

Hydrogen-Bonded Organic Frameworks

π - π Stacking as Electron-Transfer Channels in Hydrogen-Bonded Organic Frameworks for Boosting Photocatalysis

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Abstract: Photocatalysis provides a promising approach to produce green energy, by which the intermittent solar energy can be converted into storable chemical energy. It is well-known that the electron-transfer rate has great influence on the photocatalytic efficiency. Revealing the influence of electron-transfer rate on the photocatalytic efficiency from a molecular level is of great significance but a challenge. Herein, we give solid evidence to show that the π - π stacking can serve as an electron-transfer channel to boost photocatalysis. Specifically, two hydrogen-bonded organic frameworks (HOFs) with similar structures but slightly different intermolecular interactions have been weaved. Interestingly, the HOF with π - π stacking interactions shows much higher photocatalytic activity for hydrogen evolution than the one without. Further structural and spectroscopic analyses revealed that the much-enhanced photocatalytic activity of the former can be attributed to the π - π stacking, which can really serve as an electron-transfer channel, thus accelerating the electron transfer and achieving a remarkably enhanced activity in photocatalytic hydrogen evolution. The work, from a molecular level, reveals the role of π - π stacking in photocatalysis and gives new insights into the electron-transfer in photocatalysts.

Introduction

Solar energy-driven water splitting and/or CO₂ reduction is considered a promising strategy to convert and store the intermittent solar energy.^[1–30] However, the currently low photocatalytic conversion efficiency limits the industrial application of this technology. It is well-known that accelerating the electron transfer in photocatalysts is beneficial for enhancing the photocatalytic efficiency. In this aspect,

diverse strategies have been developed recently to expedite electron transfer and achieve remarkable photocatalytic efficiency.^[6–14] For instance, the introduction of an additional redox mediator as an electron relay can accelerate the electron transfer from the excited photosensitizer to catalyst, resulting in much enhanced photocatalytic efficiency.^[11–14] In addition, the covalent connection of photosensitizer and catalyst can also achieve ultrafast electron transfer.^[15–21] As a representative example, Nakada et al. have coupled Re/Mn catalyst and Ru/Os photosensitizer via covalent bonds to facilitate the intermolecular electron delivery and thus enhance photocatalytic activity.^[15–19] Ouyang group designed an Ir(III) photosensitizer featuring a pyridine-type ligand to connect molecular catalysts, which also achieved improved photocatalytic efficiency.^[21] In heterogeneous systems, grafting molecular catalysts onto organic semiconductors such as g-C₃N₄ has also achieved rapid charge transfer and high activity in photocatalysis.^[22–25]

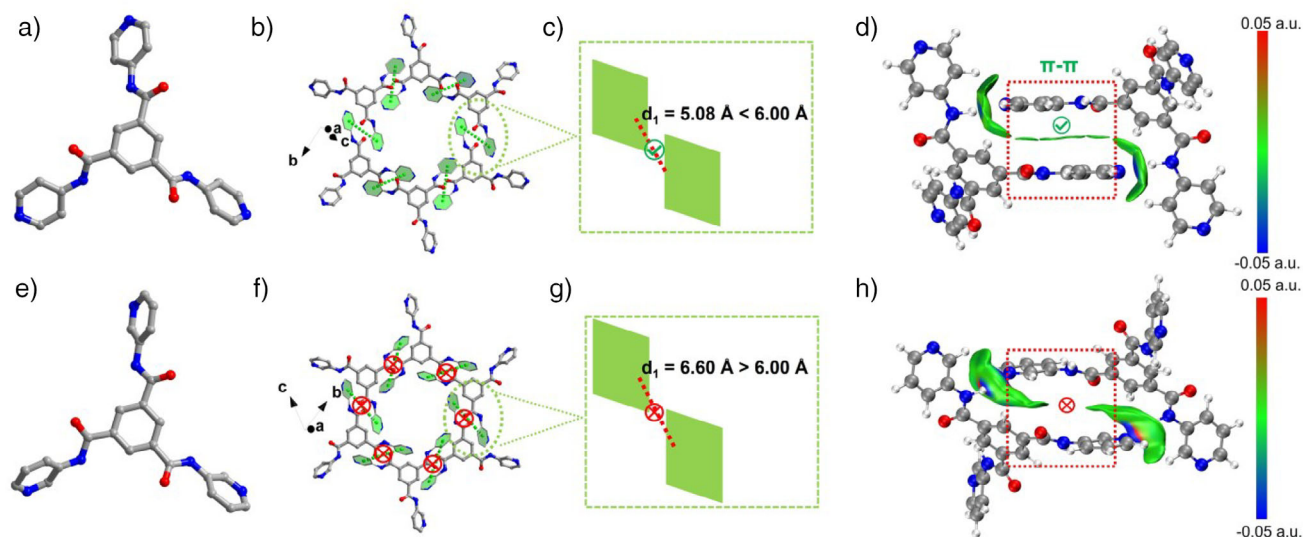
In addition to the traditional covalent strategy, non-covalent interactions can also facilitate the electron transfer to boost photocatalysis, which has been demonstrated in homogeneous photocatalytic systems.^[26–30] Kubiak group has found that the hydrogen-bonding interactions between a Re bipyridine catalyst and a Ru photosensitizer contribute to the intermolecular electron transfer, thus greatly enhancing the photocatalytic activity for CO₂ reduction.^[26] Ouyang and coworkers have reported that a Cu(I) photosensitizer and a pyrene-appended Co(II) catalyst can be preassembled by π - π stacking interactions, which expedites the intermolecular electron transfer and thus boosts the CO₂ photoreduction.^[27] Despite the non-covalent interactions being reasoned for the activity enhancement in these homogeneous photocatalytic systems, such non-covalent interactions were determined by spectroscopic analyses.^[27–30] The contribution of non-covalent interactions in accelerating electron transfer and boosting catalytic activity has not been directly observed.

Hydrogen-bonded organic frameworks (HOFs) are a new class of porous crystalline materials.^[31–35] Owing to well-defined and tailorable structures, semiconductor-like behavior, and self-healing ability, HOFs have currently shown potential application in photocatalysis.^[36–41] These features of HOFs also provide a good platform for studying the effect of non-covalent interactions on accelerating electron transfer and boosting photocatalytic activity. In this article, we demonstrate that π - π stacking can serve as an electron-transfer channel to boost photocatalysis, based on the fact that two HOFs with similar structures but slightly different

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 Additional supporting information can be found online in the Supporting Information section



Scheme 1. Schematic of the π - π stacking modes in HOF-8 a-d) and HOF-TUT-8 e-h) (the color of the bar in d and h, red: prominent repulsive interaction; green: van der Waals interaction; blue: prominent attractive weak interaction).

intermolecular interactions as well as big different photocatalytic activity in hydrogen evolution. Specifically, HOF-8, a reported HOF based on N^1 , N^3 , N^5 -tri(pyridin-4-yl)benzene-1,3,5-tricarboxamide (L_1 ; Scheme 1a),^[42] and HOF-TUT-8, a new HOF based on N^1 , N^3 , N^5 -tri(pyridin-3-yl)benzene-1,3,5-tricarboxamide (L_2 ; Scheme 1e) have been assembled, in which the only difference between them is the π - π stacking interactions (Scheme 1b-d,f-h). Interestingly, HOF-8 with π - π stacking interactions exhibits outstanding photocatalytic activity for water splitting, with H_2 evolution rate of 3.3 times higher than that of HOF-TUT-8 with negligible π - π stacking interactions, highlighting the π - π stacking interactions in boosting photocatalysis. The combined results of linear sweep voltammetry (LSV) and time-resolved fluorescence spectroscopic measurements reveal that the electron transfer in HOF-8 is really faster than that in HOF-TUT-8, well supporting the higher photocatalytic activity of HOF-8 for H_2 evolution. This study for the first time structurally shows π - π stacking interactions as electron-transfer channels in boosting photocatalysis.

Results and Discussion

L_1 and L_2 were synthesized by modified condensation amidation reactions, respectively (see the Supporting Information).^[42,43] The nuclear magnetic resonance hydrogen spectra (1H NMR) and Fourier transform infrared spectroscopy (FTIR) spectra of L_1 and L_2 revealed that they were successfully synthesized with high purity (Figures S1-S3). Recrystallization of L_1 and L_2 in the mixed solvent of $CHCl_3/CH_3OH$ (3:1, v/v) and $CHCl_3/CH_3CN/CH_3OH$ (6:1:1, v/v/v), respectively, affords single crystals of HOF-8^[42] and HOF-TUT-8, respectively (see the Supporting Information). The scanning electron microscopy (SEM) images show that the morphologies of

both HOF-8 and HOF-TUT-8 are block-shaped with similar sizes (Figure S4).

Single-crystal X-ray diffraction analysis reveals that HOF-8 and HOF-TUT-8 crystallize in the monoclinic space group of $C2/c$ ^[42] and the triclinic space group of $P-1P\bar{1}$, respectively (Table S1). As shown in Figure 1a,b, each L_1 in HOF-8 connects with three other L_1 through three pairs of hydrogen bonds ($N1-H1\cdots N6$, $N3-H3\cdots N2$, and $N5-H5\cdots N4$), generating a two-dimensional (2D) layer structure (Table S2).^[42,44-49] Adjacent layers are stacked through π - π stacking interactions to form a three-dimensional (3D) porous framework with the pore size of $6.8 \times 4.5 \text{ \AA}$ (Figure 1c,d and Figure S5; Tables S3 and S4). Similar to HOF-8, each L_2 in HOF-TUT-8 also links three adjacent L_2 by three pairs of hydrogen bonds ($N1-H1\cdots N6$, $N3-H3\cdots N2$, and $N5-H5\cdots N4$) to form a 2D layer structure (Figure 1e,f). The adjacent 2D layers in HOF-TUT-8 are further connected through hydrogen bonds ($C10-H10\cdots O2$, $C16-H16\cdots O3$, $C22-H22\cdots O1$, and $C24-H24\cdots O3$) to generate a 3D porous framework (Figure 1h and Figure S6), rather than π - π stacking interactions as in HOF-8 because of the long distances and large dihedral angles between the pyridine rings (Tables S5 and S6). The pore size of HOF-TUT-8 is approximately $6.2 \times 4.2 \text{ \AA}$, which is similar to that of HOF-8 (Figure 1f-h). Energy decomposition analysis was further carried out to quantitatively calculate the intermolecular interactions between L_1 monomers in HOF-8, and L_2 monomers in HOF-TUT-8 (see the Supporting Information). The results show that dispersion force dominates the total interactions in HOF-8, with the energy of $-101.80 \text{ kJ mol}^{-1}$, higher than that in HOF-TUT-8 (Scheme 1d,h, Table S7). This result further illustrates the stronger supramolecular interactions in HOF-8 over HOF-TUT-8.

Powder X-ray diffraction (XRD) patterns show that the measured patterns of HOF-8 and HOF-TUT-8 closely match those of the simulated ones generated from their single crystal data, indicative of their high purity (Figure 2a). The FT-IR

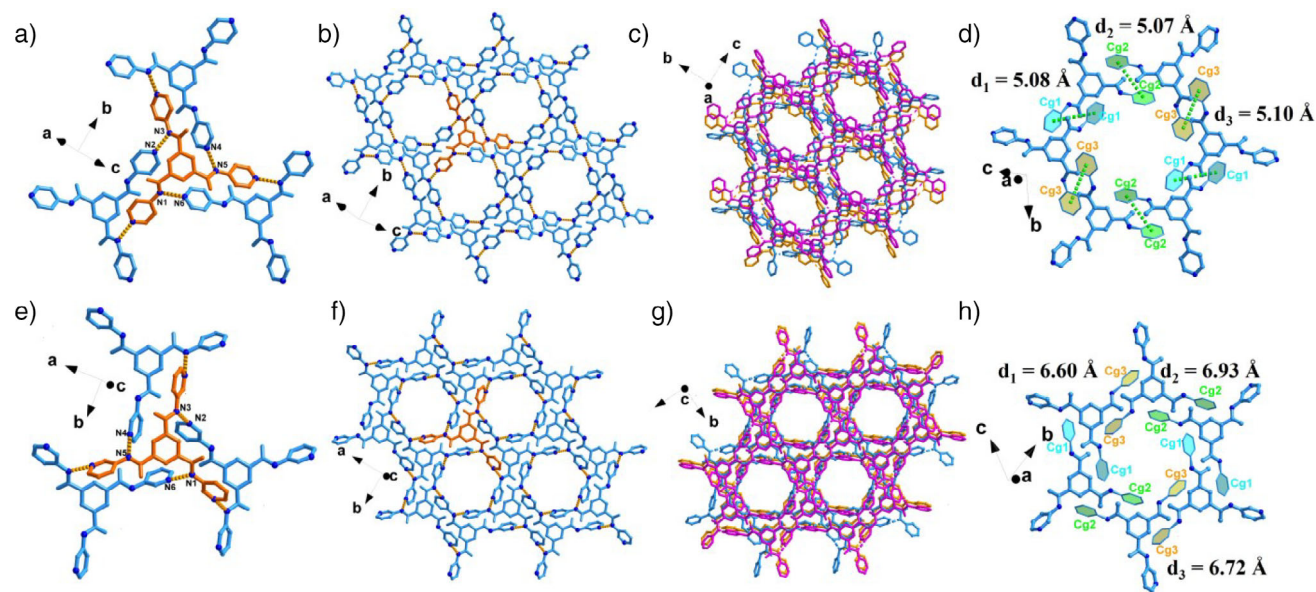


Figure 1. a) Hydrogen bonds in HOF-8. b) 2D supramolecular layer of HOF-8. c) 3D supramolecular microporous structure of HOF-8. d) π - π stacking interactions in HOF-8 (d: $C_g \cdots C_g$ distance). e) Hydrogen bonds in HOF-TUT-8. f) 2D supramolecular layer of HOF-TUT-8. g) 3D supramolecular microporous structure of HOF-TUT-8. h) The negligible π - π stacking interactions in HOF-TUT-8 (d: $C_g \cdots C_g$ distance).

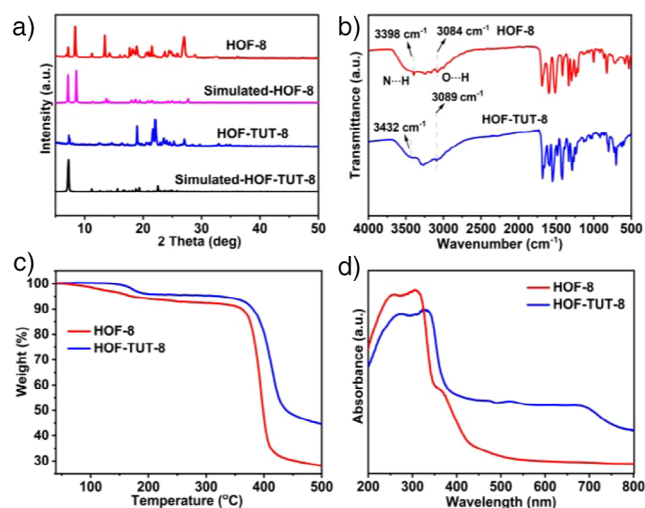


Figure 2. a) Powder XRD patterns, b) FTIR spectra, c) TG curves, and d) solid UV-vis spectra of HOF-8 (a new sample of HOF-8 was synthesized, and these data were obtained by repeated measurements) and HOF-TUT-8.

spectra of HOF-8 and HOF-TUT-8 display N-H stretching vibration peaks at 3398 and 3432 cm^{-1} respectively, corresponding to N-H $\cdots$ N hydrogen bonds (Figure 2b).^[44–49] These results agree with their crystal structures (Tables S2–S6). X-ray photoelectron spectroscopic (XPS) measurements were performed to identify the chemical compositions of HOF-8 and HOF-TUT-8 (Figures S7–S9). The XPS spectra show the C 1s spectra display characteristic peaks at approximately 284 and 288 eV, corresponding to C=C/C=O and N=C=O, respectively. For O 1s, two characteristic peaks at approximately 531 and 533 eV were observed, which can be assigned

to C=O and C–O, respectively. For N 1s, two characteristic peaks at approximately 399 and 400 eV appeared, corresponding to pyridine N and N=C=O, respectively.^[37,44,50–53] Thermogravimetric analysis (TGA) revealed that the two HOFs exhibit good thermal stability, with the decomposition temperature over 350 °C (Figure 2c).

The porous features of HOF-8 and HOF-TUT-8 were evaluated by CO_2 sorption tests at 196 K and 1 atm. As shown in Figures S10 and S11, HOF-8 and HOF-TUT-8 exhibit similar CO_2 adsorption capacity at 196 K with adsorption amounts of 24.99 and 24.09 $\text{cm}^3 \text{g}^{-1}$, respectively. The corresponding Brunauer–Emmett–Teller (BET) surface areas are 109.46 and 90.88 $\text{m}^2 \text{g}^{-1}$, respectively.^[37,41,54–57] To further examine their porosity, the I_2 adsorption experiments were conducted by soaking HOF-8 and HOF-TUT-8 in *n*-hexane solution of I_2 (Figures S12 and S13). The adsorption of HOF-8 and HOF-TUT-8 to I_2 was clearly observed by the color change of the solution from pink to colorless after 8 and 12 h, respectively. Moreover, the UV-vis spectra show that the intensity of I_2 characteristic peak at about 521 nm gradually decreases with increasing soaking time, further confirming the presence of porosity in HOF-8 and HOF-TUT-8 (Figures S12 and S13).

The results of solid UV-vis spectra demonstrate that HOF-8 and HOF-TUT-8 exhibit main light absorption in the UV region and weak light absorption in visible region (Figure 2d). The band gap energies (E_g) of HOF-8 and HOF-TUT-8 are determined based on their solid UV-vis spectra, which are 3.48 and 3.33 eV, respectively (Figures S14 and S15). In addition, the lowest unoccupied molecular orbital (LUMO) levels of HOF-8 and HOF-TUT-8 are estimated as -0.98 and -1.02 V versus NHE, respectively, by Mott–Schottky measurements (Figure S16). Hence, their highest occupied molecular orbitals (HOMOs) could be calculated

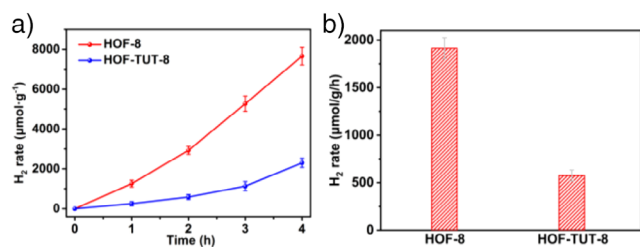


Figure 3. a) Kinetic profiles of photocatalytic H_2 evolution over HOF-8 and HOF-TUT-8. b) Comparison of the photocatalytic activity of HOF-8 and HOF-TUT-8 for H_2 evolution. The error bars are standard deviations calculated from the results of three repeated experiments.

to be 2.50 and 2.31 V versus NHE, respectively. Notably, the LUMO positions of HOF-8 and HOF-TUT-8 are lower than the proton reduction needed (-0.42 V vs. NHE, pH 7), suggesting that they are thermodynamically capable of photocatalytic proton reduction (Figure S17).^[58,59]

On the basis of the above results, photocatalytic hydrogen evolution experiments of HOF-8 and HOF-TUT-8 were conducted in aqueous solution under UV–visible light irradiation ($\lambda \geq 320$ nm), with $51 \mu\text{L}$ 0.014 M K_2PtCl_4 aqueous solution and triethylamine (TEA) as the sacrificial agent (see the Supporting Information). Interestingly, despite the packing modes of HOF-8 and HOF-TUT-8 are almost the same, HOF-8 exhibits a much higher hydrogen production rate of $1914.4 \mu\text{mol g}^{-1} \text{h}^{-1}$, which is over three times of HOF-TUT-8 (Figure 3 and Table S8, entries 1–2). Moreover, the H_2 production rate of HOF-8 is also superior to most of the reported photocatalysts under similar reaction conditions (Table S9).

A series of control experiments of photocatalytic H_2 evolution with HOF-8 revealed that negligible or even no H_2 was detected in the absence of HOF-8, TEA, or light irradiation (Table S8, entries 3–5), indicating that HOF-8, TEA and light are all indispensable to the photocatalytic H_2 evolution. The photocatalytic durability of HOF-8 was evaluated via recycling experiments. No obvious decrease in the H_2 evolution process was observed during the four consecutive cycles (Figure S18). SEM images reveal that the morphologies of HOF-8 and HOF-TUT-8 after photocatalytic reaction change to microcrystals, which are similar to those freshly prepared (Figure S19). Furthermore, the powder XRD patterns reveal almost unchanged crystallinity and structural integrity of HOF-8 and HOF-TUT-8 after photocatalytic H_2 evolution reaction (Figures S20 and S21), and the UV–vis spectra show almost no organic monomers were leached during the photocatalytic process (Figures S22 and S23). In addition, the FT-IR spectra of HOF-8 and HOF-TUT-8 before and after the photocatalytic reactions are also similar (Figures S24 and S25). These results demonstrate the excellent stability of HOF-8 and HOF-TUT-8 during the photocatalytic H_2 evolution processes.

To elucidate the better photocatalytic activity of HOF-8 over HOF-TUT-8 for H_2 evolution, photocurrent, electrochemical impedance spectroscopy (EIS), photoluminescence (PL), and time-resolved PL (TRPL) measurements were performed.^[60–64] As shown in Figure 4a, HOF-8 exhibited a

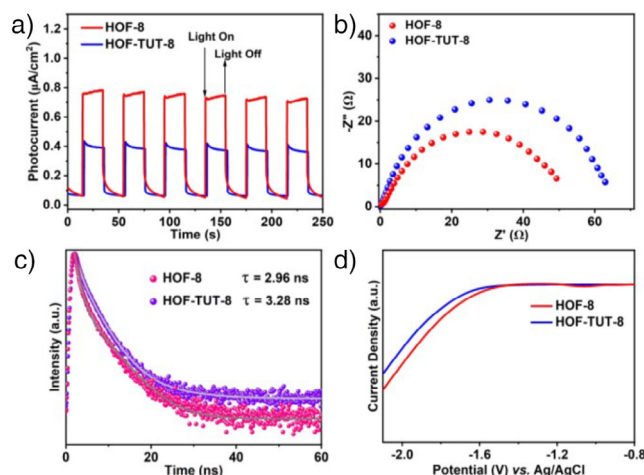


Figure 4. a) Photocurrent tests, b) EIS plots, c) time-resolved fluorescence spectroscopy ($\lambda_{\text{ex}} = 365$ nm and $\lambda_{\text{em}} = 420$ nm), and d) linear sweep voltammetry (LSV) curves for HOF-8 and HOF-TUT-8.

higher photocurrent response than HOF-TUT-8, indicating that HOF-8 has a faster electron transfer-rate. EIS results demonstrated that compared with HOF-TUT-8, HOF-8 showed a smaller semicircle radius, indicating lower charge-transfer resistance of HOF-8 (Figure 4b).

Moreover, the PL and TRPL spectra displayed that the emission intensity and PL lifetime of HOF-8 were weaker and shorter, respectively, than those of HOF-TUT-8, suggesting more efficient charge separation and transfer for HOF-8 than for HOF-TUT-8 (Figure S26, Figure 4c, and Table S10). Besides, the linear sweep voltammetry (LSV) measurements of HOF-8 and HOF-TUT-8 were conducted in Ar atmosphere to study the thermodynamics of H_2 evolution. As shown in Figure 4d, HOF-8 exhibited lower onset overpotential and higher current density than HOF-TUT-8, implying that HOF-8 is thermodynamically superior to HOF-TUT-8. Moreover, the terephthalic acid photoluminescence probing technique (TA-PL) of HOF-8 and HOF-TUT-8 was used to investigate the formation of $\cdot\text{OH}$ species. As shown in Figure S27, both HOF-8 and HOF-TUT-8 display PL signals, indicative of $\cdot\text{OH}$ species formation. HOF-8 shows stronger signal than HOF-TUT-8, demonstrating that HOF-8 possesses more photogenerated electrons, which suggests better charge separation efficiency.^[62,65,66] The above results clearly demonstrated that HOF-8 exhibited more efficient charge separation and transfer than HOF-TUT-8, thus accounting for the higher photocatalytic activity for H_2 evolution.

The possible mechanism for photocatalytic H_2 evolution over HOF-8 or HOF-TUT-8 was elucidated by in situ electron paramagnetic resonance (EPR) and XPS measurements. The results of EPR demonstrated that both HOF-8 and HOF-TUT-8 exhibited stronger signals at $g = 2.00$ under light compared with those in the dark, implying that some holes were produced upon light illumination (Figures S28 and S29).^[67,68] In this case, the photogenerated electrons can easily transfer to the Pt cocatalyst to reduce H^+ to H_2 . Furthermore, the N 1 s XPS spectrum of Pt/HOF-8 displays two characteristic peaks at 398.8 and 400.1 eV in the dark,

corresponding to the binding energies of pyridine-N and N=C=O, respectively. Upon light illumination, the signal of pyridine-N shifts to 399.2 eV (Figure S30).^[41,69] Moreover, the signals of both C 1 s and O 1 s keep unchanged upon light illumination compared with those in the dark (Figure S31). These results imply that the photogenerated electrons in HOF-8 transfer to Pt to reduce H⁺ to H₂.

Conclusion

In summary, two HOFs (HOF-8^[42] and HOF-TUT-8) with similar 3D structures were successfully constructed, which can be used as heterogeneous photocatalysts for H₂ evolution. HOF-8 possesses abundant π - π stacking interactions, exhibiting more efficient charge separation and transfer than HOF-TUT-8 without π - π stacking. As a result, HOF-8 achieves a higher H₂ production rate of 1914.4 $\mu\text{mol g}^{-1} \text{h}^{-1}$, which is 3.3 times higher than that of HOF-TUT-8. Systematic studies demonstrate that the π - π stacking in HOF-8 can serve as an electron-transfer channel to fast transfer electrons to achieve high-efficiency photocatalytic H₂ evolution. This study directly evidences the intrinsic role of π - π stacking as electron transfer-channels in photocatalysis and highlights an efficient way to enhance photocatalytic activity for H₂ evolution.

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Conflict of Interests

The authors declare no conflict of interest.

Data Availability Statement

The data that support the findings of this study are available in the supplementary material of this article.

Keywords: H₂ evolution • Hydrogen-bonded organic frameworks • Photocatalysis • π frameworks • π - π stacking interaction

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