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Supporting Information

Visible-Light-Driven Hydrogen Peroxide Production from Water and Dioxygen by Perylenetetracarboxylic Diimides Modified Titanium-Based Metal–Organic Frameworks

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Electrochemical measurements

Electrode preparation

25 mg of catalyst and 5 mg of Polyethylene glycol were dispersed in 200 μL EtOH, then grinded and mixed evenly. The as-prepared slurry was dropped on FTO with an active area of ca. 1.0 cm^2 (1.0 * 1.0 cm) to achieve a uniform coverage with thickness of about 50 μm, and then dried at 200 ^{o}C for 2 h. All electrodes were prepared through the same process.

Electrochemical measurements

The photocurrents and electrochemical impedance spectroscopy (EIS) measurements were performed on an electrochemical station (CHI760E) with a traditional three electrode system in a single-compartment quartz cell. The Ag/AgCl and platinum sheet were the reference electrode and counter electrode, respectively. Samples with an active area of ca. 1.0 cm^2 (1.0 *1.0 cm) on an FTO glass were served as working electrode. Na_2SO_4 (0.5 M) aqueous solution was used as the electrolyte. A bias voltage (0.50 V) was used for driving the photo-generated electron-transfer. A 300 W Xe lamp with an ultraviolet filter ($\lambda > 420$ nm) was used as the visible light source and positioned 10 cm away from the photoelectrochemical cell. The EIS tests were carried out at the open-circuit voltage of 0.3 V and recorded over a frequency ranged from 0.01 to 1*10^5 Hz with an amplitude at 5 mV.

Fitted time-resolved PL results

Table S1. Time-resolved PL results.

Samples	τ_1	τ_2	B_1%	B_2%	$\tau_{av.}$	χ^2
MIL-125-NH_2	1.15	19.79	35.27	64.73	19.22	1.21
MIL-125-PDI	0.82	9.12	43.08	56.92	8.59	1.28

The fitting process was conducted on the professional software provide by the instrument, and the fitting quality was judged by the factor χ^2. After fitting, we take the Rel% as the "B%" to calculate the average decay lifetime ($\tau_{av.}$). The data was fitted with using following multiple exponential formulas (1). The $\tau_{av.}$ was calculated by the formula (2).

$$R(t) = B_1 e^{\frac{-t}{\tau_1}} + B_2 e^{\frac{-t}{\tau_2}} + B_3 e^{\frac{-t}{\tau_3}} + \cdots\cdots(1)$$

$$\tau_{av.} = \frac{B_1\% \times \tau_1^2 + B_2\% \times \tau_2^2 + B_3\% \times \tau_3^2}{B_1\% \times \tau_1 + B_2\% \times \tau_2 + B_3\% \times \tau_3}\cdots\cdots(2)$$

Calculation of apparent quantum efficiency (AQY)

By assuming a two-electron reduction of O_2, the AQY was calculated as:

$$AQY = \frac{2 \times (molecule\ number\ of\ H2O2)}{incident\ photon\ number} \times 100\% \cdots\cdots(3)$$

H_2O_2 molecule number = $C[H_2O_2] \times V_{solution} \times N_A$, $C[H_2O_2]$ is the H_2O_2 concentration, $V_{solution}$ is the solution volume (5 mL), N_A is the Avogadro number (6.02×10^{23} mol^{-1}).

$$N = I \times A \times t / hv = I \times A \times t \times \lambda / (hc) = \int_{\lambda_1}^{\lambda_2} \frac{IAt}{hc} d\lambda \cdots\cdots(4)$$

Incident photon number (N):

I is the light intensity (0.305 $J \cdot s^{-1} \cdot cm^{-2}$). A is the incident area (~1.767 cm^2), t is the reaction time (4.5 h = 16200 s), λ is the light wavelength (λ_1–λ_2): 400, 420, and 450–1100 nm for Xe lamp with a light filter, h is the Planck constant (6.626×10^{-34} J·s), and c is the light speed (3.0×10^{17} $nm \cdot s^{-1}$).

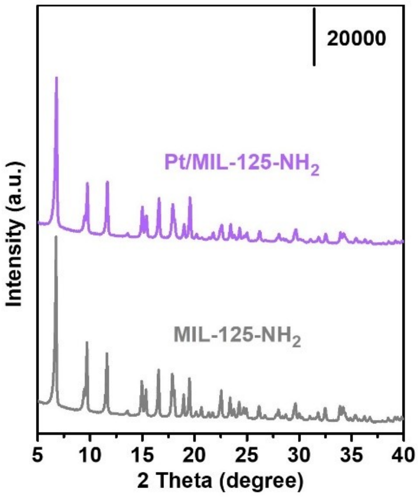

Fig. S1 XRD patterns of Pt/MIL-125-NH_2.

Due to the very small size of Pt nanoparticles, XRD peaks of Pt cannot be observed clearly.

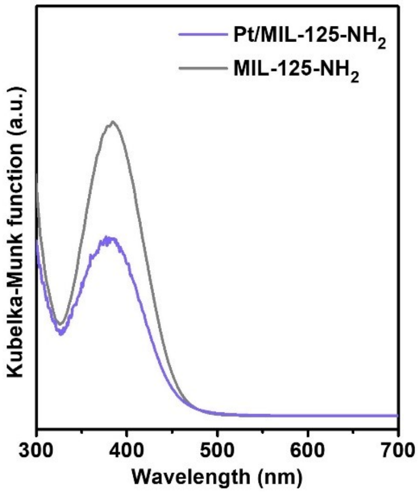

Fig. S2 UV–Vis DRS of Pt/MIL-125-NH$_2$.

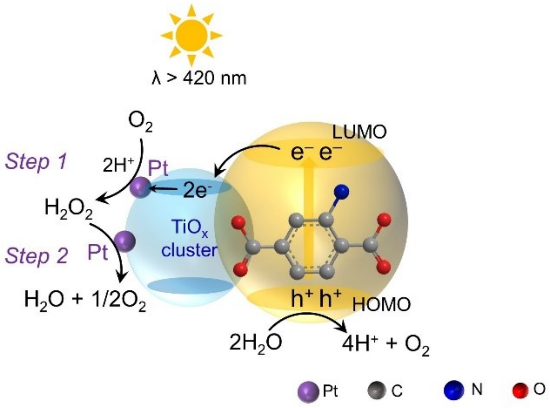

Fig. S3 Promotion effect of Pt on the H_2O_2 production and decomposition using Pt/MIL-125-NH$_2$.

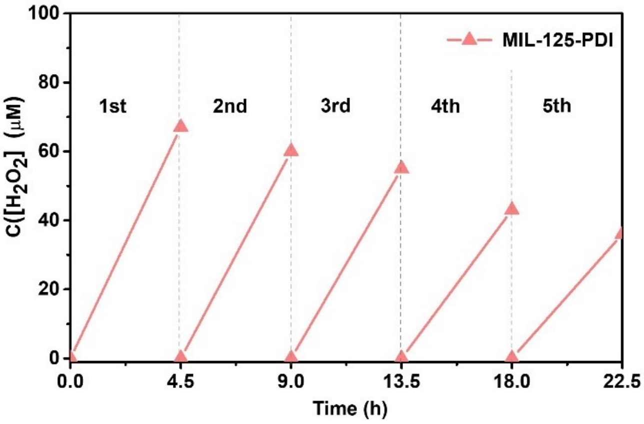

Fig. S4 Results of the recycling test using MIL-125-PDI as a photocatalyst. Reaction conditions: 10 mg of photocatalysts, 1 mL of H_2O, 9 mL of CH_3CN, $\lambda > 420$ nm, O_2: 15 min, 20 mL/min.

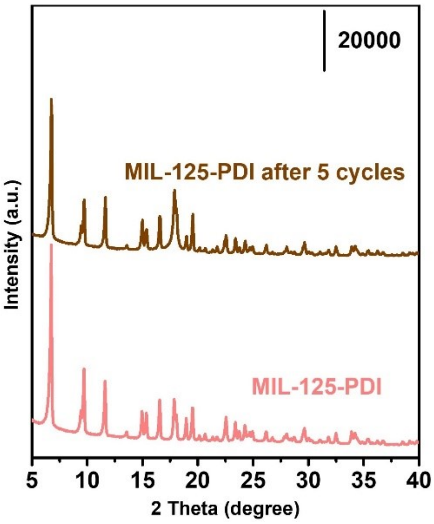

Fig. S5 XRD patterns of MIL-125-PDI before and after five cycles.

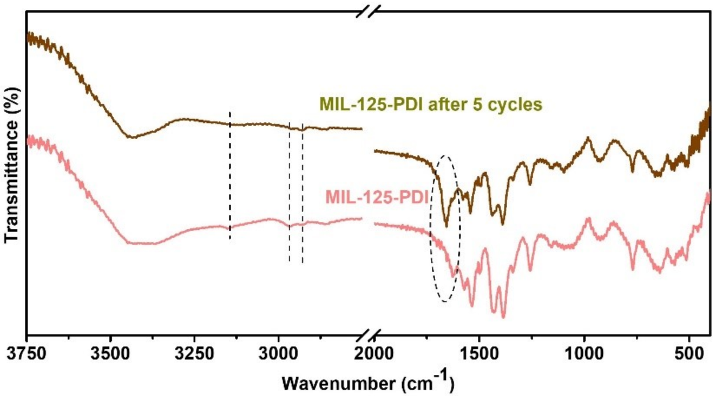

Fig. S6 FT-IR of MIL-125-PDI before and after five cycles.

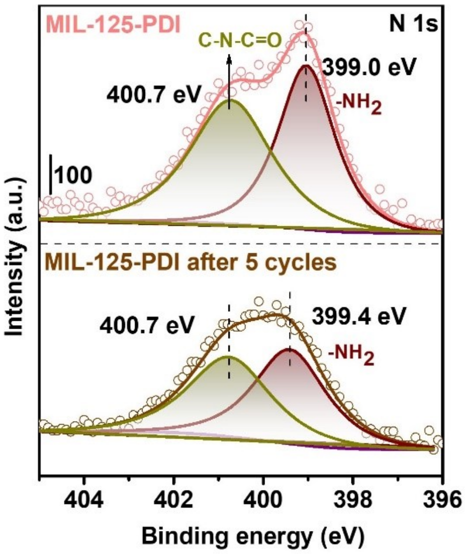

Fig. S7 XPS spectra: N 1s of MIL-125-PDI before and after five cycles.

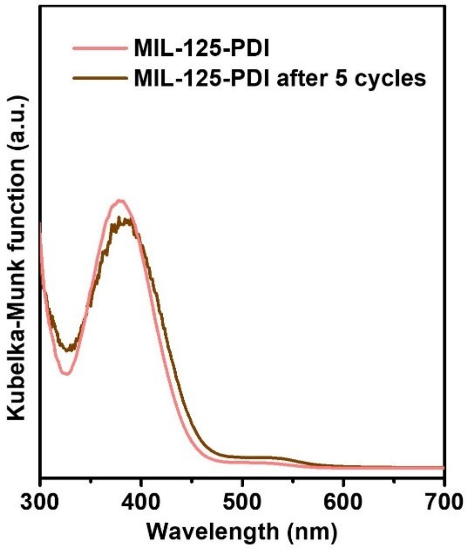

Fig. S8 UV−Vis DRS of MIL-125-PDI before and after five cycles.

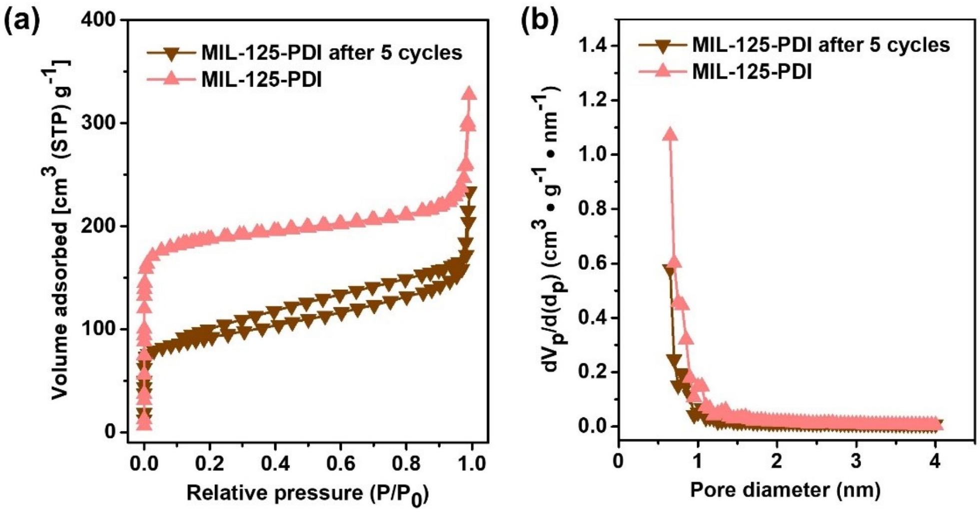

Fig. S9 (a) N_2 adsorption/desorption isotherms and (b) pore distribution of MIL-125-PDI before and after five cycles.

Table S2. Structural parameters of the MIL-125-PDI before and after five cycles.

Samples	S_{BET} ($cm^2 \cdot g^{-1}$)[a]	D_p (nm)[b]	V_p ($cm^3 \cdot g^{-1}$)[c]
MIL-125-PDI	527	0.65	0.28
After five cycles	278	0.65	0.13

[a] Surface area (S_{BET}) calculated by the BET method. [b] Average pore diameter (D_p) calculated using the Saito Foley (SF) method. [c] Pore volume (V_p) calculated using the SF method.

Table S3. Activity comparison of the photocatalytic H_2O_2 production from O_2 and H_2O with different type of photocatalysts.

Photocatalysts	**Reaction system (catalyst/solution)**	**Light**	**Activity ($\mu M \bullet g^{-1} \bullet h^{-1}$)**	**Ref.**
BM-Au/TiO_2	10 mg/10 mL	$\lambda > 430$ nm	3500	1
CdS-graphene	50 mg/50 mL	$\lambda > 420$ nm	213	2
g-C_3N_4	50 mg/30 mL	$\lambda > 420$ nm	< 2.8	3
g-C_3N_4/PDI_{51}	50 mg/30 mL	$\lambda > 420$ nm	703	3
C-N-g-C_3N_4	20 mg/15 mL	420 nm $\leq \lambda \leq$ 700 nm	3367	4
Cu-doped g-C_3N_4	200 mg/200 mL	$\lambda > 400$ nm	1333	5
Resins	50 mg/30 mL	$\lambda > 420$ nm	2750	6
Graphene oxide	320 mg/L	$\lambda \geq 420$ nm	104.2	7
MIL-125-NH_2 (This work)	5 mg/5 mL	$\lambda > 420$ nm	1111	–
MIL-125-PDI (This work)	5 mg/5 mL	$\lambda > 420$ nm	4800	–

References

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