

# Amino-functionalized Conjugated Porous Polymers for Improved Photocatalytic Hydrogen Evolution

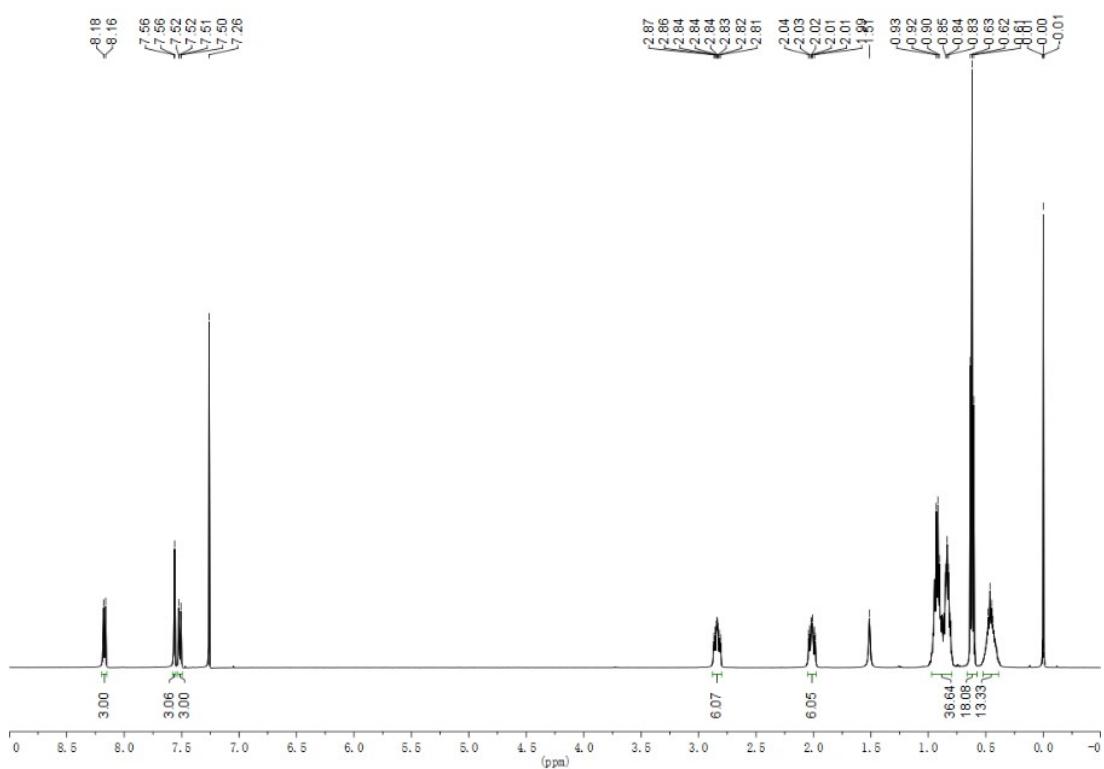
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Muhammad Rafiq, Fei Huang\* and Yong Cao

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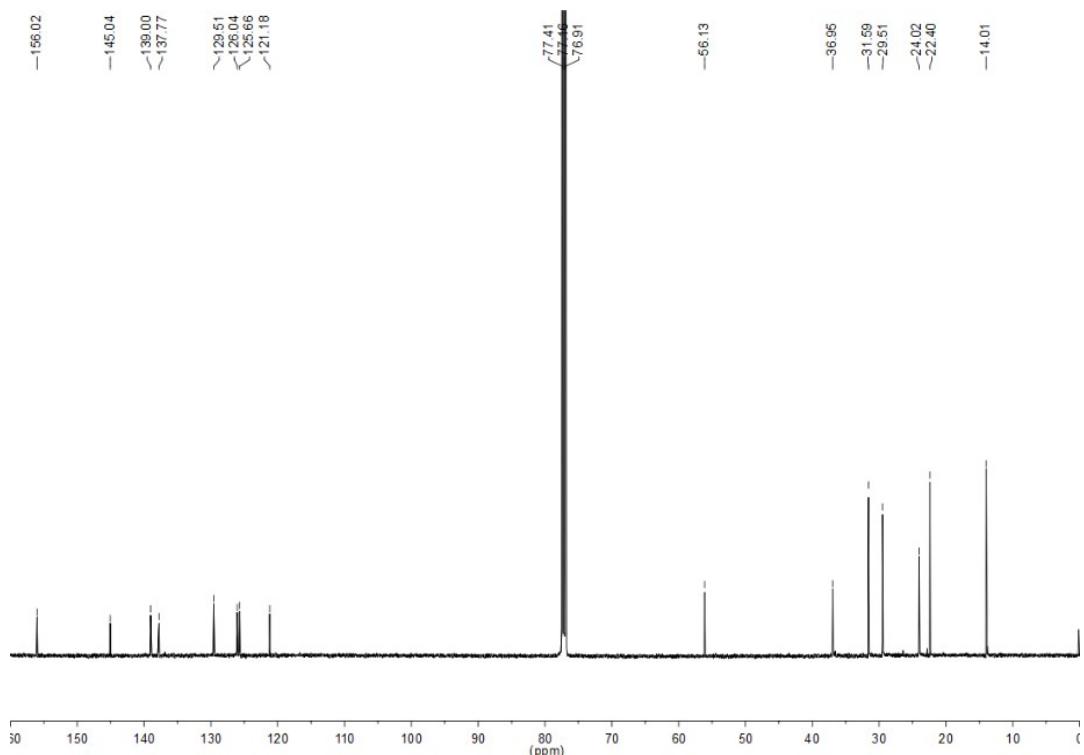
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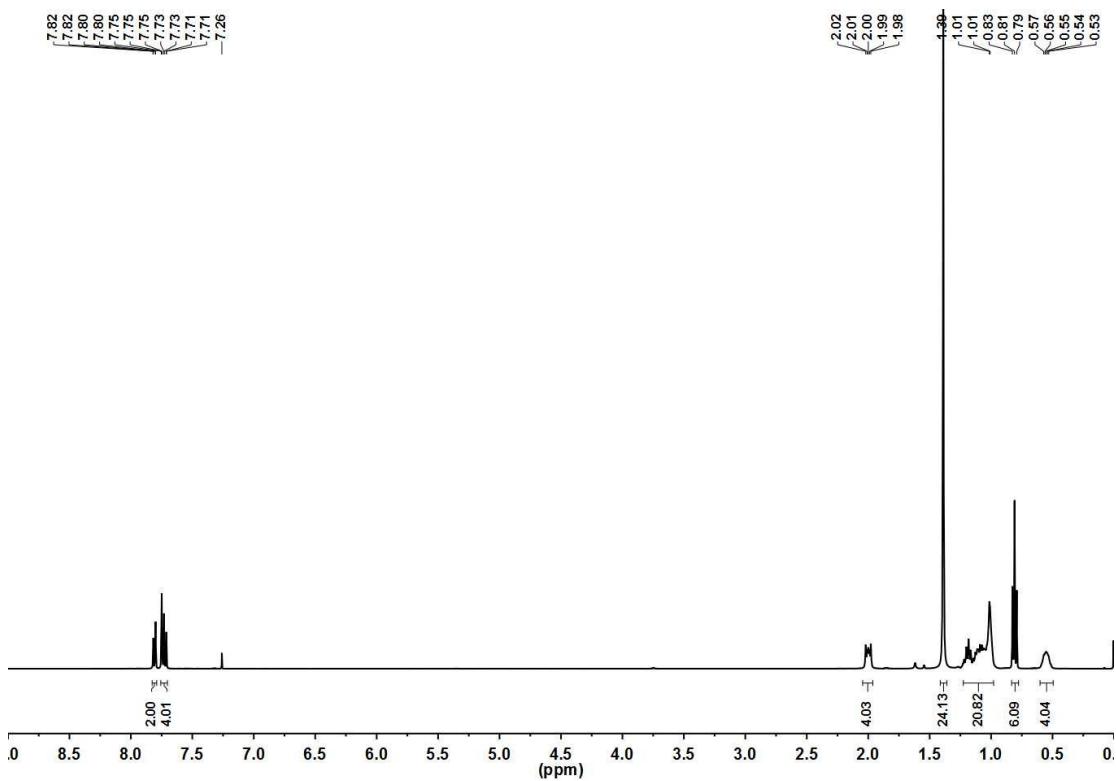
## Support Information



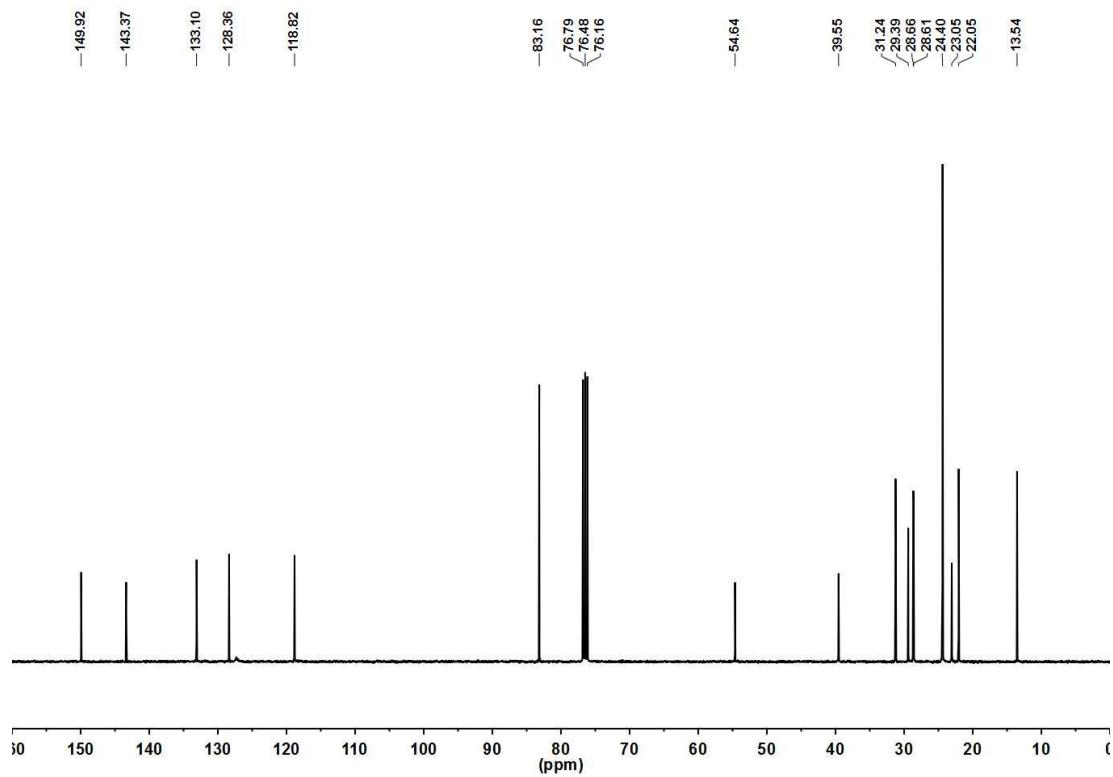
**Fig. S1**  $^1\text{H}$  NMR spectrum of Tr-3Br.



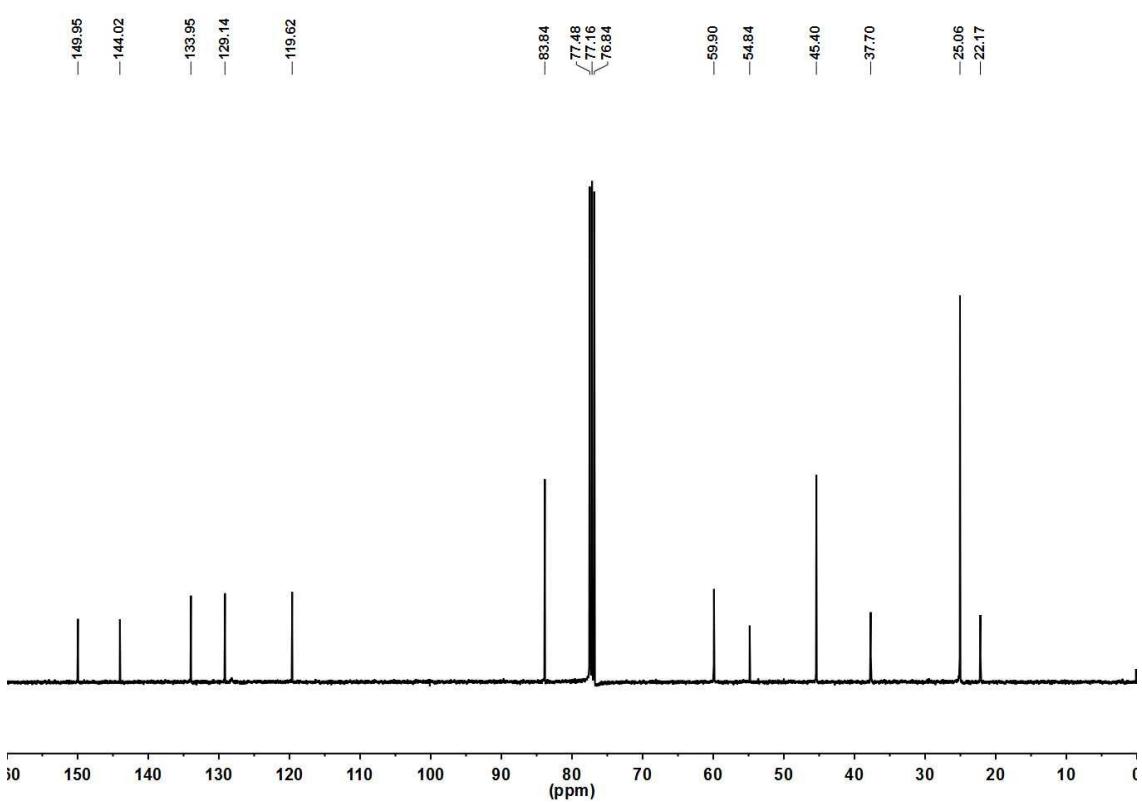
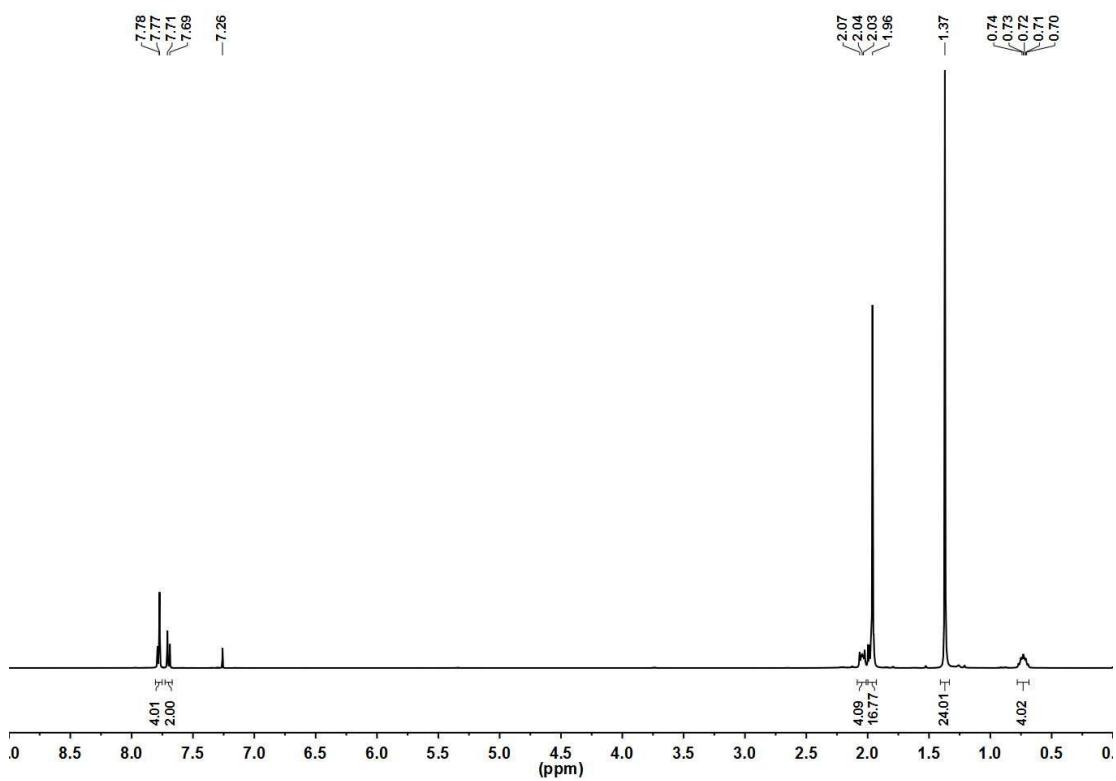
**Fig. S2**  $^{13}\text{C}$  NMR spectrum of Tr-3Br.

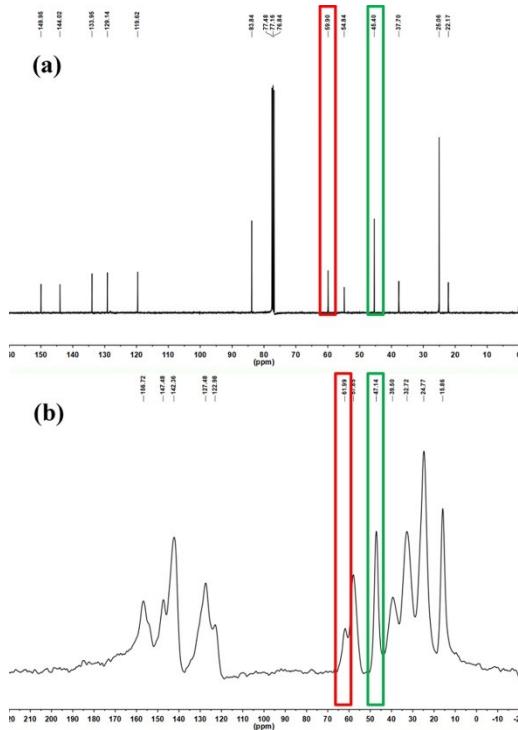


**Fig. S3**  $^1\text{H}$  NMR spectrum of F8-2BO.

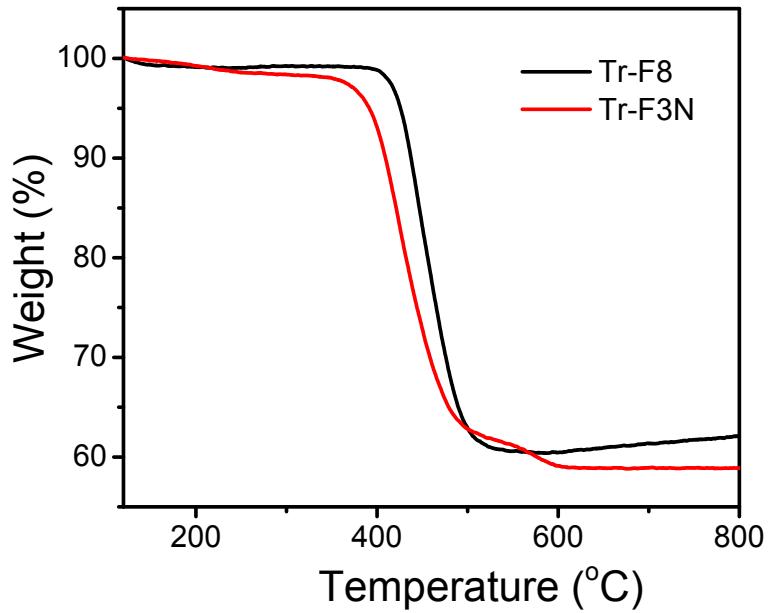


**Fig. S4**  $^{13}\text{C}$  NMR spectrum of F8-2BO.

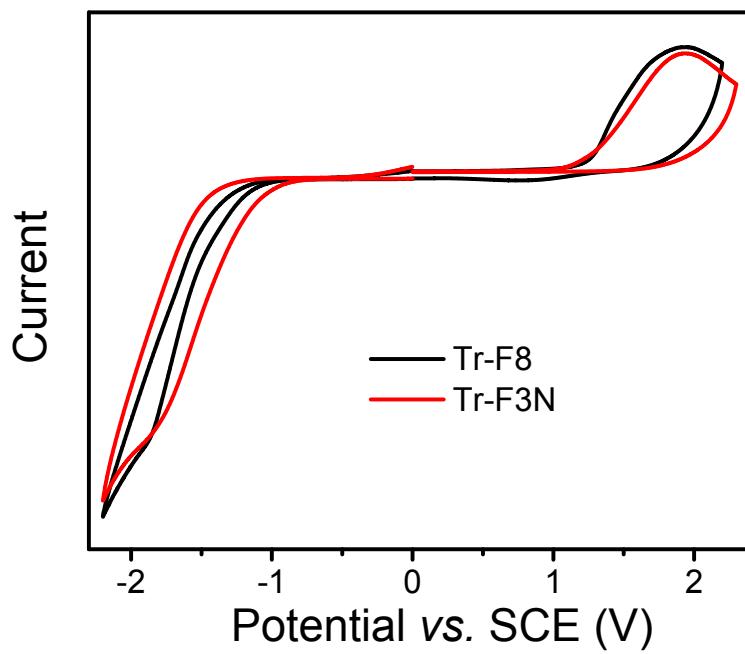




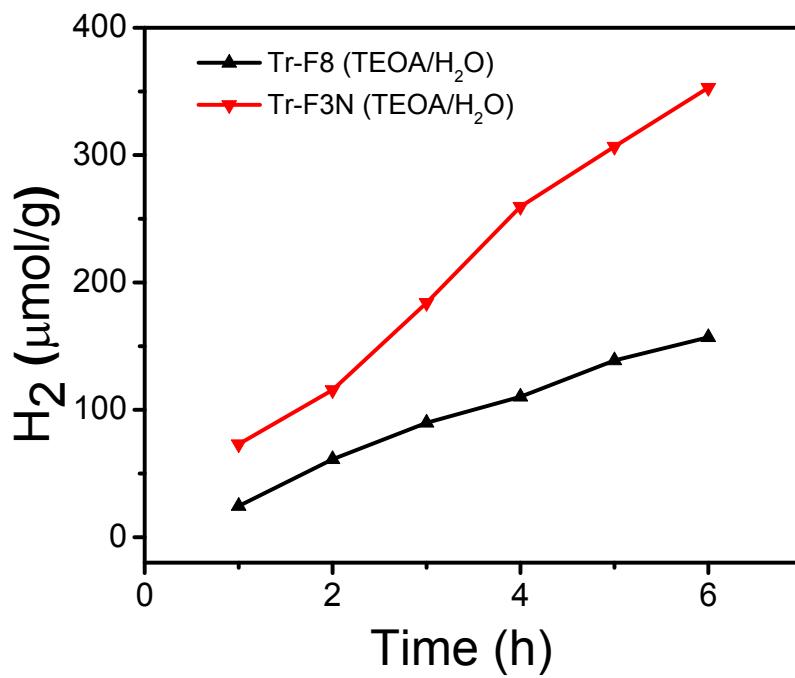
**Fig. S7** (a)  $^{13}\text{C}$  NMR spectrum of F3N-2BO and (b) the solid-state  $^{13}\text{C}$  NMR spectra of Tr-F3N.



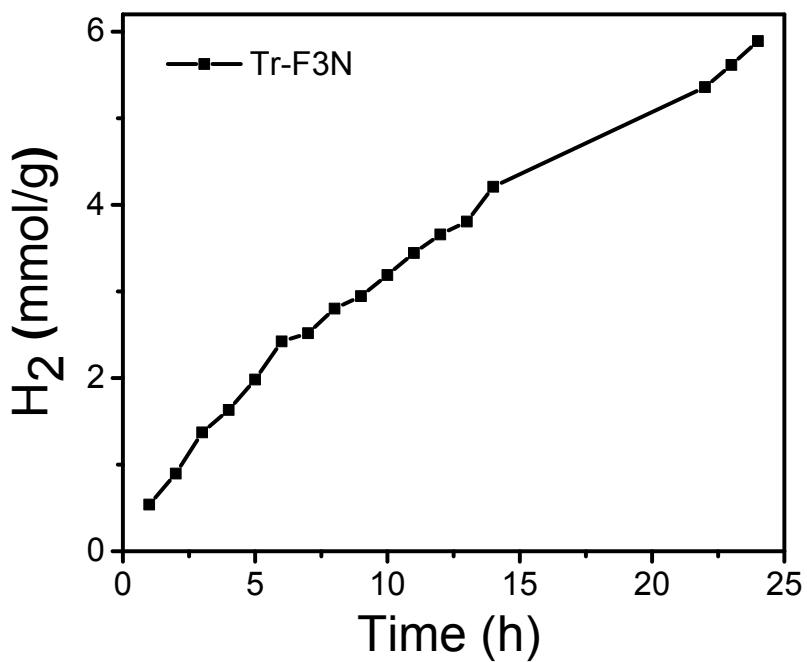
**Fig. S8** TGA of the Tr-F8 and Tr-F3N.



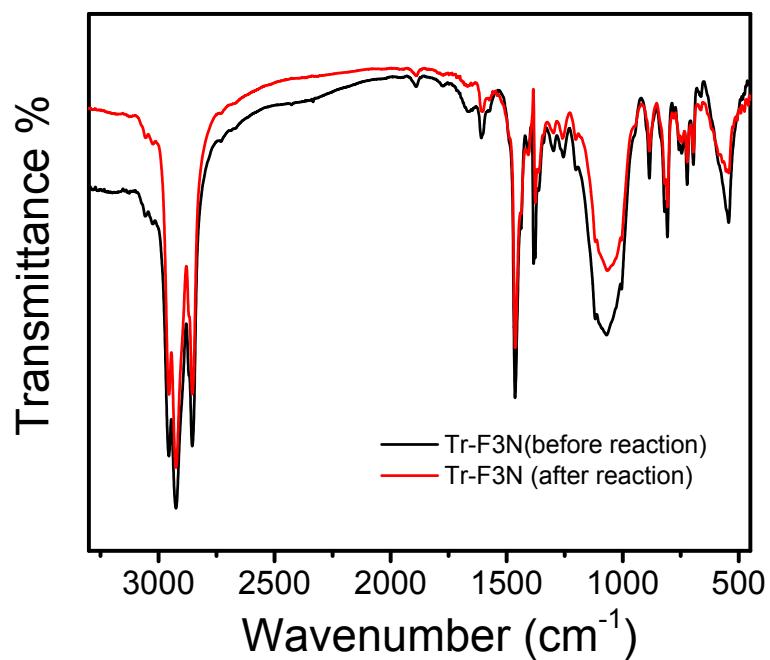
**Fig. S9** Cyclic voltammetry measurement of the Tr-F8 and Tr-F3N.



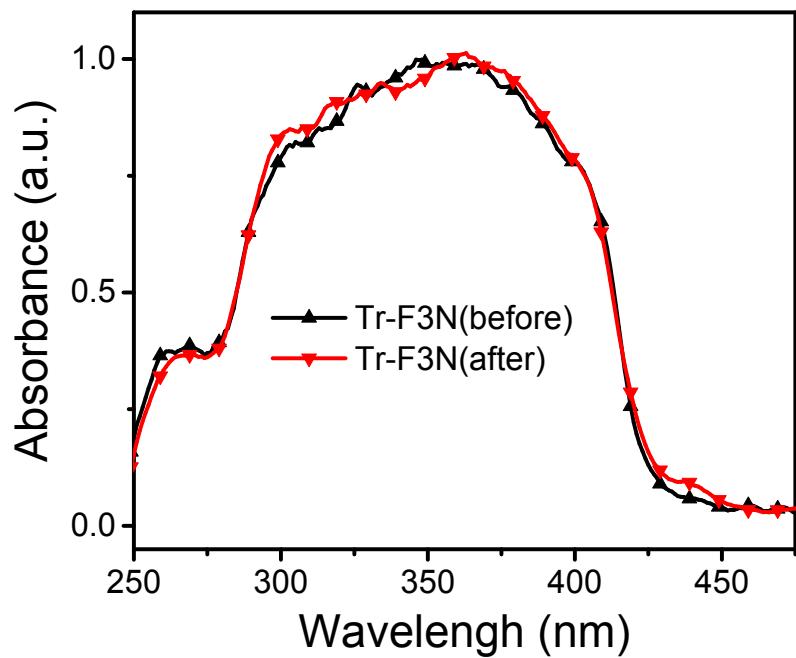
**Fig. S10** Hydrogen evolution for Tr-F8 and Tr-F3N as a function of time (50mL of TEOA/H<sub>2</sub>O, 1:9 (v:v)).



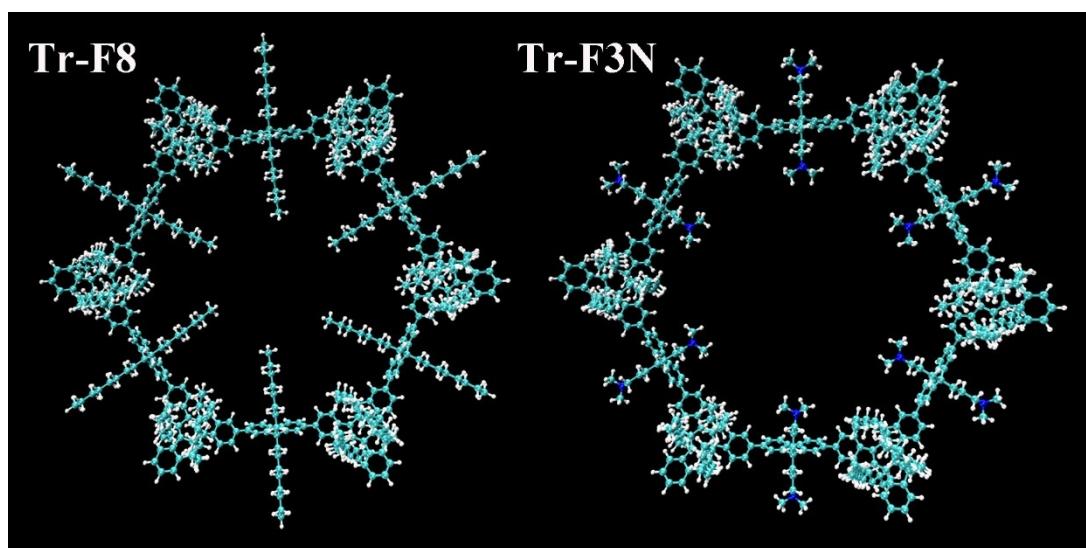
**Fig. S11** Hydrogen evolution as a function of time of Tr-F3N (50mL of TEOA/ethylene glycol (EG)/H<sub>2</sub>O, 1:3:6 (v:v)).



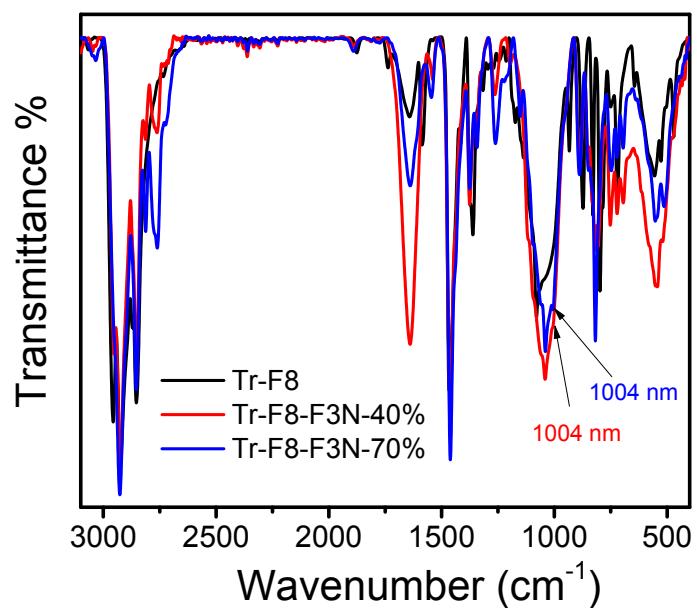
**Fig. S12** FTIR spectra of Tr-F3N before and after reaction.



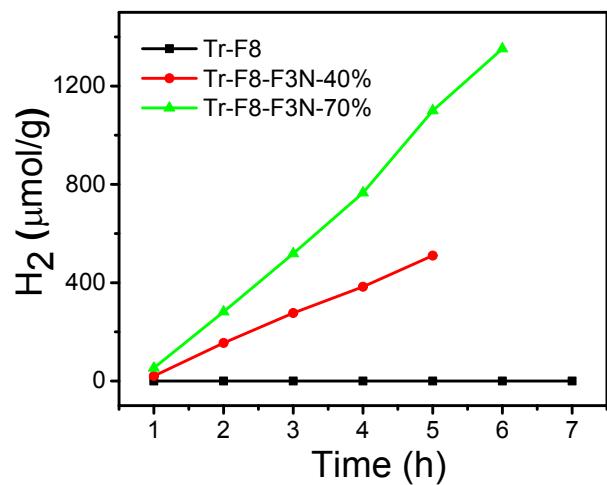
**Fig. S13** The UV-vis diffuse reflectance spectra of Tr-F3N as synthesized and after 24-h photocatalysis.



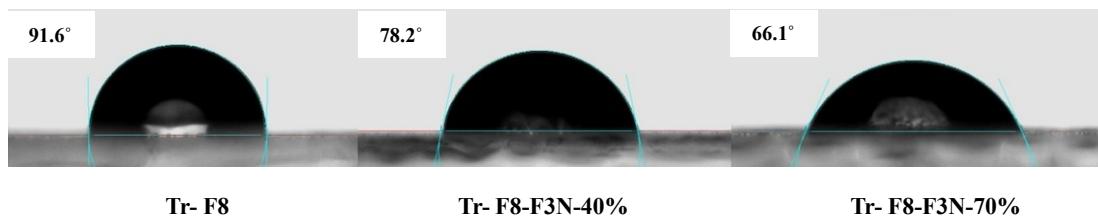
**Fig. S14** DFT calculated molecular geometries of M-F8 and M-F3N.



**Fig. S15** FTIR spectra of Tr-F8, Tr- F8-F3N-40%, and Tr- F8-F3N-70%.

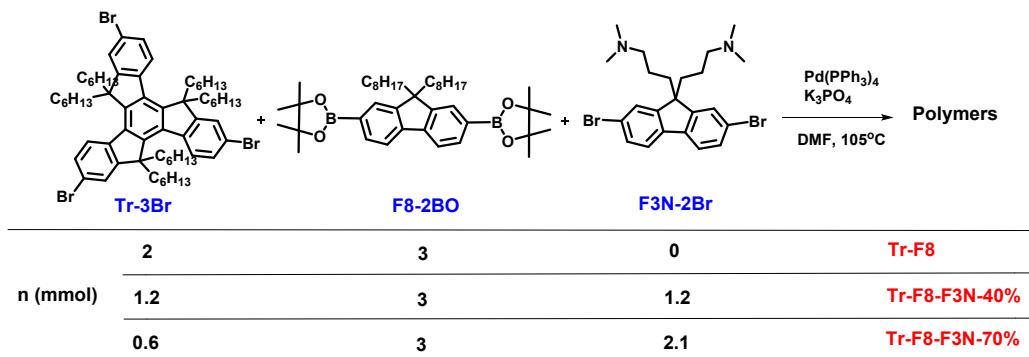


**Fig. S16** Hydrogen evolution as a function of time of Tr- F8, Tr- F8-F3N-40% and Tr- F8-F3N-70% (with ascorbic acid as sacrificing electron donor).



**Fig. S17.** Water contact angle measurements of Tr-F8, Tr-F8-F3N-40% and Tr-F8-F3N-70%.

**Scheme S1** Synthetic routes to the CPPs of Tr-F8, Tr-F8-F3N-40% and Tr-F8-F3N-70%.



**Table S1** Element analysis and Pd residue results for Tr-F8 and Tr-F3N.

CMPs	Tr-F8			Tr-F3N		
	Calcd. (%)	Found (%, before reaction)	Found (%, after reaction)	Calcd. (%)	Found (%, before reaction)	Found (%, after reaction)
C	89.49	90.48	88.15	86.86	85	85.5
H	10.21	9.52	11.85	10.02	11.2	11.54
N	--	--	--	3.12	2.8	2.96
Pd <sup>a</sup>	--	8.9 ppm	--	--	6.9 ppm	--

<sup>a</sup> (ppm), Pd residue in the polymers was obtained by ICP-MS measurements.

**Table S2** Summary of the HER without Pt as a co-catalyst for the reported CPPs.

CPPs	HER ( $\mu\text{mol h}^{-1} \text{g}^{-1}$ )	Ref.
CP-CMP10	174	1
NP-2	194	2
PCP2-100%PDI	2057	3
PrCMP-3	25	4
PCP4e	9428	5
CTF-2	0	6
PE-CMP	716	7
PCTF-8	136	8
NP-5	200	9
PyBT-0~7	54~525	10
PhBT-0~10	9.5~471	10
DBTD-CMP1	2460	11
DBTD-CMP2	188	11
DBTD-CMP3	116	11
L-PyBT	556	12
S-CMP3	6076	13

**Table S3** Element analysis and Pd residue results for Tr-F8, Tr-F8-F3N-40%, and Tr-F8-F3N-

70%.

CMPs	Tr-F8		Tr-F8-F3N-40%		Tr-F8-F3N-70%	
	Calcd. (%)	Found (%)	Calcd. (%)	Found (%)	Calcd. (%)	Found (%)
C	89.49	90.48	88.30	88.58	87.23	87.61
H	10.21	9.52	10.40	10.05	10.30	10.11
N	--	--	1.30	1.37	2.47	2.28
Pd <sup>a</sup>	10.4		8.9		7.3	

<sup>a</sup> (ppm), residue in the polymers was obtained by ICP-MS measurements.

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