Supporting Information

Defect Engineering in MIL-125-(Ti)-NH₂ for Enhanced Photocatalytic H₂ Generation

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Figure S1. Cluster of a) Ti-MOF and b) Ti₈Ph. Ti; yellow, O; red, C; brown, N; light blue, H atoms are omitted for clarity.



Figure S2. PXRD patterns of as-synthesized Ti₈Ph and simulated Ti₈Ph.



Figure S3. Photographs of a) Ti-MOF, b) Ti_8Ph -MOF, and c) Ti_8Ph -BA-MOF.



Figure S4. PXRD patterns of Ti-MOF, and Ti_8 Ph-MOF synthesized at 70 °C as compared with the simulated reference of MIL-125-NH₂.



Figure S5. PXRD patterns of Ti_8Ph -BA-MOF synthesized at 70 °C for 24, 48, and 72 h.



Figure S6. N₂ (99.999%) adsorption–desorption isotherms at 77 K, of Ti-MOF, Ti₈Ph-MOF, and Ti₈Ph-BA-MOF. Free space of the sample tube was determined prior to measuring each isotherm using helium (99.999%).



Figure S7. Pore size distributions for Ti-MOF, Ti_8 Ph-MOF, and Ti_8 Ph-BA-MOF. Distributions were derived by fitting the N_2 isotherms with sets of calculated isotherms (kernel) derived from non-local DFT (NLDFT) based methods. Fitting was done via the 3Flex Software Version 5.01 by Micromeritics Instrument Corp. using a kernel for cylindrical pores ('oxide cyl pores, strong potential') provided with the software.



Figure S8. a) BET plot with linear fit control parameters and calculated monolayer capacity (Q_m) , and b) Tabular BET plot data including amounts adsorbed in mmol/g for reference of Q_m for Ti-MOF.



Figure S9. a) BET plot with linear fit control parameters and calculated monolayer capacity (Q_m) , and b) Tabular BET plot data including amounts adsorbed in mmol/g for reference of Q_m for Ti₈Ph-MOF.



Figure S10. a) BET plot with linear fit control parameters and calculated monolayer capacity (Q_m), and b) Tabular BET plot data including amounts adsorbed in mmol/g for reference of Q_m for Ti₈Ph-BA-MOF.



Figure S11. TGA curves of Ti-MOF, Ti₈Ph-MOF, and Ti₈Ph-BA-MOFafter activation under Ar atmosphere.



Figure S12. Overlayed a) IR and b) Raman spectra of Ti-MOF, Ti₈Ph-MOF, and Ti₈Ph-BA-MOF.



Figure S13. UPS spectra of Ti-MOF, Ti₈Ph-MOF, and Ti₈Ph-BA-MOF.



Figure S14. Schematic diagram of energy levels of component of Ti_8Ph -BA-MOF.



Figure S15. a) Result of photocatalytic reactions and b) PXRD patterns of recycling tests on Ti_8Ph -BA-MOF with re-addition of 1.25 mL TEOA, 1 ml H₂O, and 22.75 mL CH₃CN.



Figure S16. Photoluminescence spectra of Ti-MOF, Ti₈Ph-MOF, and Ti₈Ph-BA-MOF (excited at 370 nm).



Figure S17. Model used for EXAFS analysis derived from local coordination environment of a) Ti₈Ph cluster and b) MIL-125-NH₂ (Ti-MOF). Ti; yellow, O; red, C; brown, N; light blue, H atoms are omitted for clarity. O₁, O₂, and O₃ in Ti₈Ph cluster presented μ_2 -O at the 1st shell, O_{the carboxylate group of linkers at the 1st shell, and O_{the carboxylate group of linkers at the 3rd shell from Ti₁ centre, respectively. Ti-MOF, O₁ and O₂ presented both μ_2 -O & μ_2 -OH at the 1st shell and O_{the carboxylate group of linkers at the 1st shell from Ti₁ centre. O₃ revealed O_{the carboxylate group of linkers at the 3rd shell.}}}}



Figure S18. DRIFT spectra of pyridine of Ti₈Ph-BA-MOF before and after reaction. Inset: High magnification presented the relative ratio of L-Py at 1454 cm⁻¹ to B-Py at 1560 cm⁻¹. DRIFT spectra of pyridine of used sample were found similar to the fresh catalyst which indicates structural durability under photocatalysis condition.



Figure S19. $Ti_8O_8(OH)_4(COOH)_{11}(H_2O)_1(OH)_1)$ cluster model.

To investigate the reaction mechanism, the Ti-oxide cluster model representing the active site was taken from the crystal structure of MIL-125(Ti)-NH₂.¹ To simulate the missing linker defect, one carboxylate linker, BDC-NH₂ was removed from the cluster. H₂O and hydroxide (OH⁻) were then placed at the defect site with the intention of neutralizing the charge. To minimize computational expenses, all remaining BDC-NH₂ linkers were replaced with formate. The resultant Ti-oxide cluster with the formula Ti₈O₈(OH)₄(COOH)₁₁(H₂O)₁(OH)₁ (as illustrated in Figure S19) was used as the catalyst model to represent the missing linker defect in MIL-125(Ti)-NH₂.



Figure S20. Energy profile for HER.

Table S1. Sorption Data of Ti-MOF, Ti₈Ph-MOF, and Ti₈Ph-BA-MOF

Sample	S _{BET} (m²/g)ª	V _{micro} (cm³/g) ^b	V _{total} (cm³/g)
Ti-MOF	1001.51 ± 0.70	0.36	0.39
Ti ₈ Ph-MOF	1483.53 ± 1.05	0.54	0.56
Ti ₈ Ph-BA-MOF	1356.76 ± 0.83	0.49	0.50

^a BET surface areas were calculated by applying the BET model and Rouquerol criteria. ^bMicropore and total pore volume were calculated using a NLDFT kernel (see Figure S5).

Table S2. VBM levels (measured by UPS) and energy gaps (obtained via Tauc's plot) for Ti-MOF, Ti₈Ph-MOF, and Ti₈Ph-BA-MOF.

Sample	Energy gap (eV)	VBM level (eV)	CBM level (eV)ª
Ti-MOF	2.81	5.80	2.99
Ti ₈ Ph-MOF	2.63	5.79	3.16
Ti ₈ Ph-BA-MOF	2.61	5.79	3.18

^a Levels were estimated per MOF upon subtracting the energy gap to the VBM.

Table S3. Selected reports for photocatalytic hydrogen evolution reaction under visible light irradiation.

Sample	Solvent	Electron	Light	H ₂	Ref.
		source	Source	(µmol/g/h)	
CdS	H ₂ O	Lactic acid	500 W Xe lamp	~150	[2]
			(> 420 nm)		
	H ₂ O	$Na_2S + Na_2SO_3$	350 W Xe lamp	~60	[3]
			(> 400 nm)		
N-doped TiO ₂ P25	H ₂ O	Formic acid	15 W visible	~10	[4]
			fluorescent lamp		
Cu ²⁺ -porphyrin MOF	H ₂ O	Ascorbic acid	300 W Xe lamp	~2	[5]
			(> 420 nm)		
Porphyrin Ti-MOF	H ₂ O	Ascorbic acid	300 W Xe lamp	-	[6]
			(> 420 nm)		
MIL-100(Fe)	H ₂ O	MeOH	300 W Xe lamp	~6	[7]
			(> 420 nm)		
MIL-101(Cr)-NH ₂			500 W Xe lamp	-	[8]
MIL-101(Cr)-NH ₂ +	H ₂ O	TEOA	(> 420 nm)	~60	
RuN ₃ ^a (dye)					
Co-ZIF-67			blue LED	-	
Co-ZIF-67 + RhB ^b	$CH_3CN + H_2O$	TEOA	(405nm)	~10	[9]
(dye)					
UiO-66(Zr)-NH ₂				~1	
defective UiO-	$CH_3CN + H_2O$	TEA	500 W Xe/Hg lamp	~2	[10]
66(Zr)-NH ₂			(> 385 nm)		
MIL-125(Ti)-NH ₂	$CH_3CN + H_2O$	TEOA	300 W Xe lamp	~20	[11]
			(>380 nm)		
Ti ₈ Ph-BA-MOF	$CH_3CN + H_2O$	TEOA	300 W Xe lamp	~150	This
			(430-740 nm)		Work

^a(cis-diisothiocyanato-bis (2,2'-bipyridyl-4,4'-dicarboxylic acid) ruthenium(II)).

^bRhodamine B.

Table S4 The HOMO and LUMO, at the isosurface values of 0.03 of the intermediate species along the HER pathway.

Sustam	Leve of calculations: MP2-6-31G**/LANL2DZ(Ti)		
System	НОМО	LUMO	
3			

Table S5 Mulliken charges and spin densities ($\rho_{\alpha} - \rho_{\beta}$) calculated at MP2-6-31G**/LANL2DZ level of theory of Ti of Ti-OH and Ti-OH₂ of the intermediate species along the HER pathway.

	Charge (e)		Spin density ($\rho_{\alpha} - \rho_{\beta}$)	
System	MP2-6-31G**/LANL2DZ		MP2-6-31G**/LANL2DZ	
	Ti-OH	Ti-OH ₂	Ti-OH	Ti-OH ₂
1	2.27	2.30	-	-
2	2 27	2 27	0.00	0.00
	2.27	2.27	0.00	(Ti5 = 0.98)*
3	2.22	1.90	0.00	1.00
III	1.31	2.31	_	-
4	2.23	1.94	-	-

*Ti5 as shown in Figure S19

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