Supporting Information

Integrating Single-Site Co Catalytic Center into Zr-MOF without Sacrificing Light-Harvesting Units for Enhanced Photocatalysis

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S1. Supplementary Figures

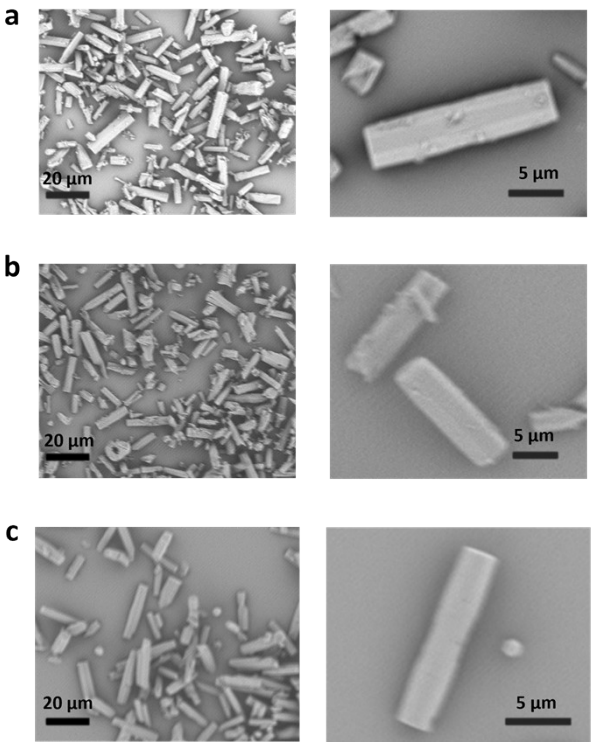

Fig. S1 SEM images of (a) NU-1000, (b) NU-1000-NIS, and (c) NU-1000-NIS-Co. Note: The crystal morphology of NU-1000-NBDC was clearly observable during 3D ED measurements. Therefore, additional SEM characterization was not performed.

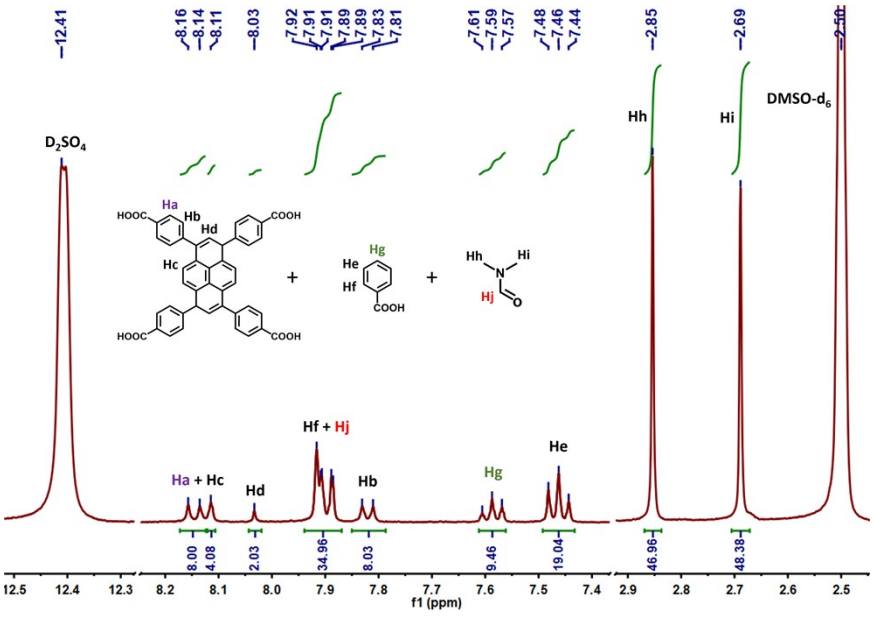

Fig. S2 The ^{1}H-NMR spectrum of digested NU-1000.

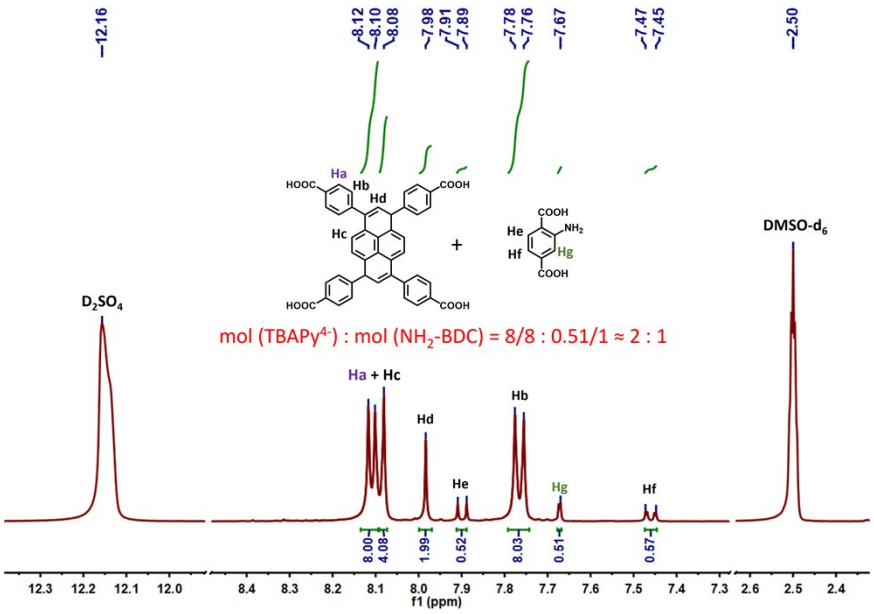

Fig. S3 The ^{1}H-NMR spectrum of digested NU-1000-NBDC.

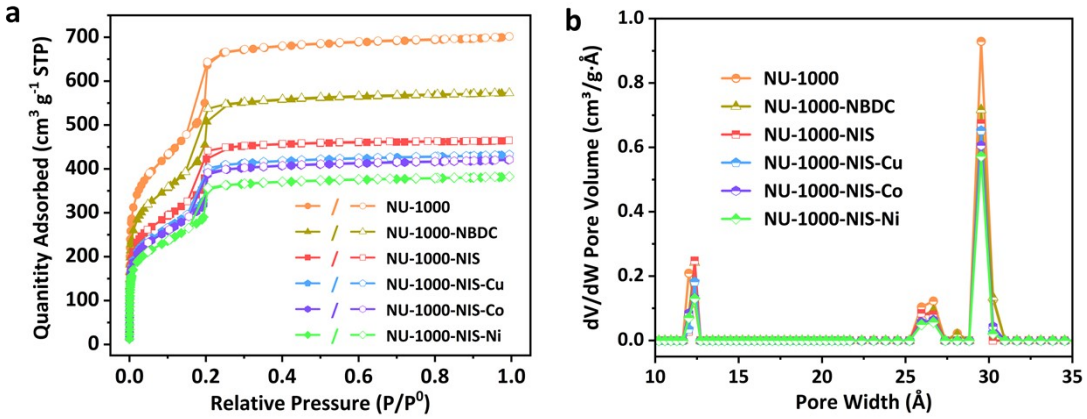

Fig. S4 The 77 K N_2 adsorption-desorption isotherms of NU-1000, NU-1000-NBDC, NU-1000-NIS, NU-1000-NIS-Cu, NU-1000-NIS-Co and NU-1000-NIS-Ni.

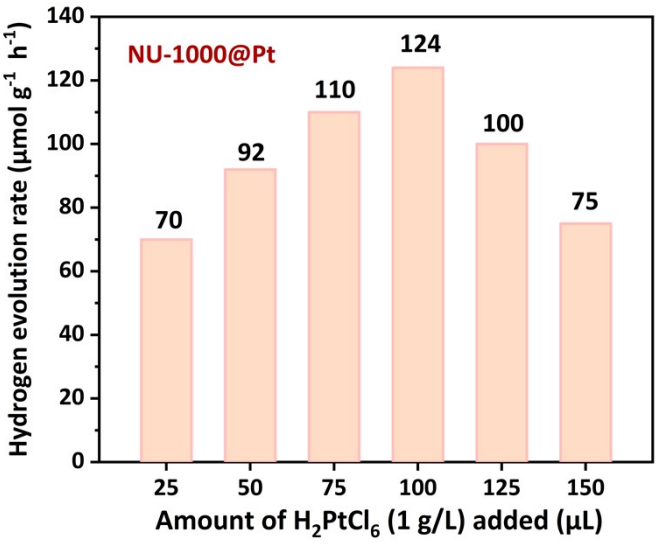

Fig. S5 The relationship between the amount of H_2PtCl_6 (1 g/L) added and the photocatalytic hydrogen evolution rate.

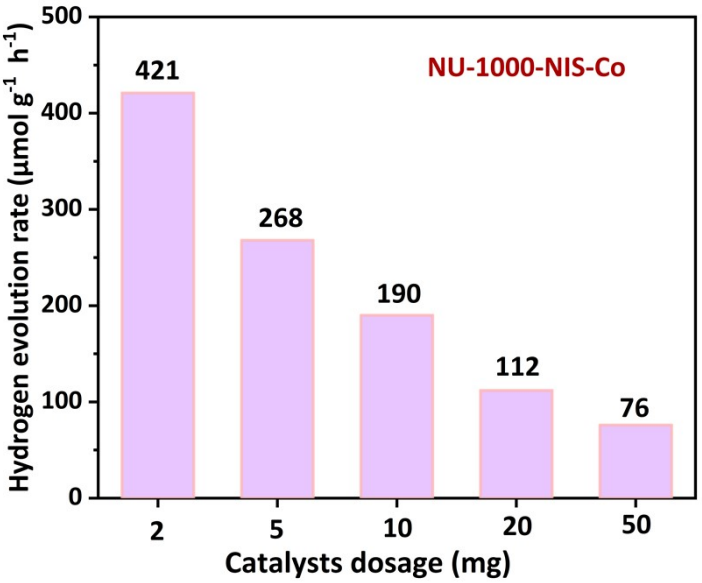

Fig. S6 The relationship between the catalysts dosage (NU-1000-NIS-Co) and the photocatalytic hydrogen evolution rate.

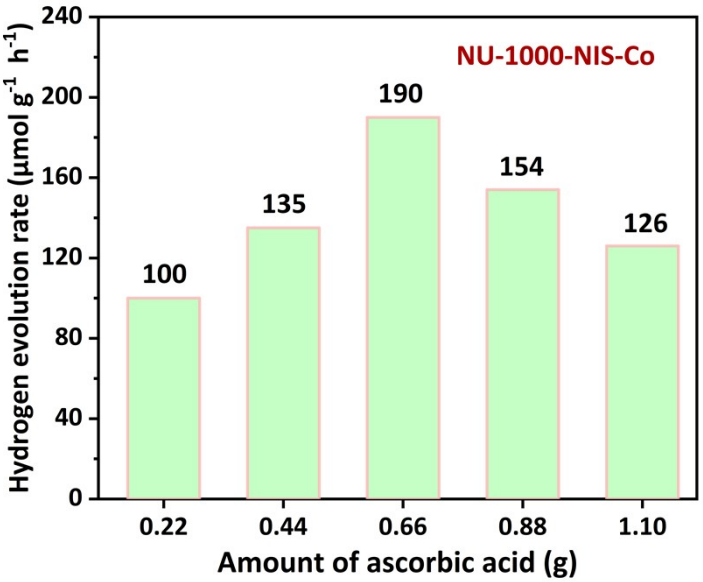

Fig. S7 The relationship between the amount of ascorbic acid and the photocatalytic hydrogen evolution rate.

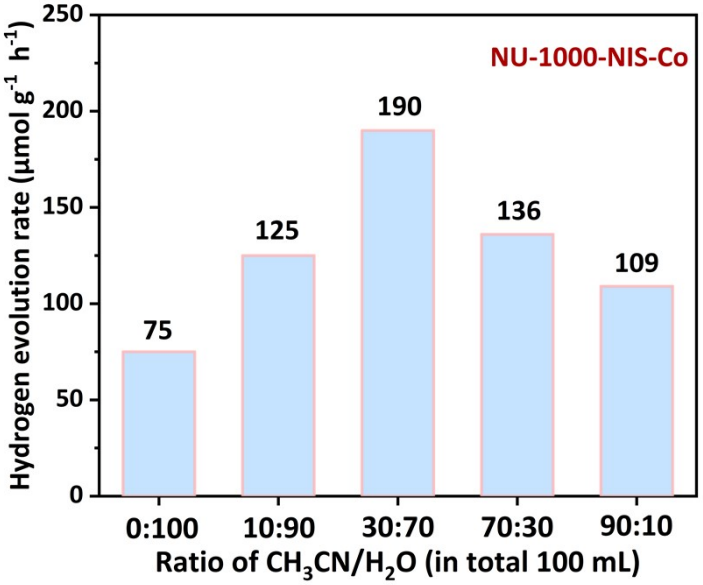

Fig. S8 The relationship between the ratio of CH_3CN/H_2O and the photocatalytic hydrogen evolution rate.

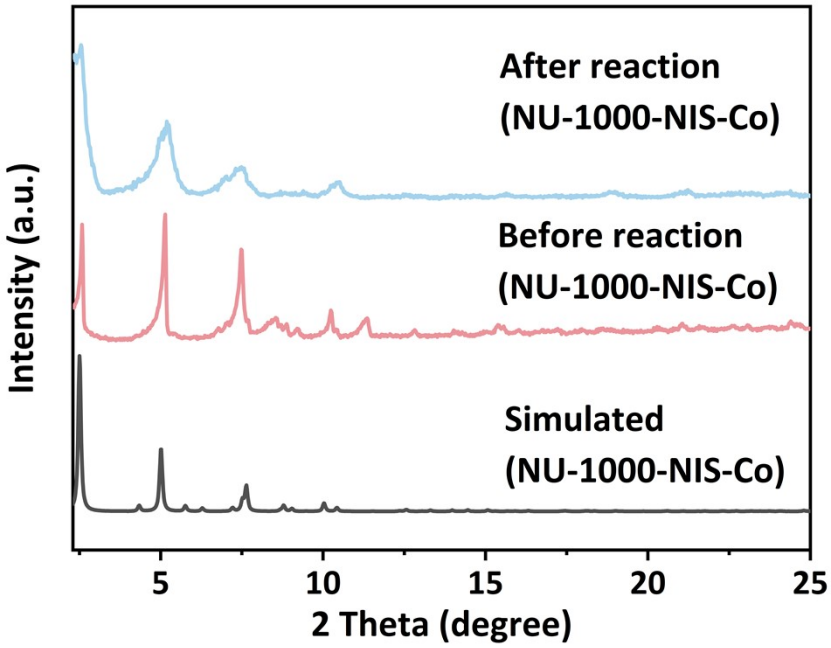

Fig. S9 The PXRD patterns of NU-1000-NIS-Co after photocatalysis.

S2. Supplementary Table

Table S1: Crystal data and structure refinements of NU-1000-NBDC

Identification Code	NU-1000-NBDC
CCDC	2537622
Empirical formula	$C_{48}H_{26}NO_{16}Zr_3$
Formula weight	1146.40
Temperature (K)	293(2)
Crystal system	hexagonal
Space group	*P*-62m
Unit cell dimensions	*a* = 40.70(18) Å
	c = 15.33(15) Å
Volume (Å^3), Z	21989(289)
Density (calculated)	0.519 g/cm^3
F(000)	1227.0
Radiation	transmission electron microscope (λ = 0.0251)
2θ range for data collection/°	0.192 to 1.798
Index ranges	$-50 \leq h \leq 50$, $-43 \leq k \leq 43$, $-19 \leq l \leq 19$
Reflections collected	68152
Data/restraints/parameters	15658/150/106
Goodness-of-fit on F^2	1.119
Final R indexes [I>=2σ (I)]	R_1 = 0.2628, wR_2 = 0.5312
Final R indexes [all data]	R_1 = 0.4626, wR_2 = 0.6252
Largest diff. peak/hole / e Å^{-3}	0.38/-0.32

Table S2. The unit cell parameters of NU-1000, NU-1000-NBDC and NU-1000-NIS-Co.

MOFs	*a*/Å	*b*/Å	*c*/Å	*α*/°	*β*/°	*γ*/°
NU-1000	39.62	39.62	16.64	90	90	120
NU-1000-NBDC	40.70	40.70	15.33	90	90	120
NU-1000-NIS-Co	40.59	40.59	15.48	90	90	120

Table S3. ICP-OES results of NU-1000-NIS-Co before and after photocatalytic reaction.

Samples	**Zr (wt%)**	**Co (wt%)**
NU-1000-NIS-Co (before photocatalytic reaction)	23.12	1.84
NU-1000-NIS-Co (after photocatalytic reaction)	23.59	1.76