



Visible light-driven hydrogen evolution using dye–semiconductor hybrids: effects of peripheral substituents and central metals of chlorophyll-*a* derivatives as photosensitizers

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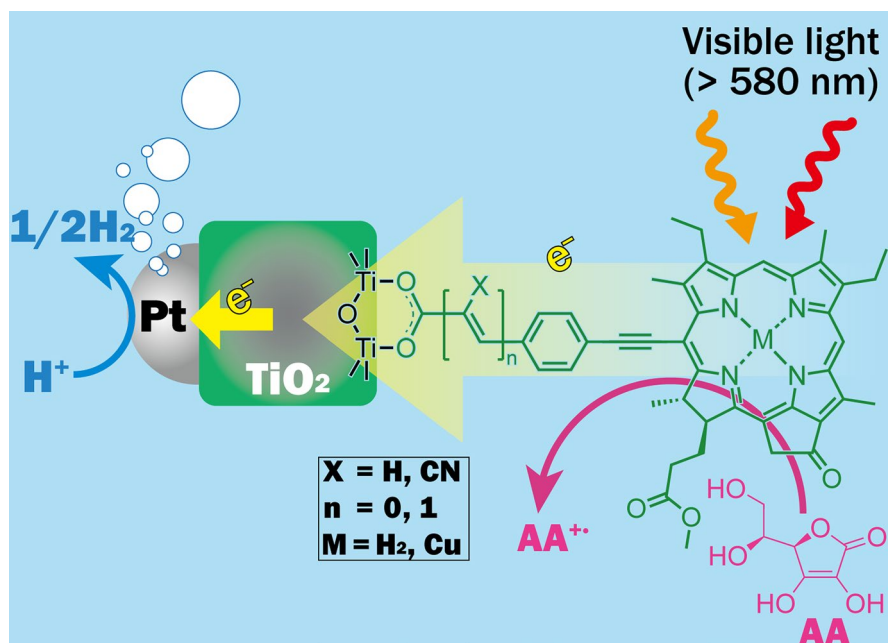
Abstract

Chlorophyll (Chl)-*a* derivatives possessing a carboxylated substituent at the peripheral 20-position were prepared as photosensitizers. The synthetic pigments were adsorbed onto the surface of titanium oxide particles loaded with platinum nanoparticles through the bonding of the carboxy group of the Chls with the oxygen functional groups of TiO₂. In an aqueous ascorbic acid solution, the resulting Chl-attaching Pt-TiO₂ was illuminated with orange and red light to generate hydrogen gas. The hydrogen evolution reaction was initiated by the electron injection of the Chl photosensitizers excited with the visible light to the TiO₂ semiconductor and was completed by the reduction of aqueous protons into H₂ on the Pt cocatalyst, while ascorbic acid functioned as an electron donor to the Chl species. The hydrogen evolution activity was dependent on the spacer between the core chlorin π -system and the terminal carboxy group in the Chls. An increase in the spacer length suppressed the undesired back electron transfer from the TiO₂ surface to the Chl cation radical to enhance the amount of evolved H₂. The facile insertion of a copper atom at the central position of a Chl sensitizer boosted the photocatalytic activity, but its zincation and nickelation diminished the photosensitizing abilities.

Dedicated to the late Professor Katsuhiko Takagi

Extended author information available on the last page of the article

Graphical abstract



Keywords Carboxylated chlorophylls · Dye sensitization · Hydrogen evolution reaction · Metal complexes · Substitution effect · TiO_2 semiconductor

Introduction

Fossil fuels including coal (solid), petroleum (liquid), and natural gas are utilized all over the world. After the combustion of these fuels, heat energy is obtained, but carbon dioxide gas causing global warming and toxic gases such as NO_x and SO_x are produced concomitantly. To avoid their production, hydrogen gas has been focused as an alternative fuel, because its combustion gave sole water along with a large amount of heat (286 kJ mol^{-1} , 33.9 kcal g^{-1}). At present, hydrogen fuel is primarily supplied by chemical modification of fossil fuels, so undesired CO_2 is inevitably generated as the by-product. Such hydrogen gas obtained cost-effectively is thus called gray hydrogen. Before release of CO_2 gas into environmental atmosphere, the greenhouse gas is captured or stored to make blue hydrogen. Green hydrogen produced from water and renewable energy is highly desired. In particular, solar energy is attracted from the generation of green hydrogen. Electrolysis of water using solar battery is one of the green hydrogen productions, which required two systems. Photolysis of water requisite for only one system is simple and was first reported by Fujishima and Honda [1]. Illumination with ultraviolet (UV) light on the surface of titanium oxide succeeded water photolysis into oxygen and hydrogen gases. Since

UV light is limited for the solar spectrum, photolysis of water using illumination with visible (Vis) light as the major part of solar radiation on the Earth has been developed by band gap engineering [2, 3] and dye-adsorbed semiconductor catalysis [4–6].

A variety of organic dyes and pigments are utilized as Vis light-absorbing sensitizers on photocatalysts for hydrogen evolution reactions (HERs) [7, 8]. For example, eosin Y (a commercially available dye) [9] and an acrylated phenothiazine (a synthetic pigment) [10] were adsorbed on platinum-loaded titanium oxide particles through the interaction of their carboxy groups with the TiO_2 surface. When the resulting particles in an aqueous solution of triethanolamine (TEOA) were illuminated with Vis light, hydrogen gas was generated by the reduction of the protons in the aqueous solution. In the systems, Pt was a cocatalyst for HER, and TEOA was a sacrificial agent for an electron donor toward the sensitizers. Recently, some C3-acrylated derivatives of naturally occurring chlorophyll (Chl) pigments (compounds A in Fig. 1) were employed as the HER sensitizers due to their ready availability and environmental friendliness [11–16]. The methyl ester at the C17-propionate residue ($\text{R}'=\text{Me}$ in compound A) was typical of the HER in an aqueous ascorbic acid (AA, an electron-donating reagent) solution ($\text{pH}=2.8$) to give H_2 at $0.39 \text{ mmol g}^{-1} \text{ h}^{-1}$ under $>580 \text{ nm}$ light illumination [14]. Instead of the Pt- TiO_2 particles, two-dimensional MXene nanosheets of Nb_2CT_x without any cocatalyst could be utilized as the HER catalyst [17]. Self-aggregates of zinc Chl-*a* derivative (compound B) [18, 19] or the other Chl pigments [20] on another $\text{Ti}_3\text{C}_2\text{T}_x$ MXene with(out) cocatalysts (graphitic C_3N_4 [21] or Cu_2O particles [22]) were furthermore effective as dye-sensitized HER catalysts.

In our previous report [23], Chl-*a* derivatives possessing carboxylated substituents at the 20-position (compounds C in Fig. 1) were examined as the photosensitizers for the Pt- TiO_2 -type HER systems. Such C20 substituents with a carboxy terminal were also useful for the anchors of the sensitizers similarly to the aforementioned C3 substituent. Methyl 20-[(4-carboxyphenyl)ethynyl] mesopyropheophorbide-*a* (H_2 -**1a**, $\text{Y}=\text{C}\equiv\text{C}-p\text{-C}_6\text{H}_4$ of compound C) afforded a better performance for the HER on Pt- TiO_2 in aqueous AA than its isomer ($\text{Y}=p\text{-C}_6\text{H}_4\text{-C}\equiv\text{C}$), its

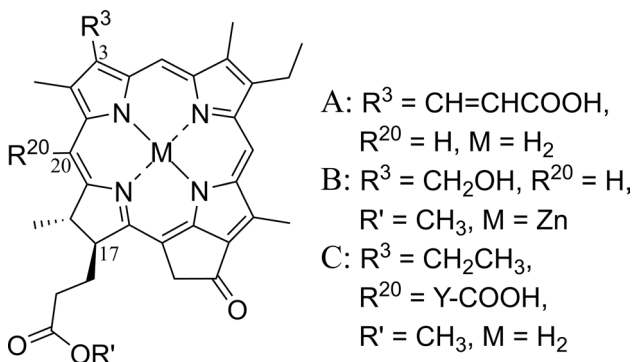


Fig. 1 Chl-*a* derivatives as the HER photosensitizers

deethynylated derivative ($Y = p\text{-C}_6\text{H}_4$), and its dephenylated counterpart ($Y = \text{C}\equiv\text{C}$). Herein, we report the HER activities of synthetic free base 20-arylethynylated analogs of $\text{H}_2\text{-1a}$ and its metal complexes. The HER effects of the peripheral C20 substituents ($Y = \text{C}\equiv\text{C-C}_6\text{H}_4\text{-Z-COOH}$ of compound C) and the central metals (M) were revealed.

Experimental

General

All melting points were measured with a Yanaco MP-S3 micromelting apparatus and were uncorrected. UV–Vis absorption spectra in a solution were measured by a Hitachi U-3500 spectrophotometer. Fluorescence emission spectra excited at Soret maxima and lifetimes excited at 403 nm were obtained by a Hamamatsu Photonics C9920-03G spectrometer and a Hamamatsu Photonics C7990S system, respectively. ^1H NMR spectra were recorded by a JEOL AL400 (400 MHz) or ECA-600 (600 MHz) spectrometer; tetramethylsilane ($\delta = 0.00$ ppm) was an internal standard in CDCl_3 or $(\text{CD}_3)_2\text{SO}$ ($\text{DMSO-}d_6$), and residual pentadeutero-acetone ($\delta = 2.05$ ppm) was used as a standard. Mass spectra (MS) were obtained using laser desorption/ionization (LDI) in positive mode by a Shimadzu AXIMA-CFR+ spectrometer. High-resolution mass spectra (HRMS) were recorded on a Bruker micrOTOF II spectrometer: atmospheric pressure chemical ionization (APCI) or electrospray ionization (ESI) and positive mode in acetonitrile.

Chl-*a* derivative $\text{H}_2\text{-1a}$ [23] and methyl 20-bromo-mesopyropheophorbide-*a* ($\text{H}_2\text{-4}$) [24–27] were prepared according to reported procedures. Flash column chromatography (FCC) was performed with silica gel (Wakogel C-300, 45–75 μm). Dry *N,N*-dimethylformamide (DMF) was obtained as super dehydrated grade from FUJIFILM Wako Pure Chemical. Dichloromethane and pyridine for optical measurements were purchased from Nacalai Tesque as reagents prepared specially for spectrometry and used without further purification.

Molecular structures of Chl-*a* derivatives were optimized by density functional theory (DFT) calculation [28]. The excitation energies were estimated by time-dependent (TD) DFT with the CAM-B3LYP exchange–correlation functional based on the Gaussian 16 W program. The basis set was used the effective core potential 6–31(D) for C, H, N, and O atoms and LanL2DZ for Ni, Cu, and Zn atoms.

Synthesis of methyl 20-[(4-formylphenyl)ethynyl]mesopyropheophorbide-*a* ($\text{H}_2\text{-3}$)

20-Bromo-chlorin $\text{H}_2\text{-4}$ (20.5 mg, 32.6 μmol), 4-ethynylbenzaldehyde (11.2 mg, 86.1 μmol), tris(dibenzylideneacetone)dipalladium(0) [$\text{Pd}_2(\text{dba})_3$, 7.1 mg, 7.8 μmol], and tri(*o*-tolyl)phosphine [$(o\text{-tol})_3\text{P}$, 9.8 mg, 28.8 μmol] were placed in a two-necked round flask, whose inside was fully replaced with argon gas. After the addition of triethylamine (0.5 ml) and dry DMF (1.5 ml), the solution was stirred at

70 °C for 3 h in the dark [23]. The reaction mixture was cooled down to room temperature (rt), and all the solvents were evaporated in vacuo. The residue was purified with FCC (CH_2Cl_2 : Et_2O = 100 : 0.5–4) and precipitation (CH_2Cl_2 and hexane) to give 20-adduct $\text{H}_2\text{-3}$ (8.2 mg, 12.1 μmol , 37%): bluish black solid; 276–278 °C; Vis (CH_2Cl_2) $\lambda_{\text{max}}/\text{nm}$ = 680 (relative intensity, 0.29), 623 (0.11), 574 (0.19), 426 (1.00); ^1H NMR (CDCl_3 , 400 MHz) δ/ppm = 10.12 (1H, s, 4-CHO of 20^2-Ph), 9.36 (1H, s, 10-H), 9.23 (1H, s, 5-H), 8.04 (2H, d, J = 8 Hz, 3,5-H of 20^2-Ph), 7.94 (2H, d, J = 8 Hz, 2,6-H of 20^2-Ph), 5.15, 5.08 (each 1H, d, J = 19 Hz, 13^2-CH_2), 4.82 (1H, q, J = 7 Hz, 18-H), 4.17 (1H, dd, J = 8, 2 Hz, 17-H), 3.83 (2H, q, J = 8 Hz, 3- CH_2), 3.62 (2H, q, J = 8 Hz, 8- CH_2), 3.61 (3H, s, 2- CH_3), 3.60 (3H, s, 12- CH_3), 3.58 (3H, s, 17^2-COOCH_3), 3.21 (3H, s, 7- CH_3), 2.60–2.49, 2.23–2.16 (each 2H, m, 17- CH_2CH_2), 1.75 (3H, d, J = 7 Hz, 18- CH_3), 1.71 (3H, t, J = 8 Hz, 8^1-CH_3), 1.67 (3H, t, J = 8 Hz, 3^1-CH_3), –0.68 (1H, s, NH) [Another NH signal was invisible.]; HRMS (APCI) found: m/z = 679.3270, calcd. for $\text{C}_{43}\text{H}_{43}\text{N}_4\text{O}_4$: MH^+ , 679.3279.

Synthesis of methyl 20-{4-[2-(*tert*-butoxycarbonyl)ethenyl]phenyl} ethynyl-mesoporphorophorbide-*a* ($\text{H}_2\text{-2}$)

Aldehyde $\text{H}_2\text{-3}$ (21.6 mg, 31.8 μmol) and (*tert*-butoxycarbonylmethylene) triphenylphosphorane (35.4 mg, 94.0 μmol) were dissolved in toluene (20 ml), and the solution was refluxed for 3 h under argon in the dark [29]. After cooled to rt, all the solvent was evaporated in vacuo, and the residue was purified with FCC (CH_2Cl_2 : Et_2O = 100: 0.5–4) and precipitation (CH_2Cl_2 and hexane) to give 20-adduct $\text{H}_2\text{-2}$ (22.9 mg, 29.5 μmol , 93%): bluish black solid; mp 167–169 °C; Vis (CH_2Cl_2) $\lambda_{\text{max}}/\text{nm}$ = 679 (relative intensity, 0.31), 622 (0.10), 582 (0.20), 427 (1.00); ^1H NMR (CDCl_3 , 600 MHz) δ/ppm = 9.36 (1H, s, 10-H), 9.22 (1H, s, 5-H), 7.81 (2H, d, J = 8 Hz, 3,5-H of 20^2-Ph), 7.68 (1H, d, J = 15 Hz, 4-CH of 20^2-Ph), 7.67 (2H, d, J = 8 Hz, 2,6-H of 20^2-Ph), 6.48 (1H, d, J = 15 Hz, 4-CCH of 20^2-Ph), 5.15, 5.09 (each 1H, d, J = 19 Hz, 13^1-CH_2), 4.81 (1H, q, J = 7 Hz, 18-H), 4.16 (1H, dd, J = 9, 3 Hz, 17-H), 3.83 (2H, q, J = 8 Hz, 3- CH_2), 3.63 (2H, q, J = 8 Hz, 8- CH_2), 3.61 (3H, s, 2- CH_3), 3.60 (3H, s, 12- CH_3), 3.57 (3H, s, 17^2-COOCH_3), 3.21 (3H, s, 7- CH_3), 2.58–2.50, 2.23–2.16 (each 2H, m, 17- CH_2CH_2), 1.74 (3H, d, J = 7 Hz, 18- CH_3), 1.71 (3H, t, J = 8 Hz, 8^1-CH_3), 1.67 (3H, t, J = 8 Hz, 3^1-CH_3), 1.58 (9H, s, $\text{C}(\text{CH}_3)_3$), –0.75 (1H, s, NH) [Another NH signal was invisible.]; HRMS (APCI) found: m/z = 777.4004, calcd. for $\text{C}_{49}\text{H}_{53}\text{N}_4\text{O}_5$: MH^+ , 777.4010.

Synthesis of methyl 20-{[4-(2-carboxyethenyl) phenyl] ethynyl} mesoporphorophorbide-*a* ($\text{H}_2\text{-1b}$)

Tert-butyl ester $\text{H}_2\text{-2}$ (21.0 mg, 27.0 μmol) was dissolved in trifluoroacetic acid (TFA, 10 ml), and the solution was stirred at rt for 2 h under nitrogen in the dark [29]. The reaction mixture was diluted with chloroform, neutralized with an aqueous solution saturated with sodium hydrogen carbonate, washed with distilled water, dried over sodium sulfate, and filtrated. After evaporation, the residue was precipitated from dichloromethane and hexane to give carboxylic acid $\text{H}_2\text{-1b}$

(16.6 mg, 23.0 μmol , 85%): bluish black solid; mp > 300 °C; Vis (CH_2Cl_2) $\lambda_{\text{max}}/\text{nm}$ = 679 (relative intensity, 0.31), 622 (0.10), 582 (0.20), 427 (1.00); ^1H NMR ($\text{DMSO}-d_6$, 600 MHz) δ/ppm = 9.50 (1H, s, 10-H), 9.15 (1H, s, 5-H), 7.90 (2H, d, J = 8 Hz, 3,5-H of 20^2-Ph), 7.86 (2H, d, J = 8 Hz, 2,6-H of 20^2-Ph), 7.71 (1H, d, J = 16 Hz, 4-CH of 20^2-Ph), 6.68 (1H, d, J = 16 Hz, 4-CCH of 20^2-Ph), 5.09, 5.02 (each 1H, d, J = 19 Hz, 13^1-CH_2), 4.78 (1H, q, J = 7 Hz, 18-H), 4.16 (1H, br-d, J = 10 Hz, 17-H), 3.68 (2H, q, J = 8 Hz, 3- CH_2), 3.54 (2H, q, J = 8 Hz, 8- CH_2), 3.50 (3H, s, 17^2-COOCH_3), 3.48 (3H, s, 12- CH_3), 3.45 (3H, s, 2- CH_3), 3.09 (3H, s, 7- CH_3), 2.64–2.58, 2.39–2.31, 1.94–1.87 (1H + 2H + 1H, m, 17- CH_2CH_2), 1.63 (3H, d, J = 7 Hz, 18- CH_3), 1.56, 1.55 (each 3H, t, J = 8 Hz, 3^1- , 8^1-CH_3), –1.20 (1H, s, NH) [Another NH and COOH signals were invisible.]; HRMS (ESI) found: m/z = 721.3377, calcd. for $\text{C}_{45}\text{H}_{45}\text{N}_4\text{O}_5$: MH^+ , 721.3384.

Synthesis of methyl 20-[(4-(2-carboxy-2-cyanoethenyl)phenyl)ethynyl-mesopyropheophorbide-a ($\text{H}_2\text{-1c}$)

Aldehyde $\text{H}_2\text{-3}$ (23.6 mg, 34.8 μmol) was dissolved in tetrahydrofuran (THF, 25 ml), to which were added cyanoacetic acid (560 mg, 6.58 mmol) and piperidine (289 μl , 2.92 mmol). The resulting solution was refluxed for 2 h under argon in the dark, cooled down to rt, and evaporated [30]. The residue was dissolved in dichloromethane, washed with distilled water, dried over sodium sulfate, and fully evaporated in vacuo. The residue was purified with FCC (CH_2Cl_2 : MeOH = 100 : 0.5–5) and precipitation (CH_2Cl_2 and hexane) to give $\text{H}_2\text{-3}$ (1.7 mg, 2.5 μmol , 7% recovery) and adduct $\text{H}_2\text{-1c}$ (23.6 mg, 31.6 μmol , 91%) in 98% based on recovered starting material (brsm): bluish black solid; mp > 300 °C; Vis (CH_2Cl_2) $\lambda_{\text{max}}/\text{nm}$ = 679 (relative intensity, 0.33), 622 (0.13), 579 (0.22), 425 (1.00); ^1H NMR (acetone- d_6 , 600 MHz) δ/ppm = 9.67 (1H, s, 10-H), 9.39 (1H, s, 5-H), 8.41 (1H, s, 4-CH of 20^2-Ph), 8.29 (2H, d, J = 8 Hz, 3,5-H of 20^2-Ph), 8.10 (2H, d, J = 8 Hz, 2,6-H of 20^2-Ph), 5.15, 5.11 (each 1H, d, J = 19 Hz, 13^1-CH_2), 5.03 (1H, q, J = 7 Hz, 18-H), 4.33 (1H, dd, J = 10, 3 Hz, 17-H), 3.90 (2H, q, J = 8 Hz, 3- CH_2), 3.68 (2H, q, J = 8 Hz, 8- CH_2), 3.66 (3H, s, 2- CH_3), 3.57 (3H, s, 12- CH_3), 3.53 (3H, s, 17^2-COOCH_3), 3.22 (3H, s, 7- CH_3), 2.75–2.69, 2.60–2.54, 2.46–2.41, 2.19–2.15 (each 1H, m, 17- CH_2CH_2), 1.80 (3H, d, J = 7 Hz, 18- CH_3), 1.71 (3H, t, J = 8 Hz, 8^1-CH_3), 1.65 (3H, t, J = 8 Hz, 3^1-CH_3), –0.83 (1H, s, NH) [Another NH and COOH signals were invisible.]; HRMS (ESI) found: m/z = 746.3340, calcd. for $\text{C}_{46}\text{H}_{44}\text{N}_5\text{O}_5$: MH^+ , 746.3337.

Synthesis of methyl 20-[(3-carboxyphenyl) ethynyl]mesopyropheophorbide-a ($\text{H}_2\text{-1d}$)

Similar to the synthesis of $\text{H}_2\text{-3}$, palladium-catalyzed cross-coupling of $\text{H}_2\text{-4}$ (22.2 mg, 35.3 μmol) with 3-ethynylbenzoic acid (11.0 mg, 75.3 μmol) in triethylamine (5 ml) and dry DMF (15 ml) for 1.5 h and purification with FCC (CH_2Cl_2 : MeOH = 95 : 5) and precipitation (CH_2Cl_2 and hexane) to give 20-adduct $\text{H}_2\text{-1d}$ (11.4 mg, 16.4 μmol , 47%): bluish black solid; mp > 300 °C; Vis (CH_2Cl_2) $\lambda_{\text{max}}/\text{nm}$ = 677 (relative intensity, 0.35), 619 (0.10), 571 (0.20), 422 (1.00); ^1H NMR ($\text{DMSO}-d_6$, 600 MHz) δ/ppm

ppm=9.54 (1H, s, 10-H), 9.15 (1H, s, 5-H), 8.37 (1H, s, 2-H of 20²-Ph), 8.09, 8.08 (each 1H, d, $J=7$ Hz, 4-, 6-H of 20²-Ph), 7.73 (1H, t, $J=7$ Hz, 5-H of 20²-Ph), 5.10, 5.02 (each 1H, d, $J=19$ Hz, 13¹-CH₂), 4.80 (1H, q, $J=7$ Hz, 18-H), 4.18 (1H, dd, $J=10, 2$ Hz, 17-H), 3.69 (2H, br-q, $J=7$ Hz, 3-CH₂), 3.56 (2H, br-q, $J=7$ Hz, 8-CH₂), 3.50 (3H, s, 12-CH₃), 3.49 (3H, s, 17²-COOCH₃), 3.47 (3H, s, 2-CH₃), 3.10 (3H, s, 7-CH₃), 2.62–2.56, 2.42–2.29, 1.98–1.89 (1H+2H+1H, m, 17-CH₂CH₂), 1.65 (3H, d, $J=7$ Hz, 18-CH₃), 1.56 (6H, t, $J=7$ Hz, 3¹-, 8¹-CH₃), –1.24 (1H, s, NH) [Another NH and the COOH signals were invisible.]; MS (APCI) found: $m/z=695.3$, calcd. for C₄₃H₄₃N₄O₅: MH⁺, 695.3.

Synthesis of nickel methyl 20-(4-carboxyphenylethynyl) mesopyropheorbide-*a* (Ni-1a)

Free base H₂-1a (30.1 mg, 43.3 μmol) was dissolved in 1,2-dichloroethane (10 ml), to which was added a methanolic solution (10 ml) of nickel(II) acetate tetrahydrate (100 mg). The solution was fully dispersed with nitrogen gas, refluxed for 15 h in the dark, cooled down to rt, washed with distilled water, dried over sodium sulfate [31]. After evaporation in vacuo, the residue was purified with FCC (CH₂Cl₂ : MeOH=95 : 5) and precipitation (acetone and hexane) to give nickel complex Ni-1a (7.1 mg, 9.5 μmol, 22%): dark green solid; mp>300 °C; Vis (CH₂Cl₂) λ_{max}/nm=660 (relative intensity, 0.54), 617 (0.18), 570 (0.19), 428 (1.00); ¹H NMR (600 MHz, DMSO-*d*₆) δ/ppm=9.31, 8.92 (each 1H, s, 5-, 10-H), 8.08 (2H, d, $J=8$ Hz, 3,5-H of 20²-Ph), 7.84 (2H, d, $J=8$ Hz, 2,6-H of 20²-Ph), 4.85, 4.59 (each 1H, d, $J=20$ Hz, 13²-CH₂), 4.72 (1H, q, $J=7$ Hz, 18-H), 3.94 (1H, t, $J=7$ Hz, 17-H), 3.56, 3.51 (each 2H, q, $J=7$ Hz, 3-, 8-CH₂), 3.47 (3H, s, 17²-COOCH₃), 3.33 (3H, s, 12-CH₃), 3.27 (3H, s, 2-CH₃), 3.04 (3H, s, 7-CH₃), 2.5–2.4, 2.0–1.9 (each 2H, m, 17-CH₂CH₂), 1.50, 1.47 (each 3H, t, $J=7$ Hz, 3¹-, 8¹-CH₃), 1.42 (3H, d, $J=7$ Hz, 18-CH₃) [The COOH signal was invisible.]; MS (ESI) found: $m/z=751.2424$, calcd. for C₄₃H₄₁N₄O₅Ni: MH⁺, 751.2425.

Synthesis of copper methyl 20-(4-carboxyphenylethynyl) mesopyropheorbide-*a* (Cu-1a)

Similar to the synthesis of Ni-1a, H₂-1a (30.1 mg, 43.3 μmol) in dichloromethane (10 ml) was metalated with a methanolic solution (10 ml) of copper(II) acetate monohydrate (100 mg) with stirring at rt for 30 min to give Cu-1a (30.7 mg, 40.6 μmol, 94%): dark green solid; mp>300 °C; Vis (CH₂Cl₂) λ_{max}/nm=663 (relative intensity, 0.57), 616 (0.16), 575 (0.18), 432 (1.00), 420 (0.98); MS (ESI) found: $m/z=756.2364$, calcd. for C₄₃H₄₁N₄O₅Cu: MH⁺, 756.2367.

Synthesis of zinc methyl 20-(4-carboxyphenylethynyl)mesopyropheorbide-*a* (Zn-1a)

Similar to the synthesis of Ni-1a, H₂-1a (10.0 mg, 14.4 μmol) in dichloromethane (20 ml) was metalated with a methanolic solution (2 ml) saturated with zinc(II) acetate dihydrate with stirring at rt for 1 h. The reaction mixture was washed with

an aqueous solution saturated with sodium hydrogen carbonate and distilled water, dried over sodium sulfate. After evaporation in vacuo, the residue was purified with FCC (CH_2Cl_2 : MeOH = 95 : 5) and precipitation (CH_2Cl_2 and hexane) to give zinc complex **Zn-1a** (7.1 mg, 9.4 μmol , 65%): dark green solid; mp > 300 °C; Vis (CH_2Cl_2 –1% $\text{C}_5\text{H}_5\text{N}$) $\lambda_{\text{max}}/\text{nm}$ = 668 (relative intensity, 0.53), 636 (0.18), 437 (1.00); ^1H NMR (CDCl_3 –3% $\text{C}_5\text{D}_5\text{N}$, 600 MHz) δ/ppm = 9.39 (1H, s, 10-H), 9.24 (1H, s, 5-H), 8.40 (2H, br, 3,5-H of 20^2-Ph), 7.86 (2H, br, 2,6-H of 20^2-Ph), 5.16, 5.10 (2H, d, J = 20 Hz, 13^1-CH_2), 4.85 (1H, br-q, 18-H), 4.17 (1H, br-d, 17-H), 3.85 (2H, br-q, 3- CH_2), 3.65 (2H, br-q, 8- CH_2), 3.64 (3H, s, 12- CH_3), 3.62 (3H, s, 17 2 - COOCH_3), 3.57 (3H, s, 2- CH_3), 3.22 (3H, s, 7- CH_3), 2.2–2.1 (4H, m, 17- CH_2CH_2), 1.77 (3H, d, J = 8 Hz, 18- CH_3), 1.72, 1.68 (3H, d, J = 8 Hz, 8^1 -, 3^1-CH_3) [The COOH signal was invisible.]; MS (LDI) found: m/z = 757.26, calcd. for $\text{C}_{43}\text{H}_{41}\text{N}_4\text{O}_5\text{Zn}$: MH^+ , 757.24.

Photocatalyst preparation

One gram of commercially available TiO_2 powder (Evonik P-25, 55 $\text{m}^2 \text{g}^{-1}$) was suspended in an aqueous 20% methanol solution (125 ml) of $\text{H}_2\text{PtCl}_6 \cdot 6\text{H}_2\text{O}$ (26.8 mg, 51.8 μmol) and irradiated for 2 h with UV–Vis light (300–500 nm) from a 300 W Xe lamp (PerkinElmer; Cermex-PE300BF). During the illumination, all the amounts of Pt ion were reduced to metallic Pt nanoparticles on the TiO_2 surface. The obtained powders were thoroughly washed with pure water and dried in air to give 1 wt% Pt-loaded TiO_2 particles. The Pt- TiO_2 powder (0.1 g) was dispersed in a mixed acetonitrile (15 ml) and *tert*-butyl alcohol (15 ml) solution of Chl-*a* derivative photosensitizers (0.48 μmol). The suspension was stirred for 24 h in the dark using a rotary evaporator. The obtained powders were filtered, washed with the acetonitrile/*tert*-butyl alcohol mixture, and dried in vacuum overnight at rt. All the dyes were adsorbed on the particle, because the filtrates were colorless.

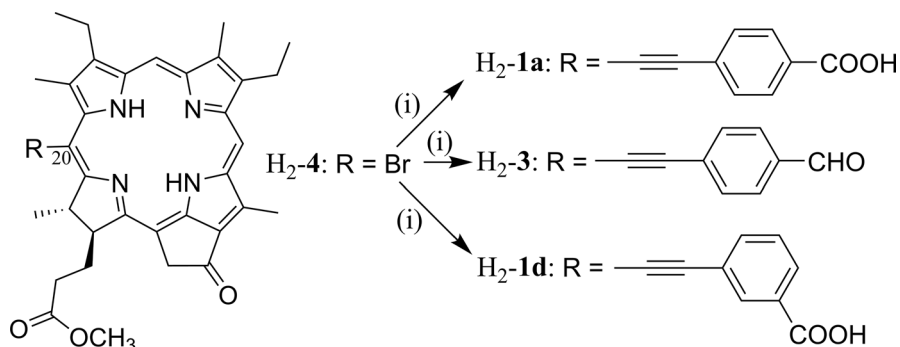
Photocatalytic reaction

Photocatalytic HERs were carried out in a Pyrex reactor connected to a closed gas circulation system. The dye-adsorbed Pt- TiO_2 powder (50 mg) was suspended in an aqueous 50 mM AA solution (100 ml, pH = 2.8). The suspension was stirred and irradiated with Vis light (580–800 nm) using the above 300 W Xe lamp with a cold mirror CM1 and a cutoff filter R-60. The produced hydrogen amount was quantified by online Shimadzu GC-8A gas chromatograph: thermal conductivity detector, 5 Å molecular sieve column packing, and Ar carrier gas.

Results and discussion

Synthesis of Chl-*a* derivative photosensitizers

Carboxylated Chl-*a* derivative **H₂-1a** was prepared according to reported procedures [23]. Its synthetic pathway is briefly described as follows. Chl-*a* was obtained from commercially available spirulina powders, dry cells of cultured cyanobacteria,

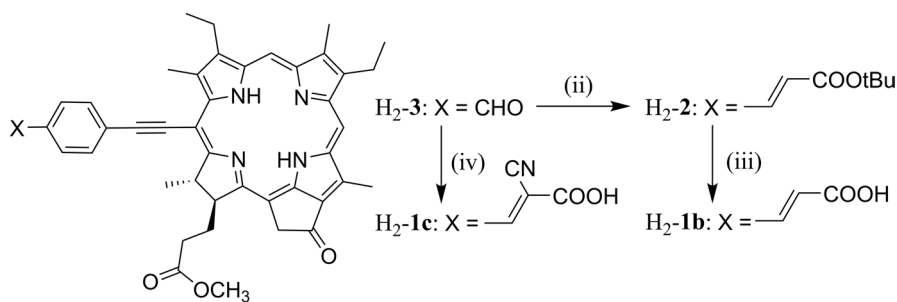


Scheme 1 Sonogashira coupling of 20-bromide H_2-4 with arylacetylenes to $H_2-1a/3/1d$: (i) $p-HC\equiv C-C_6H_4COOH$ (for H_2-1a), $p-HC\equiv C-C_6H_4CHO$ (for H_2-3), or $m-HC\equiv C-C_6H_4COOH$ (for H_2-1d), $Pd_2(dba)_3$, (*o*-tol) $_3P$ / Et_3N , dry DMF, 70 °C

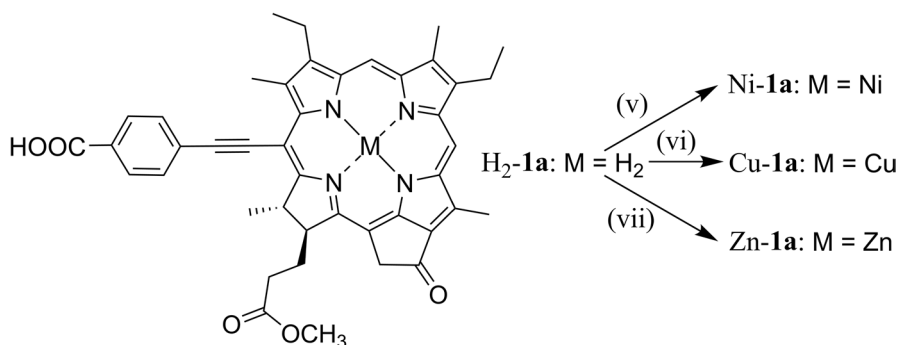
and chemically modified to give 20-bromo-chlorin H_2-4 (Scheme 1) [24–27]. The bromide was reacted with *p*-ethynylbenzoic acid under conventional copper-free Sonogashira coupling conditions [step (i) in Scheme 1] to afford H_2-1a in 42% yield. A similar palladium-catalyzed cross-coupling of H_2-4 with *m*-ethynylbenzoic acid yielded H_2-1d (47%) as the *m*-isomer of *p*-substituted H_2-1a . The substitution position of a carboxy group on the phenyl ring did not largely affect the coupling yields.

Another carboxylated Chl-*a* derivative H_2-1b as the ethylene-inserted version of H_2-1a was prepared by the following procedures. The aforementioned Sonogashira coupling of H_2-4 with *p*-ethynylbenzaldehyde gave H_2-3 (Scheme 1) in 37% yield, which was comparable to that for the synthesis of the corresponding carboxylic acid H_2-1a (42%). The aldehyde was reacted with (*tert*-butoxycarbonylmethylene)triphenylphosphorane [step (ii) in Scheme 2] [29] to afford H_2-2 (93%) as the Wittig reaction product. The *tert*-butyl ester in H_2-2 was cleaved by TFA [step (iii)] [29] to yield H_2-1b (85%) possessing an acrylic acid residue. In addition, cyanoacrylated Chl-*a* derivative H_2-1c as the cyanated version of H_2-1b was synthesized by Knoevenagel reaction of aldehyde H_2-4 with cyanoacrylic acid in the presence of piperidine [step (iv)] [30]. The reaction was so clean that H_2-1c was obtained in 98% brsm yield.

Insertion of a nickel atom at the central position of H_2-1a was performed by the treatment of a methanolic nickel acetate solution in refluxing 1,2-dichloroethane (bp = 84 °C) for 19 h [31] as shown in the step (v) in Scheme 3. The chemical yield of Ni-**1a** was 22%. Copper metalation of H_2-1a occurred by simply stirring at rt in dichloromethane with a methanolic cupric acetate solution for 30 min [step (vi)] [31] to give Cu-**1a** in a higher 94% yield. The implemented milder conditions were required, because the copper was inserted into a chlorin chromophore more readily than the corresponding nickelation. Similarly, Zn-**1a** was obtained by stirring at rt in dichloromethane with a methanolic zinc acetate solution for 1 h [step (vii)] [31]. The isolated yield of Zn-**1a** was 65%, which was lower than that of Cu-**1a**. The double reaction time and lower yield of Zn-**1a** over Cu-**1a** were ascribable to less metalation of zinc than copper atom. The present metalation order of Cu > Zn > Ni was



Scheme 2 Synthesis of H_2-1b/c by chemical modification of H_2-3 : (ii) $CH(COOtBu)=PPh_3$ / $PhCH_3$, reflux; (iii) TFA, rt; (iv) $CH_2(CN)COOH$, $(CH_2)_5NH$ / THF, reflux



Scheme 3 Metalation of H_2-1a to Ni/Cu/Zn-1a: (v) $Ni(OAc)_2 \cdot 4H_2O$ / MeOH, CH_2ClCH_2Cl , reflux; (vi) $Cu(OAc)_2 \cdot H_2O$ / MeOH, CH_2Cl_2 , rt; (vii) $Zn(OAc)_2 \cdot 2H_2O$ / MeOH, CH_2Cl_2 , rt

consistent with the metalation of porphyrinoids [32]. It is noted that copper insertion to H_2-1b/c was similarly treated with $Cu(OAc)_2$, but the pure samples of desired $Cu-1b/c$ could not be obtained due to their chemical instabilities.

Optical properties of Chl-*a* derivatives

In dichloromethane, H_2-1a with the *p*-carboxy group exhibits intense Soret and Qy bands at 424 and 679 nm, respectively (red line in Fig. 2). Between the two bands, relatively small bands are observed, including a Qx band at 573 nm. The other free bases H_2-1b-d afforded similar UV-Vis absorption spectra to that of H_2-1a (Fig. S8). Their substituents on the 20²-phenyl group hardly affected the spectral shapes. The Soret and Qy maxima of the three *p*-substitutes H_2-1a-c were almost the same (Table 1, left), indicating that the insertion of an ethynylene group from H_2-1a to H_2-1b and the additional introduction of a cyano group from H_2-1b to H_2-1c gave limited effects on the UV-Vis absorption spectra. By contrast, H_2-1d bearing the *m*-carboxy group exhibited slightly blueshifted Soret and Qy maxima, comparing with those of *p*-carboxylated H_2-1a . This hypsochromic effect on the

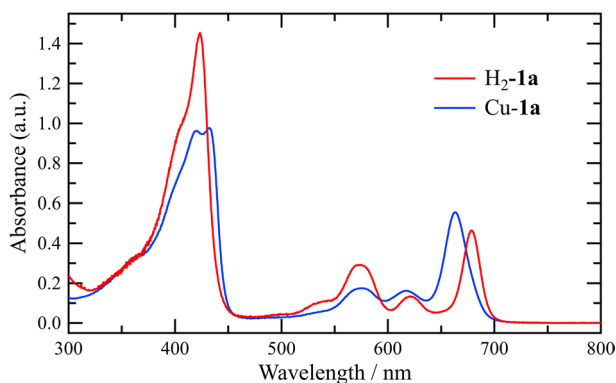


Fig. 2 UV-Vis absorption spectra of **H₂-1a** (red line) and **Cu-1a** (blue line) in CH_2Cl_2 at 10 μM

Qy maxima was supported by molecular model calculations: $\Delta\lambda_{\text{max}}(\text{Qy}) = -2$ nm observed in CH_2Cl_2 and -7 nm estimated by TD-DFT calculation.

The insertion of a copper atom at the central position of **H₂-1a** to **Cu-1a** moved the main Soret and Qy maxima to longer and shorter wavelengths, respectively: $\Delta\lambda_{\text{max}}(\text{Soret}) = +8$ nm and $\Delta\lambda_{\text{max}}(\text{Qy}) = -16$ nm in CH_2Cl_2 (Fig. 2). The intensities of the Soret and Qx peaks were suppressed, and that of Qy peak 1.2-fold enhanced. TD-DFT calculation estimated the blueshift of Qy maxima by 16 nm and the 1.1-fold increase in Qy peak, which were nearly identical to the observed values. The nickelation and zincation of **H₂-1a** to **Ni-1a** and **Zn-1a**, respectively, also displayed similar alteration (Table 1 and Fig. S9). The changes in their Vis absorption bands are consistent with those for the metalation of related Chl-*a* derivatives [31].

As reported in the previous report [23], **H₂-1a** was highly fluorescent in an aerated solution. All the diluted dichloromethane solutions of free bases **H₂-1a-d** strongly emitted fluorescence light at the red side of the Qy region by the excitation at their Soret maxima. In a diluted organic solution at rt, **Zn-1a** was fluorescent, but emission from **Ni-1a** and **Cu-1a** could not be observed (Fig. S10). Fluorescence emission lifetimes decreased in the order of **H₂-1a**, **Zn-1a**, and **Ni/Cu-1a** (Fig. S10, insert).

Table 1 Electronic absorption data of **H₂-1a-d** (left) and **M-1a** (right) in CH_2Cl_2

Compound	$\lambda_{\text{max}}/\text{nm}$		Compound	$\lambda_{\text{max}}/\text{nm}$	
	Soret	Qy ^a		Soret	Qy ^a
H₂-1a	424	679 (0.32)	Ni-1a	428	660 (0.54)
H₂-1b	427	679 (0.31)	Cu-1a	432	663 (0.57)
H₂-1c	425	679 (0.33)	Zn-1a^b	437	668 (0.53)
H₂-1d	422	677 (0.35)	H₂-1a^b	423	678 (0.34)

^aThe values in parentheses indicate the relative intensity of Qy over Soret absorbance

^bIn 1%(v/v) pyridine and CH_2Cl_2

Hydrogen evolution by Pt-loaded TiO₂ with photoexcited Chl-*a* derivatives

Photosensitizer H₂-**1a** (0.24 μmol) was adsorbed onto 1 wt% Pt-loaded TiO₂ particles (50 mg) through the bonding of the *p*-carboxy group at the 20²-phenyl group with the hydroxy (or oxo) group on the TiO₂ surface. The resulting particles were suspended in an aqueous 50 mM AA solution (100 ml, pH=2.8) and irradiated with longer wavelength Vis light than 580 nm which was produced by a 300 W Xe lamp and an R-60 cutoff filter. During the illumination, hydrogen gas evolved, and the amount linearly increased with time [23]. After illumination for 10 h, 75 μmol of hydrogen molecules was obtained (Fig. 3), and turnover number (TON) of the HER catalysis based on the pigment sensitizer was calculated to be 625. Under the same conditions, the use of *p*-acrylated H₂-**1b** instead of *p*-carboxylated H₂-**1a** afforded approximately twice hydrogen gas (134 μmol) with TON=1120. Considering that the Vis absorption spectra of H₂-**1a/b** resembled each other, their absorption amounts of orange and red light were the same. Therefore, the ethylene insertion of H₂-**1a** to H₂-**1b** enhanced the HER catalytic activity. The addition of a cyano group at the *p*-acrylate residue in H₂-**1b** to H₂-**1c** further increased the photocatalytic activity to give 213 μmol of hydrogen molecules (TON=1780) after 10-h illumination. The evolved H₂ volume by *m*-carboxylated H₂-**1d** was halved to 38 μmol (TON=317), compared with that of *p*-counterpart H₂-**1a**. Although the movement of a carboxy group from the *p*- to *m*-position as in H₂-**1a** to H₂-**1d** blueshifted the Vis absorption maxima (vide supra), the absorbed light amounts in the present system were almost the same for both the photosensitizers. The half suppression was ascribable to the decrease in the HER catalytic activity of H₂-**1d** over H₂-**1a**. It is noted that any chlorophyllous photosensitizers were not desorbed from the TiO₂ surface during the illumination.

Since the optical properties of H₂-**1a–d** fluctuated slightly, their lowest unoccupied molecular orbital (LUMO) energy levels would hardly change, indicating that the energy difference from their photoexcited states to the TiO₂ conduction band (CB) would be similar and the forward electron injection from their photoexcited states to TiO₂ would be so rapid. The injected electron is moved to the Pt site on

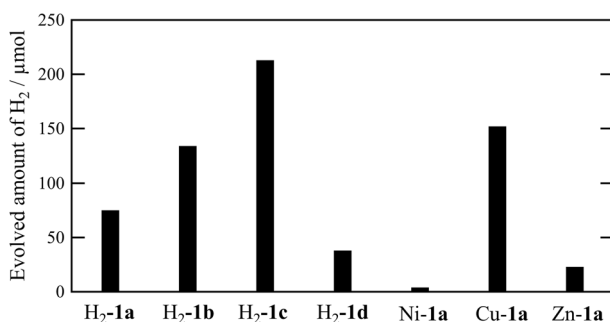


Fig. 3 Evolved amounts of hydrogen gas using 1 wt% Pt-loaded TiO₂ particles (50 mg) adsorbing seven Chl-*a* derivative photosensitizers H₂-**1a–d** and Ni/Cu/Zn-**1a** (0.24 μmol) in an aqueous 50 mM AA solution (100 ml, pH=2.8) under Vis light irradiation ($\lambda > 580$ nm) for 10 h

TiO₂ and transferred into aqueous protons to evolve hydrogen gas. The resulting cation radical of the photosensitizer on TiO₂ accepts an electron from AA in an aqueous solution to reproduce the neutral species. Before the desired reproduction, the cation radical species of the photosensitizers can obtain an electron from TiO₂. The back electron transfer notably disturbs the desired HER process. Similar to the forward electron injection mentioned above, the energy difference between the highest occupied molecular orbital (HOMO) and TiO₂ CB levels is not changed largely for H₂-**1a–d**. The undesired back electron transfer should be dependent on the distance between their HOMO electron distribution and TiO₂ surface. TD-DFT calculation revealed that the electron of the HOMO in H₂-**1a–d** were distributed around their core chlorin and peripheral 20-ethynylene π -systems (Fig. S11). The distance between the carbon at the 20²-position and the carboxy terminal increased in the order of H₂-**1d**, H₂-**1a**, and H₂-**1b**, so the back electron transfer quenching was suppressed, and their HER activities increased in the same order. Although the estimated distance of H₂-**1c** was identical to that of H₂-**1b**, the former catalytic activity was higher than the latter. The cyano group neighbor to the carboxy group in H₂-**1c** fixed the chlorin π -system more tightly on the TiO₂ surface [33] than observed in H₂-**1b**, so the average distance between the chlorin π -system and the TiO₂ surface increased in the order of H₂-**1b** and H₂-**1c**. Due to suppression of the back electron transfer quenching of H₂-**1c** over H₂-**1b**, the HER activity of H₂-**1c** would enhance comparing with that of H₂-**1b**. It is noted that the adsorption of H₂-**1a** on the TiO₂ surface hardly affected the Qy band as shown in the previous report [23].

The HER activities of some divalent metal complexes of H₂-**1a** were examined under the identical conditions mentioned above. The utilization of nickel complex Ni-**1a** as the photosensitizer evolved only 4 μ mol of H₂ (TON=33) after 10-h illumination (Fig. 3). The nickelation approximately 20-fold diminished the photocatalysis. By contrast, the copper insertion into H₂-**1a** twice enhanced the activity (152 μ mol of H₂ and 1270 of TON), indicating that Cu-**1a** was useful for the photosensitizer. Zinc complex Zn-**1a** afforded 23 μ mol of H₂ (TON=192), which was one-third lower than that by the corresponding free base, H₂-**1a**. The HER activities decreased in the order of Cu-**1a**, H₂-**1a**, Zn-**1a**, and Ni-**1a**. Although these metal complexes M-**1a** absorbed orange and red light (> 580 nm) more by at most 1.5-fold than H₂-**1a** (vide supra), their inherent activity order remained the same. Based on the oxidation potentials of the related compounds [34] and their Vis absorption spectra (Fig. S9), the HOMO and LUMO levels fell in the order of Ni/Cu-**1a**, Zn-**1a**, and H₂-**1a**, which was consistent with the TD-DFT results (Fig. S11). These energy differences could not account for their catalytic HER activities. The electron of their HOMOs was distributed on the 20-ethynylchlorin, and the distance between the C20² atom and the TiO₂ surface was identical for all the four systems, the back electron transferring quenching was not responsible for the activity difference. In addition, the aforementioned order of their fluorescence lifetimes (H₂-**1a**>Zn-**1a**>>Ni/Cu-**1a**) was inconsistent with the HER activity order. The lifetime of Cu-**1a** was significantly shorter than that of H₂-**1a**, but the former HER activity was higher than the latter, supporting that the forward electron injection from H₂/Cu-**1a** to TiO₂ was so quick and rationalizing that the HER activities of free bases H₂-**1a–d** was dependent on the back electron transfer

quenching (vide supra). In this study, the enhancement of the HER photocatalysis by the copper metalation of H₂-**1a** to Cu-**1a** could not be explained, and this will be explained in the future.

Conclusions

Methyl 20-arylethynyl-mesopyropheophorbide-*a* possessing *p*-carboxy H₂-**1a**, *p*-(2-carboxyethenyl) H₂-**1b**, *p*-(2-carboxy-2-cyanoethenyl) H₂-**1c**, and *m*-carboxy groups H₂-**1d** on the 20²-phenyl ring were readily prepared by the chemical modification of naturally occurring and environmentally friendly Chl-*a*. These synthetic Chl-*a* derivatives were useful for the HER photosensitizers connected onto the surface of TiO₂ loaded with Pt in an aqueous AA solution. The HERs proceeded through sequential electron transfer from the excited states of Chl sensitizers with Vis light (> 580 nm) to the TiO₂ particles, from the TiO₂ semiconductor to the loaded Pt nanoparticles, and from the Pt cocatalyst to the aqueous protons, while AA donated an electron to the Chl species (see Graphical abstract). The HER activity increased in the order of H₂-**1d** (TON / h = 32), H₂-**1a** (63), and H₂-**1b** (112), which was consistent with the length between the carboxy group anchored to TiO₂ and the 20-ethynylchlorin π -system. The enhancement of the spacer length suppressed back electron transfer quenching from TiO₂ to Chl sensitizers to generate H₂ gas more largely. The additional cyano group neighbor to the carboxy anchor in H₂-**1b** fixed the orientation of H₂-**1c** sensitizer on the TiO₂ surface to decrease the above quenching and increase the HER activity at 0.43 mmol g⁻¹ h⁻¹, which was comparable to that of the C3-acrylated Chl sensitizer reported previously (see Introduction section). Furthermore, the swift and smooth copper metalation at the central position of H₂-**1a** doubled the HER activity (0.30 mmol g⁻¹ h⁻¹ and TON / h = 127), but the zinc/nickel insertion significantly diminished their photocatalysis.

Supplementary Information The online version contains supplementary material available at <https://doi.org/10.1007/s11164-025-05887-9>.

Author contributions Yudai Hoshi, Yuki Hashimoto, and Nobuyuki Hara conducted the investigation. Shin Ogasawara carried out investigation and visualization. Hajime Suzuki was responsible for investigation and writing—reviewing and editing. Ryu Abe was involved in writing—reviewing and editing, supervision, project administration, and funding acquisition. Hitoshi Tamiaki took care of writing—reviewing and editing, writing—original draft, supervision, project administration, and funding acquisition.

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Data availability Data will be made available on request.

Declarations

Conflict of interest The authors declare that they have no known competing financial interests or personal relationships that could have appeared to influence the work reported in this paper.

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