Supplementary Information

Photostability of a dyad of magnesium porphyrin and fullerene and its application to photocurrent conversion

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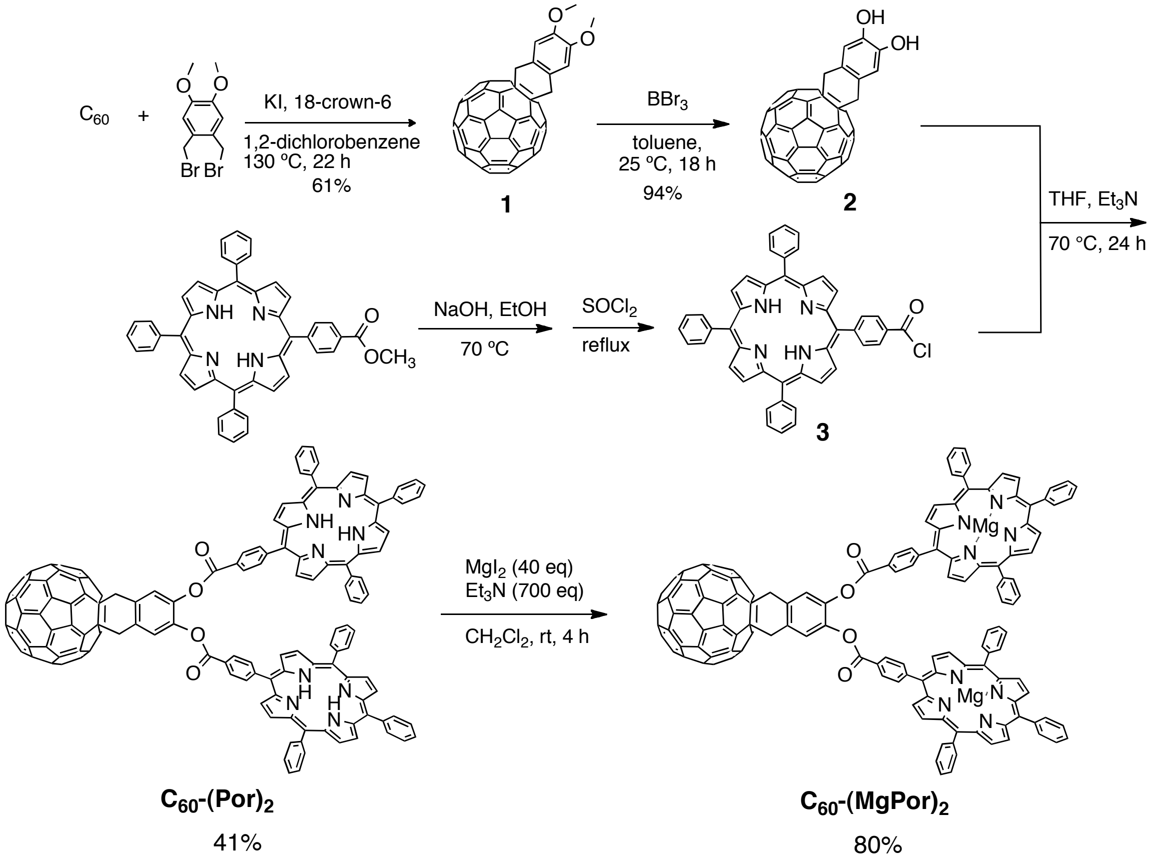
1. Synthetic Procedures

General. Syntheses were carried out under a nitrogen or argon atmosphere with standard Schlenk techniques. The water contents of the solvents were determined, using a Karl Fischer moisture titration (MK-210, Kyoto Electronics Co.), to be less than 30 ppm. All of the reactions were monitored by HPLC (column, Cosmosil-Buckyprep, 4.6 × 250 mm, Nacalai Tesque; flow rate, 2.0 mL/min; eluent, toluene/isopropanol; detector, Shimadzu SPD-M10Avp). Preparative HPLC was performed on a Buckyprep column (20 x 250 mm) using toluene/isopropanol as the eluent (detected at 350 nm with a UV spectrophotometric detector, Shimadzu SPD-6A). Flash column chromatography was performed on silica gel (Kanto Kagaku, silica gel 60N, 40–100 μm). The isolated yields were calculated on the basis of the starting fullerene compounds. The NMR spectra were measured with JEOL ECA-500 (500 MHz) instruments. Spectra are reported in parts per million from the internal tetramethylsilane (δ 0.00 ppm) or residual protons of the deuterated solvent for ^{1}H NMR. Mass spectra were measured on a JEOL JMS-T100LC APCI/ESI-TOF mass spectrometer. UV-vis absorption spectra are recorded on a JASCO V-570 spectrometer. Photoluminescence spectra are recorded on a HITACHI F-4500 spectrometer. Cyclic voltammetry (CV) was performed using HOKUTO DENKO HZ-5000 voltammetric analyzer.

Materials. Methyl viologen (MV^{2+}) was purchased from Sigma-Aldrich Co. and used as received. ^{n}Bu$_4$NClO$_4$, for electrochemical measurements, was purchased from Kanto Chemicals and used after recrystallization from ethanol. Na_2SO_4 was purchased from Kanto Chemicals and used as received. A THF solution of KO*t*Bu was purchased from Sigma-Aldrich Co. Transparent indium–tin oxide (ITO) electrodes (10 W/cm^2, ITO on glass plate, Ra = 0.7 nm and R_{max} = 8.1 nm) were obtained from GEOMATEC Inc. (Japan).



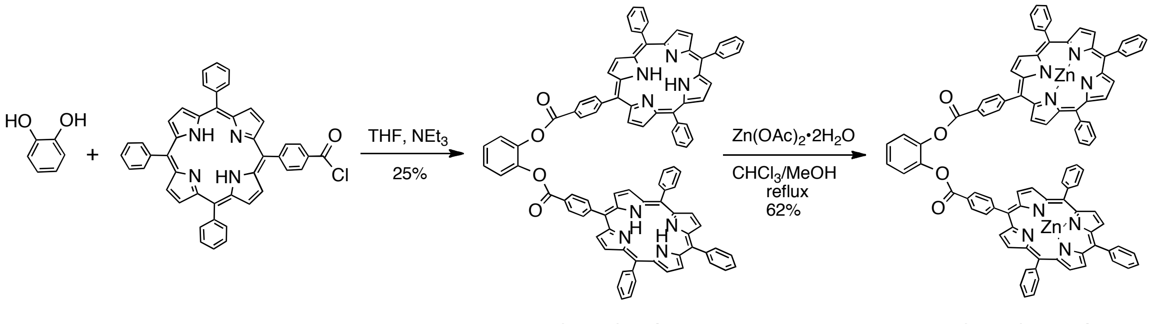
Synthesis of $C_{60}(C_2H_4C_6H_2(OMe)_2)$ (1). C_{60} (387 mg, 0.537 mmol), 1,2-bis(bromomethyl)-4,5-dimethoxybezene (174 mg, 0.537 mmol), KI (200 mg, 0.6 mmol), and [18]crown-6 (1.14 g, 4.29 mmol) in 1,2-dichlorobenzene (120 mL) were heated at 130 °C for 22 h. The reaction mixture was cooled to room temperature, and concentrated by evaporation. After adding hexane to the concentrated solution, brown precipitate was collected by filtration. The crude was purified by silica gel chromatography with CS_2/toluene as eluent. Monoadduct **1** (291 mg, 0.329 mmol, 61%) and diadduct (25 mg, 0.024 mmol) were obtained. Monoadduct (**1**): ^{1}H NMR (500 MHz, $CDCl_3$): δ 4.03 (s, 6H, OCH_3), 4.36 (d, broadened, 2H, CH_2), 4.75 (d, broadened, 2H, CH_2), 7.19 (s, 2H, Ph). APCI-MS (–): calcd for $C_{70}H_{12}O_2$ ($[M - H]^-$) 884.0837, found 884.0911. Diadduct : APCI-MS (–): calcd for $C_{80}H_{24}O_4$ ($[M - H]^-$) 1048.1675, found 1048.1662.

Synthesis of $C_{60}(C_2H_4C_6H_2(OH)_2)$ (2). Compound **1** (571 mg, 0.645 mmol), 40 mL of BBr_3 (1.0 M in CH_2Cl_2) and toluene (250 mL) were placed in a flask. The solution was warmed from 0 °C to 25 °C gradually. The reaction was quenched by water after stirring for 18 h. The crude was extracted with ethyl acetate, and purified by silica gel chromatography with toluene as eluent. A brown solid (519 mg, 0.604 mmol, 94%) was obtained by silica gel chromatography with toluene/ethanol as eluent. ^{1}H NMR (500 MHz, THF-d_8/CS_2): δ 4.28 (d, J = 13.75 Hz, 2H, CH_2), 4.74 (d, J = 13.75 Hz, 2H, CH_2), 7.02 (s, 2H, Ph), 7.95 (s, 2H, OH). APCI-MS (–): cacld for $C_{68}H_7O_2$ ($[M - H]^-$) 855.0446, found 855.0520.

Synthesis of Fullerene–Bisporphyrin (C_{60}-(Por)$_2$). Hydrolysis of 5-(4-methoxycarbonylphenyl)-10,15,20-triphenylporphin (100 mg, 0.115 mmol) was carried out with NaOH (400 mg, 10 mmol) in 2 mL of ethanol and 10 mL of toluene at 70 °C for 2 h. After evaporating the ethanol, 1 N HCl aqueous solution was added until the pH of solution was less than 5. The precipitate was collected by filtration and washed with water. After drying the purple solid, 2 mL of thionyl chloride was added to the solid. The solution was refluxed for 4 h. After removing unreacted $SOCl_2$ under reduced pressure, the residual was further dried for 4 h. Without further purification, the acid chloride (**3**) was used to react with **2** (52 mg, 0.061 mmol) and triethylamine (80 μL) in 8 mL of THF. After stirring for 24 h, **C_{60}-(Por)$_2$** (54 mg, 0.025 mmol, 41%) was obtained through silica gel column with toluene/chloroform as eluent, and further purified with HPLC (column, Cosmosil-Buckyprep, 20 × 250 mm, eluent: toluene). ^{1}H NMR (500 MHz, $CDCl_3$): δ -2.89 (s, 4H, inner), 3.81 (s, broadened, 4H, CH_2), 7.17 (s, broadened, 8H, Ph), 7.36 (t, *J* = 7.42 Hz, 4H, Ph), 7.61–7.77 (m, 16H), 8.14 (d, *J* = 6.85 Hz, 4H, Ph), 8.34 (d, *J* = 7.45 Hz, 4H, Ph), 8.41 (d, *J* = 4.6 Hz, 4H, Ph), 8.61 (d, *J* = 4.0 Hz, 4H, pyrrole), 8.71 (m, 8H, pyrrole), 8.75 (d, *J* = 4.6 Hz, 4H, pyrrole). APCI-MS (+): calcd for $C_{158}H_{65}N_8O_4$ ([M + H]$^+$) 2137.5129, found 2137.4994.

Synthesis of Fullerene-Bisporphyrin Magnesium Complex (C_{60}-(MgPor)$_2$). **C_{60}-(Por)$_2$** (30 mg, 0.014 mmol), MgI_2 (155 mg, 0.56 mmol), and Et_3N (1 mL) in CH_2Cl_2 (100 mL) were stirred for 2 h at room temperature. The color of solution changed from dark red to green. The crude was purified by silica gel chromatography with toluene as eluent. A dark green solid was obtained in 80% yield. ^{1}H NMR (500 MHz, 1,2-dichlorobenzene-*d*$_4$): δ 4.28 (4H, CH_2), 7.61 (8H, Ph), 7.88 (4H, Ph), 8.00–8.20 (m, 16H), 8.55–8.92 (m, 16H), 9.10 (8H, pyrrole), 9.14 (4H, pyrrole).

Synthesis of Fullerene–Bisporphyrin Zinc Complex (C_{60}-(ZnPor)$_2$). The title compound was prepared by refluxing a $CHCl_3$/MeOH (20 mL/10 mL) solution of **C_{60}-(Por)$_2$** (35 mg, 0.016 mmol) and $Zn(OAc)_2\cdot 2H_2O$ (70 mg, 0.32 mmol) for 1 h. After concentration, the crude was purified by silica gel chromatography with $CHCl_3$ as eluent. A dark red solid (20 mg) was obtained in 55% yield ^{1}H NMR (500 MHz, $CDCl_3$): δ 3.51 (s, broadened, 4H, CH_2), 7.30–7.52 (m, 12H, Ph), 7.68–7.86 (m, 16H, Ph), 8.12 (d, *J* = 6.3 Hz, 4H, Ph), 8.33 (d, *J* = 8.05 Hz, 4H, Ph), 8.65 (d, *J* = 4.55 Hz, 4H, Ph), 8.75 (m, 8H, pyrrole), 8.84 (d, *J* = 4.55 Hz, 4H, pyrrole), 8.88 (d, *J* = 4.6 Hz, 4H, pyrrole). APCI-MS (+): calcd for $C_{158}H_{61}N_8O_4Zn_2$ ([M + H]$^+$) 2265.3416, found 2265.3342.



Synthesis of Bisporphyrin Zinc Complex (C_6H_4-(ZnPor)$_2$). Porphyrin acid chloride (**3**) from its carboxylic acid (56 mg) was used to react with catechol (4.4 mg, 0.04 mmol) and triethylamine (100 μL) in 1.5 mL of THF. After stirring for 24 h, the linked product **C_6H_4-(Por)$_2$** was obtained through silica gel column with chloroform as eluent. Then, **C_6H_4-(Por)$_2$** was reacted with $Zn(OAc)_2 \cdot 2H_2O$ to afford **C_6H_4-(ZnPor)$_2$** in 62% yield. ^{1}H NMR (500 MHz, $CDCl_3$): δ 6.98 (t, *J* = 7.72 Hz, 8H, Ph), 7.12 (t, *J* = 7.75 Hz, 4H, Ph), 7.50–7.52 (m, 2H, Ph), 7.57 (d, *J* = 7.45 Hz, 8H, Ph), 7.61–7.63 (m, 2H, Ph), 7.72–7.77 (m, 6H, Ph), 8.23 (d, *J* = 7.15 Hz, 4H, Ph), 8.32 (d, *J* = 4.60 Hz, 4H, pyrrole), 8.38 (d, *J* = 8.05 Hz, 4H, Ph), 8.58 (d, *J* = 8.0 Hz, 4H, Ph), 8.74 (d, *J* = 4.60 Hz, 4H, pyrrole), 8.77 (d, *J* = 4.55 Hz, 4H, pyrrole), 8.92 (d, *J* = 4.55 Hz, 4H, pyrrole). APCI-MS (+): calcd for $C_{96}H_{58}N_8O_4Zn_2$ ([M]$^+$) 1517.3285, found 1517.3240.

2. Photophysical, Electrochemical, Photoelectrochemical Properties and Self-assembled Monolayer Formation

Kinetic Experiments. Solutions of porphyrin-linked compounds in THF (38 μM) were air-saturated. The solutions were irradiated with a 60 W tungsten lamp at room temperature. The progress of the reaction was monitored by measuring the UV/vis spectra.

Preparation of Imidazole Monolayer on ITO. The preparation of self-assembled first molecular layers of imidazole carboxylic acid was carried out using a simple dipping method: an ITO electrode (25 mm × 20 mm; UV–O_3 treated before use) was immersed in a 0.1 mM DMF solution of the imidazole carboxylic acid at room temperature for 3 day. Then the ITO electrode was washed with DMF and *o*-dichlorobenzene and dried in an argon gas stream.

Preparation of the Supramolecular Bilayer on ITO. The functionalized ITO electrode was immersed in a 0.01 mM *o*-dichlorobenzene solution of the metalloporphyrin-linked molecules at room temperature for 3 h. Then the ITO electrode was washed with *o*-dichlorobenzene and dried in an argon gas stream.

Electrochemical Measurements. Electrochemical measurements were carried out with a Hokuto HZ-5000 voltammetric analyzer. A glassy-carbon, a platinum coil, and a Ag/Ag^+ electrode were used as the working, counter, and reference electrodes, respectively, in THF with 0.1 M $^{n}Bu_4NClO_4$ as the supporting electrolyte. CV was performed at a scan rate of 100 mV/s. The potential was corrected against a standard reference, the ferrocene/ferrocenium couple (Fc/Fc^+). Surface coverage of the supramolecular bilayer was estimated from the redox peak area, indicating the amount of redox active spices on ITO.

Measurement of photocurrent. Photoelectrochemical measurements were carried out in a one-compartment cell, being irradiated with monochromatic excitation light (light intensity at 430 ± 10 nm was 207 ± 5 mW for systems of ITO electrodes). The photocurrent was detected with an HZ-5000 voltammetric analyzer. 50 mM methyl viologen (MV) was used as an electron acceptor in an oxygensaturated 0.1 M Na_2SO_4 aqueous solution. Quantum efficiencies of photocurrent was obtained by the following equation,

$\phi = (i / e) / [I(1-10^{-A})]$

where $I = (W\lambda / hc)$. I is the number of photons per unit area and unit time, A is the absorbance of the adsorbed dyes at λ nm, i is the photocurrent density, e is the elementary charge, W is the light power irradiated at λ nm, λ is the wavelength of light irradiation, h is the Planck constant, and c is the speed of light. A was estimated from the next equation,

$A = \varepsilon c'l$

where ε was measured from the UV-vis spectrum of the compound in THF solution and $c'l$, the amount of photoreactive molecules, was estimated from cyclic voltammogram (see above).

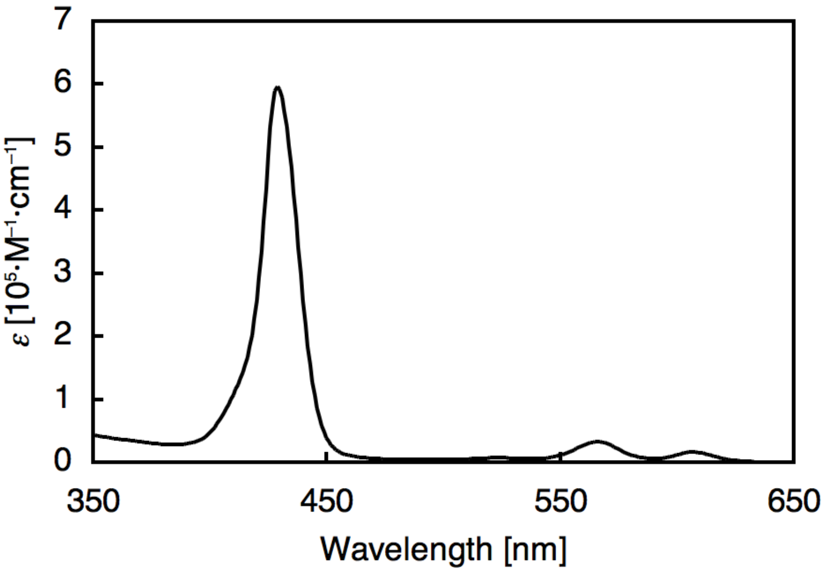


Figure S1. UV/vis spectrum of **C_{60}-(MgPor)$_2$** in ODCB at room temperature. λ (nm) = 429 (Soret band), 566 (Q-band), 607 (Q-band).

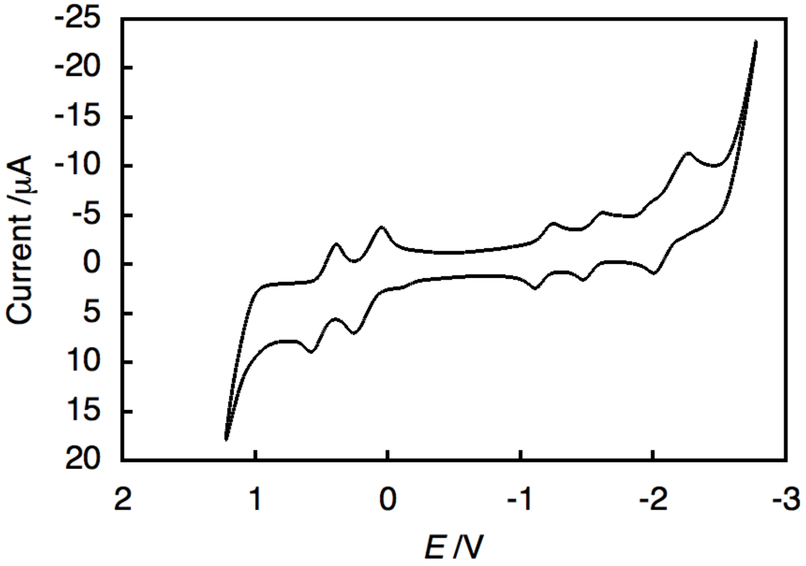


Figure S2. CV of **C_{60}-(MgPor)$_2$** at 25 °C in ODCB solution containing $^{n}Bu_4NClO_4$ as supporting electrolyte (vs Fc/Fc$^+$). $\boldsymbol{E_{ox}^{1}}$ = 0.15, $\boldsymbol{E_{ox}^{2}}$ = 0.48, $\boldsymbol{E_{red}^{1}}$ = -1.18, $\boldsymbol{E_{red}^{2}}$ = -1.53

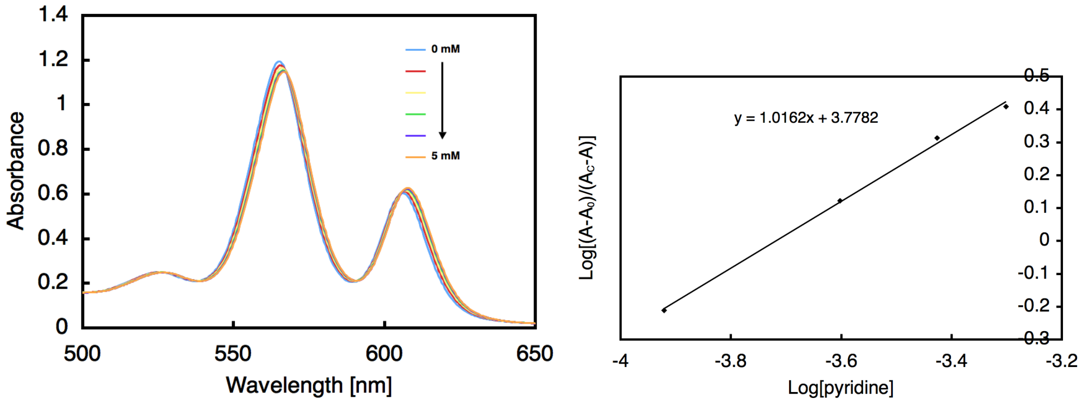


Figure S3. Spectroscopic titration of **C_{60}-(MgPor)$_2$**, with pyridine in ODCB at 25 °C. [**C_{60}-(MgPor)$_2$**] = 3.8×10^{-5} M. [pyridine] = 0 –5.0×10^{-3} M (left). Jaffe-Orchin plot (right).

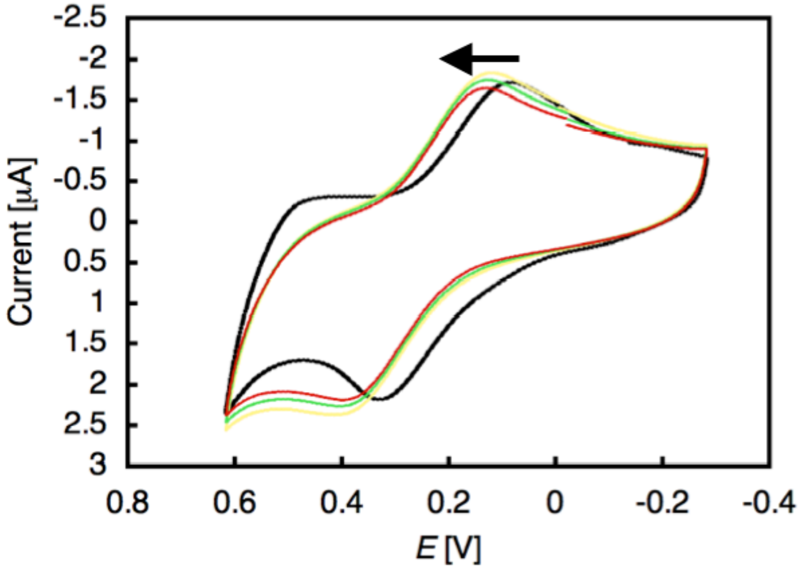


Figure S4. Changes in CV curve in ODCB with addition of pyridine. [**C_{60}-(MgPor)$_2$**] = 0.13 mM, [pyridine] = 0–15 mM

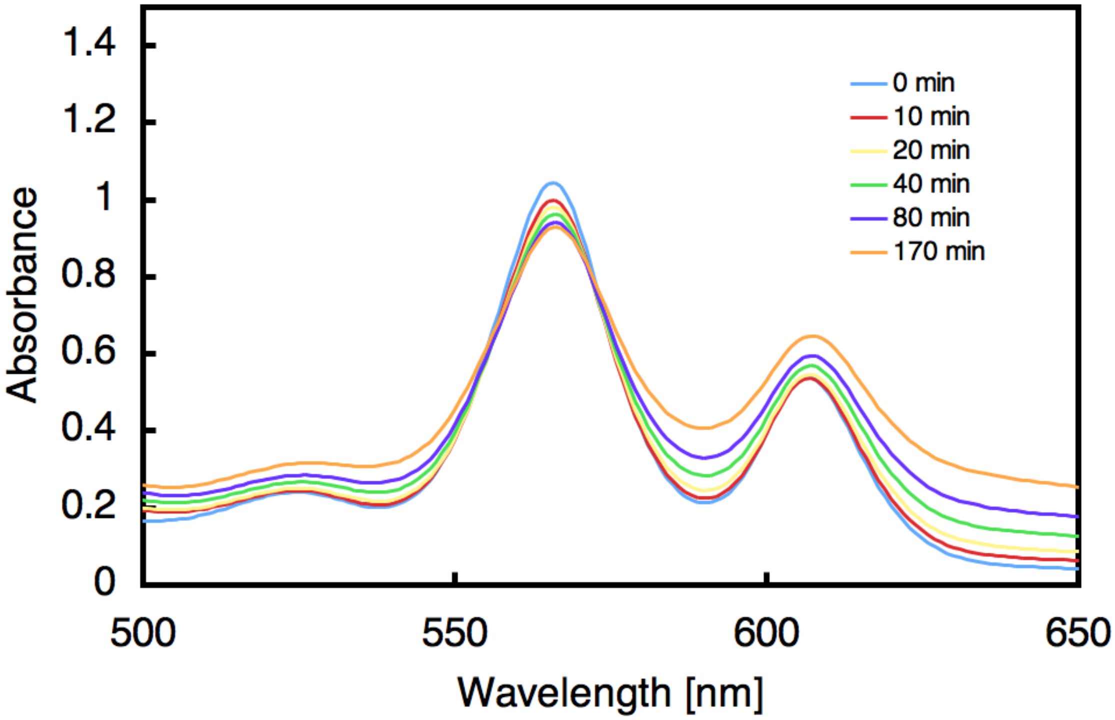


Figure S5. UV-vis spectral change during photooxidation of **C_{60}-(MgPor)$_2$** without pyridine.

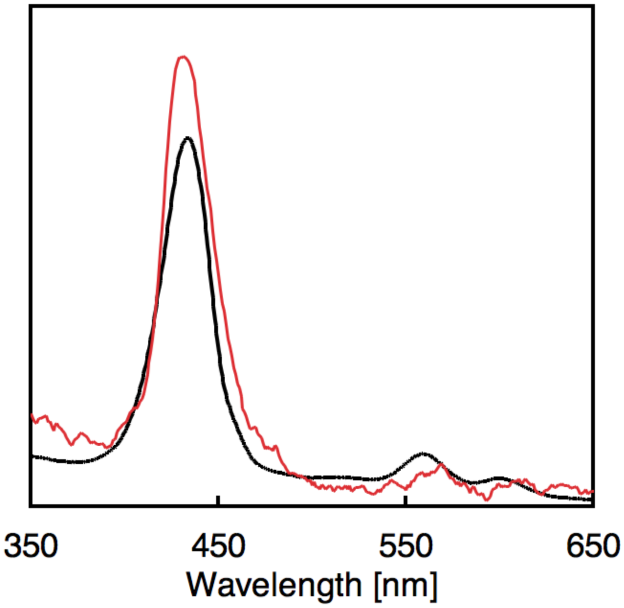


Figure S6. Comparison of action spectrum (red line) and UV/vis spectrum (black line) of **C_{60}-(MgPor)$_2$**/imidazole carboxylic acid/ITO.

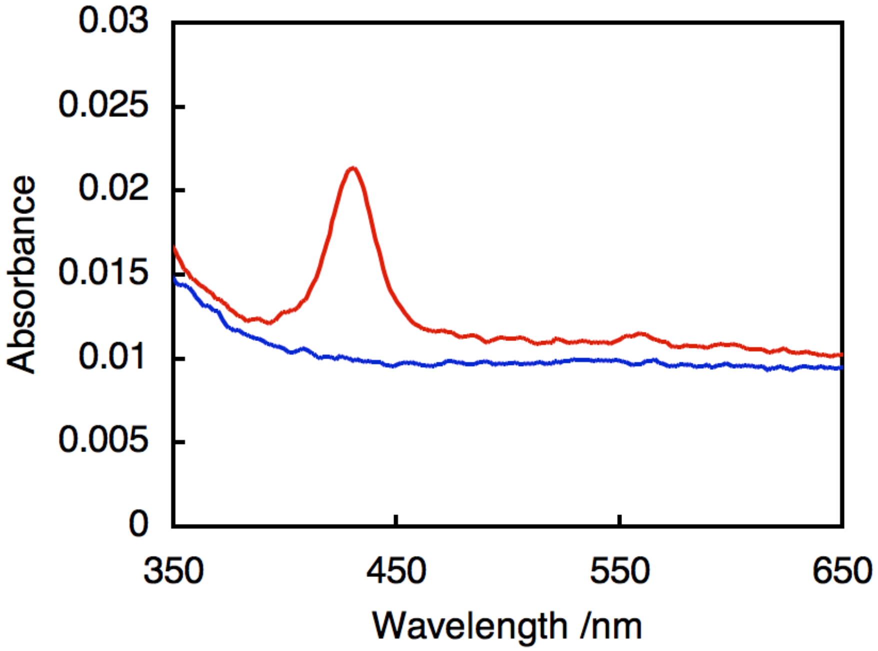


Figure S7. UV/vis spectrum of ITO substrate functionalized by imidazole carboxylic acid before and after the immersion into the solution of **C_{60}-(ZnPor)$_2$** for 3 h.

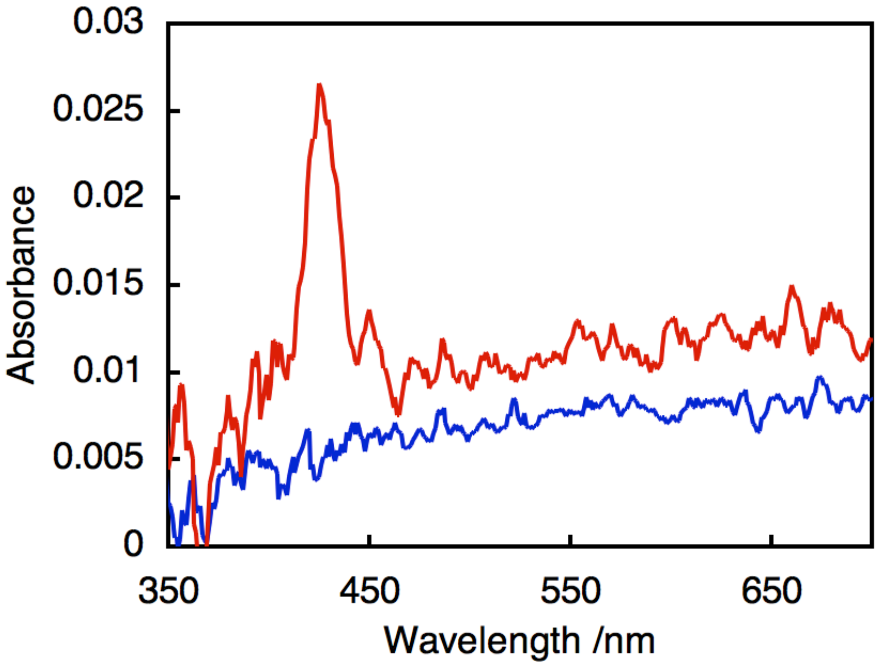


Figure S8. UV/vis spectrum of ITO substrate functionalized by imidazole carboxylic acid before and after the immersion into the solution of **C_6H_4-(ZnPor)$_2$** for 3 h.

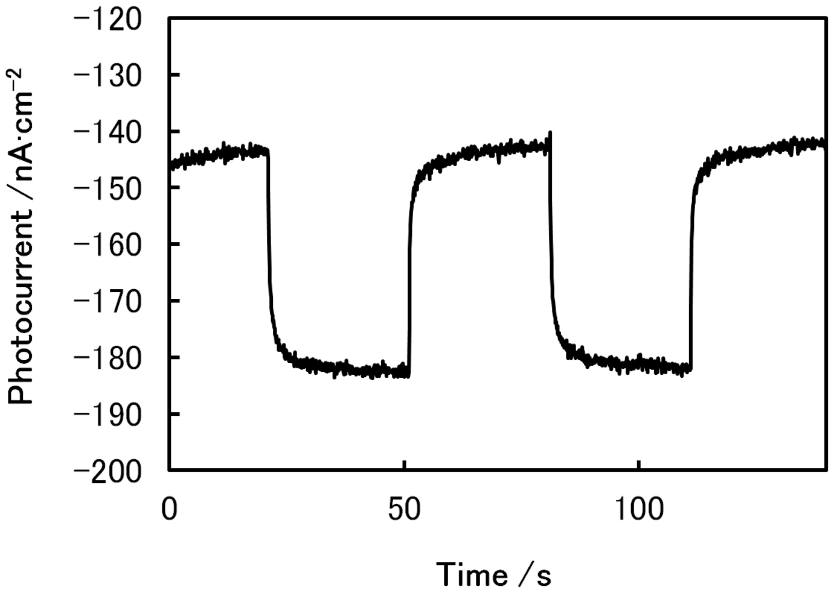


Figure S9. Photocurrent generation of **C_{60}-(ZnPor)$_2$** /imidazole carboxylic acid/ITO in the presence of MV^{2+} in aqueous solution containing Na_2SO_4 at –100 mV applied bias voltage vs Ag/AgCl reference electrode.

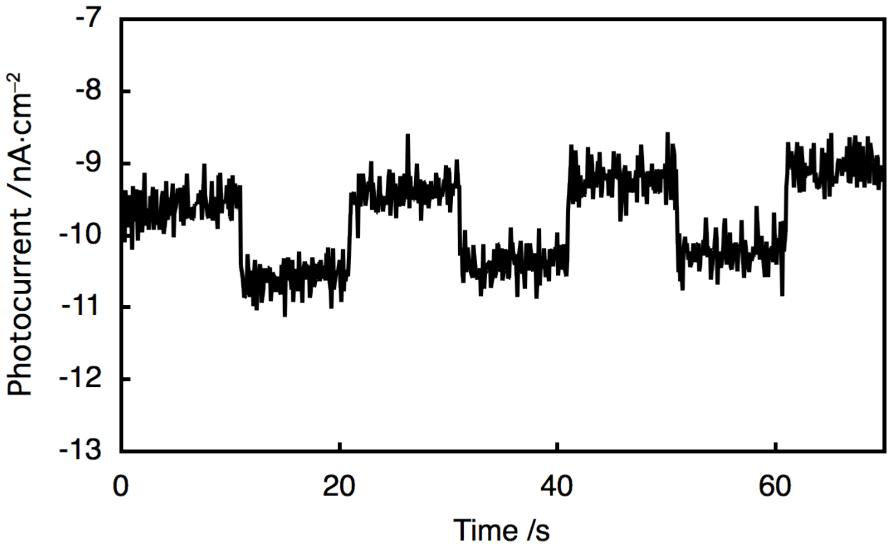


Figure S10. Photocurrent generation of **C_6H_4-(ZnPor)$_2$** / imidazole carboxylic acid /ITO in the presence of MV^{2+} in aqueous solution containing Na_2SO_4 at –100 mV applied bias voltage vs Ag/AgCl reference electrode.