# **Electronic Supplementary Information**

# P-type Ti(IV)-Based Metal-Organic Framework with Visible-Light Photo-Response

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# 1. Experimental Details

#### **Experimental Section**

**Materials.** All chemicals were purchased from Alfa Aesar, TCI chemical and Aldrich and used without further purification.

**Characterization.** Powder X-ray diffraction data were recorded on a Bruker D8 Advance diffractometer with a graphite-monochromatized Cu *Ka* radiation. FTIR spectra were recorded from KBr pellets by using a Perkin Elmer FTIR SpectrumGX spectrometer. Thermogravimetric analysis (TGA) was carried out on a TA Instrument Q500 Thermogravimetric Analyzer at a heating rate of 10°C/min up to 800°C under N<sub>2</sub> atmosphere. UV-Vis absorption spectra were obtained using a Shimadzu UV-2450 spectrophotometer. The optical diffuse reflectance spectra were measured on a PerkinElmer Lambda 750s UV-vis spectrometer equipped with an integrating sphere. BaSO<sub>4</sub>was used as the reference material, and the polycrystalline samples were ground well before the measurement. The absorption ( $\alpha$ /S) data were calculated from the reflectance using the Kubelka–Munk function:  $\alpha$ /S = (1-R)<sup>2</sup>/2R, in which R is the reflectance at a given wavelength,  $\alpha$  is the absorption coefficient, and S is the scattering coefficient.<sup>1</sup>Simulation of the XRD pattern was carried out by the single-crystal data and diffraction-crystal module of the Mercury (Hg) program version 3.1 available free of charge via the Internet http://www.ccdc.cam.ac.uk.

**Synthesis of Ti<sub>2</sub>(DOBDC)<sub>3</sub> (NTU-9).**H<sub>4</sub>DOBDC (0.75 mmol, 0.15 g), was added to acetic acid (3 mL) in a 23 mL Teflon-lined stainless-steel autoclave. Then, Ti(i-OPr)<sub>4</sub>(0.67mmol, 0.20 mL) was added to the solution with stirring and a dark red slurry formed. The mixture was heated at 120 °C for 5 days.

Then, the mixture was naturally cooled to room temperature and washed with ethanol to give darkred crystals of **NTU-9**. Yield: 59 % (based on DOBDC).

**Crystallographic measurements.** Data collections were performed on an Agilent SuperNova CCD diffractometer using graphite-monochromated Cu $K\alpha$  radiation source ( $\lambda$ =1.5418 Å). Empirical absorption was performed, and the structure was solved by direct methods and refined with the aid of a SHELXTL program package. All hydrogen atoms were calculated and refined using a riding model. The guests in the pores are disordered and cannot be assigned by single crystal XRD. So the contributions from the disordered guests were removed from the reflection data using the SQUEEZE routine of PLATON.

**Computational methods.** The band structure and DOS of **NTU-9** crystal were studied by density functional theory based quantum chemical calculations using Cambridge Series Total Energy Package (CASTEP) program, implemented in the Materials Studio 5.0. Single crystal structural data determined by single-crystal XRD analysis was used to generate the geometry of **NTU-9**. All the calculations were done using the GGA-PBE functional and ultrasoft pseudo-potentials with a kinetic energy cut off of 400 eV.

Electrode preparation. To prepare the photoelectrodes, 10 mg of NTU-9 was first ground using a marble mortar and pestle, and then added into 1 ml of 98% ethanol (Merck). The as-prepared solution was placed on a 60°C hotplate stirrer overnight to ensure that the NTU-9 was completely dissolved in the solution. Meanwhile, the fluorine-doped tin oxide (F:SnO<sub>2</sub>, Tec 15,  $10\Omega/\Box$ , Hartford Glass Company) were cleaned thoroughly by sonication in 5% detergent for 30 min first and then rinsed with de-ionized water (DI water) for several times, which were followed by sonication in DI water for 15 min. The sonication in DI water process was repeated for three times. Before coating with NTU-9, the FTO substrates were cleaned with UV-ozone plasma for 15 min to remove the organic residues. After that, 10 µl of the 10 mg/ml NTU-9 solution was dropped onto the surface of FTO substrate, which was masked by a 3M scotch tape with an exposed area of  $1.0 \times 1.0 \text{ cm}^2$ , and then dried in air at 60°C on a hotplate. This step was repeated four times to achieve a uniform coverage of NTU-9 on FTO as shown in Figure S7.

**Photoelectrochemical measurements.** The photoelectrochemical tests were performed using an electrochemical workstation (CHI 660B). A three-electrode set-up, with a platinum plate  $(1 \times 2 \text{ cm}^2)$  and a saturated calomel electrode (SCE, in 3 M KCl) as the counter and reference electrodes,

respectively, was used to study the photovoltage response (illuminated open circuit potential). Meanwhile, the photocurrent test was carried out using a two-electrode set-up, in which the working electrode (**NTU-9**/FTO) and the counter electrode (Pt) were short-circuited. 0.5 M Na<sub>2</sub>SO<sub>4</sub>solution (pH = 7.0) was used as the electrolyte throughout the photoelectrochemical tests. Prior to each measurement, the electrolyte was deaerated by purging it with argon continuously for 30 minutes. A 150 W tungsten halogen lamp (Filtered,  $\lambda$ >400nm) was used as the visible light source, and the illumination intensity on the surface of the electrode was approximately 100 mW/cm<sup>2</sup>.

**Photocatalytic experiments.** The evaluation of photocatalytic activities of the samples for the visible light photocatalytic degradation of organic dyes was performed at ambient temperature (25°C). The procedure was as follows: 5mg of sample was dispersed into 10mL of Rhodamine B (RB) aqueous solution (10<sup>-4</sup> mol L<sup>-1</sup>), followed by the addition of five drops of hydrogen peroxide solution(H<sub>2</sub>O<sub>2</sub> 30%). The photocatalytic dye degradation was carried out by irradiating the suspension with a 300-W xenon lamp coupled with a UV cut-off filter ( $\lambda$ > 420 nm).During the degradation, the mixture was stirred continuously by means of a magnetic stirrer. The samples were withdrawn regularly from the reactor, and dispersed powders were removed by centrifugation. At different time intervals, analytical samples were withdrawn and analyzed by UV-Vis spectroscopy. The degradation efficiency was determined by dividing C/C<sub>0</sub>, where C is the remained RB concentration and C<sub>0</sub> is the starting RB concentration. The recycle of photocatalytic degradation of RB was performed by centrifuging the reaction solution and reusing the catalyst for three times. The degradation of methylene blue (MB, 10<sup>-4</sup> mol L<sup>-1</sup>) was prepared using the method similar to that of RB.

# 2. Summary of crystal and structure refinement data for MOF NTU-9.

Compound	NTU-9
Empirical formula	$C_{24}H_6O_{18}Ti_2$
Formula weight	678.09
T (K)	293(2)
λ	1.54178
Crystal system	Trigonal
Space group	P-31c
a	14.620(2)
b	14.620(2)
с	11.698(2)
α	90
β	90
γ	120
V	2165.5(6)
Z	2
Dc (g/cm3)	1.040
GOF on F2	1.102
R1a [I>2σ(I)]	0.0310
$\omega R2b[I>2\sigma(I)]$	0.0949

Table S1. Summary of crystal and structure refinement data for NTU-9.

3. Powder-XRD pattern, TGA curves and IR spectra forNTU-9.



Figure S2. The simulated and experimental powder XRD patterns for NTU-9.



Figure S3. The IR spectrum of NTU-9.

4. Band structure and DOS of NTU-9.



Figure S4.Band structure of MOFNTU-9.



Figure S5. Total and partial DOS of MOFNTU-9.



Figure S6. Total and partial DOS by elements of MOFNTU-9.



Figure S7.The as-prepared NTU-9/FTO electrode for photoelectrochemical measurements.

5. Photodegradation spectra forNTU-9.



Figure S8. The time dependent UV-Vis spectra of RB over photocatalyst NTU-9.



Figure S9.Photo-degradation of RB in solution over different condition with visible light irradiation.



Figure S10. The time dependent UV-Vis spectra of MB over photocatalyst NTU-9.

Impedance Spectroscopy



**Figure S11**. Electrochemical impedance spectrum of NTU-9 photoelectrode (Blue squares: data points, red dotted line: fitted curve). Inset is the model that we used to study this spectrum.

### **Impedance Measurement**

The impedance measurements were performed using perturbation amplitude of 10 mV under visible-light illumination, and the frequency was ranged from 100 kHz to 0.1 Hz. Figure S# shows the Nyquist plot of NTU-9/FTO electrode. The equivalent circuit shown in the inset of Figure S# was used to fit the data points, where the double layer behavior is modelled by a CPE component. The estimated series resistance  $R_s$  is about 30.15 ohms, while the charge transfer resistance  $R_{ct}$  (labeled as  $R_p$ ) is ~3664 ohms.

**Cyclic-Voltammetry** 



Figure S12. The CV curves of NTU-9/FTO photoelectrode under dark (black) and illuminated (red) conditions.

### **CV** measurement

The CV curves of NTU-9/FTO electrode were recorded using a three-electrode setup. 0.5 M  $Na_2SO_4$  was used as the electrolyte, and the scan was performed with a scanning rate of 50 mV/s. Two-step hydrogen evolution can be clearly seen from the CV curves, and we found that the H<sup>+</sup> adsorption process was significantly improved under visible light illumination.

## **Reference:**

1. G. Kortüm, Reflectance Spectroscopy, Springer, New York, 1969.