Supplementary Information (SI) for New Journal of Chemistry.
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Cu-modifiled Th_6-basesd Framework for Regulating Products in Photocatalytic Oxidation of Tetrahydroisoquinoline

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Experimental section

1. Material

All solvents and reagents were commercially available analytical grade solvents and reagents, which did not require further purification during use. Th $(NO_3)_4·4H_2O$ was purchased from McLin. Nitric acid (HNO_3) was purchased from Guangzhou Chemical Reagent Company. N,N-Dimethylformamide (DMF), methanol (CH_3OH), ethanol (C_2H_5OH), dichloromethane (CH_2Cl_2), acetonitrile (CH_3CN), tert-butyl hydroperoxide (TBHP), and $CuCl_2·2H_2O$ were all purchased from Sinopharm Chemical Reagent Co., Ltd. 2,2'-Bipyridyl-5,5'-dicarboxylic acid (H_2BPYDC) and organic substrates such as 1,2,3,4-tetrahydroisoquinoline and its derivatives were purchased from Adamas-beta.

2. Material characterization

The powder X-ray diffraction (PXRD) measurements were conducted on a Bruker D8 Advance diffractometer (λ = 1.54060 Å, 40 kV, 40 mA), equipped with a copper target tube and a graphite monochromator, with a diffraction angle range of 1.5 to 50°. The Fourier transform infrared spectroscopy (FTIR) was recorded on a Thermo Scientific Nicolet iS50 using KBr pellets in the range of 4000-400 cm^{-1}. The X-ray photoelectron spectroscopy

(XPS) was recorded using an Escalab 250Xi instrument (Thermo Scientific) equipped with an Al Kα microfocus X-ray source. The ultraviolet-visible (UV-Vis) absorption spectra were obtained on a Varian Cary 5000 using $BaSO_4$ as a reflectance standard in the wavelength range of 200-800 nm. The electron paramagnetic resonance (EPR) experiments were performed on a Bruker EMX PLUS instrument. The electrochemical tests were conducted using an EC-Lab SP-150 workstation (Bio-Logic) and a CHI660E (CH Instruments). The photocatalytic liquid products were analyzed using a gas chromatography-mass spectrometer (GC-MS) (Agilent 8890 and 5977B, equipped with HP-5-MSUI or HP-PLOT Molesieve capillary columns).

The photoelectrochemical measurements were conducted on a CHI660E electrochemical workstation using a standard three-electrode system. A platinum sheet was used as the counter electrode, and a saturated Ag/AgCl electrode served as the reference electrode. The electrolyte used was sodium sulfate solution at a concentration of 0.5 M. The light source was a Xe lamp with a wavelength (λ) of 300 nm or greater.

Preparation of the working electrode: Firstly, 2 mg of ground crystal powder was mixed with 990 μL of ethanol and 10 μL of Nafion D-520 dispersion solution. The mixture was then subjected to ultrasonic treatment for 30 minutes. Subsequently, 200 μL of the solution was transferred and coated onto ITO glass (1 cm × 2 cm), which was then dried at room temperature.

Mott-Schottky curve testing was conducted on an electrochemical workstation (Bio-Logic, VSP) using a standard three-electrode system, which comprised the working electrode, a platinum sheet as the counter electrode, and a saturated Ag/AgCl electrode as the reference electrode. Mott-Schottky plots were generated at various frequencies of 500 Hz, 1000 Hz, and 1500 Hz in 0.5 M Na_2SO_4 aqueous solution. The preparation of the working electrode was identical to that used for photoelectrochemical measurements.

3. Material synthesis

Care was taken! Th was radioactive and was handled according to standard protective measures for radioactive materials.

Th_6-BPYDC was synthesized by combining 24 mg of $Th(NO_3)_4 \cdot 4H_2O$, 12.21 mg of 2, 2-bipyridine-5, 5-dicarboxylic acid (H_2BPYDC), and 150 μL of nitric acid (HNO_3)

with DMF (3 mL), which was then ultrasound-dissolved. The mixture was sealed in a 10 mL glass vial and heated at 120 °C for 72 h. Upon cooling to room temperature, the Th_6-BPYDC colorless octahedral crystals were gathered by filtration and washed thoroughly several times with DMF.

$CuCl_2$@Th_6-BPYDC was synthesized by employing acetonitrile as the solvent and placing 10 mg of the previously prepared Th_6-BPYDC crystals into a 10 mL glass vial containing 5 mL of saturated $CuCl_2 \cdot 2H_2O$ solution. The mixture was then heated at 80 °C for 7 days, resulting in the crystals turning green.

4. Photocatalytic experiments

Photocatalytic oxidation of 1, 2, 3, 4-tetrahydroisoquinoline (THIQ):

(1) Typically, a photocatalyst (20 mg) was dispersed in 1 mL of CH_3CN containing 0.1 mmol of THIQ, which was then placed into a 25 mL quartz reactor. The mixture was bubbled with oxygen for 10 minutes, and then the photoreactor was sealed. A 300 W xenon lamp (light intensity: 200 $mW \cdot cm^{-2}$) was used as the reaction light source. The reaction temperature was controlled at 298K by circulating cooling water. After the reaction, the solution was collected, centrifuged, and filtered through a 0.22 μM filter to remove the catalyst particles. The filtrate was identified by GC-MS and analyzed for conversion rate as well as selectivity. Other derivatives with the same concentration were prepared using a similar method and analyzed for corresponding conversion rate and selectivity by GC-MS.

(2) Typically, a photocatalyst (20 mg) was dispersed in 1 mL of CH_3CN containing 0.1 mmol of THIQ, which was then placed into a 10 mL quartz reactor. Afterward, 50 μL of tert-butyl hydroperoxide (TBHP) was added to the mixture. The solution was bubbled with argon for 10 minutes, and then the photoreactor was sealed. A 300 W xenon lamp (light intensity: 200 $mW \cdot cm^{-2}$) was used as the reaction light source. The reaction temperature was maintained at 298K by circulating cooling water. After the reaction, the solution was collected, centrifuged, and filtered through a 0.22 μM filter to remove the catalyst particles. The filtrate was identified by GC-MS and analyzed for conversion rate as well as selectivity. Other derivatives with the same concentration were prepared using a similar method and analyzed for corresponding conversion rate and selectivity by GC-MS.

The conversion rates of 1, 2, 3, 4-tetrahydroisoquinoline (THIQ), dihydroisoquinoline (DHIQ), and isoquinoline (IQ), along with the selectivity of the products, were calculated using the following equations (1), (2), and (3):

$$Conversion\ (\%) = \frac{C_{0} - C_{THIQ}}{C_{0}} \times 100\%$$ （1）

$$Selectivity\ of\ DHIQ\ (\%) = \frac{C_{DHIQ}}{C_{total\ products}} \times 100\%$$ （2）

$$Selectivity\ of\ IQ\ (\%) = \frac{C_{IQ}}{C_{total\ products}} \times 100\%$$ （3）

Where C_0 represented the initial concentration of THIQ. C_{THIQ}, C_{DHIQ}, and C_{IQ} denoted the concentrations of THIQ remaining and the corresponding DHIQ and IQ products after a certain period of catalytic reaction, respectively. $C_{total\ products}$ were the sum of the concentrations of all products.

Support Figures.

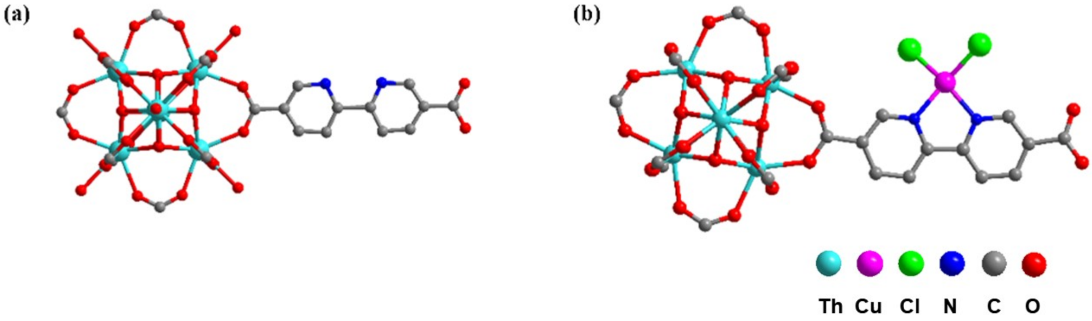


Fig. S1 (a) Asymmetric unit of the Th$_6$-BPYDC. (b) Asymmetric unit of the Cu@Th$_6$-BPYDC.

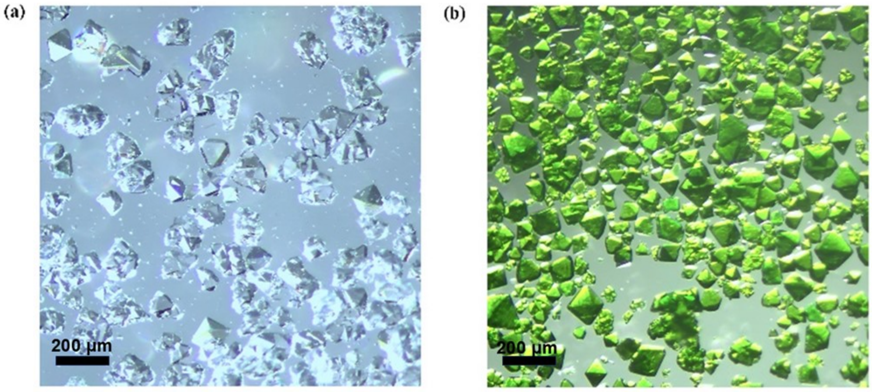


Fig. S2 (a) Microscopic crystal photograph of Th$_6$-BPYDC. (b) Microscopic crystal photograph of Cu @Th$_6$-BPYDC.

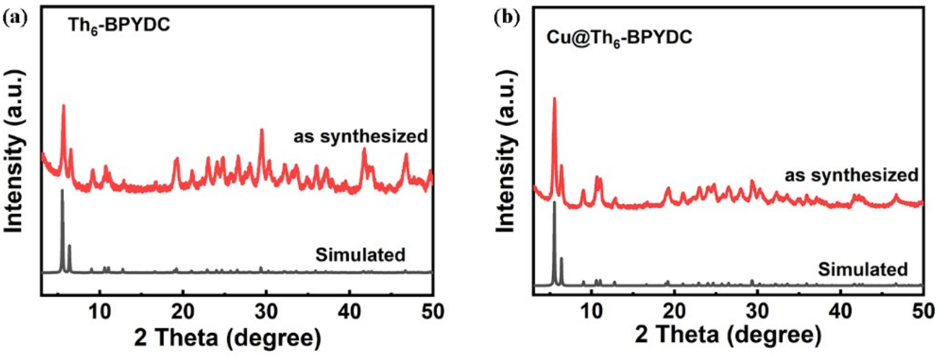


Fig. S3 (a) The PXRD spectra of Th$_6$-BPYDC. (b) The PXRD spectra of the Cu@Th$_6$-BPYDC."Simulated" represents the simulated sample, and "as synthesized" represents the synthetic sample.

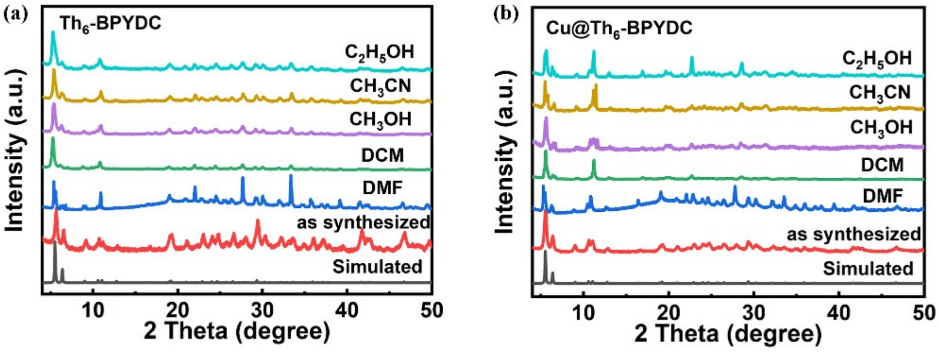


Fig. S4 (a) The PXRD spectra of Th$_6$-BPYDC soaked in different organic solvents for more than 24 h. (b) The PXRD spectra of Cu@Th$_6$-BPYDC soaked in different organic solvents for more than 24 h.

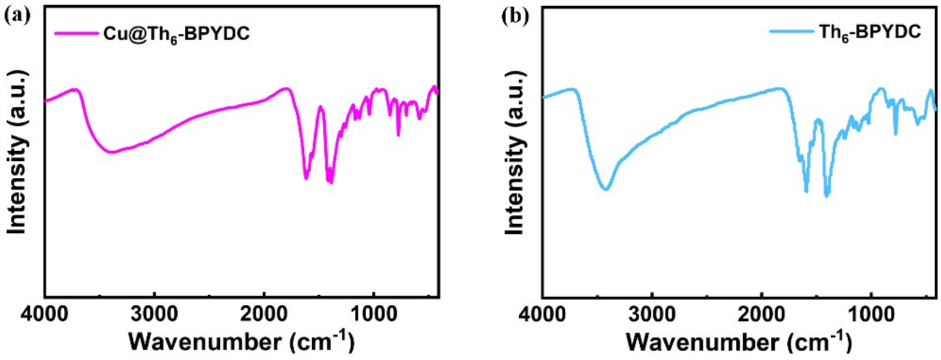


Fig. S5 (a) The FTIR spectra of Cu@Th$_6$-BPYDC. (b) The FTIR spectra of Th$_6$-BPYDC.

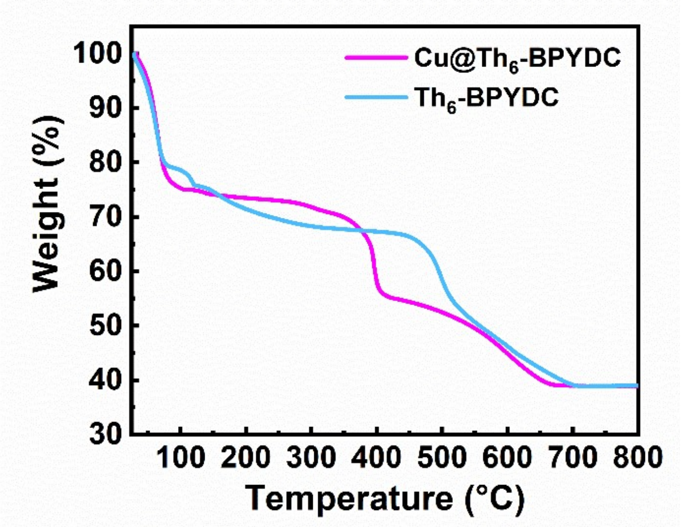


Fig. S6 TG curves of Th$_6$-BPYDC and Cu@Th$_6$-BPYDC.

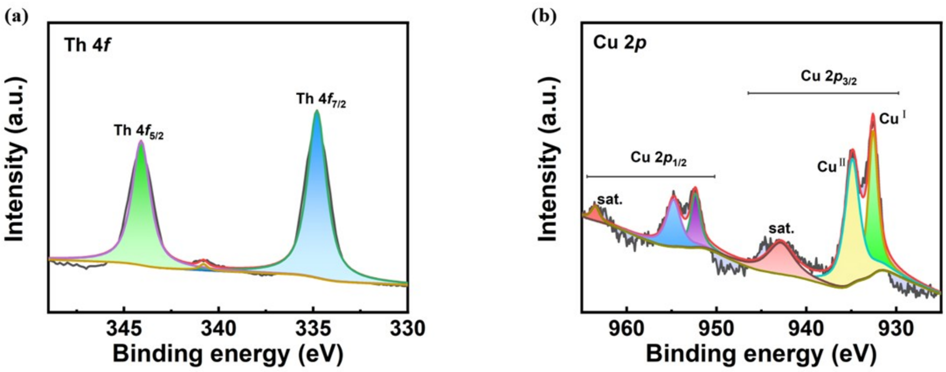


Fig. S7 The XPS spectra of Cu@Th_6-BPYDC.

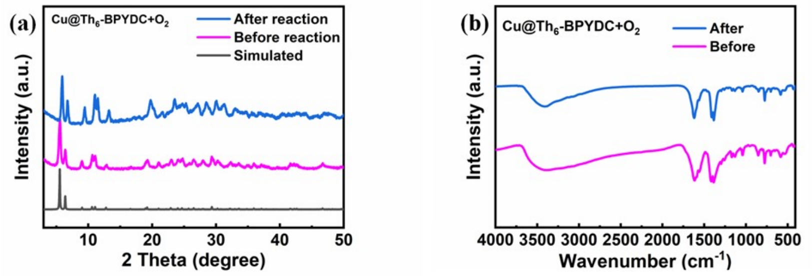


Fig. S8 (a) PXRD spectra of Cu@Th_6-BPYDC before and after the reaction. (b) The FTIR spectra of Cu@Th_6-BPYDC before and after the reaction.

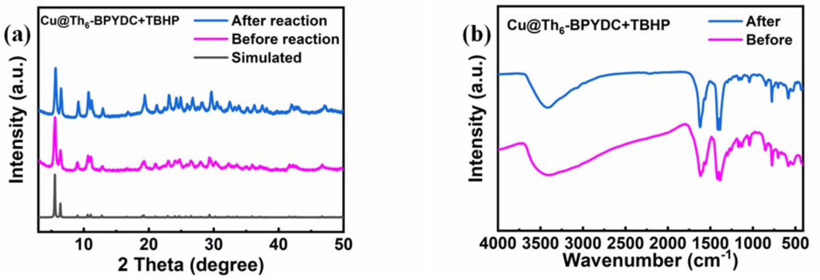


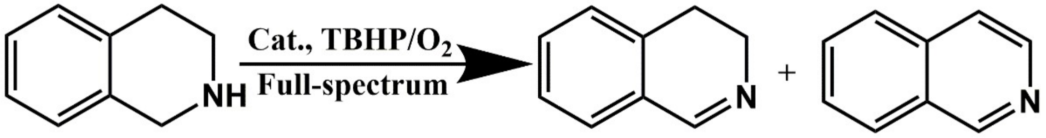
Fig. S9 (a) PXRD spectra of Cu@Th_6-BPYDC before and after the reaction. (b) The FTIR spectra of Cu@Th_6-BPYDC before and after the reaction.

Support Tables.

Table S1 ICP-OES data for Cu@Th_6-BPYDC.

Cat.	Weight Percent（wt%）
Cu@Th_6-BPYDC	7.2

Table S2 Some control experiments to demonstrate the importance of the catalyst when using O_2 as the oxidant.[a]



Entry	Deviation from standard conditions	Conversion[b] (%)	Selectivity[b] of DHIQ (%)	Selectivity[b] of IQ (%)
1	Cu@Th_6-BPYDC	94.6	81.0	19.0
2[c]	$CuCl_2$	66.2	74.3	25.7
3[d]	No cat.	65.9	84.4	15.6
4[e]	Th_6	64.4	81.0	19.0
5[f]	Ar instead of O_2	27.6	84.2	15.8
6[g]	No light	0	-	-
7[h]	BQ	98.9	89.5	10.5
8[i]	DABCO	27.0	92.7	7.3

[a] Reaction conditions: 0.1 mmol THIQ, 20 mg catalyst, 1 mL CH_3CN, in an O_2 atmosphere, at room temperature (rt), with xenon lamp full-spectrum illumination for 12h (standard conditions). [b] Qualitative and quantitative analysis was carried out using gas chromatography-mass spectrometry. [c] $CuCl_2$ was used as the catalyst. [d] Without a catalyst. [e] Th_6 was used as the catalyst. [f] The reaction was conducted in an argon atmosphere. [g] The reaction was carried out in a light-proof condition. [h] BQ was added as an $O_2{}^{\cdot -}$ scavenger. [i] DABCO was added as a $^1O_2$ scavenger.

Table S3 Oxidant screening form for the photocatalytic oxidation reaction of THIQ.[a]

Entry	Deviation from standard conditions	Conversion[b] （%）	Selectivity[b] of DHIQ （%）	Selectivity[b] of IQ （%）
1	O_2	94.6	81.0	19.0
2[c]	TBHP	99.4	0.3	99.7
3[d]	H_2O_2	65.0	81.9	18.1

[a] Reaction conditions: 0.1 mmol THIQ, 20 mg catalyst, 1 mL CH_3CN, in an O_2 atmosphere, at room temperature (rt), with full-spectrum xenon lamp illumination for 12 hours. [b] Qualitative and quantitative analyses were carried out using gas chromatography-mass spectrometry. [c] TBHP was used as the oxidant. [d] H_2O_2 was used as the oxidant.

Table S4 Some control experiments demonstrating the importance of the catalyst when using TBHP as the oxidant.[a]

Entry	Deviation from standard conditions	Conversion[b] （%）	Selectivity[b] of DHIQ （%）	Selectivity[b] of IQ （%）
1	Cu@Th_6-BPYDC	99.4	0.3	99.7
2[c]	$CuCl_2$	92.5	69.5	30.5
3[d]	No cat.	75.7	82.3	17.7
4[e]	Th_6	76.1	83.5	16.5
5[f]	Ar instead of TBHP	32.3	85.3	14.7
6[g]	No light	99.2	75.1	24.9
7[h]	BHT	>99	63.7	36.3

[a] Reaction conditions: 0.1 mmol THIQ, 20 mg catalyst (Cu@Th_6-BPYDC), 1 mL CH_3CN, 50 μL TBHP, in an Ar atmosphere, at rt, with xenon lamp full-spectrum illumination for 12 h (standard conditions). [b] Qualitative and quantitative analysis was carried out using gas chromatography-mass spectrometry. [c] $CuCl_2$ was used as the catalyst. [d] Without a catalyst. [e] Th_6 was used as the catalyst. [f] The reaction was carried out in an argon atmosphere. [g] The reaction was carried out in a light-proof condition. [h] BHT was added as a tert-butyl radical scavenger.