[FeFe]hydrogenase mimics for proton reduction catalysis: Supramolecular proton reduction catalysts with appended redox-active and proton-responsive ligands towards application in a molecular artificial leaf

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A Phosphoramidite-Containing [FeFe]H$_2$ase Functional Mimic Displaying Fast Electrocatalytic Proton Reduction

ABSTRACT. A phosphoramidite modified [FeFe]H$_2$ase mimic is studied as a model for photodriven production of H$_2$. On cathodic activation, the pyridyl-phosphoramidite complex exhibits a strongly enhanced rate of proton reduction over the previously reported pyridylphosphine model at the same overpotential. Analysis of the cyclic voltammograms shows an apparent H$_2$ evolution rate strongly influenced by the presence of both side-bound pyridyl and phosphorus-bound dimethylamino moieties at the phosphoramidite ligands. This difference is ascribed to the basic amines acting as proton relays.
Introduction

Efficient photochemical generation of molecular hydrogen is one of the key technologies our society needs in order to move to a sustainable hydrogen-based economy.\textsuperscript{1–3} As a consequence, a great deal of attention has been devoted to (photo-redox) catalysts performing proton reduction, and both homogeneous and heterogeneous systems have been developed.\textsuperscript{4–9} [FeFe]Hydrogenases (H\textsubscript{2}ase) are natural-occurring enzymes that catalyze the reduction of protons in an extremely efficient way (TOF around 10,000 s\textsuperscript{-1}).\textsuperscript{10} Models of their bimetallic core based on cheap and abundant materials are easily synthesised, which has led to a plethora of di-iron mimics.\textsuperscript{11–18} So far, the majority of studies on mimicking the function of these biological systems has focused on electrocatalysis,\textsuperscript{19} while the direct photodriven catalysis, using a light-harvesting chromophore coupled to the [FeFe] core, has only recently been addressed.\textsuperscript{20–25}

The few initial attempts to assess light-driven H\textsubscript{2} production with homogeneous systems are roughly based on four approaches: (i) simple mixing of the chromophore with the catalyst in solution, (ii) electron-transfer mediation by addition of an electron relay in donor-mediator-catalyst systems, (iii) covalent attachment of the chromophore to the catalyst or (iv) supramolecular coordination of the catalyst to the chromophore.\textsuperscript{25} The first two strategies offer ease of screening but limit the control over the spatial arrangement between the moieties. However, advantages of a well-defined system in the covalent case come at the price of tedious syntheses and more rapid charge recombination.

We envisaged a supramolecular approach combining the chromophore with the precatalyst to be most advantageous. With this philosophy in mind, we recently introduced 1-ZnTPP, a supramolecular dyad which (after disproportionation into a

\begin{figure}
\centering
\includegraphics[width=\textwidth]{figure1.png}
\caption{The active [FeFe]H\textsubscript{2}ase biomimetic supramolecular assembly formed under photo-reductive conditions from complex 1 in the presence of two different porphyrins.}
\end{figure}
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Figure 2. The novel [FeFe]H$_2$ase biomimetic catalyst 2 based on the phosphoramidite ligand appended with two 3-pyridyl groups (mPyPA) and the reference complexes 1, 3 and 4.

disubstituted complex, Figure 1) is capable of photocatalytic conversion of protons into H$_2$.$^{25}$ In that case, ZnTPP was chosen as the photosensitizer, while the catalytic mimic 1 was the (μ-pdt)Fe$_2$(CO)$_5$L precursor (Figure 2). L represents the template ligand$^{26-32}$ PPyPPh$_3$ (PPy = 4-pyridyl), which is coordinated to the di-iron center via the phosphorus atom and to ZnTPP via the PPy group (Figure 1). Under photocatalytic conditions, i.e. upon irradiation in the presence of a sacrificial proton donor and electron donor, the supramolecular assembly 1-ZnTPP exhibits H$_2$ evolution, whereas the reference complex (3; L = PPh$_3$) is inactive.

Results and discussion

Herein, we report development of our supramolecular dyad approach, using mPyPA, a recently reported phosphoramidite template ligand based on the 2,2'-binapthol motif and decorated with two pyridyl groups (Figure 2, complex 2).$^{33}$ We have been intrigued by the properties such a ligand could impart onto the di-iron core. Phosphoramidites have better π-acceptor properties compared to the related phos-
phines, likely removing electron density from the diiron core. This would lead to less negative reduction potentials of the complex and, therefore, smaller overpotential for H₂ production. Furthermore, the two pyridyl side groups on the ligand may facilitate the association of macrocyclic chromophores to the metal center and/or participate in proton transfer.

Complex 2 [(μ-pdt)Fe₂(CO)₅(mPyPA)] was synthesised together with the pyridyl-free

Table 1. The IR ν(CO) wavenumbers of complexes 1 to 4 in CH₃CN.

<table>
<thead>
<tr>
<th>Complex</th>
<th>ν(CO) [cm⁻¹]</th>
</tr>
</thead>
<tbody>
<tr>
<td>1²⁵</td>
<td>2048 (s), 1985 (s), 1966 (sh), 1937 (m)</td>
</tr>
<tr>
<td>2</td>
<td>2047 (s), 1993 (s), 1975 (s), 1962 (m)</td>
</tr>
<tr>
<td>3³⁴</td>
<td>2044 (s), 1984 (s), 1931 (m)</td>
</tr>
<tr>
<td>4</td>
<td>2045 (s), 1992 (s), 1973 (m), 1961 (sh)</td>
</tr>
</tbody>
</table>
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complexes 3 [(μ-pdt)Fe$_2$(CO)$_5$(PPh$_3$)]$^{3+}$ and 4 [(μ-pdt)Fe$_2$(CO)$_5$(PhPA)], which will be used for control experiments (Figure 2). The syntheses of 2 and 4 involve substitution of one carbonyl ligand in (μ-pdt)Fe$_2$(CO)$_6$ for the phosphoramidite ligand: $^{31}$P NMR spectra as well as MS of the new compounds revealed single CO displacement and phosphoramidite coordination to the Fe centre via the phosphorus atom, leaving, when present, both pyridyl groups on the phosphoramidite free for coordination to the photosensitizer.

The IR spectra show a characteristic ν(CO) pattern of (μ-pdt)Fe$_2$(CO)$_5$L (Table 1) and carbonyl stretching frequencies that are shifted ca. 30 cm$^{-1}$ to lower wavenumbers with respect to (μ-pdt)Fe$_2$(CO)$_6$. Surprisingly, the ν(CO) values are very close to those for the pyridylphosphine derivative 1, demonstrating that the electronic difference between the pyridylphosphine and phosphoramidite ligands is not translated into Fe-to-CO π-back-donation and hence into differences in electron density at the iron core.

In line with this observation, cyclic voltammetry shows that 1–4 have their (irreversible) first cathodic waves placed at roughly the same electrode potential (Table 2). The electrocatalytic activity of these complexes towards proton reduction was studied at a static mercury drop electrode by examining the growth of their cathodic waves upon addition of acetic acid under identical experimental conditions (Figure 3). Again, catalytic waves for all four compounds were found at roughly the same potential (−2.4 V to −2.5 V vs Fc/Fc$^+$). Adsorption of the pyridine-functionalized complexes to the mercury surface was not observed.$^1$

Although both cathodic and catalytic wave potentials for all four studied complex-

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1 It is known that pyridine (and pyridine-functionalized molecules) can adsorb to mercury surfaces.$^{44}$ If this were the case for complexes 1 and 2, their cyclic voltammograms would diverge significantly from those recorded for complexes 3 and 4, respectively. Namely, the cathodic peaks would be broadened$^{45}$ and diffusion-related behaviour would be suppressed. However, we have observed almost identical cyclic voltammograms for 1 and 3, and 2 and 4 which are in their turn similar to cyclic voltammograms published in literature (on platinum and glassy carbon electrodes).$^{34}$ Furthermore, we have conducted cyclic voltammetry of complex 2 at different scan rates (0.05 to 5.0 V/s) using both static mercury drop and platinum working electrodes and found a linear relationship between the cathodic peak current and the square root of the scan rate. Since this behaviour is in line with the Randles-Ševčík equation, we assume no significant adsorption for the major species in the electrolyte solution.
es are similar, the current maxima and shapes of the catalytic waves have indicated that there is a remarkable difference in activity. To understand this difference, in-depth analysis was performed on the cyclic voltammograms for each complex. The observed rate constant $k_{\text{obs}}$ has been determined by the method of DuBois and co-workers (Equation 1), using the ratio between the second cathodic peak current ($i_{\text{pc,2}}$) and the catalytic peak current ($i_{\text{cat}}$) under the assumption that $\text{H}_2$ formation is irreversible ($E_{\text{C}^{i-}}$ mechanism). Remarkably, catalytic efficiency is much higher for catalyst precursor 2, as reflected in the much larger $k_{\text{obs}}$ (ca. 6000 s$^{-1}$ at 7 mM acetic acid) compared to 1, 3 and 4 (Figure 4). Since all catalysts operate at similar potentials, the effect of differences in overpotential on the catalytic rate can be neglected, and therefore the rate increase might well be caused by differences in particular mechanisms of the $\text{H}_2$ evolution. It should be stressed here that the absolute values of the rate constant $k_{\text{obs}}$ (and therefore $k'$) have little physical meaning, since the analysis techniques are only valid for rate quantification under pure kinetic conditions. Therefore, the values are only used to compare the catalysts under study.

$$k_{\text{obs}} = 0.0497 \cdot \frac{F \nu}{RT} \left( \frac{i_{\text{cat}}}{i_{\text{p}}} \right)^2$$

Equation 1

$$\frac{\partial [\text{H}_2]}{\partial t} = k' [\text{H}^+]^n$$

Equation 2

In line with behaviour of the natural system and observations from recent model complexes, it seems eminent that proton preorganization plays a role in accelerating the catalytic reduction. To get more insight into the proton-reactive behaviour, a relation between the rate of the $\text{H}_2$ formation and acid concentration was sought by equating $k_{\text{obs}}$ to $\partial [\text{H}_2]/\partial t$. The obtained curve ($k_{\text{obs}}$ vs. $[\text{H}^+]$) is then characterised

<table>
<thead>
<tr>
<th>Complex</th>
<th>$E_{\text{pc,1}}$ [V]</th>
<th>$E_{\text{pc,2}}$ [V]</th>
<th>$n$</th>
<th>$k'$</th>
</tr>
</thead>
<tbody>
<tr>
<td>1</td>
<td>-1.78</td>
<td>-2.24</td>
<td>1.79</td>
<td>17.8</td>
</tr>
<tr>
<td>2</td>
<td>-1.88</td>
<td>-2.28</td>
<td>3.58</td>
<td>6.00</td>
</tr>
<tr>
<td>3</td>
<td>-1.81</td>
<td>-2.26</td>
<td>2.31</td>
<td>1.44</td>
</tr>
<tr>
<td>4</td>
<td>-1.90</td>
<td>-2.38</td>
<td>2.85</td>
<td>0.93</td>
</tr>
</tbody>
</table>

Table 2. Electrochemical data of compounds 1 to 4 in butyronitrile.
For an explanation on electrochemical reaction orders ($n$) and rate constants ($k'$), see text. All potentials are vs. Fc/Fc$^+$.
by the rate constant $k'$ and reaction order $n$ in a pseudo rate equation proportional to the kinetics of the reaction under study. Fitting our data points to a power function (Equation 2) has yielded values for $k'$ and $n$ for each complex under study (Table 2) with $R^2$ values between 0.993 and 0.999.

The obtained pseudo rate equation for (electro)catalysis takes into account the step(s) just before the rate determining step, including additional protonation equilibria (if any). On this basis a correlation between rate order and constant, and Brønsted basic sites has been found: Phosphine complexes 1 and 3 show a reaction order close to 2, whereas for phosphoramidite complexes 2 and 4, $n$ has been found closer to 3, suggesting additional protonation equilibria. Since phosphoramidites can be protonated on the dimethylamine moiety, proton preorganization might explain the differences in the reaction order. It has been shown for multiple proton reduction catalysts that a proton relay close to the active site can indeed increase their activity, supporting the hypothesis of proton preorganization in the case of the phosphoramidite complexes.  

Figure 4. Kinetic fits. Plotted dependence of the rate constant $k_{\text{obs}}$ on acetic acid concentration for complexes 1 to 4. Dashed lines are curve fits of the form $y = a \cdot x^n$.

Figure 5. Spectral titrations. UV-vis spectra showing the titration of ZnTPP with $m$PyPA (left) and 2 (right) in CH$_2$Cl$_2$. Only the Q-bands of the porphyrins are shown. The purple line corresponds to pure ZnTPP (ca. 80 μM); the last point corresponds to total addition of 10.5 equivalents $m$PyPA (left) and 4.7 equivalents 2 (right).
Still, this does not explain why complex 2 is much more active than its phenyl analogue 4. However, it has been found that the pseudo rate constants for phenyl-functionalized 3 and 4 are considerably smaller than those for pyridyl-functionalized 1 and 2. This pyridyl-induced rate increase might be explained by an electronic communication between the ligand and iron core or by stabilisation of the mono-reduced intermediate.\textsuperscript{26,33} From this analysis, it is believed that for the high electrocatalytic rate observed for 2, both phosphoramidite and pyridyl functionalities are mandatory. The dimethylamino moiety might act as a proton relay, whereas the role of the pyridyl functionality remains unclear. This distinct ligand effect also implies that the active species contains at least one ligand moiety. However, since it is known that (\(\mu\)-pdt)Fe\(_2\) complexes undergo a variety of transformations on one-electron reduction, it is unclear whether the active species is in fact one-electron reduced 2 or one of its secondary reduction products.\textsuperscript{11} Although its exact structure remains elusive, the active species formed after reduction of precatalyst 2 shows a much higher electrocatalytic activity than its phosphine analogue.

Having established that compound 2 is a precursor to a good proton reduction catalyst, we analysed its photocatalytic behaviour when combined with zinc tetraphenylporphyrin (ZnTPP). Comparison of the catalytic potential of 2 (roughly −2.5 V \(\text{vs. Fc/Fc}^+\)) with the second reduction potential of the porphyrin belonging to its singlet excited state (−1.75 V \(\text{vs. Fc/Fc}^+\)) shows that the quenching of ZnTPP\(^*\) by 2 is thermodynamically uphill, making photocatalysis for this system unfeasible. To verify this, a luminescence titration was carried out, monitoring the light emission of ZnTPP in the presence of an increasing amount of 2 (Appendix, Figure 8). Instead of static quenching by electron transfer, a red shift of the emission was observed which can be assigned to emission of the assembly 2-ZnTPP. Preliminary photocatalysis experiments using this system led, in all cases, to decomposition of the catalyst with evolution of 0.5 equivalents of H\(_2\) with respect to the catalyst.

Complex 2 shows an irreversible one-electron reduction wave, consistent with previously reported mono-substituted pentacarbonyl (\(\mu\)-pdt)Fe\(_2\) complexes.\textsuperscript{34} Furthermore, on one-electron reduction, complex 1 has been shown to disproportionate into the parent hexacarbonyl and the dissubstituted tetracarbonyl complex.\textsuperscript{25} Spectroelectrochemistry (SEC) on 2 shows identical behaviour. However, on the short time scale of cyclic voltammetry (defined by \(\nu = 100 \text{ mV/s as opposed to 2 mV/s for SEC}\)), it is reasonable to assume that during catalysis a rather complex chemical mixture is present, consisting of precatalyst 2, one-electron reduced 2\(^-\), its disproportionation products (the hexacarbonyl and the dissubstituted complexes 5), their respective decomposition products (a mixture of Fe\(_5\) and Fe\(_4\) clusters with or without bridging CO and thiolate ligands) plus all possible protonated species.
Despite these results, we still trust that the overall supramolecular strategy is worth investigating, as using e.g. aromatic dithiolates instead of the propanedithiolate bridge in the studied complexes (Figure 2), the catalytic potential may well be shifted towards a range well-accessible for ZnTPP. Therefore, we studied the supramolecular assemblies of the pyridyl-functionalised phosphoramidite ligand and its di-iron pentacarbonyl complex with ZnTPP. First, the binding of ZnTPP to the pyridyl groups at the \( m \)PyPA ligand in complex 2 was determined by means of UV-Vis titration (Figure 5). Free \( m \)PyPA binds two ZnTPP macrocycles with equal (microscopic) association constants of \( 1.1 \times 10^4 \) M\(^{-1} \) (Appendix, Figure 6), which also applies for the assembly with complex 2, which shows identical association constants (Appendix, Figure 7). These data suggest that the interaction is a regular pyridyl-ZnTPP association (typical value in \( \text{CH}_2\text{Cl}_2 \) is \( 6.9 \times 10^3 \) M\(^{-1} \)).

**Conclusions**

In summary, we report the synthesis and properties of a novel 3-pyridylphosphoramidite-ligated [FeFe]H\(_2\)ase model. Compared to the previously reported 4-pyridylphosphine analogue, complex 2 is much more active in the reduction of protons at a similar overpotential, which could be attributed to the dimethylamine moiety acting as a proton relay. The pyridyl functionality on the phosphoramidite ligand also plays a crucial role in accelerating proton reduction, although its exact function has not yet been elucidated.

Furthermore, the supramolecular host-guest-host assembly ZnTPP\( \cdot \)ZnTPP forms in non-coordinating solvents without any cooperative behaviour. However, it was shown that complex 2 neither quenches the excited state of the chromophore, nor reaches the thermodynamic potential needed for photocatalysis. Further matching of redox levels of the catalyst core and the associated chromophore will show if photo-driven hydrogen formation is viable using the same phosphoramidite ligand. One way to achieve this goal would be the replacement of the propanedithiolate bridge by an aromatic bridge, effectively shifting the cathodic potential to less negative values.\(^{19,40} \)
Experimental

General procedures and materials

All syntheses were carried out under an argon atmosphere, using standard Schlenk techniques. For all purifications involving column chromatography, a column with dry silica was prepared beforehand and left under vacuum overnight; the chromatography was performed under inert atmosphere with degassed solvents. All $^1$H and $^{31}$P NMR spectra were recorded on a Bruker AV 400 MHz spectrometer. IR spectra were recorded on a Bruker Vertex 70v FTIR spectrometer. Unless stated otherwise, all chemicals were commercially available and employed without further purification. All solvents were purified via SPS (Solvent Purification System) or via distillation and degassed by means of argon bubbling prior to use. The phosphoramidite linkers mPyPA and PhPA,[33] the hexacarbonyl complex ($\mu$-pdt)Fe$_2$(CO)$_6$,[42,43] and the di-iron catalysts 1 and 3[34] were prepared according to the previously published methods.

Electrochemistry

Cyclic voltammetry was performed on 1 mM solutions of the Fe$_2$ complexes in butyronitrile containing 0.1 M nBu$_4$NPF$_6$ as the supporting electrolyte. The voltammograms were recorded using a Metrohm 663 VA stand in conjunction with a PGSTAT302N potentiostat, a static mercury drop electrode (SMDE; drop size 2) as a working electrode, a glassy carbon rod as an auxiliary electrode and a double-junction reference electrode (inner compartment: 3 M KCl/Ag; outer compartment: 0.1 M nBu$_4$NPF$_6$ in butyronitrile). Before every measurement, the solution was purged with nitrogen for 1 minute. Single equivalents of acetic acid were added as a 10% v/v solution in butyronitrile. To convert the potential values of the 3 M KCl/Ag reference to Fc/Fc$,^+$, a correction factor of −0.43 V was used.

Synthesis

($\mu$-pdt)Fe$_2$(CO)$_6$(mPyPA) (2). CH$_3$CN (10 mL) was added to a Schlenk vessel, charged with ($\mu$-pdt)Fe$_2$(CO)$_6$ (165 mg, 0.428 mmol), mPyPA (223 mg, 0.428 mmol) and dry Me$_3$NO (53 mg, 0.48 mmol). The red solution was stirred and full conversion was achieved in 1 h, as monitored by IR spectroscopy. The solvent was removed under
vacuum, and the resulting red-brown solid was purified on a silica gel column, using 3% CH$_3$OH in CH$_2$Cl$_2$ as the eluent. The product was collected as an intense red band. Yield: 60%. IR (CH$_3$CN, cm$^{-1}$): 2047(s), 1993(s), 1975(s), 1962(m). $^1$H NMR (400 MHz, CDCl$_3$, aromatic region) δ 8.91 (dd, 2H), 8.59 (dd, 1H), 8.45 (dd, 1H), 8.21 (dt, 1H), 8.02 (dt, 1H), 7.34 (m, 2H), 7.30 (s, 1H), 7.24 (s, 1H) ppm. $^{31}$P NMR (162 MHz, CDCl$_3$) δ 187.5 ppm. MS (FAB$^+$) for C$_{40}$H$_{38}$Fe$_2$N$_3$O$_7$PS$_2$: m/z 879.06 (calculated), 880.07 (observed; MH$^+$). UV-vis (CH$_2$Cl$_2$) 349 nm (ε = 12320 cm$^{-1}$ M$^{-1}$), shoulder at 491 nm (ε = 1230 cm$^{-1}$ M$^{-1}$).

(μ-pdt)Fe$_2$(CO)$_5$(PhPA) (4). CH$_3$CN (10 mL) was added to a Schlenk vessel, charged with (μpdt)Fe$_2$(CO)$_6$ (202 mg, 0.523 mmol), PhPA (300 mg, 0.577 mmol) and Me$_3$NO (64 mg, 0.57 mmol). The red solution was stirred and abundant precipitate formed within one hour. The reaction was monitored by IR spectroscopy. The solvent was removed under vacuum, and the crude solid was purified on a silica gel column, using pure CH$_2$Cl$_2$ as the eluent. The desired product eluted in the first fraction and was isolated as a bright red solid. Yield: 62%. IR (CH$_3$CN, cm$^{-1}$): 2045 (s), 1992 (s), 1973 (m), 1961 (sh). $^1$H NMR (400 MHz, CD$_2$Cl$_2$, aromatic region) δ 7.82 (dd, 2H), 7.77 (dd, 2H), 7.47 (td, 2H), 7.38-7.31 (m, 5H) and 7.24 (tt, 1H) ppm. $^{31}$P NMR (162 MHz, CD$_2$Cl$_2$) δ 186.1 ppm. MS (FAB$^+$) for C$_{42}$H$_{40}$Fe$_2$NO$_7$PS$_2$: m/z 877.07 (calculated), 878.09 (observed; MH$^+$).

(μ-pdt)Fe$_2$(CO)$_4$(mPyPA)$_2$ (5). The disubstituted complex 5 was synthesized as a disproportionation product of 2. A Schlenk vessel was charged with 2 (108 mg, 123 mmol) and decamethylcobaltocene (CoCp$_2$). The solids were dissolved in THF (8 mL) and the resulting solution was stirred for 2 h. The solvent was removed under vacuum and the product was purified by chromatography on a silica column, using 4% CH$_3$OH in CH$_2$Cl$_2$ as the eluent. The product eluted as the last, third band. Yield: 22%. IR (CH$_3$CN, cm$^{-1}$): 2011 (s), 1965 (s), 1948 (s). $^1$H NMR (400 MHz, CDCl$_3$, aromatic region) δ 8.89 (dd, 1H), 8.82 (m, 3H), 8.63 (dd, 1H), 8.53 (dd, 1H), 8.29 (dd, 1H), 8.18 (dd, 1H), 7.97 (m, 3H), 8.01 (td, 2H), 7.32 (m, 4H), 7.14 (m, 2H) and 7.10 (m, 2H) ppm. $^{31}$P NMR (162 MHz, CDCl$_3$) δ 187.5 ppm. MS (FAB$^+$) for C$_{71}$H$_{70}$Fe$_2$N$_6$O$_8$P$_2$S$_2$: m/z 1372.29 (calculated), 1373.30 (observed; MH$^+$).
Appendix – Spectroscopic titrations

Figure 6. Association constant fitting using Matlab for the titration of mPyPA with ZnTPP.

Figure 7. Association constant fitting using Matlab for the titration of 2 with ZnTPP.
Figure 8. Luminescence spectra for the titration of ZnTPP with 2 in CH$_2$Cl$_2$.
Excitation is at 555 nm, i.e. the isosbestic point seen during the UV-vis titration of the same solutions. The first point of the titration corresponds to pure ZnTPP (8.8 x 10$^{-5}$ M, pink curve); the last point corresponds to a total addition of 2.4 equivalents of 2 (violet line).
References

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