ABSTRACT: Covalent organic frameworks (COFs) are a new class of crystalline organic polymers that have garnered significant recent attention as highly promising H₂ evolution photocatalysts. This Perspective discusses the advances in this field of energy research while highlighting the underlying peremptory factors for the rational design of readily tunable COF photoabsorber–cocatalyst systems for optimal photocatalytic performance.

Fossil fuels have been the driving force for economic growth in our world since the dawn of the industrial revolution. At present, more than 80% of the world energy requirement is derived from fossil fuels. However, overexploitation and hence the ever increasing depletion of these natural resources, in addition to the anthropogenic climate change caused by the release of greenhouse gases by combustion of fossil fuels, is a matter of profound concern. Of the renewable alternative energy resources available, solar power is arguably the most promising one. However, solar energy is diffuse and thus requires large collection areas for harvesting meaningful amounts. Also, solar energy is intermittent in nature. Thus, as a probable primary energy source, it would need to be coupled to energy storage mechanisms in an exceptional scale. In nature, photosynthesis converts solar energy into stored chemical energy in the form of carbohydrate fuels and oxygen. While too complex to duplicate in all its detail, it is an excellent inspiration to keep pace with the increasing energy demands on our planet, as it offers a blueprint for the design of artificial photosynthetic systems where the goal is to use (and hence convert) solar energy to make solar fuels like H₂ by driving thermodynamically uphill chemical reactions like splitting of water (Scheme 1), as shown in eqs 1−3.1−9

\[
2\text{H}^+ + 2e^- \rightarrow \text{H}_2
\]  

(1)

\[
\text{H}_2\text{O} + 2\text{H}^+ \rightarrow \frac{1}{2}\text{O}_2 + 2\text{H}^+
\]  

(2)

\[
\text{H}_2\text{O} \rightarrow \text{H}_2 + \frac{1}{2}\text{O}_2 \quad \Delta G = +237.2 \text{kJ/mol}
\]  

(3)

Scheme 1. Artificial Photosynthetic Water Splitting

Under standard conditions, the free-energy change of 237.2 kJ/mol for the conversion of one molecule of water to H₂ and \(\frac{1}{2}\text{O}_2\) (eq 3) corresponds to \(\Delta E = 1.23 \text{V}\) per electron transferred. Thus, for a photosystem to drive this reaction upon photoexcitation, it must absorb light with photon energies \(>1.23 \text{eV}\), corresponding to wavelengths \(\lesssim 1000 \text{nm}\). This
process should produce two and four electron–hole pairs per molecule of H₂ and O₂, respectively. An ideal photosystem, with its band gap larger than that required to split water, and with appropriately positioned conduction band and valence band energies with respect to E(H⁺/H₂) and E(O₂/H₂O), respectively, should be able to drive the hydrogen evolution (eq 1) and the oxygen evolution (eq 2) reactions using e⁻/h⁺ generated upon illumination. Honda and Fujishima were the first to report water splitting by band gap excitation of titanium dioxide in 1972.10 Substantial progress has been made in subsequent years, but the intense complications associated with the complete water-splitting reaction has led to only a handful of successful systems.4 On the other hand, studying the oxidative and the reductive half reactions separately enables detailed investigations and optimizations and thus greatly facilitates the ultimate endeavor.

A typical photocatalytic hydrogen production scheme (Scheme 1) starts with absorption of light by the photosensitizer to generate electron–hole pairs. Charge separation occurs subsequently; a cocatalyst is usually added for carrying out the proton reduction reaction, while a sacrificial electron donor is added as a source of electrons, replacing water as a thermodynamically and kinetically challenging reducing agent. The sacrificial donor then regenerates the photosensitizer by undergoing irreversible decomposition and thus prevents back electron transfer. Direct photocatalytic hydrogen production following this mechanism has been explored under homogeneous conditions and using particulate photoabsorbers alike, each with their pros and cons. Molecular photocatalytic systems based on redox active metal complexes are highly tunable, but they are poorly stable and have comparatively low efficiencies.9,11–14 Heterogeneous systems, on the other hand, have limited light-harvesting abilities and tunability.9,13–18 However, they are robust and long-lived and show decent photocatalytic efficiencies.

The past few years have witnessed increasing interest in organic polymers for photocatalytic H₂ evolution, the study of which had been dominated by inorganic materials so far.15–20 Graphitic carbon nitride, represented by Liebig’s “Melon” is the most prominent example in this category.21,22 While it features good H₂ evolution activity, the scope for fine-tuning the structure and photophysical properties, and hence H₂ evolution activity, is rather limited and mechanistic insights are accordingly scarce.23–25 This is because carbon nitrides, made by polycondensation of the precursors at high temperatures, are mostly amorphous or semicrystalline 1D or 2D polymers with a large dispersity index. In addition, the molecular backbone of carbon nitrides is composed of either heptazine or triazine units, thus limiting their molecular tunability. The need to overcome these inherent limitations with carbon nitrides, while still retaining the well-defined molecular backbone in a heterogeneous system, marks the advent of covalent organic framework (COF) photocatalysis (Scheme 2).

In 2005, Yaghi and co-workers showed the utility of topological design principles in reticulation of molecular building blocks via covalent bonds, to form crystalline COFs.26 COFs were thus a new class of highly porous organic polymers with 2D or 3D network topologies, similar to metal–organic frameworks, but composed solely of light elements and potentially more robust in nature. The suitably chosen functionalized molecular building units are linked to each other in a reversible fashion by thermodynamically controlled dynamic covalent chemistry.27–31 The reversibility in bond formation under the network-forming reaction conditions imparts self-healing ability for the repair of structural defects and facilitates reorganization of the framework structure to produce long-range order and crystallinity, not seen in typical organic polymers which are formed by kinetically driven, irreversible bond formation reactions such as C–C cross coupling.

COFs are one of the most significant discoveries pertaining to heterogeneous photocatalysis because (i) they are composed of molecular building blocks and hence possess almost unlimited chemical tunability of the different functions fundamental to the photocatalytic process, namely, light harvesting, charge separation, charge transport and electrocatalysis. (ii) They possess permanent, nanometer-sized structural pores which can be precisely tuned by choice of appropriate molecular building blocks and their reticulation. The high structural porosity entails high surface areas, enabling both rapid diffusion of charges to the surface and a very high interaction surface for enhanced accessibility of sensitizers, electrolytes, sacrificial components, and cocatalysts throughout the sample. (iii) Unlike molecular systems, the photoactive building blocks can be locked in a rigid architecture, and this can enhance the lifetimes of the excited states by preventing deactivation through collisions. Possible conjugation, both in-plane and in the stacking direction, can also contribute to increased charge carrier mobility. (iv) The crystallinity, in other words, the local and the long-range order in these systems, facilitates charge transport, can prevent recombination of charge carriers, and minimizes charge trapping at defect sites. (v) COFs are composed of covalent bonds and thus are very stable and robust. They are largely impermeable to solvents and, with appropriately chosen linking schemes, can be stable to hydrolysis, extremes of pH, and oxidative and reductive environments, and (vi) being composed of lightweight elements, COFs have an extremely low density and can offer high gravimetric performance. The exceptional blend of solid-state character together with modularity, porosity, and crystallinity means that COFs actually have the potential to be avant-garde in photocatalysis research.32–34

In 2013, Jiang and co-workers synthesized a squaraine linked porphyrin COF featuring extended π-conjugation and charge-carrier mobility. With a 1,3-diphenylisobenzofuran label, this

**Scheme 2. Photocatalytic H₂ Evolution with Metallic Pt (left) and Molecular Cocatalysts (right)"**

"The sacrificial electron donor molecules have been omitted for clarity."
COF showed steady generation of singlet oxygen from molecular oxygen. Molecular oxygen being in the triplet state, this showed that a triplet excited state of the COF photocatalyst, which did not contain any noble metals, can be populated upon visible light excitation and can actually be harvested in a subsequent reaction.

Indeed, this ability of COFs to harvest light energy laid the foundation for their development as platforms for photocatalytic hydrogen evolution. In 2014, we reported the first COF (Figure 1a) observed to produce H₂ in the presence of ascorbic acid as the sacrificial electron donor. Photodeposition of Pt nanoparticles of roughly 5 nm size (Figure 1d). While photoactivity was retained, the COF lost its crystallinity as seen in a 92 h postphotocatalysis sample, likely because of exfoliation in water. Interestingly, the amorphous product filtered out of the photocatalysis reaction mixture could be reconverted to the crystalline and porous TFPT-COF by subjecting it to the original synthesis conditions without addition of new building blocks, thus suggesting that the connectivity of the COF remained intact throughout the catalytic conversion. The H₂ evolution activity could be improved by replacing the sacrificial electron donor ascorbic acid with triethanolamine (TEOA), however at an expense of a quicker deactivation of the COF. With 10 vol % TEOA, the H₂ evolution rate was 1970 μmol h⁻¹ g⁻¹ (Figure 1c) corresponding to a quantum efficiency of 2.2%. This rate was almost 3 times higher than those with benchmark photocatalytic systems such as Pt-modified amorphous melan, other carbon nitrides, and crystalline poly(triazine imide).

As discussed before, the most remarkable feature of COFs pertinent to photocatalysis research is their tunability down to the atomic level in an otherwise heterogeneous backbone. This was exemplified in the engineering of azine-linked Nₓ-COFs with triphenylaryl nodes for photocatalytic water reduction. Four COFs, with the number of nitrogen atoms in the central aryl ring increasing from 0 to 3, were synthesized by reaction of the corresponding aldehydes with hydrazine under reversible conditions (Figure 2a). Substitution of the C–H units with N atoms gradually decreased the dihedral angle between the central aryl ring and the peripheral phenyl rings in the COF nodes, thus increasing planarity. As a direct result, the peaks in the powder X-ray diffraction (PXRD) pattern become sharper and the stacking reflection at 2θ = 26° becomes more and more prominent along the series from N₀-COF to N₃-COF, thus indicating a gradual increase in crystallinity with increasing nitrogen content (Figure 2b). This finding is significant in that it shows that a bulk property such as crystallinity can be controlled precisely by a modulation at the molecular, i.e., the building block level. The porosity of the COFs as measured by the BET surface area increased as well along this series, again reflecting the increasing degree of order with increasing nitrogen content. The increase in planarity and hence crystallinity can effect more facile exciton migration not only along the COF plane but also along the axial direction. The observed increase in planarity also leads to an obvious increase in electronic conjugation; however, with the simultaneous increasing degree of order with increasing nitrogen content. The increase in planarity and hence crystallinity can effect more facile exciton migration not only along the COF plane but also along the axial direction. The observed increase in planarity also leads to an obvious increase in electronic conjugation; however, with the simultaneous increasing degree of order with increasing nitrogen content.

Figure 1. Molecular structure (a) of the TFPT-COF hexagonal pore as seen by TEM at 300 kV (b). Visible light-mediated H₂ evolution (c) with TFPT-COF using sodium ascorbate donor and Pt cocatalyst. The inset shows H₂ evolution using TEOA as an electron donor. Photodeposited Pt nanoparticles (d) on TFPT-COF after photocatalysis for 84 h. Adapted with permission from ref 36. Copyright 2014 Royal Society of Chemistry.
Unlike TFPT-COF, the postphotocatalysis samples did not show any significant structural change in the material; framework connectivity, structure, and crystallinity were nearly fully retained with only a slight loss in the long-
range order. Also, upon replacing the sacrificial donor with ascorbic acid, long-term experiments with N$_3$-COF for over 120 h showed sustained H$_2$ evolution and thus evidence the remarkable stability of the COF under photocatalytic conditions.

The robust solid-state crystalline structure of COFs is fully modular and can be tuned for the different functions fundamental to the photocatalytic process at an atomic level precision.

Computational methods are a powerful tool in predicting and analyzing electronic properties of COF photocatalysts pertinent to their photocatalytic activity. Using representative semixtended model systems for the N$_x$-COF series, it was found that, in line with the observed H$_2$ evolution activities, the highest occupied molecular orbital (HOMO) was stabilized gradually from N$_0$- to N$_3$-COF, suggesting a progressive increase in the thermodynamic driving force for hole extraction by TEOA. The simultaneous decrease in the lowest unoccupied molecular orbital (LUMO) energy, however, indicated a gradual decrease in the driving force for electron transfer to Pt up the series, contrary to the increasing H$_2$ evolution rate. Molecular orbital calculations in unit cells of N$_x$-COFs after optimization with periodic single-point conditions at the DFTB +/−mio-1-0 level of theory reveal that the HOMO is localized only on the azine-linker moiety, thus suggesting it to be a possible hole-quenching site through hydrogen bonding interactions with TEOA. The LUMO was seen to be delocalized across the conjugated π system of the framework. For hydrazone-terminated model hexagons on the PBE0-D3/def2-SVP level of theory, electron affinities were of the order of −2 eV, rendering anionic quenching of the photoexcited COF as the likely reaction pathway. The ionization potential values were estimated to be very high, around +10 eV in vacuum. Thus, oxidative quenching of the photoexcited COF, i.e., the necessity of efficient hole-transfer reactivity by optimizing the COF−sacrificial donor interactions, for the design of a potent photocatalytic system.

The complex interplay of structural, morphological, and electronic factors for photocatalytic H$_2$ evolution in COF-based systems is further demonstrated with PTP-COF, having the same total number of N atoms as N$_3$-COF, but distributed instead on the peripheral rather than the central ring (Figure 2a). Under similar conditions as for the N$_x$-COFs, PTP-COF produces H$_2$ at a rate of only 83.83 mol h$^{-1}$ g$^{-1}$ after an initial activation period corresponding to the photodeposition of Pt nanoparticles. The lower symmetry of PTP-COF, compared to that of N$_3$-COF, most likely leads to disorder in the former system due to a higher number of possible molecular conformations involving the torsion angle between the central and the peripheral aryl rings in the PTP nodes (Figure 2e). Such molecular arrangements could have a detrimental influence on the stacking interactions, thus causing stacking disorder. Further disorder can be induced into the PTP-system by a possible donor (phenyl)−acceptor (pyridyl) stacking interactions, as opposed to face-to-face interactions in the N$_x$- system (Figure 2f). Also, the higher basicity of pyridyl Ns in the PTP nodes, compared to that of the triazine Ns in the N$_x$-nodes, could lead to oligomers or molecules occluding the pores of PTP-COF (Figure 2g). As a consequence of a possible combination of these factors, the overall crystallinity of PTP-COF was seen to be very low as compared to that of N$_3$-COF, resulting in a BET surface area of only 84.21 m$^2$ g$^{-1}$ for the former, the theoretical surface area being 2147 m$^2$ g$^{-1}$. The low crystallinity and porosity further induce morphological changes: as compared to small, well-dispersible aggregates for N$_x$-COF, PTP-COF forms large spheres and macroscopic intergrown monoliths that are very hard to disperse in water during photocatalysis. Because dispersibility affects the efficiency of light absorption and scattering, the amount of COF photosensitizer needed to absorb all light now becomes a variable and puts comparison of the H$_2$ evolution rate with N$_x$-COFs in perspective. Photophysical measurements and quantum chemical calculations call attention to additional factors responsible for the poor performance of PTP-COF: As compared to N$_x$-COF, measured fluorescence quantum yield and lifetime imply possibly a less efficient nonradiative deactivation of the photoexcited state of PTP-COF via charge-transfer pathways involved in H$_2$ evolution. That the nonradiative excited-state decay rates might actually correspond to these charge-transfer steps was confirmed in an analogous experiment where the emission quantum yield of PTP-COF was observed to be significantly lower and its luminescence decay significantly faster under photocatalytic conditions (i.e., with added TEOA and photodeposited Pt), compared to that in water. Interestingly, while all N$_x$-COFs have a band gap of around 2.6−2.7 eV, PTP-COF has a band gap of only 2.1 eV and thus a more extended absorption in the visible region. However, the underlying factors discussed above, which apparently challenge charge transport and the efficiency of light absorption in PTP-COF, seemingly emasculate this effect. In addition, from the calculations of frontier molecular orbitals for the PTP-CHO building block at the PBE0-D3/def2-TZVP level of theory, the HOMO and the LUMO were seen to have a similar energy of light absorption in PTP-COF, seemingly emasculate this effect. In addition, from the calculations of frontier molecular orbitals for the PTP-CHO building block at the PBE0-D3/def2-TZVP level of theory, the HOMO and the LUMO were seen to be in line with the observed trend in the H$_2$ production activity of the COFs. Increased stability of the COF radical anion also suggests more effective charge separation. This highlights the importance of the interface between the COF and the electron donor, i.e., the necessity of efficient hole-transfer reactivity by optimizing the COF−sacrificial donor interactions, for the design of a potent photocatalytic system.

A wide range of structural and optoelectronic factors need to be well-orchestrated to maximize the H$_2$ evolution efficiency of a COF photocatalyst.
It is thus evident that there are a myriad of variables that need to be modulated and orchestrated to have the "perfect" H\textsubscript{2} evolving COF photocatalyst. This includes structural factors such as crystallinity and porosity on the one hand and optoelectronic factors like charge separation, charge migration, charge recombination, and stability of the radical cationic or anionic intermediates on the other. Our research highlights the structure–property–activity relationship in such systems and accentuates the importance of the best possible optimization of the said factors for best performance. While these can be potential hurdles, they can be actually engineered to the desired extent at a molecular level in COFs, as mentioned at the beginning.

The development of robust COFs is the most basic step toward the development of photocatalytically active systems. In this context, it is important to remember that crystallinity in COFs is generated through reversible bond formation. Under conditions of dynamic covalent chemistry, bond breaking is thus as facile as the bond formation process, and stability and crystallinity act in opposite ways. The choice of the linkage in a COF, as well as the COF synthesis conditions (including choice of catalyst, solvent and temperature), is thus of significant importance, and linkages which are more prone to hydrolysis, such as boronic acid ones, might render the photocatalytic system unstable. In that regard, supra-molecular interactions to strengthen the intra- and interlayer interactions and irreversible lock-in strategies such as post synthetic stabilization of crystalline COFs could be promising tactics to rigidify the framework with a desired complexity. The competition between stability and crystallinity quite reasonably generates COFs with structural disorder and defects, the roles of which in the charge-transfer processes during photocatalysis need to be explored in detail and precisely controlled, as this could be the key to establish a precise structure–property correlation.

COF as the photosensitizing scaffold has to be able to harvest light energy efficiently and transfer charges to the electrocatalyst. For optimal performance, this mandates extended absorption in the visible and near-infrared region while still maintaining the driving force necessary for proton reduction as well as the overpotential for electron transfer. Conjugation, in other words the delocalization of the \pi-electron system, both in the axial direction and in-plane, should lower the band gap and also render charge transport more efficient by quick dissipation of the excitation energy, thus emphasizing the importance of planar and conjugated chromophores as the building blocks. An appropriate choice of the linker is also necessary for a fully conjugated COF layer. Achieving efficient charge separation is another challenge in such low dielectric constant polymers that typically show facile recombination of charges created upon photoexcitation. In that regard, our frontier molecular orbital calculations of model oligomeric systems indicate that electron-rich terminal groups could actually assist in charge separation. Another way to circumvent this issue would be to work with molecules having long-lived excited states to possibly increase the excited-state lifetimes of the COF. However, while systematic and thorough studies are yet to be done, our studies have generated examples where COFs with longer-lived excited states are less efficient as H\textsubscript{2} evolution photocatalysts. It must however be mentioned that it is very difficult to ascribe the H\textsubscript{2} evolution activity to a single variable, as discussed above.

The unique advantage of COFs over molecular systems is their ability to transport photogenerated charges efficiently, thus reducing the likelihood of recombination. An interesting research exemplifying the superior charge transport properties of COFs was reported by Banerjee and co-workers where the authors used the COF synthesized from 1,3,5-triformylphloroglucinol and 2,5-dimethyl-phenylenediamine as a support for CdS nanoparticles. For a CdS:COF ratio of 90:10, the authors observed a H\textsubscript{2} evolution rate of $3678 \mu$mol h\textsuperscript{-1} g\textsuperscript{-1}, which was ascribed by emission quenching experiments and Mott–Schottky measurements to an efficient transport of the photogenerated electrons from the CdS photosensitizer via the COF layers, which further prevented charge recombination losses seen in bare CdS. A H\textsubscript{2} evolution rate of only $128 \mu$mol h\textsuperscript{-1} g\textsuperscript{-1} was observed for CdS alone under the same conditions. In more general terms, the charge transport and the carrier mobilities can be maximized in a COF by improving the overall crystallinity; by refining stacking interactions for optimal overlap of \pi-orbitals in the axial direction; and by increasing in-plane conjugation preferably with precursors having high native charge carrier mobilities, such as thiophene, perylene, etc.

Optimization of the interaction of the COF with the sacrificial electron donor is necessary as well for optimal H\textsubscript{2} evolution photocatalysis (Scheme 3). The appropriate choice of the donor could be very specific for a particular COF photosensitizer and has to be optimized for high cage escape yields (for reductive quenching) and faster degradation than charge recombination, in addition to the solvent, pH, concentrations, etc. While quantum chemical calculations point to a reductive quenching mechanism in the azine-based
COF photocatalytic systems developed by us,\textsuperscript{40} a thorough photophysical investigation of the mechanism and identification of the reaction intermediates is necessary. This could be all the more important because of the possible role of these Lewis basic electron donors in some other steps in the intricate photocatalytic cycle or its possible role in poisoning the nanoparticulate electrocatalysts.

Engineering the chemistry of COF—sacrificial electron donor and the COF—cocatalyst interfaces would be vital for further improvement of H\textsubscript{2} evolution efficiency.

Optimization of the COF—electrocatalyst interface would be equally important for efficient H\textsubscript{2} evolution photocatalysis (Scheme 3). This is because without an added electrocatalyst, COFs have not yet been observed to produce H\textsubscript{2}. While charge recombination is an aspect, the major factor seems to be the kinetic overpotential associated with the charge-transfer and bond formation processes for H\textsubscript{2} evolution. Thus, in the absence of dedicated catalytic sites right at the COF backbone, suitable cocatalysts for hydrogen evolution need to be identified. Metallic Pt, with a large work function and a low Fermi level, is traditionally employed as the electron sink to trap electrons from the COF.\textsuperscript{58} It further provides effective proton reduction sites and makes H\textsubscript{2} formation facile. In this regard, coordination sites for platinum on the COF backbone might lead to more specific interaction of platinum with the COF and can result in improved charge transfer. This was observed in studies with phenyl-triazine oligomers (PTOs) where the smaller oligomers were observed to be more efficient H\textsubscript{2} evolution photocatalysts because of the increased number of terminal nitrile moieties which possibly act as coordination sites for platinum while also assisting in the dispersion of the photocatalyst by H-bonding.\textsuperscript{59} Unfortunately, platinum is an extremely rare element and hence very expensive. In the long run, it thus needs to be replaced with cocatalysts based on earth-abundant nonprecious elements.\textsuperscript{11,12} In our recent work we demonstrated the feasibility of this approach using N\textsubscript{2}-COFs and the hydrazone-based COF-42 as photosensitizers and a series of molecular cobaloxime cocatalysts as biomimetic hydrogenase mimics (Figure 3a,b, Table 1).\textsuperscript{60} Composed entirely of molecular building blocks, this system represents the first single-site heterogeneous COF photocatalyst with a unique level of molecular tunability. H\textsubscript{2} evolution activity was found to be dependent on the solvent used, and acetonitrile was observed to be important for better performance. Further dependencies on reaction pH, choice of sacrificial donor, and the crystallinity and porosity of the COF were noted. Using N\textsubscript{2}-COF as the photosensitizer and chloro(pyridine)cobaloxime cobaloxime cocatalyst, H\textsubscript{2} evolution rates as high as 782 \(\mu\text{mol h}^{-1} \text{g}^{-1}\) were obtained, corresponding to an apparent quantum efficiency (AQE) of 0.16% at 400 nm. The H\textsubscript{2} evolution rates were comparable to the previously discussed benchmark photocatalytic systems like Pt-modified amorphous melon,\textsuperscript{17} other graphitic carbon nitrides,\textsuperscript{38} and crystalline poly(triazine imide) (PTI).\textsuperscript{37} The turnover number (TON) was 54.4 at 20 h. Interestingly, for the same mol % of metallic Pt as the cobaloxime catalyst Co-1, a three times lower H\textsubscript{2} evolution rate was observed with the former when measured under the same conditions in 4:1 acetonitrile/water. However, the H\textsubscript{2} evolution rate of N\textsubscript{2}-COF with Pt cocatalyst was more than 8 times higher in water than in 4:1 acetonitrile/water, and a poorer distribution of Pt nanoparticles on the COF surface and/or a poorer photodeposition from the hexachloroplatinic acid precursor in the latter solvent was observed to be the probable reason. Photodeposition of Pt nanoparticles,\textsuperscript{61} their distribution on the COF surface, as well as the sizes of the nanoparticle clusters, only the surface atoms of which are catalytically active, thus are important factors that affect the H\textsubscript{2} evolution rate in such cases and will need to be optimized. The decisive role of the kinetics and thermodynamics of the charge-transfer processes between the COF photosensitizer and the cocatalyst was illustrated in the lower H\textsubscript{2} evolution rate with N\textsubscript{2}-COF than N\textsubscript{2}-COF, using Co-1 cocatalyst (Figure 3b). With molecular cocatalysts, an important advantage will be the possibility of studying the photocatalytic processes in detail and resolving the reaction intermediates experimentally to further fine-tune the photocatalytic activity of the hybrid system. Using COF-42 photosensitizer and Co-1 cocatalyst, successive reduction of Co\textsuperscript{III} to Co\textsuperscript{II} and then to Co\textsuperscript{II} and/or the final formation of the possible H\textsubscript{2} evolving Co\textsuperscript{III–II} species could be verified (Figure 3c,d). The Co\textsuperscript{III–II} and/or Co\textsuperscript{II}–H species were further observed to produce H\textsubscript{2} in a heterolytic pathway (Figure 3e). Characterization of the H\textsubscript{2} evolving species and optimization of its integrity during photocatalysis with...
molecular cocatalysts will be important. This is because many molecular cocatalysts are known to be photoreduced to the corresponding metallic species during photocatalysis which instead act as the heterogeneous H₂-evolving species. Furthermore, the deactivation of the catalyst, for example by formation of cobalt oxide from cobaloximes, could be a limiting factor in the long run. With cocatalysts like cobaloximes featuring labile ligands and the molecular heterogeneous structure of COFs having potential coordinating framework atoms, it is important to probe whether the complex actually binds to the COF, because if it binds it can mediate an inner shell electron transfer to the catalyst. As studied for the N₂-COF system with Co-1 cocatalyst, we could confirm that neither metallic Co nor cobalt oxide nanoparticles were formed during photocatalysis, nor does the catalyst bind chemically to the COF at any stage during photocatalysis. Improving upon this weak and nonspecific interaction between the cocatalyst and the COF by covalently binding the two could be the next step forward. A more directional binding is expected to optimize the kinetics of electron transfer to the cocatalyst and surpass the diffusion-controlled limits. Our work also shows that the simpler path of optimizing the COF and the cocatalyst as independent modules has potential as well. With molecular cocatalysts the biggest challenge is however the search for a system that is stable and has limited photodecomposition over time.

In conclusion, the molecular and hence the modular nature of the heterogeneous COF backbone creates enormous prospects for H₂ evolution photocatalysis as demonstrated by the first promising steps outlined above. However, these results mark just the beginning of a prospering area of research, and every aspect of these complex architectures needs to be scrutinized to push the limits of COF photocatalysis further. Optimization of the solid-state factors such as robustness, crystallinity, porosity, and defect engineering of COFs will be important and are expected to ameliorate the desired bottom-up design for enhancing the light-harvesting and charge transport properties of such materials (Scheme 3). Thus, the development of this field will be driven by the overall progress in COF research; its success will be contingent on our ability to engineer ordered complexity within a stable, photoactive COF framework.

**AUTHOR INFORMATION**

**Corresponding Author**

*E-mail: b.lotsch@ift.mpg.de.*

**ORCID**

Tanmay Banerjee: 0000-0002-4548-2117

Gökce Savasci: 0000-0002-6183-7715

Christian Ochsenfeld: 0000-0002-4189-6558

Bettina V. Lotsch: 0000-0002-3094-303X

**Notes**

The authors declare no competing financial interest.

**Biographies**

Tanmay Banerjee has been a scientist in theLotsch Group at MPI for Solid State Research, Stuttgart since 2016. He received his Ph.D. from National Chemical Laboratory, Pune, India in 2014. His research interests include electron- and energy-transfer processes pertinent to photocatalysis and DSSC applications.

Kerstin Gottschling received her B.Sc. and M.Sc. from the Ludwig-Maximilians-Universität München (LMU) and has worked as a Ph.D. candidate in the group of Bettina V. Lotsch at MPI for Solid State Research since 2015. Her research interests include synthesis and modification of porous 2D frameworks for applications in (photo)-catalysis.

Gökce Savasci received his B.Sc. and M.Sc. degrees from the Ludwig-Maximilians-Universität München (LMU) and works as a PhD candidate in the group of Christian Ochsenfeld at LMU since 2014. His research interests include electronic structure and dynamics of covalent organic frameworks for photocatalysis.

Christian Ochsenfeld received his Ph.D. from University of Karlsruhe in 1994. After postdoctoral work at UC Berkeley, he was a Liebig- and Emmy-Noether-fellow at University of Mainz and became professor for theoretical chemistry at University of Tübingen in 2001. Since 2010 he has held the chair of theoretical chemistry at LMU Munich. Since 2017 he has also been a Max-Planck-Fellow at MPI-FKF, Stuttgart and an elected member of the “International Academy of Quantum Molecular Sciences” (IAQMS) and the board of the “World Association of Theoretical and Computational Chemists” (WATOC). His research focuses on developing and applying linear-scaling quantum-chemical methods for studying molecular processes for large, complex systems such as COFs and DNA/RNA.

Bettina V. Lotsch received her Ph.D. from LMU Munich in 2006. After a postdoctoral stay at the University of Toronto she was appointed associate professor at LMU Munich. Since 2017 she has been Director at the Max Planck Institute for Solid State Research in Stuttgart. Her research interests are at the interface between solid-state chemistry, nanochemistry, and molecular chemistry and include porous frameworks and 2D materials for sensing and energy conversion. Bettina was named Fellow of the Royal Society of Chemistry in 2014 and is recipient of an ERC Starting grant (2014) and the EU-40 Materials Prize 2017 from the European Materials Research Society (EMRS).

**ACKNOWLEDGMENTS**

Financial support was provided by an ERC Starting Grant (Project COF Leaf, Grant Number 639233), the Max Planck Society, the cluster of excellence Nanosystems Initiative Munich, and the Center for Nanoscience (CeNS). C.O. acknowledges financial support by the excellence cluster EXC114 (DFG).

**REFERENCES**

(1) Berardi, S.; Drouet, S.; Français, L.; Gimbert-Suriñach, C.; Gutten-tag, M.; Richmond, C.; Stoll, T.; Llobet, A. Molecular Artificial Photosynthesis. Chem. Soc. Rev. 2014, 43, 7501−7519.

(2) Tachibana, A. Y.; Vayssieres, L.; Durrant, J. R. Artificial Photosynthesis for Solar Water-Splitting. Nat. Photonics 2012, 6, 511−518 and references therein.

(3) Jafari, T.; Moharreri, E.; Amin, A. S.; Miao, R.; Song, W.; Suib, S. L. Photocatalytic Water Splitting—The Untamed Dream: A Review of Recent Advances. Molecules 2016, 21, 900.

(4) Chen, S.; Takata, T.; Domen, K. Particulate Photocatalysts for Overall Water Splitting. Nat. Rev. Mater. 2017, 2, 17050.

(5) Jiang, C.; Moniz, S. J. A.; Wang, A.; Zhang, T.; Tang, J. Photoelectrochemical Devices for Solar Water Splitting – Materials and Challenges. Chem. Soc. Rev. 2017, 46, 4645−4660.

(6) Roger, I.; Shipman, M. A.; Symes, M. D. Earth-Abundant Catalysts for Electrochemical and Photocatalytic Water Splitting. Nat. Rev. Chem. 2017, 1, 0003.

(7) Li, X.; Hao, X.; Abudula, A.; Guan, G. Nanostructured Catalysts for Electrochemical Water Splitting: Current State and Prospects. J. Mater. Chem. A 2016, 4, 11973−12000.
Cobalt Complexes as Artificial Hydrogenases for the Reductive Side of Renewable Hydrogen from Photo-Catalytic Water Splitting Process: A review.

Challenges.

Elements (Co, Ni, Fe) for Water Splitting: Recent Progress and Future Improvements. 

Dalton Trans. 2012, S902−918.

Nitride: Photochemistry of the Heptazine Carbon Nitride Photocatalysts.

Electron-Transfer Cascade That Improves Hydrogen Evolution with Closer To Achieving Sustainability?

ACS Energy Lett. 2016, 6, 1601189.

Mullangi, D.; Dhavale, V.; Shalini, S.; Nandi, S.; Collins, S.; Woo, T.; Kurungot, S.; Vaidhyananath, R. Low-Overpotential Electrocatalytic Water Splitting with Noble-Metal-Free Nanoparticles Supported in a sp3 N-Rich Flexible COF. Adv. Energy Mater. 2016, 6, 1601110.

Nagai, A.; Chen, X.; Feng, X.; Ding, X.; Guo, Z.; Jiang, D. A Squaraine-Linked Mesoporous Covalent Organic Framework. Angew. Chem., Int. Ed. 2013, 52, 3770−3774.

Stegbauer, L.; Schwinghammer, K.; Lotts, B. V. A Hydrazone-Based Covalent Organic Framework for Photocatalytic Hydrogen Production. Chem. Sci. 2014, 5, 2789−2793.

Schwinghammer, K.; Tuffy, B.; Mesch, M. B.; Wrinhier, E.; Martineau, C.; Taulelle, F.; Schnick, W.; Senker, J.; Lotts, B. V. Triazine-Based Carbon Nitrides for Visible-Light-Driven Hydrogen Evolution. Angew. Chem., Int. Ed. 2013, 52, 2435−2439.

Zhang, J.; Chen, X.; Takanabe, K.; Maeda, K.; Domen, K.; Epping, J. D.; Fu, X.; Antonietti, M.; Wang, X. Synthesis of a Carbon Nitride Structure for Visible-Light Catalysis by Copolymerization. Angew. Chem. Int. Ed. 2010, 49, 441−444.

Bishey, R. P.; Dichtel, W. R. Covalent Organic Frameworks as a Platform for Multidimensional Polymerization. ACS Cent. Sci. 2017, 3, 533−543.

Ong, V. S.; Haase, F.; Stegbauer, L.; Savasci, G.; Podjaski, F.; Ochsenfeld, C.; Lotts, B. V. A Tunable Azine Covalent Organic Framework Platform for Visible Light-Induced Hydrogen Generation. Nat. Commun. 2015, 6, 8508.

Haase, F.; Banerjee, T.; Savasci, G.; Ochsenfeld, C.; Lotts, B. V. Structure−Property−Activity Relationships in a Pyridine Containing Azine-Covalent Organic Framework for Photocatalytic Hydrogen Evolution. Faraday Discuss. 2017, 201, 247−264.

DeBlase, C. R.; Dichtel, W. R. Moving Beyond Boron: The Emergence of New Linkage Chemistries in Covalent Organic Frameworks. Macromolecules 2016, 49, 5297−5305.

Chen, X.; Addicott, M.; Irie, S.; Nagai, A.; Jiang, D. Control of Crystallinity and Porosity of Covalent Organic Frameworks by Managing Interlayer Interactions Based on Self-Complementary π-Electronic Force. J. Am. Chem. Soc. 2013, 135, 546−549.

Kandambeth, S.; Shinde, D. B.; Panda, M. K.; Lukose, B.; Heine, T.; Banerjee, R. Enhancement of Chemical Stability and Crystallinity in Porphyrin-Containing Covalent Organic Frameworks by Intramolecular Hydrogen Bonds. Angew. Chem. Int. Ed. 2013, 52, 13052−13056.

Chen, X.; Addicott, M.; Jin, E.; Zhai, L.; Xu, H.; Huang, N.; Guo, Z.; Liu, L.; Irie, S.; Jiang, D. Locking Covalent Organic Frameworks with Hydrogen Bonds: General and Remarkable Effects on Crystalline Structure, Physical Properties, and Photochemical Activity. J. Am. Chem. Soc. 2015, 137, 3241−3247.

Kandambeth, S.; Mallick, A.; Lukose, B.; Mane, M. V.; Heine, T.; Banerjee, R. Construction of Crystalline 2D Covalent Organic Frameworks with Remarkable Chemical (Acid/Base) Stability via a Combined Reversible and Irreversible Route. J. Am. Chem. Soc. 2012, 134, 19524−19527.
(47) Waller, P. J.; Lyle, S. J.; Osborn Popp, T. M.; Diercks, C. S.; Reimer, J. A.; Yaghi, O. M. Chemical Conversion of Linkages in Covalent Organic Frameworks. *J. Am. Chem. Soc.* 2016, **138**, 15519–15522.

(48) Lukose, B.; Kuc, A.; Heine, T. The Structure of Layered Covalent-Organic Frameworks. *Chem. - Eur. J.* 2011, **17**, 2388–2392.

(49) Zwanenburg, N. A. A.; Pawlak, R.; Abel, M.; Catalin, D.; Gignes, D.; Bertin, D.; Porte, L. Organized Formation of 2D Extended Covalent Organic Frameworks at Surfaces. *J. Am. Chem. Soc.* 2008, **130**, 6678–6679.

(50) Gutzler, R.; Walch, H.; Eder, G.; Kloft, S.; Heckl, W. M.; Lackinger, M. Surface Mediated Synthesis of 2D Covalent Organic Frameworks: 1,3,5-tris(4-bromophenyl)benzene on Graphite(001), Cu(111), and Ag(110). *Chem. Commun.* 2009, **4456**–**4458**.

(51) Butchosa, C.; McDonald, T. O.; Cooper, A. I.; Adams, D. J.; Zwijnenburg, M. A. Shining a Light on s-Triazine-Based Polymers. *J. Phys. Chem. C* 2014, **118**, 4314–4324.

(52) Guo, J.; Xu, Y.; Jin, S.; Chen, L.; Kaji, T.; Honsho, Y.; Addicoat, M. A.; Kim, J.; Saeki, A.; Ihee, H.; et al. Conjugated Organic Framework with Three-Dimensionally Ordered Stable Structure and Delocalized π Clouds. *Nat. Commun.* 2013, **4**, 2736.

(53) Medina, D. D.; Petrus, M. L.; Jumabekov, A. N.; Margraf, J. T.; Weinberger, S.; Rotter, J. M.; Clark, T.; Bein, T. Directional Charge-Carrier Transport in Oriented Benzothiophene Covalent Organic Framework Thin Films. *ACS Nano* 2017, **11**, 2706–2713.

(54) Ding, X.; Guo, J.; Feng, X.; Honsho, Y.; Guo, J.; Seki, S.; Maitarad, P.; Saeki, A.; Nagase, S.; Jiang, D. Synthesis of Metallophthalocyanine Covalent Organic Frameworks That Exhibit High Carrier Mobility and Photoconductivity. *Angew. Chem., Int. Ed.* 2011, **50**, 1289–1293.

(55) Wan, S.; Gándara, F.; Asano, A.; Furukawa, H.; Saeki, A.; Dey, S. K.; Liao, L.; Ambrogio, M. W.; Botros, Y. Y.; Duan, X.; et al. Covalent Organic Frameworks with High Charge Carrier Mobility. *Chem. Mater.* 2011, **23**, 4094–4097.

(56) Thote, J.; Aiyappa, H. B.; Deshpande, A.; Diaz, D. D.; Kurungot, S.; Banerjee, R. A Covalent Organic Framework—Cadmium Sulfide Hybrid as a Prototype Photocatalyst for Visible-Light-Driven Hydrogen Production. *Chem. - Eur. J.* 2014, **20**, 15961–15965.

(57) Pellegrin, Y.; Odobel, F. Sacrificial Electron Donor Reagents for Solar Fuel Production. *C. R. Chim.* 2017, **20**, 283–295.

(58) Yang, J.; Wang, D.; Han, H.; Li, C. Roles of Cocatalysts in Photocatalysis and Photoelectrocatalysis. *Acc. Chem. Res.* 2013, **46**, 1900–1909.

(59) Schwinghammer, K.; Hug, S.; Mesch, M. B.; Senker, J.; Lotsch, B. V. Phenyl-triazine Oligomers for Light-Driven Hydrogen Evolution. *Energy Environ. Sci.* 2015, **8**, 3345–3353.

(60) Banerjee, T.; Haase, F.; Savasci, G.; Gottschling, K.; Ochsenfeld, C.; Lotsch, B. V. Single-Site Photocatalytic H2 Evolution from Covalent Organic Frameworks with Molecular Cobaloxime Co-Catalysts. *J. Am. Chem. Soc.* 2017, **139**, 16228–16234.

(61) Jiang, Z.; Zhang, Z.; Shangguan, W.; Isaacs, M. A.; Durandell, L. J.; Parlett, C. M. A.; Lee, A. F. Photodeposition as a Facile Route to Tunable Pt Photocatalysts for Hydrogen Production: on the Role of Methanol. *Catal. Sci. Technol.* 2016, **6**, 81–88.

(62) Lei, P.; Hedlund, M.; Lomoth, R.; Rensmo, H.; Johansson, O.; Hammarström, L. The Role of Colloid Formation in the Photoinduced H2 Production with a Ru3/Pd2 Supramolecular Complex: A Study by GC, XPS, and TEM. *J. Am. Chem. Soc.* 2008, **130**, 26–27.

(63) Cao, S.-W.; Liu, X.-F.; Yuan, Y.-P.; Zhang, Z.-Y.; Fang, J.; Loo, S. C. J.; Barber, J.; Sun, T. C.; Xue, C. Artificial Photosynthetic Hydrogen Evolution Over g-C3N4 Nanosheets Coupled with Cobaloxime. *Phys. Chem. Chem. Phys.* 2013, **15**, 18363–18366.