Dehydrogenation of anhydrous methanol at room temperature by \(\text{o-aminophenol-based photocatalysts}\)

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Dehydrogenation of anhydrous methanol is of great importance, given its ubiquity as an intermediate for the production of a large number of industrial chemicals. Since dehydrogenation of methanol is an endothermic reaction, heterogeneous or homogeneous precious-metal-based catalysts and high temperatures are usually required for this reaction to proceed. Here we report the photochemical dehydrogenation of anhydrous methanol at room temperature catalysed by \(\text{o-aminophenol (apH\textsubscript{2}), o-aminophenolate (apH}^-\text{)}\) and the non-precious metal complex \(\text{trans-[Fe}^{\text{II}}(\text{apH})\text{\textsubscript{2}(MeOH)}\text{\textsubscript{2}]})\). Under excitation at \(289\pm10\text{ nm}\) and in the absence of additional photosensitizers, these photocatalysts generate hydrogen and formaldehyde from anhydrous methanol with external quantum yields of \(2.9\pm0.15\%\), \(3.7\pm0.19\%\) and \(4.8\pm0.24\%\), respectively, which are the highest values reported so far to the best of our knowledge. Mechanistic investigations reveal that the photo-induced formation of hydrogen radicals triggers the reaction.
Molecular hydrogen (H₂) is one of the most promising energy sources of the future. As gaseous H₂ is difficult to handle and store, hydrogen storage materials have been the subject of intensive investigation in recent years. Among a number of materials, methanol (MeOH) represents one of the most fascinating hydrogen carriers, which is used in fuel cells due to its high-gravimetric H₂ content (12.6 wt % H₂). Since the generation of H₂ from MeOH is an endothermic reaction, both dehydrogenation catalysts and high temperatures are usually required for this reaction to proceed, and several heterogeneous and homogeneous catalyst systems have been investigated in this context. Homogeneous catalytic systems for the dehydrogenation of MeOH can be classified into three types: (1) thermal dehydrogenation catalysts for hydrous MeOH (MeOH reforming), (2) thermal dehydrogenation catalysts for anhydrous MeOH and (3) photochemical dehydrogenation catalysts for anhydrous MeOH. Beller et al. reported that the use of [Ru(H)(Cl)(PNP)] (PNP = HN(C₆H₄Fv-Pr₂)₂) and of the non-precious metal complex [Fe(H)(BH₄)(PNP)] allowed a dehydrogenation of the MeOH/H₂O mixture to CO₂ (or CO₂⁺) at 91 °C. Other examples were reported by Grützmacher and co-workers and Crabtree and co-workers who demonstrated that the dehydrogenation of MeOH is catalysed at 91 °C by [RuH₂(H)(1,4-bis(5H-diambenzo[a,d] cyclohepten-5-yl)-1,4-diazabuta-1,3-diene)]⁻ or [Ir₂(CO)₆(N,N-dimethylheterocyclic carbene)]⁺ complexes, respectively. Milstein and co-workers observed the formation of H₂ from mixtures of MeOH/H₂O/THF in the presence of [Ru(H)(Cl)(CO)(BPY·PNN)] (BPY·PNN = 6-di-tort-butylphosphinomethyl-2’,2’-bipyridine) at 60 °C. Conversely, Saito et al. and Shinoda et al. reported several Ru-complexes as thermal dehydrogenation catalysts for anhydrous MeOH, which operate at 64–79 °C (TONs H₂/MeOH = 8–34; TOF₁H₂ = 0.94–1.23 h⁻¹).

One promising strategy to lower the undesirably high reaction temperatures are photochemical reactions. Photochemical dehydrogenations of anhydrous MeOH should be highly attractive for two reasons: anhydrous HCHO, produced form anhydrous MeOH, is an important intermediate for the production of a large number of industrial chemicals, and the lack of effective catalysts for the removal of H₂O from aqueous HCHO renders this process relatively cost intensive. To the best of our knowledge, only six homogenous photocatalysts or catalyst precursors for the photochemical dehydrogenation of anhydrous MeOH have been reported during the past three decades (Supplementary Table 1). Saito and co-workers reported the dehydrogenation of anhydrous MeOH under concomitant formation of H₂ at 64–65 °C, using Rh, Pd and Ir-based precious metal catalysts. The reaction could also be carried out at 20 °C using cis-[Rh₂(µ₂-H)(CO)₄](dmpe) as the single Ru-complexes for anhydrous MeOH, which operate at 64–79 °C (TONs H₂/MeOH = 8–34; TOF₁H₂ = 0.94–1.23 h⁻¹).

The reaction could also be carried out at 20 °C using cis-[Rh₂(µ₂-H)(CO)₄](dmpe), albeit that the presence of acetonitrile as an additional photosensitizer was required, which led to the formation of considerable amounts of by-products, such as HOC(CH₂)₃C(CH₃)₂OH. These pioneering studies motivated us to develop a new catalytic platform for the dehydrogenation of anhydrous MeOH at ambient temperature, which requires neither precious metals nor additional photosensitizers.

We have recently reported that [Fe(H)(opda)]⁺ (opda = o-phenylenediamine) is able to photochemically generate H₂ in tetrahydrofuran. In this reaction, opda does not only act as a chelating ligand via the two amino groups, but also as a multi-electron and proton-pooling site for the photochemical generation of H₂ at ambient temperature. We proposed that H₂ is released as a result of the photochemical activation of the N–H bonds in the amino moieties of opda, accompanied by an oxidation to afford the oxidized semi-benzoquinodimine or o-benzoquinodimine species.

In contrast to the homoleptic coordination of opda via two amino groups, the corresponding o-aminophenolato ligand (apH⁻) displays a heteroleptic coordination pattern via one amino and the deprotonated hydroxyl group, which should facilitate the transfer of two electrons and one proton (Fig. 1). Pino and co-workers have reported the 1–π* initiated photochemical activation of the O–H bond of o-aminophenol (apH⁻) in the gas phase. This characteristic reactivity, which occurs on the picosecond timescale in the gas phase at 65–90 °C, has recently been labelled ‘excited state hydrogen detachment (ESHD)’. However, there is a considerable gap between the ESHD of aromatic amines and alcohols and the photochemical hydrogen evolution reaction (PHER) of [Fe(H)(opda)]⁺, because the generation of H₂ has not yet been reported for the ESHD system.

Recently, successful examples on the elucidation of electron- and proton-transfer properties of transition metal complexes of apH⁻, together with the characterization of corresponding complexes with o-iminosemiquinonate (isq⁻) have been reported, and these studies are currently under extensive investigation as models for non-haem-type iron dioxygenase. In contrast to these sophisticated examples for the reactivity of apH⁻ derivatives, which proceed under the exclusion of light, examples on photochemical reactions still remain elusive. Here we report the photochemical dehydrogenation of anhydrous MeOH at room temperature catalysed by apH₂ and apH⁻ and the non-precious metal complex trans-[Fe(H)(apH)(MeOH)] (1). These photocatalysts promote the PHER from MeOH in the absence of additional photosensitizers, and generated H₂ and HCHO with the highest external quantum yields (φH₂) reported so far. Mechanistic investigations revealed that the photo-induced formation of hydrogen radicals triggers the PHERs. Moreover, the complexion between FeII and apH⁻ facilitates the photochemical generation of H₂ at longer wavelengths. The observed PHER activity promises potential for these compounds to serve as a new photocatalyst platform.

Results

PHERs of MeOH by apH₂ and apH⁻. Figure 2 shows the ultraviolet–visible–near infrared spectra of apH₂ (2.00 mM) and apH⁻ (2.00 mM), whereby the latter was generated in situ by the treatment of apH₂ with one equivalent of tetra-n-butyl ammonium hydroxide (TBAOH). For both apH₂ and apH⁻, two absorptions were observed at λmax (ε⁻¹/M⁻¹ cm⁻¹) = 230 (6,260) and 285 nm (3,020), as well as at 230 (5,540) and 288 nm (2,630), respectively (Supplementary Table 2). These bands were assigned to two π–π* transitions, and the observed similarity of the spectral profiles indicates a negligible effect of the deprotonation of apH₂ on the π–π* transitions.

MeOH solutions of both apH₂ and apH⁻ did not exhibit any signs of gas evolution under the exclusion of light. However, the photolysis of a MeOH solution of apH₂ induced the evolution of gas, and a gas chromatography (GC) analysis of a gaseous sample taken from
accomplished spectrum of shows a magnification for the 300–900 nm region of the solution spectrum of $^1$ up to 6.5 were obtained (Fig. 3, Table 1, and Supplementary Fig. 2), while $^{3.7}$-$^{3.9}$ and CO$_2$ are also produced as minor products. After PHER of apH$_2$ (5 h), a high-performance liquid chromatography (HPLC) analysis revealed that 3.3 ± 0.08 equiv. of HCHO were generated per molecule of apH$_2$ (Table 1 and Supplementary Fig. 4a). Taking the experimental errors (3 standard deviation (s.d.)) into account, the difference between the quantities of the two products is statistically not significant, corroborating the photochemical dehydrogenation of MeOH. Furthermore, prolonged PHER (24 h) afforded a small amount of HCO$_2$H and/or HCO$_2$Me (HCO$_2$H/HCO$_2$Me), which was produced from dehydrogenation of HCHO in the presence of trace amounts of residual H$_2$O, in addition to H$_2$ and HCHO (Table 1 and Supplementary Fig. 4b). This reaction thus represents the first example of an organophotocatalyst promoting the photochemical dehydrogenation of MeOH to generate H$_2$. In particular, the external quantum yields (apH$_2$: $^{3.7}$-$^{3.9}$) are the highest value in those of previously reported molecular photocatalysts (for more details, see Supplementary Table 1).
Fig. 2. For the apH interactions between the CO0 contain the Fe II centre in the high levels of planarity in the five-membered rings that moieties via the p-orbitals of Fe II and the p-orbitals on the O atom(s) 43. It is also noteworthy that the observed differences with respect to the symmetry operation 2–.2 –.

Table 1 | PHER products from the photochemical reactions of apH2-based photocatalysts*.

| Compound          | \(\lambda_{irr}\) (nm) | \(t_{irr}\) (h) | Mols per mol of catalyst | \(\Phi_{H2}\) (%) |
|-------------------|------------------------|----------------|--------------------------|-----------------|
| apH2              | 289 ± 10               | 5              | 4.1\(^{\dagger}\)       | 3.3\(^{\dagger}\) | 2.9\(^{\ddagger}\) |
| apH–               | 289 ± 10               | 5              | 5.2\(^{\dagger}\)       | 4.0\(^{\dagger}\) | 3.7\(^{\ddagger}\) |
| 1                 | 289 ± 10               | 5              | 6.7\(^{\dagger}\)       | 6.7\(^{\dagger}\) | 4.8\(^{\ddagger}\) |
| apH2              | 289 ± 10               | 24             | 6.5\(^{\ddagger}\)      | 4.9\(^{\dagger}\) | 0.7\(^{\ddagger}\) |
| apH–               | 289 ± 10               | 24             | 14.1\(^{\ddagger}\)     | 14.2\(^{\dagger}\) | 0.73\(^{\ddagger}\) |
| 1                 | 289 ± 10               | 24             | 14.9\(^{\ddagger}\)     | 9.9\(^{\dagger}\) | 0.97\(^{\ddagger}\) |
| apH2              | 350 ± 10               | 24             | ND                       | ND              | ND |
| apH–               | 350 ± 10               | 24             | ND                       | ND              | ND |
| 1                 | 350 ± 10               | 24             | 0.48\(^{\ddagger}\)     | 1.4\(^{\ddagger}\) | ND |

ND, not detected.

*\([\text{apoH}^2] = [\text{apoH}^– + 2 \text{mM}]; [1] = 1 \text{mM}.

†Detected as 3,5-diacetyl-1,4-dihydro-2,6-lutidine.

‡Detected as methyl formate.

§Estimated relative standard deviation (s.d.) for H2 (0%), HCHO (1.4-2.5%) and HCHO/HCO2Me (19.2-9.9%) per eq.

10 24 ND ND ND ND
10 24 ND ND ND ND
10 24 14.9 ± 0.75 (24 h) mols of H2 per mol of 1, respectively (Supplementary Fig. 3). In addition to H2 and HCHO, prolonged PHER (24 h) also afforded small amounts of HCO2H/HCO2Me (Table 1), while evidence for the formation of CO2 was not observed. Control reactions under the same conditions, using a MeOH solution of Fe II(ClO4)2 (Table 1) did not show any PHER activity (Fig. 3 and Supplementary Fig. 2). Moreover, a MeOH solution of Fe II(ClO4)2 *6H2O containing 2 equiv. of opda generated only minor amounts of H2, indicating a lower activity of the opda complex of Fe(II) relative to that of 1 (Supplementary Fig. 9). For the PHER of a MeOH solution of 1, a \(\Phi_{H2}\) value of 4.8 ± 0.24% (5 h) was estimated. Considering these PHER results and the aforementioned absorption spectra, it is feasible to suggest that the photoexcitation of the apH– ligand in 1 initiates the PHER. Even when the PHER of 1 was carried out at 45 °C, no temperature dependence was observed, which in turn suggests that the photochemical process should be the rate-determining step of the PHER (Supplementary Fig. 10). Interestingly, the photocatalytic activity on apH– was not

Figure 4 Molecular structure of 1. Atomic displacement parameters set at 50% probability; colour code: C, dark grey; Fe, orange; N, light blue; O, magenta; ball-and-stick plots for N-bound hydrogen atoms (light blue), suggesting the presence of a high-spin FeII centre 43–46. These observations, in their entirety, suggest that 1 adopts a structure that is consistent with trans-[FeII(apoH)2(MeOH)]2.

In the solid state, the absorption bands of Fe II(ClO4)2 (2.204–2.234(2) Å), whereas the dihedral angle between the O1–Fe1–N1 and O1–Fe1–N2 planes in 1 (1.06°) is relatively small compared with those in [FeII(opda)](ClO4)2 (35.90, 38.17 and 44.15°)44. The high levels of planarity in the five-membered rings that contain the FeII centre in 1 are indicative for the presence of interactions between the d-orbitals of FeII and the π-orbitals of the apH– moieties via the p-orbitals on the O atom(s) 43. It is also possible to suggest that the photoexcitation of the apH– ligand in 1 initiates the PHER. Even when the PHER of 1 was carried out at 45 °C, no temperature dependence was observed, which in turn suggests that the photochemical process should be the rate-determining step of the PHER.
suppressed even after the complexation with the FeII centre, implying the possibility to tune the reactivity of the system via a variation of the metal ion.

To determine the excitation that initiates the PHER of 1 in MeOH, we examined the correlation between the PHER performance and the wavelength of the irradiation source. Exposing a MeOH solution of 1 to photoirradiation at 460 ± 10 nm (E460 nm = 483 M\(^{-1}\)cm\(^{-1}\), 24 h) did not generate any H\(_2\). However, exposing a MeOH solution of 1 to photoirradiation at 350 ± 10 nm (21.8 mW, E350 nm = 932 M\(^{-1}\)cm\(^{-1}\), 24 h) initiated PHER and resulted in the formation of 0.48 ± 0.02 equiv. of H\(_2\) with an estimated \(\Phi_{\text{H2}}\) value of 0.019 ± 0.001% (Fig. 5 and Supplementary Fig. 11). Although the \(\Phi_{\text{H2}}\) value for an irradiation at 350 ± 10 nm (0.019 ± 0.001%) is lower than that at 289 ± 10 nm (4.8 ± 0.24%), these results imply that the PHER may be driven by lower-energy light sources, given a suitable combination of apH\(^-\)-type ligands and metal ions.

**A reaction mechanism for the PHERs.** For the photochemical dehydrogenation of anhydrous MeOH, reports on detailed investigations regarding the mechanism on a molecular level remain scarce so far\(^{5-39}\). Therefore, we wanted to shed some light on the fundamental PHER mechanism that is operative in the MeOH solutions of apH\(_2\), apH\(^-\) and 1, and we were especially interested in the source of the evolved H\(_2\). In this system, it is pertinent to distinguish proton and electron sources according to: (i) the hydroxyl and methyl protons of MeOH, (ii) the aromatic protons of apH\(_2\), apH\(^-\) and apH\(^-\) in 1, and (iii) the amino protons of apH\(_2\), apH\(^-\) and apH\(^-\) in 1. Taking the amount of photochemically generated H\(_2\) and HCHO into account (Table 1), together with the small amounts of HCO\(_2\)H/HCO\(_2\)Me, it seems plausible to consider (i) as the most probable source of the evolved H\(_2\). To experimentally confirm this hypothesis, PHERs were carried out in MeOH-d\(_2\), and the evolved gas was analysed by GC at 77 K (Fig. 6). For H\(_2\), D\(_2\) and HD standards, retention times of 5.0 (p-H\(_2\)), 6.3 (o-H\(_2\)), 7.8 (p-D\(_2\)), 8.4 (o-D\(_2\)) and 6.4 min (HD) were observed (Fig. 6a–c). Photoirradiation of apH\(_2\) in MeOH-d\(_2\) at 289 ± 10 nm afforded gas samples that exhibited a single peak with a retention time of 6.4 min. (Fig. 6d), suggesting the selective formation of HD under such PHER conditions. Clearly, the D atom in the evolved HD originates from an \(\alpha\)-hydrogen of MeOH-d\(_3\), thus suggesting a C–H(D) bond cleavage during PHER. The PHER of apH\(^-\) and 1 (Fig. 6e,f), as well as the photoirradiation of a MeOH-d\(_3\) solution of 1 at 350 ± 10 nm (Fig. 6g) furnished samples that displayed similar HD peaks in the GC analysis. These results confirm that the PHER of MeOH solutions of apH\(_2\), apH\(^-\) and 1 generate H\(_2\) from MeOH.

As apH\(_2\) and apH\(^-\) can promote one-proton and two-electron transfers, it is not surprising that these can generate electron(s), hydrogen radical(s) or a hydride (Fig. 1). To gain a better mechanistic understanding of the observed PHERs, photochemical reactions were carried out in the presence of 2-methylethanol-2-thiol (t-BuSH), which is able to act as a hydrogen radical scavenger on account of the relatively low-bond dissociation energy of the S–H bond, resulting in the formation of di-tert-butyl disulfide (t-BuS\(_2\))\(^{24}\).

The \(^1\)H NMR spectrum of t-BuSH prior to photoirradiation at 289 ± 10 nm (24 h) in MeOH-d\(_4\) is shown in Fig. 7a. A singlet peak was observed at \(\delta = 1.40\) p.p.m. and assigned to the protons of the t-Bu group. After photoirradiation, no considerable change was observed in the spectrum (Supplementary Fig. 12), which is consistent with the absence of an absorption ~289 nm (Supplementary Fig. 13). The \(^1\)H NMR and ultraviolet–visible spectra of t-BuS\(_2\) in MeOH-d\(_4\) and MeOH are shown in Fig. 7b...
peaks emerged at 1.71, 1.29, 1.22 and 0.88 p.p.m. (Fig. 7e). The photoirradiation of a MeOH-

\[ -\text{BuSH} \] demonstrates the photochemical reactivity of 1.29 and 0.88 p.p.m. together with several minor peaks, which interaction between apH 2 and photoirradiation of this solution at 289 ± 10 nm (5 h), new singlet peaks were observed at 1.71, 1.29, 1.22 and 0.88 p.p.m. (Fig. 7e). These peaks are comparable to those of the photoirradiation product obtained from t-BuSH and apH2 (Fig. 7e), and these results thus suggest the formation of t-Bu2S2 from t-BuSH in the presence of 1.

At this point, it should be beneficial to consider possible formation mechanisms for the formation of t-Bu2S2 from t-BuSH. One possibility is the oxidation of t-BuSH by apH2 in the excited state, while another is the generation of hydrogen radicals from photoirradiated apH2, followed by the abstraction of a hydrogen radical from t-BuSH. On excitation at 285 nm in MeOH, apH2 exhibits an emission peak at 342 nm (Supplementary Fig. 16a). This emission was tentatively assigned to the \( \pi-\pi^* \) excited state, which was not quenched by t-BuSH. Therefore, the generation of a hydrogen radical from an alternative excited path represents a more likely mechanism compared with an electron transfer via the \( \pi-\pi^* \) excited state. Similar to the case of apH2, the emission peak of 1 in MeOH was not influenced by the presence of t-BuSH on excitation at 285 nm (Supplementary Fig. 16b). This result suggests that the PHER of 1 does not include the oxidation of t-BuSH by the excited state of 1, but the generation of a hydrogen radical from 1.

Furthermore, the characteristic singlet peak for t-Bu2S2 at 1.29 p.p.m. was observed after photoirradiation of 1 at 350 ± 10 nm (24 h; Fig. 7h). These results suggest that the pathway for the generation of hydrogen radicals is also included in the excitation of 1 at 350 ± 10 nm, similarly to the excitation of 1 and apH2 at 289 ± 10 nm. The photoirradiation of 1 in MeOH at 350 ± 10 nm in the presence of 3-carbamyl-1-methylpyridinium chloride (NADCl), which is an electron or hydride scavenger\(^{55,56} \), revealed no considerable change in the \( ^1\text{H} \) NMR spectra prior and posterior to the photoreaction (Supplementary Fig. 17). These results indicate that the photoreaction of 1 at 350 ± 10 nm does not include any electron transfer or generation of hydrides, and these are thus consistent with a mechanism based on hydrogen radicals (for a plausible reaction mechanism in the presence of t-BuSH, see Supplementary Fig. 18).

In general, hydrogen can be generated from MeOH using an electron donor, a hydrogen radical or a hydride. Reactions between MeOH-\(d_4 \) and sodium metal (electron donor) or NaNBH4 (hydride donor) showed that under these conditions, H2 was produced selectively (equations 1 and 2, Fig. 6a–c, and Supplementary Fig. 19). In contrast, the formation of HD was negligible, as the \( \sigma-\text{H}_2/\rho-\text{H}_2 \) peak area ratio was almost identical to that of the H2 standard (Supplementary Table 5). Hydrogen radicals have previously been reported to react with the \( x \)-hydrogen atoms of MeOH to produce H2 and the corresponding \( ^{\text{CH}_3}\text{OH} \) radical (equation 3)\(^{57} \). The \( ^{\text{CH}_3}\text{OH} \) radical is a good reducing agent and able to react with electron acceptors (EA) such as Fe(III) or Co(III), which affords HCHO as the oxidized species (equation 4).

\[
\begin{align*}
2\text{CD}_3\text{OH} + 2e^- & \rightarrow 2\text{CD}_2\text{O}^- + \text{H}_2 & (1) \\
\text{CD}_3\text{OH} + \text{H}^- & \rightarrow \text{CD}_2\text{O}^- + \text{H}_2 & (2) \\
\text{CH}_3\text{OH} + \text{H}^+ & \rightarrow ^*\text{CH}_3\text{OH} + \text{H}_2 & (3) \\
^*\text{CH}_3\text{OH} + \text{EA} & \rightarrow \text{HCHO} + \text{H}^+ + \text{EA}^- & (4)
\end{align*}
\]
For apH$_2$, proton- and electron-transfer properties should be expected, and apH$_2$ should thus be able to donate electrons, hydrides and/or hydrogen radicals. The ability to photochemically generate hydrogen radicals from the hydroxyl protons has already been reported for apH$_2$ (ref. 47). As previously mentioned, we confirmed that PHERs of MeOH-$d_3$ solutions of apH$_2$, apH$^-$ and 1 selectively generate HD (Fig. 6), which suggests a selective abstraction of the $\alpha$-hydrogen atoms from MeOH. Actually, the generation of hydrogen radicals was confirmed in the photochemical reactions of apH$_2$ and 1 in the

Figure 8 | Plausible PHER mechanisms. Reaction cycles catalysed by (a) apH$_2$, (b) apH$^-$ and (c) 1 upon irradiation at 289 ± 10 nm.
presence of the scavengers (Fig. 7). Consequently, all PHERs should be initiated by the generation of a hydrogen radical.

Figure 8a shows a plausible mechanism for the PHER involving apH₂. It seems reasonable to assume that PHER (289 ± 10 nm) proceeds via the initial photochemical generation of hydrogen radicals from the hydroxyl moieties of apH₂. Subsequently, H₂ and HCHO should be formed by the selective abstraction of x-hydrogen atoms from MeOH (Fig. 6). The additional oxidation products (HCO₂H/HCO₂Me) would then be generated from the dehydrogenation of HCHO or from the dehydrogenation of HCHO in the presence of residual trace amounts of water.

In the case of apH−, a hydroxyl proton is not present, and therefore, O–H bond cleavage in apH− should not occur during PHER. Previous studies on aromatic amines, such as aniline and opda, revealed characteristic photo-reactions, which are initiated by the p–π* excitation through the 3s Rydberg states of the nitrogen atom in the amino group[58–60]. Eventually, the N–H σ-bonds in these amino moieties are photochemically activated to generate hydrogen radicals via the p–π*/p–σ* conical intersection in these reactions, similar to the case of apH₂ (ref 62). The formation of a hydrogen radical may also be possible from the homolytic cleavage of an N=H bond in the p–σ* exited state from a p–π* excitation (Fig. 8b), and subsequent reactions indicate the generation of H₂ and HCHO, similar to the case of apH₂.

Furthermore, complex 1, containing apH− ligands, should also generate hydrogen radicals from the homolysis of an N–H bond in the apH− moiety under photoradiation conditions (289 ± 10 nm: Fig. 8c). In the plausible mechanism for 1, the MeOH molecule coordinated to the Fe(II) centre and/or that not directly bound to the Fe(II) centre may be included in the reaction as described in routes A and B (Fig. 8c). Remarkably, the complexation of apH− with Fe(II) does not inhibit its PHER activity. It should also be noted here that the PHER proceeding via exciations including π–π* transitions show higher Φ₁₂ values (4.8 ± 0.24%) relative to CT excitations (0.019 ± 0.001%).

Discussion

In this paper, we report the first examples for the photocatalytic dehydrogenation of anhydrous MeOH at room temperature, using apH₂, apH−, and an Fe(II) complex of apH− (1) as photocatalysts. These photocatalysts promote the PHER from MeOH in the absence of additional photosensitizers, and generate hydrogen and formaldehyde. For these PHERs, Φ₁₂ values based on the amount of generated H₂, HCHO and HCO₂H/HCO₂Me were estimated using defined excitations at 289 ± 10 or 350 ± 10 nm. The observed PHER activity and the comparable Φ₁₂ values of apH₂ and apH− promise potential for these compounds as a new organophotocatalyst platform. Furthermore, 1 demonstrated a comparable photochemical reactivity and Φ₁₂ value relative to apH−, despite the presence of a paramagnetic Fe(II) centre. The PHER activity on photoexcitation of the CT band of 1 suggested that the complexation between FeIl and apH− allows access to unprecedented photoactivity that is able to realize the photochemical generation of H₂ at longer wavelengths compared with apH₂ and apH−. The central issues to be addressed in the immediate future concern improvements of the catalytic activity and the use of visible light as a driving force. These topics are currently under investigation in our laboratory, using various combinations of metal ions with apH−-type ligands and extended π-systems.

Methods

General procedures. Unless noted otherwise, all synthetic operations and measurements were carried out under an atmosphere of N₂ using Schlenk-line techniques. Fe⁷(ClO₄)₂·6H₂O, Cu⁶(OAc)₂·H₂O (OAc = acetate), HCO₂H, acetic acid (AcOH), ammonium acetate (NH₄OAc), acetyl aceton (CoAc) and H₂SO₄ were purchased from Wako Pure Chemical Industries (Japan). Deuterated MeOH, dichromemone (CH₃Cl) and MeOH-d₄ were purchased from Kanto Chemical Co. Inc. (Japan). TBAOH in MeOH (37%), which was used after the removal of MeOH, an aqueous solution of HCHO (37%), t-BuOH, t-BuSO₂N and NADCl and apH₂ were purchased from Tokyo Chemical Industry Co. Ltd. (Japan). Prior to use, apH₂ was washed with CH₃Cl and dried in vacuo for several minutes, while t-BuSO₂N was used after stirring with CaO for 12 h, followed by distillation. MeOH-d₄ was purchased from Sigma-Aldrich. APX was prepared according to a reported procedure[53]. All solvents that were used under anaerobic conditions were thoroughly degassed at least by five freeze–pump–thaw cycles immediately prior to use. Although we did not experience any difficulties with perchlorate salts, these should be regarded as potentially explosive, and therefore handled with utmost care.

trans-[Fe⁶(μ³-p₄)₂(μ=O)(MeOH)₂] (1). A colourless MeOH solution (5 ml) of apH₂ (144 mg, 1.31 mmol) and TBAOH (340 mg, 1.31 mmol) was slowly deposited onto an aqua-blue MeOH (5 ml) solution of Fe⁶(ClO₄)₂·6H₂O (240 mg, 0.661 mmol) under an atmosphere of N₂. After leaving the solution to stand at 3°C for 5 days, colourless crystals of 1, suitable for X-ray crystallographic analysis, were obtained (see also Supplementary Methods and Supplementary Data 1). Crystalline 1 was isolated by filtration, washed with MeOH (2 × 4 ml), and dried in vacuo (yield: 59%). Crystals of 1 were found to be highly hygroscopic, and always contained small amounts of water. Anal. Calc. for C₁₂H₁₄CuN₂O₃·H₂O (1+0.2 H₂O): C, 49.49; H, 6.05; N, 8.24. Found: C, 49.49; H, 6.08; N, 8.27.

trans-[Cu⁶(μ³-p₄)₂(μ=O)(MeOH)₂] (2). A colourless MeOH solution (10 ml) of apH₂ (200 mg, 1.83 mmol) was added to 20 ml of a blue aqueous solution of Cu⁶(ClO₄)₂·H₂O (184 mg, 0.92 mmol), resulting in the formation of an aqua-blue powder after stirring the reaction mixture for 5 min. Complex 2 was isolated as an aqua-blue powder by filtration, washed with MeOH (3 × 3 ml) and Et₂O (2 × 3 ml), before being dried in vacuo (yield: 83%). Anal. Calc. for C₁₀H₁₄CuN₂O₄ (2): C, 48.40; H, 7.47; N, 9.17. Single crystals, suitable for X-ray crystallographic analysis, were obtained by layering an aqueous solution of apH₂ onto an aqueous solution of Cu⁶(OAc)₂·H₂O (see also Supplementary Methods and Supplementary Data 2).

Equipment for the PHERs. A 200 W Hg–Xe lamp (LC8, Hamamatsu Photonics) with a quartz light guide (Φ 1.9588) was used as the light source. For photoradiation at 289 ± 10 nm, a 289 nm band pass filter (BPF) was used, while a 350 nm BPF (03 type filter) was used for irradiation at 350 ± 10 nm. For photoradiation at 460 ± 10 nm, a 100 W Xe lamp (LAX-103, Asahi Spectra Co., Ltd.) with a quartz light guide (Φ 5.1000; UD0300), a VISIBLE-type mirror module and a 460 nm BPF were used. The intensity of the light was measured using a power meter (NOVA, Ophir optronics Ltd.) and a thermopile sensor (3A, Ophir optronics Ltd.). The released quantities of H₂, HD and D₂ were measured using a gas chromatograph (GC, Shimadzu GC-2014), equipped with a 2 m column packed with either MS 5A (T = 343 K; carrier gas: Ar) or 8% KOH alumina (T = 77 K; carrier gas: He).

PHER by apH₂ in MeOH. A handmade Schlenk-flask-equipped quartz vessel (V = 115 ml) was charged with 1 ml of a methanolic apH₂ solution that was prepared by dissolving apH₂ (4.36 mg, 0.04 mmol) in MeOH (20 ml). Subsequently, the solution was exposed to photoradiation in a water bath at room temperature. Gas samples (0.3 ml) were collected from the headspace of the vessel using a gas-tight syringe (Tokyo Garasu Kikai Co. Ltd.) and analysed by GC (MS 5A column). Estimated relative s.d. for H₂ (mol)/apH₂ (mol) and φH₂ (mol) 5%. 5%

PHER by apH− in MeOH. The quartz vessel was charged with 1 ml of a methanolic apH− solution that was prepared by dissolving apH− (4.36 mg, 0.04 mmol) and TBAOH (10.4 mg, 0.04 mmol) in MeOH (20 ml). Subsequently, the solution was exposed to photoradiation in a water bath at room temperature. Gas samples (0.3 ml) were collected from the headspace of the vessel using a gas-tight syringe and analysed by GC, similar to the aforementioned procedure. Estimated relative s.d. for H₂ (mol)/apH− (mol) and φH− (mol) 5%. 5%

PHER by 1 in MeOH. Crystals of 1 were filtered and washed with MeOH (2 × 4 ml), before being dissolved in MeOH (4 ml) to afford a saturated pale-orange MeOH solution of 1. Subsequently, 1 ml of this solution was transferred into the quartz vessel. The reaction and analysis were carried out as described above. Estimated relative s.d. for H₂ (mol)/apH− (mol) and φH− (mol) 5%. 5%

Analysis of HCHO in PHER solutions. An aqueous solution of AcOH (100 ml, 2.26 M) was prepared by dissolving 12.9 ml of AcOH (226 mmol) in water under an atmosphere of air. Subsequently, an aqueous solution of MeOH (2.25 M) was prepared by dissolving NH₄OAc (34.68 g, 450 mmol) in water (200 ml). An AcOH/NH₄OAc buffer solution was prepared by combining 8 ml of the aqueous
AcOH solution with 200 ml of the aqueous NH₄OAc solution. An aqueous solution (1.000 ml) of acetyl acetone and ethanol was prepared by dissolving 7 ml of acetyl acetone and 14 ml of ethanol in water (979 ml). Methanolic standard solutions of HCHO (0, 1, 5 and 10 mM) were prepared by diluting a methanolic HCHO solution (37%) with appropriate amounts of dehydrated MeOH. A mixture of the methanolic standard solutions of HCHO (0.1 ml), the AcOH/NH₄OAc buffer solution (2.0 ml) and the aqueous acetyl acetone solution (2.0 ml) was heated to 60 °C for 15 min. Then, the solution was cooled to room temperature, and 20 μl of the reaction mixture was analysed by HPLC, using a Synergi 4u Hydro-RP18A column (Phenomenex) and H₂O/MeCN (v/v = 85/15) at a flow rate of 1.0 ml min⁻¹. The targeted 3,5-diacyt-1,4-dihydro-2,6-lutidine, which was generated in situ, was detected at 6.4 min (Fig. 6c). D₂ gas was generated from the reaction of MeOH-D₂ and was dissolved in MeOH-D₂) and MeOH. Solutions of apH₂ apH (v/v = 95/5) at a flow rate of 1.0 ml min⁻¹. Quantities of HCO₂H/HCO₂Me in the PHER solutions should be possible (Supplementary Fig. 4b). To estimate the mol number of H₂, the mol number of the evolved H₂, the Avogadro constant, the speed of light in vacuum and the absorbance of the catalyst in MeOH, respectively. The absorbance throughout the photo-reaction was assumed to be constant at an optical density of 1.0 cm: apH₂ (5.72 at 289 nm), apH⁻ (5.39 at 289 nm) and I (5.76 at 289 nm, 1.15 at 350 nm).

Data availability. The data supporting the results of this study are available from the article and its Supplementary Information file, or from the authors upon request. The X-ray crystallographic coordinates used for the structure determination reported in this article have been deposited at the Cambridge Crystallographic Data Centre (CCDC) under deposition numbers CCDC-1062112 (1) and CCDC-1418335 (2). These data can be obtained free of charge from The Cambridge Crystallographic Data Centre via www.ccdc.cam.ac.uk/data_request/cif.

Analysis of HCO₂H/HCO₂Me in the PHER solutions. Methanolic standard solutions of HCO₂H (0, 0.5, 1, 2 and 4 mM) were prepared by diluting formic acid with MeOH in water under an atmosphere of air. About 500 μl of each solution were treated with 5 μl of H₂SO₄ at room temperature and stirred for 15 min. These HCO₂H standard solutions were analysed by HPLC using a Synergi 4u Hydro-RP18A column and H₂O/MeCN (v/v = 95/5) at a flow rate of 1.0 ml min⁻¹. The targeted 3,5-diacyt-1,4-dihydro-2,6-lutidine, which was generated in situ, was detected at 6.4 min (Fig. 6c). D₂ gas was generated from the reaction of MeOH-D₂ and was dissolved in MeOH-D₂) and MeOH. Solutions of apH₂ and 1 in the presence of scavengers. All reactions were carried out as described above for the PHER procedures, except for using a quarts NMR tube as the reaction vessel and MeOH-D₂ as the solvent. For that purpose, apH₂ or 1 was dissolved in degassed MeOH-D₂ (apH⁻ 2 mM; I: 1 mM) with tBuSH or NADCl (2 mM), before the solutions were analysed by ¹H NMR spectroscopy prior and posterior to photochemical reactions.

Physical measurements. ¹H NMR (500 MHz) spectra were measured on a JEOL EX-500 spectrometer. Elemental analyses were carried out on a Perkin-Elmer 2400 II CHN analyzer. Ultraviolet–visible–near infrared spectra (200–3,300 nm) in solution or in the solid state (KBr pellets) were recorded on a Hitachi U-4100 spectrophotometer at 296 K. HPLC measurements were carried out on a Shimadzu LC-20AT liquid chromatograph, equipped with an SPD-20A ultraviolet–visible detector. Emission spectra were recorded on a Horiba fluorometer using MeOH solutions of apH₂ and 1 at 296 K.

Calculations of external quantum yields (Φₑ). MeOH solutions of apH⁻ and 1 were irradiated at 289 ± 10 or 350 ± 10 nm. The amount of H₂ evolved during the subsequent 5 h was used to calculate the Φₑ according to the following equations: Φₑ = Nₑ/N₀ (5) N₀ = E₀/Eₚ (6) Nₑ = μₑNₐ (7) E₀ = hν/c (8) Φₑ = hν/c (9) R = 1 − 10⁻¹⁴ (10) wherein, Nₑ, N₀, Eₚ, E₀, R, Mₑ, Nₐ, h, c, and A refer to the number of molecules of evolved H₂ per mol of catalyst, the number of absorbed photons, the energy of the irradiation source, the energy of the irradiation photons, the proportion of the catalyst that is absorbing light, the mol number of the evolved H₂, the Avogadro constant, the optical intensity of the light, the irradiation time, the Planck constant, the speed of light in vacuum and the absorbance of the catalyst in MeOH, respectively. The absorbance throughout the photo-reaction was assumed to be constant at an optical density of 1.0 cm: apH₂ (5.72 at 289 nm), apH⁻ (5.39 at 289 nm) and I (5.76 at 289 nm, 1.15 at 350 nm).

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