Electronic Supplementary Material (ESI) for Journal of Materials Chemistry A.

Electronic Supporting Information

A dual-functional catalyst of organic p-n Bilayer comprising perylene derivative and cobalt phthalocyanine working under illumination and in the dark

Toshiyuki Abe,* Masato Okumura, Yuko Kikuchi, Takashi Itoh and Keiji Nagai

Contents:

Experimental details

Supplemental explanation for experimental setup

2-mercaptoehanol ($HS-CH_2CH_2-OH$, denoted as R-SH) must be dissociated to $R–S^-$ prior to its oxidation. Considering the acid dissociation constant of R-SH (cf. $pK_a = 9.72$ [1]), an alkaline thiol solution needed to be employed in the oxidation site.

As reported recently by the authors [2], the PTCBI/CoPc bilayer successfully induced the photocatalytic decomposition of hydrazine (N_2H_4) into N_2 and H_2. The evolution of H_2 occurred by the reducing power generated at PTCBI in the organo-bilayer. The previous work exhibited that the reducing power of PTCBI results in a decreasing amount of H_2 with an increasing pH. That is, the magnitude of the reducing power is pH-independent, although the formal potential for H^+/H_2 couple is forced on a negative shift with an increasing pH (i.e. –0.059 V/pH). Therefore, an acidic solution was employed in the reduction site.

[1] E.P. Serjeant, B. Dempsey, *Ionisation Constants of Organic Acids in Aqueous Solution (IUPAC Chemical Data Series No. 23)*, Pergamon Press, New York, 1979.

[2] T. Abe, N. Taira, Y. Tanno, Y. Kikuchi and K. Nagai, *RSC Adv.*, 2015, 5, 46325-46329.

I-V curves in the ITO/PTCBI/CoPc and Pt system with and without irradiation

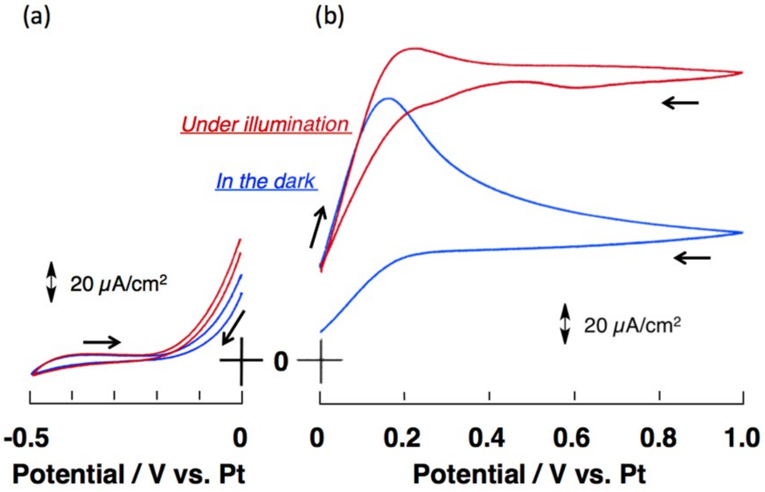

Fig. S1 I-V curves with and without irradiation (a, negative scan; b, positive scan). The I-V curves were measured in the cell depicted in Scheme 2 (i.e. in the two-electrode system). Working electrode, ITO/PTCBI/CoPc; reference and counter electrode, Pt wire; film thickness, 210 nm for PTCBI and 75 nm for CoPc; electrolyte solution in the oxidation site, 5 mM 2-mercaptoethanol solution (pH = 11); electrolyte solution in the reduction site, aqueous H_3PO_4 solution (pH = 0); light intensity, 100 mW·cm^{-2}; irradiation direction: from backside of ITO-coated face; scan rate, 5 mV·s^{-1}.

I-V curves for the ITO/PTCBI/CoPc and Pt system are shown with the negative (a) and positive (b) scans. In the negative scan, the I-V characteristics were almost independent of irradiation, where an onset potential was observed to appear around at –0.2 V vs. Pt. This is reasonable because the magnitude of the dark catalysis (active species: Co^{II}Pc, Entry 1 in Table 1) was almost equal to that of the photocatalysis (active species: Co^{III}Pc, Entry 3 in Table 1) in terms of activity. Therefore, no change of the onset potential is considered to occur.

Time-course of currents generated at ITO/PTCBI/CoPc

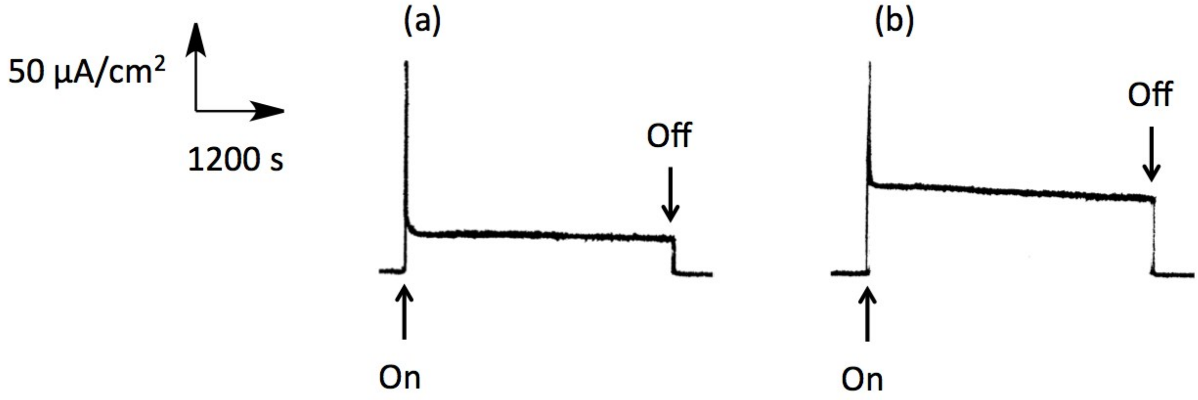

Fig. S2 Time-course of currents generated at ITO/PTCBI/CoPc in the dark (a) and under illumination (b). Employing the conditions of the Entries 1 and 2 in Table 1, the I-T curves were measured, where no electric bias was applied for the system.

Absorption spectra of PTCBI/CoPc bilayer before and after catalytic reaction

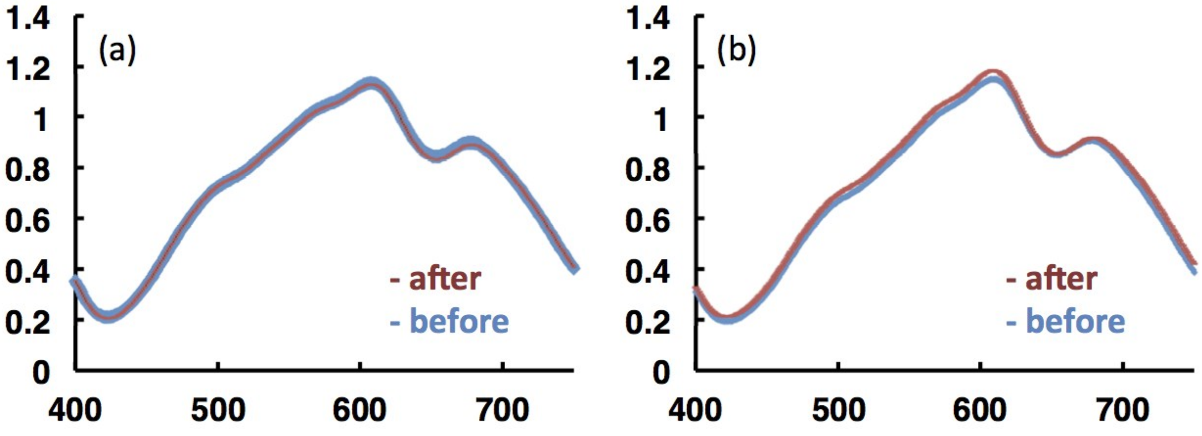

Fig. S3 Absorption spectra of PTCBI/CoPc bilayer before and after the catalytic reactions under illumination (a) and in the dark (b). The red-colored absorption spectrum was measured after the catalytic reaction under the condition of Entry 1 or Entry 2 in Table 1.