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Electronic Supplementary Information

Metal-free Azo-bridged Porphyrin Porous Organic Polymers for Visible-light-driven CO_2 Reduction to CO with High Selectivity

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1. Physical measurements

Fourier transform infrared (FT-IR) spectra were performed as KBr pellets using a Bruker Tensor 37 spectrometer with 2 cm^{-1} resolution. Powder X-ray diffraction (PXRD) data were collected on a Bruker D8 Advance XRD diffractometer using Cu-Ka radiation (I = 1.54060 Å) at room temperature. Transmission electron microscopy (TEM) images were measured on a JEOL JEM-2100 electron microscope operated at 200 kV. Scanning electron microscopy (SEM) images were obtained using a JEOL JEM-6510A scanning electron microscopy. For TEM imaging, a drop of freshly prepared sample solution was cast onto a carbon copper grid. For SEM imaging, a drop of freshly prepared sample solution was cast onto a silicon slice, and then Au (1-2 nm) was sputtered onto the grids to prevent charging effects and to improve the image clarity. X-ray photoelectron spectroscopy (XPS) was carried out on PHI 5300 ESCA System (Perkin-Elmer, USA). The excitation source is Al Kα radiation. ^{13}C CP/MAS NMR experiments were performed on Bruker AVANCE III 600 spectrometer at a resonance frequency of 150.9 MHz.

2. **Photoelectrochemical characterization.**

The photocurrent measurement were performed on three-electrode system using an electrochemical workstation. The cleaned ITO glass deposited with samples, Pt and Ag/AgCl electrode were used as working electrode, counter electrode, and reference electrode, respectively. The light source was a 300 W Xe lamp equipped with an ultraviolet cutoff filter (> 400 nm) and 0.05 M Na_2SO_4 aqueous solution acted as the electrolyte.

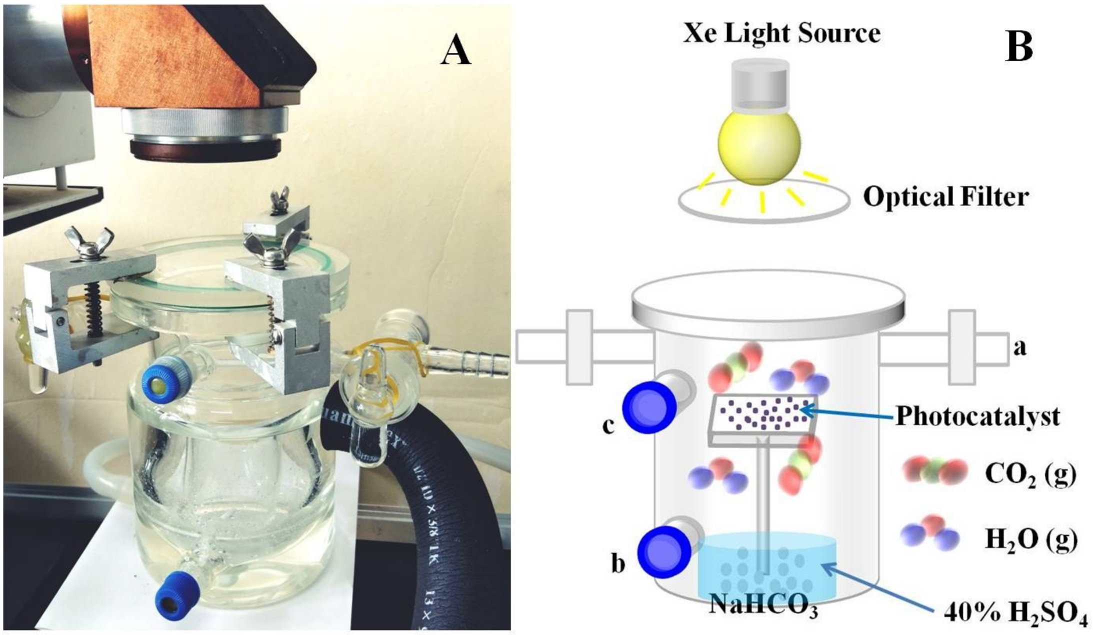

Fig. S1 (A) The photograph of the photoreactor and the schematic of the photocatalysis test process.

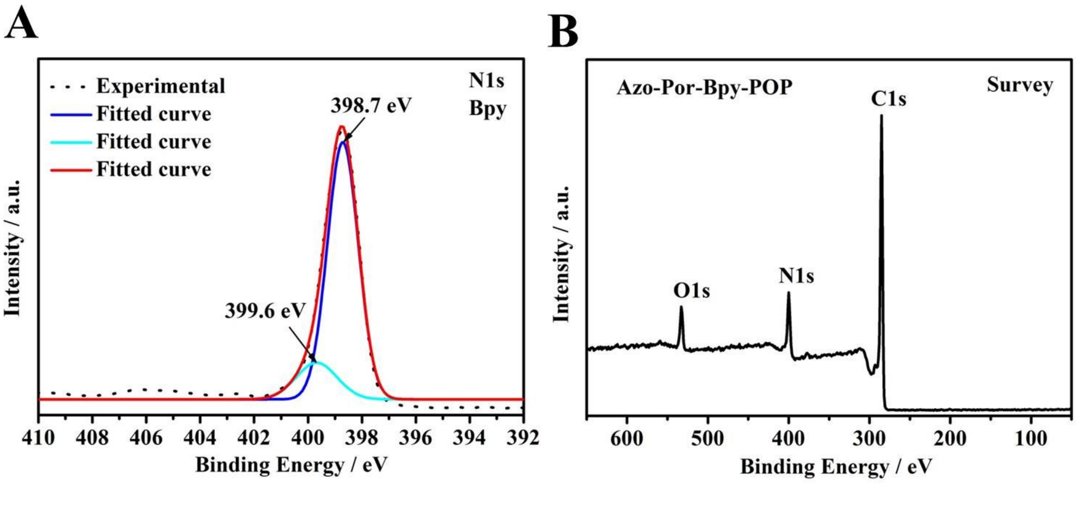

Fig. S2 (A) the XPS spectrum of Bpy and (B) XPS survey spectrum of Azo-Por-Bpy-POP.

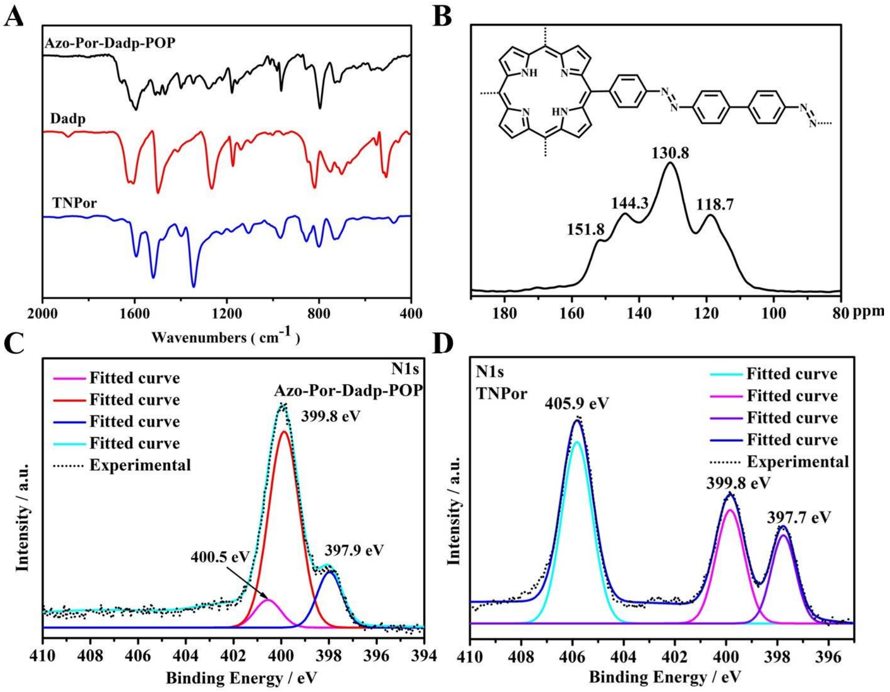

Fig. S3 (A) FT-IR spectra of Dadp, TNPP, and **Azo-Por-Dadp-POP**; (B) ^{13}C CP-MAS NMR spectrum of **Azo-Por-Dadp-POP**; (C, D) the XPS spectra of **Azo-Por-Dadp-POP** and TNPor.

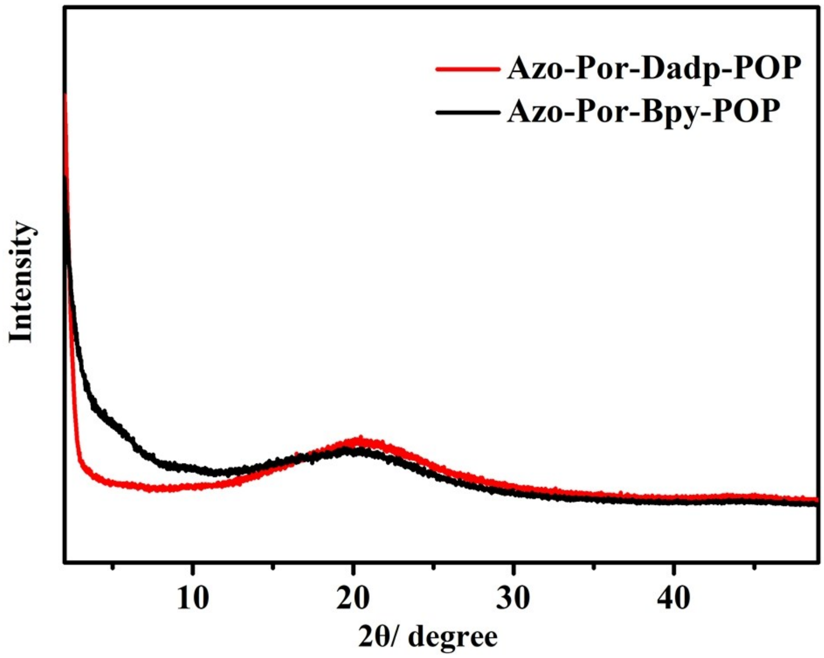

Fig. S4 Experimental PXRD patterns of **Azo-Por-Bpy-POP** (black) and **Azo-Por-Dadp-POP** (red).

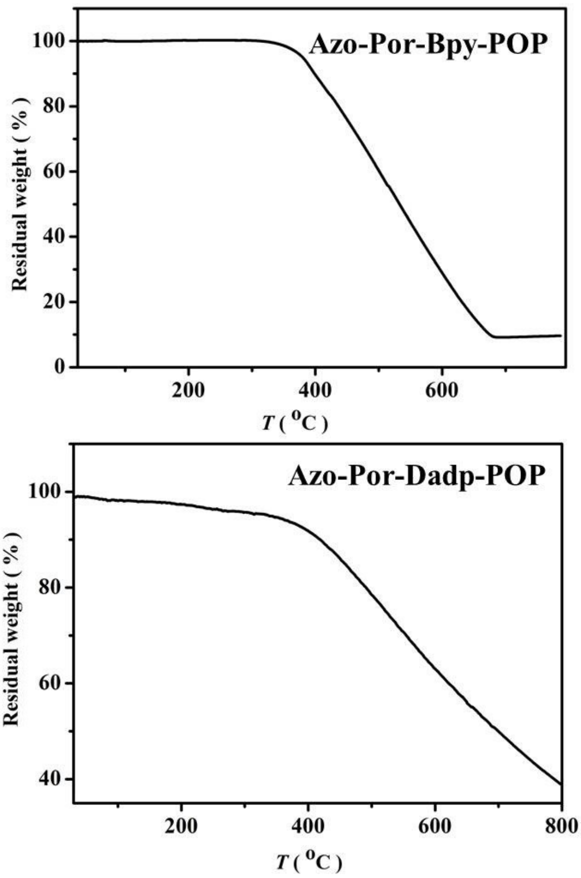

Fig. S5 Thermogravimetric analysis (TGA) data of **Azo-Por-Bpy-POP** and **Azo-Por-Dadp-POP**.

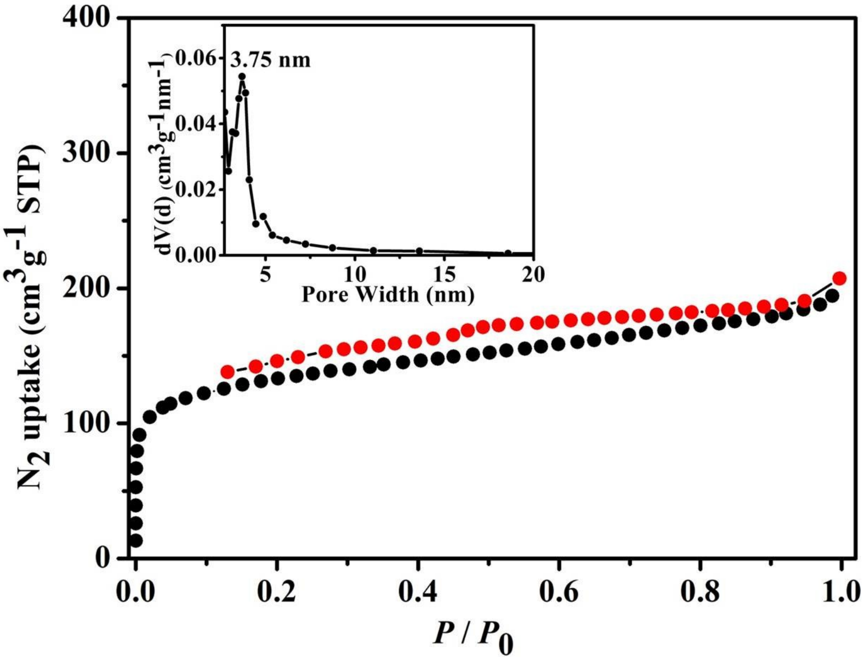

Fig. S6 Nitrogen adsorption-desorption isotherms of **Azo-Por-Dadp-POP** (A), insets: the pore size distribution.

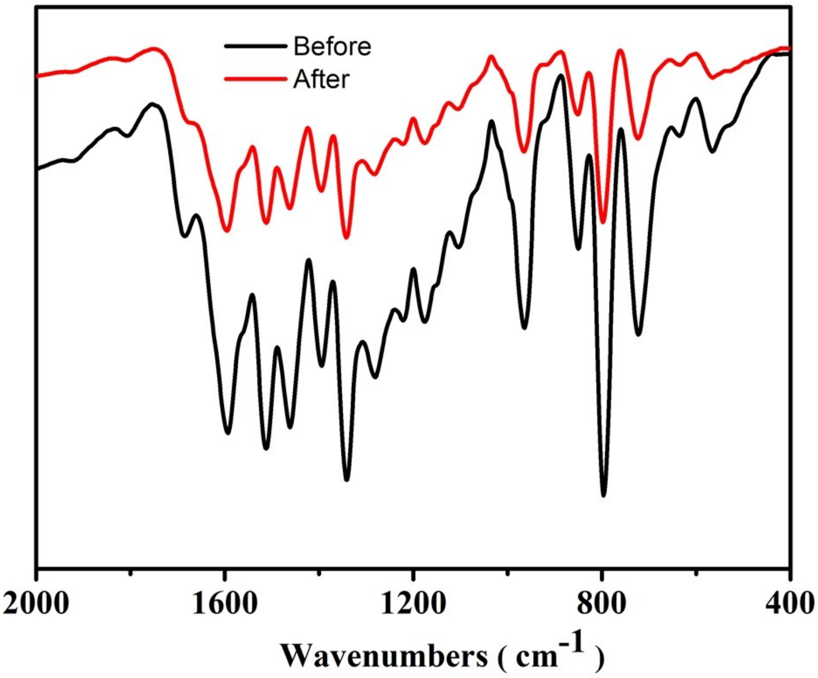

Fig. S7 the FT-IR spectra of **Azo-Por-Bpy-POP** before (black) and after (red) photocatalysis.

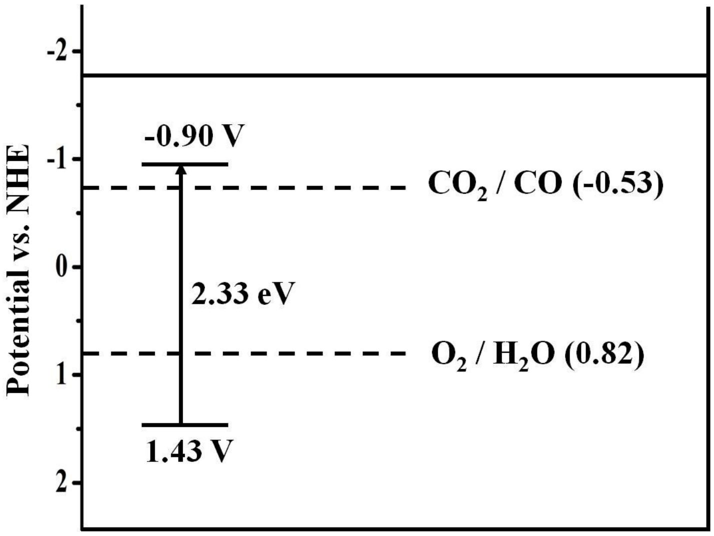

Fig. S8 The electronic band structure of **Azo-Por-Bpy-POP**.