Supporting Information

Modification Effect of *meso*-Hexakis(pentafluorophenyl) [26]Hexaphyrin Aggregates on the Photocatalytic Water Splitting

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**Fig. S8** Amount of H$_2$ and O$_2$ formed on RhO$_x$ (0.1 wt%), NiO (0.1 wt%)/hexaphyrin 3 (0.5 wt%)/IrO$_2$(0.1 wt%)-GaN:ZnO as a function of reaction time under a 300 W Xe lamp (Full arc).

**Fig. S9** Photocurrent-potential characteristics of IrO$_2$-GaN:ZnO (blue) and hexaphyrin 3/ IrO$_2$-GaN:ZnO electrodes (red) measured (scan rate, 10 mV/s) with chopped light (300 mW/cm$^2$ Xe lamp, 0.5 Hz).
Experimental procedures

Photocatalyst preparation.

A GaN:ZnO solid solution was prepared according to a reported method.[13] A mixture of Ga$_2$O$_3$ (Koujundo Chemical Lab. Co., Ltd., 3.0 g) and ZnO (Koujundo Chemical Lab Co., Ltd., 2.6 g) was heated under NH$_3$ gas flow (200 mL min$^{-1}$) at 1143 K for 20 h on an alumina boat. The crystal structure of the obtained powder was confirmed as a wurtzite structure by X-ray diffraction (XRD) measurements (Figure S8). The IrO$_2$ co-catalyst was loaded on the GaN:ZnO powder by an evaporation to dryness method with a Na$_2$IrCl$_6$•6H$_2$O (Wako Pure Chemical Industry) aqueous solution. After calcination at 673 K for 1 h in air, IrO$_2$ (0.1 wt%)-GaN:ZnO was obtained. Expanded porphyrins were prepared in accordance with the literature.[12b] A solution of pentafluorobenzaldehyde (0.51 mL, 4.11 mmol) and pyrrole (0.26 mL, 4.11 mmol) in 60 mL of dichloromethane was placed in a 100 mL round-bottomed flask under nitrogen. To the solution, 30 $\mu$L of BF$_3$OEt$_2$ (0.26 mmol) was added, and the resulting mixture was stirred for 2 h. After adding DDQ, the solution was stirred for 10 h and then passed through a short alumina column. The reaction mixture was separated by silica gel column chromatography. The obtained expanded porphyrins were purified by recrystallization. The dye modification of IrO$_2$-GaN:ZnO was performed by an evaporation to dryness method with pyridine as the solvent. The IrO$_2$-GaN:ZnO powder was suspended in dye-solved pyridine (0.5 mM) and the solvent was evaporated to dryness by stirring with a glass rod at 400 K. The amounts of modification dyes were standardized as 0.5 wt% on the amount of IrO$_2$-GaN:ZnO in this study. Co-catalysts were loaded on the dye-modified IrO$_2$-GaN:ZnO by an evaporation to dryness method with an aqueous solution of Na$_3$RhCl$_6$•12H$_2$O (Mitsuwa Chemicals) and Ni(NO$_3$)$_2$•6H$_2$O (Kanto Chemical). The amounts of co-catalysts on the dye-modified GaN:ZnO photocatalyst were 0.1 wt%. Further details of the photocatalyst are described in the Supplementary Information.

Photocatalytic water splitting reaction.

Photocatalytic water splitting was performed with a closed circulating glass reactor. The catalyst (50 mg) was suspended in 30 mL of pure water, which was pre-saturated with argon gas. KOH was used to adjust the pH to 11. A quartz reaction cell including photocatalyst suspension was irradiated by a 300 W Xe lamp (Cermax PE300UV, Perkin Elmer Inc.). During the reaction, the suspension was mixed using a magnetic stir bar. Argon gas (10.67 kPa) was used as the circulating carrier gas. The amount of gases formed was measured by a gas chromatograph with a thermal conductivity detector (GC-8A, Shimadzu Corp.), which was connected to a volumetric circulating line with a vacuum pump.

UV-Vis and Fluorescence spectroscopy.

UV-vis absorption spectra were obtained by a transmission method or a reflection method using a spectrometer (U-3310, Hitachi High-Tech. Corp.) with an integrating sphere attachment. A KBr pellet was used as the reference. Fluorescence spectra were measured with a spectrophotofluorometer (F-7000, Hitachi High-Tech. Corp.).

Fluorescence lifetime measurements.

The fluorescence lifetime was measured using a lifetime spectrofluorometer (Fluorocube, Horiba Co., Ltd.) with a pulsed light emitting diode ($\lambda = 370$ nm) as the excitation light source. A band-pass filter (600 nm) was used to remove the influence of the excitation light and the fluorescence from the porphyrin dye. The powder sample was placed in a quartz cell with a screw cap. The measurements were performed at room temperature.

Cyclic voltammetry.

Cyclic voltammetry was performed using an automatic polarization system (HSV-100, Hokuto Denko Corp.) with a three-electrode configuration consisting of a Pt-wire working electrode ($\varnothing = 0.3$ mm), a Pt-wire counter electrode, and a commercially available Ag/AgCl electrode as a reference electrode. Porphyrins were dissolved in CH$_2$Cl$_2$ containing 0.1 M tetrabutylammonium perchlorate (Strem Chemicals, Inc.) as a supporting electrolyte. Sample solutions were presaturated with N$_2$, and the measurements were performed under N$_2$ atmosphere. The sweep rates were 50-100 mV/s. Redox potential values were calculated as the average of the anodic and cathodic peak potentials, $(E_{pa} + E_{pc})/2$, and converted to those versus normal hydrogen electrode (NHE).

TEM observations

TEM observations and STEM-EDX analyses were performed at an acceleration voltage of 200 kV (JSM-ARM200F, JEOL Ltd.). The catalyst powder was dispersed on a Cu micro-grid (Nissin EM Corp.).
Preparation of GaN:ZnO electrodes

The GaN:ZnO film electrodes were prepared by electrophoretic method on conducting glass (FTO, Asahi Glass Co.). The electrophoretic method was performed in an aqueous solution (50 ml) containing GaN:ZnO powder (40 mg), which was dispersed by sonication for 10 minutes. Two FTO electrodes (2×3 cm) were immersed parallel in the solution with 10 mm of distance, and then 50 V of bias was applied for 3 min using a DC power supply (GPR-11H30D, Good Will Instrument Co., Ltd.). The area of GaN:ZnO film was controlled to be ca. 2×2.5 cm. The average weight of GaN:ZnO deposited on FTO was 10 mg. The IrO$_2$ co-catalyst was loaded on the GaN:ZnO powder by an evaporation to dryness method with a Na$_2$IrCl$_6$•6H$_2$O (Wako Pure Chemical Industry) aqueous solution. The electrode was dried and then calcined at 673 K for 1 h. After the IrO$_2$ loading, porphyrin3-solved pyridine solution (0.05 mM) was dropped on the IrO$_2$-GaN:ZnO/FTO electrode and then dried at 400 K to evaporate the solvent.

Photoelectrochemical measurements

The electrochemical cell used for photocurrent measurements consisted of the dye-modified GaN:ZnO electrode, a counter electrode (Pt wire), a Ag/AgCl reference electrode, and an electrolyte (0.1 M Na$_2$SO$_4$ aqueous solution). The potential of the working electrode was controlled by the potentiostat (ECstat-300, EC Frontier Inc.). Sample solutions were presaturated with N$_2$, and the measurements were performed under N$_2$ atmosphere. The electrodes were irradiated through the conducting glass by a Xe lamp (300 W, Cermax PE300UV, Perkin Elmer Inc.).
**Fig. S1** UV-vis absorption spectra for compounds 1-6 in CH$_2$Cl$_2$ solvent.

**Table S1** Absorption maximum wavelengths and molar absorbance coefficients for synthesized porphyrin (1) and expanded porphyrins (2-6).

<table>
<thead>
<tr>
<th>Compound</th>
<th>$\lambda_{\text{max}}$/nm</th>
<th>$\varepsilon_{\text{max}}$/M$^{-1}$cm$^{-1}$</th>
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<tr>
<td>1</td>
<td>410</td>
<td>4.03×10$^4$</td>
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<tr>
<td>2</td>
<td>558</td>
<td>6.37×10$^4$</td>
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<tr>
<td>6</td>
<td>706</td>
<td>8.45×10$^4$</td>
</tr>
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</table>
General information of the porphyrin-modified GaN:ZnO photocatalyst

The crystal structure of the GaN:ZnO powder was confirmed as a wurtzite structure by X-ray diffraction (XRD) measurements [Fig. S2(a)]. As previously reported,[1] diffraction peaks for GaN:ZnO were observed between the peaks attributed to ZnO and GaN [Fig. S2(b)]. The Ga:Zn ratio in the GaN:ZnO powder was determined by an energy dispersive X-ray spectroscopy (EDX) analyzer attached to a scanning electron microscope (VE-7800, KEYENCE Corp.) as 88:12. The specific surface area of the GaN:ZnO powder measured by using a B.E.T. surface area analyzer (BELLSORP-mini, Bell Japan Inc.) with N$_2$ adsorption was 2.3 m$^2$g$^{-1}$.

**Fig. S2** XRD patterns for ZnO, GaN, and GaN:ZnO solid solutions prepared in this study (a), and expanded figure (b).

Reference
Fig. S3 TEM images of (a) meso-tetrakis(pentafluorophenyl)porphyrin (compound 1), (b) N-fused pentaphyrin (compound 2), (c) meso-hexakis(pentafluorophenyl) [26] hexaphyrin (compound 3), (d) meso-heptakis(pentafluorophenyl) heptaphyrin (compound 4) (e) meso-octakis(pentafluorophenyl) octaphyrin (compound 5), and (f) meso-nonakis(pentafluorophenyl) nonaphyrin (compound 6) on IrO$_2$-GaN:ZnO photocatalysts.
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**Fig. S5** Dye amount dependency of the photocatalytic activity of hexaphyrin 3 modified GaN:ZnO photocatalysts.
**Fig. S6** $^1$H NMR spectra of residual species of 3 after water splitting reaction. Asterisk denote impurities or spinning side band. Circle denote hexaphyrin. Closed circle denote new peaks after water splitting reaction.

**Fig. S7** $^1$H NMR spectra of residual species of blank condition (green), bulk hexaphyrin 3 (blue), after deposit of hexaphyrin 3 by solution process (black), and after water splitting reaction (black). Asterisk denote impurities or spinning side band. Circle denote hexaphyrin peaks. Closed circle denote new peaks after water splitting reaction.

**NMR measurements**

The $^1$HNMR were recorded on a Bruker AV400 (400 MHz). The $^1$H chemical shift was reported as $\delta$ values (ppm) relative to tetramethysilane (TMS).
Fig. S8 Amount of $H_2$ and $O_2$ formed on $\text{RhO}_x$ (0.1 wt%), $\text{NiO}$ (0.1 wt%)/hexaphyrin 3 (0.5 wt%)/$\text{IrO}_2$ (0.1 wt%)–GaN:ZnO as a function of reaction time under a 300 W Xe lamp (Full arc).
Fig. S9 Photocurrent-potential characteristics of IrO$_2$-GaN:ZnO (blue) and hexaphyrin 3/IrO$_2$-GaN:ZnO electrodes (red) measured (scan rate, 10 mV/s) with chopped light (300 mW/cm$^2$ Xe lamp, 0.5 Hz).

CE: Pt wire
RE: Ag/AgCl
Electrolyte: 0.1M Na$_2$SO$_4$ aq.
pH: 6.8
Sweep rate: 10 mV/s