

## Electronic Supplementary Information

### Noble Metal-Free Porphyrin Covalent Organic Framework Membrane for CO<sub>2</sub> Photoreduction to CO

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## S1. Physical measurements

Fourier transform infrared (FT-IR) spectra were measured by a Bruker Tensor 27 infrared spectrometer. Scanning electron microscopy (SEM) analysis was conducted on the HITACH SU8220 electron microscope. Transmission electron microscopy (TEM) images of the samples were obtained using a JEOL JEM 2100F microscope (JEOL, Japan). Atomic Force Microscope (AFM) images were collected from a Bruker Dimension ICON microscope. X-ray photoelectron spectroscopy (XPS) measurements were performed on an Axis Ultra DLD using C 1s (284.8 eV) as a reference to correct the binding energy. Powder X-ray powder diffraction (XRD) patterns were performed on a Bruker D8 Advance A25 X-ray diffractometer with Cu K $\alpha$  radiation ( $\lambda=0.154$  nm). A spectrophotometer (JASCO-V750, Japan) was used to collect the UV-vis diffuse reflectance spectra (UV-vis DRS) with BaSO<sub>4</sub> as the non-absorbing reference material. Using the CHI 660 E electrochemical workstation as a three-electrode system, i-t curves of the samples were obtained at 0.5 M Na<sub>2</sub>SO<sub>4</sub> solution with a test voltage of 0 V (relative to Ag/AgCl). Electron paramagnetic resonance (EPR) measurement was performed at room temperature using a Magnettech ESR5000 spectrometer (Bruker). <sup>13</sup>C CP/MAS NMR experiments were performed on Bruker AVWB III 600 spectrometer. N<sub>2</sub> adsorption-desorption isotherms of CuDAPP-TP-COF were measured on a Micromeritics ASAP 2460 apparatus. The catalytic products were analysed using gas chromatograph (GC-7890II, Beijing CEAULIGHT Co.) with a flame ionized detector (FID) and gas chromatograph-mass spectrometer (Agilent 7890A-5975C) with a thermal

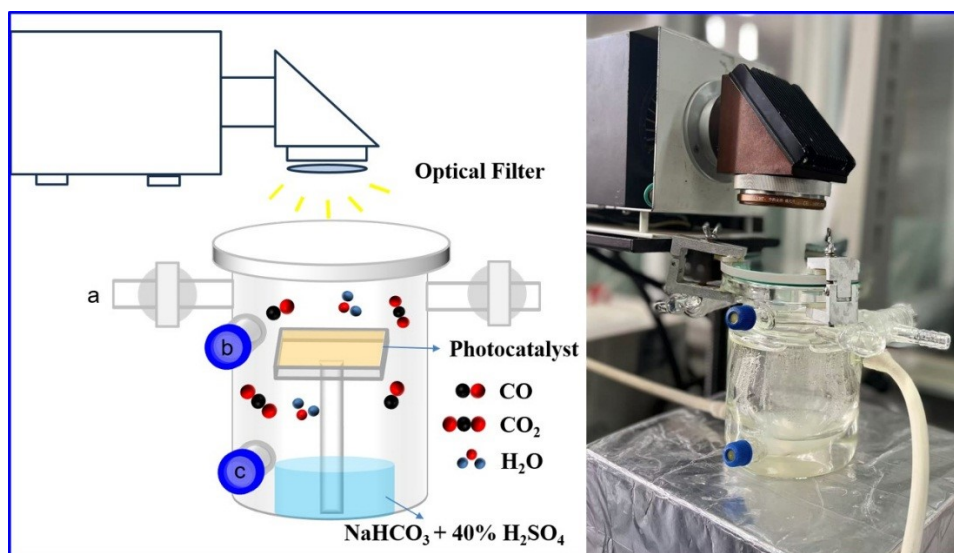
conductivity detector (TCD), and the equipped columns were TDX-01 and HP-PLOTQ, respectively. Other hydrocarbon product was measured by the n-butyl alcohol solution as extraction agent and analyzed by the GC with HP-FFAP column, FID detector and H<sub>2</sub> carrier gas.

## **S2. Synthesis of CuDAPP**

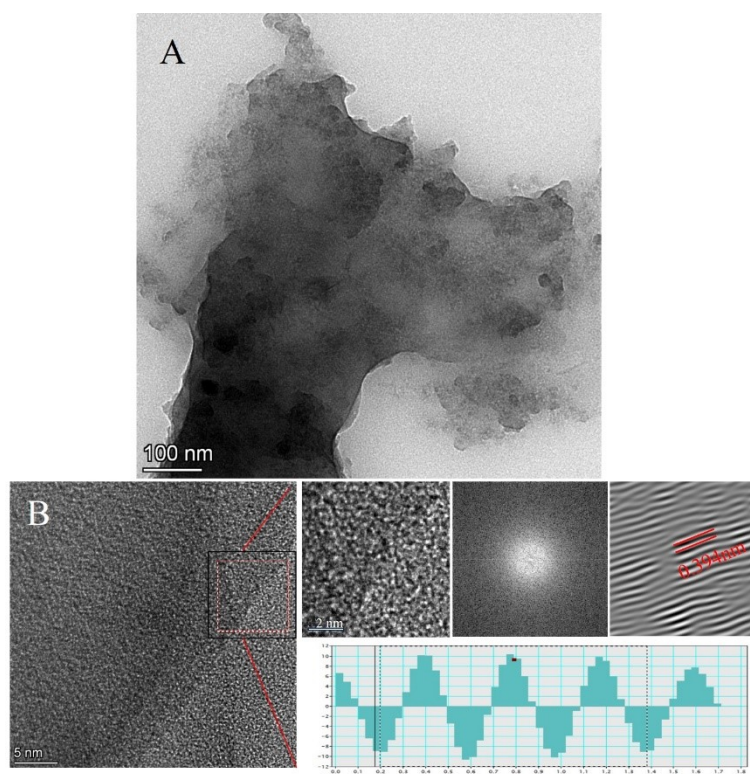
DAPP (100 mg 0.155mmol) and CHCl<sub>3</sub> (50 ml) were placed in a three-neck flask under magnetic stirring until condensation and reflux, then Cu(OAc)<sub>2</sub>•2H<sub>2</sub>O (296 mg 1.48mmol) was dissolved in methanol (15 ml), and the methanol solution was poured into the above three-neck flask and reacted for 90min, and samples were taken for thin layer. The sample is analysed by chromatography and compared with the feedstock solution and if there is no feedstock solution, the reaction is considered to be over. The reaction solution was extracted three times with water as extractant to extract the unreacted copper acetate and incorporate anhydrous sodium sulfate into the trichloromethane solution and allowed to stand for three hours before being subjected to filtration and recrystallisation. Finally, a red solid was obtained and dried in vacuum at 80°C for 24h.

**Table. S1** Photocatalytic activity and selectivity of CO<sub>2</sub> reduction in the reported literature.

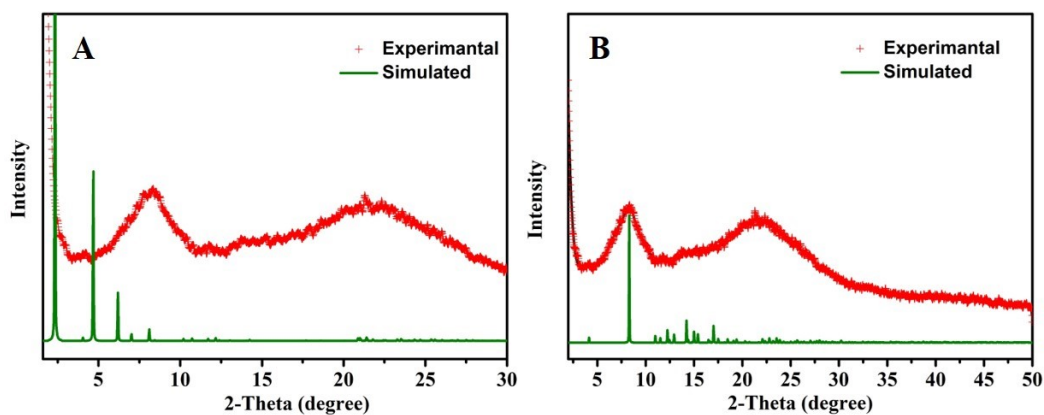
Photocatalyst	Sacrificial Agent	Light Source	Main Product	Activity (μmol g <sup>-1</sup> h <sup>-1</sup> )	Ref
TAPPB-COF	H <sub>2</sub> O	Xe Lamp	CO	24.6	1
COF-366	H <sub>2</sub> O	Xe Lamp	CO	8.5	1
TpPa/ZIF-8	H <sub>2</sub> O	40 W LED lamp	CO	43.94	2
DhaTph-Cu Tubes	H <sub>2</sub> O	-	CO	15.9	3
TiO <sub>2</sub> -INACuP-PhCOF	H <sub>2</sub> O	300W Xe Lamp	CO	50.5	4
PD-COF-23-Ni	TEOA	300W Xe Lamp	CO	40	5
APTES-TiO <sub>2</sub> @TMP	H <sub>2</sub> O	300W Xe Lamp	CO	6.67	6
PCN-224 (Cu)/TiO <sub>2</sub>	H <sub>2</sub> O	300 W Xe Lamp	CO	37.21	7
TTCOF(Zn)	H <sub>2</sub> O	300 W Xe Lamp	CO	2.1	7
CuDAPP-TP-COF	H <sub>2</sub> O	300W Xe Lamp	CO	47.1	<b>This work</b>



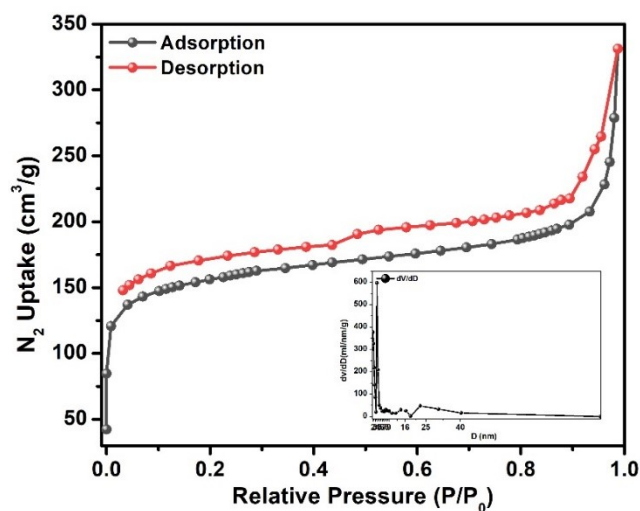
**Fig. S1** The schematic of the photocatalysis test process and the photograph of the photoreactor.



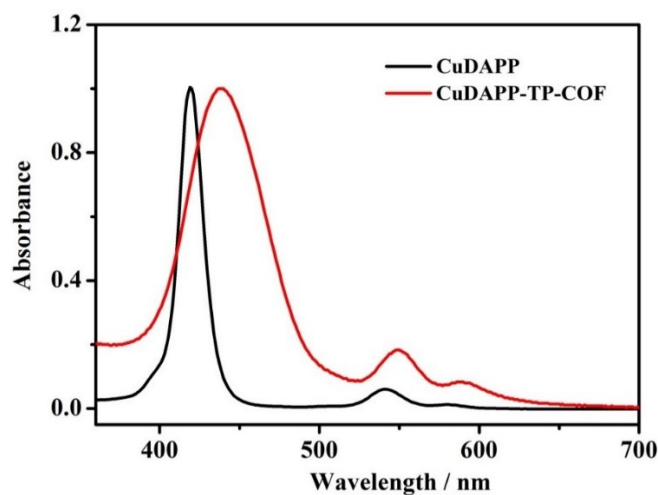
**Fig. S2** (A) TEM images of CuDAPP-TP-COF layer; (B) HR-TEM images of CuDAPP-TP-COF layer.



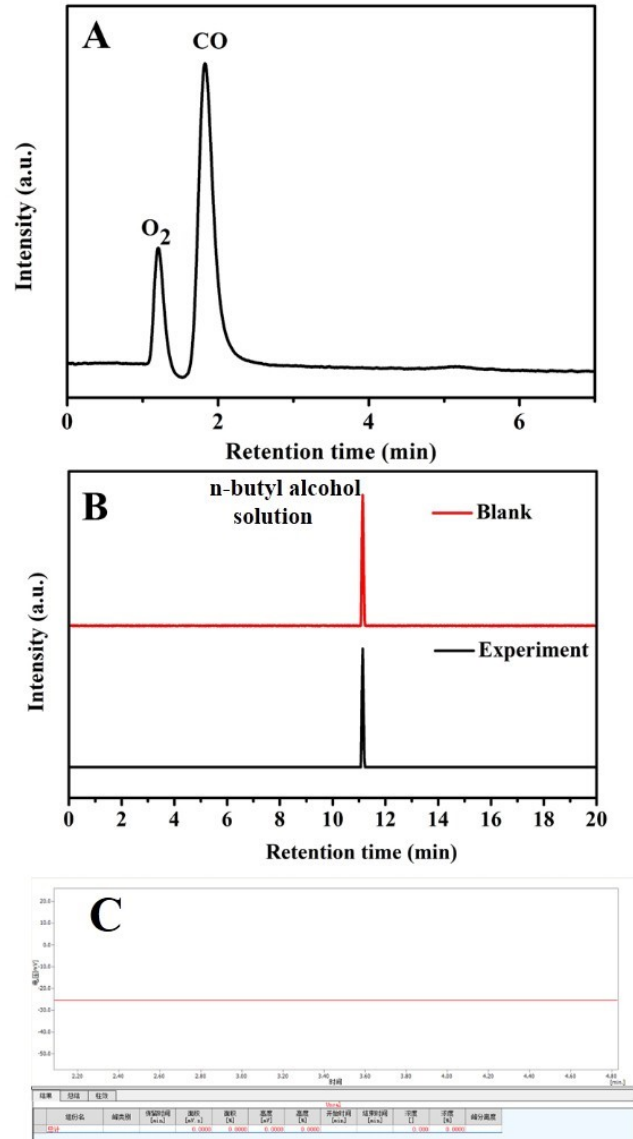
**Fig. S3** Experimental PXRD patterns of CuDAPP-TP-COF layer and the simulated ones according to AA stacking model (A) and AB stacking model (B).



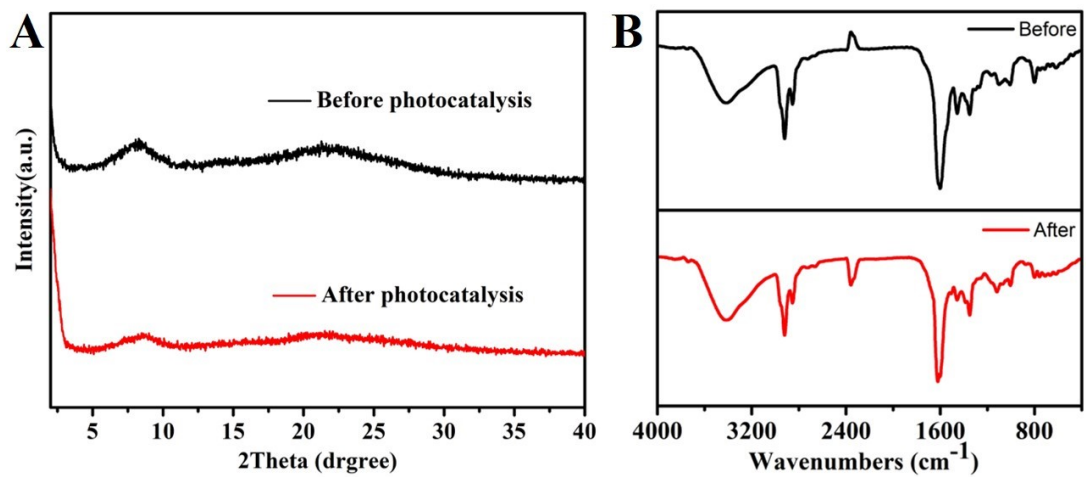
**Fig. S4** N<sub>2</sub> adsorption and desorption isotherms (inset: pore size) for CuDAPP-TP-COF.



**Fig. S5** The UV-vis spectra of CuDAPP-TP-COF layer and CuDAPP.



**Fig. S6** GC spectra of gaseous (A) and liquid products (B) of CO<sub>2</sub>, and H<sub>2</sub> (C) photoreduction using CuDAPP-TP-COF layer as catalyst.



**Fig. S7** (A) The XRD spectra of CuDAPP-TP-COF layer after (red) and before (black) photocatalysis. (B) The FT-IR spectra of CuDAPP-TP-COF layer after (red) and before (black) photocatalysis.



1. L.-j. Wang, R.-l. Wang, X. Zhang, J.-l. Mu, Z.-y. Zhou and Z.-m. Su, *ChemSusChem*, 2020, **13**, 2973-2980.
2. R. G. Yang, Y. M. Fu, H. N. Wang, D. P. Zhang, Z. Zhou, Y. Z. Cheng, X. Meng, Y. O. He and Z. M. Su, *Chem. Eng. J.*, 2022, **450**, 9.
3. Z. Zhang, J. Lu, K. Yang, J. Cao, Y. Zhao, K. Ge, S. Wang, Y. Yang, Y. Zhang and Y. Yang, *ChemistrySelect*, 2022, **7**, e202201203.
4. L. Wang, G. F. Huang, L. Zhang, R. Lian, J. W. Huang, H. D. She, C. L. Liu and Q. Z. Wang, *J. Energy Chem.*, 2022, **64**, 85-92.
5. N. F. Xu, Y. X. Diao, X. H. Qin, Z. T. Xu, H. Z. Ke and X. J. Zhu, *Dalton Transactions*, 2020, **49**, 15587-15591.
6. L. Wang, H. Y. Cheng, Z. T. Zhang, Y. Zhang, J. W. Huang, H. D. She, C. L. Liu and Q. Z. Wang, *Chem. Eng. J.*, 2023, **456**, 11.
7. R. Das, P. Kumar Verma and C. M. Nagaraja, *Coordination Chemistry Reviews*, 2024, **514**, 215944.