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Towards photocatalytic water splitting in homogeneous solutions using molecular metalloporphyrin photosensitizers and catalysts

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Towards Photocatalytic Water Splitting in Homogeneous Solutions Using Molecular Metalloporphyrin Photosensitizers and Catalysts

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Introduction

1.1 Artificial photosynthesis

The development of sustainable energy is necessary for solving the global energy crises.^[1-5] Solar energy, one of the most widespread renewable energy sources, is receiving more and more attention due to its abundance.^[6-7] Since the amount of available solar energy far exceeds the energy demands of human activities, the conversion and storage of solar energy is a significant opportunity for the future development of mankind.^[4,8-10] In recent decades, artificial photosynthesis has been considered as a promising strategy to store solar energy in a chemical form.^[11-15] What is more, one of the artificial photosynthetic reactions, CO₂ reduction, may also plays a significant role to solve the “greenhouse” problem and achieve a “carbon neutral” society.^[10,16-17]

Artificial photosynthesis is inspired from nature. Its basic idea is to achieve the conversion of light into chemical fuels.^[3,16] However, understanding all details of the natural photosynthetic mechanisms took a long time to many scientists all over the world. Thanks to past efforts, the mechanism of photosynthesis in green plants and bacteria is now well understood. The widely accepted mechanism distinguishes photosystem II (PSII), where water oxidation takes place; photosystem I (PSI), where the light-induced electron-transfer across the photosynthetic membrane happens, which happens at PSII as well; and a set of catalytic dark reactions, where the reduction of CO₂ into carbohydrate proceeds.^[1,3,12,14,16] Two combinations of simple photocatalytic reactions would represent a simplified scheme for artificial photosynthesis: either water splitting into O₂ and H₂, which can be used to further reduce CO₂ using known industrial catalytic processes; or, water oxidation and CO₂ reduction into carbon fuels or organic products (Figure 1.1).^[3,9,16]

Generally speaking, artificial photosynthesis is designed for directly capturing and storing solar energy into chemical bonds. However, recently people have been developing a technologically simplified approach, i.e., using electricity from photovoltaics as the driving energy for electrocatalytic water splitting or CO₂ reduction, with focus on developing molecular or material catalysts to realize these electrocatalytic processes efficiently. Although direct solar conversion into photoelectricity is by itself a renewable process, it is often argued that photovoltaic electricity generation, followed by electrocatalysis, inevitably causes energy loss, and that it would be more desirable to drive artificial photosynthetic reactions directly.^[7,10]

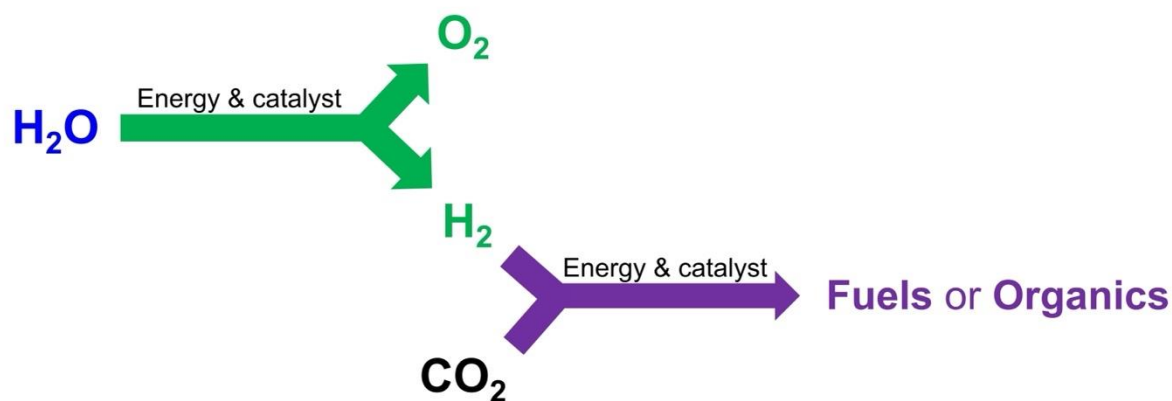


Figure 1.1 Simplified processes of artificial photosynthesis.

1.2 Molecular catalysts for homogeneous light-driven water oxidation using $[\text{Ru}(\text{bpy})_3]^{2+}$ as photosensitizer and $\text{S}_2\text{O}_8^{2-}$ as sacrificial electron acceptor

1.2.1 Molecular three-component systems for homogeneous light-driven water oxidation

Water oxidation to O_2 ($\Delta G^0 = 1.23 \text{ eV}$) is a four-electron half reaction indispensable for water splitting. It is often argued that this process is both thermodynamically and kinetically demanding, therefore, a catalyst is needed to reduce the energy barrier and speed up kinetics.^[15,18] However, in a photocatalytic water oxidation system, a light-harvesting component that can adsorb and utilize light energy is also critical.^[9] A minimal three-component system for photocatalytic water oxidation consists hence in a photosensitizer (PS), a water oxidation catalyst (Cat) and a sacrificial electron acceptor (EA); this type of systems has been considered worldwide as the best model for catalyst and photosensitizer development.^[4,9,14,18] The catalytic mechanism usually proposed for these systems is shown in Figure 1.2. In this mechanism, PS is first excited upon adsorbing a photon, then it is oxidized by giving an electron to the EA and forms an oxidized state, PS^+ . PS^+ can further oxidize Cat into Cat^+ , which, after four turnovers also releasing protons, finally generates a species capable to release O_2 .^[19-20]

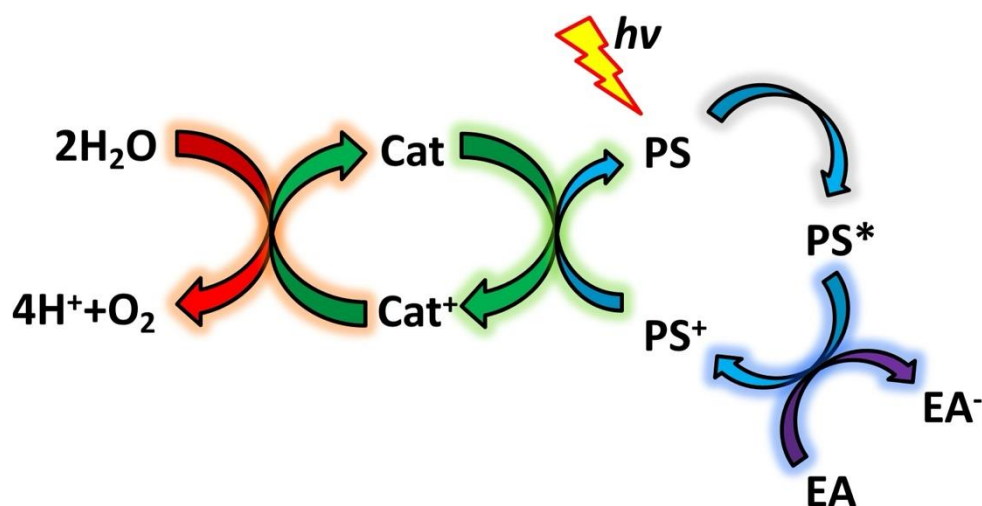


Figure 1.2 Simplified three-component photocatalytic water oxidation system. EA: sacrificial electron acceptor; PS: photosensitizer; Cat: water oxidation catalyst.

Recently, three-component molecular photocatalytic systems have been widely studied because 1) each individual component can be clearly defined, 2) the free Gibbs energy relationships between the components, and the electron transfer driving forces, can be calculated, 3) individual electron transfer between some of these components can be studied, and 4) the reactions in solution can be followed by spectroscopy.^[9,13-15,17,21-22] Current research based on this type of systems are mainly focusing on 1) finding the mechanism of water oxidation at the catalyst, 2) developing more robust and more efficient photosensitizers and catalysts, in particular using earth-abundant metals, 3) assembling supramolecular systems or immobilizing molecular catalysts onto functional materials in order to improve the overall performance of photocatalysis.^[13,20,23-26]

The most widely accepted photocatalytic water oxidation system for catalyst developments is a homogeneous system consisting of $[\text{Ru}(\text{bpy})_3]^{2+}$ (bpy = 2,2'-bipyridine) as photosensitizer, $\text{S}_2\text{O}_8^{2-}$ as sacrificial electron acceptor, and the water oxidation catalyst of interest.^[19] Although this system is not ideal since the photogenerated $[\text{Ru}(\text{bpy})_3]^{3+}$ (PS^+) has a poor stability in aqueous solutions at neutral or basic pH's, it is still widely applied as a standard system due to its well-studied mechanism. Basically, $[\text{Ru}^{\text{II}}(\text{bpy})_3]^{2+}$ absorbs a photon and is excited to an excited state that transfers an electron to $[\text{S}_2\text{O}_8]^{2-}$ to afford $[\text{Ru}^{\text{III}}(\text{bpy})_3]^{3+}$, SO_4^{2-} , and a $\text{SO}_4^{\cdot-}$ radical that subsequently oxidizes a second equivalent of $[\text{Ru}^{\text{II}}(\text{bpy})_3]^{2+}$ to $[\text{Ru}^{\text{III}}(\text{bpy})_3]^{3+}$.^[19] In such a mechanism, a single photon yields two molecules of $[\text{Ru}^{\text{III}}(\text{bpy})_3]^{3+}$, which can oxidise Cat twice. Therefore, in theory, one molecule of O_2 only needs two photons to be absorbed in such systems.

1.2.2 Noble metal-based molecular catalysts for homogeneous light-driven water oxidation using $[\text{Ru}(\text{bpy})_3]^{2+}$ as photosensitizer and $\text{S}_2\text{O}_8^{2-}$ as sacrificial electron acceptor

Based on $[\text{Ru}(\text{bpy})_3]^{2+}$ as photosensitizer and $\text{S}_2\text{O}_8^{2-}$ as sacrificial electron acceptor, molecular catalysts based on noble metals such as ruthenium(II) and iridium(III) were developed first, reaching impressively high stabilities and activities. In 2010, Sun et al. reported a Ru-based molecular catalyst **1** (known as “Ru-bda”, bda = 2,2'-bipyridine-6,6'-dicarboxylate, Figure 1.3) that was able to catalyze water oxidation using $\text{Na}_2\text{S}_2\text{O}_8$ as sacrificial electron acceptor.^[27] In the same year, they reported **2** and **3** that could catalyze water oxidation under both chemical and photochemical conditions.^[28] Another Ru-based water oxidation catalyst, **4**, which was based on a terpyridine analogue of bda called tda (tda = 2,2':6',2''-terpyridine-6,6''-dicarboxylate), was reported to be very efficient for water oxidation using a modified $[\text{Ru}(\text{bpy})_3]^{2+}$ as photosensitizer.^[18] Interestingly, Ir-based water oxidation catalysts have been widely studied in electrocatalytic conditions, however, there are fewer examples of Ir-based water oxidation catalysts were studied in this $[\text{Ru}(\text{bpy})_3]^{2+}$ and $\text{S}_2\text{O}_8^{2-}$ based photocatalytic system, only **6** (synthesized from complex **5**) was reported by Bonchio et al.^[29]

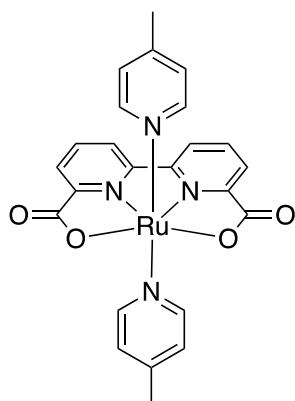
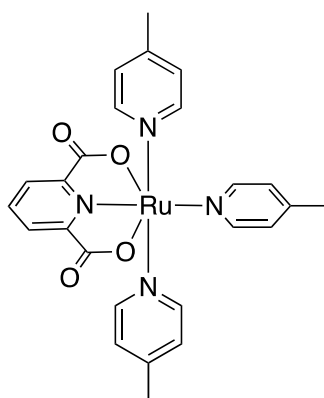
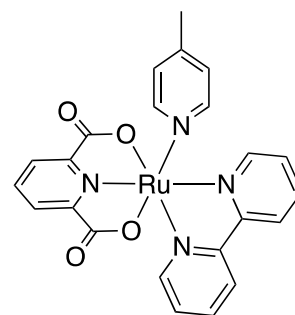
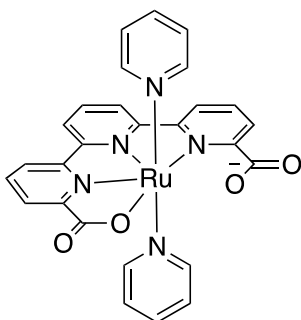
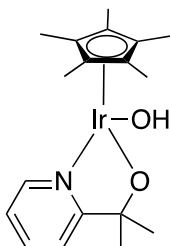
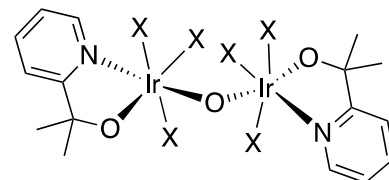
**1****2****3****4****5****6**

Figure 1.3 Chemical structures of noble metal-based water oxidation catalysts for photocatalytic systems based on $[\text{Ru}(\text{bpy})_3]^{2+}$ as PS and $\text{S}_2\text{O}_8^{2-}$ as sacrificial EA. In 6 X represents solvent ligands.

1.2.3 Earth-abundant metal-based molecular catalysts for homogeneous light-driven water oxidation using $[\text{Ru}(\text{bpy})_3]^{2+}$ as photosensitizer and $\text{S}_2\text{O}_8^{2-}$ as sacrificial electron acceptor

Compared with photocatalysts based on noble metals, those made of first-row transition metals are much cheaper and more desirable if one wants water oxidation to be widely applied in industry. The first vanadium-based water oxidation catalyst active in photocatalytic conditions was reported by Campagna et al. in 2014, still using $[\text{Ru}(\text{bpy})_3]^{2+}$ as photosensitizer and $\text{S}_2\text{O}_8^{2-}$ as EA. However, this mixed-valence $[(\text{V}^{\text{IV}}_5\text{V}^{\text{V}}_1)\text{O}_7(\text{OCH}_3)_{12}]^-$ species was only photoactive in a mixture of acetonitrile and water, and still today it remains unclear whether MeCN only plays a solubilising role, or if plays an active role in the catalytic mechanism of water oxidation.^[30] Another molecular cluster made of vanadium and manganese, $[\text{Mn}_4\text{V}_4\text{O}_{17}(\text{OAc})_3]^{3-}$, was reported to work for photocatalytic water oxidation. Although it provided a high turnover number (TON) of 1150 after 15 min irradiation and a high maximum turnover frequency (TOF) of 1.75 s^{-1} , it could also only work in an acetonitrile/water = 9:1 (v/v) mixture.^[31] Akermark and co-workers explored a binuclear manganese complex as molecular water oxidation catalyst in 2011. This binuclear $\text{Mn}^{\text{II}}\text{Mn}^{\text{III}}$ complex was able to catalyse oxygen evolution at pH 7.2 in a phosphate buffer, both when $[\text{Ru}(\text{bpy})_3]^{3+}$ was used as chemical oxidant, or in photochemical conditions using $[\text{Ru}(\text{bpy})_3]^{2+}$ as photosensitizer and $\text{S}_2\text{O}_8^{2-}$ as EA.^[32] Two iron-based molecular photocatalysts were reported by the Dhar and Thapper groups in 2014 and 2016, respectively. In Dhar's work, the homogeneous catalyst was an Fe^{III} complex based on the biuret-modified tetra-amidomacrocyclic ligand known as TAML, which generated a high-valent $\text{Fe}^{\text{V}}(\text{O})$ intermediate as the active species for the water oxidation catalysis at pH 8.7.^[33] Thapper and co-workers used two iron complexes based on the pyridine-2,6-diylbis[di(pyridine-2-yl)methanol] (Py5OH) ligand as catalysts for chemical water oxidation using either $[\text{Ru}(\text{bpy})_3]^{3+}$ at pH 8.0, Ce^{IV} ammonium nitrate (CAN) at pH 1.5, and for photochemical water oxidation at pH 8.0 using $[\text{Ru}(\text{bpy})_3]^{2+}$ as PS.^[34]

Molecular cobalt-based catalysts were studied mostly in photocatalytic systems based on $[\text{Ru}(\text{bpy})_3]^{2+}$ and $\text{S}_2\text{O}_8^{2-}$. Four types of structures have been investigated: 1) Co-porphyrin complexes; 2) Co-salophen complexes (structures shown in Figure 1.4); 3) Co_4O_4 cubane

analogues; and 4) Co-polypyridine complexes. Sakai and co-workers reported a series of Co-porphyrin complexes that were active for photocatalytic water oxidation. They first reported **9**³⁻ as the most active catalyst for photocatalytic oxygen evolution reaction (OER), in particular compared with **7**⁴⁺ and **8**⁴⁺ at pH 11.0.^[35] Then, they found that modifying the *meso*-sulfonatophenyl groups of the Co-porphyrin complex with fluoro groups in ortho position (**10**³⁻ in Figure 1.4) highly improved the photostability of the catalysts; they proposed that such stability was due to the better resistance of these complexes towards the attack of the ligand by the singlet oxygen produced during photocatalytic OER.^[36] Finally, they demonstrated that replacing the fluoro substituents by chloro groups (**11**³⁻) further improved the photostability of the sulfonated Co-porphyrin, which they also attributed to the higher resistance of the ligand towards attack by singlet oxygen due to the larger Cl substituents.^[37]

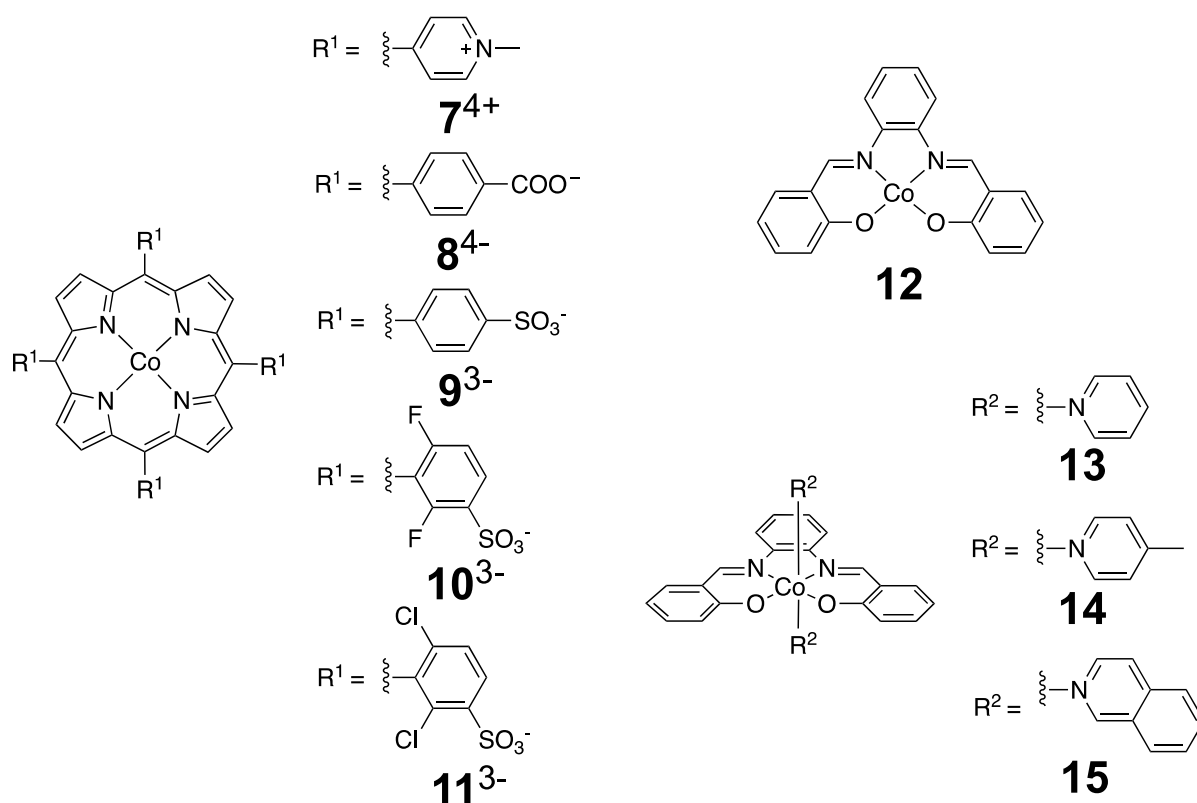


Figure 1.4 Chemical structures of Co-porphyrin and Co-salophen-based water oxidation catalysts for photocatalytic systems based on $[Ru(bpy)_3]^{2+}$ as PS and $S_2O_8^{2-}$ as sacrificial EA.

The first Co-salophen catalyst **12** for light-driven oxygen evolution at neutral pH was reported by Sartorel et al. in 2013.^[38] Modifying the Co-salophen with three different axial ligands, complexes **13**, **14** and **15** were found to be active for photocatalytic water oxidation at both pH 7.0 and pH 9.0.^[39] However, Verpoort and co-workers found that these Co-salophen complexes decomposed at pH 9.0 forming cobalt hydroxide nanoparticles, which actually

catalyzed the OER. In neutral condition, these complexes showed a much better photo-stability as homogeneous catalysts with TONs in the order of **13** > **14** > **15**.

Co₄O₄ cubane analogues are a family of structurally related molecular water oxidation catalysts. The first Co₄O₄ cubane catalyst Co₄O₄(OAc)₄(py)₄ was reported by Dismukes and co-workers in 2011, which worked under both neutral and acidic conditions.^[40] Bonchio et al. then modified the coordinated *p*-pyridine of Co₄O₄(OAc)₄(py)₄ with Me, *t*-Bu, OMe, Br, COOMe and CN groups in order to study the electronic effect of the ligand on the quantum efficiency of the photocatalytic system. However, no straightforward trend was found, probably due to a complicated overall balance between the diverse electron transfer steps of the catalytic system.^[41] A Co^{II}-based Co₄O₄ cubane water oxidation catalyst was synthesized by Patzke and co-workers as [Co^{II}₄(hmp)₄(OAc)₄(H₂O)₂] species (hmp = 2-(hydroxymethyl)pyridine). It showed a catalytic activity increasing with pH, reaching its highest TOF of 7.0 s⁻¹ at pH 9.0.^[42] Later on, Patzke and co-workers reported another Co^{II}-based Co₄O₄ cubane [Co^{II}₄(dpy{OH}O)₄(OAc)₂(H₂O)₂](ClO₄)₂ (Co₄O₄-dpk) and its Co/Ni mixed analogues [Co^{II}_xNi_{4-x}(dpy{OH}O)₄(OAc)₂(H₂O)₂](ClO₄)₂ that were active for photocatalytic water oxidation.^[43] However, the optimum pH of Co₄O₄-dpk was 8.5, which highlighted the significant disadvantage of these Co^{II}-based Co₄O₄ cubane catalysts, compared with the Co^{III} based ones: they demand an alkaline environment to be active, where proton or CO₂ reduction is more challenging.

Co-polypyridine complexes have recently attracted broad attentions due to their simple synthesis and well-defined coordination sites. Based on a typical polypyridine ligand tris(2-pyridylmethyl)amine (TPA), a binuclear Co complex [(TPA)Co(μ-OH)(μ-O₂)Co(TPA)] **16**³⁺ (Figure 1.5) was reported as a catalyst for photo-induced oxygen evolution with a TOF of 1.4±0.1 s⁻¹ and a maximum TON of 58 ± 5 after 80 s irradiation at pH 8.0 by Thapper and co-workers.^[44] More recently, a similar complex with two hydroxide bridges between the two Co-TPA molecules (complex **17**⁴⁺) instead of one –OH⁻ and one –O–O– bridges as in complex **16**³⁺, was reported by Kojima et al. to afford a high quantum yield of 44% and a large TON of 742 after 2 h irradiation at pH 9.3.^[45] A mononuclear Co-based photocatalyst **18**⁺ with a di(2-pyridyl)-ketone (DPK) ligand was reported by Ding and co-workers, which showed a very high TON for photocatalytic water oxidation (up to 1610 after 9 min irradiation at pH 9.0).^[46] A quaterpyridine- (qpy) based Co complex **19**²⁺ was reported as a catalyst for oxygen evolution in photocatalytic conditions by Lau and co-workers, with a maximum TON of 335 after 2 h irradiation at pH 8.0.^[47]

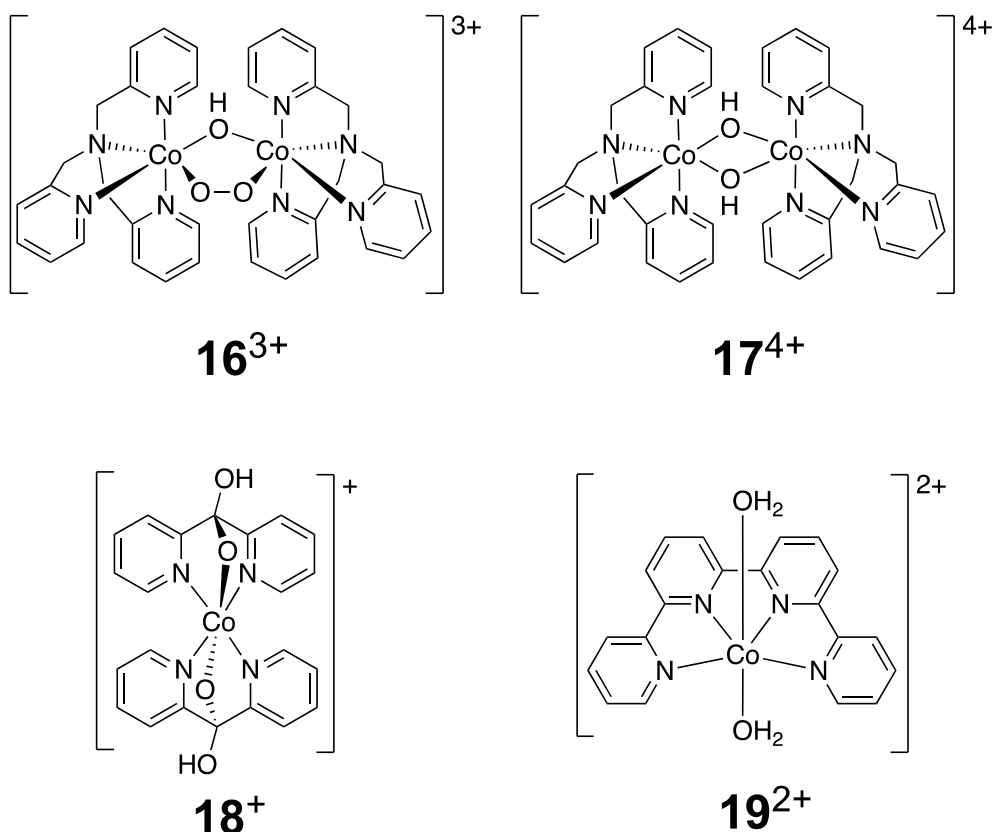


Figure 1.5 Chemical structures of Co-polypyridine based water oxidation catalysts for photocatalytic systems based on $[\text{Ru}(\text{bpy})_3]^{2+}$ as PS and $\text{S}_2\text{O}_8^{2-}$ as sacrificial EA.

Examples of copper-based molecular photocatalysts are far scarcer than those based on cobalt; in fact, to date there are only two. One is based on a phthalocyanine ligand,^[48] the other one is based on the TPA ligand.^[49] Sakai and co-workers reported a copper tetrasulfonatophthalocyanine (CuPcTS) that catalyzed water oxidation via a radical coupling mechanism at pH 9.5, in which axial chloride coordination to the copper center greatly prevents O-O bond formation. Cao and co-workers reported a catalyst based on a fluorine-modified TPA ligand, $[\text{Cu}(\text{F}_3\text{TPA})(\text{ClO}_4)_2]$, (F_3TPA = tris(2-fluoro-6-pyridylmethyl)-amine) that was capable of catalyzing water oxidation under both electrocatalytic and photocatalytic conditions at pH 8.5. Thus, an alkaline environment is also necessary for both known Cu-based molecular catalysts to catalyze the OER efficiently.

Table 1.1 Catalysts, turnover numbers, turnover frequencies and pH for selected photocatalytic water oxidation systems based on $[Ru(bpy)_3]^{2+}$ and $S_2O_8^{2-}$.

Catalyst (μM)	PS ^[a] (μM)	TON ^[b] (time)	TOF ^[b]	pH	Reference
1 (5.5)	111a ²⁺ (67)	N.R.	0.347 s ⁻¹	7.2	27
2 (50)	111a ²⁺ (500)	62.0 (1 h)	N.R.	7.2	28
3 (50)	111a ²⁺ (500)	3.7 (1 h)	N.R.	7.2	28
4 (4)	111a ²⁺ (200)	1050 (1 h)	50 s ⁻¹	7.0	18
6 from 5 (50)	111a ²⁺ (1000)	32.0±1.5 (20 min)	12.9±0.5 ×10 ³ s ⁻¹	5.2	29
7 ⁴⁺ (10)	111a ²⁺ (1000)	88.7 (30 min)	0.118 s ⁻¹	11.0	35
8 ⁴⁺ (10)	111a ²⁺ (1000)	103.4 (30 min)	0.138 s ⁻¹	11.0	35
9 ³⁻ (10)	111a ²⁺ (1000)	121.8 (30 min)	0.170 s ⁻¹	11.0	35
10 ³⁻ (1)	111a ²⁺ (200)	570 (30 min)	1.1 s ⁻¹	9.0	36
11 ³⁻ (0.25)	111a ²⁺ (200)	836 (30 min)	1.7 s ⁻¹	9.0	37
13 (12.5)	111a ²⁺ (1000)	110 (5 h)	N.R.	9.0	39
14 (12.5)	111a ²⁺ (1000)	98 (5 h)	N.R.	9.0	39
15 (12.5)	111a ²⁺ (1000)	38 (5 h)	N.R.	9.0	39
16 ³⁺ (1.7)	111a ²⁺ (400)	58±5 (80 s)	1.4±0.1 s ⁻¹	8.0	44
17 ⁴⁺ (400)	111a ²⁺ (100)	742 (2 h)	N.R.	9.3	45
18 ⁺ (0.2)	111a ²⁺ (1000)	1610 (9 min)	11.1 s ⁻¹	9.0	46
19 ²⁺ (0.2)	111a ²⁺ (128)	335 (2 h)	4 s ⁻¹	8.0	47

^[a]structures could be found in Section 1.4.^[b]N.R. = not reported

In general, most first-row transition metal-based molecular catalysts applied for photocatalytic water oxidation based on $[Ru(bpy)_3]^{2+}$ as PS and $S_2O_8^{2-}$ as sacrificial EA, only work in alkaline environment. This is a limitation for a photocatalytic solar energy conversion system combining water oxidation and either hydrogen evolution or CO₂ reduction. Indeed, CO₂-saturated solutions are usually acidic, and the hydrogen evolution reaction (HER) typically requires an environment with high concentration of protons to efficiently proceed. In principle, neutral conditions near pH 7.0 would be optimal for the combination of the OER and either the HER or the CO₂ reduction reaction. Therefore, one of the main questions asked in

this PhD thesis was whether it was possible to develop molecular catalysts that can efficiently catalyze water oxidation at pH 7.0, or even in acidic conditions. Though very rare, molecular catalysts based on nickel, which is one of the earth-abundant metals, have been reported that were active for electrocatalytic water oxidation. The first experimental chapter of this thesis explores the catalytic properties near neutral pH of nickel-based porphyrin complexes.

1.3 Cobalt-based molecular catalysts for homogeneous light-driven hydrogen evolution

1.3.1 Molecular three-component systems for homogeneous light-driven water oxidation

The overuse of fossil fuels generates a considerable proportion of the global CO₂ emissions and air pollution.^[10] Thus, the replacement of fossil fuels by clean and sustainable energies is imperative and extremely urgent. Green dihydrogen is a promising substitute to carbon-based fuels since its combustion produces only water and its production is (by definition) carbon-free. To produce H₂ sustainably and environmentally friendly, light-driven H₂ evolution from water appears as a particularly attractive approach.

Like for light-driven water oxidation system, photocatalytic hydrogen evolution system has also been developed using three-component model systems, containing a photosensitizer (PS) to harvest light, a hydrogen evolution catalyst (HEC), and a sacrificial electron donor (ED).^[3-4,10,16] Such three-component systems typically start from the ground-state PS absorbing light and being excited into an excited state PS* (Figure 1.6). Then PS* can either be oxidized by the HEC or reduced by the ED, two processes known as “oxidative” and “reductive” quenching, respectively. Whether the former or the latter of these two quenching pathways occurs depends on the redox properties of these components, and on concentrations. For example, the oxidation potential of ED, the redox properties of the PS⁺/PS and PS/PS⁻ couples, the triplet excited state energy of PS, and the potential at which the catalyst is in practice capable to catalyze the HER. When both pathways are thermodynamically feasible, the one that operates will be the faster one, which is often determined by the higher concentration of either the ED or the HEC. In the oxidative quenching mechanism, the oxidized PS⁺ is finally reduced by the ED back to the ground state PS. In the reductive quenching mechanism, the reduced PS⁻ gives an electron to HEC, thereby being oxidized back to PS.^[10]

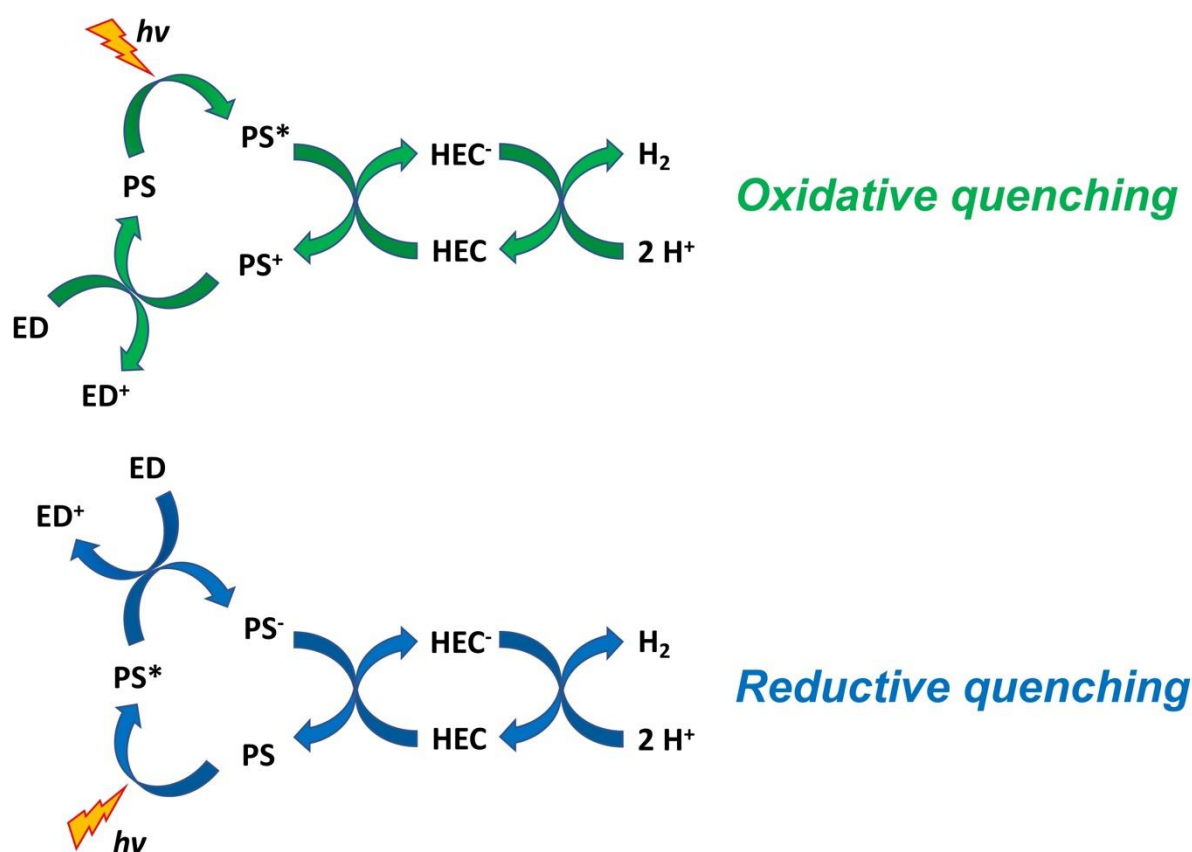


Figure 1.6 Simplified mechanisms of photocatalytic hydrogen evolution of a three-component system.

The photochemically reduced catalyst, HEC^- , which is capable to catalyze the HER, usually proceeds to generate H_2 via two mechanisms: the heterolytic and the homolytic pathways. In the heterolytic pathway, after the HEC (hereafter written M^{n+}) has been reduced once by PS^- , $M^{(n-1)+}$ can either be reduced further by a second PS^- molecule, forming $M^{(n-2)+}$; or, it undergoes oxidative protonation to yield a hydride complex, $H-M^{(n+1)+}$, whereby the formal oxidation number of the metal increases by two (Figure 1.7a). Then, $M^{(n-2)+}$ undergoes oxidative protonation or $H-M^{(n+1)+}$ is reduced a second time by PS^- , to form a key intermediate metal complex hydride $H-M^{n+}$. Finally, $H-M^{n+}$ reacts with a proton to produce H_2 in a step known as protonolysis, which regenerates the starting metal complex M^{n+} .^[4,50] For the alternative homolytic pathway, the key metal complex hydride $H-M^{n+}$ reacts with another molecule of $H-M^{n+}$ to give H_2 and the $1-e^-$ reduced starting complex $M^{(n-1)+}$ for the next catalytic circle (Figure 1.7b).^[50] In some cases, the catalysts need a 3-electron reduction to be capable of driving the HER, which makes the one-electron reduced $M^{(n-1)+}$ actually act as the starting species for the heterolytic HER catalytic cycles (Figure 1.7c).^[10] Similarly, in homolytic HER catalytic

pathway, the two key complex hydride $\text{H-M}^{(n-1)+}$ react with each other producing H_2 and $\text{M}^{(n-2)+}$ accordingly.^[10] All mechanisms are summarized in Figure 1.7.

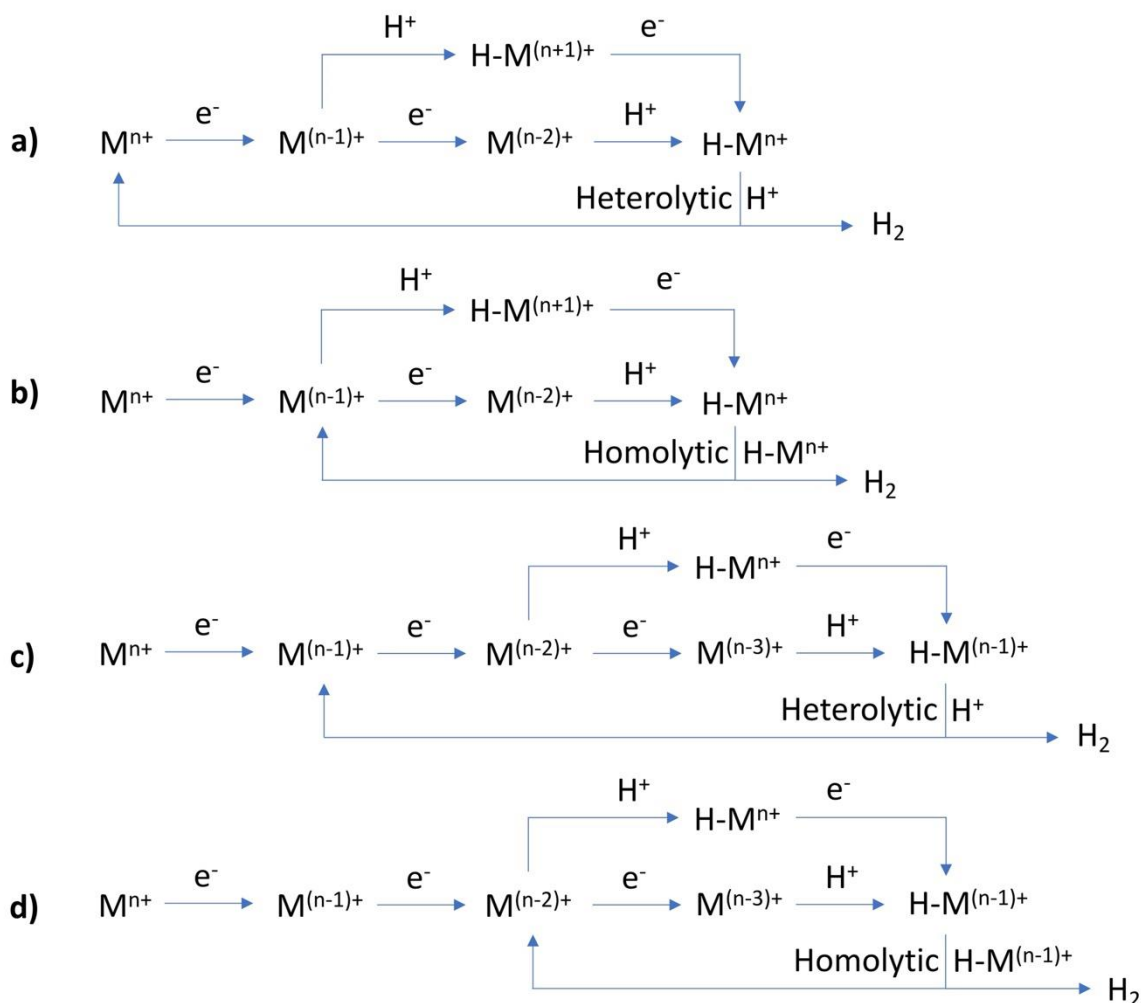


Figure 1.7 Simplified mechanisms for the catalytic cycles of hydrogen evolution. M^{n+} is a metal center, ligands are not shown for simplicity.

It is worth noting that the elementary steps of 1-e^- reduction and oxidative protonation in Figure 1.7 are not necessarily separate, since proton-coupled electron transfer (PCET) may also proceed.^[51] For example, after 1-e^- reduction from M^{n+} , there could be a PCET take place to form H-M^{n+} from $\text{M}^{(n-1)+}$. Another simplification of the general mechanisms indicated in Figure 1.7 needs to be mentioned here: that the ligand bound to the metal center are assumed here to be redox-innocent, which means that the electron transfer involving the catalyst only take place at the metal centers. However, examples where the ligand was shown to be redox active are not rare.^[52-54] In such cases, the so-called “redox non-innocent” ligand can 1) facilitate electron transfer; 2) act as proton relays; and/or 3) cooperate in electron transfer via the second

coordination sphere.^[10] Of course, the electronic effects of substituents on a ligand can fine-tune the electronic density of the metal center; on the other hand, it may also turn a redox innocent ligand into a redox non-innocent one, overall avoid the formation of high-energy intermediate species.

The influence of pH is widely considered to be particularly significant for the HER, because a higher concentration of proton (lower pH) usually favors the formation of the key hydride complex, and also promotes protonolysis, hence hydrogen evolution in a heterolytic pathway.^[4,10] Thus, a large proportion of the reported molecular HECs were reported to be more active in acidic conditions. However, it is simplistic to consider that lower pH's are always better for the HER, in particular when using an ED in a 3-component photocatalytic system. Indeed, the electron transfer from ED to PS* is usually unfavorable when the ED is protonated, which happens at pH values that are lower than its pKa. For example, in the systems using ascorbic acid (AA, pKa = 4.1), the catalytic activity usually decreases when the pH of solution is lower than 4.1, due to the lower reducing ability of AA, compared to ascorbate.^[55]

Recently, molecular catalysts for photocatalytic HER have received great attention due to their numerous advantages: 1) molecular HEC allows to approach catalytic mechanism with atomic precision, which is often more tricky to do with the more stable but less well-defined solid-state catalysts,^[13,56-57] 2) the ligands of molecular catalysts allow for fine-tuning of the coordination sphere and electronic density of the metal center, which can be used to reveal the relation between the modifications of the ligands and the photocatalytic performance of the catalysts,^[13,20] 3) molecular catalysts can be integrated in supramolecular system or immobilized onto functional materials using the powerful tools of synthetic chemistry. Overall, combining these strategies may overcome the inconvenience (e.g. low stability and activity) of existing molecular catalysts, while maintaining their advantages (e.g. high selectivity and well-defined active sites).^[12,23]

The current developments of water reduction molecular catalysts mainly focus on molecular design. In principle, a good metal-based molecular hydrogen evolution catalyst should contain 1) a metal center that can switch between different oxidation states;^[4] 2) a ligand that can provide a stable coordination environment to the metal center;^[10] 3) a fine-tuned electronic density that can balance the reaction rates and overpotential of the different steps of the catalytic mechanism.^[20] Benefits from the high abundance and low cost of first-row transition metal are undeniable, so that catalysts for the HER based on such metals have been, and are still, extensively studied. Cobalt-based catalysts, in particular, were the most studied ones; most

reported catalysts belong to a few families of molecules: cobaloximes, cobalt polypyridine complexes, cobalt dithiolene complexes, or cobalt porphyrins.

1.3.2 Cobaloximes molecular catalysts for homogeneous light-driven hydrogen generation

Cobaloximes have been widely reported as molecular HEC with notable activity for light-driven hydrogen evolution. The standard catalyst $\text{Co}(\text{dmgH})_2(\text{py})\text{Cl}$ **20a** (Figure 1.8) was first reported as photocatalysts for HER by Eisenberg and co-workers using triethanolamine (TEOA) as sacrificial electron donor in a mixture solution containing acetonitrile (MeCN) and water.^[58] (**20a-d**)^{z+} ($z = 0$ or 1), **21a** and **21b** with different axial ligands were tested using Pt(II) complexes as molecular PS at pH 8.5. **20a** was found the most efficient and **20d** was shown to lead to the fastest quenching of PS*. Later on, Sun et al. reported that **21b** was much more efficient than **21c** with a TON up to 327 after 5 h irradiation at pH 10.0 with 10% triethylamine (TEA) as ED and Rose Bengal as PS.^[59]

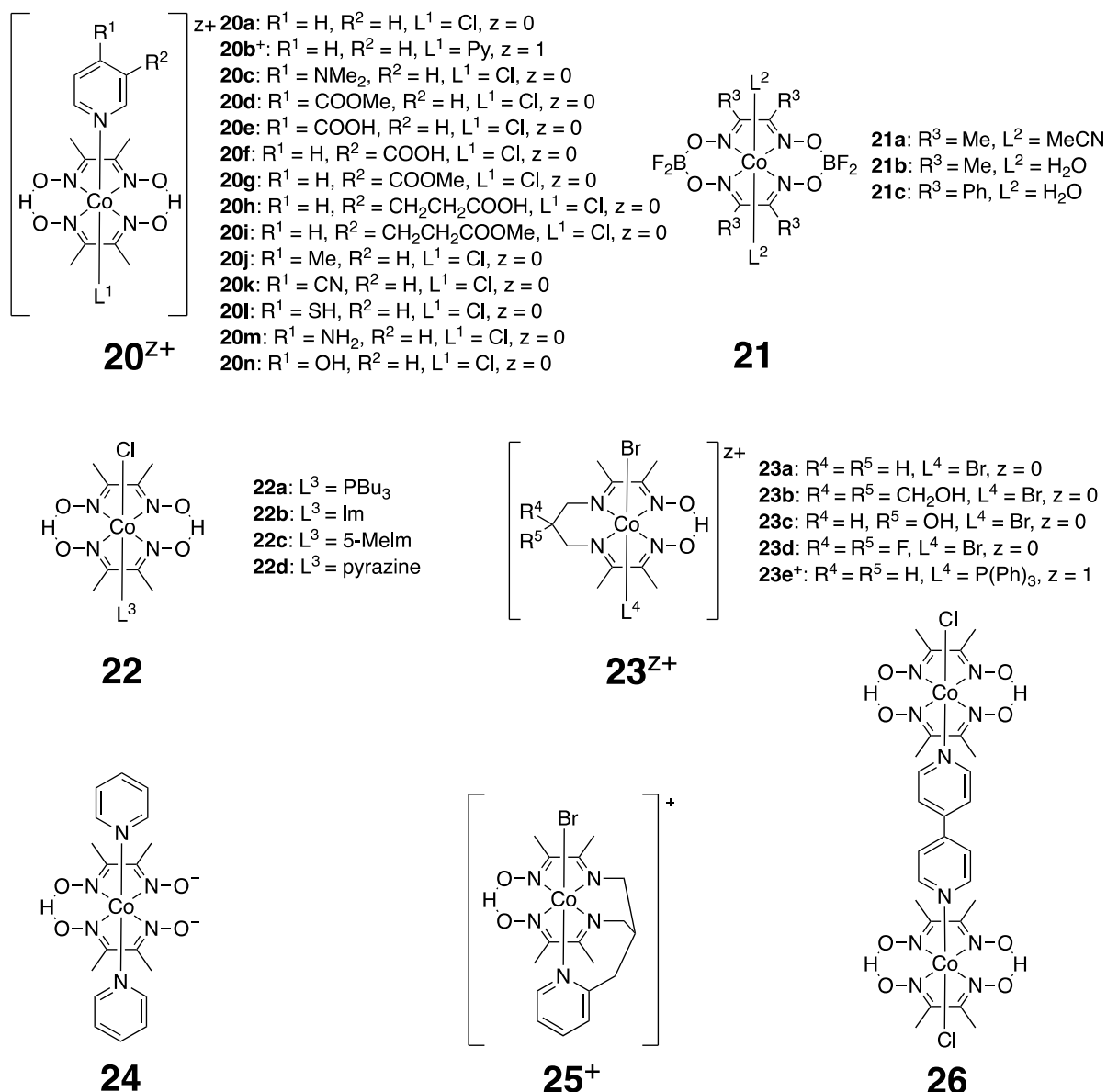


Figure 1.8 Chemical structures of selected cobaloxime catalysts for photocatalytic hydrogen evolution.

At pH 7.5, Wang and co-workers studied the effect of axial pyridine ligand on cobaloxime using **20a,d-i** for photocatalytic HER^[60] In this study, the pyridine ligand was modified with different substituents at the *para* and *meta* positions. **20h**, which bears CH_2CH_2COOH group at the *meta* position, was the most active one. In addition, according to these studies the electron-withdrawing or electron-donating ability of the substituents did not influence the HER performance significantly; it was the action of the ligand as a proton relay via hydrogen bonding that explained why **20d-i** were more active than **20a**. The Panagiotopoulos group then further studied the influence of axial N-ligand of cobaloxime with **20a,e,j-n** and **22b-c** using a Zn-porphyrin complex as PS in a pH 7.0 $H_2O:MeCN$ 1:1 solution.^[61] They found that the axial

ligand with more electron-donating ability, such as N-methyl imidazole, was more stable for photocatalytic HER, while with electron-withdrawing substituents were not able to catalyze the hydrogen evolution. Importantly, guided by density functional theory (DFT), Xu and co-workers recently designed **22d** that was efficient for light-induced HER in pH 7.0 aqueous solution using TEOA as ED, Eosin Y (EY) as PS and xenon lamp ($\lambda \geq 420$ nm). This is one of the rare example where DFT was used to develop improved HER photocatalyst.^[62]

Alberto and co-workers developed catalysts **23a-d**, **24** and **25**⁺ for homogeneous photocatalytic systems containing Re-based PS and ascorbic acid as ED. These systems were found to be most efficient at pH 4.5.^[63-65] The authors of these studies further found out that cobaloxime with triphenylphosphine (PPh₃) axial ligands, such as **23e**⁺, significantly stabilized the photocatalytic HER because PPh₃ stabilized the Co^I intermediates.^[66]

Finally, examples of binuclear molecular cobaloxime catalysts for homogeneous photocatalytic hydrogen production are limited. In the last decade, catalyst **26**, based on a bipyridine linker, was the only reported one. It was able to catalyze hydrogen evolution under visible light ($\lambda > 420$ nm) at pH 10.0 in the presence of EY as PS and TEOA as ED.^[67]

Table 1.2 Catalysts, photosensitizers, turnover numbers, turnover frequencies and solvents for a selection of homogeneous cobaloxime-based photocatalytic hydrogen evolution systems.

HEC (μM)	PS ^[a] (μM)	PTON ^[b] (time)	TOF ^[c]	Solvent ^[d]	Reference
20a (199)	115a ⁺ (11.1)	1000 (10 h)	N.R.	pH 8.5, 1:1 MeCN/H ₂ O	58
20h (100)	120a ²⁻ (25)	111 (5 h)	44 h ⁻¹	pH 7.5, 1:1 MeCN/H ₂ O	60
21b (400)	120b ²⁻ (400)	327 (5 h)	N.R.	pH 10.0, 1:9 MeCN/H ₂ O	59
22b (490)	130a ⁴⁺ (40)	1131 (50 h)	N.R.	pH 7.0, 1:1 MeCN/H ₂ O	61
23e ⁺ (100)	113a ⁺ (100)	700 (10 h)	N.R.	pH 10.0, 1:1 MeCN/H ₂ O	66

^[a]structures could be found in Section 1.4.^[b]PTON: photocatalytic turnover number = mol(H₂)/mol(PS).^[c]N.R.: not reported.^[d]H₂O: water not buffered.

1.3.3 Cobalt polypyridine complexes as molecular catalysts for homogeneous light-driven hydrogen generation

Cobalt polypyridine complexes also have remarkable properties as catalysts for photocatalytic HER. First, cobalt polypyridine complexes can provide a more stable coordination environment of the metal center than cobaloximes; on top of that, they are also considered to be more photostable than cobaloximes.^[6] Second, they display better water solubility than the cobaloxime catalysts, which is particularly important for homogeneous aqueous HER systems.^[10] Last but not least, the polypyridine ligands also have well-defined coordination sites and redox non-innocent property, which can be fine-tuned by geometrical considerations and electron-withdrawing or donating groups.^[68]

The first cobalt polypyridine molecular catalyst for homogeneous photocatalytic hydrogen evolution, [Co(bpy)₃]²⁺ (**27**²⁺, Figure 1.9), was used by Sutin et al in a system containing [Ru(bpy)₃]²⁺ as PS and ascorbate as ED at pH 5.0.^[69] Since the stability of this photocatalytic system was limited by the formation of dihydrobipyridine during light irradiation, Sutin and co-workers improved the stability of the system using para-methyl bipyridine ligands and TEOA as sacrificial ED at pH 8.0 in a MeCN-H₂O = 1:1 solution.^[70] The Zhan group recently developed a series of cobalt bis-bipyridine (bibpy) complexes (**28**^{z+}) (z = 0 or 1) bearing two cyanide ligands (**28a**⁺),^[71] one thiocyanate and one chloride (**28b**),^[72] or a bidentate nitrate ligand (**28c**⁺).^[73] These complexes were highly active for light-driven HER at pH 5.0 via a reductive quenching pathway. Replacing the bibpy ligand with two phenanthroline ligands, the

same group also reported 29^+ as a catalyst for HER under identical photochemical conditions.^[74] Using a similar strategy, Holder et al. developed catalysts 30^{2+} and 31^{2+} for photocatalytic hydrogen generation in DMF in the presence of TEOA as ED and $[\text{Ru}(\text{bpy})_3]^{2+}$ as PS.^[75] The more complicated bisterpyridine- and trisbipyridine-based molecular catalysts 32^{2+} and 33^{2+} used pyrazine and triazine rings; they were reported by Bauer and co-workers.^[76] These complexes were active homogeneously working with $[\text{Ru}(\text{bpy})_3]^{2+}$ as PS and ascorbic acid as ED.

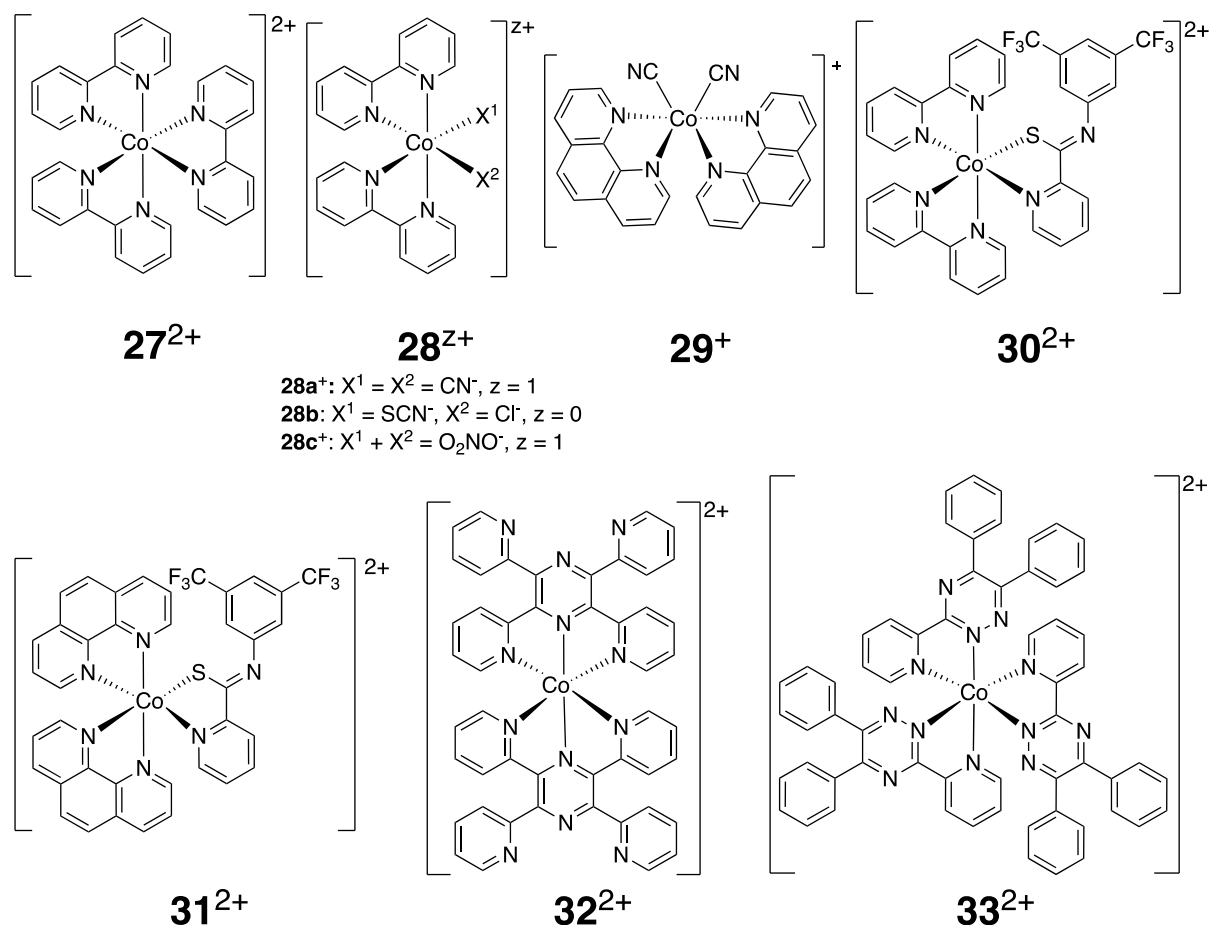


Figure 1.9 Chemical structures of selected cobalt polypyridine based catalysts ($27-33)^{z+}$ ($z = 0-2$) for photocatalytic hydrogen evolution.

Next to the six-coordinated cobalt polypyridine catalysts, tetradentate and pentadentate analogues have also widely been studied. The cobalt quaterpyridine complex 19^{2+} was first reported as a photocatalyst for HER by Lau and co-workers in 2012.^[47] 19^{2+} was much more active than 27^{2+} (Figure 1.9) in MeCN using an Ir-based photosensitizer due to the labile axial coordination sites, which was important for the formation of the key hydride intermediate. With similar structures, a propyl-linked analogue **34** (Figure 1.10),^[77] and the conjugates (**35-38**)^{z+} ($z = 0$ or 1),^[78-79] were reported to be more robust in acidic conditions using $[\text{Ru}(\text{bpy})_3]^{2+}$ as

PS. Alberto and co-workers developed a series of bipyridine-based cobalt complexes (**39-42**)^{z+} ($z = 0-2$), which were active for photocatalytic HER using [Ru(bpy)₃]²⁺, TCEP and ascorbate at pH 5.0.^[80] The most active complex of this series was **42a**, a complex characterized by *trans* cyanomethylene linkers. Later on, Probst, Alberto and co-workers further studied (**40-49**)^{z+} ($z = 0-2$) for blue light-driven hydrogen evolution under the same conditions.^[81] In particular, **43** was found to be more active because of its more flexible ligand structure.

The Alberto group also reported catalyst **50**²⁺, which is based on a macrocyclic polypyridine ligand, as a proton-reducing catalyst.^[82] With this catalyst at hand, the catalytic hydrogen evolution of a photocatalytic H₂ production scheme was not the rate-determining step (RDS) when the catalyst concentration was higher than 1 μM. In such conditions, the photon flux indeed controlled the maximum H₂ evolution rate. The bapbpy-based cobalt tetrapyrindine **51**²⁺ developed by Chavarot-Kerlidou and co-workers, was applied in a noble metal-free photocatalytic system from fully aqueous solutions.^[83] In this work a Zn porphyrin complex was used as PS, ascorbate/TCEP were used as ED, and the activity of the system was optimum at pH 4.5. More recently, the Mulfort group reported another macrocyclic HEC **52**²⁺ and an acyclic, bis(bipyridyl)amine (bbpya) based HEC **53**²⁺ in a photocatalytic system using [Ru(bpy)₃]²⁺ as PS and AA/TCEP as ED.^[84] They found that the ligand was redox active, serving as proton relay in the second coordination sphere, which improved the catalytic activity due to a intramolecular proton-transfer from the ligand to the metal center and a intramolecular electron-transfer from the metal center to the ligand. However, the proposed mechanism of the more active catalyst **52**²⁺ invoked protonation of the ligand before reduction of the resting state of the catalyst proceeded, which required acidic conditions (pH 5.0).

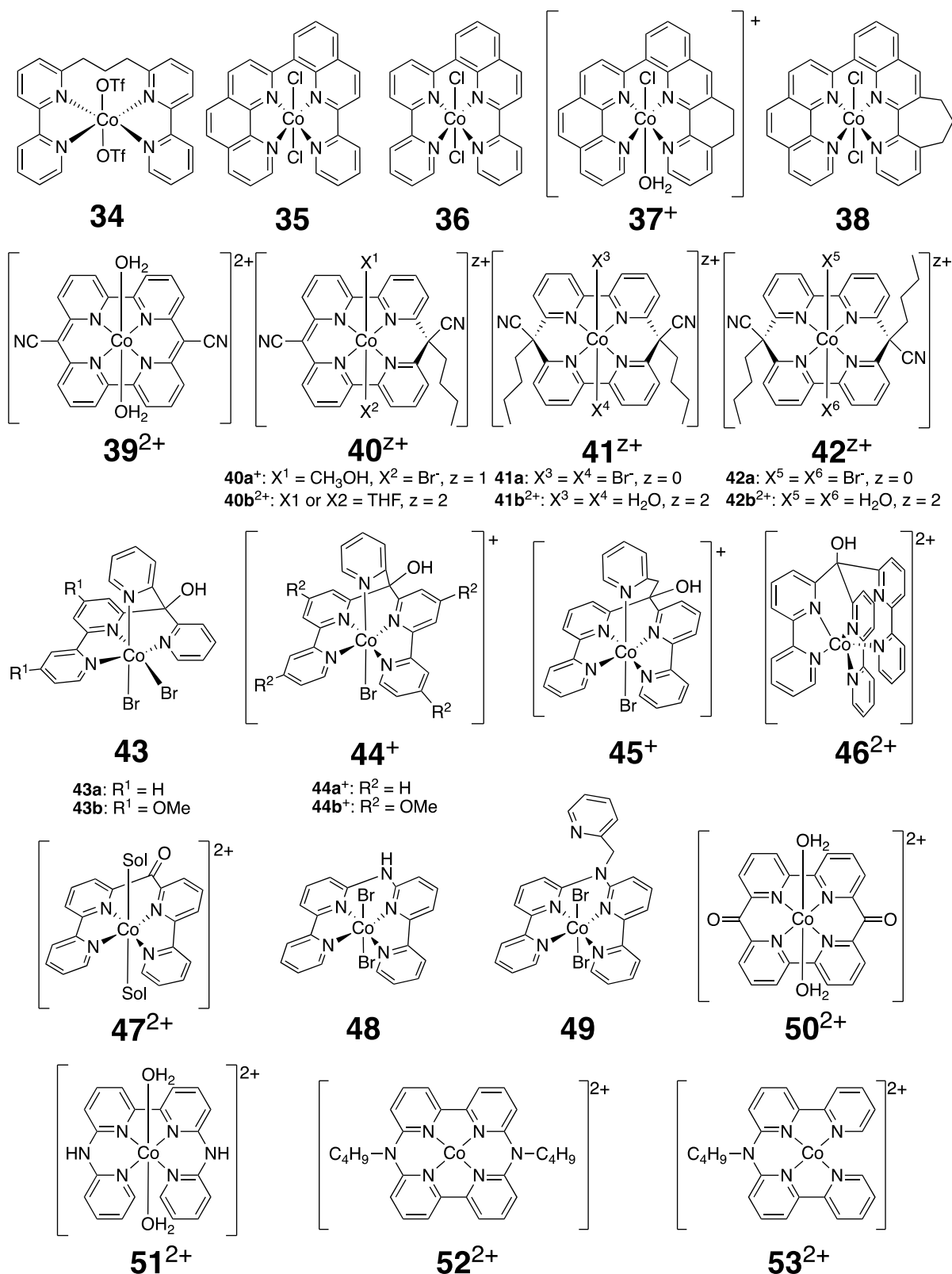


Figure 1.10 Chemical structures of selected cobalt polypyridine based catalysts (34-53)^{z+} (z = 0-2) for photocatalytic hydrogen evolution.

Duong and co-workers recently reported **54²⁺** and **55²⁺** (Figure 1.11), which bore more nitrogen-rich ligands compared to tetrapyridine or bipyridine complexes. In these reports the

authors used amine-substituted pyrazine and triazine heterocycles instead of pyridines, and obtained light-driven H_2 generation at pH 8-9 in a DMF / HBF_4 / H_2O mixture using $[\text{Ru}(\text{bpy})_3]^{2+}$ as PS and TEOA as ED.^[85-86] As a note as such pH's several OEC are also quite active, which in theory opens the possibility of full photocatalytic water splitting systems. These opportunities have not been pursued yet. With substituted methylene-bridged tetrapyrroline ligands, the series of HEC (**56a-c**)^{z+} and (**57a-g**)^{z+} ($z = 0-2$) were reported to be active in photocatalytic conditions.^[68,77,87-88] These cobalt polypyridine catalysts could all work in acidic or alkaline aqueous solutions, using Ru- or Rh-based PS and AA or TEOA as ED. Ott et al. explored a py-N-bpy type ligand-based cobalt complex **58** as a HEC working at pH 4.0 in an acetate buffer.^[89] Zonta and co-workers reported TMPA type ligand based complexes (**59a-e**)²⁺ and **60**²⁺ for light-induced hydrogen generation.^[90-91] These studies indicated that 1) a higher stability of the catalytic system may be linked with a higher water solubility of the catalyst; and 2) the additional electron density provided by the dangling oxygen may reduce the overall performance of the catalyst. The Lau group explored a cobalt pyridyl-diimine catalyst (**61a-b**)^{z+} ($z = 1$ or 3) with both chloride or water axial ligand for water photoreduction using an iridium-based PS, TEOA as ED, and AA as proton source, in MeCN-water mixture solutions.^[92-93] Afterwards, the same group developed **62**²⁺, finding that one more amine did not improve the photocatalytic activity, while no benefit was obtained from more proton relays involving the amine groups.^[94]

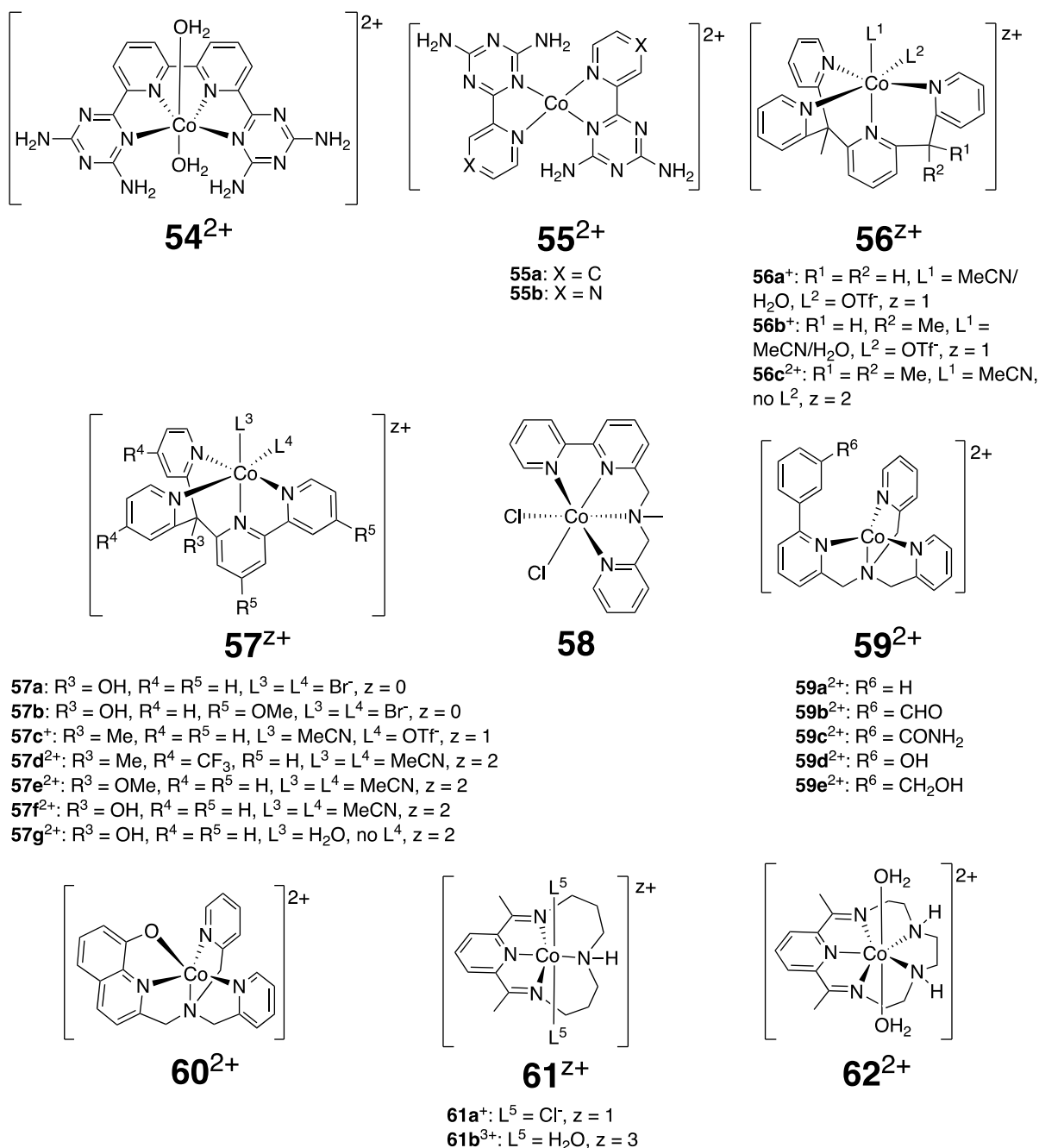


Figure 1.11 Chemical structures of selected cobalt polypyridine based catalysts (**54-62**)^{z+} (z = 0-3) for photocatalytic hydrogen evolution.

Studies on the influence of the ligand geometry on the catalytic activity of cobalt complexes were also explored by the Chang, Scandola and Alberto groups using penta-pyridyl ligand-based cobalt catalysts (**63a-b**)⁺ and (**64a-g**)^{z+} (z = 1 or 2) (Figure 1.12).^[68,95-98] It is worth noting that complex **64e**²⁺ with one pyrazine instead of a pyridine, showed better hydrogen-evolving properties in photocatalytic conditions, compared with **64f**²⁺ and **64g**²⁺, probably due to an unfavorable *trans* effect of pyridine.

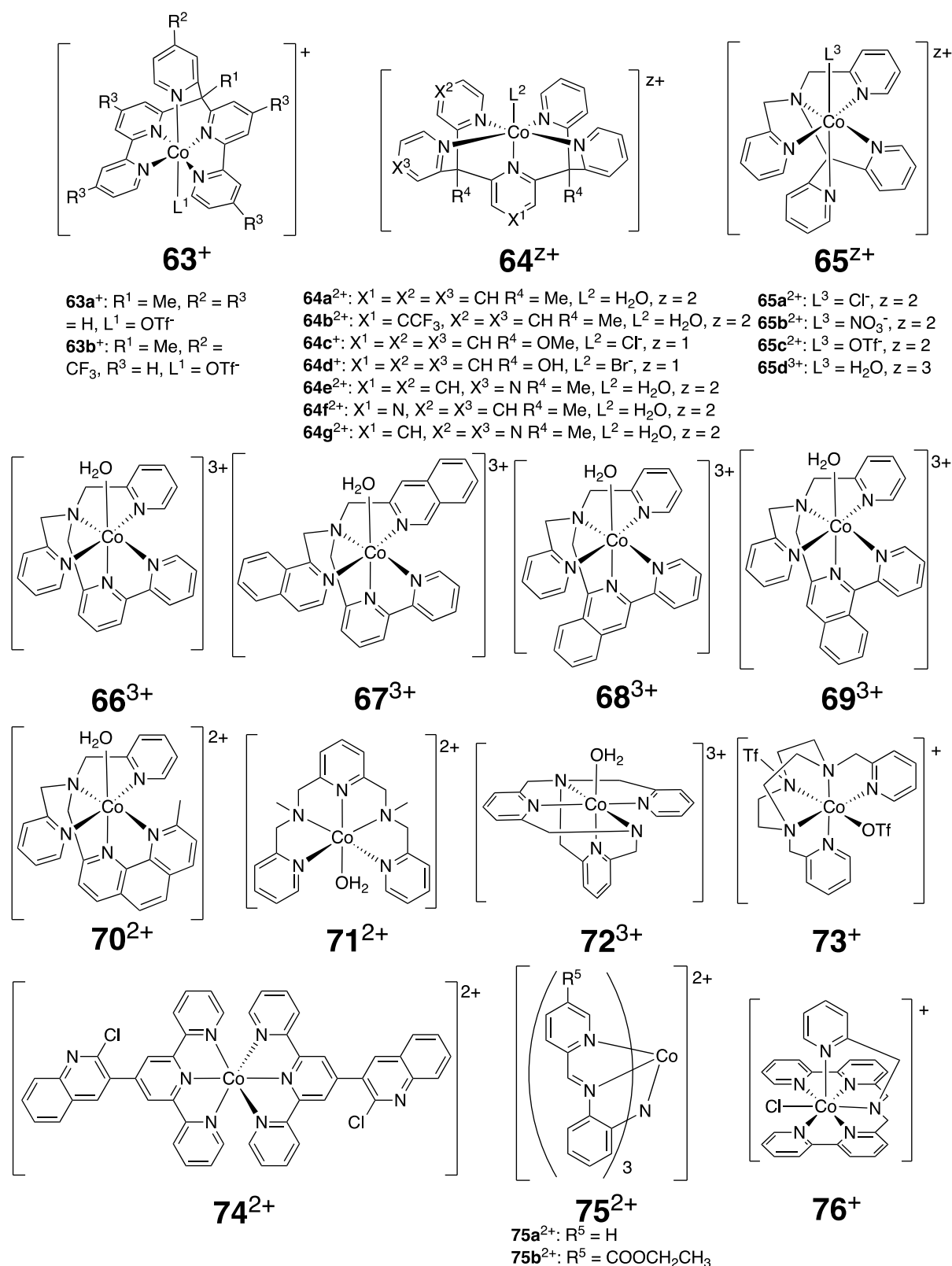


Figure 1.12 Chemical structures of selected cobalt polypyridine based catalysts (**63-76**)^{z+} (z = 1-3) for photocatalytic hydrogen evolution.

Wang and co-workers designed a N4Py pentadentate ligand with one amine and four pyridine coordination sites. Its cobalt complex (**65a-d**)^{z+} (z = 2 or 3), to which a series of

different sixth ligands has been coordinated, were studied as catalysts for photocatalytic hydrogen evolution.^[99] **65a**²⁺ showed the best activity at pH 4.0 in the presence of [Ru(bpy)₃]²⁺ as PS and AA as ED, and in such conditions the key intermediate for the catalytic HER was suggested to be a Co(III) hydride species. Under the same conditions, **66**³⁺ with a DPA-Bpy ligand, which was reported by Zhao et al., was found to be active for photocatalytic hydrogen production.^[100] Then, these authors modified the DPA-bpy ligand of **66**³⁺ with isoquinoline at different positions making **67**³⁺, **68**³⁺, and **69**³⁺.^[101] In this series of molecules, **68**³⁺ was found to be the most active due to the strong electron-donating properties of the planar isoquinoline scaffold, which made the key Co(I) species more nucleophilic and more likely to be protonated. Based on a similar structure, a phenantroline based DPA-bpy ligand was used by Chen and co-workers, who developed **70**²⁺ for hydrogen photogeneration from a MeCN and water mixture solution using Ir-based PS and TEA as ED.^[102]

Based on 2N3Py-type ligands, complexes **71**²⁺ and **72**³⁺ were also reported to be active for the photochemical HER.^[103-104] **71**²⁺ was used at pH 10.0 in a MeCN/water = 1:1 (v/v) mixture solution using Ir based PS and TEA as ED. **72**³⁺ was more active at pH 6.0 using Ru-based PS and AA as donor. **73**⁺, which is based on a 3N2Py-type ligand, was reported by Lloret-Fillol and co-workers to catalyze H₂ production using visible light in a 2:8 MeCN:H₂O solution with Ir based PS and TEA.^[105] Recently, a cobalt terpyridine (tpy) based **74**²⁺ [Co(tpy)₂]²⁺ was reported to be a very efficient catalyst for photocatalytic proton reduction by the Padhi group.^[106] The proposed mechanism involved partial dechelation of one tridentate tpy ligand. The heptacoordinated complexes (**75a-b**)²⁺ and **76**⁺ were developed by the Chen group and Ruggi group as efficient photochemical hydrogen evolution catalysts.^[107-108] The former ones were active at pH 10.0 in a MeCN/water (1/1, v/v) mixture in the presence of [Ir(ppy)₂(bpy)]⁺ (ppy = 2-phenylpyridine) as PS and TEA as ED. By contrast, the later was found to be efficient in a pH 4.0 aqueous system using [Ru(bpy)₃]²⁺ as PS and AA as ED. A selection of TON and conditions are summarized in Table 1.3.

Table 1.3 Catalysts, photosensitizers, turnover numbers, turnover frequencies and solvents for selected cobalt polypyridine-based catalysts used in homogeneous light-driven hydrogen evolution systems.

HEC (μM)	PS ^[a] (μM)	TON ^[b,c] (time)	TOF ^[c]	Solvent ^[d]	Reference
19 ²⁺ (600)	113c ⁺ (30)	1730 (20 h)	N.R.	MeCN	47
28a ⁺ (20)	111a ²⁺ (700)	7.3×10^5 (12 h)	N.R.	pH 5.0, PB	71
28b (20)	111a ²⁺ (1000)	12000 (10 h)	900 h ⁻¹	pH 5.0, PB	72
28c ⁺ (20)	111a ²⁺ (100)	7000 (3 h)	403 h ⁻¹	pH 5.0, AcB	73
29 ⁺ (20)	111a ²⁺ (600)	1232 (10 h)	N.R.	pH 5.5, PB	74
30 ²⁺ (10)	111a ²⁺ (100)	140 (2.5 h)	2.6 min ⁻¹	DMF	75
31 ²⁺ (10)	111a ²⁺ (100)	91 (2.5 h)	2.7 min ⁻¹	DMF	75
35 (1-5)	111a ²⁺ (400)	N.R.	586 h ⁻¹	pH 4.0, PB	78
42a (1)	111a ²⁺ (500)	22000 (65 h)	2750 h ⁻¹	pH 5.0, AsB	80
50 ²⁺ (0.5)	111a ²⁺ (500)	2500 (24 h)	1083 h ⁻¹	pH 4.0, AsB	82
51 ²⁺ (490)	130a ⁴⁺ (40)	443 (24 h)	N.R.	pH 4.5, AsB	83
52 ²⁺ (5)	111a ²⁺ (500)	7800 (60 h)	6870 h ⁻¹	pH 5.0, PBS	84
57a (0.1)	118c ⁺ (500)	9000 (20 h)	19000 h ⁻¹	pH 4.1, AsB	87
61a ⁺ (1)	111a ²⁺ (500)	2832 (6 h)	N.R.	pH 4.5, AsB	94
64e ²⁺ (20)	111a ²⁺ (330)	450 (8h)	N.R.	pH 5.5, PB	97
68 ³⁺ (5)	111a ²⁺ (500)	2770 (150 min)	N.R.	pH 4.0, AcB	101
69 ³⁺ (5)	111a ²⁺ (500)	90 (150 min)	N.R.	pH 4.0, AcB	101
72 ³⁺ (5)	111a ²⁺ (500)	200 (180 min)	N.R.	pH 6.0, AcB+PB	104
74 ²⁺ (5)	111a ²⁺ (250)	2115 (22 h)	0.063 s ⁻¹	pH 4.0, 1:1 MeCN/AsB	106
76 ⁺ (0.1)	111a ²⁺ (500)	16300 (2 h)	5000 h ⁻¹	pH 4.0, AcB	108

^[a]structures could be found in Section 1.4.

^[b]TON: turnover number based on HEC = mol(H₂)/mol(HEC).

^[c]N.R.: not reported.

^[d]PB: phosphate buffer, AcB: acetate buffer, AsB: ascorbate buffer, PBS: phosphate buffer saline

1.3.4 Binuclear and multinuclear cobalt complexes as molecular catalysts for homogeneous light-driven hydrogen generation

The development of binuclear or multinuclear cobalt-based HEC is also attractive since cooperative interaction may take place within molecules containing several metal centers, such as intramolecular H-H bond formation from two close M-H species.^[109] However, in such molecules it is crucial to control the metal-metal distance and orientation, as well as the local environment of the metal center, which make cooperative catalysis difficult to achieve.^[110] Several binuclear cobalt catalysts were explored for photoinduced hydrogen production. The cobaloxime type binuclear cobalt catalyst **26** (Figure 1.8), which was already discussed in 1.3.2, was reported to be active for HER under photocatalytic conditions. Llobet and co-workers reported polypyridine-based complex **77**²⁺ (Figure 1.13) as a binuclear amine and tetrapyridine catalyst.^[111] When the concentration of catalyst was higher than 55 μM , the activity of the system decreased because of the formation of polynuclear cobalt species and high-nuclearity aggregates. When the concentration was lower than 10 μM , the system performed better, and it was optimum in terms of TON and TOF at 7 μM . The hydrogen production rate was not improved by adding higher concentration of $[\text{Ru}(\text{bpy})_3]^{2+}$ or ascorbate at pH 4.1, which indicated that the RDS did not involve the light reactions.

The Brooker group developed a variety of binuclear hydrogen evolution photocatalysts (**78-83**)^{z+} ($z = 1, 3$ or 4).^[109] All these catalysts worked in both DMF and pH 5.0 aqueous solution using $[\text{Ru}(\text{bpy})_3]^{2+}$ as PS, TEOA as ED, and either HBF_4 or AA as proton donor for DMF and aqueous systems, respectively. **78a**⁴⁺ with phenyl substituent was found to be very active in aqueous solution, while **78c**⁴⁺ with alkyl substituent was showed to have better performances in DMF. For the more active (**79a-c**)^{z+} ($z = 3$ or 4) series, **79a**³⁺ performed best in aqueous media, with a maximum TOF of 5.7 min^{-1} , TON of 140 after 2.9 h irradiation, but it behaved the worst in organic media, with a maximum TOF of 3.6 min^{-1} , TON of 30 after 10 h irradiation. The series of complexes (**80a-c**)⁴⁺ also showed higher activities in aqueous solution, **81**⁺ and **82**³⁺ performed the worst in water and gave modest activity in DMF. The tetranuclear cobalt catalyst **83a**⁴⁺ showing a similar activity as (**80a-c**)⁴⁺ in aqueous media with a TOF of 2.0 min^{-1} , the mixed valence **83b**⁶⁺ and **83c**⁶⁺ performed similar TOF in aqueous and DMF solution of 1.1 and 2.1 min^{-1} , respectively.

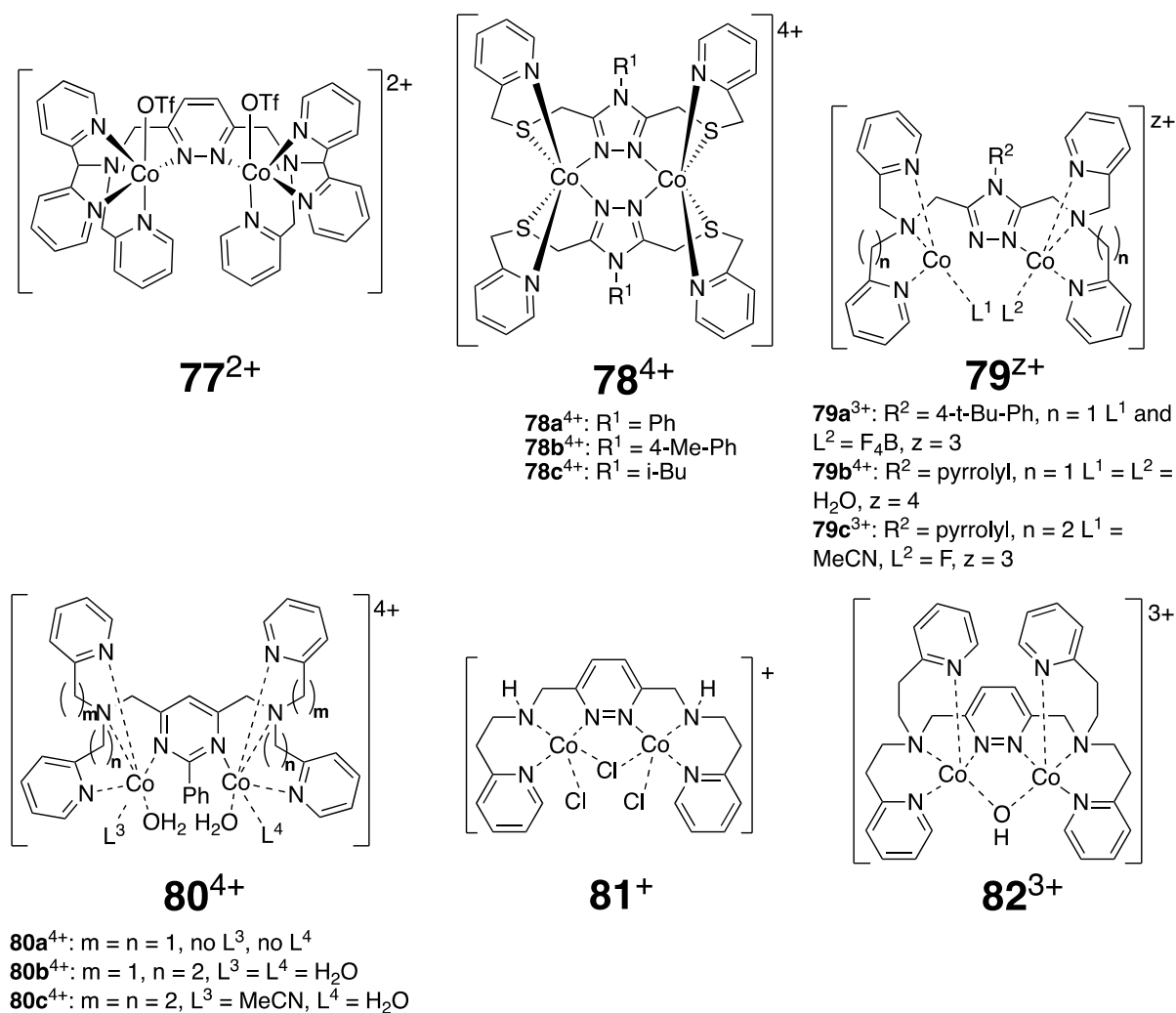


Figure 1.13 Chemical structures of selected molecular binuclear cobalt catalysts (**77-82**)^{z+} (z = 1-4) for photocatalytic hydrogen evolution.

The Zhan group explored four binuclear cobalt complexes for blue light-driven hydrogen production in the presence of [Ru(bpy)₃]²⁺ and AA in acidic aqueous solutions: **84⁺** with amino-carboxy ligands,^[112] **85** with amine-bis-phenolate ligands,^[113] **86** with triazenido ligands,^[114] and **87⁺** with polyhydroxy ligands.^[115] A bio-inspired molybdopterin-like binuclear cobalt complex **88²⁻** was applied as a catalyst for light-driven hydrogen evolution by Fontecave and co-workers.^[116] This complex displayed good activity in MeCN solution with [Ru(bpy)₃]²⁺ as PS and TEOA as ED. The hydrogen generation benefitted from the adjacent S atom of the dithiolene ligand as a proton relay, which enhanced protonation of the Co-H hydride intermediate. Bearing the same coordination unit as **88²⁻**, another binuclear cobalt dithiolene complex **89²⁻** was reported by the Eisenberg group together with (**90-92**)⁻ as photocatalysts for proton reduction.^[117-118] In a pH 4.0 MeCN:H₂O = 1:1 (v/v) mixture solution with [Ru(bpy)₃]²⁺ as PS and AA as ED, the order of photocatalytic activity for these cobalt catalysts was found

to be $89^{2-} > 92^- > 90^- > 91^-$, which indicated that the modification of a catalyst with electron-withdrawing substituents resulted in a faster system. The driving force of electron transfer from the reduced catalyst to protons was not the key factor for this photocatalytic hydrogen evolution system; the turnover limiting step was identified to be the electron transfer from the reduced PS to the $[\text{CoL}_2]^-$ species. These binuclear and tetranuclear cobalt complexes were not showing significantly better photocatalytic hydrogen evolution activities compared to mononuclear cobalt complexes based on macrocyclic ligands, and no evidence of cooperation between the different Co metal centers has been reported.

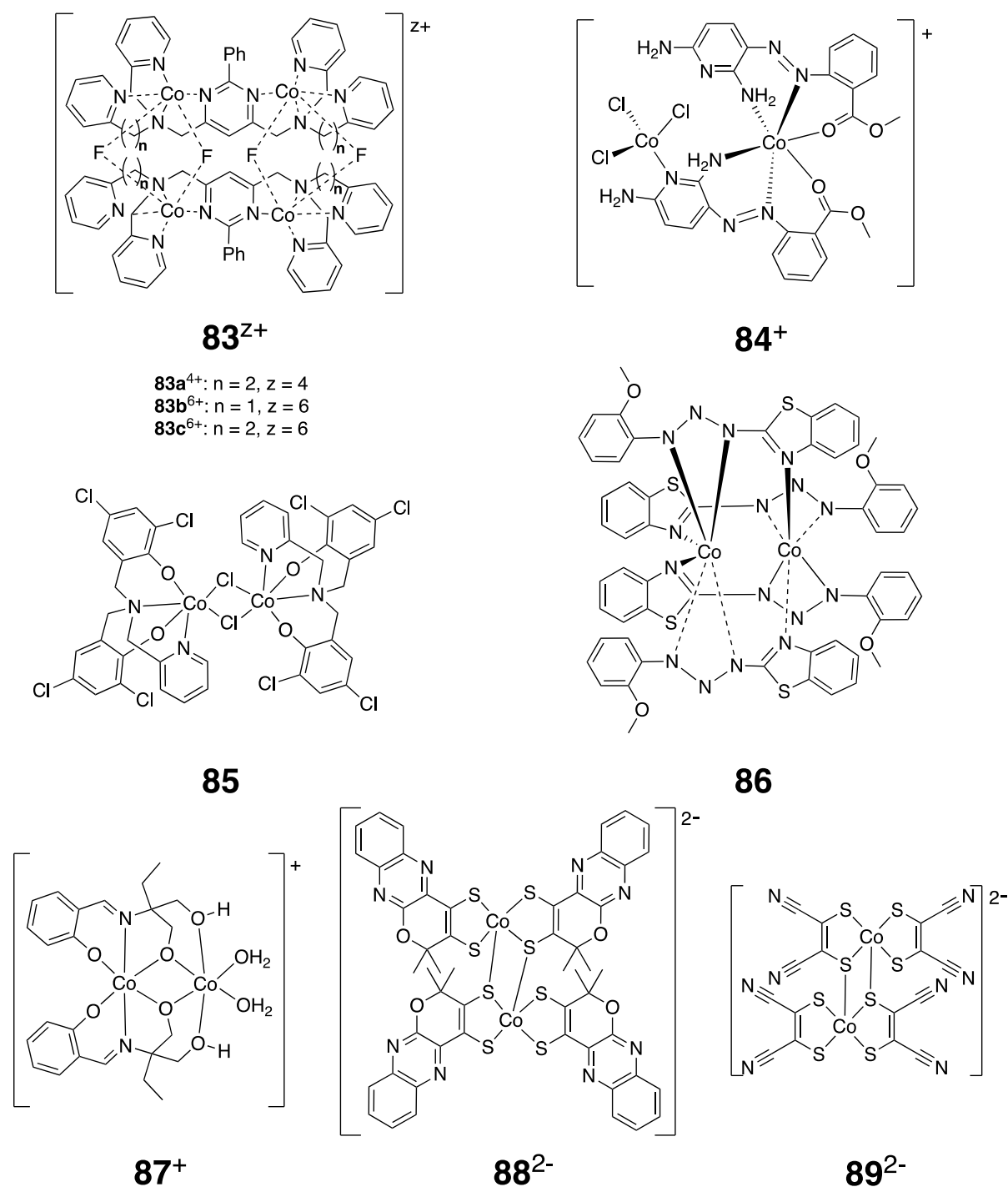


Figure 1.14 Chemical structures of selected molecular tetranuclear molecular binuclear cobalt catalysts (**83-87**)^{z+} ($z = 0, 1, 4, \text{ or } 6$), **88²⁻** and **89²⁻** for photocatalytic hydrogen evolution.

1.3.5 Cobalt dithiolene complexes as molecular catalysts for homogeneous light-driven hydrogen generation

As discussed above, the cobalt catalysts (**88-92**)^{z-} ($z = 1 \text{ or } 2$), which were based on the dithiolene ligands, were found to be a good series of HEC under photocatalytic conditions.

Another cobalt dithiolene catalyst **93⁻** was developed for light-driven H₂ evolution by the Hou group using xanthene dyes as PS and TEA as ED in a pH 10.0 MeCN/H₂O (1:1, v/v) solution.^[119] The hydrogen production was proposed to occur via an oxidative quenching mechanism, and the photoactivity of this noble metal-free catalytic system was limited by the decomposition of PS. Two cobalt bipyridine and phenanthroline dithiolene catalysts **94** and **95** were used in pH 11.6 ethanol (EtOH) and water 1:1 (v/v) mixture solutions by Cai and co-workers for H₂ photogeneration.^[120] In this study, 5% TEA was used as ED and fluorescein was used as PS, an oxidative quenching mechanism was proposed; here as well the deactivation of the system was mainly due to the decomposition of the catalyst. Using the same PS and ED as **94** and **95** systems, the *fac*- and *mer*-Co(III)-tris(thiosemicarbazide) geometrical isomers **96** and **97** were studied as catalysts for visible light-driven hydrogen production from water by Luo and co-workers.^[121] At pH 11.5, the catalytic systems deactivated due to catalyst decomposition after 8 h irradiation (xenon lamp, $\lambda > 420$ nm). A reductive quenching mechanism was proposed since the concentration of TEA was much higher than that of the catalyst.

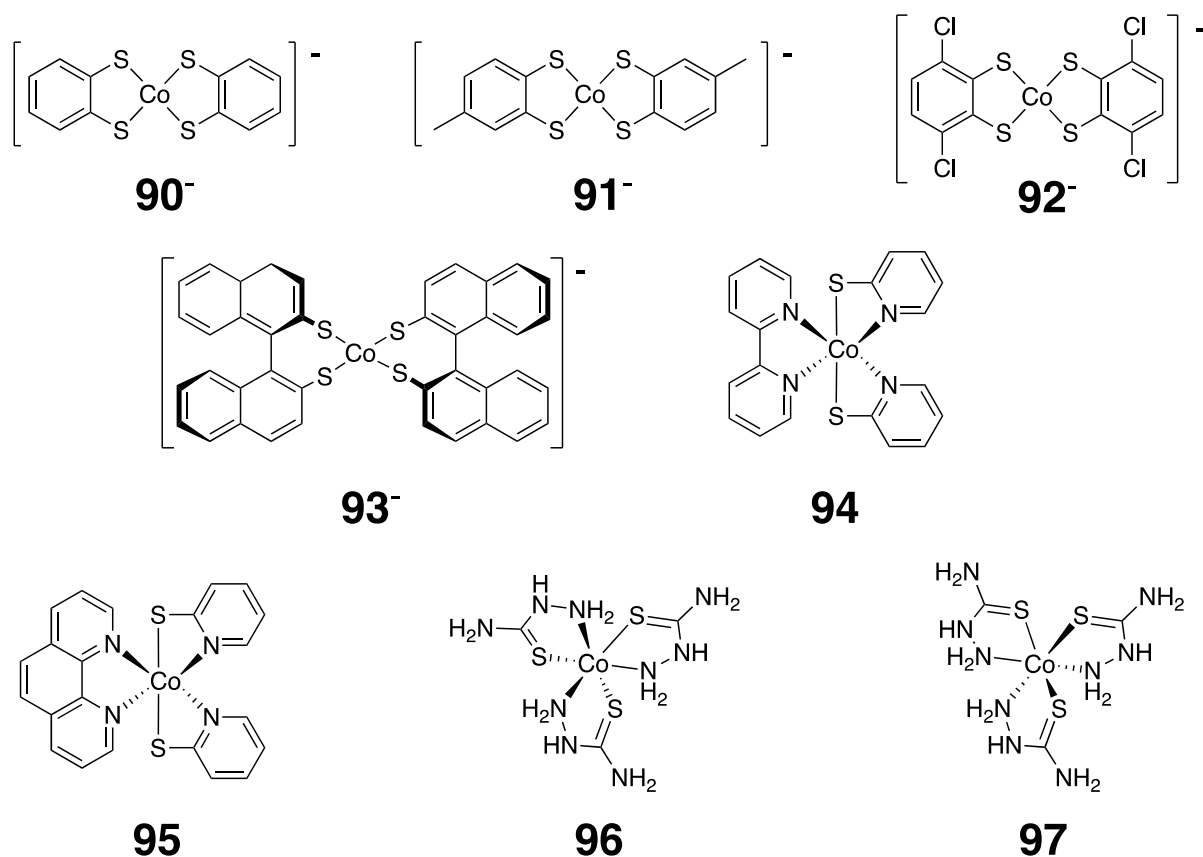


Figure 1.15 Chemical structures of selected cobalt dithiolene catalysts for photocatalytic hydrogen evolution.

Table 1.4 Catalysts, photosensitizers, turnover numbers, turnover frequencies and solvents for selected multinuclear cobalt complexes and cobalt dithiolene complexes-based catalysts used in homogeneous light-driven hydrogen evolution systems.

HEC (μM)	PS ^[a] (μM)	TON ^[b] (time)	TOF ^[c]	Solvent ^[d]	Reference
26 (370)	120a ²⁻ (400)	160 (2 h)	N.R.	pH 10, 1:1 MeCN/H ₂ O	67
77 ²⁺ (7)	111a ²⁺ (600)	350 (4 h)	N.R.	pH 4.1, AsB	111
79a ³⁺ (10)	111a ²⁺ (330)	104 (2.9 h)	5.7 min ⁻¹	pH 5.0, AsB	109
83a ⁴⁺ (10)	111a ²⁺ (330)	150 (5.5 h)	2.0 min ⁻¹	pH 5.0, AsB	109
83b ⁶⁺ (10)	111a ²⁺ (330)	120 (5.5 h)	1.1 min ⁻¹	pH 5.0, AsB	109
83c ⁶⁺ (10)	111a ²⁺ (330)	16 (16 h)	2.1 min ⁻¹	DMF	109
84 ⁺ (50)	111a ²⁺ (700)	425 (3 h)	N.R.	pH 4.0, AcB	112
85 (20)	111a ²⁺ (900)	912 (3 h)	N.R.	pH 6.0, PB	113
86 (20)	111a ²⁺ (700)	4367 (3 h)	N.R.	pH 4.0, AcB	114
87 ⁺ (20)	111a ²⁺ (900)	4314 (3 h)	N.R.	pH 6.0, PB	115
88 ²⁻ (20)	111a ²⁺ (2000)	200 (3 h)	163 h ⁻¹	MeCN	116
89 ²⁻ (6.5)	111a ²⁺ (500)	9000 (12 h)	3400 h ⁻¹	pH 4.0 1:1 MeCN/AsB	117
90 ⁻ (6.5)	111a ²⁺ (500)	2700 (12 h)	880 h ⁻¹	pH 4.0 1:1 MeCN/AsB	117
91 ⁻ (6.5)	111a ²⁺ (500)	2300 (12 h)	690 h ⁻¹	pH 4.0 1:1 MeCN/AsB	117
92 ⁻ (6.5)	111a ²⁺ (500)	6000 (12 h)	1400 h ⁻¹	pH 4.0 1:1 MeCN/AsB	117
93 ⁻ (100)	120a ²⁻ (400)	495 (4 h)	N.R.	pH 10, 1:1 MeCN/H ₂ O	119
96 (10)	120c ²⁻ (1000)	900 (15 h)	128 h ⁻¹	pH 11.5, H ₂ O	121
97 (10)	120c ²⁻ (1000)	890 (15 h)	125 h ⁻¹	pH 11.5, H ₂ O	121

^[a]structures could be found in Section 1.4.

^[b]TON: turnover number based on HEC = mol(H₂)/mol(HEC).

^[c]N.R.: not reported.

^[d]AsB: ascorbate buffer, AcB: acetate buffer, PB: phosphate buffer, H₂O: water not buffered.

1.3.6 Cobalt porphyrin and structurally related complexes as molecular catalysts for homogeneous light-driven hydrogen generation

Since porphyrin ligands have stable and rigid coordination sites, can readily be functionalized by electron-withdrawing or -donating substituents, and can act as redox-active ligands, metal porphyrin complexes have been seriously considered as promising noble metal-free photosensitizers and molecular catalysts for oxygen reduction, water oxidation, hydrogen

evolution, and carbon dioxide reduction.^[4,7,10,20,23] However, only a few cobalt porphyrin, as well as the cobalt phthalocyanine and corrole complexes have been explored as catalysts for photocatalytic hydrogen evolution so far.

Two simple water-soluble cobalt porphyrin complexes Co(II) *meso*-tetra(4-*N*-methylpyridyl)porphyrin **98**⁴⁺ and Co(II) *meso*-tetra(4-sulphonatophenyl)porphyrin **99**⁴⁻ were reported as efficient catalysts for light-driven hydrogen evolution using [Ru(bpy)₃]²⁺ as PS and AA as ED. The reaction proceeded via reductive quenching at pH 7.0 and pH 6.8, respectively.^[122-123] The catalytic activity of **98**⁴⁺ was limited by catalyst decomposition after 5 h xenon lamp irradiation ($\lambda > 400$ nm); by contrast, the photoactivity of **99**⁴⁻ was limited by PS decomposition after 40 min LED lamp (420 nm) irradiation. In the presence of the same PS and ED, the cobalt chlorin complex **100** was reported to be active for photocatalytic H₂ evolution by Fukuzumi and co-workers via a reductive quenching mechanism in a 1:1 MeCN:water solution.^[124] The RDS of this system was supposed to be the Co-H bond cleaving prior to react with a proton to evolve H₂. Bearing N atoms instead of C atoms in *meso* positions of a porphyrin, phthalocyanine cobalt complex **101** was also applied as a catalyst for photocatalytic HER working with [Ru(bpy)₃]²⁺ or xanthene dyes as PS in 4:1 EtOH:H₂O solution.^[125-126] The catalysis was found to proceed via an oxidative quenching pathway. Interestingly, TEA as the ED was observed to be better than TEOA in these studies.

Structurally related cobalt corrole complexes were also studied as catalysts for light-induced HER as Co-porphyrin analogues. Liu and co-workers reported a cobalt tris(ethoxycarbonyl)corrole catalyst **102** for both electrochemical and photochemical hydrogen evolution.^[127] Importantly, in the presence of O₂, **102** was still able to efficiently catalyze HER using [Ru(bpy)₃]²⁺ and AA at pH 4.5. Doctorovich et al. developed Co-corrole complexes **103a-c** series for homogeneous photocatalytic H₂ generation in a dioxane solution using terphenyl as PS, TEA as ED and water as proton source.^[128] The different derivatives did not differ much in terms of performances for hydrogen evolution; more interestingly, the cobalt corrole **103b** photo-electrochemically evolved H₂ in absence of PS when working with carbon nanotube.

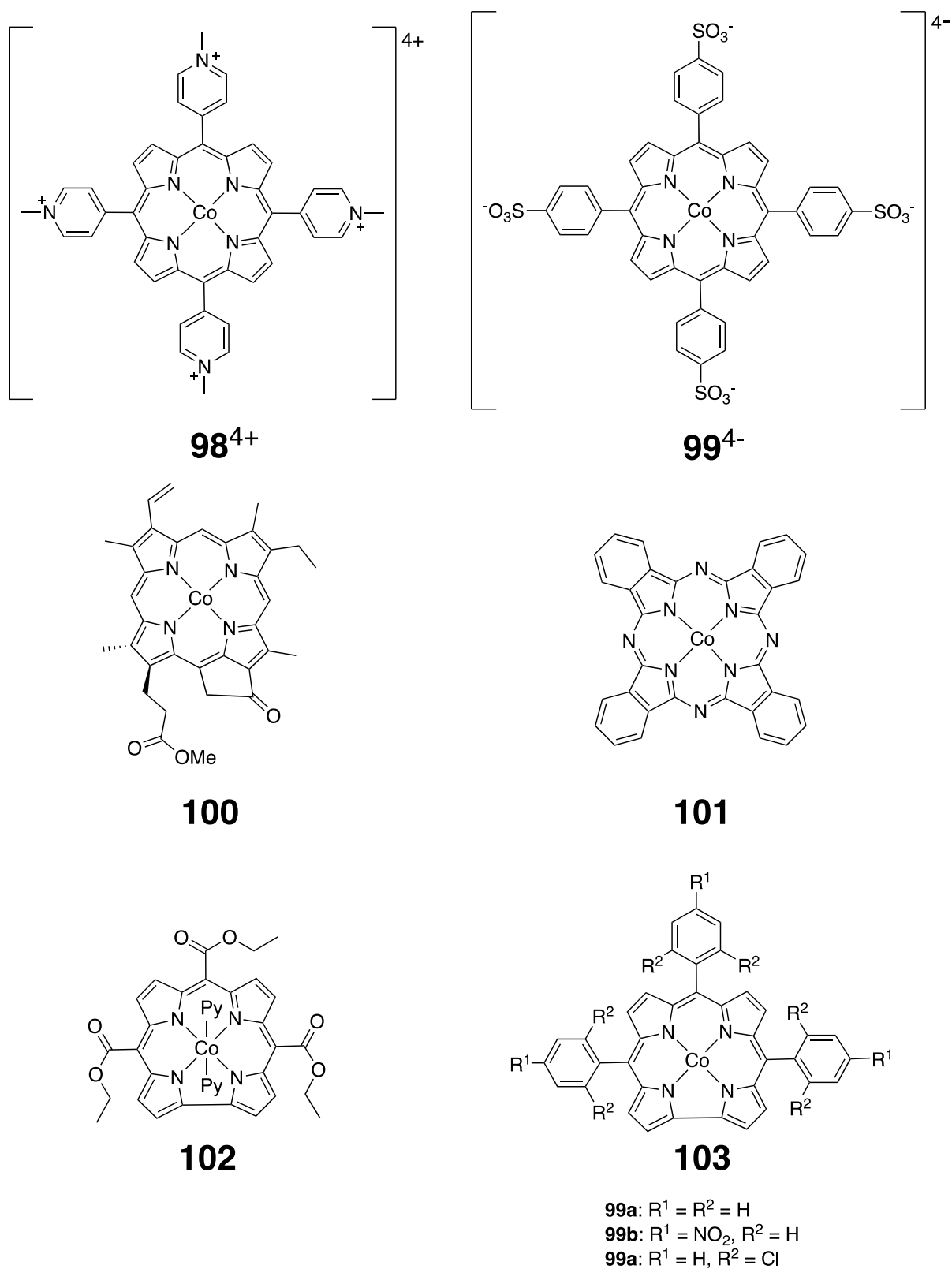


Figure 1.16 Chemical structures of selected cobalt porphyrin and structurally related catalysts for photocatalytic hydrogen evolution.

1.3.7 Other types of cobalt complexes as molecular catalysts for homogeneous light-driven hydrogen generation

Finally, miscellaneous cobalt complexes that cannot be put in the families discussed above, were reported as hydrogen-evolving catalysts. The Sakai group reported a macrocyclic N-heterocyclic carbene (NHC) type cobalt complex **104**⁺, which worked in photocatalytic conditions in a pH 5.0 acetate buffer aqueous solution with [Ru(bpy)₃]²⁺ as PS and methylviologen as redox acceptors.^[129] The HER activity was successfully driven by a very low driving force of 150 mV. Significantly, the cobalt metal center did not reach Co(I) due to a PCET process take place to form the Co(III)-H species from Co(II): $\text{Co(II)} + \text{H}^+ + \text{e}^- \rightarrow \text{Co(III)-H}$. Next to **(78-83)**^{z+} (z = 1, 3, 4 or 6), Brooker and co-workers also developed the series of complexes **(105a-c)**⁺ as mononuclear cobalt catalysts for light-driven HER using diphenylamine macrocyclic ligands.^[109] This series of mononuclear catalysts were all more efficient than the multinuclear complexes **(78-83)**^{z+} at pH 5.0 in the presence of [Ru(bpy)₃]²⁺ and AA. What is more, the **(105a-c)**⁺ series was also found to be active with TEOA and HBF₄ in DMF solution; in such conditions **105a**⁺ displayed the highest activity. Using a distinctive PN₃P type pincer ligand, Richeson group explored **106**⁺ as a catalyst for both electrochemical and photochemical hydrogen evolution.^[130] The photocatalytic system was applied in a 5% water of DMF solution, using [Ru(bpy)₃]²⁺ as PS, N-benzyl-1,4-dihydronicotinamide and TEOA or ascorbate as ED.

Li and co-workers developed a series of Co(II)-salen complexes **107-109** for efficient photocatalytic hydrogen production.^[131] In this noble metal-free photocatalytic system, a pH 10 1:1 methanol:water solution with xanthene dyes (Eosin Y, Rose Bengal and fluorescein) as PS and TEA as ED was utilized. Eosin Y performed better than fluorescein, and **107** was found to be the most active catalyst. Both reductive and oxidative quenching pathways were thermodynamically feasible, but reductive quenching was proposed due to a higher concentration of ED than that of the catalyst. A cobalt metalloprotein type catalyst **110** was reported by Bren and co-workers for photochemical hydrogen evolution from neutral water.^[132] The cobalt Gly-Gly-His tripeptide complex could efficiently work with [Ru(bpy)₃]²⁺ and AA for 48 h via a reductive quenching mechanism. In this system the decomposition of PS was responsible for the catalytic system deactivation.

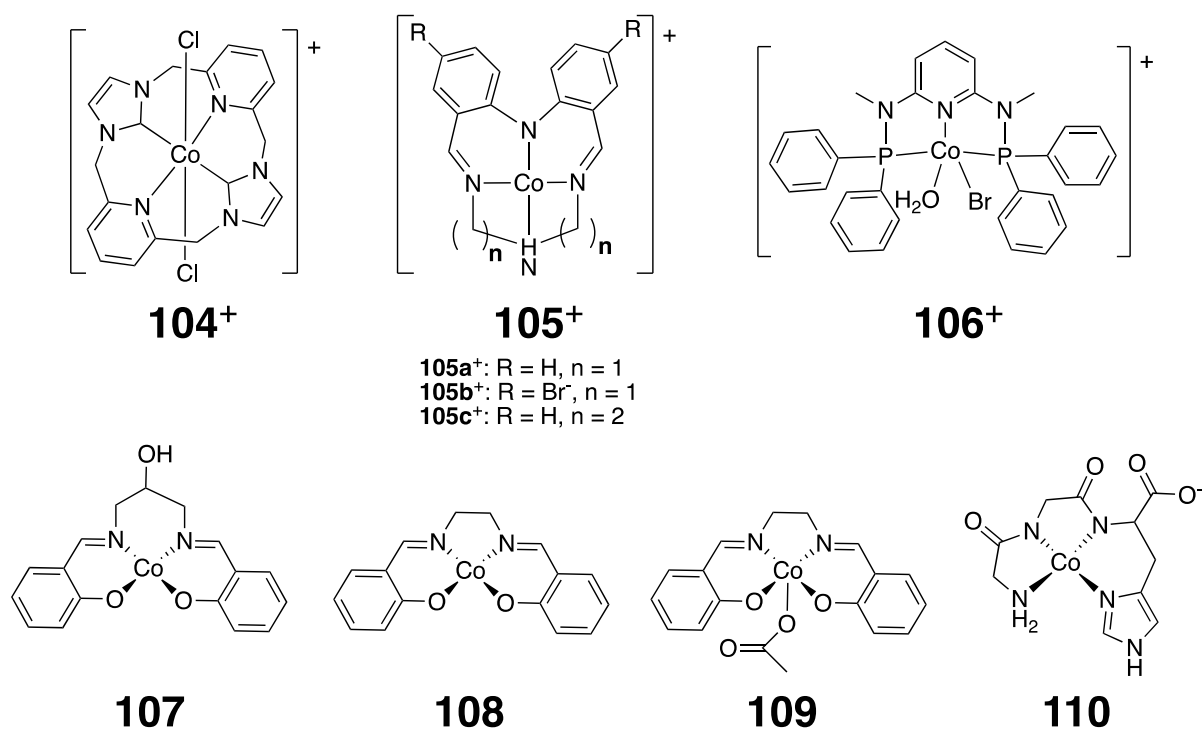


Figure 1.17 Chemical structures of other types of cobalt catalysts for photocatalytic hydrogen evolution.

Table 1.5 Catalysts, photosensitizers, turnover numbers, turnover frequencies and solvents of selected structurally related cobalt porphyrin complexes and other types of cobalt complexes-based catalytic systems for homogeneous light-driven hydrogen evolution.

HEC (μM)	PS ^[a] (μM)	TON ^[b] (time)	TOF ^[c]	Solvent ^[d]	Reference
98 ⁴⁺ (2.5)	111a ²⁺ (1000)	725 (5 h)	8.8 min ⁻¹	pH 7.0, PB	122
99 ⁴⁺ (1.5)	111a ²⁺ (1200)	6410 (40 min)	120.8 min ⁻¹	pH 6.8, PB	123
101 (2)	111a ²⁺ (600)	2400 (10 h)	680 h ⁻¹	pH 10.0, 4:1 EtOH/H ₂ O	125
102 (2.28)	111a ²⁺ (400)	152 (3 h)	N.R.	pH 4.5, AsB	127
103a (7.5)	122 (3000)	80.4 (100 min)	1.79 min ⁻¹	dioxane	128
103b (7.5)	122 (3000)	113.3 (100 min)	3.76 min ⁻¹	dioxane	128
103c (7.5)	122 (3000)	83.1 (100 min)	3.30 min ⁻¹	dioxane	128
104 ⁺ (100)	111a ²⁺ (40)	16.8 (40 h)	N.R.	pH 5.0, AcB	129
107 (10)	120a ²⁻ (100)	319 (9 h)	N.R.	pH 10.0, 1:1 MeOH/H ₂ O	131
110 (5)	111a ²⁺ (1000)	2200 (35 h)	N.R.	pH 7.1, MOPS	132

^[a]structures could be found in Section 1.4.

^[b]TON: turnover number based on HEC = mol(H₂)/mol(HEC).

^[c]N.R.: not reported.

^[d]PB: phosphate buffer, H₂O: water not buffered, AsB: ascorbate buffer, AcB: acetate buffer, MOPS: 3-(N-morpholino)propanesulfonic acid.

1.3.8 Overview of the cobalt-based molecular catalysts for photocatalytic hydrogen evolution

To sum up, comparing with other metals, cobalt based HECs have been the source of the most intense investigations. Most reports on cobalt catalysts for the HER focus on: 1) ligand development and design, to introduce novel geometries, tuning the electron density of the complex, providing proton relays, or changing the coordination environment; 2) investigating catalytic mechanisms using different techniques, determining the rate determining step, characterizing the key intermediate, or exploring the balance between different catalytic steps; 3) reporting new components for photocatalytic systems: noble-metal-free systems, novel photosensitizers, new types of electron donors or redox acceptors. From the staggering number of studies in this field a few trends can be drawn: first, [Ru(bpy)₃]²⁺ remains one of the most

used photosensitizers, and often limits the stability of the photocatalytic system; it is a precious metal hence not sustainable. Second, it remains exceptional difficult to use first-row transition metal photosensitizers for photocatalytic HEC. Third, the photocatalytic system which obtained the highest TON of 730000 is still limited to a very low PTON of 86,^[71] which is probably insufficient if one wants to place an artificial photosynthetic system on a roof to produce green hydrogen.

The design of new redox non-innocent ligands is a promising strategy to further improve HEC because this kind of ligands may help avoiding the formation of high-energy intermediates with low valence state metal ions during catalysis.^[4,10,20,53-54] Proton-coupled electron transfer (PCET) processes can be introduced by introducing flexible proton acceptor groups; this is also a promising way to avoid reaching very low oxidation states of a metal center,^[51] which are often unstable. However, this kind of flexible groups may also result in unstable catalysts.^[10] Therefore, a complex with a redox-active ligand that can provide a rigid coordination environment with less than 6 coordination sites (at least one coordination site is needed to bind a proton), will be more likely to lead to robust and efficient molecular catalysts.

Another point of concern is to design catalysts that are fully soluble in aqueous solutions, in order to obtain photocatalytic system that do not require acetonitrile or DMF to function. For example, most cobaloxime proton reduction catalysts were applied in mixtures of organic solvent and water, and most cobalt polypyridine catalysts were active in acidic mixtures of organic and aqueous solutions. All other types of cobalt catalysts required organic solvent systems or non-neutral aqueous systems to be active. So far, only a few cobalt catalysts can really work in a homogeneous neutral aqueous medium.^[122,133] On the other hand, sea water, which is the most abundant source of water in nature, is weakly alkaline. When coupling water reduction with water oxidation to achieve a whole water splitting photocatalytic scheme, utilizing sea water would be much preferable than (acidic) drinking water. This consideration requires HEC to work in near-neutral or even weakly alkaline conditions, so that both half-reactions can occur simultaneously. Overall, the quest towards robust and efficient cobalt HEC that can work in neutral or weakly alkaline homogeneous aqueous systems is important, and it will form part of this PhD thesis.

1.4 Molecular photosensitizers for homogeneous light-driven hydrogen evolution

1.4.1 Quenching mechanisms

Photosensitizers form a key component of three-component HER photocatalytic systems. They are responsible for harvesting light, and trigger electron transfer from a sacrificial electron donor (reductive quenching) or to a hydrogen evolution catalyst (oxidative quenching).^[3-4,6,10,16,134] For classical ruthenium-based photosensitizers such as $[\text{Ru}(\text{bpy})_3]^{2+}$, the highest occupied molecular orbital (HOMO) is a metal-localized t_{2g} -orbitals, and the lowest unoccupied orbital (LUMO) is the bipyridine ligand-localized antibonding π^* -orbital. When absorbing a photon, an electron of the t_{2g} -orbitals is promoted to the π^* -orbital forming the metal-to-ligand charge transfer (MLCT) excited state, in a step formally corresponding to charge separation.^[134] For organic chromophores, charge separation is also required. Then, the excited PS^* can either obtain an electron from the ED, to become a reductant PS^- and further reduce the HEC, or behave as a reductant, to transfer an electron to the HEC via oxidative quenching and be further regenerated by electron transfer from the ED. The microscopic state where one electron donor is oxidized into ED^+ and the catalyst is reduced to HEC^- , formally represents another form of charge-separated state.

As discussed above (Section 1.3), understanding which quenching pathway is favorable requires understanding the thermodynamic features of the different components of the photocatalytic system (Figure 1.18). For example, in reductive quenching mechanism (Figure 1.18, left), the oxidation potential E of the electron donor, or redox potential of the ED^+/ED couple, should be more negative than the reduction potential $E_{\text{PS}^*,\text{red}}$ of the couple involving the excited photosensitizer, PS^*/PS^- . By contrast, in the oxidative quenching mechanism (Figure 1.18, right) the oxidation potential $E_{\text{PS}^*,\text{ox}}$ of the couple involving the excited photosensitizer PS^+/PS^* , should be more negative than the potential E_{HEC} at which the catalytic HER experimentally occurs, which is η lower than the (Nernst) thermodynamical potential $E_0(\text{H}^+/\text{H}_2)$ at which proton reduction should occur at that pH. In this notation, η is often called the “overpotential” of the catalyst. What is more, the potential at which ED is oxidized should also be more negative than the potential E_{PS} at which PS is oxidized (PS^+/PS), so that regeneration of the photosensitizer can occur. The values of E (ED^+/ED), $E_{\text{PS},\text{red}}$ (PS/PS^-), $E_{\text{PS},\text{ox}}$ (PS^+/PS) and E_{HEC} (H^+/H_2) are usually obtained by electrochemistry. The triplet excited state energy $E(\text{T})$, which corresponds to the free Gibbs energy difference between the vibrational ground state of the lowest triplet excited state of the photosensitizer, T1, and the vibrational ground

state of its electronic ground state S_0 , can be calculated according to eqn (1), where $E(T)$ is the triplet excited energy (eV), “ h ” is the Planck constant (4.1357×10^{-15} eV s $^{-1}$), “ c ” is the speed of light (2.9979×10^{17} nm s $^{-1}$), $\lambda(p)$ is the maximum wavelength (nm) of the phosphorescence emission spectrum of the PS. Another option to calculate $E(T)$ is to use density functional theory (DFT). Once $E(T)$ is known, the redox potentials involving the excited states of the photosensitizer, $E_{PS^*,red} (PS^*/PS^-)$ and $E_{PS^*,ox} (PS^+/PS^*)$ can be calculated from the redox potentials $E_{PS,red} (PS/PS^-)$, $E_{PS,ox} (PS^+/PS)$ and $E(T)$ according to eqn (2) and (3). In the excited state the photosensitizer is hence both a better oxidant and a better reducing agent than in the ground state, thus driving electron processes that are impossible in the dark. When the electron transfer of Step 1 and 2 of the two quenching mechanisms are both thermodynamically feasible, the dominant mechanism will be the one that has a faster electron transfer for Step 1.^[6,10,134]

- $$E(T) = hc/\lambda(p) \quad (1)$$
- $$E_{PS^*,red} (PS^*/PS^-) = E_{PS,red} (PS/PS^-) + E(T) \quad (2)$$
- $$E_{PS^*,ox} (PS^+/PS^*) = E_{PS,ox} (PS^+/PS) - E(T) \quad (3)$$

Overall, the redox properties in the ground state, and the excited state energy of the PS, should be such that the PS can thermodynamically drive electron transfer in the photocatalytic system. In particular, $E_{PS,red} (PS/PS^-)$ and $E_{PS^*,ox} (PS^+/PS^*)$ should be as negative as possible in the reductive and oxidative quenching mechanisms, respectively, to provide the driving force necessary to reduce the HEC with a high driving force, hence quickly.

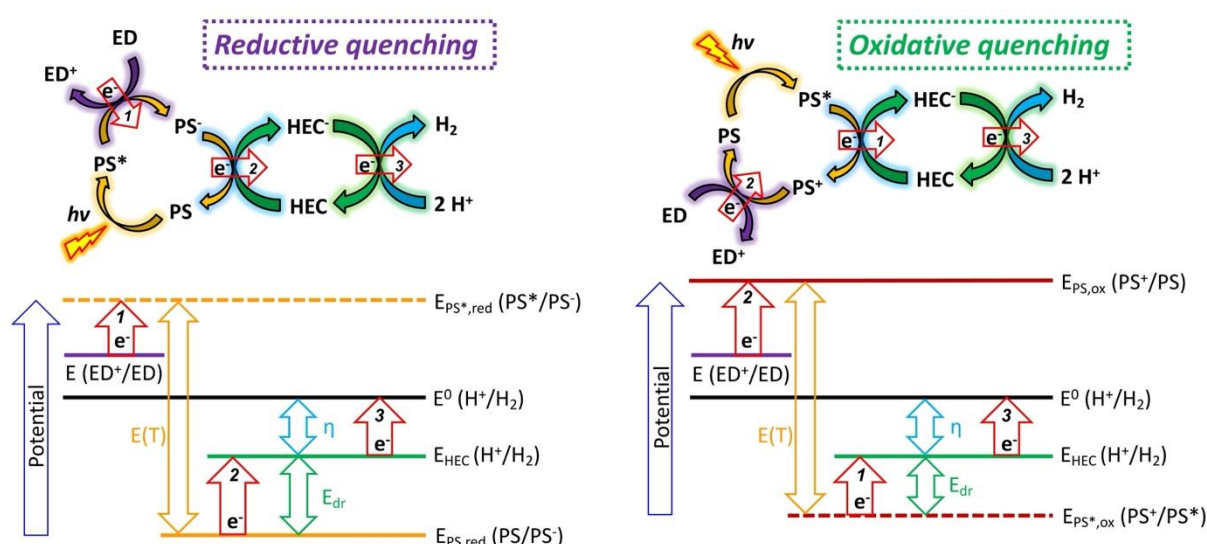


Figure 1.18 Simplified photocatalytic mechanism and energy scheme of a three-component molecular homogeneous photocatalytic hydrogen evolution system. ED: sacrificial electron donor; PS: photosensitizer; HEC: hydrogen evolution catalyst; $E(T)$: triplet excited state energy;

η : overpotential of HEC; E_{dr} : driving force of the electron transfer from the photosensitizer to the catalyst.

On the other hand, optimized redox properties are not the only requirements of a good photosensitizer for proton reduction. It should also have the following properties: 1) a broad absorption band, overlapping as much as possible with the solar spectrum, and with a high extinction coefficient at the maximum absorption, in order to maximize solar energy usage; 2) a long excited state lifetime, to ensure there is enough time to transfer an electron to or from the excited state; often, triplet excited states are hence preferred; 3) a high photostability, to be able to run long-term hydrogen evolution in photocatalytic conditions; 4) a good solubility in the solvent system, to reduce the possibility of PS aggregation, which may decrease the activity of the photocatalytic system and influence its mechanism.

1.4.2 Noble metal-based molecular photosensitizers for light-driven hydrogen evolution

Noble metal-based photosensitizers have been widely studied and are currently the most efficient chromophores for homogeneous photocatalytic hydrogen generation, in particular those based on Ru, Ir, Pt and Re. $[\text{Ru}(\text{bpy})_3]^{2+}$ (**111a**²⁺ in Figure 1.19) is a prototypical example, which has also been used as PS for water oxidation.^[10,20] This complex has three main advantages: 1) it absorbs well visible light ($\lambda_{\text{max}} = 452 \text{ nm}$ in aqueous solutions); 2) its excited state has a very long lifetime ($\tau = 1.1 \text{ }\mu\text{s}$), which is long enough for electron transfer; 3) it has a strongly negative reduction potential ($\sim -1.3 \text{ V}$ vs NHE), which provides the necessary driving force to transfer electrons to most hydrogen evolution catalysts.^[134] Durrant and co-workers modified one bipyridine ligand of **111a**²⁺ with two $\text{PO}(\text{OH})_2$ groups to afford photosensitizer **111b**²⁺ that works with a Ni-based catalyst for photocatalytic HER.^[135] The reductive quenching process transferring electrons from ED to PS*, was found to be more favorable at higher pH, as protonation of the ED at low pH decreased the activity of the catalytic system. Using phenanthroline instead of bipyridine, the Ru-based PS **112**²⁺ was reported by the Bernhard group for photoinduced hydrogen production with a much higher PTON of 580 compared with 100 PTON of **111a**²⁺.^[136]

The same work also investigated (**113a-b**)⁺ and (**114a-d**)⁺ series as Ir-based photosensitizers for water reduction. Importantly, the Ir-based PS's gave much higher PTON of 800-920 compared to the common PS **111a**²⁺.^[47,136] Thereafter, **113a**⁺ has developed as a new, widely used PS for light-induced HER.^[66,91-92,102-103,105,107] Later on, the same group further explored **113c**⁺ and **113d**⁺ as PS for HER, which contained CF_3 groups on the ligands.^[137] More recently,

the Zou group developed **113e⁺** as PS using [Ni(bpy)₃]²⁺ as catalyst and TEOA as ED for photocatalytic hydrogen production in a pH 9.0 8:2 MeCN:water solution.^[138] In general, the Ir-based photosensitizers can give a higher PTON than the Ru-based ones; their excited state energy is also 0.1 eV~ 0.2 eV higher than that of Ru-based PS, accordingly, they require higher energy to be excited.

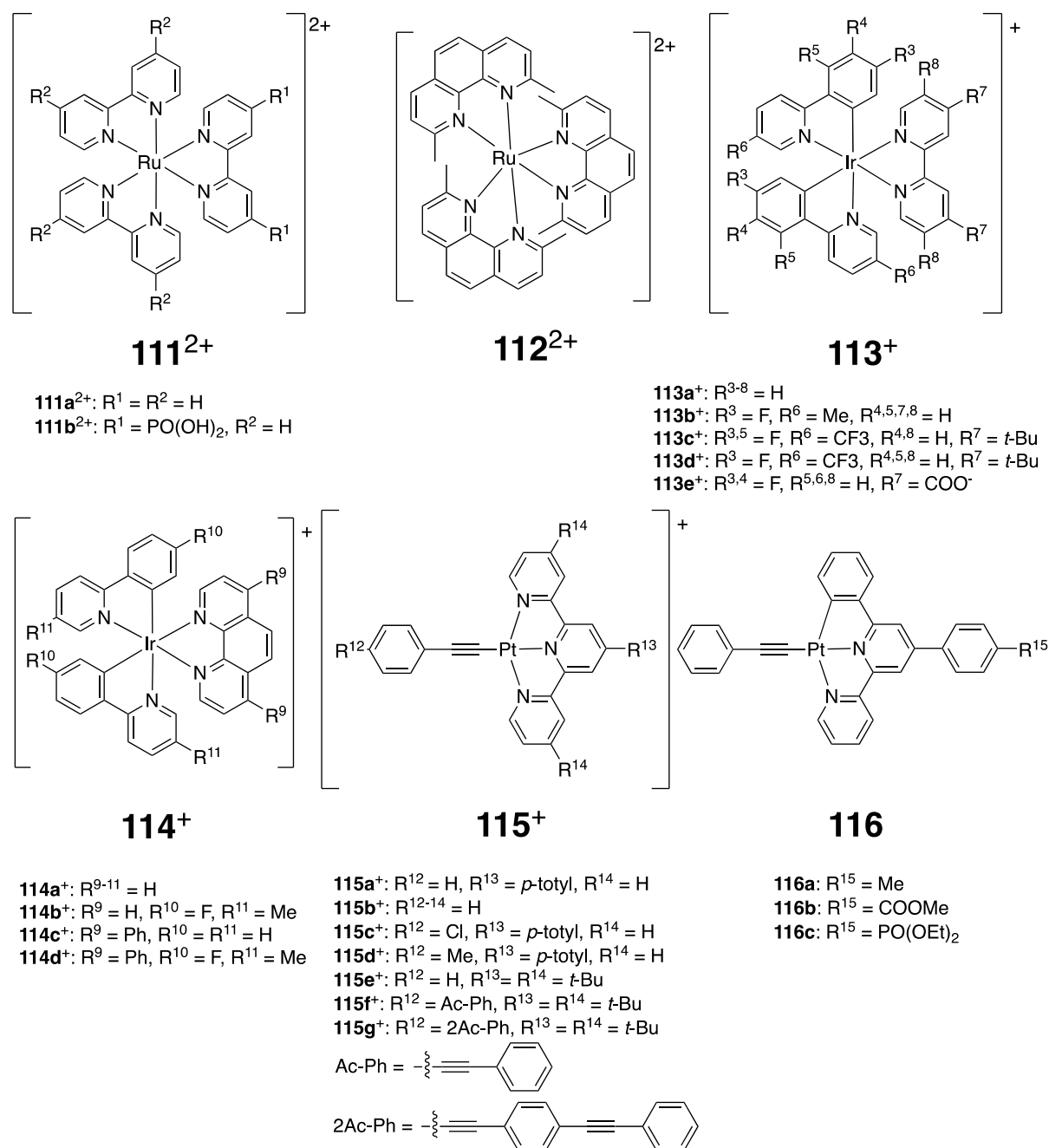


Figure 1.19 Chemical structures of selected Ru, Ir and Pt based photosensitizers for photocatalytic hydrogen evolution.

Next to PSs based on ruthenium(II) and iridium(III) the Eisenberg group developed a series of platinum(II)-based photosensitizers (**115a-d**)⁺ and **116a-c** for H₂ photogeneration, which were efficient using TEOA as ED in a MeCN:water 2:3 mixture solution.^[58,139] However, the activities of the photocatalytic systems using Pt-based PS were usually lower than those based on Ir PS's. Castellano and co-workers tried to improve Pt-based PS's via modifying the π -conjugated ligands of the initial PS **115a**⁺, and studied (**115e-g**)⁺ (Figure 1.19).^[140] Unfortunately, working with cobaloxime catalysts and TEOA, the PTON of this series of Pt-based PS was still limited up to 800 (mol_{H₂}/mol_{PS}) for 3h irradiation.

Regarding rhenium(I) the Alberto group explored two series of photosensitizers (**117a-e**)^{z+} and (**118a-f**)^{z+} (z = 0 or 1) (Figure 1.20) that were much more efficient compared with the common Ru-based PS **111a**²⁺ for photocatalytic production of H₂.^[63-64,141-142] For example, **118a** gave a much higher PTON than **111a**²⁺ (146 vs. 62) in 9 h photo reaction using Co(OAc)₂ as the HEC.^[142] Due to its high PTON property as a photosensitizer, **118c**⁺ was then used as a standard PS to develop hydrogen evolution catalysts by the same group.^[65,88,95] Che and co-workers reported organogold based photosensitizers (**119a-b**)⁺ with long-lived triplet excited states, which were able to work with cobaloxime and TEOA for hydrogen photoproduction in 4:1 MeCN:water solutions.^[143] The Re-based photosensitizers in general perform better PTON than the Ru-based ones, some of them even performed a higher PTON than that of the Pt-based PSs, for example, **118b** could reach a very high PTON of 6000 after 100 h irradiation. The activity of Au-based photosensitizers was reported with a highest PTON of 350 for 4 h light irradiation, which is not high as the other noble metal-based photosensitizers.

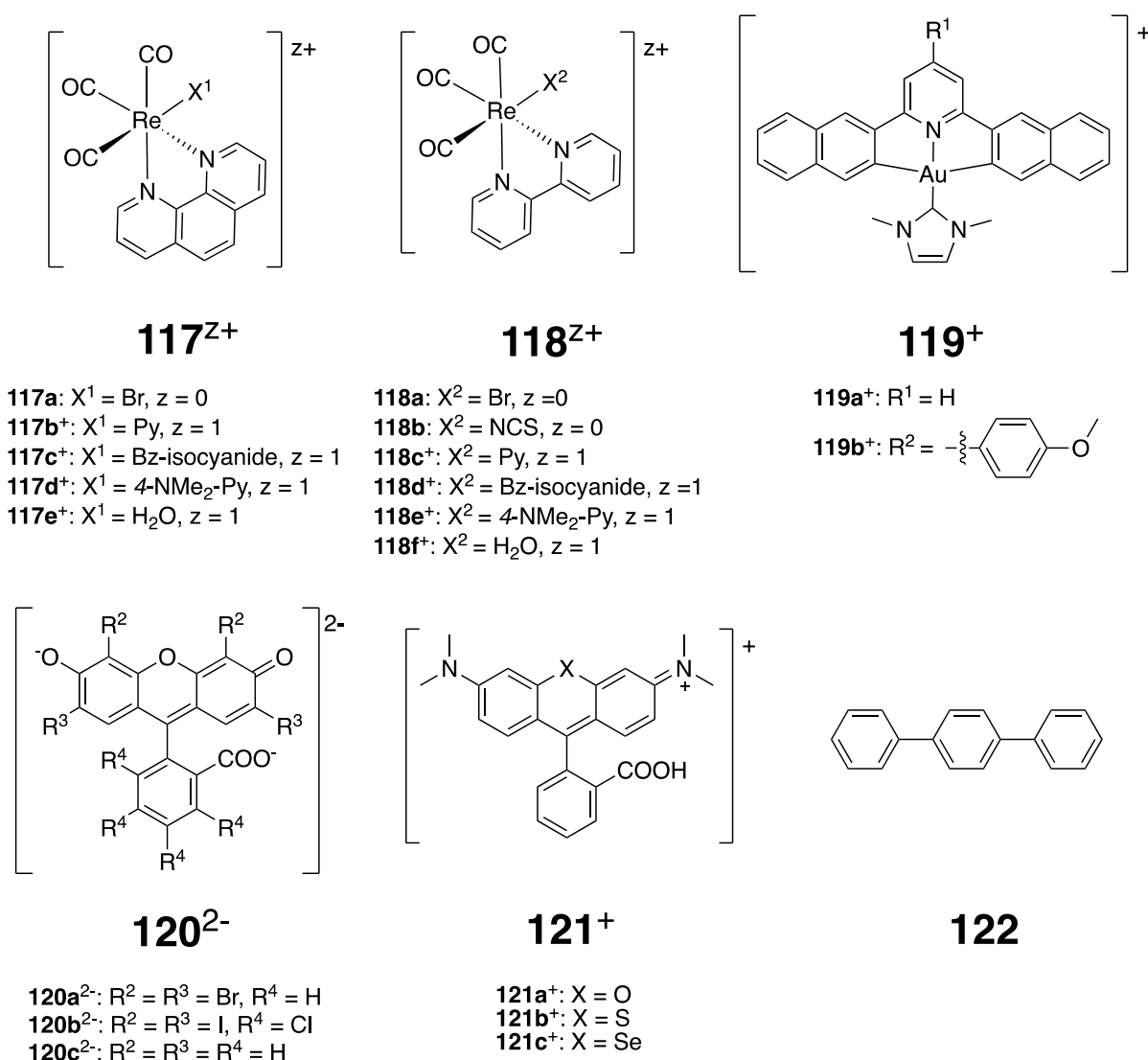


Figure 1.20 Chemical structures of selected Re-, Au-based, and organic photosensitizers for photocatalytic hydrogen evolution.

1.4.3 Noble metal-free molecular photosensitizers for light-driven hydrogen evolution

Although many noble metal-based molecular photosensitizers are very efficient in homogeneous HER photocatalytic systems, they are usually considered as too expensive and scarce for industrial scale energy applications. Therefore, people are paying more and more attention to the development of noble metal-free chromophores. Organic photosensitizers, for example xanthene dyes and terphenyl, are seriously considered as potential replacement (Figure 1.20).^[119,126] Eosin Y **120a²⁻**,^[60,62,67,131] Rose Bengal **120b²⁻**,^[59,131] and Fluorescein **120c²⁻**,^[120-121,131] are three classic types of xanthene dyes that have been widely applied in noble metal-free photocatalytic hydrogen evolution systems. Another series of xanthene-based organic PS, **121⁺**, were reported by Eisenberg and co-workers to work with cobaloxime

catalysts for H₂ evolution via a reductive quenching mechanism.^[144] Doctorovich et al. also reported terphenyl **122** as an organic PS for hydrogen production from water, working with iron and cobalt corrole catalysts deposited on carbon nanotubes.^[128] However, the photostability of these organic chromophores is far from ideal, as most of them can only last a few hours under irradiation.

As a consequence, molecular complexes based on earth-abundant metals are also being investigated thoroughly for the replacement of the ones based on noble metals. Aluminium porphyrin photosensitizer **123** (Figure 1.21) was reported by Scandola and co-workers for photocatalytic H₂ evolution in the presence of cobaloxime as HEC and ascorbic acid as ED in 3:7 water:organic solvents mixture solutions.^[145] Cu(I) based noble metal-free photosensitizer was first reported by Sauvage and co-workers for photocatalytic hydrogen generation in 1984.^[146] Recently, based on Cu(I) as well, the Beller group developed the series of complexes (**124a-e**)⁺, **125f**⁺ and **126f**⁺ as PS working with [Fe₃(CO)₁₂] as HEC and TEA as ED in a pH 11.5 THF/TEA/H₂O 4:1:1 solution.^[147,148] **125f**⁺ and **126f**⁺ showed much higher maximum PTONs close to 800 compared with 58 of the common Ru-based **111a**²⁺ and 576 of the Ir-based PS **113a**⁺. Then the same group further investigated the series (**125a-f**)⁺ and (**126a-f**)⁺ and found that **126a**⁺ and **126b**⁺ performed with the highest initial hydrogen evolution rates, but could only last for 5 h under irradiation.^[149] The highest maximum PTON of 1330 was observed by **125b**⁺, which was more photostable compared with the other complexes and remained active for over 60 h. Modifying the phenanthroline ligands of (**125a-f**)⁺ and (**126a-f**)⁺ with sulfonato groups afforded (**127a-b**)⁺ and (**128a-b**)⁺, two series of Cu(I)-based PSs that were further studied by the same group working with or without titanium dioxide for HER in mixture solutions of THF/TEA/H₂O = 4:3:1.^[150] In the catalytic systems without TiO₂, **127b**⁺ was found to be the most active one with a maximum PTON of 1530 after 24 h irradiation. However, when the Cu(I) complex was immobilized to TiO₂, **127a**⁺-TiO₂ gave the highest maximum PTON of 2452 after 24 h photocatalysis. Finally, a different type of Cu(I)-based PS (**129**⁺) was reported by Castellano and co-workers for hydrogen photogeneration working with cobaloxime.^[151] This very robust cuprous biphenanthroline photosensitizer could efficiently work with N,N-dimethyl-*p*-toluidine as ED in a pH 6.0 1:1 MeCN:H₂O solution for 5 day under visible light irradiation.

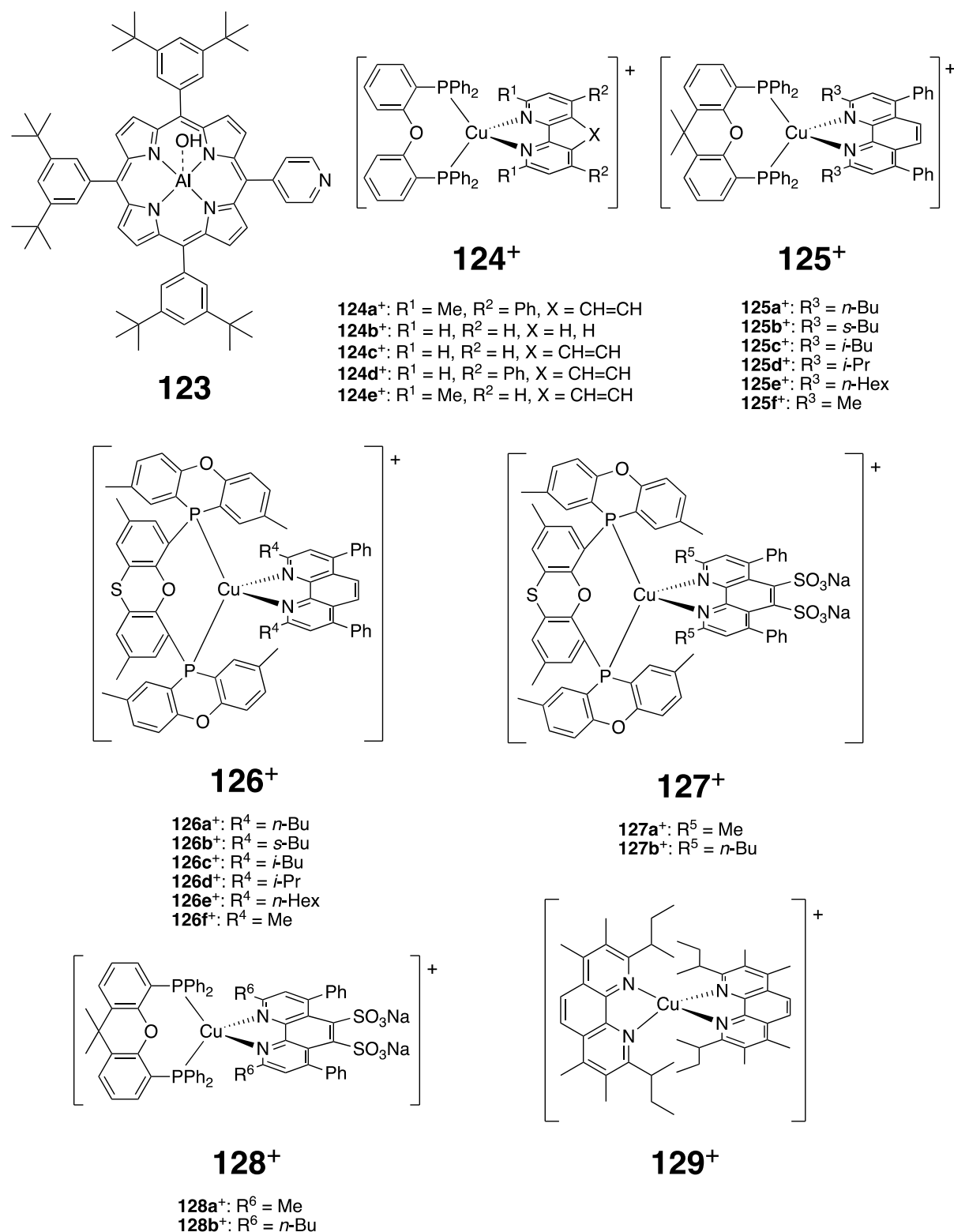


Figure 1.21 Chemical structures of selected Al and Cu(I) based photosensitizers for photocatalytic hydrogen evolution.

Of course, aluminum porphyrins and chromophores based on Cu(I) are cheaper than those based on noble metals, but 1) phosphorus ligands are expensive, 2) phosphorus is considered

now as a scarce element, 3) Cu(I) complex is not easy to store, and 4) the highest PTON of Al-porphyrin based PS was only 280 after 2 h photoreaction, which is far less than ideal. Although some photocatalytic systems based on the Cu(I) photosensitizers (e.g., **126a**⁺ and **126b**⁺) have shown encouraging rates, their short lifetime limits maximum PTONs. In recent years, many types of molecular Zn porphyrins have been developed as well, as they seem to be more robust and efficient PSs for solar driven HER. The simple water-soluble Zn-porphyrin **130a**⁴⁺ was applied by the Coutsolelos group as PS working with cobaloxime and cobalt catalyst **51**²⁺ for hydrogen production in MeCN/water mixture and aqueous solutions respectively.^[61,83,152] More recently, the same group further investigated different Zn and Sn porphyrins (**130a-b**)^{z+} to (**134a-b**)^{z+} (z = 0, 2, 4 or 6) as charged or neutral PS for light-driven hydrogen evolution in the presence of cobaloxime as HEC.^[153] In these studies, systems based on Zn(II) and Sn(IV) porphyrin photosensitizers showed a quite high photostability, in particular, most of them could last longer than 24 h with PTONs that higher than 200 and 120. However, working with cobaloxime **20a** as the HEC, the highest PTON was obtained by **130a**⁴⁺ with only 280 for 35 h irradiation. Obviously, it is not ideally high, efforts still should be done on developing more efficient Zn or Sn porphyrin chromophores for molecular noble metal-free HER photocatalytic systems, and on better understand what limits photocatalytic rates and stabilities.

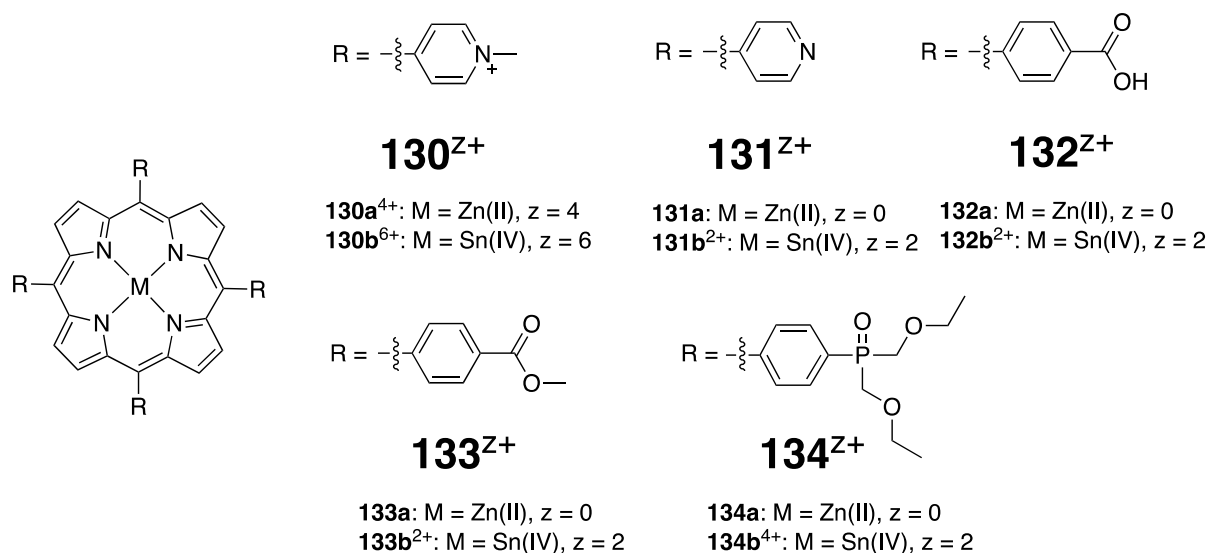


Figure 1.22 Chemical structures of selected Zn(II) and Sn(IV) porphyrin-based photosensitizers for photocatalytic hydrogen evolution.

From past studies, porphyrin-based molecular photosensitizers combine several advantages: 1) they show intense absorption of visible light due to their large conjugated ring and allowed pi-pi* transitions;^[4,7] 2) they trigger photocatalysis with good stability due to the rigid,

multidentate coordination site;^[4] 3) they are easy to modify with functional substituents, for example to introduce more water solubility or more lipophilicity; 4) they can be fine-tuned in terms of redox properties by introducing electron-withdrawing or electron-donating substituents. Thus, they represent the most promising scaffold for the development of noble-metal free PS's for photocatalytic hydrogen production. As discussed above, Zn and Sn porphyrins have already shown promising photoactivity for HER with outstanding photostability, but little is known on the kinetic details of these photocatalytic systems; it is hence highly desirable to modify them to try to improve their photocatalytic activities (TOF) without detrimental modifications on their stability (PTON). A systematic approach, which will be described in **Chapter 4** of this PhD thesis, is to first study the redox property of Zn(II) or Sn(IV) porphyrin-based PSs and their ability to sensitize a standard HEC. Then, I will come up with mechanistic insights, which will highlight the possible effect of electron-donating or electron-withdrawing groups on the efficacy of these PS. Finally, I will modify the porphyrin ligand of these PSs with such substituents, and verify their influence on the photocatalytic hydrogen evolution activity.

1.5 Aim and outline of this thesis

Artificial photosynthesis is widely accepted to be very important for the future, and thousands of research groups all over the world are working on it. Studies on photocatalytic water oxidation, hydrogen evolution, and carbon dioxide reduction, mainly focus on the development of new catalysts, photosensitizers, and devices, to optimize activity and stability, and on mechanistic studies to understand where the problems lie. Molecular systems are not only ideal to investigate photocatalytic mechanisms, they also perform well in terms of selectivity and activity.

The initial impetus of this PhD thesis was based on several concomitant observations: 1) Ni-based molecular catalysts for homogeneous photocatalytic water oxidation in aqueous solutions needs to be developed; 2) the optimal balance between the driving force of electron transfer from water to the oxidized catalyst (Cat^+) and from the catalyst to the oxidized photosensitizer (PS^+) in a homogeneous photocatalytic system, needs to be found; 3) efficient cobalt-based photocatalytic hydrogen evolution catalysts that can work in particular in neutral homogeneous aqueous solutions free from organic solvents, still need to be found; 4) the catalytic mechanism of the photocatalytic HEC in neutral conditions (pH 7.0) and the strategy to design a catalyst optimized such neutral condition, still need to be revealed; 5) the

development of more efficient and more robust noble metal-free molecular photosensitizers for light-driven H_2 generation is desirable, but general strategies to design such better PS's, are still needed.

Thus, a series of four water-soluble tetra-anionic porphyrin ligands bearing 8 strong electron-donating methoxy substituents ($\text{Na}_4[\text{H}_2\text{-OMeP}]$), 8 weak electron-donating methyl groups ($\text{Na}_4[\text{H}_2\text{-MeP}]$), and either 8 or 16 electron-withdrawing fluoro substituents ($\text{Na}_4[\text{H}_2\text{-F8P}]$, $\text{Na}_4[\text{H}_2\text{-F16P}]$) were prepared (Figure 1.26), and used for the synthesis of Ni(II) (**Chapter 2**), Co(III) (**Chapter 3**), Zn(II) (**Chapter 3-4**), and Sn(IV) (**Chapter 4**) metalloporphyrin complexes.

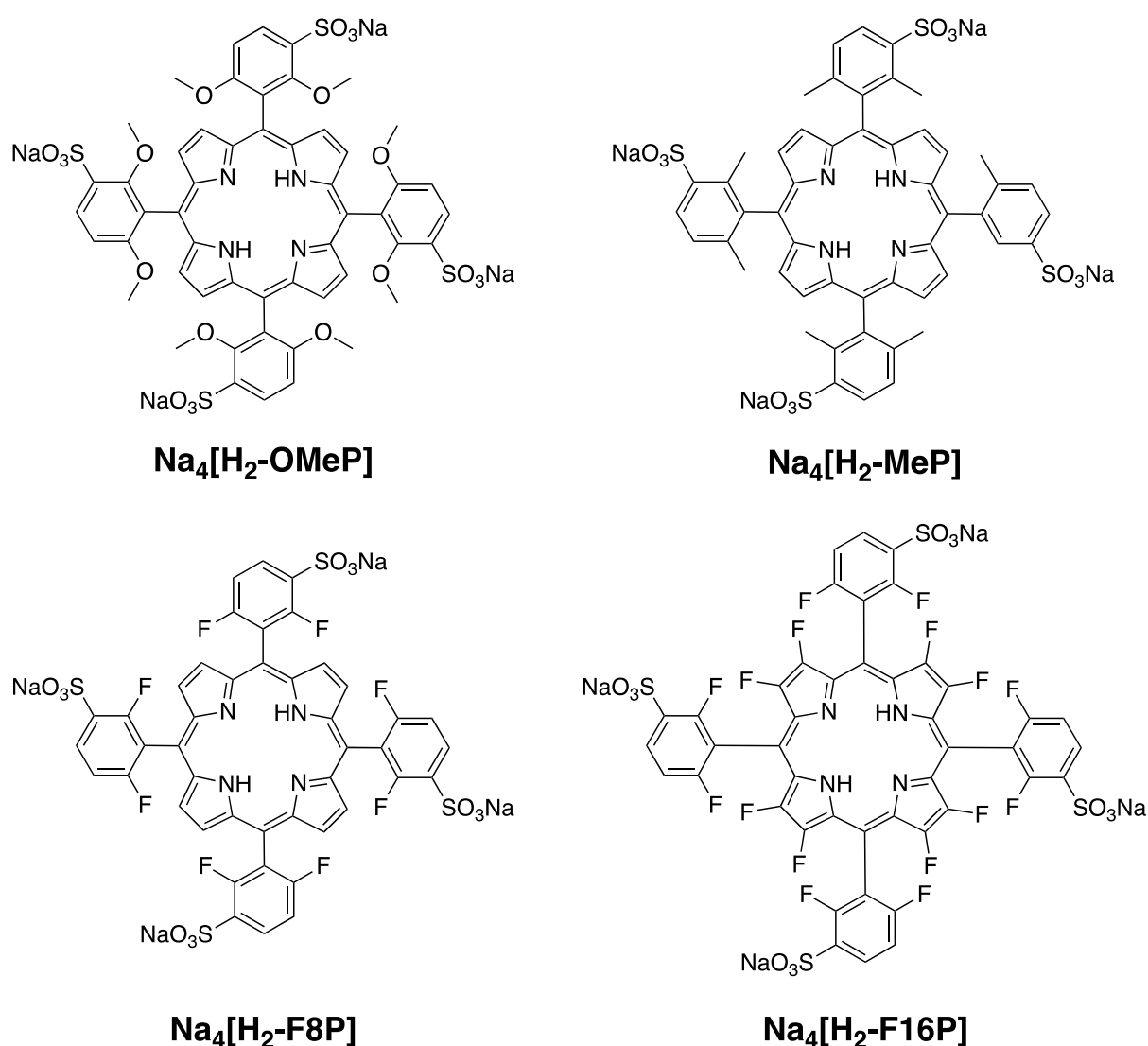


Figure 1.23 Chemical structures of porphyrin ligands used in this thesis.

The nickel complexes in **Chapter 2** were used as the first Ni-based molecular catalysts for visible light-driven water oxidation in neutral and acidic homogeneous aqueous solutions. In

particular, a balance between the driving force for the nickel-catalyzed OER and that of the electron transfer from the Ni-based catalyst to the photo-oxidized species PS^+ , was identified. New rules for the molecular design of catalysts for photocatalytic oxygen evolution are proposed, where the electron-density of the catalytic centre must be fine-tuned by appropriate substituents, to balance these two driving forces.

In **Chapter 3**, the two analogous series of Co(III) and Zn(II) porphyrin complexes were studied and compared as molecular catalysts for homogeneous photocatalytic hydrogen evolution from neutral and acidic water, using **111a**²⁺ as standard photosensitizer. Coporphyrin catalysts with either strong electron-donating or strong electron-withdrawing substituents were found to be photocatalytic active at different optimum pH, probably via different mechanisms. The redox non-innocence of the porphyrin ligands were also demonstrated with the series of zinc complexes, some of which ($\text{Na}_4[\text{Zn-F16P}]$) were found to be catalytically active for photocatalytic hydrogen production in neutral aqueous solutions. Catalytic mechanisms for proton reduction using $\text{Na}_3[\text{Co-OMeP}]$ and $\text{Na}_3[\text{Co-F16P}]$ in acidic and neutral conditions, respectively, are also proposed, with a full kinetic study.

In **Chapter 4**, the analogous series of Zn(II) and Sn(IV) porphyrin complexes were studied for their properties as photosensitizers for hydrogen photoproduction, using cobaloxime as standard catalyst. Under green light irradiation, $\text{Na}_4[\text{Zn-F16P}]$ was found to be the most active PS, followed by $\text{Na}_4[\text{Sn-MeP}]$, while $\text{Na}_4[\text{Sn-OMeP}]$ showed very limited photosensitizing activity. No activity at all was found with all other Zn- and Sn-porphyrin PSs. Mechanistic studies revealed that the HER activity for all photocatalytically active systems were following a reductive quenching pathway. This work provides innovative ideas towards strategies to develop new, noble metal-free molecular photosensitizers for water splitting, using electronic effect on porphyrin ligands.

In the final **Chapter 5**, a summary, a general discussion, and an outlook of this thesis are presented.

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2

Ligand Controls the Activity of Light-driven Water Oxidation Catalyzed by Ni(II)-porphyrin Complexes in Neutral Homogeneous Aqueous Solutions

Finding photostable, first-row transition metal-based molecular systems for photocatalytic water oxidation is a step towards sustainable solar fuel production. This chapter discovered that nickel(II) hydrophilic porphyrins are molecular catalysts for photocatalytic water oxidation in neutral to acidic aqueous solutions using $[\text{Ru}(\text{bpy})_3]^{2+}$ as photosensitizer and $[\text{S}_2\text{O}_8]^{2-}$ as sacrificial electron acceptor. Electron-poorer Ni-porphyrins bearing 8 fluorine or 4 methylpyridinium substituents as electron-poorer porphyrins afforded 6-fold higher turnover frequencies (TOFs; ca. 0.65 min^{-1}) than electronricher analogues. However, the electron-poorest Ni-porphyrin bearing 16 fluorine substituents was photocatalytically inactive under such conditions, because the potential at which catalytic O_2 evolution starts was too high (+1.23 V vs. NHE) to be driven by the photochemically generated $[\text{Ru}(\text{bpy})_3]^{3+}$. Critically, these Ni-porphyrin catalysts showed excellent stability in photocatalytic conditions, as a second photocatalytic run replenished with a new dose of photosensitizer, afforded only 1–3% less O_2 than during the first photocatalytic run. Overall, optimizing the balance between the overpotential of the water oxidation catalyst and the driving force of electron transfer between the catalyst and the photogenerated oxidant $[\text{Ru}(\text{bpy})_3]^{3+}$, appears as critical for photocatalytic water oxidation kinetics.

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2.1 Introduction

Photochemical water oxidation plays a critical role in artificial photosynthesis and solar fuel production, as water represents the most sustainable source of electrons for CO₂ and proton reduction.^[1-10] In particular, molecular water-oxidation catalysts capable of generating O₂ in homogeneous conditions and under the action of light have generated great attention, because they form the basis for integrated supramolecular solar-fuel generating devices. In principle, such molecular complexes offer fascinating possibilities of varying the ligands with atomic precision, which allows for fine-tuning the coordination sphere and electron density of the metal-based catalyst, to optimize catalytic efficacy.^[11,12] However, many molecular catalysts that were initially developed to act as molecules in photocatalytic water oxidation systems, were later shown to decompose in the harsh conditions of photocatalytic water oxidation into metal oxides, which are themselves catalytically active in the oxygen-evolution reaction (OER). It is hence critical to demonstrate the stability of a molecular catalyst in photocatalytic conditions, before claiming that it is catalytically active as a molecule.

Although molecular catalysts based on ruthenium or iridium still offer the highest stabilities and activities for photocatalytic water oxidation to date,^[13-16] recently those made of first-row transition metals such as V,^[17,18] Mn,^[18,19] Fe,^[20,21] Co,^[22-35] and Cu^[36,37] have received increased attention because of their lower cost and greater abundance on earth. However, most of them are only active in alkaline environment, which is sub-optimal for photocatalytic solar fuel generation systems combining water oxidation and either proton or CO₂ reduction, which typically require more neutral or even acidic (CO₂-saturated) conditions. Nickel is earth-abundant as well, and a number of Ni(II) complexes have been recently proposed as molecular catalysts for electrocatalytic OER,^[38-41] where they showed high activities in pH-neutral aqueous solutions. However, molecular nickel-based water oxidation catalysts remain rare in artificial photosynthesis.^[11] There is to our knowledge no demonstration of the use of Ni(II) complexes for the OER in photocatalytic conditions, with the exception of a report from Chen et al,^[41] showing photocatalytic water oxidation with Ni-based precursor complexes that clearly serve as pre-catalysts that become active only after decomposition into Ni oxide.

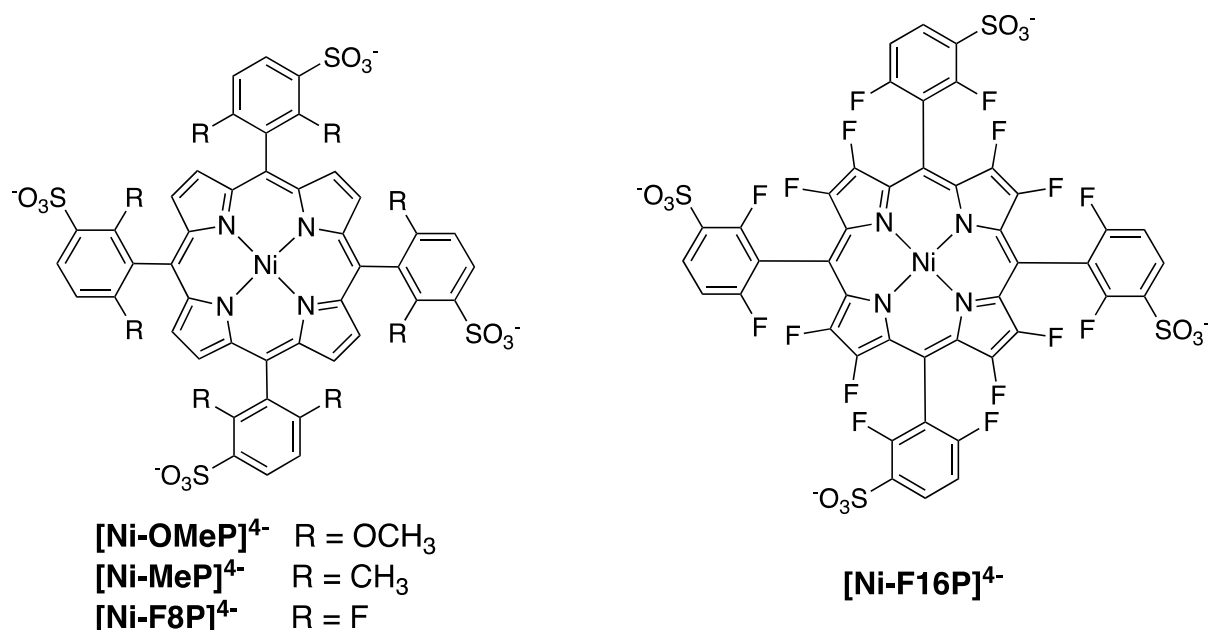


Figure 2.1 Chemical structures of water soluble Ni(II)-porphyrin complexes used in this work, isolated with Na⁺ counter ions.

Herein, we report a series of four tetraanionic Ni(II)-porphyrin complexes bearing either electron-donating ([Ni-OMeP]⁴⁻, [Ni-MeP]⁴⁻) or electron-withdrawing ([Ni-F8P]⁴⁻, [Ni-F16P]⁴⁻) substituents (Figure 2.1). These catalysts were found to be active in the photocatalytic OER in homogeneous aqueous solutions in presence of [Ru(bpy)₃]Cl₂ as photosensitizer (PS), Na₂S₂O₈ as sacrificial electron acceptor (EA), blue light (450 nm), and at neutral to acidic pH. The four substitution patterns, from electron-rich [Ni-OMeP]⁴⁻ to the electron poor [Ni-F16P]⁴⁻, were designed based on the simplified photocatalytic mechanism for water oxidation shown in Figure 2.2. In Step 1, the photosensitizer PS absorbs a photon and is excited to an excited state that transfers an electron to [S₂O₈]²⁻ to afford PS⁺ ([Ru^{III}(bpy)₃]³⁺), SO₄²⁻, and a SO₄^{•-} radical that subsequently oxidizes a second equivalent of PS to PS⁺ (Figure AI.1).^[42,43] In Step 2, PS⁺ oxidizes with an electron-transfer driving force E_{df} the water oxidation catalyst (Cat) to Cat⁺, which, after several repetitions of the same process, affords higher oxidation states of the catalyst capable to catalytically oxidize water, which corresponds to Step 3. The driving force for this last step, usually referred to as the overpotential η, corresponds to the potential at which the catalyst turns over significantly, to afford O₂ and four protons. The exceptional stability of the nickel(II) catalysts presented here enabled us to study the influence of the electron-donating and -withdrawing substituents of the nickel complexes on its redox properties,^[44] on the interplay between E_{df} and η, and to relate these redox properties to the overall performance of the photocatalytic system (Figure 2.2). Since the charge of the catalyst may affect the electron-

transfer rate of Step 2,^[45] two known positively charged Ni(II)-porphyrin complexes 5,10,15,20-tetrakis(4-N-methylpyridyl)porphyrin-nickel(II) tetratriflate ([Ni-MPyP]⁴⁺) 5,10,15,20-tetrakis(4-(N,N,N-trimethylammonio)phenyl)porphyrin-nickel(II) tetratriflate ([Ni-TMAP]⁴⁺) were included in this study as well. The chemical structures of these compounds are shown in Figure AI.2. By interrogating the mechanism shown in Figure 2.2, we established a design principle on how η and E_{df} should be balanced to develop molecular catalysts that maximize the performance of photocatalytic water oxidation.

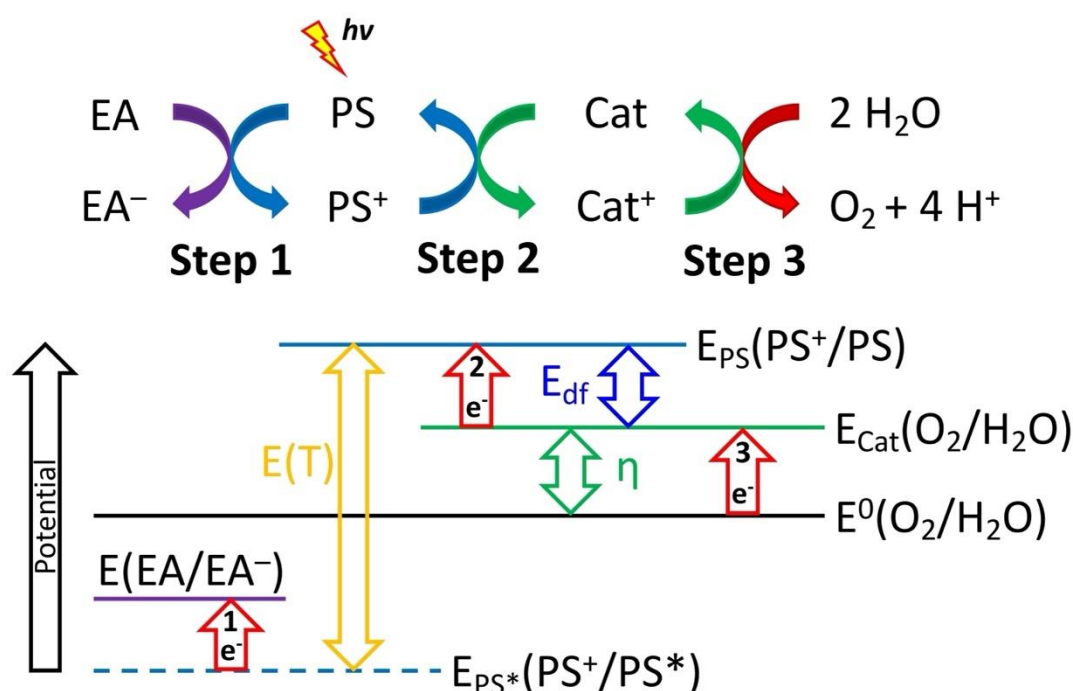


Figure 2.2 Simplified photocatalytic mechanism and energy scheme of a three-component molecular homogeneous photocatalytic water oxidation system. EA: sacrificial electron acceptor; PS: photosensitizer; Cat: water oxidation catalyst; $E(T)$: triplet excited state energy; η : overpotential of Cat; E_{df} : driving force of the electron transfer from the catalyst to the oxidized photosensitizer.

2.2 Results and discussion

The tetrasulfonated porphyrin ligands [H₂-MeP]⁴⁻, [H₂-F8P]⁴⁻, and [H₂-F16P]⁴⁻ were synthesized according to reported procedures,^[46-50] while ligand [H₂-OMeP]⁴⁻ was synthesized by sulfonation of 5,10,15,20-Tetrakis(2,6-dimethoxyphenyl)-21*H*,23*H*-porphyrin (OMeTPP) using chlorosulfonic acid in anhydrous CH₂Cl₂ at room temperature. All four Ni(II) complexes were obtained by refluxing the free-base tetrasulfonatoporphyrin ligands with Ni(II) acetate in

Milli-Q water for 12 h under N_2 . A Na^+ -loaded ion-exchange resin was used to enforce the presence of Na^+ counter ions, and the complexes were finally purified by size-exclusion chromatography in order to remove the excess inorganic salts. The analytical purity of $[H_2-OMeP]^{4-}$, $[Ni-OMeP]^{4-}$, $[Ni-MeP]^{4-}$, $[Ni-F8P]^{4-}$ and $[Ni-F16P]^{4-}$, isolated to Na^+ salt, was established by NMR spectroscopy (Figure AI.3-10), high-resolution mass spectrometry, and elemental analysis.

In photocatalytic conditions using $[Ru(bpy)_3]Cl_2$ as the PS, $Na_2S_2O_8$ as EA, and blue light irradiation (450 nm), most molecular nickel catalysts tested in this study were found to produce O_2 , but the oxygen evolution performances of the electron-poor nickel complexes $[Ni-F8P]^{4-}$ and $[Ni-MPyP]^{4+}$ were found to be significantly better than that of the relatively electron-rich complexes $[Ni-OMeP]^{4-}$ and $[Ni-MeP]^{4-}$ (Figure 2.3). Quite surprisingly, the electron-poorest complex, $[Ni-F16P]^{4-}$, showed no photocatalytic activity at all in these conditions, while nickel(II) acetate ($Ni(OAc)_2$), used as control, showed very low photocatalytic activity. This last result suggests that the homogeneous $[Ni(OH_2)_6]^{2+}$ ions or potential nickel oxide nanoparticles derived from decomposition of these ions in photocatalytic conditions are not active.

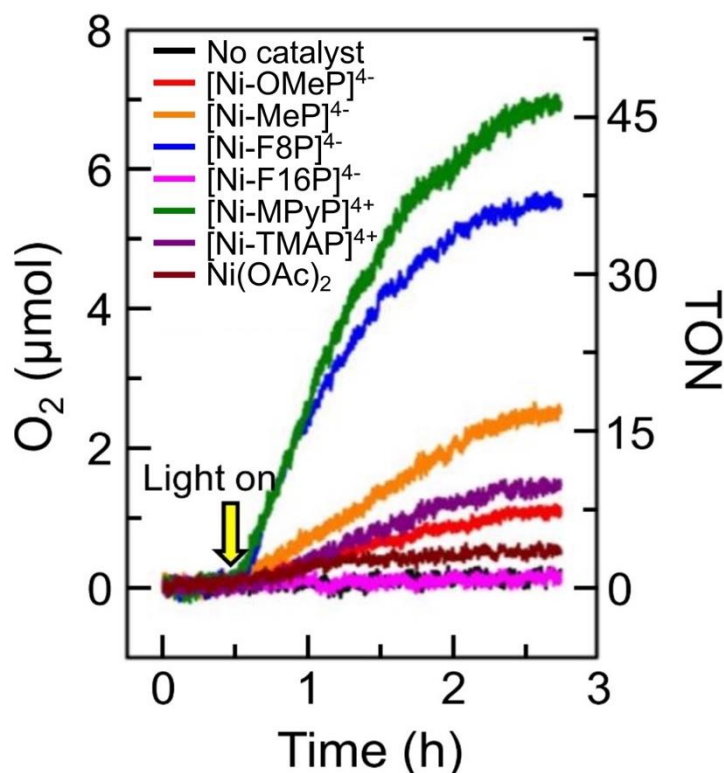


Figure 2.3 Dioxygen evolution during photocatalytic water oxidation in presence of 0.05 mM catalyst $[\text{Ni-OMeP}]^{4+}$, $[\text{Ni-MeP}]^{4+}$, $[\text{Ni-F8P}]^{4+}$, $[\text{Ni-F16P}]^{4+}$, $[\text{Ni-MPyP}]^{4+}$, $[\text{Ni-TMAP}]^{4+}$, or Ni(OAc)_2 , using 0.67 mM $[\text{Ru(bpy)}_3]\text{Cl}_2$ as photosensitizer, 50 mM $\text{Na}_2\text{S}_2\text{O}_8$ in 0.1 M pH 7.0 sodium phosphate buffer, and LED lamp (450 nm, 15.8 mW) for irradiation. $T = 298\text{ K}$.

Considering the interesting photocatalytic activity of some of the Ni-porphyrin complexes, it was essential to test whether these compounds are catalytically active as homogeneous molecular species, or simply are pre-catalysts that decompose to nickel oxide nanoparticles, which have been shown repeatedly to catalyze the OER.^[41] Several experiments were realized to investigate this question. First, phosphate-buffered solutions of each Ni-porphyrin complex at pH 7.0 were irradiated with blue light (450 nm, 15.8 mW) and their UV-vis spectrum was monitored in time during 3 h. The spectra did not change during irradiation (Figure AI.11-16), showing the intrinsic photostability of these molecules in absence of electron acceptor and photosensitizer. Second, dynamic light scattering (DLS) analysis was performed for full photocatalytic mixtures containing, next to PS and $\text{Na}_2\text{S}_2\text{O}_8$, either a Ni-porphyrin complex or Ni(OAc)_2 . From these measurements we concluded that NiO_x nanoparticles were not formed when photocatalysis was realized at an initial neutral pH (7.0) and run for 0.5, 1.0, 1.5, or 2.0 h. As a positive control, photocatalytic experiments using Ni(OAc)_2 as the catalyst but realized at an initial basic pH (8.5), did show significant formation of NiO_x nanoparticles (Figure 2.4a). Hence, in the photocatalytic conditions of the experiments shown in Figure 2.3 none of the Ni(II)-porphyrin catalysts decomposed into nickel oxide nanoparticles. In a third experiment, after a first 2.75 h photocatalytic run with $[\text{Ni-F8P}]^{4+}$ for example, the photocatalytic mixture was clearly deactivated and did not produce O_2 anymore; the final pH was significantly reduced (typically ~ 2.8) and the TON was 36.5. O_2 production resumed with very similar rates as during the first photocatalytic run after neutralization of this solution by addition of NaOH, as well as a new batch of photosensitizer and of $\text{Na}_2\text{S}_2\text{O}_8$, and irradiated further in the same conditions (Figure 2.4b). After 2.25 h light irradiation the final O_2 evolution for $[\text{Ni-MPyP}]^{4+}$ was only 7% lower than in the first run, and for $[\text{Ni-OMeP}]^{4+}$, $[\text{Ni-MeP}]^{4+}$, $[\text{Ni-F8P}]^{4+}$, and $[\text{Ni-TMAP}]^{4+}$ loss of activity was only 1-3% (see Figure 2.4b for $[\text{Ni-F8P}]^{4+}$, and Figure AI.17 for $[\text{Ni-OMeP}]^{4+}$, $[\text{Ni-MeP}]^{4+}$, $[\text{Ni-MPyP}]^{4+}$ and $[\text{Ni-TMAP}]^{4+}$).

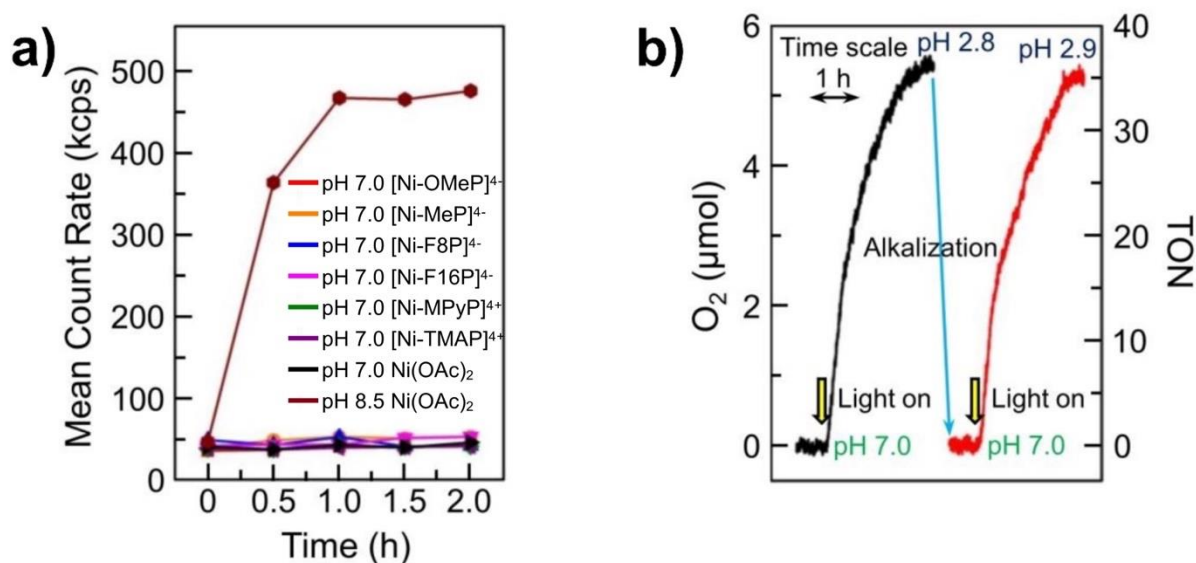


Figure 2.4 a) Dynamic light scattering analysis after various times of photocatalytic water oxidation with different catalysts. Conditions: 50 mM Na₂S₂O₈, 0.67 mM [Ru(bpy)₃]Cl₂ and 0.05 mM water oxidation catalyst [Ni-OMeP]⁴⁻, [Ni-MeP]⁴⁻, [Ni-F8P]⁴⁻, [Ni-F16P]⁴⁻, [Ni-MPyP]⁴⁺, [Ni-TMAP]⁴⁺, or Ni(OAc)₂ in 0.1 M pH 7.0 phosphate buffer, and 50 mM Na₂S₂O₈, 0.67 mM [Ru(bpy)₃]Cl₂ or 0.05 mM Ni-Ac in 0.1 M pH 8.5 phosphate buffer. Conditions: blue light (450 nm, 15.8 mW), T = 298 K. b) Repetitive photocatalytic water oxidation using a homogeneous mixture containing 0.05 mM [Ni-F8P]⁴⁻ with 0.67 mM [Ru(bpy)₃]Cl₂ and 50 mM Na₂S₂O₈ in 0.1 M sodium phosphate buffer (initial pH 7.0), using blue light (450 nm, 15.8 mW), T = 298 K. Between the two irradiation experiments, the solution was neutralized by adding solid NaOH and checking pH, after which 2.0 μmol fresh [Ru(bpy)₃]Cl₂ and 150 μmol Na₂S₂O₈ were added as solids.

As a side note, the pH change during Ni-catalyzed photocatalytic water oxidation is remarkable, but was reported before.^[13] Actually, the pH change from 7.0 to 2.8 was also observed when irradiating, in the same conditions as above, a solution containing the Ru photosensitizer and Na₂S₂O₈ but deprived of Ni catalyst (Figure AI.18). The pH change in photocatalytic conditions can hence essentially be explained by photosensitizer decomposition. Ghosh *et al* reported that formic acid may form by oxidation of the bipyridine ligands when [Ru(bpy)₃]³⁺ is dissolved in aqueous solutions.^[51] We indeed found both acetic and formic acid by ¹H NMR analysis of a D₂O solution containing 0.67 mM [Ru(bpy)₃]Cl₂ and 50 mM Na₂S₂O₈ irradiated for 2.25 h with blue light (450 nm, 15.8 mW, Figure AI.19), which suggests that the reasons causing the pH decrease is at least partly due to the formation of small organic acids derived from oxidation of the bipyridine ligands of the photosensitizer. It was repeatedly

reported that $[\text{Ru}(\text{bpy})_3]\text{Cl}_2$ is not photostable in aqueous photocatalytic conditions.^[42] Such instability obviously explains the limited TON observed in Figure 2.3; one should note, however, that another possible consequence of a lowered pH could be catalyst inactivation, because for some water oxidation catalysts (WOCs) the onset oxidation potential of the catalyst may shift upwards at lower pH.^[13] The cyclic voltammetry (CV) and differential pulse voltammetry (DPV) of Ni-F8 at pH 2.8 (Figure AI.20) showed that OER indeed starts at a higher potential at pH 2.8 (+1.24 V vs. NHE) than at pH 7.0 (+1.12 V vs. NHE), but that the catalyst is still active for the OER, even in such acidic conditions.

In presence of all four components of the photocatalytic system using the catalyst $[\text{Ni-F8P}]^{4-}$, a second photocatalytic run realized after adding fresh PS showed good activity (Figure AI.21). This experiment suggested that photosensitizer decomposition is the main reason for the loss of photocatalytic activity, while the $[\text{Ni-F8P}]^{4-}$ catalyst could indeed cope with the lower pH 2.8 obtained at the end of the first photocatalytic run. In addition, the second photocatalytic run was limited by the low concentration of $\text{Na}_2\text{S}_2\text{O}_8$ remaining in the solution after the first photocatalytic run. Indeed, adding only a new batch of fresh PS to the deactivated solution, did not reactivate the system, while after adding another batch of fresh $\text{Na}_2\text{S}_2\text{O}_8$ as well, the system evolved O_2 for a third time, demonstrating the good stability of the catalyst. In this photocatalytic system, the depletion of photosensitizer and electron acceptor were the main reasons that limited the turnover numbers. Overall, this series of Ni-porphyrin complexes show great photostability not only in absence of photosensitizer and electron acceptor, but also in full photocatalytic conditions. This stability is in great contrast with that of for example $[\text{Ru}(\text{bda})(\text{isoq})_2]$ (H_2bda = 2,2'-bipyridine-6,6'-dicarboxylic acid; isoq = isoquinoline), which decomposes in parallel with the $[\text{Ru}(\text{bpy})_3]^{2+}$ photosensitizer.^[52] These results also demonstrate that the catalytic water-oxidation activity is indeed due to the presence of molecular species dissolved in a homogeneous solution, rather than nickel oxide nanoparticles.

As photocatalysis seems to be run by molecular species, it should be possible to correlate the (photo)catalytic activities to the molecular formulae of the complexes and the electron density of their metal centre. Their redox properties were hence determined by a combination of cyclic voltammetry (CV) and differential pulse voltammetry (DPV) in 0.1 M pH 7.0 phosphate buffer using a glassy-carbon (GC) electrode (Figure AI.22). According to the CV, the electron-rich complexes $[\text{Ni-OMeP}]^{4-}$ and $[\text{Ni-MeP}]^{4-}$ showed slower kinetics for the electrocatalytic OER than the electron-poor $[\text{Ni-F8P}]^{4-}$ and $[\text{Ni-F16P}]^{4-}$, as demonstrated by their lower catalytic current density compared with the blanks. Second, while $[\text{Ni-OMeP}]^{4-}$

showed a single DPV wave, all other complexes showed two waves, with electron-poor Ni-porphyrin complexes having higher DPV oxidation wave potentials. The second DPV wave is usually proposed as the potential at which electrocatalytic O₂ production actually starts.^[1] To check this hypothesis, a controlled potential electrolysis (CPE) experiment was realized in a pH 7.0 phosphate-buffered solution using a system equipped with a Clark electrode for O₂ quantification. Using [Ni-F8P]⁴⁻ (2 mM), a CPE experiment run at the potential of the first DPV wave (+0.98 V vs. NHE) did not evolve any oxygen. However, at the potential of the second DPV wave (+1.12 V vs. NHE) the solution indeed produced significant amounts of O₂ and the current was stable (Figure AI.23a-b). This observation suggests that the first oxidation of [Ni-F8P]⁴⁻ results in the formation of oxidized species Ni^{II}-(por^{•+}) or Ni^{III}-por (por is the porphyrin ligand of [Ni-F8P]⁴⁻) that is not able to catalyze water oxidation and hence can be reduced back to Ni^{II}-por, thus explaining the quasi-reversible redox process at E_{1/2} = +0.98 V vs. NHE. Upon a second electron transfer at the potential of the second DPV wave, a catalytically active species is formed, which may be either Ni^{IV}-por or Ni^{III}-(por^{•+}).^[1,39] No OER activity was observed when the GC electrode used in a first electrolytic run was rinsed with Milli-Q water and used in a second electrocatalytic run using fresh buffer (Figure AI.23c). In addition, the UV-vis spectra of the solution before and after CPE showed no difference (Figure AI.23d). Finally, the faradaic yield of the catalytic system, as determined in CPE was 95%±5%. Overall, Ni-F8 is hence stable in electrocatalytic conditions, and the oxygen evolution as determined in CPE is actually catalyzed by the molecular [Ni-F8P]⁴⁻ complex, at the potential of the second DPV wave.

The complex [Ni-F16P]⁴⁻ behaved quite differently. This electron-poor complex shows, as expected from the higher number of electron-withdrawing substituents, higher oxidation wave potentials in DPV (+1.23 and +1.42 V vs. NHE) than [Ni-F8P]⁴⁻. However, in a 30 min CPE experiment, a 2 mM [Ni-F16P]⁴⁻ solution electrocatalytically catalyzed the OER already at the first DPV wave potential (+1.23 V vs. NHE, see Figure AI.24) with a high faradaic yield (83±3%) showing that [Ni-F16P]⁴⁻ forms a species that is active in OER upon one-electron oxidation. We speculate that this electron-poor species may catalyse water oxidation *via* a binuclear radical coupling mechanism,^[53,54] and that the second DPV wave, which corresponds to further one-electron oxidation to Ni^{IV}-por or Ni^{III}-por^{•+}, may catalyse water oxidation *via* a water nucleophilic attack, potentially with a higher energy barrier than the species formed by the first oxidation.^[1,39] As a note, [Ni-F16P]⁴⁻ is also stable during electrocatalytic OER according to UV-vis spectroscopy (Figure AI.24d). In photocatalytic conditions the photo-

oxidized sensitizer PS^+ ($[\text{Ru}(\text{bpy})_3]^{3+}$) has only a very low driving force $E_{\text{df}} = 30 \text{ mV}$ to trigger hole transfer from PS^+ (+1.26 V vs. NHE) to the catalyst (+1.23 V vs. NHE), and photocatalysis does not take place. Thus, photocatalytic water oxidation can be driven by Ni(II)-porphyrin complexes provided that the redox properties of the catalyst find an optimum: the complex should have a DPV oxidation wave potential that is high enough to be able to drive water oxidation (Step 3 in Figure 2.2) at appreciable overpotential η , but it should be low enough to keep an appreciable driving force E_{df} for the photosensitizer to drive Step 2. In this photocatalytic system, an electron-transfer driving force E_{df} of 30 mV (for $[\text{Ni-F16P}]^{4-}$) is not high enough to drive photocatalysis, while an E_{df} of 140 mV (for $[\text{Ni-F8P}]^{4-}$) appears to be close to the optimum.

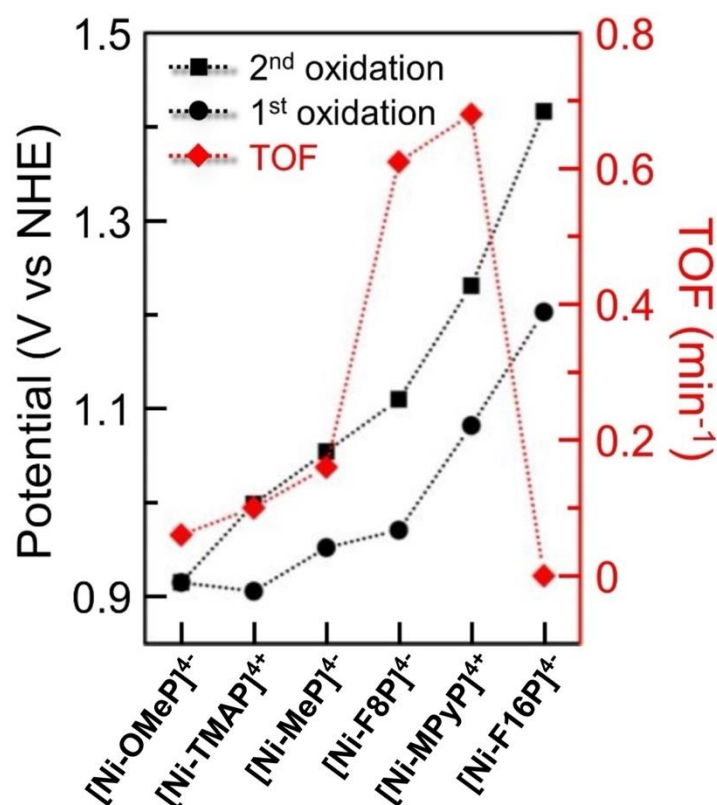


Figure 2.5 DPV oxidation wave potentials (left axis, first and second oxidation shown by circles and squares, respectively) for $[\text{Ni-OMeP}]^{4-}$, $[\text{Ni-MeP}]^{4-}$, $[\text{Ni-F8P}]^{4-}$, $[\text{Ni-F16P}]^{4-}$, $[\text{Ni-MPyP}]^{4+}$, $[\text{Ni-TMAP}]^{4+}$, and maximum TOF (right axis, red diamonds, min^{-1}) obtained in the photocatalytic water oxidation experiments shown in Figure 2.3.

Interestingly, the relative sign of the charge of the molecular catalyst and that of the photosensitizer were found to play a limited role in the relation between redox potentials and photocatalytic rates. Replacing a tetraanionic Ni-porphyrin catalyst by tetracationic Ni-

porphyrin complexes such as $[\text{Ni-MPyP}]^{4+}$ or $[\text{Ni-TMAP}]^{4+}$, did not introduce outliers in the trend discussed above (Figure 2.5). The potential of the second DPV oxidation wave of $[\text{Ni-MPyP}]^{4+}$ is slightly higher (0.12 V) than that of $[\text{Ni-F8P}]^{4-}$, but still lower than the redox potential of the $[\text{Ru}(\text{bpy})_3]^{3+}/[\text{Ru}(\text{bpy})_3]^{2+}$ couple, and indeed a slightly higher TOF was found in photocatalytic conditions for this complex. On the other hand, the potential of the second DPV oxidation wave of $[\text{Ni-TMAP}]^{4+}$ is lower than that of $[\text{Ni-MeP}]^{4-}$, and indeed a slightly lower TOF was found in photocatalysis. Hence it seems that in the series of nickel water-oxidation catalysts $[\text{Ni-OMeP}]^{4-}$, $[\text{Ni-MeP}]^{4-}$, $[\text{Ni-F8P}]^{4-}$, $[\text{Ni-F16P}]^{4-}$, $[\text{Ni-MPyP}]^{4+}$ and $[\text{Ni-TMAP}]^{4+}$, the electron-donating and -withdrawing nature of the porphyrin substituents is the main variable responsible for the variation in the photocatalytic efficiency, while the charge of the complex plays a minor role. Overall, $[\text{Ni-F8P}]^{4-}$ and $[\text{Ni-MPyP}]^{4+}$ were found to be the most active catalysts of this series of nickel complexes for photocatalytic OER. They offer the best compromise in terms of redox potential, i.e., an electrocatalytically active DPV oxidation wave potential that is high enough to maximize η and the rate of Step 3, but low enough for fast electron transfer to occur in Step 2 (Table AI.1).

As $[\text{Ni-F8P}]^{4-}$ appeared to be the most active catalyst for the series of new anionic complexes presented here, the mechanism of the photocatalytic OER in pH 7.0 phosphate buffer solution was further investigated. First, a first-order dependence of the O_2 evolution rate on catalyst concentration was observed using a fixed PS concentration of 0.67 mM (Figure 2.6a, 6b and Figure AI.25a), suggesting that the rate-determining step of the reaction involves a single nickel centre. Second, a first-order dependence of the O_2 evolution rate on PS concentration was found using a fixed $[\text{Ni-F8P}]^{4-}$ catalyst concentration of 50 μM (Figure 2.6c, 6d and Figure AI.25b), indicating that the rate-determining step of the photocatalytic system also involves one molecule of PS. Third, the TOF of the system is not significantly influenced by the photon flux when the light power is higher than 11 mW (Figure AI.26), showing that the photon density is in excess in such conditions, and that Step 1 does not limit the reaction rate. This result was confirmed by an experiment showing that there was very limited change of the rate of O_2 production when the concentration of $\text{Na}_2\text{S}_2\text{O}_8$ was varied in the range 25-100 mM (Figure AI.27). Finally, when $[\text{Ru}(\text{bpy})_3](\text{ClO}_4)_3$ was used as chemical oxidant, the maximum O_2 evolution rate of the catalytic system was found to be linearly dependent on both the concentrations of $[\text{Ru}(\text{bpy})_3]^{3+}$ and that of the $[\text{Ni-F8P}]^{4-}$ catalyst (Figure AI.28), suggesting that the role of the sulfate radical liberated by one-electron transfer from PS^* to $\text{S}_2\text{O}_8^{2-}$, is minimal, i.e., that the photocatalytic O_2 -evolution reaction is indeed driven by the

photochemical generation of $[\text{Ru}(\text{bpy})_3]^{3+}$. Altogether, these results strongly suggest that under such photocatalytic conditions it is the electron transfer from the catalyst to the photo-oxidized photosensitizer PS^+ , i.e. Step 2 in Figure 2.2, that is the rate-determining step of the photocatalytic system. This result, which is reminiscent of a study published by our group using Sun's catalyst $[\text{Ru}(\text{bda})(\text{isoq})_2]$,^[52] is not only important mechanistically speaking; it also demonstrates that the $[\text{Ni-F8P}]^{4-}$ catalyst is fast enough for homogeneous photocatalytic water oxidation. Such a result is important because the catalytic activity of molecular water oxidation catalysts (hence the rate of Step 3) is often presented as the most important parameter to improve for achieving efficient production of solar fuels, while we here confirm that the rate of electron transfer can also be the bottleneck of the reaction. Assuming that only two photons are needed to produce four molecules of $[\text{Ru}(\text{bpy})_3]^{3+}$ that can further be used to evolve one O_2 molecule, the quantum yield for O_2 production using 0.05 mM $[\text{Ni-F8P}]^{4-}$ as the catalyst, 0.67 mM $[\text{Ru}(\text{bpy})_3]\text{Cl}_2$ as PS, 50 mM $\text{Na}_2\text{S}_2\text{O}_8$ as EA and 15.8 mW of blue light (450 nm), is $0.29\% \pm 0.05\%$. This modest value should be considered as strongly encouraging, as it is accompanied by an exceptional stability of the nickel catalysts in photocatalytic conditions, whereas decomposition of the photosensitizer and the depletion of peroxodisulfate limit the turnover number of the system.

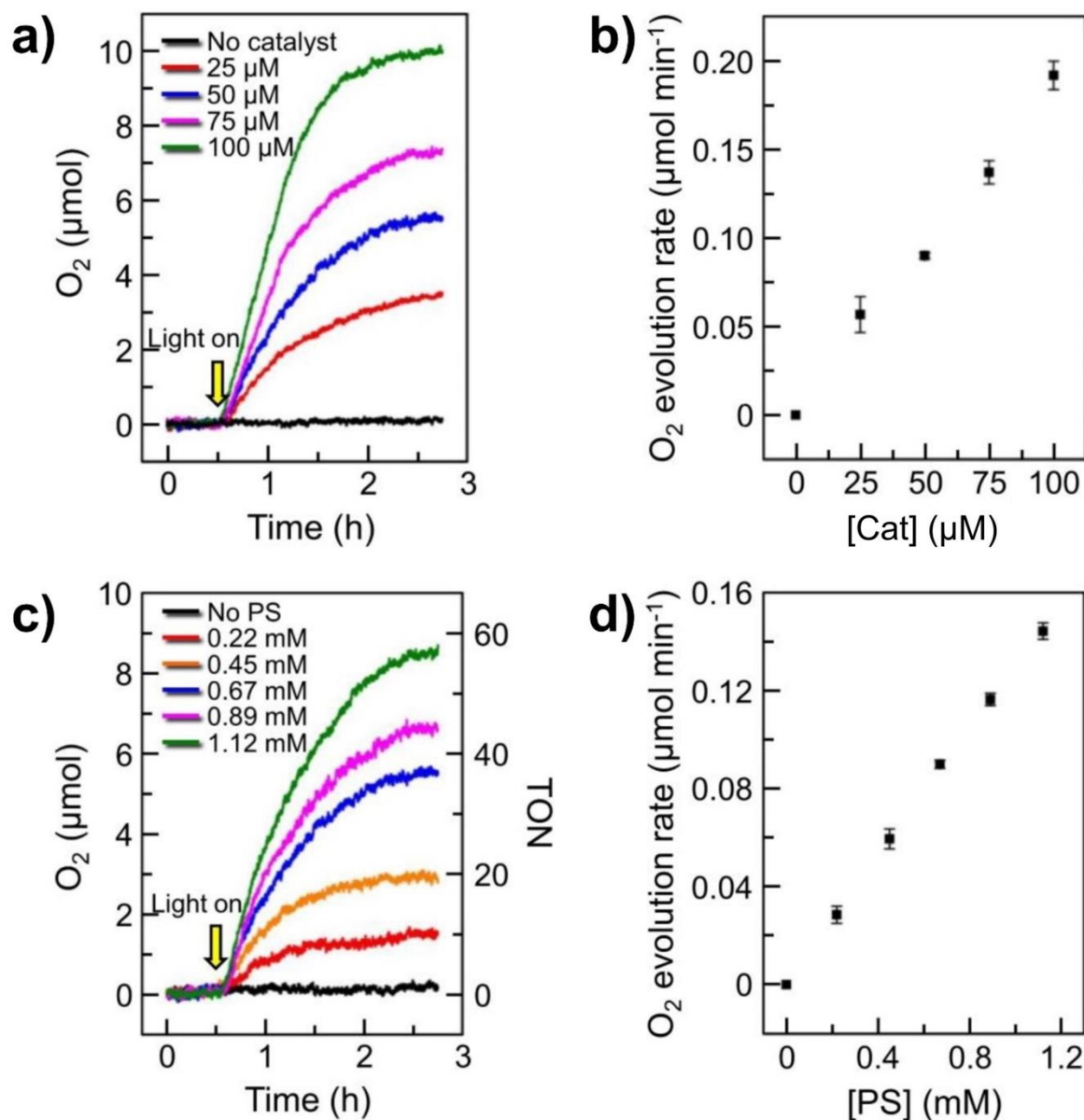


Figure 2.6 Photocatalytic oxygen evolution vs. irradiation time with a) different concentrations of $[\text{Ni-F8P}]^{4-}$ with 0.67 mM $[\text{Ru}(\text{bpy})_3]\text{Cl}_2$ as photosensitizer, and c) different concentrations of PS with 50 μM $[\text{Ni-F8P}]^{4-}$ as WOC. b) and d) maximum O₂ evolution rate during photocatalytic O₂ evolution plotted as a function of b) the concentration of $[\text{Ni-F8P}]^{4-}$ and d) the concentration of $[\text{Ru}(\text{bpy})_3]\text{Cl}_2$. Conditions: 50 mM $\text{Na}_2\text{S}_2\text{O}_8$ in 0.1 M sodium phosphate buffer (initial pH 7.0), blue light (450 nm, 15.8 mW), $T = 298$ K.

2.3 Conclusion

A series of four anionic Ni-porphyrin complexes was prepared that show promising catalytic properties for electrocatalytic and photocatalytic water oxidation in neutral to acidic phosphate-

buffered homogeneous aqueous solutions. Electrochemical studies revealed that modifications of the tetrasulfonatoporphyrin ligand with more electron-withdrawing substituents increased the potentials of the DPV oxidation waves, and strongly influenced the rate of the OER in photocatalytic conditions. A balance has to be found between increasing these oxidation potentials, which provide a higher driving force (η) for the nickel-catalyzed OER reaction itself, and lowering it, to keep the driving force for electron transfer from the catalyst to the oxidized photosensitizer PS^+ (E_{df}), high enough. $[Ni-F16P]^4-$, for example, is too electron-poor, which inactivates photocatalysis by blocking the electron transfer of Step 2. A photosensitizer with a higher oxidation potential than the $[Ru(bpy)_3]^{3+}/[Ru(bpy)_3]^{2+}$ couple may alleviate this problem and unravel the otherwise excellent electrocatalytic OER properties of this complex. By contrast, $[Ni-F8P]^4-$ and $[Ni-MPyP]^4-$ were found close to the optimum, at least for $[Ru(bpy)_3]^{2+}$ as photosensitizer, and offered excellent activity for the photocatalytic OER. Critically, these first-row transition metal complexes showed great stability both in photocatalytic and electrocatalytic conditions, and for $[Ni-F8P]^4-$ the TON of the photocatalytic system appeared to be limited predominantly by decomposition of the ruthenium photosensitizer. This work represents a significant advance in the field of solar fuel production, since it provides a rare example of homogeneous light-driven water oxidation catalyzed by Ni-based molecular catalyst, and this in neutral to acidic aqueous solutions. Last but not least, it provides a clear framework to design molecular catalysts for photocatalysis: the electron-density of the catalytic centre should be fine-tuned with appropriate substituents, to balance the driving forces of catalytic water oxidation vs. electron transfer from the catalyst to PS^+ .

2.4 Experimental section

2.4.1 Materials and methods

All reagents were purchased from Sigma-Aldrich and used as received unless otherwise noted. The compounds 5,10,15,20-tetrakis(2,6-dimethoxyphenyl)-21*H*,23*H*-porphyrin (OMeTPP),^[55] tetrasodium-5,10,15,20-tetrakis(2,6-dimethylphenyl-3-sulfonatophenyl)-21*H*,23*H*-porphyrin ($[H_2-MeP]^4-$),^[56] tetrasodium-5,10,15,20-tetrakis(2,6-difluoro-3-sulfonatophenyl)-21*H*,23*H*-porphyrin ($[H_2-F8P]^4-$),^[57] tetrasodium-2,3,7,8,12,13,17,18-octafluoro-5,10,15,20-tetrakis(2,6-difluoro-3-sulfonatophenyl)-21*H*,23*H*-porphyrin ($[H_2-F16P]^4-$),^[58] 5,10,15,20-tetrakis(4-*N*-methylpyridyl)porphyrin-nickel(II) tetratriflate ($[Ni-MPyP]^4-$),^[39,59] 5,10,15,20-tetrakis(4-(*N,N,N*-trimethylammonio)phenyl)porphyrin-nickel(II) tetratriflate ($[Ni-TMAP]^4-$),^[59] and $[Ru(bpy)_3](ClO_4)_3$ ^[60,61] were prepared according to

published methods. ^1H NMR spectra were recorded on a Bruker 400DPX-liq spectrometer operating at 400 MHz. ^{13}C NMR spectra and ^{19}F NMR spectra were recorded on a Bruker 500DPX spectrometer operating at 500 MHz. Mass spectra were obtained using a Finnigan Aqueous Mass Spectrometer (MS) with electrospray ionization (ESI) in negative ion mode. High-resolution mass spectrometric measurements were made on a Bruker Fourier Transform Ion Cyclotron Resonance Mass Spectrometer APEX IV at Leiden University. Elemental analyses were performed at the Mikroanalytisches Laboratorium Kolbe, Germany. Electronic absorption spectra were obtained on a Varian Cary 60 spectrophotometer at 25 °C during the spectrophotometric measurements. The LED optical power was measured using an OPHIR Nova-display laser power meter.

2.4.2 Synthesis

Tetrasodium 5,10,15,20-tetrakis(2,6-dimethoxyl-3-sulfonatophenyl)-21*H*,23*H*-porphyrin ($\text{Na}_4[\text{H}_2\text{-OMeP}]$)

5,10,15,20-Tetrakis(2,6-dimethoxyphenyl)-21*H*,23*H*-porphyrin (85 mg, 0.10 mmol) and anhydrous CH_2Cl_2 (100 mL) were placed under N_2 in a 250 mL three-neck round-bottom flask equipped with a magnetic stirring bar and rubber stoppers. Chlorosulfonic acid (58 mg, 34 μL , 0.50 mmol) was injected into the stirred solution using a microsyringe and the reaction mixture was stirred for 3 h at room temperature. Water (100 mL) was then added to the solution and the water phase was collected using a separating funnel. A few drops of saturated aqueous NaHCO_3 solution were used to neutralize the solution to $\text{pH} \geq 8$. The water was evaporated at 40 °C using a rotary evaporator and the residue was redissolved in cold methanol (20 mL). The solution was filtered over filter paper to remove excess NaHCO_3 , and the solvent was evaporated. The crude product was then purified on a Sephadex-20H size exclusion chromatography column to remove remaining salts (eluent: methanol) and methanol was finally rotary evaporated and the solid dried in vacuo afforded $\text{Na}_4[\text{H}_2\text{-OMeP}]$ as a dark red solid. Yield (115 mg, 91%); ^1H NMR (400 MHz, CD_3OD): δ = 8.85 (br, 8H; β -pyrrole-H), 8.41 (d, J = 9 Hz, 4H; p -Ph-H), 7.36 – 7.24 (m, 4H; m -Ph-H), 3.69, 3.67, 3.65, 3.64, 3.63, 3.61 (6 “s”, ca. 1:2:1:1:2:1, 12H; OCH_3), 3.06, 3.00, 2.99, 2.96, 2.93, 2.87 ppm (6 “s”, ca. 1:2:1:1:2:1, 12H; OCH_3); ^{13}C NMR (126 MHz, CD_3OD): δ = 163.9, 159.6, 132.2, 131.7, 127.0, 111.9, 106.7, 68.7, 62.3, 56.5, 27.0 ppm; MS (ESI neg. ion): m/z calcd for $\text{C}_{52}\text{H}_{42}\text{N}_4\text{O}_{20}\text{S}_4^{4-}$: 292.5 [$M-4\text{Na}$] $^{4-}$; found: 292.7; $\text{C}_{52}\text{H}_{42}\text{N}_4\text{O}_{20}\text{S}_4^{4-} + \text{H}^+$: 390.4 [$M-4\text{Na} + \text{H}$] $^{3-}$; found: 390.5; $\text{C}_{52}\text{H}_{42}\text{N}_4\text{O}_{20}\text{S}_4^{4-} + \text{CH}_3\text{OH} + \text{H}^+$: 401.1 [$M-4\text{Na} + \text{CH}_3\text{OH} + \text{H}$] $^{3-}$; found: 401.2; $\text{C}_{52}\text{H}_{42}\text{N}_4\text{O}_{20}\text{S}_4^{4-} + \text{Na}^+ + \text{H}^+$: 597.1

$[M-3Na+H]^{2-}$; found: 597.2; HRMS (ESI): m/z calcd for $C_{52}H_{47}N_4O_{20}S_4^+$: 1175.1661 $[M-4Na+5H]^+$; found: 1175.1665.

Tetrasodium 5,10,15,20-tetrakis(2,6-dimethoxyl-3-sulfonatophenyl)porphyrin nickel(II) ($Na_4[Ni-OMeP]$)

The ligand $Na_4[H_2-OMeP]$ (115 mg, 0.09 mmol) and Milli-Q water (40 mL) were placed under N_2 in a 100 mL round-bottom flask equipped with a magnetic stirring bar and a condenser. A solution of Ni(II) acetate tetrahydrate (112 mg, 0.45 mmol) in Milli-Q water (10 mL) was added to the stirred solution, and the mixture was refluxed for 12 h under N_2 . After cooling to room temperature, water was rotary evaporated at 40 °C and the residue was redissolved in cold methanol (15 mL). After filtration on a filter paper, methanol was rotary-evaporated, the residue was redissolved in cold methanol (5 mL). The solution was filtered by filter paper, rotary-evaporated, and the crude product was redissolved in Milli-Q water (5 mL) then passed onto an Amberlite IR 120 Na^+ form ion exchange resin column (10 cm), washed with Milli-Q water and further purified on Sephadex-20H size exclusion chromatography to remove excess nickel acetate (methanol). Methanol was finally rotary evaporated and the solid dried in vacuo. Yield (113 mg, 89%); 1H NMR (400 MHz, CD_3OD): δ = 8.82 – 8.65 (m, 8H; β -pyrrole-H), 8.36 – 8.32 (m, 4H; p -Ph-H), 7.33, 7.30, 7.23, 7.14 (4 “d”, J = 9 Hz, ca. 1:3:3:1, 4H; m -Ph-H), 3.83 (“s”), 3.76 (“d”), 3.63 (“d”), 3.48 (“s”) (ca. 1:3:3:1, 12 H; OCH_3), 3.24, 3.01, 2.99, 2.82, 2.75, 2.69 ppm (6 “s”, ca. 1:1:2:2:1:1, 12 H; OCH_3); MS (ESI neg. ion): m/z calcd for $C_{52}H_{40}N_4NiO_{20}S_4^{4-}$: 306.5 $[M-4Na]^{4-}$; found: 306.7; $C_{52}H_{40}N_4NiO_{20}S_4^{4-}+H^+$: 409.0 $[M-4Na+H]^{3-}$; found: 409.2; $C_{52}H_{40}N_4NiO_{20}S_4^{4-}+CH_3OH+H^+$: 419.7 $[M-4Na+CH_3OH+H]^{3-}$; found: 419.8; $C_{52}H_{40}N_4NiO_{20}S_4^{4-}+2Na^+$: 636.0 $[M-2Na]^{2-}$; found: 636.1; HRMS (ESI): m/z calcd for $C_{52}H_{44}N_4NiO_{20}S_4Na^+$: 1153.0677 $[M-3Na+4H]^+$; found: 1153.0668; elemental analysis calcd (%) for $C_{52}H_{40}N_4Na_4NiO_{20}S_4 \cdot 5H_2O$: C 44.30, H 3.57, N 3.97; found: C 44.29, H 3.31, N 3.93. UV-vis (H_2O): $\lambda_{max}(\epsilon)$ 409 nm (3.4×10^5), 525 nm (2.3×10^4), 558 nm ($9.5 \times 10^3 M^{-1} cm^{-1}$).

Tetrasodium 5,10,15,20-tetrakis(2,6-dimethyl-3-sulfonatophenyl)porphyrin nickel(II) ($Na_4[Ni-MeP]$)

Tetrasodium 5,10,15,20-tetrakis(2,6-dimethyl-3-sulfonatophenyl)-21*H*,23*H*-porphyrin·9*H*₂O (130 mg, 0.10 mmol) and Milli-Q water (40 mL) were placed under N_2 in a 100 mL round-bottom flask equipped with a magnetic stirring bar and a condenser. A solution of Ni(II) acetate tetrahydrate (124 mg, 0.50 mmol) in Milli-Q water (10 mL) was added to the

stirred solution and the mixture was refluxed for 12 h under N₂. After cooling to room temperature, water was rotary evaporated and the residue was redissolved in cold methanol (15 mL). After filtration on a filter paper, methanol was rotary-evaporated, the residue was redissolved in cold methanol (5 mL), the solution was filtered a second time by filter paper and rotary-evaporated, then the crude product was then passed onto an Amberlite IR 120 Na⁺ form ion exchange resin column (10 cm), washed with Milli-Q water and finally purified on Sephadex-20H size exclusion chromatography (methanol). Methanol was finally rotary evaporated and the solid dried in vacuo. Yield (120 mg, 92%); ¹H NMR (400 MHz, CD₃OD): δ = 8.60 – 8.57 (m, 8H; β -pyrrole-H), 8.33 – 8.29 (m, 4H; *p*-Ph-H), 7.52 – 7.47 (m, 4H; *m*-Ph-H), 2.38 – 2.23 (m, 12H; CH₃), 1.86 – 1.76 ppm (m, 12H; CH₃); MS (ESI neg. ion): *m/z* calcd for C₅₂H₄₁N₄NiO₁₂S₄⁴⁻+H⁺: 366.4 [M-4Na+H]³⁻; found: 366.4; C₅₂H₄₀N₄NiO₁₂S₄⁴⁻+Na⁺: 373.7 [M-3Na]³⁻; found: 373.9; C₅₂H₄₀N₄NiO₁₂S₄⁴⁻+2Na⁺: 572.0 [M-2Na]²⁻; found: 572.3; HRMS (ESI): *m/z* calcd for C₅₂H₄₅N₄NiO₁₂S₄⁺: 1103.1264 [M-4Na+5H]⁺; found: 1103.1259; C₅₂H₄₃N₄NiO₁₂S₄+2Na⁺: 1169.0723 [M-2Na+3H]⁺; found: 1169.0732; elemental analysis calcd (%) for C₅₂H₄₀N₄NiO₁₂S₄·6H₂O: C 48.05, H 4.03, N 4.31; found: C 47.95, H 4.14, N 4.33. UV-vis (H₂O): λ_{max} (ϵ) 411 nm (2.0×10^5), 521 nm (1.1×10^4), 615 nm (4.1×10^3) 646 nm (3.2×10^3 M⁻¹ cm⁻¹).

Tetrasodium 5,10,15,20-tetrakis(2,6-difluoro-3-sulfonatophenyl)porphyrin nickel(II) (Na₄[Ni-F8P])

Tetrasodium 5,10,15,20-tetrakis(2,6-difluoro-3-sulfonatophenyl)-21*H*,23*H*-porphyrin·4H₂O (124 mg, 0.10 mmol) and Milli-Q water (40 mL) were placed under N₂ in a 100 mL round-bottom flask equipped with a magnetic stirring bar and a condenser. A solution of Ni(II) acetate tetrahydrate (124 mg, 0.50 mmol) in Milli-Q water (10 mL) was added to the stirred solution and the mixture was refluxed for 12 h under N₂. After cooling to room temperature, the water was rotary evaporated and the residue was redissolved in cold methanol (15 mL), and filtered on a filter paper. After filtration, methanol was rotary-evaporated, the residue was redissolved in cold methanol (5 mL), the solution was filtered by filter paper and rotary-evaporated. The crude Na₄[Ni-F8P] product was finally passed through an Amberlite IR 120 Na⁺ form ion exchange resin column (10 cm), washed with Milli-Q water and purified on a Sephadex-20H size exclusion chromatography column (eluent: methanol). Methanol was finally rotary evaporated and the solid dried in vacuo. Yield (115 mg, 90%); ¹H NMR (400 MHz, CD₃OD): δ = 9.03 – 8.99 (m, 8H; β -pyrrole-H), 8.45 – 8.38 (m, 4H; *p*-Ph-H), 7.56

– 7.50 ppm (m, 4H; *m*-Ph-H); ^{19}F NMR (471 MHz, CD_3OD): δ = -105.95 – -106.10 (m, 4F; *o*-F), -106.35 – -106.50 ppm (m, 4F; *o*-F); MS (ESI neg. ion): m/z calcd for $\text{C}_{44}\text{H}_{16}\text{F}_8\text{N}_4\text{NiO}_{12}\text{S}_4^{4-}$: 282.5 [$M-4\text{Na}$] $^{4-}$; found: 282.7; $\text{C}_{44}\text{H}_{16}\text{F}_8\text{N}_4\text{NiO}_{12}\text{S}_4^{4-}+\text{H}^+$: 377.0 [$M-4\text{Na}+\text{H}$] $^{3-}$; found: 377.2; $\text{C}_{44}\text{H}_{16}\text{F}_8\text{N}_4\text{NiO}_{12}\text{S}_4^{4-}+\text{Na}^+$: 384.3 [$M-3\text{Na}$] $^{3-}$; found: 384.6; $\text{C}_{44}\text{H}_{16}\text{F}_8\text{N}_4\text{NiO}_{12}\text{S}_4^{4-}+2\text{Na}^+$: 587.9 [$M-2\text{Na}$] $^{2-}$; found: 587.9; HRMS (ESI): m/z calcd for $\text{C}_{44}\text{H}_{20}\text{F}_8\text{N}_4\text{NiO}_{12}\text{S}_4\text{Na}^+$: 1156.9078 [$M-3\text{Na}+4\text{H}$] $^+$; found: 1156.9063; elemental analysis calcd (%) for $\text{C}_{44}\text{H}_{16}\text{F}_8\text{N}_4\text{Na}_4\text{NiO}_{12}\text{S}_4 \cdot 3\text{H}_2\text{O}$: C 41.37, H 1.74, N 4.39; found: C 41.53, H 1.68, N 4.36. UV-vis (H_2O): $\lambda_{\text{max}}(\epsilon)$ 400 nm (3.1×10^5), 521 nm (1.9×10^4), 562 nm ($7.9 \times 10^3 \text{ M}^{-1} \text{ cm}^{-1}$).

Tetrasodium 2,3,7,8,12,13,17,18-octafluoro-5,10,15,20-tetrakis(2,6-difluoro-3-sulfonatophenyl)porphyrin nickel(II) ($\text{Na}_4[\text{Ni-F16P}]$)

Tetrasodium 2,3,7,8,12,13,17,18-octafluoro-5,10,15,20-tetrakis(2,6-difluoro-3-sulfonatophenyl)-21*H*,23*H*-porphyrin·5 H_2O (140 mg, 0.10 mmol) and Milli-Q water (40 mL) were placed under N_2 in a 100 mL round-bottom flask equipped with a magnetic stirring bar and a condenser. A solution of Ni(II) acetate tetrahydrate (124 mg, 0.50 mmol) in Milli-Q water (10 mL) was added to the stirred solution and the mixture was refluxed for 12 h under N_2 . After cooling to room temperature, the water was rotary evaporated and the residue was redissolved in cold methanol (15 mL). After filtration over a filter paper, methanol was rotary-evaporated, the residue was redissolved in cold methanol (5 mL), and filtered by filter paper again. The filtrate was rotary-evaporated and the $\text{Na}_4[\text{Ni-F16P}]$ complex was then passed through an Amberlite IR 120 Na^+ form ion exchange resin column (10 cm) and washed with Milli-Q water before being purified on Sephadex-20H size exclusion chromatography (eluent: methanol). Methanol was finally rotary evaporated and the solid dried in vacuo. Yield (124 mg, 86%); ^1H NMR (400 MHz, CD_3OD): δ = 8.89 (s, 4H; *p*-Ph-H), 8.00 ppm (s, 4H; *m*-Ph-H); ^{19}F NMR (471 MHz, CD_3OD): δ = -106.55 (s, 4F; *o*-F), -107.20 ppm (s, 4F; *o*-F) (the β -pyrrole-F atoms are not observed because of the nearby Ni^{2+} metal centre); MS (ESI neg. ion): m/z calcd for $\text{C}_{44}\text{H}_8\text{F}_{16}\text{N}_4\text{NiO}_{12}\text{S}_4^{4-}$: 318.5 [$M-4\text{Na}$] $^{4-}$; found: 318.9; $\text{C}_{44}\text{H}_8\text{F}_{16}\text{N}_4\text{NiO}_{12}\text{S}_4^{4-}+\text{Na}^+$: 432.3 [$M-3\text{Na}$] $^{3-}$; found: 432.3; $\text{C}_{44}\text{H}_8\text{F}_{16}\text{N}_4\text{NiO}_{12}\text{S}_4^{4-}+2\text{Na}^+$: 659.9 [$M-2\text{Na}$] $^{2-}$; found: 659.9; HRMS (ESI): m/z calcd for $\text{C}_{44}\text{H}_{12}\text{F}_{16}\text{N}_4\text{NiO}_{12}\text{S}_4\text{Na}^+$: 1300.8325 [$M-3\text{Na}+4\text{H}$] $^+$; found: 1300.8313; elemental analysis calcd (%) for $\text{C}_{44}\text{H}_8\text{F}_{16}\text{N}_4\text{Na}_4\text{NiO}_{12}\text{S}_4 \cdot 4\text{H}_2\text{O}$: C 36.71, H 1.12, N 3.89; found: C 36.41, H 0.85, N 3.85. UV-vis (H_2O): $\lambda_{\text{max}}(\epsilon)$ 338 nm (3.9×10^4), 408 nm (3.0×10^5), 539 nm ($1.9 \times 10^4 \text{ M}^{-1} \text{ cm}^{-1}$)

2.4.3 Cyclic voltammetry and differential pulse voltammetry

Cyclic voltammetry (CV) and differential pulse voltammetry (DPV) measurements were performed using an Autolab PGstart10 potentiostat controlled by GPES4 software. All the CV and DPV measurements were recorded in 0.1 M sodium phosphate buffer (pH 7.0) using a three-compartment cell possessing a 0.07 cm² glassy-carbon electrode as the working electrode, Pt wire as the auxiliary electrode, Ag/AgCl (saturated KCl aq.) as the reference electrode, and K₃[Fe(CN)₆] was added at the end of the measurements as internal standard ($E([Fe(CN)_6]^{3-}/[Fe(CN)_6]^{4-}) = +0.361$ V vs NHE).^[62] Unless otherwise indicated, the potential was converted relative to NHE, the solutions were bubbled with high-purity argon for at least 30 min before analysis.

2.4.4 Photo-induced oxygen production

Photo-induced oxygen production from water was analyzed by a Clark oxygen electrode (Unisense OX-NP) controlled by x-5 UniAmp using Logger software. The irradiation source was an OSRAM Opto Semiconductors LD W5SM LED (λ_{irr} 450 nm, $\Delta\lambda_{1/2} = 25$ nm) with water cooling. All the photochemical oxygen production measurements were carried out in a thermostated (298 K) photochemical reactor (total volume 25.0 mL). [Ru(bpy)₃]Cl₂·6H₂O (1.5 mg, 0.67 mM), the catalyst [Ni-OMeP]⁴⁺, N [Ni-MeP]⁴⁺, [Ni-F8P]⁴⁺, [Ni-F16P]⁴⁺, [Ni-MPyP]⁴⁺, [Ni-TMAP]⁴⁺ or Ni(II) acetate (0.05 mM), and Na₂S₂O₈ (35.7 mg, 50 mM) were added as solids in the reactor, and dissolved using sodium phosphate buffer (0.1 M, pH 7.0, 3.0 mL). Under constant stirring, the reactor was equipped with 1 rubber septum and 2 silicon septa in order to make an air-tight system (the set-up is shown in Figure AI.29). The Clark oxygen electrode was then inserted through the septum, to measure the dioxygen concentration in the head space (gas phase) of the photochemical reactor, and the whole system was deaerated by high-purity argon for at least 30 min. After removing the argon, the Clark oxygen electrode was calibrated by a four-time injection of 100 μ L (4.46 μ mol at 1 atm) of high-purity O₂ into the closed system, thereby limiting the overpressure to <2%; the calibration was adapted with the pressure change using Logger software, affording direct reading of the volume of dioxygen (μ L) produced in the gas phase of the reactor ($V_{gas} = 22.0$ mL). Following calibration, the three used septa were replaced by new ones and Clark oxygen electrode was inserted into the system again. The system was degassed for 30 min with argon, then data recording was started, first keeping the system in the dark for another 30 min prior to starting light irradiation. Unless otherwise indicated, the data recording was stopped after 2.25 h of light irradiation.

2.4.5 Catalytic dioxygen production in the dark using $[\text{Ru}(\text{bpy})_3](\text{ClO}_4)_3$ as chemical oxidant

Dark oxygen production from water using $[\text{Ru}(\text{bpy})_3](\text{ClO}_4)_3$ as chemical oxidant was analyzed by a Clark oxygen electrode (Unisense OX-NP) controlled by x-5 UniAmp using Logger software. The $[\text{Ru}(\text{bpy})_3](\text{ClO}_4)_3$ was synthesized according to published methods,^[7,8] stored as solid under vacuum in the fridge, and used within two days. All the chemical oxygen production measurements were carried out in a thermostated (298 K) reactor (total volume 10.0 mL). Sodium phosphate buffer (0.1 M, pH 7.0, 4.5 mL) was added in the reactor and under constant stirring, the reactor was equipped with a rubber septum and two silicon septa in order to make an air-tight system. The Clark oxygen electrode was then inserted through the septum, to measure the dioxygen concentration in the head space (gas phase) of the reactor, and the whole system was deaerated by high-purity argon for at least 30 min. After removing the argon, the Clark oxygen electrode was calibrated by a four-time injection of 100 μL (4.46 μmol at 1 atm) of high-purity O_2 into the closed system, thereby limiting the overpressure to <8%; the calibration was adapted with the pressure change using Logger software, affording direct reading of the volume of dioxygen (μL) produced in the gas phase of the reactor ($V_{\text{gas}} = 5.5$ mL). The reactor was cleaned and dried after calibration, $\text{Na}_4[\text{Ni-F8P}]$ was then added as solids in the reactor and dissolved using sodium phosphate buffer (0.1 M, pH 7.0, 4.0 mL), three new septa and Clark oxygen electrode were adapted to the system again. The system was degassed for 30 min with argon, at the same time 5 mL sodium phosphate buffer (0.1 M, pH 7.0) was degassed in a 10 mL flask equipped with a rubber septum, $[\text{Ru}(\text{bpy})_3](\text{ClO}_4)_3$ was weighed as solid and stored in a Schlenk tube equipped with a rubber septum under argon. 0.5 mL degassed buffer was quickly transferred to the Schlenk tube to dissolve $[\text{Ru}(\text{bpy})_3](\text{ClO}_4)_3$ and the resulting solution was injected to the reactor using an air-tight syringe, then the data recording was started. Unless otherwise indicated, the data recording was stopped after 40 min reaction.

2.4.6 Controlled-potential electrolysis equipped with a Clark electrode

Controlled-potential electrolysis (CPE) experiments coupled with a Clark oxygen electrode were CPE systems for oxygen evolution from water analysed by a Clark oxygen electrode (Unisense OX-NP) controlled by x-5 UniAmp using Logger software. The Clark oxygen electrode was two points calibrated in air saturated water and deaerated water before use. Different functional potentials were controlled by an Autolab PGstart10 potentiostat using GPES4 software to electrocatalyze OER using possessing a 0.07 cm^2 glassy-carbon electrode

as the working electrode, Pt wire as the auxiliary electrode, Ag/AgCl (saturated KCl aq.) as the reference electrode from a solution contains [Ni-F8P]⁴⁻ or [Ni-F16P]⁴⁻ (2.0 mM) in 0.1 M sodium phosphate buffer (pH 7.0, 6 mL) in a thermostated (298 K) electrochemical reactor (total volume 25 mL). A calibrated Clark oxygen electrode was set into the constant stirring solution to analyse the oxygen produced from the CPE system in aqueous phase. The whole system was deaerated by high-purity argon for at least 30 min and the top part of the reactor (gas phase) was always kept in argon atmosphere via argon flowing. Data recording of both systems started together, after electrolysis for 30 min, the two systems were stopped at the same time. Unless otherwise indicated, the data recording was stopped at the end of the 30 min electrolysis.

2.4.7 Calculation of Faradaic yield of CPE

The Faradaic yield (FY) was calculated using the amount of charge (It) passed in the electrochemical reactor, calculated by integrating the current (I) vs. electrolysis time (t), and the number of mol of dioxygen produced n_{O_2} according to the following equation:

$$FY = \frac{4 \times 96485 n_{O_2}}{It}$$

in which n_{O_2} is the number of mol of dioxygen calculated from the concentration of the dioxygen produced in the CPE experiment as indicated by the calibrated Clark oxygen electrode in solution ($\mu\text{mol L}^{-1}$), times with the volume of CPE solution (6 mL); I is the current, t is the CPE time.

2.4.8 Dynamic Light Scattering

Dynamic Light scattering (DLS) was chosen to determine the numbers of particles in 0.1 M initial pH 7.0 sodium phosphate buffer solutions contain 0.67 mM [Ru(bpy)₃]Cl₂, 50 mM Na₂S₂O₈ and 0.05 mM 1) [Ni-OMeP]⁴⁻, 2) [Ni-MeP]⁴⁻, 3) [Ni-F8P]⁴⁻, 4) [Ni-F16P]⁴⁻, 5) [Ni-MPyP]⁴⁺, 6) [Ni-TMAP]⁴⁺, or 7) Ni(II) acetate and 8) 0.1 M initial pH 8.5 sodium phosphate buffer solution contains 0.67 mM [Ru(bpy)₃]Cl₂, 50 mM Na₂S₂O₈ and 0.05 mM Ni(II) acetate after 0, 0.5, 1.0, 1.5, 2.0 hours using a ZEN 1600 Zetasizer Nano instrument (Malvern Instruments Limited) operating with a 633 nm laser.

2.4.9 Turnover number determination

The turnover number (TON) of oxygen evolution was determined by a Clark oxygen electrode (Unisense OX-NP) controlled by x-5 UniAmp using Logger software. The amount of oxygen formed during 2.25 h illumination was used to calculate the TON. The TON were calculated from the oxygen production data by the following equation:

$$TON = \frac{n_{O_2}}{n_{cat}}$$

in which n_{O_2} is the number of mol of dioxygen calculated from the volume of the dioxygen produced in the photocatalytic experiment as indicated by the calibrated Clark oxygen electrode in the gas phase (μL), divided by 22.4 L/mol, and n_{cat} is the number of mol of nickel catalyst used in the photocatalytic experiment.

The maximum turnover frequency TOF_{max} (in min^{-1}) of photocatalytic oxygen evolution was obtained using Origin 9.1 software by 1) nonlinear curve fitting of the time evolution of the TON, starting at $t = 30$ min for photocatalytic reactions (category: Growth/Sigmoidal, function: logistic Fit); 2) calculating the first derivative $TOF = f(t)$ using mathematics, differentiate, and 3) identify the maximum value TOF_{max} of $TOF = f(t)$ (example of $[\text{Ni-F8P}]^{4-}$ see Figure 2.7).

The maximum O_2 evolution rate (in min^{-1}) of photocatalytic oxygen evolution was obtained using Origin 9.1 software by 1) nonlinear curve fitting of the time evolution of the mol of oxygen evolved, starting at $t = 30$ min and at $t = 0$ for dark oxygen production using $[\text{Ru}(\text{bpy})_3](\text{ClO}_4)_3$ as chemical oxidant (category: Growth/Sigmoidal, function: logistic Fit); 2) calculating the first derivative O_2 evolution rate = $f(t)$ using mathematics, differentiate, and 3) identify the maximum O_2 evolution rate value of O_2 evolution rate = $f(t)$ (example for $[\text{Ni-F8P}]^{4-}$: see Figure 2.8).

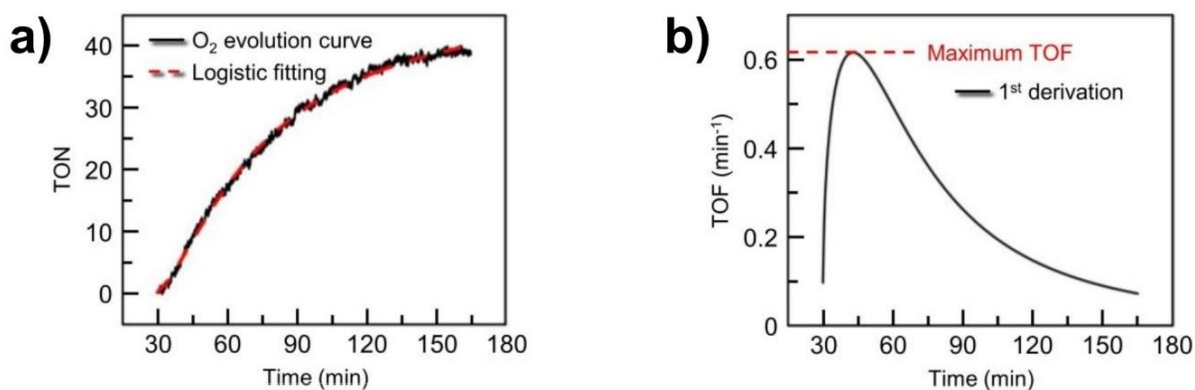


Figure 2.7 Calculation of maximum turnover frequency of $[\text{Ni-F8P}]^{4-}$.

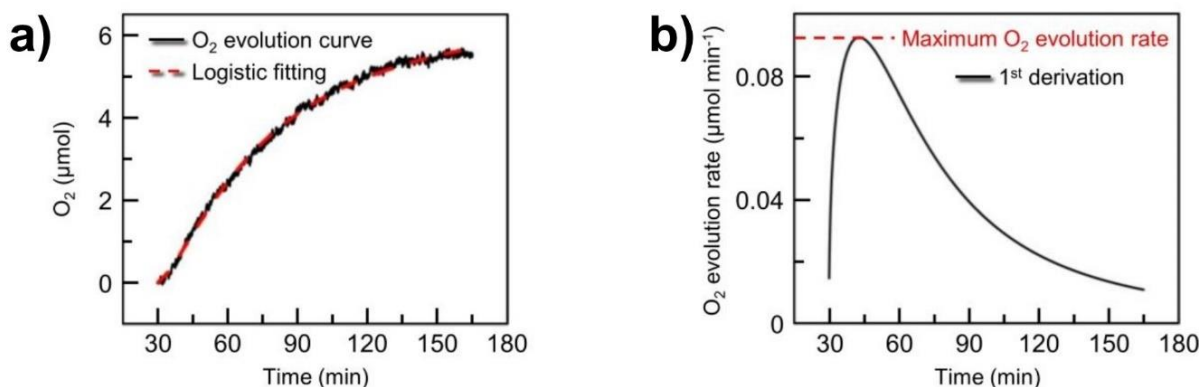


Figure 2.8 Calculation of maximum O_2 evolution rate of $[Ni-F8P]^{4-}$.

2.4.10 Calculation of photochemical O_2 production quantum yield

The O_2 generation quantum yield was calculated using the TOF_{max} , n_{cat} and the rate of photons absorption:

$$\varphi = \frac{2n_{cat}TOF_{max}}{60\Phi(1 - 10^{-A_e})(A_{PS}/A_e)}$$

in which TOF_{max} (min^{-1}) is the maximum turnover frequency of the photocatalytic oxygen evolution reaction, n_{cat} (in μmol) is the number of mol of nickel catalyst used in the photocatalytic experiment, Φ is the photon flux ($\mu\text{mol s}^{-1}$) determined by standard ferrioxalate actinometry (typically $1.05 \mu\text{mol s}^{-1}$, 15.8 mW),^[63] A_e is the total absorption of the photocatalytic solution at 450 nm ($A_e > 3$), A_{PS} is the absorption of photosensitizer only in buffer at 450 nm ($A_{PS}/A_e \sim 1$), and 60 is the number of seconds per minute. In this calculation we assumed 2 photons were needed for each molecule of O_2 produced.

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2.6 References

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3

Effects of Electron-Withdrawing and Electron-Donating Substituents on the pH Dependence of Co(III)-porphyrin Catalysts for Homogeneous Photocatalytic Hydrogen Evolution

A series of anionic Co(III)- and Zn(II)-porphyrin complexes bearing either electron-donating ($[M-OMeP]^{n-}$, $[M-MeP]^{n-}$, $M = Co$, $n = 3$ or $M = Zn$, $n = 4$) or electron-withdrawing ($[M-F8P]^{n-}$, $[M-F16P]^{n-}$) substituents were prepared to study the role of electronic effects on homogeneous photocatalytic hydrogen evolution in presence of $[Ru(bpy)_3]^{2+}$ as photosensitizer (PS), blue light irradiation (450 nm), and ascorbate and tris(2-carboxyethyl)phosphine hydrochloride (TCEP) as sacrificial electron donor. Electronic effects not only controlled the redox properties of the metal-porphyrin catalysts, they also changed the photocatalytic hydrogen evolution mechanism. Electrochemical studies and kinetic studies in photocatalytic conditions indicated that the two best catalysts, i.e., the electron-rich $[Co-OMeP]^{3-}$ and electron-poor $[Co-F16P]^{3-}$ compounds, catalyzed the hydrogen evolution reaction (HER) via two different mechanisms: one centered on the metal for $[Co-OMeP]^{3-}$, whereas for $[Co-F16P]^{3-}$ HER catalysis more likely proceeds via a mechanism involving both the metal center and the porphyrin ligand. Strikingly, the pH dependence of the photocatalytic activity of these two catalysts was found to be very different. For $[Co-F16P]^{3-}$ the highest activity and stability was observed at pH 7.0, with a maximum TOF of $6.7 \pm 0.3 \text{ h}^{-1}$ and a TON of 70 ± 3 after 39.5 hours of irradiation, while $[Co-OMeP]^{3-}$ performed more classically, with better performances at pH 4.1: in such conditions the maximum TOF was $7.2 \pm 0.4 \text{ h}^{-1}$ and the TON 175 ± 5 after 39.5 h irradiation. In this family of hydrogen-evolution catalysts, it is hence preferable to functionalize the complex with electron-withdrawing groups to maximize photocatalytic activity at neutral pH. With $[Co-F16P]^{3-}$ or $[Co-OMeP]^{3-}$ as catalyst, photocatalysis was limited by the PS decomposition.

3.1 Introduction

Light-induced H_2 evolution in aqueous solutions has generated great attention since it could contribute to providing a sustainable and environmentally friendly energy conversion system.^[1] In order to drive this photoreaction efficiently, well-performing hydrogen-evolving catalysts (HECs) must be prepared, the design of which is not yet fully understood.^[2-4] Recently, studies on molecular hydrogen evolution catalysts have multiplied due to their numerous advantages: 1) they mimic the active sites of heterogeneous catalysts and allow to approach catalytic mechanisms with atomic precision;^[5-7] 2) ligand functionalization allows for fine-tuning of the coordination sphere and electronic density of the metal center, which is a powerful tool to establish relationships between the properties of the metal center and its photocatalytic performances;^[7,8] and 3) they can be integrated in supramolecular water splitting systems, also in combination with solid-state materials and catalysts.^[9-11]

In principle, a good molecular HEC should have three characteristics: 1) it should include a metal center that can switch between different oxidation states;^[1] 2) it should be made with a ligand set that provides a stable coordination environment to the metal ion, especially for labile low-valent metal ions;^[1,4] and 3) its electronic density should balance the reaction rates and over-potential of the different catalytic steps, to achieve the highest possible rate.^[7,8] In the last decade, molecular HECs have been extensively studied for photocatalytic hydrogen evolution, especially those made of first-row transition metals.^[12-28] Many of those catalysts are based on cobalt, which is available in large quantities on Earth and has more than five available oxidation states.^[29,30] Usually, these catalysts show better catalytic properties in mildly acidic conditions (pH = 4-5), where enough protons are available for the fast generation of H_2 . On the other hand, coupling proton reduction and water oxidation to achieve a full water splitting scheme, may be more favorable in neutral conditions, because water oxidation becomes very challenging at low pH. Still, examples of cobalt-based HECs working at pH 7.0 in homogeneous aqueous solutions are very rare.^[31,32]

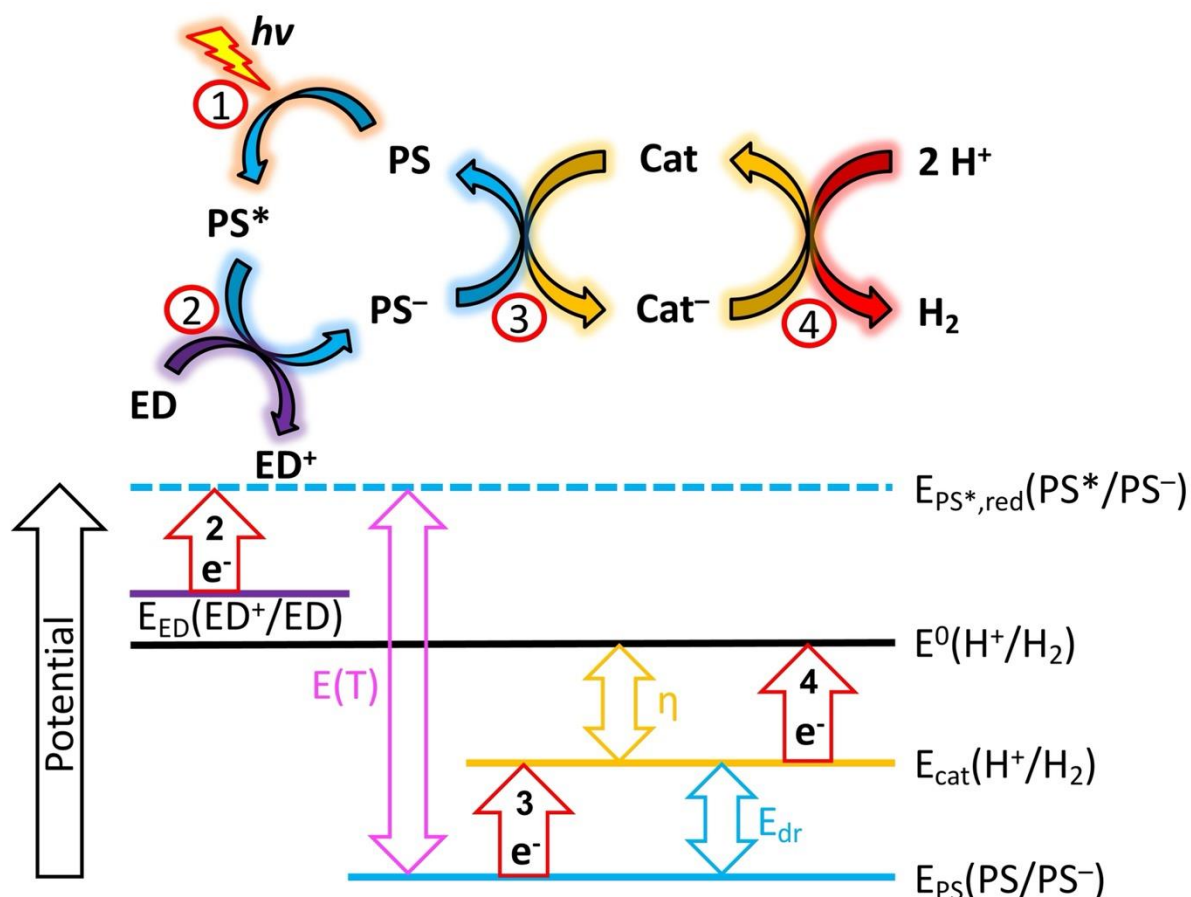


Figure 3.1 Energy scheme and simplified photocatalytic mechanism of the reductive quenching pathway in a three-component molecular photocatalytic hydrogen-evolution system. ED: sacrificial electron donor; PS: photosensitizer; Cat: hydrogen evolution catalyst; $E(T)$: triplet excited state energy of the PS; η : overpotential of the catalyst; E_{dr} : driving force of the electron-transfer step from the reduced photosensitizer PS^- to the catalyst.

Photocatalytic H_2 -evolving systems contain, next to the catalyst, a photosensitizer (PS) and a sacrificial electron donor (ED). In such 3-component systems the much higher concentration of the ED, compared to the catalyst (Cat), usually favors kinetically the excited state PS^* to be quenched reductively by ED to afford PS^- (Step 2 in Figure 3.1).^[4] PS^- then reduces Cat to Cat^- (Step 3), an electron-transfer step driven by the driving force E_{dr} . This process, when repeated twice, catalytically leads to the formation of an H_2 molecule (Step 4). In such a system a good balance between E_{dr} and the overpotential of the catalyst (η) is needed to keep both Step 3 and Step 4 fast enough.^[8] Functionalization of the catalyst with electron-donating or electron-withdrawing groups in principle allows for optimization of E_{dr} and η . However, for synthetic reasons it is not always easy to vary systematically the redox properties of a cobalt complex to optimize its redox potential for catalytic hydrogen reduction. In addition, the pH dependence

of the highest activity of a cobalt catalyst (Step 4 in Figure 3.1) may also depend strongly on the electron-density on the metal catalyst. In the two studies where systematic ligand functionalization by electron-donating or -withdrawing groups has been realized,^[19,33] the pH dependence of the activity of the HEC has not been investigated. In general, it remains poorly understood which influence electron-withdrawing or electron-donating groups have on the (photo)catalytic activity of HEC, and in particular on their pH dependence.

Porphyrin ligands offer stable and rigid coordination sites for cobalt ions, while being readily tunable with electron-donating or -withdrawing substituents, which makes them very attractive for the fine-tuning of molecular catalysts.^[1,34,35] In this work, a family of water-soluble Co(III) porphyrin complexes was prepared bearing either electron-donating ([Co-OMeP]³⁻, [Co-MeP]³⁻) or electron-withdrawing ([Co-F8P]³⁻, [Co-F16P]³⁻) substituents (Figure 3.2). This series of compounds was used to investigate the effect of the electron-richness of the ligand on homogeneous photocatalytic hydrogen evolution in presence of [Ru(bpy)₃]Cl₂ as photosensitizer (PS), and ascorbic acid (AA) and tris(2-carboxyethyl)phosphine hydrochloride (TCEP) as sacrificial electron donor (ED).^[12,36] The pH dependence of their (photo)catalytic properties was investigated and compared to those of their Zn²⁺ analogues, in which the metal center cannot accommodate any changes of the oxidation state. This study demonstrates that the cooperation of the ligand during HEC and the pH dependence of the catalyst both strongly depend on the electron-richness of the porphyrin ligand. Thus, we show that good catalysts can be obtained for the HER at pH 7, provided that the ligand is very electron-poor.

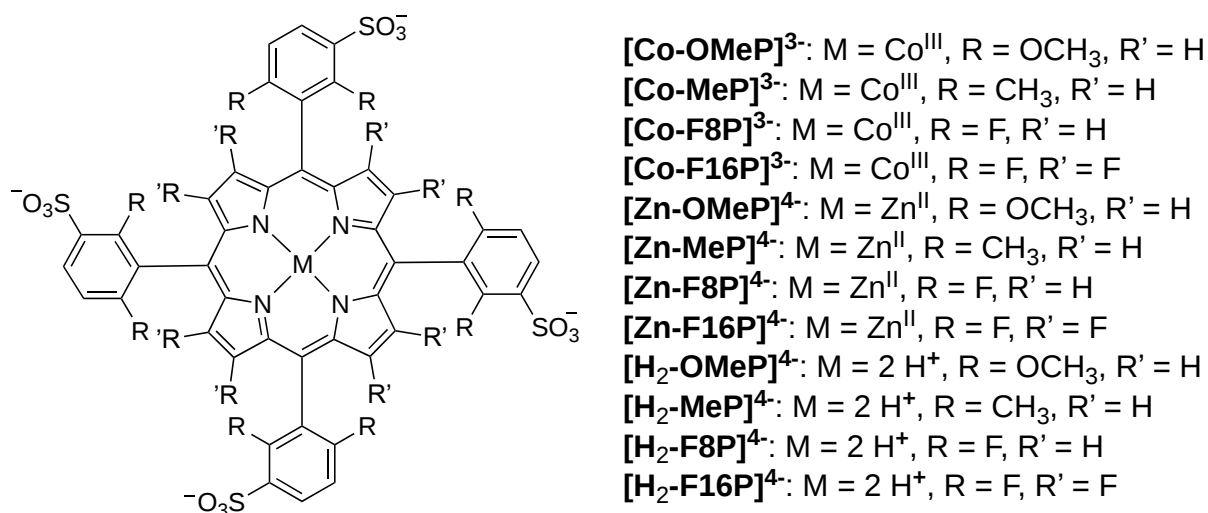


Figure 3.2 Chemical structures of the water-soluble metal porphyrin complexes and free base ligands used in this work. All compounds were isolated as Na⁺ salts.

3.2 Results and Discussion

3.2.1 Synthesis

The tetra-sulfonated free-base porphyrin ligands $\text{Na}_4[\text{H}_2\text{-OMeP}]$,^[8] $\text{Na}_4[\text{H}_2\text{-MeP}]$,^[37] $\text{Na}_4[\text{H}_2\text{-F8P}]$,^[38] $\text{Na}_4[\text{H}_2\text{-F16P}]$,^[39] and their metal complexes $\text{Na}_4[\text{Co-F8P}]$,^[40,41] $\text{Na}_4[\text{Zn-F8P}]$,^[42] $\text{Na}_4[\text{Zn-F16P}]$,^[39] were synthesized according to reported methods. The other Co(III) and Zn(II) porphyrin compounds described in this Chapter are new and were synthesized via refluxing the free-base ligands with Co(II) sulfate or Zn(II) dichloride in Milli-Q water for 12 h. Na^+ -loaded ion exchange resin was used to exchange the counter ions with Na^+ , and the complexes were finally purified by size-exclusion chromatography in order to remove all inorganic salts in excess. According to NMR all cobalt compounds are diamagnetic and hence contain low-spin Co(III) ions. The Co(III) porphyrin complexes were supposedly formed due to the oxidation of Co(II) by air during purification.^[40,41,43] Full characterization is given in the Supplementary Information (Figure AII.1 - Figure AII.6).

3.2.2 Electrochemical properties

In principle, the electron-richness of a ligand influences the redox and electrocatalytic properties of its metal complex.^[7,32] Another classical idea in hydrogen-evolution catalysis is that lower pH values render most catalysts more efficient at catalyzing the HER. The redox properties of the Co(III) and Zn(II) porphyrin complexes were hence studied with electrochemical methods at pH 7.0 and pH 4.1. Cyclic voltammetry (CV), linear sweep voltammetry (LSV), and differential pulse voltammetry (DPV), were recorded, using a phosphate buffer and a glassy-carbon (GC) working electrode (Figure 3.3). DPV of the four Co(III)-porphyrin complexes at pH 7.0, show that lowering of the electron-richness of the complex leads to a decrease of the potential of the first reduction wave that turns the Co(III)-porphyrins ($\text{Co}^{\text{III}}\text{-P}$) into Co(II)-porphyrins ($\text{Co}^{\text{II}}\text{-P}$). This reduction wave was observed at -0.53 V vs. NHE for the most electron-poor complex $[\text{Co-F16P}]^{3-}$, and at -0.75 V vs. NHE for the most electron-rich compound $[\text{Co-OMeP}]^{3-}$ (Figure 3.3a). Cyclic voltammograms recorded at pH 7.0 revealed that the second reduction of the cobalt porphyrin complexes, which leads either to Co(I)-porphyrins ($\text{Co}^{\text{I}}\text{-P}$) or to Co(II)-porphyrin radical anion ($\text{Co}^{\text{II}}\text{-P}^{\bullet-}$) species, induces electrocatalytic hydrogen evolution, with an onset potential (with catalytic current higher than -20 μA) at -0.84 to -1.04 V vs. NHE depending on the substituents (Figure 3.3b). Since the redox potential of the $[\text{Ru}(\text{bpy})_3]^{2+}/[\text{Ru}(\text{bpy})_3]^+$ couple is reported to lie between -1.26 and -1.32 V vs. NHE,^[13,44,45] the one-electron reduced species PS^- , corresponding to $[\text{Ru}(\text{bpy})_3]^+$, is capable to thermodynamically drive the reduction of all four Co(III)-porphyrins

to a potential where the catalytic HER occurs, with an electron-transfer driving force E_{dr} (Figure 3.1) being larger than 160 mV. It is worth noting that for $[\text{Co-F16P}]^{3-}$ a small reduction wave is present at -0.80 V vs. NHE at the foot of the catalytic wave (Figure 3.3b). Interestingly, a similar reduction wave was observed for the $[\text{Zn-F16P}]^{4-}$ analogue, for which metal-based reduction is nearly impossible (Figure 3.3c). This reduction must hence be ligand-based.

LSV of the Zn-porphyrin complexes were measured at pH 7.0 to focus on their electrochemical reduction processes. As expected, the more electron-poor $[\text{Zn-F16P}]^{4-}$ showed the least negative reduction potential (-0.80 V vs. NHE, see Figure 3.3c). The reduction current did not increase significantly with more negative potential until -1.10 V vs. NHE, which suggested this reduction was a reduction process of the complex without catalysis. In addition, the reduction current was around -8 μA which was similar to the current of 1-e^- reduction of Co^{III} to Co^{II} -7 μA (Figure AII.7). Thus, this first reduction process was considered to be 1-electron; it was also observed for $[\text{Zn-F8P}]^{4-}$ but not for the more electron-rich zinc porphyrin complexes $[\text{Zn-MeP}]^{4-}$ and $[\text{Zn-OMeP}]^{4-}$. Significant reduction of $[\text{Zn-MeP}]^{4-}$ and $[\text{Zn-OMeP}]^{4-}$ was observed below -1.20 V vs. NHE with reduction current higher than -16 μA ; these two compounds hence underwent a reduction process with more than 2e^- (Figure AII.8). We tentatively ascribe this process to the electrocatalytic HER, which takes place at the same potential as the reduction of $[\text{Zn-F8P}]^{4-}$ and $[\text{Zn-F16P}]^{4-}$. Overall, in aqueous solution at pH 7.0 the reduced form of the photosensitizer, $[\text{Ru}(\text{bpy})_3]^+$, should also be capable to drive the 2-electron reduction of the Zn-porphyrin complexes and the HER, with a driving force E_{dr} that is higher than 60 mV.

CVs recorded at pH 4.1, show that all Co-porphyrin complexes are also electrocatalytically active for the HER at this pH (Figure 3.3d). As expected, the compounds $[\text{Co-OMeP}]^{3-}$, $[\text{Co-MeP}]^{3-}$ and $[\text{Co-F8P}]^{3-}$ show a higher catalytic current at pH 4.1 than at pH 7.0. However, the electrocatalytic current obtained with $[\text{Co-F16P}]^{3-}$ was lower at pH 4.1 (< -100 μA) than at pH 7.0 (> -200 μA), with 200 mV more over potential. This unexpected result strongly suggests that this electron-poor catalyst may catalyze the HER at neutral pH more efficiently than at pH 4.1, possibly by following a different mechanism than the other complexes.

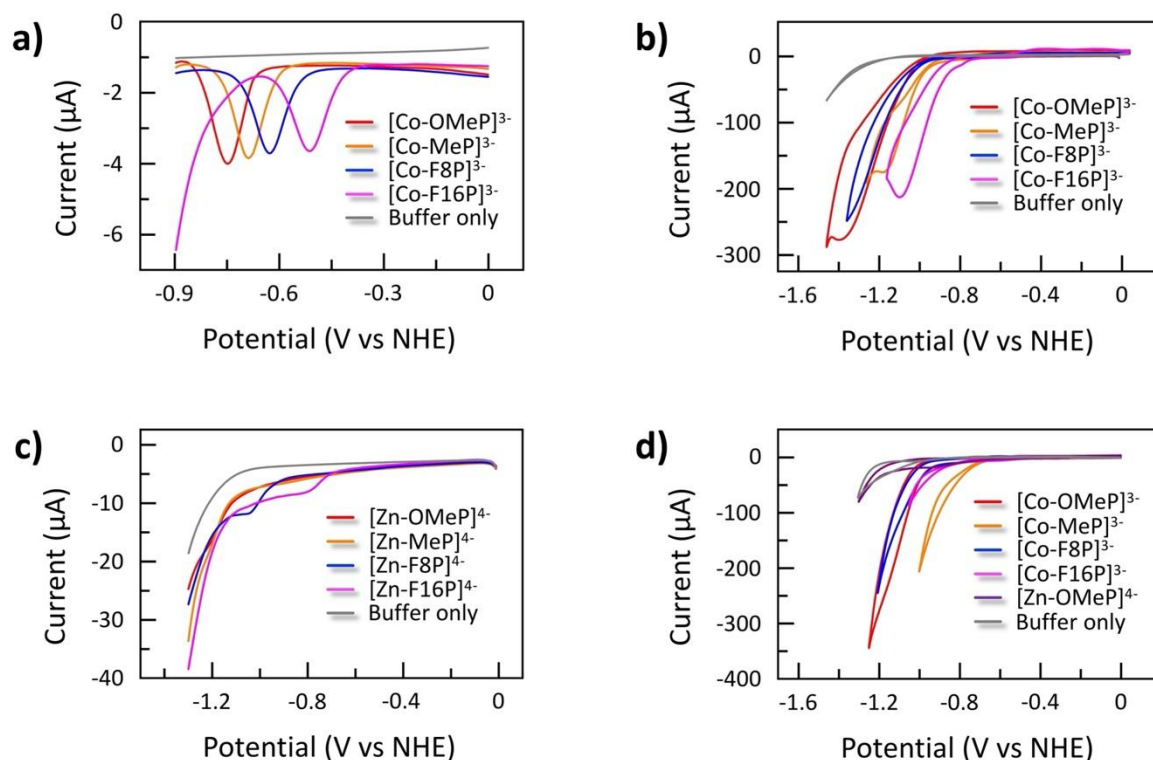


Figure 3.3 Electrochemistry at pH 7.0 and 4.1 of the water-soluble metal porphyrin complexes studied in this work. a) Differential pulse voltammetry (DPV) and b) cyclic voltammetry (CV) of the Co(III) complexes at pH 7.0; c) linear sweep voltammetry (LSV) of the Zn(II) porphyrin complexes at pH = 7.0 and d) CV of the Co-porphyrin complexes at pH = 4.1. Conditions: 0.1 M phosphate buffer, 0.07 cm² glassy-carbon working electrode, Pt wire auxiliary electrode, Ag/AgCl reference electrode, CV and LSV scan rate 50 mV s⁻¹, T = 298 K. DPV experimental parameters: 0.004 V increase potential, 0.05 V amplitude, 0.05 s pulse width, 0.0167 s sampling width, 0.5 s sample period.

3.2.3 Photocatalysis

Considering the encouraging electrocatalytic results described above, the photocatalytic activity of all metal porphyrin complexes in HER was tested in homogeneous aqueous solutions using [Ru(bpy)₃]Cl₂ as PS (0.5 mM), AA and TCEP (100 mM each) as the sacrificial electron donors, under blue light (450 nm, 16 mW) irradiation. Unlike under electrocatalytic conditions, where all Co-porphyrins showed catalytic activity for proton reduction, in photocatalytic conditions at pH = 7.0 only the most electron-poor and the most electron-rich complexes showed significant activity. The electron-poorest Co-porphyrin complex, [Co-F16P]³⁻, showed the highest turnover number (TON, see Section 3.4.5) after 39.5 h irradiation, of 70 ± 3 mol_{H₂}/mol_{HEC} and a maximum turnover frequency (TOF, see Section 3.4.5), of 6.7 ± 0.3 h⁻¹.

By contrast, the most electron-rich complex $[\text{Co-OMeP}]^{3-}$ had a lower activity than $[\text{Co-F16P}]^{3-}$, while the electron-poor $[\text{Co-F8P}]^{3-}$ complex only showed negligible activity and the electron-rich $[\text{Co-MeP}]^{3-}$ was not active at all (Figure 3.4a). At that stage it was surprising to find $[\text{Co-F16P}]^{3-}$ so active at pH 7.0, as for this complex the driving force for electron transfer E_{dr} (Figure 3.1) was 110 mV stronger than that found for $[\text{Co-MeP}]^{3-}$ according to their onset potential of -0.84 and -0.95 V vs. NHE (Table 3.1), while $[\text{Co-MeP}]^{3-}$ showed no photocatalytic activity in such conditions.

Table 3.1 Electrochemical properties of Co-porphyrin complexes at pH 7.0 and pH 4.1.

	1 st reduction potential at pH 7.0 (at pH 4.1) ^[a]	HER on-set potential at pH 7.0 (at pH 4.1) ^[b]	η at pH 7.0 (at pH 4.1) ^[c]	E_{dr} at pH 7.0 (at pH 4.1) ^[d]
$[\text{Co-OMeP}]^{3-}$	-0.75 (-0.78)	-1.04 (-0.95)	630 (710)	220 (310)
$[\text{Co-MeP}]^{3-}$	-0.70 (-0.73)	-0.95 (-0.74)	540 (500)	310 (520)
$[\text{Co-F8P}]^{3-}$	-0.64 (-0.66)	-1.01 (-0.94)	600 (700)	250 (320)
$[\text{Co-F16P}]^{3-}$	-0.53 (-0.55)	-0.84 (-0.88)	430 (640)	420 (380)

^[a] data according to DPV, V vs. NHE. ^[b] data according to CV, V vs. NHE. ^[c] calculated according to the HER on-set potential, in mV. ^[d] calculated according to $E_{\text{PS}}(\text{PS/PS}^-) = -1.26$ V vs. NHE, in mV.

At pH 4.1, the photocatalytic HER activity of electron-rich compounds $[\text{Co-OMeP}]^{3-}$ and $[\text{Co-MeP}]^{3-}$ as well as the electron-poor compound $[\text{Co-F8P}]^{3-}$, all improved compared with pH 7. After 39.5 h irradiation, $[\text{Co-OMeP}]^{3-}$ showed the highest TON of 175 ± 5 mol_{H₂}/mol_{HEC} with a maximum TOF of 7.2 ± 0.4 TON/h, while $[\text{Co-MeP}]^{3-}$, which was not active at pH 7.0, at pH 4.1 showed a TON of 22. $[\text{Co-F8P}]^{3-}$ showed a very fast turnover at the beginning of the reaction (12.7 h^{-1}), but the system was not stable resulting after 39.5 h in a TON of only 80. Surprisingly, however, the electron-poorest complex $[\text{Co-F16P}]^{3-}$ showed a significantly lower photocatalytic activity at pH 4.1 (Figure 3.4b), characterized by a TON of 10 after 39.5 h irradiation, while at pH 7.0 in otherwise identical conditions a TON of 70 was reached.

All together, these photocatalytic results are consistent with those observed in electrochemical conditions. The electron-withdrawing fluorine substituents not only seem to influence the electron density of the metal center, but also to change the pH dependence of the catalytic activity, which are reversed to that of electron-rich cobalt catalysts. This, in turn, suggests that the mechanism of catalytic proton reduction at the porphyrin complexes are different for the electron-rich and electron-poor cobalt compounds.

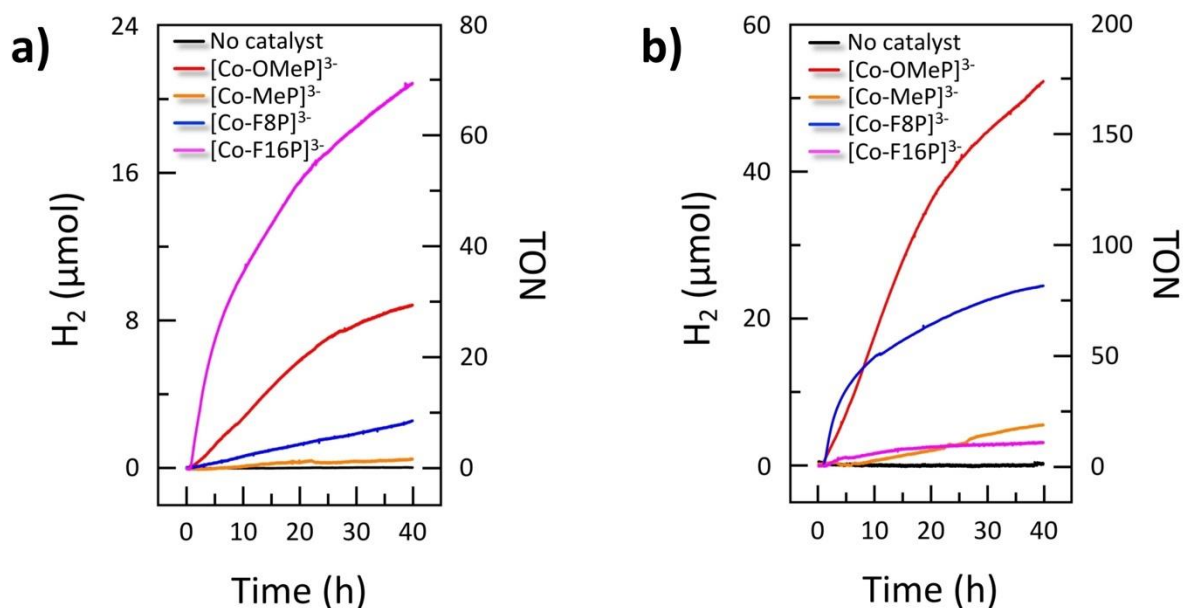


Figure 3.4 Hydrogen evolution during photocatalytic water reduction in homogeneous aqueous solution in presence of 0.1 mM catalyst [Co-OMeP]³⁻, [Co-MeP]³⁻, [Co-F8P]³⁻ or [Co-F16P]³⁻, 0.5 mM [Ru(bpy)₃]Cl₂ as photosensitizer, 0.1 M ascorbate and TCEP as electron donor, at pH 7.0 (a) or 4.1 (b), using blue light irradiation (450 nm, 16 mW). Conditions: *T* = 298 K, phosphate aqueous buffer.

Photocatalytic hydrogen evolution using the Zn-porphyrin complexes as catalysts was also investigated using the same conditions as described above. In the zinc complexes, only the ligand may lead to HEC activity, as the metal center is unable to accommodate different redox states. At pH 7.0 only use of the electron-poor Zn-porphyrin complexes resulted in significant HER activity. [Zn-F16P]⁴⁻ reached a TON of 9.5 after 39.5 h irradiation (Figure AII.9), while [Zn-F8P]⁴⁻ showed lower activity (TON = 6.5). This observation confirmed not only that a ligand-based catalytic pathway for HER is possible with these porphyrins, but also that catalysis becomes faster when more electron-withdrawing groups are added to the porphyrin ring. As a note, in these neutral conditions [Zn-F16P]⁴⁻ and its free-base analogue [H₂-F16P]⁴⁻ (which is also active for photocatalytic HER) showed lower photocatalytic activity than [Co-F16P]³⁻ (Figure AII.10a). Therefore, the mechanism of HER with [Co-F16P]³⁻ as catalyst must not only involve the ligand, but also the cobalt center in the different intermediates. In contrast, at pH 4.1 [Zn-OMeP]⁴⁻ was found to be inactive (Figure AII.10b), while [Co-OMeP]³⁻ showed the highest photocatalytic activity. This result suggests that for the most electron-rich cobalt catalyst of this series the high activity in acidic conditions involves mainly the metal center.

The influence of pH on the photocatalytic activity of $[\text{Co-OMeP}]^{3-}$ and $[\text{Co-F16P}]^{3-}$ was further studied at different pH values between 4.1 and 9.0, using otherwise identical conditions. Upon increasing the pH from 4.1 to 7.0, the TON after 39.5 h for $[\text{Co-F16P}]^{3-}$ increased from 10 to 70, but the TON decreased to 12 upon further increase of the pH to 9.0 (Figure 3.5a and AII.11a). Thus, for this complex pH 7.0 appears to be optimal for the stability of the photocatalytic system, although a higher maximum TOF of 8.9 TON/h was found at pH 6.0 (Figure AII.11b). By contrast, the electron-rich complex $[\text{Co-OMeP}]^{3-}$ clearly showed increasing TON and TOF with more acidic pH, culminating in a TON of 175 and a TOF of 7.2 TON/h at pH 4.1 (Figure 3.5b and AII.11).

Thus, classical behavior is observed for the electron-rich complex $[\text{Co-OMeP}]^{3-}$, with faster H_2 generation at low pH values. For the electron-poor complex $[\text{Co-F16P}]^{3-}$, at pH values higher than 7.0 the HER activity becomes (of course) limited by the low proton concentration hampering the formation of a Co(III) hydride species. More striking, however, is the observation that a high proton concentration significantly inhibits catalytic activity as well. The most favorable condition for this catalyst is pH 7.0, in which use of $[\text{Co-F16P}]^{3-}$ results in a two times higher TON than the use of $[\text{Co-OMeP}]^{3-}$.

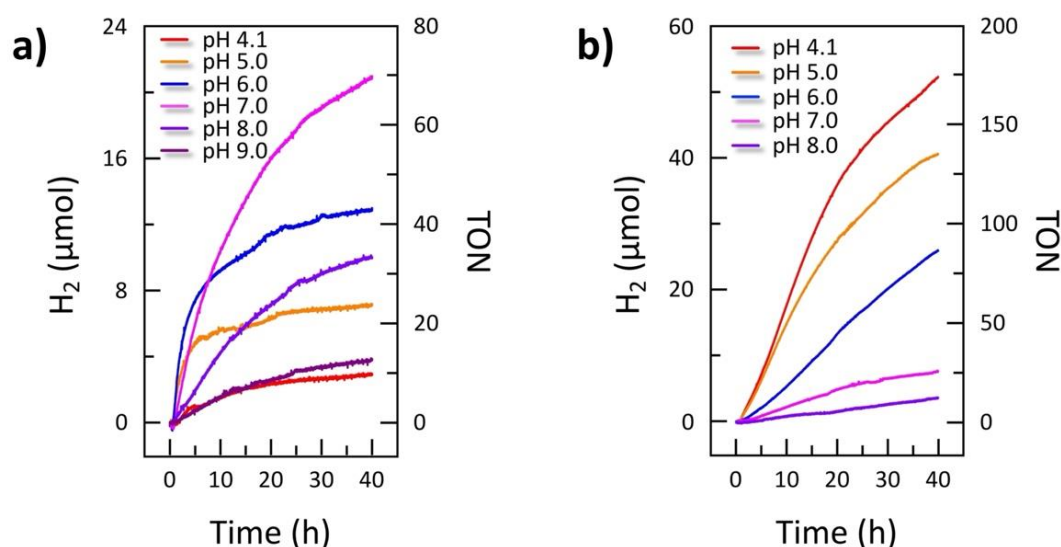


Figure 3.5 Hydrogen evolution during photocatalytic water reduction in presence of a) 0.1 mM catalyst $[\text{Co-F16P}]^{3-}$ and b) $[\text{Co-OMeP}]^{3-}$ at different pH in aqueous solution using 0.5 mM $[\text{Ru}(\text{bpy})_3]\text{Cl}_2$ as photosensitizer, 0.1 M ascorbic acid and TCEP as electron donor, and blue light irradiation (450 nm, 16 mW). Conditions: $T = 298 \text{ K}$, phosphate buffer.

In order to check the photostability of $[\text{Co-F16P}]^{3-}$ and $[\text{Co-OMeP}]^{3-}$, the UV-vis spectra of solutions of complexes in 0.1 M phosphate buffer (pH 7.0) were monitored either in the dark

or upon blue light irradiation for 48 h (450 nm, 16 mW). After 48 h irradiation, the UV-vis spectra of $[\text{Co-F16P}]^{3-}$ and $[\text{Co-OMeP}]^{3-}$ had changed only slightly (Figure AII.12 and AII.13), in contrast with $[\text{Zn-OMeP}]^{4-}$, which lost 80% of its absorption properties after 48 h of irradiation at 423 nm. In another experiment using $[\text{Co-F16P}]^{3-}$ or $[\text{Co-OMeP}]^{3-}$ as the catalyst, two consecutive photocatalytic runs were performed, adding a fresh batch of PS between the two runs to compensate for possible PS decomposition. Only 3-5% lower TON were found after the second photocatalytic run (Figure AII.14). As widely reported, $[\text{Ru}(\text{bpy})_3]^{2+}$ decomposes quickly in photocatalytic aqueous conditions,^[13,46] which is responsible for the deactivation of the HER photocatalytic system. Overall, these results confirm the excellent photostability of both $[\text{Co-F16P}]^{3-}$ and $[\text{Co-OMeP}]^{3-}$.

3.2.4 Kinetic study

A full kinetic study was performed of the photocatalytic system at pH 7.0 using the catalyst $[\text{Co-F16P}]^{3-}$. The light intensity and the concentration of the electron donors, the PS, and the catalyst, were systematically varied. It appeared that the maximum rate of hydrogen evolution of the system did not change significantly when the light power was higher than 10 mW (Figure 3.6a), when the concentration of ascorbate and TCEP was higher than 0.075 M (Figure 3.6b), or with a PS concentration higher than 0.25 mM (Figure 3.6c). However, a first-order dependence of the maximum H_2 evolution rate was found on catalyst concentration (Figure 3.6d). The observation that the photon flux, the concentration of sacrificial electron donor, and the photosensitizer concentration, do not influence, in our standard photocatalytic conditions (0.1 mM catalyst, 0.5 mM $[\text{Ru}(\text{bpy})_3]\text{Cl}_2$, 0.1 M ascorbate and TCEP, 450 nm, 16 mW), the maximum rate of hydrogen evolution of this system means that Step 1, Step 2 and Step 3 in Figure 3.1 are not limiting the photocatalytic reaction rate. The rate-determining step (RDS) of the system appears to be Step 4, i.e., the catalytic H_2 -evolving step. Considering the linear dependence of the H_2 production rate with catalyst concentration, it appears that the rate-determining step of the catalytic cycle involves one molecule of $[\text{Co-F16P}]^{3-}$. Using 0.1 mM $[\text{Co-F16P}]^{3-}$ in the standard conditions at pH 7.0, the quantum yield for H_2 evolution was calculated to be $0.10 \pm 0.01\%$. This low quantum yield highlights the occurrence of many charge-recombination events that are characteristic of homogeneous photocatalytic systems.

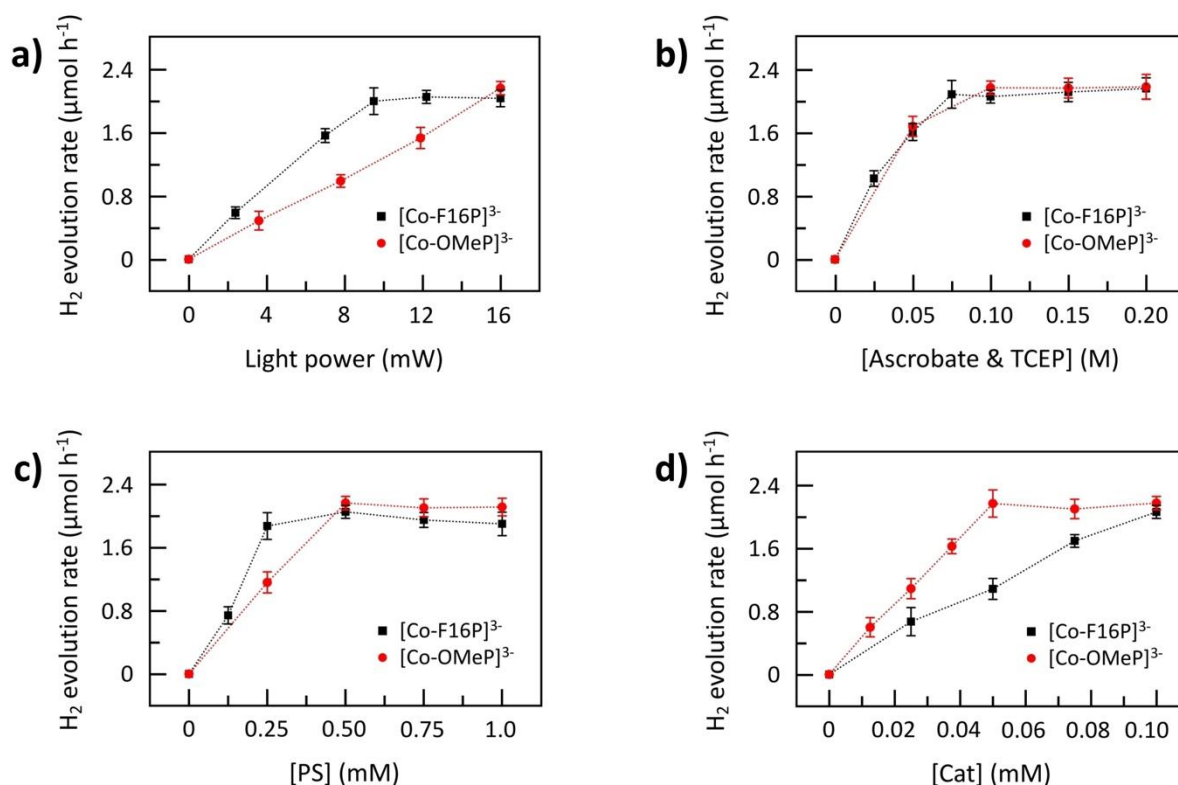


Figure 3.6 Maximum H₂ evolution rate during photocatalytic H₂ evolution using the catalyst [Co-F16P]³⁻ at pH 7.0 (black squares) or [Co-OMeP]³⁻ at pH 4.1 (red circles) plotted as a function of a) the light power, b) the concentration of ascorbate and TCEP, c) the concentration of the photosensitizer [Ru(bpy)₃]Cl₂ and d) the concentration of the catalyst. Standard conditions: 0.1 mM catalyst, 0.5 mM [Ru(bpy)₃]Cl₂, 0.1 M ascorbate and TCEP, blue light (450 nm, 16 mW), T = 298 K.

A similar kinetic study was performed at pH 4.1 using the catalyst [Co-OMeP]³⁻, for which significantly different results were obtained. A first-order dependence of the maximum H₂ evolution rate on light power was found (Figure 3.6a), indicating that the RDS of this catalytic system involves the photon flux, and thus is related to Step 1 in the mechanism. Clearly, for this electron-rich catalyst and at that low pH, Step 4 is relatively fast, at least as soon as the catalyst concentration is high enough ([Cat] > 0.05 mM). In addition, a first-order dependence of the maximum hydrogen evolution rate on the catalyst concentration was found at low concentrations of [Co-OMeP]³⁻, i.e. 0.05 mM or lower (Figure 3.6d), suggesting that the catalytic H₂ evolution involves one molecule of catalyst, but that at higher HEC concentrations the photon flux becomes limiting, which is similar as the result reported by Alberto and coworkers.^[47] Using 0.1 mM [Co-OMeP]³⁻ in the standard conditions at pH 4.1, the quantum yield for H₂ evolution was calculated to be 0.12 ± 0.01%, which is very similar to that for [Co-

F16P]³⁻ at pH 7.0. Clearly, while their mechanisms seem to be different, the performances of both catalysts in optimized conditions were actually comparable.

3.2.5 Discussion

On the one hand, the electrochemical properties of the Co-porphyrin complexes show that the electron-richness of the ligand controls the first reduction potential of the complex, i.e, from Co^{III}-P to Co^{II}-P, which does not lead to hydrogen evolution (note that hereafter and in Figure 3.8, the notation P represents the hexaanionic porphyrin ligand). The second reduction, on the other hand, does lead to catalytic hydrogen evolution, but its dependence on the electronic properties of the substituents is less straightforward to establish. The electron-richest complex [Co-OMeP]³⁻ has the most negative onset potentials of -1.04 and -0.95 V vs. NHE at pH 7.0 and pH 4.1, respectively (Table 3.1). However, the electron-poorest complex [Co-F16P]³⁻ has the least negative onset potential of -0.84 V vs. NHE only at pH 7.0. At pH 4.1 it is [Co-MeP]³⁻ that has the least negative onset potential of -0.74 V vs. NHE. Therefore, the E_{dr} value of these Co-porphyrin systems, calculated by the difference between $E_{PS}(PS/PS^-)$ and the hydrogen evolution onset potential of the catalyst, does not simply depend on the electron-richness of the catalyst. This observation is valid at both pH 7.0 and pH 4.1. The lower value of E_{dr} for [Co-F16P]³⁻ when the pH goes from 7.0 (420 mV) to 4.1 (380 mV) suggests that a faster electron transfer from the photo-reduced species PS⁻ to [Co-F16P]³⁻ may occur at pH 7.0 than at pH 4.1. Indeed, the kinetic study in photocatalytic conditions demonstrated that when using standard concentrations (0.1 mM catalyst, 0.5 mM [Ru(bpy)₃]Cl₂, 0.1 M ascorbate and TCEP) and light intensities (450 nm, 16 mW), the rate of the photocatalytic system using [Co-F16P]³⁻ as HEC at pH 7.0 was limited by the catalytic HER. As a consequence, the electron transfer between PS⁻ and HEC does not limit the HER rate, and the E_{dr} value of this system is “high enough”. At pH 4.1 and using identical concentrations and light intensity, the catalytic step of the photocatalytic system using [Co-OMeP]³⁻ as HEC was limited by the photon flux; in other terms, this HEC was “fast enough”, and E_{dr} was also high enough. Overall, both at pH 7.0 and 4.1 the onset potential of the catalyst in electrocatalytic conditions did not allow to predict the activity in photocatalytic conditions. In fact, the difference in performance between the photocatalytic systems using [Co-OMeP]³⁻ at pH 4.1 and that using [Co-F16P]³⁻ at pH 7.0 appears to be mainly due to the differences in their HER catalytic mechanisms.

For the electron-rich HEC [Co-OMeP]³⁻, the better catalytic properties at lower pH and the absence of catalytic activity of the zinc analogue suggest that catalytic hydrogen generation

occurs via a metal-based pathway.^[4] This behavior is typical for many metal-based catalysts,^[9] and the generally accepted mechanism is shown in Figure 3.8. $\text{Co}^{\text{III}}\text{-P}$ is first reduced by PS^- to $\text{Co}^{\text{II}}\text{-P}$, after which a second reduction by PS^- results in formation of $\text{Co}^{\text{I}}\text{-P}$. Protonation of this species then forms the cobalt(III)-hydride intermediate $\text{H-Co}^{\text{III}}\text{-P}$. Alternatively, protonation of $\text{Co}^{\text{II}}\text{-P}$ to $\text{H-Co}^{\text{IV}}\text{-P}$ may occur first, which is followed by a second reduction to form the same intermediate $\text{H-Co}^{\text{III}}\text{-P}$. Reaction with a second proton releases H_2 via a heterolytic route known as protonolysis, regenerating $\text{Co}^{\text{III}}\text{-P}$.^[9] The ability of the metal center to accommodate several oxidation states is critical for this mechanism to take place.

On the other hand, porphyrin ligands can be redox non-innocent,^[1,48,49] in particular when they are modified with strong (or many) electron-withdrawing substituents, which makes the porphyrin ring more likely to be reduced to a radical anion. Next to the metal-based pathway alternative catalytic pathways have been suggested for the HER catalyzed by Co-porphyrins, based on reduction of either the ligand alone, or on a combination of the metal and the ligand. Here we hypothesize that ligand reduction may be the reason for $[\text{Co-F16P}]^{3-}$ having an additional reduction wave at the foot of its catalytic current at -0.80 V vs. NHE at pH 7.0 (Figure 3.3b), which is tentatively attributed to formation of a $\text{Co}(\text{II})\text{-(P}^{\bullet-})$ radical ligand species. This reduction wave is also present in the LSV of the $[\text{Zn-F16P}]^{4-}$ compound at a similar potential (Figure 3.3c), as both complexes share the same ligand. In addition, the zinc analogue $[\text{Zn-F16P}]^{4-}$ is also photocatalytically active, albeit to a lesser extent. In photocatalytic conditions, such redox non-innocence of the ligand leads to a very different pH dependence of the H_2 -evolution properties of the complex. We hence propose $[\text{Co-F16P}]^{3-}$ to catalyze hydrogen evolution via a mixed metal- and ligand-based mechanism. In such a mechanism (Figure 3.8), the $\text{H-Co}^{\text{IV}}\text{-P}$ species can be reduced to a $\text{H-Co}^{\text{IV}}\text{-(P}^{\bullet-})$ species via a one-electron reduction of the porphyrin ring.^[1] Here a ligand-to-metal charge transfer (CT) may take place to transfer the $\text{H-Co}^{\text{IV}}\text{-(P}^{\bullet-})$ species to $\text{H-Co}^{\text{III}}\text{-P}$ and then release H_2 after reacting with a second electron; or directly be protonated again forming a $\text{Co}^{\text{IV}}\text{-H-H-(P}^{\bullet+})$ species that evolves H_2 by the so-called “homolytic” route (Figure 3.8). Since the 1 e^- -reduction of $\text{Co}^{\text{II}}\text{-P}$ may also take place at the porphyrin ring, $\text{Co}^{\text{II}}\text{-(P}^{\bullet-})$ may be formed first, which is protonated to form a ligand-based hydride species $\text{Co}^{\text{II}}\text{-(P}^{\bullet+})\text{-H}$ that could either react on the metal with a proton to form a $\text{Co}^{\text{IV}}\text{-H-H-(P}^{\bullet+})$ species, or undergo a metal-to-ligand CT forming a $\text{Co}^{\text{III}}\text{-P-H}$ species to finally give H_2 and $\text{Co}^{\text{III}}\text{-P}$. This kind of metal-to-ligand CT may also occur when $\text{Co}^{\text{II}}\text{-P}$ undergoes protonation forming a $\text{Co}^{\text{III}}\text{-P(P}^{\bullet+})\text{-H}$ analogue intermediate, which could be further reduced by 1 e^- to $\text{Co}^{\text{II}}\text{-(P}^{\bullet+})\text{-H}$ or $\text{Co}^{\text{III}}\text{-P-H}$. The $\text{Co}^{\text{III}}\text{-P-H}$ species finally could release H_2 by protonation

via a “heterolytic”, ligand-based pathway. Since neutral pH was optimum for the photocatalytic HER using $[\text{Co-F16P}]^{3-}$, the key $\text{Co}^{\text{IV}}\text{-H-H-(P}^{++})$ species is proposed to be generated more likely in neutral conditions. A high proton concentration may cause decooordination of the cobalt center from the porphyrin ligand, leading to the deactivation of the catalytic system. Alternatively, a high concentration of proton may prevent the formation of some key intermediates for hydrogen generation; this hypothesis is currently investigated in a collaboration to perform a DFT modeling study.

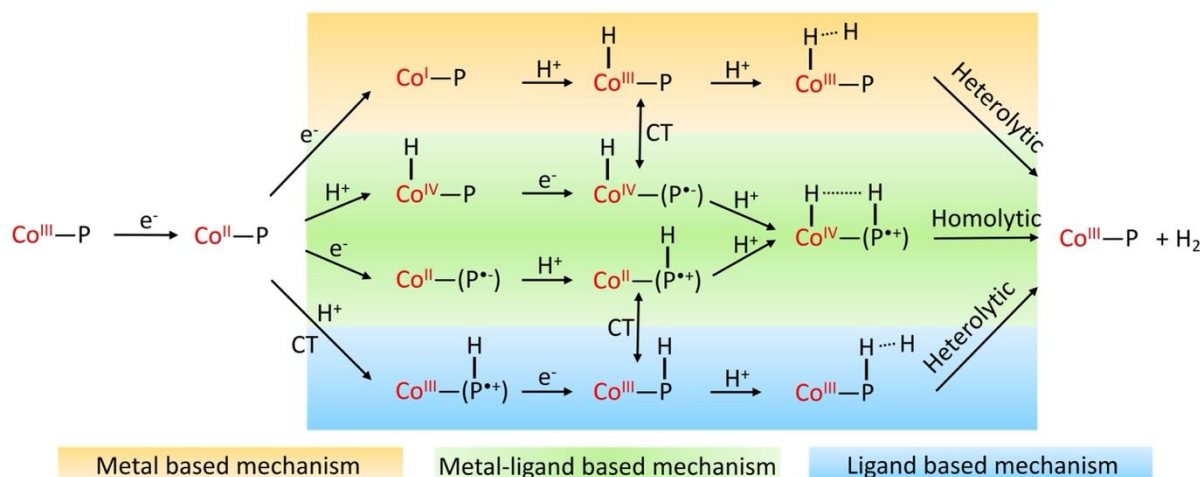


Figure 3.8 Proposed hydrogen evolution mechanisms with Co-porphyrin complex as catalyst. P represents a hexaanionic porphyrin ligand. CT = charge transfer.

3.3 Conclusion

A series of tetra-anionic Co- and Zn-porphyrin complexes were prepared and tested as catalysts for homogeneous photocatalytic hydrogen evolution from water in neutral and acid conditions. Their catalytic activity and catalytic mechanism were strongly dependent on the presence of electron-withdrawing or electron-donating substituents on the porphyrin. For the electron-richest catalyst $[\text{Co-OMeP}]^{3-}$, which has on paper a stronger driving force to reduce water, higher photocatalytic activities were observed as expected, but only at low pH (4.1). In neutral conditions, its activity was much lower, and completely vanished when the cobalt center was replaced by zinc. By contrast, for the electron-poorest catalyst $[\text{Co-F16P}]^{3-}$, photocatalytic hydrogen evolution was comparatively low at pH 4.1, but it was much better than $[\text{Co-OMeP}]^{3-}$ at neutral pH, resulting in comparable photocatalytic H_2 production quantum yields, compared to that obtained with $[\text{Co-OMeP}]^{3-}$ at pH 4.1. For $[\text{Co-F16P}]^{3-}$, the second catalyst reduction step by PS^- probably occurred via a pathway involving both the metal and the ligand, and when

replacing cobalt for zinc, part of the ligand-based photocatalytic activity was retained. This work represents a significant advance in the understanding of how molecular hydrogen evolution catalyst should be designed, because it indicated that it is not necessary to functionalize HER catalysts with electron-donating groups to enhance their catalytic activity, in particular in pH-neutral conditions. Electron-withdrawing groups lead to good catalysts at pH 7.0, too, but with a mechanism that differs from that obtained with electron-rich complexes at lower pH. In systems coupling photocatalytic HEC and OEC near pH 7.0, electron-poor proton reduction catalysts may represent a better optimum than the usually proposed electron-rich catalysts.

3.4 Experimental section

3.4.1 Materials and methods

All reagents were purchased from Sigma-Aldrich and used as received unless otherwise noted. The compounds tetrasodium-5,10,15,20-tetrakis(2,6-dimethoxyphenyl-3-sulfonatophenyl)-21*H*,23*H*-porphyrin ($\text{Na}_4[\text{H}_2\text{-OMeP}]$),^[8] tetrasodium-5,10,15,20-tetrakis(2,6-dimethylphenyl-3-sulfonatophenyl)-21*H*,23*H*-porphyrin ($\text{Na}_4[\text{H}_2\text{-MeP}]$),^[37] tetrasodium-2,3,7,8,12,13,17,18-octafluoro-5,10,15-20-tetrakis(2,6-difluoro-3-sulfonatophenyl)-21*H*,23*H*-porphyrin ($\text{Na}_4[\text{H}_2\text{-F16P}]$),^[39] trisodium-5,10,15,20-tetrakis(2,6-difluoro-3-sulfonatophenyl)porphyrin-Co(III) ($\text{Na}_3[\text{Co-F8P}]$),^[40,41] tetrasodium-5,10,15,20-tetrakis(2,6-difluoro-3-sulfonatophenyl)porphyrin-Zn(II) ($\text{Na}_4[\text{Zn-F8P}]$),^[42] tetrasodium-2,3,7,8,12,13,17,18-octafluoro-5,10,15-20-tetrakis(2,6-difluoro-3-sulfonatophenyl)porphyrin-Zn(II) ($\text{Na}_4[\text{Zn-F16P}]$),^[39] were prepared according to published methods. ¹H NMR spectra were recorded on a Bruker 400DPX-liq spectrometer operating at 400 MHz. ¹⁹F NMR spectra were recorded on a Bruker 500DPX spectrometer operating at 500 MHz. High-resolution mass spectrometric measurements were made on a Bruker Fourier Transform Ion Cyclotron Resonance Mass Spectrometer APEX IV at Leiden University. Elemental analyses were performed at the Mikroanalytisches Laboratorium Kolbe, Germany. Electronic absorption spectra were obtained on a Varian Cary 60 spectrophotometer at 25 °C during the spectrophotometric measurements. The LED optical power was measured using an OPHIR Nova-display laser power meter.

3.4.2 Synthesis

Trisodium 5,10,15,20-tetrakis(2,6-dimethoxyl-3-sulfonatophenyl)porphyrin cobalt(III) (Na₃[Co-OMeP])

The ligand Na₄[H₂-OMeP] (115 mg, 0.09 mmol) and Milli-Q water (40 mL) were placed under N₂ in a 100 mL round-bottom flask equipped with a magnetic stirring bar and a condenser. A solution of cobalt(II) sulfate heptahydrate (126 mg, 0.45 mmol) in Milli-Q water (10 mL) was added to the stirred solution, and the mixture was refluxed for 12 h under N₂. After cooling to room temperature, water was rotary evaporated at 40 °C and the residue was redissolved in cold methanol (15 mL). After filtration on a filter paper, methanol was rotary-evaporated, the residue was redissolved in cold methanol (5 mL). The solution was filtered by filter paper, rotary-evaporated, and the crude product was redissolved in Milli-Q water (5 mL) then passed onto an Amberlite IR 120 Na⁺ form ion exchange resin column (10 cm), washed with Milli-Q water and further purified on Sephadex-20H size exclusion chromatography to remove excess cobalt sulfate (methanol). Methanol was finally rotary evaporated and the solid dried in vacuo. Yield (115 mg, 88%); ¹H NMR (400 MHz, CD₃OD): δ = 9.37 – 9.19 (m, 8H; β -pyrrole-H), 8.48 – 8.40 (m, 4H; *p*-Ph-H), 7.52 – 7.15 (m, 4H; *m*-Ph-H), 3.92 – 3.49 (m, 12 H; OCH₃), 3.24 – 2.29 ppm (m, 12 H; OCH₃); HRMS (ESI): *m/z* calcd for C₅₂H₄₄N₄CoO₂₀S₄⁺: 1231.0758 [*M*-3Na+4H]⁺; found: 1231.0750; elemental analysis calcd (%) for C₅₂H₄₀N₄Na₃CoO₂₀S₄•Na₂SO₄•H₂O: C 42.86, H 2.91, N 3.85; found: C 43.01, H 2.79, N 3.84. UV-vis (H₂O): λ_{max} (ϵ in M⁻¹ cm⁻¹) 426 nm (8.8 × 10⁴), 542 nm (5.8 × 10³).

Trisodium 5,10,15,20-tetrakis(2,6-dimethyl-3-sulfonatophenyl)porphyrin cobalt(III) (Na₃[Co-MeP])

Tetrasodium 5,10,15,20-tetrakis(2,6-dimethyl-3-sulfonatophenyl)-21*H*,23*H*-porphyrin•9H₂O (130 mg, 0.10 mmol) and Milli-Q water (40 mL) were placed under N₂ in a 100 mL round-bottom flask equipped with a magnetic stirring bar and a condenser. A solution of cobalt(II) sulfate heptahydrate (141 mg, 0.50 mmol) in Milli-Q water (10 mL) was added to the stirred solution and the mixture was refluxed for 12 h under N₂. After cooling to room temperature, water was rotary evaporated and the residue was redissolved in cold methanol (15 mL). After filtration on a filter paper, methanol was rotary-evaporated, the residue was redissolved in cold methanol (5 mL), the solution was filtered a second time by filter paper and rotary-evaporated, then the crude product was then passed onto an Amberlite IR 120 Na⁺ form ion exchange resin column (10 cm), washed with Milli-Q water and finally purified on Sephadex-20H size exclusion chromatography (methanol). Methanol was finally rotary

evaporated and the solid dried in vacuo. Yield (109 mg, 90%); ^1H NMR (400 MHz, CD_3OD): δ = 9.18 – 9.09 (m, 8H; β -pyrrole-H), 8.43 – 8.38 (m, 4H; *p*-Ph-H), 7.68 – 7.55 (m, 4H; *m*-Ph-H), 2.42 – 2.09 (m, 12H; CH_3), 2.07 – 1.74 ppm (m, 12H; CH_3); HRMS (ESI): m/z calcd for $\text{C}_{52}\text{H}_{43}\text{N}_4\text{NaCoO}_{12}\text{S}_4^+$: 1125.0985 [$M-2\text{Na}+3\text{H}$] $^+$; found: 1125.0977; elemental analysis calcd (%) for $\text{C}_{52}\text{H}_{40}\text{N}_4\text{Na}_3\text{CoO}_{12}\text{S}_4\cdot 2\text{H}_2\text{O}$: C 51.83, H 3.68, N 4.65; found: C 52.08, H 3.43, N 4.66. UV-vis (H_2O): λ_{max} (ϵ in $\text{M}^{-1}\text{cm}^{-1}$) 428 nm (2.3×10^5), 545 nm (1.2×10^4).

Trisodium 2,3,7,8,12,13,17,18-octafluoro-5,10,15,20-tetrakis(2,6-difluoro-3-sulfonatophenyl)porphyrin cobalt(III) ($\text{Na}_3[\text{Co-F16P}]$)

Tetrasodium 2,3,7,8,12,13,17,18-octafluoro-5,10,15,20-tetrakis(2,6-difluoro-3-sulfonatophenyl)-21*H*,23*H*-porphyrin $\cdot 5\text{H}_2\text{O}$ (140 mg, 0.10 mmol) and Milli-Q water (40 mL) were placed under N_2 in a 100 mL round-bottom flask equipped with a magnetic stirring bar and a condenser. A solution of cobalt(II) sulfate heptahydrate (141 mg, 0.50 mmol) in Milli-Q water (10 mL) was added to the stirred solution and the mixture was refluxed for 12 h under N_2 . After cooling to room temperature, the water was rotary evaporated and the residue was redissolved in cold methanol (15 mL). After filtration over a filter paper, methanol was rotary-evaporated, the residue was redissolved in cold methanol (5 mL), and filtered by filter paper again. The filtrate was rotary-evaporated and the Co-F16 complex was then passed through an Amberlite IR 120 Na^+ form ion exchange resin column (10 cm) and washed with Milli-Q water before being purified on Sephadex-20H size exclusion chromatography (eluent: methanol). Methanol was finally rotary evaporated and the solid dried in vacuo. Yield (135 mg, 90%); ^1H NMR (400 MHz, CD_3OD): δ = 6.80 (s, 4H; *p*-Ph-H), 5.60 – 5.37 ppm (m, 4H; *m*-Ph-H); ^{19}F NMR (471 MHz, CD_3OD): δ = -111.97 (d, J = 236.0 Hz, 8F; β -pyrrole-F), -112.74 (s, 4F; *o*-F), -113.26 ppm (s, 4F; *o*-F); HRMS (ESI): m/z calcd for $\text{C}_{44}\text{H}_{12}\text{F}_{16}\text{N}_4\text{CoO}_{12}\text{S}_4^+$: 1278.8406 [$M-3\text{Na}+4\text{H}$] $^+$; found: 1278.8407; elemental analysis calcd (%) for $\text{C}_{44}\text{H}_8\text{F}_{16}\text{N}_4\text{Na}_3\text{CoO}_{12}\text{S}_4\cdot \text{Na}_2\text{SO}_4\cdot \text{H}_2\text{O}$: C 35.12, H 0.67, N 3.72; found: C 35.06, H 0.61, N 3.82. UV-vis (H_2O): λ_{max} (ϵ in $\text{M}^{-1}\text{cm}^{-1}$) 402 nm (1.4×10^5), 535 nm (6.3×10^3)

Tetrasodium 5,10,15,20-tetrakis(2,6-dimethoxyl-3-sulfonatophenyl)porphyrin zincate(II) ($\text{Na}_4[\text{Zn-OMeP}]$)

The ligand L-OMe (115 mg, 0.09 mmol) and Milli-Q water (40 mL) were placed under N_2 in a 100 mL round-bottom flask equipped with a magnetic stirring bar and a condenser. A solution of zinc(II) chloride (61 mg, 0.45 mmol) in Milli-Q water (10 mL) was added to the

stirred solution, and the mixture was refluxed for 12 h under N₂. After cooling to room temperature, water was rotary evaporated at 40 °C and the residue was redissolved in cold methanol (15 mL). After filtration on a filter paper, methanol was rotary-evaporated, the residue was redissolved in cold methanol (5 mL). The solution was filtered by filter paper, rotary-evaporated, and the crude product was redissolved in Milli-Q water (5 mL) then passed onto an Amberlite IR 120 Na⁺ form ion exchange resin column (10 cm), washed with Milli-Q water and further purified on Sephadex-20H size exclusion chromatography to remove excess zinc chloride (methanol). Methanol was finally rotary evaporated and the solid dried in vacuo. Yield (107 mg, 85%); ¹H NMR (400 MHz, CD₃OD): δ = 8.82 – 8.77 (m, 8H; β -pyrrole-H), 8.40 – 8.35 (m, 4H; *p*-Ph-H), 7.31 – 7.23 (m, 4H; *m*-Ph-H), 3.67 – 3.54 (m, 12 H; OCH₃), 3.07 – 2.76 ppm (m, 12 H; OCH₃); HRMS (ESI): *m/z* calcd for C₅₂H₄₅N₄ZnO₂₀S₄⁺: 1237.0796 [*M*-4Na+5H]⁺; found: 1237.0792; elemental analysis calcd (%) for C₅₂H₄₀N₄Na₄ZnO₂₀S₄•4H₂O: C 44.66, H 3.46, N 4.01; found: C 44.79, H 3.19, N 3.99. UV-vis (H₂O): λ_{max} (ϵ in M⁻¹ cm⁻¹) 422 nm (1.4 × 10⁵), 557 nm (6.5 × 10³).

Tetrasodium 5,10,15,20-tetrakis(2,6-dimethyl-3-sulfonatophenyl)porphyrin zincate(II) (Na₄[Zn-MeP])

Tetrasodium 5,10,15,20-tetrakis(2,6-dimethyl-3-sulfonatophenyl)-21*H*,23*H*-porphyrin•9H₂O (130 mg, 0.10 mmol) and Milli-Q water (40 mL) were placed under N₂ in a 100 mL round-bottom flask equipped with a magnetic stirring bar and a condenser. A solution of zinc(II) chloride (68 mg, 0.50 mmol) in Milli-Q water (10 mL) was added to the stirred solution and the mixture was refluxed for 12 h under N₂. After cooling to room temperature, water was rotary evaporated and the residue was redissolved in cold methanol (15 mL). After filtration on a filter paper, methanol was rotary-evaporated, the residue was redissolved in cold methanol (5 mL), the solution was filtered a second time by filter paper and rotary-evaporated, then the crude product was then passed onto an Amberlite IR 120 Na⁺ form ion exchange resin column (10 cm), washed with Milli-Q water and finally purified on Sephadex-20H size exclusion chromatography (methanol). Methanol was finally rotary evaporated and the solid dried in vacuo. Yield (110 mg, 90%); ¹H NMR (400 MHz, CD₃OD): δ = 8.63 – 8.59 (m, 8H; β -pyrrole-H), 8.35 (m, 4H; *p*-Ph-H), 7.56 – 7.49 (m, 4H; *m*-Ph-H), 2.40 – 2.26 (m, 12H; CH₃), 1.94 – 1.79 ppm (m, 12H; CH₃); HRMS (ESI): *m/z* calcd for C₅₂H₄₅N₄ZnO₁₂S₄⁺: 1109.1203 [*M*-4Na+5H]⁺; found: 1109.1204; elemental analysis calcd (%) for C₅₂H₄₀N₄Na₄ZnO₁₂S₄•H₂O:

C 51.34, H 3.48, N 4.61; found: C 51.54, H 3.39, N 4.61. UV-vis (H₂O): $\lambda_{\text{max}}(\epsilon \text{ in M}^{-1} \text{ cm}^{-1})$ 423 nm (6.0×10^5), 557 nm (1.8×10^4), 599 nm (4.6×10^3).

3.4.3 Cyclic voltammetry, differential pulse voltammetry and linear sweep voltammetry

Cyclic voltammetry (CV), differential pulse voltammetry (DPV) and linear sweep voltammetry (LSV) measurements were performed using an Autolab PGstart10 potentiostat controlled by GPES4 software. All the CV, DPV and LSV measurements were recorded in 0.1 M sodium phosphate buffer (pH 7.0) or 1.0 M sodium phosphate buffer (pH 4.1) using a three-compartment cell possessing a 0.07 cm² glassy-carbon electrode as the working electrode, Pt wire as the auxiliary electrode, Ag/AgCl (saturated KCl aq.) as the reference electrode, and K₃[Fe(CN)₆] was added at the end of the measurements as internal standard ($E([\text{Fe}(\text{CN})_6]^{3-}/[\text{Fe}(\text{CN})_6]^{4-}) = +0.361 \text{ V vs NHE}$).^[50] Unless otherwise indicated, the potential was converted relative to NHE, the solutions were bubbled with high-purity argon for at least 30 min before analysis.

3.4.4 Photo-induced hydrogen evolution

Photo-induced hydrogen evolution from water was analysed by a hydrogen electrode (Unisense H2-NP) controlled by x-5 UniAmp using Logger software. The irradiation source was an OSRAM Opto Semiconductors LD W5SM LED (λ_{irr} 450 nm, $\Delta\lambda_{1/2} = 25 \text{ nm}$) with water cooling. All the photochemical hydrogen evolution measurements were carried out in a thermostated (298 K) photochemical reactor (total volume 25.0 mL). [Ru(bpy)₃]Cl₂·6H₂O (1.3 mg, 0.5 mM), the catalyst Na₃[Co-OMeP], Na₃[Co-MeP], Na₃[Co-F8P], Na₃[Co-F16], Na₄[Zn-OMeP], Na₄[Zn-MeP], Na₄[Zn-F8P], and Na₄[Zn-F16P] (0.1 mM), and ascorbic acid (53 mg, 0.1 M) and tris(2-carboxyethyl)phosphine hydrochloride (86 mg, 0.1 M) were added as solids in the reactor, and dissolved using sodium phosphate buffer (0.1 M, pH 7.0, 3.0 mL), the pH value of the mixture solution was then controlled with sodium hydroxide solid by checking pH. Under constant stirring, the reactor was equipped with 1 rubber septum and 2 silicon septa in order to make an air-tight system (the set-up is shown in Figure AI.29). The hydrogen electrode was then inserted through the septum, to measure the hydrogen concentration in the head space (gas phase) of the photochemical reactor, and the whole system was deaerated by high-purity argon for at least 30 min. After removing the argon, the hydrogen electrode was calibrated by a four-time injection of 100 μL (4.46 μmol at 1 atm) of high-purity H₂ into the closed system, thereby limiting the overpressure to <5%; the calibration was adapted with the pressure change

using Logger software, affording direct reading of the volume of dioxygen (μL) produced in the gas phase of the reactor ($V_{\text{gas}} = 22.0 \text{ mL}$). Following calibration, the three used septa were replaced by new ones and hydrogen electrode was inserted into the system again. The system was degassed for 30 min with argon, then data recording was started, first keeping the system in the dark for another 30 min prior to starting light irradiation. Unless otherwise indicated, the data recording was stopped after 39.5 h of light irradiation.

3.4.5 Turnover number determination

The turnover number (TON) of oxygen evolution was determined by a hydrogen electrode (Unisense OX-NP) controlled by x-5 UniAmp using Logger software. The amount of oxygen formed during 39.5 h illumination was used to calculate the TON. The TON were calculated from the oxygen production data by the following equation:

$$TON = \frac{n_{O_2}}{n_{cat}}$$

in which n_{O_2} is the number of mol of hydrogen calculated from the volume of the dioxygen produced in the photocatalytic experiment as indicated by the calibrated hydrogen electrode in the gas phase (μL), divided by 22.4 L/mol, and n_{cat} is the number of mol of cobalt and zinc porphyrin catalyst used in the photocatalytic experiment. Errors in triplicate measurements.

The maximum H_2 evolution rate (in h^{-1}) or the maximum turnover frequency TOF_{max} (in h^{-1}) of photocatalytic oxygen evolution was obtained using Origin 9.1 software by 1) nonlinear curve fitting of the time evolution of the TON, starting at $t = 30 \text{ min}$ for photocatalytic reactions (category: Growth/Sigmoidal, function: logistic Fit); 2) calculating the first derivative $TOF = f(t)$ using mathematics, differentiate, and 3) identify the maximum value of H_2 evolution rate or TOF_{max} of $TOF = f(t)$ (example of $[\text{Co-OMeP}]^{3-}$ see Figure 3.9). Errors in triplicate measurements.

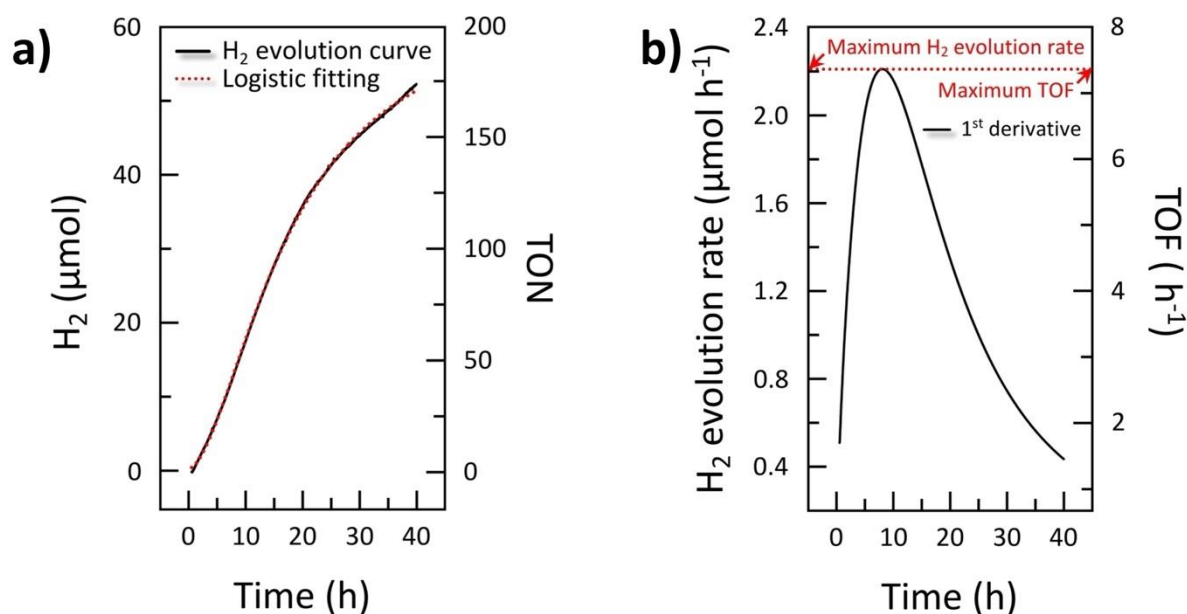


Figure 3.9 Calculation of maximum O_2 evolution rate and maximum TOF of $[Co-OMeP]^{3-}$.

3.4.6 Calculation of photochemical H_2 production quantum yield

The H_2 generation quantum yield was calculated using the TOF_{max} , n_{cat} and the rate of photons absorption:

$$\varphi = \frac{2n_{cat}TOF_{max}}{3600\Phi(1 - 10^{-A_e})(A_{PS}/A_e)}$$

in which TOF_{max} (h⁻¹) is the maximum turnover frequency of the photocatalytic oxygen evolution reaction, n_{cat} (in μmol) is the number of mol of cobalt catalyst used in the photocatalytic experiment, Φ is the photon flux (μmol s⁻¹) determined by standard ferrioxalate actinometry (typically 1.05 μmol s⁻¹, 16 mW),^[51] A_e is the total absorption of the photocatalytic solution at 450 nm ($A_e > 3$), A_{PS} is the absorption of photosensitizer only in buffer at 450 nm ($A_{PS}/A_e \sim 1$), and 3600 is the number of seconds per hour. In this calculation we assumed 2 photons were needed for each molecule of H_2 produced. Errors in triplicate measurements.

3.5 Acknowledgement

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4

Electronic Effects in Water-soluble Zn(II)- and Sn(IV)-Porphyrin Photosensitizers for Homogeneous Photocatalytic Hydrogen Evolution at pH 7.0

A series of tetra-anionic Zn(II)- and Sn(IV)-porphyrin complexes bearing either electron-donating ($[M-OMeP]^{4-}$, $[M-MeP]^{4-}$, $M = Sn^{IV}Cl_2$ or Zn^{II}) or electron-withdrawing ($[M-F8P]^{4-}$, $[M-F16P]^{4-}$) substituents were prepared. The role of electronic effects on the photosensitizer (PS) was studied of a homogeneous photocatalytic hydrogen evolution system using cobaloxime as hydrogen evolution catalyst (HEC), green light irradiation (550 nm), and triethanolamine (TEOA) as sacrificial electron donor in a 1:1 pH 7.0 water/acetonitrile solution. Electronic effects on the one hand fine-tune the redox properties of the ground state of the PS; on the other hand, they also affect its triplet excited state energy, which further changes the potentials of the redox couples involving the excited state of the PS. These effects appear to have an effect both on the thermodynamics of the photocatalytic hydrogen evolution reaction and on the quenching mechanism. The electron-poorest PS, $[Zn-F16P]^{4-}$, was the only zinc-based PS of this series to result in active catalytic system, leading to a high photocatalytic turnover number (PTON) of 850 after 20 h irradiation with a high maximum photocatalytic turnover frequency (PTOF) of 59 h^{-1} . In the Sn-porphyrin series the compounds $[Sn-OMeP]^{4-}$ and $[Sn-MeP]^{4-}$ both resulted in active catalytic systems, the latter being a much more efficient sensitizer than the former; both were less efficient than $[Zn-F16P]^{4-}$ in otherwise identical conditions. The best PS of these two series of complexes, $[Zn-F16P]^{4-}$, showed great photostability in optimized conditions, driving photocatalytic hydrogen evolution for more than 100 h under green light irradiation.

4.1 Introduction

Reducing the CO₂ emission originating from the use of fossil fuels is important for achieving a “carbon neutral” society. To achieve this goal, the utilization of a carbon-free replacement of fossil fuels, such as dihydrogen, is imperative and extremely urgent.^[1,2] Photocatalytic hydrogen generation could convert and store superfluous solar energy into chemical energy by the production of H₂ in a sustainable and environmentally friendly manner.^[2-4] The photoinduced hydrogen evolution reaction (HER) typically requires three components: a photosensitizer (PS), which is responsible for light harvesting and triggering electron transfer; a hydrogen evolving catalyst (HEC); and a sacrificial electron donor (ED), which in a full photocatalytic water splitting scheme should be replaced by an electron relay that is reduced with electrons derived from water oxidation.^[5,6] Recently, efforts on developing new photocatalytic systems have mainly focused on the catalysts, while comparatively less work has been dedicated to the optimization of the photosensitizer.^[2,6] However, the PS plays a significant role for solar H₂ generation, and it is as important to develop more robust and more efficient photosensitizers as it is to find stable and fast catalysts.^[7-9]

Noble-metal based molecular chromophores have been well studied for homogeneous light-driven hydrogen production, in particular those based on Ru,^[9,10] Ir,^[11,12] Pt,^[13,14] Re,^[15,16] and Au^[17], which have shown excellent sensitizing properties. However, these noble-metal-based photosensitizers are too expensive for use on an industrial scale due to their low natural abundance. Therefore, the development of noble-metal-free chromophores is receiving more and more attention.^[18-20] Although xanthene dyes, for example Eosin Y,^[21,22] Rose Bengal,^[23,24] or Fluorescein,^[25,26] are cheap and active, most of them only last a few hours under visible light irradiation, which drastically limits their practical applications. Next to these compounds, molecular photosensitizers based on earth-abundant metals are considered in parallel. Cu(I)-based chromophores, first reported for photocatalytic hydrogen generation by Sauvage and co-workers,^[27] have recently been re-introduced and explored in great detail, and indeed demonstrate promising sensitizing properties for photocatalytic HER.^[28-32] However, most of the photocatalytic systems described to date containing a Cu(I)-based PS still suffer from low photostability due to decomposition of the Cu(I) photosensitizers.^[6] Improvements of the stability of these PSs and optimization of their sensitizing properties for hydrogen evolution remains necessary.

Another family of photosensitizers based on abundant metals has been considered: porphyrin-based metal complexes. These molecules not only show intense absorption of visible light due to their large conjugated ring and allowed $\pi-\pi^*$ transitions, but they also have good stability due to the tetradentate, rigid coordination environment containing the metal center.^[3, 33] Porphyrin ligands can be readily functionalized with substituents for fine-tuning the electronic density of the metal centers, or for improving water solubility. This versatility allows porphyrin-based PSs to be tunable both in terms of redox and aggregation properties in aqueous media.^[3,6] However, although noble-metal-free porphyrin-based PSs, and in particular those based on Zn(II) and Sn(IV), have already been considered as PS in catalytic systems for photocatalytic hydrogen production,^[7,34-36] full understanding is still lacking of the effects that electronic properties of the porphyrin ligand have on their sensitizing properties and stability for the photocatalytic HER.

In the work reported in this chapter, we have prepared two series of water-soluble Zn(II)- and Sn(IV)-porphyrin complexes bearing either electron-donating ([M-OMeP]⁴⁻, [M-MeP]⁴⁻, M = Zn^{II} or Sn^{IV}Cl₂) or electron-withdrawing ([M-F8P]⁴⁻, [M-F16P]⁴⁻) substituents (Figure 4.1). These complexes were tested as photosensitizers for the photocatalytic HER in homogeneous 1:1 pH 7.0 water/acetonitrile (MeCN) solutions, using green light (550 nm) irradiation, cobaloxime as standard HEC, and triethanolamine (TEOA) as the ED. The synthetic availability of these two series of complexes with electron-poor or electron-rich ligands allowed for systematically evaluating the influence of electronic effects on the redox potentials and excited-state energy of the PS, and for studying how these molecular properties influence the overall kinetics of photocatalytic HER. A typical three-component system for photocatalytic hydrogen generation contains a PS, a HEC, and an ED. In this system, the excited state of the photosensitizer, PS*, can either first be reduced by the ED (“reductive quenching”), to become a reductant (PS⁻) that further reduces the HEC, or behave as a reductant to first transfer an electron to the HEC (“oxidative quenching”), before being regenerated by electron donation by the ED (Figure 4.2).^[2,5,6] Which quenching pathway is occurring in a particular photocatalytic system depends notoriously on the thermodynamics of its components, hence on the electron richness of the PS. For example, for reductive quenching the reduction potential of the ground state of the photosensitizer, $E_{\text{PS,red}}(\text{PS}/\text{PS}^-)$, should be more negative than the reduction potential of the HEC, $E_{\text{HEC}}(\text{H}^+/\text{H}_2)$; meanwhile, the reduction potential of the excited state of PS, $E_{\text{PS}^*,\text{red}}(\text{PS}^*/\text{PS}^-)$, should be more positive than the oxidation potential of the sacrificial electron donor $E(\text{ED}^+/\text{ED})$. By contrast, for oxidative quenching the oxidation

potential of the ground state of the PS, $E_{\text{PS,ox}}(\text{PS}^+/\text{PS})$, should be higher than $E(\text{ED}^+/\text{ED})$ and the oxidation potential of the excited state of PS, $E_{\text{PS}^*,\text{ox}}(\text{PS}^+/\text{PS}^*)$, should be more negative than the $E_{\text{HEC}}(\text{H}^+/\text{H}_2)$. Here, we describe our study of how these thermodynamic aspects evolve when changing the electron density of the PS, in which we identified one particular complex that shows improved stability in photocatalytic conditions, compared to reported systems.

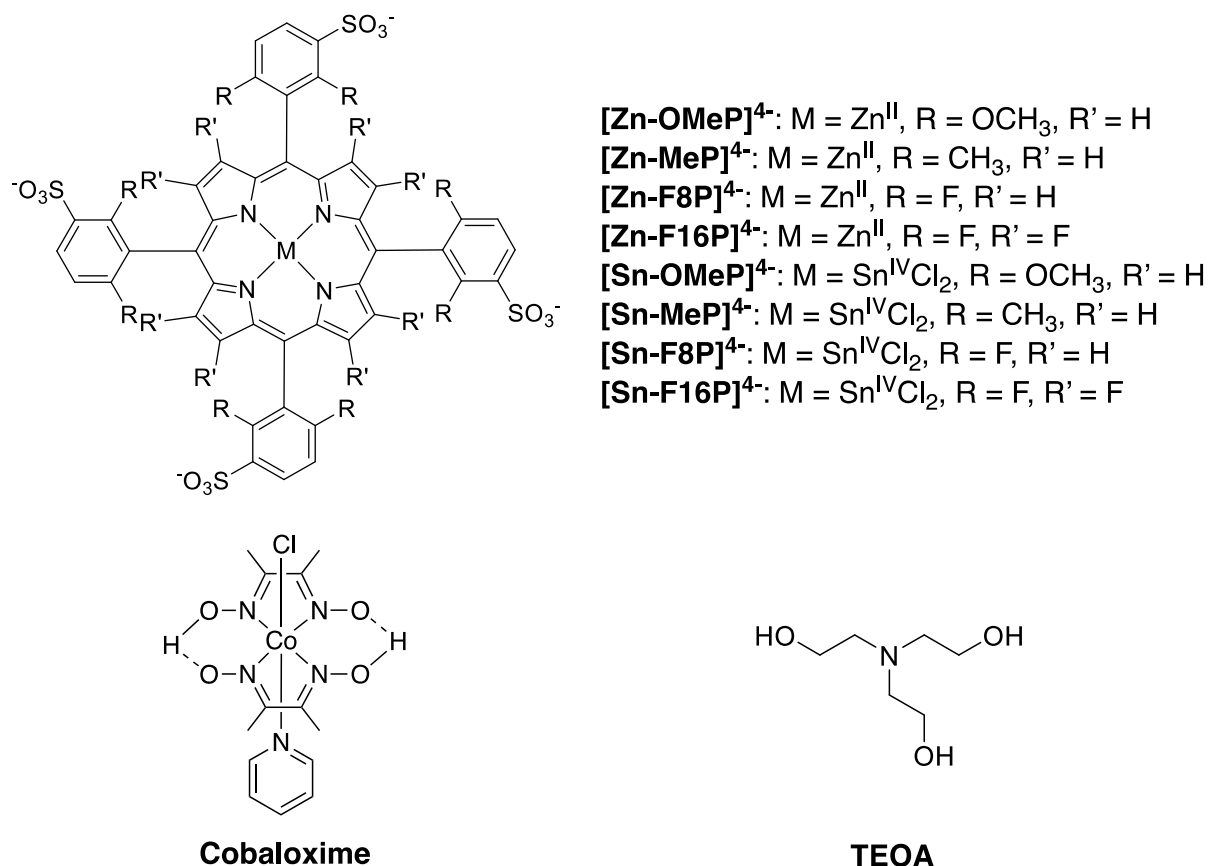


Figure 4.1 Chemical structures of water-soluble metal porphyrin photosensitizers reported in this work, the cobaloxime hydrogen-evolving catalyst, and the sacrificial electron donor TEOA. All porphyrin compounds were isolated as their Na^+ salts.

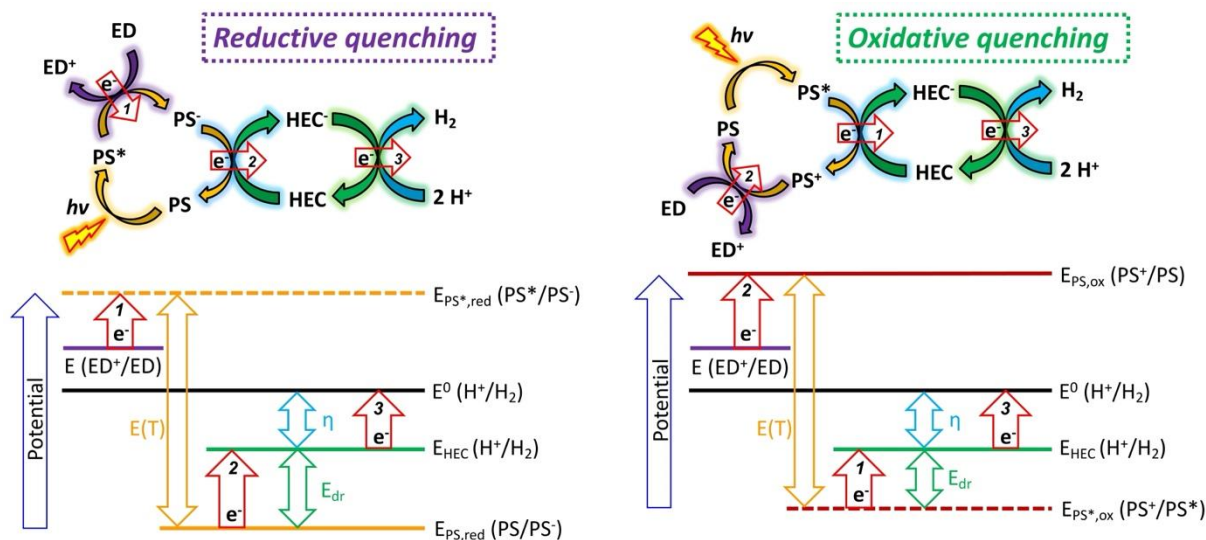


Figure 4.2 Simplified mechanism of reductive quenching and oxidative quenching pathways and their corresponding energy schemes for three-component photocatalytic hydrogen evolution. ED: sacrificial electron donor; PS: photosensitizer; HEC: hydrogen evolving catalyst; $E(T)$: triplet excited state energy of PS; η : overpotential of HEC; E_{dr} : driving force of the electron transfer from the photosensitizer to the catalyst.

4.2 Results and Discussion

4.2.1 Synthesis

The tetrasulfonated free-base porphyrin ligands Na₄[H₂-OMeP],^[37] Na₄[H₂-MeP],^[38] Na₄[H₂-F8P],^[39] Na₄[H₂-F16P],^[40] and the metal complexes Na₄[Zn-F8P],^[41] Na₄[Zn-F16P],^[40] were synthesized according to reported methods. The synthesis of Na₄[Zn-OMeP] and Na₄[Zn-MeP] is described in **Chapter 3**. The four Sn(IV)-porphyrin compounds discussed in this chapter are new and were synthesized via refluxing the free-base ligands with Sn(II) dichloride in Milli-Q water for 12 h. An Na⁺-loaded ion exchange resin was used to introduce Na⁺ counter cations, and finally the Sn-porphyrin complexes were purified by size-exclusion chromatography in order to remove excess SnCl₂. Full characterization is given in the Supplementary Information (Figure AIII.1 - Figure AIII.6).

4.2.2 Photochemical properties

The light absorption properties of the Zn- and Sn-porphyrin complexes were studied via steady-state UV-vis measurements in 1:1 pH 7.0 water/MeCN solutions in the presence of 5% (v/v) TEOA. For both series, the intense Soret band characteristic of porphyrin ligands and

complexes was observed between 409 and 424 nm and the Q band between 540—615 nm (Figure 4.3). For both the Soret and the first Q bands, a small blue shift of the absorption peaks was found with increasing electron-withdrawing properties of the substituents, from the electron-richest [M-OMeP]⁴⁻ to the electron-poorest [M-F16P]⁴⁻ (M = Zn^{II} or Sn^{IV}Cl₂). As shown in Table 4.1, in the Zn-porphyrin series the Soret and the first Q bands shifted by 15 nm and 16 nm, respectively, while in the Sn-porphyrin series the shift was only 12 and 13 nm, respectively. From [M-OMeP]⁴⁻ to [M-MeP]⁴⁻, the peak shift was very limited in both series (≤ 2 nm), while from [M-F8P]⁴⁻ to [M-F16P]⁴⁻ and [M-MeP]⁴⁻ to [M-F8P]⁴⁻, the peak shift was more significant (≥ 5 nm). Overall, the electron-withdrawing substituents influenced the absorption properties of these compounds moderately.^[8]

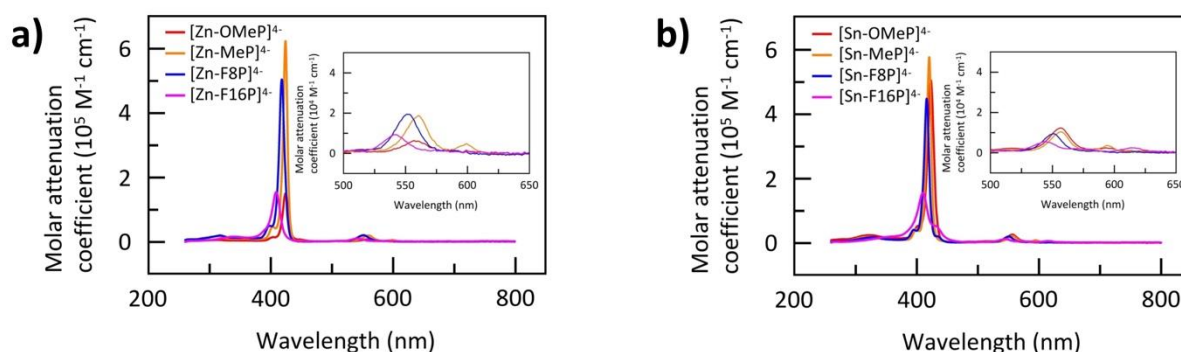


Figure 4.3 Absorption spectra of a) Zn- and b) Sn-porphyrin complexes in 1:1 pH 7.0 water/MeCN solution under air with 5% (v/v) TEOA, $T = 298$ K.

Table 4.1 Light absorption properties of Zn- and Sn-porphyrin complexes

	$\lambda_{\text{Sor}}^{[\text{a}]}$ ($\epsilon_{\text{Sor}}^{[\text{b}]}$)	$\lambda_{\text{Q}}^{[\text{a}]}$ ($\epsilon_{\text{Q}}^{[\text{b}]}$)	$\epsilon^{[\text{b}]}$ at 550 nm
[Zn-OMeP]⁴⁻	424 (140)	557 (6.4)	4.0
[Zn-MeP]⁴⁻	424 (630)	557 (19) / 599 (4.9)	11
[Zn-F8P]⁴⁻	418 (510)	551 (20)	19
[Zn-F16P]⁴⁻	409 (150)	541 (10)	6.0
[Sn-OMeP]⁴⁻	423 (430)	557 (22) / 595 (5.0)	18
[Sn-MeP]⁴⁻	421 (590)	556 (19) / 595 (7.3)	15
[Sn-F8P]⁴⁻	416 (440)	551 (19)	19
[Sn-F16P]⁴⁻	411 (310)	544 (22) / 615 (4.8)	9.2

^[a] λ_{Sor} and λ_{Q} are the absorption maxima (in nm) for the Soret and Q bands, respectively; both were measured in the condition of Figure 4.3.

^[b] molar attenuation coefficient, $\times 10^3 \text{ M}^{-1} \text{ cm}^{-1}$.

4.2.3 Photocatalysis

Cobaloxime is an efficient catalyst for light-driven hydrogen evolution, which has been used as a standard HEC for photosensitizer development.^[7] Unfortunately, due to its poor solubility in water it can only be used in water/MeCN mixtures. Therefore, we run all photocatalytic reactions in 1:1 water/MeCN solutions containing 5% (v/v) TEOA (~0.38 M) as sacrificial electron donor, to which HCl was added until reaching pH 7.0. The pK_{a} of TEOA in a 1:1 water/MeCN solution was reported to be 7.0,^[7,42] we hence consider the photocatalytic solutions used in this work to be buffered at pH 7.0 by TEOA. Since all porphyrin complexes absorb 540–560 nm light (Q band), a 550 nm green LED (9 mW, >80% intensity in range 540–560 nm) was used as the light source, which allowed for comparing photocatalytic properties of the different photosensitizers. The molar attenuation coefficient of all 8 PS is

indicated in Table 4.1. Under irradiation, using 0.49 mM cobaloxime and 0.04 mM PS, $[\text{Zn-F16P}]^{4-}$ was the only compound of the Zn series to give significant photocatalytic activity (Figure 4.4a). In the Sn series, both $[\text{Sn-OMeP}]^{4-}$ and $[\text{Sn-MeP}]^{4-}$ were found to result in photoactive systems (Figure 4.4b). $[\text{Zn-F16P}]^{4-}$ showed the best efficiency of the three photosensitizers that effectively resulted in hydrogen evolution, with a photocatalytic turnover number (PTON) of 850 ($\text{mol}_{\text{H}_2}/\text{mol}_{\text{PS}}$) after 20 h irradiation, and a maximum photocatalytic turnover frequency (PTOF, determined as explained in the Experimental Part, 4.4.5) of 59 h^{-1} . $[\text{Sn-MeP}]^{4-}$ resulted in a lower photocatalytic activity (PTON of 430 after 20 h irradiation and a maximum PTOF of 35 h^{-1}), and the photoactivity observed for $[\text{Sn-OMeP}]^{4-}$ as PS only lasted for 4 h of irradiation, with a low PTON of 30 and a low maximum PTOF of 13 h^{-1} . It is worth noting that for $[\text{Zn-F16P}]^{4-}$ in the absence of the cobaloxime HEC the photocatalytic system was not active for hydrogen evolution (Figure 4.4a). In addition, the system did not show any photocatalytic activity when replacing $[\text{Zn-F16P}]^{4-}$ by $[\text{Sn-F16P}]^{4-}$ (in the presence of cobaloxime) (Figure 4.4b). These results indicate that in the most active system using $[\text{Zn-F16P}]^{4-}$, $[\text{Zn-F16P}]^{4-}$ indeed played the role of PS, even if we demonstrated in **Chapter 3** that in different conditions, and in association with $[\text{Ru}(\text{bpy})_3]^{2+}$ as photosensitizer, it can also work as a HEC.

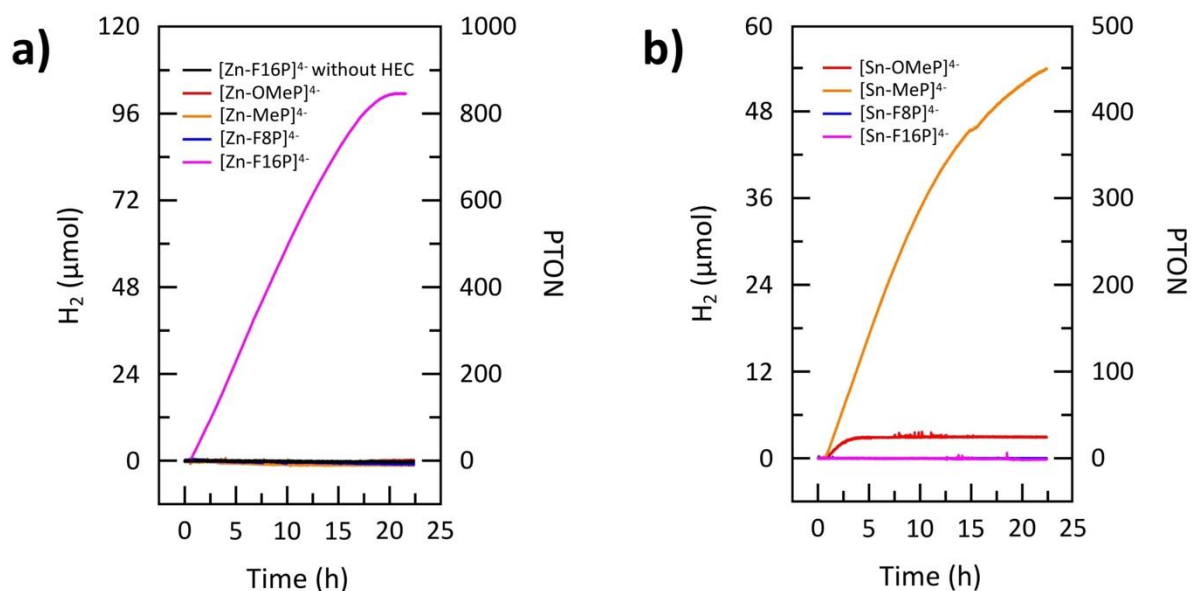


Figure 4.4 Hydrogen evolution during photocatalytic water reduction in the presence of 0.04 mM of the photosensitizer a) $[\text{Zn-OMeP}]^{4-}$, $[\text{Zn-MeP}]^{4-}$, $[\text{Zn-F8P}]^{4-}$ and $[\text{Zn-F16P}]^{4-}$, b) $[\text{Sn-OMeP}]^{4-}$, $[\text{Sn-MeP}]^{4-}$, $[\text{Sn-F8P}]^{4-}$ and $[\text{Sn-F16P}]^{4-}$, 5% (v/v) TEOA as sacrificial electron donor, with or without (a) 0.49 mM cobaloxime as catalyst, in a 1:1 pH 7.0 water/MeCN

solution, using green light irradiation (550 nm, 9 mW), $T = 298$ K. Light was switched on at $t = 0.5$ h.

In all cases, photocatalysis slowed down (Sn) or stopped (Zn) after ~22 h photocatalysis. Additional experiments were performed to understand whether deactivation of the most active system containing the PS [Zn-F16P]⁴⁻ was due to the decomposition of the PS. First, 0.12 μmol of fresh [Zn-F16P]⁴⁻ was added as solid into 3 mL of the photocatalytic mixture containing 0.04 mM [Zn-F16P]⁴⁻, 0.49 mM cobaloxime and 5% (v/v) TEOA, after the first 22 h irradiation. When green light irradiation was resumed, no hydrogen generation was observed (Figure 4.5a). Second, when a twice higher concentration (0.08 mM) of [Zn-F16P]⁴⁻ was used, an almost twice higher maximum PTOF (109 h^{-1}) was observed (Figure 4.4a), resulting in almost double PTON of 1690 after 20 h (Figure 4.5b). However, the lifetime of the system (~20 h) was not significantly changed. These two results strongly suggest that decomposition of the photosensitizer [Zn-F16P]⁴⁻ is not the cause of deactivation of the photocatalytic system, and that catalyst decomposition might be the problem instead.

In a third experiment, a twice higher concentration (0.98 mM) of the cobaloxime HEC was used; the resulting photocatalytic system, still using 0.04 mM [Zn-F16P]⁴⁻ as PS and 5% (v/v) TEOA as ED, was active this time for more than 100 h under green light irradiation (Figure 4.5c). However, the total PTON of this catalytic system after 100 h irradiation was 920, which is close to the maximum PTON 850 of the system with 0.49 mM cobaloxime after 20 h irradiation. In addition, only minor changes of the UV-vis spectra of the catalytic solution were observed after irradiating for 100 h: ~95% of the characteristic absorption peaks of [Zn-F16P]⁴⁻ at 409 and 541 nm was retained, compared to the initial absorbance (Figure 4.5d). These results demonstrate that [Zn-F16P]⁴⁻ has a great stability in photocatalytic conditions, and that when combined with cobaloxime as HEC, it remains photoactive at least for 100 h under green light irradiation.

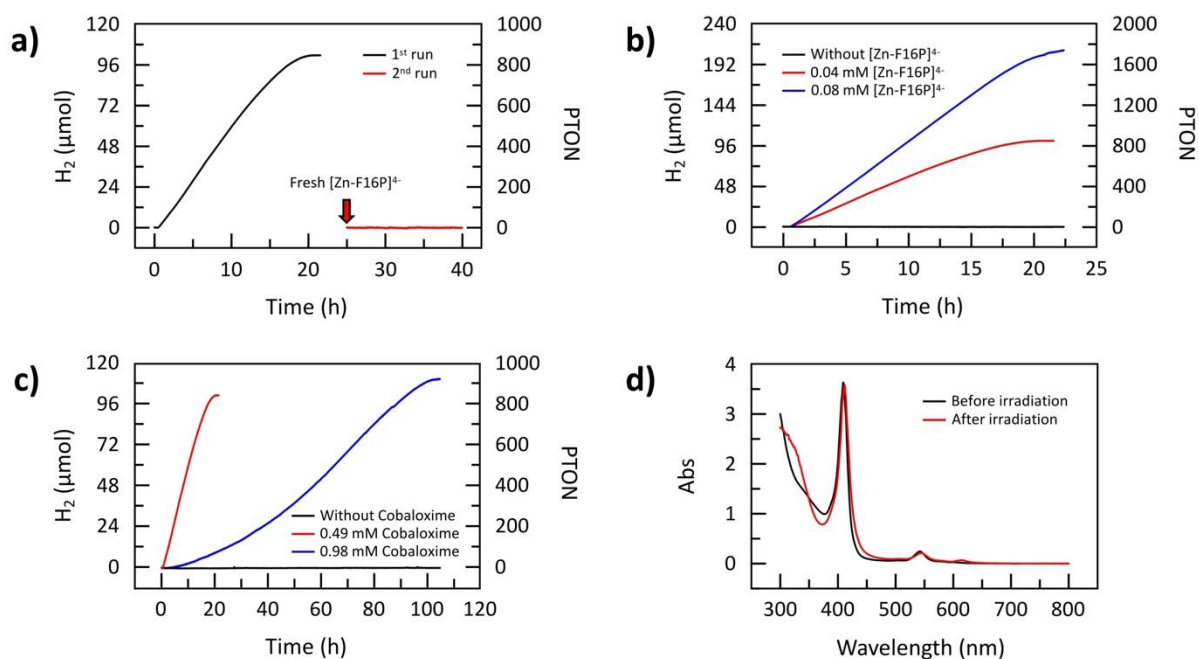


Figure 4.5 Stability of $[\text{Zn-F16P}]^{4-}$ in photocatalytic hydrogen evolution. a) Hydrogen evolution during two consecutive photocatalytic runs, adding 1 eq. more of PS at the end of the first run. b) and c) Photocatalytic hydrogen production when doubling the initial concentration of PS (b) or that of the cobaloxime catalyst (c). d) UV-vis absorption of the photocatalytic solution used in c) before (black) and after (red) irradiation. Conditions: a) 0.04 mM $[\text{Zn-F16P}]^{4-}$, 0.49 mM cobaloxime, b) 0.04 or 0.08 mM $[\text{Zn-F16P}]^{4-}$, 0.49 mM cobaloxime, c) 0.04 mM $[\text{Zn-F16P}]^{4-}$, 0.49 or 0.98 mM cobaloxime, d) 0.04 mM $[\text{Zn-F16P}]^{4-}$, 0.98 mM cobaloxime, 5% (v/v) TEOA in 1:1 pH 7.0 water/MeCN solutions and green light irradiation (550 nm, 9 mW), $T = 298$ K. For all photocatalytic experiments, light was switched on at $t = 0.5$ h. Between the two irradiation experiments in a), 0.12 μmol fresh $[\text{Zn-F16P}]^{4-}$ was added as a solid.

4.2.4 Electrochemical properties

In order to investigate the thermodynamics of the photocatalytic systems and the quenching mechanisms at play, the reduction and oxidation potentials of all metalloporphyrin complexes were determined using differential pulse voltammetry (DPV) measurements with a 0.07 cm^2 glassy-carbon (GC) working electrode, an Ag/AgCl reference electrode, and a Pt-wire counter electrode. As the photocatalytic experiments were always performed in a 1:1 pH 7.0 water/MeCN solution due to the poor solubility of cobaloxime in water, all the DPV measurements were performed in a 1:1 0.1 M pH 7.0 phosphate buffer/MeCN solution to mimic the photocatalytic conditions.

The photosensitizers are usually considered to accept or donate one electron at a time from or to the other components in the photocatalytic system. Therefore, in this work, we only measured the first redox potentials of all Zn- and Sn-porphyrin complexes. For the first reduction potential in the Zn porphyrin series, when going from the electron-richest complex [Zn-OMeP]⁴⁻ to the electron-poorest [Zn-F16P]⁴⁻ a less negative ground-state reduction potential $E_{PS,red}(PS/PS^-)$ was found (Table 4.2 and Figure AIII.7a). In contrast, the ground-state oxidation potential $E_{PS,ox}(PS^+/PS)$ of the complexes were found to be more and more positive (Table 4.2 and Figure AIII.7b); only the potential of [Zn-OMeP]⁴⁻ and [Zn-MeP]⁴⁻ appeared to be the same. Similar trends were observed for the Sn-porphyrin series, with ground state reduction potentials of [Sn-OMeP]⁴⁻ and [Sn-MeP]⁴⁻ that were identical within the precision of the measurement (Table 4.2 and Figure AIII.8a), and ground state oxidation potentials that only slightly increased with the electron-withdrawing ability of the substituents (Table 4.2 and Figure AIII.8b). It is worth mentioning that, as reported by Coutsolelos and co-workers^[7], the ground state oxidation potentials of the Sn(IV)-porphyrin complexes generally were found to be higher than those of the Zn(II)-porphyrin complexes. This observation probably is related to the higher oxidation state of Sn, which makes the complexes of the Sn compounds more electron poor and thus more difficult to oxidize.

4.2.5 Excited state energies

For both of the Zn- and Sn-porphyrin series, modifying the porphyrin complex with electron-withdrawing or electron-donating substituents not only changes their ground-state oxidation potential $E_{PS,ox}(PS^+/PS)$ and ground-state reduction potential $E_{PS,red}(PS/PS^-)$, but also affects the Gibbs free energy of their triplet excited state, $E(T)$. Here, we assumed that longer lifetimes are typically required in homogeneous solution to obtain a significant rate for intermolecular photoelectron transfer. Considering that the presence of a metal center in the photosensitizers increased the rate of intersystem crossing to the triplet state, we hypothesized that efficient sensitization could only take place from the triplet state (PS^*) of the photosensitizer, which is longer lived than the singlet ground state (PS). $E(T)$ was hence calculated by minimizing the geometry of the triplet state and that of the singlet ground state of each molecule using DFT, and by calculating the difference of their Gibbs free energy (Table 4.2). These DFT calculations reveal that the estimated triplet excited-state energy $E(T)$ of the zinc(II) or tin(IV) complexes increased with the electron-withdrawing properties of the porphyrin ligand (Table 4.2), with

the exception of $[M-OMeP]^{4-}$, which showed almost identical values of $E(T)$, compared to $[M-MeP]^{4-}$.

From these $E(T)$ values, the potential of the redox couples involving the excited state of the photosensitizers, $E_{PS^*,red}(PS^*/PS^-)$ and $E_{PS^*,ox}(PS^+/PS^*)$, were estimated (Table 4.2). The increase of the electron-withdrawing properties of the porphyrin ligand resulted in a strong increase of the ground-state reduction potential of the PS/PS^- couple, but also in a milder but clearly increasing triplet-state energy, which altogether led to a strongly increasing reduction potential for the PS^*/PS^- couple involving the excited triplet state. This trend leads to very positive reduction potential values $E_{PS^*,red}(PS^*/PS^-)$ of +1.16 V vs. NHE for $[Zn-F16P]^{4-}$ and +1.43 V vs. NHE for $[Sn-F16P]^{4-}$, highlighting the excellent photo-oxidizing properties of these two metal porphyrin molecules. On the other hand, the increasing electron-withdrawing properties of the ligand also resulted in a strong increase of the oxidation potential of the PS^+/PS^* couple. Here, however, the already mentioned mild increase of $E(T)$ along these two series of complexes slightly lowered the resulting increase of the oxidation potential of the PS^+/PS^* couple. For example, $E_{PS,ox}(PS^+/PS)$ was increased by 0.15 V from $[Sn-OMeP]^{4-}$ to $[Sn-F16P]^{4-}$, but their oxidation potentials $E_{PS^*,ox}(PS^+/PS^*)$ could not be distinguished: they were both -0.07 V vs. NHE.

Table 4.2 Calculated triplet excited state energies and redox potentials for redox couples involving the ground state and the triplet excited state of Zn- and Sn-porphyrin complexes.

PS	$E_{PS,red}(PS/PS^-)^{[a]}$	$E_{PS,ox}(PS^+/PS)^{[a]}$	$E(T)^{[b]}$	$E_{PS^*,red}(PS^*/PS^-)^{[a]}$	$E_{PS^*,ox}(PS^+/PS^*)^{[a]}$
[Zn-OMeP] ⁴⁻	−1.18 V	0.94 V	1.69	0.51 V	−0.75 V
[Zn-MeP] ⁴⁻	−1.10 V	0.94 V	1.69	0.59 V	−0.75 V
[Zn-F8P] ⁴⁻	−0.95 V	1.20 V	1.75	0.80 V	−0.55 V
[Zn-F16P] ⁴⁻	−0.61 V	1.57 V	1.77	1.16 V	−0.20 V
[Sn-OMeP] ⁴⁻	−0.60 V	1.51 V	1.58	0.98 V	−0.07 V
[Sn-MeP] ⁴⁻	−0.60 V	1.52 V	1.53	0.93 V	−0.01 V
[Sn-F8P] ⁴⁻	−0.41 V	1.53 V	1.67	1.26 V	−0.14 V
[Sn-F16P] ⁴⁻	−0.30 V	1.66 V	1.73	1.43 V	−0.07 V

^[a] V vs. NHE, as measured experimentally by DPV. Conditions: 1.0 mM PS in 1:1 (v/v) 0.1 M pH 7.0 phosphate buffer/MeCN solution, 0.07 cm² glassy-carbon working electrode, Pt wire auxiliary electrode, Ag/AgCl reference electrode, ± 0.004 V increase potential, 0.05 V amplitude, 0.05 s pulse width, 0.0167 s sampling width, 0.5 s sample period, T = 298 K.

^[b] in eV, as calculated by DFT calculation at the B3LYP-D3(BJ)/ZORA-TZ2P level using COSMO to simulate solvent effects.

4.2.6 Discussion

Following absorption of a photon, the excited photosensitizer PS* can be either reduced by the sacrificial electron donor TEOA (reductive quenching) to form PS[−], or oxidized by the HEC cobaloxime (oxidative quenching) to form PS⁺. The reduction potential of cobaloxime E(Co^{III}/Co^{II}) was found to be located at −0.59 V vs. NHE, and the second reduction E(Co^{II}/Co^I) was found at −0.74 V vs. NHE in a 1:1 0.1 M pH 7.0 phosphate buffer/MeCN solution (Figure AIII.9), similar as that reported previously.^[7] For an oxidative quenching pathway, the potential of the couple involving the triplet excited state of the photosensitizer, $E_{PS^*,ox}(PS^+/PS^*)$, should be at least more negative than E(Co^{III}/Co^{II}) and even than E(Co^{II}/Co^I), considering that more than 2 electrons are needed to drive hydrogen evolution. With a potential of −0.75 V vs. NHE,

only $[\text{Zn-OMeP}]^{4-}$ and $[\text{Zn-MeP}]^{4-}$ fulfill this criterion. The other six porphyrin-based photosensitizers are too electron-poor even to be able to proceed with the electron transfer Step 1 (Figure 4.2 right), i.e., reduction of Co^{III} to Co^{II} . The second condition for oxidative quenching, that the ground-state oxidation potential $E_{\text{PS,ox}}(\text{PS}^+/\text{PS})$ is positive enough to have PS^+ reduced by TEOA, is also met for both $[\text{Zn-OMeP}]^{4-}$ and $[\text{Zn-MeP}]^{4-}$: the oxidation potential of TEOA was reported to be around 0.82 V vs. NHE,^[42] which is lower than the 0.94 V vs. NHE necessary to reduce PS^+ back to PS. In spite of the favorable thermodynamic driving forces, however, none of the two photosensitizers $[\text{Zn-OMeP}]^{4-}$ and $[\text{Zn-MeP}]^{4-}$ showed any photoactivity for light-driven hydrogen evolution in our conditions. This might be a consequence of unfavorable kinetics at the concentrations used in our experiments, or might be due to short excited-state lifetimes, which have not been determined yet. Overall, photocatalysis seems not to proceed via an oxidative quenching pathway for any of the porphyrin-based photosensitizers in these series.

Since the oxidation potential of TEOA is around 0.82 V vs. NHE,^[42] the potentials $E_{\text{PS}^*,\text{red}}(\text{PS}^*/\text{PS}^-)$ for $[\text{Zn-OMeP}]^{4-}$, $[\text{Zn-MeP}]^{4-}$ and $[\text{Zn-F8P}]^{4-}$, are not sufficiently positive for reductive quenching to occur (Step 1 in Figure 4.2 left); only the most electron poor zinc complex $[\text{Zn-F16P}]^{4-}$ has a potential of $E_{\text{PS}^*,\text{red}}(\text{PS}^*/\text{PS}^-)$ that is positive enough for reductive quenching to occur. In contrast, all tin porphyrin compounds have a potential $E_{\text{PS}^*,\text{red}}(\text{PS}^*/\text{PS}^-)$ that is high enough for reductive quenching to proceed. However, once reductive quenching has occurred not all photo-reduced porphyrins PS^- offer favorable redox properties to complete the catalytic cycle. Indeed, the PS^- intermediates need to be able to transfer electrons to the HEC as Step 2. According to our data, only the PS^- species of $[\text{Zn-F16P}]^{4-}$, $[\text{Sn-OMeP}]^{4-}$, and $[\text{Sn-MeP}]^{4-}$, have reduction potentials $E_{\text{PS,red}}(\text{PS}/\text{PS}^-)$ that are negative enough to reduce cobaloxime from Co^{III} to Co^{II} , which is necessary for photocatalysis to proceed.

Overall, according to this analysis of redox potentials and the results of photocatalytic HER experiments, the reductive-quenching pathway seems to be the most realistic for the three porphyrin photosensitizers found active in photocatalytic conditions ($[\text{Zn-F16P}]^{4-}$, $[\text{Sn-OMeP}]^{4-}$, and $[\text{Sn-MeP}]^{4-}$). At this point two remarks should be made. First, since the redox properties and estimated excited-state energy of $[\text{Sn-OMeP}]^{4-}$ and $[\text{Sn-MeP}]^{4-}$ are similar, the low H_2 production obtained with $[\text{Sn-OMeP}]^{4-}$ is probably due to its poor photostability. As is clear from Figure 4.4b, the photocatalytic activity of the system containing $[\text{Sn-OMeP}]^{4-}$ only lasted 4 h, while for the system containing $[\text{Sn-MeP}]^{4-}$ it lasted for more than 20 h. Second, for none of these three active photosensitizers the potential of the photo-reduced PS^- species is sufficiently negative to reduce Co^{II} in cobaloxime to Co^{I} , which is considered to be the H_2 -

releasing active species of this catalyst at -0.74 V vs. NHE.^[7] Two reasons are proposed here that may explain the hydrogen evolution that is experimentally observed with these three sensitizers. First, in photocatalytic conditions the cobaloxime may decompose into more active HEC species, such as cobalt nanoparticles, characterized by an overpotential η (Figure 4.2) that is lower than that measured in the dark by electrochemistry. Possibly, such species may then be driven by the photo-reduced Zn- and Sn-porphyrin photosensitizers. Second, a TEOA-derived alkyl radical species ($\text{TEOA}^{\bullet+}$) forms during the first electron transfer step of the photocatalytic mechanism, which has a lower reduction potential (around -0.79 V vs. NHE in MeCN) than the potential of the PS/PS^- couple. This radical may reduce the Co^{II} species of cobaloxime to Co^{I} , further leading to dihydrogen evolution, in a second step that does not involve the formation of a second excited state of the photosensitizer PS^* .^[7,43] In this hypothesis, light would serve as a way to trigger the reaction and generate the radical $\text{TEOA}^{\bullet+}$, and only one photon would be needed per photogenerated molecule of H_2 .

4.3 Conclusion

A series of tetra-anionic Zn(II)- and Sn(IV)-porphyrin complexes were prepared and tested as photosensitizers for homogeneous photocatalytic hydrogen evolution in the presence of cobaloxime as the catalyst and TEOA as the sacrificial electron donor in 1:1 pH 7.0 water/acetonitrile solutions. The catalytic activity of the systems containing these photosensitizers appeared to be strongly dependent on the presence of electron-withdrawing or electron-donating substituents on the porphyrin ligand. The Zn(II)-porphyrin complexes in general are more electron rich than the Sn(IV)-porphyrin analogues, and based on our studies we conclude that the reductive-quenching mechanism is followed for all PS molecules. As a consequence, in the Zn series only the electron-poorest complex, $[\text{Zn-F16P}]^{4-}$, was photoactive. It actually showed a very high photostability, as it could work for more than 100 h under green light irradiation without significant decomposition, and showed also the highest PTON (850 after 20 h irradiation) and highest PTOF (59 h^{-1}). For the electron-poorer Sn series, only the most electron-rich compounds of the series, $[\text{Sn-OMeP}]^{4-}$ and $[\text{Sn-MeP}]^{4-}$, appeared to result in a system that was active for HER; photocatalytic activities were lower than with $[\text{Zn-F16P}]^{4-}$, however. Our general understanding of these trends is that the electronic effects introduced by the functional groups on the porphyrin ligands control both their ground-state redox properties and their triplet excited state energies. These effects further control the redox properties of their excited state, and hence their activity when used in photocatalytic systems. We also note that

the oxidation state of the metal plays an important role, too, as Sn(IV) compounds were in average more electron-poor (in the ground state) than those based on Zn(II). This work brings important information for the design of molecular photosensitizers for hydrogen evolution: it demonstrated that a balance between the redox potentials of the ground-state and that of the excited state must be found, which can be fine-tuned by introduction of electron-donating or electron-withdrawing substituents.

4.4 Experimental section

4.4.1 Materials and methods

All reagents were purchased from Sigma-Aldrich and used as received unless otherwise noted. The compounds tetrasodium-5,10,15,20-tetrakis(2,6-dimethoxyphenyl-3-sulfonatophenyl)-21*H*,23*H*-porphyrin ($\text{Na}_4[\text{H}_2\text{-OMeP}]$),^[37] tetrasodium-5,10,15,20-tetrakis(2,6-dimethylphenyl-3-sulfonatophenyl)-21*H*,23*H*-porphyrin ($\text{Na}_4[\text{H}_2\text{-MeP}]$),^[38] tetrasodium-5,10,15,20-tetrakis(2,6-difluorophenyl-3-sulfonatophenyl)-21*H*,23*H*-porphyrin ($\text{Na}_4[\text{H}_2\text{-F8P}]$),^[41] tetrasodium-2,3,7,8,12,13,17,18-octafluoro-5,10,15-20-tetrakis(2,6-difluoro-3-sulfonatophenyl)-21*H*,23*H*-porphyrin ($\text{Na}_4[\text{H}_2\text{-F16P}]$),^[40] tetrasodium-5,10,15,20-tetrakis(2,6-difluoro-3-sulfonatophenyl)porphyrin-Zn(II) ($\text{Na}_4[\text{Zn-F8P}]$),^[41] tetrasodium-2,3,7,8,12,13,17,18-octafluoro-5,10,15-20-tetrakis(2,6-difluoro-3-sulfonatophenyl)porphyrin-Zn(II) ($\text{Na}_4[\text{Zn-F16P}]$),^[40] were prepared according to published methods. Tetrasodium-5,10,15,20-tetrakis(2,6-dimethoxyphenyl-3-sulfonatophenyl)porphyrin-Zn(II) ($\text{Na}_4[\text{Zn-OMeP}]$) and tetrasodium-5,10,15,20-tetrakis(2,6-dimethylphenyl-3-sulfonatophenyl)porphyrin-Zn(II) ($\text{Na}_4[\text{Zn-MeP}]$) were prepared according to **Chapter 3**. Cobaloxime and TEOA were purchased from Sigma-Aldrich and used without further treatments. ¹H NMR spectra were recorded on a Bruker 400DPX-liq spectrometer operating at 400 MHz. ¹⁹F NMR spectra were recorded on a Bruker 500DPX spectrometer operating at 500 MHz. High-resolution mass spectrometric measurements were made on a Bruker Fourier Transform Ion Cyclotron Resonance Mass Spectrometer APEX IV at Leiden University. Elemental analyses were performed at the Mikroanalytisches Laboratorium Kolbe, Germany. Electronic absorption spectra were obtained on a Varian Cary 60 spectrophotometer at 25 °C. The LED optical power was measured using an OPHIR Nova-display laser power meter.

4.4.2 Synthesis

Tetrasodium dichlorido-5,10,15,20-tetrakis(2,6-dimethoxyl-3-sulfonatophenyl)porphyrin stannate(IV) ($\text{Na}_4[\text{Sn-OMeP}]$)

The ligand $\text{Na}_4[\text{H}_2\text{-OMeP}]$ (115 mg, 0.09 mmol) and Milli-Q water (40 mL) were placed under N_2 in a 100 mL round-bottom flask equipped with a magnetic stirring bar and a condenser. A solution of tin(II) chloride heptahydrate (85.3 mg, 0.45 mmol) in Milli-Q water (10 mL) was added to the stirred solution, and the mixture was refluxed for 12 h. After cooling to room temperature, water was rotary evaporated at 40 °C and the residue was redissolved in cold methanol (15 mL). After filtration on a filter paper, methanol was rotary-evaporated, the residue was redissolved in cold methanol (5 mL). The solution was filtered by filter paper, rotary-evaporated, and the crude product was redissolved in Milli-Q water (5 mL) then passed onto an Amberlite IR 120 Na^+ form ion exchange resin column (10 cm length). Washed the resin with 50 mL Milli-Q water and collected the solution, then removed the water by rotary evaporator and the product was further purified on Sephadex-20H size exclusion chromatography to remove excess SnCl_2 (methanol). Yield (123 mg, 90%); ^1H NMR (400 MHz, CD_3OD): δ = 9.28 – 9.16 (m, 8H; β -pyrrole-H), 8.50 – 8.43 (m, 4H; *p*-Ph-H), 7.44 – 7.28 (m, 4H; *m*-Ph-H), 3.72 – 3.49 (m, 12 H; OCH_3), 3.22 – 2.68 ppm (m, 12 H; OCH_3); HRMS (ESI): m/z calcd for $\text{C}_{52}\text{H}_{45}\text{N}_4\text{O}_{21}\text{S}_4\text{Sn}^+$: 1309.0483 [$M-4\text{Na}-2\text{Cl}+3\text{H}+\text{H}_2\text{O}$] $^+$; found: 1309.0483; elemental analysis calcd (%) for $\text{C}_{52}\text{H}_{40}\text{Cl}_2\text{N}_4\text{Na}_4\text{O}_{20}\text{S}_4\text{Sn}\cdot 4\text{H}_2\text{O}$: C 41.02, H 3.18, N 3.68; found: C 40.82, H 3.16, N 3.61. UV-vis (1:1 $\text{H}_2\text{O}/\text{MeCN}$): λ_{max} (ϵ in $\text{M}^{-1}\text{cm}^{-1}$) 423 nm (4.7×10^5), 557 nm (2.2×10^4), 595 nm (5.0×10^3).

Tetrasodium dichlorido-5,10,15,20-tetrakis(2,6-dimethyl-3-sulfonatophenyl)porphyrin stannate(IV) ($\text{Na}_4[\text{Sn-MeP}]$)

$\text{Na}_4[\text{H}_2\text{-MeP}]\cdot 9\text{H}_2\text{O}$ (130 mg, 0.10 mmol) and Milli-Q water (40 mL) were placed under N_2 in a 100 mL round-bottom flask equipped with a magnetic stirring bar and a condenser. A solution of tin(II) chloride (94.8 mg, 0.50 mmol) in Milli-Q water (10 mL) was added to the stirred solution and the mixture was refluxed for 12 h under N_2 . After cooling to room temperature, water was rotary evaporated and the residue was redissolved in cold methanol (15 mL). After filtration on a filter paper, methanol was rotary-evaporated, the residue was redissolved in cold methanol (5 mL), the solution was filtered a second time by filter paper and rotary-evaporated, then the crude product was then passed onto an Amberlite IR 120 Na^+ form ion exchange resin column (10 cm length), washed the resin with 50 mL Milli-Q water and collected the solution, then removed the water by rotary evaporator and the product was finally

purified on Sephadex-20H size exclusion chromatography (methanol). Methanol was finally rotary evaporated and the solid dried in vacuo. Yield (128 mg, 92%); ^1H NMR (400 MHz, CD_3OD): δ = 9.18 – 9.09 (m, 8H; β -pyrrole-H), 8.43 – 8.38 (m, 4H; *p*-Ph-H), 7.68 – 7.55 (m, 4H; *m*-Ph-H), 2.42 – 2.09 (m, 12H; CH_3), 2.07 – 1.74 ppm (m, 12H; CH_3); HRMS (ESI): m/z calcd for $\text{C}_{52}\text{H}_{45}\text{N}_4\text{O}_{13}\text{S}_4\text{Sn}^+$: 1181.0882 $[\text{M}-4\text{Na}-2\text{Cl}+3\text{H}+\text{H}_2\text{O}]^+$; found: 1181.0881; m/z calcd for $\text{C}_{52}\text{H}_{44}\text{N}_4\text{NaO}_{13}\text{S}_4\text{Sn}^+$: 1203.0702 $[\text{M}-3\text{Na}-2\text{Cl}+2\text{H}+\text{H}_2\text{O}]^+$; found: 1203.0702; elemental analysis calcd (%) for $\text{C}_{52}\text{H}_{40}\text{Cl}_2\text{N}_4\text{Na}_4\text{O}_{12}\text{S}_4\text{Sn}\cdot 4\text{H}_2\text{O}$: C 44.78, H 3.47, N 4.02; found: C 44.97, H 3.43, N 3.96. UV-vis (1:1 $\text{H}_2\text{O}/\text{MeCN}$): $\lambda_{\text{max}}(\epsilon \text{ in } \text{M}^{-1}\text{cm}^{-1})$ 421 nm (5.9×10^5), 556 nm (1.9×10^4), 595 nm (7.3×10^3).

Tetrasodium dichlorido-5,10,15,20-tetrakis(2,6-difluoro-3-sulfonatophenyl)porphyrin stannate(IV) ($\text{Na}_4[\text{Sn-F8P}]$)

$\text{Na}_4[\text{H}_2\text{-F8P}]\cdot 4\text{H}_2\text{O}$ (124 mg, 0.10 mmol) and Milli-Q water (40 mL) were placed under N_2 in a 100 mL round-bottom flask equipped with a magnetic stirring bar and a condenser. A solution of tin(II) chloride (94.8 mg, 0.50 mmol) in Milli-Q water (10 mL) was added to the stirred solution and the mixture was refluxed for 12 h under N_2 . After cooling to room temperature, the water was rotary evaporated and the residue was redissolved in cold methanol (15 mL). After filtration over a filter paper, methanol was rotary-evaporated, the residue was redissolved in cold methanol (5 mL), and filtered by filter paper again. The filtrate was rotary-evaporated and the Co-F16 complex was then passed through an Amberlite IR 120 Na^+ form ion exchange resin column (10 cm length) and washed with Milli-Q water before being purified on Sephadex-20H size exclusion chromatography (eluent: methanol). Yield (124 mg, 89%); ^1H NMR (400 MHz, CD_3OD): δ = 9.49 – 9.40 (m, 8H; β -pyrrole-H), 8.60 – 8.48 (m, 4H; *p*-Ph-H), 7.72 – 7.61 ppm (m, 4H; *m*-Ph-H); ^{19}F NMR (471 MHz, CD_3OD): δ = -106.42 ppm (d, J = 348.2 Hz, 8F; *o*-F); HRMS (ESI): m/z calcd for $\text{C}_{44}\text{H}_{21}\text{F}_8\text{N}_4\text{O}_{13}\text{S}_4\text{Sn}^+$: 1212.8881 $[\text{M}-4\text{Na}-2\text{Cl}+3\text{H}+\text{H}_2\text{O}]^+$; found: 1212.8879; m/z calcd for $\text{C}_{44}\text{H}_{20}\text{F}_8\text{N}_4\text{NaO}_{13}\text{S}_4\text{Sn}^+$: 1234.8696 $[\text{M}-3\text{Na}+2\text{H}+\text{H}_2\text{O}]^+$; found: 1234.8693; elemental analysis calcd (%) for $\text{C}_{44}\text{H}_{16}\text{Cl}_2\text{F}_8\text{N}_4\text{Na}_4\text{O}_{12}\text{S}_4\text{Sn}\cdot 2\text{H}_2\text{O}$: C 38.01, H 1.45, N 4.03; found: C 38.27, H 1.59, N 4.02. UV-vis (1:1 $\text{H}_2\text{O}/\text{MeCN}$): $\lambda_{\text{max}}(\epsilon \text{ in } \text{M}^{-1}\text{cm}^{-1})$ 416 nm (4.4×10^5), 551 nm (1.9×10^4).

Tetrasodium dichlorido-2,3,7,8,12,13,17,18-octafluoro-5,10,15,20-tetrakis(2,6-difluoro-3-sulfonatophenyl)porphyrin stannate(IV) ($\text{Na}_4[\text{Sn-F16P}]$)

$\text{Na}_4[\text{H}_2\text{-F16P}]\cdot 5\text{H}_2\text{O}$ (140 mg, 0.10 mmol) and Milli-Q water (40 mL) were placed under N_2 in a 100 mL round-bottom flask equipped with a magnetic stirring bar and a condenser. A solution of tin(II) chloride (94.8 mg, 0.50 mmol) in Milli-Q water (10 mL) was added to the stirred solution, and the mixture was refluxed for 12 h under N_2 . After cooling to room temperature, water was rotary evaporated at 40 °C and the residue was redissolved in cold methanol (15 mL). After filtration on a filter paper, methanol was rotary-evaporated, the residue was redissolved in cold methanol (5 mL). The solution was filtered by filter paper, rotary-evaporated, and the crude product was redissolved in Milli-Q water (5 mL) then passed onto an Amberlite IR 120 Na^+ form ion exchange resin column (10 cm length), the resin washed with Milli-Q water and the product was further purified on Sephadex-20H size exclusion chromatography to remove excess tin(II) chloride (methanol). Yield (133 mg, 87%); ^1H NMR (400 MHz, CD_3OD): 8.36 – 8.27 (m, 4H; *p*-Ph-H), 8.43 – 8.35 ppm (m, 4H; *m*-Ph-H); ^{19}F NMR (471 MHz, CD_3OD): δ = -107.17 – -107.83 (m, 4F; *o*-F), -108.40 – -109.14 (m, 4F; *o*-F), -150.19 (s, 4F; β -pyrrole-F), -151.52 ppm (s, 4F; β -pyrrole-F); HRMS (ESI): m/z calcd for $\text{C}_{44}\text{H}_{13}\text{F}_{16}\text{N}_4\text{O}_{13}\text{S}_4\text{Sn}^+$: 1356.8127 [$\text{M}-4\text{Na}-2\text{Cl}+3\text{H}+\text{H}_2\text{O}$] $^+$; found: 1356.8123; elemental analysis calcd (%) for $\text{C}_{44}\text{H}_8\text{Cl}_2\text{F}_{16}\text{N}_4\text{Na}_4\text{ZnO}_{12}\text{S}_4\text{Sn}\cdot 2\text{H}_2\text{O}$: C 34.44, H 0.79, N 3.65; found: C 34.46, H 0.72, N 3.64. UV-vis (1:1 $\text{H}_2\text{O}/\text{MeCN}$): λ_{max} (ϵ in $\text{M}^{-1}\text{cm}^{-1}$) 411 nm (3.1×10^5), 544 nm (2.2×10^4), 615 nm (4.8×10^3).

4.4.3 Electrochemistry

Differential pulse voltammetry (DPV) measurements were performed using an Autolab PGstart10 potentiostat controlled by GPES4 software. All the DPV measurements were recorded in 1:1 0.1 M pH 7.0 sodium phosphate buffer/acetonitrile solution using a three-compartment cell possessing a 0.07 cm^2 glassy-carbon electrode as the working electrode, Pt wire as the auxiliary electrode, Ag/AgCl (saturated KCl aq.) as the reference electrode, and $\text{K}_3[\text{Fe}(\text{CN})_6]$ was added at the end of the measurements as internal standard ($E([\text{Fe}(\text{CN})_6]^{3-}/[\text{Fe}(\text{CN})_6]^{4-}) = +0.361 \text{ V vs NHE}$).^[44] Unless otherwise indicated, all potentials were converted to the scale relative to NHE. The solutions were bubbled with high-purity argon for at least 15 min before running DPV.

4.4.4 Photo-induced hydrogen evolution

Photo-induced hydrogen evolution from water was analysed by a hydrogen electrode (Unisense H2-NP) controlled by x-5 UniAmp using Logger software. The irradiation source

was an OSRAM Opto Semiconductors LD W5SM LED (λ_{irr} 550 nm, 9 mW) with water cooling. All the photochemical hydrogen evolution measurements were carried out in a thermostatic (298 K) photochemical reactor (total volume 25.0 mL). The photosensitizer $\text{Na}_4[\text{Zn-OMeP}] \cdot 4\text{H}_2\text{O}$ (0.04 mM, 0.17 mg), $\text{Na}_4[\text{Zn-MeP}] \cdot \text{H}_2\text{O}$ (0.04 mM, 0.15 mg), $\text{Na}_4[\text{Zn-F8P}] \cdot 3\text{H}_2\text{O}$ (0.04 mM, 0.15 mg), $\text{Na}_4[\text{Zn-F16P}] \cdot 5\text{H}_2\text{O}$ (0.04 mM, 0.18 mg), $\text{Na}_4[\text{Sn-OMeP}] \cdot 4\text{H}_2\text{O}$ (0.04 mM, 0.18 mg), $\text{Na}_4[\text{Sn-MeP}] \cdot 4\text{H}_2\text{O}$ (0.04 mM, 0.17 mg), $\text{Na}_4[\text{Sn-F8P}] \cdot 2\text{H}_2\text{O}$ (0.04 mM, 0.17 mg), or $\text{Na}_4[\text{Sn-F16P}] \cdot 2\text{H}_2\text{O}$ (0.04 mM, 0.18 mg) and the catalyst cobaloxime (0.49 mM, 0.60 mg) were added as solids in the reactor, and dissolved using 1.5 mL 10% (v/v) TEOA aqueous solution neutralized with concentrated HCl to pH 7.0, and 1.5 mL acetonitrile. Under constant stirring, the reactor was equipped with 1 rubber septum and 2 silicon septa in order to make an air-tight system (the set-up is shown in Figure AI.29). The hydrogen electrode was then inserted through the septum, to measure the hydrogen concentration in the head space (gas phase) of the photochemical reactor, and the whole system was deaerated by high-purity argon bubbling through the solution for at least 15 min. After removing the needle bringing argon, the hydrogen electrode was calibrated by a four-time injection of 100 μL (4.46 μmol at 1 atm) of high-purity H_2 into the closed system; the calibration was adapted with the pressure change using Logger software, affording direct reading of the volume of dihydrogen (μL) produced in the gas phase of the reactor ($V_{\text{gas}} = 22.0 \text{ mL}$). Following calibration, the three used septa were replaced by new ones and the hydrogen electrode was again inserted into the system. The system was degassed for 15 min with argon, then data recording was started, first keeping the system in the dark for 30 min prior to starting light irradiation. Unless otherwise indicated, the data recording was stopped after 22 h of light irradiation.

4.4.5 Photocatalytic turnover number and turnover frequency determination

The experimental dihydrogen evolution was determined by a hydrogen electrode (Unisense OX-NP) controlled by x-5 UniAmp using Logger software. The amount of H_2 formed during illumination was used to calculate the photocatalytic turnover number (PTON) using the following equation:

$$PTON = \frac{n_{\text{H}_2}}{n_{\text{PS}}}$$

in which n_{H_2} is the number of mol of hydrogen calculated from the volume of the dioxygen produced in the photocatalytic experiment as indicated by the calibrated hydrogen electrode in

the gas phase (μL), divided by 22.4 L/mol, and n_{PS} is the number of mol of Zn- or Sn-porphyrin complex used in the photocatalytic experiment.

The maximum photocatalytic turnover frequency PTOF (in h^{-1}) for photocatalytic hydrogen evolution was obtained using Origin 9.1 software by 1) nonlinear curve fitting of the time evolution of the PTON, starting at $t = 30$ min for photocatalytic reactions (category: Growth/Sigmoidal, function: logistic Fit); 2) calculating the first time derivative $\text{PTOF} = f(t)$ of the $\text{PTON} = g(t)$ function using mathematics, differentiate, and 3) identify the maximum value of $\text{PTOF} = f(t)$ (an example for $[\text{Sn-MeP}]^{4-}$ is shown in Figure 4.7).

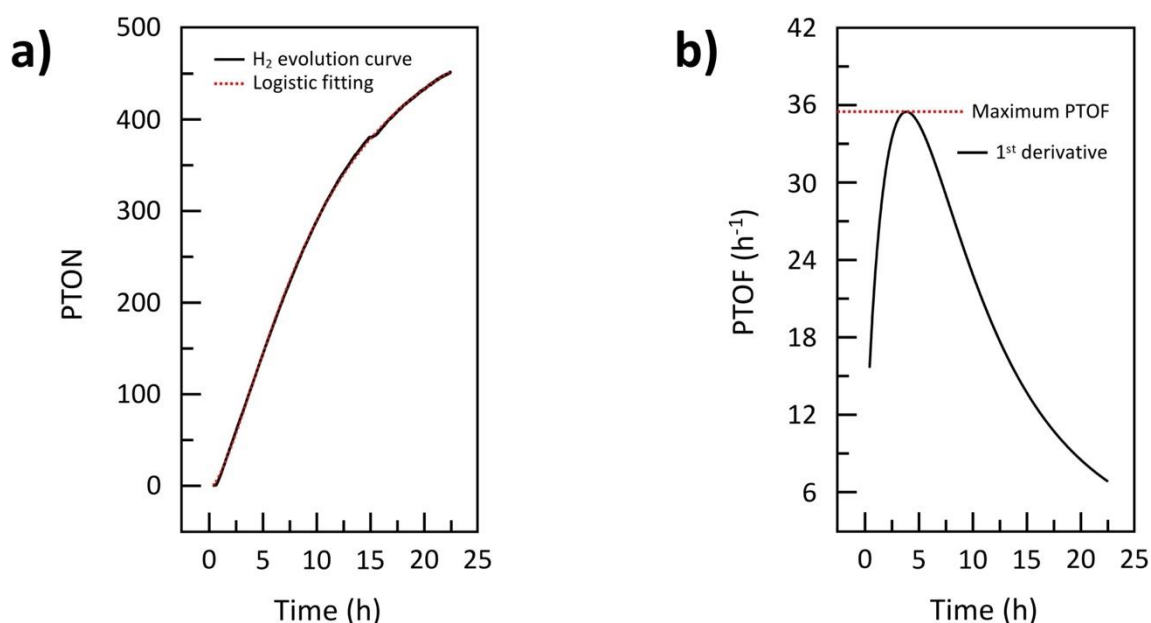


Figure 4.7 Calculation of maximum PTOF of the $[\text{Sn-MeP}]^{4-}$ -based photocatalytic hydrogen evolution system.

4.4.6 Density functional theory calculations

All density functional theory (DFT) calculations were performed within the AMS2020 package published by SCM.^[45] The X,Y,Z geometries of the ground-state singlet and lowest triplet excited states of each complex were optimized using the (GGA-type) OPBE density functional approximation,^[46] projected onto a triple- ζ polarized (TZP) Slater-type basis set, including scalar relativistic effects by means of the zero-order regular approximation (ZORA).^[47] To speed up the calculations, the 1S electrons of C, N, O, F, S and Cl, the 1S-2P electrons for Zn, and the 1S-4P electrons for Sn were frozen. Grimme3 BJDAMP (-D3(BJ)) dispersion corrections were used.^[48] Water solvation was modelled implicitly via the conductor-like screening model (COSMO).^[49,50]

The energies of the obtained geometries were then re-evaluated by performing a single-point calculation, employing the (hybrid) B3LYP-D3(BJ) functional^[51-54] in a ZORA triple- ζ Slater-type basis with two polarization functions (ZORA-TZ2P). Again, the COSMO model was employed to account for solvent effects.

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5

Summary, General discussion & Outlook

5.1 Summary of this thesis

Artificial photosynthesis (AP) is one of the scientific challenges that could help us achieving a global “carbon neutral” society. It will obviously remain an important research topic at least in the next 30 years. The general idea of AP is to use solar energy to either split water or reduce CO₂ into carbon fuels or organic products. Considering the argument that photovoltaic electricity generation followed by electrocatalysis inevitably causes energy losses, it is in principle more desirable to realize the AP reactions directly, preferably using earth-abundant elements. It is widely accepted that a photocatalytic system needs a minimum of three components: a photosensitizer (PS), a catalyst (Cat) and a sacrificial electron donor or acceptor (SE). In such a photocatalytic system, at least three electron-transfer steps can be identified: one between the SE and the excited PS (PS*), one between the photo-reduced or photo-oxidized PS and the Cat, and one between the Cat and its substrate. Since it is difficult to investigate the stability, activity, and catalytic mechanisms, of new molecular components in two photocatalytic processes running in parallel, half-reactions are often preferred. In addition, a well-defined homogeneous solution is simpler, hence better suited for the developments of molecular components, compared with heterogeneous or hybrid photocatalytic systems composed of self-assembled and/or solid-state components, in which the reacting species are sometimes difficult to identify. Therefore, all the research described in this thesis focused on developing improved molecular components for one of the two half reactions of water splitting, based on photocatalytic studies in purely homogeneous systems.

Although [Ru(bpy)₃]²⁺ is based on a relatively rare metal it is also one of the best-known molecular photosensitizers capable of sensitizing both the light-driven oxygen-evolution reaction (OER) and the light-driven hydrogen-evolution reaction (HER). Thus, in this thesis it was used as standard PS for the development of new first-row transition metal catalysts for OER and HER. On the other hand, cobaloxime is a well-studied catalyst for photocatalytic HER, and it was selected as a standard hydrogen evolution catalyst (HEC) to develop new molecular photosensitizers based on earth-abundant elements. We combined both approaches to develop new catalysts and photosensitizers based on tetrasulfonated porphyrin ligands. Considering that for optimizing a photocatalytic system, a balance needs to be found between the driving force of electron transfer from the SE to the PS*, and that of electron transfer between the catalyst and the oxidized or reduced photosensitizer (PS⁺ or PS⁻), we systematically varied the electron richness of the porphyrin ligand by adding either electron-

donating (8 methoxy or 8 methyl) or electron-withdrawing (8 or 16 fluorine) groups in ortho positions on the meso-phenyl rings (Figure 1.23 in **Chapter 1**).

In **Chapter 2**, the synthesis of a series of four tetra-anionic Ni(II)-porphyrin complexes using these ligands is described. These compounds were used as molecular catalysts for light-driven water oxidation in homogeneous neutral or acidic aqueous solutions. Electrochemical and kinetic studies demonstrated that more electron-withdrawing substituents increased the oxidation potentials of the Ni-porphyrin complexes, and controlled the oxygen-evolution rate in photocatalytic conditions. A balance had to be found between increasing these oxidation potentials, which provide a higher driving force for the catalytic OER itself, and keeping them low enough to make sure that the driving force for the electron transfer from the catalyst to the oxidized photosensitizer PS^+ is high enough. For example, when using $[Ru(bpy)_3]^{2+}$ as the photosensitizer and $S_2O_8^{2-}$ as the sacrificial electron acceptor, $[Ni-F16P]^{4-}$ was found to be too electron-poor, which blocked electron transfer between the nickel catalyst and the photo-oxidant $[Ru(bpy)_3]^{3+}$, thereby inactivating the photocatalytic system. The properties of $[Ni-F8P]^{4-}$ were found to be close to the optimum, resulting in excellent activity for the photocatalytic OER. Critically, these nickel porphyrin catalysts showed great stability in photocatalytic conditions, the TON of the photocatalytic system using $[Ni-F8P]^{4-}$ as catalyst was limited by the decomposition of the Ru-based photosensitizer. This work not only provides a rare example of homogeneous light-driven water oxidation catalysed by a Ni-based molecular catalyst in neutral to acidic aqueous solutions; it also provides new rules to design molecular catalysts for photocatalysis: the electron-density of the catalytic centre should be fine-tuned with appropriate substituents, to balance the driving forces of catalytic water oxidation vs. that of the electron transfer from the catalyst to PS^+ .

In **Chapter 3** the synthesis is reported of analogous series of tetra-anionic Co(III)- and Zn(II)-porphyrin complexes, which were studied as molecular catalysts for homogeneous photocatalytic hydrogen generation in neutral and acid aqueous solutions. Although many cobalt-based molecular catalysts have been reported that can catalyze the HER, most of them have not been optimized for neutral aqueous solutions. This is unfortunate, because pH 7.0 is ideal for combining the water-oxidation and proton-reduction reaction into full water splitting. What is more, the catalytic mechanism of the HER in neutral conditions is not necessarily the same as in acidic solution, so that the strategy to design a catalyst optimized for neutral conditions may be different from one used to develop catalysts for acidic solutions. The photocatalytic activity and mechanism of the Co(III) and Zn(II) complexes were found to be

strongly dependent on the presence of electron-withdrawing or electron-donating substituents on the porphyrin ring; they also were strongly dependent on the pH of the aqueous solution. In the series of zinc complexes the porphyrin ligands were found to be redox non-innocent, leading to significant photocatalytic HER for $[\text{Zn-F16P}]^{4-}$ in spite of the inability of the metal center to change its oxidation state. The electron-richest complex $[\text{Co-OMeP}]^{3-}$ had the highest driving force to reduce water in the series of cobalt porphyrin complexes, according to electrochemical analysis, but a higher photocatalytic activity was observed only at pH 4.1 that nearly vanished upon replacing the cobalt center by a zinc ion. At neutral pH, its activity was much lower than at low pH, and more interestingly much lower than that of the electron-poorest complex of the series, $[\text{Co-F16P}]^{3-}$. The activity of the latter compound in photocatalytic hydrogen evolution appeared to be comparatively low at pH 4.1, but excellent at neutral pH, resulting in comparable photocatalytic H_2 production quantum yields compared to that obtained with $[\text{Co-OMeP}]^{3-}$ at pH 4.1. According to our mechanistic studies the second reduction of $[\text{Co-F16P}]^{3-}$ by the photo-reduced species PS^- , which leads to hydrogen evolution, probably occurs via a pathway involving both the metal and the ligand; notably, it was partially retained when cobalt was replaced by zinc. Overall, this work represents a significant advance in our understanding of how to design a molecular hydrogen-evolution catalyst, because it indicated that it is not necessary to functionalize HER catalysts with electron-donating groups to enhance their catalytic activity, in particular in near-neutral aqueous conditions. Electron-withdrawing groups can also lead to excellent catalysts, although these follow a mechanism that differs from that obtained with electron-rich complexes. In photocatalytic systems aimed at driving full water splitting near pH 7.0, electron-poor cobalt-based hydrogen evolution catalyst (HEC) may be preferred, rather than the usually proposed electron-rich HEC which are only more active in acidic conditions.

Finally in **Chapter 4**, the synthesis of the analogous series of tetra-anionic Sn(IV)-porphyrin complexes is described. The photosensitizing properties of this new series of complexes, together with that of the Zn(II) analogues described in **Chapter 3**, were studied for the homogeneous photocatalytic HER in the presence of cobaloxime as standard HEC and TEOA as sacrificial electron donor in 1:1 pH 7.0 water/acetonitrile solutions. The photocatalytic activity obtained using these new PS molecules appeared to be highly depended on the electronic properties of the porphyrin ligand. Electrochemical studies and DFT calculations revealed that all photocatalytically active systems followed a reductive quenching pathway. For the Zn-porphyrin series, only the electron-poorest complex $[\text{Zn-F16P}]^{4-}$ led to significant

hydrogen production, as characterized by a high activity (850 PTON after 20 h irradiation, 59 h⁻¹ maximum PTOF) and a very high photostability: the complex remained active over 100 h under green light irradiation without observable decomposition. For the Sn-porphyrin series, the two electron-richest complexes [Sn-OMeP]⁴⁻ and [Sn-MeP]⁴⁻ showed significant sensitizing properties, but with a lower activity than [Zn-F16P]⁴⁻ under the same conditions. Here as well the different electron-withdrawing and electron-donating ability of the substituents on the porphyrin ligand were found to control the redox properties and triplet excited state energies of the complex, which affected the thermodynamics and rates of electron transfer. This work is significant for the design and understanding of the mechanism of noble-metal-free molecular photosensitizers for hydrogen evolution. Indeed, it shows that a balance between the redox potentials of the ground-state PS and that of the excited state must be found, which are both controlled by the electron-donating or electron-withdrawing properties of the substituents.

5.2 General discussion

5.2.1 Strategy for the improvement of a homogeneous photocatalytic water-oxidation system via an oxidative quenching pathway

A homogeneous photocatalytic system for water splitting contains a photosensitizer (PS), and either a water-oxidation catalyst (WOC) and a sacrificial electron acceptor (EA) for water oxidation, or a hydrogen-evolution catalyst (HEC) and a sacrificial electron donor (ED) for hydrogen generation.^[1] In theory, both oxidative and reductive quenching of the excited state PS* may take place for both photocatalytic OER and HER.^[2] However, throughout the work reported in this thesis we only found an oxidative quenching pathway for the water-oxidation reaction and a reductive quenching pathway for hydrogen generation. In a simple but general approach, three types of electron-transfer steps can be distinguished between the three components of a photocatalytic system: the initial charge separation between PS* and either EA or ED (Step 1, in Figure 5.1); the electron transfer between PS⁺ or PS⁻ and the catalyst (Step 2); and a series of catalytic electron-transfer steps between the oxidized or reduced catalyst and its substrate, sometimes coupled to proton transfer, to afford the products (Step 3).^[3] According to the kinetic study described in **Chapter 2**, the oxygen-evolution rate using [Ni-F8P]⁴⁻ as the WOC was limited by Step 2, i.e. electron transfer from the WOC to the PS⁺. In **Chapter 3**, the hydrogen-generation rate using [Co-F16P]³⁻ as catalyst at pH 7.0 appeared to be limited by Step 3, i.e., the catalytic proton reduction step. The hydrogen-evolution rate

using $[\text{Co-OMeP}]^{3-}$ as catalyst at pH 4.1 appeared to be limited by the photon flux generating the excited photosensitizer PS^* , which further affected the electron transfer Step 1, i.e., the generation of PS^- . Thus, the work described in this thesis clearly shows that in principle any of the three steps of a photocatalytic system can be the rate-determining step (RDS). Another important demonstration of this work is that an overall balance between these steps should be found in order to maximize the global rate of a photocatalytic system. In other words, there is no point in developing a faster catalyst if the rate-determining step (RDS) of the system is the intermolecular electron-transfer step of Step 2; it is not useful to look for a photosensitizer with a higher molar attenuation coefficient if the RDS is the catalytic step (Step 3); and it is naive to develop advanced supramolecular tools to increase local concentrations and speed up Step 2 if the RDS is photon absorption.^[4]

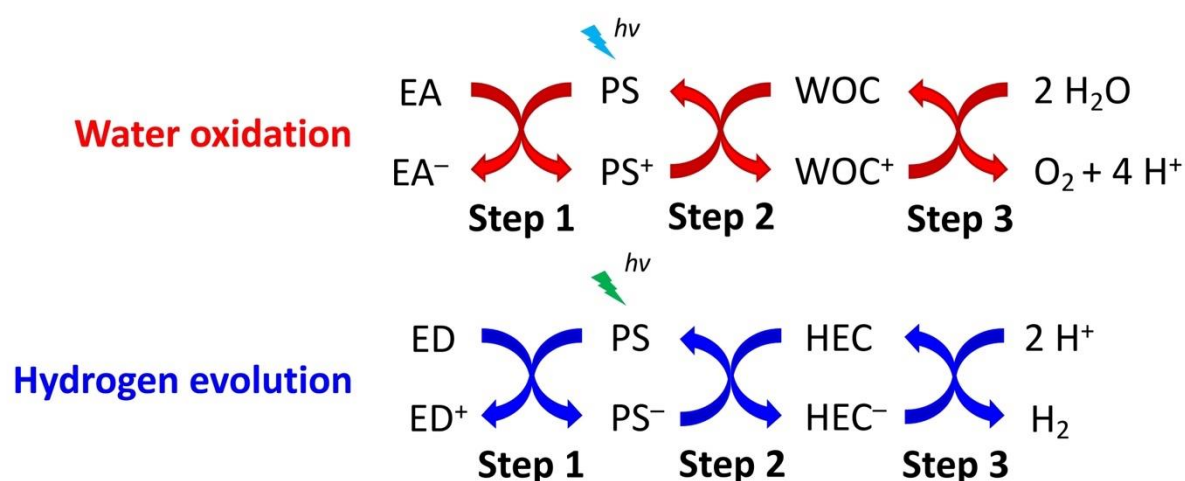


Figure 5.1 Simplified mechanisms for homogeneous photocatalytic water oxidation and hydrogen evolution described in this thesis. EA: sacrificial electron acceptor; ED: sacrificial electron donor; PS: photosensitizer; WOC: water oxidation catalyst; HEC: hydrogen evolution catalyst; Step 1,2 or 3 are electron transfer steps.

For a water-oxidation system in which PS^* is oxidatively quenched, at a given pH the rate of Step 1 will be mostly controlled by the matching properties of EA and PS, that of Step 2 by the matching properties of PS and WOC, and the rate of Step 3 is only controlled by the properties of the WOC. The thermodynamics (i.e., the driving forces) of all three steps of a photocatalytic system are determinant to realize light-induced oxygen evolution. For example, a WOC with a higher overpotential, i.e., a higher potential at which the electrocatalysis starts to be significant (also known as onset potential), will have a higher driving force to obtain electrons from water. Similarly, a PS with a higher oxidation potential provides a higher driving

force to oxidize the catalyst, resulting (in the normal region of Marcus' electron-transfer theory) in faster oxidation of the WOC to higher oxidation states, noted here symbolically WOC^+ . Finally, an EA with a higher oxidation potential can offer more driving force to oxidize PS^* to PS^+ .

Thus, in theory, when the kinetics of the photocatalytic system is limited by Step 3, a WOC with a more positive oxidation potential will improve the overall photocatalytic oxygen evolution rate, which can be achieved by functionalizing the catalyst with electron-withdrawing substituents. When Step 2 is the RDS instead of Step 3, it is the PS that must be modified with electron-withdrawing groups if one wants to enhance the photocatalytic oxygen evolution. Finally, choosing an EA with a more positive reduction potential will lead to a faster oxygen generation only when Step 1 is the RDS of the system. However, for such modifications to lead to faster oxygen evolution important conditions are to be met: 1) the catalytic conditions should not be changed (for example, the pH or the concentrations); 2) modification of the molecule should not significantly change the photostability of the components, and 3) the catalytic mechanism of Step 3 should not change.

Still, it is worth noting that modifications on the electron density of one of the components in a photocatalytic system may change its kinetics appreciably. For example, modifying a PS with strong electron-withdrawing substituents on the one hand will make the PS^+ more prone to oxidize the WOC (Step 2), on the other hand it may make the triplet state oxidation potential more positive, which may make Step 1 slower. Similarly, a WOC with a higher overpotential may boost the rate of Step 3, but the driving force of Step 2 will be lower, thus leading to an overall oxygen evolution rate that may be lower or even zero. **Chapter 2** is a typical example of this effect: although the electron-poorest $[\text{Ni-F16P}]^{4+}$ has a very positive overpotential that could in principle lead to a very fast Step 3, but it was not active for photocatalytic oxygen evolution using $[\text{Ru}(\text{bpy})_3]^{2+}$ as the PS because Step 2 was too slow, blocking the system. One should note that in such a case a photosensitizer with a higher oxidation potential than that of the $[\text{Ru}(\text{bpy})_3]^{3+}/[\text{Ru}(\text{bpy})_3]^{2+}$ couple may alleviate this problem and unravel the otherwise excellent electrocatalytic OER properties of this complex. Overall, one cannot emphasise enough that the global performances of a photocatalytic system is the result of the interplay between Step 1, Step 2, and Step 3. As a consequence, details of the photocatalytic mechanism need to be known before one is able to predict which influence substituting the PS or catalyst with electron-donating or electron-withdrawing groups will have on the photocatalytic properties of the system.

5.2.2 Strategy for the improvement of a homogeneous photocatalytic hydrogen evolution system via a reductive quenching pathway

At first sight, a very similar analysis can be made for photocatalytic hydrogen evolution in the case of reductive quenching. In **Chapter 3**, the cobalt porphyrin HEC with higher electron richness indeed made the photocatalytic system more active in acidic conditions: the electron-richest catalyst $[\text{Co-OMeP}]^{3-}$ led to better photocatalytic activity than $[\text{Co-MeP}]^{3-}$ at pH 4.1. On the other hand, the electron-poor $[\text{Co-F8P}]^{3-}$ led to faster photocatalytic H_2 production than $[\text{Co-MeP}]^{3-}$ (Figure 3.4). Although we did not do a full kinetic study for these two catalysts, we can hypothesize that the less negative onset potential of $[\text{Co-MeP}]^{3-}$, compared to all three other complexes of the series (Figure 3.3d), might explain its poor performance in photocatalytic conditions, as it may limit the rate of Step 3.

Overall, the fact that the influence of the electron richness of the HEC on photocatalytic HER is complicated, was best demonstrated by our pH-dependent studies. $[\text{Co-OMeP}]^{3-}$ has the highest overpotential η of the series, which according to our analysis leads to a fast Step 3 at pH 4.1, and as Step 2 is also fast, the hydrogen-evolution rate of the system was limited by the photon flux (Step 1). In contrast, the electron-poorest HEC $[\text{Co-F16P}]^{3-}$ gave a higher TON and TOF in photocatalytic conditions at pH 7.0, compared with that of $[\text{Co-OMeP}]^{3-}$, because the electron-withdrawing effect of 16 fluoro substituents changes the catalytic hydrogen generation mechanism of Step 3. Although these electron-withdrawing substituents give to $[\text{Co-F16P}]^{3-}$ unexpected high activity, according to our kinetic study, this photocatalytic system is still controlled by Step 3. We interpret this observation as a consequence on the one hand of the low H_2 generation overpotential η for this complex, which limits the rate of Step 3, and on the other hand of the strongly reducing properties of $[\text{Ru}(\text{bpy})_3]^+$ that provide a high driving force for Step 2. Clearly, though many people would claim that electron-donating substituents are better for HEC, our work demonstrates that electron-withdrawing groups can also lead to surprisingly good HEC, which is one of the most striking findings in this thesis.

For the PS, introducing electron-donating groups generates a more negative reduction potential, which in principle provides more driving force to transfer electron from PS^- to the HEC. However, in **Chapter 4** we found that modifications of the electron density of the PS had to be performed carefully. Indeed, an electron-rich porphyrin ligand not only made the PS more difficult to be reduced in the ground state, but it also decreased the triplet excited energy of the PS^* slightly, which made the reduction potential of the triplet state of the PS less positive. This kind of changes generated a lower driving force for the electron transfer of Step

1, which may block the photocatalytic system. For example, for the system based on $[\text{Zn-F8P}]^{4-}$ the electron transfer of Step 1 was not thermodynamically feasible, while in the system containing the electron-poor PS $[\text{Zn-F16P}]^{4-}$, Step 1 did occur. On the other hand, in the Sn-porphyrin series, $[\text{Sn-F8P}]^{4-}$ and $[\text{Sn-F16P}]^{4-}$ were found to be too electron-poor: they did not have a sufficiently negative reduction potential to provide enough driving force to drive Step 2. In this case, the introduction of electron-donating substituents, such as in $[\text{Sn-OMeP}]^{4-}$ or $[\text{Sn-MeP}]^{4-}$, led to a more negative reduction potential of these otherwise electron-poor PSs, which was more efficient for the overall photocatalytic scheme.

To sum up, the optimization of a homogeneous photocatalytic hydrogen evolution system characterized by a reductive quenching pathway can only be achieved by increasing the driving force and rate of the RDS. In particular, this effect can be obtained using a HEC with a more negative on-set potential, a PS modified with more electron-donating groups, or an ED with a more negative oxidation potential, when Step 3, 2, or 1, limits the catalytic system, respectively; alternatively, better light absorption properties could also contribute to faster Step 1. Like adding electron-withdrawing groups to a WOC for water oxidation, adding electron donating groups to PS or HEC should be done carefully, making sure that: 1) the photocatalytic conditions and the RDS do not change, 2) the modifications do not significantly change the photostability of the components of the system, and 3) the hydrogen evolution catalytic mechanism of the HEC (Step 3) does not change. Clearly, for $[\text{Co-F16P}]^{3-}$ at pH 7.0 the first and third condition were not met, and electron-withdrawing groups led to an enhancement of the photocatalytic H_2 evolution, compared to $[\text{Co-OMeP}]^{3-}$.

5.3 Outlook

In the work described in this thesis, different homogeneous photocatalytic systems were investigated in particular for photocatalytic water oxidation and hydrogen evolution. In order to achieve the target of artificial photosynthesis, efforts on photocatalytic CO_2 reduction reaction (CO_2RR) are still needed. Iron porphyrin complexes have been reported to perform the CO_2RR with high activity and selectivity.^[5] It would be interesting to prepare the iron analogues of the nickel, cobalt, zinc, and tin porphyrin complexes reported in this thesis, and to study them as catalysts for the photocatalytic CO_2RR , to investigate the effects of the electron density of the catalyst on this reaction. We should mention that the analogous series of copper(II) complexes was prepared during the work described in this thesis, and these were sent to different collaborators for evaluating their catalytic properties for the CO_2RR and for the dioxygen reduction reaction.

The homogeneous photocatalytic water described in **Chapter 2** was only studied using $[\text{Ru}(\text{bpy})_3]^{2+}$ as the PS. Since this photosensitizer is notoriously unstable under the harsh conditions of the light-driven OER,^[6] and since its oxidation potential in the ground state is only +1.26 V vs. NHE,^[4] it would be interesting to develop a more robust photosensitizer that would be free of any noble metal and that would have a more positive oxidation potential in the ground state. Such a PS could be prepared for example using the electron-poor $[\text{H}_2\text{-F16P}]^{4-}$ ligand described in this thesis with a specifically chosen metal center that would provide enough driving force to oxidize a WOC having a high overpotential such as $[\text{Ni-F16P}]^{4-}$. For example, $[\text{Zn-F16P}]^{4-}$ and all 4 tin(IV)-porphyrin complexes described in **Chapter 4** have a higher oxidation potential in the ground state than $[\text{Ru}(\text{bpy})_3]^{2+}$. They also have less energy in their excited state E(T), but the resulting excited state potentials $E_{\text{PS}^*,\text{ox}}(\text{PS}^+/\text{PS}^*)$, which culminates at -0.01 V vs. NHE for $[\text{Sn-MeP}]^{4-}$, are still more negative than the potential necessary for reducing the $\text{S}_2\text{O}_8^{2-}$ anion (+0.6 V vs. NHE). Hence, all 5 molecules are, in theory, eligible for sensitizing the OER catalyzed by $[\text{Ni-F16P}]^{4-}$.

Last but not least, an overall photocatalytic water-splitting system may be established using the catalysts reported in **Chapter 2** and **Chapter 3**, and the photosensitizers described in **Chapter 4**. When this PhD work was completed, both half-reactions of water splitting (OER and HER) worked independently, in the presence of sacrificial electron acceptor and donor. In theory, both half-reactions might be bridged into a single water-splitting system provided that an electron relay (or a couple of electron relays) can be found that transports electrons (and protons) from the WOC to the HEC. Two systems are suggested in Figure 5.2. First, solid electrodes could be used to transport electrons (system A), while protons would be moved from one side of the system to the other via a proton-conducting membrane.^[7] It is noteworthy that in such a photoelectrochemical system, a single PS might be used for both half-reactions if its photo-redox properties are sufficient to drive both the OER and the HER. This is a well-known advantage of $[\text{Ru}(\text{bpy})_3]^{2+}$, but it still remains to be proven that the same property can be obtained with a more stable PS based on an earth-abundant metal. Second, the combination of tetrachlorobenzoquinone/tetrachlorobenzo-hydrosemiquinone (TCBQ/TCBQH) embedded in the lipid membrane of a negatively charged liposome, with $\text{Fe}^{3+}/\text{Fe}^{2+}$ dissolved in the aqueous solution around the membrane, may be used (system B).^[8] In such a negatively charged liposome-supported system, the protons would be transported together with the electron through the membrane by the hydrophobic hydrosemiquinone electron relay, as quinones are usually reduced by proton-coupled electron transfer. The PS on the HER side should be

positively charged in order to stay close to the membrane and allow electron transfer to the quinone relay in the membrane. Commercially available $[\text{Ru}(\text{bpy})_3]^{2+}$ or 5,10,15,20-tetrakis(4-N-methylpyridinium)porphyrin zinc(II) compounds are potential candidates for such photosensitizers. All in all, although the development of new molecular photosensitizers and catalysts is a great advance in the field of artificial photosynthesis, combining both half-reactions in a single photocatalytic system remains one of the greatest challenges of the photochemistry and supramolecular chemistry of the 21st century.

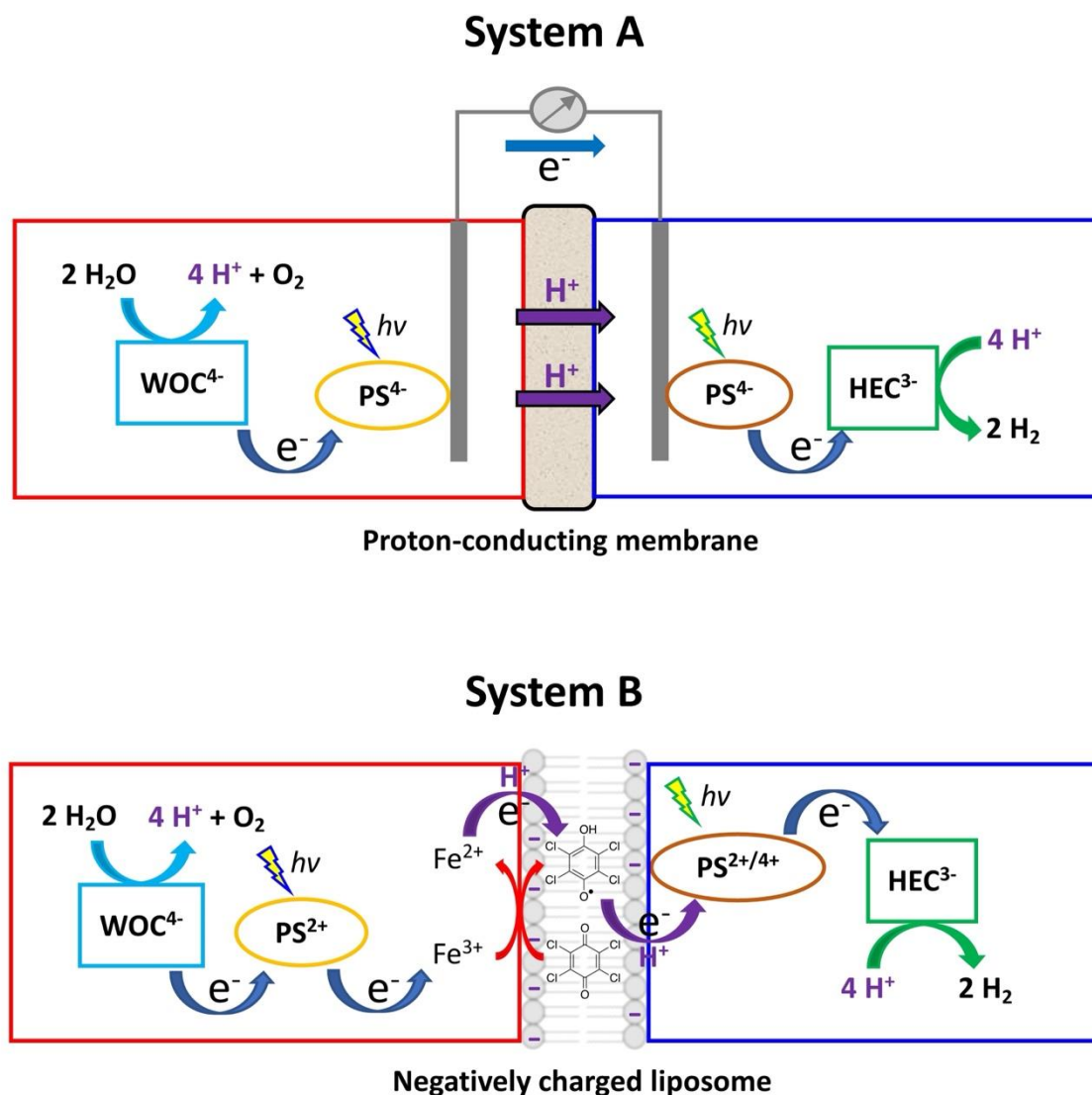


Figure 5.2 Two general architectures for full photocatalytic water splitting. PS: photosensitizer; HEC: hydrogen evolution catalyst; WOC: water oxidation catalyst.

5.4 References

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APPENDIX I: SUPPORTING INFORMATION FOR CHAPTER 2

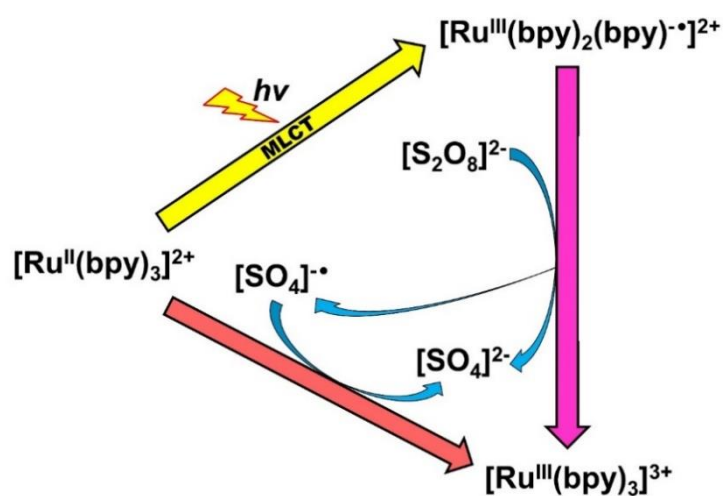


Figure AI.1 Simplified mechanism of Step 1 of Figure 2.2 in $[\text{Ru}(\text{bpy})_3]^{2+}$ coupled with $[\text{S}_2\text{O}_8]^{2-}$ system for molecular homogeneous photocatalytic water oxidation. MLCT: Metal-to-ligand charge transfer.

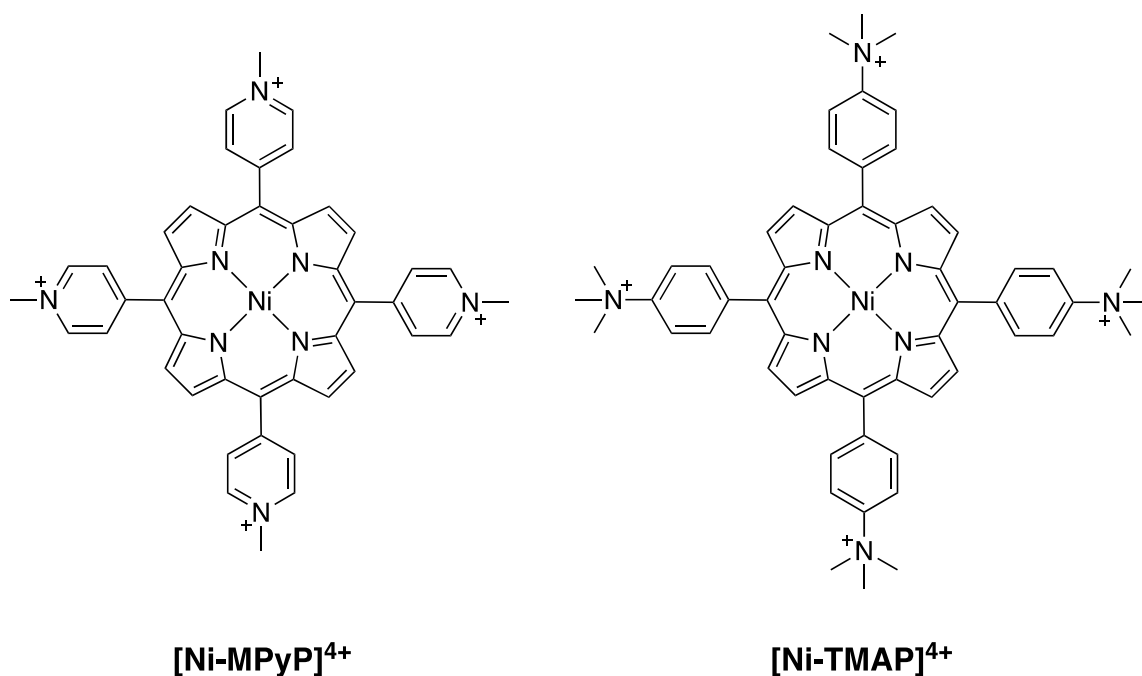


Figure AI.2 Chemical structures of two positively charged water-soluble Ni(II)-porphyrin complexes as controls in this work, isolated as trifluoromethanesulfonate salts.

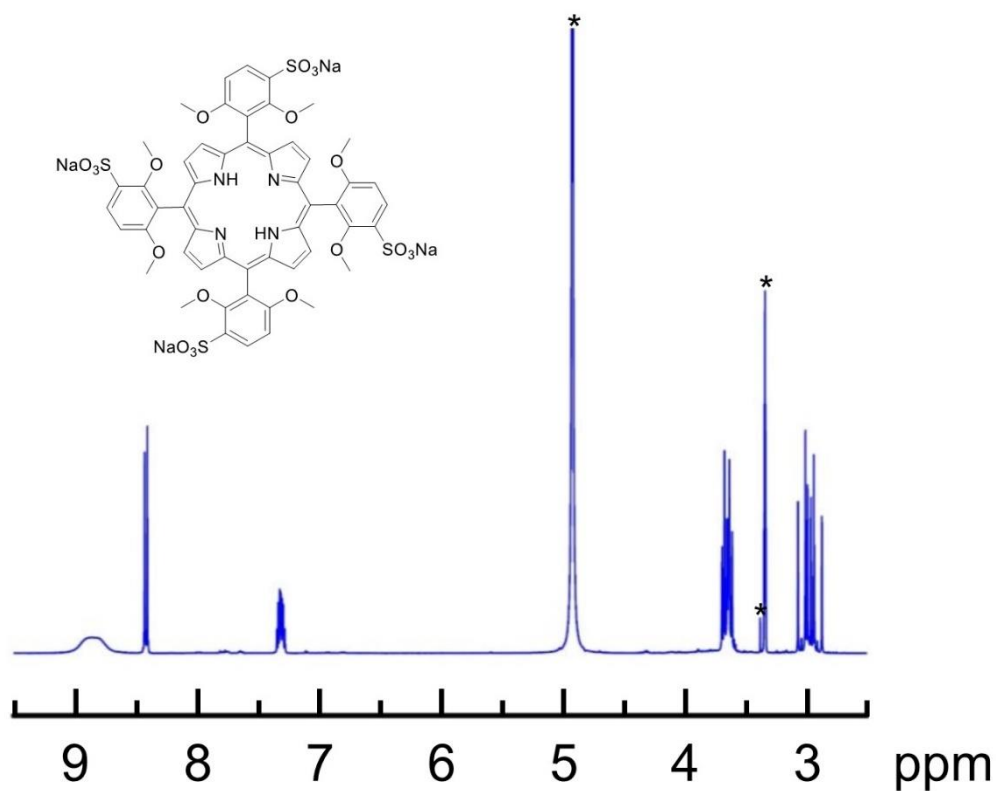


Figure AI.3 ^1H NMR of $\text{Na}_4[\text{H}_2\text{-OMeP}]$ in CD_3OD . * Methanol and water.

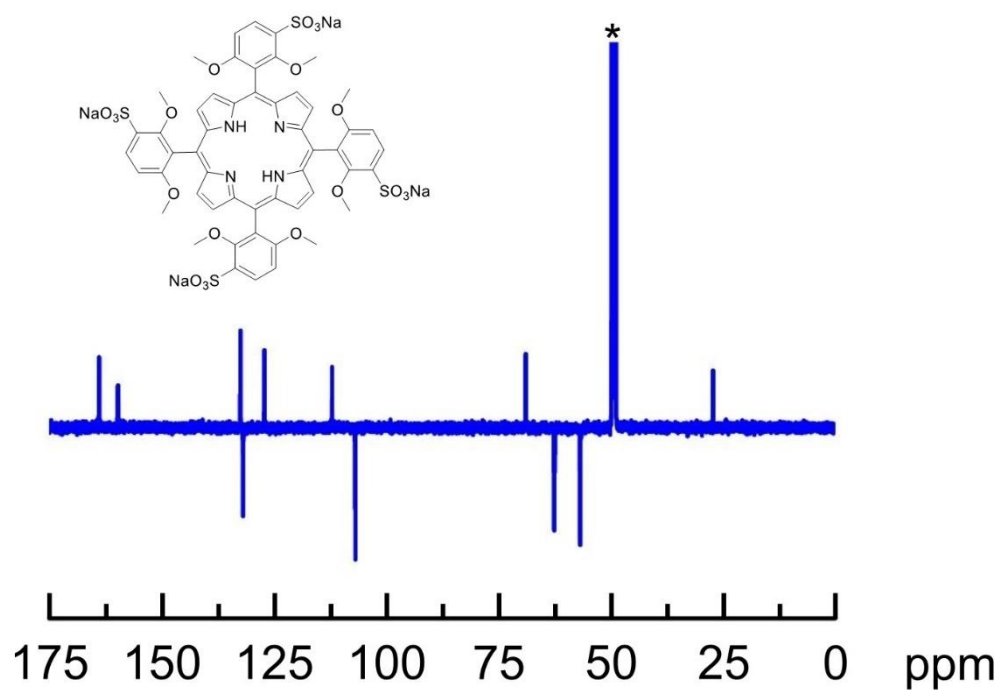


Figure AI.4 ^{13}C NMR of $\text{Na}_4[\text{H}_2\text{-OMeP}]$ in CD_3OD . * Methanol.

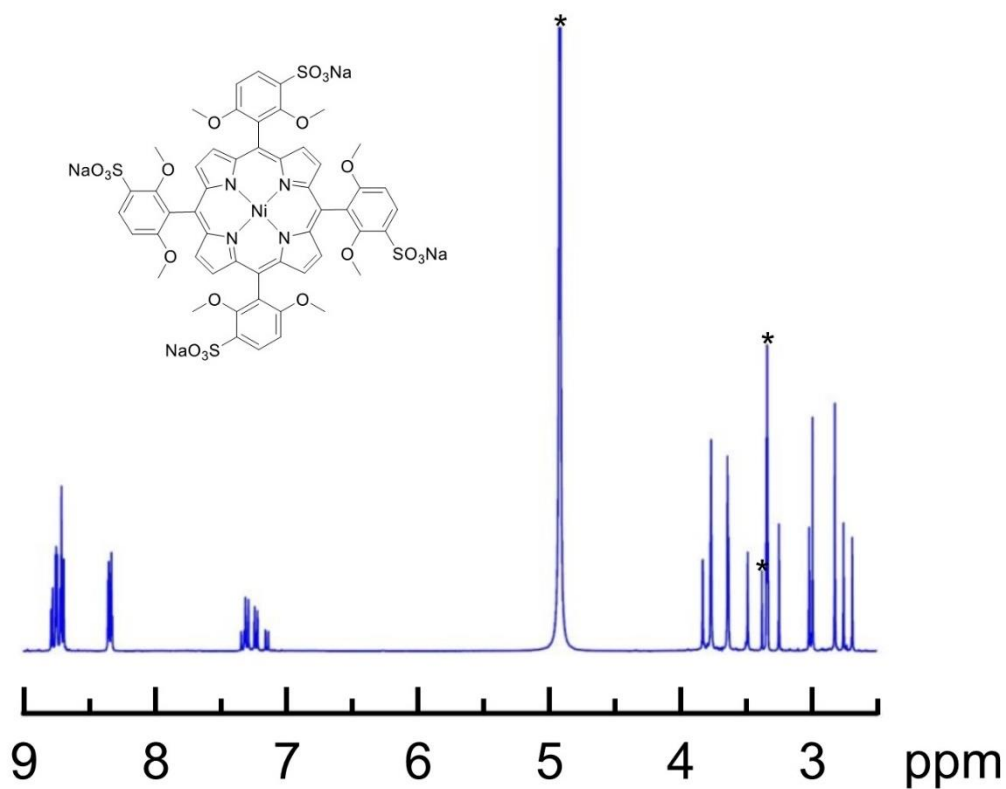


Figure AI.5 ^1H NMR of $\text{Na}_4[\text{Ni-OMeP}]$ in CD_3OD . * Methanol and water.

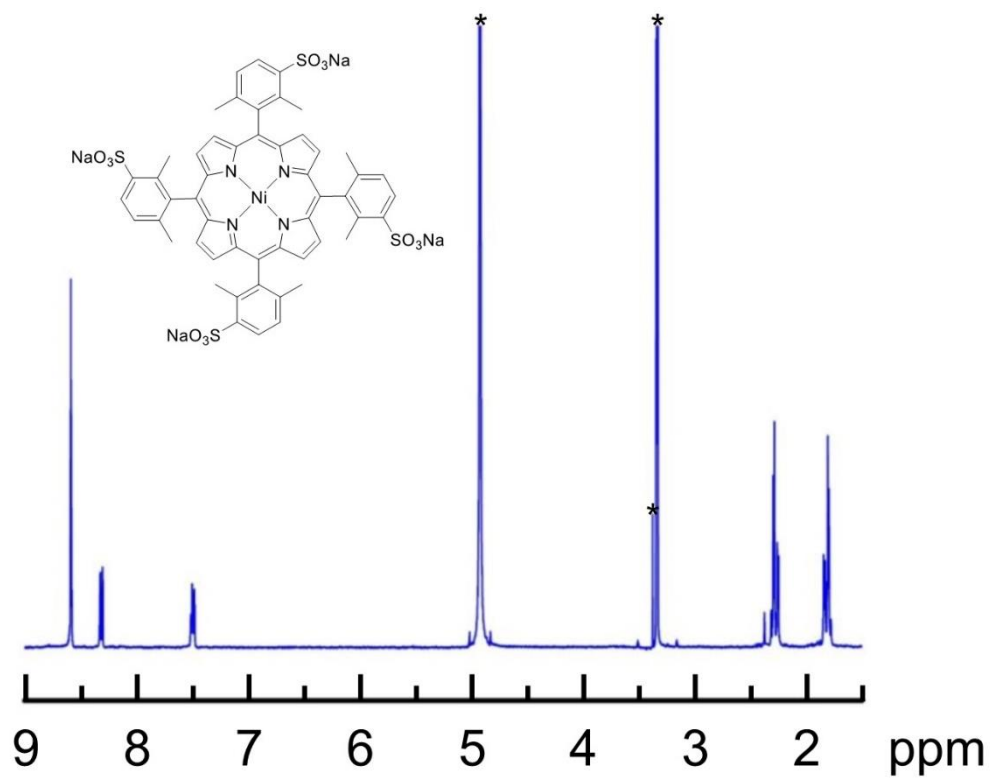


Figure AI.6 ^1H NMR of $\text{Na}_4[\text{Ni-MeP}]$ in CD_3OD . * Methanol and water.

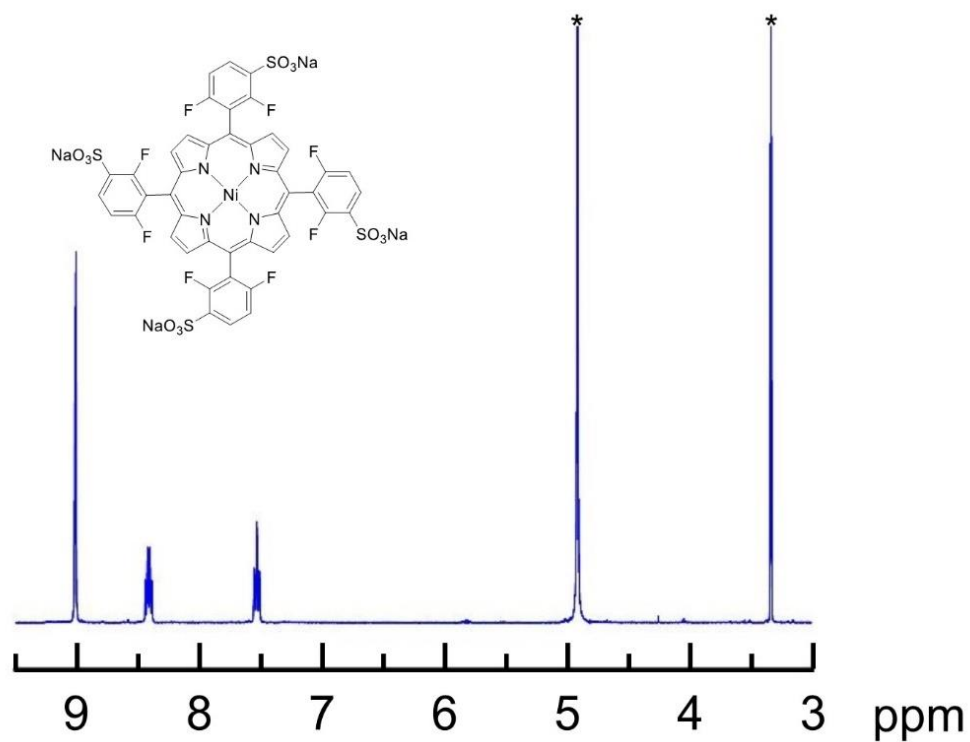


Figure AI.7 ^1H NMR of $\text{Na}_4[\text{Ni-F8P}]$ in CD_3OD . * Methanol and water.

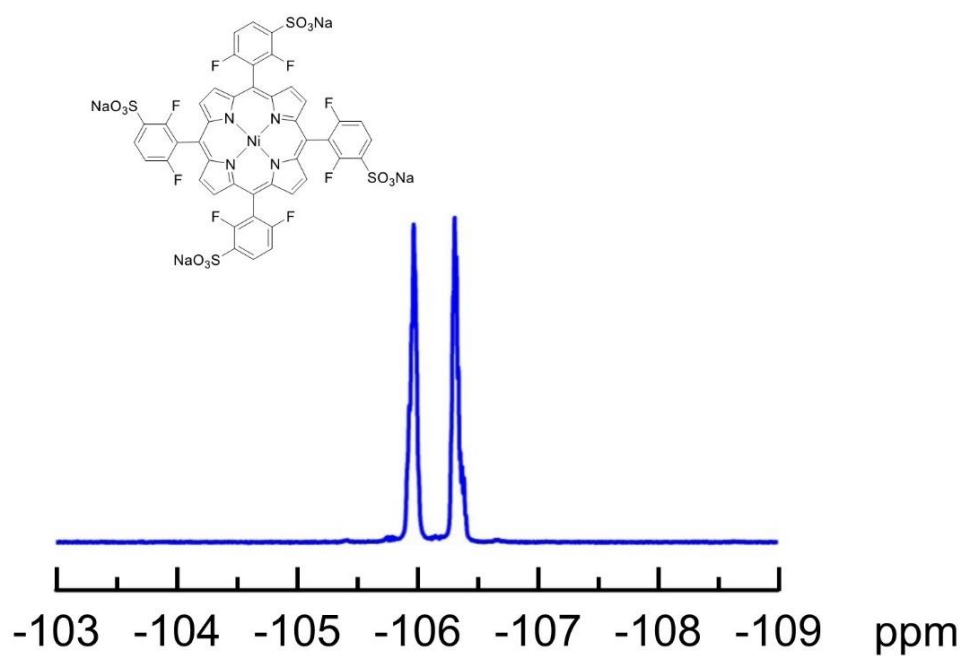


Figure AI.8 ^{19}F NMR of $\text{Na}_4[\text{Ni-F8P}]$ in CD_3OD . * Methanol and water.

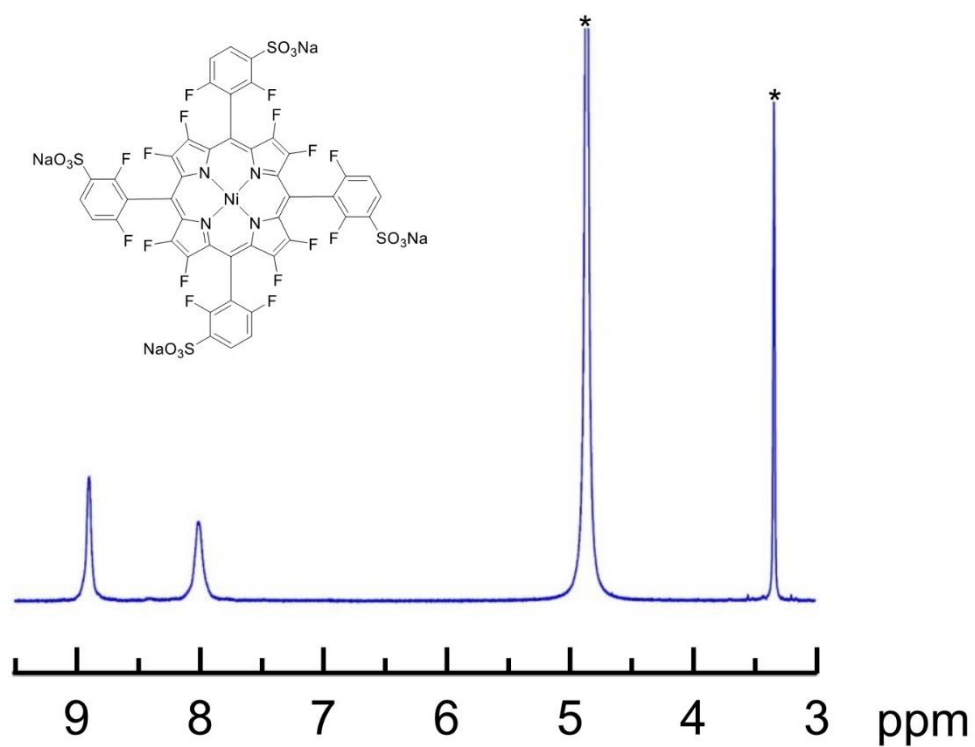


Figure AI.9 ^1H NMR of $\text{Na}_4[\text{Ni-F16P}]$ in CD_3OD . * Methanol and water.

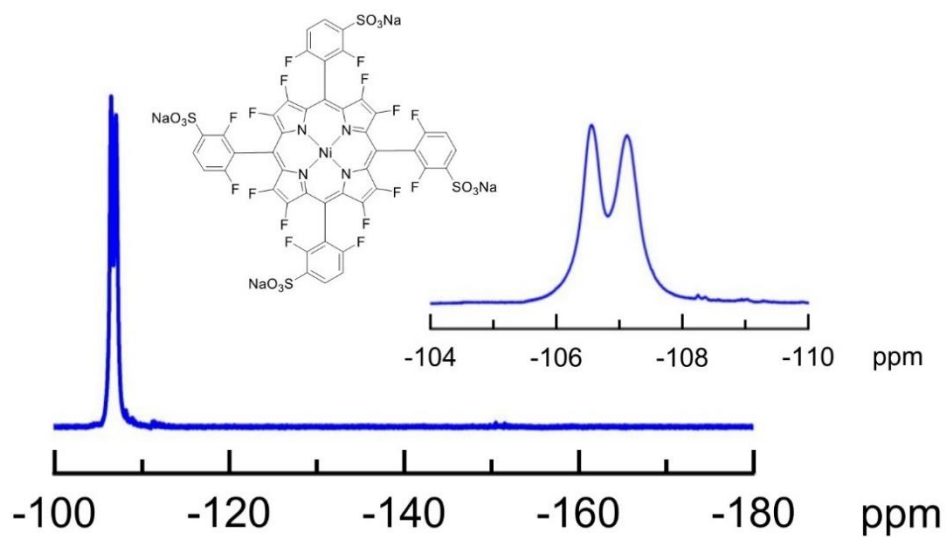


Figure AI.10 ^{19}F NMR of $\text{Na}_4[\text{Ni-F16P}]$ in CD_3OD .

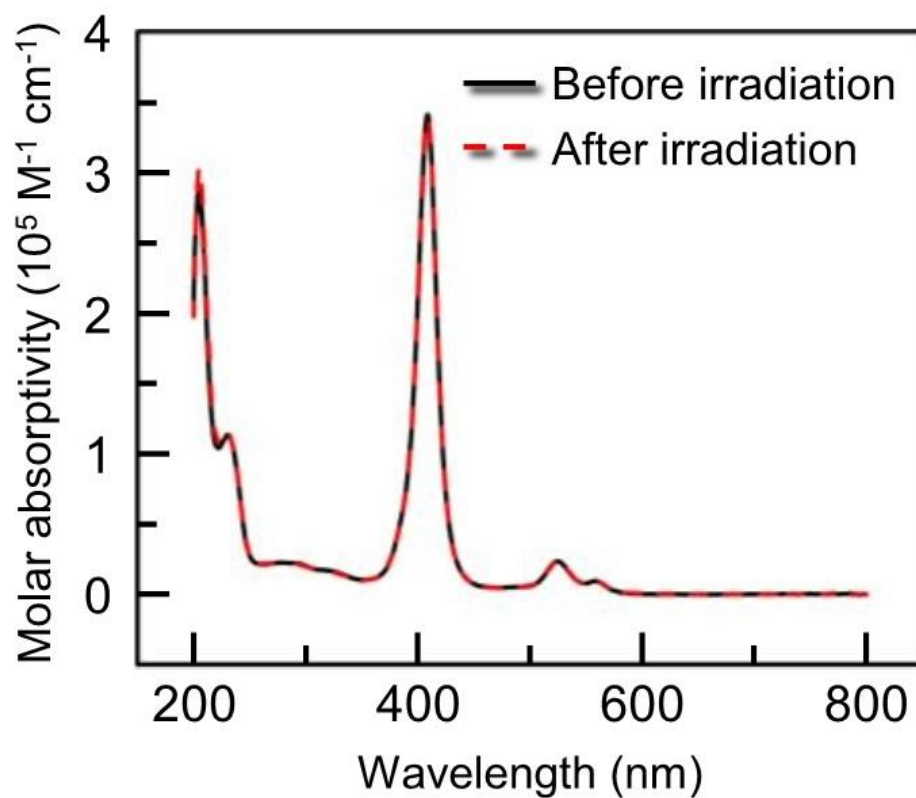


Figure AI.11 Absorption spectra of $[\text{Ni-OMeP}]^{4-}$ before (black solid) and after (red dash) 3 hours irradiation (LED, 450 nm, 15.8 mW) in phosphate buffer (0.1 M, pH 7.0) under air, $T = 298 \text{ K}$.

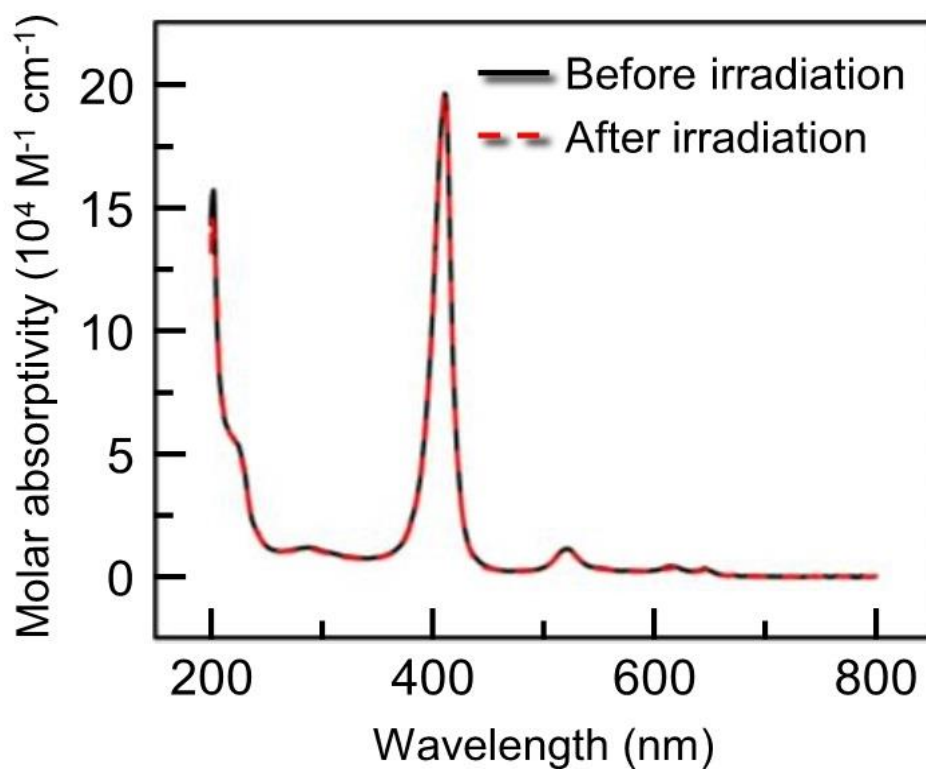


Figure AI.12 Absorption spectra of $[\text{Ni-MeP}]^{4-}$ before (black solid) and after (red dash) 3 hours irradiation (LED, 450 nm, 15.8 mW) in phosphate buffer (0.1 M, pH 7.0) under air, $T = 298 \text{ K}$.

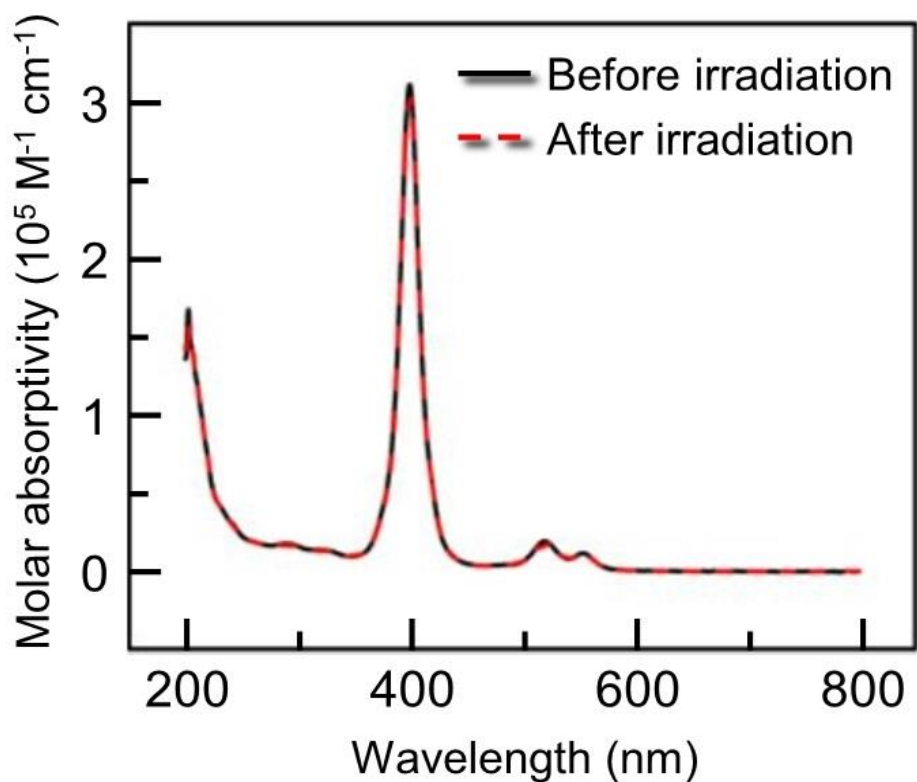


Figure AI.13 Absorption spectra of $[\text{Ni-F8P}]^{4-}$ before (black solid) and after (red dash) 3 hours irradiation (LED, 450 nm, 15.8 mW) in phosphate buffer (0.1 M, pH 7.0) under air, $T = 298 \text{ K}$.

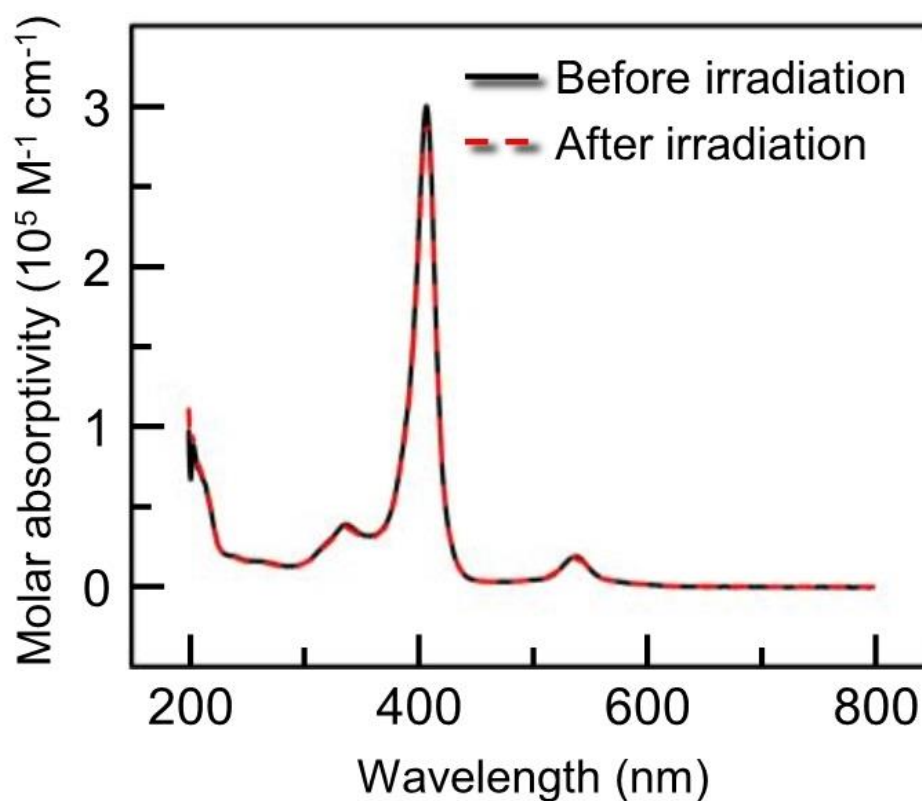


Figure AI.14 Absorption spectra of $[\text{Ni-F16P}]^{4-}$ before (black solid) and after (red dash) 3 hours irradiation (LED, 450 nm, 15.8 mW) in phosphate buffer (0.1 M, pH 7.0) under air, $T = 298 \text{ K}$.

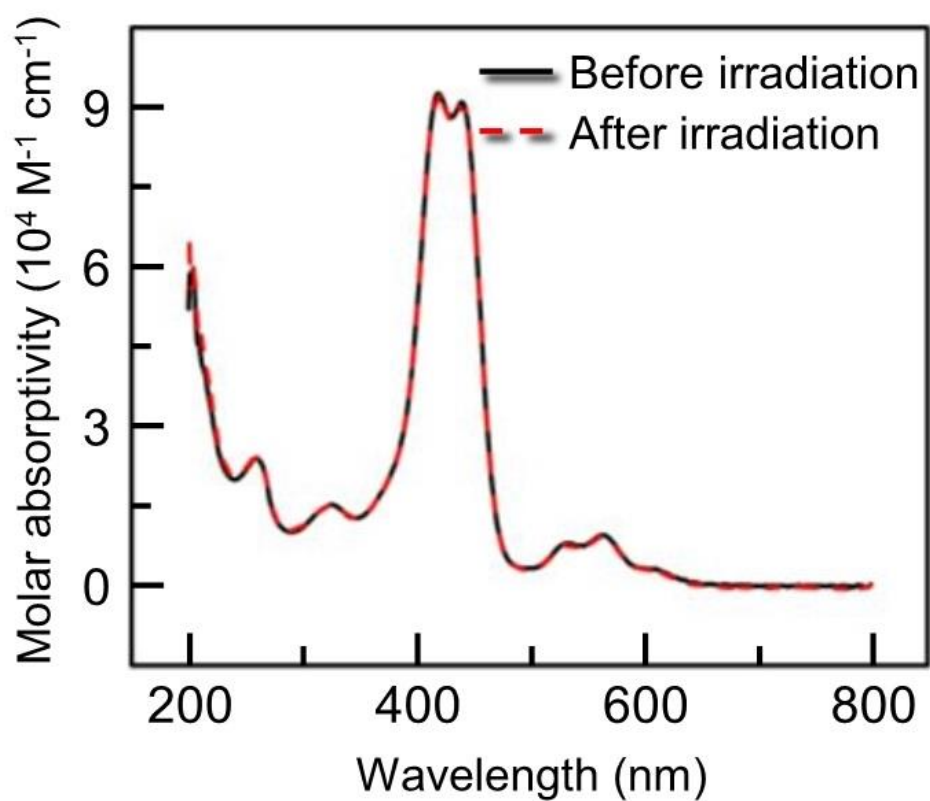


Figure AI.15 Absorption spectra of $[\text{Ni-MPyP}]^{4+}$ before (black solid) and after (red dash) 3 hours irradiation (LED, 450 nm, 15.8 mW) in phosphate buffer (0.1 M, pH 7.0) under air, $T = 298 \text{ K}$.

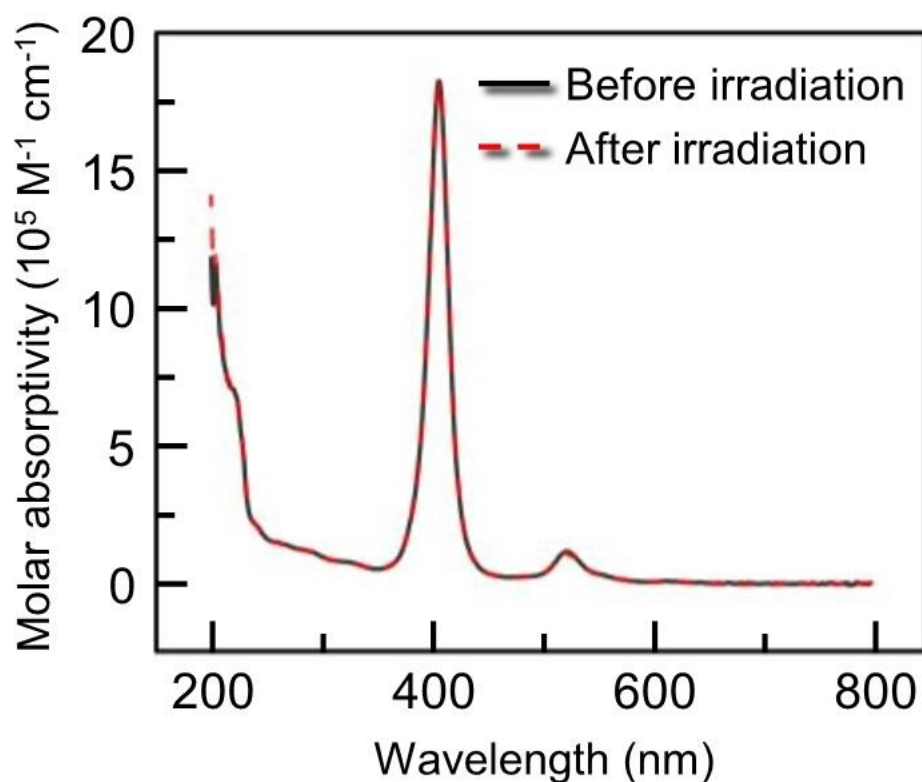


Figure AI.16 Absorption spectra of $[\text{Ni-TMAP}]^{4+}$ before (black solid) and after (red dash) 3 hours irradiation (LED, 450 nm, 15.8 mW) in phosphate buffer (0.1 M, pH 7.0) under air, $T = 298 \text{ K}$.

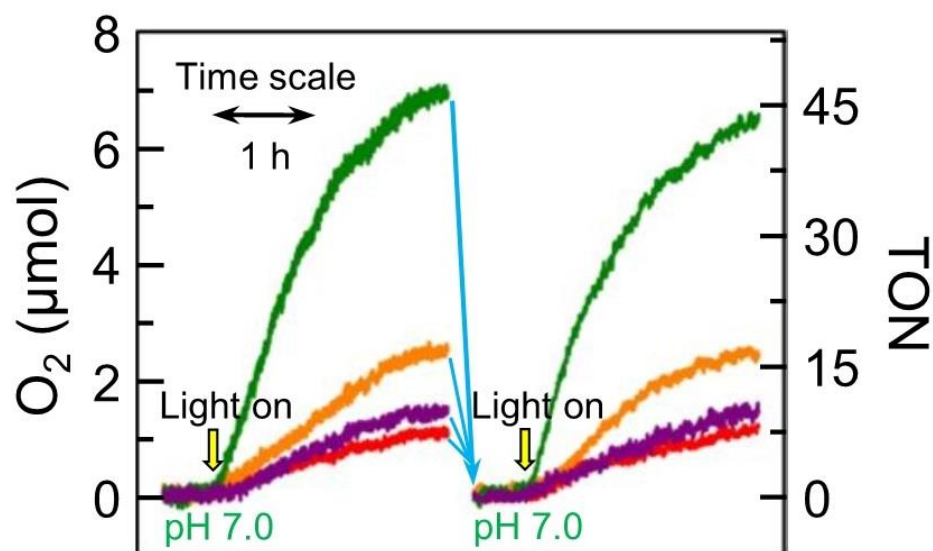


Figure AI.17 Repetitive photocatalytic water oxidation using a homogeneous mixture containing 0.05 mM $[\text{Ni-OMeP}]^{4+}$ (red), $[\text{Ni-MeP}]^{4+}$ (orange), $[\text{Ni-MPyP}]^{4+}$ (green) or $[\text{Ni-TMAP}]^{4+}$ (purple) with 0.67 mM $[\text{Ru}(\text{bpy})_3]\text{Cl}_2$ and 50 mM $\text{Na}_2\text{S}_2\text{O}_8$ in 0.1 M sodium phosphate

buffer (initial pH 7.0), using blue light (450 nm, 15.8 mW), $T = 298$ K. Between the two irradiation experiment, neutralization (cyan arrow) was realized by adding NaOH solid by checking pH, 0.67 mM fresh $[\text{Ru}(\text{bpy})_3]\text{Cl}_2$ and 50 mM $\text{Na}_2\text{S}_2\text{O}_8$ as solids were added.

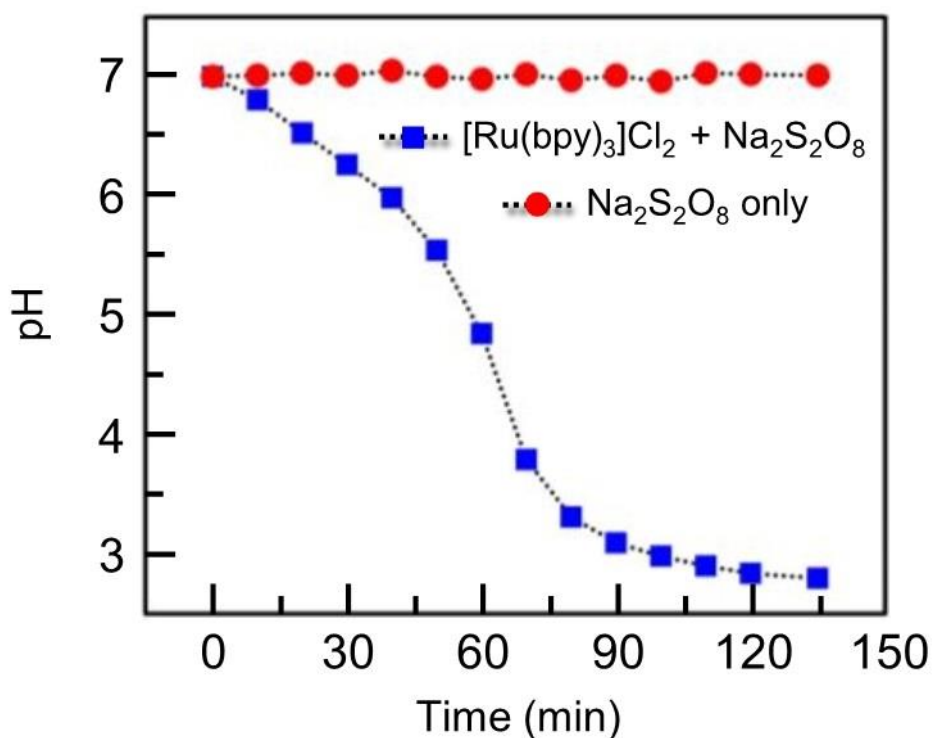


Figure AI.18 pH change of 0.1 M sodium phosphate buffer (initial pH 7.0) solution containing 50 mM $\text{Na}_2\text{S}_2\text{O}_8$ (red solid circle) or 0.67 mM $[\text{Ru}(\text{bpy})_3]\text{Cl}_2$ and 50 mM $\text{Na}_2\text{S}_2\text{O}_8$ (blue solid square) during blue light (450 nm, 15.8 mW) irradiation, $T = 298$ K.

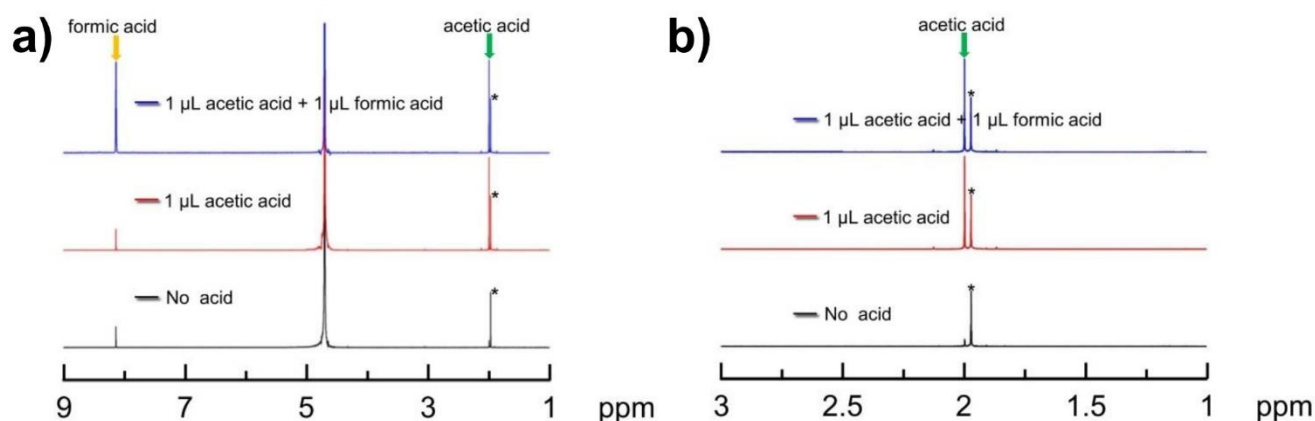


Figure AI.19 a) ^1H NMR of 0.67 mM $[\text{Ru}(\text{bpy})_3]\text{Cl}_2$ and 50 mM $\text{Na}_2\text{S}_2\text{O}_8$ in D_2O after 135 min blue light (450 nm, 15.8 mW) irradiation (black), and adding 1 μL acetic acid (red), 1 μL acetic acid and 1 μL formic acid (blue) into the 0.5 mL D_2O solution. b) zoom of spectra shown in a). * represents the 0.5 μL acetonitrile added as internal standard.

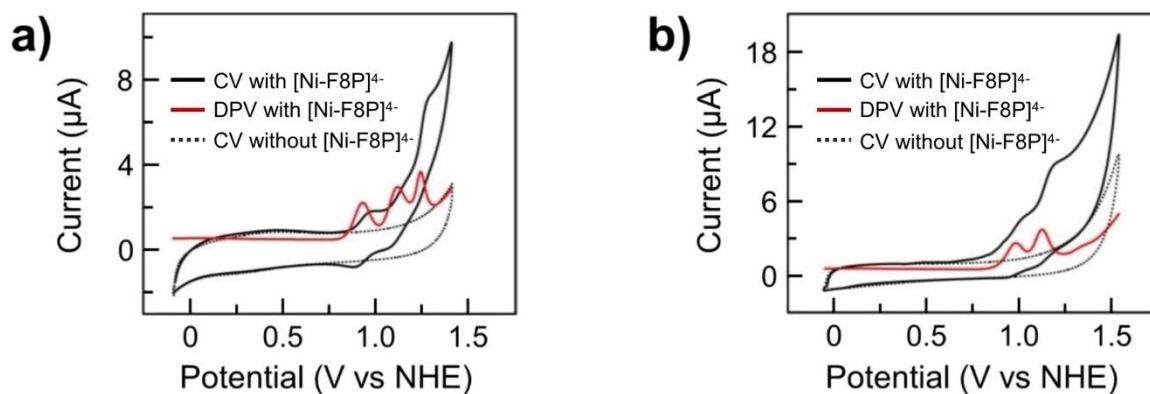


Figure AI.20 CV and DPV of 0.25 mM $[\text{Ni-F8P}]^{4-}$ in 0.1 M a) pH 2.8 and b) pH 7.0 phosphate buffer. Conditions: 0.07 cm^2 working electrode, Pt wire auxiliary electrode, Ag/AgCl reference electrode, 50 mV s^{-1} CV scan rate, $T = 298\text{ K}$. DPV experimental parameters: 0.004 V increase potential, 0.05 V amplitude, 0.05 s pulse width, 0.0167 s sampling width, 0.5 s sample period.

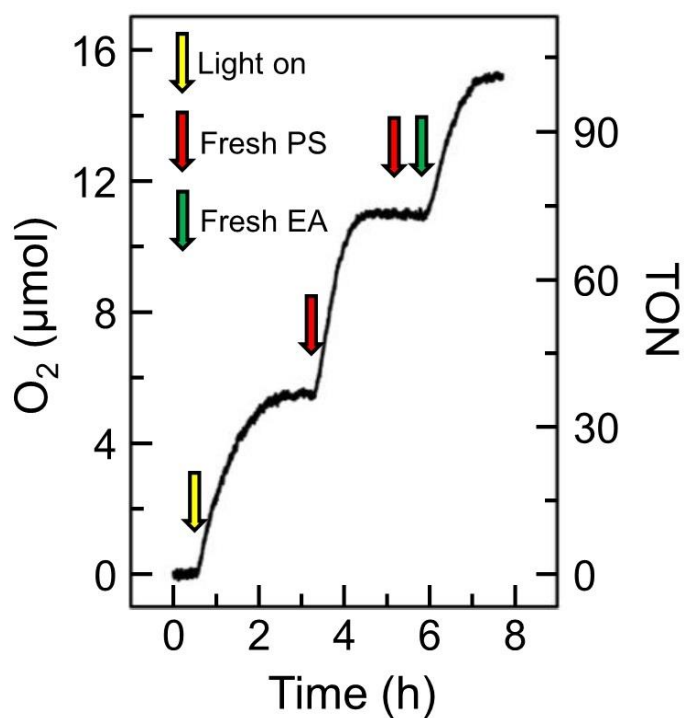


Figure AI.21 Repetitive photocatalytic water oxidation using a homogeneous mixture containing 0.05 mM $[\text{Ni-F8P}]^{4-}$, 0.67 mM $[\text{Ru}(\text{bpy})_3]\text{Cl}_2$ and 50 mM $\text{Na}_2\text{S}_2\text{O}_8$ in 0.1 M sodium phosphate buffer (initial pH 7.0), using LED lamp (450 nm, 15.8 mW), $T = 298 \text{ K}$. Fresh 0.67 mM $[\text{Ru}(\text{bpy})_3]\text{Cl}_2$ was added at $t = 3.5 \text{ h}$ and $t = 5.5$, another batch of 50 mM $\text{Na}_2\text{S}_2\text{O}_8$ was added at $t = 6.0 \text{ h}$.

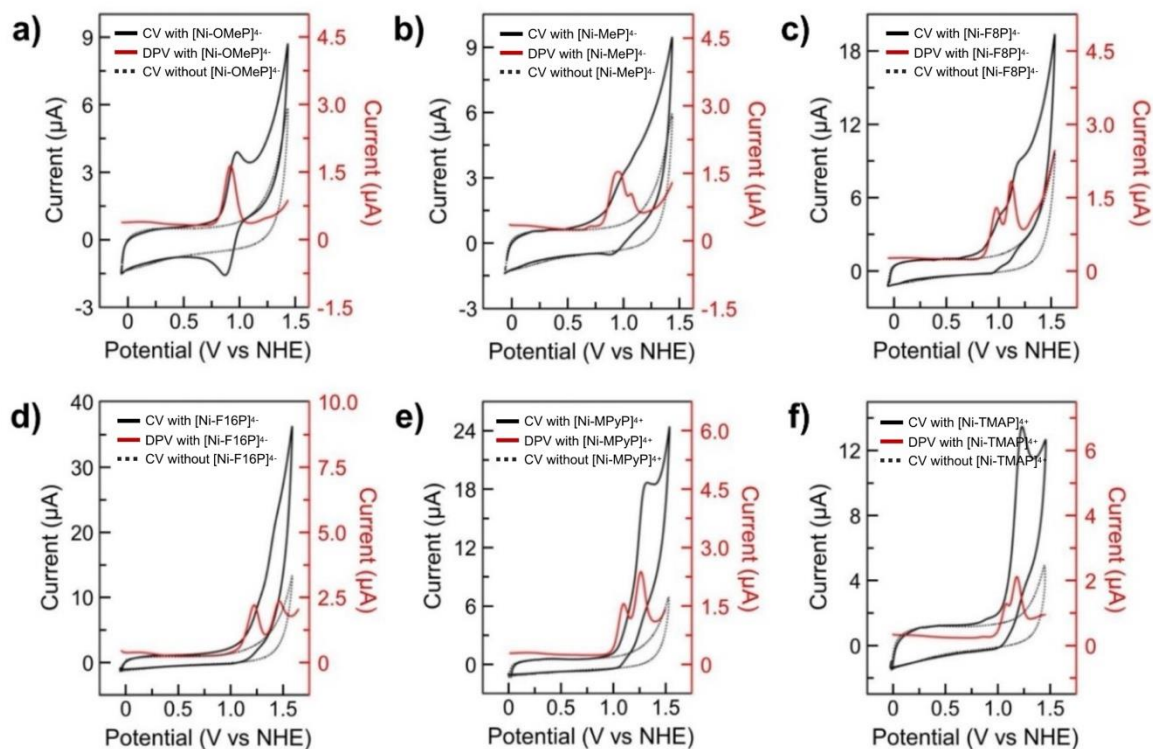


Figure AI.22 Cyclic voltammetry (CV, black traces) and differential pulse voltammetry (DPV, red traces) of aqueous solutions of a) $[\text{Ni-OMeP}]^{4-}$, b) $[\text{Ni-MeP}]^{4-}$, c) $[\text{Ni-F8P}]^{4-}$, d) $[\text{Ni-F16P}]^{4-}$, e) $[\text{Ni-MPyP}]^{4+}$, and f) $[\text{Ni-TMAP}]^{4+}$ (concentration: 0.25 mM) in 0.1 M phosphate buffer (pH 7.0). Conditions: 0.07 cm^2 working electrode, Pt wire auxiliary electrode, Ag/AgCl reference electrode, CV scan rate 50 mV s^{-1} , $T = 298 \text{ K}$. DPV experimental parameters: 0.004 V increase potential, 0.05 V amplitude, 0.05 s pulse width, 0.0167 s sampling width, 0.5 s sample period.

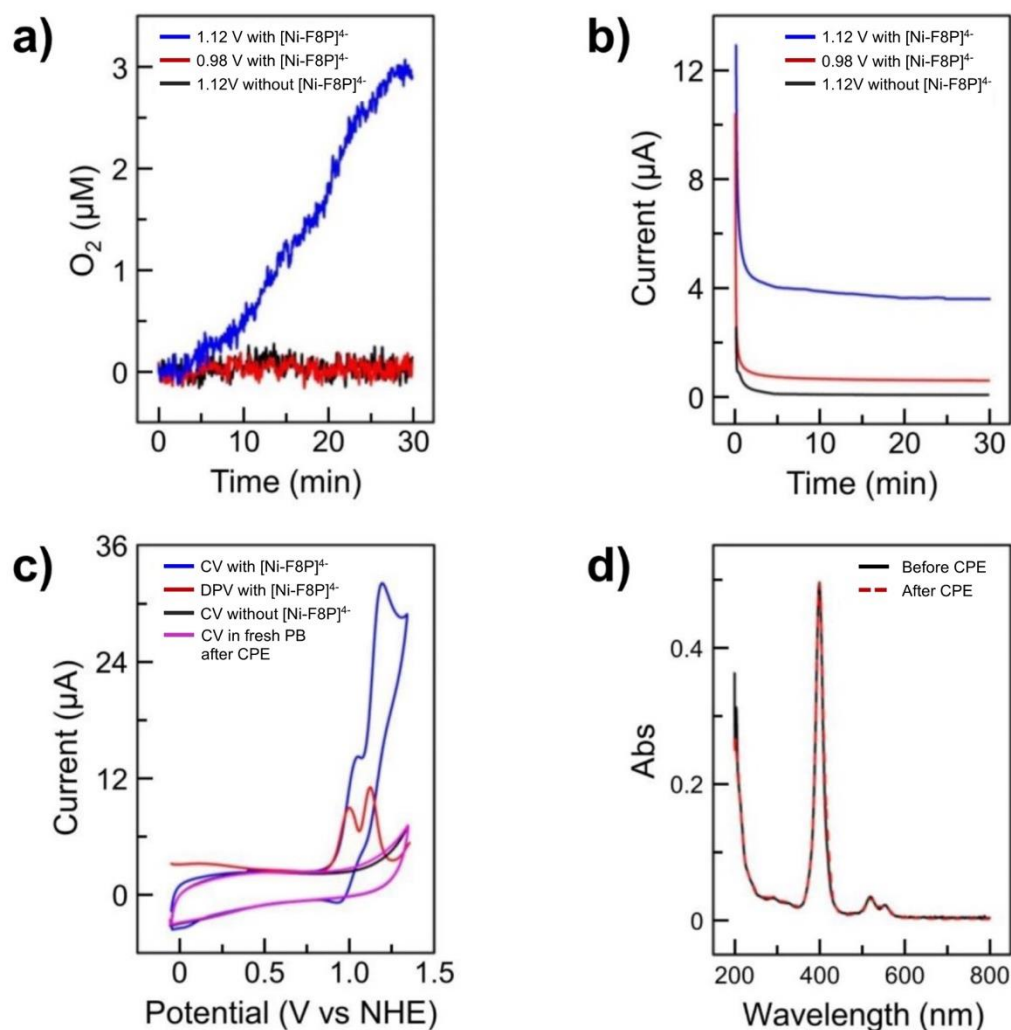


Figure AI.23 a) The oxygen evolution of the catalytic system comprising $[\text{Ni-F8P}]^{4-}$ as determined with CPE. b) Controlled potential electrolysis of a GC electrode with under 0.98 V and 1.12 V (vs NHE) and without 2 mM $[\text{Ni-F8P}]^{4-}$ at 1.12 V (vs NHE) in 0.1 M phosphate buffer (pH 7.0). c) CV (blue) and DPV (red) of a freshly cleaned GC electrode with 2 mM $[\text{Ni-F8P}]^{4-}$ and CV of a GC electrode without 2 mM $[\text{Ni-F8P}]^{4-}$ before (black) and after (magenta) 30 min electrolysis under 1.12 V (vs NHE) with 2 mM $[\text{Ni-F8P}]^{4-}$ in 0.1 M phosphate buffer (pH 7.0). d) UV-vis spectra of the solution before and after CPE at 1.12 V (vs NHE), diluted 1000 times by 0.1 M phosphate buffer (pH 7.0). Conditions: 0.07 cm^2 working electrode, Pt wire auxiliary electrode, Ag/AgCl reference electrode, 50 mV s^{-1} CV scan rate, $T = 298 \text{ K}$. DPV experimental parameters: 0.004 V increase potential, 0.05 V amplitude, 0.05 s pulse width, 0.0167 s sampling width, 0.5 s sample period. Clark oxygen electrode were set in solution.

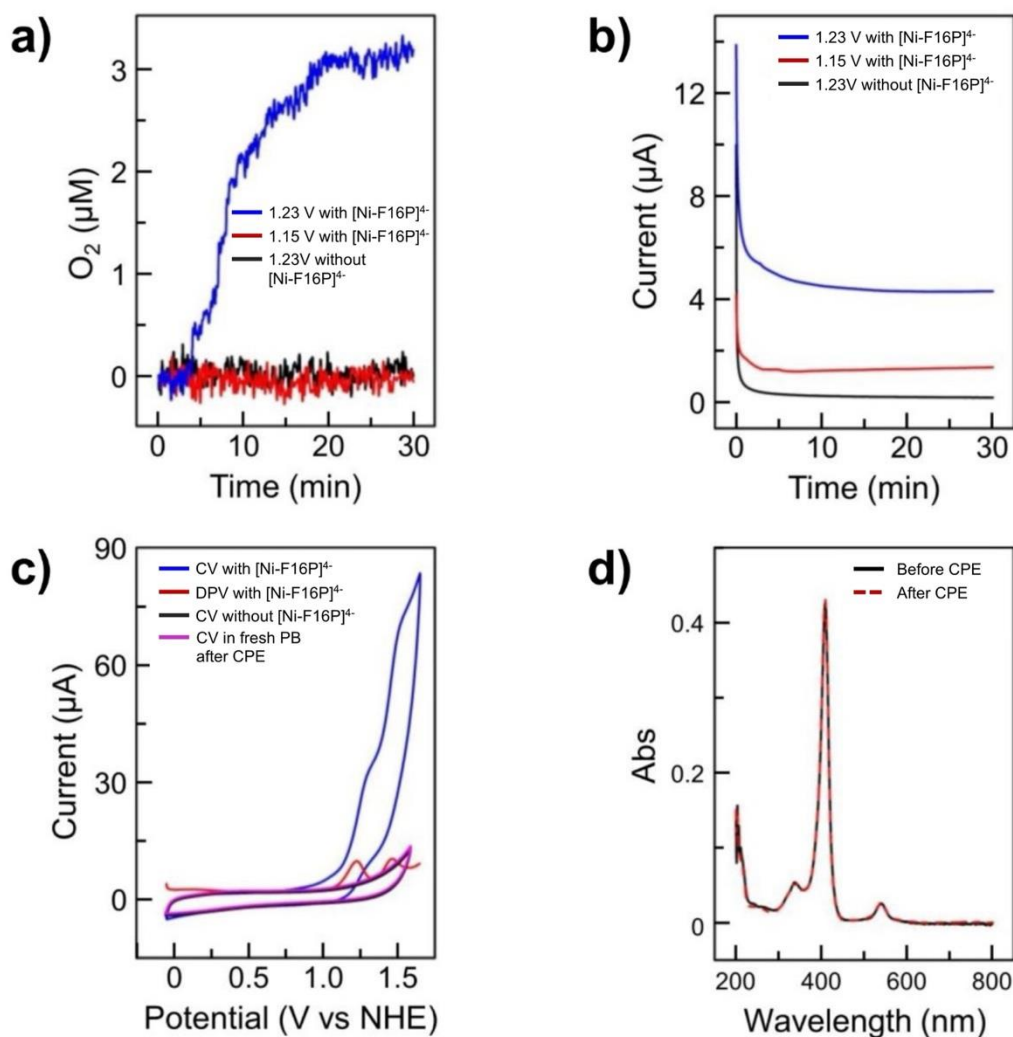


Figure AI.24 a) The oxygen evolution of the catalytic system comprising [Ni-F16P]⁴⁻ as determined with CPE. b) Controlled potential electrolysis of a GC electrode with under 1.15 V and 1.23 V (vs NHE) and without 2 mM [Ni-F16P]⁴⁻ under 1.23 V (vs NHE) in 0.1 M phosphate buffer (pH 7.0). c) CV (blue) and DPV (red) of a freshly cleaned GC electrode with 2 mM [Ni-F16P]⁴⁻ and CV of a GC electrode without 2 mM [Ni-F16P]⁴⁻ before (black) and after (magenta) 30 min electrolysis under 1.23 V (vs NHE) with 2 mM [Ni-F16P]⁴⁻ in 0.1 M phosphate buffer (pH 7.0). d) UV-vis spectra of the solution before and after CPE at 1.12 V (vs NHE), diluted 1000 times by 0.1 M phosphate buffer (pH 7.0). Conditions: 0.07 cm² working electrode, Pt wire auxiliary electrode, Ag/AgCl reference electrode, 50 mV s⁻¹ CV scan rate, *T* = 298 K. DPV experimental parameters: 0.004 V increase potential, 0.05 V amplitude, 0.05 s pulse width, 0.0167 s sampling width, 0.5 s sample period. Clark oxygen electrode were set in solution.

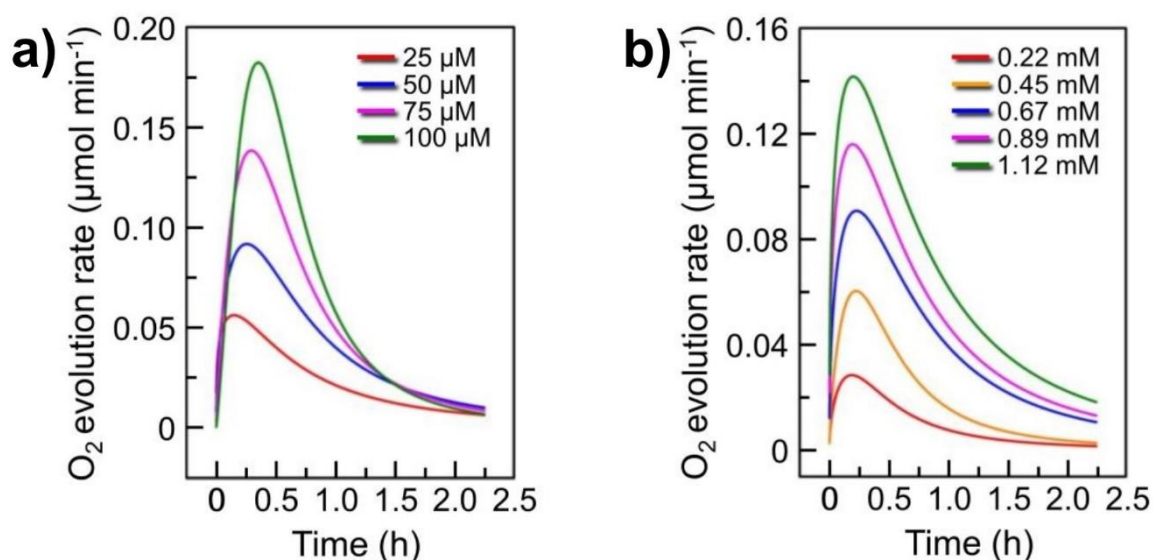


Figure AI.25 The calculated O_2 evolution rate vs. time during photocatalytic water oxidation in presence of a) different concentrations of $[Ni-F8P]^{4-}$ with 0.67 mM $[Ru(bpy)_3]Cl_2$ and 50 mM $Na_2S_2O_8$ and b) 0.05 mM $[Ni-F8P]^{4-}$ with different concentrations of $[Ru(bpy)_3]Cl_2$ and 50 mM $Na_2S_2O_8$ in 0.1 M sodium phosphate buffer (initial pH 7.0), using LED lamp (450 nm, 15,8 mW), $T = 298$ K.

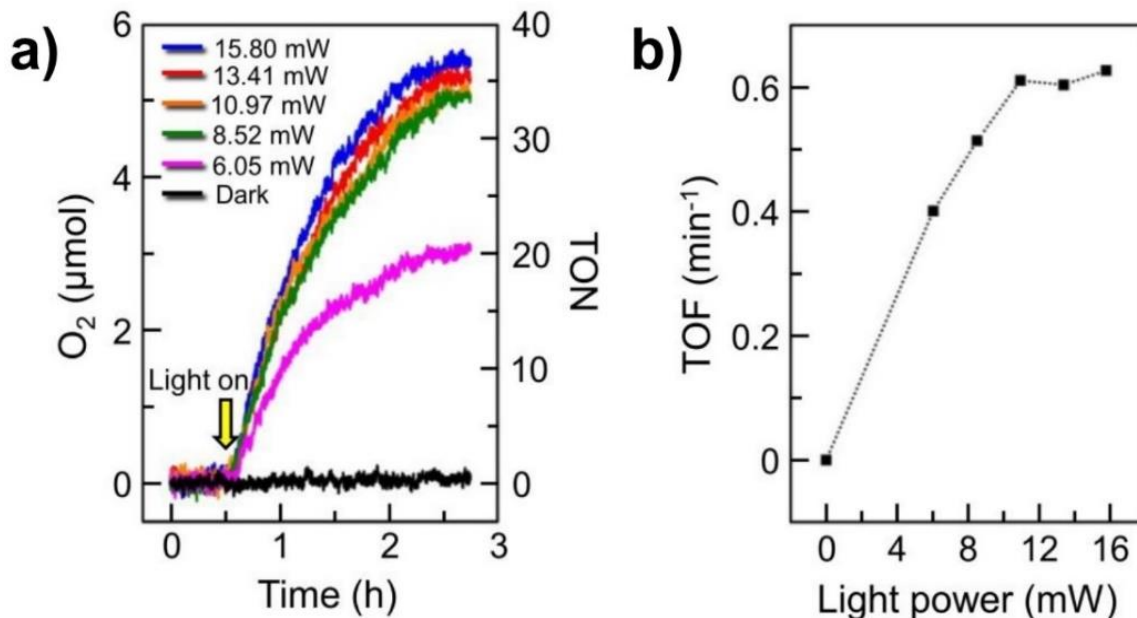


Figure AI.26 a) Dioxygen evolution during photocatalytic water oxidation in presence of 0.05 mM $[Ni-F8P]^{4-}$ with 0.67 mM $[Ru(bpy)_3]Cl_2$ and 50 mM $Na_2S_2O_8$ in 0.1 M sodium phosphate buffer (initial pH 7.0), using LED lamp (450 nm) with different optical power, $T = 298$ K. b) The maximum TOF of the O_2 evolution plotted as a function of the light power.

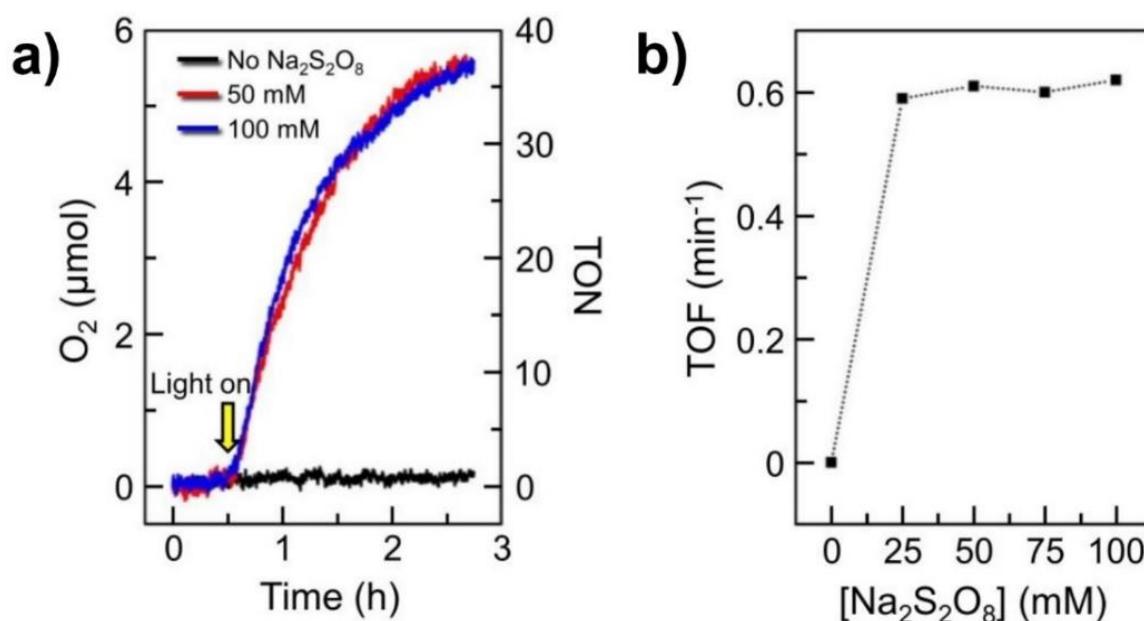


Figure AI.27 a) Dioxygen evolution during photocatalytic water oxidation in presence of 0.05 mM $[Ni-F8P]^{4-}$ with 0.67 mM $[Ru(bpy)_3]Cl_2$ and 0, 50 mM and 100 mM $Na_2S_2O_8$ in 0.1 M sodium phosphate buffer (initial pH 7.0), using LED lamp (450 nm, 15.8 mW), $T = 298$ K. b) The maximum TOF of the O_2 evolution plotted as a function of the concentration of $Na_2S_2O_8$.

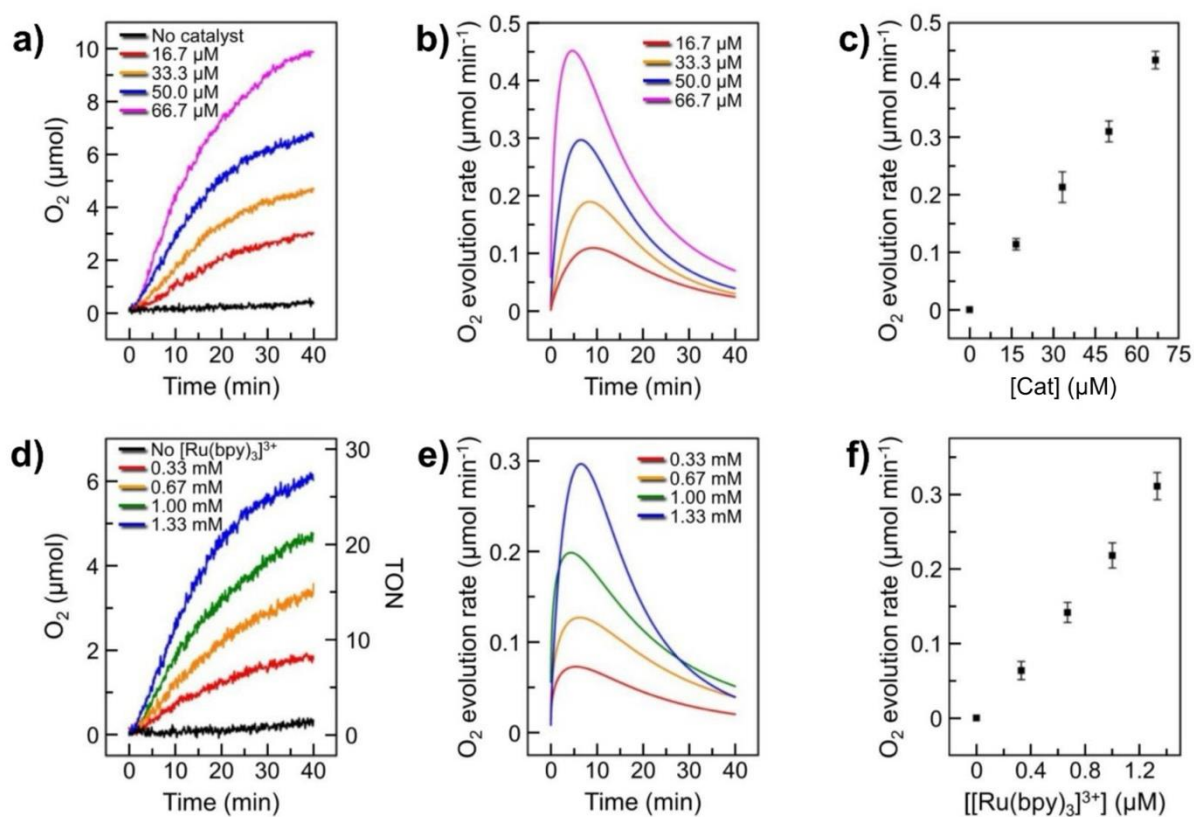


Figure AI.28 Catalytic oxygen evolution vs. time driven by chemically prepared $[\text{Ru}(\text{bpy})_3](\text{ClO}_4)_3$. a) different concentrations of $[\text{Ni-F8P}]^{4+}$ with 1.33 mM $[\text{Ru}(\text{bpy})_3](\text{ClO}_4)_3$ as chemical oxidant, and d) different concentrations of $[\text{Ru}(\text{bpy})_3](\text{ClO}_4)_3$ with 0.05 mM $[\text{Ni-F8P}]^{4+}$ as WOC in 0.1 M sodium phosphate buffer (initial pH 7.0), $T = 298 \text{ K}$. b) and e) the calculated O_2 evolution rate vs. time of a) and d). c) and f) the maximum O_2 evolution rate during catalytic O_2 evolution plotted as a function of c) the concentration of $[\text{Ni-F8P}]^{4+}$ and f) the concentration of $[\text{Ru}(\text{bpy})_3](\text{ClO}_4)_3$.



Figure AI.29 The photocatalytic set-up.

Table AI.1 DPV oxidation wave potentials of Ni-porphyrin complexes and $[\text{Ru}(\text{bpy})_3]\text{Cl}_2$

	$[\text{Ni-OMeP}]^{4+}$	$[\text{Ni-MeP}]^{4+}$	$[\text{Ni-F8P}]^{4+}$	$[\text{Ni-F16P}]^{4+}$	$[\text{Ni-MPyP}]^{4+}$	$[\text{Ni-TMAP}]^{4+}$	$[\text{Ru}(\text{bpy})_3]^{2+}$
First oxidation	0.92 V	0.96 V	0.98 V	1.23 V	1.10 V	0.91 V	1.26 V
Second oxidation		1.07 V	1.12 V	1.46 V	1.25 V	1.01 V	

Potentials versus NHE, DPV measurements were measured in pH 7.0 sodium phosphate buffer, 298

APPENDIX II: SUPPORTING INFORMATION FOR CHAPTER 3

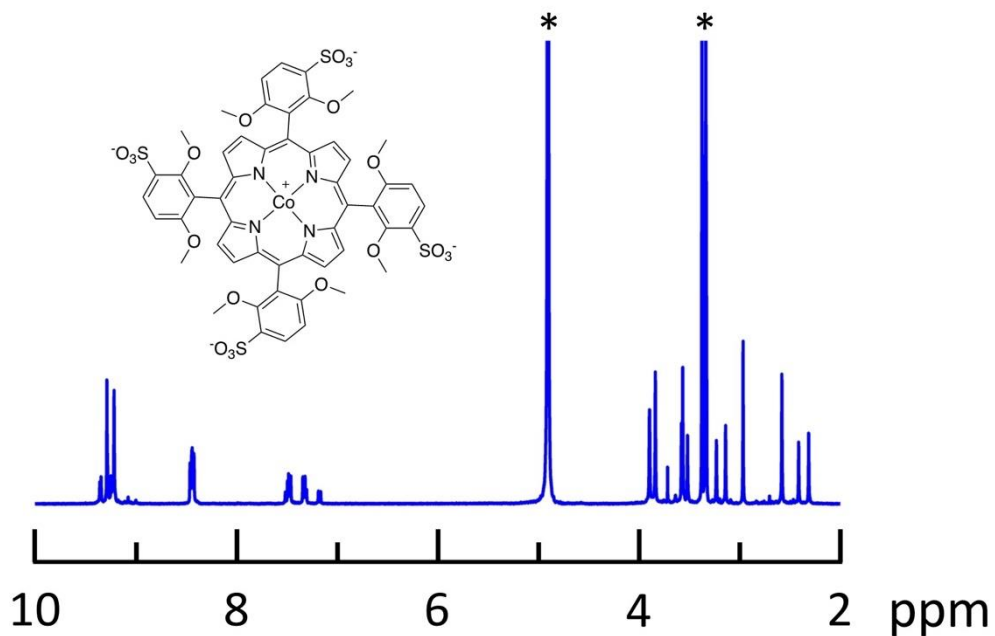


Figure AII.1 ^1H NMR of $[\text{Co-OMeP}]^{3-}$ in MeOD. * Methanol and water.

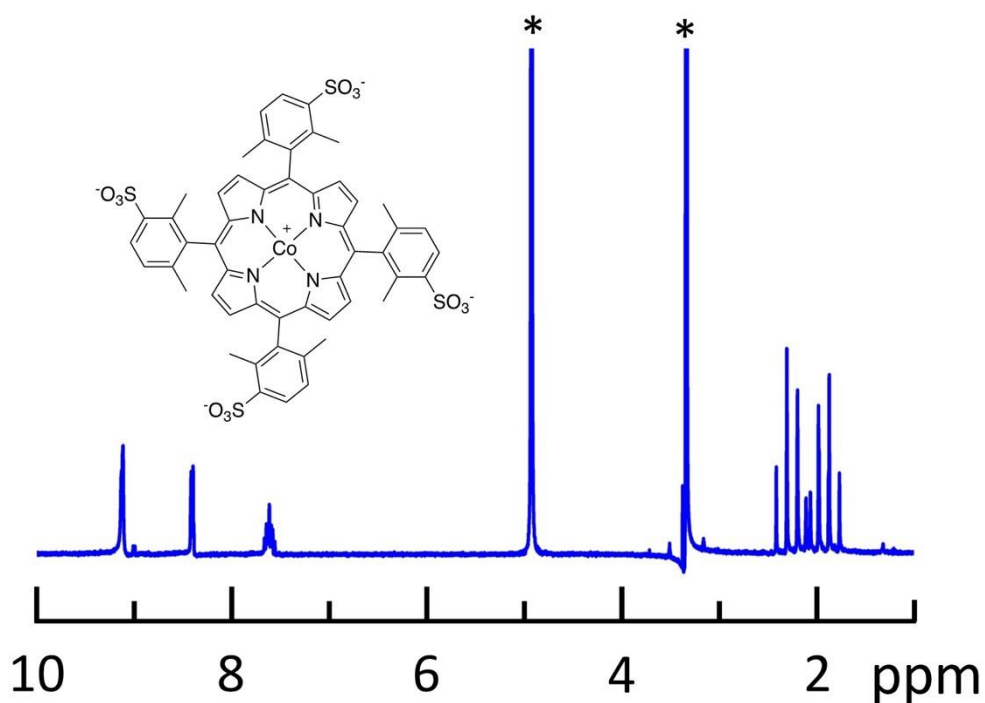


Figure AII.2 ^1H NMR of $[\text{Co-MeP}]^{3-}$ in MeOD. * Methanol and water.

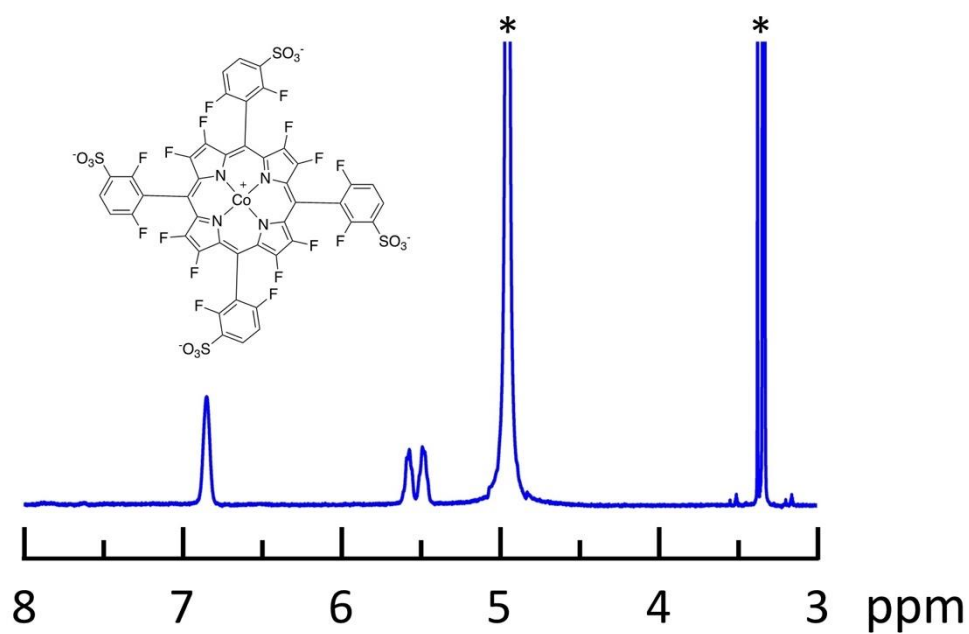


Figure AII.3 ^1H NMR of $[\text{Co-F16P}]^{3-}$ in MeOD . * Methanol and water.

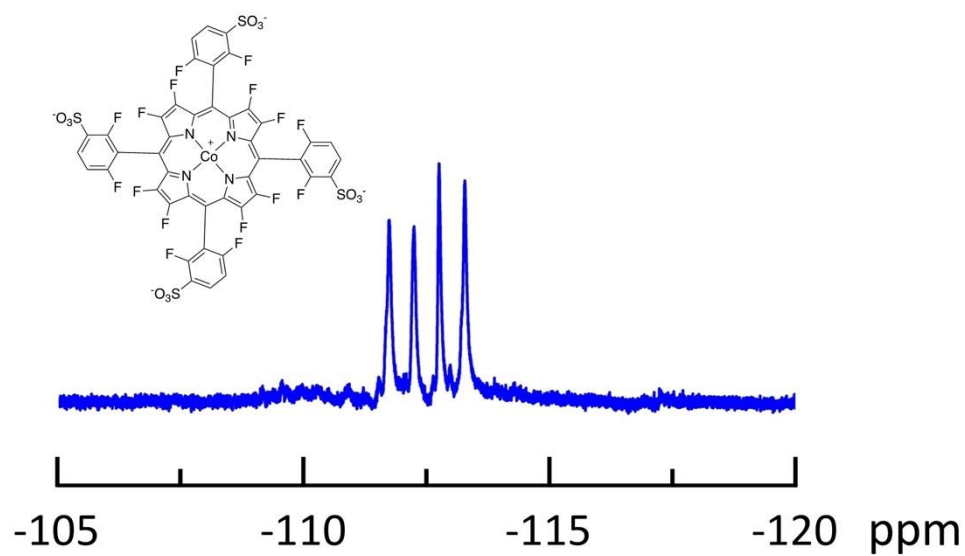


Figure AII.4 ^{19}F NMR of $[\text{Co-F16P}]^{3-}$ in MeOD .

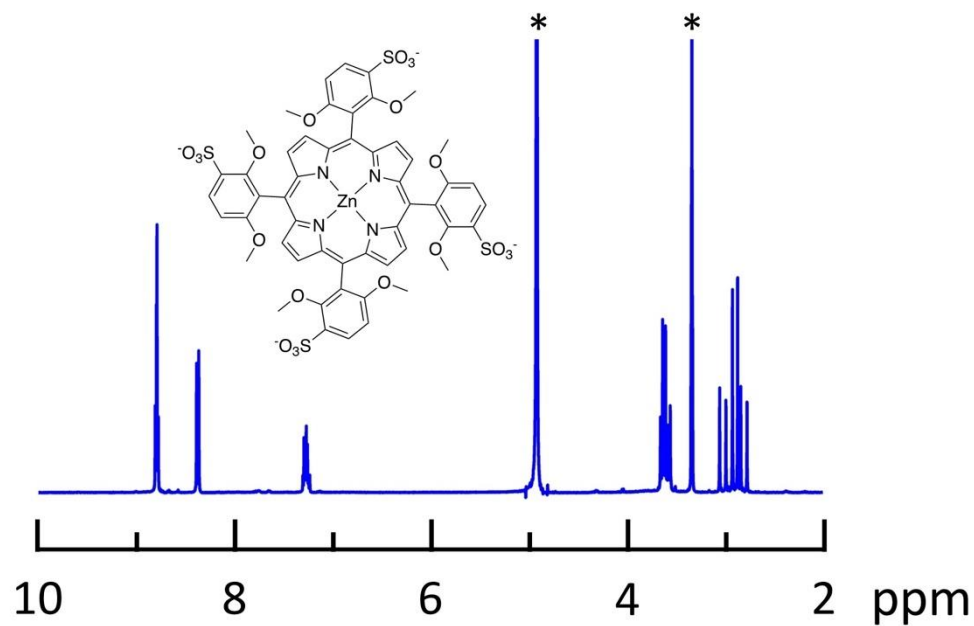


Figure AII.5 ^1H NMR of $[\text{Zn-OMeP}]^{4-}$ in MeOD . * Methanol and water.

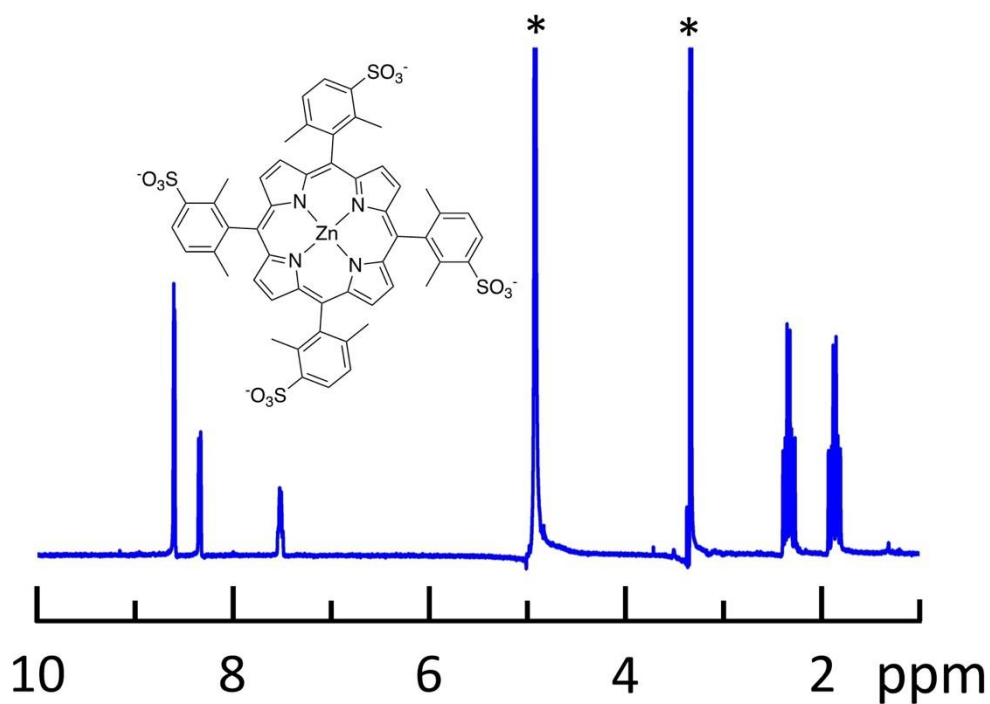


Figure AII.6 ^1H NMR of $[\text{Zn-MeP}]^{4-}$ in MeOD . * Methanol and water.

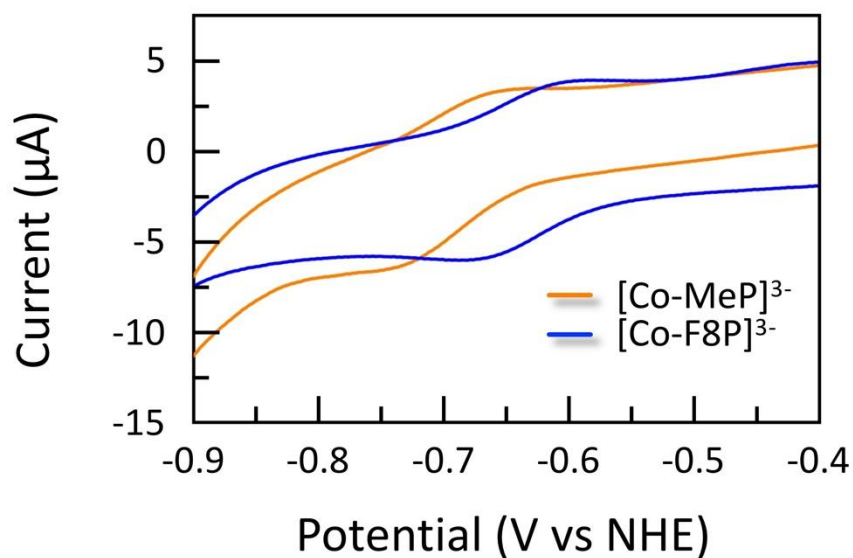


Figure AII.7 Cyclic voltammetry from -0.9 to -0.4 V vs. NHE of the $[\text{Co-MeP}]^{3-}$ and $[\text{Co-MeP}]^{3-}$ in Figure 3.3b.

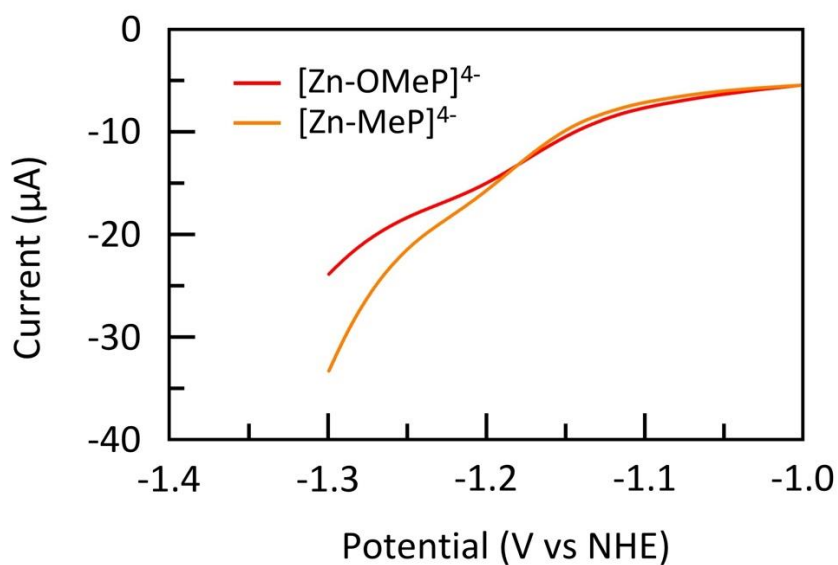


Figure AII.8 Linear sweep voltammetry from -1.3 to -1.0 V vs. NHE of the $[\text{Zn-OMeP}]^{4-}$ and $[\text{Zn-MeP}]^{4-}$ in Figure 3.3c.

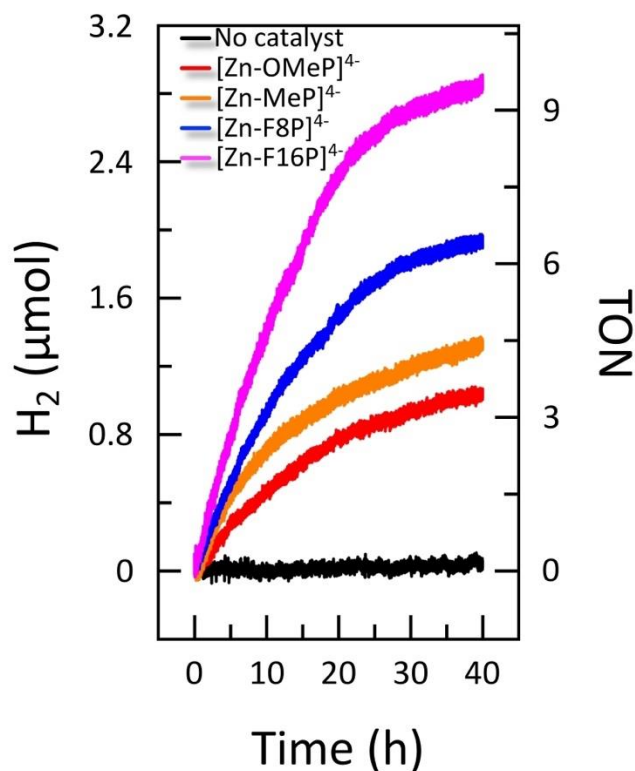


Figure AII.9 Hydrogen evolution during photocatalytic water reduction in presence of 0.1 mM catalyst $[\text{Zn-OMeP}]^{4-}$, $[\text{Zn-MeP}]^{4-}$, $[\text{Zn-F8P}]^{4-}$ and $[\text{Zn-F16P}]^{4-}$, using 0.5 mM $[\text{Ru}(\text{bpy})_3]\text{Cl}_2$ as photosensitizer, 0.1 M ascorbate and TCEP, in pH 7.0 aqueous solution, and LED lamp (450 nm, 16 mW) for irradiation, $T = 298\text{ K}$.

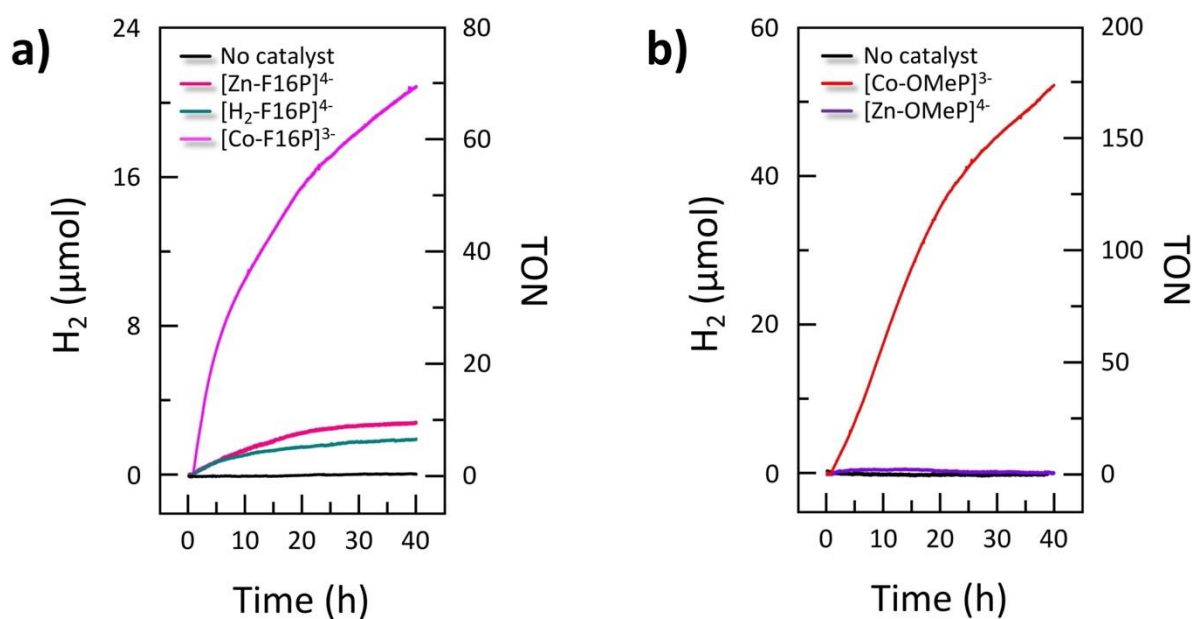


Figure AII.10 Hydrogen evolution during photocatalytic water reduction in presence of a) 0.1 mM catalyst $[\text{Co-F16P}]^{3-}$, $[\text{H}_2\text{-F16P}]^{4-}$ and $[\text{Zn-F16P}]^{4-}$ in pH 7.0 aqueous solution, and b)

0.1 mM catalyst $[\text{Co-OMeP}]^{3-}$ and $[\text{Zn-OMeP}]^{4-}$ in pH 4.1 aqueous solution using 0.5 mM $[\text{Ru}(\text{bpy})_3]\text{Cl}_2$ as photosensitizer, 0.1 M ascorbate and TCEP, and LED lamp (450 nm, 16 mW) for irradiation, $T = 298 \text{ K}$.

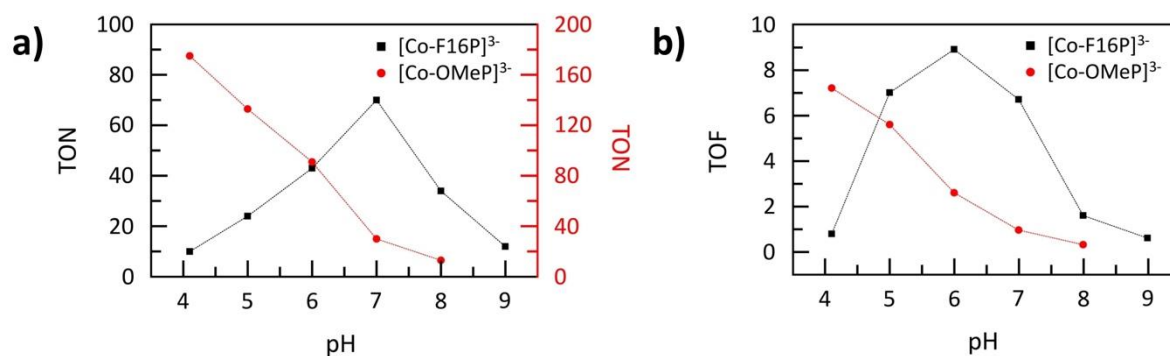


Figure AII.11 a) Turnover numbers and b) turnover frequencies of photocatalytic H_2 evolution systems in Figure 3.5 plotted as a function of the pH.

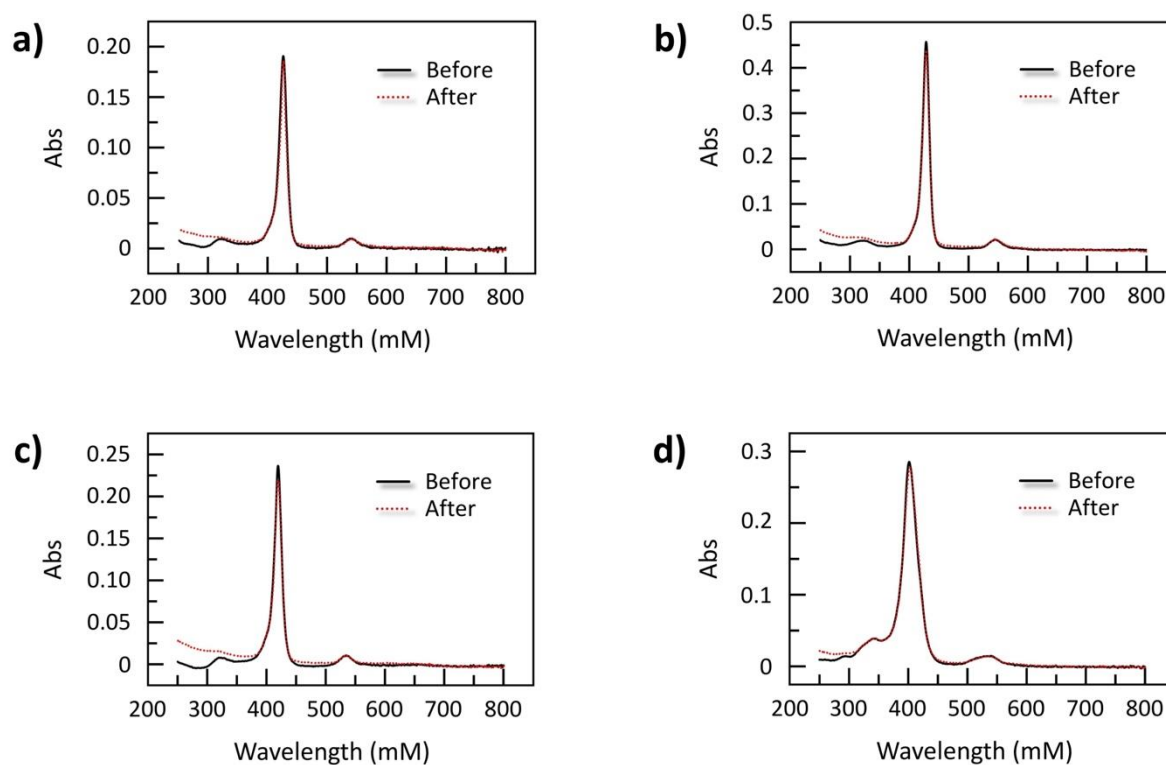


Figure AII.12 Absorption spectra of 2 μM a) $[\text{Co-OMeP}]^{3-}$, b) $[\text{Co-MeP}]^{3-}$, c) $[\text{Co-F8P}]^{3-}$, and d) $[\text{Co-F16P}]^{3-}$ before (black solid) and after (red short dot) 48 hours irradiation (LED lamp, 450 nm, 16 mW) in 0.1 M sodium phosphate buffer (pH 7.0) under air, $T = 298 \text{ K}$.

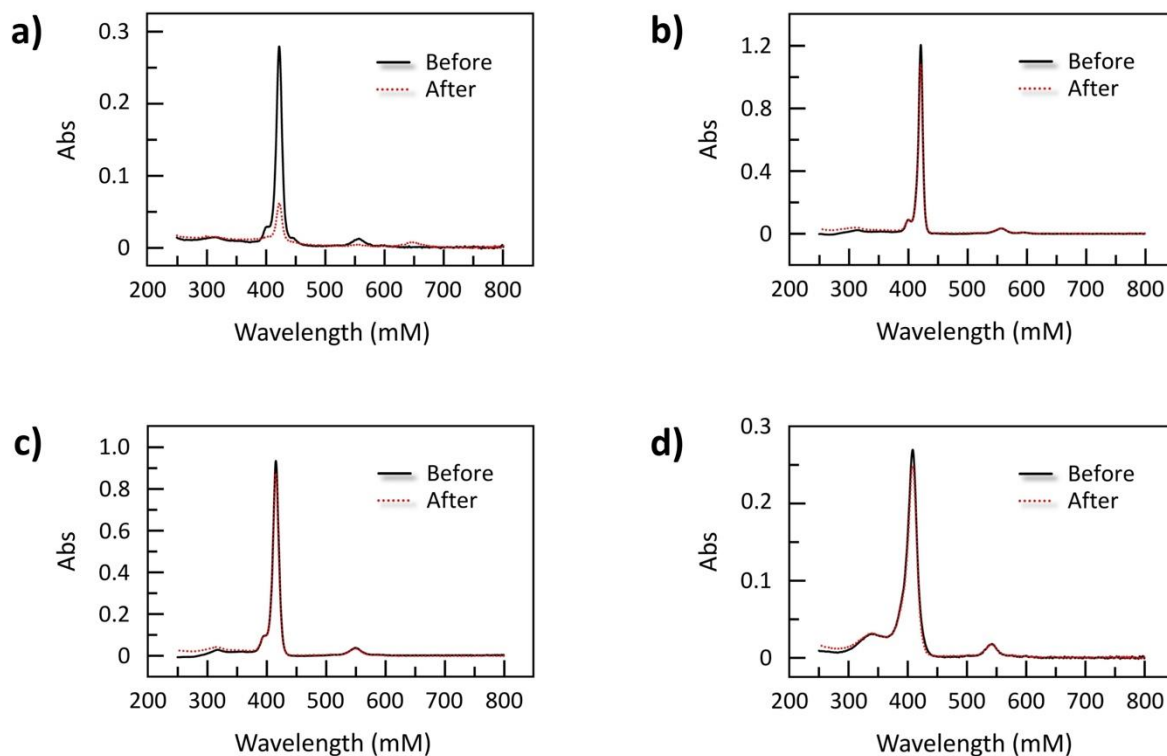


Figure AII.13 Absorption spectra of 2 μM a) $[\text{Zn-OMeP}]^{4-}$, b) $[\text{Zn-MeP}]^{4-}$, 3) $[\text{Zn-F8P}]^{4-}$, and 4) $[\text{Zn-F16P}]^{4-}$ before (black solid) and after (red short dot) 48 hours irradiation (LED lamp, 450 nm, 16 mW) in 0.1 M sodium phosphate buffer (pH 7.0) under air, $T = 298 \text{ K}$.

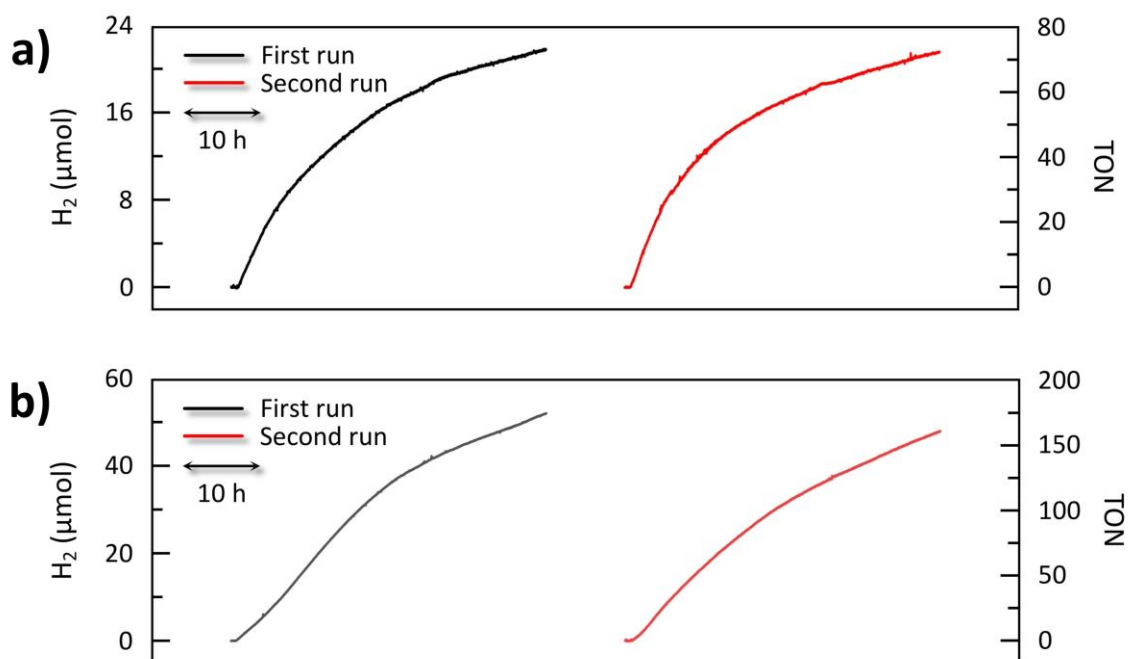


Figure AII.14 Repetitive photocatalytic hydrogen evolution in presence of a) 0.1 mM [Co-F16P]³⁻ in pH 7.0 and b) [Co-OMeP]³⁻ in different pH 4.1 aqueous solution using 0.5 mM [Ru(bpy)₃]Cl₂ as photosensitizer, 0.1 M ascorbate and TCEP, and LED lamp (450 nm, 16 mW) for irradiation, T = 298 K. Between the two irradiation experiments, 1.5 μmol fresh [Ru(bpy)₃]Cl₂ was added as solids.

APPENDIX III: SUPPORTING INFORMATION FOR CHAPTER 4

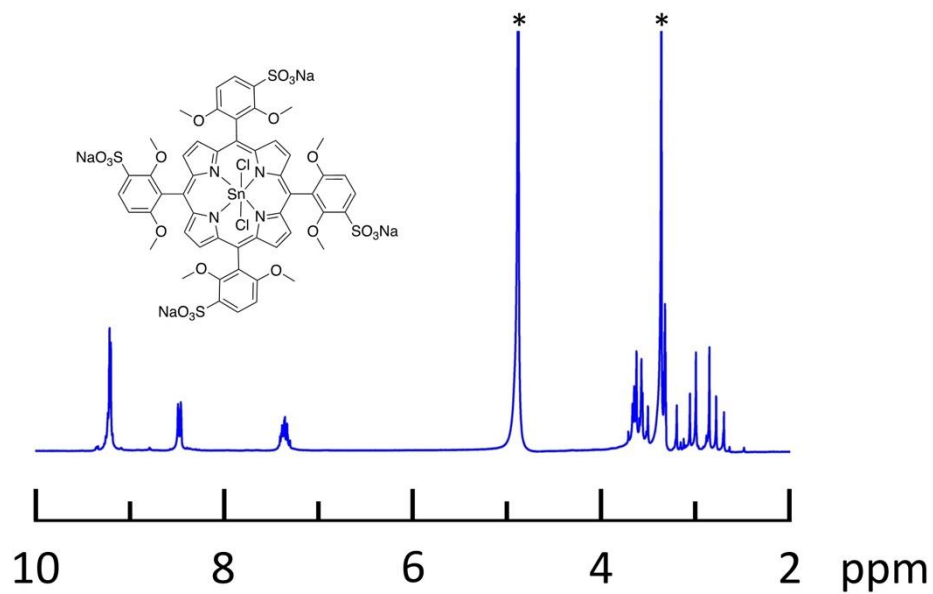


Figure AIII.1 ^1H NMR of $[\text{Sn-OMeP}]^{4-}$ in MeOD . * Methanol and water.

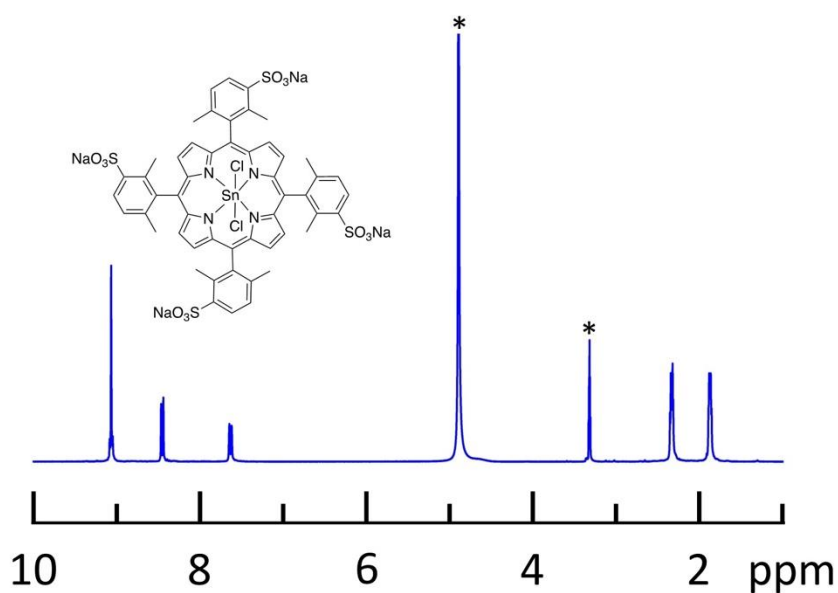


Figure AIII.2 ^1H NMR of $[\text{Sn-MeP}]^{4-}$ in MeOD . * Methanol and water.

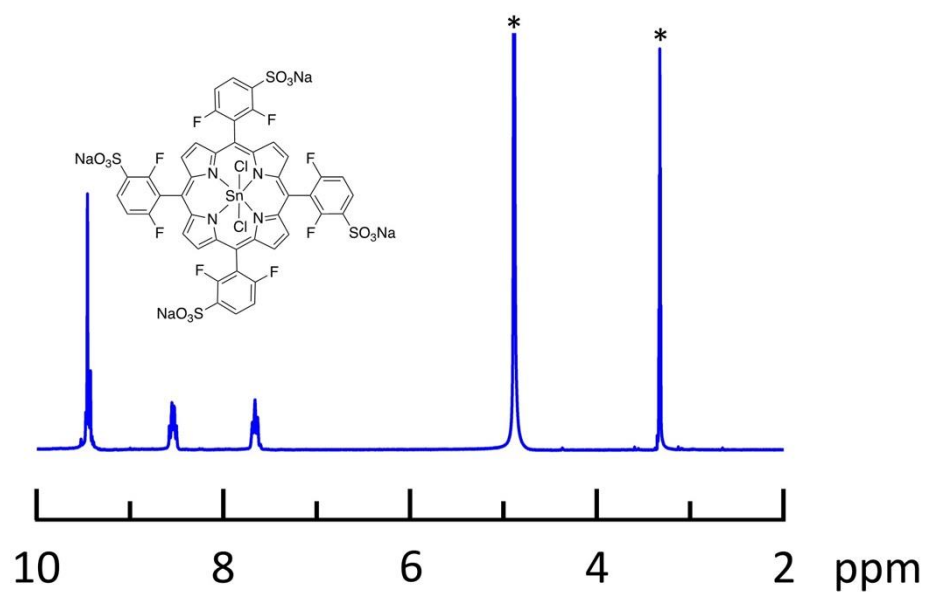


Figure AIII.3 ^1H NMR of $[\text{Sn-F8P}]^{4-}$ in MeOD . * Methanol and water.

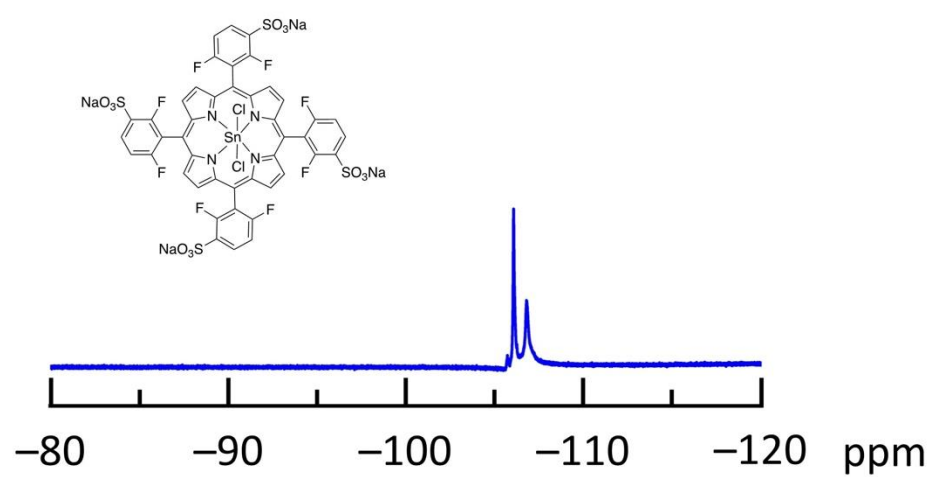


Figure AIII.4 ^{19}F NMR of $[\text{Sn-F8P}]^{4-}$ in MeOD .

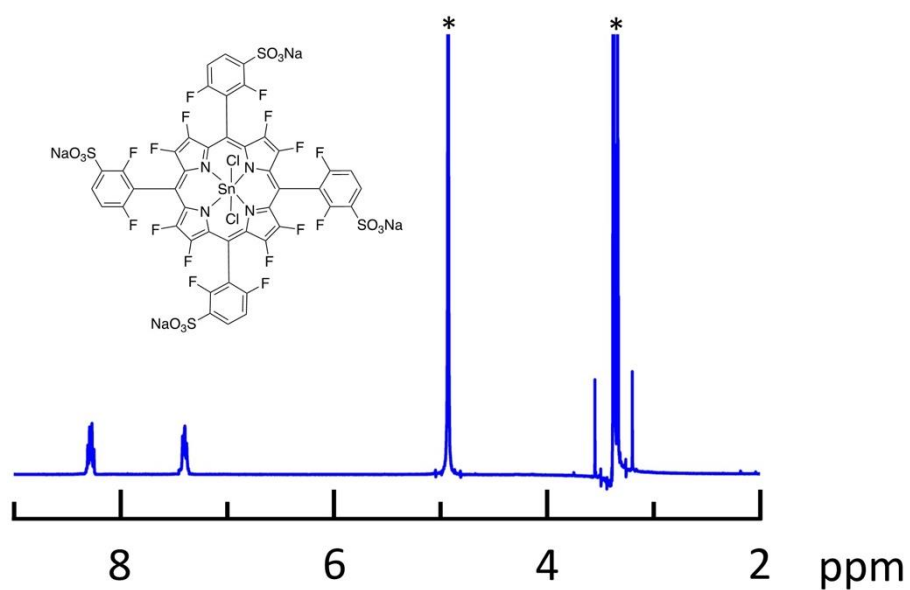


Figure AIII.5 ^1H NMR of $[\text{Sn-F16P}]^{4-}$ in MeOD . * *Methanol and water.*

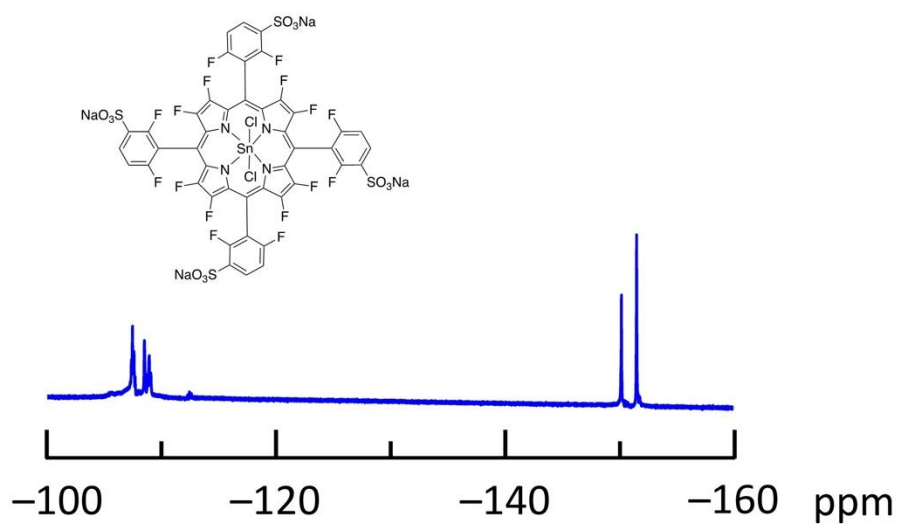


Figure AIII.6 ^{19}F NMR of $[\text{Sn-F16P}]^{4-}$ in MeOD .

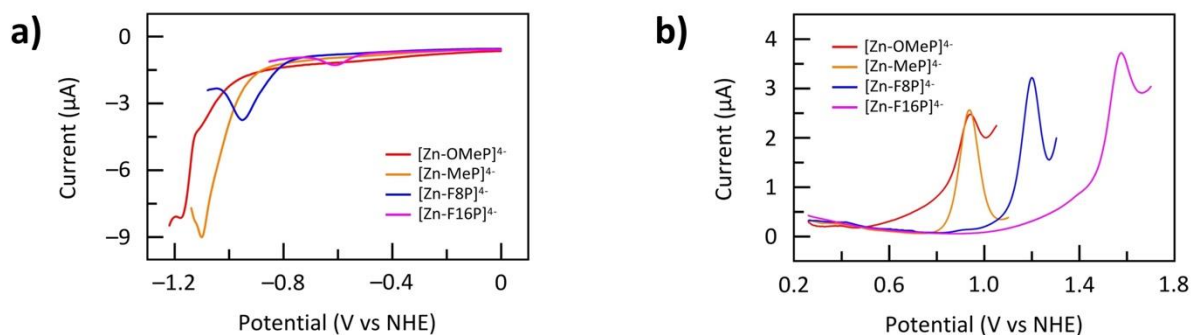


Figure AIII.7 DPV of 1.0 mM [Zn-OMeP]⁴⁻, [Zn-MeP]⁴⁻, [Zn-F8P]⁴⁻ or [Zn-F16P]⁴⁻ in 1:1 0.1 M pH 7.0 PB/MeCN solution. Conditions: 0.07 cm² glassy-carbon working electrode, Pt wire auxiliary electrode, Ag/AgCl reference electrode, ± 0.004 V increase potential, 0.05 V amplitude, 0.05 s pulse width, 0.0167 s sampling width, 0.5 s sample period, $T = 298$ K.

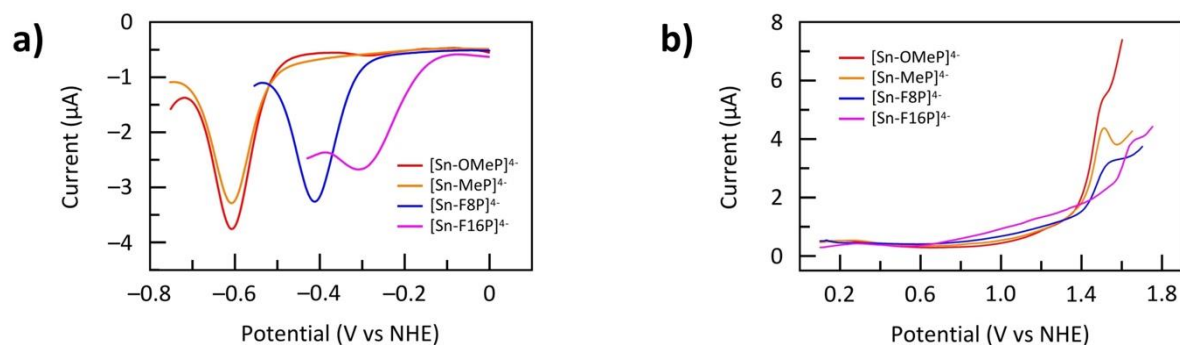


Figure AIII.8 DPV of 1.0 mM [Sn-OMeP]⁴⁻, [Sn-MeP]⁴⁻, [Sn-F8P]⁴⁻ or [Sn-F16P]⁴⁻ in 1:1 0.1 M pH 7.0 PB/MeCN solution. Conditions: 0.07 cm² glassy-carbon working electrode, Pt wire auxiliary electrode, Ag/AgCl reference electrode, ± 0.004 V increase potential, 0.05 V amplitude, 0.05 s pulse width, 0.0167 s sampling width, 0.5 s sample period, $T = 298$ K.

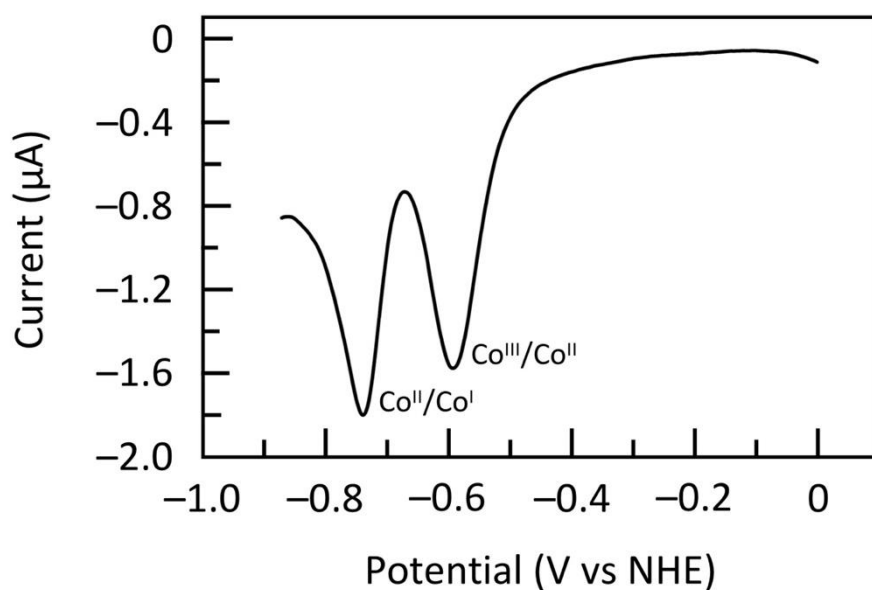


Figure AIII.9 DPV of 0.5 mM cobaloxime in 1:1 0.1 M pH 7.0 PB/MeCN solution. Conditions: 0.07 cm² glassy-carbon working electrode, Pt wire auxiliary electrode, Ag/AgCl reference electrode, -0.004 V increase potential, 0.05 V amplitude, 0.05 s pulse width, 0.0167 s sampling width, 0.5 s sample period, $T = 298$ K.

Samenvatting van dit proefschrift

Kunstmatige fotosynthese (AP) is een van de wetenschappelijke uitdagingen die ons zouden kunnen helpen om een wereldwijde "koolstofneutrale" samenleving tot stand te brengen. Het zal een belangrijk onderzoeksthema blijven voor tenminste de komende 30 jaar. Het algemene idee van AP is om water te splitsen of CO₂ om te zetten in koolwaterstoffen of organische producten met behulp van zonne-energie. Aangezien fotonvoltaïsche elektriciteitsopwekking gevolgd door elektrolyse onvermijdelijk energieverliezen met zich meebrengt, is het in principe wenselijker de AP-reacties rechtstreeks te realiseren, bij voorkeur met behulp van elementen die op aarde veel voorkomen. In het algemeen wordt aangenomen dat een fotokatalytisch systeem minimaal drie componenten nodig heeft: een fotosensibilisator (PS), een katalysator (Cat) en een opofferings-elektronendonor of -acceptor (SE). In een dergelijk fotokatalytisch systeem kunnen ten minste drie elektronenoverdrachtstappen worden onderscheiden: één tussen de SE en het geëxciteerde PS (PS*), één tussen het gefotoreduceerde of gefotooxideerde PS en de kat, en één tussen de kat en zijn substraat. Aangezien het moeilijk is de stabiliteit, activiteit en katalytische mechanismen van nieuwe moleculaire componenten in twee parallel verlopende fotokatalytische processen te onderzoeken, wordt vaak de voorkeur gegeven aan het onderzoeken van één van de individuele halfreacties. Een goed gedefinieerde homogene oplossing is eenvoudiger te analyseren en dus beter geschikt voor de ontwikkeling van moleculaire componenten, in tegenstelling tot heterogene of hybride fotokatalytische systemen die bestaan uit zelfgeassembleerde en/of vastestofcomponenten, waarin de reagerende moleculen soms moeilijk te identificeren zijn. Daarom was al het in dit proefschrift beschreven onderzoek gericht op de ontwikkeling van verbeterde moleculaire componenten voor één van de twee halfreacties van watersplitsing, gebaseerd op fotokatalytische studies in zuiver homogene systemen.

Hoewel [Ru(bpy)₃]²⁺ gebaseerd is op een relatief zeldzaam metaal, is het ook een van de bekendste moleculaire fotosensibilisatoren die in staat is zowel de lichtgedreven zuurstof-evolutiereactie (OER) als de lichtgedreven waterstof-evolutiereactie (HER) te sensibiliseren. Daarom werd het in dit proefschrift gebruikt als standaard PS voor de ontwikkeling van nieuwe eerste-rij overgangsmetaalkatalysatoren voor OER en HER. Anderzijds is cobaloxime een goed bestudeerde katalysator voor fotokatalytische HER, en werd het geselecteerd als standaard waterstofevolutiekatalysator (HEC) om nieuwe moleculaire fotosensibilisatoren te ontwikkelen op basis van veelvoorkomende elementen. Wij combineerden beide manieren van

aanpak om nieuwe katalysatoren en fotosensibilisatoren te ontwikkelen op basis van tetragesulfoneerde porfyryne liganden. Aangezien voor het optimaliseren van een fotokatalytisch systeem een evenwicht moet worden gevonden tussen de drijvende kracht van elektronenoverdracht van de SE naar de PS*, en die van elektronenoverdracht tussen de katalysator en de geoxideerde of gereduceerde fotosensitizer (PS⁺ of PS⁻), varieerden we systematisch de elektronendichtheid van het porfyryne ligand door toevoeging van ofwel elektron-donerende (8 methoxy of 8 methyl) ofwel elektron-onttrekkende (8 of 16 fluor) groepen op de ortho posities van de meso-fenyl ringen (Figuur 1.23 in **hoofdstuk 1**).

In **hoofdstuk 2** wordt de synthese beschreven van een serie van vier tetra-anionische Ni(II)-porfyryne complexen met deze liganden. Deze verbindingen werden gebruikt als moleculaire katalysatoren voor licht-gedreven water oxidatie in homogene neutrale of zure waterige oplossingen. Elektrochemische en kinetische studies toonden aan dat meer elektron-onttrekkende substituenten de oxidatiepotentiaal van de Ni-porfyryne complexen verhoogden, en de zuurstof-evolutiesnelheid controleerden in fotokatalytische omstandigheden. Er moest een evenwicht worden gevonden tussen het verhogen van deze oxidatiepotentiëlen, die een hogere drijvende kracht leveren voor de katalytische OER zelf, en ze laag genoeg houden om ervoor te zorgen dat de drijvende kracht voor de elektronenoverdracht van de katalysator naar de geoxideerde fotosensibilisator PS⁺ hoog genoeg blijft. Bij gebruik van [Ru(bpy)₃]²⁺ als fotosensibilisator en S₂O₈²⁻ als opofferingselektronenacceptor, bleek [Ni-F16P]⁴⁻ bijvoorbeeld te elektronarm te zijn. Hierdoor werd de elektronenoverdracht tussen de nikkelkatalysator en de foto-oxidant [Ru(bpy)₃]³⁺ geblokkeerd, wat het fotokatalytische systeem inactief maakte. De eigenschappen van [Ni-F8P]⁴⁻ bleken dicht bij het optimum te liggen, wat resulteerde in een uitstekende activiteit voor de fotokatalytische OER. De gerapporteerde nikkelporfyrynekatalysatoren vertoonden een grote stabiliteit onder fotokatalytische omstandigheden. Zo werd bijvoorbeeld de TON van het fotokatalytische systeem met [Ni-F8P]⁴⁻ als katalysator beperkt door ontleding van de op Ru gebaseerde fotosensibilisator. Dit werk beschrijft niet alleen een zeldzaam voorbeeld van homogene lichtgestuurde wateroxidatie gekatalyseerd door een Ni-gebaseerde moleculaire katalysator in neutrale tot zure waterige oplossingen; het levert ook nieuwe regels op voor het ontwerp van moleculaire katalysatoren voor fotokatalyse: de elektronendichtheid van het katalytische centrum moet nauwkeurig worden afgesteld met geschikte substituenten, om de drijvende krachten van katalytische wateroxidatie versus die van de elektronenoverdracht van de katalysator naar PS⁺ in evenwicht te brengen.

In **hoofdstuk 3** wordt de synthese gerapporteerd van analoge series tetra-anionische Co(III)- en Zn(II)-porfyrine complexen, die werden bestudeerd als moleculaire katalysatoren voor homogene fotokatalytische waterstofproductie in neutrale en zure waterige oplossingen. Hoewel er veel kobalt katalysatoren zijn gerapporteerd die HER kunnen faciliteren, zijn de meeste van hen niet geoptimaliseerd voor neutrale waterige oplossingen. Dit is jammer, want pH 7,0 is ideaal voor het combineren van de water-oxidatie en proton-reductie reactie tot een volledige watersplitsingsreactie. Bovendien is het katalytische mechanisme van HER in neutrale omstandigheden niet noodzakelijkerwijs hetzelfde als in zure oplossingen. Dit zorgt er voor dat de strategie om een katalysator te ontwerpen die geoptimaliseerd is voor neutrale omstandigheden anders kan zijn dan de strategie die wordt gebruikt om katalysatoren te ontwikkelen voor zure oplossingen. De fotokatalytische activiteit en het mechanisme van de Co(III) en Zn(II) complexen bleken sterk afhankelijk te zijn van de aanwezigheid van elektron-onttrekkende of elektron-donerende substituenten op de porfyrine ring en van de pH van de waterige oplossing. In de serie zinkcomplexen bleken de porfyrineliganden redox-actief te zijn, wat leidde tot significante fotokatalytische HER voor $[\text{Zn-F16P}]^{4-}$ ondanks het onvermogen van het metaalcentrum om zijn oxidatietoestand te veranderen. Het elektron-rijkste complex, $[\text{Co-OMeP}]^{3-}$, had de hoogste drijvende kracht om water te reduceren in de serie van kobaltporfyrinecomplexen volgens elektrochemische analyse, maar een hogere fotokatalytische activiteit werd alleen waargenomen bij pH 4,1 die verdween bijna volledig bij het vervangen van het kobaltcentrum door een zinkion. Bij neutrale pH was de activiteit veel lager dan bij lage pH, en interessanter, ook veel lager dan die van het elektron-armste complex van de reeks, $[\text{Co-F16P}]^{3-}$. De activiteit van laatstgenoemde verbinding in fotokatalytische waterstofevolutie bleek relatief laag te zijn bij pH 4,1, maar uitstekend bij neutrale pH, wat resulteerde in vergelijkbare fotokatalytische H_2 productiekwantumrendementen vergeleken met die verkregen met $[\text{Co-OMeP}]^{3-}$ bij pH 4,1. Volgens onze mechanistische studies verloopt de tweede reductie van $[\text{Co-F16P}]^{3-}$ door de gefotokatalyseerde soort PS^- , die leidt tot waterstofevolutie, waarschijnlijk via een route waarbij zowel het metaal als het ligand betrokken zijn. Opvallend is dat de activiteit gedeeltelijk behouden bleef wanneer kobalt werd vervangen door zink. In het algemeen zet dit werk een belangrijke stap voorwaarts in ons begrip van het ontwerpen van een moleculaire waterstofevolutiekatalysator omdat het heeft aangetoond dat het niet nodig is HER-katalysatoren te functionaliseren met elektron-donerende groepen om hun katalytische activiteit te verhogen, in het bijzonder in bijna-neutrale waterige omstandigheden. Elektrononttrekkende groepen kunnen ook leiden tot uitstekende katalysatoren, hoewel deze een ander mechanisme volgen dan elektronrijke complexen. In

fotokatalytische systemen die gericht zijn op volledige watersplitsing in de buurt van pH 7,0 kan de voorkeur worden gegeven aan een elektronarme waterstofevolutiekatalysator op basis van kobalt (HEC) boven de gewoonlijk voorgestelde elektronrijke HEC die alleen in zure omstandigheden actiever zijn.

Tenslotte wordt in **hoofdstuk 4** de synthese beschreven van de analoge serie van tetra-anionische Sn(IV)-porfyrine complexen. De fotosensibiliserende eigenschappen van deze nieuwe serie complexen, samen met die van de Zn(II) analogen beschreven in **hoofdstuk 3**, werden bestudeerd voor de homogene fotokatalytische HER in aanwezigheid van cobaloxime als standaard HEC en TEOA als opofferende elektronendonor in een 1:1 pH 7.0 water/acetonitril oplossingen. De fotokatalytische activiteit verkregen met deze nieuwe PS moleculen bleek sterk afhankelijk te zijn van de elektronische eigenschappen van het porfyrine ligand. Elektrochemische studies en DFT-berekeningen toonden aan dat alle fotokatalytisch actieve systemen een reductieve quenching-route volgden. Voor de Zn-porfyrine-reeks leidde alleen het elektron-arme complex $[\text{Zn-F16P}]^{4-}$ tot significante waterstofproductie, zoals gekenmerkt door een hoge activiteit (850 PTON na 20 uur bestraling, 59 uur^{-1} maximale PTOF) en een zeer hoge fotostabiliteit: het complex bleef actief gedurende 100 uur onder bestraling met groen licht zonder waarneembare ontleding. Voor de Sn-porfyrine-reeks vertoonden de twee elektron-rijkste complexen, $[\text{Sn-OMeP}]^{4-}$ en $[\text{Sn-MeP}]^{4-}$, significante sensibiliserende eigenschappen, maar met een lagere activiteit dan $[\text{Zn-F16P}]^{4-}$ onder dezelfde omstandigheden. Ook hier bleken de verschillende elektron-onttrekkende en elektron-donerende capaciteiten van de substituenten op het porfyrine ligand de redox eigenschappen en triplet aangeslagen toestand energieën van het complex te controleren, wat de thermodynamica en de snelheid van elektronenoverdracht beïnvloedde. Dit werk is belangrijk voor het ontwerpen en het begrijpen van het mechanisme van edelmetaal-vrije moleculaire fotosensibilisatoren voor waterstof evolutie. Het toont namelijk aan dat een evenwicht moet worden gevonden tussen de redoxpotentiëlen van de grondtoestand PS en die van de aangeslagen toestand, die beide worden gecontroleerd door de elektron-donerende of elektron-onttrekkende eigenschappen van de substituenten.

总结

人工模拟光合作用是可以帮助我们实现全球“碳中和”的科学挑战之一。至少在未来 30 年内，它仍将是一个重要的研究方向。人工模拟光合作用的总体思路是利用太阳能分解水并将二氧化碳还原为碳燃料或有机产品。考虑到光伏发电会不可避免地导致能量损失，直接用光驱动人工模拟光合作用的反应会比用电驱动更具吸引力，当然如果可以使用地球富含的元素就会更加理想。人们普遍认为，光催化系统至少需要三个组分：光敏剂（PS）、催化剂（Cat）和牺牲电子供体或受体（SE）。在这样的光催化系统中，至少可以确定会有三个电子转移步骤：一个在 SE 和激发的 PS（PS*）之间，一个在光还原或光氧化的 PS 和 Cat 之间，一个在 Cat 和它的底物之间。由于在两个并行的光催化过程中很难研究新组分的稳定性、活性和催化机制，因此半反应通常是研究的首选。此外，自组装或固态组分组成的多相混合光催化系统中反应物种有时难以来识别，相比之下定义明确的均相溶液体系组分更简单，也更适合分子组分的开发。因此，所有本论文中的研究都基于均相光催化系统，为水分解的两个半反应开发分子组分。

尽管 $[\text{Ru}(\text{bpy})_3]^{2+}$ 基于一种相对稀有的金属，但它是最著名的分子光敏剂之一，能够同时用来驱动析氧反应（OER）和析氢反应（HER）。因此，在本论文中，它被用作标准光敏剂来开发新型的 OER 和 HER 第一周期过渡金属催化剂。另一方面，钴酞菁是一种经过充分研究的光催化 HER 催化剂，它被选为标准的析氢催化剂（HEC），用于开发基于地球富含元素的新型分子光敏剂。我们结合这两种方法来开发基于四碘化卟啉配体的新型催化剂和光敏剂。为了优化光催化系统，需要找到从 SE 到 PS* 的电子转移驱动力和催化剂与氧化或者还原的光敏（PS⁺或 PS⁻）之间的电子转移驱动力的平衡，

我们通过在卟啉分子中苯环的 2, 6 位置添加给电子 (8 个甲氧基或 8 个甲基) 或吸电子 (8 或 16 个氟) 基团, 系统性地改变了卟啉配体的电子丰度 (第 1 章中的图 1.23.)

在第 2 章中, 本文描述了使用这些配体合成一系列四种带四个负电荷的 Ni(II)-卟啉配合物。这些化合物被用作光催化分子催化剂在中性或酸性水溶液中均相催化水氧化。电化学和动力学研究表明, 更多的吸电子取代基增加了镍卟啉配合物的氧化电位, 并控制了光催化条件下的析氧速率。但是必须找到增加氧化电位的平衡点, 一方面使催化 OER 本身拥有更高的驱动力, 另一方面确保电子从催化剂转移到氧化的光敏剂 PS⁺的驱动力足够高。例如, 当使用[Ru(bpy)₃]²⁺作为光敏剂 S₂O₈²⁻作为牺牲电子受体时, [Ni-F16P]⁴⁻由于太缺电子阻碍了镍催化剂和光氧化的光敏剂之间的电子转移, 从而使整个光催化系统失活。相较之下, [Ni-F8P]⁴⁻的氧化还原性质更接近最佳值, 使其光催化 OER 具有更优异的活性。重要的是, 这些镍卟啉催化剂在光催化条件下表现出很高的稳定性, 使用 [Ni-F8P]⁴⁻作为催化剂的光催化体系中催化转换数 (TON) 仅被 Ru 基光敏剂的分解限制。这项工作不仅提供了在中性至酸性水溶液中由镍基分子催化剂催化均相光驱动水氧化的罕见例子; 它还为设计光催化水氧化分子催化剂提供了新规则: 催化中心的电子密度应使用适当的取代基进行微调, 用以平衡催化水氧化和从催化剂到 PS⁺的电子转移驱动力。

在第 3 章中, 本文使用类似的带四个负电荷的 Co(III)-和 Zn(II)-卟啉配合物作为分子催化剂, 用于研究在中性和酸性水溶液中进行的均相光催化析氢反应。尽管已经有许多可以催化 HER 的钴基分子催化剂被报道过, 但不幸的是它们中的大多数都没有针对中性水溶液的条件进行优化。因为只有 pH 7.0 同时适合水氧化和质子还原反应, 是催化水分解全反应的最佳条件。更重要的是, HER 在中性条件下的催化机制不一定与酸性溶液中相同, 因此针对中性条件的催化剂的设计策略可能与用于酸性溶液中的不同。本文发现 Co(III)和 Zn(II)配合物的光催化活性和机理与卟啉环上吸电子或给电子取

代基相关，同时它们还与水溶液的 pH 值相关。在锌配合物系列中，卟啉配体是可以被氧化还原的，尽管锌金属中心的氧化态几乎不会变化，但 $[\text{Zn-F16P}]^4$ 被发现有着显著的光催化 HER 活性。根据电化学分析，最富电子的络合物 $[\text{Co-OMeP}]^3$ 在钴卟啉络合物中具有最高的质子还原驱动力，但仅在 pH 4.1 时观察到相对较高的光催化活性，将钴中心换成锌之后卟啉络合物的催化活性几乎全部消失。在中性条件下，它的活性远低于酸性条件。更有趣的是，它远低于该系列中最缺电子的复合物 $[\text{Co-F16P}]^3$ 的活性。后者的光催化析氢活性在 pH 4.1 时相对较低，但在中性 pH 时表现优异，与在 pH 4.1 下用 $[\text{Co-OMeP}]^3$ 获得的光催化产氢量子产率相当。我们的机理研究表明， $[\text{Co-F16P}]^3$ 被光还原的 PS 还原两次而产生析氢活性，两次还原可能是分别在金属中心和配体上进行的。值得注意的是，当钴中心被锌取代时，催化活性被部分保留了下来。总而言之，这项工作代表了析氢分子催化剂设计策略上的重大进展，因为它表明想要增强 HER 催化剂的催化活性，修饰推电子基团不是必须的。特别是在近-中性水溶液条件下，修饰吸电子基团也可以产生性质优异的催化剂。在旨在 pH 7.0 附近驱动水的全分解的光催化系统中，缺电子钴基析氢催化剂 (HEC)可能是更好选择，而不是通常仅在酸性条件下更具活性的富电子催化剂。

最后在第 4 章中，本文描述了类似的带四个负电荷的 Sn(IV)-卟啉配合物的合成。在钴酞作为标准 HEC 和 TEOA 作为牺牲电子供体条件下，在中性水和乙腈 1:1 的混合溶液中，研究了这一系列锡配合物以及第 3 章中描述的锌类似物的催化 HER 的光敏特性。使用这些新的 PS 分子获得的光催化活性似乎高度依赖于卟啉配体的电子丰度。电化学研究和 DFT 计算表明，所有有光催化活性的系统都遵循还原淬灭途径。对于 Zn-卟啉系列，只有最缺电子的配合物 $[\text{Zn-F16P}]^4$ 的光催化系统有着显著的产氢活性，并体现出较高的活性（光照 20 小时内有 850 的光催化转换数和 59 h^{-1} 的光催化转换率）和非常高的光稳定性：在绿光照射下保持活性超过 100 小时，并且没有观察到明显的

分解。在 Sn-卟啉系列中，两个富电子的配合物[Sn-OMeP]⁴⁺和[Sn-MeP]⁴⁺表现出析氢反应的光敏特性，但在相同条件下系统的活性低于[Zn-F16P]⁴⁺。此外，卟啉配体上，取代基不同的吸电子和给电子能力可以控制配合物的氧化还原性质和三重激发态的能量，从而可以进一步影响催化系统的热力学和电子转移速率。这项工作对于设计和理解非贵金属分子光敏剂析氢机理具有重要意义。它表明在设计分子光敏剂时，必须找到由取代基的给电子和吸电子特性控制的基态 PS 的氧化还原电位和激发态的氧化还原电位之间的平衡，以确保光敏剂相关的电子转移步骤能够高效地进行。

总之，本论文通过对水溶性卟啉配体的设计，开发出了一系列拥有不同电子丰度的非贵金属分子光敏剂和催化剂，并将它们成功应用在了均相光催化水氧化和析氢反应中。与此同时，揭示了不同的电子丰度的光敏剂和催化剂对光催化水氧化和析氢反应的机理和活性的影响，为分子光敏剂和催化剂的开发提供了切实可行的设计策略，也为光催化水分解和人工模拟光合作用领域提供了不可或缺的理论基础。

CURRICULUM VITAE

Chengyu Liu was born in Jilin, China in September 1990. He obtained his bachelor degree from the Faculty of Chemistry of Jilin University in 2013. His research topic was “Inorganic synthesis of nanocrystals as materials for lithium-ion battery electrodes”. During his BSc study, he was awarded with the “Excellent Student” prize of the faculty and the “2nd-class scholarship” of Jilin University. Then, he moved to Beijing in 2014, where he started his research on “Electrocatalytic oxygen reduction using molecular catalysts” as a master student at the Faculty of Science of Renmin University of China, supervised by Prof. Rui Cao. In 2017, he obtained his Master’s degree in chemistry with the award of “Outstanding Graduate of the Universities in Beijing”. The same year, he moved to Leiden University in the Netherlands where he started his PhD study under the supervision of Prof. Sylvestre Bonnet and Prof. Elisabeth Bouwman. His research work in the Metals in Catalysis, Biomimetics & Inorganic Materials (MCBIM) group was entitled “Towards the light-driven water splitting in homogeneous solutions using molecular metalloporphyrin photosensitizers and catalysts”. During his PhD, he supervised two BSc students (Barthold den Hartog and Dennis van der Meij) and two MSc students (Daan van den Bos and Roy Maas). He had several collaborations, working with Dr. Santiago Rodriguez Jimenez, Marion Isabelle May and Prof. Erwin Reisner from the University of Cambridge (UK), and Titus de Haas, Dr. Francesco Buda, Dr. Mingchuan Luo, and Prof. Marc T. M. Koper from Leiden University. He followed the courses “Advanced Metal-Organic Chemistry” and Catalysis and “High Impact Writing Course”, provided by the Holland Research School of Molecular Chemistry (HRSMC), and the “Scientific Conduct” course provided by the Graduate School of Leiden University. He also attended and presented some of his research work at the following conferences:

- The Netherlands’ Catalysis and Chemistry Conference (**NCCC**), **2018, 2019** and **2020**, in Noordwijkerhout, The Netherlands
- Chemistry as Innovating Science (**CHAINS**), **2018** and **2019**, in Veldhoven, The Netherlands
- Holland Research School of Molecular Chemistry (**HRSMC**) **Symposium**, **2018** and **2019**, in Amsterdam, The Netherlands
- **Reedijk Symposium**, **2019**, Leiden, The Netherlands
- The International Solar Fuels Conference (**ISFC**), **2021**, Online, UK

LIST OF PUBLICATIONS

Published:

1. **Liu, C.**; van den Bos, D.; den Hartog, B.; van der Meij, D.; Ramakrishnan, A.; Bonnet, S., Ligand Controls the Activity of Light-Driven Water Oxidation Catalyzed by Nickel(II) Porphyrin Complexes in Neutral Homogeneous Aqueous Solutions. *Angew. Chem. Int. Ed.* **2021**, *60* (24), 13463-13469.
2. **Liu, C.**; Lei, H.; Zhang, Z.; Chen, F.; Cao, R., Oxygen reduction catalyzed by a water-soluble binuclear copper(II) complex from a neutral aqueous solution. *Chem. Commun.* **2017**, *53* (22), 3189-3192.
3. Lei, H.; **Liu, C.**; Wang, Z.; Zhang, Z.; Zhang, M.; Chang, X.; Zhang, W.; Cao, R., Noncovalent Immobilization of a Pyrene-Modified Cobalt Corrole on Carbon Supports for Enhanced Electrocatalytic Oxygen Reduction and Oxygen Evolution in Aqueous Solutions. *ACS Catal.* **2016**, *6* (10), 6429-6437.
4. Lei, H.; Chen, M.; Liang, Z.; **Liu, C.**; Zhang, W.; Cao, R., Ni₂P hollow microspheres for electrocatalytic oxygen evolution and reduction reactions. *Catal. Sci. Technol.* **2018**, *8* (9), 2289-2293.

In preparation:

1. **Liu, C.**; de Haas, T.; Amati, A.; Buda, F.; Bonnet, S., Electronic Effect in Water-soluble Zn(II) and Sn(IV) Porphyrin Photosensitizers for Homogeneous Photocatalytic Hydrogen Evolution at pH 7.0.
2. **Liu, C.**; de Haas, T.; Bouwman, E.; Buda, F.; Bonnet, S., Effects of Electron-Withdrawing and Electron-Donating Substituents on the pH Dependence of Co(III)-porphyrin Catalysts for Homogeneous Photocatalytic Hydrogen Evolution.
3. **Liu, C.**; Amati, A.; Klein, D. M.; Bonnet, S., A Simple Approach Towards the Application of Lipophilic Molecular Catalysts for Light-driven Hydrogen Evolution from Neutral Aqueous Solutions.