

Supporting Information

Photosynthesis of hydrogen peroxide from dioxygen and water using aluminium-based metal–organic framework assembled with porphyrin- and pyrene-based linkers

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Experimental Section

Characterization

Powder X-ray diffraction (XRD) patterns were recorded using a Rigaku Ultima IV diffractometer with Cu K α irradiation ($\lambda = 1.54056$ Å, 40 kV to 40 mA). Nitrogen sorption isotherms were acquired at -196 °C using a BELSORP-max system (MicrotracBEL Corp.). Samples were preheated at 150 °C for 16 h before the measurement. Specific surface areas were calculated by the Brunauer-Emmett-Teller (BET) method using nitrogen adsorption data based on ISO 9277 standard. Pore distribution was calculated by the Non-Local Density Functional Theory (NLDFT) method. Proton nuclear magnetic resonance ($^1\text{H-NMR}$) spectra were obtained on a JEOL JNM-ECS 400 spectrometer operating at 400 MHz. UV-Vis spectra were collected on a Shimadzu UV-2600 spectrometer equipped with an integrating sphere. BaSO $_4$ was used as a reference, and absorption spectra were obtained using the Kubelka-Munk function. Steady-state photoluminescence (PL) spectra were obtained using a Horiba Fluorolog-3 spectrofluorometer at room temperature. The excitation wavelength of PL measurements was 420 nm. Time-resolved PL measurements and time-resolved emission spectroscopy (TRES) measurements were performed using a Horiba DeltaFlex.

Determination of the molar ratio between TCPP and TBAPy linkers

A MOF sample (1.0 mg) was dissolved in dimethylsulfoxide- d_6 (DMSO- d_6) containing 10 vol% deuterium sulfate (D $_2$ SO $_4$). The supernatant liquid was transferred to a NMR tube.

Photocatalytic H $_2$ O $_2$ production

MOF samples (5.0 mg) and distilled water (5.0 mL) were added into a Pyrex reaction vessel (30 mL). The mixture was bubbled with O $_2$ for 15 min under dark condition after sonication. Thereafter, the reaction solution was irradiated from the side with a Xe lamp (100 mW/cm 2 , 500 W, SAN-EIELECTRIC XEF-501S) through a glass filter ($\lambda > 420$ nm) for 3 h with magnetic stirring at ambient pressure and temperature.

H₂O₂ decomposition test

Al-TCPP10, Al-TCPP4-TBAPy6, and Al-TBAPy10 (5.0 mg) and 0.5 mmol·L⁻¹ H₂O₂ aqueous solution (5.0 mL) were added to a Pyrex reaction vessel (30 mL), which was sealed with a rubber septum. The mixture solution was stirred under dark conditions at ambient pressure and temperature.

Quantification of produced H₂O₂

The amount of H₂O₂ produced was determined by spectroscopic titration with an acidic solution of [TiO(tpypH₄)]⁴⁺ complex (Ti-TPyP reagent). The [TiO(tpypH₄)]⁴⁺ complex (3.4 mg) was dissolved in 50 mmol·L⁻¹ HCl aqueous solution (100 mL). This solution was used as the Ti-TPyP reagent. The sample solution was diluted with purified water. The diluted sample solution (0.25 mL) was mixed with 4.8 mol·L⁻¹ HClO₄ aqueous solution (0.25 mL) and Ti-TPyP reagent (0.25 mL). After a few minutes, the mixture was diluted to 2.5 mL with purified water. The absorbance of this solution at $\lambda = 434$ nm (A_S) was measured using a Shimadzu UV-2600 UV-Vis spectroscope. A blank solution was prepared by adding purified water in place of the sample solution (0.25 mL) and its absorbance was defined as A_B . The difference in absorbance (ΔA_{434}) was determined by the following equation: $\Delta A_{434} = A_B - A_S$. Based on ΔA_{434} and the volume of the solution, the amount of hydrogen peroxide was determined according to the literature.¹

The detection of active oxygen using ESR measurements

For trapping superoxide radicals (O₂^{·-}), Al-TCPP4-TBAPy6 powder (1.0 mg) was suspended in a 100 mmol·L⁻¹ DMPO water/acetonitrile (1:4) solution (1.0 mL). For trapping singlet oxygen (¹O₂) species, Al-TCPP4-TBAPy6 powder (1.0 mg) was suspended in a 50 mmol·L⁻¹ TEMPO water/acetonitrile (1:4) solution (1.0 mL). All solutions were mixed, transferred into a quartz ESR cell, and bubbled O₂ for 15 min. The ESR measurements were performed by using an ESR spectrometer (JEOL RESONANCE JES-TE200) at room temperature. Test samples were irradiated by using a light focused from a xenon arc-lamp (Ushio Co., UXL10, Tokyo, Japan) through a glass filter ($\lambda > 420$ nm). ESR measurements were conducted under the following conditions: microwave power, 1.0 mW; center of magnetic field, 336.0 mT; sweep width, 7.5 mT; sweep time, 1 min; modulation width, 0.1 mT; amplitude, 400; time constant, 0.1 s. Signal intensities were normalized to a MnO marker.

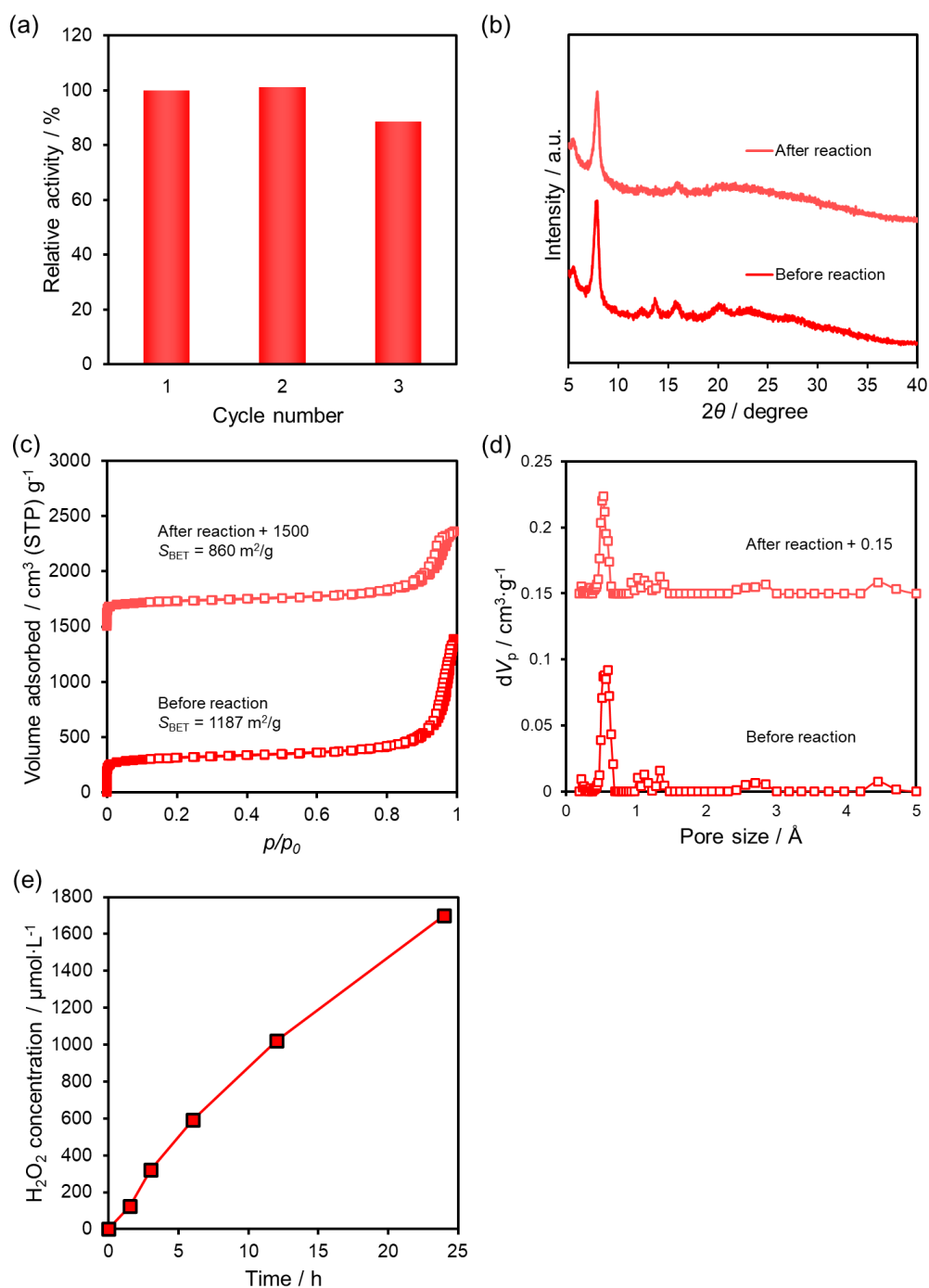


Fig. S1 (a) Recycle tests using Al-TCPP4-TBAPy6 in distilled water in O₂ atmosphere under visible-light ($\lambda > 420$ nm) irradiation. (b) PXRD patterns, (c) N₂ physisorption isotherms and (d) pore distributions calculated using NLDFT method of Al-TCPP4-TBAPy6 before and after the reactions. (e) Time course of H₂O₂ production under visible-light ($\lambda > 420$ nm) irradiation of Al-TCPP4-TBAPy6 during the long-term reaction.

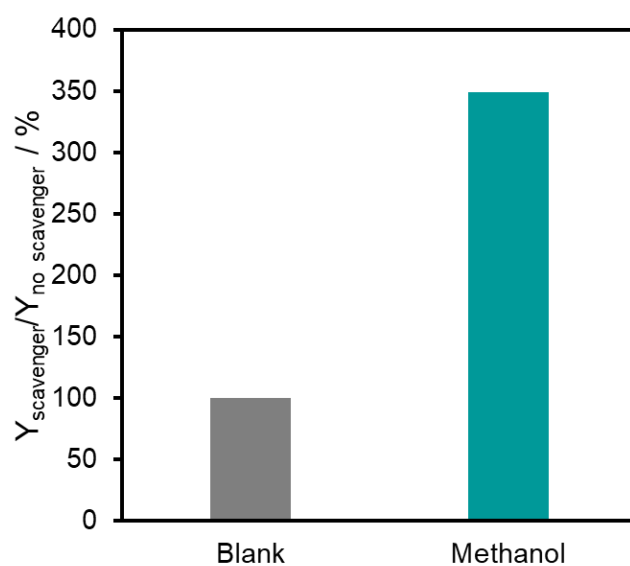


Fig. S2 Comparison of H_2O_2 concentration generated over Al-TCPP4-TBAPy6 under visible-light ($\lambda > 420$ nm) irradiation for 3 h with and without methanol as a hole scavenger.

Table S1 The molar ratio of TCPP and TBAPy linkers in Al-TCPP(10-X)-TBAPyX samples added during synthesis.

Sample	TCPP / mg	TBAPy / mg
Al-TCPP10	50	0.0
Al-TCPP8-TBAPy2	40	9.0
Al-TCPP6-TBAPy4	30	18
Al-TCPP4-TBAPy6	20	27
Al-TCPP2-TBAPy8	10	36
Al-TBAPy10	0	48

Table S2 Comparison of photocatalytic activities on H₂O₂ production from O₂ and water over MOF photocatalysts.²⁻⁴

Sample	H ₂ O ₂ production rate / $\mu\text{mol}\cdot\text{L}^{-1}\cdot\text{h}^{-1}$	Reaction condition	Ref.
Al-TCPP4-TBAPy6	127	MOF 5.0 mg, distilled water 5.0 mL, Xe lamp ($\lambda > 420$ nm, 100 mW·cm ⁻¹)	This work
MIL-125-PDI	24	MOF 5.0 mg, distilled water/acetonitrile (1:4) 5.0 mL, Xe lamp ($\lambda > 420$ nm, 800 mW·cm ⁻¹)	2
MIL-001*	7.0	MOF 5.0 mg, distilled water 5.0 mL, Xe lamp ($\lambda > 420$ nm, 100 mW·cm ⁻¹)	3
Ni/Hf-0.5	10.7	MOF 5.0 mg, distilled water 5.0 mL, Xe lamp ($\lambda > 420$ nm, 100 mW·cm ⁻¹)	4

*We could not replicate the activity in the reference paper (Ref. 9), so we conducted a photocatalytic test under the above condition.

Table S3 PL lifetimes and contribution rates of Al-TBAPy10 and Al-TCPP4-TBAPy6 excited at 405 nm.

Sample	τ_1 / ns	τ_2 / ns	τ_3 / ns	τ_4 / ns
Al-TBAPy10	0.28 (4.55)	2.28 (35.54)	11.48 (32.04)	39.55 (27.88)
Al-TCPP4-TBAPy6	0.07 (11.51)	2.09 (88.49)	-	-

References

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