Electronic Supplementary Information (ESI)

Bandgap Engineering of Covalent Organic Frameworks for Boosting Photocatalytic Hydrogen Evolution from Water

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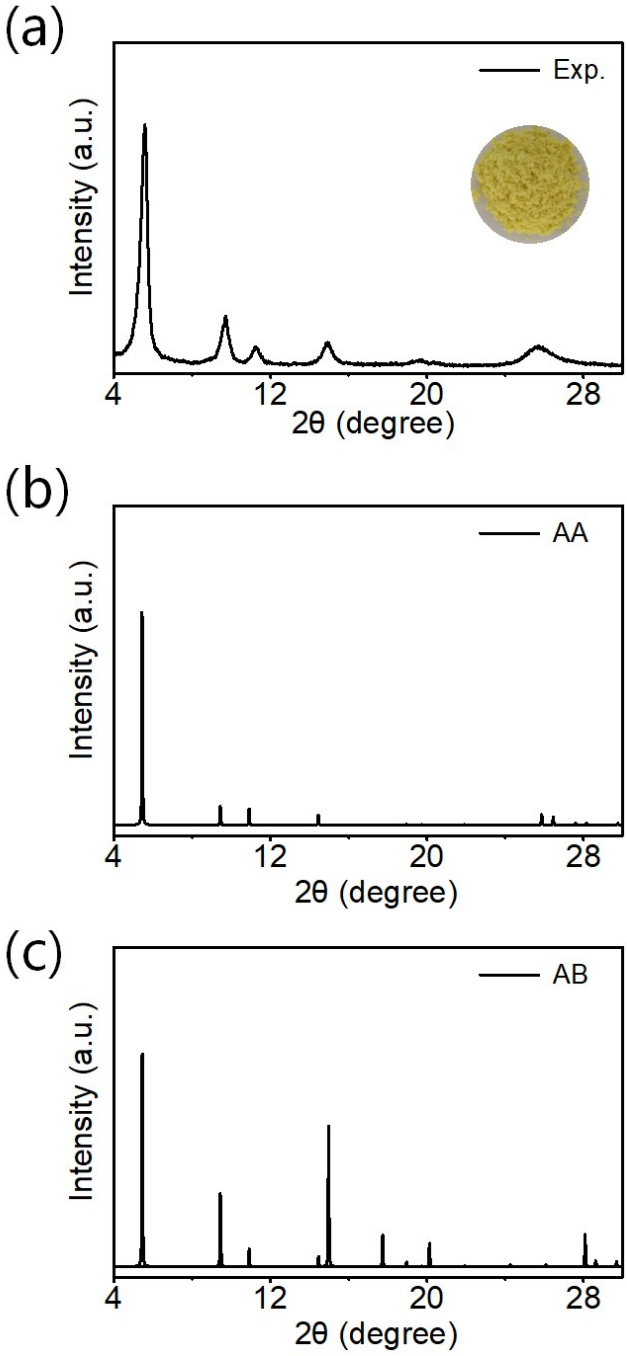

Fig. S1. PXRD patterns with corresponding powder photo for **COF-OH-0** in experimental (a), simulated with AA stacking mode (b) and for simulated with AB stacking mode (c).

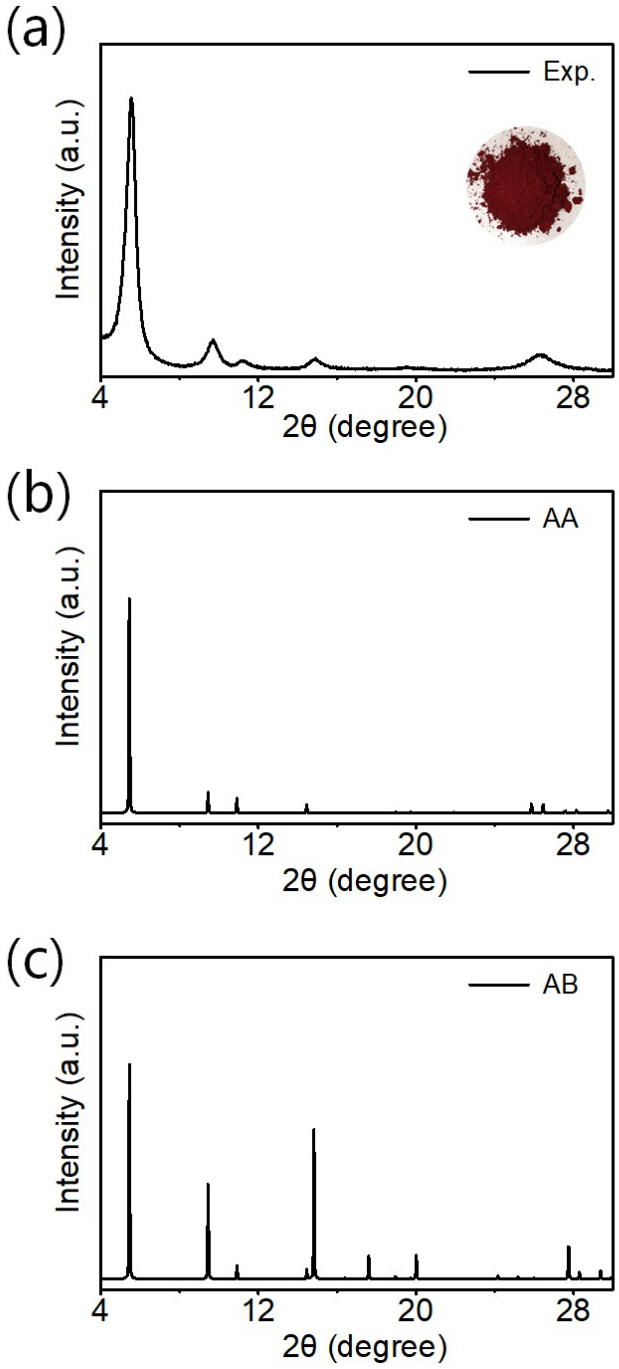

Fig. S2. PXRD patterns with corresponding powder photo for **COF-OH-1** in experimental (a), simulated with AA stacking mode (b) and for simulated with AB stacking mode (c).

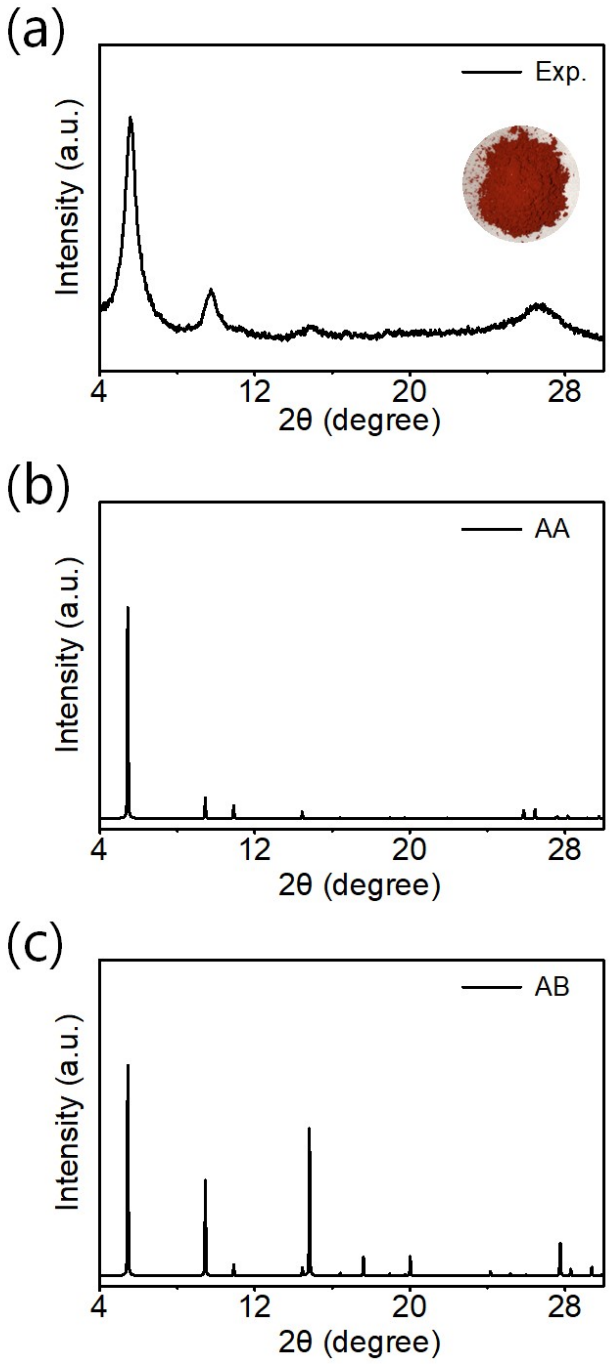

Fig. S3. PXRD patterns with corresponding powder photo for **COF-OH-2** in experimental (a), simulated with AA stacking mode (b) and for simulated with AB stacking mode (c).

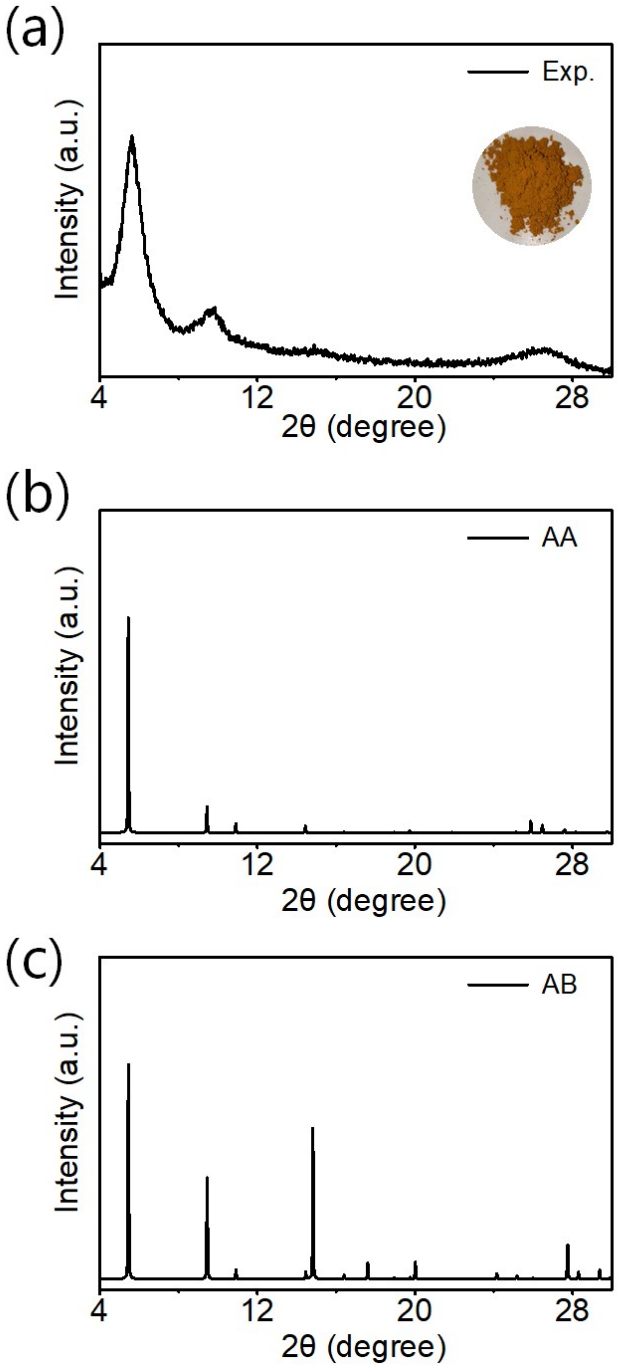

Fig. S4. PXRD patterns with corresponding powder photo for **COF-OH-3** in experimental (a), simulated with AA stacking mode (b) and for simulated with AB stacking mode (c).

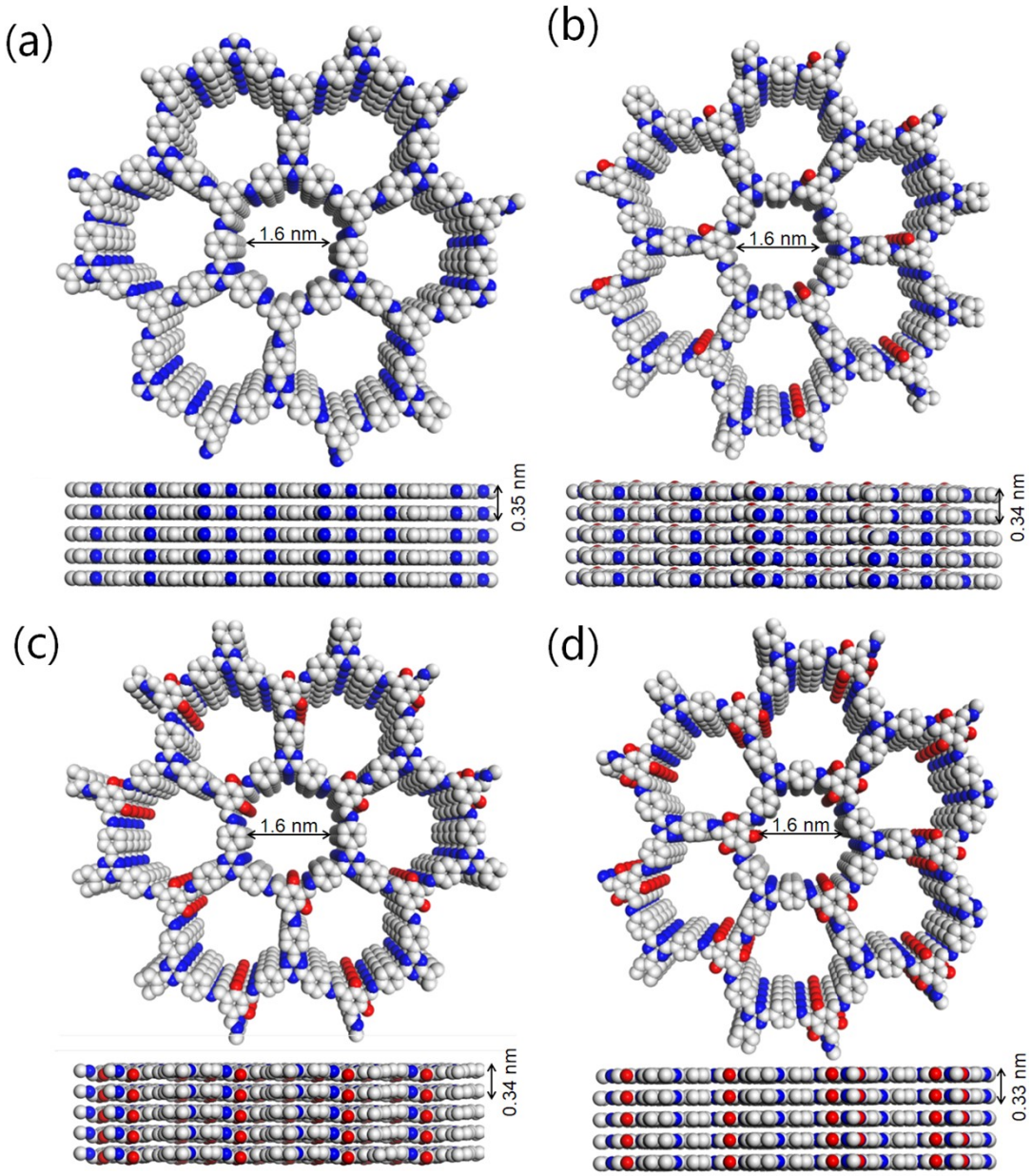

Fig. S5. Simulated packing structures (O: red; N: blue; C: white; hydrogen were omitted for clarity) for **COF-OH-0** (a), **COF-OH-1** (b), **COF-OH-2** (c), **COF-OH-3** (d), respectively.

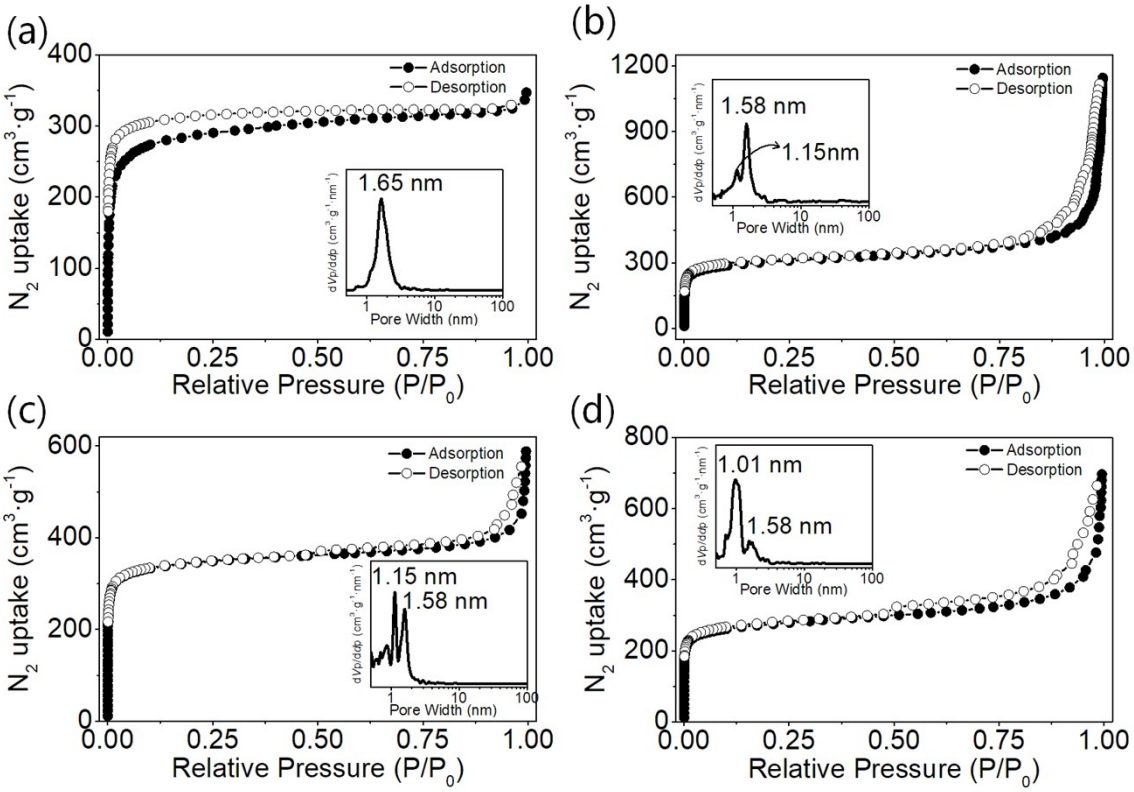

Fig. S6. N_2 adsorption (filled symbols) and desorption (open symbols) isotherm with the pore size distribution (inset) for **COF-OH-0** (a), **COF-OH-1** (b), **COF-OH-2** (c), **COF-OH-3** (d), respectively.

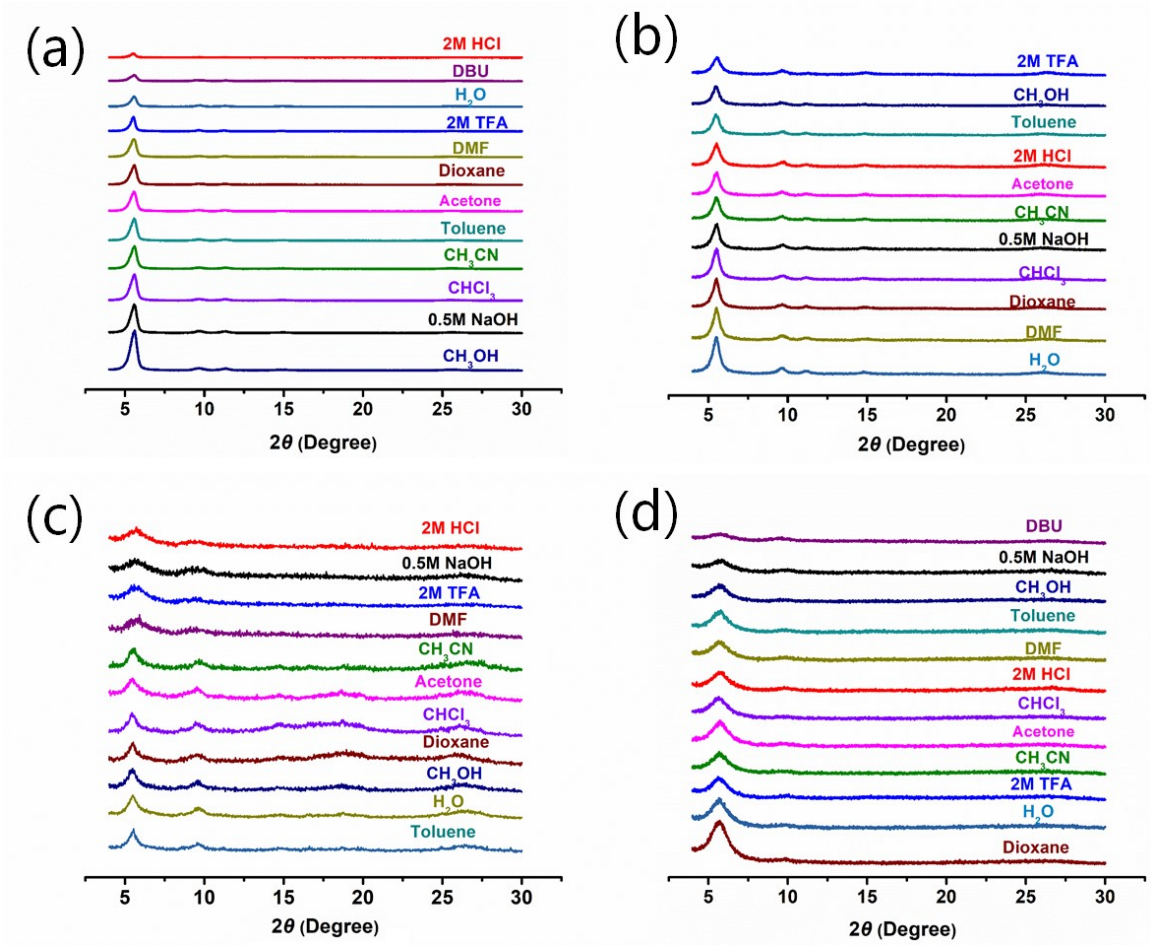

Fig. S7. Experimental PXRD patterns after 3-day exposure to various solvents for **COF-OH-0** (a), **COF-OH-1** (b), **COF-OH-2** (c), **COF-OH-3** (d), respectively.

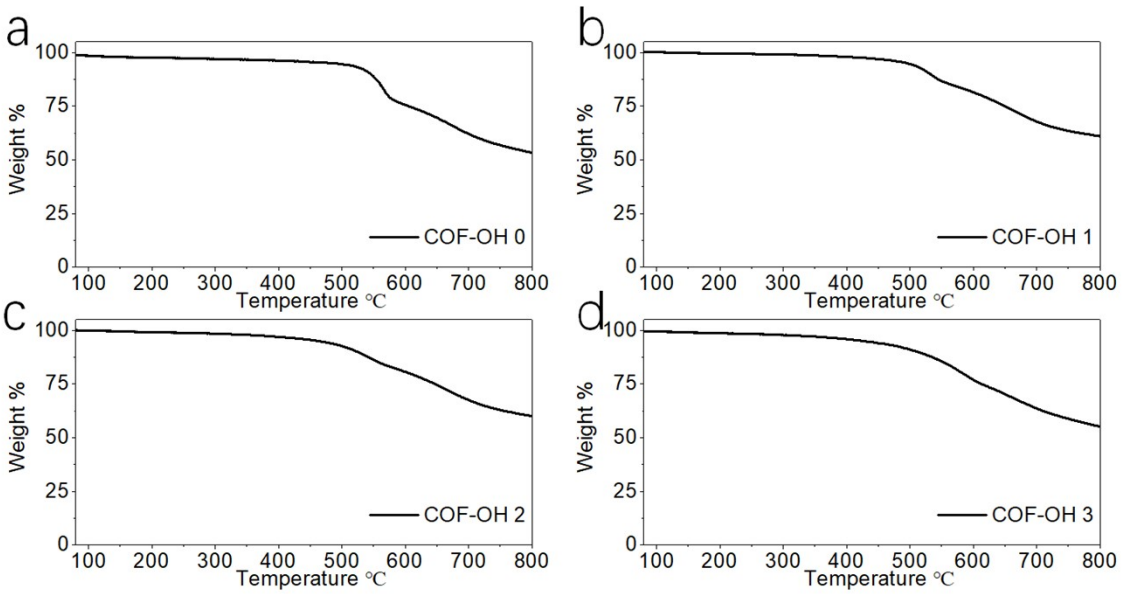

Fig. S8. The thermogravimetric analysis (TGA) plot of **COF-OH-0** (a), **COF-OH-1** (b), **COF-OH-2** (c), **COF-OH-3** (d), respectively.

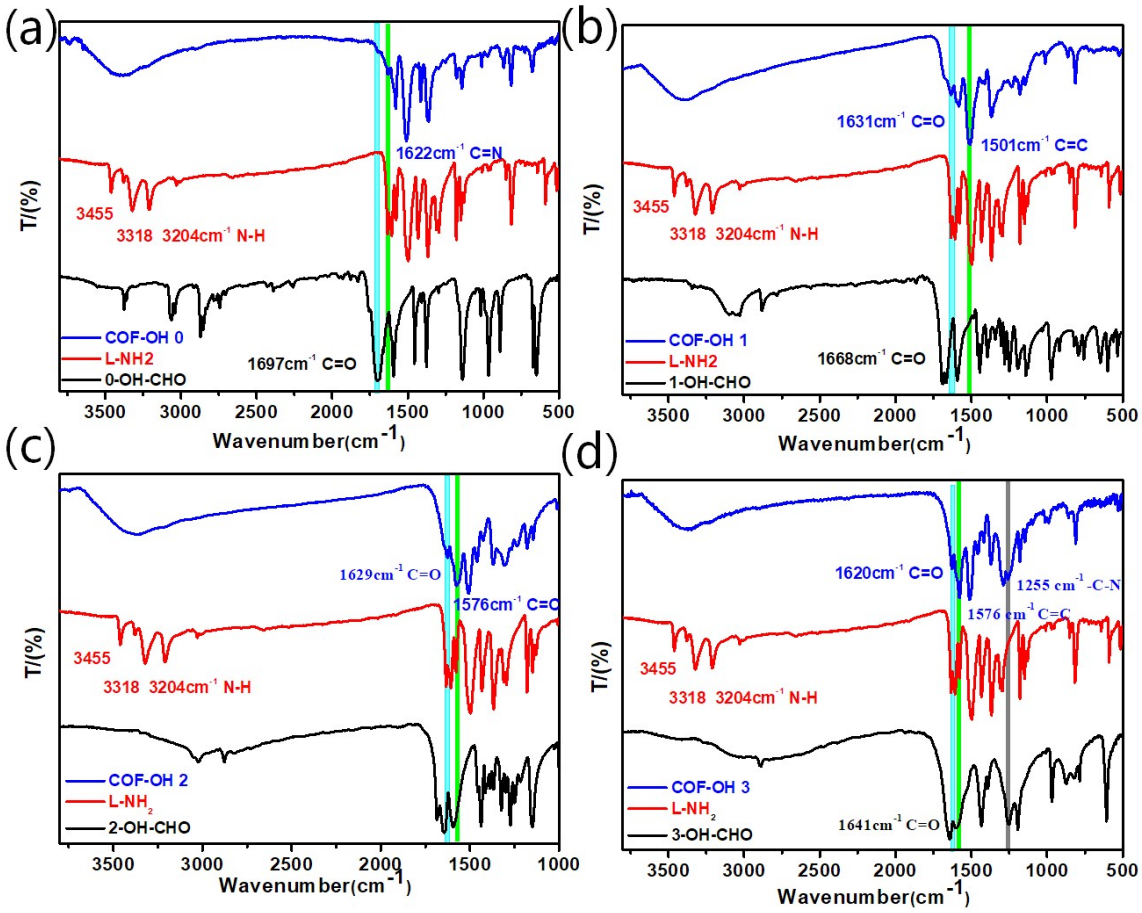

Fig. S9. FT-IR spectra of the four COFs with their corresponding precursors **COF-OH-0** (a), **COF-OH-1** (b), **COF-OH-2** (c), **COF-OH-3** (d), respectively.

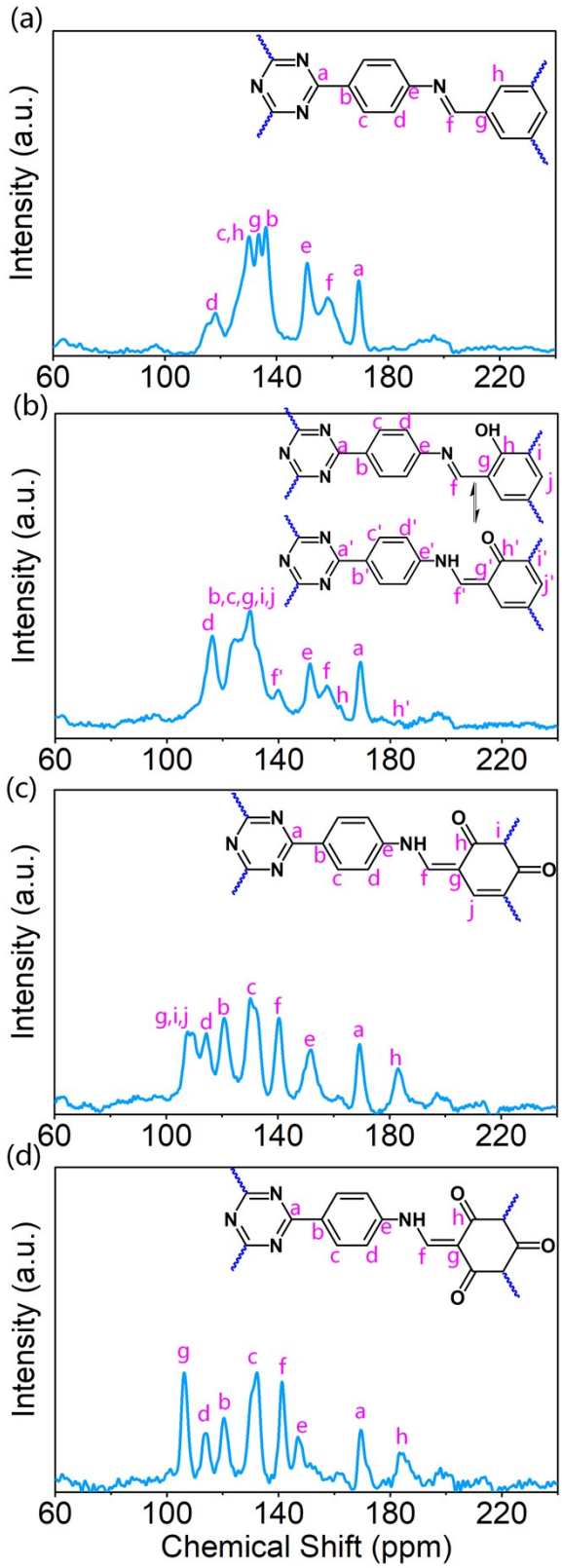

Fig. S10. CP/MAS ^{13}C solid-state NMR spectra of **COF-OH-0** (a), **COF-OH-1** (b), **COF-OH-2** (c), **COF-OH-3** (d), respectively.

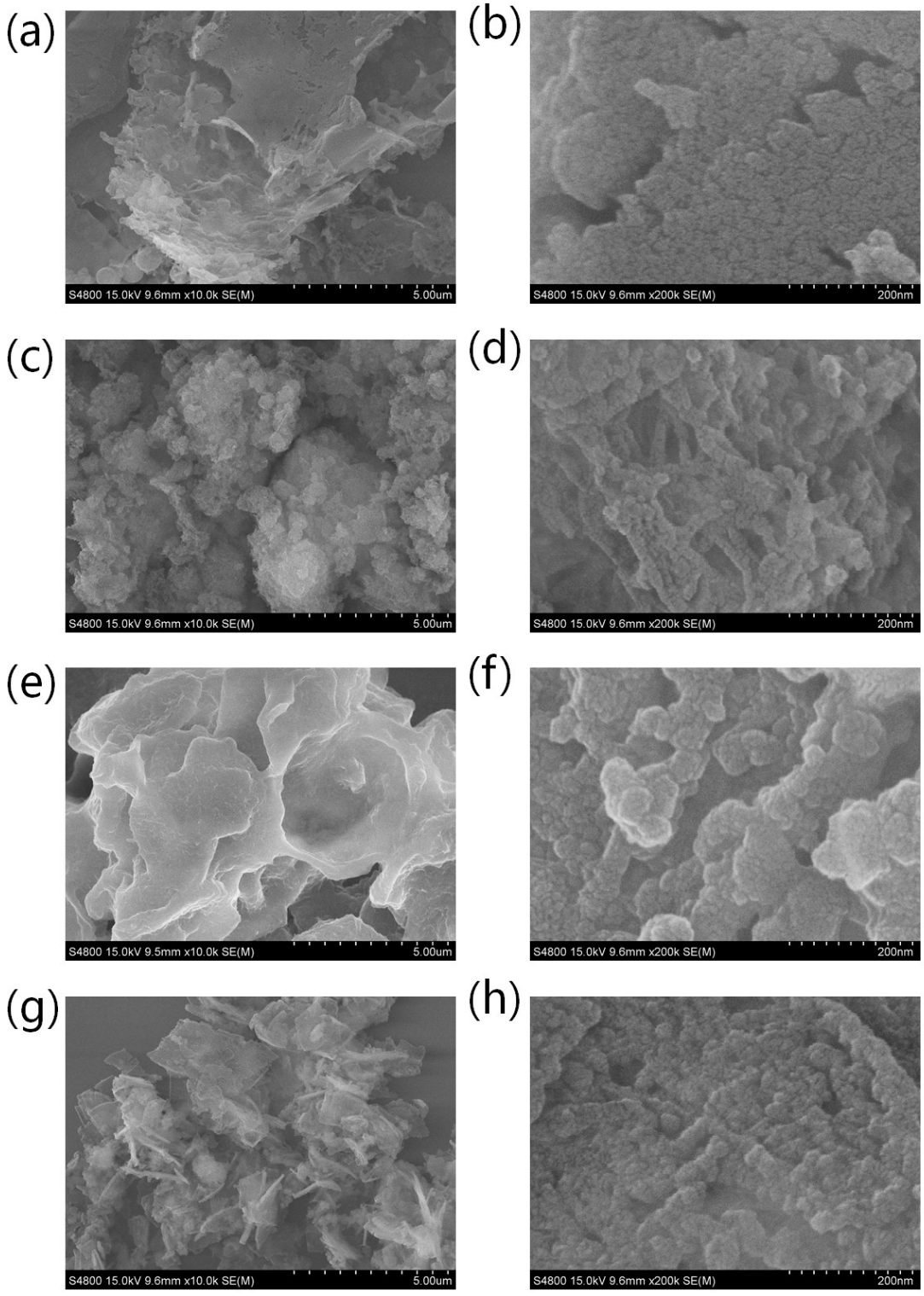

Fig. S11. SEM images of **COF-OH-0** (a, b), **COF-OH-1** (c, d), **COF-OH-2** (e, f), **COF-OH-3** (g, h), respectively.

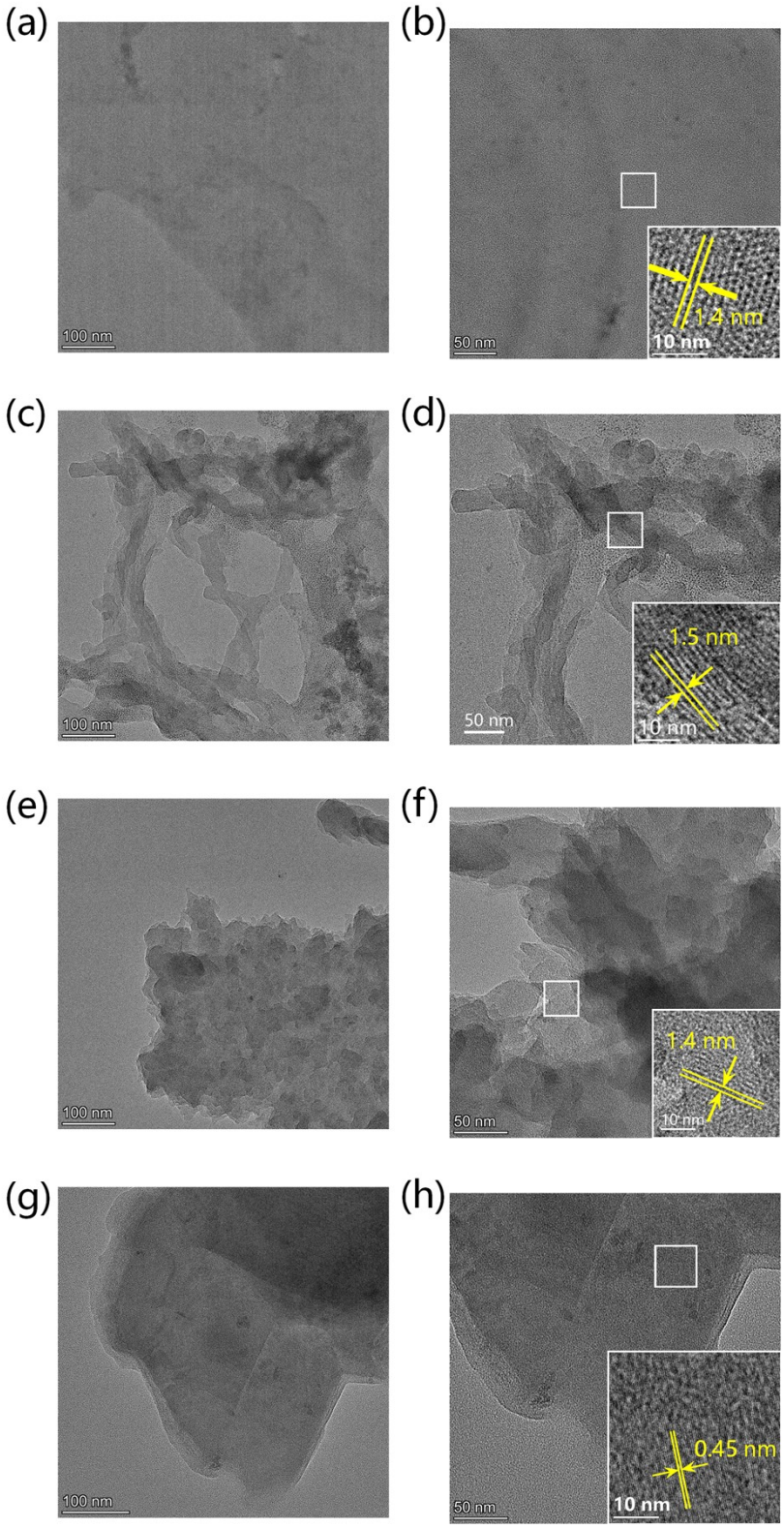

Fig. S12. TEM images with the lattice fringes (inset of the right one) for **COF-OH-0** (a, b), **COF-OH-1** (c, d), **COF-OH-2** (e, f), **COF-OH-3** (g, h), respectively.

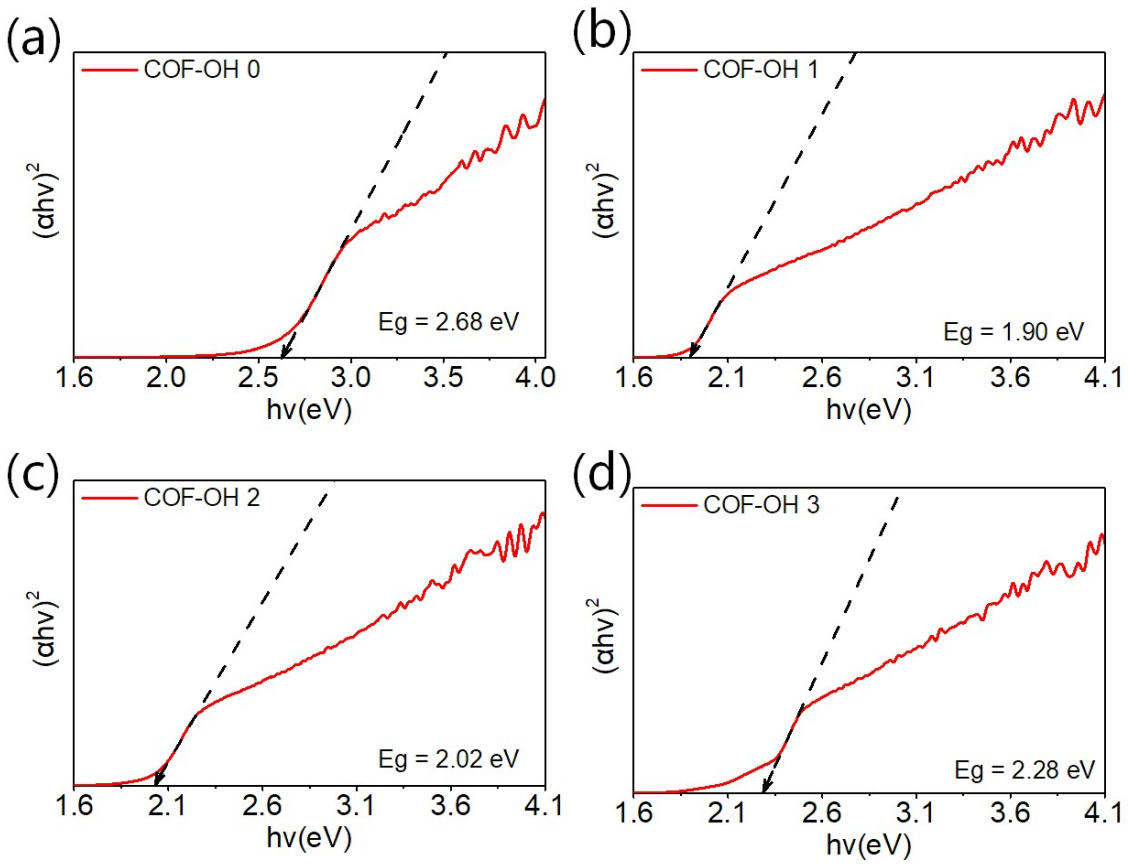

Fig. S13. The Tauc plots for the band gaps of **COF-OH-0** (a), **COF-OH-1** (b), **COF-OH-2** (c), **COF-OH-3** (d), respectively.

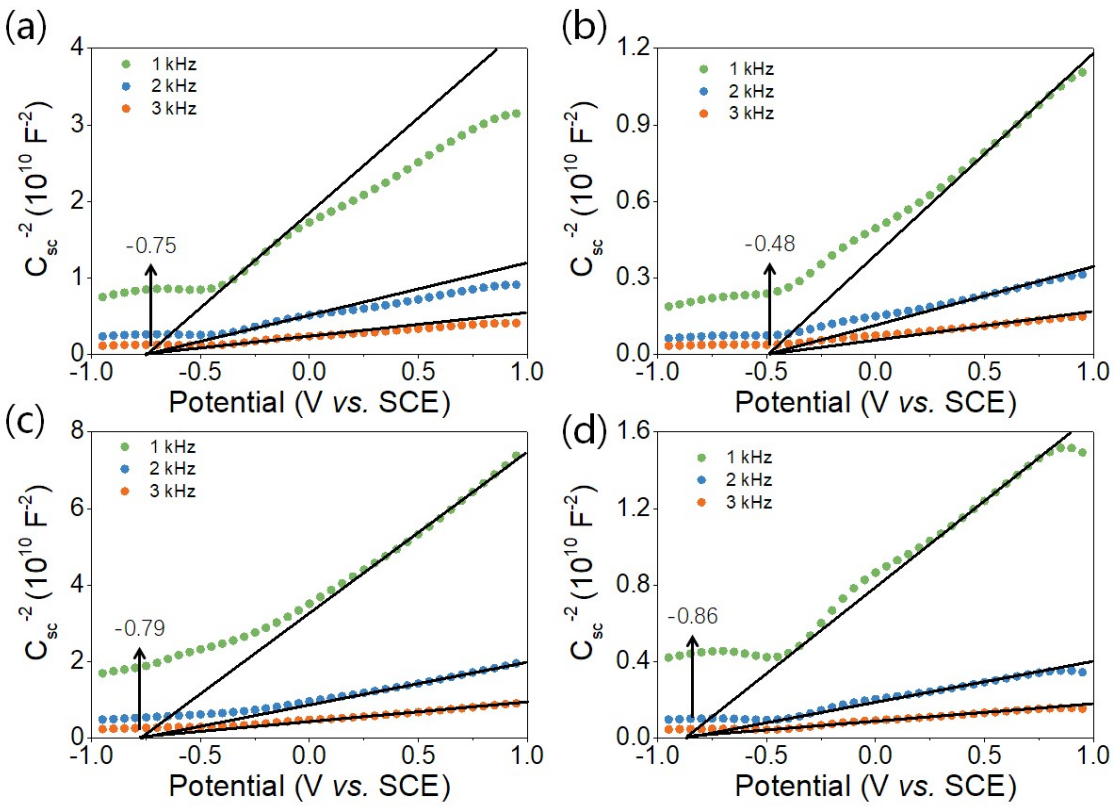

Fig. S14. Mott-Schottky plots for **COF-OH-0** (a), **COF-OH-1** (b), **COF-OH-2** (c), **COF-OH-3** (d), respectively.

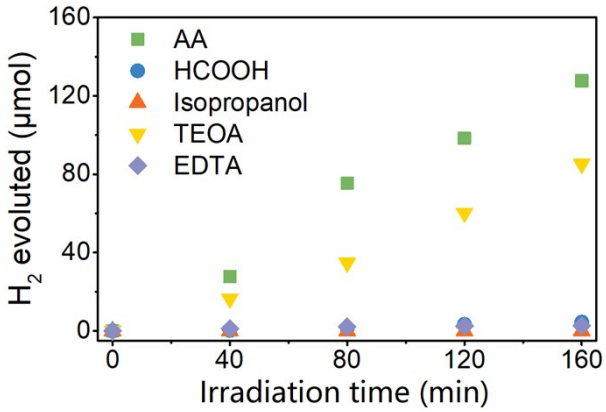

Fig. S15. Hydrogen evolution plots for **COF-OH-3** with 1% Pt using different sacrificial electron donor reagents (AA: ascorbic acid; TEOA: triethanolamine; EDTA: ethylenediaminetetraacetic acid disodium salt dihydrate).

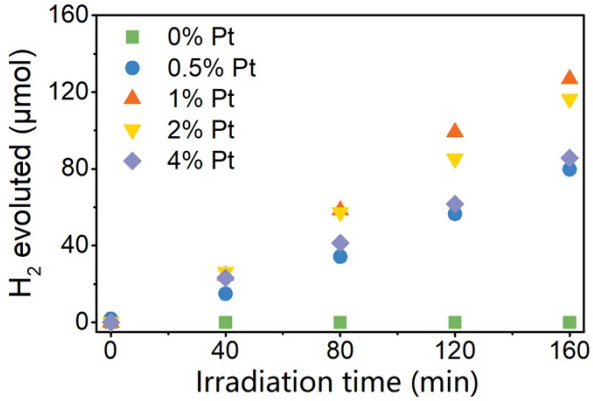

Fig. S16. Hydrogen evolution plots for **COF-OH-3** using ascorbic acid as sacrificial electron donor reagents with different platinum contents.

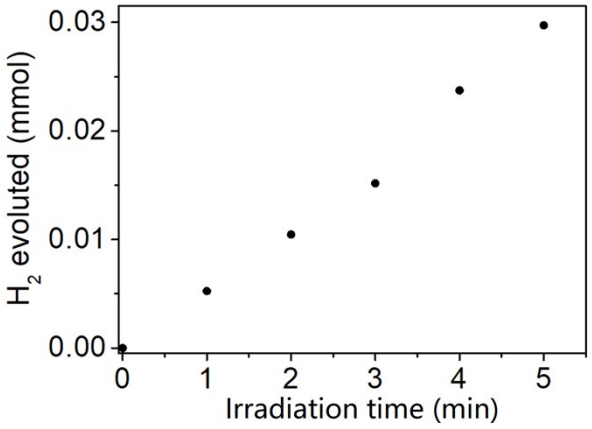

Fig. S17. Time course for photocatalytic H_2 production of **COF-OH-3** (50 mg of catalyst with 1 wt % Pt in 50 mL 0.1 M ascorbic acid aqueous solution) under λ = 420 nm light (300 W Xe lamp equipped with a band-pass filter λ = 420 nm).

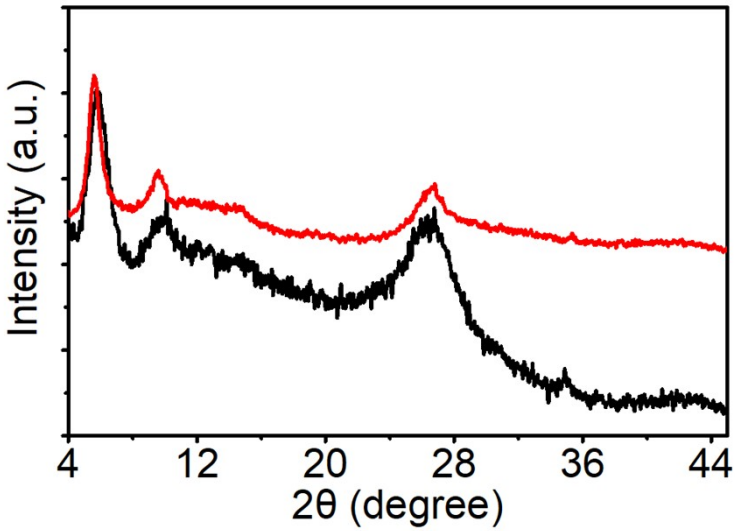

Fig. S18. PXRD patterns for **COF-OH-3** before (red line) and after (black line) the 30 hours irradiation reaction.

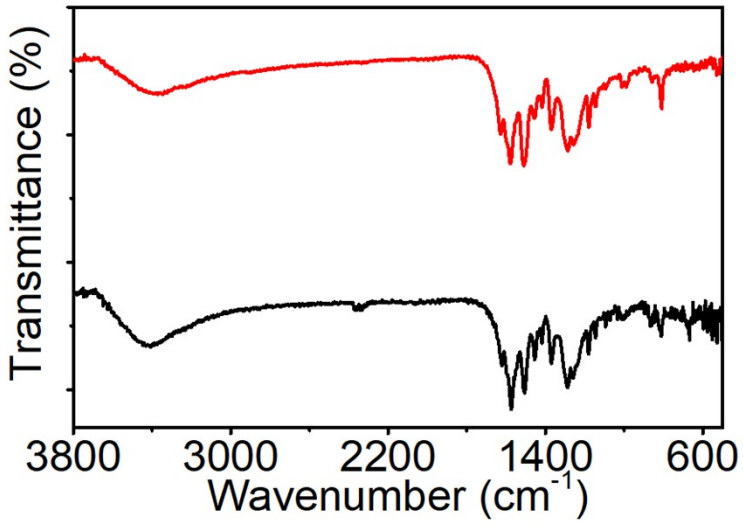

Fig. S19. FT-IR spectrum for **COF-OH-3** before (red line) and after (black line) the 30 hours irradiation reaction.

Table S1. Experiment PXRD data for **COF-OH-0–3**.

Samples	**COF-OH-0**	**COF-OH-1**	**COF-OH-2**	**COF-OH-3**
(100)	5.58°	5.54°	5.58°	5.64°
(110)	9.72°	9.70°	9.74°	9.86°
(200)	11.26°	11.16°	11.24°	–
(210)	14.98°	14.92°	14.74°	14.88°
(220)	19.62°	19.61°	–	–
(001)	25.68°	26.28°	26.60°	26.32°

Table S2. The crystal structure and refinement data for **COF-OH-0–3**.

Sample	a, b, c (Å)	*α, β, γ* (°)	V (Å^3)	Space group	R_p, R_{wp}
COF-OH-0	18.7121 18.7121 3.4416	90 90 120	1043.6	*P*-6	12.47%, 9.39%
COF-OH-1	3.4131 18.7075 18.7075	120 90 90	1034.4	*P* 1	5.11%, 4.04%
COF-OH-2	3.4566 18.5924 18.5924	120 90 90	1034.8	*P* 1	5.03%, 3.99%
COF-OH-3	18.7251 18.7251 3.4397	90 90 120	1044.5	*P*-6	6.86%, 5.49%

Table S3. The flat band and band gap data for **COF-OH-0–3**[a].

Sample	Flat band (V)	Calculated valence band (V)	Band gap (eV)[b]
COF-OH-0	–0.51	2.17	2.68
COF-OH-1	–0.24	1.66	1.90
COF-OH-2	–0.55	1.47	2.02
COF-OH-3	–0.62	1.66	2.28

[a] All the potentials (V) have been calculated *vs.* SHE; [b] Calculated from the solid UV−vis diffuse reflectance spectra.

Table S4. Summary of the representative COFs as photocatalysts for photocatalytic hydrogen evolution under visible-light irradiation[a].

COFs	Sacrificial agent	HER ($mmol \cdot g^{-1} \cdot h^{-1}$)	Ref.
COF-JLU100	AA	100	1
CYANO-COF	AA	60.85	2
Tp-2C/BPy^{2+}-COF	AA	34.6	3
COF TtaTfa	AA	20.7	4
SonoCOF-3	AA	16.6	5
BTH-3	AA	15.1	6
COF TpaTfa	AA	14.9	4
NKCOF-108	AA	11.6	7
COF TtaTpa	AA	10.8	4
BTH-1	AA	10.5	6
FS-COF	AA	10.1	8
COF-OH-3	AA	9.89	This work
TF-HUST-A1	TEOA	9.2	9
Py-ClTP-BT-COF	AA	8.875	10
TP-COF	AA	8.42	11
TpPa-COF-$(CH_3)_2$	SA	8.33	12
TpPa-Cl_2	SA	7.6	13
TpPa-1-COF[b]	AA	5.585	14
TpPa-1	AA	5.479	14
CTF-HUST-C1	TEOA	5.1	15
S-COF	AA	4.44	8
TpPa-COF-CH_3	SA	3.07	12
COF-OH-2	AA	2.91	This work
Py-FTP-BT-COF	AA	2.875	10
sp^2c-COF_{ERDN}	TEOA	2.12	16
PyTz-COF	AA	2.0724	17
TFPT-COF	TEOA	1.97	18
N_3-COF	TEOA	1.703	19
TP-COF (Ref.[8])	AA	1.6	8
TpPa-COF	SA	1.56	12
sp^2c-COF	TEOA	1.36	16
TpPa-1-COF	SA	1.223	20
BTH-2	AA	1.2	6
NTU-BDA-THTA	AA	1.127	21
Py-HTP-BT-COF	AA	1.078	10
BT-TAPT-COF	AA	0.949	22
N_2-COF[c]	TEOA	0.782	23
BtCOF150	TEOA	0.75	24
N_2-COF	TEOA	0.438	19
N_2-COF[d]	TEOA	0.414	23
ZnPor-DETH-COF	TEOA	0.413	25

TP-BDDA	TEOA	0.324	26
COF-42	TEOA	0.233	23
TpPa-COF-NO_2	SA	0.22	12
COF(ERDN)	TEOA	0.212	16
N_3-COF[c]	TEOA	0.163	23
COF-OH-0	AA	0.11	This work
N_1-COF[c]	TEOA	0.1	23
A-TEBPY-COF	TEOA	0.098	27
N_1-COF	TEOA	0.09	19
BT-COF	AA	0.076	11
N_0-COF	TEOA	0.023	19

[a] The reactions were performed with Pt as co-catalyst; [b] The co-catalyst is MoS_2; [c] The co-catalyst is $[Co(dmgH)_2pyCl]$; [d] The co-catalyst is $[Co(dmgBF_2)_2(OH_2)_2]$; AA: Ascorbic acid; SA: Sodium ascorbate; TEOA: triethanolamine.

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