

## Supporting Information

### **Design of Titanium-Oxide Cluster-Based Metal-Covalent Organic Frameworks for Efficient Photocatalytic CO<sub>2</sub> Reduction**

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#### **1. Reagents and solvents**

All reagents and solvents used in the experiments were commercially available and were used as received. The reagents and solvents used include p-aminobenzoic acid, diethylenetriamine (DETA), titanium (IV)-isopropoxide ( $\text{Ti}(\text{OCHCH}_3\text{CH}_3)_4$ ), 1,3,5-triformyl-phloroglucinol (Tp), ethyl acetate, N,N-dimethylformamide, dichloromethane, methanol, 2-propanol, 5% Nafion solution, sodium sulfate, and polyvinylidene fluoride (PVDF).

## 2. Material characterization

Fourier transform infrared (FT-IR) spectra were collected using an FT-IR 850 spectrometer with KBr as the background. X-ray diffraction (XRD) patterns were recorded on a Bruker D8 Advance diffractometer using  $\text{Cu K}\alpha$  radiation ( $\lambda = 1.5418 \text{ \AA}$ ) over a  $2\theta$  range of  $5^\circ$  to  $90^\circ$ . The surface morphology of the samples was analyzed using a field emission scanning electron microscope (SEM, Quanta 250) operated at an accelerating voltage of 10 kV. Mott–Schottky plots and photocurrent measurements were performed using a CHI 760E electrochemical workstation. X-ray photoelectron spectroscopy (XPS) was conducted on a K-Alpha scanning X-ray microprobe (Thermo Scientific) with  $\text{Al K}\alpha$  radiation, using the C 1s peak at 284.8 eV as the internal reference. UV–visible diffuse reflectance spectra (UV–vis DRS) were obtained using a Persee TU-1901 spectrophotometer with  $\text{BaSO}_4$  as the reflectance standard.

## 3. Photocurrent measurements

The electrochemical measurements were conducted using a CHI 760E electrochemical workstation with a standard three-electrode system for photoelectrochemical and Mott–Schottky tests. A 0.2 mol/L sodium sulfate solution served as the electrolyte. The working electrode was prepared by dispersing 1 mg of the photocatalyst and 10  $\mu\text{L}$  of a 5% Nafion solution in 1 mL of ethanol, followed by sonication for 1 hour. The resulting suspension was subsequently drop-cast onto a  $1 \text{ cm} \times 2 \text{ cm}$  ITO conductive glass. The  $\text{Ag}/\text{AgCl}$  electrode served as the reference electrode, while the platinum electrode functioned as the counter electrode.

## 4. Photocatalytic measurements

The synthesized sample (1 mg) was dispersed in 1 mL of dichloromethane and sonicated for 30 minutes to achieve a uniform distribution. The resulting suspension was drop-cast onto a  $1 \text{ cm} \times 3 \text{ cm}$  glass slide, ensuring full coverage. The prepared sample was placed in a custom-made photocatalytic reactor, where approximately 100  $\mu\text{L}$  of deionized water was added at the bottom as a reducing agent. The reactor was purged with  $\text{CO}_2$  gas to fully displace the air inside. An LED lamp was used as the light source to irradiate the sample for 2 hours. After the reaction, 0.5 mL and 1.0 mL of the generated gas mixture were collected and analyzed using a gas chromatograph (GC 1120) to determine the concentrations of CO and  $\text{H}_2$ .

## 5. Synthesis of $\text{Ti}_6\text{O}_6(\text{O}^i\text{Pr})_6(\text{abz})_6$

The  $\text{Ti}_6\text{O}_6(\text{O}^i\text{Pr})_6(\text{abz})_6$  cluster (where  $\text{O}^i\text{Pr}$  = isopropoxide;  $\text{Habz}$  = 4-aminobenzoic acid, denoted as  $\text{Ti}_6$ ) was synthesized based on a previously reported method,<sup>1</sup> with an adjusted reaction time. Specifically, 4-aminobenzoic acid (192.1 mg, 1.40 mmol) was first dissolved in 6.0 mL of 2-propanol, followed by the addition of titanium (IV) isopropoxide (103.6 mL). The mixture was stirred at room temperature for 30 minutes until an orange suspension formed. The solution was then transferred to a sealed glass

tube and heated at 100 °C for 24 hours, a reduced reaction time compared to the reported method. Upon completion of the reaction, the bright yellow crystalline product was collected, washed with 2-propanol, and vacuum-dried for 3 hours.

#### **6. Synthesis of MCOF-TDT-X**

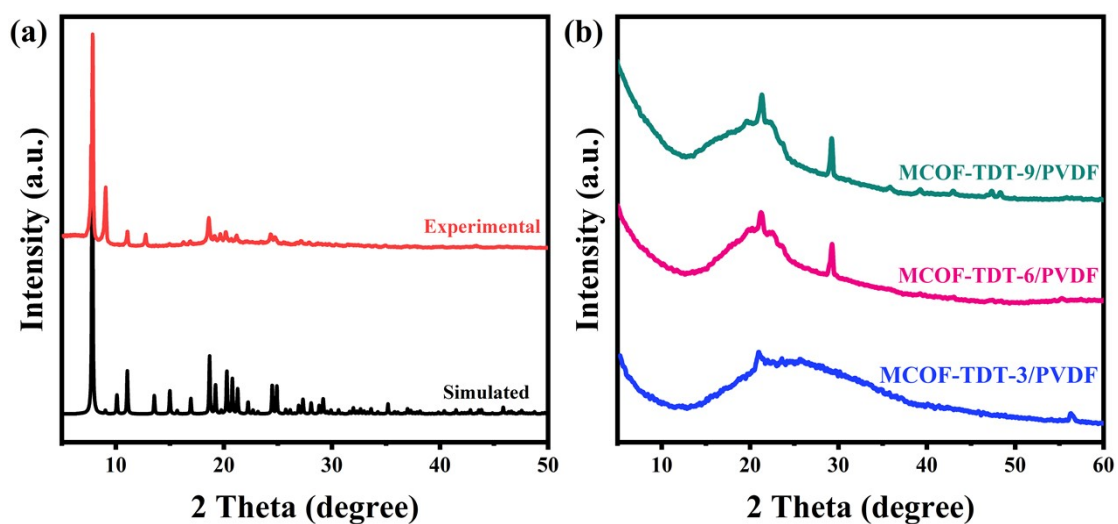
**Ti<sub>6</sub>** (3 mg, 6 mg, and 9 mg) and 1,3,5-triformyl-phloroglucinol (Tp, 16 mg) were dispersed in a 6 mL solvent mixture composed of dichloromethane, ethyl acetate, and methanol in a volume ratio of 1:1:8. Immediately afterward, 43  $\mu$ L of diethylenetriamine (DETA) was added to the dispersion. The resulting mixture was stirred at room temperature for 15 minutes and then filtered. The solid was washed three times with methanol and then soaked in methanol for 12 hours. This procedure produced the **MCOF-TDT-3**, **MCOF-TDT-6**, and **MCOF-TDT-9** samples.

#### **7. Synthesis of MCOF-TDT-X/PVDF**

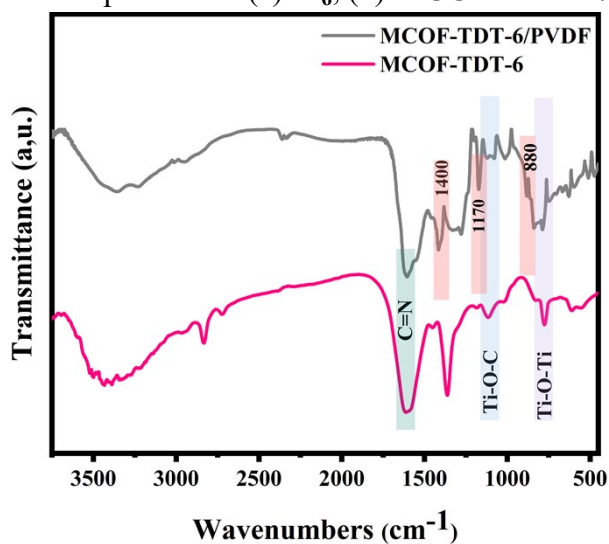
**Ti<sub>6</sub>** samples (15 mg, 30 mg, and 45 mg) were each dissolved in 2 mL of N,N-dimethylformamide (DMF), followed by the addition of 80 mg of poly(vinylidene fluoride) (PVDF). The mixtures were stirred for 15 minutes and uniformly cast onto glass slides using a 200  $\mu$ m film applicator. The resulting films were dried at 60 °C for 15 minutes and carefully removed, **Ti<sub>6</sub>**/PVDF membranes with varying **Ti<sub>6</sub>** contents were successfully obtained. Subsequently, 12 mg of 1,3,5-triformyl-phloroglucinol (Tp) was dissolved in 6 mL of a DMF/methanol mixture (v/v = 1:5), and each pre-formed film (3 mg) was immersed in the solution for 2 minutes. Then, 64.5  $\mu$ L of diethylenetriamine (DETA) was added, and the system was heated at 60 °C for 15 minutes. The membranes were subsequently transferred into a methanol solution containing 4.8 mg of Tp, 6 mg of **Ti<sub>6</sub>**, and 13  $\mu$ L of DETA (total volume: 6 mL), gently stirred to ensure full contact between the membrane surface and the solution, and then heated at 60 °C for an additional 30 minutes to complete the synthesis. This procedure successfully produced **MCOF-TDT-3/PVDF**, **MCOF-TDT-6/PVDF**, and **MCOF-TDT-9/PVDF** membrane materials.

#### **8. Synthesis of MCOF-TDT-6 Interface Film**

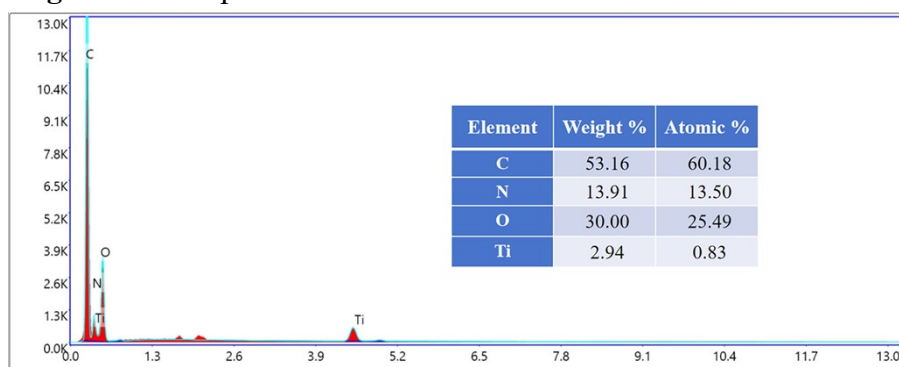
Dispersion A was prepared by dispersing 3 mg of **Ti<sub>6</sub>** and 21.5  $\mu$ L of diethylenetriamine (DETA) in 4 mL of deionized water, followed by ultrasonication for 5 minutes. Dispersion B was prepared by sonicating 8 mg of 1,3,5-triformyl-phloroglucinol (Tp) in 4 mL of dichloromethane for 5 minutes. Both dispersions were prepared in 10 mL vials. Subsequently, dispersion A was slowly added dropwise onto the surface of dispersion B and left undisturbed for 6 hours to facilitate interfacial polymerization. The resulting light-yellow interfacial film was carefully collected and immersed in methanol for 12 hours to remove unreacted residues.



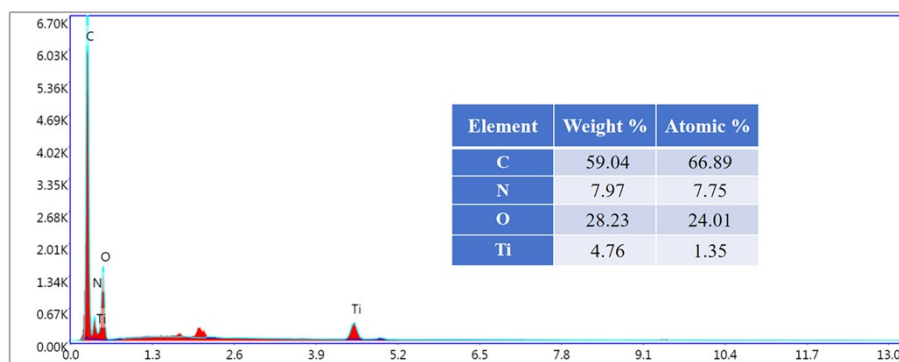
**Fig. S1** PXRD patterns of (a)  $\text{Ti}_6$ , (b) MCOF-TDT-X/PVDF.



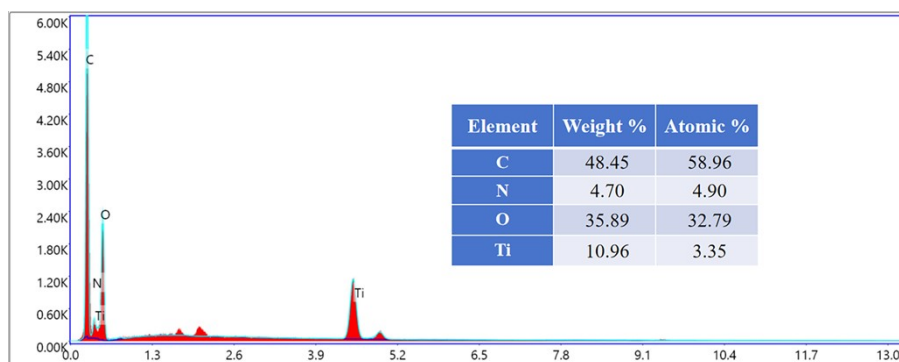
**Fig. S2** FT-IR spectra of MCOF-TDT-6/PVDF and MCOF-TDT-6.



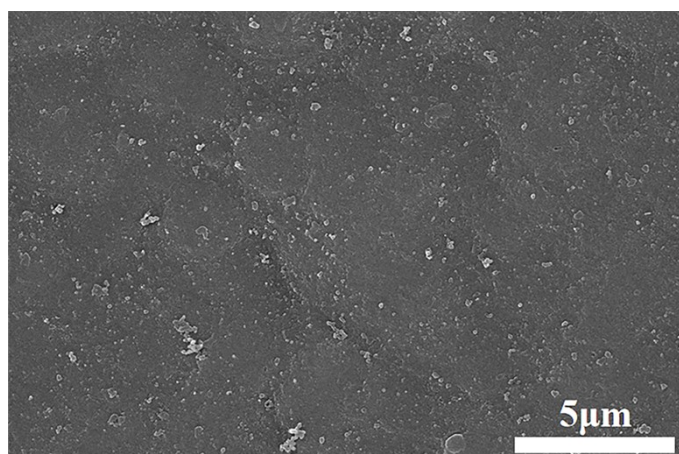
**Fig. S3** The content of C, N, O and Ti in MCOF-TDT-3.



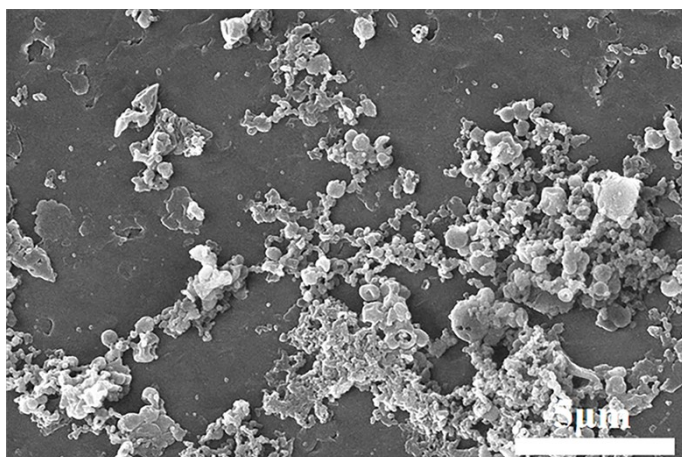
**Fig. S4** The content of C, N, O and Ti in **MCOF-TDT-6**.



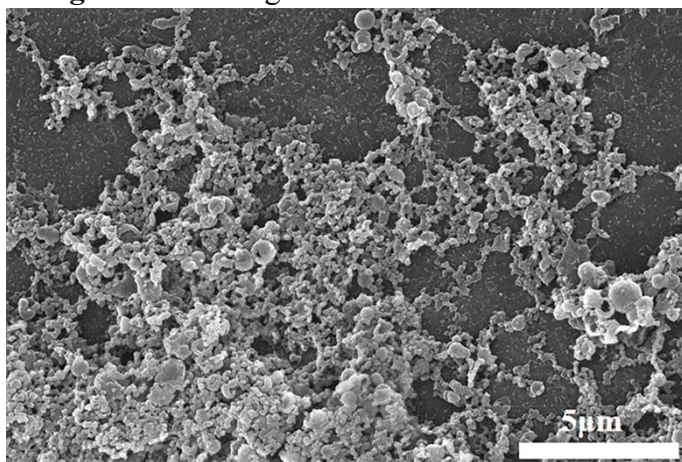
**Fig. S5** The content of C, N, O and Ti in **MCOF-TDT-9**.



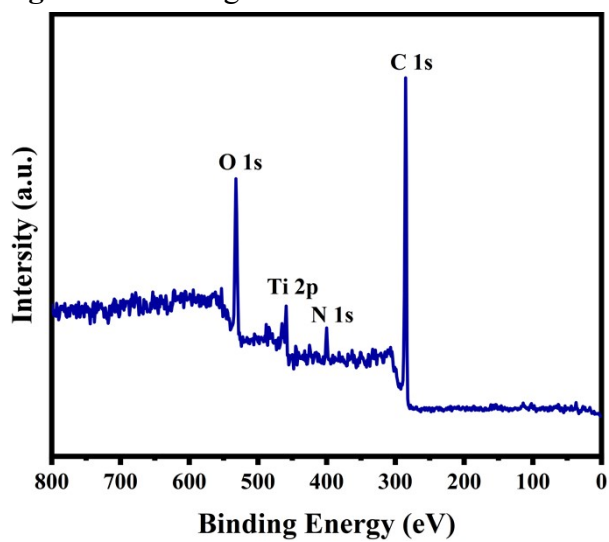
**Fig. S6** SEM images of **MCOF-TDT-3/PVDF**.



**Fig. S7** SEM images of MCOF-TDT-6/PVDF.



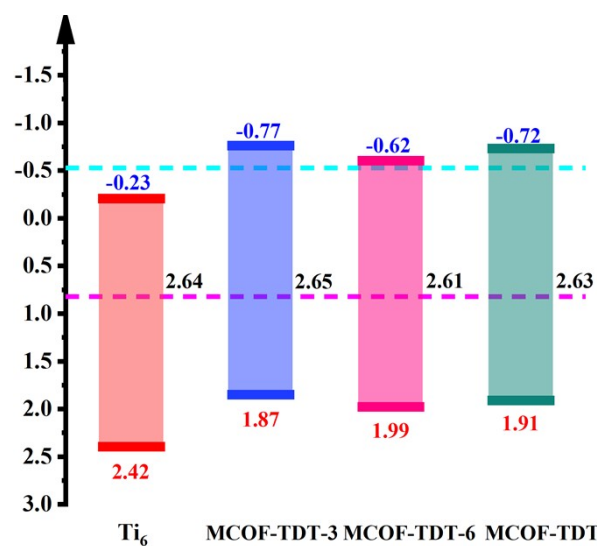
**Fig. S8** SEM images of MCOF-TDT-9/PVDF.



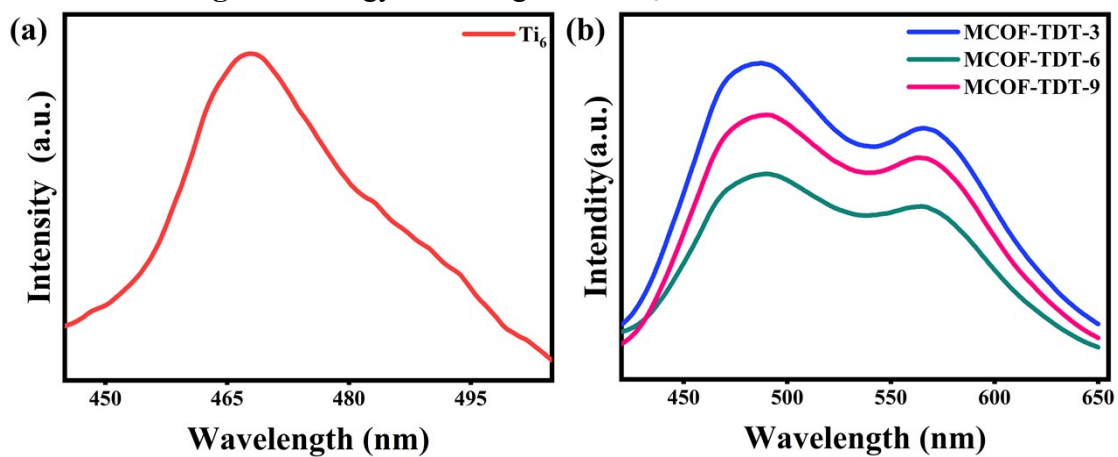
**Fig. S9** XPS spectra of MCOF-TDT-6.



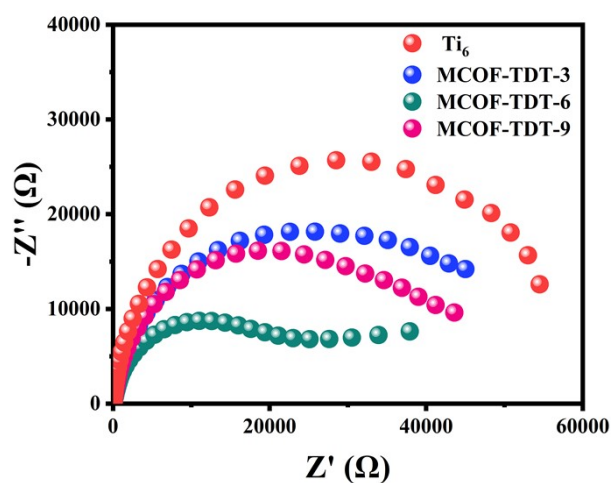




**Fig. S12** Energy level diagram of  $\text{Ti}_6$  and MCOF-TDT-X.

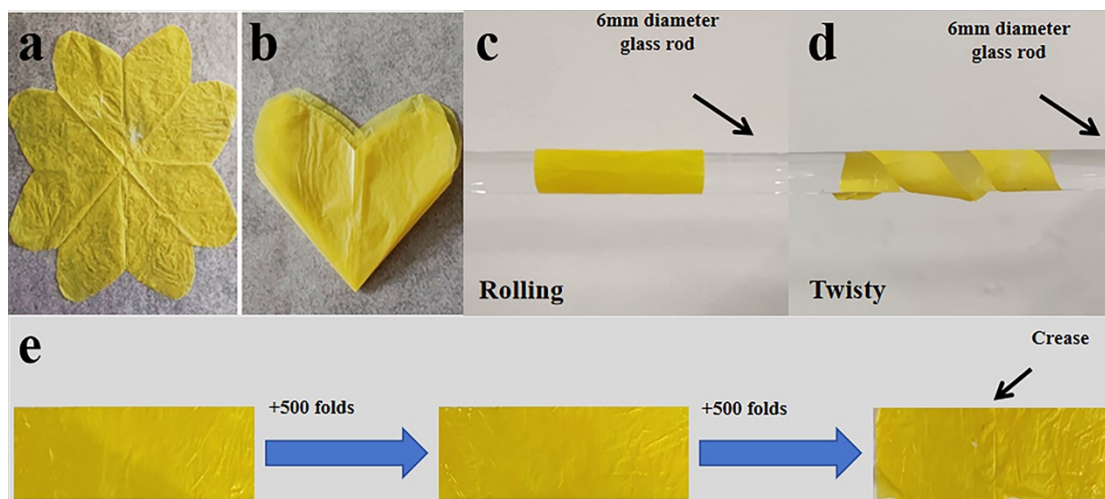


**Fig. S13** PL spectra of (a)  $\text{Ti}_6$  and (b) MCOF-TDT-X.

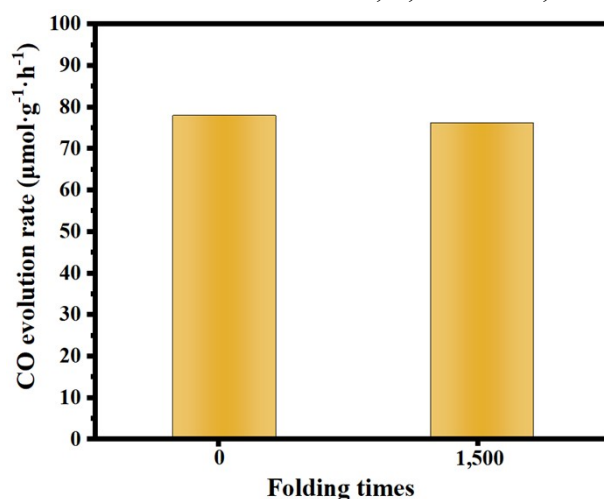


**Fig. S14** Nyquist plots of MCOF-TDT-X and  $\text{Ti}_6$ .

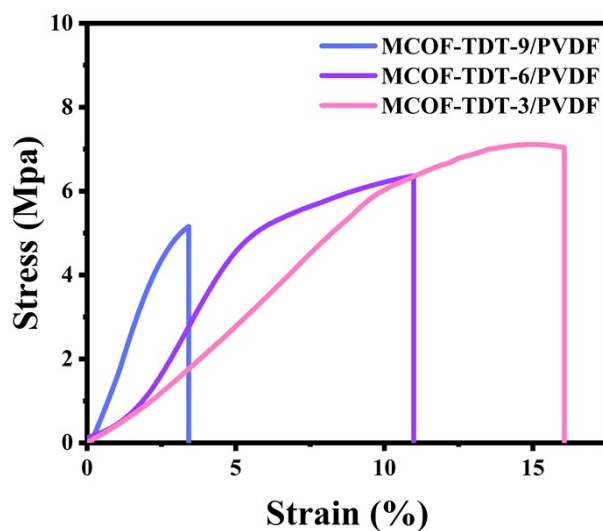




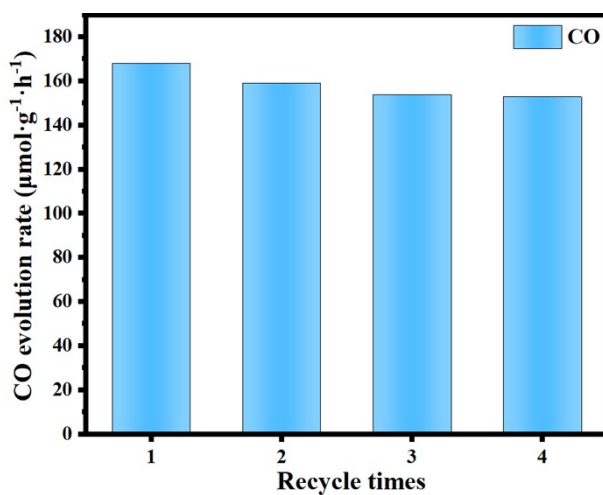
**Fig. S15** Optical images of (a) The petal-like morphology of the unfolded **MCOF-TDT-6/PVDF** membrane, (b) The heart-like morphology of the folded **MCOF-TDT-6/PVDF** membrane, (c) **MCOF-TDT-6/PVDF** membrane rolled  $\approx 6$  mm diameter glass rod, (d) **MCOF-TDT-6/PVDF** membrane twisted  $\approx 6$  mm diameter glass rod, (e) **MCOF-TDT-6/PVDF** folded 500, 1,000 and 1,500 times.



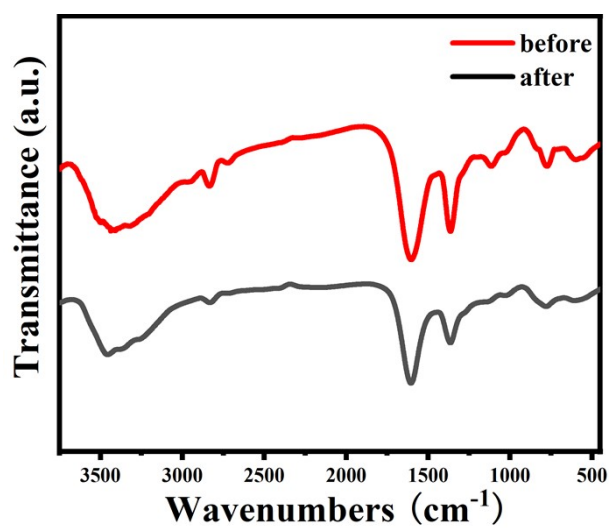
**Fig. S16** CO formation rates of **MCOF-TDT-6/PVDF** before and after 1,500 repeated foldings.



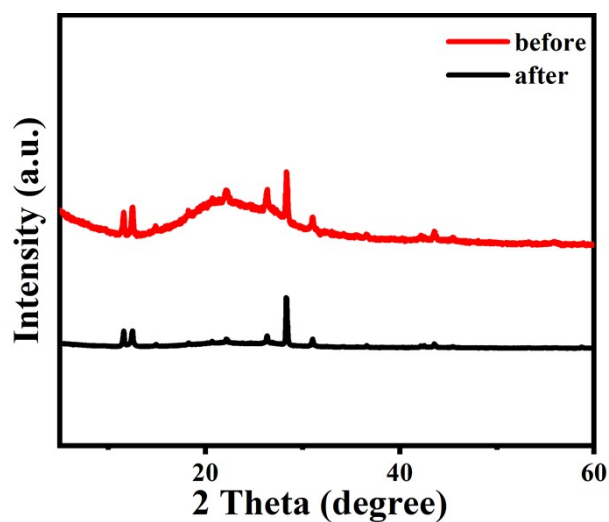
**Fig. S17** Stress-strain curves of **MCOF-TDT-X/PVDF**.



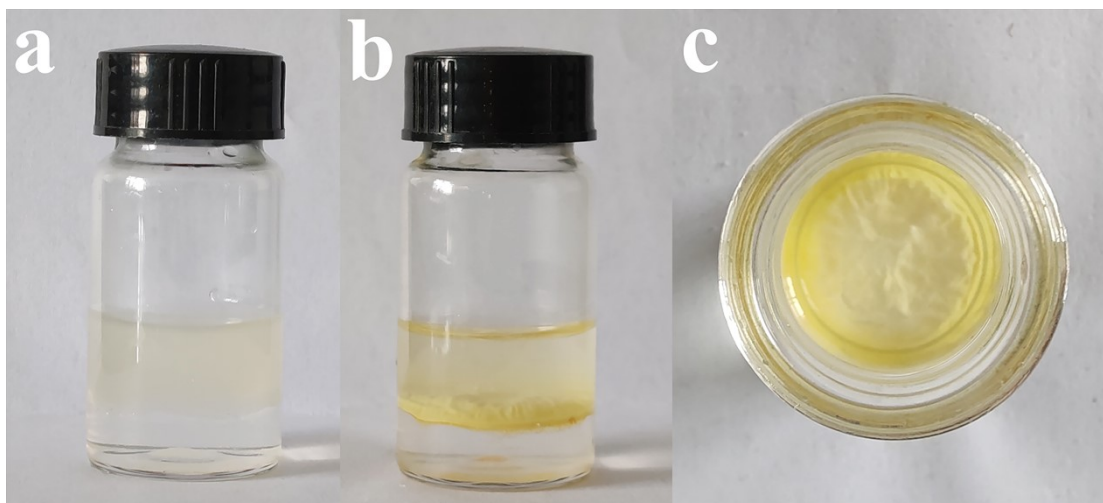
**Fig. S18** CO evolution rate within four cycles in the presence of **MCOF-TDT-6**.



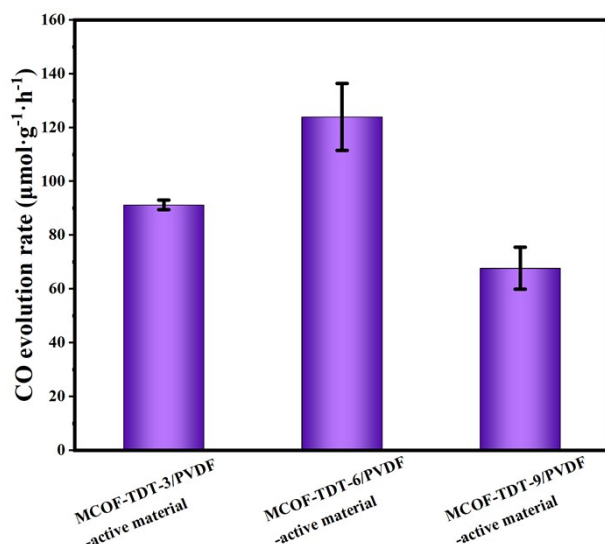
**Fig. S19** FT-IR spectra of **MCOF-TDT-6** after photocatalysis.



**Fig. S20** PXRD spectra of MCOF-TDT-6 after photocatalysis.



**Fig. S21** (a) Photograph of the organic–aqueous system immediately after contact, (b) Photograph of the interfacial film formed after 6 hours of contact, (c) Top-view image of the interfacial film in a vial.



**Fig. S22** CO formation rates **MCOF-TDT-X/PVDF-active material**.

**Table S1** Comparison of the performance of **MCOF-TDT-6** with the reported catalysts for CO<sub>2</sub> photoreduction with H<sub>2</sub>O

Photocatalyst	Products	yield (μmolg <sup>-1</sup> h <sup>-1</sup> )	Light source	Ref
<b>MCOF-TDT-6</b>	<b>CO</b>	<b>168</b>	<b>40 W LED lamp</b>	<b>This work</b>
MCOF-Ti <sub>6</sub> Cu <sub>3</sub>	HCOOH	77.3	PLS-SXE 300 Xe lamp	1
Cu <sub>6</sub> -NH	CO	24.8	Xe lamp (400≤λ≤800 nm)	2
TCOF-MnMo <sub>6</sub>	CO	37.3	Xe lamp (400≤λ≤800 nm)	3
PCN-601	CO	6.0	Xe lamp (λ≥410nm)	4
	CH <sub>4</sub>	10.1		
UJN-1	CO	28.7	300 W Xe lamp (λ≥420nm)	5
CZ-TAPT COF	CO	107	300 W Xe lamp (λ≥420nm)	6
TTCOF-Zn	CO	2.06	300 W Xe lamp (λ≥420nm)	7
TpBb-COF	CO	89.9	Visible Ligh (λ=380nm)	8
CTF-BP	CH <sub>4</sub>	7.81	Xe Lamp(λ> 420 nm)	9
	CO	4.60		
TTCOF/NUZ	CO	6.56	300 W Xe lamp	10
EPPT-COF	CH <sub>4</sub>	14.7	300 W Xe lamp (λ ≥ 420 nm)	11

TAPBB-COF	CO	24.6	Xe lamp	12
MAF-34-CoRu	CO	5.43	300 W Xe lamp	13
	CH <sub>4</sub>	0.66	( $\lambda \geq 420\text{nm}$ )	
COF-318-TiO <sub>2</sub>	CO	69.67	Simulated Sunlight	14
			Irradiation	
N <sub>3</sub> -COF	HCOOH	0.57	800 $\geq \lambda \geq$ 380	15
			500 W Xe lamp ( $\lambda \geq$ 420 nm)	
NNU-31-Zn	HCOOH	26.3	300 W Xe-lamp (400 $\leq \lambda \leq$ 800 nm)	16
TpPa/ZIF-8	CO	43.94	40 W LED lamp	17
C-TiO <sub>2</sub> -x@g-C <sub>3</sub> N <sub>4</sub>	CO	205	300 W Xe lamp	18
[Emim]BF <sub>4</sub> @Zn-S-COF	CO	267.95	300 W Xe lamp ( $\lambda \geq$ 420 nm)	19
viCOF-bpy	CO	190.6	300 W Xe lamp ( $\lambda =$ 420–800 nm)	20

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