

Supporting Information

Imidazole-Linked Porphyrin-based Conjugated Microporous Polymers for Metal- Free Photocatalytic Oxidative dehydrogenation of N-Heterocycles

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Materials and instruments

All chemicals and solvents were commercially available without further purification unless specified. Anatase TiO₂ was purchased from Energy Chemical Co. Ltd. BiVO₄,¹ FeVO₄,² CdS,³ and g-C₃N₄⁴ were prepared according to the reported literature.

Solid-state ¹³C CP/MAS NMR spectrum was obtained using a Bruker Avance III 400 MHz spectrometer. XPS spectra were conducted in a Thermo Fisher Scientific ESCALab250 using mono AlK α radiation ($h\nu = 1486.6$ eV) as the excitation source under a base pressure of 2×10^{-9} mbar. The binding energies were referenced to the C 1s peak at 284.8 eV. The X-ray diffraction (XRD) patterns were recorded on a Rigaku Smartlab instrument using Cu K α radiation (40 kV) with a scan rate of 10°/min in the 2 θ range from 5° to 85°. The morphology was investigated using a Field Emission Scanning Electron Microscopy (Thermo Scientific Apreo 2C). N₂ sorption isotherm was recorded using an ASAP2020M adsorption instrument. Before measurement, the as-prepared sample was outgassed in vacuum at 100 °C for 10 h. UV-Vis DRS spectra were conducted in a Lambda 950 spectrophotometer in the wavelength range of 200-2000 nm. UPS spectra were performed with an unfiltered HeI (21.22 eV) gas discharge lamp. PL emission spectra were scanned on a FLS980 photoluminescence spectrometer with excitation at 420 nm. Photocatalysis was carried out on a CEL-LAB200E7 multichannel photochemical reaction system equipped with a circulating cooling water system and ten of white LED lamps (4.0 A, 40 mW/cm²), which was provided by Beijing China Education Au-light Co. Ltd. The spectrum of white LED was shown in Figure S1. Reaction products were analyzed by Agilent Agilent GC7890B equipped with DB-1 capillary column (0.25 μ m \times 320 μ m \times 30 m) and FID detector. Standard analysis condition: oven temperature 50 °C, injector temperature 300 °C, detector temperature 300 °C, heating rate 10 °C/min, final temperature 250 °C and hold time 1 min. ESR measurements were performed on a Bruker EMXplus ESR spectrometer.

UV-Vis measurements

TCPP-TAB (10 mg) was dispersed in H₂O containing NBT (0.4 mM). The mixture was irradiated under white LED and air atmosphere. UV-Vis spectra of the sample were recorded on a Shimadzu UV-1800 spectrophotometer in the wavelength range of 200-450 nm.

TCPP-TAB (10 mg) was dispersed in a DMA (5 mL) solution containing DPD (25 mg) and POD (1 mg). The mixture which was bubble with O₂ was irradiated under white LED for 5 min. After reaction, UV-Vis spectra of the sample were recorded on a Shimadzu UV-3600 spectrophotometer in the wavelength range of 400-600 nm.

ESR measurements

TCPP-TAB (10 mg) was dispersed in DMA (5 mL) containing TEMP (100 μL). The mixture was irradiated under air atmosphere and white LED for 2 h. Next, the sample was analyzed on ESR spectrometer at microwave frequency of 9.85 GHz at room temperature. The blank experiment was conducted under same conditions in the absence of TCPP-TAB.

TCPP-TAB (10 mg) was dispersed in DMA (5 mL) containing DMPO (50 μL). The mixture was irradiated under air atmosphere and white LED for 2 h. Next, the sample was analyzed on ESR spectrometer at microwave frequency of 9.85 GHz at room temperature. The blank experiment was conducted under same conditions in the absence of TCPP-TAB.

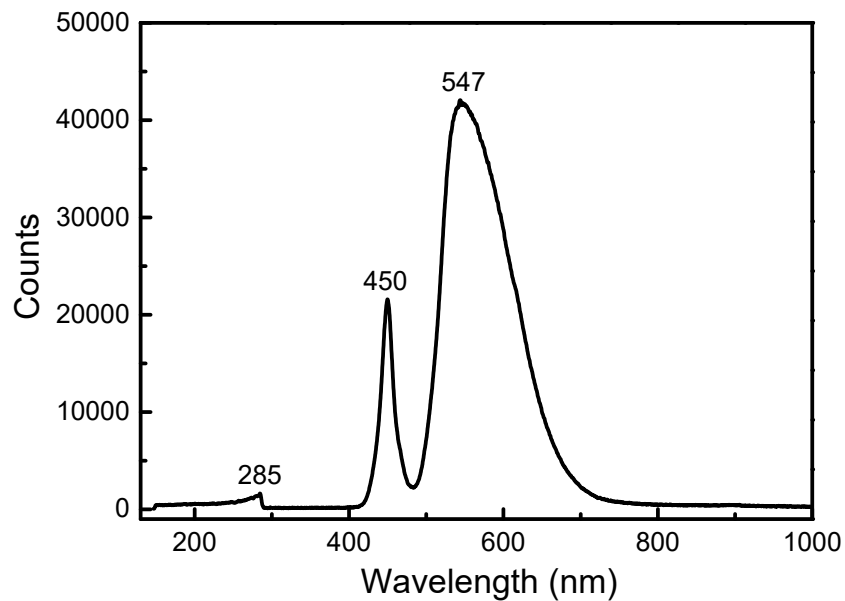


Figure S1. The spectrum of white LED

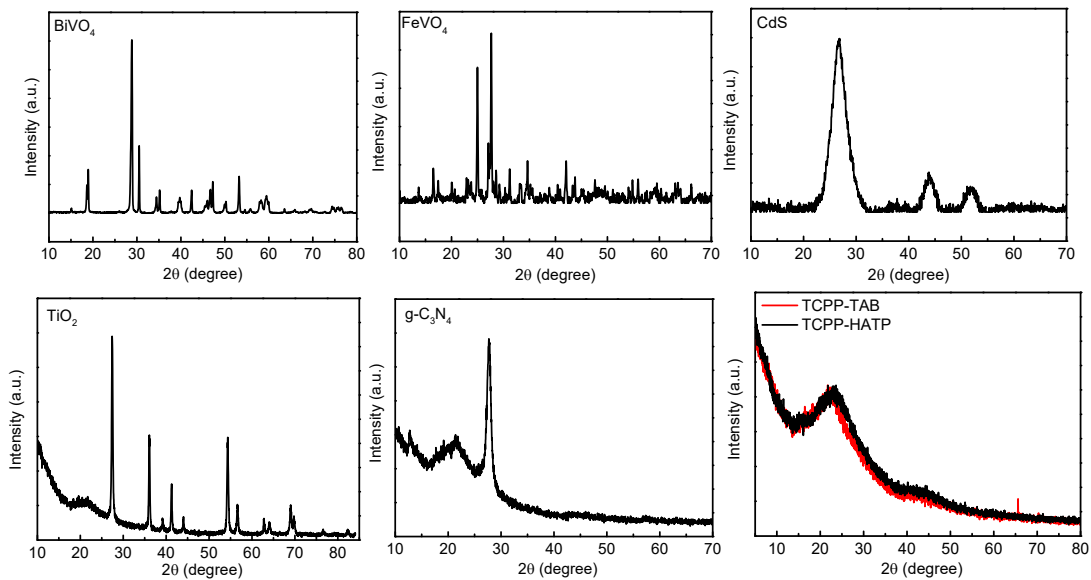


Figure S2. XRD patterns of BiVO₄, FeVO₄, CdS, TiO₂, g-C₃N₄, TCPP-TAB and TCPP-HATP

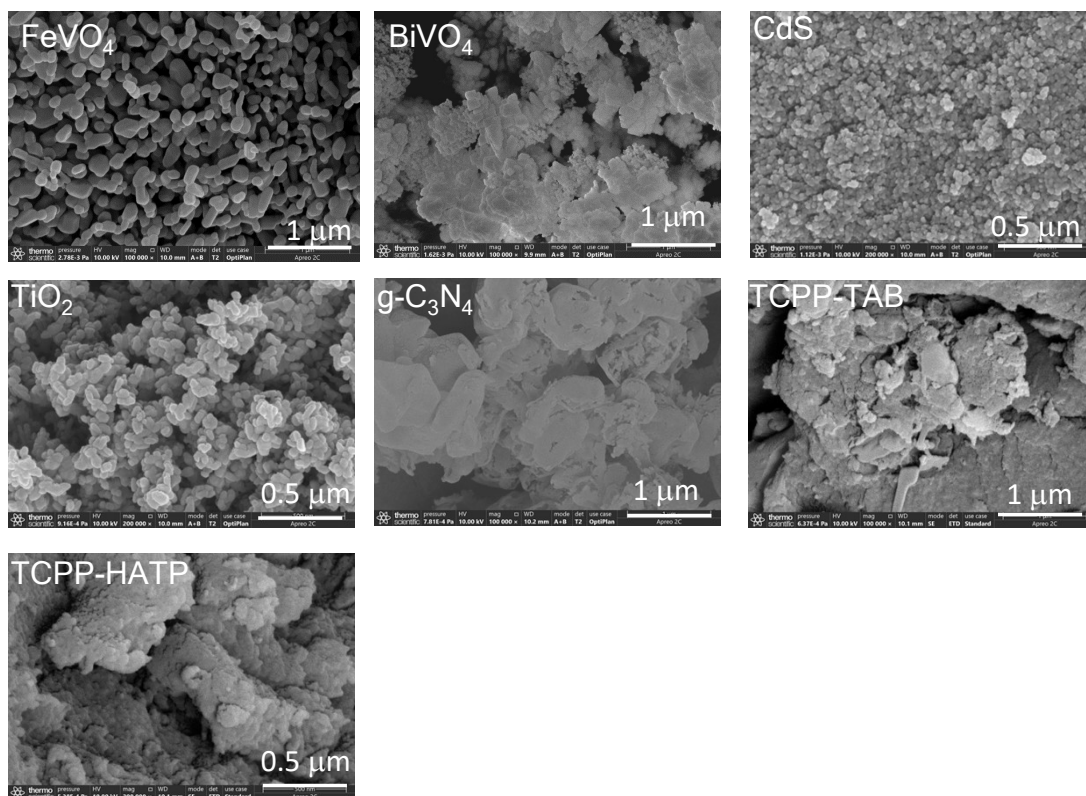


Figure S3. SEM images of BiVO₄, FeVO₄, CdS, TiO₂, g-C₃N₄, TCPP-TAB and TCPP-HATP

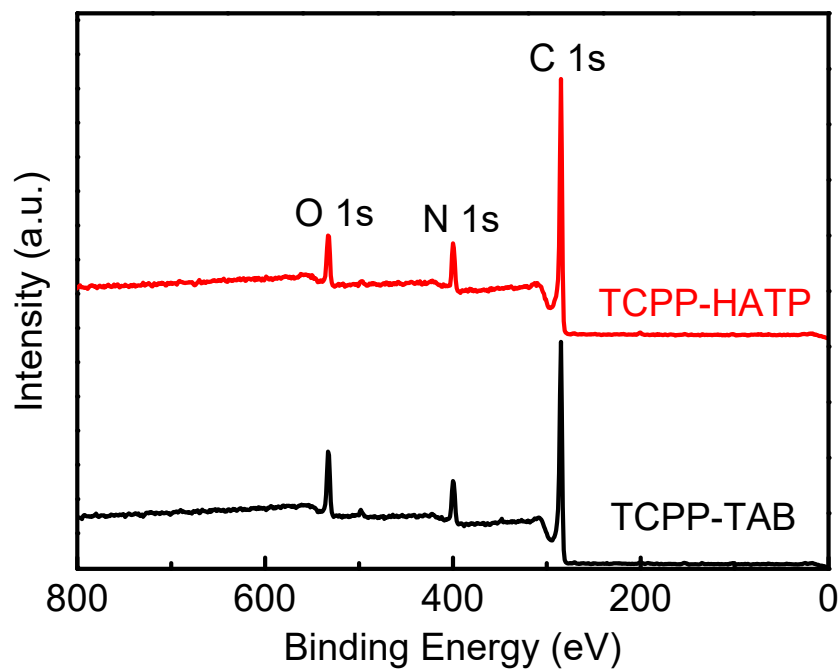


Figure S4. XPS spectra of TCPP-TAB and TCPP-HATP

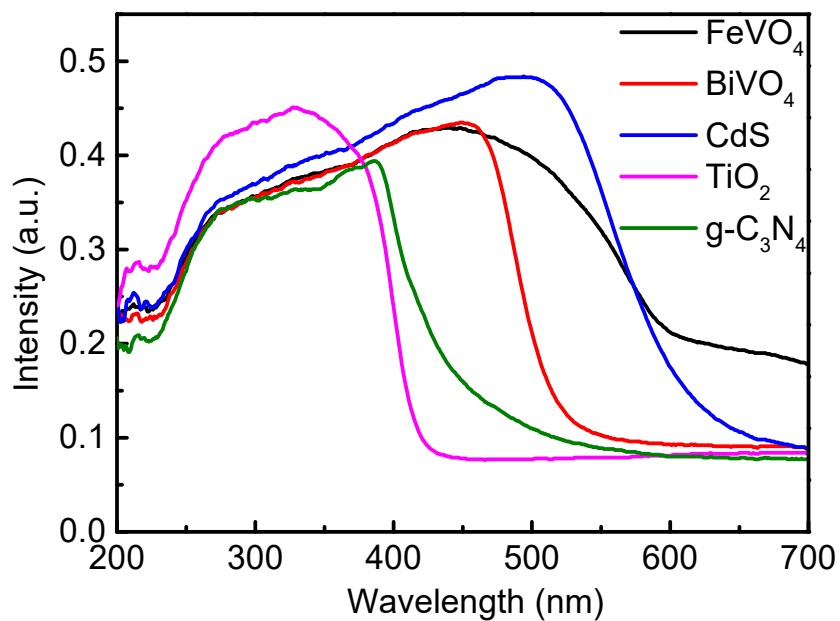


Figure S5. UV-Vis DRS spectra of BiVO₄, FeVO₄, CdS, TiO₂ and g-C₃N₄

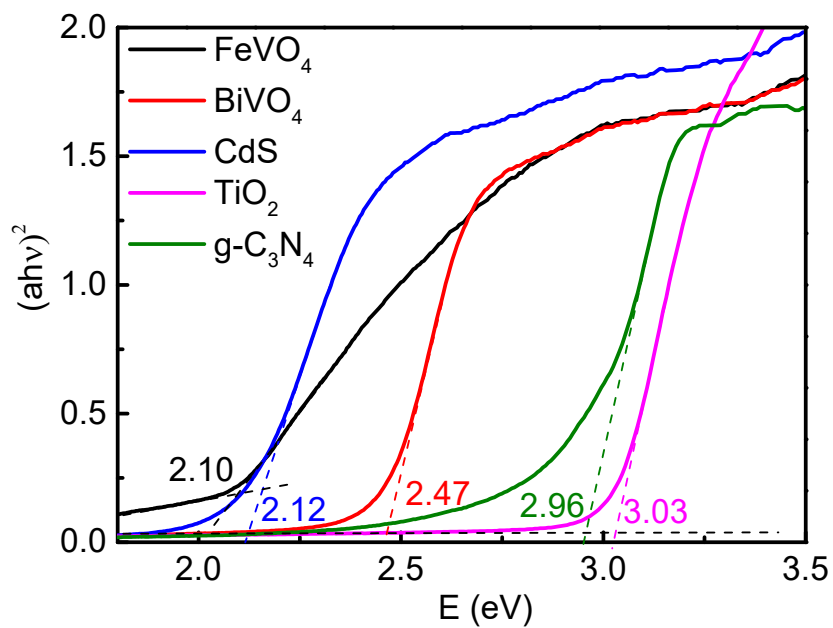


Figure S6. Band gap of BiVO₄, FeVO₄, CdS, TiO₂ and g-C₃N₄

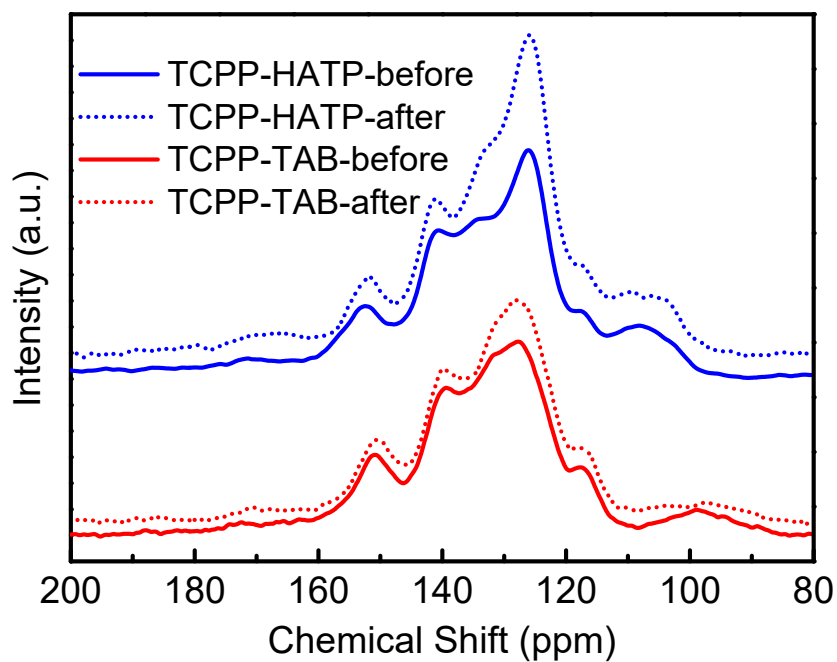


Figure S7. Solid state ^{13}C CP/MAS NMR spectra of TCPP-TAB and TCPP-HATP before and after photocatalytic reaction

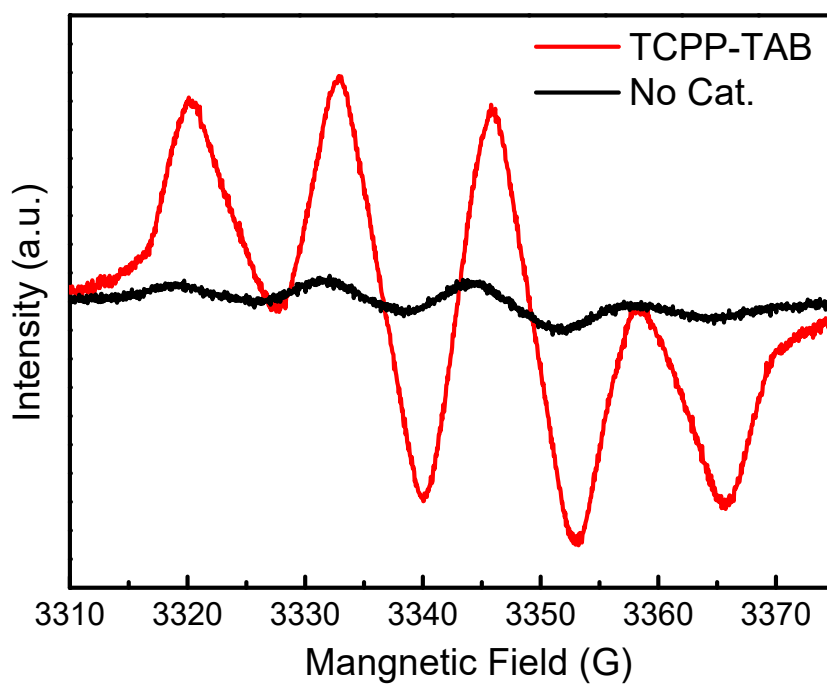


Figure S8. Determination of $\text{O}_2^{\bullet-}$ using DMPO as the trapping agent by ESR spectrometer.

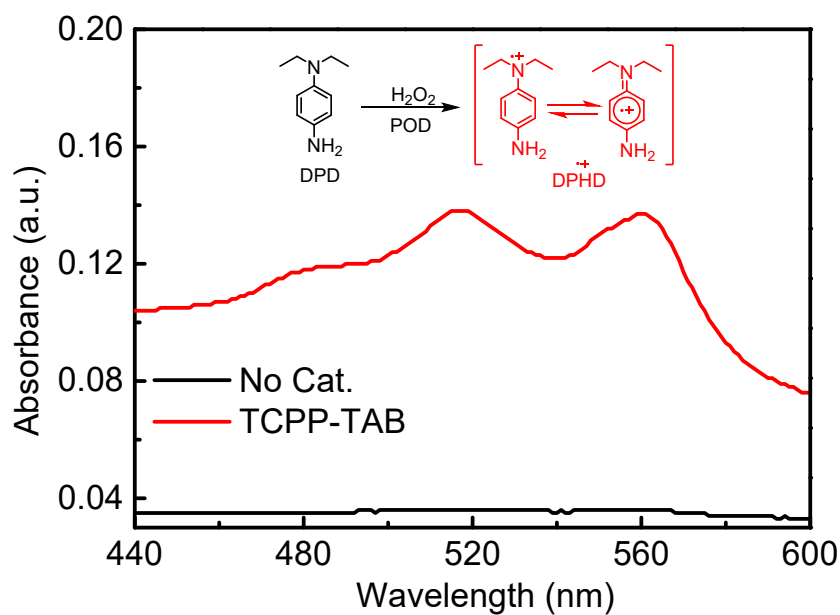
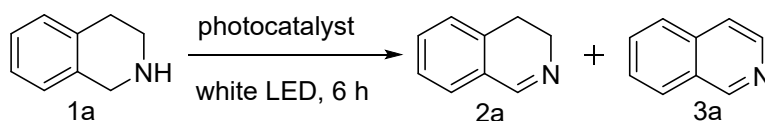


Figure S9. The ultraviolet-visible absorption spectra of reaction system with or without catalyst after adding DPD and POD

Table S1. Comparative experiments



Entry	Photocatalyst	O ₂	hν	Conv.(%)	Yield (%) ^c	
					2a	3a
1	–	+	+	n.d.	n.d.	n.d.
2	+	–	+	n.d.	n.d.	n.d.
3	+	+	–	n.d.	n.d.	n.d.
4	TCPP	+	+	99	74	25

Reaction conditions: 1,2,3,4-tetrahydroisoquinoline (0.5 mmol), photocatalyst (10 mg), air atmosphere, white LED, dimethylacetamide (5 mL), room temperature and 6 h.

Table S2. VB and CB potentials of FeVO₄ and BiVO₄

Photocatalyst	E _g (eV)	E _{VB} (V vs. NHE)	E _{CB} (V vs. NHE)
FeVO ₄	2.10	1.47	-0.63
BiVO ₄	2.47	2.775	0.305

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2. S. Samanta and R. Srivastava, *Appl. Catal. B: Environ.*, 2017, **218**, 621-636.
3. J. Jin, J. Yu, D. Guo, C. Cui and W. Ho, *Small*, 2015, **11**, 5262-5271.
4. J. W. Sun, J. Bian, J. D. Li, Z. Q. Zhang, Z. J. Li, Y. Qu, L. L. Bai, Z. D. Yang and L. Q. Jing, *Appl. Catal. B: Environ.*, 2020, **277**.