Supporting Information

Tunable Covalent Triazine-Based Frameworks (CTF-0) for Visible Light-Driven Hydrogen and Oxygen Generation from Water Splitting

Dan Kong, [a] *Xiaoyu Han,* [b] *Jijia Xie,* [a] *Qiushi Ruan,* [a] *Christopher D. Windle,* [a] *Srinivas Gadipelli,* [b] *Kai Shen,*[c] Zhiming Bai, [a,d,]* *Zhengxiao Guo,* [b,]* *Junwang Tang* [a,]*

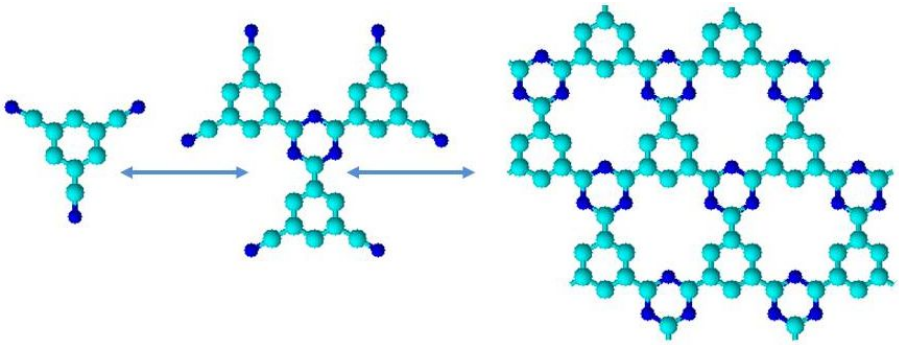
[a] Department of Chemical Engineering, University College London, Torrington Place, London, WC1E 7JE, UK.

[b] Department of Chemistry, University College London, 20 Gordon St, London, WC1H 0AJ, UK.

[c] Department of Electronic and Electrical Engineering, University College London, Torrington Place, London WC1E 7JE, UK.

[d] The school of Material Science and Engineering, Beihang University, No.37 Xueyuan Road, Haidian district, Beijing, China.

*Corresponding Author E-mails: junwang.tang@ucl.ac.uk; z.x.guo@ucl.ac.uk; bzm@buaa.edu.cn



Scheme S1. Polymerization reaction of 1,3,5-tricyanobenzene to an intermediate trimer and the ideal extended CTF-0.

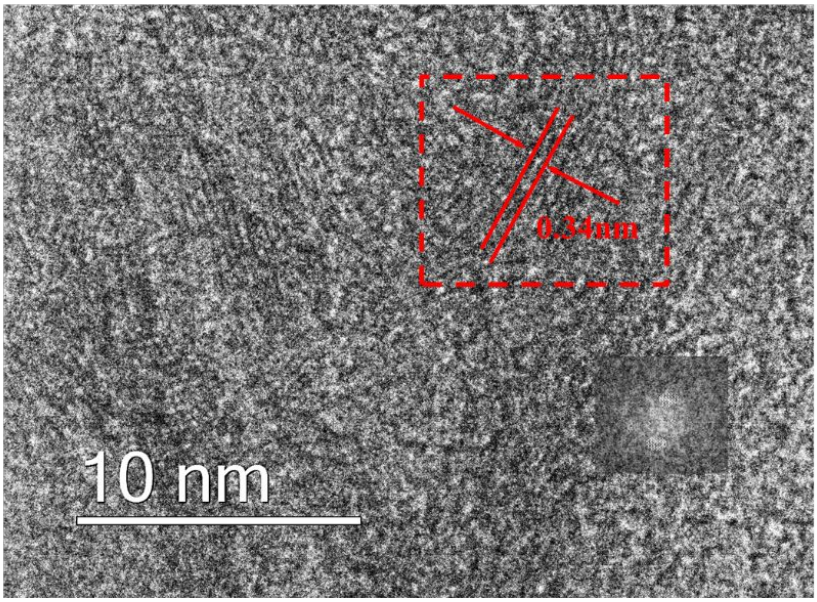


Figure S1. Transmission electron microscopy (TEM) image of CTF-0-M_2.

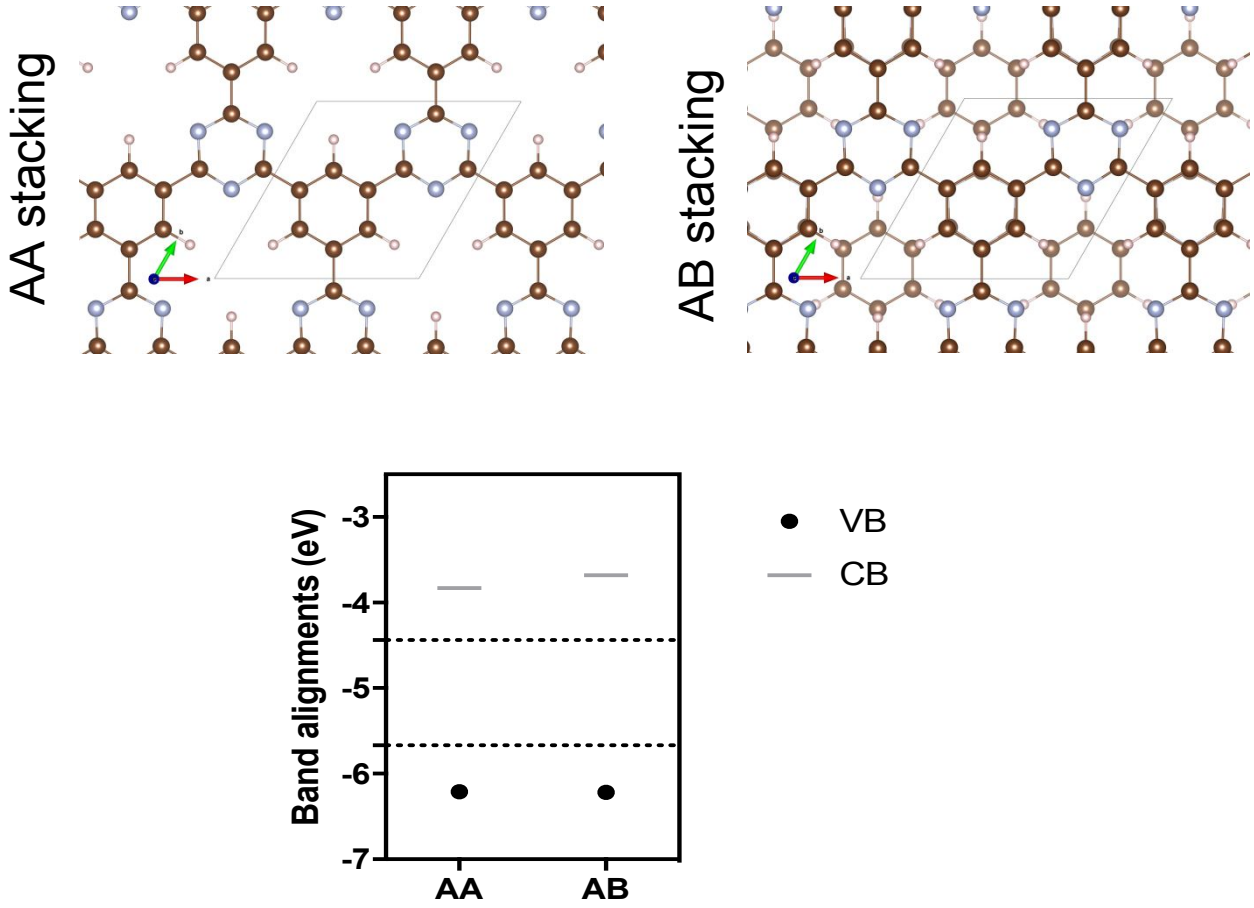


Figure S2 Estimated band positions of CTF-0 with three-layer AA stacking and AB stacking.

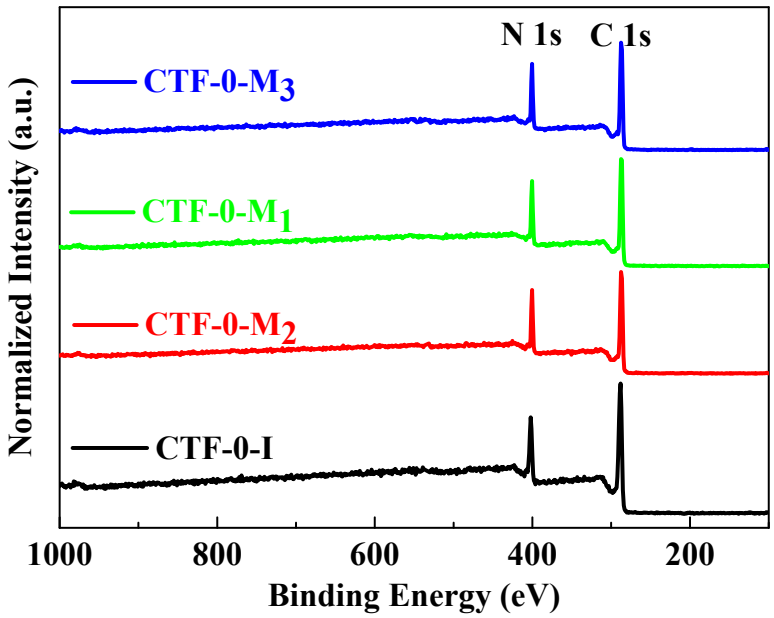


Figure S3. XPS survey spectra of CTF-0-I, CTF-0-M_1, CTF-0-M_2 and CTF-0-M_3.

Table S1. Elemental analysis data of the polymers CTF-0-I, CTF-0-M_1, CTF-0-M_2 and CTF-0-M_3.

Polymer	Acid catalyst	TCB	Experimental %				Theory %		
			C	H	N	N/C	C	H	N
CTF-0-I	0.9 g	1 g	76.8	2.5	20.0	0.26	70.6	2.0	27.4
CTF-0-M_2	2 mL	1 g	71.4	2.0	26.3	0.36	70.6	2.0	27.4
CTF-0-M_1	1.5 mL	1 g	72.1	2.1	25.3	0.35	70.6	2.0	27.4
CTF-0-M_3	2.5 mL	1 g	72.3	2.2	24.8	0.34	70.6	2.0	27.4

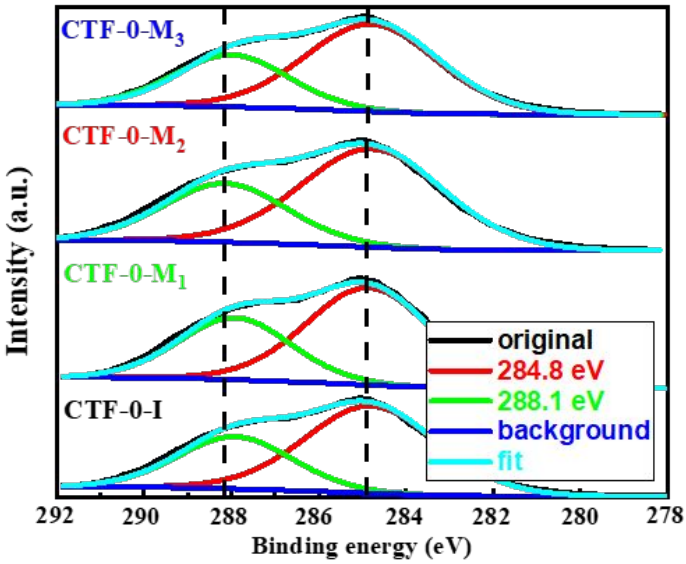


Figure S4. C1*s* XPS spectra with applied peak and cumulative fits of CTF-0-I, CTF-0-M_1, CTF-0-M_2, and CTF-0-M_3.

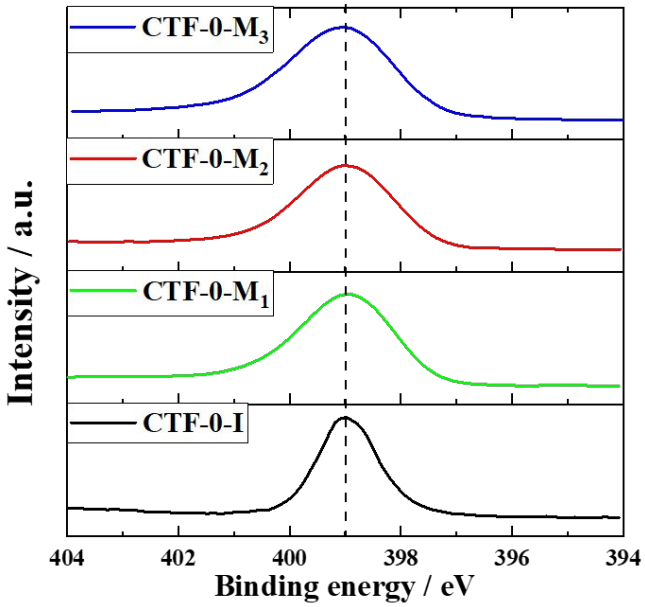


Figure S5. N1*s* XPS spectra with applied peak and cumulative fits of CTF-0-I, CTF-0-M_1, CTF-0-M_2, and CTF-0-M_3.

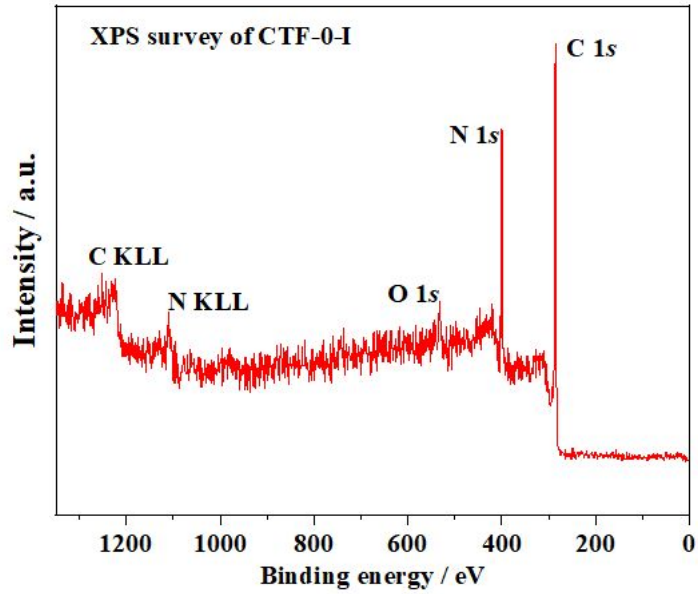


Figure S6. XPS survey spectra of CTF-0-I.

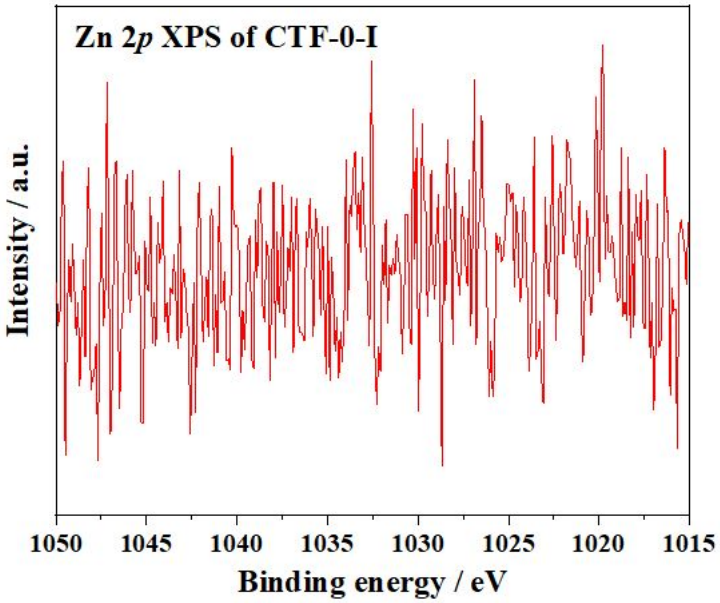


Figure S7. Zn 2*p* XPS spectrum of CTF-0-I

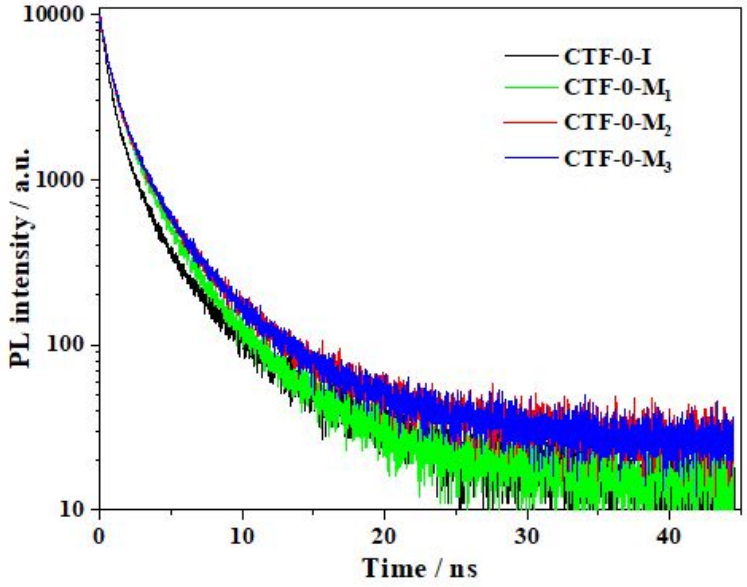


Figure S8. Log-linear plot of time-resolved photoluminance

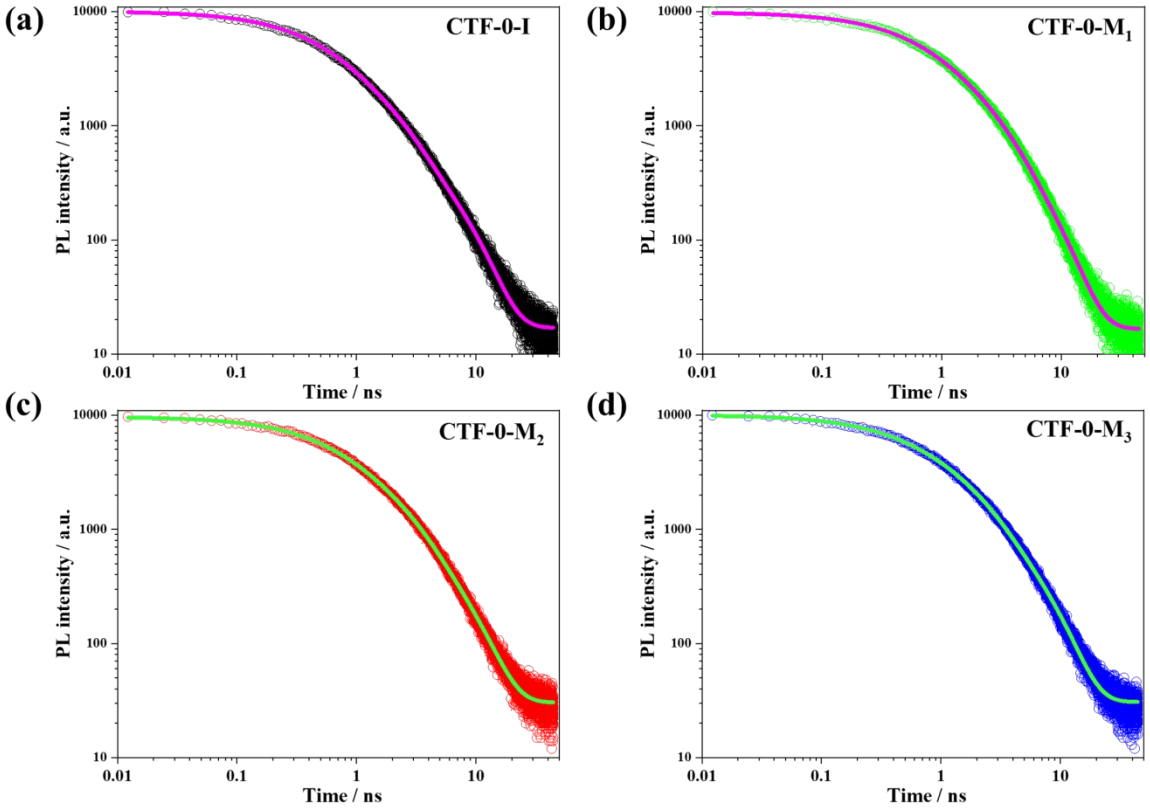


Figure S9. Triple-exponential fits to PL kinetics

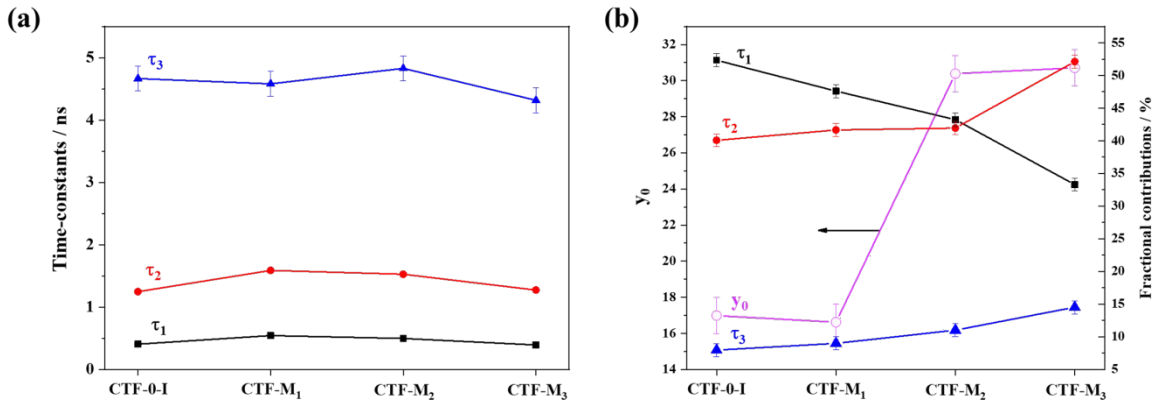


Figure S10. Fitting parameters of PL kinetics

Table S2 Fitting parameters of PL kinetics

Sample	τ_1 (contribution) / ns (%)	τ_2 (contribution) / ns (%)	τ_3 (contribution) / ns (%)	y_0 / ns	$\tau_{average}$ / ns
CTF-0-I	0.41 (52)	1.25 (40)	4.66 (8)	17.0	1.09
CTF-0-M_1	0.54 (48)	1.59 (42)	4.58 (9)	16.6	1.34
CTF-0-M_2	0.50 (43)	1.53 (42)	4.82 (11)	30.4	1.39
CTF-0-M_3	0.39 (33)	1.27 (52)	4.32 (15)	30.7	1.44

y_0 represents y-offset which can be interpreted as a long-lived PL component with time-constant.

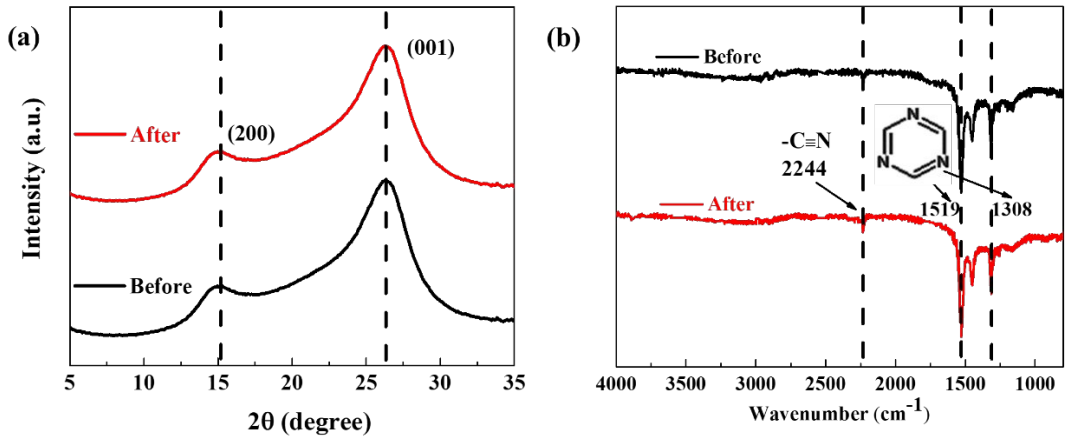


Figure S11. XRD patterns (a) and FTIR spectra (b) of CTF-0-M_2 before and after photocatalytic reactions.

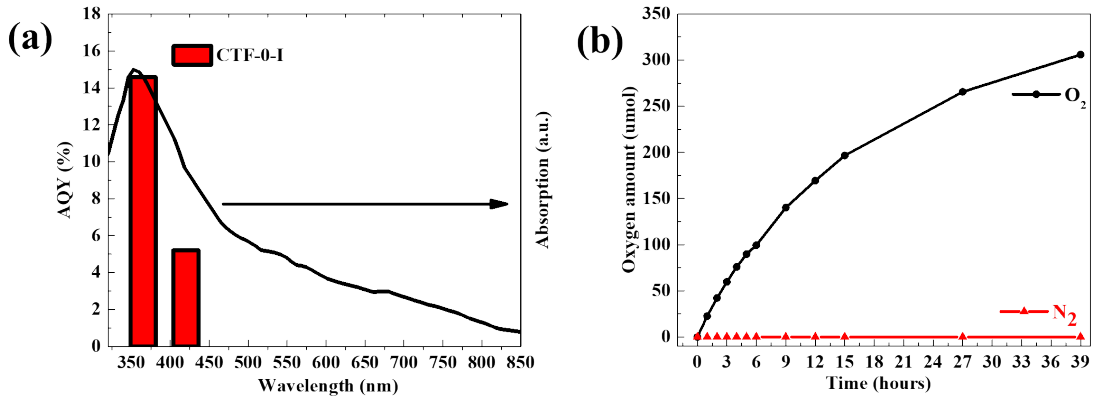


Figure S12. (a) Apparent quantum yield (AQY) for oxygen generation and (b) Stability test of CTF-0-I under ambient conditions.

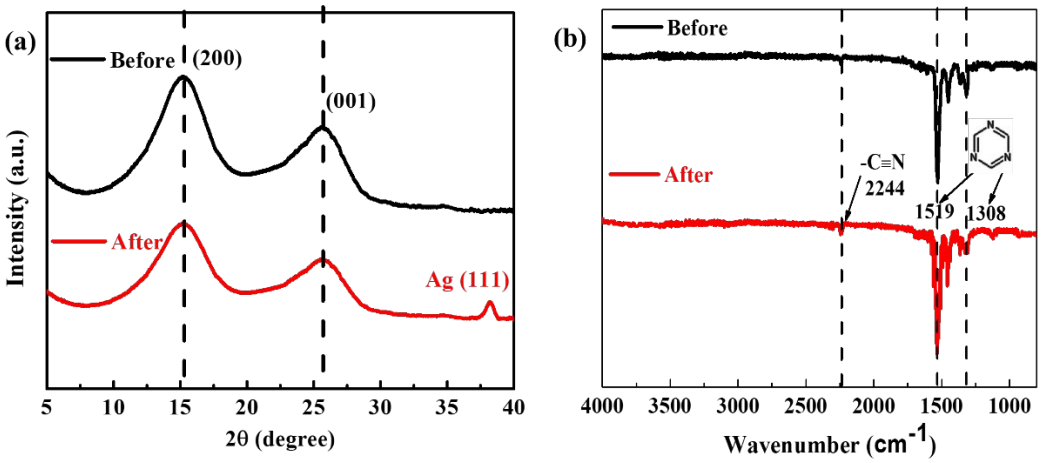


Figure S13. XRD patterns (a) and FTIR spectra (b) of CTF-0-I before and after photocatalytic water oxidation reactions.

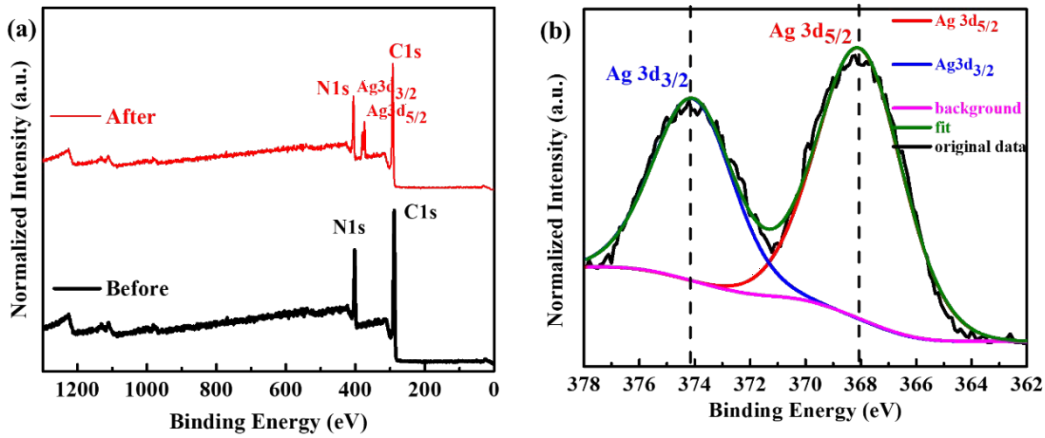


Figure S14. XPS survey spectra of CTF-0-I before and after photocatalytic reactions (a) and Ag 3d XPS spectra of CTF-0-I after photocatalytic reaction (b). Charge referenced to adventitious C1s peak at 284.8 eV.0

Table S3. Nitrile rings to benzene rings ratio according to the ^{13}C ssNMR spectra of the polymers CTF-0-I, CTF-0-M_1, CTF-0-M_2 and CTF-0-M_3.

Polymer	Amount of Lewis acid	TCB	Nitrile to benzene ratio
CTF-0-I	0.9 g	1 g	0.91
CTF-0-M_2	2 mL	1 g	1.23
CTF-0-M_1	1.5 mL	1 g	0.79
CTF-0-M_3	2.5 mL	1 g	0.15

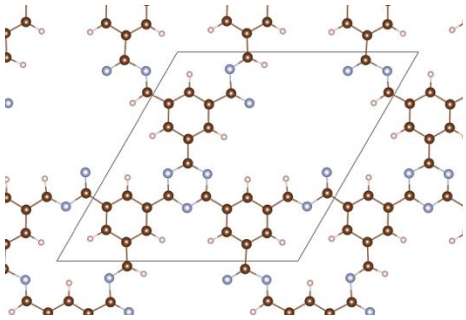


Figure S15. The CTF-0 with the unreacted CN terminals. The model was built on a 2×2 supercell with distracting one 1,3,5-tricyanobenzene group.

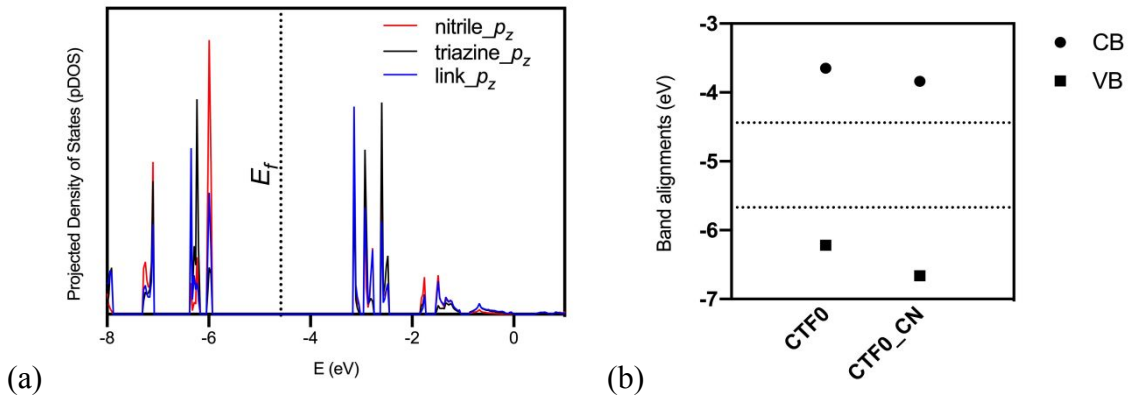


Figure S16. (a)The projected Density of States of different N in the CTF-0 with nitrile framework. The dot line represents the Fermi level. (b)The calculated band alignments of pristine CTF-0 and CTF-0 with nitrile terminals in the framework.

Table S4. The detailed parameters for calculating AQY data.

AQY of Hydrogen evolution				
wavelength(nm)	365	420	500	600
light intensity (mw/cm^2)	1.58	1.25	1.82	1.93
the amount of gas (μmol)	18.7	11.96	5.08	1.94
AQY (%)	10.98	7.72	1.89	0.57
AQY of Oxygen evolution				
wavelength(nm)	365	420		
light intensity (mw/cm^2)	1.16	1.01		
the amount of gas (μmol)	9.17	3.25		
AQY (%)	14.59	5.21		
Both reactions have the same irradiation time and area				
irradiation area(cm^2)	19.63			
irradiation time(s)	3600			