Supporting information

Band Structure Regulation and Photocatalytic Degradation of Tetracycline by Covalent Organic Frameworks†

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1. Chemicals

1,3,5-Tris(4-aminophenyl) benzene (TAPB) , 2,5-divinylterephthalaldehyde (DVA), 2,5-dihydroxyterephthaldeyde (DHTP), 2,5-dimethoxyterephthalaldehyde (DMTP), were purchased from Jilin Chinese Academy of Sciences-Yanshen Technology Co. Ltd. Acetonitrile (C_2H_3N, 99.9%, Shanghai Macklin Biochemical Co. Ltd), Folic Acid ($C_{19}H_{19}N_7O_6$, 97%, Shanghai Macklin Biochemical Co. Ltd), Acetic acid ($C_2H_4O_2$, 99.8%, Shanghai Macklin Biochemical Co. Ltd), Polyvinylpyrrolidone (PVP-K90, Sigma-Aldrich), Ethanol (99.8%, Shanghai Macklin Biochemical Co. Ltd), Tetracycline (TC, Shanghai Macklin Biochemical Co. Ltd), Isopropanol (IPA, HPLC, Shanghai Macklin Biochemical Co. Ltd), Methanol (MeOH, HPLC, Shanghai Macklin Biochemical Co. Ltd), N,N-Dimethylformamide (DMF, 99.8%, Shanghai Macklin Biochemical Co. Ltd) Ascorbic acid (VC, Shanghai Macklin Biochemical Co. Ltd) and Glutathione (GSH, Shanghai Macklin Biochemical Co. Ltd).

2. Characterization

The crystal structures of COFs-R were analyzed by powder X-ray diffraction (PXRD) using a Rigaku MiniFlex 600-C diffractometer equipped with a graphite-monochromatized Cu Kα radiation source (λ = 0.15405 nm). Scans were recorded at room temperature over a 2θ range of 2-15° with a scanning rate of 5° min^{-1}. Chemical bonding information was obtained *via* Fourier-transform infrared spectroscopy (FT-IR, Nicolet iS50, Thermo Fisher Scientific, USA) using the KBr pellet method. The UV-visible absorption properties were measured on a UV-2600 spectrophotometer (Shimadzu, Japan) to investigate the optical response of the materials. Furthermore, to explore the active species generated during the reaction, electron paramagnetic resonance (EPR) spectroscopy was employed to analyze the reaction intermediates.

3. Photocatalytic degradation of tetracycline

In this study, three covalent organic frameworks, namely TAPB-DVA-COF, TAPB-DMTP-COF, and TAPB-DHTP-COF, were employed as photocatalysts to systematically evaluate their photocatalytic performance toward the degradation of tetracycline. A 300 W xenon lamp equipped with a 420 nm cut-off filter (light intensity: 427.7 mW cm^{-2}) was used as the irradiation source. In the photocatalytic reaction system, a fixed amount of catalyst was dispersed in a tetracycline solution of predetermined concentration. Prior to illumination, the suspension was subjected to a dark reaction to achieve adsorption–desorption equilibrium, followed by visible-light irradiation for 30 min. The variation in tetracycline concentration during the reaction was monitored by UV-vis spectroscopy, and the corresponding degradation kinetics were plotted to quantitatively assess the photocatalytic activity of each catalyst.[1]

4. Electron Paramagnetic Resonance (EPR) Measurements

2,2,6,6-Tetramethylpiperidine (TEMP) was employed as a spin-trapping agent to detect singlet oxygen ($^1O_2$) generated in the presence of TC and COFs under xenon lamp irradiation. Specifically, a mixture containing 70 μL of deionized water, 100 μL of a TC (8 mg L^{-1}) and COF (3 mg) mixed dispersion, and 10 μL of TEMP solution (0.8 M) was prepared and transferred into a plastic tube, followed by irradiation under a xenon lamp for 5 min. The resulting solution was then loaded into a quartz capillary tube and analyzed using an electron paramagnetic resonance (EPR) spectrometer.

5,5-Dimethyl-1-pyrroline N-oxide (DMPO) was used as the spin-trapping agent to detect hydroxyl radicals (·OH) in the presence of TC and COFs. A mixture containing 70 μL of deionized water, 100 μL of a TC (8 mg L^{-1}) and COF (3 mg) mixed dispersion, and 10 μL of DMPO solution (0.8 M) was prepared, transferred into a plastic tube, and irradiated under a xenon lamp for 5 min. The mixture was subsequently loaded into a quartz capillary tube for EPR analysis.

A 300 W xenon lamp equipped with a 420 nm cutoff filter was used as the light source, with a light intensity of 427.7 mW cm^{-2}.

5. Identification of Reactive Species

The reactive species involved in the photocatalytic system were identified through quenching experiments. Specifically, 3 mg of COF powder was dispersed in 100 mL of an aqueous tetracycline (TC, 8 mg L^{-1}) solution, followed by the addition of Isopropanol (IPA, 100 mmol L^{-1}), Methanol (MeOH, 100 mmol L^{-1}), N,N-Dimethylformamide (DMF, 100 mmol L^{-1}), Ascorbic acid (VC, 100 mmol L^{-1}) and Glutathione (GSH, 100 mmol L^{-1}) as quenchers.[2,3] Prior to illumination, the mixed suspension was magnetically stirred for 30 min to establish adsorption equilibrium. Photocatalytic reactions were carried out under irradiation with a 300 W xenon lamp equipped with a cut-off filter ($\lambda \geq 420$ nm). During the reaction, 3 mL of the suspension was withdrawn at designated time intervals, filtered through a 0.45 μm cellulose acetate membrane, and subsequently analyzed for photocatalytic degradation.

6. Electrochemical properties characterizations.

All the electrochemical properties were detected on a CHI760E electrochemical analyzer in a three-electrode system, which uses platinum foil and an Ag/AgCl electrode as the counter electrode and reference electrode, respectively. The electrolyte was 0.1 mol L^{-1} Na_2SO_4 aqueous solution and the working electrode was prepared as follows: i) 2 mg catalysts were dispersed in 2 mL ethanol followed by addition of 30 μL Nafion/ethanol solution, then sonicated for 30 min, ii) 50 μL as-prepared mixture was dropped onto the surface of conductive glass substrate and then dried at room temperature. The frequency of electronic impendence spectroscopy (EIS) ranged from 0.1 Hz to 100 kHz.

7. Stability and Recycling Tests.

The recyclability of TAPB-DVA-COF was evaluated by monitoring its degradation efficiency over Five consecutive cycles.[4,5] After each cycle, the photocatalyst was

recovered by washing twice with ethanol and water, followed by drying for reuse (approximately 91 % of the catalyst could be recovered). In the first cycle, four parallel experiments were conducted (total amount: 12.0 mg), with Groups 1 and 2 serving as duplicates (recovered: 5.43 mg), while Groups 3 and 4 were tested without sampling (recovered: 5.39 mg). In the second cycle, another four experiments were carried out under the same conditions (total amount: 12.0 mg), where Groups 1 and 2 were duplicates (recovered: 5.33 mg), and Groups 3 and 4 were tested without sampling (recovered: 5.39 mg). The third, fourth, and fifth cycles were all performed using the same procedure.

Sample	TC Initial Concentration ($mg \cdot L^{-1}$)	Photocatalyst Concentration	Time (min)	Removal Rate (%)	k (min^{-1})	Ref.
PCN	**10.0**	**0.5 $g \cdot L^{-1}$**	**60**	**62.70**	**-**	**[6]**
PCN/CN	**10.0**	**0.5 $g \cdot L^{-1}$**	**60**	**89.70**	**-**	**[6]**
CoPCPA-COF	**20.0**	**0.6 $g \cdot L^{-1}$**	**60**	**95.15**	**4.5×10^{-2}**	**[7]**
Py-NH_2-COF	**20.0**	**0.2 $g \cdot L^{-1}$**	**90**	**3.10**	**5.0×10^{-4}**	**[2]**
COF-2	**20.0**	**5.0 mg**	**360**	**50.80**	**1.84×10^{-3}**	**[8]**
CTF	**10.0**	**5.0 mg**	**50**	**40.0**	**4.01×10^{-3}**	**[9]**
TAPB-DMTP-COF	**10.0**	**0.03 $g \cdot L^{-1}$**	**30**	**63.4**	**3.43×10^{-2}**	**This work**
TAPB-DHTP-COF	**10.0**	**0.03 $g \cdot L^{-1}$**	**30**	**16.7**	**5.09×10^{-3}**	**This work**
TAPB-DVA-COF	**10.0**	**0.03 $g \cdot L^{-1}$**	**30**	**83.2**	**6.5×10^{-2}**	**This work**

Table S1. Comparation of photocatalysts for TC degradation.

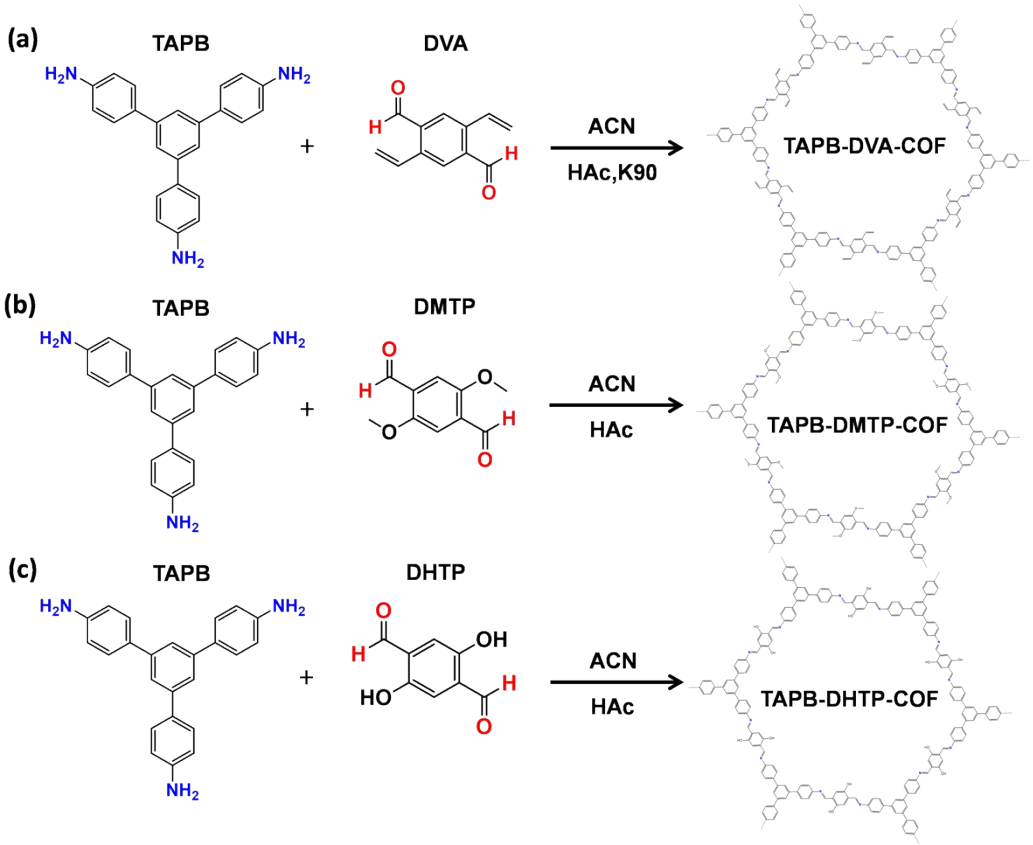


Fig. S1 Schematic illustration of the synthesis and molecular structures of the TAPB-COF series: (a) TAPB-DVA-COF, (b) TAPB-DMTP-COF, and (c) TAPB-DHTP-COF.

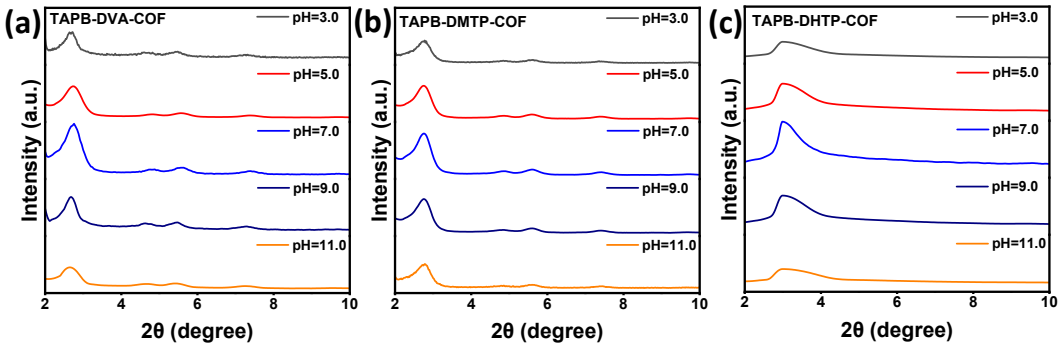


Fig. S2 PXRD of the COFs after treatment in aqueous solutions with pH= 3.0, 5.0, 7.0, 9.0, and 11.0.

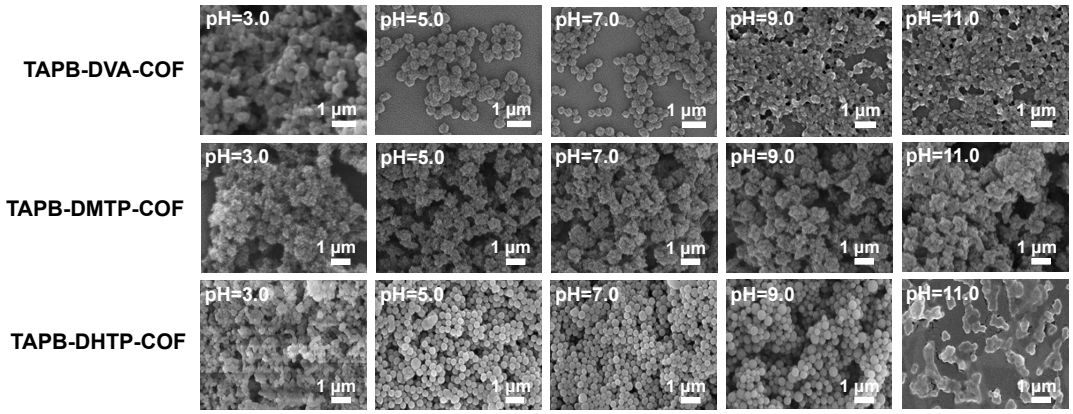


Fig. S3 SEM images of the COFs after treatment in aqueous solutions with pH= 3.0, 5.0, 7.0, 9.0, and 11.0.

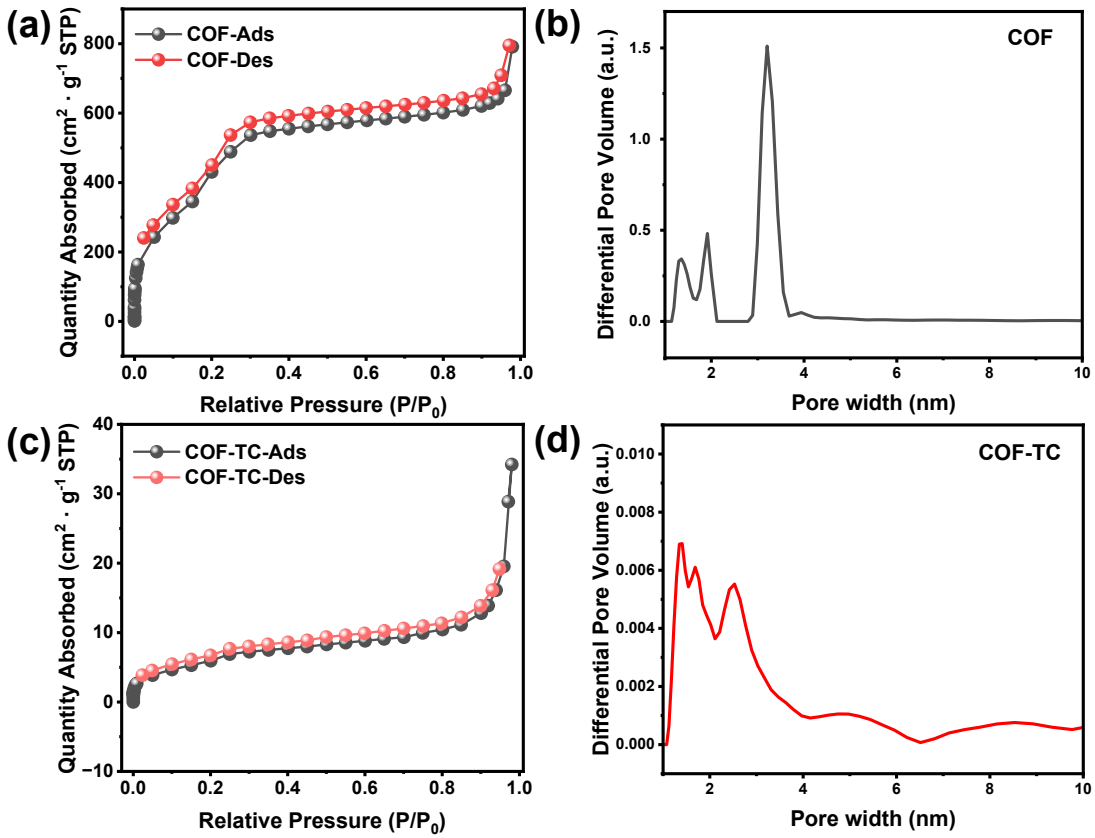


Fig. S4. N_2 adsorption-desorption isotherms and pore size distribution of TAPB-DVA-COF before and after TC treatment

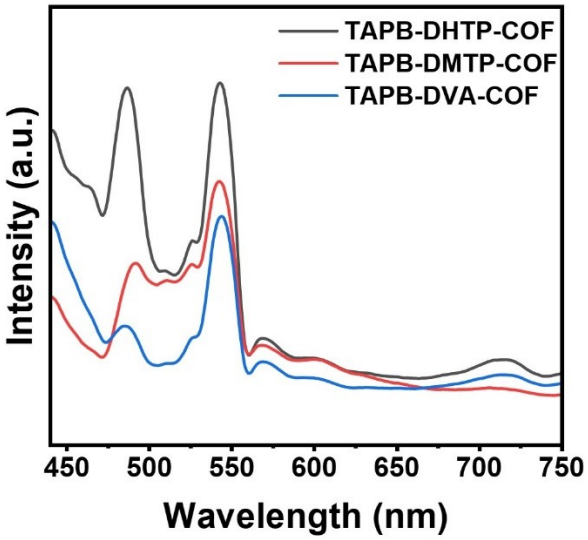


Fig. S5 Steady-state fluorescence emission under excitation at 542 nm. The TAPB-DVA-COF, TAPB-DMTP-COF and TAPB-DHTP-COF are represented by blue, red and black colours, respectively.

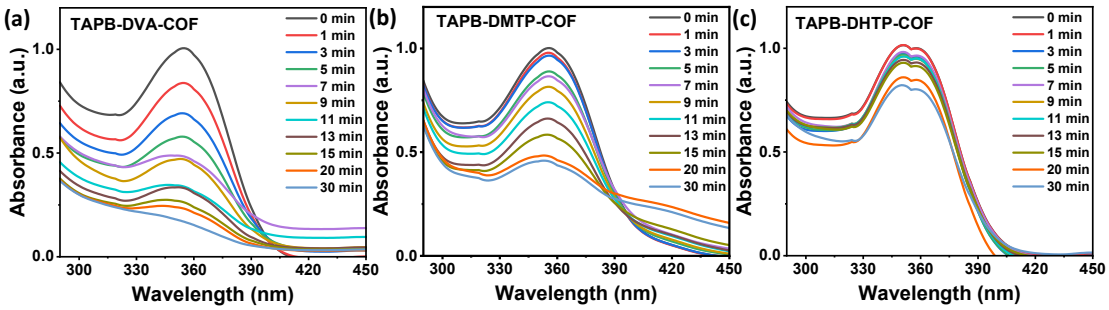


Fig. S6 UV-vis Degradation of TC Using Different COFs.

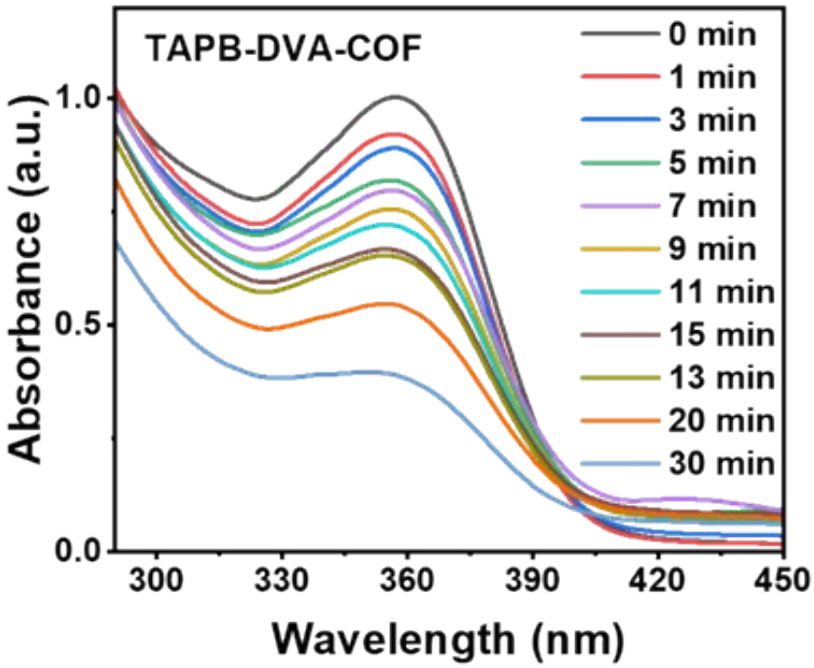
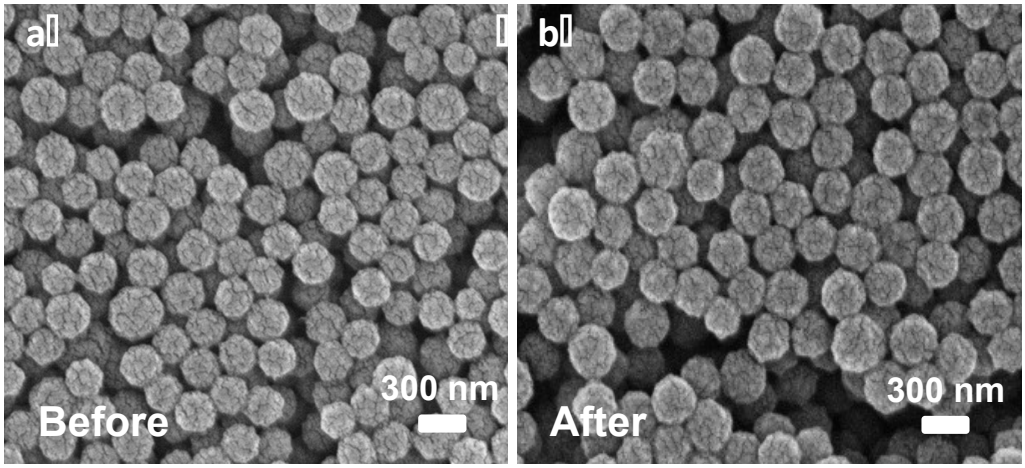


Fig. S7 The UV-vis spectrum of TC degradation by TAPB-DVA-COF during the cyclic process.

Fig. S8



SEM images of TAPB-DVA-COF before and after the catalytic test.

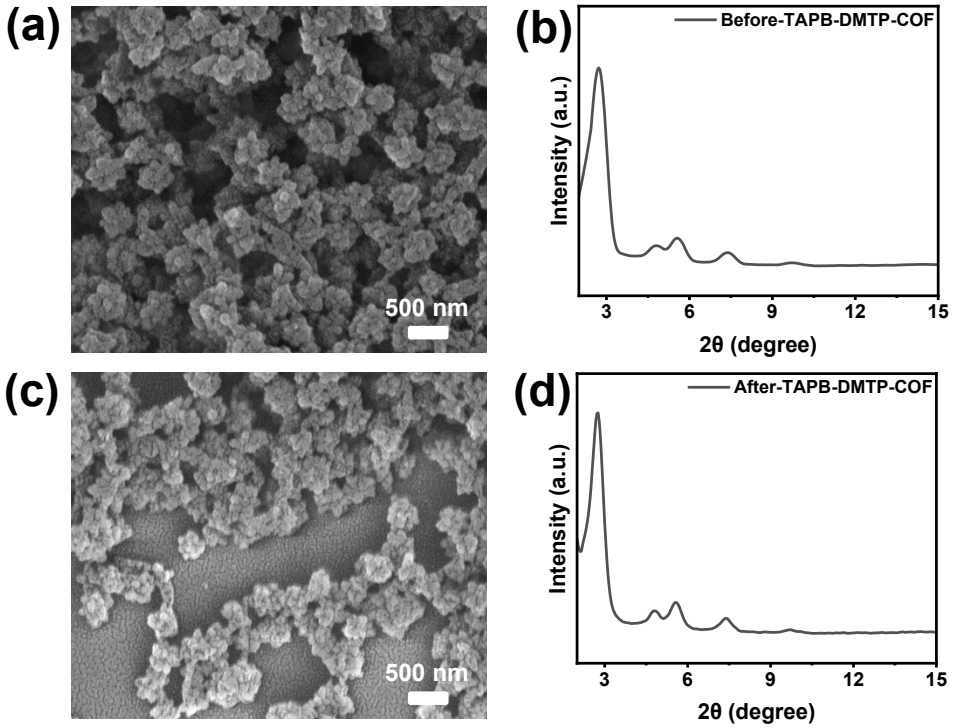


Fig. S9 (a), (c) SEM images of TAPB-DMTP-COF before and after the catalytic test. (b), (d) PXRD patterns before and after degradation.

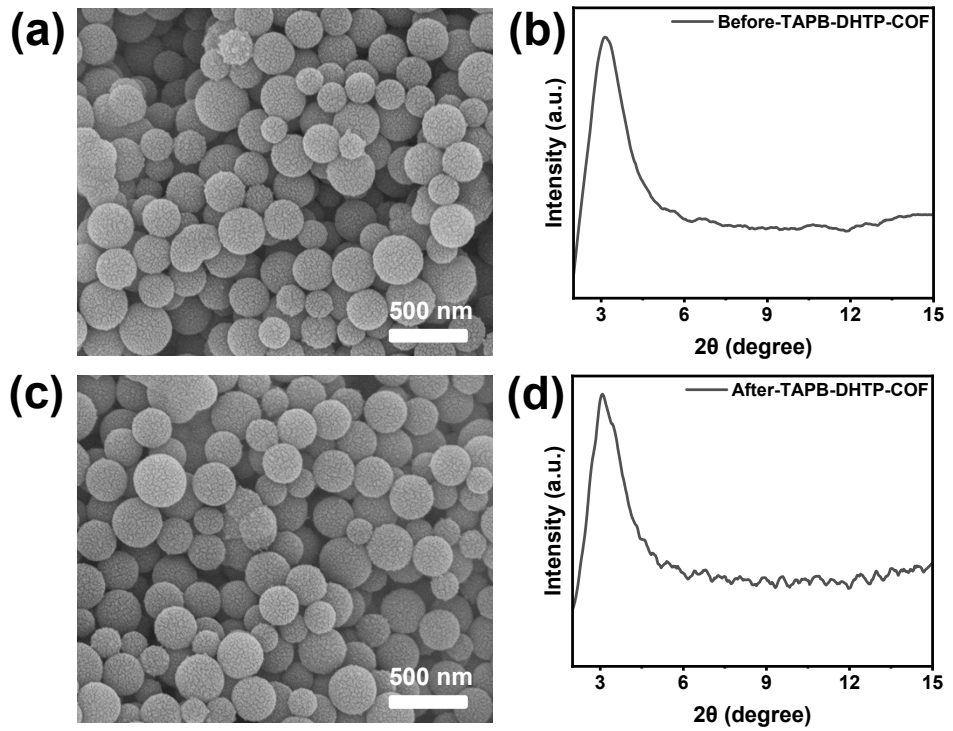


Fig. S10 (a), (c) SEM images of TAPB-DHTP-COF before and after the catalytic test. (b), (d) PXRD patterns before and after degradation.

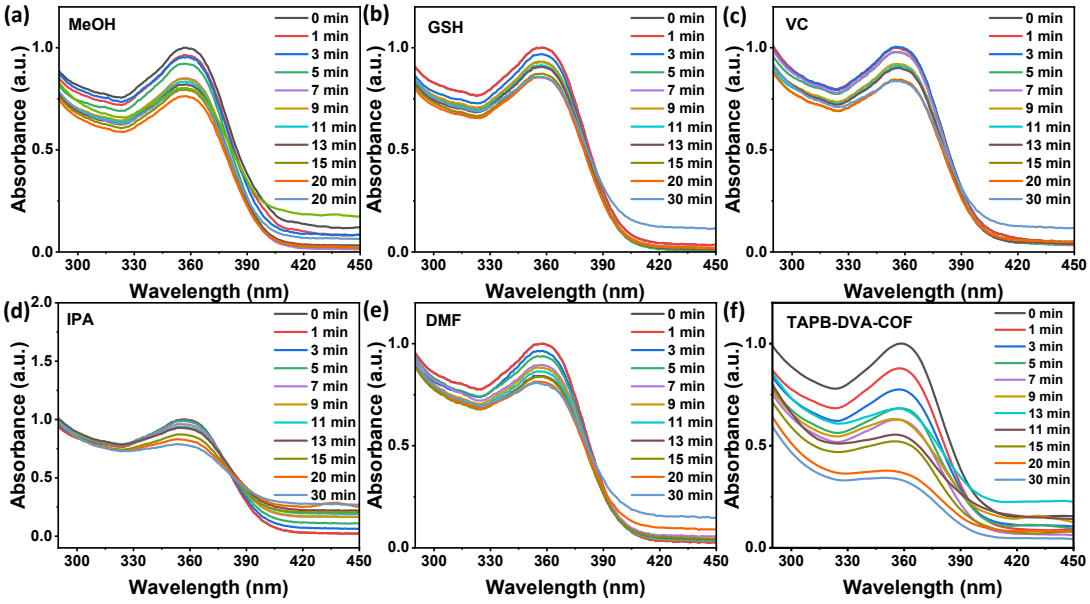


Fig. S11 UV-vis spectra of TC degradation with different quenchers.

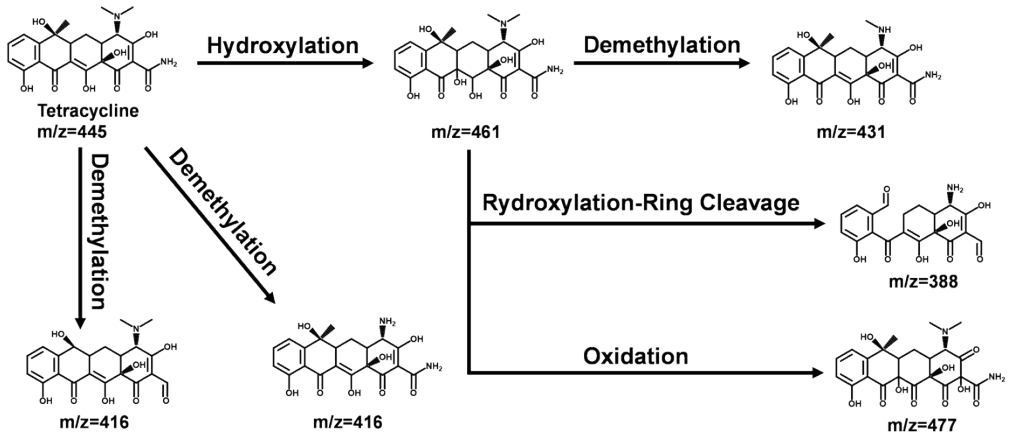


Fig. S12 Molecular structure of tetracycline (TC) and its possible degradation pathways.[10,11]

Reference

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