

Electronic Supplementary Information

Efficient organo-photocatalysis system of an n-type perylene derivative/p-type cobalt phthalocyanine bilayer for the production of molecular hydrogen from hydrazine

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Experimental details

Chemicals: PTCBI was synthesised and purified according to a previously described procedure [1]. Commercially available CoPc (Tokyo Kasei Co., Ltd.) was used as received. N₂H₄ and a 5 wt% Nafion alcoholic solution were purchased from Kanto Chemical Co., Inc. and Sigma-Aldrich Co., respectively. The ITO-coated glass plate (sheet resistance, 8 Ω·cm⁻²; transmittance, >85%; ITO thickness, 174 nm) was obtained from Asahi Glass Co., Ltd.

Procedure for coating Nafion onto the surface of a photocatalyst device: A 1 wt% Nafion solution was prepared by diluting commercial Nafion with methanol (density of Nafion in the resulting solution: 8.74 × 10⁻³ g·cm⁻³). Typically, 23 μl of this solution was cast onto the CoPc surface (effective area: 1 cm²), and the solvent was evaporated under air. The resulting thickness of Nf was estimated to be ca. 1 μm by assuming a membrane density of 2 g·cm⁻³ [2].

Measurements: Absorption measurements were performed using a Hitachi U-2010 spectrophotometer. The resulting absorption spectra of PTCBI [3] and CoPc [4] were identical to those reported previously, and their absorption coefficients were used to determine the thickness of the obtained film [5]. In view of its spectral characteristics, the resulting CoPc film may be assigned as the α-phase (*vide infra*). On the basis of a comparison of the absorption spectrum of the PTCBI (200 nm)/CoPc (150 nm) bilayer with the summed absorption spectra of each single layer, the formation of a charge transfer complex at the heterojunction was confirmed to be absent.

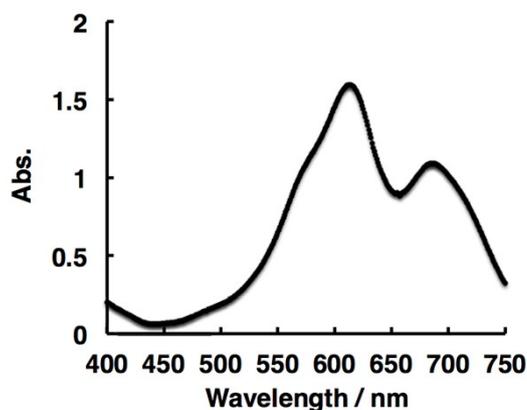


Figure Absorption spectrum of a single-layered CoPc.

The photoelectrochemical and photocatalytic studies were usually conducted under an Ar atmosphere. A halogen lamp was typically used as the light source, and irradiation was performed from the back-side of the ITO-coated face. For irradiation with monochromatic light, the lamp was used in conjunction with a monochromator (Soma Optics, Ltd., S-10). Light intensity was measured using a power metre (type 3A, Ophir Japan, Ltd.).

As depicted in Scheme S1 and Scheme 1, a twin-compartment cell was used in the photoelectrolysis and photocatalysis experiments. The use of such a cell facilitated the clear analysis of the reaction products. For the preparation of the salt bridge (in Scheme S1 and Scheme 1), agar (1.3 g) and KNO₃ (4.74 g) were first dissolved in hot water ($1.0 \times 10^{-2} \text{ dm}^3$); the resulting mixture was then allowed to flow into the bridging part of the cell and solidify at room temperature. Cyclic voltammograms were obtained using a single-compartment electrochemical glass cell equipped with a modified ITO working electrode (effective area, 1 cm²), a spiral Pt counter electrode and an Ag/AgCl (in saturated KCl electrolyte solution) reference electrode (see Fig. S1).

Voltammetric measurements and potentiostatic electrolysis were performed under illumination using a potentiostat (Hokuto Denko, HA-301) with a function generator (Hokuto Denko, HB-104), coulomb metre (Hokuto Denko, HF-201) and X–Y recorder (GRAPHTEC, WX-4000).

Gaseous products were analysed using a gas chromatograph equipped with a thermal conductivity detector (Shimadzu, GC-8A); the chromatograph was equipped with a 5-Å molecular sieve column, and Ar was used as the carrier gas. Quantification of gaseous products was performed using a chromatogram analyser (Shimadzu, C-R8A) equipped on the chromatograph.

Calculation methods:

The Faradaic efficiency (F.E.) of N₂ evolution was calculated according to the following procedure:

i) During the photoelectrochemical decomposition of N₂H₄, the amount of charge passed was measured using a coulomb metre. On the basis of the measured charge amount, the theoretical amount of evolved N₂ was estimated.

ii) After the photoelectrochemical reaction, the amount of N₂ evolved was quantified using a gas chromatograph.

Therefore, the F.E. value was estimated using the following equation:

$$\begin{aligned} \text{F.E. (\%)} &= [\text{amount of N}_2 \text{ evolved}]/[\text{theoretical amount of N}_2] \times 100 \\ &= [\text{amount of N}_2 \text{ evolved}]/[(\text{amount of charge passed})/(nF)] \times 100 \end{aligned}$$

where n is the number of electrons that participated in the evolution of N₂ (n = 4 for the oxidation of N₂H₄ into N₂), and F is the Faraday constant ($9.65 \times 10^4 \text{ C}\cdot\text{mol}^{-1}$).

The external quantum efficiency (EQE) of H₂ evolution was estimated as follows:

$$\text{EQE (\%)} = (N_A \times M)/(I \times A) \times 100,$$

where N_A is Avogadro's number (particles·mol⁻¹), M is the amount of reacted electrons in H₂ evolution (mol), I is the number of incident photons at a given wavelength (particles·cm⁻²) and A is the effective area of the photocatalyst film (1 cm²).

References

1. T. Maki and H. Hashimoto, *Bull. Chem. Soc. Jpn.*, 1952, **25**, 411.
2. H. S. White, J. Leddy and A. J. Bard, *J. Am. Chem. Soc.*, 1982, **104**, 4811.
3. T. Morikawa, C. Adachi, T. Tsutsui and S. Saito, *Nippon Kagaku Kaishi*, 1990, 962.
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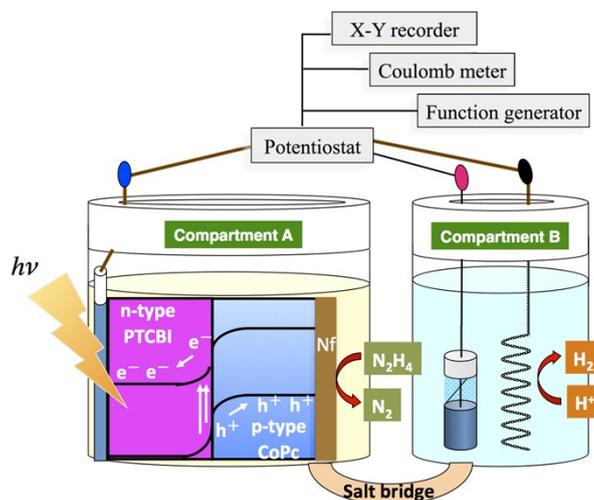
Function of Nf as absorbent

The Nf absorbent employed in this study can increase the surface concentration of N_2H_4 , effectively enhancing the rate-limiting oxidation reaction. Given the acid dissociation constant (pK_a) of the terminal sulfonic acid in Nf ($pK_a = -6$) [1] and those of the hydrazinium ions [pK_{a1} ($H_3N^+-NH_3^+/H_3N^+-NH_2$) = -0.9 , pK_{a2} ($H_3N^+-NH_2/H_2N-NH_2$) = 7.9] [2], N_2H_4 dissolved in the electrolyte solution ($pH = 11$) is incorporated into Nf, likely followed by the protonation of N_2H_4 to form $H_3N^+-NH_3^+$ in the hydrophilic environment surrounded by sulfonic ions. Through such a process, N_2H_4 can be considered to be concentrated in Nf; however, the hydrazinium ions (i.e. the protonated species of N_2H_4) cannot undergo oxidation into a N_2 molecule because the oxidation point on the hydrazinium ion(s) is blocked. As the concentration of the hydrazinium ions in Nf increases, some ions are pushed into the interfacial region (between the hydrophilic and hydrophobic regions) [3] where the deprotonated species, N_2H_4 , can be oxidised to N_2 .

References

1. A. G. Ryder, S. Power and T. Glynn, *J. Appl. Spec.* 2003, **57**, 73.
2. R. M. Smith and A.E. Martel, "Critical Stability Constants" Vol. 4, Plenum Press, New York, 1976.
3. K. A. Mauritz and R. B. Moore, *Chem. Rev.* 2004, **104**, 4535.

Photoelectrolysis cell



Scheme S1 Twin-compartment cell used for photoelectrolysis experiments.

Cyclic voltammograms

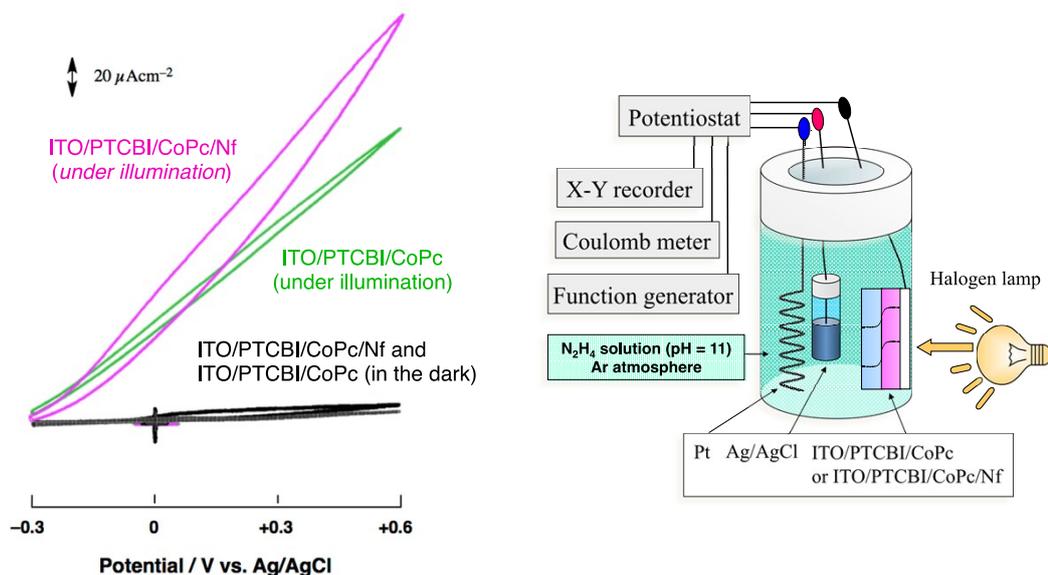


Figure S1 Cyclic voltammograms measured at ITO/PTCBI/CoPc/Nf and ITO/PTCBI/CoPc. Film thickness n-type PTCBI, 200 nm; p-type CoPc, 150 nm; Nf, 1 μm ; hydrazine solution, 5 mM (pH = 11); light intensity, ca. 70 $\text{mW}\cdot\text{cm}^{-2}$; scan rate, 20 $\text{mV}\cdot\text{s}^{-1}$. A schematic of a single-compartment cell employed for the voltammogram measurements is also depicted.

Dependence of the amount of H_2 evolved on film thickness in the photocatalytic decomposition of N_2H_4

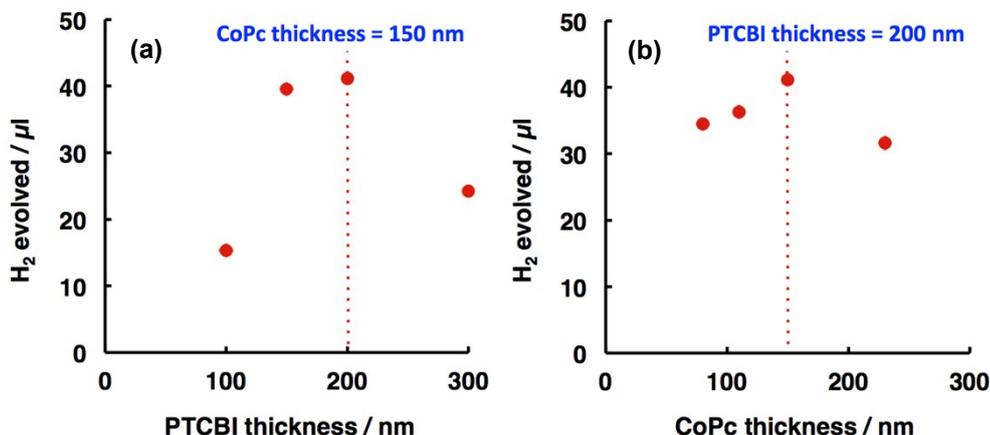


Figure S2 Relation between the film thickness of PTCBI/CoPc/Nf and amount of H_2 evolved during the photocatalytic decomposition of N_2H_4 . The conditions for Entry 1 in Table 2 were applied in this study, except that the film thickness was varied. In (a) and (b), the thickness of only one layer (i.e. PTCBI (a) or CoPc (b)) in the bilayer was changed.

Film thickness of Nf (for a and b), 1 μm ; N_2H_4 solution in compartment A, 5 mM (pH = 11); electrolyte solution in compartment B, H_3PO_4 (pH = 0); light intensity, ca. 70 $\text{mW}\cdot\text{cm}^{-2}$; irradiation time, 1 h. The dashed line indicates the conditions employed in Entry 1 of Table 2. Irradiation was performed from the back side of the ITO-coated face.

The optimal thickness of the PTCBI layer was investigated using a constant thickness of CoPc (150 nm) (Fig. S2a). The results of this experiment indicated that a 200-nm-thick PTCBI layer was most effective. A PTCBI layer thicker than 200 nm may induce an optical filter effect, thus disturbing the light absorption of PTCBI near the heterojunction and consequently leading to decreased H_2 evolution.

When the thickness of PTCBI was 200 nm, the amount of H_2 generated was independent of the CoPc thickness (Fig. S2b), indicating that absorption by CoPc was not involved in the evolution of H_2 . The roles of CoPc in the PTCBI/CoPc bilayer are discussed in the main text.

Dependence of the amount of H_2 evolved in the photocatalytic decomposition of N_2H_4 on light intensity

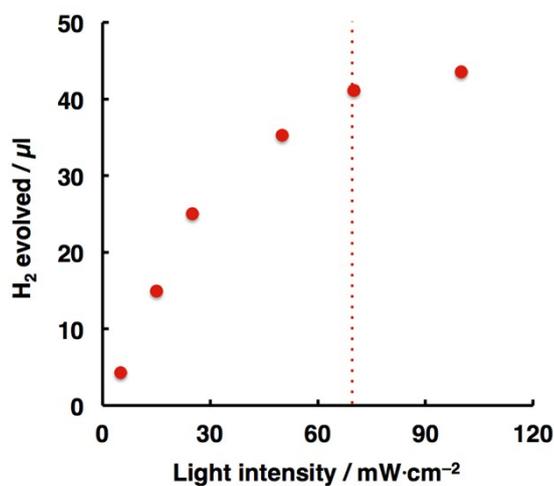


Figure S3 Relation between the intensity of irradiated light and amount of H_2 evolved in compartment B. Film thickness of PTCBI, 200 nm; CoPc, 150 nm; Nf, 1 μm ; geometrical area of photocatalyst device (ITO/PTCBI/CoPc/Nf), 1 cm^2 ; hydrazine solution in compartment A, 5 mM (pH = 11); electrolyte solution in compartment B, H_3PO_4 (pH = 0); irradiation time, 1 h. The dashed line indicates the conditions employed in Entry 1 of Table 2.

For intensities greater than 30 $mW \cdot cm^{-2}$, the amount of H_2 evolved was not proportional to the light intensity, indicating that the generation of carriers within the bilayer employed is not the rate-limiting step under the given experimental conditions.

Dependence of the amount of H_2 evolved in the photocatalytic decomposition of N_2H_4 on the concentration of N_2H_4

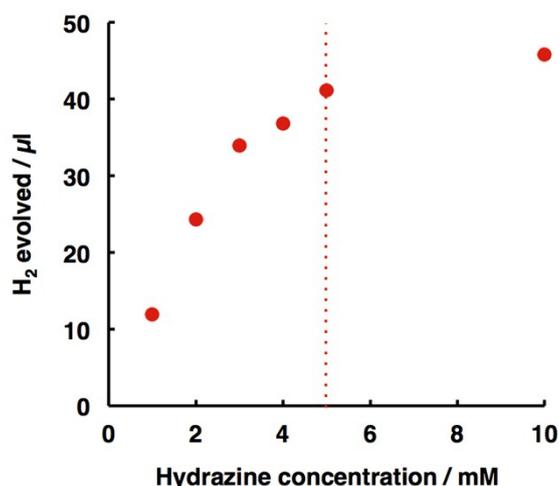


Figure S4 Relation between the N_2H_4 concentration in compartment A and amount of H_2 evolved in compartment B. Film thickness of PTCBI, 200 nm; CoPc, 150 nm; Nf, 1 μ m; geometrical area of photocatalyst device (ITO/PTCBI/CoPc/Nf), 1 cm^2 ; electrolyte solution in compartment B, H_3PO_4 (pH = 0); light intensity, ca. 70 $mW \cdot cm^{-2}$; irradiation time, 1 h. The dashed line indicates the condition employed in Entry 1 of Table 2.

At concentrations greater than 3 mM, the amount of H_2 evolved was not proportional to the concentration of N_2H_4 , indicating that the overall kinetics of the reaction were not dominated by the mass transport of N_2H_4 under the typical experimental conditions.

Absorption of visible light by PTCBI/CoPc

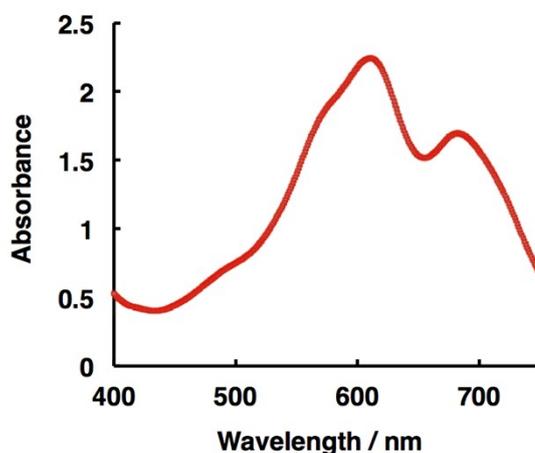


Figure S5 Absorption spectrum of the PTCBI/CoPc bilayer used in the experiments.

Action spectrum for photocurrent generated at ITO/PTCBI/CoPc/Nf

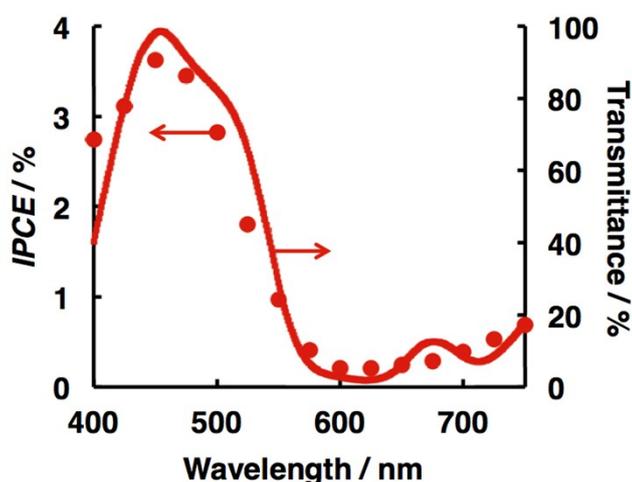


Figure S6 Action spectrum for photocurrents generated by the oxidation of N_2H_4 (closed circles), and the transmittance spectrum of CoPc (solid line).

Working electrode, ITO/PTCBI/CoPc/Nf; film thickness, PTCBI = 200 nm, CoPc = 150 nm and Nf = 1 μ m; electrolyte solution, 5 mM N_2H_4 solution (pH = 11); irradiation, side of the CoPc surface; applied potential, +0.3 V vs. Ag/AgCl.

In the presence of N_2H_4 , the action spectrum for photoanodic currents generated at ITO/PTCBI/CoPc/Nf was measured in the system shown in Figure S1, where monochromatic light was irradiated from the side of the CoPc surface. Consequently, the resulting action spectrum coincided with the transmittance spectrum of CoPc, indicating that CoPc absorption contributed little to the generated photocurrent. This supplemental result supports the results in Figure 1.

Dependence of the amount of H_2 evolved in the photocatalytic decomposition of N_2H_4 on pH

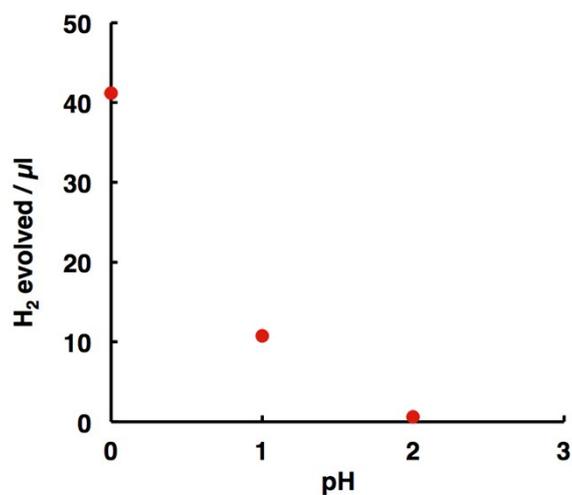


Figure S7 Relation between the amount of H_2 evolved and pH in compartment B. These experiments were performed under the same conditions listed in Entry 1 of Table 2, except that the pH values in compartment B were varied.

Film thickness of PTCBI, 200 nm; CoPc, 150 nm; Nf, 1 μm ; geometrical area of photocatalyst device (ITO/PTCBI/CoPc/Nf), 1 cm^2 ; hydrazine solution in compartment A, 5 mM (pH = 11); light intensity, ca. 70 $\text{mW}\cdot\text{cm}^{-2}$; irradiation time, 1 h.