Electronic Supplementary Information

In-situ construction of hydrazone-linked COF-based core-shell hetero-frameworks for enhanced photocatalytic hydrogen evolution

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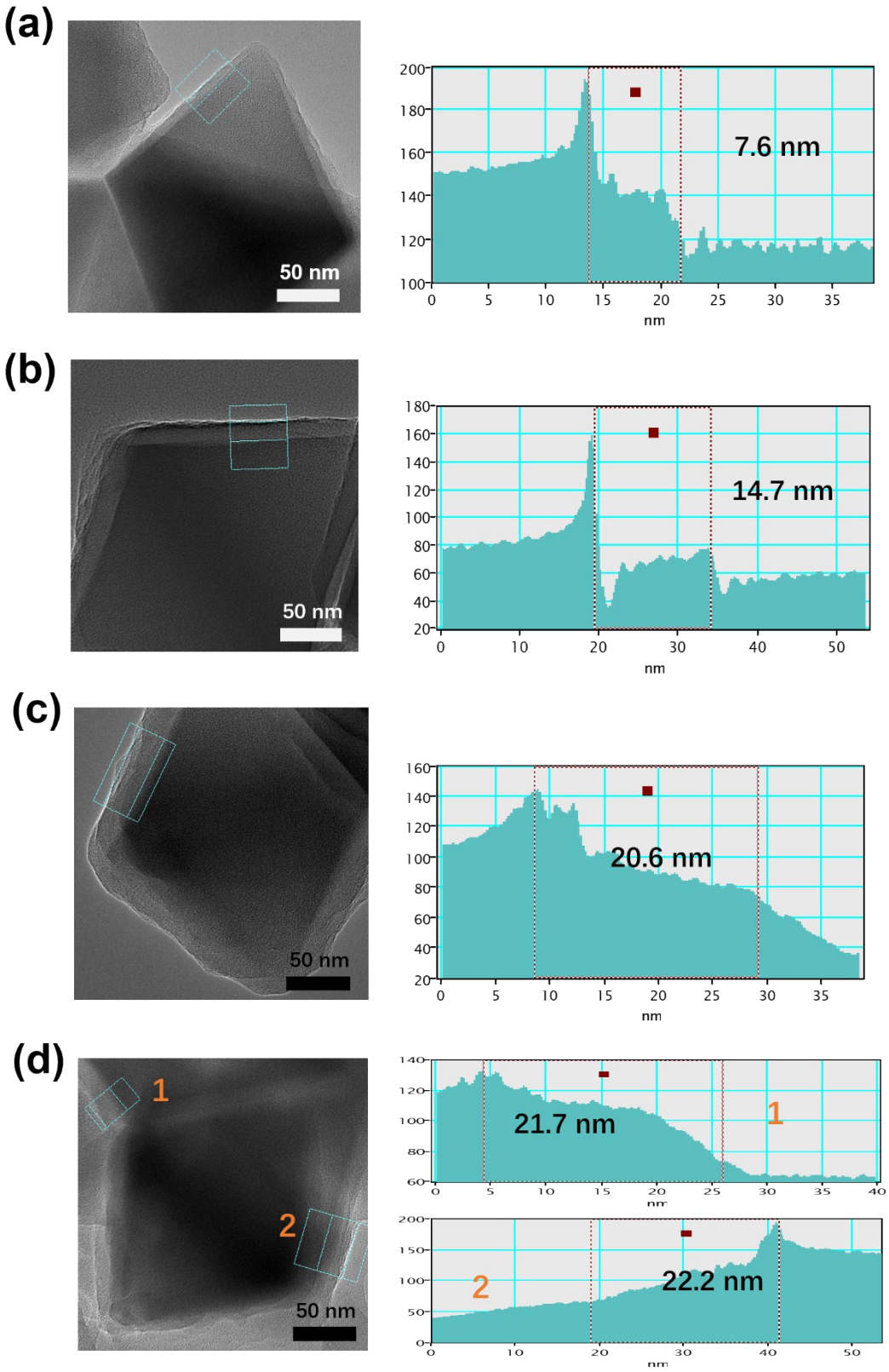

Fig. S1. TEM images (a) U@TDE1, (b) U@TDE2, (c) U@TDE4 and (d) U@TDE6. The right of each TEM image is the thickness profile of boxed regions obtained by Digital Micrograph software.

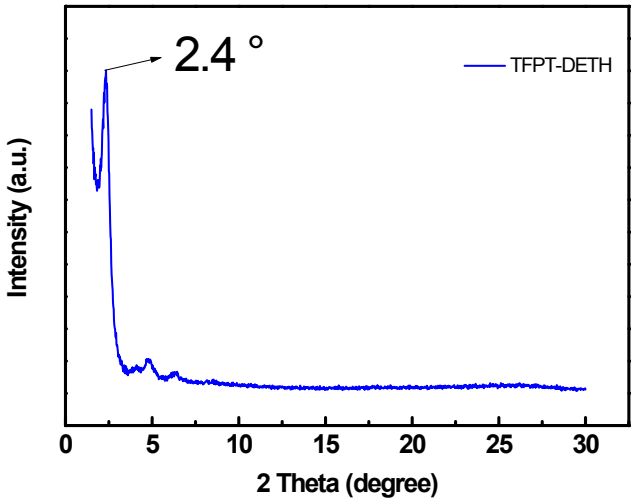

Fig. S2. Small-angle XRD patterns of TFPT-DETH.

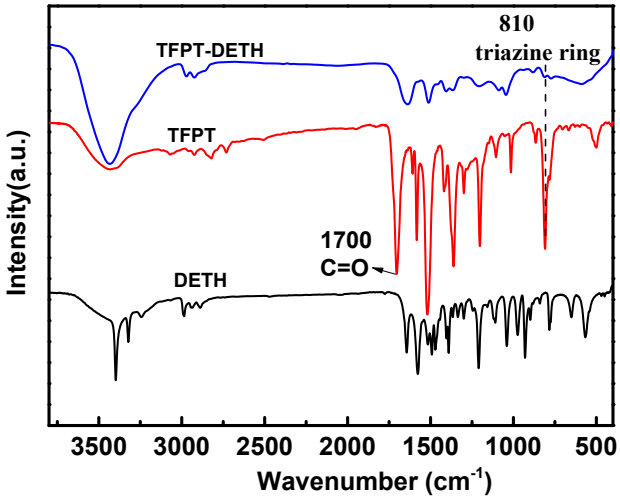

Fig. S3. FT-IR spectra of TFPT, DETH and TFPT-DETH.

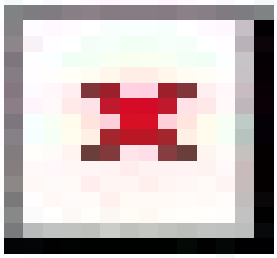

Fig. S4. Solid state ^{13}C NMR spectra of TFPT-DETH and U@TDE4.

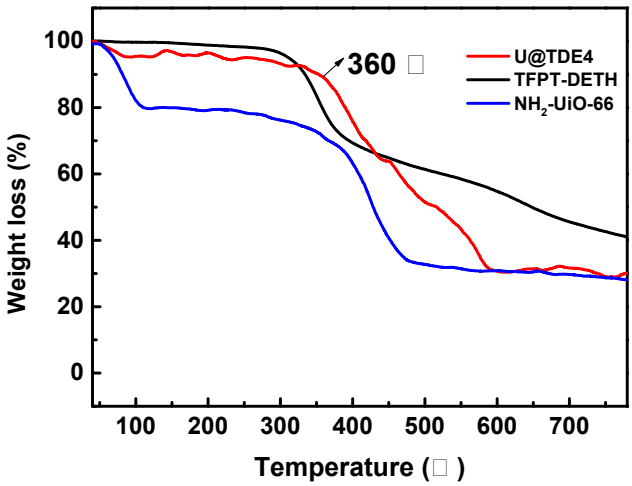

Fig. S5. TGA curves of NH_2-UiO66, TFPT-DETH and U@TDE4.

Table S1. Photocatalytic hydrogen evolution activity of the U@TDE4 hetero-framework compared with published work of pure COFs and COF-based photocatalysts.

Catalyst	Co catalyst	Sacrificial agent	Solvent	Illumination	Activity ($\mu molg^{-1}h^{-1}$)	AQE	Ref
CdS NPs/CTF-1	Pt	Lactic acid	Water	≥420 nm, 300 W	12150	□	1
CTF-BT/Th-1	Pt	TEOA	Water	≥ 420 nm, 300 W	6600	7.3% at 420 nm	2
CdS/TPPA-2	Pt	Lactic acid	Water	≥ 420 nm, 400 W	3678	□	3
TiO_2@BpZn-COP	Pt	TEOA	Water	≥420 nm, 300 W	1333	2.5% at 420 nm	4
NH_2-MIL-125(Ti)/B-CTF-1	Pt	TEOA	Water	≥ 420 nm, 300 W	360	□	5
FS-COF	Pt	SA	Water	≥ 420 nm, 300 W	10100	3.2% at 420 nm	6
TpPa-1-COF	MoS_2	SA	Water	≥ 420 nm, 300 W	5585	0.76% at 420 nm	7
g-$C_{40}N_3$-COF	Pt	TEOA	Water	≥420 nm, 300 W	4120	4.84% at 420nm	8
COP-TF@ CNi_2P	CNi_2P	Na_2SO_3/Na_2S	Seawater	≥ 400 nm, 300 W	2500	□	9
NUS-55*	$[Co(bpy)_3]Cl_2$	TEA	Water/Ethanol	≥420 nm, 300 W	2480		10
TFPT-COF*	Pt	TEOA	Water	≥420 nm, 300 W	1970	2.2% at 400 nm	11

TpPa-2-COF	$Ni(OH)_2$	SA	PBS Buffer	≥420 nm, 300 W	1896	□	12
N_3-COF	Pt	TEOA	PBS Buffer	≥420 nm, 300 W	1703	0.15% at 400 nm	13
TpDTz-COF	Ni-thiolate	TEOA	Water	AM 1.5	941	□	14
TTR-COF*	Au	TEOA	Water	≥420 nm, 300 W	430	□	15
TP-BDDA-COF	Pt	TEOA	Water	≥ 395 nm, 300 W	324	1.30% at 420 nm	16
COF-42*	$[Co(dmgH)_2pyCl]$	TEOA	ACN/Water	AM1.5	233	□	17
A-TEBPY-COF	Pt	TEOA	PBS Buffer	AM 1.5	98	□	18
PTP-COF	Pt	TEOA	PBS Buffer	AM 1.5	83.83	□	19
U@TDE4	Pt	SA	PBS Buffer	≥420 nm, 300 W	7178	1.11% at 420 nm	This work
TFPT-COF	Pt	SA	PBS Buffer	≥420 nm, 300 W	2301	□	This work

* represents hydrazone-linked COFs.

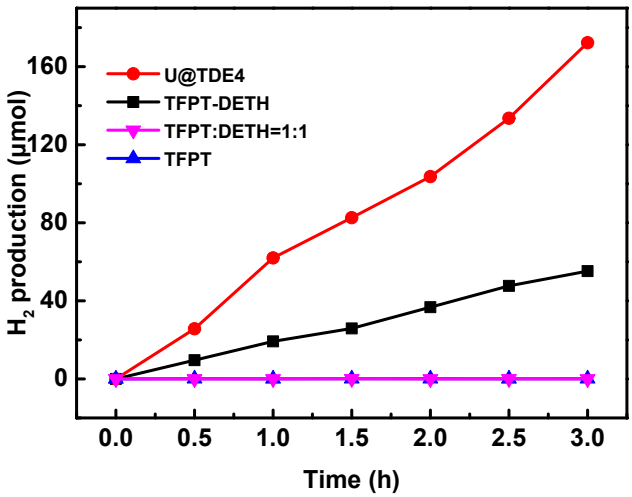

Fig. S6. Hydrogen evolution curves of TFPT, physical mixture of DETH and TFPT (1: 1), TFPT-DETH and U@TDE4 under visible light irradiation (λ≥420 nm).

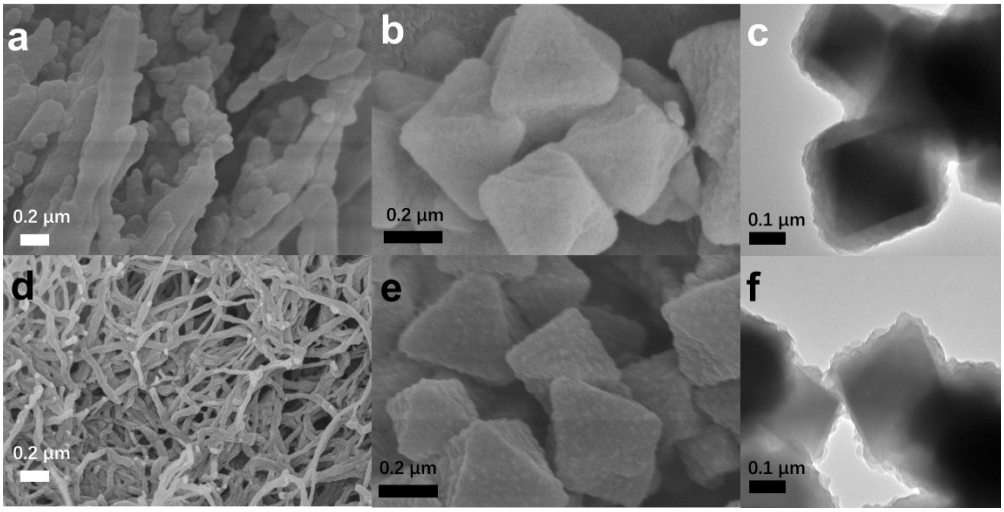

Fig. S7. SEM images of (a) TFPT-DMTH and (b) U@TDM4; (c) TEM images of U@TDM4; SEM images of (d) TFPT-DPP and (e) U@TDP4; (f) TEM images of U@TDP4.

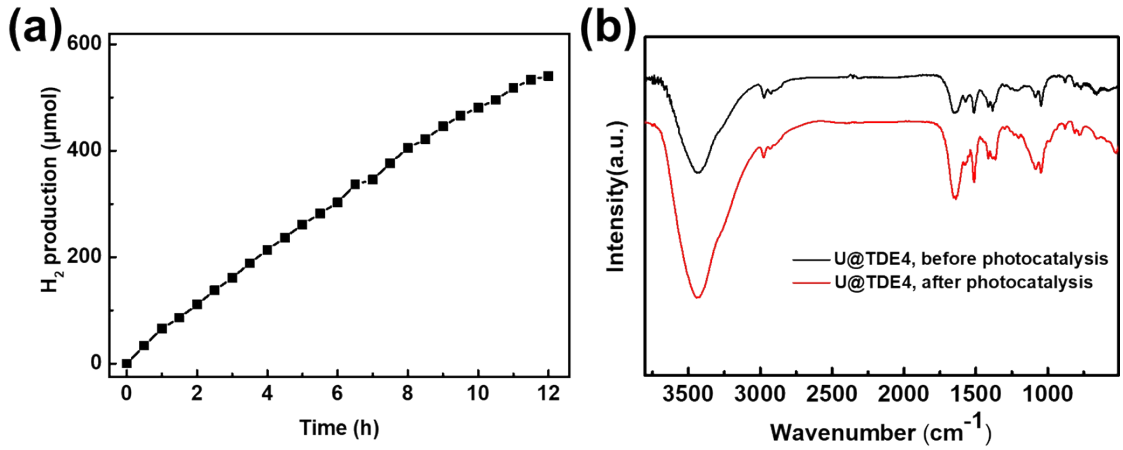

Fig. S8. (a) Long-term hydrogen evolution curve over U@TDE4 under visible light (≥420 nm) irradiation; (b) FTIR spectra of U@TDE4 before and after photocatalysis for 12 h.

Notes and references

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