

A coumarin-linked conjugated covalent organic framework for enhanced photocatalytic hydrogen evolution

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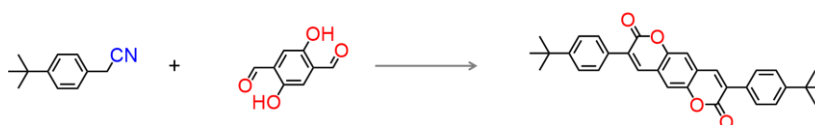
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Supplementary Methods

Reagents and Solvents

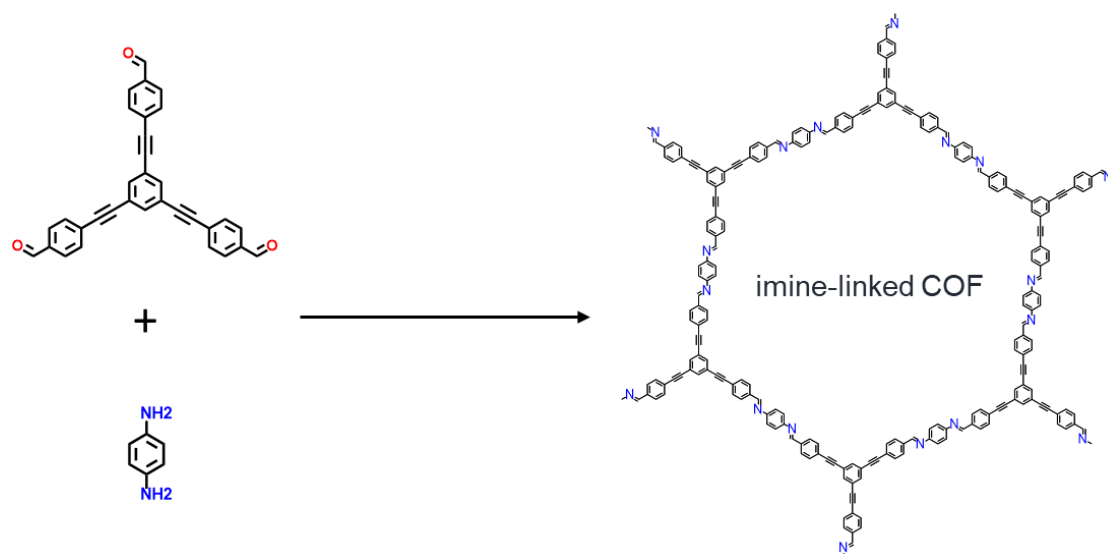
p-phenylenediamine, 1,4-phenylenediacetonitrile, 1,2-dichlorobenzene(98%), 1-butanol (AR, 99%), tetrahydrofuran (AR, 99%), N,N-dimethylformamide, 1,8-Diazabicyclo[5.4.0]undec-7-ene (DBU) were purchased from Shanghai Aladdin Biochemical Technology Co., Ltd. 1,4-phenylenediacetonitrile, 2,5-dihydroxyterephthalaldehyde, 1,3,5-tri(3-hydroxy-4-formylethynylphenyl)benzene, 4,4',4''-(benzene-1,3,5-triyltris(ethyne-2,1-diyl))tribenzaldehyde, were purchased from Bide Pharmatech Co., Ltd. All chemicals and solvents were used as received without further purification.

The synthetic procedures of model molecule. A Pyrex tube was charged with 4-tert-butylphenyl-acetonitrile (0.09 mmol, 15.59 mg) and 2,5-dihydroxyterephthalaldehyde (0.18 mmol, 29.9 mg) in a mixed solution of 1,2-dichlorobenzene and 1-butanol (v/v=3:7, 1 mL). The tube was sonicated for 5 minutes then added 3 M DBU (0.1 mL) as the base catalyst. The mixture was degassed by at least three “freeze-pump-thaw” cycles. After that, the tube was sealed under vacuum and heated at 120 °C for 1 day. When cooled to room temperature, the precipitate was isolated by filtration and washed with ethanol several times to afford the model compound (Yield: 89%). ¹H NMR (600 MHz, Chloroform-d) δ 7.84 (s, 2H), 7.69 (d, J = 8.3 Hz, 4H), 7.50 (d, J = 8.3 Hz, 4H), 7.49 (s, 2H), 1.36 (s, 18H).



Scheme S1. The synthesis of model molecule.

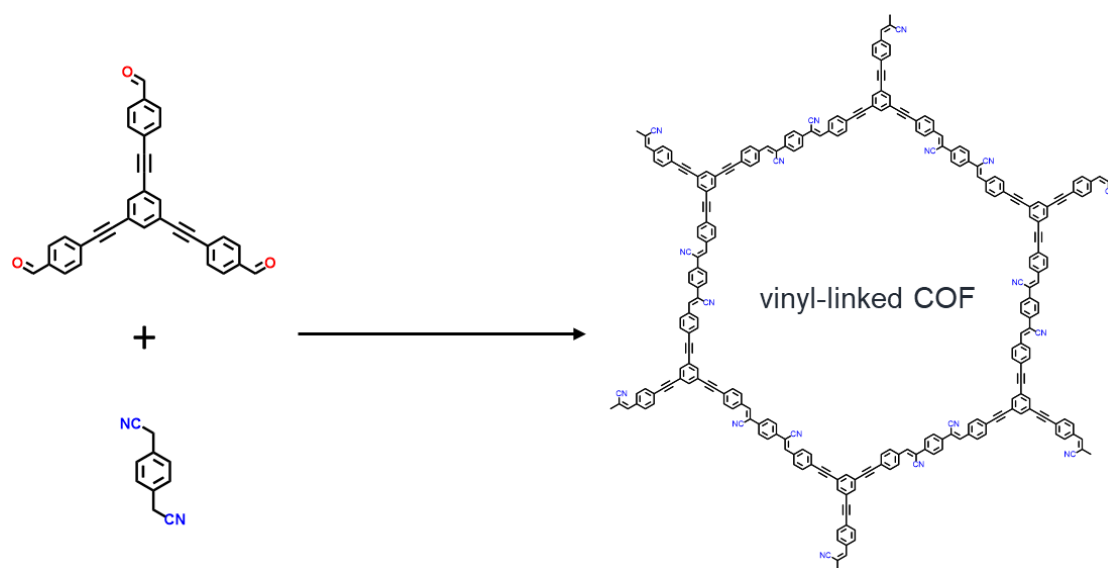
The synthetic procedures of imine-linked COF. A quartz tube was charged with 4,4',4''-(benzene-1,3,5-triyltris(ethyne-2,1-diyl))tribenzaldehyde (0.03 mmol, 13.88 mg) and p-phenylenediamine (0.045 mmol, 4.87 mg) in a mixed solution of 1,2-dichlorobenzene and 1-butanol (v/v=5:5, 1 mL). The tube was sonicated for 5 minutes then added 6 M acetic acid (0.1 mL) as the catalyst. The mixture was degassed by at least three “freeze-pump-thaw” cycles. After that, the tube was sealed under vacuum and heated at 120 °C for 3 days. When cooled to room temperature, the precipitate was isolated by filtration and washed with DMF and THF several times until the filtrate was colorless. The resulting solid was further extracted with THF and finally dried at 60 °C under vacuum to yield a yellow powder in 90%¹.



Scheme S2. The synthesis of imine-linked COF.

The synthetic procedures of vinyl-linked COF. A quartz tube was charged with 4,4',4''-(benzene-1,3,5-triyltris(ethyne-2,1-diyl))tribenzaldehyde (0.03 mmol, 13.88 mg) and 1,4-phenylenediacetonitrile (0.045 mmol, 7.03 mg) in a mixed solution of 1,2-dichlorobenzene and 1-butanol (v/v=7:3, 1 mL). The tube was sonicated for 5 minutes

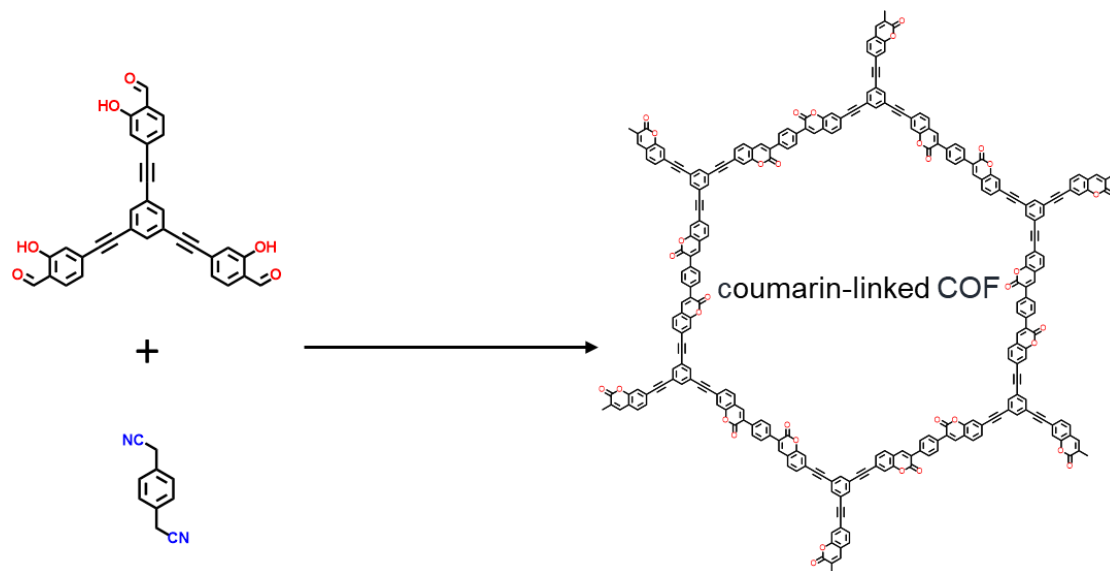
then added 3 M DBU (0.1 mL) as the base catalyst. The mixture was degassed by at least three “freeze-pump-thaw” cycles. After that, the tube was sealed under vacuum and heated at 150 °C for 3 days. When cooled to room temperature, the precipitate was isolated by filtration and washed with DMF and THF several times until the filtrate was colorless. The resulting solid was further extracted with THF and finally dried at 60 °C under vacuum to yield a yellow powder in 87%.



Scheme S3. The synthesis of vinyl-linked COF.

The synthetic procedures of coumarin-linked COF. A quartz tube (10 mL) was charged with 1,3,5-tri(3-hydroxy-4-formylethynylphenyl)benzene (0.03 mmol, 15.3 mg) and 1,4-phenylenediacetonitrile (0.045 mmol, 7.03 mg) in a solution of 1-butanol (0.7 mL). The tube was sonicated for 5 minutes and then added 1,2-dichlorobenzene (0.3 mL). After mixing evenly, 3 M DBU (0.1 mL) was added as the base catalyst. The mixture was degassed by at least three “freeze-pump-thaw” cycles for 15 minutes. After that, the tube was sealed under vacuum and heated at 120 °C for 5 days. When cooled to room temperature, the precipitate was isolated by filtration and washed with DMF

(10 mL) and THF (10 mL) 5 times until the filtrate was colorless. The resulting solid was further extracted with THF and finally dried at 60 °C under vacuum to yield an orange-red powder in 85%².



Scheme S4. The synthesis of coumarin-linked COF.

Supplementary Notes

Supplementary Note 1: Band structure measurement.

First, we measured the UV-vis absorption spectra and calculated the bandgap of three COFs by the Tauc equation.

$$(\alpha h\nu)^{n/2} = A(h\nu - E_g)$$

Where h is the Planck constant, ν is the frequency of light, A is the proportionality constant, α is the absorbance index, and E_g is the bandgap. For direct semiconductors, $n=1$.^{3,4}.

The valence band (VB) is calculated by VB-XPS and conduction band (CB) was calculated by the equation:

$$E_{CB} = E_{VB} + E_g$$

Supplementary Note 2: Photocatalytic hydrogen evolution reaction measurements

1.5 mg photocatalyst was dispersed into 10 mL 0.14 M ascorbic acid solution and then added into a reaction tube. Through ultrasonic dispersion for 30 min, a well-dispersed suspension was obtained. Then 1 μ L 8 wt% H_2PtCl_6 was added to the suspension, by which the cocatalyst Pt was loaded by the in-situ photodeposition approach. The system was degassed with argon for 30 minutes, followed by 100 μ L methane injected into the system as standard gas. 440 nm LED lamp or Xe lamps with a cutoff filter ($\lambda > 420$ nm) were used as the light source for testing H_2 evolution performance. Cyclic condensed water was used to keep the reaction at room temperature. The generated gases were measured by gas chromatography equipped with a thermal conductive detector (TCD) with argon as the carrier gas⁵⁻⁷.

Supplementary Note 3: Photoelectrochemical/electrochemical measurements

The photocurrent response profiles and electrochemical impedance spectra (EIS) were recorded on the CHI 760E electrochemical workstation with a standard three-electrode system, using the N₂ purged 0.1 M Na₂SO₄ as the electrolyte, sample-coated indium-tin oxide (ITO) as the working electrode, Pt wire as the counter electrode and Ag/AgCl electrode as the reference electrode. For the preparation of the working electrodes, the as synthesized COF samples (10 mg) were added into 0.1 mL 5% Nafion and 0.9 mL ethanol mixed solution were sonicated for 5 min, then the catalyst suspension (100 μ L) was dropped onto ITO glass (1 cm $\times$ 1 cm), forming a film after drying naturally for 24 h. The 300 W Xe lamp ($\lambda > 420$ nm) with a power density of 300 mW cm⁻² was used as the light source. Note that the working electrodes were immersed in the electrolyte for 60 s before any measurements were taken^{8,9}.

Supplementary Note 4: Apparent quantum yield (AQY)

The AQY for H₂ was measured under the irradiation of LED lights with different wavelengths (405, 440, 490, and 550nm), followed by using the equation¹⁰⁻¹²:

$$AQY = \frac{10^9 \times 2 \times M \times N_A \times h \times c}{P \times S \times t \times \lambda} \times 100\%$$

Where M is the amount of H₂ (mol), N_A is Avogadro constant (6.02 $\times 10^{23}$ mol⁻¹), h is the Planck constant (6.626 $\times 10^{-34}$ J·s), c is the speed of light (3 $\times 10^8$ m·s⁻¹), S is the irradiation area (cm²), P is the intensity of irradiation light (W·cm⁻²), t is the photoreaction time (s), λ is the wavelength of the monochromatic light (nm).

Supplementary Note 5: Femtosecond transient absorption spectra (fs-TA)

TAS, a pump-detection technique, is used to detect the excited state dynamics

information and ultrafast spectral processes of photocatalysts. The charge carrier dynamics is tracked by a pump-probe configuration with a 400 nm pump and a white light probe (400-780 nm). The measurements for suspension, three COFs in the mixed solvent of acetone and water, are performed in 1 mm pathlength quartz cuvettes.

Three kinds of COFs exhibit positive signals indicating excited state absorption (ESA), and negative signal confirming the ground state bleach (GSB) at different wavelengths. In the *fs*-TA spectra of imine-linked COF, after pump pulse excitation, only broad positive peaks are observed after pump pulse excitation. As for vinyl-linked COF, there were negative features at around 450 nm and positive peaks at around 700 nm.

Correspondingly, due to the fast recombination of photogenerated electron-hole pairs, the *fs*-TA kinetics of three COFs are fitted using a biexponential function. Respectively, τ_1 and τ_2 correspond to electron capture and effective exciton dissociation. And theoretically, the kinetics of ESA (originating from the increased absorption from the excited state) peak can reflect the lifetime of charge separation (τ_{avg})^{13,14}.

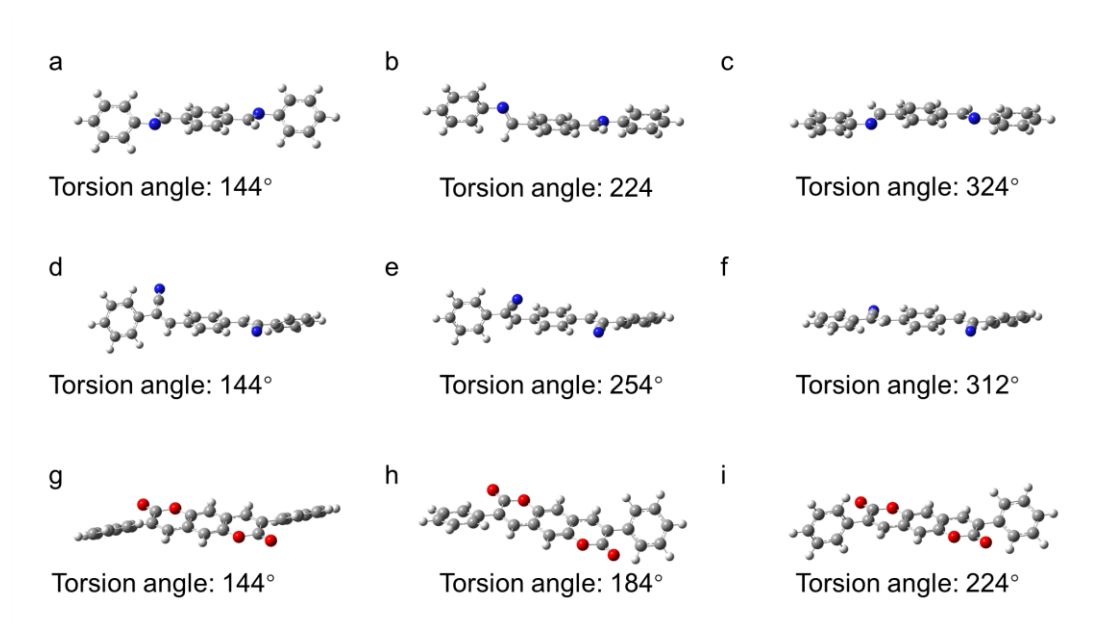
Supplementary Note 6: Theoretical calculation

For calculating the potential energy surface of the imine, vinyl, and coumarin linkers with different torsion angles in water. We performed DFT calculations using the Gaussian 16 (Revision C.01) program¹⁵. The minimum energy structures of the linkers and the torsion path along the dihedral angle of the linkers were obtained using the B3LYP functional¹⁶ and the D3 version of Grimme's dispersion¹⁷ with the 6-311g (d, p) basis sets¹⁸ and solvation model based on density¹⁹.

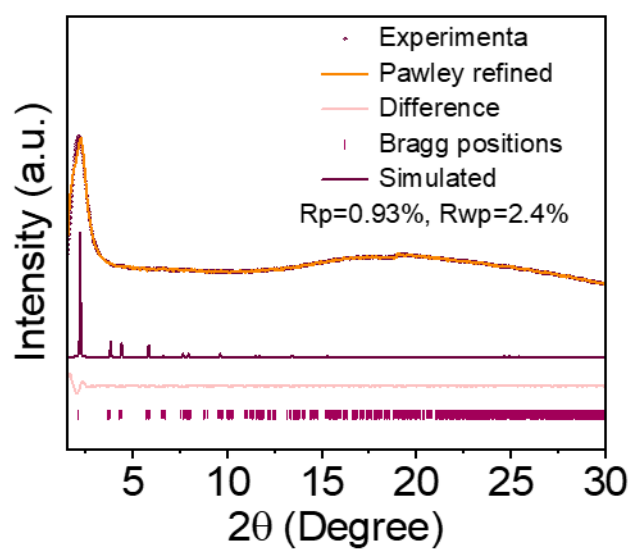
The photo-response of the COFs was assessed by combining ground-state DFT with excited-state TD-DFT. Instead of using the full periodic framework, we employed a representative fragment, because describing a charged system in a periodic setting is challenging. All DFT computations were performed with the Gaussian 16 package. Ground-state geometries were optimized at the B3LYP-D3 level, using the 6-31G(d) basis set for C, H, O, and Cl, and the Stuttgart/Dresden (SDD) basis set together with an effective core potential (ECP) for Pt. On the basis of these optimized structures, single-point energies were subsequently refined with the PBE0-D3 functional, where the basis set was upgraded to 6-311+G(d,p) for C, H, O, and Cl, while SDD with ECP was kept for Pt. Aqueous solvation was accounted for by the PCM model; solvent effects were included during geometry optimizations, single-point calculations, and TD-DFT calculations alike. Excited-state calculations were carried out using TD-DFT at the PBE0-D3 level, as PBE0 provides more reliable excitation energies than B3LYP. The adsorption Gibbs free energy (ΔG_{ads}) was computed according to the following equations:

$$\Delta G_{\text{ads}} = G_{\text{COF-PtCl}_6^{2-}} \quad (1)$$

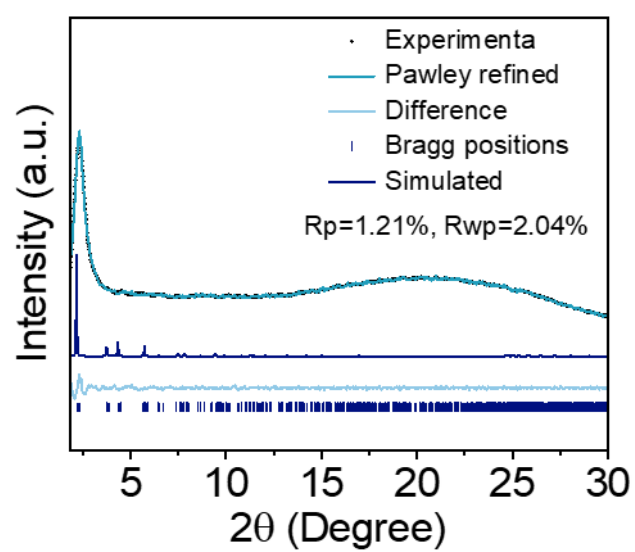
Supplementary Figures



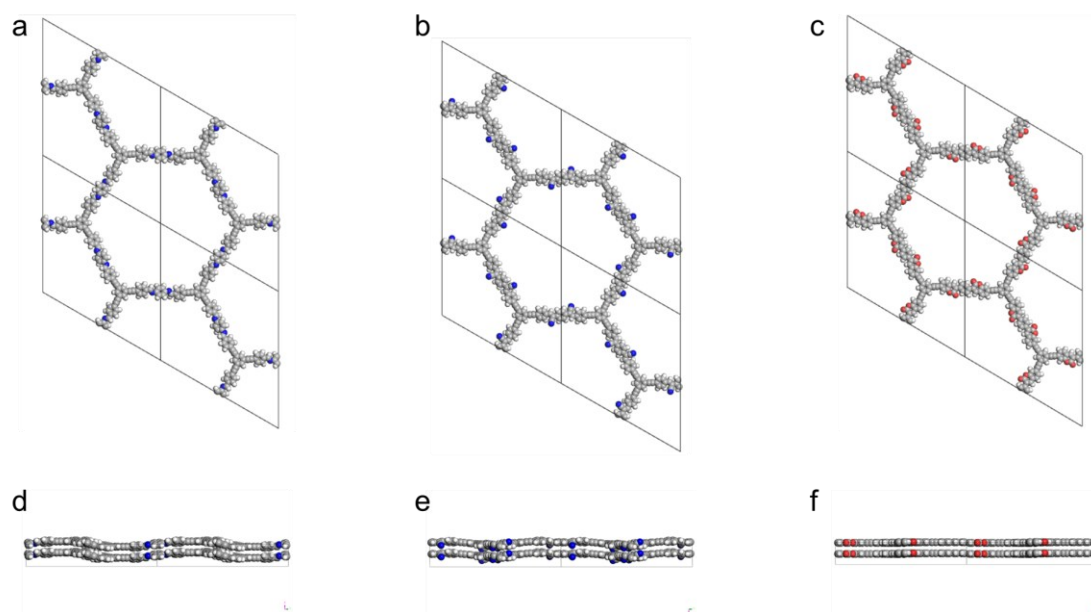
Supplementary Fig. 1 (a-c) The two typical conformers and transition state of imine-linked COF. (b) The two typical conformers and transition state of vinyl-linked COF. (c) The two typical conformers and transition state of coumarin-linked COF.



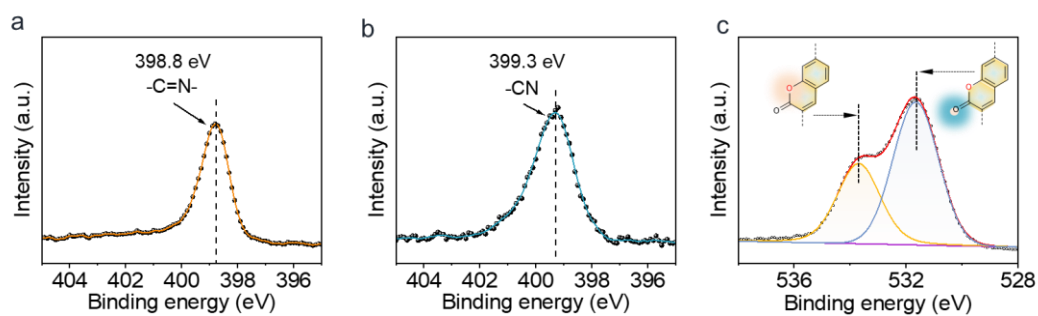
Supplementary Fig. 2 Experimental, simulated, and refined PXRD patterns of imine-linked COF.



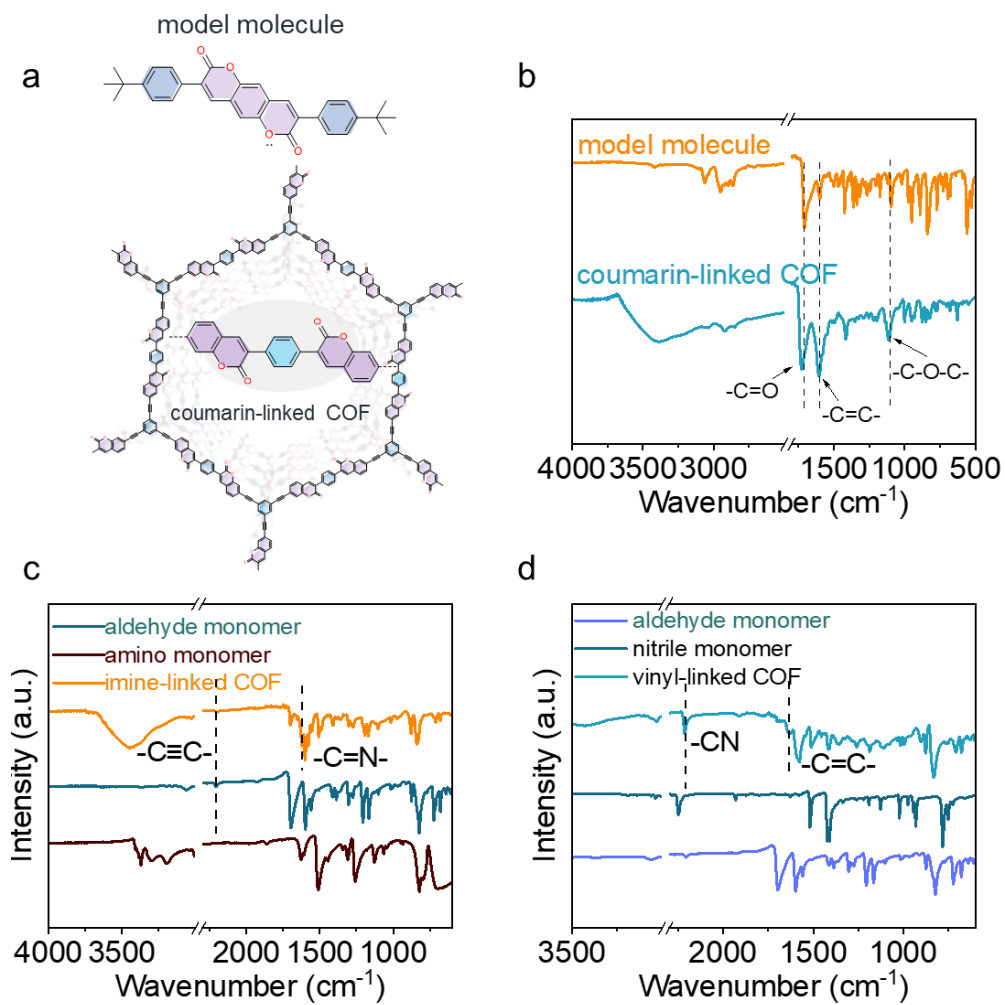
Supplementary Fig. 3 Experimental, simulated, and refined PXRD patterns of vinyl-linked COF.



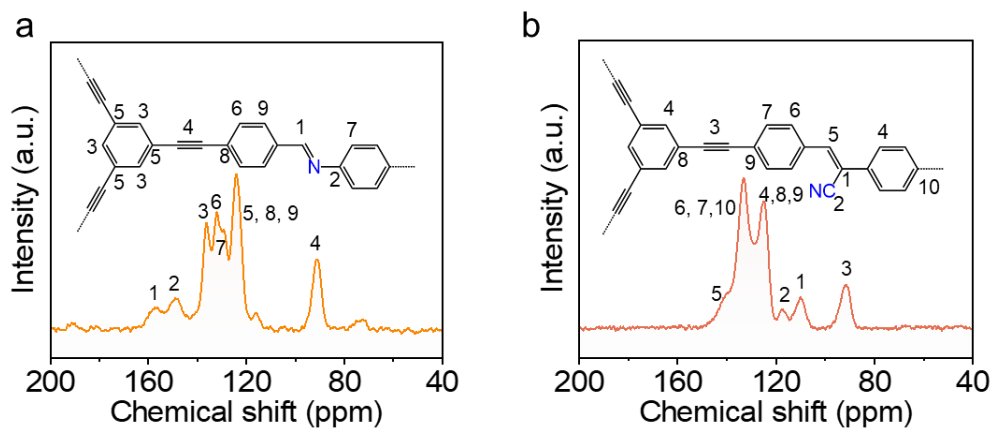
Supplementary Fig. 4 The top view of unit cells of (a) imine-linked COF, (b) vinyl-linked COF and (c) coumarin-linked COF. The side view of unit cells of (d) imine-linked COF, (e) vinyl-linked COF and (f) coumarin-linked COF.



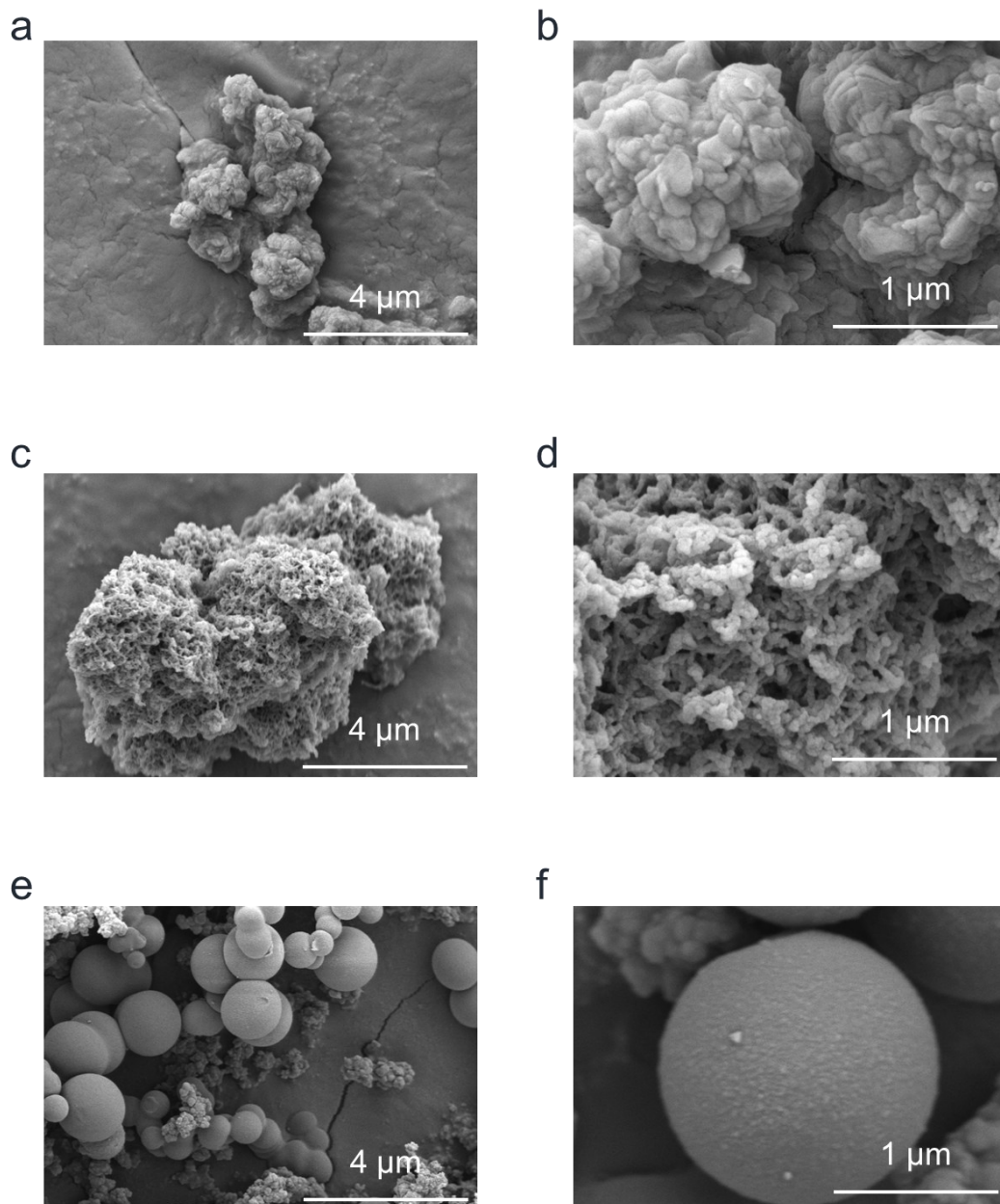
Supplementary Fig. 5 (a) N 1s XPS spectra of imine-linked COF, corresponding to imine bond. (b) N 1s XPS spectra of vinyl-linked COF, corresponding to cyano groups. (c) O 1s XPS spectra of coumarin-linked COF, corresponding to coumarin units.



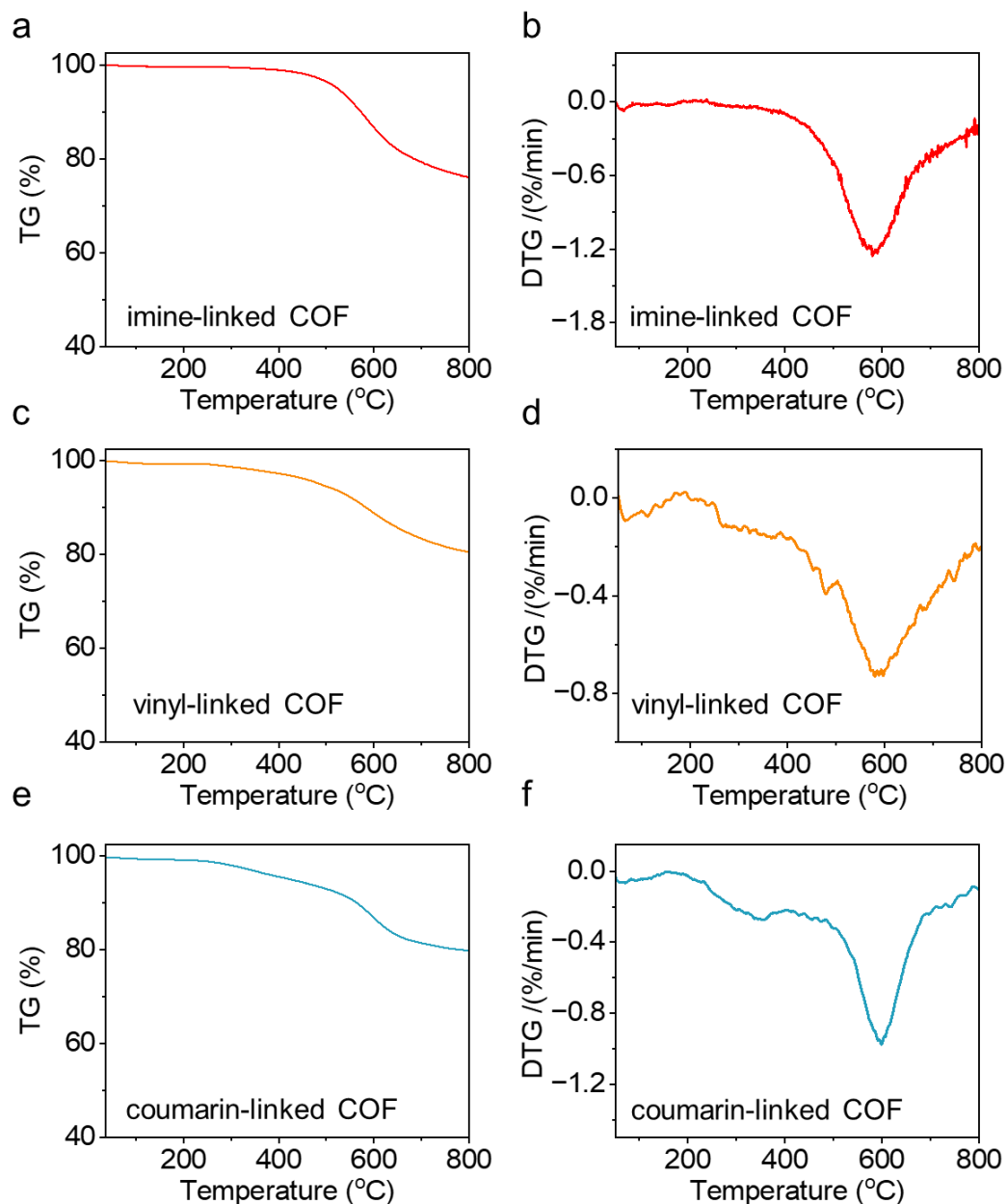
Supplementary Fig. 6 (a-b) FT-IR spectra of model molecule and coumarin-linked COF. (c-d) FT-IR spectra of imine-linked COF and vinyl-linked COF.



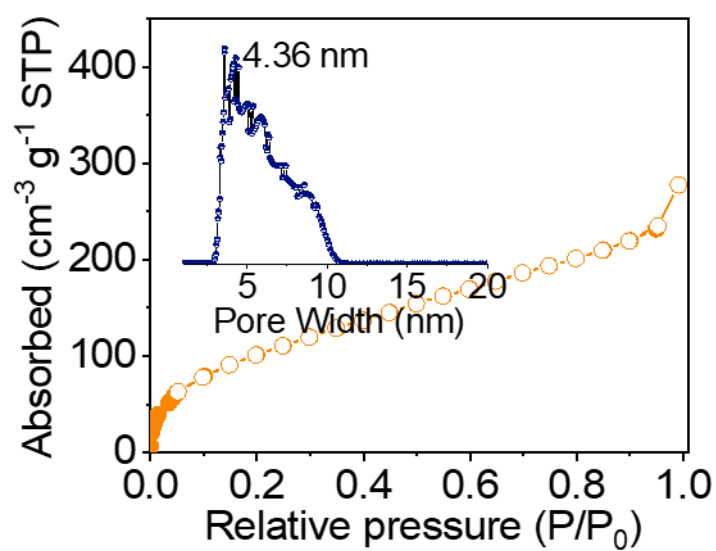
Supplementary Fig. 7 (a) ^{13}C NMR spectra of imine-linked COF. (b) ^{13}C NMR spectra of vinyl-linked COF.



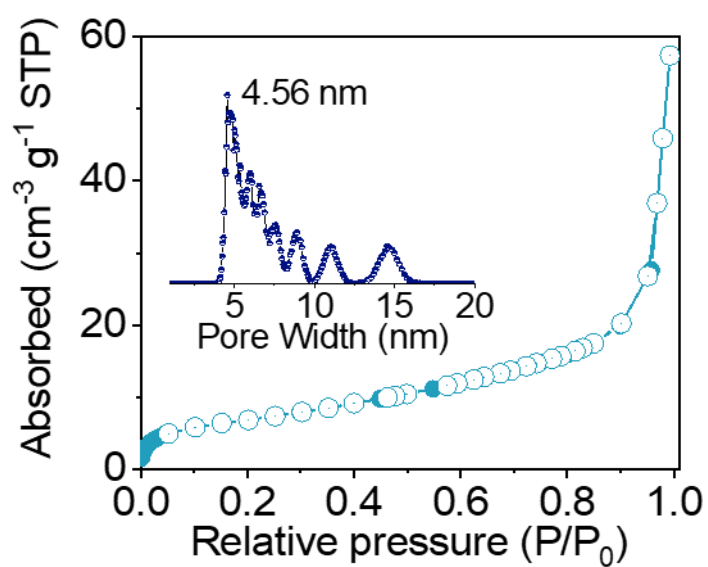
Supplementary Fig. 8 SEM images of imine-linked COF (a, b), vinyl-linked COF (c, d), and coumarin-linked COF (e, f). Scale bars: a, c, e 4 μm ; b, d, f 1 μm .



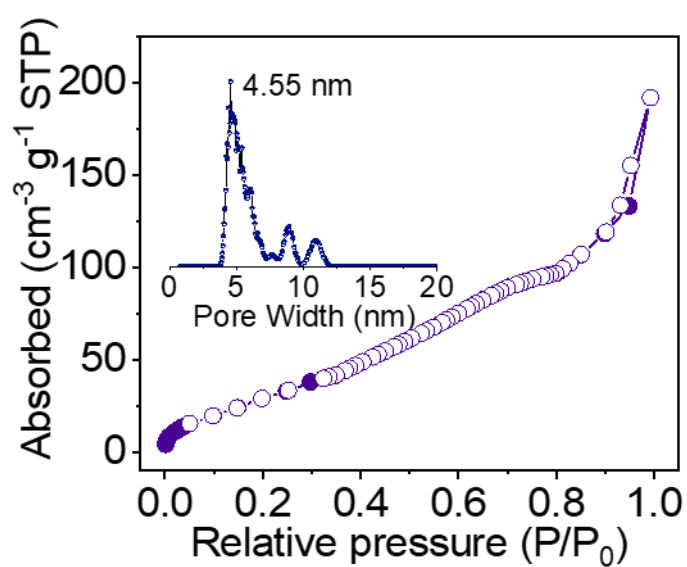
Supplementary Fig. 9 TGA trace and derivative of the weight loss measured under continuous flow of argon. The curve shows that the weight loss of (a) imine-linked COF, (b) vinyl-linked COF and (c) coumarin-linked COF are 25%, 20% and 20% until 800 °C. (b, d, f) are the weight loss of imine-linked COF, vinyl-linked COF and coumarin-linked COF.



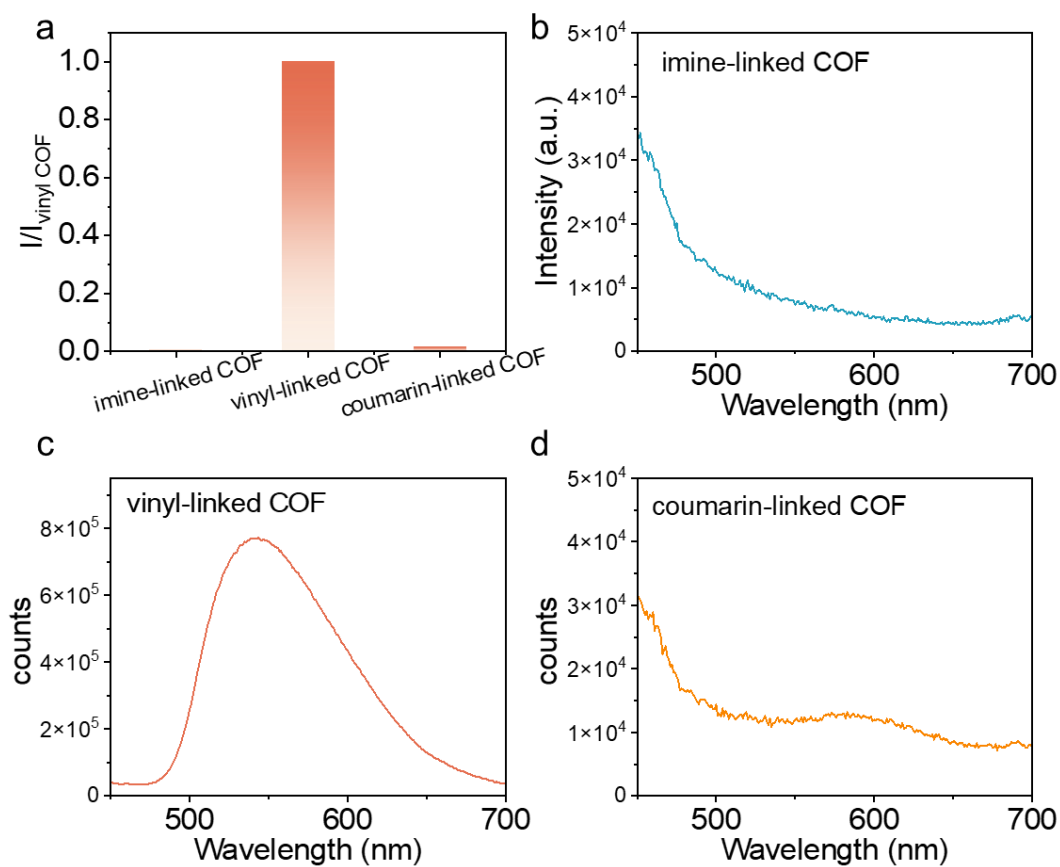
Supplementary Fig. 10 Nitrogen adsorption and desorption isotherms with pore size distribution of imine-linked COF (BET Surface Area: $399 \text{ m}^2 \text{g}^{-1}$).



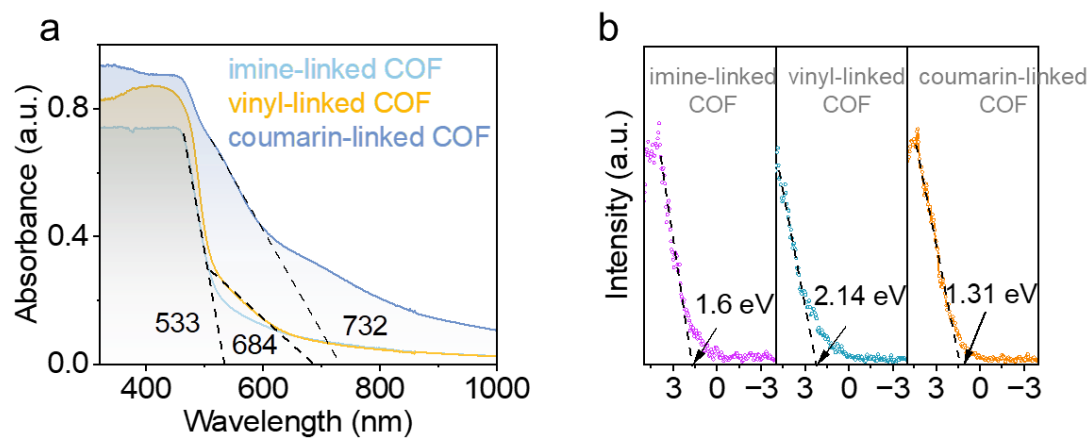
Supplementary Fig. 11 Nitrogen adsorption and desorption isotherms with pore size distribution of vinyl-linked COF (BET Surface Area: $41 \text{ m}^2 \text{ g}^{-1}$).



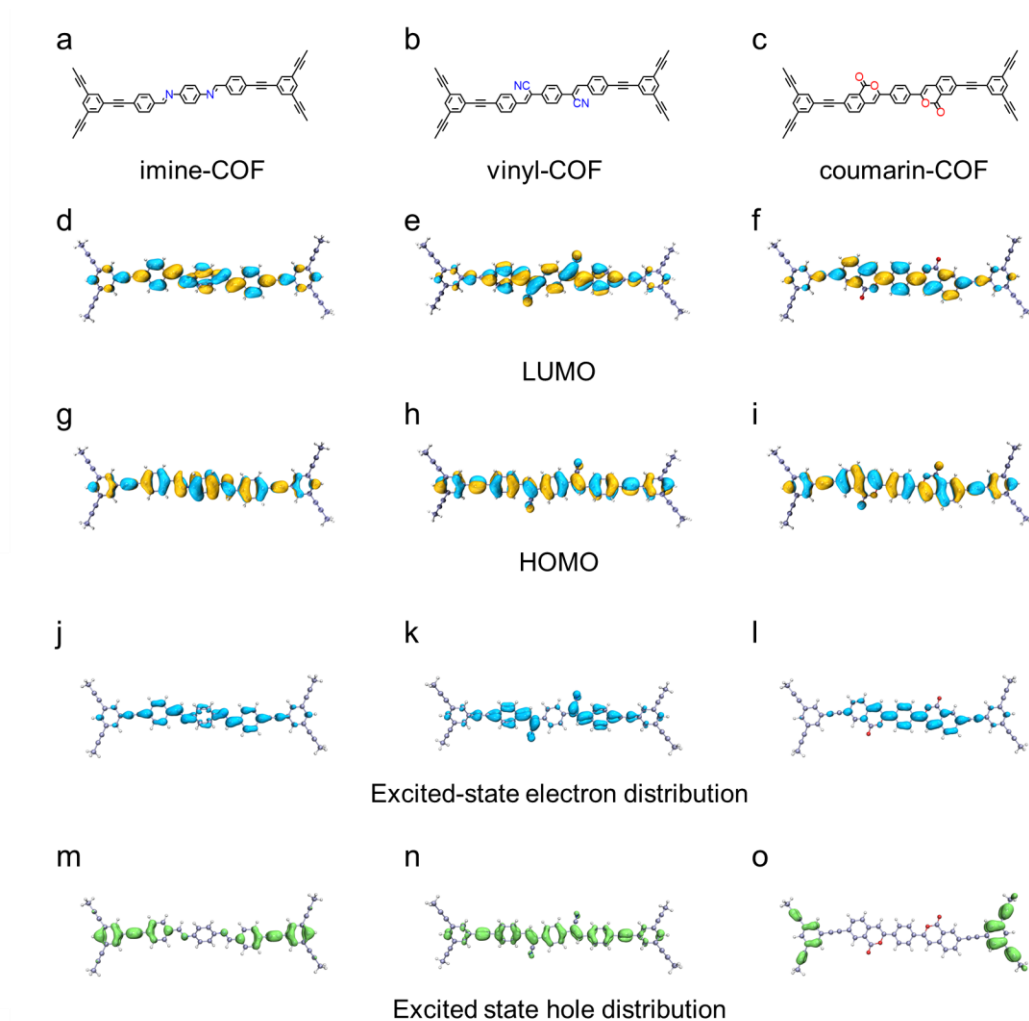
Supplementary Fig. 12 Nitrogen adsorption and desorption isotherms with pore size distribution of coumarin-linked COF (BET Surface Area: $143 \text{ m}^2 \text{g}^{-1}$).



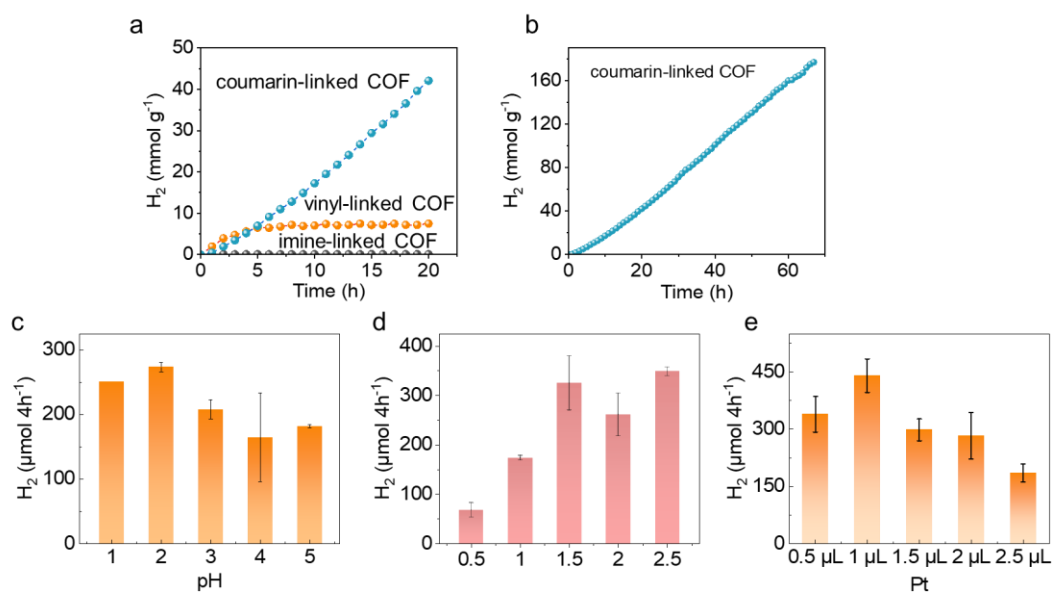
Supplementary Fig. 13 (a) The fluorescence intensity ratio of COFs. (b-d) Steady-state PL spectra of imine-linked COF, vinyl-linked COF and coumarin-linked COF.



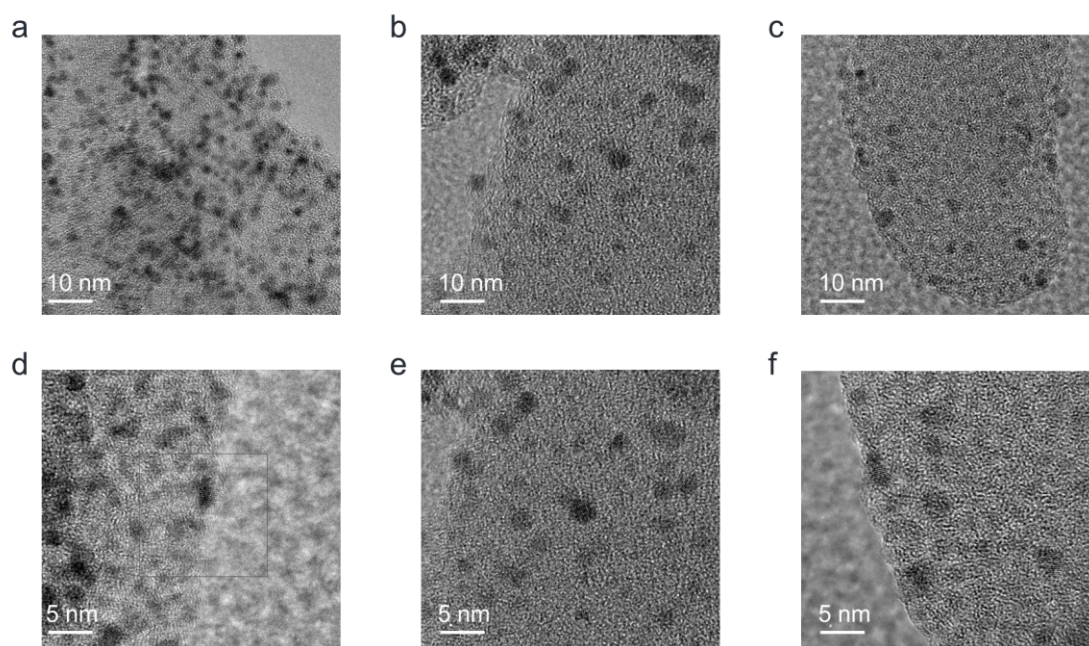
Supplementary Fig. 14 (a) UV Visible Absorption Spectroscopy of imine-linked, vinyl-linked and coumarin-linked COF. (b) VB-XPS spectra of imine-linked, vinyl-linked and coumarin-linked COF.



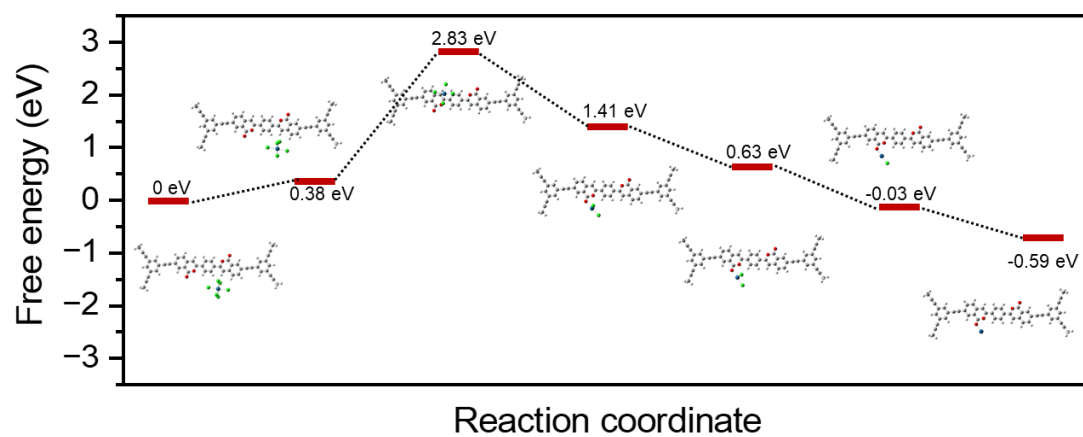
Supplementary Fig. 15 The structure fragment of (a) imine-linked COF, (b) vinyl-linked COF and (c) coumarin-linked COF. The LUMO of (d) imine-linked COF, (e) vinyl-linked COF and (f) coumarin-linked COF. The HOMO of (g) imine-linked COF, (h) vinyl-linked COF and (i) coumarin-linked COF. The excited-state electron distribution of (j) imine-linked COF, (k) vinyl-linked COF and (l) coumarin-linked COF. The excited-state hole distribution of (m) imine-linked COF, (n) vinyl-linked COF and (o) coumarin-linked COF. The charge centroid distance (D value) between the hole and electron of imine-, vinyl- and coumarin-linked COFs are 0.003, 0.176 and 5.366 respectively.



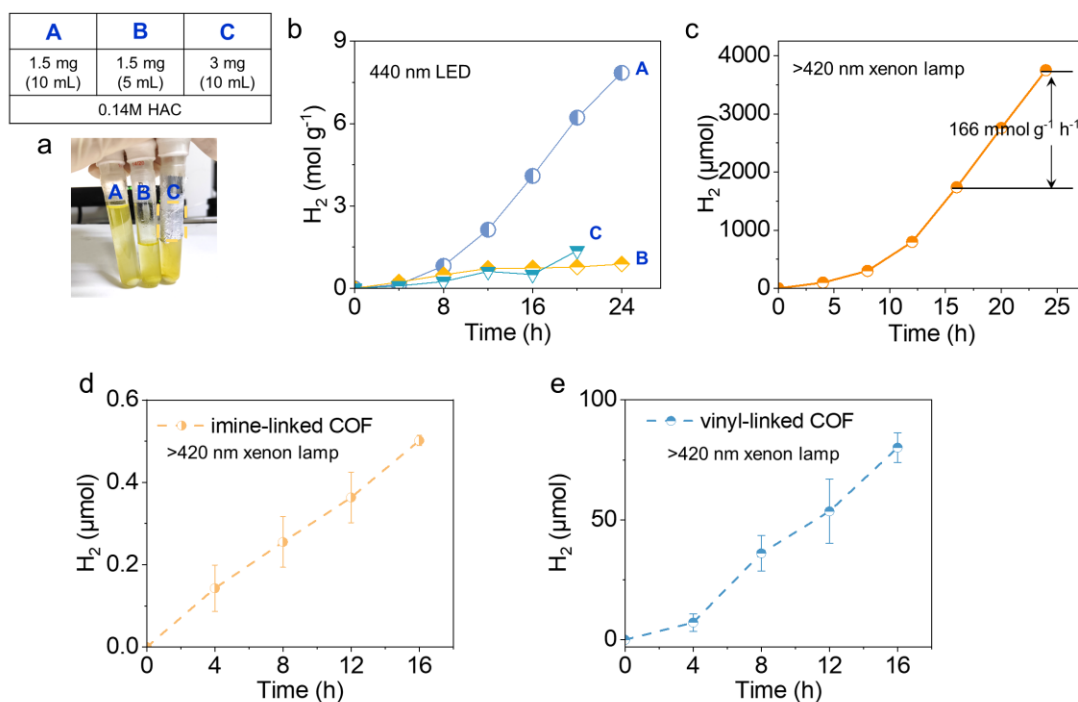
Supplementary Fig. 16 (a-b) Hydrogen production rate of imine-, vinyl- and coumarin-linked COF in ascorbic acid aqueous solution from real-time online monitoring (Labsolar-6A system, Beijing Perfectlight). (c-e) A series of controlled screening experiments (pH values and dosage of COFs and cocatalyst) performed under 440 nm LED light.



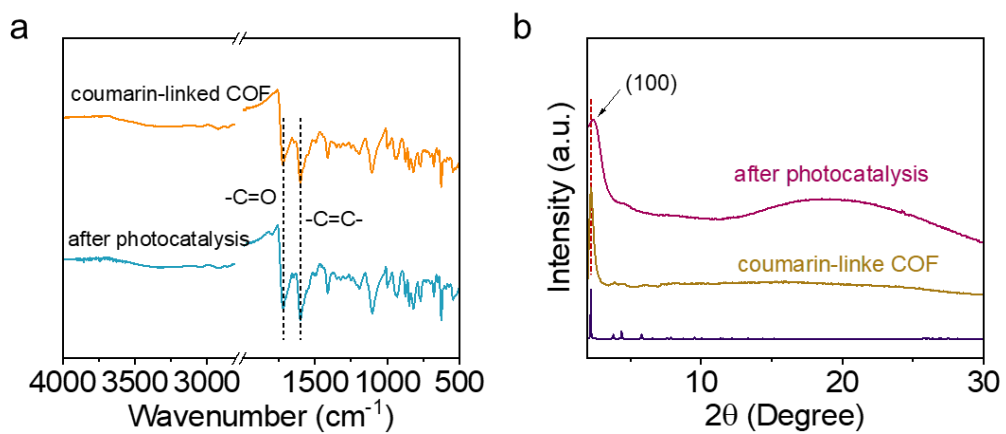
Supplementary Fig. 17 TEM image of Pt@COF hybrid material after light irradiation
(a, d) imine-linked COF, (b, e) vinyl-linked COF and (c, f) coumarin-linked COF.



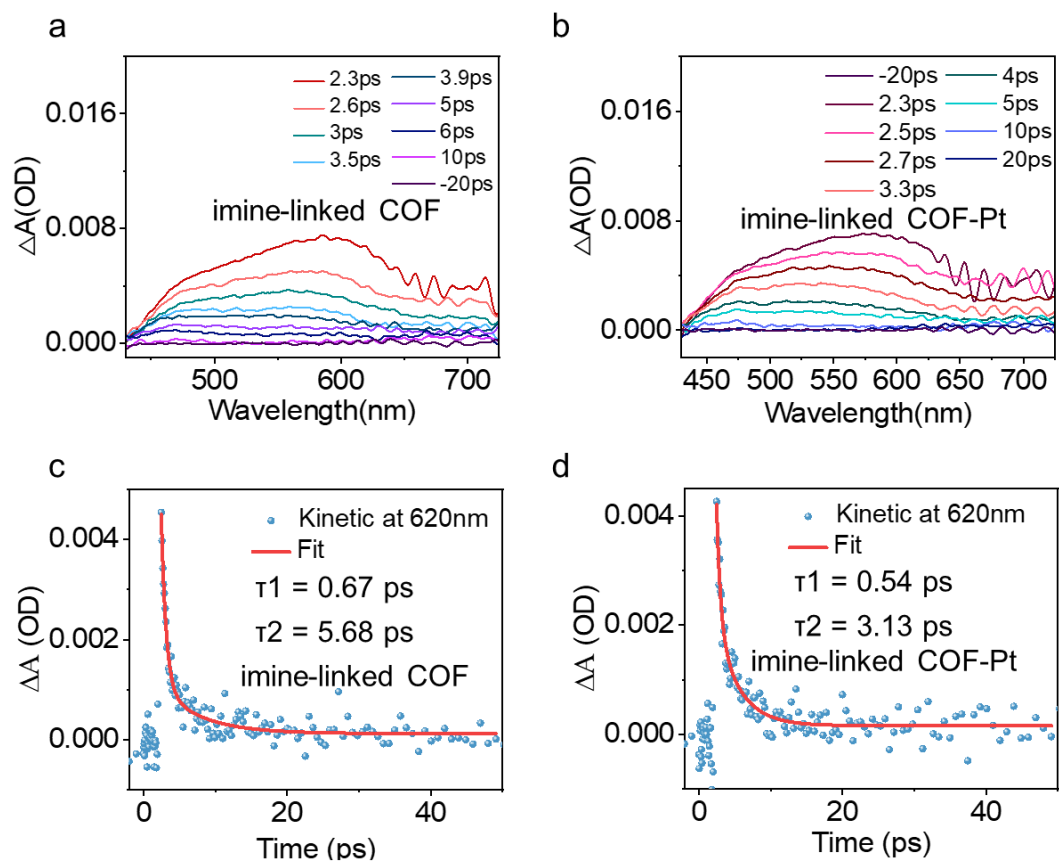
Supplementary Fig. 18 Free energy diagrams of photo-deposition reaction paths.



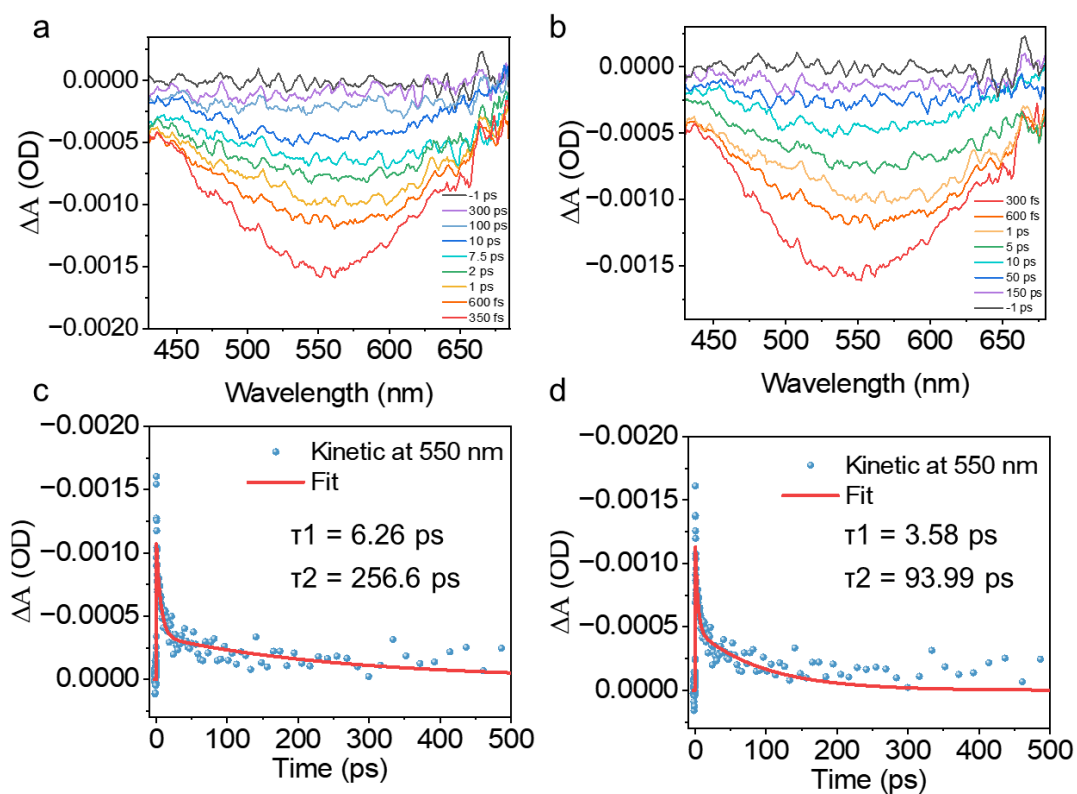
Supplementary Fig. 19 (a-b) Effect of coumarin-linked COF dosage and ascorbic acid concentration on hydrogen production rate. A, B, C correspond to 1.5 mg 10 mL⁻¹, 1.5 mg 5 mL⁻¹, and 3 mg 10 mL⁻¹, respectively. Hydrogen production performance of 1.5 mg coumarin-linked COF (c), imine-linked COF (d) and vinyl-linked COFs (e) under >420 nm light.



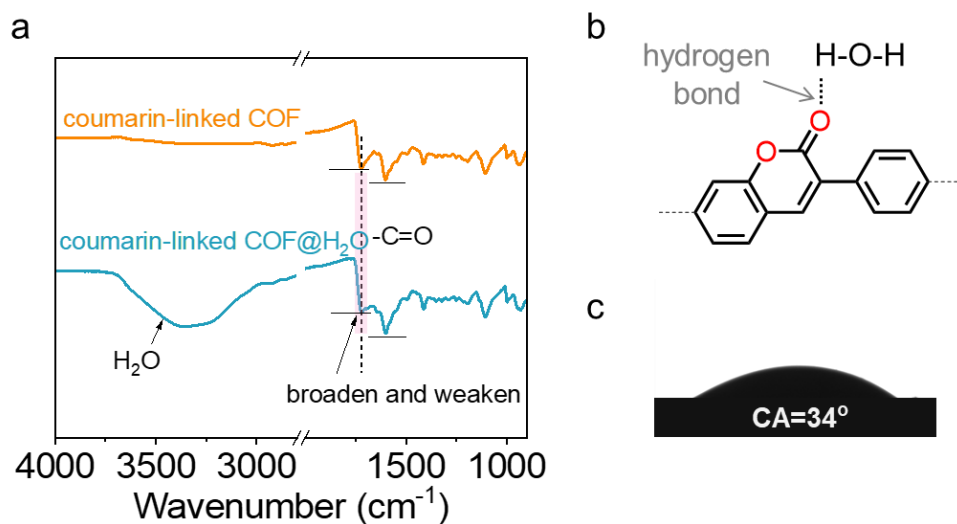
Supplementary Fig. 20 FT-IR (a) and PXRD (b) spectra of coumarin-linked COF before and after photocatalytic reaction under 440 nm.



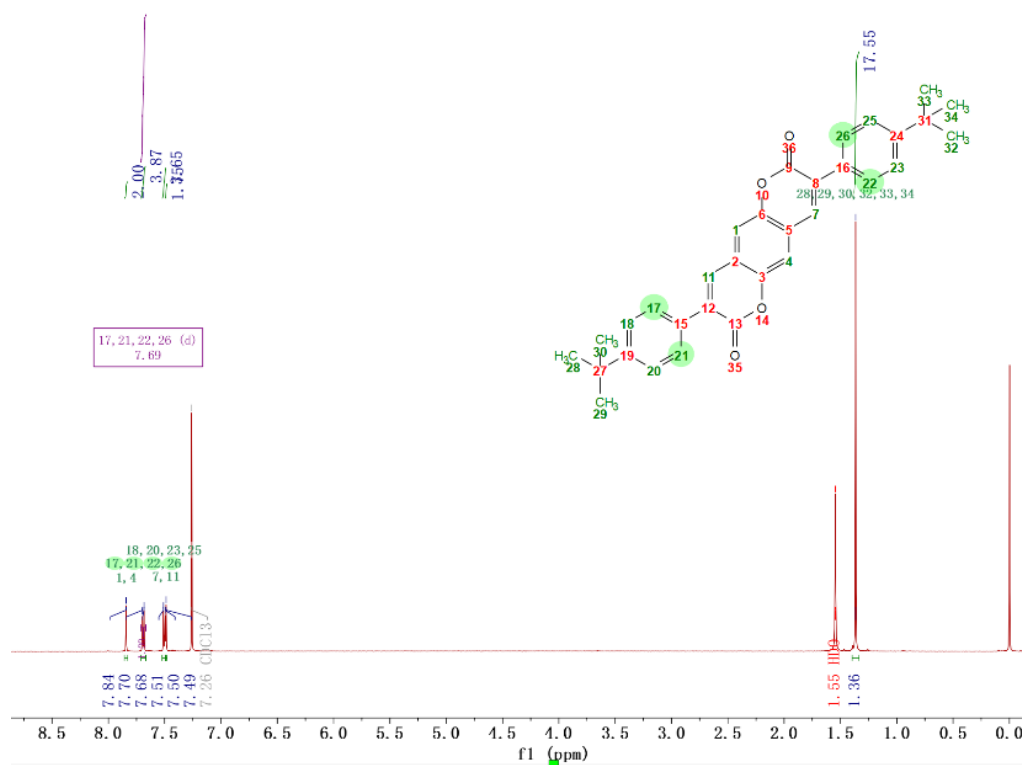
Supplementary Fig. 21 (a-b) Fs-TA spectra curves with excitation spectrum at 400 nm of imine-linked COF and imine-linked COF-Pt dispersed in the mixed solvent of acetone and water, respectively. (c-d) Decay kinetics of imine-linked COF and imine-linked COF-Pt at 620 nm.



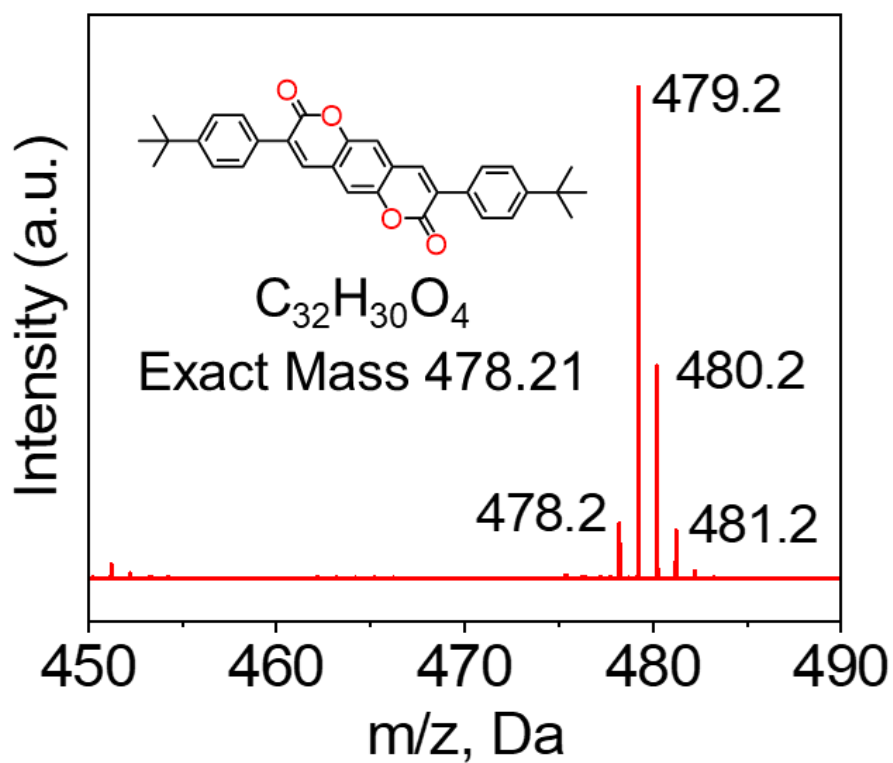
Supplementary Fig. 22 (a-b) Fs-TA spectra curves with excitation spectrum at 400 nm of vinyl-linked COF and vinyl-linked COF-Pt. (c-d) Decay kinetics of vinyl-linked COF and vinyl-linked COF-Pt at 550 nm.



Supplementary Fig. 23 (a) FTIR spectra of coumarin-linked COF and coumarin-linked COF@H₂O. (b) Illustration of hydrogen-bonding interactions between water molecules and the coumarin unit. (c) Water contact angle of coumarin-linked COF.



Supplementary Fig. 23 ^1H NMR of 3,8-bis(4-(tert-butyl)phenyl)pyrano[2,3-g]chromene-2,7-dione.



Supplementary Fig. 24 Mass spectrum of 3,8-bis(4-(tert-butyl)phenyl)pyrano[2,3-g]chromene-2,7-dione.

Supplementary Tables

Supplementary Table 1. Optimization of synthesis conditions of coumarin-linked COF.

Entry	Condition	Temperature (°C)	Crystallinity
1	mesitylene/1,4-dioxane/TFA	120	No
2	o-dichlorobenzene/n-butanol/K ₂ CO ₃	120	No
3	o-dichlorobenzene/n-butanol/Cs ₂ CO ₃	120	No
4	o-dichlorobenzene/n-butanol/potassium t-butoxide	120	No
5	o-dichlorobenzene/n-butanol/KOH	120	No
6	o-dichlorobenzene/n-butanol/Piperidine	120	No
7	o-dichlorobenzene/n-butanol/DMAP	120	Low
8	o-dichlorobenzene/n-butanol/6M DBU	120	Low
9	o-dichlorobenzene/n-butanol/3M DBU	150	Low
10	o-dichlorobenzene/n-butanol/3M DBU	120	Hight

Supplementary Table 2. Fractional atomic coordinates of incline model of imine-linked COF.

Crystal system: Hexagonal

Space group: P1

$a = 45.9984 \text{ \AA}$; $b = 46.1879 \text{ \AA}$; $c = 3.3980 \text{ \AA}$; $\alpha = 90.0575^\circ$; $\beta = 90.1579^\circ$; $\gamma = 119.9892^\circ$

C1	0.39268	0.8037	-0.22658
C2	0.42654	0.82363	-0.12285
C3	0.44144	0.8582	-0.11267
C4	0.42326	0.87421	-0.20813
C5	0.38951	0.85415	-0.31436
C6	0.37435	0.81951	-0.32222
N7	0.46878	0.92985	-0.07333
C8	0.43871	0.9108	-0.19658
C9	0.3179	0.63169	-0.23591
C10	0.35297	0.65142	-0.23615
C11	0.26217	0.62662	-0.234
C12	0.23185	0.60947	-0.22954
C13	0.03496	0.51901	-0.04342
C14	0.01502	0.53356	-0.11764
C15	0.98045	0.51512	-0.08292
H16	0.30613	0.60463	-0.23453
H17	0.44095	0.81177	-0.04739
H18	0.37499	0.86591	-0.39123
H19	0.34831	0.80455	-0.40508
H20	0.42306	0.92108	-0.30383
H21	0.02686	0.55922	-0.21451
H22	0.96566	0.52668	-0.15474
C23	0.19609	0.58925	-0.22223
C24	0.17621	0.60322	-0.11949
C25	0.14164	0.58356	-0.10951
C26	0.12556	0.54935	-0.20417

C27	0.14558	0.53562	-0.30921
C28	0.18022	0.55508	-0.31688
N29	0.06996	0.53928	-0.07113
C30	0.08896	0.52822	-0.19314
C31	0.36815	0.68647	-0.23752
C32	0.3484	0.70181	-0.23817
C33	0.37323	0.63584	-0.2332
C34	0.39038	0.62267	-0.22855
C35	0.48084	0.51621	-0.03853
C36	0.46627	0.48175	-0.11392
C37	0.48471	0.4656	-0.07826
H38	0.39522	0.70176	-0.23731
H39	0.18812	0.6295	-0.04472
H40	0.13377	0.50932	-0.38537
H41	0.19514	0.54397	-0.3989
H42	0.07863	0.50227	-0.29985
H43	0.44059	0.46795	-0.21235
H44	0.47314	0.43927	-0.15103
C45	0.41061	0.60713	-0.22053
C46	0.39665	0.57329	-0.11854
C47	0.4163	0.55836	-0.10772
C48	0.45051	0.5765	-0.20073
C49	0.46423	0.61023	-0.30505
C50	0.44476	0.62542	-0.31358
N51	0.46058	0.53095	-0.06731
C52	0.47163	0.56101	-0.1887
C53	0.31334	0.68193	-0.23794
C54	0.298	0.64686	-0.23654
C55	0.36398	0.73764	-0.23704
C56	0.37715	0.76795	-0.23348
C57	0.4835	0.96484	-0.04463
C58	0.51796	0.98475	-0.11791
C59	0.53409	0.01932	-0.082
H60	0.29804	0.6937	-0.23807

H61	0.37037	0.55892	-0.04494
H62	0.49052	0.62471	-0.38002
H63	0.45586	0.65144	-0.39508
H64	0.49758	0.57662	-0.29402
H65	0.53177	0.97288	-0.21497
H66	0.56042	0.03409	-0.15315
C67	0.60713	0.19632	0.22066
C68	0.57328	0.1764	0.1168
C69	0.55838	0.14183	0.10616
C70	0.57656	0.12581	0.20121
C71	0.61031	0.14586	0.30751
C72	0.62547	0.1805	0.31584
N73	0.53104	0.07018	0.06593
C74	0.56111	0.08922	0.18933
C75	0.68164	0.36831	0.2338
C76	0.64656	0.3485	0.23512
C77	0.73743	0.37354	0.22917
C78	0.76774	0.39077	0.22385
C79	0.96462	0.48151	0.03603
C80	0.98456	0.46696	0.11025
C81	0.01913	0.4854	0.07554
H82	0.69334	0.39536	0.23289
H83	0.55886	0.18826	0.04167
H84	0.62484	0.1341	0.38406
H85	0.65151	0.19545	0.39883
H86	0.57675	0.07893	0.29658
H87	0.97271	0.4413	0.20701
H88	0.03393	0.47385	0.1473
C89	0.80349	0.41107	0.21584
C90	0.82342	0.39716	0.1128
C91	0.85799	0.41688	0.10239
C92	0.87401	0.45109	0.19685
C93	0.85395	0.46476	0.30206
C94	0.81931	0.44524	0.31016

N95	0.92963	0.46124	0.06376
C96	0.9106	0.47227	0.18568
C97	0.63148	0.31345	0.23574
C98	0.6513	0.2982	0.23448
C99	0.62623	0.36399	0.23368
C100	0.60901	0.37708	0.23001
C101	0.51834	0.48335	0.04288
C102	0.53291	0.51781	0.11827
C103	0.51447	0.53396	0.08263
H104	0.60441	0.2981	0.23632
H105	0.81155	0.37087	0.03825
H106	0.86571	0.49107	0.37799
H107	0.80435	0.45631	0.39238
H108	0.9209	0.49822	0.29226
H109	0.55859	0.53161	0.21666
H110	0.52604	0.56029	0.15538
C111	0.58874	0.39258	0.22292
C112	0.60265	0.42642	0.12119
C113	0.58295	0.4413	0.11092
C114	0.54876	0.42312	0.20425
C115	0.53509	0.38939	0.30839
C116	0.55459	0.37424	0.31636
N117	0.53861	0.46862	0.07144
C118	0.52759	0.43856	0.19272
C119	0.68636	0.31816	0.23322
C120	0.70161	0.35322	0.23268
C121	0.63579	0.26238	0.23247
C122	0.62265	0.23207	0.22828
C123	0.51632	0.03518	0.03723
C124	0.48185	0.01528	0.11053
C125	0.46573	0.98071	0.07464
H126	0.70171	0.30645	0.23205
H127	0.62892	0.44082	0.04737
H128	0.5088	0.37487	0.38356

H129	0.54352	0.34821	0.39755
H130	0.50166	0.42292	0.29825
H131	0.46804	0.02714	0.20753
H132	0.43939	0.96593	0.14573
H133	0.12664	0.59459	-0.02729
H134	0.40528	0.53234	-0.02599
H135	0.87302	0.40589	0.01994
H136	0.59393	0.46732	0.02942
H137	0.46748	0.87324	-0.02954
H138	0.53234	0.1268	0.02296

Supplementary Table 3. Fractional atomic coordinates of incline model of vinyl-linked COF.

Crystal system: Hexagonal

Space group: P1

$a = 47.1895 \text{ \AA}$; $b = 47.1185 \text{ \AA}$; $c = 3.6157 \text{ \AA}$; $\alpha = 89.1889^\circ$; $\beta = 90.2563^\circ$; $\gamma = 119.7308^\circ$

C1	0.3952	0.8012	-0.2069
C2	0.42903	0.81948	-0.28486
C3	0.44531	0.85355	-0.29292
C4	0.42842	0.8708	-0.22441
C5	0.39425	0.85222	-0.16133
C6	0.37794	0.81817	-0.1487
C7	0.47537	0.92969	-0.12803
C8	0.44399	0.90674	-0.22112
C9	0.31737	0.63269	-0.02711
C10	0.35164	0.65093	-0.06821
C11	0.26379	0.62989	0.01694
C12	0.23419	0.61395	0.05437
C13	0.03477	0.52186	0.12774
C14	0.0129	0.5329	0.22483
C15	0.97946	0.51116	0.25786
H16	0.30524	0.60623	0.00769
H17	0.44257	0.8068	-0.33949
H18	0.3805	0.86482	-0.11185
H19	0.3518	0.80458	-0.09158
H20	0.42747	0.91589	-0.29307
H21	0.0222	0.55874	0.28237
H22	0.96368	0.52075	0.34231
H23	0.13385	0.60509	0.28315
C24	0.4988	0.92029	-0.00489
C25	0.19921	0.59516	0.09103
C26	0.18094	0.61057	0.17892

C27	0.147	0.5925	0.20583
C28	0.1299	0.55825	0.14589
C29	0.14851	0.54286	0.07028
C30	0.18241	0.56087	0.03984
C31	0.07052	0.54573	0.09278
C32	0.09408	0.53764	0.16652
C33	0.3673	0.68521	-0.11246
C34	0.34884	0.70128	-0.11379
C35	0.37054	0.63457	-0.06101
C36	0.38644	0.62064	-0.04855
C37	0.4763	0.51132	0.16388
C38	0.46591	0.4782	0.08495
C39	0.48777	0.46648	0.08747
H40	0.39373	0.69934	-0.1452
H41	0.19352	0.63686	0.22804
H42	0.13603	0.51645	0.02657
H43	0.19603	0.54846	-0.02534
H44	0.08551	0.51218	0.24503
H45	0.44048	0.46144	0.01325
H46	0.47827	0.44078	0.01982
H47	0.39398	0.52684	-0.09411
C48	0.07848	0.57805	-0.0356
C49	0.40484	0.60388	-0.02811
C50	0.38922	0.56957	-0.0747
C51	0.4068	0.55314	-0.0481
C52	0.44081	0.57032	0.0258
C53	0.45641	0.60483	0.06171
C54	0.43887	0.62132	0.0388
C55	0.45237	0.5233	0.15385
C56	0.46105	0.55473	0.05623
C57	0.3146	0.68292	-0.07019
C58	0.29878	0.64861	-0.02707
C59	0.36497	0.73634	-0.15473
C60	0.37871	0.76607	-0.18442

C61	0.48766	0.96563	-0.13001
C62	0.52164	0.98805	-0.14677
C63	0.53388	0.02172	-0.14169
H64	0.30032	0.69527	-0.07008
H65	0.36313	0.5558	-0.13403
H66	0.48264	0.61878	0.11579
H67	0.45147	0.64779	0.07354
H68	0.48695	0.57117	-0.00473
H69	0.53887	0.9791	-0.1658
H70	0.56034	0.03769	-0.15082
H71	0.47121	0.8667	-0.36135
C72	0.41938	0.49927	0.26298
C73	0.60507	0.19967	-0.15902
C74	0.57133	0.18147	-0.24072
C75	0.55513	0.14743	-0.25529
C76	0.57204	0.13012	-0.18914
C77	0.60612	0.14864	-0.12161
C78	0.62233	0.18266	-0.10291
C79	0.52519	0.07091	-0.10533
C80	0.5566	0.0942	-0.19472
C81	0.68341	0.36802	0.03376
C82	0.64904	0.34983	0.00551
C83	0.73706	0.37072	0.04521
C84	0.7668	0.3865	0.06682
C85	0.9662	0.47734	0.19199
C86	0.98811	0.46626	0.09749
C87	0.02155	0.48801	0.06457
H88	0.69566	0.39445	0.06939
H89	0.55778	0.19419	-0.29387
H90	0.61988	0.13601	-0.07395
H91	0.64841	0.1962	-0.04284
H92	0.5733	0.08539	-0.27066
H93	0.97882	0.44043	0.03971
H94	0.03733	0.47841	-0.01987

H95	0.86822	0.39484	-0.01371
C96	0.50184	0.08016	0.02459
C97	0.80189	0.40496	0.08696
C98	0.82065	0.38959	0.02745
C99	0.85464	0.40741	0.04387
C100	0.87134	0.4414	0.11974
C101	0.85232	0.45671	0.17275
C102	0.81833	0.43892	0.16067
C103	0.93036	0.45354	0.2142
C104	0.90719	0.46194	0.12976
C105	0.63322	0.31558	-0.03967
C106	0.65162	0.29949	-0.05635
C107	0.63017	0.3662	0.02247
C108	0.61417	0.38001	0.03631
C109	0.52123	0.48709	0.17398
C110	0.53141	0.52016	0.25676
C111	0.50962	0.53197	0.25153
H112	0.6067	0.30149	-0.06188
H113	0.80844	0.36355	-0.03592
H114	0.86449	0.4829	0.2302
H115	0.80435	0.45129	0.20685
H116	0.91622	0.48765	0.05914
H117	0.55679	0.53706	0.32859
H118	0.51874	0.55752	0.32445
H119	0.60435	0.4723	-0.06865
C120	0.92187	0.4209	0.33569
C121	0.59538	0.39639	0.0515
C122	0.61025	0.43037	-0.01819
C123	0.59215	0.44631	-0.00305
C124	0.55834	0.42893	0.08233
C125	0.54349	0.3947	0.14325
C126	0.56156	0.37873	0.13181
C127	0.54527	0.47535	0.17876
C128	0.5374	0.44381	0.097

C129	0.68598	0.31781	-0.02777
C130	0.70195	0.35208	0.01727
C131	0.63535	0.26445	-0.09931
C132	0.62152	0.23476	-0.13175
C133	0.51287	0.035	-0.11882
C134	0.47888	0.01255	-0.10328
C135	0.46662	0.97887	-0.10876
H136	0.70024	0.30546	-0.04064
H137	0.63615	0.44427	-0.08779
H138	0.51745	0.38059	0.20735
H139	0.54955	0.35249	0.18524
H140	0.51166	0.42646	0.04111
H141	0.4616	0.02145	-0.08687
H142	0.44022	0.96283	-0.08955
H143	0.52933	0.13435	-0.32738
C144	0.5782	0.49929	0.29111
N145	0.51783	0.91397	0.11117
N146	0.08318	0.60278	-0.15638
N147	0.39405	0.47948	0.3707
N148	0.48304	0.08659	0.14478
N149	0.91668	0.3959	0.45255
N150	0.60385	0.51847	0.39619

Supplementary Table 4. Fractional atomic coordinates of incline model of coumarin-linked COF.

Crystal system: Hexagonal

Space group: P1

$a = 47.2547 \text{ \AA}$; $b = 47.1489 \text{ \AA}$; $c = 3.4280 \text{ \AA}$; $\alpha = 89.7784^\circ$; $\beta = 90.3804^\circ$; $\gamma = 120.6576^\circ$

C1	0.38966	0.79975	-0.00688
C2	0.42398	0.8197	-0.0048
C3	0.43891	0.85408	-0.00526
C4	0.41939	0.86854	-0.00782
C5	0.38497	0.84854	-0.0099
C6	0.37017	0.81424	-0.00943
O7	0.47326	0.87319	-0.00314
C8	0.48798	0.9077	-0.00363
C9	0.4682	0.9247	-0.00634
C10	0.43516	0.90459	-0.0083
O11	0.51781	0.92338	-0.00173
C12	0.31714	0.63084	-0.00453
C13	0.35147	0.65079	-0.00244
C14	0.2623	0.62477	-0.00926
C15	0.23276	0.60762	-0.01103
C16	0.03552	0.51726	-0.02427
C17	0.01379	0.52952	-0.02691
C18	0.9753	0.52192	0.0615
H19	0.30572	0.60421	-0.00416
H20	0.43919	0.8086	-0.00282
H21	0.3696	0.85944	-0.0119
H22	0.34359	0.79904	-0.01106
H23	0.41842	0.91363	-0.01031
H24	0.02181	0.55523	-0.02754
H25	0.96163	0.53443	0.05959
C26	0.19751	0.58717	-0.01316

C27	0.17793	0.60158	-0.01572
C28	0.1436	0.58181	-0.01781
C29	0.12881	0.54746	-0.01734
C30	0.14844	0.533	-0.01477
C31	0.1827	0.55282	-0.01268
O32	0.12486	0.5971	-0.02034
C33	0.09039	0.57698	-0.02242
C34	0.07304	0.53979	-0.02203
C35	0.09281	0.52684	-0.01954
O36	0.07503	0.59119	-0.02459
C37	0.36622	0.68516	-0.00293
C38	0.34664	0.69959	-0.00548
C39	0.37158	0.63598	0.00015
C40	0.38842	0.62355	0.00237
C41	0.47655	0.5161	0.01616
C42	0.46394	0.48175	0.01683
C43	0.4844	0.46839	0.01942
H44	0.39281	0.70061	-0.00132
H45	0.18928	0.62818	-0.01609
H46	0.13729	0.50645	-0.01438
H47	0.19761	0.5414	-0.01072
H48	0.08351	0.50079	-0.019
H49	0.43823	0.4638	0.01544
H50	0.47164	0.44191	0.01966
C51	0.40849	0.60871	0.00501
C52	0.39375	0.57435	0.00549
C53	0.41315	0.55974	0.00804
C54	0.44746	0.57963	0.01012
C55	0.46224	0.61409	0.00964
C56	0.44279	0.62857	0.00709
O57	0.39754	0.52534	0.00844
C58	0.41729	0.51095	0.01101
C59	0.45442	0.53113	0.01334
C60	0.46769	0.5642	0.01279

O61	0.40281	0.48106	0.01128
C62	0.3123	0.67963	-0.00757
C63	0.29755	0.64526	-0.00708
C64	0.36178	0.73488	-0.00601
C65	0.37448	0.76446	-0.0064
C66	0.48359	0.96227	-0.00693
C67	0.51793	0.98435	-0.00496
C68	0.53163	0.02732	0.04721
H69	0.29714	0.6908	-0.00956
H70	0.36719	0.55885	0.00388
H71	0.48877	0.62974	0.01123
H72	0.45447	0.65519	0.00674
H73	0.49373	0.58121	0.01427
H74	0.53562	0.9766	-0.00293
H75	0.55805	0.04128	0.04888
C76	0.606	0.20467	0.04458
C77	0.57168	0.18472	0.0425
C78	0.55675	0.15034	0.04297
C79	0.57627	0.13588	0.04552
C80	0.61069	0.15588	0.04761
C81	0.62549	0.19018	0.04714
O82	0.5224	0.13123	0.04083
C83	0.50768	0.09673	0.04132
C84	0.52746	0.07972	0.04404
C85	0.5605	0.09983	0.04599
O86	0.47785	0.08104	0.03943
C87	0.67852	0.37358	0.04224
C88	0.64419	0.35363	0.04016
C89	0.73336	0.37965	0.0469
C90	0.7629	0.3968	0.04871
C91	0.96015	0.48716	0.06197
C92	0.98187	0.4749	0.06461
C93	0.02036	0.4825	-0.02381
H94	0.68994	0.40021	0.04186

H95	0.55647	0.19582	0.04052
H96	0.62606	0.14498	0.04959
H97	0.65207	0.20538	0.04876
H98	0.57724	0.09079	0.04801
H99	0.97385	0.44919	0.06524
H100	0.03403	0.46999	-0.02189
C101	0.79815	0.41725	0.05086
C102	0.81773	0.40284	0.05342
C103	0.85207	0.42261	0.05551
C104	0.86685	0.45696	0.05503
C105	0.84722	0.47142	0.05247
C106	0.81296	0.4516	0.05039
O107	0.8708	0.40732	0.05803
C108	0.90527	0.42744	0.06012
C109	0.92262	0.46463	0.05973
C110	0.90285	0.47758	0.05723
O111	0.92063	0.41323	0.06228
C112	0.62944	0.31926	0.04063
C113	0.64902	0.30483	0.0432
C114	0.62408	0.36844	0.0375
C115	0.60724	0.38087	0.03531
C116	0.51911	0.48832	0.02153
C117	0.53172	0.52267	0.02086
C118	0.51127	0.53603	0.01828
H119	0.60285	0.30381	0.03902
H120	0.80638	0.37624	0.05379
H121	0.85837	0.49798	0.05207
H122	0.79805	0.46302	0.04841
H123	0.91215	0.50363	0.0567
H124	0.55743	0.54062	0.02226
H125	0.52402	0.56251	0.01804
C126	0.58717	0.39571	0.0327
C127	0.60191	0.43007	0.03222
C128	0.58251	0.44468	0.02966

C129	0.5482	0.42479	0.02758
C130	0.53342	0.39033	0.02806
C131	0.55287	0.37585	0.03061
O132	0.59812	0.47908	0.02926
C133	0.57837	0.49347	0.02668
C134	0.54125	0.47329	0.02436
C135	0.52797	0.44022	0.0249
O136	0.59285	0.52336	0.02642
C137	0.68336	0.32479	0.04528
C138	0.69811	0.35917	0.0448
C139	0.63388	0.26954	0.04365
C140	0.62118	0.23996	0.04408
C141	0.51207	0.04215	0.04463
C142	0.47773	0.02007	0.04266
C143	0.46403	0.9771	-0.00951
H144	0.69852	0.31362	0.04725
H145	0.62847	0.44557	0.03382
H146	0.50689	0.37468	0.02646
H147	0.54119	0.34923	0.03096
H148	0.50193	0.42321	0.02343
H149	0.46004	0.02782	0.04063
H150	0.43761	0.96314	-0.01119

Supplementary Table 5. Comparison of photocatalytic hydrogen production performance of organic photocatalysts

Photocatalyst	Amount	Cocatalyst Pt	Irradiation condition	Sacrificial reagent	HER mmol h ⁻¹ g ⁻¹	Reference
coumarin-linked COF	1.5 mg	2 wt %	440nm LED lamp	Ascorbic acid	531.2	This work
HOF-H4TBAPy	1.5 mg	5 wt %	300 W Xe lamp Full-arc 300 W	Ascorbic acid	357	Nat. Catal. 2023, 6, 574.
PY-TP-BTDO	10 mg	3 wt %	Xe lamp $\lambda > 300$ nm	Ascorbic acid	331	ACS Catal. 2023, 13, 204.
ZVCOF-1	1 mg	1 wt %	300 W Xe lamp $\lambda > 420$ nm	Ascorbic acid	289	J. Am. Chem. Soc. 2023, 145, 25222.
COF-JLU45	5 mg	1 wt %	300 W Xe lamp $\lambda > 420$ nm	Ascorbic acid	273	Angew. Chem. Int. Ed. 2025, 64, e202501869.
coumarin-linked COF	1.5 mg	2 wt %	300 W Xe lamp $\lambda > 420$ nm	Ascorbic acid	166	This work
COF-954	5 mg	5 wt %	300 W Xe lamp $\lambda > 420$ nm	Ascorbic acid	137	Adv. Mater. 2024, 36, 2308251.
CYANO-CON	20 mg	1 wt %	300 W Xe lamp $\lambda > 420$ nm	Ascorbic acid	134	Nat Commun 2022, 13, 2357.
IT-PMI NPs	45 μ g	6 wt %	LED lamp 420-750 nm	Ascorbic acid	126	Nat. Chem. 2026, 10.1038/s41557-025-02035-z
COF-JLU-100	3 mg	12 wt %	300 W Xe lamp $\lambda > 420$ nm	Triethanolamine	107	Angew. Chem. Int. Ed. 2022, 61, e202208919.
TpDTz-2D-COF	1.25 mg	5 wt %	525 nm LED lamp	Ascorbic acid	106	J. Am. Chem. Soc. 2026, 148, 1316.

Variations in experimental conditions (catalyst loading, Pt content, reactor geometry, photon flux) make strict cross-comparisons inherently challenging

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