

Substituent Effects in Iron Porphyrin Catalysts for the Hydrogen Evolution Reaction**

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Abstract: For a future hydrogen economy, non-precious metal catalysts for the water splitting reactions are needed that can be implemented on a global scale. Metal-nitrogen-carbon (MNC) catalysts with active sites constituting a metal center with fourfold coordination of nitrogen (MN₄) show promising performance, but an optimization rooted in structure-property relationships has been hampered by their low structural definition. Porphyrin model complexes are studied to transfer insights from well-defined molecules to MNC systems. This work combines experiment and theory to evaluate the influence of porphyrin substituents on the

electronic and electrocatalytic properties of MN₄ centers with respect to the hydrogen evolution reaction (HER) in aqueous electrolyte. We found that the choice of substituent affects their utilization on the carbon support and their electrocatalytic performance. We propose an HER mechanism for supported iron porphyrin complexes involving a [Fe^{II}(P*)]⁻ radical anion intermediate, in which a porphyrinic nitrogen atom acts as an internal base. While this work focuses on the HER, the limited influence of a simultaneous interaction with the support and an aqueous electrolyte will likely be transferable to other catalytic applications.

Introduction

To halt the global temperature increase, drastic transitions in energy production and storage are required. During the last decade, the global electricity production by renewable energy duplicated and is predicted to keep growing rapidly.^[1] However a major problem for the large scale implementation of renew-

able energies is the mismatch between production and demand. Compensating this discrepancy requires matching buffer capacities. The key principle for a hydrogen-fueled society is to facilitate hydrogen (H₂) as a storable energy carrier. In this scenario, excess energy is used in water electrolysis to produce hydrogen. Alternatively, a direct conversion of solar energy to hydrogen in a photo-electrochemical cell (PEC) promises higher overall efficiency by utilizing synergetic effects of photoabsorption and water splitting,^[2] so that the system can be operated in a decentralized way. In such systems, photoabsorbers can generate the required photovoltage, while catalysts decrease the overpotential of the oxygen and hydrogen evolution reaction (OER, HER) for overall water splitting.^[3]

The maximum photon flux from solar irradiation limits the current density to 10 mA cm⁻² on a flat substrate with an electrode area equal to its photoabsorber size.^[2,4] For low current densities, cheap and earth abundant metal-nitrogen-carbon (MNC; M=Mn, Fe, Co, Ni, Mo) catalysts hold promise to replace platinum-type catalysts for the hydrogen evolution reaction (HER).^[5] MNC catalysts are better known for their excellent activity in the oxygen reduction reaction (ORR).^[6] They are also attractive for the CO₂ reduction reaction (CO₂RR) yielding valuable green fuels or base chemicals.^[5,7] One notable property of these materials is that the selectivity of the reduction process can be manipulated by varying the nature of the metal center or its chemical environment.^[5b,7c,8]

Almost all MNC catalysts are prepared via a high temperature pyrolysis which results in a material with varying degrees of structural disorder. The low definition and the presence of side phases (e.g. carbides, nitride or oxides) hinders systematic investigations.^[9] This impedes the development of structure-property-relationships and consequently a knowledge-based

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optimization of the preparation process towards optimal catalyst activity. Intense structural characterization has shown the active center in MNC catalysts to be constituted of single metal atoms incorporated into an amorphous carbon structure by coordination of N donor atoms, which are covalently doped into the carbon layers, see Figure 1a for a schematic depiction. The configuration of the N atoms surrounding the metal center and the geometry of the ligand sphere are still under debate,^[6c,9b,10] but most suggestions for the active site structure have a square planar nitrogen coordination environment in common.^[5b,6f,7a,9b,10a,b,11]

Porphyrins have discrete MN_4 architectures that render them classical precursors for MNC catalyst preparation and spectroscopic models,^[12] in particular to better understand the influence of porphyrin substituents on the M–N bonding character and resulting properties. The literature on porphyrins contains many examples that describe the effect of such chemical variations, for instance on the redox potentials,^[13] or on the reactivity of the complex.^[14]

Considering first the homogeneous catalysed HER on porphyrins: Most processes catalysed by porphyrin metal complexes take place in the M–X axial binding sites.^[15] For the HER, substitution effects have been reported, for example by incorporating internal acids in the vicinity of the axial binding sites.^[16] However, not only metal centered HER mechanisms are described in organic electrolytes. Specifically for nickelporphyrins the competition between a Ni–hydride and a β -hydrogenation (Ni–N–H intermediate) mechanism,^[17] or HER with ligand-based mechanisms with participation of peripheral carbon atoms are described in the presence of strong acids.^[18] The HER on iron porphyrins involves two initial reduction steps of the Fe(III) center to Fe(I) with subsequent oxidative protonation of the active site.^[16a,c,i]

Switching to an aqueous electrolyte and heterogeneous catalyst systems, for example Pt/C, the HER is thought to

proceed via consecutive proton-coupled electron transfer (PCET) steps. In this case porphyrins are supported on a conducting substrate, e.g. carbon and considered as catalyst. To the best of our knowledge, no systematic study of substitution effects on metal porphyrins exists for such systems in the HER to date. This represents a significant gap in knowledge, because the simultaneous interaction of porphyrins with the aqueous electrolyte and with a carbon support may influence the hydrogen evolution reactivity significantly.^[19] This study makes a contribution towards closing this gap by building a bridge between homogeneous catalysis and heterogeneous systems such as MNC catalysts. Focusing on iron porphyrins, we investigate the influence of substituents and the effect that the immobilization on a high-surface area carbon support has on the redox characteristics, spectroscopic properties and electrocatalytic HER behaviour. The catalytic activity is correlated with structural characteristics extracted from X-ray photoelectron spectroscopy (XPS) and nuclear resonance vibrational spectroscopy (NRVS). Additionally, density functional theory (DFT) calculations on all iron porphyrin complexes complement the experimental findings and shed light on the HER mechanism in supported porphyrin complexes.

Results and Discussion

For this systematic study of substituent effects on the properties and catalytic activity of iron porphyrin complexes, six variants of the phenyl rings in the parent complex [Fe(TPP)Cl], TPP: tetraphenylporphyrin, were chosen. The phenyl substituents are expected to increase the electron density at the FeN_4 center from 1 to 6, see Figure 1b. For 1 and 2, a mesomeric or inductive electron withdrawing effect is expected, whereas the substituents of 4–6 are electron donating. Since inductive effects are considered rather weak, substitution patterns with

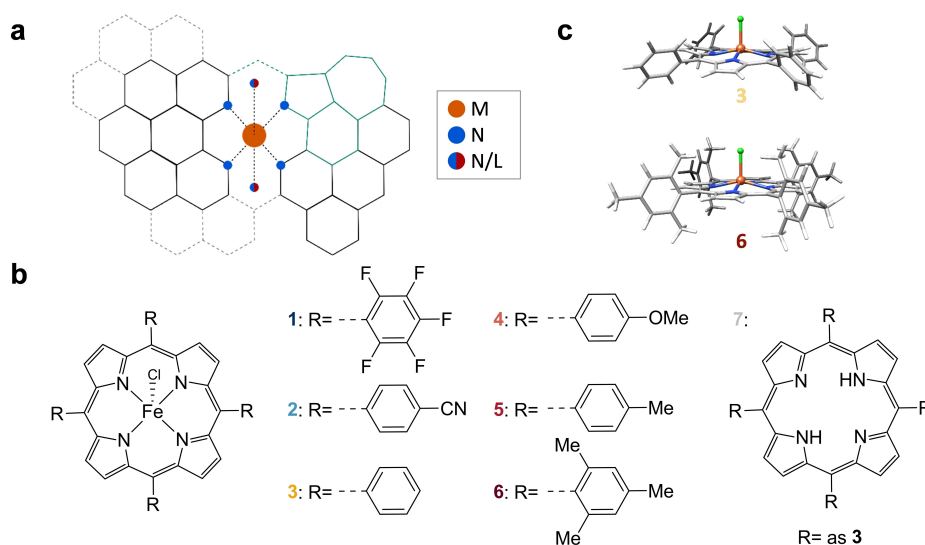


Figure 1. a) Structural motif of an MNC catalyst, b) the complexes studied herein with the substituents R = (1) TPP(F)₂₀–FeCl, (2) TPP(CN)₄–FeCl, (3) TPP–FeCl, (4) TPP(OMe)₄–FeCl, (5) TPP(Me)₄–FeCl, (6) TPP(Me)₁₂–FeCl and free base porphyrin (7) TPP–H₂, c) three dimensional side view of the geometries optimized by DFT exemplarily shown for complexes 3 and 6.

multiple groups were chosen for **1** and **6**. To assess the importance of rotational degrees of freedom of the phenyl group relative to the porphyrin ring, porphyrin complex **5** is used as an additional example for electron donation via an inductive effect. The parent complex **3** serves as a reference substance, and the free porphyrin **7** as a reference for activity measurements to confirm that the observed catalytic activity stems from the metal center as the active site (see section 'mechanistic insights' below).

The substituents influence the orientation of the phenyl ring relative to the porphyrin plane (Supporting Information-Figure S1), as is exemplarily shown in Figure 1c for complexes **3** and **6**. This tilt affects the conjugation between the phenyl π -electrons and the π -electrons of the porphyrin ring (Supporting Information-Figure S2a) and hence the properties of the complexes. Furthermore, it can be reasonably expected that this aspect of the structure can alter the porphyrin-support interface: it affects the distance between the metal center and the underlying graphene plane, the adsorption of the porphyrin on the carbon support, their electronic interaction or a partial rotation/distortion of the substituents. Vice versa, the degree of interaction with the support may result in altered electronic properties or stabilities of the complexes.

Redox properties in organic solvent

The electrochemical properties of porphyrins and other MN_4 macrocycles in organic solvents have been investigated previously.^[20] Clear correlations between redox properties and catalytic activity are evident.^[14,20d,21] Nevertheless, to determine the redox properties of the porphyrins without any support effects, a first set of measurements was conducted in organic solvent. Dichloromethane (DCM) with tetrabutylammonium perchlorate (TBAP) as a conductive agent was chosen as the electrolyte as it makes a large potential range accessible. Figures 2a and b show the cyclic voltammograms (CVs) of **1–7** at 100 mVs^{-1} and 10 mVs^{-1} , respectively.

Three main redox events can be distinguished. Depending on the substituent, the first feature around 1.2 to 1.7 V vs. RHE corresponds to the redox event in the porphyrin π -system.^[20a] This transition appears stable and reversible for all porphyrin complexes except for **1** where an irreversible decomposition takes place. The strong electron withdrawing effect of the fluoro substituents suggests that their presence destabilizes a higher oxidation state of either the iron center (i.e. Fe^{IV}) or the delocalized π -system.

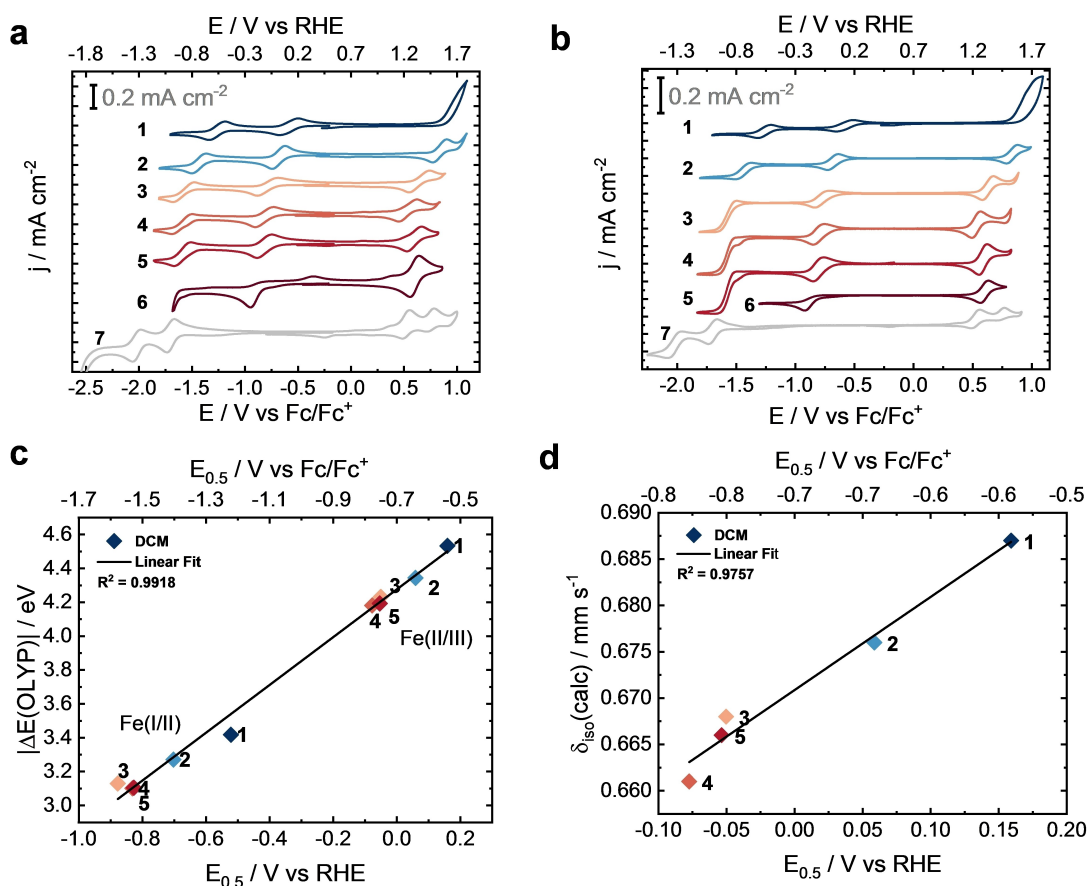


Figure 2. Cyclic voltammograms of 1 mM $\text{Fe}(\text{III})\text{Cl}$ -porphyrin and 0.1 M TBAP in DCM with a scan rate of a) 100 mVs^{-1} and b) 10 mVs^{-1} . Correlation between redox potentials of $\text{Fe}(\text{II/III})$ and $\text{Fe}(\text{I/II})$ with c) electronic energy differences from DFT calculations with the OLYP density functional (linear regression with slope: $1.41 \pm 0.05\text{ eV V}^{-1}$, intercept: $4.28 \pm 0.02\text{ eV}$) and d) isomer shift values of the $\text{Fe}(\text{II})$ species computed with the B3LYP density functional (linear regression with slope: $0.101 \pm 0.009\text{ mm s}^{-1}\text{ V}^{-1}$, intercept: $0.6708 \pm 0.0008\text{ mm s}^{-1}$).

The second redox feature around 0.3 and -0.3 V vs. RHE corresponds to the $\text{Fe}^{\text{II}}/\text{Fe}^{\text{III}}$ redox transition. Consequently, no redox event is found in reference compound **7**. The $\text{Fe}(\text{II}/\text{III})$ redox potentials for **1**,^[14] **3**,^[14,23] **4**,^[14] **5**^[14] and **6**^[23] determined here are in good agreement with literature data. To the best of our knowledge, there is no suitable reference data with comparable choices of solvent and conducting agent available for **2**.

The separation between anodic and cathodic peak and their similar intensities indicate that the $\text{Fe}^{\text{II}}/\text{Fe}^{\text{III}}$ redox transition is a reversible transition for all iron porphyrin complexes except for **6**. The highly electron donating effect of the mesityl groups in **6** may destabilize the reduced state, which can be understood as a highly reactive Fe^{II} species.

Since after the reduction peak, no anodic peak appears in the reverse direction, the follow-up reaction has to be of non-electrochemical nature. This is also indicated by the small oxidation peak at ~ 0.35 V vs. RHE which only appears in the anodic sweep at 100 mVs^{-1} , but is absent at 10 mVs^{-1} of **6**. This peak is likely not associated with the oxidation back to the intact Fe^{III} porphyrin. Instead, we suggest that the cathodic sweep at $U < -0.3$ V vs. RHE produces an unspecified intermediate from **6**, the decay products of which can be oxidized at high sweep rates.

The third main redox event in the potential range of -0.3 to -1.0 V vs. RHE is assigned to the transition between Fe^{II} and Fe^{I} . For the $\text{Fe}(\text{I}/\text{II})$ redox potentials determined here, reference data is only available for **3**^[22] and **6**,^[23] which is in good agreement. For **1** and **2**, the transition is reversible, whereas **3** to **5** show a distorted pair of redox peaks at 100 mVs^{-1} and a narrow step at 10 mVs^{-1} . The latter can be interpreted as a synproportionation of Fe^{I} generated on the electrode and Fe^{III} from solution to Fe^{II} which also explains the lack of a reoxidation peak on the back sweep.^[16a] This observation indicates a higher reactivity at reduced states where additionally the substitution pattern induces a higher electron density at the iron center.

We note that the assignment of Fe^{I} as a formal oxidation state should be treated with caution. The electronic structure may be formulated in terms of either the formal oxidation state $[\text{Fe}^{\text{I}}(\text{P})]^-$ or the physical or spectroscopic oxidation state $[\text{Fe}^{\text{II}}(\text{P}^*)]^-$.^[24] Both resonance structures have been assigned from spectroscopic experiments,^[25] and their formation is heavily dependent on the substitution pattern.^[25,26] The electronic structures obtained from density functional theory (DFT) calculations show π -radical anion character throughout the series. In all species, the spin delocalized over the porphyrin ring is antiparallel to the unpaired electrons on the iron ion, in line with previous reports of this type of electronic structure.^[26b] Nevertheless, this reduced state will be referred to both as Fe^{I} and $[\text{Fe}^{\text{II}}(\text{P}^*)]^-$ in the following.

The free base porphyrin **7** shows two reversible redox potentials at -0.9 V vs. RHE and -1.3 V vs. RHE that are associated with the radical anion and dianion formation; respectively, as shown by spectroelectrochemistry.^[27] The first reduction potential of **7** and therefore formation of the radical anion lies just a few mV below the half wave potentials ($E_{0.5}$) of

the discussed $\text{Fe}^{\text{I}}/\text{Fe}^{\text{II}}$ transition. The observed trends indicate that the radical anion character is more pronounced the lower the $E_{0.5}$ of the $[\text{Fe}^{\text{II}}(\text{P}^*)]^-/\text{Fe}^{\text{II}}$ couple and hence the tendency for synproportionation with Fe^{III} porphyrin from solution is.

The experimental redox potentials (100 mVs^{-1}) are compared against the electronic energy differences from DFT single point calculations of the reduced and oxidized species using the OLYP density functional. This straightforward approach does not consider a reference redox couple and thus cannot yield absolute redox potentials. Nevertheless, it has been applied successfully in the past and is therefore used in this work.^[28] The resulting energy differences, reported in eV, correlate extremely well with the redox potentials obtained experimentally in organic solvent (linear regression with $R^2 > 0.99$, see Figure 2c). Consequently, the computational approach chosen here could be employed as a calibration for future predictions of redox events in similar catalyst models.

Since the isomer shift from Mössbauer spectroscopy is inversely proportional to the electron density at the nucleus, it can serve as a further measure of the electron density in the series.^[29] Figure 2d shows that the predicted isomer shift values of the Fe^{II} species correlate well with the experimentally determined half wave potentials of the $\text{Fe}^{\text{II}}/\text{Fe}^{\text{III}}$ couple in organic solvent.^[30] The iron porphyrin complexes with electron donating substituents have a lower isomer shift and therefore a higher electron density at the iron center than the iron porphyrins with electron withdrawing groups. These results confirm the expected trend and furthermore establish a direct correlation between the half wave potentials and the electron density at the FeN_4 moiety. It is thus possible to link the predicted electronic structures and electron densities to the measured redox potentials via a spectroscopic property.

Note that no experimental $E_{0.5}$ was determined for **6** due to the irreversibility of $\text{Fe}(\text{III})$ reduction and therefore this data point is absent in Figures 2c and d. From the predicted value of the electronic energy difference, 4.23 eV, an $E_{0.5}$ data point at -0.03 V vs. RHE for $\text{Fe}^{\text{II}}/\text{Fe}^{\text{III}}$ can be predicted. For the same redox event, the $\text{Fe}(\text{II})$ isomer shift at 0.678 mms^{-1} would correspond to an $E_{0.5}$ data point at 0.07 V vs. RHE. For the $[\text{Fe}^{\text{II}}(\text{P}^*)]^-/\text{Fe}^{\text{II}}$ transition, the computed electronic energy difference is 3.02 eV which would correspond to -0.887 V vs. RHE in the experiment.

Support effects detected by nuclear resonance vibrational spectroscopy

In the literature, the influence of the support on the structural and electronic properties of MN_4 macrocycles has been investigated on (single crystal) surfaces like TiO_2 ^[31], Ag ^[32], Au ^[33], Si ^[34] by scanning tunneling microscopy (STM) or X-ray photoelectron spectroscopy (XPS)^[35]. With respect to carbonous supports, distinct interactions with porphyrins (P) and phthalocyanines (Pc) have been described by electrochemistry and theoretical calculations only for CNTs.^[36]

To better understand the transferability of our findings from homogeneous electrochemistry in organic solvent to heterogeneous electrochemistry of the carbon-supported porphyrins in aqueous electrolyte, nuclear resonance vibrational spectroscopy (NRVS) was performed on selected ^{57}Fe -enriched porphyrins (**2**, **3**, **5** and **6**) with and without carbon support. NRVS selectively probes the vibrational modes involving iron and has been used to characterize heme-type complexes and FeNC materials.^[9c,37]

NRV spectra of iron porphyrins can generally be divided into three main ranges: (i) below 200 cm^{-1} , there are mostly out-of-plane modes including the doming mode, (ii) between $200\text{--}400\text{ cm}^{-1}$, most modes have in-plane character, (iii) between $400\text{--}600\text{ cm}^{-1}$, modes typically involving the axial ligand are found.^[37a] Below 50 cm^{-1} , phonon modes resulting from translation of the molecule in the solid state are found; since these cannot be predicted by DFT calculations of a single molecule, they will not be discussed below.

For heme-type molecules, the highly symmetric (D_{4h}) iron porphyrin Fe(P) core serves as a reference compound for assigning and discussing the most important vibrational modes.^[37a,c,38] A_1 symmetric out-of-plane motions of iron such as the doming mode (γ_9) or the inverse doming modes (γ_6 , γ_7) are thought to influence reactivity in axial direction.^[37c,38a,b] The stretching mode of the Fe–L bond, where L denotes the axial ligand, gives further information on the bond strength. In-plane modes of E symmetry stretching the Fe–N bonds are referred to as ν_{50} and ν_{53} , and result in dominating features due to the high relative motion of Fe within these modes and are located at $407\text{ to }426\text{ cm}^{-1}$.^[37c] From the work of Barabanschikov *et al.* on how the NRVS changed from unsubstituted Fe(P)Cl to substituted Fe(OEP)Cl and Fe(PPIX)Cl, it is known that asymmetric substitutions can have a strong impact on modes that influence ligand binding and dissociation.^[37c] For aryl substituted Fe(P), namely the Fe(TPP) family, various NRVS studies for different axial ligands and aryl substitution patterns were performed.^[38,39] These studies found that vibrational modes of biorelevant axial ligands such as O_2 , NO, CO or imidazole derivatives couple with those of the rest of the molecule.^[38] The distortion of the aryl rings was found to couple strongly with in-plane modes, so that ν_{50} and ν_{53} split into several signals.^[38b] For the aryl-substituted Fe(P)Cl complexes with C_{4v} symmetry- (such as **3**), it is usually assumed that the symmetry of the molecule does not change which would allow an easier assignment of the modes.^[40] However, the aryl rings are not likely to be oriented perpendicular to the porphyrin plane, but at

a smaller angle, thus lifting the symmetry and hence the degeneracy of E symmetric vibrations.

The NRV spectra of **2**, **3**, **5** and **6** are shown in Figure 3; the experimental vibrational frequencies are given in Supporting Information-Table S1, and the predicted vibrational frequencies and modes are described in Supporting Information-Table S2. By comparison to the NRVS of Fe(P)Cl and the predicted DFT spectra, the doming mode γ_9 , the inverse doming mode γ_6 , the Fe–Cl stretch and two in-plane vibrations ν_{50} can be assigned (see Table 1).

The signals in the NRV spectrum of complex **3** are consistent with spectra for similar complexes with different axial ligands,^[38] and the Fe–Cl stretch fits previous Raman spectroscopy data.^[40] Moreover, the experimental and calculated pDOS of all four complexes are in excellent agreement except for the vibrations involving the chlorine ligand, which are underestimated as has been seen previously in the literature.^[37c,40] A clear effect of the aryl ring substituents on the Fe–Cl stretch is not observed.

The doming modes γ_9 are sensitive to the substitution pattern, although the influence of electronic effects and differing molecular weights cannot be discerned (exp: 112 cm^{-1} , 117 cm^{-1} , 107 cm^{-1} , and 106 cm^{-1} for **2**, **3**, **5**, and **6**). This shift is also observed for predicted positions of the inverse doming mode γ_6 which cannot be clearly assigned in the experiment due to overlay with more intense in-plane vibrations. The less intense in-plane modes show a shift to higher frequency for ν_{50} or no significant change for ν_8 (breathing mode).

A general substituent effect for the more intense in-plane Fe–N stretching modes is more difficult to state. Substitution in *para* position of the aryl rings has a similar effect for **2** and **5**. The bending (and rotation) motions of the $-\text{CN}$ or $-\text{CH}_3$ substituents are coupled to the in-plane Fe–N stretching modes, which likely further lifts the degeneracy of these vibrations. In contrast to that, **6** shows a larger number of degenerate Fe–N stretching vibrations and fewer, but more well-defined modes. As the aryl rings have methyl substituents in both *ortho* positions, steric effects enforce an almost perpendicular orientation to the porphyrin plane, which brings **6** closer to C_{4v} symmetry than its analogues in which the aryl rings are rotated. Another observation is that for **6**, the modes around 200 cm^{-1} are less intense than in **2**, **3** and **5**; this is because the aryl motion dominates these modes rather than the iron motion.

The experimental data show no (**2**, **3**) or at most a minor (**5**, **6**) effect of the carbon support on the positions and intensities

Table 1. Assignment and energetic position of vibrational modes for NRV spectra of **2**, **3**, **5** and **6** and the frequencies predicted by DFT. Frequencies are given in cm^{-1} .

	2		3		5		6	
	exp.	calc.	exp.	calc.	exp.	calc.	exp.	calc.
γ_9 (doming)	112	94, 121	117	104	107	93, 94	106	90
Fe–Cl stretch	366	335	387	329	366	328, 336	363, 373	334
ν_{50}	420	425, 426	407	409, 412	426	420, 420	422	424, 427
γ_6 (inverse doming)		208, 260		237, 266		199, 233, 253		161, 233
ν_8 (breathing)		385		392		390		398

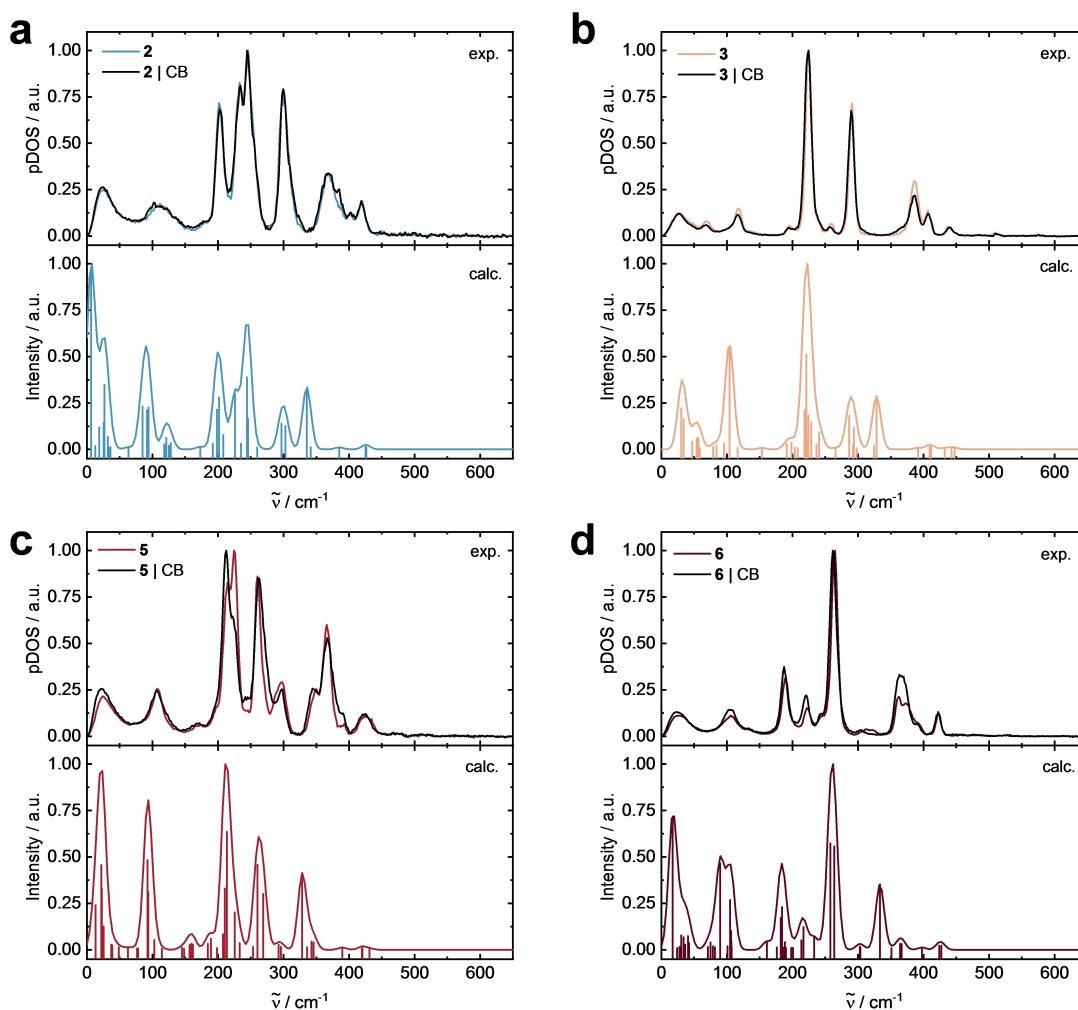


Figure 3. ^{57}Fe -pDOS derived from NRVs measurements (exp.) of a) **2**, b) **3**, c) **5** and d) **6** between 17 and 28 K. Compared are as-prepared porphyrins and their carbon-supported counterparts labeled “| CB” in the upper panels with predicted NRV spectra from DFT (calc.) in the lower panels.

of the vibrational modes. It can thus be concluded that the carbon support interacts only weakly with the systems investigated here. This is further corroborated by the excellent agreement between experiment and calculation, and hence the use of a molecular model appears fully justified to analyze the spectroscopic, electrochemical and catalytic data presented in the following.

Structural investigation by XPS

The near-surface composition was investigated by XPS. The results for the characteristic N 1s and Fe 2p signals can be found in Figures 4a and b, the survey spectra are shown in Supporting Information-Figure S3. The impregnated model catalysts were investigated as powders by pressing them onto an indium foil as the sample carrier (see experimental details for more information). In consequence, the In 3p signal (~ 704 eV) occurs in all Fe 2p spectra in varying intensities depending on the quality of the catalyst layer on In.

It is well known that the energetic position of the N 1s peak related to metal-nitrogen coordination is quite sensitive to the electronic state of the coordinating iron atom.^[41] Besides the main Fe–N₄ peak, a second peak arises at higher binding energy values and is attributed to the same origin, but broadened by π -stacking. The Fe–N₄ signal of **1** shows a further broadening which could indicate the presence of a further signature. With this assumption, it was deconvoluted into two narrow main signals and a minor signal. The additional species is assumed to be a side product of the purchased iron porphyrin, i.e. with varying fluorine bonds on the phenyl substituents (see also the XP spectra for the as-received porphyrin **1** Supporting Information-Figure S4).

Once more, a correlation between the spectroscopic results and the electrochemical characteristics can be observed. Figure 4c shows a good correlation between increasing binding energy of the related N 1s peak and increasing redox potential (linear regression with $R^2 > 0.99$; note: the value for **1** is averaged for the two main Fe–N₄ components; **6** is again not included due to irreversibility of Fe(III) reduction in DCM). The

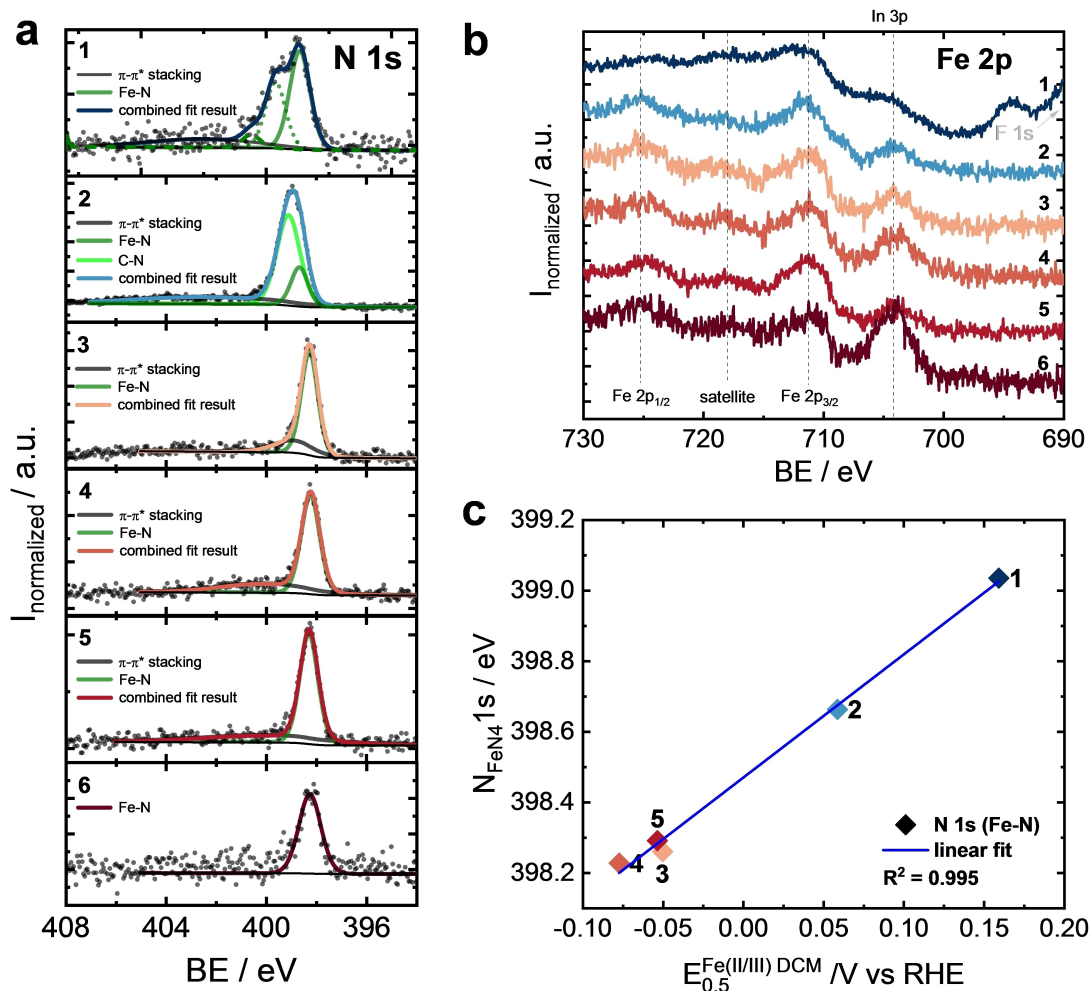


Figure 4. XPS results of porphyrins 1–6 impregnated on CB; HR-XPS of the a) N 1s region; b) Fe 2p region; c) correlation between the binding energy associated with the FeN_4 peak and the redox potential $E_{0.5}$ of Fe(II/III) in DCM.

calculated N 1s orbital energies for the chlorides 1–6 also fit well to the binding energies obtained from XPS (see Supporting Information-Figure S5).

Redox properties of the supported porphyrins in aqueous electrolyte

Having clarified the structural characteristics and shown that there is only a minor influence of the carbon support, the CVs of the carbon supported systems in alkaline and acidic electrolyte were measured, see Figures 5a and b. The measurements were performed in a much smaller potential range of 0.0 to 1.1 V vs. RHE (compare –1.8 to 1.7 V vs. Fc in DCM) defined by the stability window of the aqueous electrolyte. The capacitive current of the supported porphyrins is similar throughout the series and systematically lower than for the carbon support. This is attributed to micro pore blockage by porphyrin molecules. One redox transition can be identified in the iron porphyrin CVs and is assigned to $\text{Fe}^{\text{II}}/\text{Fe}^{\text{III}}$.^[15b,20d,42] The general

trend observed in aqueous electrolyte is the same as in organic electrolyte: electron withdrawing groups shift the $E_{0.5}$ values to higher potentials while electron donating substituents shift the potentials to lower values (see Supporting Information-Table S3 for the exact redox potential values).

The $E_{0.5}$ determined in both aqueous electrolytes correlate well with the values obtained from the measurements in DCM, see Figure 5c. The slope of the regression line deviates from 1, indicative of a solvent or support effect on the redox behavior. While identifying the dominant effect is beyond the scope of this work, it is noted that a more pronounced deviation of the potentials is seen in the acidic vs. organic media. A plausible explanation may lie in a stronger interaction of the material with the acidic environment: substituents with free electron pairs (2 and 4) may be (partially) protonated, which could bias the comparison, and similarly a (partial) protonation of the CB surface is expected to affect the porphyrin-support interface.

We note that the energy differences predicted by DFT correlate better with $E_{0.5}$ in alkaline than for acidic electrolyte (see Supporting Information-Figure 5d), but are overall best correlated with the half wave potentials in organic electrolyte. It

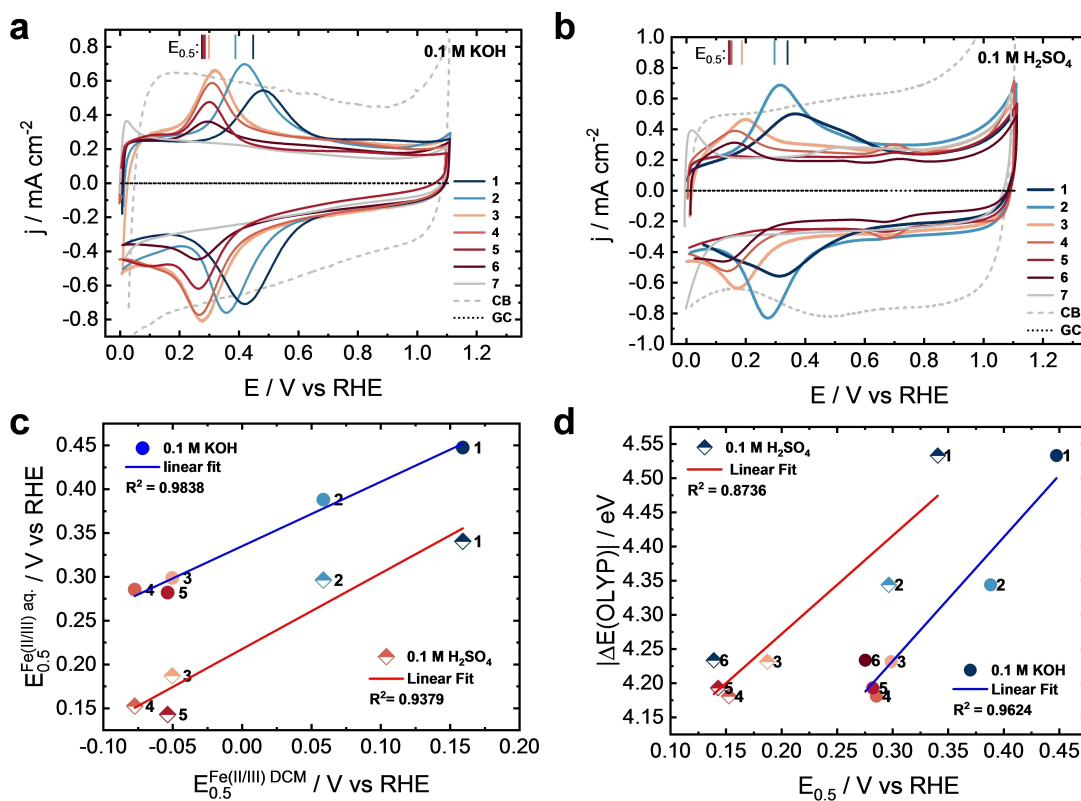


Figure 5. Representative cyclic voltammograms of carbon-supported Fe(III)Cl-porphyrins, carbon supported free base porphyrin, carbon support without porphyrin (CB) and the bare glassy carbon electrode (GC) a) in KOH of pH = 13 and b) in H₂SO₄ of pH = 1 where the vertical lines above the CVs indicate the position of Fe(II/III) half wave potentials $E_{0.5}$; all measurements performed with an electrode loading of 0.5 mgcat cm⁻². c) Correlation between $E_{0.5}$ of Fe(II/III) at pH = 13 and pH = 1 vs. the corresponding $E_{0.5}$ of Fe(II/III) values in DCM. d) Correlation between electronic energy differences from OLYP single point calculations and $E_{0.5}$ of Fe(II/III) at pH = 13 and pH = 1.

is likely that the simplified description of the redox events (no explicit solvent-solute interactions, no counter ion effects) reaches its limits here. The HER activity data in acidic media are shown in Supporting Information-Figure S6a and indicate lower activity than in alkaline media. Additionally, the carbon support and the carbon-supported free base porphyrin have a similar activity as the Fe(P) systems. Thus, the assumption that the FeN₄ moiety is the only active center is invalid for this electrolyte. HER studies in organic media describe that in the presence of acids porphyrin ligands can participate via a ligand-based hydrogenation reaction in the catalytic cycle.^[18] This impedes the deduction of structure-property relationships for the FeN₄ center and therefore, we refrain from a further discussion of the activity data obtained in acidic electrolyte.

In the following, we will focus on the data obtained in 0.1 M KOH. In the CVs in KOH (Figure 5a), it can be noted that the peak shape and area of the redox signals varies depending on the porphyrin. All systems are compared in terms of the electrochemically active amount of iron on the electrode which can be calculated by integrating the peak area of the oxidation signal. The reduction peak was not considered as in most cases the baselines were less well defined leading to larger errors. Supporting Information-Figure S6b shows exemplarily for 4 how the charge q_a was determined, which is used in

Equation (1) to determine the electrochemically active amount of Fe on the electrode $n_{\text{Fe-EC}}$

$$n_{\text{Fe-EC}} = \frac{q_a}{vF} \quad (1)$$

with the scan rate v and the Faraday constant F . It is assumed that each electrochemically active FeN₄ center contributes with a full electron transfer to the redox peak and the individual FeN₄ centers do not affect each other. The values of $n_{\text{Fe-EC}}$ were then compared to the stoichiometrically calculated amount expected on the electrode (n_{theo}) based on catalyst loadings. In Figure 6a, the electrochemically active amount of iron and the theoretically possible value are compared.

The electrochemically active iron, $n_{\text{Fe-EC}}$, amounts to only a fraction of the theoretical amount n_{theo} . The ratio of both values is the electrochemical utilization of iron, see Figure 6b where this quantity is plotted against the half wave potential of the Fe^{II}/Fe^{III} couple. This illustrates that the quality of the porphyrin-support interaction is influenced by the substituent induced chemical changes of the porphyrin structure. The utilization of iron ranges from 6–28% across the porphyrin series. The interaction with the carbon support is most favorable for electron poor FeN₄ porphyrins, while a high electron density leads to a weaker interaction with the support. Clearly, steric

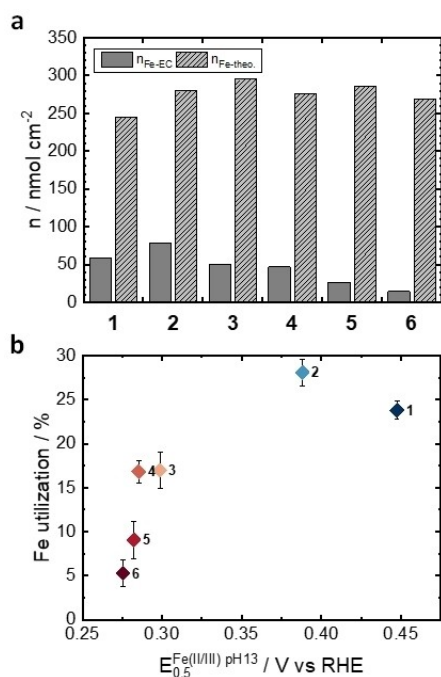


Figure 6. a) Theoretically expected iron amount on the electrode vs. electrochemically determined amount in 0.1 M KOH, b) Fe utilization (percentage of electrochemically contacted iron = $n_{\text{Fe-EC}} n_{\text{theo}}^{-1}$) over the Fe(II/III) redox potential.

and electronic effects will play a role here, which might be one reason for the deviations from ideal correlation lines in Figure 5 c and d. Steric effects are especially important for ortho-substituted porphyrins 1 and 6, where the phenyl groups are almost perpendicular to the porphyrin plane (see Supporting Information-Table S4, and Figure S2b). Electronic effects may take the form of polarizability effects in the highly fluorinated 1, where smaller van der Waals forces would be expected.

Mechanistic insights

The activity measurements of the carbon-supported iron porphyrin complexes towards water splitting in alkaline media are shown in Figure 7a. For comparison, the data of 7, the carbon support and the bare glassy carbon (GC) electrode were measured. The free base porphyrin 7 has a similar capacitance current density as the Fe(P) systems (Figures 5a and b), but does not reveal any significant HER activity. The carbon support reaches slightly higher current densities. Both the higher intrinsic surface area as indicated from the CV or a partial passivation of the amorphous carbon with 7 might be at the origin. Identifying the exact origin goes beyond the scope of this work, since it is sufficiently clear that the main activity can be attributed to the Fe(P) systems at the relevant potentials. Also, the Faradaic efficiency (FE) was determined for carbon-supported complex 3 and 7, as well as the carbon support. The results are given in the Supporting Information-Figure S7 clearly

indicates a much higher transient FE at the relevant potentials for the metalated iron porphyrin system.

While it was expected that the current density would scale with the electron density on the metal center, no such trend can be derived. As we assume the change in utilization to be responsible for this observation (Figure 6b), the relevant quantities were considered when calculating the turnover frequency (TOF, Equation (2)):

$$\text{TOF} = \frac{j A_{\text{disk}}}{n_{\text{Fe-EC}} F f} \quad (2)$$

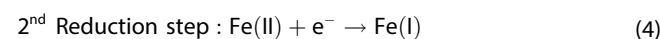
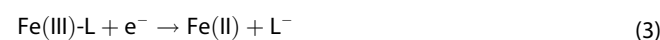
From the product of the current density and the geometric electrode area A_{Disk} the current is determined and then divided by $n_{\text{Fe-EC}}$ Faraday constant F and the stoichiometric factor f derived from the reaction equation of hydrogen formation. Figure 7b shows the logarithmic of the TOF at overpotentials of 0.7 V and 0.8 V plotted against the $E_{0.5}^{\text{Fe}^{\text{II}}/\text{Fe}^{\text{III}}}$.

As the electron donating effect of the substituent increases, the redox potential of the $\text{Fe}^{\text{II}}/\text{Fe}^{\text{III}}$ transition decreases and the TOF increases. To translate this direct structure-property-relationship into systematic improvements of HER catalysts, a detailed understanding of the reaction mechanism is essential. Currently, only a few reports are available, specifically on Fe(P)s in neutral or alkaline electrolyte.^[43] During the past ten years, Beyene *et al.* extensively investigated the homogeneous HER on metal porphyrins.^[16b,c,21a,44] They concluded that water acts as a proton source like a weak Brønsted acid for the oxidative protonation of the $[\text{Co}^{\text{0}}\text{N}_4]^{2-}$ ^[16b] and $[\text{Cu}^{\text{0}}\text{N}_4]^{2-}$ ^[44] species.

In analogy to the behaviour of the cobalt porphyrin case, a generalized reaction mechanism was deduced for the reduction in organic solvents, i.e. homogeneous catalysts: the HER is initiated by a two electron reduction of the metal center (equations 3, 4).^[16c,45] According to Bhugun *et al.* in case of fivefold coordinated complexes the axial ligand L (here initially Cl^-) is removed during the first reduction step and does not further interfere with the catalytic reaction.^[45] Subsequently, the intermediate $[\text{M}^{n-2}]$ undergoes an oxidative protonation yielding a metal hydride $[\text{M}^n\text{-H}]$ (Eq. (5)). In organic electrolyte, a homolysis of two $[\text{M}^n\text{-H}]$ is also possible.^[16d] The hydricity of metal hydrides was suggested as a descriptor for their HER activity.^[46]

In aqueous electrolyte, metal hydrides are not expected to be stable, so that a rapid protonation is likely (Eq. (6)). Furthermore, the combination of two hydrides appears very unlikely for supported systems. It is therefore assumed that the reaction proceeds via two reduction steps followed by two consecutive protonation steps at the same site. The $[\text{M}^n]$ complex formed can then either directly undergo a further catalytic cycle or become stabilized by a ligand L from the electrolyte.

1st Reduction step: ^[a]



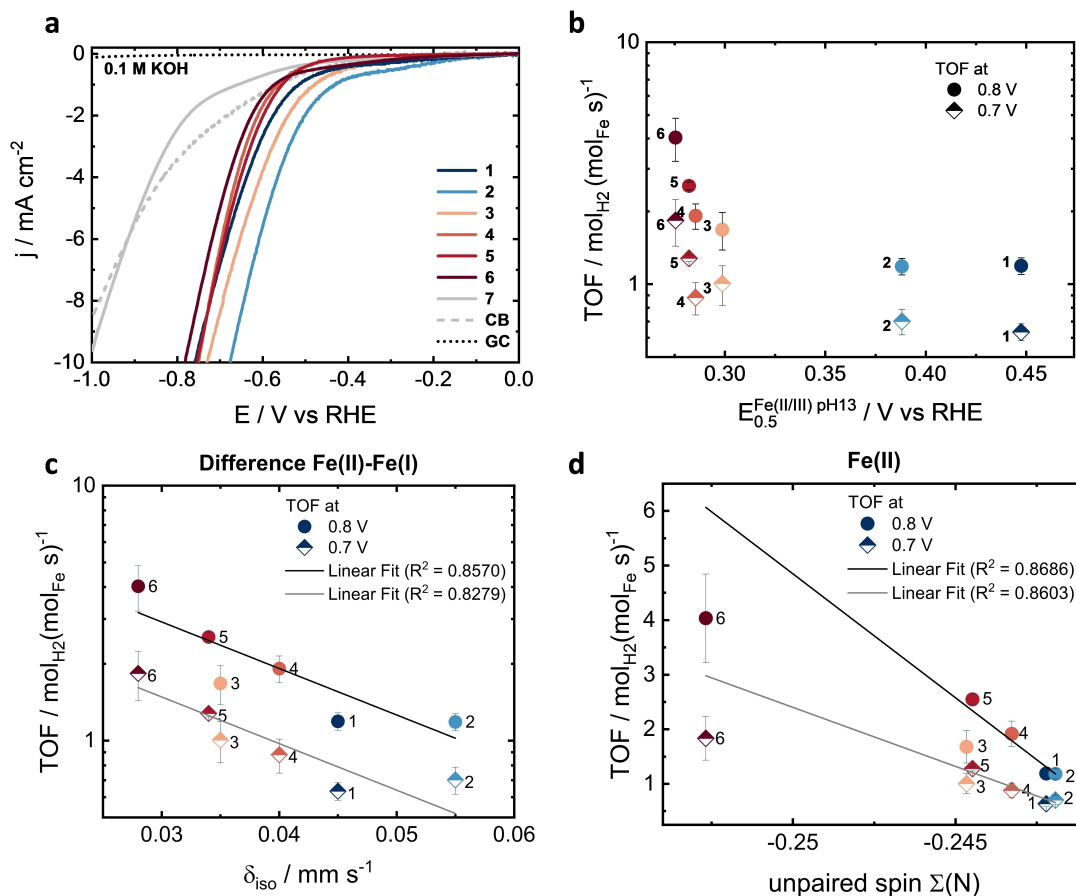
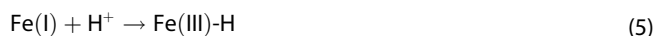


Figure 7. a) Representative LSVs of the heterogenized systems of carbon-supported Fe(III)Cl-porphyrins, or free base porphyrin, carbon black (CB) support without porphyrin and the bare glassy carbon electrode (GC) in 0.1 M KOH to determine the HER activity at pH 13; correlation attempts between TOF and b) $E_{0.5}^{\text{Fe(II/III)}}$, c) difference in δ_{iso} obtained for Fe(II)P and Fe(I)P (in spectroscopic oxidation state notation: [Fe^{II}(P^{*})⁻]), and d) sum of Mulliken spin populations on porphyrinic N in the Fe(II) complexes.

Oxidative protonation



Hydride protonation and H₂ release



[a] For the sake of simplicity, the porphyrin ligand and the total charge of the systems are not stated explicitly in the reaction equations.

The mechanism is thought to be heavily dependent on the porphyrin complex, the electrolyte and the proton source. It was suggested that the formation of an M^{n-2} species Fe^I (or [Fe^{II}(P^{*})⁻]) by two consecutive reduction steps (Eq. (3) and (4)) is rate-determining for porphyrin complexes in organic electrolyte, i.e. as a homogeneous catalyst.^[16a,45]

Both assumptions seem to be invalid for the supported iron porphyrins in this study. Porphyrin 1 has the lowest overpotential towards [Fe^{II}(P^{*})⁻] formation in DCM, but overall lowest TOF (at 0.7 V) in 0.1 M KOH. Further, complex 3 with the highest [Fe^{II}(P^{*})⁻] overpotential only shows mediocre TOF. This

leads to the conclusion that [Fe^{II}(P^{*})⁻]/Fe^{II} potentials determined in organic electrolyte cannot be translated to HER activities in alkaline electrolyte. A possible explanation is that the stability of the doubly reduced [Fe^{II}(P^{*})⁻] state with π -radical-anion character, which is documented in spectroscopic investigations of similar systems, differs in different media.^[25,26c] This suggests that the [Fe^{II}(P^{*})⁻]/Fe^{II} transition mostly depends on the ability of the π -system to stabilize the radical anion, making it a ligand centered transition in contrast to the metal centered Fe^{II}/Fe^{III} transition. The stability of the radical anion is not only influenced by the substituents but also by the solvent. For this reason, a comparison of the [Fe^{II}(P^{*})⁻]/Fe^{II} potential determined in DCM and the HER activity in 0.1 M KOH is not reported in this study.

From the experimental results, a structure-property-relationship can be drawn: electron donating effects cause an increase in HER reactivity, presumably by destabilizing the Fe^{II} species. However, this effect seems to be not of purely electronic nature as the calculated isomer shift, a direct measure for the electron density at the iron center, does not correlate with the TOF, nor do the number of unpaired electrons and the charge at the iron ion (see Supporting Information-Figure S8). The solvent inter-

actions discussed above are thus not systematic throughout the series which would suggest water or hydroxide involved in the HER mechanism and in the rate-determining step.

DFT calculations were performed to obtain further insights into the mechanism. The calculated Gibbs free enthalpies of all reaction steps for the mechanism expected in organic electrolyte (A, B, C, E, J) are shown in Figure 8. The Gibbs free enthalpies of each reaction step for each complex are plotted vs. the TOF in the Supporting Information-Figure S9.

Similarly to the homogeneous system, the abstraction of the chlorine ligand (A→C in Figure 8b) is assumed to take place during the initial reduction of the pre-catalyst via an intermedi-

ate species A-2.^[45] These processes take place during the initial conditioning of the electrode and are likely irreversible. Alternatively, a ligand exchange reaction (A→B→PFe(III)-L) with molecules from the electrolyte could take place. Incorporating explicit electrolyte interactions is beyond the scope of the current study.

Under operating conditions, B is deemed the starting point of the catalytic cycle. Correlating the predicted ΔG with the TOF shows the same behavior as the correlation of the experimental redox potentials with the TOF for the first reduction step $\text{Fe}^{\text{II}}/\text{Fe}^{\text{III}}$ (B→C). The second reduction step $[\text{Fe}^{\text{II}}(\text{P}^*)]/\text{Fe}^{\text{II}}$ (C→E) and the further reaction from $[\text{Fe}^{\text{II}}(\text{P}^*)]$ to the hydride $\text{Fe}^{\text{III}}\text{-H}$ (E→J) both show linear trends in correlation of predicted ΔG with the TOF, but with relatively poor R^2 values. Note that the comparison of TOF with the Gibbs enthalpy as a purely thermodynamic property is only meaningful for small reaction barriers; transition states are required to link directly to kinetic information from experiments.

In further attempts to identify species involved in the rate-determining step (RDS), we investigated properties related to the electron densities of Fe^{II} and $[\text{Fe}^{\text{II}}(\text{P}^*)]^-$ (E, formally $\text{Fe}(\text{I})$), since the reduction step is associated with the onset of the HER.^[16a,c,i,47] Supporting Information-Figures S8 and S10 show that properties of the iron atom extracted from OLYP calculations, such as the charge, the Mulliken spin population as a measure of the number of unpaired electrons, and the isomer shift of both Fe^{II} and $[\text{Fe}^{\text{II}}(\text{P}^*)]^-$, again correlate poorly with the TOF. We note that the changes in these properties between Fe^{II} and $[\text{Fe}^{\text{II}}(\text{P}^*)]^-$ (see Supporting Information-Figure S11) show clearer correlations with the TOF, in particular the isomer shift (see also Figure 7c). The less electron density at the iron nucleus is shifted during the Fe^{II} to $[\text{Fe}^{\text{II}}(\text{P}^*)]^-$ transition, the more active the complex. This indicates an involvement of the porphyrin ring in the RDS. We note that complex 6, which shows destabilized Fe^{II} in organic solvent, achieves higher HER activity in aqueous conditions compared to complexes with stable Fe^{II} .

Considering previous suggestions that the nitrogen ligand atoms can be involved in the reaction mechanism as internal bases,^[17,48] this possibility was investigated more closely by us. Experimentally, the involvement of the N atoms is indicated by observations made in organic electrolyte. The highly instable Fe^{II} species of 6 in DCM results in the highest TOF of 6 in 0.1 M KOH. Due to the absence of other reactants in the inert organic electrolyte, the porphyrin decomposes. In contrast to this, Fe^{II} and even $[\text{Fe}^{\text{II}}(\text{P}^*)]^-$ species are very stable in case of 1 and 2. Here, the reduced species are stabilized by the electron withdrawing groups. In 0.1 M KOH, 1 and 2 show low TOFs compared to the other iron porphyrins. These trends support our working hypothesis.

At the electronic structure level, this idea can be evaluated by correlating the number of unpaired electrons at the nitrogen ligand atoms with the TOF (see Figure 7d). To this end, the Mulliken spin population was extracted from OLYP single point calculations for the species Fe^{II} (C) and $[\text{Fe}^{\text{II}}(\text{P}^*)]^-$ (E, denoted as $\text{Fe}(\text{I})$ in Figure 8b and in the Supporting Information), and summed for all four nitrogen atoms. The sum was used because

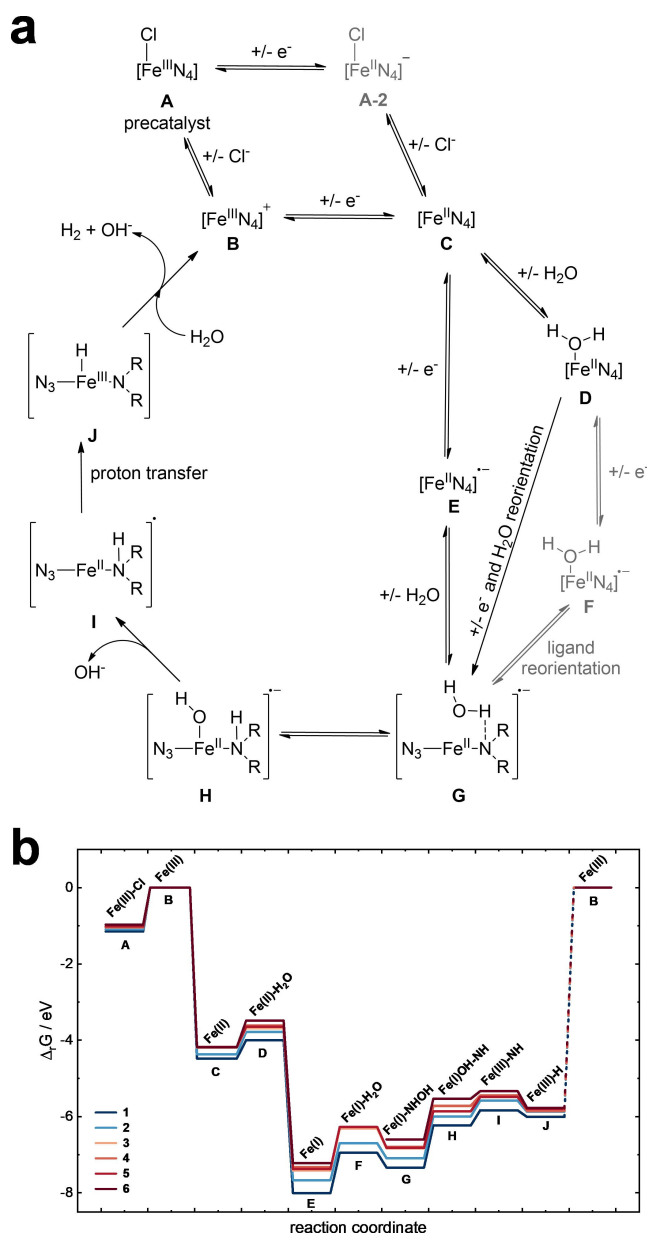


Figure 8. a) Proposed HER mechanism under alkaline conditions. b) Calculated Gibbs free enthalpies of HER intermediates relative to the Fe^{III} species. To improve legibility, the labels in (b) use the formal oxidation states, i.e. $[\text{Fe}(\text{I})\text{P}^*]^-$ instead of $[\text{Fe}(\text{II})\text{P}^*]^-$.

the differences between the substituted complexes are very small; we emphasize here that this measure should only be understood as an indicator and should not be used as a quantitative predictor. Similar to that, the predicted charge on the nitrogen atoms, as well as the spin population of the porphyrin plane seem to vaguely correlate with the TOF for both Fe^{II} and $[\text{Fe}^{\text{II}}(\text{P}^{\bullet})]^{-}$ (see Supporting Information-Figures S8 and S10). Even though the variation across the substituents is again very small, we propose that the anion radical character is important for the HER activity, and furthermore that nitrogen is involved in the rate-determining step in alkaline solution. Similar intermediates were found by Wu *et al.* conducting HER on nickel porphyrins in organic electrolyte in the presence of acids, where a key denominator for the probability to form $[\text{Ni}-\text{N}-\text{H}]$ intermediates was the electron density on the ligand N.^[17]

With this hypothesis in hand, we put forward a new mechanistic proposal for adsorbed iron porphyrin complexes in aqueous electrolyte. As a first step, the role of water in the catalytic cycle is further investigated, namely by coordination to Fe^{II} or Fe^{I} , forming **D** and **F**, and further reaction via a transition state where OH is coordinated to Fe and H binds to one of the four nitrogen atoms, using the formal oxidation state notation $\text{Fe}^{\text{I}}\text{OH}-\text{NH}$ (**H**) (see Figure 8, Supporting Information-Figure S12). Geometries of these intermediates are exemplarily shown for **3** in Supporting Information-Figure S13. Surprisingly, the coordination of water to Fe^{II} (**D**) and Fe^{I} (**F**) is disfavored by 0.5–0.7 eV and 1.0–1.1 eV, respectively. Additionally, the coordination of water to Fe^{I} (**F**) only resulted in stable geometries for complexes **1**, **2**, **3**, and **5**. These structures have a total spin $S_{\text{total}} = 3/2$, i.e. a similar electronic configuration as for Fe^{I} (**E**, namely $[\text{Fe}^{\text{I}}(\text{P}^{\bullet})]^{-}$), but with a parallel alignment of the unpaired electrons on the porphyrin plane and the iron ion. We observed that geometry optimizations for this and other spin states repeatedly resulted in the coordination of H_2O towards one of the N atoms. Therefore, such a geometry, labeled $\text{Fe}^{\text{I}}-\text{NHOH}$ (**G**), was added to the systematic study. The energetic cost for the coordination of water at a porphyrin nitrogen atom (**E**→**G**) was found to be only 0.5–0.7 eV and the electronic configuration matches that of $[\text{Fe}^{\text{I}}(\text{P}^{\bullet})]^{-}$, i.e. antiparallel alignment of spins on the iron ion and the porphyrin plane.

For the intermediate $\text{Fe}^{\text{I}}\text{OH}-\text{NH}$ (**H**), two energetically close-lying spin states were found: doublet and sextet. After consideration of the entropy contribution to the Gibbs free enthalpies, $S_{\text{total}} = 5/2$ was found to be more stable by 0.1–0.2 eV. The only exceptions are complex **6**, where only $S_{\text{total}} = 5/2$ could be converged, and complex **3**, for which a different, energetically unfavored electron configuration is found for $S_{\text{total}} = 5/2$ (see Supporting Information Table S4–S5).

Even though the identification of the rate-determining step within this mechanism by computational means is beyond the scope of this work, some estimates can be made: the highest thermodynamic obstacle for the reaction is the second reduction step (**C**→**E**, 3.0–3.4 eV), and the second largest is the O–H bond breaking step (**G**→**H**, 0.9–1.1 eV).

The reduction step from Fe^{II} (**C**) to Fe^{I} (**E**) by itself does not explain a possible involvement of porphyrinic nitrogen in the

rate-determining step. Relaxed surface scans for the O–H bond breaking process from $\text{Fe}-\text{NHOH}$ (**G**) to $\text{Fe}^{\text{I}}\text{OH}-\text{NH}$ (**H**; scan with $S_{\text{total}} = 1/2$) do not show a transition state (see Supporting Information-Figure S14). Capturing the spin state change for this reaction from the $S_{\text{total}} = 1/2$ species to the $S_{\text{total}} = 5/2$ product would require a scan with $S_{\text{total}} = 5/2$. Since the method we chose for the relaxed surface scan does not capture the stabilizing entropic contributions for the high spin species, a complete comparison is outside the scope of this work. Consequently, this reaction step cannot be excluded as the RDS *per se*, but would require a barrier exceeding the Gibbs free enthalpy of 3.0–3.4 eV associated with the second reduction step.

From the exemplary surface scans for H migration from $\text{Fe}^{\text{III}}-\text{NH}$ (**I**) to $\text{Fe}^{\text{III}}\text{H}$ (**J**), a reaction barrier of <0.3 eV was estimated (see Supporting Information-Figure S15), excluding this reaction step to be rate-determining.

The barriers for OH^- abstraction from $\text{Fe}^{\text{I}}\text{OH}-\text{NH}$ (**I**) and the reaction of $\text{Fe}^{\text{III}}-\text{H}$ (**J**) to Fe^{III} (**B**) forming H_2 cannot be estimated via relaxed surface scans. However, these reaction steps do not require the involvement of N and thus do not fit with the reaction model derived above.

Another plausible RDS might be - after the first reduction step - a combined second reduction and water migration step from $\text{Fe}^{\text{II}}-\text{H}_2\text{O}$ (**D**) to $\text{Fe}^{\text{I}}-\text{NHOH}$ (**G**). If the applied potential is sufficiently high for the coordination of water, forming **D**, the coordinated water is destabilized upon further reduction, forming the instable species **F**. The water molecule may therefore migrate to a porphyrinic nitrogen atom (**F** to **G**). This reaction may occur concertedly from **D** to **G**. Either would explain nitrogen involvement in the rate-determining step. The Gibbs free enthalpies of the differently substituted complexes correlate remarkably well for this reaction step ($\text{Fe}^{\text{II}}-\text{H}_2\text{O} + e^- \rightarrow \text{Fe}^{\text{I}}-\text{NHOH}$; **D** to **G**), $R^2 = 0.9026$ for TOF at 0.8 V and $R^2 = 0.9136$ for TOF at 0.7 V (see Supporting Information-Figure S9f). Consequently, we propose the second reduction combined with water migration as the rate-determining step. Further experiments will be required to verify this statement and to fully elucidate the HER mechanism on these model systems.

Conclusion

The influence of substituents in iron porphyrin complexes on the electrochemical characteristics, the interaction with a support, and the hydrogen evolution reaction was investigated by a combination of theory and experiment. The redox potentials determined in DCM/TBAP and in alkaline media correlate well with the electronic energy differences obtained from DFT calculations for the differently substituted porphyrin complexes. The partial density of states related to iron with and without support are similar and compare well with NRV spectra predicted for the isolated complexes. These findings show that the carbon support studied here has a limited or no effect on the pDOS. However, it is found that the choice of substituent alters the utilization: electron poor porphyrins connect better to the carbon support, resulting in a higher utilization.

Correlating the substituent properties with the observed catalytic activity, we find that an increase in the electron donating power is associated with a decrease in the $\text{Fe}^{\text{II}}/\text{Fe}^{\text{III}}$ redox potential and an increase of the TOF. DFT calculations show that the formal Fe(I) state is better described as an Fe(II) ion with a porphyrin radical ligand $[\text{Fe}^{\text{II}}(\text{P}^{\bullet})]^{-}$ with the unpaired electrons aligned antiparallel to those of the iron ion. Porphyrins that promote a shift of electron density in this reduced state towards the ligand π -system are more active in the HER. We connected experimental information with the predicted properties of plausible catalytic intermediates and suggest that one of the porphyrinic nitrogen atoms acts as an internal base towards a water molecule. This interaction facilitates an O–H bond breaking step of a water molecule in alkaline conditions, thus enabling higher TOF values.

Our results provide insights on the support effects of carbon supported porphyrin systems and thereby help to close the gap between homogeneous and heterogeneous catalysis. Our findings on the reaction mechanism are furthermore relevant in the context of MN_4 moieties integrated in amorphous carbon frameworks, where they might aid in the knowledge-based design of MNC catalysts as promising materials in PEC.

Experimental Section

Materials: All reagents are commercially available and were used without further purification. The iron and free base porphyrins (> 95 %) were purchased from Porphyrin-Laboratories GmbH, isotopically enriched ^{57}Fe metal powder (> 95 % Fe-57) from CHEMGAS, 5 wt.% Nafion solution NS-5 from QuinTech, BLACK PEARLS 2000 from CABOT and 0.25 mm thick Indium foil (99.99 % metal basis) from AlfaAesar. All other chemicals were obtained from Carl Roth.

All electrochemical testing and structural investigations by XPS were carried out using (non-enriched) purchased iron porphyrins (Porphyrin Laboratories). However, to enable NRVS measurements, an Fe-57 isotopic enrichment was required. Therefore, ^{57}Fe iron(III) chloride was prepared in a first step and then used in the metalation of the porphyrins, which were then immobilized on carbon black following the same procedure as used for the commercial iron porphyrins.

$^{57}\text{Fe}(\text{III})\text{Cl}_3$ anhydrous preparation: The preparation was conducted by adapting the textbook synthesis.^[49] Therefore, metallic ^{57}Fe (150 mg, 2.63 mmol, 1 equiv.) was dispersed in 2 mL water and dissolved in concentrated hydrochloric acid (2.15 mL, 26 mmol, 10 equiv.). The solution was stirred at 60 °C until a clear colourless solution is obtained. 30 % H_2O_2 solution (2.6 mL, 26 mmol, 10 equiv.) was added slowly to the mixture and yielded a dark brown solution. To complete the reaction, the mixture was stirred at 60 °C for 60 min. Under N_2 flow at 120 °C the reaction mixture was dried. Under N_2 atmosphere the solid residue was dispersed in thionyl chloride (1.9 mL, 26 mmol, 10 equiv.) and stirred for 60 min. Subsequently the solvent was evaporated at 100 °C under a N_2 flow. A black solid with metallic shine was obtained and stored under inert atmosphere.

Porphyrin metalation: Fully enriched ^{57}Fe -porphyrins **2**, **3**, **5** and **6** were prepared by a synthesis adapted from literature.^[50] The isotopically pure $^{57}\text{Fe}(\text{III})\text{Cl}_3$ anhydrous (70 mg, 0.44 mmol, 2.7 equiv.) was solved in dry dimethylformamide (50 mL) together with the respective free base porphyrin (0.163 mmol, 1 equiv.) under inert atmosphere. The reaction was stirred at 160 °C for 6 to 8 h. The

reaction progress was monitored by TLC. When no free base porphyrin was detected the reaction was deemed complete and the solvent was removed under reduced pressure. The obtained solid was then solved in DCM and consecutively washed with 2 M HCl (50 mL), water (3 × 50 mL) and dried (MgSO_4). The solvent was then removed again under reduced pressure and the solid product was dried overnight under high vacuum. The product was characterized by mass spectrometry, the related mass spectra can be found in the Supporting Information, Supporting Information-Figure S17.

ESI-MS:

2: m/z: calc. for $\text{C}_{48}\text{H}_{24}\text{N}_8^{57}\text{Fe}$ 769.14724, found 769.14832

3: m/z: calc. for $\text{C}_{48}\text{H}_{36}\text{N}_4^{57}\text{Fe}$ 669.16624, found 669.16651

5: m/z: calc. for $\text{C}_{48}\text{H}_{36}\text{N}_4^{57}\text{Fe}$ 725.22884, found 725.22946

6: m/z: calc. for $\text{C}_{56}\text{H}_{52}\text{N}_4^{57}\text{Fe}$ 837.35404, found 837.35468

Catalyst preparation: The iron porphyrin (0.23 mmol) was dissolved in 15 mL dichloromethane and treated in an ultrasonic bath for 5 min before BlackPearls2000 (100 mg, $1635 \text{ m}^2\text{g}^{-1}$) was added. Under ultrasonic treatment the solvent was allowed to evaporate completely. The drying process was completed by an overnight treatment at 80 °C in a drying oven. Finally, the obtained powder was homogenized in a mortar.

Electrochemistry: For electrochemical investigations a Princeton Applied Research set up was used, consisting of a PARSTAT 3000 A DX, a 636 A rotator and a ring disk electrode with a glassy carbon disk electrode ($d_{\text{disk}} = 5.5 \text{ mm}$, $A_{\text{disk}} = 0.2376 \text{ cm}^2$). The potentials were referenced versus an Ag|AgCl|3 M NaCl electrode in acid electrolyte and a Hg|HgO|1 M NaOH electrode in alkaline electrolyte. Both types of reference electrodes were purchased from ALS via C3 Analytics. The reference electrodes were calibrated every day vs. a HydroFlex reversible hydrogen electrode from Gaskatel to correct the measured potential and reference it to RHE. In general, the correction can be calculated theoretically as given in Equation (7) and for the specific pH values in Equation (8) and 9.

$$E_{\text{RHE}} = E_{\text{measured}} + E_{\text{Reference}}^0 + 0.059 \text{ pH} \quad (7)$$

$$\text{pH } 13 : E_{\text{RHE}} = E_{\text{measured}} + 0.907 \text{ V} \quad (8)$$

$$\text{pH } 1 : E_{\text{RHE}} = E_{\text{measured}} + 0.289 \text{ V} \quad (9)$$

The applied corrections as determined on basis of the Gaskatel RHE were close to 0.9 V for the Hg|HgO|1 M NaOH reference electrode and close to 0.3 V for the Ag|AgCl|3 M NaCl reference electrode, which is in good agreement with the calculation. As counter electrode glassy carbon rods purchased from HTW-Germany were used. For measurements in dichloromethane an Ag|AgNO₃ reference electrode from ALS was used and calibrated after every set of measurements in the same electrolyte mixture against ferrocene as an internal standard. The counter electrode was a platinum wire.

Measurements in organic electrolyte were conducted by producing a solution of 1 mM porphyrin and 0.1 M of tetrabutylammonium perchlorate (TBAP) as conducting agent in dichloromethane. The measurements were performed under constant saturation with N_2 in a custom made 5 necked cell with a filling capacity of 4 to 10 mL. An initial survey measurement was performed to determine the anodic and cathodic decomposition potentials. Then the vortex potentials for CVs were set below the decomposition potentials and one CV was measured at 100 mVs^{-1} and 10 mVs^{-1} each.

Afterwards ferrocene was added as internal standard to calibrate the reference electrode.

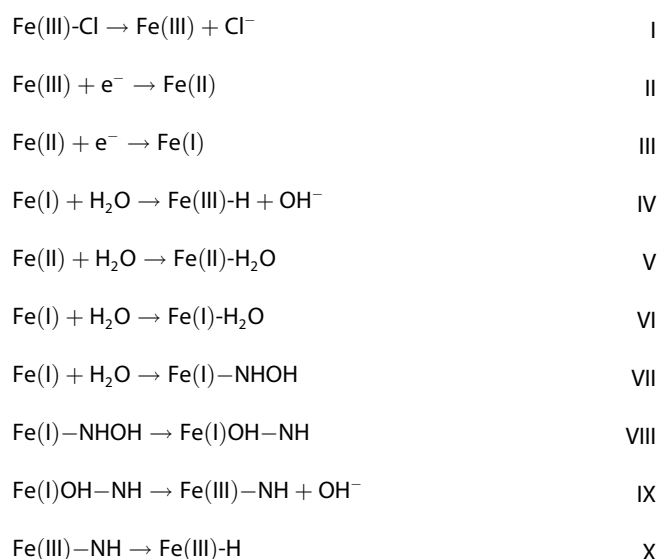
0.1 M H₂SO₄ aqueous electrolyte was prepared from concentrated (> 98 %) acid by dilution with ultra-pure water with a resistance of 18.2 Ω or higher. 0.1 KOH electrolyte was prepared by dissolving KOH pellets in ultra-pure water. The catalyst layer was deposited on a freshly polished glassy carbon disk electrode by deploying an ink. 0.05 μm alumina polish and a MasterTex polishing pad were used in preparation for the ink deposition. For the ink preparation 5 mg of catalyst are dispersed in 142 μL water and then subsequently 25 μL 5 wt.% Nafion solution, 83.3 μL and 125 μL 0.1 M H₂SO₄ were added. For ideal dispersion the mixture is placed alternately into an ice cooled ultrasonic bath (USB) and on an orbital shaker. After 45, 15 and 1 min in the USB the ink is placed for 1 min in the shaker. 9 μL of the freshly prepared ink was then drop casted on the glassy carbon disk electrode and left to dry to obtain a loading of 0.51 mg cm⁻². Close before complete drying of the catalyst layer, the process is quenched by a drop of electrolyte, to reach a homogeneous catalyst layer. The electrode was then mounted on the rotator and positioned in the electrolyte. A beaker like cell was used filled with 50 mL N₂ saturated premixed electrolyte. The measurements were performed under constant saturation of the electrolyte with N₂. For conditioning of the catalyst layer a set of cyclic voltammetry measurements were performed between 0 and 1.1 V vs. RHE, namely 20 cycles at 300 mVs⁻¹, and one at 100 mVs⁻¹, 50 mVs⁻¹ and 10 mVs⁻¹ each. The hydrogen evolution reaction was measured in a potential range from 0.1 V to -1 V vs. RHE. Three cycles were performed, but only the second one was evaluated for interpretation of the activity. The first cycle serves as an activation and the third is used to check the reproducibility of the evaluated cycle. Both are not further discussed here. In general, the activity in the third cycle was slightly lower than in the second cycle. With an overpotential drop of less than 30 mV at 10 mA cm⁻², we consider the electrode layer sufficiently stable. E_{0.5} potentials and HER activities were calculated from multiple determinations on two to four separately prepared catalyst layers. The averaged results are always used to determine correlations and shown in the scatter plots. For the CVs in Figure 5 and LSVs in Figure 7 a representative measurement is plotted for simplicity and readability.

Nuclear Resonance Vibration Spectroscopy: (alternative nomenclature: nuclear resonance inelastic X-ray scattering NRIXS or nuclear inelastic scattering NIS) was performed at the P01 High Resolution Dynamics beamline at PETRA III (Deutsches Elektronen-Synchrotron, DESY) during the beamtime I-20200863.^[51] The synchrotron operated with a 40 bunches filling mode and a photon energy of 14.4 keV (⁵⁷Fe resonance) is selected at the P01 beamline. The energy is tunable in the meV range by a high-resolution monochromator. Thin packages of 1–3 mg sample powder were prepared by pressing in the sample between two layers of Mylar aluminium foil. These packages were placed on a copper sample holder in a closed cycle cryostat (6–800 K). The NRVS scans were performed at a temperature between 17 and 28 K. The exact measurement temperature was determined from the original measured data and differed due to variation in thermal contacting. Scattered photons were detected by an avalanche photodiode (APD). From the NRVS scans the partial density of states (pDOS) related to iron was calculated.^[37a,52]

X-ray photoelectron spectroscopy: XPS samples were prepared by pressing a homogenized powder onto an 8 by 8 mm piece of indium foil, which is then mounted on a stainless-steel sample holder. Afterwards, the sample was introduced into ultra-high vacuum (UHV) at the Darmstadt Integrated System for Fundamental research (DAISY-FUN).^[53] It is equipped with a PHOIBOS 150 hemispherical analyser, CEM 9 Channeltron analyser and a XR50 M

x-ray source, all three from SPECS Surface Nano Analysis GmbH. The XPS measurements were performed at pressures below 1·10⁻⁹ mbar with monochromatic excitation by Al Kα (1486.64 eV) radiation. The pass energy was set to 20 eV for the survey scans, to 20 eV for high resolution (HR) Fe 2p scans and to 10 eV for all other HR scans. The setup is calibrated using Cu 2p, Ag 3d and Au 4f core levels and valence band edges. The used evaluation software was Igor Pro. The obtained spectra were analysed with CasaXPS. The background in HR-XPS was determined as Shirley type, to accommodate for inelastic electron scattering. The signals were fitted with a Gaussian/Lorentzian (70/30) line shape model.

Computational Details: All calculations were carried out using version 4.2.1. of the ORCA suite of programs.^[54] Geometry optimizations and subsequent frequency calculations were performed using the TPSS^[55] density functional in unrestricted Kohn–Sham density functional theory and Ahlrichs' basis set def2-SVP^[56] for the description of C and H atoms while def2-TZVP^[56] was used for all other atoms, namely Fe, O and Cl. Split-RJ approximation was employed using the def2/J basis set.^[57] The convergence criteria for SCF and geometry optimisation were set to "tight" in ORCA nomenclature. The size of the radial grid and the angular grid was to 6.0. Dispersion correction by Grimme with Becke–Johnson damping (D3BJ) was employed^[58] and water was used as an implicit solvent within the SMD model.^[59] Single point calculations using the B3LYP^[60] functional were performed on the optimized geometries for the prediction of Mössbauer parameters as previously described by the authors.^[30] The electronic structures were evaluated with single point calculations using the same settings as the Mössbauer predictions, but with the OLYP density functional^[60b,61] and excluding dispersion corrections. This approach was verified on structurally and electronically similar test cases, as documented in the Supporting Information of Ref.^[61] From the optimized geometries and frequency calculations Gibbs free enthalpies were obtained and corrected using the electronic energies obtained from the OLYP calculations. Reaction enthalpies were calculated for the following reactions:



The corrected Gibbs free enthalpies of formation of small molecules, namely Cl⁻, H₂O and OH⁻, were computed using the same settings and are given in Table S6 where required for the reaction. Relaxed surface scans were performed for reaction VIII and X fixing the bond length of O–H and Fe–H, respectively, starting from the optimized geometry of the reactant. For each step of the relaxed surface scan, the bond length was fixed for each step (0.98

to 2.50 Å, 20 steps for VIII and 2.10 to 1.45 Å, 45 steps for X) followed by a geometry optimization of the rest of the molecule with the same settings as stated above.

For NRVS, optimized geometries were reoptimized using the B3LYP^[60] density functional and RIJCOSX^[62] approximation with otherwise identical settings. A frequency calculation was performed on these structures with the same approach. The spectra were extracted from the Hessian file using the *orca_mapspc* subprogram and the NRVS keyword and a Gaussian band broadening of 15 cm⁻¹ was chosen. Visualisations were carried out in Chimera 1.13.1 and Origin 2020b.

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Conflict of Interest

The authors declare no conflict of interest.

Data Availability Statement

The data that support the findings of this study are available from the corresponding author upon reasonable request. Please send your request view <https://tudatalib.ulb.tu-darmstadt.de/handle/tudatalib/3674>

Keywords: density functional theory · electrochemistry · heterogeneous catalysis · hydrogen · molecular electrochemistry · renewable resources

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