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Determining the Fate of a Non-Heme Iron Oxidation Catalyst Under Illumination, Oxygen, and Acid

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S Supporting Information

ABSTRACT: We analyze the stability of the non-heme water oxidation catalyst (WOC), Fe(bpmcn)Cl₂ toward oxygen and illumination under nonaqueous and acidic conditions. Fe(bpmcn)Cl₂ has been previously used as a C-H activation catalyst, a homogeneous WOC, and as a cocatalyst anchored to WO₃ for photoelectrochemical water oxidation. This paper reports that the ligand dissociates at pH 1 with a rate constant $k = 19.8(2) \times 10^{-3}$ min⁻¹, resulting in loss of catalytic activity. The combination of UV-vis experiments, ¹H NMR spectroscopy, and cyclic voltammetry confirm free bpmcn and Fe²⁺ present in solution under acidic conditions. Even under nonaqueous conditions, both oxygen and



illumination together show slow oxidation of iron over the course of a few hours, consistent with forming an $Fe^{3+}-O_2^{-1}$ intermediate as corroborated by resonance-enhanced Raman spectroscopy, with a rate constant of $k = 3.03(8) \times 10^{-3}$ min⁻¹. This finding has implications in both the merits of non-heme iron complexes as WOCs as well as cocatalysts in photoelectrochemical schemes: the decomposition mechanisms may include both anchoring group hydrolysis and instability under illumination.

INTRODUCTION

A great deal of focus has been given to molecular water oxidation catalysts (WOCs) in the pursuit of a high-efficiency water splitting system to generate oxygen and hydrogen fuel.¹⁻⁹ Solutions of these catalysts typically require a sacrificial oxidant such as Ce^{IV} in the form of ceric ammonium nitrate (CAN), a hazardous and wasteful compound, in order to generate the high oxidation state active species needed to drive the oxygen evolution reaction (OER). The need for a sacrificial oxidant limits this pathway as a viable alternative for achieving largescale water splitting. Nevertheless, the mechanism by which molecular WOCs operate using Ce^{IV} as the sacrificial oxidant is well understood for many systems, 10-13 and they are known to be quite selective toward water oxidation. Although it is assumed that cerium serves only to oxidize the complex to its catalytically active form in outer-sphere reactions, there is evidence that cerium does participate in key mechanistic steps of water oxidation.^{11,12} These benefits are in contrast to photoelectrochemical approaches on visible light absorbing metal oxide semiconductors like tungsten oxide, which has notoriously low OER efficiency^{14–19} and the reaction pathway is difficult to probe.^{16–18} However, photoactive metal oxides do serve as highly stable WOCs that use sunlight as the driving force with no sacrificial oxidant needed. Because of their distinct advantages, many researchers have tried to get the best of both worlds by anchoring molecular catalysts to metal oxides to improve the water oxidation efficiency while also eliminating the need for a sacrificial reagent such as Ce^{IV 19-24} These molecular/solid-state architectures show higher efficiencies toward the OER under both acidic and neutral conditions,

but with lifetimes of only a few hours for most cases. Here, cues are taken from the many examples of anchoring molecular dyes and organic oxidation catalysts to semiconductor surfaces for dye-sensitized solar cells $(DSSCs)^{25-27}$ and photoelectrosynthetic (PES) cells.^{28–30}

Our group recently developed such a molecular/solid-state electrode, FelWO₃, where the iron species is the non-heme iron WOC, Fe(tebppmcn)Cl₂ (tebppmcn = tetraethyl N,N'-bis(2-methylpyridyl-4-phosphonate)-N,N' dimethylcyclohexyl-diamine), with a phosphonate anchoring group to attach the molecule to a tungsten oxide surface (Scheme 1).¹⁹ The intent of creating this system was to eliminate the need for a sacrificial







reagent to oxidize the iron complex, while also improving the OER efficiency for WO₃ in a PEC cell. Indeed, we observe a 60% increase in the photocurrent generated, coupled with a 30% increase in the OER efficiency over the first 3 h of operation. Using an iron complex is preferable to more common ruthenium complexes in DSSCs, PEC cells, and PES cells because of their significantly lower cost. However, the true active species and the fate of the iron complex could not be identified with confidence, as the molecule was no longer observed spectroscopically or electrochemically on the surface of WO₃ after 3 h of operation in aqueous sulfate solution at pH 3 under low loadings (15 nmol/cm²). Similar disappearances of other Ru-based complexes have also been observed, and decomposition is typically ascribed either to hydrolysis of the anchoring group, forcing the molecule to leave the surface, or to chromophore decomposition. $^{21-23,29,31}$ In addition, many of the aforementioned homogeneous catalysts have reported ligand dissociation of the η^1 ligands as the primary deactivation pathway.4,5,7,24

Specifically, Hong et al. have probed Fe(bqen)OTf₂ and $Fe(bqcn)OTf_2$ (bqen = N,N'-dimethyl-N,N'-bis(8-quinolyl)ethane-1,2-diamine, bqcn = N,N'-dimethyl-N,N'-bis(8-quinolvl)-cyclohexane-1,2-diamine), other non-heme iron WOCs, for their decomposition during the OER using Ce^{IV.2} They concluded that catalyzing the OER by these iron complexes competes with ligand degradation by Ce^{IV} and that iron dissociates during catalysis under acidic conditions. Moreover, under basic conditions, the complex decomposes to an iron hydroxide species that can be used as an OER catalyst in the presence of the photoactive dye, $[Ru(bpy)_3]^{2+}$. This report focuses on the dark reactivity, with no discussion of the direct effects of light on the molecule's stability in water. Reports from other groups have also examined the identity and stability of the active species of non-heme iron, manganese, and ruthenium-based complexes during homogeneous water oxidation using Ce^{IV} , $S_2O_8^-$, and IO_4^{-32-36} However, the stability of these complexes in acid as well as under illumination are critical in determining the long-term viability of these catalysts for molecular/solid-state PEC cells.

Outside of WOCs, many chemists have also used these nonheme iron complexes in C–H activation of organic substrates.^{37–47} These examples typically rely on NaIO₄, H₂O₂, and PhIO as sacrificial oxidants, although there are examples of using CAN for similar reactivity. In many cases, the sacrificial oxidant is typically dissolved in a small amount of water prior to adding it to the reactants. The ideal scenario is to use dissolved O₂ as the oxidant, eliminating the need for wasteforming higher-energy oxidants. There are additional reports of photodriven oxidation reactions using non-heme iron complexes with O₂ as the oxidant through either adding a dye^{37,48,49} or through direct absorption by the iron complex itself.⁵⁰ This bodes well for chemists looking to use O₂ as a direct oxygen source for C–H activation using sunlight as the driving force instead of a wasteful, sacrificial component.

Although emphasis has been placed on attaching molecules to surfaces and understanding their desorption, relatively little attention has been paid to how light alters molecular WOCs and what the fate of these catalysts is. This is a problem of particular importance in molecule/electrode architectures. In this paper, we present data showing that even the unanchorable complex, Fe(bpmcn)Cl₂ (bpmcn = (15,2S)-N,N'-dimethyl-N,N'-bis(2-pyridinylmethyl)cyclohexane-1,2-diamine) is inherently unstable under acidic conditions, and that free ferrous ion

is released as a decomposition product. We discuss the effects of oxygen and solar illumination on this complex in acidic water and in nonaqueous conditions. Our results provide further information toward identifying the true active species on the surface of our previously reported FelWO₃ electrode,¹⁹ and possibly on other WOCs with similar ligand scaffolds on highly oxidizing photoactive semiconductor surfaces. We recognize that our findings also have an impact on the use of non-heme iron complexes in organic oxidation reactions in water, as has been proposed in the literature,⁵¹ and we expose how O₂ reacts with iron in the presence of light even under nonaqueous conditions. For the scope of this paper, we will be focusing on the implications toward water oxidation, and will not be directly applying this to organic oxidation reactions.

EXPERIMENTAL SECTION

General Considerations. FeCl₂, bpmcn ligand, and distilled acetonitrile were all stored in an N2 glovebox prior to synthesis. Acetonitrile was purchased from Fisher Scientific, and was previously dried over powdered 4 Å molecular sieves for 3 days prior to distilling over CaH₂ under N₂ and stored on molecular sieves in an N₂ glovebox. Anhydrous FeCl₂ (99.5%) was purchased from Alfa Aesar, and used without further purification. Trifluoromethanesulfonic acid (reagent grade, 98%) was purchased from Sigma-Aldrich, stored under N₂, and used without further purification. For isotopic labeling experiments, ³⁶O₂ (97 atom % ¹⁸O, 99% purity) was purchased from Sigma-Aldrich. For all experiments involving water, Millipore 18.2 M Ω H₂O was used. Elemental analysis was conducted by Atlantic Microlab, Inc. UV-vis spectroscopy was conducted using a Varian Cary 5000 spectrophotometer. FTIR spectroscopy was conducted using a ThermoScientific Nicolet 6700, and samples were prepared in dried KBr pellets. Resonance-enhanced Raman spectroscopy was conducted in a quartz electron paramagnetic resonance tube and immersed in liquid nitrogen using a custom-made coldfinger apparatus. The laser was a 413.1 nm continuous-wave Kr-ion laser from a Spectra Physics. The detector used for resonance Raman spectroscopy was a Princeton Instruments TriVista Spectrometer System. NMR spectroscopy was performed with Varian MR400 spectrometer equipped with a 5 mm PFG AutoX Dual Broadband probe. Electrospray Ionization Mass Spectrometry (ESI-MS) was conducted using a Micromass AutoSpec Ultima Magnetic Sector mass spectrometer. Characterization data for the synthesized compounds are included in the Supporting Information (SI) as Figures S1-S5.

Synthesis of N^1 , N^2 -Dimethyl- N^1 , N^2 -bis(pyridin-2-ylmethyl)cyclohexane-1,2-diamine (bpmcn). Synthesis of this compound was taken from a previously reported procedure.¹⁹ Briefly, 1,2dimethylcyclohexane-1,2-diamine (162 mg, 1.14 mmol) was dissolved in acetonitrile (15 mL) in a round-bottom flask. Triethylamine (0.78 mL, 5.6 mmol) was charged to the solution, and 2-(chloromethyl)pyridine (374 mg, 2.27 mmol) was added. The solution as brought to reflux in air overnight, then cooled to room temperature and condensed under reduced pressure. The resulting crude solid was dissolved in 30 mL of dichloromethane, and washed with 30 mL of saturated NaHCO₃(aq). The organic layer was extracted, and the aqueous layer was washed 2×30 mL with dichloromethane. The organic layers were collected, dried over Na2SO4, filtered, and condensed under reduced pressure to yield a brown oil. The crude product was purified using silica gel chromatrography with 86% EtOAc/10% MeOH/4% NH4OH to yield the desired product as a light brown oil; yield: 155 mg (0.479 mmol, 42%). ¹H NMR (CDCl₃): δ (ppm) = 8.47 (d, 2H), 7.55 (d, 4H), 7.09 (m, 2H), 3.84 (q, 4H), 2.63 (d, 2H), 2.27 (s, 6H), 1.97 (2H), 1.75 (d, 2H), 1.27 (m, 2H), 1.14 (t, 2H). ¹³C NMR (CDCl₂): δ (ppm) = 161.6, 148.7, 136.4, 122.9, 121.7, 64.7, 60.6, 36.8, 26.0, 25.9. EA C₂₀H₂₈N₄: (calc.) C 74.03, H 8.70, N 17.27 (found) C 73.29, H 8.69, N 16.96 ESI-MS+: [bpmcn $+H]^+ = 325.24 \ m/z^+.$

Synthesis of Fe(bpmcn)Cl₂. Synthesis of this compound was adapted from a previously reported procedure,¹⁹ and was performed

under N₂. Briefly, the bpmcn ligand (162 mg, 0.5 mmol) was dissolved in dry, degassed acetonitrile (5 mL). Separately, a slurry of anhydrous FeCl₂ (63.3 mg, 0.5 mmol) in a solution of dry, degassed acetonitrile (5 mL) was made. The bpmcn solution was added to the vigorously stirring FeCl₂ solution, and the resulting solution was allowed to stir overnight under N₂. The solution changed from a pale yellow solution to an opaque yellow-orange solution over the course of the reaction. The resulting yellow suspension was filtered, washed with acetonitrile, and dried under high vacuum. After synthesis, the powder was stored in the N₂ glovebox in the dark; yield: 172 mg (0.382 mmol, 76%). ¹H NMR (CD₃CN): δ (ppm) = 147.0, 108.2, 62.8, 50.6, 50.1, 20.3, 16.0, 1.3, -0.3, -0.4, -8.1, -25.8. EA C₂₀H₂₈N₄FeCl₂: (calc.) C 52.20, H 6.35, N 12.17, Cl 15.41 (found) C 52.40, H 6.22, N 12.25, Cl 15.31. ESI-MS⁺: [Fe(bpmcn) (OEt)]⁺ = 425.16 m/z⁺.

UV-vis Spectroscopy of Fe(bpmcn)Cl₂ in Dry Acetonitrile. The sealed quartz vial used in this experiment was previously cleaned with aqua regia, and dried prior to use. A 0.2 mM solution of Fe(bpmcn)Cl₂ was made in dry acetonitrile under N₂. Dry acetonitrile under N₂ was used as a baseline for the UV-vis measurements, and Fe(bpmcn)Cl₂ solutions were prepared immediately prior to measuring the UV-vis spectra, where the solution was placed into the quartz vial, sealed under N₂. The solution was either kept in the dark or illuminated with 1-sun using a Newport Oriel 150 W Xe lamp equipped with an AM 1.5G filter, and kept under positive N₂ pressure.

Determining Stability of Fe(bpmcn)Cl₂ under Illumination via ¹H NMR Spectroscopy. A saturated solution of Fe(bpmcn)Cl₂ was made in the N₂ glovebox with dry d_3 -CD₃CN. This solution was then placed in a dry J-Young tube and sealed under N₂ with a Teflon seal. The solution was monitored by ¹H NMR spectroscopy while illuminating the NMR tube using a Newport Oriel 150 W Xe lamp at 100 mW/cm² equipped with an AM 1.SG solar filter. The solution was illuminated for a total of 24 h under N₂.

Exposure of Fe(bpmcn)Cl₂ to O_2 and Light for UV-vis Kinetics. The sealed quartz vial used in this experiment was previously cleaned with aqua regia, and dried prior to use. A dilute solution (0.2 mM) of Fe(bpmcn)Cl₂ was made in dry acetonitrile previously saturated with O_2 . The solution was placed in a clean sealed quartz cuvette, and exposed to 100 mW/cm² of illumination at the front of the quartz cuvette using a Newport Oriel 150 W Xe lamp with an AM 1.5G filter for 24 h. The reaction was monitored by UV-vis spectroscopy. Dry acetonitrile saturated with O_2 was used as a baseline for the UV-vis measurements, and Fe(bpmcn)Cl₂ solutions were prepared immediately prior to measuring the UV-vis spectra.

Exposure of Fe(bpmcn)Cl₂ to O₂ and Light at Preparative Scale. 50 mg of Fe(bpmcn)Cl₂ was dissolved in 200 mL of dry acetonitrile previously saturated with pure O₂ in a dry 250 mL Erlenmeyer flask. The solution was then placed under positive O₂ pressure with a balloon, and allowed to stir vigorously under 1.5 W of illumination using a Newport Oriel 150 W Xe lamp equipped with an AM 1.5G filter. The reaction was monitored by UV–vis spectroscopy, and took approximately 2 days given the experimental setup. For this experiment, the entirety of the solution was not capable of being illuminated. The resulting orange solution was condensed under reduced pressure and dried under high vacuum to yield a dark brown solid. The product was characterized without any further purification.

UV-vis Spectroscopy of Fe(bpmcn)Cl₂ in Acidic Water at Various pH. The sealed quartz vial used in this experiment was previously cleaned with aqua regia. A 0.2 mM solution of Fe(bpmcn)Cl₂ was made in 0.1 M triflate adjusted to various pH with mixtures of TfOH and TfONa. The TfOH solution was prepared under an inert N₂ atmosphere and degassed prior to adding the metal complex. TfOH solutions under N₂ were used as a baseline for the UV-vis measurements, and Fe(bpmcn)Cl₂ solutions were prepared immediately prior to measuring the UV-vis spectra, where the solution was placed into the quartz vial, and sealed under N₂. The solution UV-vis spectra were collected until the change in absorbance over time approached zero.

Electrochemistry. A solution of 2.5 mM $Fe(bpmcn)Cl_2$ was made under N₂ with pH 1 TfOH. This solution was placed in a three-necked cell equipped with a glassy carbon working electrode, a Pt wire counter electrode, and a Ag/AgCl (sat'd KCl) reference electrode. The cell was sealed under N₂, and connected to a CH Instruments CHI-1000 potentiostat. A macro command was programmed to take measurements every 30 min starting at the original open circuit potential, and scan at 100 mV/s from -0.2 to 1.2 V vs Ag/AgCl with negative polarity. After measuring cyclic voltammograms for 4 h, 3 equiv of 2,2'-bipyridine was added and monitored over the same potential range at the same scan rate over 10 min.

Oxygen Evolution Reaction Measurements. Oxygen was quantified using a FOSSPOR fluorescence probe using two-point calibration at 20.90% and 0.00% O2. A 12.5 µM solution of Fe(bpmcn)Cl₂ was made either in degassed unbuffered water or in pH 1 TfOH under N₂. The 20 mL solution was poured into a threenecked round-bottom flask and purged of air with N₂ until the oxygen probe read 0.00%. Data was collected for 10 min under N₂ prior to the injection of 0.8 mL of 1.25 M CAN (4000 equiv, previously degassed with N₂). Measurements were taken until the oxygen evolved had plateaued, typically at the 4 h mark. For unbuffered solutions, the OER experiment was conducted immediately after the solution was made. For Fe(bpmcn)Cl₂ dissolved in pH 1 TfOH, the solution was allowed to stir under N2 in the dark for 4 h prior to the injection of CAN. For Fe(bpmcn)Cl₂ dissolved in acetonitrile under illumination and O₂, the complex was illuminated for 24 h, and then isolated under reduced pressure. A 12.5 μ M solution of the final product was made in 20 mL of degassed, unbuffered Millipore water. 0.8 mL of 1.25 M CAN was then added to the solution, and the amount of oxygen in the headspace was measured by the FOSSPOR fluorescence probe. Oxygen measurements and calculations accounted for the solubility of oxygen in water and the overall headspace of the reaction vessel.

Magnetic Susceptibility Measurements. DC susceptibility was measured with a Quantum Design MPMS-XL7 SQUID equipped with an Evercool dewar. Fe(bpmcn)Cl₂ pre- and post-exposure to O_2 and 1.5 W of light from a Newport Oriel 150 W Xe lamp equipped with an AM 1.5G filter were used for these measurements. The sample was suspended in a known quantity of eicosane and placed in a small polycarbonate capsule. Total moment was measured from 30 to 300 K every 5 K, and were converted to X_M T by accounting for the susceptibility of eicosane and the diamagnetic components of the complex using Pascal's constants.

RESULTS

The effects of sunlight, O_2 , and water typically encountered during the OER in PEC cells have been examined in solutions of Fe(bpmcn)Cl₂ to assess their effects on the complex's stability. We isolated each variable independently, and monitored structural stability by UV–vis, ¹H NMR, and resonance Raman spectroscopies along with ESI-MS analysis in positive-ion mode. For the freshly prepared complex stored in the dark, the ¹H NMR spectra in D₂O and dry d_3 -MeCN show significantly deshielded protons with chemical shifts as large as 146 ppm (vs tetramethylsilane) as the result of high-spin Fe²⁺. SQUID magnetometry was used to determine the spin-state of the iron complex exposed to oxygen and sunlight.

Effects of Light and O₂. We start with the key control experiment: illuminating Fe(bpmcn)Cl₂ in dry acetonitrile under N₂ for 24 h shows no observable structural isomerism or decomposition by ¹H NMR spectroscopy (Figure S6), as expected. For comparison, structural isomerism from the cis- α conformation to a cis- β conformation would result in the loss of C_2 symmetry (Scheme 2), and the ¹H NMR spectrum in that case would show twice the number of resonances—from 12 to 24. Also, the cis- β form is not active for catalyzing the OER.¹² In addition, oxidation of Fe²⁺ to Fe³⁺ can result in C–N bond cleavage by oxidative N-dealkylation, resulting in hemiaminal complexes.⁵² The lack of drastic chemical shifts in the ¹H NMR rules out this reaction under 1-sun illumination during a 24 h period. Finally, the UV–vis spectrum in Figure 1 (red trace)

Scheme 2. Possible Conformal Rearrangement of Fe(bpmcn)Cl₂



Figure 1. (a) UV-vis spectra of $Fe(bpmcn)Cl_2$ in dry, degassed acetonitrile for t = 0 (black) and 24 h (red) in the dark and under 1-sun illumination (blue). (b) UV-vis spectra of $Fe(bpmcn)Cl_2$ in acetonitrile with no added cerium (black), 1 equiv of CAN (red), and 2 equiv of CAN (blue).

shows that $Fe(bpmcn)Cl_2$ is stable under completely inert conditions in dry acetonitrile under N_2 .

When exposed to 24 h of 1-sun illumination (but still under N₂ in acetonitrile), the ¹H NMR spectrum is unchanged, but the UV-vis spectrum presented as the blue trace in Figure 1 indicates a small, hypsochromic shift in the MLCT band over a 24 h period. This shift in similar to what is observed in Fe²⁺ in solution as well as Fe²⁺ in enzymes as it slowly photo-oxidizes to Fe^{3+, 53-55} However, when we add 1 and 2 equiv of CAN oxidant to a solution of Fe(bpmcn)Cl₂ in acetonitrile, a similar blue shift and the appearance of higher energy bands appear but with molar extinction coefficients that are approximately an order of magnitude higher. Therefore, we surmise that even for illumination times \geq 24 h, little photoinduced oxidation of Fe²⁺ in the complex is observed, which is consistent with the ¹H NMR spectra in Figure S6.

When exposed to a saturated solution of O₂ in dry acetonitrile in the dark, a similar Fe²⁺ oxidation is observed by UV–vis spectroscopy, illustrated in Figure 2. Here, new absorption maxima appear at $\lambda_{max} = 294$, 328, and 374 nm, with



Figure 2. UV-vis spectra of a $Fe(bpmcn)Cl_2$ solution in dry acetonitrile saturated with O_2 over time in the dark.

an isosbestic point at 417 nm. Given that this hypsochromic shift in the UV–vis spectrum does not occur in the absence of O_2 and light (see Figure 1a, blue trace), we surmise that O_2 reacts with the complex in the dark, albeit slowly.

Irradiating a dry acetonitrile solution of Fe(bpmcn)Cl₂ that is saturated with O_2 results in the onset of a spectral shift in the UV-vis response, with a new peak appearing at 342 nm. Further, a clear isosbestic point at 419 nm is present in the series of spectra, indicating that only one reaction is proceeding with Fe(bpmcn)Cl₂. In separate experiments, spectral changes resulting from iron oxidation upon exposure to either saturated O_2 or to light do not emerge until after 1 day. In contrast, Figure 3 shows that when both light and O_2 are present, iron



Figure 3. UV-vis spectra of a $Fe(bpmcn)Cl_2$ solution in dry acetonitrile under O_2 with of 1-sun illumination.

oxidation proceeds with a pseudo-first-order rate constant $k = 3.08(3) \times 10^{-3} \text{ min}^{-1}$ by monitoring the absorbance at 342 nm (see inset). After 3 h, the reaction rate drops either as we approach equilibrium or as the concentration of O₂ in solution decreases. The changes in ¹H NMR chemical shifts and new peaks appearing near 7 ppm after exposure to both O₂ and light corroborate this reactivity (Figure S7). The faster oxidation with both O₂ and light present implies that both sunlight and O₂ react with the iron together.

When we irradiate a dry acetonitrile solution of Fe(bpmcn)-Cl₂ under O₂ through a 550 nm cutoff filter, only the slow oxidation of the iron from the presence of O₂ is observed over the first 24 h (Figure S8). Then, preparing Fe(bpmcn)Cl₂ in acetonitrile with excess H₂O₂ results in an absorption maximum at 340 nm, similar what we observe with both O₂ and light (Figure S9). All three spectra in Figure S9 also show an isosbetic point at 422 nm, suggesting that reacting with H₂O₂ and with O₂ and light result in the similar products. We note that adding H2O2 to similarly structured non-heme iron complexes is commonly used in organic oxidation catalysis, and these oxidations proceed through an Fe³⁺-peroxo intermediate. 40,41,51,56 In addition, the spectra produced do not correspond to any FeCl₂ solvated complex in acetonitrile (Figure S10), discounting ligand dissociation as a potential decomposition pathway. Previous examples of non-heme iron complexes exposed to O2 at low temperatures have yielded similar UV-vis spectral responses, with the emergence of a strong absorption band between 340 and 350 nm that corresponded to an $Fe^{3+}-O_2^-$ species.⁵⁷⁻⁶⁰ We therefore surmise that that a $Fe^{3+}-O_2^-$ (superoxo) species is generated with O_2 and light at room temperature.

To corroborate forming a superoxo intermediate, we recorded resonance Raman spectra after illumination with 1.5 W of AM 1.5 G filtered light (Figure 4). Spectra were recorded



Figure 4. Resonance Raman spectra of (black) $Fe^{-32}O_2^-$ and (red) $Fe^{-36}O_2^-$ with 413 nm laser at 77 K. Starred peaks indicate acetonitrile solvent peaks.

on samples taken directly from solution under illumination (0.5 mM) and frozen immediately in liquid nitrogen (77 K). Cosmic rays were manually removed for clarity in Figure 4, and the raw data is shown in Figure S11. A resonance-enhanced vibration near 1051 cm^{-1} appears as a shoulder to the acetonitrile solvent peak for the Fe $-^{32}O_2^-$ complex. As expected, a 56 cm $^{-1}$ shift in this peak occurs when $^{32}O_2$ is replaced with $^{36}O_2$ under illumination, with a peak appearing at 995 cm $^{-1.58-60}$ This is strong evidence for an end-on ferric superoxo species generated photochemically in dry organic solvent. Control experiments showed that neither of these peaks are present in the solvent nor in the starting material (Figure S12).

The SQUID magnetometry of the product formed after exposing Fe(bpmcn)Cl₂ to O₂ and light shows a significant decrease in the χT product from 3.89 cm³ K mol⁻¹ in the freshly prepared sample to 0.59 cm³ K mol⁻¹ (Figure S13). This result is indicative of a spin-state change from high-spin Fe²⁺ (*S* = 2) to low-spin Fe³⁺ (*S* = 1/2) that is uncoupled to the superoxo radical. Furthermore, ESI-MS⁺ analysis shows fragments at m/z < 400 from Fe(bpmcn)Cl₂ exposed to illumination under O₂ for 24 h that are consistent with amide formation on the ligand (m/z = 339.22), and C–N bond cleavage (m/z = 262.19) (Figure S14). When ³²O₂ is replaced with ${}^{36}O_2$, clear isotopic labeling is observed in the mass spectra corresponding to the amide formation under soft ionizing conditions (Figure S15). Moreover, FTIR spectra of Fe $-{}^{32}O_2$ vs Fe $-{}^{36}O_2$ show this amide bond in the crude material, with a shift in the vibrational signal at 1660 cm⁻¹ into the signals from the pyridine ring near 1600 cm⁻¹, consistent with the difference in reduced mass when substituting C=¹⁶O with C=¹⁸O in the amide bond (Figure S16).

Since these products are observed only through exciting electrons from the MCLT band absorption, reactivity *must* include the Fe-center of the molecular complex. Although we observe iron oxidation through varying spectroscopic techniques, the activity of the resulting complex toward the OER does not completely diminish (Figure 5). Rather, oxidation decreases



Figure 5. OER data collected using an O₂ probe of solution of 12.5 μ M Fe(bpmcn)Cl₂ (black) in unbuffered 18.2 M Ω H₂O and (red) after exposing Fe(bpmcn)Cl₂ to O₂ and light for 2 days. 4000 equiv of CAN was added to the solution to initiate chemical oxidation of water, and the solution pH is ~0.9 after adding excess oxidant.

the turnover number (TON) by only 35% after 3 h and decreases the turnover frequency (TOF, measured by the initial rate) from 3.24 to 2.30 min⁻¹. We conclude that although O_2 binds to the iron complex, the resulting $Fe^{3+}-O_2^{-}$ is active for catalyzing the OER, but that it slowly oxidizes itself. It is likely that this decomposition leads to the decreased activity of the OER observed in Figure 5. Nevertheless, adding CAN to the Fe³⁺- O_2^{-} species illustrated in Scheme 3 releases O_2 and generates a species active for the OER.

Effects of Water and Acid. Dissolving Fe(bpmcn)Cl₂ in D₂O with 0.1 M deuterated trifluoroacetic acid (*d*-TFA) results in the rapid disappearance of ¹H NMR signals downfield of 10 ppm. Instead, the 12 peaks appear between 0 and 10 ppm upon monitoring the reaction for 4 h (Figures S17 and 18), and no deshielded signals indicative of a paramagnetic center remain after 8 h. Furthermore, the final ¹H NMR spectra matches closely to that of free bpmcn in the presence of 1 equiv FeCl₂ in pH 1 d-TFA. In addition, the UV-vis spectra in Figure 6a show a decreasing MLCT band at 367 nm over 3 h in the dark in pH 1 trifluoromethanesulfonic acid (TfOH). The existence of a clear isosbestic point at 287 nm suggests that only two species contribute to the absorption spectrum-the starting iron complex and a single product. A plot of $\log[Fe(bpmcn)Cl_2]$ vs t for the MLCT band at 367 nm is linear, consistent with a first-order decay with a rate constant of $k_{\rm obs} = 19.8(2) \times 10^{-3}$ min⁻¹. Disappearance of the MLCT band hints at ligand dissociation, leaving behind free bpmcn and $[Fe(H_2O)_6]^{2+}$. To demonstrate that indeed the bpmcn ligand dissociates from Fe^{2+} upon reacting with acid, we added 2,2'-bipyridine to the solution after 3 h. This reaction results in a new UV-vis

Scheme 3. Proposed Mechanism for Photoinitiated Binding of O_2 to Fe(bpmcn)Cl₂ in Acetonitrile



Figure 6. (a) Fe(bpmcn)Cl₂ in pH 1 TfOH over time from 0 to 3 h. (b) UV–vis spectra of Fe(bpmcn)Cl₂ after 3 h in pH 1 TfOH before and after the addition of 2,2'-bipyridine.

spectrum in Figure 6b with absorbances at 349, 496, and 523 nm, all of which match closely with $[Fe(bpy)_3]^{2+,61}$ This observation is consistent with what has been observed during the OER catalysis for similar non-heme iron complexes.² The increasing absorptivity of the $\pi-\pi^*$ transition at 261 nm of the ligand is consistent with the inherent higher absorptivity of the free *intact* bpmcn ligand (Figure S19). Adding 2,2'-bpyridine to a solution of FeCl₂ in pH 1 TfOH produced the same result as presented in Figure 6 (also in Figure S9). Moreover, cyclic voltammetry of the pH 1 TfOH solution over time shows a disappearance of the Fe^{3+/2+} reversible wave having $E_{1/2} = 0.578$ V vs Ag/AgCl (0.775 V vs NHE) associated with the Fe(bpmcn)Cl₂ complex over a similar time-scale as the ¹H

NMR and UV–vis spectroscopy experiments, illustrated in Figure 7a. Within 4 h, the ${\rm Fe}^{3+/2+}$ wave associated with



Figure 7. (a) Cyclic voltammetry of $Fe(bpmcn)Cl_2$ in pH 1 TfOH over 4 h block. WE: Glassy carbon, CE: Pt wire, RE: Ag/AgCl (sat'd KCl). (b) Same solution after the 4 h mark (black) prior to (red) and after (blue) adding 3 equiv 2,2'-bipyridine to the solution.

Fe(bpmcn)Cl₂ completely disappears, and a very broad wave centered at ~0.6 V vs Ag/AgCl appears. Figure 7b shows that after adding 3 equiv of 2,2'-bipyridine to this solution, a new clearly distinct and reversible wave with $E_{1/2} = 0.886$ V vs Ag/AgCl results; this wave is consistent with the $[Fe(bpy)_3]^{2+/3+}$ couple.⁶² Together, these data show unequivocally that bpmcn dissociates at pH 1 through the reaction outlined in Scheme 4.

Scheme 4. Proposed Mechanism for Dissociation of Fe²⁺ from bpmcn Ligand under Acidic Conditions

$$4 \text{ Ce}^{4+} + 2\text{H}_2\text{O}$$

$$L_4\text{Fe}^{\parallel} \xrightarrow{2\text{H}^+} L_4\text{-H}_2^{2+} + [\text{Fe}(\text{H}_2\text{O})_6]^{2+}$$

$$O_2 + 4\text{H}^+ + 4\text{Ce}^{3+}$$

As expected, free Fe²⁺ in solution that results from adding 0.1 M acid (pH 1) yields no OER activity, illustrated in Figure 8. However, ligand dissociation is slower when the pH is raised to pH 3, similar to the conditions used for FelWO₃ electrodes in our previous work.¹⁹ Monitoring the disappearance of the MLCT band in Figure 9a shows that ligand dissociation now occurs over the course of several days, not hours. By plotting first-order kinetics for the first hour, the rate constant, $k_{obs} = 93(5) \times 10^{-5} \text{ min}^{-1}$ reflects this increased stability, decreasing by 2 orders of magnitude (inset of Figure 9a). After 1 h, the reaction deviates from first-order kinetics (Figure S20), which we attribute to the reversible ligand dissociation at pH 3 and



Figure 8. OER data collected using an O₂ probe of solution of 12.5 μ M Fe(bpmcn)Cl₂ in unbuffered 18.2 M Ω H₂O (black) and in pH 1 TfOH for 4 h (red). 4000 equiv CAN was added to the solution to initiate dark oxidation of water, which is marked as t = 0 in the plot. The solution pH is ~0.9 after adding excess oxidant.



Figure 9. UV–vis spectra of Fe(bpmcn)Cl₂ in 0.1 M HOTf/NaOTf pH 3 under N₂ (a) in the dark over 4 days, and (b) under 1-sun illumination under N₂ at (black) t = 0, (red) 8 h.

the relatively similar concentrations of Fe(bpmcn)Cl₂ and H⁺. With prolonged exposure to sunlight at pH 3, the complex also undergoes acid-driven ligand dissociation and light-driven oxidation occurring simultaneously, presented in Figure 9b. The absorption band growing in at ~300 nm can be attributed to the MLCT band absorption from the newly formed Fe³⁺ complex, and the decrease in intensity of the MLCT band from the Fe²⁺ complex can be attributed to ligand dissociation.

DISCUSSION

By isolating the three major variables for water oxidation $(O_2, light, and acid)$, we have determined the viability of Fe(bpmcn)Cl₂, and perhaps other non-heme iron complexes for water oxidation. To recap, UV–vis- and resonance-enhanced Raman spectroscopies, coupled with magnetic susceptibility measurements indicate that Fe(bpmcn)Cl₂ reacts

to form an end-on $Fe^{3+}-O_2^{-}$ species in the presence of O_2 at room temperature; the reaction is slow in the dark. Moreover, the iron complex is stable under illumination alone. Of note, these non-heme iron complexes have been used previously with H₂O₂ for epoxidation of alkenes and for aliphatic C-H bond oxidation, and visible light coupled with O2 has shown reactivity for non-heme {FeNO}⁷ complexes in the oxidation of thiolates in organic solvents as described in the Introduction. Although this background reaction occurs significantly faster than when $Fe(bpmcn)Cl_2$ is exposed to O_2 and light separately, it still requires at least 24 h to completely react in solution and it forms ~ 6 times more slowly than acid-driven ligand dissociation. This reaction could be accelerated by adding an acid in nonaqueous media to yield an Fe-OOH intermediate for use in organic substrate oxidation. In this regard, further exploration is needed to generate photocatalysis in organic media, using similar reaction conditions as reported herein and examples from the literature such as the recently reported {FeNO}⁷ complexes for thiolate oxidation.⁵⁰

To put the results into proper context for our own previous work, we note that ligand dissociation does not occur on the same time scale as our 3 h bulk electrolysis experiments on Fel WO₃ electrodes (data reproduced in Figure S21).¹⁹ Rather, in that time frame, we observe hydrolysis and desorption of the phosphonate-anchored tebppmcn complex from WO₃. Given that Fe(bpmcn)Cl₂ does not exist as an Fe²⁺ in the proposed mechanism of water oxidation, and an increased oxidation state of the iron center would result in a substitutionally inert intermediate, it is unlikely that ligand dissociation occurs *during* the OER. However, prolonged exposure of the complex to light, oxygen, and/or acid prior to using it for catalytic water oxidation will significantly reduce the activity of this catalyst due to ligand dissociation—whether as a homogeneous catalyst or when anchored to a semiconductor.

The implication of these findings are as follows: (1) the instability of $Fe(bpmcn)Cl_2$ to acid requires caution especially when handling the complex in aqueous solution since, as prolonged storage (order of minutes) in acid will significantly degrade the complex; (2) Fe^{2+} oxidation to a photogenerated $Fe^{3+}-O_2^{-}$ at t = 0 could potentially lead to deleterious reactivity with the metal oxide semiconductor surace, and the activity after prolonged exposure on the surface at various pH should be measured systematically in future work; and (3) WOCs with similar ligand scaffolds must be tested for their stability in acid, O_2 , and under illumination to advance the chemistry of PEC, PES, and DSSC approaches to catalyzing the OER.

In a more general sense, the current design of non-heme iron complexes does not allow for a long-lived species in solution under acidic conditions (pH \leq 3), without oxidation to a more substitutionally inert Fe⁴⁺ complex prior to ligand dissociation.² In order to apply non-heme iron WOCs to metal oxide semiconductors for improved OER efficiency in PEC cells practically, the ligand scaffold must first be modified to increase the stability of the coordination complex. One straightforward way to do so would be to generate an anionic ligand scaffold, although alkoxide and carboxylate groups on non-heme iron complexes are completely inactive toward the OER.⁶³ Nevertheless, examples of ruthenium-based WOCs that contain alcohol and carboxylic acid groups within the binding pocket have been explored.^{4–8}

As an example, the most active OER catalyst to date, Ru(bda) (isoq)₂ (bda = 2,2'-bipyridine-6,6'-dicarboxylic acid, isoq = isoquinoline) contains a dianionic equatorial ligand and two neutral, axial ligands. This catalyst has a turnover frequency of 303 s⁻¹, comparable to that of photosystem II.⁵ This activity is 2 orders of magnitude higher than most WOCs reported in the literature. In this paper, Duan et al. describe the major deactivation pathway as isoquinoline dissociation within a few minutes, with the inactive Ru(bda) moiety staying intact. One recommendation by the authors to solve this issue is to use pincer-type ligands in place of monodentate ligands in order to increase the binding affinity of the axial ligands. It is important to note that the equatorial ligand in the Ru(bda) complexes is incredibly stable during the OER, and that the decomposition mechanism does not involve the dissociation or decomposition of the bda ligand. Catalysts with this basic Ru(bda) structure have been used previously in molecular/solid-state photoanodes for the PEC OER with significantly higher OER efficiencies;²⁴ however, the inherent stability of these complexes under illumination in the absence and presence of oxygen have vet to be tested.

It is therefore imperative that ruthenium-based WOCs with similar scaffolds as non-heme iron complexes as well as those with anionic ligands undergo similar scrutiny as $Fe(bpmcn)Cl_2$ toward their long-term stability under acidic conditions as well as under illumination in the presence of O₂. Because molecular Ru-based complexes contain MLCT absorption bands within the visible spectrum, it is crucial that we probe potential photoinduced ligand dissociation given that they are commonly attached to metal oxide surfaces for improved OER efficiency.

CONCLUSIONS

The complex $Fe(bpmcn)Cl_2$ is easily oxidized under the action of solar illumination and O2. It is also prone to ligand dissociation at pH 1. These findings have profound implications on the stability and structural identity of non-heme iron WOCs anchored to semiconductor photoelectrodes such as WO₃. Oxygen in the dark oxidizes Fe(bpmcn)Cl₂ in nonaqueous conditions (acetonitrile) over the course of days, and under illumination, an $Fe^{3+}-O_2^{-}$ complex forms within a few hours. This new complex remains active for the OER, albeit slower than the original Fe(bpmcn)Cl₂ complex. In contrast, Fe-(bpmcn)Cl₂ is inherently unstable in water at pH \leq 3. There, bpmcn dissociates. At pH 3, this reaction is slow, so it may not lead to direct drastic decomposition of anchorable catalysts such as Fe(tebppmcn)Cl₂ tethered to WO₃. Although several analytically challenging questions remain such as whether the ligand backbone is oxidized by WO3 and what is the catalytically active species oxidized in the ligand backbone by WO₃, this paper introduces a new possible pathway for degradation of molecular WOCs on semiconductors or solid supports irrespective of anchoring group hydrolysis. We aim to begin a larger discussion of what is feasible in proposing the true active species of molecular/solid-state electrodes in PEC and PES cells over short and long time periods. These considerations are also quite relevant to using non-heme complexes as photocatalysts for oxidizing organic substrates.

ASSOCIATED CONTENT

Supporting Information

The Supporting Information is available free of charge on the ACS Publications website at DOI: 10.1021/acs.inorg-chem.6b01538.

Spectra, kinetics plot, OER data (PDF)

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The authors declare no competing financial interest.

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ABBREVIATIONS

CAN, ceric ammonium nitrate; DSSC, dye-sensitized solar-cell; WOC, water oxidation catalyst; PEC, photoelectrochemical; PES, photoelectrosynthetic; OER, oxygen evolution reaction

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