Electronic Supplementary Information (ESI)

High performance photoanodic catalyst prepared from an active organic photovoltaic cell -high potential gain from visible light-

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**Experimental details**

Regioregular poly(3-hexylthiophene) (P3HT) (Mn 54,000–75,000) was purchased from Sigma-Aldrich. Poly(3,4-ethylenedioxylenethiophene):poly(4-styrene sulfonic acid) (PEDOT:PSS) dispersion in water (Clevios® P) (1.3 wt %) was purchased from H.C. Starck. PCBM and ZnPc were purchased from Frontier Carbon and Tokyo Kasei Co., Ltd, respectively. These were used as received. All of the other reagents were of the extra-pure grade. Glass–ITO substrates (sheet esistance = 10 Ω sq⁻¹) was purchased from Furuuchi Chemical.

An ITO/ZnO/PCBM:P3HT (4:5 by weight)/PEDOT:PSS/Au organic photovoltaic cell (OPV) was fabricated in air and was mechanically protected by lamination with a film (moisture-proof sheet “CELLEL F1550H,” Kureha Extech Co., Ltd.) at 150 °C for 5 min under reduced pressure, as described elsewhere [S1], and its I-V curves under illumination (Figure S1 in the supplement information) and in the dark were identical with the reported there. After removing the PEDOT:PSS/Au coated film mechanically, the ITO/ZnO/PCBM:P3HT electrode was dipped into water to remove water-soluble PEDOT:PSS which slightly lefts on the PCBM:P3HT film. The electrode is denoted as a BHJ electrode. After drying the electrode, ZnPc layer was coated by vapor deposition (degree of pressure <1.0 × 10⁻³ Pa; deposition speed: 0.03 nm s⁻¹). The electrode is denoted as a ZnPc coated BHJ electrode.

Absorption spectra were acquired using a spectrophotometer (MCPD-7000, Otsuka). To measure cyclic voltammograms, rest potentials, and photocurrent action spectra, a single-compartment cell was used with a working electrode (effective area: 1 cm²), a Pt spiral wire as the counter electrode, and an Ag/AgCl (in saturated KCl electrolyte) as the reference electrode. The photovoltaic experiments were operated using a potentiostat (Hokuto Denko, HSV-100). The electrolyte was 2-mercaptoethanol (in KOH, pH 11) and was stirred during the measurement. Halogen light source (Megalight 100, SCHOTT) was used to irradiate white light, at intensity of 70 mW/cm², whose spectrum is shown in Figure S4. The monochromator (SM-GTD, BUNKOUKEIKI Co. Ltd.) was used for the action spectrum photocurrent measurement, with controlled photon number = 1 x 10¹⁶ photons cm⁻² s⁻¹.

The incident photon-to-current conversion efficiency (IPCE) was calculated using the following equation:

\[
\text{IPCE} (\%) = \left\{ \left[ \frac{I_{\text{light}} - I_{\text{dark}}}{e} \right] / \left[ W / e \right] \right\} \times 100
\]  

(S1)
where $I_{\text{light}}$ (A·cm$^{-2}$) and $I_{\text{dark}}$ are the photocurrent and dark current density, respectively, $e$ (C) is the elementary electric charge, $W$ (W·cm$^{-2}$) is the light intensity, and $\varepsilon$ is the photon energy of a monochromatic light.

Atomic force microscopy (AFM) observations were performed in ambient condition with an Asylum Cypher S with a controller to stabilize environment temperature. The operation mode for the scanning Kelvin probe force microscopy (SKPM) measurement was based on the amplitude modulation (AM) mode. The non-contact mode cantilevers (OCML-AC240TM, OLYMPUS) were used with typical resonant frequency and spring constant about 70 kHz and 2 N/m, respectively. The tip-sample distance and applied AC voltage were set to 50 nm and 3 V, respectively.

Figure S1.  \textit{I-V} curve under 1 sun illumination of AM-1.5G for an inverted type ITO/ZnO/(PCBM:P3HT)/PEDOT:PSS/Au OPV device. The $J_{sc}$, $V_{oc}$, $FF$ and PCE are 9.50 mA/cm$^2$, 0.58 V, 0.61 and 3.35\%, respectively.

Other characteristics such as action spectra of incident photon-to-current efficiency (IPCE) are shown in the literature below.

Figure S2. FESEM images for (a) crosssection and (b) surface of the BHJ electrode ITO/ZnO/(PCBM:P3HT).
Figure S3  Visible-near infrared absorption spectra for the BHJ electrode, ZnPc coated BHJ electrode, ITO/ZnPc, and ITO.
Figure S4. Spectrum of white light using the experiments in Figs 1, S5 and S8. The light source was a halogen lamp irradiated through a thermal cut filter and neutral density filters to adjust the light intensity. The integrated light intensity was 20 mW/cm², and the photon quanta was estimated to be $3.1 \times 10^{16}/(s \text{ cm}^2)$ from the spectrum.
Figure S5 Cyclic voltammograms for the BHJ (a) and ZnPc coated BHJ (b) electrodes for the scan rate of 20 mV/s. Concentration of 2-mercaptoethanol (thiol), 10 mM (pH = 11); light intensity, 70 mW/cm² (Fig. S4); thickness of ZnPc, 8 nm.
Figure S6. Potential diagram for the ZnPc coated BHJ electrode in the dark. These values are shown in elsewhere [S2, S3].

Figure S7. Cyclic voltammogram for the ZnPc electrode in the dark. Scan rate, 20 mV/s.
Figure S8 Rest potential change for the white light illumination (70 mW/cm$^2$). The arrows show the time to start light illumination.

Discussion for the Figure.

Figure S8 shows the rest potential depending on time. Initially the experimental set up was kept in the dark, and the white light was illuminated at the time shown as the arrows in the figure. The rest potential values were changed by the light illumination. While the BHJ and ZnPc coated BHJ electrodes exhibited shifts to negative potential direction, the ZnPc electrode did to positive potential direction. The difference would be caused by semiconductor polarity \[^{[S4]}\]. Because the ZnPc solid in air behaves as a p-type semiconductor, the ZnPc electrode forms a typical Schottky barrier junction between ZnPc layer and electrolyte. Since the light illumination induces an electron transfer to electrolyte from ZnPc, the generated holes in ZnPc were collected to ITO resulting about 0.03 V of positive potentials shift. The rest potential for the BHJ electrode was -0.25 V under the illumination compared to -0.1 V vs. Ag/AgCl in the dark. For the ZnPc coated BHJ electrode, it was slightly (0.05 V) more positive than that without ZnPc coating, that is, the shift values for the light illumination were almost similar regardless of the ZnPc coating. The photogenerated holes may be transferred to ZnPc from BHJ layer, and the remained electrons would be collected to ITO to result the rest potential shift to negative direction.