Photocatalysts Based on Organic Semiconductors with Tunable Energy Levels for Solar Fuel Applications

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The photocatalytic synthesis of solar fuels such as hydrogen and methane from water and carbon dioxide is a promising strategy to store abundant solar energy in order to overcome its intermittency. Although this approach has been studied for decades using inorganic semiconductor photocatalysts, organic semiconductors have only recently gained notable attention. The tunable energy levels of organic semiconductors can enable the design of photocatalysts with optimized solar light utilization. However, the solar conversion efficiency of organic semiconductor photocatalysts has so far been limited by their low quantum efficiencies. To address this issue, various photocatalyst design strategies including semiconductor energy level optimization, surface modification, and the fabrication of heterojunctions have been applied, resulting in substantial increases in photocatalytic efficiency. This progress report systematically describes the strategies employed to increase the efficiency of organic semiconductor photocatalysts for the generation of solar fuels from water and carbon dioxide. Particular attention is given to describing strategies to enhance quantum efficiency, and insights are provided on the mechanisms underlying their success to aid the rational design of future organic photocatalysts. Perspectives on the future challenges and promising research directions for the design of efficient organic photocatalysts for the generation of solar fuels are also provided.

1. Introduction

Averting the effects of impending climate change resulting from global population and economic growth requires the development of sustainable energy sources. Among these, solar energy has the greatest potential, with more solar energy irradiating the surface of the Earth in one hour than human society consumes in one year. However, the intermittency of solar energy limits its utility. In order for solar energy to provide power on a scale commensurate with that currently generated from fossil fuels, it must be stored and supplied to users on demand. On short timescales (seconds to days) this is possible to achieve using batteries, which can store electricity generated from solar photovoltaics. However, the expensive materials required and their relatively high rates of self-discharge make batteries unsuitable for seasonal energy storage. Storing solar energy in the chemical bonds of a fuel, which can be stored indefinitely at low cost, transported, and converted to electrical or heat energy on demand is therefore highly desirable. Solar fuels such as H₂, CH₃OH, and CH₄ can be generated from abundant and renewable feedstocks such as water and CO₂ using semiconductor photocatalysts. The vast majority of research to date has focused on photocatalysts fabricated from wide bandgap semiconductors such as TiO₂,[8] SrTiO₃,[9] and carbon nitride (CN).[10–14] Photocatalysts based on some of these semiconductors have achieved operational stabilities exceeding 1000 h and maximum external quantum efficiencies (EQEs) of over 50% for overall water splitting.[9,15–18] However, their wide and difficult to tune bandgaps mean that photocatalysts fabricated from these semiconductors are almost exclusively active at UV wavelengths, which carry <5% of solar energy.[19] This fundamentally limits their efficiency below what is required for many practical solar fuels applications. For example, an estimated solar-to-hydrogen efficiency (ηH₂) of 5–10% would be required to photocatalytically produce H₂ at a cost that meets the U.S. Department of Energy’s target of $2–4 kg⁻¹, which is difficult or impossible to achieve with the aforementioned wide bandgap semiconductors.[20] This has stimulated interest in developing novel photocatalysts based on semiconductors with narrower bandgaps that are able to absorb a greater proportion of the solar spectrum and can therefore achieve higher maximum theoretical solar energy conversion efficiencies.[18] Among these, non-CN organic semiconductors have recently gained prominence due to the Earth abundance of their constituent elements, and their high extinction coefficients and...
precisely tunable energy levels. This progress report will introduce the theory of photocatalysis and provide an overview of the recent advances in the design of photocatalysts based on non-CN organic semiconductors for the production of solar fuels from water and CO₂.

2. The Principles of Photocatalytic Solar Fuel Generation

Photocatalysts are materials that absorb light and convert it to electrical charges that can drive reductions and oxidations of species at the photocatalyst surface. Most photocatalysts are a composite of one or more semiconductors, in which photogenerated charges are formed upon bandgap excitation, and one or more cocatalysts, which extract the photogenerated charges from the semiconductor(s) and use them to oxidize or reduce the substrates of interest. If the overall redox reaction driven by the photocatalyst has a positive Gibbs free energy ($\Delta G$), the photocatalytic process converts light to chemical energy. This is the basis for generating solar fuels. The potential difference available for a photocatalytic reaction is determined by the bandgap(s) of the semiconductor(s) that the photocatalyst is fabricated from. In order for a photocatalyst to drive an electrolytic reaction, the most negative conduction band (CB) or lowest unoccupied molecular orbital (LUMO) energy level of the semiconductor(s) used to fabricate the photocatalyst must be less negative (on the absolute electrochemical scale) than the half-cell reduction potential of the species to be reduced, and the least negative valence band (VB) or highest occupied molecular orbital (HOMO) energy level of the semiconductor(s) used to fabricate the photocatalyst must be more negative (on the absolute electrochemical scale) than the half-cell reduction potential of the species to be oxidized. The photocatalyst must also provide sufficient overpotential ($\eta$) to overcome the kinetic barriers associated with each half-reaction, which widens the minimum bandgap required to drive the overall reaction (Figure 1). The $\eta$ required for each half-reaction depends on how efficiently the photocatalyst surface catalyzes that half-reaction and can be minimized by the use of suitable cocatalysts. The use of cocatalysts will be discussed in more detail next. The two half-reactions can either be driven simultaneously by a single photocatalyst (Figure 1a) or occur individually on two separate photocatalysts that operate in series (Figure 1b,c). The latter configuration is known as a Z-scheme and is analogous to natural photosynthesis.

Because both semiconductors in a Z-scheme must be photoexcited in order for both half-reactions to take place, Z-schemes must absorb twice as many photons to generate the same amount of product as a single semiconductor that can drive both half-reactions. However, if they utilize narrow bandgap semiconductors with complementary absorptions, Z-schemes can achieve higher maximum theoretical solar conversion efficiencies than single photocatalyst systems by harvesting a larger fraction of the solar energy.  

Figure 1. Schematic energy level diagram of a) a single photocatalyst and b,c) a Z-scheme (formed from photocatalysts b and c) for the generation of solar fuels and value-added products from CO₂ and H₂O. Each photocatalytic reaction consists of water oxidation coupled to the reduction of either H⁺ or CO₂. Solid horizontal lines represent the reduction potentials at pH 7 of the half-reactions detailed in Table 1. All energy levels and electrochemical potentials are expressed on the absolute electrochemical scale (0 V vs NHE = −4.44 V vs vac.).
The conversion of solar to chemical energy in all photocatalytic reactions in both single semiconductor and Z-scheme configurations consists of four major steps: 1) photoexcitation of semiconductor to generate an electron–hole pair, 2) charge separation, 3) charge transport to catalytic sites at the photocatalyst surface, and 4) electrocatalytic reduction and oxidation of species in the surrounding matrix (Figure 2).[18,25]

To maximize photocatalytic efficiency, it is essential to design photocatalysts in a way that maximizes the efficiency of each of these consecutive steps. The remainder of this progress report will describe the numerous strategies that have been developed to optimize these steps in photocatalysts based on non-CN organic semiconductors for the generation of solar fuels. General strategies that are applicable to all photocatalysts will be discussed first, followed by a discussion of how specific strategies have been applied to increase the efficiency of photocatalysts for H₂ evolution, overall water splitting (OWS), O₂ evolution, and CO₂ reduction.

3. General Strategies to Enhance Photocatalytic Efficiency

3.1. Tuning Semiconductor Energy Levels

Regardless of which reaction a photocatalyst is designed to drive, efficient harvesting of solar photons by the light absorbing semiconductor(s) is essential to maximize its efficiency. A major research focus has therefore been to design organic semiconductors that have suitably aligned energy levels to drive their specific half-reactions (Figure 1) while also retaining narrow bandgaps and broad absorptions in the 400–1000 nm wavelength range, where solar energy is most concentrated and solar photons are most abundant (Figure 3).

To achieve this, the structures of most modern semiconductors often incorporate extended aromatic units and heterocycles with stabilized quinoid resonance structures that narrow their bandgaps through extended π-conjugation.[26–28] Copolymerization of electron-rich and electron-deficient aromatic units (referred to as donor and acceptor units) is also often
employed to further optimize the semiconductor bandgap through molecular orbital hybridization and enable precise tuning of the HOMO and LUMO.[29–36] The ability to tune energy levels through synthetic design is a key advantage of non-CN organic semiconductors, because it can be used to design photocatalysts that have strong visible light absorptions while retaining suitable energy level alignments to drive the desired photocatalytic reactions.

3.2. The Use of Cocatalysts

Similarly, regardless of which reaction a semiconductor is designed to drive, its photocatalytic efficiency (the rate at which it transfers charges from its surface to substrates in the surrounding gas or liquid phase) can be improved by interfacing it with a suitable cocatalyst. Cocatalysts accelerate charge transfer by providing sites for charge accumulation, required for multielectron transfer reactions, and lowering the activation $\eta$ required to drive the desired photocatalytic reaction by lowering the activation energy required for charge transfer.[38–41] An ideal cocatalyst will efficiently extract photo-generated electrons or holes from the semiconductor, and use them to rapidly and specifically drive the desired reduction or oxidation reaction while avoiding the competing charge recombination. Nanoparticles (NPs) of metals or metal oxides that are efficient photocatalysts for the desired half-reactions are commonly employed as cocatalysts.[38–41] These nanoparticles can often be present within the semiconductor as impurities following polymerization (e.g., Pt, Ni, or Cu)[33,41,42] or interfaced with the semiconductor surface in a subsequent deposition step (e.g., Pd).[43–45] As well as minimizing the $\eta$ required to drive the desired photocatalytic reaction, the cocatalyst can also improve charge separation at the semiconductor/cocatalyst interface.[21,46] Therefore, designing the cocatalyst deposition method to minimize the cocatalyst particle size can increase photocatalytic activity as this both maximizes the semiconductor/cocatalyst interfacial area and the surface area of cocatalyst available to drive the desired half-reaction. This can enhance the photocatalyst’s external quantum efficiency (EQE) by enabling more efficient exciton dissociation at the semiconductor/cocatalyst interface and can improve the co-catalyst’s turnover frequency (TOF) by exposing more surface area per unit mass of cocatalyst.[40,47–50] Furthermore, because a particular semiconductor can have suitably aligned energy levels to drive a wide range of redox reactions (Figure 1) the addition of a cocatalyst which preferentially catalyzes the desired half-reaction can be crucial to improve a photocatalyst’s selectivity. This is particularly important when designing photocatalysts for CO$_2$ reduction, where reduction cocatalysts such as Ir$_2$O$_3$, NiO, and Cu are used to control selectivity between the various competing CO$_2$ reduction pathways (Table 1) and to suppress H$_2$ evolution—an undesired side reaction.[42,51–53] Similarly, core–shell cocatalysts such as Ni-NiO and Rh-Cr$_2$O$_3$ can selectively promote proton reduction while suppressing superoxide formation (Equation (I)) O$_2$ reduction, and the thermal recombination of H$_2$ and O$_2$, thereby improving the efficiency of OWS in both single semiconductor systems and Z-schemes.[54–56]

| Product                  | Half-reaction                        | $E$ (pH 7) [V vs NHE] | $E$ (pH 7) [eV vs vac.] | Equation |
|--------------------------|-------------------------------------|-----------------------|-------------------------|----------|
| Superoxide               | $O_2 + e^- \rightarrow O_2^-$       | $-0.16$               | $-4.28$                 | (1)      |
| Methane                  | $CO_2 + 8H^+ + 8e^- \rightarrow CH_4 + 2H_2O$ | $-0.24$               | $-4.20$                 | (2)      |
| Ethane                   | $2CO_2 + 14H^+ + 14e^- \rightarrow C_2H_4 + 4H_2O$ | $-0.27$               | $-4.17$                 | (3)      |
| Ethanol                  | $2CO_2 + 12H^+ + 12e^- \rightarrow C_2H_2O + 3H_2O$ | $-0.33$               | $-4.11$                 | (4)      |
| Methanol                 | $CO_2 + 6H^+ + 6e^- \rightarrow CH_2OH + H_2O$ | $-0.39$               | $-4.05$                 | (5)      |
| Hydrogen                 | $2H^+ + 2e^- \rightarrow H_2$       | $-0.41$               | $-4.03$                 | (6)      |
| Carbon monoxide          | $CO_2 + 2H^+ + 2e^- \rightarrow CO + H_2O$ | $-0.51$               | $-3.93$                 | (7)      |
| Formic acid              | $CO_2 + 2H^+ + 2e^- \rightarrow HCOOH$ | $-0.58$               | $-3.86$                 | (8)      |
| Oxalic acid              | $2CO_2 + 2H^+ + 2e^- \rightarrow H_2C_2O_4$ | $-0.87$               | $-3.57$                 | (9)      |
| Oxygen                   | $2H_2O \rightarrow O_2 + 4H^+ + 4e^-$ | $+0.82$               | $-5.26$                 | (10)     |
| Hydrogen peroxide        | $2H_2O \rightarrow H_2O_2 + 2H^+ + 2e^-$ | $+1.20$               | $-5.64$                 | (11)     |

*Values converted to the absolute electrochemical scale using the relation: 0 V versus NHE = −0.44 V versus vac.

4. Organic Photocatalysts for Hydrogen Production

H$_2$ production via photocatalytic OWS is an attractive method to generate H$_2$, a highly versatile clean burning fuel and a valuable chemical feedstock.[61,62] Since the first report of photocatalytic water splitting by Fujishima and Honda,[63] the goal has been to develop a stable photocatalytic system synthesized from Earth-abundant elements that is capable of efficiently splitting water into H$_2$ and O$_2$ using solar energy. Although the final photocatalytic system is required to simultaneously drive both the hydrogen evolution reaction (HER, Equation (6)) and the oxygen evolution reaction (OER, Equation (10)), it is common to initially test photocatalysts for either the HER or the OER in the presence of a sacrificial hole or electron scavenger, respectively. The role of these scavengers is to rapidly extract the charges that are not being used for the desired half-reaction (holes for the HER or electrons for the OER) in order to allow the desired half-reaction to take place. This simplifies testing and allows hydrogen evolution photocatalysts (HEPs) and OER photocatalysts (OEPs) to be individually optimized without requiring the construction of a complete Z-scheme.

When choosing a hole scavenger for a particular semiconductor, it is essential that the redox potential of the hole scavenger is less negative (on the absolute electrochemical scale) than the HOMO energy level of the semiconductor so that photogenerated holes in the semiconductor HOMO have sufficient thermodynamic potential to oxidize the hole scavenger. Similarly, when choosing an electron scavenger, it is essential that the scavenger redox potential is more negative (on the absolute electrochemical scale) than the semiconductor LUMO energy level so that photogenerated electrons in the
semiconductor LUMO have sufficient thermodynamic potential to reduce the electron scavenger. Typical hole scavengers used during photocatalytic hydrogen evolution include amines such as diethylamine (DEA), triethylamine (TEA), and triethanolamine (TEOA) as well as ascorbic acid (AA) and methanol (MeOH).\[^{63}\] Commonly used electron scavengers include Ag\(^+\), Fe\(^{3+}\), and IO\(_3\)^\(-\).\[^{64}\] The hole or electron scavengers employed can greatly influence the H\(_2\) and/or O\(_2\) evolution rates achieved with a given photocatalyst, and are usually empirically selected to maximize the production of the desired product. The mechanisms of hole and electron scavenging are still poorly understood, but factors including the scavenger redox potential, its affinity for the semiconductor surface, and its effect on the solution pH all play a role in determining which scavengers are optimal for a particular photocatalyst.\[^{63-67}\]

### 4.1. Linear Conjugated Polymers for Hydrogen Evolution

The linear conjugated polymer 1 (Figure 4) was the first reported organic semiconductor to be used as a HEP.\[^{68}\] Its HER rate (2.08 µmol h\(^{-1}\)) under broad spectrum irradiation (>290 nm) was low due to its wide bandgap (2.9 eV) that limited its activity to wavelengths <430 nm and low EQE (<3.3% at 313 nm). This HER rate was achieved without the addition of a cocatalyst, but it is likely that the insoluble polymer contained a substantial amount of residual Ni (originating from its synthesis via Ni-catalyzed Yamamoto polymerization) that could have acted as a cocatalyst.\[^{64,68-70}\] Since this first report, substantial efforts have been made to improve both the active wavelength range and the EQE of linear conjugated polymer HEPs. Initial studies focused on using the aforementioned molecular design techniques to narrow the bandgap of 1 in order to extend light absorption further into the visible spectrum. Incorporating the planarized dibenzo[b,d]thiophene unit into the polyphenylene backbone resulted in polymer 3 with a bandgap of 2.77 eV and a HER rate seven times greater than 1 when measured under identical conditions (>420 nm broad spectrum irradiation).\[^{30}\] More importantly, it was found that when the dibenzo[b,d]thiophene unit was replaced with dibenzo[b,d]thiophene sulfone (4), the HER rate increased by a factor of 3. This observation could be partly explained by the more efficient light absorption of 4 versus 3 due to its narrower bandgap (2.70 eV) but it was later shown that the hydrophilicity of the sulfone group may have also increased the EQE of 4 by creating a more water-rich environment near the polymer backbone, which enabled more efficient oxidation of the TEA hole scavenger, and hence a higher yield of photogenerated electrons in the polymer capable of driving H\(_2\) evolution.\[^{67}\] This effect was further exploited by the synthesis of the dibenzo[b,d]thiophene sulfone homopolymer 5 which achieved a 160% EQE increase at 420 nm compared to 2 (11.6% vs 7.2%) that was attributed to the increased

![Figure 4. Chemical structures of the linear conjugated polymer semiconductors 1–12 and EH-IDTBR (13).](image-url)
hydrophilicity of 5. Using miniemulsion polymerization to decrease the particle size of 5 further increased its EQE by a factor of 2.5 versus the bulk polymer because the greater semiconductor/electrolyte interfacial area enabled more efficient hole scavenging.[71] These results demonstrate that making the semiconductor surface more accessible to hole scavengers can improve a HEP’s EQE by increasing the efficiency of exciton dissociation at the semiconductor/electrolyte interface.[21,67]

Unlike the insoluble polymers 1–5, the size and shape of photocatalysts fabricated from polymers bearing solubilizing side chains can be controlled using a variety of solution processing techniques. Most notably, NP formation using the reprecipitation[41,72,73] and miniemulsion[32,74] methods has been widely employed to reduce the particle size of HEPs formed from soluble conjugated polymers in order to maximize their surface area.[31,75] In one study, the HER rate of NP photocatalysts formed from polymer 6 showed an initial HER rate improvement of five orders of magnitude versus the bulk polymer, demonstrating the efficacy of this technique.[71] However, a rapid HER rate decrease was observed, possibly due to aggregation of the NPs. It should also be noted that the presence of hydrophobic alkyl side chains on the polymer backbone may impede H₂ evolution, possibly by reducing the efficiency of hole scavenging, and that unless solution processing is used to reduce the photocatalyst particle size, the efficiency of photocatalysts based on soluble conjugated polymers bearing alkyl side chains can become lower than that of their insoluble counterparts.[76] Combining NP formation with an enhancement of the semiconductor’s hydrophilicity can further improve a HEP’s EQE. The oligoethylene glycol side chains on polymer 8 increased both its hydrophilicity and water dispersibility compared to the alkyl side chain bearing polymer 7, leading to a smaller average particle diameter (6 nm vs 24 nm) and a surface that was more accessible to both the Pt cocatalyst and the AA hole scavenger. The combination of these factors increased its HER rate (39.75 μmol h⁻¹) by a factor of almost 90 compared to the hydrophobic alkyl side chain bearing analogue 7.[77] A similar effect was observed upon partial substitution of the hydrophobic tertiary amine side chains on polymer 9 with side chains bearing hydrophilic quaternary ammonium cations.[78] The resulting decrease in particle size and increase in surface hydrophilicity of HEPs fabricated from polymer 10 resulted in a 50-fold improvement in its HER rate compared to polymer 9. Because the side chain variation had almost no impact on the absorption spectra of polymers 7 or 9, the substantial HER rate increases observed were due primarily to the increased EQE of the HEPs fabricated from their more hydrophilic analogues, which indicates that hydrophilicity enhancement of HEPs is an effective technique to increase their EQE and a promising direction for further research.

The photocatalysts based on polymers 1–8 utilized residual metals and/or photodeposited Pt NPs as HER cocatalysts. However, it is also possible to attach cocatalysts to the polymer backbone covalently or via chelation.[79–81] Polymer 11 utilized the Pt complex ([5-bromo-2-(5-bromo-thio-phen-2-yl)pyridinato-N,C₃](2,4-pentanedionato-O,O)-platinum(II)) as a cocatalyst to covalently link the Pt cocatalyst to the conjugated polymer backbone.[82] Increasing the mole fraction of the Pt-containing unit in polymer 11 from 0% to 15% increased the EQE of NP HEPs fabricated from the polymer by a factor of 10 (0.04–0.4% at 515 nm) with a corresponding ninefold increase in the HER rate (0.88–8.16 μmol h⁻¹). It remains unclear whether covalent attachment of Pt on the semiconductor backbone is more effective at increasing the HER rate than photodeposition of Pt NPs on the semiconductor surface. However, the increased synthetic control over both the cocatalyst structure and attachment location that covalent binding of a molecular complex provides may yet prove to be highly advantageous. For example, photocatalysts could be designed with covalently attached molecular catalysts tailored for a wide range of specific organic reductions and oxidations.[82]

The strategies mentioned previously all focus on increasing a photocatalyst’s efficiency by increasing its light absorption, or increasing its EQE by improving charge separation at the semiconductor/electrolyte or semiconductor/cocatalyst heterojunctions at its surface. However, they do not address the problem of inefficient charge separation in the semiconductor bulk, which was determined to be the key factor limiting quantum efficiency in particulate photocatalysts.[83] This is because, in a typically sized NP with a diameter of 100 nm, most excitons are generated in the NP bulk, further than the exciton diffusion length (typically 5–10 nm in organic semiconductors)[84] from the heterojunctions at the NP surface that can facilitate their dissociation. Therefore, most excitons recombine in the semiconductor bulk and do not contribute to photocatalysis. This issue was recently overcome by utilizing the concept of the bulk heterojunction, originally developed to enhance exciton dissociation in organic solar cells,[85] to fabricate NP HEPs from a blend of the donor polymer 12 and the small molecule nonfullerene acceptor 13.[86,87] Following Pt photodeposition, NP HEPs fabricated from the optimized donor/acceptor blend achieved a HER rate of 128.9 μmol h⁻¹, over 20 times that of analogous HEPs fabricated from the individual semiconductors, and an EQE of 6.2% at 700 nm. The activity increase was attributed to the type II heterojunction formed between domains of 12 and 13 inside the NP that greatly enhanced exciton dissociation in the NP bulk compared to single-component NPs. Optimization of the heterojunction morphology was required to maximize the HER rate and was achieved by varying the stabilizing surfactant employed during the miniemulsion NP fabrication process. It was found that in order to avoid the commonly observed core–shell morphology (Figure 5a) in which electrons remained trapped inside the acceptor domain in the NP core, it was necessary to tune the interfacial tensions between 12 and 13 and the aqueous phase such that they were equal to one another. This removed the thermodynamic driving force for the radial segregation of the two semiconductors, disrupting the core–shell structure and resulting in a more intimately mixed bulk heterojunction morphology with both donor and acceptor domains present at the NP surface (Figure 5b). This morphology allowed efficient exciton dissociation as well as efficient extraction of both photogenerated holes (by AA) and electrons (by the Pt cocatalyst) increasing the EQE by an order of magnitude compared to the core–shell structure, and leading to a proportionately large increase in the HER rate.[87] These results suggest that low quantum efficiency rather than inefficient light absorption may limit the efficiency of many organic photocatalysts and present bulk heterojunction formation as
a way to help overcome this limitation. Furthermore, the use of bulk heterojunctions in photocatalyst design enables the application of both the materials, and the well-understood photophysical principles developed through organic photovoltaic research to the construction and optimization of organic photocatalysts for the generation of H₂ and other solar fuels.

4.2. Conjugated Network Polymers for Hydrogen Evolution

Another strategy to increase EQE by improving charge separation at the semiconductor/electrolyte or semiconductor/cocatalyst interface is increasing its area, which lowers the average distance excitons must diffuse to reach it. Highly porous conjugated polymer networks, where the cocatalyst can also be incorporated in the bulk of the network have been proposed as a means of achieving this.[90–92]

Microporosity can arise in conjugated linear polymers owing to their rigid sp² hybridized backbones with restricted conformational flexibility,[93] impairing packing and resulting in free volume or void formation.[94] Conjugated polymer networks further enhance this intrinsic microporosity with extensive rigid crosslinking via the copolymerization of branched monomers containing more than two polymerizable groups. This enhances porosity by building rigid amorphous networks involving a large amount of void space. While not all crosslinking imparts porosity, short rigid crosslinking as achieved by incorporation of branched monomers can impart 3D character and prevents pore collapse after solvent removal, imparting permanent porosity.[93–95] Although these microporous conjugated polymeric networks are not solution processable, they have received widespread attention as photocatalysts for H₂ production owing to their π-conjugated backbones and high porosity.[94,96,97] Their synthesis, outlined in several reviews,[90,98,99] chiefly utilizes kinetically controlled cross-coupling reactions, allowing incorporation of a diverse range of organic semiconductor building blocks to generate amorphous polymer networks.[93,98–100]

Varying the ratio of monomers with different connectivities and lengths was shown to be an effective strategy to tune the pore dimensions and surface area of conjugated network polymers in a continuous fashion.[101,102] The statistical Suzuki copolymerization of pyrene and phenyl-based monomers was shown to continuously tune the optical bandgap of conjugated polymer networks for photocatalytic hydrogen evolution from 2.95 to 1.94 eV.[29] This optical bandgap tuning was shown to be the dominant factor in determining photocatalytic activity, peaking at 2.33 eV in polymer 14 (Figure 6); however, a correlation between surface area measured by Brunauer–Emmett–Teller (BET) N₂ adsorption and photocatalytic activity was not found.[29] Similar studies also reflect this, whereby the measured surface area showed no relationship to photocatalytic activity.[33,103–107]
Formation of highly porous conjugated network polymers requires the incorporation of branching monomers, capable of polymerization in more than two positions. The connectivity of these crosslinking units, while often enabling high porosity, simultaneously affects other structural parameters. For photocatalysts incorporating benzene units, higher activity is reported for those incorporating linear 1,2-linkages (para), in comparison to branched 1,3,5- (meta) and 1,2,4,5-linkages (ortho).\[103,108,109\] Meta linkages confer cross-conjugation and can incorporate kinks into the backbone.\[106,108,110\] while ortho linkages can impose severe twisting between adjacent units.\[108,109,111\] This branching can have the effect of reducing planarity and decreasing the extent of conjugation, hence widening the optical bandgap, leading to poorer utilization of visible light and diminished photocatalytic activity. The reduced planarity in polymer backbones caused by high degrees of torsion also impedes intramolecular charge transport along the backbone.\[104,109,111\] given that conjugated network polymers with greater adjacent unit planarity have improved intramolecular charge transport.\[112,113\] Taken together, this could explain how the advantages of porosity can be outweighed by these other factors, and contorted porous network polymers are often less photocatalytically active than their low or nonporous linear polymer equivalents.

Nonetheless, polymer 15 demonstrates the potential of highly porous network polymers to dramatically outperform their nonporous linear polymer analogues in photocatalytic H\(_2\) production. Here, the crosslinking is via the nonconjugated bridging sp\(^3\)-hybridized carbon atom of the fluorene unit, rather than directly on the conjugated backbone as is often the case. This mode of crosslinking avoids significant twisting between adjacent units along the polymer backbone, supported by density functional theory (DFT) calculations showing negligible changes in the adjacent unit dihedral angle between the network polymer 15 and its non-crosslinked linear analogue.\[109\] Given that the optical bandgaps of the linear and network polymers were almost identical (2.75 and 2.77 eV, respectively), it can be concluded that the increase in surface area from 11 m\(^2\) g\(^{-1}\) in the nonporous linear polymer to 596 m\(^2\) g\(^{-1}\) in 15 brought about by the crosslinking was the chief cause of the improved photocatalytic activity.\[109\] However, in this study the most marked improvement in photocatalytic activity was achieved by incorporation of polar sulfone units in the form of dibenzo[b,d]thiophene sulfone, shown by polymer 16, the most active polymer in the study.\[109\] These findings in part, can be explained by increased hydrophilicity due to the polar sulfone group, with sulfone-containing porous network 16 measured to have greater water uptake compared to non sulfone porous network 15, and also a higher water uptake compared to the analogous sulfone-containing linear polymers in the study.\[109\] This highlights that, in order for the increased porosity of network polymers to have the greatest impact on photocatalytic activity, the aqueous reaction medium containing sacrificial hole scavenger and hydrated protons must be able to access and diffuse within those pores, suggesting that increasing hydrophilicity is an important design consideration for the benefits of porosity to be fully realized, and that dry surface area BET measurements should be considered alongside wettability measurements, such as water uptake, swelling, and contact angle measurements where possible.\[93,109,114,115\] In addition, sulfone substitution brought about a narrowing of optical bandgap, enhancing visible light harvesting.\[109\] Another factor explaining the greater activity of the sulfone-containing polymers is that the electron-withdrawing character of the dibenzo[b,d]thiophene sulfone units drives the HOMO and LUMO deeper in energy,\[106,107,116\] which can increase the thermodynamic driving force for hole scavenger oxidation,\[109\] thus, increasing the efficiency of hole scavenging leading to a greater population of electron polarons available to drive the HER.\[67\]

Dibenzo[b,d]thiophene sulfone units have been utilized extensively in network polymers for photocatalytic H\(_2\) production, showing success in network polymers with greater planarity between adjacent units.\[107,112,114,117\] Of these, polymer 17 using dibenzo[b,d]thiophene sulfone units to link pyrene cores reported the highest EQE.\[117\] In addition to the previously discussed advantages of this unit for its hydrophilicity and use in energy level tuning, it was also proposed that favorable interactions between the sulfone units and residual Pd cocatalyst improved the transport of electron polarons to cocatalyst, further accounting for the success of this unit.\[107\]

Other combinations of electron-rich and electron-deficient monomers in copolymers to improve light harvesting of the solar spectrum have been applied to conjugated network polymers. These include donors such as spirofluorene,\[106\] pyrene,\[29,117,118\] perylene,\[119\] carbazole,\[120\] dibenzo[b,d]thiophene,\[114\] and acceptors such as benzothiadiazole,\[101,103,121\] phenanthroline,\[118\] triazines,\[122\] as well as the use of cyano and fluorene substitution.\[105,115,120\] Investigating the role of donor–acceptor combinations, a series of conjugated network polymers were synthesized from a range of monomer pairs of differing electron-donating abilities, showing the highest activity when strong donors were matched with weak acceptor units.\[134\] Further study of optimizing the acceptor units reported polymer 18 with the highest EQE,\[108\] where it was claimed that internal polarization in the conjugated donor–acceptor copolymers reduced exciton binding energy, better facilitating exciton dissociation and charge separation, given such internal dipoles lead to more polarized excited states with greater spatial separation of photogenerated electrons and holes.\[31,108\] This highlights the importance of well-matched donor and acceptor units for facilitating charge separation and optical bandgap tuning in these materials.

### 4.3. Covalent–Organic Frameworks (COFs) and Covalent–Triazine Frameworks (CTFs) for Hydrogen Evolution

In contrast to conjugated network polymers, COFs combine both crystallinity and porosity. COFs are formed through thermodynamically controlled polymerization of a wide variety of conjugated subunits, whose geometry determines the key structural parameters. Broadly, COFs are either 3D frameworks or \(\pi\)-stacked eclipsed 2D sheets. Their structures are highly crystalline, owing to reversible bond formation under solvothermal reaction conditions, allowing formation of the most stable ordered structure, which minimizes charge trapping at defect sites.\[100,123\] 2D COFs are of particular interest for photocatalytic applications, due to the possibility for axial charge...
transport through electronically coupled \( \pi \)-orbitals, as well as high porosity in the form of well-defined channels that increase the semiconductor/electrolyte interfacial area.\(^{[92,100,123,124]} \)

Hexagonal COFs 19 to 22 (Figure 7) synthesized through condensation of hydrazine with trialdehydes of varying N atom substitution illustrate the atomic tunability of COFs, whereby sequential substitution of C-H units with N atoms in the central ring could satisfy several design principles at once: increasing planarity, crystallinity, surface area, and energy level tuning. This led to a concomitant increase in photocatalytic activity after photodeposition of Pt cocatalyst: in the order of 19 < 20 < 21 < 22.\(^{[125]} \) This was primarily attributed to the planarization of the structures by decreasing the steric clash of the central rings with adjacent phenyl groups by substitution of C-H units with N atoms, decreasing the biaryl dihedral angle. As a consequence, sharper X-ray diffraction (XRD) peaks were observed along the series as stacking was made more efficient and the COFs increased in crystallinity, improving photocatalytic activity by bringing about greater axial and lateral charge transport. In addition, surface area showed a general increase across the series as well as due to the formation of more ordered structures. Computational modeling showed electron donation by hole scavenger to be the lowest energy exciton dissociation pathway, where hole scavenger reduced exciton bound holes, liberating electron polarons in the COF to subsequently migrate to Pt cocatalyst. Higher degrees of N atom substitution in the core were predicted to better stabilize these electron polarons, improving the efficiency of this charge separation process, also accounting for the increase in activity across the series.\(^{[125]} \) This example highlights the improvements in photocatalytic activity brought about through planarization of the stacked 2D COF sheets, which improved charge transport and in this case surface area. Although such planarization would be expected to be accompanied by a decrease in optical bandgap, this was not a significant factor here due to the electron-withdrawing character imparted by N atom substitution counteracting this. This means that absorption does not play a part in explaining the differences across the series, supporting its explanation in terms of charge separation and transport alone.\(^{[123]} \) Other COFs have further demonstrated the importance of planarity for improving crystallinity and photocatalytic activity.\(^{[126]} \)

**Figure 7.** Chemical structures of COFs and CTFs 19–31.
Imine linkages are common in COFs but are susceptible to hydrolysis.\textsuperscript{[127-129]} 1,3,5-Triformylphenololigocinol is widely utilized as a trifunctional building block, which undergoes condensation with aromatic diamines followed by irreversible tautomerization to produce stable \(\beta\)-ketoenamine hexagonal COFs.\textsuperscript{[130]} The COF structure can be tuned via variation of the aromatic diamines. Using this approach and building on the success of sulfone-containing units for linear and network polymers, the aromatic diamine units in \(\beta\)-ketoenamine were varied, with COFs 23 to 25, presenting \(H_2\) evolution activity in the order 23 < 24 < 25.\textsuperscript{[131]} In comparison to the triphenyl linker in 23 which was twisted, the fused sulfone units in 24 and 25 increased planarity. This has the effect of increasing crystallinity as well as surface area with this effect being strongest in 25, potentially due to the parallel external bonds of the linking unit allowing more ordered structures. In addition, the extra polar sulfone unit enhanced hydrophilicity. These increases in wettability and surface area increased the area of the semiconductor surface accessible to the aqueous reaction medium, as evidenced by increased water vapor adsorption. Furthermore, the increased crystallinity and planarized structure narrowed the bandgap of the 25, enhancing light harvesting.\textsuperscript{[127,131]} Interestingly, an almost amorphous analogue of 25 was also synthesized under different conditions, showing nine times lower photocatalytic activity, providing further evidence for the benefits of crystallinity for the reasons previously discussed.\textsuperscript{[130,131]} It was also found that the addition of an equal mass of the organic dye WSSF to 25 enabled the utilization of longer wavelength photons which increased the activity, giving modest EQEs at longer wavelengths where previously it was zero. Given that there was no overlap of fluorescence spectra of the dye with the absorbance of the COF, the effective quenching of dye fluorescence was attributed to interfacial electron transfer to the COF, given the favorable energy level alignment which boosted light harvesting.\textsuperscript{[133]} The postsynthetic dye sensitization of porous organic semiconductors such as COFs represents an effective strategy to boost the performance of organic semiconductor photocatalysts. The maximum benefit is derived when the dye has a narrower optical bandgap and a higher energy LUMO than the organic semiconductor. This allows electron transfer from the LUMO of the dye to the LUMO of the semiconductor minimizing recombination, while absorbing a complementary portion of the visible spectrum. The HOMO of the dye must however be deep enough to oxidize the hole scavenger to allow dye regeneration.\textsuperscript{[133]}

CTFs are a related material to COFs. Indeed, CTFs with a high degree of crystallinity could be considered COFs, while amorphous CTFs more closely resemble network polymers incorporating triazine units, where the synthetic conditions determine the degree of crystallinity. Trimerization of aromatic nitriles often produces amorphous triazine networks due to the strength and irreversibility of the stable aromatic triazine unit formed. While beneficial for stability, this precludes formation of crystalline frameworks. However, with the use of molten ZnCl\(2\) as a solvent and catalyst, dynamic trimerization has been demonstrated, enabling the formation of crystalline CTFs owing to the greater reversibility of triazine formation under these conditions.\textsuperscript{[134,132]} When conditions are carefully controlled to minimize the partial carbonization of materials,\textsuperscript{[135]} the use of molten ZnCl\(2\) has been shown to dramatically increase photocatalytic performance of the crystalline triazine frameworks produced, in comparison to their amorphous counterparts.\textsuperscript{[136,137]} This increase in photocatalytic activity of crystalline CTFs is due to the increase in the degree of polymerization, extending conjugation which decreases the optical bandgap to better harvest solar photons.\textsuperscript{[136]} It also suppresses the presence of defects which are detrimental for charge transport.\textsuperscript{[21]}

In a study investigating factors relating to CTF performance, triphenyl triazine linkers were combined with a large variety of bifunctional linker units via Suzuki coupling in a high-throughput rapid screening technique to produce 39 different CTFs (as was done with linear polymers in a similar study).\textsuperscript{[138]} Dibenzo[b,d]thiophene sulfone featured again (26) as one of the best performing linkers, along with 27. The property requirements for photocatalysts are complex, and no single variable can alone predict photocatalytic activity. Nonetheless, through screening a large number of structures, this study showed that LUMO energy was the best predictor of activity under these conditions, where all of the most active CTFs had LUMOs higher in energy than \(-3.1\) eV. At the same time the HOMO energy was found not to correlate well to activity. This was attributed to the use of basic TEA as hole scavenger, which shifted the reduction potential for hydrogen evolution to more negative potentials, underlining the importance of high energy LUMOs to provide enough thermodynamic driving force for HER under the given pH conditions. By contrast, all of the HOMOs provided sufficient thermodynamic driving force for TEA oxidation.\textsuperscript{[139]} The second parameter found to most closely predict activity was the dispersibility of the triazine networks as measured by light transmittance.\textsuperscript{[139]} This property is relevant to the activity of many of the materials discussed in this review, since they are generally hydrophobic powders suspended in an aqueous testing medium, which if poorly dispersible, will aggregate and fail to absorb the full cross section irradiated during photocatalytic testing.\textsuperscript{[93]} Given that wettability is favorable for dispersibility, it further highlights the advantages of hydrophilicity for these semiconductors.\textsuperscript{[93,127,138]} Nonetheless, due to the use of kinetically controlled coupling reactions, these networks can be expected to possess low crystallinity, and activity would be expected to improve by the synthesis of such structures through thermodynamically controlled conditions to generate crystalline CTFs. A detailed summary of the photocatalytic performance of all of the photocatalysts discussed in this section is shown in Table 2.

5. Photocatalysts for Oxygen Evolution

The organic semiconductors in this section were used to fabricate OEPs and were tested in the presence of sacrificial electron scavengers such as Ag\(^+\) or IO\(3^-\).

\(O_2\) evolution is a key reaction in both OWS and \(CO_2\) reduction (Figure 1), where the oxidation of water (or \(OH^-\) under basic conditions) liberates proton equivalents that can be reduced to \(H_2\) in the HER, or take part in the proton-coupled electron transfer reactions required for \(CO_2\) reduction (Table 1).\textsuperscript{[140]} Furthermore, in photocatalytic OWS systems, oxygen evolution is generally the rate determining half-reaction due to its slow
Table 2. Summary of the photocatalytic activities of HEPs based on semiconductors 1–27.

| Semiconductor | HOMO/LUMO | Bandgap [eV] | Sacrificial reagent | HER rate [µmol h⁻¹] | Cocatalyst [wt%] | Semiconductor mass [mg] | Light source | EQE [%] [wavelength, nm] | Stability [h] | Ref. |
|---------------|-----------|-------------|---------------------|---------------------|------------------|------------------------|--------------|--------------------------|--------------|------|
| 1             | –/–       | 2.9         | DEA                 | 2.08                | Ni⁺              | 10                     | >290 nm Xe lamp | 3.33 (313), 0.60 (366), 0.82 (313), 0.48 (366), 0.04 (313) | 19.5         | [68] |
|               | –/–       | 2.78        | MeOH/TEA            | 3.9                 | Pd⁺              | 25                     | >420 nm 300 W Xe lamp | –           | 5            | [30] |
|               | –/–       | 2.79        | MeOH/TEA            | 8.3                 | Pd⁺ (0.53)       | 25                     | >420 nm 300 W Xe lamp | –           | 5            |      |
|               | –/–       | 2.77        | MeOH/TEA            | 26.6                | Pd⁺ (0.60)       | 25                     | >420 nm 300 W Xe lamp | 1.10 (420)  | 5            |      |
|               | –/–       | 2.7         | MeOH/TEA            | 92                  | Pd⁺ (0.38)       | 25                     | >420 nm 300 W Xe lamp | 2.25 (420)  | 65           |      |
|               | –/–       | 2.62        | MeOH/TEA            | 81.5                | Pd⁺ (0.40)       | 25                     | >420 nm 300 W Xe lamp | 11.6 (420)  | 40           | [67] |
| 6             | −5.85/−3.33 | 2.32       | DEA                 | 0.35                | Pt (5) Pd⁺ (1.2) | 2                      | 385–700 nm Xe lamp | 0.02 (340)  | 24           | [46] |
| 7             | −5.41/−3.36 | 2.05       | AA                  | 0.45                | Pt (3) Pd⁺       | 2.5                    | Xe lamp full spectrum (162.4 mW cm⁻²) | –           | 5            | [77] |
| 8             | −5.27/−3.39 | 1.88       | AA                  | 39.75               | Pt (3) Pd⁺       | 2.5                    | Xe lamp full spectrum (162.4 mW cm⁻²) | 0.18 (380), 0.11 (420), 0.14 (450), 0.25 (550), 0.30 (600), 0.24 (650), 0.09 (700) | 36           |      |
|               | AA        | 34.5        | Pt (3) Pd⁺          | 2.5                 | AM1.5            | (162.4 mW cm⁻²)        | –           | 44           |      |
| 9             | −5.44/−2.37 | 3.07       | AA                  | 0.23                | Pt (3) Pd⁺       | 2.5                    | Xe lamp > 300 nm (162.4 mW cm⁻²) | –           | 5            | [78] |
| 10            | −5.46/−2.41 | 3.05       | AA                  | 11.5                | Pt (3) Pd⁺       | 2.5                    | Xe lamp > 300 nm (162.4 mW cm⁻²) | –           | 5            |      |
| 11            | −5.64/−3.01 | 2.03       | DEA                 | 8.16                | Pd⁺ (0.013)      | 0.8                    | LED 6500 K, >420 nm | 0.40 (315)  | 12           | [80] |
| 12           | −5.04/−3.42 | 2.02       | AA                  | 128.9               | Pt (10) Pd⁺ (0.94) | 2                      | Xe lamp 350–800 nm (2.0 (400), 2.3 (500), 4.3 (620), 5.6 (660), 6.2 (700)) | 36           | [87] |
| 13           | −5.68/−4.08 | 1.60       | –/–                 | 17.4                | Pd⁺ (0.42)       | 100                    | >420 nm 300 W Xe lamp | –           | 6            | [29] |
| 14           | −5.28/−2.08 | 2.77       | MeOH/TEA            | 13.5                | Pd⁺ (0.62)       | 25                     | >420 nm 300 W Xe lamp | –           | 5            | [109] |
| 15           | −5.28/−2.08 | 2.77       | MeOH/TEA            | 13.5                | Pd⁺ (0.62)       | 25                     | >295 nm 300 W Xe lamp | –           | 5            |      |
Increasing the efficiency of O2 evolution photocatalysts could be the most effective way to improve the η_{STH} of current OWS Z-schemes. However, organic semiconductor based OEPs have so far received far less attention than their HEP counterparts. O2 evolution can either occur directly via the OER (Equation (10)) or via the formation of hydrogen peroxide (Equation (11)) and its subsequent decomposition into H2O and O2.[141]

Compared to the HER, the OER requires a greater activation energy due to its kinetically demanding four-electron oxidation mechanism.[140] Hydrogen peroxide formation requires a lower energy than the OER, due to its less kinetically demanding two-electron oxidation pathway, but has a substantially higher redox potential (–5.64 eV vs vac. at pH 7) than the OER (–5.26 eV vs vac. at pH 7).[140] Therefore, regardless of which oxygen evolution pathway takes place, the semiconductors used to fabricate OEPs must have HOMOs substantially deeper than the –5.26 eV OER redox potential at pH 7 in order for the OEP to function at this pH. Perhaps for this reason, the organic semiconductors used to fabricate OEPs have so far been limited to CN and polymer networks containing heterocycles such as triazine and heptazine that are rich in pyridinic nitrogens.[132,142–144] These highly electron-deficient units give rise to the deep HOMO energy levels required to drive the OER, and efforts have been made to further improve the efficiency of these systems.

### Table 2. Continued.

| Semiconductor | HOMO/LUMO (eV vs vac.) | Bandgap (eV) | Sacrificial reagent | HER rate [µmol h⁻¹] | Cocatalyst [wt%] | Semiconductor mass [mg] | Light source | EQE [%] (wavelength, nm) | Stability [h] | Ref. |
|---------------|------------------------|--------------|---------------------|--------------------|-----------------|-------------------------|--------------|-------------------------|---------------|-----|
| 16            | –5.63/–2.53[11]        | 2.56         | MeOH/TEA            | 77.7               | Pd* (0.72)      | >420 nm 300 W Xe lamp   | 13.2 (420)   | 151.9                   | 35            |     |
| 17            | –5.85/–3.48[12]        | 2.37         | TEOA                | 426.2              | Pt (3)          | >420 nm 300 W Xe lamp   | 6.1 (400)    | 649.3                   | 24 [117]      |     |
| 18            | –/–                    | –            | TEA                  | 103.6              | Pt (2)          | >420 nm 150 W Xe lamp   | 1.93 (400)   | 12                      | 14 [108]      |     |
| 19            | –/–                    | 2.6–2.7      | TEOA                | 0.32               | Pt (2.14)       | >420 nm 300 W Xe lamp   | 0.0016 (400), 0.0017 (500), 0.0003 (550) | 8 [125]       |     |
| 20            | –/–                    | 2.6–2.7      | TEOA                | 0.45               | Pt (1.70)       | >420 nm 300 W Xe lamp   | 0.038 (400), 0.007 (450), 0.083 (500), 0.020 (550) |     |     |
| 21            | –/–                    | 2.6–2.7      | TEOA                | 2.19               | Pt (0.94)       | >420 nm 300 W Xe lamp   | 0.088 (400), 0.190 (450), 0.083 (500), 0.020 (550) |     |     |
| 22            | –/–                    | 2.6–2.7      | TEOA                | 8.5                | Pt (0.68)       | >420 nm 300 W Xe lamp   | 0.17 (400), 0.44 (450), 0.26 (500), 0.039 (550) | 120           |     |
| 23            | –/–                    | 2.28         | AA                  | 8                  | Pt (3.1)        | >420 nm 300 W Xe lamp   | –            | 5 [133]                 |     |     |
| 24            | –/–                    | 2.1          | AA                  | 22.2               | Pt (3.1)        | >420 nm 300 W Xe lamp   | –            | 5 [134]                 |     |     |
| 25            | –/–                    | 1.85         | AA                  | 50.5               | Pt (3.1)        | >420 nm 300 W Xe lamp   | 3.2 (420)    | 50 [135]                |     |     |
| 25 + WSSF     | –/–                    | –            | AA                  | 81.5               | Pt (3.1)        | >420 nm 300 W Xe lamp   | 0.6 (600), 0.7 (700) | 5 [136]              |     |     |
| 26            | –/–                    | 2.7          | MeOH/TEA            | 59.33              | Pt (3)          | >420 nm 300 W Xe lamp   | 5 [137]      |                         |     |     |
| 27            | –/–                    | 2.58         | MeOH/TEA            | 73.65              | Pt (3)          | >420 nm 300 W Xe lamp   | 15.9 (420)   |                         |     |     |

*Value expressed is the longest time H2 evolution was recorded under continuous operation and does not necessarily reflect the maximum stability of the photocatalyst; †Value expressed is the internal quantum efficiency (IQE); ‡Energy levels measured using photoelectron spectroscopy; §Energy levels measured using electrochemical techniques; ‡Energy levels predicted by density functional theory; *Metal impurity present in semiconductor.

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**Kinetics.** Therefore, increasing the efficiency of O2 evolution photocatalysts could be the most effective way to improve the η_{STH} of current OWS Z-schemes. However, organic semiconductor based OEPs have so far received far less attention than their HEP counterparts.
made to increase their OER activity by tuning their bandgaps to improve light absorption, and by increasing their EQE through increased crystallinity. A study in which the number of phenyl units was increased from 1 to 3 in structures 28 to 30 illustrates the need for a compromise between maximizing a semiconductor’s light absorption by decreasing its bandgap and retaining a deep enough HOMO to provide sufficient overpotential to drive the OER. By increasing the number of electron-donating phenyl units it was possible to gradually narrow its bandgap from 2.98 eV in 28 to 2.66 eV in 29 and 2.36 eV in 30, leading to a corresponding increase in light absorption. However, increasing the concentration of the relatively electron-rich phenyl units in the CTF also raised its HOMO energy level, which decreased the η available to drive the OER. This led to an optimum OER rate (3.0 μmol h⁻¹) for 29 when the Co cocatalyst loaded CTFs were used as OEPs in the presence of AgNO₃. This occurred because although the light absorption was more efficient for 28, the shallower HOMO provided a lower η for the OER, which led to a 75-fold decrease in the OER rate (0.4 μmol h⁻¹) compared to 29, and a 2.5-fold decrease compared to 28 (1.0 μmol h⁻¹).[145] It was later shown that the crystallinity of CTF 29 could be altered by tuning the microwave power provided during its microwave-assisted polymerization, and that the most crystalline structure also gave rise to the highest OER rate when the CTF interfaced with a RuOₓ cocatalyst was used as an OEP in the presence of AgNO₃.[146] The most crystalline structure achieved an EQE of 3.8% at 420 nm, and its increased OER rate was attributed to less charge recombination in the photocatalyst bulk, possibly due to a longer exciton diffusion length in the more crystalline domains. However, its wide bandgap (2.48 eV) limited light absorption mostly to wavelengths <500 nm. Polymer 31 with a bandgap of 1.22 eV overcame the issue of poor light absorption while also retaining a deep HOMO energy level (~6.1 eV), possibly due to the higher concentration of electronegative N atoms in the conjugated π system compared to 29. As a result of its suitably aligned energy levels, when polymer 31 in the form of nanosheets interfaced with a Co(OH)₂ cocatalyst was used as an OEP, it remained active up to wavelengths >800 nm. However, its EQE (1.5% at 420 nm) remained low, and may have been limited by high rates of exciton recombination in its amorphous structure.[147] These initial results demonstrate that organic semiconductors synthesized using rational design principles can be used to fabricate OEPs with superior light absorption and O₂ evolution activity than CN. However, the adoption of known strategies for the enhancement of EQE such as hydrophilicity enhancement and heterojunction formation would be required to gain further substantial improvements in their O₂ evolution activity. Furthermore, advanced surface modification strategies such as the incorporation of protective interlayers between the organic semiconductor and the O₂ evolution catalysts may be required to protect the organic semiconductors from photocorrosion by the reactive oxygen species generated as intermediates during O₂ evolution in order to achieve long-term stability.[148, 149] A detailed summary of the photocatalytic performance of all of the photocatalysts discussed in this section is shown in Table 3.

### 6. Photocatalysts for Overall Water Splitting

Given the sparsity of examples of non-CN organic semiconductor photocatalysts reported to achieve water oxidation, it is unsurprising that even fewer have been reported to achieve OWS, though these reports are yet to be reproduced.[21] This is because the HER and OER in all of the above examples are made possible with the use of sacrificial agents, which serve to rapidly and irreversibly accept or donate electrons from/to the semiconductor at relatively unchallenging redox potentials. This reduces charge recombination and prevents the backreaction of O₂ and H₂ because they are not produced simultaneously.[64] Hole scavenger concentration is also often high in the case of H₂ evolution,[93] to maximize the efficiency of hole scavenging which generates higher concentrations of electron polarons available to drive H₂ evolution.[22] Therefore, removing sacrificial reagents entirely to achieve overall water splitting is much more challenging than driving the individual reactions under sacrificial conditions. OWS is well established for wide bandgap inorganic semiconductor photocatalysts,[9,15,16,150–152] While their wide bandgaps limit solar light harvesting, they also provide large η for both half-reactions, in particular for the demanding OER. For single semiconductor photocatalysts, there exists a bandgap

| Table 3. Summary of the photocatalytic activities of OEPs based on semiconductors 28–31. |
|---------------------------------|-----------------|-----------------|-----------------|-----------------|-----------------|-----------------|-----------------|-----------------|-----------------|-----------------|-----------------|-----------------|
| Semiconductor                   | HOMO/LUMO       | Bandgap         | Sacrificial reagent | O₂ evolution rate | Cocatalyst      | Semiconductor mass | Light source     | EQE [%]         | Stability [h]    | Ref.  |
|---------------------------------|-----------------|-----------------|-----------------|-----------------|-----------------|-----------------|-----------------|-----------------|-----------------|-----------------|
| 28                              | –6.58/–3.6      | 2.98            | AgNO₃           | 3               | Co (3)          | 30              | >300 nm 300 W Xe lamp | –               | 8               | [145]           |
| 29                              | –6.09/–3.43     | 2.66            | AgNO₃           | 1               | Co (3)          | 30              | >300 nm 300 W Xe lamp | –               | 8               | [145]           |
| 29                              | –6.24/–3.74     | 2.5             | AgNO₃           | 7               | RuOₓ (3)        | 50              | >420 nm 300 W Xe lamp | 4.0 (400), 3.8 (420) | 18              | [146]           |
| 30                              | –5.53/–3.17     | 2.36            | AgNO₃           | 0.4             | Co (3)          | 30              | >300 nm 300 W Xe lamp | –               | 8               | [145]           |
| 31                              | –6.08/–4.86     | 1.22            | AgNO₃           | 14.3            | Co(OH)₂ (3)     | 25              | >420 nm 300 W Xe lamp | 1.48 (420)       | 6               | [147]           |

*Energy levels measured using photoelectron spectroscopy. *Value expressed is the longest time O₂ evolution was recorded under continuous operation and does not necessarily reflect the maximum stability of the photocatalyst.
compromise between being narrow enough for improved solar light harvesting, but also wide enough to drive both HER and OER efficiently. It is estimated that the minimum feasible bandgap will be 1.6 eV to provide this driving force for both reactions, though this will depend to a large extent on the optimum deployment of dual cocatalysts to drive the HER and OER, both for lowering the overpotential and also hindering charge recombination. Z-schemes may present a suitable solution to the problem of balancing competing demands on bandgaps, given that Z-schemes can utilize two semiconductors with narrow bandgaps, together providing suitable overpotentials which straddle the potentials for the HER and OER, albeit at the expense of requiring the absorption of twice as many photons per excited electron. This could greatly expand the range of semiconductors both inorganic and organic which could be utilized for OWS. While OWS Z-schemes have been reported for CNs in conjunction with inorganic catalysts, this strategy is yet to be adequately explored for other organic semiconductors due to their structural complexity, though could be a promising future research direction.

7. Photocatalysts for Carbon Dioxide Photoreduction

Solar photoreduction of CO₂ is an elegant method to synthesize useful carbon-based products from CO₂ and water. Carbon neutral fuels generated via CO₂ reduction can be directly used to replace fossil fuels, while using chemicals derived from CO₂ as feedstocks for the chemical industry captures CO₂, making the process carbon negative. CO₂ photoreduction is a more challenging process than photocatalytic water splitting, because as well as the hurdles presented by H₂ evolution, the large number of proton-coupled electron transfer steps that must occur to generate useful products such as methane or ethane.

Due to its inert nature, activation of the CO₂ molecule is particularly more complex and kinetically more challenging, which typically raises the overpotentials required to drive CO₂ reduction. This is due to the high activation energy required to break the strong C=O bonds, and the large number of proton-coupled electron transfer steps that must occur to generate useful products such as methane or ethane. Elemental doping with sulfur was also able to increase the rate of photocatalysis for CO₂ to methanol by 2.5 times. The sulfur-doped system was found to have a narrower bandgap than the pristine system, and as a result gave a broadened light response, so more electrons could be generated upon light irradiation. Since the process of forming methanol from CO₂ requires multiple electrons (Table 1), more photogenerated electrons could be used for CO₂ reduction per unit time, thus increasing the rate of photocatalysis in comparison to the pristine CN.

7.1. Carbon Nitrides for Carbon Dioxide Photoreduction

CN-based composites have been reported for CO₂ photoreduction, in the pristine state and doped state. Structural modifications of CNs have shown increased performances for photoreduction. For example, an increase in performance due to the presence of N vacancies has been reported. At 41% humidity, CO₂ reduction to CO was demonstrated with an average production rate of 0.54 µmol h⁻¹ and a selectivity of 78%, with the material tested in the gas phase with no sacrificial agent. This was attributed to an accumulation of electrons within the vacancies, to benefit the multielectron nature of CO₂ photoreduction. It was reported that carbon vacancies within the CN structure generated a CO evolution rate of 0.13 µmol h⁻¹, more than two times that of graphitic CN. The carbon vacancies within the structure allowed for an increased adsorption of CO₂, as well as an increase in charge carrier formation. Elemental doping with sulfur was also able to increase the rate of photocatalysis for CO₂ to methanol by 2.5 times. The sulfur-doped system was found to have a narrower bandgap than the pristine system, and as a result gave a broadened light response, so more electrons could be generated upon light irradiation. Since the process of forming methanol from CO₂ requires multiple electrons (Table 1), more photogenerated electrons could be used for CO₂ reduction per unit time, thus increasing the rate of photocatalysis in comparison to the pristine CN.

7.2. Conjugated Network Polymers for Carbon Dioxide Photoreduction

Porous conjugated network polymers, which have shown promise in CO₂ capture, have also attracted interest for use in photocatalysis. They give the desired porosity for CO₂ reactive and thus aid photoreduction. Furthermore, as well as more favorable energetics, CO₂ activation in these ways results in more facile adsorption of the CO₂ molecule onto the catalytic surface, which in turn enables electron transfer from the catalyst surface into the molecule. Consequently, heteroatoms such as N and O, which have been shown to interact with the CO₂ molecule, incorporated into the structures of organic photocatalysts can aid adsorption and activation, and can therefore increase photocatalytic efficiency. The incorporation of oxygen and nitrogen-containing functional groups can also increase the selectivity of the reactions due to favorable interactions with specific reaction intermediates. Selective binding to a specific intermediate can favor specific products, thus increasing photoreduction selectivity. Another important factor to be considered in the design of organic photocatalysts for CO₂ photoreduction is the effect of having a high surface area material. To the best of our knowledge, all materials published for CO₂ photocatalysis display a high surface area, especially by incorporation of a porous structure within the photocatalytic system. This property supplies enough reaction sites for electron transfer from the photocatalyst to carbon dioxide.
reduction, supply sites for electron transfer, and often hold favorable interactions with carbon dioxide, enabling activation. Most current examples focus on selectively forming CO. Although this product is not the most desirable, the proof of concept supports the feasibility of using organic semiconductors in CO2 photoreduction and offers some direction in understanding the factors that can lead to increased photocatalytic activity. Trace amounts of metal impurities in some of these conjugated networks, introduced by their synthesis via metal-catalyzed polymerization reactions should be noted, since even trace amounts of metals such as palladium and copper can act as cocatalysts in photocatalysis.

The CTFs 32–34 (Figure 8) have been synthesized and tested for CO2 reduction using CoCl2 as a cocatalyst in aqueous solution, with TEOA as a hole scavenger. CTF 34 was the highest performing with an EQE of 1.75% at 405 nm and a selective production of carbon monoxide of 18.4 µmol h⁻¹. In this study, the CO evolution rate did not have a direct correlation with increased surface area, since framework 34 containing the electron-deficient benzothiadiazole unit showed the highest CO evolution rate, despite having a surface area of only 37 m² g⁻¹, almost ten times lower than the phenyl-containing analogue 33, which achieved a lower CO evolution rate of 10 µmol h⁻¹.

In this example, improved charge separation, facilitated by the electron-withdrawing benzothiadiazole unit was shown to be of more efficacy than a higher surface area. A study involving the pyrene-based networks 35 to 39 also used TEOA as a hole scavenger, with no added cocatalyst reported. The reaction occurred within an ionic liquid, which was able to directly capture CO2 and water from air and was reported to decrease H2 evolution in favor of CO2 photoreduction. The CO evolution rate was found to increase in direct relation to a higher lying LUMO level, perhaps due to the higher overpotential provided for CO2 reduction. As the LUMO level became less negative (−3.66 eV for 35 to −2.92 eV for 39) the performance for CO2 photoreduction increased. Polymer 39 displayed the highest rate of CO2 reduction, with a CO evolution rate of 2.37 µmol h⁻¹ and a CO selectivity of 98.7%.

A study involving the conjugated networks 40 and 41 showed over a threefold increase in rate of methane production from

Figure 8. Chemical structures of the network polymers 32–47.
structure 40 compared to 41, with 40 showing a methane production rate of 1.13 μmol h⁻¹, while 41 had a methane production rate of 0.33 μmol h⁻¹. The semiconductors were tested in aqueous solution, using TEOA as a hole scavenger. The increased activity of 40 was attributed to the presence of phosphorous groups. First, the phosphorous-containing conjugated polymer showed an increased affinity toward the CO₂ molecule, causing more to be trapped and activated in the active site to facilitate conversion. Second, it was found that 40 had a near threefold increase in photoluminescence compared to 41. It was reported that this increase in free charges available for site to facilitate conversion. Second, it was found that 40 had a near threefold increase in photoluminescence compared to 41.

It was reported that dipole interactions between N and O atoms on 43, from the oxadiazole, contributed to an increased carbon dioxide adsorbing ability for 43. The oxadiazole unit on the backbone of 43 was also credited for decreased charge recombination. DFT calculations showed that in polymer 43 photogenerated holes were located predominantly on the electron-donating triphenylamine unit, while photogenerated electrons were delocalized throughout the conjugated network. The highest performance for CO₂ production was achieved by network 44 and was 0.33 μmol h⁻¹ with a selectivity of 92%. In this study, DFT was used to show that the Eosin Y moiety was able to adsorb carbon dioxide and water molecules, via its COO− and −OH functional groups. This work highlights the importance of effective electron transfer into adsorbed CO₂ for efficient CO₂ photocatalysis.

When polymer 47 was employed as a photocatalyst for CO₂ reduction, a CO evolution rate of 5.14 μmol h⁻¹ was achieved, almost 70 times higher than when CN was tested under the same conditions. Notably, this activity was achieved without the use of a cocatalyst, and the framework was formed in a metal-free synthesis. Interestingly, the CO evolution rate was found to decrease by more than half when using an amorphous analogue of the structure. It was reported that the amorphous structure contained the same functionalities, but with a decreased surface area, and it was hypothesized that this decrease in surface area led to a decrease in active sites and by extension a lower photocatalytic activity. Furthermore, DFT calculations suggest that N atoms on the triazine moiety were able to both stabilize negative charge and adsorb carbon dioxide, thus facilitating the transfer of electrons into the activated carbon dioxide molecule, improving photocatalytic efficiency. The study makes a strong case for the importance of electron transfer within a material for effective photocatalysis. A detailed summary of the photocatalytic performance of all of the photocatalysts discussed in this section is shown in Table 4.

It is undeniable that there is a lack of standardization both in testing conditions and result reporting in the emerging field of organic photocatalysts for CO₂ photocatalysis. This makes comparisons difficult between studies and can hinder reproducibility, due to the sheer number of variants at play. Despite this, the studies reported above address key factors that affect CO₂ photocatalysis and highlight the importance of specific functional groups, such as amines or carboxylates, effective electron transfer, by incorporation of electron-rich and electron-poor groups such as triphenylamine units and oxadiazoles or carbazoles, and high surface area. These studies suggest that organic materials may have useful properties for applications in CO₂ photoreduction and offer some useful considerations for future research that should be applied to material design to better understand CO₂ photocatalysis. This, together with a better insight of testing media and reaction conditions should lead to the generation of more useful CO₂ reduction products to be used as solar fuels.

8. Conclusions and Outlook

The ability to precisely tune the HOMO and LUMO energy levels of non-CN organic semiconductors is a major advantage that has only recently begun to be exploited for the photocatalytic generation of solar fuels. An ever-increasing number of photocatalysts based on a wide range of non-CN semiconductor classes including linear conjugated polymers and a variety of crosslinked polymer networks and frameworks are being tested for H₂ evolution, O₂ evolution, OWS, and CO₂ reduction. The measurement conditions under which their photocatalytic performance is evaluated can vary greatly between research groups, as can the morphology and form factor of the photocatalysts themselves. This can make it challenging to make reliable comparisons between photocatalytic activities measured by different research groups based solely on the reported data. Furthermore, a single change in the chemical structure of a semiconductor can often have more than one effect on its properties. For example, altering a semiconductor’s chemical structure to modify its bandgap in order to improve light absorption can also impact properties that affect its EQE, such as its crystallinity or surface area. As a result, unless the property change that has the dominant effect on photocatalytic performance is unambiguously identified, clear structure–activity relationships are difficult to establish, even when the photocatalysts are tested under identical conditions. The adoption of standardized testing conditions to measure photocatalytic activities under AM1.5G irradiation with a well-defined illumination area, the reporting of EQEs over a broad wavelength range, and the careful design of experiments to isolate the effects of specific properties could greatly alleviate these issues and accelerate the development of efficient photocatalysts.

Nevertheless, several design strategies that are effective at increasing the activity of organic semiconductor photocatalysts have emerged and have been discussed in detail in this progress report. While the specific strategies vary depending on which half-reaction(s) the photocatalyst is designed to drive, they all follow similar themes. Narrowing the semiconductor...
Table 4. Summary of the photocatalytic activities of CO₂ reduction photocatalysts based on semiconductors 32–47.

| Semiconductor | HOMO/LUMO (eV vs vac.) | Bandgap [eV] | Reaction conditions | Cocatalyst [wt %] | BET surface area (N₂) [m² g⁻¹] | CO₂ uptake | Product evolution rate [µmol h⁻¹] | Selectivity [%] (product) | EQE (%) [wavelength, nm] | Semiconductor mass [mg] | Light source | Stability [h] | Ref. |
|---------------|------------------------|-------------|---------------------|------------------|------------------------|-----------|-----------------------------------|------------------------|--------------------------|------------------------|--------------|-------------|------|
| 32            | 5.63/−3.57⁴       | 2.24        | Acetonitrile: water 4 | CoCl₂ (0.01) | Pd | 52 | – | 10.0 | 76.9 (CO) | – | 15 | >420 nm 300 W Xe lamp | – | [173] |
| 33            | 5.68/−3.38⁵       | 2.08        | Room temperature    | CoCl₂ (0.01) | Pd | 409 | – | 4.0 | 66.7 (CO) | – | 15 | – | – | [174] |
| 34            | 5.92/−3.49⁵       | 2.43        | Atmospheric pressure | CoCl₂ (0.01) | Pd | 37 | – | 18.2 | 81.6 (CO) | 1.75 (405) | 15 | 24 | – | [175] |
| 35            | 6.20/−3.72⁵       | 2.48        | Ionic Liquid medium treated with air and CO₂ | Ni | – | – | 0.73 | 71.1 (CO) | – | 50 | >420 nm 220 W Xe lamp | – | [176] |
| 36            | 5.76/−3.59⁴       | 2.17        | TEOA hole scavenger | Ni | – | – | 1.37 | 95.9 (CO) | – | 50 | – | – | [177] |
| 37            | 5.9/−3.04⁴        | 2.86        | Room temperature | Ni | – | – | 2.07 | 97.2 (CO) | – | 50 | – | – | [178] |
| 38            | 6.11/−3.35⁴       | 2.76        | Atmospheric pressure | Ni | – | – | 1.59 | 96.5 (CO) | – | 50 | – | – | [179] |
| 39            | 6.64/−2.98⁴       | 2.66        | Ni | – | – | 2.37 | 93.3 (CO) | – | 50 | – | 50 | [180] |
| 40            | 6.33/−3.69⁴       | 2.32        | Aqueous solution treated with air and CO₂ | Ni | – | 44.5 | 7.21 wt % | 1.13 | 90.2 (CH₄) | 0.32 (405) | 50 | >420 nm 300 W Xe lamp | 120 | [181] |
| 41            | 6.34/−3.82⁴       | 2.34        | Room temperature | Atmospheric pressure | – | 33.5 | 5.06 wt % | 0.33 | – | 0.09 (405) | 50 | 120 | – | [182] |
| 42            | 6.47/−4.09⁴       | 2.38        | Gas phase with CO₂ passing first through a water bubbler | Pd | Cu | 512 | 24 cm³ g⁻¹ | 0.56 | ≈100 (CO) | – | 15 | – | [183] |
| 43            | 6.28/−4.08⁴       | 2.22        | Room temperature | Atmospheric pressure | Pd | 686 | 30 cm³ g⁻¹ | 0.01 | – | – | 15 | 20 | [184] |
| 44            | 6.15/−2.55⁴       | 2.45        | Aqueous solution | Pd (0.1) | Cu (0.13) | 445 | 39 cm³ g⁻¹ | 0.33 | 92 (CO) | – | 10 | 50 | [179] |
| 45            | 6.07/−3.54⁴       | 2.53        | Room temperature | Pd (0.07) | Cu (0.06) | 131 | – | – | – | – | – | – | – |
| 46            | 5.98/−3.56⁴       | 2.42        | Atmospheric pressure | Pd (0.13) | Cu (0.18) | 610 | – | – | – | – | – | – | – |
| 47            | 5.66/−3.62⁵       | 2.04        | Acetonitrile: water 4 | Ni | – | 521 | 43 cm³ g⁻¹ | 5.34 | 98 (CO) | 0.704 (420) | 50 | 20 | [180] |

⁴Value expressed is the longest time CO₂ reduction was recorded under continuous operation and does not necessarily reflect the maximum stability of the photocatalyst; ⁵Energy levels measured using photoelectron spectroscopy. ⁶Metal impurity present in semiconductor; ⁷Energy levels measured using photoelectron spectroscopy.
bandgap can improve photocatalytic efficiency by enabling the utilization of more solar photons. However, care should be taken to retain the required energy level alignments to drive the desired half-reactions. Therefore, to maximize photocatalytic efficiency, the development of semiconductors with energy levels tailored to drive specific half-reactions will be required, taking into account the substantial activation overpotentials required to drive kinetically demanding half-reactions such as O₂ evolution and CO₂ reduction. The use of cocatalysts can minimize these overpotentials and enable the use of narrower bandgap semiconductors to further enhance photocatalytic efficiency. Inefficient charge separation has emerged as the key factor that limits the EQE of current organic photocatalysts, and in future more effort should be put into designing semiconductors or semiconductor assemblies that enhance exciton dissociation and enable efficient charge transport to the photocatalyst surface. Enhancing the crystallinity of COFs and CTFs can enhance exciton separation, as can increasing the accessible surface area of the photocatalyst. Interactions between the reaction substrates and the semiconductor surface also play an important role, and increasing the hydrophilicity of photocatalysts that operate in an aqueous environment, or introducing functional groups capable of strong CO₂ adsorption or activation have all been shown to increase photocatalytic efficiency. The use of bulk heterojunctions can greatly enhance the formation of valuable products such as CH₄ and CH₃OH while suppressing the formation of H₂ and CO.

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Conflict of Interest

The authors declare no conflict of interest.

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