

## Electronic Supplementary Information

### **Photocatalytic Production of Hydrogen Peroxide through Selective Two-Electron Reduction of Dioxygen Utilizing Amine-Functionalized MIL-125 Deposited with Nickel Oxide Nanoparticles**

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## Experimental section

### 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%) and 5,5-dimethyl-1-pyrroline N-oxide (97%) were supplied from Tokyo Chemical Industry Co., Ltd. (TCI). Titanium isopropoxide, N,N-dimethylformaldehyde (>99.5%), methanol (>99%),  $\text{Ni}(\text{NO}_3)_2 \cdot 6\text{H}_2\text{O}$  (>97%),  $\text{H}_2\text{PtCl}_6$ , hydrazine hydrate, 2-aminobenzoic acid, benzylalcohol (>97%), triethanolamine (>98%), hydrogen peroxide (30%), hydrochloric acid (16.9%), perchloric acid (60%) and biphenyl were purchased from Nacalai Tesque.

### Synthesis of MIL-125-NH<sub>2</sub>

MIL-125-NH<sub>2</sub> was synthesized according to a reported method.<sup>1</sup> First, 2-aminoterephthalic acid (6 mmol) and titanium isopropoxide (3 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 16 h at 423 K. After the reaction, the product of the synthesis was collected by centrifugation and washed with DMF to remove unreacted organic linker followed by washing with methanol. The obtained yellow solid was dried under vacuum overnight and activated by calcination in vacuum overnight at 423 K.

### Synthesis of M/MIL-125-NH<sub>2</sub>

M/MIL-125-NH<sub>2</sub> (M = Ni and Pt) was synthesized by applying a reported method.<sup>2</sup> To a suspension containing 500 mg of activated MIL-125-NH<sub>2</sub> in 50 mL of methanol, 0.17 mmol of metal source was added and stirred overnight in dark. Metal sources used in the synthesis were  $\text{Ni}(\text{NO}_3)_2 \cdot 6\text{H}_2\text{O}$  (0.17 mmol) for Ni/MIL-125-NH<sub>2</sub> and  $\text{H}_2\text{PtCl}_6$  (0.17 mmol) for Pt/MIL-125-NH<sub>2</sub>. The product was collected centrifugally and washed with methanol to remove unreacted metal ions. The solid was then suspended in 50 mL of methanol. To the suspension, hydrazine hydrate (1.0 mL) was added dropwise with vigorous stirring. After stirring for 30 min, the product was isolated by centrifugation, washed with methanol, and dried under vacuum at room temperature.

### Synthesis of MIL-125 and Ni/MIL-125

Amine-free MIL-125 was synthesized according to a reported method.<sup>3</sup> 1 g (6 mmol) of terephthalic acid was dissolved in solution containing 18 mL of DMF and 2 mL of methanol. 0.568 mL (2 mmol) of titanium isopropoxide was then added into the terephthalic acid containing solution. The solution was mixed and then sonicated for 20 min until it became transparent. The solution was then transferred into Teflon-lined reactor (100 mL) and kept at 423 K for 18 h. The white slurry was collected by centrifugation and washed 3 times with ethanol. Ni/MIL-125 was synthesized by following the same procedure used to synthesize Ni/MIL-125-NH<sub>2</sub> from MIL-125-NH<sub>2</sub>. The XRD pattern of MIL-125 is shown in Figure S9.

### **Synthesis of Ni/TiO<sub>2</sub>**

TiO<sub>2</sub> (ST-01) deposited with NiO<sub>x</sub> was synthesized by impregnation method. To an aqueous suspension (50 mL) containing ST-01(500 mg), Ni(NO<sub>3</sub>)<sub>2</sub>•6H<sub>2</sub>O (35.2 mg) was added. After stirring overnight, 10 eq. of NaBH<sub>4</sub> was added. The solid was then collected centrifugally, dried overnight under vacuum and employed for the reaction.

### **Measurement of X-ray powder diffraction patterns**

X-ray powder diffraction patterns were recorded using a Rigaku RINT2500 diffractometer with Cu K radiation ( $\lambda = 1.5406 \text{ \AA}$ ).

### **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 423 K for 16 h prior to data collection.

### **Transmission Electron Microscopy (TEM) images**

Transmission Electron Microscopy (TEM) images were obtained using a Hitachi H-800 electron microscope equipped with an energy-dispersive X-ray (EDX) detector, operated at 200 kV.

### **Spectroscopic measurements in solution**

The UV-visible absorption spectra were recorded using a Shimadzu UV-2600 UV-Vis spectrophotometer with a quartz cuvette (light-path length = 1.0 cm) at 298 K.

### **UV-Vis absorption spectrum measurements of MIL-125-NH<sub>2</sub> and M/MIL-125-NH<sub>2</sub>**

The ultraviolet visible diffuse reflectance (UV-Vis) spectra of the powdered samples were collected using a Shimadzu UV-2450 spectrophotometer. Using BaSO<sub>4</sub> as a reference, absorption spectra were obtained using the Kubelka-Munk function.

### **Photocatalytic reaction**

In a typical reaction setup, the photocatalyst (5.0 mg), TEOA (1.0 mL), and acetonitrile (4.0 mL) were added to a Pyrex<sup>®</sup> reaction vessel (30 mL), which was sealed with a rubber septum. The resulting mixture was sonicated and bubbled with oxygen for 15 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) for 24 h with magnetic stirring at ambient pressure and temperature. An aliquot of the reaction solution was collected and analysed as following.

### **Quantification of produced H<sub>2</sub>O<sub>2</sub>**

From spectroscopic titration with an acidic solution of [TiO(tpypH<sub>4</sub>)]<sup>4+</sup> complex (Ti-TPyP reagent), the amount of produced H<sub>2</sub>O<sub>2</sub> was determined.<sup>4</sup> The [TiO(tpypH<sub>4</sub>)]<sup>4+</sup> 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  $\mu$ L) of the reaction solution was diluted with water and used as 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 (AS). 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 AB. The difference in absorbance was determined by following the equation:  $\Delta A_{434} = AB - AS$ . Based on  $\Delta A_{434}$  and the volume of the solution, the amount of hydrogen peroxide was determined according to the literature.<sup>3</sup>

### **Quantification of produced benzaldehyde**

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

### **XAFS measurement**

The data for the structural transformation of Ni species as catalytic active sites were collected using X-ray absorption fine structure analysis (XAFS). The Ni K-edge XAFS spectra were recorded at the BL-01 at SPring-8, JASRI, Harima, Japan (Pro. Nos. 2017B1081 and 2017B1084). In XAFS measurements, a Si(111) double crystal was used to mono-chromatize the X-rays from the 2.5 GeV electron storage ring. In XAFS measurement, a sample is loaded into the cell and measured in fluorescence mode. The EXAFS data were examined using the EXAFS analysis program, Rigaku REX2000.

### **EPR measurement**

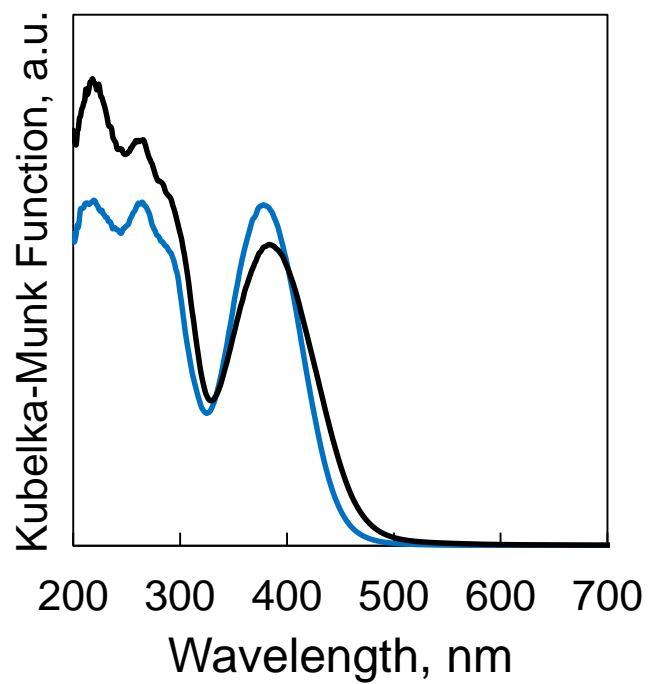
MIL-125-NH<sub>2</sub> was suspended in ethanol (1.0 mg mL<sup>-1</sup>) and mixed with DMPO (10 mM). All solutions were freshly prepared, mixed, immediately transferred into a quartz ESR cell, and measured in an ESR spectrometer (JEOL RESONANCE JES-TE200) at 25°C. Test samples were directly irradiated in a micro-wave cavity with a light focused from a xenon arc-lamp (Ushio Co., UXL10, Tokyo, Japan) operating at 500 W. ESR measurements were conducted under the following conditions: magnetic field, 336.250 mT; modulation width, 0.1 mT; time constant, 0.3 s; microwave power, 1.0 mW; sweep width, 7.5 mT; sweep time, 8 min; amplitude, 400. Signal intensities were normalized to a MnO marker.

### **Identification of TEOA oxidation product**

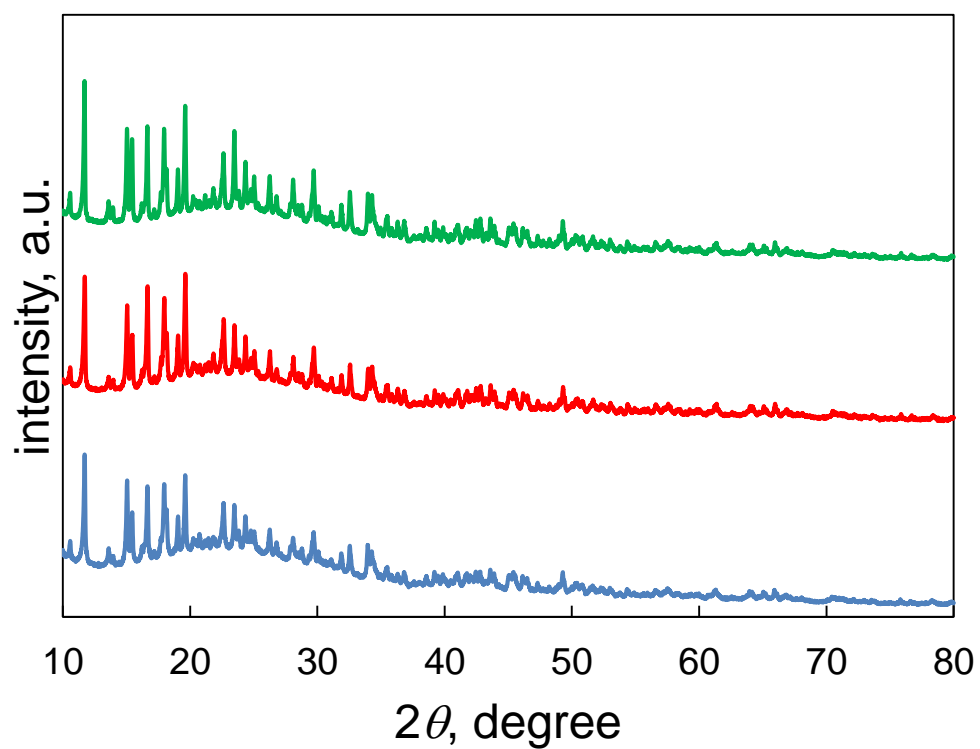
MIL-125-NH<sub>2</sub> (10.0 mg) was dispersed in O<sub>2</sub>-saturated acetonitrile (5.0 mL) solution. An aliquot of reaction solution was diluted with same amount of acetonitrile and used for gas chromatography/mass spectrometry (Shimadzu GCMS-2010 plus) equipped with TC-5HT column.

### **Repetitive H<sub>2</sub>O<sub>2</sub> production**

Repetitive H<sub>2</sub>O<sub>2</sub> production was performed to examine the stability of Ni/MIL-125-NH<sub>2</sub> in water. Acetonitrile suspension (7.5 mL) containing water (1.5 mL) and MIL-125-NH<sub>2</sub> (7.5 mg) was irradiated with Xe lamp. The catalyst was collected centrifugally every 20 h, and employed for the second run after addition of 7.5 mL of the reaction solution. H<sub>2</sub>O<sub>2</sub> concentration of the reaction solution was measured prior to the second and third run to confirm that only negligible amount of H<sub>2</sub>O<sub>2</sub> was in the reaction solution.

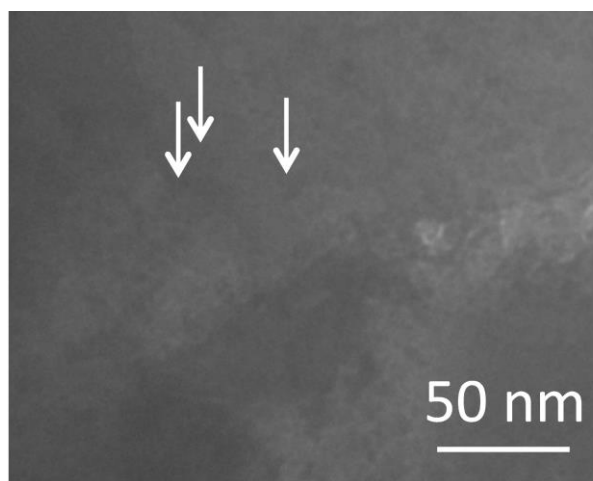


**Figure S1.** UV-Vis spectrum of MIL-125-NH<sub>2</sub> (blue) and Pt/MIL-125-NH<sub>2</sub> (black).

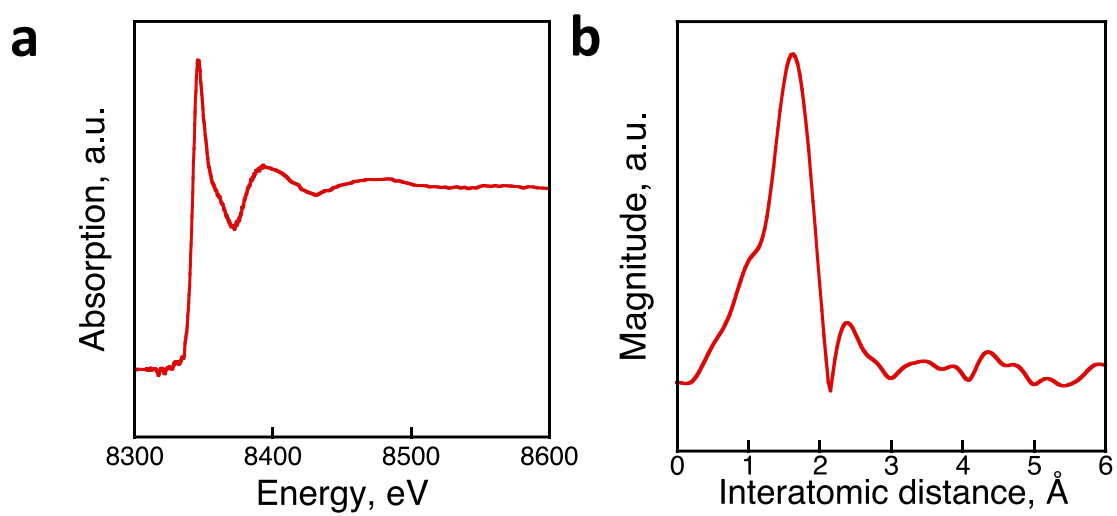


**Figure S2.** X-ray diffraction (XRD) patterns of MIL-125-NH<sub>2</sub> (blue), Ni/MIL-125-NH<sub>2</sub> (red) and Pt/MIL-125-NH<sub>2</sub> (green).

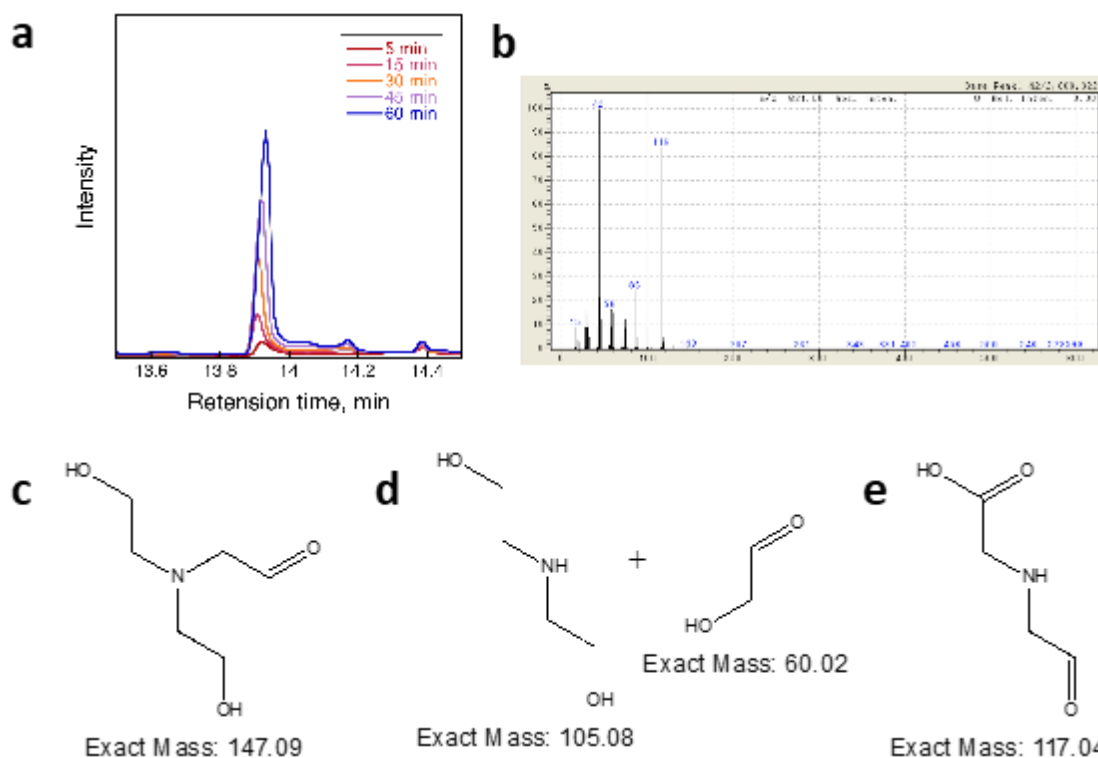




**Figure S3.** TEM image of Pt/MIL-125-NH<sub>2</sub>.

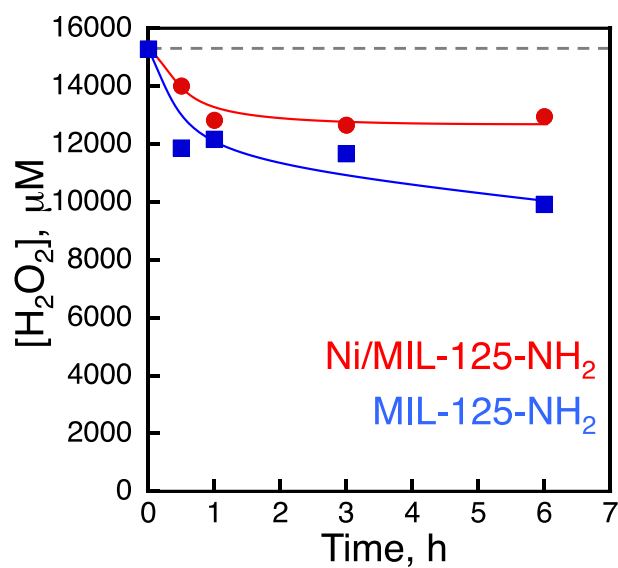


**Figure S4.** Ni K-edge (a) XAFS and (b) FT-EXAFS spectra of Ni/MIL-125-NH<sub>2</sub>.

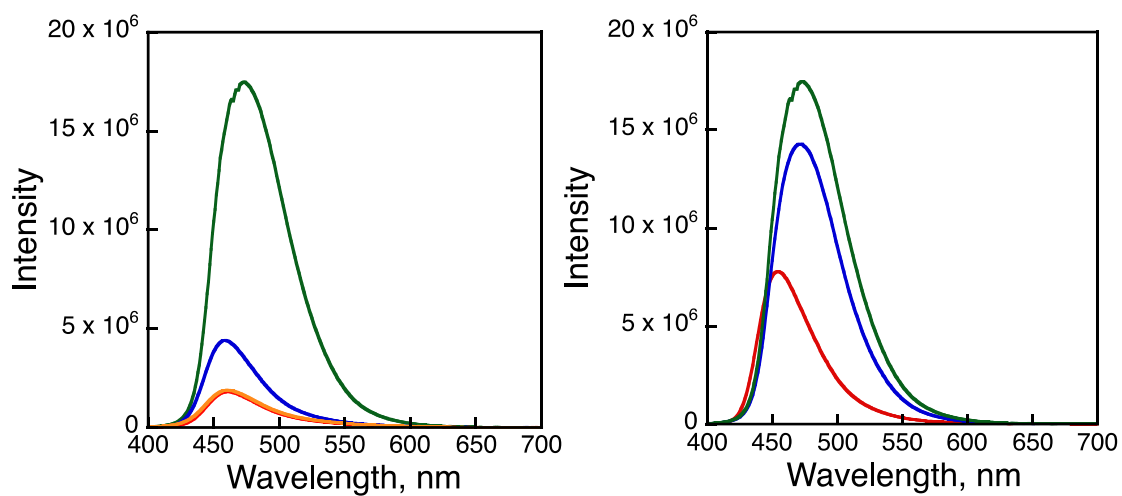


**Figure S5.** (a) Time course of TEOA oxidation product formation after visible-light ( $\lambda > 420$  nm) irradiation of MIL-125-NH<sub>2</sub> (10.0 mg) dispersed in an O<sub>2</sub>-saturated acetonitrile solution (5.0 mL) of TEOA (1.0 mL). (b) Mass spectrum of the peak shown in Figure S6a after 60 min of photoirradiation. (c, d) Reported oxidation products of TEOA. (e) Plausible product of TEOA oxidation.

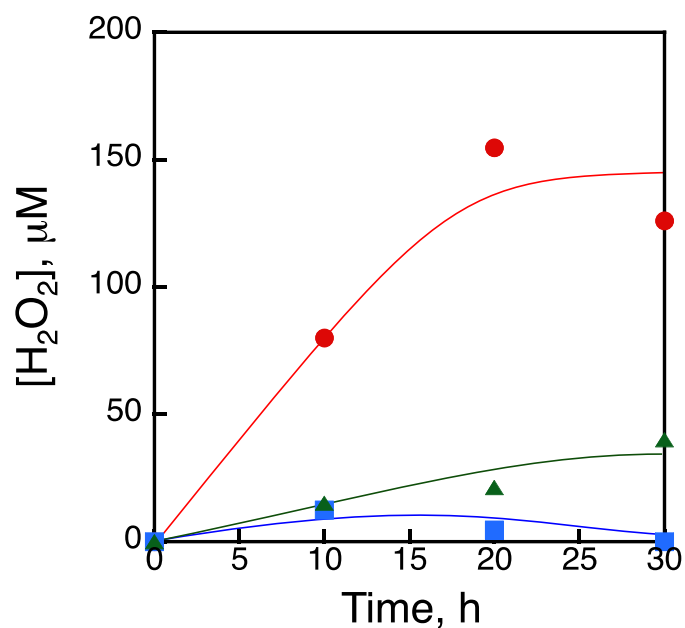
A fragment with  $m/z = 116$  was observed after photoirradiation of MIL-125-NH<sub>2</sub> dispersed in an O<sub>2</sub>-saturated acetonitrile solution of TEOA. Previously, formation of molecules shown in Figure S5c and S5d were reported as oxidation products of TEOA.<sup>5,6</sup> The molecules are formed as the result of oxidation of alcohol moiety to an aldehyde and successive hydration, respectively. On the other hand, complete oxidation of an alcohol moiety to carboxylic acid in addition to hydration is expected to form the molecule shown in Figure S5e, which is suggested to be the oxidation product of TEOA detected in this work as it is able to yield a fragment with  $m/z = 116$  after deprotonation.



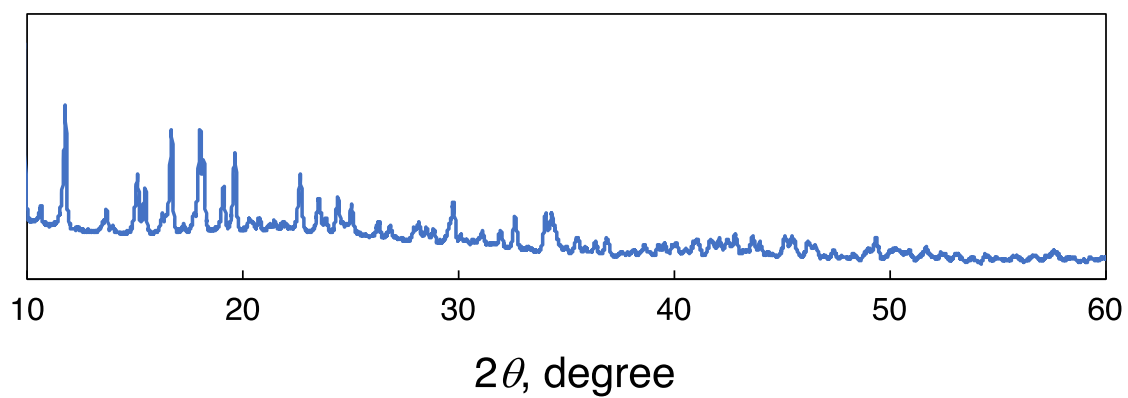
**Figure S6.** Time courses of  $H_2O_2$  (15 mM) decomposition dissolved in 5.0 mL of acetonitrile suspension of 5.0 mg of MIL-125-NH<sub>2</sub> (blue square) or Ni/MIL-125-NH<sub>2</sub> (red circle) at 313 K.



**Figure S7.** Photoluminescence emission spectra of MIL-125-NH<sub>2</sub> (2.0 mg) dispersed in acetonitrile (2.0 mL) irradiated with visible-light ( $\lambda_{\text{ex}} = 380 \text{ nm}$ ) in the presence of various concentrations of (a) TEOA [0 mM (green), 75 mM (blue), 360 mM (red) and 840 mM (orange)] or (b) oxygen [N<sub>2</sub> atmosphere (green), air-saturated (blue) and O<sub>2</sub>-saturated (red)].



**Figure S8.** Time courses of  $H_2O_2$  production under UV and visible light irradiation of 5.0 mg of photocatalyst [MIL-125-NH<sub>2</sub> (green triangle) or Ni/MIL-125-NH<sub>2</sub> (red circle and blue square)] dispersed in an O<sub>2</sub>-saturated acetonitrile solution (5.0 mL) of water [1.0 mL (red circle and green triangle) or 0 mL (blue square)].



**Figure S9.** XRD pattern of synthesized MIL-125.

## References

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