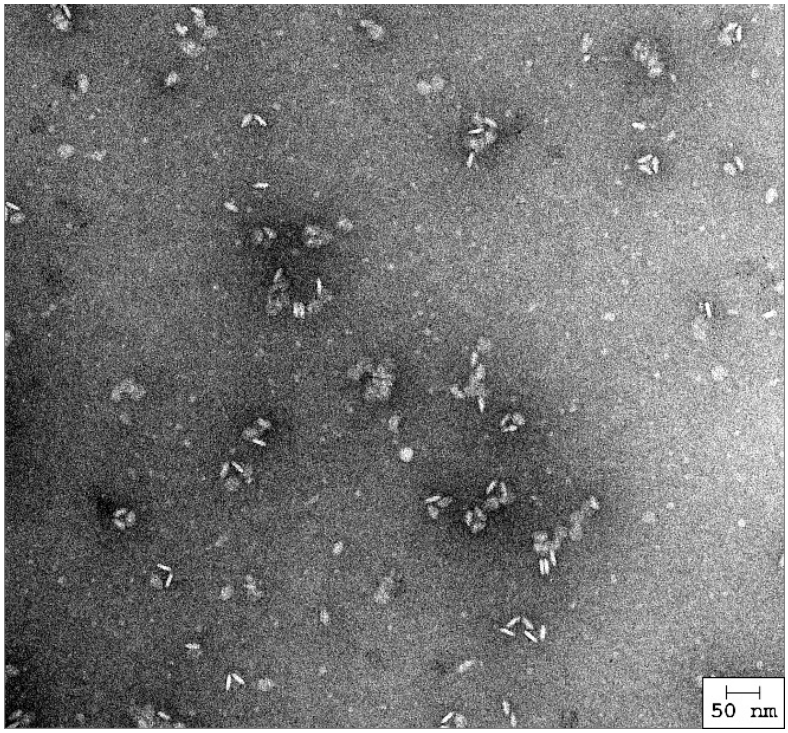

Figure S9. TEM image of PSI–PtNP (magnification: ×20,000).

Figure S10. Negative-stain TEM 2D class averages of PSI–PtNP. Numbers in parentheses indicate the number of particles contributing to each class-average image. A total of 1,281 particle images extracted from 65 micrographs were classified into three classes in RELION, followed by 2D class averaging.

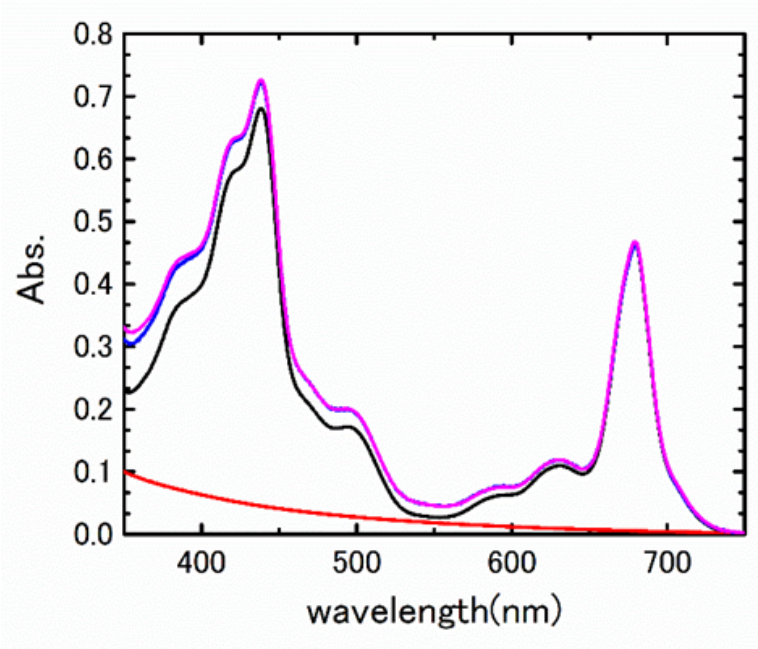

Figure S11. UV–vis absorption spectra of PSI (0.084 μmol L^{-1}; black) and PtNP (0.084 μmol L^{-1}; red). The calculated spectrum obtained by arithmetically summing the PSI and PtNP spectra at a 1:1 stoichiometric ratio (pink) closely matches the spectrum of the synthesized PSI–PtNP complex (blue), consistent with a 1:1 binding stoichiometry between PSI and PtNP.

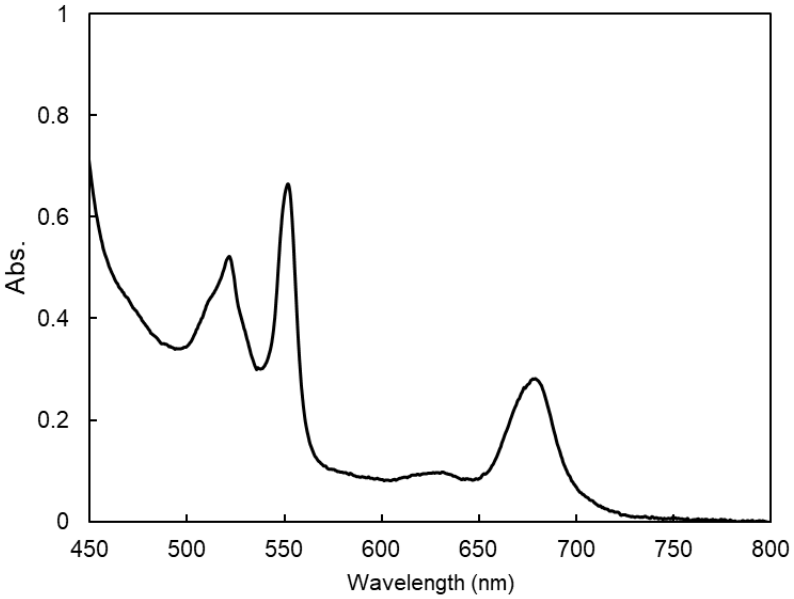

Figure S12. UV–vis absorption spectrum of a PGP co-immobilized with PSI–PtNP and cyt c_6.

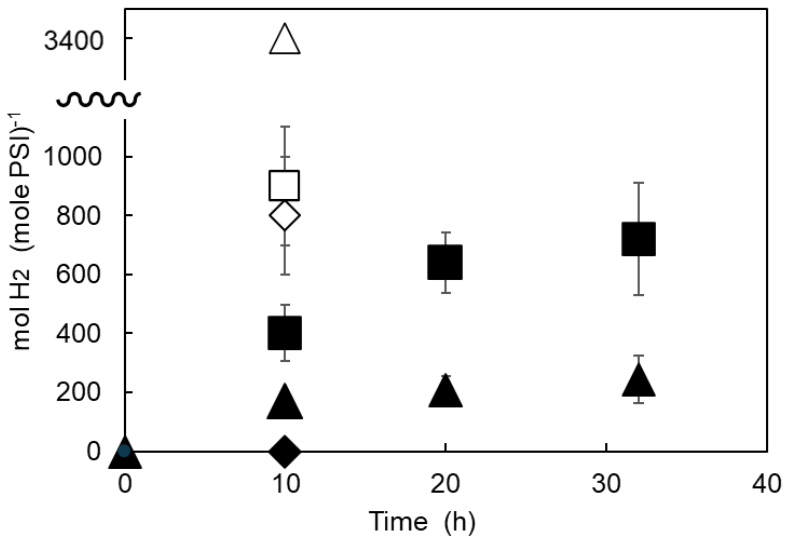

Figure S13. Light-driven H_2 evolution in solution and PGP systems. Squares represent the PGP system with co-immobilized PSI–PtNP and cyt c_6. The solution-phase system is represented by triangles (stirred) and diamonds (unstirred). Filled symbols indicate aerobic conditions, whereas open symbols indicate anaerobic conditions (data shown only at 10 h).

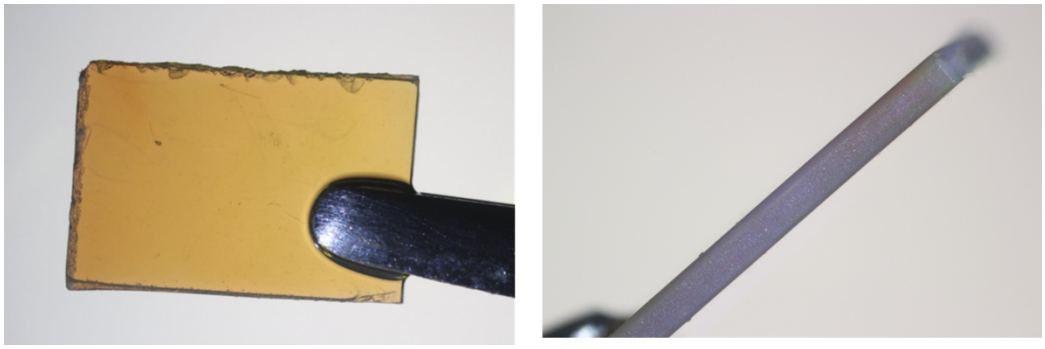

Figure S14. PGP co-immobilized with PSI–PtNP and cyt c_6. The left panel shows the surface of the plate, and the right panel shows the side view.