Supporting information

Linker length-dependent hydrogen peroxide photosynthesis performance over crystalline covalent organic frameworks

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Figure S1. Synthetic route of COF-BPDA-DTP, COF-BPDA-BD and COF-BPDA-PA.



Figure S2. (a) The LSV curves at different rotate speeds. (b) The calculated collection efficiency (N) for RRDE



Figure S3. (a) Eclipsed (AA) stacking mode of COF-BPDA-DTP. (b) Comparison between experimental PXRD pattern and simulated pattern. White, gray, blue, and red spheres represent H, C, N, and O atoms, respectively.



Figure S4. (a) Staggered (AB) stacking mode of COF-BPDA-DTP. (b) Comparison between experimental PXRD pattern and simulated pattern. White, gray, blue, and red spheres represent H, C, N, and O atoms, respectively; the second layer is highlighted in bule for clarity.



Figure S5. (a) Eclipsed (AA) stacking mode of COF-BPDA-BD. (b) Comparison between experimental PXRD pattern and simulated pattern. White, gray, blue, and red spheres represent H, C, N, and O atoms, respectively.



Figure S6. (a) Staggered (AB) stacking mode of COF-BPDA-BD. (b) Comparison between experimental PXRD pattern and simulated pattern. White, gray, blue, and red spheres represent H, C, N, and O atoms, respectively; the second layer is highlighted in bule for clarity.



Figure S7. (a) Eclipsed (AA) stacking mode of COF-BPDA-PA. (b) Comparison between experimental PXRD pattern and simulated pattern. White, gray, blue, and red spheres represent H, C, N, and O atoms, respectively.



Figure S8. (a) Staggered (AB) stacking mode of COF-BPDA-PA. (b) Comparison between experimental PXRD pattern and simulated pattern. White, gray, blue, and red spheres represent H, C, N, and O atoms, respectively; the second layer is highlighted in bule for clarity.



Figure S9. TEM images of COF-BPDA-BD (a and b) and COF-BPDA-PA (c and d)



Figure S10. The pore size distributions of (a) COF-BPDA-DTP, (b) COF-BPDA-BD, and (c) COF-BPDA-PA.



Figure S11. FT-IR spectra of COF-BPDA-DTP, COF-BPDA-BD and COF-BPDA-PA.



Figure S12. The water contact angle of (a) COF-BPDA-DTP, (b) COF-BPDA-BD and (C) COF-BPDA-PA.



Figure S13. The time-amount curves for photocatalytic H_2O_2 production over COF-BPDA-DTP (35mg, 40 mL pure water).



Figure S14. (a) C 1s, (b) N 1s and (c) O 1s XPS spectra of COF-BPDA-DTP before and after undergoing photocatalysis.

H₂O₂ yield Irradiated Test Samples rate (µmol Solvent Ref. conditions conditions $h^{-1} g_{cat}^{-1}$) 30 mg catalysts $\lambda{>}420~nm$ 97 **CTF-BDDBN** H_2O **S**1 and 50 mL water 5 mg catalysts $\lambda{>}420~nm$ COF-TfpBpy 695 H_2O S2 and 10 mL water 50 mg catalysts $\lambda > 420 \text{ nm}$ **MRF-250** 582 H_2O S3 and 30 mL water 10 mg catalysts N₀-COF 1570 $\lambda = 495 \text{ nm}$ H_2O S4 and 20 mL water 30 mg catalysts $\lambda \!>\! 420 \ nm$ 1H-COF 700 H_2O S5 and 30 mL water 30 mg catalysts $\lambda \!>\! 420 \text{ nm}$ DE7-M 266 H_2O S6 and 50 mL water

Table S1. The comparison of H_2O_2 production rate with other reported photocatalysts without sacrificial reagents.

SonoCOF-F2	1244	3 mg catalysts	$\lambda \!>\! 420 \text{ nm}$	H ₂ O	S7
		and 5 mL			
		water			
HEP-TAPT- COF	1750	50 mg	$\lambda > 420 \text{ nm}$	H ₂ O	S8
		catalysts			
		and 100			
		mL water			
FS-COFs	3904	5 mg	$\lambda \!>\! 420 \text{ nm}$	H ₂ O	S9
		catalysts			
		and 20 mL			
		water			
TTF-BT-COF	2760	5 mg	$\lambda \!>\! 420 \text{ nm}$	H ₂ O	S10
TTF-pT-COF	996	catalysts			
TPE-BT-COF	592	and 10 mL			
		water			
COF-BPDA-	450		λ>420 nm	H ₂ O	
РА		5 mg			This work
COF-BPDA-	1040	catalysts		H ₂ O	
BD		and 40 mL			
COF-BPDA-	1164	water		H ₂ O	
DTP					

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