Hydrogen-bonded organic framework with the extended conjugate system for boosted photocatalytic degradation

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Section S1. Chemicals and materials

All chemical reagents applied in this paper are of analytical purity.

1,2,4-Benzenetricarboxylic anhydride ($C_9H_4O_5$, 99.8%, Aladdin), urea (H_2NCONH_2, 99%, Sinopharm), ammonium molybdate tetrahydrate (($NH_4)_6Mo_7O_{24}\cdot4H_2O$, AR, Sinopharm), cobalt(II) chloride hexahydrate ($CoCl_2\cdot6H_2O$, AR, Sinopharm), hydrochloric acid (HCl, AR, Sinopharm), sodium hydroxide (NaOH, AR, Sinopharm), methanol (CH_3OH, HPLC eluent, 99.8%, Macklin), formate (CH_2O_2, 98%, Macklin), ethanol (CH_3CH_2OH, 95%, Aladdin), tert-Butanol ($C_4H_{10}O$, AR, Sinopharm),p-benzoquinone($C_6H_4O_2$, AR, Macklin), ethylenediamine tetraacetic acid disodium salt($C_{10}H_{14}N_2O_8Na_2\cdot2H_2O$, AR, Sinopharm), sulfamethoxazole ($C_{10}H_{11}N_3O_3S$, 98%, Aladdin). Sodium hydroxide(NaOH, 97%, Aladdin), Hydrochloric acid(HCl, 37%, Aladdin).

Section S2. Photocatalytic performance test

The detection wavelength was 270 nm, and the removal rate of SMX was calculated as follows:

$$\alpha = ((C_0 / C_t) / C_0) * 100\% \qquad (1)$$

where α represents the degradation rate of SMX; C_0 is the concentration of sulfamethoxazole when the adsorption-desorption equilibrium was reached in the dark; C_t is the concentration of sulfamethoxazole at the time t of light. LC-MS was recorded on Ultimate 3000 UHPLC - Q Exactive liquid-mass spectrometer (Thermo Scientific，US), consisting of a Dinonex Ultimate 3000 UHPLC chromatography. Separation was accomplished using an Eclipse Plus C18 column (4.6 × 100 mm). Elution was performed at a flow rate of 0.3 mL min^{-1} with 0.1 vol% formic acid aqueous solution as eluent A and ethyl hydrazine as eluent B. The separation of the analytes was achieved by a mixture solution with 80.0 vol% eluent A and 20.0 vol% eluent B, injected volume of 10.0 μl. Mass spectra analysis was operated in positive mode using a HESI source, and the mass analyzer was operated in full scan mode (m/z range 200–600).

Section S3. Electrochemical experiment details

The photocurrent measurement, Mott-Schottky (MS) plots, and Electrochemical impedance spectroscopy (EIS) were conducted on a CHI 660B electrochemical system (Shanghai, China) using a standard three-electrode cell with a working electrode, a platinum wire counter electrode,

and a standard calomel electrode (SCE) reference electrode. The electrolyte solution used was Na_2SO_4 (1 M). The working electrode was prepared according to the following process. Five milligrams of the as-prepared sample were dispersed in 1 mL of H_2O, and the resulting mixture was sonicated for 30 min before drop-casting onto a 10 mm × 20 mm indium tin oxide (ITO) glass electrode. Subsequently, the electrode was annealed at 200 °C for 300 min. Visible light irradiation was provided by MVL-210 with a UV cutoff filter. Electrochemical impedance spectroscopy (EIS) was applied to the electrode over the frequency range of 0.05 to 1×10^5 Hz with a sinusoidal ac perturbation of 5 mV.

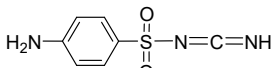**Section S4. Calculation of the apparent rate constants**
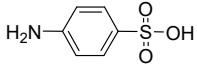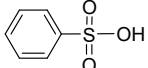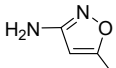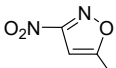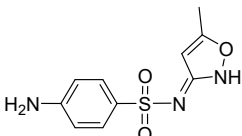
$$\ln(C_t / C_0) = -K_{obs}\, t \qquad\qquad (2)$$

Where C_0 and C_t represent the SMX concentration at the initial (t=0) and time t.

Table S1. Apparent reaction rate constants of CoPcTc and its HOF material to SMX in water under visible light irradiation
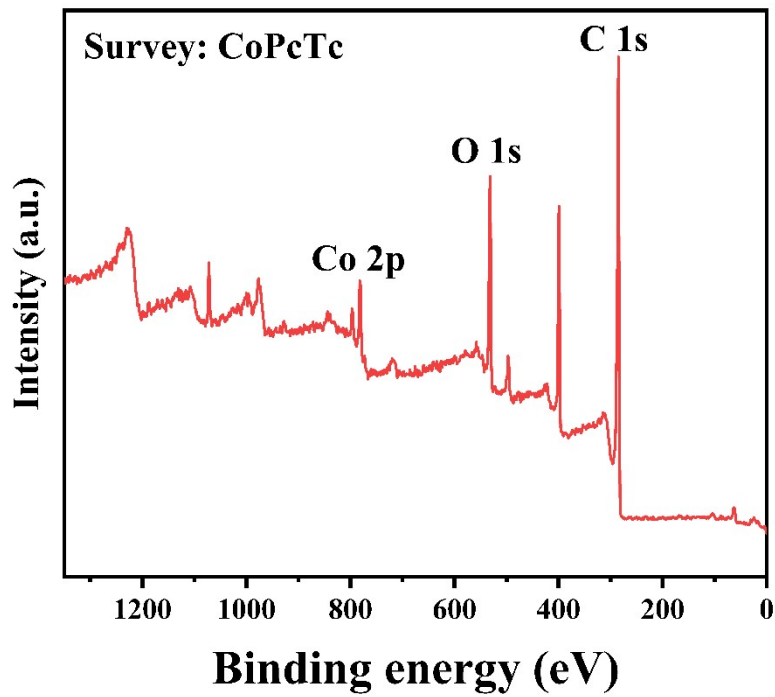
Catalysts	K_{obs} (min^{-1})	$1 / K_{obs}$ (min)	R^2
CoPcTc	0.00886	112.86	0.99693
HOF-CoPcTc	0.0198	50.5	0.9999

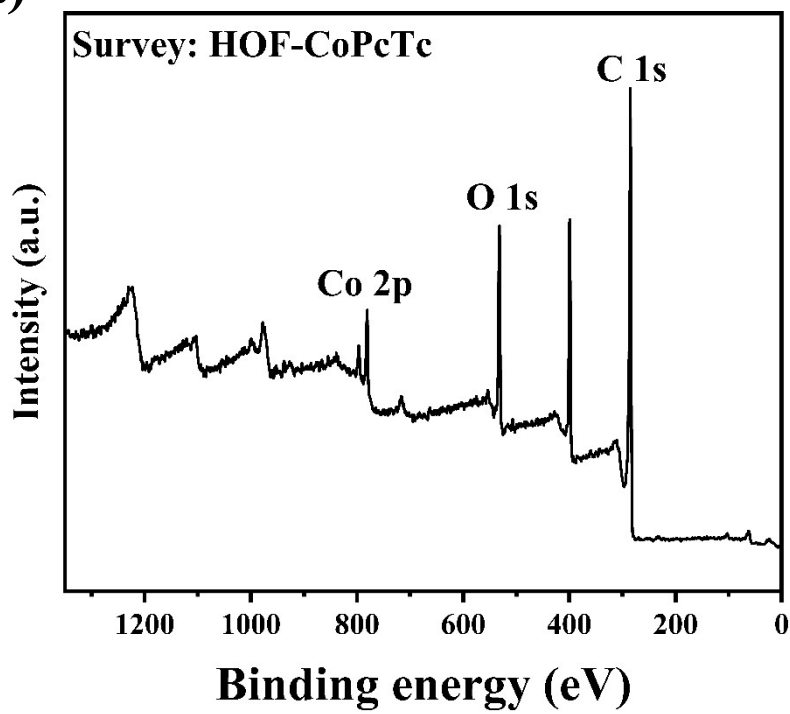**Table S2. Chemical formulas and relative molecular mass of intermediate products.**

ID	Chemical Formula	m/z	Proposed structure
SMX			
I	$C_6H_7NO_3S$	172	
II	$C_6H_6O_3S$	159	
III	$C_4H_6N_2O$	99	
IV	$C_4H_4N_2O_3$	128	
V	$C_{10}H_{11}N_3O_3S$	254	
VI	$C_7H_7N_3O_2$	199	
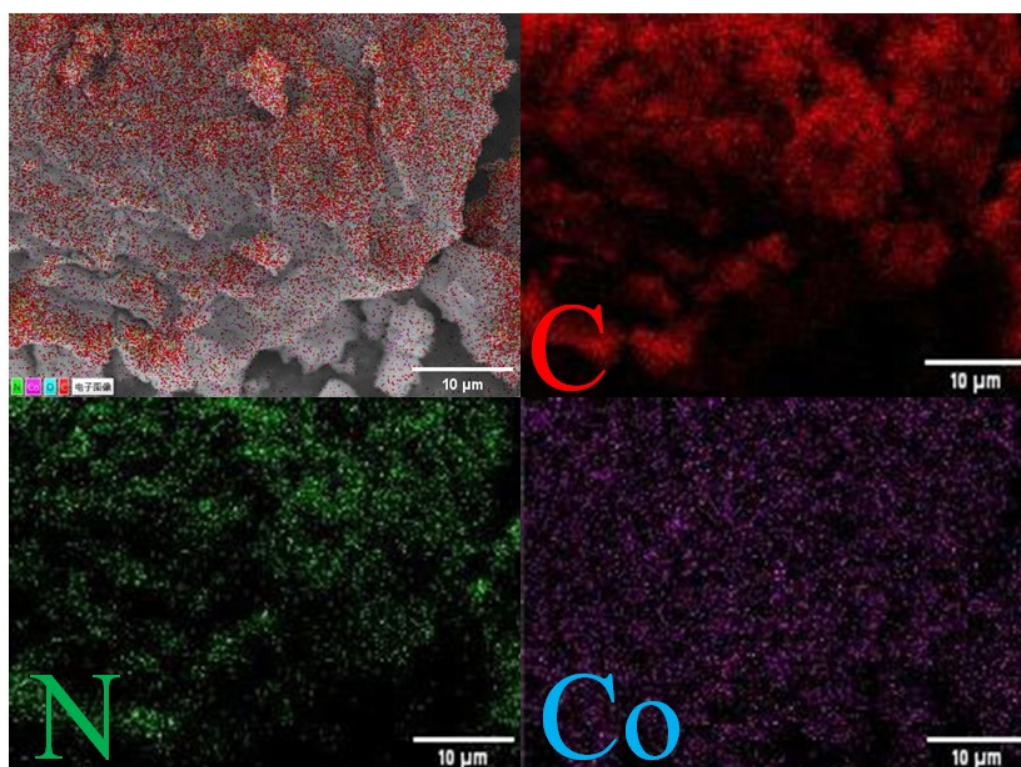
Figure S1. SEM-EDS analysis of CoPcTc.
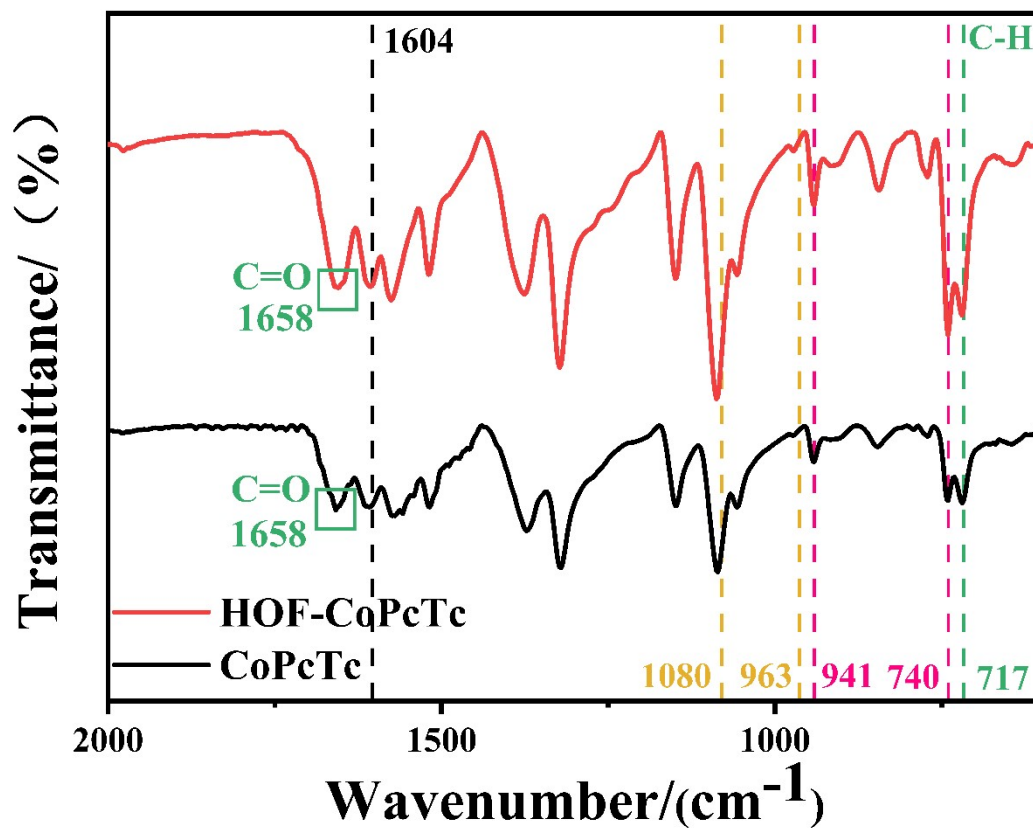
(a)

(b)

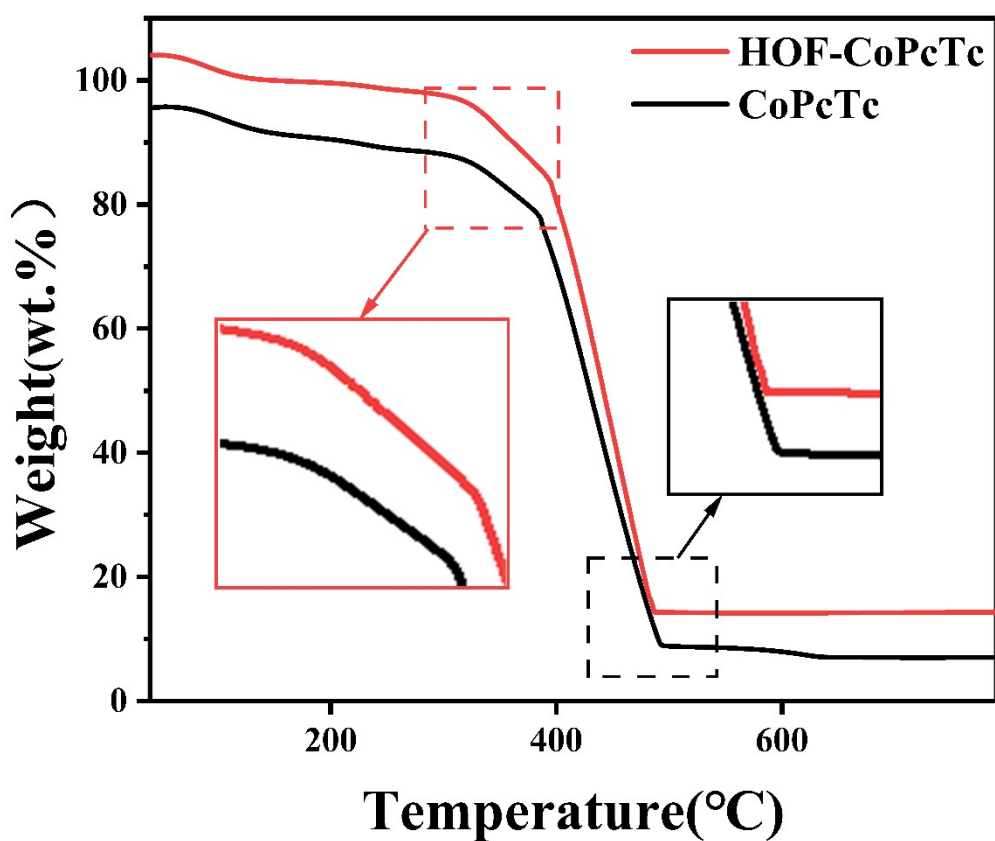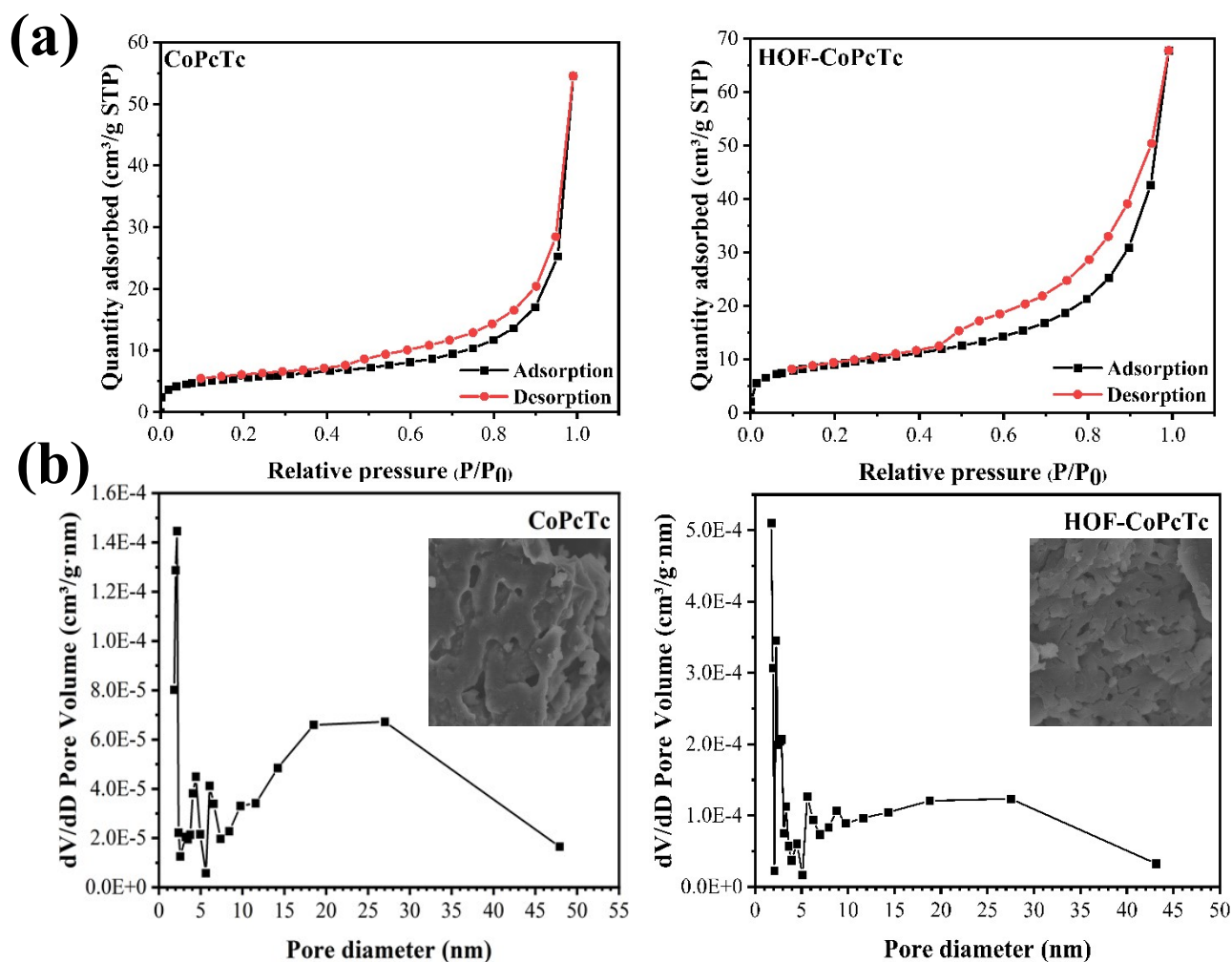**Figure S2.** XPS survey spectra of CoPcTc(a) and HOF-CoPcTc (b).
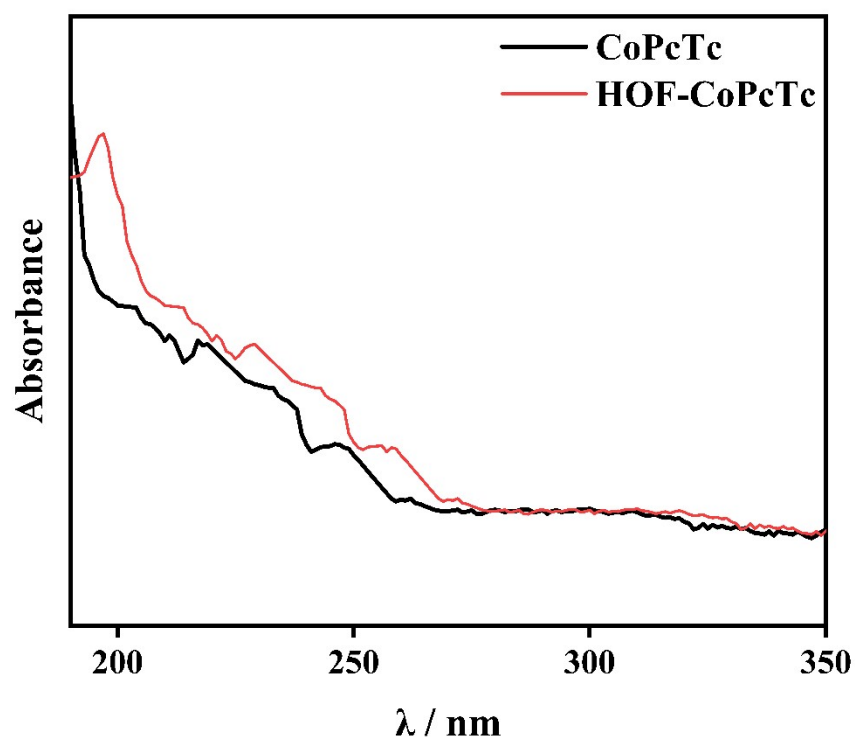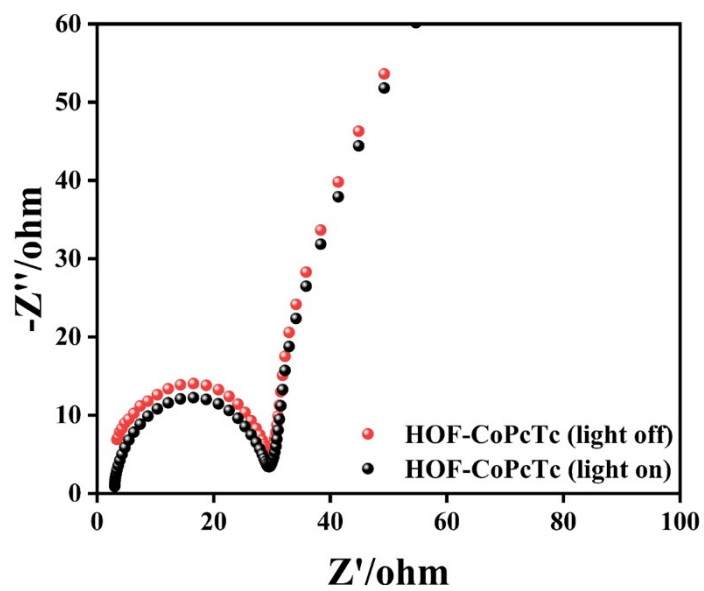
Figure S3. Enlarged view of FT-IR spectra.

Figure S4. Enlarged view of TGA curves.

Figure S5. (a)N$_2$ sorption isotherms and (b) pore size distributions of the CoPcTc and HOF-CoPcTc.
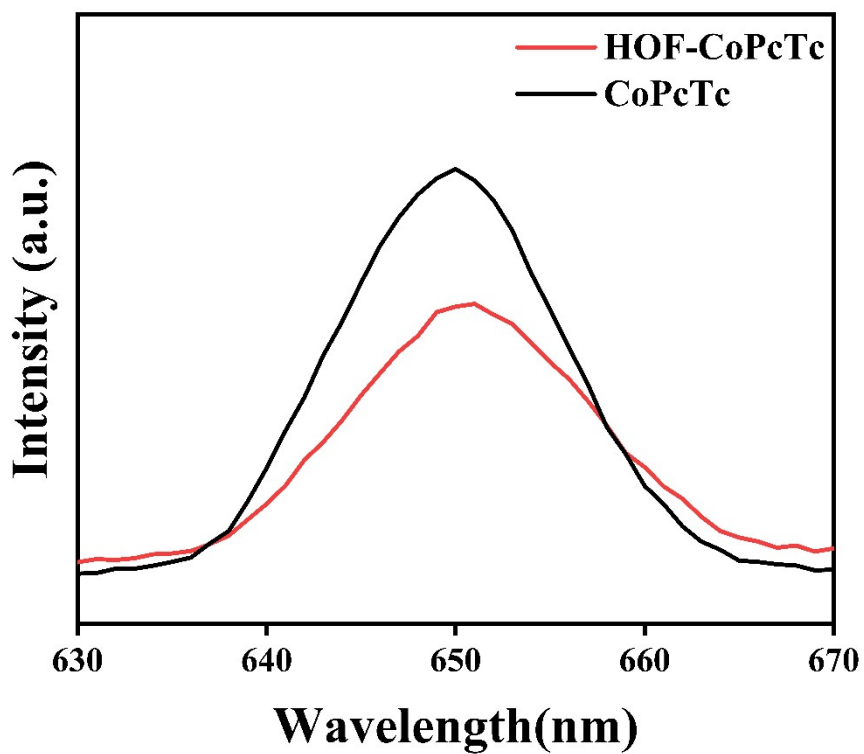
Figure S6. UV-vis absorption spectra for CoPcTc and HOF-CoPcTc in the CIP solution.
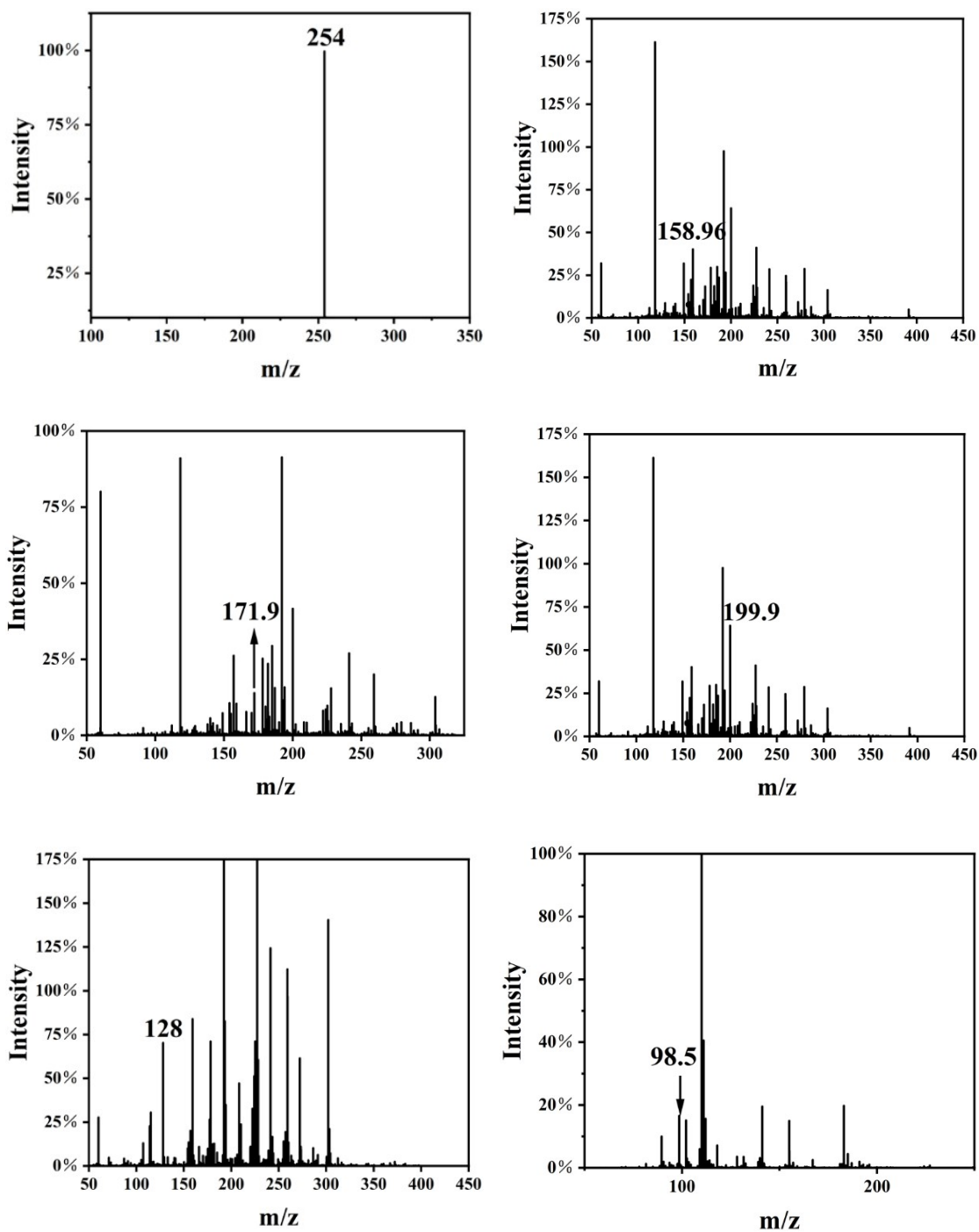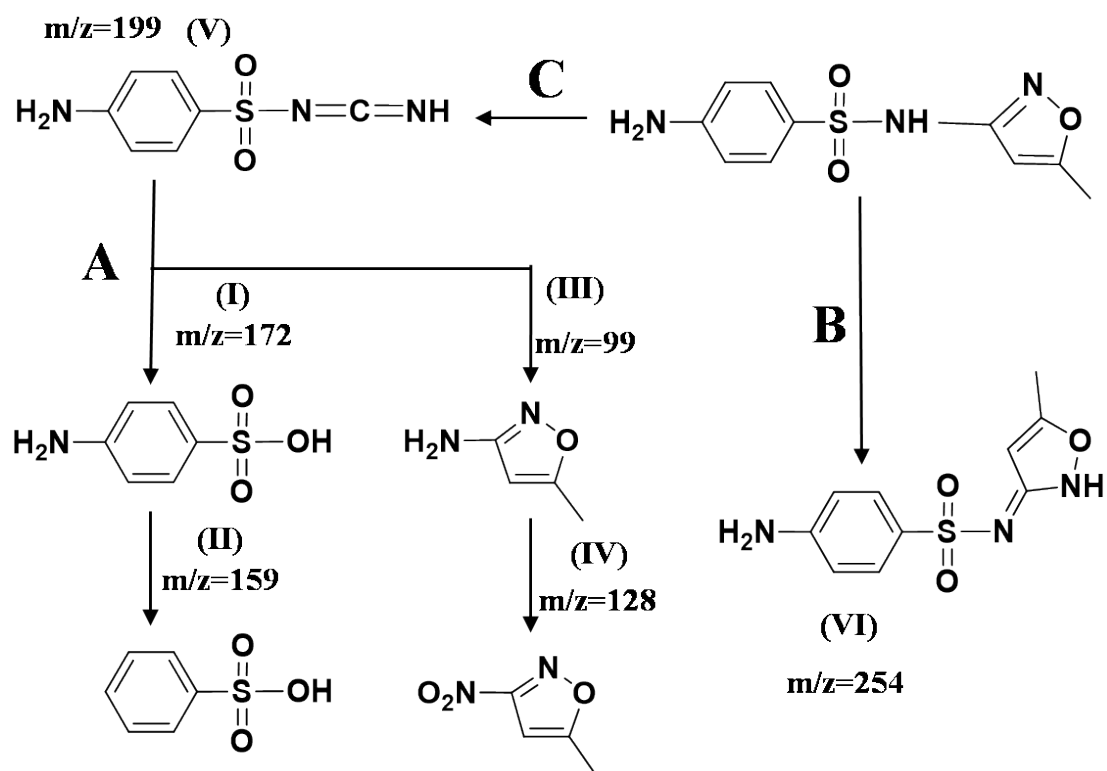
Figure S7. EIS Nyquist plots of HOF-CoPcTc with the light on and light off under irradiation in the light ($\lambda > 380$ nm, $[Na_2SO_4] = 0.1$ M)

Figure S8. PL spectra of CoPcTc, HOF-CoPcTc.

Figure S9. MS spectra of SMX degradation intermediates of HOF-CoPcTc.

Figure S10. Proposed transformation pathways for SMX photocatalytic degradation.