

Electronic Supplementary Information

**Ti cluster-alkylated hydrophobic MOFs for photocatalytic production
of hydrogen peroxide in two-phase systems**

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Table of contents

	Pages
Materials	□□□ S2
Materials Synthesis	□□□ S2 – S3
Experimental	□□□ S3 – S4
Characterization	□□□ S5 – S9
Results	□□□ S10 – S12
References	□□□ S12

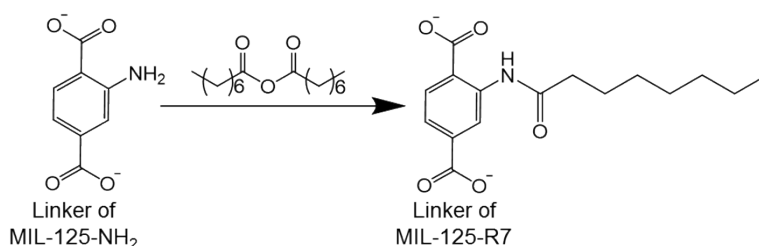
Materials

All chemicals commercially available were used without further purification unless otherwise noted. Oxo[5,10,15,20-tetra(4-pyridyl)porphinato]titanium(IV) ($[\text{TiO}(\text{tpypH}_4)]^{4+}$), 2-aminoterephthalic acid (98%), n-octanoic anhydride (>98 %) and octadecylphosphonic acid were supplied from Tokyo Chemical Industry Co., Ltd. (TCI). Acetonitrile (99%), Titanium isopropoxide, N,N-dimethylformaldehyde (>99.5%), ethanol (99.5%), methanol (>99%), benzyl alcohol (>97%), hydrogen peroxide (30%), hydrochloric acid (16.9%) and perchloric acid (60%) were purchased from Nacalai Tesque.

Materials synthesis

MIL-125-NH₂. MIL-125-NH₂ was synthesized according to a reported method.¹ First, 2-aminoterephthalic acid (6.0 mmol) and titanium isopropoxide (3.0 mmol) were added to a solution of N,N-dimethylformamide (25 ml) and methanol (25 ml). The mixture was stirred at ambient temperature for 30 min, transferred to 50 ml Teflon lined stainless steel autoclave, and heated for 16 h at 423 K. After the reaction, the product of the synthesis was collected by centrifugation and washed with DMF followed by methanol to remove unreacted organic linkers. The obtained yellow solid was dried under vacuum overnight.

MIL-125-R7. Prepared MIL-125-NH₂ was modified by n-octanoic anhydride by following the steps published elsewhere (Scheme S1).² MIL-125-NH₂ (49 mg) was activated prior to the modification at 423 K for 5 h. Then the MOF was dispersed in 5.0 mL of acetonitrile, to which 40 equivalent of n-octanoic anhydride was added. The suspension was stirred for 24 h at 353 K. The solid was collected centrifugally and washed with CH₂Cl₂ to yield linker-modified hydrophobic MOF (MIL-125-R7).



Scheme S1. Alkylation of linker of MIL-125-NH₂ to form MIL-125-R7.

OPA/MIL-125-R7. OPA/MIL-125-R7 was synthesized in the same manner as steps which synthesized OPA/MIL-125-NH₂. MIL-125-R7 was immersed in OPA ethanol solution for 24

h at room temperature. The mixture was stirred for 5 minutes every 2 hours. Then, the solution was decanted and washed with ethanol to remove free OPA. The washed material was dried under vacuum overnight at room temperature and activated at 393 K for 24 h.

Experimental

UV-Vis absorption spectrum measurements of MIL-125-NH₂ and OPA/MIL-125-NH₂. The ultraviolet visible diffuse reflectance (UV-Vis) spectra of the powdered samples were collected using a Shimadzu UV-2450 spectrophotometer. Absorption spectra were obtained using the Kubelka-Munk function using BaSO₄ as the reference.

Nitrogen adsorption measurements. Nitrogen adsorption measurements were performed using BELSORP-max system (Microtrac BEL Corp., Inc.) at 77 K. Samples were degassed under vacuum at 453 K for 20 h prior to data collection.

TG/DTA measurements. TG-DTA was carried out using a Rigaku thermogravimetry unit, Rigaku Thermo Plus EVO II series high-temperature differential thermal balance TG/DTA, with temperature increasing at a ramping rate of 1.0 K min⁻¹ up to 1273 K in air.

FT-IR spectrum measurements of MIL-125-NH₂ and OPA/MIL-125-NH₂. Fourier transform infrared spectroscopy (FT-IR) was performed with a JASCO FTIR-6100. Samples were mixed with KBr and compressed into thin disk-shaped pellets prior to acquiring FT-IR spectra.

XPS spectrum measurements of MIL-125-NH₂ and OPA/MIL-125-NH₂. X-ray photoelectron microscopy (XPS) was performed with a Shimadzu XPS system, ESCA-3400, using the Mg K α line (1253.6 eV). The designated closed container was utilized for sample setting to prevent reoxidation. Binding energy was calibrated using C 1s photoelectronic peak at 285 eV.

Photocatalytic reaction. In a typical reaction setup, the photocatalysts (5.0 mg), water (2.0 mL), and benzyl alcohol (BA) (5.0 mL) (in case of the two-phase system) or the photocatalysts (5.0 mg), acetonitrile (5.0 mL) and BA (1.0 mL) (in case of the single-phase system) were added to a Pyrex® reaction vessel (30 mL), which was sealed with a rubber septum. The resulting mixture was sonicated and bubbled with oxygen for 20 min in the dark. Subsequently the sample was irradiated from the side with an Xe lamp (500 W; SAN-EI ELECTRIC XEF-501S) through a glass filter ($\lambda > 420$ nm) with magnetic stirring at

ambient pressure and temperature. An aliquot of the reaction solution was collected and analyzed.

Recycling test. The MOF (10 mg) was added to a two-phase reaction system composed of water (4.0 mL) and benzyl alcohol (10 mL). The mixture was bubbled with oxygen for 20 min in the dark. Then, the system was irradiated with visible light ($\lambda > 420$ nm) for the photocatalysis. After 2 h, the quantification of produced H_2O_2 was conducted and the reaction suspension was filtrated to collect the MOF. The collected MOF was dried and activated at 423 K for 40 min in a vacuum prior to next cycle.

Quantification of produced H_2O_2 . From spectroscopic titration with an acidic solution of $[\text{TiO}(\text{tpypH}_4)]^{4+}$ complex (Ti-TPyP reagent), the amount of produced H_2O_2 was determined. The $[\text{TiO}(\text{tpyp})]$ complex (34 mg) was dissolved in 1.0 L of 50 mM hydrochloric acid to be used as Ti-TPyP reagent. An aliquot (e.g., 10 μL) of the reaction solution was diluted with water and used as a sample solution. 0.25 mL of the sample solution was mixed with 0.25 mL of 4.8 M perchloric acid and 0.25 mL of the Ti-TPyP reagent. After 5 min at room temperature, the mixture was diluted to 2.5 mL with water and used for the spectroscopic measurement. Absorbance at $\lambda = 434$ nm was measured using a Shimadzu UV-2600 UV-Vis spectrophotometer (A_S). In the similar manner, a blank solution was prepared by adding distilled water in place of the sample solution in the same volume with its absorbance designated as A_B . The difference in absorbance was determined by following the 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.³

Quantification of produced benzaldehyde. The amount of produced benzaldehyde was analysed by gas chromatography (Shimadzu, GC-14B with Phenomenex ZB-FFAP columns).

Characterization

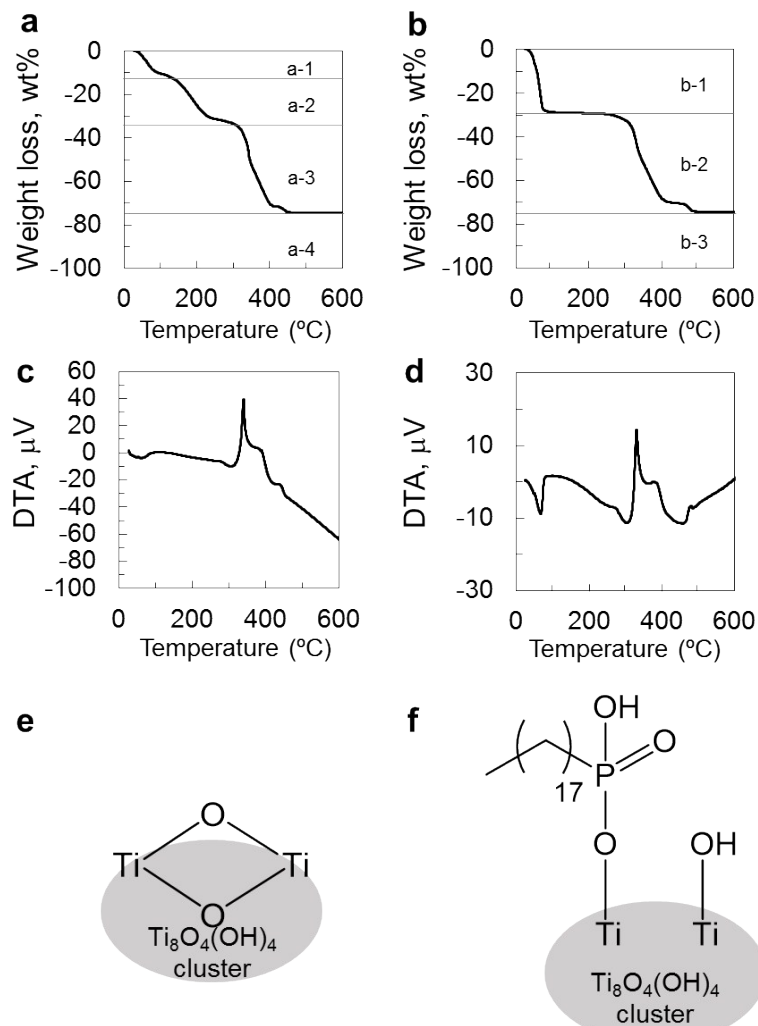


Figure S1. (a, b) TG profiles of MIL-125-NH₂ and OPA/MIL-125-NH₂. (c, d) DTA profiles of MIL-125-NH₂ and OPA/MIL-125-NH₂. Chemical structures of (e) clusters in very surface of MIL-125-NH₂, (f) alkylated clusters in OPA/MIL-125-NH₂.

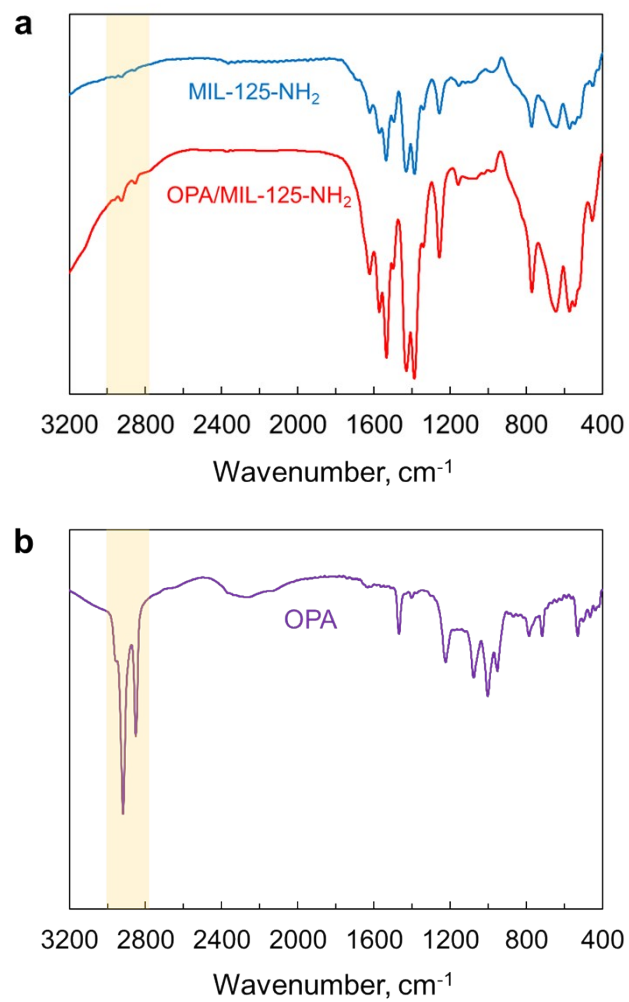


Figure S2. FT-IR spectra of (a) MIL-125-NH₂ and OPA/MIL-125-NH₂ and (b) OPA.

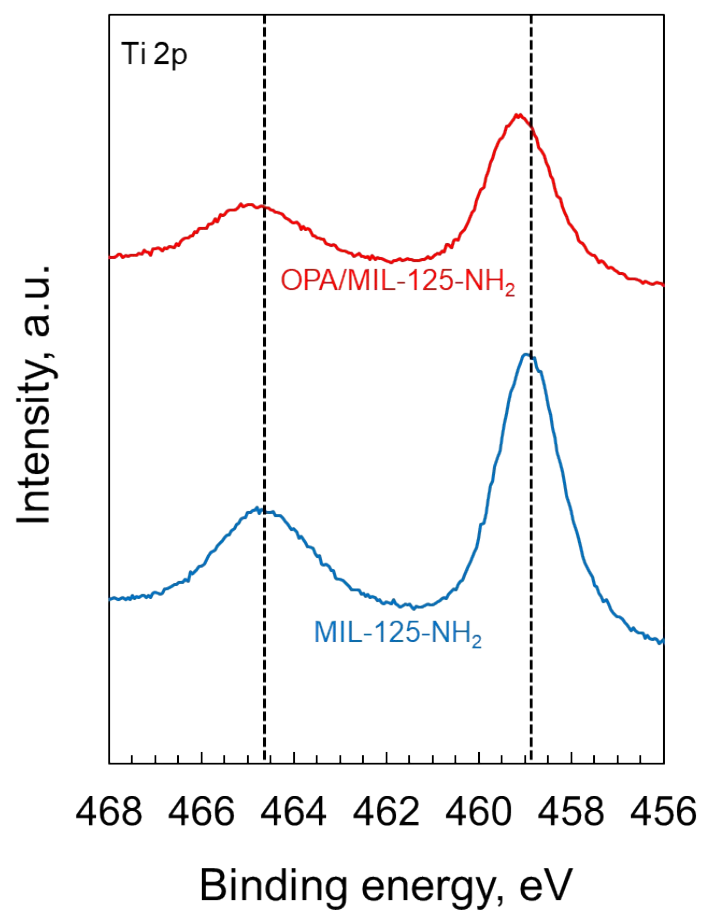


Figure S3. Ti 2p XPS spectra of OPA/MIL-125-NH₂ (red) and MIL-125-NH₂ (blue).

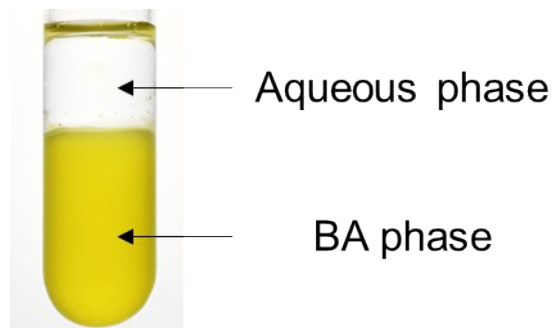


Figure S4. The digital picture of two-phase systems composed of BA/water phase containing OPA/MIL-125-NH₂ in BA phase.

Calculation of population of alkylated clusters in OPA/MIL-125-NH₂.

TG-DTA measurement was carried out to determine the population of alkylated clusters in OPA/MIL-125-NH₂. A unit cell of MIL-125-NH₂ can be expressed as Ti₈O₈(OH)₄-L₆, where L is 2-aminoterephthalic acid linker. After combustion, this unit cell is expected to yield 8TiO₂. The theoretical ratio of weight of 6L (1075 g mol⁻¹) to 8TiO₂ (638.9 g mol⁻¹) can be calculated to be 1.682. In the result of TG-DTA measurements for MIL-125-NH₂, the endothermal weight losses in regions indicated as a-1 and a-2 were attributed to desorption of H₂O and residual DMF from synthesis step, respectively. Exothermal weight loss in a-3 and residual a-4 were attributed to the weight loss due to combustion of organic linkers and weight of residual TiO₂, respectively. The experimental ratio of weight loss due to combustion of organic linkers (41.8%) to 8TiO₂ (25.8%) was determined to be 1.62, which is in good agreement with the expected value calculated above (1.682).

For MIL-125-R_n, a unit cell can be expressed as OPA_{*n*}Ti₈O₈(OH)₄-L₆, where *n* is an average number of OPA that modify the clusters per unit cell. The structure of OPA is indicated in (f) for OPA/MIL-125-NH₂. When combusted, assuming the monodentate species (f), 1 mol of this unit cell loses [179.1*6 + 334.5**n*] g due to combustion of organic linkers and OPA and leaves 638.9 g due to residual 8TiO₂. The weight losses due to combustion of organic linkers and OPA of OPA/MIL-125-NH₂ can be found in regions b-2 (64.7%). The weight of residual 8TiO₂ of OPA/MIL-125-NH₂ can be found in regions b-3 (35.3%). By comparing the ratios of these values with the theoretically calculated values, *n* can be calculated as 0.283 for OPA/MIL-125-NH₂. This yields the conversion of Ti atoms in Ti₈O₈(OH)₄ clusters alkylation to be 3.54% for OPA/MIL-125-NH₂.

Results

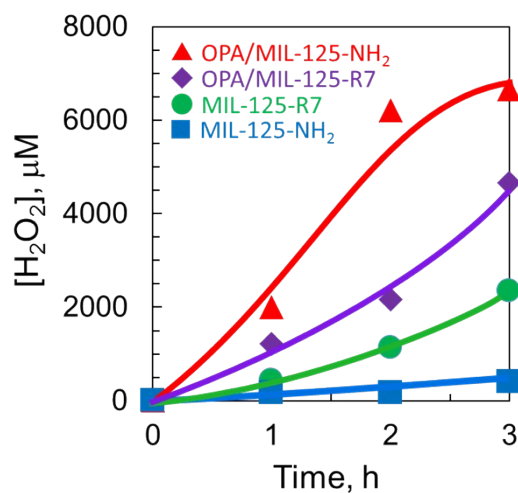


Figure S5. Time courses of H₂O₂ production and under photoirradiation ($\lambda > 420$ nm) of the two-phase system composed of BA (5.0 mL) and water (2.0 mL) catalyzed by 5.0 mg of OPA/MIL-125-NH₂ (red triangle), OPA/MIL-125-R7 (purple diamond), MIL-125-R7 (green circle) and MIL-125-NH₂ (blue square).

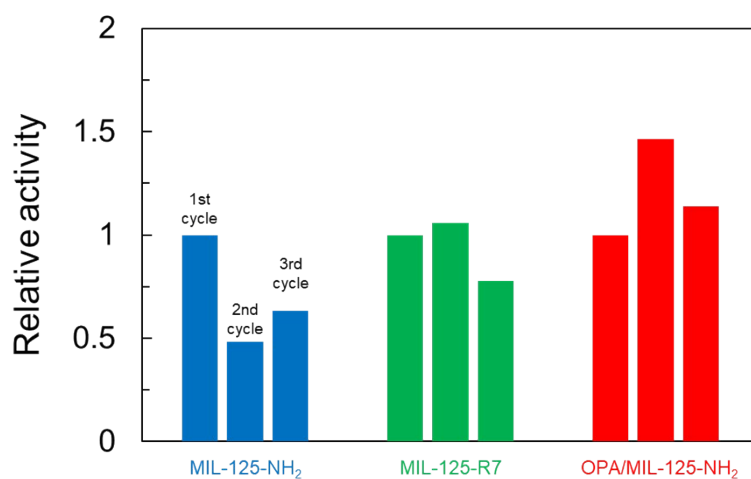


Figure S6. Recycling tests of MIL-125-NH₂ (blue), MIL-125-R7 (green) and OPA/MIL-125-NH₂ (red)

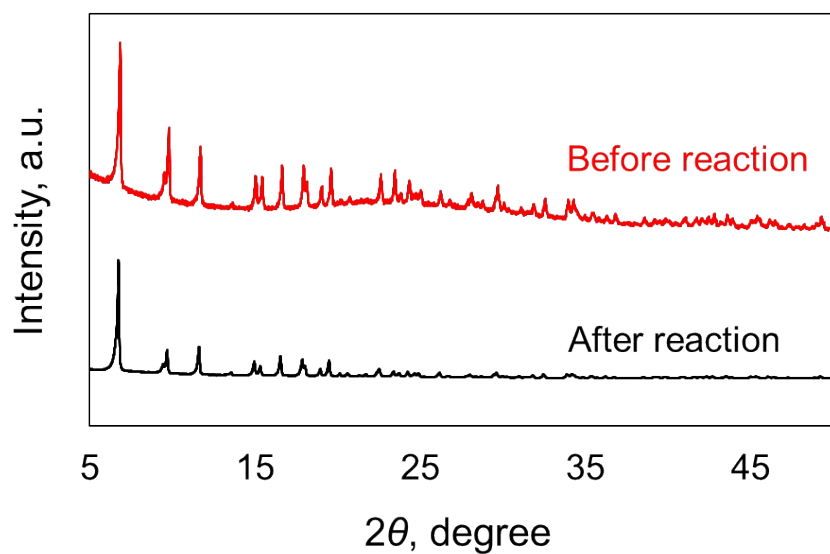


Figure S7. XRD patterns of OPA/MIL-125-NH₂ before and after the reaction.

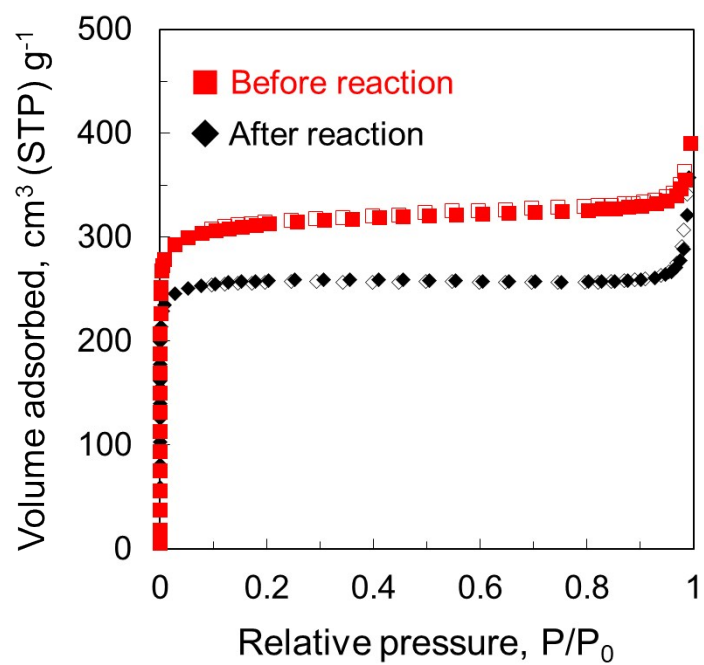


Figure S8. N₂ adsorption isotherms at 77 K for OPA/MIL-125-NH₂ before and after the reaction.

Table S1. Textual properties of OPA/MIL-125-NH₂ before and after the reaction.

Sample	S _{BET} (m ² g ⁻¹)	d _{pore} (nm)	V _{pore} (cm ³ g ⁻¹)
Before reaction	1242	0.54	0.48
After reaction	1038	0.65	0.39

References

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- 2 J. G. Nguyen and S. M. Cohen, *J. Am. Chem. Soc.*, 2010, **132**, 4560–4561.
- 3 C. Matsubara, N. Kawamoto and K. Takamura, *Analyst*, 1992, **117**, 1781–1784.