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Covalent Organic Frameworks

Celebrating Ten Years of Covalent Organic Frameworks for Solar Energy Conversion: Past, Present and Future

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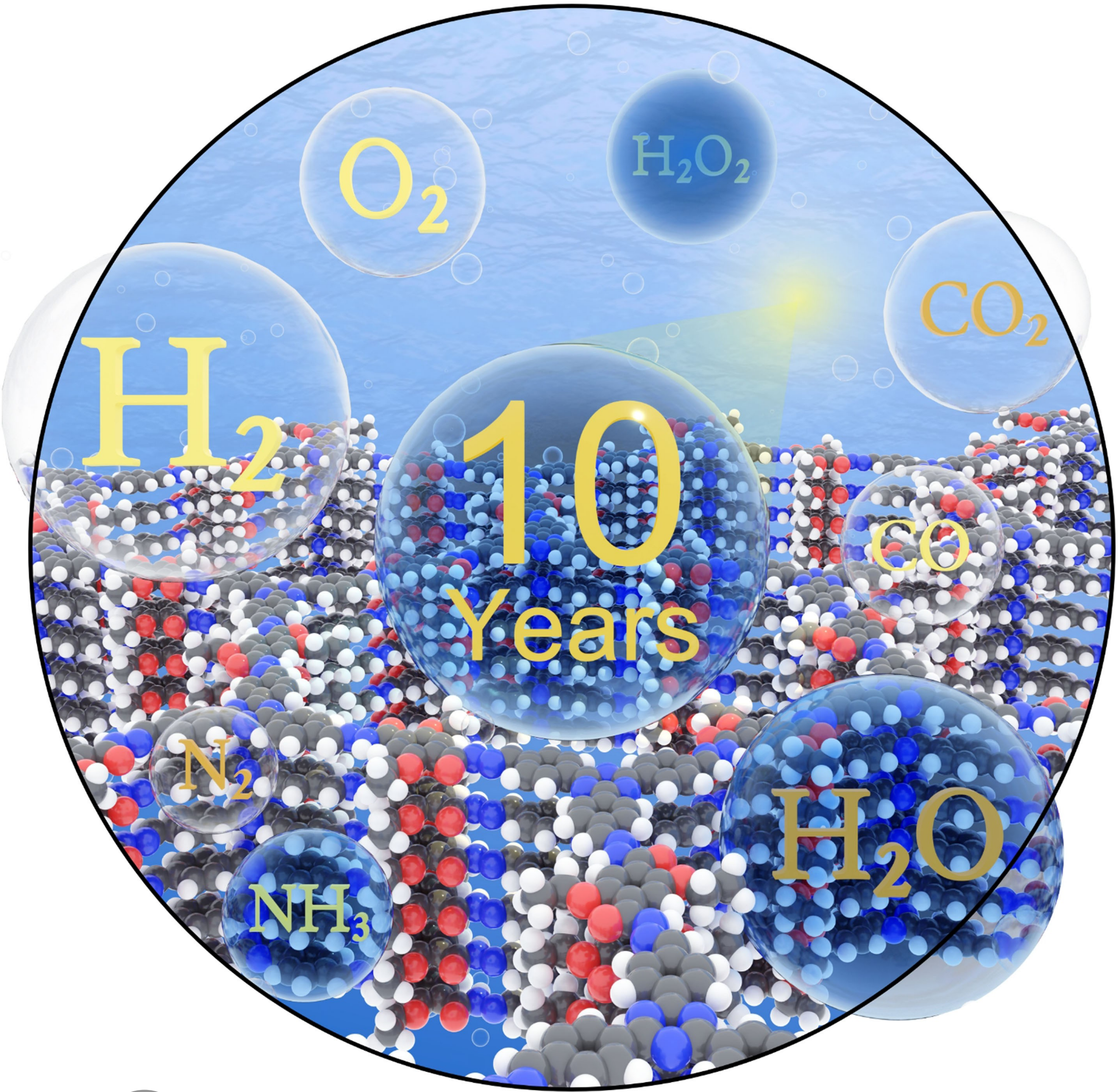

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Abstract: Accelerated anthropogenic emission of greenhouse gases due to increasing energy demands has created a negative impact on our planet. Therefore, the replacement of fossil by renewable energy resources has become of paramount interest, both societally and scientifically. It is within this setting that organic photocatalysts have emerged as a new generation of earth-abundant catalysts for the conversion of solar radiation into chemical energy. In 2014, the first example of a covalent organic framework (COF) photocatalyst for the hydrogen evolution reaction was reported by our group, which has not only marked the beginning of COF photocatalysis for solar fuel production but also helped to accelerate research into "soft photocatalysis" based on porous polymers in general. In the last decade, significant progress has been made toward developing COFs as robust, molecularly precise platforms emulating artificial photosynthesis. This mini-review commemorates the 10th anniversary of COF photocatalysis and gives a brief historical overview of the milestones in the field since its inception in 2014. We review milestones in the development of COFs for solar fuel production and related photocatalytic transformations, including hydrogen evolution, oxygen evolution, overall water splitting, CO_2 reduction, N_2 fixation, oxygen reduction, and alcohol oxidation. We discuss lessons learned for the design of structure-property-function relationships in COF photocatalysts, and future perspectives and challenges for the field of "soft photocatalysis" are given.

1. Introduction

The rapid development of our standard of living, including advanced technology, has required large amounts of energy and natural resources, generating a significant impact on our planet. Anthropogenic global warming is a concern that has existed in society for more than 50 years and has motivated researchers to develop sustainable alternatives for the world's energy supply. As early as 1972, Fujishima and Honda published visionary work on the use of solar radiation for the generation of "solar fuels" such as hydrogen as sustainable resources of energy. They reported the use of TiO_2 as a catalyst to carry out the water-splitting reaction using a photoelectrochemical system.[1] In the following years, a large body of work was published on the photocatalytic water splitting reaction where the most prominent types of photocatalysts were inorganic materials composed primarily of transition metals such as titanates, tungstates, or vanadates. Already early on, carbon-based materials such as organic polymers[2] and carbon nitrides[3] were investigated as well. Tunable and strong visible light absorption, low overall toxicity, and structural diversity promoted the rapid growth of the field of organic semiconductor photocatalysis for energy conversion.

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In 2005, Yaghi et al. reported the first covalent organic framework (COF), marking the discovery of a new class of crystalline and porous organic polymers.[4] In fact, COFs display a suite of useful characteristics that render them interesting candidates for a range of applications spanning from sorption to sensing, and from catalysis to energy storage.[5] Drawing on the rapidly evolving understanding of structure-property-activity relationships in COFs and their unique modularity and versatility, our group developed the first COF photocatalyst for the hydrogen evolution reaction (HER) in 2014. The suitable band gap, along with beneficial photophysical and structural properties including (meso)porosity and stability under photocatalytic conditions, enabled this hydrazone-COF to efficiently capture visible photons and transfer them to a Pt nanoparticle-based proton reduction co-catalyst (PRC) for the generation of molecular hydrogen from water.[6] This seminal work opened the door to the photocatalytic conversion of solar into chemical energy using COFs as photocatalysts. As a consequence, this idea was rapidly taken up and developed further by the scientific community, as demonstrated by the exponential growth of scientific publications on the topic over the past decade (Figure 1a), including remarkable progress in terms of photocatalytic efficiencies and expanding photocatalysis beyond HER research.

This mini-review highlights important milestones in COF photocatalysis research, using our own contributions as a frame of reference while recognizing that the rapid emergence of this field has been a truly collective endeavor. We include covalent triazine frameworks (CTFs) in this review due to their high chemical stability and well-documented photocatalytic activity, even though they often exhibit relatively low tunability and reduced crystallinity compared to COFs. With this "historic" perspective, we review the key developments in the field over the last decade, which in their entirety document the remarkable success of a community effort towards developing a new class of semiconductor photocatalysts for solar energy conversion. We provide an overview of how the field has grown since the first report in 2014, highlighting some landmark achievements in solar fuel generation, ranging from the prototypical hydrogen evolution reaction (HER) to the CO_2 reduction reaction

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(CO_2RR), N_2 fixation reaction, oxygen reduction reaction (ORR), and alcohol oxidation to achieve value-added products (Figure 1b–c). Additionally, we briefly discuss structure–property-function relationships and share our view on what is next in this maturing, yet still burgeoning field.

2. Solar Fuel Production

2.1. Hydrogen Evolution Reaction

In 2014, our team reported a hydrazone-based COF (TFPT-COF) which is capable of producing hydrogen gas from water under visible light illumination and in conjunction with a Pt co-catalyst, marking the first hydrogen-evolving COF photocatalyst.[6] COFs based on hydrazone linkages tend to be more stable against hydrolysis compared to most imine COFs,[7] a key factor for photocatalysis in aqueous media. Therefore, a hydrazone-COF formed by the condensation of 1,3,5-tri-(4-formyl-phenyl)triazine (TFPT) and 2,5-diethoxy-terephthalohydrazide (DETH) was selected as the photo-absorber (Figure 2a). Besides the stability of the hydrazone linkage, the triazine unit was chosen due to its reported stability, high electron mobility, and electron-accepting nature,[8] which was thought to enhance charge separation in local donor-acceptor type arrangements, a hypothesis that turned out to be a valuable ingredient for the rational design of COF photocatalysts in recent years.[9] The as-synthesized COF presented a considerable crystallinity (Figure 2b) and Brunauer–Emmett–Teller (BET) surface area of 1603 $m^2 g^{-1}$. In fact, a high surface area can enhance the catalytic activity since it promotes the interaction between the COF backbone, reactant (i.e. protons), and sacrificial agent. In addition, TFPT-COF has an absorption edge around 450 nm with an absorption tail beyond 600 nm (Figure 2c), thus facilitating the absorption of a relatively large fraction of visible light. Considering all the above, TFPT-COF was tested as a photocatalyst for hydrogen evolution. In that work, triethanolamine (TEoA) was used as a sacrificial electron donor, and in situ photogenerated Pt nanoparticles (Pt NPs) as PRC (Figure 2d). Considerable hydrogen evolution was observed, reaching up to 2.0 $mmol\,g^{-1}h^{-1}$ (Figure 2e). Since the COF's activity compared favorably to the graphitic carbon nitride (melon, g-C_3N_4) benchmark systems (e.g. 0.7 $mmol\,g^{-1}h^{-1}$),[6] the development of COF photocatalysts marked an important milestone in the field of carbon-based photocatalysts for the hydrogen evolution reaction for two reasons: First, the possibility to rationally design the structure, electronic and photophysical properties of COFs through molecular design sets them apart from carbon nitrides which are exclusively triazine or heptazine based and notoriously difficult to functionalize. Second, the structural definition and high porosity of COFs—in contrast to predominantly amorphous polymers and essentially non-porous carbon nitrides—facilitates their structural characterization and amplifies the catalytic surface area—both key ingredients for the rational design of new and improved photocatalysts.

This seminal work has laid the grounds for the use of COFs as photoabsorbers for the photocatalytic hydrogen evolution, and inspired numerous subsequent studies, as

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Dr. Kenichi Endo is a postdoctoral fellow at the Max Planck Institute for Solid State Research, Stuttgart, Germany, funded by a Humboldt Research Fellowship. He earned his Ph.D. degree from the University of Tokyo, Japan, in 2020 on coordination chemistry. Then he served as a postdoctoral researcher at Kyoto University, Japan in the field of nanochemistry and photocatalysis. Since 2021 he has been working in his current position, studying metal–organic frameworks and covalent organic frameworks for photo- and electrocatalysis.

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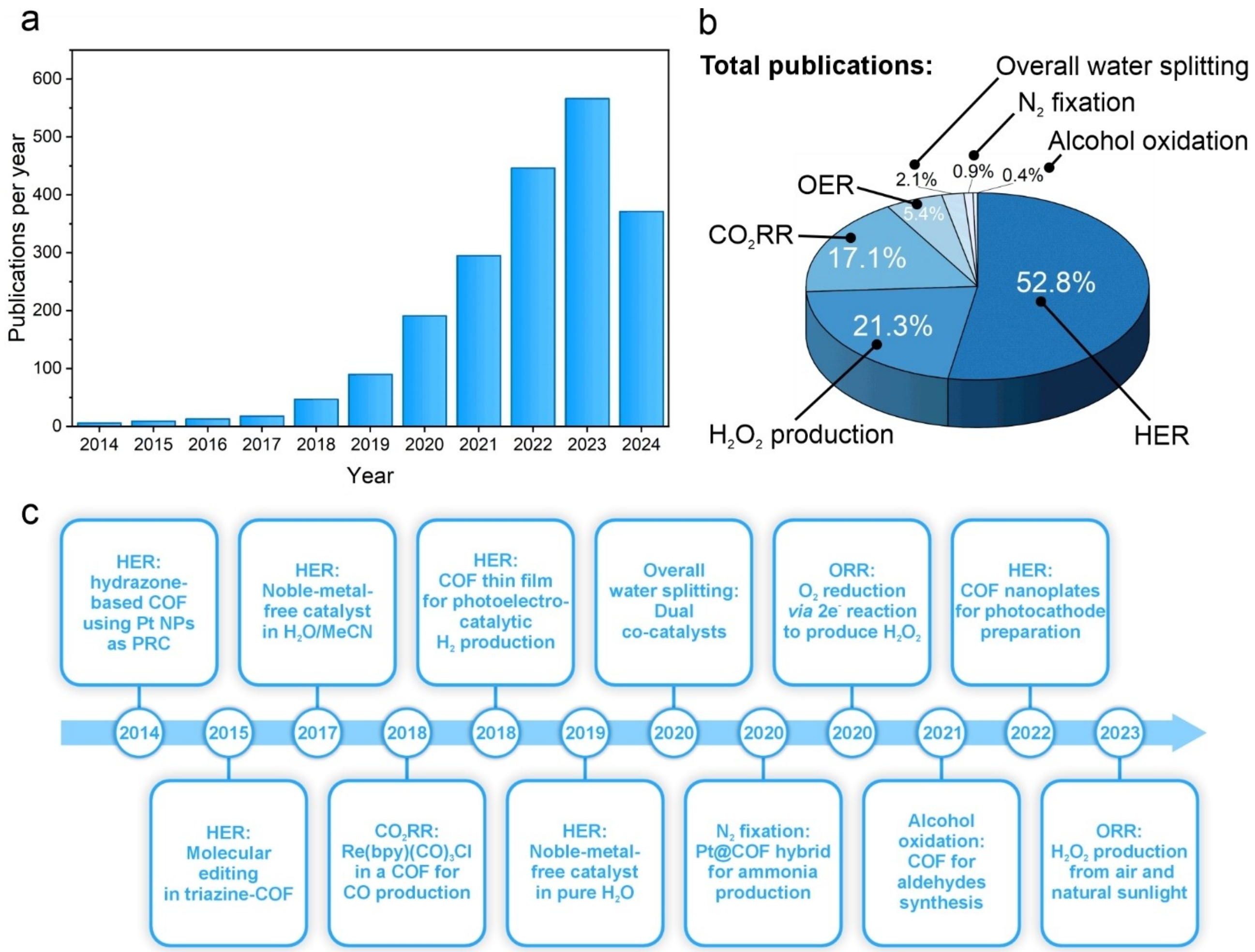

Figure 1. a) Number of scientific publications per year registered in SciFinder with the keywords (“Covalent organic framework” OR “Covalent triazine framework” AND photocat*). June 18th, 2024. b) Distribution of total publications related to relevant photocatalytic reactions and covalent frameworks. Data analysed from SciFinder on June 18th, 2024 with the keywords: (“covalent organic framework” OR “Covalent triazine framework” AND photocat* AND hydrogen NOT peroxide) for HER, (“Covalent organic framework” OR “Covalent triazine framework” AND photo* AND “hydrogen peroxide”) for H_2O_2 production, (“Covalent organic framework” OR “Covalent triazine framework” AND photocat* AND “CO2 reduction”) for CO_2RR, (“Covalent organic framework” OR “Covalent triazine framework” AND photocat* AND “oxygen evolution” OR “water oxidation”) for OER, (“Covalent organic framework” OR “Covalent triazine framework” AND photocat* AND “overall water splitting”) for overall water splitting, (“Covalent organic framework” OR “Covalent triazine framework” AND photocat* AND “N_2 fixation” OR “nitrogen reduction”) for N_2 fixation and (“Covalent organic framework” OR “Covalent triazine framework” AND photocat* AND “alcohol oxidation”) for alcohol oxidation. c) Timeline with selected benchmark contributions in COF photocatalysis since the first publication in 2014.

predicted in the outlook of this article: “We expect this new application of COFs in photocatalysis to open new avenues to custom-made heterogeneous photocatalysts, and to direct and diversify the ongoing development of COFs for optoelectronic applications.”[6]

Once the “coarse” groundwork had been done, refinement was the order of the day: In the following years, the focus shifted towards generating a fundamental understanding of the mechanism of the catalytic process and the structure-property-activity relationships of COFs for light-driven hydrogen production. While a hallmark of COFs is their bottom-up rational design, this principle had not been put to use for photocatalysis in a systematic fashion. To exploit its potential for photocatalysis, we developed a series of four aryl azine-linked COFs, in which the number of nitrogen atoms in the central aryl ring of the tris(4-formylphenyl)arene linkers was systematically varied (from 0 for phenyl, N_0, to 3 for triazine, N_3) (Figure 3a). This substitution of carbon atoms by nitrogen significantly influenced the steric properties of the building blocks, having a clear impact on the dihedral angle between the central and peripheral rings (from 38.7° for N_0 to 0.0° for N_3, Figure 3b). Notably, this local, molecular-level engineering of the linker also affects the long-range crystallographic features of the COFs, thus highlighting the character of COFs as “molecular materials”: The PXRD signals became sharper and the 001 reflections more evident (ca. $2\theta = 26°$) as the number of nitrogen atoms increased (Figure 3c). We speculate that besides a favorable impact of layer planarity on crystallization, the planarity of the linker may also have a

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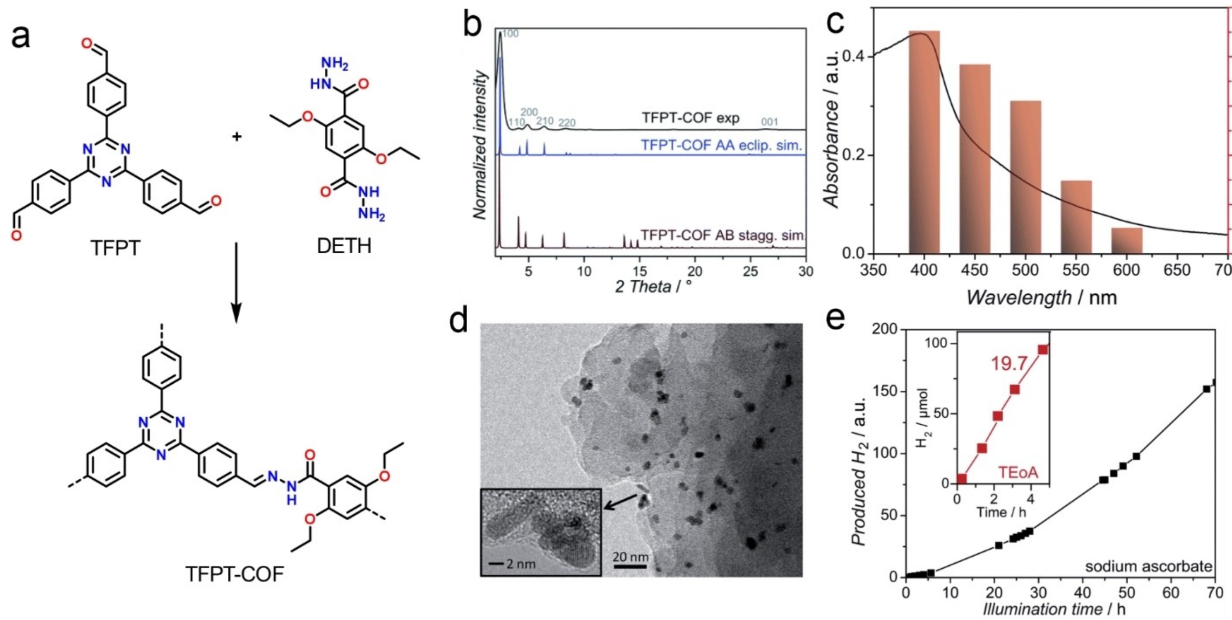

Figure 2. a) Chemical structure of the TFPT and DEHT linkers and TFPT-COF. b) Diffraction patterns of experimental TFPT-COF and the simulated AA and AB stacking structures. c) Absorbance and quantum efficiency (QE) in hydrogen production of TFPT-COF at different wavelengths. d) TEM image of TFPT-COF decorated with Pt NPs after photodeposition of H_2PtCl_6. The inset shows a magnification of Pt NPs. e) Produced hydrogen by TFPT-COF and Pt NPs using sodium ascorbate (main graph) and TEoA (inset) as sacrificial electron donors. Reproduced from Ref. [6] with permission from the Royal Society of Chemistry.

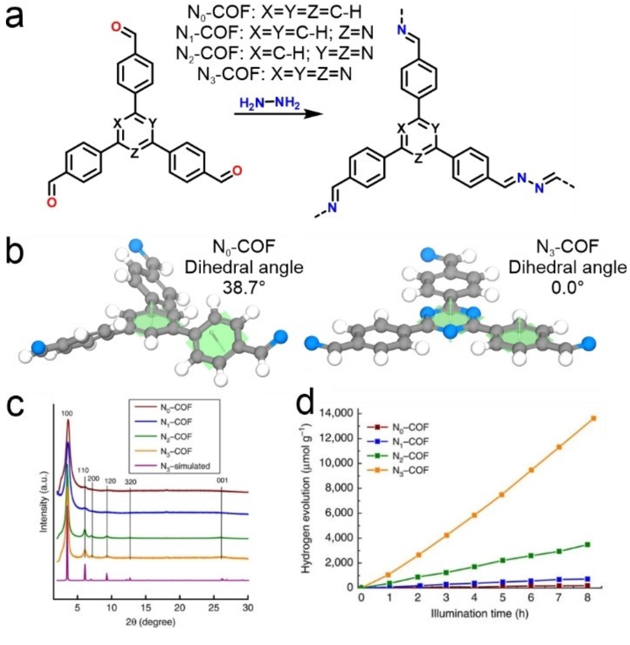

Figure 3. a) Chemical structures of azine N_m-COFs. b) Schematic of a COF fragment in which the DFT calculated dihedral angle between the central aryl ring and the peripheral phenyl ring is changed as a function of the number of nitrogen atoms in the central ring. Nitrogen atoms are represented in blue, hydrogen atoms in white, carbon atoms in grey, and the ring planes and plane vectors in green. c) Diffraction patterns of experimental Nm-COFs and the N3-COF simulation. d) Photocatalytic hydrogen evolution of N_m-COFs as a function of irradiation time. Reproduced from Ref. [10] with permission from Springer Nature.

structure-directing ("templating") effect on the COF crystallization process as observed in related systems where non-covalent interactions can assist in COF crystallization.[10] In terms of hydrogen production, effectively a direct and surprisingly linear correlation of produced hydrogen and the number of nitrogen atoms in the linker was observed: 0.023, 0.090, 0.438, and 1.703 $mmol\,g^{-1}h^{-1}$ for N_0-COF, N_1-COF, N_2-COF, and N_3-COF, respectively (Figure 3d). In spite of the pronounced structural differences in terms of planarity and hence electronic conjugation of the backbone, the 2D stacked COFs show similar optical gaps of 2.6–2.7 eV, indicating that in this case, the difference in photocatalytic performance does not primarily correlate with differences in light-harvesting capability. On the other hand, we note that photocatalytic activity is a result of a complex interplay of many different structural (e.g. crystallinity, porosity, surface area) and (opto)electronic properties, which are highly correlated, and hence catalytic activity is hard to predict and needs to be assessed on a case-by-case basis. For example, in subsequent work, we demonstrated that the number of nitrogen atoms in the peripheral rings of the aryl-triphenyl linker of PTP-COF does not show a clear correlation with the H_2 production.[11] This suggests that in this case other factors, such as long-range order, porosity, and morphology—and their interplay—are the dominant factors that have to be considered to understand photocatalytic performance.

Up to this point, great efforts were made in the exploration of COF as photoabsorbers in the HER reaction; however, in all those cases, platinum had been used as PRC. Pt is among the most active catalysts for reactions involving hydrogen, including proton reduction. Nevertheless, as a

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rare noble metal, the use of platinum in the catalytic process constitutes a downside from a sustainability as well as economical point of view. The incorporation of non-noble metals as PRC has therefore been defined as an obvious next step in the development of COF-co-catalyst couples. At the same time, leveraging the power of molecular PRCs could give rise to all-single-site photocatalytic systems, where both the COF photoabsorber and the co-catalyst are molecularly precise. This strategy of COFs as single-site photocatalysts was extensively investigated in the following years.[12]

In 2017, we reported the first example of a noble-metal-free photocatalytic system where H_2 was produced using a triazine-based COF as a photoabsorber in conjunction with a series of cobaloximes, a well-established family of molecular HER catalysts. The cobaloxime molecular catalyst was added to the photocatalytic reactor within a mixture of water and acetonitrile, thus resulting in weak physisorption and accordingly outer-sphere charge transfer between the COF photoabsorber and the co-catalyst. While not capable of operating in pure water, this COF was the first to produce hydrogen from water in the absence of noble metals. Hydrogen evolution rates up to 0.782 mmol $g^{-1}h^{-1}$ were competitive with other non-metal photocatalysts such as the benchmark system melon ("g-C_3N_4") with Pt as the PRC (0.840 mmol $g^{-1}h^{-1}$).[13] Nevertheless, several drawbacks were observed in this system: On the one hand, cobaloximes are photoactive, and prolonged irradiation leads to their reductive decomposition and, as a consequence, deactivation of the co-catalyst. On the other hand, physisorption of the molecular co-catalyst may suffer from limited diffusion through the COF pores and in particular, sluggish electron transfer between COF and co-catalyst, which only occurs upon (infrequent) collisional encounters between the two.

To address these challenges, in a subsequent study the cobaloxime molecular co-catalyst was immobilized onto the COF pore wall through covalent bonding.[14] This work synergistically combines the benefits of heterogeneous catalysis and the tunability of molecular catalysts. Specifically, a hydrazine-bonded COF with propargyl groups in the linker was synthesized to enable post-synthetic immobilization of molecular catalysts using click chemistry (Figure 4a). Through the combined use of advanced 1D and 2D solid-state nucelar magnetic resonance (ssNMR) techniques and calculations, a permanent close contact between the ethoxy groups on the COF pore wall and the oxime moiety was revealed. To evaluate the impact of chemical anchoring of cobaloxime on HER performance, covalently bonded systems were compared to samples in which a similar amount of molecular catalyst was physisorbed into the COF. An approximately two-fold improvement in catalytic performance for the covalently bound cobaloxime compared to the physisorbed counterpart was observed (photonic efficiency of 0.14 % and 0.06 %, respectively, Figure 4b). This work demonstrates that covalent immobilization of cobaloximes enhances the catalytic process, potentially by optimizing

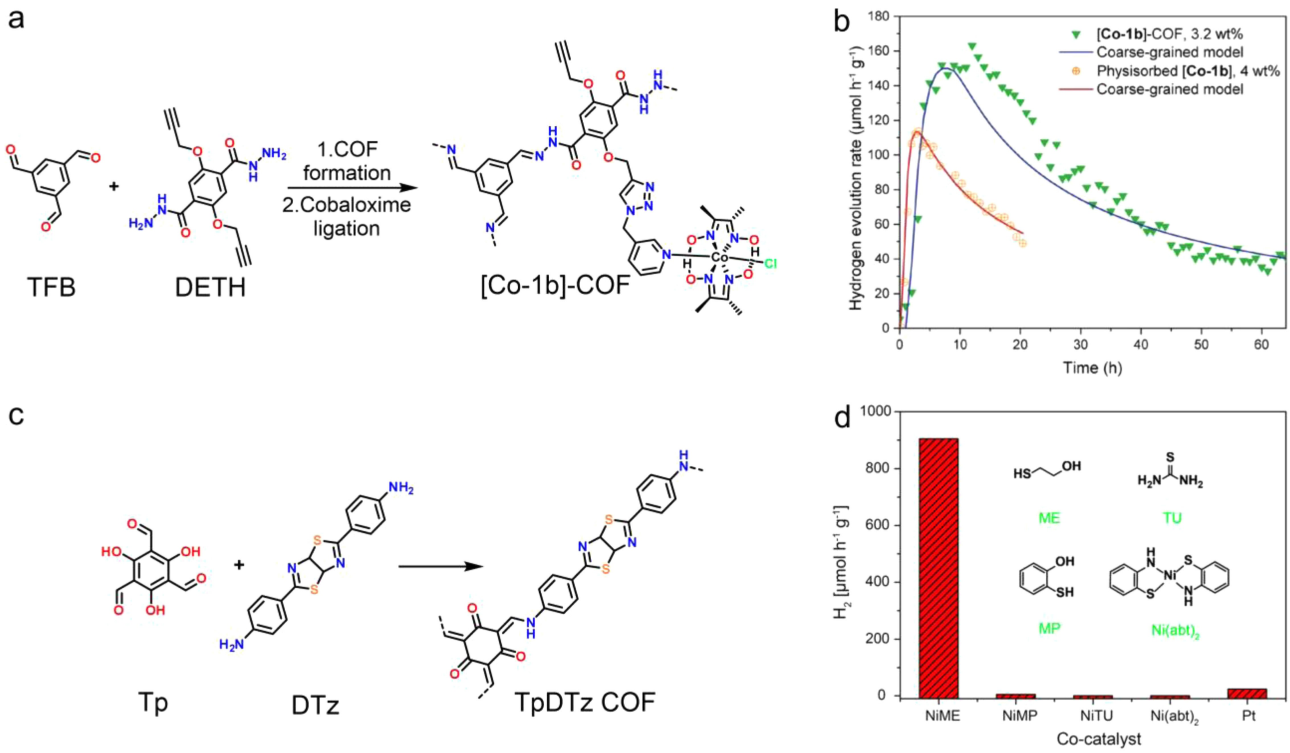

Figure 4. a) Reaction Scheme for the synthesis of [Co-1b]-COF from TFP and DETH linkers. b) Photocatalytic hydrogen evolution rate of [Co-1b]-COF and physisorbed cobaloxime [Co-1b] and fits based on a coarse-grained microkinetic model. Reproduced from Ref. [14] with permission from the American Chemical Society. c) Reaction scheme for TpDTz COF from Tp and DTz linkers. d) Photocatalytic hydrogen evolution rate of TpDTz COF using different co-catalysts. Reproduced from Ref. [15] with permission from the American Chemical Society.

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electron transfer between the COF and the PRC by keeping the metal center in close proximity, hence facilitating direct interaction. In addition, confinement of the molecular catalyst within the pores of the COF improves the long-term stability of the complex as it reduces degradation during catalysis by facilitating the re-coordination of the axial ligand.[14]

Although the evolution of hydrogen from water by noble metal-free photocatalysis is the first step towards more sustainable photocatalytic systems, the described cobaloxime-based photocatalysts only work in a mixture of water and acetonitrile, conditions that are not ideal for green and sustainable solar fuel production.

We thus introduced a COF system designed for H_2 production in pure water, using a hexameric nickel cluster (NiMe) as PRC and triethanolamine (TEoA) as electron donor sacrificial.[15] This was accomplished through the synergistic effect of the nickel co-catalyst and a new thiazole-based TpDTz COF (Figure 4c). The combination of DTz linker planarity, extended conjugation, and electron-deficient properties, along with significant long-range order (confirmed by powder X-ray diffraction (PXRD)), high BET surface area ($356\,m^2g^{-1}$), and hydrophilic nature of TpDTz COF, which enhances the dispersibility of the COF powder in water, led to photocatalytic activities superior to those observed for the cobaloxime-based systems. Interestingly, the TpDTz COF exhibited a substantial H_2 production rate of $0.941\,mmol\,g^{-1}h^{-1}$ when NiMe was used, in contrast to the much lower H_2 production rate with Pt as a co-catalyst ($0.023\,mmol\,g^{-1}h^{-1}$) (Figure 4d); this result confirmed the high affinity between the photoabsorber (COF) and the PRC (NiMe).[15] In summary, this work set the stage for the development of all-single-site photocatalysts capable of producing H_2 from water using a noble-metal-free co-catalyst, a crucial step in the sustainable production of solar fuels. Building on this approach, Jiang et al. reported an impressive activity of $11\,mmol\,g^{-1}h^{-1}$ using a Zn-porphyrin-based COF conjugated with thiomolybdate ($(NH_4)_2Mo_3S_{13}$) as a non-noble metal co-catalyst.[16]

An alternative process for converting solar energy into chemical energy involves the process of photoelectrocatalysis (PEC). In PEC, the charges generated through light absorption are extracted by applying an electric potential. This method combines the solar energy harvesting characteristics of a photoabsorber with the charge separation and extraction steps of electrocatalysis. In 2018, Bein et al. demonstrated the first COF photocathode for PEC proton reduction.[17] In this work, it was demonstrated that the processability of COFs into thin films is crucial for the preparation of photoelectrodes. In a subsequent work, we developed a strategy to fabricate colloidal nanofilms suitable for PEC based on morphology control by adjusting the nucleation and growth process during COF synthesis. Specifically, reducing the concentration of the linker 1,3,5-tris(4-aminophenyl)benzene (TAPB) and 2,5-dimethoxyterephthalaldehyde (MeOTP) favors the formation of colloidally stable nanoplates over nanospheres. MeOTP shows a strong tendency to self-assemble in solution via π–π stacking even at low concentrations, thus leading to shape anisotropic growth along the interlayer stacking direction. The as-obtained long-term stable colloid served as a source for preparing smooth and homogeneous COF films with controllable thicknesses from ~120 nm to ~660 nm through spin coating (4 and 20 cycles, respectively). In fact, this COF film preparation method allowed for the assembly of suitable heterojunction architectures with a polymer electron donor (P3HT), a CuSCN nanowire hole transport layer, and a SnO_2 electron collection layer to fabricate photocathodes with very positive onset potentials for PEC hydrogen evolution (more than $+1$ V vs. reversible hydrogen electrode (RHE) in 0.5 M NaH_2PO_4 aqueous electrolyte).[18] Although this study showcases the power of solution processing for the fabrication of multilayer COF-based optoelectronic devices, it puts the spotlight on COF processability and film formation as a key development area.

After the initial demonstration of COFs as promising photocatalysts for energy conversion, there has been a surge of concerted research activity to advance the understanding and development of this field over the past 10 years. For instance, Jiang and co-workers have contributed substantially to rationalizing the photophysical and photochemical behavior of COFs in the context of the vast structural diversity of those materials, with a particular emphasis on critical factors such as light harvesting, exciton splitting, charge transport, and charge transfer.[19] Although a direct comparison of H_2 generation by COFs is not trivial, we would like to highlight the enormous progress in terms of hydrogen production activity to date (Figure 5a–b). As mentioned above, the first hydrazone-based COF showed a H_2 production rate of $2.0\,mmol\,g^{-1}h^{-1}$ with an apparent quantum yield (AQY) of 2.2 % at 400 nm.[6] Subsequently, Cooper et al. synthesized COFs inspired by a previously reported sulfone-containing linear polymer, in which the sulfone moiety imparted to the COF broad visible light absorption, high hydrophilicity, and proper alignment of energy bands to efficiently carry out proton reduction, with H_2 rates reaching $10.1\,mmol\,g^{-1}h^{-1}$ (AQY of 3.2 % at 420 nm).[20] In 2022, a 2D COF based on benzobisthiazole was presented by Zhao et al., in which the electron-deficient property of benzobisthiazole units was combined with an electron-rich moiety such as benzotrithiophene to generate a strong donor-acceptor (D–A) structure, facilitating separation of light-induced charge carriers towards HER. This COF showed a H_2 production of as high as $15.1\,mmol\,g^{-1}h^{-1}$ (AQY of 1.6 % at 420 nm), but more importantly, it set the stage for the exploitation of D–A structures as a powerful design concept for photoactive COFs.[21] Along similar lines, Thomas et al. presented an elegant strategy to enhance the efficacy of COF photocatalytic systems, based on the in situ protonation of the imine bond by adding ascorbic acid as an electron-donor sacrificial. This protocol exploits imine protonation as a means to enhance visible light absorption as well as charge separation after photoexcitation, and—crucially—to increase hydrophilicity and hence wettability. After combining all these features, the H_2 production amounted to $20.7\,mmol\,g^{-1}h^{-1}$ (AQY of 1.4 % at 450 nm).[22] In 2023, Cao et al. presented a novel linkage conversion

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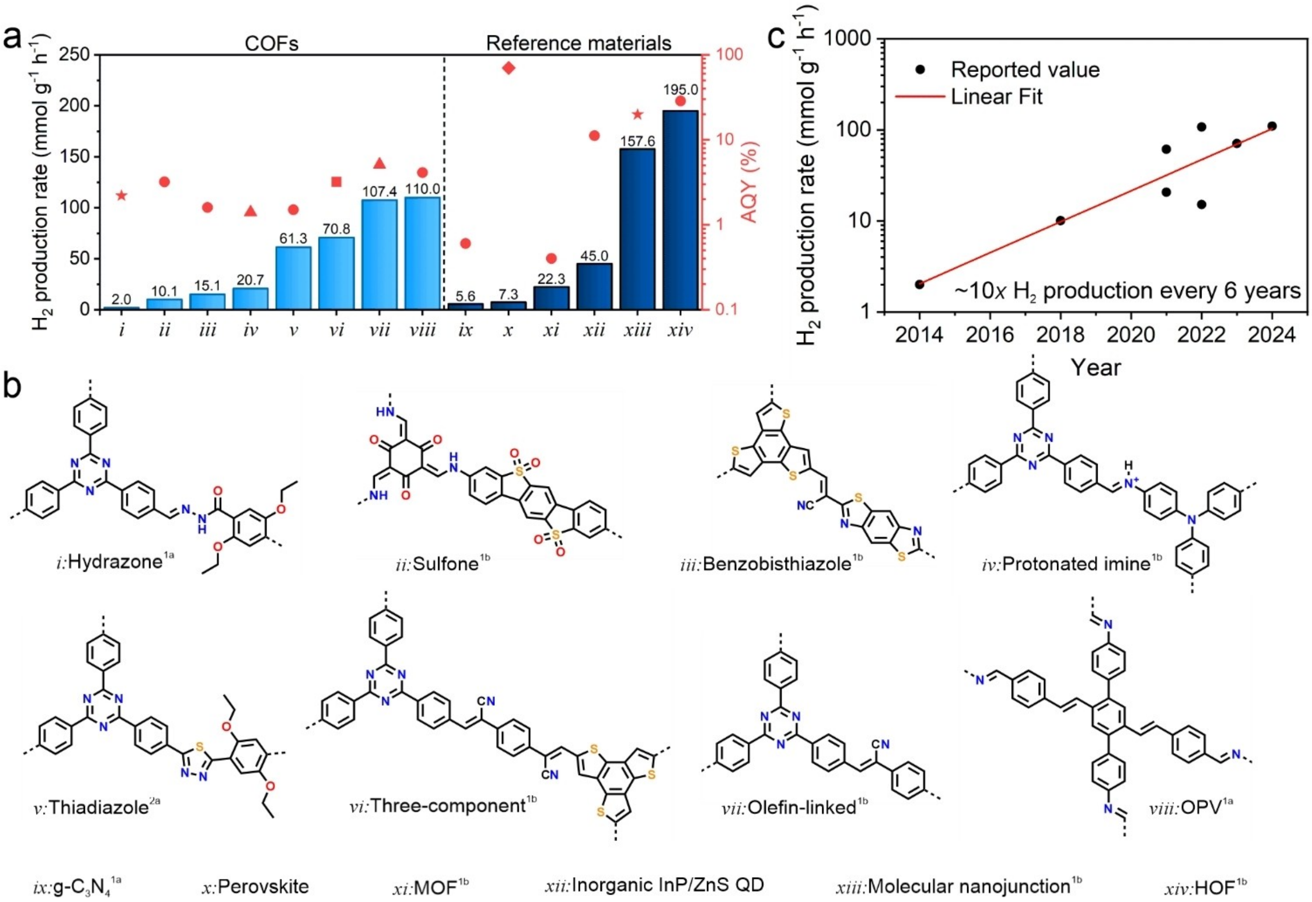

Figure 5. a) Photocatalytic hydrogen production rates and apparent quantum yields (AQY). The AQYs were calculated at different wavelengths according to the symbols: star: 400 nm, circle: 420 nm, triangle: 450 nm, square: 500 nm, and rhombus: 410 nm. Note that while the hydrogen production rates have clearly increased over the years, the AQEs show a less obvious trend. b) Chemical structures of some notable COF HER photocatalysts (*i–viii*), along with some reference material categories *ix–xiv*. Superscripts refer to the experimental conditions according to: 1 for Pt NPs and 2 for Au NPs as co-catalyst, and a for TEoA and b for ascorbic acid as sacrificial electron donor. c) Logarithmic plot of photocatalytic hydrogen production by COFs per year and its linear fit.

strategy, which turned out to be highly effective in enhancing the HER. Thiadiazole moieties were prepared post-synthetically from a hydrazine-based COF, featuring extended π-electron delocalization as well as improved thermal and chemical stability. This COF exhibited a further increased H_2 evolution rate of 61.3 mmol g^{-1} h^{-1} (AQY of 1.5 % at 420 nm).[23] Recently, a three-component donor-π-acceptor COF was published by Liu et al. in which the use of an electron-deficient triazine unit and an electron-rich benzotrithiophene moiety linked by an olefin bond work synergistically to extend the π-conjugation and enhance charge transfer and charge separation efficiency. In particular, the olefin bond showed much higher HER activity than its imine counterpart, reaching a H_2 rate of 70.8 mmol g^{-1} h^{-1} (AQY of 3.2 % at 500 nm).[24] In fact, olefin-linked COFs, synthesized by Knoevenagel condensation reactions, have been shown to be effective photocatalysts for the HER thanks to their extended π-delocalization, which confers excellent photophysical properties for HER. A case in point is the work of Liu et al., in which an olefin-based COF showed remarkable activity up to 107.4 mmol g^{-1} h^{-1} (AQY of 5.1 % at 450 nm).[25] Furthermore, Li et al. presented a notable HER catalyst in which a conjugated oligo(phenylenevinylene)-based COF (OPV COF) with kagome topology showed a HER rate of 110.0 mmol g^{-1} h^{-1} (AQY of 4.1 % at 420 nm).[26] By now, the H_2 production rates of COF systems exceed those of other prototypical organic, inorganic, and hybrid semiconductors, such as g-C_3N_4 (5.6 mmol g^{-1} h^{-1}),[27] certain types of perovskites (7.3 mmol g^{-1} h^{-1}),[28] metal–organic frameworks (MOFs, 22.3 mmol g^{-1} h^{-1}),[16] or inorganic quantum dots (InP/ZnS QD, 45.0 mmol g^{-1} h^{-1}),[29] and are comparable to highly active organic molecular systems such as nanojunctions (157.6 mmol g^{-1} h^{-1})[30] or hydrogen-bonded organic frameworks (HOFs, 195.0 mmol g^{-1} h^{-1}).[31] The HER activity of COFs has increased substantially over the last decade, with an increase of almost an order of magnitude every 6 years (Figure 5c), demonstrating how much this vast field can be explored.

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2.2. Oxygen Evolution Reaction

The second half-reaction of water splitting is the oxygen evolution reaction (OER). This four-electron oxidation reaction is kinetically and thermodynamically more challenging and often the main bottleneck in carrying out overall water splitting. In fact, COFs are no exception. The inherent difficulty of OER for electron-rich organic systems with relatively shallow highest occupied molecular orbital (HOMO)/valence band (VB) positions, together with the known issue of parasitic oxygen evolution observed with typical sacrificial electron acceptors, warrants special scrutiny when assessing the OER performance of COFs. To date, there are only a few reports of COFs as photocatalysts for oxygen evolution, demonstrating the enormous challenge of this reaction. Typically, silver nitrite ($AgNO_3$), sodium iodate ($NaIO_3$), or sodium persulfate ($Na_2S_2O_8$) are used as electron scavengers and a transition metal center such as Ru or Co is employed as a co-catalyst.[32] Once the photocatalytic OER was achieved, coupling with HER was the natural step to perform overall water splitting, as discussed below.

2.3. Overall Water Splitting

Moreover, identifying systems that are able to perform oxygen evolution and at the same time can reduce protons from water to form hydrogen is challenging. Nevertheless, in 2020 Jin et al. published the first example of full water splitting using a CTF (Figure 6a) as a photoabsorber and different co-catalysts for OER (nickel phosphide) and HER (Pt NPs). The use of the strong base potassium *tert*-butoxide (tBuOK) led to the formation of a highly crystalline triazine material (CTF-HUST-A1) as evidenced by high-resolution transmission electron microscopy (HRTEM, Figure 6b). This ordered structure, combined with well-defined porosity and high hydrophilicity resulted in coupled H_2 and O_2 production rates of 0.0254 mmol g^{-1} h^{-1} and 0.0129 mmol g^{-1} h^{-1}, respectively. In addition, CTF-HUST-A1 showed stable water-splitting activity for more than 24 h (Figure 6c).[33] This benchmark study demonstrated for the first time the simultaneous oxygen and hydrogen evolution without incorporating any sacrificial agent in an overall water-splitting process. Subsequently, a limited number of other examples were published, pointing to the relevance of COFs in solar water splitting.[34] From a more practical standpoint, there are still some challenges to overcome to achieve high performance in overall water splitting. The requirement for multiple co-catalysts opens the door to setbacks if not carefully considered. For example, the use of a noble metal such as Pt and the limited COF-co-catalyst interaction in a co-dispersed configuration call for further system optimization. On the other hand, the separation of H_2 and O_2 gases after photocatalytic water splitting is a general challenge that requires creative solutions.

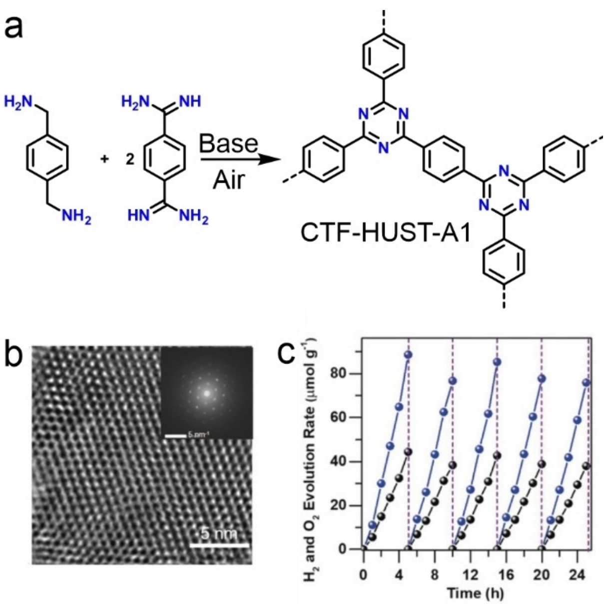

Figure 6. a) Reaction scheme for the synthesis of CTF-HUST-A1. b) HRTEM image and fast Fourier transform (FFT) of CTF-HUST-A1. c) Hydrogen and oxygen evolution rates resulting from the overall water splitting reaction by CTF-HUST-A1. Reproduced from Ref. [33] with permission from John Wiley and Sons.

2.4. CO_2 Reduction Reaction

The general idea of mimicking the natural photosynthesis process in plants in which CO_2 and H_2O are transformed into carbohydrates and oxygen, using sunlight is a major challenge in the field of energy conversion. At the same time, global warming caused by, among others, the greenhouse gas carbon dioxide, makes CO_2RR a promising alternative to mitigate the climate crisis and at the same time generate value-added products such as methanol, methane, or C_{2+} species such as ethylene or ethanol, which are commodity chemicals produced on a global scale.[35] However, the complexity of the CO_2RR and the competition with the kinetically less challenging HER impose the need to develop efficient and selective catalysts. In this context, COFs have been widely used as photocatalysts, where transition metals are incorporated as active sites to carry out such catalytic processes. To date, CO_2RR with COFs has been summarized in a number of reviews.[36] Our intention is thus not to expand on this topic here, but instead to mention a few benchmark studies which have started and progressed the field. In 2018, Huang et al. published the first example of a bipyridine-based 2D COF functionalized with the classical tricarbonylchloro(2,2'-bipyridine) rhenium (Re(bpy)-(CO)$_3$Cl) molecular complex known as Lehn's catalyst for photocatalytic CO_2 reduction.[37] Immobilization of Lehn's catalyst on the COF backbone improved charge separation after illumination through electron transfer from the COF skeleton to the Re center, enhancing the stability and activity towards CO_2RR. The enormous interest attracted by this work in the use of COFs as CO_2RR catalysts has led to important achievements in the following years. For example, a remarkable CO production rate of 18.0 mmol g^{-1} h^{-1} with

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95.7% CO selectivity was achieved by a triazine-based COF using coordinated Co(II) as a co-catalyst and TEoA as a sacrificial reagent.[38] However, further advances are needed to achieve the desired CO_2 reduction beyond CO. Although the production of CH_4 and HCOOH by a Co-porphyrin-based COF has been reported,[39] higher efficiencies and the formation of additional products such as methanol or C_{2+} such as ethanol and ethylene are lacking in this field.

2.5. N_2 Fixation

The photosynthetic generation of ammonia from atmospheric nitrogen is an attractive process since ammonia is a vital commodity for daily life and can be used to store energy in chemical bonds in a sustainable fashion. However, the very stable triple bond of molecular nitrogen and the competition with HER make this process an enormous challenge. Accordingly, only a few works have been reported where CTF or COF act as photocatalysts in the N_2 fixation reaction. An early report in 2020 used a CTF with well-defined Pt centers to achieve N_2 fixation in the absence of an additional sacrificial electron donor reagent in aqueous media, defining water oxidation as the counter-reaction.[40] Subsequently, Zhao et al. studied the influence of functional groups incorporated into an Au-porphyrin-based COF. The isolated gold atom in the porphyrin unit allows for tuning the electronic environment surrounding the active site molecular design of the COF structure. The authors found that the addition of electron-withdrawing groups proximally to the porphyrin center (pentafluorophenyl rings) and distally to the active site (benzothiadiazole linker) enabled nitrogen reduction to ammonia with a rate of $0.333\ mmol\,g^{-1}h^{-1}$ in pure water using K_2SO_3 as sacrificial agent.[16] Still, the formidable challenges of realizing photocatalytic N_2 fixation, including inefficient N_2 adsorption, triple bond activation, and charge carrier separation, as well as recurring issues with false positives due to nitrogen or ammonia contamination, have resulted in limited progress in recent years.

2.6. H_2O_2 Production

Hydrogen peroxide can be used in multiple applications, such as disinfection processes, water treatment, and energy conversion. Therefore, the use of COFs as photocatalysts has become an attractive method for H_2O_2 generation. The production of H_2O_2 takes place mainly via two pathways: through the oxygen reduction reaction (ORR) and through the oxidation of water. In 2020, Van Der Voort et al. reported the first example of a COF with kagome topology for the metal-free photocatalytic generation of H_2O_2 by the ORR.[41] In the following years, the high interest in this topic resulted in a rapid growth in the number of publications, about doubling each year (Figure 7a).[42] Among some benchmark contributions, the use of high-throughput synthesis for the screening of a large number of COFs towards H_2O_2 production has demonstrated the importance of

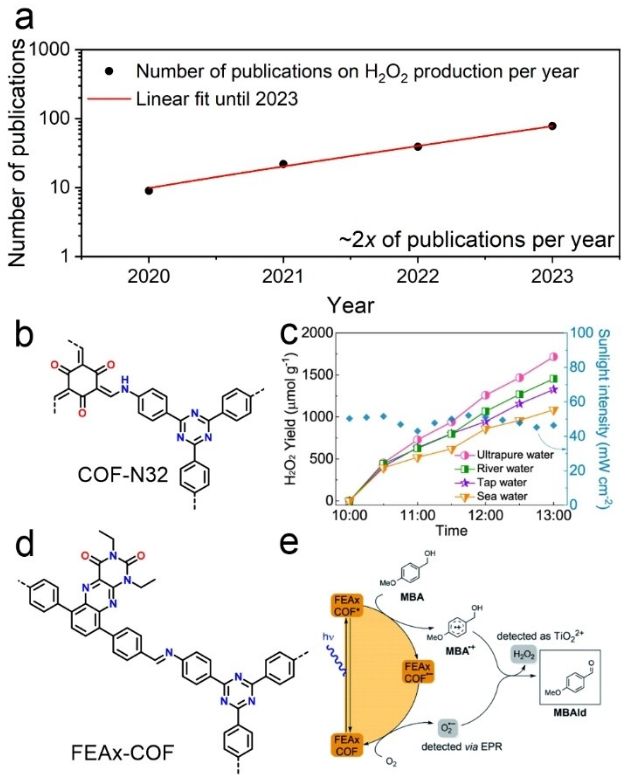

Figure 7. a) Number of scientific publications per year registered in SciFinder with the keywords "Covalent organic framework" AND "hydrogen peroxide" AND photo*. April 4th 2024. b) Chemical structure of the triazine-based COF-N32. c) H_2O_2 production with natural sunlight, air, and different water sources by COF-N32. Reproduced from Ref. [44] with permission from Springer Nature. d) Chemical structure of FEAx-COF. e) Proposed mechanism for the photocatalytic oxidation of *p*-methoxybenzyl alcohol (MBA) by FEAx-COF. EPR, electron paramagnetic resonance. Reproduced from Ref. [48] with permission from the Royal Society of Chemistry.

developing new technologies—here AI-assisted, robotic synthesis—for the accelerated discovery of new materials and catalysts.[43] In addition, the work of Ni et al. in which a triazine-based COF (Figure 7b) can produce a significant amount of H_2O_2 from water, air, and natural sunlight ($0.605\ mmol\,g^{-1}h^{-1}$), has attracted significant attention (Figure 7c).[44] H_2O_2 production in the absence of sacrificial agents is an attractive way to store solar energy since this reaction is thermodynamically uphill ($\Delta G^\circ = 204\ kJ\,mol^{-1}$).[45] Therefore, the fact that metal-free COFs can produce H_2O_2 in a photosynthetic reaction under natural sunlight suggests a promising future for this topic. The remaining challenges include the transition from batch to flow reactions for optimal H_2O_2 utilization,[46] and the development of strategies to efficiently extract the produced H_2O_2 solution from the photocatalytic setup.

2.7. Alcohol Oxidation

An alternative oxidation reaction to couple with any of the reduction reactions mentioned above is the oxidation of

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alcohols to value-added products including carbonyl species such as aldehydes, ketones, or carboxylic acids. Using alcohol oxidation bypasses the need for sacrificial electron donors or the challenging water oxidation reaction while providing organic products that can be fed into the value chain of commodity chemicals. This however requires highly selective oxidation reactions for which the use of COFs may be especially fruitful, due to their molecular-level tunability. For example, a cobaloxime-functionalized COF was used to carry out the HER coupled to ethanol oxidation to produce acetaldehyde.[47] Furthermore, in 2021 we developed a nature-inspired COF for the selective oxidation of benzyl alcohols to their corresponding aldehydes. Here, the incorporation of a flavin-based chromophore (alloxazine) into the COF skeleton (Figure 7d) led to broad visible light absorption and enabled the photocatalytic oxidation of benzyl alcohols to aldehydes, using ORR as the corresponding reduction reaction (Figure 7e).[48] As mentioned above, water oxidation is usually a limiting step for the overall redox reaction (coupled with HER, CO_2RR, or ORR). However, it has been shown that the facile oxidation of alcohols can be combined with solar fuel production such as hydrogen in a photoreforming process, thus mitigating the bottleneck of water oxidation while yielding valuable oxidized products. Such processes open up interesting perspectives when linked for example to the selective degradation of biomass or microplastics.[49]

3. Summary and Perspectives

The surge in activity on COF photocatalysis since the seminal work in 2014 vividly demonstrates the enormous potential of COFs as molecularly precise semiconductor photocatalysts in energy conversion reactions. The great structural diversity and the possibility to rationally design their molecular composition and extended structure allows for the fine-tuning and orchestration of properties vital for photocatalysis such as light absorption, charge carrier generation, separation, etc. However, what sets COFs apart from other organic semiconductors is their well-ordered structure and structurally precise porosity, which in tandem increase the accessibility of active sites and facilitate the electron transfer process between COF and reactants. Although each reaction follows a different mechanism, we identify some common features in the structure of COFs that based on aggregated evidence enhance their photocatalytic performance: For example, the incorporation of suitable heterocycles in the COF skeleton can lead to powerful donor-acceptor structures which reduce the band gap, enhance visible light absorption and assist in charge carrier separation, akin to an internal heterojunction. Widely used examples include triazine, benzothiadiazole, sulfone, benzodithiophene, etc, and their combinations (Figure 8). In fact, triazine units tend to improve the structural and photophysical properties of these photocatalysts. On the one hand, the robustness of the triazine moiety confers superior chemical stability to the COF and its planarity allows crystallization driven by the "templating" effect that often results in a more ordered structure. At the same time, electron-poor triazine units provide a platform for donor-acceptor structures that promote charge separation and enhance light absorption. In addition, the COF linkage plays a critical role not only in the stability of the COF during catalysis, but also in modulating its electronic properties: Specifically, it has been shown that the olefin bond and hydrazone unit are competent linkages that increase pi-conjugation, decrease the energy gap and reduce the exciton binding energy compared to imine linkages, leading to more efficient charge separation after light absorption (Figure 8).[50]

And yet, although COFs are highly promising photocatalysts, some of their properties—both structural and (opto)electronic—need to be improved to achieve higher performance. For example, further reducing the binding energy of the photogenerated excitons, enhancing charge transport through a less defective, more conjugated COF backbone supporting high charge carrier mobilities, increasing the stability of the COF backbone and maintaining the interaction between the metal center and the COF skeleton are key development areas, among many others.[51] Fortunately, great strides have been made over the past years to broaden the palette of COF formation and post-synthetic stabilization reactions, and towards introducing functional groups of all stripes into COFs. Among the many interesting strategies, linkage modification stands out as a powerful tool to achieve a more stable backbone structure while at the same time introducing functionality into the framework *post*-synthetically, for example, to enhance its hydrophilicity and hence wettability in water.[16,52] In addition, controlling the COF morphology—especially particle size, shape, and aggregation behavior—can significantly improve the interaction of active sites with the reactants and improve the dispersibility and colloidal stability of the material during catalysis.[53] Moreover, creating thin films and their heterostructures which synergistically combine the features of different materials and control charge separation via heterojunctions could further increase the catalytic performance.[18] For instance, hybrid materials composed of COFs and MOFs, carbon nanomaterials, or metal NPs to achieve plasmonic enhancement of catalytic reactions come to mind, among others.[54]

As COFs are coming of age, we would like to emphasize the ever-greater need for improving the understanding, processability, and scalability of COFs while exploring alternative photocatalytic setups to extend the utility of COFs as catalysts. For example, COFs are well-known as (micro-meso)porous materials that can provide a well-controllable catalytic environment. However, studying a catalytic process in a confined pore space is a major challenge to address. Therefore, innovative approaches are needed to systematically study confinement effects within COF pores on photocatalytic processes. On the other hand, developing strategies to process COFs into scalable particle-based and thin film systems presents an extraordinary opportunity to incorporate these porous materials into large-scale photocatalytic reactors, such as film-based,[55] flat-panel-based[56] or even floating systems which require

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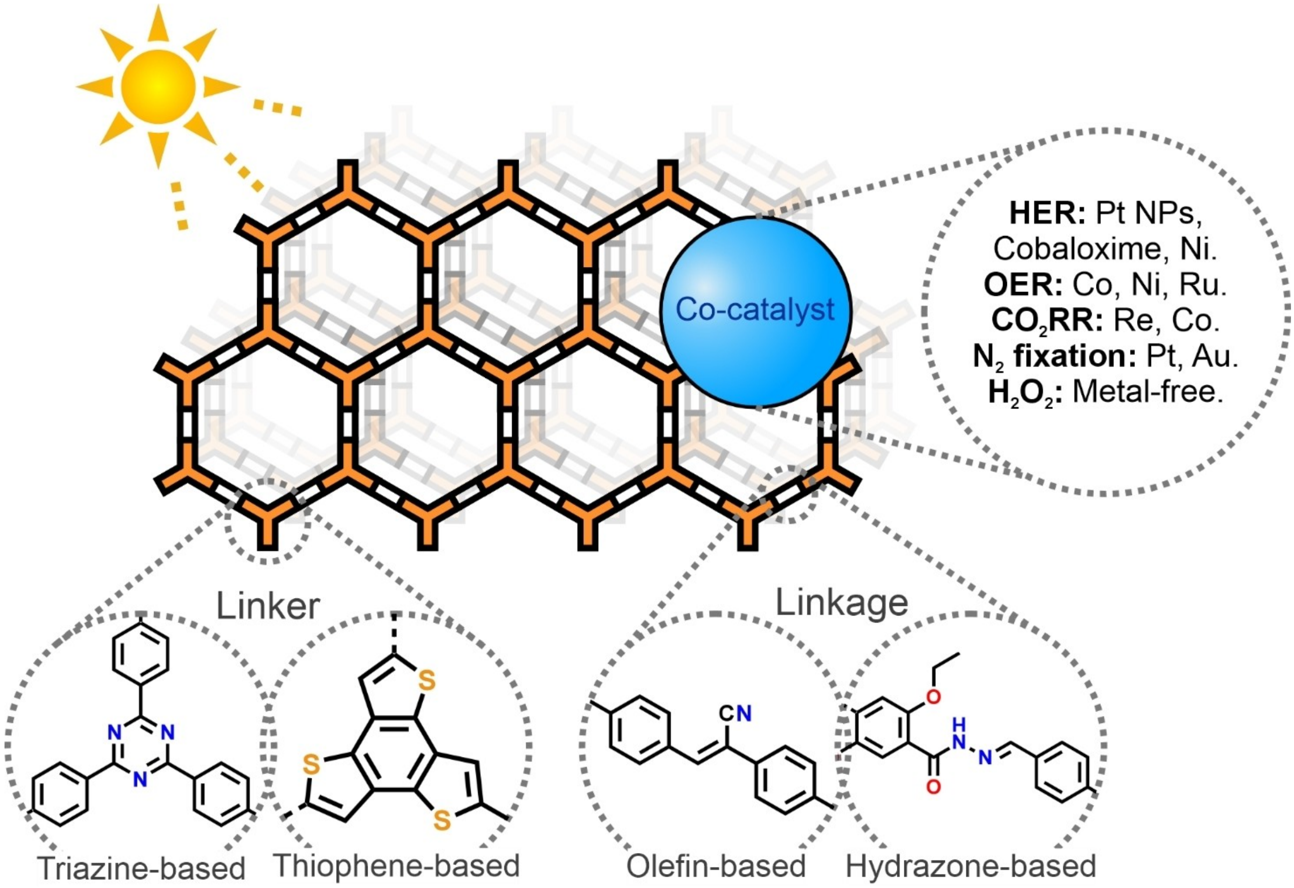

Figure 8. Scheme and chemical structure of some notable types of ligands, linkers, and co-catalysts present in COFs as photocatalysts.

dedicated morphologies and, hence, processing strategies.[57] In summary, there are plenty of opportunities for further growth in this field—the future of COF photocatalysis is bright.

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Conflict of Interest

The authors declare no conflict of interest.

Data Availability Statement

Data sharing is not applicable to this article as no new data were created or analyzed in this study.

Keywords: Solar energy conversion · covalent organic frameworks · covalent triazine frameworks · photocatalysis · organic semiconductor

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