

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

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This file contains all reviewer reports in order by version, followed by all author rebuttals in order by version.

Version 0:

Reviewer comments:

Reviewer #1

(Comments for the Author)

This manuscript has reported the enhanced photocatalytic hydrogen evolution via various linkages in COFs. The result is interest and this manuscript can be accepted after major revisions.

1. How does the linkage reduce the recombination of electrons and holes, which is very important for hydrogen production performance and needs to be explained in detail!
2. Based on fig. 3e, the influence of linkage on photocurrent is not very great. Why is there such a big difference in hydrogen production performance?
3. How calculation to obtain 532.1 mmol/g/h based on the hydrogen production and time per gram in Figure 4b? The hydrogen production per gram of catalyst is 8 mmol/g within 24 hours, and its hydrogen production rate should be 333.3 mmol/g/h. In addition, why is the initial hydrogen production rate slow and the hydrogen production energy accelerated later? Is it related to the reaction of sacrificial agent?

Reviewer #2

(Comments for the Author)

In this manuscript, the authors report three COFs with different linkages (imine, vinylene, and coumarin) for photocatalytic H₂ evolution, with the coumarin-linked COFs achieving a notable H₂ production rate of 531 mmol·g⁻¹·h⁻¹ (under 440 nm monochromatic light). However, the authors fail to demonstrate advancement and novelty over the prior coumarin COF system by Yaghi et al. (<https://www.nature.com/articles/s44160-025-00859-8>), as evidenced by inferior crystallinity and BET surface area relative to reported benchmarks. Furthermore, direct comparison of monochromatic-light performance with literature values obtained under broadband illumination (Fig. 4c) is not justified, and when evaluated under visible-light conditions, the activity of the coumarin-linked COF (166 mmol·g⁻¹·h⁻¹) is not superior to leading benchmark photocatalysts. Crucially, the evidence in the mechanism discussion section is not sufficiently compelling; the authors ascribe the high photocatalytic performance of the coumarin-linked COF to long-lived excited-state electrons observed in TAS measurements, but they do not assign or thoroughly analyze the transient spectral features to substantiate this claim. For the reasons stated above, I do not think this manuscript meets the standard of novelty and innovation required for publication in Nature Synthesis.

Additional concerns:

1. The hydrogen evolution data is confusing, as there are inconsistencies across different figures. For example, the HER in Supplementary Fig. 15a is around 2 mmol·g⁻¹·h⁻¹, while the values in Supplementary Fig. 15b-d are approximately 50-80 mmol·g⁻¹·h⁻¹, and the HER in Fig. 4b is as high as 531 mmol·g⁻¹·h⁻¹, which is an order of magnitude higher than the others. These discrepancies require clarification.
2. In Fig. 4b, the average HER in the initial 4 h is markedly lower (34.6 mmol·g⁻¹·h⁻¹) than during the 12-20 h period (531 mmol·g⁻¹·h⁻¹), which is unusual and requires further explanation.
3. The AQY at 405 nm is higher than at 440 nm (Fig. 4d), yet the authors have chosen to focus their main discussion on the H₂ evolution data at 440 nm, and the rationale for this selection should be clarified.
4. The claim of "represent the separation of photo generated electrons/holes" (line 175) is not convincingly supported by the HOMO/LUMO theoretical calculations in Supplementary Fig. 14, as the spatial separation of HOMO and LUMO is not

evident in calculated results and the results are inconsistent with the cited literature (Ref. 27).

5. The reported band gap of 1.69 eV (Fig. 4a) for the coumarin-linked COFs appears inconsistent with the bright yellow color of the photocatalytic dispersion (Supplementary Fig. 17), and it is recommended to re-measure the band gap.

6. It is recommended to provide the PXRD or FT-IR data of COFs after photocatalysis.

Reviewer #3

(Comments for the Author)

In this manuscript, the authors present novel and fully conjugated coumarin-linked COFs synthesized via a one-pot topological polycondensation method. The resultant material exhibits exceptional photocatalytic performance for hydrogen evolution, achieving a remarkable solar-to-hydrogen efficiency with an AQY of 37.95% at 405 nm and a hydrogen production rate of up to 531 mmol g⁻¹ h⁻¹. In addition, this study unveils the profound linkage-dependent enhancement in photocatalytic activity, as the coumarin-linked COF largely outperforms its imine- and vinyl-linked analogues. The study not only provides a novel synthetic strategy but also highlights the critical role of linkage engineering in designing high-performance COF photocatalysts. Overall, the results presented are highly compelling, and the manuscript is well-written and logically organized. I recommend publication in Nature Synthesis after the authors address the following comments:

1. While the one-pot synthesis approach is commendable yet challenging, the authors should further discuss how crystallinity is controlled and demonstrate the general applicability of this method to other coumarin-based COFs.
2. The authors should clarify whether the hydrophilicity of the coumarin-linked COF contributes to its photocatalytic performance. Moreover, a more in-depth analysis of the hydrogen evolution mechanism is warranted, particularly focusing on the role of the coumarin moiety's intrinsic chemical structure.
3. A direct comparative analysis of the FTIR spectra between the coumarin model compound and the resulting coumarin-linked COF should be provided to confirm structural fidelity.
4. The FTIR spectra of the key monomers used in synthesizing the imine- and vinyl-linked COFs should also be included to enable direct assessment of linkage formation and reaction completeness.
5. In Figure 2d, each peak in the ¹³C NMR spectrum should be assigned to the corresponding carbon atoms in the coumarin-linked COF structure. In addition, the C=C peak should be clearly labeled in the FTIR spectrum.
6. The author should provide fs-TA spectra for the vinyl-linked COF in the presence of co-catalysts to directly elucidate the interfacial electron transfer dynamics. This data is paramount to substantiating the proposed relationship between the bonding nature of the linkages and the resulting photocatalytic performance.
7. A schematic diagram illustrating the electron-transfer pathway upon co-catalyst loading, supported by theoretical calculations, should be included to fully clarify the reaction mechanism.
8. The photocatalytic hydrogen evolution performance of the imine- and vinyl-linked COFs under visible-light irradiation should also be provided for comparison.
9. The color scheme in Figure 4a should be revised to maintain consistency with the other figures.

Version 1:

Reviewer comments:

Reviewer #1

(Comments for the Author)

After revised in details, this manuscript has clarified questions and it can be accepted as current form.

Reviewer #2

(Comments for the Author)

The reviewer appreciates the revisions made by the authors. However, two major concerns remain. First, the authors emphasize the advantage of their one-pot approach over Yaghi's method (Nat. Synth. 2025, 4, 1376). However, despite the synthetic simplicity, the quality of the resulting material appears unsatisfactory. In particular, the BET surface area is only 143 m² g⁻¹ (page 9), which is substantially lower than the value reported by Yaghi et al. (~981 m² g⁻¹). Therefore, the claimed synthetic advantage is not convincing if the simplified route leads to an inferior material.

Second, the reported high hydrogen evolution rate of 531 mmol g⁻¹ h⁻¹ is based on irradiation with a 440 nm LED. Although monochrome LED sources are commonly used in organic photocatalysis studies, photocatalytic water splitting for hydrogen production is intended for solar energy conversion and is more appropriately evaluated under simulated sunlight, typically using Xe lamps with AM 1.5G filters or cutoff filters ($\lambda > 420$ nm). The authors also acknowledge in the Response Letter (Table R1) that the literature examples used for comparison were all measured under Xe lamp irradiation. Under the more relevant visible-light condition (Xe lamp, $\lambda > 420$ nm), the coumarin COF exhibits an activity of 166 mmol g⁻¹ h⁻¹ (page 12), which does not surpass several leading organic photocatalysts listed in Table R1 and Figure 4c.

Reviewer #3

(Comments for the Author)

The authors have conducted a comprehensive revision of the manuscript, incorporating new experimental data and theoretical backing. The responses to all referees' concerns are satisfactory and have notably strengthened the work. I therefore recommend publication pending the minor revisions below:

1. The authors should provide calculation details for Supplementary Fig. 17 in the Supporting Information.
2. In Fig. 3c, the fluorescence signal of coumarin COF is largely obscured by the intense signal of vinyl COF. The authors should consider moving the coumarin COF spectra to the Supporting Information to allow clearer visualization on a suitable scale.
3. The caption “2D framework” in Fig. 1c should be revised to “2D covalent organic framework”.
4. In Fig. 3, “imine-COF”, “vinyl-COF” and “coumarin-COF” should be revised to “imine COF”, “vinyl COF” and “coumarin COF” respectively, for consistency with the main text.
5. The term “recombination” in Fig. 3a should be revised to “radiative recombination”.
6. In Fig. 2a, the authors should more clearly highlight the one-step synthetic strategy of the coumarin linkage.

Version 2:

Reviewer comments:

Reviewer #2

(Comments for the Author)

The reviewer has no further comments.

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We address the concerns of Reviewer 1# as follows:

Comments:

This manuscript has reported the enhanced photocatalytic hydrogen evolution via various linkages in COFs. The result is interest and this manuscript can be accepted after major revisions.

Response:

We sincerely thank you for your constructive comments. The manuscript has been revised accordingly, with careful consideration given to all of your suggestions.

Question 1:

How does the linkage reduce the recombination of electrons and holes, which is very important for hydrogen production performance and needs to be explained in detail!

Response:

Thank you for your constructive comment. The coumarin linkage reduces electrons/holes recombination primarily through two synergistic mechanisms (Figure R1):

(i) **Enhanced Spatial Charge Separation:** The coumarin unit acts as an electron acceptor, forming a donor-acceptor (D-A) structure with the electron-rich moieties of the framework (*J. Am. Chem. Soc.* 2023, 145, 8364). This creates a built-in electric field that drives charge separation (Figure R1a). The degree of separation is quantified by the charge centroid

distance (D). The calculated D value for the coumarin-linked structure (5.366) is significantly larger than those for the imine (0.003) and vinyl (0.176) analogues, confirming its superior capability in spatially separating electrons/holes.

(ii) **Promoted Charge Delocalization and Transport:** The coumarin linkage could extend the overall π -conjugation, as evidenced by the calculation of orbital delocalization index (ODI) (*Adv. Mater.* 2026, 38, e07961). The ODI value of coumarin-linked structure (4.38) is lower than that of the imine (7.05) and vinyl-linked (4.71) structures (Figure R1b), indicating the enhancement of conjugation. This enhanced conjugation could improve the mobility of photogenerated charge carriers to reaction sites before recombination.

Action:

We added the following discussion in **Page 13 of the revised manuscript:**

“Enhanced photocatalytic hydrogen evolution in coumarin COF can be attributed to four factors: (i) a D-A structure established for efficient charge separation; (ii) the planar, rigid coumarin extends π -conjugation, boosting charge mobility; (iii) suppressed structural torsion minimizes vibrational energy loss; (iv) carbonyl-water hydrogen bonding promotes proton adsorption and reduction.”

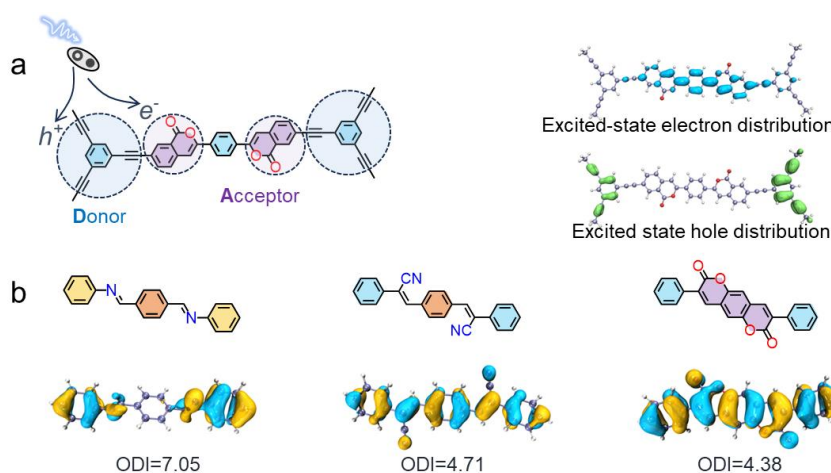


Figure R1. Advantages of coumarin COF in photocatalytic hydrogen production. (a) The D-A structure facilitates the separation of photo-generated electrons/holes. (b) Highly conjugated structures promote the delocalization of electrons.

Question 2:

Based on fig. 3e, the influence of linkage on photocurrent is not very great.

Why is there such a big difference in hydrogen production performance?

Response:

Thank you for the insightful comment. The influence of linkage on the photocurrent density in Fig. 3e appears limited because that photocurrent measurements are conducted under an applied bias, which drives the migration of photogenerated electrons towards the electrode. Therefore, the photocurrent response is limited to reflecting the generation trend of photo generated electrons across the electrode interface. Photocurrent is positively correlated with photocatalytic activity, but not directly equivalent. Under certain testing conditions, the magnitude of photocurrent can semi-quantitatively reflect photocatalytic activity of hydrogen

production performance under bias-free conditions.

As for the big difference in hydrogen production performance, which stems from the complex catalytic kinetics. As in Fig. 5 and Supplementary Fig. 21-22, the fs-TA spectroscopies show that the excited-state electron lifetime of coumarin COF is extended to 1080 ps, approximately 1000 times than that of the imine COF (1.07 ps) and 4 times than that of the vinyl COF (252 ps). These long-lived electrons are subsequently transferred to the cocatalyst within ~407 ps, facilitating efficient hydrogen production. In addition, the -C=O of coumarin has obvious hydrophilicity and electron withdrawing properties, which promotes the adsorption/activation of water (*Angew. Chem. Int. Ed.* 2025, 64, e202502821) and the coordination/photo-deposition of Pt cocatalysts (*Angew. Chem. Int. Ed.* 2023, 62, e202217989), for efficient electron transfer in photocatalytic hydrogen production.

In summary, while the applied bias in photocurrent measurements equalizes electron extraction, the photocatalytic hydrogen production under zero bias is kinetically controlled. The coumarin linkage excels here by profoundly extending charge carrier lifetimes, accelerating electron transfer to cocatalysts, and optimizing the reaction microenvironment; these factors are collectively responsible for the dramatically enhanced hydrogen evolution performance.

Question 3:

How calculation to obtain 532.1 mmol/g/h based on the hydrogen production and time per gram in Figure 4b? The hydrogen production per gram of catalyst is 8 mol/g within 24 hours, and its hydrogen production rate should be 333.3 mmol/g/h. In addition, why is the initial hydrogen production rate slow and the hydrogen production energy accelerated later? Is it related to the reaction of sacrificial agent?

Response:

Thank you for your careful and insightful comment. In Fig. 4b, the maximum hydrogen production rate of 532.1 mmol g⁻¹ h⁻¹ was calculated based on the stable hydrogen production interval (8-12 hours) (per gram of catalyst is 4.25 mol g⁻¹), while the hydrogen production rate of 333.3 mmol g⁻¹ h⁻¹ that you mentioned represents the average value calculated within 24 hours. We are sorry for this confusion, which has been clarified in this revision.

In addition, the slow hydrogen production rate during the initial hours is due to the consumption of a lot of photogenerated electrons for the photo-deposition of the platinum cocatalyst (Figure R2) (*Nat. Mater.* 2020, 19, 559; *Nat. Energy* 2022, 7, 340), thus the photocatalytic hydrogen production rate reaches its optimal level only after establishing the necessary active sites for proton reduction.

Meanwhile, the sacrificial agent (ascorbic acid) is indeed related to the

overall high hydrogen production. It rapidly scavenges photogenerated holes to suppress the charge recombination, which is essential for enabling the initial reduction/deposition of the Pt co-catalyst and driving sustained proton reduction. We have clarified this point in the revised manuscript and caption.

Action:

We added the following discussion in **Page 12 of the revised manuscript**:

“The optimal hydrogen production rate at 440 nm calculated from the stable hydrogen production interval (approximately 12-20 hours) was 531 mmol g⁻¹ h⁻¹. ”

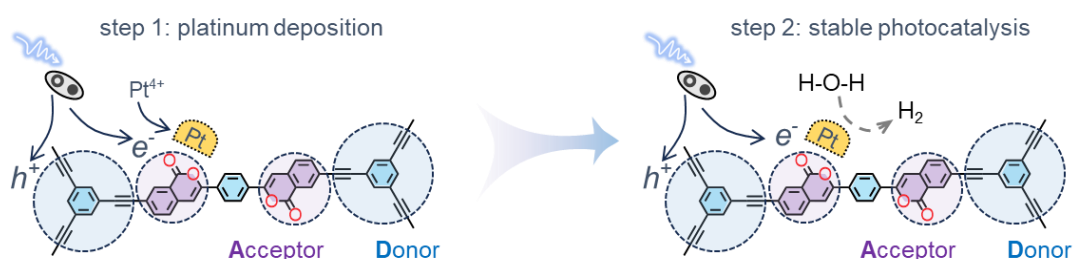


Figure R2. Schematic diagram of photocatalytic hydrogen production. The first step is the deposition of platinum, and the second step is stable photocatalytic hydrogen production.

We address the concerns of Reviewer 2# as follows:

Comments:

In this manuscript, the authors report three COFs with different linkages (imine, vinylene, and coumarin) for photocatalytic H₂ evolution, with the coumarin-linked COFs achieving a notable H₂ production rate of 531 mmol·g⁻¹·h⁻¹ (under 440 nm monochromatic light).

Response:

We sincerely appreciate your careful assessment and valuable suggestions. All the points you raised have been carefully addressed in the revised manuscript, as detailed in our responses below.

Question 1:

However, the authors fail to demonstrate advancement and novelty over the prior coumarin COF system by Yaghi et al. (<https://www.nature.com/articles/s44160-025-00859-8>), as evidenced by inferior crystallinity and BET surface area relative to reported benchmarks.

Response:

Thanks for your careful comments. In brief, our work differs fundamentally from the Yaghi's work (*Nat. Synth.* 2025, 4, 1376) in both synthesis mechanism and photocatalytic applications.

(i) **For synthesis mechanism.** Yaghi's work reported a two steps route (pre-crystallization and post-cyclization) to synthesize coumarin COF because they emphasized that the irreversible coumarin linkage is

negative for forming ordered frameworks (Figure R3a). In contrast, we report a simple one-pot strategy via base-catalyzed polycondensation with kinetic modulation. By tuning catalyst, monomer ratio, and solvent, the crystallization and cyclization steps were resolved under a single condition (Figure R3b). The direct synthesis strategy eliminates the complex hydroxyl protection step compared to Yaghi's work.

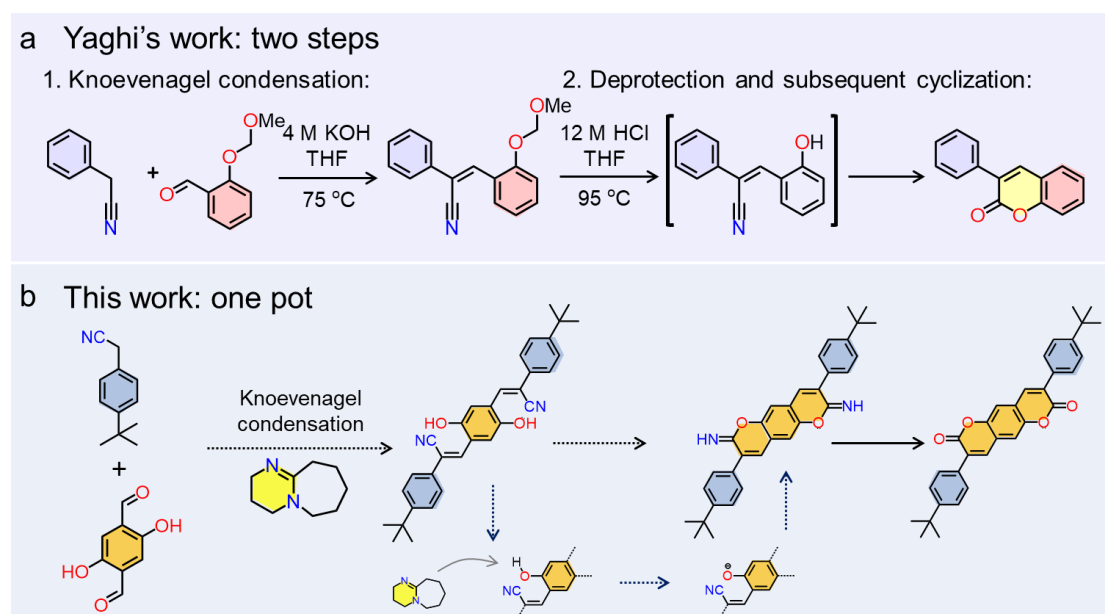


Figure R3. Comparison of synthetic strategies. (a) The previous approach requires sequential hydroxyl protection, Knoevenagel condensation, deprotection, cyclization. (b) Our method achieves direct construction via a single-step, base-catalyzed reaction.

(ii) **For photocatalytic applications.** Yaghi's work primarily focuses on synthesis method and structural characterization of coumarin COFs, without investigation on the structure-activity relationship. Our work innovatively reveals the correlation between linkages and photocatalytic performance from the π conjugation, structural torsion and active site. We demonstrated the enhanced π conjugation of coumarin linkage by the

optimally decoupled index (ODI) calculation (smaller ODI values correspond to higher conjugation) (Figure R4a). Meanwhile, the calculation of torsional energy barrier shows that the coumarin linkage could minimize non radiative vibrational energy loss, contributing to the extended excited state lifetime (Figure R4b). Additionally, the intrinsic electron-withdrawing and hydrophilic coumarin units facilitate efficient photo-deposition of cocatalysts (*Angew. Chem. Int. Ed.* 2023, 62, e202217989) and favor proton reduction (Figure R4c) (*Angew. Chem. Int. Ed.* 2025, 64, e202502821). Therefore, the coumarin COF exhibited a prominent hydrogen production rate of up to 531 mmol·g⁻¹·h⁻¹.

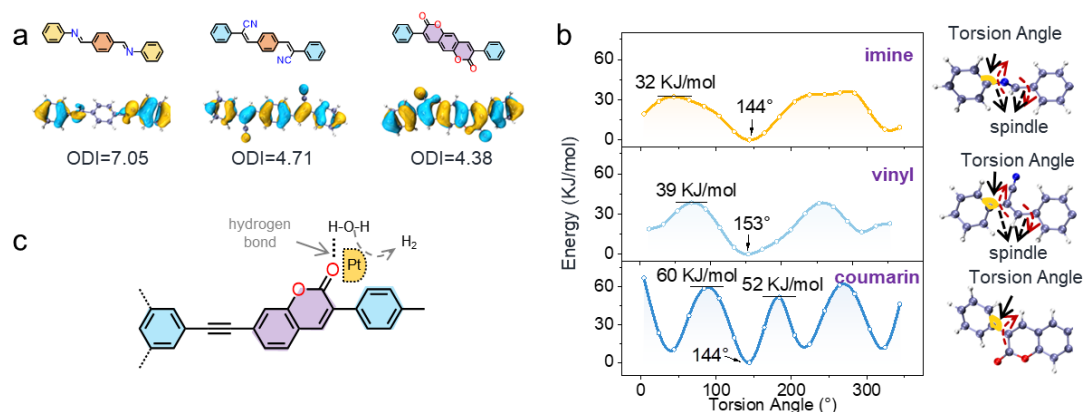


Figure R4. The influence mechanism of linkages on photocatalytic hydrogen production. (a) Electron delocalization. (b) The in-plane vibrational losses. (c) The water adsorption and Pt deposition on carbonyl site.

In summary, compared with previously reported work by Yaghi and coworkers, our work not only represents significant progress in synthetic strategy but also provides an important reference for expanding the application of coumarin-based COFs and elucidating their structure-

activity relationships in comparison to imine- and vinyl-linked counterparts.

Question 2:

Furthermore, direct comparison of monochromatic-light performance with literature values obtained under broadband illumination (Fig. 4c) is not justified, and when evaluated under visible-light conditions, the activity of the coumarin-linked COF ($166 \text{ mmol}\cdot\text{g}^{-1}\cdot\text{h}^{-1}$) is not superior to leading benchmark photocatalysts.

Response:

Thank you for this insightful comment. We agree that direct comparison between monochromatic-light-driven performance and literature values obtained under broadband illumination requires careful consideration. We would like to clarify the following points:

i) Currently, there is no universally accepted standard for evaluating photocatalytic hydrogen evolution performance. Reported activities are strongly influenced by multiple experimental parameters beyond the light source, including catalyst loading, cocatalyst type, sacrificial agents, reactor configuration, and photon flux. Therefore, most literature reports present the optimal performance under their respective conditions.

ii) Monochromatic light sources (e.g., LEDs) are widely adopted in photocatalysis studies due to their well-defined wavelength, low cost, energy efficiency, and compatibility with scalable device integration.

Recent high-impact studies (e.g., *Science* 2026, 391, 267; *Science* 2022, 378, 889) have also employed such systems. Importantly, monochromatic illumination enables precise evaluation of wavelength-dependent activity and quantum efficiency, which is critical for mechanistic understanding and rational material design, and is increasingly considered relevant for practical applications due to low cost and easy device integration.

iii) Regarding to your concern, in this revision, we performed the hydrogen evolution rate of coumarin COF under visible light in Figure 4c. In addition, we added a comparison Table of HER performance of organic photocatalysts, including detailed testing information.

Action:

We added the **Table R1** in **Supplementary Table 5 of the revised SI**.

Table R1. Comparison of HER performance of organic photocatalysts.

Photocatalyst	Amount	Cocatalyst Pt	Irradiation condition	Sacrificial reagent	HER mmol h ⁻¹ g ⁻¹	Reference
coumarin 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 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.

Question 3:

Crucially, the evidence in the mechanism discussion section is not sufficiently compelling; the authors ascribe the high photocatalytic performance of the coumarin-linked COF to long-lived excited-state electrons observed in TAS measurements, but they do not assign or thoroughly analyze the transient spectral features to substantiate this claim.

Response:

We greatly appreciate for your constructive comments. Regarding your concern, in this revision, we have enhanced our discussion on the mechanism section from both transient spectral characteristics and catalytic kinetics analysis:

(i) **For transient spectral characteristics.** As revealed by the fs-TAS spectroscopy (Figure 5b), the negative features at ~ 450 nm signify the ground-state bleaching (GSB) according to UV-vis absorption spectroscopy, confirming the photoexcitation of electrons. Concurrently, a broad excited-state absorption at ~ 550 -650 nm can be attribute to the

characteristic excited-state absorption (ESA), indicating the highly delocalized excitons within the conjugated framework.

(ii) **For catalytic kinetics analysis.** The distinct kinetic behaviors of three COFs were demonstrated via the decay kinetics fitting. The imine COF shows the fastest decay ($\tau_1 = 0.67$ ps, $\tau_2 = 5.68$ ps, where τ_1 and τ_2 represent electron trapping and exciton dissociation) (Figure R5a) due to the polarization of -C=N. The vinyl COF shows a moderate carrier lifetime ($\tau_1 = 6.26$ ps, $\tau_2 = 256.6$ ps) because the enhanced π -density promotes the generation of excited-state electrons (Figure R5c). However, excited-state electrons will also rapidly return to the ground state. In contrast, the coumarin COF exhibits dramatically prolonged lifetimes ($\tau_1 = 45.42$ ps, $\tau_2 = 1031.39$ ps) (Figure R5e) because further enhanced delocalization could stabilize charge-separated states. Additionally, the long-lived electrons can be rapidly transferred to the catalytic sites within 407 ps, which was demonstrated by the decay kinetics after Pt loading (Figure R5f).

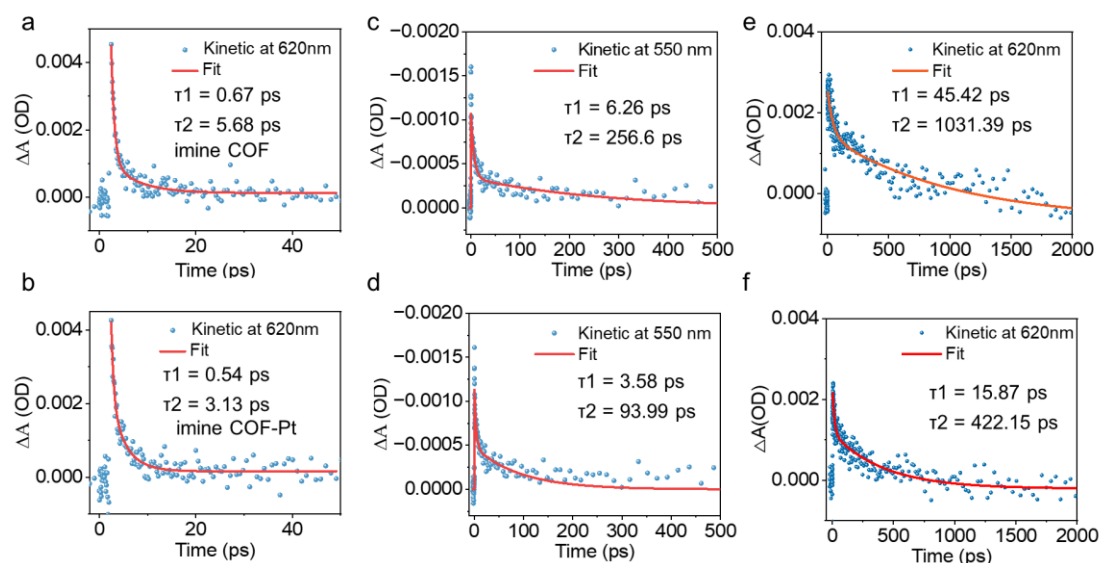


Figure R5. (a-b) Decay kinetics of imine COF and imine COF-Pt. (c-d) Decay kinetics of vinyl COF and vinyl COF-Pt. (e-f) Decay kinetics of coumarin COF and coumarin COF-Pt.

In summary, TAS measurements revealed the separation and transfer behavior of photo generated electrons in three COFs, which shows that coumarin COF exhibits higher electron utilization efficiency, contributing to enhanced photocatalytic hydrogen production.

Action:

We added the following discussion in **Page 14 of the revised manuscript**:

“The imine-linked COF shows the fastest decay ($\tau_1 = 0.67$ ps, $\tau_2 = 5.68$ ps, where τ_1 and τ_2 represent electron trapping and exciton dissociation) due to bond polarization. The vinyl-linked COF exhibits moderate improvement ($\tau_1 = 6.26$ ps, $\tau_2 = 256.6$ ps) due to the high π -density, which promotes the generation of excited-state electrons. However, excited-state electrons will still rapidly return to the ground state. In contrast, the coumarin-linked COF displays dramatically prolonged lifetimes ($\tau_1 =$

45.42 ps, $\tau_2 = 1031.39$ ps), resulting from enhanced delocalization that effectively stabilizes charge-separated states.”

Question 4:

The hydrogen evolution data is confusing, as there are inconsistencies across different figures. For example, the HER in Supplementary Fig. 15a is around $2 \text{ mmol}\cdot\text{g}^{-1}\cdot\text{h}^{-1}$, while the values in Supplementary Fig. 15b-d are approximately $50\text{-}80 \text{ mmol}\cdot\text{g}^{-1}\cdot\text{h}^{-1}$, and the HER in Fig. 4b is as high as $531 \text{ mmol}\cdot\text{g}^{-1}\cdot\text{h}^{-1}$, which is an order of magnitude higher than the others. These discrepancies require clarification.

Response:

We are sorry for this confusion. The discrepancies of hydrogen evolution data are due to distinct experimental conditions for specific objectives:

(i) **For long-term HER stability.** The lower hydrogen production rate (around $2 \text{ mmol}\cdot\text{g}^{-1}\cdot\text{h}^{-1}$) in Supplementary Fig. 15a-b is due to a relatively high dosage of COF (15 mg), which is to ensure a sustained and detectable hydrogen signal in the real-time online monitoring (Labsolar-6A system, Beijing Perfectlight). The enhancement light scattering effect of the COF suspension under high dosage results in inefficient photon absorption efficiency per unit mass of photocatalyst.

(ii) **For performance optimization.** The hydrogen production rates of $50\text{-}80 \text{ mmol}\cdot\text{g}^{-1}\cdot\text{h}^{-1}$ in Supplementary Fig. 15b-d were conducted in a multi-channel photoreactor under 440 nm LEDs to screen for the optimal

reaction conditions. After identifying the optimal combination of sacrificial agent (0.14 M ascorbic acid solution), COF dosage (1.5 mg), and cocatalyst precursor loading (1.0 μL 8 wt% H_2PtCl_6), yielding a maximum hydrogen production rate of $531 \text{ mmol}\cdot\text{g}^{-1}\cdot\text{h}^{-1}$ (Figure 4a).

To avoid future confusion, we have updated the discussion in the manuscript. For more details, please refer to the Actions section below.

Actions:

1. We revised the figure legends of **Supplementary Fig. 15**.
2. We added the following discussion in **Page 12 of the revised manuscript**: *“Supplementary Fig. 15a presents the hydrogen production rate monitored in real time using the Labsolar-6A online analysis system. In contrast, Supplementary Fig. 15 b-d detail a series of controlled optimization experiments at 440 nm LED light to identify the optimal conditions.”*

Question 5:

In Fig. 4b, the average HER in the initial 4 h is markedly lower ($34.6 \text{ mmol}\cdot\text{g}^{-1}\cdot\text{h}^{-1}$) than during the 12-20 h period ($531 \text{ mmol}\cdot\text{g}^{-1}\cdot\text{h}^{-1}$), which is unusual and requires further explanation.

Response:

Thank you for the comment. The lower hydrogen production in the initial 4 h is due to the in-situ photo-deposition of the Pt co-catalyst, representing

a necessary activation period (*Nat. Mater.* 2020, 19, 559; *Nat. Energy* 2022, 7, 340). During the initial 4 hours (the so-called induction period), the majority of photogenerated electrons are consumed to reduce cocatalyst precursors, rather than for proton reduction, which is a common phenomenon in the field of photocatalysis.

To further elucidate the platinum deposition mechanism, in the revision, we have supplemented the additional calculations (Figure R6), which shows the thermodynamic spontaneity of Pt deposition onto the carbonyl sites of coumarin unit (*Angew. Chem. Int. Ed.* 2023, 62, e202217989).

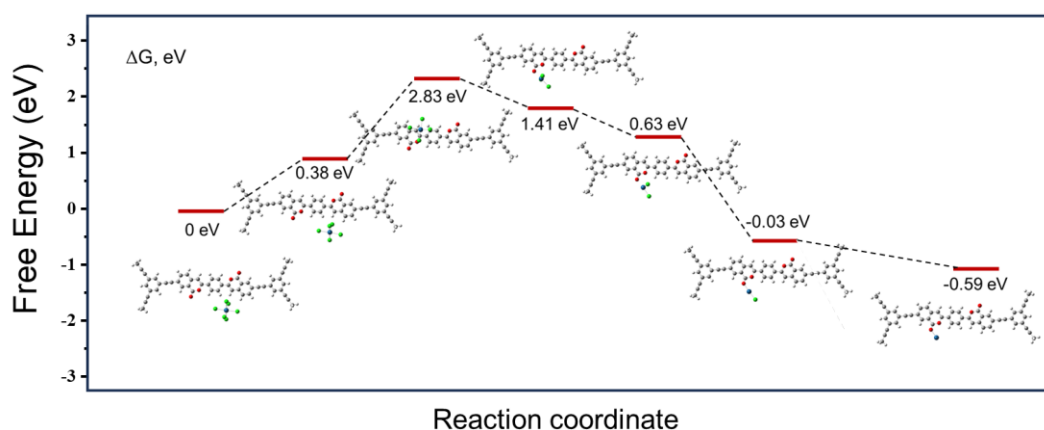


Figure R6. The photo deposition process of platinum on C=O within coumarin bond (free energy diagrams).

Action:

We added the **Figure R6** in **Supplementary Fig. 17 of the revised SI**.

Question 6:

The AQY at 405 nm is higher than at 440 nm (Fig. 4d), yet the authors have chosen to focus their main discussion on the H₂ evolution data at 440

nm, and the rationale for this selection should be clarified.

Response:

Thank you for the constructive comment. The 440 nm LEDs was chosen to evaluate hydrogen production performance for avoiding the possible [2+2] photocycloaddition reaction of coumarin under UV irradiation (e.g., 405 nm) (*Adv. Mater.* 2021, 33, 2008057), which will disrupt the π conjugated structure during long-term testing.

Question 7:

The claim of “represent the separation of photo generated electrons/holes” (line 175) is not convincingly supported by the HOMO/LUMO theoretical calculations in Supplementary Fig. 14, as the spatial separation of HOMO and LUMO is not evident in calculated results and the results are inconsistent with the cited literature (Ref. 27).

Response:

Thank you for the constructive comments. Regarding to your concern, in this revision, we have supplemented new calculations on the spatial distributions of excited-state electrons and holes using time-dependent density functional theory (TDDFT) with hole–electron analysis (Figure R8). In contrast to the previous HOMO–LUMO orbital analysis, which only provides a static description of ground-state charge distribution, the new calculations in Figure R8 reveal that electrons and holes are

completely separated on the electron-withdrawing coumarin and the electron-donating benzene ring.

To quantify the spatial separation of electrons/holes, we further calculated the charge centroid distance (D value). The results mean that the D value of coumarin linkage (5.366) is higher than that of imine (0.003) and vinyl (0.176), representing an enhancement of charge separation. The cited literature 27 (Ref. 27) has also been replaced (*Nat Commun*, 2025, 16, 2457).

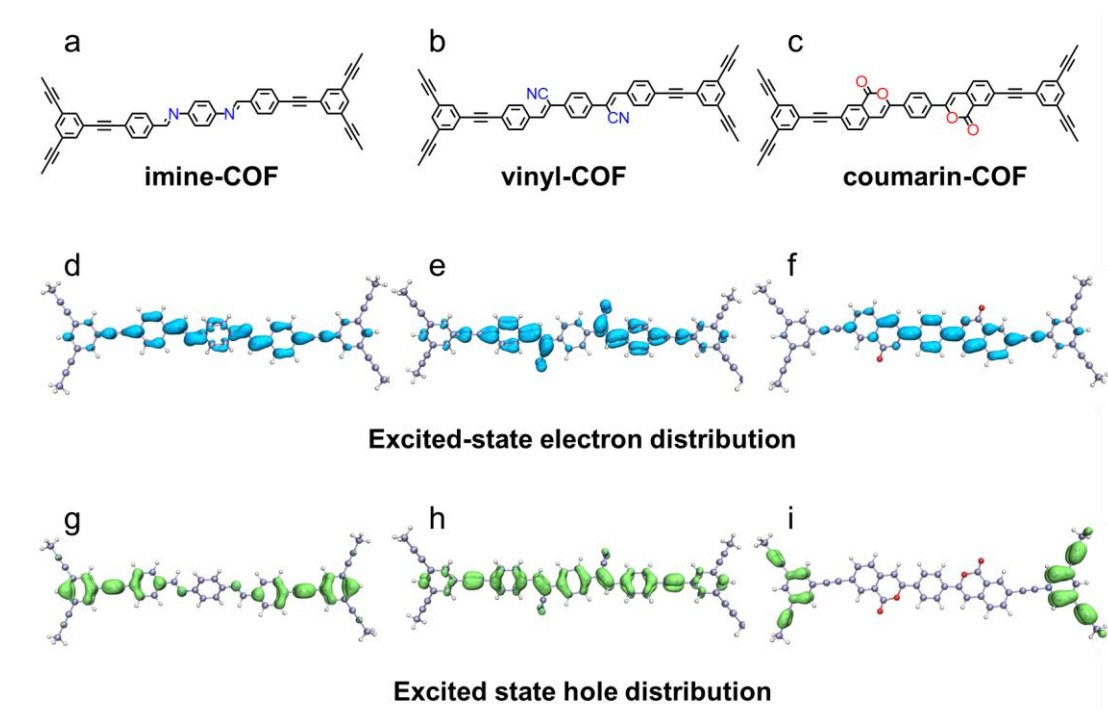


Figure R7. The structure fragment of (a) imine COF, (b) vinyl COF and (c) coumarin COF. The excited-state electron distribution of (d) imine COF, (e) vinyl COF and (f) coumarin COF. The excited-state hole distribution of (g) imine COF, (h) vinyl COF and (i) coumarin COF. The charge centroid distance (D value) between the hole and electron of imine, vinyl and coumarin COFs are 0.003, 0.176 and 5.366 respectively.

Actions:

1. We supplemented the **Figure R7** in **Supplementary Fig. 14 of the revised SI**.
2. We added the following discussion in **Page 10 of the revised manuscript**: *“Meanwhile, the extent of spatial separation was quantified by calculating the charge centroid distance (D value) between the hole and electron, which means that the coumarin linkage ($D=5.366$) facilitates superior separation of photo-generated charge carriers (0.003 for imine COF and 0.176 for vinyl COF).”*

Question 8:

The reported band gap of 1.69 eV (Fig. 4a) for the coumarin-linked COFs appears inconsistent with the bright yellow color of the photocatalytic dispersion (Supplementary Fig. 17), and it is recommended to re-measure the band gap.

Response:

Thank you for the careful comment. We would like to note that the pristine coumarin COF powder is orange (Figure. R8), which is consistent with the 1.69 eV bandgap calculated by the Tauc plot of the solid-state UV-Vis spectrum. In contrast, in dispersion, light absorption follows the Lambert-Beer law, correlating with concentration and optical path length, while the contribution of scattering is minimized. Additionally, solvent molecules (such as H₂O in our system) can to some extent passivate surface defects

of COFs through coordination or hydrogen bonding, rendering the optical properties of the material closer to the ideal structure and resulting in a lighter color. Therefore, in experiments, we frequently observe that the color of 2D COFs in dispersion is lighter than that in the powder state. Accordingly, in the revised manuscript, we further specify the conditions for bandgap determination to avoid potential misunderstandings for readers.

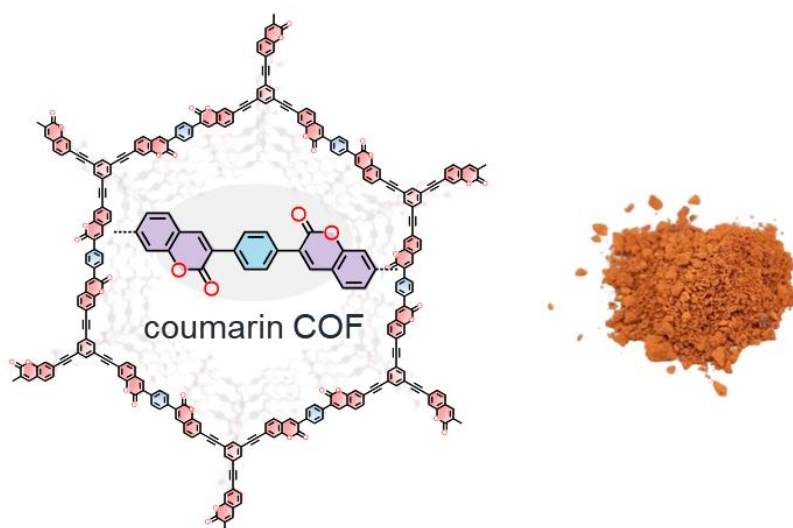


Figure R8. Digital photograph of the as-synthesized coumarin COF powder.

Question 9:

It is recommended to provide the PXRD or FT-IR data of COFs after photocatalysis.

Response:

Thank you for this valuable suggestion. As recommended, in the revision, we have provided the FT-IR and PXRD spectra of coumarin COF after 24 hours of photocatalytic hydrogen production to confirm the chemical and crystal stability.

(i) **The chemical stability.** The FT-IR characterization shows that all characteristic peaks after photocatalysis, including the -C=O (1723 cm^{-1}) and -C=C- (1610 cm^{-1}) stretches, remain consistent with those of the pristine coumarin COF, confirming that the chemical structure is preserved (Figure R9a).

(ii) **The crystal stability.** The peak of (100) face shifted 0.1° , accompanied by a decrease in intensity due to the breaking of interlayer stacking, caused by continuous hydrogen evolution and magnetic stirring (Figure R9b). Solvation effects can also reduce interlayer interactions, leading to exfoliation of COF materials into thinner morphologies. Nevertheless, the retention of the primary diffraction peak at 2.3° demonstrates that the coumarin COF maintains good crystallinity.

Actions:

1. We supplemented the **Figure R9** in **Supplementary Fig. 19 of the revised SI**.
2. We added the following discussion in **Page 13 of the revised manuscript**: *“The FT-IR spectra of the coumarin COF after the photocatalysis showed that the key lactone -C=O and -C=C- peaks remain consistent, indicating the chemical stability. Meanwhile, the crystal stability also been proven through PXRD characterization.”*

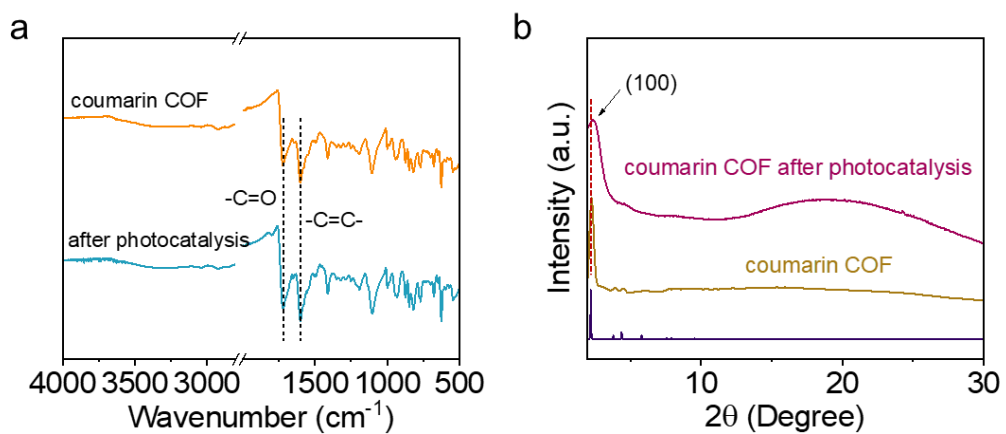


Figure R9. (a) FT-IR and (b) PXRD spectra of coumarin COF before and after 24 hours photocatalytic reaction under 440nm.

We address the concerns of Reviewer 3# as follows:

Comments:

In this manuscript, the authors present novel and fully conjugated coumarin-linked COFs synthesized via a one-pot topological polycondensation method. The resultant material exhibits exceptional photocatalytic performance for hydrogen evolution, achieving a remarkable solar-to-hydrogen efficiency with an AQY of 37.95% at 405 nm and a hydrogen production rate of up to 531 mmol g⁻¹ h⁻¹. In addition, this study unveils the profound linkage-dependent enhancement in photocatalytic activity, as the coumarin-linked COF largely outperforms its imine- and vinyl-linked analogues. The study not only provides a novel synthetic strategy but also highlights the critical role of linkage engineering in designing high-performance COF photocatalysts. Overall, the results presented are highly compelling, and the manuscript is well-written and logically organized. I recommend publication in Nature Synthesis after the authors address the following comments:

Response:

We sincerely thank you for your constructive comments. The manuscript has been revised accordingly, with careful consideration given to all of your suggestions.

Question 1:

While the one-pot synthesis approach is commendable yet challenging, the

authors should further discuss how crystallinity is controlled and demonstrate the general applicability of this method to other coumarin-based COFs.

Response:

Thank you for the valuable comment. The challenge of the one-pot synthesis approach is due to the inherent irreversibility of lactonization, which lead to a poor crystallinity of coumarin COF. Regarding this issue, this work functionally decoupled the process into two stages. The reaction initiates with a reversible Knoevenagel condensation between aldehyde and phenylacetonitrile groups, allowing for error correction and the assembly of an ordered pre-framework for the irreversible cyclization by optimizing solvent composition, catalyst, and temperature. This principle has been successfully generalized for synthesizing other coumarin-linked COFs in our subsequent works.

Question 2:

The authors should clarify whether the hydrophilicity of the coumarin-linked COF contributes to its photocatalytic performance. Moreover, a more in-depth analysis of the hydrogen evolution mechanism is warranted, particularly focusing on the role of the coumarin moiety's intrinsic chemical structure.

Response:

Thank you for your constructive suggestion. Following your suggestion, we have confirmed the hydrophilicity of coumarin COF by water contact (CA) angle testing, showing a CA value of 34°. Furthermore, to analyze the interaction between coumarin units and water, we measured the FT-IR spectroscopy of coumarin COF after wetting. The results reveal that the characteristic lactone -C=O stretch broadens and redshifts upon hydration, confirming the formation of hydrogen-bond between the carbonyl groups and water molecules (Figure R10). The hydrogen-bonded network enhances the adsorption and activation of water at the active site for efficient hydrogen production (*Angew. Chem. Int. Ed.* 2025, 64, e202502821). In addition, the coumarin unit also serve as active sites for cocatalyst deposition, further facilitating charge transfer and surface reaction kinetics (see detailed discussion in response to Question 7).

Actions:

1. We supplemented the **Figure R10** in **Supplementary Fig. 22 of the revised SI**.
2. We added the following discussion in **Page 14 of the revised manuscript**: “*The hydrophilicity of the coumarin COF (CA=34°) is also contribute to the photocatalytic hydrogen production. Mechanistically, FT-IR spectroscopy showed that the characteristic lactone C=O stretch*

broadens and redshifts upon hydration, confirming the formation of hydrogen-bond between carbonyl groups and water molecules.”

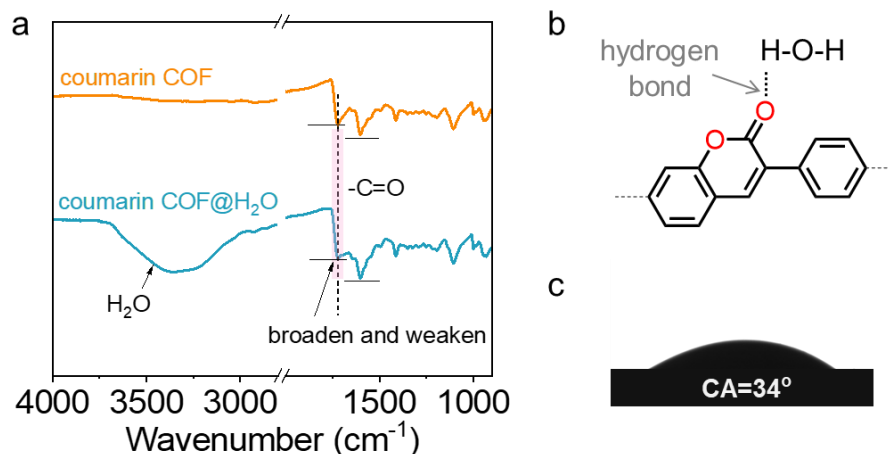


Figure R10. (a) FTIR spectra of coumarin COF and coumarin COF@H₂O. (b) Illustration of hydrogen-bonding interactions between water molecules and the coumarin unit. (c) Water contact angle of coumarin COF.

Question 3:

A direct comparative analysis of the FTIR spectra between the coumarin model compound and the resulting coumarin-linked COF should be provided to confirm structural fidelity.

Response:

Thank you for your valuable suggestion. Following your suggestion, in this revision, we have provided the FT-IR spectra of the coumarin model compound (Figure R11), which exhibits distinct -C=O and -C=C- stretching vibrations at 1723 cm^{-1} and 1610 cm^{-1} , respectively. The consistent positions of characteristic peak between the model compound and the coumarin COF confirm the structural fidelity of the synthesized framework.

Actions:

1. We supplemented the **Figure R11** in **Supplementary Fig. 6** of the **revised SI**.
2. We added the following discussion in **Page 8** of the **revised manuscript**: *“New characteristic peaks at 1111, 1610 and 1723 cm^{-1} correspond to C-O-C, -C=C- and C=O, which matches the model molecule, demonstrating the successful synthesis of coumarin.”*

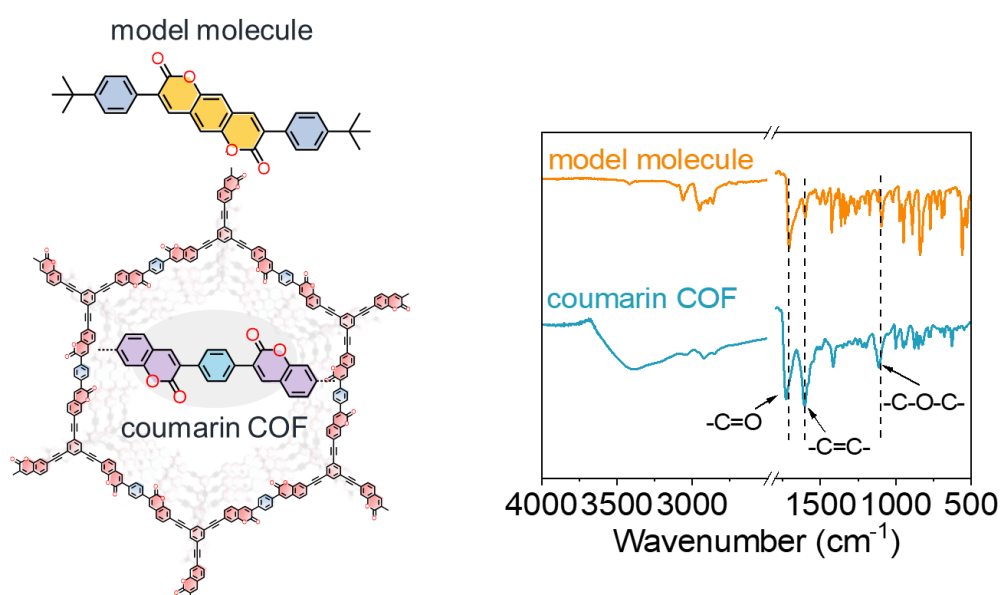


Figure R11. FT-IR spectra of coumarin COF and model molecule.

Question 4:

The FTIR spectra of the key monomers used in synthesizing the imine- and vinyl-linked COFs should also be included to enable direct assessment of linkage formation and reaction completeness.

Response:

Thank you for your constructive suggestion. Following your suggestion, in this revision, we have included the FT-IR spectra of the monomers used in synthesizing the imine and vinyl COFs (Figure R12). The result reveals that the peaks of amino and the aldehyde groups disappeared after polymerization. Concurrently, the prepared imine and vinyl COFs exhibit new peaks at 1617 and 1623 cm^{-1} corresponding to -C=N- and -C=C- bonds, respectively.

Action:

We added the **Figure R12** in **Supplementary Fig. 6 of the revised SI**.

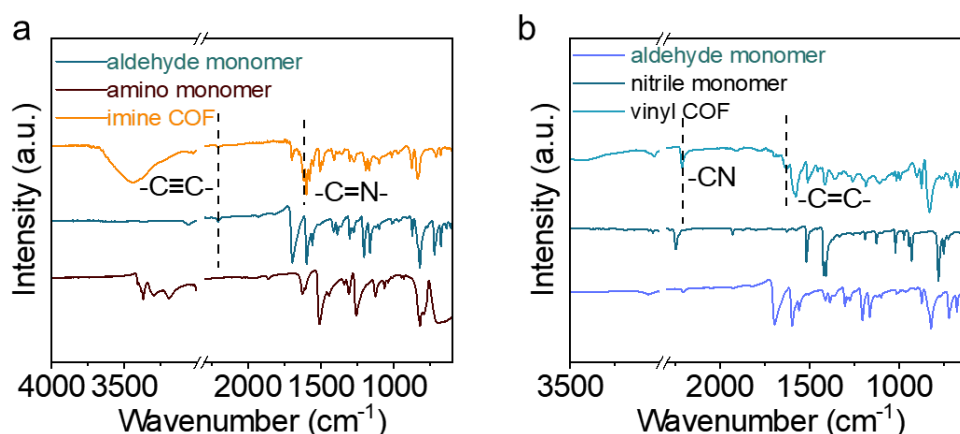


Figure R12. (a) FT-IR spectra of imine COF and key monomers. (b) FT-IR spectra of vinyl COF and key monomers.

Question 5:

In Figure 2d, each peak in the ^{13}C NMR spectrum should be assigned to the corresponding carbon atoms in the coumarin-linked COF structure. In addition, the C=C peak should be clearly labeled in the FTIR spectrum.

Response:

Thank you for your constructive suggestion. In the revision, we have clearly assigned all major peaks in the ^{13}C NMR spectrum to their corresponding carbon atoms in coumarin COF (Figure R13a). Regarding the FTIR spectrum, the stretching vibration of the C=C bond within the coumarin ring have also been labeled (1610 cm^{-1}) (Figure R13b).

Action:

We added the **Figure R13** in **Figure 2 of the revised manuscript**.

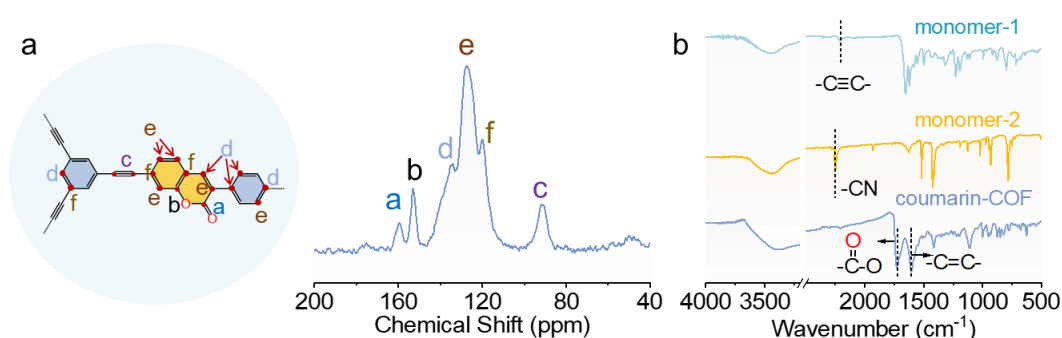


Figure R13. (a) Major peaks in the ^{13}C NMR spectrum and their corresponding carbon atoms in the coumarin COF. (b) FTIR spectra of coumarin COF. The stretching vibration of the C=C bond is 1610 cm^{-1} .

Question 6:

The author should provide fs-TA spectra for the vinyl-linked COF in the presence of co-catalysts to directly elucidate the interfacial electron transfer dynamics. This data is paramount to substantiating the proposed relationship between the bonding nature of the linkages and the resulting photocatalytic performance.

Response:

Thank you for your valuable comments. Following your suggestion, in this revision, we have added the fs-TA spectra of the Pt-loaded vinyl COF (Figure R14b and R14d). The spectra of vinyl COF after Pt loading shows a faster decay process ($\tau_1 = 3.58$ ps, $\tau_2 = 93.99$ ps) than vinyl COF ($\tau_1 = 6.26$ ps, $\tau_2 = 256.6$ ps) (Figure R14a-b), indicating that Pt nanoparticles can promote the transfer of electrons for the hydrogen evolution reaction.

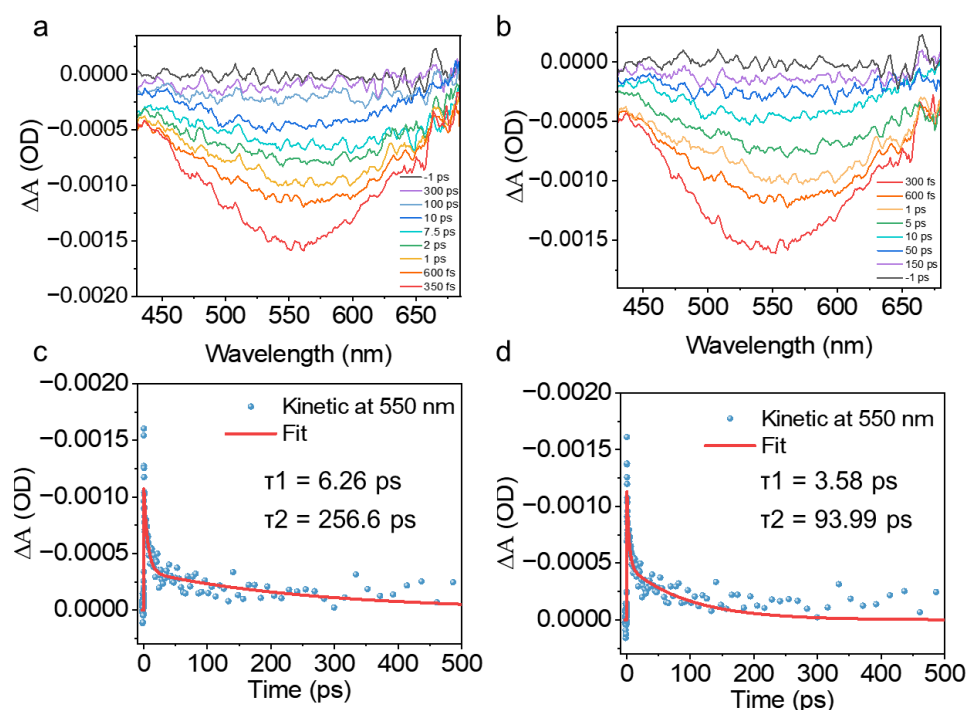


Figure R14. (a-b) The fs-TA spectra curves with excitation spectrum at 400 nm of vinyl COF and vinyl COF-Pt. (c-d) Decay kinetics of vinyl COF and vinyl COF-Pt at 550 nm.

Action:

We supplemented the **Figure R14** in **Supplementary Fig. 21** of the revised SI.

Question 7:

A schematic diagram illustrating the electron-transfer pathway upon co-catalyst loading, supported by theoretical calculations, should be included to fully clarify the reaction mechanism.

Response:

Thank you for the constructive comment. Following your suggestion, we have supplemented the free energy diagrams of the photo-deposition reaction paths based on the theoretical calculations (Figure R15), which shows the thermodynamic spontaneity of Pt deposition onto the coumarin COF. Furthermore, our calculation results reveal that the Pt species preferentially adsorb and anchor at the carbonyl sites of the coumarin-based COF during this process.

Actions:

1. We supplemented the **Figure R15** in **Supplementary Fig. 17 of the revised SI**.
2. We added the following discussion in **Page 12 of the revised manuscript**: *“The free energy diagrams of the photo-deposition reaction paths based on the theoretical calculations also establish the thermodynamic spontaneity of Pt deposition onto the coumarin units.”*

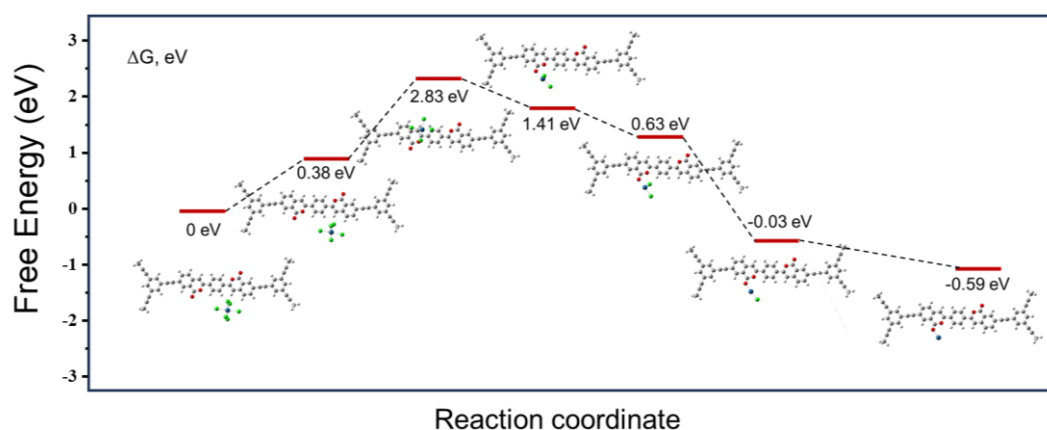


Figure R15. Free energy diagrams of photo-deposition reaction paths.

Question 8:

The photocatalytic hydrogen evolution performance of the imine- and vinyl-linked COFs under visible-light irradiation should also be provided for comparison.

Response:

Thank you for the valuable suggestion. Following your suggestion, we have supplemented the hydrogen evolution performance of imine- and vinyl-linked COFs under the visible-light irradiation (Figure R16). In the tests under visible light (>420 nm), both the imine- and vinyl-linked COFs exhibited significantly lower activity ($0.016 \text{ mmol g}^{-1} \text{ h}^{-1}$ and $3.5 \text{ mmol g}^{-1} \text{ h}^{-1}$) compared to coumarin-linked COF, consistent with the superior charge dynamics of the coumarin linkage.

Actions:

1. We supplemented the **Figure R16** in **Supplementary Fig. 18** of the revised SI.

2. We added the following discussion in **Page 12 of the revised manuscript**: “In addition, the hydrogen production rate of coumarin COF under >420 nm visible light could reach $166 \text{ mmol g}^{-1} \text{ h}^{-1}$, higher than that of the imine COF ($0.016 \text{ mmol g}^{-1} \text{ h}^{-1}$) and vinyl COF ($3.5 \text{ mmol g}^{-1} \text{ h}^{-1}$).”

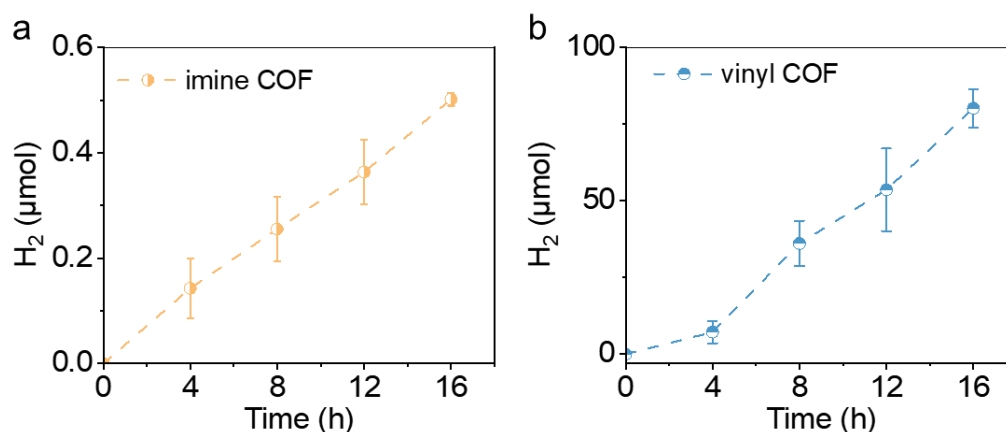


Figure R16. The photocatalytic hydrogen evolution performance of the imine COF (a) and vinyl COFs (b).

Question 9:

The color scheme in Figure 4a should be revised to maintain consistency with the other figures.

Response:

Thank you for the constructive comment. Following your suggestion, in the revision, the color scheme in Figure 4a has been revised to ensure consistency with other figures in the manuscript (Figure R17).

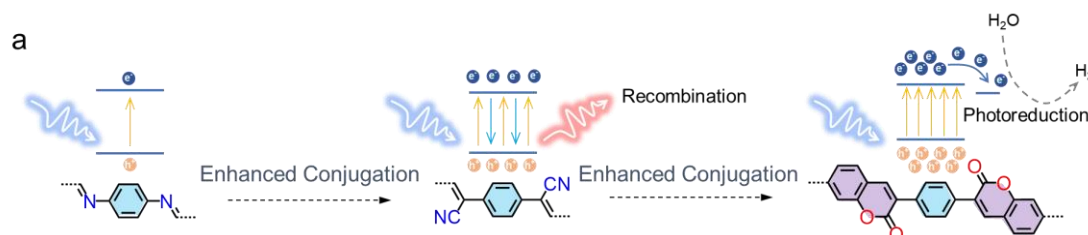


Figure R17. Schematic diagram of photoelectric conversion of imine COF,

vinyl COF and coumarin COF. Coumarin COF shows higher concentration of excited state electrons for photocatalysis.

Reviewer comments:

Reviewer #1 (Comments for the Author):

After revised in details, this manuscript has clarified questions and it can be accepted as current form.

Response:

We sincerely thank you for all of your constructive comments to improve the quality of our manuscript.

Reviewer #2 (Comments for the Author):

1. The reviewer appreciates the revisions made by the authors. However, two major concerns remain. First, the authors emphasize the advantage of their one-pot approach over Yaghi's method (Nat. Synth. 2025, 4, 1376). However, despite the synthetic simplicity, the quality of the resulting material appears unsatisfactory. In particular, the BET surface area is only $143 \text{ m}^2 \text{ g}^{-1}$ (page 9), which is substantially lower than the value reported by Yaghi et al. ($\sim 981 \text{ m}^2 \text{ g}^{-1}$). Therefore, the claimed synthetic advantage is not convincing if the simplified route leads to an inferior material.

Response:

We sincerely thank you for your insightful comment. We agree that the BET surface area of our coumarin-linked COF ($143 \text{ m}^2 \text{ g}^{-1}$) is lower than that reported in the work by Yaghi et al. ($\sim 981 \text{ m}^2 \text{ g}^{-1}$). However, we would like to clarify that the difference arises from both the intrinsic structural characteristics and the distinct synthetic strategies, and does not necessarily indicate inferior framework formation or photocatalytic functionality:

First, compared with Yaghi's two-step protocol, which requires a conventional solvothermal crystallization (3 days) followed by concentrated HCl treatment at 50°C for 5 days to achieve deprotection and cyclization, our strategy establishes a one-pot synthetic pathway under substantially milder conditions. This approach streamlines the synthesis, shortens the total reaction time to 5 days, and avoids the additional yield

loss associated with the post-synthetic transformation step. Importantly, the overall isolated yield of our method (~85%) is comparable to the yield of the first step in Yaghi's procedure.

Second, the coumarin-linked COF reported here is structurally different from that in Yaghi's work, and therefore direct comparison of BET surface areas may not be appropriate. As reported in their study (Nat. Synth. 2025, 4, 1376), coumarin-linked COFs with larger pore sizes often exhibit substantially reduced experimental BET surface areas because of weakened interlayer π - π interactions and stacking limitations (see Supplementary information, Page S47, Line 11-20). Notably, the measured BET surface areas of COF-994-CN and COF-995-CN decrease to 97 and 22 m² g⁻¹ (Table R1, in this response), respectively, despite their well-defined framework structures. Since the coumarin-linked COF in our work possesses an even larger pore size, the relatively low BET surface area is likely associated with similar stacking limitations rather than unsuccessful framework construction. Moreover, PXRD, FT-IR, and solid-state ¹³C NMR collectively confirm the successful formation of the crystalline coumarin-linked COF.

Most importantly, the primary objective of this work is not to maximize BET surface area, but to establish a systematic structure-property-activity relationship among imine-, vinyl-, and coumarin-linked COFs with comparable structural dimensions. Within this framework, the coumarin

linkage exhibits distinct advantages in electronic delocalization, charge separation, and photocatalytic hydrogen evolution.

Accordingly, regarding to your concern, we have further revised the manuscript to clarify that the main advantages of our strategy lie in synthetic simplicity and mechanistic insight, rather than superior porosity alone.

Actions:

1. We added the following discussion in **Page 7 of the revised manuscript**: *“The one pot synthetic pathway with a new catalytic mechanism compare to Yaghi’s work, streamlines the synthesis, and eliminates the concentrated HCl treatment step.”*
2. We added the following discussion in **Page 9 of the revised manuscript**: *“The specific surface areas are low ($399\text{ m}^2\text{ g}^{-1}$, $41\text{ m}^2\text{ g}^{-1}$ and $143\text{ m}^2\text{ g}^{-1}$) due to weakened interlayer π - π stacking.”*

Table R1. Summary of theoretical and measured BET surface areas of COFs in Yaghi’s work.

Sample	BET surface area ($\text{m}^2\text{ g}^{-1}$)		Pore size (nm)	
	Theoretical	Measured	Theoretical	Measured
COF-992-CN	2330	218	1.8	1.9
COF-993-CN	2491	325	2.4	2.2

COF-994-CN	2493	97	2.6	2.3
COF-995-CN	2570	22	3.5	3.6
COF-992	2080	872	2.5	1.8
COF-993	2129	695	3.1	1.8
COF-994	2230	591	3.2	1.8
COF-995	2223	459	4.0	3.4

2. Second, the reported high hydrogen evolution rate of 531 mmol g⁻¹ h⁻¹ is based on irradiation with a 440 nm LED. Although monochrome LED sources are commonly used in organic photocatalysis studies, photocatalytic water splitting for hydrogen production is intended for solar energy conversion and is more appropriately evaluated under simulated sunlight, typically using Xe lamps with AM 1.5G filters or cutoff filters ($\lambda > 420$ nm). The authors also acknowledge in the Response Letter (Table R1) that the literature examples used for comparison were all measured under Xe lamp irradiation. Under the more relevant visible-light condition (Xe lamp, $\lambda > 420$ nm), the coumarin COF exhibits an activity of 166 mmol g⁻¹ h⁻¹ (page 12), which does not surpass several leading organic photocatalysts listed in Table R1 and Figure 4c.

Response:

We sincerely thank you for your important comment regarding the evaluation conditions for photocatalytic hydrogen production.

We fully agree that simulated sunlight conditions (e.g., Xe lamp irradiation with $\lambda > 420$ nm or AM 1.5G filters) provide a more application-relevant assessment for solar energy conversion. At the same time, monochromatic LED irradiation is also widely used in COF photocatalysis studies to evaluate intrinsic photocatalytic activity and wavelength-dependent performance (J. Am. Chem. Soc. 2026, 148, 1316). Therefore, in this work, we intentionally included both monochromatic (440 nm LED) and visible-light ($\lambda > 420$ nm) measurements to provide a more comprehensive evaluation of the photocatalytic behavior.

Under visible-light irradiation ($\lambda > 420$ nm), the coumarin-linked COF exhibits a hydrogen evolution rate of $166 \text{ mmol g}^{-1} \text{ h}^{-1}$. We agree that this value does not surpass the highest-performing organic photocatalysts reported to date. Nevertheless, it is necessary to note that: (1) the activity remains competitive among representative COF-based and organic photocatalysts summarized in Supplementary Table 5; (2) Variations in experimental conditions (e.g., catalyst loading, Pt content, reactor geometry, photon flux) make strict cross-comparisons inherently challenging.

In addition, as we stated above in the Response to your Coment 1, the central contribution of our work is to establish a clear structure-property-activity relationship among imine-, vinyl-, and coumarin-linked COFs. Through combined experimental and theoretical analyses, we

demonstrated that the coumarin linkage exhibits: (1) enhanced electronic delocalization; (2) promoted cocatalyst deposition and water adsorption; and (3) improved charge separation and utilization. These insights provide a design principle for future COF-based photocatalysts, which we believe is of broader significance beyond absolute activity metrics.

To address your concern, all the hydrogen production data mentioned in the manuscript have been clearly marked with the light source conditions to avoid confusion.

Actions:

1. We added the following annotations in the caption of **Fig. 4 of the revised manuscript**: “**b**, *Hydrogen evolution of coumarin COF ($\lambda = 440$ nm; monochromatic LED) under the optimized conditions, monitored over 24 hours. c, Comparison of hydrogen evolution rate for coumarin COF (under visible light and monochromatic light) with the recently reported representative organic photocatalysts.*”

2. We added the following content in **Page 7 of the revised SI**: “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.”

Reviewer #3 (Comments for the Author):

The authors have conducted a comprehensive revision of the manuscript, incorporating new experimental data and theoretical backing. The responses to all referees' concerns are satisfactory and have notably strengthened the work. I therefore recommend publication pending the minor revisions below:

Response:

We sincerely thank you for the positive comments on the revised manuscript. All the suggestions and concerns from you have been carefully addressed and modifications have been made accordingly.

1. The authors should provide calculation details for Supplementary Fig. 17 in the Supporting Information.

Response:

Thank you for your careful comment. As requested, we have added the detailed calculation methods for Supplementary Fig. 17 in the Supporting Information.

Action:

We added the following content in **Page 10 of the revised SI**: *“The photoresponse 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:

$$\Delta G_{ads} = G_{COF-PtCl_6^{2-}} \quad (1)''$$

2. In Fig. 3c, the fluorescence signal of coumarin COF is largely obscured by the intense signal of vinyl COF. The authors should consider moving the coumarin COF spectra to the Supporting Information to allow clearer visualization on a suitable scale.

Response:

Thank you for your valuable comment. As recommended, we have moved the coumarin COF fluorescence spectra to the Supplementary materials

(now provided as Supplementary Fig. 13) and displayed them on an appropriate y-axis scale.

Action:

We added the **Figure R1** in **Supplementary Fig. 13** of the revised SI.

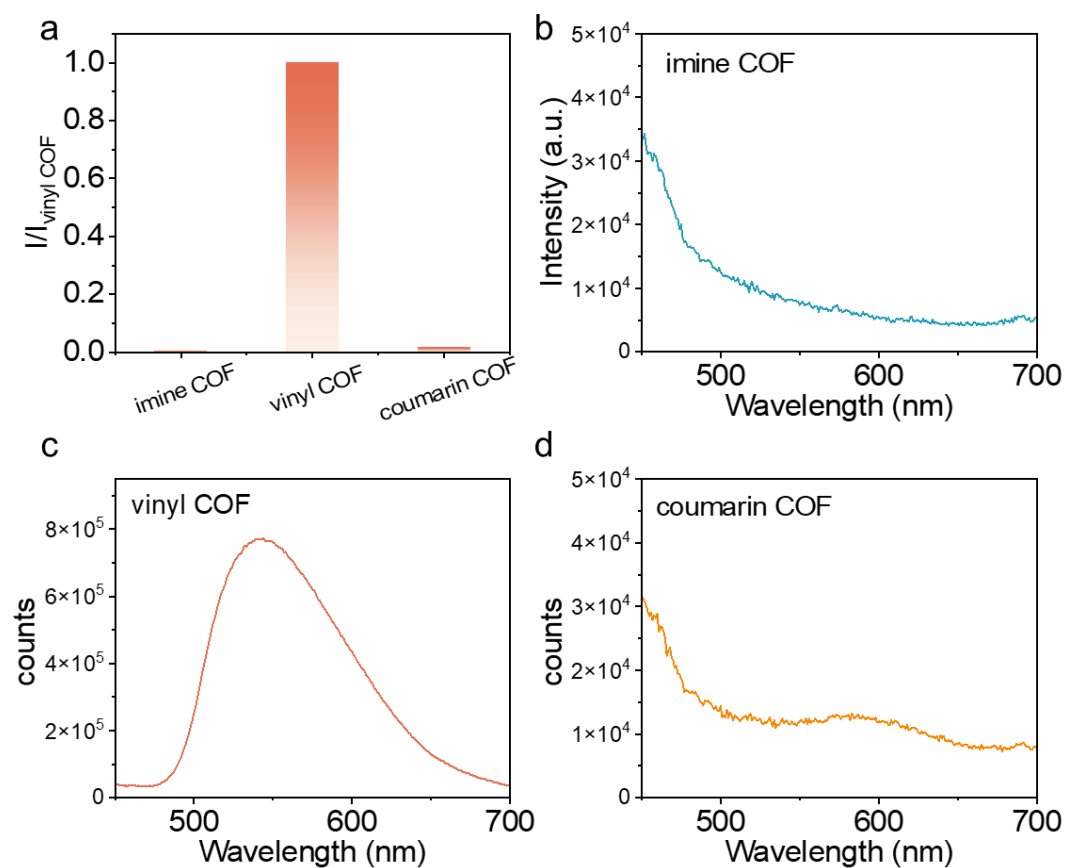


Figure R1. (a) The fluorescence intensity ratio of COFs. (b-d) Steady-state PL spectra of imine COF, vinyl COF and coumarin COF.

3. The caption “2D framework” in Fig. 1c should be revised to “2D covalent organic framework”.

Response:

Thank you for the helpful comment. As recommended, in the revision, we have revised the caption “2D framework” in Fig. 1c to “2D covalent organic framework” to ensure terminological accuracy.

4. In Fig. 3, “imine-COF”, “vinyl-COF” and “coumarin-COF” should be revised to “imine COF”, “vinyl COF” and “coumarin COF” respectively, for consistency with the main text.

Response:

Thank you for your suggestion. In the revision, we have unified the formatting of all COF-related terms throughout the entire manuscript to ensure consistency with the main text.

5. The term “recombination” in Fig. 3a should be revised to “radiative recombination”.

Response:

Thank you for your comment. Following your suggestion, we have revised the term “recombination” in Fig. 3a to “radiative recombination” for greater accuracy.

6. In Fig. 2a, the authors should more clearly highlight the one-step synthetic strategy of the coumarin linkage.

Response:

Thank you for your comment. As recommended, we have revised Fig. 2a to more clearly highlight the one-step synthetic strategy of the coumarin linkage by adding an explicit annotation to the scheme.