A Non-Heme Iron Photocatalyst for Light-Driven Aerobic Oxidation of Methanol

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Abstract: Non-heme (L)FeIII and (L)FeIII-O-FeIII(L) complexes (L = 1,1-di(pyridin-2-yl)-N,N-bis(pyridin-2-ylmethyl)ethan-1-amine) underwent reduction under irradiation to the FeII state with concomitant oxidation of methanol to methanal, without the need for a secondary photosensitizer. Spectroscopic and DFT studies support a mechanism in which irradiation results in charge-transfer excitation of a FeIII-μ-O-FeIII complex to generate [FeII=O]3+ (observed transiently during irradiation in acetonitrile), and an equivalent of (L)FeII. Under aerobic conditions, irradiation accelerates reoxidation from the FeIII to the FeII state with O2, thus closing the cycle of methanol oxidation to methanal.

Photocatalysis has emerged as a versatile method to access highly reactive species in a selective and clean manner.1-2 The redox-active photosensitizers available include organic dyes,3 inorganic clusters,4 and transition-metal complexes, such as [Ru(bpy)3]2+ and its derivatives,5,6 whose redox potentials can be fine-tuned by ligand modification.7-9 Photocatalysis can bypass reactive stoichiometric oxidants, such as H2O2 and ClO-, to generate high-valent transition-metal oxido species by electron-transfer oxidation. Non-heme iron complexes that are well-known catalysts for a wide range of oxidation reactions have been combined with photocatalysts, such as [Ru(bpy)3]2+, for light-driven oxidation reactions.6-10 In this multicatalyst strategy (Scheme 1a), excitation of the photocatalyst sensitizer is followed by electron-transfer oxidation of the catalyst to raise it to a higher oxidation state so that it can subsequently oxidize substrates. The photocatalyst sensitizer is reoxidized by an electron acceptor (EA); however, the use of atom-economical terminal oxidants (e.g., O2) is a key challenge, and it would be preferable to use a single catalyst that is driven directly by light through the entire redox cycle. Furthermore, the generation of other species, such as singlet oxygen, by the organic and RuII/III photosensitizers is difficult to avoid.11-17

The photochemistry of iron complexes and especially the reduction of complexes from the FeIII to the FeII state when irradiated is well-established,18-20 not least in the widely used chemical actinometer [FeIII(oxalato)]18-20 and other iron(III) carboxylato complexes.20 Photoreduction in such systems is irreversible and accompanied by ligand oxidation (e.g., CO2 formation from carboxylate ligands), and hence FeIII complexes are of limited use in the photocatalytic oxidation of organic substrates. Notable exceptions (see below) are to be found in the reports of Richman21,22 Karlin,23 and co-workers on the photochemistry of μ-oxido-bridged diiron(III) complexes.

Previously, we reported that non-heme FeII complexes (such as [(MeN4Py)FeII(CH3CN)]+)1, Figure 1) are photoinert in acetonitrile, but undergo light-driven oxidation (from the FeII to the FeIII redox state) with O2 in solvents in which the CH3CN ligand is displaced by the solvent used.24 The photochemically driven oxidation of an FeIII complex together with the earlier reports of photoreduction of FeII complexes.

Scheme 1. a) Multicatalyst strategy for photocatalytic reactions, and b) the single-catalyst photocatalytic oxidation described herein. L = MeN4Py, X = OMe or Cl.

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raises the possibility that a fully light driven photocatalytic oxidation cycle can be achieved without the need for a separate photosensitiser, for example, [Ru(bpy)]2+. However, simple non-heme Fe(III) systems lack the distinct photophysics and chromophoric properties of the heme unit present in the systems of Richman, Karlin, and co-workers, and hence it would seem unlikely that a fully non-heme Fe(III) complex would show similar photoactivity.

Herein, we show that a single iron-based catalyst can promote catalytic oxidation reactions without the use of a secondary photosensitizer (Scheme 1b). We report a light-driven double photocycle capable of high-turnover oxidation of methanol with O2 as the terminal oxidant. Photoreduction of the non-heme iron(III) complexes to the Fe(I) state occurs concomitantly with the oxidation of methanol and is followed by light-driven reoxidation of the iron(II) complex, with O2 as the terminal oxidant (Scheme 1b). The whole cycle proceeds without significant ligand degradation.

Density functional (DFT) methods support the assignment of the µ-oxy diiron(III) complex 2a (Figure 1) as the photochemically reactive species with photoreduction proceeding via a [(L)FeIV=O]2+ intermediate analogous to that reported for the heme-based systems [(L)FeIV=O]2+ (4) is itself photoreactive, as we have shown recently. However, under certain conditions this species can also be observed during the irradiation of 2a in acetonitrile. The formation of ([(L)FeIV=O])2+ (4) during irradiation opens the possibility for selective photocatalytic oxidation reactions.

Irradiation of the Fe(III) complexes [(L)FeIII(OCH3)]2+ (2) and [(L)FeIII(OCN)]2+ (3) in argon-purged methanol at 365 nm resulted in a decrease in absorbance at 310 nm and concomitant increase in absorbance at 380 and 480 nm corresponding to the formation of Fe(II) complexes (Figure 2; see also Figure S3 in the Supporting Information). Irradiation of 3 at 300 nm resulted in similar changes; however, there was a pronounced wavelength dependence of the photochemical yield [(L)FeIII(OCH3)]2+ (Φ300 nm = 0.31 ± 0.01, Φ315 or 355 nm = 0.07 ± 0.01). Irradiation at 490 nm did not affect the absorption spectrum (see Figure S4) even though this wavelength is in resonance with a weak absorption band. Changes in absorbance were not observed without irradiation (Figure 2; see also Figure S5). Essentially identical changes were observed upon irradiation of 2a in methanol at 365 nm as with 2 and 3 (see Figure S6). The identical behavior of all three complexes in argon-purged methanol reflects the rapid equilibration of 2a and 3 with methanol to form predominantly 2, as confirmed by resonance Raman (λres = 355 nm; see Figure S7), EPR, and UV/Vis absorption spectroscopy (see the Supporting Information, Figures S8–S13, for further details).

The addition of acetonitrile (to 2.5 vol%) after irradiation confirmed the integrity of the ligands by yielding the corresponding [(L)FeII(CH3CN)]2+ complex (1) quantitatively, as shown by comparison with the absorption spectrum of [(L)FeII(CH3CN)]2+ (1) in acetonitrile (Figure 2; see also Figure S14). The concomitant formation of 0.5 equivalents of formaldehyde (see the Supporting Information) confirmed that methanol was the source of electrons for the reduction.

The dependence of the photochemistry on wavelength (see above) indicates that not all of the species (2a, 3, etc.) present in solution are photoactive (see below). Although the expected S = 1/2 Fe(III) (X-band) EPR signals of 2 were observed at 77 K (see Figure S8), quantification indicates that in deoxygenated methanol, only 40% of the Fe(III) is present as a mononuclear S = 1/2 Fe(III)–OCH3 complex. The remaining 60% is EPR-silent, possibly present in the Fe(III)–O–Fe(II) form, for example, 2a, or as mononuclear complexes with coordination modes that lead to fast electron-spin relaxation (and hence EPR silence as observed for 3 in acetonitrile; see the Supporting Information). Hence the UV/Vis absorption spectrum of 2 (and 3) in deoxygenated methanol and in acetonitrile is a weighted sum of the spectra of [(L)FeIII(OCH3)]2+ (2) or [(L)FeIII(OCN)]2+ (3; see Figures S8 and S23), [(L)FeIII–µ-O–FeIII(L)]2+ (2a), and other related species.

The addition of NaOAc (50 equiv) to 2 in argon-purged methanol resulted in a slight but immediate change in its UV/Vis absorption spectrum (Figure 3; for 3, see Figure S15), but thereafter no further thermally induced changes were observed. The rate of photoreduction was, however, increased fourfold (Figure 3). Again, subsequent addition of acetonitrile (see above, Figure S16) resulted in the quantitative formation of [(L)FeIV(CH3CN)]2+ (1), thus confirming the integrity of the ligand (L).

CH3CN did not significantly displace CH3O–, µ-O2– (see below), or Cl– in the ferric state, as confirmed, for example, by the EPR spectrum of 2, which shows the characteristic low-spin S = 1/2 signal (g = 2.28, 2.12, 1.96) for Fe(III)–OCH3 (see Figure S17; see the Supporting Information for further discussion). Nevertheless, photoreduction of 2, 2a, and 3 was also observed in acetonitrile; however, in contrast to
methanol, the initial form of the FeIII complex used played an important role in the observed photochemistry (see below). Furthermore, adventitious water could displace CH₃OH, μ-O²⁻, or Cl⁻ to form [(L)Fe[III]-OH]²⁺, as manifested in weaker signals, g = 2.36, 2.16, and 1.94 (see Figure S17).

The photoreduction of 2 in acetonitrile was orders of magnitude slower than in methanol (Figure 4), with a kobs value (from fitting of the change in the absorbance at 310 nm as an exponential decay) of 0.15 s⁻¹ in methanol and 0.0066 s⁻¹ in acetonitrile (with the same incident light flux). The addition of H₂O (2 vol%; see Figure S18) or triflic acid (1.0, 5.0, or 50 equiv; see Figure S19) to 2 in acetonitrile resulted in a substantial decrease in the rate of photo-reduction.

Irradiation of 3 at 365 nm in acetonitrile resulted in an almost linear decrease and increase in absorbance at 310 and 480 nm, respectively, due to formation of 1, and was again much slower than observed in methanol (Figure 4). The lower rate is due to the stronger binding of the chlorido ligand of 3 (see the Supporting Information for a discussion) and hence a reduced extent of exchange with adventitious water to form aqua and dinuclear complexes, such as 2a. This conclusion was confirmed by the addition of chloride to 2 in acetonitrile, which resulted in a lower rate of reduction. The observed rate is dependent on irradiation power, thus confirming photo-kinetic control (see Figure S20), and the linear decay indicates that the photoreactive species maintains a steady-state concentration throughout most of the reaction.

The 1H NMR spectrum of 2a in CD₃CN (see Figure S21) is similar to that reported for its N4Py analogue[29] and shows moderate paramagnetic line broadening and shift, which is consistent with strong antiferromagnetic coupling of the FeIII centers, and also further confirmed by the absence of signals in its EPR spectrum at 77 K (see Figure S22). The UV/Vis absorption spectrum of 2a in anhydrous acetonitrile shows the strong absorption at 312 nm (see Figure S23), which has been assigned as an oxo → Fe charge-transfer band,[30] with symmetric and asymmetric bands of a near-linear Fe–O–Fe core[31] at 407 and 810 cm⁻¹, respectively, observed in its resonance Raman (λexc = 355 nm) spectrum (see Figure S24). The data confirm that the complex retains its dinuclear structure in anhydrous acetonitrile, in contrast to the equilibration with mononuclear complexes observed in methanol (see above).

Irradiation of 2a in anhydrous acetonitrile resulted in an increase in the absorbance at 458 nm due to formation of the FeII complex (1). At higher concentrations, that is, 0.5 mm, an absorption band at 686 nm, characteristic of [(L)FeIV=O]²⁺ (4), appeared also (Figures 5; see also Figure S25). The addition of excess H₂O to 2a in acetonitrile had a minor effect on the resonance Raman and EPR spectra (see Figure S22 and S24, respectively), thus indicating that the dinuclear structure is largely retained, but accelerated the rate and extent of the increase in absorbance at 686 nm (Figure 5; see also Figure S26). The subsequent decrease in absorbance at 686 nm after 300 s is due to the photochemical reduction of [(L)FeIV=O]²⁺ formed.[23] The absence of [(L)FeIV=O]²⁻ under irradiation of 2a at lower concentrations in acetonitrile (see Figure S25) or in methanol (see Figure S6) is expected considering its low molar absorptivity (400 M⁻¹ cm⁻¹) and its own photoreactivity.[28] At higher
concentrations of 2a in acetonitrile, at which the absorbance at 365 nm is above 2, the inner-filter effect allows only partial penetration of light into the solution and the buildup of a significant steady-state concentration of 4 within the bulk. Overall, the non-heme iron(III) complexes 2, 2a, and 3 equilibrate rapidly with argon-purged methanol and show identical photochemical reduction to the FeIII oxidation state without ligand degradation. Both EPR spectroscopy and the wavelength dependence of \( \Phi \) indicate that there are several species present in solution, not all of which are photochemically reactive. In non-heme systems, the equilibrium between mononuclear and \( \mu \)-oxido-bridged dinuclear FeIII complexes with pentadentate ligands (N4Py, P2DA, 6-OC\(_2\)H\(_7\)-TPA, etc.)\(^{29,32,33}\) has been shown earlier to be rapid. Addition of base (NaOAc) and proton sources (H\(_2\)O or TIOH) shifts the equilibrium towards complexes, such as mononuclear FeIII-OH and FeIII-OH, and dinuclear FeIII-O-FeIII complexes. In the present reaction, conditions which favor dimer formation (base addition) are accompanied by an increase in the rate of photoreduction, while an added proton source or added chloride favor the formation of mononuclear FeIII complexes and retard photoreduction. A possible mechanism for the photoreduction is shown in Scheme 2.

Photoinduced heterolysis was reported first by Richman and co-workers. In the case of \( \mu \)-oxido-bridged diiron(III) porphyrin complexes, visible irradiation resulted in the reduction of both FeIII centers to the FeII redox state via an intermediate FeIV/FeII species\(^{21-23}\) in the presence of oxidizable substrates\(^{31,34}\). Reoxidation of the dinuclear FeII complex was not spontaneous, thus limiting the potential for catalytic turnover. In the absence of substrates with weak C-H bonds, the quantum yield for the reduction was negligible due to rapid recombination of the FeIV=O/FeII centers to the FeIII-O-FeIII state. Karlin and co-workers\(^{23}\) have shown that photocatalytic oxidation and aromatic dehalogenation are possible with turnover by using a nonsymmetric dinuclear FeIII complex based on a non-heme FeIII unit and an FeII porphyrin, which were bridged by both a \( \mu \)-oxido unit and a covalent link between the heme and non-heme ligands. As in the double iron(III) porphyrin systems,\(^{34}\) an intermediate FeIV=O/FeII species was observed by flash photolysis. The FeIV=O/FeII species was sufficiently long-lived to react with organic substrates with relatively strong C-H bonds, and the FeIII-\( \mu \)-O-FeIII complex was recovered subsequently by aerobic oxidation. The formation of tetranuclear complexes bearing an inert non-heme FeIII-\( \mu \)-O-FeIII unit was observed especially in dechlorination reactions.

For heme cofacial porphyrin \( \mu \)-oxido-bridged diiron(III) complexes, irradiation into the oxido \( \rightarrow \) FeIII charge-transfer band\(^{35}\) results in photoinduced disproportionation to FeIII and FeIV=O monomers.\(^{21,22,34}\) In the present non-heme system, an analogous model would see an FeIV=O species formed upon excitation of 2a in methanol or acetonitrile, which can recombine with the FeII fragment to reform 2a or react with methanol to form methanol and a second equivalent of an FeII complex. The electronic nature of the photoreaction and the thermodynamic energies of possible dissociation products were explored by DFT methods (see the Supporting Information). In brief, the electronic structure of the \( \mu \)-oxido-bridged dinuclear complex 2a and all accessible spin states revealed an antiferromagnetically coupled ground state (see Table S4 in the Supporting Information), in accordance with the experimental data.\(^{29}\) The excited states of 2a are predicted to result in Fe-O bond elongation owing to the charge-transfer character of the spin-allowed transitions to low-lying excited states. For possible dissociation products formed following photoexcitation, that is, [(L)FeIII=O + (L)FeIII] and [(L)FeIV=O + (L)FeII], a triplet ground state for (L)FeIV=O and quartet ground state for (L)FeIII=O is indicated, whereas for (L)FeII and (L)FeIII low-spin ground states were found both with and without coordinated CH\(_3\)CN (see Tables S5–S10). The electronic and Gibbs free energies indicate that both dissociation pathways are stabilized through solvent coordination; however, the (L)FeIV=O + (L)FeIII charge-transfer path is substantially more favorable. Importantly, when coordination of CH\(_3\)CN is included explicitly, both 2a and (1 + FeIV=O) are similar in energy (see Tables S11–S14).

The oxidation of [(MeN4Py)FeIV(CH\(_3\)CN)]\(^{2+}\) (1) in methanol to its FeIII state (i.e., 2) with O\(_2\) as the terminal oxidant was reported by our group earlier with visible and UV light.\(^{24}\) In the present study, we have shown that the iron(III) complexes of the ligand N4Py undergo reduction upon irradiation in methanol. This observation prompted us to explore whether both reactions could proceed under the same conditions simultaneously and thereby enable the catalytic use of O\(_2\) as a terminal oxidant. Irradiation of [(MeN4Py)FeIV(CH\(_3\)CN)]\(^{2+}\) (1) at 365 nm in methanol at room temperature under aerobic conditions resulted in a steady increase in the amount of formaldehyde formed over time (Scheme 2 and Figure 6) with a relatively minor decrease in visible absorbance (33 % after irradiation for 3 h; see Figure S29). Over 50 turnovers were observed with respect to 1, thus confirming that the process is catalytic.

In summary, the photoreduction of non-heme FeIII complexes proceeds via an intermediate formed from the mononuclear complexes 2 and 3 or the \( \mu \)-oxido-bridged diiron(III) complex 2a. DFT calculations indicate that photoexcitation of 2a would result in the population of antibonding orbitals and drive heterolytic cleavage to form a five-coordinate FeII species and an FeIV=O species in an excited electronic state (HS) rather than in its intermediate-spin (IS) ground state.
Recombination to reform 2a competes with solvent coordination (e.g., in acetonitrile to form 1) and oxidation of solvent (e.g., methanol to methanol) by the Fe$^{IV}=O$ species formed. This mechanism is analogous to those proposed for the heme Fe$^{III}$ systems reported earlier. Importantly, we show that the present system can use light to achieve a full catalytic cycle in methanol without the need for a secondary photosensitizer. In the presence of O$_2$, the Fe$^{III}$ species formed undergoes light-driven oxidation by O$_2$ to close a full photocatalytic cycle with a single catalyst, and oxidation of methanol with O$_2$ occurs with high turnover numbers. The present system opens opportunities for selective photocatalytic reactions with a single catalyst.

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**Conflict of interest**

The authors declare no conflict of interest.

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