Supplementary Information

Ionic Porous Organic Polymer as a Bifunctional Platform for CO_2 photoreduction and Proton Conduction

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Materials and methods

All materials are commercially available and can be used directly. The used materials are listed here: cyanuric chloride, anhydrous 4,4'-bipyridine (BPy), Molybdenum(VI) oxide (MoO_3), Vanadium pentoxide (V_2O_5), phosphoric acid (H_3PO_4), potassium iodide (KI), absolute methanol, absolute ethanol, N,N-dimethylformamide (DMF), potassium bromide (KBr), barium sulfate ($BaSO_4$).

Powder X-ray Diffraction (PXRD) patterns were acquired with Bruker D8 Advance X-ray diffractometer (Cu Kα radiation, λ = 1.5418 Å) in the range of 5-90° (2θ). Fourier Transform Infrared (FT-IR) spectroscopy was tested with Gangdong FT-IR 850 using KBr as background. The morphology of the sample was analyzed via Thermo Scientific Apreo S Scanning Electron Microscope (SEM). UV-Vis Diffuse Reflection Spectrum (UV-Vis DRS) were tested with Persee TU-1901 UV-Vis Spectrophotometer.

Preparation of POP-BPy

POP-BPy was synthesized according to reported literature[1] with minor modification. Typically, 1.12 g (*ca.* 6 mmol) cyanuric chloride was dissolved in 30 mL DMF as Solution A; 1.50 g (*ca.* 8 mmol) BPy was dissolved in 20 mL DMF as Solution B. The solution B was added dropwise to solution A with continuous stirring, then the slurry was stirred and refluxed under 120℃ for 2 h. The precipitate was filtered and washed with methanol for 3 times, then dried under room temperature.

Preparation of $PMo_{10}V_2$

Vanadium-substituted phosphomolybdic acid $H_5PMo_{10}V_2O_{40}$ ($PMo_{10}V_2$) were synthesized according to reported literature[2]. Typically, 7.2 g (*ca.* 50 mmol) MoO_3 was dispersed in 50 mL of deionized water, and a solution of 0.91 g (*ca*. 5 mmol) V_2O_5 in 50 mL of deionized water was added. The slurry was heated to 120 ℃ under continuously stirring. Afterward, 0.6 g H_3PO_4 (85% wt., *ca.* 5 mmol) was added dropwise to the mixture within 30 minutes, and the reaction was continued for another 20 h. After cooling to room temperature, the solution was filtered to removed unreacted reactants or insoluble impurities. The solution was evaporated, and orange-pink

products were obtained. The product $PMo_{10}V_2$ was dried at 80 ℃ to remove moisture.

Preparation of POP-BPy-PMV-x

The POP-BPy-PMV-x samples were prepared via the ion exchange between $PMo_{10}V_2$ anion and Cl^- anion. 200 mg of POP-BPy was dispersed in 10 mL methanol with 5 min of sonication, then 5 mL $PMo_{10}V_2$/methanol solution with certain amount (x mg, x = 12.5, 25 and 50) of $PMo_{10}V_2$ was added into POP-BPy/methanol solution, and the mixture was followed with 4 h stirring. Finally, the solid product was filtered, washed with methanol and dried under 60 ℃.

Photocatalytic CO_2 Reduction Performance Test

The sample (2 mg) was dispersed in 1 mL ethanol with 30 min of sonication to make it uniformly distributed, and then drip it on a 1 cm × 3 cm glass slide with a coverage area of 10×30mm. The prepared sample was placed in a self-made photocatalytic reactor, and 2 drops (*ca.* 100 μL) of deionized water was added to the bottom as a reducing agent. The CO_2 gas was used to replace the air inside the reactor and full of the reactor. The LED lamp was used as the light source and irradiated the sample for 2 h. 0.5 mL and 1.0 mL of the photocatalyzed mixed gas were injected into the gas chromatograph to determine the CO content in the gas respectively.

Electrochemical Analysis

The electrochemical analysis was carried out by the electrochemical analyzer (CHI 760E), using a standard three-electrode system for photocurrent response test and Mott-Schottky test. The electrolyte solution is 0.2 $mol \cdot L^{-1}$ Na_2SO_4 solution, Ag/AgCl electrode is used as reference electrode, platinum electrode is used as counter electrode, and ITO glass coated with photocatalyst is used as working electrode. The working electrode was prepared by adding photocatalyst (1 mg) and 5% Nafion (10 μL) to 1 mL ethanol and ultrasonic treatment for 1 h, and then dripping the resulting suspension on 1 cm × 2 cm ITO glass.

Proton Conductivity Measurement

The sample was placed in a homemade press die (10 mm in diameter), and the sample was pressed under a pressure of 0.6 MPa to obtain the block in the form of a round tablet. After measuring the thickness of the disc-shaped block, copper conductive adhesive is glued on both sides and fixed on the electrode. AC Impedance Spectroscopy analysis was carried out on the compressed pellet samples to evaluate the proton conductivity, which was calculated using the following equation:

$$\sigma = \frac{L}{RS}$$

Where L and S are the length (cm) and cross-sectional area (cm^2) of the samples respectively. R is the proton conduction resistance (Ω) of the sample, which was extracted directly from the Nyquist plot. Activation energy (E_a) for the materials conductivity was estimated from the following equation:

$$\ln(\sigma T) = \ln A - \frac{E_a}{kT}$$

Where σ is the proton conductivity (S/cm), A is the pre-exponential factor, T is the temperature (K), k is the Boltzmann constant.

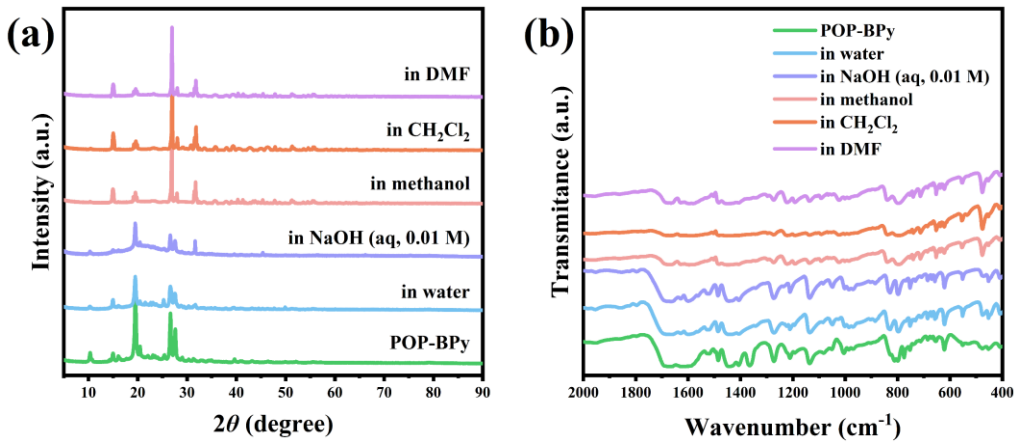

Fig. S1 The PXRD patterns (a) and FT-IR spectra (b) of original POP-BPy and POP-BPy soaked in different solutions or solvents.

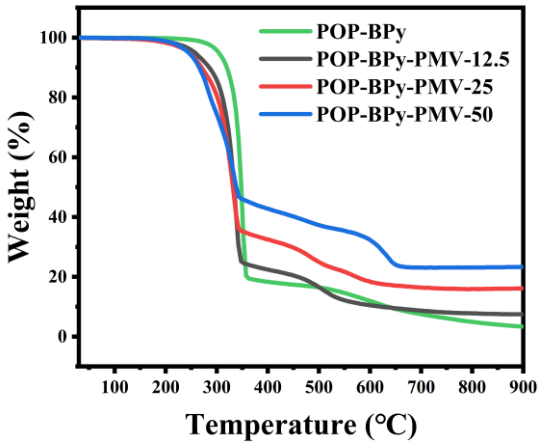

Fig. S2 The TGA curves of POP-BPy and POP-BPy-PMV-x

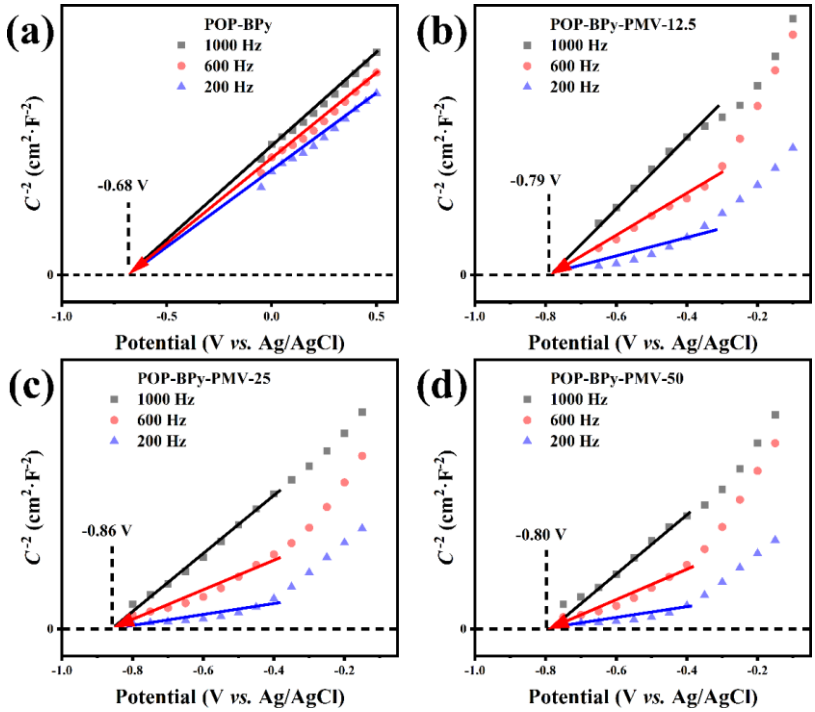

Fig. S3 Mott-Schottky plot of POP-BPy (a), POP-BPy-PMV-12.5 (b), POP-BPy-PMV-25 (c) and POP-BPy-PMV-50 (d)

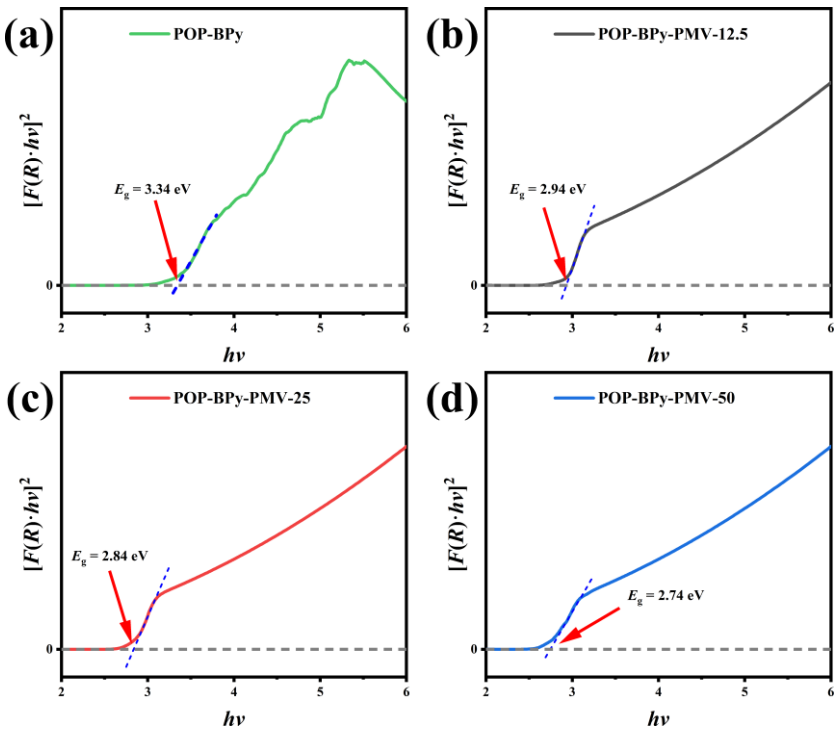

Fig. S4 Tauc plot of POP-BPy (a), POP-BPy-PMV-12.5 (b), POP-BPy-PMV-25 (c) and POP-BPy-PMV-50 (d)

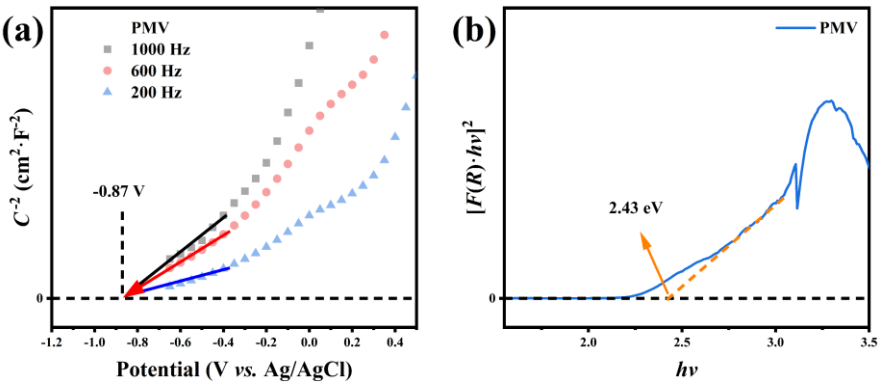

Fig. S5 Mott-Schottky plot (a) and Tauc plot (b) of PMV

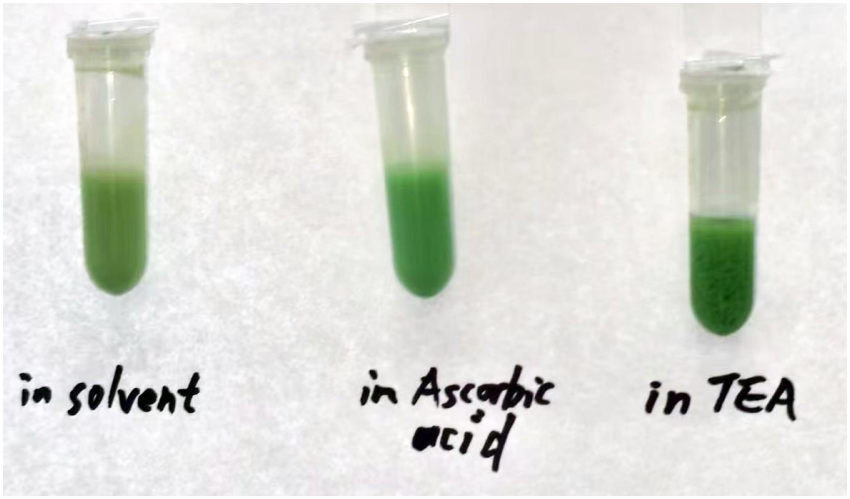

Fig. S6 The behavior of POP-BPy in acidic or alkaline conditions (solvent=deionized wateer)

Table S1 Photocatalytic CO_2 reduction performance

Samples	CO evolution rate $\mu mol \cdot g^{-1} \cdot h^{-1}$	O_2 evolution rate $\mu mol \cdot g^{-1} \cdot h^{-1}$	H_2 evolution rate $\mu mol \cdot g^{-1} \cdot h^{-1}$	Selectivity %
POP-BPy	7.300	9.803	4.921	59.73
POP-BPy-PMV-12.5	14.00	16.40	4.780	74.55
POP-BPy-PMV-25	22.75	12.63	5.132	81.60
POP-BPy-PMV-50	18.75	21.31	4.887	79.32

Table S2 Summary of photocatalysts for CO2 reduction in other works

Photocatalyst	Product	Production Rate $\mu mol \cdot h^{-1} \cdot g^{-1}$	Ref.
POP-BPy-PMV-25	CO	22.75	This work
PD-COF-23-Ni	CO	40.0	[3]
HB-TAPT + Co	CO	19.6	[4]
g-C_3N_4/$FeWO_4$	CO	6	[5]
NiAl-LDH/Ti_3C_2	CO	11.82	[6]
Ultrathin $Bi_4O_5Br_2$	CO	31.565	[7]
MTCN-H (ys)	CO	18.12	[8]
TAPBB-COF	CO	24.6	[9]
TTCOF-Zn	CO	2.06	[10]

Table S3 Summary of proton conductive materials in other works

Material	Proton Conductivity $S \cdot cm^{-1}$	Condition	Ref.
POP-BPy	1.18×10^{-2}	90 °C, 100% RH	This work
BIP	3.2×10^{-2}	95 °C, 95% RH	[11]
GS-COF-2-COOH	1.38×10^{-3}	80 °C, 90% RH	[12]

TPB-DPPA-COF	4.96×10^{-4}	90 °C, 98% RH	[13]
NH_4Br@COF-Im^+-SO_3^-	3.7×10^{-3}	90 °C, 100% RH	[14]
PA@Tp-Azo	9.9×10^{-4}	59 °C, 98% RH	[15]
EB-COF:PW_{12}	3.32×10^{-3}	25 °C, 97% RH	[16]
aza-COF-2_H	4.8×10^{-3}	50 °C, 97% RH	[17]
P^2PV (H_2SO_4 doped)	1.7×10^{-2}	21 °C, 75% RH	[18]

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