

Deciphering the structure-function nexus of metal-integrated covalent organic frameworks for solar H₂ production

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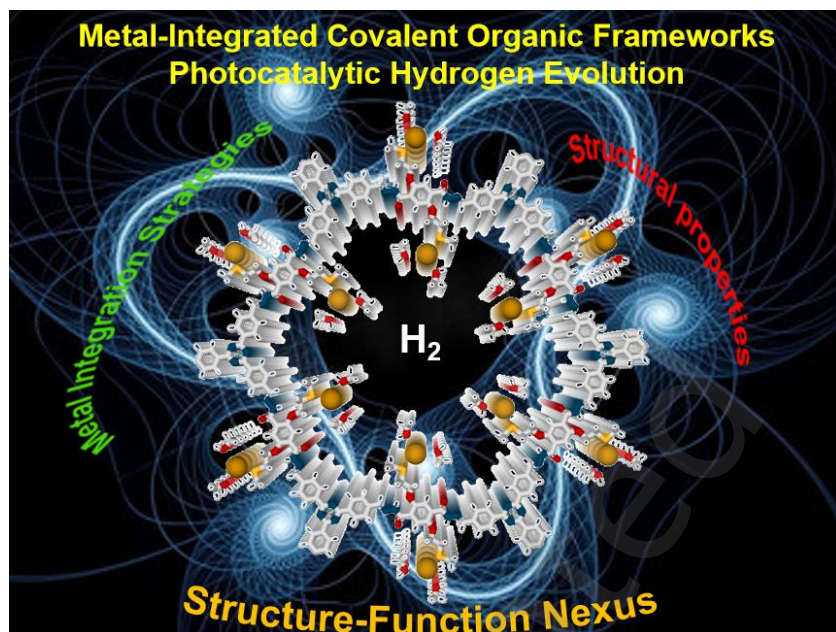
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We highlight how the rational integration of metallic species into COFs establishes a structure–function nexus that enhances light harvesting, charge separation, and catalytic active sites for efficient solar-driven H₂ evolution. It comprehensively discusses metal integration strategies, underlying photocatalytic mechanisms, and future design principles for developing high-performance and durable COF-based H₂ evolution photocatalysts.

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ABSTRACT: Covalent organic frameworks (COFs) are increasingly recognized as promising crystalline platforms for solar-driven H₂ evolution because of their unique architectures, extended conjugation characteristics, adjustable pore environments, and structural regularity. Nevertheless, unmodified frameworks generally exhibit inadequate photocatalytic functionality and rapid recombination of photoinduced charge carriers, limiting their performance during H₂ evolution processes. To address these limitations, extensive investigations have explored the incorporation of metallic entities into COF networks to improve light absorption, carrier mobility, interfacial redox behavior, and surface catalytic dynamics. Despite rapid developments in this area, an integrated understanding linking metallic incorporation approaches with H₂ evolution activity remains insufficient. This review therefore provides a comprehensive overview connecting the structural characteristics and catalytic functions of metal-containing COF systems for photocatalytic H₂ evolution. The fundamental chemistry and framework features of COFs are first introduced, followed by representative methodologies for incorporating metallic species and their corresponding functional effects in regulating light absorption, charge separation, proton reduction, and H₂ evolution kinetics. Finally, future research directions toward constructing highly efficient and durable COF-based photocatalysts for sustainable H₂ evolution are critically highlighted.

KEYWORDS: photocatalyst; covalent organic frameworks; H₂ evolution; metal integration; nanoclusters.

Introduction

Escalating global energy consumption together with the environmental burden associated with carbon-intensive fuel utilization has intensified the pursuit of sustainable energy vectors capable of supporting long-term technological development without aggravating atmospheric pollution [1]. Among emerging clean fuels, H₂ occupies a distinctive position because its combustion generates only water while simultaneously delivering exceptionally high gravimetric energy density [2, 3]. In this context, photocatalytic H₂ evolution has attracted sustained attention as a direct route for converting abundant solar energy into storable chemical fuels through proton reduction under light irradiation [4, 5]. Since the seminal discovery of semiconductor-assisted water splitting, extensive efforts have been devoted to engineering photocatalysts with broadened visible-light absorption, accelerated charge transport, and enhanced surface reaction kinetics [6]. Considerable advances have consequently been achieved using inorganic semiconductors, molecular photosensitizers, polymeric photocatalysts, and hybrid photoactive systems [7]. Among the

diverse photocatalytic platforms developed for solar H₂ evolution, inorganic semiconductors such as TiO₂, CdS, ZnO, etc. have long dominated the field because of their excellent photostability and well-established electronic structures. Nevertheless, many inorganic photocatalysts suffer from limited visible-light absorption, rapid recombination of photoinduced charge carriers, photocorrosion, or insufficient density of catalytically active sites. In parallel, g-C₃N₄ has emerged as an attractive metal-free photocatalyst owing to its suitable band structure, low cost, and chemical stability; however, its relatively low surface area, moderate electrical conductivity, and severe charge recombination often restrict its photocatalytic efficiency [8]. Metal-organic frameworks (MOFs) and conjugated polymers have also attracted significant attention for photocatalytic H₂ evolution because of their tunable molecular structures and versatile chemical compositions. MOFs provide exceptionally high porosity and abundant coordination environments but are frequently limited by inadequate hydrolytic stability and relatively poor charge transport [9]. Conjugated polymers exhibit broad visible-light absorption and structural flexibility, yet their generally amorphous nature and

limited crystallinity can impede efficient exciton dissociation and long-range charge migration. Compared with these photocatalytic systems, COFs uniquely integrate permanent crystallinity, ordered porosity, extended π -conjugation, and highly programmable molecular architectures, providing a distinctive platform for simultaneously optimizing light harvesting, charge transport, and catalytic-site accessibility [10]. Nevertheless, practical solar-to-hydrogen conversion remains constrained by several persistent obstacles, including inefficient utilization of visible photons, rapid recombination of photoinduced charge carriers, sluggish proton-coupled electron-transfer processes, and limited accessibility of catalytically active surface sites [11–13]. Furthermore, many conventional photocatalysts possess structurally heterogeneous surfaces and poorly defined reaction environments, complicating mechanistic interpretation and limiting precise regulation of catalytic pathways [14]. These limitations have stimulated increasing interest in crystalline photocatalytic platforms with programmable molecular architectures and controllable electronic structures.

Covalent organic frameworks (COFs) have emerged as highly attractive photocatalytic materials because they integrate long-range structural periodicity with molecular-level synthetic tunability [15, 16]. Constructed through the reticular assembly of organic building units connected by covalent linkages, COFs possess ordered nanochannels, permanent porosity, high surface areas, and well-defined π -conjugated frameworks [17]. Their modular structural characteristics permit deliberate manipulation of light-harvesting properties, charge-transport pathways, pore environments, and catalytic functionalities through rational monomer design [18]. In particular, the incorporation of donor–acceptor (D–A) motifs, heteroatom-containing units, and extended aromatic systems enables effective modulation of band structures and exciton migration behaviors [19]. Unlike many amorphous organic photocatalysts, crystalline COFs facilitate directional charge transport through ordered π -columnar stacking and periodic electronic coupling, thereby favoring photoinduced carrier separation under visible-light irradiation [20]. Simultaneously, their porous architectures provide abundant accessible interfaces for mass diffusion and surface catalytic reactions [21]. These advantages have established COFs as promising candidates for diverse photocatalytic transformations, including CO_2 reduction, organic synthesis, pollutant degradation, O_2 evolution, and H_2 evolution [22–24]. Pristine metal-free COFs have been widely recognized as efficient photocatalysts for H_2 evolution due to their structural tunability and tailorable electronic properties. Nevertheless, their photocatalytic performance remains framework-dependent, and some COFs still suffer from limited proton reduction kinetics, rapid charge-carrier recombination, and insufficient proton adsorption, which restrict overall H_2 evolution efficiency [25, 26].

To address these intrinsic limitations, substantial attention has been directed toward the integration of metal species into COF architectures [27]. Metal incorporation fundamentally alters the electronic and catalytic characteristics of COFs by introducing localized charge centers, redox-active orbitals, and catalytic reaction sites [28, 29]. Transition-metal species such as Co, Ni, Fe, Cu, Mo, and Pt possess partially occupied d orbitals capable of facilitating proton adsorption and lowering the energetic barrier associated with hydrogen evolution [30–32].

Simultaneously, strong coordination interactions between metal centers and heteroatom-rich COF frameworks stabilize highly dispersed catalytic sites while regulating electron-density distribution across the conjugated skeleton [33]. Such electronic interactions can substantially improve visible-light harvesting, accelerate exciton dissociation, and promote directional migration of photoinduced electrons toward reduction centers [34]. Depending on the integration strategy, metals can be introduced into COFs as isolated single atoms (SAs), molecular complexes, nanoclusters (NCs), nanoparticles (NPs), or heterostructured cocatalysts [35–37]. Single-atom (SA) coordination environments maximize atomic utilization efficiency while generating well-defined catalytic microenvironments that enable mechanistic regulation at molecular scales [38]. Metal NCs can function as electronic relay domains that prolong charge-carrier lifetime and facilitate multielectron transfer processes [39]. Noble-metal NPs additionally induce localized surface plasmon resonance, thereby intensifying electromagnetic fields and improving solar-energy utilization efficiency [40]. Moreover, coupling COFs with metal sulfides, phosphides, oxides, or metal–organic frameworks enables construction of type-II, Z-scheme, or S-scheme heterojunctions that effectively suppress electron–hole recombination through interfacial band alignment [41–43].

Recent advances have further demonstrated that the photocatalytic behavior of metal-integrated COFs is strongly dependent on the coordination chemistry and spatial organization of incorporated metal species [44]. The electronic communication established between catalytic metal centers and π -conjugated organic backbones directly governs exciton dynamics, proton adsorption energetics, and interfacial reduction pathways [45]. For example, coordination motifs such as M–N_4 , $\text{M–N}_2\text{S}_2$, or $\text{M–N}_3\text{O}$ environments can markedly influence hydrogen adsorption free energies and regulate proton-coupled electron-transfer kinetics [46]. Likewise, D–A engineering within COF skeletons can synergistically interact with metal sites to enhance long-range charge delocalization and broaden spectral response into the visible and near-infrared regions [47]. Structural parameters including crystallinity, pore accessibility, linkage chemistry, stacking arrangement, and framework dimensionality additionally influence metal dispersion and catalytic accessibility [48]. Highly ordered layered COFs generally exhibit superior charge-transport capability because eclipsed π -stacking facilitates directional electron migration along periodic conjugated channels [49]. Hierarchically porous architectures can further improve electrolyte diffusion and proton accessibility during photocatalytic reactions [50]. Importantly, metal integration also enhances framework robustness by stabilizing reactive intermediates and suppressing photocorrosion under prolonged irradiation conditions [12–16, 51]. Hence, these developments indicate that rational integration of metal functionality with crystalline organic frameworks provides an exceptionally versatile strategy for constructing next-generation photocatalysts with highly tunable physicochemical properties.

The rapid expansion of this field has generated diverse metal integration approaches, catalytic mechanisms, and structure–activity relationships that require systematic interpretation from both synthetic and mechanistic perspectives. In particular, understanding how distinct metal species regulate electronic structures, charge-transfer dynamics, proton adsorption, and H_2

evolution pathways is essential for the rational design of highly efficient photocatalytic systems. Therefore, this review summarizes recent advances in metal-integrated COFs for photocatalytic H_2 evolution, emphasizing the relationships among framework structures, metal coordination environments, optoelectronic properties, and catalytic functions (Fig. 1). First, the structural characteristics and photocatalytic fundamentals of COFs are introduced, followed by representative strategies for incorporating metal SAs, molecular complexes, metal clusters, NPs, and heterostructured cocatalysts into crystalline frameworks. Subsequently, the mechanistic roles of integrated metals in regulating light absorption, charge separation, proton reduction, and H_2 evolution kinetics of different COFs photocatalytic systems are critically discussed. Finally, future opportunities are highlighted toward the development of highly efficient COF-based photocatalysts for sustainable solar H_2 evolution.

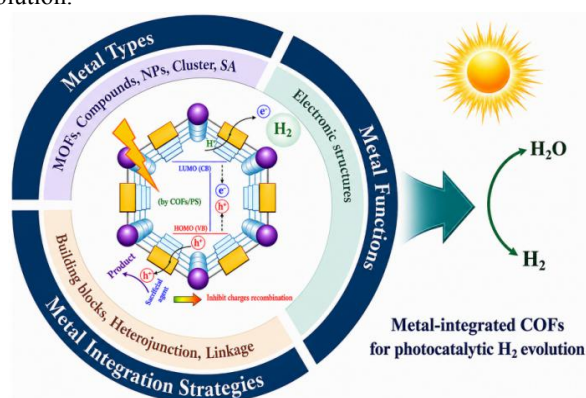


Figure 1 Summary illustration this review for photocatalytic H_2 evolution.

2. Structural properties of COFs

Framework networks identified as COFs emerge through integrating assorted molecular precursors into organized porous systems using multiple chemical joining patterns. Detailed examination regarding composition, topology, and native behavior remains crucial toward expanding solar-assisted catalytic technologies because that understanding permits deliberate tuning of reaction efficiency after metallic incorporation. Consequently, this passage presents foundational characteristics connected with those frameworks, addressing precursor selection, connective chemistries, together with architectural properties relevant for investigation and optimization.

2.1. Basic structures of COFs

The framework architecture of COFs originates from the covalent integration of geometrically defined monomers containing reactive functional groups. Through precise molecular design, these monomers can assemble into highly ordered two-dimensional (2D) or three-dimensional (3D) porous networks with tunable electronic structures and controllable catalytic interfaces. The structural diversity achievable in COFs enables the deliberate regulation of D–A interactions, π -conjugation length, pore accessibility, and metal-binding motifs. For photocatalytic systems, the framework geometry strongly influences charge separation pathways and the accessibility of catalytic centers. The incorporation of metal-coordination sites within the framework further enables the formation of atomically dispersed catalytic centers or multinuclear metal clusters. Such structural integration not only facilitates

photoinduced electron migration but also promotes substrate adsorption and activation. Studies on metal-functionalized COFs have demonstrated that carefully engineered coordination environments, including Co–N–O, Co–N₂–O₂, Zn–N, and Cu-cluster motifs, can substantially reduce kinetic barriers for photocatalytic reduction processes [51–53]. The structural organization of COFs can therefore be understood through two major components: covalent linkage chemistry and functional building blocks capable of regulating electronic distribution and metal integration.

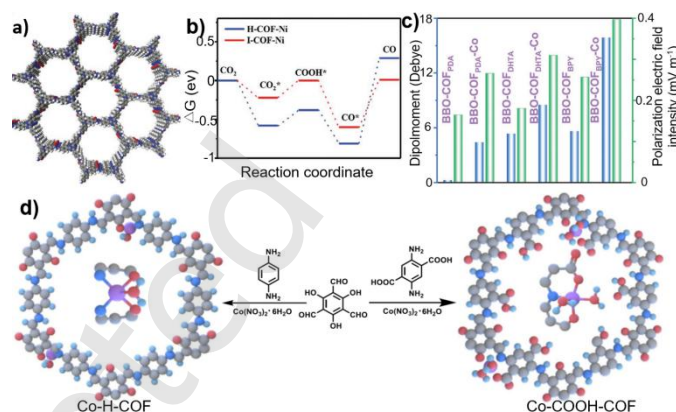


Figure 2 (a) Top view and (b) Gibbs free energy calculation of H-COF-Ni and I-COF-Ni [50]. Reprinted with permission from Ref. [50]. Copyright 2022, John Wiley and Sons. (c) Dipole moment and intensity polarization of BBO-based COFs [51]. Reprinted with permission from Ref. [51]. Copyright 2025, John Wiley and Sons. (d) Preparation of Co-COOH-COF nanosheets [54]. Reprinted with permission from Ref. [54]. Copyright 2025, John Wiley and Sons.

2.1.1. Covalent linkages of COFs

Covalent linkages serve as the structural backbone of COFs and play a decisive role in determining crystallinity, chemical durability, electronic communication, and catalytic stability. In photocatalytic COFs, linkage chemistry directly influences π -electron delocalization, exciton dissociation behavior, and the stabilization of metal active sites. Among the reported linkage systems, Schiff-base-derived imine and hydrazone structures remain widely employed because they enable facile synthesis and provide coordination sites for transition metals. However, recent studies indicate that subtle differences in linkage microenvironments can substantially alter photocatalytic behavior. For instance, Yang et al. demonstrated that N-acylhydrazone-linked H-COF-Ni exhibited significantly stronger CO_2 adsorption and activation capability than its imine-linked analogue I-COF-Ni (Figs. 2a & 2b) [50]. The enhanced catalytic behavior originated from the stronger interaction between Ni centers and CO_2 molecules mediated by the N-acylhydrazone environment. Interestingly, the catalytic performance was not solely governed by charge-separation efficiency, emphasizing the importance of local linkage chemistry in determining reaction energetics. Linkage-associated coordination environments also regulate excitonic dissociation within D–A COFs. Zhang et al. prepared BBO-based COFs containing programmable coordination motifs, including Co–N–O₂, Co–N–O₃, and Co–N₂–O₂ structures [51]. The incorporation of cobalt altered the polarization electric field within the frameworks (Fig. 2c), thereby accelerating singlet exciton dissociation and facilitating charge migration toward catalytic sites. Among the investigated systems, the bipyridine-coordinated Co–N₂–O₂

configuration displayed the highest CO evolution activity and selectivity owing to superior electron delocalization and lower energy barriers for intermediate formation. Vinylene-linked COFs have emerged as an important class of photocatalytic materials because their fully conjugated carbon-carbon backbones provide efficient pathways for long-range charge transport while improving structural robustness under prolonged irradiation. Li et al. developed vinylene-linked donor- π -acceptor metal COFs incorporating electron-deficient Cu cyclic trinuclear units (Cu-CTUs) [52]. In these architectures, the vinylene bridge promoted rapid migration of photogenerated charge carriers throughout the conjugated framework, whereas the Cu clusters served as electron-mediating centers that facilitated interfacial charge transfer and promoted the utilization of photoexcited electrons during photocatalysis. The synergistic interaction between the conjugated linkage and the embedded metal sites enhanced charge separation and reduced carrier recombination, both of which are essential prerequisites for efficient photocatalytic performance. This study further illustrates that optimizing the electronic coupling between the organic backbone and metal centers is as important as increasing the density of catalytic sites, since balanced carrier transport ultimately determines photocatalytic efficiency. The influence of linkage engineering is also evident in tridentate ligand-containing COFs. Deng et al. synthesized imine-linked Co-COOH-COF nanosheets possessing asymmetric tridentate coordination motifs (Fig. 2d) [54]. The expanded coordination environment surrounding the cobalt centers generated a greater population of accessible catalytic sites while facilitating rapid electron transfer across the framework, thereby improving photocatalytic reaction kinetics and enhancing the overall stability of the catalytic process. Beyond regulating photocatalytic activity, linkage chemistry also plays a decisive role in framework formation and synthetic scalability. One-step synthetic strategies for metallosalen COFs have demonstrated that preserving crystallinity during metal incorporation is essential for maintaining efficient charge transport and long-term photocatalytic performance [55]. Compared with post-synthetic metalation, direct integration of metal-containing linkages produced more ordered crystalline frameworks with stronger electronic communication between the organic skeleton and metal centers. Hence, these studies demonstrate that covalent linkages function not only as structural connectors but also as molecular regulators of electronic structure, charge-transfer behavior, metal-site stabilization, and photocatalytic durability, making linkage engineering a central design principle for developing highly efficient metal-integrated COFs for solar H₂ evolution.

Beyond framework stabilization, linkage engineering also directly influences local electronic polarization and exciton-binding energy within photocatalytic COFs. Electron-rich linkage environments can facilitate rapid electron delocalization across conjugated domains, whereas electron-deficient motifs often enhance directional charge migration toward catalytic metal centers. In D-A structured systems, the covalent bridge serves as the principal pathway for carrier transport between donor and acceptor units [56]. Consequently, subtle modifications in bond polarity and conjugation length can profoundly regulate photoinduced carrier mobility. Recent investigations further revealed that coordination-assisted linkage modulation is highly effective for suppressing recombination

losses. In Co-functionalized BBO-COFs, distinct coordination geometries surrounding cobalt centers altered local polarization fields and accelerated the dissociation of tightly bound excitons into free carriers [51]. Similarly, the introduction of tridentate coordination motifs into imine-linked COFs generated higher densities of accessible catalytic sites and weakened adsorption energies of key intermediates, thereby promoting continuous catalytic turnover during syngas generation [54]. The role of linkage chemistry is also evident in one-pot synthesized metallosalen COFs, where preserving ordered covalent assembly during metal incorporation resulted in improved crystallinity and enhanced photocatalytic performance compared with post-synthetically modified analogues [57]. These findings cooperatively indicate that linkage chemistry simultaneously governs framework order, charge-transport pathways, and the stability of catalytically active coordination environments. Moreover, extended π -conjugated linkages substantially broaden visible-light absorption and promote efficient migration of photoinduced carriers throughout the framework. Vinylene-linked D- π -A architectures containing Cu-CTUs exhibited highly efficient charge separation because the continuous carbon-carbon conjugated bridges reduced carrier-transport resistance and strengthened electronic communication between the organic backbone and metal catalytic centers [52]. Such structural features are particularly advantageous for photocatalytic H₂ evolution, where sustained accumulation and transfer of photoinduced electrons are essential for efficient proton reduction. Hence, these studies establish linkage chemistry as a fundamental molecular design parameter for metal-integrated COFs. Rational optimization of coordination environments, electronic conjugation, and bond polarity provides a versatile strategy for simultaneously enhancing light harvesting, exciton dissociation, long-range charge transport, and catalytic durability, all of which are indispensable for achieving high-performance solar H₂ evolution.

2.1.2. Building blocks of COFs

The physicochemical characteristics of COFs are fundamentally governed by the molecular design of their organic building units, making building-block selection a decisive factor in the development of efficient photocatalysts for solar H₂ evolution. Beyond defining framework geometry and pore architecture, functional monomers regulate optical absorption, D-A interactions, electronic delocalization, and metal-coordination behavior, thereby influencing the generation, migration, and utilization of photoinduced charge carriers. Consequently, rational molecular engineering has emerged as an indispensable strategy for constructing high-performance metal-integrated COFs. Electron-rich donor components and electron-deficient acceptor fragments are frequently combined to establish internal D-A heterojunctions that strengthen charge separation and prolong carrier lifetimes. For example, Li et al. fabricated three-component vinylene-linked D- π -A metal COFs using triphenylamine donors, Cu-CTU acceptors, and conjugated π -bridges [52]. The electron-deficient Cu clusters promoted efficient intramolecular charge redistribution, broadened visible-light absorption, and facilitated rapid electron transport toward catalytically active metal centers, features that are equally advantageous for photocatalytic proton reduction. Likewise, porphyrin- and salen-derived monomers remain among the most extensively explored building blocks because they provide highly ordered coordination environments capable of stabilizing

isolated metal sites. Zhou et al. synthesized a series of metallosalen COFs featuring mononuclear and binuclear coordination motifs [55], demonstrating that the well-defined M–N₂O₂ environments effectively regulate electronic structures while promoting charge mobility throughout the crystalline framework. Bipyridine-containing monomers exhibit similar importance because their nitrogen-rich coordination sites efficiently anchor isolated transition-metal ions. Xu et al. prepared hierarchically porous TB-COFs containing bipyridine units capable of coordinating Co²⁺, Ni²⁺, and Cu²⁺ ions [58]. Among these materials, Co-TB-COF displayed the most favorable electronic characteristics, including enhanced electron-accepting ability and accelerated carrier migration, highlighting the value of bipyridine ligands for constructing robust photocatalysts designed for efficient H₂ evolution.

Triazine-containing acceptor units further strengthen the electronic functionality of metal-integrated COFs by serving as effective electron-withdrawing centers within conjugated frameworks. Fu et al. synthesized a TPy-COF incorporating both triazine acceptors and bipyridine coordination sites [59]. Following cobalt immobilization, the resulting Co–N₄Cl₂ active centers promoted efficient charge redistribution across the framework and facilitated directional electron transfer under visible-light irradiation, thereby improving overall photocatalytic efficiency. Three-dimensional cage-based COFs constructed from porphyrinic and nitrogen-rich building units further expand the structural versatility of these materials. Cage-PorCOF(Co) combined an interconnected porous architecture with uniformly distributed cobalt centers, providing rapid molecular diffusion, abundant accessible catalytic sites, and efficient charge transport throughout the framework [60]. Metal-cluster-based building units offer another effective design strategy. Xu et al. constructed Cu–S–N cluster-based 3D COFs using tetrahedral Cu₄ cluster nodes [61]. Strong electronic communication between the conjugated organic linkers and copper clusters enhanced visible-light harvesting, accelerated carrier migration, and reinforced structural robustness, cooperatively benefiting photocatalytic activity. In addition, heteroatom-containing building units introduce localized electronic polarization within the framework. Liao et al. developed phosphazene-containing 3D COFs incorporating N, O, and P active sites [62]. Under illumination, photoinduced electrons and holes became spatially separated between different functional domains, enabling efficient redox reactions while minimizing recombination losses. Overall, these studies demonstrate that molecular building-block engineering dictates the electronic architecture and photocatalytic behavior of COFs. Precise integration of donor–acceptor units, heteroatoms, and metal-coordination motifs enables simultaneous optimization of light harvesting, charge transport, catalytic-site accessibility, and long-term photocatalytic stability, all of which are essential requirements for efficient solar H₂ evolution.

Recent advances have increasingly focused on D–A topology engineering because internally polarized conjugated frameworks create built-in electric fields that facilitate directional charge migration. The spatial separation of electron-rich and electron-deficient segments promotes efficient exciton dissociation while suppressing undesirable electron–hole recombination. Such electronic asymmetry provides continuous electron delivery toward catalytically active metal centers, thereby enhancing proton reduction kinetics during photocatalytic H₂ evolution.

Bipyridine-containing monomers have emerged as particularly versatile structural components because they simultaneously function as electron-withdrawing units and coordination ligands for isolated transition metals [63]. Their nitrogen-rich coordination environments stabilize atomically dispersed catalytic centers while facilitating rapid interfacial electron transfer throughout the conjugated framework. In Co-TB-COF and TPy-COF-Co systems, bipyridine motifs significantly accelerated charge migration and optimized the electronic environment surrounding the coordinated metal atoms [64]. Porphyrinic and phthalocyanine-like macrocycles likewise contribute substantially to visible-light harvesting because of their highly delocalized π -electron systems and broad optical absorption. These macrocycles stabilize transition-metal ions within well-defined coordination environments, where the embedded metal centers simultaneously function as catalytic sites and charge-transfer mediators. Metallosalen COFs further demonstrate that the combination of conjugated macrocyclic structures with isolated metal centers generates highly efficient photocatalytic systems exhibiting excellent electronic communication, rapid carrier transport, and remarkable structural robustness under prolonged illumination [65].

Three-dimensional building blocks further enhance framework accessibility by creating interconnected diffusion channels that facilitate rapid mass transport and expose a larger proportion of catalytically active sites [66, 67]. These structural characteristics become increasingly important during photocatalytic hydrogen evolution because efficient proton diffusion and continuous removal of evolved hydrogen contribute directly to sustained catalytic performance. Incorporation of metal clusters into framework nodes provides an additional opportunity to tailor the electronic structure of COFs. Cu-CTU units and Cu₄ cluster nodes introduce electron-deficient coordination environments that strengthen electronic coupling with conjugated organic linkers, broaden visible-light absorption, and promote efficient separation of photogenerated charge carriers [68, 69]. Such synergistic interactions improve carrier utilization while maintaining structural integrity during repeated photocatalytic cycles. Furthermore, heteroatom-rich building blocks containing nitrogen, sulfur, oxygen, or phosphorus further diversify the electronic functionality of COFs by regulating local electron density and stabilizing transient charge distributions during photocatalysis. Phosphazene-containing 3D COFs demonstrate that the coexistence of N, O, and P functionalities enables spatially separated oxidation and reduction domains, thereby promoting efficient utilization of photoinduced carriers while minimizing recombination losses [70]. Consequently, building-block selection extends well beyond framework construction. Their electronic characteristics, coordination capability, steric configuration, and heteroatom composition collectively determine light absorption, carrier mobility, catalytic-site accessibility, and overall photocatalytic efficiency, establishing molecular design as the cornerstone for developing next-generation metal-integrated COFs for solar H₂ evolution.

2.2. Characteristics of COFs

COFs exhibit a unique combination of crystallinity, structural tunability, porosity, and electronic conjugation, making them highly promising platforms for photocatalytic applications. These intrinsic characteristics collectively determine light-harvesting efficiency, exciton dissociation behavior, reactant

accessibility, and catalytic durability. High crystallinity is one of the most significant structural features of COFs because ordered π -stacked architectures facilitate directional carrier transport and suppress charge recombination. The influence of crystallinity on photocatalysis was demonstrated in several metal-functionalized systems, where ordered coordination environments promoted rapid electron migration toward catalytic metal sites [71]. Porosity and interconnected transport channels are equally important because they improve the diffusion of reactants and expose catalytic active centers. Hierarchically porous COFs containing cage-like or 3D interconnected structures have shown particularly strong photocatalytic performance due to enhanced substrate accessibility [72]. In addition, the confinement effect generated by ordered channels stabilizes isolated metal species and suppresses aggregation during photocatalysis. Another defining characteristic of COFs is their extensive π -conjugated structure. Delocalized electronic networks broaden visible-light absorption and promote intramolecular charge transfer. D–A engineering within conjugated backbones has proven especially effective for enhancing photocatalytic efficiency. For example, D– π –A Cu-CTU-based metal COFs displayed accelerated carrier separation and enhanced CO₂ activation owing to strong internal electron pull–push interactions [52].

The integration of metal centers further amplifies the optoelectronic properties of COFs. SA metal incorporation can generate localized polarization electric fields that accelerate exciton dissociation and improve electron transfer kinetics [73]. In Zn-SAC@COF systems, isolated zinc centers reduced the energy barriers associated with *OOH intermediate formation and promoted electron delocalization, thereby significantly increasing photocatalytic H₂O₂ generation [53]. COFs also exhibit highly tunable coordination microenvironments capable of regulating adsorption behavior and catalytic selectivity. Cd-modified N-heterocyclic COFs demonstrated that introducing high-valence metal ions can alter local electronic structures, reduce charge-transfer resistance, and strengthen oxygen adsorption capability [74]. Similarly, dual-metal ZnZn-Salen-COFs achieved remarkable photocatalytic performance under diluted CO₂ atmospheres because neighboring metal sites cooperatively stabilized reaction intermediates and lowered activation barriers [75]. Another important feature of COFs is their chemical robustness. The covalent framework enables structural stability under prolonged irradiation conditions while maintaining catalytic activity. Metal-cluster-containing COFs and SA catalysts confined within porous channels exhibited strong resistance against metal aggregation and structural degradation during repetitive photocatalytic cycles [76, 77]. Beyond stability and porosity, COFs provide exceptional flexibility for constructing multifunctional catalytic systems. Trimetallic COFs integrating Ru photosensitizers, Co catalytic sites, and Cu reduction centers established tandem photocatalytic pathways capable of converting CO₂ into CH₄ with high selectivity [66]. Such multifunctional architectures highlight the ability of COFs to spatially organize multiple catalytic processes within a single crystalline framework. Overall, the distinctive characteristics of COFs, including high crystallinity, tunable conjugation, ordered porosity, stable covalent backbones, and adaptable coordination environments, establish them as highly versatile photocatalytic platforms. Through rational structural engineering and controlled metal integration, these materials can achieve efficient light harvesting,

accelerated charge separation, optimized intermediate stabilization, and enhanced catalytic conversion efficiency.

One of the defining advantages of COFs lies in their ability to stabilize atomically dispersed catalytic sites through spatial confinement and strong coordination interactions. The ordered porous channels and periodic heteroatom distribution create highly uniform microenvironments that prevent metal aggregation while maintaining maximum atomic utilization efficiency. SA catalytic centers embedded within COFs can therefore act as highly active electron-capture and substrate-activation sites [78, 79]. The incorporation of transition metals further induces localized polarization electric fields that accelerate carrier migration. In cobalt-modified BBO-COFs, the intensified polarization environment significantly enhanced singlet-exciton dissociation and promoted free-charge transfer from the bulk framework toward catalytic surfaces [51]. Similar phenomena were observed in Zn-SAC@COF systems, where isolated zinc atoms disrupted local electronic symmetry and lowered the energy barrier associated with *OOH intermediate generation [53]. Another remarkable feature of COFs is their ability to accommodate multifunctional catalytic architectures. By spatially integrating photosensitizing units, electron-transfer channels, and reduction-active sites within a single framework, tandem catalytic pathways can be established. Trimetallic COFs incorporating Ru, Co, and Cu centers successfully achieved cooperative CO₂-to-CH₄ conversion through sequential catalytic processes [66]. In these systems, Ru sites accelerated photoinduced carrier separation, Co centers facilitated CO generation, and trinuclear Cu units promoted subsequent multielectron reduction reactions.

The confinement effect generated by ordered porous structures also contributes to intermediate stabilization during photocatalysis. Restricted pore environments can increase local reactant concentration near catalytic centers while suppressing undesired side reactions. Such effects become especially beneficial in CO₂ photoreduction systems, where stabilization of *COOH and *CO intermediates strongly influences product selectivity and catalytic efficiency [80, 81]. Furthermore, the tunable D–A arrangement within COFs enables precise modulation of band structures and interfacial charge-transfer behavior. Electron-deficient acceptor units act as electron sinks that facilitate directional migration of photoinduced electrons, whereas donor units broaden visible-light absorption and improve carrier mobility. This cooperative electronic interaction is central to the exceptional photocatalytic activity observed in D– π –A metal COFs [52]. Chemical robustness is another critical feature supporting long-term photocatalytic applications. The strong covalent backbones of COFs enable structural stability under prolonged irradiation and repetitive catalytic cycling. Frameworks containing coordinated SA metals or cluster nodes maintained excellent recyclability and retained catalytic activity over multiple reaction cycles without significant structural degradation [82, 83]. Additionally, the modular nature of COFs enables precise molecular-level regulation of catalytic microenvironments. Metal identity, coordination number, heteroatom composition, pore topology, and D–A distribution can all be independently tailored to optimize photocatalytic pathways. Such structural versatility provides unparalleled opportunities for designing next-generation photocatalysts with controllable selectivity, high quantum efficiency, and enhanced solar-energy utilization. Overall, these structural characteristics

position COFs as highly adaptable and functionally programmable materials for artificial photosynthesis and solar-fuel generation. Continuous advances in molecular design, metal integration, and electronic-structure engineering are expected to further expand their role in sustainable photocatalytic conversion technologies.

3. Metal integration strategies in COFs

Although pristine COFs possess ordered porosity, structural periodicity, and extended π -conjugation, their limited density of intrinsically active catalytic sites restricts photocatalytic efficiency. Incorporation of metal species has therefore become a central strategy for converting COFs into highly efficient and electronically tunable photocatalysts by promoting light harvesting, charge separation, and surface redox kinetics. Based on the coordination environment and framework architecture, metal integration in COFs can be classified into three major approaches: (i) anchoring metals at framework linkages, (ii) coordinating metals with functional building units, and (iii) constructing COF-based heterostructures with metal-containing materials. The introduced metals may exist as, NCs, SAs, NPs, metal compounds, or MOFs, each imparting distinct electronic interactions and catalytic functionalities.

3.1. Metal on linkage

Linkage-directed metal anchoring utilizes electron-rich moieties such as imine, bipyridine, triazine, or β -ketoenamine units to stabilize isolated metal centers through strong coordination interactions, thereby suppressing aggregation and facilitating directional charge transfer. In contrast, metal coordination to predesigned building blocks enables precise regulation of the local electronic configuration and catalytic microenvironment, resulting in improved band alignment, accelerated exciton dissociation, and enhanced photocatalytic reactivity [85]. Beyond isolated coordination strategies, COFs are also widely employed as crystalline scaffolds for assembling heterostructured photocatalysts with metal-based semiconductors, MOFs, and metallic NPs. The resulting interfacial electronic coupling and built-in electric fields promote spatial charge separation and broaden visible-light utilization, leading to superior photocatalytic performance [86]. Nevertheless, precise control over metal dispersion, coordination geometry, electronic states, and operational stability remains a major challenge. Accordingly, advanced synthetic methodologies combined with operando characterization and theoretical analysis are essential for elucidating structure–property relationships and guiding the rational design of next-generation metal-integrated COF photocatalysts [87]. Metal incorporation within covalent linkage domains has emerged as a powerful strategy for constructing COF photocatalysts with finely regulated electronic structures and uniformly accessible catalytic sites. Unlike frameworks assembled from pre-metalated monomers, linkage-directed metalation exploits the intrinsic coordination ability of heteroatom-rich linkages already embedded in the polymer backbone [88]. Imine, hydrazone, β -ketoenamine, acylhydrazone, and related N/O-containing motifs provide localized lone-pair donor environments capable of anchoring transition-metal species directly inside ordered channels without disrupting framework crystallinity. Because metal incorporation occurs after framework construction, this approach offers broad structural compatibility, synthetic versatility, and efficient suppression of uncontrolled metallic

aggregation [89–92]. The resulting atomically dispersed centers promote directional charge migration, exciton dissociation, substrate accessibility, and localized polarization within conjugated networks, thereby enhancing photocatalytic carrier utilization and interfacial redox kinetics.

A representative example was reported by Hu et al. through post-synthetic cyclometalation of an imine-linked pyrene COF using iridium precursors to generate organometallic catalytic domains within the pore walls [90]. Under alkaline reflux conditions, selective coordination of Ir species occurred at Schiff-base linkages while preserving long-range crystallinity and framework topology. Spectroscopic analyses confirmed direct participation of imine nitrogen atoms in iridacycle formation, whereas diffraction measurements demonstrated structural retention after metal insertion. Incorporation of Ir broadened visible-light absorption and extended the photoresponse region while slightly reducing pore dimensions and BET surface area, consistent with confinement of isolated organometallic species inside the channels. The cyclometalated framework displayed markedly enhanced H_2 evolution from aqueous formate media under photo-assisted thermal conditions owing to efficient electronic coupling between hydride-forming Ir centers and the π -conjugated backbone. The coordinated Ir sites promoted photon harvesting, carrier transport, and proton reduction while exhibiting negligible metal leaching during prolonged operation, highlighting the stabilizing effect of linkage-confined coordination on single-site catalytic architectures.

Linkage-regulated photodeposition has likewise been employed to generate highly dispersed Pt species in imine-linked COFs [91]. In pyrene-derived frameworks containing neighboring hydroxyl and imine functionalities, in situ photoreduction of H_2PtCl_6 under visible-light irradiation produced atomically dispersed Pt centers together with ultrasmall Pt clusters uniformly distributed throughout the channels. Cooperative O/N coordination sites acted as preferential precursor adsorption and nucleation domains, suppressing uncontrolled particle growth and strengthening electronic communication between Pt and the conjugated framework. Compared with randomly deposited Pt NPs, the confined Pt species provided higher exposure of catalytically accessible atoms and significantly reduced interfacial charge recombination, leading to superior H_2 evolution activity. Theoretical calculations further revealed that the adjacent hydroxyl–imine environment increased precursor binding affinity and induced localized electron accumulation around Pt anchoring sites, thereby accelerating photodeposition kinetics and facilitating proton-coupled reduction pathways. Sulfur-containing linkage environments provide an additional means of regulating the electronic structure of immobilized metal centers. For instance, Peng et al. developed sulfur-rich hydrazone-linked COFs capable of stabilizing isolated Pt species through mild post-immobilization reduction [42]. Following incorporation of H_2PtCl_6 into the S-TFPT framework, atomically dispersed PtSA@S-TFPT formed without detectable nanoparticle aggregation. X-ray absorption analyses revealed asymmetrically coordinated low-valence Pt species embedded within polarized Pt– S_2O_2 coordination domains (Fig. 3a). The asymmetric donor environment promoted rapid carrier separation and reduced the thermodynamic barrier for hydrogen desorption, resulting in substantially enhanced visible-light-driven H_2 evolution and

excellent long-term stability. These findings demonstrate that incorporation of soft donor atoms such as sulfur can effectively tune local electron density distributions and optimize interfacial charge-transfer energetics around isolated catalytic centers.

Hydrazone-linked COFs have also enabled construction of highly polarized Pt SA photocatalysts through cryogenic photoreduction strategies. For instance, Xia et al. synthesized mesoporous triazine-containing TCOF frameworks enriched with hydrazone coordination sites and subsequently immobilized Pt precursors within frozen aqueous dispersions under Xe-lamp irradiation [93]. Rapid cryogenic confinement effectively inhibited precursor diffusion and suppressed metallic aggregation during photoreduction (Fig. 3b). Structural characterization XANES (Fig. 3c) identified isolated $\text{Pt}^{\delta+}$ species stabilized within an unusual N1–Pt–C₂ coordination environment rather than conventional Pt ensembles. The optimized TCOF-Pt SA3 catalyst simultaneously promoted H₂ evolution and selective benzylamine oxidation, affording H₂ and N-benzylidenebenzylamine production rates of 501.8 and 477.3 $\mu\text{mol g}^{-1} \text{ h}^{-1}$, respectively. Mechanistically, the atomically dispersed Pt centers generated localized polarization fields, enhanced dielectric response, lowered exciton-binding energy, and accelerated charge separation throughout the framework. Excessive Pt loading, however, induced cluster formation and partially disrupted electronic homogeneity, underscoring the importance of balancing atomic-site density with structural integrity during linkage-confined metalation. Beyond noble metals, linkage-coordinated SA engineering has been extended to earth-abundant transition metals. For instance, Wen et al. reported rapid plasma-assisted synthesis of bipyridine-containing TpBpy COFs followed by post-synthetic coordination of isolated Ni centers [94]. Under dielectric barrier discharge plasma conditions, crystalline frameworks formed within one hour and subsequently coordinated Ni species through bipyridine nitrogen donors distributed along the conjugated skeleton. Spectroscopic analyses confirmed the presence of atomically dispersed N₂–Ni–Cl₂ sites rather than metallic or oxide clusters. Incorporation of isolated Ni narrowed the optical bandgap, accelerated carrier transport, and enhanced generation of reactive oxygen intermediates, particularly superoxide radicals, thereby markedly improving visible-light-driven acetaminophen degradation. Strong electronic coupling between Ni centers and the conjugated backbone simultaneously preserved crystallinity and photocatalytic stability during repeated operation.

Similarly, Tu et al. introduced isolated Cu centers into two-dimensional DHTA-TTA COF nanobelts through spontaneous coordination between CuCl_2 and framework heteroatoms under ambient conditions [95]. Coordinative interactions involving imine nitrogen and methoxy oxygen functionalities generated atomically dispersed Cu–O/N active sites without detectable nanoparticle formation, as confirmed by EXAFS analysis (Fig. 3d). Incorporation of Cu substantially enhanced interfacial

electron transport, strengthened electronic coupling between the coordinated metal atoms and the conjugated framework, and improved the separation efficiency of photogenerated charge carriers while maintaining excellent structural stability. The uniformly dispersed Cu catalytic domains also increased the accessibility of active sites throughout the ordered porous architecture, providing continuous pathways for efficient carrier migration under visible-light irradiation. From the perspective of photocatalytic H₂ evolution, these characteristics are highly desirable because rapid electron transfer toward proton-reduction sites represents one of the principal requirements for achieving high hydrogen-generation efficiency. This work therefore highlights that rational control of coordination chemistry can significantly improve photocatalytic performance even when the original catalytic application differs from hydrogen production. The catalytic behavior of linkage-confined metal centers can be further optimized through deliberate regulation of their local coordination microenvironment. Zhang et al. demonstrated this concept by employing hydroxyl-substituted aldehyde precursors to engineer distinct Co coordination geometries within triazine-based COFs [96]. Post-synthetic coordination with $\text{Co}(\text{NO}_3)_2$ generated highly dispersed Co–O₄ and Co–O₃N motifs uniformly distributed throughout the porous framework. Comparative analyses showed that the Co–O₄ coordination environment provided more favorable electronic characteristics, including accelerated directional electron transport, enhanced carrier separation, and improved utilization of photogenerated electrons. These structural features contributed to superior photocatalytic efficiency by facilitating rapid charge migration while minimizing recombination losses across the conjugated framework. The study clearly demonstrates that subtle variations in atomic coordination geometry can substantially influence the electronic structure and photocatalytic behavior of metal-integrated COFs. Consequently, future catalyst design should emphasize precise manipulation of local coordination environments as a practical route for optimizing hydrogen-evolution kinetics without altering the overall crystalline architecture.

Linkage-confined coordination has also enabled the development of cooperative bimetallic catalytic architectures capable of promoting more efficient charge redistribution within crystalline COF frameworks. Zhou et al. employed electrostatically guided self-assembly to immobilize neighboring La and Ni centers within boronate-linked COF-5 using phenanthroline ligands as coordination bridges [97]. Sequential incorporation of NiCl_2 , phenanthroline, and LaCl_3 generated atomically dispersed La–Ni diatomic centers stabilized through La–N₃ and Ni–N₃ coordination environments. HAADF-STEM and XAFS analyses (Figs. 3e & 3f) confirmed the homogeneous distribution of neighboring bimetallic sites without detectable metallic aggregation. The close spatial arrangement of the two metal centers promoted synergistic electron redistribution,

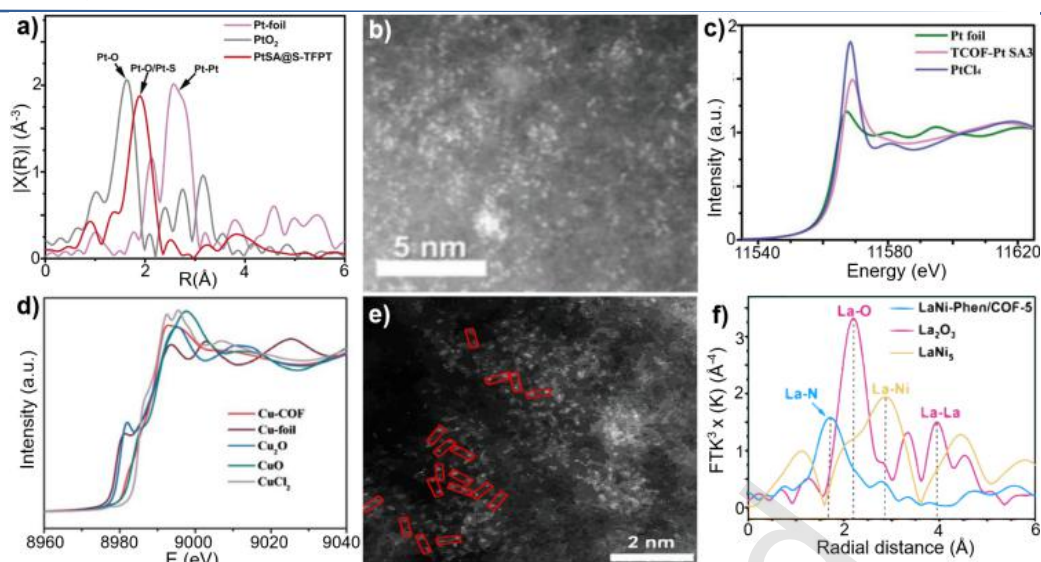


Figure 3 (a) EXAFS spectra of PtSA@S-TFPT [42] and (d) DHTA-TTA COF [95]. Reprinted with permission from Refs. [42] and [95]. Copyright 2025, Springer Nature and Copyright 2023, John Wiley & Sons. (b) STEM image and (c) XANES spectra of TCOF-Pt SA3 [93]. Reprinted with permission from Ref. [93]. Copyright 2023, John Wiley & Sons. (e) HAADF-STEM and (f) XAFS analyses of boronate-linked COF-5 [97]. Reprinted with permission from Ref. [97]. Copyright 2023, Springer Nature.

accelerated carrier migration across the conjugated framework, and strengthened electronic communication between adjacent catalytic sites under visible-light irradiation. Confinement within the highly ordered porous channels further preserved structural integrity and prevented catalyst deactivation during prolonged photocatalytic operation. These observations demonstrate that cooperative bimetallic coordination represents an attractive strategy for improving photocatalytic efficiency by integrating complementary electronic functions within a single crystalline framework. Such architectures are expected to provide additional opportunities for optimizing proton-reduction kinetics and long-term H_2 evolution stability through rational regulation of intermetallic electronic interactions.

To sum up, direct coordination of transition metals within covalent linkage domains represents an effective route for integrating catalytically active electronic centers into crystalline COF architectures without sacrificing structural periodicity. The sterically confined coordination environments intrinsically favor isolated atomic dispersion over large metallic aggregates, making metals with strong coordination affinity and moderate aggregation tendencies, including Fe, Co, Ni, Cu, and Pt, particularly suitable for linkage-functionalized systems. These atomically dispersed centers operate as localized charge-polarization nodes that regulate electron redistribution, promote substrate activation, accelerate exciton dissociation, and tune photocatalytic selectivity through local electronic-field effects. Simultaneously, linkage-confined metalation frequently modifies the electronic band structure of the host framework, narrows optical bandgaps, and enhances carrier mobility across conjugated channels. Nevertheless, intrinsic challenges remain. Coordination interactions between organic linkages and metal species may undergo reconstruction or gradual leaching under prolonged photocatalytic operation, especially in aqueous or oxidative environments. In addition, the limited steric space available within linkage domains restricts achievable metal loading and complicates precise control of coordination uniformity at elevated atomic densities. Consequently, future progress will depend on developing more robust coordination

motifs, dynamically adaptive linkage environments, and structurally resilient single-site architectures capable of sustaining long-term photocatalytic operation under demanding reaction conditions.

3.2. Metals on building blocks

The deliberate incorporation of catalytically active metal centers into COFs has become a central strategy for engineering integrated photocatalytic platforms with synchronized light harvesting, charge migration, and catalytic conversion. In contrast to conventional post-synthetic metalation, direct framework-level coordination design enables precise regulation of electronic coupling, local coordination geometry, and long-range carrier transport within the crystalline skeleton. Using this concept, Jiang et al. developed nickel-incorporated pyridyl-quinoline COFs in which the conjugated linkage simultaneously functioned as a structural connector, photosensitizer, and coordination domain for atomically dispersed Ni sites (Fig. 4a) [98]. The resulting Ni-PQCOFs combined extended visible-light absorption with highly ordered porosity and exceptional framework robustness arising from the chemically resilient pyridyl-quinoline backbone. Cooperative electronic communication between the photoactive linker and embedded Ni centers promoted efficient visible-light-driven $C(sp^2)$ -based C-C and C-heteroatom cross-coupling reactions while preserving catalytic stability, recyclability, and minimal metal leaching over repeated cycles. An alternative preorganization strategy was reported by Niu et al., who incorporated presynthesized Cu-containing single crystals into a bipyridine-functionalized COF through Schiff-base condensation to generate the heteroporous Bpy-COF-Cu architecture [99]. Unlike postmetalation methods that frequently compromise pore regularity and crystallinity, this route preserved ordered framework assembly and enabled uniform distribution of catalytically active Cu sites. The hierarchically porous AA-stacked structure integrated mesoporous diffusion channels with Cu-enriched microporous domains, thereby simultaneously accelerating substrate transport and concentrating uranium species near catalytic centers (Figs. 4b-e). Relative to the

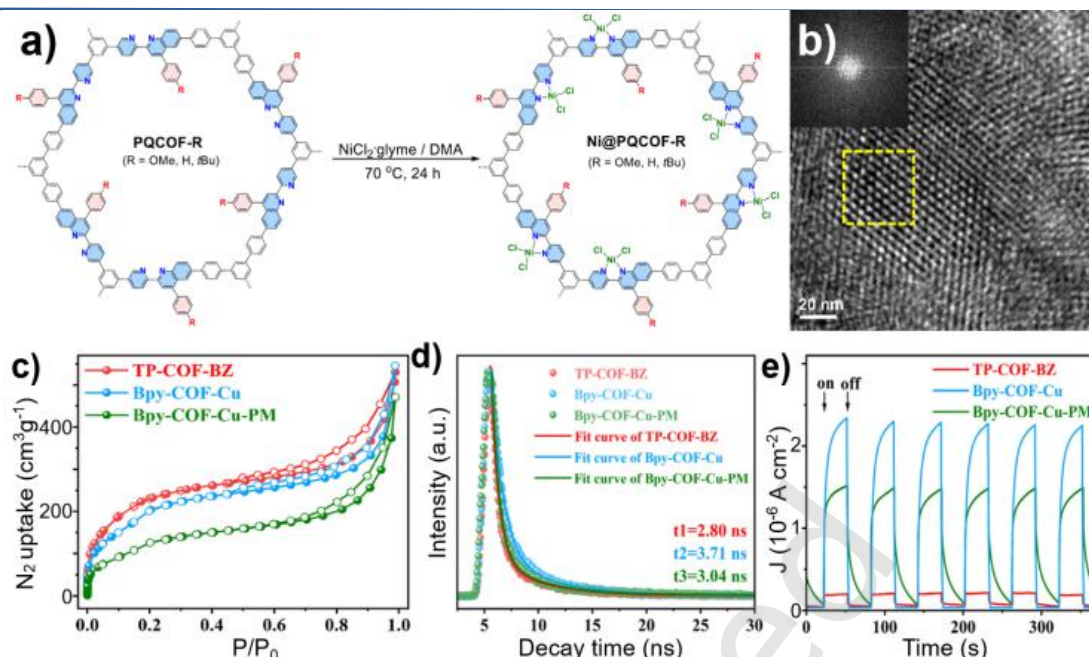


Figure 4 (a) Incorporation of nickel SA into PQCOF [98]. Reprinted with permission from Ref. [98]. Copyright 2025, Springer Nature. (b) HR-TEM image, (c) N₂ adsorption-desorption isotherms, (d) time resolved PL spectra, and (e) photocurrent response of Bpy-COF-Cu [99]. Reprinted with permission from Ref. [99]. Copyright 2025, Chinese Chemical Society.

postmodified analogue, the pre-engineered framework displayed higher surface area, lower charge-transfer resistance, broadened visible-light absorption, and prolonged carrier lifetimes, ultimately delivering superior photocatalytic uranium reduction efficiency together with remarkable cycling durability.

Beyond isolated SA sites, cyclic trinuclear coinage-metal units have emerged as highly effective intrinsic catalytic motifs for noble-metal-free photocatalysis. For instance, Luo et al. synthesized Cu-CTU-based covalent metal-organic frameworks through integrated polycondensation and polycoordination reactions, affording hydroxyl-regulated n-OH-JNM architectures with tunable electronic structures [100]. Modulation of hydroxyl substitution directly influenced the β -ketoenamine configuration, internal electric field distribution, and interfacial charge dynamics. Among the series, 2-OH-JNM exhibited the most favorable band structure, enhanced carrier-separation efficiency, reduced electron-transfer resistance, and broadened visible-light response. The Cu-CTU domains served as proton-reduction centers, whereas the hydroxyl-engineered framework environment facilitated directional electron redistribution and suppressed recombination losses. Consequently, 2-OH-JNM achieved highly efficient photocatalytic H₂ evolution in both pure water and seawater without Pt cocatalysts or sacrificial reagents while retaining long-term structural and catalytic stability. Spectroscopic characterization and DFT calculations further correlated its enhanced activity with optimized local charge-transfer pathways and reduced reaction free-energy barriers. Periodic organization of metalloporphyrin building blocks within conjugated COFs has also emerged as an effective strategy for regulating charge transport and catalytic activity at the molecular level. For instance, Lv et al. constructed metalloporphyrin-linked MP-TPE-COFs by integrating tetraphenylethene donor units with porphyrinic acceptors containing H₂, Co, or Ni centers [101]. The periodically arranged metalloporphyrin domains significantly broadened visible-light absorption, promoted efficient charge migration through the extended π -conjugated

framework, and established highly accessible metal coordination environments throughout the porous architecture. Compared with the metal-free analogue, incorporation of Co and Ni substantially modified the electronic structure, strengthened donor-acceptor interactions, and facilitated more effective separation of photoinduced electron-hole pairs. Although the original investigation emphasized photocatalytic CO₂ conversion, the enhanced electronic communication observed within CoP-TPE-COF and NiP-TPE-COF is equally advantageous for photocatalytic H₂ evolution because efficient migration of excited electrons toward catalytically active metal centers represents the key requirement for sustained proton reduction. Time-resolved spectroscopic measurements confirmed rapid transfer of photoexcited carriers toward the metalloporphyrin domains, while density functional theory calculations demonstrated that the coordinated transition metals effectively regulated local electronic structures and reduced the energetic barriers associated with interfacial charge transport. These findings emphasize that metalloporphyrin-based building blocks provide an attractive molecular platform for designing highly efficient metal-integrated COFs dedicated to solar H₂ evolution.

The periodic arrangement of porphyrinic active sites has likewise proven highly beneficial for improving framework conductivity and long-range carrier transport. Hou et al. fabricated vertically aligned CuDAPP-TP-COF through layer-by-layer assembly of Cu-porphyrin monomers with triformylphloroglucinol, generating a crystalline β -ketoenamine-linked architecture containing uniformly distributed Cu catalytic centers [102]. The extended π -conjugated framework established continuous pathways for directional electron migration while maintaining highly ordered porosity and excellent structural stability. Compared with the corresponding monomeric compounds and physically mixed systems, CuDAPP-TP-COF exhibited markedly improved visible-light absorption, accelerated carrier transport, efficient electron-hole separation, and prolonged charge-carrier lifetimes. The

uniformly dispersed Cu porphyrin domains acted as electronically coupled catalytic centers that efficiently accepted photogenerated electrons from the conjugated backbone while suppressing charge recombination throughout the framework. These characteristics are highly desirable for photocatalytic H_2 evolution because rapid electron delivery toward proton-reduction sites directly governs hydrogen-production efficiency. Furthermore, the ordered crystalline architecture maintained excellent catalytic durability during repeated photocatalytic cycles, illustrating the importance of integrating photoactive metal-containing building blocks directly into the COF skeleton rather than relying on external cocatalyst deposition. Integration of multiple metal complexes into a single crystalline framework provides an additional opportunity to regulate intraframework charge-transfer pathways through cooperative electronic interactions. Han et al. developed a three-dimensional Ru/Re metal COF by incorporating Ru(II) photosensitizing units together with Re(I) coordination sites into a conjugated lvt-topological framework [103]. The Ru-containing bipyrimidine precursor was first polymerized into crystalline MCOF-Ru, followed by post-coordination with $Re(CO)_3Cl$ to generate MCOF-Ru/Re. The close spatial proximity between Ru and Re centers established highly efficient intraframework electron-transfer channels and significantly prolonged the lifetime of photoexcited charge carriers. Relative to the parent MCOF-Ru, the heterometallic framework displayed narrower optical bandgaps, broader visible-light absorption, reduced radiative recombination, and substantially improved charge-separation efficiency. Femtosecond transient absorption spectroscopy further revealed ultrafast migration of excited electrons from Ru photosensitizing domains toward neighboring Re coordination centers, highlighting the effectiveness of molecularly integrated bimetallic architectures in promoting directional carrier transport. Although originally investigated for a different photocatalytic transformation, the fundamental electronic principles demonstrated in this work, including efficient light harvesting, rapid intermetallic charge transfer, and prolonged carrier lifetimes, are directly relevant to the rational design of advanced COFs for solar hydrogen evolution. More broadly, this study illustrates that cooperative interactions between complementary metal centers can provide a powerful strategy for maximizing photocatalytic efficiency while preserving excellent structural stability under prolonged illumination.

Cluster-engineered photocatalytic COFs have recently attracted increasing attention because atomically defined metal clusters can simultaneously function as structural nodes and electronically active centers [104]. An amino-functionalized Cu_4 cluster was epitaxially integrated into a 3D COF network through Schiff-base polymerization, producing the electronically coupled Cu_4 COF-2 architecture [61]. Strong orbital hybridization between Cu 3d states and the conjugated framework elevated the valence-band edge and narrowed the bandgap, thereby enhancing visible-light absorption and interfacial charge generation. The intimate electronic coupling between the cluster core and the extended π -system further promoted directional carrier transport and suppressed electron-hole recombination. Nevertheless, despite the substantial enhancement in optoelectronic responsiveness, the long-term photochemical stability of cluster-integrated frameworks under continuous catalytic operation remains insufficiently understood. Noble-metal cluster incorporation has similarly emerged as an

effective route for tailoring interfacial charge-transfer pathways. Ultrasmall Au NCs were immobilized within a thiol-functionalized imine-linked COF through in situ growth, affording the hybrid Au@COF photocatalyst [105]. Electronic communication between the confined Au domains and the semiconducting framework established a Z-scheme charge-transfer pathway that accelerated carrier separation while preserving strong redox potentials. As a result, Au@COF exhibited substantially enhanced photocatalytic RhB degradation compared with the parent framework. Although the precise mechanistic role of ultrasmall Au clusters remains under debate, their contribution as interfacial electron mediators and charge-separation centers appears central to the observed enhancement in photocatalytic performance.

Main-group metal clusters have also emerged as electronically programmable framework vertices for photocatalytic COF design. For instance, Lan et al. introduced an eight-connected amino-functionalized Al_8 cluster precursor as a multitopic node for constructing 3D AlCCOF materials [106]. The highly polarized Al-O and Al-N coordination environments induced significant electronic localization and stabilized the valence-band edge, enabling efficient photoinduced electron transfer from the Al-cluster domains toward the conjugated organic segments. This intercomponent charge migration promoted selective two-electron O_2 reduction to H_2O_2 . The study highlights the broader conceptual evolution of cluster-based COF photocatalysis, in which metal clusters operate not only as structural connectors but also as electronically active nodes that govern carrier distribution and reaction selectivity. However, the hydrolytic stability of highly polarized Al-based coordination environments under prolonged aqueous photocatalytic conditions remains to be systematically evaluated. Further functional complexity can be achieved through heterometallic cluster integration, where distinct redox processes are spatially compartmentalized within a single framework. This concept was demonstrated in the mixed-cluster MCOF- Ti_6Cu_3 system, assembled from Ti_6 oxo clusters and Cu_3 catalytic units through imine-linked condensation [107]. Within the hybrid architecture, Ti-O domains preferentially mediated oxidative half-reactions, whereas Cu-containing sites promoted reductive transformations. Such spatially differentiated catalytic functionality enabled simultaneous photocatalytic CO_2 reduction to formic acid and water oxidation for O_2 evolution while minimizing charge recombination losses. The biomimetic separation of oxidation and reduction centers substantially improved utilization of photoinduced carriers. Nonetheless, achieving balanced carrier-transfer kinetics between the two catalytic compartments remains a critical challenge, emphasizing the need for more precise regulation of intercluster electronic communication and exciton transport in future multicluster photocatalytic COFs.

To sum up, COFs assembled directly from metal-containing nodes are commonly categorized as metal-based COFs (MCOFs). Relative to SA incorporation strategies, MCOFs accommodate a higher density of metal sites and exhibit more diverse electronic characteristics and adsorption properties because multinuclear clusters contain chemically inequivalent surface environments. Such structural complexity is advantageous for cooperative and multifunctional catalysis. In most SA-modified COFs, isolated metal centers primarily function as charge-capture sites for photoinduced carriers and as

localized adsorption centers for substrate activation, thereby improving photocatalytic selectivity and reaction efficiency. Transition metals including Fe, Co, Ni, Cu, Zn, Au, and Ir have been extensively explored in this context. By contrast, metal clusters possess multiple adjacent active centers that can simultaneously mediate electron transfer and proton binding, enabling tandem catalytic pathways and multistep transformations. In addition, intracluster metal–metal interactions can influence d-orbital electronic states, thereby regulating the band structure of the framework and often reducing the bandgap to improve visible-light absorption. Nevertheless, although cluster-based MCOFs offer clear advantages in catalytic versatility, excessive metal incorporation may also generate charge-recombination sites or reduce framework stability, indicating that precise control over cluster geometry and electronic coupling remains essential for achieving optimal photocatalytic performance.

3.3. COF heterojunction with metals

Metal-integrated COF heterojunctions have emerged as versatile photocatalytic platforms for regulating interfacial charge transport and excited-state carrier dynamics. These hybrid architectures are commonly constructed either through post-synthetic assembly or concurrent solvothermal growth. Post-assembly approaches, typically based on stirring, impregnation, or ultrasonic treatment, offer compositional flexibility and synthetic simplicity but often suffer from weak interfacial coupling and metal aggregation [108]. In contrast, in situ self-assembly simultaneously drives framework crystallization and metal incorporation, generating intimate electronic communication across the heterointerface and facilitating directional migration of photoinduced carriers. Through integration of metallic NPs, SAs, alloy clusters, molecular catalysts, or semiconductor domains within crystalline COF matrices, these heterostructures establish internal electric fields and efficient electron-transport pathways that suppress electron–hole recombination, broaden visible-light utilization, and reduce interfacial resistance. Meanwhile, the ordered porosity and periodically conjugated skeletons of COFs stabilize catalytic species, prevent aggregation, and promote substrate diffusion during photocatalytic conversion [109].

Metal incorporation into COFs generally proceeds through three principal modes. The first involves direct coordination of metals at covalent linkages, generating atomically dispersed catalytic centers that act as electron-accepting and substrate-activation sites. The second strategy introduces metals into framework building units either before polymerization or via targeted post-synthetic modification, thereby enabling precise regulation of the coordination environment while preserving long-range crystallinity. The third approach constructs heterojunctions between COFs and external metallic or semiconducting components, where the interfacial electronic structure dictates carrier-transfer behavior and catalytic selectivity. Representative interfacial charge-regulated metal deposition was demonstrated by Li et al., who achieved visible-light-driven photodeposition of Pt clusters within hydroxyl- and imine-functionalized PY-DHBD-COFs (Fig. 5a) [110]. Under irradiation, PtCl_6^{2-} species were selectively reduced by CB electrons to form uniformly dispersed Pt NCs anchored within O/N-rich channels. Cooperative hydroxyl oxygen and imine nitrogen functionalities served simultaneously as electron-

enrichment and nucleation domains, promoting rapid charge extraction from the pyrene-conjugated framework toward Pt catalytic sites. Strong electronic coupling between Pt clusters and the COF backbone effectively suppressed recombination losses and enabled highly efficient photocatalytic H_2 evolution with excellent operational stability. Molecular catalyst/COF heterointerfaces provide an alternative strategy for ultrafast carrier separation. Pan et al. coordinated $\text{Re}(\text{CO})_3\text{Cl}$ units into bipyridine-containing TpBpy COFs to construct periodically ordered D–A architectures for photocatalytic CO_2 reduction [111]. In this system, the conjugated COF functioned as a light-harvesting electron donor, whereas $\text{Re}(\text{I})$ centers operated as catalytic electron-accepting domains. Ultrafast transient spectroscopy revealed sub-picosecond electron transfer from the excited framework to Re sites, producing long-lived charge-separated states favorable for multielectron CO_2 conversion. The spatially ordered D–A arrangement markedly suppressed exciton recombination and improved catalytic durability relative to homogeneous molecular analogues.

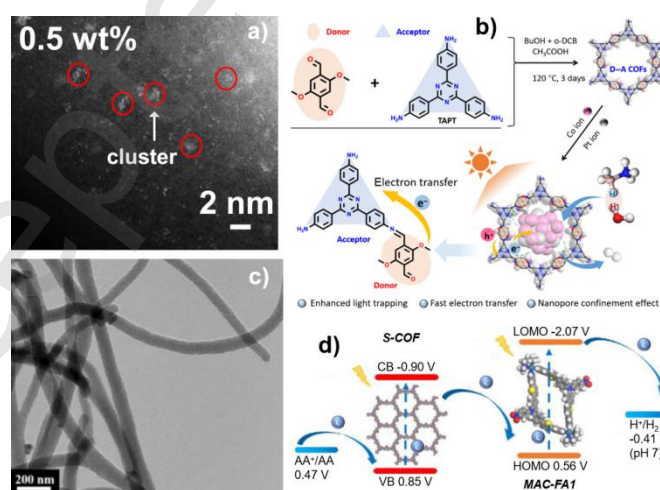


Figure 5 (a) HAADF-STEM image of PY-DHBD-COFs [110]. Reprinted with permission from Ref. [110]. Copyright 2022, Springer Nature. (b) Ultrafine PtCo_2 NCs into triazine-based D–A COFs through double-solvent infiltration followed by liquid-phase reduction [112]. Reprinted with permission from Ref. [112]. Copyright 2024, SciOpen. (c) HR-TEM image and (d) mechanism of Z-scheme MAC-FA1/S-COF [113]. Reprinted with permission from Ref. [113]. Copyright 2024, John Wiley & Sons.

Alloy nanocluster confinement within D–A COFs further strengthens framework–metal electronic communication. For instance, Liu et al. introduced ultrafine PtCo_2 NCs into triazine-based D–A COFs through double-solvent infiltration followed by liquid-phase reduction (Fig. 5b) [112]. The confined alloy clusters closely matched the intrinsic pore dimensions, producing intimate interfacial contact and rapid extraction of photoinduced electrons from the framework. Simultaneously, the D–A skeleton promoted intramolecular push–pull charge transfer and enhanced visible-light harvesting, while the porous confinement inhibited nanocluster aggregation during photocatalytic H_2 evolution. The resulting hybrid displayed accelerated carrier separation together with prolonged catalytic stability. Supramolecular heterointerface engineering has likewise proven effective for regulating charge-migration pathways. For instance, Li et al. assembled a direct Z-scheme MAC-FA1/S-COF heterostructure by integrating a sulfur-containing COF with a photoactive Pd_2L_2 metal–organic ring through solvothermal-assisted supramolecular assembly [113].

Cooperative π - π interactions and hydrogen bonding enabled homogeneous distribution of Pd SA domains across the porous framework while preserving crystallinity (Fig. 5c). The resulting Z-scheme heterojunction promoted efficient spatial separation of oxidative and reductive charge carriers (Fig. 5d), broadened visible-light absorption, and facilitated directional carrier transport. Within the architecture, the Pd-based ring acted as the reduction-active domain, whereas the conductive porous COF provided rapid carrier-transport pathways and proton-access channels during photocatalytic H₂ evolution. Compared with post-assembly methodologies, in situ growth generally yields stronger interfacial electronic coupling because metallic domains nucleate concurrently with framework formation. For instance, Deng et al. demonstrated this principle through construction of a Cu NP/TpPa-1 Schottky heterojunction via coordinated growth followed by photochemical reduction [114]. Uniformly distributed Cu NPs embedded within the β -ketoenamine-linked framework generated intimate metal-semiconductor interfaces capable of continuously extracting photoinduced electrons from the COF matrix toward Cu domains. Formation of the Schottky barrier effectively suppressed charge recombination, lowered interfacial resistance, and accelerated proton-reduction kinetics, thereby markedly enhancing photocatalytic H₂ evolution activity and long-term durability.

Semiconductor/COF integration has similarly emerged as an efficient strategy for tuning band alignment and interfacial carrier migration. For instance, Liu et al. fabricated a CdS/TTCOF heterostructure through solvothermal incorporation of CdS nanospheres into a triazine-rich TTCOF matrix [115]. Intimate semiconductor-framework contact enabled rapid electron transfer from the conjugated COF toward CdS reduction sites, significantly suppressing electron-hole recombination under visible-light irradiation. The COF component provided broad optical absorption and long-range charge-transport capability, whereas CdS acted as an energetically favorable proton-reduction domain. Reduced charge-transfer resistance and prolonged carrier lifetimes collectively resulted in substantially enhanced photocatalytic H₂ evolution and excellent operational stability. The electronic nature of the heterojunction critically governs photocatalytic performance. Type-II heterostructures spatially separate electrons and holes across different semiconducting domains, whereas S-scheme systems preserve strong redox capability while suppressing recombination. Interfacial functionalization further modulates carrier-transfer efficiency; for example, BPDA-COF forms stronger N-Ti-O interfacial bonding with TiO₂ than BD-COF, thereby facilitating more efficient energy transfer across the heterointerface [116, 117]. To overcome the limitations of isolated SA catalysts in complex multielectron CO₂ reduction, dual-atom catalytic motifs embedded within crystalline COFs have recently attracted substantial attention. For instance, Zhou et al. introduced paired La-Ni centers into COF-5 through ligand-mediated electrostatic assembly, initially anchoring Ni species followed by incorporation of La ions to generate confined LaNi catalytic motifs [97]. The ordered porous framework suppressed metal aggregation and ensured homogeneous distribution of the bimetallic active sites. Lanthanum enhanced visible-light absorption and electronic delocalization, whereas Ni served as the catalytic center for CO₂ activation. Electronic coupling between the two metals

promoted rapid charge separation and directional carrier migration, resulting in significantly improved photocatalytic CO formation efficiency and selectivity relative to pristine and monometallic analogues.

Single-site cyclometalated architectures have also demonstrated exceptional catalytic stability and charge-transport characteristics. For instance, Hu et al. incorporated isolated iridium centers into a pyrene-derived imine COF through direct cyclometalation of Schiff-base units, affording the Py-1P-Ir framework [118]. Metal incorporation preserved the crystallinity and permanent porosity of the parent COF while enabling homogeneous dispersion of iridacycle active sites throughout the conjugated network. The embedded Ir centers broadened visible-light absorption and promoted efficient charge transport between the photoactive pyrene scaffold and catalytic domains [119]. Consequently, the cyclometalated framework displayed markedly enhanced H₂ evolution from aqueous formate solutions under photothermal and photocatalytic conditions relative to molecular Ir complexes and physically mixed systems. Programmable coordination engineering provides another powerful route for tuning local catalytic environments within COFs. For instance, Zhang et al. designed cobalt-functionalized Schiff-base COFs containing distinct Co-O₄ and Co-O₃N coordination structures through hydroxyl-directed modular assembly [96]. Structural analyses confirmed atomically dispersed Co sites uniformly distributed within the porous framework without formation of metallic aggregates. Among the two coordination motifs, the symmetric oxygen-rich Co-O₄ environment established stronger electronic coupling with the π -conjugated skeleton, accelerated interfacial electron transport, and promoted more efficient charge separation under visible-light irradiation. In situ infrared spectroscopy identified *COOH and *CO intermediates during photocatalytic CO₂ reduction, whereas DFT calculations demonstrated that the oxygen-coordinated Co structure lowered the free-energy barrier associated with ligand exchange and CO₂ activation. As a result, the Co-O₄-functionalized framework exhibited highly selective and efficient CO generation. Tu et al. further demonstrated the effectiveness of isolated Cu centers through post-synthetic coordination engineering of a 2D COF nanobelt photocatalyst [95]. Atomically dispersed Cu sites coordinated through imine nitrogen and methoxy oxygen functionalities were uniformly distributed throughout the ultrathin framework without nanoparticle formation. The Cu-functionalized COF retained its crystallinity and porous morphology while exhibiting enlarged interlayer spacing and enhanced CO₂ adsorption capability. Under visible-light irradiation, the coordinated Cu sites promoted rapid electron migration and selective CO₂ activation, resulting in substantially enhanced CO evolution and suppressed competing H₂ evolution without requiring external photosensitizers.

Nitrogen-rich COF matrices have also proven highly effective for stabilizing isolated transition-metal sites and regulating reactive oxygen species generation. For instance, Wen et al. reported a bipyridine-linked COF containing atomically dispersed Ni centers stabilized within an N₂-Ni-Cl₂ coordination environment for photocatalytic degradation of pharmaceutical contaminants [121]. The isolated Ni atoms broadened visible-light absorption, enhanced photocurrent response, reduced charge-transfer resistance, and facilitated O₂ adsorption for efficient •O₂⁻ generation. Consequently, the Ni-

functionalized framework exhibited markedly improved degradation of acetaminophen relative to the pristine COF while maintaining excellent structural stability during repeated catalytic cycles. Similarly, Roudsari et al. developed a hollow bipyridine-based COF containing atomically dispersed Cu centers through template-assisted synthesis followed by Cu coordination [122]. The hollow architecture increased accessible surface area, enhanced light harvesting, and facilitated CO₂ diffusion, whereas the coordinated Cu sites accelerated charge migration and selective CO₂ activation. Spectroscopic and electrochemical analyses confirmed reduced bandgap energy, suppressed recombination, and enhanced interfacial electron-transfer kinetics after Cu incorporation. Benefiting from the synergistic interplay between the hollow porous framework and isolated Cu catalytic centers, the resulting Cu-HCOF exhibited substantially enhanced visible-light-driven CO₂-to-CO conversion and high product selectivity.

Interfacial electronic regulation extends beyond photocatalysis into electrochemical energy systems. For instance, Zhang et al. fabricated a lithiophilic Pt@NF heterostructure through ion-sputtering deposition of ultrathin Pt layers onto conductive nickel foam [123]. During electrochemical cycling, in situ Li/Pt alloy formation lowered nucleation barriers, promoted uniform Li deposition, and suppressed dendritic growth. Strong electronic coupling between Pt and the hierarchical conductive scaffold enhanced charge-transfer kinetics, minimized polarization, and improved long-term structural stability. Although distinct from COF photocatalysts, this study further emphasizes the broader importance of engineered interfacial electric fields and conductive architectures for controlling carrier migration and catalytic durability. Importantly, the synthetic methodology used for COF construction fundamentally determines subsequent metal integration and photocatalytic behavior. Solvothermal synthesis generally affords highly crystalline porous frameworks favorable for uniform metal dispersion and efficient electronic coupling, whereas microwave-assisted synthesis enables rapid crystallization and defect regulation that influence carrier transport. Ionothermal methods can improve thermal stability and fluorescence characteristics, while mechanochemical routes provide solvent-free fabrication with tunable morphologies. Consequently, synthesis-dependent structural parameters, including crystallinity, pore accessibility, dimensionality, and framework morphology, directly govern metal stabilization, interfacial charge-transfer efficiency, and catalytic-site accessibility, making precise synthetic control essential for the rational design of advanced metal-integrated COF photocatalysts for solar-driven CO₂ conversion.

To sum up, metal/COF heterojunctions constitute a versatile platform for manipulating photocatalytic charge dynamics, interfacial electronic structure, and reaction selectivity. Metallic NPs, alloy NCs, molecular catalytic complexes, and semiconducting domains integrated with conjugated COF matrices can simultaneously broaden light absorption, accelerate directional carrier transport, stabilize reactive intermediates, and improve substrate activation kinetics. Ordered porosity and crystalline periodicity further enable homogeneous dispersion of catalytic species while minimizing aggregation-induced deactivation. Nevertheless, maintaining durable interfacial coupling under prolonged irradiation remains challenging because lattice mismatch, nanoparticle coalescence, and

interface reconstruction can gradually deteriorate charge-transfer efficiency. Excessive metal loading may additionally obstruct pore accessibility and disrupt intrinsic framework conjugation. Future development of high-performance metal/COF heterostructures will therefore require precise regulation of nanoscale interface geometry, electronic band alignment, and dynamic structural stability under realistic photocatalytic operating conditions.

4. Mechanism of photocatalytic H₂ evolution

Photocatalytic H₂ evolution from water represents an attractive route for converting intermittent solar energy into sustainable chemical fuels. Despite the favorable thermodynamics of proton reduction, practical H₂ evolution systems are often restricted by insufficient visible-light utilization, rapid recombination of photoinduced carriers, sluggish surface redox kinetics, and limited accessibility of catalytically active sites. Consequently, the development of efficient photocatalysts requires simultaneous optimization of light harvesting, charge separation and migration, proton adsorption, interfacial electron transfer, and long-term structural stability [124]. Within this context, metal-integrated COFs have emerged as highly promising photocatalytic platforms because they combine the structural periodicity of crystalline porous materials with the electronic tunability of conjugated organic semiconductors. The modular and reticular nature of COFs enables precise incorporation of catalytically active metal species into periodically ordered frameworks, thereby generating well-defined coordination environments and controllable charge-transport pathways [125]. Furthermore, extended π -conjugated architectures promote broad visible-light absorption and facilitate electronic delocalization throughout the framework, while high surface areas and interconnected porous channels enhance mass diffusion and expose abundant accessible catalytic sites [126]. These collective features make metal-functionalized COFs particularly advantageous for photocatalytic H₂ evolution.

Photocatalytic H₂ evolution over metal-integrated COFs generally proceeds through a series of sequential elementary processes involving photon absorption, photoinduced electron-hole generation and separation, proton adsorption, interfacial electron transfer, and molecular H₂ evolution. Upon light irradiation, the conjugated framework absorbs photons and excites electrons from the VB-like highest occupied molecular orbital (HOMO) to the CB-like lowest unoccupied molecular orbital (LUMO), leaving corresponding holes within the VB region [11]. Efficient solar-energy conversion at this stage requires strong visible-light absorption and appropriate band-gap energies, both of which are closely associated with π -electron delocalization and D-A interactions within the COF skeleton. Following photoexcitation, the generated electrons and holes must undergo rapid spatial separation to suppress recombination losses [3,5]. Directional migration of photoinduced electrons from photoactive organic segments toward coordinated metal centers plays a decisive role in prolonging carrier lifetime and maintaining continuous proton-reduction processes. Therefore, strong interfacial electronic coupling between the organic backbone and catalytic metal sites is mechanistically essential for facilitating ultrafast electron extraction and minimizing energy dissipation. Simultaneously, the energetic alignment of the CB and VB must satisfy the thermodynamic requirements for proton reduction and hole

consumption [2, 13]. In particular, the CB minimum should remain sufficiently negative relative to the H^+/H_2 reduction potential to provide the driving force necessary for H_2 evolution (Fig. 6) [4, 14].

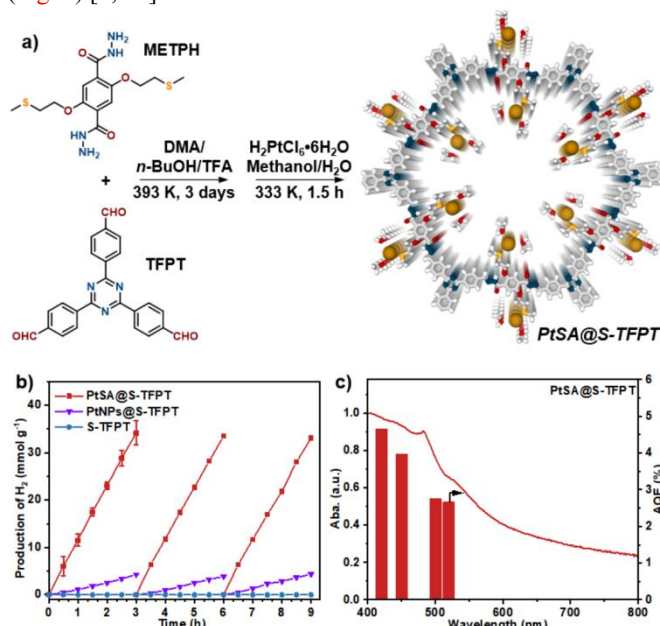


Fig. 6 (a) Synthesis of PtSA@S-TFPT. (b) Time course and cycling stability of photocatalytic H_2 productions. (c) Diffuse reflectance UV/Vis spectrum and wavelength-dependent AQE of photocatalytic H_2 production for PtSA@S-TFPT. [42] Reprinted with permission from Ref. [42]. Copyright 2024, Springer Nature.

After charge separation and migration, protons originating from water molecules or proton-containing electrolytes become adsorbed onto catalytically active metal centers embedded within the COF framework. The adsorption behavior and stabilization of hydrogen intermediates critically determine H_2 evolution kinetics because both excessively weak and excessively strong hydrogen binding are detrimental to catalytic turnover [21]. According to the Sabatier principle, optimal catalytic performance is achieved only when the interaction strength between hydrogen intermediates and active sites remains appropriately balanced [17]. Consequently, regulation of the electronic structure and coordination environment surrounding isolated or multinuclear metal centers has become a key strategy for improving H_2 evolution activity. Subsequently, adsorbed proton intermediates undergo sequential proton-coupled electron-transfer processes to generate molecular H_2 [23]. Efficient proton-coupled electron transfer is indispensable because synchronized proton and electron migration lowers activation barriers and stabilizes transient reaction intermediates during hydrogen formation. High crystallinity and ordered pore structures further facilitate directional charge transport and rapid proton diffusion toward catalytically active domains, thereby enhancing overall reduction efficiency. Once molecular H_2 is generated, it desorbs from the catalyst surface and diffuses into the surrounding reaction medium [19].

Throughout the entire photocatalytic process, suppression of charge recombination and enhancement of carrier utilization efficiency remain central mechanistic requirements. To improve photoresponse behavior, catalytically active transition metals such as Pt, Co, Ni, Mo, and Cu are frequently incorporated into the COF architecture to accelerate electron extraction and reduce the kinetic barrier for proton reduction. In some systems,

additional photosensitizers, including ruthenium- or iridium-based complexes, are introduced to enhance visible-light harvesting and generate strongly reducing excited-state electrons [12, 26]. Under such conditions, the photosensitizer absorbs incident photons and subsequently transfers excited electrons to the COF photocatalyst, while sacrificial reagents consume photoinduced holes to inhibit reverse recombination pathways. Effective energetic matching among the photosensitizer, metal centers, and COF framework is therefore indispensable for thermodynamically favorable and kinetically efficient electron-transfer processes. Mechanistic investigations have further demonstrated that the catalytic activity of metal-integrated COFs is strongly influenced by the local coordination environment and electronic density surrounding the metal centers [23, 35]. Isolated single-metal sites can provide highly uniform catalytic domains with tunable electronic structures, whereas multinuclear configurations may induce cooperative catalytic effects through synergistic electron redistribution and proton activation [41]. Therefore, precise molecular-level engineering of coordination structures is increasingly recognized as an effective strategy for regulating H_2 evolution kinetics and improving hydrogen-production efficiency.

Long-term structural and photochemical stability also constitutes a critical mechanistic requirement for practical H_2 evolution systems. Under prolonged irradiation conditions, photocatalysts may undergo framework degradation, photocorrosion, metal aggregation, or leaching of catalytically active species, resulting in gradual deterioration of catalytic performance [40]. Accordingly, robust covalent linkages, chemically stable coordination environments, and rigid framework architectures are essential for sustaining continuous H_2 evolution under operational conditions [33]. Despite substantial progress, efficient utilization of photoinduced carriers remains a major challenge limiting the overall solar-to-hydrogen conversion efficiency of metal-integrated COF photocatalysts. Reverse electron transfer, parasitic light absorption, and competing side reactions can significantly reduce catalytic selectivity and electron utilization efficiency [22]. Therefore, future advances in this field should focus on the integrated optimization of framework crystallinity, electronic delocalization, metal-site dispersion, interfacial charge-transfer kinetics, proton-transport pathways, and photochemical stability. Comprehensive mechanistic understanding combined with rational molecular engineering is expected to provide valuable guidance for constructing next-generation metal-integrated COF photocatalysts capable of highly efficient and durable solar H_2 evolution.

5. Metal integrated COFs for photocatalytic H_2 evolution

The continuously increasing global energy demand together with the environmental consequences associated with extensive fossil-fuel consumption has intensified the search for sustainable solar-to-fuel conversion technologies. In this context, photocatalytic H_2 evolution has attracted considerable attention because hydrogen possesses high gravimetric energy density, carbon-neutral combustion characteristics, and strong potential as a clean secondary energy carrier for future energy infrastructures [11, 23]. Among the diverse classes of photocatalytic materials explored for solar-driven H_2 evolution, COFs have emerged as particularly promising candidates owing

to their tailorable π -conjugated architectures, high surface areas, ordered porosity, tunable electronic structures, and excellent structural modularity. These characteristics collectively facilitate visible-light harvesting, exciton migration, charge separation, and mass transport during photocatalytic reactions [34]. More importantly, incorporation of metal species into COF frameworks provides additional opportunities to regulate photocatalytic H_2 evolution through modulation of electronic structures, interfacial charge-transfer pathways, proton-adsorption energetics, and catalytic-site accessibility. Depending on the coordination environment and spatial distribution of the incorporated metals, these hybrid systems can effectively accelerate carrier migration, suppress recombination losses, and promote proton-reduction kinetics. In the following sections, recent advances in metal-functionalized COFs for photocatalytic H_2 evolution are discussed with emphasis on the mechanistic roles of metal species in governing catalytic activity, charge-transfer behavior, and reaction selectivity within structurally engineered COF platforms.

5.1. Metal-COF heterostructures

Metal-COF heterostructures have emerged as an important strategy for enhancing photocatalytic H_2 evolution by integrating efficient light harvesting, charge separation, and catalytic functionality within a single architecture. Although COFs possess ordered π -conjugated frameworks and tunable electronic structures, their performance is often limited by strong exciton binding and rapid charge recombination. Interfacial coupling with metal-containing components overcomes these limitations by promoting directional carrier migration and accelerating proton-reduction kinetics [127]. Through optimized band alignment, internal electric fields, and strong interfacial electronic interactions, these hybrid systems facilitate efficient electron extraction and suppress recombination losses. Advanced architectures including MOF/COF hybrids, Schottky junctions, S-scheme systems, MXene-integrated composites, and MIS interfaces further regulate exciton dissociation and interfacial charge transfer at the molecular level. Consequently, interfacial junction engineering has become a central design principle for developing highly efficient COF-based photocatalysts for solar H_2 evolution [128]. Although metalated COFs synthesized through either pre-coordination or post-synthetic metalation exhibit considerable promise for photocatalytic H_2 evolution, strong excitonic interactions within these conjugated frameworks still restrict efficient utilization of photoinduced carriers. Consequently, suppressing exciton recombination while accelerating exciton dissociation remains a central challenge in the development of high-performance COF photocatalysts [129]. 2D MXenes, including transition-metal carbides, nitrides, and carbonitrides, possess outstanding electrical conductivity, broad solar-light absorption, rich surface chemistry, and ultrathin morphologies, rendering them highly attractive for interfacial charge-engineering applications. Constructing heterojunctions between metal-containing COFs and conductive MXenes therefore provides an effective strategy for generating energetically disordered interfacial domains capable of destabilizing tightly bound excitons and promoting free-carrier generation. Along this direction, Li et al. synthesized one-dimensional trinuclear Cu-based COFs nanorods through coordination assembly of Cu_3L_3 clusters with tris(4-aminophenyl)amine, followed by integration with ultrathin

Ti_3C_2 , Ti_3CN , and Nb_2C MXene nanosheets to afford 1D/2D TCOF-MXene heterostructures (Fig. 7a) [48]. The highly conductive MXene layers efficiently extracted photoinduced electrons and markedly accelerated interfacial charge-transfer kinetics, thereby suppressing electron-hole recombination.

Benefiting from synergistic coupling between photoactive Cu-cluster sites and conductive MXene interfaces, the optimized TCOF/ Ti_3C_2 , TCOF/ Ti_3CN , and TCOF/ Nb_2C composites achieved H_2 evolution rates of 190.3, 162.8, and 59.5 $\mu\text{mol h}^{-1}$, respectively, representing dramatic improvements over pristine TCOF. Comprehensive spectroscopic investigations further established the structure-function relationship, revealing that the preserved Cu coordination environment, together with photoinduced interfacial electron transfer from the TCOF framework to conductive MXene sheets, promoted efficient exciton dissociation, prolonged carrier lifetime, and accelerated long-range charge transport (Fig. 7b). This study demonstrates that integrating conductive 2D electron-accepting platforms with metal-coordinated COFs effectively overcomes excitonic limitations while enhancing long-range carrier transport and catalytic efficiency.

The integration of metallic NPs with conjugated COFs provides a highly effective route for constructing Schottky heterojunctions capable of accelerating charge separation and interfacial proton reduction. In such architectures, COFs function as visible-light-responsive n-type semiconductors with ordered porous channels that facilitate directional carrier transport as well as rapid diffusion of reactants and products. Simultaneously, uniformly distributed Cu NPs introduce electron-accepting interfaces, plasmon-enhanced light harvesting, and abundant catalytic sites. For instance, Deng et al. exploited these advantages by constructing Cu NP/TpPa-1 Schottky heterojunctions through photochemical decomposition and in situ reduction of Cu-cluster coordination precursors on β -ketoenamine-linked TpPa-1 COFs (Fig. 7c) [130]. The strong electronic coupling and intimate nanoscale contact between Cu NPs and the COF framework markedly improved visible-light absorption and promoted directional migration of photoinduced electrons toward proton-reduction sites. Although pristine TpPa-1 and isolated Cu NPs individually exhibited negligible photocatalytic activity, the optimized Cu NP/TpPa-1(40) heterojunction achieved a H_2 evolution rate of 16.89 $\text{mmol g}^{-1} \text{h}^{-1}$, significantly exceeding that of physically mixed Cu/COF systems owing to the absence of efficient interfacial contact in the latter. The shortened electron-migration distance within the Schottky interface reduced transfer resistance to increase the charge separation (Fig. 7d) and accelerated charge kinetics, while the uniformly dispersed Cu NPs increased both active-site density and light-utilization efficiency, resulting in increased H_2 evolution performance. Comprehensive photophysical and spectroscopic investigations further substantiated the interfacial charge-transfer mechanism, with PL and TRPL analyses demonstrating suppressed electron-hole recombination and prolonged carrier lifetime, photocurrent and impedance measurements confirming accelerated carrier transport with reduced interfacial resistance, and in situ XPS together with DFT calculations verifying directional electron migration from the TpPa-1 framework to Cu nanoparticles across the Schottky junction. This work demonstrates that rationally engineered

noble-metal-free Schottky junctions can substantially enhance photocatalytic H_2 evolution through synergistic interfacial

electronic interactions.

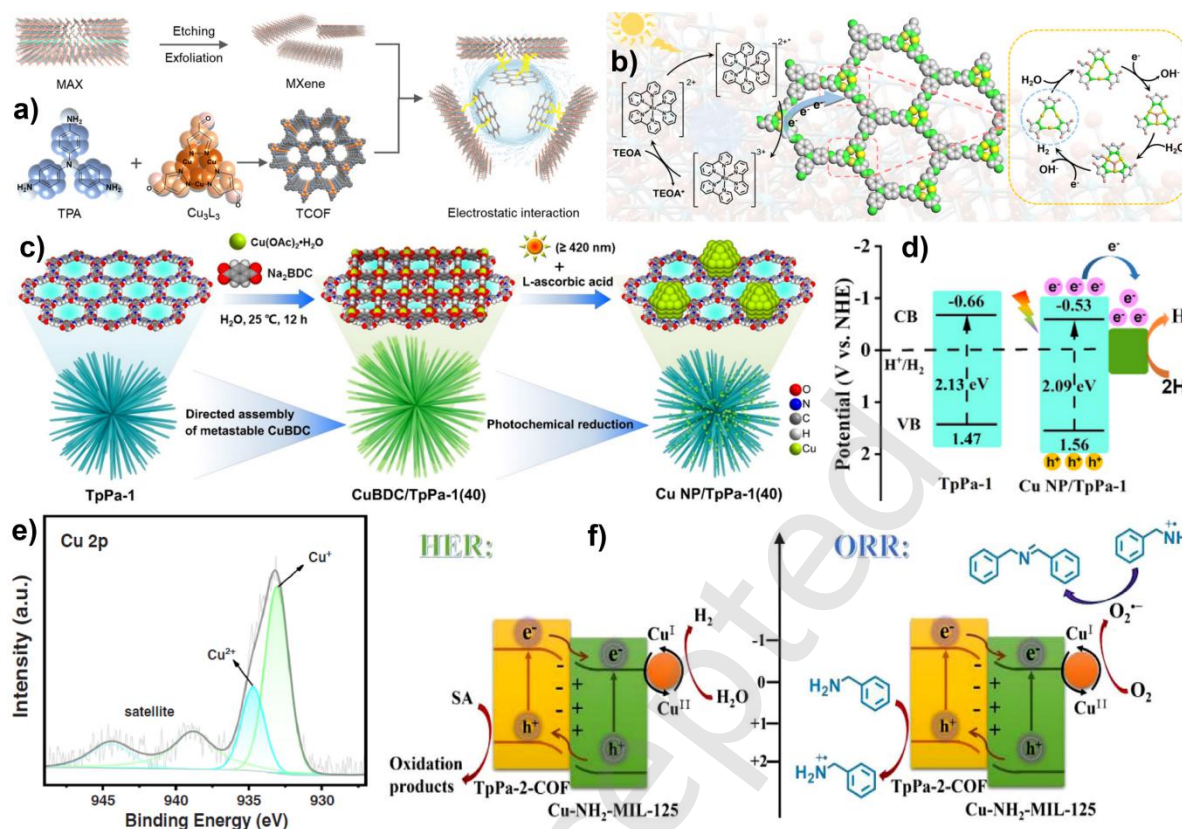


Fig. 7 Synthesis and mechanism of (a,b) TCOF–MXene [48] and (c,d) Cu NP/TpPa-1 [130] for H_2 production. Reprinted with permission from Refs. [48] and [130]. Copyright 2025, Elsevier B.V. (e) Cu XPS spectra and (f) mechanism of Cu-NH₂-MIL-125/TpPa-2-COF for H_2 evolution.

Despite significant progress in MOF/COF heterojunctions, many systems still rely heavily on noble-metal cocatalysts because sluggish surface proton-reduction kinetics at the MOF component limit overall catalytic efficiency. Constructing intrinsically active, noble-metal-free catalytic centers within MOF/COF heterostructures therefore represents a critical objective for sustainable photocatalysis. For instance, Han et al. addressed this issue by introducing monodisperse Cu active centers into NH₂-MIL-125 and subsequently integrating the modified MOF into TpPa-2-COF through in situ covalent assembly [131]. The amino-functionalized MOF provided well-defined coordination environments that stabilized isolated Cu species (Fig. 7e) with suitable spatial distribution. The resulting Cu-NH₂-MIL-125/TpPa-2-COF heterostructure exhibited highly efficient photocatalytic activity for both H_2 evolution and selective amine oxidation under visible-light irradiation. The optimized hybrid generated hydrogen at a rate of $9.21 \text{ mmol g}^{-1} \text{ h}^{-1}$, approximately 17.7 times higher than pristine TpPa-2-COF, together with an apparent quantum efficiency of 8.6% at 500 nm. Simultaneously, the photocatalyst achieved highly selective oxidation of amines to imines with conversion exceeding 91%. Mechanistic investigations revealed that the cooperative interaction between the covalent heterojunction and robust $\text{Cu}^+/\text{Cu}^{2+}$ redox centers accelerated carrier separation, prolonged excited-state lifetimes, and strengthened proton-reduction activity. Electrochemical impedance spectroscopy and transient photocurrent measurements demonstrated reduced interfacial charge-transfer resistance and more efficient charge migration, while PL quenching and time-resolved PL analyses

confirmed suppressed electron–hole recombination and extended carrier lifetimes. Furthermore, XPS binding-energy shifts and cyclic voltammetry verified directional electron transfer from TpPa-2-COF to Cu-NH₂-MIL-125 and established the $\text{Cu}^+/\text{Cu}^{2+}$ redox couple as the active proton-reduction center with reduced HER overpotential. ESR measurements further confirmed enhanced generation of reactive oxygen species during amine oxidation, highlighting the multifunctional role of the Cu centers in both reduction and oxidation half-reactions. The monodisperse Cu sites functioned as efficient noble-metal-free catalytic centers while the MOF/COF interface facilitated rapid interfacial charge migration (Fig. 7f). This work demonstrates that combining covalent heterojunction engineering with atomically dispersed transition-metal centers offers an effective strategy for developing multifunctional noble-metal-free photocatalysts with superior activity and stability.

Although MOF/COF heterostructures have demonstrated substantial potential in photocatalytic H_2 evolution, efficient utilization of interfacial catalytic sites remains challenging because the cooperative interaction between MOF metal nodes and conventional cocatalysts is often insufficiently optimized. In particular, metallic Ni and Pt possess complementary electronic functions, where Pt efficiently captures photoinduced electrons while Ni facilitates electron donation and interfacial transfer. Guided by this concept, Ren et al. constructed an S-scheme heterojunction integrating Ni-TBAPy-MOF with TpPa-COF to maximize interfacial charge separation and catalytic-site synergy [40]. The resulting crystalline porous hybrid exhibited

favorable band alignment, abundant accessible active centers, and enhanced internal electric fields across the heterointerface. The π -conjugated framework further functioned as an efficient carrier-transport network, promoting directional migration of photoinduced charges. Mott–Schottky and UPS analyses established the staggered band alignment and Fermi-level equilibration essential for S-scheme formation, while in situ XPS directly verified light-driven interfacial electron redistribution from Ni-TBAPy-MOF toward TpPa-COF, thereby confirming the proposed charge-transfer pathway. Benefiting from the synergistic cooperation between Ni nodes and Pt cocatalyst sites, the optimized MOF/COF heterostructure achieved a H_2 evolution rate of $276.01 \text{ mmol g}^{-1} \text{ h}^{-1}$ under visible-light irradiation, exceeding the activity of both pristine TpPa-COF and Ni-TBAPy-MOF while outperforming most previously reported COF-based photocatalysts. Complementary photophysical investigations further revealed that suppressed photoluminescence, enhanced transient photocurrent response, reduced charge-transfer resistance, lower exciton-binding energy, and femtosecond transient absorption spectroscopy collectively evidenced accelerated carrier migration, efficient exciton dissociation, and inhibited electron–hole recombination across the S-scheme interface. Electrostatic-potential and frontier-orbital calculations further demonstrated that coupling with Ni-TBAPy-MOF strengthened the built-in electric field and promoted directional charge migration, thereby maximizing the utilization of catalytically active Ni nodes and Pt cocatalyst sites. This work demonstrates that rationally engineered S-scheme heterojunctions provide an effective platform for simultaneously optimizing charge dynamics and catalytic-site utilization in solar-driven H_2 evolution.

The deliberate integration of metalloporphyrinic motifs into Ti-based multivariate metal–organic frameworks has emerged as an effective route for regulating photoredox dynamics within porous photocatalysts. Concurrently, imine-linked COFs have attracted substantial interest because their crystalline π -conjugated skeletons, permanent porosity, and chemically tailorable backbones collectively favor solar-energy conversion [132]. The ordered π -stacking channels in these frameworks promote long-range carrier migration and interfacial electronic communication, whereas uniformly distributed nitrogen sites provide robust coordination environments for catalytic species [133]. Combining metalloporphyrin-functionalized MTV-Ti-MOFs with imine-bridged COFs therefore enables the construction of integrated heterostructures that simultaneously optimize light harvesting, exciton dissociation, and charge transport. On this basis, Chen et al. established a covalently integrated MTV-Ti-MOF/COF platform for visible-light-driven H_2 evolution [5]. A Pd-porphyrinic linker was incorporated into PCN-415(NH_2) through a coordination-assisted one-pot assembly to yield PdTCPP%PCN-415(NH_2), followed by covalent coupling with the TpPa COF through interfacial condensation between amino and aldehyde functionalities. The resulting hybrid architectures exhibited broadened visible-light absorption, favorable band alignment, enlarged accessible surface area, and accelerated electron–hole separation. Among the prepared composites, the optimized material delivered an H_2 evolution rate of $13.98 \text{ mmol g}^{-1} \text{ h}^{-1}$ with a TOF of 227 h^{-1} , substantially surpassing those of the parent PdTCPP%PCN-415(NH_2) and TpPa frameworks. Extended irradiation further afforded a TON of

24,508 over 120 h, highlighting the remarkable structural durability and catalytic persistence of the covalently fused system. Steady-state PL measurements revealed markedly suppressed radiative recombination after covalent integration, while Mott–Schottky analysis verified favorable type-II band alignment with increased electron density, enabling efficient interfacial charge separation. Complementary DFT calculations further demonstrated a ligand-to-metal charge-transfer pathway in which photoexcited electrons migrated from the Pd-porphyrinic linker to Ti–oxo clusters before being transferred across the covalent junction to the TpPa framework and ultimately to Pt cocatalyst sites for proton reduction, thereby accounting for the enhanced photocatalytic performance. This study provides a viable molecular-level strategy for engineering cooperative MOF/COF heterostructures with highly efficient solar-to-fuel conversion characteristics.

To sum up, the construction of metal–COF heterostructures has emerged as an effective strategy for overcoming the intrinsic excitonic limitations and sluggish interfacial reaction kinetics that commonly restrict the photocatalytic efficiency of pristine COFs. Through rational integration of conductive MXenes, metal NPs, MOFs, and multicomponent catalytic interfaces, these hybrid systems establish favorable interfacial electric fields, optimized band alignment, and accelerated charge-transfer pathways that collectively promote exciton dissociation and suppress carrier recombination. In particular, conductive 2D platforms and covalently integrated heterointerfaces significantly enhance long-range electron migration and interfacial catalytic accessibility, while Schottky and S-scheme junctions further improve directional charge separation and proton-reduction dynamics. Simultaneously, incorporation of atomically dispersed or coordinatively confined transition-metal centers provides efficient electron-capture sites and robust catalytic redox centers without excessive dependence on noble metals. Despite these advances, precise regulation of interfacial electronic coupling, stabilization of isolated metal sites, and prevention of metal aggregation or leaching remain critical challenges for sustaining long-term photocatalytic activity. Therefore, future development of metal–COF heterostructures will require deeper mechanistic understanding of interfacial carrier dynamics together with molecular-level control over coordination environments, heterojunction architecture, and catalytic-site distribution to fully exploit their potential for efficient solar-to- H_2 conversion.

5.2. Single-/dual-atom metal catalysts in COFs

SA and dual-atom catalysts have become an important strategy for improving photocatalytic H_2 evolution in COFs because they maximize atomic utilization and provide precisely defined catalytic environments. Compared with metal NPs, atomically dispersed sites offer more accessible active centers, regulated electronic structures, and optimized hydrogen-adsorption energetics, leading to enhanced catalytic efficiency [134]. The heteroatom-rich and porous frameworks of COFs enable strong stabilization of isolated metal atoms and dual-metal sites while suppressing aggregation during catalysis. Simultaneously, strong metal–framework interactions promote charge separation, accelerate carrier migration, and improve interfacial electron transfer. In dual-atom systems, cooperative coupling between adjacent metal centers further enhances catalytic kinetics and charge-transport behavior [135]. As a result, atomic-scale metal engineering has emerged as a central approach for developing

highly efficient and durable COF-based photocatalysts for solar H_2 evolution. Despite the attractive optoelectronic characteristics of COFs, their composition from lightweight elements often restricts intrinsic catalytic activity. Metal incorporation has therefore become an effective strategy for increasing active-site density and improving charge-transfer efficiency. While isolated SAs can enhance catalytic performance, post-synthetic incorporation frequently involves complicated procedures and may induce aggregation or structural deterioration. In contrast, metal-COFs (MCOFs) constructed from atomically defined metal clusters offer predictable coordination environments, high atomic utilization, and improved structural robustness. Nevertheless, sluggish interlayer electron migration remains a major limitation. To overcome this challenge, the concept of a SA electron bridge (SAEB) has been introduced to transform charge transport from conventional π -stacking conduction into ligand-mediated interlayer transfer. For instance, Li et al. reported the first in situ generation of an SAEB-containing MCOF for photocatalytic H_2 evolution [9]. A Cu^I cluster and a nitrogen-rich guanidine ligand were rationally assembled to produce COF- Cu_3TG , followed by the formation of N_2 -Ru- N_2 interlayer electron bridges through controlled anchoring of Ru atoms at predefined nitrogen sites. The Cu_3 clusters served as catalytically active centers for proton reduction (Fig. 8a), whereas the Ru-SAEB units operated as rapid electron-transport channels between adjacent layers. In the presence of $[Ru(bpy)_3]Cl_2$ and triethylamine, the material exhibited progressively enhanced visible-light-driven H_2 evolution, reaching hourly production rates of approximately $11.88 \text{ mmol g}^{-1}$ during prolonged irradiation. Comprehensive spectroscopic investigations, including XANES/EXAFS analyses, verified the atomically dispersed N_2 -Ru- N_2 bridge configuration, while photoelectrochemical measurements demonstrated that SAEB formation strengthened photocurrent responses, lowered charge-transfer resistance, and prolonged carrier lifetimes. DFT calculations further revealed that the Ru-mediated electron bridge established a built-in electric field that promoted directional interlayer electron migration toward the Cu_3 catalytic nodes, where proton reduction preferentially occurred with a substantially reduced hydrogen adsorption energy barrier. Spectroscopic characterization together with density functional theory calculations confirmed the spatial distribution of Ru SAs and clarified their decisive role in accelerating directional electron migration. The cooperative interaction between Cu-cluster catalytic nodes and Ru-mediated electron bridges substantially reduced charge-transfer resistance and improved carrier utilization, thereby enabling efficient photocatalytic H_2 evolution.

The extensive reliance on Pt NPs in photocatalytic H_2 evolution inevitably increases noble-metal consumption because only a fraction of surface atoms participate catalytically. COFs provide an attractive solution to this limitation owing to their structural programmability and capacity to immobilize isolated catalytic centers within photoactive backbones. Incorporating accessible coordination sites into conjugated COFs enables subsequent anchoring of atomically dispersed metal species, thereby maximizing metal utilization while strengthening electronic communication between photosensitizing and catalytic domains. Along this direction, Zhang et al. constructed a porphyrin-bipyridine-based COF (PB-COF) integrating visible-light-harvesting chromophores with open coordination

sites for SA Pt immobilization [18]. The porphyrinic units acted as efficient photosensitizers, whereas bipyridine moieties remained coordinatively unsaturated during framework formation and subsequently served as anchoring centers for isolated Pt atoms. XPS and Pt LIII-edge EXAFS analyses verified that Pt was stabilized as Pt(II) in a PtN_2Cl_2 coordination environment, while AC-HAADF-STEM directly confirmed the atomic dispersion of Pt species throughout the crystalline framework. The resulting PB-COF-Pt photocatalyst exhibited excellent stability, recyclability, and highly efficient H_2 evolution, achieving a production rate of $80.4 \text{ mmol h}^{-1} \text{ g}_{Pt}^{-1}$ together with a turnover frequency of 15.7 h^{-1} , markedly exceeding those of Pt-free analogues and physically mixed Pt systems. Post-catalytic PXRD, TEM, and AC-HAADF-STEM further confirmed that PB-COF-Pt-1% retained its crystalline framework and isolated Pt sites after repeated irradiation, distinguishing the active SA configuration from nanoparticle-derived Pt species observed at higher metal loadings. The enhanced activity originated from efficient interfacial charge transfer between the conjugated framework and atomically dispersed Pt centers, as supported by PL quenching, stronger photocurrent response, reduced electrochemical impedance, and more negative flat-band potential after Pt anchoring, which collectively indicate faster electron migration from Zn-porphyrin photosensitizers to Pt(bpy) catalytic sites for proton reduction.

The atomically precise coordination environment accessible within COFs has also positioned these frameworks as ideal hosts for SA photocatalysts. Their high surface area, ordered channels, and abundant heteroatom coordination sites enable stabilization of isolated metal centers while preserving rapid charge transport within the conjugated network. For instance, Chen et al. exploited this concept by constructing a D-A type 2D COF (COF-BP) from benzothiadiazole and dihydroxybiphenyl building units [24]. The resulting framework combined electron-rich and electron-deficient components to generate a narrow-band-gap conjugated architecture containing N,O-chelating sites suitable for metal coordination. Subsequent immobilization of isolated Ni atoms produced COF-BP-Ni1, whereas additional coordination with salicylideneaniline ligands generated a Schiff-base-type SA system denoted COF-BP-Ni2. The modified coordination environment lowered the oxidation state of Ni and substantially improved charge separation and interfacial electron transfer. XPS and Ni K-edge XANES analyses confirmed the altered Ni electronic state after ligand modulation, while EXAFS fitting verified atomically dispersed Ni-N/O coordination without detectable Ni-Ni contributions, demonstrating that the catalytic improvement originated from isolated Ni sites rather than aggregated nickel species. Consequently, COF-BP-Ni2 exhibited a H_2 evolution rate of $12.21 \text{ mmol g}^{-1} \text{ h}^{-1}$, corresponding to 4.6- and 2.2-fold enhancements relative to the parent COF and COF-BP-Ni1, respectively. Remarkably, even in the absence of Pt cocatalysts, COF-BP-Ni2 maintained efficient photocatalytic activity with an H_2 evolution rate of $1.27 \text{ mmol g}^{-1} \text{ h}^{-1}$, demonstrating the effectiveness of coordination-environment engineering for noble-metal-free H_2 evolution. Photocurrent, EIS, steady-state PL, time-resolved fluorescence, and EPR analyses further showed that the salicylideneaniline-regulated Ni coordination environment enhanced carrier density, suppressed electron-hole recombination, prolonged excited-state lifetime, and accelerated

interfacial charge migration toward catalytic sites. This strategy establishes ligand-regulated SA modulation as a versatile route for tailoring photocatalytic activity in COF-based systems.

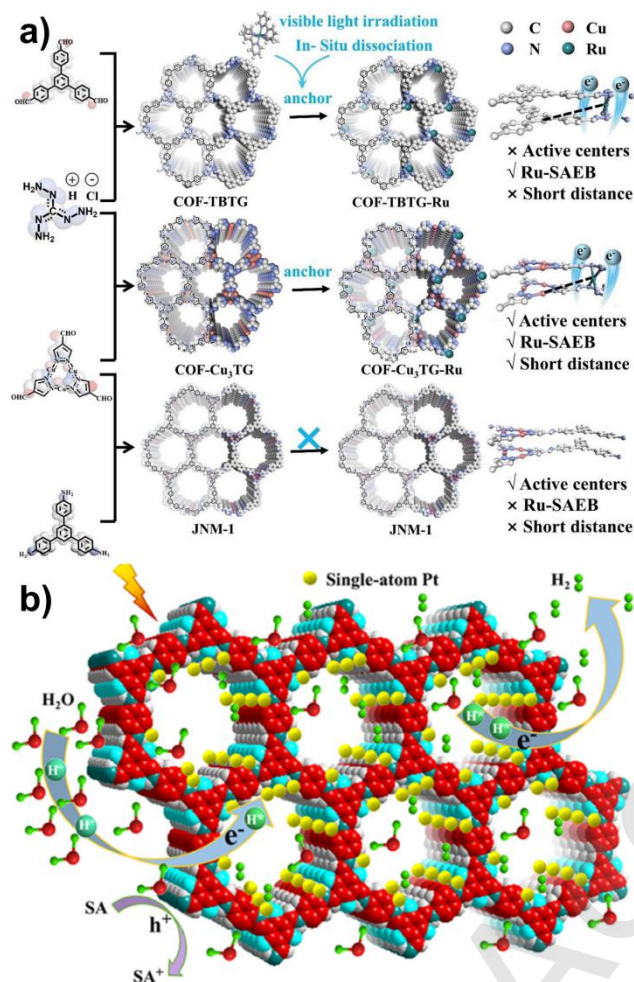


Figure 8 The mechanisms of (a) SAEB-containing MCOF [9] and (b) Pt₁@TpPa-1 [25] for photocatalytic H₂ evolution. Reprinted with permission from Refs. [9] and [25]. Copyright 2024, John Wiley & Sons and Copyright 2021, American Chemical Society.

Among structurally robust COFs, β -ketoenamine-linked TpPa-1 frameworks provide particularly advantageous platforms for stabilizing isolated noble-metal atoms because of their periodic coordination cavities, intrinsic porosity, and extended π -conjugated stacking channels. The ordered 2D architecture promotes both high metal dispersion and efficient charge migration toward catalytic sites. Building upon these features, Dong et al. anchored atomically dispersed Pt species onto TpPa-1-COF to construct a highly efficient SA photocatalyst for water splitting [25]. Aberration-corrected HAADF-STEM directly confirmed the isolated nature of Pt atoms, while X-ray absorption spectroscopy identified an unusual C₃N–Pt–Cl₂ coordination environment within the framework. Owing to the unsaturated nitrogen coordination sites and confined microporous structure, the Pt loading reached 0.72 wt%, exceeding that of many previously reported SA photocatalysts. The optimized Pt₁@TpPa-1 system achieved a H₂ evolution activity of 99.86 mmol g⁻¹ h⁻¹ with a turnover number of 304 after prolonged irradiation. PL quenching, shortened time-resolved PL lifetime, enhanced photocurrent response, and reduced electrochemical impedance collectively demonstrated

that isolated Pt sites served as efficient electron-accepting centers, accelerating photogenerated charge extraction from TpPa-1 while suppressing recombination losses. Advanced spectroscopic characterization together with density functional theory calculations revealed that the six-coordinated Pt centers possessed an optimal hydrogen adsorption free energy ($\Delta G_H^* = -0.092$ eV), thereby substantially reducing the kinetic barrier for H^{*} formation. The enhanced photocatalytic performance was therefore attributed to the synergistic combination of efficient carrier separation, rapid charge migration through π -stacked channels, and highly accessible SA catalytic sites (Fig. 8b). Post-reaction XRD, FTIR, and Pt 4f XPS analyses further confirmed the retention of the β -ketoenamine framework and Pt²⁺ single-atom state, highlighting the structural durability of the coordination-confined Pt₁@TpPa-1 photocatalyst. This work highlights the importance of coordination microenvironment engineering for developing stable and highly active COF-supported SA photocatalysts.

Beyond cocatalyst substitution, manipulation of excitonic behavior has emerged as a critical strategy for improving photocatalytic efficiency in metal-decorated COFs. In many conjugated frameworks, strong Coulombic attraction between photoinduced electrons and holes leads to tightly bound Frenkel excitons that hinder spontaneous carrier dissociation and suppress photocatalytic performance. Therefore, reducing exciton-binding energy is essential for promoting free-carrier generation and directional charge transport. Addressing this issue, Xia et al. developed a hydrazone-linked 2D COF containing atomically dispersed Pt centers to investigate the influence of metal-support interactions on exciton dynamics [33]. The framework, constructed from triazine aldehyde and terephthalohydrazide building blocks, provided abundant hydrazone coordination sites that stabilized isolated Pt atoms through unique N1–Pt–C2 environments. HAADF-STEM and EXAFS analyses verified the atomic dispersion and N₁–Pt–C₂ coordination of Pt, while XANES and XPS revealed partially oxidized Pt^{δ+} species and strong Pt–framework electronic interaction. Strong electronic coupling between Pt SAs and the conjugated framework induced local polarization and enhanced the dielectric constant, thereby significantly lowering exciton-binding energy. Temperature-dependent PL measurements showed that the exciton-binding energy decreased from 104 meV for pristine TCOF to 32 meV for TCOF-Pt SA3, confirming that isolated Pt sites facilitated exciton dissociation more effectively than Pt nanoparticles. As a consequence, spontaneous exciton dissociation and rapid bulk-to-surface carrier migration became energetically favorable. The optimized TCOF-Pt SA catalyst achieved H₂ and N-benzylidenebenzylamine production rates of 501.8 and 477.3 $\mu\text{mol g}^{-1} \text{h}^{-1}$, respectively, exceeding those of both pristine COF and Pt nanoparticle-loaded analogues by more than an order of magnitude. PL quenching, prolonged TRPL lifetime, enhanced photocurrent density, reduced EIS resistance, and KPFM-derived surface photovoltage collectively confirmed accelerated charge separation and surface accumulation of photogenerated carriers after Pt single-atom incorporation. DFT calculations further confirmed that isolated Pt sites effectively promoted carrier separation and transfer by weakening electron–hole interactions and lowering the H₂ evolution energy barrier, thereby coupling efficient proton reduction at Pt centers with benzylamine oxidation on the TCOF framework. This study

highlights excitonic regulation through SA metal-support coupling as an effective route toward highly efficient photocatalytic systems.

Precise cocatalyst anchoring within COFs has likewise proven crucial for maximizing proton-reduction activity while minimizing noble-metal consumption. Nitrogen-rich heteroaromatic motifs are particularly attractive because they can immobilize isolated metal species, inhibit nanoparticle aggregation, and strengthen interfacial electronic interactions. For instance, Tang et al. exploited this concept through heteroatomic structural engineering of COFs containing triazine units, β -ketoenamine linkages, and secondary amine groups strategically positioned within the framework [34]. Theoretical calculations predicted that incorporation of these heteroatomic functionalities would simultaneously narrow the band gap and increase the adsorption affinity for Pt species. Experimental analyses subsequently confirmed efficient dispersion of Pt SAs throughout the COF network together with enhanced visible-light absorption and improved charge separation. AC HAADF-STEM, Pt 4f XPS, and Pt L₃-edge XANES/EXAFS analyses further verified that Pt was stabilized as isolated atomic species rather than nanoparticles, with heteroatomic N/O sites providing strong anchoring interactions and preventing Pt aggregation under photocatalytic conditions. Importantly, Pt anchored as isolated atoms displayed substantially lower H₂ evolution barriers than Pt NPs or the pristine framework. Benefiting from the synergistic combination of optimized electronic structure and atomically dispersed catalytic centers, the resulting photocatalyst achieved a turnover frequency of 150.4 h⁻¹ with an ultralow Pt loading of only 0.31 wt%. Fluorescence quenching, shortened fluorescence lifetime, reduced EIS resistance, and enhanced transient photocurrent response demonstrated that heteroatomic engineering accelerated interfacial charge migration from the COF backbone to Pt single atoms, thereby correlating improved carrier separation with the enhanced H₂ evolution activity. The study demonstrates that heteroatomic framework engineering enables simultaneous regulation of photoelectronic properties and catalytic-site distribution, thereby providing an effective strategy for highly efficient SA photocatalysis.

Stabilizing isolated metal atoms or ultrasmall clusters within COFs remains intrinsically challenging because weak confinement forces often permit metal migration and aggregation during synthesis or catalysis. Although the angstrom-scale interlayer spacing of 2D COFs appears suitable for immobilizing atomically dispersed species, strong π - π stacking interactions generally hinder penetration of metal precursors into the interlamellar region. To overcome these limitations, Ren et al. engineered Pd SAs and clusters within TP-TTA COF nanosheets supported on fumed SiO₂ NPs [36]. Detailed mechanistic investigations revealed that the controlled deposition of Pd-containing TP-TTA colloids on SiO₂ rather than simple impregnation or excessive Pd precursor addition, was essential for generating Pd SAs/Cs and preventing their conversion into larger Pd nanoparticles. The resulting Pd SA/Cs-TP-TTA photocatalyst exhibited substantially enhanced charge separation relative to Pd nanoparticle analogues, leading to markedly improved photocatalytic H₂ evolution. AC-HAADF-STEM and CO-adsorbed FTIR analyses verified the coexistence of atomically dispersed Pd and ultrasmall Pd clusters without detectable Pd nanoparticle features, while PL

quenching, enhanced photocurrent response, and reduced EIS resistance confirmed that Pd SAs/Cs mainly promoted charge separation and migration rather than simply accelerating proton reduction. Specifically, the optimized system achieved a H₂ evolution rate of 156 mmol g_{COF}⁻¹ h⁻¹ with an apparent quantum efficiency of 7.3% despite an ultralow Pd loading of only 0.033 wt%. In addition, thin-film architectures fabricated from the photocatalyst enabled continuous H₂ evolution under static visible-light irradiation without mechanical stirring. The stable 20 h powder-photocatalysis test and linearly increasing H₂ evolution from the PAN-based photoactive film further highlighted the operational durability and device-relevant potential of this low-noble-metal COF system. These findings demonstrate that coupling atomically dispersed cocatalysts with ultrathin COF layers provides an effective strategy for minimizing noble-metal consumption while maximizing interfacial charge utilization in photocatalytic systems.

Precise regulation of active-site size and dispersion has likewise emerged as a decisive factor governing photocatalytic efficiency. Catalytic centers ranging from NPs to SAs exhibit profoundly different coordination environments, surface energies, and reaction kinetics, with atomically dispersed sites generally providing the highest catalytic utilization. For instance, Guan et al. addressed this challenge by synthesizing a porphyrin-linked COF, PCOF-18, through direct coupling of aryl bromide-functionalized porphyrin units [39]. The resulting framework exhibited exceptional chemical stability, large surface area, and highly accessible microporosity favorable for reactant diffusion and catalytic turnover. More importantly, PCOF-18 accommodated an ultrahigh density of isolated Pt atoms with an experimentally confirmed loading of 19.4 wt%, representing one of the highest SA contents reported for COF-based photocatalysts. Aberration-corrected HAADF-STEM, elemental mapping, Pt L₃-edge XANES/EXAFS, and WT-EXAFS analyses confirmed the atomically dispersed Pt-N₄ coordination environment without detectable Pt-Pt contributions, verifying that the high Pt content was retained as isolated porphyrinic Pt centers rather than aggregated nanoparticles. The high density of Pt SAs substantially improved interfacial charge transfer and lowered the energy barriers associated with proton reduction and H₂ evolution. When integrated with semiconductor photosensitizers such as CdS, TiO₂, ZnO, and ZnIn₂S₄, the resulting composites exhibited remarkable versatility and operational stability under diverse water conditions and natural sunlight. Among them, CdS@PCOF-18(Pt)-30 delivered H₂ evolution rates of 240.3 and 110 mmol g⁻¹ h⁻¹ under Xe-lamp and visible-light irradiation, respectively. The corresponding AQY values reached 62.17% at 420 nm and 64.84% at 450 nm, while cycling tests and post-reaction PXRD/XPS analyses confirmed sustained activity and structural stability after repeated photocatalysis. Mechanistic analyses supported by density functional theory demonstrated that CdS supplied photoinduced carriers, whereas the isolated Pt sites within PCOF-18 acted as highly efficient proton-reduction centers. XPS binding-energy shifts, charge-density-difference calculations, EIS, and photocurrent measurements further verified directional electron transfer from CdS to porphyrinic Pt sites, reduced interfacial resistance, and enhanced light-driven carrier utilization, thereby directly linking the dense SA architecture with accelerated proton coupling and H₂ release. This study illustrates the potential of densely populated SA COF

architectures for constructing next-generation photocatalysts with exceptional catalytic efficiency and long-term stability.

Precise regulation of the valence state and coordination environment of SA catalysts within COFs has likewise emerged as a key strategy for improving photocatalytic stability and efficiency. Most previously reported COF-supported SA catalysts contain highly oxidized metal centers strongly coordinated by electronegative heteroatoms, which often undergo reduction and aggregation during H_2 evolution. To address this instability, Chen et al. developed a sulfur-containing COF capable of stabilizing low-valence Pt SAs through asymmetric coordination interactions [42]. Using methanol as a mild reducing agent, isolated Pt atoms were incorporated into the sulfur-rich framework without nanoparticle formation, yielding a photocatalyst denoted PtSA@S-TFPT. AC-HAADF-STEM, CO-probe infrared spectroscopy, XPS, and Pt L-edge XANES/EXAFS analyses confirmed that Pt remained atomically dispersed in a partially positive low-valence state, with no Pt–Pt coordination and an asymmetric Pt–S/O four-coordination environment. Contrary to the conventional view that sulfur coordination weakens noble-metal catalytic activity, the low-valence Pt centers exhibited remarkable photocatalytic H_2 evolution with a rate of $11.4 \text{ mmol g}^{-1} \text{ h}^{-1}$ together with excellent operational stability over repeated irradiation cycles. The catalyst also delivered an AQE of 4.65% at 420 nm, while post-reaction PXRD, AC-HAADF-STEM, STEM, TGA, XPS, and FTIR analyses verified retention of the crystalline framework and isolated Pt state after photocatalysis. Dynamic carrier analysis, transient photocurrent measurements, impedance spectroscopy, and density functional theory calculations collectively revealed that the atomically dispersed Pt species reduced hydrogen-desorption barriers while simultaneously accelerating photoinduced charge separation. PL quenching, prolonged carrier lifetime, enhanced photocurrent response, reduced EIS resistance, and spatially separated HOMO/LUMO distributions further demonstrated that low-valence Pt SAs promoted charge extraction and suppressed recombination more effectively than Pt nanoparticle analogues. The unique asymmetric S/O coordination environment effectively stabilized the low-valence Pt state and suppressed particle aggregation throughout catalysis. This work introduces a new design principle for low-valence SA photocatalysts within conjugated COF matrices and challenges traditional assumptions regarding sulfur-coordinated noble-metal centers.

Dual-atom catalysts have recently emerged as an advanced extension of SA catalytic systems because adjacent bimetallic centers provide greater electronic tunability, cooperative adsorption behavior, and flexible coordination environments [136]. Nevertheless, the controlled stabilization of isolated diatomic sites remains intrinsically difficult, as effective synthesis requires simultaneous suppression of metal aggregation and prevention of atomically dispersed mononuclear species [137]. In photocatalytic systems, these challenges are further amplified by the requirement that the support must also sustain efficient photoinduced charge generation and transport. Addressing this issue, Niu et al. established a versatile strategy for constructing atomically dispersed Cu dual sites within a β -ketoenamine-linked COF for photocatalytic H_2 evolution [12]. Carboxylate ligands were employed as molecular bridges to spatially confine neighboring Cu atoms inside the O/N-coordinated framework, thereby

generating Cu-DAs@COF with highly stable dual-metal configurations. The β -ketoenamine backbone not only imparted excellent chemical robustness but also electronically regulated the Cu active centers through strong coordination interactions. Structural analyses confirmed the formation of uniformly distributed carboxylate-bridged Cu dimers embedded within the crystalline matrix. HAADF-STEM, Cu K-edge XANES/EXAFS, WT-EXAFS, and XPS analyses further distinguished paired Cu dual sites from isolated Cu single atoms and metallic Cu aggregates, confirming a Cu–N/O first-shell coordination environment together with a Cu–Cu interaction consistent with carboxylate-bridged dinuclear sites. Under visible-light irradiation, the catalyst achieved an H_2 evolution rate of $33.3 \text{ mmol g}^{-1} \text{ h}^{-1}$, approaching the activity of benchmark Pt-containing systems. The corresponding apparent quantum yield reached 7.19% at 420 nm, and five-cycle tests together with post-photocatalysis characterization verified retention of the framework structure and catalytic durability. In situ X-ray absorption spectroscopy together with theoretical calculations further revealed the generation of a photoinduced asymmetric mixed-valence state during catalysis, which accelerated intersite charge transfer and optimized hydrogen adsorption energetics. Transient photocurrent, EIS, steady-state PL quenching, time-resolved PL, and ultrafast TAS analyses demonstrated that the dual-Cu configuration promoted faster electron extraction from the TpBD-COF framework, stabilized the charge-transfer state, prolonged carrier lifetime, and suppressed recombination more effectively than Cu single-site analogues. In situ XAS, in situ XPS, and EPR further showed reversible Cu(II)/Cu(I) evolution under illumination without formation of metallic Cu clusters, while DFT calculations gave an optimized ΔG_H value of -0.078 eV and stronger charge redistribution at the binuclear Cu sites, directly correlating dynamic electronic asymmetry with improved proton-reduction kinetics. The study therefore highlights the critical role of dynamically reconstructed dual-atom electronic structures in promoting efficient proton-reduction kinetics.

To sum up, atomically dispersed metal centers and dual-atom catalytic configurations have emerged as highly effective approaches for regulating the photocatalytic behavior of COFs at the molecular scale. By exploiting the periodic porosity, heteroatom-rich coordination environments, and extended π -conjugated channels of COFs, isolated metal species can be stabilized with high atomic efficiency while simultaneously promoting directional charge migration and interfacial electron transfer. In particular, SA incorporation not only maximizes catalytic-site accessibility and optimizes hydrogen-adsorption energetics, but also enables precise modulation of local electronic structures, exciton dissociation behavior, and carrier-separation dynamics through strong metal–framework interactions. Furthermore, coordination-environment engineering involving N-, O-, and S-containing ligands provides effective control over the valence state, geometric configuration, and catalytic stability of atomically dispersed metals, thereby substantially improving proton-reduction kinetics while minimizing noble-metal consumption. Beyond mononuclear systems, dual-atom catalytic sites introduce cooperative electronic coupling and dynamically tunable adsorption characteristics that further accelerate interfacial charge redistribution and H_2 evolution pathways. Nevertheless, maintaining long-term structural stability of isolated atomic sites

remains a major challenge because insufficient confinement and weak coordination interactions can induce metal migration, reduction, or aggregation under photocatalytic conditions. Therefore, future progress in single-/dual-atom COF photocatalysts will depend on developing robust coordination architectures capable of simultaneously stabilizing atomically dispersed active centers, regulating excitonic processes, and optimizing multiscale charge-transfer pathways to achieve highly efficient and durable solar-driven H₂ evolution.

5.3. Metal cluster-integrated and multinuclear metal COFs

Metal cluster-integrated and multinuclear metal COFs have emerged as advanced photocatalytic platforms because cooperative interactions between multiple metal centers enable efficient charge transport, optimized adsorption energetics, and enhanced catalytic activity. Unlike isolated metal sites, multinuclear clusters provide electronically coupled active centers that facilitate directional electron migration and accelerate proton-reduction kinetics. In these systems, metal clusters are directly integrated into the crystalline COF backbone, generating strong electronic communication between catalytic nodes and conjugated frameworks. This integration improves visible-light absorption, promotes charge separation, and reduces exciton recombination [138]. Simultaneously, the ordered porous architecture of COFs ensures uniform distribution and accessibility of multinuclear active sites. As a result, cluster-integrated and multimetallic COFs have become an important strategy for constructing highly efficient and stable photocatalysts for solar-driven H₂ evolution. The structural precision and modularity of crystalline organic semiconductors also provide unique opportunities for integrating multiple photosensitizing motifs within a single photocatalytic architecture [139]. Owing to their atomically defined frameworks and programmable optoelectronic properties, COFs represent ideal platforms for investigating structure–activity relationships in solar-energy conversion. In this regard, Lu et al. developed a family of 3D metal-complex-based COFs incorporating two distinct photosensitizing units through covalent integration (Fig. 9a) [13]. Conventional bipyridine Ru/Fe complexes and porphyrinic chromophores were simultaneously embedded into imine-linked [6+4] 3D frameworks with soc topology, yielding dual-photosensitizer MCOFs including Rubpy-2HPor COF, Rubpy-ZnPor COF, Febpy-2HPor COF, and Febpy-ZnPor COF. The coexistence of complementary photoactive centers enabled cooperative light harvesting and dual photoexcitation processes, while the covalent linkage facilitated rapid electron migration throughout the crystalline network. Consequently, the resulting MCOFs exhibited broad visible-light absorption, efficient charge separation, and favorable band energetics for photocatalytic water reduction. PXRD refinement, FTIR, solid-state ¹³C NMR, N₂ sorption, TEM/HRTEM, XPS, ICP, and stability tests confirmed the formation of porous crystalline 3D MCOFs with preserved metal-complex units, imine linkages, permanent porosity, and solvent-resistant frameworks. Among the series, Rubpy-ZnPor COF displayed exceptional activity, affording an H₂ evolution rate of 30,338 μmol g⁻¹ h⁻¹ with an apparent quantum efficiency of 9.68% at 420 nm, positioning it among the highest-performing COF-based photocatalysts reported thus far. PL quenching, the longest fluorescence lifetime, enhanced transient photocurrent response, and Mott–Schottky-derived

band positions demonstrated that Rubpy-ZnPor COF possessed superior charge separation, more efficient carrier transport, and thermodynamically favorable redox energetics compared with the Fe- or free-base porphyrin analogues. Moreover, the in situ generated H₂ was directly utilized for tandem hydrogenation of alkynes with nearly quantitative conversion efficiency. The catalyst maintained activity over at least five cycles, and post-reaction PXRD, FTIR, and TEM analyses verified retention of the crystalline and chemical structure after photocatalysis, supporting its operational durability. Time-dependent density functional theory and spin-density analyses demonstrated that photoexcited electrons accumulated predominantly at the Rubpy moieties after cooperative excitation of both Rubpy and ZnPor units, thereby enabling highly efficient proton reduction (Fig. 9b). Mechanistically, visible-light excitation of either Rubpy or ZnPor generated convergent Rubpy-localized triplet states through direct excitation or triplet–triplet energy transfer, after which electron donation and transfer to Pt cocatalyst sites promoted H⁺ reduction to H₂. This work establishes a new paradigm for constructing multifunctional COF photocatalysts through molecular-level integration of synergistic photosensitizers.

Beyond active-site engineering, modulation of π -conjugation within MCOFs provides a powerful approach for regulating excitonic behavior and carrier dynamics. Extending conjugated pathways can profoundly influence charge separation, interfacial transfer, and electronic coupling between framework linkers and metal-cluster nodes. However, systematic evaluation of conjugation effects is often complicated by simultaneous variations in topology, stacking arrangement, and defect density. To isolate the intrinsic contribution of π -extension, Zhang et al. developed an isorecticular series of Cu₃-cluster-based MCOFs using aromatic diamine linkers with progressively elongated conjugation lengths [19]. Solvothermal imine condensation between preorganized Cu₃ aldehyde nodes and the corresponding diamines generated highly crystalline Cu₃-PDA, Cu₃-NDA, and Cu₃-ADA frameworks while preserving identical topology and interlayer organization. PXRD refinement, FTIR, solid-state ¹³C NMR, XPS, XAFS, and WT-EXAFS analyses confirmed the formation of structurally comparable imine-linked frameworks containing mixed-valence Cu(I)/Cu(II) trinuclear nodes with Cu–N coordination and without detectable metallic Cu aggregation. The resulting materials displayed tunable visible-light absorption and optimized band alignment without compromising structural stability. Among them, Cu₃-NDA achieved an exceptional noble-metal-free H₂ evolution rate of 31,328 μmol g⁻¹ h⁻¹ under visible-light irradiation, outperforming most previously reported crystalline photocatalysts. Control experiments verified the indispensable roles of light irradiation, fluorescein photosensitizer, triethylamine donor, and the Cu₃-NDA catalyst, while five-cycle testing and post-reaction PXRD, XPS, SEM, and TEM analyses confirmed sustained activity, framework retention, and absence of copper nanoparticle formation. Experimental observations combined with theoretical calculations revealed that moderate π -extension minimized exciton-binding energy while maintaining rapid intraframework carrier transport, thereby establishing an optimal balance between charge separation and interfacial electron utilization. Specifically, variable-temperature PL analysis showed that Cu₃-NDA

possessed the lowest exciton-binding energy of 8.2 meV compared with Cu₃-PDA and Cu₃-ADA, while transient photocurrent and EIS measurements demonstrated the highest photocurrent response and lowest charge-transfer resistance. Excited-state calculations further revealed long-range electron-hole separation and favorable electron delocalization in Cu₃-NDA, explaining why excessive conjugation in Cu₃-ADA induced charge localization and reduced catalytic efficiency. This work introduces a clear reticular design principle in which precise conjugation engineering governs node-framework electronic synergy and ultimately determines photocatalytic efficiency.

The incorporation of cooperative bimetallic sites has also emerged as an effective strategy for overcoming the intrinsic limitations of monometallic nonprecious-metal photocatalysts. Single-metal active centers often cannot simultaneously optimize intermediate adsorption, carrier migration, and product desorption during photocatalytic proton reduction. Bimetallic systems, in contrast, benefit from electronic coupling effects that regulate adsorption energetics and facilitate charge separation. In this context, Wang et al. synthesized a Cu₃-cluster-based 2D COF through Schiff-base condensation and subsequently introduced Zn²⁺ ions via post-synthetic coordination to generate a Pt-free bimetallic photocatalyst [20]. Structural characterization confirmed that Zn incorporation preserved the crystallinity and electronic state of the parent Cu₃-BPY-COF while modifying pore characteristics and electronic distribution around the bipyridine coordination sites. XPS deconvolution of N 1s and Zn 2p spectra further indicated that Zn²⁺ was mainly coordinated to bipyridine nitrogen sites, while SAXS, FTIR, solid-state ¹³C NMR, SEM/TEM, EDS mapping,

ICP-AES, and N₂ sorption analyses verified framework preservation, uniform Cu/Zn distribution, reduced pore dimensions, and stable Zn anchoring after post-synthetic metallization. Under visible-light irradiation ($\lambda > 420$ nm), the resulting Cu₃-BPY-COF(Zn) achieved an H₂ evolution rate of 23.04 mmol g⁻¹ h⁻¹ with an apparent quantum efficiency of 15.2%, significantly surpassing the pristine framework and ranking among the most efficient noble-metal-free COF photocatalysts reported to date. Eight consecutive cycling tests over 32 h, together with post-reaction SAXS, FTIR, SEM, and ICP-AES analyses, confirmed that the long-range ordered framework, imine linkage, morphology, and Cu/Zn composition were retained without obvious metal leaching or aggregation. Combined experimental and theoretical analyses demonstrated that Cu₃ clusters functioned as efficient electron-conduction channels, whereas coordinated Zn²⁺ species optimized the electronic structure of the bipyridine ligands and promoted charge separation. Transient photocurrent measurements showed a higher photocurrent density for Cu₃-BPY-COF(Zn), while UPS/UV-vis-derived band structures, EIS Nyquist plots, and LSV curves confirmed a more negative conduction band, lower charge-transfer resistance, and improved proton-reduction kinetics after Zn coordination. Simultaneously, the Cu₃-Zn cooperative interaction regulated hydrogen-intermediate adsorption energetics, thereby accelerating proton-reduction kinetics. DFT calculations further showed that Zn incorporation decreased the H-intermediate adsorption free energy from 0.56 to 0.37 eV, directly linking bimetallic electronic modulation with enhanced HER activity. This study broadens the structural scope of multinuclear-cluster COFs and highlights the potential of bimetallic synergy for constructing efficient Pt-free photocatalytic systems.

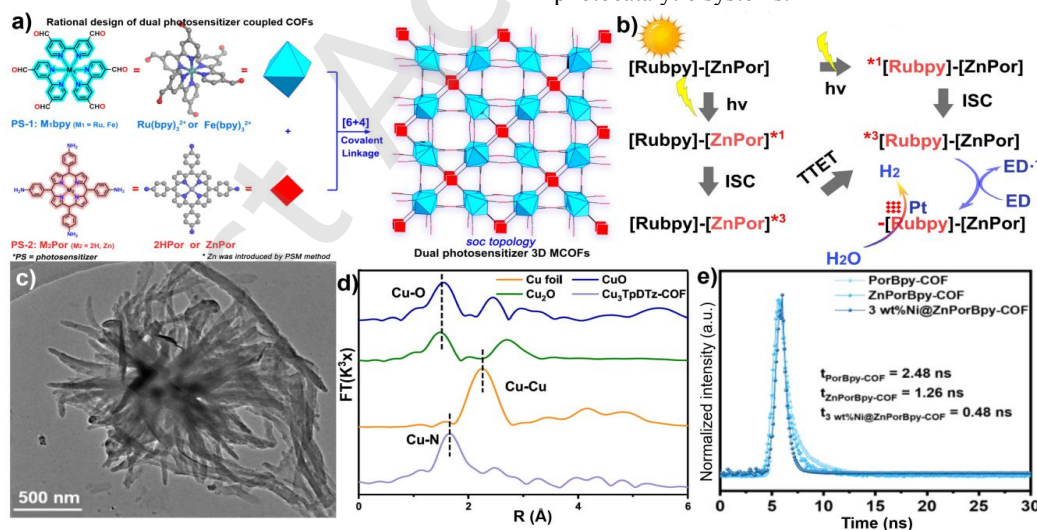


Figure 9 (a) Synthesis of various 3D COFs. (b) Charge transfer mechanism of Rubpy-ZnPor COF for H₂ evolution [13]. Reprinted with permission from Ref. [13]. Copyright 2023, John Wiley & Sons. (c) TEM image and (d) XFA spectra of Cu₃TpDTz-COF [38]. Reprinted with permission from Ref. [38]. Copyright 2026, Elsevier B.V. (e) Time resolved PL spectra of PorBpy-COF [88]. Reprinted with permission from Ref. [88]. Copyright 2025, American Chemical Society.

Despite extensive progress in cocatalyst engineering, many COF photocatalysts still suffer from strong excitonic effects and dependence on noble metals for efficient proton reduction. In conjugated polymeric systems, tightly bound Frenkel excitons often undergo rapid recombination before dissociation into free carriers, thereby limiting photocatalytic efficiency. Simultaneously, the absence of intrinsically active catalytic sites necessitates external cocatalysts. To address these issues

simultaneously, Qiu et al. developed a cluster-integrated COF through direct incorporation of trinuclear Cu clusters into a conjugated framework (Fig. 9c) [38]. A preassembled Cu₃(PyCA)₃ complex was introduced as a structural building block during one-pot Schiff-base polymerization to afford Cu₃TpDTz-COF with atomically integrated catalytic clusters uniformly distributed throughout the framework. PXRD refinement, FTIR, solid-state ¹³C NMR, Raman spectroscopy,

EDS mapping, HAADF-STEM, XAFS, WT-EXAFS, and XPS analyses confirmed that the Cu₃ clusters were covalently embedded as dispersed mixed-valence Cu⁺/Cu²⁺ units with N–Cu–N coordination, rather than being externally deposited or aggregated. The embedded Cu clusters reduced dielectric confinement and substantially lowered exciton-binding energy, thereby promoting spontaneous exciton dissociation and efficient free-carrier generation. Temperature-dependent PL analysis showed that the exciton-binding energy decreased from 64.6 meV for TpDTz-COF to 44.7 meV for Cu₃TpDTz-COF, while PL quenching, prolonged TRPL lifetime, stronger photocurrent response, and reduced EIS resistance verified suppressed recombination and accelerated charge migration. In parallel, strong electronic coupling between the Cu clusters and organic backbone established directional charge-transfer pathways that steered photoinduced electrons toward catalytically active Cu centers. Because the Cu clusters also possessed near-optimal hydrogen adsorption energetics, external cocatalysts became unnecessary. As a consequence, Cu₃TpDTz-COF achieved a remarkable cocatalyst-free H₂ evolution rate of 106.03 mmol g⁻¹ h⁻¹. The catalyst further delivered an AQY of 19.7% at 420 nm and retained stable H₂ evolution over five consecutive cycles, with post-reaction XRD, FTIR, TEM, and EDS mapping confirming preservation of the framework and Cu distribution. Ultrafast spectroscopy (Fig. 9d) together with theoretical calculations confirmed that atomically integrated Cu clusters simultaneously accelerated exciton dissociation, prolonged carrier lifetimes, and enhanced proton-reduction kinetics. Femtosecond TAS revealed an intense long-lived charge-separated state and substantially extended carrier-decay components after Cu₃ integration, while in situ EPR, XAFS, and XPS directly verified light-induced electron migration from the COF skeleton to Cu clusters. DFT calculations further showed spatially separated frontier orbitals, cluster-centered electron accumulation, and near-ideal ΔGH at Cu sites, directly linking cluster-mediated charge trapping with efficient proton reduction. This work establishes cluster-mediated exciton engineering as a powerful strategy for constructing all-in-one photocatalytic architectures without noble-metal assistance.

Combining D–A COFs with coordinated transition-metal centers also provides an effective pathway for simultaneously regulating light harvesting, charge transport, and catalytic-site distribution. Bipyridine units, owing to their electron-deficient nature and strong coordination ability, can suppress exciton recombination while serving as anchoring sites for catalytic metal species [140]. Porphyrin derivatives, by contrast, possess highly conjugated macrocyclic π-systems with excellent visible-light absorption and tunable redox properties [141]. Nevertheless, isolated porphyrin monomers often suffer from insufficient light-harvesting capability because of limited intermolecular electronic communication. For instance, Su et al. addressed these limitations through the construction of D–A porphyrin–bipyridine COFs, namely PorBpy-COF and ZnPorBpy-COF, in which Zn²⁺ ions were coordinated within porphyrin cores to rigidify the macrocycles and modulate electronic transitions [88]. Subsequent postsynthetic incorporation of Ni²⁺ ions at bipyridine sites enabled precise tuning of catalytic-site density and electronic-band structure. In the resulting dual-metallic framework, Zn–porphyrin units acted as visible-light absorbers and photoinduced-electron sources, whereas Ni–bipyridine centers functioned as proton-reduction

catalytic sites. The synergistic interaction between the two metal centers substantially accelerated charge separation and carrier migration (Fig. 9e), ultimately leading to an optimal H₂ evolution rate of 13.40 mmol g⁻¹ h⁻¹ for 3 wt% Ni@ZnPorBpy-COF, which markedly exceeded that of the metal-free analogue and most previously reported porphyrinic COFs. Theoretical analyses further revealed that photocatalytic efficiency was governed primarily by carrier-transport dynamics rather than solely by light-absorption capability. This work highlights the importance of molecular-level charge-transport engineering in determining the photocatalytic behavior of D–A COF architectures.

To sum up, integration of multinuclear metal centers and atomically defined metal clusters within COF backbones has emerged as a highly effective strategy for simultaneously regulating light harvesting, exciton dissociation, charge migration, and catalytic proton reduction. In contrast to isolated monometallic sites, electronically coupled multinuclear architectures provide cooperative catalytic environments that facilitate directional electron delocalization, optimize hydrogen-intermediate adsorption energetics, and accelerate interfacial redox kinetics. The crystalline and periodically ordered nature of COFs further enables homogeneous distribution of cluster-based active centers while maintaining intimate electronic communication between conjugated organic linkers and metal nodes. In particular, incorporation of multinuclear clusters directly into the framework skeleton effectively reduces excitonic confinement, promotes free-carrier generation, and establishes rapid intraframework charge-transport pathways, thereby substantially improving photocatalytic efficiency without excessive dependence on external cocatalysts. Moreover, synergistic interactions between different metal components within bimetallic or dual-photosensitizer systems provide additional opportunities for tuning band structures, extending visible-light absorption, and strengthening interfacial carrier-transfer dynamics. Nevertheless, precise control over cluster nuclearity, spatial distribution, and electronic coupling within highly crystalline frameworks remains a considerable synthetic challenge. In addition, maintaining long-term structural integrity and preventing electronic deactivation of multinuclear active centers under photocatalytic conditions are critical issues that continue to limit practical implementation. Therefore, future development of cluster-integrated and multinuclear metal COFs will require advanced molecular-level design strategies capable of synchronizing framework conjugation, multimetallic cooperation, and excitonic regulation to realize highly efficient, stable, and fully integrated photocatalytic systems for solar H₂ evolution.

5.4. Transition-metal coordination engineering in COFs

Transition-metal coordination engineering has emerged as an effective strategy for regulating the electronic structure and photocatalytic behavior of COFs. Coordination of metal ions within heteroatom-rich frameworks can tailor band alignment, enhance visible-light absorption, and promote charge separation, thereby improving photocatalytic H₂ evolution performance. The ordered and tunable coordination environments of COFs enable precise incorporation of transition metals while preserving framework crystallinity and structural stability. Strong metal–ligand interactions facilitate carrier migration, accelerate interfacial electron transfer, and optimize proton-reduction energetics [142]. Furthermore, modulation of

coordination geometry and metal valence states provides additional control over catalytic activity and excited-state dynamics. Consequently, transition-metal coordination engineering has become a key molecular-level approach for developing efficient and durable COF-based photocatalysts for solar H₂ evolution. Beyond framework engineering, modulation of metal-coordination geometry within 2D COFs has proven highly effective for extending spectral response and improving photocatalytic performance [143]. D–A conjugation and dye sensitization are widely employed to enhance visible-light utilization in 2D COFs, whereas transition-metal coordination can introduce energetically favorable metal-to-ligand charge-transfer pathways. However, conventional post-metalation strategies often suffer from weak visible-light enhancement and instability caused by metal leaching. To overcome these limitations, Zhang et al. investigated the coordination-state evolution of Ni²⁺ ions in a bipyridine-containing 2D COF under solvothermal treatment [14]. Under mild coordination conditions, only limited improvement in light absorption and H₂ evolution was observed. In contrast, solvothermal processing induced conformational planarization of the twisted 2,2'-bipyridine units and rearrangement of the layered framework, thereby promoting strong coordination with Ni²⁺ centers. FTIR, N 1s XPS, Ni K-edge XANES/EXAFS, and HAADF-STEM analyses confirmed atomically dispersed Ni²⁺ species coordinated through Ni–N/O environments, with shorter Ni–N bonds in the solvothermally treated sample indicating stronger orbital overlap between planarized bipyridine and Ni²⁺ centers. The resulting COF–Ni complex exhibited substantially red-shifted absorption spanning the full visible region together with pronounced metal-to-ligand charge-transfer characteristics. As a consequence, photocatalytic H₂ evolution increased by approximately 2.5-fold relative to the pristine framework, and H₂ evolution persisted even under irradiation beyond 700 nm. The optimized TpBpy–Ni2% delivered an AQE of 5.3% at 475 nm and retained reliable H₂ evolution over 12 cycles for 48 h, while post-reaction FTIR, PXRD, N₂ sorption, XPS, ICP, and HRTEM-EDS analyses verified preservation of the coordinated framework and uniform Ni distribution. PL quenching, prolonged time-resolved PL lifetime, enhanced photocurrent response, smaller EIS semicircle, ns-TA evidence of long-lived electron accumulation, and calculated electron–hole separation collectively demonstrated that solvothermal Ni coordination accelerated charge separation and strengthened MLCT-driven carrier transport. The study demonstrates that unlocking coaxial stacking and rotational flexibility within 2D COFs provides an effective route for regulating multidentate coordination environments and tailoring photochemical driving forces for panchromatic photocatalysis.

Postsynthetic metalation of COFs has emerged as an effective strategy for integrating catalytically active metal centers into ordered organic semiconductors without disrupting their crystallinity or structural periodicity. Because COFs possess tunable supramolecular coordination environments, electron-rich ligands, and permanent porosity, they can efficiently stabilize metal ions while simultaneously modulating the electronic characteristics of the framework. Such cooperative regulation between metal species and conjugated skeletons enables precise tuning of charge distribution, carrier migration, and catalytic reactivity. In this context, Punniyamoorthy et al. developed a triazine-centered β -ketoenamine-linked COF

through Schiff-base condensation and subsequently introduced transition-metal ions via postsynthetic coordination (Fig. 10a) [22]. Systematic evaluation of Ni-, Co-, and Fe-functionalized materials demonstrated that Ni incorporation generated the most active bifunctional electrocatalyst rather than a photocatalyst for both H₂ and O₂ evolution. PXRD and FTIR analyses confirmed that postmetalation preserved the COF framework, while Ni 2p, O 1s, and N 1s XPS shifts verified Ni²⁺ coordination with β -ketoenamine-derived O/N sites and charge redistribution between the metal centers and organic skeleton. In acidic electrolyte, Ni-COF exhibited significantly reduced overpotentials for H₂ and O₂ evolution, requiring only 208 and 302 mV, respectively, to achieve 10 mA cm⁻². Electrochemical impedance and Tafel analyses further showed that Ni-COF possessed the lowest charge-transfer resistance and fastest reaction kinetics among the Fe-, Co-, and pristine COF analogues, directly correlating metal coordination with improved HER/OER activity. The oxygen-evolution turnover frequency increased approximately fivefold relative to the pristine framework, highlighting the decisive role of the coordinated Ni centers in accelerating catalytic kinetics. Moreover, the catalyst maintained stable H₂ evolution activity over extended electrolysis, confirming the robustness of the metal–framework interaction. Chronoamperometry and accelerated durability tests demonstrated 24 h stability for both HER and OER, while post-OER XPS, HR-TEM, HAADF imaging, and elemental mapping confirmed retention of the ordered morphology, homogeneous Ni distribution, and active Ni²⁺/Ni³⁺ redox environment under harsh alkaline operation. This work illustrates how coupling redox-active 3d metal sites with conductive COF backbones can effectively enhance catalytic efficiency and operational durability.

Porphyrinic COFs have emerged as highly attractive photocatalytic platforms because their extended π -macrocyclic architectures combine intense visible-light absorption with tunable redox properties and long-range charge delocalization. Precise incorporation of different metal ions into porphyrin subunits enables systematic regulation of carrier dynamics and excited-state electronic structures, thereby directly influencing photocatalytic activity. Along this direction, Chen et al. synthesized a family of isostructural hydrazone-linked 2D porphyrinic COFs, denoted MPor-DETH-COF (M = H₂, Co, Ni, Zn), to investigate the influence of metal-centered electronic modulation on photocatalytic H₂ evolution [28]. All frameworks exhibited high crystallinity, permanent porosity, and robust structural stability (Fig. 10a) under photocatalytic conditions. PXRD refinement, FTIR, solid-state NMR, N₂ sorption, SEM, and HR-TEM analyses confirmed that the four COFs retained comparable AA-stacked mesoporous architectures, allowing their metal-dependent photocatalytic behavior to be correlated mainly with electronic and charge-transport differences rather than structural variation. Visible-light-driven water reduction in the presence of H₂PtCl₆ and triethanolamine demonstrated strongly metal-dependent catalytic behavior, following the activity sequence CoPor-DETH-COF < H₂Por-DETH-COF < NiPor-DETH-COF < ZnPor-DETH-COF. Among them, ZnPor-DETH-COF achieved the highest H₂ evolution rate of 413 $\mu\text{mol g}^{-1} \text{h}^{-1}$, whereas CoPor-DETH-COF displayed substantially suppressed activity. The optimized ZnPor-DETH-COF further showed an AQE of 0.32% after Pt/sacrificial-agent optimization and maintained H₂ production over 120 h, while post-reaction

PXRD and XAS analyses verified preservation of the crystalline framework and metalloporphyrin coordination environment. Detailed photophysical investigations revealed that incorporation of different transition metals modulated charge-carrier lifetimes and separation efficiencies (Fig. 10b) within the porphyrinic network, establishing charge-transfer dynamics as a decisive parameter governing photocatalytic proton reduction. Time-correlated single-photon counting and chopped photocurrent measurements showed the same activity-related order of carrier lifetime and photoresponse, ZnPor-DETH-COF > NiPor-DETH-COF > H₂Por-DETH-COF > CoPor-DETH-COF, confirming that longer-lived charge-separated states and stronger photocurrent responses directly accounted for higher H₂ evolution activity. XAS R-space and CCWT analyses further ruled out metal-cluster formation after photocatalysis, confirming that the embedded metalloporphyrin sites retained single-metal coordination, while DFT calculations indicated that Zn²⁺ suppressed ligand-to-metal charge-transfer losses and enabled more efficient electron migration through Zn-Zn columns and hole transport through porphyrin macrocycle channels toward Pt-assisted proton reduction. This work provides a clear molecular-level strategy for tailoring photocatalytic functionality through rational metalloporphyrin engineering in crystalline COF frameworks.

Chiral COFs have recently introduced a new dimension into photocatalytic H₂ evolution by enabling enantioselective interactions between sacrificial electron donors and catalytic interfaces. Although conventional 2D COFs exhibit excellent visible-light absorption and charge mobility, their intrinsic proton-reduction kinetics often remain insufficient without noble-metal cocatalysts. Inspired by biomimetic catalytic systems, Weng et al. designed a chiral β -ketoenamine-linked COF incorporating atomically dispersed Cu(II) centers as electron-transfer mediators for visible-light-driven H₂ evolution [30]. The Cu ions were coordinated to N-salicylideneaniline units embedded within the chiral hexagonal framework, generating isolated redox-active sites capable of mediating cyclic Cu(II)/Cu(I) conversion during photocatalysis (Fig. 10c). XPS, Cu K-edge EXAFS, wavelet-transform analysis, HAADF-STEM, and elemental mapping confirmed that Cu species were atomically dispersed through Cu–O/N coordination without detectable Cu–Cu scattering or nanoparticle formation, while PXRD and N₂ sorption verified retention of the ordered porous COF structure after metal coordination. Upon enantioselective interaction with L-/D-cysteine sacrificial donors, the chiral framework promoted accelerated donor oxidation and efficient hole extraction through stereochemically favored molecular recognition. XPS/Auger analysis and EPR measurements further demonstrated that cysteine reduced coordinated Cu(II) to Cu(I) in the dark, followed by photoinduced Cu(I)-to-Cu(II) regeneration and sulfanyl-radical formation under irradiation, establishing a Cu-mediated cyclic hole-extraction pathway. Simultaneously, the ordered chiral stacking arrangement reduced proton-reduction overpotentials and facilitated directional charge migration. As a result, the enantiomeric TpPa(Δ)-Cu(II)-COF/L-cysteine system achieved a remarkable H₂ evolution rate of 14.72 mmol g⁻¹ h⁻¹ without any precious-metal cocatalyst, outperforming both achiral analogues and several Pt-assisted COF photocatalysts. The corresponding sacrificial-oxidation TOF reached 9.0 h⁻¹,

and the AQE at 600 nm increased to 0.78%, substantially higher than the achiral TpPa-Cu(II)-COF/L-cysteine system. Long-term irradiation tests also confirmed stable H₂ evolution over 24 h, while recycled COF retained its crystallinity, porosity, chemical structure, optical response, and chirality after regeneration. The enhanced activity originated from synergistic acceleration of sacrificial-donor oxidation and proton-reduction kinetics enabled by chiral recognition and optimized interfacial electron transfer (Fig. 10d). Theoretical binding-energy calculations and isothermal titration calorimetry verified stronger interaction between matched chiral COF/cysteine pairs, whereas electrochemical polarization and DFT analyses showed that parallel chiral stacking shortened the distance between adjacent H-adsorbed sites and lowered the kinetic barrier for H₂ formation. This work establishes chiral COFs as a promising platform for constructing nonprecious-metal photocatalytic systems through stereochemically controlled reaction pathways.

In addition to postsynthetic metal coordination, synchronized incorporation of metal ions during COF formation offers a simplified route for constructing highly conjugated metal-containing frameworks. Conventional post-coordination approaches often require secondary solvothermal treatment, during which reversible bond cleavage and reconstruction may occur, complicating synthesis and limiting structural precision. To overcome these limitations, Qiu et al. introduced a one-pot solvothermal strategy for directly integrating Co ions into bipyridine-containing COFs during framework assembly [47]. Simultaneous coordination between Co ions and bipyridine ligands during polymerization produced Syn-Co-COF with a substantially higher proportion of N–Co–N coordination motifs than analogous post-coordinated materials. PXRD, N₂ sorption, SEM/TEM, elemental mapping, solid-state ¹³C NMR, FTIR, ATR-SEIRAS, ICP, and XPS analyses confirmed that the synchronized route retained the TpBpy-COF-type framework while uniformly incorporating Co species through pyridinic-N coordination. The rigid N–Co–N environment suppressed pyridine-ring torsion, enhanced π -electron delocalization, broadened visible-light absorption, and accelerated charge separation and migration throughout the framework. Co 2p and N 1s XPS shifts, charge-density-difference analysis, and Bader-charge calculations demonstrated stronger electron donation from bipyridine N atoms to Co centers in Syn-Co-COF, while the calculated pyridine-ring torsion angle decreased to 1.307° for N–Co–N compared with 11.974° for Co–N coordination, directly explaining the improved planarity and conjugation. Compared with Post-Co-COF and pristine TpBpy-COF, the synchronized coordination architecture exhibited significantly prolonged excited-state lifetimes (Fig. 10e) and superior photocatalytic H₂ evolution. In the presence of 3 wt% Pt, Syn-Co-COF@Pt achieved a hydrogen-production rate of 47.2 mmol g⁻¹ h⁻¹, corresponding to approximately 2.4-fold enhancement relative to the parent framework. Syn-Co-COF also showed AQE values of 1.71, 1.01, 0.68, and 0.54% at 365, 400, 420, and 500 nm, respectively, and retained stable H₂ evolution over 20 h; post-reaction PXRD, FTIR, SEM, TEM, and Co 2p XPS analyses verified preservation of the framework morphology and coordination environment. Both experimental investigations and theoretical calculations confirmed that the abundance of rigid N–Co–N coordination structures was primarily responsible for the enhanced photocatalytic activity (Fig. 10f). Mechanistically, Syn-Co-COF displayed the most

negative conduction-band potential, highest photocurrent response, lowest EIS resistance, largest carrier density, lowest exciton-binding energy of 26.6 meV, strongest PL quenching, and longest TAS-derived carrier lifetime of 434.41 ps, confirming that synchronized Co coordination promoted exciton dissociation, charge separation, and electron transport toward

Pt-assisted proton reduction. This work provides important mechanistic insight into the influence of coordination pathways on framework conjugation and establishes synchronized metal coordination as an efficient strategy for constructing high-performance metal-containing COF photocatalysts.

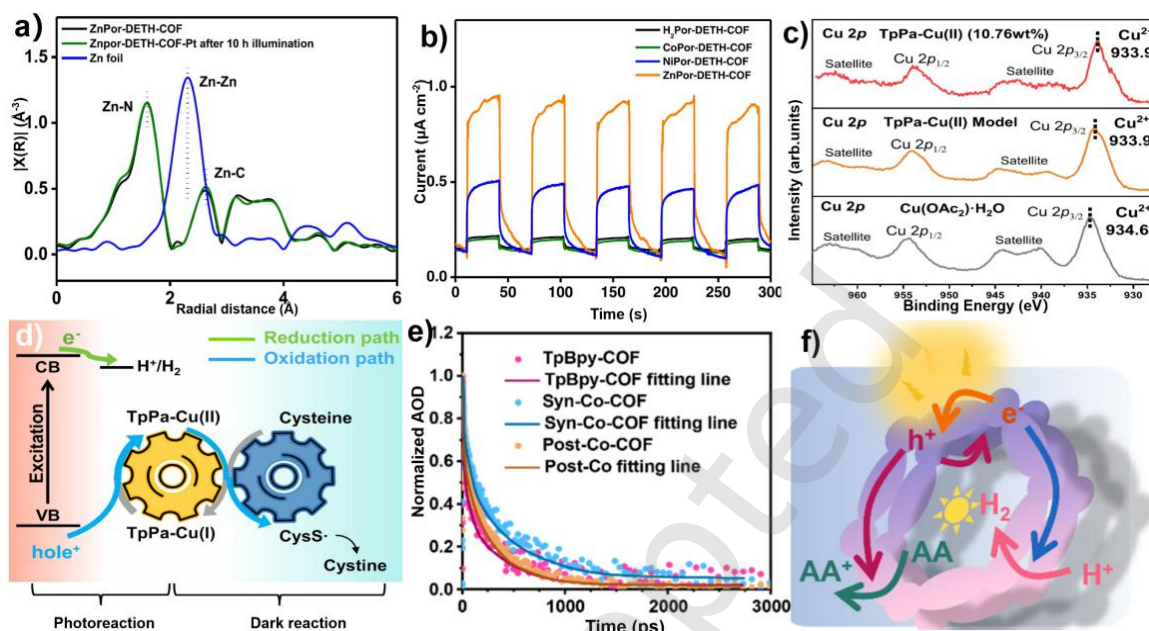


Fig. 10 (a) XAS Fourier transform R-space curve of ZnPor-DETH-COF. (b) Photocurrent curves of different COFs [28]. Reprinted with permission from Ref. [28]. Copyright 2023, Royal Society of Chemistry. (c) Cu 2p XPS spectra, and (d) charge migration mechanism of Cu-mediated COF [30]. Reprinted with permission from Ref. [30]. Copyright 2022, Springer Nature. (e) Time resolved PL spectra and (f) charge transfer mechanism of Syn-Co-COF@Pt for H₂ evolution [47]. Reprinted with permission from Ref. [47]. Copyright 2026, Elsevier B.V.

Coordination of transition-metal ions within nitrogen-rich COF frameworks provides another effective approach for enhancing visible-light absorption and promoting photoinduced charge separation. Nitrogen-containing ligands such as bipyridine possess strong coordination affinity toward transition metals and can stabilize isolated catalytic centers within conjugated frameworks. Compared with porphyrinic systems, bipyridine-based COFs are generally synthesized under milder conditions while retaining excellent tunability for electronic modulation. For instance, Cui et al. designed an olefin-linked bipyridine-containing COF, denoted sp²c-COFdpy, capable of coordinating Co, Fe, or Ni ions to generate metal-functionalized photocatalysts [144]. Metal coordination substantially broadened visible-light absorption and improved photoinduced carrier separation relative to the pristine framework. Among the investigated systems, Co coordination produced the most efficient photocatalyst. After loading 1 wt% Pt cocatalyst, Pt@sp²c-COFdpy-Co achieved a H₂ evolution rate of 324.4 μmol h⁻¹ following optimization, greatly exceeding the activities of pristine COF, Fe- and Ni-containing analogues, and many previously reported COF and g-C₃N₄ photocatalysts. Spectroscopic analyses and photocurrent measurements confirmed that Co incorporation enhanced both charge-separation efficiency and visible-light harvesting. Moreover, the catalyst exhibited an apparent quantum yield of 2.1% at 500 nm, highlighting the effectiveness of transition-metal coordination in regulating the electronic structure and photocatalytic properties of conjugated COFs. This study establishes bipyridine-mediated metal coordination as a versatile strategy for constructing highly efficient H₂ evolution photocatalysts.

Manipulation of interfacial charge-transfer pathways between COFs and cocatalysts also represents a powerful strategy for maximizing photocatalytic efficiency while minimizing noble-metal usage. Transition-metal ions can act as intermediate electron-transfer relays between semiconducting frameworks and cocatalyst NPs because their adjustable redox states and positive electrode potentials facilitate directional carrier migration. For instance, Zhang et al. exploited this concept by constructing a series of TpBpy-based COF/transition-metal/Pt interfaces through stepwise coordination and photodeposition processes [145]. The bipyridine-containing TpBpy framework served as a highly crystalline and water-stable platform for anchoring transition-metal ions including Rh³⁺, Ag⁺, Au³⁺, and Cu²⁺ prior to Pt deposition. Among the investigated systems, Rh-mediated interfaces displayed the most efficient electron-transfer characteristics. Comprehensive spectroscopic and theoretical analyses, including in-situ XPS, XANES/EXAFS, femtosecond transient absorption spectroscopy, UPS, and DFT calculations, consistently demonstrated that Rh species establish an energetically favorable interfacial bridge that accelerates carrier migration while suppressing recombination. Mechanistic investigations revealed that Rh ions functioned as dynamic electron-transfer mediators through reversible Rh³⁺/Rh⁺ redox cycling, while simultaneously lowering the Schottky barrier between TpBpy and Pt NPs. Furthermore, the interfacial transition-metal species suppressed undesirable back-electron transfer by introducing favorable energy-level alignment. These complementary characterizations directly correlated the improved charge-separation dynamics with the enhanced photocatalytic activity, thereby providing convincing evidence

for the proposed structure–function relationship. As a consequence, the optimized Pt@TpBpy-Rh photocatalyst achieved a H₂ evolution rate of 52.5 mmol h⁻¹ g⁻¹ together with an apparent quantum yield of 12.8% at 450 nm using an ultralow Pt loading of only 0.25 wt%, representing one of the highest activities reported for TpBpy-based photocatalysts. This work demonstrates that atomic-level interfacial engineering using transition-metal bridges provides a highly effective strategy for directing photoinduced electron flow and improving cocatalyst utilization in COF photocatalysis.

Electronic asymmetry engineering through partial fluorination has additionally emerged as an effective route for activating inert π -conjugated frameworks and enhancing nonprecious-metal photocatalysis. Conventional pyrene-based COFs often suffer from centrosymmetric electron distribution and limited active-site accessibility despite excellent light-harvesting capability. For instance, Yan et al. addressed these limitations by combining asymmetric fluorination, D–A optimization, and transition-metal coordination within pyrene-based COFs to construct highly polarized photocatalytic frameworks [146]. Controlled ortho-fluorination of pyrene units generated partially fluorinated TF0.5CN-COF, in which local symmetry breaking induced strong charge polarization and directional electron localization toward bipyridyl-diacetonitrile acceptor domains. Subsequent coordination of earth-abundant Cu, Ni, and Co ions to bipyridine motifs further strengthened metal–support electronic interactions and eliminated dependence on noble-metal cocatalysts. Among the resulting systems, TF0.5CN-Cu exhibited the highest photocatalytic activity, achieving a H₂ evolution rate of 10.5 mmol h⁻¹ g⁻¹ under visible-light irradiation together with excellent operational stability over extended reaction periods. Comprehensive spectroscopic and theoretical analyses, including XPS, UV–vis diffuse reflectance spectroscopy, PL, TRPL, three-dimensional excitation–emission matrix fluorescence spectroscopy, transient photocurrent measurements, Kelvin probe force microscopy, fluorescence-quenching studies, and density functional theory calculations, consistently demonstrated that asymmetric fluorination generated a directional built-in electric field, promoted exciton dissociation, accelerated interfacial charge-transfer dynamics, prolonged carrier lifetimes, and facilitated electron migration toward Cu coordination sites. Combined experimental analyses and theoretical calculations confirmed that asymmetric fluorination enhanced built-in electric fields, promoted charge separation, and improved accessibility of catalytic sites by disrupting the electronic symmetry of the framework. Furthermore, post-photocatalytic XRD, FT-IR, XPS, and ICP analyses verified that both the framework architecture and Cu coordination environment remained largely unchanged after repeated hydrogen-evolution cycles, providing strong evidence that the optimized electronic structure was retained during photocatalysis. Importantly, partially fluorinated structures outperformed both fully fluorinated and nonfluorinated analogues, demonstrating that moderate asymmetric polarization optimally balances electronic localization and carrier mobility. This study establishes asymmetry-driven fluorination engineering as a highly effective strategy for constructing efficient noble-metal-free COF photocatalysts with precisely tunable electronic structures.

To sum up, transition-metal coordination engineering has become a versatile molecular-level strategy for tailoring the

optoelectronic properties and catalytic functionality of COF-based photocatalysts. Through rational coordination of transition-metal ions within heteroatom-rich conjugated frameworks, these systems can simultaneously regulate band structures, broaden visible-light absorption, and promote directional charge migration. In particular, strong metal–ligand electronic interactions generate favorable charge-transfer pathways and internal polarization effects that accelerate exciton dissociation while suppressing nonradiative recombination. Precise modulation of coordination geometry, metal valence states, and ligand-field environments further enables fine control over carrier lifetimes, interfacial electron-transfer kinetics, and proton-reduction energetics. Moreover, incorporation of redox-active transition metals into ordered porous architectures provides efficient electron-relay centers capable of enhancing cocatalyst utilization and reducing noble-metal dependence. Advanced strategies including synchronized coordination assembly, chiral coordination environments, interfacial metal-bridge engineering, and asymmetric electronic polarization additionally demonstrate that subtle regulation of local coordination chemistry can profoundly influence photocatalytic performance. Nevertheless, maintaining robust metal–framework interactions under prolonged photocatalytic conditions remains a substantial challenge because dynamic coordination environments may induce metal leaching, structural distortion, or deactivation of catalytic centers. Therefore, future development of transition-metal-coordinated COFs will require deeper understanding of coordination-induced excited-state dynamics together with precise control over coordination symmetry, electronic polarization, and interfacial charge-transfer pathways to achieve highly efficient and durable solar-driven hydrogen-production systems.

5.5. Donor-Acceptor engineering and exciton regulation

D–A engineering has become a central strategy for improving photocatalytic H₂ evolution in COFs by promoting charge separation and regulating exciton dynamics. Incorporation of electron-rich donor units and electron-deficient acceptor moieties generates internal polarization fields that facilitate directional carrier migration and suppress electron–hole recombination. Simultaneously, exciton regulation through electronic asymmetry, heteroatom incorporation, and nanosheet engineering reduces exciton-binding energy and enhances free-carrier generation [147]. The extended π -conjugated and crystalline nature of COFs further supports long-range charge transport and efficient utilization of photoinduced carriers. As a result, D–A modulation and exciton engineering have emerged as powerful molecular-design approaches for constructing highly efficient COF photocatalysts for solar-driven H₂ evolution [148]. The electronic versatility of COFs has further stimulated the development of donor–acceptor (D–A) and donor–acceptor–donor (D–A–D) architectures for photocatalytic CO₂ reduction. Their extended conjugation pathways and interlayer π – π interactions not only broaden optical absorption but also enable anisotropic charge migration across both in-plane and stacking directions. Nevertheless, conventional D–A systems frequently suffer from rapid charge recombination, limiting the generation of long-lived reactive carriers [149]. To overcome this limitation, introducing electron-rich and electron-deficient units with progressively aligned energy levels has been proposed to strengthen internal electric fields and accelerate exciton dissociation. In particular, D–A–D configurations

possessing spatially separated donor domains can direct charge flow toward catalytically active acceptor centers while suppressing reverse electron transfer. Guided by this principle, Lan et al. constructed a family of imine-linked COFs based on trinuclear copper pyrazolate clusters and linkers with tunable electron-withdrawing ability, affording Cu₃-TPA-COF, Cu₃-TAPB-COF, and Cu₃-TAPT-COF [6]. The frameworks enabled the formation of interlayer Co–imine–N single-site motifs in which atomically dispersed cobalt centers remained highly accessible within the ordered channels. These localized coordination environments generated electron-enriched states favorable for CO₂ adsorption and activation. Among the series, Co/Cu₃-TPA-COF displayed the highest photoreduction efficiency owing to its distinctive D1–A–D2 electronic topology. The coexistence of mixed-valence Cu^I/Cu^{II} species and the electron-donating triphenylamine unit promoted efficient charge separation and directed electron migration toward the interlayer cobalt centers, thereby enhancing catalytic turnover. Upon modulation with 4,4'-dimethyl-2,2'-bipyridine, the catalyst achieved an excellent performance, outperforming previously reported COF-derived photocatalytic systems. Comprehensive spectroscopic and theoretical analyses, including XPS, XANES, EXAFS, UV–vis diffuse reflectance spectroscopy, transient photocurrent measurements, electrochemical impedance spectroscopy, PL, TRPL, in situ DRIFTS, and density functional theory calculations, demonstrated that the D1–A–D2 electronic architecture together with the interlayer Co–imine–N coordination environment established highly separated electron–hole states, accelerated directional charge migration through both the in-plane conjugated network and π -stacked interlayers, strengthened Co–N electronic coupling, facilitated CO₂ adsorption and activation, and lowered the energetic barrier for the key COOH intermediate, thereby promoting interfacial catalytic kinetics. Furthermore, post-reaction PXRD, FT-IR, XPS, and ICP analyses confirmed that the crystalline framework, coordination environment, and atomically dispersed Co sites remained well preserved after repeated photocatalytic cycles, highlighting the excellent structural stability of the catalyst during operation. These findings underscore the decisive influence of precisely engineered D–A–D electronic structures on carrier dynamics and interfacial catalytic kinetics during photocatalytic solar conversion.

Despite rapid advances in COF photocatalysis, photocatalytic H₂ evolution remains governed by a complex interplay of light absorption, exciton migration, carrier generation, charge transport, stacking arrangement, crystallinity, morphology, cocatalyst proximity, and framework stability. Because these parameters are strongly interdependent, identifying the

dominant descriptors controlling catalytic performance is essential for rational materials design. To address this issue, Ghosh et al. established a comprehensive structure–property–activity relationship using a series of molecularly engineered isorecticular COFs with systematically varied D–A interactions, torsional configurations, and stacking arrangements [21]. Through careful modulation of conjugation and reaction conditions, the authors independently examined the influence of optical absorption, electronic structure, crystallinity, surface area, morphology, and carrier mobility on photocatalytic H₂ evolution (Fig. 11a). Comprehensive spectroscopic, electrochemical, and theoretical analyses, including UV–vis diffuse reflectance spectroscopy, photo-yield spectroscopy, Mott–Schottky measurements, electron paramagnetic resonance, flash-photolysis time-resolved microwave conductivity, electrochemical impedance spectroscopy, PXRD refinement, solid-state NMR, and DFT/DFTB calculations, enabled direct correlation of band alignment, photogenerated carrier density, interfacial resistance, and intrinsic charge mobility with H₂ evolution rates. Correlation of photophysical measurements with catalytic performance revealed that light harvesting, charge generation, and carrier transport exerted substantially greater influence on H₂ evolution than surface area or morphology alone. In particular, AA'-stacked frameworks displayed superior exciton migration and charge mobility compared with AB or ABC arrangements, emphasizing the importance of interlayer electronic coupling. Among the synthesized materials, BtCOF150 delivered the highest H₂ evolution rate of $750 \pm 25 \mu\text{mol g}^{-1} \text{h}^{-1}$ using only 1 wt% Pt cocatalyst and triethanolamine as sacrificial donor while maintaining long-term stability. Its enhanced activity was quantitatively linked to stronger visible-light absorption, light-induced EPR signal intensification, the highest FP-TRMC photoconductivity, and the lowest EIS-derived charge-transfer resistance, confirming that efficient carrier generation and transport, rather than surface area alone, dominate the overall photocatalytic output. Interestingly, introducing mixed linkers improved optical absorption but reduced catalytic activity because of impaired carrier mobility, further confirming that efficient charge transport dominates overall photocatalytic performance. Post-photocatalytic FT-IR, solid-state NMR, PXRD, SEM, and HR-TEM analyses further verified preservation of molecular connectivity and morphology, while Pt nanoparticles were retained on the COF surface, supporting the operational robustness of the optimized system. These findings provide a quantitative framework for understanding structure-dependent photocatalytic behavior and establish key design principles for next-generation COF-based H₂ evolution systems.

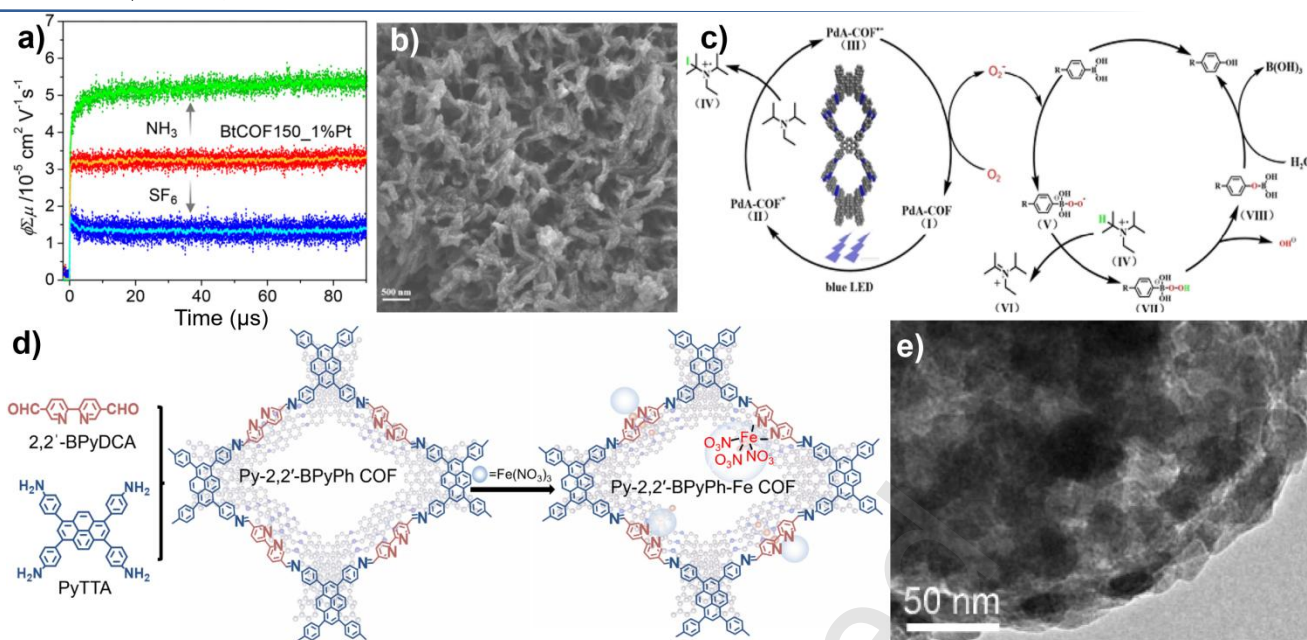


Figure 11 (a) Transient photoconductivity of BtCOF150 [21]. Reprinted with permission from Ref. [21]. Copyright 2020, American Chemical Society. (b) SEM image, and (c) charge transfer mechanism of Pd-COF for H₂ evolution [27]. Reprinted with permission from Ref. [27]. Copyright 2026, American Chemical Society. (d) Synthesis and (e) TEM image of Fe-CONs [153]. Reprinted with permission from Ref. [153]. Copyright 2024, Elsevier B.V.

Heteroatom incorporation into conjugated COFs has further emerged as a powerful molecular-engineering strategy for regulating electronic structure and catalytic selectivity. In particular, nitrogen doping can modify framework polarity, alter D–A characteristics, accelerate electron transfer, and introduce Lewis-basic sites favorable for adsorption and redox activation. For instance, Wang et al. investigated the influence of nitrogen-position engineering by synthesizing a family of one-dimensional COFs using nonlinear V-shaped C₂-symmetric building units containing distinct pyrimidine or pyrazine configurations coupled with pyrene-based tetratopic monomers (Fig. 11b) [27]. Through precise control over the spatial location of nitrogen atoms inside and outside the pore channels, the authors systematically correlated heteroatom positioning with photocatalytic behavior. Comprehensive spectroscopic, electrochemical, and theoretical analyses, including PXRD refinement, FT-IR, XPS, UV–vis diffuse reflectance spectroscopy, Mott–Schottky measurements, transient photocurrent response, EIS, steady-state PL, TRPL, water-contact-angle analysis, and DFT-based HOMO–LUMO and electrostatic-potential calculations, confirmed that nitrogen positioning directly regulates band gaps, conduction-band potentials, charge recombination, carrier lifetime, hydrophilicity, and intramolecular charge-transfer direction. Among the prepared materials, Pd-COF exhibited the highest H₂ evolution activity, reaching 99.6 mmol g^{−1} h^{−1}, whereas PdA-COF showed superior activity in photocatalytic oxidation of arylboronic acids to phenols. Mechanistic investigations demonstrated that meta-positioned nitrogen atoms within pyrimidine units facilitated charge separation and proton-reduction kinetics, while nitrogen functionalities located inside the pores preferentially promoted substrate activation during organic transformation (Fig. 11c). Specifically, Pd-COF combined broader visible-light absorption, the smallest optical band gap, suppressed PL intensity, the longest TRPL lifetime, and improved aqueous dispersibility, explaining its superior hydrogen-evolution performance despite the higher photocurrent

response of Pz-COF. Post-reaction PXRD and FT-IR analyses further verified that Pd-COF retained its crystallinity and imine-linked framework after H₂-evolution cycling, while PdA-COF preserved its structure during repeated arylboronic-acid oxidation cycles, supporting the operational stability of these nitrogen-position-engineered 1D COFs. These findings reveal that heteroatom spatial distribution can selectively regulate photocatalytic pathways and provide an important design principle for multifunctional COF photocatalysts capable of simultaneously optimizing solar-fuel production and organic conversion reactions.

Exciton regulation within conjugated COFs has become increasingly recognized as a decisive factor controlling photocatalytic efficiency. In layered polymeric semiconductors, strong exciton binding energies frequently hinder free-carrier generation and accelerate recombination. Nanosheet engineering and D–A molecular design therefore provide effective strategies for improving exciton dissociation and extending carrier lifetimes. For instance, Li et al. demonstrated this concept through the synthesis of a cyano-functionalized ketene–cyano D–A COF (CYANO-COF) derived from triformylphloroglucinol and dicyano-biphenyl diamine monomers [45]. Exfoliation of the bulk framework into nanosheets (CYANO-CON) significantly shortened carrier diffusion pathways and enhanced exposure of catalytically active surfaces. Comprehensive spectroscopic, electrochemical, and theoretical analyses, including FT-IR, solid-state ¹³C CP-TOSS NMR, PXRD refinement, HRTEM, AFM, UV–vis DRS, Mott–Schottky measurements, temperature-dependent PL, femtosecond transient absorption spectroscopy, EIS, isotope tracing, and charge-distribution calculations, verified the formation of a stable β-ketoenamine-linked ketene–cyano D–A framework and directly connected its electronic structure with enhanced exciton dissociation and charge utilization. Temperature-dependent PL spectroscopy revealed substantially reduced exciton-binding energy in CYANO-CON relative to non-cyano analogues, while femtosecond transient absorption

measurements demonstrated markedly prolonged carrier lifetimes arising from efficient D–A induced charge separation. Specifically, CYANO-CON exhibited a lower exciton-binding energy than BD-CON and a markedly longer trapped-carrier lifetime, while ascorbic acid (AA) rapidly extracted photogenerated holes and enabled long-lived electron accumulation, explaining the exceptional proton-reduction efficiency. As a consequence, CYANO-CON achieved an exceptional apparent quantum efficiency of 82.6% at 450 nm, representing one of the highest AQE values reported for COF-based H₂ evolution photocatalysts. Moreover, reducing the framework thickness to approximately 12–15 layers produced more than a twofold increase in H₂ evolution activity. Post-photocatalytic TEM, PXRD, and FT-IR analyses confirmed that CYANO-CON retained its nanosheet morphology, crystallinity, and chemical structure after repeated hydrogen-evolution cycles, supporting the operational robustness of the exciton-engineered photocatalyst. This study establishes exciton engineering through D–A modulation and nanosheet construction as a highly effective strategy for maximizing photocatalytic charge utilization in conjugated COFs.

The development of fully conjugated sp² carbon-linked COFs has additionally opened new opportunities for constructing robust metal-free photocatalysts with highly ordered electronic structures. Embedding D–A motifs into extended π -conjugated frameworks promotes directional carrier migration, suppresses charge recombination, and enhances exciton dissociation, while crystalline porous channels facilitate efficient reactant diffusion and active-site accessibility. In this context, Wu et al. synthesized two cyano-functionalized sp² carbon-conjugated COFs, Py-CN-BZTD and Py-CN-TZTZ, through Knoevenagel condensation between pyrene-based donor units and electron-deficient benzothiadiazole or thiazolothiazole acceptors, respectively [126]. The fully conjugated D–A frameworks exhibited high crystallinity, large surface areas, and strong visible-light absorption. Comprehensive spectroscopic, electrochemical, and theoretical analyses, including PXRD refinement, FT-IR, solid-state ¹³C NMR, XPS, TGA, N₂ sorption, SEM/TEM-EDS mapping, UV–vis DRS, UPS, cyclic voltammetry, PL, TRPL, EIS, transient photocurrent response, water-contact-angle measurements, EPR spin-trapping experiments, and DFT-based electrostatic-potential calculations, confirmed the formation of stable cyano-vinylene-linked D–A frameworks and clarified how linker electronics and heteroatom distribution regulate light harvesting, band alignment, charge separation, interfacial resistance, carrier lifetime, and Pt anchoring behavior. Among the pristine materials, Py-CN-BZTD displayed superior photocatalytic H₂ evolution owing to the stronger electron-withdrawing nature of the benzothiadiazole unit, which generated a narrower band gap and promoted more efficient charge separation and carrier transport. However, after Pt photodeposition, Py-CN-TZTZ exhibited a dramatic increase in catalytic performance, reaching a H₂ evolution rate of 61 577 $\mu\text{mol g}^{-1} \text{h}^{-1}$, substantially exceeding that of Pt-loaded Py-CN-BZTD. The enhanced activity originated from the more homogeneous distribution of sulfur and nitrogen heteroatoms within the TZTZ-based framework, which generated extended regions of negative electrostatic potential favorable for uniform Pt dispersion and increased catalytic-site density. EPR analyses further indicated that Pt-assisted Py-CN-TZTZ enabled more efficient electron

extraction and suppressed radical-mediated charge loss, while TRPL, photocurrent, and EIS results quantitatively linked the improved interfacial charge-transfer dynamics with the enhanced HER output. Experimental observations together with theoretical calculations confirmed that heteroatom spatial distribution critically influenced cocatalyst anchoring behavior, interfacial electron transfer, and overall photocatalytic efficiency. Long-term cycling, FT-IR, and SEM analyses after photocatalysis further verified that both COFs retained their characteristic cyano-vinylene framework vibrations and original morphologies after prolonged visible-light operation, demonstrating strong chemical and morphological stability under HER conditions. This study establishes heteroatom-regulated D–A engineering as a powerful design principle for next-generation sp² carbon-conjugated COF photocatalysts with ultrahigh H₂ evolution activity.

Manipulating excitonic behavior through atomic-level interfacial engineering has recently emerged as an effective strategy for overcoming the intrinsic carrier-recombination limitations of conjugated COFs. In D–A COFs, tightly bound singlet excitons often coexist with free carriers under visible-light excitation, thereby restricting efficient utilization of photoinduced charges for H₂ evolution. For instance, Shen et al. addressed this challenge by inserting Ni atoms into the interlayer D–A interface of a newly developed pyrene–fluorenone COF, denoted COF-SCAU-1 [2]. In this framework, electron-rich pyrene units functioned as donor moieties, whereas fluorenone fragments served as electron acceptors, generating an internal D–A electronic architecture. Coordination of Ni atoms with nitrogen sites at the interfacial region profoundly altered the excitonic behavior of the framework by strengthening the local polarization electric field. Comprehensive spectroscopic, photophysical, electrochemical, and theoretical analyses, including PXRD refinement, solid-state ¹³C CP/MAS NMR, FT-IR, XPS, XANES, EXAFS, WT-EXAFS, TEM/HRTEM, elemental mapping, UV–vis spectroscopy, VB-XPS, temperature-dependent PL, delayed fluorescence/phosphorescence, EPR, Mott–Schottky analysis, transient absorption spectroscopy, surface photovoltage, EIS, photocurrent response, and DFT calculations, confirmed Ni–N coordination at the imine-linked D–A interface and directly connected interfacial polarization with exciton dissociation, charge accumulation, and carrier migration. Combined experimental analyses and theoretical calculations revealed that incorporation of Ni enhanced the internal polarization intensity by approximately 3.23-fold, thereby facilitating rapid dissociation of singlet excitons into free charge carriers and accelerating carrier migration from the bulk framework toward surface catalytic sites. Specifically, Ni incorporation lowered the exciton-binding energy, shortened delayed fluorescence lifetime, increased EPR-detected free-carrier density, reduced charge-transfer resistance, enhanced surface photovoltage and photocurrent response, and prolonged transient-absorption-derived trapped-electron lifetimes, collectively verifying more efficient conversion of excitonic states into mobile charge carriers. As a consequence, Ni-COF-SCAU-1 exhibited a H₂ evolution rate of 197.46 $\text{mmol g}^{-1} \text{h}^{-1}$ under visible-light irradiation in the presence of 3 wt% Pt cocatalyst, representing a more than threefold enhancement relative to the pristine framework. The Ni-intercalated material also delivered an AQE of 43.2% at 420 nm and maintained stable cyclic H₂ evolution,

while control tests without Pt confirmed that Ni primarily regulated exciton and charge-transfer dynamics rather than serving as the proton-reduction cocatalyst. The study demonstrates that atomic interface modulation can effectively regulate exciton dynamics and charge-transfer behavior in D–A COFs, thereby offering a versatile strategy for designing highly efficient photocatalytic systems based on exciton engineering.

To sum up, D–A modulation and exciton regulation have emerged as fundamental molecular-engineering strategies for overcoming the intrinsic carrier-recombination limitations of conjugated COF photocatalysts. By integrating electron-rich donor segments with electron-deficient acceptor units, these frameworks generate internal polarization fields that promote directional charge separation, accelerate carrier migration, and suppress reverse electron transfer. Simultaneously, precise tuning of conjugation length, heteroatom distribution, stacking configuration, and interfacial electronic asymmetry enables effective reduction of exciton-binding energy and facilitates spontaneous generation of free charge carriers. In particular, D–A-donor configurations, nanosheet engineering, and atomic-level interfacial modulation have demonstrated strong capability for enhancing exciton dissociation and prolonging excited-state lifetimes within highly ordered π -conjugated networks. Moreover, regulation of heteroatom positioning and electronic polarization provides additional control over cocatalyst anchoring behavior, charge-transport pathways, and proton-reduction kinetics, thereby substantially improving photocatalytic H₂ evolution efficiency. Nevertheless, the highly coupled relationship among framework crystallinity, stacking mode, carrier mobility, excitonic interactions, and interfacial charge-transfer dynamics continues to complicate rational optimization of photocatalytic performance. Therefore, future advances in D–A-engineered COFs will require deeper mechanistic understanding of exciton evolution and multiscale carrier dynamics together with precise electronic-structure control to construct highly efficient, stable, and fully integrated solar-to-hydrogen conversion systems.

5.6. Structural, morphological, and conjugation engineering

Structural, morphological, and π -conjugation engineering have emerged as fundamental strategies for optimizing photocatalytic H₂ evolution in COFs. Precise regulation of framework planarity, stacking arrangement, pore architecture, and conjugation length can significantly influence light absorption, exciton dissociation, and carrier-transport behavior [150]. Morphological modulation, particularly nanosheets construction and exfoliation, shortens carrier-diffusion pathways and increases exposure of catalytically accessible surface sites. Simultaneously, extension of π -conjugation and enhancement of framework crystallinity improve charge delocalization and suppress recombination losses [151]. Control over interlayer stacking and molecular ordering further facilitates directional carrier migration across the framework. As a result, structural and conjugation engineering have become essential design principles for developing highly efficient and durable COF-based photocatalysts. Photocatalytic H₂ evolution over COF-based semiconductors is generally governed by sacrificial-agent-assisted kinetics, where rapid hole scavenging and sufficiently negative conduction-band potentials are both essential for sustaining proton reduction [152]. Although numerous COFs possess energetically suitable band structures, many remain

photocatalytically inactive even after noble-metal loading, indicating that efficient H₂ evolution depends not only on thermodynamic feasibility but also on the nature of charge extraction and transport within the conjugated framework. In particular, β -ketoenamine-linked COFs generated through Schiff-base condensation have recently revealed unconventional photocatalytic behavior; nevertheless, the molecular origin of electron delivery toward proton-reduction sites has remained insufficiently clarified. Addressing this issue, Wu et al. identified phenolic keto moieties as effective π -electron injection centers in β -ketoenamine COFs for visible-light-driven H₂ evolution [8]. A series of frameworks with progressively varied hydroxyl substitution were synthesized from hydroxylated benzene trialdehydes and p-phenylenediamine, followed by enol–keto tautomerization to generate β -ketoenamine-linked structures with different keto densities. Comprehensive spectroscopic, photoelectrochemical, and theoretical analyses, including PXRD, SEM, N₂ sorption, FT-IR, solid-state ¹³C CP/MAS NMR, XPS, UV–vis DRS, Mott–Schottky measurements, steady-state and time-resolved photoluminescence, transient photocurrent response, EIS, zeta-potential analysis, TEM, and DFT calculations, confirmed that alkaline reconstruction preserved the crystalline porous framework while converting enol-rich domains into keto-dominated β -ketoenamine units. Under alkaline conditions, thermodynamically favored keto reconstruction produced highly conjugated TP-COFs, which were subsequently integrated with polyvinylpyrrolidone-coated Pt NPs to establish insulated photocatalytic assemblies. Visible-light irradiation triggered efficient tunneling of photoexcited π -electrons from keto-active domains to Pt catalytic sites across the insulating interlayer, thereby enabling proton reduction. The reconstructed keto motifs shifted the conduction-band potential negatively, prolonged fluorescence lifetimes, lowered interfacial resistance, enhanced photocurrent response, and generated an inhomogeneous electrostatic-potential distribution, demonstrating that keto sites promote charge separation and serve as preferential electron-emission domains rather than merely altering optical absorption. The H₂ evolution activity increased systematically with the concentration of keto functionalities, and TP-COFs-3 delivered an H₂ evolution rate of 53.0 mmol g^{−1} h^{−1} at pH 11.0. Long-term cycling further showed stable hydrogen evolution over keto-rich BT-COFs-3/TP-COFs-3, supporting the structural durability of the keto-switched photocatalytic system under visible-light operation. This work established phenolic keto groups as direct charge-injection motifs and provided mechanistic insight into electron-emission pathways in β -ketoenamine COF photocatalysts.

Interfacial assembly between COFs and molecular chromophores offers another effective strategy for regulating photocatalytic performance through controlled supramolecular organization. In addition to improving mechanical and interfacial properties, such hybridization can modulate hydrophobicity, exciton migration, and aggregation-dependent photophysical behavior. For instance, Han et al. demonstrated this concept through co-assembled systems composed of COF NPs and metalloporphyrins for visible-light-driven H₂ evolution [16]. The porous COF surface served as a template for organizing porphyrinic assemblies, while simultaneously regulating aggregation behavior through interfacial interactions. Comprehensive spectroscopic, morphological, electrochemical,

and theoretical analyses, including PXRD, FT-IR, N₂ sorption, SEM/TEM, EDS elemental mapping, ICP, XPS, UV-vis DRS, Tauc analysis, Mott-Schottky measurements, PL spectroscopy, transient photocurrent response, EIS, water-contact-angle measurements, Gibbs free-energy evaluation, and molecular-dynamics calculations, confirmed that COF/porphyrin co-assembly preserved the COF framework while strongly modulating porphyrin loading, aggregation thickness, band alignment, charge-transfer resistance, and interfacial photophysical behavior. Depending on the coordinated metal center, distinct surface-covering modes and aggregation states were generated. Notably, NiTCPP formed a predominantly monolayer distribution over the COF surface, minimizing intermolecular aggregation and facilitating efficient charge separation and migration. As a result, COF/NiTCPP achieved the highest H₂ evolution rate of 29.71 mmol g⁻¹ h⁻¹ under visible-light irradiation, outperforming analogous PtTCPP- and CoTCPP-based systems despite the intrinsically superior photophysical properties of the latter chromophores. The superior activity of COF/NiTCPP was further supported by its more negative conduction-band position, stronger photocurrent response, smaller EIS semicircle, weaker aggregation-induced energy dissipation, and smoother photon-to-electron transfer pathway from the monolayer porphyrin interface to the COF scaffold. Excessive porphyrin stacking in COF/PtTCPP and COF/CoTCPP induced severe aggregation-caused quenching, thereby diminishing photocatalytic efficiency. Recycling experiments over 25 h, together with post-reaction FT-IR, TEM/EDS mapping, and ICP analyses, verified that COF/NiTCPP retained its chemical integrity and metal distribution with only slight activity attenuation, although weakened PXRD reflections indicated partial loss of long-range ordering after photocatalysis. These findings emphasize that controlling supramolecular assembly and aggregation states can be equally important as intrinsic chromophore properties in determining the activity of COF-based photocatalytic systems.

Morphological engineering of COFs into ultrathin nanosheets has also emerged as an efficient strategy for improving photocatalytic performance because reduced thickness shortens carrier-diffusion pathways and exposes more catalytically accessible surface sites. Compared with bulk COF powders, covalent organic nanosheets exhibit larger surface areas, enhanced contact with water molecules, and accelerated interfacial charge transport. For instance, Guo et al. reported an unusual self-driven photochemical exfoliation process in which iron-coordinated imine-linked COFs gradually transformed into ultrathin covalent organic nanosheets during photocatalytic water splitting (Fig. 11d) [153]. Two Fe-containing COFs, Py-2,2'-BPyPh-Fe and Py-3,3'-BPyPh-Fe, were employed together with eosin Y as both photosensitizer and intercalation agent. Comprehensive spectroscopic, morphological, photoelectrochemical, and mechanistic analyses, including PXRD, FT-IR, XPS, ICP-MS, UV-vis DRS, Mott-Schottky measurements, SEM, TEM, AFM, BET analysis, Raman spectroscopy, steady-state PL, TRFL, EIS, transient photocurrent response, isotope-labeling experiments, and outdoor sunlight tests, confirmed Fe-N coordination, visible-light-responsive band structures, water-derived hydrogen formation, and progressive nanosheets generation during catalysis. During photocatalytic H₂ evolution, insertion of eosin Y between stacked COF layers weakened van der Waals

interactions, while the rapid release of H₂ gas mechanically exfoliated the layered structures into nanosheets with thicknesses reduced from hundreds of nanometers to sub-2 nm dimensions (Fig. 11e). The resulting Fe-CONs exhibited dramatically enhanced carrier separation and transport, leading to a H₂ evolution rate of 67.94 mmol g⁻¹ h⁻¹ for the optimized Py-2,2'-BPyPh-Fe nanosheets, surpassing most previously reported non-noble-metal COF photocatalysts and even many noble-metal-containing systems. Photophysical and electrochemical comparisons showed that Fe-CONs possessed lower charge-transfer resistance, stronger photocurrent response, more efficient EY photoluminescence quenching, and shorter EY excited-state lifetime than the corresponding Fe-COF powders, directly linking nanosheet exfoliation with faster electron transfer and suppressed recombination. Importantly, H₂ evolution progressively increased during repeated catalytic cycles as exfoliation proceeded further, directly linking nanosheet formation with photocatalytic enhancement. Post-cycling XRD and FT-IR analyses further verified that the Fe-COF framework was retained after repeated photocatalytic operation, while outdoor solar irradiation demonstrated measurable hydrogen production under natural sunlight, supporting both operational stability and practical relevance. This work introduces a sustainable strategy in which photocatalytic H₂ evolution simultaneously drives the in situ generation of highly active COF nanosheets.

Porphyrin-based COFs have likewise emerged as highly effective photocatalytic platforms because conjugated porphyrinic macrocycles possess strong visible-light absorption, excellent redox tunability, and efficient π -electron delocalization. Moreover, ordered self-assembly of porphyrin units within crystalline 2D frameworks enhances charge mobility and suppresses recombination of photoinduced carriers. For instance, Liu et al. explored the influence of molecular conjugation on photocatalytic activity through the synthesis of two structurally analogous imine-linked porphyrin COFs, TPB-TAPP-COF and TFPPY-TAPP-COF, which differed only in the degree of conjugation and planarity of their donor building units [154]. Because the two frameworks exhibited nearly identical crystallinity, porosity, and surface area, they provided an ideal model system for establishing direct structure-activity correlations. The more planar and strongly conjugated TFPPY-based framework exhibited enhanced electron delocalization, narrower bandgap characteristics, and red-shifted light absorption relative to TPB-TAPP-COF. Comprehensive structural, spectroscopic, and photoelectrochemical investigations, including PXRD with Pawley refinement, FT-IR, solid-state ¹³C NMR, BET surface-area analysis, SEM, TEM, UV-vis diffuse reflectance spectroscopy, water-contact-angle measurements, time-correlated single-photon counting, XPS, Mott-Schottky analysis, electrochemical impedance spectroscopy, transient photocurrent response, time-resolved EPR spectroscopy, apparent quantum yield measurements, and post-photocatalytic FT-IR, UV-vis, and XRD analyses, collectively demonstrated that the enhanced π -conjugation and coplanarity of the TFPPY donor optimized the electronic structure, strengthened donor-acceptor interactions, lowered the optical bandgap, promoted charge separation and interfacial carrier transport, and reinforced electronic coupling with photodeposited Pt cocatalyst through stronger Pt-N coordination. These features substantially improved carrier

separation and migration under illumination, ultimately resulting in a H_2 evolution rate of $8700.2 \mu\text{mol g}^{-1} \text{h}^{-1}$, approximately double that of the TPB analogue. The longer excited-state lifetime, reduced charge-transfer resistance, higher transient photocurrent density, stronger light-induced EPR response, and suitable band-edge positions derived from Mott–Schottky measurements consistently established a direct correlation between molecular conjugation, accelerated charge-transfer dynamics, suppressed carrier recombination, and the superior hydrogen evolution performance of TFPPY-TAPP-COF, while post-reaction structural characterization confirmed preservation of the covalent framework despite a moderate reduction in crystallinity after prolonged photocatalysis. This work highlights precise molecular conjugation engineering as a decisive factor governing the photocatalytic efficiency of porphyrin-containing COFs.

To sum up, structural modulation, morphological regulation, and π -conjugation engineering have become indispensable strategies for optimizing the photocatalytic behavior of COF-based H_2 evolution systems. Fine control over framework planarity, interlayer stacking, conjugation pathways, and pore organization can effectively regulate light harvesting, carrier delocalization, and directional charge migration within crystalline organic networks. In particular, enhancement of π -electron conjugation and molecular ordering promotes rapid intraframework charge transport while suppressing recombination losses associated with localized excitonic states. Simultaneously, nanosheet engineering and morphological exfoliation significantly shorten carrier-diffusion distances, increase accessibility of catalytic interfaces, and strengthen interfacial contact with reactants, thereby improving overall photocatalytic efficiency. Regulation of supramolecular aggregation and interfacial assembly additionally demonstrates that photocatalytic activity is strongly influenced not only by intrinsic chromophore properties but also by the spatial organization and electronic communication of photoactive components within the framework. Moreover, localized electronic motifs such as keto-functionalized conjugated domains can serve as efficient charge-injection centers, providing alternative pathways for photoinduced electron extraction and proton reduction. Nevertheless, achieving simultaneous optimization of crystallinity, structural stability, charge mobility, and exciton dissociation remains highly challenging because these parameters are strongly interconnected at multiple length scales. Therefore, future advances in structurally engineered COF photocatalysts will require integrated molecular and morphological design approaches capable of synchronizing framework conjugation, nanoscale architecture, and interfacial charge-transfer dynamics to realize highly efficient and durable solar-driven hydrogen-production systems.

5.7. Cocatalyst engineering and noble-metal-free systems

Cocatalyst engineering has become a crucial strategy for enhancing photocatalytic H_2 evolution in COFs by accelerating charge separation and proton-reduction kinetics. While noble metals such as Pt remain highly effective electron sinks and catalytic centers, their scarcity and cost have driven the development of earth-abundant alternatives including transition-metal phosphides, Cu-based species, and molecular metal catalysts. Integration of noble-metal-free cocatalysts within

COF frameworks improves interfacial electron transfer, promotes carrier utilization, and optimizes hydrogen-adsorption energetics [155]. Simultaneously, the ordered and tunable structure of COFs enables uniform dispersion and stabilization of catalytic sites, preventing aggregation and improving long-term stability. Consequently, cocatalyst engineering and noble-metal-free design strategies have emerged as key approaches for constructing sustainable and high-performance COF photocatalysts for solar H_2 evolution [156]. Although noble-metal cocatalysts such as Pt, Pd, and Au remain highly effective for suppressing charge recombination through Schottky-junction formation, their scarcity, high cost, and aggregation tendency severely limit large-scale photocatalytic H_2 evolution. Consequently, the development of efficient noble-metal-free cocatalysts has become a major focus in COF-based photocatalysis [157]. Among emerging alternatives, transition-metal phosphides possess distinct advantages including earth abundance, rich catalytic sites, rapid charge-transfer capability, and tunable electronic structures. For instance, Yan et al. pioneered the integration of transition-metal phosphides with a visible-light-responsive TpPa-1-COF to construct fully noble-metal-free photocatalysts for water splitting [32]. Through a direct solvothermal strategy (Fig. 12a), several phosphide/COF composites were prepared, among which $\text{Ni}_{12}\text{P}_5/\text{TpPa-1-COF}$ exhibited the highest photocatalytic activity because of its abundant reactive surface sites and favorable hydrogen-adsorption energetics. Comprehensive structural, spectroscopic, photoelectrochemical, and theoretical analyses, including PXRD, FT-IR, N_2 sorption, TGA, SEM, TEM/HRTEM, EDS elemental mapping, XPS, UV–vis diffuse reflectance spectroscopy, Tauc analysis, Mott–Schottky measurements, transient photocurrent response, EIS, LSV, and DFT+U calculations, confirmed the successful anchoring of Ni_{12}P_5 nanoparticles on TpPa-1-COF and clarified their role as electron-collecting cocatalytic sites rather than light-absorbing framework components. Under visible-light irradiation, the optimized composite delivered an H_2 evolution rate of $31.6 \mu\text{mol h}^{-1}$, approximately nineteen times greater than pristine TpPa-1-COF and comparable to Pt-loaded analogues. Photoelectrochemical analysis (Fig. 12b) and theoretical calculations demonstrated that incorporation of Ni_{12}P_5 substantially enhanced framework conductivity, accelerated carrier migration, and promoted interfacial charge separation. The positive shifts of C 1s and N 1s signals together with the negative shift of P 2p peaks indicated directional electron transfer from TpPa-1-COF to Ni_{12}P_5 , while the strongest photocurrent response and smallest EIS arc among Ni_{12}P_5 -, Ni_2P -, and CoP-based composites directly correlated the superior HER activity with more efficient charge separation and lower interfacial resistance. The lowered thermodynamic barrier for H^* formation on Ni_{12}P_5 further facilitated proton reduction kinetics (Fig. 12c). DFT+U calculations further showed that the $\text{Ni}_{12}\text{P}_5(312)$ surface possessed the most favorable H-binding energetics and the lowest H formation barrier among the investigated phosphides, explaining why Ni_{12}P_5 outperformed Ni_2P and CoP under identical conditions. Recycling tests, together with post-photocatalytic PXRD, FT-IR, and SEM analyses, verified that the TpPa-1-COF framework and $\text{Ni}_{12}\text{P}_5/\text{TpPa-1-COF}$ composite structure were largely retained after repeated hydrogen-evolution cycles, supporting the operational stability of this noble-metal-free system. This work established transition-metal phosphides as highly promising

cocatalysts for constructing efficient noble-metal-free COF photocatalytic systems.

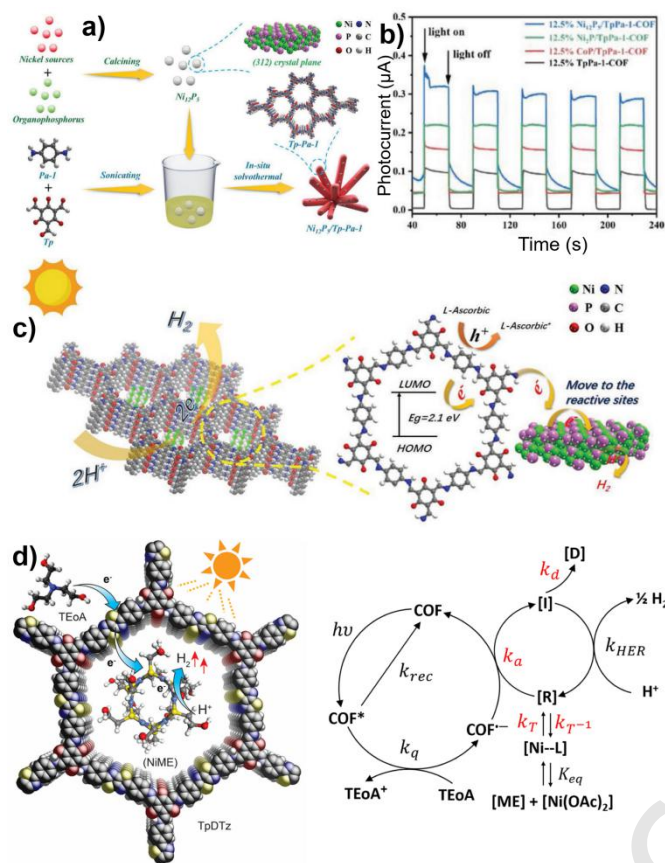


Figure 12 (a) Synthesis, (b) photocurrent response, and (c) charge transfer route of $\text{Ni}_{12}\text{P}_5/\text{TpPa-1-COF}$ for H_2 evolution [32]. Reprinted with permission from Ref. [32]. Copyright 2022, John Wiley & Sons. (d) Charge transfer mechanism of TpDTz/NiME for H_2 evolution [35]. Reprinted with permission from Ref. [35]. Copyright 2019, American Chemical Society.

The development of cocatalyst-free multifunctional photocatalysts is highly desirable because simplified catalytic architectures can simultaneously reduce system complexity, lower material cost, and maximize intrinsic synergistic interactions between catalytic centers. Owing to their atomically defined structures, high crystallinity, tunable porosity, and broad visible-light responsiveness, COFs provide an exceptional platform for constructing integrated photocatalytic systems. In particular, D–A engineering within COFs promotes efficient spatial separation of photoinduced carriers and enables directional charge migration toward catalytically active sites. Guided by these principles, Xiao et al. designed a dual-functional COF integrating cobalt porphyrin donor units with fluorenone acceptor moieties to construct a cocatalyst-free photocatalyst for simultaneous hydrogen and oxygen evolution [158]. The resulting Co-TPFO-COF possessed a highly crystalline mesoporous architecture with large surface area and efficient visible-light harvesting capability. Comprehensive structural, spectroscopic, photoelectrochemical, and theoretical investigations, including PXRD, FT-IR, SEM, TEM, BET, UV–vis diffuse reflectance spectroscopy, Mott–Schottky analysis, femtosecond transient absorption spectroscopy, light-induced XPS, photocurrent response, electrochemical impedance spectroscopy, linear sweep voltammetry, Bader charge analysis, and DFT calculations, collectively verified the successful integration of donor–acceptor building blocks and established

favorable band alignment for efficient charge separation and dual half-reaction catalysis. Femtosecond transient absorption spectroscopy revealed ultrafast intramolecular charge transfer from electron-rich Co-TP domains toward electron-deficient fluorenone sites, leading to spatially separated reduction- and oxidation-active centers. The transient absorption dynamics exhibited rapid electron-transfer and prolonged charge-separated states, while illumination-induced XPS peak shifts, enhanced photocurrent response, reduced interfacial charge-transfer resistance, and Bader charge analysis consistently demonstrated electron migration from Co-TP donor units toward fluorenone acceptors, thereby suppressing charge recombination and promoting directional carrier transport. Consequently, accumulated electrons at the fluorenone units promoted proton reduction, whereas holes localized at cobalt porphyrin sites efficiently drove water oxidation. The optimized photocatalyst achieved H_2 - and O_2 -evolution rates of 1015 and 2399 $\text{mmol g}^{-1} \text{h}^{-1}$, respectively, together with stable multicycle operation. The corresponding apparent quantum efficiencies reached 0.47% for H_2 evolution and 1.06% for O_2 evolution at 450 nm, providing quantitative evidence that the improved photophysical properties translated directly into enhanced photocatalytic performance. DFT calculations further demonstrated that the framework simultaneously lowered water-oxidation barriers and strengthened proton adsorption energetics, thereby facilitating both half-reactions within a single integrated architecture. Theoretical free-energy analyses further identified proton adsorption on fluorenone moieties and oxygen evolution at cobalt porphyrin sites as energetically favorable pathways, providing a quantitative structure–function relationship that rationalizes the experimentally observed bifunctional photocatalytic activity. This study establishes D–A-regulated bifunctional COFs as promising all-in-one photocatalytic systems for solar-to-fuel conversion.

To sum up, cocatalyst engineering has become a pivotal strategy for overcoming the kinetic and charge-transfer limitations of COF-based photocatalytic H_2 evolution systems. Although noble metals remain highly efficient proton-reduction centers, increasing emphasis has been directed toward developing earth-abundant alternatives capable of delivering comparable catalytic performance while reducing material cost and improving sustainability. Integration of transition-metal phosphides, Cu-based species, and coordinated molecular catalysts within crystalline COF architectures effectively enhances interfacial electron extraction, accelerates carrier migration, and optimizes hydrogen-adsorption energetics. In particular, strong electronic coupling between cocatalysts and conjugated frameworks promotes efficient charge separation and suppresses recombination losses, while the ordered porous structures of COFs provide spatial confinement that improves catalytic-site dispersion and stability. Furthermore, synergistic coupling between D–A electronic architectures and nonprecious-metal cocatalysts enables directional carrier transport and more efficient utilization of photoinduced electrons for proton reduction. The emergence of cocatalyst-free integrated systems additionally demonstrates that rational framework design can spatially separate reduction and oxidation centers within a single architecture, thereby enabling simultaneous multielectron photocatalytic reactions without external noble-metal assistance. Nevertheless, achieving long-term operational stability and maintaining efficient interfacial

charge-transfer dynamics in noble-metal-free systems remain major challenges because catalytic activity is highly sensitive to cocatalyst dispersion, electronic structure, and metal–framework interactions under irradiation conditions. Therefore, future progress in cocatalyst-engineered COFs will require precise regulation of interfacial electronic coupling, catalytic-site accessibility, and reaction-pathway energetics to develop highly efficient, stable, and economically viable photocatalytic hydrogen-production systems.

5.8. Molecular metal complexes

Integration of molecular metal complexes into COFs has emerged as an effective strategy for constructing well-defined single-site photocatalytic systems with tunable electronic structures and high catalytic selectivity. Unlike conventional nanoparticle cocatalysts, molecularly dispersed active sites provide uniform coordination environments, maximized metal utilization, and controllable proton-reduction pathways [159]. The crystalline and porous nature of COFs enables precise immobilization of molecular catalysts while facilitating efficient light harvesting and charge transport. Strong electronic coupling between the framework and coordinated metal complexes accelerates interfacial electron transfer and suppresses carrier recombination [160]. In addition, spatial confinement within ordered channels improves catalyst stability and prevents leaching during photocatalysis. Consequently, molecular and single-site catalytic architectures have become promising platforms for developing efficient, structurally precise, and noble-metal-efficient COF photocatalysts for H₂ evolution [161]. In parallel with SA engineering, molecularly defined noble-metal-free cocatalysts have emerged as promising alternatives for sustainable solar H₂ evolution. Nevertheless, coupling molecular catalysts with COF photosensitizers remains challenging because many molecular systems suffer from limited water stability, poor photochemical durability, and sluggish multielectron proton-reduction kinetics. Biswal et al. addressed these limitations by integrating a thiazolo[5,4-d]thiazole-linked COF (TpDTz) with a Ni-thiolate molecular cocatalyst generated in situ from Ni²⁺ salts and mercaptoethanol [35]. The rigid planar TzTz units endowed the COF with strong visible-light absorption, excellent oxidative stability, and efficient π -overlap for carrier transport, while the molecular Ni-thiolate clusters acted as robust proton-reduction centers reminiscent of [Ni–Fe] hydrogenase active sites. Comprehensive structural, spectroscopic, optoelectronic, and theoretical characterizations, including PXRD, solid-state ¹³C/¹⁵N NMR, FT-IR, electron microscopy, gas-sorption analysis, UV–vis diffuse reflectance spectroscopy, photoluminescence spectroscopy, cyclic voltammetry, and quantum-chemical calculations, confirmed the highly crystalline porous framework, extended visible-light harvesting, favorable band-edge alignment, and efficient electronic communication between the COF photosensitizer and the molecular cocatalyst. Under simulated solar irradiation in water using triethanolamine as sacrificial donor, the hybrid TpDTz/NiME system achieved sustained H₂ evolution with a rate of 941 $\mu\text{mol h}^{-1} \text{g}^{-1}$ and a turnover number exceeding 10³ over 70 h. Comprehensive parameter screening further established strong structure–property relationships involving cocatalyst composition, pH, sacrificial donors, and ligand environments. Photophysical investigations further demonstrated that the TzTz-bridged

framework exhibited broadened visible-light absorption, suitable conduction-band energetics for electron injection into the Ni-thiolate catalyst, and efficient hole scavenging by triethanolamine, while quantum-chemical calculations and kinetic modeling identified interfacial electron transfer from the COF to the molecular cocatalyst as the rate-determining process governing long-term hydrogen production. Importantly, implementation of a continuous-flow photocatalytic reactor enabled accurate real-time kinetic analysis and provided mechanistic insight into charge-transfer behavior within the hybrid system (Fig. 12d). The flow-reactor platform further enabled quantitative kinetic modeling with significantly improved measurement accuracy over conventional batch methods, revealing catalyst activation, deactivation, kinetic isotope effects, and charge-transfer kinetics that established a quantitative correlation between interfacial charge-transfer dynamics and sustained photocatalytic H₂ evolution. This work demonstrates the viability of combining molecularly defined earth-abundant cocatalysts with crystalline COF photoabsorbers to construct efficient and durable single-site photocatalytic platforms for sustainable H₂ evolution.

The rational integration of molecular catalysts within photoactive frameworks has also become an effective strategy for minimizing interfacial resistance in photocatalytic H₂ evolution. Although molecular cocatalysts exhibit high intrinsic activity, weak interfacial contact and energetically mismatched coupling with photosensitizers often impede rapid electron delivery and intensify charge recombination. COFs offer a unique platform to address these limitations because their chemically programmable architectures allow catalytic sites and light-harvesting units to be integrated within a single crystalline lattice. In this regard, Zhou et al. incorporated Salen-metal complexes into conjugated COF skeletons to construct M/Zn-Salen-COFs (M = Fe, Co, Ni) for photocatalytic H₂ evolution [7]. Comprehensive structural, spectroscopic, photoelectrochemical, and theoretical analyses, including PXRD/Pawley refinement, FT-IR, solid-state ¹³C NMR, BET, HR-TEM/AC-TEM, EDS mapping, XPS, XANES/EXAFS, wavelet-transform EXAFS, UV–vis DRS, Mott–Schottky, UPS, EIS, steady-state fluorescence, nanosecond transient absorption spectroscopy, EPR, and DFT calculations, confirmed the preservation of crystalline Salen-COF structures after metalation and clarified the metal-dependent charge-transfer and proton-reduction behavior. X-ray absorption fine structure analysis verified the formation of metal–N₂O₂ coordination environments, while spectroscopic investigations demonstrated efficient charge separation between the pyrene photosensitizer and adjacent proton-reduction centers. EXAFS fitting and WT-EXAFS verified atomically dispersed Co–N/O coordination without detectable Co–Co bonding, although post-photocatalytic characterization showed partial framework degradation, indicating that the Salen-Co sites remain chemically relevant but long-term structural integrity still requires careful evaluation. Spatial confinement of the catalytic sites within the ordered framework substantially shortened electron-transfer pathways and lowered interfacial transport resistance. Among the prepared materials, Co/Zn-Salen-COF exhibited the highest activity, achieving an H₂ evolution rate of 1378 $\mu\text{mol g}^{-1} \text{h}^{-1}$ without the assistance of noble-metal cocatalysts. Its superior performance was supported by the smallest EIS semicircle, nearly complete fluorescence quenching, a longer nanosecond

transient-absorption electron lifetime of 370 ns, light-induced Co^{II} -to- Co^{I} reduction observed by EPR, and improved activity relative to Pt-loaded analogues, collectively demonstrating more efficient electron utilization at the endogenous Salen-Co centers. The superior performance originated from the favorable H_2 evolution energetics of the cobalt Salen unit together with enhanced charge delocalization and reduced transfer resistance after cobalt incorporation. DFT calculations further identified the Salen-Co site as the most favorable proton-reduction center, with a lower H formation energy barrier than the corresponding Fe-, Ni-, and Zn-Salen analogues, providing a quantitative structure–activity relationship consistent with the experimental HER trend. This work highlights the effectiveness of embedding molecular catalytic motifs directly into crystalline COF backbones for constructing atom-economical photocatalysts with efficient proton-reduction capability.

Beyond covalent metal incorporation, precise immobilization of molecular catalysts on 2D COFs has emerged as an effective approach for constructing highly active single-site photocatalytic systems. Owing to their crystalline layered structures, broad visible-light absorption, prolonged carrier lifetimes, and low exciton-binding energies, 2D COFs provide versatile platforms for engineering catalytic interfaces. However, post-synthetic metalation often suffers from steric congestion within densely stacked layers, while pore confinement strategies are limited by catalyst leaching and sluggish outer-sphere electron-transfer kinetics. To address these issues, Huang et al. developed an enantioselective surface-assembly strategy for immobilizing a noble-metal-free molecular catalyst onto a chiral β -ketoenamine-linked COF for photocatalytic H_2 evolution [11]. A Co(salen) complex containing a chiral cyclohexane segment was selectively assembled onto a conformationally chiral COF surface through stereospecific interactions. The narrow microporous channels prevented catalyst penetration into the interior framework, thereby favoring ordered surface localization. Comprehensive structural, spectroscopic, electrochemical, photophysical, and theoretical analyses, including circular dichroism spectroscopy, PXRD, FT-IR, ICP-AES, XPS, Co K-edge XANES/EXAFS, wavelet-transform EXAFS, TEM/STEM, UV–vis DRS, Mott–Schottky analysis, transient photocurrent response, EIS, steady-state PL, femtosecond transient absorption spectroscopy, and DFT calculations, verified surface-confined Co(salen) immobilization, single-site Co dispersion, and chirality-induced electronic coupling at the COF–catalyst interface. Enantiomeric recognition induced the formation of additional chelating environments capable of axially coordinating the Co(salen) units, which established intimate electronic coupling between the catalyst and the photoactive framework. As a consequence, efficient inner-sphere electron transfer occurred across the COF–Co(salen) interface, markedly enhancing photocatalytic performance. XPS and XANES analyses showed an increased $\text{Co}^{2+}/\text{Co}^{3+}$ ratio in the enantiomeric assembly, while EXAFS and WT-EXAFS confirmed Co–O/N coordination without Co–Co scattering, excluding nanoparticle formation and supporting the single-site nature of the immobilized Co(salen) centers. The resulting hybrid system achieved an H_2 evolution rate of $5.70 \text{ mmol g}^{-1} \text{ h}^{-1}$ under visible-light irradiation together with excellent operational stability, outperforming previously reported noble-metal-free COF photocatalysts. This activity was further supported by a TOF of 6.7, an AQE of 0.48% at 475 nm,

the strongest photocurrent response, the smallest EIS semicircle, pronounced PL quenching, and a prolonged fs-TAS-derived carrier lifetime of 91.4 ps, directly linking stereoselective interfacial assembly with enhanced charge separation and faster electron utilization. Post-photocatalytic FT-IR, UV–vis DRS, PXRD, HR-TEM, DF-STEM, Co 2p XPS, and ICP-AES analyses confirmed that most immobilized Co(salen) remained attached without forming Co nanoparticles after cycling, although slight Co detachment was detected, making this system stable but still worthy of long-term leaching evaluation. This work demonstrates that stereochemically directed catalyst immobilization can precisely regulate interfacial charge-transfer pathways and offers a new conceptual framework for designing highly efficient single-site photocatalytic architectures.

The replacement of noble-metal cocatalysts with earth-abundant molecular catalysts represents another critical objective for sustainable COF-based artificial photosynthesis. However, integrating molecular proton-reduction catalysts with photoactive COFs remains challenging because efficient multielectron transfer requires favorable thermodynamic coupling, rapid charge migration, and sufficient catalyst photostability. Banerjee et al. addressed these limitations by coupling azine-linked COFs with cobaloxime molecular catalysts for visible-light-driven H_2 evolution [31]. In the presence of triethanolamine as sacrificial donor, the combination of the N_2 -COF photosensitizer and a chloro(pyridine)cobaloxime cocatalyst generated efficient photocatalytic H_2 evolution under simulated solar irradiation. Comprehensive structural, spectroscopic, electrochemical, and theoretical analyses, including PXRD, FT-IR, solid-state NMR, SEM, TEM, EDX, UV–vis spectroscopy, EPR, TCSPC lifetime measurements, Gibbs-free-energy estimation, and quantum-chemical calculations, verified the retained COF framework after photocatalysis and established thermodynamically feasible electron transfer from the photoexcited COF to the cobaloxime catalyst. Mechanistic analyses confirmed that the dissolved cobaloxime species acted as the true proton-reduction catalyst, whereas metallic cobalt formation through decomposition could be excluded. The unchanged post-reaction PXRD, FT-IR, solid-state NMR, SEM/TEM, and absence of cobalt deposition confirmed structural preservation of N_2 -COF and ruled out cobalt nanoparticles or cobalt oxide as the active phase. The molecular cocatalyst accepted photoinduced reducing equivalents from the COF and subsequently mediated proton reduction through multielectron redox cycling. Quantum-chemical modeling further supported an outer-sphere electron-transfer pathway rather than covalent coordination between N_2 -COF and cobaloxime, while UV–vis/EPR detection of reduced cobalt intermediates and the linear dependence of H_2 evolution on cobaloxime concentration supported a monometallic Co-hydride-based proton-reduction mechanism. Importantly, the strategy proved applicable to a broader family of azine- and hydrazone-linked COFs as well as structurally diverse cobaloxime derivatives. After optimization of solvent composition, pH, sacrificial donor concentration, and ligand stabilization, the system reached a H_2 evolution rate of $782 \text{ } \mu\text{mol h}^{-1} \text{ g}^{-1}$, TON of 54.4, initial TOF of 3.96 h^{-1} , and AQE of 0.16% at 400 nm, providing quantitative evidence for the role of COF crystallinity, porosity, and electronic coupling in determining catalytic output. This work demonstrates the feasibility of constructing noble-metal-free single-site

heterogeneous photocatalytic systems based entirely on molecularly defined components. More broadly, it highlights the fundamental requirements governing efficient COF–molecular cocatalyst integration, including framework stability, effective

carrier separation and transport, energetically favorable interfacial electron transfer, and compatibility between single-electron photophysical events and multielectron catalytic processes.

Table 1 Comparative summary of representative metal-integrated COF photocatalysts for H₂ evolution.

To sum up, incorporation of molecular metal complexes into crystalline COF architectures has emerged as an effective strategy for constructing atomically precise photocatalytic systems with highly tunable electronic structures and catalytic functionalities. In contrast to conventional nanoparticle

electron-transfer dynamics and catalytic efficiency. Nevertheless, maintaining long-term photochemical stability of molecular catalysts under irradiation conditions remains a major challenge because weak catalyst–framework interactions and multielectron reaction pathways may induce catalyst

Catalyst system	Metal type	Sacrificial agent	H ₂ evolution rate (mmol g ⁻¹ h ⁻¹)	AQE	TOF/TON	Stability	Ref.
Ni-COF-SCAU	Ni	AA	272.2	43.2%@420 nm	-	30 h	[2]
Pd MOF/COF	Pd	AA	13.98	5.9%@515 nm	227 h ⁻¹ /1136	120 h	[5]
COF-Cu ₃ TG/Ru	Ru	TEOA	11.88	0.62%@420 nm	-	32 h	[9]
COF-Co(salen)	Co	AA	5.70	0.48%@475 nm	n.r/6.7	12 h	[11]
TpBpy-Ni2%	Ni	AA	0.513	5.3%@475 nm	-	48 h	[14]
PB-COF-Pt-1%	Pt SA	AA	80.4	-	15.7 h ⁻¹ /n. r	35 h	[18]
ZnPor-DETH-COF	Zn+Pt	TEOA	0.413	0.32%	-	120 h	[28]
Co-PVP@TpPa-1-COF/SnS	Co	Glycerol	6.39	18.4%@400 nm	-	16 h	[29]
TpPa(Δ)-Cu	Cu	L-cysteine	14.72	0.78%@600 nm	9.0 h ⁻¹ /n.r	24 h	[30]
N ₂ -COF/cobaloxime	Co	TEOA	0.782	0.16%@400 nm	3.96 h ⁻¹ /54.4	8 h	[31]
TpDTz/NiME	Ni-thiolate	TEOA	0.941	0.2%@400 nm	2.3 h ⁻¹ /1000	70 h	[35]
Cu ₃ TpDTz-COF	Cu	AA	106.0	19.7%@420 nm	-	25 h	[38]
Cu-NH ₂ -MIL-125/TpPa-2	Cu	AA	276.0	51.25%@500	-	12 h	[40]
PtSA@S-TFPT	Pt SA	TEOA	11.4	4.65%@420 nm	-	9 h	[42]
Syn-Co-COF@Pt	Co+Pt	AA	47.2	1.71%@365	-	20 h	[47]
Pt-TAPT-COF	Pt SA	TEOA	670	0.8%@420 nm	-	40 h	[56]
COF-Py-H (Pt)	Pt	AA	488.5	9.53%@420 nm	-	n.r	[78]
TCOF-Pt SA3	Pt	Oxidative coupling	0.502	-	-	3 cycle	[93]
TPDA-BiPy@NiBr ₂	Ni	AA+ TEOA	34.13	5.9%@370 nm	-	8 h	[129]
TF _{0.5} CN-Cu	Cu	TEOA	10.5	-	-	12 h	[146]
TFFPY-TAPP@Pt	Pt	AA	8.70	0.12%@420 nm	-	16 h	[154]

cocatalysts, molecularly dispersed active centers provide uniform coordination environments, maximized metal utilization efficiency, and well-defined proton-reduction pathways. The ordered porosity and programmable topology of COFs further enable spatial confinement and stable immobilization of molecular catalysts while simultaneously promoting visible-light harvesting and long-range charge transport within the conjugated framework. Strong electronic coupling between molecular catalytic units and photoactive COF backbones significantly accelerates interfacial electron transfer and suppresses recombination losses, thereby improving utilization of photoinduced carriers. In particular, integration of noble-metal-free molecular catalysts such as cobaloxime, cobalt salen, and Ni-thiolate complexes demonstrates that efficient proton reduction can be achieved through cooperative regulation of coordination environments, charge-transfer pathways, and multielectron redox processes. Moreover, stereochemical assembly and framework-directed surface immobilization strategies reveal that precise control over catalyst localization and interfacial geometry can strongly influence inner-sphere

degradation, leaching, or deactivation. Therefore, future development of molecular-complex-integrated COFs will require deeper mechanistic understanding of interfacial electron-transfer processes together with precise coordination engineering to synchronize catalytic-site stability, carrier dynamics, and multielectron proton-reduction kinetics for efficient and durable solar H₂ evolution.

6. Gaps, targets, and promising avenues

6.1. Mechanistic comprehension and strategic design of metal-integrated COFs for H₂ evolution

Gaps:

(i) Despite rapid progress, the mechanistic picture of photocatalytic H₂ evolution over metal-integrated COFs remains insufficiently resolved. In many reports, the incorporated metal center is treated simply as a catalytic proton-reduction site, whereas its simultaneous roles in light absorption, exciton dissociation, charge trapping, interfacial electron delivery, and local proton management are rarely disentangled. This ambiguity is particularly critical for metalloporphyrin-,

bipyridine-, salen-, phenanthroline-, and glyoxime-based COFs, where the metal node is electronically coupled to the π -conjugated skeleton rather than being a passive cocatalyst. Recent examples, including nickel glyoximate-based metal-COFs and Ni-embedded bipyridine COFs, show that molecularly defined metal sites can promote H₂ evolution without relying exclusively on Pt, but the elementary sequence from photoexcitation to H-H bond formation remains only partially verified under operating conditions.

(ii) A central unresolved issue is how photogenerated charges migrate through the framework and reach the integrated metal centers before recombination. In metal-integrated COFs, charge transport is governed by the D-A strength of the organic backbone, interlayer π -stacking, crystallinity, linkage chemistry, metal-ligand orbital hybridization, and pore-level solvation. However, these parameters are often optimized empirically. For example, imine, β -ketoenamine, hydrazone, olefin, thiazole, and triazine linkages differ strongly in chemical robustness, conjugation, and polarity, yet their influence on exciton binding, carrier diffusion length, and electron residence time at the metal site is seldom quantified. Nanosized COFs and interfacially engineered COF photocatalysts have demonstrated that morphology and interface design can strongly alter H₂ evolution activity, underscoring that the active process is not dictated by molecular structure alone.

(iii) Another gap concerns the true chemical identity of the active metal state. Metal centers embedded in COFs may undergo photoinduced reduction, ligand-field distortion, axial coordination by water or sacrificial donors, protonation of adjacent heteroatoms, or partial demetallation. Yet many studies infer activity from post-reaction characterization, which cannot capture transient M-H, M-H₂, M-OH, or protonated ligand intermediates. This limitation is especially important for Ni, Co, Fe, Cu, and Pt-integrated COFs, where changes in oxidation state and coordination geometry can determine whether proton reduction occurs at the metal center, at a ligand radical, at a metal-ligand cooperative site, or at deposited metallic clusters.

(iv) Productivity is also frequently reported without sufficient distinction between intrinsic and apparent activity. H₂ evolution rates can be enhanced by high surface area, improved dispersion, residual metal salts, photodeposited NPs, or sacrificial-agent oxidation kinetics. Consequently, the field still lacks rigorous correlations between metal-site density, quantum efficiency, turnover frequency, long-term structural integrity, and catalytic selectivity for proton reduction over competing photodegradation or side reactions. The continued reliance on noble-metal cocatalysts in many COF systems further obscures whether the integrated metal site is the primary catalytic center or merely a photosensitizing/charge-relay component.

Targets:

(i) A primary target should be the direct identification of catalytic intermediates and charge-separated states under photocatalytic conditions. Operando X-ray absorption spectroscopy, electron paramagnetic resonance, transient absorption spectroscopy, time-resolved photoluminescence, in situ infrared spectroscopy, and resonance Raman spectroscopy should be combined to follow metal oxidation-state changes, ligand radical formation, proton-coupled electron transfer, and M-H generation. Such measurements would move the field beyond static structure-activity comparisons and reveal whether

the decisive step is exciton separation, electron migration, proton adsorption, hydride formation, or H₂ desorption.

(ii) A second target is to establish design rules that connect framework electronics with metal-site catalysis. The optical band gap, CB potential, exciton lifetime, metal-centered redox potential, and proton-reduction overpotential should be treated as coupled descriptors rather than isolated parameters. In this context, metalloporphyrin COFs, bipyridine-metal COFs, and nickel glyoxime COFs offer powerful model platforms because their coordination geometry and electronic structure can be synthetically varied while retaining ordered porosity.

(iii) A further target is to clarify the role of the pore microenvironment. Metal-integrated COFs should be designed not only as light absorbers but also as proton-delivery architectures. Hydrophilic channels can facilitate water access and proton transport, whereas locally hydrophobic regions may suppress nonproductive recombination and stabilize reactive hydride-like species. Systematic variation of pore size, pendant acid/base groups, axial ligands, interlayer spacing, and sacrificial donor compatibility will be essential for converting structural tunability into predictable H₂ evolution performance.

(iv) Finally, reliable benchmarking is needed. Future reports should provide wavelength-dependent apparent quantum yields, solar-to-hydrogen metrics where applicable, isotope-labeled experiments using D₂O or H₂O/D₂O mixtures, metal leaching tests, poisoning controls, post- and operando structural analysis, and turnover numbers normalized to accessible metal sites. These data are necessary to distinguish a genuine metal-integrated COF photocatalyst from a COF-supported metal residue or in situ-generated NPs system.

Promising avenues:

(i) One promising direction is the construction of electronically coupled metal-ligand catalytic pockets within D-A COFs. Rather than placing a metal complex as an isolated pendant unit, the metal center should be integrated into the conjugated pathway so that photoinduced electrons are funneled toward the catalytic site. Bipyridine-Ni/Co, porphyrin-Co/Ni/Fe, salen-Co, and glyoxime-Ni motifs are particularly attractive because their redox potentials and coordination geometries can be tuned at the molecular level.

(ii) A second avenue is noble-metal-free cooperative catalysis. Dual-site COFs that combine a photosensitizing metal unit with a separate proton-reduction metal center can mimic molecular dyads while retaining heterogeneous stability. Recent dual non-noble-metal COF designs, such as Cu-based photosensitizer units paired with Co catalytic sites, point toward modular architectures in which light harvesting and proton reduction are spatially organized but electronically connected.

(iii) A third opportunity lies in interfacial and morphological engineering. Nanoscale COFs, COF/MOF hybrids, COF/MXene composites, and covalently coupled heterojunctions can shorten carrier-migration distances and improve charge extraction. However, these architectures should be designed with mechanistic precision: the interface must provide directional electron flow to the metal site rather than merely increase surface area or light scattering.

(iv) A fourth promising route is dynamic coordination chemistry. Axially labile metal centers, proton-responsive ligands, and redox-active linkers could allow the COF to reorganize during catalysis, stabilizing key hydride or protonated intermediates only under illumination. This strategy would transform metal-

integrated COFs from static crystalline scaffolds into adaptive photocatalytic matrices.

6.2. Materials engineering for performance optimization Gaps:

(i) Metal-integrated COFs have created a powerful platform for photocatalytic H₂ evolution because they can combine ordered light-harvesting skeletons with molecularly defined catalytic metal sites. However, many reported systems still operate as COF-metal composites rather than truly integrated photocatalytic architectures. In several cases, the metal center improves activity, but its precise role in exciton dissociation, electron accumulation, proton adsorption, and H-H bond formation remains insufficiently resolved. This makes it difficult to distinguish whether the enhanced H₂ evolution originates from genuine metal-mediated catalysis, improved crystallinity, altered hydrophilicity, suppressed recombination, or residual noble-metal co-catalysts.

(ii) A major bottleneck is the weak electronic communication between the COF backbone and the incorporated metal unit. Metal porphyrins, phthalocyanines, bipyridines, terpyridines, salen motifs, and diimine pockets can introduce catalytic centers, but if orbital coupling with the π -conjugated framework is poor, photoinduced electrons remain localized in the organic scaffold and recombine before reaching the proton-reduction site. Therefore, merely increasing the metal content does not guarantee higher photocatalytic efficiency. The critical issue is whether the framework can deliver electrons to the metal center rapidly, directionally, and repeatedly under illumination.

(iii) Another unresolved problem is the structural instability of metal sites under photocatalytic turnover. Earth-abundant Ni, Co, Fe, Cu, and Mo centers are attractive alternatives to Pt, yet they can undergo demetallation, ligand exchange, photoreduction, oxidation, or aggregation during irradiation. Such transformations may generate NPs or amorphous metal species that obscure the identity of the real active site. For review-level discussion, this is especially important: without post-catalytic PXRD, XPS, EXAFS/XANES, ICP analysis, TEM, and recycling data, claims of “single-site” or “molecularly integrated” catalysis remain incomplete.

(iv) A further limitation lies in the mismatch between light absorption and catalytic turnover. Many COFs absorb visible light, but their excitons are strongly bound, and charge transport is often limited by imperfect π -stacking, grain boundaries, interlayer disorder, and poor contact with the aqueous phase. Recent nano-COF studies show that reducing COF dimensions can improve water dispersibility and light harvesting, demonstrating that morphology can be as decisive as chemical composition for photocatalytic H₂ evolution.

(v) The field also lacks sufficient control over the local proton-transfer environment. Photocatalytic H₂ evolution requires not only electrons but also continuous proton supply to the active site. Hydrophobic pores, blocked channels, dense stacking, or poorly wetted crystallites can limit proton diffusion even when the COF has favorable optical absorption. Thus, the pore wall, linkage polarity, hydrogen-bonding network, and local acid-base functionality must be considered part of the catalytic design rather than passive structural features.

(vi) Finally, many studies still rely on sacrificial electron donors such as triethanolamine, ascorbic acid, methanol, or lactic acid. Although useful for benchmarking, these systems do not fully reflect overall water splitting. The next challenge is to design

metal-integrated COFs that can operate with reduced dependence on sacrificial reagents, ideally through coupling with suitable water-oxidation components, S-scheme architectures, or redox-balanced tandem systems.

Targets:

(i) A primary target is to transform metal-integrated COFs from metal-decorated absorbers into electronically coupled photocatalytic lattices. The metal site should be embedded within the conjugated pathway so that photoexcitation of the COF directly promotes charge transfer toward the catalytic center. Metalloporphyrin and metallophthalocyanine COFs are particularly valuable because the macrocyclic metal center can tune visible-light absorption, charge separation, and proton-reduction energetics within one periodic framework. Recent reviews emphasize that metalloporphyrin COFs combine porphyrinic light absorption with metal-centered catalytic functionality and ordered charge-transport channels.

(ii) A second target is the deliberate construction of D-A metalated frameworks. Electron-rich units such as pyrene, triphenylamine, benzotrithiophene, or porphyrin donors can be paired with electron-deficient triazine, benzothiadiazole, quinoxaline, cyano-vinylene, diimide, or bipyridine-metal acceptor sites. This arrangement can generate internal polarization, accelerate exciton separation, and direct electrons toward metal centers. D-A COF design is now recognized as a major route to improve charge separation in photocatalytic H₂ evolution.

(iii) A third target is to replace Pt co-catalysts with framework-confined base-metal catalytic centers. Nickel bipyridine, cobalt porphyrin, cobalt diimine, iron porphyrin, molybdenum sulfide-like motifs, and Cu- or Ni-coordinated N-rich pockets should be engineered with suitable proton affinity and hydride-formation energetics. A recent nickel-embedded COF study showed that post-synthetic Ni coordination with imine and bipyridine nitrogen atoms can improve planarity, conjugation, and photocatalytic H₂ evolution, illustrating how metalation can modify both catalytic and electronic properties.

(iv) Another important target is to stabilize the metal site through strong coordination and spatial confinement. Instead of weakly adsorbed metal ions or NPs, the preferred structures should contain chelating N₄, N₂O₂, N₄S₂, porphyrinic, phthalocyaninic, bipyridyl, or salen-like coordination pockets. These motifs can suppress metal migration, aggregation, and leaching while maintaining defined catalytic geometry. For higher credibility, the stability claim should be supported by metal-leaching quantification, identical-location microscopy where possible, operando spectroscopy, and comparison between pre- and post-reaction coordination environments.

(v) A further target is morphology-directed charge utilization. Ultrathin COF nanosheets, nanofibers, hollow spheres, oriented films, and crystalline thin layers can shorten exciton diffusion distances, expose more active metal sites, and improve contact with water. Nanoscale COFs have been reported to outperform bulk analogues because downsizing improves dispersibility and light harvesting, making size control a rational performance parameter rather than a secondary synthetic feature.

(vi) Finally, metal-integrated COFs should be assessed using more rigorous photocatalytic metrics. In addition to H₂ evolution rate, reports should include apparent quantum yield, turnover number per metal site, turnover frequency, wavelength-dependent action spectra, long-term cycling, isotope or control

experiments when relevant, and post-catalytic structural verification. These metrics are essential for distinguishing genuine materials optimization from apparent activity increases caused by higher surface area, residual metal salts, or uncontrolled co-catalyst formation.

Promising avenues:

(i) One promising avenue is the design of single-site metal COFs for molecularly interpretable H_2 evolution catalysis. Periodic Co-N₄, Ni-N₄, Fe-N₄, Cu-N₄, and Mo-containing coordination environments can act as uniform proton-reduction centers when they are electronically connected to the photoactive skeleton. Such systems allow systematic comparison of metal identity, spin state, coordination geometry, axial ligation, and proton-binding energy. This direction is especially powerful because it can bridge homogeneous molecular catalysis and heterogeneous photocatalysis within one crystalline platform.

(ii) A second avenue is the development of metalloporphyrin and metallophthalocyanine COFs with built-in light-harvesting and catalytic functions. Porphyrin- and phthalocyanine-based frameworks provide intense visible absorption, extended π -conjugation, and tunable central metals. Isostructural porphyrin COFs containing different metals have already been used to study how metal identity affects photocatalytic H_2 evolution, offering a model strategy for structure-activity correlation.

(iii) A third strategy is post-synthetic metalation of preorganized coordination pockets. This approach allows the same parent COF to be metalated with different ions, enabling direct comparison of Ni, Co, Fe, Cu, Zn, or Pd centers without changing the overall topology. It is particularly useful for bipyridine-, terpyridine-, phenanthroline-, salen-, and catechol-containing COFs. However, the metalation degree must be quantified carefully, and uncoordinated metal salts must be removed thoroughly to avoid misleading activity assignments.

(iv) Another promising direction is pore-environment engineering for proton delivery. Proton relays such as imidazole, pyridine, sulfonic acid, phenolic OH, carboxyl, triazole, or amide groups can be positioned near the metal center to facilitate proton-coupled electron transfer. In this design, the pore does not simply host reactants; it regulates hydration, proton mobility, local polarity, and intermediate stabilization. Such microenvironmental control could be decisive for lowering kinetic barriers to H-H bond formation.

(v) A further avenue is the creation of 2D metalated COF nanosheets and oriented films. Exfoliated layers reduce charge-transport distances and expose metal sites on accessible surfaces, while oriented films can align π -stacked columns with the direction of electron extraction. These architectures are particularly relevant for photoelectrochemical H_2 evolution, where intimate contact between the COF, conductive substrate, and electrolyte is required.

(vi) Heterojunction construction also offers a strong route forward. Metal-integrated COFs can be coupled with g-C₃N₄, TiO₂, CdS, ZnIn₂S₄, black phosphorus, perovskite-inspired semiconductors, or conductive carbon supports to form type-II, S-scheme, or Z-scheme charge-transfer pathways. Recent work on COF-based heterojunction photocatalysts highlights their value in improving light harvesting, charge separation, and surface redox reactions.

(vi) Plasmonic enhancement is another selective but useful strategy. Au, Ag, or Cu nanostructures can be incorporated near

metalated COF domains to intensify visible absorption through localized surface plasmon resonance, near-field amplification, or hot-electron injection. However, such systems should be discussed cautiously: the plasmonic component must be positioned to support charge delivery to the metal catalytic site, not merely to increase optical absorption.

(vii) Finally, the most forward-looking avenue is the integration of metalated COFs into overall water-splitting or tandem photocatalytic systems. For this purpose, H_2 evolution active metalated COFs must be paired with O₂ evolution catalysts, redox mediators, or complementary photoabsorbers. Photocatalytic overall-reaction studies involving MOFs and COFs increasingly emphasize the need to move beyond half-reaction H_2 evolution toward redox-balanced solar fuel production.

6.3. Targeting selective, scalable, and sustainable photocatalytic H_2 evolution

Gaps:

(i) Despite substantial advances in metal-integrated COFs for photocatalytic H_2 evolution, most reported systems still prioritize apparent H_2 evolution rates over mechanistic selectivity and catalytic sustainability. In many cases, the measured activity reflects a convolution of light absorption, sacrificial-agent oxidation, NPs-assisted proton reduction, and framework sensitization, rather than a clearly defined metal-centered H_2 evolution pathway. Consequently, the true catalytic contribution of the incorporated metal site frequently remains ambiguous.

(ii) A central limitation arises from the insufficient control over proton-coupled electron transfer (PCET) within the COF architecture. Efficient H_2 evolution requires synchronized proton delivery, electron accumulation, and H-H bond formation at the catalytic center. However, many metal-integrated COFs possess poorly organized proton-transport pathways, heterogeneous hydration environments, or energetically mismatched redox states, resulting in sluggish proton reduction kinetics and elevated recombination losses. Even when charge separation is improved, the absence of spatially coordinated proton relays often prevents efficient conversion of long-lived electrons into molecular H_2 .

(iii) Another persistent issue is the lack of precision in intermediate binding energetics at the metal center. The catalytic performance of Ni, Co, Fe, Mo, Cu, or molecularly dispersed bimetallic sites is governed by the adsorption free energy of H^* , yet many current COFs cannot regulate this parameter with sufficient electronic fidelity. Overly weak H^* adsorption suppresses proton reduction, whereas excessively strong binding hinders H_2 desorption and promotes catalyst poisoning. Because the electronic density surrounding the metal site is strongly influenced by linker conjugation, coordination geometry, heteroatom distribution, and interlayer interactions, even subtle structural disorder can substantially alter HER kinetics.

(iv) The field also faces a major challenge in distinguishing intrinsic molecular-site catalysis from in situ generated metal NPs. Under prolonged irradiation, coordinated metal ions may undergo reduction, cluster formation, or photochemical reconstruction. Such transformations are particularly problematic for cobalt, nickel, and copper systems, where photogenerated electrons can induce metal aggregation under sacrificial conditions. As a result, many reports claiming atomically dispersed HER sites lack sufficient operando

evidence to confirm catalytic-site integrity during turnover.

(v) Scalability represents another critical bottleneck. Most metal-integrated COFs are synthesized as microcrystalline powders through solvothermal methods requiring dilute conditions, prolonged heating, and limited batch reproducibility. These materials often exhibit poor dispersibility, low processability, and weak adhesion to conductive supports, hindering their integration into continuous-flow photoreactors or photoelectrochemical devices. Moreover, photocatalytic performance obtained in small-volume batch systems under high sacrificial-reagent concentrations frequently deteriorates under realistic irradiation intensity, neutral pH conditions, or scaled-up reactor geometries.

(vi) In addition, long-term operational stability remains inadequately addressed. Continuous illumination can trigger linker oxidation, hydrolysis of dynamic covalent bonds, interlayer exfoliation, metal leaching, or pore collapse. Particularly under aqueous H_2 evolution conditions, accumulated radicals and reactive oxygen-containing intermediates may progressively degrade framework crystallinity and disrupt metal coordination environments. Therefore, many currently reported systems demonstrate impressive short-term activity but insufficient durability for practical solar-fuel generation.

(vii) Another unresolved issue is the dominance of sacrificial-agent-driven half reactions. Triethanolamine, methanol, ascorbic acid, sulfides, and amines are widely employed to consume photoinduced holes, thereby artificially enhancing H_2 evolution efficiency. However, these conditions bypass the kinetic complexity of overall water splitting and obscure the true oxidative stability of the photocatalyst. Consequently, catalyst designs optimized under sacrificial conditions may not translate into sustainable solar-to-hydrogen systems.

(viii) Finally, the field lacks sufficiently standardized benchmarking protocols. Differences in light intensity, reactor geometry, catalyst loading, sacrificial-agent concentration, dissolved gases, and metal quantification often make direct comparison between studies unreliable. Without normalization to active-site density, apparent quantum yield, or turnover frequency per metal center, the rational evaluation of structure–performance relationships remains difficult.

Targets:

(i) A major target is the development of electronically programmable metal-integrated COFs in which the coordination environment, redox properties, and proton affinity of the metal center can be deliberately engineered. Rather than functioning as passive catalytic decorations, the incorporated metal units should operate as electronically coupled reaction centers capable of mediating sequential proton-coupled electron-transfer events with minimal energetic loss.

(ii) An equally important objective is to establish precise control over H_2 adsorption energetics through coordination-environment modulation. Tailoring ligand-field strength, π -backbonding interactions, heteroatom polarization, and local electron density around the metal center can regulate H^* stabilization and H_2 desorption kinetics. This strategy is especially relevant for Ni– N_4 , Co– N_4 , Fe– N_4 , Mo– S_x -like, and Cu–N coordination motifs embedded within conjugated COF lattices.

(iii) Another critical target is the integration of spatially organized proton-transport networks within the pore architecture. Proton relays based on imidazole, pyridine, triazole, sulfonic

acid, phenolic hydroxyl, carboxylate, or amide functionalities can facilitate directional proton migration toward catalytic metal sites. Such microenvironment engineering is essential for synchronizing proton transport with photoinduced electron delivery, thereby accelerating H–H bond formation and minimizing kinetic mismatch.

(iv) The field must also move toward noble-metal-minimized or noble-metal-free H_2 evolution systems. Although Pt remains the benchmark co-catalyst because of its near-optimal H_2 binding energy, sustainable photocatalytic H_2 evolution requires the replacement of Pt with earth-abundant alternatives. Achieving this objective demands atomically precise coordination environments that can emulate Pt-like proton-reduction energetics while preserving structural stability under prolonged irradiation.

(v) Another major target involves constructing intrinsically conductive and highly conjugated metalated COFs. Conventional COFs often suffer from low carrier mobility due to localized electronic states and inefficient interlayer transport. Therefore, extended π -conjugated frameworks containing porphyrins, phthalocyanines, tetrathiafulvalene, quinones, acetylene bridges, fused aromatic motifs, or ladder-type backbones should be developed to support rapid electron migration toward catalytic centers.

(vi) Equally important is the engineering of directional charge-transport pathways. Ordered π -columnar stacking, anisotropic crystallization, in-plane d– π conjugation, and oriented thin-film growth can minimize trap-state formation and facilitate vectorial electron flow from the photoinduced framework toward proton-reduction sites. Such directional transport is particularly critical for suppressing bulk recombination in highly crystalline systems.

(vii) Another target is the realization of photocatalytic overall water splitting without sacrificial reagents. This requires coupling efficient H_2 evolution active metalated COFs with complementary oxidation catalysts, S-scheme architectures, or tandem photoabsorbers capable of sustaining balanced redox chemistry under solar illumination. Achieving stable overall water splitting would represent a decisive transition from laboratory H_2 evolution benchmarking to practical solar-fuel production.

(viii) Furthermore, scalable fabrication strategies must become a priority. Continuous-flow synthesis, interfacial polymerization, vapor-assisted crystallization, electrophoretic deposition, and layer-by-layer assembly should be explored to produce large-area metal-integrated COF films with controlled thickness, crystallinity, and substrate adhesion. These processing strategies are essential for integrating COFs into industrially relevant photoelectrochemical platforms.

(ix) Finally, future catalyst evaluation should incorporate rigorous operando methodologies. Time-resolved spectroscopy, transient absorption analysis, operando X-ray absorption spectroscopy, in situ infrared measurements, isotope-labeled proton tracking, and electrochemical impedance studies should be routinely combined with photocatalytic testing to establish unambiguous structure–activity correlations.

Promising avenues:

(i) One particularly promising avenue is the construction of single-site metal-integrated COFs with crystallographically defined catalytic environments. Periodically distributed Co– N_4 , Ni– N_4 , Fe– N_4 , Mo– N_2S_2 , or Cu–N coordination motifs can

function as uniform proton-reduction centers while enabling direct investigation of electronic-structure effects on H₂ evolution kinetics. Such systems bridge the conceptual gap between homogeneous molecular catalysis and heterogeneous photocatalysis.

(ii) Another impactful strategy involves the design of D–A metalated COFs with built-in internal electric fields. Electron-rich units such as pyrene, triphenylamine, benzodithiophene, or tetrathiafulvalene can be coupled with electron-deficient triazines, benzothiadiazoles, quinoxalines, cyano-vinylene units, or metal-coordinated acceptor nodes. This D–A polarization can facilitate exciton dissociation, directional electron migration, and preferential charge accumulation at H₂ evolution active metal sites.

(iii) The emergence of fully conjugated and ladder-type COFs offers another transformative opportunity. In these architectures, rigid covalent fusion and extended π -delocalization minimize energetic disorder and support high carrier mobility. When combined with embedded metal catalytic centers, such electronically coherent frameworks may approach semiconductor-like charge-transport behavior while maintaining molecular-level tunability.

(iv) A highly promising direction is the fabrication of oriented COF thin films and nanosheets on conductive substrates. Interfacial crystallization, solvothermal epitaxy, and layer-by-layer deposition can produce vertically aligned or in-plane oriented films with reduced grain boundaries and enhanced interfacial charge transfer. Such architectures improve carrier extraction efficiency and are particularly attractive for photoelectrochemical H₂ evolution.

(v) Another compelling strategy involves multifunctional heterojunction engineering. Metal-integrated COFs can be interfaced with graphitic carbon nitride, TiO₂, black phosphorus, MXenes, transition-metal sulfides, or perovskite-inspired absorbers to construct type-II, S-scheme, or Z-scheme charge-transfer pathways. Rational band alignment within these heterostructures can spatially separate oxidative and reductive carriers while prolonging electron lifetime at H₂ evolution active sites.

(vi) The incorporation of dual-metal or heterobimetallic catalytic centers also represents a significant opportunity. Cooperative interactions between adjacent metal sites may facilitate sequential proton adsorption, electron accumulation, and H–H coupling steps more efficiently than isolated single-metal centers. For example, Ni–Co, Fe–Co, or Mo–Ni combinations could synergistically balance proton affinity and electron-transfer kinetics.

(vii) Another forward-looking avenue is microenvironment-directed catalysis within COF nanopores. Tailoring pore polarity, hydration behavior, proton accessibility, and local dielectric properties can influence catalytic intermediate stabilization and regulate proton-coupled electron transfer. Hydrophobic domains may suppress competitive water adsorption, whereas hydrophilic proton-relay channels can accelerate proton transport toward catalytic centers.

(viii) Machine-learning-assisted catalyst discovery also provides enormous potential. Closed-loop workflows integrating DFT-derived descriptors, automated synthesis, high-throughput photocatalytic screening, and operando characterization can accelerate the identification of optimal metal–linker combinations, band structures, and proton-transfer motifs. Such

data-driven approaches are expected to dramatically reduce empirical trial-and-error experimentation.

(ix) Finally, the ultimate frontier lies in the development of integrated solar-fuel platforms based on metalated COFs. Rather than functioning solely as suspended photocatalyst powders, future systems should be incorporated into membrane reactors, tandem photoelectrochemical assemblies, or wireless artificial-photosynthesis devices capable of continuous H₂ evolution under natural sunlight. Achieving this transition will require simultaneous optimization of catalytic activity, charge transport, structural robustness, interfacial engineering, and scalable processability within a unified materials-design framework.

7. Techno-economic perspectives

Although remarkable improvements in photocatalytic H₂ evolution have been achieved through rational metal integration within COFs, the practical implementation of these materials will ultimately depend on their techno-economic viability in addition to laboratory-scale catalytic performance. Presently, most reported metal-integrated COFs remain at an early stage of technological development, where catalyst synthesis, reactor design, long-term stability, and manufacturing costs continue to represent major barriers to commercial deployment. Consequently, evaluating these factors alongside photocatalytic activity is essential for identifying realistic pathways toward industrial application. The economic competitiveness of metal-integrated COFs is strongly influenced by the complexity of framework synthesis. Most highly crystalline COFs are prepared through conventional routes requiring high-purity organic monomers, elevated temperatures, extended reaction periods, and considerable solvent consumption. These synthetic requirements increase production costs compared with conventional inorganic photocatalysts. Additional post-synthetic metal incorporation, purification, activation, and solvent recovery further increase processing complexity. Consequently, the development of rapid, scalable, and environmentally benign synthetic methodologies, including continuous-flow production, mechanochemical synthesis, microwave-assisted crystallization, and solvent-minimized approaches, could substantially improve manufacturing efficiency while lowering production expenses. Metal selection also plays a decisive role in overall process economics. Noble metals such as Pt, Pd, Ru, Ir, and Au frequently deliver exceptional catalytic activity because of their favorable electronic structures and low overpotentials for proton reduction. However, their limited natural abundance and high market prices significantly increase catalyst cost and may restrict large-scale deployment.

In contrast, earth-abundant transition metals including Co, Ni, Fe, Cu, and Mo provide a more economically attractive alternative. Recent studies have demonstrated that appropriately engineered coordination environments within COFs can substantially improve the intrinsic activity of these non-noble metals, thereby narrowing the performance gap while reducing dependence on critical raw materials. Increasing the utilization efficiency of individual metal atoms through single-atom or atomically dispersed catalytic sites represents another promising strategy for minimizing metal consumption without sacrificing catalytic performance. Catalyst durability is equally important

from an economic perspective because replacement frequency directly influences operating costs. Although many metal-integrated COFs exhibit satisfactory stability during laboratory recycling experiments, most investigations evaluate catalyst performance over relatively short irradiation periods under controlled conditions. Industrial implementation will require prolonged operation under continuous solar irradiation, repeated wet-dry cycling, fluctuating temperatures, and natural water matrices. Potential framework degradation, metal leaching, photocorrosion, and loss of crystallinity may reduce catalyst lifetime and increase replacement costs. Accordingly, future studies should prioritize long-duration stability testing together with standardized durability protocols that better represent practical operating environments.

Reactor engineering constitutes another critical component of techno-economic performance. Most reported photocatalytic H₂ evolution experiments employ suspended catalyst powders irradiated within small batch reactors under simulated sunlight. Although these systems provide valuable mechanistic information, they are not readily transferable to large-scale hydrogen production. Practical deployment will require efficient photoreactor configurations capable of maximizing photon utilization, minimizing mass-transfer limitations, facilitating catalyst recovery, and ensuring uniform light distribution over large illuminated areas. The integration of immobilized COF films, structured supports, membrane-assisted reactors, and continuous-flow photoreactors may significantly improve process efficiency while reducing operational costs associated with catalyst separation and recycling. Beyond catalyst preparation, the overall economic performance of solar H₂ evolution depends on solar-to-hydrogen conversion efficiency, quantum efficiency, catalyst lifetime, and H₂ productivity under natural sunlight. Improvements in any single parameter are unlikely to ensure commercial competitiveness if accompanied by poor durability or expensive catalyst fabrication. Therefore, future optimization should simultaneously target efficient visible-light harvesting, rapid charge separation, minimized noble-metal loading, robust structural stability, and scalable manufacturing methods.

Comprehensive techno-economic assessments should additionally incorporate catalyst synthesis energy demand, raw-material availability, solvent recycling, operational lifetime, H₂ evolution rate, and end-of-life catalyst recovery to establish realistic estimates of process feasibility. Life-cycle considerations further strengthen the attractiveness of metal-integrated COFs. Compared with conventional hydrogen production based on fossil fuels, photocatalytic water splitting offers the possibility of direct solar energy utilization without greenhouse-gas emissions during hydrogen generation. Nevertheless, the environmental benefits depend on sustainable catalyst production, reduced solvent consumption, efficient recovery of valuable metals, and extended catalyst service life. The adoption of renewable feedstocks for organic monomer synthesis, recyclable reaction media, and circular strategies for recovering incorporated metals could further improve both environmental sustainability and economic competitiveness. Hence, metal-integrated COFs represent an emerging class of photocatalysts with considerable potential for sustainable solar

hydrogen production. However, their transition from laboratory demonstrations to industrial implementation will require simultaneous advances in catalyst synthesis, material durability, reactor engineering, and system-level economic optimization. Future research should therefore complement photocatalytic performance evaluation with standardized techno-economic and life-cycle analyses, enabling direct comparison with established H₂ evolution technologies and accelerating the practical development of COF-based solar fuel systems.

8. Conclusion

Metal-integrated COFs have emerged as one of the most conceptually versatile platforms for photocatalytic H₂ evolution because they unite the structural order of crystalline organic semiconductors with the catalytic precision of molecular and atomic metal centers. Unlike conventional heterogeneous photocatalysts, these materials offer an unusual degree of synthetic programmability, enabling simultaneous regulation of framework topology, pore architecture, π -conjugation, exciton dynamics, coordination geometry, and catalytic-site distribution within a single integrated system. As a result, metal-integrated COFs are no longer viewed merely as porous light absorbers, but rather as tunable photocatalytic reaction matrices capable of orchestrating light harvesting, charge separation, proton transport, and H₂ evolution in a spatially coordinated manner. Throughout this review, it becomes evident that the photocatalytic behavior of metal-integrated COFs is fundamentally governed by the interplay between framework structure and metal-site electronics. Parameters such as linkage chemistry, stacking arrangement, D-A polarization, pore microenvironment, and crystallographic order directly influence exciton dissociation and carrier migration, while the identity, nuclearity, and coordination environment of incorporated metal centers dictate proton-reduction kinetics and H₂ binding energetics. Consequently, the integration of metal species into COFs should not be interpreted as a simple cocatalyst-loading process; instead, it represents a deliberate strategy to construct electronically coupled photocatalytic architectures with controllable catalytic functionality.

Significant progress has been achieved through multiple integration strategies. The incorporation of isolated single-metal sites within periodically ordered coordination pockets has enabled atomically dispersed catalytic centers with well-defined electronic structures and maximized metal utilization efficiency. Dual-metal and heterobimetallic systems have further demonstrated that cooperative interactions between adjacent metals can regulate proton adsorption, electron accumulation, and H-H coupling pathways more effectively than isolated active sites. Meanwhile, multinuclear metal clusters and subnanometric metal aggregates integrated into COF matrices provide opportunities to bridge molecular and nanoscale catalysis, often delivering enhanced charge delocalization and multielectron transfer capability. Equally important, molecular metal complexes, including metalloporphyrins, metallophthalocyanines, bipyridines, salens, terpyridines, and diimine motifs, have established a highly modular route toward photocatalytic H₂ evolution systems with tunable redox behavior and coordination environments. In these architectures, the framework not only immobilizes catalytically active complexes but also modulates their electronic structure through conjugation and long-range lattice effects. Such electronic communication

between the metal center and the COF backbone is increasingly recognized as a prerequisite for efficient proton-coupled electron transfer.

Beyond active-site engineering, structural and morphological regulation has emerged as another defining factor governing HER performance. Donor–acceptor engineering, extended π -conjugation, ladder-type architectures, ordered π -stacking, and in-plane d – π delocalization have collectively improved visible-light absorption and directional carrier transport. Simultaneously, nanosheet formation, oriented thin films, hierarchical porosity, and interfacial heterostructure construction have shortened charge-diffusion pathways and increased accessibility of catalytically active sites. Such advances demonstrate that photocatalytic efficiency is not determined solely by the intrinsic activity of the metal center, but also by the ability of the framework to direct exciton migration and regulate interfacial charge-transfer kinetics. The development of noble-metal-free systems has also substantially expanded the sustainability prospects of metal-integrated COFs. Although Pt-based cocatalysts still provide benchmark H_2 activity, increasing attention has shifted toward earth-abundant Ni, Co, Fe, Cu, and Mo centers capable of mediating proton reduction through appropriately engineered coordination environments. Nevertheless, reproducing Pt-like H_2 adsorption energetics while preserving long-term structural integrity remains a major challenge. In many cases, instability arising from demetallation, ligand dissociation, photoreduction, or NPs aggregation continues to obscure the true identity of catalytically active species under operational conditions.

Despite these advances, several critical barriers still limit the transition of metal-integrated COFs from laboratory materials to practically relevant solar-fuel platforms. First, many systems continue to rely heavily on sacrificial hole scavengers, making the measured H_2 evolution performance only partially representative of genuine solar water splitting. Second, the charge-transport characteristics of many COFs remain insufficient for rapid long-range carrier migration, particularly in bulk microcrystalline materials where interlayer disorder and trap-state formation promote recombination losses. Third, the long-term stability of coordinated metal sites under continuous irradiation and aqueous conditions remains inadequately understood, especially for atomically dispersed base-metal systems. Finally, the lack of standardized photocatalytic benchmarking protocols complicates direct comparison across different reports and often obscures meaningful structure–activity relationships. Looking forward, the future of metal-integrated COFs for photocatalytic H_2 evolution will likely depend on the convergence of several complementary directions. One particularly promising pathway involves the construction of fully conjugated and electronically coherent frameworks in which catalytic metal centers are intrinsically integrated into directional charge-transport networks. Such architectures could simultaneously optimize exciton separation, electron mobility, and catalytic turnover. Another emerging strategy is the development of multifunctional heterostructures that couple metalated COFs with semiconductors, conductive carbons, MXenes, or molecular photosensitizers to create spatially separated redox domains and prolonged carrier lifetimes.

In parallel, the integration of atomically precise metal clusters, single-/dual-atom catalysts, and multinuclear catalytic motifs within crystalline COF lattices offers a powerful

opportunity to bridge homogeneous and heterogeneous photocatalysis. Covalent anchoring, coordination confinement, pore-directed encapsulation, post-synthetic metalation, and in situ growth strategies collectively provide a versatile synthetic toolbox for regulating catalytic-site geometry and framework–metal electronic coupling. These approaches are particularly attractive because they enable simultaneous control over local catalytic events and long-range mass/charge transport processes. Equally transformative will be the increasing integration of operando characterization, computational modeling, and data-driven catalyst discovery. Advanced spectroscopic methods, including transient absorption spectroscopy, operando X-ray absorption analysis, electron paramagnetic resonance, and time-resolved photoluminescence, will be indispensable for identifying active intermediates and elucidating dynamic charge-transfer pathways. Concurrently, density functional theory, machine-learning-assisted screening, and automated synthesis platforms are expected to accelerate the rational discovery of optimized metal–framework combinations with predictable catalytic behavior.

Ultimately, the evolution of metal-integrated COFs is moving beyond the conventional paradigm of porous photocatalyst design toward a broader concept of programmable solar-fuel materials. The most successful next-generation systems will not simply maximize H_2 evolution rates; rather, they will integrate efficient light harvesting, directional charge transport, controlled proton delivery, durable catalytic-site stabilization, and scalable processability within a unified crystalline platform. Achieving this level of integration could position metal-integrated COFs among the most important material classes for sustainable solar-to- H_2 energy conversion in the coming decade.

Data availability

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Declaration of competing interest

All the contributing authors report no conflict of interests in this work.

Author contribution statement

Yifei Zhang: Writing–original draft, Investigation. Zheqiang Li: Writing–original draft. Ayman Al-Qattan: Writing–original draft. Khalid Aljohani: Visualization, Funding acquisition. Ahmad M. Alghamdi: Visualization. Zhen Zhao: Project administration, Funding acquisition. Gao Li: Writing–review & editing, Supervision, Conceptualization. All the authors have approved the final manuscript.

Informed consent

Not applicable.

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Use of AI statement

None

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