Supporting Information

Amine-functionalized zirconium metal-organic framework as efficient visible light photocatalyst for aerobic organic transformations

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Experimental section

Chemical reagents include $ZrCl_4$, N, N-dimethylformamide, methanol, 1, 4-benzenedicarboxylic acid, and 2-amino-1, 4-benzenedicarboxylic acid were purchased from Alfa Aesar. All these chemicals used in this work are analytical grade purity without further purification.

Synthesis of amine-functionalized Zr-MOF materials. UiO-66 and UiO-66-NH_2 have been prepared following the procedure described in the literature[4] with slight modification. For the synthesis of UiO-66, $ZrCl_4$ (53 mg, 0.227 mmol) and 1,4-benzenedicarboxylic acid (34 mg, 0.227 mmol) were dissolved in DMF (25 mL), and then the resulting solution was heated inside an autoclave at 393 K for 48 h. After this, the autoclave was cooled down to room temperature in air, and the obtained solid was soaked in methanol with robust stirring for several days and then dried at 353 K under vacuum. UiO-66-NH_2 was achieved by replacing 1, 4-benzenedicarboxylic acid by 2-amino-1, 4-benzenedicarboxylic acid, while keeping all other synthetic conditions unchanged.

Catalyst characterizations. X-ray powder diffraction patterns were recorded on a Bruker D8 Advance X-ray diffractometer using Cu $K\alpha1$ radiation (λ=1.5406 Å), 40 kV, 40 mA with a scanning speed of 0.2° (2θ) min^{-1}. PL spectra were surveyed by an Edinburgh FL/FS900 spectrophotometer. The UV/Vis diffuse reflectance spectrum was recorded by Perkin Elmer Lambda 950 UV-Vis-NIR system. The ESR spectra were performed on a Bruker A300 EPR spectrometer.

Electrochemical characterizations. The Zr-MOF-NH_2 particulate film electrodes were prepared by applying 50 μL of Zr-MOF-NH_2 slurry to the surface of an optically transparent electrode and covering approximately 0.25 cm^2. The Zr-MOF-NH_2 slurry was prepared by mixing 0.1 g Zr-MOF-NH_2 powder and 1 g ethanol. The electrode was then dried on a warm plate. Electrochemical measurements were conducted with a BAS Epsilon Electrochemical System in a conventional three electrode cell, using a Pt plate as the counter electrode and Ag/AgCl electrode (3 M KCl) as the reference electrode. The working electrode was prepared by spreading the slurries over 0.25 cm^2 of indium tin oxide (ITO) glass substrate. Then the film was dried in air. The electrochemical measurement was carried out in a Na_2SO4 (0.2 M) electrolyte, which was purged with nitrogen gas for 2 h prior to the measurements. A 500 W xenon lamp (Beijin Changtuo, CHF-XM500) fitted with a UV (420 nm) cut-off filter was used as the light source. All electrochemical potentials are reported vs. NHE.

Photocatalytic activity testing. The aerobic photocatalytic oxidation reactions were carried out at 1.0 atm O_2 partial pressure in a flask containing 5 mL solvent, 200 ul reacting substrate, and 100 mg catalyst by stirring with a magnetic stirrer and irradiated under a 300 W Xe lamp with a 420-450 nm band-pass filter. Unless otherwise indicated, the aerobic photocatalytic oxidation reactions are conducted at 274 K with an oxygen balloon as an oxygen source. The reaction solution was sampled, then analyzed and quantified on Agilent 6890 GC-MS equipped with a flame ionization detector.

The determined concentration data of reactants and products are further treated with expressions given as follows, where the conversion of substrates is expressed by X:

$$X\,(\%) = 100 \times (C_0 - C_i)/C_0 \qquad (1)$$

Where C_0 and C_i are the molar concentrations of substrates before and after the photocatalytic reaction, respectively. The selectivity to product is shown by S_j:

$$S_j\,(\%) = 100 \times C_j/(C_0 - C_i) \qquad (2)$$

Where C_j is the molar concentration of product. The turnover frenquency (TOF) value of the reaction is calaculated by an expression as follows:

$$\mathrm{TOF}\,(h^{-1}) = X \times 200 \times 10^{-6} \times \rho \times M_c / 100 \times 10^{-3} \times M_r \times T \qquad (3)$$

Where ρ, M_c, and M_r are the density of the reactive substrate (g/L), the molar molecular weight of the UiO-66-NH_2 catalyst, and the molar molecular weight of the reactive substrate (g/Mol), respectively. T represents the reaction time (h). The formula of UiO-66-NH_2 is $Zr_{24}O_{120}C_{192}H_{96}N_{24}$ which have a formula weight of 6848.10 g/Mol.

Fig. S1 Isothermal adsorption-desorption plot (A) and TEM image (B) of UiO-66-NH_2.

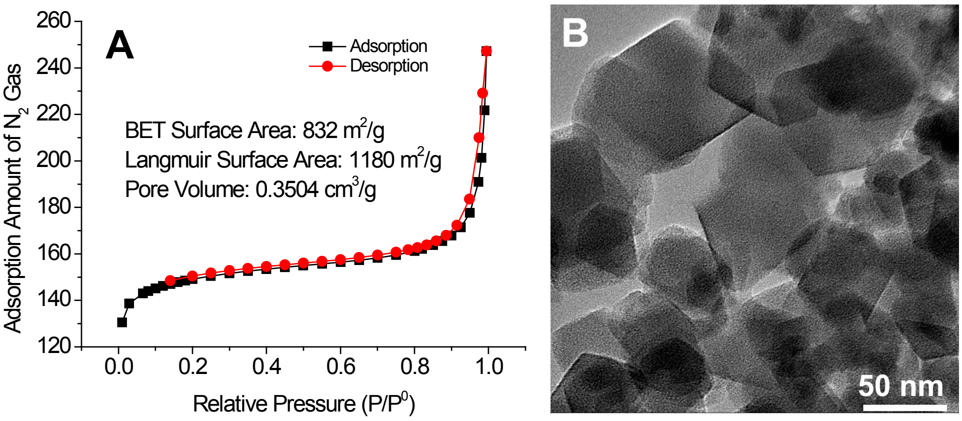


Fig. S2 XPS spectra of UiO-66, UiO-66-NH_2, and ATA precursor (the XPS spectra were carried out on a PHI5000 Versa Probe XPS System).

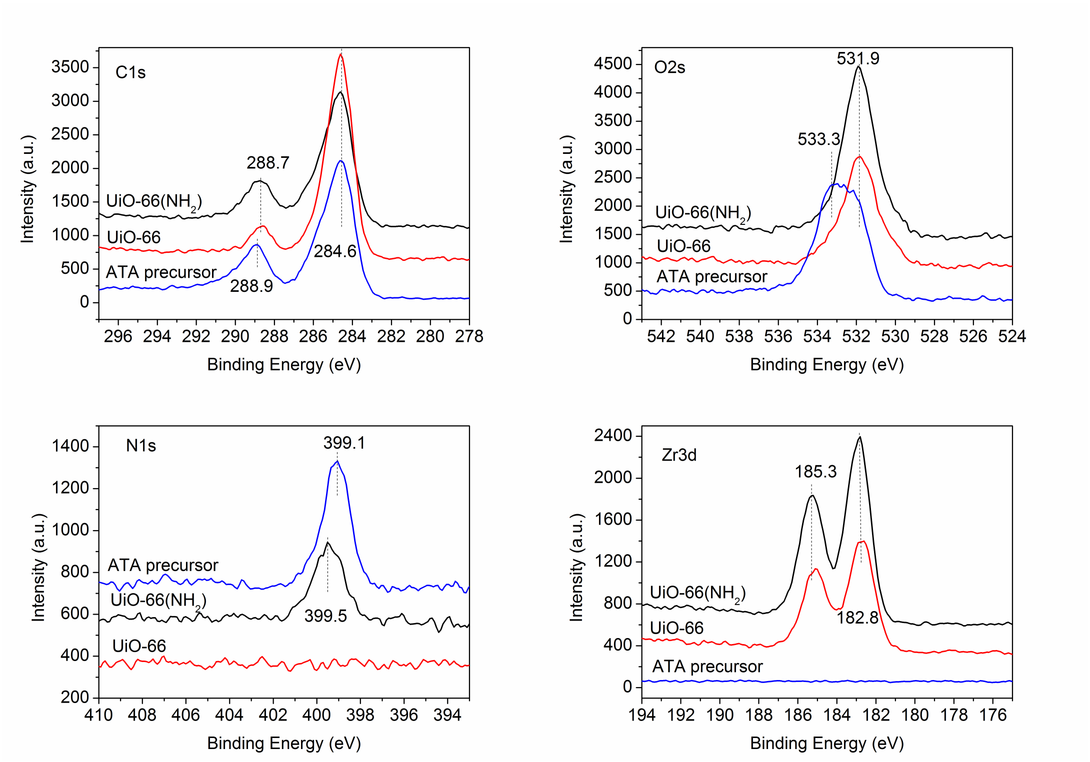


Fig. S3 XRD pattern (left) and SEM image (right) of UiO-66.

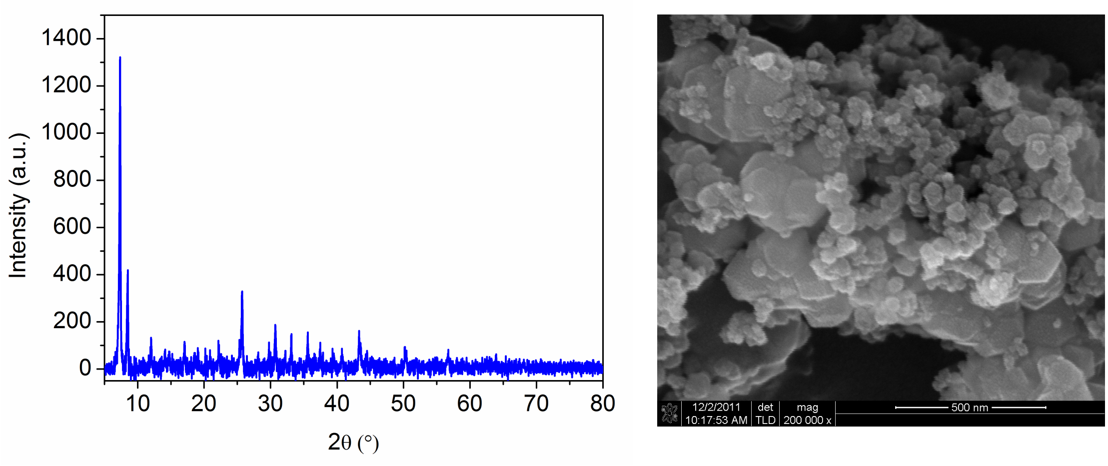


Fig. S4 UV-Vis DRS spectrum of UiO-66.

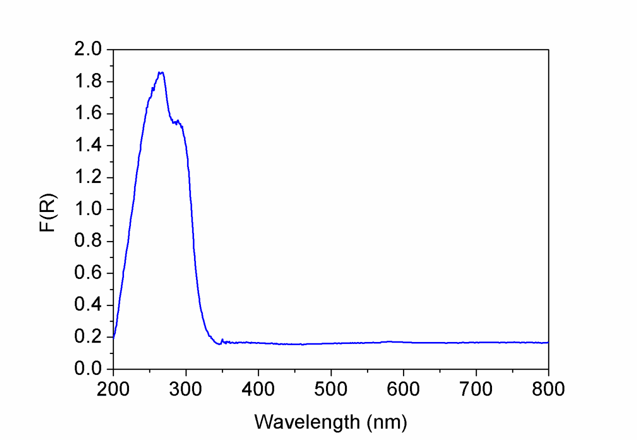


Fig. S5 Impedance spectrum of UiO-66-NH_2 before and after visible light irradiation.

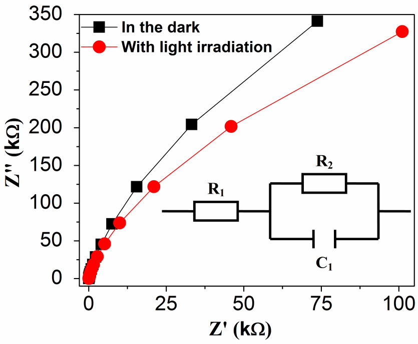
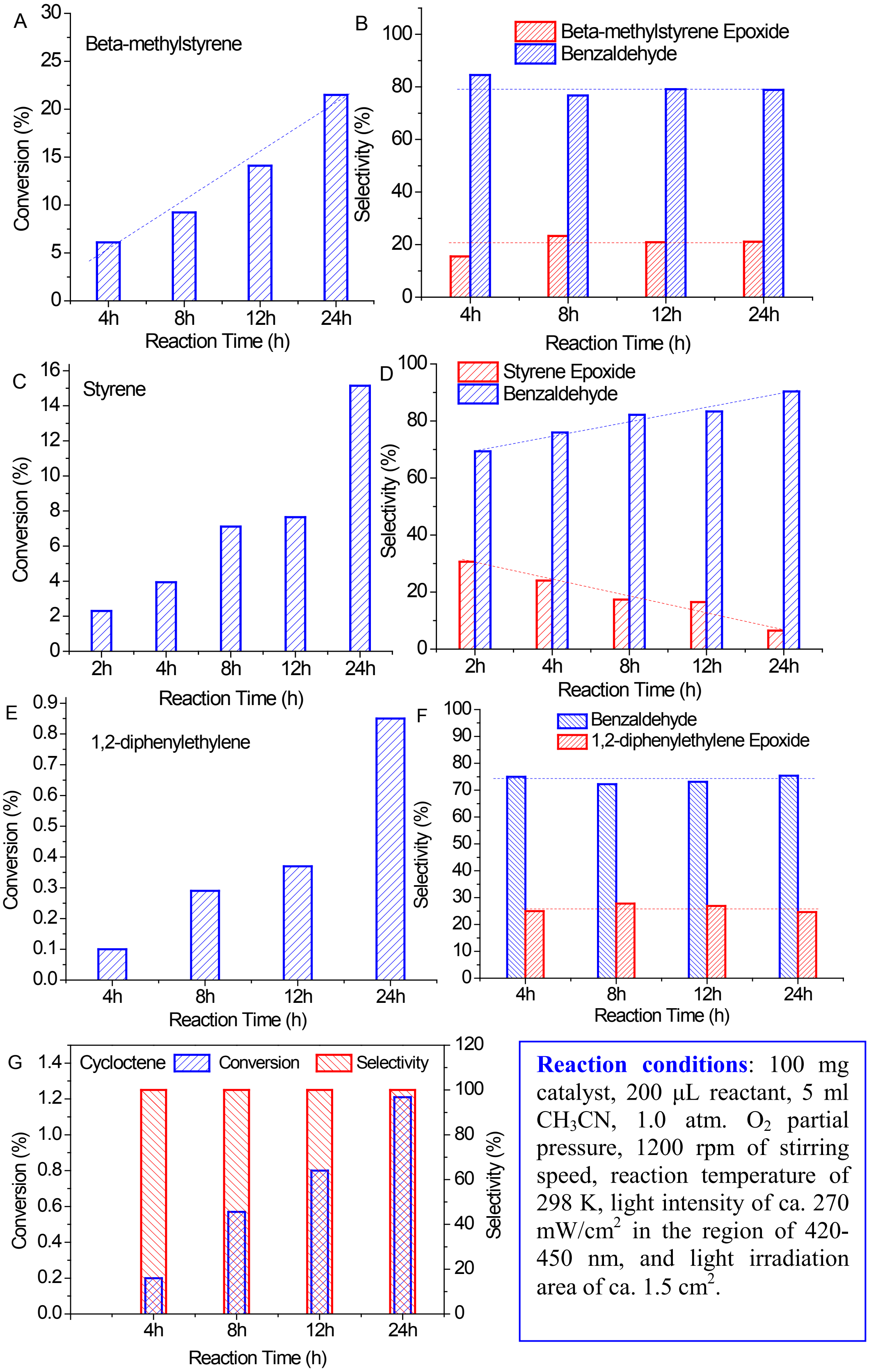


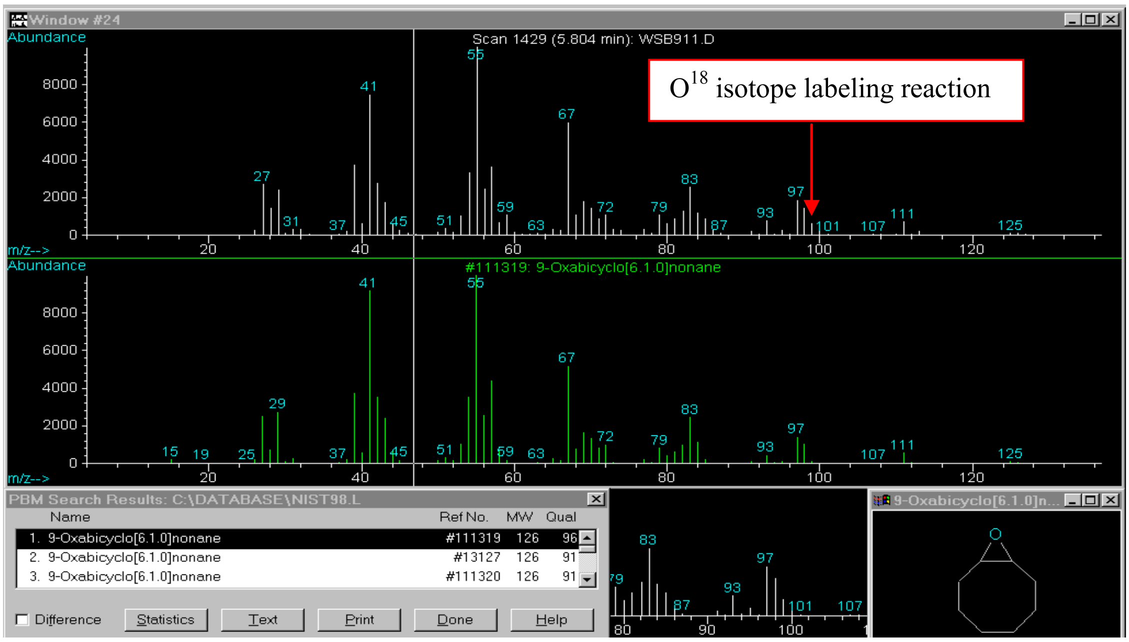
Fig. S5 shows the impedance spectroscopy of UiO-66-NH_2 before and after visible light irradiation. The measured data were fitted to an equivalent model consisting of the solution resistance (R1), the capacitance of the double layer (C_1), and its resistance (R_2), as illustrated in the inset of Fig. S5. The fitting results (Table S1) further confirm that UiO-66-NH_2 is a semiconductor with a relatively large resistance of 1.34×10^6 Ω. Upon visible light irradiation, its resistance decreases to 9.73×10^5 Ω because of the formation of electron-hole pairs.

Fig. S6 Photocatalytic activity as a function of reaction time.



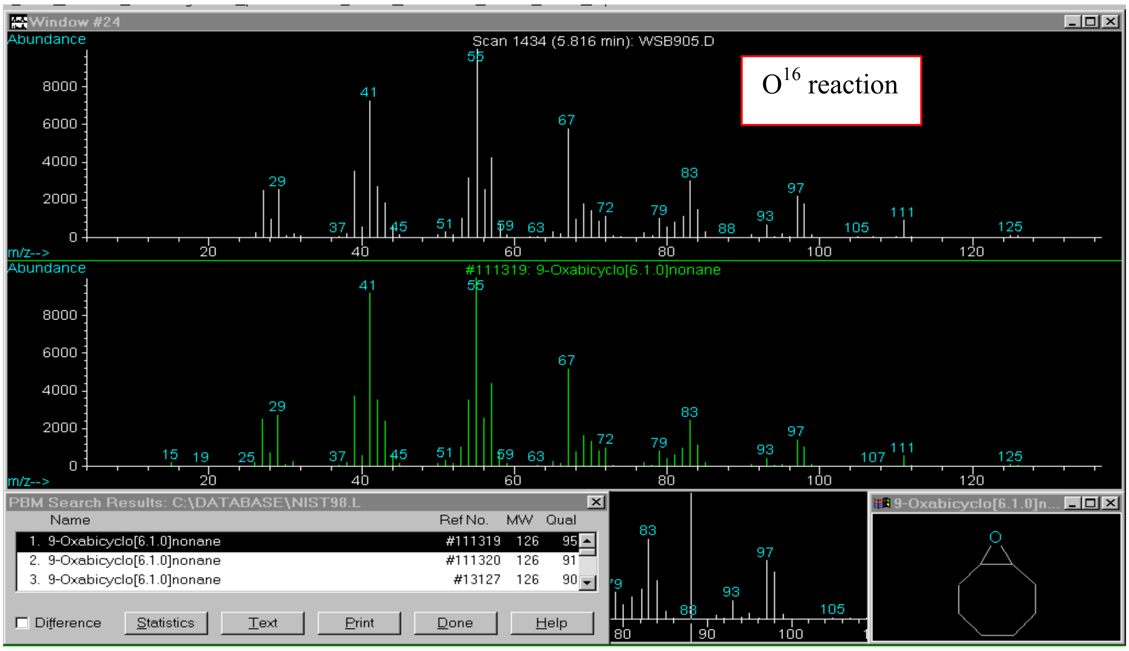
Reaction conditions: 100 mg catalyst, 200 μL reactant, 5 ml CH_3CN, 1.0 atm. O_2 partial pressure, 1200 rpm of stirring speed, reaction temperature of 298 K, light intensity of ca. 270 mW/cm^2 in the region of 420-450 nm, and light irradiation area of ca. 1.5 cm^2.

Fig. S7 GC-MS results of O^{18} isotope labeling experiment.



O^{18} isotope labeling reaction

Name	Ref No.	MW	Qual
1. 9-Oxabicyclo[6.1.0]nonane	#111319	126	96
2. 9-Oxabicyclo[6.1.0]nonane	#13127	126	91
3. 9-Oxabicyclo[6.1.0]nonane	#111320	126	91



O^{16} reaction

Name	Ref No.	MW	Qual
1. 9-Oxabicyclo[6.1.0]nonane	#111319	126	95
2. 9-Oxabicyclo[6.1.0]nonane	#111320	126	91
3. 9-Oxabicyclo[6.1.0]nonane	#13127	126	90

To clarify the role of molecular oxygen in these photocatalytic oxidation reactions, an O^{18} isotope labeling experiment was performed using the photocatalytic epoxidation of cyclooctene as a model reaction and the 50 % enrichment of $^{18}O_2$. The GC-MS analysis results exhibit a significantly-enhanced abundance of O^{18} in the product cyclooctene epoxide as shown by the higher line at m/z = 99, indicating clearly the source of oxidant for these organic oxygenations and offering a powerful evidence for the involvement of molecular oxygen in the photocatalytic oxidation.

Fig. S8 EPR spectra of the solid state UiO-66-NH_2 (A) and ATA ligand (B).

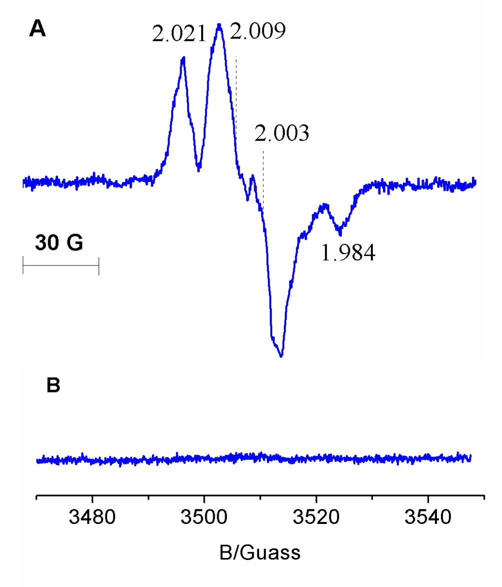


Fig. S9 EPR spectra of the solid state UiO-66 before and after UV light irradiation.

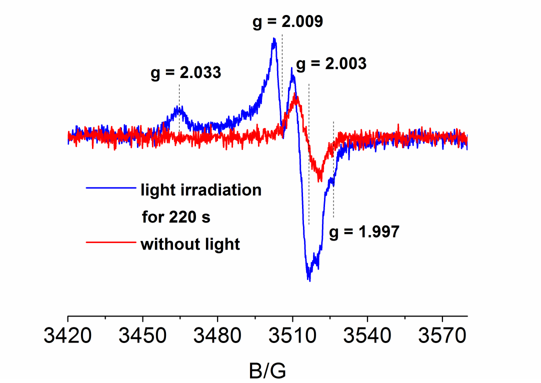


Table S1 Fitted results derived from **Fig. S5**.

Conditions	R_1[Ω]	R_2[Ω]	C_1[F]
In the dark	72.5	1.34×10^{6}	3.51×10^{-6}
With visible light	72.1	9.73×10^{5}	3.46×10^{-6}

R_1: Solution resistance, R_2: Resistance of the MOF material, C_1: Electrical double layer capacitance