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Conjugated porphyrin materials for solar fuel generation

Yang Bai,^{1,*} and Reiner Sebastian Sprick,^{2,*}

¹ Institute of Materials Research and Engineering, Agency for Science Technology and Research, #08-03, 2 Fusionopolis Way, Innovis, Singapore 138634, Singapore. Email: bai_yang@imre.a-star.edu.sg.

² Department of Pure and Applied Chemistry, University of Strathclyde, Thomas Graham Building, 295 Cathedral Street, Glasgow G1 1XL, UK. Email: sebastian.sprick@strath.ac.uk.

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Abstract: Conjugated materials have emerged as a new class of photocatalysts for solar fuel generation, thus allowing for the Sun's energy to be converted into a storable fuel that can be used without further emissions at the point of use. Many different building blocks have been used to make conjugated materials that act as photocatalysts allowing for efficient light absorption and tuing of photophysical properties. The porphyrin moiety is a very interesting building block for photocatalysts as the large π -conjugated system allows efficient light absorption. Metalation of porphyrins allows for further tuning of the materials' properties, thus further expanding the property space that these materials can cover. This allows to design and better control over the properties of the materials, which is discussed in this review together with the state-of-the-art in porphyrin photocatalysts and hybrid systems.

Introduction

The energy used by humans for industrial processes, transportation, and domestic use has released large amounts of carbon dioxide, a major contributor to climate change.[1] In order to prevent catastrophic effects that originate from the increased Earth's surface temperature due to the greenhouse effect, we need to replace our fossil fuel-based energy sources with clean and renewable energy that does not release carbon dioxide.[2] This renewable energy source is already widely available: The total annual energy of the sun reaching the Earth's surface is 8,000 times the annual energy needs of humanity, and we need innovative solutions to access this energy. As such, solar energy has the potential to meet global energy needs, but the intermittency of sunlight due to the day/night cycle, and changes in light intensity during the year as well as due to cloud cover make it challenging to provide consistent energy through an electric grid.[3] For this reason, the alternative of storing solar energy as chemical fuels has been widely considered. [4,5] They can be obtained by using the electricity generated in a solar cell to drive electrolysis to generate hydrogen from water. Hydrogen can be used directly in fuel cells to generate electricity or industrial processes. Hydrogen can also be produced in photoelectrochemical cells or through photocatalytic processes.[6,7] The photochemical approach is of particular interest because it provides a technically simple solution that requires only water and a photocatalyst to facilitate the water splitting making it in principle more cost effective for large scale application.[8]

Natural photocatalysts

For billions of years, nature has used photosynthesis to convert solar light into chemical compounds such as carbohydrides to store energy. This allows to convert light to energy in a relatively efficient process with an efficient of approximately 6%. This process is ubiquitous in plants and other organisms and can be maintained over long periods of time due to the presence of self-repair mechanisms in cells.[9]

Chlorophylls, which are organized into supramolecular structures via self-assembly, have been identified as a key component in photosynthesis, which can absorb solar energy, and catalyze the conversion of carbon dioxide and water converted into sugars and oxygen, as shown in Figure 1a. The exact orientation of porphyrinoids ensures an efficient stepwise energy transfer to the reaction center where charge separation occurs.[10] The porphyrin unit as the main component in chlorophyll has attracted the attention of researchers for application in photochemical conversions.[11–14] Here, we discuss porphyrin-based materials for artificial photosynthesis – mainly focusing on photocatalytic water splitting.



Figure 1. Schematic diagram for a) photosynthesis in nature with chlorophyll molecular structure;[15,16] b) Reactions taking place during water splitting and carbon dioxide reduction on a semiconductor photocatalyst.[17]

Artificial photocatalysts

Science has always been inspired by nature, this is also true for artificial photosynthesis which aims to mimic the photosynthetic process of nature by storing solar energy in chemical energy.[18,19] As mentioned above, photosynthesis produces sugars while artificial photocatalyst aims to produce hydrogen from water via water splitting. Hydrogen produced using renewable solar light has significant potential to be used in energy generation allowing for decarbonisation of transport.[8,17,20] In order to allow this, photocatalytic processes that significantly exceed the light to energy conversion efficiency of nature are required, potentially as high as 10 to 20%, used on very large scale and with long-term stability.[5,21,22] For this reason, many scientific reports have been published over the last 50 years studying the conversion of sunlight into hydrogen via water splitting.^[23-27]

In photocatalytic water splitting, semiconductors are dispersed in water under light irradiation to promote simultaneous proton reduction and water oxidation. Photons that have sufficient energy promote an electron from the HOMO (the highest occupied molecular orbital) to the LUMO (the

lowest unoccupied molecular orbital) of the photocatalyst forming a so-called exciton.[28] The exciton is then separated into individual charge carriers with the electrons transferred to protons or carbon dioxide producing hydrogen or carbon monoxide and/or other carbon reduction products.[29–31] The holes are transferred to water resulting in the production of oxygen.[32,33] Metal catalysts play an important role as most reported systems require a catalyst that transfers charges from the semiconductor to protons or water in both half reactions.[34,35] These catalysts are either loaded onto the materials or in the case of many polymer photocatalysts they are already present within the material originating from the catalyst used in the material synthesis, such as residual palladium that was used in the Suzuki-Miyaura coupling reaction.[36,37] The water oxidation half-reaction is very challenging given that it is a four-hole process with very sluggish kinetics and the fact that low LUMO levels are required to fulfil thermodynamic requirements.[17,38] For this reason, often sacrificial hole scavengers are used that are oxidized instead of water.[39,40] This allows for the study of these systems to gain understanding, but scavengers ultimately have to be replaced with water to make the process energetically viable.

Most of the semiconductors studied as artificial photocatalysts so far are inorganic, with the best systems such as lanthanum-doped SrTiO₃ having relatively low solar-to-hydrogen efficiencies (STH, the percentage of solar energy converted into fuels) of up to 0.65%. This is despite their very high external quantum efficiencies (AQYs) under ultraviolet radiation (AQY = 96% at 350 nm),[41] and simply the result of the poor match of the light absorption of these materials with sunlight. As an organic alternatives, carbon nitride was first reported in 2009 to have photocatalytic activity for proton reduction and is one of the first examples of a polymeric material used for this purpose.[25] In recent years, a variety of other organic polymer photocatalysts, such as linear conjugated polymers,[29,42–46,61] conjugated polymer networks,[47,48] covalent organic frameworks,[49,50] oligomers,[51] and molecular crystals,[52] as well as various other types of photocatalysts, have been used as photocatalysts for sacrificial water oxidation in the presence of electron scavengers with some systems being translated into overall water splitting systems that do not require any sacrificial reagents.

Porphyrin-based photocatalysts

Porphyrin materials have been extensively studied as photocatalysts as they are closely related to natural systems and their large π -conjugated systems allow for efficient light absorption. The properties of porphyrin materials can be tuned by co-polymerization with a range of organic building blocks. This allows to, for example, to tune the energy levels, light absorption onset, or interaction with water to be tuned. The ability of the porphyrin ring to ligate metal ions via coordination to the nitrogen atoms inside the ring is highly relevant as these metal centers in metalated porphyrins has also the potential to be active as the electrocatalyst that is required in the proton reduction[53] or water oxidation process.[54,55] Metal ions can be coordinated in the plane of porphyrin rings when the metal ion radius is in the range of 55–80 pm, while the out-of-plane or sitting-atop metalloporphyrins can be formed when the metal ion radius is larger than 80 pm.[56–59]

The copolymerization of tetraphenylporphyrin cobalt(II) with squaraine has been reported to give a material with a very narrow optical gap of 1.82 eV.[60] The photocatalytic activity was determined in the presence of a sacrificial reagent, which is either oxidized or reduced instead of water. The tetraphenylporphyrin cobalt(II) monomer shows photocatalytic activity for hydrogen production in the presence of methanol as the sacrificial hole scavenger under visible light ($\lambda > 420$ nm). The copolymer with squaraine was found to be more active due to enhanced light absorption matching

the light source output better compared to the building block and exhibited increased stability, possibly as deactivation pathways are not accessible. By using additional platinum, which is an excellent catalyst for electron transfer to protons, the rates were to 1 μ mol h⁻¹ in the presence of triethanolamine (TEOA) acting as the hole scavenger. The system was also tested for water oxidation using silver nitride as the hole scavenger and under visible light ($\lambda > 420$ nm) a rate of 0.65 μ mol h⁻¹ was observed. While this rate is somewhat low compared to other reports, it is an interesting system as most other polymer systems rely on metal particles, such as CoO_x to be added to the surface of the material to make it active for water oxidation.[32] Here, the system appears to be using a coordinated cobalt species, but more work is required to study if the metal remains coordinated throughout the photocatalytic process.

The wettability of the photocatalysts plays a key role in photocatalytic water splitting as organic materials are fairly hydrophobic, which reduces the ability of the materials to intact with water on the surface.[39] Thus usually organic photocatalysts with increased wettability show higher photocatalytic proton reduction rates.[45,64] Oligomers of conjugated porphyrins with water solubiliszing side-chains have been reported for hydrogen evolution from water.[65] Platinum-loaded materials were found to have little activity in water with TEOA and only upon the addition of sodium chloride significant activity was determined with the highest rate of 10.9 mmol g⁻¹ h⁻¹ in 0.5 M NaCl (2 mg photocatalyst, 1 sun irradiation, 3 wt. % Pt, H₂O/TEOA, 9:1 v/v). The increase in activity upon the addition of sodium chloride coincides with aggregation of the photocatalyst into larger particles, which has also been observed for other systems to result in higher activity due to increased light scattering.[66]

The incorporation of polar side-chains into polymeric porphyrin materials has also been shown to give materials with high photocatalytic performance. A series of porphyrin-based conjugated polyelectrolytes (CPEs) with different coordinated metals for the efficient photocatalytic hydrogen evolution has been reported.[67] These CPEs also undergo aggregation under photocatalytic conditions and the use of different metals coordinated in the porphyrin unit can be used to tune the photocatalytic activity. The Pt-porphyrin CPE (PPF-Pt-Br, Fig. 3a) has a hydrogen evolution rate of 5.39 μ mol g⁻¹ h⁻¹, and an even higher hydrogen evolution rate of 37.9 μ mol h⁻¹ upon addition of 3 wt. % Pt co-catalyst under (Reaction conditions: 1 mg of CPE in 50 mL of water with 0.2 M ascorbic acid as the sacrificial agent, pH = 2.0, full arc, 300 W light source). An apparent quantum yield (AQY) at 420 nm was determined to be 3.33% using this Pt coordinated porphyrin-based CPE. Another porphyrin-based conjugated polymer example showed a higher AQY value of 7.36% at 400 nm using Zn and Co as the dual central metal in a porphyrin framework polymer synthesized by Sonogashira coupling (Figure 3b).[68]



Figure 2. a) Molecular structure of porphyrin derivatives with different dipoles (top), and diagram of molecular dipoles and electron distribution in three porphyrin derivatives, units of dipole moment: Debye (bottom) [Figure adapted with permission from ref.[62] Copyright 2019 Wiley-VCH]; b) Orbital splitting of metal centers in CoTCPP, NiTCPP, and ZnTCPP, and the interaction between porphyrin and central metal (top), and energy-band alignment diagram for supramolecular porphyrins (bottom) [Figure adapted with permission from ref.[63] Copyright 2019 Wiley-VCH].



Figure 3. a) Chemical structures of PPF-H-Br, PPF-Ni-Br, PPF-Cu-Br, and PPF-Pt-Br, Adapted with permission from reference[67]. Copyright 2021 American Chemical Society; b) Synthesis of CoP-nph-CMP, Adapted with permission from reference.[51] Copyright 2019 American Chemical Society; c) Synthesis of MPor-DETH-COFs.[69]

Polymeric photocatalysts are usually amorphous or show a low degree of order at best due to the fact that irreversible reactions are used to make these materials or conditions are used that are not near equilibrium resulting in defects within the structure and 3-dimentional growth. In recent years, covalent organic frameworks have attracted significant attention in photocatalytic hydrogen generation from water as they combine a relatively high degree of crystallinity and large surface areas.[49,70,71] Four isostructural porphyrinic two-dimensional covalent organic frameworks have been reported as photocatalysts for sacrificial hydrogen evolution from water. The AQY for hydrogen evolution from water can reach to 0.32% at 450 nm using porphyrin photocatalyst, ZnPor-DETH-COF (Fig. 3c), bearing Pt cocatalyst with TEOA as the sacrificial reagent. The photocatalytic activity of NiPor-DETH-COF is nearly half of ZnPor-DETH-COF, while CoPor-DETH-COF has the lowest activity in this report. Further than a high photocatalytic activity of material, the tuneable photocatalytic performance can be mainly explained by their tailored charge-carrier dynamics via molecular engineering has been clear shown in this report.[69]

Most conjugated systems reported to date require a metal cocatalyst to drive the proton reduction and water oxidation process as these allow to overcome kinetic barriers that typically exist.[17,72] In 2019, metal-free porphyrin-based photocatalysts for hydrogen evolution and oxygen evolution from water has been reported (Fig. 2a).[62] Different nanocrystal structures with so-called 'built-in electric fields' were presented using porphyrin bearing materials with three different terminal groups (pyridyl, cyanophenyl, or carboxyphenyl). This is the first report for metal-free porphyrin photocatalyst, and the SA-TCPP photocatalyst was reported with a hydrogen evolution rate of 40.8 μ mol g⁻¹ h⁻¹ (50 mg photocatalyst, 90 mL H₂O and 10 mL TEOA) and an oxygen evolution rate of 36.1 μ mol g⁻¹ h⁻¹ (50 mg photocatalyst, 100 mL 0.05 M AgNO₃ aqueous solution) under visible irradiation with a 500 W Xe light source. The authors state that the molecular dipoles give rise to the built-in electric field which increases charge separation efficiency of the photogenerated excitons which is responsible for the high photocatalytic efficiency.[63] It is unclear though how the electron and hole transfer to water occur when no metal catalyst is present. This requires further investigation in the future as other reports have shown the crucial role that metals have in photocatalytic processes with conjugated materials.[37,44,73] Following this work, the same group presented a nanosheet photocatalyst, SA-TCPP coordinating zinc ions (Fig. 2b). SA-TCPP produced hydrogen from water with a rate of 3487.3 μ mol g⁻¹ h⁻¹ under the same conditions, which is an 85-time increase compared to the metal-free porphyrin photocatalyst.

Composites of porphyrins



Figure 4. a) Chemical structures of the semiconductor CN (A) and of the porphyrins TPP (B), pTCPP (C) and mTCPP (D);[74] b) Structure of the g-C₃N₄-Cu-TCPP composite.[75]

Porphyrins and porphyrin-based materials have also been extensively used in composites with other materials. Using this approach allows to combine favorable properties from more than one material and to create interfaces that result in additional benefits, such as increased driving forces for charge separation of excitons.[76]

Carbon nitride (C₃N₄) has been widely studied for photocatalytic water splitting due to its suitable energy band structure and easy synthesis from low-cost precursors. However, the photoactivity of pristine C₃N₄ is low because of its wide band gap (~2.7 eV) limiting the activity under visible light illumination.[25,77,78] As porphyrin exhibit high absorption coefficients in the visible and near IR region they can be used to sensitize C₃N₄ making the composite active under visible light. As a result of this, composites of porphyrins with carbon nitride have been relatively well studied: For example, hybrids of C₃N₄ sensitized with three different porphyrins (*meso*-tetraphenylporphyrin, *meso*tetrakis(*meta*-carboxyphenyl)porphyrin and *meso*-tetrakis(*para*-carboxyphenyl)porphyrin) for photocatalytic hydrogen evolution from water (Fig. 4a).[74] All hybrids show higher hydrogen evolution rates than pristine carbon nitride, and the *meso*-tetrakis(*meta*-carboxyphenyl)porphyrin hybrid with carbon nitride had the highest amount of evolved hydrogen (48.4 µmol) under visible light ($\lambda > 400$ nm) illumination in 6 hours. These hybrid systems rely on non-covalent π - π interactions between both components. As an example of an alternative approach, a hybrid of *meso*-tetra(4carboxyphenyl) porphyrin and C₃N₄ using copper as the interfacial linker was reported (Fig. 4b).[75] This resulted in increased light absorption efficiency for the carbon nitride-copper-porphyrin hybrid compared to carbon nitride alone as well as increased charge-transfer rates increasing the hydrogen evolution rate more than 10-times higher compared to pristine carbon nitride. By changing the linker to tetrakis-(4-hydroxyphenyl)porphyrin in the carbon nitride hybrid, a more than 17-times higher hydrogen evolution rate compared to pristine carbon nitride hybrid, a more than 17-times higher hydrogen evolution rate compared to pristine carbon nitride was reported from the same group.[79]

Hybrid systems of porphyrins with TiO₂ have been reported for hydrogen production, improving the photocatalytic performance by acting as light absorbers[80,81] and through increased charge separation.[82] Systems that are simple mixtures of porphyrins and TiO₂[80,81] as well as systems with porphyrins anchored on the TiO₂ surface have been reported,[82] with the latter showing increased stability. Similarly, porphyrin-based polymers can be used in conjunction with TiO₂. TpTph, the condensation product of triformylphloroglucinol and tetrakis(4-aminophenyl)-porphyrin, was loaded mechanochemically onto TiO₂.[83] The resulting hybrid had a maximum hydrogen evolution rate of 5602 µmol g⁻¹ h⁻¹ under visible light ($\lambda > 420$ nm, 400 W Xe light source) in the presence of platinum acting as the co-catalyst and ascorbic acid as the hole scavenger. Control experiments show that the TiO₂ and TpTph are nearly inactive under the same conditions, indicating that this is a truly synergistic effect.

Fully organic composites with porphyrins have also been studied for their potential.[84,85] A recent report has demonstrated that a composite of tetraphenylporphinesulfonate and a fullerene derivative allows for light harvesting up to 843 nm and increased charge separation efficiency resulting in sacrificial hydrogen evolution rates of up to 34.57 mmol g⁻¹ h⁻¹, and an AQY is 1.64 % at 650 nm.[85]

Overall water splitting system

In contrast to sacrificial photocatalytic hydrogen production which has been extensively studied, there are only a few examples of overall water splitting with organic materials. Z-Scheme water splitting allows to couple an organic photocatalyst that performs hydrogen production with an inorganic semiconductor to perform overall water splitting.[86,87] Using such a system a 2D hybrid nanocomposite composed of monoclinic BiVO₄ nanosheets and an asymmetric Cr(III) porphyrin derivative (CrmTPP) act as a photocatalytic system for overall water splitting. The optimized hybrid nanocomposite produced stoichiometric amounts of hydrogen and oxygen with rates of 42.6 and 22.3 μ mol h⁻¹ under visible light irradiation (λ > 400 nm, 300 W Xe light source) and atmospheric pressure with Pt as co-catalyst, and the AQY reach to 8.67% at 400 nm.[12] Following work has been reported from the same group, that a Z-scheme overall water splitting system, that the heterometallic porphyrin conjugated polymer (ZnPtP-CP) was grafted onto ultrathin BiVO₄ nanosheets through an *in* situ Sonogashira coupling polymerization, giving a system capable of overall water splitting (Fig. 5). BiVO₄ acts as an oxygen evolution photocatalyst and ZnPtP-CP nanosheet as a hydrogen evolution photocatalyst, respectively. Zn-O-V bridging bonds were formed to promote charge transfer between ZnPtP-CP and BiVO₄. Overall water splitting rates under visible-light irradiation (λ > 400 nm, 300 W Xe light source) of 77.3 (H₂) and 39.5 (O₂) μ mol h⁻¹ were reported. A apparent quantum yield of 9.85% at 400 nm was determined by the authors, which is one of the highest solar-to-hydrogen efficiencies reported for organic photocatalysts.[88]



Figure 5. Schematic diagram of the synthesis route, structure and charge transfer mechanism of the ZnPyP-CP/BiVO₄ composite [Figure adapted with permission from ref.[88] Copyright 2021 Wiley-VCH].

Conclusions and outlook

Conjugated porphyrin-based materials have clearly shown that they have significant potential as photocatalysts for solar fuel generation, even though there are only relatively few reports so far. Advantages of these materials are the typically broad light absorption profiles originating from the extended π -conjugation in porphyrin units, which can be further tuned by metalation and intrinsic wettability due to the polar nature of the heterocycle.

Most conjugated materials rely on physiosorbed metal particles to facilitate water oxidation and/or proton reduction half reactions. Typically, platinum or palladium metal particles either loaded onto the photocatalyst or are residual metals originating from the synthesis. This is different from metalated porphyrins that can coordinate defined metal centres that can act as active sites. This is interesting as it allows for much better control, unlike for conjugated materials that are loaded with metal particles of varied sizes. It will also allow to gain better insight into the underlying photocatalytic processes as the exact nature of the catalyst is known, allowing to establish structure-property relationships and the design of more active systems going forward. In all reports, no system coordinating metal ions so far has outperformed systems that are loaded with platinum particles, however, effects such as longer-term stability have not been explored. Here, direct coordination might be beneficial as the risk of detachment of metal particles from the surface can be circumvented. Overall, it is clear that more work on metalated porphyrin photocatalysts is required.

Only a few reports on porphyrin materials have demonstrated for water oxidation, despite the large number of molecular porphyrin electrocatalysts that have been reported for water oxidation.[54,55,89,90] Water oxidation is very challenging for conjugated materials and usually archived by the addition of metal co-catalysts, such as CoO_x[32] or NiP_x.[91] Metalated porphyrins also offer exciting possibilities here that should be further explored as the development of such systems will allow to build up supramolecular systems and/or complex structures with both water oxidation and reduction catalysts to facilitate overall watersplitting. Finally, developing such hybrid systems is also highly relevant to photocatalytic carbon dioxide reduction[30] and hydrogen peroxide production[92] as water oxidation is likely to be the key bottleneck.

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References

- [1] T. J. Crowley, R. A. Berner, CO2 and Climate Change. *Science* **2001**, *292*, 870.
- [2] D. Gielen, F. Boshell, D. Saygin, M. D. Bazilian, N. Wagner, R. Gorini, The Role of Renewable Energy in the Global Energy Transformation. *Energy Strateg. Rev.* **2019**, *24*, 38.
- [3] J. Gong, C. Li, M. R. Wasielewski, Advances in Solar Energy Conversion. *Chem. Soc. Rev.* **2019**, *48*, 1862.
- [4] M. Grätzel, Photoelectrochemical Cells. Electrochem. *Nature* **2001**, *414*, 338.
- [5] Z. Wang, C. Li, K. Domen, Recent Developments in Heterogeneous Photocatalysts for Solar-Driven Overall Water Splitting. *Chem. Soc. Rev.* **2019**, *48*, 2109.
- [6] B. A. Pinaud, J. D. Benck, L. C. Seitz, A. J. Forman, Z. Chen, T. G. Deutsch, B. D. James, K. N. Baum, G. N. Baum, S. Ardo, H. Wang, E. Miller, T. F. Jaramillo, Technical and Economic Feasibility of Centralized Facilities for Solar Hydrogen Production via Photocatalysis and Photoelectrochemistry. *Energy Environ. Sci.* **2013**, *6*, 1983.
- [7] J. Joy, J. Mathew, S. C. George, Nanomaterials for Photoelectrochemical Water Splitting– Review. *Int. J. Hydrogen Energy* **2018**, *43*, 4804.
- [8] Q. Wang, K. Domen, Particulate Photocatalysts for Light-Driven Water Splitting: Mechanisms, Challenges, and Design Strategies. *Chem. Rev.* **2019**, *120*, 919.
- [9] V. Krewald, M. Retegan, D. A. Pantazis, Principles of Natural Photosynthesis, *Top Curr Chem.* **2016**, 371, 23.
- [10] J. Z. Zhang, E. Reisner, Advancing Photosystem II Photoelectrochemistry for Semi-Artificial Photosynthesis. *Nat. Rev. Chem.* **2020**, *4*, 6.
- [11] Y. Zhang, K. Ren, L. Wang, L. Wang, Z. Fan, Porphyrin-Based Heterogeneous Photocatalysts for Solar Energy Conversion. *Chinese Chem. Lett.* **2021**, DOI:10.1016/j.cclet.2021.06.013.
- [12] J. Wang, L. Guo, L. Xu, P. Zeng, R. Li, T. Peng, Z-Scheme Photocatalyst Based on Porphyrin Derivative Decorated Few-Layer BiVO₄ Nanosheets for Efficient Visible-Light-Driven Overall Water Splitting. *Nano Res.* 2021, 14, 1294.
- [13] L. Wang, H. Fan, F. Bai, Porphyrin-Based Photocatalysts for Hydrogen Production. *MRS Bull.* 2020, 45, 49.
- [14] M. Joseph, S. Haridas, Recent Progresses in Porphyrin Assisted Hydrogen Evolution. *Int. J. Hydrogen Energy* **2020**, *45*, 11954.
- [15] J. Min Park, J. H. Lee, W. D. Jang, Applications of Porphyrins in Emerging Energy Conversion Technologies. *Coord. Chem. Rev.* **2020**, *407*, 213157.
- [16] X. Li, J. Wen, J. Low, Y. Fang, J. Yu, Design and Fabrication of Semiconductor Photocatalyst for Photocatalytic Reduction of CO₂ to Solar Fuel. *Sci. China Mater.* **2014**, 57, 70.
- [17] Y. Bai, K. Hippalgaonkar, R. S. Sprick, Organic Materials as Photocatalysts for Water Splitting.

J. Mater. Chem. A 2021, 121.

- [18] Y. Fang, Y. Zheng, T. Fang, Y. Chen, Y. Zhu, Q. Liang, H. Sheng, Z. Li, C. Chen, X. Wang, Photocatalysis: An Overview of Recent Developments and Technological Advancements. *Sci. China Chem.* 2020, *63*, 149.
- [19] Y. Wang, H. Suzuki, J. Xie, O. Tomita, D. J. Martin, M. Higashi, D. Kong, R. Abe, J. Tang, Mimicking Natural Photosynthesis: Solar to Renewable H₂ Fuel Synthesis by Z-Scheme Water Splitting Systems. *Chem. Rev.* 2018, 118, 5201.
- [20] V. Andrei, B. Reuillard, E. Reisner, Bias-Free Solar Syngas Production by Integrating a Molecular Cobalt Catalyst with Perovskite–BiVO₄ Tandems. *Nat. Mater.* **2020**, *19*, 189.
- [21] H. Lyu, T. Hisatomi, Y. Goto, M. Yoshida, T. Higashi, M. Katayama, T. Takata, T. Minegishi, H. Nishiyama, T. Yamada, Y. Sakata, K. Asakura, K. Domen, An Al-Doped SrTiO₃ Photocatalyst Maintaining Sunlight-Driven Overall Water Splitting Activity for over 1000 h of Constant Illumination. *Chem. Sci.* 2019, 10, 3196.
- [22] H. Nishiyama, T. Yamada, M. Nakabayashi, Y. Maehara, M. Yamaguchi, Y. Kuromiya, H. Tokudome, S. Akiyama, T. Watanabe, R. Narushima, S. Okunaka, N. Shibata, T. Takata, T. Hisatomi, K. Domen, Photocatalytic Solar Hydrogen Production from Water on a 100 m²-Scale. *Nature* **2021**, DOI:10.1038/s41586-021-03907-3.
- [23] A. Fujishima, K. Honda, Electrochemical Photolysis of Water at a Semiconductor Electrode. *Nature* **1972**, *238*, 37.
- [24] T. Takata, J. Jiang, Y. Sakata, M. Nakabayashi, N. Shibata, V. Nandal, K. Seki, T. Hisatomi, K. Domen, Photocatalytic Water Splitting with a Quantum Efficiency of Almost Unity. *Nature* 2020, 581, 411.
- [25] X. Wang, K. Maeda, A. Thomas, K. Takanabe, G. Xin, J. M. Carlsson, K. Domen, M. Antonietti, A Metal-Free Polymeric Photocatalyst for Hydrogen Production from Water under Visible Light. *Nat. Mater.* 2009, *8*, 76.
- [26] W.-H. Wang, L.-Y. Ting, J. Jayakumar, C.-L. Chang, W.-C. Lin, C.-C. Chung, M. H. Elsayed, C.-Y. Lu, A. M. Elewa, H.-H. Chou, Design and Synthesis of Phenylphosphine Oxide-Based Polymer Photocatalysts for Highly Efficient Visible-Light-Driven Hydrogen Evolution. *Sustain. Energy Fuels* **2020**, *4*, 5264.
- [27] Z. Qian, Z. J. Wang, K. A. I. Zhang, Covalent Triazine Frameworks as Emerging Heterogeneous Photocatalysts. *Chem. Mater.* **2021**, DOI:10.1021/acs.chemmater.0c04348.
- [28] P. Guiglion, C. Butchosa, M. A. Zwijnenburg, Polymeric Watersplitting Photocatalysts; A Computational Perspective on the Water Oxidation Conundrum. J. Mater. Chem. A 2014, 2, 11996.
- [29] Y. Bai, L. Wilbraham, H. Gao, R. Clowes, H. Yang, M. Zwijnenburg, A. Cooper, R. S. Sprick, Photocatalytic Polymers of Intrinsic Microporosity for Hydrogen Production from Water. J. Mater. Chem. A 2021, 121.
- [30] Z. Fu, A. Vogel, M. A. Zwijnenburg, A. I. Cooper, R. S. Sprick, Photocatalytic Syngas Production Using Conjugated Organic Polymers. *J. Mater. Chem. A* **2021**, *9*, 4291.
- [31] Q. Wang, J. Warnan, S. Rodríguez-Jiménez, J. J. Leung, S. Kalathil, V. Andrei, K. Domen, E. Reisner, Molecularly Engineered Photocatalyst Sheet for Scalable Solar Formate Production from Carbon Dioxide and Water. *Nat. Energy* 2020, *5*, 703.
- [32] R. S. Sprick, Z. Chen, A. J. Cowan, Y. Bai, C. M. Aitchison, Y. Fang, M. A. Zwijnenburg, A. I.

Cooper, X. Wang, Water Oxidation with Cobalt - Loaded Linear Conjugated Polymer Photocatalysts. *Angew. Chem. Int. Ed.* **2020**, *59*, 18695.

- [33] J. Xie, S. A. Shevlin, Q. Ruan, S. J. A. Moniz, Y. Liu, X. Liu, Y. Li, C. C. Lau, Z. X. Guo, J. Tang, Efficient Visible Light-Driven Water Oxidation and Proton Reduction by an Ordered Covalent Triazine-Based Framework. *Energy Environ. Sci.* 2018, 11, 1617.
- [34] N. Aiga, Q. Jia, K. Watanabe, A. Kudo, T. Sugimoto, Y. Matsumoto, Electron-Phonon Coupling Dynamics at Oxygen Evolution Sites of Visible-Light-Driven Photocatalyst: Bismuth Vanadate. *J. Phys. Chem. C* **2013**, *117*, 9881.
- [35] Z. Pan, T. Hisatomi, Q. Wang, M. Nakabayashi, N. Shibata, C. Pan, T. Takata, K. Domen, Application of LaMg1/3Ta2/3O2N as a Hydrogen Evolution Photocatalyst of a Photocatalyst Sheet for Z-Scheme Water Splitting. *Appl. Catal. A Gen.* **2016**, *521*, 26.
- [36] R. S. Sprick, Y. Bai, A. A. Y. Guilbert, M. Zbiri, C. M. Aitchison, L. Wilbraham, Y. Yan, D. J.
 Woods, M. A. Zwijnenburg, A. I. Cooper, Photocatalytic Hydrogen Evolution from Water Using Fluorene and Dibenzothiophene Sulfone-Conjugated Microporous and Linear Polymers. *Chem. Mater.* 2019, *31*, 305.
- [37] J. Kosco, M. Sachs, R. Godin, M. Kirkus, L. Francas, M. Bidwell, M. Qureshi, D. Anjum, J. R. Durrant, I. McCulloch, The Effect of Residual Palladium Catalyst Contamination on the Photocatalytic Hydrogen Evolution Activity of Conjugated Polymers. *Adv. Energy Mater.* 2018, 8, 1802181.
- [38] K. Maeda, Z-Scheme Water Splitting Using Two Different Semiconductor Photocatalysts. *ACS Catal.* **2013**, *3*, 1486.
- [39] M. Sachs, R. S. Sprick, D. Pearce, S. A. J. Hillman, A. Monti, A. A. Y. Guilbert, N. J. Brownbill, S. Dimitrov, X. Shi, F. Blanc, M. A. Zwijnenburg, J. Nelson, J. R. Durrant, A. I. Cooper, Understanding Structure-Activity Relationships in Linear Polymer Photocatalysts for Hydrogen Evolution. *Nat. Commun.* 2018, 9, 1.
- [40] V. S. Vyas, F. Haase, L. Stegbauer, G. Savasci, F. Podjaski, C. Ochsenfeld, B. V Lotsch, A Tunable Azine Covalent Organic Framework Platform for Visible Light-Induced Hydrogen Generation. *Nat. Commun.* 2015, 6, 8508.
- [41] Y. Goto, T. Hisatomi, Q. Wang, T. Higashi, K. Ishikiriyama, T. Maeda, Y. Sakata, S. Okunaka, H. Tokudome, M. Katayama, S. Akiyama, H. Nishiyama, Y. Inoue, T. Takewaki, T. Setoyama, T. Minegishi, T. Takata, T. Yamada, K. Domen, A Particulate Photocatalyst Water-Splitting Panel for Large-Scale Solar Hydrogen Generation. *Joule* **2018**, *2*, 509.
- [42] R. S. Sprick, B. Bonillo, R. Clowes, P. Guiglion, N. J. Brownbill, B. J. Slater, F. Blanc, M. A.
 Zwijnenburg, D. J. Adams, A. I. Cooper, Visible-Light-Driven Hydrogen Evolution Using
 Planarized Conjugated Polymer Photocatalysts. *Angew. Chem. Int. Ed.* 2016, 55, 1792.
- [43] D. J. Woods, S. A. J. Hillman, D. Pearce, L. Wilbraham, L. Q. Flagg, W. Duffy, I. McCulloch, J. R. Durrant, A. A. Y. Guilbert, M. A. Zwijnenburg, R. S. Sprick, J. Nelson, A. I. Cooper, Side-Chain Tuning in Conjugated Polymer Photocatalysts for Improved Hydrogen Production from Water. *Energy Environ. Sci.* 2020, 13, 1843.
- [44] M. Sachs, H. Cha, J. Kosco, C. M. Aitchison, L. Francàs, S. Corby, C.-L. Chiang, A. Wilson, R. Godin, A. Fahey-Williams, Tracking Charge Transfer to Residual Metal Clusters in Conjugated Polymers for Photocatalytic Hydrogen Evolution. J. Am. Chem. Soc. 2020, 142, 14574.
- [45] R. S. Sprick, K. J. Cheetham, Y. Bai, J. Alves Fernandes, M. Barnes, J. W. Bradley, A. I. Cooper, Polymer Photocatalysts with Plasma-Enhanced Activity. *J. Mater. Chem. A* **2020**, *8*, 7125.

- [46] A. Vogel, M. Forster, L. Wilbraham, C. L. Smith, A. J. Cowan, M. A. Zwijnenburg, R. S. Sprick, A.
 I. Cooper, Photocatalytically Active Ladder Polymers. *Faraday Discuss.* **2019**, *215*, 84.
- [47] R. S. Sprick, J. X. Jiang, B. Bonillo, S. Ren, T. Ratvijitvech, P. Guiglion, M. A. Zwijnenburg, D. J. Adams, A. I. Cooper, Tunable Organic Photocatalysts for Visible-Light-Driven Hydrogen Evolution. J. Am. Chem. Soc. 2015, 137, 3265.
- [48] Y. Bai, D. J. Woods, L. Wilbraham, C. M. Aitchison, M. A. Zwijnenburg, R. S. Sprick, A. I. Cooper, Hydrogen Evolution from Water Using Heteroatom Substituted Fluorene Conjugated Co-Polymers. J. Mater. Chem. A 2020, 8, 8700.
- X. Wang, L. Chen, S. Y. Chong, M. A. Little, Y. Wu, W.-H. Zhu, R. Clowes, Y. Yan, M. A.
 Zwijnenburg, R. Sebastian Sprick, A. I. Cooper, R. S. Sprick, A. I. Cooper, Sulfone-Containing
 Covalent Organic Frameworks for Photocatalytic Hydrogen Evolution from Water. *Nat. Chem.* 2018, 10, 1180.
- [50] H. Zhong, R. Sa, H. Lv, S. Yang, D. Yuan, X. Wang, R. Wang, Covalent Organic Framework Hosting Metalloporphyrin-Based Carbon Dots for Visible-Light-Driven Selective CO2 Reduction. Adv. Funct. Mater. 2020, 30, 2002654.
- [51] C. M. Aitchison, M. Sachs, M. Little, L. Wilbraham, N. J. Brownbill, C. Kane, F. Blanc, M. Zwijnenburg, J. Durrant, R. S. Sprick, Structure-Activity Relationships in Well-Defined Conjugated Oligomer Photocatalysts for Hydrogen Production from Water. *Chem. Sci.* 2020, 11, 8744.
- [52] C. M. Aitchison, C. M. Kane, D. P. McMahon, P. R. Spackman, A. Pulido, X. Wang, L.
 Wilbraham, L. Chen, R. Clowes, M. A. Zwijnenburg, R. S. Sprick, M. A. Little, G. M. Day, A. I.
 Cooper, Photocatalytic Proton Reduction by a Computationally Identified, Molecular
 Hydrogen-Bonded Framework. J. Mater. Chem. A 2020, 8, 7158.
- [53] K. Ladomenou, M. Natali, E. Iengo, G. Charalampidis, F. Scandola, A. G. Coutsolelos, Photochemical Hydrogen Generation with Porphyrin-Based Systems. *Coord. Chem. Rev.* 2015, 304–305, 38.
- [54] Y. Han, Y. Wu, W. Lai, R. Cao, Electrocatalytic Water Oxidation by a Water-Soluble Nickel Porphyrin Complex at Neutral PH with Low Overpotential. *Inorg. Chem.* **2015**, *54*, 5604.
- [55] T. Nakazono, A. R. Parent, K. Sakai, Cobalt Porphyrins as Homogeneous Catalysts for Water Oxidation. *Chem. Commun.* **2013**, *49*, 6325.
- [56] M. J. Latter, S. J. Langford, Porphyrinic Molecular Devices: Towards Nanoscaled Processes. *Int. J. Mol. Sci.* **2010**, *11*, 1878.
- [57] E. Barton Cole, P. S. Lakkaraju, D. M. Rampulla, A. J. Morris, E. Abelev, A. B. Bocarsly, Using a One-Electron Shuttle for the Multielectron Reduction of CO₂ to Methanol: Kinetic, Mechanistic, and Structural Insights. J. Am. Chem. Soc. **2010**, 132, 11539.
- [58] M. Imran, M. Ramzan, A. K. Qureshi, M. Azhar Khan, M. Tariq, Emerging Applications of Porphyrins and Metalloporphyrins in Biomedicine and Diagnostic Magnetic Resonance Imaging. *Biosensors* **2018**, *8*, 1.
- [59] Y. Liu, L. Wang, H. Feng, X. Ren, J. Ji, F. Bai, H. Fan, Microemulsion-Assisted Self-Assembly and Synthesis of Size-Controlled Porphyrin Nanocrystals with Enhanced Photocatalytic Hydrogen Evolution. *Nano Lett.* **2019**, *19*, 2614.
- [60] K. C. Ranjeesh, L. George, V. C. Wakchaure, Goudappagouda, R. N. Devi, S. S. Babu, A Squaraine-Linked Metalloporphyrin Two-Dimensional Polymer Photocatalyst for Hydrogen

and Oxygen Evolution Reactions. Chem. Commun. 2019, 55, 1627.

- [61] Y. Bai, C. Li, L. Liu, Y. Yamaguchi, B. Mounib, H. Yang, A. Gardner, M. A. Zwijnenburg, N. Browning, A. J. Cowan, and A. Kudo, A. I. Cooper, R. S. Sprick, Photocatalytic overall water splitting under visible light enabled by a particulate conjugated polymer loaded with iridium. *ChemRxiv*. 2022, DOI 10.26434/chemrxiv-2022-8vr18.
- [62] Z. Zhang, Y. Zhu, X. Chen, H. Zhang, J. Wang, A Full-Spectrum Metal-Free Porphyrin Supramolecular Photocatalyst for Dual Functions of Highly Efficient Hydrogen and Oxygen Evolution. *Adv. Mater.* **2019**, *31*, 1.
- [63] J. Jing, J. Yang, Z. Zhang, Y. Zhu, Supramolecular Zinc Porphyrin Photocatalyst with Strong Reduction Ability and Robust Built-In Electric Field for Highly Efficient Hydrogen Production. *Adv. Energy Mater.* **2021**, *2101392*, 1.
- [64] R. S. Sprick, L. Wilbraham, Y. Bai, P. Guiglion, A. Monti, R. Clowes, A. I. Cooper, M. A.
 Zwijnenburg, Nitrogen Containing Linear Poly(phenylene) Derivatives for Photo-Catalytic
 Hydrogen Evolution from Water. *Chem. Mater.* 2018, *30*, 5733.
- [65] X. Yang, Z. Hu, Q. Yin, C. Shu, X. X. F. Jiang, J. Zhang, X. Wang, J. X. Jiang, F. Huang, Y. Cao, Q. Yin, Y. Cao, Water-Soluble Conjugated Molecule for Solar-Driven Hydrogen Evolution from Salt Water. Adv. Funct. Mater. 2019, 29, 1.
- [66] C. M. Aitchison, R. S. Sprick, A. I. Cooper, Emulsion Polymerization Derived Organic Photocatalysts for Improved Light-Driven Hydrogen Evolution. *J. Mater. Chem. A* 2019, *7*, 2490.
- [67] X. Zhao, X. Zhang, Y. Liang, Z. Hu, F. Huang, Porphyrin-Based Conjugated Polyelectrolytes for Efficient Photocatalytic Hydrogen Evolution. *Macromolecules* 2021, DOI: 10.1021/acs.macromol.1c00489.
- [68] Z. Chen, J. Wang, S. Zhang, Y. Zhang, J. Zhang, R. Li, T. Peng, Porphyrin-Based Conjugated Polymers as Intrinsic Semiconducting Photocatalysts for Robust H₂ Generation under Visible Light. ACS Appl. Energy Mater. 2019, 2, 5665.
- [69] R. Chen, Y. Wang, Y. Ma, A. Mal, X. Y. Gao, L. Gao, L. Qiao, X. B. Li, L. Z. Wu, C. Wang, Rational Design of Isostructural 2D Porphyrin-Based Covalent Organic Frameworks for Tunable Photocatalytic Hydrogen Evolution. *Nat. Commun.* **2021**, *12*, 1.
- [70] K. Gottschling, G. Savasci, H. Vignolo-González, S. Schmidt, P. Mauker, T. Banerjee, P. Rovó, C. Ochsenfeld, B. V. Lotsch, Rational Design of Covalent Cobaloxime-Covalent Organic
 Framework Hybrids for Enhanced Photocatalytic Hydrogen Evolution. J. Am. Chem. Soc. 2020, 142, 12146.
- K. Wang, Z. Jia, Y. Bai, X. Wang, S. E. Hodgkiss, L. Chen, S. Y. Chong, X. Wang, H. Yang, Y. Xu, F. Feng, J. W. Ward, A. I. Cooper, Synthesis of Stable Thiazole-Linked Covalent Organic Frameworks via a Multicomponent Reaction. *J. Am. Chem. Soc.* 2020, 142, 11131.
- Y. Wang, A. Vogel, M. Sachs, R. S. Sprick, L. Wilbraham, S. J. A. Moniz, R. Godin, M. A.
 Zwijnenburg, J. R. Durrant, A. I. Cooper, J. Tang, Current Understanding and Challenges of
 Solar-Driven Hydrogen Generation Using Polymeric Photocatalysts. *Nat. Energy* 2019, *4*, 746.
- [73] L. Li, Z. Cai, Q. Wu, W. Y. Lo, N. Zhang, L. X. Chen, L. Yu, Rational Design of Porous Conjugated Polymers and Roles of Residual Palladium for Photocatalytic Hydrogen Production. J. Am. Chem. Soc. 2016, 138, 7681.
- [74] E. S. Da Silva, N. M. M. Moura, M. G. P. M. S. Neves, A. Coutinho, M. Prieto, C. G. Silva, J. L.

Faria, Novel Hybrids of Graphitic Carbon Nitride Sensitized with Free-Base Meso-Tetrakis(Carboxyphenyl) Porphyrins for Efficient Visible Light Photocatalytic Hydrogen Production. *Appl. Catal. B Environ.* **2018**, *221*, 56.

- [75] K. Zhu, M. Zhang, X. Feng, L. Qin, S. Z. Kang, X. Li, A Novel Copper-Bridged Graphitic Carbon Nitride/Porphyrin Nanocomposite with Dramatically Enhanced Photocatalytic Hydrogen Generation. *Appl. Catal. B Environ.* **2020**, *268*, 118434.
- J. Kosco, M. Bidwell, H. Cha, T. Martin, C. T. Howells, M. Sachs, D. H. Anjum, S. Gonzalez
 Lopez, L. Zou, A. Wadsworth, W. Zhang, L. Zhang, J. Tellam, R. Sougrat, F. Laquai, D. M.
 DeLongchamp, J. R. Durrant, I. McCulloch, Enhanced Photocatalytic Hydrogen Evolution from
 Organic Semiconductor Heterojunction Nanoparticles. *Nat. Mater.* 2020, 19, 559.
- [77] G. Zhang, G. Li, Z. A. Lan, L. Lin, A. Savateev, T. Heil, S. Zafeiratos, X. Wang, M. Antonietti, Optimizing Optical Absorption, Exciton Dissociation, and Charge Transfer of a Polymeric Carbon Nitride with Ultrahigh Solar Hydrogen Production Activity. *Angew. Chem. Int. Ed.* 2017, 56, 13445.
- [78] G. Zhang, L. Lin, G. Li, Y. Zhang, A. Savateev, S. Zafeiratos, X. Wang, M. Antonietti, Ionothermal Synthesis of Triazine–Heptazine-Based Copolymers with Apparent Quantum Yields of 60 % at 420 Nm for Solar Hydrogen Production from "Sea Water.". Angew. Chem. Int. Ed. 2018, 57, 9372.
- [79] M. Zhang, K. Zhu, L. Qin, S. Z. Kang, X. Li, Enhanced Electron Transfer and Photocatalytic Hydrogen Production over the Carbon Nitride/Porphyrin Nanohybrid Finely Bridged by Special Copper. *Catal. Sci. Technol.* **2020**, *10*, 1640.
- [80] W. Kim, T. Tachikawa, T. Majima, C. Li, H.-J. Kim, W. Choi, Tin-Porphyrin Sensitized TiO2 for the Production of H 2 under Visible Light. *Energy Environ. Sci.* **2010**, *3*, 1789.
- [81] E. A. Malinka, G. L. Kamalov, S. V. Vodzinskii, V. I. Melnik, Z. I. Zhilina, Hydrogen Production from Water by Visible Light Using Zinc Porphyrin-Sensitized Platinized Titanium Dioxide. J. Photochem. Photobiol. A Chem. 1995, 90, 153.
- [82] X. Guo, X. Li, L. Qin, S.-Z. Kang, G. Li, A Highly Active Nano-Micro Hybrid Derived from Cu-Bridged TiO2/Porphyrin for Enhanced Photocatalytic Hydrogen Production. *Appl. Catal. B Environ.* 2019, 243, 1.
- [83] G. Mukherjee, J. Thote, H. B. Aiyappa, S. Kandambeth, S. Banerjee, K. Vanka, R. Banerjee, A Porous Porphyrin Organic Polymer (PPOP) for Visible Light Triggered Hydrogen Production. *Chem. Commun.* 2017, 53, 4461.
- [84] X. Li, T. Goto, K. Nomura, M. Zhu, T. Sekino, Y. Osakada, Synthesis of Porphyrin Nanodisks from COFs through Mechanical Stirring and Their Photocatalytic Activity. *Appl. Surf. Sci.* 2020, 513, 145720.
- [85] J. Yang, J. Jing, Y. Zhu, A Full-Spectrum Porphyrin–Fullerene D–A Supramolecular Photocatalyst with Giant Built-In Electric Field for Efficient Hydrogen Production. *Adv. Mater.* 2021, 33 (31), 1–8.
- [86] Z. Pan, G. Zhang, X. Wang, Polymeric Carbon Nitride/Reduced Graphene Oxide/Fe₂O₃: All-Solid-State Z-Scheme System for Photocatalytic Overall Water Splitting. *Angew. Chem. Int. Ed.* 2019, *58*, 7102.
- [87] Y. Bai, K. Nakagawa, A. Cowan, C. M. Aitchison, Y. Yamaguchi, M. Zwijnenburg, A. Kudo, R. S. Sprick, A. Cooper, Photocatalyst Z-Scheme System Composed of a Linear Conjugated Polymer and BiVO₄ for Overall Water Splitting under Visible Light. *J. Mater. Chem. A* **2020**, *6*, 4883.

- [88] J. Wang, L. Xu, T. Wang, R. Li, Y. Zhang, J. Zhang, T. Peng, Porphyrin Conjugated Polymer Grafted onto BiVO4 Nanosheets for Efficient Z-Scheme Overall Water Splitting via Cascade Charge Transfer and Single-Atom Catalytic Sites. *Adv. Energy Mater.* **2021**, *11*, 1.
- [89] A. N. Marianov, Y. Jiang, Effect of Manganese Porphyrin Covalent Immobilization on Electrocatalytic Water Oxidation and Oxygen Reduction Reactions. ACS Sustain. Chem. Eng. 2019, 7, 3838.
- [90] D. Wang, J. T. Groves, Efficient Water Oxidation Catalyzed by Homogeneous Cationic Cobalt Porphyrins with Critical Roles for the Buffer Base. *Proc. Natl. Acad. Sci.* **2013**, *110*, 15579.
- [91] S. Zhang, G. Cheng, L. Guo, N. Wang, B. Tan, S. Jin, Strong-Base-Assisted Synthesis of a Crystalline Covalent Triazine Framework with High Hydrophilicity via Benzylamine Monomer for Photocatalytic Water Splitting. *Angew. Chem. Int. Ed.* **2020**, *59*, 6007.
- [92] Y. Shiraishi, T. Takii, T. Hagi, S. Mori, Y. Kofuji, Y. Kitagawa, S. Tanaka, S. Ichikawa, T. Hirai, Resorcinol–Formaldehyde Resins as Metal-Free Semiconductor Photocatalysts for Solar-to-Hydrogen Peroxide Energy Conversion. *Nat. Mater.* **2019**, *18*, 985.